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Synthesis of Electrode Materials

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Content

Synthesis of Electrode Materials based on $BaLaInO_4$ with the Ruddlesden-Popper structure

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The environmental situation is getting worse year by year, and the use of electronic devices is increasing, so there is an urgent need for an alternative source of electricity. Recently, among the alternative methods of generating electricity, hydrogen energy has attracted much attention. The environmental friendliness, availability and widespread use of hydrogen are the main advantages of hydrogen energy. In addition, fuel cell technology is about converting chemical energy into electrical energy without releasing carbon dioxide into the environment. The major aim of hydrogen energy is the creation of fuel cells (FC). According to the type of electrolyte used, fuel cells are classified into alkaline FC, proton exchange membrane FC, phosphoric acid FC, carbonate melt FC, and solid oxide FC (SOFC). Among the listed fuel cells, the SOFC is interesting from the point of view of fuel flexibility.

Today, the lowest operating temperature for SOFCs is about 600 °C. However, this temperature is quite high for routine use. Therefore, the search for materials for SOFCs is of high relevance nowadays. Of the known SOFC materials, those with a perovskite structure and its derivatives are the most studied in terms of transport properties. The Ruddlesden-Popper (RP) structure is a derivative of the perovskite structure. The general formula of the structure of RP is $AA'BO_4$, where A are the atoms of the alkali element, A' are the atoms of the rare earth element, B are the atoms of the element in oxidation state 3+ and O are the oxygen atoms.

In this work, an Fe-doped compound with the Ruddlesden-Popper structure was synthesized for the first time. The sample was synthesized using a modified glycine nitrate method. The precursors used were metal nitrates: $Ba(NO_3)_2$, $In(NO_3)_3 \cdot 4.5H_2O$, $La(NO_3)_3 \cdot 6H_2O$, $Fe(NO_3)_3 \cdot 9H_2O$. The resulting powder was accurately ground and annealed at 1050 °C for 24 hours. This was followed by annealing at temperatures of 1100°C to 1300°C with intermediate grinding of the samples in an agate mortar. It has been identified that the conductivity character is mixed hole/oxygen ionic at dry air and hole/oxygen ionic/protonic and wet air. The complex oxide $BaLa_{0.9}Fe_{0.1}InO_{4-\delta}$ can be regarded as a triple conductivity material for SOFC as an electrode material.

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The synthesis of new sodium-ion polyanionic conductors $Na_2Ln(MO_4)(PO_4)$ (Ln = Er, Y, Tb, Ho; M = Mo, W) discovered as a result of high-throughput ICSD screening

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The development of new crystal materials for sodium-ion batteries is considered one of the most promising areas in solid-state electrochemistry. In order to search for new sodium-ion conductors, we selected over 200 crystal structures from the Inorganic Crystal Structure Database (ICSD, version 2023/1), which consist of four-, five- and six-element compounds with several oxygen anionic groups. We selected 45 unique structures with periodic 1D, 2D, and 3D migration maps through geometrical-topological analysis in ToposPro software (https://topospro.com/). Then, using the bond valence site energy method within the softBV program (http://www.softbv.net/), we calculated the sodium migration barriers (E_m, eV) and crystal chemical stability indices for each compound. Finally, we determined the room-temperature ionic conductivities (σ_{rt}, S cm^{-1}) of 21 compounds using a kinetic Monte Carlo approach in softBVCL (https://www.dmse.nus.edu.sg/asn/softBVCL.html). This led to the identification of seven substances with conductivities greater than 10^{-5} S cm^{-1}, including a new class of compounds $Na_2Ln(MO_4)(PO_4)$ (Ln = Er, Y, Tb, Ho; M = Mo, W; sp.gr. Ibca) with layered sodium diffusion, which were not previously considered as possible conductors (Table 1). The screening results are described in more detail in our recent work [1].

Table 1. Theoretical conductivity in $Na_2Ln(MO_4)(PO_4)$ (Ln = Er, Y, Tb, Ho; M = Mo, W).

ICSD code	Composition	Theoretical capacity, mAh g^{-1}	Em(Na$^+$), eV			σrt, S cm^{-1}
			1D	2D	3D	
250440	$Na_2Er(MoO_4)(PO_4)$	171	0.33	0.49	-	2.56×10^{-4}
424743	$Na_2(Y_{0.86}Eu_{0.14})(WO_4)(PO_4)$	220	0.30	0.32	-	1.81×10^{-4}
183506	$Na_2Y(MoO_4)(PO_4)$	206	0.30	0.37	-	1.06×10^{-4}
424739	$Na_2Tb(WO_4)(PO_4)$	232	0.30	0.31	-	8.27×10^{-5}
424738	$Na_2Ho(WO_4)(PO_4)$	230	0.32	0.32	-	1.05×10^{-5}

Then, we have been engaged in the synthesis of these substances for experimental verification of theoretical results. The synthesis of $Na_2Ln(MO_4)(PO_4)$ (Ln = Er, Y, Tb, Ho; M = Mo, W) was performed according to equation [2]:

$$Ln_2O_3 + 2Na_2MO_4 \bullet 2H_2O + 2(NH4)2HPO_4 \rightarrow 2Na_2Ln(MO_4)(PO_4) + 4NH_3 + 7H_2O$$

Starting with stoichiometric amounts of ammonium hydrogen phosphate and rare-earth oxide with an excess of sodium was transferred into a platinum crucible. Then this mixture was heated to 1220 K with a rate of 60 K h^{-1}. After 2 h the mixture was cooled to

1010 K with a rate of 15 K h^{-1} before it was allowed cooling to room temperature with a rate of 180 K h^{-1}. The excess of sodium was dissolved in hot water.

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Ammonia-free coprecipitation synthesis of Ni-rich layered cathode materials for lithium-ion batteries

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The rapid development of technologies dramatically increases the requirements for energy storage systems. The higher energy density, lifetime and low cost of lithium-ion batteries (LIBs) leads to the fact that complex layered lithium and transition metal oxides $LiNi_xMn_yCo_zO_2$ ($x + y + z = 1$, $x \geq 0.6$), so-called Ni-rich NMCXYZ, are becoming one of the promising cathode materials for LIBs. Nevertheless, Ni-rich NMCs (>90%) are still very limited in terms of practical applications due to rapid capacity fade during electrochemical cycling with more than 80-90% lithium extraction, as well as low thermal and structural stability causing safety problems in battery performance. These disadvantages are mainly due to the mechanical failure of agglomerates consisting of submicron primary particles.

The most common method for the preparation of NMCs is the method based on the controlled co-precipitation of mixed hydroxide precursor $Ni_xMn_yCo_z(OH)_2$ followed by high temperature calcination with a lithium source[1]. Moreover, the diffusion properties of Li^+ ions in nickel-rich layered cathode materials are largely determined by the crystallographic structure of their primary particles, which is formed during the synthesis process. And mostly inherited from the microstructure of primary precursor particles [2]. Therefore, one of the most important parameters of co-precipitation synthesis is the control of the concentration of the used complexing agent, most often ammonia. However, maintaining the $NH_3 H_2O$ concentration can be difficult due to the high volatility of ammonia, which makes it difficult to control the reaction precisely. In addition, ammonia is a toxic substance that can be harmful to the environment and human health. Therefore, the development of a method to produce cathode materials without the use of ammonia is a promising area of research.

In this work, high nickel layered $LiNiO_2$ oxides will be obtained, using an optimised concentration of ammonia as a complexing agent, to produce radially oriented primary particles. And ammonia-free techniques will also be applied, where, for example, citric acid will be used as a chelating agent [3], or citric acid with the addition of sodium glutamate [4]. Furthermore, exploration of alternative ammonia-free complexing agents for the preparation of Ni-rich positive electrode materials for lithium-ion batteries via co-precipitation.

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Influence of synthesis methods on the electrochemical properties of $La_{0.9}Sr_{0.1}Sc_{0.4}Mn_{0.6}O_{3-\delta}$ cathode

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Solid oxide fuel cells (SOFCs) are devices generating electrical energy through the electrochemical reaction between oxygen and fuel. A single fuel cell in SOFCs is composed of anode to which fuel is supplied, an electrolyte, and a cathode to which oxygen is supplied. At the cathode, the oxygen reduction reaction (ORR) occurs, which is the limiting process that constrains the operation of the entire cell. The polarization losses at the cathode of SOFCs are estimated as ~50% of the total polarization resistance of the cell [1].

Optimization of the cathode powders morphology by various synthesis methods can increase the ORR rate and improve the performance of SOFCs [2]. The increase in the ORR rate occurs due to the formation of catalytic activity centers on the surface of powder particles and pore systems in the cathode layer. The develop pore systems increase the contact area of the material with oxygen and facilitating the diffusion of the flow to the three-phase boundary (cathode/ electrolyte/ oxygen).

In recent work [3] we investigated the electrical properties of high-density (>95%) $La_{0.9}Sr_{0.1}Sc_{1-x}Mn_xO_{3-\delta}$ materials. We suggested that $La_{0.9}Sr_{0.1}Sc_{0.4}Mn_{0.6}O_{3-\delta}$ may be a promising cathode material. In this work, the influence of microstructure on ohmic and polarization resistance of the $La_{0.9}Sr_{0.1}Sc_{0.4}Mn_{0.6}O_{3-\delta}$ material is investigated. The powders were obtained by various synthesis methods, such as citrate-nitrate, coprecipitation, and solid-phase. The synthesis method influence on the morphology of the obtained powders was estimated. The electrochemical characteristics of cathodes on symmetric cells (cathode/ electrolyte/ cathode) were studied by impedance spectroscopy.

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Study of the influence of titanium (IV) oxide on the electrochemical properties of high-nickel cathode materials

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Layered transition metal oxides with high nickel content, which include $LiNi_{1-x-y}Co_xMn_yO_2$ ($1-x-y \geq 0.6$) are promising materials for creating cathode materials with high energy density [1-2]. However, as the Ni content increases, structural instability increases, which leads to a decrease in the electrochemical characteristics and thermal instability of the material. One of the options for reducing the tendency to degradation of cathode materials is the introduction of doping components. In the literature, the range of proposed doping additives is quite wide and includes Al, Ti, V, Ta, etc.

In this work, the influence of TiO_2 introduction on the electrochemical characteristics of the cathode material was studied. The compound $Ni_xCo_yMn_z(OH)_2$ was used as a precursor of the cathode material. The introduction of doping additives was carried out at the stage of high-temperature heat treatment of the precursor with a lithium source. The obtained materials were studied by ICP, scanning electron microscopy, X-ray spectral microanalysis, X-ray phase analysis, etc. In order to determine the specific discharge capacity, electrochemical tests of the obtained samples were carried out.

