 <b>MLF Experimental Report</b>	提出日 Date of Report 2016/6/10
課題番号 Project No. 2014B0016 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 2016/4/1-4/4

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/dm<sup>3</sup> LiPF<sub>6</sub> in a 1:1 volumetric mixture of ethylene carbonate and diethyl carbonate.

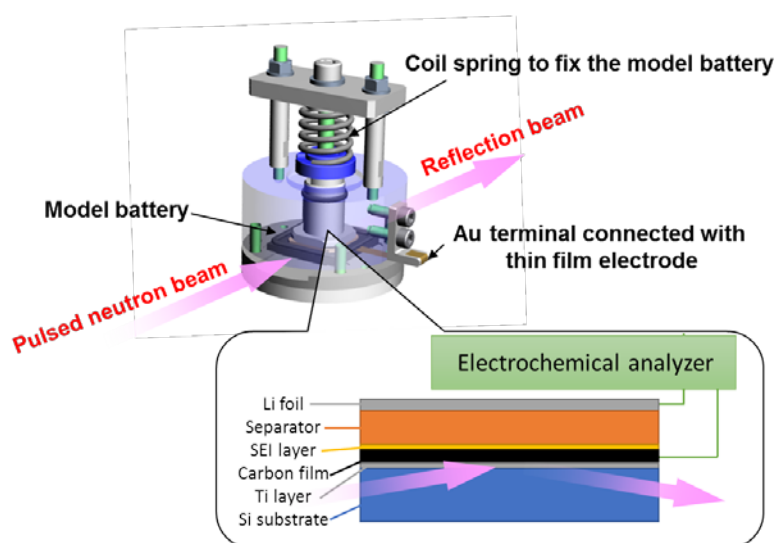


Figure 1. Schematic illustration of the electrochemical cell and cross-section of the model battery system for *in situ* NR measurements.

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 neutrons were introduced from the substrate side for *in situ* neutron reflectivity (NR) measurement at 200 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. 3.3 V) and 0.05 V (vs. Li/Li<sup>+</sup>) during the NR measurement. The NR data was acquired every 5 minutes at an incident angle  $\theta$  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  $\lambda$  from 0.10 to 0.45 nm<sup>-1</sup>.

**Figure 2** shows cyclic voltammograms between 3.3 V and 0.05 V. In the first charge cycle, the current  $I$ , didn't change from OCV (3.3 V) to 1.5 V, i.e., no characteristic reaction occurred. Next,  $I$  began to decrease around 1.5 V, reached a local minimum at 1.1 V, and then slightly increased until 0.6 V. The negative value of  $I$  indicates that the Li<sup>+</sup> 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 1.5 V with a peak around 1.1 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. The positive value of  $I$  indicates that the Li<sup>+</sup> deintercalation reaction is a oxidative reaction for carbon, so that 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 3.3 V with a peak around the 1.4 V. During second charging reaction, the negative value of  $I$  indicates that the Li<sup>+</sup> intercalation reaction is a reductive reaction for carbon in the  $E$  range between 0.05 and 1.5 V. The change of  $I$  during second discharge reaction indicates the same change mostly during first charge/discharge.

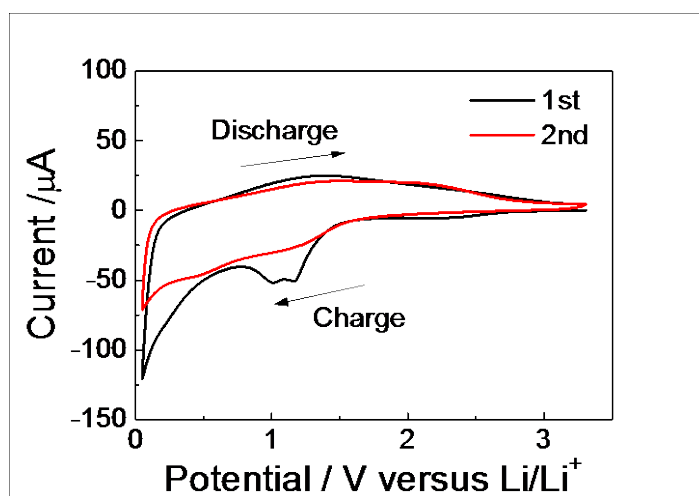


Figure 2. Voltammogram of the carbon thin film electrode in 1 mol dm<sup>-3</sup> LiPF<sub>6</sub> dissolved in a 1:1 volumetric mixture of ethylene carbonate and diethyl carbonate.

