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Lectures

Computational modeling of materials for energy storage

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One emerging and promising approach for the discovery and improvement of materials is computer modeling. Traditionally, providing a deep understanding of materials' properties, computer modeling helped to rationalize the process of materials development. Nowadays, with the emergence of high throughput screening techniques, computer modeling allows the discovery of completely new materials with the desired properties [1].

In this talk, a history of computational modeling and its role in materials science is shortly presented. The basic principles of modeling and main methods used for modeling of inorganic solids are reviewed.

An emphasis is made on density functional theory (DFT) – a method that became a must-have tool in materials science studies. We show how DFT is used for predicting numerous properties of functional materials including catalysts for fuel cells and electrode materials for Li-ion batteries. An examples for calculating atomic and electronic structure, thermodynamics, mechanical properties, ionic and electronic conductivity are given.

The talk is concluded by discussing the future of computational modeling based on machine-learning and high-throughput approaches [2].

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Na-ion batteries: be or definitely be?

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Nowadays, autonomous small-to-large-scale devices are driven by two mature power sources: Lead-acid and Li-ion batteries (LABs and LIBs, respectively). Despite being widely used in scooters and bikes, as automotive starters and uninterruptible power supply (UPS), electric vehicles, stationary storage systems, both technologies suffer from some disadvantages. For example, LABs have generally low specific energy, typically short lifetimes, particularly slow charging rate and obligation to be stored in a charged state, not excluding an undesirable ecological damage made if the poisonous lead or concentrated sulfuric acid used are not properly recycled. The widespread implementation of LIBs is hindered by rare and isolated raw resources, expensive recycling, inferior performance at low temperatures, flammability and toxicity of some components. In terms of energy density, recyclability and costs, sodium-ion batteries (SIBs) are a tradeoff between LABs and LIBs rendering this technology alternative for LABs if superior specific energy is required or for LIBs if the price per kWh is preferential over the energy density.

In fact, the SIB technology appears more sustainable compared to both LABs and LIBs since SIB electrode materials can be manufactured from abundant metals such as sodium, iron, manganese, vanadium, titanium and aluminum, eliminating expensive cobalt, nickel, and copper that makes Na-ion batteries affordable worldwide. Moreover, SIBs tolerate deep overdischarge so that they can be fully discharged to "zero" volts, kept in this state without maintenance and then easily recovered to its full operation. Overall, SIBs set forth a number of advantages being competitive or even superior to LABs and LIBs in specific niches. In this lecture, current status of the SIB technology, its further development and perspectives will be discussed along with the underlying chemistry and physics. A variety of materials for SIB electrodes will also be covered in detail, including those designed and upscaled at Skoltech.

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Fire Safety of Lithium Ion Batteries

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Self-heating of lithium ion batteries to high temperatures, often accompanied by smoke, flames, and even explosion presents a risk for those who use the batteries. The process of the uncontrolled increase of the battery temperature leading to the battery failure with the possible ignition is known as thermal runaway. It may occur either when the operation conditions of the battery go beyond the safety limit (mechanical damage, cycling at exceedingly high or low temperature, too high voltage at the cell terminals), or spontaneously resulting from the development of internal defects of the lithium ion cell.

The thermal runaway events have been observed in the lithium ion batteries of various dimensions, capacities and electrochemical systems. Both small cells of smartphones and laptops and the large batteries of the electric vehicles and energy storage systems may exhibit the thermal runaway.

In order to increase the safety of the lithium ion cells, three protection levels are introduced. On the first level, special cell materials are used (for example, a three-layer separator, electrolyte additives). On the second level, safety devices are added to the cell design. Finally, on the level of the lithium-ion battery, safety is provided by the battery management system, the electronic device, which disconnects the battery from the external circuit when the operation conditions are beyond the safe limits. This three-level protection works well against overcharge or the external short circuit, however the battery fires are still not uncommon.

In most cases, the lithium ion battery ignitions result from the development of an internal short circuit, followed by thermal runaway. Internal defects of the cells or lithium metal dendrites growing from the negative electrode are responsible for the internal short circuit. The battery protection is not efficient against the internal short circuits. During the thermal runaway, the cell temperature rises quickly and the process becomes irreversible at the temperature of about 150°C when the separator fails. The battery may heat up to 900°C within seconds. It is extremely difficult to extinguish the fires of large lithium ion batteries, although certain solutions have been developed in the recent years.

Although the concept of “dangerous” and “safe” lithium ion battery electrochemical systems is widespread, the actual level of the battery safety depends on many factors, such as the size of the cell, the materials used for the electrodes, electrolyte, and separator, and the presence of safety devices. The consequences of a possible internal short circuit may be evaluated using the nail penetration test. However, its practical significance has been criticized, and alternative tests have been proposed.

As for the user, the safety of the whole battery pack is the thing that matters. The safety evaluation of the battery pack is a complex task involving a number of costly tests such as crash test, vibration test, etc. For the reasonable safety assessment it is necessary to take into account various hazardous factors of the battery thermal runaway (high temperature, flame, smoke) in relation to the actual operation conditions of the battery (working indoors, presence of people nearby, evacuation conditions).

Electrocatalysis: Fundamentals and Applications

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Electrocatalysis is concerned with electrochemical reactions at the interface between an electrolyte and an electrode. Electrocatalytic processes are technologically rather relevant as they occur in fuel cells or electrolyzers. Even in electrochemical energy storage in batteries, electrocatalytic processes occur, in particular in metal–air batteries. Hence, electrocatalytic processes are of an immense technological relevance in the context of our future sustainable energy technology.

In this lecture, we will survey the basic concepts of electrochemical thermodynamics and kinetics, in order to have a basic perception of the range of relevant electrochemical phenomena and the key kinetic parameters, which dictate the sluggishness of the most important electrocatalytic reactions: the oxygen evolution/reduction reactions and the hydrogen oxidation/evolution reactions. We will discuss the mechanisms underlying the reaction rate enhancement by using a suitable catalyst and outline the differences between heterogeneous catalysis and electrocatalysis. Examples of application of electrocatalytic reactions in energy conversion devices will be provided. Finally, we will emphasize the complexity of the relevant electrocatalytic interfaces, the difficulties of deducing the true rate-controlling factors, and the ways to overcome these difficulties.

Industrial application of electrochemical energy storage systems

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Electrochemical Energy Storage Systems (EESSs) are widely used in many industrial applications [1,2]. EESSs provide a wide range of services for solar and wind integration, absorbing energy at high generation and providing it when needed thus ensuring stable energy supply in the grid. EESSs are applied in electrical vehicles being charged form the grid and providing energy to electrical engines during the trip. EESSs are used for capacity and ancillary services markets, offering grid services related to primary and secondary reserves. Indirectly EESSs can support cost reduction, cutting down the need for generation and transmission capacity by reducing the need for peaking plants and easing line congestion [3]. EESSs can also support the integration of distributed renewables and the active participation of prosumers in demand management, reducing average electricity bills of households. All of these tasks have different requirements for applied storage system and thus different EESSs technologies should be considered. In addition to EESSs, Hydrogen Energy Storage Systems (HESSs) are seen as a possible solution for some of the tasks described above due to relatively high energy density and flexibility of power and energy ratings [4]. However, this technology also has a number of limitations that should be taking into account for proper application [2,3].

The topic of the lecture is the application of EESSs for industrial tasks. First, different EESSs technologies will be considered focusing on their specifics, advantages and limitations. After that, that main industrial applications will be discussed with specific requirements for each task. Finally, comparison of EESSs with HESSs will be considered and pros and cons of each of the technology will be discussed deriving the areas of their application.

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Main characteristics and features of redox flow batteries

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Vanadium Redox Flow Batteries (VRFB) are considered as one of the most promising solutions for stationary electric energy storage systems. A VRFB stores electric energy in the chemical form of vanadium solutions converting it in the electrochemical cells and storing the electrolytes in two separated external tanks. As a results, VRFB has very low self-discharge [1], long life time, up to 20 years / 2000000 cycles [2], and independent scalability of capacity and power ratings [3] making this technology attractive for development of solutions "all in one" when the same storage unit can be used for multiple services simultaneously being suitable either for bulk electric energy management for electric power quality services. In addition, the VRFB presents the key technology for Russian energy industry, as Russia has nearly 25% of the world's vanadium reserves as well as all materials required for all other components of the battery [4]. Thus, VRFB systems can be produced in Russia under conditions of economic sanctions and export limitations. Therefore, development of VRFB technology as a crucial issue for sovereignty of our country.

