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Effect of ball milling parameters on the morphological and structural properties of $LiFePO_4$ cathode materials

Abanina A.V. [1], Styuf E.A. [1], Abakumov A.M. [1]

[1] Center for Energy Science and Technology, Skolkovo Institute of Science and Technology, Moscow, Russia

A.Abanina@skoltech.ru

The tap density of electrode materials plays a pivotal role in determining their performance in energy storage systems. In the realm of lithium iron phosphate (LFP), a prominent cathode material for lithium-ion batteries, tap density directly influences electrode packing density, porosity, and consequently, overall electrochemical performance [1]. The ball size used during the milling process significantly influences the characteristics of lithium iron phosphate (LFP) electrode materials due to its impact on particle size reduction, homogenization, and structural properties [2]. The size of milling balls directly affects the mechanical forces exerted on the material being milled, leading to a range of effects that influence LFP's characteristics. Smaller milling balls tend to impart higher levels of energy during collisions with the LFP particles, resulting in more effective particle size reduction. Finer particles offer larger surface areas, which can enhance electrode performance by facilitating faster ion and electron transport. The energy input from milling balls influences not only particle size but also the crystallinity and defect structure of LFP.

Utilizing a systematic approach, we conducted a series of experiments involving varying sizes of milling balls and time of milling during the preparation of LFP. $LiFePO_4/C$ was prepared by a mechano-chemical activation, spray-drying, and further annealing process. All the starting materials were put into a ceramic cylindrical container with zirconia balls (ball-to-powder weight ratio of 8:1) and ground in a planetary ball mill for 2–6 h. The mixture was initially spray-dried and then calcined at 750°C. Three ball milling ways were tried, i.e., ball milling with 0.5, 1, and 3 mm zirconia balls. The structures of the samples were characterized by X-ray powder diffraction. The morphologies of the samples were observed by transmission electron microscopy. The particulate morphologies of the synthesized $LiFePO_4/C$ were also examined by a scanning electronic microscope. The tap density was measured on the Quantachrome Autotap device. During the study, it was determined that the optimal size of zirconium balls is 1 mm (tap density is 1.54 g/cm^3). When using balls with a diameter of 0.5 and 3 mm, the tap density of the material decreased. Smaller balls with higher energy impacts can lead to more intense collisions between particles, potentially causing particle agglomeration or sticking. Agglomerated particles might not pack as effectively, resulting in lower tap density (tap density is 1.28 g/cm^3). In the case of balls with a diameter of 3 mm, they are disproportionately large relative to the agglomerates that need to be crushed (tap density is 1.36 g/cm^3).

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Synthesis and characterization of catalysts with the structure of perovskites and Ruddlesden-Popper for the electrochemical oxidation of carbamide

Atoian Edita [1], **Pavel Sinitsyn** [1], **Vitaly Kuznetsov** [2]

[1] Center for Energy Science and Technology, Skolkovo Institute of Science and Technology, Moscow 121205, Russian Federation
[2] Mendeleev University of Chemical Technology of Russia, Moscow 125047, Russian Federation

edita.atoian@skoltech.ru

The purpose of this work was to choose the most efficient method for the synthesis of catalysts with the structure of perovskites and Ruddlesden-Popper from the ones presented to date. The literature review presents the characteristics of the structure, properties, and various methods for the synthesis of perovskites and Ruddlesden-Popper phases.

Target single-phase products, namely $LaNiO_3$, La_2NiO_4, $LaSrNi_{0.5}Co_{0.5}O_4$, $LaSrNiO_4$, $LaSrCo_{0.5}Fe_{0.5}O_4$, were obtained using the ultrasonic spray pyrolysis method, which showed the highest efficiency, exactly with the accuracy of solid-phase synthesis and sol-gel. Quantitative and qualitative analysis of all obtained phases, carried out using X-ray diffraction analysis, namely the method of powder X-ray diffraction.

The structure was refined using the Jana2006 program using the Rietveld and LeBaile methods.

In the section "Chapter 2" all the experimental methods used in this work are discussed in detail.

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Analysis of the effect of cultivation conditions and pretreatment on the nanofibrillar structure of the surface of bacterial cellulose using scanning electron microscopy

Bulkina A.M. [1]

[1] ITMO University, Lomonosova 9, 191002 Saint-Petersburg, Russia

bulkina@scamt-itmo.ru

Bacterial cellulose (BC) is an extracellular polysaccharide synthesized by prokaryotes belonging to different taxa (Acetobacter and Komagataeibacter) at the liquid-air interface [1,2]. Unlike cellulose of plant origin, BC is synthesized by microorganisms of chemical purity, that is, it does not contain impurities such as lignin and hemicelluloses [1]. BC is characterized by a 3D mesh highly crystalline nanofibrillar structure, which provides water absorption capacity of up to 1000% and mechanical strength [3]. However, bacteria synthesize BC inhomogeneously, which affects the surface structure and subsequently complicates the process of its assessment. This study focused on the influence of the cultivation conditions of bacterial producers of BC K. *xylinus* on the structure of synthesized biofilms using scanning electron microscopy (SEM). The influence of the following conditions was evaluated: nutrient medium, temperature, static and dynamic cultivation, and a directed magnetic field. The influence of the process of BC sample preparation (washing and drying) on the quality of the obtained SEM images was also considered.

It was found that the cultivation conditions have a significant effect on the structure of BC, including depending on the presence (upper) or absence (bottom) of surface contact with air. The orientation and compaction of BC fibrils was found perpendicular to the directed magnetic field. In addition, the influence of BC preprocessing for SEM was assessed, which showed that the most optimal for the preservation and visualization of the nanofibrillar structure was the washing of BC from the remains of the nutrient medium and bacteria in 0.1 M NaOH for a day at room temperature, followed by incubation of the biofilm in a 0.5% citric acid solution and washing in distilled water until neutral pH.

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Influence of planar defects on superconducting properties in $NaFe_{1-x}Co_xAs$ single crystal

A. Yu. Degtyarenko[1], I.V. Morozov[2], E. O. Rakhmanov[2], A.V. Sadakov[1], A.I. Shilov[1], S. Yu. Gavrilkin[1], A. Yu. Tsvetkov[1], S. A. Kuzmichev[3,1], T.E. Kuzmicheva[1]

[1] V.L. Ginzburg Centre for High-Temperature Superconductivity and Quantum Materials P.N. Lebedev Physical Institute of the Russian Academy of Sciences, 53, Leninsky Ave., 119991 Moscow, Russia
[2] Department of Chemistry, Moscow State University, 1, Leninskiye Gory 119234 Moscow Russia
[3] Faculty of Physics, Moscow State University, 1, Leninskiye Gory 119234 Moscow Russia

degtyarenkoayu@lebedev.ru

The 111 iron-based superconductors are interesting for its unique properties The compound NaFeAs has long-range antiferromagnetic ordering as well as structural phase transition along with superconductivity [1]. The substitution of Co atoms for Fe atoms in this compound leads to bulk superconductivity, whereby the superconducting transition temperature increases significantly from 10 K to ~22 K. [2, 3].

In this work [4], the microstructure of the $NaFe_{1-x}Co_xAs$ compound by high-resolution transmission electron microscopy (HRTEM) and the superconducting properties by vibrational magnetometry in fields up to 9 Tesla in a wide temperature range from 2 to 16 K were studied. The single crystallinity of $NaFe_{0.955}Co_{0.045}As$ was confirmed by X-ray diffraction. The temperature dependence of the magnetic susceptibility shows sharp superconducting transition with the critical temperature Tc~21 K. It was observed the planar defects along the ab plane by high angle annular dark field (HAADF) STEM images. 2D defects are typical for layered materials [5], and additionally for superconductors they act as pinning centers. The M(H) hysteresis loops obtained over a wide temperature range from 2 to 16 K in fields from 0 to 9 Tesla at H||c show a second magnetization peak. The critical current density calculated from the Bean critical state model [6] is Jc ~ 105A/cm^2. Thus, since the obtained M(H) hysteresis loops are symmetrical, the samples are dominated by bulk pinning.

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Microstructural features of Ni-rich layered oxides with different transition metals distribution through the particles as cathode materials for Li-ion batteries

Dikhtyar Yu.Yu. [1], Savina A.A. [1]

[1] Center for Energy Science and Technology, Skolkovo Institute of Science and Technology, Nobel Str. 3, 121205 Moscow, Russia

yurydikhtyar@gmail.com

Over the last decade, the production of electric-powered transport has increased in an attempt to reduce human impact on the environment. The energy source in electric vehicles is traditionally Li-ion batteries (LIBs) due to their high specific energy density. The positive electrode (cathode) is known to play key role in determining both final cost and performance of LIBs. Currently, layered oxides of Li and transition metals $LiNi_xMn_yCo_z$ (NMCxyz, x+y+z = 1) with high Ni content, so-called Ni-rich NMCs, have become one of the preferred cathode materials for advanced LIBs due to their high reversible electrochemical capacity (up to 220 mAh/g), energy density (up to 800 Wh/kg) and low cost [1]. Improving the performance characteristics by doping the structure with different ions has been widely investigated [2]. Therefore, it is of interest to develop chemical approaches for directed microstructure design.

In this work, the influence of different variants of cation distribution through the spherical-like particles on their microstructural features of Ni-rich layered oxides is investigated. The layered oxide $LiNi_{0.75}Mn_{0.25}O_2$ was chosen as a model system. First, three samples $Ni_{0.75}Mn_{0.25}(OH)_2$ were obtained by co-precipitation technique: the mixed hydroxide with a uniform cation distribution (1), with gradient concentration structure (2), and a core-shell structure (3, core – $Ni(OH)_2$, shell – $Mn(OH)_2$). The precursors were further mixed with Li source and annealed in oxygen flow. The obtained polycrystalline samples were investigated by powder X-ray diffraction (PXRD), scanning and transmission electron microscopy (SEM, TEM). Research results can be used for further improving of LIBs industry in Russian Federation.

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Ni-rich layered oxides with core-shell structure as positive electrodes for next generation Li-ion batteries

Dolzhikova E.A.[1], Sitnikova L.A.[1], Savina A.A.[1], Abakumov A.M.[1]

[1] Skolkovo Institute of Science and Technology, Bolshoy Boulevard 30, bld. 1, 121205, Moscow, Russia

Ekaterina.Dolzhikova@skoltech.ru

Layered lithium and transition metals oxides $LiNi_xMn_yCo_zO_2$ ($x + y + z = 1$) with high nickel content ($x>0.6$) demonstrate high electrochemical capacity (~220-240 mAh/g at 2.7-4.3 V vs. Li/Li^+) and high energy density (800-900 Wh/kg) and are considered to be the most promising candidates as cathode materials for next generation Li-ion batteries (LIBs). However, due to low cycling life and low thermal stability, these materials are limited in practical application in LIBs [1]. One of the promising approaches to solve the mentioned problems is development of core-shell structured NMCs, where Ni-rich NMC as high-capacity sources act as the core, while more stable layered oxides are chosen as the shell [2-3].

In this work, a series of core–shell structured cathode materials $Li[(Ni)_{1-x}(Ni_{0.6}Co_{0.2}Mn_{0.2})x]O_2$ and $Li[(Ni_{0.95}Co_{0.025}Mn_{0.025})_{1-x}(Ni_{0.6}Co_{0.2}Mn_{0.2})x]O_2$ with different thickness ($x = 0.1$, 0.2) of the shell were prepared via co-precipitation synthesis technique. Based on the powder X-ray analysis, all samples are single-phase without foreign impurities. According to SEM and EDX analysis, the prepared materials are near spherical particles with the local compositional change from the particle center to the surface consistent with the designed particle structure. The electrochemical performance of the $Li[(Ni)_{1-x}(Ni_{0.6}Co_{0.2}Mn_{0.2})x]O_2$ and $Li[(Ni_{0.95}Co_{0.025}Mn_{0.025})_{1-x}(Ni_{0.6}Co_{0.2}Mn_{0.2})x]O_2$ ($x = 0, 0.1, 0.2$) was evaluated via prolonged galvanostatic cycling test. Thus, capacity retention increased by 20% for core-shell structured Ni-rich NMCs compared to unmodified samples.

