Project Report

"A system for neutron *operando* monitoring and diagnostics of materials and interfaces for electrochemical energy storage devices at the IBR-2 reactor"

ELCHEM_NR

Theme: Investigations of Condensed Matter
by Modern Neutron Scattering Methods (04-4-1121-2015/2020).

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2020

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ABSTRACT

At present, the continuous growth of the use of electrochemical energy storage devices requires the development of special approaches for studying the processes taking place inside these devices, including electrodes and hidden boundaries of charge separation, during their functioning (*operando* mode). This project was aimed at a wide adaptation of neutron scattering methods (diffraction, reflectometry, small angle scattering) and sample environment systems to study the evolution of the structure of electrochemical interfaces and electrode materials in *operando* mode.

The project objectives were to develop approaches for the effective use of neutron scattering methods for various types of electrochemical interfaces and electrodes, to create specialized experimental cells, as well as to adapt sample environment systems for *operando* research. The high penetrating power of thermal neutrons makes it possible to study complex systems that are closest in conditions to real batteries, fuel cells and other electrochemical devices. Neutron scattering experiments required the development of special approaches to the creation of electrochemical cells for simultaneous monitoring of voltage/current at the interface/electrode under study together with the organization of the neutron beam passing through the interface/electrode, followed by the detection and analysis of scattering. The application of common approaches to solving problems for different types of interfaces/electrodes in the scattering methods used has significantly improved the quality and level of structural information in the study of electrochemical processes.

The neutron scattering experiments were carried out at the IBR-2 reactor of FLNP JINR using HRFD, RTD diffractometers, GRAINS reflectometer, and YuMO small-angle diffractometer. The work was done at the Frank Laboratory of Neutron Physics, JINR, in collaboration with the Department of Chemistry of Moscow State University and Dubna State University.

The project was performed in the framework of the theme 04-4-1121-2015/2020 ‘Investigations of Condensed Matter by Modern Neutron Scattering Methods’.

INTRODUCTION

The production and storage of energy from electrochemical sources play an extremely important role in creating a wide range of devices, from portable phones, laptops and power tools to sophisticated machines such as railway locomotives and automobiles. Sources of this type demonstrate a competitive combination of a fairly high energy capacity, low price and better compliance with environmental requirements, which is reflected, in particular, in the steady growth in sales of electric vehicles worldwide over the past five years. The importance of this type of energy storage devices was recently recognized by the Nobel Committee, which awarded the 2019 Nobel Prize in Chemistry to J. Goodenough, S. Whittingham, and A. Yoshino for the development of lithium-ion batteries.

The performance characteristics of electrochemical batteries and accumulators are largely determined by the processes occurring at the boundaries of the charge separation, in electrode materials and the corresponding chemical reactions. The evolution of the structure, composition and chemistry of electrodes and electrolytes affects all the functional parameters of the devices, including specific energy capacity, power, stability, and lifetime. The solution of modern problems of electrochemistry requires the development of experimental approaches that would reliably describe the structure of electrode materials and interfaces during their operation.

This project was aimed at developing neutron scattering techniques, which allowed us to study the structure of electrochemical interfaces and electrode materials of various types in the process of their functioning (*operando* mode). The application of this kind of techniques made it possible at a new scientific level to monitor the influence on the evolution of electrochemical interfaces and materials of the initial characteristics of surfaces and environmental parameters, electrolyte composition, overvoltage, current density and other parameters. The high penetrating power of neutrons makes it possible to study complex systems that are closest in conditions to real batteries. Neutron scattering experiments required the development of special approaches to the creation of electrochemical cells for simultaneous monitoring of voltage/current at the interface/electrode under study together with the organization of the neutron beam passing through the interface/electrode, followed by the detection and analysis of scattering. Moreover, for different types of interfaces/electrodes and scattering methods used, common tasks were identified that made it possible to combine approaches to their solution and thus increased the quality and level of structural information obtained when studying various aspects of electrochemical processes.

In the course of this project, promising (from the point of view of applications to electrochemical interfaces) neutron scattering techniques were considered. The approaches to their effective use for various types of interfaces/electrodes were developed, followed by the creation of specialized experimental cells and sample environment systems for *operando* research. The project included: (i) consideration and extensive adaptation of thermal neutron scattering methods, including diffraction, reflectometry, and small-angle scattering, to solve the problems of electrochemistry; (ii) creation of specialized electrochemical cells and sample environment systems for studying materials and interfaces for different types of electrochemical energy storage devices using non-aqueous electrolytes and alkali metals, in particular lithium.

Work with such systems requires special equipment and infrastructure, which were introduced into the sample environment at neutron scattering instruments.

1. PROJECT OBJECTIVES AND STRUCTURE

Two main directions of structural research of lithium energy-storage devices are naturally associated with the study of the evolution of the structure of electrodes and electrochemical interfaces. This is especially important for functioning cells, so the development of methods that allow studying the corresponding processes in *ex situ*, *in situ*, and *operando* modes is of current interest.

The project objectives were:

1) Development of general approaches to the effective use of neutron scattering methods (diffraction, reflectometry, small-angle scattering) in the analysis of the structural evolution of electrodes of various types and interfaces for electrochemical energy storage devices during operation (*operando* mode).

2) Design and development of specialized electrochemical cells and sample environment systems for *operando* research in neutron scattering experiments.

The conceptual scheme of the project is presented in Fig. 1. The following instruments at the IBR-2 reactor were used in the project: HRFD, RTD diffractometers; GRAINS reflectometer; YuMO small-angle diffractometer.

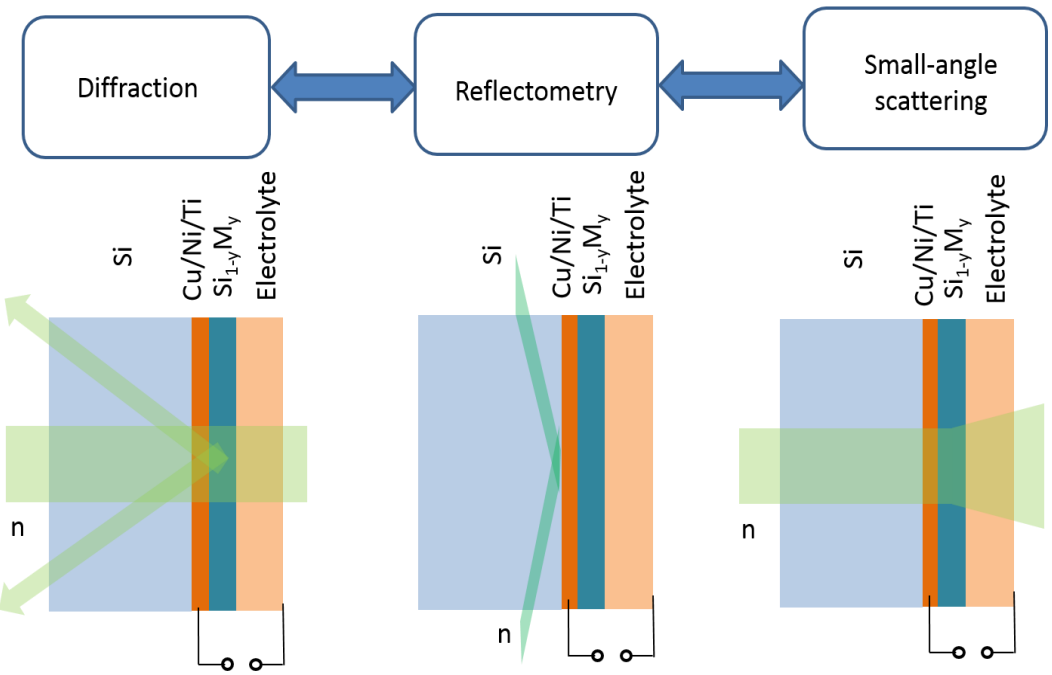

Fig. 1. Conceptual scheme of the ELCHEM_NR project.

