 MLF Experimental Report	提出日 Date of Report 2017/1/6
課題番号 Project No. 2016A0036 実験課題名 Title of experiment In-situ analysis on electrode/electrolyte interfaces in Li-ion batteries by neutron reflectometry 実験責任者名 Name of principal investigator Hiroyuki Kawaura 所属 Affiliation Toyota Central R&D Labs., Inc.	装置責任者 Name of responsible person Norifumi Yamada 装置名 Name of Instrument/(BL No.) SOFIA/BL16 実施日 Date of Experiment 2016/5/26-11/7

試料、実験方法、利用の結果得られた主なデータ、考察、結論等を、記述して下さい。(適宜、図表添付のこと)
 Please report your samples, experimental method and results, discussion and conclusions. Please add figures and tables for better explanation.

1. 試料 Name of sample(s) and chemical formula, or compositions including physical form.

Figure 1 shows a schematic of the electrochemical cell used for the present work. A carbon/titanium multilayer thin film on a 3 mm thick silicon substrate with an area of 30×30 mm was used as the working electrode. After cleaning, a 20 nm titanium adhesion layer and a 70 nm carbon layer were deposited on the flat silicon wafer using a magnetron sputtering instrument. The carbon electrode used in these experiments consisted of an amorphous carbon film. The substrate was set in an electrochemical cell with a lithium foil, counter/reference electrode. The electrodes were separated by a microporous polypropylene membrane (separator) soaked with an electrolyte consisting of 1 mol/dm³ LiPF₆ in a 1:1 + 0.1wt%LiBOB dissolved in a 1:1 volumetric mixture of ethylene carbonate and diethyl carbonate.

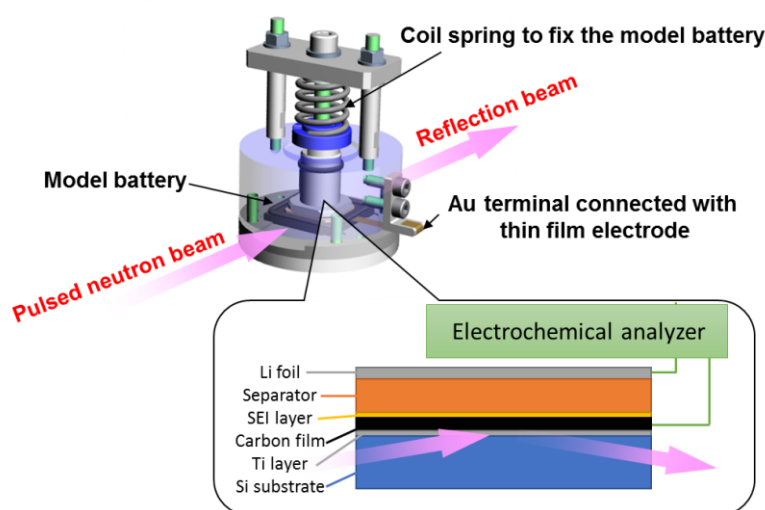


Figure 1. Schematic illustration of the electrochemical cell and cross-section of the model battery system for *in situ* NR measurements.

2. 実験方法及び結果（実験がうまくいかなかった場合、その理由を記述してください。）

Experimental method and results. If you failed to conduct experiment as planned, please describe reasons.

The electrochemical cell was mounted on the sample stage of the neutron reflectometer and the neutrons were introduced from the substrate side for *in situ* neutron reflectivity (NR) measurements at 300 kW. Charge and discharge tests were carried out using the two-electrode cells. Cyclic voltammetry (CV) was performed at a slow sweep rate of 0.2 mV/s between the open circuit voltage (OCV; ca. 3.2 V) and 0.05 V (vs. Li/Li⁺) during the NR measurement. The NR data was acquired every 5 minutes at an incident angle θ of 0.4°, whereby the reflectivity profile as a function of the momentum transfer normal to the basal plane Q_z ; $Q_z = (4\pi\sin\theta)/\lambda$, can be obtained by taking into account wavelength of neutrons λ from 0.10 to 0.45 nm⁻¹.

Figure 2 shows the cyclic voltammograms between 3.2 V and 0.05 V. In the first charge process, the current I , didn't change from OCV (3.2 V) to 1.8 V, i.e., no characteristic reaction occurred. Next, I began to decrease around 1.7 V, and reached a local minimum at 1.0 V, and then slightly increased until 0.6 V. The negative value of I indicates that the Li⁺ intercalation reaction is a reductive reaction for carbon, so that the $I(E)$ curve shows the presence of a broad reductive peak in the E range between 0.6 and 1.7 V with a peak around 1.0 V.

