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Content

Stabilization of [Ni(*R*Salen)] Polymer Complexes in Water-in-Salt Electrolytes

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Most modern lithium-ion batteries employ a variety of technical solutions based on non-renewable, toxic and hazardous resources, which, among other issues, complicate batteries disposal. One of the problems is the high flammability and toxicity of the electrolyte based on organic carbonate solvents.

This work is devoted to an alternative approach to lithium-ion energy systems, which makes them more versatile in their field of application and working conditions by replacing an electrolyte based on an organic solvent with superconcentrated aqueous salt solutions, also called "water-in-salt electrolytes" (WiSE) [1]. Their use allows both to achieve a wide range of operating potentials and to ensure the stability of organic electrode materials, such as polymeric complexes of nickel with salen-type ligands (poly[Ni(*R*Salen)], *R* = H, Me, MeO) polymer complexes, which usually irreversibly degrade in the presence of even trace amounts of water [2].

A 21 mol/kg LiTFSI solution was used as a WiSE, which showed significant polymer stabilization in the case of poly[Ni(MeSalen)]. The performance of other polymer complexes, i.e., poly[Ni(Salen)] and poly[Ni(MeOSalen)], did not show notable improvement. After 100 cycles, poly[Ni(MeSalen)] retained 99% of the initial capacity, while poly[Ni(MeOSalen)] showed less stability with only 60% over the same number of cycles.

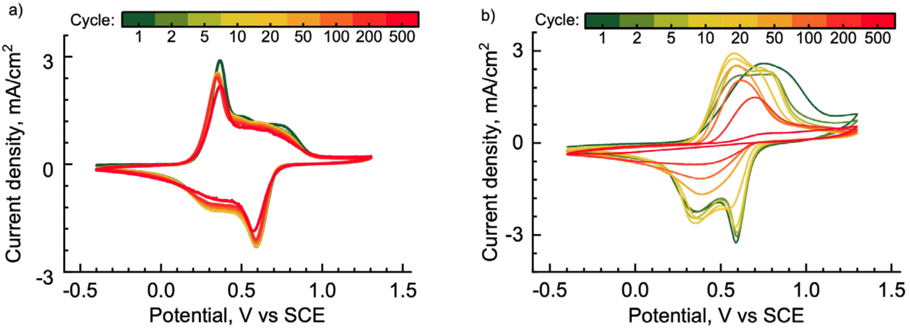

Fig. 1. CVs of (a) poly[Ni(MeSalen)] and (b) poly[Ni(MeOSalen)] on a glassy carbon electrode in 21 mol/kg LiTFSI solution.

The financial support of Russian Science Foundation (project No 24-73-00160) is gratefully acknowledged.

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Theoretical insight into lithiation of N-doped molybdenum disulfide

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Molybdenum disulfide (MoS_2) is a promising anode material due to its layered structure and high theoretical capacity.[1] Low electrical conductivity and poor reversibility of the conversion reaction are the main disadvantages of pure MoS_2 anodes, which can be overcome by doping with heteroatoms. In this work, we use quantum chemical calculations to study the effect of replacing part of the sulfur atoms with nitrogen, which is quite easily realized during synthesis or post synthetic treatment with appropriate nitrogen containing compounds, on the interaction of MoS_2 with lithium. Several experimental works showed that the presence of nitrogen heteroatoms leads to enhanced electrochemical capacity in MoS_2. [2,3] We first sampled possible nitrogen arrangements in $MoN_{0.125}S_{1.875}$ and $MoN_{0.375}S_{1.625}$ monolayers (~4.2 and ~12.5 at.% N, respectively) and determined the energetically preferred nitrogen configurations in 1H and 1T crystals using density functional theory. Calculations showed that replacing sulfur with nitrogen increases the stability of 1T phase and narrows the band gap of MoS_2. Then, we tested the possibility of Li atom trapping near nitrogen sites by considering different Li positions in the interlayer space of the 1T N MoS_2. Molecular dynamics simulations were employed to probe the stability of nitrogen-doped MoS_2 upon interaction with lithium. The results demonstrated that nitrogen doping narrows the MoS_2 band gap, promoting electron transfer. However, insights into lithium interactions with nitrogen active sites and the stability of the nitrogen-doped MoS_2 lattice unable to demonstrate an evident benefit of nitrogen doping, which allows us to suggest that electrical and ionic conductivity may have a more substantial impact on electrochemical performance.

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Synthesis and structural research of Li-rich oxides

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In 2007, M. Thackeray proposed a new class of cathode materials for Li-ion batteries: lithium-rich layered oxides. These materials integrate components such as $LiMO_2$ (where M = Ni, Mn, Co) and Li_2MnO_3 [1]. $LiMO_2$ forms a layered solid solution of the α-$LiFeO_2$ structural type and exhibits a broad homogeneity region based on rhombohedral lithium cobaltate (III) and nickelate (III), as well as orthorhombic lithium manganate (III). Lithium manganate (IV), Li_2MnO_3, in its monoclinic modification (space group C2/m), possesses a layered structure similar to $LiMO_2$ with comparable interlayer distances [2]. On the one hand, this structural similarity enables the isomorphic substitution of transition metals (e.g., Mn), resulting in the formation of extensive homogeneous solid solutions based on the rhombohedral $LiMO_2$ structure with minimal disordering in the transition metal sublattice. On the other hand, it significantly complicates the identification of the crystal structure of these lithium-rich oxides.

The aim of this work was synthesis, structural and phase identification of Li-rich oxides $Li_{1.149}Mn_{0.519}Co_{0.055}Ni_{0.277}O_2$ (LR-1) and $Li_{1.149}Mn_{0.574}Ni_{0.277}O_2$ (LR-2).

Samples were synthesized by coprecipitation of Mn, Ni and Co carbonates in specified ratios from an aqueous solution. Precursors were dried in an argon steam then were mixed with LiOH. Next samples were annealing at 480°C for 6 hours after at 900°C for 12 hours.

Powder diffraction patterns of the samples were recorded on a Bruker D8 Advanced X-ray diffractometer (Ni-filtered Cu K_α radiation) in the range 2θ from 10° to 80°. The step was 0.01° with exposition time 7.2 seconds per point. Powder diffraction patterns are reliably indicated in hexagonal system. The diffraction pattern can be described as obtained from a solid solution based on the rhombohedral structure of $LiCoO_2$ (space group $R\bar{3}m$, Pearson symbol *hR3*). Due to the overage of Li against stoichiometry, the obtained material can be characterized as a solid solution with simultaneous of Li atoms for the positions of the transition metal $3a$ and the possibility of antistructural disordering in the position Li($3b$) and M($3a$) (relative to the group $R\bar{3}m$ *(H))*.

Lattice parameters were calculated by using the method of the least squares (based on 10 reflections): 0.28570 ± 0.00001 nm (a), 1.42221 ± 0.00010 nm (c) – for the first sample and 0.28589 ± 0.00001 nm (a), 1.42315 ± 0.00010 nm (c) – for the second.

Low-intensity reflections (close to 20.80° and 21.70°) testify about an existence of coherent scattering spread, which are probably connected with the formation of local structures with monoclinic symmetry (corresponding to the structure type of Li_2MnO_3).

We express our gratitude to E. V. Makhonina and A. V. Naumov for participation in the discussion of the work.

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Optimization of ionomer content in the catalyst layer of a low-temperature fuel cell

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Proton exchange membrane fuel cells (PEMFCs) are promising power sources due to their environmentally friendly operation and the high mass-dimensional characteristics of power plants. Electricity generation in PEMFCs occurs in membrane-electrode assemblies (MEAs), included in their structure. The current-generating reactions in MEAs take place on the catalytic layers, whose structure significantly affects their performance efficiency. The latter can be increased by optimizing composition and structure of the catalytic layer [1]. One of the key characteristics of the catalytic layer's composition is its ionomer content. The optimal proportion of ionomer depends on the platinum loading of the electrode, the type of carbon support for the catalyst, as well as the platinum content in the catalyst itself [2, 3].

