Studies of electrochemical interfaces by TOF neutron reflectometry at the IBR-2 reactor

V I Petrenko\textsuperscript{1,2,}\ast, I V Gapon\textsuperscript{1,2}, A A Rulev\textsuperscript{3}, E E Ushakova\textsuperscript{3,4}, E Yu Kataev\textsuperscript{3}, L V Yashina\textsuperscript{3}, D M Itkis\textsuperscript{3,5}, M V Avdeev\textsuperscript{1,5}

\textsuperscript{1}Frank Laboratory of Neutron Physics, Joint Institute for Nuclear Research, Dubna, Moscow Reg., Russia
\textsuperscript{2}Taras Shevchenko National University of Kyiv, Kyiv, Ukraine
\textsuperscript{3}Department of Chemistry, Lomonosov Moscow State University, Moscow, Russia
\textsuperscript{4}Engineering Incubator Ltd., Dubna, Moscow Reg., Russia
\textsuperscript{5}Dubna University, Dubna, Moscow Reg., Russia

E-mail: vip@nf.jinr.ru

Abstract. The operation performance of electrochemical energy conversion and storage systems such as supercapacitors and batteries depends on the processes occurring at the electrochemical interfaces, where charge separation and chemical reactions occur. Here, we report about the tests of the neutron reflectometry cells specially designed for operando studies of structural changes at the electrochemical interfaces between solid electrodes and liquid electrolytes. The cells are compatible with anhydrous electrolytes with organic solvents, which are employed today in all lithium ion batteries and most supercapacitors. The sensitivity of neutron reflectometry applied at the time-of-flight (TOF) reflectometer at the pulsed reactor IBR-2 is discussed regarding the effect of solid electrolyte interphase (SEI) formation on metal electrode surface.

Keywords: electrochemical interfaces; neutron reflectometry; specular reflectivity; lithium ion batteries; liquid electrolytes; solid-electrolyte interphase.

1. Introduction
Electrochemical energy conversion and storage systems often play a crucial role in overall performance of a wide variety of devices that we face in our everyday life ranging from portable phones, laptops and power tools, to rather big facilities including power / heat cogeneration fuel cell systems, railway locomotives, power grid leveling facilities. The operation of the most of these systems such as supercapacitors [1], rechargeable batteries [2] is based on the electrochemical interfaces, where charge separation and chemical reactions occur. The evolution of the structure, composition and chemistry at the interfaces between electrodes and electrolytes affects all the functional parameters of the device including power and long-term performance stability. That motivates the researchers to study the chemical processes at the interface itself and transport phenomena in bordering layers under operando conditions. The methods that allow effective monitoring of internal electrode-electrolyte interfaces in operando conditions are of current interest [3]. Among such methods, neutron reflectometry (NR) is one of few techniques that provide a sensitivity to such interfaces due to high penetration power of thermal neutrons into matter. An additional important feature of NR is a possibility to vary ‘electrode-
electrolyte’ scattering contrast based on isotope substitution of hydrogen for deuterium in the liquid component to better resolve near-surface layers of interest.

An in-deep understanding of atomistic mechanisms underlying different electrochemical process, including electric double layer formation, Faradic processes involving heterogeneous electron or ion transfer, often require that data are to be recorded in situ. Ex situ studies in lots of cases are almost irrelevant, since the chemical reactions occurring during operation of electrochemical devices result in intermediates and products that cannot be quenched for post-process studies. The desired parameters include (i) the chemical composition at the interface, (ii) the chemical state of atoms and it is variation due to the chemical / electrochemical reactions, and (iii) structural evolution in the interface region.

Here, we report about the tests of the NR cells specially designed for operando studies of the structural changes at the electrochemical interfaces between solid electrodes and liquid electrolytes. The cells are compatible with anhydrous electrolytes with organic solvents, which are employed today in all lithium ion batteries and most supercapacitors. The concept of the cells mainly repeats the ideology of the previous devices for this purpose [4, 5]. It uses the horizontal layout of the interface with the neutron beam passing through a massive single crystal silicon block and falling to a thin (thickness below 100 nm) electrode film on silicon which is in contact with a liquid electrolyte containing lithium. The experiment can be done when the electrodes are in close electric circuit under potentiostatic control. As a first step, homogeneous metal film (copper) is used as a working electrode. The task of the experiment was to determine the possibilities of these units applied at the GRAINS time-of-flight (TOF) reflectometer [6], with horizontal sample plane at the IBR-2 pulsed reactor.

2. Experimental

The tested NR cells used the horizontal ‘from the top’ layout (Fig.1) or ‘from the bottom’ layout with the neutron beam passing through a massive (dimensions 8 × 5 × 1.5 cm) single crystal silicon block and falling to the interface between a thin electrode film (working electrode) on the silicon substrate and liquid electrolyte. As a working electrode, a metal (copper) film was used. The electrode deposition (magnetron sputtering) on several Si substrates was made at PNPI NRC KI (Gatchina, Russia) in two steps including the deposition of an intermediate Ti layer (nominal thickness 5 nm) for better copper adhesion and the deposition of the Cu layer itself (nominal thickness 50 nm) on the working silicon surface (plane orientation <111>, nominal roughness < 0.5 nm).