2. 実験方法及び結果(つづき) Experimental method and results (continued)

This reductive current is presumably due to decomposition of the electrolyte and/or the organic solvent, which contributes to SEI formation. Finally, I decreased again with an increase in the dI/dE slope below 0.6 V, which mainly indicates the intercalation of Li ions.

In the first discharge reaction, I increased in the E range between 0.05 V and 0.4 V. Then the $I(E)$ curve shows the presence of a broad oxidation peak in the E range the plus electric current between 0.4 V and 3.2 V with a peak around the 1.4 V.

During second charging reaction, the negative value of I in the E range between 0.05 and 1.5 V indicates that the Li⁺ intercalation reaction is a reductive reaction for carbon. The change of I during second discharge process indicates is almost same with that of the first charge/discharge process.

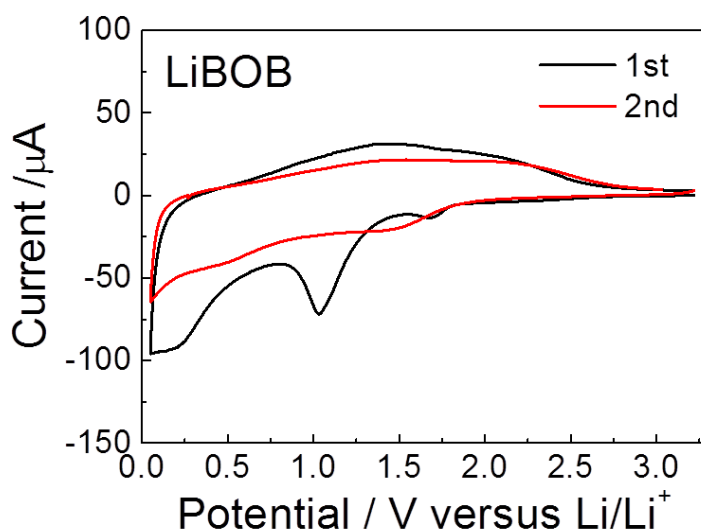


Figure 2. Cyclic voltammograms of carbon thin film in 1 M LiPF₆/EC:DEC=1:1 containing 0.1 wt % LiBOB.

Figure 3 shows reflectivity (R) profiles as a function of E during the charge and discharge reaction, in which the period of fringes and the critical value of Q_z at the total reflection in the profiles indicate the thickness, d , and the scattering length density, ρ , of the carbon layers, respectively. In contrast to the lack of change even with a decrease in E from OCV (=3.2 V) to 1.5 V, the change in the period and critical value began in the range of E from 1.5 V to 0.6 V and was more pronounced at E from 0.6 V to 0.05 V during first charge reaction. On the other hand, R profile slightly changes during first discharge reaction from 2.5 V to 3.2 V were indicated. During second charging reaction, while almost no change in R profiles is admitted from 3.2 V to 1.5 V like the first charge reaction, and the amount of change is promoted from 1.5 V to 0.05 V. The change during second discharge reaction was as same as that of first discharge reaction. To convert the change in reciprocal space to that in real space, the R profile at each E was analyzed to obtain a depth profile of ρ based on a least-squares fitting with the Parratt formalism.

Figure 4a shows typical NR profiles and their fitting curves at different potentials, at the OCV (3.2 V), at 0.5 V during first charge, and at 0.05 V during first charge (vs. Li/Li⁺). **Figure 4b** shows the evolution of the scattering length density profiles as a function of potential, whereby the change in the carbon electrode and the SEI on the electrochemical reaction at the interface is observed. **Figure 5** and **Figure 6** show the dependence of d_1 and ρ_1 obtained by the least-squares fitting, where the subscripts I indicate the interfacial layer. NR profiles were obtained as a function of E and analyzed with the Motofit analysis package based on the Parratt formalism. For the analysis, it was assumed that there were three layers on the silicon surface (titanium, carbon, and the electrode/electrolyte interface layers) and the fitting of all the profiles to minimize χ^2 using Levenberg-Marquardt algorithm was performed. The scattering length densities of silicon and the electrolyte are fixed to be those calculated from their densities and their scattering lengths of the component atoms. The fitting parameters for the top layers, the scattering length density and the roughness of the carbon and electrode/electrolyte interface layers of each reflectivity profiles are changed to fit the R profiles.