The aim of this work is to study the effect of the m(Nafion)/m(C) ratio in the cathode catalytic layer of MEA for a PtCo/C catalyst on a nitrogen-doped Ketjen Black EC300J carbon carrier on the electrochemical characteristics of MEA.

The catalyst layers were applied using an airbrush onto the GORE-SELECT® M765.08 proton exchange membrane. The m(Nafion)/m(C) ratio at the cathode varied from 0.7 to 1.0 in 0.1 increments. The platinum loading at the cathode was 0.4 mg(Pt)/cm^2. A commercial PM40 catalyst (40% Pt, Prometheus R&D LLC) with a platinum loading of 0.2 mg(Pt)/cm^2 was used as the anode catalyst in all MEAs. The m(Nafion)/m(C) ratio at the anode was maintained at 0.7. The current-voltage curves and electrochemical impedance spectra of the obtained MEAs were measured at a temperature of 80 °C, 1.5 bar back pressure, hydrogen and air flow rates of 220 ml/min and 680 ml/min, respectively, and 100% relative gas humidity. The electrochemical active surface area (ECSA) of the cathode catalyst was measured in an argon atmosphere at 100% humidity.

According to the measurement results, the m(Nafion)/m(C) ratio that provides the highest maximum MEA power is in the range of 0.8–0.9. Impedance spectroscopy data relieved that reducing the m(Nafion)/m(C) ratio to 0.7 leads to an increase in charge transfer resistance, which negatively affects the electrochemical activity of the catalyst. On the other hand, when the ratio is increased to 1.0, mass transfer resistance sharply increases, reducing the MEA's performance at high current densities.

This research was supported by the Ministry of Education and Science of the Russian Federation (project No FENW-2023-0016).

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Analysis of solid oxide fuel cell impedance spectra under load

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Analysis of polarization resistance is one of the main challenges in the study of solid oxide fuel cells (SOFC). The electrochemical impedance method is used to separate the total polarization resistance into partial contributions of individual limiting electrochemical processes [1]. The impedance spectra taken under electrical load conditions are of the greatest interest, since their analysis makes it possible to determine the behavior of limiting processes in conditions close to real operating conditions [2]. However, it is not always possible to completely separate the polarization processes and determine their localization analyzing the spectra taken under load. Therefore, the purpose of this work is to identify the localization of polarization processes using impregnation of tubular SOFC electrodes, as well as their separation using distribution relaxation times (DRT) method [3].

The paper shows the effect of electrode impregnation on the polarization resistance of limiting processes in a tubular solid oxide fuel cell. Based on the analysis of the impedance spectra, the main limiting processes are determined, their localization is determined by their reaction to the activation of the electrodes, and their nature is determined by the corresponding capacitances of the processes. Thus, the cathode electrochemical stage is experiencing the greatest difficulties due to the heterogeneity of the cathode-electrolyte interface, which is also the reason for the appearance of interface processes in this area. On the other hand, the difficulties at the anode are caused by the low porosity of the functional anode layer.

The conclusions of the work are based on the analysis of impedance spectra using equivalent circuit and DRT methods. The combination of methods made it possible to separate processes that are not available in the framework of the analysis using only the equivalent schemes method, and also improved the quality and reliability of the analysis. The results of the analysis of the impedance spectra are in good agreement with the results of electron microscopy, which confirms their reliability.

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Covalent organic frameworks based on pyrazinoporphyrazine for high-performance potassium-ion batteries

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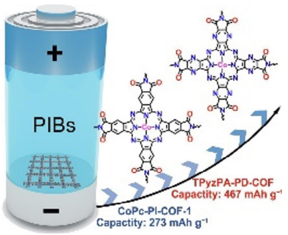
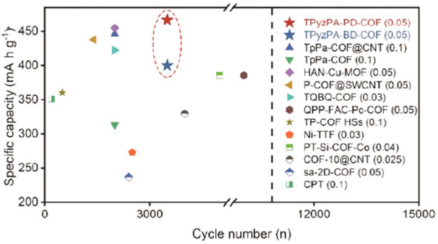
Lithium-ion batteries (LIBs) have almost occupied the global market share of energy storage devices, the sharp expansion of requirement is followed from the wide application in the mobile appliances, electric vehicles, and stationary energy storage. The low abundance of element (0.0017 wt%) and unbalanced distribution of lithium bring the concern to develop the secondary batteries composed of earth-abundant elements for complementing LIBs. Potassium ion batteries (PIBs) have emerged as a promising alternative due to its rich abundance (2.09 wt%), cheap cost of the electrolyte, and high voltage operation, but similar energy storage mechanism to LIBs [1].

Reticular materials, in particular covalent organic frameworks (COFs) based on macrocycles constructed by strong covalent bonds, show high crystallinity and outstanding robustness, representing good platforms to immobilize functional organic building blocks. The stable redox-active macrocycles such as phthalocyanines have good potassium ion storage capacity. As a result, COFs have attracted increasing interests in fabricating superior organic electrodes for PIBs, illustrating the bright prospects of COFs as an emerged kind of electrode materials. Particular, excellent PIB performance has been demonstrated previously for the electrode modified with highly stable fully aromatic conjugated COF QPP-FAC-Pc-COF [2].

This report focuses on the synthesis of carboxyl-substituted Co pyrazinoporphyrazine ($(COOH)_8TPyzPACo$) and its reaction with diamines for the design of COFs. In this case, crystalline rich-N/O 2D-COFs possess microporous and polyimide conjugated nature. In particular, TPyzPA-PD-COF, as a PIB anode, displays an outstanding reversible capacity of 467 $mA*h*g^{-1}$ at 50 $mA*g^{-1}$. The robustness of pore and polyimide conjugated framework enable the superior cycling performance with nearly 100% capacity retention at 2000 $mA*g^{-1}$ after 3500 cycles [2]. The identification of 2D-COFs and specific binding of COF for K^+-ion has been further verified by ex situ XPS and ex situ FTIR studies as well as DFT calculations.

This work was supported by the Russian Science Foundation (grant RNF 23-43-00136).





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Ether electrolytes unlock bismuth all-metal anodes for high-energy LIBs

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Metals and their intermetallic compounds represent promising anode materials for lithium-ion batteries owing to their substantially greater volumetric energy densities, which are directly related to the intrinsic density of the metal. These materials also possess higher theoretical capacities, ranging from 385 mAh g^{-1} for bismuth to 3860 mAh g^{-1} for lithium, compared with conventional graphite anodes. The combination of high energy density and large capacity facilitates the design of more compact batteries with enhanced energy storage per unit area, rendering them particularly suitable for applications where space and mass are critical constraints.

However, the development of metal anodes continues to face significant challenges, including substantial volumetric expansion during cycling, electrode material pulverization, and low energy efficiency [1]. Various strategies have been proposed to address these issues, such as the fabrication of nanostructured Bi@C composites [2] or the use of microsized particles [3], although these approaches are often complex and difficult to implement. To fully unlock the potential of metal-anode systems, research must also focus on optimizing electrolyte composition.

In this study, we demonstrate that Bi||LFP cells employing 100% metal anodes prepared by physical vapor deposition exhibit promising performance when combined with tailored ether-based electrolyte formulations.

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Synthesis and investigation of the electrochemical properties of $NaLi_xVPO_4F$ as cathode materials for sodium-ion batteries

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Metal-ion batteries play a crucial role in modern energy storage, yet the limited availability of lithium resources motivates the search for alternative systems. Sodium-ion batteries (SIBs) are considered a promising direction, with vanadium-based fluorophosphate cathodes demonstrating good electrochemical performance.

