



XXII MENDELEEV CONGRESS  
ON GENERAL AND APPLIED CHEMISTRY

# BOOK OF ABSTRACTS

IN 7 VOLUMES

VOLUME 4

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**XXII MENDELEEV CONGRESS  
ON GENERAL AND APPLIED CHEMISTRY**

*Dedicated to the 190<sup>th</sup> anniversary  
of D.I. Mendeleev and the 300<sup>th</sup> anniversary  
of the Russian Academy of Sciences*

**BOOK OF ABSTRACTS**

**Volume 4**

*Book of abstracts in 7 volumes*

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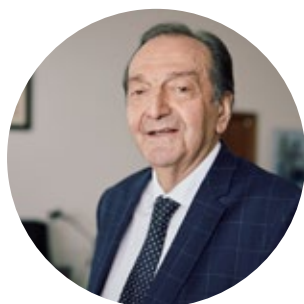
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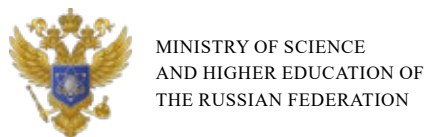
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An abstract, high-energy visualization of particle interactions. The scene is set against a solid black background. Numerous small, glowing particles in shades of magenta, red, orange, yellow, and blue are scattered throughout. These particles form complex, swirling patterns and dense clusters, suggesting a dynamic process like a chemical reaction or a chromatographic separation. The overall effect is one of intense energy and complex, organic-looking structures.

# SYMPOSIUM ON CHROMATOGRAPHY

# ION CHROMATOGRAPHY – PAST, PRESENCE, AND FUTURE

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Ion chromatography (IC) has been introduced in 1975 by Small et al. In its earliest embodiments IC was focused primarily on the analysis of inorganic anions and cations. Over the past almost fifty years, ion chromatography has undergone enormous changes. Although separations of ions by ion-exchange chromatography prevail, other liquid chromatography techniques such as ion-exclusion chromatography, reversed-phase liquid chromatography in the ion-suppression mode, and even hydrophilic interaction and mixed-mode liquid chromatography are also used today for the separation of ions. Thus, the definition of the term ion chromatography became much broader over the years to be an umbrella term nowadays for all liquid chromatographic techniques that are suitable for separating and detecting ionic and ionizable species. Today, the method of ion chromatography is well matured and widely accepted by international regulatory authorities.

The past decades have seen a number of exciting developments in ion chromatography that further established this analytical technique. Of particular importance is the progress in stationary phase design with hyperbranched condensation polymers developed for anion-exchange chromatography and cation exchangers for improved separations of amines. In general, we observe the development of stationary phases with improved selectivities and chromatographic efficiencies. In terms of eluent preparation, electrolytic eluent generation (RFIC™) has been well established as an alternative to manually prepared eluents. RFIC not only facilitates the use of gradient elution techniques in ion chromatography, but also provides the user with more consistent data. Along with the RFIC technology, hydroxide eluents, which are particularly suitable for concentration gradients in anion-exchange chromatography, are increasingly replacing classical carbonate/bicarbonate eluents predominantly used so far. In contrast to carbonate/bicarbonate buffers, which are still used for relatively simple applications that only require isocratic elution, higher sensitivities are achieved with hydroxide eluents. This trend is supported by the development of hydroxide-selective stationary phases for anion-exchange chromatography.

For the majority of applications, conductivity detection with suppression devices represents the most versatile detection system augmented today. Periodically regenerated packed-bed suppressors used in the early days of IC have been replaced by continuously regenerated membrane-based devices for chemical and electrolytic suppression. In addition to conductivity detection, UV/Vis detection is also used today for analyzing ions with an intrinsic UV absorption or in combination with post-column derivatizations for a number of compound classes such as oxyhalides, aminopolycarboxylic acids, aminopolyphosphonic acids, and others. and amperometry. Particular progress has been made in amperometric detection, utilizing pulsed amperometry for analyzing carbohydrates and related compounds as well as integrated pulsed amperometry for the analysis of amino acids and sulfur components.

Current and future trends in the development of IC include the introduction of ion-exchange packing materials with smaller particle sizes down to 4 µm, which allows method speedup or high-resolution IC. This pathway follows the one used in conventional HPLC with the transition to UHPLC techniques. In ion chromatography, however, the pathway of using smaller particle sizes and smaller column formats can only be followed to a certain extent due to the limited back pressure tolerance of metal-free components in the fluidic system of IC instruments. A growing number of applications are based on hyphenation, thus coupling ion chromatography with ICP–OES, ICP–MS, and ESI–MS. The advantage of coupling ICP with ion chromatography includes the ability to separate and detect metals with different oxidation states. The analytical interest in chemical speciation is based on the fact that the oxidation state of an element determines toxicity, environmental behavior, and biological effects. Hyphenation with ESI–MS provides the analyst with mass-selective information. Challenging applications such as the determination of emerging contaminants such as haloacetic acids, bromate, and perchlorate in water at trace levels by IC–ESI–MS/MS or the identification and the quantification of polar pesticides by coupling IC to high-resolution MS clearly demonstrate the need for MS hyphenation to achieve the required sensitivity and specificity.

Thus, ion chromatography has become an almost indispensable tool for the analysis of low- and high-molecular weight inorganic and organic anions and cations.

# RUSSIAN CHROMATOGRAPHY AND ITS PROSPECTS

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Chromatography, together with spectroscopy, is the most demanded and actively developing analytical method. It is known that the founder of world chromatography is the Russian scientist M.S. Tsvet (1903). Since its creation, Russian chromatography has occupied a worthy place in world science. Everyone knows the chromatographic works of N.A. Izmailov, M.S. Schreiber, V.A. Davankov, A. Makarov and other Russian scientists. The most active centers of chromatography development are located in Moscow, St. Petersburg, Voronezh, Samara, Novosibirsk, Krasnodar, Arkhangelsk and a number of other cities. These centers carry out serious scientific researches aimed at solving important fundamental and applied problems, train highly qualified young professionals.

To coordinate research in the field of chromatography, the Joint Commission on Chromatography was established in 2023 on the basis of the Scientific Councils of the Russian Academy of Sciences on Analytical and Physical Chemistry. The Commission considers the following tasks to be the most important in its work:

- activation of creation of Russian chromatographic equipment;
- increasing the number of training centers for specialists in the field of chromatography;
- restoration of the scientific specialty “chromatography and chromatographic instruments”;
- active participation of young scientists in solving the problems of Russian chromatography;
- creation of specialized chromatography centers to solve the problems of the main sectors of the Russian economy.

The Commission hopes that these tasks will be successfully solved in the coming years.

# THE ROLE OF CHROMATO-MASS SPECTROMETRIC MONITORING IN THE DEVELOPMENT AND IMPLEMENTATION OF ADVANCED TECHNOLOGIES IN INTENSIVE CARE

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The capabilities of modern chromatography-mass spectrometry equipment make it possible to overcome the difficult problems of determining low-molecular compounds in clinical samples with a complex composition, such as blood serum, cerebrospinal fluid, etc. Thanks to GC-MS and HPLC-MS, accurate measurement methods have been developed and validated for a number of metabolites of microbial origin, in particular, derivatives of aromatic amino acids, which are contained in biological fluids at very low concentrations (mmol/L or ng/L). It has been shown that the dynamics of concentrations of these metabolites is directly related to the frequency of complications and the risk of death in intensive care, and their significance exceeds all previously known biomarkers. Today, for an objective assessment of the effectiveness of certain life-saving therapeutic technologies or new medicines, monitoring of diagnostically significant metabolites based on GC-MS and/or HPLC-MS methods comes to the fore. It is difficult to overestimate the prospects of their implementation and new opportunities for the survival of patients at the highest risk.

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# NOVEL EFFICIENT STATIONARY PHASES FOR HYDROPHILIC INTERACTION LIQUID CHROMATOGRAPHY AND THEIR APPLICATION

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Hydrophilic interaction liquid chromatography (HILIC) is successfully used for solving complex analytical problems involving the separation of multicomponent mixtures. Due to the combination of various mechanisms such as partitioning, adsorption, ion exchange, and other types of interactions, it provides the simultaneous determination of substances from different classes in one analysis. A variety of hydrophilic stationary phases facilitates identifying and isolating polar substances, as well as separating structurally related compounds. Other advantages of HILIC mode involve simplifying sample preparation, avoiding derivatization, good compatibility with mass spectrometric detection, efficiency and rapidity of analysis. HILIC can solve various problems from many industries, being suitable for a wide range of analytical objects. Nowadays, this modern method has almost replaced affinity and size exclusion chromatography.

In this work, novel highly efficient stationary phases for HILIC were developed providing unique selectivity toward some classes of polar substances. Methods for hydrophilization of various substrates were proposed. The applicability for several HPLC modes was demonstrated for the obtained phases including reversed-phase, hydrophilic, chiral, and ion chromatography.

Approaches to separating multicomponent mixtures containing substances from different classes in one analysis were developed providing increased efficiency and significantly reduced time and labor costs. Application of the developed stationary phases to solving analytical problems from food, pharmaceutical, and biochemical industry was demonstrated including the kinetics study for enzymatic reactions, the composition and quality control of beverages, nutritional supplements, and pharmaceuticals.

*This work was supported by Russian Science Foundation through the grant № 20-13-00140.*

# EFFECT OF PRESSURE ON SORBATE RETENTION AND DESIGN CHARACTERISTICS IN «MONOMERIC» REVERSED-PHASE HPLC

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The only measured parameter in HPLC, retention time, is not convenient for characterizing the retention of sorbates, since it depends on the size of the chromatographic column and the feed rate of the mobile phase for the selected mobile phase compositions and the separation temperature. In addition, this parameter is not applicable for further calculations, since it includes the «dead time» of the column. Therefore, in a chemical experiment, «dead time» is also measured, for example, by the retention of a non-sorbed substance and the retention factor, its decimal or natural logarithm, is calculated for subsequent calculations.

However, in a series of studies in recent years, it has been shown that the retention factor may depend on the feed rate of the mobile phase, since this characteristic determines the pressure at the inlet to the column. At the same time, there are several theoretically justified reasons for this dependence at high pressures (hundreds of bar) for small molecules, and such a dependence is understandable for macromolecules prone to pressure-induced conformational transitions. In the work performed in our laboratory, it was found that the retention of anthocyanins significantly depends on pressure, whereas no such dependence was found for betacyanins. According to experimental data, these two types of glycosides differ in retention mechanisms: anthocyanins (glycosides of anthocyanidins) are retained by a float mechanism, penetrating into the grafted phase, while betacyanins (glycosides of betalaines) are retained by an adsorption mechanism.

Therefore, it was suggested that the dependence of sorbate retention on pressure (at relatively low pressures – up to 200 bar) depends on their structure and on the retention mechanism. In a series of subsequent studies, it was found that if the sorbate is retained by the adsorption mechanism, its retention does not depend on pressure. At the same time, the retention of sorbates with alkyl groups does not depend on pressure due to the specifics of the structure of the grafted reversed phase and the dependence of retention on pressure increases as the proportion of the absorption mechanism in retention increases.

# APPLICATION OF MATERIALS WITH SUPRAMOLECULAR CHIRALITY IN ADSORPTION AND CHROMATOGRAPHY

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The problem of separating enantiomers under chromatographic conditions remains relevant due to the insufficient enantioselectivity of chiral stationary phases, especially at high analyte concentrations. At the same time, the potential for increasing the applicability of chiral selectors based on molecular chirality in chromatography is almost exhausted. Therefore, the search for new enantioselective materials based on new approaches to chiral recognition is relevant. There are materials that do not have an asymmetric carbon atom, but exhibit supramolecular chirality. However, such materials have not become widespread in adsorption and chromatography. The reason for this is the lack of sufficient information about the mechanism of enantiomers separation.

Non-porous enantiomorphic crystals (quartz, retgersite, cytosine, etc.), zeolite-like porous structures, as well as various MOFs can serve as materials with supramolecular chirality. Based on a significant amount of accumulated data, the following conclusions were made about the possibilities of chiral recognition on such materials. It has been established that for enantioselectivity to occur, adsorption must be localized. Also, the concentration of adsorbate molecules on the crystals surface must be sufficient to form an ordered layer of enantiomer molecules. No enantioselectivity was observed during the formation of the second adsorbate layer. Chiral recognition occurs not to a single adsorbate molecule, but to an object of similar size - a layer of localized adsorbed molecules.

The adsorbents developed were used for the separation of enantiomers under both gas and liquid chromatography conditions. It has been shown that in liquid chromatography separations are accompanied by greater enantioselectivity due to the greater stability of the adsorption layer. The enantiomeric composition of a number of fine organic synthesis products was successfully analyzed under normal phase HPLC conditions.

*The financial support of Russian Science Foundation (project No 23-73-00119) is gratefully acknowledged.*

# THE PHYSICAL MEANING OF THE CORRECTED RETENTION VOLUME - POSSIBLE SOLUTION TO THE KNOWN PROBLEM

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Recently published in the Journal of Chromatography, articles by A. Kondor et. al.<sup>1</sup> and J. Sygusch et. al.<sup>2</sup> have again attracted the attention of chromatographers to the issue of the correct representation of the corrected retention volume  $V_R^o$ , which returns us to an intense discussion about the physical meaning of the corrected retention volume, held on the pages of «Chromatographia» more than 20 years ago<sup>3</sup>. The current IUPAC recommendation<sup>4</sup> does not provide for any other temperature correction other than bringing the temperature at which the retention volume is measured to the temperature of the column. However, in an effort to provide standard conditions for comparing retention data, Littlewood et al.<sup>5</sup> proposed to bring the values of the corrected retention volumes  $V_R^o$  reduced to a standard temperature of 0°C. Although the thermodynamic inconsistency of such «standardization» was noted during the above-mentioned discussion, and recently confirmed once again by experimental measurements<sup>1</sup>, it still remains a widely used method of «standardization» of results in IGC. The reason for such popularity of «standardization» implemented using gas laws can be seen in the fact that the IUPAC recommendation treats the corrected retention volume as the volume of gas measured at strictly defined pressure and temperature. At the same time, the IUPAC recommendation<sup>4</sup> emphasizes that the corrected retention volume does not depend on pressure, and this directly contradicts the gaseous nature of the corrected retention volume: after all, a gas whose volume does not depend on pressure does not exist in nature. Compressibility is an inherent property of gases. The nature of the corrected retention volume can be understood if we consider two chromatographic systems for which analytical solutions of mass-balance equations have been reported. The first system can be considered as an ideal chromatographic system with an incompressible mobile phase<sup>6</sup>. In such a system, the retention volume of analyte  $V_R^*$  is directly proportional to the constant of analyte distribution K between the mobile and the stationary phases:

$$V_R^* = V_M + V_S \times K, \quad \text{where } V_M \text{ and } V_S \text{ are volume of the mobile and the stationary phases, correspondingly.} \quad (1)$$

The second GC system meets all the requirements of the previous ideal system, but uses a compressible mobile phase<sup>7</sup>. For such a system, the distribution constant K correlates not with the measured retention volume of  $V_R$ , but with the corrected retention volume  $V_R^o$ :

$$V_R^o = V_M + V_S \times K \quad (2)$$

The right parts of equations 1 and 2 are identical and, accordingly, the left ones are equal, i.e.  $V_R^* = V_R^o = V_R \times j_3^2$  (3)

Thus, the James-Martin compressibility coefficient  $j_3^2$  allows us to move from the actually measured retention volume of the compressible mobile phase VR to the retention volume of the incompressible mobile phase in an ideal chromatographic system and, accordingly, to finding thermodynamic parameters. The mobile phase in an ideal GC system is not compressible, and no gas laws apply to it. Accordingly, they are not applicable to the corrected retention volume either. Unfortunately, this property of the corrected retention volume was very often ignored, which makes it necessary to make clarifications and corrections to the results obtained using «standardized» corrected volumes.

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# SORPTION AND CHROMATOGRAPHIC METHODS FOR RECOVERY AND SEPARATION OF RADIOACTIVE ELEMENTS AND DECONTAMINATION OF LIQUID RADIOACTIVE WASTE

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Currently, sorption and chromatographic methods are used for the recovery and separation of various radioactive elements, as well as for the decontamination of liquid radioactive wastes.

Since the mid-1980s of the 20th century, FSUE PO Mayak has been using sorption technology based on FS-10 ferrocyanide sorbents to recover cesium-137 from solutions after spent nuclear fuel reprocessing. By now, about two million curies of <sup>137</sup>Cs are produced in high-quality cesium salts for ionizing radiation sources.

The method of displacement complexing chromatography (DCC) is used for the radioactive rare earth and transplutonium elements recovery and separation. High-purity isotopes of americium, curium, promethium, samarium, etc., are needed to manufacture ionizing radiation sources, remote transplutonium elements, and fundamental research in nuclear physics. Several technologies based on the DCC method for producing these elements are created and implemented. A DCC technique is successfully tested to obtain high-purity lutetium and terbium isotopes for radiopharmaceutical production. Low and medium-activity level liquid radioactive waste (LRW) poses a high environmental hazard.

Sorption methods are also used for decontaminating various LRW types. Sorption-selective studies of a wide range of sorption materials resulted in a number of technologies for handling LRW at Rosatom enterprises.

Thus, the fundamental studies of sorption and chromatographic methods for recovering and separating various radioactive elements allowed for addressing several challenging issues in the radiochemical industry. The created technologies were of great importance for improving the industrial and defense capabilities of the Russian Federation.

# CHROMATOGRAPHIC METHODS FOR SEPARATION OF ISOTOPOLOGUES

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Organic compounds labeled with hydrogen isotopes (deuterium and tritium) are of great practical significance in various research investigations, including the study of the mechanism of complex chemical reactions, identification of products of catalytic transformations, pharmacokinetics and medicinal chemistry, various kinetic effects in biochemistry, applications in analytical chemistry as an almost ideal internal standards and for the isotope dilution method in mass spectrometry analysis and in many other areas of science and technology. Accordingly, the effectiveness of the use of compounds labeled with hydrogen isotopes is connected with the purity of the individual isotologues used and the possibility of their simple selective purification, separation and isolation at the preparative scale.

To solve this important and urgent problem, it is necessary to find out new ways to the separation and isolation of isotopologues, which is not an easy task, since deuterated compounds have only a slight change in the molecular weight of compounds and in some of the chemical properties of compounds.

This report is devoted to the use of HPLC for the separation of isotopologues with similar properties on various adsorbents<sup>1</sup>. Particular attention is paid to the possibility of using new microporous aluminosilicate sorbents (zeolites), as well as metal-organic frameworks and covalent organic frameworks, for which the condition of maximum compliance of the size of the compound molecule and its geometry with the size of the windows, pores and channels of the zeolites is met. In this case, any minor change in the configuration of the compounds and their properties can lead to a noticeable increase in the selectivity of separation. An additional increase in separation selectivity is expected due to a new kinetic selectivity effect.

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# MICROFLUIDIC ANALYTICAL SYSTEMS IN GAS ANALYSIS

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A pronounced trend in the development of modern instrument making is the miniaturization of analytical equipment in order to carry out specific types of analysis.<sup>1</sup> The advantages of micro-instruments include small dimensions, weight and rapidity of analysis. In addition, the use of micro-instruments allows for on-site analysis and real-time results, while significantly reducing the likelihood of changing the sample during storage and transportation, saving time and money for preservation and transportation of samples. The available field instruments and gas analyzers are significantly inferior to laboratory ones in terms of analytical characteristics and the range of analyzed objects. The use of miniature gas chromatographic modules through the use of modern technologies and materials, including microelectromechanical systems, opens up new opportunities, for example, remote control of technological processes, the state of the environment, ensuring safety in production, in mechanical engineering, in astronautics, as well as solving the problems of the oil and gas processing complex.

The report discusses the possibilities of creating detection devices based on microelectromechanical systems, gas chromatographic columns on various types of substrates, new types of dosing devices, including microfluidic thermal desorbers. Various methodological approaches to filling gas chromatographic columns with new sorbents and adsorbents using nanocarbon materials are considered. Sufficient attention is paid to the behavior of high-speed measurements, including two-dimensional gas chromatography.

The possibilities of implementing developed portable analytical systems in vital areas of medicine, food production and quality control, pharmaceuticals, ecology, etc. are discussed.

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# MACHINE LEARNING FOR MODELING RETENTION PARAMETERS OF PHARMACEUTICAL COMPOUNDS UNDER REVERSED-PHASE AND HYDROPHILIC CHROMATOGRAPHY CONDITIONS

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Pharmaceutical substances are complex mixtures containing structurally related impurities. While their analytical standards are not always available, retention ( $\log k$ , RT) modeling can provide additional support for the peak annotation. There are numerous ways to construct such models in a Quantitative Structure Retention Relationship (QSRR) approach and there are a lot of available web-applications and software which allow computing the basic physico-chemical properties and other molecular features and performing machine learning (ML). We employed nine different descriptor calculation tools combined with different feature selection methods (genetic algorithm (GA), stepwise, Boruta) and various ML modeling approaches (support vector machine (SVM), multiple linear regression (MLR), random forest (RF), XGBoost) in order to provide a reliable molecular interpretation of chromatographic retention behavior in different conditions. GA showed the most suitable performance as descriptor selection method, while in most cases SVM and XGBoost modeling gave satisfactory predictive characteristics. ChemoPy/RF approach demonstrated the best elution order predictivity through calculating complex 3D descriptors.

For larger datasets neural networks (NNs) can be applied to predict RT. The effectiveness and generalization ability of the constructed 1D CNN model was demonstrated with a transfer learning approach. Thus, we believe that the results of these studies can be used as a solid basis for retention modeling of small drug-like molecules in different LC conditions.

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# DOMESTIC SORBENTS AND COLUMNS FOR ANALYTICAL AND INDUSTRIAL CHROMATOGRAPHY

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Sorbents based on chemically modified silica have been developed. To use them in analytical practice and real industrial production, we have organized their manufacture, as well as the production of HPLC columns with a diameter from 2 to 110 mm.

Columns with the brand name **Diasfer®** and **Nautilus®** are popular both in scientific research and in regulatory analysis: pharmaceutical production, environmental monitoring, control of the safety and authenticity of food and feed.

Columns for reverse-phase chromatography are represented by sorbents with grafted alkyl radicals of various lengths (C1-C18), phenyl or cyanodecyl (C10CN) groups. Columns with nitrile, diol and amino groups are available for the normal phase, and **Nautilus® HILIC** sorbent is available for hydrophilic chromatography.

**Nautilus® E** is a sorbent for the enantiomer separations of amino acid, profens and  $\beta$ -blockers. Sorbent with immobilized iminodiacetic acid **Nautilus® IDA** is able to separate all lanthanides. For the analysis of anions by ion chromatography, we have started the production of **Nautilus® ION** columns.

The HPLC column of dynamic axial compression **AXIOMA®-100-HP** has a capacity sufficient for industrial purification of all therapeutic peptides produced in the country.

Low-pressure chromatographs and glass columns with a volume of up to 50 liters make it possible to implement technologies for the purification of recombinant and natural proteins. The technology of obtaining highly purified, virus-free immunoglobulin G, currently forms the basis for the preparation of the drug «Covid-globulin». During the pandemic, up to 56 tons of plasma per year from patients after covid were processed at the chromatographic complex. Our technology, equipment and columns are also used for the production of Fortelysin, an effective remedy for heart attacks and strokes.

# STRUCTURAL SELECTIVITY IN GAS ADSORPTION CHROMATOGRAPHY: ACHIEVEMENTS AND PROSPECTS

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The paper systematizes data on the structural selectivity of a large number of adsorbents used in modern gas adsorption chromatography. A critical analysis of the concept of adsorbent selectivity was performed, which is determined by their sensitivity to the features of the molecular structure of adsorbates, as well as the ability to various types of intermolecular interactions. It has been shown that the range of selectivity of adsorbents is determined by a combination of various factors - the spectrum of the manifested intermolecular interactions, geometric structure, fractality, as well as a number of physicochemical parameters. Analysis of a large array of GAC data on various sorbents allows us to talk about structural, energy, dimensional, and other types of selectivity.

We have developed a classification approach based on the concept of nD-dimensional structural selectivity of sorbents. The basis of the approach we are developing is the idea of the two-dimensional (2D) and three-dimensional (3D) nature of adsorption and absorption phenomena, respectively. Obviously, as in the case of classification by the type of intermolecular interactions implemented (according to A.V. Kiselev), the selectivity of the adsorbent should be evaluated for specific compounds. Obviously, among all the variety of molecular forms, one can find such compounds that have the most pronounced geometric similarity with respect to the dimension of the space of intermolecular interactions realized by the adsorption system. One of the criteria for choosing such selection molecules may be the principle of structural similarity in the spatial structure of the adsorbate and the field of adsorbent forces. So, flat or linear molecules will have the greatest affinity for the surface of a flat adsorbent (2D-selectivity), in the case of rough or volumetric sorbents (porous bodies, macrocyclic complexing agents, etc.), on the contrary, volumetric molecules will be characterized by greater affinity for the surface, the geometric dimensions of which are close to the size of the cavity or surface fractal in the sorbent.

# FEATURES OF GAS CHROMATOGRAPHIC ANALYSIS OF THERMALLY UNSTABLE COMPOUNDS

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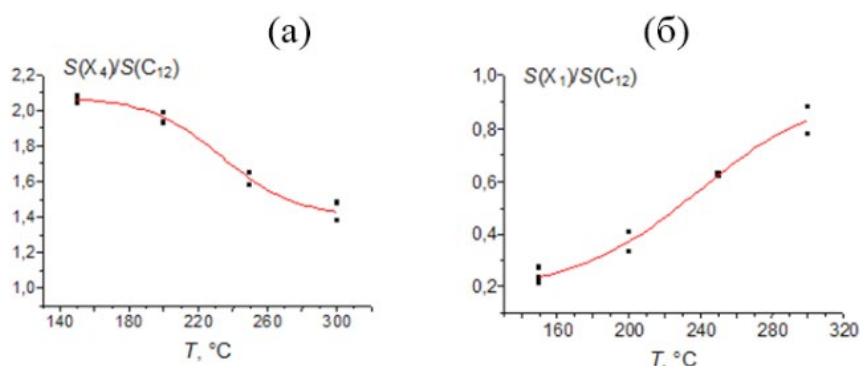
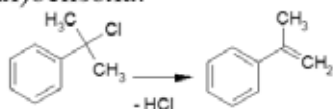
Thermal instability of analytes seems to be the principal restriction of chromatographic separation methods. In gas chromatography the main reasons of this is thermal decomposition of analytes, or their interaction with other constituents of samples. Such processes should be taken into account, for example, for products of free radical chlorination of hydrocarbons.

The variations of absolute areas of chromatographic peaks cannot be a control criterion for decomposition of unstable analytes due to so-called discrimination effects when dosing them using split ratio. However, it has been shown that their ratios to peak areas of thermally stable compounds follow the regularities of logistic regression<sup>1</sup>:

$$y = \frac{a}{1+b \exp(-kx)} + c \quad \lim_{x \rightarrow 0} y = \frac{a}{1+b} + c, \quad \lim_{x \rightarrow \infty} y = c \text{ при } k < 0 \quad \lim_{x \rightarrow \infty} y = a + c \text{ при } k > 0.$$

Approximation of the results using such regression model allows calculating the limiting values of the areas at  $T \rightarrow 0$  и  $T \rightarrow \infty$ , which are not distorted by thermal decomposition of components or their formation from other ones.

Образование  $\alpha$ -метилстирола  
в результате термического  
разложения (1-метил-1-хлор-  
этил)бензола:



**Figure 1.** The logistic approximation plots of the dependencies of the ratio of (1-methyl-1-chloroethyl)benzene peak areas  $[S(X_4)]$  and 1-methylethenylbenzene  $[S(X_1)]$  to the peak areas of n-dodecane  $C_{12}$  on temperature of injector of gas chromatograph: a) the higher (left) limit  $[\lim(S_{rel})]_L$  is  $2.08 \pm 0.04$ , the lower (right) limit  $[\lim(S_{rel})]_R$  is  $1.40 \pm 0.05$ ; б) the lower (left) limit  $[\lim(S_{rel})]_L$  is  $0.18 \pm 0.08$ , the higher (right) limit  $[\lim(S_{rel})]_R$  is  $0.94 \pm 0.14$ . Split ratio is 10 : 1.

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# CHROMATOGRAPHY-MASS SPECTROMETRIC (GC-MS) DETERMINATION OF HYDROXYLATED PAHS IN URINE

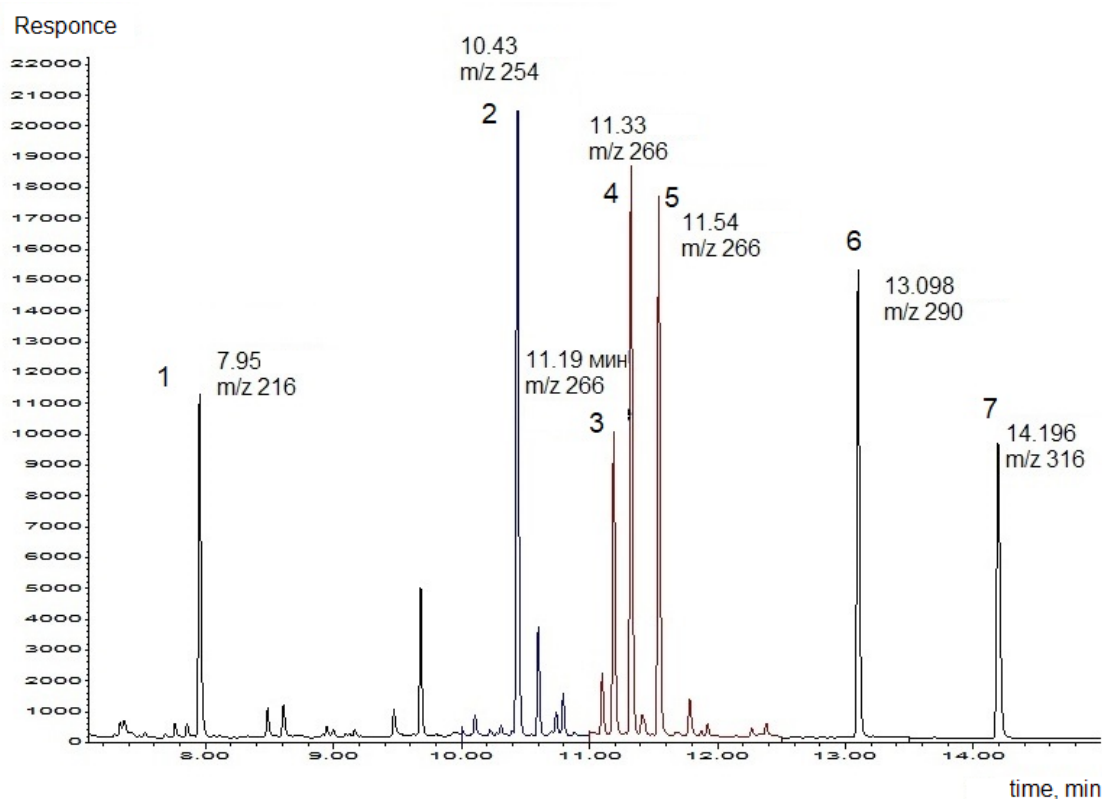
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Carcinogenic polycyclic aromatic hydrocarbons (PAHs) are excreted in the urine in the form of their hydroxylated derivatives (OH-PAHs) during metabolism in the human body.

A simple and sensitive method has been developed for the determination of OH-PAHs (2-hydroxynaphthalene, 2-hydroxyfluorene, 9-hydroxyphenanthrene, 3-hydroxyphenanthrene, 2-hydroxyphenanthrene, 1-hydroxypyrene, 6-hydroxychrysene) in urine by GC-MS in the range of 0.5 – 100 ng/ml.

Analytes were extracted by dispersion liquid-liquid microextraction (DLLME) with trichloromethane in an acidic medium. Derivatization was performed with a silylating reagent BSTFA in the injector port at 300 °C. Ethanol was experimentally selected as a dispersing solvent, and using a three-factor experiment, the optimal ratio of the following factors was determined according to a predetermined plan: pH, ethanol volume, extraction time. GC-MS measurement was carried out on a high-temperature HT-8 capillary column in the mode of temperature gradient and selective ion monitoring (Fig.1).



**Figure 1.** Chromatogram of a mixture of OH-PAHs in urine with concentrations of 10 ng/ml (1 – 2-hydroxynaphthalene, 2 – 2-hydroxyfluorene, 3 – 9-hydroxyphenanthrene, 4 – 3-hydroxyphenanthrene, 5 – 2-hydroxyphenanthrene, 6 – 1-hydroxypyrene, 7 – 6-hydroxychrysene)

# THEORETICAL FOUNDATIONS AND PARTICULARITIES OF THE APPLICATION OF THE VAN'T HOFF EQUATION IN CHROMATOGRAPHY

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The van't Hoff equation relates the equilibrium constant ( $K$ ) of a process its heat effect ( $\Delta X^0$ ):

$$\left( \frac{d \ln K}{dT} \right)_{\Pi} = \frac{\Delta X^0}{RT^2}, \Pi = P, V$$

Under isobaric conditions ( $\Pi = P$ ), the equilibrium constant  $K_p$  is used, and the heat effect is the change in enthalpy, but under isochoric conditions ( $\Pi = V$ ), the equilibrium constant  $K_c$  is used, and the heat effect is the change in internal energy. In chromatography, the heat effect of adsorption is derived from the temperature dependence of the retention factor ( $k$ ) that is related to the Henry constant ( $K_H$ ) by the relation  $k = K_{H\phi}$ , where  $\phi$  is the phase ratio. The problem with this application of the van't Hoff equation is that it describes equilibrium processes, whereas a chromatographic experiment carried out in an open flow system is nonequilibrium. Other important issues are the dependence of  $\phi$  on temperature and, in the case of liquid chromatography, the non-identity of the Henry constant and the adsorption equilibrium constant<sup>1</sup>. This report shows that a chromatographic column can be considered as a quasi-isobaric system and, thus, the application of the van't Hoff isobar equation to it is justified. The physical meaning of the quantity of the adsorption heat effect obtained under conditions of a pressure gradient is discussed, and an equation for the average heat effect over the column is given. Various sources of errors in determining the thermodynamic characteristics of adsorption and ways to eliminate them are considered.

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# GAS CHROMATOGRAPHY WITH ATMOSPHERIC AIR AS CARRIER GAS

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The relevance of using atmospheric air as carrier gas arose due to the need to have express gas chromatographs (GCs) that are more convenient in field work for the detection of explosives. In the process of completing the task, the main components of the GC were developed and tested. Vortex sampling device; injection device with interchangeable injectors: concentrator, syringe and gas loop with gas sampling by a built-in pump; multicapillary gas chromatographic column (M-GCC); ion detector with tunable selectivity (IDTS); a source of clean air with a small-sized compressor and an original filter, restored from the device's network<sup>1,2</sup>. Based on the listed elements, the explosive detector «EKHO-V» was created. By order of the Federal Security Service of the Russian Federation, the «Shpinat» explosive detector was developed. It is produced by the Federal State Unitary Enterprise «SPA Analitpribor» in Smolensk.

Further development of the GC series «EKHO-V» is associated with the use of a photo-ionization detector (PhID). GCs with air as carrier gas have been developed: «EKHO-V-PhID» for analysis of the content of organic compounds in various media (gases, water and solids); a complex based on the «EKHO-V-PhID» GC with a personal exhalation sampling device, followed by analysis of exhaled air for the content of risk markers for the first type diabetes mellitus; complex based on GC «EKHO-V-PhID» and passive concentrators for the analysis of dispersed hydrocarbons when searching for oil fields<sup>1,2</sup>.

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# FEATURES OF EXTRACTION-CHROMATOGRAPHIC SEPARATION OF YTTERBIUM AND LUTETIUM USING 2-ETHYLHEXYLPHOSPHONIC ACID MONO(2-ETHYLHEXYL) ESTER

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Extraction-chromatographic isolation of  $^{177}\text{Lu}$  from irradiated ytterbium target using 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester HEH [EHP] as an extractant was proposed in work<sup>1</sup>. A significant influence of ytterbium on the behavior of lutetium was noted by the authors of the method, but this aspect of separation was not studied quantitatively. The purpose of this work was to assess the influence of the mass of ytterbium on the behavior of ytterbium and lutetium during their separation in a column with a diameter of 10 and a height of 100 mm containing a sorbent – an analogue of the commercially available LN2 Resin.

It has been shown that for a column of selected size, an increase in the Yb mass from 1 to 25 mg leads to a shift in the onset of the output, the position of the maximum, and the width of the Yb peak. The distribution coefficient of ytterbium ( $D_{Yb}$ ), calculated from the elution curve, is related to its mass ( $m_{Yb}$ ) with the following expression:  $\lg D_{Yb} = -0.023m_{Yb} + 1.442$

This dependence allows of calculation of the elution curve maximum position. The onset of Yb yield, expressed in column volumes, is described by the expression:  $\lg A_{Yb} = -0.02m_{Yb} + 0.63$

The position of the maximum of the lutetium peak remains unchanged until the mass of ytterbium is increased to 10 mg, but a significant distortion of the peak shape and an earlier release of Lu are noted. The beginning of the yield of lutetium is related to the mass of ytterbium by the expression:  $\lg A_{Lu} = -0.015m_{Yb} + 0.85$

The obtained dependencies are useful for scaling-up of the separation procedure, however, taken together they indicate the limited productivity of extraction chromatography as an independent method for separating macro amounts of ytterbium and micro amounts of lutetium.

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# EXHALED BREATH LUNG CANCER DIAGNOSTICS USING GAS CHROMATOGRAPHY-MASS SPECTROMETRY

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Development and implementation of non-invasive approaches for lung cancer diagnosing can significantly improve a quality of treatment due to the simplicity of the analysis procedure and absence of additional requirements for the sterility of equipment and qualifications of medical personnel.

Exhaled breath, as a noninvasive diagnostic tool, is one of the most interesting objects of analysis. Potential exhaled breath is being actively studied by many scientific groups for the various diseases diagnostics. As a rule, the studies are conducted as follows: exhaled breath analysis of both cohorts: patients suffering from the disease and healthy individuals is conducted with subsequent identification of biomarkers. Nonetheless, many factors can influence on exhaled breath composition besides the disease. Additionally, diagnostic model, based on «norm -pathology» principle, does not consider influence of comorbidities as well as not sensitive to the patients with other diseases. On the other hand, variability inside of cohort of lung cancer patients can exist, which can affect diagnostic model accuracy.

This study presents the results of exhaled breath GC-MS analysis of 4 cohorts of volunteers: patients with lung cancer, patients with cancer of other localizations, patients with non-malignant tumors and other lung diseases and healthy individuals. The factors, which can potentially influence the exhaled breath composition, are analyzed with subsequent estimation of possibility to diagnose cancer and other lung diseases by exhaled breath.

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# RETENTION OF SOME AZOLES AND AZINES IN REVERSED-PHASE AND HYDROPHILIC HPLC-MS

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The separation of various azoles and azines is an urgent problem in biochemistry, medicine, food and environmental analysis. There are many techniques to solve this problem using high-performance liquid chromatography-mass spectrometry, while the main sorbent for separation is octadecylsilyl silica gel<sup>1</sup>. However, many azoles and azines, due to their polarity, demonstrate poor separation on reversed phases when eluting from aqueous-organic mixtures without additives. The solution of this problem may be the switch from reversed-phase to hydrophilic chromatography<sup>2</sup>.

In the present work, a comparative retention characterization of 19 azoles and azines in reversed-phase and hydrophilic HPLC-MS modes was carried out. Elution for reversed-phase systems was done from water-acetonitrile solutions with and without acid-base additives. Elution in hydrophilic mode was performed using buffer containing 5 mM aqueous solution of ammonium formate. It was shown that the use of unsupported silica gel in the hydrophilic chromatography allows satisfactory separation of azoles, including isomeric ones, with obtaining narrow symmetric peaks. However, unsupported silica gel does not have a pronounced selectivity advantage over octadecyl silica gel for the separation of azine molecules in this technique. The effect of acid-base additives in the mobile phase on reversed-phase separation was also examined. It was found that the most optimal results of chromatographic separation and ionization in electrospray mode are achieved with the introduction of 0.1% formic acid solution.

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# SOME ALGORITHMS OF CHROMATOGRAPHIC DATA PROCESSING

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The publication discusses algorithms, developed by Ampersand Ltd. team during 36 years of its history, resolving several typical problems of chromatographic data processing:

- How to evaluate Signal/Noise ratio? Pharmacopeia uses peak-to peak measure of noise, but this measure is biased and inconsistent<sup>1</sup>.
- To smooth or not to smooth? Explicit and implicit smoothing. Does optimal filter exist, and, if YES, how does it look like? What is the price of optimality<sup>2-5</sup>?
- How to process data in the case of very narrow peaks<sup>6</sup>?
- How to calculate the shape of chromatographic peak<sup>7</sup>?
- What to do, if the peaks are overlapped in the case of one and multi-channel chromatography? How can one evaluate peak homogeneity<sup>8-10</sup>?
- How to implement internal standard calculations properly<sup>11-14</sup>

## **Literature**

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# ANALYTICAL CAPABILITIES OF SMART MATERIALS IN COMBINATION WITH HPLC METHODS IN THE ANALYSIS OF NATURAL OBJECTS

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Recent years, scientists have successfully solved the problem of complex matrix analysis using so-called smart materials. These materials have properties that can significantly affect the selectivity of analytes extraction and concentration, as well as simplify the sample preparation process. For natural objects such as medicinal plants, it is important to develop methods for profiling in order to obtain characteristic chromatographic profiles. This can help confirm the authenticity of the raw materials and identify promising biologically active substances (BAS). Another important area is the search for materials for selective solid-phase microextraction of BAS from natural objects.

The analytical capabilities of ionic liquids (IL) and their closest analogues deep eutectic solvents (DES) are being actively explored as promising extractants for BAS from plant materials. The search for these solvents, combined with approaches of design of experiment, can increase sensitivity and shorten the analytical cycle. Equally significant is the compatibility of these materials with subsequent mass spectrometry detection of the extracted products.

The goal of the study was to develop and validate methods for extracting BAS from natural samples using smart materials such as imidazolium ILs and DESs based on choline chloride, along with magnetic nanoparticles, followed by HPLC analysis.

A new method for microextraction of polar analytes was proposed using pH-switching DES. The method was validated for an extraction system containing choline chloride and urea (1:2 molar ratio). The analytical potential of this approach was demonstrated on various plant samples, including *Iris sibirica* L., *Citrus reticulata* B., *Scutellaria baicalensis* G., *Hypericum perforatum* L. Compatibility with HPLC-MS was also shown. Optimization of extraction conditions was performed, and comparative evaluation of the method was conducted for two samples: *Iris sibirica* L. leaf and *Scutellaria baicalensis* G. root. LOD of the method was 50 ng/mL.

For extraction low-polarity compounds from aqueous extracts, salts of 1-hexyl-3-methylimidazolium were found to be promising. Using HPLC methods, the influence of various factors was revealed, such as the type of anion, mass of IL (ionic liquid), stage of salting, type of dispersion, and dispersing solvent. By optimizing the dispersion time, extract volume, and dispersing solvent volume using a central composite design, we were able to optimize the process. The proposed approach was validated and tested for *Iris sibirica* L. and *Scutellaria baicalensis* G., resulting in comparative quantitative characteristics such as enrichment factor and matrix effect. LOD of the method was 21 ng/mL.

Additionally, first syntheses of composite magnetic nanoparticles with selective coatings were carried out, and the potential applications of these nanoparticles in the analysis of natural objects were demonstrated.

Thus, the usage of DES and IL as receiving phases in the analysis of plant samples allow to selectively extract polar and low-polar analytes from complex plant matrices for subsequent sensitive determination of biologically active substances (BAS) using HPLC-UV and HPLC-MS.

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# HEATRESISTANT POLYMER SORBENTS POLYNAPHTHAYLENEBENZIMIDAZOLES FOR GAS CHROMATOGRAPHIC SEPARATION AND CONCENTRATION OF VOLATILE SUBSTANCES

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The use of heat-resistant polymer sorbents of polynaphthaylenebenzimidazoles (PNBI-1-4) for gas chromatographic separation and concentration of volatile substances with a boiling point from -56 to +400°C from poorly sorbed gases, such as air. The temperature limit for the use of sorbents is 480-500°C, the specific surface is 20-30 m<sup>2</sup>/g<sup>1</sup>.

PNBI-1-4 can be used to concentrate impurities of volatile compounds released from wood, composite and polymer materials, to analyze mixtures of compounds of different geometric structures, to determine impurities of cyclic and branched compounds in compounds of normal structure, for the separation of saturated, unsaturated, aromatic and heterocyclic compounds, for the determination of water in organic compounds, for the analysis of air, CO and CO<sub>2</sub>.

It has been established that PNBI-1-4, compared to tenax, have large retention volumes V<sub>g</sub> (ml/g) for organic substances: formaldehyde, ammonia, methanol, phenol, vinyl chloride, benzene, toluene, ethylbenzene, styrene and others released during production and operation of composite, wood and polymer materials. For example, at 20°C, the specific retention volume (ml/g) is equal on tenax for ammonia - 13, formaldehyde - 46, methanol - 231, on PNBI-1-4 for ammonia - 360-402, formaldehyde - 736-794, methanol - 25130-26700. A similar increase in V<sub>g</sub> is observed for other organic substances.

This makes it possible to accumulate significant amounts of these components in a concentrator with PNB-1-4 before breakthrough during sanitary-chemical studies and is a significant advantage compared to Tenax. To ensure compact input of concentrated volatile organic substances into the column for separation, desorption is carried out at a temperature of 200-320°C. It is important to note that the shape of the chromatographic peaks of the analyzed substances practically does not change compared to direct injection of the vapor mixture with a gas syringe.

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# ROLE OF CHROMATOGRAPHY IN THE DEVELOPMENT OF MODERN VACCINOLOGY

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Vaccine prophylaxis is an integral part of life in modern society. The National Calendar of Preventive Vaccinations (NCPV) is based on the use of 12 mandatory vaccines to prevent the most serious childhood infections and 10 vaccines to protect adults from the most dangerous infections.

The use of safe and effective vaccines is therefore an important strategic aspect of protecting the population from the serious consequences of infectious diseases, and chromatography plays a special role in the development of modern vaccines and their production.

In the technological process of vaccine production, chromatography is used to purify antigens contained in vaccines and to control all technological steps of vaccine production.

Chromatography has proven to be an indispensable method in the production and control of recombinant vaccines against pandemic infections such as influenza and COVID-19.

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# STUDYING VOLATILE ORGANIC COMPOUNDS THE COMPLEX FORMATION WITH CYCLODEXTRINS IN POLYMER SYSTEMS BY REVERSE GAS CHROMATOGRAPHY METHOD

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The relevance of studying the properties of cyclodextrin-containing systems is due to the ability of these macrocycles to form «guest-host» inclusion complexes with a variety of inorganic and organic compounds. This property is widely used in sorption and separation technologies, in particular, for isomeraselective separation of optical and structural isomers of organic substances by gas chromatography.

The purpose of this work was to study the sorption and complexing properties of polymer-macrocyclic systems in relation to organic compounds by inverse gas chromatography.

Two polymers of different polarity were considered as a polymer matrix: polyphenylmethylsiloxane (PFMS) and polyethylene glycol (PEG-400).  $\beta$ -Cyclodextrin derivatives (*heptakis*(2,3,6-tri-*O*-methyl- $\beta$ -cyclodextrin, *heptakis*(2,6-di-*O*-methyl- $\beta$ -cyclodextrin and 2-hydroxypropyl- $\beta$ -cyclodextrin) were considered as macrocyclic components.

Analysis of the thermodynamic functions of sorption indicates the implementation of inner-sphere and/or outer-sphere «guest-host» complex formation in the studied phases.

It has been established that systems with permethylated  $\beta$ -cyclodextrin have high selectivity towards structural isomers of xylene ( $\alpha_{m/p} > 1.1$  at 80 °C). High meta-para selectivity is maintained throughout the entire temperature range studied (80-130 °C) for a system based on low-polar PFMS. High enantioselectivity towards low-polar isomers of terpene compounds was found for the stationary phase «PEG – 2-hydroxypropyl- $\beta$ -cyclodextrin». This is explained by the hydrophobic effect, as a result of which it is preferable for non-polar and low-polar terpene molecules to be in the hydrophobic cavity of the macrocycle than in a polar solvent.

# APPLICATION OF STIR-BAR SORPTIVE EXTRACTION IN GAS CHROMATOGRAPHY-MASS SPECTROMETRIC ANALYSIS OF ARCTIC SNOW

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A key challenge in using GC-HRMS for studying Arctic snow is sample preparation, which must ensure efficient extraction and concentration of analytes present in ultra-trace concentrations. Traditional methods of sample preparation (LLE and SPE) involve the use of large volumes of extractant, the concentration of which leads to the appearance of background signals of microimpurities in chromatograms, making it difficult to search for minor compounds in snow. To solve this problem, we have proposed an alternative approach to snow sample preparation, based on stir-bar sorptive extraction (SBSE), implemented using a magnetic stirrer with a sorption coating. For its testing, a test mixture of 76 priority semi-volatile organic pollutants of various classes was used (in accordance with EPA method 8270). The use of a polydimethylsiloxane coating during extraction of 100 ml of an aqueous solution for 3 hours followed by direct thermal desorption of analytes and GC-HRMS analysis made it possible to reliably detect more than 60 analytes of various classes, among which quantitative assessment is possible for 15 analytes. Comparison the effectiveness of the developed approach with the LLE and SPE methods showed an increase in the sensitivity of SBSE by several orders of magnitude.

Application of the developed approach to the analysis of priority organic pollutants in snow sampled in the Arctic zone made it possible to identify 29 components from the list of priority air pollutants in concentrations from 0.09 to 51 ng/l. Based on the results of non-target screening, over 200 organic compounds of various classes were detected, the concentration of which ranged from 0.01 to 500 ng/l.

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# APPLICATION OF THE PLANAR MICROFLUIDIC THERMAL DESORBER FOR THE ANALYSIS OF VOLATILE ORGANIC COMPOUNDS IN AMBIENT AIR

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A current trend in modern instrument engineering is the creation of hardware for conducting analytical analysis in the sampling area. However, the detection limits of portable devices do not provide the required detection limit. To solve this problem, it is necessary to use concentration methods, one of which is thermal desorption.

The goal of the work was to develop a portable planar microthermal desorber with the ability to perform on-site analysis.

The designed microthermal desorber includes a planar column, which is a sorption cartridge, gas communications and an electronic board.

A mixture of PGS pentane and iso-pentane with concentrations of 2.5 ppm and 2.2 ppm, respectively, was used as the studied volatile organic compounds for analysis.

At the sorption stage, the planar column was cooled ( $-10^{\circ}\text{C}$ ) and the temperature stabilized.

At the next stage, a volume of 300 ml of the analyzed gas was passed through the planar column.

At the desorption stage ( $85^{\circ}\text{C}$ ), a sample was taken and introduced into a portable gas chromatograph for the purpose of gas chromatographic analysis. The volume of the gas sample taken from the planar microthermal desorber was 5 ml.

The full operating cycle time of the developed planar microthermal desorber was 23 minutes. The process was controlled automatically.

In the process of studying the concentration of pentane and iso-pentane, the concentration of pentane after concentration was 117 ppm, and iso-pentane - 96 ppm. This fact indicates a concentration coefficient equal to  $K = 45$ .

# SORPTION OF PETROLEUM VOLATILE ORGANIC COMPOUNDS ON CARBON SORBENT FROM RICE HUSK

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Sorption purification methods are widely used in petroleum pollution of the environment. Rice husk, a by-product of the rice processing industry, is produced in large quantities as waste every year. Due to its surface characteristics, activated carbon adsorbent obtained from rice husk ash can be used as a sorbent for various pollutants, including those of petroleum origin. The purpose of this work is to study the sorption properties of a carbon sorbent obtained from rice husks using the example of volatile organic compounds (VOCs) of oil.

In this work, the physicochemical characteristics of a carbon sorbent obtained from rice husk were studied, the optimal time for passive sorption of oil VOCs was determined using thermal desorption GC-MS (GC-MS/TD), and the possibility of its practical use was assessed.

The specific surface area of the sorbent is 590 m<sup>2</sup>/g; basically, the surface of the sample is represented by mesopores with a diameter of 2÷10 nm. The elemental composition of the surface is represented by atoms of oxygen, carbon, nitrogen with microimpurities of calcium and silicon. In turn, oxygen and nitrogen are in different chemical environments with a predominance of hydroxyl, carboxyl, ester and amino groups.

The kinetics of the adsorption of oil vapors on a carbon sorbent from rice husk was studied and it was found that the kinetic dependence is described by a pseudo  $n$ -th order model with a reaction order of  $n = 2.1$  and a maximum saturation  $m_{\max} = 0.1620$  g/g of sorbent.

The dependence of the sorption time on the amount of sorbed components was obtained using GC-MS/TD, the optimal passive sorption time is 200 min. The relative standard deviation corresponds to the error of the method.

The completeness of desorption of oil VOCs from a carbon sorbent has been assessed: for 6 stages, the completeness of desorption is more than >80%. Thus, this carbon sorbent is suitable only for one-time use (for example, for treating wastewater from oil pollution or for forecasting during geological exploration).

# FAST GC SEPARATION ON MULTICAPILLARY COLUMNS IN COMBINATION WITH ATMOSPHERIC PRESSURE CHEMICAL IONIZATION MASS SPECTROMETRIC DETECTOR

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Atmospheric pressure chemical ionization (APCI) mass spectrometry is often considered as a promising method for detecting trace amount of hazardous substances, since it is characterized by high sensitivity and specificity.

Despite the high selectivity of APCI, the presence of concomitant substances in the samples may distort the results of the analysis. This problem is significantly aggravated for samples taken by the contact method containing matrix substances in an abnormal amount.

The report presents the results of the development of an analytical scheme that increases the reliability of the analysis of samples of complex composition, combining fast GC separation on multicapillary columns (MCC) with a small-sized mass spectrometric detector with APCI, previously developed in the Laboratory of Field Analytical and Measuring Technologies of IPGG<sup>1</sup>.

The issues of practical implementation of this tandem scheme from the point of view of adaptation of a mass spectrometric APCI ion source and selection of optimal parameters of the MCC are discussed. The advantages of a MCC for use in such a configuration are noted: low gas dynamic resistance, the ability to operate in a wide range of carrier gas speeds, high capacity, small dimensions. In the context of import substitution, it is important to have our own technology for manufacturing MCC based on materials of domestic production.

As an example, the result of the analysis of the composition of free fatty acids C12-C18 in the lipid layer on human skin with a GC separation time of less than 1 minute is presented.

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# DETERMINATION OF AROMATIC, FATTY AND DICARBOXYLIC ACIDS IN BLOOD SERUM AND CEREBROSPINAL FLUID BY GAS AND HIGH- PERFORMANCE LIQUID CHROMATOGRAPHY-MASS SPECTROMETRY METHODS FOR THE PURPOSES OF PREDICTION AND MONITORING THE CONDITION OF PATIENTS IN REANIMATOLOGY

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Critically ill patients admitted to intensive care units, either after planned surgery or during emergency hospitalization, are patients at high risk of developing infectious complications and unfavorable outcome. Along with the use of clinical scales and the use of various biomarkers, a scientific search is being conducted for new markers of critical illness with high sensitivity and specificity and a noticeable response to treatment. Microbial (metabolites of aromatic  $\alpha$ -amino acids tyrosine, phenylalanine and tryptophan and short-chain fatty acids) and mitochondrial metabolites (dicarboxylic acids from the Krebs cycle) are potentially significant markers, since they reflect dysfunction of the gut microbiota in critical conditions, and can be used in clinical practice in patients of different groups. To date, a number of methodological solutions have been developed for the simultaneous determination of metabolites of different groups (phenyl-, indole-containing, short-chain fatty and dicarboxylic acids) in biological samples (blood serum of healthy donors and critically ill patients with various pathologies, cerebrospinal fluid of neurosurgical patients) by gas and high-performance liquid chromatography-mass spectrometry with subsequent use for the purposes of characterization, monitoring and prognosis of the outcome and development of postoperative complications in critically ill patients. The results obtained demonstrate that targeted monitoring of low-molecular-weight metabolites measured by chromatography-mass spectrometry methods can objectify indications and provide predictability in the treatment of patients in intensive care units, and the most diagnostically significant metabolites can be used as target markers in life-threatening conditions.

# PASSIVE SORPTION OF VOLATILE COMPOUNDS ON NEW COMPOSITE MATERIALS BASED ON SILICON CARBIDE AND THEIR SUBSEQUENT IDENTIFICATION BY GC/MS METHOD WITH THERMAL DESORPTION

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One of the application areas of passive sorption is areal geochemical survey (AGS) - search for oil fields. The method consists of sorption of soil air components using sorption cartridges, which are placed in small depressions in the soil. The sorbents are then analyzed using gas chromatography (GC) with thermal desorption. Since volatile components of oil migrate to the surface layers of the soil, their presence or absence in the soil air can be used to judge the presence of oil in a given area.

Currently, most oil field identification applications use commercially available polymer materials such as Tenax-TA. However, such sorbents often have some disadvantages: they cannot work in conditions of high humidity, and are thermally unstable at temperatures above 280°C. In addition, such sorbents are not produced in Russia, so they have a high price.

Therefore, currently an urgent task in analytical chemistry is the search for alternative materials for creating sorbents for capturing volatile substances, in particular, hydrocarbon markers of oil. Scientists from MSU and NUST MISIS develop composite materials based on silicon carbide, which have not previously been used for oil exploration geochemistry. Sorbents based on silicon carbide and styrene-butadiene rubber (SR) have a monolithic structure, high mechanical strength, the ability to regenerate and chemical resistance in acidic and alkaline environments.

Thus, the purpose of this work is to evaluate the possibility of using new composite sorbers based on silicon carbide and SBR for the passive sorption of VOCs with their subsequent gas chromatographic analysis with thermal desorption.

# THERMAL DESORPTION GAS CHROMATOGRAPHY - MASS SPECTROMETRY: A NEW APPROACH TO MONITORING THE CONTAMINATION OF PEAT BOG SOILS WITH ROCKET FUEL TRANSFORMATION PRODUCTS

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One of the key aspects of the functioning of ground-based space infrastructure is the environmental support of rocket space-rocket activity, an important place in which is given to solving the problems of controlling the pollution of environmental objects with highly toxic rocket fuel based on 1,1-dimethylhydrazine and its transformation products. Such objects primarily include peat bog soils, characteristic of most areas where spent parts of launch vehicles fall on the territory of the Russian Federation. In this regard, there is a need to create a set of methods for the rapid and highly sensitive determination of transformation products of 1,1-dimethylhydrazine in this type of soil.

This study proposes an approach for the simultaneous determination of a wide range of nitrogen-containing UDMH oxidation products based on direct thermal desorption of analytes from peat soil and subsequent determination by high-resolution GC-MS. The approach is characterized by its simplicity, lack of sample preparation, and is also a «green» alternative to existing methods, while benefiting in sensitivity. It has been established that the introduction of 10 µl of 10% NaOH into a 3 mg soil sample with moisture content 70% ensures the achievement of high (30-100%) degrees of extraction at relatively low thermal desorption temperatures (200°C) for a duration of 30 minutes. Testing was carried out on real objects, in which 11 out of 13 analytes were detected in the concentration range of 50-196100 µg/kg. As a result of non-target screening, 40-100 nitrogen-containing transformation products were detected in soil samples contaminated with rocket fuel.

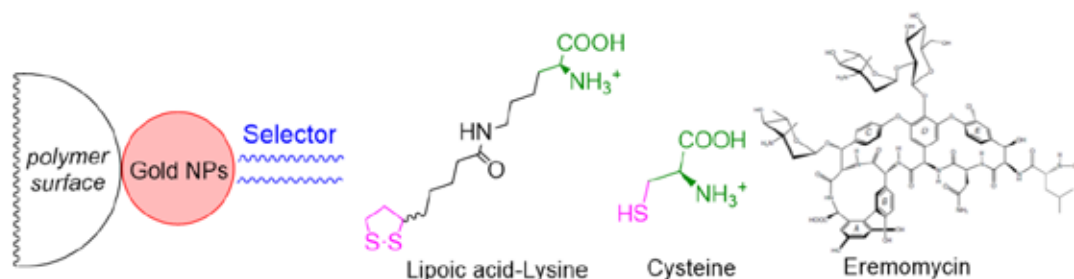
*This work was supported by the Ministry of Science and Higher Education of the Russian Federation (state assignment project FSRU-2024-0003)*

# FUNCTIONAL MATERIALS WITH GOLD NANOPARTICLES AS STATIONARY PHASES FOR HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY

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The use of functional nanohybrid materials for preparation of new stationary phases is one of the intensively developing directions in liquid chromatography<sup>1</sup>. The creation of chiral stationary phases is an topical challenge. A new approach to the synthesis of polymeric nanohybrid materials with gold nanoparticles (GNPs) is presented and the application of such sorbents in HPLC is investigated. GNPs allow easy functionalization of the polymer matrix. Two types of amino acids – bare and with the spacer to remove them from the matrix surface, as well as macrocyclic antibiotics act as selectors.



Studies by various instrumental methods have shown that the use of GNPs allows to increase the functional surface area. The immobilization efficiency of selectors is comparable to covalent bonding.

**Table 1.** Comparison of column efficiency

| Stationary phase     | N/m     |         |
|----------------------|---------|---------|
|                      | Acetone | Toluene |
| PS-DVB-Au-Eremomycin | 1830    | 810     |
| PS-DVB-Eremomycin    | 690     | 420     |

The obtained materials were used for the separation of mixtures of different nature in reversed-phase, polar organic and hydrophilic modes of chromatography. The sorbents showed enantioselectivity to profens,  $\beta$ -blockers, amino acids and their derivatives, which suggests the versatility of the resulting chiral stationary phases.

# MASS SPECTROMETRY AS A TOOL FOR PHYSICAL AND CHEMICAL RESEARCH AND A MEANS FOR CONTROL OF MODERN MATERIALS

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Modern analytical methods include gas chromatography-mass spectrometry techniques, which in most cases are used when it is necessary to identify compounds in a complex mixture (often in trace quantities). Chromatography-mass spectrometry has proven to be indispensable in this area. Also, separately, mass spectrometry is widely used for quantitative analysis and identification in high-resolution mode. For such work, soft ionization methods are used, since it is necessary to obtain a molecular ion.

Mass spectrometry is also used in the field of surface physicochemistry. The authors showed that the laser desorption/ionization mass spectrometry method allows surface monitoring over a wide area and with high resolution. In this case, not only a targeted search is possible, but also the identification of unknown compounds with structure confirmation in high resolution mode. The authors have developed a method for constructing surface diagrams with the ability to extract distributions of specific compounds. The method is successfully used to study structural materials to search for contaminants, technological impurities and toxic products introduced as a result of operation. The method is also successfully used to search for corrosion damage to metal surfaces and study the mechanisms of operation of inhibitors. The work also shows the possibility of studying non-metallic materials.

Also, mass spectrometry allows you to study the ionization processes themselves that take place in the source and provide a lot of useful information about metastable forms of existence. The authors examined a number of inorganic and organic compounds using laser desorption/ionization mass spectrometry and electrospray mass spectrometry and found that the nature of the compounds significantly influences the ionization mechanisms. It has been shown that during ionization, not only the disintegration of molecules is possible, but also their association, and this process can be controlled by changing the parameters of the device or the composition of the sample.

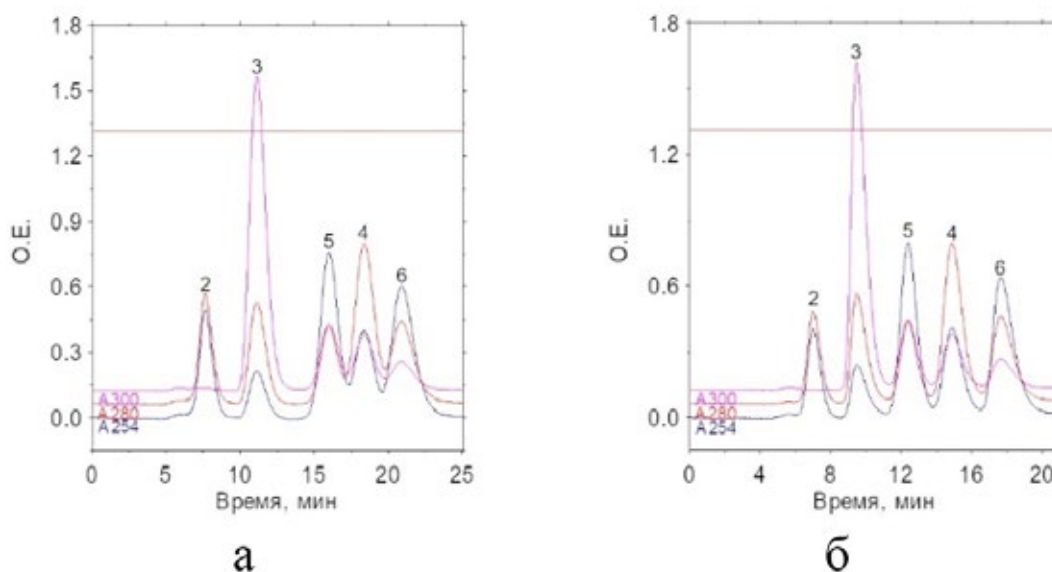
# INFLUENCE OF THE NATURE OF IONIC LIQUIDS ON THE RETENTION OF AROMATIC ACIDS ON HYPERCARB™ UNDER RP HPLC CONDITIONS

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HYPERCARB™ is a promising graphite-like adsorbent for HPLC, characterized by high selectivity, mechanical strength and chemical inertness, wide pH range.



**Figure 1.** Chromatograms of acid mixture separation in systems without addition of ILs (a) and with addition of 1 Butyl-2,3-dimethylimidazolium bromide (b).

2 - benzoic acid, 3 – salicylic acid, 4 – 4-nitrobenzoic acid, 5 – vanillic acid, 6 – cinnamic acid.

In this work, the effect of imidazolium ionic liquids (ILs) of different nature and structure on the sorption of aromatic acids (gallic acid, benzoic acid, salicylic acid, vanillic acid, 4 nitrobenzoic acid, cinnamic acid) from water-acetonitrile solutions (water/acetonitrile – 35/65, 30/70, 25/75, 20/80, 15/85 vol.%, 0.1% TFA) on HYPERCARB™ at 35°C was studied.

It was found that the addition of ILs to the mobile phase leads to both a decrease and an increase in the retention of the studied aromatic acids depending on the structure of the ILs used. This can be explained by the formation of ion pairs and the change of hydrophobic effect during sorption of the studied acids in systems with ILs. It was found that additions of some ILs to the mobile phase increase the selectivity of acid mixture separation and decrease the chromatographic analysis time (Fig. 1).

When analyzing the dependence of the retention factor on the acetonitrile content in the mobile phase, it was shown that some retention anomalies are observed for gallic and vanillic acids: the retention of gallic acid increases with increasing acetonitrile content in the mobile phase on HYPERCARB™. Retention of vanillic acid increases at high content of acetonitrile in the mobile phase (more than 85 vol.%).

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<https://rscf.ru/en/project/23-23-00397/>.*

# ENANTIOSELECTIVE CHROMATOGRAPHY OF DIPEPTIDES ON ADSORBENTS WITH GRAFTED ANTIBIOTICS

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Short peptides are important compounds in biological systems. Peptide optical isomers can have different biological activities. The presented study is of interest for the development of chromatographic methods for preparing enantiomerically pure dipeptides (DPs). Chiral chromatography is an effective technique for solving this task. Chiral stationary phases (CSPs) based on macrocyclic antibiotics (MA) have evinced advantages in enantioseparation of the low molecular weight peptides, in particular DPs.

There was studied the chromatographic behavior of CSPs Chirobiotic-T and Nautilus-E with MAs – teicoplanin and eremomycin – grafted onto fully porous silica gel particles of 5  $\mu\text{m}$  in size, as well as that of CSPs Chiral-T and Chiral-V with MAs- teicoplanin and vancomycin grafted onto superficially porous silica particles of 2.7  $\mu\text{m}$  in size, towards the DP stereoisomers. The studies were performed on an Agilent 1260 Series liquid chromatograph with a diode-matrix detector. The DP stereoisomers were used as aqueous or methanol solutions at a concentration 0.2-0.5 mg/ml, with a sample volume 2  $\mu\text{l}$ . Water-methanol mixtures with addition of  $2 \cdot 10^{-4}$  M  $\text{CH}_3\text{COONa}$  served as eluents. There were used the following DP stereoisomers (Sigma Aldrich): Leu-Leu, Leu-Phe, Phe-Leu, Phe-Gly, Gly-Phe, Leu-Gly, Gly-Leu, Ala-Ala.

There was evinced the complementary enantioselectivity of CSPs with MAs towards the DP stereoisomers. There was investigated the effect of solvent compositions in the eluent on retention and enantioseparation of the DPs. The lipophilicity of the DPs was found to essentially affect the dependence of their retention on methanol concentration in the eluent. A theoretical model taking into account interaction of the both solvents of a binary MP with both an analyte and adsorption sites was successfully applied so as to approximate and interpret the dependences of DP retention (monotonic and U-shaped) on the modifier content in the MP.

*This study was financially supported by the Russian Science Foundation (Grant No. 23-23-00085).*

# DEVELOPMENT AND APPLICATION OF THE APPROACHES FOR THE DESCRIPTION OF RETENTION MECHANISM IN HYDROPHILIC INTERACTION LIQUID CHROMATOGRAPHY

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Hydrophilic interaction liquid chromatography is a convenient method for analyzing multicomponent mixtures containing polar substances of different structure and charge. Understanding the ways for governing selectivity is important for selecting separation conditions. Prediction of the effect of a particular parameter on the analyte's behavior is possible when the retention mechanism is known. In hydrophilic interaction liquid chromatography, it is a combination of partitioning, electrostatic, and other adsorption interactions.

In this work the approaches were developed for evaluating the contribution of these interactions into the retention of the analytes of various acid-base properties. The influence of the eluent buffer solution components nature on retention mechanism was preliminary assessed. The applicability of the approaches was shown for silica, diol and amino phases, silica modified with eremomycin, zwitterionic, and polyamine groups. The key idea was to vary one parameter of the mobile phase while fixing the others. We used models proposed for other types of chromatography with corresponding retention mechanisms to assess the contribution of ion exchange mechanism and partitioning to the overall retention of the test substances. We also established thermodynamic parameters of retention using the Van't Hoff equation.