When comparing the results for the specific discharge capacity of the first cycle, it is worth noting the decrease in this indicator with a titanium content in the resulting material above 0.5% by weight. The observed decrease in electrochemical characteristics has a high degree of correlation with the intensity of the I(003)/I(104) peaks, which has a similar tendency to decrease with an increase in the consumption of the doping additive. An increase in cationic mixing between lithium and nickel ions may be the cause of deterioration in the cyclability of nickel-containing oxide cathode materials.

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The effect of high-temperature sintering on the electrochemical properties of a thin solid electrolyte based on garnet-type $Li_7La_3Zr_2O_{12}$

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The next generation of all-solid-state lithium-ion batteries is based on the use of solid electrolytes, which leads to increased energy density and battery safety. One of the most promising materials for use in solid-state batteries is $Li_7La_3Zr_2O_{12}$ (LLZO) with a cubic garnet structure. This compound has been demonstrated to exhibit high ionic conductivity (up to 10^{-3} Sm/cm), a wide range of stability of operating potentials (0.05 – 6 V), and non-flammability [1].

However, there are a number of difficulties preventing their practical application due to problems with sintering electrolyte films. It is all about the fact that SSEs need to be sintered at high temperatures (up to 1200°C) for several hours in order to obtain a high-density membrane with a cubic crystal structure required for high ionic conductivity. However, prolonged sintering also results in significant Li loss and corresponding decrease in ionic conductivity. As a result, SSE ceramic films typically exhibit either poor crystallinity or noticeable lithium losses.

A common strategy employed in conventional ceramic film deposition methods is to reduce the processing temperature in order to prevent significant lithium loss, or to add excess lithium to compensate for it. However, this approach often results in poor compositional control.

In this study, a garnet-type $Li_7La_3Zr_2O_{12}$ (LLZO) freestanding ceramic electrolyte film is prepared via tape casting technique followed by sintering [2]. Conventional sintering process was conducted in different atmospheres. Additionally, a high-temperature and short-time approach was implemented, reaching temperatures up to 1500°C [3]. The rapid heating permitted the formation of a dense polycrystalline film structure, with minimal loss of volatile elements due to the brief sintering time. The influence of different sintering methods on the electrochemical properties and chemical composition of thin solid electrolyte membranes will be discussed in this report.

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Synthesis of cathode materials for sodium-ion batteries by spray drying

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In recent years, the issue of replacing lithium-ion electrochemical systems, which are widely used today, with sodium-ion ones has become acute. This will help to solve the problems of lithium shortage on Earth and the high cost of lithium-based materials. The most promising area of application for sodium-ion batteries (SIB) is large-sized stationary energy storage devices, where the availability of raw materials and their low cost, high service life and fire safety are of crucial importance.

One of the main problems in the synthesis of materials is, on the one hand, obtaining the necessary characteristics, primarily bulk density, electrochemical capacity and particle size, and, on the other hand, the cheapest and most environmentally friendly production method.

The spray drying method is currently gaining popularity, the main advantages of which are good reproducibility, significantly smaller particle size and cheaper production costs in mass production [1]. Spray drying is a universal synthesis method that is usually used to produce commercial materials based on transition metal oxides on a large scale; However, it is not widely used in academic research laboratories due to the high cost and complexity of laboratory equipment. The disadvantages of the method include low bulk density of particles, which requires additional processes to improve this parameter. In addition, the literature does not clearly show how various synthesis parameters (concentration, pH of the solution, temperature and flow time) affect the final morphology of the particles [2].

Our team tried this method to synthesize various cathode materials for sodium-ion batteries, varying the above parameters. The main conclusions are as follows: in general, increasing the concentration of the initial solutions for the spray drying method leads to an increase in the size of the primary particles and an improvement in the electrochemical characteristics. The effect of the solvent for the initial solutions needs to be further studied, since no direct correlation was found.

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Developing Liquid Metal-based materials to power flexible and wearable electronics

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Due to the growing demand for wearable electronics and flexible displays, flexible batteries and energy harvesters have become increasingly relevant in recent years. In this regard, the proposed research aims to develop a simple and efficient approach to the creation of energy materials to power textile electronics and smart devices. Our projects aim to collect best practices and trends in this field to create basic technologies for large-scale production of energy storage materials. At the center of the project is the development of a core technology for the processing of liquid metal composites to create and develop flexible electronics for batteries and energy harvesters (triboelectric nanogenerators). In terms of batteries, liquid metals have the significant advantage of inhibiting the dendritic growth of lithium compounds within the battery device compared to conventional materials. Such dendrites are one of the main reasons for the uncontrolled behavior of batteries. Moreover,

liquid metals have the property of self-healing. Unfortunately, the handling of pure gallium is limited by uncontrolled volume changes and phase transformations during electrochemical reactions in the battery, as well as insufficiently high capacity. It is also worth noting that the assembly and testing technologies for conventional batteries are not suitable for liquid metal batteries, which entails the need for research in this area. Therefore, the proposed project is primarily focused on the creation of composite liquid structures, as well as on the search for methods for their molding into materials for energy applications.
The proposed research aims to develop flexible "semi-fluid" composites based on gallium and its alloys with such promising elements in the context of lithium-ion batteries as germanium, silicon, tin, antimony and bismuth. The resulting composites will be adapted for printing to create flexible and efficient battery electrodes. In the field of energy harvesting technologies, we have constructed TENG of various shapes, including fibers and flat structures, which have become an important area of research.

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Electrochemical processing of natural zircon to obtain $ZrSi_2$

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The unique properties of zirconium silicides determine the possibility of their application in various industries. However, the currently known methods for their production are multi-stage and energy-consuming, therefore they cannot be used for large-scale production. One of the promising methods is the production of zirconium silicides from oxide raw materials by electrolysis of molten salts. In this paper, the possibility of obtaining zirconium silicides by electrolysis of $KCl-K_2SiF_6$ melt with the addition of 0.33 and 0.66 wt.% ZrO_2 is considered. For this purpose, the kinetics of the cathode process on a glassy carbon electrode in $KCl-K_2SiF_6$ and $KCl-K_2SiF_6-ZrO_2$ melts at a temperature of 790 ° C was studied by cyclic chronovoltammetry and chronoamperometry, the parameters of silicon and zirconium electrodeposition were determined, and some features of the mechanism of silicon and zirconium ion reduction were established.

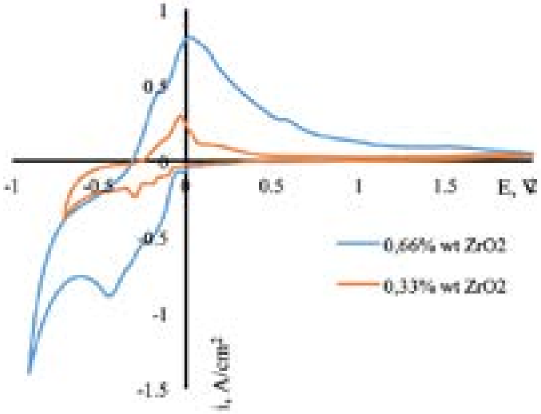

Figure 1. Cyclic voltammograms obtained on glassy carbon in $KCl-K_2SiF_6-ZrO_2$ melts at a temperature of 790°C and a scan rate of 0.5 V/s

Based on the selected parameters, a series of experiments on the electrolysis of the $KCl-K_2SiF_6-ZrO_2$ melt in the galvanostatic mode at a current density of 20 mA/cm^2 were performed. As a result, cathode deposits were obtained, which, after separating the electrolyte residues, were studied by X-ray phase analysis, scanning electron microscopy and micro-X-ray spectral analysis. The cathode deposits were represented by 57-62 wt.% zirconium silicides ($ZrSi$, $ZrSi_2$), as well as the corresponding silicon and zirconium oxides, which indicates the fundamental possibility of obtaining zirconium silicides from oxide raw materials and the need for further optimization of the method.

Application of the $KCl-K_2SiF_6$ liquid salt system for the opening and processing of natural zircon

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In nature, zirconium is most often found in the form of zirconium orthosilicate, which is part of natural zircon. There is also a form of oxide assigned as part of the natural heritage, which accounts for no more than 3-5% of the world's zirconium reserves. The main difficulty in processing zircon is its appearance and subsequent purification. One of the proposed methods of zircon inclusion are liquid crystal systems such as: $KCl-K_2zrf_6$, KCl-KF, $KCl-K_2CO_3-K_2SiF_6$ [1].

The purpose of this work is to establish the applicability of the $KCl-K_2SiF_6$ liquid salt system for the opening and processing of natural zircon.

The study of electrochemical kinetics was carried out using cyclic voltammetry, deposition was carried out in galvanostatic mode, and the study of the obtained precipitation was carried out using X-ray phase analysis, as well as electron scanning microscopy.

Figure 1 shows the most representative voltammogram obtained at a scanning speed of 0.1 V/s.

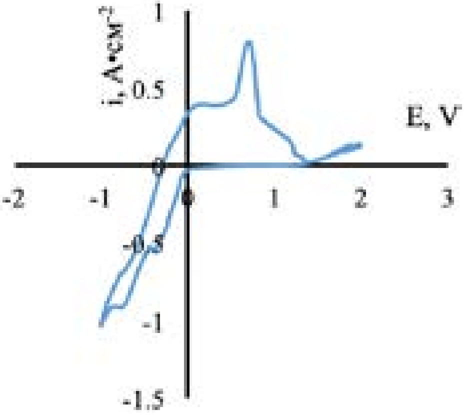

Figure 1. A voltammogram obtained at a scanning speed of 0.1 V/s in the $KCl\text{-}K_2SiF_6\text{-}ZrSiO_4$ *system on a glass-carbon working electrode.*

The presented voltammogram clearly shows a reflex at a potential of 0.7 v relative to silicon, presumably anodic dissolution of silicon. No distinct peaks were recorded in the cathode region, the most likely reason being the inability to achieve unsteady diffusion conditions. The second possible explanation for the results obtained is the large number of possible chemical reactions on the surface of the cathode deposit.

Based on the data obtained, it can be concluded that it is possible to open the processing of natural zircon in the $KCl\text{-}K_2SiF_6$ melt.

