PROJECT

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

M.V. Avdeev, I.A. Bobrikov, I.V. Gapon, A.I. Ivankov, V.I. Petrenko, D.V. Soloviev, S.V. Sumnikov, A.V. Tomchuk (FLNP JINR , Dubna)

D.M. Itkis (Moscow State University, Moscow)

F.S. Napolsky (Dubna University, Dubna)

ABSTRACT

The performance characteristics of modern electrochemical energy storage devices (energy capacity, power, stability of operation, service life) are largely determined by the processes occurring at charge separation interfaces and by corresponding chemical reactions, as well as the evolution of the structure, composition and chemistry of electrodes and electrolytes. The project is aimed at developing neutron scattering techniques that would allow studying the structure of electrochemical interfaces and electrode materials of different types in the course of their operation (*operando* mode) and monitoring the influence of various factors on it. The high penetrating power of neutrons makes it possible to study complex systems that are the closest to real batteries. Neutron scattering experiments require the development of specialized approaches and the creation of electrochemical cells for simultaneous monitoring of voltage/current at an interface/electrode under study and the formation of a neutron beam passing through the interface/electrode, followed by detection and analysis of scattering. At the same time, for various types of interfaces/electrodes and the scattering methods used (diffraction, reflectometry, small-angle scattering), it is possible to formulate common tasks that allow one to some extent to combine approaches to their solution and thus improve the efficiency of obtaining structural information and enlarge the scope of investigations of various aspects of electrochemical processes. Thus, the purpose of this project is to develop approaches for the effective use of neutron scattering methods for various types of electrochemical interfaces and electrodes, with the subsequent creation of specialized experimental cells and a sample environment system for *operando* research.

Neutron scattering experiments will be carried out at the IBR-2 reactor at FLNP JINR on HRFD and RTD diffractometers, GRAINS reflectometer, and YuMO small-angle instrument. The long-term experience in electrochemical studies of a wide range of interfaces at the Chemical Faculty of Moscow State University (Moscow) and the experience in diffraction studies of electrodes in lithium-ion batteries at FLNP JINR will be used to develop new cells. Facilities and equipment for electrochemical testing of the cells, as well as application of additional methods (spectroscopy, microscopy, etc.) will be available in specialized laboratories at the Engineering Centre of Dubna University. The infrastructure developed during the project implementation will be employed in the framework of the User Program at the IBR-2 reactor for a wide range of tasks related to materials and interfaces for electrochemical energy storage.

The project cost is estimated to be about 450 k$ for 3 years.

1. INTRODUCTION

The production and storage of energy from electrochemical sources play an extremely important role in the creation of a wide range of present-day devices, from portable mobiles, laptops and electric tools to sophisticated machines such as railway locomotives and cars. The performance characteristics of modern electrochemical energy storage devices are largely determined by the processes occurring at charge separation interfaces and in electrodes and by corresponding chemical reactions. The evolution of the structure, composition and chemistry of electrodes and electrolytes has an impact on all functional parameters of the devices, including specific energy capacity, power, stability of operation and service life. The solution of the problems of modern electrochemistry requires the development of experimental approaches that would allow one to reliably describe the structure of electrode materials and interfaces during their operation.