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Tortuosity in sodium-vanadium phosphate cathodes as a performance limiting factor

Dyakonov A.K. [1], Zakharkin M.V. [1], Nikitina V.A. [2, 1]

[1] M. V. Lomonosov Moscow State University, Leninskie gory GSP-1, 11991 Moscow, Russia
[2] Center for Energy Science and Technology, Skolkovo Institute of Science and Technology, Nobel Str. 3, 143026 Moscow, Russia

andrei.diakonov@chemistry.msu.ru

Nowadays metal-ion batteries (MIB) have become a crucial part of energy sources. However, one of the main challenges for battery R&D is to achieve higher power with minimal capacity losses and higher active material loading. With the increase of the current density, kinetic obstacles arise, which hampers battery performance. Many studies treat the rate limitations at the particle level, analyzing the rates of solid-state diffusion, interfacial charge transfer and other microscopic events. However, under certain conditions, such as high current densities or low temperatures, other types of limitations prevail. The electrodes used in metal-ion batteries are porous composites, consisting of active material particles, conductive additive and a binder. For such objects, the major sources of rate limitations are diffusional losses in pores, filled with the electrolyte solution, and ohmic losses, due to low electronic conductivity of the composites [1]. Our study is focused on minimizing kinetic hinderances in MIB cathodes on the electrode level.

To characterize the porous structure quantitatively, the values of porosity and tortuosity are used, which are the fraction of empty space in the composite and the ratio of the real ion path in the electrode to the electrode thickness, respectively. While the porosity could be easily evaluated from the electrode volume and composite material density, tortuosity of a composite electrode is non-isotropic and can hardly be accurately calculated [2]. Here we propose a method for experimental electrode tortuosity evaluation using electrochemical impedance spectroscopy in symmetric two-electrode setup. Sodium-vanadium phosphate ($Na_3V_2(PO_4)_3$) [3] has been chosen as a model material for this study, as it demonstrates high theoretical capacity of 118 mAh/g for two Na^+-ions deintercalation per formula unit and superior capacity retention. To test this method, we prepared electrodes with close porosity values, but different mass loading: 2, 9, 18 mg/cm^2. We concluded that the obtained tortuosity values do not depend on mass loading, which validates our approach.

As a continuation of this study, we attempted to prepare electrode with different architectures containing channel-like pores to minimize the tortuosity values and improve the rate capability [4]. Tortuosity values and high-rate performance were compared between samples with reduced tortuosity and samples with randomly distributed pores to draw conclusions about the effect of electrode architecture on battery performance.

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Template synthesis of hard carbon anode materials for sodium-ion batteries

Fefelov M.A. [1], Lakienko G.P. [1], Bobyleva Z.V. [2], Drozhzhin O.A. [2]

[1] Faculty of Materials Sciences of MSU by Lomonosov M.V., 119991 Moscow, Russia
[2] Department of Chemistry of MSU by Lomonosov M.V., 119991 Moscow, Russia

fefelovm19@gmail.com

Sodium-ion batteries (SIBs) are the most promising post-lithium technology currently under development. They possess several advantages over other post-lithium systems as well as lithium-ion batteries themselves.
For instance, SIBs are more environmentally friendly and less expensive due to the widespread availability of sodium in the Earth's crust. High initial coulombic efficiency (ICE), high specific capacity, and good stability are required for the electrode materials to commercialize this technology. Hard carbon is a non-graphitizable form of carbon that contains curved graphene-like layers in its structure.
The structural disorder of hard carbon enables sodium ions to intercalate into expanded interlayer space of carbon and occupy other positions, such as closed pores. This material is the best candidate for the role of anode material in SIBs due to its high electrochemical capacity compared to graphite, which has limited sodium ion intercalation [1].
Numerous routes for synthesis of hard carbon exist, some

of which aim to increase the specific capacity of hard carbon. Template-based synthesis methods are used to create materials with a high microporosity, where different salts such as magnesium gluconate or citrate can serve as templates. This approach enables the production of materials with very high specific capacities of up to 480 mAh/g [2]. The aim of this work is to carry out template synthesis of hard carbon with high specific capacity using magnesium and calcium salts as template. For the synthesis of hard carbon, evaporation and caramelization of a glucose solution in air followed by high-temperature annealing was employed. After the initial annealing, which took place at temperatures of 600/800 °C in an inert atmosphere, the templates were removed by hydrochloric acid. Following that, the material was subjected to a secondary annealing at temperatures of 1300/1500 °C in an inert atmosphere. The samples were analyzed using low temperature nitrogen adsorption, X-ray diffraction, and scanning electron microscopy techniques. Additionally, electrochemical tests were conducted on the obtained materials in sodium half-cells. The obtained samples exhibited a discharge capacity of 260 mAh/g and an ICE of 59% for the magnesium-based material, and a discharge capacity of 228 mAh/g with an ICE of 58% for the calcium-based material. Based on galvanostatic testing results, hard carbons obtained through annealing at 600°C followed by a secondary annealing at 1300°C demonstrated the highest values of discharge capacity and ICE. It was found that insufficient removal of oxides reduces the discharge capacity of materials. In the future, the work will be aimed at optimizing the removal conditions to improve the discharge capacity.

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Application of Transmission Electron Microscopy in Heterogeneous Catalysis

Gerasimov E.Yu.

[1] Boreskov Institute of Catalysis SB RAS, Lavrentiev Ave. 5
Novosibirsk, Russia, 630090

gerasimov@catalysis.ru

For the development of new functional materials used in modern technologies a detailed knowledge of the structure of these materials is essential.
Understanding structure at the nanoscale, as well as the analysis of various parameters, including the interface, the effect of alloying, defects, etc. largely determines the set of necessary properties and, consequently, the technology of creating the resulting materials.
Nowadays, analytical transmission electron microscopy, as one of the best experimental methods, attracts a lot of attention due to the high spatial resolution (about 0.1 nm) and the large set of related methods. The use of transmission electron microscopes in various fields of science and technology such as materials science, biology, chemistry, geology, etc. determines different approaches to the design of devices and the number of their experimental capabilities. Thus, modern electron microscopes allow experiments to be carried out in a wide temperature range, to study various types of materials (from biological samples to metal alloys and ceramics) and even work in the mode of chemical reactors. To achieve the various parameters required for the study, various accelerating voltages are used and special sample holders are designed.
The set of experimental techniques possessed by the transmission electron microscopy is not limited only to diffraction and direct image observation, but allows you to obtain up-to-date information about the quantitative content of elements (EDX), electronic structure (EELS), the mutual orientation of atoms in the material structure (HAADF – STEM). Using a combination of these techniques allows to obtain information that is often not available for analysis by other chemical and physical methods.
The report will show the scope of transmission electron microscopy in the study of the structure of various catalytic systems. In particular, composite, carbon materials, supported catalysts, etc. will be discussed.

Physico-chemical properties of Langmuir monolayers based on α, ω-hydridoligo-dimethyl-siloxanes

Griscenco P. [1], Raitman O.A. [2]

[1] Skoltech, Bolshoy Boulevard, 30, b.1 Moscow 121205, Russia
[2] MUCTR, Miusskaya square, 9, b. 6 Moscow 125047, Russia

Piotr.Griscenco@skoltech.ru

Siloxanes are a broad class of organosilicon compounds that possess a set of unique properties that make them widely used in various industries and everyday life. For example, the traditional member of this family, polydimethylsiloxane (PDMS), has unique thermal stability, biocompatibility, chemical inertness and excellent insulating properties. PDMS is widely used in defoamers, dielectric and sealant formulations and is also a constituent of cushioning and damping fluids[1]. In recent decades, considerable efforts of scientists have been directed towards the development of durable hydrophobic coatings. Currently, one of the most common ways to obtain superhydrophobic coatings is modification of mechanically rigid matrices with perfluorinated organic compounds. However, such matrices have a thickness of the order of one hundred micrometres or more, which makes it impossible to apply the resulting coatings in nanoengineering and molecular electronics[2]. In addition, industrial companies refuse to use fluorine-containing organic compounds due to their toxicity to humans and nature, as well as the high reactivity of fluorine[3]. A potential alternative to perfluorinated compounds are silicones, which have comparable hydrophobic characteristics, but unlike perfluorinated compounds, their synthesis is faster and is not associated with the above risks. At the same time, one of the promising methods for the formation of functional monomolecular coatings on solid substrates is the Langmuir-Blodgett (LB) technique, which makes it possible to obtain nanoscale films with controlled thickness and a given degree of molecular ordering. One of the advantages of the LB technique over various coating methods is the versatility of the method and the possibility of transferring monolayers to almost any surface[4].

We have for the first time carried out the transfer of monolayers of hydride-terminal ODMCs onto solid substrates and studied their hydrophobic characteristics. We have shown that the use of ODMCs with higher molecular weight allows to obtain thermally stable hydrophobic coatings.

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Single crystal Ni-rich layered cathode materials for LIBs with reduced cation disordering

E. Ivanova [1], A. Pavlova [1], I. Moiseev [1], A. Savina [1], A. Abakumov [1]

[1] Skolkovo University of Science and Technology, 121205 Moscow, Russia

El.Ivanova@skoltech.ru

The electromechanical capacity fade of polycrystalline cathode materials with the general formula $LiNi_xCo_yMn_zO_2$ (x+y+z=1, so-called NMCs) is known to cause by the destruction of secondary agglomerates along the intergranular boundaries of primary particles during lithium (de)intercalation. In contrast, the so-called "single crystal" cathodes are characterized by long cycling life due to the absence of an intergranular

boundary and microcrack growth along those.
It is necessary to note the direct proportional relationship between the nickel content in NMCs and the number of defects that affect the cyclic stability of the material and capacity retention. The standard temperature annealing of single-crystal NMCs is around 900°C. Due to such extremely conditions ultra-high Ni-rich NMCs exhibit a large number of anti-site defects in the layered structure. For such a reason, the aim of this work is to investigate the influence of synthesis temperature on the formation of anti-site disordering for single crystal Ni-rich NMC with ultra-high Ni content ($LiNi_{0.95}Mn_{0.025}Co_{0.025}O_2$, SC-NMC95).
A series of single crystal SC-NMC95 materials were obtained at different temperature (750-900°C). According to powder X-ray diffraction analysis, a highly ordered hexagonal structure with α-$NaFeO_2$ structural type (*R*-3*m* space group) was confirmed for all samples. The unit cell parameters and degree of Li^+/Ni^{2+} disordering, occurred from partial exchange of the Li^+ (r_{IV} = 0.76 Å) and Ni^{2+} (r_{IV} = 0.69 Å) cations between the Li (3*b*) and Ni (3*a*) sites were calculated for all obtained samples via Rietveld refinement. The degree of Li^+/Ni^{2+} disordering is found to reduce with decreasing temperature annealing (from 4% (900°C) to 0.1% (750°C)). However, the particle growth is also reduced and the average size particles does not exceed 3 μm. The results of galvanostatic cycling with potential limitation show that the obtained material with the lowest anti0site disordering demonstrates specific discharge capacity of 218 mAh/g at 0.1C (2.7-4.3 V vs. Li/Li^+).
The research work is supported by Russian Science Foundation (RSF) (Grant # 23-73-30003).

Electrocatalysis of the reaction of oxygen release on materials with a Ruddlesden-Popper structure in alkaline solutions

Ivchenko S. S. [1]; Sinitsyn P. A. [2]; Kuznetsov V. V. [3]

[1] Skoltech, Bolshoy Boulevard, 30, b.1 Moscow 121205, Russia
[2] Skoltech, Bolshoy Boulevard, 30, b.1 Moscow 121205, Russia
[3] MUCTR, Miusskaya square, 9, b. 6 Moscow 125047, Russia

S.Ivchenko@skoltech.ru

The purpose of this work was to study the catalytic activity of Ruddlesden-Popper phases under the conditions of the oxygen release reaction by potentiodynamic and potentiostatic studies in 5 molar alkali. The literature review considers different patterns of dependence of catalytic activity on the structure and morphology of the material, as well as different ways of increasing catalytic activity [1-3]. The materials studied with the Ruddlesden-Popper phase structure were obtained by ultrasonic spray pyrolysis from reagents manufactured by Sigma Aldrich. Electrochemical measurements were carried out in a standard three-electrode Teflon cell (V = 100 ml) using a Metrohm Autolab PGSTAT302N potentiostat equipped with a linear sweep generator module. A rotating disk electrode (RDE [glass-carbon (GC) disk]) with $S_{geom} = 0.07\ cm^2$ was used as the working electrode.