As a result, the influence of the mobile phase composition and the structure of stationary phase on the ratio of different types of solute-adsorbent interactions was demonstrated for organic ions, weak acids, and bases. Positive enthalpies of transfer from mobile to stationary phase were established for the analytes which retained significantly via ion exchange interactions. The obtained trends for the retention factors and the contribution of retention mechanisms made it possible to interpret the changes in separation selectivity when varying the eluent composition. Finally, the separation conditions for the test multicomponent mixture were selected.

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# MACHINE LEARNING IN GAS CHROMATO-MASS SPECTROMETRY – A FASHIONABLE TREND OR A WORKING TOOL?

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In recent years, machine learning and artificial intelligence have been extremely popular and are being used in a wide variety of fields. The application of machine learning to tasks to which it has not previously been applied has long become a trend, and the works in which it is mentioned always arouse interest. However, every time the question arises whether machine learning can really influence the state of affairs in a particular area or whether its use is just a tribute to fashion.

One of the main methods used in non-targeted analysis is gas chromatography-mass spectrometry (GC/MS). This method allows one to obtain a significant amount of information about the composition of the mixture, but is not able to unambiguously establish the structure of the unknown component. Machine learning greatly enhances the capabilities of GC/MS and can be used to predict retention indices, to rank candidates when searching mass spectral databases, to predict and interpret mass spectra, to generate possible new candidate structures, to process «raw» mass chromatograms and to predict the properties of molecules that have been identified in a mixture.

One of the problems that arise when training models is errors in databases, which affect the accuracy of further prediction. We found errors in the NIST database for relatively simple compounds - triazole, imidazole and their derivatives. Correcting erroneous values in the training data set and retraining models will allow for even more reliable determination of compound structures in untargeted GC/MS analysis.

The effectiveness of the combination of GC/MS and artificial intelligence methods was demonstrated by the example of identifying transformation products of unsymmetrical dimethylhydrazine, which is an important task. Verification of the proposed candidate structures using standards showed the reliability of the described methods.

*The research is supported by Russian Science Foundation, project No. 22-73-10053*

# STUDYING THE ADSORPTION PROPERTIES OF MESOPOROUS SILICA GEL DOPED WITH TERBIUM, MODIFIED WITH NICKEL AND SILVER (Ag-Ni/Tb-MS) BY REVERSE GAS CHROMATOGRAPHY

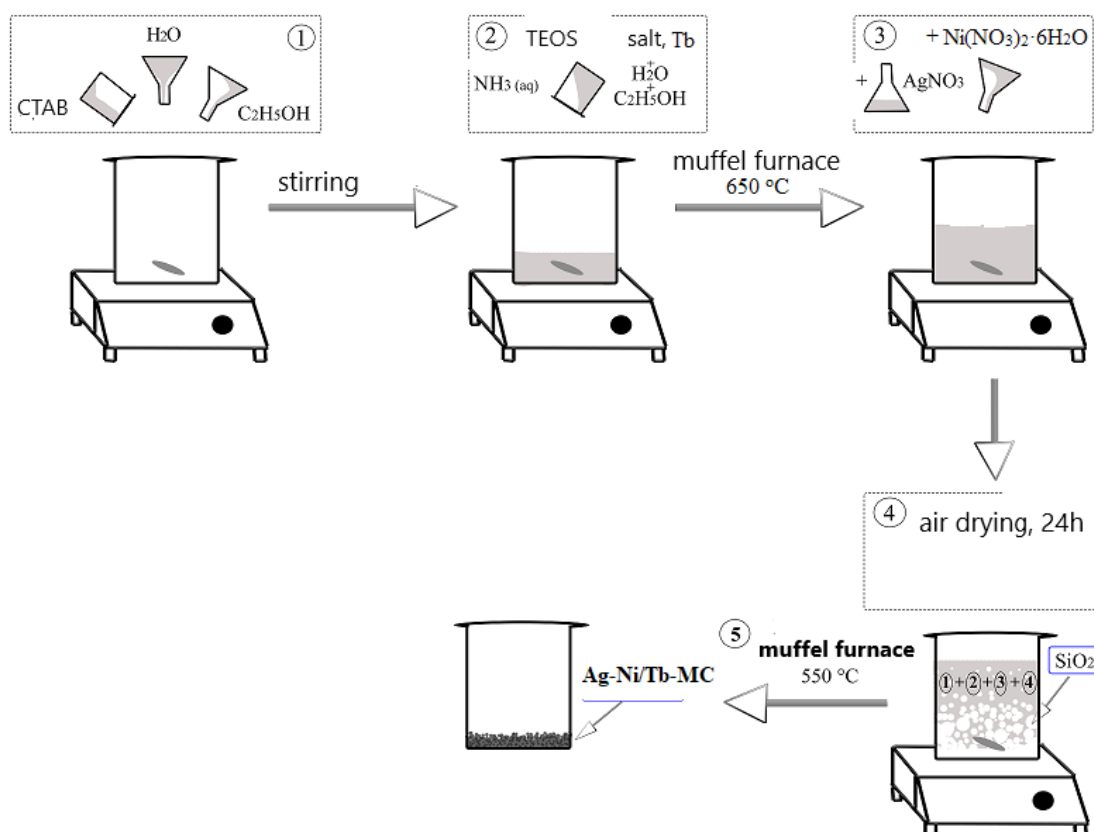
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The simplest and most universal method for producing mesoporous silica gels is template synthesis, during which it is possible to control the textural and morphological characteristics of the resulting porous silica material (Fig. 1).



**Figure 1.** Synthesis scheme for Ag - Ni / Tb -MS.

In recent years, materials containing both an active metal (palladium, nickel) and an inactive one (silver) deposited on aluminum or silicon oxides have become widely used in industry. It is assumed that promotion is of an electronic nature and is due to the transfer of electron density from silver to the active metal, which leads to a decrease in the adsorption of test adsorbate, or a geometric nature associated with the blocking of low-coordinated atoms of the active metal.

# NON-TARGETED SCREENING OF SULFONAMIDE ANTIBIOTICS IN WASTEWATER BY HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY-TANDEM MASS SPECTROMETRY IN THE PRECURSOR ION SCAN MODE

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Antibiotic contamination of the environment is of particular concern due to the greatly increased risk of the spread of resistant genes among bacteria. Sulfonamides are one of the oldest groups of antibiotics, which are widely used in animal husbandry, agriculture and medicine for the treatment and prevention of microbial infections.

Since sulfonamide antibiotics have a similar structure, these compounds can form the same product ions during fragmentation. This feature served as the basis for the development of an approach to non-targeted screening of sulfonamides using high-performance liquid chromatography–tandem mass spectrometry (HPLC-MS/MS) in the precursor ion scan mode (PrecIS). The developed approach of non-targeted search of sulfonamide antibiotics was successfully applied to the analysis of municipal wastewater of the city of Arkhangelsk. Five sulfonamide antibiotics and their derivatives were found in wastewater after biological treatment. The content of sulfonamides for which standard samples were not available was estimated semi-quantitatively from the calibration curves of the structurally closest commercially available sulfonamides. The total content of sulfonamides in the wastewater was 900 ng/l.

Thus, this study proposes a new approach for the non-targeted screening and semi-quantitative determination of sulfonamides in wastewater using HPLC-MS/MS in the precursor ion scan mode.

*The work was carried out using the equipment of the Core Facility Center «Arktika» of Northern Federal University named after M.V. Lomonosov with financial support from the Ministry of Science and Higher Education of the Russian Federation, state assignment project FSRU-2024-0003.*

# THEORETICAL DESCRIPTION OF INTERMOLECULAR INTERACTIONS IN GAS CHROMATOGRAPHY

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To solve the problems of separation and identification of substances with similar properties using gas chromatography, a theoretical method has been developed for describing the properties of chromatographic stationary phases.<sup>1,2</sup> The three-parameter characteristic (TPC) method is based on a general expression for the adsorption energy in a system, which includes three independent contributions to the energy - the energies of nonpolar and polar interactions and the energy of hydrogen bonding. The stationary phase is described by two parameters, designated in the method as polarity and hydrophilicity. This method allows you to correctly determine the characteristics of stationary phases based on experimental data on chromatographic retention indices and make an a priori calculation using the structural formula of the substance, and select a selective phase without conducting experiments. A convenient way to present the results of calculations is a diagram called a stationary phase selectivity map.<sup>1</sup>

The proposed method makes it possible to abandon the known empirical and semi-empirical methods for classifying chromatographic stationary phases due to the fact that all the parameters used have a physical meaning, are portable and do not require experiments to determine them.<sup>1,2</sup>

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# CHROMATOGRAPHIC METHODS AND INSTRUMENTATION IN ANALYTICAL CONTROL REFINING PROCESSES

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Oil, crude oil, processed products (technological flows), target products as a commodity are complex, multicomponent objects of research.

Various types of chromatography have found wide application both in the daily analytical support of technological processes - monitoring the quality of streams, and in conducting research.

The personnel of chemical analytical and testing laboratories are guided by standardized testing procedures, taking into account the recommended instrumentation and software. The report provides a number of regulatory documents (GOST, ASTM D, EN, etc.) for assessing the composition and properties of petroleum raw materials and refined products based on chromatographic methods.

The method of simulated distillation, which has recently become widespread for predicting the potential of oil entering the country's refineries, is specifically considered. The results of determining the fractional composition of various oil samples using chromatographic complexes from a number of manufacturers, including domestic ones, are presented.

It is emphasized that for the analysis of oil, «light» petroleum products and medium distillates, unified methods in the form of GOST with a description of the completeness of hardware and software complexes are used in laboratory practice. To determine the group hydrocarbon composition of heavy petroleum fractions – oils, vacuum gas oil, fuel oil, tar, cracking residues, oxidized and natural bitumen, a single type of instrumental equipment is used – the Gradient-M installation (JSC Institute of Petrochemical Processing, Ufa). But the domestic market has complexes for the implementation of the «SARA» method (IP 469, etc.), which are not universal, for each specific «heavy» product, the development of a methodological option is required, etc.

The primary tasks of chromatographers and analytical instrument companies in the field of import substitution, which, as time requires, must be solved together.

# STUDY OF THE SORPTION OF DICLOFENAC FROM AQUEOUS SOLUTIONS ON CARBON SORBENT FROM RICE HUSK

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The anti-inflammatory drug diclofenac takes one of the leading positions in terms of concentration and prevalence in water reservoirs around the world.<sup>1</sup> A by-product of rice production - rice husk can be used as the unique sorbent the potentially hazardous diclofenac during water purification<sup>2</sup>.

In the course of the work, the characteristics of the activated carbon sorbent obtained from the rice husks were studied: the content and chemical state of the elements in the surface layer (with XPS method), surface area and pore size distribution (with low-temperature sorption-desorption method).

The efficiency of diclofenac sorption from an aqueous solution with activated carbon was evaluated by quantitative analysis using HPLC:

|                                  |      |      |      |      |      |      |      |      |      |      |      |
|----------------------------------|------|------|------|------|------|------|------|------|------|------|------|
| $c_0^*$ , $\mu\text{g/ml}$       | 10   | 25   | 50   | 75   | 100  | 125  | 150  | 175  | 200  | 250  | 300  |
| $c_{ad}^{**}$ , $\mu\text{g/ml}$ | 9    | 20   | 28   | 33   | 35   | 37   | 40   | 41   | 43   | 44   | 46   |
| $R=c_{ad}^{**}/c_0^*$ , %        | 90.0 | 80.0 | 56.0 | 44.0 | 35.0 | 29.6 | 26.7 | 23.4 | 21.5 | 17.6 | 15.3 |

\*the initial concentration of diclofenac in an aqueous solution

\*\*the concentration of diclofenac adsorbed from an aqueous solution

Based on the chromatographic analysis data, the detection limits (0.1 mg/ml) and determination limits (0.3 mg/ml) of diclofenac were calculated.

The dependence between the duration of the adsorption process and the proportion of the adsorbed substance has been established. The adsorption isotherm has been classified as the Freundlich isotherm.

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# FACTORS AFFECTING THE ACCURACY OF PREDICTION OF GAS CHROMATOGRAPHIC RETENTION INDICES USING MACHINE LEARNING

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Retention indices can be used as an additional factor to confirm or reject a candidate structure in the non-target analysis of complex mixtures. Many deep neural network models have been presented to predict retention indices. The mean accuracy of such models is usually assessed on large data sets. However, for a particular category of molecules, the accuracy may differ greatly from the mean. The aim of this work is to find ways to evaluate the reliability of the retention index prediction for a specific molecule.

The first factor affecting prediction accuracy that was considered was the similarity of the molecule being predicted to molecules from the training set. Four algorithms for calculating molecular similarity were considered; the best results were shown by the ECFP6-type molecular fingerprints. The higher the similarity between a given molecule and the closest molecule from the training set, the better the prediction accuracy. For compounds for which this value is higher than the median, in ~10% of cases the prediction error is above 100 (for the polar stationary phase).

It was also examined how the difference between predictions made using different models is related to the accuracy of the prediction (when compared with a reference value). In addition, to assess the accuracy of the prediction, clustering of molecules into clusters of similar structures was used. Accuracy varies greatly among different clusters.

In one of the previously published works, the prediction of retention indices for polar and non-polar stationary phases was used to determine the structure of unknown transformation products of unsymmetrical dimethylhydrazine. It has been shown that for many of those structures, predictions for the polar stationary phase can be quite unreliable and should be used with great caution.

*The work was carried out with the financial support of the Russian Science Foundation, project 22-73-10053*

# STUDYING THE POSSIBILITY OF OBTAINING CONSTANT CONCENTRATIONS OF ORGANICALLY SOLUBLE ANALYTES IN ORGANIC MEDIA DURING THE OPERATION OF MONOLITHIC CHROMATO-DESORPTION SYSTEMS

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Correctness, accuracy and precision of quantitative chromatographic analysis is determined by the quality of preparation of standard composition samples, the development and use of which allows analytical laboratories to solve a wide range of applied problems.

The paper presents the results of research of chromato-desorption systems (CDS), which allow to create solutions with normalized amount of organically soluble analytes. Manufactured experimental samples represent a composite material obtained as a result of polymerization of two-component epoxy resin, in which the analyte, previously applied to nanodispersed adsorbent, is uniformly distributed in the volume of the polymer. A number of carboxylic acids serve as analytes.

Extraction of analytes from CDS under different temperature and barometric conditions in static and dynamic extraction modes using a specially designed extraction unit was carried out. A comparative evaluation of the amount of desorbed organically soluble analyte by the extractant in static and dynamic modes was carried out. It is shown that the dynamic mode of extraction is characterized by the possibility to create flows of organic solvents for a longer period of time, and the output to the working quasi-stationary mode, which is characterized by a deviation of analyte concentration not more than 10%, is achieved faster.

The obtained results allow us to recommend the manufactured CDS for the creation of organic media with known content of the target substance.

# HYDROPHILIC AND MIXED-MODE ADSORBENTS FOR THE SEPARATION AND DETERMINATION OF SWEETENERS IN VARIOUS OBJECTS

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Sugars and sugar alcohols (polyols) are an integral part of the diet. Together they are called natural sweeteners. Artificial sweeteners are synthetically produced substances used as low-calorie supplements. Excessive consumption of both natural and artificial sweeteners can have negative effects on human health. It is therefore important to develop new approaches for their determination and to monitor their levels in different food products.

The retention of natural and artificial sweeteners on different mixed-mode adsorbents based on a polymer substrate as well as on hydrophilic phases based on silica was studied. Stationary phases based on polystyrene-divinylbenzene with covalently grafted polyethylenimine and polyelectrolytes showed significant retention of polyols in hydrophilic mode and high selectivity for the sorbitol/mannitol pair, with the same Hansch hydrophobicity parameter ( $\log P = -4.67$ , Epiweb 4.1). However, the efficiency of amide phases based on silica obtained by Ugi reaction, as well as phases modified with linear polymers: a copolymer of acrylic and maleic acid and polyethylene glycol, is significantly higher than those based on a polymer substrate. The possibility of simultaneously separating 10 carbohydrates and sugar alcohols on a highly efficient amide silica column using an evaporative light scattering detector was demonstrated. With respect to artificial sweeteners, the best chromatographic characteristics were demonstrated by mixed-mode columns on a polymer substrate. The developed stationary phases were used to analyze mouthwashes from different manufacturers.

*The work was supported by Russian Science Foundation through the grant № 20-13-00140.*

# METHODS OF GRADIENT ELUTION OF HYDROPHILIC ORGANIC SUBSTANCES USING POROUS GRAPHITIZED CARBON

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The separation of hydrophilic organic substances present in aqueous solutions in ionic and molecular forms is quite a difficult task due to the weak retention of such substances in many stationary phases. To separate/determine a number of hydrophilic acidic components (carboxylic and phosphonic acids, some organophosphorus pesticides), it is proposed to apply gradient modes of elution with aqueous solutions of formic acid using porous graphitized carbon as a stationary phase.

The chromatographic separation conditions and the gradient shape are selected, under which the best separation of mixtures of these analytes is achieved. It is shown that an increase in the concentration of formic acid in the mobile phase to 0.5% and above leads to a deterioration in the shape of peaks and an increase in noise.

The parameters of separation of hydrophilic analytes in isocratic and gradient elution modes are compared. It was found that the use of a concentration gradient of formic acid increases the retention time of analytes and improves their separation compared with the isocratic mode on the Hypercarb column. Using the example of organophosphorus pesticides, it is shown that gradient elution affects the separation of analytes in a neutral medium in the form of anions, while the retention of analytes-cations does not change. It is shown that the replacement of formate in the mobile phase with bicarbonate during column conditioning before sample injection does not lead to a change in analyte yield times.

It is suggested that the peculiarities of the retention of analytes on the Hypercarb sorbent under selected conditions can be explained by the displacing «quasi-ion exchange» mechanism of elution and the effect of the addition of anions in the mobile phase on the interaction of analytes of an acidic nature with the surface of the sorbent.

*The work was carried out as part of the work on the topic of the state task No. AAAAA-A21-121011990021-7*

# RETENTION REGULARITIES OF NORMAL ALCOHOLS ON MICROPOROUS SORBENTS

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A growing interest for the use of microporous sorbents in HPLC, in particular, wide-porous inorganic zeolites has been noted in the recent years. Pore size ( $D_{pore}$ ) of zeolites is only 2-3 times larger than the size of molecules of the compounds with a molecular weight less than 60-70 daltons, that increases their separation selectivity due to the molecular sieve effect. In present work the mechanism of adsorption on wide-porous zeolite 13X and common mesoporous silica gel is studied under normal-phase HPLC conditions.

Columns packed with microspherical zeolite 13X (50×4.6 mm, 5  $\mu$ m,  $D_{pore}$  = 0.74 nm)<sup>1</sup> and with mesoporous silica gel Partisil P10 (250×4.6 mm, 10  $\mu$ m,  $D_{pore}$  = 8.5 nm) were used in the work. Methanol and acetonitrile were used as eluents. It is shown that the retention of alcohols on zeolite 13X<sup>1</sup> and silica gel is determined by the polarity ( $P'$ ) and a combination of specific and non-specific intermolecular interactions. When using the acetonitrile eluent for both sorbents, a significant dependence of the retention ( $k'$ ) of normal alcohols on the length of the hydrocarbon chain ( $n_C$  = 1-12) was observed. The dependence of  $n$ -alcohols retention on zeolite 13X corresponds to the size-exclusion mechanism. On mesoporous silica gel  $n$ -alcohols are retained less strongly, the dependence  $\log k - n_C$  is not too steep due to the large  $D_{pore}$  of this adsorbent. Similar dependences are obtained for ketones confirming the molecular sieve effect for zeolite 13X, but not for silica gel.

The values of the relative enthalpy of adsorption ( $\Delta H^0$ ) were calculated for the homologous series of alcohols on zeolite 13X. The change in the values of  $\Delta H^0$  with  $n_C$  increase is opposite to the order obtained reported for the heats of adsorption of alcohols measured by GC method<sup>2</sup>. The possibility for the separation of several compounds and their fully deuterated analogues was also considered on zeolite 13X column.

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# ESTIMATION OF INITIAL PARAMETERS FOR ITERATIVE APPROXIMATION OF CHROMATOGRAPHIC PEAKS WITH EXPONENTIALLY MODIFIED GAUSSIAN

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Iterative approximation with exponentially modified gaussian (EMG) function is widely used to describe chromatographic peaks<sup>1</sup>. EMG has four parameters: peak height ( $h$ ), position of unmodified gaussian ( $\mu$ ), standard deviation ( $\sigma$ ), and relaxation time ( $\tau$ )<sup>2</sup>. Peak asymmetry is most often described by the ratio of the right and the left half-width at 10% of peak height. The equations to estimate initial parameters of EMG from experimental data date back to the 1980s<sup>3</sup>. Nevertheless, modern papers often omit recommendations for setting initial values for approximation of chromatographic peaks. While the choice of initial values is not so important for EMG, it can be crucial for iterative approximation of the peak using more sophisticated functions with more parameters<sup>1</sup>. That is why we revised and improved some of the previously suggested approaches<sup>3</sup>. For example, we used interpolation with splines instead of approximation with equations, which allowed us to drastically increase the range of valid values obtained from experimental data without losing accuracy. Moreover, we explored some aspects of estimating peak apex coordinates and half-widths. We also compared the accuracy of estimation of initial parameters using half-widths at various heights (from 10% to 50%).

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# REGULARITIES OF ENANTIOSEPARATION OF DERIVATIZED AMINO ACIDS ON CHIRAL STATIONARY PHASES BASED ON CHEMICALLY MODIFIED QUININE ALKALOIDS

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Amino acids are natural biomarkers in physiological studies. The ratio of enantiomers of certain amino acids can serve as an important diagnostic sign of various pathological conditions. To determine this ratio the method of direct chromatographic separation on chiral stationary phases (CSP) is often used. To increase the sensitivity of determination amino acids are derivatized with reagents containing chromophore or fluorophore groups. In the presented work the possibility of separating derivatized enantiomers of amino acids into new CSPs with grafted zwitterionic ligands obtained by modifying quinine alkaloids (quinine and quinidine) with dipeptides was studied. The influence of mobile phase composition and temperature on the separation of mixtures of serine and aspartic acid enantiomers selected as model objects due to their importance for physiological and medical research was considered. It was shown that the best separation is achieved on quinidine-based CSP with the dipeptide

L– Leu –L– Ala when using 100% MeOH as a mobile phase with the addition of 25 mM formic acid and 12.5 mM triethylamine and column temperature 35 °C.

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# REGULARITIES OF RETENTION OF LOW MOLECULAR ALIPHATIC AMINES ON CARBOXYL CATION EXCHANGER

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Currently, ion chromatography (IC) is the main method for determining inorganic and organic ions in natural waters<sup>1</sup>. The IC method is distinguished by low cost of analysis and high efficiency of separation of multicomponent mixtures.

Short-chain aliphatic amines are often found in the environment due to their use as intermediates in the chemical and pharmaceutical industries. These compounds may be hazardous to human health, and they can also form carcinogenic nitrosamines. Thus, there is a need to determine aliphatic amines in various environmental objects. To determine aliphatic amines in water, chromatographic methods are usually used. There are few known determination methods using GC and HPLC. However, these methods include a time consuming sample preparation. The derivatization is often required to increase sensitivity in HPLC, since aliphatic amines do not have strong UV absorbance or fluorescent properties.

In this work, the chromatographic retention of 16 aliphatic primary, secondary, tertiary amines and quaternary ammonium base with  $n_c < 4$  was studied on a 250 x 4.0 mm column filled with PS-DVB based cation exchanger having grafted carboxyl groups and average particle size of 5  $\mu\text{m}$ .

The dependences of amines retention on temperature, eluent concentration and of methanol content were obtained and used for the elucidation of the retention mechanism. The possibility of simultaneous separation of six amines and six cations of alkali and alkaline earth metals was demonstrated. Also the retention of some deuterated aliphatic amines was studied under these conditions.

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# APPLICATION OF ELECTROSPRAY IONIZATION MASS SPECTROMETRY FOR THE SYNTHESIS AND STUDY OF METASTABLE OLIGOPEPTIDE CLUSTERS

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Mass spectrometric methods find many applications in modern analytical chemistry, as a highly sensitive and versatile method for quantitative analysis and identification of compounds in complex mixtures. Reproducible ionization methods such as electron impact are used for quantitative analysis. Methods that are less reproducible and, at the same time, softer allow us to obtain mass spectra of the equilibrium state of various molecules and record the formation of intermediate forms of their existence.

This paper presents the results of a study of oligopeptides in an aqueous acetonitrile solution using electrospray ionization and laser desorption mass spectrometry. It has been shown that peptides, such as triglycine, alanylglutamine and prolylleucine, can form associates of two or three molecules, which are identified in the mass spectrum as protonated or cationized ions. Such results are obtained in the presence of alkali and alkaline earth metals in the solution. It is noted that when d-metals with variable oxidation states are added, in addition to cationization processes, aggregation of molecules around the coordination center of the copper atom is observed. The mass spectra revealed large associates of 5-6 peptide molecules, including those with several copper atoms. When associates are formed from three or more peptide molecules, the replacement of not one, but several protons can occur, which is confirmed by high-resolution mass spectra. It should be noted that the number of replaced protons can sometimes exceed the number of mobile protons in the associated molecules.

The mechanism of this process is not completely clear and has not been described in the literature. To establish this mechanism, we used tandem mass spectrometry methods, which allow for forced fragmentation of selected cluster ions to establish their structure and, in particular for our work, the position and charge transition of the ion during fragmentation and formation.

# COMPOSITE CHROMATO-DESORPTION SYSTEMS FOR OBTAINING CONSTANT ANALYTE CONCENTRATIONS IN AQUEOUS AND AQUEOUS- ORGANIC ENVIRONMENTS WITH SUBSEQUENT ANALYTICAL CONTROL

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One of the promising dynamic methods for creating solutions of known concentration is chromato-desorption, which makes it possible to obtain streams containing the analyte in the required concentrations for a sufficiently long time.

The chromato-desorption method of creating solutions of known concentration is carried out in two stages: 1 - chromato-sorption consists in the equilibrium saturation of the sorbent or polymer material with the analyte; in the case of a sorbent, saturation occurs at a temperature above the operating temperatures of the system; in the case of using a polymer material, the system is saturated with the analyte at manufacturing process, forming a composite material; 2 – chromato-desorption consists in the desorption of the analyte when passing through the mobile phase system. By changing the temperature, it is possible to regulate the distribution constant of the analyte in the sorbent-mobile phase system, ensuring the production of streams with a given analyte content.

In this work, we studied the patterns of operation of polymer composite chromato-desorption systems (CDS), made from a polymer resin with the addition of a water-soluble dye applied to the surface of the adsorbent, in aqueous and organic media, both under static and dynamic conditions. The concentrations of analytes after operation of the CDS were monitored by reverse -phase HPLC with diode array detection.

The patterns of desorption of 10 analytes from polymer matrices into distilled water under static conditions were determined; in addition, the desorption of water-soluble analytes into a mixture of distilled water and acetone was studied, the acetone content was 1, 10, 50, 100%. It was found that as the acetone content increases, the desorption rate under static conditions decreases. Dynamic extraction of the analyte was also carried out at 25 and 80°C and a pressure of 10 MPa. As a result, it was found that during long-term operation, the CDS begins to desorb a quasi-stationary mass of the analyte per unit time under stationary conditions, regardless of the flow rate.

# APPLICATION OF STIR-BAR SORPTIVE EXTRACTION IN GAS CHROMATOGRAPHY-MASS SPECTROMETRIC ANALYSIS OF ARCTIC SNOW

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A key challenge in using GC-HRMS for studying Arctic snow is sample preparation, which must ensure efficient extraction and concentration of analytes present in ultra-trace concentrations. Traditional methods of sample preparation (LLE and SPE) involve the use of large volumes of extractant, the concentration of which leads to the appearance of background signals of microimpurities in chromatograms, making it difficult to search for minor compounds in snow. To solve this problem, we have proposed an alternative approach to snow sample preparation, based on stir-bar sorptive extraction (SBSE), implemented using a magnetic stirrer with a sorption coating. For its testing, a test mixture of 76 priority semi-volatile organic pollutants of various classes was used (in accordance with EPA method 8270). The use of a polydimethylsiloxane coating during extraction of 100 ml of an aqueous solution for 3 hours followed by direct thermal desorption of analytes and GC-HRMS analysis made it possible to reliably detect more than 60 analytes of various classes, among which quantitative assessment is possible for 15 analytes. Comparison the effectiveness of the developed approach with the LLE and SPE methods showed an increase in the sensitivity of SBSE by several orders of magnitude.

Application of the developed approach to the analysis of priority organic pollutants in snow sampled in the Arctic zone made it possible to identify 29 components from the list of priority air pollutants in concentrations from 0.09 to 51 ng/l. Based on the results of non-target screening, over 200 organic compounds of various classes were detected, the concentration of which ranged from 0.01 to 500 ng/l.

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# REVEALING THE FACTORS GOVERNING SEPARATION SELECTIVITY TOWARD POLAR SUBSTANCES ON SILICA COLUMNS IN HYDROPHILIC INTERACTION LIQUID CHROMATOGRAPHY

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The key factor influencing separation selectivity in hydrophilic interaction liquid chromatography (HILIC) is the composition of mobile phase. Namely, a strong eluent content, a concentration of the buffer solution, and acidity, which is especially important for the analytes providing acid-base behavior. This work offers an approach to describing solute-adsorbent interactions in HILIC by varying the composition of mobile phase. It also allows to compare the properties of stationary phases of different structure.

Buffer solutions in the pH range from 3 to 6 containing sodium salts of acetic, monochloroacetic, formic, and propionic acids were used. The contribution of electrostatic interactions to the retention of substances was additionally assessed by varying the eluting ion concentration at a fixed acidity.

The proposed approach was used for comparing retention mechanisms and predicting selectivity on bare silica and neutral diol-modified column Diasphere-300-Diol (particle diameter 6  $\mu\text{m}$ , pore size 300 Å, «BioChemMack ST»). Eleven compounds of diverse properties were used as test analytes. Actually, both columns showed similar retention dependence on pH. Increased retention with increasing pH was observed for neutral compounds, weak acids, and cations. The dependence of weak bases retention on pH had a maximum. The silica substrate shielding with diol groups reduced cations and bases retention factors due to decreasing electrostatic interactions and ion exchange contribution by 20% as compared to bare silica.

The obtained patterns are useful for choosing the stationary phase for a particular analytical task, as well as for predicting the conditions providing required selectivity toward compounds of different acid-base properties.

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# OBTAINING BIOLOGICALLY ACTIVE COMPOUNDS FROM EXTRACTS OF COMPRESSED WOOD OF CONIFEROUS AND DECIDUOUS USING PREPARATIVE SUPERCRITICAL FLUID CHROMATOGRAPHY

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Isolation of valuable components in pure form from wood extracts using classical versions of column chromatography is an extremely labor-intensive and complex task. The use of preparative reverse phase HPLC in this case has limitations due to the insufficient polarity differences between the isomers present. As an alternative to isolating phenolic extractives from wood, supercritical fluid chromatography (SFC) can be considered. It offers orthogonal selectivity compared to HPLC and has been successfully used for the separation of optical isomers. One of the key tasks in the separation of structurally similar compounds (such as lignans or flavonoids) using the SFC method is selecting the most appropriate stationary phase. The best results were achieved using of «classical» normal-phase polar stationary phases, specifically diol (for coniferous) and 2-ethylpyrrolidine (for deciduous).

The isolated phenolic metabolites were identified by high-resolution mass spectrometry and NMR spectroscopy. The data obtained indicate that the dominant lignans in compression coniferous wood (nortrachelogenin, hydroxymatairesinol and secoisolariciresinol) can be isolated in the form of pure preparations with high yields. In the case of deciduous compression wood, the main components were flavonoid structures, among which aromadendrin and naringenin, as well as their glycosylated derivatives, stand out.

The presented results indicate that supercritical fluid chromatography holds great potential for isolating polar secondary metabolites from compression wood in individual form. This opens up opportunities not only for reliable identification of these compounds, but also for studying their properties, including biological activity.

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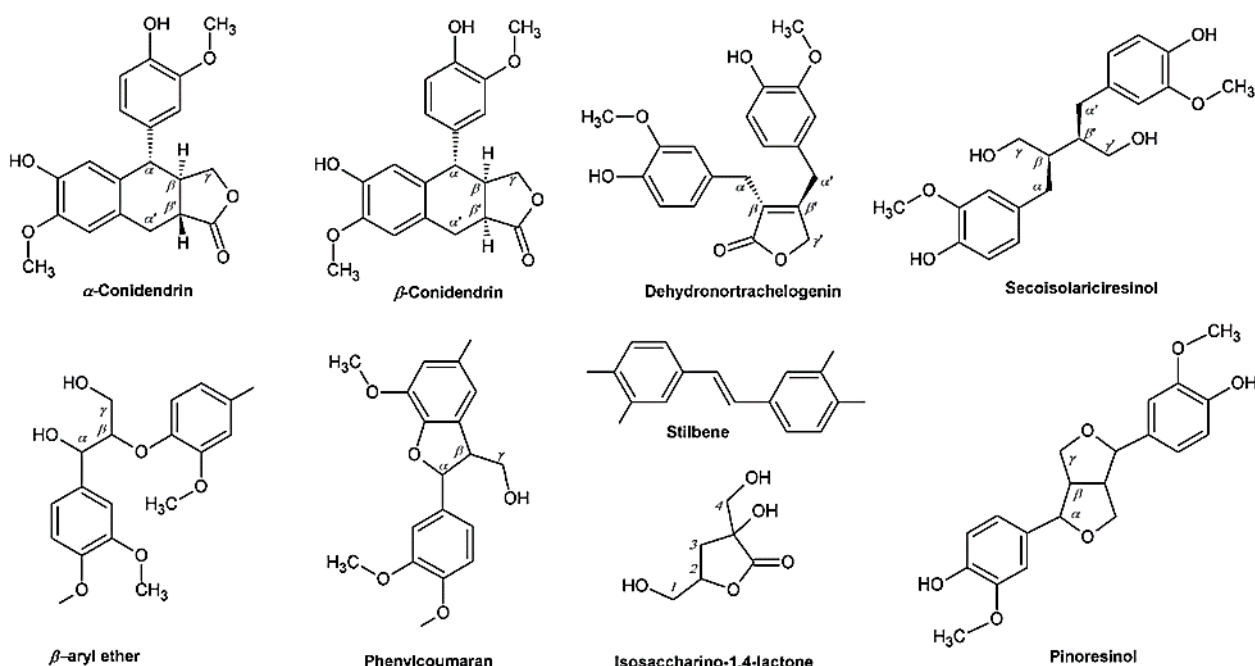
# LIGNANS IN SULPHATE PROCESS WASTES: COMPONENT COMPOSITION AND BIOLOGICAL ACTIVITY

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Undercooked pulp, which is formed due to incomplete removal of lignin from compression wood during the sulfate process of producing cellulose, has been considered as a promising source of polyphenolic compounds, particularly lignans. The exact composition of the extractive substances in undercooked pulp has not been determined yet, which makes it difficult to use these raw materials to isolate valuable compounds.

Using high-performance liquid chromatography (size exclusion, reverse phase) with spectrophotometric and high-resolution mass spectrometric detection (HPLC-HRMS), it was established the composition of the aqueous and acetone extracts. It has been shown that lignin with a molecular weight of 5–7 kDa (up to 30% of the uncooked mass) is one of the main compounds extracted by water. Acetone extract is characterized by the presence of low molecular weight polyphenolic compounds, namely lignans, the main ones are  $\alpha$ - and  $\beta$ - conidendrin, dehydronortrachelogenin, secoisolariciresinol and todolactol (Figure).



**Figure 1.** Structural formulas of lignans found in extracts

The antioxidant activity of acetone extracts, as determined by photochemiluminescence and electrochemical methods, yields high values – 379 mg/g (in Trolox units) and 215 mg/g (in gallic acid units), respectively. The discovered lignans have significant potential for use in the pharmaceutical, cosmetic and food industries. Undercooked pulp, in this regard, can be considered an industrial source for valuable compounds.

*The study was carried out at the expense of the NArFU Development Program for 2021-2035, contract D-389.2024*

# DETERMINATION OF THE QUANTITATIVE CONTENT OF ATALUREN AND SELEXIPAG BY HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY METHOD WITH UV DETECTION

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As part of the preparation of methods for quality control of active pharmaceutical ingredients (APIs) ataluren and selexipag when creating new technologies for the synthesis of APIs for the further production of orphan drugs based on small molecules, analytical methods were developed for the quantitative determination of the active substance by HPLC-UV.

To achieve optimal values for the suitability parameters of the chromatographic system, literature data were studied, and during testing, an *InfinityLab Poroshell 120 EC-C18* chromatographic column was selected, which is characterized by good efficiency, selectivity and stability. The performance of the methods is characterized by the parameters of the peak of the main substance (asymmetry factor, number of theoretical plates, relative standard deviation), which take into account the basic requirements of the Pharmacopoeia of Russian Federation<sup>1</sup>. To establish the «resolution» criterion when assessing the suitability of the chromatographic system, stress tests of the API were carried out and selected, followed by preparative isolation of the required impurity and determination of the structure by nuclear magnetic resonance. The developed methods were qualified with confirmation of specificity, precision and linearity. This shows that the developed analytical methods meet the requirements of modern chromatographic analysis.

The advantage of the methods is the analytical range: from 1.0% to 150.0% of the working concentration, which allows further use of the methods both for studying the kinetics of dissolution of substances and for determining the maximum permissible levels of contamination of production equipment. In turn, the stationary and mobile phases in the methods for ataluren and selexipag are absolutely identical and are suitable for solving various problems in pharmaceutical production, which increases the productivity of the substances.

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# THE STUDY OF LEMON MYRTLE AS A POTENTIAL RAW MATERIAL FOR THE PREPARATION OF BEVERAGES

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Lemon myrtle (*Backhousia Citriodora*) is a poorly studied plant. To study the composition of the aroma of lemon myrtle, an analysis of the gas extract of crushed leaves was carried out. Extraction was also carried out with water, an aqueous-ethanol mixture and under conditions close to the conditions of the gastrointestinal tract. The study was conducted using the method of gas chromatography with mass spectrometric detection (GC-MS). The components of the aqueous extract were re-extracted with ethyl acetate, then the resulting extract was derivatized by BSTFA and injected into a chromatograph.

It was determined that lemon myrtle contains 29 aromatic compounds, the predominant isomers of citral. Melonal, geraniol and rosefuran are also present in the gas extract. The analysis of the aqueous extract revealed linalool, geraniol, and citronellol – citral derivatives providing similar flavor and aromatic characteristics with dry raw materials. The aqueous extracts largely repeat each other, but the extract obtained by boiling contains more alkanes, as well as L-methionine, epicatechin and lignoteryl alcohol. Subcritical extracts expand the range of substances found. Thus, fumaric acid, lucene-2, 2-phenylserine were found in the extract obtained at 110 °C, and resorcinol,  $\alpha$ -terpinene, lysine were found in the extract obtained at 130 °C. The analysis of the alcohol extract showed the predominance of various sugars: glucose, D-fructose, D-ribose, as well as fatty acids. L-proline,  $\beta$ -cytostyrol,  $\alpha$ -tocopherol have also been found, which can pass into an aqueous extract in trace amounts during the preparation of the drink. The analysis of samples prepared in the environment inside the gastrointestinal tract repeated previous analyses, however, in the acidic environment of the stomach, esters are hydrolyzed, polyatomic alcohols and carboxylic acids are released.

Based on the established component composition, it can be assumed that lemon myrtle has antiseptic, antiviral, bactericidal, antimycotic properties, sedative and expectorant effects and is an excellent raw material in the preparation of beverages, flavoring additives and, possibly, can become a good additive to functional nutrition products.

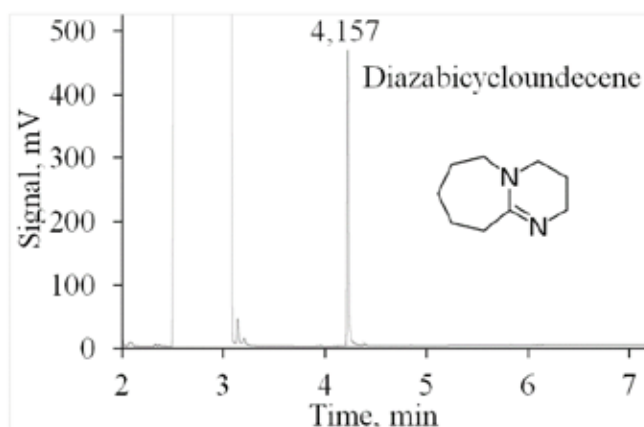
# DETERMINATION OF DIAZABICYCLOUNDECENE IN THE PHARMACEUTICAL SUBSTANCE SELEXIPAG

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Diazabicycloundecene is used in the synthesis of the substance selexipag as a catalyst for the acylation reaction of mesylamide with imidazolidine acid. Methods for its determination in selexipag substance have not been found in the literature. The physicochemical properties of this substance allow the use of the standardization and determination methodology adopted for residual organic solvents<sup>1</sup>. The maximum permissible content in the substance is set at 5000 ppm.

We have developed an express method for the determination of diazabicycloundecene by gas chromatography (GC)<sup>2</sup> using liquid sample injection and flame ionization detection. Identification was performed by retention time and GC with mass spectrometric detection.



**Figure 1.** Chromatogram of a solution of a standard sample of diazabicycloundecene

In the range from 5 to 120% of the normalized value, a linear relationship was established between the mass fraction values and the peak area of diazabicycloundecene, expressed by the equation  $y=769.91x-7.0879$ . The correlation coefficient is 0.9995. At analyte content levels from 250 to 6000 ppm, specificity is ensured with respect to the main substance and solvents used for synthesis.

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# APPLICATION OF GAS CHROMATOGRAPHY-MASS SPECTROMETRY TO ASSESS THE ABILITY OF THE GUT MICROBIOTA TO BIOTRANSFORM SEPSIS-ASSOCIATED METABOLITES

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The gas chromatography-mass spectrometry method (GC-MS) has powerful potential and used in intensive care more often for a comprehensive analysis of metabolites in critical conditions and for predicting the outcome of critically patients with high sensitivity. This study is based on a hypothesis that excess sepsis-associated AMM in patients with sepsis is caused by metabolic alterations (dysfunction) in the intestinal microbiota (pathobiota vs normobiota). Microbial metabolites of aromatic amino acids (AMM) composition was investigated in healthy volunteers (N=9) and sepsis patients (N=10) before and after incubation of feces in thioglycol medium (TGM) supplemented with sepsis-associated microbial metabolites at clinically relevant concentrations (25  $\mu$ M phenyllactic acid (PLA) or 25  $\mu$ M 4-hydroxyphenyllactic acid (4-HPLA)) for 24 hours at 37°C with using the gas chromatography-mass spectrometry (GC-MS) method. After incubation, the tubes were vortexed, centrifuged at 1000 rpm for 10 minutes, and the supernatant was frozen at -20°C. The concentration of metabolites in feces of healthy volunteers and sepsis patients before and after incubation in TGM was measured by the GC-2010 Plus gas chromatograph and a GCMS-QP2020 mass spectrometer (both from Shimadzu, Japan)<sup>1</sup>. Comparison of the metabolomic profiles of normobiota and pathobiota in an experiment showed that when loaded with sepsis-associated metabolites of PLA and 4-HPLA, the microbiota of a healthy subject's biotransforms them into the end products of microbial metabolism, whereas the pathobiota of a septic patient is unable to perform this function. GC-MS method provides an indicator of the putative mechanisms of AMM formation in sepsis.

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# DEVELOPMENT OF OPTIMAL FORMULATIONS AUTOMOTIVE FUELS BASED ON CHROMATOGRAPHIC ANALYSIS INFORMATION

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It is known that automobile fuels are produced according to technical specifications, which specify the basic physico-chemical and operational characteristics. There are certain regulatory restrictions on quality, including on the component and hydrocarbon composition. For example, in GOST 32513-2013 "Motor fuels. Unleaded gasoline. Technical conditions" prescribed – volume fraction, %, no more than: olefin hydrocarbons 18.0; aromatic 35.0; oxygenates, including esters ( $C_5$  and above) 15.0. Chromatography is used to assess the content of the above-mentioned groups of hydrocarbons and octane-enhancing additives - esters.

In order to increase the efficiency of one of the petrochemical enterprises by involving low-demand products in the production of automotive fuel, research work was carried out. The tasks of the researchers included: a detailed study of gasoline components - real samples from technological installations of a number of oil refining enterprises; a comprehensive analysis of the product of a petrochemical enterprise – oxygenate; selection of the ratio of gasoline components and a high-octane additive based on the results of gas chromatographic analysis.

During the experiment, an array of data was accumulated, and model samples of gasoline were prepared in the laboratory. In order to confirm the correctness of the selected compounding formulation of the studied components, each sample of the model range was determined by the octane number according to the motor (GOST 511) and research (GOST 8226) methods.

This work is the initial stage in the process of setting up the production of motor fuel. The role of chromatography as a research method is obvious.

# CHARACTERISATION OF THE COMPOSITION OF BREWING HOP VARIETIES USING HPLC-HRMS AND MOLECULAR NETWORKING

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*Humulus lupulus* is perennial climbing plant of the hemp family. Hops are used in beer brewing as a flavoring and preservative, as well as in bioactive additives. The unique profile of the biological activity of this plant is formed by the diversity of its secondary metabolites, which include alpha-, beta-bitter acids and flavonoids. The main method for analyzing the bioactive components of hops is HPLC-MS with reversed-phase separation. Moreover, the use of high-resolution mass analyzers increases the information content of the analysis<sup>1</sup>. In case of plants, limited information presented in public mass-spectrometry databases leads researchers to use instruments for mass-spectra characterization, such as molecular networking, in cases, when target metabolite is unknown.

The aim of the present work was to characterize the metabolome of brewing hop varieties based on the results of sample analysis by HPLC-HRMS and further visualization of the experimental data by molecular network construction. The analysis was carried out using HPLC-MS with an orbital-ion trap mass analyzer in the 'data-dependent' mode of accumulation of fragmentation spectra. The obtained data underwent chromatographic peak picking and filtering procedures, after which molecular networks were constructed using the GNPS service. The components were identified based on the set of observed fragments, retention information, comparison with databases and literature sources.

Based on the results, more than 50 components of the studied extracts were characterized, including proposed structures for compounds not previously described in the literature. The present work demonstrates the efficiency of using molecular networks in the characterization of complex samples.

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# APPLICATION OF SUPERCRITICAL FLUID CHROMATOGRAPHY-TANDEM MASS-SPECTROMETRY FOR DETERMINATION OF TRANSFORMATION PRODUCTS OF 1,1-DIMETHYLHYDRAZINE IN SOILS

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1,1-Dimethylhydrazine is a highly reactive and toxic substance widely used in rocket and space activities. The long period of its usage has resulted in contamination of areas located in launch vehicle crash sites not only with rocket fuel, but also with its transformation products. To monitor the content of formed toxic compounds, GC and HPLC techniques in combination with mass spectrometric detection are currently used, but have disadvantages such as long analysis time in case of GC and high consumption of organic solvents in case of HPLC. An alternative for the determination of the formed compounds can be SFC, which has proved to be a green, rapid and selective method.

We have proposed two approaches based on the SFC-MS/MS technique for the determination of transformation products of 1,1-dimethylhydrazine, namely 2-Formyl-1,1-dimethylhydrazine and two dimethylureas, as well as 20 heterocyclic nitrogen-containing compounds of different classes - pyrazoles, imidazoles, triazoles and pyridines. Both approaches combine rapidity, selectivity and high sensitivity. Separation was performed using BEH-2EP and HSS Cyano stationary phases (silica gels with grafted 2-ethylpyridine and cyanopropyl groups). The analysis times are 2 and 8 min, respectively. Combined with pressurized liquid extraction, the limit of quantification of the analyzed compounds ranges from 0.03 to 1.8 mg/kg with no significant matrix effects for both peat and sandy soils, 75-115%.

Analysis of peat bog and sandy soils contaminated with rocket fuel showed the presence of some detectable compounds with concentrations ranging from 0.27-10 mg/kg and 1-190 mg/kg, respectively.

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# SOLID-PHASE EXTRACTION OF FLAVONOIDS BY ORDERED MESOPOROUS SILICA SYNTHESISED IN THE PRESENCE OF POTENTIAL SORBATES AS A STAGE OF CHROMATOGRAPHIC ANALYSIS

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The development of sample preparation methods is related to the use of new materials with controlled properties. The appearance of silica with ordered nanostructures makes it possible to increase the efficiency of sorption concentration, especially in solid-phase extraction under dynamic conditions<sup>1</sup>. The control of pore size, specific density of sorption sites and their distribution on the surface of mesopores allows to choose the optimal sorbent for the analysis of a certain group of substances. The selectivity of target substances extraction can be significantly increased by synthesizing sorbents in the presence of target sorbates.

Ordered mesoporous silica was prepared by sol-gel synthesis with hydrothermal treatment. Polyphenolic substances were determined in various natural objects with sample preparation by solid-phase extraction and its modern variants (matrix solid-phase dispersion and dispersive solid-phase extraction) using ordered mesoporous silica as sorbents. The determination of substances was carried out by HPLC with diode-matrix detection.

The application of nanostructured silica with highly enhanced surface allows to increase the completeness of analytes extraction from complex matrices. The parameters of their separation are improved, high desorption degrees are achieved at minimum solvent volumes.

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# DETERMINATION OF SERINE AND ASPARAGIC ACID ENANTIOMERS IN HUMAN BRAIN TISSUE

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D-amino acids can act as biomarkers for a number of serious neurodegenerative diseases, such as Alzheimer's disease, schizophrenia, Parkinson's disease<sup>1</sup>. A popular method for the determination of D-amino acids in the presence of L-amino acids in biological samples is chromatography on chiral columns. Columns with chiral stationary phases (CSPs) with grafted cyclodextrins are often used for this purpose, which are characterized by a significant analysis time<sup>2</sup>. In this work, it is proposed to use a new CSPs with a zwitterionic type ligand, which will reduce the time of the chromatographic stage of analysis by 2 times. The work was carried out on a chromatograph Ultimate 3000 (Thermo Fisher, Germany). The separation of serine and asparagine enantiomers was carried out on CSPs with a quinidine adduct grafted to silica gel and Leu-Ala (column ASTRA CHSAK 58B 150 mm x 3 mm). Methanol with formic acid additives was used as the mobile phase (50 mM) and triethylamine (25 mM). Samples were derivatized with dansyl chloride<sup>3</sup>. Issues of accuracy, precision, and reproducibility of the analysis are discussed. The influence of the matrix of biological samples on the accuracy and precision of the determination of amino acid enantiomers is considered.

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# CYANOACETOHYDRAZIDE IS A NOVEL DERIVATIZATION REAGENT FOR STEROID HORMONES DETERMINATION IN URINE

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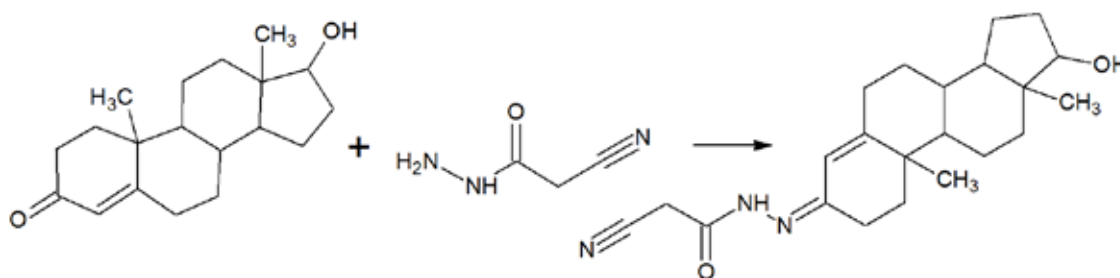
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Steroid hormones play a vital role in human body, as a result they are of great interest to clinical diagnostics of various diseases. Unfortunately, the possibility of simultaneous determination of steroid hormones belonging to various classes by high-resolution mass spectrometry is difficult, since the ionization efficiency of many estrogens and a number of corticosteroids is significantly higher in negative ion mode.

To solve this problem, derivatization can be used. This approach allows to obtain derivatives of target compounds that can be effectively ionized in positive ion mode, meanwhile to improve sensitivity.

The application of cyanoacetohydrazide for derivatization of steroid hormones is discussed in this work. It is a convenient candidate for the role of potential derivatization reagent due to its prevalence, availability and wide application in organic synthesis. The derivatization scheme is shown in Fig. 1.



**Figure 1.** The scheme of testosterone derivatization with cyanoacetohydrazide

The proposed approach has been used for UHPLC-HRMS analysis of real urine samples. The new derivatization reagent made it possible to simultaneously determine steroid hormones belonging to various classes and also to significantly reduce the detection limits in comparison with ones of native steroids.

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# PHTHALYLGLYCYL CHLORIDE IS A NOVEL DERIVATIZATION REAGENT FOR AMINO ACIDS DETERMINATION IN URINE

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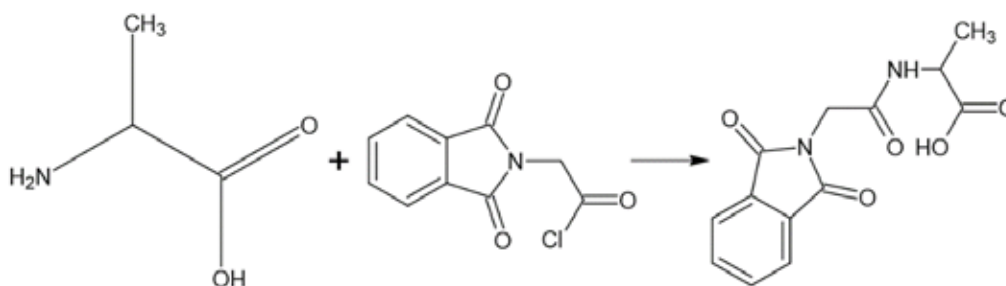
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Amino acids are the main structural elements of proteins. Their abnormal concentration levels in human biological fluids may indicate the presence of pathologies associated with inborn errors of metabolism, such as phenylketonuria, thus the determination of amino acids is vital for clinical diagnostic purposes.

At present, the most common method for amino acids determination is reversed-phase HPLC with mass spectrometric detection. Due to polar nature of the analytes, the application of this method requires derivatization, which allows to introduce a non-polar fragment into amino acid molecules. Existing reagents have several disadvantages, including the inability to derivatize secondary amino groups due to steric hindrance and long incubation times. There is a need to develop new derivatizing reagents to make it possible to offset the above disadvantages.

In this work, phthalylglycyl chloride, a reagent widely used in organic synthesis, is studied as a novel derivatizing reagent. The derivatization scheme is shown in Fig. 1.



**Figure 1.** The scheme of alanine derivatization with phthalylglycyl chloride

Real urine samples were analyzed by UHPLC-HRMS. The efficiency of amino acid derivatization with a new reagent and researched reagents – dansyl chloride, o-phthalaldehyde and 9-fluorenylmethylchloroformate – was assessed. The obtained results indicate that further research of a new reagent is promising.

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An abstract, vibrant, and complex structure composed of numerous small, colored particles (red, orange, yellow, green, blue, and purple) arranged in a swirling, organic, and somewhat crystalline form against a dark background. The structure has a central core with various arms and loops extending outwards, resembling a molecular model or a complex crystal lattice. The overall effect is one of dynamic energy and intricate detail.

**11<sup>TH</sup> INTERNATIONAL  
FRUMKIN SYMPOSIUM  
ON ELECTROCHEMISTRY**

# THE CHALLENGE OF RECHARGEABLE BATTERIES WITH VERY HIGH ENERGY DENSITY AND PROLONGED CYCLE LIFE: FROM BASIC SCIENCE TO PRACTICAL DEVICES

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Electro-mobility is a major challenge today in the field of electrochemical power sources. However, we encounter too many unsupported promises! Examples: Many publications on ‘novel’ nano-materials, not suitable for practical battery applications. A lot of words on “beyond Li-ion batteries”. Beyond... for what purposes? Hard to see what can be relevant for electrochemical propulsion beyond Li-ion batteries, except  $H_2/O_2$  fuel cells. The main theme of this presentation is to examine what is the true horizons for advanced high energy density batteries that can promote the electro-mobility revolution. The limiting factor in Li-ion batteries in terms of energy density, cost, potential, durability and cycling efficiency are the cathode materials used. We will examine most energetic cathode materials and novel approaches we developed for their stabilization. We describe in this lecture which electrode materials can be relevant, methodologies of doping, coating cathode materials such as Li & Mn rich NCM, Ni rich NCM, high voltage LCO and LMNO.<sup>1,2</sup> We will discuss the renaissance of Li metal-based rechargeable batteries.<sup>3</sup> We have learned how to stabilize Li metal anodes in rechargeable batteries using reactive electrolyte solutions that induce excellent passivation through controlled surface reactions. The emphasis is on fluorinated co-solvents that open the door for a very rich surface chemistry that forms passivating surface films that behave as ideal solid electrolyte interphase on both anodes and cathodes in advanced secondary Li batteries.

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# ELECTRON TRANSFER REACTIONS AND ELECTROACTIVE MATERIALS FOR LATENT FINGERPRINT VISUALIZATION

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A fingerprint is a unique time-invariant biometric feature and is the most frequent physical evidence used to identify an individual in a criminal investigation. Most fingermarks are *latent* (non-visible) marks: they require chemical treatment to generate a visible image. The reagent must be delivered with high spatial selectivity to *either* the fingerprint residue *or* the bare substrate. This presentation describes the contribution of electrochemical processes to achievement of this aim using metallic and polymeric materials.

We describe mechanistic insights into metal nanoparticle deposition rates on ridge vs furrow regions that dictate image contrast in the physical developer (PD) and multi-metal deposition (MMD) processes. PD involves Ag deposition on fingerprint residue on paper substrates. In MMD, Au pre-deposited on the residue creates nucleation sites for Ag deposition on plastic substrates.

An alternative strategy is to use the fingerprint residue as a “mask” to direct electrochemically generated reagent to the *bare surface* between the deposited ridges; this creates a negative image of the fingerprint. When the surface is a reactive metal (Cu or Fe), ions of a more noble metal (Ag<sup>+</sup> on Cu or Cu<sup>2+</sup> on Fe) can undergo galvanic exchange, generating an image in the more noble metal.

When the surface is an inert metal, electrodeposition of a metal or polymer is effective. We show formation of Ag nanoparticle rafts on bare regions of fingerprinted metal surfaces; image analysis quantifies spatial selectivity.<sup>1</sup> Electropolymerisation of aromatic monomers creates negative images of latent marks *via* polyaniline,<sup>2</sup> PEDOT,<sup>3</sup> or poly(pyrrole-co-EDOT),<sup>4</sup> electrochromic films. We demonstrate dye encapsulation in polymer films, using FTIR surface compositional mapping of polymer and dye components. These molecular data are correlated with image quality of macroscopically visualized fingermarks.

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# HYDROGEN PEROXIDE SOL GEL PROCESSING OF Li, Na, AND K METAL ION BATTERY ANODES

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Hydrogen peroxide sol-gel processing (PSGP) is a low-temperature, waste-free process used to control the growth of peroxy-nanoparticles and their deposition on particulates. Hydrogen peroxide acts as a capping agent to control nanoparticle growth and promote their hydrogen bonding to the substrate. Different metal oxides, metal sulfides, and zero-valent metal nanoparticles can be readily synthesized directly from hydrogen peroxide-rich solutions or indirectly from intermediates produced by PSGP. These nanoparticle coatings form useful alloys for lithium, sodium, and potassium, thus serving as promising high-charge-capacity ion battery anodes. Particularly, metal sulfides can utilize both alloying and conversion reactions to double the charge capacity.

We demonstrate the utility of the PSGP approach for coating various 2-D conductive substrates, such as conductive reduced graphene oxide and  $\text{Ti}_3\text{C}_2\text{T}_2$  MXenes, with different metal ion hosts, and evaluate their electrochemical performance as lithium, sodium, and potassium ion battery anodes. In a related approach, we synthesize by PSGP a highly soluble germanium oxide intermediate that can be readily dissolved in aqueous solution and converted to germanium nitride, germanium phosphide, and germanium sulfide hosts.

Remarkable performance as metal ion battery anodes can be readily achieved through this approach.

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# PORE FORMATION IN LIPID MEMBRANES: INFLUENCE OF TENSION, SUPPORT, SOLVENT

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Lipid bilayers are the main structural element of cell membranes. The amphiphilicity of lipid molecules provides an extremely low permeability of lipid membranes, which allows them to perform their main barrier function in cells. Through pores can be formed in membranes when subjected to external stress. The sharp increase in membrane permeability is used in a number of cellular processes, as well as in various biotechnological and biomedical applications. Using the theory of elasticity of lipid membranes, we theoretically analyzed the process of pore formation under various conditions. The formation of a pore requires overcoming an energy barrier, the height of which is determined both by the structure of membrane deformations at the edge of the pore and by the external stress causing pores. We described the formation of pores under the influence of lateral tension applied either symmetrically or asymmetrically to membrane monolayers. The influence of spontaneous curvature of lipid monolayers in membranes asymmetric in lipid composition on poration was determined. For model membranes, the influence of the presence of a solid support and an organic solvent used in the formation of membranes on the formation of pores was studied. Analysis of the trajectories of the pore formation process under various external conditions made it possible to understand the mechanisms underlying the experimentally observed phenomena.

# ELECTROCHEMICAL NOISE: OBJECTS AND PROBLEMS

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Electrochemical noise is a fluctuation of potential or current that occurs as a result of physical and chemical processes taking place in the electrochemical system. They are generated by non-equilibrium phenomena arising from changes in the states of any components of the electrochemical cell.

The method has gained the greatest popularity in the field of corrosion, due to the sufficiently high noise amplitudes (up to hundreds of millivolts in potential) observed during active corrosion of metals. By their nature, corrosive noises occur mainly from the processes of phase formation, in particular the release of gaseous products, and the formation of solid films, which led to independent studies of these phenomena.

There is also a certain interest in the study of electrochemical noise in the field of chemical current sources. The amplitudes of noise in primary elements of various types under load can reach units and even hundreds of microvolts. In this case, the frequency dependences of the spectral power density have the form of  $1/f^n$ . Lithium-ion batteries are characterized by an increase in noise amplitude only at the very end of the discharge process. There is also an increase in the amplitude of noise during the aging process (cycling). Frequency dependences of noise with several plateaus were obtained for fuel cells, and models based on electrochemical impedance data were proposed<sup>1</sup>. There is currently no generalized and self-consistent theory of electrochemical noise for objects such as chemical current sources. This is largely due to the insufficient amount of experimental material, the collection of which is limited by the lack of commercial equipment.

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# CURRENT INTERRUPTION TECHNIQUES IN ELECTROANALYSIS

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Interruption methods, or measurement methods associated with the periodic opening of an electrical circuit, are characterized by a significant signal gain (3 or more orders of magnitude) in relation to measurements in direct current mode. In interruption amperometry, there is no interference in the form of a charging current of the DES, since the recorded current, depending on the concentration of the analyte, is capacitive in nature. On the other hand, such high current amplification coefficients lead to a significant narrowing of the “electrochemical window” due to the electrochemical stability of the solvent and the electrode material, therefore, the choice of solvent and electrode material is key in the development of measurement techniques. In addition, the method is extremely sensitive to electrochemically active impurities. Switching amperometry is promising for measurements with UME.

Another option for interruption measurements is Interruption conductometry, which also has high sensitivity, allows you not to use high-frequency alternating current, due to the use of low voltages. The theory of the method is considered, it is shown that the method is free from the “eternal enemies” of conductometry of the DES capacity and parasitic capacity, which increases with decreasing concentration. It is proved that the use of switching conductometry to measure currents through small holes: ion channels, capillaries, nanopores eliminates interference in the form of double-layer and parasitic capacitance and significantly increases the measured current. A nanopore model was created, on which measurements were carried out and a linear dependence of the current on the electrolyte concentration was obtained.

The use of interruption conductometry is especially promising for measuring the current of nanopores during electrochemical DNA sequencing, since it allows measurements to be carried out in solutions with a low concentration of potassium chloride, use low voltage values and obtain currents at the nanoampere level, instead of traditional picoampere values. Current measurements on alpha-hemolysin nanopores were carried out. The results obtained prove the validity of the assumptions made.

# ELECTROCHEMICAL SYNTHESIS OF NEW PHOTOCONDUCTIVE MATERIALS BASED ON POLY-3,4-ETHYLENEDIOXYTHIOPHENE

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Electrochemical synthesis of electroactive polymers and their composites is an actual approach to creating thin-film functional layers for modern optoelectronic devices. We were the first to demonstrate the possibility of electrodeposition of composites of electroactive polymers with metal phthalocyaninate or fullerene with ionic substituents as charge-compensating anions in aqueous solutions without the use of supporting electrolyte.

Using the example of poly-3,4-ethylenedioxythiophene (PEDOT), as one of the most promising electroactive polymers, and zinc or copper phthalocyaninates containing 16 ionic carboxylate groups, a series of electrodepositions of composite layers was performed. Phthalocyanines are known to be photoactive in the UV-Vis region of the spectrum. Electropolymerization of 3,4-ethylenedioxythiophene in the presence of different content of water-soluble sodium salts of zinc or copper phthalocyaninates makes it possible to control the efficiency of photogeneration of charge carriers in the layers.

Also, a composite layer was obtained by electrodeposition of PEDOT in the presence of a water-soluble Na<sup>+</sup>-containing fullerenes with ionogenic groups. Electroconductive PEDOT absorbs radiation in the near-IR region due to the presence of polarons and bipolarons, the levels of which are inside the polymer bandgap. The composite layer exhibits photoconductivity in the near-IR region of the spectrum. In this case, the fullerene acts as an electron acceptor and contributes to increasing the concentration of free charge carriers.

The electrodeposition processes were studied by UV-Vis spectroelectrochemistry. The layers were characterized by cyclic voltammetry, spectroscopy and spectroelectrochemistry in the UV-Vis-NIR regions, Raman spectroscopy, and photoelectric conductivity measurements.

*The work was carried out with the financial support of the Russian Science Foundation, project No. 23-19-00884.*

# PLATINUM-CONTAINING ELECTROCATALYSTS FOR HYDROGEN-AIR PEMFC: SYNTHESIS AS A SCIENCE, MICROSTRUCTURE, AND ELECTROCHEMICAL PERFORMANCE

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In hydrogen-air fuel cells with a proton exchange membrane (PEM FC), Pt-containing electrocatalysts will not be replaced by platinum-free analogues, at least in the medium term<sup>1</sup>. In this case, it is necessary to increase the activity of catalysts in current-generating reactions, especially in the oxygen electroreduction reaction (ORR), increase stability and reduce the Pt content in their composition. The functional characteristics of catalysts are determined by their composition and structure, which, in turn, strongly depend on the synthesis method.

The report presents the results of research in the field of development of liquid-phase synthesis methods for Pt/C and PtM/C (M = Cu, Ni, Co) catalysts, studying their microstructure and electrochemical behavior, obtained in recent years in the laboratory “Nanostructured materials for electrochemical power engineering” SFedU and in the PROMETHEY R&D company – catalysts manufacturer for electrolyzers and PEM FC.

An original technique has been developed for in-situ monitoring of the kinetics of the multi-stage transformation of Pt(IV) → Pt(0)<sub>x</sub> in the processes of liquid-phase synthesis of platinum-containing nanoparticles (NPs) and platinum-carbon catalysts. This made it possible to optimize synthesis conditions, improve control of the shape and size of NPs, and increase the uniformity of their distribution over the surface of the carrier. Pt/C and PtM/C catalysts have been obtained that are superior to foreign commercial analogues both in activity in the ORR and in stability. Tests of catalysts in PEM FC membrane-electrode assemblies were carried out.

In general, significant progress has been made in understanding the relationship between “synthesis method → microstructure → electrochemical behavior” of the catalyst.

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# INTERCALATION PROCESSES IN $\text{Al}_x\text{V}_2\text{O}_5$ CATHODES IN $\text{Mg}^{2+}$ - AND $\text{Zn}^{2+}$ - CONTAINING AQUEOUS ELECTROLYTES

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Among various post-lithium metal-ion systems, magnesium-ion and zinc-ion batteries can be considered attractive for grid-scale energy storage due to their economic viability, satisfactory energy performance, and improved battery life.

Guest ion-doped vanadium oxides are currently considered promising cathode materials because they have a tunable interlayer space due to the pillaring effect of the doping ion, expanding the interplanar space and thus stabilizing the oxide structure and allowing to accommodate intercalated ions and solvent molecules. At the same time, it can lower the energy barrier of ion diffusion, potentially enabling rapid diffusion of multivalent ions.

The electrochemical behavior of novel  $\text{Al}_x\text{V}_2\text{O}_5$  ( $x=0.059\text{--}0.072$ ) cathode materials in magnesium- and zinc-containing mild acidic electrolytes (pH 4-5) based on simple metal salts will be reported.

The application of combined methods for studying the mechanism of charge-discharge processes to determine the role of proton injection into the  $\text{Al}_x\text{V}_2\text{O}_5$  cathode material will be considered together with the results on the functional energy storage properties of these materials obtained by standard electrochemical methods.

In particular, in situ monitoring of the pH of the supporting electrolyte with a pH indicator (bromocresol green) additive by UV-vis spectroscopy and the use of a pH-microelectrode to monitor local pH changes in the near-electrode layers during charge-discharge will be demonstrated.

The measured electrolyte pH values have been shown to correlate with the reduction-oxidation peaks of vanadium in the  $\text{Al}_x\text{V}_2\text{O}_5$  composition and indicate the processes of proton injection and expulsion in the corresponding charge-discharge cycles. The issues of co-intercalation of metal ions and protons and the differences in the mechanisms of the processes for zinc- and magnesium-containing electrolytes will be discussed.

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# PROBLEMS OF CORRECT MEASUREMENTS OF NANOSTRUCTURED ELECTRODES

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Currently, in most cases, the subject of research is electrodes obtained by applying various nanostructured substances to a conductive substrate, and the main way to study such electrodes is the method of cyclic voltammetry (CV). However, an analysis of publications shows that authors often either do not fully use its capabilities, or in the interpretation of the data obtained go far beyond the permissible limits, not taking into account both the electrochemical heterogeneity of such electrodes and their effective porosity in the interpretation of the results. At the same time, in the literature one can find theoretical studies devoted to the application of this method to a complex electrode surface often correlated with corresponding experiments. It is important to note that the results obtained by the CV method, in addition to classifying the mechanism of electrode processes, are the basis for the determination of a number of significant parameters of electrochemical characterization of nanostructured electrodes, such as the electrochemically active surface area (ECSA) and the “double-layer” capacity of the electrode (C), values of rate constants of electrode reactions ( $\kappa$ ), etc. For this reason, the correctness of CV measurements is of key importance for obtaining reliable information about the values of ECSA, C and  $\kappa$ .