The project is aimed at developing neutron scattering techniques that would allow studying the structure of electrochemical interfaces and electrode materials of different types in the course of their operation (*operando* mode). The application of this kind of techniques will allow us to monitor, at a new scientific level, the influence of the initial characteristics of surfaces and environmental parameters, the composition of electrolytes, overvoltage, current density and other parameters on the evolution of electrochemical interfaces and materials. The high penetrating power of neutrons makes it possible to study complex systems that are the closest to real batteries. Neutron scattering experiments require the development of specialized approaches and the creation of electrochemical cells for simultaneous monitoring of voltage/current at an interface/electrode under study and the formation of a neutron beam passing through the interface/electrode, followed by detection and analysis of scattering. At the same time, for various types of interfaces/electrodes and the scattering methods, it is possible to formulate common tasks that allow one to some extent to combine approaches to their solution, improve the efficiency of obtaining structural information and enlarge the scope of investigations of various aspects of electrochemical processes. Thus, the purpose of this project is to develop approaches for the effective use of neutron scattering methods for various types of electrochemical interfaces and electrodes, with the subsequent creation of specialized experimental cells and a sample environment system for *operando* research. The project includes consideration and enhanced adaptation of thermal neutron scattering methods, including diffraction, reflectometry and small-angle scattering, to solve electrochemical problems. In particular, it is planned to create 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. The corresponding experiments demand special equipment and infrastructure, which should be adopted to the sample environment systems of available neutron scattering instruments. The creation of an appropriate system for neutron monitoring and diagnostics of materials and interfaces at the IBR-2 reactor will allow one to carry out structural investigations at a new higher level and significantly expand the range of tasks solved in the field of electrochemistry. In turn, the implementation of this project will make a significant contribution to the development of the User Policy at the IBR-2 reactor.

2. STATUS OF STUDIES ON THE DESIGNATED SCIENTIFIC PROBLEM

The most common today lithium-ion batteries are electrochemical energy storage devices with the highest (up to 220 - 240 Wh / kg) accumulated specific energy among other types of accumulators. One of the most attractive ways to further increase the specific energy of batteries is a change-over to systems which use a metal lithium electrode as a negative electrode. Such systems include lithium-metal accumulators with positive electrodes of intercalation type and new electrochemical systems, such as lithium-sulfur or lithium-oxygen, being developed today. Advanced anode materials are also nanostructured silicon and alloys based on it. The development of rechargeable and safe electrodes with high capacity for new generation electrochemical batteries based on lithium-containing electrolytes requires a deep understanding of the processes occurring in the vicinity of the internal electrode-electrolyte interfaces during their operation. This is currently of great interest in the development of methods that allow effective monitoring of electrochemical interfaces where intercalation and electrodeposition of lithium occurs. The complexity in the application of any methods for these purposes is related to the high chemical activity of lithium, which demands a specialized infrastructure providing safe work with experimental electrochemical cells (both during their assembly/preparation for experiments and during experiments).

Nowadays, scattering of thermal neutrons is beginning to be actively used in the study of lithium energy storage devices [1, 2]. This is due to the high penetrating power of this type of radiation, which makes it possible to perform experiments in the *operando* mode, and due to the possibilities of the contrast variation approach based on isotope (primarily hydrogen/deuterium) substitution. There are two main research directions in this field which are (i) monitoring of the changes in the structure of electrodes in charge-discharge processes and (ii) monitoring of the evolution of interfaces between electrodes and liquid electrolytes. Thus, neutron diffraction (ND) is actively used [3-5] to follow the changes in the crystal structure of the electrodes in the processes of lithium incorporation/extraction. Neutron reflectometry (NR) makes it possible to track the growth of thin layers deposited in the course of electrochemical processes (in particular, transitional solid electrolyte interphase (SEI) layer) at the interfaces of electrodes with liquid electrolytes [6-10], and near-surface lithium incorporation into electrodes [11]. Finally, small-angle neutron scattering (SANS) is used to determine the structural properties of deposited discharge products and by-products in porous electrodes [12].

In recent survey works of the project participants [1,2] it has been shown that:

- Methods of scattering of thermal neutrons make it possible to investigate ‘hidden’ structures of electrode materials and interfaces in electrochemical energy storage devices.
- An important, from the practical point of view, feature of neutron scattering is the ‘averaged’ information on the volume or surface of electrodes, which avoids artifacts associated with the ‘locality’ of information and the influence of various factors on it in many other methods of research.
- Implementation of high-quality experiments requires an appropriate ‘electrochemical infrastructure’.

The latter imposes limitations on experiments in this respect at reactors and, in particular, at IBR-2. The project is aimed at solving this problem by significantly improving the experimental capabilities in regard to this topic and creating a specialized system for neutron *operando* monitoring and diagnostics of materials and interfaces for electrochemical energy storage devices. Its implementation will significantly increase the competitiveness of the IBR-2 reactor as a modern research neutron source.