In this lecture, the main working principle of the VRFBs will be explained. After that, their main features will be discussed and compared with other main battery technologies. A special attention will be devoted to internal physical process taking place in the electrochemical cells and their affect to polarization behavior of the cell as well as on the integral battery characteristics. In addition, main aspects for electrochemical testing of the VRFB systems will be discussed considering characterization of internal components (e.g. membranes, electrodes) highlighting the most important points for redox flow batterers.

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Materials synthesis methods for electrochemical systems

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The synthesis method and approach are known to affect directly their physicochemical parameters (bulk density, tap density, primary and secondary particle size and shape, crystallinity, and size distribution) as well as electrochemical properties (charge/discharge capacity, rate capability, capacity retention, and cycle stability) of materials used in promising electrochemical systems such as metal-ion batteries (MIBs). Several wet chemical and solid-state synthesis techniques have been developed in the last couple of decades including the sol-gel method, solid-state reaction, hydro- and solvothermal synthesis, and its microwave-assisted variation, spray pyrolysis, combustion, and co-precipitation for the synthesis of electrode materials. All these methods are in a different stage of development and application having their own advantages and disadvantages. However, in term of an industrial scale, an ideal synthesis method should meet several important criteria such as simple operation, low cost, ability to selectively design material properties (e.g., particle shape and size, porosity, stoichiometry), and should be environmentally friendly.

In this talk, main aspects of most of the synthesis methods will be highlighted and analyzed to understand the effect of various parameters on the properties and performance of the developed electrode materials. Furthermore, the main steps of synthesis in each method, key differences in the process, advantages and drawbacks, and their effects on the performance of materials will be discussed. Finally, a comparative assessment of the existing synthesis methods to evaluate their feasibility for industrial application will be carried out.

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Participants

Oxygen isotopic exchange with $Ba_{0.5}Sr_{0.5}Co_{0.8-x}Fe_{0.2}Me_xO_3-$ (Me – Nb, Ta, Mo, W)

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Owing to high values of oxygen permeability [1] and electron conductivity [2], complex oxide $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) is well known as a promising material for air electrodes of solid oxide electrochemical devices and mixed conducting membranes. Despite prominent advantages, the widespread usage of this material is restricted by its metastability in the conditions of operation of high-temperature devices [3]. The doping of high-charged cations into the cobalt and iron sublattice is reliable method of stabilizing of cubic structure of BSCF. But the influence of such cations on the kinetics of exchange and diffusion of oxygen remains poorly studied. Therefore, the purpose of this work was to investigate the effect of highly charged cations such as Ta, W, Nb, Mo in oxides based on $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ on the crystal structure, oxygen content and kinetics of the interaction of oxides with oxygen of the gas phase.

All oxides were synthesized by the standard solid-phase method. To obtain dense ceramics, all powders were pressed into tablets and sintered at 1300°C. The phase composition, crystal structure and microstructure of synthesized oxides were studied by X-ray diffraction

and scanning electron microscopy.
The kinetics of oxygen exchange with synthesized oxides in the temperature range of 600-800°C at oxygen pressure pO2 = 6.7 mbar was studied by the method of oxygen isotope exchange. The mechanism of oxygen exchange with oxides was analyzed within the framework of a two-stage model of oxygen exchange, which includes the stage of dissociative oxygen adsorption ra and the stage of oxygen incorporation ri.

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ZnV_2O_4 spinel as prospective cathode material for metal-ion batteries

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The current trends in battery materials science are related to the search for prospective resource-efficient, high-energy-density, and safe post- or beyond-lithium battery chemistries.
Zn-ion batteries attract attention due to potentially larger theoretical volumetric capacity, safety and lower cost than lithium ion batteries. We performed a step-by-step search for new cathode materials for zinc-ion batteries. We used ToposPro package for geometrical–topological screening of the ICSD database and selected

the compounds whose structure is suitable for the zinc ions migration. Next, the Bond Valence Site Energy theory (softBV program) and Density Functional Method (VASP program) were applied to calculate the Zn^{2+}-ion migration energy. As a result, few interesting cathode materials were identified, mostly with spinel structure. Among them, ZnV_2O_4 was selected for the synthesis due to high energy density and low zinc migration energy [1]. The spinel ZnV_2O_4 was synthesized by a hydrothermal method. According to the X-ray diffraction data the best result for ZnV_2O_4 (Fig. 1a) was obtained under the following synthesis conditions: 1 mmol $Zn(NO_3)_{2.6}H_2O$, 2 mmol NH_4VO_3 and 1 mmol hydrazine hydrate were dissolved in 15 mL deionized water. The mixture was then stirred strongly to homogeneous solution and transferred into a 22 mL Teflon-lined autoclave and maintained at 180°C for 2 days. After cooled down to room temperature naturally, the product was centrifuged, washed with deionized water several times and finally dried at 50°C overnight [2]. The measured conductivity within electrochemical impedance spectroscopy method was 5.57×10^{-6} S cm^{-1} at room temperature (Fig. 1b)

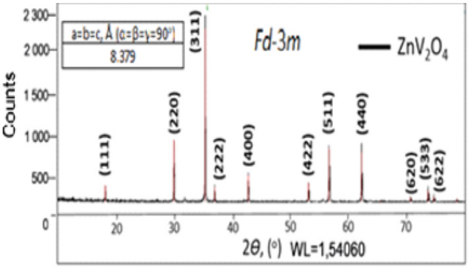

Fig. 1 (a)XRD of the spinel-like ZnV_2O_4.

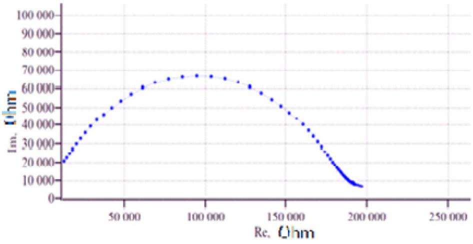

Fig. 1b Nyquist plots of the ZnV_2O_4 electrode.

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The nature of NASICON-structured materials degradation during cycling in different potential ranges

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NASICON-structured $Na_3V_2(PO_4)_3$ is considered as a cathode for sodium-ion batteries. The capability of de/intercalation of more than two sodium ions per formula unit could be provided by partial substitution of vanadium by the metals in 2+ oxidation state. Such materials of compositions $Na_{3+x}V_{2-x}Mex(PO_4)_3$ (Me = Mn, Mg, x = 0.5, 1) demonstrate structural stability and capacity retention after multiple charge/discharge cycles, even at high current densities in the potential window of 2.5-3.8 V with respect to Na/Na^+, but only with 2 sodium ions reversible de/intercalation. However, the deintercalation of additional amount of sodium ions accompanied with an increase of the anode potential limit above 3.8 V causes a loss of capacity on subsequent cycling [1]. Yet, the increase of potential hysteresis during subsequent cycling could be observed in case of substitution of one vanadium atom per formula unit. It was previously approved the degradation of $Na_4VMn(PO_4)_3$ correlates with the reduced values of the calculated charge transfer rate constant and of the diffusion of sodium ions what apparently caused by the formation of a new amorphous phase at potentials above 3.8 V [2]. Still, the degradation process, which is taken place in potential window of 2.5 – 4.4 V is reversible. After the discharge to 1.0 V the shape of the galvanostatic curves returns to its origin. Furthermore, the cathode materials when cycling in the most expanded potential range of 1.0 – 4.4 V show the same capacity loss as for the 2.5-3.8 V.

The crystalographical insights on the nature of different electrochemical kinetics of discussed set of materials caused by extra sodium ions extraction and discharging to 1.0 V could be manifested using *operando* and *ex-situ* X-ray diffraction.

This is confirmed by *ex situ* diffraction studies of electrodes based on $Na_4MnV(PO_4)_3$ after cycling in various charge-discharge modes. A capacity decrease during cycling with the limit of the anode potential of 4.1 V is accompanied by an increase in the proportion of the sodium-deficient phase in the volume of the material. Our study demonstrates that hysteretic effects in $Na_4MnV(PO_4)_3$ materials originate from the thermodynamic instability of the deeply desodiated material, rather than from the kinetic limitations due to irreversible structural changes, as it was suggested in previous studies.

The study was supported by the Russian Science Foundation (Grant № 17-73-30006-P).

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Swelling degree and supramolecular organization of Nafion membrane in water and aprotic solvents

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Sulfofluorinated membranes of the Nafion family with proton conductivity are widely used in low-temperature fuel cells, sensors, vanadium redox batteries, ionistors, and in organic catalysis [1]. Polymer electrolytes based on the lithium form of membranes are promising for creating a new generation of lithium-ion batteries suitable for use in electric vehicles due to increased safety and an extended operating temperature range [2].