Based on comparison of the shape of calculated and experimental voltammograms and a review of literature data, the main reasons that complicate the interpretation of CV data were established. These are inadequate selection of the potential scan interval, insufficient range of potential scan rates, virtually universal ignorance of experimental errors, lack of measurements at different depolarizer concentrations, and the use of idealized criteria to determine the mechanism of the process under study. It is concluded that even in the simplest case, a correct analysis of CV data makes it possible to semi-quantitatively determine  $\kappa$ , reliably estimate the characteristic times of chemical stages only for CE or EC processes, estimate the absolute value of ECSA, obtain relatively reliable data on the value of C and quantitatively precise values of formal potentials of redox reactions.

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# CHEMICAL AND ELECTROCHEMICAL ASPECTS OF UTILIZING THE BUFFER LAYERS IN SOLID OXIDE FUEL CELLS

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Research and development of solid oxide fuel cells (SOFCs) and solid oxide electrolysis cells (SOECs) are currently of paramount importance in terms of realizing hydrogen energy and carbon emission reduction programs, which many countries have committed to. Although, there are many outstanding results in the fabrication and characterization of SOFCs and SOECs with promising oxygen-ionic and proton-conducting electrolytes, conventional zirconia electrolytes are still widely used not only in a lab-scale setup, but also in the form of enlarged cells and stacks, with the experimental operation of the latter during 10 000–100 000 h. To ensure good performance stability and microstructural integrity of such multilayer cells, a special attention should be paid to the chemical activity of functional materials toward their interaction with each other, especially in long-term focus. The literature analysis has shown that many undesirable processes occur in SOFCs and SOECs with the classical pairs of zirconia electrolytes and strontium-containing electrodes, including element segregation and interdiffusion, insulating phase formation, microscopic defect appearance, and delamination. Some of these processes can be efficiently eliminated by using so-called interlayers designed from doped ceria materials. Due to their numerous beneficial functions, such interlayers have several synonymous names: blocking, barrier, buffer, or protecting layers. In the present report, the recent progress and achievements in the fundamental and applied research on ceria interlayers and their impact on chemistry and electrochemistry of solid oxide cells based on classical zirconia electrolytes as well as promising oxygen-ionic and proton-conducting analogs.

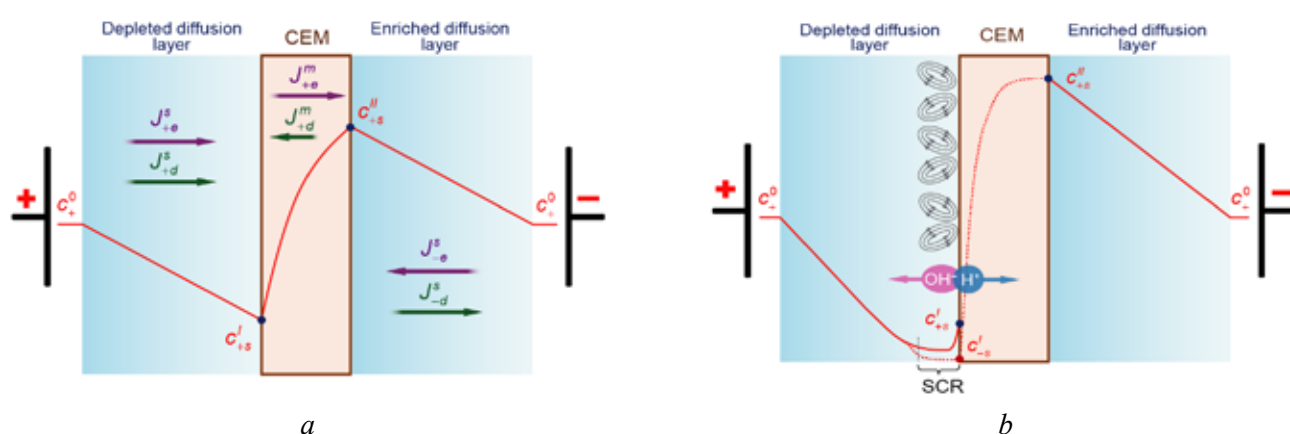
# CONCENTRATION POLARIZATION IN ELECTROMEMBRANE SYSTEMS

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In membrane science, concentration polarization (CP) is understood as the phenomenon of the formation of concentration gradients near membrane/solution interfaces under the influence of an external driving force<sup>1</sup>. The cause of the CP is the selectivity of ion transport through the membrane: the retained substances are concentrated at the solution/membrane interface. Interestingly, the term appears to have come from electrode kinetics.

CP is an inevitable consequence of membrane permselectivity. However, reducing the CP is an important issue. The report discusses phenomena associated with CP, methods of modifying the membrane surface to enhance electroconvection and weaken the dissociation of water molecules (Fig. 1), the use of separators, membrane surface profiling and other techniques, including the application of a pressure field.



**Figure 1.** Concentration profiles in a cation-exchange membrane (CEM) and diffusion layers at an underlimiting (a) and overlimiting current (b); space charge region (SCR) and electroconvective vortices are shown

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# FEATURES OF INTERPRETING THE RESULTS OF ELECTROCHEMICAL EXPERIMENTS

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Cyclic voltammetry (CVA) and electrochemical impedance spectroscopy (EIS) are very popular research methods in modern electrochemical experimentation. Both methods have a reliable theoretical basis and strictly defined limits of applicability. In many publications, the results obtained using these methods are processed and discussed without taking into account the limits of applicability, which catastrophically reduces the reliability of the conclusions.

The CVA method records the change in current over time when a potential is applied that varies linearly with time. This produces curves with a maximum. When creating the theory, it was assumed that the electrode process rate is controlled by diffusion (Randles, Ševčík) and/or charge transfer (Matsuda and Ayabe). In all cases, conditions of plane semi-infinite diffusion were considered, and the electrode surface was assumed to be equally accessible. The relationship between the equilibrium potential and concentration was described by the simplified Nernst equation, where activity is identified with concentration. In most real experiments, these conditions are not met, and the only criterion of applicability is considered to be the linear dependence of the maximum current on the root of the potential scan rate. Almost never is the experimental curve compared with the theoretical one, and the characteristic size of the electrode roughness is not compared with the diffusion length.

The EIS method assumes the same diffusion conditions and the same relationship between the equilibrium potential and the concentration of the diffusing species. All comments related to the CVA method are valid here. When analyzing EIS data, an equivalent circuit is usually proposed and specific values of some of its elements are given. It is sometimes possible to compare experimental values of certain elements (electrolyte resistance, double layer capacitance) with values calculated from independent data, but such comparisons are rarely made.

# SUPERCAPACITORS BASED ON CARBON MATERIALS OBTAINED FROM WASTE PROCESSING PLANT RAW MATERIALS

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A unique feature of carbon materials (CM) is the possibility of their production from plant raw materials, products and even waste from its primary processing. The wide range of possible applications of CM necessitates the development of technology that makes it possible to obtain materials with a certain morphology and composition depending on the scope of their practical use. Particular attention should be paid to the possibility of preserving the molecular complexity of the original natural compound in the finished CM during the thermochemical conversion process, as well as the preservation or transformation of the original organic and inorganic components, acting, in this case, as doping agents. On the other hand, an important factor influencing the physicochemical properties of carbon materials is the presence of non-metal heteroatoms such as N, P, B and S in their structure.

The paper discusses the prospects for obtaining CMs for use in supercapacitors. CMs are obtained from waste chemical processing of plant raw materials into 5-hydroxymethylfurfural – solid<sup>1</sup> and liquid<sup>2</sup> humins. Another source of carbon-containing raw materials is sugar beet processing waste<sup>3</sup>. Mushrooms (*Fomes fomentarius*)<sup>4</sup> can be used as a biotemplate for the production of carbon fibers.

Correlations have been established between the composition of raw materials, production conditions, and the structural and electrochemical properties of the resulting carbon materials in supercapacitors.

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# THE FAST TRANSFER OF PROTONS LIBERATED FROM PHOTOACTIVATE COMPOUND ON THE BOUNDARY OF THE LIPID MEMBRANE

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The protons on the membrane/water interface have unique properties, such as a possibility to move along the membrane, thereby influencing on their transport by the membrane proteins. Such behavior is provided by a potential barrier due to water molecules bound on the membrane surface. The height of the barrier can be evaluated by measuring the rate of exchange of protons between the membrane surface and water, using the photoactivated compounds. One of them – 2-methoxy-5-nitrosulfate of sodium (MNPS) liberating the proton and sulfate under exciting by UV light was studies by us earlier. We have observed by the method of inner field compensation the change of boundary potential and capacitance of the bilayer lipid membrane, one side of which contained the MNPS molecules bound on its surface. However, the protons on the membrane remained in the equilibrium with water, and the kinetics of the process was limited by the slowest step – the change of pH in the unstirred layer adjacent to the membrane.<sup>1</sup>

To evaluate the rate of a faster stage, presumably assigned with the transfer of protons across the barrier on the membrane surface, the change of the boundary potential was measured by the electrometer, and the MNPS molecules were activated by the UV light flash. We observed a fast change of the potential after the flash coupled with a restoration of equilibrium of protons and MNPS anions between the membrane and water followed by a slow relaxation due to restoring of concentration of protons, buffer and MNPS in the unstirred layer. The magnitude of fast phase of the potential change decreased with increase of the concentration of buffer in solution and decrease its pH indicating on the assignment of this phase with the transfer of protons from water to the membrane.

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# APPROACHES TO THE DEVELOPMENT OF ELECTROLYTES FOR SUPERCAPACITORS WITH EXTENDED OPERATION TEMPERATURE RANGE

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Supercapacitors (SC) are increasingly used in alternative energy, backup power supply systems, braking energy recovery in electric vehicles, etc. The use of organic electrolytes allows not only to increase the operating voltage, but also to expand the temperature range of operation of the SC. Electrolytes containing two- or three-component systems of aprotic organic co-solvents based on acetonitrile and providing high SC performance characteristics at temperatures from  $-70\text{ }^{\circ}\text{C}$  to  $+65\text{ }^{\circ}\text{C}$  have been developed<sup>1</sup>.

At the same time, taking into account the climatic conditions of the Russian Federation, there is a need to create electrolytes for other temperature ranges, in particular, from  $30\text{ }^{\circ}\text{C}$  to  $+85\text{ }^{\circ}\text{C}$ . The main method of their development is the selection of co-solvents for cyclic alkyl carbonates in order to increase the electrical conductivity of electrolytes at low temperatures. An approach has been proposed that makes it possible to predict changes in the electrical conductivity of organic electrolytes with a multicomponent system of cosolvents with decreasing temperature based on the activation energy of electrical conductivity, dielectric characteristics and viscosity of the cosolvent system, interactions between ions, their solvation and association<sup>2</sup>.

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# HYBRID NANOCOMPOSITE SOLID ELECTROLYTES

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It is known that the use of solid electrolytes in chemical power sources can significantly increase mechanical and thermal stability, prevent dendritic growth, undesirable effects of mixing active anodic and cathodic reagents, and increase the reliability of the device. The solid electrolyte must serve as a separator, have high ionic conductivity and electrochemical stability with respect to electrode materials. Composite solid electrolytes are a promising class of solid electrolytes, the properties of which can be varied within wide limits by changing the morphology and composition of the electrolyte.<sup>1</sup> The use of composites makes it possible to form a gradient transition to the electrode material and significantly increase the electrode/electrolyte contact area. However, even in this case, the contact between the solid phases of the electrode and electrolyte is gradually broken down during cyclic operation of the electrochemical device.

To solve this problem, hybrid nanocomposite materials<sup>2</sup>, nanoheterogeneous systems consisting of organic and inorganic components connected to each other by relatively strong non-covalent bonds, can be used as a solid electrolyte. Examples of such systems are nanocomposites based on organic salts or polymers with nano-sized particles of inorganic phases included in them, which have high ionic conductivity. The report provides a review of the literature and our own experimental data on the conductivity of such materials<sup>3,4</sup> and their use in chemical current sources.

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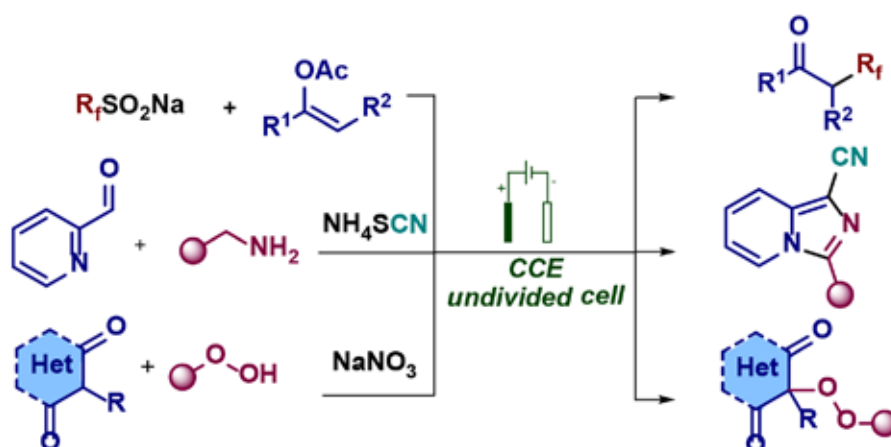
# ELECTROCHEMICALLY MEDIATED FORMATION OF C-C AND C-HET BONDS

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Nowadays, electroorganic synthesis is considered as one of the most actively developing areas of modern organic chemistry. This study develops state-of-the-art synthetic organic electrochemistry – methods for C-C and C-Het bonds formation.

The electrochemical synthesis of fluorinated ketones from enol acetates and  $R_fSO_2Na$  in an undivided cell under constant current conditions was developed.<sup>1</sup> The electrosynthesis proceeded *via* perfluoroalkyl radical generation from sodium perfluoroalkyl sulfinate followed by addition to the enol acetate and transformation of the resulting C radical to a fluorinated ketone.



[CN] species were generated in the course of electrochemical oxidation of SCN anion and used in the three-component electrosynthesis of 1-cyano-imidazo[1,5-a]pyridines from pyridine-2-carboxaldehydes, amines, and  $NH_4SCN$ .<sup>2</sup> In contrast to previously known electrochemical methods,  $NH_4SCN$  acts as a CN source rather than a SCN source.

We have disclosed the electrochemical generation of the *tert*-butyl peroxy radical from TBHP and developed the preparative electrosynthesis of organic peroxides with TBHP.<sup>3</sup> Electric current allowed radical peroxidation to occur without the traditional initiators: transition metals, iodine sources, high temperature or irradiation. The applicability of the developed electrochemical peroxidation to various C-H structures and 1,3-dicarbonyls was evaluated.

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# GALVANIC METALLIZATION OF HOLES OF MULTILAYER PRINTED CIRCUIT BOARDS

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Taking into account modern requirements for the dimensions and compactness of products, multilayer printed circuit boards (MPCB) are becoming more and more in demand in the industry. With the development of the electronic industry, their designs become more complicated, namely, the diameter of the transition holes decreases, the thickness and the distance between the paths of the conductive pattern) and the requirements for the quality of manufacture increase<sup>1,2,3</sup>.

The quality of PCB is determined, among other things, by the uniformity of the distribution of the galvanic copper coating in the holes. In modern PCB production technologies, high-tech electrolytes with high throwing power (TP) are used to form conductive pattern and metallize holes. Electrolytes based on copper salts, sulfuric acid, (II) and organic additives (suppressor, leveller and accelerator) are used at the stage of galvanic copper plating.

In the work, an electrolyte of the composition (g/l) was chosen as the base: 100  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ; 200  $\text{H}_2\text{SO}_4$  (96%); 0,11 NaCl. The effect of polyethylene glycol (PEG) as an inhibitory additive has been studied on the character of cathode polarization curves of the copper reduction process. It was found that the optimal molecular weight for polyethylene glycol is 4000 g/mol and a concentration of 1 g/l, at which the greatest polarization is ensured of the copper reduction process.

It was found that the gloss of coatings is affected by the length of the polyethylene glycol chain and when using PEG with a low molecular weight, less shiny coatings are obtained. The maximum gloss value of the coating (610 Gloss Unit) was obtained when PEG 4000 (1 g/l) was introduced into the base electrolyte in combination with a diazotized dye (leveller) and 3-mercaptopropyl sulfonate sodium (accelerator), which surpasses similar characteristics of a foreign electrolyte.

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# SELF-DIFFUSIOPHORESIS OF CATALYTIC MICROSWIMMERS

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Catalytic Janus swimmers have drawn a considerable interest during last decades<sup>1,2</sup> because of their ability to move autonomously as a result of the conversion of chemical energy into mechanical energy. The potential applications include drug delivery, lab-on-a-chip devices and nano-robotics. Microswimmers move due to the heterogeneous catalytic properties of the surface and inhomogeneous fluxes of active ions (reaction products).

Ion concentrations and electric potential near particles are governed by a system of nonlinear Nernst-Planck and Poisson partial differential equations. Since microswimmers are typically large relative to Debye length, our theoretical approach<sup>2,3</sup> utilizes the limit of thin electric diffuse layer (EDL). We consider two experimentally relevant cases when only one type of ion is released from the particle surface (type I microswimmers) or equal fluxes of cations and anions (type II microswimmers). We show that the electric field arises both in a thin EDL and at distances of the order of the particle size (outer region). Analytical solutions are obtained for the potential in the outer region as a function of the dimensionless ion flux from the surface (Damköhler number). Nonlinear effects cause a number of unusual physical phenomena, such as a change in the direction of particle motion with increasing Damköhler number, as well as the self-propulsion of uncharged particles.

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# SENSING OF MOLECULES AND MOLECULAR MACHINES WITH ELASTIC NANOPORES

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The recognition of single molecules using nanopores represents a pivotal tool in the field of proteomics. However, its application is currently limited to water-soluble analytes that are capable of passing through the pore lumen. In this study, we demonstrate that nanopore technology can be extended to the realm of membrane proteins by employing biomimetic membrane nanotubes that have been miniaturized to the dimensions of a nanopore. These elastic nanopores (ENPs), in contrast to their solid-state counterparts, possess an easily deformable elastic wall. Therefore, the ionic current flowing through them changes not only when a molecule enters the pore lumen, but also when it deforms its wall. This allows the detection of transmembrane proteins and proteins that bind to the outside of the ENP. Analyte molecules move along the ENP membrane under the action of an electric field, which can also be transmitted to proteins bound to the outer side of ENP by synthetic bolaamphiphilic transmembrane molecules specially designed for this purpose. We demonstrated the feasibility of recognizing single transmembrane and membrane-bound proteins by ENPs. The molecular parameters of the analytes were correctly determined in terms of their size, deformation capabilities, and conformational dynamics. Therefore, the different molecular sensing modes offered by ENPs allow the detection and analysis of different types of membrane proteins and interactomes in their natural environment.

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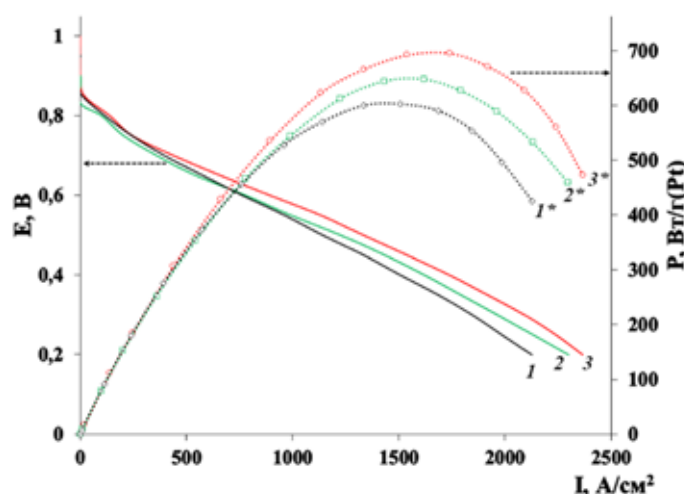
# INFLUENCE OF HEAT TREATMENT ON THE STRUCTURE AND ACTIVITY OF PTCU/C ELECTROCATALYSTS ON DIFFERENT CARBON CARRIERS

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Fuel cells (FC) are alternative power sources that are promising for use in transport. Platinum-based catalysts play a key role in fuel cells; doping them with various d-metals can significantly improve their functional characteristics.

Based on the results of the study, it was established that, regardless of the type of carbon support used, heat treatment of PtCu/C catalysts at 350 °C leads to a transformation of the structure of bimetallic NPs and an increase in activity in the ORR up to 1.6 times due to a change in the chemical composition of the surface<sup>1</sup>. The use of heat treatment for the PtCu/C catalyst made it possible to increase the maximum power of the membrane-electrode unit by 15% to 696 W/g (Pt), which exceeds the level of the commercial analogue (Fig. 1).



**Figure 1.** Current-voltage and power characteristics of the MEA with the catalysts under study: (1) Pt(Cu)/CN, (2) JM40, (3) Pt(Cu)/CN<sub>350</sub>

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# RESOLVING SOME CONTROVERSIES IN WATER AND ION TRANSPORT IN POLYMER MEMBRANES FOR WATER DESALINATION: HOW DO IONS AND WATER MOLECULES MOVE AND PARTITION?

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There is at the moment a big controversy worldwide about the nature of ion and water transport in ion-exchange membranes and especially nanofiltration and reverse osmosis. One side of the argument is strongly defended by scientists from the University of Austin, Texas, USA, and the other side from scientists at Yale, New Haven, USA. The discussion centers around the question how water absorbs in a membrane and flows across it. Does it first dissolve as in a dissolution process, and then diffuse across it? This is the “solution-diffusion” (SD) model. The other model says, no, water flows as cohesive fluid through the pores of the membrane, more like continuum or viscous flow. This is the “pore flow” model, related to the solution-friction (SF) model. Whereas the SD model dates back to 1965, the SF model is older, dating back to papers from around 1960 by A. Katchalsky.

An important argument for the SF model is the supposed existence of a water concentration gradient that drives diffusion. However, new calculations by Yale show that this is due to physical compression of the membrane, and in line with the pore flow mechanism, and does not lead to a concentration gradient.

A related question is how to describe activity coefficients of ions in the membrane. Based on a “Manning condensation” model, again from the Austin group, a model was proposed where ions arrange around strands of polymer in the membrane, leading to strong activity effects. A new model from the Yale group made a new model for ion activity in the membrane and concludes the opposite. Both groups agree activity effects in solution are important to calculate Donnan equilibrium.

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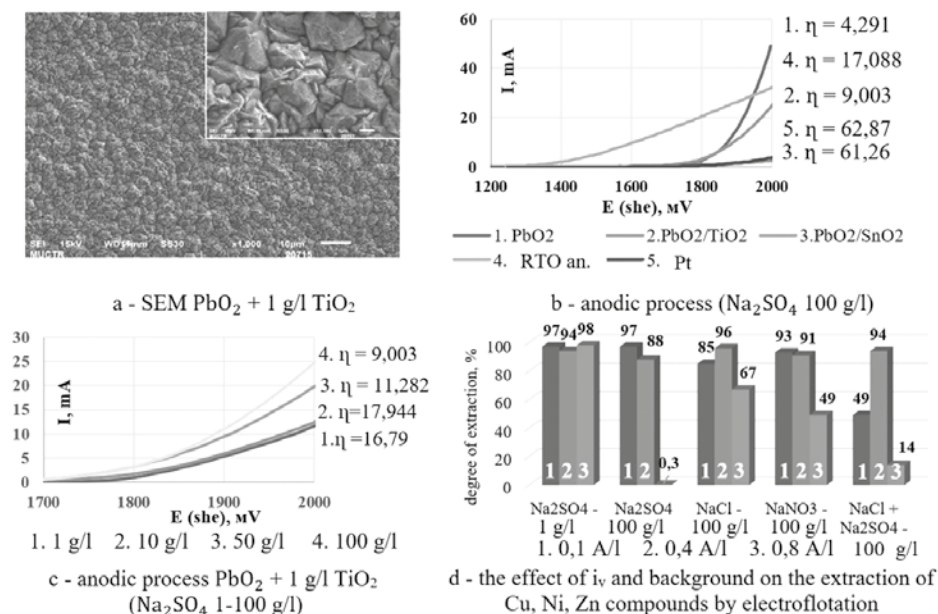
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# THE USE OF ELECTRODE MATERIALS BASED ON PbO<sub>2</sub> DOPED WITH TiO<sub>2</sub> AS A REPLACEMENT FOR RTO ANODE IN THE ELECTROFLOTATION PROCESS

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An important task is to produce anodes to exchange anode (RTO) in processes with low  $i_a$ , including for electroflotation (EF). Anodes made of lead dioxide with additives of Me<sub>x</sub>O<sub>y</sub> are prospective for this problem. It can be seen from the SEM (Fig. 1, a), that PbO<sub>2</sub> + TiO<sub>2</sub> (1 g/l) coatings on steel have a low voltage. The process of oxygen release on electrodes with various additives in sodium sulfate solutions (1–100 g/l) has been researched by the CVA method (Fig. 1, b, c)<sup>1</sup>.



**Figure 1.** Physical and chemical action of electrodes PbO<sub>2</sub> + TiO<sub>2</sub> (1 g/l)

In the presence of sodium sulfate 100 g/l (Fig. 1, d), the efficiency of the extraction process of copper, nickel and zinc compounds reaches 98–99% (10 minutes,  $i_v$  0,4 A/l), the PbO<sub>2</sub> + TiO<sub>2</sub> (1 g/l) electrode meets the demands of the electroflotation process.

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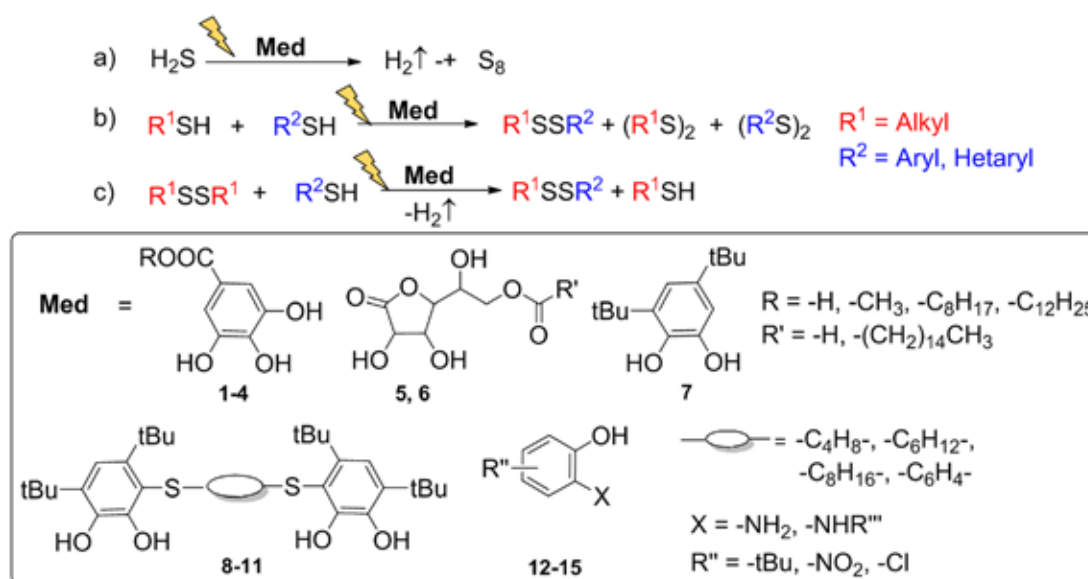
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# REDOX-TRANSFORMATIONS OF H<sub>2</sub>S, RSH AND RSSR IN THE PRESENCE OF ORGANOCATALYSTS

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The use of H<sub>2</sub>S, alkanethiols (C<sub>3</sub>, C<sub>4</sub>) and their dimers in the synthesis of organosulfur derivatives is relevant from the point of view of recycling waste from oil and gas desulfurization process into high added value products. Reactions of decomposition of H<sub>2</sub>S to hydrogen and sulfur, an oxidation of RSH to RSSR, as well as a thiol-disulfide exchange can be implemented under electrochemical conditions, in particular using organic redox-mediator systems.<sup>1</sup> The electrochemical transformations of H<sub>2</sub>S, RSH and RSSR in the presence of organic electrocatalysts (**Med**): gallic, ascorbic acids and their esters (**1–6**), sterically hindered mono- and bis-catechols (**7–11**), substituted *o*-aminophenols (**12–15**) were investigated. Anodic activation of **Med** leads to the formation of their oxidized forms—the corresponding *o*-(imino)benzoquinones, which participate in the interaction with sulfur substrates, completing the catalytic redox cycle.



**Figure 1.** Studied pathways of H<sub>2</sub>S, RSH and RSSR redox-transformations

For the first time, natural compounds and their derivatives (**1–6**) have been considered as redox-mediators for the production of H<sub>2</sub> and S<sub>8</sub> from H<sub>2</sub>S (Fig. 1, a). The main advantage of using organic catalysts **1–15** in the electrosynthesis of unsymmetrical disulfides is a reduction in the anodic overvoltage of the thiol oxidation by 0.5–1.2 V (Fig. 1, b–c) and, as a consequence, an increase in the energy efficiency of the process.

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# N, S CO-DOPED CARBON ELECTRODE MATERIALS FROM PLANT BIOMASS CHEMICAL PROCESSING WASTES

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Various carbon materials (CMs), including those derived from plant biomass and its processing wastes, are investigated as electrode materials in double-layer supercapacitors (SCs)<sup>1-3</sup>. To increase the specific characteristics of SCs, doping of CMs with various heteroatoms (N, S, P, etc.), which, being embedded in the carbon skeleton, form defects and surface functional groups contributing to the increase of capacitance, wettability, conductivity and stability of electrode materials, is used<sup>1,3</sup>. Previously, we showed the prospect of using the liquid fraction of humins (wastes of chemical processing of plant biomass into furan derivatives, so-called platform chemicals) as a universal basis for direct doping of CMs with nitrogen<sup>3</sup>.

In the present work, we investigated for the first time the possibility of obtaining simultaneously N, S codoped CMs based on copolymers of humins and thiourea. The influence of CM production conditions on the porosity structure and the character of nitrogen and sulfur incorporation into the carbon framework was analyzed. Comparison of electrochemical properties of CMs doped with only one heteroatom (nitrogen or sulfur) and CMs containing two heteroatoms at once has shown, that the material obtained as a result of chemical activation of carbonized copolymer synthesized by polycondensation of humins and thiourea has the best specific capacitance and excellent stability during long-term cycling (25000 cycles in charge/discharge mode) in a two-electrode SC cell.

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# PERMEABILITY OF CHARGED MACROPOROUS GLASSES

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The cell model of an ion-exchange membrane<sup>1</sup> has been successfully applied to the description of the filtration process of NaCl aqueous solutions with concentrations from  $10^{-4}$  to  $10^{-1}$  M using macroporous glass (PG) membranes prepared from sodium borosilicate glass. These membranes were obtained by additional alkaline treatment of microporous glasses with KOH solution<sup>2</sup>. Alkaline treatment led to the removal of “secondary silica” from the pore space and partial dissolution of the silica membrane matrix. Numerical values of the model parameters were determined for glass-like membranes of the grades PG-26, PG-42, PG-66, PG-160 and a good correspondence between theoretical predictions and experimental data on the hydrodynamic permeability of glass-like membranes versus the electrolyte concentration was obtained.

Porous glass-like membranes hold a number of advantages over other porous materials: homogeneity of chemical composition; low level of impurities; thermal, chemical, and microbiological resistance; transparency in visible region of the spectrum; and adjustable structural characteristic. Porous glass-like membranes are also favorable materials for solving the problems of the membrane separation of mixtures. When using membranes in the baro-electromembrane separations of liquid mixtures, along with the adsorption and surface electrical properties, the structural characteristics of the pore space of the membrane are particularly important, which largely determine the membrane’s transport mechanisms upon application of external forces like gradients of pressure, electric and chemical potentials. It is well known that the size of the globules and their packing density determine the hydrodynamic permeability of the macroporous membrane. In this concern, the task of this work was to study and compare the structural parameters of macroporous glass-like membranes, made from sodium borosilicate glass, in the aqueous solution of NaCl electrolyte of different concentrations based on the cell model of a charged membrane in comparison with the capillary model.

The presence of a volume charge of porous glass granules makes it possible to increase the coefficient of hydrodynamic permeability of membranes by 3–25% with an increase in electrolyte concentration by 3 orders of magnitude.

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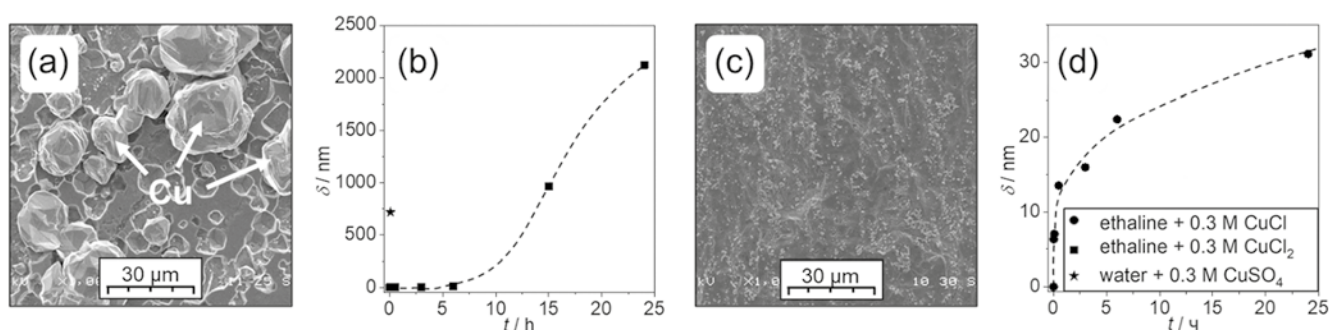
*The work is supported by RSF (grant No. 23–19–00520, <https://rscf.ru/project/23-19-00520/>).*

# COPPER GALVANIC REPLACEMENT PROCESS IN ETHALINE-BASED SOLUTIONS

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Due to a number of useful properties, deep eutectic solvents (DESs) are promising media for the electrochemical deposition of metals and alloys<sup>1</sup>. Despite the considerable interest in these media, the process of galvanic replacement (GR) in DES has been studied very little. In this work, for the first time, the GR reaction between Fe substrate and Cu ions in solution based on ethaline (DES, a mixture of choline chloride and ethylene glycol in a molar ratio 1:2) was investigated. It has been shown that GR on Fe proceeds in solutions containing both Cu(I) and Cu(II) ions. In the first case, large Cu crystallites are gradually grown on the substrate and surrounded by pits that appeared during the dissolution of Fe (Fig. 1, *a*). This type of deposition leads to a gradual acceleration of the process, which is confirmed by inductively coupled plasma mass spectrometry (Fig. 1, *b*). In the second case, on the contrary, relatively uniform Cu layers are formed (Fig. 1, *c*), shielding the substrate and slowing down the GR (Fig. 1, *d*). It should be noted that the GR in ethaline proceeds much slower than in aqueous solutions (Fig. 1, *b*). The exposure of Fe in Cu(I) and Cu(II) solutions in ethaline at Cu deposition potentials leads to the formation of deposits with a pronounced crystalline structure and good adhesion to the substrate.



**Figure 1.** SEM of Fe substrate after 24 h in the solutions (*a*) 0.3 M CuCl and (*c*) 0.3 M CuCl<sub>2</sub> in ethaline, (*b*, *d*) effective thickness ( $\delta$ ) of Cu deposits as a function of the GR duration

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*The work was supported by the Ministry of Science and Higher Education of the Russian Federation.*

# ELECTROCHEMICAL FORMATION OF NANOSTRUCTURES BASED ON GERMANIUM

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Ge nanowires (Ge NWs), due to their electrophysical and optical properties, have a wide range of applications in lithium-ion batteries, photovoltaics, memory devices, optics, and nanoelectromechanical systems. Vapor phase deposition is mainly used to form Ge NWs. However, these processes often require complex process equipment and high temperatures. Also, toxic and expensive precursors are used in the process. In turn, the use of electrochemical deposition is a good alternative. However, it is known, that electrodeposition of Ge from aqueous solution in practice the growth is restricted to a few monolayers. At the same time, the use of molten metal particles, such as Hg and Ga, as crystallization centres allows to obtain films of sufficient thickness and Ge NWs. In this case, the liquid metal serves as an electrode for the reduction of ions containing Ge to germanium in the atomic state, with their subsequent dissolution and formation of a melt of eutectic composition. The continuous cathodic reduction reaction provides concentration supersaturation of the melt with germanium. As a result, on the liquid metal-substrate boundary, precipitation of germanium occurs by analogy with the growth of whiskers from the gas phase (vapor-liquid-solid mechanism).

In this work the features of the Ge NWs formation using different metal particles are considered. In addition, the results of the influence of adding cobalt, antimony and tellurium ions to the electrolyte solution on the morphology and composition of the formed structures are obtained. The presented results will make it possible to expand the range of materials obtained by the proposed method, which, in turn, will contribute to further research in this field.

*The work was supported by a grant from Russian Science Foundation No 20-79-10312, <https://rscf.ru/en/project/20-79-10312/>*

# HYBRID COATINGS OF A NEW GENERATION WITH THE FUNCTION OF TARGETED DELIVERY OF ACTIVE COMPONENTS ON THE SURFACE OF MAGNESIUM ALLOYS

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The research aims to develop methods for active corrosion protection of magnesium alloys, promising for application in industries such as automotive manufacturing, aircraft production, electronics, and implant surgery.

One of the primary challenges in using magnesium and its alloys is their susceptibility to intense corrosion when exposed to the environment. This study focuses on enhancing the corrosion resistance and bioactive properties of these materials through targeted functionalization of a protective layer initially formed via plasma electrolytic oxidation (PEO). This enhancement involves subsequent chemical treatment of the coating with substances that reduce the degradation rate<sup>1</sup>. Novel hybrid coatings were formed and optimized. These layers contain a corrosion inhibitor embedded in the coating composition, along with a biodegradable polymer material, representing a unified protective system.

The incorporation of carefully selected biocompatible components into the PEO-coating actively and controllable protects implants against corrosion by delivering a passivating substance to areas of defects. Additionally, this hybrid coating enhances integration of the treated implant with the human body by providing antibacterial properties and increasing bioactivity<sup>2-3</sup>.

The scientific novelty is related to the application of advanced local scanning electrochemical methods. These methods enable the evaluation of the selected inhibitor's effectiveness at the microscale and provide insights into the mechanism of *in situ* corrosion degradation of the biomaterial

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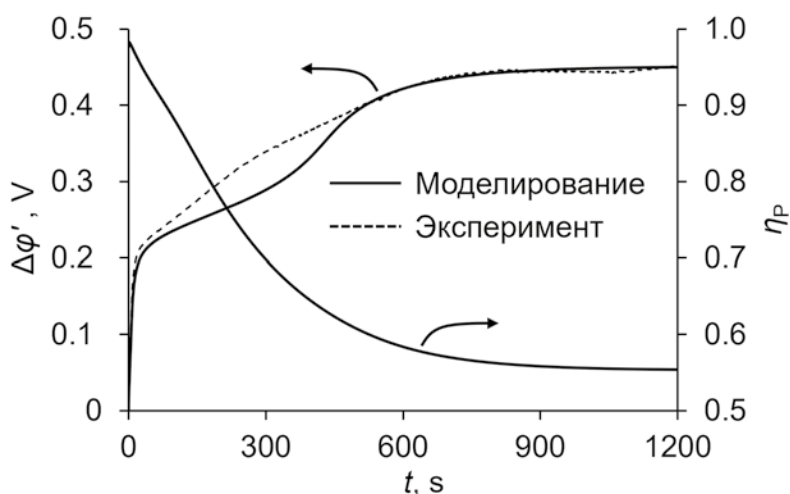
# NON-STATIONARY PHOSPHATE TRANSPORT THROUGH AN ANION-EXCHANGE MEMBRANE DURING ELECTRODIALYSIS: EXPERIMENTS AND MODELING

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Every year, the amount of phosphates entering the environment as wastes is steadily increasing, causing eutrophication of water bodies. The reason is the widespread use of phosphorus fertilizers and discharges of municipal and livestock farming wastewater. At the same time, phosphate rock reserves are declining<sup>1</sup>. Recovering phosphates from wastewater will not only prevent pollution of water bodies but will also provide secondary raw materials to produce new fertilizers. Electrodialysis (ED) can solve this problem, but phosphate transport during ED is complicated by protolysis reactions. The complex mechanisms of such transfer have not been sufficiently studied, which hinders the widespread use of ED of phosphate-containing solutions.

This work is devoted to study of the mechanisms of non-stationary transfer of phosphoric acid anions through anion-exchange membranes in an applied electric field to increase the efficiency of ED phosphorus recovery from phosphate-containing solutions. It has been established that protolysis reactions involving phosphate anions significantly slow down the achievement of the membrane system stationary state and cause a decrease in the current efficiency of pentavalent phosphorus recovery (Fig. 1).



**Figure 1.** Chronopotentiograms of the system Neosepta AMX membrane / 0.02 M  $\text{KH}_2\text{PO}_4$  at a current density of  $2.2j_{\text{lim}}$  ( $j_{\text{lim}}$  is the limiting current density), as well as the time dependence of the current efficiency of pentavalent phosphorus ( $\eta_p$ ) in this system

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# PHOTOELECTROCHEMISTRY OF COPPER OXIDES ANODICALLY FORMED ON BRASSES WITH DIFFERENT PHASE COMPOSITION

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Copper oxides are considered as promising materials for photoelectrochemical converters due to their optimal band structure. However, they are characterized by low conversion efficiency, which is associated with chemical instability and short lifetime of charge carriers. Increased efficiency is achieved by creating protective layers and heterostructures, for example, with zinc oxide. The anodic oxidation of brass in an alkaline solution can serve as a one-stage method to obtain such structures.

The purpose of this work is to determine the photoelectrochemical characteristics of Cu(I) oxide anodically formed in 0.1 M KOH on alloys of the Cu-Zn system with a zinc concentration of 34 to 50 at.%. Electrodes designated as Cu34Zn and Cu50Zn are homogeneous, including only the  $\alpha$ - or  $\beta$ -phase, respectively. Cu38Zn and Cu44Zn electrodes contain elements of both phases in their structure.

Photoelectrochemical characteristics (photocurrent and photopotential) were recorded under conditions of pulsed illumination of the electrode surface with a 470 nm LED at a radiation power of 0.1 mW/cm<sup>2</sup>. The photocurrent and photopotential depend on the thickness of the oxide films. Correct assessment of the thickness is possible with using the data on the current efficiency values of the anodic oxide formation. The current efficiency  $\psi$  for Cu(I) oxide was calculated based on the results of coulometry during the potentiostatic oxidation of brasses at  $-0.17$  V (s.h.e.) and their subsequent potentiodynamic reduction in a renewed solution containing no soluble alloy oxidation products.

With increasing of zinc concentration from 34 to 50 at.% and the share of beta phase from 0 to 100%, the value of  $\psi$  decreases from 99 to 45%. Nevertheless, it is the alloy containing 50 at.% of zinc that produces the maximum values of the cathode photocurrent (3.54  $\mu$ A/cm<sup>2</sup>) and positive photopotential (340  $\mu$ V). Thus, the highest zinc content in the alloy, which most likely ensures the highest content of zinc oxide in the film, leads to an increase in its photoelectrochemical parameters.

*The work was carried out with the financial support of the Ministry of Science and Higher Education of the Russian Federation within the framework of the state assignment No. 075-15-2021-1351.*

# APPLICABILITY OF STRUCTURED CARBON MATERIALS FOR PERFORMANCE AND DURABILITY IMPROVEMENT OF THE PEMFC ELECTRODES

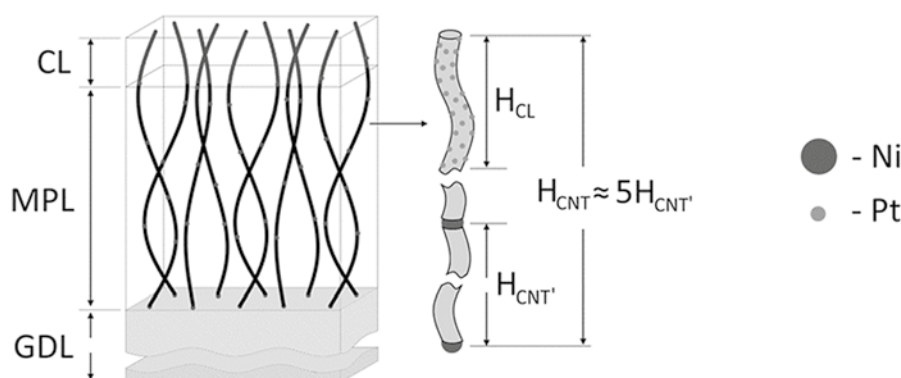
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The global issue for the proton exchange membrane fuel cell (PEMFC) market development is decreasing in devices cost due to increase the efficiency of the oxygen reduction reaction (ORR) occurring at the cathode, as well as the service life of the electrochemical device<sup>1</sup>. The losses in fuel cell performance caused by various degradation processes in the catalytic layers (CL) that occur under the overpotential, temperature, and humidity.

Application of structured carbon supports (which are graphene, its oxides, and derivatives, including CNTs and their arrays) looks promising solution due to their structure and high degradation resistance. Catalysts based on graphene-like (GL) materials also show better electrocatalytic activity due to the increased dispersion of the platinum particles distribution. However, some mass and gas transfer problems take place in catalytic layers based on GL, which negatively affects the performance of the fuel cell. This problem is can partially solved by using carbon nanotubes, especially arrays, due to their optimized structure, high adhesion to gas diffusion layers and the presence of mass transport channels<sup>2</sup>.



**Figure 1.** Structure of Pt-electrocatalyst based on carbon nanotubes array as a part of gas diffusion layer

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*The work was carried out within the state assignment of NRC “Kurchatov Institute”.*

# ELECTRODEPOSITION OF PHOTOACTIVE LAYERS BASED ON POLYPYRROLE AND ZINC PHTHALOCYANINATE

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Hybrid materials based on polypyrrole (PPy) and sodium salt of zinc octa(3',5'dicarboxyphenoxy)phthalocyaninate (ZnPc) were synthesized using electrochemical polymerization. The resulting layers combine the high hole conductivity of PPy and the photoelectric properties of ZnPc.

Phthalocyaninate is a water-soluble compound containing 16 ionogenic carboxylate groups that can act as a charge-compensating anions for charged fragments of the PPy chain.

The process of pyrrole electropolymerization was studied using in situ electrochemistry and spectroelectrochemistry in the visible and near-IR spectral regions. It was shown that the electrosynthesis of PPy-ZnPc hybrid layers occurs more efficiently on the sublayer of a complex of poly(3,4-ethylenedioxythiophene) (PEDOT) with the Na salt of poly(2-acryamido-2-methyl-1-propanesulfonic) acid (PAMPSNa) in galvanostatic and potentiostatic modes. During the electrosynthesis of PPy-ZnPc layers on the PPy-PAMPSNa sublayer, the latter degrades, slowing down the process and preventing the formation of layers of sufficient thickness.

Using electron absorption and Raman spectroscopies, it was shown that the resulting PPy hybrid layers contain ZnPc.

In the process of studying the photoelectric properties of the PPy-ZnPc layers, it was found that they demonstrate photosensitivity, which suggests the prospects of their use for creating photodiode devices.

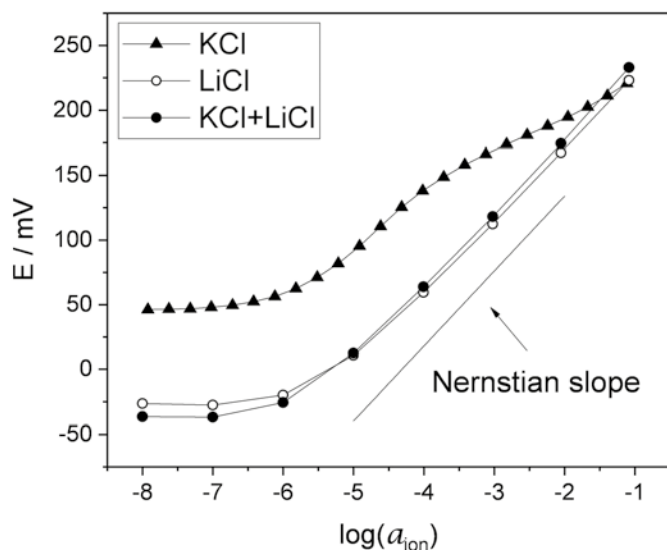
*The work was carried out with the financial support of the Russian Science Foundation, project No. 23-19-00884.*

# THE STUDY OF THE POTENTIOMETRIC RESPONSE OF ION-SELECTIVE ELECTRODES CONTAINING TWO NEUTRAL IONOPHORES AND ION-EXCHANGER

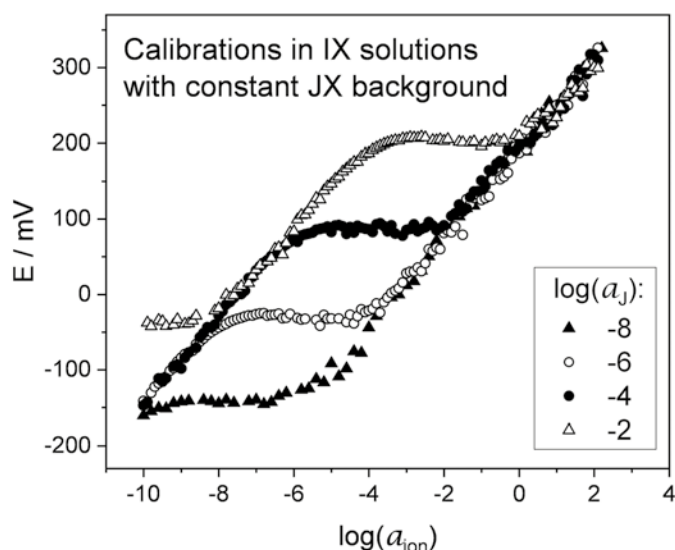
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Cyclic voltammetry is a promising method of using ion-selective electrodes (ISEs) in non-zero current mode. Voltammetry with ISEs involves the use of electrodes equipped with membranes containing several ionophores, which allows for multianalyte measurements with a sole sensor.<sup>1-3</sup> The proposed membrane compositions differ significantly from those traditionally used in potentiometry: the ion-exchanger is in excess over the ionophores. We will report on the unusual potentiometric response of membranes containing two ionophores (valinomycin and Li VIII) and an ion-exchanger in excess over the ionophores, Fig. 1. To explain these peculiarities, the results of computer simulation, based on our model, with ion-ionophore complex formation constants estimated by the sandwich membrane method will be presented, Fig. 2. A surprisingly strong influence of pH on the response of such ISEs will be discussed.



**Figure 1.** Experimental potentiometric calibrations of ISEs in pure KCl and LiCl solutions, and in mixed solutions of KCl and LiCl



**Figure 2.** Simulated potentiometric calibrations of ISEs in IX solutions with different background of JX

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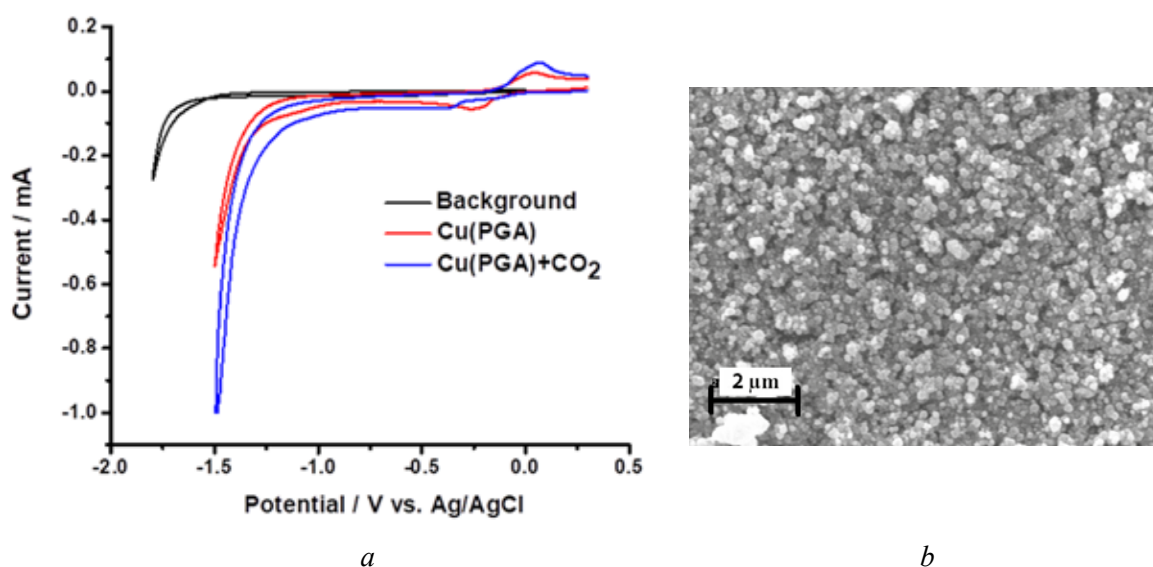
# ELECTROCATALYTIC REDUCTION OF CO<sub>2</sub> WITH COPPER-CONTAINING NANOSTRUCTURED ELECTRODE AND SODIUM PECTATE COMPLEXES.

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Copper occupies a special place in homo- and heterogeneous CO<sub>2</sub>RR catalysts, since it allows the production of hydrocarbons and alcohols as products in some cases.<sup>1</sup>



**Figure 1.** Cyclic voltammograms in the absence and presence of sodium pectate complex with copper in solution (a), image of the surface of a glassy carbon electrode nanostructured with copper-containing particles (b)

We have demonstrated the catalytic properties of sodium pectate complexes with copper in CO<sub>2</sub>RR. Glassy carbon electrodes coated with copper-containing nanoparticles were obtained by electrolysis of solutions of these complexes. The nanostructured electrodes exhibit heterocatalytic properties in CO<sub>2</sub>RR. CO and CH<sub>4</sub> is the main reaction products.

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# ONE-STEP PLASMA-ASSISTED ELECTROCHEMICAL SYNTHESIS OF NANOCOMPOSITES OF GRAPHENE STRUCTURES WITH COBALT/MANGANESE OXIDES – PROMISING ELECTROCATALYSTS OF OXYGEN REDUCTION REACTION

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One of the promising approaches to production of highly efficient and inexpensive catalysts of oxygen reduction reaction (ORR) is the development of composite materials based on graphene nanostructures doped with various *p*-elements, primarily N, with transition metal oxides deposited on their surface, for example Mn, Co. Such materials along with high catalytic activity are characterized by low cost, non-toxicity and large natural reserves of raw materials for their production. Currently, the usage of electrochemical methods of synthesis of such materials is becoming increasingly popular due to the variety of modes of synthesis of carbon nanostructures.

In the present work, a nanocomposite of nitrogen-doped few-layer graphene structures (FLGS) with complex cobalt/manganese oxide– $\text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_4$ /FLGS-N was obtained in a one-step process. The synthesis method was a plasma-assisted electrochemical exfoliation of graphite electrodes carried out by applying alternating high-voltage pulses of different polarities in solutions containing sodium nitrate and melamine as a source of nitrogen, as well as transition metal salts. Complete reduction of oxygen was found to occur on the resulting catalyst in a wide range of potentials. And at the same time  $\text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_4$ /FLGS-N has better stability characteristics than the commercial platinum-containing analogue.

Thus, the presented results indicate the possibility of production of effective platinum-free ORR catalysts based on nanocomposites of carbon nanostructures with transition metal oxides by plasma-assisted electrochemical exfoliation of graphite.

*The study was carried out in the framework of the State Assignment no. 124013000692-4 using the equipment of the Multi-User Analytical Center of FRC PCP MC RAS.*

# SPECIFIC FUNCTIONING OF BIFUNCTIONAL ELECTROCATALYSTS BASED ON NICKEL SULPHIDE UNDER CONDITIONS OF CYCLIC CHANGE OF THE ELECTRODE PROCESS

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Bifunctional electrocatalysts (BFE) based on transition metals for the electrolysis of water in alkaline solutions represent a promising solution both for reducing the cost of hydrogen production in classical alkaline and solid polymer electrolyzers, and for use in fundamentally new systems of decoupled membraneless electrolysis, in which oxygen (OER) and hydrogen (HER) evolution reactions are separated in space and time, and electron transport is carried out through a solid mediator<sup>1</sup>. In this case, during the process of decoupled electrolysis, a periodic change in the polarity of the electrodes occurs to recharge the mediator, and therefore it is necessary to develop BFE materials capable of operating effectively under these conditions.

One of the promising BFE materials is nickel sulfide  $\text{Ni}_3\text{S}_2$ , due to its high electrocatalytic activity, good electrical conductivity and low cost<sup>2</sup>, but the behavior of this catalyst under the conditions of cyclic flow of OER and HER has not been studied. It is expected that the production of mixed electrocatalysts based on Ni, Fe, Co will lead to an increase in electrocatalytic activity due to an increase in the number and change in the energy of active centers.

In this work, nickel sulfide and mixed Ni-M sulfides (where M=Fe, Co) were prepared by electrodeposition. Conditions have been found that make it possible to obtain  $\text{M}_x\text{S}_y$  deposits with different metal:sulfur ratios. It has been established that compounds based on nickel sulfide exhibit high electrocatalytic activity under conditions of cyclic flow of OER and HER. Factors have been identified that influence the recovery time of the activity of electrocatalysts after a change in the electrochemical process occurring on the surface of the material.

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# IONIC MOBILITY IN THE COMPOSITE (IONIC LIQUIDS)@MOF ELECTROLYTES PROBED BY SOLID STATE NMR

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The current strategy for a sustainable development dictates the technological shift towards wider use of electric power storage and transfer systems, which motivates the development of new electrolytes. These advanced electrolytes, used in hydrogen fuel cells or Li-ion batteries, are subject to strict ecological restrictions such as being free from volatile compounds and the risk of leakage. In the same time, these materials have to be good conductors with high ionic mobility. One of ways to unite these concurrent requirements is to use a composite electrolyte based on ionic liquids confined in ordered porous host matrices, such as the metal-organic frameworks.<sup>1-2</sup> Herein we report the first case study of the microscopic molecular mobility of the Protic Ionic Liquids (PILs) confined within the MOF pore. We apply conductivity measurements and solid state <sup>2</sup>H NMR to probe mobility of the [(C<sub>n</sub>H<sub>2n+1</sub>)ND<sub>3</sub>]<sup>+</sup>[TFSI]<sup>-</sup> (n=4–10) PILs within the MIL-100 (Al) MOF. We relate the molecular mobility of the confined PILs with the ionic conductivity of the composite. Finally, we show how the PILs mobility and ionic conductivity depends from the steric size of the cations hydrocarbon alkyl-chain.

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# TOLERANT CATALYSTS FOR HYDROGEN OXIDATION IN ALKALINE ENVIRONMENTS

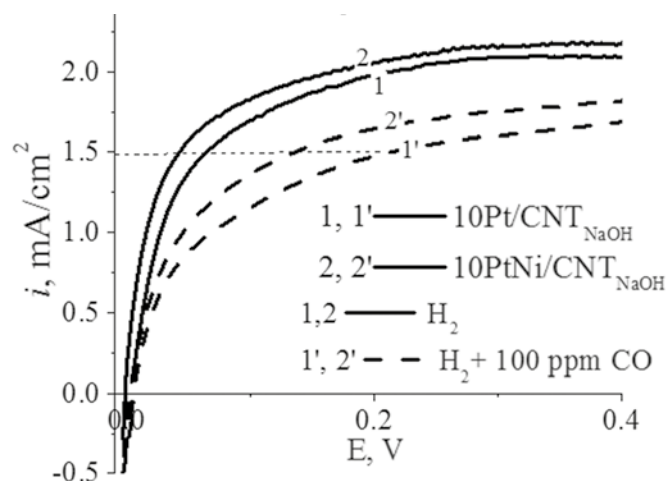
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Bimetallic PtNi/CNT<sub>NaOH</sub> catalysts synthesized on nanotubes have been developed to reduce the platinum content in the catalyst composition. These catalysts are characterized by increased activity and stability. The most important property of catalysts is their tolerance to CO impurities in hydrogen in the oxidation reaction of hydrogen in an alkaline electrolyte.

PtNi catalysts with Pt contents of 10 and 40 wt.% were synthesized. The electrochemically active surface ( $S_{\text{EAS Pt}}$ ) of PtNi catalysts is significantly reduced ( $\sim 37 \text{ m}^2/\text{g}$ ) compared to Pt/CNT<sub>NaOH</sub> ( $76 \text{ m}^2/\text{g}$ ), with a similar Pt content in the composition (10 wt. %). Consequently, part of the Pt surface is covered with nickel oxides, which is confirmed by XPS data. Nickel dioxide provides a large hydrophilic surface area, exceeding the total specific surface area. A similar effect was considered in<sup>1</sup>. The presence of OH<sup>-</sup> ions near the active sites of H<sub>2</sub> adsorption ensures<sup>2</sup> effective oxidation of H<sub>2</sub>. Tests of the synthesized PtNi/CNT<sub>NaOH</sub> catalysts were carried out as part of membrane-electrode assembly of alkaline fuel cells.



**Figure 1.** Polarization curves of H<sub>2</sub> oxidation in 0.1M KOH. 5 mV/s, 1500 rpm

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# KINETICS OF NUCLEATION AND GROWTH DURING CATHODIC CO-DEPOSITION OF ZINC AND NICKEL FROM AMMONIUM CHLORIDE ELECTROLYTES

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Corrosion-resistant zinc-based galvanic Zn-Ni coatings can be obtained by electrodeposition from ammonium chloride electrolytes, which proceeds by the mechanism of anomalous co-deposition, in which the rate of deposition of the electropositive component (nickel) is lower than the electronegative component (zinc). To obtain coatings with certain morphology, chemical and phase composition, it is necessary to know the kinetics of cathodic deposition of Zn-Ni alloy at the stage of heterogeneous nucleation, the determination of which is the purpose of this work.

The nucleation mechanism was determined using voltammetry and chronoamperometry methods: for electrodeposition of Zn and Ni within the Palomar-Pardavé approach, taking into account the hydrogen reduction reaction and charging of the double electric layer contributions to the total cathodic current, and for Zn-Ni coatings using the Scharifker model for electrodeposition of a binary alloy, modified taking into account the dependence the composition of the alloy on time.

It has been established that both the electrodeposition of zinc and nickel from individual solutions and their anomalous co-deposition mainly implements the mechanism of progressive nucleation, the rate constant of which increases with the cathodic potential. The growth of a new phase, regardless of the chemical composition of the resulting deposit, is limited by the 3D diffusion of zinc and nickel ions to the electrode surface. The density of nucleation sites is weakly dependent on the deposition potential, decreasing with the transition from individual metals to zinc-nickel coatings. The contribution of the side reaction of hydrogen evolution is maximal in the case of electrocrystallization of nickel, probably due to its high catalytic activity, and decreases with the transition to Zn-Ni and zinc alloys, increasing with a shift of the deposition potential to the more negative values, which is consistent with the current efficiency.

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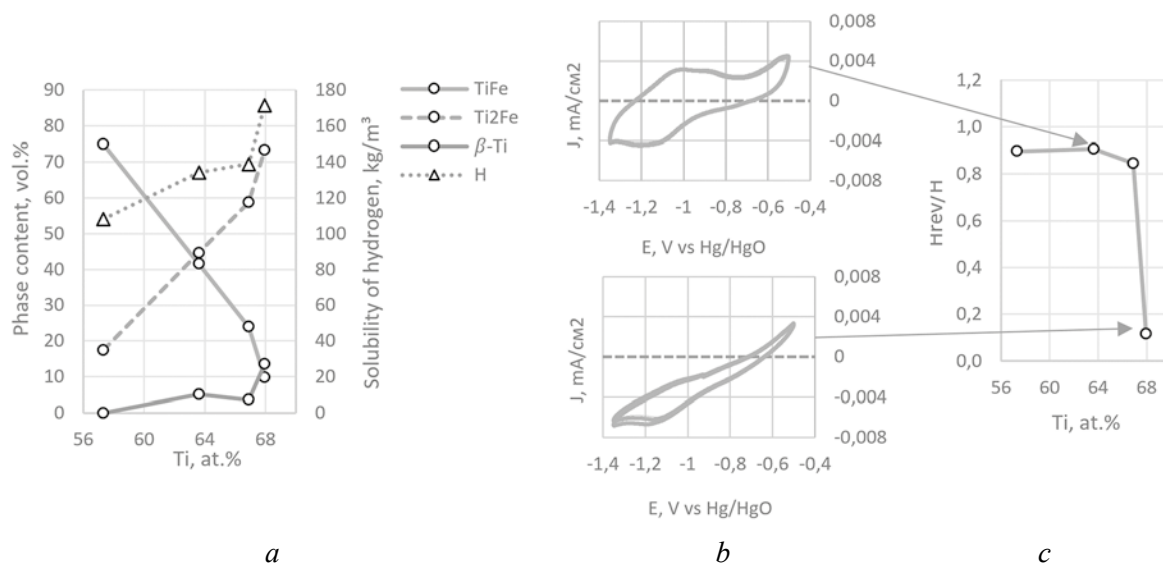
# INFLUENCE OF PHASE COMPOSITION OF MATERIALS OF “TI-FE” SYSTEM WITH INCREASED TITANIUM CONTENT ON THEIR HYDROGEN CAPACITY

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Materials obtained by explosive pressing and subsequent sintering at 1100 °C of powder mixtures of Fe and Ti with the content of the latter exceeding the stoichiometric one for TiFe were investigated. The sintered materials had a structure consisting of TiFe and Ti<sub>2</sub>Fe intermetallides with minor amounts of β-Ti. Hydrogen adsorption properties of the samples were determined by electrochemical method. The measurements were carried out in a three-electrode cell with 9M aqueous KOH solution as an electrolyte, Ni(OH)<sub>2</sub>/NiOOH-anti-electrode and Hg/HgO-comparison electrode on Electrochemical Instruments P-40X potentiostat. The reversibility of the process of hydrogenation was checked by taking voltammetry at cyclic change of potential.

It is shown that up to Ti content equal to 66.9 at.%, the obtained materials retain the ability to reversible hydrogenation. The hydrogen capacity reaches 138.9 kg/m<sup>3</sup>, which is noticeably higher than the capacity of TiFe and LaNi<sub>5</sub>, which does not exceed 120 kg/m<sup>3</sup>.



**Figure 1.** Phase content and hydrogen solubility during primary hydrogenation (a); voltammetry view (b) and ratio of reversible hydrogen capacity to primary hydrogenation capacity (c) of the studied materials

# THE APPEARANCE OF ELECTRICAL PHENOMENA IN AN ENERGETIC SUBSTANCE UNDER SHOCK LOADING

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There are many views on the reasons of the explosive decomposition initiated by mechanical action on an energetic substance (ES). The most common explanation is the theory of “hot spots”, according to which explosive transformation occurs during adiabatic compression of gas or liquid bubbles, accompanied by local heating to high temperatures.<sup>1</sup>

An alternative approach explains the occurrence of a local hot zone by electrical breakdown resulting from the piezoelectric properties of crystals of a substance.<sup>2</sup> The goal of this work is to prove the existence of the piezoelectric effect for some ES.<sup>3</sup>

Using a specially developed method, guanidine nitrate (GN) and triaminoguanidine nitrate (TAGN), compounds representing organic salts, were studied. The measured oscillograms contain specific electrical signals indicating the presence of the piezoelectric effect even under low-energy shock loading of samples.

The discovered effects were comprehensively analyzed, the differences in the peculiar features of oscillograms depending on the thickness of the samples, the orientation of the crystals of the substance and its anisotropic properties were justified.

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# PRODUCTION OF ELECTRO- AND CATALYTICALLY ACTIVE MATERIALS BY PULSE ELECTROLYSIS

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Materials with electrochemical and catalytic activity are commonly used in chemical and electrochemical production processes, as well as in electrochemical energy technologies. They are also used in catalytic technologies for neutralising gas emissions and purifying water. These materials can be obtained through condensation or dispersion approaches. Electrochemical methods are used in both groups of approaches.

In the field of electrochemical processes, the use of alternating current was a key factor in the development of a new scientific area known as unsteady electrolysis. This includes pulse electrolysis as a special case. Currently, the scientific community has accumulated experience and systematized knowledge in the use of pulse electrolysis for catalytic processes and metal electrodeposition. Pulse electrolysis can effectively produce dispersed materials, including metallic (or oxide-metallic) and non-metallic materials such as carbon. This method combines processes occurring in both liquid and solid phases.

This report examines the electrochemical behaviour of platinum, palladium, tin and carbon materials in aqueous solutions of electrolytes containing alkali metal cations during pulse electrolysis and establishes the conditions necessary to obtain dispersed non-hydrated crystalline products with electro- and catalytic activity without the use of organic solvents, capping agents or thermal post-treatment of the materials.

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# INVESTIGATION THE JOINT ELECTROCHEMICAL REDUCTION MECHANISM OF RARE-EARTH IONS AND IRON TRIAD METALS IN THE KCl-NaCl-CsCl EUTECTIC MELT

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The electroreduction mechanism of rare earth metal ions ( $\text{Dy}^{3+}$ ,  $\text{Nd}^{3+}$ ,  $\text{La}^{3+}$ ) and iron triad metals ions ( $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Fe}^{3+}$ ) and their joint electroreduction on inert tungsten and active nickel electrodes in the melt was studied in this work using cyclic and square-wave voltammetry and open-circuit chronopotentiometry in KCl-NaCl-CsCl at 823 K temperature.

The potential of electrodeposition of the metal triad of iron and rare earth metals in the KCl-NaCl-CsCl melt were determined and differed by approximately 1.5 V. The kinetic regularity of the electroreduction of  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Fe}^{3+}$  ions and rare earth metal ions  $\text{Dy}^{3+}$ ,  $\text{Nd}^{3+}$ ,  $\text{La}^{3+}$  in the KCl-NaCl-CsCl melt at 823 K have been established. It has been shown that with the combined content of metal ions, the triad of iron ( $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Fe}^{3+}$ ) and rare earth metals ( $\text{Dy}^{3+}$ ,  $\text{Nd}^{3+}$ ,  $\text{La}^{3+}$ ) there is a certain depolarization of the electroreduction of rare earth metal ions on the pre-formed on a tungsten electrode of the iron triad metals with the formation of intermetallic phases of different compositions based on rare earth metals and iron triad metals.