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Fabrication of plasmonic nanoobjects that amplify the electromagnetic field

E. I. Kameneva [1]*, A. A. Lizunova[1], E. M. Filalova[1], A. G. Musaev[1], D. V. Kornyushin[1], D. Malo[1], V. V. Ivanov[1]

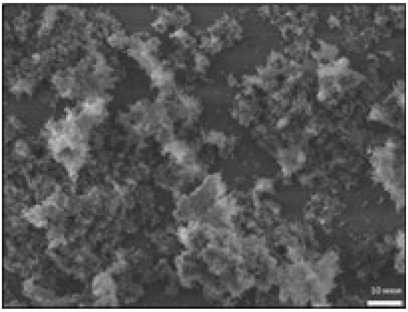
[1] Moscow Institute of Physics and Technology, Dolgoprudny, Russia

* kameneva.ei@phystech.edu

Recently, it has been of great interest to obtain nanoparticles from metals such as Au, Ag, Cu, Al, as well as hybrid nanostructures with different morphologies. Such nanostructures are used in nanoelectronics, nonlinear optics and other fields [1] due to their ability to amplify SERS (surface-enhanced Raman spectroscopy) signals and luminescence [2-3]. Plasmonic metal nanostructures were created by dry aerosol printing. This method [4] has a number of advantages over known methods: electron lithography, vapor deposition [5], photochemical deposition [6]. The most valuable in the application of particles by dry aerosol method is the ability to control the process of synthesis of nanoparticles in real time due to a wide range of parameters of the spark discharge. Aluminum is one of the metals that we used to create plasmonic nanostructures.

To enhance the electromagnetic field in the ultraviolet range, thin-film nanostructures with different morphologies from aluminum nanoparticles were fabricated. The peak of aluminum instinct is in the range of 200-300 nm [7]. The optical density of the obtained aluminum nanostructures was studied using a JASCO V-770 spectrophotometer (Japan) and morphology of the nanostructures surface by scanning electron microscopy (JSM 7001F, JEOL). We have the opportunity to obtain plasmonic nanoobjects with different morphology, thickness, amplifying ability and patterns by changing the printing parameters.

This work was funded by the Russian Science Foundation as part of the investigation into the fabrication technology of plasmon nanostructures by aerosol dry printing (project No. 22-19-00311, https://rscf.ru/project/22-19-00311/).



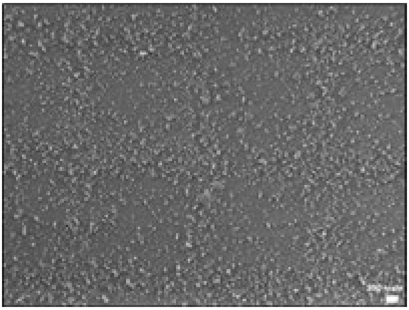


Figure 1. SEM images of nanostructures (pattern – grid).

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The microscopic study of the omniphobic photoresist patterning resolution

Kartsev D.D. [1]

[1] ITMO University, International Institute “Solution Chemistry of Advanced Materials and Technologies” (SCAMT), 9 Lomonosova St., St. Petersburg, 191002, Russia

kartsev@scamt-itmo.ru

Omniphobic surfaces are repellent to both water and low surface tension liquids, demonstrating low contact angle hysteresis and low sliding angles for water and liquids with lower surface tension. Micropatterning of omniphobic properties can provide a wide range of applications, including miniaturized experiments using both aqueous and organic media [1]. Thus, arrays of microdroplets formed on a surface using wettability patterns represent a modern method for the miniaturization of various types of chemical and biological experiments.

Herein, an approach for creating omniphobic micropatterns based on selective photoacid polymerization of octa(3-glycidyloxypropyl) polyhedral oligomeric silsesquioxane modified with mono-aminopropyl-terminated polydimethylsiloxane (GPOSS-PDMS) is presented. Though the utilized approach was already published [2], the micropatterning of GPOSS-PDMS is firstly presented. The aim of the current work is to describe the accuracy of the performed approach with the means of AFM, SEM and EDX approaches.

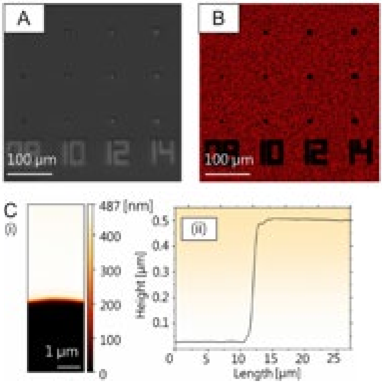

Figure 1. Microscopic characterization of the omniphobic GPOSS-PDMS patterns.

The selective polymerization was achieved with photolithography of the GPOSS-PDMS composition, which was prepared according to the method [2]. For this, the pronounced composition, which acted as a negative photoresist, was spincoated onto silicon wafers. MJB4 mask-aligner was used in exposure process. AFM analyses were performed using an NT-MDT Solver NEXT (NT-MDT, Russia) in the non-contact mode. The images were obtained using cantilever with force constant of 34 N m^{-1} and resonance frequency of 345 kHz.
No organic leftovers from the GPOSS-PDMS composition remained in the omniphilic spots after development, which was confirmed by EDX analysis (Figure 1B) (2.1 ± 1.6 % carbon content inside the developed areas). Almost no microdefects were observed in the profiles (Figure 1C.ii) and AFM topography images (Figure 1C.i) of the omniphilic-omniphobic boundaries. Therfore the smallest lateral dimensions of omniphilic features developed using this method were 8 µm.

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Optimization of the method for obtaining cathode materials based on layered oxides in the form of single-crystal particles for lithium-ion batteries

Yu. A. Klychevskikh [1], E. D. Ivanova [1], A. D. Pavlova [1], I. A. Moiseev [1], A. A. Savina [1], A. M. Abakumov [1]

[1] Skolkovo Institute of Science and Technology, Bolshoy Boulevard 30, bld. 1, 121205 Moscow, Russia

Yuliya.Klychevskikh@skoltech.ru

Ni-rich layered oxides $LiNi_xCo_yMn_zO_2$ ($x \geq 0.6$, $x + y + z = 1$) attract significant attention as cathode materials due to their high specific capacity, high operating voltage and reasonable cost [1]. However, such materials suffer from strong anisotropic lattice distortion during the charge-discharge process which leads to microcracks formation [2]. Obtaining single crystal particles allows to overcome the issue of intergranular cracking providing better performance of the material. Particle size as well as particle morphology affects the performance of the material: smaller particle sizes provide shorter lithium diffusion passage and it has been demonstrated that single-crystal Ni-rich NMC with a particle size of 2-5 μm are sufficient to supress intergranular cracking [3]. To obtain the desired properties and decrease the amount of Li/Ni exchange defects synthesis parameters can be varied.

In the present study the influence of synthesis parameters such as flux composition and flux amount and precursor on the properties of NMC95 ($LiNi_{0.95}Co_{0.025}Mn_{0.025}O_2$, space group *R*-3*m*) material was investigated. Increase in initial concentration of NH_4OH from 1.0 M to 2.0 M during co-precipitation of precursor lead to increase in particle sizes of corresponding NMC95 samples as well as the number of defects (Ni in 3a site goes up from 3.34(7) to 4.78(5) %). The increase in flux amount from 0.4375 mol to 1.75 mol has similar effect on particle size distribution and the number of defects of corresponding samples. The amount of K-source in the flux was varied to demonstrate that with its increase from 10 to 20 % average particle size decreases while the number of defects lowers (from 4.04(7) to 3.34(7) %). Precursor with initial concentration of NH_4OH 1.0 M, 0.875 mol of flux of 80% LiOH, 20% K-salt proved to be the acceptable parameters to obtain NMC95 material at this stage. For the next stage of the research temperature of the first annealing is going to be optimized simultaneously with nflux and electrochemical performance of synthesized materials will be studied.

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Microwave-solvothermal and conventional synthesis of Cu-Zn-Al-Ce-Zr oxides as CO_2-to-methanol hydrogenation catalysts

Korneeva E.Yu. [1], Kustov A.L. [1]

[1] Lomonosov Moscow State University, Leninskie gory GSP-1, 119991 Moscow, Russia

catherina.korneeva@student.msu.ru

The excess of carbon dioxide emissions caused by anthropogenic factors poses a serious danger to the environment: it is associated with the acidification of the oceans and global climate change [1]. Despite this, the current dynamics of greenhouse gas emissions is not improving, which is an urgent task for the capture and disposal of CO_2. One of the ways of carbon dioxide utilization is its catalytic hydrogenation into hydrocarbons of various structures, including methanol, which is a promising product for further synthesis of various organic compounds [2]. One of the most commonly used catalysts for the hydrogenation of carbon dioxide into methanol are Cu/ZnO systems, often with Al_2O_3 in the composition. Among the promoters of such catalysts, oxides CeO_2 and ZrO_2 are used.

The purpose of this work was to obtain highly efficient catalysts for the hydrogenation of CO_2 to methanol using the microwave-solvothermal method. Template synthesis makes it possible to obtain a porous structure of the catalyst, and the use of microwave radiation in the synthesis process makes it possible to accelerate the process of obtaining catalytic materials several times. As part of the work, the following tasks were set, namely: the synthesis of Cu-Zn-Al-Ce-Zr oxide systems with varying molar ratios (x(Cu):x(Zn):x(Me)=4(2):2:1, Me=Al, Ce, Zr, Ce/Zr), synthesis time; investigation of the obtained systems by physicochemical analysis methods; investigation of the activity of the obtained systems in the reaction of hydrogenation of carbon dioxide into methanol.
The synthesis of catalysts was carried out by a modified sol-gel method using P123 as a template. The obtained samples were characterized by XRD, SEM-EDS, IR probe molecules, and TEM methods. The textural characteristics of the samples by adsorption-desorption of N_2 were also investigated. The study of catalytic activity was carried out in a flow-through installation.
X-ray diffraction analysis (XRD) of the obtained oxide systems showed that the size of CuO crystallites, estimated by the coherent scattering region, is 12-15 nm. The particle size, which is in the range of 3-30 nm, was determined using the TEM method.
The obtained samples demonstrate high selectivity for CH_3OH in the CO_2 hydrogenation reaction, and the productivity of the main product exceeds the productivity obtained on industrial catalysts for the production of methanol from synthesis gas and is about 0.5 g(CH_3OH)/(g(cat)*h)). The catalysts CuO-ZnO-Al_2O_3 showed the best activity ($x(Cu):x(Zn):x(Al)_{theor}$=4:2:1) with a productivity above 0.7 g(CH_3OH)/(g(cat)*h)) in the high temperature range (above 250 °C).

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β-amyloids' study using atomic force microscopy

Kuanaeva R. M [1], Vaneev A. N. [1,2], Erofeev A. S. [1,2]

[1] NUST MISIS, Leninsky prospect 6s7, 119049 Moscow, Russia
[2] Lomonosov Moscow State University, Leninskie gory 1s3, 119991 Moscow, Russia

rmkuanaeva@misis.ru

The Alzheimer's disease is associated with the spontaneous aggregation of β-amyloid monomers into insoluble fibrils and plagues that form on the surface of neuronal cells disrupting their functions [1]; therefore, innovative approaches are needed to determine β-amyloid peptide in various forms in biological fluids. Atomic force microscopy (AFM) is widely used to characterize structural and mechanical properties of β-amyloid, with easy sample preparation [2].

Monomers of β-amyloid peptides (25 μM) were incubated for the day, week, and month, after that, 10 μl of 2,5 μM solution was applied to purified mica substrates and adhered for 10 minutes in a closed Petri dish to avoid drying out a drop of solution. After adhesion, the substrate with the sample was dried in an argon stream. To characterize the aggregation stage of β-amyloid peptide, an atomic force microscope NTEGRA II (NT-MDT S.I., Russia) was used, the measurement was carried out by a semi-contact method, the amplitude of the probe swing is 20-30 nm, the scanning size is from 800 nm to 5 microns, 512 dots, the scanning speed is 0.5 Hz.