The aim of this work was to characterize the thermodynamics and kinetics of the process of swelling of the protonated and lithiated forms of the Nafion membrane in water and aprotic dipolar solvents.

The objects of study were commercially available extrusion membranes H^+-Nafion 115, H^+-Nafion 212 casting membranes, as well as membranes obtained by casting from a water-alcohol dispersion and a polymer solution in N-methylformamide (NMF). The chemical substitution of mobile membrane protons for lithium ions was carried out by keeping the samples in an aqueous solution of LiOH [3]. The dependence of the degree of swelling of the protonated and lithiated forms of Nafion on temperature was studied by film gravimetry. The plasticizers were water, ethylene carbonate (EC) and sulfolane (SL). The degree of crystallinity of the protonated Nafion membrane was studied by X-ray diffraction analysis and differential scanning calorimetry.

It was found that with increasing temperature, the swelling capacity of Nafion increases regardless of the nature of the solvent and the method of obtaining the membrane. Upon transition to the lithiated form of the polymer, the absorption of EC doubles at a holding temperature of +40...+60°C. With a further increase in temperature H^+-Nafion 212 begins to dissolve in EC, in contrast to Li^+-Nafion 212.

It is shown that films cast from a true solution H^+-Nafion in NMF do not demonstrate the endothermic effect of dissociation of ionic clusters, in contrast to films from water-alcohol dispersion. It is assumed that Nafion macromolecules in NMF solution have an unperturbed coil conformation. When the solvent evaporates, a uniform physical network of entanglements with a lower degree of crystallinity is formed, which can be seen from the ratio and shape of the peaks according to the X-ray diffraction analysis.

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Ph_3BiBr_2 – a bifunctional mediator of discharge/charge of lithium-oxygen battery

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Lithium-oxygen batteries (LOBs) due to their high specific energy can be used in electric vehicles while maintaining the same mileage as internal combustion engine vehicles [1]. However, there are significant difficulties that arise during discharge and charge of LOBs, and which associated with the main discharge product – lithium peroxide. During discharge of LOBs, cathode is passivated by Li_2O_2, and during charge of LOBs, oxidation of Li_2O_2 becomes difficult due to its low electronic conductivity and low solubility in electrolyte. To solve these problems bifunctional mediators could be introduced into the system that lead to the formation of lithium peroxide in the volume of electrolyte solution, instead of cathode surface during discharge. Also, mediators could facilitate Li_2O_2 decomposition during charge.

In this work, Ph_3MeHal_2 (Me=Bi, Sb; Hal=Cl, Br) and Ph_3MeCl (Me=Sn, Pb) were studied as bifunctional mediators of LOB discharge/charge. For each compound, we studied the mechanism of the oxygen reduction/evolution reactions using a glassy carbon working electrode in an electrolyte based on dimethyl sulfoxide with the addition of lithium ions and without it. Lithium-oxygen cells based on a carbon paper positive electrode and tetraethylene glycol dimethyl ether (TEGDME)-based electrolyte were discharged and charged.

It was found that under the operating conditions of a LOB Ph_3PbCl is electrochemically unstable, therefore, this compound has not been studied further. The absence of anodic peaks in the CV for Ph_3SbCl_2 in presence of O_2 and Li^+ indicates that the binding force between Sb and oxygen derivates is so large that it interferes with the formation of Li_2O_2. Consequently, this compound does not exhibit the properties of a discharge mediator. Addition of Bi and Sn based compounds to electrolyte leads to an increase in the discharge capacity, and for the former one it turns out to be larger. Thereby these compounds can be performed as discharge mediators. Comparison of discharge curves of chloride and bromide compounds shows that the halide ion does not affect the discharge capacity. The use of bromide compounds leads to a decrease in the charge voltage by 0.4 V compared to chloride ones.

Thus, of all the above compounds, only Ph_3BiBr_2 can be used as a bifunctional mediator of discharge/charge of a lithium-oxygen battery, since its addition to the cell leads to a significant increase in the discharge capacity by 8 times in TEGDME-based electrolyte and an essential decrease in the charge voltage.

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Electrocarboxylation of Imines to α-Amino Acids on Various Metal Surfaces

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α-Amino acids (α-AA) are the most important class of natural substances with a variety of biological activities. In addition, α-AAs are important building blocks in the processes of biological and chemical synthesis of peptides, proteins, and pharmaceuticals [1-3]. Due to the variety of applications, much attention is paid to the development of new approaches to the synthesis of α-AA. The electrochemical method for the synthesis of α-amino acids is a reductive combination of CO_2 with imines (or electrocarboxylation, EC), which directly gives the target carboxylic acids. This approach is gaining a lot of attention as a "green" solar-powered synthesis method and allows the synthesis to be combined with a beneficial anodic reaction such as oxidative wastewater treatment.

We have studied the effect of the nature of the catalyst, its surface morphology, and operating parameters on the efficiency and selectivity of imine ECs. In particular, EC of N-benzylideneaniline in an aprotic medium was carried out on 11 different metals. The efficiency of the studied catalytic materials was determined by NMR analysis of the reaction mixture after potentiostatic electrolysis at optimal potentials determined by cyclic voltammetry (hereinafter CV). In addition, nanostructured Pd catalysts of various shapes (cubes and branched star-shaped nanoparticles) were synthesized and electrochemically studied. The activity of the synthesized nanoparticles was determined under conditions similar to those previously used for polycrystalline Pd.

As a result, the EC of imines on Ag, Zn, Fe, Ti, and Cu surfaces is accompanied by the most efficient formation of α-AA. Electrocarboxylation reactions on Pd nanomaterials are accompanied by an increase in the Faraday yield of the formation of target reaction products with increasing potential. Branched star-shaped Pd nanoparticles demonstrated the highest current density at each potential. All materials show structural stability during electrolysis.

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On improvement of electrochemical performance of sodium-manganese-chromium phosphate

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Nowadays with the development of electric vehicles and portable devices the demand on cathode materials with high energy density, durability and safe cycling broadens. NASICON-type phosphates of d-metals and sodium may become a solution to the latest challenges, as its structure provides long and safe operation [1]. However, the common NVP ($Na_3V_2(PO_4)_3$) cathodic material provides relatively low energy density of about 400 Wh/kg, hence the NMCP ($Na_4MnCr(PO_4)_3$)

compound with energy density of more than 500 Wh/kg has been proposed. [2]

Such high energy density comprise of three redox processes: at 3.7, 4.2 and 4.5 V (Figure 1). In order to improve the cyclic performance of NMCP in the potential range 2.5-5.0 V we have optimized the electrolyte composition. After obtaining the NMCP by sol-gel method and annealing, its electrochemical properties were studied using galvanostatic charge-discharge, unveiling the cyclic stability of (de) intercalation processes corresponding to different redox processes. Following that, the structural changes during the cell operation have been investigated using *ex-situ* and *in-situ* X-ray diffraction.

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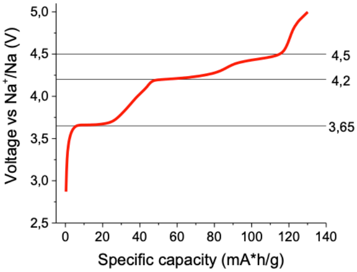

Figure 1. Galvanostatic charge curve of NMCP in 2.5-5.0 range

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Ionic mobility in triple molybdates and tungstates with a NASICON-type structure

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The development of advanced technologies for electric energy storage (battery technologies) is a crucial problem in the field of world energy. This is due to the widespread occurrence of portable electronic devices, increased interest in creating electrical and hybrid vehicles, to renewable energy sources, etc. Today, the technology based on lithium-ion batteries appears to be the most promising in terms of performance (high values of discharge voltage and specific energy capacity, small size, and light weight). It should be noted however that the search for lithium substitutes is continuing because of expensiveness of lithium-based devices. Sodium, being chemically similar to lithium, is much cheaper and less toxic. Although sodium-ion batteries have a considerably lower specific energy than lithium-ion analogs, the former are of choice for stationary units with a high power consumption.