Several designs of NR cells have been developed. The main common features of the cells are demonstrated in Fig.2, where a cell for the from the top experimental configuration is presented. The cell is designed airtight with o-ring sealing between silicon single crystal and the cell enclosure. The sealing is important as the electrolytes used should contain no more than 10 ppm humidity. The cell enclosure is fabricated of polyether ether ketone (PEEK), the polymer which comprises proper mechanical properties together with high chemical stability in contact with organic solvents and does not react with metallic lithium that is used as a counter electrode (Li foil from China Energy Lithium, ltd., pressed on Ni mesh). The important feature of the cell is the introduction of Vycor-frit separate reference electrode (RE) that allows accurate potential control of the working electrode (WE). We use Ag/Ag+ RE prepared in-house by sealing a silver wire in a tube with a solution of 0.01M AgNO3 (Aldrich) and 0.1M tetrabutylammonium perchlorate (Aldrich, for electrochemical analysis) in acetonitrile (Aldrich, anhydrous). The RE potential was calibrated against a ferrocene / fferrocenium redox couple prior to the cell assembly. The cell was assembled including the electrolyte filling in the controlled atmosphere Ar-filled glovebox (humidity and oxygen concentrations below 0.1 and 1.0 ppm, respectively). The potential between the electrodes of the NR cell was controlled using a Bio-logic SAS SP-200 potentiostat / galvanostat in three-electrode configuration.
Figure 1. Principal ‘from the top’ layout of the NR experiment with the electrochemical cell. The plane neutron beam passes single-crystal Si and falls on interface between thin electrode film (working electrode) on the silicon substrate and liquid electrolyte. The ratio between the specular reflected (wave vector $\vec{k}$) and incident (wave vector $\vec{k}_0$) neutron beams known as reflectivity is measured as a function $R(q_z)$ of the Z-projection of the momentum transfer, $q_z = (4\pi/\lambda) \sin \alpha \approx 4\pi \alpha/\lambda$, where $\lambda$ is the neutron wavelength and $\alpha$ is the grazing angle. The potential between the working electrode (copper film) and the counter electrode (lithium foil) is remotely controlled.

In the first tests of the cells, 0.1 M solution of LiClO$_4$ (Aldrich, battery grade) in propylene carbonate (PC) was used as an electrolyte. Two kinds of solvents in the electrolyte were probed including protonated PC (h-PC, CH$_3$C$_2$H$_3$O$_2$CO) and deuterated PC (d-PC, CD$_3$C$_2$D$_3$O$_2$CO) both purchased from EQ Laboratories GmbH. The required electrolyte volume was about 6 ml (cell with the from the top configuration) and < 3 ml (cell with the from the bottom configuration) per one cell filling.

Figure 2. The design of electrochemical cell for neutron reflectometry, ‘from the top’ configuration.

The NR measurements were carried out at the GRAINS time-of-flight reflectometer at the IBR-2 pulsed reactor of FLNP JINR (Dubna, Russia) [7] in the thermal mode of the moderator.
The inclination ($\approx 5$ mrad) of the plane-incident beam (collimated by several slit apertures) against the interface was provided by a deflecting neutron mirror (mirror-sample distance 3 m). The specular beam was detected by a 2D position-sensitive detector (size $20 \times 20$ cm$^2$, resolution $2 \times 2$ mm$^2$, sample-detector distance 3 m) [8] with the averaging of the reflected beam along the horizontal direction. The intensity was plotted as a function of the momentum transfer, $q_z = (4\pi/\lambda) \sin \theta \approx 4\pi \theta/\lambda$, where $\theta$ is the fixed (5 mrad) incident grazing angle (see Fig.2) and $\lambda$ is the neutron wavelength varied in the working interval of 0.1 - 0.6 nm. The calibration against the incident spectrum was performed by a separate measurement of an empty beam (after removing the cell from the beam). The obtained NR curves were processed in terms of the Parratt formalism using the Motofit package for the IGOR Pro software [9].

3. Results

Prior the experiment with liquid electrolytes the structure of the pristine working electrode film deposited on the silicon substrate was determined by NR in the ‘beam from air’ experiments (Fig.3). Found from the fitting, the SLD profile (see inset to Fig.3) gives the best parameters collected in Table 1. The fitting procedure requires the introduction of an additional small transitional layer with respect to the boundary between Cu and Ti layers with high roughness and intermediate (between Cu and Ti) SLD-value. The parameters of the SLD profile of the working electrode film were fixed in the fitting of the next experimental curves obtained when the electrode was in contact with liquid electrolytes.

