

Book of abstracts

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New cathode materials for Li-ion batteries

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Li-ion batteries originally developed for portable devices can now be found in applications as diverse as power tools, electric vehicles and stationary energy storage. To satisfy the need of current and new applications, Li-ion batteries require further improvement in terms of performance properties (energy and power density, safety and cost).

First generation of cathode materials for Li-ion batteries represents the ternary mixed oxides belonging to spinel or rock-salt derivatives structures: LiM_2O_4 or LiMO_2 , respectively, has been already widely commercialized. However, these materials have severe limitations in further improvements of their properties related to their structural features. Transition metal compounds containing different polyanion units $(\text{XO}_4)^{m-}$ (X=B, P, S, Si) are now considered as the most promising cathode materials for next generation of Li-ion batteries due to increased redox potential caused by an inductive effect and remarkable electrochemical and thermal stability ascribed to a three-dimensional structure. Further advances in the polyanion-containing cathode materials are related to combining $(\text{XO}_4)^{m-}$ and F^- in the anion sublattice, which is expected to enhance the operating voltage due to the increasing ionicity of the M-F bond. Indeed, various fluorophosphates and fluorosulphates have been reported to exhibit attractive electrochemical performance.

The overview of various types of cathode materials for Li-ion batteries will be presented and possible directions of their development will be discussed.

Structure Analysis of Disordered Systems by Small-Angle Scattering

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The lecture covers present day possibilities of the small-angle scattering (SAS) technique for structural studies of disordered systems. The principles of the method (which is highly sensitive to the length scale of 1-100 nm) are introduced. The peculiarities of X-ray (including synchrotron radiation) and neutron scattering are emphasized. Specific details of the contrast variation procedure in small-angle neutron scattering (SANS) from dispersed systems are given taking into account the polydispersity of the nanostructures under study. It is demonstrated that the SAS method is to be used as a part of complex investigations which comprise several complementary methods. Examples on the SAS structure analysis of the carbon nanostructures and catalysts are demonstrated.

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Neutron scattering as a tool for atomic and magnetic structural characterization

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Extremely high efficiency of neutron scattering as a tool for analysis of atomic and magnetic structures of materials is conditioned by well known features of slow neutrons interaction with matter: sensitivity to light elements, ability to distinguish between adjacent elements, huge magnetic scattering cross-section, and high penetration depth. All they are topical for electrochemical materials used in batteries, fuel cells etc. Just light elements (hydrogen, lithium, carbon, oxygen) are required for electrochemical devices and we need to know their positions in a structure for understanding of redox-processes. Cathode materials usually contain cations with close atomic numbers and their distribution (redistribution processes) in a unit cell can be traced up by neutron diffraction only. Magnetism of the 3d-elements (Mn, Fe, Co, Ni) is in many respects crucial for macroscopic properties of the oxides and magnetic neutron scattering is able to provide data about magnetic structure – properties correlations. Finally, the high penetrability of neutrons in matter, due to their lack of charge, is helpful for studies on samples in special environments and *in situ* studies with model electrochemical cell and real current sources.

This paper reviews the state of the art in neutron scattering (mainly diffraction) experiments, facilities available to researchers, and some applications of neutron scattering for studies of electrochemical materials and processes both *ex* and *in situ*. Besides, the construction of the specialized facility RTD (Real Time Diffractometer) at the IBR-2 pulsed reactor in Dubna is reported, which offers a substantially new possibility for real-time experiments [1]. Often only this mode with a continuous recording of experimental information allows obtaining the necessary data for the interpretation of an irreversible process. The minute and sometimes second range of collecting diffraction and SANS patterns has already been realized in Dubna [2]. Estimations show that at the upgraded IBR-2 reactor the conditions exist for a significant improvement in temporal resolution while reducing the mass of the sample.

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The Microscopic Model of Electron Transfer Reaction in Disordered Solid Matrices

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The original model of the hopping mechanism for electronic conduction in photosensitive organic materials is considered. The electron transfer (ET) in active centers of such systems proceeds via local intra- and intermolecular modes. The active modes, as a rule, operate beyond the kinetic regimes, which are usually postulated in the existing theories of the ET. Our alternative dynamic ET model for local modes immersed in the continuum harmonic medium is formulated for both classical and quantum regimes, and accounts explicitly for the mode/medium interaction. The kinetics of the energy exchange between the local ET subsystem and the surrounding environment determine essentially the total ET rate. The efficient computer code for rate computations is elaborated. The computations are available in the wide range of system parameters, such as the temperature, external field, the local mode frequency and the characteristics of the mode/medium interaction.

The relation of the present approach to the Marcus ET theory and to the underlying quantum-statistical reaction rate theory (Levich-Dogonadze, 1959) will be discussed and illustrated by the results of computations for practically important target systems.

Processes in Lithium-Air Battery Cathodes as Seen by *in situ* Raman Scattering and Photoemission Spectroscopy

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The lithium-air batteries attract a lot of attention worldwide as a promising power source for electric vehicle propulsion as it could provide extremely high specific energy in comparison with other battery systems developed to date [1]. The main features of lithium-air system include metallic lithium as an anode, and air cathode where oxygen reduction during battery discharge and its evolution at recharge occurs. Conventional cathode material for lithium-air cell comprises oxygen reduction catalyst (transition metal oxide or complex) mixed with electronically conductive carbon. In this case, active reaction sites would be boundaries between conductive carbon particles, absorbed oxygen species on the catalyst surface, and lithium-ion-conductive electrolyte. Thus, the discharge process could be limited by the electronic, ionic or oxygen transport in the positive electrode. The main discharge product is believed to be the lithium peroxide, that was confirmed using spectroscopic techniques [2]. However, the electrode reaction pathways are not yet understood so the search for effective electrode materials is embarrassed and performed by trial-and-error route. High pressure XPS and Raman spectroscopy studies under electrochemical conditions provides unique tool to probe unusual chemistry at true *operando* conditions. The aim of the experiment is to get an insight to the cathode direct and reverse reaction pathways and to identify discharge products formed at the surface using high-pressure XPS and Raman scattering. Among different cathode materials we are focused on a reduced graphene oxide (RGO) as a convenient model electrode: it provides high performance for Li-air batteries, could be easily deposited on the substrate and has good electrical conductivity. In this work simple cell design for carrying out spectroscopic and electrochemical measurements was used: metallic lithium foil (anode) was brought into a contact with lithium-ion-conductive NASICON-type glass-ceramic membrane (solid electrolyte), graphene layer (cathode) was deposited on the opposite side of the membrane. Such electrode design provide developed 3-phase interface where Li^+ , e^- and O_2 can react thus making it possible to explore the reactions occurring in real air cathodes with high-pressure XPS and Raman techniques.

Electrochemical and spectroscopic measurements were carried out in vacuum, argon and oxygen atmosphere in galvanostatic regime. Using *operando* XPS at high oxygen pressure (0.1 mbar) we have confirmed that the discharge product stoichiometry $\text{Li}:\text{O} = 1:1$. At the same time the appearance of lithium peroxide bands in Raman spectra makes us believe that discharge product is Li_2O_2 . We demonstrated that RGO could effectively promote the discharge reaction as a catalyst. It was demonstrated that the discharge process involves the formation of intermediate compounds including carbonyl, carboxyl and other oxygen containing groups at the cathode surface.

The work was supported by Russian Foundation for Basic Research (grant No. 10-03-00997) and FM Lab company.

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Low Signal Electrochemical Methods Application for the Investigation of the Systems with High Currents and Voltages

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POLYCOM Company represents on the Russian market different products of AMETEK (USA) Company – the famous manufacturer of precision electrochemical test systems Princeton Applied Research (PAR) and Solartron Analytical. The testing equipment of these brands have high quality and outstanding characteristics. In particular, PAR potentiostats allow to measure low potential of reference electrodes against the background of high (up to 100 V) voltage drop at counter. Impedancemeters Solartron allow to carry out the impedance measurements by 3- and 4-terminals methods at high resistance of current electrodes as well as to study the systems in non-equilibrium conditions.

POLYCOM specialists have great experience in experimental research work in field of classic voltammetry and corrosion measurements, impedance analysis of electrochemical systems and in pulse measurements.

For example, the non-standard problem for voltammetry and impedance measurements arises during investigation of the electro dialysis processes and ion migration through the ion-exchange membrane. For this experiment it's necessary to measure CVA and impedance spectra of the membrane that has rather low voltage drop (about 1-3 V). At the same time the electrolyte is very dilute, and the voltage drop between current electrodes is very high (up to 100 volts).

This kind of problems require both special cell geometry and the instrument, which would provide high suppression of the co-phasal component (up to 100 V). The instrument PARSTAT 2273 was selected for this purpose and the special scheme of the measurements was proposed. Application of this tool allows measuring the frequency response in the range of 0.01 Hz – 1 MHz at the background of voltage of the counter electrode equal to 100 V.

The other complex problem of low signal electrochemical methods is the investigation of the electrochemical current sources (ECS). The investigation of these systems usually has to be done in their operating mode under load. These systems are in non-equilibrium conditions and they change during the operation time.

Unfortunately classic impedance theory [1] does not allow interpreting the spectra received far from the equilibrium. They are hard to be described by separate stages of the process due to non-linearity of the current-voltage dependence of the electrochemical process, as at high perturbations the processes are not additive. Moreover in order to study the processes in the ECS against the background parameters drift in time it is important to measure the impedance at very low frequencies [2,3]. In spite of imperfect mathematical validity it is possible to propose the methods of experimental planning and data interpretation, which provide the possibility of application of impedance spectroscopy for ECS investigation. That is why the Solartron division proposes to the customers the power boosters for measurements under high currents.

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Применение Малосигнальных Электрохимических Методов для Исследования Систем с Большими Токами и Напряжениями

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Компания Поликом представляет на Российском рынке продукцию АМТЕК (США) - производителя знаменитых приборов для электрохимических измерений Princeton Applied Research (PAR) и Solartron. Эти приборы являются уникальными в своей области и обладают высоким качеством и непревзойденными характеристиками. В частности, потенциостаты PAR позволяют измерять малые значения потенциала измерительных электродов на фоне большого (до 100 В) падения напряжения на вспомогательном электроде. Импедансметры Solartron имеют возможность измерения импеданса 4-х электродным методом на фоне больших сопротивлений токовых электродов а также проведения измерений в неравновесных условиях.

Специалисты компании Поликом имеют опыт в планировании и проведении измерений как в области классической вольтамперометрии и коррозионных измерений, так и в анализе импеданса электрохимических систем и импульсных измерениях.

Например, при изучении процессов электролиза и миграции ионов через ионообменную мембрану возникает необходимость измерения ЦВА и импедансных спектров мембраны, на которой падает достаточно низкое напряжение (1-3 В). В то же время электролит является сильно разбавленным и падение напряжения на участках между токовыми электродами достигает нескольких десятков вольт.

Подобная задача требует приборов с компенсацией синфазной составляющей с уровнем до 100 В. Для этих измерений была подобрана схема включения и прибор PARSTAT 2273, допускающие измерения частотного отклика в диапазоне 0,01 Гц - 1 МГц при потенциале вспомогательного электрода до 100 В.

Другой сложной проблемой малосигнальных измерений является исследование ХИТ. Исследования таких систем обычно проводятся в режиме работы источника тока, под нагрузкой. Соответственно система не находится в равновесии и изменяется во времени. При этом измерения проводятся на неравновесных системах, изменяющихся во времени под нагрузкой.

Классическая теория импедансных измерений [1] не позволяет интерпретировать спектры, полученные вдали от равновесия, в терминах отдельных стадий процесса в силу нелинейности вольтамперной зависимости электрохимического процесса, так как при больших возмущениях перечисленные процессы не являются аддитивными. Более того, для изучения процессов в ХИТ на фоне дрейфа параметров во времени важны измерения инфранизкочастотного импеданса [2-3]. Однако, несмотря на неполную математическую обоснованность, можно предложить методы интерпретации и постановки эксперимента, позволяющие использовать импедансную спектроскопию для исследования ХИТ. В связи с этим в номенклатуре приборов Solartron присутствуют бустеры, позволяющие вести измерения ЦВА и импедансных спектров при больших токах нагрузки.

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Model and Experimental Approaches to Solid State Diffusion Studies in Intercalation Materials

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The diffusional processes proceeding in an intercalation electrode on applying a potential or current step are theoretically treated. The theory of chronopotentiometry and chronoamperometry (in the variants of potentiostatic intermittent titration technique (PITT) and galvanostatic intermittent titration technique (GITT) for lithium-ion batteries (LIB)) is shown to require the necessary account of the contribution of the surface solid-state film to the overall diffusion resistance of the electrode. For the case of small deviations from equilibrium, analytical solutions of the diffusion problem have been obtained. Ignoring the retarding contribution of the surface film is shown to bring about an error into the diffusion coefficient of lithium in its alloys and intercalates [1 – 5].