Our group previously put forwards a new modification of $NaVPO_4F$ stabilized in the $KTiOPO_4$-type structure, showing both high reversible capacity (125–135 mAh • g^{-1}) and average voltage (4.0 vs. Na^+/Na). Introducing additional lithium ions into the structure ($NaLi_xVPO_4F$) offers the potential to further increase specific capacity by partially reducing vanadium. Partial substitution of sodium by lithium may also modify the composition and structure of the CEI, prolongating electrolyte's lifespan. $NaLi_xVPO_4F$ compounds ($x = 0.15$) were synthesized by thermal treatment of corresponding homogeneous mixtures of $NaVPO_4F$ with LiI and HCOOLi. The obtained materials were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), and various elemental analysis techniques (ICP-OES, EDX). Electrochemical tests in coin-type cells versus sodium showcased that the materials deliver a specific capacity of approximately 120 mAh • g^{-1} at 0.1C. Galvanostatic cycling on low voltages didn't demonstrate additional redox activity, which would have marked on the reduction of V^{3+}. Several samples exhibited long-term cycling stability significantly exceeding results for pristine $NaVPO_4F$ (the time of work for mew materials increased by 250-300 cycles with capacity retention ~z75%. Also, there is an increase of peak CE by 0.1–0.2%), confirming the effectiveness of this modification.

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Development of quasi-solid polymer electrolytes based on mixed compositions of PVDF/HNBR

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The development of highly efficient electrochemical power sources is a pressing issue, as reality dictates ever higher demands on the entire energy industry. One of the most important parts of a battery is the electrolyte, as it is where the migration of alkali metal ions between the electrodes takes place, ensuring the battery functions properly. Today, the main disadvantage of traditional liquid electrolytes is their low boiling point and high rate of lithium dendrite formation, which leads to battery degradation or spontaneous combustion. A promising method for solving these problems is the use of solid polymer electrolytes (SPE).

Solid-state polymer-based electrolytes provide increased safety and allow the use of high-capacity lithium metal anodes, but their practical application is hampered by low ionic conductivity. This limitation is due to the low mobility of ions within the polymer matrix, especially in the presence of crystalline regions.

To create TPE with ionic conductivity comparable to that of liquid electrolyte, we propose an approach to creating quasi-solid polymer electrolytes with high ionic conductivity through the use of a mixed polymer matrix and liquid plasticisers. This approach utilised a mixture of polymers (polyvinylidene fluoride and butadiene-nitrile rubber) and selective high-boiling solvents (such as propylene carbonate and isopropyl 2,2, 3,3-tetrafluoropropyl carbonate) with an affinity for lithium salts that do not dissolve the polymer matrix and promote the formation of stable ion-conducting channels in the solid polymer framework. The electrolytes were obtained by solution casting and the dependence of conductivity on solvent content was studied using electrochemical impedance spectroscopy (EIS).

We have shown that the use of mixed systems based on polyvinylidene fluoride and butadiene-nitrile rubber leads to an increase in ionic conductivity to 1.16×10^{-4} S/cm at a polymer ratio of 50:50 by mass and 15 mass % of residual solvent. Studies have shown that ionic conductivity directly depends on the content and composition of the residual solvent, while the introduction of up to 10% by mass of high-boiling additives contributes to an increase in ionic conductivity to 1.95×10^{-4} S/cm with a total residual solvent content of 15% by mass.

Functional and structural analysis of the omniphobic photoresist

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Functional materials with controlled wettability are becoming more and more relevant in modern science. Based on such materials, it is possible to create complex microfluidic devices used for miniaturized experiments with living cells, synthesis in micro-volumes, and even immobilization of various biological molecules such as proteins or DNA [1].

Earlier, we described a material wettability of which can be controlled using photolithography. The precursor material containing monomers, surfactants, and a photoinitiator acts as a negative photoresist. When exposing thin precursor layers obtained by spin-coating, it is possible to obtain wettability patterns with high surface energy in masked areas and low surface energy in exposed areas [2].

In this paper, the mechanism of wettability contrast formation in the studied material during its selective application by photolithography is inspected. The low surface energy of this material is, theoretically, formed due to the inclusion of surfactant monomers in the precursor structure. In this work, the distribution of the surfactant in the polymerized composite was studied for the first time. For this purpose, the adhesion of the AFM probe to surfaces in various layers of the material was studied. The samples for study were obtained by photolithography. The exposure time was adjusted for easier access to the inner layers of the material.

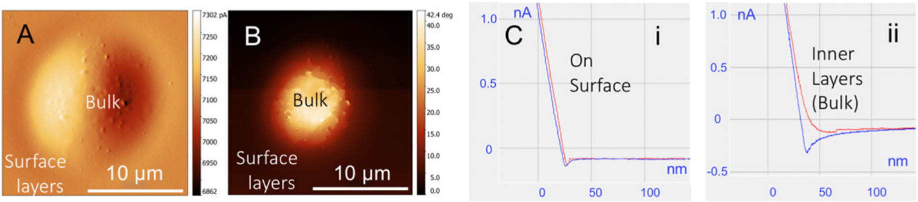

Figure 1. AFM study of the developed area of the pattern obtained with photolithography.

In non-contact mode scanning, (Fig. 1.A, B) the contrast of the oscillation phase of the cantilever is noticeable between the surface layer and the bulk of the material, (Fig. 1.B) which indicate different adhesion of the probe to these surfaces. Also, in the contact mode, the probe landing and removal curves were recorded to determine the relation of the deflection of the cantilever on the distance of the probe from the sample DFL(Z). In the case of the surface layer, there is practically no difference for the corresponding curves. (Fig. C.i) In contrast, in the bulk layers of the material, there is a noticeable difference between the landing and the removal curves. (Fig. C.ii) This indicate the occurrence of more significant adhesive forces between the probe and the sample when the probe comes into contact with the surface of the bulk layers of the material. The results obtained confirm the concentration of the surfactant component at the surface and in the pores of the material. Thus, we can state that the occurrence of omniphobic properties of the surface of composites is due to the self-assembly of surfactant monomers.

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Potentioresistive polymer layer as a way to protect lithium-ion battery from thermal runaway in case of internal short circuit

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Lithium-ion batteries (LIBs) are the most widely used portable power sources due to their high energy density, long cycle stability, and good power capacity. However, one of the major drawbacks of LIBs is their susceptibility to thermal runaway, which can lead to battery inflammation.

Various safety strategies have been developed to prevent thermal runaway, including external devices such thermal fuses or safety vents, as well as internal components such as thermal separators, temperature-sensitive electrodes, and temperature-sensitive electrolytes [1, 2].

One of the possible solutions to overcome thermal runaway and its consequences is the modification of the internal structure of the LIB cell through the introduction of a voltage-controlled protective (potential-resistive) layer with switchable resistance. When the applied potential exceeds the stability range of the polymer, the conductivity of the layer sharply decreases by several orders of magnitude. This characteristic of the potential-resistive layer has been shown to be effectively utilized for protecting LIBs against overcharging and external short circuits.

In this work, we demonstrated that the incorporation of a polyNiMeOSalen layer modifies the degradation pathway of the cathode material, shifting it from thermal decomposition to electrochemical delithiation. X-ray diffraction analysis revealed that, in cells lacking a protective layer, a cobalt oxide phase emerges after short-circuiting, formed via oxidation of cobalt in the temperature range of 200–660 °C [3]. Elevated temperatures also promote electrolyte decomposition, which in turn leads to partial reduction of cobalt to the metallic state and the formation of lithium carbonate through reactions involving lithium oxide, electrolyte decomposition products, and the conductive graphite additive. In contrast, the presence of even a thin potential-resistive layer induces partial delithiation of the rhombohedral phase without disrupting the parent layered structure or producing distinct cobalt oxide phases. This process, however, is accompanied by the appearance of a spinel-type phase, arising from contraction of the CoO_6 interlayer spacing, which indicates a substantial degree of delithiation ($x<0.5$ in Li_xCoO_2). Increasing the thickness of the potential-resistive layer up to fourfold suppresses the formation of spinel-type lithium cobalt oxide, highlighting the complete mitigation of the thermal contribution to cathode material degradation.