References

[1] A.M.Balagurov, I.A.Bobrikov, N.Y.Samoylova, O.A.Drozhzhin, E.V.Antipov, Neutron scattering for analysis of processes in lithium-ion batteries, *Russ. Chem. Rev.* 83 (2014) 1120

[2] D.M.Itkis, J.J.Velasco-Velez, A.Knop-Gericke, A.Vyalikh, M.V.Avdeev, L.V.Yashina, Probing of electrochemical interfaces by photons and neutrons in operando. Review. *ChemElectroChem* 2 (2015) 1427

[3] A. Senyshyn, et al., *J. Electrochem. Soc.* 160, A3198 (2013)

[4] V. Zinth, C. von Lüders, M. Hofmann, J. Hattendorff, I. Buchberger, S. Erhard, J. Rebelo-Kornmeier, A. Jossen, R. Gilles, Lithium plating in lithium-ion batteries at sub-ambient temperatures investigated by in situ neutron diffraction, *Journal of Power Sources* 271 (2014) 152

[5] Bobrikov I.A., Balagurov A.M., Chih-Wei Hu, Chih-Hao Lee, Sangaa Deleg, Structural evolution in LiFePO4-based battery materials: in-situ and ex-situ time-of-flight neutron diffraction study, *Journal of Power Sources* 258 (2014) 356-364

[6] S. C. DeCaluwe, B. M. Dhar, L. Huang, Y. He, K. Yang, J. P. Owejan, Y. Zhao, A. A. Talin, J. A. Dura, H. Wang, Pore collapse and regrowth in silicon electrodes for rechargeable batteries, *Phys.Chem.Chem.Phys.,* 2015, 17, 11301

[7] T. M. Fears, M. Doucet, J. F. Browning, J. K. S. Baldwin, J. G. Winiarz, H. Kaiser, H.Taub, R. L. Sacci, G. M. Veith, Evaluating the solid electrolyte interphase formed on silicon electrodes: a comparison of *ex situ* X-ray photoelectron spectroscopy and *in situ* neutron reflectometry, *Phys. Chem. Chem. Phys.*, 2016,18, 13927-13940

[8] H. Kawaura, M. Harada, Y. Kondo, H. Kondo, Y. Suganuma, N. Takahashi, J. Sugiyama, Y. Seno, N. L. Yamada, Operando Measurement of Solid Electrolyte Interphase Formation at Working Electrode of Li-Ion Battery by Time-Slicing Neutron Reflectometry, *ACS Appl. Mater. Interfaces*, 2016, *8* (15), pp 9540–9544

[9] G. M. Veith, M. Doucet, J. K. Baldwin, R. L. Sacci, T. M. Fears, Y. Wang, J. F. Browning, Direct Determination of Solid-Electrolyte Interphase Thickness and Composition as a Function of State of Charge on a Silicon Anode, *J. Phys. Chem. C*, 2015, 119 (35), 20339–20349

[10] Avdeev M.V., Rulev A.A., Bodnarchuk V.I., Ushakova E.E., Petrenko V.I., Gapon I.V., Tomchuk O.V., Matveev V.A., Pleshanov N.K., Kataev E.Yu., Yashina L.V., Itkis D.M. Monitoring of Lithium Plating by Neutron Reflectometry. *Appl. Surf. Sci.*, 2017, in press.

[11] B.-K. Seidlhofer, B. Jerliu, M. Trapp, E. Hüger, S. Risse, R. Cubitt, H. Schmidt, R. Steitz, M. Ballauff, Lithiation of Crystalline Silicon As Analyzed by Operando Neutron Reflectivity, ACS Nano, 2016, 10 (8), 7458–7466

[12] C. A. Bridges, X.-G. Sun, J. Zhao, M. P. Paranthaman, S. Dai, In Situ Observation of Solid Electrolyte Interphase Formation in Ordered Mesoporous Hard Carbon by Small-Angle Neutron Scattering, *J. Phys. Chem. C* 2012, *116*, 7701–7711

3. DESCRIPTION OF PROPOSED RESEARCH

3.1. Physical background

The development of the experimental instrumentation for electrochemical research at the IBR-2 reactor during the project will be carried out in the following areas of modern research of electrochemical energy storage devices in the *operando* mode:

I. Evolution of the crystal structure of electrodes;
II. Evolution of interfaces of flat electrodes with liquid electrolytes;
III. Evolution of developed interfaces of porous electrodes with liquid electrolytes;

In regard to item I, the most promising approach is the application of neutron diffraction. The corresponding range of topical applied problems for this method includes the study of:

- Intercalation/deintercalation of lithium into electrodes based on new advanced materials for increasing the discharge capacity, such as nanostructured silicon and its alloys, vanadium oxide V_2O_5, etc.;
- Degradation of electrodes based on the analysis of the evolution of the microstructure of electrode materials both in the process of a single operating cycle and during long-term operation.
- Moreover, it is possible to set more fundamental problems related to phase transitions in materials for electrodes during electrochemical cycling.

Item II implies the application of neutron reflectometry. The range of tasks in this area includes:

- Creation and testing of complex heterogeneous thin-film electrodes based on metals and silicon;
- Analysis of the formation and evolution of a passivation SEI layer on the surface of such electrodes;
- Development of a methodology for contrast variation based on the use of electrolytes with deuterated solvents;
- Analysis of the appearance and growth of inhomogeneities, including the formation of needle-type deposits (‘dendrites’), at interfaces with various electrolytes and the development for this purpose of the techniques of specular reflection, diffuse scattering, and grazing incidence small-angle scattering (GISANS).

While optical methods allow one to observe dendritic formations at their final stages of growth (micron level), neutron reflectometry is sensitive to nanoscale structural alterations, i.e. there is a fundamental opportunity to track the initial stages of dendrite formation, which will make it possible to clarify the mechanisms of their appearance and growth. Then, one can test the influence of various factors on these processes when studying the suppression of this parasitic energy phenomenon in electrochemical storage devices.

In the framework of item III, small-angle neutron scattering is used to solve urgent problems:

- Study of deposition of discharge products in porous positive electrodes for lithium-air and lithium-sulfur batteries;
- Development of methods for analyzing the pore filling in the electrode by the products of electrochemical processes;
- Development of a contrast variation technique based on the use of electrolytes with deuterated solvents.

The effective application of the above-mentioned neutron scattering techniques (diffraction, reflectometry, and small-angle scattering) to solve the formulated problems requires the creation and systematic testing of specialized electrochemical cells and sample environment systems for *operando* research.

3.2. Methodological background

The methodological aspects of the project concern the following directions.

- Development of common approaches to the effective use of neutron scattering methods (diffraction, reflectometry, small-angle scattering) in the analysis of the evolution of the structure of various types of electrodes and interfaces for electrochemical energy storage devices during their operation (*operando* mode).
- Creation and improvement of specialized electrochemical cells and sample environment systems for *operando* research in neutron scattering experiments.

Within the project, the following tasks in regard to the involved methods are assigned.

<u>Neutron diffraction</u>

- Optimization of existing electrochemical cells for diffraction experiment.
- Installation of a specialized collimation system for incoming and scattered neutron beams.
- Development of a sample environment system, including the electrode preparation line, for electrochemical studies.

<u>Neutron reflectometry</u>

- Optimization of a neutron experiment with respect to the selection of electrode and electrolyte compositions in combination with electrochemical characteristics of interfaces under study.
- Optimization of reflectometry cells and sample environment systems.
- Organization of synthesis of complex heterogeneous film electrodes.
- Diagnostics of dendritic formations after neutron scattering experiments.
- Organization of storage and processing of crystalline substrates after neutron scattering experiments.

<u>Small-angle neutron scattering</u>

- Development of an electrochemical cell for neutron experiments.
- Development of a sample environment system for in-situ neutron experiments.