The transfer processes proceeding in intercalation electrode materials with surface control on the application of a potential or current step are considered theoretically. The theoretical relationships have been verified by the determination of the kinetic and diffusion parameters of electrochemical lithium intercalation into thin-film electrodes such as Li_xC_6 , Li_xSn , Li_xTiO_2 , and Li_xWO_3 as well as composite electrode such as $\text{Li}_x\text{Mn}_2\text{O}_4$, LiFePO_4 , etc. The overall electrode polarization is divided, both theoretically and experimentally, into the kinetic component, related to hindered ion transfer in the passive surface layer, and the diffusion one, related to decelerated lithium diffusion in the intercalated matrix. The polarization dependence of kinetic current is shown to obey the same regularities that the current-potential function of the lithium electrode. The concentration dependencies of the surface layer parameters and of the Li^+ diffusion coefficient have been determined [1 – 9].

A new model of lithium-ion transport processes in the LiFePO_4 electrode (and other similar LIB's electrodes that undergo a phase transition) is proposed. This model takes into account the phase transition $\text{LiFePO}_4 \leftrightarrow \text{FePO}_4$ accompanying reversible lithium intercalation into the electrode during potential or current steps. The diffusion coefficient of Li^+ ion and its dependence on the $\text{LiFePO}_4/\text{FePO}_4$ phase ratio have been determined by means of processing of experimental potential and current transients in accordance with the model's equations. The PITT & GITT results are in good agreement [10].

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Application of low voltage Cs-corrected TEM for nanocarbon materials

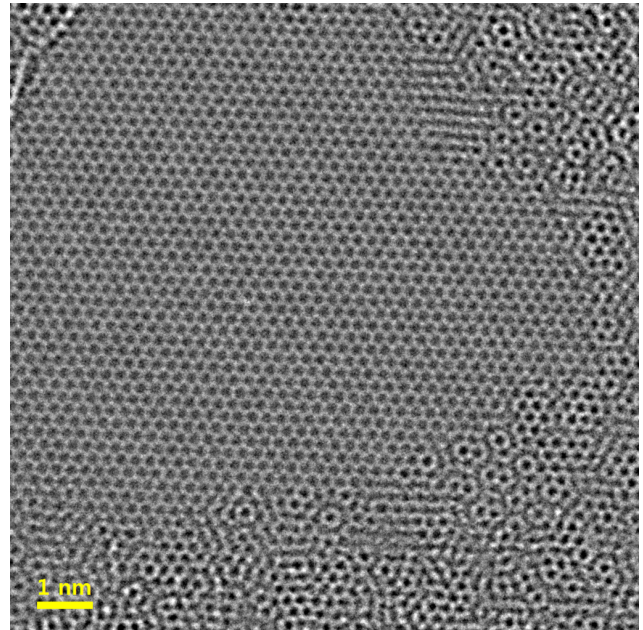
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Theory, state of the art and prospective of aberration corrected low voltage transmission electron microscopy in application to carbon materials will be discussed.

Being one of the main methods for studying the atomic structure of carbon materials, high resolution TEM suffers from a serious flaw as the energy of electrons, necessary to obtain atomic resolution (200-300 keV), is far above the knock-on damage threshold for graphitic carbon (about 80 keV), which means that carbon nanostructures are always observed more or less damaged by electron beam. Practical implementation of Cs correctors in the last decade opened the possibility to decrease acceleration voltage of the microscopes significantly, yet preserving the resolution at reasonable level. This opens a possibility for direct observation of pristine structure of nanocarbons at atomic level.

We present the examples of application of 80kV aberration corrected electron microscopy for studying carbon nanotubes, peapods and graphene. We show that nano-structures composed of graphitic carbon are stable under the conditions of observation, which opens the possibility for monitoring of single atom dynamics, diffraction studies and EELS measurements without radiation damage induced by the electron beam. Time resolved imaging at atomic scale opens a perspective for direct observation of chemical reactions on atomic level, a few examples of this kind will be presented. Unprecedented stability of graphene under electron beam allows acquisition of the images with extremely high signal-to-noise ratio, which in turn makes it possible to observe subtle contrast related to electron redistribution between atoms, namely the chemical bond.



AC-TEM image of graphene monolayer

Li⁺ Intercalation Into Nb₉PO₂₅

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Search and study of the materials for reversible intercalation of Li⁺ is an actual problem. The purpose of this work was investigation of the intercalation kinetics of lithium ions in complex niobium phosphate Nb₉PO₂₅ with crystallographic shear structure (s.c. Wadsley-Roth phases), which possesses rather large channels for Li⁺ diffusion and stability during Li⁺ intercalation/deintercalation [1], Fig. 1.

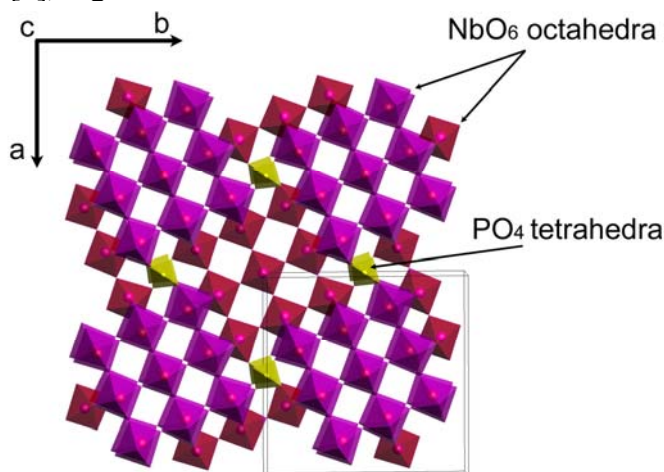


Figure 1. Crystal structure of Nb₉PO₂₅

Method of sintering of Nb₉PO₂₅ was optimized for obtaining the monodisperse material (≈ 1 μm particle size) suitable for electrochemical experiments.

An electrode material with reversible capacity about 170 mAh/g (≈ 0.8 Li:Nb) at potential range of 1.2-2.5 V was prepared. This sample was investigated by means of different electrochemical methods: galvanostatic cycling, potential intermittent titration technique, impedance spectroscopy. Dependence of chemical diffusion coefficient D_{chem} on lithium content was determined, it varies between 10^{-10} - 10^{-11} cm^2/s . Values of D_{chem} obtained using different techniques are fit with each other. The kinetic parameters defined in this work are comparable or even exceed those for well known materials (for example, D_{chem} of Li⁺ in Li₄Ti₅O₁₂ is 10^{-11} - 10^{-12} cm^2/s [2,3]).

This work was financially supported by Russian Foundation for Basic Research (10-03-00970-a), grant of the President of the Russian Federation for young PhD scientists (MK-5679.2011.3) and M.V. Lomonosov Moscow State University Program of Development.

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Determination Of Li⁺ Chemical Diffusion Coefficients In LiFePO₄/C Composites

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The value of Li⁺ chemical diffusion coefficient (LCDC) is a significant parameter of cathode materials of Li-ion batteries because it characterizes the velocity of electrode processes and therefore defines power efficiency of the battery in whole. Different theoretical and empirical models based on corresponding electrochemical measurements are used for LCDC determination. The aim of this work was determination of LCDC in LiFePO₄/C using PITT (potentiostatic intermittent titration technique) data.

LiFePO₄/C samples were synthesized by a sol-gel route implementing polyethylene glycol as a carbon additive. The content of residual carbon in the composites was estimated by TG/DSC analysis. The morphology was investigated by scanning electron microscopy.

Electrochemical behavior of LiFePO₄/C electrodes was analyzed by means of galvanostatic and potentiostatic experiments.

The model suggested in [1] in its approximation [2] was used to calculate LCDC. According to the model, ohmic resistance and charge transfer resistivity contribute significantly to the experimental PITT data. The advanced model presented in [3] was also applied. It allowed separating the diffusive contribution from the total charge transferred.

The magnitudes of LCDC were obtained in range from 10⁻¹¹ to 10⁻¹⁷ cm²/s depending on the applied potential. We carried out the comparison of two electrochemical models. It has been shown that the LCDC values obtained by two models correlate with each other but differ by two orders of magnitude.

Acknowledgements

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Physics and Chemistry of Solvated Electron

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The behavior of excess electrons in condensed dielectric media is among the key problems of chemical physics with numerous implications [1]. The studies on localization and dynamics of excess electrons in molecular liquids and solids with negative intrinsic electron affinity led to the concept of *solvated electron*. Actually, the species of this kind was first introduced as a chemical entity existing in solutions of alkali metals in liquid ammonia more than 100 years ago [2]. However, it was usually considered as a sort “chemical exotics” before the discovery of hydrated electron in 1962 [3]. This finding stimulated extensive experimental and theoretical efforts for elucidation of solvation dynamics and structure of solvated electrons in liquid and glassy media and numerous studies on kinetics of chemical reactions of such species. Nevertheless, after fifty years, it is still a hot topic, with a number of controversial issues and challenges [4, 5].

This lecture will present an overview of the state of the art, including both physical and chemical aspects. The following points will be considered briefly: (1) basics of excess electron localization and transport in disordered media; (2) spectroscopic signs of solvated electrons and their interpretation; (3) critical survey of existing models; (4) solvation dynamics; (5) kinetic peculiarities. Finally, unresolved issues will be addressed and the directions of future studies will be outlined, with particular impact to the role of local interactions (“microsolvation”). The latter aspect will be illustrated by some recent results obtained in our laboratory

Acknowledgements

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Mathematical Modeling of Ion Transport through One- and Bi-Layer Ion-Exchange Systems

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Mathematical modeling is a powerful instrument to describe quantitatively the variety of membrane processes like as reverse osmosis, nano-, ultra-, microfiltration, electro dialysis and etc. The goal of mathematical modeling is to provide simple but effective model of the process under consideration. The original method for governing electro-mass-transfer through asymmetric membranes taking into account physico-chemical properties of their layers was proposed recently [1]. Boundary value problem for the bi-layer system was set up for the Nernst-Planck equations under validity of electroneutrality conditions through all regions and equality of the electrochemical potentials at the interfaces. It was shown that the difference between effective densities of the fixed charges inside the layers is the main factor which is responsible for the asymmetry degree of the diffusion permeability. Confirmation of the suggested approach was approved by comparing theoretical and experimental results for the diffusion permeability of reverse osmosis, bipolar, bi-layer and modified ion-exchange membranes on polystyrene and per-fluorinate matrix [2, 3]. However the comparison between optical measured and calculated thicknesses of modified layers [3] let us to conclude on inhomogeneous distribution of fixed charges of synthesized nanocomposite MF-4SC/PANI – i.e. to discover the existence of gradient of these charges along the membrane thickness. SEM study [4] confirmed the hypothesis of penetration of the polyaniline chains from the modified side to the opposite side of the membrane even in the case of the one hour modification [3]. The bi-layer model with different charge densities of layers showed good correspondence with experiments for the case of thin-layering during little time modification. In the case of long time modification (> 1 hour) it looks like obligatory to adopt the linear profile of the fixed charges density along the membrane thickness in order to reach a good quantitative description of experimental results. The new linear model [5] has allowed us to present better interpretation of experiments on the diffusion permeability of nanocomposites membranes MF-4SC/PANI than bi-layer model. We applied that model successfully for description of asymmetry of current-voltage curves (CVC) for abovementioned membranes. Note that asymmetry of CVC was also observed in the case of asymmetric conic pore of track-etched membrane [6] within acid range of pH and it also confirms that the hypothesis of heterogeneously charged membrane is the reason of asymmetry of the current-voltage curves.

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Oxygen Diffusion Simulation in $\text{Pr}_{2-x}\text{Sr}_x\text{CuO}_{4-\delta}$ ($x = 0; 0.4; 1$)

by Molecular Dynamics

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Computer simulation techniques have been used to investigate the defect and transport properties of the $\text{Pr}_{2-x}\text{Sr}_x\text{CuO}_{4-\delta}$ ($x = 0; 0.4; 1$) phases which pertain to the three structural types (T' , T^* and T respectively) [1]. Molecular dynamic (MD) simulations have been performed to study the diffusion mechanisms of oxygen atoms by using hard spheres model with effective pair (Buckingham) potential. MD simulation successfully visualized the oxygen diffusion in Pr_2CuO_4 lattice and allowed to reveal distinctions in contributions of various oxygen species to the total diffusion coefficient.

The structural parameters and calculated thermal expansion coefficients ($\sim (10-13) \times 10^{-6} \text{ K}^{-1}$) are good agreed with experimental data at high temperatures ($T > 800 \text{ K}$) [2].

MD calculations disclosed anisotropic nature of oxygen diffusion in $\text{Pr}_{2-x}\text{Sr}_x\text{CuO}_{4-\delta}$. Oxygen diffusion coefficients of $\text{Pr}_{2-x}\text{Sr}_x\text{CuO}_{4-\delta}$ layered cuprates have varied in the range of $\sim 10^{-7}$ - $10^{-6} \text{ cm}^2/\text{s}$ at the temperatures of 1100-2100 K. The obtained values of oxygen diffusivity and activation energies are comparable with the ones for other SOFC electrodes. From this fact, we could suppose that the $\text{Pr}_{2-x}\text{Sr}_x\text{CuO}_{4-\delta}$ matrix can be considered as a potential cathode material for SOFCs.