The electrode potentials  $\text{Ln}^{3+}/\text{Ln}$  were determined using open-circuit chronopotentiometry, where (Ln- Dy, Nd, La), as well as a number of other potentials corresponding to the equilibrium of two intermetallic phases of different compositions are found. By measuring the potentials corresponding to the equilibrium of two different intermetallic phases from the electrode potential  $\text{Ln}/\text{Ln}^{3+}$ , the EMF of each two-phase coexisting state is obtained. Based on the EMT results, the relative partial molar Gibbs energies and the activity of the rare earth metal in  $\text{Ln}_x\text{Me}_y$  intermetallic compounds (where Me–Ni, Co, Fe) were calculated.

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# PHOTONIC CRYSTAL STRUCTURES BASED ON ANODIC ALUMINIUM OXIDE

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Photonic crystals (PhC) are of significant interest to researchers owing to their ability to control the propagation of light. Electrochemical techniques are employed to produce PhC based on porous silicon or oxides of valve metals (Al, Ti, etc.). The cyclic variation of the anodizing voltage or current density over time produces periodic modulation of the effective refractive index perpendicular to the surface of the porous film, which is essential for the appearance of photonic band gap (PBG). Nevertheless, conventional anodizing regimes are not appropriate to direct control of the optical path length of the forming porous structure, which is required to precisely determine the position of the PBG and achieve their narrow width in the optical spectrum.

In the course of the research, we developed anodizing regimes with voltage modulation depending on the anodizing charge density ( $U(q)$ ) and the optical path length ( $U(L)$ ), which allow one to precisely control the parameters of the porous structure of anodic aluminium oxide (AAO) and the spectral properties of the resulting PhC. Using these techniques, we have obtained materials with exceptional properties, including: PhCs (Q factor of 60–70) and optical microcavities (Q factors of 200–270 over the wavelength range of 250–1500 nm); PhC heterostructures composed of up to 21 PBG. Three-dimensional PhCs based on AAO were fabricated for the first time. The growth rate of AAO varies with the crystallographic orientation of Al grains, causing the stained glass effect, which can be seen with the naked eye in PhCs. With an increase in the anodizing voltage, the growth rate crossover is observed for the main crystallographic orientations.

The potential for creating PhC barcodes that encode 10-letter words and store 47 bits of data, as well as the use of bright decorative coatings on aluminium alloy surfaces in a wide variety of colours, are identified as promising applications of the materials produced.

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# ELECTROCHEMICAL METHODS FOR PORPHYRIN SEMICONDUCTOR FILMS FORMATION AND INVESTIGATION

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The thin films formation processes are considered for amino phenyl porphyrins when the polymerization initiating step is electrochemical oxidation of porphyrin and/or interaction of porphyrin with electrochemically synthesized superoxide. The electro physical characteristics of the films obtained were studied. We have shown the film formation conditions influence on the film thickness, morphology and electro physical characteristics. Using the combination of electrochemical and non-electrochemical approaches the specific conductivity of the resulting materials, the band gap, the concentration and the type of majority charge carriers in the semiconductor material, and the flat band potential were evaluated. The Mott-Schottky method<sup>1,2</sup> is appeared one of the most useful approaches for estimating a lot of electro physical parameters. According the literature<sup>3</sup> and our researches results the Mott-Schottky method can be also used to characterization of localized states which are at the film–solution interfaces.

The suitable approaches to the accurate determination of the semiconductor depletion layer capacitance from the electrochemical impedance spectroscopy data are analyzed.

Mott-Schottky method limitations and experimental conditions which allow as avoiding some artifacts are discussed.

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# NIOBIUM AND TANTALUM IN MOLTEN SALTS: TWINS OR BROTHERS?

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Niobium and tantalum are to a certain extent chemical analogs. Nevertheless, electrode processes and cathodic products of carried out in similar niobium and tantalum-containing melts are very different. By electrolysis of NaCl-KCl or KCl melts containing  $K_2NbF_7$ , it is impossible to obtain niobium with a small content of oxygen even at very low values of O/Nb.<sup>1</sup> In the case of tantalum electrolysis in chloride-fluoride melts a relatively high concentration of oxygen does not lead to significant its concentration in tantalum metal, because the discharge potential of oxofluoride complexes has more negative value than fluoride one.<sup>1,2</sup>

In our studies<sup>3-4</sup> was established the possibility to obtain new, previously unknown compounds by electrolysis from oxohalide melts in systems: Nb-O, Nb-O-F, Nb-O-F-Me, Ta-O, Ta-O-Me, Ta-O-F-Me (Me – alkali metal). For niobium-containing melts the most typical cathodic products are low valence compounds: Nb, Nb(O), NbO', Nb<sub>4</sub>O<sub>5</sub>, tetragonal suboxide Nb<sub>6</sub>O, rhombohedral suboxide Nb<sub>x</sub>O (x < 6), composite (laminated) compounds "NbO"·n"MeF" (Me = K, Rb; n = 1.2). For tantalum-containing melts, the most characteristic cathodic products are metal-like conducting oxide bronzes of three structural types: cubic, tetragonal and hexagonal for the potassium compounds K<sub>1+x</sub>TaO<sub>3</sub>, K<sub>6-x</sub>Ta<sub>10.8</sub>O<sub>30</sub> and K<sub>6</sub>Ta<sub>6.5</sub>O<sub>15+x</sub>F<sub>6+y</sub>, respectively, while the cesium phases, with pyrochlore type crystal lattice, have the general formula Cs<sup>n+</sup><sub>2+z</sub>O<sub>5+y</sub>F<sub>1-y</sub>.

Electrochemical studies have shown that niobium and tantalum in molten salts are not twins.

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# POLYANILINE/CARBON COMPOSITE AS ELECTRODES FOR SUPERCAPACITORS

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Supercapacitors (SC) are electrochemical energy storage devices with a wide range of applications from consumer electronics to heavy industrial machinery.

The report summarizes data on the study of composite materials (CM) based on a conductive polymer, polyaniline (Pani), and activated carbon materials (ACM) obtained from carbonized rice husks and their use as supercapacitor electrodes. Regularities of Pani formation on course of oxidative polymerization on ACM surface have been studied. It has been shown that the formation of a high molecular weight polymer on ACM surface depends on the  $S_{\text{BET}}$  value of ACM and monomer loading<sup>1</sup>.

Performance study of CM as SC electrodes in an acidic aqueous electrolyte showed that the specific capacitance of CM increases consistently with increasing polymer content, while the stability decreases. Material balanced with capacitance/stability is based on ACM with  $S_{\text{BET}} = 2290 \text{ m}^2/\text{g}$  and a Pani content of 61 wt%, which has a specific capacitance of 465 F/g with a capacitance retention 90% after 1,000 charge/discharge cycles<sup>2</sup>.

Symmetrical (CM//CM) and asymmetric (ACM//CM) SC were assembled in the body of a CR2032 battery using an ionic liquid (BMIMBF<sub>4</sub>/ACN) as electrolyte. The specific capacitance values are 42–47 F/g and are high for this type of device compared to literature data. It has been shown that the main reason for the decrease in cell efficiency is the accumulation of a non-conducting form of the polymer during charge/discharge cycles<sup>3</sup>.

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# ELECTROLYTIC DISPERSION OF ALLOYS. PRODUCTION OF COMPOSITE PDNI-ELECTROCATALYSTS OF METHANOL OXIDATION REACTION

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Recently, due to the progress in “green” energy, much attention has been paid to the development of direct methanol fuel cells. Platinum or its alloys are used as catalysts of methanol oxidation reaction (MOR) in such devices. As an alternative to platinum, attempts have been made to use palladium which has fewer poisoning problems in MOR. Among the numerous methods of synthesis of metallic and bimetallic structures, the electrochemical approach attracts special attention in recent years. The interest in the studies using this method is caused by its simplicity and technological efficiency.

The synthesis of composites was carried out in one stage due to simultaneous electrolytic sputtering of the PdNi alloy and electrochemical exfoliation of graphite initiated by 2 ms long voltage pulses with an amplitude of up to 75 V applied to the metallic Pd<sub>0.37</sub>Ni<sub>0.63</sub> and graphite electrodes. As a result, the alloy was dispersed and few-layer graphene structures (FLGS) were produced which served as a substrate for the deposition of nanoalloy particles. Part of the PdNi/FLGS suspension was treated with sulfuric acid to obtain a modified PdNi<sub>mod</sub>/FLGS catalyst. According to X-ray photoelectron spectroscopy data, the content of Pd and Ni in PdNi/FLGS is at 2.8 and 5.5 at. %, respectively, and only palladium is present on the surface of the PdNi<sub>mod</sub>/FLGS sample. The catalytic activity of the composites towards MOR was studied in a solution of 0.1 M KOH + 1 M CH<sub>3</sub>OH. The treatment of PdNi/FLGS in acid has been established to lead to an increase in its activity to the level of a commercial Pt/C catalyst.

Thus, the combination of electrolytic dispersion of the alloy and electrochemical exfoliation of graphite makes it possible to obtain a catalyst demonstrating high catalytic activity towards methanol oxidation reaction.

*The study was carried out in the framework of the State Assignment no. 124013000692-4 using the equipment of the Multi-User Analytical Center of FRC PCP MC RAS.*

# ION-SELECTIVE ELECTRODES IN NON-ZERO CURRENT MODE: CAN WE USE THE NERNST EQUATION IF CURRENT FLOWS THROUGH THE ELECTRODE?

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Ion-selective electrodes with membranes containing ionophores (ISEs) are widely used as potentiometric sensors in analysis of various samples<sup>1</sup>. However, in recent years these sensors are increasingly applied in non-zero current modes – voltammetry and chronoamperometry<sup>2,3</sup>. On the other hand, the interpretation of the signals recorded implies use of the Nernst equation for the potential at the membrane/solution interface. To its turn, the Nernst equation implies an electrochemical equilibrium at this interface.

In this work the kinetics of interfacial transfer of ions is studied by means of electrochemical impedance spectroscopy and chronopotentiometry with Na<sup>+</sup>-selective electrode as a model system. The obtained regular dependence of the low-frequency resistance on the concentration of Na<sup>+</sup> ions in aqueous solution allowed obtaining exchange current densities at the membrane/solution interface. These currents turned to be significantly higher than currents which flow across ISEs in analytical use in chronoamperometric mode. This finding is in favor of the applicability of the Nernst equation for the interpretation of the chronoamperometric analysis with ISEs.

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# THE EFFECTIVENESS OF PROTEIN-FREE FUSION OF LIPID DROPLETS IS DETERMINED BY THE LIPID COMPOSITION OF THEIR SHELLS

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In this work we analyzed the fusion of lipid droplets (LDs), organelles consisting of a core of fatty acids such as triolein surrounded by a monolayer of phospholipids. During metabolism, the size of LDs is regulated by their controlled fusion, i.e. merging of droplet nuclei and their monolayers. In this work, protein-free fusion of lipid droplets was studied. This process requires overcoming the energy barrier  $E$  associated with the topological rearrangement of merging lipid monolayers and overcoming hydration repulsion. We calculated the energy barrier and studied the effect of lipid composition on the height of this barrier. Calculations were carried out using the theory of elasticity of lipid membranes and molecular dynamics methods. As part of the construction of the model, a generalization of the theory of bilayer fusion<sup>1</sup> to the case of monolayer fusion was made.

The lipids that make up the LD shell largely consist of two components—dioleoylphosphatidylethanolamine (DOPE) and dioleoylphosphatidylcholine (DOPC). Our calculations show that an increase in the fraction of DOPE in the LD shell leads to a decrease in the height of the fusion barrier, which is consistent with previously obtained results for bilayer and bilayer-monolayer fusion<sup>2</sup>. At the same time, in contrast to bilayer fusion, the height of the energy barrier decreases and the number of barriers decreases from three to one. As part of our calculations, we also showed that the height of the energy barrier is determined to the greatest extent by hydration repulsion between monolayers; due to this the monolayers at the point of contact have almost vertical shape. These results are confirmed by molecular dynamics calculations.

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# THE INFLUENCE OF THE CRYSTAL STRUCTURE OF NICKEL AND IRON-BASED ELECTROCATALYSTS ON THEIR ACTIVITY IN OXYGEN EVOLUTION REACTION IN ALKALINE MEDIA

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Anion exchange membrane electrolyzers have emerged as a promising technology for water electrolysis due to their ability to operate at higher current densities and lower temperatures compared to traditional alkaline electrolyzers. However, the performance of these electrolyzers heavily relies on the efficiency of the electrocatalysts used at the electrodes. Efforts to develop highly efficient electrocatalysts for anion exchange membrane electrolyzers are crucial for advancing the commercial viability of hydrogen production through electrolysis.

This presentation delves into the development of highly efficient electrocatalysts based on nickel and iron for anion exchange membrane electrolyzers.<sup>1,2</sup> We explore how the crystal structure of Ni,Fe-based electrocatalysts (spinel, perovskite, rock salt, etc.) impacts their electrocatalytic performance in the oxygen evolution reaction in alkaline medium. Our evaluation of intrinsic electrocatalytic activity considers factors such as differences in the true surface area of oxyhydroxide catalytic layers, the conductivity of composite electrodes, and the material/support contact. A key focus of this discussion is emphasizing the significance of performance testing of electrocatalysts in a membrane electrode assembly.

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# SYNTHESIS AND PHYSICAL PROPERTIES OF THE OXYGEN-CONDUCTING $MLn_4Mo_3O_{15}F$ ( $M = Li, Na, K$ ; $Ln = La-Dy$ ) COMPOUNDS FAMILY

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Rare earth molybdates of the composition  $Ln_5Mo_3O_{16+\delta}$  ( $Ln = La-Gd$ ; sp. gr.  $Pn-3n$ )<sup>1</sup>, which have variable oxygen stoichiometry, are being studied as potential electrode materials for solid oxide fuel cells operating in the medium temperature range<sup>2,3</sup>. The interstitial conductivity of such materials is sensitive to the oxygen content ( $\delta$ ), which can be controlled, in particular, by heterovalent doping. Of particular interest is the effect of cation-anion co-doping with an alkali metal and fluorine on the polymorphism, structure, and physical properties of compounds of the  $Ln_5Mo_3O_{16+\delta}$  family.

Compounds with the nominal composition  $MLn_4Mo_3O_{15}F$  ( $M = Li, Na, K$ ;  $Ln = La-Dy$ ) were synthesized in air or in evacuated sealed quartz ampoules in the form of ceramics. The samples were characterized using a set of methods including X-ray diffraction, simultaneous thermal analysis, scanning electron microscopy and impedance spectroscopy in dry and humid atmospheres.

The synthesized ceramics are isostructural with fluorite-like compounds of the  $Ln_5Mo_3O_{16+\delta}$  family. It has been shown that replacing the lanthanide cation with an alkaline element and oxygen with fluorine leads to the occurrence of a reversible phase transition in the samples, accompanied by a jump in anion conductivity by several orders of magnitude for all F-containing ceramics. Samples with large lanthanides are capable of dissociative water absorption and proton transport in a humid environment. As the radius  $Ln$  decreases, fluorine-containing compounds lose their ability to hydrate and proton transfer.

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# IMPACT OF S-PROTEIN FUSION PEPTIDES OF CORONAVIRUSES ON THE STABILITY AND SHAPE OF LIPID MEMBRANES

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To create effective antiviral drugs that prevent cell infection by viruses, it is necessary to understand the molecular mechanisms of action of their fusion proteins<sup>1</sup>. One of the most relevant research objects is the SARS-CoV-2 coronavirus S-protein, which recognizes the ACE2 receptor in human cells and initiates the fusion of viral and cellular lipid membranes. The fusion process is induced by a conformational rearrangement of the S-protein, a crucial step of which is the insertion of its hydrophobic segment, the fusion peptide, into the cell membrane<sup>2</sup>. The high conservation of the amino acid sequence of the fusion peptide indicates its importance in catalyzing membrane fusion. This study investigates the effects of two consecutive segments of the SARS-CoV-2 coronavirus S-protein fusion peptide: FP1 and FP2 on the barrier properties, as well as the mechanical and geometric characteristics of model lipid bilayers. It is shown that the insertion of FP1 into the lipid bilayer leads to its destabilization, causing the formation of defects. Furthermore, when interacting with membranes with low lateral tension, the fusion peptides alter their geometry, leading to the formation of highly curved membrane structures—tubules. The influence of lipid composition on the outcome of the interaction of fusion peptides with membranes has been studied. Based on the obtained data, an explanation for the role of the fusion peptide in lowering the energy barrier of membrane fusion is proposed.

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# MOLECULAR DYNAMICS METHOD FOR DETERMINATION OF ELASTIC PARAMETERS OF MULTICOMPONENT LIPID MEMBRANES

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Lipid membranes, which play the role of the envelope of living cells and their organelles, are subject to various deformations that play an important role in cell life. Elastic parameters of membranes determine the energy barriers and temporal characteristics of deformation processes. The multicomponent nature of membranes allows cells to regulate these parameters by altering lipid composition. Therefore, the study of these parameters is important for understanding the regulation of cellular processes associated with membrane deformations.

In this work<sup>1</sup> we have developed a molecular dynamics method for determining the elastic parameters of multicomponent lipid membranes based on the measurement of lateral pressure profiles of planar lipid bilayers. The planar configuration prevents spatial redistribution of lipids, a problem that complicates the determination of intrinsic elastic parameters of lipid membranes by other methods<sup>2</sup>.

The proposed method is an improved version of the method developed in Ref.<sup>3</sup> An important correction to the bending modulus is taken into account, thus avoiding a systematic error of up to 25%. Instead of determining the local stretching-compression modulus as in Ref.<sup>3</sup>, a simpler method based on finding the derivatives of the local tension moments is used. An expression for the local Poisson's ratio, which characterizes the local volume change under strain, is also derived. The method is applied to membranes composed of dipalmitoylphosphatidylcholine, dioleoylphosphatidylcholine and their mixture. It is shown that the bending modulus and spontaneous curvature of the mixture do not obey the assumption of additivity of elastic parameters.

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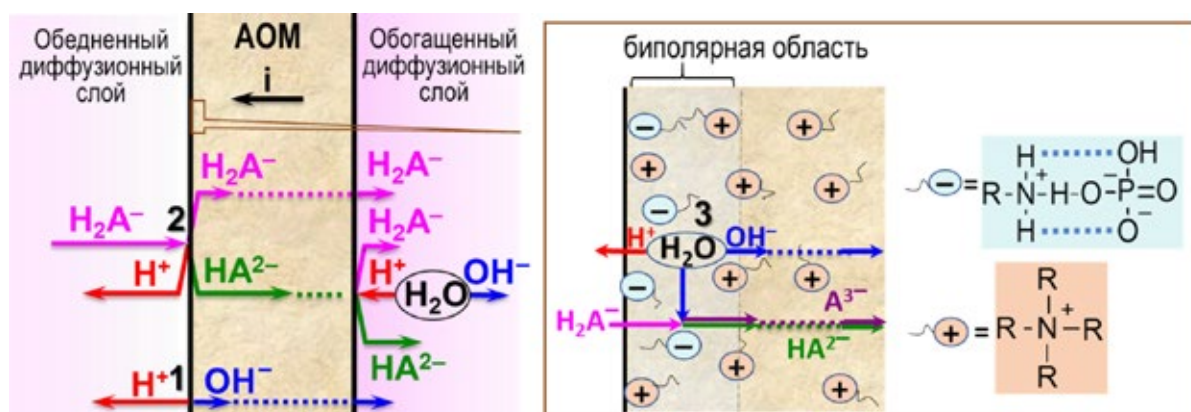
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# MECHANISMS OF ION TRANSFER IN ION EXCHANGE MEMBRANE/AMPHOLYTE SOLUTION SYSTEMS IN ELECTRODIALYSIS

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Electrodialysis, dialysis, membrane capacitive deionization and membrane bioreactors are increasingly used for the purification, concentration and separation of ampholytes, that is, substances capable of participating in proton transfer reactions. Participation in these reactions makes the structure and electrical charge of ampholytes extremely sensitive to the pH of the media and leads to a number of peculiarities in the development of concentration polarization compared to membrane systems, where the transfer of electrical charge is carried out by strong electrolytes (NaCl), which are not involved in proton transfer reactions. We have discovered two previously undiscussed phenomena that develop under any current modes. They lead to enhanced generation of  $H^+$ ,  $OH^-$  ions in anion exchange membrane (AEM)/ampholyte solution systems compared to solutions of strong electrolytes (Fig. 1) and cause a reduce of electroconvection, a decrease in current efficiency, an increase in energy consumption and progressive degradation of membranes during electrodialysis processing of ampholyte containing solutions.



**Figure 1.** Schemes for the generation of protons and hydroxyl ions in the system AOM/ampholyte solution according to the known mechanism of water splitting with the participation of fixed membrane groups (index 1), as well as the discovered mechanisms of “acid dissociation” (index 2) and “bipolar dissociation” in the junction formed by positively charged fixed AOM groups and negatively charged “bound species” (index 3). A is the acidic residue of a hydroxy acid (phosphoric, tartaric, citric, etc.)

*The work was carried out with the financial support of the Russian Science Foundation, project 24-19-00451.*

# ELECTROCHEMICAL BEHAVIOR OF CYCLIC OZONIDE AND AMINOPEROXIDE IN ACETONITRILE MEDIUM ON GOLD

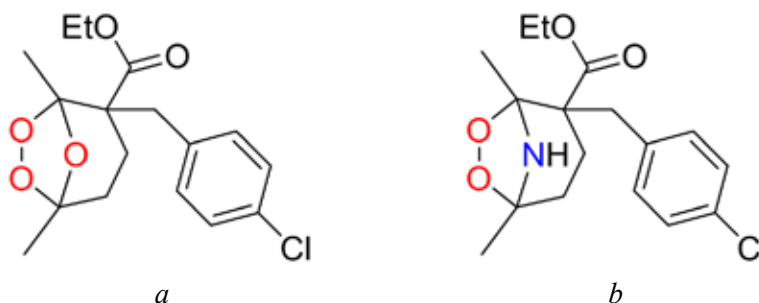
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Cyclic organic peroxides are an important object of research, since these compounds have different biological activity. The structure of peroxides determines the electrochemical behavior, which can be studied using the cyclic voltammogram (CV) method, which allows determining the redox properties of such compounds.

We studied the electrochemical behavior of two structures of cyclic organic bridged peroxides: 1,2,4-trioxalane (*a*) and 1,2,4-dioxazolidine (*b*), on a gold electrode in a medium of dehydrated acetonitrile. The CV registered by us on the gold electrode made it possible to obtain the clearest and most separated reduction peaks and the ability to fix peaks in the anode region.



In the cathode region of the CV, the peroxide bond of the molecules of the studied compounds is restored with the transfer of a total of two electrons and followed by a break in the cycle, resulting in the formation of a 1,5-diketone fragment. During gravimetric studies using a gold anode, the formation of colloidal particles (3–8 nm) and the absence of a gold deposit on the cathode surface were recorded.

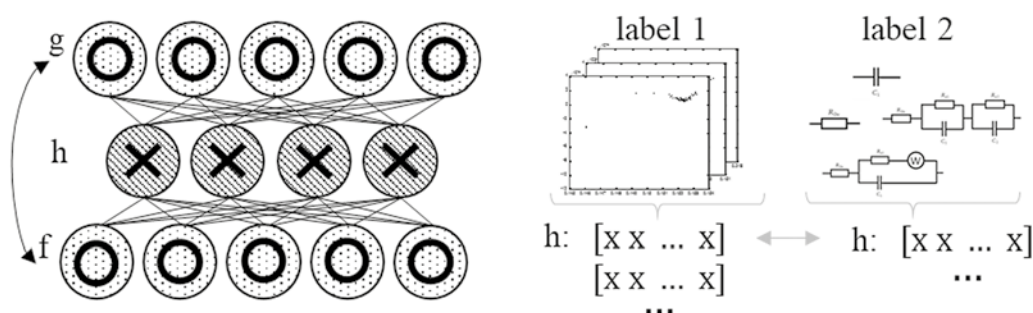
# AUTOENCODER NETWORK FOR ANALYSIS OF ELECTROCHEMICAL IMPEDANCE OF LITHIUM-ION BATTERIES

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We developed a new technique of analysis of electrochemical impedance spectra of lithium-ion batteries by application of an autoecoder neural network. The architecture of the created network is presented at Fig. 1. It consists of an encoder *g*, hidden state *h* and decoder *f*. The network combines LSTM-layers and convolutional layers and utilizes data-labels to perform comparative study of impedance of batteries and equivalent circuits.



**Figure 1.** The architecture and the main principles of functioning of the autoencoder network for electrochemical impedance analysis of lithium-ion power sources

To verify the technique, we performed a study of impedance of lithium-ion batteries of type LG 18650 3500 mAh in frequency area from 1 mHz to 1 kHz. The advantages of the proposed method over other methods<sup>1</sup> of sorting and management of battery packs were shown.

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# CONDITIONS FOR DEPOSITING OF ELECTROACTIVE COATINGS BASED ON DYES FROM DEEP EUTECTIC SOLVENTS

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Electrochemical sensors and biosensors have found great application in medicine, ecology, biotechnology and food industry. Such sensors often use modifying electroactive coatings that can be obtained by electropolymerization from phenothiazine, phenoxazine, phenazine and acridine dyes solutions. Moreover, sensor coating can contain various carbon nanomaterials and bioreceptors to detect target analytes—medications, neurotransmitters and toxicants with high specificity. Low solubility of organic monomers in aqueous medium limits the opportunities for stable layers obtaining, reduces the concentrations of precursors and leads to their aggregation in reaction mixture. Deep eutectic mixture use—the mixture of compounds that are donors and acceptors of hydrogen bonds—allows to overcome these limitations.

Polymer coatings from dye solutions in deep eutectic solvents were received and electrochemically characterized. Influence of monomer nature and reaction media content on coatings morphology was established. Methods of carbon nanomaterials and dyes co-incorporation in deep eutectic mixtures were developed and the possibility of “one-step” electropolymerization resulted in nanocomposites “polymer–carbon nanomaterial” formation was demonstrated. Electropolymerization in deep eutectic solvents medium allowed to obtain molecularly imprinted coatings for biologically active low molecular compounds determination. The sensors developed were tested in epinephrine, anthracycline anticancer drugs determination and DNA damage registration.

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# ELECTROCHEMICAL SIMULATORS OF $\text{Am}^{2+}$ AND $\text{Cm}^{3+}$ IONS IN A MOLTEN $\text{LiCl-KCl}$ EUTECTIC

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Spent nuclear fuel (SNF) contains americium and curium among other fission products (FP). Although the content of these two FPs is approximately 0.1 and 0.01% (irradiation with fast neutrons to a burnup depth of 4.5% h.a.), their activity exceeds the total activity of uranium and plutonium<sup>1</sup>. When reprocessing SNF, they must be separated, because Am can be afterburned in molten salt reactors, or even reintroduced into the nuclear fuel cycle, but Cm must be stored. The half-life of  $^{244}\text{Cm}$  is 18 years, and after 100 years it will decay to  $^{240}\text{Pu}$ , which can be introduced into the nuclear fuel. Operations with americium and curium are complicated due to their high  $\alpha$ -activity, which causes intense radiolysis of almost any media: aqueous, organic, glassy. Molten salts have significant radiation resistance. Therefore, it is advisable to separate Am and Cm in molten salts. First of all, the separation technology should be developed and it is important to find appropriate Am and Cm simulators to perform experiments.

The purpose of this work is to search for electrochemical simulators of  $\text{Am}^{2+}$  and  $\text{Cm}^{3+}$  ions in the molten  $\text{LiCl-KCl}$  eutectic.

As can be seen from the Periodic table, europium and gadolinium have the closest electronic structure to americium and curium ( $\text{Eu} [\text{Xe}]4f^76s^2 \sim \text{Am} [\text{Rn}]5f^77s^2$  and  $\text{Gd} [\text{Xe}]4f^75d^16s^2 \sim \text{Cm} [\text{Rn}] 5f^76d^17s^2$ ). Americium, like europium, has two oxidation states, and both of them have the most stable oxidation state of two in melts.

However, the potentials of Eu and Gd were found to be far from those of Am and Cm, respectively. In the molten  $\text{LiCl-KCl}$  eutectic, the  $\text{Eu}^{2+}/\text{Eu}$  potential is almost 0.5 V more negative than that of  $\text{Am}^{2+}/\text{Am}$ , and the  $\text{Gd}^{3+}/\text{Gd}$  potential is approximately 150 mV more negative than that of  $\text{Cm}^{3+}/\text{Cm}$ .<sup>2-5</sup>

In the present work possible simulators with potentials differing from those of Am and Cm by ~40 mV are suggested.

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# ELECTROKINETIC LENGTH SELECTION IN ELECTRODEPOSITION

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We discuss the mechanism of electrokinetic regularization of the shortwave catastrophe in electrodeposition. Without suitable regularizations, both morphological and nonequilibrium electroosmotic instabilities occurring in electrodeposition are singular for shortwave perturbations in the following sense. In morphological instability the infinitesimal wavelength perturbation grows the fastest. In the electroosmotic instability in terms of the local electroneutrality approximation, the quiescent state is least stable for infinitesimal wavelength perturbations. Regularization of electroosmotic instability requires considering the finite width of the electric double layer. It was recently shown that in electrodeposition too, taking into account the finite width of the electric double layer combined with the finite electrode reaction rate constant, yields selection of a finite critical perturbation wavelength for instability, thus providing a regularization mechanism alternative to surface tension. We discuss the physical mechanism of this length selection, along with the effect exerted by the nonequilibrium electroosmotic flow which emerges in the limiting/overlimiting current regime.

# WAYS TO SUPPRESS OF SELF-DISCHARGE IN A NON-FLOWING ZINC-BROMINE BATTERY

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The development of metal halide batteries is one of the more important areas of electrochemical energy study today. The zinc-bromine system, produced in both flow (stationary) and non-flow<sup>1</sup> (portable) versions, has reached practical realization. The main advantages of the portable zinc-bromine system are power and resource, which exceed other types of batteries. The main disadvantage of such a storage device is a high self-discharge, primarily due to the transfer of bromine through the separator. The methods of dealing with this type of self-discharge are divided into two fundamentally different groups. The selection of separators that prevent the bromine diffusion<sup>2</sup> and the modification of activated carbons (AC) in order to increase their sorption capacity to bromine<sup>3</sup>.

The principle of AC modification is based on the blocking of the surface of macro- and mesopores by large organic molecules adsorbed on the reduced surface of microporous AC. Quaternary ammonium salts of bromine or glycol-based polymers are most often used for this purpose. Low-porous and cation-exchange membranes are used as separators that reduce self-discharge by bromine. This method, as a rule, significantly increases the internal resistance of the battery.

Within the framework of the presented work, we proposed and tested a method for modifying AC with polyethylene glycol and a method for using a porous heterogeneous membrane replaced with tetrabutylammonium ions. As a result, a significant decrease in self-discharge was shown. Laboratory cells showed an energy efficiency of close to 80% in a daily charge-discharge cycle.

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# ELECTRO / BAROMEMBRANE PROCESS FOR SEPARATION OF IONIC DYES SOLUTIONS USING ELECTRICALLY CONDUCTIVE MEMBRANES

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The baromembrane processes are widely used for separation, purification and concentration of solutions. In a recent decade, the electrically conductive membranes were applied in ultrafiltration and nanofiltration<sup>1</sup>. Such membranes combine the sieving filtration mechanism with Donnan exclusion of charged components (ions) by varying the electrical potential of membrane surface. It provides an efficient way to control membrane selectivity and permeability<sup>2,3</sup>.

This work deals with the preparation of ceramic membranes with electrically conductive selective layer and application of these membranes for separation of ionic dyes from aqueous solutions. The membranes consist of a substrate prepared from a fraction of fly ash microspheres (~10 µm) and a selective layer composed from alumina nanofibers (d~10 nm) covered by conductive carbon coating with the help of chemical vapour deposition<sup>2,4</sup>. The average pore size of the selective layer is about 33 nm and 26 nm before and after carbon deposition, respectively.

The filtration experiments with aqueous solutions of cationic and anionic dyes (Brilliant Blue R, Victoria Blue B, Methylene Blue, Methyl Orange) were carried out in a laboratory setup with filtration cell, where the membrane served as the working electrode, while the titanium porous plate served as the counter electrode. The transmembrane pressure was varied in the range 5–8 bar. It is found that the rejection of dyes occurs due to adsorption, which can be modified by applying the prescribed potential to the membrane surface. In particular, when positive potential was imposed to the membrane, the rejection of cationic dyes decreased with time from 99.9% to 80–85%, while at negative potentials, the rejection was stable at the level of 99.9%. Our results indicate that electro/baromembrane process is promising for selective separation / purification of molecular mixtures.

The work is supported by the Russian Science Foundation, project 23-19-00269.

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# A MODEL DESCRIPTION OF THE POTENTIAL DISTRIBUTION AT THE INTERFACE OF A RENEWABLE GRAPHITE ELECTRODE WITH ELECTROLYTE SOLUTIONS

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The behavior of a graphite electrode in aqueous and propylene carbonate<sup>1</sup> solutions of surface inactive electrolytes is studied by the method of electrochemical *in situ* measurements on electrodes with the mechanically renewable surface. The potential regions are found in which the electrode behaves as ideally polarizable. It is noted that the capacitance curves ( $C$  vs.  $E$  dependences, where  $C$  is the differential capacitance and  $E$  is the potential) demonstrate the following characteristic features: at potentials corresponding to the positive surface charges, the capacitance of the electric double layer of the graphite electrode is approximately 1.5–2 times lower as compared with the typical mercury-like metals; at the same time, as the potential shifts to the region corresponding to the negative surface charges, the aforementioned values come closer and even merge together.

The analysis of the results has shown that the peculiarities of  $C$  vs.  $E$  curves on the graphite electrode are associated with the semiconductor properties of this material. A new approach is proposed to the model description of experimental data that allows one to assess the characteristics (parameters) of the electrode material important as regards its semiconductor properties such as the flat band potential and the concentration of charge carriers in the conduction zone.

The proposed procedure of processing the capacitance curves was used for processing the literature data<sup>2,3</sup> on the interface of the Bi electrode with solutions of surface-inactive electrolytes. The results allowed us to compare the semiconductor properties of the Bi and graphite electrodes and assess their role in the formation of the electrode/solution interfaces.

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# PHOTOCATALYSTS BASED ON ANODIC TITANIA PHOTONIC CRYSTALS

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Titanium dioxide is a promising photocatalyst for water splitting and degradation of organic pollutants in the environment due to high photocatalytic activity, low cost, high chemical stability and low toxicity. Photonic crystals (PhCs) based on anodic titanium oxide (ATO) are attracting great interest. PhCs are characterized by the photonic band gaps (PBGs) – frequency ranges in which light cannot propagate in the material. The PBG spectral position is one of the important parameters that determine the photocatalytic activity of the ATO PhC.

In this work, an anodizing regime with modulation of voltage ( $U$ ) on the optical path length ( $L$ ) has been developed. Proposed  $U(L)$  regime<sup>1</sup> was successfully applied for the synthesis of ATO PhCs with the reflectance close to 100% and the desired PBG position in a wavelength range of 400–1500 nm. Deviation of the experimental PBG position from the desired one was less than 10%. Post-treatment of the ATO PhC has a significant effect on its photocatalytic activity in methylene blue (MB) degradation under the ultraviolet radiation<sup>2</sup>. An increase in the MB decomposition rate constant up to ~60% was observed for the PhC after annealing in  $H_2/Ar$  atmosphere due to an increase in the concentration of single-electron-trapped oxygen vacancies (SETOV) and surface hydroxyl groups. Electrochemical reduction and annealing in  $NH_3$  led to a decrease in the photocatalytic activity of the PhC.

ATO PhCs are promising for use not only as photocatalysts but also as SERS substrates and photoanodes in solar cells.

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# FAST-ACTIVATING RESERVE POWER SOURCES: THE ROLE OF PHYSICO-CHEMICAL PROPERTIES OF ELECTRODE MATERIALS IN THE IMPROVEMENT OF DISCHARGE PERFORMANCE

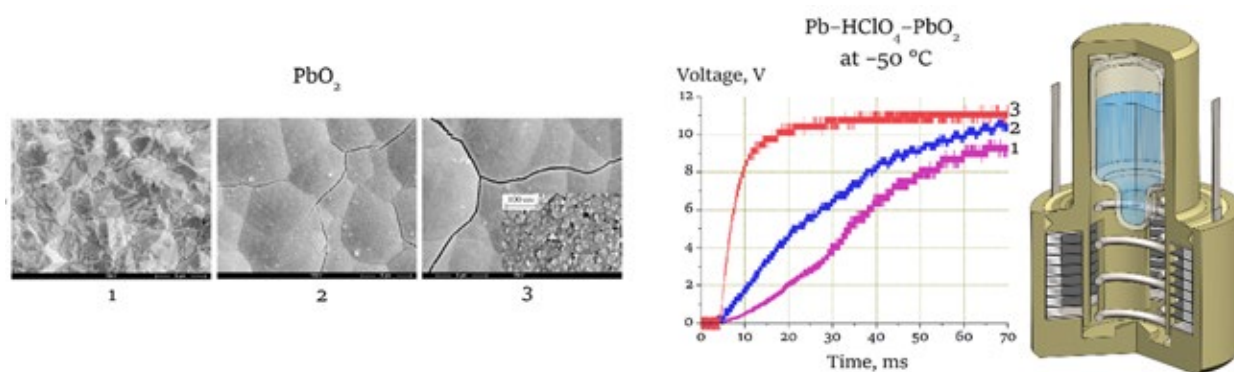
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The work deals with the development of small-sized reserve power sources for the autonomous technical devices operating under extreme conditions<sup>1</sup>. Two approaches were applied to modification of the system Pb/HClO<sub>4</sub>/PbO<sub>2</sub>: (i) substitution of lead with zinc as anodic material; (ii) application of highly active PbO<sub>2</sub> coatings as cathodic material.

The influence of physico-chemical properties of electrode materials (including microstructure, phase and chemical composition, porosity) on the performance of electrodes was investigated<sup>2-4</sup>. The application of nanoporous nano-crystalline PbO<sub>2</sub> coatings helps approach proper operating ability of power sources at the lower temperature (down to –50 °C) and provides short activations time (less than 30 ms) (Fig. 1). The results were transferred into the industrial production of power sources.



**Figure 1.** Surface microstructure of cathodes, discharge curves  
of power sources at –50 °C and design scheme of small-sized power sources

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# QUANTUM CHEMICAL MODELLING REDUCTIVE METALLATION OF ORGANIC CATHODE MATERIALS

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Currently, organic cathode materials for chemical energy sources are of particular interest as a cheaper and more efficient alternative to traditional inorganic materials. However, despite high theoretical capacities of up to 400 mAh/g, there is a problem of poor stability of organic cathodes. The use of quantum chemical approaches makes it possible to see changes in the structure of organic molecules during their reductive metalation at the molecular level<sup>1,2</sup>, as well as to identify the relationship between the structure of molecules and energy effects during reductive metalation. In addition, molecular design using quantum chemical modeling allows new promising materials to be tested a priori for undesirable effects<sup>3,4</sup>.

In the process of metalation of polymeric organic materials, many intramolecular and intermolecular coordination bonds arise with the participation of intercalated alkali metal ions. Their total energy is quite high, which makes possible significant structural rearrangements due to conformational changes, which serve as an obstacle to good reversibility of the processes of intercalation and deintercalation of metal ions, even if they are energetically favorable. However, in some cases it is possible to perform a charge/discharge cycle in ~80 s for various alkali metals<sup>5</sup> with excellent cyclic stability, especially in the case of potassium, where there is no capacity fade after 4000 cycles.

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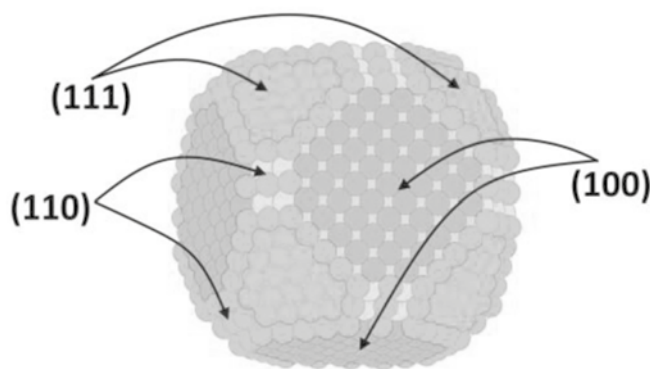
# STUDY OF PLATINUM ELECTROCATALYSTS ON CARBON SUPPORT USING FRUMKIN ADSORPTION ISOTHERMS

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Cyclic voltammetry is an effective tool for rapidly analysing the structural and electrochemical properties of platinum carbon-based electrocatalysts, an important stage in their development. The cyclic voltammetry curve's shape in the hydrogen adsorption region is determined by the total contribution from various surface structures of platinum nanoparticles in the electrocatalyst sample. This curve can be used to screen the crystal structure of active centres<sup>1</sup>.

The Frumkin adsorption isotherms were used to deconvolute the hydrogen adsorption peaks of various samples of platinum electrocatalysts on nanostructured carbon supports. This allowed for the calculation of the adsorption energy and surface fraction corresponding to the crystal structure of platinum nanoparticles. The impact of various degradation mechanisms on the change of sites with different types of crystal structure was evaluated by analyzing the dependence of calculated peak parameters on the number of cycles of accelerated stress testing. Additionally, the stability and structure of platinum nanoparticles were assessed in relation to the type of carbon support used<sup>2</sup>.



**Figure 1.** Crystal structure of a platinum nanoparticle

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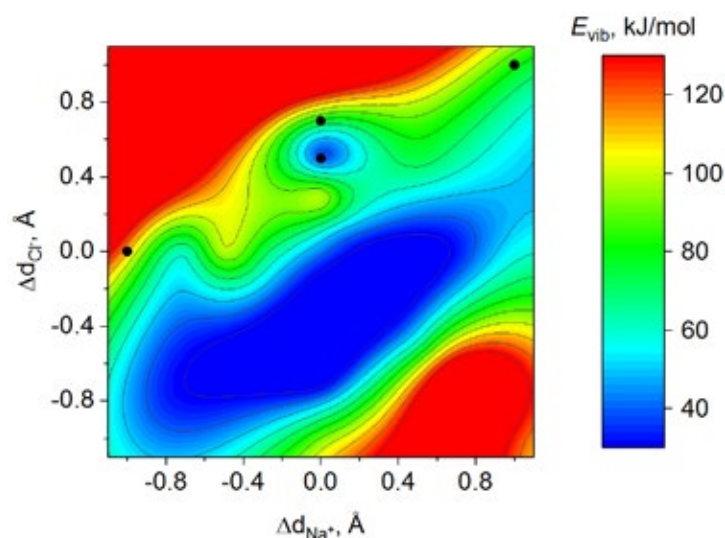
*The work was carried out within the framework of the state assignment to the National Research Center “Kurchatov Institute”.*

# THEORETICAL-EXPERIMENTAL STUDY OF CHARGE TRANSFER PROCESS IN SAMARIUM-CONTAINING MELTS

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One of the promising methods of spent nuclear fuel handling is its pyrometallurgical reprocessing. The key process of this technology is electrorefining in molten salts to separate actinoids from lanthanides. The electrorefining process requires data on the electrochemical behavior of these closely related elements in salt melts of different compositions. Electrochemical studies were performed by cyclic and linear voltammetry methods in NaCl-KCl, KCl and CsCl melts containing  $\text{SmF}_3$ . Quantum-chemical studies were carried out using the quantum-chemical program package Firefly, by DFT/B3LYP density functional theory methods. The influence of the second coordination sphere of samarium complexes on the diffusion coefficients and standard charge transfer rate constants ( $k_s$ ) of the  $\text{Sm(III)/Sm(II)}$  redox pair in halide melts was studied by electrochemical methods and the corresponding activation energies were calculated. Quantum chemical analysis of the structure of the boundary molecular orbitals allowed us to identify the most probable transition state structures for the electron transfer process (Fig. 1).



**Figure 1.** Potential energy surface at different shifts of ions ( $\text{Na}^+$  and  $\text{Cl}^-$ ) of the double layer, Sm-F bonds stretched by 0.10 Å. Black dots indicate transition states for the electron transfer process

# CHANGING IN THE SHAPE OF THE LIPID MEMBRANE BY INTERACTION OF AMPHIPATHIC HELICES AND CONICAL LIPIDS

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Changes in the shape of membrane structures in cells occur as a result of the temporally and spatially coordinated action of specialized proteins. Proteins can create geometric curvature of the membrane by forcing their shape on it<sup>1</sup> or through steric interactions which occur between protein molecules on the surface of the membrane<sup>2</sup>. In this work we consider another mechanism that may be involved in the regulation of the shape and curvature of biological membranes—the incorporation of amphiphilic regions of peripheral proteins at the interface between the polar and hydrophobic area of the lipid bilayer. We show that integration into a flat membrane H0 peptide ENTH domain of the epsin protein and model peptides with a similar hydrophilic-hydrophobic profile can lead to a change in shape of the membrane—to the spontaneous formation of tubular structures. Also, the most important role of so-called non-bilayer lipids in this process has been shown. The presence of phosphatidylethanolamine (a lipid with negative spontaneous curvature) significantly increased the value of lateral tension which could resist spontaneous membrane tubulation by the peptide. In addition, the radius of the formed tubules was decreased. We have proposed a model to explain the observed lipid-protein synergism in the regulation of the shape of biological membranes.

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# LITHIUM-ION CONDUCTIVE MATERIALS BASED ON N-METHYL-N-PROPYLPYPERIDINIUM SALT

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Organic plastic crystals represent a new and unique class of solid materials that combine a crystalline structure, moderate plasticity, and relatively high ionic conductivity. At the molten state, organic salts are ionic liquids with high ionic conductivity. The high-temperature plastic phases of these salts, existing below the melting point, can be considered as an intermediate state between ionic liquids and solids with a completely ordered structure. Local disorder of the crystal lattice and high orientational mobility of molecular fragments facilitate the transport of ions in organic salts; charge carriers can be relatively large organic cations or anions.

At this work, we studied the effect of the addition of lithium salt  $\text{LiX}$  ( $\text{X} = \text{ClO}_4^-$ ,  $\text{BF}_4^-$ ) on the physicochemical properties of N-methyl-N-propylpyperidinium salt  $[\text{N}_{13}\text{pip}]\text{X}$ . The thermal properties, crystal structure and ionic conductivity of the phases of the  $[\text{N}_{13}\text{pip}]\text{X}$ - $\text{LiX}$  binary system were studied, electrochemical and impedance measurements were carried out in order to determine the possibility of using the systems under study as electrolytes in lithium current sources.

Addition of  $\text{LiX}$  leads to a decrease in the melting point and the formation of eutectics, as well as a new compound representing a double salt.

A study of electrochemical stability relative to lithium showed that the most conducting binary systems are stable up to 4.5–4.9 V (rel. Li). The results of galvanostatic cycling of symmetric  $\text{Li}/[\text{N}_{13}\text{pip}]\text{X}$ - $\text{LiX}/\text{Li}$  cells indicate that lithium transport is realized in these binary systems.

The research results will be presented in more detail in the report.

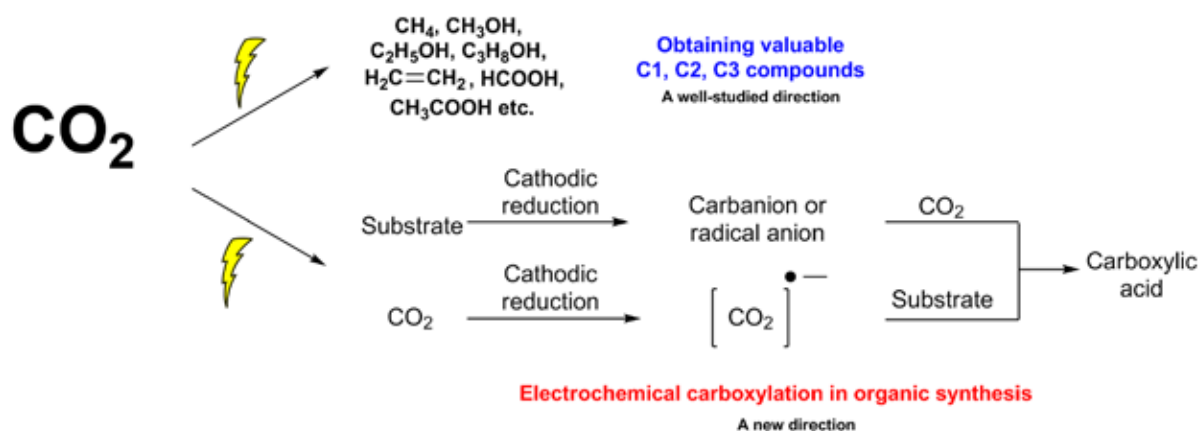
*The work was carried out with the financial support of the Russian Science Foundation, project 20-13-00302.*

# ELECTROCHEMICAL CARBOXYLATION USING CARBON DIOXIDE

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One of the approaches to CO<sub>2</sub> utilization and conversion is based on the transformation of carbon dioxide into valuable C1, C2, C3 products under the action of an electric current. Along with this, the direction of carbon dioxide involvement in electrochemical organic synthesis is developing, in which CO<sub>2</sub> is introduced into various substrates to form valuable carboxylic acids.



This work is aimed at studying the processes of CO<sub>2</sub> involvement in electroorganic synthesis, in particular studies of the processes of electrochemical hydrocarboxylation of enol derivatives of carbonyl compounds using CO<sub>2</sub>.

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*The work was carried out with financial support Subsidy 01-10, topic is "Development of adsorption-catalytic systems for air purification from greenhouse and acid gases"*

# EXPRESS METHOD FOR DETERMINATION OF CROSSOVER PARAMETERS OF SOLUTE ELECTROACTIVE COMPONENTS

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Crossover of a solute component, B, across an ion-exchange membrane is characterized by its distribution constant at the membrane/solution boundary,  $K(B)$ , and by its diffusion coefficient inside the membrane,  $D(B)$ . We have proposed<sup>1,2</sup> to determine these parameters for any electroactive component of the system, B, by means of measurements of its discharge current on an (immobile) disk electrode through the membrane which is pressed mechanically towards the electrode surface while the external surface of the membrane is in contact with a solution containing this electroactive component, B. First, the equilibrium for the mobile ions (including B) has been established both at the membrane/solution boundary and inside the membrane. Then, the electrode potential changes in a stepwise manner to the value where the species, B, discharges at the electrode surface ( $B - ne^- = C$ ) under the non-stationary limiting-current regime. After that a steady-state current has been attained the electrode potential changes again in a stepwise way to a value where a backward transformation of the C component into B takes place. Measurement of the non-stationary current during two stages of the process enables one to determine crossover parameters of both electroactive components, B and C.

Such measurements have been performed for a series of mixed aqueous solutions:  $x \text{ M HBr} + 2 \text{ M H}_2\text{SO}_4$ ,  $0.125 \leq x \leq 0.75$  in contact with Nafion-212 membrane. Transport parameters have been found:  $D(\text{Br}^-) = (2.98 \pm 0.27) \cdot 10^{-6} \text{ cm}^2/\text{s}$ ,  $D(\text{Br}_2) = (1.10 \pm 0.07) \cdot 10^{-6} \text{ cm}^2/\text{s}$ ,  $K(\text{Br}^-) = 0.190 \pm 0.005$ , which have turned out to be practically independent of the HBr concentration with the above range.

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*Financial support of the Russian Science Foundation is acknowledged (project 23-13-00428).*

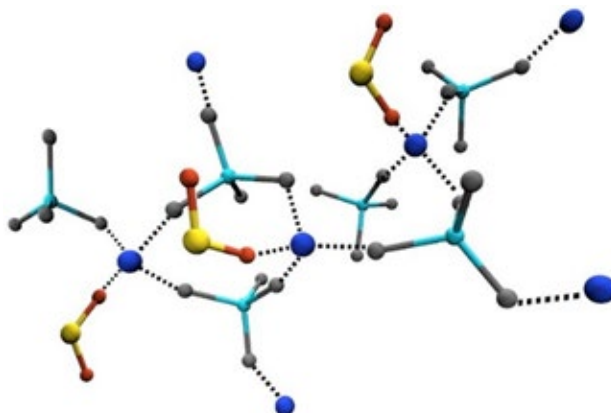
# STRUCTURE AND PROPERTIES OF SOLVATE COMPLEX OF LITHIUM TETRACHLOROALUMINATE WITH SULFUR DIOXIDE

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In order to create fireproof electrolytes for lithium-ion and lithium batteries, solvate complexes of lithium tetrachloroaluminate with sulfur dioxide<sup>1</sup> were studied. For the first time, the physicochemical properties (electrical conductivity, viscosity, density, melting points) and the structure of the  $\text{LiAlCl}_4 \cdot \text{SO}_2$  solvate complex were studied using experimental and theoretical methods.

It has been shown that  $\text{LiAlCl}_4 \cdot \text{SO}_2$  has high electrical conductivity ( $4.7 \cdot 10^{-2} \text{ Ohm}^{-1} \text{ cm}^{-1}$ ) and dynamic viscosity ( $1.9 \cdot 10^{-2} \text{ Pa s}$ ) at 30 °C. The solvate complex  $\text{LiAlCl}_4 \cdot \text{SO}_2$  is stable at atmospheric pressure. Sulfur dioxide is associated with the lithium cation and is included in its internal coordination sphere (Fig. 1).



**Figure 1.** Structure of the solvate complex  $\text{LiAlCl}_4 \cdot \text{SO}_2$   
(blue—Li, cyan—Al, gray—Cl, yellow—S, red—O, the dashes line shows  
the coordination of the lithium cation with  $\text{AlCl}_4^-$  and  $\text{SO}_2$ )

It has been established that  $\text{LiAlCl}_4 \cdot \text{SO}_2$  monosolvate has high fire safety and can be recommended as an inorganic electrolyte for high-power lithium-ion batteries.

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# ENANTIOSELECTIVE SENSORS: ANALYTICAL CAPABILITIES AND PROSPECTS

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Modern advances in the study of the molecular mechanisms of diseases and methods of pharmacological treatment confirm the need for the use of optically active substances. An important role in this context is played by the development of accessible analytical methods for the analysis of these substances. In recent years, there has been growing interest in the development of electrochemical analytical methods using enantioselective voltammetric sensors<sup>1–5</sup>. However, when developing such sensors, certain difficulties always arise related to the discrimination of analytical signals, since the voltammograms of enantiomers often have similar characteristics. Obtaining an enantiodifferentiated analytical signal of an optically active analyte is ensured by a chiral selector, but there are no universal selectors and methods for their creation due to the complexity of the processes occurring on the sensor surface.

The report provides an overview of the most interesting trends associated with methods of development, research and practical application of enantioselective voltammetric sensors based on new chiral materials for recognizing enantiomers of biologically active compounds. Enantioselective sensors based on chiral metal nanoparticles<sup>1</sup> have been considered; mesoporous metals with molecular imprints; single-walled carbon nanotubes<sup>2</sup>; “smart” polymers; metal-organic framework structures; metal complexes<sup>3</sup> and their composites; chiral ionic liquids, zeolites<sup>4,5</sup>. The problems and prospects for their use in the analysis and recognition of optically active compounds are discussed, highlighting the main problems facing the scientific community and possible directions for further development in this area.

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# ELECTRODEPOSITION OF NICKEL-BASED HIGH-ENERGY COMPOSITE COATINGS WITH DIFFERENT KINDS OF FILLERS

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High energy composites are composites with a high calorific efficiency. The simplest and most processible method of their manufacturing is their deposition in the form of composite electrochemical coatings (CEC) from nickel-plating electrolytes. The method allows obtaining composite coatings with high adhesion to the support and easily regulated thickness. In the course of this study, electrolyte compositions have been developed that allow plating such composites, as Ni-Al, Ni-B, Ni-B<sub>4</sub>C, Ni-Ti-2B, Ni-Mg. The maximum energy of calorific efficiency in composites is achieved at a certain ratio of components in the coating. In the case of Ni-B and Ni-B<sub>4</sub>C composites, the thermal energy is released as a result of interaction between Ni and B with formation of Ni<sub>3</sub>B at the component ratio of 75 at.% Ni and 25 at.% B (ideal stoichiometry), while 20 at.% B in the coating are to be obtained in the case of the Ni-Ti-2B CEC, and the Ni-Al CEC contains 50 at.% Ni and 50 at.% Al. Well-known aqueous nickel-plating electrolytes (sulfate, sulfamate etc.) can be used for formation of the Ni-B, Ni-B<sub>4</sub>C composites. However, the electroplating of the Ni-Al composites from aqueous electrolytes is complicated due to the high rate of the aluminum powder oxidation. Accordingly, we suggest using nickel-plating electrolytes based on deep eutectic solvents (DES). In this case, an advantage of these electrolytes is the low concentration of water: in point of fact, DES include only the crystallization water from nickel salt hydrates. The prospects of applying DES-based electrolytes for CEC formation are obvious and are related to the radical decrease in the oxidation rate of the aluminum component. For the same reason, these electrolytes allow obtaining high-quality Ni-Ti-2B and Ni-Mg composites by introducing the corresponding dispersed phase powders.

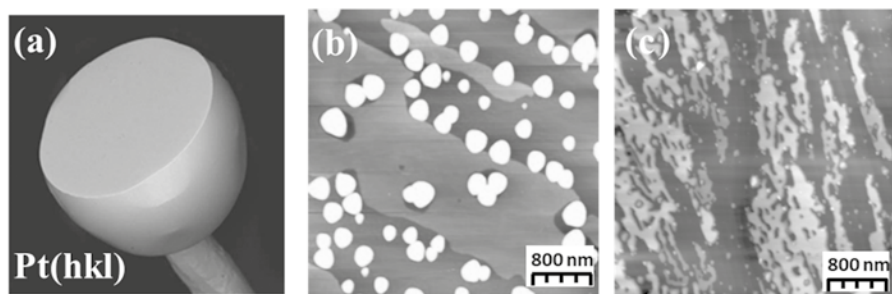
# INITIAL STAGES OF SILVER ELECTRODEPOSITION FROM ETHALINE ON SINGLE CRYSTAL AND POLYCRYSTALLINE PLATINUM ELECTRODES

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Despite the numerous publications on electrodeposition of metals and alloys from deep eutectic solvents (DES), the nature of electrosorption and initial stages of electrodeposition from DES still requires detailed investigation. The aim of This work was to study the regularities of electrosorption and phase deposition of metals from DES on the example of silver onto model Pt single crystals with a controlled surface structure (Fig. 1, *a*). For this, we used a complex experimental approach including registration of formation of adlayers and growth of phase deposits under different conditions using voltammetric methods and in situ and ex situ scanning probe microscopy with control of the deposit morphology.

A protocol of single crystal Pt(hkl) preparation for work in nonaqueous media was suggested that excludes the oxidation and disordering of the single crystal surface. Additionally, a procedure was developed for single crystal activation that allowed removing from their surface thermal oxides formed in the course of single crystal cooling. Electrosorption and initial stages of Ag phase deposition from ethaline onto basal Pt(hkl) single crystals were studied depending on the electrode single crystal surface structure, preparation procedure, and activation degree (Fig. 1, *b*, *c*).



**Figure 1.** SEM image of the Pt(hkl) electrode; (*b*, *c*) AFM images of the Ag deposit on (*b*) nonactivated and (*c*) activated Pt(111) surface

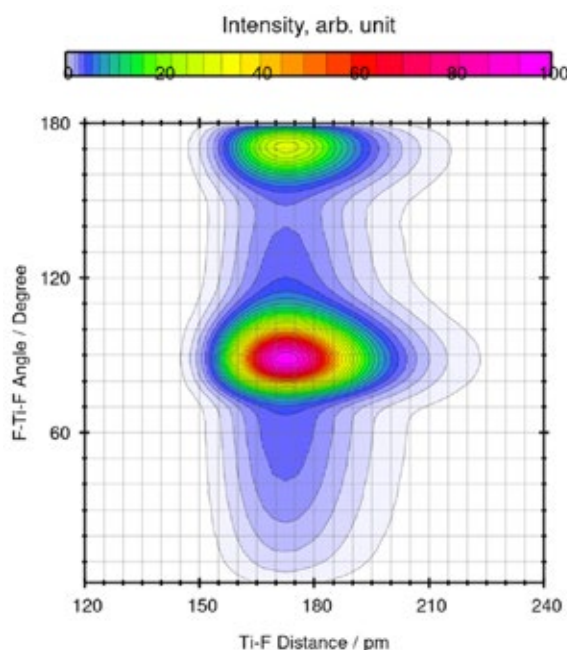
*The work was supported by the Russian Science Foundation project no. 23-23-00248, <https://rscf.ru/project/23-23-00248/>.*

# STRUCTURE AND LOCAL ION DYNAMICS OF $\text{TiF}_4$ IN ALKALI FLUORIDE MELTS

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Electrorefining in molten salts is a promising pathway for producing affordable high-grade titanium for industrial purposes. To optimize this process, a thorough understanding of the structure and dynamic properties of titanium complexes in various molten salts is necessary. Therefore, we employed molecular dynamics simulations to investigate the structure and local ion dynamics of  $\text{TiF}_4$  in individual molten alkali fluorides and commonly used eutectic composition FLiNaK. It is shown, that the  $[\text{TiF}_6]^{2-}$  complexes with distorted octahedral geometry are mainly formed in the melts with low concentration of Ti (Fig. 1). The formation of polyatomic fluorotitanate complexes along with  $[\text{TiF}_6]^{2-}$  is observed in the melts containing large amounts of Ti. The effect of the outer coordination sphere of titanium complexes on the structure and dynamics (i.e., Ti-F bond strength, formation of the polyatomic fluorotitanate complexes, diffusion coefficients, etc.) of the studied melts is investigated.



**Figure 1.** Combined distribution function for the  $[\text{TiF}_6]^{2-}$  complexes in the  $\text{TiF}_4$ -NaF melt at  $T=1323\text{K}$ . The mole fraction of  $\text{TiF}_4$  is 0.05

# SUPERCAPACITOR ELECTRODE MATERIALS OBTAINED BY MICROWAVE CARBONIZATION OF COTTON WASTE

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The study focuses on the electrochemical properties of double-layer electrochemical supercapacitor electrodes made from carbon materials produced through microwave carbonization of textile wastes (cotton fluff) and compares them to similar materials made through carbonization and activation in a laboratory-scale tubular furnace. Microwave carbonization and activation were carried out in two steps: during the first step, heating process took place in a flow of CO<sub>2</sub>, N<sub>2</sub> or Ar and during second step, activation was carried out in an air flow (total process duration is approximately 5 min). In the tubular furnace, carbonization was sequentially performed in an inert atmosphere during heating starting from room temperature to 900 °C at a rate of 15 °C/min and then material was activated in a CO<sub>2</sub> flow at a temperature of 900 °C (total process duration is approximately 80 min). The electrodes made from the carbon materials obtained were examined as part of a symmetrical supercapacitor using an electrolyte based on an aqueous 1 M KNO<sub>3</sub> solution. Cyclic voltammetry and galvanostatic charge-discharge techniques were used. At scan rates less than 20 mV/s, all carbon materials obtained through microwave carbonization had lower specific capacitance values (ranging from 70 to 80 F/g at 1 mV/s) than the material produced in the tubular furnace (about 90 F/g), however, at higher scan rates (100 mV/s), the capacitance was almost 1.5 times greater for the material obtained from the microwave process (48 F/g) compared to the material produced in the tubular furnace (29 F/g). Similar trends were observed in the galvanostatic charge-discharge results. Among these, carbon material produced in an atmosphere of CO<sub>2</sub> had the best characteristics, with a capacitance of 70 F/g at an applied current of 1 A/g.

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# DENSITY OF CHLORALUMINATE IONIC LIQUID BASED ON TRIETHYLAMINE HYDROCHLORIDE

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Non-flammability and environmentally friendly aluminum-ion batteries (AIB), with ultra-fast charging function, are a promising alternative to existing types of batteries. Chloroaluminate ionic liquid (IL) based on triethylamine hydrochloride ( $\text{Et}_3\text{NHCl}$ ) can be used as an electrolyte for AIB. An analysis of literature sources showed that the concentration and temperature dependences of density of this electrolyte has not been systematically studied. Although it is necessary for optimization of the specific electrical characteristics of the battery and calculation of the molar concentrations of ions present in the electrolyte.

Synthesis and density measurements of ILs were carried out in an argon field glovebox MBraun UniLab. Experimental values of electrolyte density were measured by the dilatometric method in the range of molar ratios of  $\text{AlCl}_3$  to  $\text{Et}_3\text{NHCl}$  (N) from 0.7 to 1.95 and temperatures from 0 to 100 °C. The temperature dependence of density is described by the equation  $\rho = a + bt$ , where  $t$  is temperature,  $a$  and  $b$  are constants. Table 1 presents the values of the molar ratios of IL components, density at 25 °C, equation constants, and the minimum measurement temperature caused by IL crystallization. Thus, the density values of chloroaluminate IL based on  $\text{Et}_3\text{NHCl}$  were obtained in a wide concentration and temperature range.

**Table 1**

| N    | $\rho^{t=25\text{ }^\circ\text{C}}, \text{g}\cdot\text{cm}^{-3}$ | $a, \text{g}\cdot\text{cm}^{-3}$ | $-10^4\cdot b, \text{g}\cdot\text{cm}^{-3}\cdot^\circ\text{C}^{-1}$ | $t_{\text{min}}, ^\circ\text{C}$ |
|------|--|----------------------------------|---|----------------------------------|
| 0.7  | 1.150  | 1.167                            | 6.912   | 23                               |
| 0.8  | —  | 1.187                            | 6.854   | 32                               |
| 0.9  | —  | 1.206                            | 7.291   | 43                               |
| 1.0  | —  | 1.222                            | 7.092   | 66                               |
| 1.3  | —  | 1.257                            | 6.927   | 34                               |
| 1.5  | 1.262  | 1.281                            | 7.465   | 0                                |
| 1.7  | 1.289  | 1.310                            | 8.516   | 0                                |
| 1.95 | 1.315  | 1.337                            | 8.615   | 0                                |

*The study was supported by a grant from the Russian Science Foundation and the Government of the Sverdlovsk region № 24-23-20046, <https://rscf.ru/project/24-23-20046/>*

# ELECTROCHEMICAL AND STRUCTURAL CHARACTERISTICS OF THE NEGATIVE ELECTRODE OF A LEAD-ACID BATTERY WITH CARBON ADDITIVES

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The introduction of carbon additives into the active mass of the negative electrode of a lead-acid battery (LAB) significantly delays the sulfation of the negative plates when the battery is operated in the mode of constant undercharging and high-speed charging.

A current direction for solving the problem of irreversible sulfation of negative active mass is the search for additives to the active mass, in particular, additives of various types of carbon. In this regard, the purpose of This work was to study the mechanism of the influence of carbon additives with different structures on the electrochemical properties of the negative electrode. The following forms of carbon were selected as carbon materials: crystalline graphite, amorphous carbon product, expanded graphite and its modifications by treatment with ozone and dimethylformamide, carbon nanotubes, graphene.

Testing of the studied electrodes was carried out in lead-acid cells with one negative and two positive electrodes under study. The tests were carried out in two stages: the first stage included 10 cycles of alternating charge and discharge, the second – cycling, which simulates the high-speed partially charged state (HRPSoC) of the batteries. After cycling, the cells were disassembled and the surface morphology of the negative electrodes was studied using SEM and their porous structure using contact reference porosimetry.

Tests of battery prototypes have shown that the addition of carbon nanotubes and expanded graphite treated with dimethylformamide increases the capacity of the negative electrode and reduces the rate of degradation of the negative active mass.

# DETERMINATION OF PARTITION COEFFICIENTS OF LIPOFILIC ELECTROLYTES BETWEEN WATER AND PLASTICIZED PVC MEMBRANE

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Single-ion partition coefficients introduced by Eisenman depend on standard Gibbs energy of ion transfer from one phase to another. They demonstrate the ion affinity for one of the phases under consideration. Single-ion partition coefficients are widely used to describe the response of ion-selective electrodes and optodes, for instance, sensors with membranes, containing moderately lipophilic organic electrolytes. Addition of those electrolytes into optode<sup>1</sup> or electrode<sup>2</sup> composition allows to stabilize the phase boundary potential and opens up an opportunity to create optical sensors with single ionic activity response and reference electrodes without liquid junction. Knowledge of partition coefficients helps to create sensors with required properties and makes it possible to control their analytical characteristics. However there is few data on electrolyte partition between water and plasticized PVC membranes in the literature.

The main approaches proposed for determination of the standard Gibbs energies of transfer are based on potentiometric and voltammetric measurements as well as distribution of substance between phases. Our research deals with the latter.

Equilibrium concentrations of the examined ions in an aqueous phase and in plasticized PVC membranes were determined using spectrophotometry in ultraviolet and visible regions. The obtained data was used to calculate the partition coefficients of practically significant ions. For example, the obtained value of the partition coefficient for the tetraphenylborate ion is  $\lg k = 4.98 \pm 0.14$ , which is close to  $\lg k = 5.37$  determined for a similar system<sup>3</sup>.

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# ELECTRICAL DOUBLE LAYER AT THE Sn/ PROPYLENE CARBONATE INTERFACE

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The new results on the capacitance of the electrical double layer (EDL) obtained on the Sn electrode renewed *in situ* in propylene carbonate solutions (PC) of a surface-inactive electrolyte (TBAClO<sub>4</sub>) are demonstrated. The interest in this system is associated with the fact that tin is a promising component for thin-film electrodes of lithium-ion batteries. On the other hand, the comparison of our new results with the published data makes it possible to understand better the position of the Sn electrode in the series of mercury-like metals as regards their interaction with solvent molecules.

Using the methods of cyclic voltammetry and impedance spectroscopy, the potential region is found in which the Sn electrode can be considered as ideally polarizable in these solutions. It is shown that the capacitance curves (dependences of the EDL capacitance  $C$  on the potential  $E$ ) in the region of ideal polarizability demonstrate a characteristic minimum which deepens with electrolyte dilution. The capacitance curves are analyzed within the framework of the classical theory of the EDL. It is shown that the position of the minimum at the potential of  $-0.39 \pm 0.02$  V (vs. aqueous saturated calomel electrode) corresponds to the maximum diffusivity of the EDL at the potential of zero charge.

Our results and published data are analyzed using the correlational relationships between the zero charge potentials ( $E_{\sigma=0}$ ) of Hg and Sn electrodes in solutions of surface-inactive electrolytes in PC, acetonitrile (AN), and water, on the one hand, and the electron work functions of these metals ( $W_{\phi}$ ), on the other hand. It is shown that the chemisorption interaction of Sn with solvent dipoles increases in the series: AN < PC < H<sub>2</sub>O.