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Synthesis and investigation of the electrochemical properties of $NaLixVPO_4F$ as cathode materials for sodium-ion batteries

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Metal-ion batteries (MIBs) play a very important role in everyone’s life. They provide work of many electric portable devices, which are frequently indispensable. First commercialized and most prevalent nowadays type of MIBs are lithium-ion batteries (LIBs) [1]. However, over the last years the need of switching to energy storage system with more available resource base appeared. In this regard, sodium has both benefits and disadvantages. Its cost is lower and the quantity of sodium precursors is almost inexhaustible, but its atoms are heavier and have lower electrode potential [2].
Lately in our group a new modification of $NaVPO_4F$ composition with structural type of $KTiOPO_4$ has been synthesized and analyzed as a prospective cathode material for sodium-ion batteries (SIBs). It showed attractive values of specific capacity (125 135 mAh·g^{-1}) [2]. However, inserting additional lithium ions into the initial structure with simultaneous reduction of V^{3+} forming a group of $NaLi_xVPO_4F$ compounds could lead to specific capacity boost.
This work is devoted to the development of new KTP-$NaVPO_4F$-based cathode materials for SIBs with increased theoretical specific capacity.
Several compounds with $NaLi_xVPO_4F$ has been synthesized for $x = 0.15$ by annealing $NaVPO_4F$ with a lithium reagent. Two substances were chosen as lithium sources: LiI and HCOOLi. First one is attractive due to the presence of anion with high reduction ability and rather low melting temperature (469^{o}C). Lithium formate possesses lower melting point (273^{o}C) while also having reductive anion. Each mixture ($NaVPO_4F$ with LiI and $NaVPO_4F$ with HCOOLi) was homogenized and annealed in tabular furnaces in argon atmosphere

at the temperature around the melting point. X-Ray diffraction analysis shows single-phase product in both cases, which confirms the expected flow of the reaction. When tested in coin-type cells versus sodium, composite materials demonstrate 120 mAh/g at 0.1C rate.

This work is supported by Russian Science Foundation (RSF grant # 23 73 10125).

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Microreactor array based on wettability patterns for high-throughput organic synthesis

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Carrying out chemical reactions in solutions has its advantages and disadvantages. The presence of reagents in one phase helps to increase the rate of the process, meanwhile, interaction with the solvent appears to be an additional barrier. It has been shown that solvent content can be lowered to 1 mass% without phase separation, which results in a 10^2 – 10^4-fold increase in the reaction rate.

An even greater acceleration effect was noticed in charged microdroplets, obtained with electrospray. [1] It is assumed that the acceleration effect, in both cases, is associated with the desolvation of the reacting substances, which happens at the interface of microdroplets or in the media due to solvent evaporation. [1] To practically apply this phenomenon limitations of the existing methods concerning the collection of the product, cost-effectiveness and the optimization of reaction conditions should be addressed.

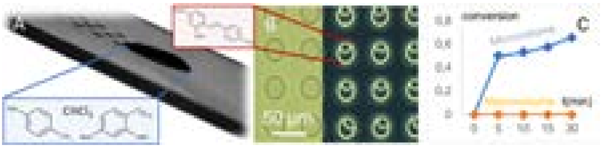

Figure 1. A. Application of droplets array using the running droplet method. B. Selective application of the reaction mass. C. Time-conversion rates for Schiff reactions: blue graph – reaction in $CHCl_3$ *on wettability pattern, orange graph – bulk reaction in* $CDCl_3$*.*

Herein, we introduce a new approach to the formation of a reaction mass droplet array. This approach is based on using photolithography of a material with omniphobic surface properties. The new method resolves the main practical limitations of the known reaction acceleration methods. It allows to generate microdroplets of a reaction mass without using any additional equipment by simply wetting the pattern (fig. 1A, B). In addition, the proposed method is convenient for conditions optimization of reactions in oversaturated solutions due to variability of experiment parameters such as droplet size and solvent.
In this study we inspected the acceleration rate of the Schiff reaction by comparing the reaction kinetics on wettability patterns and in the bulk (fig. 1C). The reaction mass (2,4-dimethoxybenzaldehyde 0.65 mmol/ml and p-toluidine 1.00 mmol/ml in chloroform) was applied onto the wettability pattern with circle wettable areas D = 15 microns, using the running drop method (fig. 1A). The resulting array of microreactors (fig. 1B) was kept at room temperature. Next,

microdroplets containing the product were collected from the pattern with $CDCl_3$. Conversion of 50% was achieved on the pattern within 5 minutes of the reaction (NMR analysis). To further characterize the new method we plan to compare the reaction kinetics on wettability patterns and in electrospray generated microdroplets.

The study was supported by State Assignment No. FSER-2022-0008 under the National Project ‘Science and Universities.

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Designing the architecture of the long-life KTP-$NaV_{1-x}M_xPO_4F$ cathode material using chromium and titanium-based doping approaches

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Keywords: sodium-ion battery; cathode material; Cr doping; Ti doping;

Currently, new materials for metal-ion batteries are being actively developed. In particular, materials based on transition metal fluoride phosphates are being studied. This work proposes chemical modifications of the $NaVPO_4F$ cathode material, which is based on the structural modification of $KTiOPO_4$ (KTP). KTP-based materials are ahead of other related compounds in terms of energy density and specific power, although it has some drawbacks. The main drawback is its instability during long cycling and low Coulombic efficiency on

the first cycle. [1] A way to increase the stability during cycling is to dope the material into the position of the transition metal with the elements having more stable MO_6 octahedral, such as Cr or Ti. Those modifications are to potentially increase the Coulombic efficiency. [2] The purpose of this work is to investigate the effect of substitution with select transition metals (Cr, Ti) of the cathode material KTP-$NaVPO_4F$ on its electrochemical properties.
During the course of the research, materials that are doped with chromium and titanium have been synthesized. KTP-$NaV_{1-x}M_xPO_4F$ (M = Cr, Ti, $0<x<1$) were obtained through ion exchange reactions in the melt of sodium glutamate. In addition to volume-level chemical substitution, the samples adopting core-shell architecture with KTP-$NaCrPO_4F$ on the surface were successfully synthesized, a content of dopant in the shell being 5, 12.5 and 20%. XRD patterns of the obtained materials were fully indexed in Pna21 space group. The ratios of vanadium to chromium and titanium were calculated using EDX method. When tested in coin-type cells versus sodium metal on anode, the materials with core-shell architecture demonstrates significant boost in degradation suppression (up to 1000 cycles on 0.5C rate).

This work is supported by Russian Science Foundation (RSF grant # 23-73-10125).

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Solvothermal synthesis of cathode material $Li_{1.2}Ni_{0.133}Mn_{0.534}Co_{0.133}O_2$

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One of the main tasks of modern materials science is to create materials for high-energy power sources for portable electronic devices, electric vehicles, and stationary energy storage systems. One of the most widespread types of energy storage devices are lithium-ion batteries (LIA), which exhibit high energy and power density, cycling stability and wide operating temperature range. At the moment, the technology of anode material manufacturing is already well developed, and the main opportunities to improve the properties of lithium-ion batteries are related to the improvement of the cathode material, which mostly determines the performance characteristics of the LIA. The most high-energy cathode materials include a class of lithium-rich layered oxides (Li-rich oxides). The reversible discharge capacity of such materials, due to the combination of crystal structure features and chemical composition, can reach more than 250 mAh/g.

The method of synthesis and its conditions determine the morphology of the synthesized material, the particle size distribution and the uniformity of distribution of the components of the composition. In this work, lithium-rich layered oxides of $Li_{1.2}Ni_{0.133}Mn_{0.534}Co_{0.133}O_2$ were prepared. The precursor for oxide preparation was obtained by solvothermal method from transition metal nitrates. In the process of solvothermal synthesis, the influence of the nature of the reaction medium (isopropyl alcohol (IPA), deionized water) and precipitant (potassium hydroxide, ammonium oxalate) were investigated. The obtained compounds were characterized by a complex of physicochemical methods: SEM, XRD, DTA, IR spectroscopy, and electrochemical tests. The relationship between precursor synthesis conditions, morphology, and electrochemical characteristics of the investigated materials was established.

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Morphology of cathode material precursors as one of the key parameters determining the characteristics of cathode material

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Over the last decades, a large number of methods have been developed and adapted for the synthesis of cathode materials of various types/generations/compositions [1-3], but not all of them are applicable for obtaining material in large-tonnage volumes, primarily due to the complexity of scaling.

At the stage of cathode material precursor (PCAM) production, if optimal synthesis parameters are selected and maintained, it is possible to obtain materials with specified functional properties, which further affect the key parameters of the final product.

In this work the influence of synthesis parameters of PCAM of different generations (6:2:2÷9:0.5:0.5) on surface morphology was investigated (Fig.1). The materials were obtained by co-precipitation from sulfate solutions in batch and continuous modes, in 5, 10 and 50-litre reactors. The main parameters varied were pH, T, stirring speed, and ratios of the main components.

The obtained materials were analysed for the main physicochemical characteristics: particle morphology, particle size distribution, density with shrinkage, chemical composition and crystal structure parameters.

The conducted studies allowed us to determine the optimal parameters for the synthesis of materials with ordered, controlled and reproducible morphology of primary particles (Figure 1), which is further more susceptible to the introduction of Li^+ ions into the structure of the material.

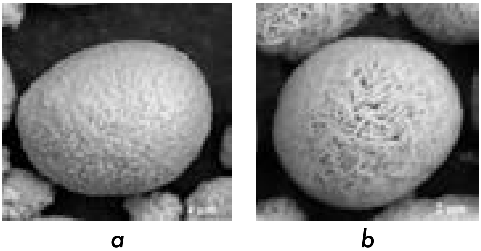

Figure 1. Microphotographs of RCAM NCMs obtained under different conditions

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Graphite regeneration from retired LIBs by closed-loop cycle recycling technology of lithium-ion batteries

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The environmentally friendly closed cycle of regeneration process of spent $LiCoO_2$ was success-fully developed and the following synthesis of $LiNi_xCo_yMn_zO_2$ was carried out by the authors earlier [1] . It was decided for further research to ensure the developed methodology on the negative electrode of Li-ion battery.

Thus, the spent graphite electrode from the same retired LIB was used in the joint leaching process in 1.5 mol/L malic acid and 3 vol. % of H_2O_2 solution with positive electrode of $LiCoO_2$. The efficiency of cobalt extraction reached 95%, lithium extraction – 99%.