The research groups involved in the project were: I. Frank Laboratory of Neutron Physics JINR (FLNP JINR); II. Department of Chemistry, Moscow State University (MSU); III. Engineering Center of Dubna State University (Dubna State University), which solved the following tasks:

I. FLNP JINR

I.1. Manufacturing:

- Electrochemical cells for neutron scattering;
- Sample environment systems for *in-situ* and *operando* neutron scattering experiments.

I.2. Organization and support of R&D line for deposition and polishing of crystalline substrates;

I.3. Organization and conduct of neutron experiments at the IBR-2 reactor;

I.4. Diagnostics and storage of samples under special conditions after experiments.

II. MSU

II.1. Design and draft projects:

- Electrochemical cells for neutron scattering;
- Sample environment systems for *in-situ* and *operando* neutron scattering experiments.

II.1. Scientific support of the project.

III. Dubna State University

III.1. Test assembly and electrochemical measurements of cells and sample environment systems for neutron experiments;

II.2. Electrochemical support of neutron experiments.

2. NEUTRON DIFFRACTION

In the previous development of the neutron diffraction technique at IBR-2 for electrochemical tasks, *operando* cells were already tested to track the evolution of diffraction patterns during intercalation/deintercolation of lithium in electrodes for lithium-ion batteries in real time. Within this project, a significant upgrade of existing cells was done, including:

1. Replacement of the case material (PTFE polytetrafluoroethylene with PEEK polyetheretherketone) with the possibility of better mechanical processing with increased accuracy.

2. Change in the internal design of the cases to increase the efficiency of the assembly.

3. Replacement of the beam attenuator material with more effective one (boron nitride with boron carbide).

4. Creation of a specialized mold for the production of seals used in PEEK-based cases.

As a result, if until now it was possible to study mainly the first discharge/charge cycle, then after the upgrade it became possible to study the full cell cycling with the help of neutron diffraction. From the point of view of electrochemistry, the cells (Fig. 2) are actually chemical storage cells with fairly good characteristics. Thus, for the new cells with $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ (NCA) / graphite (C) electrodes, the capacity lost during cycling does not exceed 30% after 700 discharge/charge cycles, the leakage current change is ~1 μA h^{-1} (at the capacity of 500 mA h). An example of the evolution of diffraction patterns obtained using such a cell when studying cathode materials of the NCA type is presented in Fig. 3.

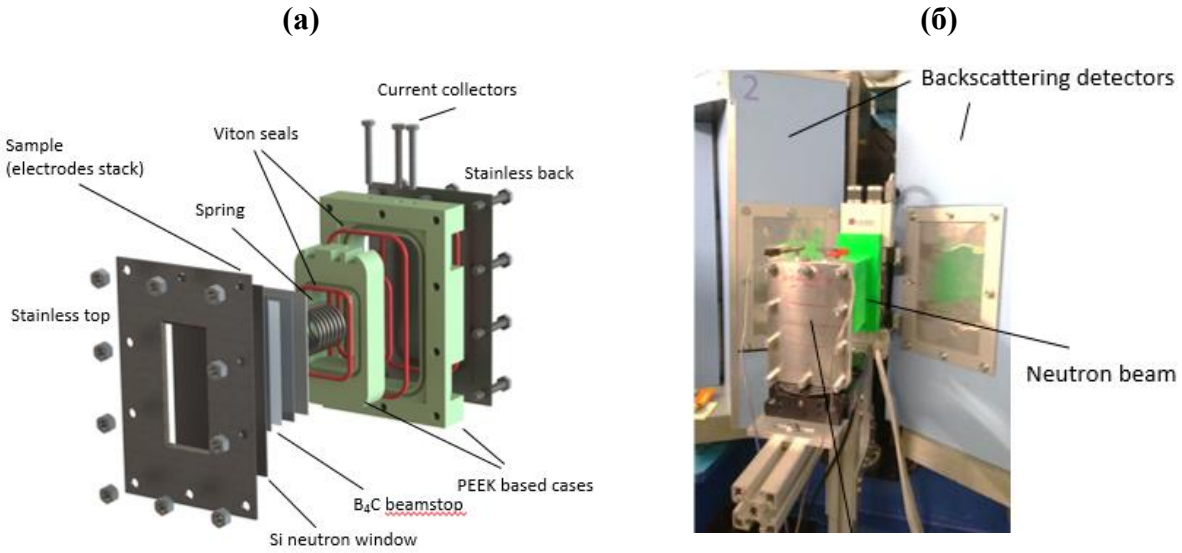

Fig. 2. **(a)** Schematic diagram of the electrochemical *operando* cell for neutron diffraction.

(b) Photo of the cell assembly at the HRFD diffractometer of the IBR-2 reactor.

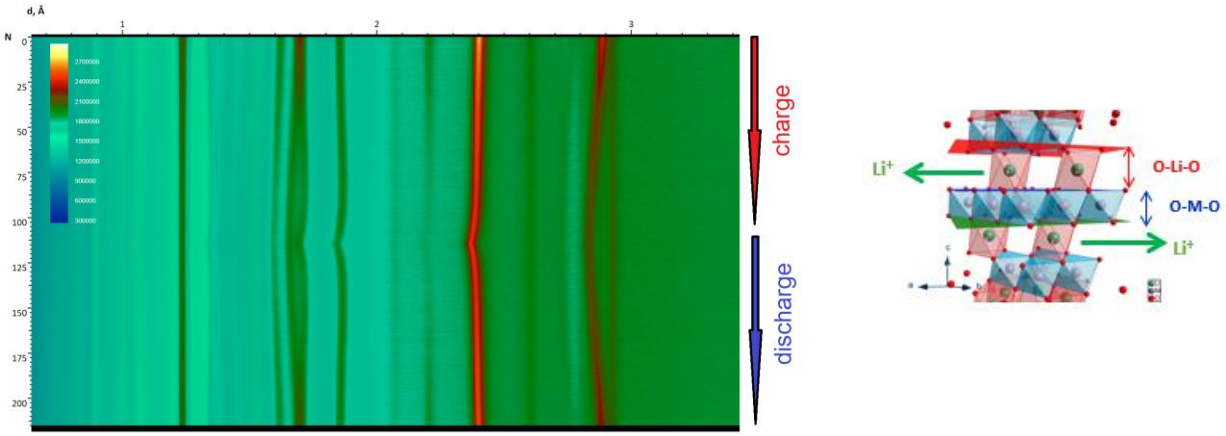

Fig. 3. Evolution of neutron diffraction patterns during cycling obtained using a new type of electrochemical cell at the HRFD diffractometer of the IBR-2 reactor. Lithium intercolation/deintercolation in cathode materials of the NCA type is studied.

During the project implementation, the capabilities of the local laboratory of electrochemical support at FLNP were expanded. In particular, the following equipment was adapted: titrator (Metrohm Fischer 917), dispergator (up to 25,000 rpm), potentiostat (BIOLOGIC SP-300), high-temperature furnace (inert gas, 1200˚C), place for storage of deuterated electrolytes (DMC, PC, EC), three-axis holders of non-standard samples (electrochemical cells) for the X-ray diffractometer. As a result, at present, the PANalytical X-ray diffractometer makes it possible to carry out full *operando* measurements along with neutron experiments. In particular, a specialized electrochemical cell with a beryllium window was developed and successfully tested for this purpose (Fig. 4).

The experience gained in the study of model cells allowed us to switch to more complex real storage devices. In Fig. 5, an example of *operando* research using neutron diffraction of industrial batteries with a NCA cathode is given.