**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,  $\rho$ , of the interfacial layers, respectively. In contrast to the lack of change from OCV ( $=3.3$  V) to  $1.5$  V in the profile, even with a decrease in  $E$ , the change in the period and critical value began at  $E$  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 changes during first discharge reaction, and the tendency small in the change quantity at  $E$  from  $2.5$  V to  $3.3$  V were indicated. During second charging reaction, almost no change is admitted by  $E$  from  $3.3$  V to  $1.5$  V like the first charge reaction, and change amount of  $R$  spectrum is promoted at  $E$  from  $1.5$  V to  $0.05$  V. The change during second discharge reaction was as same as that during 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  $\rho$  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 ( $3.3$  V), after first charge at  $0.5$  V, and after first charge at  $0.05$  V (*vs.* Li/Li<sup>+</sup>). **Figure 5a** shows typical NR profiles and their fitting curves at different potentials, after first charge/discharge cycle ( $3.3$ V), after second charge at  $0.05$  V, and after second charge/discharge cycle ( $3.3$  V *vs.* Li/Li<sup>+</sup>), respectively. **Figure 4b** and **5b** 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 6a** and **6b** shows the dependence of  $\rho_C$ ,  $\rho_I$ ,  $d_C$ , and  $d_I$  obtained by the least-squares fitting, where the subscripts C and I indicate the carbon electrode and interfacial layer, respectively. 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  $\chi^2$  using Levenberg-Marquardt algorithm was performed. The scattering length densities of silicon and electrolyte are fixed to be those calculated from their densities and scattering lengths of component atoms. The fitting parameters for the top layers, scattering density and roughness of the carbon and electrode/electrolyte interface layers of each reflectivity profile are independent of each other.

The fitting result indicated the presence of an interfacial layer, even at the OCV, with  $d_I = 25.6 \pm 1.2$  nm and  $\rho_I = (2.54 \pm 0.15) \times 10^{-4}$  nm<sup>-2</sup>. 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 SEI formation. Furthermore, the values of  $d_I$  and  $\rho_I$  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  $d_I$ , the SEI thickened with the first charge reaction up to  $38.6 \pm 1.66$  nm at  $E = 0.05$  V and thinned with first discharge reaction down to  $33.5 \pm 2.7$  nm at  $E = 3.3$  V. In the second cycles, the thickness of SEI indicated around  $33$  nm. On the other hand,  $\rho_I$  increased with first charge reaction up to  $(2.88 \pm 0.08) \times 10^{-4}$  nm<sup>-2</sup> at  $E = 0.05$  V and decreased down to  $(2.36 \pm 0.05) \times 10^{-4}$  nm<sup>-2</sup> at  $E = 3.3$  V after first discharged reaction. In the second cycles,  $\rho_I$  indicated  $(2.43 \pm 0.06) \times 10^{-4}$  nm<sup>-2</sup> at  $E = 0.05$  V and increased up to  $(2.6 \pm 0.06) \times 10^{-4}$  nm<sup>-2</sup> at  $E = 3.3$  V.

Next, we focused on the intercalation of Li<sup>+</sup> ions into the electrode during the charge reaction;  $d_C$  was  $66.7 \pm 0.1$  nm at OCV, increased monotonically up to  $80.7 \pm 0.2$  nm at  $E = 0.05$  V during first charge reaction, and decreased  $74.9 \pm 0.2$  nm at  $E = 3.3$  V after first discharge reaction, whereas  $\rho_C$  was  $(6.47 \pm 0.01) \times 10^{-4}$  nm<sup>-2</sup> at