Then the filtrated graphite, aluminum and copper foils were separated, the filtrated solution was used for the following synthesis of NCM cathode material. In this abstract we will focus predominantly on the graphite material results. The graphite was annealed in the Ar atmosphere at 1100°C. The obtained material was investigated by X-ray diffraction analysis, EDX and SEM methods. Electrochemical behavior of Regenerated Graphite (RG) was analyzed. The material demonstrated the specific discharge capacity on the 1st cycle of 368.8 mAh/g at 0.1C. After 20 cycles of charge/discharge at 0.1C the specific discharge capacity was 370.52 mAh/g. The results are shown in Figure 1(a,b). In addition, the rate performance and CVA were also used for material behavior analysis, the results are demonstrated in Figure 1 (c,d).

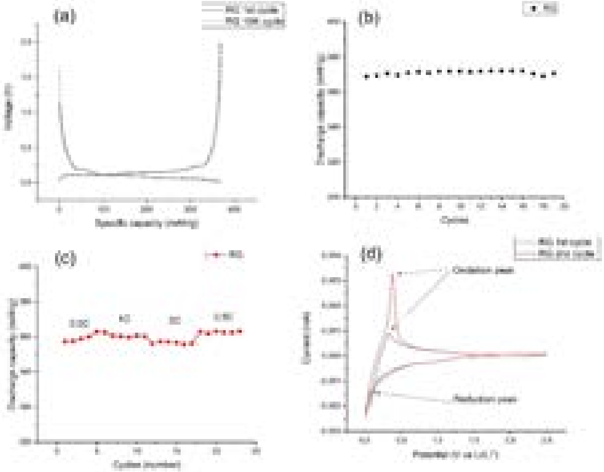

Figure 1. The electrochemical behavior of the regenerated graphite.

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Devolopment of fluorinated cyxlotriphosphazene-based additives for lithium-ion batteries

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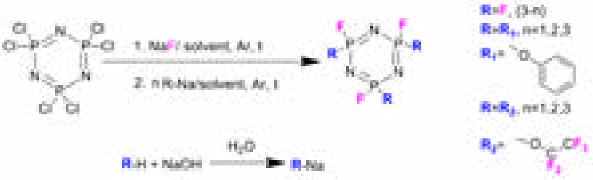
Nowadays the problem of cost-effective energy storage is indeed highly discussed topic. Every year more technologies like electric vehicles and portable electronics that demand productive electrochemical processes proceed in order to store energy appear. The effective solution for the problem is the lithium-ion batteries (LIBS). Particularly, LIBs based on Ni-rich layered transition metal oxide $LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$ (NMC622) cathode and graphite anode have attracted considerable attention due to their high electrochemical properties. However, LIB with NMC622 cathode and graphite anode degrades during electrochemical cycling. The electrolyte additives are used in order to enhance electrochemical performance of LIBs. Moreover, this approach is easily applied at manufacture. Phosphazenes showed the least degradation in battery performance comparing to other additives accompanied with the flame-retardant properties. On the other hand, chemistry of fluorine is a thing of great interest nowadays because of its' advantages. Herein, we synthesized a range of fluorinated cyclotriphosphazenes. Hexachlorocyclotriphpsphazene was undertaken bimolecular nucleophilic substitution to obtain hexafluorinated compound and then different substituents were added. (Scheme 1). The structures of the compounds were proved with different nucleus NMR. The cycling of LIB comprising of NMC622 cathode, Li metal anode and carbonate-based electrolyte with obtained fluorinated cyclotriphosphazene derivatives were performed.



Scheme 1. Synthesis of fluoridated cyxlotriphosphazene -based additives

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$LiFePO_4$-based composite cathode materials for all solid-state lithium batteries

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Recent fire and explosion accidents of electric vehicles draw more attention on battery safety. At the same time, it is extremely hard for commercial lithium-ion batteries to meet these demands. Thus, the use of solid-state batteries with high safety, high energy density, and simple packaging became a key research direction in the field of energy storage [1]. There are still many problems to be solved before the commercial application of solid-state batteries. Among them, the poor contact between the solid electrolyte (SE) and the electrode material is an important factor leading to the high impedance of solid-state batteries [2]. Therefore, the goal of this work is to design the structure of the composite cathode material by synthesizing a core-shell structure in which the cathode active material (CAM) is coated with a SE to achieve good contact between the SE and the CAM.

In this work, we chosen the $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ (LATP) with a NASICON-type structure as the solid electrolyte in the composite cathode. We developed a novel coprecipitation method to synthesize LATP. First, $LiNO_3$, $AlNO_3 \cdot 9H_2O$ and $Ti[OCH(CH_3)_2]_4$ were dissolved in isopropanol, and the pH of the solution was controlled to 9.5 by ammonia solution. After that, $NH_4H_2PO_4$ aqueous solution was slowly added to the solution, and the pH of the solution was maintained at 9.5 using ammonia solution. The solution was then stirred at 80 °C for two hours, and then dried at 90 °C for 24 hours to remove the solvent. The obtained precipitate was annealed at 800 °C for 3 hours to obtain the product LATP. The X-ray powder diffraction confirmed the pure LATP phase formation. So, our coprecipitation method is suitable for synthesis of the composite cathode. As CAM here we use widespread $LiFePO_4$ (LFP). In this work, hydrothermal and solvothermal methods were used to synthesize LFP to control the particle size, since size of CAM particles has a great influence on the capacity of the solid-state battery. We found that the particle size of LFP can be controlled from micro- to nanosize by hydrothermal method and solvothermal method based on ethylene glycol. Due to the almost insulating properties of LFP, a carbon coating is necessary to improve the conductivity of LFP and thus increase the capacity of the battery. However, the formation of the carbon coating may cause a large amount of agglomeration of the powder, which will deteriorate uniformity of the solid electrolyte coating. Therefore, here we tried to developed a synthesis method for LFP that can achieve a higher capacity without a carbon coating. We found that upon the addition 75% ethylene glycol in solvothermal synthesis, the capacity can reach 100 mAh/g, and at the same time with addition of 1% single wall carbon nanotube the capacity can further increased up to 120 mAh/g.

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NaK-78 Alloy-Assisted Synthesis of Porous Metal- and Metalloid-Based Materials as Components of Anodes for Na- and K-ion Batteries

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The growing demand on the porous functional materials is the most effective driver to the development of new synthetic approaches to their production and further application in catalysis, purification and separation systems, as well as energy storage devices [1]. Conventional solution-based techniques (such as sol-gel, co-precipitation, self-assembly, solvothermal method) are limited in the context of their versatility and scalability [2].

In this study, we suggest an alternative template-free solution-based synthetic method based on the use of the eutectic liquid NaK-78 alloy [3] emulsions for simultaneous chemical reduction, structure directing, and pore formation processes [4]. These features allow the formation of porous materials with controllable composition and porosity based on Si, C, Ge, Sb, Sn, Ru, Fe, Nb, Ta, and their oxides.

As-synthesized porous-structured materials are promising to suppress anode expansion in metal-ion batteries due to the ability of pores to adjust their volume. Sn and Sb are widely known as alloying-type anode materials [5], therefore, the synthesized porous Sn- and Sb-based materials were incorporated as active components of Na- and K-ion cells. The capacities of both the Sn- and Sb-based materials undergo fading within the first 10 cycles at C/20 rate: starting with average 353 $mAh \cdot g^{-1}$ and 221 $mAh \cdot g^{-1}$ in Na- and K-half-cells, it drops to 168 $mAh \cdot g^{-1}$ and 70 $mAh \cdot g^{-1}$ to the end of the step at C/20, respectively. The cycling stability of the material at C/10 is quite good (91% after 50 cycles) but remains only 24 $mAh \cdot g^{-1}$ in Na // Sn and 50 $mAh \cdot g^{-1}$ in K // Sn. Similar fading is observed in Sb-based materials. Thus, the produced materials should be modified and stabilized to reach the higher capacities. However, these results indicate the potential applicability of the developed synthetic approach.

In summary, we have presented an innovative and versatile platform for the template-free synthesis of metal- and metalloid-based porous materials with adjustable porosity, morphology, and composition. The proposed approach is suitable for many applications, including energy storage devices production.

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Development of flexible triboelectric nanogenerators based on gallium alloy

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Triboelectric nanogenerators (TENG) are devices that convert mechanical energy, generated from contact between different materials, into electrical energy [1]. Their main advantages, considering evolving technologies, include durability, efficiency, scalability, and integration with different systems.

The materials for TENGs must possess a certain affinity for effective energy generation. One of the materials, when in contact with another, should generate positive charges, while the second material should produce negative charges. There are large number materials and combinations available; however, we propose a combination of popular polymers such as Ecoflex-0030 and polydimethylsiloxane (PDMS), which are dielectrics and sources of negative charges. One source of positive charges is a layer based on GaInSn-Cu paste. We chose this paste for a reason: galinstan is the working name for the GaInSn alloy in the required ratio, and copper enhances the wettability of the paste to the polymer, thickening it and thus making the application of the layer not only more uniform but also allowing for thickness control. The second source of positive charges is copper electrodes, which transmit our converted mechanical energy to the device through the circuit.

We have developed two types of TENGs. The first type consists of triboelectric fibers with a supercapacitor structure that not only allows for energy generation but also charge storage if necessary. The second type is a flat TENG operating on the principle of contact separation. The method we developed for its fabrication is simple and optimized to minimize time costs, making it particularly noteworthy. This streamlined approach ensures efficient production of nanogenerators, enabling rapid scaling of the technology with minimal expenses. By focusing on ease of fabrication, we aim to accelerate the deployment and integration of triboelectric nanogenerators in various applications for energy harvesting.

This work was supported by the Russian Science Foundation (project No 24-23-00270)

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Titanoniobates $ATiNbO_5$ ($A = H^+, Li^+, Na^+$) as anode materials for metal-ion batteries: synthesis, structure and intercalation properties

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Mixed titanium niobium oxides are considered as safe anode materials for lithium-ion batteries (LIBs) with long cycling life. Their benefits are provided by both structure stability and relatively high working potentials of Ti(IV)/Ti(III) and Nb(V)/Nb(IV) redox couples (1.3 – 1.6 V vs. Li/Li^+). Direct synthesis allows obtaining only a few titanoniobates, which are very similar to $TiNb_2O_7$ and are characterized by a high relative Nb content. The use of «soft» chemistry approaches, including the ion exchange method, resulted in the discovery of a new class of layered titanoniobates $ATiNbO_5$ ($A = H^+, Li^+, Na^+$), which are promising as anode materials for LIBs. This work is aimed to the synthesis and comprehensive study of $ATiNbO_5$ as anode materials for metal-ion batteries.