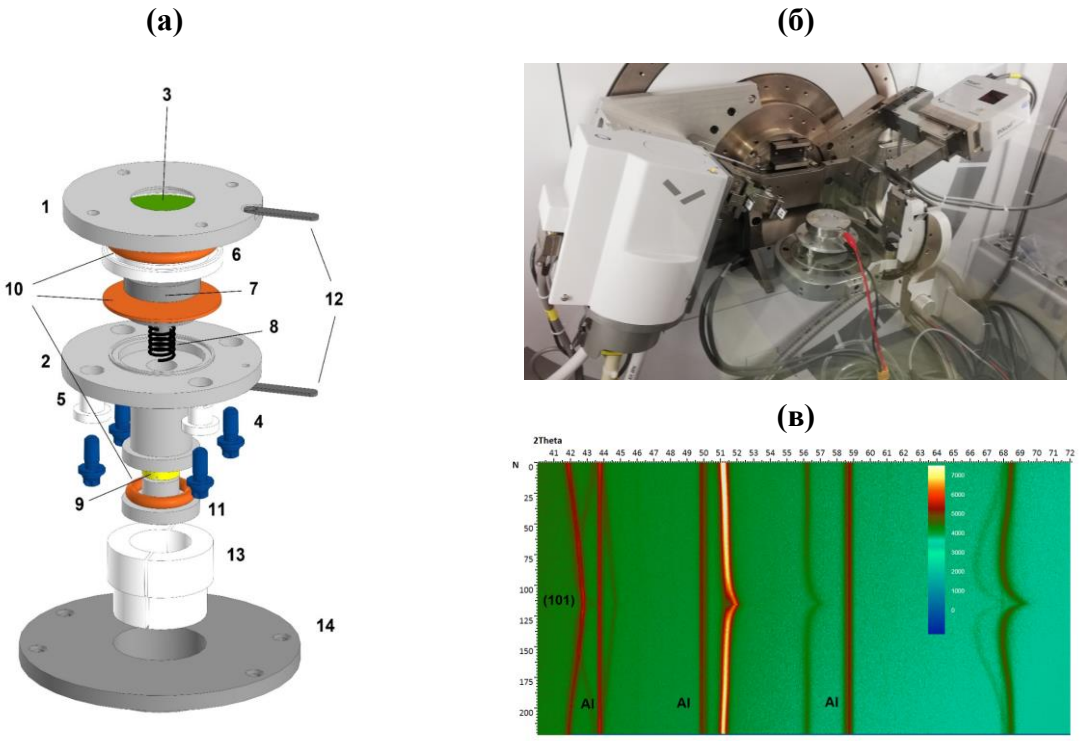

Fig. 4. **(a)** Electrochemical cell with a beryllium window for studying electrode materials in *operando* mode at X-ray diffractometer. The cell consists of two parts of the case (1, 2), beryllium disk (3) with a diameter of 36.2 mm and thickness of 0.5 mm, TORX E10 bolts with an internal hexagon with washers and bushings (4, 5), guide insert (6) made of polyetheretherketone (PEEK) with a cavity for electrolyte, composite substrate of a current collector (7), spring (8, stainless steel), adjustable limiter with a thread (9), gaskets (10) (recommended material is fluorinated rubber), screw cover (11), current collectors (12). Axial platform is fastened at the diffractometer through plastic dielectric bushings (13) and aluminum disk supports (14).
(b) Photo of the cell mounted at the PANalytical X-ray diffractometer (FLNP);
(c) Example of *operando* study using X-ray diffraction.

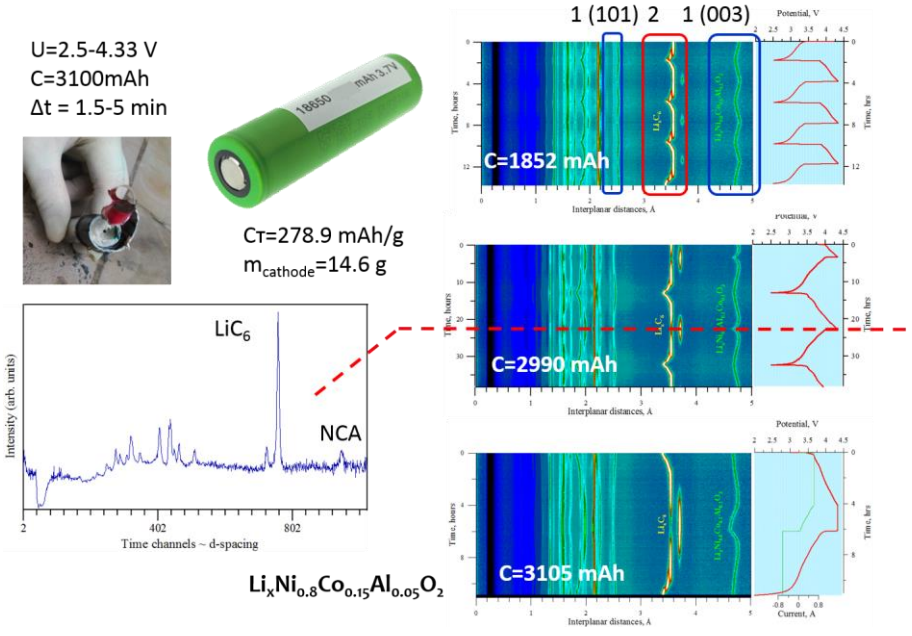

Fig. 5. *Operando* study of a real chemical energy storage device at the HRFD diffractometer of the IBR-2 reactor.

3. NEUTRON REFLECTOMETRY

The application of neutron reflectometry to planar interfaces is based on the standard scheme (Fig. 6), when a plane neutron beam is incident and reflected from the interface through a massive single-crystal silicon block coated with a thin (about 50 nm thick) electrode film that is in contact with liquid electrolyte. The electric circuit is organized using special connectors through a potentiostat, which regulates the potential at the interface. The interface modification, such as the appearance of the so-called solid electrolyte interphase (SEI) layer during the discharge process, causes small changes in the depth profiles of the scattering length density, which are, in their turn, detected by the specular reflectivity curves. To increase the efficiency of the cells of this type, the following tasks were solved:

1. Optimization of reflectometry cells and sample environment system;
2. Synthesis of complex heterogeneous film electrodes;
3. Additional diagnostics of electrode surfaces after neutron scattering experiments;
4. Processing of crystalline substrates after neutron scattering experiments.

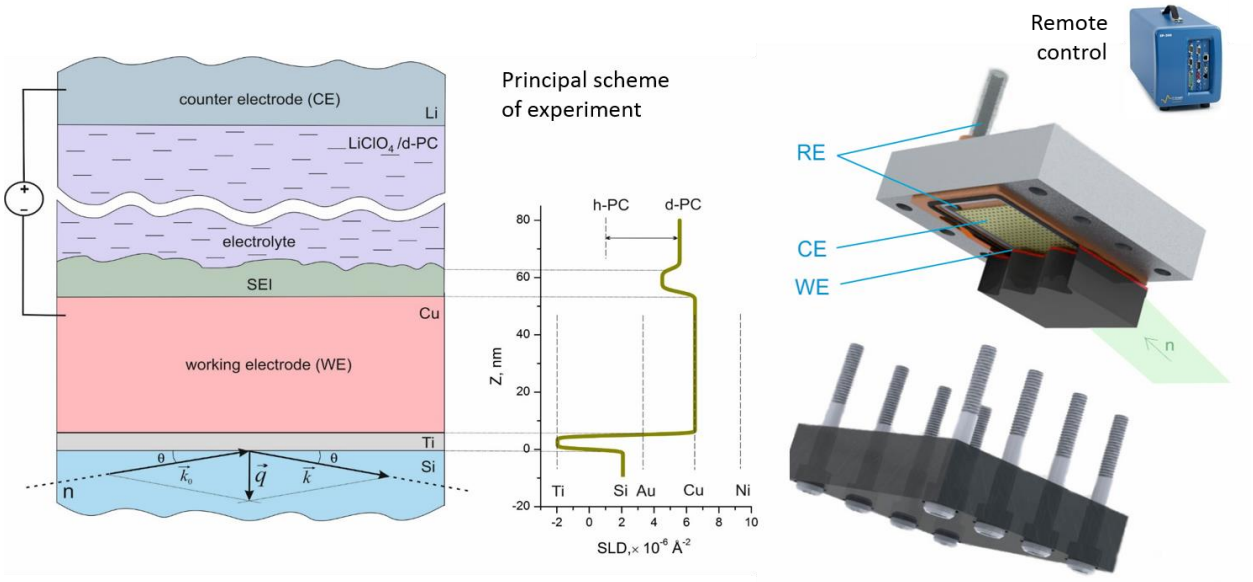

Fig. 6. Schematic diagram of a neutron reflectometry experiment on an electrochemical interface and a 3D representation of the corresponding cell: working electrode – thin-film metal electrode (Ti / Cu) – on a massive crystalline substrate (Si) in contact with a liquid electrolyte is closed through an external circuit (with remote external control via a potentiostat) with a counter electrode (lithium foil). Deposition of the colloidal layer on the surface of the working electrode is displayed on the depth profile of the scattering length density as an additional feature, which, in turn, manifests itself as changes in modulation of the reflectivity curve (not shown).