In the study of β-amyloid peptide using AFM with different incubation periods (day, week, month), protein structures were shown at all stages of aggregation from oligomers into protofibrils and fibrils.

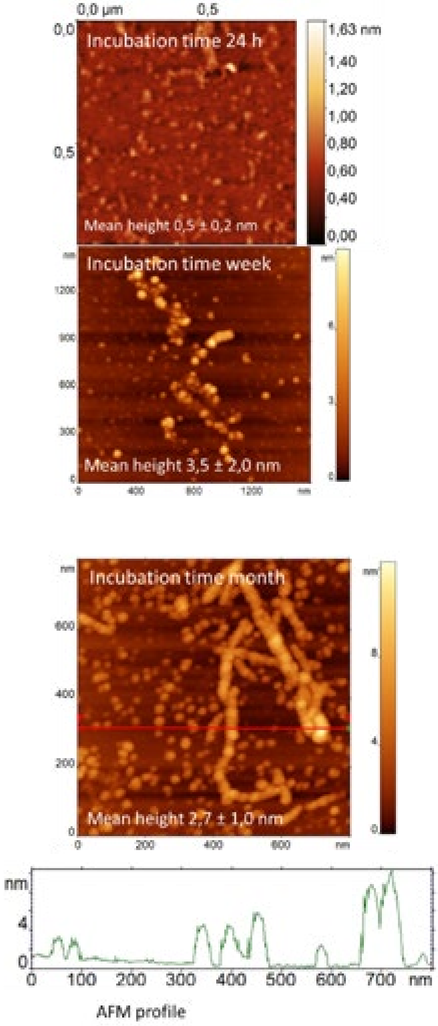

Figure 1. SEM images of aluminum nanostructures (pattern – grid).

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Investigation of MT SOFC microstructure with Scanning Electron Microscopy

E.Y. Lapushkina , V.P. Sivtsev, I.V. Kovalev, M. P. Popov, A.P. Nemudry

Institute of Solid State Chemistry and Mechanochemistry, Kutateladze, 18, Novosibirsk, 630090, Russia

elapushkina@solid.nsc.ru

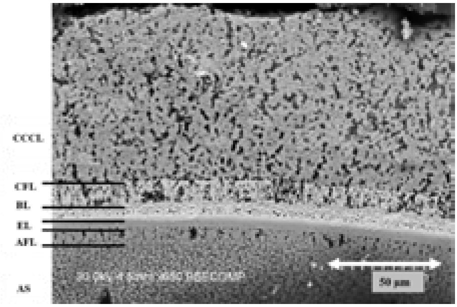
Among all types of solid oxide fuel cells (SOFCs), microtubular (MT) designs have increased resistance to thermal cycling and high-power density (from 300 to 1000 W/kg and above). Optimization of the microstructure of MT SOFC layers plays the key role to achieve high power and strength characteristics, the key role is played.

The aim of the work is to optimize the microstructure of the MT SOFC, including the manufacture of anode support (AS) for a single elements of high-temperature fuel cells, as well as the development of a technique for applying coatings of the anode functional layer (AFL), the electrolytic layer (EL), the buffer layer (BL), the cathode functional layer (CFL) and cathode current-collecting layer (CCCL).

The microstructure of MT SOFC layers is shown in Figure 1. Reducing the number of stages of high-temperature treatment while maintaining the functional characteristics of MT SOFC was achieved by co-firing of APL and EL. APL with a thickness of 7 μm has a high porosity of 26%, which helps to optimize shrinkage during sintering of a highly porous anode support and a dense electrolyte. EL has the required properties – gas tightness (only 3% of closed porosity) and a thickness of 6 μm. The electrolyte and cathode are separated by a buffer layer 7 μm thick and 15% porosity to prevent a chemical reaction between them.

It is important to obtain high porosity and maximum thickness for CFL and CCCL. In this work, the CFL shows a thickness of 12 μm and a porosity of 38%, the CCCL reaches 82 μm and has 37% of open porosity.

In this work, high adhesion between layers, certain porosity and mechanical properties were achieved due to the composition of pastes and the sintering regime optimization at each stage of applying the layers.



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Novel quaternary phosphide platinides based on $AuCu_3$ type intermetallic fragments: synthesis, crystal, and electronic structure

A.Yu. Makhaneva [1], E.Yu. Zakharova [1], S.N. Nesterenko [1], S.M. Kazakov [1], K.A. Lyssenko [1], N.N. Efimov [2], A.N. Kuznetsov [1]

[1] Department of Chemistry, Lomonosov Moscow State University, Leninskie Gory 1-3, 119991, Moscow, Russia
[2] N.S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences,
Leninsky prosp. 31, GSP-1, 119991, Moscow, Russia

nastya.makhaneva@mail.ru

The $AuCu_3$ structure type is among the five most common structural motifs for binary intermetallic compounds. It is based on centered cuboctahedra $\{AuCu_{12}\}$, connected to each other via common faces. Such fragments, or their close variations, act as building blocks in a large number of ordered ternary and more complex intermetallic compounds and their derivatives, and the blocks of the $AuCu_3$ type can be combined with binary and ternary blocks with completely different structure types. Up to date, only two quaternary compounds containing fragment of $AuCu_3$ type based on one of group 10 metals have been structurally characterized: $Eu_2Pt_7AlP_{2.95}$ and its analogue containing, $Eu_2Pt_{7.3}Mg_{0.7}P_{3.3}$ [1]. The authors of Ref.1 also mention similar compounds in several other systems, however, their composition and crystal structures have not been reliably established ever since.

In this work, we have conducted the search and synthesized a number of new compounds isostructural to the complex phosphide platinide $Eu_2Pt_7AlP_{2.95}$ in the Eu-Pt-X-P systems (X = Ti, Cr, Fe, Ni, Zn). In all investigated systems, the crystals of quaternary pnictides were grown by high-temperature ampoule technique from the elements using lead as a flux at 1050°C. The crystals were separated from the flux by centrifugation at 550°C.

In the Eu-Pt-Cr-P system we have obtained needle-shaped crystals, as opposed to all other systems where they were plate-like. The composition of the crystals was determined using the energy dispersive X-ray spectroscopy (EDX). The EDX data confirm the formation of quaternary phases in all investigated samples. The X-ray diffraction analysis on single crystals obtained (Bruker d8 quest diffractometer, MoKα radiation) shows that all new quaternary pnictides crystallize in the tetragonal space group I4/mmm with Z = 2 and belong to the $Eu_2Pt_7AlP_{2.95}$ structure type.

A new quaternary phosphide platinide $Eu_2Pt_7MnP_{4-x}$ was also obtained by direct synthesis from the elements. Its crystal structure was established by powder diffraction data using the full profile Rietveld method. Magnetic measurements show that the $Eu_2Pt_7MnP_{4-x}$ compound is a ferromagnet with a TC ≈ 140 K.

Quantum chemical calculations of the band structure of periodic crystals have been performed using density functional theory (DFT) and pseudopotentials (PAW). The band structure of ternary and quaternary phases is shown to be close to that of their binary prototypes. Based on the analysis of the electron localization function (ELF) the features of chemical bonding in intermetallic compounds and more complex structures based on them have been revealed.

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$HTiNbO_5$ as anode material for LIB's: synthesis and mechanism of Li^+ electrochemical intercalation

Marenko A.P. [1], Alekseeva A.M. [1], Drozhzhin O.A. [1], Antipov E.V. [1,2]

[1] Lomonosov Moscow State University, Leninskie gory GSP-1, 119991 Moscow, Russia
[2] Skolkovo Institute of Science and Technology, Bolshoy Boulevard 30, bld. 1, 121205 Moscow, Russia

marenko.andrey@mail.ru

Mixed oxides of titanium and niobium (TNO) are considered as safe anode materials for lithium-ion batteries (LIB's) with long cycling life. Such benefits are associated by both structural stability and relatively high working potentials of Ti(IV)/Ti(III) and Nb(V)/Nb(IV) redox couples (1.3 – 1.6 V vs. Li/Li^+) preventing SEI formation [1]. An additional attention has been attracted to $HTiNbO_5$ as the unique proton-containing anode material providing reversible capacity of ~120 mAh • g^{-1} after 50 cycles [2]. However, no detailed studying of Li^+ (de)intercalation in $HTiNbO_5$ can be found up to date. This work is devoted to synthesis and investigation of HTiNbO5 as an anode material for LIB's.

In $HTiNbO_5$ structure [3] (sp. gr. *Pnma*, *Z* = 4, a = 6.531(1) Å, *b* = 3.7756(5) Å, *c* = 16.733(6) Å, V = 412.6(2) Å3) [$(Ti,Nb)O_6$] octahedra are sharing edges forming zig-zag ribbons (M2O6)∞ (M = Ti, Nb) connected in layers by common vertices. The stability of the described lamellar structure is ensured by the presence of strong O–H-O bonds between adjacent layers.

The single phase sample of $HTiNbO_5$ was obtained using preliminary synthesized sample of $KTiNbO_5$ via ion exchange process in 1M aqueous solution of HNO_3. Applying scanning electron microscopy average particle size of 10 – 20 μm was defined. The electrochemical lithium (de)intercalation in $HTiNbO_5$ was investigated by a galvanostatic charge-discharge at 12 mA • g^{-1} rate using two-electrode cells assembled in argon-filled glove-box with 1M solution $LiPF_6$ in EC/DEC as electrolyte and a lithium metal anode. Phase and structural transformations upon (de)intercalation of Li^+ were studied by operando and ex situ X-ray powder diffraction (PXRD).

Within the potential range of 1 – 3 V vs. Li/Li+ the material exhibited stable cycling with one plateau at ~2 V. At the same time, from the first to the second cycle, the increase in the capacity was observed from 150 mAh • g^{-1} to 170 mAh • g^{-1}. From the second cycle, the reversible capacity exceeded 170 mAh • g−1 (after 10 cycles) which was the best achieved value for this material and corresponded to the reversible intercalation of 1.4 Li^+ per f.u. PXRD investigation revealed the irreversible two-phase transition during the first cycle. As a result, a new phase isostructural to $LiTiNbO_5$ [4] was formed. From the second cycle (de)lihitation proceeded via a solid solution mechanism with volume change smaller than ~6%.

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Ball-milling as a Tool For Grain Boundaries Engineering in Garnet-Type $Li_{6.4}Ga_{0.2}La_3Zr_2O_{12}$ Solid Electrolyte

Markopolskii R. [1], Timusheva N. [1], Morozov A. [1], Savina A. [1], Abakumov A. [1]

[1] Skolkovo Institute of Science and Technology, Bolshoy boulevard 30, bld.1, 121205 Moscow, Russia

Roman.Markopolskii@skoltech.ru

All solid-state batteries (ASSBs) based on ceramic solid electrolytes are deemed to be a promising alternatives to the conventional liquid organic electrolyte due to potentially high specific gravimetric and volumetric energy density and higher safety [1]. One of the main features of ASSBs is the ability to accommodate Li-metal as an anode which results in a boost of specific energy density. However, one of the problems limiting the development of ASSB is a Li dendrite formation and growth upon cycling that inevitably causes short circuit. Solid-state electrolytes are usually polycrystalline ceramic materials which contain numerous grain boundaries. It is known that Li dendrite propagation takes place along the grain boundaries, hindering electrochemical behavior of solid electrolyte [2]. Therefore, it is important to establish the correlation between the microstructural features of solid-state electrolytes and their electrochemical performance which will contribute to the development of the all-solid-state battery with high energy density and extended cycle life.

That is why this work was focused on studying the influence of synthesis parameters on the microstructural organization of cubic garnet-type $Li_{6.4}Ga_{0.2}La_3Zr_2O_{12}$ (Ga-LLZO) solid electrolyte. Ga-LLZO was chosen among different types of solid-state electrolytes because of high Li-ion conductivity (~10^{-3} – 10^{-4} S/cm at 25 °C), wide electrochemical stability window (0.05–5 V vs. Li/Li^+) and chemical stability against metallic Li [3].

We obtained single-phase Ga-LLZO electrolyte pellets with high relative density of > 90% by conventional solid-state synthesis with the implementation of ball-milling technique and isostatic pressing.