Potassium titanoniobate $KTiNbO_5$, used as a precursor, was prepared by direct high-temperature annealing and subjected to K^+/H^+ ion exchange to yield the "solid acid" $HTiNbO_5$. Then $HTiNbO_5$ was used to synthesize $LiTiNbO_5$ and $NaTiNbO_5$ by different methods. The first one is chemical ion exchange using low-temperature melts ($LiOH/LiNO_3$ or sodium glutamate). The second one is electrochemical ion exchange by charge-discharge in Li^+- or Na^+-cell. The crystal structures of $LiTiNbO_5$ (sp. gr. $P2_1/m$, $Z = 2$, $a = 6.421(1)$ Å, $b = 3.7701(6)$ Å, $c = 8.109(5)$ Å, $\beta = 92.23(2)°$, $V/Z = 98.1(2)$ Å^3) and $NaTiNbO_5$ (sp. gr. Pcmn, $Z = 4$, $a = 6.468(1)$ Å, $b = 3.7861(6)$ Å, $c = 17.652(6)$ Å, $V/Z = 108.1(2)$ Å^3) were solved by direct methods using PXRD data and refined by the Rietveld method.

In the structure of $KTiNbO_5$ the $[(Ti,Nb)O_6]$ octahedra are connected by edges and vertices in zig-zag layers. The drastic decrease in the radius of the A-cation in $HTiNbO_5$ is compensated by the formation of strong interlayer hydrogen bonds, which allows the structure motif of $KTiNbO_5$ to be preserved. The shifts and rotations of the layers during the H^+/Li^+ and H^+/Na^+ ion exchanges ensure the coordination of small Li^+ and Na^+ and the stabilization of the structure due to Coulombic interaction. The resulting monoclinic distortion of the $LiTiNbO_5$ structure leads to the formation of 1D channels accessible for Li^+-intercalation. The electrochemical behavior of $HTiNbO_5$ and $LiTiNbO_5$ was investigated in Li-ion half-cells using chronopotentiometry and PXRD in *operando* and *ex situ* regime. It was revealed that during the first charge-discharge of $HTiNbO_5$, an irreversible phase transition occurs, resulting in the formation of $LiTiNbO_5$. The intercalation of 1 Li^+ (per f.u.) in $LiTiNbO_5$ proceeds at ~1.6 V vs. Li/Li^+ with a reversible capacity of □125 $mA \cdot h \cdot g^{-1}$ (1 – 3 V vs. Li/Li^+) and is accompanied by a significant decrease in the cell volume (6%). The synthesis of nanosized $HTiNbO_5$ material made it possible to overcome diffusion limitations caused by cell shrinkage and achieve a reversible capacity of 240 $mA \cdot h \cdot g^{-1}$ in the first ten cycles.

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Synthesis and investigation of the electrochemical properties of $Na_{1-x}KxV_{1-y}MyPO_4F$ (M = Cr, Ti) as cathode materials for sodium-ion batteries

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In the last decade, fluorine-containing vanadium-based polyanionic materials have been widely recognised for use in sodium-ion batteries as high-energy positive electrodes. The $KTiOPO_4$(KTP)-structured cathode material with the general formula of $NaVPO_4F$ is one of the most attractive ones due to its high both practical capacity (136 mAh*g^{-1} at 0.1C) and average working voltage (4.0 V) [1]. However, it possesses some drawbacks to be handled by direct chemical modifications. Substitutions in alkali metal and transition metal sites are known to lead to the effect of initial coulombic efficiency increase as well as to degradation suppression on extended cycling. Notably, the possible synergetic effect of simultaneous substitutions has rarely been studied, yet being a prospective approach of direct modifications of functional materials.

In this work we put forward the synthesis and a detailed study of electrochemical properties for representatives of a family of KTP-structured materials with a general formula of $Na_{1-x}KxV_{1-y}MyPO_4F$ (M = Cr, Ti) with arbitrary degrees of substitution.

Single-phase KTP-$Na_{1-x}K_xV_{1-y}MyPO_4F$ was synthesized by a simple two-step method similar to that previously proposed by Shraer et al. [1], using ion exchange in sodium glutamate melt using hydrothermally synthesized $(NH_4)_{1-x}KxV_{1-y}MyPO_4F$. The phase composition of the samples at each stage was monitored by X-ray diffraction.

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Fabrication of thin films of solid electrolytes for all-solid-state Na-ion batteries via tape-casting technique

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One of the most promising directions for the development of the energy storage devices is all-solid-state batteries (ASSB) due to their advanced safety and, in perspective – higher power and energy densities. Among metal-ion batteries, sodium-ion batteries seem to be the most prospective as Na-ion conductive materials possess the highest ionic conductivity among all solid electrolytes; in addition, they are mostly resistant to moisture and air, their synthesis is quite facile and the precursors are quite earth-abundant [1]. Currently, the fabrication of solid electrolyte (SE) with high density and ionic conductivity and at the same time as low thickness as possible is the crucial problem. Among several classes of solid Na-ion conductive materials, NaSICON-type $Na_3Si_2Zr_2PO_{12}$ (NZSP) is considered as the most prominent showing high ionic conductivity (0.67 mS cm^{-1} and above) and moderate activation energy (0.36 eV) [2]. At the same time, it is crucial for ASSBs to obtain the electrolyte with as low thickness as possible. However, simple and scalable method for fabrication of thin (100-200 µm) layers of ceramic electrolyte has not been invented yet. Thin electrolyte layers are commonly obtained either by direct sintering (which usually leads to mechanical deformations if the thickness of the ceramic is below 0.5 mm) or by grinding of thick ceramics, which usually does not impact density, but may not to be considered as up-scalable technique for massive fabrication [3]. Thus, search for alternative fabrication routines for production of thin-film layers of solid electrolytes is required.

In this work, a relatively new method for the fabrication of thin-film layers of ceramic electrolyte from polymer-ceramic composites is proposed. In this method, ceramic (NZSP) and polymer (PAN-15) are mixed in a liquid solvent (DMF) to obtain viscous slurry which is then deposited on glass substrate via tape-casting technique with subsequent drying and coagulation from the substrate. Afterwards, the film was subjected to two-step sintering (with holding at 360°C to melt the polymer binder and at 860°C for its decomposition). The optimization of slurry composition as well as the sintering conditions led to formation of thin (>100 µm) films with sufficient density (> 80%) and ionic conductivity (> 10-4 S cm^{-1}). The impact of the suspension viscosity, sintering conditions on density, thickness of films and their electrochemical properties will be discussed and presented during the report.

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Determination of 3d transition metals redox activity in Prussian blue analogs as cathode materials for potassium-ion batteries

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Among electrochemical energy storage systems, metal-ion batteries are the most high-power, versatile, and long-life devices. In recent years, the use of lithium-ion batteries has become increasingly popular due to their high energy density. However, in stationary storage equipment with the high capacity batteries, the operational costs of lithium-ion batteries are significant. The alternative to lithium in practical applications is post-lithium-ion systems, including those based on potassium: they demonstrate closed profitable energy characteristics with the twice lower price [1]. Influencing nominal voltage and capacity, cathode materials for potassium-ion batteries based on Prussian Blue analogues (PBAs) with the formula $K_2M^1[M^2(CN)_6]\cdot nH_2O$ (M^i – 3d transition metal, $n\geq0$) are promising solution with wide variety of composition and tuning of redox reactions. However, interactions of 3d metals through CN-bonding is not studied enough as well as the understanding the sequence of their redox activity. The aim of this work is to study the mechanism of redox activities in PBAs with the compositions

$K_2M^1[M^2(CN)_6]\cdot nH_2O$ (M^1 – “inner-sphere” cations Fe, Co, Mn, Mg, M2 – “outer-sphere” cations Fe, Mn, $x=0 - 1$, $n\geq0$).
Series of single-phase samples of hexacyanoferrates and hexacyanomanganates were synthesized and studied. According to electron and X-ray diffraction analyses in hexacyanoferrates, it was found that with increasing cobalt content with more than 50 at.%, the crystal structure changes from monoclinic to cubic [2]. During an iron content increasing, in both hexacyanoferrates and hexacyanomanganates, a decrease in the unit cell volume without changing the monoclinic system was identified. In addition, a model material with no inner-sphere 3d metal influence $K_2Mg[Fe(CN)_6]\cdot nH_2O$ was synthesized and characterized. The magnetic, electronic and electrochemical properties of the obtained compounds were studied by Mössbauer spectroscopy, Fourier-transform infrared spectroscopy, magnetic and electrochemical measurements as well as the evolution of the electronic structure of transition metals in the PBAs in ex situ and operando modes during dis/charge by X-ray absorption spectroscopy. Finally, a correlation between the composition and electronic and electrochemical properties of studied materials was identified, and schemes of electronic structure evolution depending on compositions were proposed.

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Lignocellulose biomass as a source of hard carbon for metal-ion batteries

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Sodium based batteries have been considered a reliable technology for clean energy store as a promising alternative to lithium-ion batteries. Hard carbon, which is used as an anode material for metal-ion batteries, has recently attracted a lot of attention due to its potential to be obtained from cheap renewable sources, such as various biomasses. One of these sources can be lignin, which is the main component of wood (15-40%) along with cellulose and hemicellulose [1].

This study is devoted to investigating the properties of hard carbon based on lignin, its electrochemical characteristics, and the search for optimal synthesis conditions to improve performance in lithium and sodium-ion batteries. Commercial sodium lignosulfonate and kraft-lignin were used as starting materials, which are abundant waste products in the pulp and paper industry. Hard carbon was obtained through several methods: direct annealing in an inert atmosphere at 1300ºC and annealing after dissolution for both substances. In addition, hydrothermal synthesis in an alkaline medium for lignosulfonate was performed. Based on the results of electrochemical tests in the sodium-ion half-cell, it can be seen that the initial Coulombic efficiency of the dissolved sodium lignosulfonate and the washed from sodium one reaches 85%, and 74% for the sample obtained by direct annealing. The discharge capacity is in the range of 250–300 mAh/g. During redissolution, there is a change in particle size and porosity, which leads to a change in surface area from 13 m^2/g to 6 m^2/g. It can be concluded that it is the change in morphology during dissolution that affects the change in coulombic efficiency, and the sodium content has a lesser effect on electrochemical characteristics. The hard carbon based on kraft-lignin exhibits a high discharge capacity in the range of 330-350 mAh/g and ICE 60% with unchanged morphology and 70% after changing morphology by redissolution. The use of water-soluble polymers opens up great opportunities for the directional design of the resulting hard carbon. The above simple approach allows to obtain a material with improved characteristics, which can potentially be used in real batteries.