The obtained data make it possible to conclude that the Sn electrode is characterized by the very weak (close to the Hg electrode) interaction with PC molecules in a wide potential region. From the point of view of practice, this result may prove to be interesting and helpful when developing Li- and/or Na-ion batteries.

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# STRUCTURE OF CHARGED INTERPHASE ON A RENEWABLE LEAD ELECTRODE IN PROPYLENE CARBONATE SOLUTIONS

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This paper presents the results of in situ measuring the capacitance of the electrical double layer (EDL) on a mechanically renewable Pb electrode in solutions of tetrabutylammonium (TBA) salts with a surface inactive anion ( $\text{ClO}_4^-$ ) in propylene carbonate (PC).

Our interest to this system is partly connected with the following fact: according to the literature, Pb is a promising component of various nanocomposite anodes in lithium- and sodium-ion batteries as an alternative to graphite and solid carbon materials with prospects of providing higher capacitance and higher energy density at a lower cost. Lead was also considered as a dopant for cathodes with good performance characteristics.

By using the methods of cyclic voltammetry (CVA) and impedance spectroscopy, the potential region in which Pb electrode can be considered as ideally polarizable in these solutions is found. It is found that the capacitance curves (dependences of the EDL capacitance  $C$  on the potential  $E$ ) in the region of ideal polarizability demonstrate a characteristic minimum deepening with electrolyte dilution. The capacitance curves are analyzed within the framework of the classical theory of the EDL. It is shown that the position of the minimum at the potential of  $0.61 \pm 0.02$  V (vs. aqueous saturated calomel electrode) corresponds to the maximum diffusivity of the EDL at the potential of zero charge (PZC).

The results and published data were analyzed using the correlation relationships between the zero charge potentials ( $E_{\sigma=0}$ ) of Hg-, Pb-, Sn-, and Ga- electrodes in solutions of surface-inactive electrolytes in PC, acetonitrile, and water on the one hand, and the electron work functions of these metals ( $W_\phi$ ), on the other hand. It was concluded that Pb electrodes interacted weakly with the molecules of these solvents.

*This work was supported by the Program of Development for the M. V. Lomonosov Moscow State University, topic no. AAAA-A21-121011590088-4.*

# TEMPLATED ELECTRODEPOSITION OF FREE-STANDING GOLD NANOROD ARRAYS FOR PHOTONICS APPLICATIONS

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Growing interest in hyperbolic metamaterials (HMMs) stems from their potential applications in optical and sensing devices<sup>1</sup>. Examples of such materials include arrays of gold nanostructures embedded in a dielectric matrix, which can be obtained by templated electrodeposition into porous aluminium oxide (AAO) films. This method is relatively easy to implement and provides highly reproducible results. The goal of This work was to fabricate arrays of gold nanostructures and investigate their optical properties in different media. Porous templates with a thickness of 35  $\mu\text{m}$ , average pore diameter of 35 nm, and average distance between pores of 100 nm were prepared using anodic oxidation of aluminium oxide. Au nanowires arrays with different lengths ranging from 250 to 1260 nm were fabricated using templated electrodeposition. After partial dissolution of AAO in 30 mM sodium hydroxide solution and filling the remaining space with water, ethanol, glycerin, or nematic 5CB crystalline liquids, the optical properties of the HMMs were studied. The spectral minimum of transmitted light corresponding to plasmon resonance excitation in the longitudinal direction (ENZ) shifts towards longer wavelengths by approximately 15 nm as the length of gold nanostructures increases from 435 nm to 1260 nm. Additionally, the position of ENZ shifts towards longer wavelengths at a rate of approximately 86 nm/RIU change in the refractive index of the surrounding medium. The results indicate that these smart materials with controllable properties have significant potential.

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# MEMBRANE ACTIVITY OF THE HUMAN IMMUNODEFICIENCY VIRUS GAG POLYPROTEIN

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Human immunodeficiency virus (HIV) is a dangerous pathogen that causes acquired immunodeficiency syndrome (AIDS). The Gag polyprotein is the major structural protein of HIV responsible for the assembly and budding of progeny virions from the plasma membrane of the infected cell<sup>1</sup>. Thus, protein-lipid interactions play a key role in the process of viral replication.

It is generally accepted that Gag specifically binds to anionic lipids on the cytoplasmic side of the cell membrane<sup>2</sup>. However, the question about the contribution of electrostatic and hydrophobic forces to these interactions remains poorly addressed. To answer this question, we studied the adsorption process of the HIV Gag polyprotein on model bilayer lipid membranes (BLMs). One of the ways to record the electrostatic effects caused by the adsorption of molecules on the surface of a BLM is to measure the difference of the boundary potentials on the BLM by the inner field compensation (IFC) method<sup>3</sup>. Using the IFC method, we obtained adsorption isotherms and determined the thermodynamic binding constants of Gag to membranes of different lipid compositions.

The budding stage of viral particles from the surface of an infected cell is associated with the formation of curved regions on the membrane. Using a model system of lipid nanotubes pulled from BLMs<sup>4</sup>, we established a previously undescribed physicochemical mechanism for the generation of membrane curvature. The HIV Gag polyprotein can alter the lateral tension of the lipid bilayer to generate membrane curvature for budding.

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# FORMATION OF COBALT-CONTAINING NANOSTRUCTURED SURFACES ON GLASS-CARBON ELECTRODES

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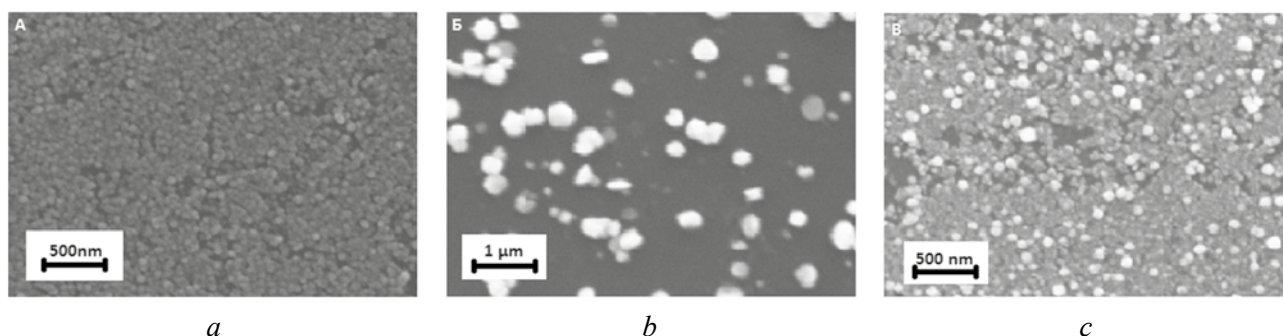
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One of the effective methods for electrochemical conversion of CO<sub>2</sub> is the use of electrodes modified with nano-catalysts.<sup>1</sup> We have investigated the surface of a glassy carbon electrode, which was modified with Co-containing nano-structures, using scanning electron microscopy.

Nanostructured surfaces of glassy carbon electrodes were obtained by electrochemical deposition from a solution of the PG-NaCo 20% complex with a controlled potential of -1.5 V.

One could argue that Co-containing structures have been successfully formed in the form of nanoparticles with average sizes of (a) 50 nm, (b) 200 nm and (c) 250 nm based on the presented SEM images (Fig. 1).



**Figure 1.** SEM images of the surfaces of glassy carbon electrodes after electrolysis in the presence of PG-NaCo 20% for (a) 1 hour, (b) 2.5 hours, (c) 4 hours

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*The work was carried out within the framework of a state assignment of the Federal Research Center “Kazan Scientific Center of the Russian Academy of Sciences”.*

# THE INHIBITORY PROPERTIES OF THE BOILING EXTRACTS FROM DIFFERENT PLANTS ON THE CORROSION OF STEEL EN Fe37-3FN IN ACIDIC ENVIRONMENTS

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Recently, many studies have appeared in the literature showing that compounds extracted from plant materials can slow down metal corrosion in aqueous environments. The use of natural compounds reduces the cost of dedicated synthesis of corrosion inhibitors, and therefore, this topic is of interest.

In the present work the boiling extracts from the aerial parts of lemon balm (*Melissa officinalis*), the beans of common bean (*Phaseolus vulgaris*) and fava bean (*Vicia faba*), the flowers of common lilac (*Syringa vulgaris*) and wild apple (*Malus sylvestris*), the aerial parts of common knotgrass (*Polygonum aviculare*) and white goosefoot (*Chenopodium album*), the fruits of rowan berry (*Sorbus aucuparia*), red elderberry (*Sambucus racemosa*), guelder rose (*Viburnum opulus*), bird cherry (*Prunus padus*), chokeberry (*Aronia melanocarpa*), common barberry (*Berberis vulgaris*), silverberry (*Elaeagnus commutata*), common hawthorn (*Crataegus laevigata*), the grains of common buckwheat (*Fagopyrum esculentum*), and the leaves of silver birch (*Betula pendula*), rowan berry (*Sorbus aucuparia*) and European purple beech (*Fagus sylvatica purpurea*).

The obtained extracts were tested as a potential inhibitor for the corrosion of mild steel EN Fe37-3FN both in 0.5 M hydrochloric acid, in 0.5 sulphuric acid, and in 0.5 nitric acid solutions with the different additions of the inhibitors. The studies include the weight loss measurements, the open circuit potential measurements, the potentiodynamic polarisation with estimation of the polarization resistance, Tafel slopes and corrosion current densities, and the recording of electrochemical impedance spectra. The sorption of the compound on the steel surface follows the Langmuir adsorption isotherm, and the nature of adsorption is physical due to the electrostatic interactions.

*This work was funded within the framework of the state assignment of the Ministry of science and higher education of Russian Federation, project registry number 1023041400091-5-3.2.10;2.4.2.*

# CONDUCTIVE AND DIFFUSION PROPERTIES OF THE MF-4SK PERFLUORINATED MEMBRANE IN THE PROCESS OF ITS MODIFICATION WITH ZIRCONIUM PHOSPHATE

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Perfluorinated membranes are commonly modified by inorganic hydrophilic or proton-conducting compounds to maintain high proton conductivity of the membrane, when it is used as a polymer electrolyte in a hydrogen-air fuel cell. During *in situ* modification, the polymer is treated with water-organic mixtures to increase the pore space for the dopant intercalation.

The purpose of this work is studying the physical-chemical and transport properties of the MF-4SK perfluorsulfonic sulfonic acid membrane (Plastpolymer JSC, St. Petersburg, Russia) in the process of its modification by zirconium phosphate (ZrP).

Modification with ZrP was carried out *in situ* by saturating the membrane with a solution of precursor (zirconyl chloride) followed by precipitation by phosphoric acid treatment. The membrane was pretreated by water-alcohol mixture during heating. The diffusion permeability and specific conductivity of the membrane after its treatment in working solutions and after dopant intercalation are studied. Treatment with working solutions leads to a significant increase in the transport properties of the membrane, which decrease after precipitation of the dopant, but retain higher values compared to the initial membrane. The discovered effect is due to an increase in the volume fraction of the internal equilibrium solution in the membrane after treatment in working solutions, which also leads to an increase in the conductivity of the gel phase due to the growth of the mobility of counterions in it. These effects are confirmed by the growth in the thickness and water content of the membranes after keeping the samples in the water-alcohol mixture, the values of which decrease after the ZrP intercalation. It is concluded that the key influence of the operation of treatment with working solutions during *in situ* modifying the perfluorinated membrane, and not the dopant intercalation.

*The study was supported by a grant from the Russian Science Foundation and the Kuban Science Foundation No. 22-19-20101, <https://rscf.ru/project/22-19-20101/>*

# GAS PERMEABILITY OF MODIFIED PERFLUORINATED MEMBRANES WHEN OPERATING IN A HYDROGEN-AIR FUEL CELL

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To increase the proton conductivity and mechanical strength of perfluorinated membranes, they are modified with hydrophilic particles. However, this may lead to an increase in the negative hydrogen crossover when operating in a hydrogen-air fuel cell (FC). The purpose of This work was to study the effect of modifying the MF-4SK membrane with zirconium phosphate (ZrP) and the inert fluoropolymer F-26 (vinylidene fluoride-co-hexafluoropropylene) on the power characteristics of a hydrogen-air FC. The gas permeability of the membranes was assessed based on the hydrogen crossover current measured by cyclic voltammetry and potential step regimes<sup>1</sup>.

It is established that the amount of F-26 inert polymer in the MF-4SK membrane should not exceed 10%. This leads to a decrease in the hydrogen crossover current and allows an increase in maximum power density by 15%. When a membrane is modified with ZrP, its gas permeability increases compared to the original membrane of the same thickness. However, in this case, there is an increase in efficiency of FC due to the higher electrical conductivity of the membrane at low humidity, which prevails over the negative factor of increasing the gas permeability of the membrane<sup>2</sup>. The optimal ZrP content in the membrane is 6%, because the surface power density increases by almost 30% compared to the non-modified membrane, and the hydrogen crossover current is minimal. Of greatest interest are samples containing both an inert fluoropolymer and ZHP and combining the advantages of both modifiers.

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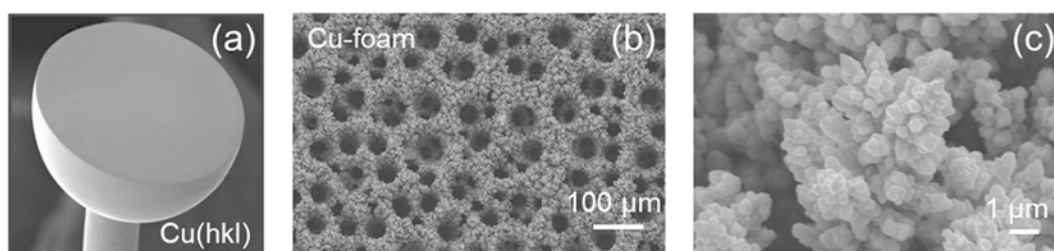
The work was financially supported by the Russian Science Foundation and the Kuban Science Foundation No. 22-19-20101, <https://rscf.ru/project/22-19-20101>

# SURFACE CHARACTERIZATION OF SINGLE-CRYSTALLINE AND DISPERSED COPPER ELECTROCATALYSTS UNDER ALKALINE CONDITIONS

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In recent years, interest in copper-based materials was increased due to the catalytic activity of Cu in the electrochemical conversion of nitrate anions to ammonia and CO<sub>2</sub> to C<sub>1</sub>-C<sub>3</sub> hydrocarbons and alcohols.<sup>1</sup> The structural effect of Cu catalysts on their activity in CO<sub>2</sub> electroreduction and on conversion selectivity has been intensively studied. Previously, Hori et al. demonstrated the structural sensitivity of the CO<sub>2</sub> reduction reaction using single-crystalline Cu(hkl) electrodes with well-structured surfaces. Rational design of dispersed Cu catalysts can be based on the voltammetric characterization of the electrodes in alkaline solutions. In these media, the voltammetric response is determined by the presence of adsorption sites of a certain geometry on the catalyst surface and allows extracting important structural information. This work compares voltammetric data for model Cu(hkl) surfaces and synthesized dispersed Cu catalysts (Fig. 1). Furthermore, we provide estimates of the electrochemically active surface area of dispersed catalysts based on capacitance values and on the charges of lead underpotential deposition.



**Figure 1.** SEM-images of (a) a Cu(hkl) electrode and (b, c) Cu foam

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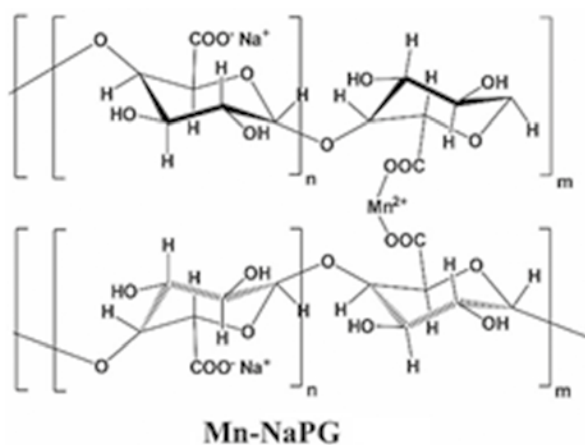
# ELECTROCHEMICAL OXYGEN REDUCTION REACTION CATALYZED BY THE MANGANESE COMPLEXES OF SODIUM PECTATE: STRUCTURAL AND MORPHOLOGICAL ASPECTS

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Manganese complexes of sodium pectate have been studied as electrocatalysts for the oxygen reduction reaction. The synthesis of Mn-NaPG complexes was carried out by analogy with the known method<sup>1</sup>.



In a series of Mn(n%)-NaPG catalysts with varying degrees of substitution of Na with manganese (from 5% to 25%), the dependence of electrochemical activity and stability on morphology and structure was studied. The morphology of film structures formed when these catalysts are applied from a liquid phase to a solid surface was studied by atomic force microscopy. The structure, size and distribution of metal ions within the sodium pectate polymer matrix were studied using a transmission electron microscope. A more branched film structure and a uniform distribution of metal particles corresponds to Mn(25%)-NaPG, which manifests itself in the form of the best electrocatalytic properties.

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# ELECTROPORATION OF LIPID MEMBRANES: A NEW PERSPECTIVE

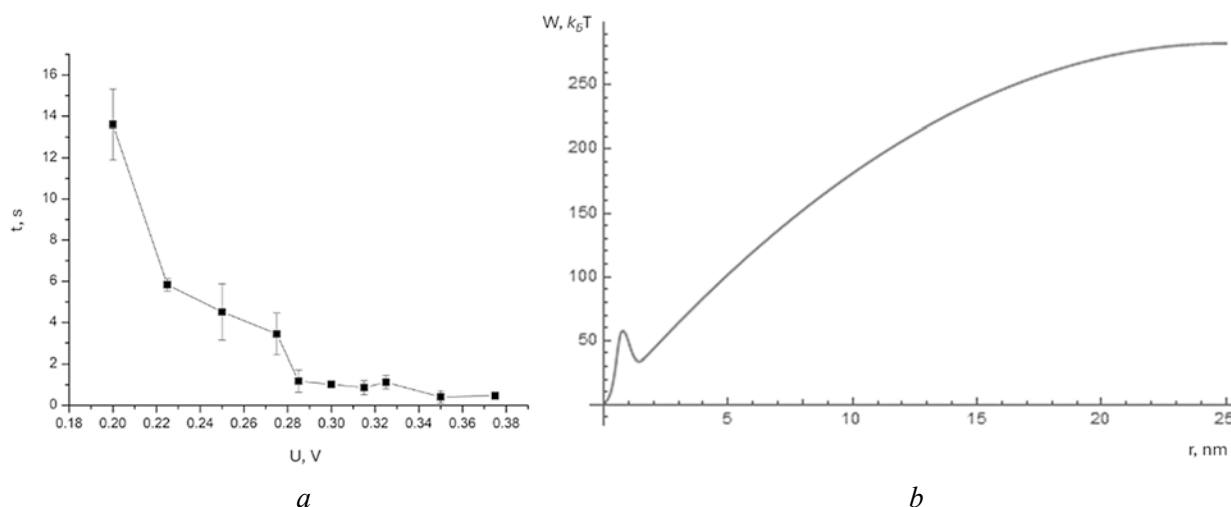
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In this work we investigated the process of electroporation of bilayer lipid membranes of various compositions. The results of experiments<sup>1</sup> showed that the dependence of the membrane lifetime on the applied potential difference for a number of lipid compositions has an inflection/break region, which cannot be described within the framework of the classical theory of electroporation<sup>2</sup>. Such conclusions are consistent with modern theoretical models of the formation of pores in lipid membranes, which take into account the structure and elastic characteristics of the lipid bilayer, as well as the dependence of the pore energy on the lateral tension of the membrane and the applied external electric field<sup>3</sup>.

In addition, we showed that the model function corresponding to the theoretically predicted pore energy profile can approximate the experimentally observed dependences (Fig. 1). These results confirm the hypothesis that there are two energy barriers along the pore formation trajectory, which requires modification of the classical theory of electroporation.



**Figure 1.** (a) The dependence of the lifetime of dioleoylphosphatidylcholine (DOPC) membranes on the applied voltage. (b) Possible form of the energy profile of pore formation for a DOPC membrane within the framework of the two-energy barrier model

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# TRANSPORT CHARACTERISTICS OF ELECTROCHEMICAL MATERIALS $(\text{La},\text{Sr})(\text{Fe},\text{Ga})\text{O}_{3-\delta}$ FOR SYMMETRICAL ELECTROCHEMICAL DEVICES

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The symmetrical design of solid oxide fuel cells and electrolyzers is attracting increasing attention from researchers. The identical chemical and structural composition of the electrode layers, in conjunction with the absence of anode reduction, allows for a significant reduction in economic costs associated with the production and operation of electrochemical cells. One potential avenue for further developing the strengths of symmetrical design is to bring the chemical composition of the electrodes and electrolyte closer together. This should result in a reduction in the occurrence of undesirable cation diffusion and chemical material interaction processes. In the present work, a series of electrode compositions based on  $\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_{3-\delta}$  with partial substitution of iron by gallium cations have been prepared. This brings the composition closer to that of the highly conductive electrolyte  $(\text{La},\text{Sr})(\text{Ga},\text{Fe},\text{Mg})\text{O}_{3-\delta}$ .

The  $\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_{1-x}\text{Ga}_x\text{O}_{3-\delta}$  materials, where  $x=0.0; 0.1; 0.2$  and  $0.3$  (LSF; LSFG-0.1; LSFG-0.2 and LSFG-0.3, respectively) exhibited a single perovskite-type structure. The results demonstrate that as the level of iron sublattice doping increases, the conductivity decreases across the entire temperature range investigated, both in air and at  $p\text{O}_2 = 10^{-20}$  atm. The investigation into the correlation between conductivity and  $p\text{O}_2$  at temperatures of 700–800 °C revealed that all samples exhibited a pronounced decline in conductivity within the low  $p\text{O}_2$  region.

Phase stability studies were conducted in a humid hydrogen atmosphere at a temperature of 700 °C. It was demonstrated that the incorporation of gallium into the iron sublattice markedly enhances the oxides' resistance to reduction. The electrochemical performance of the LSFG-0.1 electrode material is a little lower than that of the LSF. However, it displays enhanced stability in reducing atmospheres, which makes it a potential candidate for utilization in a symmetrical fuel cells.

*The research was made possible by a grant from the Russian Science Foundation (grant number 24-19-00040), <https://rscf.ru/project/24-19-00040/>.*

# TRANSPORT PROPERTIES OF NICKEL-DOPED BARIUM-PRASEODYMIUM FERRITE ELECTRODE MATERIALS

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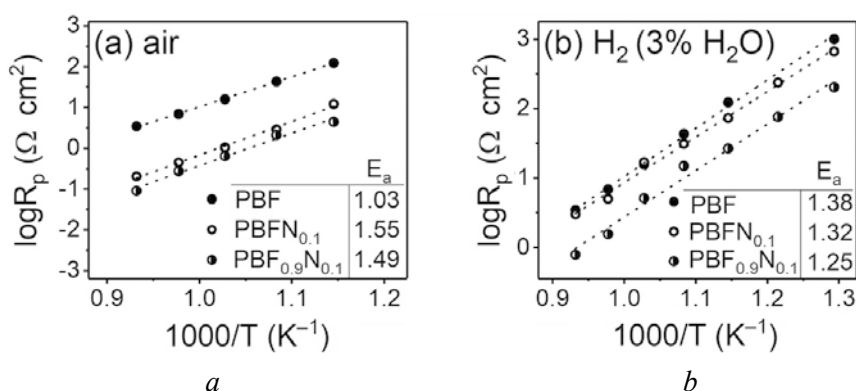
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One of the promising directions in the field of solid oxide fuel cells is the study of materials suitable for simultaneous use as oxygen and fuel electrodes (so-called quasi-symmetric electrodes). For the successful application of such materials as symmetrical electrodes, it is necessary that they exhibit desirable properties, such as phase stability, electrical conductivity, and electrochemical activity in both oxidizing and reducing atmospheres. This study focuses on evaluating the electrochemical performance of nickel-doped praseodymium- barium ferrite electrodes.

The  $\text{Pr}_{0.6}\text{Ba}_{0.4}\text{FeNi}_y\text{O}_{3-\delta}$  ( $y=0,0.1$ ) powders were prepared by the standard citrate-nitrate method. All samples were found to be single phase by X-ray diffraction analysis. The electrode inks were prepared by mixing the powder in isopropyl alcohol medium along with organic binder. Each ink was applied to the surface of a proton-conducting electrolyte  $\text{BaCe}_{0.5}\text{Zr}_{0.3}\text{Y}_{0.1}\text{Yb}_{0.1}\text{O}_{3-\delta}$  (BCZYYb) and the resulting symmetrical cells were sintered at 1100 °C for 2 h.

It was found that the Ni-doping reduces the polarization resistance values of the basic ferrite by  $\sim 3$  times (Fig. 1, *a, b*) for both air (*a*) and wet hydrogen (*b*) atmospheres.



**Figure 1.** Electrode polarization resistances depending on temperature in air (*a*) and wet hydrogen (*b*) atmospheres

# FORMATION AND CATHODIC REDUCTION OF ZINC, NICKEL(II) AND COBALT(II) COMPLEXES IN SOLUTIONS OF TAURINE

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The electrodeposition of a metal coating (zinc, cadmium, tin) is known to be normally used blocking out corrosion of steelwork. A promising way to enhance corrosion resistance of the protective coating is alloying its material with an iron subgroup metal (Fe, Co, Ni).

Using methods of cyclic voltammetry, potentiometry and calorimetry we have studied some equilibria of acid-base interaction and complex formation for taurine and cations of zinc(II), nickel(II) and cobalt(II) in aqueous solutions. The thermodynamic parameters ( $\lg K$ ,  $\Delta G$ ,  $\Delta H$ ,  $\Delta S$ ) of the reactions investigated have been evaluated at 298.15K and ionic strength values of 0.3–1.5 mole/l<sup>1-3</sup>.

The electrodeposition of zinc, nickel, cobalt and alloys of these metals have been examined by cyclic voltammetry and polarization curve measurements in order to galvanize a 08KP steel. The results were compared with the corresponding data for electrolytes containing some useful carboxylates, aminoalcohols, aminoacids and complexones investigated earlier<sup>2-5</sup>. A complex approach to the research of the solution equilibria and electrode processes allowed us to optimize the electrolytic bath compositions and electrolysis conditions. New promising electrolytes have been suggested for plating with alloys of Zn–Ni–Co, Zn–Ni and Zn–Co. The deposits obtained had excellent tribometric and anticorrosion characteristics.

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# ESTIMATION OF ELECTRONIC PARAMETERS OF Ag(I) OXIDE FROM THE IMPEDANCEMETRY OF Ag-Pd SYSTEM ALLOYS

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Silver oxides are widely used in the field of microelectronics and photoelectrocatalysis, in the production of solar cells and various kinds of sensors. The scope of application is determined by the structure-dependent properties of the oxides. As a rule, anodic oxidation of metals or alloys makes it possible to obtain oxide films with a set of properties, depending on the oxidation mode and the composition of the solution and the substrate.

The purpose of this work is the impedancemetric investigation of the electronic parameters of Ag(I) oxide anodically formed in 0.1 M KOH on alloys of the Ag-Pd system with an atomic fraction of palladium from 0.05 to 0.20.

The chemical composition of the alloys (Table 1) was determined from energy-dispersive X-ray analysis performed on a JSM-6380LV JEOL scanning electron microscope with an INCA 250 microanalysis system. Based on the results of X-ray diffractometry (ARL X'TRA, Thermo Scientific; Switzerland), it was established that the structure of all the studied alloys is represented by the alpha phase.

The impedance of the interface between the electrode and the solution was measured in a stepwise polarization mode (5 mV step, 5 s dwell time) at a constant alternating current signal frequency of 999 Hz.

The concentration of donor defects  $N_D$ , calculated from the dependence of the inverse square of the capacitance on the potential, increases with increasing palladium concentration. The flat band potential  $E_{fb}$  varies within the experimental error.

**Table 1.** Alloys composition, flat band potential  $E_{fb}$  and concentration of donor defects  $N_D$  in Ag(I) oxides

| Atomic fractions of components |                  | Electronic parameters of Ag(I) oxide |   |
|--------------------------------|------------------|--------------------------------------|---|
| $X_{Pd}$ , at. %               | $X_{Ag}$ , at. % | $E_{fb}$ , V                         | $N_D \cdot 10^{-18}$ , cm <sup>-3</sup> |
| 5.01 ± 0.01                    | 94.99 ± 1.59     | 0.60 ± 0.03                          | 4.9 ± 0.1                               |
| 9.81 ± 0.03                    | 90.19 ± 1.52     | 0.65 ± 0.03                          | 5.1 ± 0.1                               |
| 15.67 ± 0.05                   | 84.33 ± 1.23     | 0.65 ± 0.02                          | 11.7 ± 0.6                              |
| 20.51 ± 0.08                   | 79.50 ± 1.02     | 0.62 ± 0.02                          | 30.0 ± 0.7                              |

*The work was carried out with the financial support of the Ministry of Science and Higher Education of the Russian Federation within the framework of the state assignment to universities in the field of scientific activity for 2023–2025, project No. FZGU-2023-0006.*

# ELECTROCHEMICAL PROPERTIES OF REDOX-ACTIVE POLYMERS AND NANOGELS AND FOR REDOX FLOW BATTERY APPLICATIONS

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Flow batteries are one of the promising stationary energy storage systems. The use of low-molecular electroactive reagents in them requires expensive ion-exchange membranes to prevent crossover. Transition to polymer reagents with “grafted” redox-active groups can significantly reduce the requirements for membrane materials.<sup>1</sup>

In this work, it is proposed to use weakly cross-linked polymer nanogels based on poly-N-isopropylacrylamide (PNIPA) modified with redox-active groups of 4-(3-carboxypropanamido)-TEMPO as reagents in redox flow batteries. Nanogel solutions have lower viscosity than solutions of linear polymers, but the electrochemical properties of such objects have not been comprehensively studied.

Using cyclic voltammetry on stationary and rotating electrodes and impedance spectroscopy, parameters of nanogels such as diffusion coefficient and effective concentration of redox active centers, as well as the rate of electron transfer to the redox active group, were determined. The results obtained for nanogels were compared with the properties of linear polymers of similar composition.<sup>2</sup>

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*The work was carried out with the financial support of the Russian Science Foundation, project 22-13-00115.*

# ELECTROCHEMICAL SYNTHESIS OF HYBRID MATERIALS BASED ON CHITOSAN COMPLEXES AND THEIR APPLICATIONS AS ELECTROCATALYSTS FOR GLYCEROL OXIDATION

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One of the important products of biomass processing, along with glucose, furfural and 5-hydroxymethylfurfural, should be considered glycerin, which belongs to trihydric alcohols and is a by-product in the production of biofuel<sup>1</sup>.

Among the methods of glycerol oxidation, the electrocatalytic method should be considered the most promising, which is flexible of control and is characterized by both high productivity and low cost. At the same time, along with gold-containing and non-platinum metal electrocatalysts for the oxidation of glycerol, hybrid organic-inorganic materials are increasingly being developed<sup>2</sup>.

The purpose of this work is the synthesis of hybrid materials based on complexes of chitosan with oxygen-containing compounds of cobalt and nickel and the study of their electrochemical properties.

The catalytic properties of the hybrid materials were studied in a 0.1 M solution of NaOH + 0.1 M glycerol. For this purpose, a potentiostat-galvanostat SmartStat PS-50 and Autolab PGSTAT100N were used. A mercury-oxide electrode was used as a reference electrode, and a platinum plate was used as an auxiliary electrode.

The study showed that the onset of oxidation coincides in potential with 60%Ni/KB600, while the current increase begins from a potential of 1.1 V vs. RHE, and for the hybrid material it has a sharper rise than for the commercial nickel catalyst 60%Ni/KB600, which indicates its rather high catalytic activity.

The authors thank the junior researcher at the Boreskov Institute of Catalysis SB RAS, A.N. Kuznetsov, for assistance in conducting research.

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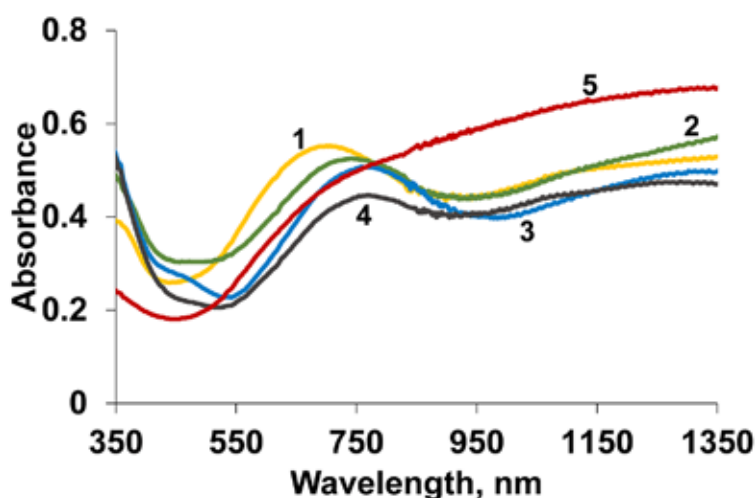
# ELECTRODEPOSITION OF COMPOSITE OF POLY-3,4-ETHYLENEDIOXYTHIOPHENE WITH FULLERENOL

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Poly-3,4-ethylenedioxythiophene (PEDOT) was electrochemically deposited in the presence of water-soluble fullerene modified with Na<sup>+</sup> ions and hydroxyl groups (fullerenol) at various fullerenol concentrations. During the electropolymerization process the electrochemical parameters and electronic absorption spectra were recorded. It was shown that fullerenol is included in the composition of the resulting PEDOT layers, independently of the concentration of fullerenol in the synthesis solution. In this case, it acts as a doping anion, compensating for the positive charges on the growing PEDOT chains.

The layers of PEDOT-fullerenol composites were studied by electron spectroscopy and spectroelectrochemistry in the UV-visible-near-IR regions, as well as by atomic force microscopy. It has been shown that with increasing fullerenol content in the synthesis solution, longer PEDOT chains are formed, which is evident from the bathochromic shift of the polaron absorption maximum (706 nm → 736 nm → 758 nm → 770 nm) (Fig. 1).



**Figure 1.** Electronic absorption spectra in air of PEDOT composite layers electrodeposited in aqueous solutions of fullerenol at 0.00017 M (1), 0.00034 M (2), 0.00067 M (3), 0.0014 M (4) concentrations and in 0.1 M aqueous solution of NaClO<sub>4</sub> (5)

The photoconductivity of the PEDOT-fullerenol composite layers in the near-IR spectral region has been demonstrated for the first time. The proposed mechanism of photoconductivity is associated with an increase in the concentration of charge carriers due to the transfer of a photoexcited electrons from PEDOT to the acceptor molecule of fullerenol.

*The work was carried out with the financial support of the Russian Science Foundation, project No. 23-19-00884.*

# INFLUENCE OF ELECTROLYTE COMPOSITION ON ELECTROCATALYTIC PROPERTIES OF CONDUCTIVE POLYMER MODIFIED WITH NITROXYL GROUPS

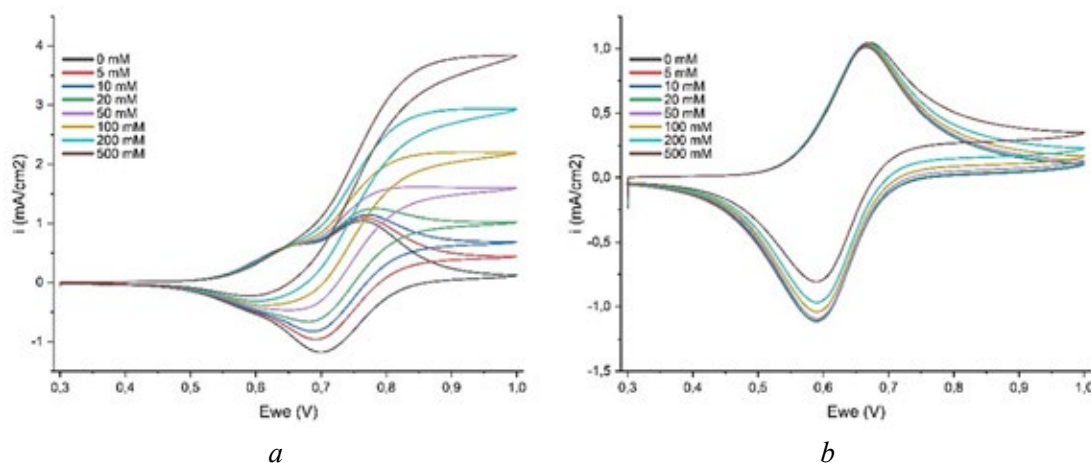
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This work comprises electrocatalytic properties of a polymer obtained by electropolymerisation of pyrrole modified with pendant 4-hydroxy-2,2,6,6-tetramethylpiperidin-N-oxyl (TEMPO) group.

Incorporated in the polymer TEMPO groups are capable of oxidizing alcohols. After the reaction TEMPO can be regenerated by electrochemical oxidation. Such catalytic cycle is described in the literature for the case of soluble nitroxides<sup>1</sup> as well as for immobilized species<sup>2</sup>.

It was found that electrochemical response of poly-TEMPO-pyrrole is strongly affected by the electrolyte composition (Fig. 1). Registered anodic current is strongly dependent on glucose concentration (Fig. 1, *a*), but becomes almost unchanged if NaClO<sub>4</sub> is present (Fig. 1, *b*)



**Figure 1.** CV of the poly-TEMPO-pyrrole at varied concentrations of glucose. Electrolyte composition: 200 mM phosphate buffer, pH=7.4 (*a*); 100 mM NaClO<sub>4</sub>, 100 mM phosphate buffer, pH=7.4 (*b*). Glucose concentration 0–500 mM. *v* = 50 mV/s

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# SEARCH FOR NEW POLYMER PRECURSORS FOR ORR ELECTROCATALYSTS

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Traditionally used oxygen reduction reaction (ORR) catalysts based on platinum group metals, despite their high efficiency, limit the commercialization of low-temperature fuel cells due to their high cost and low stability in alkaline electrolytes. Metal-free carbon materials are alternative materials for use as ORR electrocatalysts. One of the common approaches to the creation of such materials is pyrolysis of polymer precursors containing heteroatoms in their structure<sup>1</sup>.

Linear styrene homopolymer and its copolymer with 2-vinylpyridine were prepared by emulsion polymerization in an inert atmosphere, for this purpose monomers were dissolved in a mixture of toluene and water, after which sodium dodecyl sulphate and ammonium persulphate were added to the obtained mixture. Upon completion of the reaction, the polymers were dried and subjected to pyrolysis in argon atmosphere at 800 °C to obtain carbon materials. The catalytic activity of the obtained materials was investigated using the rotating disc ring electrode method. Cyclic voltammetry of glass-carbon electrode with a platinum ring was obtained in oxygen saturated solution of 0.1 M KOH at a potential sweep rate of 10 mV·s<sup>-1</sup>.

The obtained results of determination of catalytic activity show that the lowest ORR overvoltage is characteristic for the catalyst obtained by pyrolysis of nitrogen-containing polymer with vinylpyridine – the reaction onset potential on it is 781 mV, whereas on the catalyst from linear polymer the reaction onset potential has a value of 603 mV relative reversible hydrogen electrode. At the same time, the addition of pyridine increases the selectivity of the catalyst to the four-electron mechanism – a significant increase in the release of peroxide as a reaction intermediate is observed.

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# OBTAINING COATINGS OF INTERMETALLIC PHASES OF DYSPROSIUM AND NICKEL ON A NICKEL ELECTRODE IN A KCL-NACL-CSCL EUTECTIC MELT AT 823 K

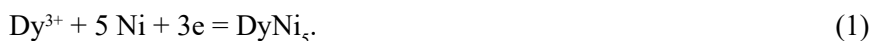
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In this work, the mechanism of joint electroreduction of dysprosium and nickel ions on an active nickel electrode in the eutectic melt KCl-NaCl-CsCl, at 823 K, was studied using electrochemical methods (cyclic voltammetry, square wave voltammetry, open-circuit chronopotentiometry).

With the combined content of  $\text{Dy}^{3+}$  and  $\text{Ni}^{2+}$  ions in the eutectic melt KCl-NaCl-CsCl, in the cyclic and square-wave voltammogram, open-circuit chronopotentiogram on the active nickel electrode, in addition to the processes of electroreduction of  $\text{Dy}^{3+}$  and  $\text{Ni}^{2+}$  ions to metal, waves were identified on which joint electroreduction of  $\text{Dy}^{3+}$  and  $\text{Ni}^{2+}$  ions occurs with the formation of intermetallic phases of dysprosium and nickel.

In this case, the phase with a high nickel content is formed first,  $\text{DyNi}_5$ , since the Gibbs free energy and the formation of this phase are the lowest among the intermetallic phases in the Dy-Ni system.



As the electrolysis potential in the cathode region or the electrolysis current density increases, the formation current of dysprosium metal increases, and intermetallic phases with a high content of dysprosium metal appear in the cathode product.



By potentiostatic electrolysis of a KCl-NaCl-CsCl melt containing various concentrations of  $\text{DyCl}_3$  and  $\text{NiCl}_2$  at potentials of  $-1.7$  V,  $-1.9$  V,  $-2.1$  V relative to the standard Ag/AgCl reference electrode at 823 K, coatings of  $\text{Dy}_x\text{Ni}_y$  intermetallic compounds of various compositions on a nickel electrode were obtained. XRD and SEM-EDS analyzes of cathode coatings show the formation of  $\text{DyNi}_5$ ,  $\text{DyNi}_3$ ,  $\text{DyNi}_2$  phases, respectively.

*The work was carried out with the financial support of the Russian Science Foundation, project 23-23-00360.*

# SYNTHESIS AND ELECTROCHEMICAL PROPERTIES OF VANADIUM OXIDE DOPED WITH ALUMINUM IONS AS CATHODES FOR AQUEOUS METAL-ION BATTERIES

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Vanadium oxide  $V_2O_5$ -based cathode materials with high theoretical capacity ( $589 \text{ mA} \cdot \text{h} \cdot \text{g}^{-1}$  for the two-electron process) and the ability to provide enhanced ion intercalation rates due to the layered structure are of considerable interest as high energy density materials. However, one of the problems affecting the performance of vanadium oxide-based cathode materials is their dissolution, resulting in unsatisfactory cycling performance. One of the ways to improve the stability of vanadium oxides is pre-doping them with foreign metal ions during synthesis.

In this work,  $Al^{3+}$ -doped vanadium oxides ( $Al_xV_2O_5$ ) with different aluminum content ( $x=0.05\text{--}0.07 \text{ at.}\%$ ) have been synthesized by hydrothermal method. The morphology and structure of the obtained compounds were characterized by SEM, XRD and XPS methods. It is shown that thin layers of  $Al_xV_2O_5$  are agglomerated in the form of “nanoflowers”. The presence of  $Al^{3+}$  in the layered structure of vanadium oxide  $Al_xV_2O_5$  was confirmed by EDS and XPS methods and the elemental ratios were evaluated. Quantitative analysis of Al content in the samples was performed by ICP-OES.

The electrochemical properties of the obtained cathode materials were studied in three-electrode cells and in CR2032 coin cells with zinc anode in aqueous solutions of  $3M \text{ ZnSO}_4$  by cyclic voltammetry and galvanostatic charge/discharge. It is shown that increasing the content of  $Al^{3+}$  ions ( $x=0.07 \text{ at.}\%$ ) leads to a decrease in discharge capacity ( $196 \text{ mA} \cdot \text{h} \cdot \text{g}^{-1}$  at  $0.05 \text{ A} \cdot \text{g}^{-1}$  compared to  $390 \text{ mA} \cdot \text{h} \cdot \text{g}^{-1}$  for low  $Al^{3+}$  contents ( $x=0.05 \text{ at.}\%$ )), but improved stability with a capacity retention of 92.8% after 300 cycles.

In addition, studies of  $Al_xV_2O_5$  cathode materials were conducted in magnesium-containing electrolyte solutions. The results of studies of the functional characteristics of the electrodes in different electrolyte compositions will be discussed.

*The work was supported by the Russian Science Foundation (grant № 24-23-00224).*

# EFFECT OF PH ON THE DESALINATION EFFICIENCY OF AMMONIUM NITRATE SOLUTION DURING ELECTRODIALYSIS

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The introduction of electrodialysis wastewater treatment at chemical enterprises is a promising option for improving production. The main by-product of the technology of nitrogen-containing mineral fertilizers is ammonium nitrate. Ammonium-containing solutions are characterized by a special behavior during electrodialysis, which is caused by protonation/deprotonation reactions involving ammonia when the pH of the solution changes during the process.

The purpose of the work is an experimental and theoretical study of the features of ammonium cation transfer through cation exchange membranes from ammonium nitrate solutions with different pH values during electrodialysis in under-limiting current modes.

The experiment was carried out in a seven-chamber electrodialyzer (Ralex AM(H)-PP, Ralex CM(H)-PP membranes, solution velocity 0.46 cm/s) for  $\text{NH}_4\text{NO}_3$  solutions with a concentration ( $\text{mol/dm}^3$ ): 0.015; 0.01; 0.001 in the pH range 4.8–7.8 at a relative current density  $i/i_{\text{lim}} = 0.8$ . Electromembrane ion transport was modeled for a system including a membrane and adjacent boundary diffusion layers, taking into account the hydrolysis of the electrolyte in solution and membrane. The non-linear effects of spatial charge were taken into account by the joint solution of the Nernst-Planck and Poisson equations in combination with additional ratios and boundary conditions establishing the physico-chemical properties of the cation exchange membrane and solution. The solution of the system of corresponding equations was found by the numerical finite element method (COMSOL Multiphysics).

It was found that with an increase in the pH of the initial solution, the degree of desalination decreases, and this is most noticeable during electrodialysis of more dilute solutions. This effect is associated with an increase in the fraction of  $\text{NH}_3$  in the system, both in the initial solution and inside the membrane, with an increase in the pH of the solution, which limits the transfer of ammonium through the cation exchange membrane. The experimental features are confirmed by numerical modeling of the transfer of ammonium and medium ions through a cation exchange membrane.

# ELECTROCHEMICAL PERFORMANCE OF $\text{Al}_2\text{O}_3$

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Nano dispersed metal oxide powders are widely used in various fields of modern industry as sorbents, catalysts, catalyst carriers<sup>1</sup>, polymer fillers, etc. Electrochemical synthesis is the most favored method for synthesizing dispersed metal oxides<sup>2</sup>.

In the present work the electrochemical behavior of aluminum under the action of alternating pulse current in chloride electrolytes with different cation composition ( $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{NH}_4^+$ ,  $\text{Ba}^{2+}$ ,  $\text{Sr}^{2+}$ ) is investigated for obtaining dispersed aluminum oxide powder. It was found that the rate of the process depends on the value of the AC pulse current density, on the cationic composition and concentration of the electrolyte. Thus, with the increase of the average density of alternating pulse current in the range of 0.5 to 3 A/cm<sup>2</sup> the rate of accumulation of aluminum dispersion products increased from 87 to 500 mg/cm<sup>2</sup>·h. The highest rate of accumulation of products of electrochemical dispersion of aluminum was observed in ammonium chloride electrolyte. Increasing the concentration of ammonium chloride in the electrolyte the accumulation rate increases by 100 mg/cm<sup>2</sup>·h. The result of electrochemical oxidation of aluminum by alternating pulse current is the formation of dispersed phase. The phase composition of the pulse electrolysis products was determined by X-ray phase and differential thermal analyses, which showed that the obtained samples corresponded to  $\text{Al}(\text{OH})_3$  or  $\text{AlOOH}$  phases depending on the cationic composition of the electrolyte. After annealing, freshly prepared  $\text{Al}(\text{OH})_3$  or  $\text{AlOOH}$  at 500 °C for 4 h, a nano dispersed phase of active  $\gamma\text{-Al}_2\text{O}_3$  is formed.

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*The work has been carried out with the financial support of the Russian Science Foundation, project 23-73-10108.*

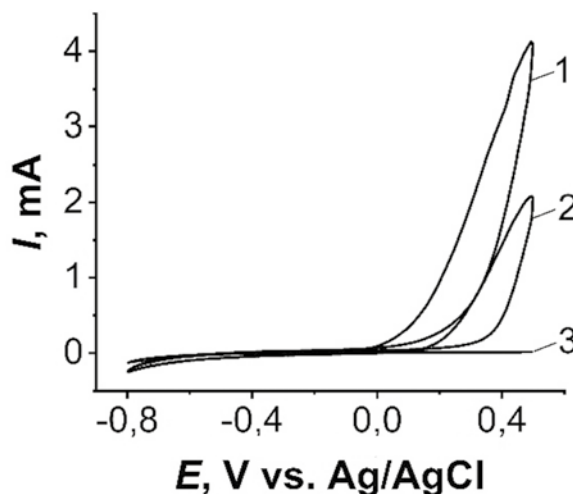
# ELECTROCHEMICAL NO<sub>2</sub> SENSOR BASED ON GLASS-CARBON/NiO ACTIVE SYSTEM

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Every year, industrial enterprises emit a large amount of harmful substances into the atmosphere, which include nitrogen oxides NO<sub>x</sub>, which pose a great danger to humans and the environment. Among nitrogen oxides, the most toxic is nitrogen dioxide NO<sub>2</sub>,<sup>1</sup> which even in small concentrations can lead to serious consequences. In this regard, timely detection of NO<sub>2</sub> is an important and mandatory task of our time. In this work, an electrochemical sensor based on a three-electrode cell with a liquid electrolyte is proposed for the detection of nitrogen dioxide. A glassy carbon electrode modified with nickel oxide (GC/NiO) is used as a working electrode. Cyclic voltammograms (CV) for GC/NiO recorded in N<sub>2</sub> and 50 ppm NO<sub>2</sub> are shown in Fig. 1.



**Figure 1.** CV curves for: GC/NiO in N<sub>2</sub> (1);  
GC/NiO in 50 ppm NO<sub>2</sub> (2); pure GC in 50 ppm NO<sub>2</sub> (3)

In the presence of NO<sub>2</sub>, a significant decrease in the anode current is observed (from 4 mA to 2 mA). This phenomenon indicates the high sensitivity of this sensor to the target gas.

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# EFFECT OF THICKNESS ON THE MEMBRANE CURRENT-VOLTAGE CURVES

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One of the main requirements for polymer materials for proton exchange membrane fuel cells is a high proton conductivity. It is depending on the membrane thickness<sup>1</sup>. Today the best properties for use as a proton exchange membrane are possessed by perfluorinated polymer systems, which include a number of commercial polymers: Nafion (DuPont, Wilmington, DE, USA), Flemion (Asahi Glass Co., Ltd., Japan), Aquivion (Solvay SA, Belgium), 3M (3M India Ltd., India), Fumion/Fumapem (FUMATECH BWT GmbH, Germany), and MF-4SK (JSC "Plastpolymer", Russia).

The aim of this work is to study of the current-voltage curve of the perfluorinated cation exchange MF-4SK membranes of various thickness to estimate the effect of their thickness on proton transport through membrane under its polarization by a direct current.

It is found that the limiting current density increases by almost in 50% with the reduction in membrane thickness from 300 to 60  $\mu\text{m}$  due to higher value of diffusion flux through thin membrane. The influence of membrane thickness on the slope of ohmic region is not observed, because the resistance of the diffusion boundary layer mainly contributes to the ohmic resistance of the system. However, the reduction of both limiting plateau length and slope of limiting region are observed at currents above the limiting one. In the case of thinner membrane, the ion flux through the membrane is higher in comparison with the membrane with higher thickness, which leads to the reduction of the electrical resistance of the membrane with increasing the current density<sup>2</sup>.

In general, the obtained results are in a good agreement with the concept, that efficiency of electromembrane processes increases with the decreasing thickness of the membrane.

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# SELECTIVE CONCENTRATION OF ELECTROLYTE SOLUTIONS USING BILAYER ION EXCHANGE MEMBRANES

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Electromembrane processes are widely used for the desalination of sea and salt waters, the concentration of dilute solutions, the production of acids and alkalis from solutions of the corresponding salts, etc. An important task is the processing of wastewater, concentration of solutions to extract valuable components, such as metal ions. The use of electrodialysis concentration makes it possible to return valuable components back into production, reducing the cost of purchasing new reagents, as well as implementing closed-cycle technologies with zero liquid discharge.

An urgent task is to develop processes for the selective concentration of electrolytes from ternary and multiionic solutions. In these processes, the concentration and separation of ions occurs simultaneously and requires ion-exchange membranes with high specific selectivity for their implementation. The work investigated the process of limited electrodialysis concentration of an equinormal mixture of sodium and calcium chlorides using anisotropic bilayer membranes with a thin selective layer on the surface of industrial membranes. A copolymer of N,N-dimethyl-N,N-diallylammonium chloride and ethyl methacrylate was chosen as a selective anion-exchange layer. Applying a thin homogeneous anion exchange layer to the surface of a cation-exchange membrane leads to a significant decrease in the maximum electric current density, but the selectivity of the membrane to singly charged ions increases significantly. Selective concentration of salts of singly charged ions from mixed solutions will reduce the risk of sedimentation in concentration chambers.

Based on the research performed, processes for selective electrodialysis concentration of electrolytes from multiionic solutions will be developed using new bilayer and industrial ion-exchange membranes.

*The study was financially supported by the Russian Science Foundation, project No. 22-13-00439, <https://rscf.ru/project/22-13-00439/>*

# LOW PERCENTAGE COBALT CATALYSTS FOR ELECTROSYNTHESIS OF HYDROGEN PEROXIDE

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Production of H<sub>2</sub>O<sub>2</sub> through electrochemical 2-e<sup>-</sup> oxygen reduction reaction (ORR) is one of the promising methods for the production of H<sub>2</sub>O<sub>2</sub> solutions of various concentrations directly at a place of potential use. Recently, single atom catalysts (SAC) have been used in various catalytic processes due to large number of active sites resulting in high catalytic activity. The non-noble metals (Co, etc.) are used as SAC, which is cost-effective. However, up to now mechanism of SAC operating is not deeply understand, especially the relationship between the structure and properties of the catalyst in the target reaction.

In this work, a study was carried out on cobalt SAC with a load of 0.5–3 wt.% in ORR. The catalysts were prepared by cobalt nitrate impregnation of N- and B-graphene. Supports were obtained by template method followed by heat treatment. The values of kinetic current and electrochemically active surface were obtained. It was established that ORR follows the 2-e<sup>-</sup> path on catalysts used. The Faraday efficiency, yield and generation rate of H<sub>2</sub>O<sub>2</sub> were determined in an H-cell with a gas-diffusion electrode in potentiostatic and galvanostatic mode. Composition and structure of SAC active sites were evaluated by set of physicochemical methods (EXAFS, HAADF STEM, XPS, etc.). Relationship between active site structure and activity and selectivity in the ORR was established.

Efficiency of ethylene glycol electrochemical oxidation using *in situ* synthesized H<sub>2</sub>O<sub>2</sub> on SAC with the addition of Fenton's reagent was studied.

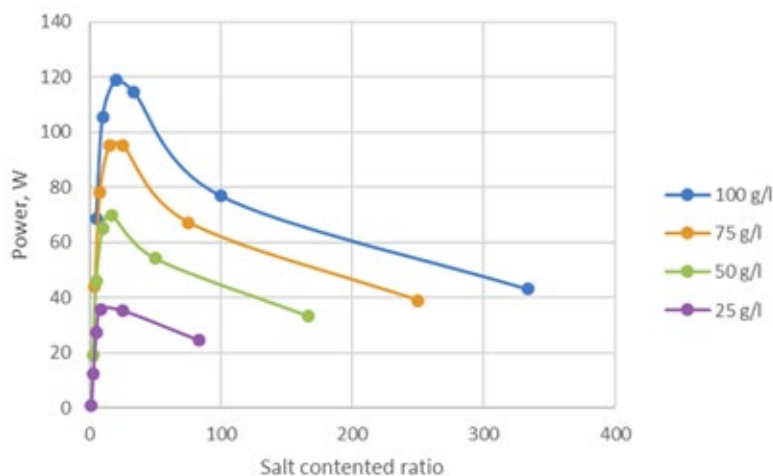
*The work was carried out with financial support from the Ministry of Science and Higher Education of the Russian Federation within the framework of a state assignment for Novosibirsk State University, project No. FSUS-2022-0022.*

# REVERS ELECTRODIALYSIS AS AN ALTERNATIVE METHOD OF ELECTRIC POWER GENERATION

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The use of non-renewable energy resources leads to the need to find alternative solutions, one of which may be the technology of reverse electrodialysis, based on pumping desalinated and salty streams through channels formed by cation- and anion-exchange membranes.<sup>1</sup> The liquids used as streams can be varied. We have obtained experimental data for the installation of the reverse electrodialyzer with flows of different salinity. The maximum power in all cases is observed at the ratio of salinity from 15 to 25 times.<sup>2</sup>



**Figure 1.** Dependence of the power obtained on the ratio of solution salinity at different salinities of the more concentrated solution

The membranes are stable over a wide range of pH so we can use acid and alkaline streams as well. And so, this technology to be applied in various chemical production facilities including metallurgical plants, oil refineries, food and cosmetic industries.

However, it should be noted that the field of application can also be extended by agriculture where produce a large number of streams suitable for technological requirements.

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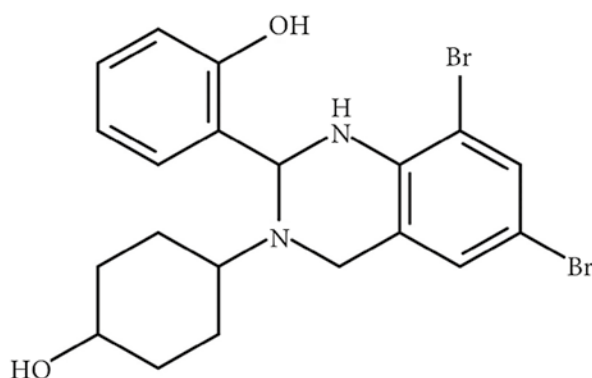
# THE INHIBITORY PROPERTIES OF 2-(6,8-DIBROMO-3-(4-HYDROXYCYCLOHEXYL)-1,2,3,4-TETRAHYDROQUINAZOLIN-2-YL)PHENOL ON THE CORROSION OF STEEL EN Fe37-3FN IN ACIDIC ENVIRONMENTS

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Burmistrov L.O.<sup>b</sup>, Amelina N.S.<sup>b</sup>**

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A derivative of ambroxol hydrochloride and salicylaldehyde, namely, 2-(6,8-dibromo-3-(4-hydroxycyclohexyl)-1,2,3,4-tetrahydroquinazolin-2-yl)phenol was synthesized, and its structure was confirmed by both UV, IR, Raman, and <sup>1</sup>H NMR spectroscopy.



This compound was tested as a potential inhibitor for the corrosion of mild steel EN Fe37-3FN both in 0.5 M hydrochloric acid and in 0.5 sulphuric acid solutions with the different additions of the compound ranging from 4 to 400 ppm. The studies include the weight loss measurements, the open circuit potential measurements, the potentiodynamic polarisation with estimation of the polarization resistance, Tafel slopes and corrosion current densities, and the recording of electrochemical impedance spectra. It was shown that the inhibitory activity of the compound increases with the increase of its concentration in a solution, and corrosion rate decreases up to 85%. The data of gravimetric and electrochemical measurements coincide each other well. The sorption of the compound on the steel surface follows the Langmuir adsorption isotherm, and the nature of adsorption is physical due to the electrostatic interactions. The chelating activity of the compound relatively to both ferrous and ferric ions in the acidic solution was also studied.

*This work was funded within the framework of the state assignment of the Ministry of science and higher education of Russian Federation, project registry number 1023041400091-5-3.2.10;2.4.2.*

# ELECTROCHEMICAL SYNTHESIS OF ACTIVE ANISATROPIC COATINGS BASED ON SUPRAMOLECULAR METAL SYSTEMS

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Currently, it is important to search for alternative energy sources, including electrochemical ones. An interesting direction is the release of hydrogen energy, as well as solar energy. An important structural element of such energy release devices are functional electrodes, which have a high specific active surface and transverse electrical conductivity. When creating such electrodes, it is important to pay attention to the specific catalytic surface of the upper layer and the ability of efficient charge transfer in the surface layer.<sup>1</sup> The work discusses the modification of electrodes for a number of problems of alternative electrochemical energy sources by electrochemical deposition from the liquid phase. The modification is carried out by electrochemical deposition of oriented metal networks with a highly developed surface and high electrical conductivity, which is achieved due to the high anisotropy of the nanowire network on the electrode surface. Deposition from metal + calixarene supramolecular systems is used to obtain high uniformity of the deposited network layer. In this work, a number of Metal (Fe, Ni, Co) –calixarene complexes were studied, and the electrochemical reduction potentials and deposition time were determined for each of them. For example, for the calixarene + CoCl<sub>2</sub> complex, it was found that at a potential of –1.7 V (AgAgCl), the electrode is modified by a system of oriented networks of nanofibers with inclusions of individual particles with sizes ranging from 70 nm to 350 nm. The networks are represented by fibers with a lateral size of 70–90 nm. A length of the fibers is about tens of micrometers. The height of the fibers is 3–5 nm.

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# PREPARATION AND ELECTROCHEMICAL PROPERTIES OF ELECTRODE MATERIAL BASED ON NITROGEN DECORATED CARBON NANOTUBES FOR HYBRID SUPERCAPACITORS

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Hybrid supercapacitors, which combine a double-layer capacitance electrode with a Faraday-type electrode, can combine correspondingly high power density with high energy density. The use of aqueous solutions as an electrolyte has a number of advantages compared to supercapacitors with organic electrolytes. The disadvantage of an aqueous electrolyte for a traditional double-layer (symmetrical) supercapacitor is the low operating voltage window. The hybrid device makes it possible to expand the operating voltage window by changing the overvoltage of water decomposition on the Faraday electrode. The capacity of a hybrid cell is limited by the capacity of the double-layer electrode due to its low energy density, so the selection of a double-layer electrode material that provides the best electrochemical performance is necessary. Various carbon materials, in particular carbon nanotubes (CNTs), are used as a double-layer electrode. Doping the surface of CNTs with heteroatoms is an effective method for increasing their specific capacity.

The purpose of this research is to develop a technique for doping carbon nanotubes with nitrogen and to study the electrochemical properties of electrodes based on the resulting material in acidic and alkaline electrolytes.

Nitrogen-doped carbon nanotubes were prepared by carbonizing CNTs coated with polyaniline, synthesized by polymerizing aniline on the surface of the nanotubes.

To assess the electrochemical characteristics of the studied electrode materials, the method of cyclic voltammetry, galvanostatic method, and impedance spectroscopy method were used.

Experiments testing electrodes with doped carbon nanotubes showed an increase in capacity compared to samples without nitrogen.

# EVOLUTION OF STRUCTURAL PARAMETERS OF OXIDE CERAMIC COATINGS ON MAGNESIUM ALLOY DURING EXPOSURE OF A CORROSIVE ENVIRONMENT

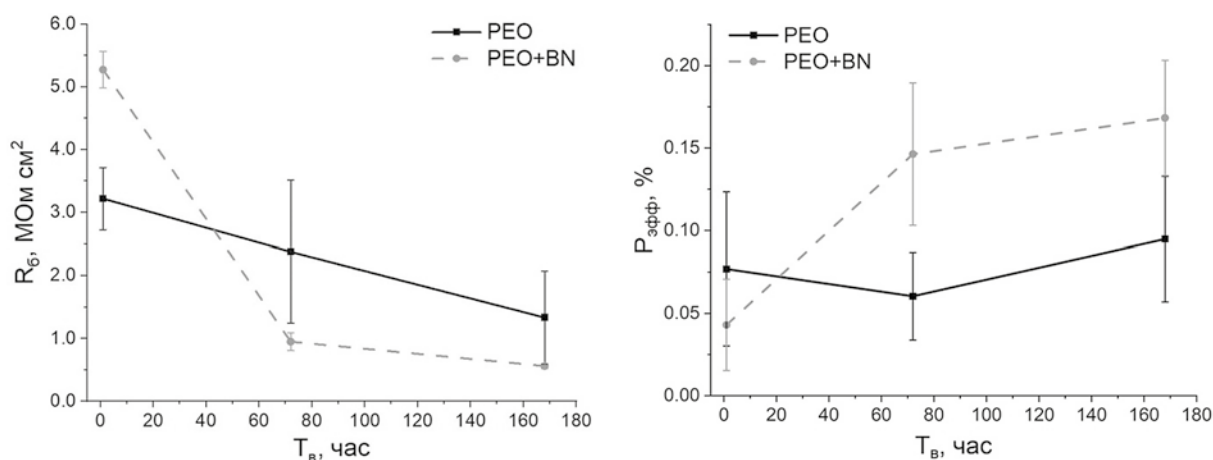
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Plasma electrolytic oxidation (PEO) is a technology for surface modification and anti-corrosion protection of magnesium alloys. The use of insoluble nanoparticles (NPs) as electrolyte modifiers has improved the properties of the formed ceramic coatings. However, the achieved effects are mainly given for coatings in their original state and do not reflect the properties of the material during long-term operation.

The purpose of the work is to study the evolution of the structure of oxide layers formed by PEO on the ML10 alloy in the base electrolyte and in the presence of BN NPs (4 g/l), when exposed to 3.5 wt.% NaCl, using impedance spectroscopy and potentiodynamic polarization.

It has been established that BN NPs increase the resistance of  $R_b$  charge transfer through the internal (barrier) layer of the coating in the initial state by  $\sim 1.6$  times, but after three days of exposure in a corrosive environment it drops by more than 5 times. The degree of heterogeneity ( $n_b$ ) of the barrier zone of the hybrid coating decreases from 0.9 to 0.73, which indicates the development of corrosion damage. The effective through porosity of the base layer does not change after 7 days of exposure, but for the coating with the BN additive it increases by  $\sim 4$  times. Thus, this modifier is suitable for use only for short-term protection of the ML10 alloy.



**Figure 1.** Resistance to charge transfer through the barrier layer and effective through porosity of the base layer and hybrid coating with the addition of BN NPs

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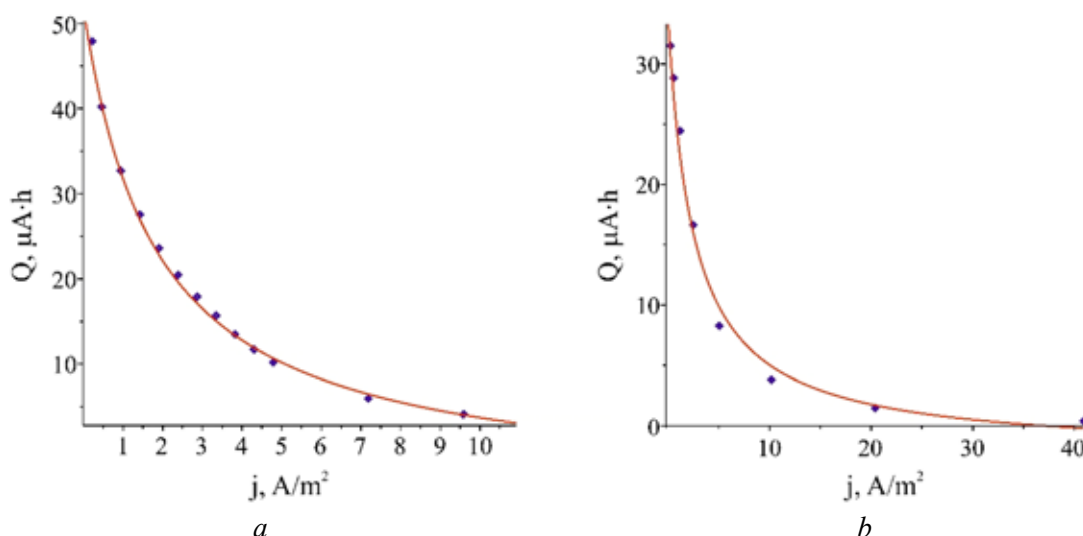
# ON THE APPLICABILITY OF PEUKERT'S LAW TO ALL-SOLID-STATE LITHIUM-ION BATTERIES

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The results from measuring the capacity of thin-film solid-state lithium-ion batteries (SSLIB) Si@O@Al-LiPON-LiCoO<sub>2</sub>, Si@O@Al-LiPON-Li<sub>x</sub>V<sub>2</sub>O<sub>5</sub> and Ti-LiPON-LiCoO<sub>2</sub> at different charge currents are reported. It is shown that the capacity dependence on the current density  $Q(j)$  follows Peukert's law and features a low value of Peukert's exponents in the region of low currents and a high value of the exponents in the region of high currents. Peukert's exponent for the anode-free cell remains constant through the entire range of current density variation. A model for SSLIB capacity based on the balance of drift, diffusion and electron currents is proposed. The model predicts a  $Q(j)$  dependence well approximating the experimental results and meeting Peukert's law. The model allows a qualitative interpretation of the change in the Peukert exponent with increasing current density, based on the effect of the charge current saturation.



**Figure 1.** The theoretical (line) and experimental (diamonds) dependences of capacity on current density: (a) Ti|Si@O@Al|LiPON|LiCoO<sub>2</sub>|Ti; (b) Ti|Si@O@Al|LiPON|Li<sub>x</sub>V<sub>2</sub>O<sub>5</sub>|Ti

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# INVESTIGATION OF THE KINETIC REGIME OF ELECTRON TRANSFER ON GRAPHENE ELECTRODES

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Graphene, a two-dimensional crystal consisting of sp<sup>2</sup>-hybridized carbon atoms, is of significant interest for various electrochemical applications due to its wide electrochemical stability window and record-low thickness. One of the most important electrochemical properties of graphene is electron transfer rate to electroactive species. The kinetic regime depends both on the nature of the reagent and the electronic structure of graphene and the substrate. However, the question of electron transfer kinetic regime on graphene and graphite and the influence of various conditions remains heavily disputed<sup>1,2</sup>.

In this study, we determined the kinetic regime of electron transfer on graphene for certain outer-sphere electrochemical systems (ferrocene, decamethylferrocene, TEMPOL, ferroin) in aqueous and aprotic environments. To achieve this, standard heterogeneous rate constants for electron transfer on samples of graphene, glassy carbon, and highly oriented pyrolytic graphite (HOPG) were determined from cyclic voltammetry data using the Nicholson method<sup>3</sup>. Comparing these constants allowed us to draw conclusions about the kinetic regime. Analysis of the obtained data showed that for ferrocene and TEMPOL, the rate constant for electron transfer on graphene is an order of magnitude lower than on glassy carbon and HOPG, indicating a non-adiabatic regime of electron transfer. Conversely, for decamethylferrocene, the rate constant practically does not depend on the electrode material, indicating an adiabatic regime.