The investigation was focused on different parameters of mechanoactivation and grinding step through ball-milling (e.g. solvent media, grinding duration, Ga-LLZO powder to grinding balls mass ratio) and their impact on the microstructural organization of the solid electrolyte. The wide range of variable parameters of the ball-milling step provided an understanding how grinding conditions affect Ga-LLZO solid-state electrolyte grain structure. Further work will be dedicated to the investigation of the correlation between solid-state electrolyte microstructure and electrochemical properties.

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Ni-rich NMC composite cathode materials containing Li_2SO_{4}-Li_3PO_4 solid electrolyte for Li-ion batteries

Mikheeva M. [1], Orlova E. [1]

[1] Skolkovo Institute of Science and Technology, Bolshoy boulevard 30, bld.1, 121205 Moscow, Russia

Maria.Mikheeva@skoltech.ru

Development of high-energy-density cathode materials for Li-ion batteries is a highly relevant field of study as a world moves towards more environmentally sustainable energy sources. Ni-rich NMC811 composite layered oxides are one of the most promising cathode materials with their high practical capacity of over 200 mAh/g and high energy density larger than 800 Wh/kg. However, Ni-rich NMCs have several drawbacks such as significant capacity drop over prolonged cycling, that prevents them from widespread application. There are several strategies that are used to enhance the performance of Ni-rich NMC cathode materials, one of them – grain boundaries engineering with a Li-conductive solid electrolytes. It allows to improve mechanical properties of cathode materials and enhance Li-ion transportation between particles in agglomerate. Thus, the present work aims at obtaining composite cathode materials based on the Ni-rich NMC ($LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$), modified via Li_2SO_4-Li_3PO_4 solid electrolyte system, with enhanced electrochemical properties.

Modified cathode materials based on $LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$ (NMC811) were synthesized via co-precipitation method with $(NH_4)_2HPO_4$ as a phosphorus source. Five samples were obtained with various concentrations of added $(NH_4)_2HPO_4$. According to XRD analysis, all synthesized materials possess well-crystalline layered structure (s.g. *R*-3*m*) with a minor presence of additional phase isostructural to γ-Li_3PO_4. Peaks of this additional phase were shifted towards the smaller angles which suggests formation of a Li_2SO_{4}-Li_3PO_4 solid solution. SAED pattern, acquired from the additional phase, also corresponds to γ-Li_3PO_4-like phase. Results of HAADF-STEM and EDX-STEM and EELS elemental mapping showed that sulfur and phosphorus are simultaneously segregated on grain boundaries and intergranular contacts, which speaks in favor of solid solution formation instead of two separate phases. Effect of this modification on morphology and electrochemical performance was also investigated. BET analysis showed that sample, containing the largest amount of solid solution (2.18 mol. %) has the smallest surface area of 1.15 m^2/g, while primary particles size remains the same of approximately 220-230 nm, indicating that solid electrolyte binder "closes" gaps between primary particles, preventing penetration of electrolyte into agglomerates. Electrochemical impedance spectra, which contain additional semi-circle, attributed to the resistance of solid electrolyte on grain boundaries, demonstrate decrease in charge transfer resistance with rise of solid electrolyte binder content.
Due to the prolonged galvanostatic charge/discharge cycling in the 2.7-4.3 V vs. Li/Li^+ potential range at different current densities from 0.1C to 1C (1C=200 mAh), it was established that composite cathode materials based on the NMC811 and $Li_{2+x}S_{1-x}P_xO_4$ possess slightly increased rate capability, compared to the one, modified by Li_2SO_4 [1], and significantly enhanced stability as the capacity retention over 300 cycles at 1C elevated from 68% to 81%.

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Hard carbon-based anode materials for anode-less sodium-ion batteries

Denis Muravev [1], researcher Dr. Zoya Bobyleva [2], leading researcher Dr. Oleg Drozhzhin [2], head of the laboratory Prof. Dr. Evgeny Antipov [2]

[1] Lomonosov Moscow State University, Faculty of Materials Science, Moscow, Russia
[2] Lomonosov Moscow State University, Faculty of Chemistry, Moscow, Russia

denis2mur@gmail.com

Sodium-ion batteries (SIBs) are being actively developed today. Such batteries can become a promising alternative for widely used lithium-ion batteries (LIBs) due to lower cost and wide sodium abundance in nature. Graphite is used as an anode material for LIBs, however its use for SIBs is limited, since sodium ions intercalation into graphite structure is thermodynamically unstable, which leads to low specific capacity values. Graphite can be replaced with hard or non-graphitized carbon. Hard carbon is a disorder form of carbon material, its structure consists of curved graphene-like layers, at the curvatures of which closed micropores are located. Such a material is characterized by high specific capacity (above 250 mAh/g), high coulombic efficiency, simple synthesis, and possibility of a large number of precursors to be used [1]. However, sodium dendritic formation on anode’s surface remains a significant problem of using hard carbon. Dendritic formation leads to short circuit and cell death, possess a serious threat to the safety of SIBs. Electrolyte composition, hard carbon morphology, as well as the type of separators used affect the solid electrolyte interface (SEI) stability, dendritic formation and sodium

deposition [2]. Optimization of these parameters can prevent dendritic grows and makes deposition uniform and reversible, which on the other hand becomes a key to anode-less systems with higher specific capacity values [3].
In this work, we study the sodium deposition on different hard carbon anode materials using different electrolytes and separators, varying the galvanostatic cycling parameters. Electrochemical properties were revealed by galvanostatic charge-discharge cycling, as well as impedance spectroscopy for interface characterization. The morphology of the interface formed on the electrode was studied by scanning electron microscopy (SEM). Thermal effects of decomposition reactions of anode materials were measured by differential scanning calorimetry (DSC). It has been demonstrated that fluoroethylene carbonate addition to the electrolyte (1 M $NaPF_6$ EC:DEC 1:1) promotes the reversible sodium deposition/dissolution on hard carbon and reduces irreversible sodium dendritic grows. Also, composite Ag-coated hard carbon electrodes were developed, and Ag/C composites showed better electrochemical cyclability presumably due to homogenous sodium deposition. The best electrochemical properties were achieved on samples with spherical carbon particles about 100 nm size. The highest discharge capacity reached at 550 mAh/g against 300 mAh/g in the system without deposition, and the coulombic efficiency of the first cycle was at 85%.

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Application of deep machine learning for microscopy image analysis: services for automatic search, identification and analysis of objects

A.V. Nartova [1,2], A.V. Matveev [2], M.Yu. Mashukov [3],
N.N. Sankova [1,2], V.Y. Kudinov [2], A.G. Okunev [2]

[1] Boreskov Institute of Catalysis SB RAS, Lavrentiev Ave.-5, Novosibirsk, Russia
[2] Novosibirsk State University, Pirogova St-1, Novosibirsk, Russia
[3] Ershov Institute of Informatics Systems SB RAS, Lavrentiev Ave.-6, Novosibirsk, Russia

nartova@catalysis.ru

Independently on the type of microscopy, the search and size analysis of objects on images is the common task that takes a lot of time for researchers. Therefore, the development of the automatic ways of image analysis is extremely important for practical applications. Deep machine learning is a promising approach for resolving this problem.

In the present work deep machine learning or artificial intelligence is used for automatic search and analysis of objects on images [1-3]. Three services were developed: web-service ParticlesNN (http://particlesnn.nsu.ru) and cloud services DLgram and No Code ML, which use Telegram messenger as an interface. For user's convenience, all developed services are consolidated in the iOk platform (http://iok.nsu.ru/). Platform allows working with any types of images (electron, probe, optical microscopy, photography) of any quality without preprocessing. The most important advantage of DLgram and No Code ML is that the users can train the neural network by itself on their own images that makes services universal. The results of image recognition – objects, its areas, sizes (effective diameter) and position on image (coordinates of centers) – are aggregated in a table that is easy-to-use for statistical analysis. If more than one type of objects were labeled at stage of neural-network training the type will be also recognized. Services were made primarily for the work with scanning probe microscopy [1] and electron microscopy [2] images, but practical check shows their applicability for any images of any quality [3]. All services are accompanied with detailed user instructions for better convenience.

The advantages of using deep learning methods for automatic particle recognition: 1) Analysis is faster (compared to manual analysis) saving a lot of time of researcher; 2) Objectivity of measurements (independent of user personality and experience); 3) The neural network takes into account specific features such as a non-uniform background due to particle projection overlapping or support thickening, etc. [1-3]. The result of recognition mainly depends on the training of neural-network. Thus, the proposed approach allows to improve the quality of recognition over time by optimization of training or / and accumulating labelled data.

Presented services are in free access, no coding skills are required. The iOk Platform is a user-friendly tool for the work with any type of images for automatic search of the objects and determination of their parameters.

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Optical and Magnetic Properties of Hybrid Nanomaterials based on $Na_2Ti_3O_7$ and α-Fe_2O_3

Neumoin A.I., Opra D.P., Tkachenko I.A., Sinebryukhov S.L., Ustinov A. Yu., Mayorov Vi. Yu., Gnedenkov S.V.

Institute of Chemistry FEB RAS, 159 Pr. 100-letiya
Vladivostoka, 690022 Vladivostok, Russia

anton_neumoin@ich.dvo.ru

Currently, researches aimed at preparing and studying the properties of novel nanostructured materials based on titanium oxides and sodium titanates are carrying out intensively. This is due to their use as the main components for so-called "smart materials", mechanical and physico-chemical properties of which can be controlled using external influences (e.g. light flux, electric or magnetic field). In addition, as thin films these materials are intensively studied for so-called diluted magnetic semiconductors due to wide application in microelectronic devices based on the electron spin effect (spintronics). In the form of nanotubes, such materials find wide practical applications, including the conversion of solar radiation, photoelectrochemical water splitting, air and water purification, medical applications, as well as the manufacture of structural parts for supercapacitors and gas sensors. Among other things, nanotubular $Na_2Ti_3O_7$ is also promising anode material for sodium-ion batteries. Despite the fact that recent advances have been reported in the synthesis of nanotubes suitable for practical use, there remains a need for simple and easily scalable methods for preparing such materials. In addition, there are not so many works in which the magnetic characteristics of modified $Na_2Ti_3O_7$ nanotubes would be consecrated. In this regard, this work was aimed at developing a method to fabricate hybrid nanotubular structure based on $Na_2Ti_3O_7$ and α-Fe_2O_3 and study its optical and magnetic characteristics. The formation of hybrid nanomaterial was carried out under hydrothermal conditions. The prepared nanotubes were multi-walled with the outer and inner diameter are 7–10 and 3.5–4 nm, respectively. The hybrid has well-defined mesopore structure with a specific surface area of about 200 m^2/g and pore volume of around

0.5 cm^3/g. The hybrid possesses improved optical activity in the visible and near infrared ranges of the electromagnetic spectrum (hyperchromic effect) as well as narrowed band gap of 2.9 eV due to the fabrication of heterojunctions between the $Na_2Ti_3O_7$ and α-Fe_2O_3 coexisted in nanotubes. The studied nanocomposite material has exchange anisotropy and superparamagnetic properties.

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Structural Features and Regularities of Thermolysis of Compounds in the U(VI)-Hydrazine System

Iurii Nevolin [1,2], Anna Krot [1], Evgeny Gerber [1]

[1] A.N. Frumkin Institute of Physical Chemistry and Electrochemistry RAS, 31/4, Leninsky pr., Moscow, 119071, Russia
[2] Lomonosov Moscow State University, Department of Chemistry, 119991 Moscow, Russia

somonka1@gmail.com

Due to their high reduction potential, hydrazine and its derivatives can be promising reagents in low-temperature processes for the synthesis of actinide dioxides and in denitration processes (removal of nitrate ions) during the processing of radioactive waste [1,2]. In the course of the work, nanosized (10-90 nm) precipitation products of uranyl nitrate with hydrazine with the general formula $xUO_3 \bullet yN_2H_4 \bullet zH_2O$ were synthesized and studied using various laboratory and synchrotron methods, which provide an opportunity for a comprehensive and consistent study of the structure of precipitation products and redox processes occurring with them when heated. According to SEM the reaction product is an aggregate of particles with an average size of 250 nm. At the same time, the size distribution of precipitate particles does not allow us to make an unambiguous conclusion about the mechanism of their growth. The structure motif of $xUO_3 \bullet yN_2H_4 \bullet zH_2O$ – uranyl layers with water and hydrazine molecules in the interlayer space — was determined from powder

X-ray diffraction, photoluminescence, and Raman spectroscopy data. According to these data, the precipitation product contains crystalline phases with a structure similar to ammonium polyuranates with a somewhat shorter U=O bond length in the uranyl cation, ~1.78 Å. An analysis of the extended x-ray absorption fine structure (EXAFS) region confirmed the similarity of the structure with the layered structure of the schoepite mineral. According to IR spectroscopy, it was determined that the predominant form of hydrazine in $xUO_3 \bullet yN_2H_4 \bullet zH_2O$ is the form of the neutral N_2H_4 molecule.