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Hydrothermal synthesis of LiFePO$_4$ cathode material using Fe$_2$O$_3$

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Hydrothermal reaction techniques have been successfully applied in commercial usage since the 20th century. Water action at elevated temperature and pressure conditions, occurring in formation of various rocks and minerals in the earth's crust, is widely used in synthesis of single crystals or nanomaterials for different applications. There are extensive possibilities of controlling the morphology, crystal structure and functional properties of materials by varying synthesis conditions.
Triphyline-type cathode materials are essential for the actual battery market with improved safety, costs and service life. As representative, lithium iron phosphate is the most commercially advanced material, so technology improvement is actual issue affected by developers. One-dimensional diffusion activity

of $LiFePO_4$ makes it challengeable for obtaining the materials with competitive electrochemical properties. Finding the most convenient conditions for forming required crystal structure and morphology is the key for successful material design.

We found an opportunity to reduce the cost and simplify synthesis process by using transition metal oxide (Fe_2O_3) as raw iron-containing reagent during the hydrothermal synthesis. Synthesis conditions are highly affected to the phase composition, crystal structure and morphology of the produced material. We researched the evolution of properties of the materials by changing the amounts of reagents, temperatures, prolongation, reaction medium and using additives.

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Atomic layer deposition as a method for high precision doping of Ni-rich cathode materials

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High-nickel (Ni-rich) cathode materials is one of the promising directions in chemical current sources. Usage of these materials in metal-ion batteries provides the battery's energy capacity growth [1], which is necessary for the electric vehicle development. Nevertheless, during the implementation of such materials, there are difficulties in ensuring their stability during cycling because of the nature of the material's layered structure. A widely used method for solving this problem is doping [2].

In the present work, atomic layer deposition (ALD) technology was used as a method of cathode's materials doping, including Ni-rich materials. The ALD technology allows obtaining thin, homogeneous and precise coatings on the developed surface [3, 4]. Using metals oxide films on the surface of cathode material precursor particles (mixed hydroxide of nickel, cobalt and manganese with given composition) as dopant and subsequent heat treatment, we propose the route to precise control of doping value. Subsequent heat treatment provides distribution of elements contained in the obtained films over the particles volume. The doping method proposed, is primarily intended to study the influence of doping elements, including their possible combinations, on physical and chemical properties of Ni-rich cathode materials.

The doping of the NMC811 material, obtained at Gipronickel Institute, with aluminum (3+) and titanium (4+) ions was studied. Aluminum and titanium oxide coatings with approximate thicknesses of 5 and 10 nm were applied on the surface of the precursor particles by ALD method. Thermal treatment of the samples was carried out at 750 °C in an oxygen atmosphere, the treatment time was varied between 5 and 25 hours. Scanning electron microscopy, X-Ray diffraction and electrochemical cycling were used to analyze the obtained results.

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Double-layer deposition of cathode mass for optimization the cathode | solid electrolyte interface in all-solid-state power source

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Today, there is growing interest in research of all-solid-state power sources due to their extended range of operating conditions and significant fire and explosion safety. The development of materials for such power sources is a promising task for researchers. However, the organization of the interface between the cathode and electrolyteis one of the main problems in the design of such batteries, because these solid materials are characterized by low contact area and high porosity and resistance.

In the presented study Al-doped $Li_7La_3Zr_2O_{12}$(LLZ) was used as the electrolyte. Based on our previous investigations of the cathode | ceramic electrolyte interface with different compositions of cathode masses containing: binder, C and cathode ($LiFePO_4$ or $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$), it was proposed to optimize the interface using doble-layer deposition. The first stage is the deposition of a thin layer of a mixture of the main compound and carbon black without a binder to increase the reaction zone at the cathode | solid electrolyte interface. The second stage consists of the cathode mass deposition with selected proportion of components to ensure mechanical retention of the cathode mass on the electrolyte (for $LiFePO_4$ – 90% the main compound, 5% C and 5% binder, and for $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ – 96% main compound, 2% C and 2% binder).

According to scanning electron microscopy data, it was found that deposition of cathode masses in two layers leads to the formation of a dense, defect-free interface between the cathode and the ceramic electrolyte. And according to the distribution maps, a clearly defined interface between the two phases was observed.

The resistance of symmetrical cells was measured using electrochemical impedance in the temperature range 25 - 150 °C. Impedance plots had a classic view without dropped points, which indicates a good contact between all components of the measuring cell. For samples with LiFePO4 and $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$, the resistance at the cathode | solid electrolyte interface decreased with increasing temperature from 10 kOhm·cm^2 at 25 °C to less than 1 kOhm·cm^2 at 150 °C. Thus, we can conclude that in the case of the formation of a cathode | solid electrolyte interface in all-solid-state power sources, the choice of the composition of the cathode mass, as well as the method of its deposition, is very important. The prospects of stage-by-stage deposition of the cathode with the formation of tight contact between the electrode and the ceramic electrolyte were shown. Heating the obtained cells to 150 °C made it possible to significantly reduce the resistance at the studied interface and did not lead to delamination of the cathode material during cooling.

Synthesis and research of $NaFePO_4F$ as a potential cathode material for sodium-ion batteries

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Nowadays the consumption of electricity consumed is rapidly growing, putting forward the issue of efficient energy storage is acute. Metal-ion batteries (MIBs) successfully solve this problem. A boost in the specific energy of MIBs is achieved by increasing the operating voltage of a single cell and/or specific capacity, which largely depends on the cathode material. In this regard, materials based on transition metal fluoride phosphates with the $KTiOPO_4$-type (KTP) structure are promising due to high theoretical energy density as well as the wide variety of compositions and high ionic conductivity [1].

Recently, sodium-ion batteries (SIBs) have been actively investigated, therefore a novel fluoride phosphate $NaFePO_4F$ with KTP-type structure was chosen as the subject of research. Iron is of interest due to its abundance and cost-efficiency. The phosphate group provides chemical, thermal and structural stability, and its inductive effect in combination with the high electronegativity of fluorine results in the increased working potential. $NaFePO_4F$ has a 3D system of energy channels in its framework with a 0.3 V activation energy.

To obtain $NaFePO_4F$, isostructural NH_4FePO_4F was preliminarily synthesized hydrothermally, followed by an ion exchange reaction. The precursor was characterized by XRD and SEM, and the product was studied with XRD and FTIR spectroscopy.

According to the XRD data, a single-phase KTP-NH_4FePO_4F was obtained, with the parameters of its unit cell corroborating well with the literature data [2]. Using SEM, it was found that NH_4FePO_4F primary particles are combined in elliptical agglomerates ranging in size from 2 to 5μm. For $NaFePO_4F$ the XRD data has confirmed the inheritance of the KTP structural type. $NaFePO_4F$ crystallizes in the orthorhombic symmetry (space group $Pna2_1$) with unit cell parameters: a = 12.7635(2) Å, b = 6.2323(1) Å, c = 10.6467(2) Å, V = 846.90(2) Å^3. The complete substitution of NH_4^+ ions by Na^+ was confirmed by FTIR spectroscopy showing no absorption bands in the range of 1400–3300 cm^{-1} related to NH_4^+ vibrations.

Electrochemical properties of $NaFePO_4F$ were investigated using galvanostatic cycling in the 2.0–4.2 V potential range vs Na^+/Na at C/10 rate for 5 cycles. For the first discharge step a conversion reaction was assumed with specific capacity reaching 80 mAh/g. The following cycles demonstrated reversible capacity of 50 mAh/g with rapid capacity fading.

In the poster, synthesis approach, conditions, structural features, results of SEM/FTIR characterization and electrochemical properties of $NaFePO_4F$ will be presented in detail.

The work was supported by Russian Science Foundation (grant #23-73-10125).

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Effective recycling of electrode materials

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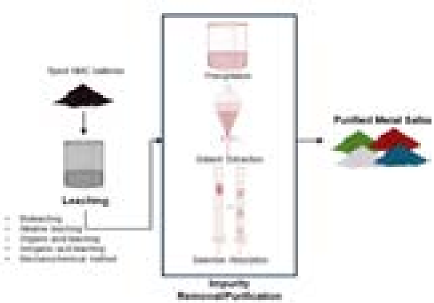
Eco-friendly utilization methods for Li-ion batteries (LIBs) is an advanced task for the efficient disposal and recycling of ever-increasing volumes in mobile device, electric vehicle, and energy storage system.
The current commercial approach for recycling NMC (LiNixMnyCozO$_2$) cathodes which offers the greatest extraction and lowest energy impacts, is the hydrometallurgical processing route [1]. The NMC cathode has become economically more desirable, the Co content has decreased (NMC 111, NMC 523, NMC 622, NMC 811) improving not only overall cost but also lessening the environmental and ethical impacts [2]. Globally, the target of recovering high purity pay metals such as Li, Co, Mn and Ni reaches greater than 99 percent, using this method. Low impurity content and a lower energy consumption are the benefits.
The processing method consists of several principal stages such as: discharging and dismantling. The plastic and steel cases are removing from the cells, and the anodes and cathodes are separating.
Dissolving of Al foils to detach the cathode materials. After filtration, washing and drying, the material is grounded and sieved for subsequent leaching process. Then the valuable metals recovered via fractional precipitation. Varying conditions of the precipitating

agent application: pH of the solution, temperature, and infusion rate affect the efficiency of the final product separation. In a laboratory scale the last stage is the most important one. The overlap of pH range for precipitation of different metals makes the attempt of single step precipitation ineffective in obtaining pure metals. As a result, the selection of deposition conditions for obtaining both pure metals and their salts for further use remains an urgent technological task.



Principal schematic steps of recycling using hydrometallurgical processing [2].

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Study of biomass derived activated carbons in the process of capacitive deionization

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The scarcity of clean fresh water is acute in many parts of the world today. Clean water is essential for sustaining life, for domestic use and for agricultural and industrial applications. The currently used purification technologies have significant drawbacks. In membrane technologies (reverse osmosis, electrodialysis), membranes are vulnerable to biofouling, processes require high pressures, and cell designs are difficult to scale. Thermal methods (multi-stage flash distillation and distillation) are associated with high energy costs. Capacitive deionization (CDI) is a promising method for desalination of water with low to moderate salt content. CDI is environmentally friendly, has both low cost and high energy efficiency due to low operating voltage. The ability to remove selectively the desired ions is an important advantage of the CDI [1]. Various types of nanostructured carbon materials such as activated carbons (ACs), nanotubes, nanofibers, aerogels, graphene, and etc. are widely used as electrodes. Among indicated materials biomass derived ACs are considered as perspective due to high electrosorption capacity [2].