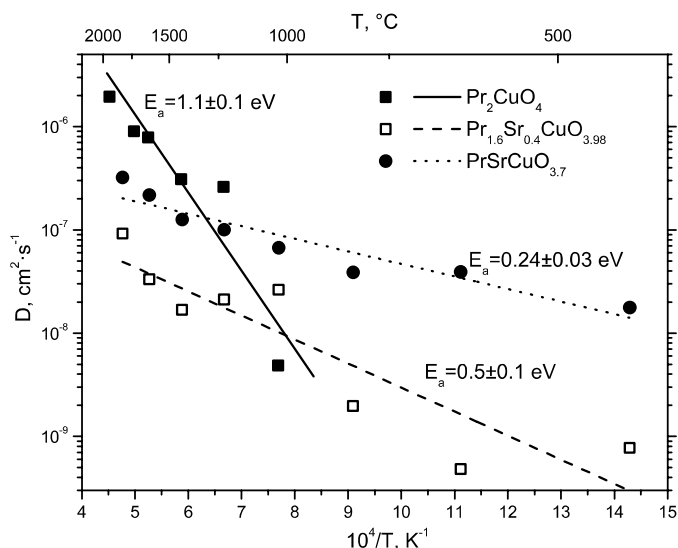


Fig. 1. Arrhenius plot of the calculated oxygen diffusivity of $\text{Pr}_{2-x}\text{Sr}_x\text{CuO}_{4-\delta}$ ($x=0; 0.4; 1$).

Acknowledgements

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Conductometric gas sensors based on nanocrystalline metal oxides

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The gas sensor performances of nanostructured semiconductor metal oxides: ZnO, SnO₂, In₂O₃, and WO₃ are discussed towards air pollutants: CO, H₂S, NO₂, and NH₃. The key role of surface modifiers in the selectivity of conductometric semiconductor gas sensors has been demonstrated. The fundamental properties of materials: structure, composition, nature and concentration of active adsorption centers, electrical behavior, work function are investigated with using of complementary techniques: X-ray diffraction, Transmission Electron Microscopy, Raman spectroscopy, Mössbauer spectroscopy, impedance spectroscopy, Kelvin probe, and probe molecules spectroscopy (TPD, TPR).

The ZnO, SnO₂, In₂O₃, and WO₃ materials with grain size of 3-50 nm and specific surface area up to 200 m²g⁻¹ have been prepared as powders or thin films by chemical and physical routes: sol-gel, aerosol pyrolysis, laser deposition, and magnetron sputtering techniques. A co-precipitation and impregnation techniques with application of surfactant were used to obtain the samples modified with clusters of noble metals: Au, PtO₂, PdO, RuO₂ as well as oxide of *d*-elements: Fe₂O₃, Co₃O₄, NiO, CuO, MoO₃, and V₂O₅. The gas sensor properties of materials were tested towards toxic reducing and oxidizing gases: NH₃, NO₂, H₂S, and CO to analyze the sensor signal depending on density and nature of active centers controlled by catalyst.

The work demonstrates the influence of catalytic clusters on the nature and density of surface active centers. Acidic and redox properties of the modified materials are strongly depended on catalyst selected. For example the concentration of acid centers on the surface of SnO₂ increases with addition of acidic oxide MoO₃ and decreases with addition of basic oxide Fe₂O₃. The sensor properties have been measured on thick films deposited on the microelectronic chips in DC mode at controlled relative humidity to detect CO, NH₃, CO(CH₃)₂, NO₂ and H₂S taken in *ppm* - level of concentration in air.

The application of catalytic clusters for modification of sensitivity and selectivity of sensor materials could be a perspective route of tailoring selective materials. The semiconductor gas sensors are used in electronic nose with pre-concentration system to detect the toxic and explosive agents in air

Challenges facing rechargeable lithium-air batteries

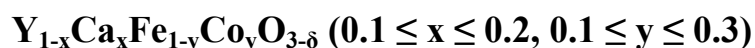
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Power sources that utilize the reaction of lithium and oxygen have become a great challenge since first works in that direction in 1980s. Today lithium-air batteries attract a new wave of attention worldwide due to its promise to provide specific energy of more than 1 kWh per kg at cell level that can lead to skyrocketing expansion of electric vehicle market. However practical use of lithium-air batteries is limited primarily by the low round-trip efficiency associated with slow kinetics of oxygen reduction on discharge and oxygen evolution on charge while the search for effective catalysts and electrode materials is performed by trial-and-error route as the current understanding of elementary processes in the positive electrode is limited because of the paucity of suitable *in situ* techniques to probe these issues. In non-aqueous Li/air cells recharge process is additionally embarrassed as the reaction product deposits are electrically insulating, and truly reversible reaction with a high Coulombs efficiency has not yet been demonstrated. Aqueous cells require water-stable lithium-protection membranes that today exhibit too high impedance for the most interesting application areas. Both aqueous and non-aqueous lithium-air cells require oxygen permeable membranes capable to separate carbon dioxide from environmental air. In addition, the low cycle life that results from both positive and negative electrode degradation and electrolyte instability must be addressed to enable the commercialization of lithium-air batteries.

Synthesis and Specific Conductivity of Solid Solutions with Perovskite Structure



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Perovskites containing transition metals are studied as possible cathode materials for solid oxide fuel cells (SOFC). One of their disadvantages is a low chemical stability to electrolyte materials (Zr,Y)O_{2-x} (YSZ) or (Ce,Gd)O_{2-x} (GDC) related to the presence of rare-earth and alkaline earth metals in the cathode material. It is interesting to synthesize transition metal perovskites containing small cations as Ca and Y in the A-position. They are expected to be more stable to electrolyte materials based on acid oxides than cathode materials containing strontium, barium and lanthanum.

The aim of this work was the synthesis of solid solutions Y_{1-x}Ca_xFe_{1-y}Co_yO_{3-δ} (0.1 ≤ x ≤ 0.2, 0.1 ≤ y ≤ 0.3), study of their homogeneity range and of the temperature dependence of specific conductivity.

As standard solid state reaction doesn't lead to pure samples, one of the soft chemistry methods – the citrate method – was used for the synthesis. The reagents were dissolved in citric acid melt, then a high temperature annealing (1150-1200 °C for 24-40h) was made after combustion of the organic components. One-phase samples were synthesized for the compositions Y_{1-x}Ca_xFe_{1-y}Co_yO_{3-δ} (0.1 ≤ x ≤ 0.2, y = 0.1 ≤ y ≤ 0.3). In the case of larger content of yttrium or calcium admixtures of Ca₂Fe₂O₅ and Y₂O₃ were formed. Replacement of iron with cobalt leads to the decrease of the unit cell parameters, for example, the cell parameters are a = 5.5807(4)Å, b = 7.5859(6)Å, c = 5.2767(3)Å for Y_{0.9}Ca_{0.1}Fe_{0.9}Co_{0.1}O_{3-δ} and a = 5.5474(3)Å, b = 7.5391(5)Å, c = 5.2515(3)Å for Y_{0.9}Ca_{0.1}Fe_{0.7}Co_{0.3}O_{3-δ}. It may be related to the smaller ionic radius of Co³⁺-cation (r(HS Co³⁺) = 0.61 Å; r(LS Co³⁺) = 0.525Å) compared to the Fe³⁺ cation radius (r(HS Fe³⁺) = 0.645 Å). When increasing the calcium content one can expect the cell parameters to decrease but this decrease is small.

The specific conductivity measurements for the samples of Y_{1-x}Ca_xFe_{1-y}Co_yO₃ (x=0.1, 0.2, y = 0.2, 0.3) was made by the four probe method with permanent current. Round ceramic tablets with the diameter 17-18 mm were used for the measurements. The temperature dependence of the specific conductivity has the semiconductor character. The specific conductivity at 900°C is in the range from 22.7 Sm/cm for Y_{0.8}Ca_{0.2}Fe_{0.7}Co_{0.3}O_{3-δ}, Y_{0.9}Ca_{0.1}Fe_{0.8}Co_{0.2}O_{3-δ} to 27.2 Sm/cm for Y_{0.9}Ca_{0.1}Fe_{0.7}Co_{0.3}O_{3-δ}. So the specific conductivity at 900°C is higher for solid state solutions Y_{1-x}Ca_xFe_{1-y}Co_yO₃ than for described in the literature [1] compounds Y_{1-x}Ca_xFeO_{3-δ} (0 ≤ x ≤ 0.1) (for example, specific conductivity is 9 Sm/cm for Y_{0.9}Ca_{0.1}FeO₃). Variation of cobalt content in the solid solutions does not significantly influence the specific conductivity. It may be related to high degree of distortion of the perovskite structure in this compound that results in the constriction of the conduction band.

Acknowledgements

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Carbon Materials Impact On Electrochemical Properties of Positive Electrode Compound Based on LiFePO₄

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Carbon materials are used as conductive additive in positive electrodes in modern Li-ion batteries. Morphology and concentration of carbon additive and also method of positive electrode synthesis have an impact on eventual electrochemical characteristics of Li-ion battery.

The object of the work is determination a degree of the aforementioned factors' impact on the electrochemical characteristics of positive electrode. LiFePO₄ coated with carbon was used as active component. Composite positive electrode was produced by the mixing of LiFePO₄, carbon additive and polyvinylidene fluoride as a plasticizer. Following carbon additives was studied with different concentrations (5 and 10 wt%): acetylene black (AB), multiwall carbon nanotubes (MWCNT) and reduced graphite oxide (RGO)

Charge-discharge curves were measured in galvanostatic mode with currents from the 20 mA/g to the 400 mA/g. Metallic lithium was used as the counter and reference electrode. The electrolyte was 1M LiPF₆ of 1:1:1 (v/v) of ethylene carbonate, dimethyl carbonate and diethyl carbonate. The results of these measurements are tabulated in Table 1.

The research of the composites microstructure was carried out using the scanning electronic microscopy (Supra 50VP).

Table 1. Specific electrochemical capacity of the positive electrode composites based on different carbon materials

Material	Concentration, %	Specific electrochemical capacity, mA*h/g								
		Current 20 mA/g			Current 200 mA/g			Current 400 mA/g		
Cycle number		1	2	20	1	2	10	1	2	10
AB	5	144	145	124	94	95	83	67	58	42
	10	144	145	145	122	121	120	106	99	93
RGO	5	146	145	137	104	102	95	86	84	73
	10	137	140	138	105	104	104	104	102	97
MWCNT	5	95	34	-	-	-	-	-	-	-

The results show that on the small current (20 mA/g) the composite based on 10 % AB and 5 % RGO demonstrates the best properties. That properties can be explained by uniform bounded microstructure of composite. However, on the high current (400 mA/g) the composite based on 5% RGO demonstrates the best properties that can be explained by higher rate of composite conductivity.

Positive electrodes based on MWCNT has the lowest capacity because of two reasons. The first reason is nanotubes coagulation and therefore not uniform distribution in composite. And the second reason is a working electrode passivation during cathode polarization. As a result only a little part of composite participate in electrochemical processes.

Solvation of conformationally flexible molecules. Experiment and computer simulations

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ABSTRACT

All drug-like molecules are conformationally flexible and their physico-chemical properties critically depend on population of conformations. These conformations may determine the polymorphic forms, which appear as result of nucleation of crystal from liquid solutions. Therefore the study of conformational manifolds of drug-like molecules is important for pharmaceutical chemistry. However, there are only few publications in the literature where this problem has been considered. The main reason is the residence time of conformations which is around of $10^{-12} - 10^{-7}$ sec and, therefore, experimental techniques (NMR, infra red spectroscopy) give a smeared picture that is difficult to resolve from the point of view the contribution of different conformations. The computational methods, in turns, either don't take into consideration solvent at molecular level (quantum chemical calculations) or use an effective potential, so the electronic structure is assumed to be constant for whole simulation. In order to overcome these problems, we apply several techniques for the study of conformational manifolds in this work. The results of the simulation of paracetamol - dimethylformamide mixture by molecular dynamics, quantum chemical calculations and metadynamics will be discussed in this presentation. The intermolecular interactions are described in the frame of a "force field" approximation. We compared three well known force fields in this work: OPLS-AA (optimized molecular potential for liquid simulations) [1], GGenFF(charmm general force field) [2], GAFF (general amber force field) [3]. The method of metadynamics has been used for effective sampling of conformational manifold. As for the experimental methods, 2-D NMR and infrared spectroscopy approaches were used for the study of the conformations. The NOESY(NMR) method estimating of internuclear distances for various pairs of protons in a molecule is based on the existence of a strong dependence of the cross-relaxation rate constant σ_{ij} on the distance r_{ij} between the interacting nuclear spins. The reason for combination of several computational and experimental techniques for the study of the conformations will be discussed in the presentation.

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Molecular Dynamics Simulation as a Powerful Tool to Investigate the Structure of Interfaces and Heterogeneous Processes

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Classical molecular dynamics (MD) simulations are known to be a milestone in computational physics and nowadays they become a standard tool in chemistry, materials science and biophysics. In this lecture we consider the basic principles of MD and dwell upon the capability of method to explore interfacial structures and heterogeneous processes. We discuss approaches to calculate reaction rates, as well as some improved sampling techniques (constrained dynamics, umbrella sampling), which enable to deal with rare events occurring in a finite MD time scale and to calculate reaction free energy. The adsorption/desorption of ions in organic electrolytes on the TiO₂ surface is addressed as example. Calculations of free energy surfaces and outer sphere reorganization energy are discussed for certain redox couples at a metal/room temperature ionic liquids (RTIL) interface. A part of the lecture is focused on our recent results on MD simulations of the structure and dynamics of solid/RTIL interfaces [1-3]. Results on the modeling of a TiO₂/acetonitrile-based electrolyte interface [4] are reported in order to illustrate the problem of dye-sensitized solar cells.