To study the redox processes and structural changes during the thermal transformations of $xUO_3 \bullet yN_2H_4 \bullet zH_2O$, thermal analysis and methods with in situ heating were used: powder X-ray diffraction and X-ray absorption spectroscopy at the L_3 edge of uranium. *In situ* measurements of powder X-ray diffraction showed significant amorphization of $xUO_3 \bullet yN_2H_4 \bullet zH_2O$ already upon heating to 90 °C. A further increase in temperature enhances this effect, and the interlayer distance decreases. At 250 °C, the layered structure is finally destroyed and an X-ray amorphous phase is formed. Further heating leads only to crystallization of the reduced U_3O_8 phase. X-ray diffraction data on uranium reduction are confirmed by X-ray absorption spectroscopy.

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Atomic layer deposition of Al-La-O films for solid-state batteries

Olkhovskii Denis Aleksandrovich [1], Maximov M. Yu. [1]

[1] Peter the Great St.Petersburg Polytechnic University, Polytechnicheskaya St. 29, 195251 St.Petersburg, Russia

Odl-ne@yandex.ru

Solid-state batteries (SSB) in perspective are the next generation of lithium-ion batteries, using solid electrolyte (SE) allows applying metallic lithium as an anode (which significantly increases the specific capacity) and increases fire and explosion safety [1]. Presented advantages allow to expand the lithium energy application, e.g., in the field of electric vehicles. In our view, the major problem of SE widespread introduction is the creation of a material that has good lithium-ion conductivity, but at the same time stable at the line with metal lithium. Known methods of solid electrolyte preparation (solid-state synthesis, melt quenching, sol-gel, coprecipitation, etc. [2]) are unable to precisely control the thickness of the solid electrolyte, which also affects the conductivity of the material. We propose to use the atomic layer deposition (ALD) method, aimed at thin films obtaining. Due to cyclic self-regulating reactions, the method allows to precisely control the thickness of applied coating. The Al-La-O system was chosen for the SE realization, we suppose La_2O_3 will exhibit electrochemical inertness to metallic lithium in the solid-state battery potential window, like Ta_2O_5 [3]. The creation of a multilayer system by ALD will be performed by supercycle realization, when oxides of different metals are alternately deposited on the substrate. Based on available literature, the most popular reagents for Al_2O_3 synthesis are the $Al(CH_3)_3$ (TMA) and water [4], for La_2O_3 are $La(^iPrCp)_3$, $La(thd)_3$ and $La[N(SiMe_3)_2]_3$ as the lanthanum-containing reagent, and ozone or water as the oxygen-containing reagent [5,6,7]. TMA and oxygen-containing reagents are not heated, the temperature of lanthanum reagent ranges from 110 to 180 °C. In the Al_2O_3 synthesis, we suppose to start from the pulse/purge times of TMA and water 0.1/4 s, in the synthesis of La_2O_3 the initial pulse/purge times of lanthanum reagent is 0.5/6 s and water is 0.5/8 s. Combining the known synthesis windows for Al_2O_3 and La_2O_3 we obtain a range of synthesis temperatures from 200 to 250 °C.

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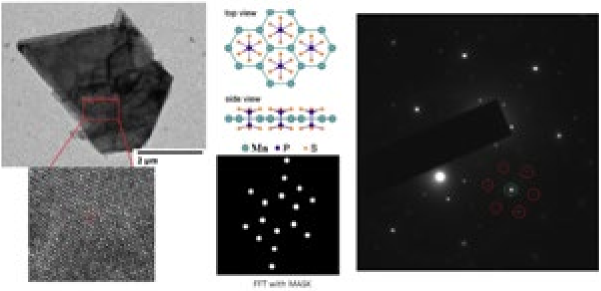
TEM study of the atomic structure of 2D Van der Waals $MnPS_3$ crystals

I.V. Pankov [1], A.A. Tsaturyan [2]

[1] Institute of Physical and Organic Chemistry, Southern Federal University, Stachki Av. 194/2, 344090 Rostov-on-Don, Russia
[2] Univ Lyon, UJM-Saint-Etienne, CNRS, IOGS, Laboratoire Hubert Curien UMR5516, F-42023 St-Etienne, France

ipankov@sfedu.ru

2D materials are at the forefront of modern research areas such as solid state physics and materials science. After the discovery of the unique electronic properties of graphene, a significant amount of experimental and theoretical data obtained has led to a deep understanding of the structural and electronic properties of these materials, as well as various systems based on them. This work presents the results of studying layered $MnPS_3$ crystals by scanning electron microscopy (SEM), high-resolution transmission electron microscopy (HRTEM), selected area electron diffraction (SAED), and energy dispersive X-ray spectroscopy (EDX). The crystals were grown by chemical transport reaction (CVT), and 75 nm thick lamellas were prepared using the focused ion beam (FIB) method for cross-sectional TEM imaging. The obtained data confirmed the quantitative and qualitative composition of the $MnPS_3$ crystals, using HRTEM it become possible to obtain atomic resolution images of the crystal in two orientations (top view and side view), and using the analysis of the SAED results, we obtained interatomic distances and compared those results with DFT simulation data.



This work is a systematic study of various data, which allows us to understand the electronic structure of Van der Waals layered crystals, which is of paramount importance for further research, providing a solid foundation in understanding the transport, optical and catalytic properties of such systems.

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Pseudo five-fold symmetry of boron carbide microcrystals

I.S. Pavlov [1], A.L. Vasiliev [1,2]

[1] Federal Scientific Research Centre "Crystallography and Photonics" of Russian Academy of Sciences, Leninsky pr. 59, 119333 Moscow, Russia
[2] Moscow Institute of Physics and Technology (State University), MIPT, 9 Institutskiy per., Dolgoprudny, 141701 Moscow Region, Russia

ispav88@gmail.com

Cyclic multiple twinning of cubic nanocrystals is a well-studied phenomenon [1]. The tendency to decrease their Gibbs free energy by the reduction of surface area leads to the twinning parallel to { 111 } planes, which results in formation of particles with pseudo five-fold symmetry (icosahedron or decahedron) [2]. Increasing of volume energy impact as the particles grow up contributes to the disappearance of the pseudo-fivefold symmetry of such crystals.

In our research, we studied a boron carbide powder synthetized from M-carboran at a pressure of 7 GPa and a temperature 1200 K. For the first time, the particles of boron carbide exhibited the rhombic hexecontahedron shape with a size of 5-15 μm were observed (fig. 1) [3]. Electron diffraction and high-resolution transmission electron microscopy analysis demonstrated that these crystals have rhombohedral symmetry ($R\bar{3}m$) and are formed by cyclic multiple twinning with close to fractal growing mechanism.

An estimate of the free energy of these particles showed that the decrease of energy by diminishing of the surface area could not be the reason of their twinning. High pressure and temperature were proposed as reasons of multiple twinning of particles, which is cyclic to minimize resulting energy.

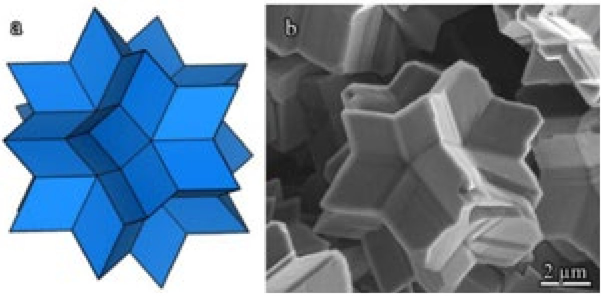

Fig. 1. Rhombic hexecontahedron (a) and scanning electron microscopy image of a particle of boron carbide with the same shape (b).

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High entropy thin film alloy cocrfenitix for electroresistive elements in microelectronics

M.V. Poliakov [1,2], A.S. Rogachev [2], D.Yu. Kovalev [2], S.G. Vadchenko [2], D.O. Moskovskikh [3], Ph.V. Kiryukhantsev-Korneev [3], L.S. Volkova [1], I.A. Mikhaylov [1], A.P. Orlov [1]

[1] Institute of Nanotechnology of Microelectronics of the Russian Academy of Sciences, Moscow, Russia
[2] Merzhanov Institute of Structural Macrokinetics and Materials Science, Russian Academy of Sciences (ISMAN), Chernogolovka, Russia
[3] National University of Science and Technology MISiS, Moscow, Russia

polyakov.m@inme-ras.ru

The main requirements for the resistive elements of microcircuits and other microelectronic devices include high accuracy of the electrical resistance value, which must depend in a controlled way on temperature [1] For pure metals, the temperature coefficient of electrical resistance (TCR) is positive and has a value about 4000 • ppm/°C. The search for alloys and compounds with a lower value of TCR is actively conducted.

In recent years, the attention of researchers has attracted the high-entropy alloys [2], which are solid solutions of five or more metals taken in equal or comparable concentrations. The combination of atoms of dissimilar metals with different radii into a single crystal lattice (FCC or BCC) leads to strong distortions of the crystal structure and, as a result, to a relatively high electrical resistance and low TCR. The beginning of the rapid development of research in the field of thin-film high-entropy alloys was reflected in review [3].

Using the method of magnetron sputtering from a multicomponent target manufactured by hot pressing of a powder mixture, thin films of a high-entropy CoCrFeNiTix alloy on silicon substrates were first obtained. The microstructure and phase composition of these films have been studied. Resistive thin-film elements are made and their electrical resistance is measured at different temperatureshe temperature coefficient of the resistivity (TCR) depends on temperature according to the simple linear law in a range from −60 °C up to 130 °C, changing its value from −78 ppm/°C at low temperatures to −6.6 ppm/°C at 130 °C. Such characteristics show the possibility of using this high-entropy alloy for resistive elements in contemporary and future microelectronic devices. The work was supported by a grant from the Russian Science Foundation project no. 20-13-00277 P.

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Correlation between micro- and macro characteristics of bacterial cellulose using scanning electron microscopy

Prilepskii A.Y.[1]

[1] ITMO University, Lomonosova 9, 191002 Saint-Petersburg, Russia

prilepskii@gmail.com

Bacterial cellulose (BC) is a type of cellulose synthesized as an extracellular matrix by several bacterial strains. It has a combination of unique properties including mechanical strength, chemical purity, and high adsorption capacity [1]. BC has been a subject of study for many years. However, it has not yet been widely applied in industry, mainly because of the high cost of production and insufficient control over its characteristics [2].

The main macroparameters of interest for biomedical applications includes Young's modulus (YM), water holding capacity (WHC), and water absorption capacity (WAC). The Young's modulus of BC lies in the typical range of 15–35 GPa; however, it can reach 130 GPa. The WHC reaches 1000%, whereas the WAC varies from 6% to 500% [3]. Such a wide range of parameters significantly complicates the selection of specific BC-producing strains and samples for use in specific areas.

Our study aimed to simplify the screening procedure for cellulose macroparameters. Using scanning electron microscopy, we plan to establish the dependence of the BC macroparameters on the microparameters. BC has a unique nanofibrillar structure, which determines its macroparameters. The microstructure depends on many other parameters such as cultivation conditions, temperature, composition of the culture medium, and methods of washing and drying of BC. Among the microparameters, we measured the average size and diameter of the fibrils, the size of the pores, and their number. In the future, we plan to use image-processing methods to quickly evaluate the macroparameters of a specific BC sample without the need to perform time-consuming experiments for YM and WHC measurements.

The work was supported by the national project "Science and Universities", project No. FSER-2022-0008.