The data on investigation of activated carbons obtained at different activation temperature from carbonized rice husk are presented in this work [3]. The materials have different specific surface areas (from 900 to 2700 m^2/g) and porous structure (average pore size from 2.2 to 4.4 nm). The electrodes consisted of AC and polyvinylidenfluoride as a binder were prepared by a «doctor blade» technique. The samples were investigated in adsorption (1 V cell voltage) and desorption (0 V cell voltage) cycles in NaCl solutions of different concentrations varied from 10 to 500 mg/L.

The potentials of zero charge (PZC) of materials were determined by impedance spectroscopy before and after adsorption-desorption cycles.

It was shown that the electrosorption equilibrium can be well described by the Langmuir equation. The adsorption capacity of the most efficient sample has reached 10.9 mg(NaCl)/g(C), which is at the level of literature data. The material was activated at 750 °C and has 2.7 nm average pore size and 2300 m^2/g specific area. It was suggested that the cyclic adsorption-desorption process results in the formation of oxygen-containing groups on the carbon surface due to its oxidation. This leads to a positive shift of the PZC by 50 – 100 mV for the cathode electrode and by 150 – 300 mV for the anode electrode. In addition, the pH of the deionized solution reaches 3.5 – 4 for oxidized samples, while for stable samples it is close to neutral (5 – 7). In this work, the specific adsorption capacity for different materials was analyzed and their relationship with physicochemical properties was investigated.

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Studying the effect of calcium doping of layered $NaCrO_2$ oxide on its electrochemical performance

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Sodium-ion batteries (SIBs) are a promising alternative to lithium-ion batteries, due to the low cost of sodium and its abundance. A wide range of cathode materials for SIBs is being studied. Notably, cathode materials based on layered oxides with the $NaxTMO_2$ (TM – transition metal) structure have several advantages, such as low cost, scalable synthesis, and suitable operating potentials. Furthermore, these oxides can be doped with different elements, which can lead to structure stabilization and to the improvement of the electronic conductivity [1].
Among the existing dopant candidates, calcium is a promising one since Ca^{2+} has an ionic radius very close to Na^+ (1.04 Å and 1.02 Å respectively), which allows us to suggest that it inserts into sodium sublattice and prevents the migration of chromium ions into sodium layers. This, in turn, leads to smoothing of the charge-discharge curves [2].
This research is focused on the study of the effect of calcium doping of layered $NaCrO_2$ on its electrochemical performance, as well as the synthesis optimization, which includes the search for optimal conditions for obtaining an electrode material with homogeneous element distribution and suitable morphology.

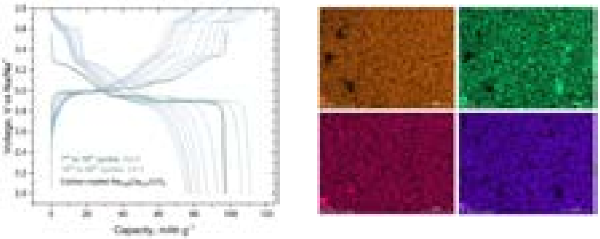

Figure 1 (a, b). Galvanostatic curves (a) and element distribution maps (b) of a $Na_{0.98}Ca_{0.01}CrO_2$.

As a result, calcium-doped material demonstrated a stable discharge capacity of 97 mAh/g during 10 cycles in the potential range of 2 to 3.6 V. Upon extending the upper potential limit to 3.8 V, an additional plateau could be observed on the charge curve, resulting in an enhanced capacity of 115 mAh/g.

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Synthesis and of a composite bifunctional catalyst for the oxygen reduction and evolution reactions

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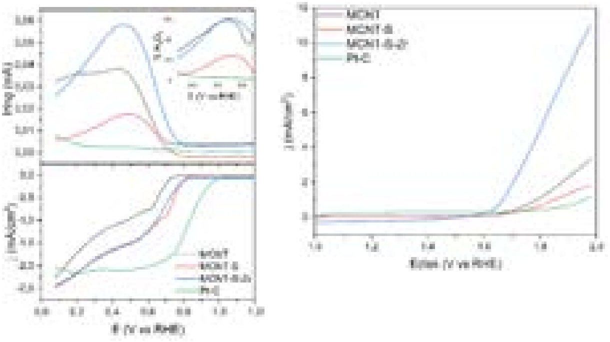
The industrial production of reversible fuel cells is currently hindered by the elevated cost and poor stability of the catalysts involved in the oxygen reduction reaction (ORR) and the oxygen evolution reaction (HER), which are utilized in alkaline electrolytes. The creation of stable and active bifunctional catalysts will facilitate the development of a reversible element that is capable of operating alternately in both electrolyzer and fuel cell modes [1].

The current study presents a methodology for the synthesis of a bifunctional catalyst based on a composite material comprising sulfonated carbon nanomaterials and zirconium dioxide. The catalytic activity of the obtained materials was investigated through the utilization of the rotating ring-disk electrode method (RRDE). The results demonstrated that the incorporation of sulfur into the multi-walled carbon nanotubes (MWCNTs) structure resulted in a reduction of the ORR overpotential by 93 mV (from 707 to 800 mV vs

reversible hydrogen electrode (RHE)). This results in a notable decrease in selectivity towards the two-electron ORR, as evidenced by a reduction in the percentage of peroxide release at 0.1 V vs RHE from 20 to 5%.
The composite material displays the highest catalytic activity in the OER among all the materials under study. The overpotential of the reaction for a bifunctional catalyst is 100 mV vs RHE less compared to single-phase carbon materials, and the current density is more than three times higher.



a b

Fig. 1. (a) Polarization curves of the ORR on a rotating GC electrode with the materials studied, the corresponding polarization curves of the peroxide reduction and the percentage of peroxide appearance as a function of potential in an O2-saturated solution of 0.1 M KOH at a speed of 1000 rpm and (b) polarization curves of the OER on a rotating GC electrode in a deaerated solution of 0.1 M KOH at a speed of 1000 rpm.

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Design and application of FeCo magnetic catalysis for enhanced water splitting

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Alkaline water electrolysis is widely recognized as an effective and reliable method for producing pure hydrogen and is considered as the best options for decarbonization. However, the slow kinetics of the oxygen evolution reaction (OER) during water splitting still hinders the widespread implementation of this technology. Ru and Ir-based oxides are highly active OER catalysts, but their high cost does not allow us to talk about their widespread implementation.

The research project is devoted to the study of the catalytic properties of iron-cobalt alloy nanoparticles, as well as to assessing the effect of an external magnetic field on the kinetics of the electrochemical reaction. For this purpose, optimal conditions for the experiment were determined, for which several parameters were varied during the experiments. The most significant characteristics were the molar ratio of elements in the catalyst, the direction and strength of the magnetic field, the presence of a crystalline structure.

Three of the most stable compositions with an iron-cobalt ratio were studied, $FexCo_{1-x}$, where x = 0.8, 0.6, 0.4. FeCo NPs were obtained by co-reduction of Fe and Co salts with sodium borohydride. Cyclic voltammetry was used to study the catalytic activity. According to the data obtained, the $Fe_{0.8}Co_{0.2}$ composition has the highest activity. The effect of an external magnetic field of 200 mT was also estimated (Fig 1A). A significant increase in current density can be due to hydrodynamic effects caused by the Kelvin force and the Lorentz force. It is assumed that this effect will be more pronounced in small volumes, where the role of mixing and renewal of the electrolyte composition near the electrode increases.

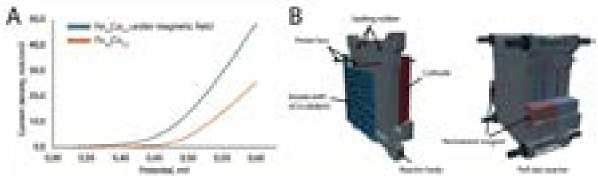

Figure 1 – A. Polarization curves (5 mV s^{-1}) in 1 M KOH electrolyte (pH 14) for Ni–foil electrodes decorated with $Fe_{0.8}Co_{0.2}$ OER catalysts, and under an applied 200 mT magnetic field. B. Design of electrochemical water splitting reactor based on magnetic catalysts.

To implement the obtained magnetic catalysts, a prototype electrochemical reactor for hydrogen production was designed (Fig. 1 B). The reactor consists of several sections separated by a non-solid partition that prevents the mixing of gaseous oxygen and hydrogen. Niches for placing permanent magnets are provided along the reactor body.

Effect of salt anions on crystallinity, glass transition temperature and conductive properties of PEO-based solid polymer electrolytes

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The liquid organic electrolytes currently used in metal-ion batteries are toxic and highly flammable. Gel, solid polymer and ceramic electrolytes can replace liquid organic electrolytes. Their use will enable the development of the battery industry by creating solid-state batteries that promise higher energy storage density, increased reliability and durability, flexibility, fast charging and increased safety in operation. However, there are some drawbacks to these electrolytes. Drying of the gel electrolyte can lead to a reduction in battery life, and a low transference number (0.1-0.4) effects the specific energy. Ceramic electrolytes have a high transference

number (~0.95), but their main problem is the high resistance at the electrode/electrolyte interface due to poor wettability. Solid polymer electrolytes (SPEs) occupy a middle position between gel and ceramic electrolytes. SPEs have good wettability and achieve high degree of alkali metal ion transfer (~0.4-0.8).
Among solid polymer electrolytes, the most widely studied polymer is polyethylene oxide (PEO), however, its conductivity is low (~10^{-7} S cm^{-1}). One of the main strategies to increase the conductivity of SPE is the introduction of a conductive salt acting as a source of alkali metal ions. The conductivity of the resulting solid polymer electrolytes varies depending on the type of salt. One of the reasons for this difference is the change in crystallinity (χ) and glass transition temperature (T_g) of the polymer, associated with the dissociation of the salt and the interaction of the polymer chains with its cations/anions. The choice of salt allows the elasticity and conductivity of polymer electrolytes to be adjusted by changing χ and Tg. In this work, a comparative study of the effect of different salts on χ and Tg, as well as on the ionic conductivity was carried out. It has been shown that the combination of different salts makes it possible to regulate the value of the ionic conductivity over a wide range.

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Mechano-chemically Assisted Solid-State Synthesis of High-Entropy Layered Oxide $NaTi_{0.2}Mn_{0.2}Fe_{0.2}Co_{0.2}N_{i0.2}O_2$ as a Cathode Material for Sodium-Ion Batteries

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The growing demand for lithium-ion batteries is driving up the price of lithium compounds, thereby increasing the price of lithium-based energy storage and conversion devices. Concerns over lithium scarcity and rising costs, coupled with the inevitable global need for energy storage devices to power the energy transition, are driving research and innovation to develop sodium-ion batteries (SIB).