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# COMPOSITE ELECTRODE MATERIALS OBTAINED BY DEPOSITION OF POLYANILINE IN THE PORES AND ON THE SURFACE OF HIGHLY POROUS CARBON CLOTH FOR SUPERCAPACITORS WITH ENHANCED CYCLING STABILITY

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The study is dedicated to composite materials that consist of fibrous carbon cloth modified by polyaniline. FTIR-spectroscopy analysis results in the composites showed that polyaniline was formed as protonated emeraldine. Polyaniline deposited as a thin layer in the pores of the carbon fabric which has a high specific surface area (1271 m<sup>2</sup>/g). The electrochemical properties of the composite materials were a combination of the high specific capacity of polyaniline and the enhanced electrochemical stability of carbon fabric. The highest value of electrical capacity equal to 4.54 F/cm<sup>2</sup> was achieved by the synthesis of polyaniline from an aniline solution with a concentration of 0.250 M in 1 M hydrochloric acid. The loss of electrical capacity after 2000 charge-discharge cycles at a current density of 10 A/cm<sup>2</sup> was about 8% with a charge efficiency of 97 to 98% which indicates the high resource stability of the composites. According to the results of Trasatti method analysis, it was revealed that 27% of the composites' specific capacitance belongs to pseudocapacitance while 73% represents double-layer capacitance.

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# TEMPLATED ELECTRODEPOSITION OF INDIUM NANOWIRES AND MEASURING THEIR ELECTRICAL RESISTANCE

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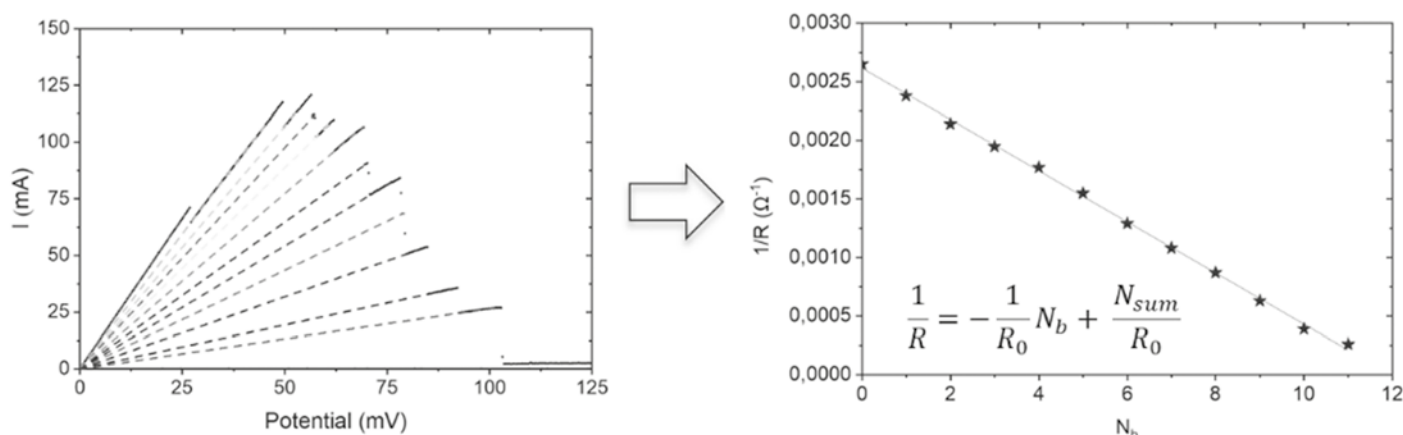
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The growing use of metal nanowires in superconducting quantum microelectronics and nanophotonics makes it necessary to study the specific physical properties of nanostructures.

Obtaining arrays of indium nanowires by template electrodeposition into a matrix of anodic aluminum oxide is one of the most effective synthesis techniques since it allows the formation of ordered arrays of cylindrical nanowires with tailored geometric parameters (diameter and length).

In this work arrays of indium nanowires with diameters of 40 nm, 50 nm and 200 nm were fabricated. The technique was proposed for measuring the resistance of single nanowires without removal from the template based on I-U curve analysis. By sweeping the potential up to 1 V, it is possible to register discrete current jumps corresponding to the sequential burnout of nanowires inside the template. This phenomenon allows one to calculate the resistance of a single nanowire (Fig. 1).



**Figure 1.** Determination of the resistance of a single nanowire

The experimental data were described by the theoretical Fuchs-Sondheimer model<sup>1</sup>. Based on the approximation the electron free path in a bulk indium was estimated to  $57 \pm 5$  nm.

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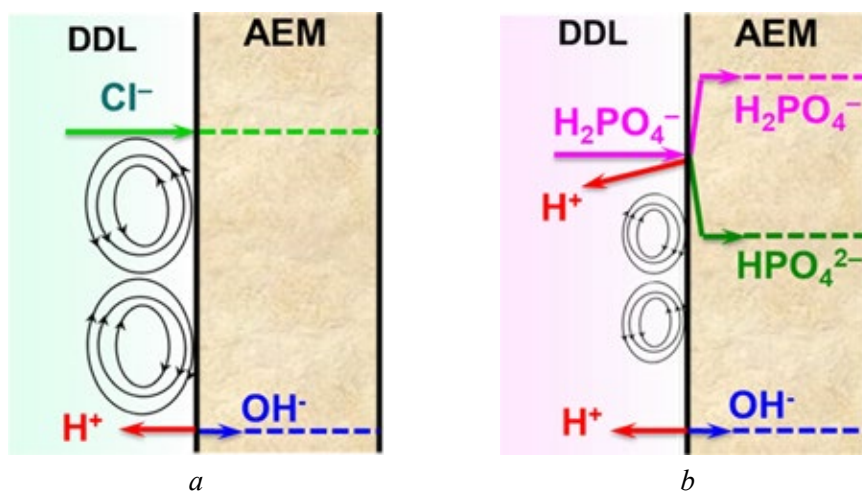
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# INVESTIGATION OF THE DEVELOPMENT OF ELECTROCONVECTION AT THE SURFACE OF ANION EXCHANGE MEMBRANE IN SODIUM DIHYDROCITRATE AND HYDROTARTRATE SOLUTIONS

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Electroconvection, EC, appears to be a phenomenon that is often mentioned when interpreting voltammetric characteristics, chronopotentiograms, or when discussing the transport patterns of ampholytes (phosphates, citrates, and tartrates) in intense current regimes. The regularities of EC development in systems with ion-exchange membranes have been studied in sufficient detail with respect to solutions of NaCl and other strong electrolytes. However, the influence of the nature of ampholyte and its propensity to generate  $H^+$  /  $OH^-$  ions in systems with ion exchange membranes on the development of electroconvection (EC) has not been discussed so far. The aim of this work is to study the influence of the development of electroconvection near the surface of anion-exchange membrane in solutions of ampholytes that engage in protonation-deprotonation reactions.



**Figure 1.** Schematic representation of the phenomena developing at the anion-exchange membrane/depleted solution interface in ultra-limit current regimes for the cases of strong electrolyte solution (a) and ampholyte solution (b)

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# ELECTROCHEMICAL MODIFICATION OF THE SURFACE OF A GLASSY CARBON ELECTRODE WITH NICKEL NANOPARTICLES

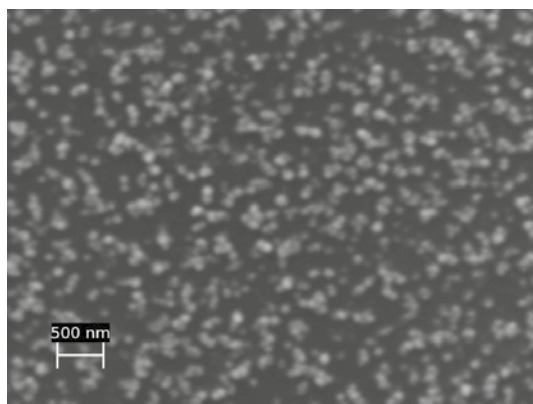
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Currently, there are several ways to obtain nickel nanoparticles on the surface, some of the most effective are: lithography, thermal vacuum evaporation method, pulsed laser deposition, electrochemical deposition<sup>1</sup>. However, among all these methods, it is worth noting electrochemical deposition, since this method is cheaper and easier to use.

In this work, we used a nickel complex formed from sodium pectate salt, where 25% of Na ions were replaced by Ni ions. The complex was dissolved in an aqueous solution of  $\text{Na}_2\text{HPO}_4$  /  $\text{NaH}_2\text{PO}_4$ , after which electrolysis was carried out at a potential of  $-1.5\text{V}$  rel.  $\text{Ag}/\text{AgCl}$  for 60 min. The modified electrode was washed, dried, and then examined on a scanning electron microscope (Fig. 1).



**Figure 1.** Image of a modified glassy carbon surface

The study showed that nanoparticles with sizes of 20–100 nm were formed on the surface, the average particle size was 60 nm.

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# GRAIN AND GRAIN BOUNDARY TRANSPORT OF THE PROTON CONDUCTING CERAMIC $\text{BaSn}_{0.8}\text{Y}_{0.2}\text{O}_{3-\delta}$ AT DIFFERENT OXYGEN PRESSURES

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Proton-conducting ceramic materials are widely studied as an alternative to traditional oxygen-conducting electrolytes for solid oxide fuel cells (SOFCs). The lower operating temperatures of such devices simplify the selection of thermally compatible materials. This has a positive impact on the SOFC lifetime.

In this work, the bulk and grain boundary transport of a promising proton conductor based on barium stannate,  $\text{BaSn}_{0.8}\text{Y}_{0.2}\text{O}_{3-\delta}$  (BSY), synthesized by the solid-state reaction at 1500 °C for 5 h using 0.5 wt% CuO as a sintering additive, has been investigated. The electrical conductivity of the ceramic sample was measured in a specially designed setup by electrochemical impedance spectroscopy (EIS) in a wide range of temperatures (400–550 °C), partial pressures of oxygen ( $10^{-22}$ –0,21 atm) and water vapour ( $10^{-5}$ –0,03 atm). The results were processed using distribution of relaxation times (DRT) analysis.

The obtained impedance spectra of the symmetrical Ag|BSY|Ag cell show two classical processes (bulk and grain boundary) along with an additional process which total contribution does not exceed 10% of the total cell resistance. The measurements carried out under reducing conditions allowed the identification of an electrolytic domain boundary with predominant ionic conductivity for all three processes. For two processes (bulk and additional with activation energies  $\approx 0.5$  eV), an increase in ionic conductivity upon humidification is observed, while the conductivity of the additional process does not change, according to the results of EIS and DRT data analysis. Taking into account the localisation of sintering additives, the additional processes with very low resistivities can be attributed to pure grain boundaries of BSY ceramics, while the low frequency process with high resistivity can be associated with grain boundaries coated with a low melting CuO phase.

# THE ROLE OF SURFACE-ACTIVE ANIONS IN THE ADSORPTION OF SUPRAMOLECULAR CATIONIC COMPLEXES OF CUCURBITURILS

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Pumpkin-shaped molecular containers of the relatively new family of cucurbiturils (CBn<sub>s</sub>) have unique properties due to the ability to simultaneously form complexes with organic particles (inclusion in a hydrophobic cavity) and with inorganic cations (interaction with carbonyl groups of portals). Almost the only source of information about their adsorption behavior is the cycle of our impedancemetric studies (the dependence of the differential capacitance  $C$  on the potential  $E$ ) for the interface of a model Hg electrode/aqueous solutions of sulfates of a number of alkali metals, where the existence of two structures of the adsorption layer, formed either by supramolecular cationic complexes ( $q < 0$ ), or these complexes and free cavitand molecules ( $q > 0$ ). The objective of this work was to identify the role of adsorption of surface-active anions ( $\text{Cl}^-$ ,  $\text{NO}_3^-$ ) in these processes. It has been established that the presence of these anions in the system leads to a sharp narrowing ( $\sim 400$  mV) of the adsorption region of cationic complexes and a weakening in the effects of the concentration of CBn and time on adsorption processes. A significant difference from systems that do not contain surface-active anions is also the formation in the region at small negative potentials ( $E = 0 \div -0.3$  V relative to Ag/AgCl) of some stable structures of the adsorption layer, which is expressed in the appearance of characteristic areas with an almost constant value  $C$ , which significantly exceeds that corresponding to the adsorption of cationic complexes at  $q < 0$ . These effects are explained by the adsorption of supramolecular cationic complexes on a layer of adsorbed surfactant anions. Similar effects of drawing inorganic cations into the layer of  $\text{Cl}^-$  and  $\text{NO}_3^-$  anions adsorbed on the electrode are described in the literature. At extremely positive potentials ( $E > 0$ ), where the adsorption of cationic complexes is impossible, a sharp change in the nature of the  $C$ – $E$  dependences is observed, which is probably due to the adsorption of free cavitand molecules.

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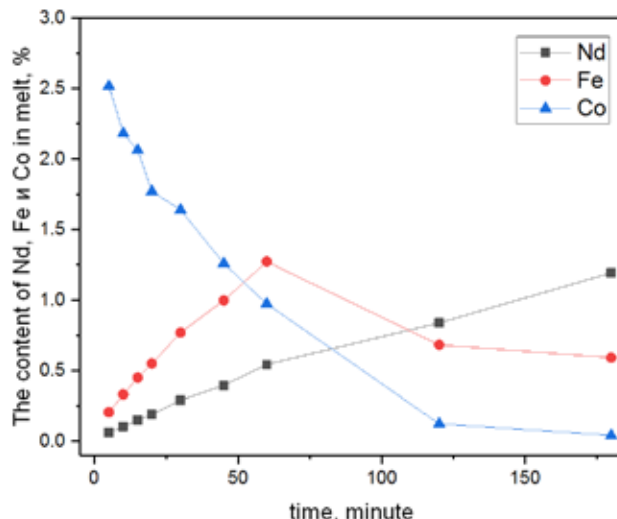
# STUDY OF NEODYMIUM EXTRACTION FROM NdFeB ALLOY IN MOLTEN SALTS

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Neodymium magnets made of NdFeB alloy are widely used in various fields of modern engineering. At the moment there are no technologies aimed at recycling decommissioned electronic devices containing NdFeB-based magnets. The technology based on the extraction of neodymium from NdFeB alloy in alkali metal chloride melts would be promising for obtaining neodymium from secondary sources.

NaCl-KCl-CoCl<sub>2</sub> melts containing 4.75, 7.75 and 10.50 wt.% cobalt chloride were used to study the interaction of NdFeB alloy with salt melts. Neodymium magnets with a composition of 79 wt.% Fe, 29 wt.% Nd and 1 wt.% B were used as NdFeB alloy samples. An approach based on the interaction of the NdFeB alloy with salts of more electropositive metals was used to transfer neodymium into the melt. The interaction of melts containing cobalt chloride with NdFeB alloy was studied. Thermodynamic calculations showed that it is favorable to carry out the process at lower temperatures to increase the extraction of neodymium in the melt. It is shown that the process of neodymium leaching from NdFeB proceeds in two stages, at the first stage CoCl<sub>2</sub> leaches Nd, Fe and B into the melt, and at the second stage, when cobalt is absent in the melt, leaching proceeds at the expense of iron. In this process, the melt is spontaneously cleared of iron (Fig. 1).



**Figure 1.** Change of Nd, Fe and Co content in the NaCl-KCl-CoCl<sub>2</sub>-NdFeB system from time, initial Co content in the melt 7.70 wt.%

# BLOCKING UNDESIREDDIFFUSION AS A WAY TO OPTIMIZE PCFC BASED ON $\text{Pr}_2\text{NiO}_{4+\delta}$

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Materials based on  $\text{Pr}_2\text{NiO}_{4+\delta}$  are considered as promising electrode materials for protonic ceramic electrochemical devices. However, possible chemical interaction between  $\text{Pr}_2\text{NiO}_{4+\delta}$  and oxides based on  $\text{Ba}(\text{Ce},\text{Zr})\text{O}_3$  at operating temperatures of PCFCs prevents their joint use. One of the promising methods of solving this problem is to reduce the difference in barium concentration between these phases due to the preliminary substitution of a part of praseodymium in nickelate with barium.

The aim of this work is to improve the functional properties of Ba-doped  $\text{Pr}_2\text{NiO}_{4+\delta}$ -based materials as air PCFC electrodes. The powders with  $\text{Pr}_{2-x}\text{Ba}_x\text{NiO}_{4+\delta}$  compositions ( $x=0, 0.1, 0.2, 0.3, 0.4$ ) were prepared using the citrate-nitrate synthesis method. Properties such as crystal structure (XRD and HT-XRD) absolute oxygen content (thermogravimetry), TCLP (dilatometry), total conductivity (4-probe method), polarization resistance (electrochemical impedance spectroscopy), and ion conductivity (oxygen flow method) were obtained for the synthesized materials. The chemical interaction of the investigated materials with  $\text{Ba}(\text{Ce},\text{Zr})\text{O}_3$ -based oxides was investigated. Based on the optimal composition, a reversible electrochemical cell was fabricated.

In the course of this work, it was found that due to the acceptor effect, barium doping increases the total conductivity of the materials up to  $125 \text{ S cm}^{-1}$  at  $700^\circ\text{C}$  for  $x=0.3$ . In addition, a slight decrease in TEC values was observed for  $x=0.1$  and  $0.2$  samples ( $12.7 \cdot 10^{-6}$  and  $12.6 \cdot 10^{-6} \text{ K}^{-1}$ , respectively). The doping was found to reduce undesirable phase formation during annealing of the electrolyte/electrode mixture. The addition of barium leads to a decrease in the polarization resistances of symmetric cells, down to  $\sim 0.17 \text{ Ohm/cm}^2$  for the samples  $x=0.2$  and  $0.3$  at  $700^\circ\text{C}$ . The reversible electrochemical cell was tested. The maximal power density values of  $\sim 430 \text{ mW cm}^{-2}$  in the PCFC mode and hydrogen flux values of  $5 \text{ mL min}^{-1} \text{ cm}^{-2}$  in the PCEC mode at  $750^\circ\text{C}$  were achieved.

# ASPECTS OF CHEMICAL STABILITY OF MIXED ION-ELECTRON CONDUCTORS AS PROMISING ELECTRODES FOR PROTON-CERAMIC FUEL CELLS

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The modern issues of environmental pollution and global warming have brought alternative energy sources to the forefront of attention. Solid oxide fuel cells are one such source, being efficient devices that convert the chemical energy of fuel into electrical energy. Mixed ion-electron conductors are found to be promising as materials for air electrodes of proton-ceramic fuel cells (PCFCs) or oxygen-permeable membranes. This work investigates the chemical stability of complex oxide materials based on  $\text{BaCe}_{0.7-x}\text{Fe}_x\text{Zr}_{0.2}\text{Y}_{0.1}\text{O}_{3-\delta}$  ( $x=0.5, 0.6, 0.7$ ) with mixed ion-electron conductivity and their interaction with other functional materials such as  $(\text{BaCe}_{0.5}\text{Zr}_{0.3}\text{Y}_{0.1}\text{Yb}_{0.1}\text{O}_{3-\delta})$  based proton conducting electrolyte) and gas components ( $\text{H}_2\text{O}$ ,  $\text{CO}_2$  and  $\text{H}_2$ ).

The high-temperature X-ray diffraction analysis indicates that there were no phase transitions in the investigated materials. Additionally, an increase in their unit cell volume was observed due to thermal expansion. Chemical compatibility studies revealed no visible chemical interaction between the electrode and electrolyte materials, even at a temperature of 1200 °C, which is significantly higher than the operating temperatures (600–800 °C) for PCFCs. Exposure of  $\text{BaCe}_{0.7-x}\text{Fe}_x\text{Zr}_{0.2}\text{Y}_{0.1}\text{O}_{3-\delta}$  to different atmospheres at 1100 °C for 10 h resulted in the formation of impurity phases. However, their extremely small amount suggests that they may not form under the working conditions of PCFCs. Therefore, the investigated materials can be considered as potential candidates for various electrochemical applications.

*This research was funded by the scholarship of the President of the Russian Federation for young scientists and postgraduate students № CII-210.2022.1.*

# ELECTROSTATIC POTENTIALS ASSIGNED TO TRANSFER OF PROTONS ALONG THE SURFACE OF LIPID MEMBRANE FROM DONOR TO ACCEPTOR

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The protons on the surface of lipid membrane separated from the bulk water by a high barrier, the study of which attracts the attention of many investigators in the world. It can be evaluated by study of the rate of transfer of protons between the surface of bilayer lipid membrane (BLM) and water using the photoactivated donors of H<sup>+</sup> (caged-H<sup>+</sup>). The study by the Inner Field Compensation Method allowed the observation the release of protons from caged-H<sup>+</sup> and their equilibration with water<sup>1</sup>. The magnitude of the potential change was determined by the dependence of surface charge of BLM on pH which was significant only in the region higher than 7. To make this method more sensitive at broader pH range, we measured the changes of potential with the pH sensors – styryl fluorescent dyes RH-421 or di-4-ANEPPS, capable to adsorb on BLM and change its dipole potential that depends on pH. Two kinds of caged-H<sup>+</sup> were studied as the donors of protons: – 2-methoxy-5-nitrophenyl sulfate (MNPS) or pyranine. The illumination of BLM containing the molecules caged-H<sup>+</sup> and dyes bound on its one side led to disappearing of the dipole potential created by the dyes, which restored after switching the light off. The rate of disappearing of the potential increased with increase of the intensity of the illumination and decreased with pH of the solution. This effect cannot be due to oxidation of the molecules of dyes, as it tested in the control experiments in the medium without oxygen. The most probable mechanism of change of the potential is the transfer of protons from donor – caged-H<sup>+</sup> to acceptors – molecules of dyes leading to their protonation and desorption from BLM.

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*Supported by the Russian National Fund, project 23-24-00571.*

# ENANTIOSELECTIVE VOLTAMMETRIC SENSOR BASED ON THE OCTAHEDRAL COMPLEX OF CO(III) AND CARBOBLACK

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The ability for enantioselective recognition in voltammetric sensors is provided by various chiral materials – selectors<sup>1-2</sup>. Transition metal complexes with chiral ligands have all the necessary characteristics of chiral selectors (reliability of enantiomer recognition, reproducibility, stability, accessibility and ease of sensor production), and therefore are in demand in the development of enantioselective voltammetric sensors (EVS)<sup>3</sup>.

In this study, we developed an EBC based on a CarboBlackC paste electrode modified with a chiral octahedral cobalt(III) complex ( $\Lambda(R,R)\text{-Co-Cl@CBPE}$ ). The developed EVS selectively recognizes L- and D-tryptophan (Trp), while achieving an oxidation potential difference ( $\Delta E_p$ ) of 35 mV and an enantioselectivity coefficient ( $i_{p1}/i_{p2}$ ) of 1.36. It was found that the determined concentrations of Trp enantiomers retain their linearity in the range of 1–500  $\mu\text{M}$  with LOD and LOQ values of 3.30 and 11.03  $\mu\text{M}$  for L-Trp and 2.42 and 8.06  $\mu\text{M}$  for D-Trp. The sensitivity coefficients for L- and D-Trp were determined to be 9.84 and 13.46. High values of  $\Delta E_p$  and  $i_{p1}/i_{p2}$  allow the determination of Trp enantiomers in their racemic mixture and a mixture with a predominance of one of the enantiomers. In this case, the peak potentials are linearly shifted towards negative values, and the peak currents increase linearly with increasing D-Trp content. The practical application of the developed EVS was tested using the “added-found” method to determine Trp enantiomers in biological fluids and tablet forms of dietary supplements. The relative standard deviation in urine did not exceed 5.1%, in plasma 5.4%, and in tablet forms 4.2%.

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*The work was carried out with the financial support of the Russian Science Foundation, grant № 23-23-00340.*

# CHIRAL VOLTAMMETRIC SENSOR BASED ON NI(II) CHELATE COMPLEX

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The main criteria for creating enantioselective voltammetric sensors (EVS) are stability, accessibility, rapidity and reliability of enantiomer recognition. These characteristics are enhanced by various chiral selectors<sup>1-2</sup>. Among them, we can highlight complex compounds of transition metals with chiral ligands, which make it possible to increase the selectivity and other characteristics of EVS at low cost<sup>3</sup>.

We have proposed a sensor based on a CarboBlackC paste electrode modified with a nickel(II) complex compound (PE/(S)-BPB-Gly-Ni(II)). Using the square wave voltammetry (SWV) method, it was found that the sensor exhibits selectivity to the enantiomers of atenolol (Atn) ( $i_{p1}/i_{p2}=1.60$  and  $\Delta E_p=20$  mV). The developed sensor is capable of determining concentrations of Atn enantiomers in the linear range of 100–1000  $\mu$ M with limits of detection (LOD) of 4.51 and 2.76  $\mu$ M for S- and R-Atn, respectively. The PE/(S)-BPB-Gly-Ni(II) sensor exhibits greater sensitivity to S-Atn (11.72). The proposed sensor was successfully tested for the determination of Atn enantiomers in test solutions and biological fluids. In all cases, the concentrations of the studied solutions were determined with high accuracy and good reproducibility –  $S_r$  did not exceed 4.1%. To assess the possibility of using the proposed sensor for analytical purposes, we studied the interfering effect of excipients present in dosage forms in various combinations and concentrations (talc, starch, lactose, calcium stearate, sucrose) on the correct determination of S- and R-Atn. In all cases, the “found” values correspond to the “added” values, while  $S_r$  ranges from 0.6–3.4% over the entire range of concentrations studied.

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*The work was carried out with the financial support of the Russian Science Foundation, grant № 23-23-00340.*

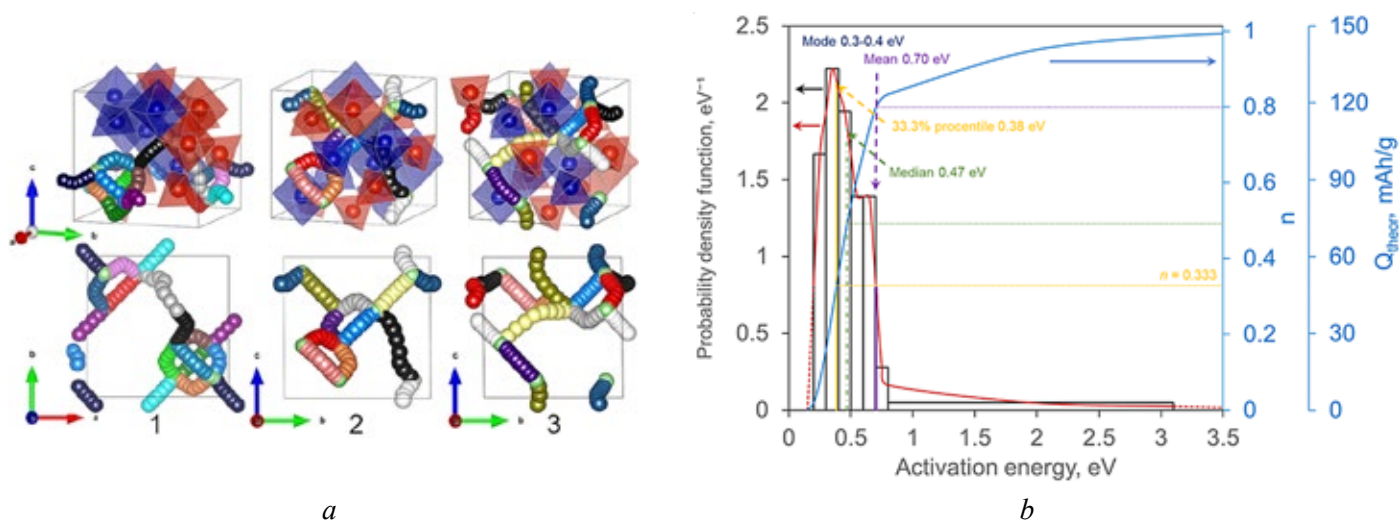
# PREDICTION OF ELECTRODE MATERIAL SPECIFIC CAPACITY FROM DISTRIBUTION OF ION DIFFUSION PATHS BY ACTIVATION ENERGY

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The development of electrode materials for metal-ion accumulators requires a combination of theoretical and experimental methods.

We compare the results of determining the activation energies of lithium ion diffusion in materials, which we obtained by density functional theory (DFT) calculations, with experimental results from electrochemical methods such as cyclic voltammetry and galvanostatic and potentiostatic pulses. As a result, for example, for  $\text{LiCoVO}_4$ , we assume that the limitation of the practically realizable capacity of the material is due to its structural constraints, which lead to the impossibility of involving all lithium ions in the current-generating process (illustrated in Fig. 1<sup>1</sup>). This reason is fixed by the modeling results, but is not revealed by the experimental results.



**Figure 1.** Illustration of possible diffusion paths of lithium ions in  $\text{LiCoVO}_4$  (a) and their activation energy distribution with prediction of specific capacity based on this distribution (b)<sup>1</sup>

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# DEVELOPMENT OF AN ELECTROCHEMICAL METHOD FOR SEPARATING <sup>99m</sup>Tc FROM A MOLYBDENUM TARGET IN THE PROCESS OF OBTAINING RADIOPHARMACEUTICALS

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When obtaining the <sup>99m</sup>Tc isotope used in radiopharmaceuticals for in vivo diagnostics, it is necessary to develop a technique for quickly separating the resulting <sup>99m</sup>Tc from a molybdenum target. This problem is usually solved using chromatography, while it is believed that the electrochemical method is less effective. During chromatographic separation, polymer compounds Mo(VI) are sorbed on a column with Al<sub>2</sub>O<sub>3</sub>, then the pertechnetate ions are not retained and pass into the eluate. To convert TcO<sub>4</sub><sup>-</sup> ions into a pharmaceutically accessible form, their subsequent reduction is necessary. When implementing the electrochemical output, separation of technetium by reduction at the cathode, it is possible to simultaneously separate molybdenum compounds from technetium and their reduction to technetium(IV) oxide in the generally accepted oilated form, which can subsequently be converted into the required ZP form.

The work carried out a study of the electrochemical reduction of pertechnetate ions in mixed alkaline solutions containing molybdate and pertechnetate ions. As a result, a fairly high percentage of recovery of technetium compounds was achieved with an electrolysis time of 30 min.<sup>1</sup>

**Table 1.**

| Experiments with estimated solution concentrations and scanning speed                        | Before electrolysis Activity, Bc/mcg | After electrolysis Activity, Bc/mcg | Before electrolysis S, mmol/l | After electrolysis S, mmol/l | Percentage of extraction, % |
|--|--------------------------------------|-------------------------------------|-------------------------------|------------------------------|-----------------------------|
| 0,0001 M KTcO <sub>4</sub><br>+ 0,01 M Na <sub>2</sub> MoO <sub>4</sub> + 0,5 M NaOH – 1 B/c | 2523                                 | 452                                 | 0,403                         | 0,072                        | 82                          |
| 0,0001M KTcO <sub>4</sub><br>+ 0,01M Na <sub>2</sub> MoO <sub>4</sub> + 0,5 M NaOH – 0,1 B/c | 817                                  | 76                                  | 0,131                         | 0,012                        | 91                          |

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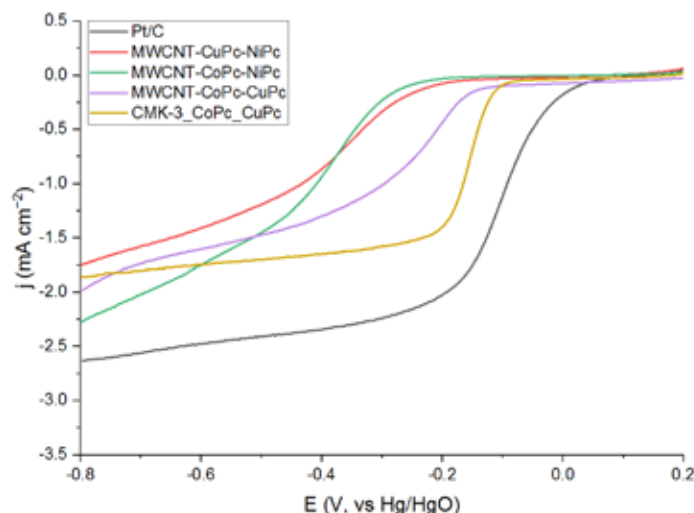
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# CATALYTIC ACTIVITY IN ORR OF CARBON MATERIALS DOPED WITH PHTHALOCYANINES OF TRANSITION METALS

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Carbon materials (carbon nanotubes and mesoporous carbon CMK-3) modified with cobalt, copper and nickel phthalocyanines by pyrolytic method at a temperature of 1000 °C were synthesized and their electrocatalytic properties in the oxygen reduction reaction (ORR) were studied. The catalytic activity of the synthesized samples was tested by linear voltammetry (LV) on a rotating disk glass-carbon electrode. The obtained LV are shown in Fig. 1.



**Figure 1.** LV for synthesized ORR electrocatalysts in oxygen-saturated 0.1 n KOH: 1000 rpm, 5 MV/s.

When comparing bimetallic systems of phthalocyanines of copper, nickel and cobalt on CNTs, the sample based on cobalt and copper shows the greatest activity. Changing the carrier from CNT to CMK-3 makes it possible to improve the characteristics of the catalyst without the use of platinum group metals.

*The research was carried out at the expense of a grant from the Russian Science Foundation No. 23-73-00063, <https://rscf.ru/en/project/23-73-00063/>*

## MECHANICAL PROPERTIES OF POROUS ANODIC ALUMINIUM OXIDE OBTAINED IN PHOSPHOROUS ACID

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Anodic aluminium oxide (AAO) porous films have a unique honeycomb structure. For several applications, such as supports for gas sensors, catalysts and solid oxide fuel cells, their mechanical characteristics are important. Phosphorous acid is an understudied promising electrolyte for preparation of AAO. Its main advantages are the high rate of oxide formation and the ability to achieve large values of interpore distance ( $D_{int}$ )  $\sim 400$  nm and pore diameter ( $D_p$ )  $\geq 150$  nm.

The aim of this work is studying the mechanical properties of AAO films obtained in phosphorous acid.

In this work, anodic oxidation of aluminium was carried out in 1 M phosphorous acid ( $H_3PO_3$ ). It is shown that the most ordered porous structure is formed at a voltage of 170 V and a temperature of 0 °C. The porosity of these films is 14%.

In tension experiments, the 200  $\mu m$  thick film obtained under these conditions can support a weight of 30 kg! The tensile strength and Young's modulus are  $93 \pm 30$  MPa and  $15 \pm 4$  GPa, respectively. Increasing the porosity of AAO by chemical etching of the pore walls to 66% leads to decrease in mechanical characteristics by 2.5 times.

The initial AAO is an amorphous material. Annealing with a maximum temperature of 950 °C leads to crystallization into a mixture of  $\gamma$ -,  $\theta$ - and  $\delta$ - $Al_2O_3$  phases. Annealing with a maximum temperature of 1310 °C leads to the formation of  $\alpha$ - $Al_2O_3$ . After annealing according to the proposed multistage program, the porous structure is preserved, Young's modulus does not change, and the tensile strength decreases by  $\sim 2$  times.

Anodic oxidation of aluminium in 1 M  $H_3PO_3$  allows obtaining mechanically stable porous structures suitable for practical use at high temperatures.

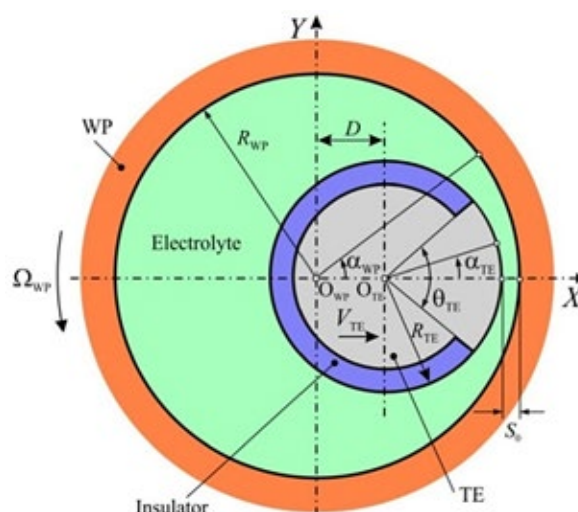
# SIMULATION OF ELECTROCHEMICAL MACHINING OF CYLINDRICAL HOLE BY PARTIALLY INSULATED ECCENTRIC CATHODE

**Volgin V.M.<sup>a,b</sup>, Gnidina I.V.<sup>a</sup>, Sidorov V.N.<sup>a</sup>, Kabanova T.B.<sup>b</sup>, Davydov A.D.<sup>b</sup>**

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Parts made of difficult-to-cut materials with inner cylindrical surfaces are used in various industries such as automotive, aerospace, die/mold, electrical or electronic appliances<sup>1,2</sup>. Along with the methods of mechanical, chemical, and physical treatment, various schemes of electrochemical machining (ECM) are used to fabricate inner cylinder surfaces<sup>3</sup>. Earlier, the regularities of ECM of cylindrical holes with an eccentric non-insulated tool-electrode (TE) were studied<sup>4</sup>. This work is devoted to the theoretical analysis of ECM of holes by an eccentric tool-electrode with a partially insulated surface (Fig. 1).



**Figure 1.** Scheme of ECM by cylindrical TE with partially insulated surface

As a result of the numerical solution, the dependences of the average current density on the angle of active TE surface, the hole radius, and the minimum interelectrode gap are obtained.

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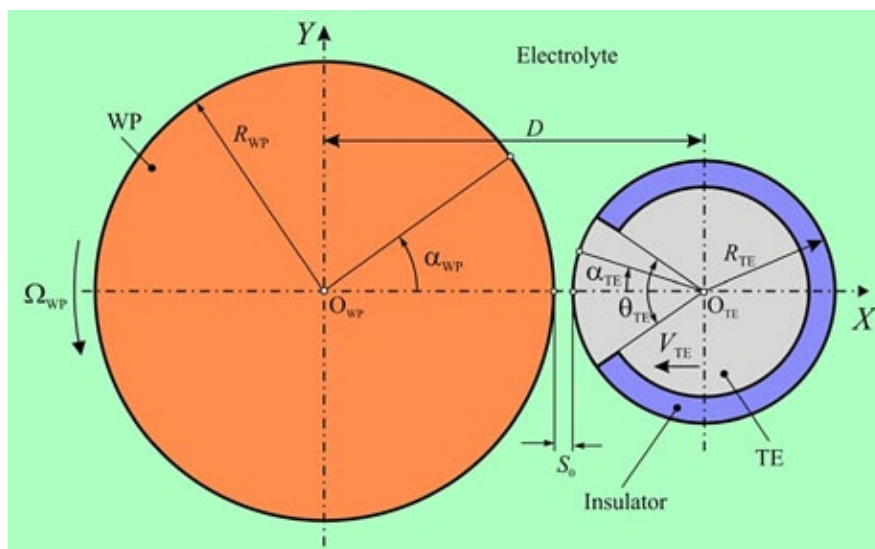
# SIMULATION OF ELECTROCHEMICAL MACHINING OF CYLINDRICAL SURFACE BY PARTIALLY INSULATED CATHODE

**Volgin V.M.<sup>a,b</sup>, Gnidina I.V.<sup>a</sup>, Sidorov V.N.<sup>a</sup>, Kabanova T.B.<sup>b</sup>, Davydov A.D.<sup>b</sup>**

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Electrochemical machining (ECM) is used to process the outer and inner surfaces of rotation of parts made of difficult-to-process materials<sup>1-4</sup>. This work is devoted to the theoretical analysis of the ECM of outer cylindrical surfaces by a tool-electrode (TE) with a partially insulated surface (Fig. 1).



**Figure 1.** Scheme of ECM of cylindrical surface by TE with partially insulated surface

The Laplace equation with boundary conditions of the first kind on the electrodes was used as a mathematical model. As a result of numerical solution by the boundary element method, the dependences of the average current density on the angle of TE active surface, the radius of cylindrical surface and the minimum interelectrode gap were obtained.

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4. Volgin V.M., Gnidina I.V., Sidorov V.N., Kabanova T.B., Davydov A.D. *J. Solid State Electrochem.* 2023, DOI: 10.1007/s10008-023-05661-0.

# APPLICATION OF STRIPPING VOLTAMMETRY FOR THE ANALYSIS OF ELECTRODEPOSITS BASED ON LEAD-BISMUTH

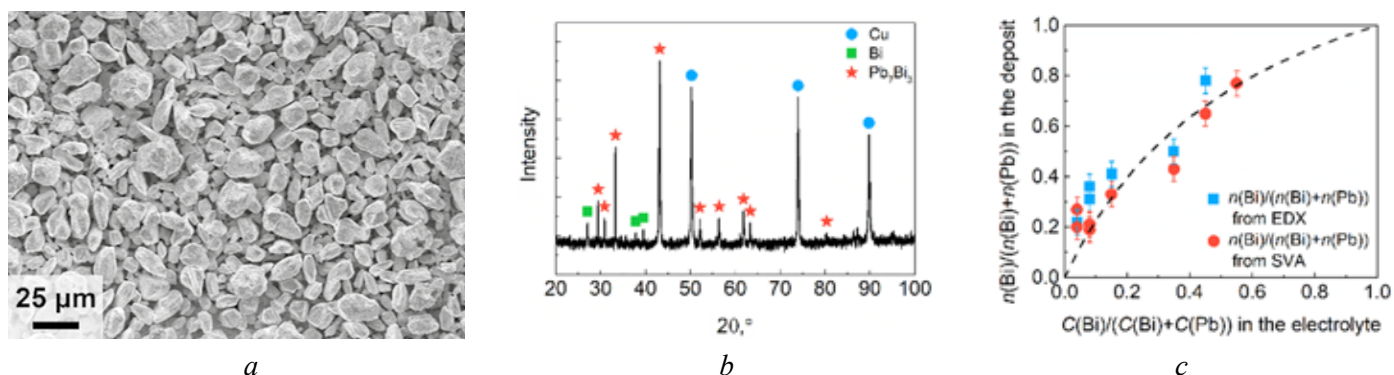
**Voronin I.A.<sup>a,b</sup>, Sotnichuk S.V.<sup>b</sup>, Kolesnik I.V.<sup>a,b</sup>, Napolskii K.S.<sup>a,b</sup>**

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Nanocrystalline materials containing lead and bismuth are promising for creating logic elements of superconducting nanoelectronics. An important analytical task is to determine the chemical composition of the materials in order to further optimize the experimental parameters and fabricate compounds with the necessary structure and physical properties.

In this work, we have analyzed the growth features of Pb-Bi electrodeposits from a trilonate electrolyte of the composition 18.4 mM Pb(NO<sub>3</sub>)<sub>2</sub>, 0.8 mM Bi(NO<sub>3</sub>)<sub>3</sub>, 24.6 mM EDTA-Na<sub>2</sub> and 625 mM NaNO<sub>3</sub> and selected the deposition conditions that allow the formation of Pb<sub>7</sub>Bi<sub>3</sub> intermetallic compound. The parameters for recording stripping voltammograms (SVA) were determined for the analysis of Pb and Bi in the joint presence in the concentration range of 10<sup>-6</sup>–10<sup>-5</sup> M: cleaning time 100 s, frequency 25 Hz, amplitude 20 mV, step 2.5 mV, potential and time of electroconcentration: –0,6 V and 150 s. At a potential of –1.0 V vs Ag/AgCl, the Pb<sub>7</sub>Bi<sub>3</sub> phase is predominantly deposited in the form of homogeneous large particles ~10 μm in size (Fig. 1, *a*, *b*). The found correlation between the electrolyte composition and the deposit composition (Fig. 1*c*) can be used for the targeted synthesis of films and nanostructures in the Pb-Bi system with a given component ratio.



**Figure 1.** SEM image of the surface of a deposit containing 27 at. % Bi (*a*) and its X-ray diffraction pattern (*b*). The molar fraction of Bi in the electrolytic deposit depending on the molar fraction of Bi in the total content of Pb and Bi in the electrolyte, determined by EDX analysis and SVA (*c*)

*The work was carried out with the financial support of the Russian Science Foundation, project 24-23-00450.*

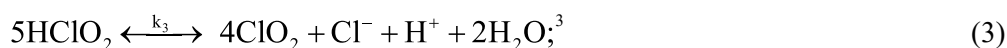
# TIME EVOLUTION OF THE SULFURIC ACID CHLORATE ELECTROLYTE COMPOSITION DURING REDUCTIVE ELECTROLYSIS

**Zader P.A.<sup>a</sup>, Goncharova O.A.<sup>a,b</sup>, Konev D.V.<sup>a,b</sup>, Vorotyntsev M.A.<sup>a</sup>**

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In this work, the process of electroreduction of chlorate anion in an acidic medium (H<sub>2</sub>SO<sub>4</sub>) was simulated. The reduction of ClO<sub>3</sub><sup>-</sup> occurred in a special cell that allowed simultaneous spectroscopic and chronoamperometric measurements. The similarity of the experimental current and chlorine dioxide concentration curves over time suggests that ClO<sub>2</sub> makes a significant contribution to the electrochemical process. To interpret the experimental results, a mechanism for the reduction of the chlorate anion through a redox mediator cycle involving one electrochemical and two chemical stages (1)–(3) is proposed.



The general shape of the chlorine dioxide concentration-time curves and the current-time curves is reproduced fairly accurately. Both the position of the maximum of the curves and their shape near the maximum are qualitatively correctly reproduced. However, at longer times, there is a slight discrepancy between the theoretical and experimental curves. Also, the peak of the theoretical curves is slightly shifted relative to the experimental data.

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# INFLUENCE OF S-MODIFICATION OF A CARBON SUPPORT ON THE DEGRADATION STABILITY OF CATALYSTS FOR PROTON EXCHANGE MEMBRANE FUEL CELLS

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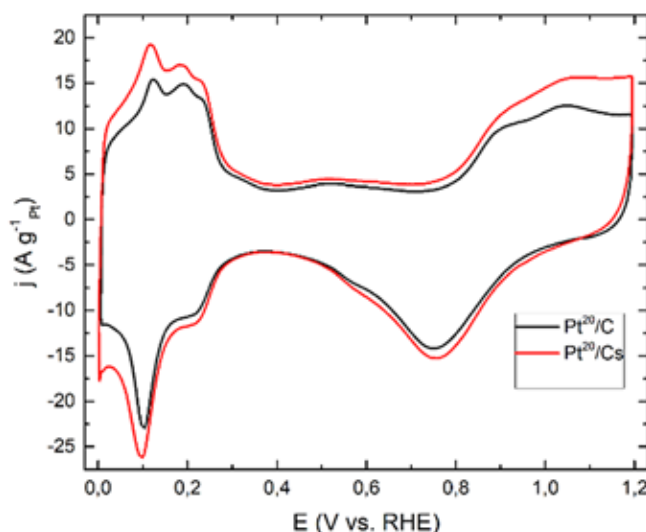
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Proton exchange membrane fuel cells (PEMFCs) are subject to gradual degradation due to corrosion of the carbon support<sup>1</sup>. In order to improve the properties of the support, modification with various compounds, in particular sulfur atoms, is applicable<sup>2</sup>.

In this work, we studied the influence of a modifying additive in the form of sulfur heteroatoms using magnetron sputtering into Vulcan XC-72 carbon black on the main characteristics of a catalyst based on it, as well as on the performance characteristics of a membrane electrode assembly (MEA). Life tests were support out in various modes and environments of a platinum catalyst based on a modified support.

It was shown that for the Pt<sup>20</sup>/Cs catalyst the value of the electrochemically active surface is higher than for the standard catalyst (Fig. 1).



**Figure 1.** Cyclic voltammograms of standard Pt<sup>20</sup>/C catalyst and a catalyst based on carbon black modified with sulfur Pt<sup>20</sup>/C<sub>s</sub>

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# CHIRAL SENSOR BASED ON NANO-SIZED MFI ZEOLITE FOR RECOGNITION AND DETERMINATION OF TRYPTOPHAN ENANTIOMERS

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It is known that the human body is a chiral environment, due to which different enantiomers of biologically active substances entering the body have different pharmacological effects. In some cases, one of the enantiomers can cause side effects or even death. For this reason, the creation of enantiomerically pure compounds has become increasingly important, increasing the importance of quality control of these compounds. To monitor enantiomeric purity, enantioselective voltammetric sensors<sup>1-5</sup> are widely used, which have high selectivity and sensitivity, low cost, and the ability to quickly detect enantiomers of biologically active molecules.

For the selective recognition and determination of tryptophan enantiomers, a voltammetric sensor based on a paste electrode made of graphitized thermal carbon black CarbolblackC and nano-sized MFI zeolite was developed. The sensor detects enantiomers of tryptophan in model solutions, mixtures of enantiomers, biological fluids and tablet forms of dietary supplements. It has been established that when determining the enantiomers of tryptophan, the linear dependence remains in the concentration range from  $5 \cdot 10^{-5}$  to  $1 \cdot 10^{-3}$  M. The detection limits for L- and D-enantiomers of tryptophan are  $4.98 \cdot 10^{-7}$  M and  $3.20 \cdot 10^{-7}$  M respectively. The sensor is more sensitive to D-tryptophan ( $\Delta E_p = 20$  mV,  $i_pD/i_pL = 1.58$ ). It was shown that the proposed sensor makes it possible to determine with high probability the ratio of L- and D-enantiomers of tryptophan in a mixture. The main advantages of the developed sensor include ease of manufacture, low cost, and storage stability.

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# EFFECT OF SIDE GROUPS ON CATIONIC PHTHALOCYANINE COMPLEXES WITH ZINC ATOM ON THEIR ADSORPTION AND INITIATION OF BLM CONDUCTIVITY

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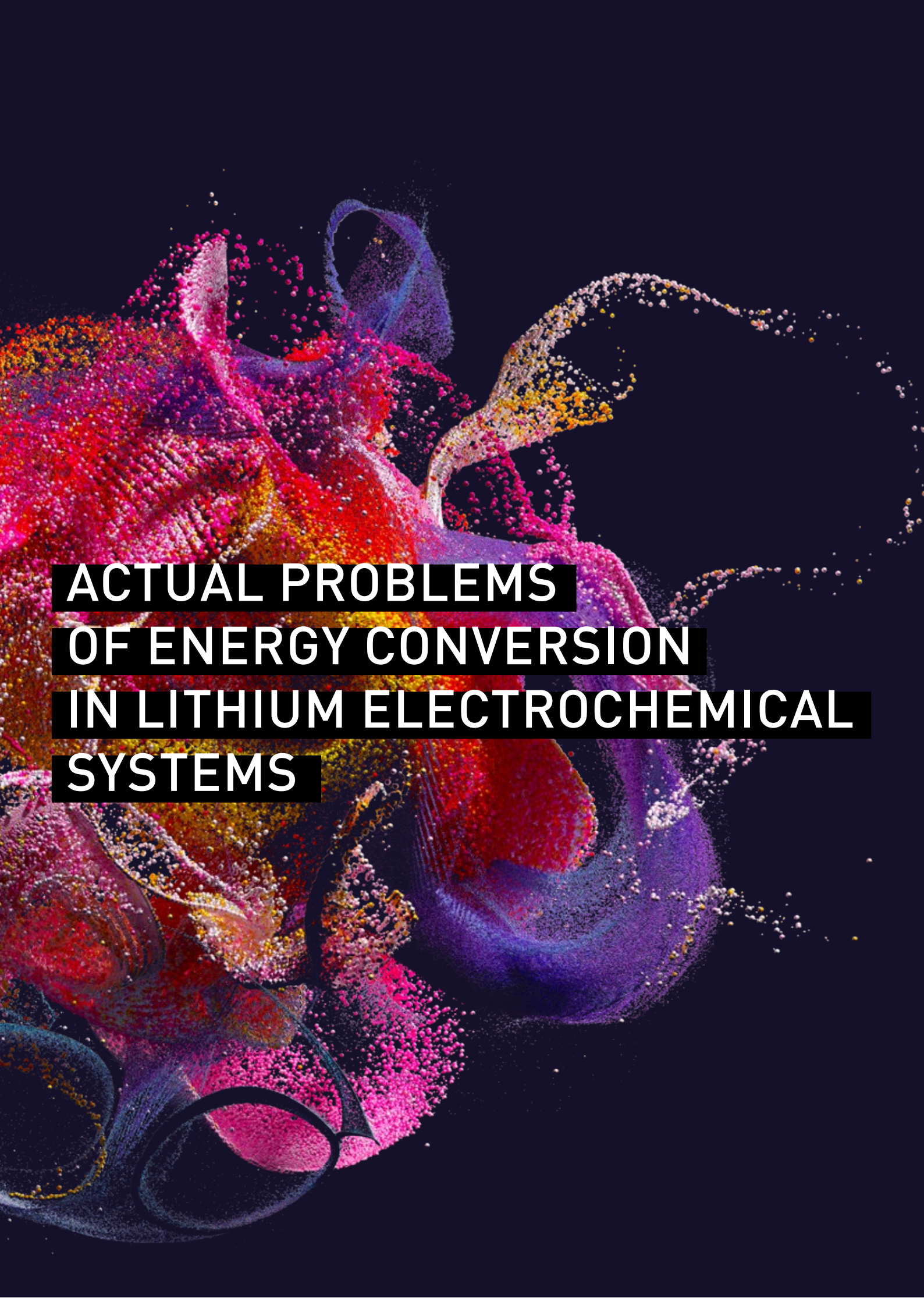
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The efficacy of photosensitizers against tumour cells and pathogenic bacteria is largely determined by their ability to adsorb on a membrane, which can be studied in vitro on models such as bilayer lipid membranes (BLMs). In this work, the adsorption on BLM of cationic complexes of phthalocyanine (Pc) with one zinc atom 8bZnPc, 8aZnPc, 4aZnPc and 4bZnPc, differing in the position and number of charged side groups, was studied. The binding of these compounds on BLM was detected by two main methods: Inner Field Compensation Method, measuring the change in the interfacial potential, and the BLM conductance measurements.

The values of the boundary potentials for 8aZnPc and 8bZnPc were practically identical, indicating that the position of the charged side groups does not affect their affinity. As it was found earlier, the incorporation of 8bZnPc into a BLM causes an increase in its conductivity which disappears with time. The conductivity value was proportional to the square of the 8bZnPc concentration in the solution. This was explained by the formation of lipid pores during the incorporation of 8bZnPc aggregates from an aqueous solution into BLM with their subsequent decomposition into monomers. The increase in conductivity was observed in BLMs formed from not only the solution of lipids in decane, but when it was changed to squalane, leading to decrease the thickness of BLM to that of cell membranes. The study of the kinetics of current relaxation during a voltage change showed that the current through lipid pores is limited by the diffusion of ions in an aqueous solution. The results of investigation indicate that 8bZnPc can increase the conductance of the lipid component of the cell membrane that attenuates its barrier capability, hence, can lead to die of the cell without illumination. This effect wasn't observed with other phthalocyanines (8aZnPc, 4aZnPc and 4bZnPc).

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# **ACTUAL PROBLEMS OF ENERGY CONVERSION IN LITHIUM ELECTROCHEMICAL SYSTEMS**

# LAYERED OXIDE CATHODES FOR LI-ION BATTERIES: RESEARCH DIRECTIONS

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Competition between the electric and internal combustion engines requires overcoming the technological barrier in specific energy of Li-ion battery cells of 300 Wh/kg by 2025, and 350 Wh/kg - by 2030, which is impossible without advanced cathode materials, such as Ni-rich layered transition metal oxides NMC811 or NMC9,0.5,0.5 (NMCxyz denotes  $\text{LiNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$ , where  $x+y+z = 1$ ), providing electrochemical capacity up to ~220 mAh/g. NMC cathode materials are still the subject of intense research aimed at increasing mass and volumetric energy density, cycle life, and performance at elevated charge/discharge rates. Almost all elements of the Periodic Table were used to dope and create protective coatings for NMC materials, with the exception of highly toxic, radioactive and chemically inert ones [1].

Future optimization directions of the NMC cathode materials, however, are significantly more diverse and include:

- creation of an optimal concentration of point defects for the simultaneous implementation of high capacity, transport of Li cations and structural stability;
- modification of grain boundaries to increase the crack resistance of agglomerates of primary particles;
- manipulation of the shape and arrangement of primary particles in agglomerates to relax mechanical stresses and straighten the Li diffusion paths;
- crystal shape design to increase tap density and volumetric energy density.

These directions will be illustrated in the talk using examples of polycrystalline NMC811 cathode materials with grain boundaries modified with lithium sulfate and borate [2, 3], with a predominant radial orientation of particles due to the creation of a concentration gradient [4], and using the example of single-crystalline materials with “spherical” crystal shape [5]. The chemistry of point defects in NMC, its dependence on synthesis conditions, and methods for determining the concentration of defects on different spatial scales will also be discussed [6].

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# PHOSPHATE CATHODE MATERIALS FOR LITHIUM-ION BATTERIES AND METHODS FOR THEIR IMPROVEMENT

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Phosphate cathode materials are a major alternative to oxide compounds as lithium-ion battery (LIB) cathodes, primarily due to the success story of lithium iron phosphate  $\text{LiFePO}_4$ , often referred to as LFP. The main difference between phosphate materials and oxide ones is the presence of phosphate ( $\text{PO}_4$ ) or pyrophosphate ( $\text{P}_2\text{O}_7$ ) groups, which form a reliable structural framework and “bind” oxygen anions. Due to these factors, phosphate-based materials demonstrate stable cycling over thousands of charge-discharge cycles, the ability to quickly charge or discharge, as well as increased thermal stability, i.e. safety of use. Currently, LFP has become the basis of an entire direction both in research activities and in the field of LIB industry - actively developing and extremely promising. However, the issue of increasing the specific energy density of batteries with the transition from oxide materials to LFP arises very acutely, and today there are three main ways to solve it: 1) increasing energy density by replacing part or all of Fe with Mn (with an increase in the average cell voltage from 3.4 to 4.1 V vs.  $\text{Li/Li}^+$ ), 2) improving the density of deposition of active layers and increasing the proportion of active material in the total mass of the battery and 3) transition to solid electrolyte and metal lithium (or so-called “anodeless” systems) at the anode.

The report discusses the results of the main ways to achieve these goals. In particular, the use of the solvothermal method for the synthesis of  $\text{Li(Fe,Mn)PO}_4$  phosphates in combination with spray drying makes it possible to obtain powders of cathode materials with a fairly high ( $\sim 1.5 \text{ g/cm}^3$ ) bulk density, and the use of water-based binders and single-walled carbon nanotubes improves the electrochemical properties of materials even with a high ( $>95\%$ ) mass fraction of phosphate in the electrode composite and a load of more than  $3 \text{ mAh/cm}^2$ .

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# ANODE-FREE LITHIUM AND SODIUM BATTERIES

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The term "anode-free batteries" was introduced for batteries in which, in the discharged state, the negative electrode consists only of a current collector. The design of such batteries includes a positive electrode current collector coated with lithiated (or sodiated) cathode material, a separator, a negative electrode current collector and an electrolyte. During charging, lithium (sodium) ions are extracted from the cathode material and deposited on the negative electrode current collector as a metal deposit. During the discharge, the resulted layer of metal lithium (sodium) dissolves and the negative electrode current collector is completely freed from metal deposits.

Recently, anode-free batteries have attracted increasing attention due to their lower cost and highest energy density. However, problems with lithium (sodium) dendrite formation and resulting degradation during cycling make it difficult to commercialize anode-free batteries. For anode-free batteries to be commercialized, it is necessary to maintain a high average Coulombic efficiency ( $>99.9\%$ ) of the lithium (sodium) deposition/dissolution process on the negative electrode current collector. Ways to solve this problem include: (1) different electrolyte compositions; (2) negative electrode current collector design; (3) control of the chemical and physical properties of the solid electrolyte interface (SEI) formed on lithium (sodium); (4) creating artificial SEI with good mechanical properties and high ionic conductivity; (5) optimization of the ratio of battery charge and discharge rates.

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# CONTROL OF CONDUCTIVITY WINDOW OF POTENTIORESISTIVE MATERIALS FOR PROTECTION OF LITHIUM-ION BATTERIES

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Feedback materials that change their properties under the influence of an external stimulus are the basis of many sensing and actuating devices. In the field of lithium-ion batteries (LIBs), materials with variable conductivity are of particular importance to prevent the development of processes leading to overheating and explosion of the battery in case of overcharging or short circuits. A promising approach to LIB protection using conjugated conductive polymers that change to a non-conductive state when the dangerous value of the electrode potential is reached has been recently proposed by the authors of the project. The key property determining the protective properties of the materials under consideration is the bell-shaped dependence of their conductivity on the applied potential. For the observed effect, the authors propose to use the term “potentioresistivity” by analogy with “thermoresistivity”. At the moment the application of potentioresistive protection is limited by the range of conductivity of known conducting polymers. However, varying the conduction window of potentioresistive materials is fundamentally possible, and can be used to create materials whose conduction window corresponds to different LIB configurations.

The report discusses the possibility of creating potentioresistive materials with predetermined parameters of the conduction window based on composites of conducting polymers with redox additives, where the composition of the composite will determine the parameters of the conduction window. By changing the composition of the composite it is possible to synthesize materials with a controlled range of potentials and amplitude of change in electrical conductivity, which is relevant for their use as protective layers in battery systems and other devices.

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# ATOMISTIC MODELING OF INTERFACES AND IONIC TRANSPORT IN METAL-ION BATTERIES

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The electrochemical performance of metal-ion batteries depends heavily on the rapid transport of metal ions not only within solid electrodes but also across electrolyte/electrode interfaces. Accurately measuring metal-ion transport experimentally is challenging due to the nanostructured composition of electrode materials and interactions with the electrolyte. This underscores the importance of employing computational methods at the atomic level to comprehend the mechanisms of ionic transport and assess the inherent activation barriers for metal ion diffusion. Analyzing ionic transfer through interfaces presents an even greater challenge. Atomistic modeling enables us to meticulously track the transfer process, but before this can be achieved, obtaining the correct interface structure is a non-trivial task.

In this presentation, we illustrate our successful calculations of migration barriers and our comprehensive understanding of the high ionic conductivity observed in polyanion cathode materials, aligning closely with experimental results<sup>1</sup>. Additionally, we delve into how we determine the equilibrium shape of crystals and the most stable surfaces through density functional theory slab calculations<sup>2</sup>. Furthermore, we address the intricate effects of chemical composition, such as surface segregation, and demonstrate our meticulous treatment to accurately incorporate these complexities<sup>3</sup>. Lastly, we showcase the construction of a complete solid metal/electrolyte interface and the calculation of charge-transfer activation energies, providing insights into the origins of interfacial resistance in solid-state batteries<sup>4</sup>.

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# RUSSIAN EQUIPMENT FOR ELECTROCHEMICAL RESEARCH SMARTSTAT

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The Russian scientific and production company SmartStat specializes in the development, serial production and supply of modern scientific equipment for electrochemistry.

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SmartStat potentiostats are being developed and assembled in Russia with 100% localization of housing and all electromechanical components. At the same time, the achievement of the highest characteristics and functional indicators of such products would be impossible today without the use of the best electronic components of Western production. SmartStat's strategic independence from international situations is ensured by a sufficient stock of such components in our warehouses. Tactical flexibility and high speed of deliveries are ensured by the mandatory availability of finished products in our warehouse in the Moscow region.

To date, our production potentiostats occupy more than 90% of the market in Russia. In many ways, this is due to the clear and well-coordinated work of the company's team, focused on the fastest and most comfortable deliveries for our customers. Our scientific competencies ensure the optimal solution of your tasks in a wide variety of fields of electrochemistry.

# CHEMICAL PROCESSES AT THE ELECTRODE/ ELECTROLYTE INTERFASE IN LITHIUM-ION BATTERIES

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A process of CEI (cathode electrolyte interphase) formation on a surface of an active material of the positive electrode of lithium-ion battery (LIB) is usually considered similar to those of SEI (solid electrolyte interphase) on the negative carbon electrode. Therefore, the formation of a film of insoluble products on the electrode surface is considered as a result of the electrochemical oxidation of electrolyte solution components. However, unlike carbon, the active materials of the positive electrode  $\text{Li}_x\text{MO}_y$  (where M is a transition metal) initially contain a large amount of lithium ions. The chemical activity of  $\text{Li}_x\text{MO}_y$  is high enough to interact with an electrolyte solution in a manner of lithium metal. For positive electrode materials, the contribution of such side chemical reactions is greatly underestimated and is most often masked by the overall degradation processes during cycling or aging of the electrode under partial charge (discharge) conditions. However, it is precisely these chemical interactions that occur during the LIB fabrication process immediately after  $\text{Li}_x\text{MO}_y$ -based electrode and electrolyte contact (i.e., under current-free conditions) leading to the formation of a primary CEI layer from the products of chemical interaction. The products of electrochemical oxidation of the electrolyte components and further chemical processes are subsequently layered onto this primary layer. The reason of side chemical reactions is mutual thermodynamic instability of  $\text{Li}_x\text{MO}_y$  and lithium salt (usually  $\text{LiPF}_6$ ). In addition, catalytic polymerization of solvent molecules on the surface of  $\text{Li}_x\text{MO}_y$  particles can take place. Similar processes can also take place in the anode half-cell if it contains non-carbon materials. The primary layer of interaction products has a decisive influence on the barrier properties of the final CEI layer formed during long-term battery operation.

*The work was carried out in accordance with the state assignment for the Institute of Solid State Chemistry of the Ural Branch of the Russian Academy of Sciences (registration no. NIOKTR 124020600047-4).*

# RECYCLING OF SPENT LITHIUM ION BATTERIES INCLUDING ELECTROLYTE AND CATHODE MATERIALS

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While large-scale recycling of waste lithium-ion batteries has been undertaken by domestic and foreign enterprises, the existing process technologies face three major issues: Firstly, research on electrolyte separation and recycling needs further reinforcement, as direct combustion can easily lead to resource wastage and secondary pollution to water bodies and the atmosphere.<sup>1</sup> Secondly, the technical route for recycling and reusing lithium-ion battery materials remains relatively intricate, involving lengthy process flows.<sup>2-3</sup> Thirdly, the recovery rates of lithium ions and transition metal ions require improvement.<sup>4-5</sup>

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# DEVELOPMENT OF NEW-GENERATION ELECTRODE MATERIALS FOR NA-ION BATTERIES

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The commercialization of sodium-ion batteries requires advanced positive electrode materials showing superior electrochemical properties<sup>1</sup>. In a competition between oxide and polyanion classes of materials, the latter show extraordinary stability and power characteristics. At the same time, the polyanion materials display a rich variety of crystal structures offering vast opportunities for designing new materials with unique properties.

In my research group, a new prospective class of positive electrode materials has been designed by fusing a promising  $\text{NaVPO}_4\text{X}$  ( $\text{X} = \text{F}, \text{O}$ )<sup>2,3</sup> chemical composition and a high-rate  $\text{KTiOPO}_4$ -(KTP)-type structural framework with attractive transport properties, enabled by a specially developed low-temperature ion-exchange synthesis approach. Depending on X materials exhibit up to 120-135 mAh g<sup>-1</sup> of reversible capacity (80-90% of the theoretical values) at average discharge potentials of 3.7-4.0 V vs. Na<sup>+</sup>/Na. The fluoride phosphate follows an advantageous solid-solution mechanism, whereas switching to oxophosphate activates several minor phase transitions. Overall, KTP-type  $\text{NaVPO}_4\text{X}$  phosphates unlock the practical specific energy in the range of 480-540 Wh kg<sup>-1</sup> offering a new benchmark for the Na-ion battery positive electrodes.

In the talk, different aspects and peculiarities of synthesis, crystal structure refinement, materials characterization and electrochemical properties of new cathode materials will be highlighted with special attention to the composition-structure-property relationships. A particular emphasis will be given to the comparison of KTP- $\text{NaVPO}_4\text{X}$  against their polymorphic modifications and other related cathode materials

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# DIAGNOSTICS OF ELECTROCHEMICAL PROCESSES IN HETEROGENEOUS INTERCALATION ELECTRODE MATERIALS AS A BASIS FOR IMPROVING OF THEIR CHARACTERISTICS

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Lithium-ion batteries (LIB) are currently considered as the most promising autonomous electrical energy storage devices. Cathode materials are the largest and most diverse group of LIB materials and components. The most energy-intensive LIB cathode materials are mixed oxides of lithium and several transition metals (Ni, Co, Mn) with a layered structure, which are often abbreviated NCM in the literature. Many researchers note that the morphology and surface state of cathode material particles have a significant impact on its electrochemical characteristics<sup>1</sup>. Immediately after synthesis, the surface of NCM is covered with a significant amount of lithium compounds:  $\text{Li}_2\text{CO}_3$ ,  $\text{LiOH}$ , which are the remains of unreacted starting substances and products of their transformation. Many researchers associate their presence on the NCM surface with accelerated degradation of the cathode material characteristics, which may be due to the hindered transport of lithium ions through the surface layer into the particles<sup>2</sup>. In the literature, such a layer is usually denoted by the abbreviation CEI (Cathode Electrolyte Interphase). A solution to the mentioned problem may be to replace native CEI with its artificial analogue – a fairly chemically inert layer with high ion-conductive characteristics. All this makes it extremely important to study mass transfer processes in such morphologically complex formations as LIB cathode materials. Approaches to studying such characteristics were discussed in detail in our recently published work<sup>3</sup>.

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# NOVEL HIGH-CAPACITY ANODE MATERIALS FOR SODIUM-ION BATTERIES

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The successful development of sodium-ion batteries (SIBs), which are considered as an alternative to rechargeable batteries for large-scale applications, is impossible without improving the electrode materials that determine the energy intensity and power of these devices. In this regard, the search for new materials with multielectron redox transitions is crucial and could lead to a significant increase in energy density of SIBs.

In this work, we introduce novel anode materials for SIBs based on niobium phosphates  $\text{NaNbM}(\text{PO}_4)_3$  (where  $\text{M} = \text{V}, \text{Cr}$ ) with the NASICON structure<sup>1,2</sup>. The obtained materials exhibit reversible electrochemical intercalation up to 3  $\text{Na}^+$  ions per formula unit, providing a high specific capacity of about  $160 \text{ mA h g}^{-1}$  at 1C rate. s Electrochemical processes corresponding to multi-electron redox transitions, such as  $\text{Nb}^{5+}/\text{Nb}^{4+}$ ,  $\text{Nb}^{4+}/\text{Nb}^{3+}$  и  $\text{M}^{3+}/\text{M}^{2+}$ , occur at an average operating potential of 1.5 V (vs.  $\text{Na}^+/\text{Na}$ ), thus eliminating the possibility of sodium plating upon cycling at high rates and providing an advantage over hard carbon anodes currently used in SIBs. Furthermore, these materials demonstrate high thermal stability superior to that of hard carbon anodes.