During the project, electrochemical cells for neutron reflectometry experiments were significantly improved (Fig. 7). The new design of the cell in the “beam from bottom” configuration provides electrolyte filling with better control, which made it possible to significantly reduce the cost

of experiments because of less volumes of expensive deuterated electrolytes required in contrast variation. A higher accuracy in respect to the control of the ratio of mixed light and heavy electrolyte components in this type of experiments was achieved. The cell is assembled in an argon box. The whole structure is air-tight. Filling of the cell and monitoring of the electrolyte level in the cell are provided by syringes with special metering taps.

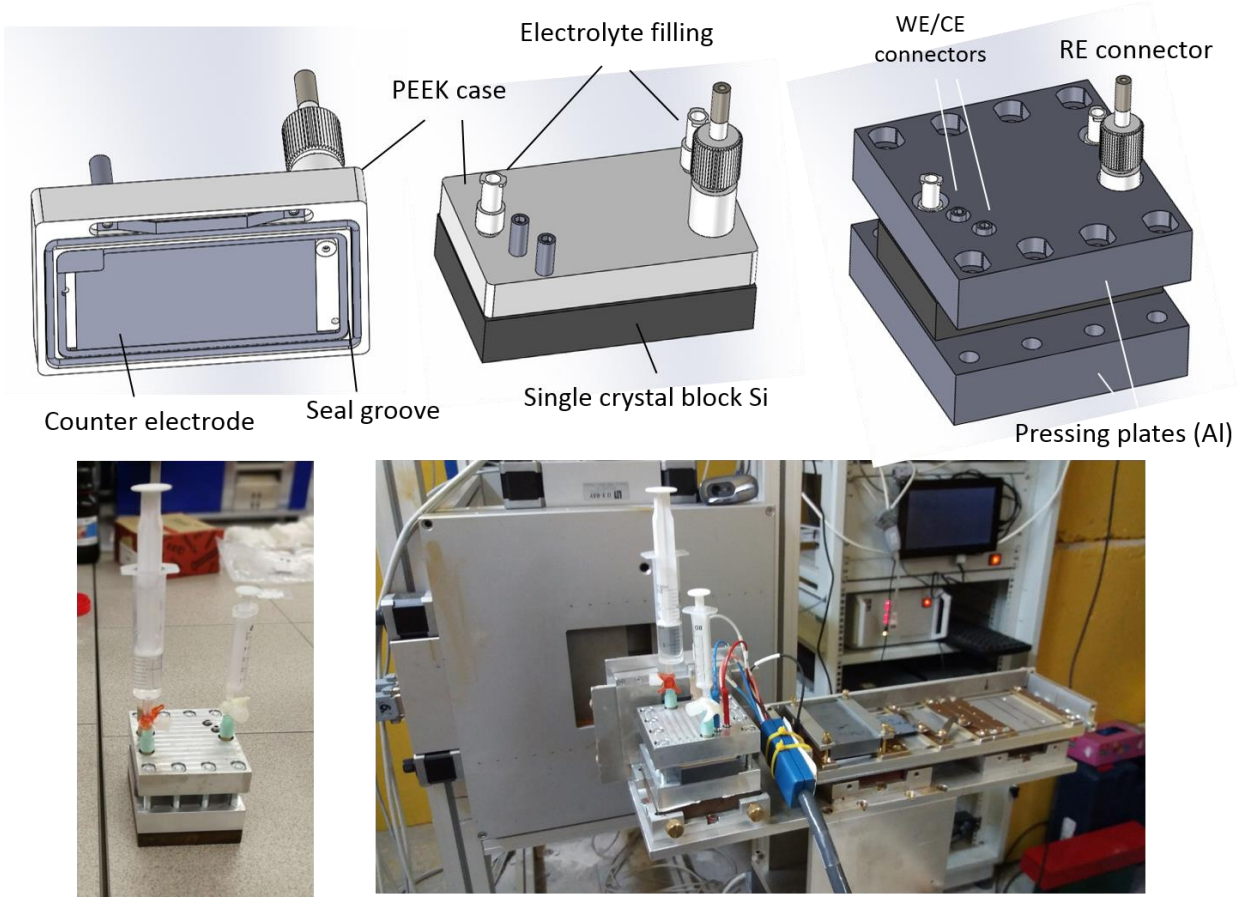

Fig. 7. Schematic diagram of the assembly of the electrochemical cell for neutron reflectometry and photos after assembly and its installation at the GRAINS reflectometer of the IBR-2 reactor.

As an example, Figure 8 illustrates the use of this cell in a pilot experiment on the contrast variation (replacing an electrolyte with a deuterated analog) to track the formation of a transitional SEI layer on the anode that occurs at the initial stage of the cell discharge as a result of the electrochemical activity of lithium ions with a liquid base. One can see that changes in the modulation of the reflectivity curves due to the new layer become more pronounced when using a deuterated electrolyte. All profile parameters, except for a new layer (thickness, roughness and average value of the scattering length density), are measured in advance, including diagnostics by X-ray reflectometry, and are fixed during the data treatment. Figure 9 shows an example of *operando* research — lithium plating on a metal electrode and the effect of various modifications of the electrolyte on this process aimed at suppressing dendritic formation on the electrode surface. In particular, electrolyte concentrating is tried, which essentially inhibits the deposition of the primary SEI layer.

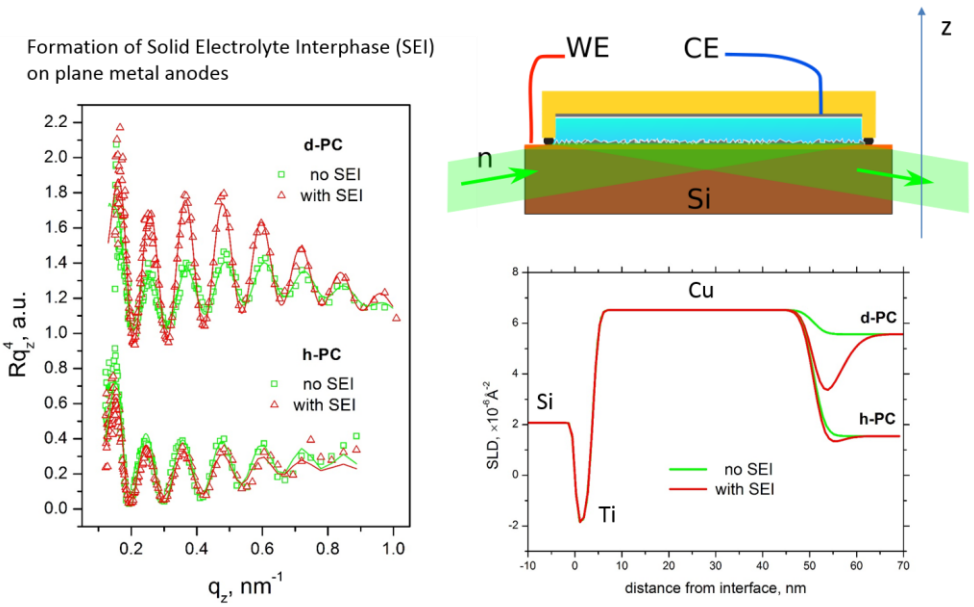

Fig. 8. Detection of SEI layer on metal working electrode by specular neutron reflectometry in a conventional electrolyte (propylene carbonate, h-PC) and its deuterated analog (d-PC). The experiment was carried out at the GRAINS reflectometer of the IBR-2 reactor.

