

Series of studies

**«Nanoscale structure of planar and developed electrochemical interfaces
for lithium power sources by neutron scattering»**

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ABSTRACT

The current rapid development of electric transport, robotics, as well as the miniaturization and enhancement of the functionality of portable electronic devices, require more advanced electrochemical energy storage devices. To date, the highest specific energy storage (up to 240 W h / kg) is achieved in lithium-ion batteries, which are based on the ability of electrode materials to include (intercalate) and extract (deintercalate) lithium ions during battery charging/discharging. Further ways of a significant increase in the specific energy of electrochemical sources are associated with non-intercalating type lithium energy storage devices, including lithium-ion sources with a metal anode, as well as lithium-oxygen cells based on carbon cathodes with a record theoretical specific energy storage (up to ~ 600 Wh / kg and above). The development of appropriate power supplies, however, encounters difficulties associated with the fact that a number of undesirable processes occur at the electrochemical interfaces, leading to a decrease in the efficiency of the power sources, as well as causing problems in their safety. In particular, the reason for this is the formation and growth of mesoscopic structures: (i) needle-like formations (often called "dendrites") during the electrodeposition of metallic lithium during charging; (ii) layers of amorphous and crystalline discharge products and supercrystalline structures in the case of lithium-oxygen cells. In this regard, the development of experimental approaches that would make it possible to describe the structure of inhomogeneities at electrochemical interfaces, primarily for the nanoscale (1-100 nm), which determines the evolution of the interface during the storage device operation, is of current interest. For this purpose, the effectiveness of the methods using the scattering of thermal neutrons was demonstrated for studying planar (neutron reflectometry, NR) and developed (small-angle neutron scattering, SANS) interfaces. The high penetrating power of neutrons makes it possible to study complex systems with interfaces hidden for many methods. The presence of a liquid component in the electrolyte made it possible to use extremely efficiently the contrast variation in neutron scattering based on hydrogen / deuterium isotopic substitution.

The presented series of studies (7 journal publications in total) is devoted to the diagnostics and investigation of electrochemical interfaces for advanced lithium energy storage devices and covers experimental structural research carried out in the period of 2017-2020 using neutron reflectometry and small-angle neutron scattering. As a result, the relationship between the microstructure of interfaces in materials used in electrochemical cells and the characteristics of the cells is shown under different conditions. Recommendations are formulated on the composition and synthesis of materials to improve the capacity, conductivity and safety of functioning of new generation lithium-ion and lithium-oxygen energy storage cells. All

experiments were carried out at the instruments of the basic JINR facility—IBR-2 pulsed reactor of FLNP, including the GRAINS reflectometer and the YuMO small-angle diffractometer. Electrochemical cells specially developed by the team of authors were used for studying model interfaces of the 'solid electrode - liquid electrolyte' type in addition to extensive electrochemical characterization performed jointly with the Department of Chemistry of Moscow State University. This series of works was awarded the First Prize in Experimental Studies of Condensed Matter at the FLNP JINR Research Competition for 2019.

Main results

1. It was shown that neutron reflectometry can be effectively used to characterize various modes of deposition of lithium on metal electrodes. A two-stage nature of deposition was found, when, at the first stage, a dense lithium-enriched layer is formed on the electrode surface from the products of the chemical interaction of lithium ions with the solvent, and at the second stage, a transition layer begins to form, which corresponds to the onset of the appearance of large mesoscopic inhomogeneities (needle-like structures). When modifying the electrolyte by adding a non-electrically active additive, there is a strong suppression of growth and a significant change in the composition of the near-surface layer. To further increase the efficiency of the NR method, a procedure is proposed for optimizing the substrate / electrode / lithium-containing electrolyte structure with respect to the maximum change in specular reflection curves in NR experiments at the electrochemical interface between the metal electrode and the liquid electrolyte during the cell operation.
2. Based on the SANS data, the blocking of oxygen transport pathways in wetted cathodes in lithium-oxygen cells occurs both due to the passivation of the inner pore surface inside the carbon grains of the cathode material and due to the growth of supramolecular structures in the intergranular space. The high solvation of lithium ions in the liquid base of the electrolyte determines the rapid diffusion of lithium-containing complexes formed during electrochemical reactions and promotes the predominant release of lithium peroxide into the intergranular space. A prime example of such a solvent is dimethyl sulfoxide. When it is used, the fraction of filled nanopores in carbon grains does not depend on the discharge current; lithium peroxide mesocrystals are also formed throughout the entire volume of the material.
3. The operation of electrochemical lithium-oxygen SANS cells can be significantly improved by using special conductive ceramic LAGP membranes of the NASICON type. To ensure the structural homogeneity of membranes during crystallization by annealing, it was proposed to use a homogenizing additive in the form of an yttrium compound, which showed very good results. With the help of SANS, it was possible to explain the mechanism for improving the conductivity of membranes when using an additive: modification of the material leads to a more uniform shape of crystal grains and a decrease in porosity; as a result, an increase in intergranular contacts takes place.