Research data for the diffusion mechanisms of Na+ ions in $Na_{1-x}Mg_{1-x}Al_{1+x(}XO_4)_3$ (X = Mo, W) compounds with the NASICON-type structure (space group $R\bar{3}c$, Z = 6) are reported. Solid solutions in the homogeneity range $0.1 \le x \le 0.5$ for X = Mo and $0.4 \le x \le 0.6$ for X = W have been prepared by solid-state synthesis. Conductivity measurements and NMR spectroscopy data indicate fast sodium diffusion in the studied samples: the ionic conductivity reaches the values of about 10^{-3} S/cm at T > 800 K. The frequency of elementary ionic jumps is on the order of 104 s^{-1} at T ≈ 500 K, and the activation energy is equal to 0.8–0.9 eV. Comparative analysis has shown that the ionic conductivity in molybdates is higher than in tungstates, as confirmedby calculations of sodium barriers. We showed that growth of magnesium concentration increases the concentration of local coordinations Mg^{2+}–Na^{+}–Mg^{2+}, acting as traps for moving sodium ions. The above conclusions are supported by ab initio calculations according to which the barrier for sodium diffusion from the Mg^{2+}–Na^{+}–Mg^{2+} position is expected to be higher than those for the Mg^{2+}–Na^{+}–Al^{3+} and Al^{3+}–Na^{+}–Al^{3+} ones.

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SiO_2-template synthesis of hard carbon anode materials for sodium-ion batteries

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Sodium-ion batteries (SIBs) can be a possible alternative to lithium-ion batteries (LIBs) due to sodium availability and low cost. Commercialization of SIBs requires electrode materials with high specific capacity, good cycling stability, low cost and low toxicity.
Hard carbon (HC) is one of the promising negative electrode material in NIBs, since HC demonstrates a high capacity in contrast to graphite [1]. Hard carbon (HC) is a non-graphitizable form of carbon material, which consist of curved graphitic domains and micropores.
There are a variety of methods to synthesize hard carbon, where template synthesis aims an increase the specific capacity of hard carbon through increasing the number of inner micropores. This approach helps to obtain HCs with extremely high specific capacity up to 480 mAh/g [2]. Porous SiO_2 is an attractive material for use as a nanoscale template because its porosity and average pore diameter can be easily adjusted [3].
This work is devoted to SiO_2-template synthesis of hard carbon. At first, the mixture of glucose and tetraethoxysilane (TEOS) as a source of SiO_2 was pretreated in hydrothermal condition. The template was removed by hydrofluoric acid, and then the material was subjected to annealing at 1300°C. The concentration of hydrofluoric acid was varied in order to achieve formation of maximum number of micropores instead of silicon dioxide. Influence of synthetic conditions, morphology on electrochemical performance was studied. Obtained SiO_2-templated HC demonstrated high specific discharge capacity of 372 mAh/g.

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Sacrificial compounds for lithium ion batteries capacity recovery

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Nowadays, lithium ion batteries (LIBs) are predominantly used in electronic devices and electro vehicles due to their relatively high specific capacity (372 mAh/g) and other technical advantages [1]. Higher production of electronics is inevitably associated with generation of a higher number of waste LIBs, which are very hazardous to the environment, if they are not recycled [2]. Common cause of LIBs throwing away is their significant capacity loss, thus capacity recovery may give LIBs the second life. One of the reasons for capacity fade in LIBs is loss of active lithium in electrode material. [3]. We assume, that recovery of active lithium and thus capacity recovery is possible if lithium intercalation on one electrode occurs simultaneously with irreversible electrochemical oxidation on opposite electrode.

We consider methyl formate, dimethyl oxalate, lithium lactate, lithium acetate, etc as a reductants for capacity recovery. Electrochemical oxidation of such carboxylic compounds is commonly irreversible. In addition, possible products of their electrochemical oxidation are gaseous or very similar to components of SEI, so they should not affect performance of recovered LIB. We studied electrochemical behavior of saturated solutions of lithium lactate, lithium acetate and 0.2M dimethyl oxalate, 5M methyl formate solutions in 1M $LiClO_4$ in EC/DC (1:1). Cyclic voltammetry of these solutions was performed on glassy carbon electrode. Each compound found to be irreversibly electrochemically oxidized near the potential range of electrolyte oxidative decomposition (approximately 5.7 V vs Li/Li^+). Side reduction reactions with significant cathodic currents were observed for methyl formate and dimethyl oxalate, that limits their use for capacity recovery. Fortunately, no side reduction reactions were observed for lithium lactate and lithium acetate. So, lithium lactate and lithium acetate could be used for capacity recovery due to irreversibility of their electrochemical oxidation and absence of side reduction reactions.

Electrochemical oxidation of lactate and acetate anions was studied by low scan rate cyclic voltammetry on glassy carbon electrode and chronoamperometry on carbon fiber microelectrode. Transfer coefficients in Butler-Volmer equation were calculated for each anion using data from cyclic voltammetry (0.13 and 0.17 for lactate and acetate respectively). Diffusion coefficients were calculated for each anion using chronoamperometry data and Shoup-Szabo equation ($4.3 \cdot 10^{-7}$ cm2/s and $1.5 \cdot 10^{-8}$ cm2/s for lactate and acetate respectively).

We found that lithium lactate and lithium acetate among the studied compounds are possible candidates for LIB capacity recovery. However, poor solubility of these salts is a big limitation, which should be overcome.

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Electroreduction of Chlorate Anion in Acidic Medium. Role of Chlorine Dioxide

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Halate anions can be used as multielectron oxidizers in power sources of a new type without the use of expensive catalysts. [1-2]. Chlorate anion has no electrical activity in the range of potentials required in energy sources. This difficulty can be overcome by a combination of chemical and electrochemical steps involving electrochemically active intermediates containing a halogen atom in an intermediate oxidation state. In this work, the possibility of implementing such a mechanism based on chlorine dioxide was studied.

In order to elucidate the fundamental regularities of the electroreduction of the chlorate anion and to find ways to accelerate this reaction, reductive electrolysis of an aqueous solution of sodium chlorate (12.5mM) in sulphuric acid (8M). The limiting current was controlled in the potentiostatic mode. The optical spectra of the solution were periodically measured, the dominant contribution was made by chlorine dioxide ClO_2. It has been established that the current and concentration of chlorine dioxide change in time according to the same law, which corresponds to the autocatalytic redox mediator mechanism [3]. It was shown that at the maximum current, typical for such a mechanism, the concentration of chlorine dioxide is a significant part of the total concentration of chlorine atoms in the system, i.e. this component plays a key role in the process of chlorate electroreduction. An almost complete conversion of chlorate to chloride was found.

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Structural features of Lanthanum Hexaboride single crystal at temperatures 85–293 K

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Hexaborides of rare earth elements (REE) have a unique variety of physical properties, depending on the composition and external conditions. It is known that at low temperatures some of these properties manifest themselves anisotropically, which contradicts the known information about the structure [1]. Studies of some polycrystals of REE hexaborides by various diffraction methods have shown nonmonotonicity of the temperature dependences of the unit cell parameters and atomic displacements in the range of 100–180 K, for example [2]. Recent studies have shown distortions in the structural characteristics of single crystals of other higher borides in the same temperature range [3].

More detailed studies of the atomic structure of hexaboride single crystals will help correlate structural information with accumulated information about physical properties at various temperatures. This work is devoted to structural features of LaB_6 single crystals. Lanthanum hexaboride occupies a leading position in the series REE hexaborides according to the number of practical applications. It is used as a material for cathodes capable of stable operation under harsh operating conditions. cathodes, in which uses lanthanum hexaboride, is used for the manufacture of electronic vacuum lamps.

The studied samples were obtained by the method of induction crucibleless zone melting. The structure of all compounds with the general formula RB_6 (R = La–Gd) can be represented as two subsystems: boron and metal. Boron atoms form the framework of the structure, which ensures the high strength of the crystals. The type of cation, in turn, determines the physical properties of the compound.

Precision X-ray diffraction experiments were performed on a Synergy DW single-crystal diffractometer with a curved HyPix-Arc 150° photon counting detector in the temperature range 85–293 K with a step of 5–10 K. The structure was refined in cubic sp. gr. $Pm\text{-}3m$. The nonmonotonicity of the temperature dependence of the unit cell period was found, which indicates possible structural transformations. An analysis of atomic dynamics was carried out using the extended models of Debye and Einstein, which made it possible, on the basis of structural data, to draw conclusions about hidden phase transitions and calculate the characteristic temperatures.