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Improving KTP-$NaVPO_4F$ cathode durability through structural substitution and surface protection

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Keywords: sodium-ion battery; cathode material; Cr substitution; core-shell-type architecture

Sodium-ion batteries (SIBs) present a promising alternative to lithium-ion batteries due to material availability and enhanced safety. The cathode material plays a key role in the characteristics of sodium-ion batteries, determining their specific capacity, energy density and durability. Among promising materials, KTP-$NaVPO_4F$ demonstrates record-high both energy density and specific power, but its practical application is limited by rapid degradation over cycling [1]. To increase stability, a strategy of replacing vanadium with chromium is proposed in this work. Chromium has greater electrochemical stability, a close ionic radius and the ability to form stable octahedral coordination. Synthesis-wise, we can divide the organization of the material of interest from macro level into two different approaches. The first one implies substitution in the bulk and the second one a creation of preferably isostructural "protective" surface layer, which may be called a "core-shell" architecture.

The purpose of this work is to develop a long-life cathode material for sodium-ion batteries based on KTP $NaVPO_4F$ by applying a dual strategy: bulk substitution to enhance structural stability and surface coating to protect against degradation. These modifications were designed to improve cycling performance while maintaining high capacity and energy density.

After systematical synthesis and investigation of solid solutions $NaV_{1-x}CrxPO_4F$ ($x<0.1$) the best result was achieved for $x=0.075$. Positive electrode material maintained 86% of specific capacity after 600 cycles. An alternative core-shell design approach resulted in obtaining particles covered with chromium-enriched phase (~11% of mass fraction). Core-shell-type cathode material showcased even more impressive results retaining 83% of specific capacity after 1000 cycles with only 7% energy density loss. Our results surpass the pristine material, proving the effectiveness of our modifications. Thus, this work offers a feasible and scalable approach towards enhancement of sodium-ion battery cathodes performance.

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NMC811-based cathode material with nano-inclusions for next-generation lithium-ion batteries

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The layered transition metal oxides with lithium ($LiNi_xMn_yCo_zO_2$ – NMC) are of significant interest for the development of the next-generation lithium-ion batteries (LIBs). Ni-rich NMCs demonstrate high discharge specific capacity (≥ 220 mAh/g in the potential window 2.7-4.3 V vs. Li^+/Li) compared to commercialized $LiCoO_2$ [1, 2]. However, an essential decrease in discharge specific capacity from the initial value during prolonged cycling is the main obstacle to their widespread commercial application. The degradation of electrochemical capacity is caused by a complex of interrelated processes affecting both the structure and chemical composition of the cathode material during lithium (de)intercalation. The main contributors to the reduction in cyclic resource are: transition metals cation migration to the lithium positions, leading to disorder in the crystal structure [3], as well as phase transitions and changes in the packing of the anion sublattice in the layered structure ($O_3 \rightarrow O_1$) [4]. In addition, during the (de)lithiation process, the volume of the unit cell changes, which initiates the accumulation of mechanical stresses, contributing to the appearance and movement of edge dislocations, as well as the formation and propagation of microcracks [5].

To solve the problem of reduced capacity retention, we develop a new approach based on the synthesis of heterogeneous system of Ni-rich NMC material with Sn-containing nanoinclusions. It is assumed that the nanoscale inclusions will act as dislocation pinning centers, preventing the formation and propagation of microcracks. The mixed hydroxide precursor $Ni_{0.8}Mn_{0.1}Co_{0.1}(OH)_2$ was synthesized by co-precipitation technique with addition of SnO_2 nanoparticles. According to powder X-ray diffraction data (PXRD), the obtained precursor consists of two phases: a mixed transition metal hydroxide (space group P3m1) and SnO_2 (space group P42/mnm).

After high temperature lithiation, inclusions of Li_2SnO_3 were confirmed in the obtained $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ sample by a combination of PXRD and transmission electron microscopy (TEM). Galvanostatic cycling in the potential window 2.7-4.3V vs. Li^+/Li demonstrated a 10% improved capacity retention over 115 cycles at 1C in comparison with the pristine material.

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Catalytic graphitization of microcrystalline cellulose

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Sodium-ion battery (SIB) technology is an important alternative to the widely used lithi-um-ion analogues. The necessity for SIBs is driven by the existence of applications that require less powerful but cheaper energy storage systems. Consequently, materials for sodium-ion bat-teries are being actively studied. The selection of anode materials is relatively limited; the most practically interesting are carbon materials, among which non-graphitizable carbon (hard car-bon) is the most in-demand due to its microstructural features that enable good electrochemical characteristics [1].

The most promising source of non-graphitizable carbon is biomass, owing to its abun-dance and low cost. However, biomass-based materials significantly underperform in their elec-trochemical characteristics compared to similar materials from other sources. This is attributed to the variability of its composition and the presence of inorganic impurities. An important feature is the possibility of low-temperature catalytic graphitization of carbon materials under the influence of certain d-metals. Catalytic graphitization induced by iron (+3) salts has been de-scribed in the literature; furthermore, iron is the most common trace element in plant biomass. The combination of these factors led us to use salts of this particular element in our work.

Thus, the aim of this work was to investigate the influence of catalytic graphitization us-ing iron on the microstructure and electrochemical properties of non-graphitizable carbon de-rived from biomass. In the course of the work, samples of non-graphitizable carbon were obtained by pyrolyzing microcrystalline cellulose doped with iron chloride ($FeCl_3$) or iron oxa-late ($Fe_2(C_2O_4)_3$) at different concentrations (from 5×10^{-5} to 1.5 wt. %). The materials were characterized in terms of their microstructure and electrochemical properties.

As a result of the work, a number of patterns were identified. The electrochemical char-acteristics of the samples monotonically deteriorated with an increase in the iron content in the doped material, and in the case of the oxalate, the characteristics were significantly worse. This is associated with more intense decomposition of the oxalate and, consequently, activation of the surface during synthesis. It was shown that the addition of small concentrations of iron somewhat improves the specific capacity and Coulombic efficiency of the material. The fact of catalytic graphitization of the material under the influence of iron salts was also confirmed: Ra-man spectroscopy established that the degree of graphitization increases with increasing iron concentration during doping. Scanning electron microscopy revealed that the particle morphol-ogy differs when doping with iron oxalate and iron chloride. This difference was explained by more substantial gas evolution during the pyrolysis of iron (+3) oxalate, resulting in finer mate-rial particles.

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Study of ion intercalation processes in electrode materials at low temperatures

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The relevance of studying the processes of ion intercalation into electrode materials at low temperatures is due to the need to create efficient energy storage devices capable of operating over a wide temperature range.

As the temperature decreases, significant changes occur in the kinetics and mechanism of ion incorporation into the crystal lattice of electrode materials, which affects their operational characteristics. The primary constraints on the operation of the electrochemical group with a carbon electrode are the electrical conductivity of the electrolyte, the ionic conductivity of the graphite layer, and the background processes at the electrolyte-graphite interface.

This study involved measuring the viscosity and electrical conductivity of a range of electrolytes, as well as determining the voltage values of their background processes. The electrochemical parameters of symmetric Li/Li^+ cells were measured at various temperatures, and the influence of the separator type was established. Furthermore, the performance dependence of the electrochemical groups on graphite properties and electrolyte composition was investigated under low-temperature conditions.

The study of graphite materials with different particle morphologies revealed comparable fundamental electrochemical properties. However, nearly identical graphite particle size parameters were found to have a negligible effect on the initial electrochemical characteristics of the material.