We acknowledge the Russian Foundation for Basic Research for financial support (project № 10-08-01123-a) and the Joint Supercomputer Center of the Russian Academy of Sciences for computer resources.

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Mechanochemical Synthesis and Investigation of Nanomaterials for Lithium-Ion Batteries

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Last years, a great deal of attention was devoted to nanosized electrode materials based on the industrial demands to increase capacity and power characteristics of lithium-ion batteries. The main advantages of nanomaterials include: increased practical capacity due to higher active mass utilization; improved structural stability because of better adaptability of nanoparticles to volume changes during insertion/extraction of lithium ions; enhanced high-rate capability owing to increased electrode/electrolyte contact surface and accelerated ionic transport, etc.

To prepare nanosized materials, solid-state eco- and energy-efficient method of mechanical activation (MA) is a real alternative to solution methods. Preliminary MA of initial mixtures in high-energy planetary mills leads to decrease in temperature and duration of their subsequent annealing, thus preventing the coarsening of particles and resulting in nanosized homogeneous final products. In the present study, MA was applied to the synthesis of electrode materials with spinel ($\text{LiMn}_{2-x}\text{M}_x\text{O}_4$, $\text{Li}_4\text{Ti}_5\text{O}_{12}$), layered ($\text{LiNi}_{1-x-y}\text{Co}_x\text{Mn}_y\text{O}_2$) and frame-work (LiMPO_4 , $\text{Li}_x\text{MPO}_4\text{F}$) structure differing by operative voltage, conductivity and chemical stability in electrolytes. The materials were prepared using ‘soft’ mechanochemical reactions [1], mechanochemically assisted carbothermal reduction [2] and ‘dimensional reduction’ approach [3] and studied by a complex of physico-chemical methods, including XRD, SEM, TEM, IRS, MAS NMR, Mössbauer, XPS, galvanostatic cycling, etc. Phase transformations under charge and discharge were investigated by *in situ* synchrotron diffraction [4].

The MA method also opens new opportunities for the development of new composite materials, i.e. ‘core-shell’ materials with inactive to electrolyte ($\text{LiCoO}_2/\text{MO}_x$) or high-conductive (LiMPO_4/C) surface coatings, as well as dual materials based on two active electrode components ($\text{LiMn}_2\text{O}_4/\text{LiCoO}_2$; $\text{LiFePO}_4/\text{L}_3\text{V}_2(\text{PO}_4)_3$), possessing some advantages in electrochemical behavior over the single ones [4].

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Electrochemical Characterization of Pr₂CuO₄-based Electrodes

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Recent trends in the research field of promising cathode materials for intermediate temperature solid oxide fuel cells (IT-SOFCs) deal with investigation of new mixed electronic-ionic conductors with layered structures.

Structurally, oxide materials based on Sr doped Pr₂CuO₄ arouse interest due to the T'→T*→T structural evolution with increasing Sr substitution in Pr_{2-x}Sr_xCuO_{4-δ}. Among them, such phases possess high mixed electronic-ionic conductivity which varies in the range of ~10-100 S/cm at the temperatures of 500-900 °C. Thermal expansion coefficients of praseodymium cuprates (~12-14×10⁻⁶ K⁻¹) are comparable with ceria solid electrolyte (for Ce_{0.9}Gd_{0.1}O_{2-δ} (CGO) – 12.4×10⁻⁶ K⁻¹). From these points of view such materials can be considered as potential cathode materials for IT-SOFCs. In this work the electrochemical behaviour of Pr_{2-x}Sr_xCuO_{4-δ} (x = 0; 0.4; 1) electrodes screen-printed on CGO electrolyte was studied at various temperatures and oxygen partial pressures.

The electrochemical characterization of porous cuprate layers on CGO electrolyte was carried out in a symmetrical cell configuration by AC impedance spectroscopy at OCV conditions in the temperature range of 500-900 °C at the oxygen partial pressures of 10⁻⁴-0.21 atm. The interrelation between composition, crystal structure and rate-determining steps of oxygen reduction reaction at the electrode/electrolyte interface was determined.

Acknowledgements

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Are There Voltammetric Criteria of the Absence of Short-Range Interactions within Electroactive Polymer Films?

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Cyclic voltammetry is perhaps the most frequently used method of electrochemical research. Its application to studies of modified electrodes is often based on the criteria developed by Laviron for reversible electrode reactions that proceed in an adsorbed state of reacting particles [1]. Here, it should be emphasized that the Laviron's consideration had been performed for compact monolayer films of adsorbed particles Ox and Red, whereas modifying films of electroactive polymers, as a rule, has a phase character, i.e. they are so thick, that the electroneutrality condition takes place practically for their all interior. Vorotyntsev, Daikhin, and Levi were probably the first authors that paid their attention to the above difference between the compared systems [2]. Having performed the corresponding analysis, they led to the conclusion that adsorption isotherms of counter-ions into conducting polymer films do not coincide with the Langmuir one and, hence, the Laviron's criteria cannot be used to treat quasi-equilibrium CV-curves of electrodes modified by such polymers. In the represented work we have extended the proper consideration over a more wide circle of modifying films and shown that, in case of one-electron exchange between Red- and Ox-forms of film fragments, the shape of CV-curves (in particular, peak current and potential values, mid-width of CV-peaks) is dependent on charge z_{ox} of the Ox-fragments and changes if the electron transfer is accompanied by binding of counter-ions with charged film fragments. Thus, the only system of voltammetric criteria of the absence of short-range interactions within electroactive films is absent; the proper formulations of such criteria depend on concrete peculiarities of charge transport within these objects.

Financial support by the Russian Foundation for Basic Research (grant # 12-03-00560) and the St. Petersburg University (grants # 12.38.77.2012, 12.38.15.2011) is gratefully acknowledged.

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Nanocomposite Carbon-Based Electrode Materials for Supercapacitors

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Supercapacitors are a novel energy-storage devices combining the advantages of the high power of dielectric capacitors and the high specific energy of rechargeable batteries. Worldwide attention is focused on supercapacitors due to their safety, short charging time, electrochemical stability, high power density and long cycle life. To develop an advanced supercapacitor device, the active electrode material with high capacity is required. The carbon materials are attractive materials applied in energy storage devices such as secondary batteries, fuel cells and pseudocapacitors, because of their chemical stability, low mass density, activated high surface area, and high conductivity. Recently asymmetric or hybrid supercapacitors attract special interest as they have advantages of both batteries and ordinary double layer capacitors and are characterized by a high specific capacity and high specific power. As electrodes in asymmetric supercapacitors one can use different nanocomposites consisted of carbon matrix with deposited nanoparticles of transitional metal oxides.

In the present work, we report results of the study of new nanocomposite electrode materials based on nanoporous carbon materials based on modify coals and cokes for application in asymmetric supercapacitors. As supporting matrixes different carbon samples with a specific surface area of 120-1000 m²/g were used. The materials were modified by treatment in acids (H₂SO₄, HNO₃, acetic acid) in order to enable surface hydrophilicity. Then nanoparticles of transition metal oxides, such as MnO₂, NiO, LiMn₂O₄ and TiO₂ were deposited on the carbon surfaces using methods of salts impregnation, mechanical treatment in ball mills and CVD followed by the precursors decomposition. The electrochemical characteristics of electrode hybrid materials were investigated in a symmetrical two-electrode cell using an impedance spectroscopy, voltammetry in both potentiodynamic and galvanostatic modes. It was shown that specific capacitance of the materials under study strongly depend on the composition of electrode materials and the type of electrolyte (H₂SO₄, KOH, LiClO₄ in acetonitril). Specific capacity was found to increase from 70 F/g for initial carbon materials to 150-200 F/g for nanocomposite materials. This result is promising and optimization of the conditions of the treatment will lead to further increase in the specific capacitance of the carbon materials.

Numerical Simulation of Diffusion of Ions in Colloidal Crystals

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The work is devoted to the calculation of effective diffusion coefficient of ions from the bulk solution to the electrode through a mask and the calculation of the distribution of the limiting current density over the electrode surface. A colloidal crystal, which is formed by orderly arranged monodispersed spherical particles, serves as a mask. It is shown that the diffusion of electroactive ions in the pores between spherical particles can be simulated by unit cells with rhombic, rectangular, or triangular cross section (Fig. 1). In the latter case, the cell side surface has no periodical boundaries. This simplifies significantly the numerical solution of the Laplace's equation by the finite element method.

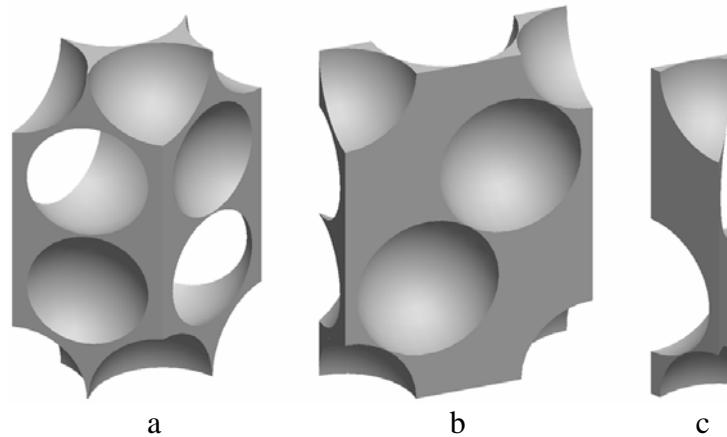


Fig. 1. Geometry of computational domain for determining effective diffusion coefficient for unit cells with (a) rhombic, (b) rectangular, and (c) triangular cross sections.

The effective diffusion coefficient in the bulk colloidal crystal is calculated at various values of its porosity. The calculated results agree well with the literature data. It is found that, for close packed spherical particles, the relative effective diffusion coefficient in the bulk colloidal crystal is 0.16. The thicknesses of transient zones adjacent to the electrode surface and outer boundary of colloidal crystal and the effective diffusion coefficients for these zones are determined. The dependence of effective diffusion coefficient on the number of spherical particle layers in the colloidal crystal is obtained (Fig. 2). The distribution of the limiting current density over the electrode surface is analyzed at various numbers of particle layers.

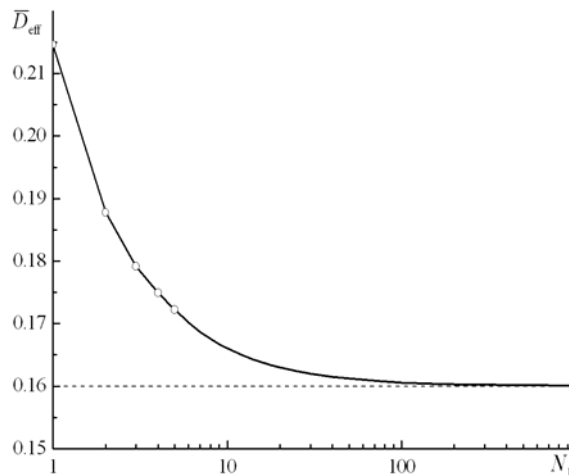


Fig. 2. The dependence of dimensionless effective diffusion coefficient on the number of particle layers in the colloidal crystal.

Molecular Dynamics Simulations of Diffusion of Na⁺ and Cl⁻ ions in concentrated Glucose Aqueous Solutions

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Mechanism of diffusion of small solute particles in dense liquid of larger particles is a challenging problem which is not properly understood so far (see, e.g. Refs.[1,2]). We made an attempt to address this issue using molecular dynamics (MD) method developed by Kast et al [3]. In this formalism a bath of virtual particles obeying the Maxwell distribution mimics the medium viscosity (friction effects) induced by solvent molecules. MD simulations were performed for Na⁺ and Cl⁻ ions dissolved in glucose aqueous solutions of different concentrations (up to 3 M). The ions and carbohydrate molecules are treated as spherical particles; the “glucose - glucose” and “ion-glucose” interactions are described by using the LJ pair potentials which are defined by two parameters (r_{\min} and ϵ). In our simulations we used a set of r_{\min} values which depend on the concentration of glucose solution. As the potential depth (ϵ) is difficult to estimate exactly, this quantity was varied in a certain region. We thoroughly investigated the influence of association of glucose molecules on mobility Na⁺ and Cl⁻ ions. The main emphasis was put on understanding the mechanism of diffusion of ions at qualitative level. The results of MD simulations are compared with predictions based on the Einstein-Smoluchowski formula, as well as with original experimental data on the electroconductivity of NaCl in glucose and sucrose aqueous solutions.

This work was supported in part by the RFBR (project № 11-03-01186-a).