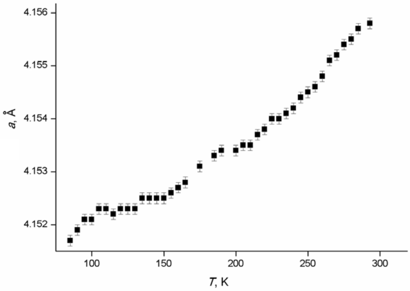

Figure 1. Unit cell period of a LaB_6 *single crystal.*

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Immobilized Nitroxyl in Combination with Molecular Redox-Mediator System for Electrocatalytic Oxygen Reduction

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The extensive developments of sustainable energy technologies is driven by the rapid expansion of global clean energy demand. Among diverse energy technologies, fuel cells (FCs) are widely considered as promising energy conversion and storage devices. However, the slow kinetics of oxygen reduction reaction (ORR) on a cathode leads to the demand of active, cheap and reliable platinum-free ORR catalyst.
This report describes a new type of ORR catalytic system. The system consists of an electrode modified by nitroxyl groups and an electrolyte with anionic redox mediators. During the catalysis of ORR, two consecutive redox mediator cycles are realized: oxidation of NOx particles in atmospheric oxygen and subsequent oxidation of TEMPO molecules by oxidized NOx particles. Amine oxide molecules are the result of oxidation of TEMPO. The oxide molecules are reduced at the carbon cathode. In the system oxygen is not reduced either at the carbon electrode or TEMPO by the mediator system. However, oxygen is effectively reduced by the NOx system. In this case, NOx particles are effectively reduced by TEMPO radicals, but practically not reduced at the electrode, while TEMPO radicals are formed during the reduction of amine oxide fragments on a carbon electrode with a low overvoltage. Such catalytic cycle is described for soluble TEMPO mediators, which can hardly be applied to FC technology [1]. In our study we have synthesized a series of redox-conducting polymers with TEMPO-based pendants. Conducting backbone based on π-conjugated polymer provides fast electron exchange between TEMPO groups and a current collector, and macromolecular structure of the catalyst prevents washing out of the catalyst. As a result, immobilization of the polymers on an electrode improves the kinetics

of the process and avoid problems with low stability of TEMPO in aqueous electrolytes. This research was funded by the Russian Foundation for Basic Research, grant number 20-33-51007.

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PEDOT:PSS-modified gel polymer electrolyte for lithium-ion batteries based on carboxymethyl cellulose

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Lithium-ion batteries (LIBs) are still the most widely used power sources for portable devices, electric vehicles. Despite their high practical capacity and energy density values, major drawback of these batteries is safety. Using the flammable liquid organic carbonates-based electrolyte is one of the main issues of LIBs. To solve this problem, all-solid or quasi-solid electrolytes can be applied. Application of quasi-solid, or gel polymer electrolytes (GPEs) is promising way because of high mechanical integrity and flexibility of polymer and high ionic conductivity of liquids [1]. Among different polymer matrixes of GPEs bio-derived polymers, in particular, cellulose and its derivatives, have attracted especial attention due to their high abundance, solubility in water, thermal stability and high amount of donor oxygen atoms which facilitate the movement of Li^+ ions along the polymer chain [2].
To enhance the functional properties like ionic conductivity, various synthetical routes can be applied to develop the oxygenated polymer chains [3]. Another way is addition a conductive additive to the polymer solution for preparation the composite

material. In this work, a dispersion of conducting polymer poly (3,4-ethylenedioxythiophene) with polystyrene sulfonate anion (PEDOT:PSS) was added to carboxymethyl cellulose (CMC) for application as GPE for lithium batteries.

The membrane were prepared by dissolving of fixed amount of CMC in solution of water with N,N-dymethyl formamide and the different amount of PEDOT:PSS dispersion was added. The resulting solution was cast on the glass form and dried under vacuum at 75 °C. Before the electrochemical tests, membranes were cut into disks and swollen in the solution of 1 M $LiPF_6$ dissolved in ethylene carbonate: diethyl carbonate (EC:DEC, 1:1 vol.).

Measurements of ionic conductivity of membranes were carried out by electrochemical impedance spectroscopy in symmetric steel/GPE/steel cells in the temperature range of 20 – 70 °C. The electrochemical stability window of GPE was determined by cyclic voltammetry in the potential range of 0.5 – 4.5 V vs. lithium electrode. The functional properties of LIBs were studied with cathode materials based on $LiFePO_4$ using galvanostatic charge/discharge and cyclic voltammetry.

The values of ionic conductivity obtained were $\approx 10^{-5} - 10^{-4}$ S·cm^{-1} and has slight dependence on the temperature. It was established by cyclic voltammetry that at potential values of $E < 1.5$ V and $E > 4.3$ V, competitive processes occur due to the presence of traces of water in the cellulose structure. The capacity values of $LiFePO_4$-based cathodes vs. lithium anode in the cell with GPE are comparable with ones obtained with liquid electrolyte.

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Facile Synthesis of Hollow Crystalline Ga-Doped Germanium Microcapsules as Anode Materials for Li- and Na-Ion Batteries

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Hollow metallic and metalloid capsules are of great interest due to their large specific surface area and optical, electrical, and catalytic properties. Issues in optimization of lithium-ion batteries and development of sodium-ion batteries can benefit from various nano- and micromaterials with hollow structure. This unique morphology of the materials allows to overcome and neutralize the anode volume expansion effect. One of the most facile and convenient approach to hollow nano- and microspheres synthesis is galvanic replacement reaction (GRR). In our previous research we proposed GRR with liquid gallium hydrocolloid to obtain a library of bi- and trimetallic functional capsules. The properties of the capsules are determined by the synthesis conditions, concentrations, precursors, and stabilizers, providing control over the surface morphology and the elemental composition and distribution [1]. Meanwhile, metals are not as interesting for battery storage devices as metalloids. Several research groups devoted their efforts to the synthesis of mesoporous carbon, silicon and germanium that can be used as highly effective materials for anodes in Li- and Na-ion batteries [2-4]. However, the synthetic approaches proposed could be simplified and made safer.

Wet synthesis of hollow germanium microcapsules was carried out using the emulsion of liquid eutectic gallium-indium alloy (GaIn) with ~ 2 μm particle size obtained through the sonication of GaIn in organic solvents: dimethylsulfoxide (DMSO), dimethylformamide (DMF), and tetrahydrofuran (THF). Germanium tetrachloride was used as a precursor. Concentrations of the reagents were varied in series consist of 6 samples. Obtained germanium powders were characterized using XRD phase analysis, SEM particle morphology and size distribution analysis, EDX elemental analysis, and surface area sorption-desorption analysis.

All the synthesized samples are represented by gallium-doped germanium ($Ge_{0.987}Ga_{0.013}$ is a prevalent phase) with high crystallinity (more than 80 %). Increase in reagents concentrations leads to a higher reaction yield and an increase in crystalline indium phase percentage (from ~ 5 % to ~ 10 %) as a side product. Nature of the solvent plays a key role in the presented synthetic approach. DMSO allows to produce germanium microcapsules with thinner shell walls. DMFA complicates the reaction and leads to hard-shell capsules formation. The highest reaction rate is observed in THF, however, the effect of this solvent results in weaker microcapsules wall structure and lower yield. It is assumed to test all the synthesized samples as anode materials in metal-ion batteries as the next step of our research.

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Гидротермальный синтез и исследование электрохимических свойств α-$Fe_{0.8}Cr_{0.2}PO_4$ в качестве катодного материала для металл-ионных аккумуляторов

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Развитие рынка литий-ионных аккумуляторов, гибридных транспортных средств, а также повышение стоимости литиевых ресурсов за последнее десятилетие мотивировало разработку более доступных систем с другим щелочным металлом, натрием. Поскольку основным лимитирующим электрохимические характеристики элементом является катодный материал, основные исследования направлены на получение новых катодных материалов для применения в натрий-ионных аккумуляторах.

Цель данной работы – синтез и исследование электрохимических свойств α-$Fe_{0.8}Cr_{0.2}PO_4$ со структурой α-$CrPO^4$, полученного термических разложением КТФ-$NH_4Fe_{0.8}Cr_{0.2}PO_4F$ в качестве катодного материала натрий-ионного аккумулятора [1,2].

Фосфат α-$Fe_{0.8}Cr_{0.2}PO_4$ был синтезирован путём термического разложения прекурсора $NH_4Fe_{0.8}Cr_{0.2}PO_4F$, кристаллизующегося в структурном типе $KTiOPO_4$ (КТФ), родственном α-$CrPO_4$, в атмосфере O_2 при температуре 600°C [3]. Продукт был охарактеризован методами рентгеновской дифракции, энергодисперсионной рентгеновской спектроскопии, сканирующей электронной микроскопии и др.