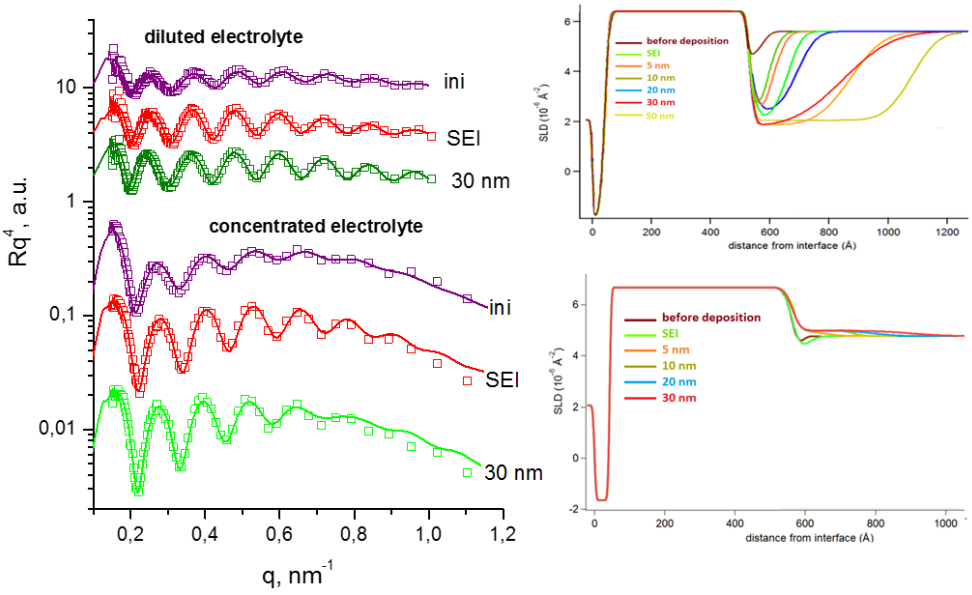

Fig. 9. *Operando* study of lithium plating on metal electrode from liquid electrolyte by specular neutron reflectometry using diluted and concentrated electrolytes (deuterated analogues). The curve captions indicate expected thicknesses of lithium layers in case of homogeneous deposition.

During the project, the problem of optimizing the initial structure of the "solid-liquid" interface in *in situ* and *operando* experiments on neutron reflectometry was considered in order to maximize weak changes in the specular reflectivity curves caused by small changes of the interface (Fig. 10). The latter is modeled as a carrier layer on a substrate, which is in contact with the solution. An adsorption layer is deposited on this layer from the solution over time (layer thickness up to 2000 Å). The proposed optimization procedure was considered for the initial configuration of typical electrochemical interfaces. The study of a specific system (electrochemical interface) made it possible

to introduce restrictions on the variation of the interface parameters, which significantly simplified the solution of the optimization problem.

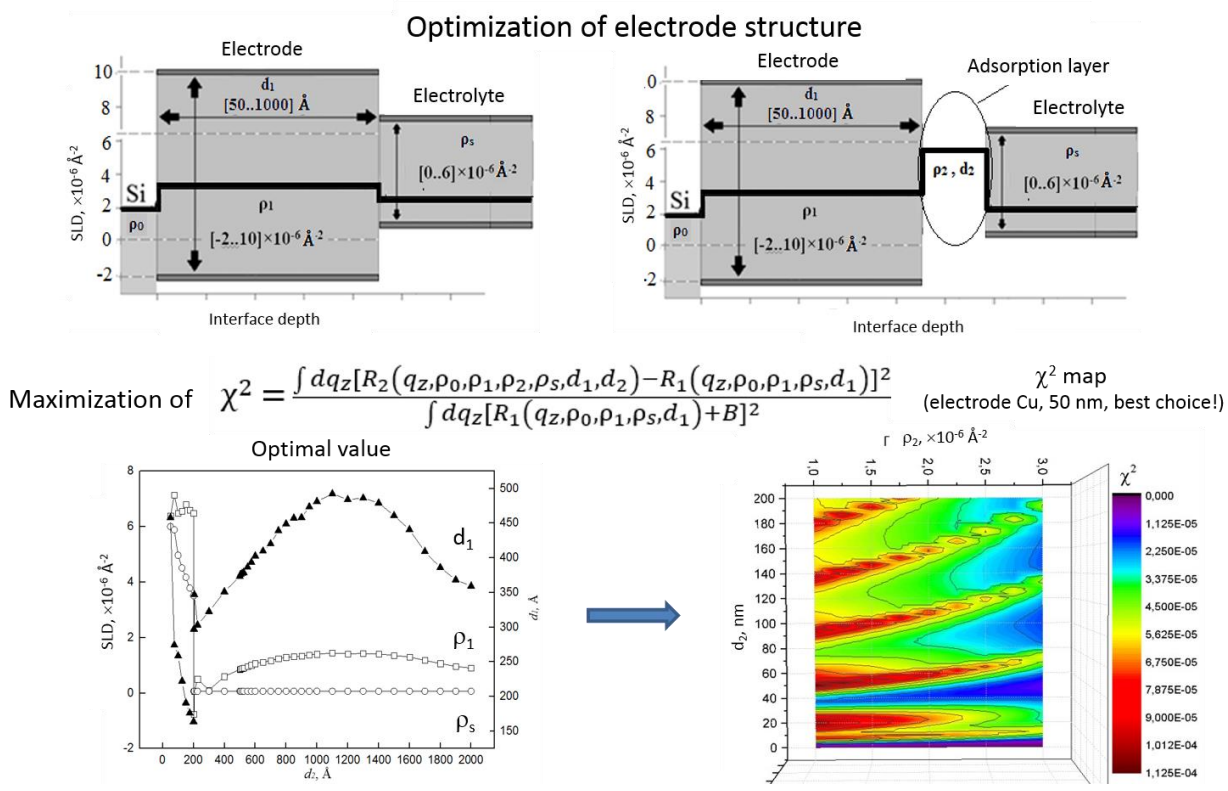

Fig. 10. Schematic representation of the problem of optimizing the initial structure of the solid – liquid interface in *in situ* and *operando* experiments on specular neutron reflectometry in order to maximize slight changes in specular reflectivity curves caused by small changes of the interface. Upon transition to the structure with an additional new layer, to determine the conditions of the highest sensitivity, the parameters of the initial interface are searched through maximizing χ^2-functional.

Possibilities for optimizing the composition of interfaces were also considered experimentally. In particular, for better adhesion of the metal layer during sputtering, an intermediate layer (for example, titanium) is required, which impairs the sensitivity of the reflectometry experiment. During the project, test systems with magnetron sputtering were manufactured (Mirrotron, Hungary) with minimization of the intermediate adhesive layer of titanium: Si (crystal) / Ti [0-10 nm] / Cu [10-50 nm]. The synthesized thin-film electrodes were characterized using neutron (GINA reflectometer, Budapest Neutron Center) and X-ray (PANalytical, LNF) reflectometry. It was found that modern experimental sputtering capabilities make it possible to obtain a homogeneous intermediate titanium film with a thickness of down to 1 nm and less. When copper was also applied directly to crystalline silicon, time-stable structures were obtained in the absence of mechanical stresses. These electrodes can be used in electrochemical cells for neutron reflectometry. The most preferred (in terms of sputtering quality) is a structure with a working electrode thickness (copper) of 50 nm.