![Figure 3.](image)

The NR experiment on the observation of the SEI layer for the cell filled with the electrolyte consists of two stages. First, the specular reflectivity curves are obtained under open circuit conditions. At the next stage, the deposition of the SEI layer on the copper electrode surface is initiated by applying to the cell a constant potential (here, + 10 mV vs. Li$^+/\text{Li}$ during 15 min period). Then, the NR curves are obtained under open circuit conditions. The experimental reflectivity curves for the two (h- and d-) cases are collected and treated in Fig.4. Slight changes in the modulation of $R(q_z)$ because of the new small layer can be seen. The fits were made by
varying reduced number of parameters of the interface layers including the thickness, roughness and SLD of the new layer, as well as the SLD of electrolyte. The last parameter was made free to be sure that the electrolyte SLD was not modified because of some parasitic effects (e.g. residual gas fraction) after cell assembly and filling.

Table 1. Parameters of the SLD profile of the studied electrode on silicon substrate obtained by NR in the beam from air experiment.

| Layer   | Mean SLD, $\times 10^{10}$ cm$^{-2}$ | Thickness, Å | Roughness, Å |
|---------|-------------------------------------|--------------|--------------|
| Cu      | 6.5243                              | 470          | 20           |
| Cu/Ti   | 4.0                                 | 7            | 10           |
| Ti      | -1.9249                             | 38           | 10           |
| Si      | 2.0737                              | -            | 5            |

Figure 4. Experimental specular NR curves from electrochemical interfaces under study with d-electrolyte (a) and h-electrolyte (b) and fitting curves. The curves ‘before deposition’ and ‘after deposition’ are shifted along the ordinate axis for convenient representation. To compare in absolute scale, the model curves are given Fig.5.

The effect of the SEI layer in the NR experiments with two kinds of electrolytes is analyzed in Fig.5, where the SLD profiles and corresponding model reflectivity curves obtained from the experimental NR curves before and after SEI deposition are compared. A new transitional (electrode-electrolyte) layer (characteristic thickness $\approx 50$ Å) can be seen reflecting the SEI formation in agreement with the previous results for the similar interface [5]. As compared to the electrolyte, a lower SLD of this layer is a result of lithium enrichment; this decreases SLD since lithium has negative scattering length. While a modification of the SLD profile after SEI
deposition takes place in both kinds of electrolyte, the effect is more pronounced in the case of the deuterated electrolyte. This is consistent with the scattering contrasts between electrolyte and electrode; the SLD difference is significantly less in the case of h-PC. The mean SLD of the SEI layers in the two electrolytes differs in absolute values showing the dependence of this parameter on the electrolyte SLD. The reason is that in the h-case hydrogen containing components of SEI decreases SLD of the layer because of low scattering length of hydrogen, while in the d-case the situation is opposite; SLD should increase because of the presence in it of deuterium with high scattering length. The additional potential factor determining this effect is a possible penetration of the liquid electrolyte into a porous at some extent structure of the SEI layer, thus increasing the effective content of hydrogen or deuterium in the layer for h- and d-solvents, respectively.

To separate the contribution from the solvent, the so-called contrast variation should be done when experiments are repeated for the electrolytes with different deuteration rates and, hence, different SLDs and contrasts against the SEI layer.

![Figure 5](image)

**Figure 5.** Effect of SEI layer in NR experiments with d-electrolytes (a) and h-electrolytes (b). The SLD profiles and corresponding model reflectivity curves obtained from the experimental NR curves before and after SEI deposition are compared. The differences in the SLD profiles before and after deposition are marked by red filling to illustrate different levels of deviations.

One can conclude that the $q_z$-range covered in the TOF experiments for the thermal ($T = 300$ K) mode of the neutron source carried out at one grazing angle is sufficient to reliably conclude about the appearance of a new layer (thickness above $40 \, \text{Å}$). It is important that this range is insensitive to the details of the inner titanium layer between the substrate and the electrode film followed from the XRR analysis. Our tests show that the SEI evolution on the metal electrode surface including thickness, roughness and mean scattering length density can be well followed in the operando experiments with deuterated electrolytes. In this connection, the ‘from bottom’ configuration of the NR cell is more preferable because of the lower volume
of comparatively expensive deuterated solvents required in the experiment.

4. Conclusions
The neutron reflectometry experiments on electrochemical interfaces have been carried out using specialized cells for operando studies at the time-of-flight reflectometer. The interfaces between metal (copper) electrode and liquid electrolyte with lithium ions (lithium perchlorate dissolved in propylene carbonate) have been probed to clarify the sensitivity of the NR method to the formation of solid electrolyte interphase (SEI) on the metal electrode when analyzing specular reflectivity curves. The $q_z$-range covered in the experiments for the thermal mode of the neutron source ($T = 300$ K) is sufficient to reliably conclude about the appearance of a new layer (thickness above 40 Å). The effect for light and heavy solvents in the electrolyte with respect to the D/H substitution have been compared in the same operando conditions. It is more pronounced for the heavy electrolyte because of the higher scattering contrast between electrode and electrolyte. The sensitivity of the scattering length density of SEI to the change in the electrolyte density after H/D substitution has been observed which is indicative of the electrolyte penetration into the structure of SEI.

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