Neutron scattering experiments will be carried out at the IBR-2 reactor at FLNP JINR using HRFD and RTD diffractometers, GRAINS reflectometer, and YuMO small-angle instrument. The long-term experience in electrochemical studies of a wide range of interfaces at the Chemical Faculty of Moscow State University (Moscow) and the experience in diffraction studies of electrodes in lithium-ion batteries at FLNP JINR will be used to develop new cells. Facilities and equipment for electrochemical testing of the cells will be available in specialized laboratories at the Engineering Centre of Dubna together with the chemical equipment already available in FLNP JINR (argon box, mixers for preparing electrodes, etc.). The close proximity of the experimental site of JINR and Dubna University will make it possible to carry out, with high efficiency, the development and testing of electrochemical cells for neutron experiments. The accomplishment of The experimental tasks of the project are among the key priority targets of the electrochemical laboratories of the involved educational institutions, where neutron scattering data can also be supplemented by a variety of laboratory methods (spectroscopy, microscopy, etc.).

3.3. Expected results

Neutron diffraction
Creation and approbation of specialized electrochemical cells and sample environment system for *operando* studies of intercalation/deintercalation of lithium into electrodes based on new advanced materials for increasing the energy capacity of lithium-ion batteries. Improvement of the cells regarding their use for multiple discharge-charge cycling.

Neutron reflectometry
Creation and approbation of specialized electrochemical cells and sample environment system for studying lithium electrochemical deposition on flat interfaces based on metal and complex heterogeneous thin-film electrodes in the *operando* mode. Optimization of the neutron experiment with respect to the choice of electrode and electrolyte composition in combination with electrochemical characteristics of interfaces under study. Analysis of the appearance and growth of heterogeneities, including the formation of filamentous deposits on interfaces with various electrolytes. The development for this purpose of techniques of specular reflection, diffuse scattering and grazing incidence small-angle scattering (GISANS). The development of the contrast variation technique based on the use of electrolytes with deuterated solvents.

Small-angle neutron scattering
Creation of specialized electrochemical cells and sample environment system for studying deposition of electrochemical cycling products in porous positive electrodes of lithium-air and lithium-sulfur batteries in the *operando* mode. Development and creation of a sample environment system for in-situ experiments.
Development of techniques for analyzing pore filling in electrodes by products of electrochemical processes. Development of the contrast variation technique based on the use of electrolytes with deuterated solvents. Improvement of the cells regarding their use for multiple discharge-charge cycling.

As the main result, a combined system for monitoring the structure of electrochemical interfaces with respect to electrodes and their interfaces with liquid electrolytes will be created. This system will allow experiments with different neutron scattering methods for the same electrochemical cells. The infrastructure developed during the project implementation will be employed in the framework of the User Program at the IBR-2 reactor for a wide range of tasks related to materials and interfaces for electrochemical energy storage. This subject is of current interest; nowadays the number of corresponding proposals to IBR-2 is ~ 10 per year. Among the research centers involved in the experiments on electrochemistry are Moscow State University; Saratov State University, Institute of Metal Physics, Ural Branch of the Russian Academy of Sciences; Petersburg Institute of Nuclear Physics, Kurchatov Institute; China Institute of Atomic Energy; University of China Academy of Sciences; Taiwan Tsinhua University. One of the project objectives is to increase the number of applications for enhanced experiments on problems in electrochemistry using more complex approaches, and, as a result, to increase the number of involved research centers in experiments in this area at the IBR-2 reactor.

3.4. Project structure

The research groups of the Frank Laboratory of Neutron Physics of JINR, the Faculty of Chemistry and the Faculty of Materials Science of Moscow State University, the Faculty of Science of the University of Dubna and its Engineering Center are involved in the project.

The groups are assigned to fulfill the following tasks.

FLNP JINR

Manufacturing:

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

Organization and support of R&D line for deposition and grinding of crystalline substrates;
Organization and conduct of neutron experiments at the IBR-2 reactor;
Diagnostics and storage of samples under special conditions after experiments.

MSU

Design and draft projects:

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

Scientific support of the project.

Dubna University/Engineering Center

Test assembly and electrochemical measurements of cells and sample environment systems for neutron experiments;
Electrochemical support of neutron experiments.