По данным рентгеновской дифракции соединение α-$Fe_{0.8}Cr_{0.2}PO_4$ изоструктурно α-$CrPO_4$. Наличие в данной системе протяженных каналов вдоль направлений [010] и [100] позволяет рассматривать α-$Fe_{0.8}Cr_{0.2}PO_4$ в качестве электродного материала для металл-ионных аккумуляторов. Измерение электрохимической активности углеродсодержащего композита α-$Fe_{0.8}Cr_{0.2}PO_4$/C проводили методом гальваностатического циклирования в литиевой и натриевой системах. В литиевой ячейке материал демонстрирует удельную емкость до ≈104 мАч/г на разряде, что составляет ≈73% от теоретической, а в натриевой ячейке достигаются значения удельной емкости до ≈108 мАч/г на разряде, что составляет ≈76% от его теоретической емкости.

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Highly soluble germanium oxide – a precursor for germanium compounds based anode materials for lithium-ion batteries

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Germanium compounds are important materials whose preparation mostly starts from germanium(IV) chloride or when slow, controlled hydrolysis is desirable from germanium alkoxides. Alkoxides are expensive and generate a waste stream that should be recycled. The solubility of amorphous and hexagonal germanium oxide (0.43 g in 100 g of H_2O at 20 °C) is higher than that of the tetragonal germania and it is also much higher than the solubility of other post transition metal oxides. Preparation of germanium compounds can therefore start by dissolution of germanium oxide in water. However, the dissolution of germania is slow. The solubility is still too low for wet materials processing, and therefore, germanium oxide deposition involves large volumes of precursors. In addition, the preparation of pure germanium oxide is a challenge, since it is difficult to get rid of ligands or chloride counterions. Here, we introduce a way to produce a highly soluble form of germanium oxide (HSGO) that can be used as a generic precursor for many germanium compounds. HSGO can be easily prepared in high yield from crystalline ammonium peroxogermanate, APG, a stable compound that can be stored under ambient conditions. We have demonstrated the possibility of quantitative deposition of germanium oxide on the surface of graphene oxide particles. Heat treatment in an inert atmosphere makes it possible to obtain a coating of amorphous germanium oxide on reduced graphene oxide. The passage of ammonia over the hegrmanium oxide-graphene oxide powder at a temperature of 700°C promotes the formation of the germanium nitride phase. Heating of GeO_2-GO in the presence of phosphorus makes it possible to obtain a material based on germanium phosphide and reduced graphene oxide. The obtained materials were studied as anodes in half-cells with a lithium counter electrode. The influence of the content of the initial germanium oxide in the composition of the material on the morphology and electrochemical performance of the final material was studied.

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Theoretical and experimental investigation of ion conductivity in the columbites MNb_2O_6, (M=Mg, Ca, Zn)

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In the last decade columbites (AB_2O_6, where A is a divalent metal; B - Nb, Ta) have been studied as promising conductive materials for solid oxide fuel cells due to their lower sintering temperatures and a relative density of more than 95% [1-2]. $MgNb_2O_6$ was selected as potential $Mg2^+$-ion conductor according to the crystallochemical analysis [3]. However, next quantitative calculations by bond valence site energy (BVSE) and density functional theory (DFT) methods proved the predominance of oxygen-ionic conductivity with low migration energies and wide migration channels in the structure (the channel size is characterized by the rchan parameter, Table 1).

Table 1. Theoretical results of ion diffusion in the columbites MNb2O6, M=Mg, Ca, Zn

Compound	r_{chan}, Å	E_m(BVSE)*, eV			ΔEm** (BVSE), eV	E_m(DFT), eV			ΔEm (DFT), eV
		1D	2D	3D		1D	2D	3D	
MgNb2O6	1.977	0.10	0.42	0.75	1.73	1.25	1.39	1.44	0.19
CaNb2O6	2.009	0.21	0.39	1.10	1.95	0.98	1.63	2.21	-0.49
ZnNb2O6	1.991	0.19	0.43	1.20	1.96	1.17	1.38	1.47	-0.33

* – the most probable dimension of ion migration maps are highlighted in bold.
** – difference between Em of oxygen and other ions, see [3] for details.

In order to demonstrate the oxygen conductivity, we synthesized $MgNb_2O_6$ and investigated the ion conductivity depended on oxygen pressure. We showed that the conductivity in the $MgNb_2O_6$ sample is ionic with oxygen working ions (~10^{-5} S/cm at 700°C). Next, we performed the same simulations for $CaNb_2O_6$ and $ZnNb_2O_6$, but quantitative calculations showed the possibility of bipolar conductivity (Table 1).

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Synthesis of binder-free hybrid electrode materials using alternating asymmetric current

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The rapid development of science and technology entails a growing demand for portable and flexible electronics, which in turn requires new approaches to the development of flexible electrode materials for chemical current sources.

Modern flexible binder-free electrode materials are based on carbon-containing materials characterized by high electronic conductivity, flexibility and low cost, combined with oxide compounds of transition metals, such as Mn_3O_4, MoO_3, CoO, $FeMoO_4$, NiO [1].

However, their significant disadvantages include insufficiently high specific capacitance values. One of the promising ways to improve the electrochemical characteristics of such electrode materials is their doping with polymers, which have electronic and ionic conductivity.

Among synthetic water-soluble anionic polymers, polyacrylic acid is of great interest – a proton-donor polymer that is readily soluble in water and is a weak polyelectrolyte [2].

This paper presents the results of studies on the production of electrode materials based on Ural T-22R carbon cloth modified with binder-free transition metal oxides and polyacrylic acid, using alternating asymmetric current.

The electrolyte, containing iron (II) sulfate ($FeSO_4$ $7H_2O$), cobalt sulfate ($CoSO_4$ $7H_2O$), nickel sulfate ($NiSO_4$ $7H_2O$), ammonium heptamolybdate ($(NH_4)_6Mo_7O_{24}$ $4H_2O$), boric acid (H_3BO_3), citric acid ($C_6H_8O_7$), was used to electrolyze. The temperature was 60–65°C, pH 4–5.

To increase adhesion, the surface of the carbon cloth was preliminarily subjected to electrochemical treatment in the electrolyte solution containing sodium metavadanate ($NaVO_3$).

According to energy dispersive X-ray analysis (EDX), the main elements of the hybrid material are carbon, oxygen, molybdenum, vanadium, iron, cobalt and nickel. The surface morphology of the obtained electrode materials has a mosaic character. According to TEM (SAED) data, the main phases of the resulting hybrid material are a mixture of molybdenum oxides MoO_2, MoO_3, Mo_4O_{11} and V_2O_5. Further study will be devoted to the obtained hybrid anode materials for lithium-ion batteries.

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Moss-Like Hierarchical Architecture Self-Assembled by Ultrathin $Na_2Ti_3O_7$ Nanotubes as an Anode for Sodium-Ion Batteries

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Recently, functional materials with a hierarchical architecture constructed by unique assemblies of constituent elements have gained increased attention. Topology benefits of hierarchical materials can provide unusual functionalities making them valuable for practical applications. The creation of materials with a hierarchical structure, which have a significant potential for practical use, is today an actively developing area of nanoengineering and the nanosystems industry. Titanium compounds are the basic components in a wide range of applications including paints, catalysts, plastics, coatings, sensors, hygienic products, cosmetics, pharmaceuticals, and even foods. Yearly world titanium demand (in TiO_2-units) is estimated around 6–8 million tons growing by about 3% per year. Furthermore, titanium compounds are already applied in battery production (e.g. spinel $Li_4Ti_5O_{12}$ that is valuable anode material for lithium storage due to its advantageous properties in long-term cycling stability). Nanocrystalline layer-structured monoclinic $Na_2Ti_3O_7$ is currently under consideration for usage in solid state electrolyte applications or electrochemical devices, including sodium-ion batteries, fuel cells, and sensors. Herein, a facile one-pot hydrothermal synthetic procedure is developed to prepare self-assembled moss-like hierarchical porous structure constructed by ultrathin $Na_2Ti_3O_7$ nanotubes with an outer diameter of 6–9 nm, a wall thickness of 2–3 nm, and a length of several hundred nanometers. The phase and chemical transformations, optoelectronic, conductive, and electrochemical properties of as-prepared hierarchically-organized $Na_2Ti_3O_7$ nanotubes have been studied. It is established that the obtained substance possesses an electrical conductivity of $3.34 \cdot 10^{-4}$ S/cm at room temperature allowing faster motion of charge carriers. Besides, the unique hierarchical $Na_2Ti_3O_7$ architecture exhibits promising cycling and rate performance as an anode material for sodium-ion batteries. In particular, after 50 charge/discharge cycles at the current loads of 50, 150, 350, and 800 mA/g, the reversible capacities of about 145, 120, 100, and 80 mA·h/g, respectively, were achieved. Upon prolonged cycling at 350 mA/g, the capacity of approximately 95 mA·h/g at the 200th cycle was observed with a Coulombic efficiency of almost 100% showing the retention as high as 95.0% initial storage. At last, it is found that residual water in the un-annealed nanotubular $Na_2Ti_3O_7$ affects its electrochemical properties. As we believed the reported strategy of hierarchically-organized $Na_2Ti_3O_7$ nanotubes may have a great potential for other fields, e.g. biomedicine, photocatalysis, and ion exchanger applications.