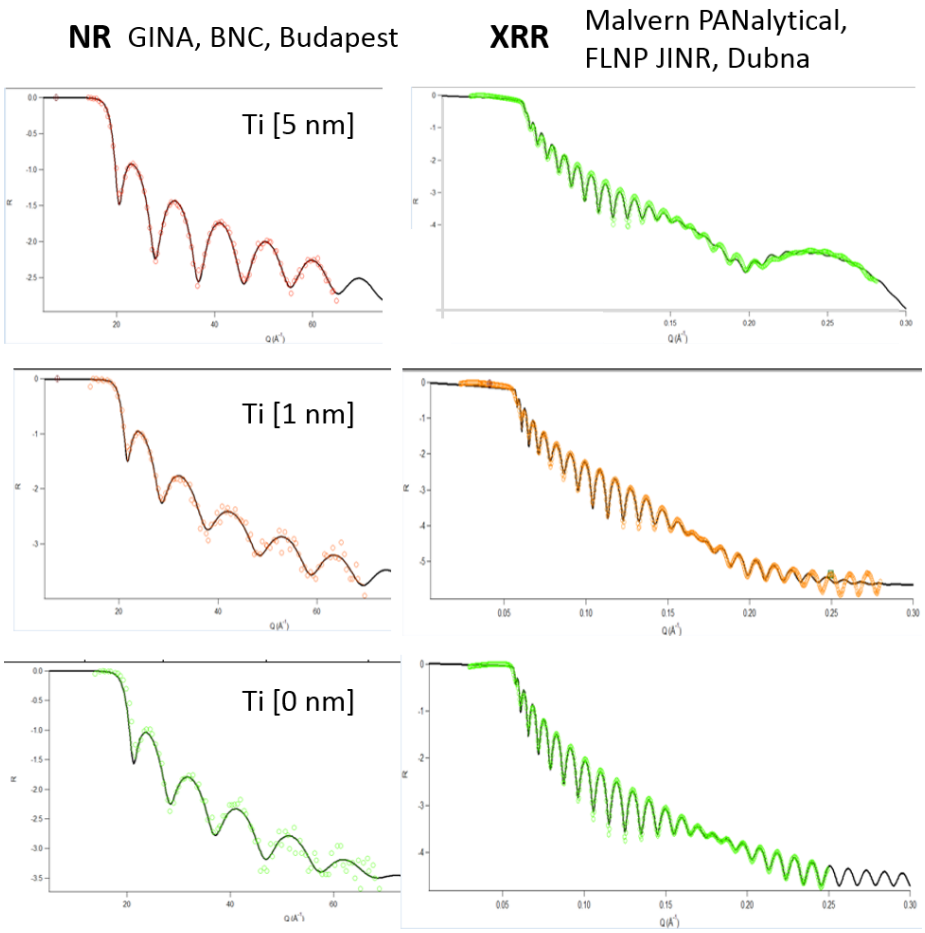

Fig. 11. Characterization of thin-film electrodes on a silicon single crystal using neutron reflectometry (NR) and X-ray reflectometry (NR) as a part of the study of the possibility for reducing the thickness of the intermediate adhesive layer of titanium.

Also, to expand the possibilities for contrast variation in neutron reflectometry, it was proposed to use multilayer structures based on ultrathin titanium-nickel sublayers to change the average electrode density in a quasihomogeneous approximation (Fig. 12). Test sputtering (Mirrotron, Hungary) and analysis of density profiles from measurements of neutron and X-ray reflectometry showed the possibility for realizing this idea. Modern equipment allows controlled sputtering of such layers with a sublayer thickness of down to 0.5 nm. In this case, the initial region of the reflectivity curves, which is covered in neutron experiments ($q < 0.1$ nm^{-1}), is well described within the quasihomogeneous approximation (systematic error does not exceed 10%). Thus, along with a change in the density of the scattering length of the electrolyte, the possibility for changing the density of the electrode was shown.

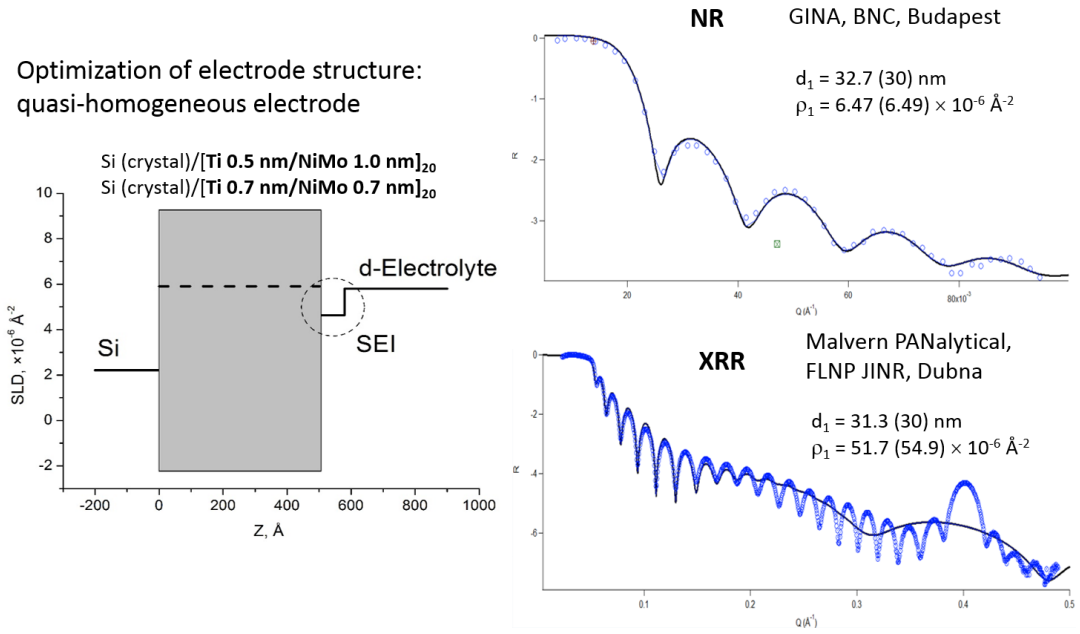

Fig. 12. Regulation of the SLD of the working electrode for additional contrast variation in the NR experiment using a multilayer of ultrathin Ti/Ni sublayers with varying thickness ratios of the sublayers. Examples of processing experimental neutron reflectometry curves (GINA, BNC, Budapest) and X-ray reflectometry curves (PANalytical, LNP JINR, Dubna) in the framework of the quasihomogeneous approximation.

4. SMALL-ANGLE NEUTRON SCATTERING

The third area of work was related to electrochemical interfaces in porous materials, which are used in promising (from the point of view of energy capacity, which is several times higher than in lithium-ion batteries) lithium-air batteries based on the reaction of chemical interaction of lithium with oxygen (Fig. 13). A serious obstacle to the development of this type of batteries, however, is the parasitic effect, passivation of the pore surface with an insoluble reaction product – lithium peroxide. For this reason, the discharge is blocked long before reaching theoretical limits.

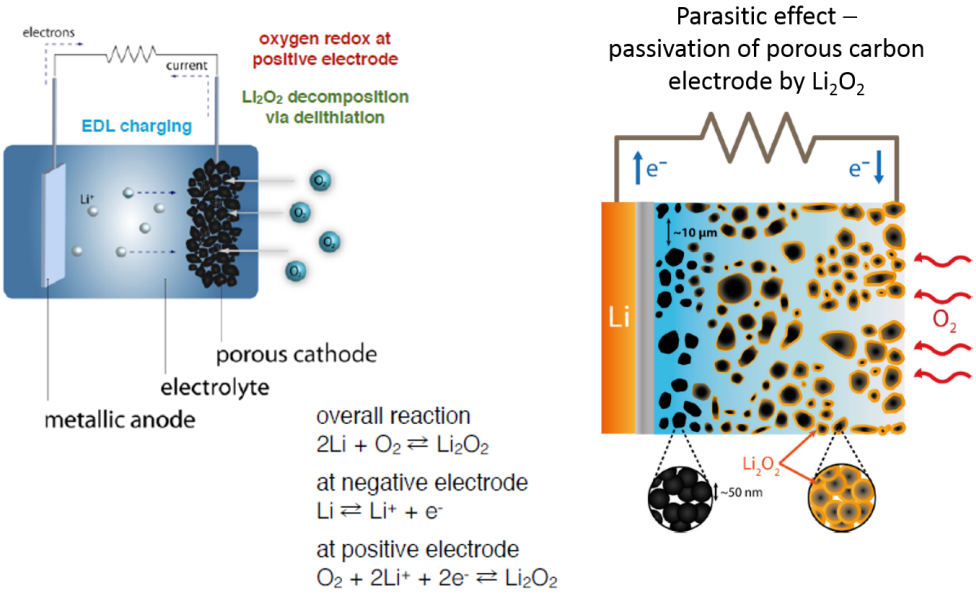

Fig. 13. Principle of operation of lithium-oxygen electrochemical cells (maximum theoretical energy capacity of up to 900 Wh / kg).