It was established that under normal conditions, the parameters of the electrochemical groups are determined by the chosen electrolyte, while at temperatures below -10 °C, it is governed by the active anode material.

Understanding the mechanisms of low-temperature intercalation will enable the design of more efficient and reliable energy storage systems for use in cold climates, space technology, and other fields that require stable power source operation at low temperatures.

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Evaluation of the cathode material $LiMn_{0.5}Fe_{0.5}PO_4$ degradation by ICP OES method

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A major issue of modern electrode materials is their degradation during long term cycling. Therefore, the search for new methods to quantitatively assess degradation is particularly important. The aim of this work was to evaluate the degradation of $LiMn_{0.5}Fe_{0.5}PO_4$ (LMFP) based cathode materials using inductively coupled plasma optical emission spectroscopy (ICP-OES).

A single-phase $LiMn_{0.5}Fe_{0.5}PO_4$ sample was synthesized via a hydrothermal method. The sample was coated with carbon using two different techniques: 1) mixing with 10% glucose followed by annealing in an argon atmosphere (sample GT), and 2) spray drying followed by annealing (sample GT_sd). The morphology of the obtained samples was investigated. Half-cells with lithium metal anodes were assembled using the prepared cathode materials and subjected to long-term galvanostatic cycling (100 cycles, C/5). After cycling, the electrodes were analyzed for manganese and iron content using ICP-OES.

The maximum discharge capacity of the sample prepared by spray drying (GT_sd) was higher than that of the sample mixed with glucose using the standard method. The degradation rate of the GT_sd sample after 100 cycles was also lower compared to the GT sample (Table 1). The obtained ICP-OES results for iron and manganese content in the lithium anodes after cycling are in good agreement with the electrochemical data. It was found that the amount of manganese and iron detected on the anode increases with the degree of cathode material degradation (Table 2).

Table 1. Electrochemical performance of the samples

Sample GT	GT_sd	
C_{max}, mAh/g	127	131
Degradation after 100 cycles, %	8	5

Table 2. Average metal content in the electrodes and relative metal content in the anodes (P = 0.95; n = 4)

Electrode	ω_{avg}(Fe), µg/mg	ω_{avg}(Mn), µg/mg	$m(Fe)_{an}/m(Fe)_{total}$	$m(Mn)_{an}/m(Mn)_{total}$
GT (cathode)	60 ± 10	50 ± 10	0.015 ± 0.002	0.018 ± 0.002
GT (anode)	0.33 ± 0.07	0.34 ± 0.07		
GT_sd (cathode)	80 ± 20	70 ± 10	0.009 ± 0.001	0.010 ± 0.002
GT_sd (anode)	0.26 ± 0.05	0.27 ± 0.05		

NaK Alloy-Assisted Synthesis of Porous Multiphase Fe/Co/Ni-based Materials for Boosted OER Magnetic Electrocatalysis

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The development of efficient, cost-effective, scalable, and stable electrocatalysts for the oxygen evolution reaction (OER) is crucial for advancing green hydrogen production [1, 2]. While magnetic fields are known to enhance OER kinetics by improving spin-polarized electron transfer and mass transport [3], conventional synthesis of magnetically active alloys (e.g., FeCo, FeNi) often involves complex, multi-step processes with limited control over porosity and composition.

This work presents a novel, template-free synthetic strategy utilizing a liquid NaK-78 eutectic alloy emulsion [4, 5] for the one-pot reduction and structuring of porous multiphase Fe-X-based (X = Co, Ni) materials. The NaK alloy acts simultaneously as a powerful reducing agent, pore-forming agent, and structure-directing medium, enabling the formation of mesoporous architectures with high specific surface areas (up to 96 m^2/g for FeCo-G2). The synthesis was optimized in different solvent systems (tetrahydrofuran – THF and diethylene glycol dimethyl ether – diglyme, G2), with diglyme yielding more homogeneous and less oxidized structures.

The as-synthesized porous Fe-Co-based and Fe-Ni-based materials contain both alloy and mixed oxide phases (spinel-type), according to XRD. The phase ratio can be controlled by the synthetic protocol adjustment. The element ratio of the metals in resulting materials is 1.0:1.0 from EDS analysis. These materials were evaluated as electrocatalysts for OER in 1 M KOH. Under an applied external magnetic field (250 mT), the Fe-

Co-based catalyst exhibited a remarkable 40-60% increase in current density at 0.55 V vs. Ag/AgCl, reaching 135 mA • cm^{-2}, compared to its performance without a magnetic field. This significant boost is attributed to the unique combination of high surface area with a magnetically active Fe-X FCC structure facilitated by the NaK-assisted synthesis.

In summary, we demonstrated that the NaK-78 alloy is a versatile reagent for fabricating porous, multiphase magnetic electrocatalysts. The developed materials show exceptional promise for application in magnetically enhanced water splitting systems due to its high activity, simplicity of synthesis, and significant response to an external magnetic field.

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Thin-film solid electrolytes $Li_{6.6}Al_{0.05}La_3Zr_{1.75}Nb_{0.25}O_{12}$ formed by electrophoretic deposition

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The development of alternative energy sources is one of the priority areas of scientific research in the modern world. Particular attention is paid to the creation of solid-state power sources, which open up new opportunities for the creation of environmentally safe energy storage devices. Solid electrolytes have increased stability to active materials, but have lower ionic conductivity compared to liquid electrolytes. The transition to thin-film technologies allow reducing the ion transfer resistance, which makes such a system more efficient for practical application and opens up new prospects for the creation of a new generation of energy devices.

This study examines the method of electrophoretic deposition (EPD), which enables the formation of homogeneous thin-film coating ranging from 10 to 30 of micrometers in thickness under the influence of an electric field on substrates of various shapes. The effect of heat treatment conditions on the phase composition, microstructure, and conductivity of $Li_{6.6}Al_{0.05}La_3Zr_{1.75}Nb_{0.25}O_{12}$ films was investigated.

The solid electrolyte $Li_{6.6}Al_{0.05}La_3Zr_{1.75}Nb_{0.25}O_{12}$ was synthesized via the citrate-nitrate method. The powder, after heat treatment at 1150°C, underwent mechanical milling at 750 rpm. The specific surface area of the milled powder was 4.0 ± 0.1 $m^{-2} \cdot g^{-1}$, with a grain size of 0.4-5 μm. Using the EPD method, the powder was deposited on a Ti substrate under a constant voltage (80 V) for 4 minutes. The resulting films were annealed in an argon atmosphere at various temperatures (300-700 °C) with a heating rate of 10 $°C \cdot min^{-1}$ and a holding time of 30 min.

XRD data indicate that annealing temperatures below 700 °C preserve a single-phase state, while at 700 °C and above, the emergence of $La_2Zr_2O_7$ impurities is observed, indicating partial lithium oxide evaporation. The resistance of the obtained single-phase solid electrolytes was measured by impedance spectroscopy in the temperature range of 25-300 °C. According to the data, heat treatment of the films up to 300 °C increased their conductivity from 1.3 • 10^{-6} to 3.4 • 10^{-6} S • cm^{-1} at 300 °C. Further temperature increases led to a decrease in film conductivity. The low conductivity values are attributed to the formation of a porous structure with numerous weakly bonded grains. These results are significant for developing technological processes for forming thin-film coatings based on LLZ-family solid electrolytes on metallic substrates via EPD. Further investigation should be aimed at the formation of highly conductive dense films of $Li_{6.6}Al_{0.05}La_3Zr_{1.75}Nb_{0.25}O_{12}$.

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Synthesis and investigation of the electrochemical properties of $Na_{1-x}K_xV_{1-y}M_yPO_4F$ (M = Cr, Al) 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 $Na_{1-x}K_xV_{1-y}M_yPO_4F$ (M = Cr, Al) with degrees of substitution not exceeding 20%.