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Theory vs molecular modelling of charge transfer reactions: some problems and challenges

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Modern quantum mechanical theory (see, for example Refs.[1-3]) constitutes a solid basis to gain a deep insight into the mechanism of charge transfer reactions in condensed media. The theory enables to estimate the rate constants of various redox processes or (at least) to make qualitative conclusions on their kinetics. Although the theory plays first fiddle, we also have to make some model assumptions and to employ methods of computational chemistry. Three pertinent issues are presented and illustrated by different examples. Firstly, we dwell on the problem of solvent coordinate and reaction free energy surfaces which is addressed in terms of stochastic theory. Secondly, effects of solvent quantum modes on the reaction rate are considered for water and ionic liquids. These effects are shown to decrease noticeably the activation barrier. In the both problems complex dielectric spectra of medium play an important role and facilitate analysis. Finally, we discuss the various aspects of model calculations of orbital overlap resting on different quantum chemical approaches; main emphasis is put on heterogeneous redox systems. This problem is crucial for estimations of electronic transmission coefficient (weak overlap limit) and predictions of catalytic properties of metal surfaces (strong overlap limit). Special attention is paid on pitfalls of some model approaches. An attempt is made to compare the results of calculations with available experimental data.

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Quantum Chemical Modeling of the Gas-Phase Adsorption of Hydrogen on (111) Face of IB Metals

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Hydrogen adsorption on metal surface plays an important part in many chemical and electrochemical processes. All of these processes begin from hydrogen adsorption on solid surface. Theoretical researchers of hydrogen adsorption afford closely understanding these acts. To study hydrogen adsorption on (111) face of IB metals density-functional calculations with PBE exchange-correlation functional were performed. LanL2DZ pseudopotential and aug-cc-pVDZ basis set were used for Cu, Ag, Au and H atom respectively. Me₃₁(19, 12) cluster was chosen as (111) adsorption surface model. Adsorption capabilities were calculated in all possible adsorption positions of hydrogen atoms on metal face (hollow, top, bridge). Results of our calculations are represented in table 1.

Table 1. Adsorption capabilities of H on (111) face IB metals without/with relaxation

Metal	position	E _{ads} , kJ/mol	R _{Me-H} , pm	Q(H), a. u.
Ag	<i>bridge</i>	-169.8/-163.8	110.9/110.2	-0.155/-0.156
	<i>top</i>	-110.9/-121.3	165.0/165.1	-0.031/-0.031
	<i>hollow 1</i>	-180.9/-185.9	89.5/86.7	-0.190/-0.193
	<i>hollow 2</i>	-196.5/-201.2	88.7/85.7	-0.215/-0.235
Au	<i>bridge</i>	-198.8/-234.9	101.4/97.9	0.015/-0.010
	<i>top</i>	-170.1/-201.3	156.9/157.0	0.131/0.134
	<i>hollow 1</i>	-209.8/-245.8	81.4/77.6	-0.031/-0.059
	<i>hollow 2</i>	-218.2/-253.0	83.9/78.4	-0.053/-0.081
Cu	<i>bridge</i>	-211.4/-217.0	107.2/106.3	-0.116/-0.137
	<i>top</i>	-143.8/-148.1	152.4/152.6	0.013/0.018
	<i>hollow 1</i>	-220.3/-238.3	90.9/87.0	-0.144/-0.179
	<i>hollow 2</i>	-234.2/-238.3	88.3/90.0	-0.179/-0.179

The calculations show that Au is the most active metal to atomic hydrogen adsorption, Ag shows the smallest activity. Consideration of surface relaxation gives visible correction to all adsorption capabilities on all investigated metals. Dependence of adsorption energy E_{ads} from position of adsorbate doesn't changes. Lengths from hydrogen atom to metal surface are in good agreement with calculated adsorption energies. *Hollow 1* and *hollow 2* positions have the smallest R_{Me-H} values, whereas the biggest length is observed in case of *top* position. Consideration of surface relaxation leads to higher values of electron density transfer from metal to adsorbate, especially for *hollow 1* and *hollow 2* positions. Adsorbate charge is changing in a series: Ag > Cu > Au, as in case of calculations without relaxation.

Polymeric Sulfonic Acids as Molecular Templates for Preparing Conducting Polymers with Tunable Morphology, Electrochemical and Spectral Properties

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Electrochemical and chemical synthesis of conducting polymers in the presence of polymeric sulfonic acids results in the formation of interpolymer complexes. Both commercial (poly(2-acrylamido-2-methyl-1-propanesulfonic acid) (PAMPSA, flexible chain), poly(styrenesulfonic acid) (PSSA, flexible chain)) and laboratory-synthesized (poly-(p,p'-(2,2'-disulfonic acid)-diphenylene-tere-phthalamide) (t-PASA, rigid chain), poly-(p,p'-(2,2'-disulfonic acid)-diphenylene-iso-phthalamide) (i-PASA, semi-rigid chain)) were used for chemical and electrochemical oxidative synthesis of polyaniline (PANI). It was shown that aniline polymerization significantly accelerates in the presence of the polyacids, which is due to preliminary association of aniline molecules with the sulfonic groups of the polyacid, which creates preforms for PANI-phase nucleation, and increased local concentration of protons near the polyacid backbone. The course and duration of PANI synthesis and the properties of obtained interpolymer complexes significantly depend on the rigidity of polyacid backbone and the structure of sulfoacid-containing side chains. The electrodeposited layers possess much better adhesion to metallic and oxide (ITO, FTO) substrates compared to ordinary PANI, which is an important advantage as far as electrochromic and electroluminescent applications are concerned. AFM studies showed that, depending on the polyacid dopant, the films possess controllable morphology, from smooth to highly-porous one and wider pH-range of electroactivity, which is useful for biological and electrocatalytic applications. Spectroelectrochemical and electrochemical studies (see Fig.) showed retarded formation of quinoid fragments and high NIR absorption in the films of interpolymer complexes of PANI with rigid-chain polyacids. The results are discussed in terms of molecular interactions between polymeric chains of PANI and the polymeric acids: flexible-chain polyacids can adapt their conformation to match the conformation of PANI macromolecule, while the rigid-chain polyacids can not.

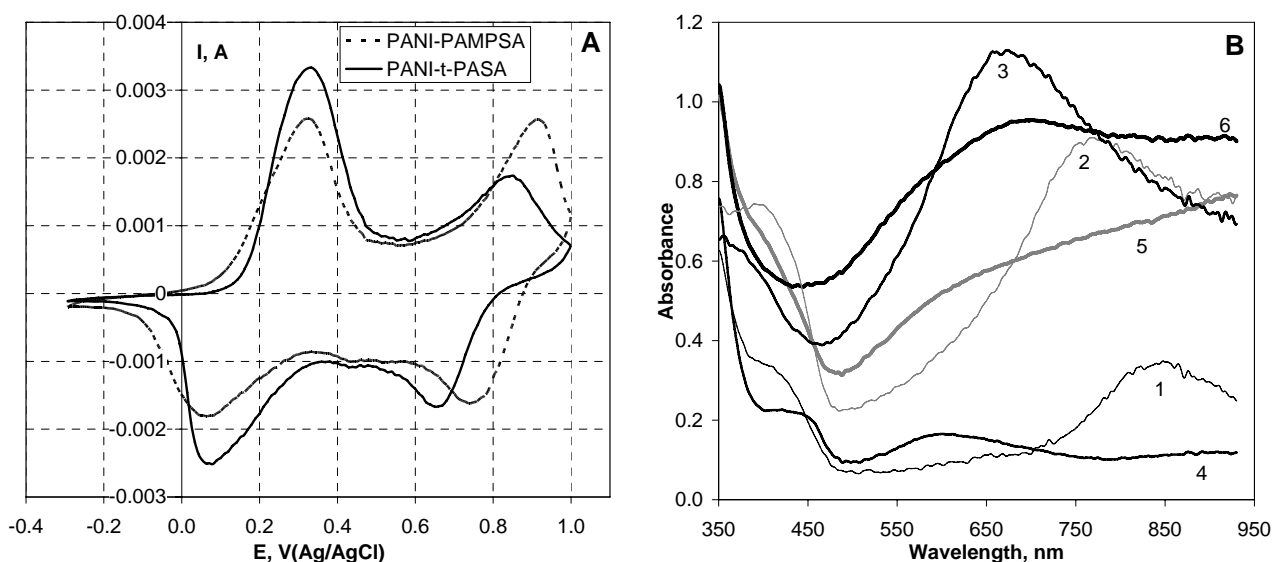


Fig. Electrochemical (A) and spectroelectrochemical (B) characteristics of electrodeposited films of interpolymer complexes of polyaniline with flexible-chain (PAMPSA) and the most rigid-chain (t-PASA) polymeric acids measured in 1M aqueous HCl: PANI-PAMPSA (B1-0.0V; B2-0.4V; B3-0.8V(Ag/AgCl)); PANI-t-PASA (B4-0.0V; B5-0.4V; B6-0.8V(Ag/AgCl)).

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Studies of electrocatalytic systems using X-ray absorption spectroscopy

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Core-shell electrocatalysts are of great interest for the oxygen reduction reaction (ORR) in proton exchange membrane fuel cells (PEMFCs) due to reported enhancements in activity when compared with the benchmark Pt/C electrocatalysts.

X-ray absorption spectroscopy offers unique insights into the electronic and geometric structure of these systems under in situ operating conditions, and how the structure can change in an electrochemical environment. XAS measurements can be combined with other in situ spectroscopic measurements, X-ray diffraction and electron microscopy to provide a fuller picture of the catalyst structure

This talk will include an overview of the technique and experimental set up and focus on some recent in situ XAS investigations of core-shell electrocatalysts. The first system is looking at the formation of core-shell catalysts in situ by means of the underpotential deposition of a sacrificial Cu shell on supported Au nanoparticles followed by the subsequent galvanic displacement of the Cu by Pd. The effect of preparation route on the catalyst structure is investigated as a function of the applied potential. The second system investigated is the aging of Pd core Pt shell supported nanoparticles, investigation the effect of shell thickness and applied potential on the electrocatalyst structure.

Ethylene Glycol - water mixtures: Information from MD Simulations

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Ethylene glycol has a flexible and symmetric H-O-C-C-O-H chain structure. The physical properties of ethylene glycol depend on chain angles and aggregation. The purpose of this work is to investigate dynamical and structural properties of pure ethylene glycol in wide temperature ranges.

Various properties of ethylene glycol (EG) were studied using molecular dynamics simulations. Two all-atom OPLS force fields were used to describe the intermolecular and intramolecular interactions of liquid EG. The average molecular dipole moment and the diffusion constants from this model are in good agreement with experimental values. The MD simulations were performed with the DL_POLY package and with GROMACS.

Trajectories of a few nanoseconds each were analyzed with respect to structural probability distributions and to dynamical properties. Results from the former can be understood in terms of intramolecular angles. For example the probability distributions of the intramolecular angles are not independent of each other. As an example of time-dependent processes, also the dynamics of angle flipping were investigated in detail. If a molecule starts to change its angles, it normally does so many times until it reaches a stationary state again.

We discuss these features as function of the temperature and of the mole-fraction in EG/H₂O mixtures. Relaxation modes of hydrogen-bond related and other processes were extracted from the trajectories and are discussed in relation with experimental spectra and analytical theory.

We have further investigated new spectral correlations and tried to find a good way to visualize the dynamic hydrogen bond network. Our aim there is to show that interactive analysis and visualization adds a new angle the analysis of such systems.

The Effect of Deposition Mode on the Oxotungstate Films Formation from highly Acidic Solutions

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During the last decade we demonstrated that it is possible to deposit oxotungstate electrochromic films from acidic oversaturated tungstate solutions avoiding peroxide as conventional additive [1,2]. This fabrication technique allows to tune electrochromic properties of the films by changing solution composition [3,4]. The most important synthetic factor affecting the behaviour of the films was found to be molecular structure of isopolytungstate anions (oxide precursors in deposition solution).

At present, we report a systematic study of the influence of solution pH, nature of supporting anion (sulfate or chloride), total tungstate concentration, additives of vanadates and molybdates, as well as of organic co-solvent (acetonitrile) on the rate of oxotungstate films growth. Degradation stability and recharging behaviour of the films in 0.5 and 2 M sulfuric acid solutions is also addressed. These properties are studied after ageing (stabilization) of the as-deposited amorphous films in supporting electrolyte. Aged films consist of defective hydrated tungstic acid $\text{WO}_3 \cdot 2\text{H}_2\text{O}$ independently on solution composition.

Main advantage of our electrodeposited oxides, as compared to wider known WO_3 electrochromic materials, consists in pronounced coloration at potentials above zero in RHE scale. In this potential region the ratio of W(V) to W(VI) is already ca. 0.1, when for usual WO_3 the pronounced reduction starts at negative RHE potentials. Optical transmittance of the films on ITO in visible and near infrared spectral range is reported in combination with in situ Raman spectra. Both techniques confirmed that the coloration of all films is defined by reduction of terminal or/and non-terminal W-atoms depending on the reduction potential.

The study is supported by RFBR, project No 11-03-00902a.