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Manganese-Incorporated Bronze Titanium Dioxide Nanotubes: Properties and Applications

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Over the past decades, titanium dioxide is widely applied in a range of applications due to its valuable properties, such as non-toxicity, availability, environmental benignity, physicochemical stability, biocompatibility, photo-reactivity, producing cheapness, and so on. In a form of nanomaterials TiO_2 has considered to be used in a range of innovative industrial arears, including hydrogen generation, sensing technologies, biomedical applications, superhydrophilic surfaces, memory storage devices, solar cells, dilute magnetic semiconductors, and metal-ion batteries. In this way, as evident, properties of nanocrystalline TiO_2 to be determined by its morphology, topology, and texture features. Therefore, tremendous efforts have been devoted to tuning and optimizing the synthetic methodologies in order to prepare the

TiO_2-based nanomaterials with required particle size, porosity, and architecture (e.g. hierarchically-organized and oriented structures). Titanium dioxide exists in nature as brookite, anatase, rutile, and bronze ($TiO_2(B)$) polymorphic phases. Among others, $TiO_2(B)$ is a best choice for batteries due to the structure organization. However, the electronic properties of TiO_2 (including nanoscopic materials) is insufficient for these purposes. Doping is an effective way to regulate the electronic properties of TiO_2 nanostructures.

We suggested to modify the electronic properties of nanotubular $TiO_2(B)$ for metal-ion batteries through doping with manganese. We showed that the preparation of Mn-containing $TiO_2(B)$ nanomaterials is occurred in the presence of NH_4HF_2 (when it is absent the anatase is formed due to phase transformation). We detected the evolution of crystal and electronic structure, ferromagnetic ordering, enhancing optical absorption under visible light, improving electrochemical performance in metal-ion batteries of manganese-doped $TiO_2(B)$ nanotubes.

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New perspectives for bismuth anode synthesis

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At present, there is active studying of sodium-ion batteries, which due to their proximity to lithium-ion batteries in chemical characteristics could become their appropriate equivalent. However, the main challenge remains the larger sodium radius, which leads to lower capacity of standard materials and as a consequence, a shorter life time. Bismuth anode has been shown as an optimal material for storing sodium-ion in battery systems in connection with the most suitable interaction force. The bismuth electrode is also shown specific characteristics including high theoretical capacity (385 mAh g^{-1}) and low redox potential (−0.8 V vs. SCE) [1]. The use of bulk bismuth material or particles results in anode pulverization. Fragmentation leads to a disconnection between the active material, the active conductive-additive material, and the collecting active ingredient. When this phenomenon occurs, the active ingredient is electrically isolated, which blocks electron transfer to carry out the reaction, so a large volume of the active ingredients remains unused to the process. Ultimately, this fact causes a dramatic decrease in capacity during the work cycle. The creation of 3-D interconnected porous bismuth alloys and the existence of mesopores and macropores are favorable for ion diffusion and electrolyte penetration. Also, the pores in the active materials and/or matrix can provide sufficient space to compensate for volumetric expansion after battery cycling [2].

Our research is aimed at solving the above mentioned problem by means of transferring metals and their compounds into nano- and microscale systems by galvanic replacement reaction [3]. Using this unique method, hollow particles of the desired metals are obtained from gallium as a sacrificial template. The reaction is controlled by values of electrochemical potentials, and bismuth is an excellent metal in these terms (E_0 Ga/Ga^{3+} = -0.549; E_0 Bi/Bi^{3+} = 0.308). Moreover, the method of galvanic replacement benefits from the fact that the formation of the new phase begins at the atomic level, providing a uniform distribution of the components. In addition the possibility of creating trimetallic anode structures, for example, alloying Bi with Sb, Sn, makes it possible to achieve stable and highly efficient SIBs and PIBs due to synergistic effects.

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Side processes in Li-O_2 batteries and their effect on GCPL curves

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Li-O_2 batteries have the highest theoretical energy density among electrochemical energy sources. Unfortunately, these batteries maintain poor cyclability, as the main discharge product – Li_2O_2, is an insulator. Introducing redox mediators (RM) into electrolyte may solve this problem: electrochemically oxidized form of RM chemically oxidizes lithium peroxide during the charge process. In order to investigate possible candidates for RM and their behavior at the positive electrode, it is necessary to understand the side reactions and their effect on discharge/charge curves. For instance, processes that occur on the Li-electrode lead to degradation of the Li-O_2, furthermore severe corrosion may affect electric conductivity and RM stability. This study is attributed to investigation of side reactions in Li-O_2 batteries.

To facilitate the interpretation of GCPL metallic Li anode could be replaced by lithium-iron phosphate (LFP) electrode – commercially available material with low-energy density yet with high stability. Since LFP has a two-phase intercalation-deintercalation mechanism, the potential remains unchanged during both lithiation and delithiation [1]. Commercially available LFP is deposited onto thin aluminum foil (LFP@Al), which exhibits corrosion during cycling in 1 M LiTFSI/DMSO. To prevent degradation preliminary cycling of LFP-Li half-cell in $LiPF_6$/EC:DMC (1:1) is necessary. This procedure results in enhanced stability towards corrosion and therefore longer battery life, which is shown in Figure 1a.

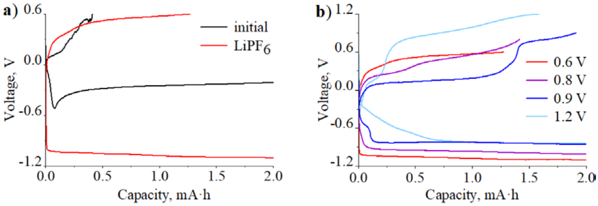

Fig. 1. GCPL curves of Li-O_2 cells with different voltage charging limits.

Cycling of Li-O_2 cell revealed that the shape of discharge curve depend on the charge voltage limit: increasing the limit leads to enlarging "step" at the beginning of the discharge. We believe that this region is a reverse process to side oxidation reactions that occur at the positive electrode surface upon charge. The charging curve include two regions at lower and higher potentials, the capacity of discharging "step" correlates to capacity of the higher-potential charging region which is demonstrated at Figure 1b.
In this work, we have applied passivation technique on LFP@Al electrode that prevents current collector corrosion. Relationship between the shape of the discharge and charge curves has been investigated, and influence of voltage upper-limit on discharge plateau is emphasized. Overall, the way is paved for further RM investigation by GCPL technique in Li-O_2 batteries.

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Nanocrystalline Oxygen-Deficient TiO_2–δ(B): synthesis and properties

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Nanocrystalline TiO_2 polymorphs with nonstoichiometry, i.e. containing intrinsic and/or impurity structural defects, attract considerable interest due to enhanced optical and catalytic activity, improved electronic properties. However, cationic or anionic doping can change the conditions of structural-phase transformations in TiO_2 during thermal treatment, provoke the nanoparticles agglomeration with decreasing in specific surface area, etc. On the other hand, the structural defects in TiO_2 can be formed through a non-doping way, e.g. via a heat treatment under controlled atmosphere (such as hydrogen, argon, nitrogen) or in a vacuum. An issue which has attracted increased attention in recent years is the defect-induced magnetic response at room temperature in nonstoichiometric semiconducting TiO_2 Regarding the latter, efforts are focused mainly on the anatase and rutile (including mixture). Herein, due to combination of hydrothermal technology followed by ion exchange process and high-temperature vacuum annealing, an oxygen-deficient bronze titanium dioxide $TiO_{2-\delta}$(B) with a belt-like nanostructure has been successfully prepared. It was found that upon vacuum heat treatment the material changes color from its original white to gray. EPR reveals that this is because of color centers (namely oxygen vacancies in the anionic sublattice) appearing in the bronze polymorph. According to spectrophotometry, the visible and near-infrared light absorption is much stronger in intensity and the band gap is narrowed from 3.23 to 3.04 eV due to existence of anionic defects. The synthesized gray $TiO_{2-\delta}$(B) exhibits room-temperature ferromagnetism, hence it belongs to the class of so-called dilute magnetic oxide semiconductors. It is remarkable that at low temperatures (4 K) the magnetic properties of defective $TiO_{2-\delta}$(B) do not differ from those for quazistoichiometric (prepared via annealing in air).