Single-phase KTP-$Na_{1-x}K_xV_{1-y}M_yPO_4F$ were synthesized by an original two-step approach similar to that previously proposed by Shraer et al. [1], using ion exchange in sodium glutamate melt with hydrothermally synthesized ammonium precursors. The phase and elemental compositions of the samples at each stage were monitored by X-ray diffraction and EDX spectroscopy accordingly. The correlations between the coulombic efficiency and the long-term cycling stability of cathode materials with a respect to the degree of substitution were proposed by analysis of galvanostatic cycling of materials in a coin-cell vs. metallic sodium.

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Formation of low-resistant anode-solid electrolyte interface in all-solid-state Na-ion batteries

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All-solid-state sodium-ion batteries (ASSSBs) have emerged as promising candidates for large-scale energy storage systems, offering advantages over conventional lithium- and sodium-ion batteries employing flammable liquid electrolytes. Among various solid electrolytes investigated for ASSSBs, the NaSICON-type electrolyte $Na_3Zr_2Si_2PO_{12}$ (NZSP) is particularly promising due to its high ionic conductivity, excellent chemical stability in air, relatively low cost, and simple synthesis [1]. However, NZSP suffers from large interfacial resistance in contact with sodium metal anode; the main reason for that are voids presenting at the sodium metal anode/solid-state electrolyte interface. This issue limits the effective use of sodium metal as the anode and complicates the fabrication of batteries with Na metal anodes. Application of the stack pressure and slight increase of the operating temperature are effective tools to activate creep deformation in sodium metal, promoting interfacial deformation and interface voids' filling with sodium [2]. This thereby necessitates detailed studies of the Na/NZSP interface under the pressure.

In this study, solid electrolyte NZSP was synthesized via solution-assisted solid-state synthesis described in [1]; as a result, dense ceramic electrolyte pellets were obtained. The impact of constant mechanical pressure on the interfacial interaction between the sodium metal anode and the NZSP electrolyte was investigated. Symmetric Na/NZSP/Na cells were fabricated by assembling sodium electrodes in a sandwich configuration under internal pressures of 1, 3, and 5 MPa. Sodium metal was deposited either by an ultrasonic welding to ensure consistent interfacial contact or by without ultrasonic assistance. Critical current density (CCD) and electrochemical impedance spectroscopy (EIS) measurements were conducted at room temperature and elevated temperatures of 40, 50, and 60°C. After cycling, the samples were examined via scanning electron microscopy (SEM) for morphological analysis.

Phase purity of the synthesized NZSP ceramic electrolyte was confirmed by X-ray diffraction (XRD), indicating a high phase purity with minor zirconium dioxide impurities (~5%). The effects of sodium deposition methodology, applied pressure, and operating temperature on the critical current density and interfacial resistance were systematically evaluated and correlated to interfacial properties. The resistance of cells at 1 MPa with ultrasound deposition and without is $2 \cdot 10^2$ and $7 \cdot 10^2$, at 3 MPa $2 \cdot 10^3$ and $2 \cdot 10^2$, at 5 MPa $7 \cdot 10^3$ and $1{,}5 \cdot 10^5$ Ohm/cm^2. The CCD results will be presented during the report.

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Conductive properties in Ti-doping MgV_2O_4: comprehensive calculations and experimental measurements

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MgV_2O_4 has been previously mentioned as a promising cathode material for magnesium and zinc-ion batteries due to its three-dimensional spinel structure [1-2]. Sugimoto et al. [3] noted that the addition of titanium could improve the conductivity, but the authors did not obtain these structures in the form of single-phase samples. We first theoretically studied Mg^{2+}-ion conductivity in structures initial MgV_2O_4 and doped $Mg_{0.8}(V_{0.8}Ti_{0.2})_2O_4$. All possible supercell configurations were generated in the Supercell program [4], and the most stable configuration was selected from the electrostatic energy data. Stable configurations were optimized by density functional theory (DFT) in the VASP software [5]. The sizes of migration channels were estimated using geometrical-topological (GT) analysis in ToposPro [6], and migration barriers were calculated using bond valence site energy (BVSE) methods in softBV [7] and in the framework of DFT with the nudged elastic band approach. Cationic conductivity was estimated as a function of temperature using kinetic Monte Carlo (KMC) simulation. Band gaps were also estimated by DFT, which turned out to be 0 eV in both cases, indicating the presence of electronic conductivity. Some simulation results are presented in Table 1.

Table 1. Calculation details of conductive properties in MgV_2O_4 and $Mg_{0.5}VTiO_4$.

Compound	GT	BVSE	KMC
	Channel radius, Å	*Em* (migration map), eV	σ300K, S cm^{-1}
MgV_2O_4	1.857	0.43 (3D)	$>10^{-10}$
$Mg_{0.8}(V_{0.8}Ti_{0.2})2O_4$	1.892	0.57 (3D)	$1.5 \bullet 10^{-5}$

We then successfully synthesized these compounds using a single-step process involving VO_2 reduction with graphite and subsequent oxidation annealing. We measured the total conductivity using impedance spectroscopy on samples that had been sintered to form dense ceramics, and the electronic conductivity contribution using direct current polarization. The experimental results showed a correlation with theoretical data.

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Acetonitrile as electrolyte additive for improving the cyclic stability of aqueous zinc-ion batteries

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Aqueous zinc-ion batteries are of great interest as an alternative to lithium-ion batteries due to their low cost, environmental friendliness, and safety. Zinc anodes have a high theoretical capacity (820 mAh/g), volumetric capacity (5854 mAh/cm^3), and a low redox potential (−0.76 V vs. SHE). Despite this, dendrite formation, which affects coulombic efficiency and cycle life, limits their application. In addition, there is the problem of hydrogen evolution and anode corrosion [1].

To solve the above-mentioned problems, several approaches have been proposed: the use of zinc alloys, application of protective coatings, construction of three-dimensional structures, and electrolyte modification [2]. The electrolyte is an important part of the battery and has a significant impact on its performance. It can influence interfacial reactions and interface formation, as well as the solvation structure. Various organic and inorganic electrolyte additives help to address the problem of non-uniform zinc deposition and suppress side reactions. Acetonitrile is of particular interest because it is an inexpensive additive and is also highly soluble in water, making it a suitable candidate for use in aqueous zinc-ion batteries [3]. It is assumed that the high solvation ability of acetonitrile increases the number of nucleation sites and provides dendrite-free morphologies of zinc. However, its role in tuning the structure and functions of aqueous electrolytes has not been fully studied.

In this work, we investigated vanadium oxide–based cathode materials versus zinc anode in 3 M $Zn(CF_3SO_3)_2$ electrolytes, tested in two solvents: pure H_2O and a mixed H_2O/AN (3/1 v/v) system. Introducing acetonitrile significantly improved the cycling stability of the batteries without reducing the capacity of the cathode, resulting in an increase of around 13% in capacity retention by the 500th cycle.

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Search for new conductive solid-state materials among halides for Mg-ion batteries

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Nowdays, the lithium-ion batteries are the most commonly used in different electrochemical technologies. However, their production faces the challenge of rising costs of lithium, which results in high prices for finished devices [1]. Magnesium-ion batteries, which use significantly less expensive materials, are presented as a more favorable alternative [2].

In this study, we carried out a search for novel magnesium-conducting materials among compounds containing halogens using theoretical screening. Such compounds are very promising due to their high stability and simple synthesis conditions and can be applied as electrode materials and solid electrolytes. We selected 77 compounds containing magnesium-containing halides from three, four, and five elements from the ICSD database (version 2024/2). Using crystal chemical analysis implemented in ToposPro [3] for the evaluation of voids and channels sizes, we identified 60 structures with periodic migration maps of Mg^{2+} ions. After literature analysis, we found that 44 out of them were not previously mentioned as conductive materials. Next, for each structure, we calculated the crystal chemical stability (GII parameter) and the magnesium migration energy (E_m, eV) using the bond valence site energy method and calculate the ionic conductivity at 300 K (σ_{rt}, S cm^{-1}) within the kinetic Monte Carlo simulation method in softBV (command line version) [4]. Some of the best data are presented in Table 1 for example.