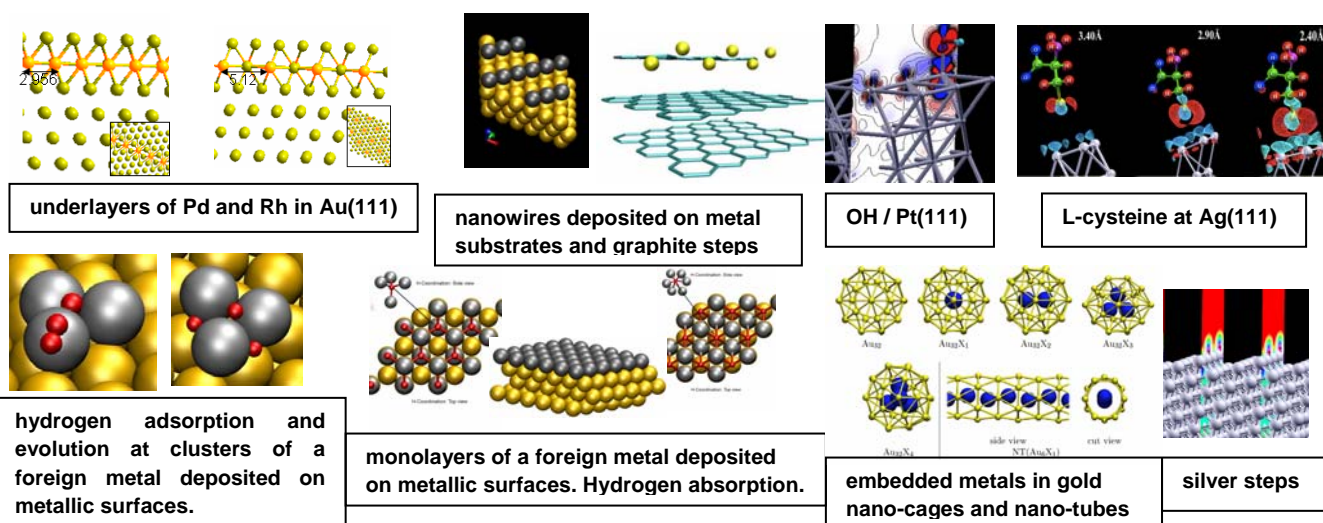
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Electrocatalytic properties of nanostructures

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Our model for d-band electrocatalysis¹ combines results of density functional theory (DFT) with quantum mechanics calculations. In this way, it is possible to analyze the reactivity of particular electrode structures in an electrochemical environment. This method is not limited to single crystal surfaces, but the effect of different nanostructures such as steps, overlayers, and alloying can be incorporated as well. The advantage of our combined methodology is that it makes possible to calculate the effect of the electronic structure on the energy of activation, while DFT alone can give very useful information about thermodynamic processes. The other important aspect is that in our model are included the solvent reorganization, which plays a fundamental role in electrochemical reactions.



Important differences between the different systems in the band structure, relative position to the Fermi level and the work function have been observed, which produce strong changes in the electrocatalytic properties. In the case of the metallic substrates the influence of the strain and the chemical interactions can also be distinguished. We have mainly investigated the electrocatalytic activity of these nanostructures for the hydrogen absorption, oxidation and evolution reactions. Recently, we have started to study other more complicated reactions such as the OH adsorption², oxygen reduction and L-cysteine adsorption³.

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Using X-Ray Photoelectron Spectroscopy for studying electrode/electrolyte interfaces

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X-Ray Photoelectron spectroscopy (XPS) is a powerful analytical method sensitive to the composition and the oxidation state of components located on the surface and in the near-surface region of materials. However, application of XPS requires ultra-high vacuum thus severely restricting the range of systems which can be investigated. The capability of the XPS for probing the chemical state of surfaces and interfaces has inspired various quasi in situ approaches for studies of electrode/electrolyte interfaces, including emersed electrodes, frozen electrolytes, etc. Recent advances in vacuum and analyzer technologies have resulted in the development of specialized instruments at synchrotron facilities which allow performing the so-called Ambient Pressure Photoelectron Spectroscopy (APPES) measurements in the pressure range of millibars [3]. Development of the APPES has boosted in situ studies of various catalytic [4] and recently also electrocatalytic [5] systems.

After a short introduction and an overview of various approaches we will concentrate on two examples of the application of the XPS to the studies of the electrode/electrolyte interface. The first refers to the investigation of Ag single crystal electrodes emersed from alkaline electrolytes which allowed us to follow the formation of various oxygen containing species at the silver/electrolyte interface [1]. The second example refers to the application of APPES to the study the interface between Pt nanoparticles and a phosphoric acid imbibed polymer membrane [6]. We will show that this approach allows one the in situ probing of the potential distribution, as well as the observation of various potential-driven processes including Pt surface oxide formation, and adsorption and migration of phosphoric acid in the catalytic layer.

Acknowledgements

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Theoretical Investigations of Oxygen Reactions

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Oxygen reduction is one of the most important electrochemical reactions; its inertia is the main obstacle to the development of efficient fuel cells. Theoretical investigations of this reaction have focused on the reaction steps in acid solutions; using density functional theory (DFT) as a tool, the thermodynamics of reaction mechanisms have been evaluated by several groups. In contrast, reactions in alkaline media have been neglected, even though the first fuel cells that were used by NASA in space technology were alkaline cells.

In alkaline media, the first step is the transfer of one electron to the oxygen molecule according to:



Often, this is also the rate determining step. The kinetics of this reaction cannot be elucidated by DFT alone. Therefore, we have developed our own theory (Santos and Schmickler, [1,2]) that combines DFT with electron transfer theory.

Specifically, we have investigated reaction (??) on a Au(100) electrode, since it is known that it is the rate-determining step for oxygen reduction on that surface [3]. The interaction of the oxygen molecule with Au(100) is very weak; in the vacuum, the energy of adsorption is almost zero. Consequently, the reaction occurs almost like an outer-sphere electron transfer; however, the O_2^- ion is attracted to the surface, and this lowers the activation energy. At the equilibrium potential for reaction (1), the reaction is quite fast, with an activation energy of the order of 0.4 eV.

Another important reaction involving oxygen is the adsorption of the hydroxyl ion in alkaline solutions:



Using the same formalism as for oxygen, we have investigated the kinetics of this reaction on Pt(111). In good accord with experimental data, we have found this reaction to be very fast.

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Photogeneration, Transport and Recombination of Charge Carriers in Organic Donor-Acceptor Solar Cells

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Intensity modulated photocurrent (IMPS) and photovoltage (IMVS) spectroscopies were used to study the mechanism of photoprocesses in P3HT:PCBM bulk heterojunction organic solar cells at various light intensities. The use of the IMPS and IMVS frequency domain techniques allowed us to separate the bulk and interfacial processes such as photogeneration, exciton separation, transport and recombination of photoexcited carriers, as well as to gain a valuable insight into the mechanism of losses in these devices. The results provide direct evidence that interfacial non-geminate recombination is one of the dominant loss and ageing mechanisms in bulk heterojunction organic solar cells. The trapping of photoexcited holes in the P3HT phase was found to contribute to the increased recombination rate. The results suggest that promising ways of improving the efficiency of bulk heterojunction solar cells may be reducing the charge trapping both at and near the P3HT:PCBM interface, as well as improving the efficiency of charge extraction at contacts.

Acknowledgements

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Proton Discharge On Charged Metal Surfaces. A Reactive Trajectory Approach

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A reactive trajectory approach for the study of proton discharge from aqueous environments on charged metal surfaces is reviewed. It is based on an extension of a minimalistic empirical valence bond (EVB) model to study proton transfer in the bulk. Extensive quantum mechanical density functional theory calculations were parametrized for the EVB force field [1]. The model is used to investigate reactive (discharging) proton trajectories that were started in the bulk of a water film adsorbed on charged metal electrodes. The results indicate a transition between a reaction-dominated regime at moderate negative charges, where the rate constant increases exponentially, to a "transport limited" regime where the transfer rate is almost independent of the surface charge density (at more negative surface charge densities) [2,3].

Recent extensions of the model to introduce background electrolytes with and without specific ion adsorption are discussed. Comparison between the electrochemically active Pt(111) surface and the much less reactive Ag(111) surface indicate that proton discharge on silver occurs only at unrealistically large negative potentials. This trend is in good agreement with experiment. The simulation results hint that part of the large differences in electrochemical behavior between the two metals might -- at least partially -- be due to the strikingly different water structure at the two interfaces.

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LiMn_xFe_{1-x}BO₃/C Composites: Synthesis and Electrochemical Properties

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Recently it was proved [1] that transition metal borates may be considered as perspective cathode materials for Li-ion batteries. Borate anion-containing structures provide an area of interest due to their low molecular weight resulting in higher electrochemical capacity and therefore higher energy density. In this study we have focused on solid solution of complex borates LiMnBO₃-LiFeBO₃.

LiMn_xFe_{1-x}BO₃ solid solution was previously studied at [1] and [2]. Our work provides an adoption of sol-gel route to the synthesis of composites LiMn_xFe_{1-x}BO₃/C. Polyethylene glycol (PEG) was used as a carbon source.

Since LiMBO₃ (M = Mn, Fe) forms 2 types of polymorphs – monoclinic (M=Mn, Fe) and hexagonal (M=Mn), one may also suggest two possible structural types for the LiMn_xFe_{1-x}BO₃ solid solutions. In our experiments we confirmed formation of the monoclinic LiMn_xFe_{1-x}BO₃ that correlates with data [2].

The control of iron oxidation state was conducted by means of Mossbauer spectroscopy. All the samples investigated were single-phase according to X-ray diffraction data. Nevertheless, each sample contained different amount of Fe(III) depending on sintering conditions. Sintering in Ar flow, sealed quartz tube and sealed quartz tube with different types of getters were performed. The best results have been achieved in sealed quartz tube with iron getter and Fe (II) content of not less than 90% was reached.

Scanning electron microscopy demonstrated that solid solution composite samples had similar morphology and had been composed of spherical particles of 200-800 nm diameter. Carbon content in the composites was determined by means of thermal analysis; it is in the range of 5-7 wt%. Preliminary electrochemical study revealed the approximately 40% of theoretical capacity at C/40 rate. Nowadays the research devoted to the increase of the capacity values is in progress.

Acknowledgements

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Quantum Chemical Modeling of the Gas-phase Adsorption of Methanal, Anion and Cation of Methandiol on (100), (110), (111) Faces of IB Metals

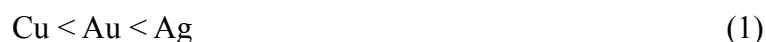
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Regularities of gas-phase adsorption of methanal on IB metals surfaces attract attention due to the rapid development of heterogeneous catalysis on transition metals. It is known that CH₂O is the main product originated in the industrial partial oxidation of methanol on silver surfaces [1] and it is an important intermediate in the industrial synthesis of methanol on supported copper surfaces.

In this work the quantum chemical modeling of the gas-phase adsorption of methanal and ionic forms of methandiol on (100), (110), (111) faces of Cu, Ag, Au is carried out in the framework of the density functional theory (B3LYP hybrid functional). 6-31G(d,p) basis set for H, C and O atoms and LanL2MB pseudopotential for metal atoms were used.

The Me(100) and Me(110) surfaces were represented in the Me₂₅(16, 9) cluster. The Me(111) surface was represented in the Me₃₁(19, 12) cluster. Results (tbl. 1) show common regularities of the faces orientation and the metal nature influence on adsorption energy:



The adsorption energy of all investigated particles, except CH₃O⁺ on (100) face decreases in a series (1). The adsorption energy of methanal on (111) face and anion methandiol on (110) face connected with (1). The adsorption energy of cation methandiol on (100) and (110) faces and methanal on (110) face changes as (2). The adsorption energy of cation methandiol on (111) face of Cu and Ag is approximately equal (3). Pattern (4) corresponds to the adsorption energy of anion methandiol on (111) face. Thus only metal nature exerts influence on the adsorption energy of methadiol cation and anion on (100) face. In other cases the adsorption energy connected with metal nature and type of faces. Adsorption activity is greatest on (110) face of all investigated metals. It is known that CH₃O₂⁻ adsorbed on IB-metals in water solutions dissociates with formation of atomic hydrogen [2]. In this work the possibility of dissociative gas-phase adsorption of anionic form of methylene glycol was examined. It was shown that CH₃O₂⁻ dissociates on (111) face of Cu and on (110) face of Au with formation of formic acid anion and two atoms of hydrogen:



Calculated energies of CH₃O₂⁻ dissociation on surface are -22.1 kJ/mol (Cu) and -2.5 kJ/mol (Au).

Table 1. Adsorption energy, kJ/mol

Particle	Cu			Ag			Au		
	(100)	(110)	(111)	(100)	(110)	(111)	(100)	(110)	(111)
CH ₂ O	-36.1	-52.9	-21.9	-24.0	-48.1	-11.1	-25.8	-42.6	-14.9
CH ₃ O ⁺	-272.7	-377.1	-238.0	-255.0	-323.5	-237.9	-172.4	-236.6	-178.4
CH ₃ O ₂ ⁻	-369.1	-463.2	-304.3	-319.3	-379.4	-276.4	-348.4	-403.1	-334.9

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Materials development for SOFC: status and development perspectives

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Solid Oxide Fuel Cells will soon turn into an important technology to directly turn natural gas and hydrogen into electricity. Due to the high temperature and challenging operating conditions, many problems of materials persist. SOFC will have to operate for 80 000 hours at high efficiencies. The presentation sketches the current status of materials development and points out main challenges and future development lines.