At the initial stage of the project, small-angle neutron scattering (SANS) in *ex situ* mode was used to track the deposition of lithium peroxide in the pores of the carbon cathode. The electrodes (soaked with liquid electrolyte) were discharged with different discharge times under laboratory conditions, placed in quartz cells, which were sealed with silicone glue to avoid electrolyte evaporation, and transferred to the beam (Fig. 14). As a result, prospects of the SANS applications were shown based on the use of a specific combination of component contrasts in the system. Figure 15 schematically illustrates three stages of the experiment with measurement of three types of scattering: from an initial dry electrode; from an electrode soaked with a fully deuterated electrolyte; from a soaked electrode after discharge in an electrochemical cell. The fully deuterated electrolyte is close by the scattering length density to the carbon matrix, which explains the decrease in the scattering for the soaked electrode because of matching of open pores filled with the electrolyte. When lithium peroxide is deposited in the pores, due to the contrast between the new component and the electrolyte/ carbon matrix, the scattering increases again.

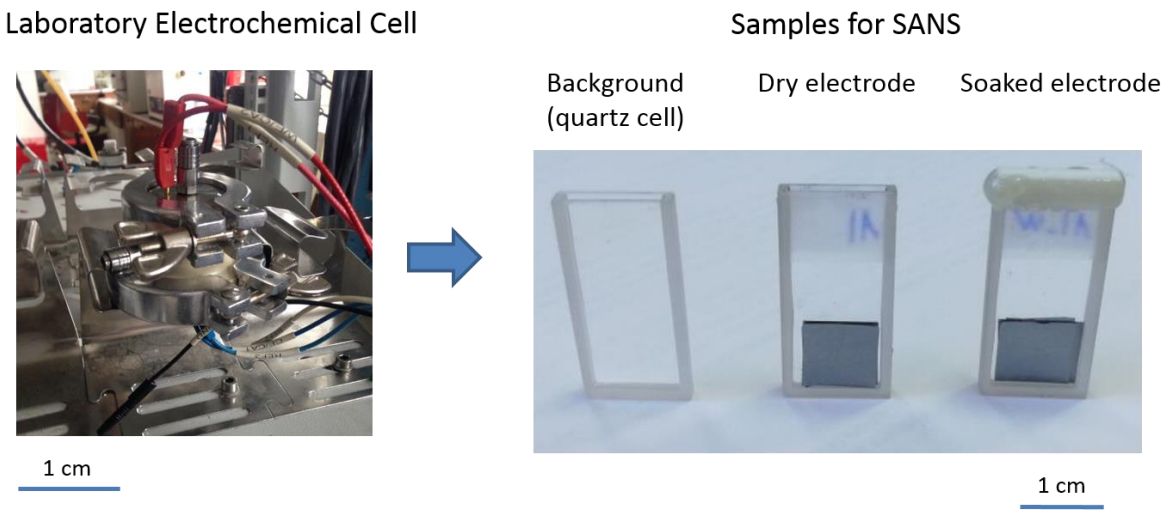

Fig. 14. Organization of *ex-situ* SANS experiments. Cathode plates were discharged in the laboratories of the Department of Chemistry of Moscow State University and the Engineering Center of Dubna State University. Further, the "wet" cathode material from the cells was transferred to quartz cuvettes, which were sealed and delivered to IBR-2.

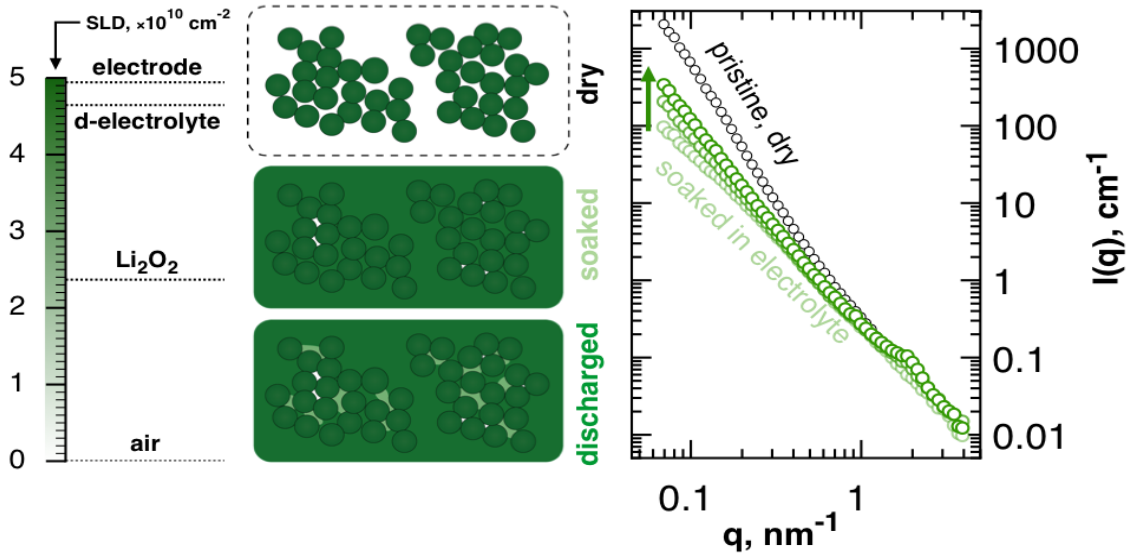

Fig. 15. Three stages of the SANS experiment for lithium-oxygen cells with measurement of scattering: from an initial dry electrode; from an electrode soaked with a fully deuterated electrolyte; from a soaked electrode after discharge in an electrochemical cell. The increase in scattering at the third stage is determined by the filling of pores with lithium peroxide. Experimental scattering curves were obtained at the YuMO instrument of the IBR-2 reactor.

Within the project, an *operando* SANS cell was developed and tested. The schematic diagram of the cell is shown in Fig. 16. The complexity of creation of such cells lies in the fact that due to the configuration of the SANS experiment (transmission type), along with the working electrode with electrolyte, additional components are present in the beam (counter electrode, polymeric membrane - separator with liquid electrolyte, regulating ion-conducting membrane, windows for the beam). These components give a background contribution to the scattering, thus reducing the sensitivity of the

experiment. Therefore, at the initial stage, the optimization of the cell regarding materials was made. SANS was measured in absolute units for various types of potential cell components with the subsequent selection of materials with a minimal scattering contribution (Fig. 16). Then, this choice was tested regarding the electrochemical characteristics of the cell to ensure the possibility of a sufficiently fast (one day) discharge. Such characteristic discharge time is necessary for the implementation of the *operando* experiment at a neutron beam; it corresponds to a typical experiment time at SANS instruments.

As a result, a cell prototype was developed (Fig. 17) and tested (Fig. 18). It is based on a standard metal crosspiece with airtight flanges and two sapphire windows on opposite flanges for a neutron beam. The cell is filled with oxygen through special fittings located on one of the flanges. On one of the flanges with a sapphire window, a cylindrical insert with the components is installed according to the scheme in Fig. 17, including electrodes, a separator and a membrane, pressed against each other by two (for anode and cathode components) springs. The first cycling (discharge/charge) was carried out, during which the scattering curves were obtained. The achieved effective time resolution is 10 min.