The fitting result indicated the presence of an interfacial layer, even at the OCV, with $d_1 = 27.8 \pm 6.8$ nm and $\rho_1 = (1.47 \pm 0.07) \times 10^{-4}$ nm⁻². Based on an *ex situ* X-ray photoelectron spectroscopy analysis of the present sample, a hydroxyl layer was detected on the surface of the carbon electrode after immersion in the electrolyte and without charging. This implies that there is an adsorption layer formed upon contact with the electrolyte before solid electrolyte interphase (SEI) formation. Furthermore, the values of d_1 and ρ_1 changed with a decrease in E , which indicates an SEI starts to form at the interface due to a decomposition reaction. The $I(E)$ curve shown in Fig. 2 indicates the reaction is decomposition of the electrolyte and/or the organic solvent. According to the trend of d_1 , the SEI thickened with the first charge reaction up to 36.5 ± 0.6 nm at $E = 1.2$ V and thinned down to 19.0 ± 1.4 nm at $E = 0.9$ V. The reason was presumed that the SEI layer formed by reaction decomposition of an additive is changing. The SEI gradually thickened with the charge reaction in the potential range from 0.9 to 0.05 V (vs Li/Li⁺) during the first charge cycle. The SEI gradually thickened with the discharge reaction during the first discharge cycle. The thickness of SEI increase and decrease repeatedly between 24.0 ± 0.7 nm and 30.1 ± 1.0 nm during the second charge/discharge cycles. On the other hand, the ρ_1 increased with first charge reaction up to $(3.29 \pm 0.08) \times 10^{-4}$ nm⁻² at $E = 1.15$ V and decreased down to $(2.55 \pm 0.06) \times 10^{-4}$ nm⁻² at $E = 0.05$ V. The ρ_1 increase during the first discharged reaction in the potential at 2.7 V, and indicates $(2.78 \pm 0.05) \times 10^{-4}$ nm⁻² at $E = 3.2$ V. The ρ_1 increase and decrease repeatedly between $(2.45 \pm 0.07) \times 10^{-4}$ nm⁻² and $(2.89 \pm 0.06) \times 10^{-4}$ nm⁻² in the potential range from 3.2 V to 0.4 V during second charge cycles. The ρ_1 decrease with charge reaction in the potential from 0.4 V to 0.05 V, and indicated $(2.41 \pm 0.1) \times 10^{-4}$ nm⁻² at $E = 0.05$ V during second charge cycles, and increased up to $(2.7 \pm 0.07) \times 10^{-4}$ nm⁻² at $E = 3.2$ V during second discharge cycles.

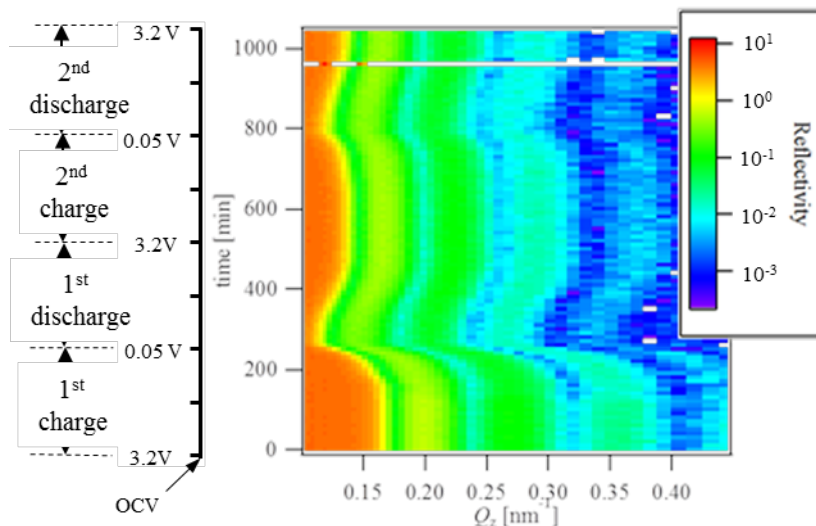


Figure 3. Contour plot of neutron reflectivity as a function of Q_z value recorded in *operando* during charge and discharge cycles between cycles 3.2V (top) and OCV (bottom).