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Application of DSA electrodes for redox flow batteries

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Redox flow batteries (RFB) are promising candidates for solving the problems of sustainable energy production and use as stationary energy storage systems. Among them, the vanadium redox flow battery (VRFB) has achieved commercial success. VRFB is a membrane-electrode block (MEB), which consists of different components All these components are important for determining the energy efficiency of the VRFB [1, 2]. The bipolar plate role (BP) plays an important role in the prevention and transport of electrons and the production of carbon materials with high electrical conductivity [3]. Traditionally, corrosive electrolytes are used in the application of VRFB, so the BP must have anticorrosive properties. Along with high corrosion resistance, carbon materials have relatively low electrochemical characteristics and mechanical strength in thin form, which increases the cost of their processing and requires the use of thick BPs. Reducing the size of the BP can create compact multi-stack VRFBs.

The solution to the described problems can be the use of dimensionally stable anodes (DSA). DSA consists of electrocatalytic oxides of noble metals such as RuO_2 and IrO_2, which are on a substrate consisting of TiO_2/Ti and increase corrosion resistance [4].

In addition to using DSA as a thin BP for VRFB, such an electrode can be used in addition to the electrolyte rebalancing circuit. In this regard, the study of the stability and corrosion resistance of DSA in relation to operating conditions is an urgent task, to which the coverage work is directed.

In this work, RuO_2-TiO_2/Ti DSA were fabricated and accelerated corrosion resistance tests were carried out according to the procedure presented in [5]. The results of the experiment are shown in fig. one.

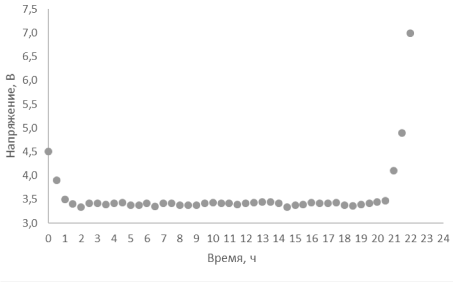

Fig. 1. Accelerated corrosion testing.

The lifetime under given conditions gives indications of about 22 hours, which, in terms of the method [6] for a possible mode of use (at a current of 0.05A/cm^2), is 1.7 years.

The resulting RuO_2-TiO_2/Ti DSAs exhibit high catalytic activity while maintaining corrosion resistance. In addition, an increase in the lifetime of food additives can promote the formation of mixed RuO_2/IrO_2 structures.

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Examination of self-discharge phenomenon for hard carbon anode materials in sodium ion-batteries

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Lithium-ion batteries (LIBs) are successfully used in portable devices, but due to the high cost of lithium raw materials there is a need to develop alternative systems. Sodium–ion system draws the most attention, since sodium is widespread in nature, and the cost of sodium-containing raw materials is two orders of magnitude lower than lithium ones [1]. For the successful commercialization of sodium-ion batteries, several fundamental and practical issues in the development of anode materials need to be solved [2]. A number of general requirements are imposed on anode materials: inexpensive cost, simplicity of synthesis, high specific capacity and Coulomb efficiency, good cyclability and durable charge retention, in other words low self-discharge rate.

Non-graphitizable carbon (also known as hard carbon) is the most promising anode material for SIBs [3]. Hard carbon is class of carbonaceous materials with highly amorphous structure consisted of curved graphene layers in strong cross-linking bonds, defect sites and open surface and internal pores. Though many electrochemical parameters of HCs are studied and presented in the literature, there is lack of information about the self-discharge phenomenon and its mechanism for this type of materials. However, several authors hypothesized higher rates of self-discharge in SIBs than in LIBs due to the higher solubility of the SEI components in electrolyte [4].

This work is devoted to the study of self-discharge of various hard carbon material. For this study, we have selected several HC samples with different nature of precursors and the synthesis method. Before the self-discharge study, electrochemical cells with hard carbon were precycled against sodium metal. After hard carbons were fully charged, open circuit potential of the cell had been recorded for one month. It was found that different HC samples demonstrate different self-discharge rates. The work presents our conclusions about the influence of the synthesis method, morphology and microstructure on the self-discharge rate of different HC samples.

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Influence of the synthesis method and type of binder on the electrochemical performances of Co_3O_4 as an anode material for lithium-ion batteries

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Commercial LIBs use graphite, which has a moderate theoretical capacity of 372 mAh/g and can promote the growth of lithium dendrites leading to a short circuit [1]. Thus, the search for anode materials alternative to graphite is an actual task. Among the potential promising anode materials, a number of transition metal oxides are considered [2, 3], which have a high theoretical capacity. In particular, a promising anode material for lithium-ion batteries is mixed cobalt oxide Co_3O_4 with a high theoretical capacity (890 mAh/g), which is 2.39 times higher than the theoretical capacity of graphite. Additional interest is caused by the possibility of using Co_3O_4 in sodium-ion batteries due to the linear dimensions of Co_3O_4 particles into which Na+ can intercalate. However, the practical use of anodes based on Co_3O_4 is difficult due to a significant drop in capacitance during long-term cycling of the electrodes and low performance at high currents. There are various ways to solve these problems, including varying the morphology of the material [3] and selecting a binder [4].

In this work, electrode materials based on Co_3O_4 with different morphologies were studied, obtained by three different synthesis methods (hydrothermal, precipitation and decomposition) using various binder compositions (PVDF, PEDOT:PSS/CMC 1:1, PAA/CMC 1:1).

The best results were shown by cobalt oxide obtained by the hydrothermal method at a temperature of 260°C using $NH_3 \cdot H_2O$ as hydroxide ions in combination with a PVDF binder. Co_3O_4 particles formed under these conditions are obtained in the form nanoprisms with an average size of 72 nm are distinguished by high crystallinity and low specific surface area relative to particles obtained under other conditions. Electrodes based on them in the first cycles give capacity of 1060 mAh/g at current of 0.2 C in potential range 0.01 – 2 V, and the capacity decreases to 910 mAh/g at current of 2 C. For 100 charge-discharge cycles at current of 0.5 C, 43% of the capacity is retained. With an aqueous binder for this sample, relatively low capacities and a noticeable deterioration in stability are observed.

The precipitation method makes it possible to obtain large highly porous particles with a diameter of 20 μm, which give high and even growing capacities of the order of 1000 mAh/g at any currents, including 2 C, with an aqueous PEDOT:PSS/CMC binder. However, in this case, no improvement in stability was achieved. At a current of 0.5 C, already in the first 50 cycles, the capacity drops by 78%.

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

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One of the most important conditions of successful development and implementation of renewable energy sources and electric vehicles is the production of efficient and accessible energy storage systems. Sodium-ion batteries (SIBs), being a promising alternative to the widely used today lithium-ion (LIBs) and lead-acid batteries (LAB), present one of the solutions to this problem. The main advantages of SIBs are that they approach LAB in terms of price and availability, and to LIBs in terms of specific energy density. The key task in the commercialization of SIBs is the development of materials, in particular cathode materials, for production of batteries with desired electrochemical characteristics.

Polyanionic compounds present one of the most promising classes of cathode materials for SIBs. This is caused by the specific structure of these compounds – it consists of 3D open robust framework, which leads to possibility of 3D-diffusion of sodium ions, higher ionic conductivity and higher stability of these compounds compared to their analogues. Among such systems, mixed phosphates are of particular interest. Mixed phosphates present class of polyanionic compounds with a framework composed of phosphate (PO_4^{3-}) and pyrophosphate ($P_2O_7^{4-}$) groups linking cations of transition metals. Interest in these compounds is caused by relatively high values of the operating potential, compared to phosphates and pyrophosphates, as well as smaller changes in the volume of the structure in the intercalation-deintercalation processes, which leads to their higher stability [1]. The aim of this work is the optimization of the synthesis method of cathode materials based on mixed phosphates with the general formula $Na_7V_4(P_2O_7)_4(PO_4)$, as well as their derivatives obtained by substitution of a transition metal cation. Single-phase samples of $Na_7V_4(P_2O_7)_4(PO_4)$ were obtained by the sol-gel method. The composition and structure of the obtained compounds were studied by powder X-ray diffraction, energy dispersive X-ray spectroscopy and scanning electron microscopy. Cathode materials for SIBs were obtained based on the synthesized compounds and their electrochemical characteristics were investigated in half-cells with sodium metal as counter electrode.

As a result of the work, the effect of the precursor composition for high-temperature annealing on the phase composition of the obtained samples was shown. It was also shown that the quenching of samples (both during synthesis and during the carbon coating process) significantly affects the electrochemical characteristics of the obtained cathode materials.

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