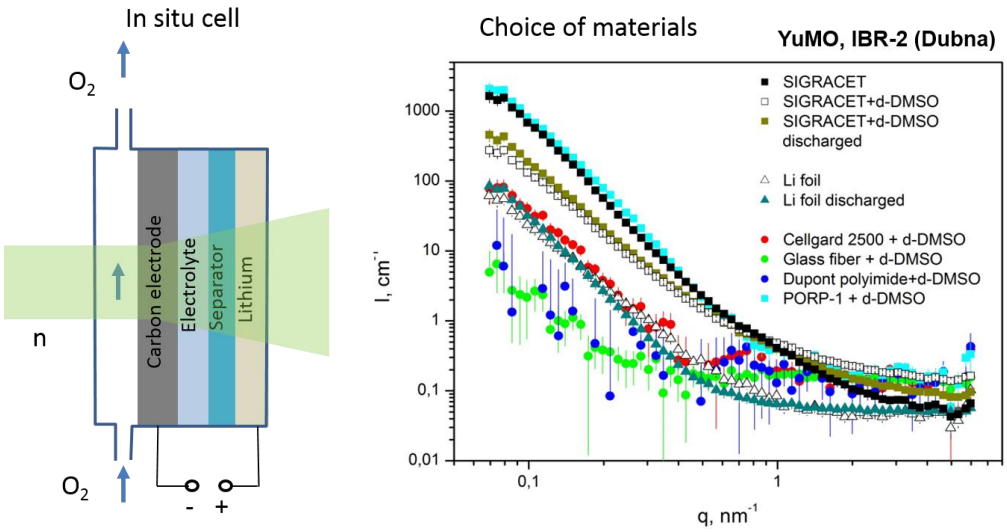

Fig. 16. Schematic diagram of the *operando* SANS cell for studying the deposition of lithium peroxide into a porous cathode material in a lithium-oxygen energy storage device and a comparative analysis of the experimentally measured contributions to scattering from various types of cell components in the dry and wetted states. Experimental scattering curves were obtained at the YuMO instrument of the IBR-2 reactor.

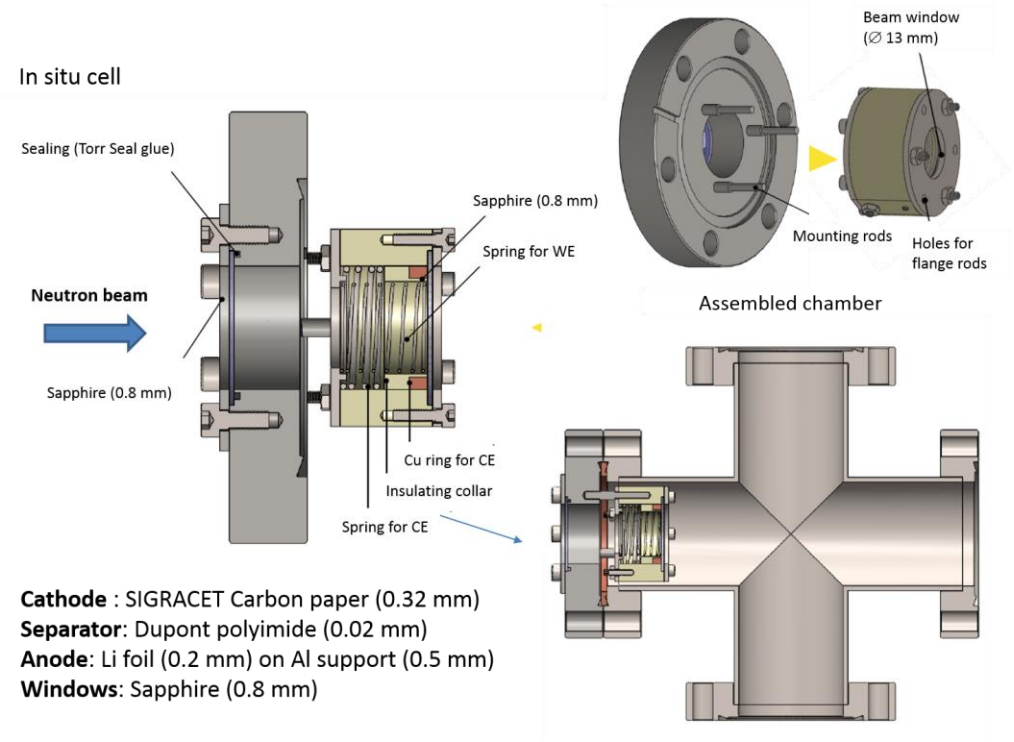

Fig. 17. Schematic design of *operando* lithium oxygen cell for SANS.

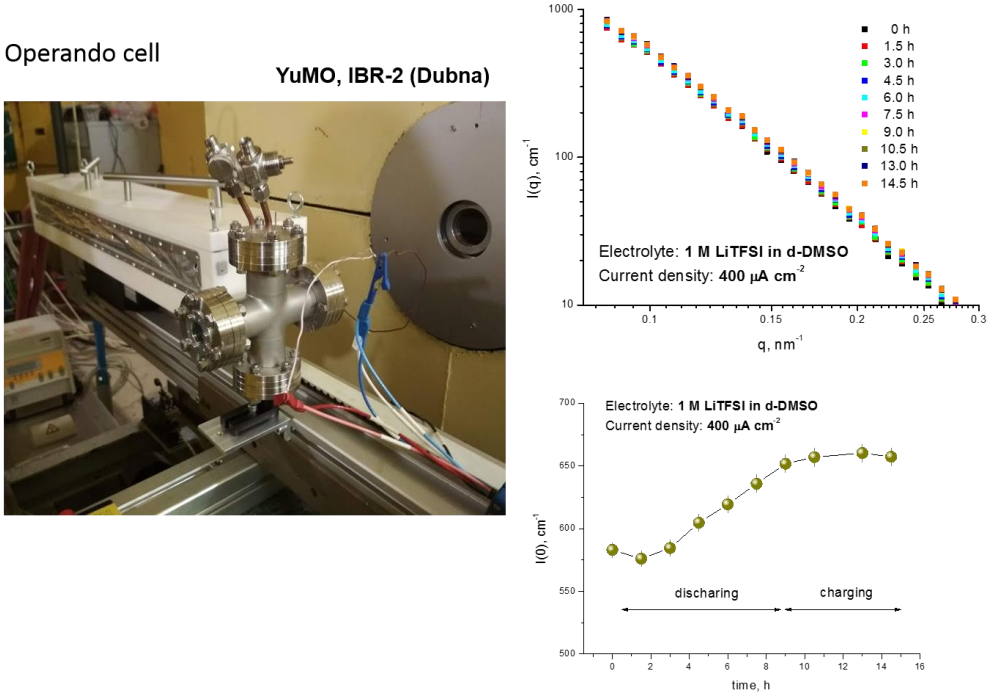

Fig. 18. Installation and test results for *operando* lithium-oxygen cell for SANS at the YuMO instrument of the IBR-2 reactor. The carbon electrode was soaked with a liquid electrolyte based on deuterated dimethyl sulfoxide (d-DMSO). The primary cycling (discharge/charge) was carried out.

SUMMARY

In the framework of the project, the following equipment was designed, manufactured and adapted:

Neutron diffraction

- Specialized lithium-ion cells for multiple charge/discharge;
- Sample environment system for experiments in *operando* mode;
- Line of multi-channel charge/discharge of electrochemical cells;
- Complementary lithium-ion cells for X-ray diffraction.

Neutron reflectometry

- Specialized lithium-ion cells with heterogeneous electrodes/liquid electrolytes;
- Sample environment system for experiments in *operando* mode;
- System for storing and processing samples after experiments;

Small-angle neutron scattering

- Specialized lithium-air cells for *operando* mode;
- Sample environment system for *ex-situ* experiments;
- Sample environment system for experiments *in operando* mode.

Within the project, cooperation was established with companies directly involved in the production of electrochemical energy storage devices, including: Engineering Incubator Ltd. (Dubna), LITION Ltd. (Dubna), LG Technology Center Moscow (Moscow). The phased expansion of the capabilities of electrochemical studies for various neutron techniques contributed to the strengthening of experimental activity. The following research centers were involved in the experimental work at IBR-2 using the developments of the project: Moscow State University; Saratov State University, Institute of Metal Physics, Ural Branch of the Russian Academy of Sciences; Petersburg Institute of Nuclear Physics, Research Center "Kurchatov Institute"; Budapest Neutron Center, Center for Energy Research, Hungary; Physical-Technical Institute of the Mongolian Academy of Sciences; China Atomic Energy Institute; University of China Academy of Sciences; Taiwan Tsinhua University. The reference list contains publications where, to a greater or lesser extent, the equipment or approaches developed and tested in the course of the project were used.

Costs related to theme 1121 within the period of 2018-2020 for the implementation of the project under the item “Materials and Equipment” amounted to 450 kUSD.

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