Electrochemical Properties of Pd and Au Nanoclusters on PEDOT Support

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Electrocatalytic activity of metal nanoparticles and nanostructured metal alloys supported on different substrates has attracted much attention during the recent years due to possible applications of such materials in electrocatalysis, fuel cells and sensor devices. In the present work, palladium and gold nanoclusters, as well as palladium-gold alloys stabilized by poly-3,4-ethylenedioxythiophene (PEDOT) were synthesized by electroless deposition of gold or palladium particles. The syntheses were carried out by immersion ($t=30-800s$) of a reduced PEDOT film into the solutions of $HAuCl_4$ or $PdCl_2$ with varied concentration ($5 \cdot 10^{-4} - 5 \cdot 10^{-3} M$) in $0.1 M H_2SO_4$. Spontaneous deposition of metals takes place due to the redox reaction of reduced fragments of PEDOT film with $AuCl_4^-$ ions or $Pd(2+)$ ions acting as oxidizing agents. The consecutive deposition of gold and palladium particles allows to obtain Au/Pd alloys on the surface of PEDOT with different ratio of Pd to Au.

X-ray photoelectron spectroscopy (XPS) data have confirmed the presence of metallic palladium or gold in the polymer films. Morphology of composite films as well as the size of Pd or Au nanoparticles and their distribution were characterized using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). It was shown that nanoparticles were non-uniformly dispersed on the surface and in the pores of polymer matrix. TEM images of composite films showed remarkable effect of loading time and concentration of metal ions on the size of metal particles and their density.

The electrochemical characterization of metal-polymer composites was performed by using cyclic voltammetry and RDE voltammetry measurements in solutions of $0.1M H_2SO_4$ and $0.1M HClO_4$.

Cyclic voltammograms of PEDOT/Pd composite film in diluted perchloric acid exhibit well-defined peaks of hydrogen adsorption/desorption that are typical for noble metals. The height of peaks was almost proportional to the deposition time. At more positive potentials CVs show cathodic peaks of the reduction of surface palladium oxide. The reduction charge is apparently related to the surface area of palladium particles available for oxygen sorption/desorption reaction. The determined charge was used for the evaluation of electrochemically active surface area of palladium particles, accounting that the charge for monolayer adsorption of oxygen on smooth Pd is known to be $C=424 \mu C/cm^2$. The electrochemically active surface area of Pd was calculated for different Pd loadings. Analogously, the real electrochemical surface area of Au particles in the PEDOT/Au composites was assessed using the charges of oxygen desorption process. The electrocatalytic activity of PEDOT/Au, PEDOT/Pd and PEDOT/Au/Pd composites in respect to the hydrogen peroxide electroreduction was measured by obtaining CVs and RDE voltammograms in phosphate buffer solution ($pH=6.86$).

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Diversity of electrochemistry: the specific problems of molecular models and their experimental verification

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Intersections of electrochemistry with various branches of chemistry, physics, and material science are briefly reviewed. The complexity of electrochemical systems is discussed, which still excludes the straightforward consideration at molecular level. In addition, for majority of electrochemical systems some basic contradictions arise between the models of electrode and electrolyte (e.g. metal and liquid solution). Under these circumstances, one is always forced to combine physical theory with computational activities, and to arrange various types of parallel indirect experimental tests.

The lecture presents some examples of experimental work related to step-by-step theory verification. These examples illustrate evolution of Tafel plots understanding, from empiric relations to various levels of theory.

Similar problems for solid state electrochemical phenomena are outlined as well.

Diffraction studies of ultrafine powders and nanostructured materials

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Diffraction method is a powerful tool for studying highly-dispersed and nanostructured materials. However, diffraction patterns of these objects have many features due to nanostructure. Therefore not only lattice parameters and atomic coordinates should be taken into account, but also shape and size of nanoparticles (nanoblocks), as well as how they come into contact with each other. Diffraction analysis requires special techniques, such as RDF method (Radial Distribution Function) [1], DFA method (Debye Function Analysis) [2-3] and modelling method for 1D nanostructures [4]. Several case studies and examples of nanostructured objects are presented [5-7].

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All-Solid-State Supercapacitors with Lithium Composite Solid Electrolytes

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Supercapacitors are able to provide a great amount of energy in a short period of time, making them useful for many applications. At present, in supercapacitors one uses acidic or basic liquid electrolytes or ion-conducting polymers. Acids and alkaline solutions are strong corrosion agents that leads to fast degradation of the electrochemical cells. Organic liquid electrolytes are flammable, they are easy to ignite with exposure to high temperatures. To solve the safety problem, it is strongly desired to replace flammable electrolytes with nonflammable electrolytes.

Inorganic solid electrolytes are essentially nonflammable and thus may be regarded as the most promising electrolytes for development of solid-state electrochemical devices. The aim of this work was to develop the solid-state supercapacitors with electrodes of activated carbon with oxide additives and solid electrolyte. As solid electrolytes we used the following systems: (i) lithium-ion conducting composites based on lithium perchlorate reported earlier [1-2]; (ii) proton-conducting nanocomposites based on acid salts of cesium prepared and investigated earlier [3]. As active electrode materials highly porous carbon was used with admixtures of metal oxide nanoparticles. Electrode materials were made by mixing of active material with solid composite electrolyte and carbon black as electron conductivity additive. The cells were prepared by hot-pressing. The cells were investigated by methods of impedance analysis, voltammetry and charge-discharge cycling. The report presents the results obtained.

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Measurement of Electrophysical Parameters of $\text{LaF}_3\text{-SrF}_2$ Solid Electrolytes In Planar Geometry

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The crystals of the fluorite MF_2 ($M=\text{Ca, Sr, Ba, Cd}$) and RF_3 phases (R -rare earth elements), and mixed fluorite crystals on their basis $\text{R}_{1-x}\text{M}_x\text{F}_{3-x}$ are materials demonstrating high ionic conductivity. The superionic conductivity in such compounds results from introduction of the anionic vacancies compensating the difference of the charges of the cations at the heterovalent replacements $\text{R}^{+3} \rightarrow \text{M}^{+2} + \text{V}_\text{F}$ [1]. Other way consists in the transition from bulk single crystals to thin films and heterostructures. For example high level of conductivity can be reached by alternation of $\text{BaF}_2\text{-CaF}_2$ layers [2].

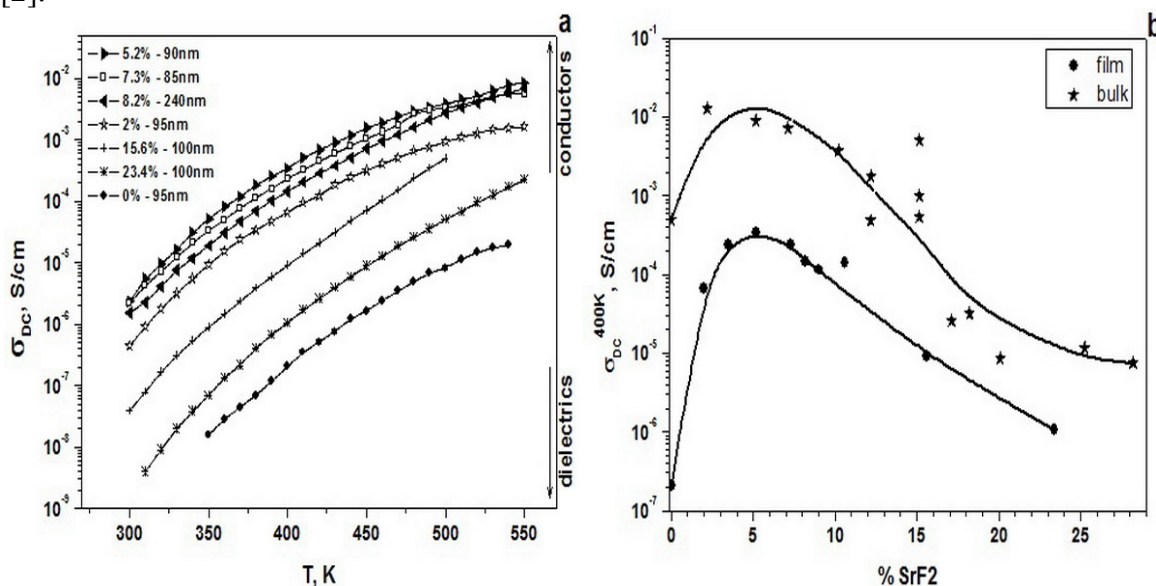


Figure 1. The temperature dependencies of DC-conductivity (a) and comparison of conductivities between bulk and thin films crystals at 400K (b).

This work is devoted to study the ionic conductivity of the thin films of the solid solutions $\text{La}_{1-x}\text{Sr}_x\text{F}_{3-x}$ with different thicknesses (from 40 to 260 nm) and different stoichiometric compositions ($x=0\div 0.24$). The thin films have been grown up by molecular-beam epitaxy (MBE) on the dielectric glassceramic substrates. The electrical properties have been studied by the dielectric spectrometer Novocontrol BDS'80 in the wide frequency (from 10^{-1} to 10^6 Hz) and temperature (from 0 to 300°C) ranges in the planar geometry using inter-digital electrodes. The temperature dependencies of different electrophysical parameters have been obtained for all investigated samples. The DC-conductivities have been estimated from the impedance hodographs $Z''(Z')$ and the temperature dependencies have been constructed for all investigated samples (fig.1a). We have studied the influence of the doping on a value of the conductivity (fig.1b). The activation energies and the characteristic time of the jumps have been estimated. The equivalent electric circuit describing processes of charge transport in the samples is proposed.

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Crystal Structure of Perovskite-Type Oxides $\text{La}_{1-x}\text{Sr}_x\text{Fe}_{2/3}\text{Mo}_{1/3}\text{O}_3$, $x=0, 0.5, 1$

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Complex transition metal oxides with perovskite-related structure $\text{A}_2(\text{B},\text{B}')_2\text{O}_6$ (double perovskites) containing two different B-cations, show important magnetic and electrical properties. These properties depend on nature of B-cations and their degree of ordering in the crystal structure. Iron-containing double perovskites attract special interest since. For example, $\text{SrFe}_{2/3}\text{Mo}_{1/3}\text{O}_3$ can be used as an anode material in solid oxide fuel cells (SOFC).

The aim of this work is synthesis of the compounds $\text{La}_{1-x}\text{Sr}_x\text{Fe}_{2/3}\text{Mo}_{1/3}\text{O}_3$, $x=0.0, 0.5$ and 1.0 and investigation of their crystal structures and magnetic properties. $\text{SrFe}_{2/3}\text{Mo}_{1/3}\text{O}_3$ ($x=1.0$) and $\text{LaFe}_{2/3}\text{Mo}_{1/3}\text{O}_3$ ($x=0.0$) have been known for a long time [1, 2, 3]. However, information on their structures and properties are controversial. In addition, crystal structure and properties of $\text{La}_{1-x}\text{Sr}_x\text{Fe}_{2/3}\text{Mo}_{1/3}\text{O}_3$ perovskite haven't been studied yet.

$\text{La}_{1-x}\text{Sr}_x\text{Fe}_{2/3}\text{Mo}_{1/3}\text{O}_3$ ($x=0, 0.5$) samples were obtained by heating stoichiometric amounts of La_2O_3 , Fe_2O_3 , MoO_2 , Mo and Sr_3MoO_6 at 1150°C in Ar/ H_2 (9%) flow for 24 hours. $\text{SrFe}_{2/3}\text{Mo}_{1/3}\text{O}_3$ was synthesized by citric method using $\text{Sr}(\text{NO}_3)_2$, $\text{Fe}(\text{C}_2\text{O}_4)\cdot 2\text{H}_2\text{O}$ and $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ with final heating at 1000°C in Ar/ H_2 (9%) flow for 24 hours. According to XRD data, ordering of Fe and Mo cations doesn't occur in $\text{LaFe}_{2/3}\text{Mo}_{1/3}\text{O}_3$ ($x = 0$) and $\text{La}_{0.5}\text{Sr}_{0.5}\text{Fe}_{2/3}\text{Mo}_{1/3}\text{O}_3$ ($x = 0.5$) crystal structures (Gd FeO_3 -type, Sp. gr. *Pbnm* ($x=0.0$: $a=5.583(3)\text{\AA}$, $b=5.611(3)\text{\AA}$, $c=7.902(3)\text{\AA}$; $x=0.5$: $a=5.564(3)\text{\AA}$, $b=5.580(2)\text{\AA}$, $c=7.872(4)\text{\AA}$). XRD pattern of $\text{SrFe}_{2/3}\text{Mo}_{1/3}\text{O}_3$ can be indexed in I-centered tetragonal cell ($a=5.577(2)\text{\AA}$, $c=7.841(3)\text{\AA}$). Crystal structure of $\text{La}_{0.5}\text{Sr}_{0.5}\text{Fe}_{2/3}\text{Mo}_{1/3}\text{O}_3$ ($x = 0.5$) was refined using neutron diffraction data (Sp. gr. *Pnma*, $a = 5.5810(2)\text{\AA}$, $b = 7.8828(2)\text{\AA}$, $c = 5.5846(2)\text{\AA}$).

