

In situ neutron reflectometry analysis of electrode/electrolyte interface for lithium batteries

Tokyo Institute of Technology, Ryoji Kanno

1. Introduction

Neutron reflectometry is a powerful technique that can provide an atomistic understanding of solid/liquid interfaces as a function of the depth, since neutrons have a sufficiently small absorption cross-section for penetrating electrochemical cells so that electrochemical interfaces can be probed. As a light element, lithium has a relatively high neutron scattering power compared to that of X-rays, and the depth profile of the neutron scattering length density (SLD) obtained by curve fitting can reveal the surface structure changes of lithium battery electrode films during electrochemical processes. In contrast, no structural information at the liquid-electrolyte side interface has been available. A high-resolution structural analysis method of the liquid-side interface is absolutely essential for further understanding of the interfacial reactions in lithium batteries. We have developed neutron reflectometry techniques for investigating the interfacial structures of lithium batteries, and have successfully clarified lithium distribution changes at the electrode-side interface from neutron reflectometry data collected at SOFIA on the 2013B and 2015A proposals. However, we have not clearly extracted the interfacial structure at the electrolyte side from the scattering length density profiles mainly due to the surface roughness of the electrode films. The model-film electrodes had a roughness of several nanometers which could be comparable to the length of electric double layer. It makes difficult to distinguish the electric double layer from the film roughness. In this proposal, we will conduct in situ neutron reflectivity measurements of electrochemical interfaces with a simple Nb:SrTiO₃ substrate with an atomically flat surface to clarify the possibility of detection of the electrolyte-side interface structure.

2. Experiment

0.5%Nb-doped SrTiO₃(111) substrates (20 × 20 × 5 mm, Crystal Base Co., Ltd.) were immersed in a HNO₃ and buffered HF (NH₄F:HF = 7:1) solution as the etchants. Etching time was 2min. The etched substrates were successfully annealed at 1000 °C for 30 min in vacuum condition (1.0×10⁻⁴~10⁻³ Pa) . Finally, AFM measurements confirmed that the etched SrTiO₃ (111) substrates had a step-terrace structure with a surface roughness of below 1 nm. It is enough flat to detect the interfacial structure at the electrolyte-side. In situ NR measurements were performed on SOFIA (BL-16), which is a time-of-flight reflectometer. An electrochemical cell was composed of a 0.5%Nb-doped SrTiO₃(111) working electrode, a Li counter electrode and deuterated propylene carbonate (PC) electrolytes containing 0.1 to 2 mol dm⁻³, with the purpose of the deuterated electrolytes being to prevent incoherent scattering (80.27 and 2.05 for ¹H and ²H, respectively). Electrochemical tests were performed via the potentiostatic method using a potentiostat/galvanostat (Hokuto denko, HZ-7000). The NR spectra were collected using the single-frame mode at 0.3, 0.6, and 1.2°, and the individual data points were combined. The cell conditions were monitored before (air) and after the cell construction (OCV) and 4.2 V (vs. Li/Li⁺) at the first cycle. The NR spectra were analyzed using the Motofit software.

3. Results

Fig. 1 shows neutron reflectometry analysis results of a Nb:SrTiO₃ (100) substrate in pristine condition, at following soaking in the 1.0 mol dm⁻³ LiPF₆ EC/DEC (3:7 vol.), and at the first 4.2 V. The reflectivity spectra were plotted as functions of the scattering vector, $Q_z = 4\pi\sin\theta/\lambda$ where λ is the neutron wavelength and θ is the glancing angle. A one-layer model consisting of surface phase/SrTiO₃ fitted closely with the reflectivity curve for the pristine film. The neutron scattering length density (SLD) of the pristine substrate was $3.51 \times 10^{-4} \text{ nm}^{-2}$, which is consistent with the theoretical value as calculated with the ICSD data. The pristine film was covered with a surface layer with a thickness of 2.5 nm, and the surface impurity had a lower neutron SLD value than the substrate bulk. The surface and interfacial roughness of the surface layer and the substrate bulk were 0.3 nm and 1.4 nm, respectively, which are flat enough to detect the interfacial structure at the electrolyte-side which could be a few nanometer thick. NR spectra collected under the OCV condition were analyzed using the two-layer model (SrTiO₃/electrode-side interface/electrolyte-side interface/electrolyte). The thickness of the electrolyte-side interface was ~ 3 nm. At the first 4.2 V, the SLD of the electrolyte-side interface decreased, which indicated a voltage dependence. This result clarified that the NR technique can detect the ionic distribution at the electrolyte-side interface when the model electrodes with a very flat surface.

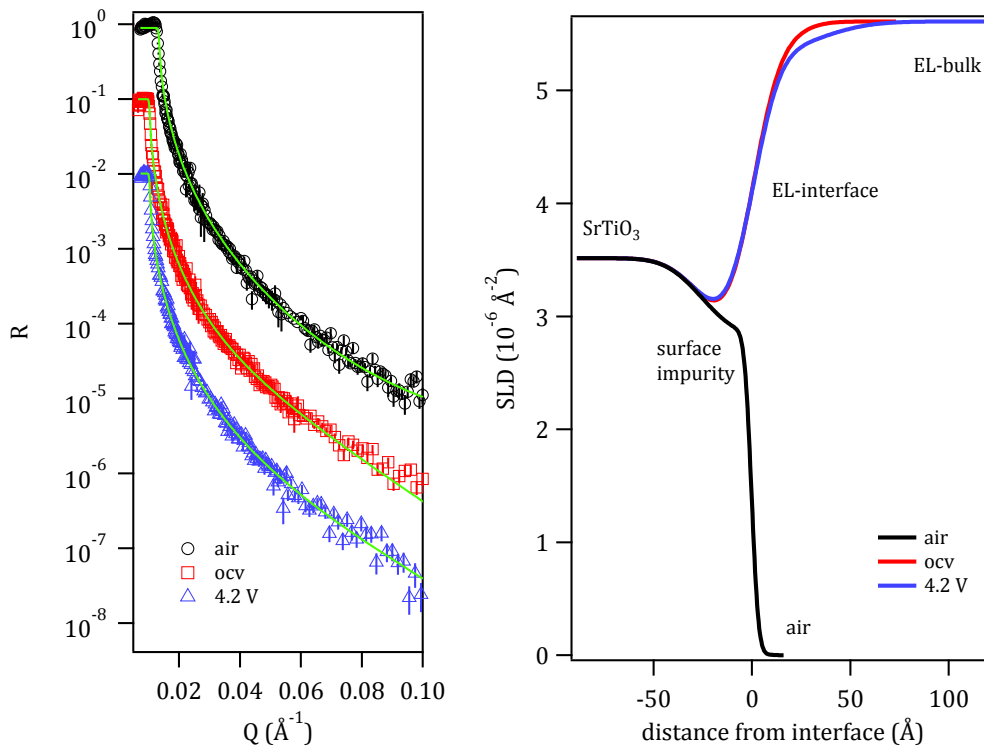


Fig. 1 NR spectra and fitting curves (left) and SLD profiles (right) of a Nb:SrTiO₃ (100) substrate (a) in air, (b) at OCV in 1 M LiPF₆ d-PC, and at 4.2 V in 1 M LiPF₆ d-PC. Substrate size was 20 x 20 x 5 mm.

4. Conclusion

The neutron reflectometry analyses revealed that the ionic distribution at the electrolyte-side interface was formed at the electrochemical interface, and it changed with the electrode potential. In future works, we will conduct further NR experiments to detect interfacial structures at the electrolyte-side using lithium battery electrodes with a very flat surface.