OCV, decreased monotonically down to  $(4.54 \pm 0.01) \times 10^{-4} \text{ nm}^{-2}$  at  $E = 0.05 \text{ V}$  during first charge reaction, and increased up to  $(5.13 \pm 0.01) \times 10^{-4} \text{ nm}^{-2}$  at  $E = 3.3 \text{ V}$  after first discharge reaction. In the second cycles,  $d_C$  increased up to  $78.2 \pm 0.2 \text{ nm}$  at  $E = 0.05 \text{ V}$  and decreased down to  $75.2 \pm 0.2 \text{ nm}$  at  $E = 3.3 \text{ V}$ , whereas  $\rho_C$  was  $(4.43 \pm 0.01) \times 10^{-4} \text{ nm}^{-2}$  at  $E = 0.05 \text{ V}$ , decreased monotonically down to  $(5.10 \pm 0.01) \times 10^{-4} \text{ nm}^{-2}$  at  $E = 3.3 \text{ V}$ . The change in  $d_C$  is consistent with the volumetric change induced by  $\text{Li}^+$  intercalation/deintercalation into carbon during charge/discharge cycles, because the  $c$ -axis length of  $\text{Li}^+$ -intercalated/deintercalated carbon is larger than that of carbon

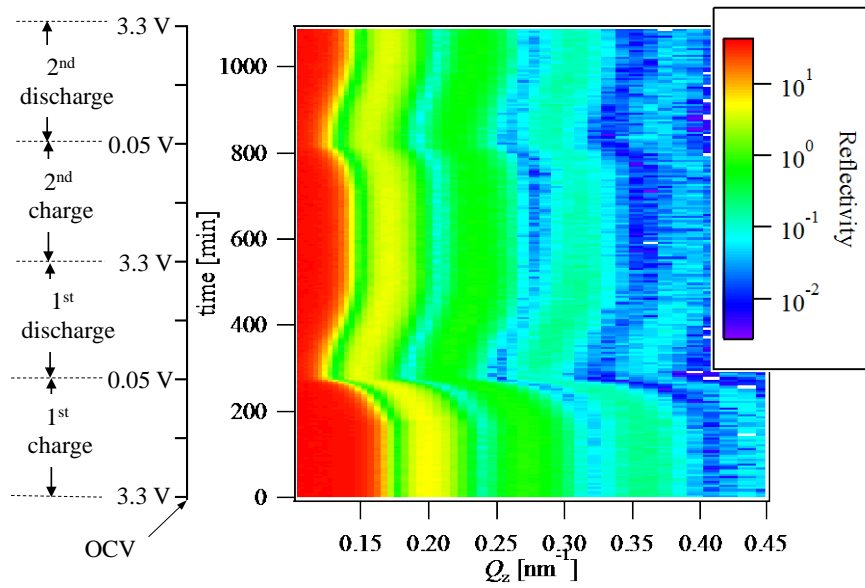


Figure 3. NR profiles as a function of potential during the charge and discharge reaction obtained by *operando* measurement.

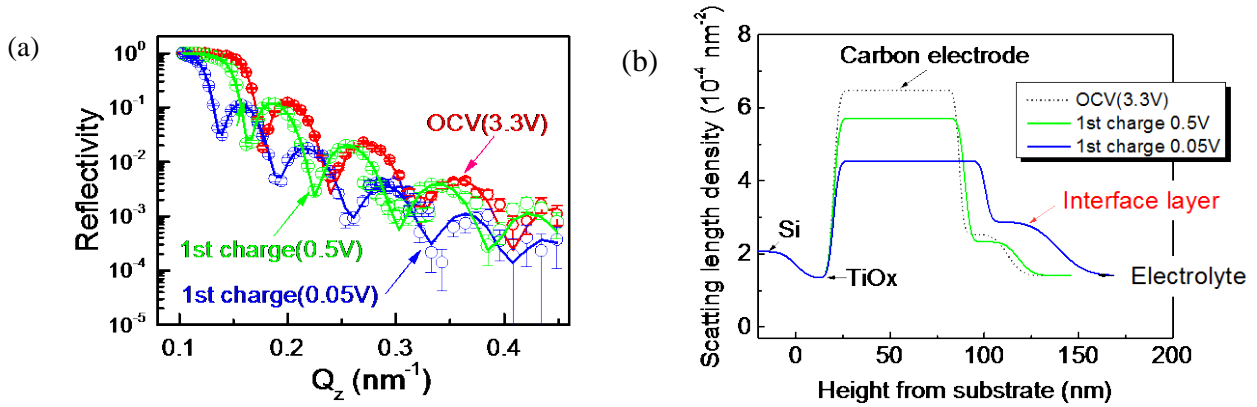


Figure 4. (a) Neutron reflectivity vs.  $Q_z$  and fitting results (solid line) at different potentials. (b) Evolution of scattering length profiles obtained by fitting of the electrochemical reaction at the model electrode.