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Morphology control investigation of single-crystal Ni-rich NMC obtained via flux technique

M.Z. Ratkovich, A.D. Pavlova, I.A. Moiseev, A.A. Savina, A.M. Abakumov

prilepskii@gmail.com

The world market of cathode materials for energy storage elements has been intensively developing recently. Despite a wide variety of different materials are presented, $LiNi_xMn_yCo_zO_2$ (x>0.6) with a high nickel content (so-called Ni-rich NMCs) layered oxides are encouraging candidates for the role of high-energy cathode materials and occupy a leading position in the market. Ni-rich NMC has a number of advantages, such as increased discharge specific capacity (up to 230 mAh/g), high energy density (up to 800 $Whkg^{-1}$), reduced content of expensive and toxic cobalt oxide. However, due to the polycrystalline morphology there are some disadvantages, including low cyclic and thermal stability, low tap density.

One of the promising approaches to solve such problems is the development of cathode materials in the form of single crystal (SC-NMC) particles with the average size >1-6 μm. SC-NMC materials demonstrate reduced surface reactivity towards electrolyte, lower stress concentration and increased resistance to mechanical cracking. It causes more stable electrochemical characteristics during battery cycling in comparison with polycrystalline particles of the same composition.

By influencing the morphology of the particles, it become possible to achieve not only the above advantages, but also physicochemical characteristics such as high tap density, which will allow the production of more compact batteries with high energy density.

A series of samples with the general formula $LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$ were obtained using different ratio of lithium and potassium sources as flux at the stage of high-temperature annealing of the material. The physicochemical properties such as particle size distribution by dynamic light scattering technique, tap density, morphology and electrochemical properties by galvanostatic cycling with potential limitation of the obtained SC-NMCs were studied.

Using powder X-ray diffraction (PXRD) was confirmed obtained samples are single-phase with a layered structure (pr. gr. *R*-3*m*). Low concentration of anti-site

defects in 3b lithium site for obtained samples was showed by Rietveld refinement. It was found that the use of inert potassium salt as a flux formation agent leads to the formation of particles with the shape of truncated octahedrons with smoothed edges and vertexes.
The optimum ratio of lithium hydroxide and potassium sulphate was found as 4:1 respectively, where the particles crystallize with spherical-like shape with a dominant (003) surface according to literature data and scanning electron microscopy (SEM) analysis.

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Ultra-high Ni content layered transition metal oxides in the form of single crystal particles of high energy density as the cathode material for lithium-ion batteries

Sergeant A. [1], A.D. Pavlova [1], A.A. Savina [1], A.M. Abakumov [1]

[1] kolkovo University of Science and Technology, 121205 Moscow, Russia

aubreylsergeant@yandex.ru

Lithium-ion batteries (LIBs) are one of the hottest topics in today’s materials science and chemistry landscape. They are incredibly important to the modern way of life; they provide power to things like electric transportation, handheld electronic devices, and even toys. The major limiting element in LIB innovation is the cathode.
By smart design of the cathode, the price and performance of the battery as a whole can be impacted most significantly.
Recent studies have been done on particular cathode materials known as layered Ni-rich mixed transition metal oxides with the common formula $LiNi_xCo_yMn_zO_2$, where $x > 0.6$ (Ni-rich NMC). These materials have proven to be a cheaper and safer alternative than the previous commercialized $LiCoO_2$ cathode material. The crystal microstructure of this new material can be synthesized in two different analogues, as secondary agglomerates known as polycrystals and as single

crystal (SC) particles. Though the polycrystalline cathode materials being investigated have showed much promise, they also have a large downfall – microcracking. Microcracking occurs over prolonged cycling and contributes to decay of cycling stability. This results in poor energy performance and poor capacity for the overall battery. It occurs due to the accumulation of electrochemical and mechanical stress within the cathode during charging and discharging. Microcracking occurs along the grain boundaries of primary particles as these regions of misalignment disrupt the paths of force vectors through the agglomerate.

The SC analogues of these materials have shown much greater resistance to microcracking due to the absence of grain boundaries. Forces moving through the crystals do not run into boundaries and are therefore more effectively dissipated without as much damage to the material structure. This results in better electrochemical and mechanical stability than observed in the polycrystalline analogue. SCs also have the advantage of higher energy density compared to polycrystalline analogues. SCs with spherical-like morphology fill space in a more ordered way and therefore results in increased tap density of the material. Aside from the interesting advantages of SC cathode materials, they are not without disadvantages.

The main concerns being poor rate capability at a high current density. This is to say that microcracks will still form in the single crystal material when cycled at a high current. Defects are also observed in these crystals and can contribute to poor performance. To correct these issues, novel synthesis approaches will be taken to involve inclusions and dopants into the crystal structure. Inclusions such as non-isostructural materials, specifically transition metal oxides, are to be used to increase the structural stability of the material over long cycling. They will do this by acting as a bolster, buttressing the structure and making it more rigid. This will help decrease collapse of ion transport pathways and thereby improve cycling stability. Dopants such as Al^{3+}, Mg^{2+}, Ti^{4+}, and Zr^{4+} are being considered for the purpose of reducing the quantity of anti-structure disordering. Pushing the boundaries of what is known from Ni-rich NMC cathode materials, a new material known as layered ultra-high Ni content NMC ($LiNi_xCo_yMn_zO_2$, where x > 0.9) with above modifications are to be synthesized. The purpose of this material being to make the new generation of lithium-ion batteries safer, longer lasting, and more cost effective.

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Intercalation of transition metal anionic malonates to layered yttrium hydroxide

E.D. Sheichenko [1,2], A.D. Yapryntsev [2], N.V. Gogoleva [2]

[1] Higher School of Economics, Myasnitskaya st., 20, 101000, Moscow, Russia
[2] Kurnakov Institute of General and Inorganic Chemistry, 119991 Moscow, Russia

kseterina@yandex.ru

Layered REE hydroxides (LRH) – a new class of layered inorganic anion-exchange materials, significant interest in which is associated with the possibility of combining the unique properties of lanthanides (luminescent, magnetic, catalytic) and intercalated anions to create multifunctional materials based on these compounds. By varying the anions intercalated in LRH, it is possible to obtain various materials, including catalysts, phosphors, nanoreactors, etc. Metal coordination compounds are promising anions for intercalation in LRHs, however, at the moment there is no universal methodology for intercalation of complexes of a wide range of metals in layered rare earth hydroxides. The universal ligand is malonate anion because it forms stable complexes with SHZM, REE and transition metals, and varying the malonate substituent allows you to control the structure of the resulting complexes. The aim of this work was to develop a methodology for the intercalation of d-metal malonates in layered yttrium hydroxide, as well as to study the influence of the malonate anion substituent on the composition, structure and thermal decomposition of the obtained hybrid compounds. For realization of the aim a number of tasks were performed, including anion-exchange reactions of layered yttrium hydroxynitrate with aqueous solutions of malonates (butylmalonate, cyclobutylmalonate, dimethylmalonate, cyclopropylmalonate and benzylmalonate) of copper, chromium, iron and vanadium; stepwise thermal annealing of LH exchange products of yttrium and malonates in air and in hydrogen atmosphere; analysis of composition, structure and properties of the obtained compounds by XRD, SEM, UV-visible spectroscopy and EDX. Methods of preparation of new hybrid compounds based on layered yttrium hydroxide intercalated with transition metal malonates are proposed. The copper content in the hybrid compounds increases with the decrease of the malonate substituent. The possibility of in situ complexation of Cu^{2+} in the interlayer space of the layered hydroxide with dimethyl- and benzylmalonate anions was shown. It is shown that annealing above 800 °C leads to the formation of a mixture of Y_2O_3, $Y_2Cu_2O_5$ and $Cu^{21+}Cu^{22+}O_3$. By reduction (H_2, 450 °C) of the annealing product of layered yttrium hydroxynitrate intercalated with copper dimethylmalonate, a nanocomposite based on yttrium oxide containing metallic copper particles on the surface was obtained.

Preparation of segmented Au/Ni nanowires for SFS Josephson junctions

Stepan V. Sotnichuk [1,2], Olga V. Skryabina [2,3], Vasily S. Stolyarov [2,3], Kirill S. Napolskii [1,2]

[1] Lomonosov Moscow State University, Leninskie gory GSP-1, 119991 Moscow, Russia
[2] National University of Science and Technology MISIS, Leninskiy Prospekt 4, 119049 Moscow, Russia
[3] Moscow Institute of Physics and Technology, Institutskiy per. 9, 141700 Dolgoprudny, Russia

sotnichuksv@my.msu.ru

Nanowire-based Josephson junctions are the new type of superconducting hybrid structures that have attracted much interest owing to low energy consumption and heat dissipation in integrated circuits. In this work, we suggest creating such structures using multilayer

metallic nanowires that contain segments of normal metal (Au) and a thin layer of ferromagnetic material (Ni). This geometry is novel and, compared with traditional sputtering techniques, can significantly minimize the lateral dimensions of superconducting circuits.
Au/Ni/Au nanowires were fabricated using templated electrodeposition into porous anodic aluminium oxide (AAO) templates. A robotic electrodeposition setup was used to fabricate metal segments from separate electrolyte solutions one after another thereby minimizing the mixing of metals at the interface between adjacent segments. The deposition of Au segments was carried out from an electrolyte solution Ecomet 04-ZG at a potential of Ed = –1.0 V. Ni segments were deposited from an electrolyte containing 0.6 M $NiSO_4$, 0.1 M $NiCl_2$, 0.3 M H_3BO_3 at a potential of Ed = – 0.9 V.
For the fabrication of the SFS Josephson junctions, individual Au/Ni nanowires were bonded to superconducting Nb electrodes following the steps comprising a seeding onto a marked Si/SiO_2 substrate, electron lithography, magnetron sputtering, and lift-off process.
We have successfully obtained 60 nm nanowires consisting of 400 nm-long Au segments and thin Ni layers of various thickness in the range of 7-50 nm. The use of a robotic electrochemical setup made it possible to achieve narrow distribution of segments along the length. According to TEM and EDS mapping data, the nanowires have a smooth surface with a good quality connection between neighboring segments. The electron diffraction pattern taken from the part of the nanowire with the Ni segment shows that sets of crystallographic planes, e.g. (220) corresponding to Au and Ni, follow each other (Fig. 1).

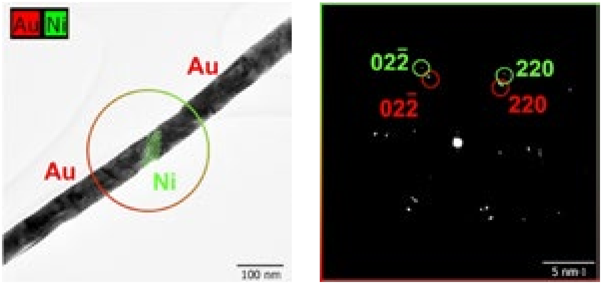

Fig. 1. TEM image of a single Au/Ni/Au nanowire and electron diffraction pattern from a highlighted area containing a thin ferromagnetic nickel layer between gold segments.

This confirms the 'epitaxial' growth of the segments. The gold parts in the obtained nanowires are single-crystal. In the presence of a ~7-nm-thick Ni segment in the Nb/Au/Ni/Au/Nb Josephson junction, a critical current of 0.85 μA has been registered.

The work was performed under financial support of the Russian Science Foundation (grant number 22-23-00984) and the National University of Science and Technology MISIS (grant number K2-2022-029).