Abstracts of contributing papers

In [1,2], experiments on neutron reflectometry (NR) of specular reflection are presented. The study of model electrochemical interfaces 'liquid electrolyte - solid electrode' has been carried out. The specular reflection curves showed the formation of a solid electrolyte layer (SEI) on the surface of a thin-film metal electrode (copper) and traced the subsequent electrodeposition of lithium over this layer. To study the ways for preventing parasitic formations on the surfaces of electrodes in lithium batteries, which improves their characteristics and increases the safety of

their operation, a similar series of NR experiments with the modification of the electrolyte by adding a non-electroactive additive (tetrabutyl ammonium perchlorate, TBAP) was carried out. It was shown that the formation of the SEI layer on the electrode surface has a two-stage nature: first, a dense lithium-rich near-surface layer is formed on the electrode surface from the products of the electrochemical interaction of lithium ions with a solvent, and then a transition layer is formed, which corresponds to the onset of the appearance of large microscopic inhomogeneities (needle-like structures). With the addition of a non-electrically active additive, there is a strong suppression of growth and a significant change in the composition of the near-surface layer.

In [3,4], the possibilities for optimizing the structure of the substrate / electrode / lithium-containing electrolyte with respect to the maximum change in the specular reflection curves in the NR experiments for the electrochemical interface between the metal electrode and the liquid electrolyte during operation, are considered. The characteristic relationships between the scattering length densities of the components, for which the reflection curves most fully convey information about the structure of the SEI layer on the electrode surface, are considered. The performed analysis of the possibilities for detecting and characterizing the SEI layer from the specular reflection curve made it possible to distinguish several relationships between the parameters of the system components, in which, despite the overall weak changes, it is possible to trace the evolution of the layer to different extent. This analysis was carried out purely from the point of view of thermal neutron reflectometry. As a first step, metal electrodes were considered for simplicity. At the next stage, the problem was extended to the more general case on optimization of the initial structure of the "solid-liquid" interface in in situ NR experiments in order to maximize weak changes in specular reflection curves with small changes in the interface. The latter is modeled as a carrier layer on a substrate, which is in contact with the solution and onto which an adsorption layer is deposited from the solution over time (thickness up to 200 nm). The proposed optimization procedure was worked out for the initial configuration of the electrochemical interface, where, when an electric circuit of a liquid electrolyte with lithium ions is closed on a metal electrode with a silicon substrate, a transition layer of a solid electrolyte SEI is deposited. The study of a specific type of interfaces allowed us to introduce restrictions on the variation of the parameters of the interface components, which significantly simplified the solution of the optimization problem.

In [5], on the basis of ex-situ SANS experiments, the filling of the pores of a carbon cathode with the final product of the overall electrochemical reaction — lithium peroxide — was studied during the discharge of lithium-oxygen cells. This type of battery has a significantly higher capacity than commonly used lithium-ion batteries. However, their use encounters a number of difficulties associated with blocking oxygen diffusion in the electrolyte due to clogging of pores with lithium peroxide. SANS data made it possible to relate nanoscale changes in the cathode to the electrochemical characteristics of the cells and helped to elucidate the mechanisms limiting the cell capacity. It has been shown that the blocking of oxygen transport pathways in a wetted cathode occurs both due to the passivation of the inner surface of the pores inside carbon grains and due to the growth of supramolecular structures (mesocrystals) in the intergranular space, and the nature of these phenomena substantially depends on the type of liquid base of the organic electrolyte, and also on the content of residual water molecules in it.

In [6, 7], SANS was used in the analysis of the structure of lithium conducting ceramic membranes, which are important components of lithium-oxygen cells. The synthesis conditions are studied in detail, allowing to achieve the homogeneity of the material and its sufficient ionic (Li^+) conductivity. Based on the availability and possibilities of synthesis, the compound $\text{Li}_{1.5}\text{Al}_{0.5}\text{Ge}_{1.5}(\text{PO}_4)_3$ (LAGP) of the NASICON type was taken as a basis, into which a compound of yttrium (Y_2O_3) was added to enhance the ionic conductivity (up to 5 times). Crystallization by

double annealing shows differences in the formation of phases without and with the addition of the yttrium compound. The microstructure of conducting ceramic membranes has been studied. It is shown that the increase in conductivity is explained by the growth of contact points of crystal grains. Based on the data obtained, the optimization of the procedure for the synthesis of membranes for cells was carried out, allowing the operando study of SANS during discharge/charge in real time.

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