Given the numerous benefits, such as working potentials, high thermal and cyclic stability, facile and scalable synthesis these high capacity anode materials could be considered as promising candidates for use in long-term application in devices of various sizes from compact uninterruptible power supplies to large-scale batteries for renewable energy storage systems.

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# IMPROVING THE SAFETY OF LITHIUM-ION BATTERIES: PROTECTION STEPS

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The use of lithium-ion batteries (LIB) is becoming more widespread every day, from small-sized current sources for portable microelectronic devices to traction batteries for electric vehicles. The wide range of LIB applications is determined by high energy density, long service life, high reliability and safety while meeting the requirements of operation. However, violation of the operating conditions of the LIB can lead to an emergency situation, up to fire and explosion. By these, lithium-ion batteries include various protection elements that prevent the development of an emergency situation at a certain stage, thus forming protection stages. The steps of protection include:

1. The type of electrochemical system that allows to set the threshold for the onset of thermal runaway;
2. The composition of the separator, which allows to set the temperature range at which the porous structure of the polymer will melt, leading to a decrease in ionic conductivity;
3. Fused current collectors, which are a metallized polymer film that collapses when a certain temperature is reached, leading to a decrease in electronic conductivity or to a circuit break;
4. Membranes that operate at a certain pressure and thus prevent rupture of the LIB case;
5. External coatings of LIB with directional heat dissipation to prevent heating of adjacent LIB in the battery;
6. External fire extinguishing coatings of LIA.

Thus, an integrated approach, namely the correct arrangement of temperature ranges at which each of the protection stages in the LIB should work, will minimize, or completely eliminate the development of an emergency situation.

# HIGH-ENERGY ELECTRODE MATERIALS WITH DISORDERED ROCK SALT STRUCTURE

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Almost all known cathode materials for lithium-ion batteries (LIB) with high energy density have a well-ordered crystal structure, in which lithium and d-metal ions occupy their own structural positions and are divided into corresponding sublattices. Materials with a disordered structure were not previously considered as candidates for LIB cathodes due to the lack of diffusion channels in them, as well as due to the metastable nature of many disordered phases. In recent years, there has been increased interest in new classes of lithium-excess cathode materials – oxides or oxifluorides with a disordered rock salt structure (DRX) of  $\text{Li}_y(\text{M}_1\text{M}_2)_{2-y}\text{O}_2$  and  $\text{Li}_{1+x}(\text{M}_1\text{M}_2)_{1-x}\text{O}_{2-y}\text{F}_y$  compositions, where  $\text{M}_1=\text{Ti}^{4+}$ ,  $\text{Nb}^{5+}$ , and  $\text{M}_2=\text{Mn}^{3+}$ , in which  $\text{Li}^+$  and transition metal (TM) ions are equally likely to occupy the same octahedral positions in the lattice, and the diffusion of  $\text{Li}^+$  ions occurs by passing from one octahedron to another through an intermediate tetrahedron. To maintain macroscopic migration of  $\text{Li}^+$  ions, O-M diffusion channels must form a percolation network. A necessary condition for the transport of  $\text{Li}^+$  ions in DRX is an excess of the content of  $\text{Li}^+$  over TM by at least 10% (percolation threshold). TM ions, in which the electronic configuration of the valence level can be written as  $d^0$ , such as  $\text{Ti}^{4+}$ ,  $\text{Nb}^{5+}$  and  $\text{Mo}^{6+}$ , increase the structural stability of DRX oxides, while the remaining TM ions are electrochemically active. The combination of TM with highly charged  $d^0$  ions contributes to the enrichment of DRX with  $\text{Li}^+$  ions and an increase in their specific capacity. The advantage of DRX over classical ordered cathode materials is their high reversible capacity (more than  $300 \text{ mAh}\cdot\text{g}^{-1}$  at elevated temperatures), which is achieved through multielectronic processes involving cationic  $\text{TM}^{(n+1)+}/\text{TM}^{n+}$  ( $\text{TM} = \text{Mn}^{3+}$ ,  $\text{Fe}^{3+}$ ,  $\text{V}^{3+}$ ,  $\text{Mo}^{3+}$ , etc.) and anionic  $\text{O}^{2-}/\text{O}^{\cdot-}$  redox couples.

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# MAIN RESULTS ON THE DEVELOPMENT OF LITHIUM-ION BATTERIES FOR SPACE AND SPECIAL APPLICATIONS AND WORK PLANS TO MODERNIZE THEIR PERFORMANCE

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One of the main challenges in developing power supply systems for modern spacecraft is providing them with efficient and reliable secondary power sources – rechargeable batteries that can operate in autonomous mode for up to 15 years.

Currently, lithium-ion batteries (LIBs) are considered to be the most promising type of battery for space applications.

The report presents the results of work carried out by Saturn JSC to develop accelerated life test methods for the LCO/C system. LCO stands for lithium cobaltate of domestic production by LLC Renera (formerly NCCP), which is part of the Rosatom State Corporation. In addition, the report presents a number of developed batteries for space applications and their specifications. The results of these batteries' flight tests since 2012 have confirmed the results of their ground life testing.

Until recently, the increase in the specific power characteristics of batteries was carried out mainly due to the improvement in battery design and manufacturing technology. The achieved specific power characteristics of the LCO/C system batteries for GEO and LEO modes are marginal, at 180 Wh/kg and 170 Wh/kg respectively. Further improvements in these characteristics are possible through use of more advanced active materials, essentially those for the positive electrode.

The report presents the results of tests (including life ones) of battery prototypes with NMC 622 active material by OOO Rustor in GEO and LEO modes in comparison with standard batteries of Saturn JSC. Assessments have been carried out to improve the energy capacity properties of space batteries by replacing LCO to NMC 622 and to NMC 811. The potential of using active materials of this type to enhance the energy capacity capabilities of space batteries has been demonstrated.

# DATE SEED-DERIVED SUPERCAPACITOR ELECTRODES IN AQUEOUS ELECTROLYTE

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Date seeds, often considered byproducts of date fruit processing, represent a significant bio-waste stream. Despite their abundance, these seeds are underutilized and typically regarded as agricultural waste. Rich in carbon content, date seeds have the inherent potential to serve as precursors for hard carbon electrodes in supercapacitors. To enhance cyclic stability and improve Coulombic efficiency, free-standing electrodes were fabricated, showcasing superior electrochemical performance. The activation process with a 1:3 KOH-to-bio-char ratio yielded a specific capacitance of 204 F/g at current density of 0.2 A/g with an energy density of 6.5 Wh/kg and a power density of 47.70 W/kg, highlighting the effectiveness of this approach in advancing both structural integrity and electrochemical attributes.

To elucidate the electrochemical performance of KOH-activated hard carbon, BET analysis, Scanning Electron Microscopy (SEM), and Raman Spectroscopy were employed. BET analysis revealed a higher surface area of 2423.4 m<sup>2</sup>/g for the hard carbon activated with a 1:3 KOH ratio. This enhancement in structural integrity was further corroborated by cyclic voltammetry (CV) and charge-discharge curves, emphasizing the favorable electrochemical attributes of the proposed method.

While previous investigations into date seed supercapacitors revealed promising results, achieving near 100% Coulombic efficiency remained a challenge. In this study, the implementation of free-standing electrodes marked a significant advancement, resulting in a remarkable Coulombic efficiency of 99.97%. This nuanced approach underscores the effectiveness of our methodology in addressing and improving the Coulombic efficiency of date seed-derived supercapacitors.

# SILICON ANODE MATERIALS FOR LITHIUM-ION BATTERIES WITH THE INCREASED SPECIFIC ENERGY

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Silicon anode materials for lithium-ion batteries attract much attention of researchers because of their high specific capacity and potentially low cost. The commercially available silicon anode materials can be divided into two groups: non-stoichiometric silicon oxides  $\text{SiO}_x$  ( $x \sim 1$ ) and silicon-carbon composites Si-C. The sample analysis has shown that  $\text{SiO}_x$  materials may contain, apart from the nanoparticles of the active material, significant amounts of magnesium silicates, while the Si-C material consists of micrometer-sized amorphous silicon particles coated with carbon. In half-cells against Li metal, samples of the commercial silicon anode materials demonstrate the discharge capacities of up to 1600 mAh/g (at the charge-discharge rate of 0.1 C) with the initial Coulombic efficiency as high as 0.87. No noticeable capacity fade has been observed for at least several tens of cycles. It is worth mentioning that thicker electrodes with the areal density of the active material exceeding 2 mg/cm<sup>2</sup> demonstrate significant decrease of the capacity with the increase of the charge-discharge rate.

Despite the large number of publications describing the synthesis of silicon anode materials by the reduction of silicon compounds with Mg metal, these methods rarely produce the materials suitable for the practical use because of the crystallization of the silicon particles and the formation of undesirable magnesium compounds. The materials synthesized in our laboratory by these methods demonstrated insufficient stability during the cycling in the test cells.

A more promising synthesis method for the stable high-capacity silicon anode materials suitable for the practical use in the lithium-ion batteries is the deposition of Si and  $\text{SiO}_x$  from the gas phase. As far as we know, such methods have been employed for the synthesis of the commercially available silicon-based anode materials tested in our laboratory.

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# WATER SOLUBLE POLYMER BINDERS FOR LITHIUM-ION BATTERY ELECTRODES

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Electrodes for lithium-ion batteries based on  $\text{LiFePO}_4$  and various water-soluble polymer binders PEDOT-PSS, hydrolyzed polyacrylonitrile (HIPAN) and carboxymethylcellulose have been developed [1,2]. The electrodes were prepared with the addition of single-walled carbon nanotubes (CNTs), which are a promising electrically conductive component. Since CNTs are prone to aggregation in an aqueous environment, the key task was to ensure uniform distribution of CNTs within the electrodes by using a binder as a dispersion stabilizer and thickener.

This work examines the ability of water-soluble binders to ensure aggregative stability of CNT dispersions in an aqueous environment at different pH. It has been established that stabilization of CNT dispersion ensures uniform distribution of CNTs within the electrodes and high capacitive characteristics.

The electrochemical characteristics of electrodes with water-soluble binders were superior to those of electrodes with the classical binder polyvinylidene fluoride. However, the use of electrically conductive binders did not lead to an improvement in the characteristics of the electrodes compared to commercially available analogues (HIPAN and carboxymethylcellulose). The developed electrodes demonstrated cyclic stability for at least 200 charge-discharge cycles.

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# POLYMER ELECTROLYTES FOR LITHIUM METAL BATTERIES

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The desire to increase the specific capacity of lithium-ion batteries leads to the need not only to improve cathode materials, but also to use a lithium metal anode. However, this increases the risk of lithium dendrite growth and battery safety problems. A promising approach to solve these problems is manufacturing all-solid-state batteries, in which solid electrolytes play a key role. In this regard, much effort has been made in recent years to develop solid electrolytes that can compete with liquid electrolytes in ionic conductivity and at the same time ensure battery safety.

Solid electrolytes can be divided into inorganic, for example, complex oxides of a garnet-type, complex phosphates with a NASICON structure, sulfide materials, and polymer (solid and gel polymer) electrolytes. The latter are the most popular because they are characterized not only by high mechanical stability and elasticity, but also in some cases demonstrate high ionic conductivity. Solid polymer electrolytes consist of inert polymers with dissolved lithium salt, while gel polymer electrolytes consist of a liquid electrolyte (more than 50 wt.%) immobilized in a polymer matrix. Liquid electrolyte commonly consists of an ionic liquid or lithium salt solution in aprotic solvents, which provides ionic conductivity of about  $\sim 10^{-3}$  S/cm at room temperature. An interesting class of polymer electrolytes are materials based on cation exchange membranes, which are usually also solvent immobilized. At the same time, the most promising studies seem to be those devoted to the development of composite electrolytes containing a polymer electrolyte with an inorganic filler (with or without their own lithium conductivity), which makes it possible to create materials that combine high conductivity and good mechanical properties.

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# STRUCTURAL MODULATION AND LARGE-SCALE PREPARATION OF PHOSPHATE-BASED COMPOUNDS FOR SODIUM ION BATTERIES

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Sodium-ion batteries possess abundant resources, high safety, and excellent low-temperature performance, rendering them promising for large-scale green energy storage. Polyanion compounds with a unique framework structure not only offer high ionic conductivity but also demonstrate exceptional structural and thermal stability during electrochemical processes, making them an ideal choice for cost-effective, long-lasting Na-ion battery cathode materials.<sup>1-2</sup> However, the poor electronic conductivity of these materials hinders their electrochemical reaction kinetics. phosphate-based cathode materials have been prepared by solid-phase synthesis method combining with advanced improvement techniques (e.g., heteroatom doping, in-situ carbon coating and nano treatment), exhibiting excellent sodium ion storage performances. The solid-phase synthesis method represents a general approach for large-scale production of polyanion-based cathode materials.<sup>3-4</sup> Heteroatom doping enhances the internal electronic conductivity of primary particles while in-situ carbon coating establishes an internal carbon micro-network for electron transport within secondary particles and suppresses structural failure during charging and discharging processes. Nanoparticle size reduction shortens the transmission path of electrons and ions within individual particles. Consequently, these approaches improve the rate capability and cycling stability of polyanionic compound cathode material. Currently, the solid-phase synthesis method is the main technology for industrial production of lithium iron phosphate. By adjusting and modifying the existing lithium iron phosphate production equipment, it is possible to achieve the scaled production of phosphate-based polyanionic cathode materials, thus accelerating the rapid development of the sodium-ion battery industry.

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# PERSPECTIVE GEL ELECTROLYTES FOR LITHIUM POWER SOURCES

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Lithium-polymer batteries are of interest to developers of new chemical power sources as a safe alternative to existing lithium-ion batteries.

This report will present the results of work on the creation of two new compositions of polymer gel electrolytes (PGE) for lithium batteries. According to the synthesis method, these PGEs belong to different classes, namely gel electrolytes with *in situ* polymerization and nanocomposites with the introduction of an ionic liquid obtained by a radical polymerization reaction of the oligomer.

Model experiments showed the promise of using a gel electrolyte obtained directly in a battery prototype by mixing two liquid electrolytes of the composition 1M LiTFSI in dioxolane/dimethoxyethane (2:1) and 1M LiPF<sub>6</sub> in ethylene carbonate/dimethyl carbonate (1:1)<sup>1</sup>.

The second type of PGE<sup>2-3</sup> consists of polyethylene glycol diacrylate, LiBF<sub>4</sub> salt, ionic liquid 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIBF<sub>4</sub>), ethylene carbonate and SiO<sub>2</sub> or TiO<sub>2</sub> nanoparticles. It was shown that the obtained PGEs, along with high thermal stability up to 350 °C, have high conductivity up to 10 mS/cm and a wide range of operating temperatures from -40 to 100 °C. SiO<sub>2</sub> and TiO<sub>2</sub> nanoparticles provide priority ion transport for lithium cations in the EMIBF<sub>4</sub> ionic liquid environment, which makes them promising for lithium batteries.

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# SPHERICAL COMPOSITE MICROPARTICLES $\text{LiFePO}_4$ FOR HIGH-POWER LITHIUM-ION BATTERIES

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Lithium– $\text{LiFePO}_4$  (LFP) ferrophosphate is one of the most promising materials for lithium-ion battery cathodes, as it has a relatively high theoretical discharge capacity of 170 mAh/g and high structural stability during long-term cycling [1]. The iron used in LFP is non-toxic and has a low cost, making LFP-based batteries more affordable and safer.

However, the key disadvantage of LFP, along with its low diffusion coefficient for lithium ions ( $\sim 10^{-15} \text{ cm}^2/\text{s}$ ), is its low electronic conductivity ( $\sim 10^{-9} \text{ Cm/cm}$ ). Solutions to this problem include forming a carbon coating on the surface of LFP particles and replacing the traditional carbon black additive with carbon nanotubes in cathode materials.

In this paper, we propose a novel technique for the preparation of iron phosphate ( $\text{FePO}_4$ ), a precursor for the synthesis of lithium iron phosphate (LFP), in the presence of single-walled carbon nanotubes (SWCNTs). The proposed method involves the encapsulation of SWCNTs within the structure of  $\text{FePO}_4$ , resulting in the formation of a composite material with enhanced electronic conductivity. This is achieved through the use of a carbon coating on the SWCNT surface. The specific discharge capacity of the resulting LFP/SWCNT cathode material is found to be 20-25% higher than that of a similar material without SWCNTs, at high current densities (10C and above).

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# FIRST-PRINCIPLES STUDY OF SURFACE SEGREGATION IN $\text{LiCoO}_2$

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Surface segregation of dopants in layered oxides used as cathode materials for metal-ion batteries has attracted increasing attention in recent years<sup>1</sup>. An increase in the surface concentration of dopants correlates with a deterioration or improvement of electrochemical characteristics, which is associated with their effect on the stability of the electrochemically active surface. However, the specific physicochemical reasons for segregation remain poorly understood.

Using density functional theory, we investigated the segregation of commercially important dopants Mg, Al, Ti, V, Cr, Mn, Fe and Ni on the low-energy (104) surface of  $\text{LiCoO}_2$  (LCO). According to our results, all considered elements, with the exception of Al and Cr, are prone to segregation. We show that the segregation effect is primarily due to the difference in surface energies between the LCO and solute lattices and is explained in terms of crystal field theory. The secondary effect is associated with the difference in elastic contributions due to the mismatch between the sizes of cobalt ions and dopant ions.

Based on the obtained results, we propose a number of descriptors to describe the tendency of dopants to surface segregation, and also discuss the influence of segregating elements on the electrochemical characteristics of layered cathodes.

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# EVALUATION OF REDOX POTENTIALS OF ELECTROLYTES OF LITHIUM-ION BATTERIES BY METHODS OF COMPUTATIONAL CHEMISTRY

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Evaluation of the oxidative and reducing potential (ORP) of lithium ion battery (LIA) electrolytes using combined computational chemistry methods can significantly speed up and simplify the process of creating high-voltage batteries. At the same time, the ORP calculation algorithm should be accurate and fast. In this work, we present theoretical principles for evaluating ORP in LIA electrolyte solutions by considering LiDFOB solutions with various salt concentrations in EC/DMC and SL/DMC solvent mixtures.

The advantage of our new algorithm, in comparison to previous theoretical definitions of ORP, is that it thoroughly analyzes the trajectories of molecular dynamics simulations of the solutions, followed by identification of statistically significant complexes that contribute significantly to the stability of the electrochemical system. The geometric parameters of the complexes were optimized using quantum chemistry methods, followed by an assessment of their reductive and oxidative stability. Finally, additive values for ORP (oxidation-reduction potential) were estimated, depending on the composition of the electrolyte and salt concentration. The results of the theoretical calculations agree with the experimental data. The compositions and structures of the complexes used in theoretical calculations correspond to NMR (nuclear magnetic resonance) spectra of electrolyte solutions with the same concentration. Calculated ORP values agree well with experimentally observed values and correctly reflect trends in changing potentials with increased salt concentration. Therefore, we believe that the proposed calculation algorithm can be used to evaluate the performance of other electrochemical systems.

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# MIXED NIOBIUM-VANADIUM PHOSPHATES AS ANODE MATERIALS FOR METAL-ION BATTERIES

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Niobium-containing compounds are being actively studied as anode materials for metal-ion batteries due to their high energy density, which is provided by multi-electron redox processes <sup>1</sup>. According to calculations, in phosphates the redox potential of the  $V^{3+}/V^{2+}$  pair is located between that of the  $Nb^{5+}/Nb^{4+}$  and  $Nb^{4+}/Nb^{3+}$  pairs <sup>2</sup>, which allows the implementation of a three-electron process. The aim of this work – research of multielectron processes in mixed niobium-vanadium phosphates with NASICON-related structures.

$LiNbV(PO_4)_3$  (*Pbcn*, Anti-NASICON) was synthesized via sol-gel route, cell parameters are in a good agreement with the literature data<sup>3</sup>. Electrochemical and *operando* measurements was conducted in Li- and Na-halfcells. *Operando*-XANES measurements confirmed that the Nb oxidation state in initial phase is +5, and Nb *K*-edge shift during the intercalation proves reduction deeper, than  $Nb^{+4}$ .  $LiNbV(PO_4)_3$  is the first example of Anti-NASICON structured phosphate with reversible electrochemical activity which is observed in the Na half-cell. It was confirmed by diffusion barriers obtained by DFT calculations: for 1D diffusion the barrier is 0.5 eV, which is comparable with other Anti-NASICONs<sup>4</sup>; the features of sodium diffusion in this frame will be discussed in more detail in the oral report.

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# PROSPECTS FOR THE TRANSITION TO THIN-FILM SOLID ELECTROLYTES IN THE CREATION OF ALL-SOLID-STATE BATTERIES

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Currently, the development of all-solid-state lithium power sources is of great interest worldwide. The transition to such power sources from traditional lithium-ion batteries (LIBs) is positioned as a possible way to solve the safety problem (especially in extreme operating conditions - elevated temperatures, pressure and aggressive environments) and increase the service life of the power source.

In traditional LIBs a thickness of used separators are equal to  $\sim 20\ \mu\text{m}$ , so to create competitive all-solid-state batteries the solid electrolytes with a thickness of  $\sim 20\ \mu\text{m}$  or less are required. All-solid-state thin-film lithium/lithium-ion microbatteries, combining solid-state battery architecture and thin-film manufacturing, are considered ideal embedded power sources for microelectronic devices. However, the dependence of the energy efficiency of the device from the thickness of the electrolyte is currently not fully determined, despite the apparent evidence of the effectiveness of thin films.

Most often in the literature, all-solid-state cells with a Li anode, cathode materials traditional for LIBs ( $\text{LiCoO}_2$ ,  $\text{LiNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$ ,  $\text{LiFePO}_4$ ) and lithium-conducting solid electrolytes (sulfide or oxide compounds) are assembled and tested. Based on the analysis literature data it can be concluded that at lower values of conductivity of a thin-film electrolyte compared to bulk ceramic samples, higher values of the discharge capacity and energy density of lithium all-solid-state batteries were observed, including electrolytes with a garnet-like structure of the  $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$  family. It should be noted that the solution to the problem of fast charging of batteries is associated with reducing the internal resistance of the cell and can be achieved using thin-film electrolytes.

# ORIGINS OF DEGRADATION OF LITHIUM-ION BATTERY WITH $\text{LiNi}_{0.6}\text{Mn}_{0.2}\text{Co}_{0.2}\text{O}_2$ LAYERED OXIDE AND GRAHITE

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Abakumov A.M.,<sup>b</sup> Ananikov V.P.,<sup>a</sup> Antipov E.V.<sup>a-c</sup>**

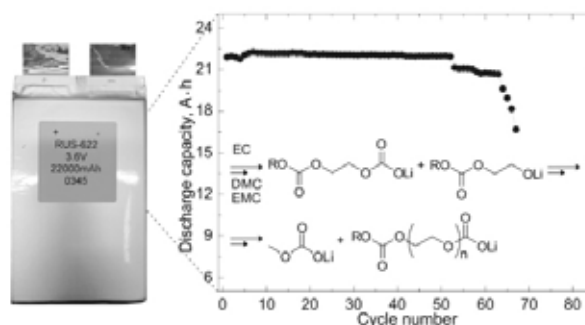
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Lithium-ion batteries (LIBs) based on Ni-rich layered transition metal oxide  $\text{LiNi}_{0.6}\text{Mn}_{0.2}\text{Co}_{0.2}\text{O}_2$  (NMC622) cathode and graphite anode are effective technology for electrochemical energy storage for electric vehicles. Nevertheless, LIB with NMC622 cathode and graphite anode degrades during electrochemical cycling. Herein, composition changes of electrolyte in LIB based on NMC622 cathode and graphite anode with nominal capacity of 22 A·h were examined after electrochemical cycling to establish origin of fast capacity decay. The combination of NMR spectroscopy with external standard and high resolution electrospray ionisation mass-spectrometry (ESI-HRMS) techniques reveals continuous decomposition of linear carbonates (dimethyl carbonate and ethylmethyl carbonate) originating from the lack of stable surface film formation on the graphite electrode. Besides, water content higher than 20 ppm leads to HF generation in the electrolyte. HF dissolves components of surface film with emergence of “fresh” surface on graphite, which further participates in electrochemical decomposition of carbonate solvents.



# SCIENTIFIC AND METHODOLOGICAL APPROACHES TO LITHIUM-ION STORAGE BATTERY SAFETY AND FAULT TOLERANCE IMPROVEMENT

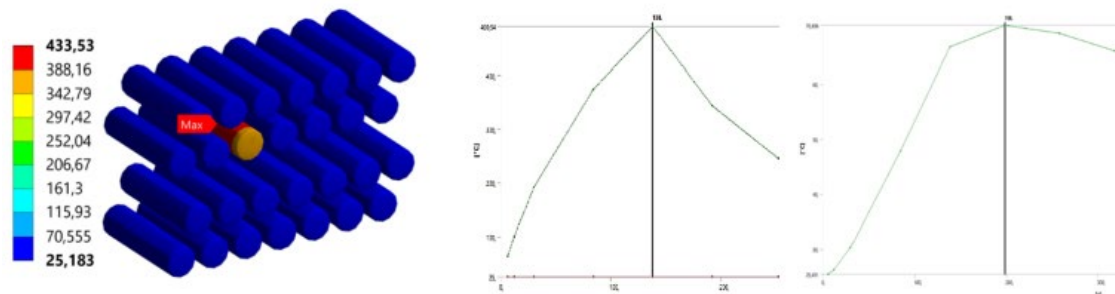
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High safety and fault tolerance of storage batteries (SBs) based on lithium-ion cells (LICs) are only ensured with a comprehensive approach to their design and use:

- optimal SB system configurations (selection of LIC electrochemical system and SB structure, use of support systems: monitoring and control<sup>1</sup>, thermal regulation, fire extinguishing systems, etc.);
- fault-tolerant LICs and current circuits elements of circuitry and design SB configurations<sup>2</sup>;
- new materials and technical solutions to protect LICs from the occurrence and consequences of internal short circuits (SCs).

LIC thermal runaway (TR) has the most dangerous consequences and is difficult to counteract. Calculations and results of a full-scale experiment on model modules have shown that the developed SB configuration during the SC of a single LIC with heat release corresponding to its TR (200 W, 3 minutes, 10 W·h) excludes the propagation of TR even in the SBs based on high-energy LICs with oxide cathodes: the temperature of the cells adjacent to the short-circuited LIC only briefly increases to 70 °C.



**Figure 1.** Change in the temperature of the short-circuited (200 W) and adjacent LICs

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# QUASI-SOLID-STATE POLYMER ELECTROLYTES FOR LI-ION BATTERIES

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Currently, the need for chemical current sources is increasing every year, and one of the current areas of research is the development of solid-state batteries based on polymer electrolytes<sup>1</sup>. Systems using solid polymer electrolytes (SPEs) are characterized by high safety and the possibility of using metallic lithium as an anode<sup>2</sup>. The main disadvantage of TPEs is low ionic conductivity, for example, TPEs based on polyethylene oxide are characterized by ionic conductivity of the order of  $10^{-7}$  S/cm. In this regard, the creation of polymer composite systems providing high ionic conductivity is an urgent issue.

In this work, to solve this problem, quasi-TPEs with a small amount of residual solvent were prepared based on blended polymer compositions of polyvinylidene fluoride and a series of poly methacrylates with electronegative groups capable of coordinating lithium ions with lithium salts  $\text{LiPF}_6$ ,  $\text{LiFSI}$  and  $\text{LiTFSI}$ . The influence of polymer blend composition on the synergistic properties, formation features, microstructure and ionic conductivity of quasi-TPEs was studied. The use of blended polymer matrix with low solvent content (up to 20 wt %) provides high values of ionic conductivity: up to  $3 \cdot 10^{-3}$  S/cm at 25°C and up to  $1 \cdot 10^{-2}$  S/cm at 80°C. The solid electrolyte provides high electrochemical characteristics of the  $\text{LiFePO}_4/\text{TPE}/\text{Li}$  cell - specific capacity of 154 mAh/g at cycling rate C/10 and cyclic stability in continuous cycling mode for at least 500 cycles at 1C rate.

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# QUANTIFYING THE IMPACT OF PHASE TRANSITION-RELATED POLARIZATION LOSSES ON METAL-ION BATTERY PERFORMANCE AT LOW TEMPERATURES

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Metal-ion batteries have become the predominant energy storage technology worldwide, known for its high energy density and long cycling life. However, their application is limited by a narrow operating temperature range, which becomes a critical drawback in a cold winter climate typical for Russia and complicates the use of devices powered by such batteries in regions with harsh weather conditions.

The deterioration of metal-ion battery performance at lower temperatures is often attributed to the manifestation of limitations associated with slow solid-state diffusion, the growth of metallic dendrites, a decrease in electrolyte conductivity in porous composite electrodes and slow charge transfer kinetics.<sup>1</sup> However, for materials undergoing phase transitions, electrode polarization at lower temperatures can also be caused by the slow kinetics of the nucleation of a new phase within the bulk of the original material particles. In our study, using  $\text{LiFePO}_4$  and  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  as model materials, we have shown for the first time that the contribution of the nucleation step to the overall polarization losses at low temperatures can determine the magnitude of the hysteresis of the charge/discharge curves. Additionally, in a study of  $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$  and  $\text{NaVPO}_4\text{F}$  model materials, which have similar chemical composition and particle morphology, yet operate via different intercalation pathways (phase transformation and single-phase intercalation, respectively), we established that capacity losses at low temperatures can be due to the slow movement of the phase boundary during phase transition.<sup>2</sup> These results have allowed for the first systematic analysis of the factors limiting the rate of reversible intercalation of ions into electrode materials undergoing phase transitions in a wide range of states-of-charge.

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# GERMANIUM NANOSTRUCTURES FOR LITHIUM- AND SODIUM-ION BATTERIES

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The tightening of energy requirements for common lithium-ion (LIA) and developing sodium-ion batteries (NIA) encourages researchers to develop new electrode materials that provide high battery capacity and operating voltage, long service life and economic feasibility of their use.

Active coatings based on nanostructured germanium, obtained as a result of cathodic reduction from aqueous solutions of  $\text{GeO}_2$ , are a high-capacity material for LIA and NIA anodes. This synthesis method does not require the use of high temperatures and complex technological equipment, as well as expensive and toxic Ge precursors, which is economically advantageous. Tests of the obtained materials have shown their ability to intercalate/deintercalate both lithium and sodium ions, good cycling stability and low electrode potential, which makes these structures a promising anode material for lithium- and sodium-ion batteries.

The theoretical capacity of germanium with the introduction of lithium and sodium is 1624 mAh/g and 1107 mAh/g, respectively. To reduce the loss of irreversible capacitance in the first cycles and increase the life of the electrodes, the addition of vinylene carbonate (VC) to electrolytes is necessary [1]. Thus, the practical capacity of electrodes based on Ge nanostructures in reversible interaction with lithium and sodium was 1300 mAh/g and 600 mAh/g, respectively [2].

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# SOLID ELECTROLYTE INTERPHASE FORMATION IN THE LI-ION BATTERY

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Solid Electrolyte Interphase (SEI) is one of the critical components of the Li-ion battery, which plays a significant role in its performance and safety. Despite nearly three decades of research, the SEI remains one of the least understood components of the Li-ion battery, particularly in the initial stage of formation. In this work, we provide microscopic evidence of a transient SEI layer forming inside graphite due to cointercalation and reduction of solvated  $\text{Li}^+$  ions.<sup>1</sup> Using scotch-tape cleavage, we directly accessed the intercalated species and products of their redox at different stages of the formation cycling inside graphite and traced their evolution. The results showed that solvated Li intercalates inside graphite in the surface vicinity at the potential above 1 V vs  $\text{Li}^+/\text{Li}$ . The reduction of the intercalated components proceeds simultaneously with the on-surface SEI formation and leads to graphite exfoliation and blistering. The internal reduction products are mostly inorganic and presumably disappear after oxidation, which constitute its transient nature.

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*This work was supported by Russian Science Foundation (RSF), grant agreement № 23-23-00041.*

# SYNTHESIS, STRUCTURE AND ELECTROCHEMICAL PERFORMANCE OF A NEW POTASSIUM-ION SOLID-CONDUCTOR $\text{KScPO}_4\text{F}$ WITH $\text{KTiPO}_4$ STRUCTURE TYPE

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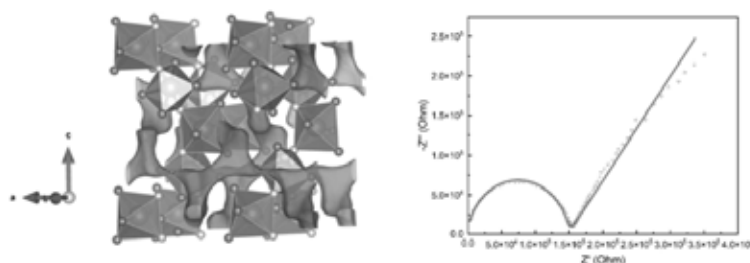
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One of the directions in the development of post-lithium electrochemical devices is the transition to solid-state batteries, in which the electrolyte containing organic solvents is replaced by an inorganic ionic conductor. In the case of potassium-ion batteries, there are few inorganic conductors that have a three-dimensional ionic conductivity higher than  $10^{-6}$  S/cm.

Compounds with the potassium titanyl phosphate (KTP) structure have one-dimensional diffusion of potassium ions in the structure, which ensures their successful use as electrodes in potassium-ion batteries. Replacing the *d* metal with scandium not only eliminates RedOx reactions but also significantly increases the cell volume. Thus,  $\text{KScPO}_4\text{F}$  has the largest cell volume among phosphate and fluoride phosphate KTPs, which provides the possibility of three-dimensional diffusion of potassium in the structure. The potassium ion conductivity of  $\text{KScPO}_4\text{F}$  is  $2.2 \cdot 10^{-6}$  S/cm at room temperature. The activation energies calculated by the BVEL method are 0.25 eV along the *c* axis and 0.89 eV along the *a* and *b* axes.

In this talk, we will discuss in detail the synthesis, structure refinement with the synchrotron X-ray powder diffraction data acquired at room temperature and 500°C and electrochemical properties of the potassium-ion conductor  $\text{KScPO}_4\text{F}$ , features of the creation of a multimodal mixture, and thermal stability.



**Figure 1.**  $\text{KScPO}_4\text{F}$  structure with illustration of potassium migration channels (left) and Nyquist plot of  $\text{KScPO}_4\text{F}$  obtained at 25°C.

# NOVEL PHOSPHATES $\alpha\text{-Na}_x\text{Fe}_{1-y}\text{Cr}_y\text{PO}_4$ AS CATHODE MATERIALS FOR SODIUM-ION BATTERIES

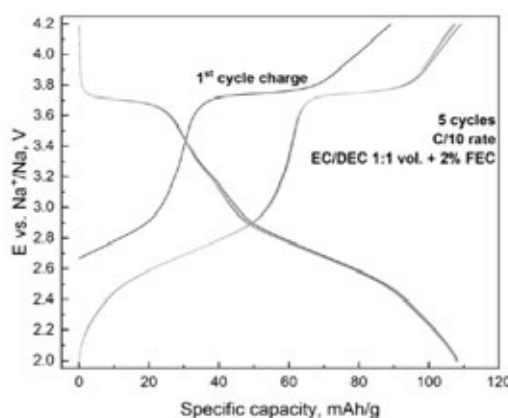
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The development of new, affordable, low-cost, and environmentally friendly iron-based cathode materials with improved energy performance is a high priority for the cost-effective commercialization of sodium-ion batteries (SIBs).

This work presents a new class of iron-containing phosphates,  $\alpha\text{-Na}_x\text{Fe}_{1-y}\text{Cr}_y\text{PO}_4$  ( $x < 1$ ,  $y \leq 0.25$ ) isotypic to  $\alpha\text{-CrPO}_4$ , proposed as promising cathode materials for SIBs. A two-stage synthesis method has been developed and optimized, combining the preparation of a special precursor using hydrothermal method and subsequent high-temperature annealing. The crystal structure of  $\alpha\text{-Na}_x\text{Fe}_{1-y}\text{Cr}_y\text{PO}_4$  was refined, the chemical composition was confirmed by energy-dispersive X-ray analysis, Mössbauer and infrared spectroscopy, and the morphology of particles of the prepared material was studied using scanning electron microscopy.

It has been shown that electrode materials based on  $\alpha\text{-Na}_x\text{Fe}_{1-y}\text{Cr}_y\text{PO}_4/\text{C}$  demonstrate reversible electrochemical activity in the 2.0–4.2 V vs.  $\text{Na}^+/\text{Na}$  range. In particular,  $\alpha\text{-Na}_{0.75}\text{Fe}_{0.75}\text{Cr}_{0.25}\text{PO}_4/\text{C}$  exhibits an average potential of 3.1 V and a specific discharge capacity of 108 mAh/g.



**Figure 1.** Galvanostatic cycling of  $\alpha\text{-Na}_{0.75}\text{Fe}_{0.75}\text{Cr}_{0.25}\text{PO}_4/\text{C}$  half-cell vs. metallic Na.

The report will discuss in detail the specific features of the synthesis, chemical composition, and crystal structure of  $\alpha\text{-Na}_x\text{Fe}_{1-y}\text{Cr}_y\text{PO}_4$ , as well as their relationship with electrochemical properties.

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# MICROCRACK GROWTH SUPPRESSION IN Mg-SUBSTITUTED Ni-RICH NMCS FOR Li-ION BATTERIES

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Layered transition metal oxides (TM)  $\text{LiNi}_{2/3+x}\text{Mn}_{4+y}\text{Co}_{3+z}\text{O}_2$  with a high nickel content ( $x \geq 0.6$ , so-called Ni-rich NMC), are considered promising cathode materials for lithium new-generation ion batteries. However, their practical application is limited due to the rapid specific capacity degradation during prolonged electrochemical cycling. This problem is a consequence of the accumulation of structural stresses in Ni-rich NMCs during electrochemical cycling, which leads to deterioration of the mechanical integrity of the cathode due to cracking of secondary particles, while the penetration of the electrolyte into the particles through microcracks accelerates the process of degradation of the material. A promising approach to suppress irreversible structural changes is the chemical modification of the cation sublattice. Elements that can occupy both Li and TM positions are selected for doping into the cationic sublattice, however, the majority of published data on the cationic substitution of Ni-rich NMC is purely empirical in nature, without clarifying the role of doping additives.

As part of this work, Mg-substituted  $\text{Li}(\text{Ni}_{0.6}\text{Mn}_{0.2}\text{Co}_{0.2})_{1-x}\text{Mg}_x\text{O}_2$  ( $x=0.05, 0.1$ ) were synthesized via flux-growth technique in the form of single crystal particles in order to suppress the formation of microcracks during galvanostatic cycling, as well as to clarify the mechanism of stabilization and suppression of crack formation process. The joint Rietveld refinement of X-ray and neutron diffraction showed that  $\text{Mg}^{2+}$  cations in the layered oxide structure occupy simultaneously the octahedral positions of lithium (3a) and TM (3b). Using the high-resolution EDX-STEM method, magnesium distribution within 3a and 3b sites was confirmed. Galvanostatic tests of the obtained samples have shown that the presence of Mg improves the stability of materials during long-term cycling. In the case of a 5% degree of substitution for magnesium, the sample demonstrates a retention of capacity from the initial 94% after 300 charge/discharge cycles versus 88% for unsubstituted one. However, Mg-doped samples show lower values of specific discharge capacity compared to  $\text{LiNi}_{0.6}\text{Mn}_{0.2}\text{Co}_{0.2}\text{O}_2$ . The report will show that Mg in Ni-rich NMCs plays the role of a "stabilizer" of the structure and suppresses the formation of microcracks, as well as their spread.

*Research funded by Russian Science Foundation (RSF) (Grant № 23-73-30003).*

# THEORETICAL AND EXPERIMENTAL STUDY OF CONDUCTIVITY IN THE $\text{Na}_6\text{M}_2(\text{CO}_3)_4\text{SO}_4$ ( $M = \text{Mg, Mn, Fe, Co, Ni}$ ) STRUCTURES

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The search for conducting materials among polyanionic compounds is a significant challenge in electrochemistry. Compounds containing transition metals have received special attention due to regulate the redox potential. Previously, we have theoretically and experimentally investigated the conductivity of tychite  $\text{Na}_6\text{Mg}_2(\text{CO}_3)_4\text{SO}_4$  (space group  $Fd-3$ ). In this work, we expand our research by selecting isostructural compounds that contain d-metals.

Using geometrical-topological analysis in the ToposPro program, we identified the possibility of 3D  $\text{Na}^+$  ions diffusion in all the structures. Next, we calculated the  $\text{Na}^+$  ions migration energy ( $E_m$ ) using the bond valence site energy (BVSE) method in the softBV program (Table 1). Then we calculated the ionic conductivity using kinetic Monte Carlo simulations. The formation energies of sodium vacancy sites calculated using density functional theory were less than 1.6 eV.

| Structure  | BVSE: $E_m(\text{Na}^+)$ , eV |      |      | KMC:<br>$\sigma$ , $\text{Cm cm}^{-1}$ | $E_g$ , eV* |
|--|-------------------------------|------|------|--|-------------|
|  | 1D                            | 2D   | 3D   |  |             |
| $\text{Na}_6\text{Mg}_2(\text{CO}_3)_4\text{SO}_4$ | 0.37                          | 0.37 | 0.37 | $2.6 \times 10^{-7}$                   | 4.53        |
| $\text{Na}_6\text{Fe}_2(\text{CO}_3)_4\text{SO}_4$ | 0.38                          | 0.38 | 0.38 | $7.2 \times 10^{-8}$                   | 0.00        |
| $\text{Na}_6\text{Ni}_2(\text{CO}_3)_4\text{SO}_4$ | 0.44                          | 0.44 | 0.44 | $2.9 \times 10^{-8}$                   | 3.25        |
| $\text{Na}_6\text{Mn}_2(\text{CO}_3)_4\text{SO}_4$ | 0.46                          | 0.46 | 0.46 | $1.3 \times 10^{-8}$                   | 3.90        |
| $\text{Na}_6\text{Co}_2(\text{CO}_3)_4\text{SO}_4$ | 0.47                          | 0.47 | 0.47 | $1.7 \times 10^{-8}$                   | 2.72        |

**Table 1.** Migration energy (BVSE calculations), ionic conductivity (KMC simulation) and band gaps  $E_g$  in tychites.

Also, the electrode potentials and the volume change degree of structures during (de)intercalation of sodium ions were studied within the DFT modeling.

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# MORPHOLOGY DESIGN FOR THE PRODUCTION OF HIGH VOLUMETRIC ENERGY DENSITY TRIPHYLITE-TYPE CATHODE MATERIALS

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Despite the intensive research and successful commercialization of  $\text{LiFePO}_4$  (LFP) triphylite-structure cathode material for Li-ion batteries (LIBs), the modifications of the production process as well as material's functional properties are necessary for the implementation in high-energy areas. The attention of the research community is focused on the materials operational properties increase such as specific capacity, working potential, cycle life, and energy density. Among all the existing strategies it is worth mentioning, substitution of Fe by higher RedOx potential 3-d metals and morphology control for the production of microspherical particles, since the two approaches make it possible to elevate both volumetric and gravimetric energy densities of the cathode materials. The object of the research is  $\text{LiFe}_{0.5}\text{Mn}_{0.5}\text{PO}_4$  (LFMP) as a promising next-generation triphylite-type cathode material.

For the microspherical production of LFMP, a dittmarite-type precursor ( $\text{NH}_4\text{Fe}_{0.5}\text{Mn}_{0.5}\text{PO}_4 \cdot \text{H}_2\text{O}$ ) was synthesized by a coprecipitation technique followed by a mild solvothermal treatment. The morphology of the asprepared precursor remains unchanged for the final LFMP and represents microspheres with mean particles diameter of 30  $\mu\text{m}$  and tap density of 1.5  $\text{g}\cdot\text{cm}^{-3}$ . The technology makes it possible to reduce the total Li consumption during the material's production and eliminate the impact of antisite defects on the materials' electrochemical performance<sup>1</sup>. The obtained material demonstrates decent electrochemical performance and exhibits more than 140  $\text{mAh}\cdot\text{g}^{-1}$  at C/10 and 90  $\text{mAh}\cdot\text{g}^{-1}$  at 5C current densities with capacity retention of 86 and 85% after 250 cycles at 1C and 5C rates.

The report will include the detailed synthesis route of the material as well as description of the dittmarite-triphylite transformation in terms of microstructure evolution.

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# HIGH ENERGY DENSITY NI-RICH LAYERED CATHODE MATERIALS WITH THE IMPROVED MICROSTRUCTURE

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Ni-rich complex layered oxides of lithium and transition metals  $\text{LiNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$  ( $x + y + z = 1$ ,  $x \geq 0.6$ ), so-called Ni-rich NMCXYZ, have become one of the preferred cathode materials for advanced Li-ion batteries due to their high reversible electrochemical capacity, energy density and relatively low cost. However, strong demand to increase driving range of electric vehicles calls for advanced cathode materials with even higher energy density ( $>800 \text{ Wh/kg}$ )<sup>1</sup>. One of the promising strategies to fit this requirement is increase of the Ni fraction in Ni-rich NMCs, which leads to layered oxides with ultra-high Ni content ( $x > 0.85$ ) demonstrating discharge capacity as high as  $230 \text{ mAh/g}$ <sup>2</sup>. Nevertheless, enhancing the Ni concentration not only boosts energy density, but also causes dramatic structure changes resulted in microstrains and, ultimately, to an initiation of microcracks disintegrating agglomerates and even primary particles<sup>3</sup>. Cracks are considered to be one of the main reasons for the rapid degradation of Ni-rich NMCs upon cycling. These issues are mainly related to widely commercialized Ni-rich NMCs with spherical-like micrometer-sized agglomerates consisting of randomly oriented primary nanoparticles. In contrast, the radially oriented primary particles seemingly allow the cathode agglomerate to contract and expand uniformly, remarkably suppressing microcracks formation and, thereby, improving cycling stability.

In this talk, main aspects of synthesis approaches to obtain Ni-rich NMCs with the stabilized microstructure will be highlighted and analyzed to understand the effect of various parameters on the properties and performance of the developed cathode materials.

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*The study was supported by the Russian Science Foundation grant No. 23-73-30003, <https://rscf.ru/project/23-73-30003/>*

# STUDY OF ALLOY FORMATION AT ALUMINUM ANODES OF LI-ION BATTERIES USING IMPEDANCE SPECTROSCOPY

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Charging of Li-ion battery with a metallic Al anode is accompanied by the alloying reaction between aluminium and lithium to form first  $\alpha$ -LiAl solid solution and then  $\beta$ -LiAl intermetallic compound. The solid solution has the same crystal structure as aluminium, whereas  $\beta$ -LiAl possesses a Zintl-type body-centered lattice<sup>1</sup>. Correspondingly, the  $\alpha$ - $\beta$  phase transition is accompanied by a significant structural rearrangement. The alloying reaction produces  $\alpha$ -LiAl first;  $\beta$ -LiAl is formed at a later stage from the  $\alpha$ -LiAl solid solution.

In this work, we performed the measurements of electrochemical impedance spectra of metallic aluminium anodes in the course of their lithiation. The values of lithium-ion concentration as well as the rate constant of  $\beta$  phase formation from  $\alpha$ -LiAl solid solution were determined as dependent of the experimental conditions. Possible ways of increasing the charge-discharge currents and specific capacities of aluminium metal anodes without jeopardizing their performance including cycle ability and coulombic efficiency were discussed.

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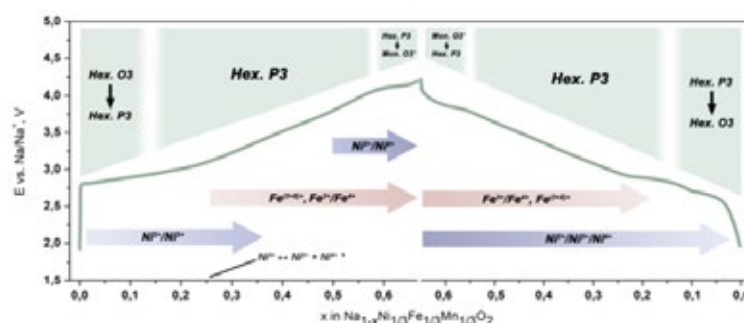
# EFFECT OF NI/FE/MN RATIO ON ELECTROCHEMICAL PROPERTIES OF THE O3- $\text{NaNi}_{1-x-y}\text{Fe}_x\text{Mn}_y\text{O}_2$ ( $0.25 \leq x, y \leq 0.75$ ) CATHODE MATERIALS FOR NA-ION BATTERIES

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Na-ion batteries are considered as future alternative to Li-ion due to low cost and wide abundance of sodium. In turn, O3-type  $\text{NaNi}_{1-x-y}\text{Fe}_x\text{Mn}_y\text{O}_2$  cathode materials are an excellent alternative to Li-containing layered oxides such as  $\text{LiCoO}_2$  and its derivatives<sup>1</sup>. These compounds are isostructural to  $\alpha\text{-NaFeO}_2$  (s.g.  $R\bar{3}m$ ) with Ni, Fe, and Mn in  $\text{NaNi}_{1/3}\text{Fe}_{1/3}\text{Mn}_{1/3}\text{O}_2$  being in the 2+, 3+, and 4+ oxidation states, respectively. The possibility of using  $\text{Fe}^{3+}/\text{Fe}^{4+}$  redox pair in cathode materials for SIBs is one of the main features of the Na-ion system in contrast to Li-ion. However, the peculiar crystal chemistry of iron cations introduces certain problems in the (de)sodiation process of layered sodium oxides.



Here, we present operando and ex situ studies using powder X-ray diffraction (PXRD) and X-ray absorption spectroscopy (XAS) combined with  $^{57}\text{Fe}$  Mössbauer spectroscopy (MS). Our approach reveals the sequence of the redox transitions that occur during the charge and discharge of O3-  $\text{NaNi}_{1/3}\text{Fe}_{1/3}\text{Mn}_{1/3}\text{O}_2$ <sup>2</sup>. Furthermore, we accurately analyzed the effect of the Mn, Fe, and Ni ratio on the electrochemical properties, thermal stability, and kinetics of  $\text{Na}^+$  (de)intercalation in O3- $\text{Na}(\text{Ni}, \text{Fe}, \text{Mn})\text{O}_2$  oxides<sup>3</sup>.

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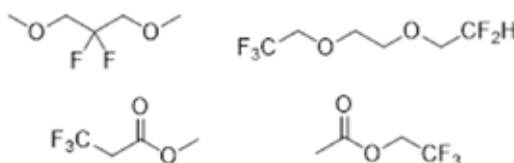
# FLUORINATED ELECTROLYTES FOR LITHIUM-ION BATTERIES

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The C–F bond is the strongest single bond in organic chemistry. As a result, fluorinated compounds are non-flammable and highly resistant to chemical transformations, including oxidation.<sup>1</sup>

Fluorinated organic solvents are widely used as electrolyte components for high-voltage and high-energy-density lithium-ion batteries because of these characteristics.<sup>2-3</sup>



**Figure 1.** Structures of fluorinated solvent molecules.

We have developed new electrolyte systems based on fluorinated ethers and esters (Fig. 1) that allow lithium-ion and lithium-metal batteries to operate up to 4.5 V for hundreds of cycles. It is worth noting that conventional carbonate electrolytes are stable only up to 4.3 V.

Pouch cells (graphite||NMC811) were tested with two developed electrolyte systems. By raising the cut-off voltage, the specific capacity and energy density of the cathode material increase by 10-15% without compromising the battery's performance.

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# THE CORRELATION BETWEEN SODIUM IONS STORAGE MECHANISM AND ANIONIC COMPOSITION IN $\text{KTP-NaVPO}_4\text{F}_{1-x}\text{O}_x$

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Vanadium-based polyanionic compounds has recommended itself as a prospective playground for the development of high-energy and high-power cathode materials for sodium-ion batteries. Family of materials with a general formula of  $\text{NaVPO}_4\text{F}_{1-x}\text{O}_x$  seems to be promising due to high theoretical specific capacity (145 mAh/g) and the possibility of members' stabilization in  $\text{KTiOPO}_4$  structural type (KTP), uniting all necessary prerequisites for increased specific characteristics realization. A particular attention should be paid to  $\text{Na}^+$  ions (de)intercalation mechanism during electrochemical reaction, which directly affects power characteristics and indirectly influences on energy density<sup>1</sup>.

The purpose of this work is to investigate the correlation between sodium ions storage mechanism and anionic composition in members of materials' family with a general formula of  $\text{NaVPO}_4\text{F}_{1-x}\text{O}_x$ .

A number of new compounds with a general formula of  $\text{NaVPO}_4\text{F}_{1-x}\text{O}_x$  were obtained via two-step solid-state ion exchange approach using hydrothermally prepared ammonium precursors<sup>2-3</sup>. According to the results,  $\text{NaVPO}_4\text{F}$  demonstrates reversible intercalation of sodium ions showing somewhat close to solid-solution mechanism, while in case of  $\text{NaVOPO}_4$  several stable intermediate phases are found within different state of charge windows. Finally, mixed valence compounds  $\text{NaVPO}_4\text{F}_{1-x}\text{O}_x$  showcase completely sloped galvanostatic curves, thus being the most attractive materials in terms of specific energy and power. In oral report a comparative analysis of the results of galvanostatic cycling and *operando* synchrotron x-ray diffraction for series of as-synthesized materials will be presented.

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# MECHANISM OF IONIC TRANSPORT IN NANOCOMPOSITE POLYMER ELECTROLYTES WITH THE INTRODUCTION OF IONIC LIQUID ACCORDING TO NMR DATA

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The development of highly conductive electrolyte systems for safe and highly efficient energy storage devices requires a detailed study of ionic and molecular transport at different spatial scales. This can be done using pulsed field gradient NMR (PFG NMR)<sup>1,2</sup>.

In this work, the features of ionic and molecular transport in 5-component electrolyte systems based on polymer (polyethylene glycol diacrylate), solvent - ethylene carbonate, LiBF<sub>4</sub> salt, ionic liquid (1-ethyl-3-methylimidazolium tetrafluoroborate) and TiO<sub>2</sub> nanoparticles (d~21nm) were studied by NMR. Two types of ion and molecule transport (fast and slow) in the electrolyte in the presence of TiO<sub>2</sub> were detected by PFG NMR. The phase occupancies are 0.7 and 0.3, respectively. Obtaining highly mobile lithium cations became possible by increasing the proportion of solvent - ethylene carbonate. This made it possible to create electrolytes with predominant lithium conductivity. They compete with imidazolium ionic liquid cations. These 5-component electrolyte systems have been successfully tested in a prototype lithium battery with a LiFePO<sub>4</sub> cathode.

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# PROSPECTS OF USING MULTICOMPONENT LIQUID ELECTROLYTES BASED ON GLYMES FOR LOW TEMPERATURE APPLICATIONS: THEORY AND EXPERIMENT

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Currently, there is a question about searching for electrolyte systems that could ensure the operation of a lithium current source at low temperatures. Solvents for such electrolytes can be ether oligomers with ethylene oxide units –  $(\text{CH}_2\text{CH}_2\text{O})_n$ –, the so-called glymes.

In this work, new electrolytes based on glymes and lithium bis(trifluoromethanesulfonyl)imide salt (LiTFSI) were obtained (Table 1). The conductivity of electrolytes was measured in the temperature range from  $-30$  to  $20^\circ\text{C}$  in increments of  $10$  degrees using conductometry. The electrolyte/Li interface was studied by electrochemical impedance spectroscopy in CR2032 cells with Li electrodes. The measurement results of the electrolyte conductivity ( $\sigma$ ) and the effective activation energy ( $E_a^{\text{ef}}$ ) calculations are presented in table 1.

| Electrolyte composition                                 | $\sigma$ , mS/cm   |                     | $E_a^{\text{ef}}$ , kJ/mol |
|---|--------------------|---------------------|----------------------------|
|   | $20^\circ\text{C}$ | $-20^\circ\text{C}$ |                            |
| 1 M LiTFSI in 1,3-dioxolane/diglyme (DOL/G2 (1:2))      | 8.6                | 3.7                 | 3.1                        |
| 1 M LiTFSI in dimethoxyethane/tetraglyme (DME/G4 (2:1)) | 7.3                | 3.0                 | 3.4                        |
| 1 M LiTFSI in DOL/G2/DME/G4 (1:2:2:1)                   | 7.2                | 2.9                 | 3.3                        |

**Table 1.** Electrolyte compositions and conductivity values

Higher conductivity values and the minimal effective activation energy are achieved with the first composition (1 M LiTFSI in DOL/G2 (1:2)).

Using the method of quantum chemical modeling, the solvation energies of the complexes  $\text{Li}^+(\text{DOL})_2(\text{G2})_4$ ,  $\text{Li}^+(\text{DME})_2(\text{G4})$ ,  $\text{Li}^+(\text{DOL})(\text{G2})(\text{DME})(\text{G4})$  are calculated, which are 148.1, 130.9, 126.8 kcal/mol, respectively. They show that at low temperatures the process of  $\text{Li}^+$  desolvation at the Li anode interphase in this sequence proceeds more easily.

*The work was supported by the Ministry of Science and Higher Education of the Russian Federation, state assignment number 124013000743-3 (FFSG-2024-0008).*

# ANODE MATERIALS AND SOLID ELECTROLYTES BASED ON OXYGEN-DEFICIENT PYROCHLORES FOR POTASSIUM-ION BATTERIES

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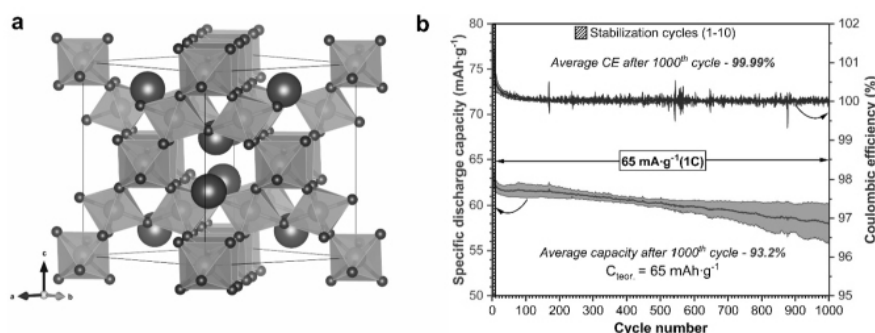
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The electrochemical properties of oxygen-deficient pyrochlores with the composition  $\text{KM}_x\text{W}_{2-x}\text{O}_6$  ( $M = \text{Ta}, \text{Nb}, \text{Ti}, \text{Cr}, \text{Al}$ ) (Fig. 1a) as applied to potassium-ion batteries (PIB) were studied for the first time. All compounds under consideration showed reversible redox activity in the low-voltage region with formal potentials of  $\sim 1.08 - 1.40$  V. The  $\text{KNbWO}_6$  composition demonstrated high stability in prolonged galvanostatic cycling (Fig. 1b). The mechanism of potassium de/intercalation into the  $\text{KNbWO}_6$  structure was studied by operando X-ray diffraction and confirmed by a set of electrochemical methods.

Additionally, the compositions  $\text{KA}_{10.33}\text{W}_{1.67}\text{O}_6$ ,  $\text{KTi}_{0.5}\text{W}_{1.5}\text{O}_6$ , and  $\text{KNbWO}_6$  were examined as potential solid electrolytes for PIB. The ionic conductivity of the  $\text{KA}_{10.33}\text{W}_{1.67}\text{O}_6$  compound was  $5.6 \text{ mS/cm}$  at  $25^\circ\text{C}$ , which is one of the highest values among inorganic potassium-ion conductors known in the literature<sup>1</sup>.

The report will discuss in detail the synthesis, structural, and electrochemical features of oxygen-deficient pyrochlores as materials for PIB.



**Figure 1.** (a) Crystal structure of  $\text{KM}_x\text{W}_{2-x}\text{O}_6$  pyrochlores:  $(\text{M}/\text{W})\text{O}_6$  octahedra and K atoms.  
(b) The prolonged galvanostatic cycling of  $\text{K} \parallel \text{KNbWO}_6$  half-cells.

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# POLYANIONIC CATHODE MATERIALS FOR SODIUM-ION BATTERIES BASED ON Mn AND Fe

**Zakharkin M.V.,<sup>a</sup> Jablanovic A.D.,<sup>a,b</sup> Alyoshin S.A.,<sup>a</sup> Popov S.P.,<sup>a</sup>  
Drozhzhin O.A.,<sup>a</sup> Antipov E.V.<sup>a,b</sup>**

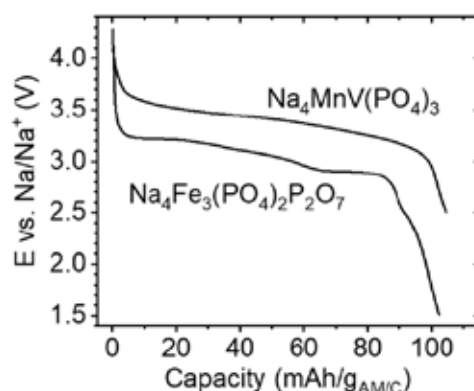
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Phosphates  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$  and  $\text{Na}_4\text{Fe}_3(\text{PO}_4)_2\text{P}_2\text{O}_7$  are considered as promising cathode materials for sodium-ion batteries, demonstrating a reversible capacity of more than 100 mAh/g at high charge and discharge rates for thousands of cycles <sup>1,2</sup>.

Replacing V with Mn in  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$  reduces the cost of materials and increases the operating potential above 3.4 V vs.  $\text{Na}/\text{Na}^+$ . When V is replaced by Fe in the NASICON framework, the  $\text{Fe}^{2+}/\text{Fe}^{3+}$  redox-process occurs at  $\sim 2.5$  V vs.  $\text{Na}/\text{Na}^+$ . Due to the presence of a pyrophosphate ( $\text{P}_2\text{O}_7^{4-}$ ) group in  $\text{Na}_4\text{Fe}_3(\text{PO}_4)_2\text{P}_2\text{O}_7$ , the potential of the  $\text{Fe}^{2+}/\text{Fe}^{3+}$  transition increases up to  $\sim 3$  V vs.  $\text{Na}/\text{Na}^+$ , which makes this material attractive for practical use.

The presentation will focus on the relationship between the chemical composition and electrochemical properties of two types of cathode materials containing widespread metals Na, Mn and Fe.



**Figure 1.** Galvanostatic curves of  $\text{Na}_4\text{MnV}(\text{PO}_4)_3$  and  $\text{Na}_4\text{Fe}_3(\text{PO}_4)_2\text{P}_2\text{O}_7$

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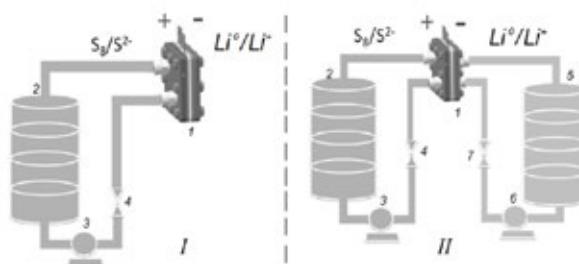
# LITHIUM SULFUR FLOW BATTERY: DEVELOPMENT AND RESEARCH

**Akhmedov M.A.,<sup>a,b</sup> Rabadanov K.Sh.,<sup>a</sup> Gafurov M.M.,<sup>a</sup> Ataev M.B.<sup>a</sup>**

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Currently, redox flow batteries are considered promising systems for safe and reliable high-capacity energy storage<sup>1</sup>. In this work, a prototype lithium-sulfur flow battery (LSFB) was developed and investigated, where the energy charge produced in lithium-sulfur cells is stored in rechargeable ion-conducting non-aqueous electrolyte, which is stored and supplied from a separate reservoir(s).



**Figure 1.** Lithium-sulfur flow battery with one (I) and two-flow (II) circuit, where: 1 - electrode cell, 2, 5 - reservoir for electrolyte, 3,6 - pumps; 4, 7 – gate valve.

It has been established that the use of a flow-through electrolyte movement system solves the problem of: suppression of the polysulfide shuttle and migration of sulfur to the anode, characteristic of conventional lithium-sulfur batteries with a fixed layer of electrolyte; increase specific power 250-680 Wh/kg, number of charge/discharge cycles withstand – 8000, energy efficiency 80%. The proposed laboratory prototype of LSPAs are inexpensive, easily scalable and can be used in energy storage systems obtained from solar, wind and other power plants.

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*The work was carried out with the financial support of the FASIE, contract 4470FC1/72582 dated*

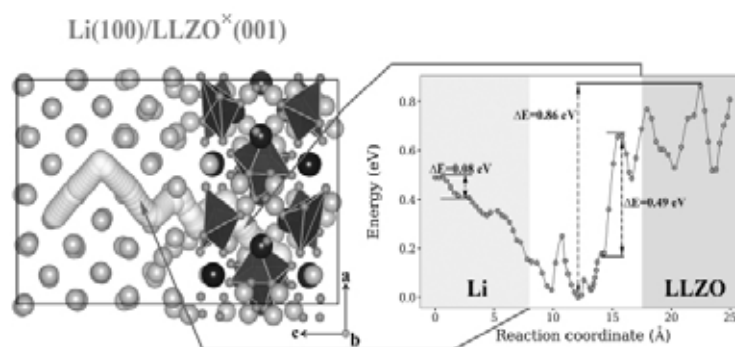
# COMPUTATIONAL MODELING OF COOPERATIVE DIFFUSION OF $\text{Li}^+$ IONS IN GARNET-TYPE STRUCTURES USING MOLECULAR DYNAMICS WITH MACHINE-LEARNING POTENTIALS

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Metal-ion batteries with solid-state electrolytes are a promising solution for the portable electronics and automobile industry due to their high energy density [1]. A limiting factor for their industrial application is the challenge of forming interfaces with low resistance that do not degrade during battery cycling. Experimental investigation of the microstructure in this area, as well as its evolution during battery cycling, is challenging.

In this study, we investigated the transport of  $\text{Li}^+$  ions within the bulk material while considering the interface between Li and the promising garnet-type solid-state electrolyte  $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$  (LLZO). To account for the lattice dynamics, temperature effects, cooperative phenomena, and to ensure high-quality statistical averaging, we conducted molecular dynamics simulations employing machine-learning interatomic potentials [2]. Our findings reveal that the activation barriers for  $\text{Li}^+$  diffusion within the bulk material are substantially lower than those obtained from our previous DFT-NEB calculations [3], and are in good agreement with the experimental data. Additionally, we explored for the first time the degradation process of the interface structure through the formation of point defects. These results will serve as a basis for the targeted design of stable interfaces.



**Fig. 1.** Charge transfer of  $\text{Li}^+$  ions at Li/LLZO interfaces.

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# IMPACT OF HIGH SYMMETRY GRAIN BOUNDARIES ON TRANSPORT AND OXYGEN RELEASE IN $\text{LiNiO}_2$

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Energy storage, particularly in the form of rechargeable batteries, is crucial for technological advancement across various domains.  $\text{LiCoO}_2$ , a common cathode material, faces challenges due to its drawbacks such as cost, toxicity, and performance, leading to the exploration of alternative materials based on  $\text{LiNiO}_2$  and furtherly doped with different metals such as Mn, Co or Al.  $\text{LiNiO}_2$ -based cathode materials offer higher specific capacity but suffer from poor cycling performance due to gradual loss of oxygen. Though the loss of oxygen is attributed to the inherent low stability of  $\text{LiNiO}_2$  in a charged state, the role of grain boundaries in oxygen loss remains elusive. Moreover, the influence of grain boundaries on mechanical stability, transport properties, and overall battery performance remains a subject of significant research interest.

An important class of special low-energy grain boundaries plays a crucial role in determining the mechanical and transport properties of cathode materials. For instance, high-symmetry boundaries, such as  $\Sigma 2(1-104)[-1-120]$ , enhance the mobility of lithium ions, while asymmetric boundaries, like  $\Sigma 5(1-10-1)[-1-120]$ , reduce ion mobility in NMC layered oxides. Nevertheless, the role of GBs in oxygen transport and loss remains poorly understood even for pure  $\text{LiNiO}_2$ .<sup>1</sup>

This study focuses on understanding the structure, formation energy of special grain boundaries and its impact on oxygen stability of  $\text{LiNiO}_2$ -based electrode material. Using  $\text{LiNiO}_2$  as a model material, grain boundaries were constructed using a GB program, and simulations were performed using Density Functional theory with Hubbard correction. We focused on  $\Sigma 2$  and  $\Sigma 3$  grain boundaries, revealing insights into their structures and energetics. The results show that higher symmetry grain boundaries exhibit lower energy and enhance ionic transport properties through the boundary and inside of it in comparison to the bulk, while both GBs have negative impact on oxygen loss. We expect these findings will be used to optimize the contribution of grain boundaries to improve the stability of cathode materials.

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# THE INFLUENCE OF THE TORTUOSITY OF SODIUM VANADIUM PHOSPHATE-BASED COMPOSITE ELECTRODES ON POLARIZATION LOSSES AT LOW TEMPERATURES

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Nowadays, one of the crucial problems of metal-ion batteries is claimed to be their losses of energy density, while operating at temperatures below 0 °C. Retaining energy density is hindered by kinetic limitations, including low electronic conductivity of a composite electrode and diffusional polarization in pores, filled with electrolyte solution.<sup>1</sup> Diffusion limitations leading to polarization of composite electrodes are caused by the increased ion path length in the electrode pores compared to that in the electrolyte bulk, i.e., the tortuosity of the pores.

This study investigates the influence of porosity and tortuosity of composite electrodes on the magnitude of polarization losses at room and reduced temperatures. The cathode material  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$  was selected for the study, demonstrating a theoretical capacity of 118 mAh/g, corresponding to the deintercalation of two sodium ions per formula unit.<sup>2</sup> Composite electrodes with a loading of 20 mg/cm<sup>2</sup> were prepared, with pores oriented perpendicular to the electrode surface. By analyzing the electrochemical impedance spectra recorded in symmetric cells,<sup>3</sup> dependencies of the tortuosity of composite electrodes with random and preferred pore orientations on temperature were obtained, and the electronic conductivity of both types of electrodes was evaluated. Based on the data obtained, conclusions were drawn about the contribution of limitations caused by high tortuosity of the pores in composite electrodes to the reduction in energy density of  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$  electrodes.