Detecting low-melting phases upon the densification of $BaSn_{0.8}Y_{0.2}O3{-}\delta$ ceramics via sintering additive-assisted sintering

Starostin G. N. [1,2], Starostina I. A. [1,2] , Akopian M. T. [1,2], Medvedev D. A. [1,2]

[1] Institute of High Temperature Electrochemistry, 620066 Yekaterinburg, Russia
[2] Ural Federal University, 620002 Yekaterinburg, Russia

gorgge23@mail.ru

Ba-based perovskites (i.e., $BaCeO_3$, $BaZrO_3$, $BaHfO_3$, $BaSnO_3$) are attracting considerable attention of researchers as proton-conducting electrolyte systems for high-temperature applications, including solid oxide fuel cells (SOFCs) and electrolysis cells (SOECs). To achieve high performance of SOFCs and SOECs at reduced operating temperatures, such electrolytes need to be fabricated in thin film form during their co-sintering with supported (mainly, Ni-cermet) electrodes. However, the co-sintering temperatures should be as low as possible to avoid possible interactions between the functional layers. For the desired densification of Ba-based perovskites as refractory materials, sintering additives (SAs) are widely used [1]. This method is based on the use of SAs in small quantities, which form a liquid phase during sintering and significantly improve diffusion processes. As guest impurity phases, SAs can adversely affect the functional materials of proton-conducting electrolytes [2]. However, the detection of SAs is often challenging due to the low concentration used (usually not more than 1 wt%). In detail, neither X-ray diffraction (XRD) analysis nor conventional scanning electron microscopy (SEM) modes can detect such impurities. To overcome this shortcoming, we present here the results of the identification and localization of SA, taking a reference system of $BaSn_{0.8}Y_{0.2}O_{3-\delta}$ + 0.5wt% CuO (BSY-Cu) into account. To achieve this goal, the corresponding dense ceramic was fabricated and then characterized by a combination of SEM and electron backscatter diffraction (EBSD) analyses. Our observations (Figure 1) show that CuO indeed improves the overall densification of BSY-Cu owing to liquid phase sintering, since the copper oxide phases (Cu_2O and CuO) are detected along the grain boundaries of the ceramics. Therefore, the combined SEM and EBSD analysis can be used as a non-destructive alternative to high-resolution transmission electron microscopy for the detection of impurity phases in various functional ceramics.

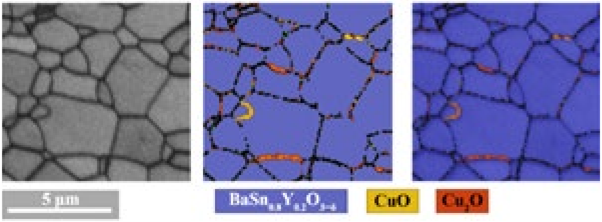

Fig. 1. SEM and EBSD analysis for the BSY-Cu ceramic.

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Structure of active centers of Pt/CeO_2 and Pt-CeO_2/MWCNTs composite catalysts for dry and wet CO oxidation at sub-ambient temperatures

Stonkus O.A. [1], Slavinskaya E.M. [1], Kibis L.S. [1],
Stadnichenko A.I. [1], Zadesenets A.V. [2], Kardash T.Yu. [1],
Lashina E.A. [1], Podyacheva O.Yu. [1], Boronin A.I [1].

[1] Boreskov Institute of Catalysis, Pr. Lavrentieva 5, 630090 Novosibirsk, Russia
[2] Nikolaev Institute of Inorganic Chemistry, Pr. Lavrentieva 3, 630090 Novosibirsk, Russia

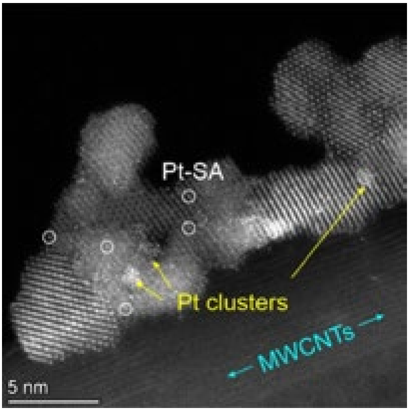
stonkus@catalysis.ru

Pt–based CeO_2 catalysts are among the most used ones in a variety of heterogeneous catalytic reactions required to purify the atmosphere from harmful pollutants, such as CO and hydrocarbons. The scope of application of Pt–based CeO_2 catalysts requires the formation of Pt active centers in a desired structural and electronic state which provides the maximum catalytic activity in a given reaction.

The formation of various active forms of platinum is primarily determined by the strong chemical interaction of platinum with ceria nanoparticles. Transmission electron microscopy (TEM) methods comprising the combined use of high-resolution TEM and scanning TEM imaging modes as well as energy-dispersive X-ray microanalysis (EDX) provide detailed information on the local structure and composition of highly dispersed catalyst particles. Combining the TEM results with the data provided by other structural, physicochemical and catalytic methods, we can distinguish different structural and electronic states of platinum in the studied samples, from isolated ions (single atoms, Pt-SA) and metallic (Ptn) or oxidized (PtO_x) subnanosized clusters, up to anchored nanoparticles (PtNP) of different sizes.

At low platinum content in the catalysts, platinum mainly forms Pt^{2+} single atoms incorporated into the ceria lattice, this state is stable and active in the CO oxidation only at T > 100 °C. The increase of platinum content leads to the formation of Pt2+ and Pt4+ cations, forming PtO_x subnanosized clusters which trigger the CO oxidation activity below 0 °C. The highly dispersed Pt-species exhibit dynamic behavior under the action of the electron beam, which requires imaging at a very low beam current. However, the observed dynamic transformations are of particular interest as they can also occur under the reducing action of the reaction medium. Fixation of these clusters can be observed on the defects of the support, such as surface steps and intercrystalline boundaries. Increasing the defectiveness of the support is one of the approaches to obtain highly dispersed states of platinum while decreasing its loading in the catalyst. The approach used in this work involves increasing the dispersity and defectiveness of CeO_2 by fixing it to the surface of the multi-walled carbon nanotubes (MWCNTs). This is accompanied by the stabilization of the platinum on the surface of the MWCNTs in the form of highly dispersed PtO_x clusters and Pt-SA. These forms of platinum, being out of contact with ceria, have no sub-ambient activity, however, they can absorb the water molecules, thus opening a new pathway of the catalytic reaction in a humid atmosphere via a CO-assisted H_2O dissociation mechanism.

This research was supported by the Ministry of Science and Higher Education of the Russian Federation within the governmental order for Boreskov Institute of Catalysis (project AAAA-A21-121011390053-4).



Effect of gas flow rate and sintering temperature on morphology of platinum nanoparticles produced in gas discharge

Vershinina O.V. [1], Novoselov A.K. [1], Sanatulina A.F. [1], Lizunova A.A. [1], Ivanov V.V. [1]

[1] Moscow Institute of Physics and Technology, National Research University, 141701 Dolgoprudny, Russia

seraia.ov@phystech.edu

Platinum nanoparticles exhibit distinct optical properties due to surface plasmon resonance which can be adjusted to a desired wavelength by modifying the size and shape of the particles. Such modifications are crucial for numerous applications in science and industrial fields, including Raman spectroscopy, optical data storage, medicine, biosensors and plasmon solar cells [1]. Numerous physical and chemical methods are employed to prepare nanoparticles for optical investigations, for example, laser ablation in liquids, polyol and green synthesis [1, 2], and gas-phase methods [3]. One of the most promising methods for obtaining nanoparticles with a high degree of chemical purity, a narrow size distribution and the possibility of flexible control over the particle size and morphology by changing the setup parameters is a gas discharge. In this study, we investigate the impact of gas flow rate and temperature of a tube furnace in a subsequent in-flow sintering process in gas discharge setup [4] on the size and shape of generated particles (fig. 1).

The morphology, size and distribution of aerosol nanoparticles were characterized by transmission electron microscopy (TEM) on a JEM-2100 device (JEOL, Japan), with an accelerating voltage of 200 kV. Diffraction patterns and high-resolution images (fig. 1, e, f) have shown that all nanoparticles are crystallized in the platinum phase of the Fm3m space group. It has been demonstrated that an increase in gas flow rate from 50 to 600 ml/min leads to decrease in sintered particles size. Subsequent exposure to a temperature of 985 °C causes the melting and fusion of primary nanoparticles, resulting in the formation of larger spherical platinum particles with sizes up to 250 nm. Huge particles are observed at lower gas flow rates, whereas at higher flow rates, the particles exhibit a more rounded shape with smaller sizes.

This work was funded by the Russian Science Foundation (project No. 22-19-00311, https://rscf.ru/project/22-19-00311/).

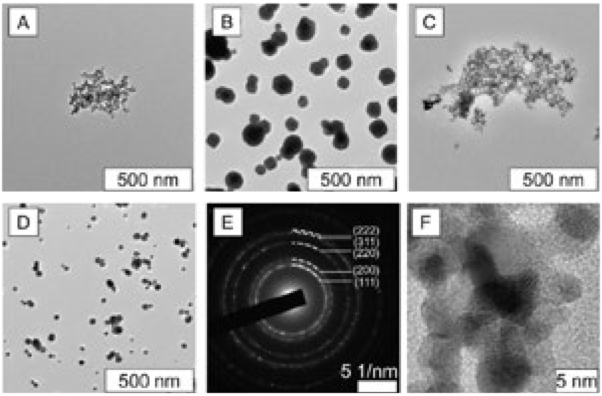


Fig. 1 – TEM images of primary Pt nanoparticles synthesized in gas discharge (a, c) with subsequent sintering at 985°C (b, d) using gas flow rates of 50 and 600 ml/min respectively; diffraction pattern (e) and high-resolution image (f)

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Composite Materials Based on Sodium-Vanadium Fluoride-Phosphate and Amorphous Carbon for Sodium-IonBatteries

Zaytsev N.I., Opra D.P., Sinebryukhov S.L., Kuryavy V.G., Zavidnaya A.G., Ustinov A.Y., Gnedenkov S.V.

Institute of Chemistry FEB RAS, 159 Pr. 100-letiya Vladivostoka, 690022 Vladivostok, Russia

zaitcev.ni@ich.dvo.ru

Among promising materials for the role of cathodes of sodium-ion batteries (SIBs), sodium-vanadium fluoride phosphates (NVPF) stand out. These compounds have a NASICON-type structure, which provides high ionic conductivity. An important representative of this group of substances is $Na_3V_2(PO_4)_2F_3$, which has relatively high performance in SIBs. Its specific energy density equals to 500 Wh/kg that is close to $LiFePO_4$ – 530Wh/kg. The synthesis of $Na_3V_2(PO_4)_2F_3$ is rather simple in implementation and does not require complex equipment or expensive reagents. The main disadvantage of sodium-vanadium fluoride-phosphate is low electric conductivity (~10–12 S*cm–1). Proven theways to solve this problem include the creation of composites with electrically conductive carbon materials, e.g. mixing with organic compounds (with subsequent annealing), carbon nanotubes or graphene. In this work, a one-step synthesis of composite material based on $Na_3V_2(PO_4)_2F_3$ and amorphous carbon has been developed. The composite was obtained by hydrothermal method. Oxalic acid acted as a carbon precursor.
The synthesized product has a complex morphology with hierarchical organization and consists of flower-shaped agglomerates with diameters of several hundred microns (Fig. 1a) constructed from parallelepiped-shaped microparticles with dimensions of tens microns (Fig. 1b). The diffractogram of the material (Fig. 1c) is dominated by reflections corresponding to the $Na_3V_2(PO_4)_2F_3$ phase. In addition, a blurred peak at ~21° from amorphous carbon is presented. These data are in agreement with the results of energy-dispersive X-ray spectroscopy and X-ray photoelectron spectroscopy (these data not presented here). The D and G peaks are observed in Raman spectrum of the investigated sample (Fig. 1d), which also confirms the presence of carbon phase in it.

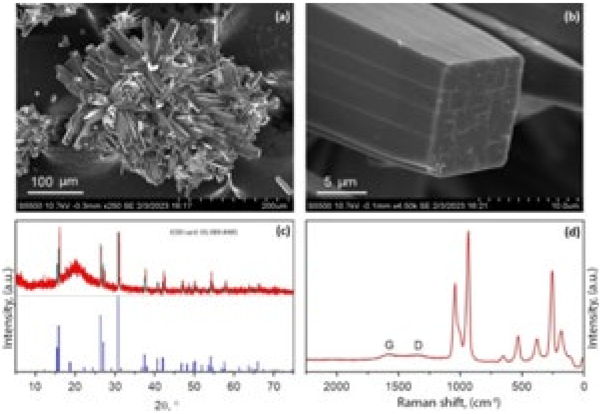

Fig. 1. SEM images of particle surface (a, b), X-ray pattern (c) and Raman spectrum (d) for composite material based on $Na_3V_2(PO_4)_2F_3$ and amorphous carbon

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Skolkovo Institute
of Science
and Technology

Bolshoy Boulevard 30, bld. 1
Moscow, Russia 121205
Tel.: +7 (495) 280 14 81