The cathode material is one of the key factors determining the SIB performance. One of the most promising cathode materials for sodium ion batteries are layered transition metal oxides Na_xMO_2 (M = transition metals) due to their high specific capacity and ease of synthesis [1]. The disadvantage of these cathodes is the complex phase transitions during the cycling process, which leads to capacity degradation and structural instability. To smooth the charge-discharge curves and simplify phase transitions, the cation substitution strategy is widely used.

Two or three transition metals in one Na_xMO_2 phase are not sufficient for improvement on stability, therefore many researchers use five or more elements to obtain high-entropy oxides (HEO) which exhibit smoother charge-discharge curves and superior cycling stability compared to those of Na_xMO_2 with 1-3 transition metals [2]. Each atom in a distorted high-entropy lattice can serve as a point obstacle to the movement of neighboring atoms, which leads to a stable local structure and strong mechanical stability.

Layered transition metal oxides can be obtained in various ways [1]. Solution methods, such as hydrothermal and sol–gel, allow one to adjust the morphology and particle size and obtain a nanosized cathode material with a uniform particle size distribution. However, these methods typically use expensive organic reagents, which limit their use in industry. Usually, cost-effective and simple solid-state synthesis is used as the most suitable way to produce cathode materials. However, this method requires heat treatment of a reagent mixture at a high temperature of 800–1000 °C for a long time (12–24 h). The use of preliminary mechanical activation makes it possible to shorten the duration of solid-phase synthesis.

The aim of this work was to obtain the high-entropy layered oxide $NaTi_{0.2}Mn_{0.2}Fe_{0.2}Co_{0.2}Ni_{0.2}O_2$ by mechanochemically assisted solid-state synthesis and to study its electrochemical properties in sodium half-cells. According to the results of galvanostatic cycling, the values of the specific discharge capacity are equal to 93 mAh g^{-1} and 67 mAh g^{-1} at 0.1C and 10C cycling rates. After 50 cycles at the 0.1C rate, the material exhibited 98.6% capacity retention.

This work was supported by the Russian Science Foundation, Grant #21-73-20064.

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Cathode materials for sodium-ion batteries based on mixed iron and sodium phosphates

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Sodium-ion batteries (SIBs) present a new promising class of energy storage systems. The key step towards the commercialization of SIBs is the development of materials, in particular cathode materials, that will allow to obtain batteries with specified electrochemical characteristics.

One of the most promising classes of cathode materials for SIBs is a group of polyanionic compounds. Polyanionic compounds are characterized by higher thermal and cycling stability as well as higher working potential values compared to layered oxides and Prussian blue analogs. Among such systems mixed phosphates are of particular interest, specifically mixed sodium iron phosphate $Na_4Fe_3(PO_4)_2(P_2O_7)$. Interest in this phase is caused by one of the highest values of the Fe^{3+}/Fe^{2+} redox pair potential: 3.4V (vs Na^+/Na). According to literature data the choice of synthesis method and synthesis conditions significantly affect the phase composition and electrochemical properties of the obtained compounds [1, 2].

One of the widely used and successfully commercialized synthesis methods of electrode materials for lithium-ion batteries is coprecipitation followed by high-temperature annealing [3]. This synthetic approach attracts attention due to its simplicity, the possibility of varying the composition of the precipitated samples, and the possibility of upscaling. In this work, an approach for obtaining $Na_4Fe_3(PO_4)_2(P_2O_7)$ mixed phosphate by coprecipitation is proposed for the first time.

At the first stage of synthesis, a precursor, iron (II) phosphate, was obtained via coprecipitation by mixing aqueous solutions of iron (II) sulfate and sodium hydrogen phosphate. According to PXRD data the obtained product was iron phosphate $Fe_3(PO_4)_2{*}nH_2O$ with a vivianite structure. The composition of the resulting crystal hydrate was determined using thermogravimetry. The resulting product was mixed with sodium pyrophosphate and subjected to high-temperature annealing under different conditions. The influence of the precursor synthesis conditions, the stoichiometry of the initial compounds, the annealing duration, as well as the presence or absence of pre-annealing on the phase composition and morphology of the resulting compounds was shown. Based on the synthesized compounds, cathode materials for sodium-ion batteries were obtained, and their electrochemical characteristics were studied by galvanostatic charge/discharge.

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Synthesis and investigation of KTP-NaVO$_{1-x}$PO$_4$F$_x$ as a prospective cathode material for sodium-ion batteries

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Within last decade vanadium-based polyanion materials are recognized as prospective cathode materials for sodium-ion batteries. Thus, KTiOPO$_4$(KTP)-structured materials with general formula of NaVOPO$_4$ and NaVPO$_4$F were thoroughly investigated [1,2]. Fluorine substitution of oxygen provides inductive effect increasing working potential. NaVOPO$_4$ exhibits lower specific energy compared to NaVPO$_4$F, but recent studies show appealing capacity retention. In attempt to merge their positive sides of electrochemical performance, partial oxygen substitution by fluorine was proposed.

In this work new KTP-structured materials with NaVO$_{1-x}$PO$_4$F$_x$ (where x= [0.25; 0.5; 0.75]) formula and theoretic capacity of ~143 mAhg-1 are put forward with investigation of their electrochemical properties. Single-phased KTP-NaVO$_{1-x}$PO$_4$Fx were obtained via solid-state ion exchange using hydrothermally synthesized NH$_4$VO$_{1-x}$PO$_4$F$_x$ with V$_2$O$_5$ as a starting vanadium source. Scanning electron microscopy analysis revealed predominant presence of agglomerates with medium size from 10 to 20 μm. X-Ray diffraction patterns of the materials were fully indexed in $Pna2_1$ space group using orthorhombic unit cell, particularly the unit cell parameters for «x=0.5» sample are a = 12.738(1) Å, b = 10.619(1) Å, c = 6.302(1) Å, V = 852.5(5) Å^3. When tested in coin-type cells versus sodium metal on anode, carbon-coated NaVO$_{1-x}$PO$_4$F$_x$/C composite materials demonstrate specific capacity of 100-110 mAh*g^{-1} at 0.1C rate. Average electrode potential is around 4.0 V for all materials. Solid-solution sodium ions intercalation mechanism was confirmed by means of operando SXRD in 2.5-4.5V potential range.

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The impact of the spray-drying parameters on microstructure and electrochemical properties of phosphate cathode materials for sodium-ion batteries

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Sodium-ion batteries are a potential alternative to lead-acid and lithium-ion batteries. Their advantages of abundant resources, low cost, high safety, excellent high and low temperature performance could be widely used with further development. The current mainstream cathode materials are layered oxides and polyanionic materials. Typically higher energy density could be achieved using layered oxides produced by co-precipitation method. Safer and longer-life batteries are based on polyanionic materials produced by solid-state method.

One of the challenges for polyanionic materials is volumetric energy density. Taking into account that the theoretical gravimetric capacity of the most advanced phosphate materials for sodium-ion batteries does not exceed 130 mAh/g, rising of the tap density of polyanionic materials becomes especially important.

Among polyanionic materials NASICON-type $Na_3V_2(PO_4)_3$ electrode materials are considered as promising candidates for high-performance sodium-ion batteries due to extremely long cyclic life and an outstanding ability to operate at high (dis)charge rates.

Because of the high phase stability Na3V2(PO4)3 is a perfect model object to develop new synthesis processes.

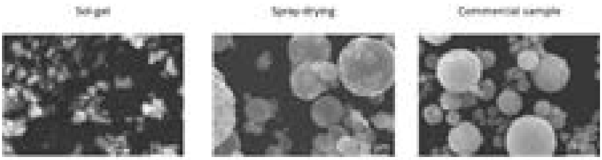

Figure 1. SEM images of the $Na_3V_2(PO_4)_3$ prepared by different synthesis procedures.

In this work a spray-drying method is applied to the synthesis of Na3V2(PO4)3. Single- and multi-step preparation procedures were developed, and the impact of the spray-drying parameters on microstructure and electrochemical properties were studied.

This work was supported by the Russian Science Foundation (Grant 24-13-00107).

Получение анодных материалов для литий-ионных аккумуляторов на основе термоактивированной углеродной ткани, модифицированной оксидами переходных металлов, с использованием переменного асимметричного тока

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Литий-ионные аккумуляторы (ЛИА) являются перспективными устройствами хранения энергии, имеющими широкую область применения, в том числе в электронных устройствах, гибридных автомобилях, благодаря высокой плотности мощности, длительному сроку службы и низкому уровню саморазряда.

Известно, что свойства ЛИА в целом во многом определяются характеристиками используемых электродных материалов, в том числе анодных.

В настоящее время большое развитие получила область исследований, связанная с разработкой анодных материалов без использования связующего на основе углеродных материалов (тканей, волокон), модифицированных оксидами переходных металлов [1]. При этом их существенным недостатком являются низкие значения удельной поверхности, что приводит к низким значениям удельной емкости.

Перспективным подходом к повышению электрохимических характеристик таких анодных материалов является предварительная активация углеродных материалов (кислотная, щелочная, термическая). При этом термическая активация приводит к появлению большого количества дефектов поверхности и образованию нанопористой структуры, не уменьшая механическую прочность волокон, а также является более экологичной.

В данной работе приведены результаты исследований по установлению влияния параметров термической активации углеродной ткани марки Урал Т-22Р с последующей модификацией оксидами переходных металлов на электрохимические

свойства получаемых анодных материалов.
Модификацию поверхности углеродной ткани оксидами переходных металлов (молибдена с металлами группы железа) проводили с использованием переменного асимметричного тока по методике [1]. Термическую активацию проводили в диапазоне температур 300-600 ºС в интервале времени 2-3 часа в атмосфере воздуха.
Было установлено, что оптимальным температурным режимом термической активации углеродной ткани следует считать температуру 300 ºС и время выдержки 2 часа, так как при данных условиях достигается максимальное значение удельной поверхности и пористости без разрушения структуры углеродных волокон (0,85 $м^2$/г).
Полученное значение разрядной емкости для готового анодного материала составило 180 мАч/г для 20 мкА/мг в диапазоне потенциалов 0,01-3 В.
Работа выполнена при финансовой поддержке программы «Старт-Взлет» Фонда содействия развитию малых форм предприятий в научно-технической сфере. Договор 5202ГС1/90912 от 26.12.2023.

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