3.5. Groundwork

To date, several series of experiments have been carried out at FLNP to study the intercalation and deintercalation of lithium in electrode materials in the *operando* mode by neutron diffraction. As a result, a framework has been organized to create an infrastructure for electrochemical research at the IBR-2 reactor, including specialized boxes for working with cells. Some experience has been accumulated on the creation of electrochemical cells for this purpose, which can be used in the design and manufacture of a new class of cells and a general monitoring system for new advanced electrode materials.

Regarding flat interfaces with thin-film metal electrodes in contact with liquid lithium-containing electrolytes, first pilot experiments on neutron reflectometry in the *operando* mode have been carried out. The possibilities of the experiment design with the matching of the scattering from the electrode by using deuterated electrolytes are considered. The sensitivity of the method with respect to thickness, roughness and density of the deposited layer has been determined. The experience gained allows us to fulfill the project objectives on creating a sample environment system in a reflectometry experiment with complex electrochemical interfaces in the *operando* mode on a full scale in a relatively short time.

Small-angle neutron scattering was used in test experiments to track the deposition of lithium peroxide in lithium-air electrochemical cells based on carbon porous matrices impregnated with liquid lithium-containing electrolytes. The experiments were conducted in ex-situ mode. The possibilities and sensitivity of the method with respect to the degree of filling of nanopores (size interval of 1 ± 100 nm) by the products of the interaction of lithium with an electrolyte during the discharge of the cells have been specified. The experience gained provides the basis for the successful implementation of the project with regard to the creation of in-situ cells for the small-angle neutron scattering method and respective sample environment for *operando* research.

4. MANPOWER

FLNP JINR
M.V. Avdeev, V.I. Petrenko, A.V. Tomchuk, I.V. Gapon,
I.A. Bobrykov, S.V. Sumnikov, A.M. Balagurov, O.Yu. Ivanshina, N.Yu. Samoylova,
D.V. Soloviev, A.I. Ivankov
The share of participation in the project is 65%.

MSU, Moscow
D.M. Itkis, E.B. Kataev, A.A. Rulev, T.K. Zakharchenko, O. Kapitanova, L.V. Yashina
The share of participation in the project is 15%.

Dubna University, Dubna
F.S. Napolsky, E.E. Ushakova, M. Erdaulethov, V.A. Krivchenko
The share of participation in the project is 20%.

5. BUDGET

Description	Cost, k$	Year 1, k$	Year 2, k$	Year 3, k$
Equipment	**240**	**80**	**80**	**80**
Development and manufacturing of electrochemical cells for neutron diffraction, neutron reflectometry and small-angle neutron scattering (~ 30 pcs.)	100	30	30	40
Sample environment systems including in situ experiments	100	30	30	40
Portable programmable potentiostat with safety control (2 pcs.)	40	20	20	-
Outside contracts	**100**	**30**	**30**	**40**
Sputtering and processing of crystalline substrates	100	30	30	40
Materials	**80**	**30**	**30**	**20**
Crystalline substrates	10	5	5	-
Targets for sputtering electrodes	10	5	5	-
Consumables	10	5	5	-
Deuterated electrolytes	25	5	10	10
^{7}Li salts	25	5	10	10
Software	**15**	**5**	**5**	**5**
Travel expenses	**15**	**5**	**5**	**5**
Total:	**450**	**150**	**150**	**150**

6. SHORT SWOT ANALYSIS

Internal strengths:

• Availability of stable high-flux pulsed neutron source.

• Balanced and experienced team for solving instrumental and methodological problems with a high level of understanding of physical problems, the solution of which is aimed at creating new equipment.

• Availability of fully equipped electrochemical laboratory in the close proximity to the neutron source.

• High scientific background on the topic of all groups participating in the project.

• Participation of a large number of young specialists trained in this field, who can immediately start implementing specific project tasks without additional preparation.

Internal weaknesses:

• Time-limited operation of the neutron source.

• High workload of the reactor instruments.

• Probability of irregular financing.

• High cost of experiments

External opportunities:

• Relevance of the topics and high demand in the respective experiments from the world scientific community.

• Prospects for financing future research at the equipment being developed in the project by various scientific and business foundations.

External threats:

• Competition in certain areas with the world's neutron centers.