Preliminary results of Mössbauer study of the prepared compounds indicates that increasing of Sr^{2+} content in $\text{La}_{1-x}\text{Sr}_x\text{Fe}_{2/3}\text{Mo}_{1/3}\text{O}_3$ does not lead to the significant change of the oxidation state of iron, which remains +3. Therefore, oxidation of molybdenum from Mo^{3+} to Mo^{6+} takes place with increasing of Sr^{2+} content. Antiferromagnetic ordering of magnetic moments of B-cations for $x=0$ ($T_N=130\text{K}$) transforms into ferromagnetic one with x . Highest $T_c=470\text{K}$ is observed for $x = 0.5$.

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Carbon-silicon composite for thin-film lithium-ion batteries

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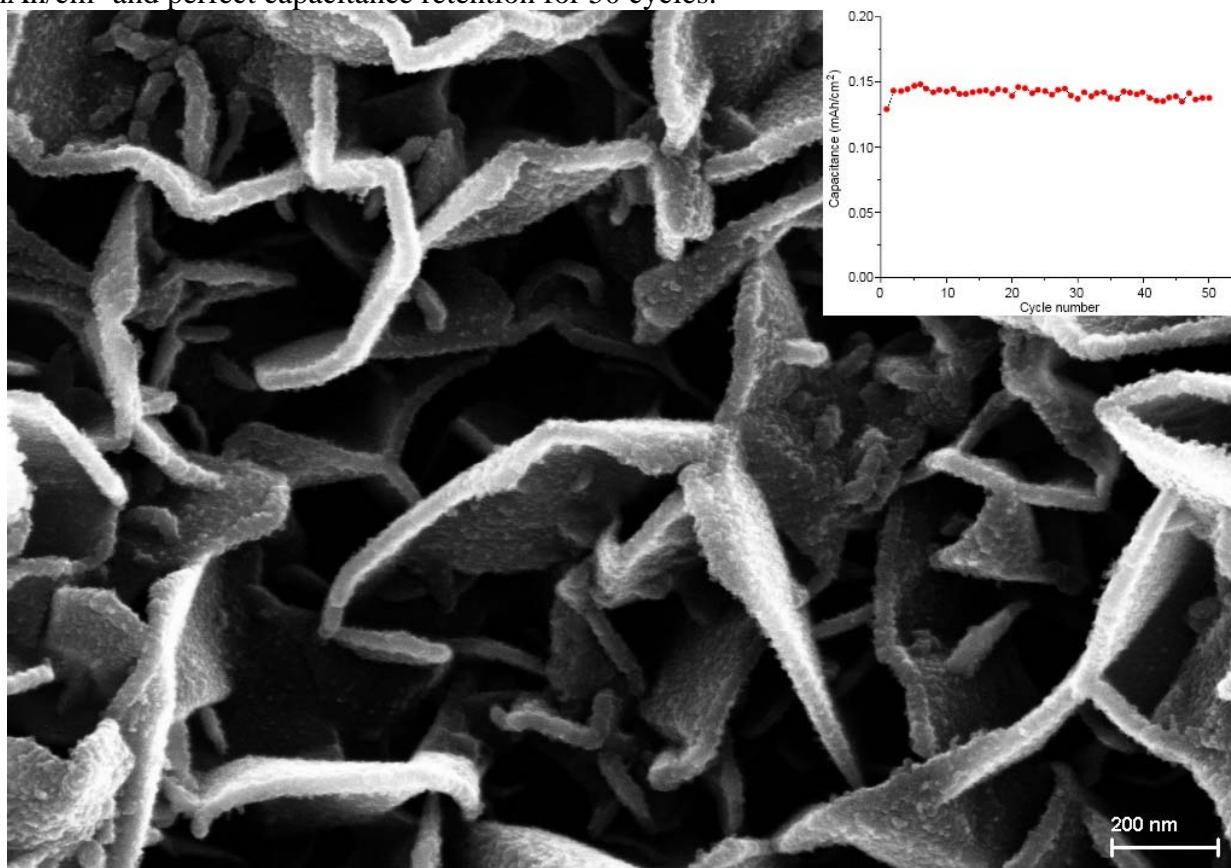
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Of all materials silicon has the largest theoretical specific lithium capacitance equal to 4200 mAh/g. Yet the mass-production of lithium-ion batteries with silicon anodes is not possible since the problem of severe capacitance fading during cycling is still not solved on a large scale. Thin silicon films has been showed to lack this disadvantage [1], and the concept of a 3D supporting framework for silicon film was proposed. We report on our realization of this concept.

We have used carbon nanowall (CNW) films grown in hydrogen-methane plasma of DC glow discharge as a support material [2]. It was covered with silicon by magnetron sputtering method. Thickness of a nanowall with silicon ranges from 20 to 30 nm, meaning silicon film thickness is 5 to 10 nm.

Resulting composite material possess large specific areal lithium capacitance of 0.14 mAh/cm² and perfect capacitance retention for 50 cycles.



SEM image of composite material. Inset - Film capacitance during cycling under 0.1 ma current.

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Visualization of the Diffusional Pathway of Mobile Ions in Ionic Conducting Ceramics through Diffraction Experiments

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Solid materials with high ionic conductivity have attracted considerable attention due to a variety of applications in solid oxide fuel cells (SOFCs), batteries, catalysts, gas sensors and oxygen separation membrane. A fundamental understanding of the nature of the superionic state has provided one of the major challenges in the fields of materials science, physics and chemistry. Geometric information of the ionic conduction and diffusion is a key to understand the conduction mechanism [1,2]. Here I review the diffusional pathway of mobile ions and crystal structure of the materials with high ionic conductivity. In the fluorite-structured ionic conductors such as ceria solid solution $\text{Ce}_{0.93}\text{Y}_{0.07}\text{O}_{1.96}$, bismuth oxide solid solution $\delta\text{-Bi}_{1.4}\text{Yb}_{0.6}\text{O}_3$ and copper iodide CuI , a similar curved diffusion pathway along the $\langle 100 \rangle$ directions is observed. In the ionic and mixed conductors with the cubic ABO_3 perovskite-type structure such as lanthanum gallate and lanthanum cobaltite solid solutions [3], the mobile ions diffuses along a curved line keeping the interatomic distance between the B cation and O^{2-} anion to some degree. The structure and diffusion path of double-perovskite-type $\text{La}_{0.64}\text{Ti}_{0.92}\text{Nb}_{0.08}\text{O}_{2.99}$, K_2NiF_4 -type $(\text{Pr}_{0.9}\text{La}_{0.1})_2(\text{Ni}_{0.74}\text{Cu}_{0.21}\text{Ga}_{0.05})\text{O}_{4+\delta}$ (Fig. 1) [4] and apatite-type $\text{La}_{9.69}(\text{Si}_{5.70}\text{Mg}_{0.30})\text{O}_{26.24}$ (Fig. 2) and $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$ [5] are described. The diffusion paths of $\text{La}_{0.62}\text{Li}_{0.16}\text{TiO}_3$ and $\text{Li}_{0.6}\text{FePO}_4$ are two- and one-dimensional, respectively.

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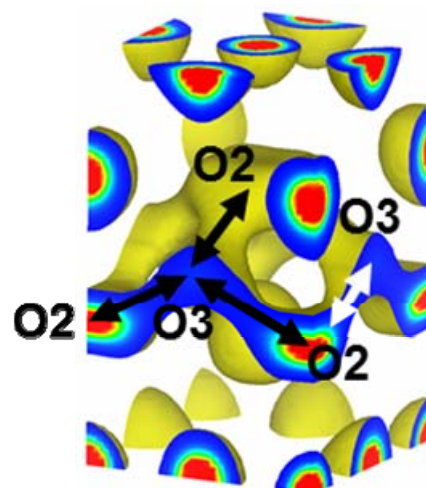


Fig. 1: Nuclear-density distribution of $(\text{Pr}_{0.9}\text{La}_{0.1})_2(\text{Ni}_{0.74}\text{Cu}_{0.21}\text{Ga}_{0.05})\text{O}_{4+\delta}$ [2,4]. The oxide ions diffuse three-dimensionally through the O2-O3-O2 sites.

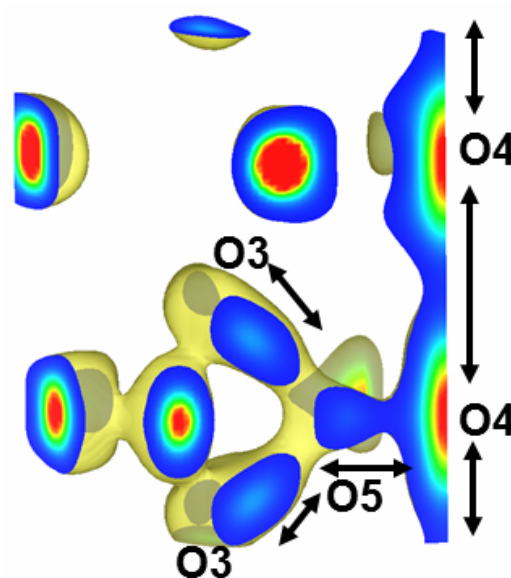


Fig. 2: Nuclear-density distribution of $\text{La}_{9.69}(\text{Si}_{5.70}\text{Mg}_{0.30})\text{O}_{26.24}$ [2]. The oxide ions diffuse one-dimensionally through the O4 site.

The Effect of Boron Oxide Addition on Lithium Conductivity of Glass-Ceramic Membranes with NASICON Structure

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Effective energy storage is highly demanded for different applications such as consumer electronics and pure electric vehicles (EV). The lithium-air batteries are among one of the most prominent solution due to high specific energy and huge capacity overcoming lithium-ion batteries by one order of magnitude.

Unfortunately, lithium-air batteries are still underestimated and could not be deployed because of safety issues and their fast degradation under ambient conditions. In particular, the highly reactive lithium must somehow be isolated from water vapor and oxygen permeating to the anode part of the cell from the surrounding atmosphere. Recently, NASICON-type lithium conductors were suggested to protect lithium anodes inside lithium-air batteries [1,2].

Preparation of NASICON glass-ceramic powders and pellets was reported by Fu [3]. Aim of our investigation was to obtain air-tight and at the same time high Li^+ -conductive glass-ceramic membranes. To avoid inevitable change of the material density during glass crystallization leading to cavities formation and thus affecting air-tightness we used boron oxide as a fusible non-crystallize additive to glass.

Glass plates were obtained by casting of the melt to the moulds preheated to 200 – 400°C. Processes of the glass crystallization were characterized by differential scanning calorimetry. Annealing of thus prepared glass plates near its crystallization temperature lead to the formation of glass-ceramics membranes with the composition $\text{Li}_{1.5}\text{Al}_{1.5}\text{Ge}_{1.5}(\text{PO}_4)_3 \cdot x\text{LiBO}_2$ ($x = 0 - 0.25$)

Electrochemical properties of the glass-ceramics were evaluated by electrochemical impedance spectroscopy and DC polarization technique. We demonstrated that conductivity of the samples vary from about 10 $\mu\text{Sm/cm}$ for 20 mol.% LiBO_2 to ca. 100 $\mu\text{Sm/cm}$ for glass-ceramics with no boron oxide added. The transference numbers for glass ceramics were estimated to be higher than 0.9. Protected lithium anodes that comprise a metallic lithium electrode, interface electrolyte layer and gas-tight glass-ceramic electrolytes with boron oxide were assembled to demonstrate lithium stability under environmental condition. It was demonstrated that round shaped anodes (20 mm in diameter) have total impedance of about 150 Ohms and no lithium corrosion is observed during weeks in humid environment.

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Structural diagnostics of functional materials in action: capabilities of X-ray synchrotron techniques

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Synchrotron radiation sources are large-scale facilities based on accelerators of light charged particles (viz., electrons or positrons) hosted by national or international research centers and open to a wide community of external users. Synchrotron radiation, especially, in the hard X-ray photon range [1], offers a versatile structural diagnostics platform applicable to diverse scientific and technological problems related to advanced functional materials. A combination of X-ray spectroscopic, diffraction, and imaging techniques augmented with a high spatial and time resolution provides detailed multiscale structural information especially valuable for complex partly ordered materials.

In the present lecture, the current status of synchrotron radiation sources worldwide as well as recent developments in X-ray instrumentation and methodology will be overviewed with the emphasis placed on the state-of-the-art X-ray techniques to probe functioning materials in the so-called *in situ* mode. More specifically, recent activities of the Structural Materials Science beamline installed at the Kurchatov Synchrotron Radiation Source (Moscow, Russia) will be briefly surveyed [2]. Powder X-ray diffraction, Small-angle X-ray scattering and X-ray absorption spectroscopy EXAFS/XANES are jointly applied to elucidate nanostructured catalysts, transition metal complexes in solutions, metal-polymer composites, etc. Selected examples on the use of anomalous diffraction, microbeam diffraction, time-resolved SAXS, and variable-temperature EXAFS will be given.

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