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Monitoring of lithium plating by neutron reflectometry

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ABSTRACT

The development of high-capacity rechargeable and safe metallic lithium negative electrodes for next-generation batteries requires an in-depth understanding of reasons for nonuniform lithium plating during lithium-metal battery charge. It drives the interest for the tools enabling efficient monitoring of electrochemical interfaces where lithium electrodeposition occurs. We report on a three-electrode electrochemical cell designed to track lithium electrodeposition from aprotic electrolytes by neutron reflectometry (NR) in the specular reflectivity mode. We performed a case study of Li plating from $LiClO_4$ solution in propylene carbonate. The sensitivity was optimized by tuning the neutron scattering contrast for a given electrode material (Cu film) and the electrolyte, which was done employing a deuterated solvent. The analysis of the scattering length density (SLD) profiles derived from the modeling of the reflectivity data clearly demonstrated that the deposition of nm-thin Li layers above initially formed solid-electrolyte interphase (SEI) layer can be detected and their roughness, which is a characterizing parameter of electrodeposition nonuniformity, can be estimated. It makes NR a proper tool for further studies of "dendritic" lithium growth.

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1. Introduction

Having the highest specific capacity among all metals (about 3.8 Ah/g) and the most negative standard electrode potential (−3.05 V) lithium can potentially enable the development of batteries possessing extraordinary high specific energy, *e.g.* lithium-metal-polymer, lithium-air or lithium-sulfur [1]. High reactivity of metallic lithium leading to active solid-electrolyte interphase (SEI) formation, and electrodeposition in the form of filaments upon battery charge cycles often referred to as "dendrite" growth, however, prevent application of metallic lithium negative electrodes [2]. The "dendrite" formation is a rather complicated process. Although being studied for decades there is still no complete understanding on whether it can or cannot be suppressed. The need for in-depth understanding of the mechanisms driving nonuniform lithium plating motivates the researchers to apply both *in situ* (optical microscopy [3], SEM [4], holography [5], and others) and *ex situ* (SEM [6], AFM [7], and others) tools to study this process. Neutron reflectometry (NR) is one of the tools, which enable *operando* studies of spatial distributions of the components at electrochemical interfaces [8]. It provides the information about the interfaces, first of all, in terms of the scattering length density (SLD) profile along the interface depth by analyzing and modeling specific modulations in the specular reflectivity of thermal neutrons as a function of their momentum transfer upon scattering. In contrast to X-ray reflectometry where because of high absorption the beam can be guided only through the electrolyte, NR makes it possible to probe electrochemical interfaces through the electrode, which is achieved due to extremely high penetration power of neutrons. Also, in contrast to the 'local' tools for microstructural investigations of electrochemical interfaces (*e.g.* SEM, AFM), the reflectivity techniques provide the information averaged over the interface at the macroscopic scale.

Here, we report the observation of metallic lithium plating by NR using a specially fabricated three-electrode electrochemi-

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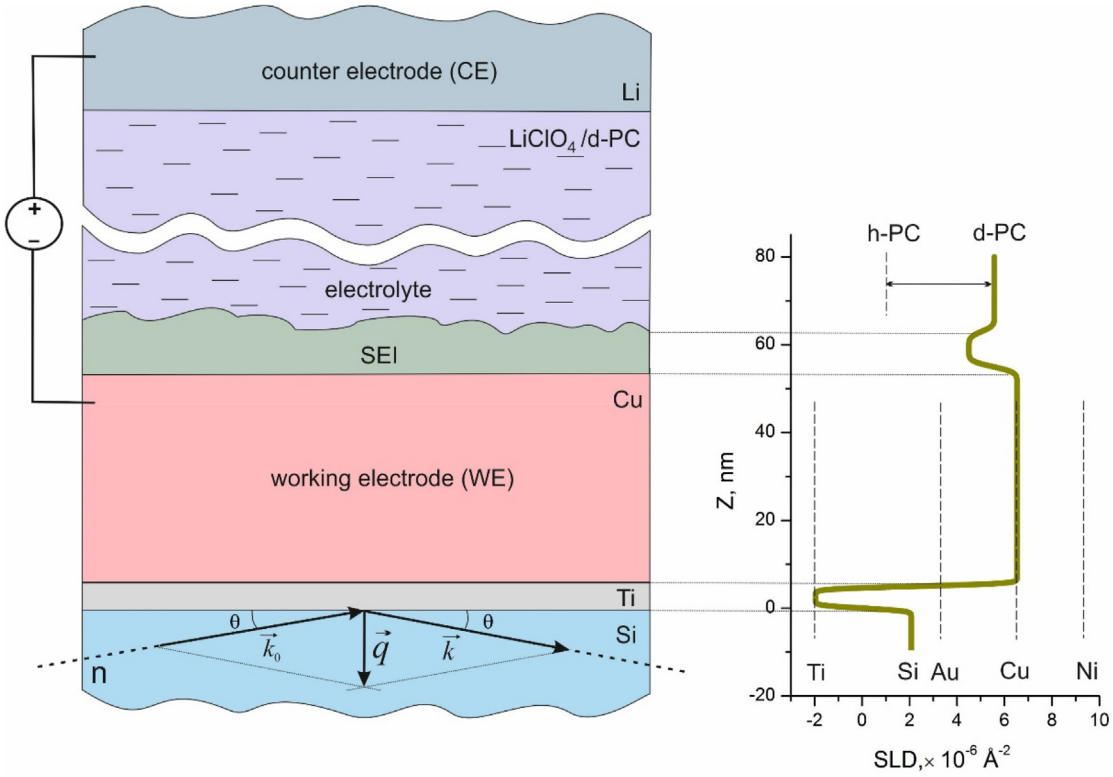