Table 1.

Compound	*GII*	E_m, eV	σ_{rt}, *S* cm^{-1}
MgW_6I_{14} ($Pn\bar{3}$)	0.23	0.41	$3.08 \bullet 10^{-5}$
$MgPdF_6$ ($P\bar{3}$)	0.15	1.17	$2.25 \bullet 10^{-6}$
$MgAu_2F_8$ ($P21/c$)	0.04	1.26	$1.91 \bullet 10^{-6}$

For stable structures with E_m less than 0.5 eV and σ_{rt} greater than 10^{-6} S cm^{-1}, the more precise calculations of migration and vacancy formation energies and the band gap values were performed in the framework of density functional theory.

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Anode Materials For Hybrid Sodium-ion/ Metal Batteries

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Currently, sodium-ion battery (SIB) technology is undergoing rapid development and is considered a promising alternative to lithium-ion batteries (LIBs). The primary advantage of SIBs lies in their significantly lower cost, which is attributed to the abundant natural availability of sodium. Hard carbon is predominantly used as the anode material for SIBs, characterized by its high specific capacity, good Coulombic efficiency, and straightforward synthesis from readily available precursors. Hard carbon is also employed in hybrid sodium-ion/ sodium-metal batteries [1]. However, the development of this hybrid technology faces a challenge related to the insufficient reversibility of metallic sodium plating and stripping, which adversely affects the Coulombic efficiency [2].

This study investigates various carbon materials to determine their electrochemical characteristics, such as capacity, Coulombic efficiency, and cycling stability, in a hybrid system. The experimental section involved the fabrication of electrodes from selected carbon materials, the assembly of electrochemical cells, and galvanostatic charge-discharge cycling tests within a current density range of 25 to 250 mA/g. Scanning electron microscopy (SEM) was employed for a detailed analysis of the electrodes' morphological features and the characteristics of the deposited sodium.

Electrochemical investigations were conducted by applying varying pressures to the electrodes within the cell, ranging from 130 to 390 kPa (equivalent to approximately 25 to 75 kgf). To prevent short circuits, separator layers of different thicknesses were tested, which enabled the establishment of a correlation between the electrochemical cell's performance and the magnitude of the applied pressure and separator thickness.

The study revealed that the hybrid system exhibits distinct electrochemical behavior depending on the type of carbon material used as the electrode and the annealing temperature of non-graphitizing carbon. Specifically, non-graphitizing carbon derived from lignin demonstrated a first-cycle Coulombic efficiency of 83%, while non-graphitizing carbon derived from glucose exhibited one of the highest reported values in the literature—90%.

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Conditions for the formation of the cathode|solid electrolyte interface with the introduction of a low-melting additive of $65Li_2O\ 27B_2O_3\ 8SiO_2$ glass

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Currently all-solid-state power sources are under great demand. The transition to a fully solid-state design is positioned as a possible way to solve the safety problem (especially in extreme conditions – high temperatures, pressure and aggressive environments) and increase the service life of the current source. The interface between cathode and solid electrolyte is one of the main problems in the design of such batteries, since these solid-state materials are characterized by a small contact area, high porosity and resistance. Formation of an optimal contact between solid particles of the cathode and solid electrolyte can be achieved by high-temperature sintering of the cathode with a solid electrolyte. To form the $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ (NMC) | solid electrolyte interface, a lithium-conducting low-melting additive of $65Li_2O \bullet 27B_2O_3 \bullet 8SiO_2$ (LBS) glass was introduced into the cathode composition, since it has high values of lithium-ion conductivity of $3.6 \bullet 10^{-6}$ S/cm at room temperature and a low melting point (640 °C) and during crystallization the main phase is lithium-conducting Li_3BO_3.

The sintering temperature of composite cathode and solid electrolyte was choosen based on the DSC data. The thermal behavior of NMC+LBS and NMC+LBS+$Li_{7.15}La_3Zr_{1.85}Al_{0.15}O_{12}$ mixtures were studied. An exothermic peak at 338 °C and an endothermic peak at 638 °C were observed on the DSC curve of NMC+LBS mixture, which correspond to LBS glass crystallization and melting respectively. Two additional endothermic peaks were observed at temperatures of 675 and 697 °C on the DSC curve of NMC+LBS+solid electrolyte mixture, which suggest the onset of interaction between the components of the mixture.

According to XRD data the additional peaks related to $La_2Zr_2O_7$ and Li_3BO_3 were observed on the XRD pattern of NMC+LBS+LLZ (1:1:1) mixture after annealing at 700 °C. Based on the obtained results data, it can be concluded that the endothermic peak at 675 °C on the DSC curve can be associated with the interaction of LLZ and LBS. Therefore, 650 °C was chosen as the sintering temperature of the composite cathode material to the solid electrolyte. According to XRD data, heat treatment at 650 ºC did not lead to the formation of any impurity phases in the composite cathode; peaks of NMC and cubic LLZ were observed. Thus, the optimal sintering temperature of the cathode with a solid electrolyte was established and the chemical stability of the LLZ electrolyte to the NMC cathode material was confirmed.

The research has been carried out with the equipment of the Shared Access Center "Composition of Compounds" of the Institute of High Temperature Electrochemistry.

Electrochemical properties of V_2O_5/PEDOT cathode in different electrolytes for aqueous zinc-ion batteries

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Lithium-ion batteries are widely used due to their high specific energy, Coulombic efficiency, and long cycle life. However, their drawbacks, including high cost, recycling challenges, and the risk of thermal runaway under short-circuit conditions, drive the search for alternative energy storage systems. A promising direction is aqueous zinc-ion batteries (AZIB), which are characterized by safety, environmental friendliness, and low production cost [1].

Among cathode materials, vanadium pentoxide (V_2O_5) has attracted considerable attention due to its low cost and high theoretical capacity (~589 mAh/g) enabled by a two-electron redox process. Nevertheless, the application of pristine V_2O_5 is limited by poor electronic conductivity, long activation periods, and rapid capacity fading. One of the strategies to improve cathode performance is modification with conducting polymers, which expand interlayer spacing, facilitate intercalation of hydrated Zn^{2+} ions, and enhance electrical conductivity [2]. Poly(3,4-ethylenedioxythiophene) (PEDOT) has proven to be the most promising among them, providing high electronic conductivity and cycling stability.

The synthesis of V_2O_5/polymer composites is most often performed via the hydrothermal method, though it requires high temperature and pressure. An alternative is the polymerization in solution method, which is simple and does not require specialized equipment, though it is time-consuming.

In this work, the V_2O_5/PEDOT composite was synthesized by prolonged polymerization in solution with ultrasonic pretreatment, a method previously applied for lithium-ion battery cathode materials [3]. Half-cells with a zinc anode were assembled and tested in two aqueous electrolytes: 3M $ZnSO_4$ and 3M $Zn(CF_3SO_3)_2$. Cycling results demonstrated that the material exhibits superior capacity and stability in sulfate electrolyte only at low current densities up to 2 A/g, whereas in triflate electrolyte it performs better at high current densities, with a capacity difference of nearly 210 mAh/g at 10 A/g.