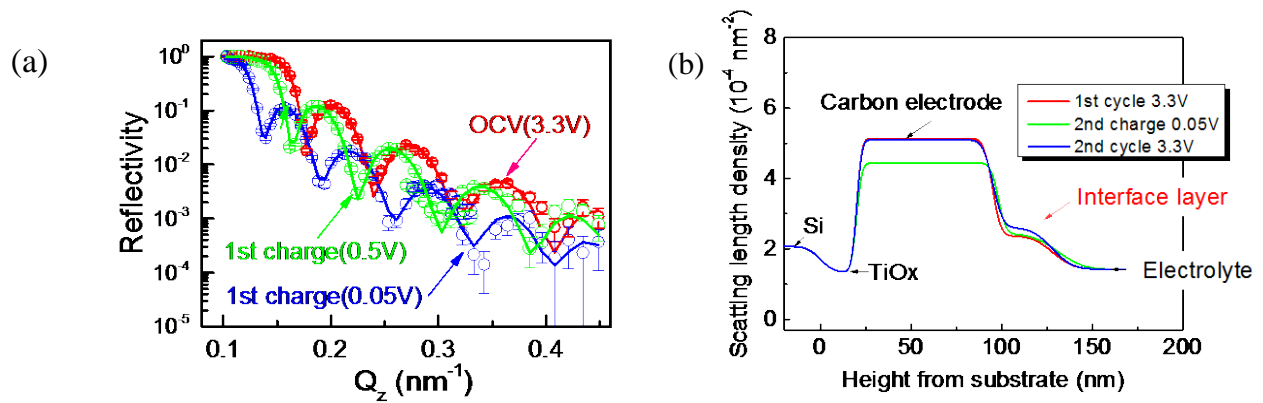


Figure 5. (a) Neutron reflectivity vs.  $Q_z$  and fitting results (solid line) at different potentials. (b) Evolution of scattering length profiles obtained by fitting of the electrochemical reaction at the model electrode.

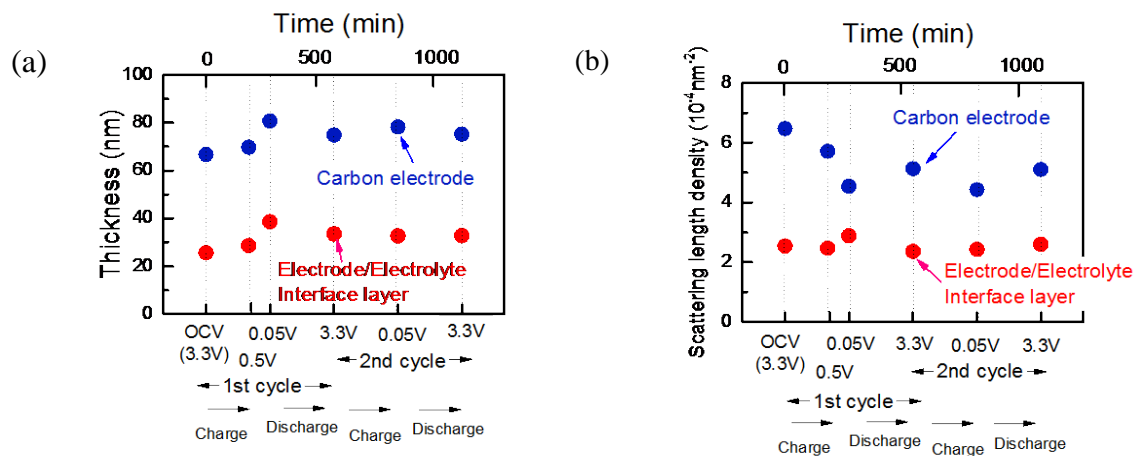


Figure 6. Evolution of the interfacial structure at the carbon electrode during electrochemical reaction: (a) thickness and (b) scattering length density as a function of potential for carbon electrode and interface layer between electrode and electrolyte.