Fig. 1. Principal layout of the specular NR experiment on electrochemical interface with a metal electrode and lithium-containing liquid electrolyte. The schematic representation of SLD profiles of the interface with possible ranges for electrode materials and h-/d- electrolyte combinations is shown.

cal cell for *in situ* studies of electrochemical interfaces involving non-aqueous Li^+-containing electrolytes. The cell adopts previously reported designs with metal [9,10] or other types of working electrodes [11–17] and uses the horizontal 'beam from the top' or 'beam from the bottom' layouts (Fig. 1) with a flat neutron beam passing through a single crystal silicon block and reaching a thin-film metal electrode (working electrode) deposited on a silicon substrate. The cell design allows using Ag^+/Ag and other reference electrodes for precise potential control. The hydrogen/deuterium isotopic substitution in electrolyte solvents is used to control the scattering contrast between the components at the interface, thus providing a possibility to enhance the sensitivity of the technique to interface changes occurring upon lithium plating. Using the solution of lithium perchlorate in deuterated propylene carbonate as the electrolyte, we tracked the SEI formation and lithium metal deposition in the thickness range of few nanometers by *in situ* NR.

2. Design of NR experiment

In specular reflectometry experiments (Fig. 1) the reflectivity (ratio between reflected and incident beam intensities) is measured as a function of q, the component of the momentum transfer vector along the normal to the interface plane (Z-axis in Fig. 1). The specular reflection takes place at very small grazing angles, which makes it possible to determine a 1D normal SLD distribution. The typical resolution of NR experiments restricts the upper limit of the thickness sensitivity interval for the studied layered structures on bulk substrates at the level of 100 nm. The lower limit in a complex manner depends on the contrast combination between the layers composing the interface against SLDs of the substrate and a liquid phase. Thus, the investigations of the electrochemical interface between a 50-nm copper film deposited on single crystal Si and 1 M $LiPF_6$ solution in the 1:2 (vol.) mixture of deuterated ethyl carbonate (d-EC) and protonated diethyl carbonate (h-DEC) showed [10] that subtle changes in the NR curves caused by the formation of a lithium-enriched SEI can be reliably detected when its SLD is lower by about 10% in comparison with that of electrolyte and the thickness exceeds ≈4 nm.

In order to maximize the changes in reflectivity upon SEI formation and further lithium plating, one needs to consider the optimization problem concerning the combination of components' SLDs in the interface depth profile in Fig. 1. Although full optimization including all the parameters of the SLD profile is rather difficult, the best SLD combination can be derived from the general terms. It corresponds to the situation when the reflection comes only from the SEI layer or deposited Li metal which can happen if SLDs of all components (substrate, electrode material and electrolyte) are equal. In this case, the simple calculations show that despite small characteristic reflectivity (<0.01) over typical q-ranges covered in the experiments with thermal neutrons, it can be well detected and analyzed by the available neutron reflectometers. As the substrate SLD is predefined in this scheme (actually, single crystal silicon has no competitors with respect to the transparency for neutrons), it should be matched by electrolyte SLD, which is easily achieved by employing deuterated solvents or its mixtures with non-deuterated analogs (see, for example, [10]). Here, among other aprotic solvents, propylene carbonate was selected for lithium-metal deposition studies. It forms rather dense SEI on a lithium surface, which prevents further decomposition of the electrolyte [18]. The composition and structure of the formed SEI, as well as its electrochemical behavior are known from literature, simplifying further NR data fitting.

The electrode SLD changes significantly depending on the electrode material. Different options are considered in the interface SLD profile in Fig. 1. The matching of the substrate SLD by the electrode is principally possible if one deposits a sufficiently thick (>10 nm) quasi-homogeneous multilayer (*e.g.* a set of Ti/Ni bilayers) with the average SLD equal to that of Si. The thickness of sublayers in this

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