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# THE MECHANISM OF FORMATION OF MICROPORES IN NON-GRAPHITIZED CARBON FROM PHENOL- FORMALDEHYDE RESIN AND GLUCOSE FOR SODIUM-ION BATTERIES RESIN AND GLUCOSE

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Sodium-ion batteries (SIBs) offer an environmentally friendly and cost-effective alternative to lithium-ion batteries. Hard carbon, with its disordered graphene-like layers, is a promising anode material for SIBs, unlike graphite, which cannot effectively embed sodium ions.

To enhance hard carbon's capacity by creating micropores, methods such as template<sup>1</sup> and solvothermal synthesis<sup>2</sup> are used. These methods produce porous structures, allowing sodium nanoclusters to form during charging, boosting performance. However, the formation of micropores and the influence of synthesis methods need further understanding.

This study examines micropore development in hard carbon from phenol-formaldehyde resin (PFR) and glucose. Two synthesis methods were used: a solvothermal process with ethanol and PFR, and glucose pretreatment at 200°C followed by annealing at 1300°C. Techniques like low-temperature adsorption (N<sub>2</sub> and CO<sub>2</sub>), galvanostatic charging/discharging, Raman spectroscopy, SEM, SAXS, TGA and IR spectroscopy analyzed the samples.

Results showed PFR-derived hard carbon had a discharge capacity of 400 mAh/g and 83% columbic efficiency in the first cycle, outperforming glucose-derived samples (300 mAh/g) due to differences in micropore structures.

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# ELECTRONIC STRUCTURE OF CATHODE MATERIALS: INSIGHTS FROM THEORETICAL SPECTROSCOPY

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In the context of understanding the path to the maximum capacity of the battery cells, the electronic structure of cathode materials plays one of the key roles<sup>1</sup>. This work focuses on x-ray spectroscopy methods in combination with first-principle calculations to investigate cathode materials based on layered transition metal oxides.

The crystal and electronic structure of LiNiO<sub>2</sub> in its ground state is a subject of ongoing debate in the literature<sup>2,3</sup>. Proposed models range from a charge-disproportionated state and local Jahn-Teller distortion to a high-entropy glass-like state<sup>3</sup>. To clarify the various contributions from electronic arrangements to the experimentally observable spectra, we employed *ab initio* calculations of X-ray absorption spectroscopy (XAS) and resonant inelastic X-ray scattering (RIXS). These complementary techniques highlight the electronic structure of both occupied and unoccupied states. To account for the excitonic effects in the excited state calculations, we used a Green's function approach based on the solution of the Bethe-Salpeter equation. Non-interacting Green's functions and light-matter interaction matrix elements were obtained from the mean-field density functional theory.

Furthermore, we also considered the dependence of XAS and RIXS signals as a function of Li concentration on both O-K and Ni-L<sub>2,3</sub> edges to obtain a complete picture of the charge transfer and redox activity during the charge/discharge process.

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# DEVELOPMENT OF $\text{Mg-O}_2$ BATTERY ELECTROLYTE COMPOSITION

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$\text{Mg-O}_2$  battery is a promising alternative to lithium-ion batteries, as it has higher theoretical specific energy. In  $\text{Mg-O}_2$  battery carbon paper often used as a positive electrode, metallic magnesium as negative electrode and solution of magnesium salt in aprotic solvent as electrolyte. Upon battery discharge electrochemical oxygen reduction reaction (ORR) occurs on a positive electrode. Solid, insoluble in electrolyte and insulating products ( $\text{MgO}_2$ ,  $\text{MgO}$ ) are formed by this reaction. Their formation on positive electrode surface blocks electron transfer that leads to impeding either discharge or charge process. It is worth noting, that  $\text{MgO}_2$  is rather favorable discharge product than  $\text{MgO}$  as  $\text{MgO}_2$  is easier to oxidize upon charge. Generally, composition of discharge products depends largely on electrolyte solution.

In this work we investigated  $\text{Mg-O}_2$  battery electrolytes based on common solvents - 1-Methoxy-2-(2-methoxyethoxy)ethane (diglyme), acetonitrile, sulfolane, dimethyl sulfoxide (DMSO). However, only in DMSO  $\text{Mg-O}_2$  cell showed noticeable discharge capacity. Further, we studied the role of electrolyte anion and water content in electrolyte on discharge process. Principally,  $\text{MgO}_2$  formation coulombic efficiency (measured by spectrophotometry of peroxotitanyl) is less than 2% in any DMSO-based electrolyte.  $\text{MgO}_2$  was earlier suggested to be one of the main  $\text{Mg-O}_2$  battery discharge products. Extremely low  $\text{MgO}_2$  yield is caused by electrolyte decomposition by reaction of solvent with ORR intermediates. This conclusion is confirmed by  $\text{Mg-O}_2$  cell discharge with pseudoreference electrode and discharge products analysis by FTIR. Thus, DMSO cannot be used as electrolyte solvent for  $\text{Mg-O}_2$  battery, despite notable discharge capacity. All in all, our results reveal that solvent stability against ORR intermediates is one of key factors for the choice of electrolyte for  $\text{Mg-O}_2$  battery.

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# SODIUM TO POTASSIUM ION EXCHANGE MECHANISM IN P2-TYPE LAYERED TRANSITION METALS OXIDE

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Potassium-ion batteries (KIBs) are considered to be an inexpensive option for large-scale stationary grid storage applications. The crystal structure of the layered type cathode materials provides a sufficient interlayer distance for hosting and effective diffusion of potassium ions, which are relatively large (1.37 Å). However, direct synthesis route for such layered cathodes faces difficulties<sup>1</sup>.

Here, a "chimie douce" (soft chemistry) method was used to obtain potassium transition metal oxide from a parent P2 type sodium transition metal oxide material. In this work, we used a combination of powder X-ray diffraction (XRD) and transmission electron microscopy (TEM) to investigate the ion exchange mechanism in detail. Both diffraction and high-resolution imaging showed the formation of an intermediate phase with approximately equal amounts of sodium and potassium. Layer-by-layer alternation of sodium and potassium ions was found to be the reason for the appearance of this intermediate phase. Additionally, another type of order was demonstrated: after full ion exchange, potassium ions and vacancies were ordered in a "honeycomb" pattern, resembling the ordering of Li and transition metals in Li-rich nickel manganese cobalt (NMC) oxides. Using electron diffraction and high-resolution imaging, we proved that the P2 structure was preserved during the entire ion exchange process. However, changes in the space group due to different orderings were observed. This study sheds light on the detailed mechanism of ion exchange in layered oxides, and can help develop new cathode materials for potassium ion batteries (KIB).

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# MIXED SODIUM AND IRON PHOSPHATES AS CATHODE MATERIALS FOR SODIUM ION BATTERIES

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An increasing demand for electricity in modern world leads to necessity for production of efficient energy storage systems. One of these systems are sodium-ion batteries (SIBs). A key task for the successful commercialization of SIBs is the development of new efficient electrode materials, which will allow the production of batteries with specified electrochemical characteristics.

Mixed phosphates (compounds containing both phosphate ( $\text{PO}_4^{3-}$ ) and pyrophosphate ( $\text{P}_2\text{O}_7^{4-}$ ) groups) attract a special attention as promising cathode materials for SIBs. A large number of publications are devoted to the study of  $\text{Na}_4\text{Fe}_3(\text{PO}_4)_2\text{P}_2\text{O}_7$  mixed phosphate compound. One of the key problems in the synthesis of this phase is the formation of impurities of various composition in the resulting samples. The formation of a number of impurity phases (for example, maricite-type  $\text{NaFePO}_4$ ) leads to a deterioration in the electrochemical characteristics of the resulting cathode material<sup>1</sup>.

This work aims to systematically investigate the conditions that ensure a minimum content of electrochemically inactive phases during the synthesis of  $\text{Na}_4\text{Fe}_3(\text{PO}_4)_2\text{P}_2\text{O}_7$ .

By variation of stoichiometric ratios of precursor and annealing temperature a number of samples of mixed phosphates were obtained. The phase composition and structure of the obtained samples were refined by Rietveld method. The content of maricite-structured impurity phase in the samples was decreased to 1.5% due to variation of the initial compounds stoichiometrical ratios and annealing temperature.

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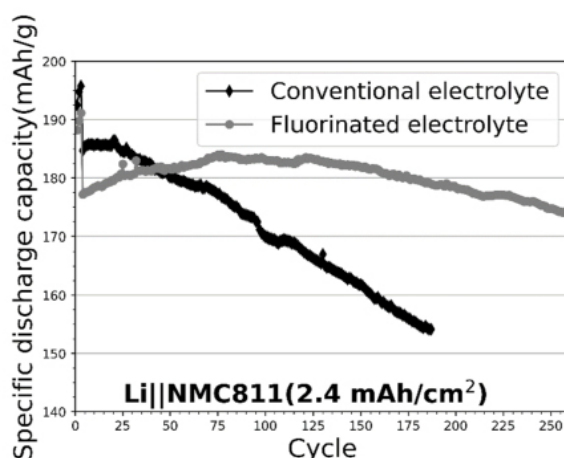
# FLUORINATED ETHERS AS COMPONENTS OF ELECTROLYTES IN LITHIUM METAL BATTERIES

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Lithium-ion batteries are widely used due to their high energy density and long lifetime. However, lithium metal batteries, which have higher energy density, are not as commonly used due to certain drawbacks related to electrolytes, such as flammability, low stability and capacity loss over cycling.<sup>1</sup>

Fluorinated ethers have advantages like increased oxidative stability, good wetting of polypropylene separators, high Coulombic efficiency, and non-flammability. These properties make fluorine-containing ethers promising components for lithium metal battery electrolytes. Moreover, compared to conventional carbonate electrolytes, fluorinated ether-based electrolytes stable at potentials above 4.3 V<sup>2</sup> and demonstrate better performance in cells with Ni-rich cathodes (Fig.1).



**Figure 1.** Specific discharge capacity dependence on cycle number.

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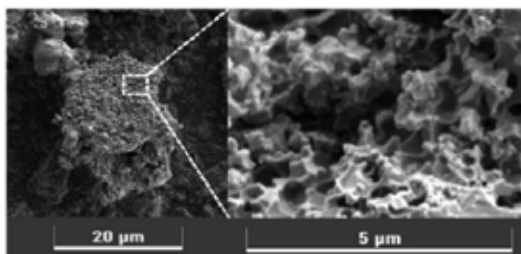
# NANOPOROUS SILICON MICROPARTICLES AS THE ANODE OF A LITHIUM-ION BATTERY

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The theoretical specific capacity of silicon is almost 10 times higher than that of traditional graphite (3579 versus 372 mAh/g, respectively). However, silicon has low cyclic stability. An effective strategy for increasing the cyclic stability of silicon is the creation of nanostructured materials<sup>1</sup>.

In this work, hierarchical nanoporous silicon microparticles were obtained by the method of magnesium-thermal reduction of silica with subsequent acid treatment (Figure 1). The influence of the microstructure of the silicon dioxide used, including industrial trademarks, and the annealing temperature on the elemental and phase composition, morphology and electrochemical properties of the materials obtained has been studied.



**Figure 1.** Scanning electron microscopy images of the obtained silicon microparticles

According to electrochemical testing in galvanostatic mode, the obtained materials demonstrate a specific charging capacity of more than 2000 mAh/g at a current density of 180 mA/g. However, the high irreversible capacity in the first cycle and an overvoltage of up to 20 mV indicate the need to continue work on optimizing the synthesis process, applying a carbon coating and using a chemical bond with a binder.

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# DEVELOPMENT OF A COMPOSITE NEGATIVE ELECTRODE CURRENT COLLECTOR FOR LITHIUM-ION BATTERIES, IN ORDER TO IMPROVE SAFETY

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Lithium-ion batteries (LI-Ion) have taken a leading position among all types of batteries in the modern world due to such advantages as: high specific capacity, cyclic life and lack of "memory" effect. Despite a number of advantages of LI-Ion, they also have a significant disadvantage – low security. In case of external and internal short circuits, overheating and overcharging, thermal acceleration, depressurization, as well as explosion with subsequent combustion of the LI-Ion occur. So, in 2022, the New York City Fire Department recorded 216 cases of LI-Ion fires, resulting in 147 injuries and 6 deaths, which is more than 2 times higher than in 2021<sup>1</sup>.

One of the ways to increase the safety of the LI-Ion is the use of fused current collectors. The principle of operation of such protection is to interrupt the flow of current through the electrode when overheating occurs as a result of melting of a polymer substrate on which a conductive metal layer is applied.

In this work, samples of fused current collectors were obtained from polyethylene terephthalate metallized using magnetron sputtering of copper. The thickness of the applied copper layer was  $\sim 1 \mu\text{m}$ . The surface resistance of the samples measured by the eddy current method was  $5.6 \text{ m}\Omega/\square$ , which is close to the value of the surface resistance of the copper foil. These results allow us to state that the obtained samples can be used as a current collector of the LI-Ion.

Further work on the study of the obtained samples will include checking the operability as a LI-Ion current collector in graphite/lithium metal and graphite/lithium-iron-phosphate systems, as well as tests for battery interruption in case of overheating.

## Literature

1. <https://www.statista.com/chart/29472/fires-caused-by-lithium-ion-batteries/>

# IMPROVING THE ELECTROCHEMICAL PERFORMANCE OF CATHODE MATERIALS WITH A TRIPHYLITE STRUCTURE VIA SURFACE MODIFICATION

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Currently, the most promising cathode materials for lithium-ion batteries include complex phosphates with a triphylite structure. Commercially successful lithium iron phosphate  $\text{LiFePO}_4$  is characterized by high chemical and electrochemical stability, but relatively low operating potential  $\sim 3.4$  V vs.  $\text{Li/Li}^+$ . On the other hand, lithium-manganese phosphate has  $\text{Li}^+$  (de) intercalation potential of 4.1 V vs.  $\text{Li/Li}^+$ , which causes a significant increase in the energy intensity of the material. However,  $\text{LiMnPO}_4$  is characterized by degradation during electrochemical cyclic charge-discharge, which is associated with the dissolution of Mn upon contact with an electrolyte and the formation of a non-conductive layer of  $\text{Li}_4\text{P}_2\text{O}_7$ <sup>1,2</sup> on the surface of particles. One of the potential solutions to this problem is to create a protective layer on the surface that prevents the interaction of the material with the electrolyte.

This work examined the possibility of the formation of particles of a gradient composition, for which an increase in the concentration of iron will occur from the center to the boundary of the particle.

For this purpose, a series of hydrothermal syntheses of  $\text{LiFePO}_4$  modified Mn(II) and  $\text{LiMnPO}_4$  modified Fe(II) materials was carried out, while the duration and temperature of synthesis, as well as the concentration of reagents varied.

The obtained samples were characterized by means of powder X-ray diffraction, scanning electron microscopy and electrochemical galvanostatic cycling. It is shown that  $\text{LiMnPO}_4$ -based materials modified in this way demonstrate improved electrochemical characteristics: increased discharge capacity and improved stability during long-term cycling, including at elevated temperatures.

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# SYNTHESIS OF NI-RICH CATHODE MATERIALS USING COORDINATION COMPOUNDS

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Nickel-rich oxides (NMC oxides) are one of the most promising as cathode materials for lithium-ion battery due to the combination of high operating voltage and specific discharge capacity. Along with the search for the most efficient composition (different combination of transition metals Ni, Co and Mn and tendency to increase Ni content in oxides), one of the most effective methods to increase electrochemical performance is morphology design.

Traditionally, oxide cathode materials are formed from inorganic salts (nitrates, sulfates) of transition metals Ni, Mn, Co by precipitation in the form of carbonates or hydroxides. Initial components and precursor precipitated form influence on the morphology of synthesized oxides. The most common methods for the preparation of NMC oxides involve two steps - synthesis of the precursor and further solid-phase reaction of the precursor with a lithium source. Multistage process, multivariant synthesis conditions - all this also contributes to the formation of morphology and obtaining the exact composition of the material.

In this work, the possibility of using new starting components based on coordination compounds of transition metals in one-step synthesis of NMC oxides was investigated. Pyvalates and acetates of transition metals and lithium were used as starting components. The starting components possessing branched structure lay down a certain pattern in the morphology of synthesized oxides and at the same time can guarantee the exact composition of the obtained oxide. The obtained materials were characterized by various physicochemical analysis methods including SEM, XRD, BET, elemental analysis. Electrochemical behavior was investigated by a complex of methods: galvanostatic cycling (at 0.1C and 0.5C), rate characteristics, electrochemical data analysis using the voltage dependence of the first derivative of capacity on voltage,  $dQ/dV$ .

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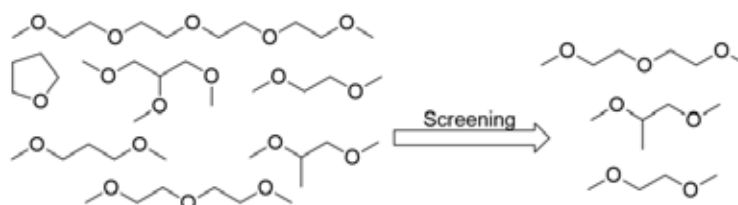
# ELECTROLYTES FOR SODIUM-ION BATTERIES WITH METAL ANODE

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Lithium-ion batteries (LIBs) are one of the most popular energy storage systems, however increasing consumer demand for portable electronic devices creates a need for new types more affordable rechargeable batteries. Sodium-ion batteries (NIBs) might serve as an alternative to LIBs due to their low cost and properties comparable to LIBs.<sup>1</sup>

SIBs with metal anodes possess an increased specific capacity, but standard carbonate electrolytes are unable to provide stable cycling performance for this type of batteries. In our work, we conducted screening of ethers (Fig. 1) as electrolyte components for NIA and developed electrolyte systems compatible with anode based on p-metals (lead, tin and bismuth).



**Picture 1.** Structural formulas of the studied organic solvents.

The proposed electrolytes demonstrated high Coulombic efficiency (up to 99.95%) and great capacity retention (up to 91.5% over 1000 cycles) in Na||Metal half-cells and full cells with the configuration Metal||Na<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>. Also, it is worth to note that such electrochemical systems can be used at subzero temperatures.

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# ELECTROLYTE REFILLING AS A WAY TO RECOVER CAPACITY OF AGED LITHIUM-ION BATTERIES

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The use of lithium-ion batteries (LIBs) in electric vehicles is increasing, which is accompanied by the corresponding increase in the number of spent batteries. Aged batteries are partially used in low-power applications, however, this extends the battery life only slightly. In this report, a novel technique is proposed to restore the capacity of aged LIBs by refilling the electrolyte.

Commercial LIBs of the NMC-C chemical system in a laminated case were aged using charge-discharge cycling with C/2 current. The cycling was carried out to two critical points, approx. 70 and 30% of the original capacity.

The aged batteries were pre-washed, refilled with electrolyte, and tested again. The impact of pre-washing of the aged electrolyte on the refilling results was also evaluated; for this purpose, a mixture of  $\text{sc-CO}_2 + \text{CH}_3\text{CN}$  or liquid  $\text{CH}_3\text{CN}$  was employed. The effects of aging and refilling were assessed through galvanostatic cycling, impedance spectroscopy, and galvanostatic titration. The influence of the pre-washing technique was investigated by ICP MS, XRD, FTIR and XPS.

The results demonstrated that electrolyte refilling allows to restore up to 50% of the lost capacity for LIBs with 30% of the remaining initial capacity after cycling and up to 28% for LIBs with 70% of the remaining initial capacity, while significantly enhancing the power characteristics of the cells. Possible reasons for such effect are discussed in detail in the report. Also, it was demonstrated that neither flushing nor refilling affects the electrode composition<sup>1</sup>. The proposed approach can be used to restore the lost capacity of LIBs.

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# THE MICROSTRUCTURAL DESCRIPTORS OF CARBON ANODE MATERIALS FOR SODIUM-ION BATTERIES

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The demand for energy storage systems is increasing growing every year. Sodium-ion batteries, or SIBs, can be used as a promising and cheaper alternative to lithium-ion batteries (LIBs). However, the key challenge in commercializing this technology is finding suitable electrode materials with good electrochemical properties. Graphite, an anode material used in lithium-ion batteries, is not a suitable electrode material for SIBs. This is because sodium ions do not intercalate between the graphite layers. This limits the potential for SIBs development.

Other sp<sup>2</sup>-hybridized carbon materials, such as hard carbon and soft carbon, can be used as anode materials for SIBs. However, the exact relationship between the microstructure and the charge storage mechanism remains unclear. This study aims to investigate the effect of the microstructural features of these materials such as microporosity and defectiveness on the insertion mechanism of sodium ions.

We compare hard carbon and soft carbon materials, based on different precursors and synthetics methods. on hard carbon obtained from different sources (glucose, phenol-formaldehyde resin) and different methods (hydrothermal and air pretreatment), as well as on soft carbon from petroleum pitch and synthetic polymers. The synthesis took place in one or two stages. In one case, the material was first pretreated in a hydrothermal reactor or in air, after which the sample was subjected to high-temperature annealing, in another case, the material was annealed without pretreatment. The materials demonstrated initial Coulombic efficiency of up to 90% and reversible capacity of up to 400 mAh/g. The mechanism of sodium insertion has been studied using entropymetry, electrochemical impedance spectroscopy, and galvanostatic intermittent titration. The microstructural features of the materials were studied using X-ray diffraction, low-temperature gas adsorption and Raman spectroscopy techniques.

*This work was supported by the Russian Science Foundation (Project No. 24-23-20052)*

# LITHIATED ANODE MATERIALS AS A PROMISING SUBSTITUTE FOR METALLIC LITHIUM IN LITHIUM-SULFUR BATTERIES

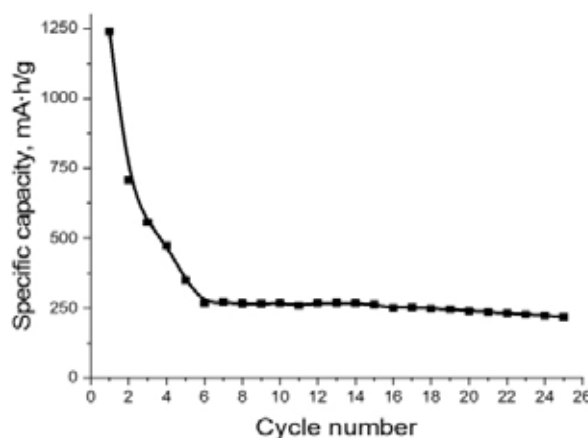
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One of the main problems hindering the commercialization of lithium-sulfur batteries is shuttle transfer: during the discharge process, electrolyte-soluble reaction intermediates - lithium polysulfides are formed, which can migrate through the electrolyte and be recovered on the anode surface from metallic lithium due to chemical interaction, leading to a rapid loss of active component and, consequently, to a rapid drop in battery capacity.

In this paper, to solve the shuttle transfer problem, a complex approach is used. Certain porous carbon materials are used in the active mass of the sulfur electrode, which limit the transport of lithium polysulfides and hold them inside the electrode, and instead of the anode made of metallic lithium, various pre-lithiated anode materials used in lithium-ion batteries are used.

This approach will achieve good cyclic stability, although at the expense of specific energy.



**Figure 1.** Dependence of discharge capacity on the cycle number of lithium-sulfur battery with lithium metal anode.

*This work was financially supported by the Russian Science Foundation, grant No. 23-19-00642, <https://rscf.ru/project/23-19-00642/>.*

# ELECTROCHEMICAL LITHIATION OF NICKEL PHYLLOSILICATE NANOSCROLLS

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Here, we report on a study nickel phyllosilicate nanoscrolls with a chrysotile structure as negative electrodes of a lithium-ion battery (LIB). To obtain the phyllosilicate, the initial composition was first synthesized by reverse precipitation from a  $\text{NiCl}_2$  solution using a NaOH solution in the presence of amorphous  $\text{SiO}_2$ . Next, hydrothermal treatment of the initial composition was carried out at  $T = 220^\circ\text{C}$  for 7 days, after which the resulting nickel phyllosilicate was subjected to heat treatment at  $T = 400^\circ\text{C}$  for 20 hours to remove excess hydroxyl groups. The composition, structure, and morphology of the synthesized  $\text{Ni}_3\text{Si}_2\text{O}_5(\text{OH})_4$  were confirmed by powder X-ray diffraction analysis, X-ray microanalysis and scanning electron microscopy. Electrodes from the resulting material were made using slurry technology. The measurements were carried out in CR2032 two-electrode coin cells, lithium was used as a counter electrode.

Galvanostatic cycling showed that during the first 20 cycles there was a gradual decrease in the discharge capacity from 700 to 130 mAh/g, after which the capacity value stabilized, and the Coulombic efficiency reached 98-99%. In addition, after several cycles, the electrochemical activity of phyllosilicate lithiation products was discovered at voltages above 3 V, which opens up prospects for the use of phyllosilicate not only as anodic, but also as cathode materials after their electrochemical lithiation.

# STUDY OF LOW-TEMPERATURE PROPERTIES OF LIQUID ELECTROLYTE SYSTEMS FOR SODIUM-ION BATTERIES

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The acceptable operating temperature range of metal-ion batteries (MIB) is from -20°C to +60°C, and the optimal is from +15 °C to +35 °C<sup>1</sup>. At the same time, the scope of sodium-ion batteries application implies their use in a wider temperature range, including up to -40 °C and below. But their operation under such conditions can be unsafe and involves a significant decrease in the capacity and Coulomb efficiency.

It is known the low-temperature characteristics of MIB significantly depend on the composition of the liquid electrolyte system<sup>2</sup>.

In this work, the methods of differential scanning calorimetry, chronopotentiometry and electrochemical impedance spectroscopy were used to study the low-temperature properties of electrolyte solutions, where sodium hexafluorophosphate (NaPF<sub>6</sub>) was used as a salt, and ethylene carbonate (EC), dimethyl carbonate (DMC), diethyl carbonate (DEC), 1,2-dimethoxyethane (DME) were used as solvents.

It is established the properties of electrolyte solutions during their cooling can strongly depend on the experimental method (a metastable state of a supercooled liquid may be observed). In the temperature range from -40 °C to -20 °C, 1M NaPF<sub>6</sub> solution in EC:DEC demonstrates satisfactory performance, although it undergoes a partial transition from liquid to solid at a temperature of  $\approx -7$  °C. For the 1M NaPF<sub>6</sub> in EC:DEC:DMC = 1:1:1 system, relatively high ionic conductivity is observed at low temperatures ( $\approx 1.5$  mSm/cm at -40 °C).

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# NEW APPROACHES TOWARDS SYNTHESIS AND MODIFICATION OF CHROMIUM-BASED LAYERED OXIDES AS CATHODES FOR SODIUM-ION BATTERIES

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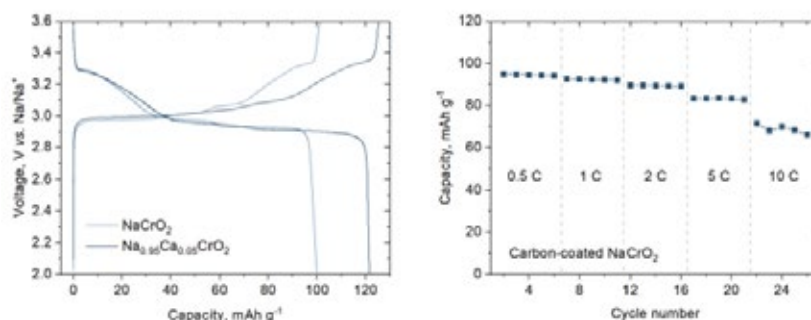
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Layered oxides with  $\text{NaFeO}_2$  structure are widely used as cathodes for sodium-ion batteries due to their high specific capacities. Modification of their chemical composition and optimization of synthesis conditions allow to control the particles size and morphology of such oxides in order to improve their electrochemical performance.

This work is devoted to the synthesis and properties investigation of O3-type sodium layered oxides with the compositions  $\text{NaCr}_{1-x-y}\text{Mn}_x\text{Fe}_y\text{O}_2$  with spherical morphology and high tap density, obtained using coprecipitation method, as well as the use of these materials as cathodes in sodium-ion batteries. Moreover, the doping of these materials with  $\text{Ca}^{2+}$  cations in order to stabilize the structure and minimize the phase transitions during  $\text{Na}^+$  deintercalation was studied. Also, the correlations between the methods of carbon coating and electrochemical properties were revealed.



**Figure 1.** Typical galvanostatic curves (left) and rate capabilities (right) of cathode materials based on modified  $\text{NaCrO}_2$

As a result, the doping of alkali metal position with  $\text{Ca}^{2+}$  cations led to a significant increase of the specific discharge capacity (by more than 20% in the case of  $\text{NaCrO}_2$ ), and the use of a carbon coating made it possible to improve capacity retention at high current densities (Fig. 1).

In the report, modern modification methods of chromium-based sodium layered oxides with  $\text{NaCr}_{1-x-y}\text{Mn}_x\text{Fe}_y\text{O}_2$  composition will be covered, and a detailed analysis of the influence of composition, morphology, dopants and coating on electrochemical characteristics will be provided.

# TITANONILOBATES $\text{LiTi}_x\text{NbO}_{(3+2x)}$ ( $x = 1, 2$ ) AS ANODE MATERIALS FOR LITHIUM ION BATTERIES

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Further development of lithium-ion batteries requires the development of new anode materials that combine high capacity with long cyclic stability and operation safety. Layered titanium-niobium oxides,  $\text{LiTi}_x\text{NbO}_{(3+2x)}$  ( $x = 1, 2$ ), are attractive anode materials due to the possibility of implementing multielectron processes in the anode potential range ( $\text{Ti}^{4+} \leftrightarrow \text{Ti}^{3+}$ ,  $\text{Nb}^{5+} \leftrightarrow \text{Nb}^{3+}$ ), the expected high Li-ions diffusion rate and crystal structure stability.

This work is devoted to the synthesis and crystal structure study of  $\text{LiTi}_x\text{NbO}_{(3+2x)}$  compounds ( $x = 1, 2$ ), as well as their electrochemical investigation as anodes in lithium-ion batteries.

Samples of  $\text{LiTiNbO}_5$  and  $\text{LiTi}_2\text{NbO}_7$  were prepared via ion exchange approach using potassium and cesium titanoniobates as precursors. At the first stage,  $\text{KTiNbO}_5$  and  $\text{CsTi}_2\text{NbO}_7$  were obtained by solid state and/or sol gel synthesis, followed by ion exchange procedures, including the preparation of “solid acids”  $\text{HTiNbO}_5$  and  $\text{HTi}_2\text{NbO}_7 \cdot x\text{H}_2\text{O}$  as intermediates. The crystal structures of  $\text{LiTiNbO}_5$  (sp. gr.  $P2_1/m$ ,  $Z = 2$ ,  $a = 6.421(1) \text{ \AA}$ ,  $b = 3.7701(6) \text{ \AA}$ ,  $c = 8.109(5) \text{ \AA}$ ,  $\beta = 92.23(2)^\circ$ ) and  $\text{LiTi}_2\text{NbO}_7$  (sp. gr.  $Pcmn$ ,  $Z = 4$ ,  $a = 9.2584(9) \text{ \AA}$ ,  $b = 3.7546(3) \text{ \AA}$ ,  $c = 17.032(5) \text{ \AA}$ ) were determined by the Rietveld method using powder X ray diffraction data.

Electrochemical properties of the materials were investigated by chronopotentiometry in lithium ion half cells within the potential range of

1–3 V vs.  $\text{Li/Li}^+$ . The  $\text{LiTiNbO}_5$  material demonstrated the reversible capacity of  $\sim 120 \text{ mA} \cdot \text{h} \cdot \text{g}^{-1}$ . In the case of the  $\text{LiTi}_2\text{NbO}_7$ , an increase in the titanium content, accompanied by a change in the structure and mutual arrangement of the octahedral layers  $[(\text{Ti},\text{Nb})\text{O}_6]$ , resulted in an increase in the reversible capacity up to  $200 \text{ mA} \cdot \text{h} \cdot \text{g}^{-1}$ . Phase and structural transformations of the materials during the charge-discharge were studied applying powder X ray diffraction and X ray absorption spectroscopy in *ex situ* an *operando* regime.

# HARD CARBON-BASED HYBRID SODIUM-ION/SODIUM-METAL BATTERIES

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The technology of sodium-ion batteries (SIB) is actively developing today as a promising alternative to the commonly used lithium-ion batteries (LIB) due to the lower cost of sodium. A more disordered compared to graphite form of carbon (hard carbon) is used as an anode material for SIB, which possesses high specific capacity and initial Coulombic efficiency<sup>1</sup>. However, premature and uneven deposition of sodium in the form of dendrites remains a significant problem, that leads to short circuit of the cell and limits the commercial application of SIB<sup>2</sup>.

In this study it was demonstrated, that by optimizing the parameters of the electrochemical system (electrolyte composition, type of separator, cycling mode, morphology and microstructure of the carbon material) it is possible to prevent dendrite formation and make the deposition/dissolution of sodium metal on the electrode's surface reversible. Such a technology represents a hybrid energy storage system with greater energy gain<sup>3</sup>. Electrochemical properties were studied by galvanostatic charge-discharge cycling and *in situ* electrochemical impedance spectroscopy. The morphology of the sodium plated was studied by *ex situ* scanning electron microscopy with the application of energy-dispersive X-ray spectroscopy.

The best results were achieved for hard carbon samples with microspherical morphology with 10 % fluoroethylene carbonate addition to the electrolyte (1 M NaPF<sub>6</sub> in EC:DEC). The highest discharge capacity reached 830 mAh/g compared to 300 mAh/g in the traditional system, initial Coulombic efficiency was 85%. Full cells with cathode material Na<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> were also assembled and demonstrated higher operating voltage and energy density (by 26 %) along with stable cyclability.

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*The work was carried out with the financial support of the Russian Science Foundation, pro-ject 24-23-20052.*

# FEATURES OF SOLVOTHERMAL SYNTHESIS OF PHOSPHATE CATHODE MATERIALS FOR LITHIUM-ION BATTERIES USING TRANSITION METAL OXIDES

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Cathode materials based on transition metals-lithium phosphates are widely used in rechargeable power supplies. In particular, the market share of LFP ( $\text{LiFePO}_4$ ) batteries has already exceeded 30% and is growing from year to year. Their outstanding advantages are improved service life, low cost of production, and relative environmental friendliness in comparison with Co-containing cathodes. Thus, there is an economic need to develop or improve industrial methods for producing lithium-metal-phosphate materials.

Solvothermal synthesis methods are considered as one of the most promising to produce phosphate materials. Due to the large number of variable parameters and, as a result, the extensive possibilities for controlling the crystal structure of materials, the size and shape of particles, there are a huge number of methods for their production. However, the issue of cost and efficient use of resources in such methods remains open.

This report addresses the use of d-cation oxides as metal-containing reagents, which are cheaper alternatives to the commonly used Fe and Mn salts in the synthesis of phosphate cathode materials. During the study, the dependences of the formation of samples with different phase composition and morphology on several synthesis conditions were established. The samples were examined by powder X-ray diffraction, scanning electron microscopy and galvanostatic electrochemical measurements. The results obtained show that the use of Fe and Mn oxides is promising for the scalable synthesis of materials with a triphylite structure.

*The work was carried out with the financial support of the Russian Science Foundation, grant 24-13-00107.*

# ANALYSIS OF THE Na<sup>+</sup>-ION MIGRATION IN THE NaNi<sub>0.67</sub>Mn<sub>0.2</sub>Co<sub>0.1</sub>O<sub>2</sub> DISORDERED LAYERED OXIDE

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NaNi<sub>0.67</sub>Mn<sub>0.2</sub>Co<sub>0.1</sub>O<sub>2</sub> (NaNMC) is a promising cathode material for sodium ion battery. NaNMC is a layered oxide, which is disordered at both sodium atomic sites and transition metals. For the modeling of Na diffusion, the several steps are necessary to create a pseudo-ordered structure. Therefore, all possible atomic configurations were created using the Supercell software and the electrostatic energies were calculated for each of them. <sup>1</sup> More than six million nonequivalent configurations were generated for the 3x2x1 supercell, and only ten structures with the lowest electrostatic energy were selected for the following density functional theory (DFT) relaxation in the VASP program.<sup>2</sup> The three most stable configurations were selected for subsequent modeling of the Na<sup>+</sup> ions' diffusion using the bond valence site energy (BVSE), kinetic Monte Carlo (KMC) and DFT calculations. <sup>3</sup> All methods prove 2D sodium ion diffusion, the results are shown in the Table 1.

| Configuration number | BVSE                         |      |                              |      | KMC at T=298K         |                       | DFT                          |                              |
|----------------------|------------------------------|------|------------------------------|------|-----------------------|-----------------------|------------------------------|------------------------------|
|                      | $E_m$ (Na <sup>+</sup> ), eV |      | $E_m$ (O <sup>2-</sup> ), eV |      | D, m <sup>2</sup> /s  | $\bar{\sigma}$ , S/cm | $E_m$ (Na <sup>+</sup> ), eV | $E_v$ (Na <sup>+</sup> ), eV |
|                      | 1D                           | 2D   | 1D                           | 2D   |                       |                       |                              |                              |
| 1                    | 0.17                         | 0.46 | 2.88                         | 3.35 | 1.8×10 <sup>-11</sup> | 2.7×10 <sup>-10</sup> | 0.47                         | 0.53                         |
| 2                    | 0.25                         | 0.30 | 3.18                         | 3.22 | 7.5×10 <sup>-10</sup> | 1.2×10 <sup>-8</sup>  | 0.50                         | 0.28                         |
| 3                    | 0.25                         | 0.33 | 3.00                         | 3.07 | 4.8×10 <sup>-18</sup> | 7.3×10 <sup>-17</sup> | 0.50                         | 0.33                         |

**Table 1.** The calculation details of Na<sup>+</sup> ion migration in NaNMC from BVSE, KMC and DFT simulations.

More accurate DFT-NEB calculations show barriers to sodium diffusion in the range 0.35-0.8 eV per elementary pathway. Each configuration has 18 elementary pathways, and the arithmetic mean of the activation energy  $E_m$  along all considered pathways is close to 0.5 eV. The average vacancy formation energy for sodium ions  $E_v$  is less than or equal to 0.5 eV, which seems favorable for ion diffusion.

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# OPTIMIZATION OF SYNTHESIS AND GRAIN BOUNDARIES FORMATION FOR ION-CONDUCTIVE CERAMICS WITH NASICON STRUCTURE FOR ALL-SOLID-STATE SODIUM-ION BATTERIES

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The replacement of conventional liquid electrolyte to solid ceramics in metal-ion batteries is one of the important direction of sodium-ion batteries (SIBs) development as it will significantly improve battery safety, lead to an increase in the electrochemical potential of the cell, and consequently, to an increase in energy density. Phosphate ceramics, in particular  $\text{Na}_3\text{Zr}_2(\text{SiO}_4)_2\text{PO}_4$  (NZSP) with NaSICON-type structure is one of the prominent candidates: this material possesses high ( $10^{-3} \Omega^{-1}\text{cm}^{-1}$  and above) ionic conductivity, is relatively stable on air and may be synthesized by facile procedure<sup>1</sup>. Recently, the alternative methodology named “solution-assisted solid-state technique” was proposed; the distribution of elements in ceramics obtained by the following method was more homogeneous resulting in the increase in ionic conductivity and material stability<sup>2</sup>. At the same time, it is necessary to thoroughly investigate the influence of synthesis parameters and sintering additives on density, grain size distribution, and ionic conductivity for reproducible production of dense ion-conductive ceramics using this synthesis method.

In this work, the influence of synthesis conditions and precursor impact on the phase composition, microstructure, and electrochemical characteristics of the ion-conductive NZSP ceramics were studied. Optimal values of precursor excess were determined to form dense ceramics with impurity content less than 3%, a volumetric density level of 95%, and ionic conductivity of about  $10^{-3} \Omega^{-1}\text{cm}^{-1}$ . The impact of sintering additives such as  $\text{B}_2\text{O}_3$  and  $\text{MgO}$  was also investigated. The dependence of material's microstructure from synthesis parameters, sintering additives as well as its correlation with grain boundary and bulk ionic conductivity will be presented during the report.

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# FLUORINATED ESTERS AS NEW ELECTROLYTE COMPONENTS FOR HIGH VOLTAGE LITHIUM BATTERIES

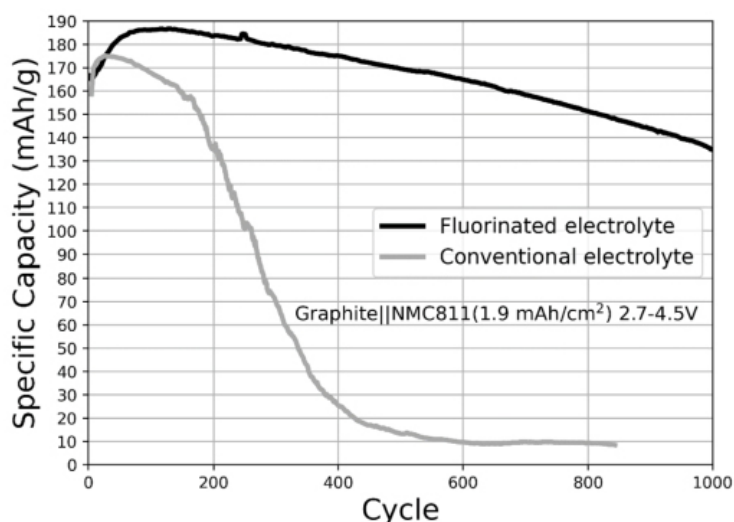
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Energy storage systems, such as lithium-ion batteries, are becoming more relevant. With the increasing popularity of portable electronics and electric vehicles, there is a growing demand for high-capacity batteries.

Fluorinated esters are known to be effective components of electrolytes for high-voltage lithium-ion batteries.<sup>1</sup> They significantly reduce the risk of electrolyte ignition and increase resistance to electrolyte degradation.<sup>2</sup>

Our results show that electrolyte systems containing organofluorine esters were found to be effective in NMC811||Graphite up to 4.5V (Fig. 1). Furthermore, pouch cells (6.9 mAh/cm<sup>2</sup>) containing fluorinated esters showed capacity retention up to 78% after 1000 cycles (2.7-4.5 V).



**Figure 1.** Specific capacity dependence on the number of cycles.

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# $\text{Na}_{2/3}\text{Ni}_{1/3-x}\text{Mg}_x\text{Mn}_{2/3}\text{O}_2$ AS A CATHODE MATERIAL FOR SODIUM-ION BATTERY

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The search of materials with high specific capacity and thermal stability for sodium-ion batteries attract an interest. One of the promising cathode materials is the  $\text{Na}_{2/3}\text{Ni}_{1/3-x}\text{Mg}_x\text{Mn}_{2/3}\text{O}_2$  phase.

On the first stage of this work  $\text{Na}_{2/3}\text{Ni}_{1/3-x}\text{Mg}_x\text{Mn}_{2/3}\text{O}_2$   $x=0, 1/9, 1/6, 2/9$  were synthesized by solid state method. A high-voltage plateau in the range of 4.2-4.5V was observed for all materials by galvanostatic cycling. The study of phase transitions by X-ray diffraction showed the presence of P2-O2 transition for  $x=0$  and P2-OP4 transition for  $x>0$ . It indicates complete deintercalation of sodium in the first case and only partial in the second one. At the same time, for  $x=1/9$ , there is the degradation rate decrease in comparison with magnesium-free material. For  $x>1/9$ , the P2-OP4 transition occurs at voltages higher than 4.35V that leads to the degradation rate increase during cycling due to electrolyte decomposition.

The study of materials thermal stability by differential scanning calorimetry showed that all materials in the uncharged state are stable until 450°C. For deintercalated materials  $x=0, 1/9$  we measured the decomposition temperatures and thermal effects.

In summary, we found that the low concentration of magnesium leads to better cyclability  $\text{Na}_{2/3}\text{Ni}_{1/3-x}\text{Mg}_x\text{Mn}_{2/3}\text{O}_2$ , but the deintercalated magnesium-containing materials are unfortunately less thermally stable compared to the magnesium-free phase.

*The work was performed under financial support of Russian Science Foundation (project 22-13-00427).*

# HIGH-CAPACITY SILICON-BASED ACTIVE MATERIALS FOR NEGATIVE ELECTRODE OF LITHIUM-ION BATTERIES

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Lithium-ion batteries (LIBs) remain the market leader due to their high energy density and long lifespan as demands for electric vehicles and portable electronics increase. The LIBs parameters depend heavily on the properties of electrode active materials. Traditional graphite anode materials cannot meet future demands for developing the LIBs with a higher energy density. Silicon-based anode materials are considered to be the most promising ones to replace the graphite in the next generation LIBs due to the high theoretical specific capacity and low lithiation potential. However, a large volume expansion of silicon during the cycling process causes the rapid degradation of the active material. And special attention is therefore given to developing the nanoscale and amorphous structures as well as their composites.

In our work, we conduct comprehensive research on both commercial composite materials based on amorphous silicon covered carbon shell (Si/C), and lab-synthesized anode Si-based materials. The Si/C-based anodes exhibit the specific discharge capacity up to 1800 mAh g<sup>-1</sup> (vs. Li) at a charge-discharge rate of 0.05C and the initial coulombic efficiency (ICE) of about 87%. The full coin cells including Si/C-based anodes and LiNi<sub>0.6</sub>Mn<sub>0.2</sub>Co<sub>0.2</sub>O<sub>2</sub> cathodes were subjected to the prolonged cycling at 0.25C in three voltage ranges. The full cells tested in the range of 2.2–4.0 V demonstrated the highest cycling stability (capacity retention is 92.4% after 300 cycles).

The silicon-based material with amorphous structure (a-Si) was synthesized by a solvothermal method. Analysis of the synthesized material showed the presence of by-products that were removed with the subsequent annealing and washing. In the first cycle, the specific discharge capacity for a-Si-based anodes was about 1120 mAh g<sup>-1</sup> (vs. Li) at 25 mA g<sup>-1</sup> current density.

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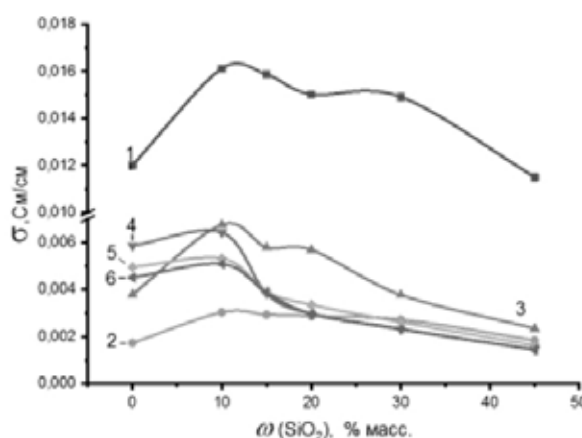
# THE VIBRATIONAL SPECTRA AND CONDUCTIVITY OF LITHIUM AND SODIUM PERCHLORATES IN NON-AQUEOUS SOLUTIONS (ACN, PC, PC – DMC AND PC – DME) WITH $\text{SiO}_2$ AND $\text{Al}_2\text{O}_3$ NANOPARTICLES

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In recent years, electrolytes of “soggy sand” systems, consisting of a liquid electrolyte in which insulating but surface active oxide nanoparticles are dispersed: silicon oxide ( $\text{SiO}_2$ ) and aluminum oxide ( $\text{Al}_2\text{O}_3$ ) have been of particular interest<sup>1</sup>. In this work, the vibrational spectra and electrical conductivity of lithium and sodium perchlorate systems in acetonitrile (AcN), propylene carbonate (PC), propylene carbonate-dimethyl carbonate (PC–DMC) and propylene carbonate-dimethoxyethane (PC–DME) in the presence of  $\text{SiO}_2$  filler were studied.



**Figure 1.** Dependence of specific ionic conductivity in systems:  
AcN – 1,0 M  $\text{NaClO}_4$  (1); PC – 1,0 M  $\text{LiClO}_4$  (2); PC – 1,0 M  $\text{NaClO}_4$  (3);  
PC – DMC – 1,0 M  $\text{LiClO}_4$  (4); PC– DMC – 1,0 M  $\text{NaClO}_4$  (5); PC–DME– 1,0 M  $\text{NaClO}_4$  (6)  
in the presence of  $\text{SiO}_2$  additives, at  $T=293$  K.

It has been established that doping the systems under study with  $\text{SiO}_2$  nanoparticles leads to the appearance of two maxima on the curve of the concentration dependence on the specific electrical conductivity (Fig. 1) and a shift in the vibration contour of the perchlorate anion in the Raman spectra. This fact may be due to some interaction of the silicon oxide nanoparticle with the perchlorate ion and a consequence of their orientational ordering.

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# THE EFFECT OF ELECTROLYTE COMPOSITION ON THE CYCLABILITY OF SODIUM-ION ELECTROCHEMICAL CELLS

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Sodium-ion batteries are a promising alternative to lithium-ion batteries. The development of sodium-ion batteries requires the search for suitable cathode and anode materials, as well as electrolytes. Much attention is paid to finding the most suitable formulation when preparing the electrolyte in order to improve both the electrochemical characteristics of the battery and the safety aspects. The aim of the study is to study electrolyte systems. The research was carried out in full cells, since this model is close to battery prototypes. In addition to the effect of the electrolyte on the electrochemical properties of the system, the influence of parameters such as the morphology of the anode material, the composition of the cathode material and the mass ratio of cathode and anode materials was studied.

During the work, electrolytes with organic carbonates as solvents and various concentrations of  $\text{NaPF}_6$  salt were prepared. We used non-graphitizable carbon (HC) as the anode materials, and  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$  (NVP) as the cathode material. Full cells were investigated by galvanostatic charge-discharge cycling and the discharge capacity, Coulomb efficiency, cyclability and power characteristics were determined.

It is shown that the morphology of non-graphitizable carbon affects the capacity and cyclability of the full cell. The full NVP/HC cell in the case of the microspherical morphology of the carbon material is characterized by better cyclability. It is shown that electrolytes based on 1M  $\text{NaPF}_6$  in a two-component (EC:DEC 1:1) and a three-component solvent system (EC:PC:DEC 1:1:2) are suitable for long-term cycling of full cells and prototypes of sodium-ion batteries. A full cell of NVP/HC and 1M  $\text{NaPF}_6$  electrolyte in EC:EC (1:1) demonstrated a discharge capacity of 60 mAh/g on the 1000th cycle.

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# THERMAL STABILITY OF MATERIALS FOR SODIUM-ION BATTERIES

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Nowadays, the technology of sodium-ion batteries (SIB) is actively developing in laboratories and in industry. The use of SIB instead of lithium-ion batteries as stationary energy storage systems may be more profitable. However, some issues related to the thermal stability of SIB have not been sufficiently studied<sup>1</sup>.

In the course of the work, the thermal stability of cathode materials (based on  $\text{Na}_3\text{V}_2\text{O}_2(\text{PO}_4)_2\text{F}$ ) and anode materials (based on hard carbon) have been studied with differential scanning calorimetry (DSC). Based on DSC model experiments between individual components, some chemical reactions corresponding to the observed thermal effects has been proposed. The temperature ranges and the thermal effects of some of them are represented in Table 1.

| Chemical process   | Temperature range, °C | Heat, J/g |
|--|-----------------------|-----------|
| The decomposition of primary SEI (solid electrolyte interphase, passivation layer emerging on the anode material during the charge and discharge of SIB) $(\text{CH}_2\text{OCO}_2\text{Na})_2 \rightarrow \text{Na}_2\text{CO}_3 + \text{C}_2\text{H}_4 + \text{CO}_2 + 1/2\text{O}_2$  | 65 – 97               | 4         |
| Cycles of regeneration of secondary SEI and its immediate thermal decomposition: $2\text{Na} + 2\text{C}_3\text{H}_4\text{O}_3 \rightarrow (\text{CH}_2\text{OCO}_2\text{Na})_2 + \text{C}_2\text{H}_4$ $(\text{CH}_2\text{OCO}_2\text{Na})_2 \rightarrow \text{Na}_2\text{CO}_3 + \text{C}_2\text{H}_4 + \text{CO}_2 + 1/2\text{O}_2$ | 100 – 165             | 252       |
| The reaction between the sodium embedded in the anode material and the electrolyte: $\text{Na} + \text{C}_3\text{H}_4\text{O}_3 \rightarrow \text{Na}_2\text{CO}_3 + \text{C}_2\text{H}_4$   | 168 – 268             | 209       |
| Thermal decomposition of $\text{Na}_3\text{V}_2\text{O}_2(\text{PO}_4)_2\text{F}$ as a main component of cathode material  | 116 – 189             | -103      |

**Table 1.** Temperature ranges and thermal effects of reactions occurring in the NIA during thermal decomposition.

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# OXIDATION OF LITHIUM PEROXIDE BY CYCLOMETALLATED RUTHENIUM COMPLEXES IN LITHIUM-OXYGEN BATTERY

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Lithium-oxygen batteries (LOB) are promising energy source since its specific energy is an order of magnitude higher than that of lithium-ion batteries. The key problem limiting the development LOB is the poor conductivity of the main discharge product - lithium peroxide ( $\text{Li}_2\text{O}_2$ ). It leads to high charging voltage and battery components degradation. To solve this problem, it was proposed to use redox mediators (RM) that oxidize electrochemically on the positive electrode surface upon battery charge, diffuse into the electrolyte volume and chemically oxidize  $\text{Li}_2\text{O}_2$  that leads to charge voltage reduce. Here we propose cyclometalated ruthenium (II) complexes (CMC Ru) with 4,4'-dimethyldicarbonylbipyridine and various 1-phenyl-2-arylbenzimidazoles as redox mediators for LOB.

The galvanostatic cycling with capacity limitation was carried out in model LOB cells with added RM. On the first cycles Ru CMCs demonstrate a charge voltage decrease in comparison with RMs known from the literature<sup>1</sup> (ferrocene, decamethylferrocene, tetrathiofulvalene). However, after the 5th cycle, the mediator effect disappears due to its chemical decomposition. It destructs by highly reactive singlet oxygen ( $^1\text{O}_2$ ) that forms during the discharge/charge of the LOB as result of lithium superoxide intermediate disproportionation. The kinetic study of  $\text{Li}_2\text{O}_2$  oxidation by oxidized forms of RMs showed an increase in the effective reaction rate constant with increasing mediator OR potential.

Here we found that ruthenium CMC reduce the LOB charging voltage but they are unsuitable RM for LOB since they are unstable to reactive oxygen species formed during cycling. Therefore, further search of LOB RM with good cyclability should be focused on complexes with inert substituents.

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# NI-RICH NMC WITH IMPROVED MECHANICAL AND ELECTROCHEMICAL CHARACTERISTICS

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The need for increasing the energy density of lithium-ion batteries (LIBs) leads to complex layered oxides of lithium and transition metals  $\text{LiNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$  ( $x + y + z = 1$ ,  $x \geq 0.6$ ), so called Ni-rich NMCXYZ, becoming one of the promising cathode materials for LIBs. Increasing the Ni content ( $x > 0.85$ ) ensures obtaining materials with high reversible specific capacity (up to 230 mAh/g at 2.7-4.3 V vs. Li/Li<sup>+</sup>) and energy density (up to 800 Wh/kg) and relatively low cost. However, despite the high electrochemical capacity, Ni-rich NMC are still highly limited in practical application due to rapid capacity fade during electrochemical cycling and low structural stability. These drawbacks are mainly associated with mechanical fracture (microcrack formation) of agglomerates consisting of sub-micron primary particles.

In order to overcome the above problem, in this work an approach based on obtaining radially oriented elongated plate-like primary particles in agglomerates and Ni/Co concentration gradient, i.e., the content of nickel and cobalt gradually changes from the center of the agglomerate to its surface, was implemented. For this purpose, a Co-rich coating layer on the surface of the mixed hydroxide precursor  $\text{Ni}_{0.95}\text{Mn}_{0.025}\text{Co}_{0.025}(\text{OH})_2$  via microwave-assisted hydrothermal synthesis based on urea as a source of hydroxide anions, was prepared, followed by high-temperature annealing with a Li source. SEM and HAADF-STEM investigation indicated differences in the formation/absence of cracks in the original and modified materials. AFM nanoindentation revealed a tendency to decrease hardness in the Co-modified material.

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# STUDY OF ELECTROLYTE SYSTEMS WITH COMPETITIVE ION TRANSPORT IN MIXED SOLVENTS ACCORDING TO NMR AND QUANTUM CHEMICAL MODELING DATA

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The work was carried out as part of the study of the mechanism of ion transport at the nanocomposite polymer electrolyte (NPE)/liquid electrolyte/porous electrode interfaces, which are critical for battery operation<sup>1</sup>. Electrolytes based on LiBF<sub>4</sub> and LiTFSI salts in gamma-butyrolactone (GBL), dioxolane (DOL) and dimethoxyethane (DME) were studied. It has been shown that “liquid-phase therapy” of the NPE/porous cathode interface effectively increases the electrode response only in the case of 1M LiTFSI in a DOL/DME mixture (1:2 by volume), while 1M LiBF<sub>4</sub> in GBL, 78 wt.% of which is included in NPE, makes the boundary non-conductive<sup>1</sup>. The following compositions of liquid electrolytes were studied: 1) 1 M LiBF<sub>4</sub> in GBL; 2) 1 M LiBF<sub>4</sub> in DOL/DME (1:1 vol); 3) 1 M LiTFSI in DOL/DME (1:1 vol); 4) 1 M LiBF<sub>4</sub> in GBL + 1 M LiTFSI in DOL/DME (1:1 vol.). The lithium self-diffusion coefficients measured by NMR together with quantum chemical calculations of the binding energies of solvation complexes of the lithium cation indicate that solvation at the interface with NPE in 1 M LiTFSI in DOL/DME is facilitated, and at the interface with 1 M LiBF<sub>4</sub> in GBL it is hindered, which is in agreement with experiment<sup>2-3</sup>.

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# THE STUDY OF DEFECTS INTERACTION IN DISORDERED CARBON ANODE MATERIALS

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Non-graphitizable (hard) carbon is a promising anode material for sodium-ion batteries, possessing high specific capacity and high coulombic efficiency. It has been established that the characteristics of a material fundamentally depend on its microstructure.

In the majority of theoretical studies, the structure of non-graphitizable carbon is presented as a set of disordered graphene layers. However, such a representation is not enough to describe the electrochemical properties of the material. In particular, the mechanism of intercalation of alkali metals in the region of low potentials poses a particular problem. For a correct theoretical description of the structure of hard carbon materials, it is necessary to take into account Stone-Wales defects, vacancies, heteroatoms N, O, etc. Currently, only a few theoretical works are known that take into account the presence of defects in the structure of non-graphitizable carbon [1,2]. However, the issue of energy stability of the previously considered model structures remains poorly studied.

In this work, a model of non-graphitizable carbon that takes into account curvature and defects under periodic conditions is developed. For a set of structures with different defect contents, a selection by energy was carried out, and the composition of the lowest-energy structures was determined within the framework of density functional theory. For selected structures, the contribution of various defects to the enthalpy of formation was assessed and their interaction was analyzed. In the future, the developed model will be used to study the mechanism of intercalation of alkali metals.

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# SYNTHESIS OF CATHODE MATERIAL $\text{LiFePO}_4/\text{C}$ BY MICROWAVE SPRAY DRYING METHOD

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Lithium-ion batteries (LIBs) are becoming increasingly popular as a secondary electrochemical power source due to their compact size, lightweight, and superior energy intensity compared to previous generations of energy storage devices.

One promising cathode material for LIBs is lithium iron phosphate ( $\text{LiFePO}_4$  or LFP), which offers increased safety, low cost, and a long service life. However, LFP has several challenges, including low volumetric energy density, poor electrical conductivity, and high degradation. One reason for the low volumetric energy density of LFP is its low density.

To increase the density of materials, spray drying is used to obtain spherical or sphere-like agglomerates with a polymodal particle size distribution, which, when tapped, have a denser packing than nano-sized primary particles [1]. In a microwave spray dryer, water is removed under the influence of magnetron radiation, unlike traditional spraying methods where moisture from a drop evaporates under an elevated temperature of 100-300°C.

The resulting  $\text{LiFePO}_4/\text{C}$  cathode material has a more uniform distribution of the carbon coating throughout the entire volume of the spherical agglomerate. This is due to a change in the moisture removal mechanism (from the center to the shell). As a result, the specific discharge capacity at a cycling rate of 0.1 C is 162 mAh/g, and the values of tap density with shaking reach 1.6 g/cm<sup>3</sup>.

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# BIOWASTE-DERIVED HARD CARBON MATERIALS FOR SODIUM-ION BATTERIES

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Non-graphitizable carbon (hard carbon, HC) is a promising anode material for sodium-ion batteries (SIBs) [1]. Secondary biomass could serve as a potential source for the production of HC [2]. Every year, more than 7 thousand tons of waste generated by the oil and fat industries in the Russian Federation are not disposed of in a rational manner. Therefore, the aim of this study is to develop a process for the manufacture of biomass-based non-graphitizable carbon.

Waste from the oil and fat industry, such as sunflower husk and cakes, and microcrystalline cellulose (MCC) were selected as precursors. Different methods of pretreatment were proposed and their effects on the composition, microstructure and electrochemical properties of the HC were studied.

MCC-based materials have shown impressive electrochemical properties (discharge capacity of 305 mAh/g and the initial Coulombic efficiency (ICE) above 90%). Sunflower husk-based materials have demonstrated characteristics acceptable for industrial use: a discharge capacity of 248 mAh/g and the ICE of 85%. The conducted research has shown that the pretreatment of high-voltage sources (cake) is a necessary stage for obtaining materials with satisfactory electrochemical properties. The effect of inorganic impurities on the electrochemical properties of materials has also been thoroughly investigated.

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# APPROXIMATION OF THE RATE CAPABILITY FOR HYBRID ELECTRODE MATERIALS AND BATTERIES

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The electrical capacity of electrochemical power sources is strongly dependent on the rate of charge or discharge. Diffusion of ions in the active material is the main factor limiting this rate. At high currents and a developed electrode surface, the influence of the capacitance of the electric double layer is significant. The authors [1, 2] propose a model according to which the reduction of the current source capacitance in comparison with the limiting maximum capacitance is proportional to  $(R\tau)^n(1 - e^{-(R\tau)^{-n}})$ , where  $R$  is the current normalized to the realized capacitance;  $\tau$  and  $n$  are, respectively, the characteristic stage time and an exponent depending on the type of limiting stage. To the expression  $(R\tau)^n(1 - e^{-(R\tau)^{-n}})$  we give the meaning of the probability of the process failure due to the limited speed of one limiting stage.

We propose to represent a complex process of accumulation or release of charge by a combination of single processes and apply the properties of probabilities. For example, if we assume that in the electrode charge accumulation is possible due to a sequence of  $N$  stages, the probability of realization of the whole process will be determined by the product of probabilities of realization of each of the sequential components of the process, so the formula for the specific capacitance of the electrode material, realized for a given time, in the analysis of probabilities of events will take the following form:

$$\frac{Q}{M} = Q_M \cdot \prod_{i=1}^N [1 - (R\tau_i)^{n_i}(1 - e^{-(R\tau_i)^{-n_i}})].$$

The model was successfully applied to approximate the dependence of electrical capacity on discharge currents of  $\text{LiFePO}_4$  anisotropic crystallites [3,4].

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# HYBRID CATION-EXCHANGE MEMBRANES FOR LITHIUM METAL BATTERY APPLICATIONS

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Lithium metal batteries with a metallic anode may allow a doubling of the energy density compared to conventional lithium-ion batteries, which currently reaches ~250 Wh/kg. The most important issue limiting their widespread application is the dendrite growth through the electrolyte, which leads to deterioration of the electrochemical performance of the battery and eventually to short circuits. The use of cation-exchange membranes solvated by organic solvents as electrolytes in lithium metal batteries allows to improve their safety, but the mechanical properties of the membranes deteriorate after solvation.

In the present work, the transport, mechanical and electrochemical properties of hybrid Nafion membranes in Li<sup>+</sup> form containing in-situ obtained zirconium oxide with neutral and sulfonated surfaces solvated by mixtures of ethylene carbonate and dimethyl carbonate, ethylene carbonate and dimethylformamide, ethylene carbonate and dimethyl sulfoxide and ethylene carbonate and *N,N*-dimethylacetamide have been studied. It was shown that the introduction of dopant leads to a decrease in the ionic conductivity of all the membranes studied, but the membrane containing sulfonated zirconium oxide shows a higher ionic conductivity for all solvents compared to the native membrane. The maximum values of ionic conductivity (2.16 mS/cm at 25°C) and Young's modulus (89.0±18.3 MPa) among the hybrid membranes were obtained for the membrane solvated by ethylene carbonate and *N,N*-dimethylacetamide mixture in Li<sup>+</sup> form. Combined with high ionic conductivity, this makes this membrane the best candidate for its application as electrolyte in lithium batteries. Symmetric Li|Li cells as well as LFP|Li batteries with membrane electrolyte showed good performance for over >200 h.

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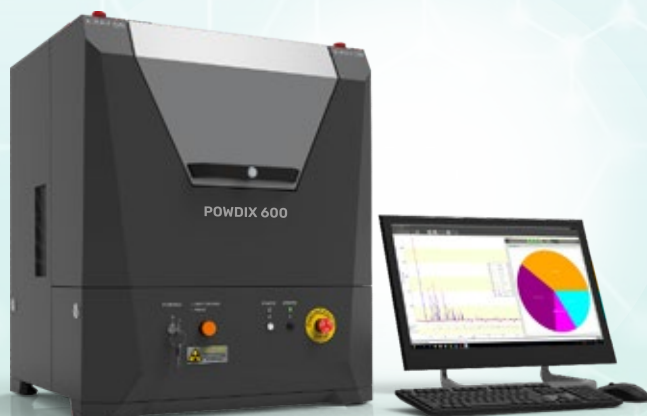
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## ПРОГРЕСС, БЕЗОПАСНЫЙ ДЛЯ ПРИРОДЫ

Компания «ФосАгро» – лидер российской химической промышленности выступила с инициативой создания фонда для финансовой и научной поддержки перспективных ученых-химиков, в сферу интересов которых попадают охрана окружающей среды, здравоохранение, продовольствие, повышение энергоэффективности и рациональное использование природных ресурсов.

В 2013 году между ЮНЕСКО, Международным союзом теоретической и прикладной химии (IUPAC) и компанией «ФосАгро» было подписано соглашение о партнерстве в создании программы грантов для ученых, занимающихся так называемой «зеленой химией». Предметом этого направления в науке является создание производственных технологий и материалов, безопасных для природы и человека.

Так родился проект «Зеленая химия для жизни», помогающий талантливой молодежи не только материальными средствами для

продолжения исследовательской работы и реализации проектов, но и плодотворным общением со старшими коллегами – видными современными химиками, и организацией информационного обмена в научной среде. Это первый проект в истории ЮНЕСКО и ООН, реализуемый за счет средств российского бизнеса. ФосАгро выделила более \$2,5 млн на развитие и реализацию проекта.

## ТРИНАДЦАТЬ МУДРЕЦОВ

Отбор заявок на участие в проекте – обязанность компетентного жюри, в которое входят 13 ученых из 11 стран. Проект-победитель должен соответствовать нескольким критериям. Оцениваются его научная новизна, глобальная и локальная значимость, соответствие принципам «зеленой химии», компетентность молодого ученого и его команды, оснащенность института и лабораторий, в которых предполагается вести проект. Качество работ очень высокое, и членам жюри приходится порой вступать в длительные диспуты по той или иной кандидатуре.

## НАУЧНЫЙ ПОИСК БЕЗ ГРАНИЦ

В 2016 году был учрежден специальный грант за исследования в области применения фосфогипса. В 2019 году в штаб-квартире ЮНЕСКО в Париже в рамках открытия Года Периодической таблицы химических элементов было принято решение продлить грантовую программу «Зеленая химия для жизни».

Проблемы экологического характера, к сожалению, есть во всем мире, и во всем мире есть ученые, которые предлагают решения для многих из этих проблем методами и технологиями «зеленой химии». Это наглядно демонстрирует география проекта «Зеленая химия для жизни». За время реализации программы на рассмотрение жюри поступило более 1000 заявок, 55 грантов было присуждено молодым ученым из 33 стран. Самый главный результат грантовой программы – практическое применение разработок молодых исследователей.



## ЖИЗНЬ ПОСЛЕ ГРАНТА

Дважды за первые 10 лет существования проекта победителями конкурса становились ученые из России. Одна из них – Галина Калашникова, заведующая лабораторией синтеза и исследования минералоподобных функциональных материалов Центра наноматериаловедения ФИЦ КНЦ РАН. В 2019 году грант «Зеленая химия для жизни» был присужден проекту «Разработка универсального и экологичного метода гранулирования синтетических титаносиликатных материалов (сорбентов, катализаторов, регенерируемых матриц), полученных на основе отходов региональных горно-обогатительных и металлургических производств».

### Галина Калашникова:

– В рамках проекта удалось опробовать 5 разных методов грануляции для новых материалов с широким функционалом свойств (сорбенты, катализаторы для органического синтеза, керамические матрицы), которые мы синтезируем именно в нашей лаборатории. Мы смогли выбрать наиболее подходящий метод получения гранул для каждого из них, а также приоритетные нетоксичные связующие. Полученные гранулы были опробованы в качестве сорбентов для очистки жидких радиоактивных отходов от радиоизотопов 137-цезия и 90-стронция совместно с лабораторией хроматографии радиоактивных элементов и станцией переработки радиоактивных отходов Института физической химии и электрохимии им. А. Н. Фрумкина РАН.

Работа по проекту продолжается, несмотря на окончание действия гранта. Все полученные средства были потрачены только на выполнение основной задачи, благодаря чему мы приобрели необходимое оборудование, получили хороший опыт в работе с зарубежными коллегами и выстроили приоритетные направления дальнейшей совместной работы со многими научно-исследовательскими организациями.

Хочется пожелать организаторам конкурса еще больше новых проектов, которые были бы направлены на самые острые вопросы взаимосвязи экологии и современной промышленности.





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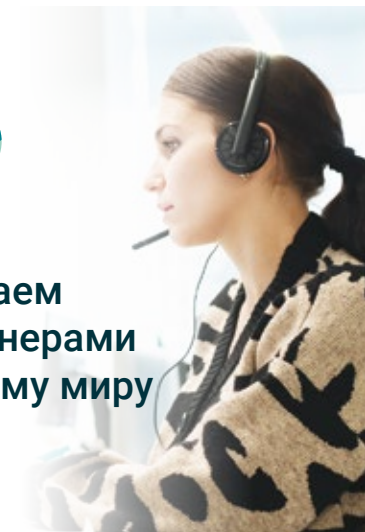
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