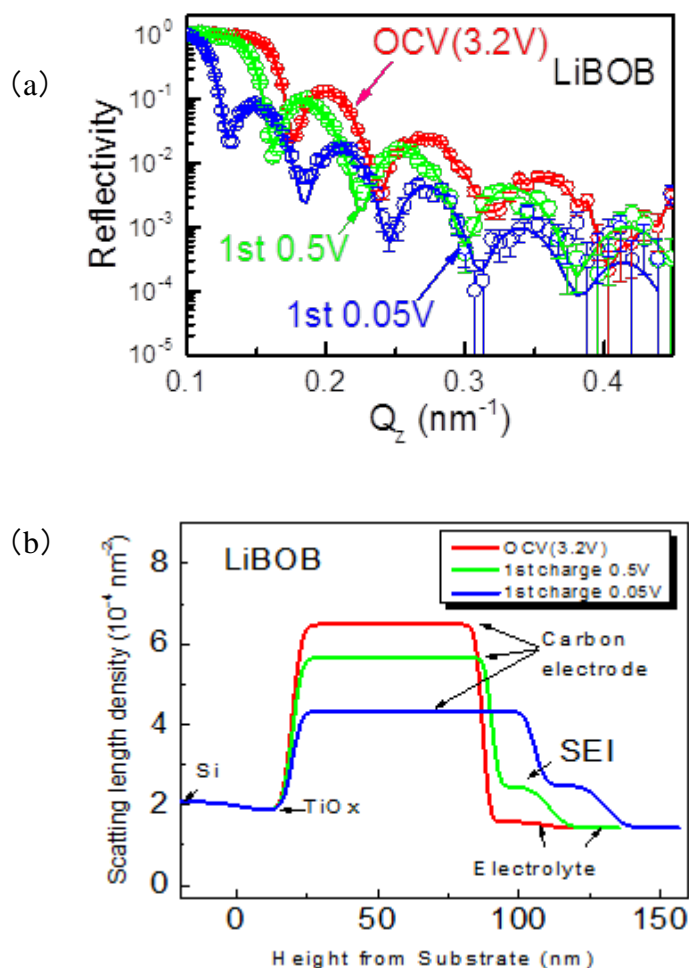


Figure 4. (a) Neutron reflectivity as a function of Q_z value for the samples at OCV, at 0.5 V in 1st cycle, and at 0.05V in 1st cycle. The solid lines are the best fit, from a simultaneous fit. (b) The SLD profiles for the best fits. The layer positions of Si, TiO_x layer, carbon electrode, SEI layer and electrolyte are indicated.

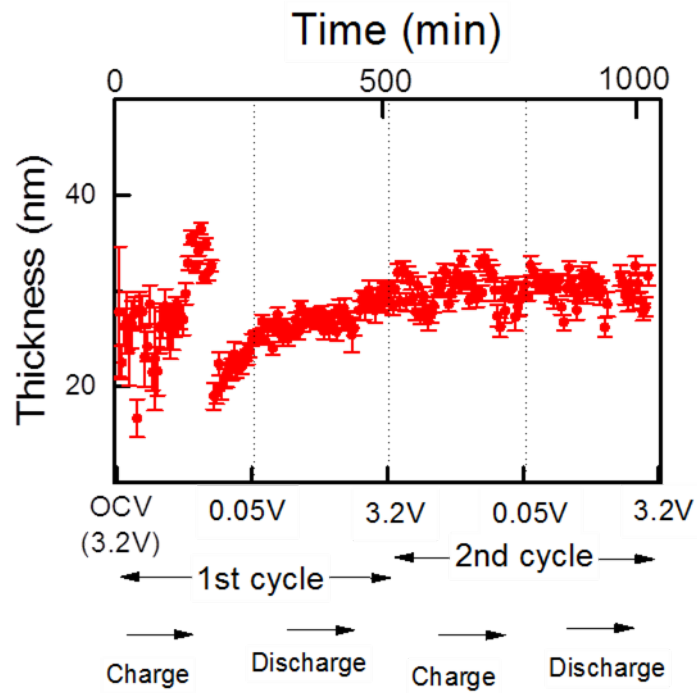


Figure 5. Evolution of the SEI thickness on the carbon electrode during the electrochemical reaction.

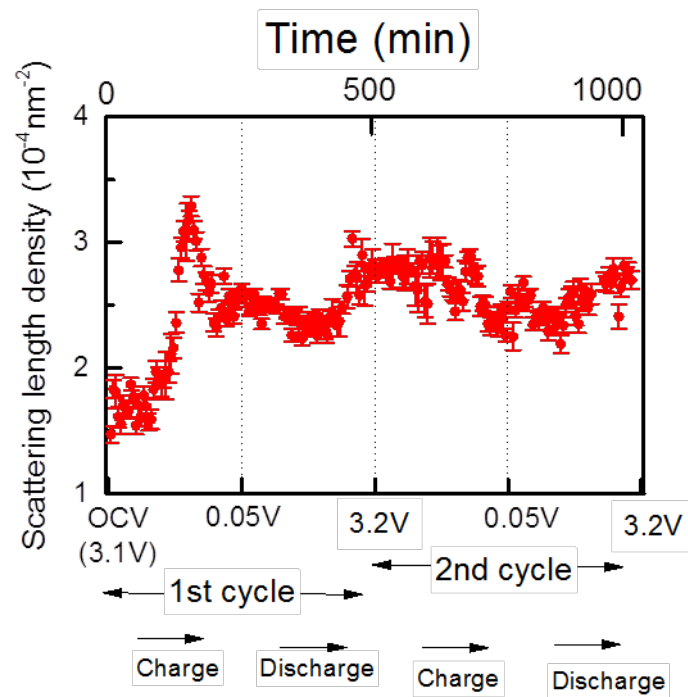


Figure 6. Evolution of the scattering length density of SEI layer on the carbon electrode during the electrochemical reaction.