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Sodium-niobium phosphate bronzes $Na_2Nb_6P_4O2_6$ and $Na_4Nb_8P_4O_{32}$ as negative electrode materials: synthesis, structure and conductive properties

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Over the past three decades, lithium-ion batteries (LIB) have been successfully used as energy storage devices. However, due to the gradual depletion of lithium resources, there is a need to find an alternative. Sodium-ion batteries (SIB) attract attention due to the uniform geographical distribution of sodium raw materials, cheapness and similar principle of operation. One of the main components of batteries is the anode material, which significantly affects the battery performance. Sodium-niobium phosphate bronzes $Na_2Nb_6P_4O_{26}$ [1] and $Na_4Nb_8P_4O_{32}$ [2] may be considered as potential anode materials for SIB. The most common method of synthesizing these compounds is long-term (from 10 hours to 2 months) high-temperature (1000 – 1200 °C) solid-state synthesis.

In this work, the optimal conditions for the solid-state synthesis of $Na_2Nb_6P_4O_{26}$ and $Na_4Nb_8P_4O_{32}$ were selected, followed by a study of the structure and electrochemical properties. It has been established that the use of a stoichiometric ratio of reagents does not lead to the production of a phase pure compound, since prolonged heat treatment result in the volatilization of Na and P. The addition of carbon to the reagent mixture avoids foaming process during degasation of reagents. The regulation of Na and P-containing reagents and the exclusion of the preliminal degasation stage made it possible to reduce the synthesis temperature and synthesis time of $Na_2Nb_6P_4O_{26}$ and $Na_4Nb_8P_4O_{32}$ to 900 °C and 1 hour. The phase composition was determined by XRD analysis followed by refinement of the crystal structure using the Rietveld method. The available migration paths of Na ions were determined and an assessment of energy barriers was carried out, according to which the barrier value for Na+ ions in $Na_2Nb_6P_4O_{26}$ was 0.6-0.8 eV, while for $Na_4Nb_8P_4O_{32}$ 0.8-0.9 eV.

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Synthesis of Hard Carbon from Glucose as an Anodic Material for Sodium-Ion Batteries

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The ever-increasing demand for high-power, more stable, and cheaper batteries is driving the development of alternatives to lithium-ion batteries and improving the properties of electrode materials. As a result, researchers have turned their attention to amorphous hard carbon as an anode material for sodium-ion batteries (SIBs) with attractive electrochemical characteristics [1]. One promising synthesis method is the hydrothermal pretreatment of carbohydrates followed by high-temperature annealing in an inert atmosphere [2]. However, the effect of hydrothermal synthesis conditions on the final characteristics of hard carbon remains poorly understood. Additionally, well-reproducible and scalable synthesis methods for selected electrode materials are necessary for subsequent research on the performance of SIBs prototypes.

Therefore, the aim of this work is to develop a hydrothermal carbonization-based synthesis method for producing hard carbon with improved electrochemical characteristics for sodium-ion batteries.

The synthesis was carried out by hydrothermal carbonization of a 2.6 M glucose solution at 200-220 °C in 0.3 and 0.5 L reactors with different fillings and stirring modes. The resulting hydrochar was washed, dried, and annealed in an argon atmosphere at 1300 °C for one hour. The materials were studied using galvanostatic charge-discharge cycling, SEM, and adsorption measurements.

Previously, the synthesis method was developed in a 0.3 L reactor, resulting in samples with a discharge capacity of approximately 320 mAh/g and a coulombic efficiency of 88% at a current density of 25 mA/g. However, increasing the autoclave volume from 0.3 to 0.5 L while maintaining the same synthesis parameters resulted in a decrease in the properties. This is most likely due to the temperature gradient caused by incomplete and uneven heating of the larger reactor volume. Because of this, the particles are submicron-sized, which is confirmed by the SEM images and the large specific surface area of the samples. Increasing the temperature to 220 °C and stirring the solution during the synthesis, as well as additional drying of the hydrochar in a vacuum oven before annealing, allowed us to achieve good electrochemical characteristics for hard carbon derived from glucose. At the same time, changes in the mixing speed and reactor fill factor do not have a significant effect on the properties and yield of the final product.

Thus, the hydrothermal synthesis conditions in a 0.5 L reactor were optimized. The resulting samples have a discharge capacity of about 310 mAh/g and a coulombic efficiency of up to 90% in the first cycle.

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Boron containing salts for electrolyte additives

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Currently, concerns about the sustainability and finite availability of lithium have prompted researchers to pursue the development of low-cost and more sustainable battery technologies. Consequently, sodium-ion batteries (NIBs) have attracted significant research interest recently [1]. In lithium-ion batteries (LIBs), lithium hexafluorophosphate ($LiPF_6$) is commonly used as the electrolyte salt, and an analogous sodium salt has been adopted for NIBs in a carbonate solvent mixture.

However, the formation of less stable solid electrolyte interphase (SEI) and cathode electrolyte interphase (CEI) passivation layers presents a challenge, largely due to the less rigid nature of the sodium cation. To improve electrode stability in NIBs, boron-containing compounds may be used. Recently, it has been demonstrated that $Na[B(hfip)_4] \bullet DME$ (hfip=hexafluoroisopropyloxy, O^iPr^F) and $Na[B(pp)_2]$ (pp=perfluorinated pinacolato, $O_2C_{2\text{-}}(CF_3)_4$) have excellent electrochemical perforwmance. Both electrolytes give more stable electrode-electrolyte interfaces than conventional $NaPF_6$, as demonstrated by impedance spectroscopy and cyclic voltammetry [2]. At the same time, the vast majority of $Na[B(OR^F)]$ salts has relatively low conductivity [2] and may be used as electrolyte additives, as far as, the boron compounds have predisposition to polymerization while the coordination number of 4 is available [3], this must influence the electrochemical and physical properties of the electrolyte systems based on them.

In this work, fluorine containing salt with views to success in electrolyte additives is synthesized in grate yields from sodium borohydride: $Na[B(Otfe)_4]$ (tfe=trifluroethoxy). The impact of the additive and its electrochemical properties will be discussed and presented during the report.

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Electrochemical performance of KTP-$NaV_{0.9}Al_{0.1}PO_4F$ || HC system in multi-layered pouch cells

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Within last decade vanadium-based polyanion materials are recognized as prospective cathode materials for sodium-ion batteries (SIBs). Thus, $KTiOPO_4$(KTP)-structured materials with general formula of $NaVPO_4F$ was thoroughly investigated [1]. $NaVPO_4F$ exhibits high specific energy compared to other polyanion materials, but lacks appealing capacity retention. In attempt to improve material's electrochemical performance, partial vanadium substitution by aluminium was proposed in our laboratory. Aluminium substitution of vanadium provides increase in crystal structure stability and thus prevents vanadium from dissolving, which is believed to be the main cause of poor long-term performance of the material. Tests in coin-type cells vs. sodium metal and vs. hard carbon (HC) were successful in proving the substitution strategy working, therefore investigation of pouch cells performance was put forward. Investigation in pouch cell with 1 Ah capacity is necessary to approach the comparison with available on market options

In this work KTP-structured material with $NaV_{0.9}Al_{0.1}PO_4F$ formula and practical capacity of ~120 mAh • g^{-1} paired with HC is investigated in multi-layered pouch cells.

Single-phased KTP-$NaV_{0.9}Al_{0.1}PO_4F$ was obtained via solid-state ion exchange using hydrothermally synthesized $NH_4V_{0.9}Al_{0.1}PO_4F$. When tested in coin-type cells vs. hard carbon on anode, carbon-coated $NaV_{0.9}Al_{0.1}PO_4F/C$ (1.5 mAh/cm^2) composite materials demonstrate specific capacity of 120 mAh • g^{-1} at 0.1C rate. Average electrode potential is around 4.0 V. 2, 10 and 20 layered pouch cells with double-sided cathode were assembled, and they've shown promising capacity retention and capacity of 55 mAh, 550 mAh and 1100 mAh respectively at 0.1C rate, which fully corresponds to expected characteristics. The cells are expected to reach specific energy greater than 100 Wh/kg which is competitive with other polyanion compound SIBs.

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