MLF Experimental Report

		提出日 Date of Report
![J-PARC logo]	**MLF Experimental Report**	2016/4/27

課題番号 Project No.	装置責任者 Name of responsible person
2015A0110	Norifumi Yamada
実験課題名 Title of experiment	装置名 Name of Instrument/（BL No.）
In-situ analysis on electrode/electrolyte interfaces in Li-ion batteries by neutron reflectometry	SOFIA/BL16
	実施日 Date of Experiment
実験責任者名 Name of principal investigator	2016/2/27-3/1
Hiroyuki Kawaura	
所属 Affiliation	
Toyota Central R&D Labs., Inc.	

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^3 LiPF$_6$ in a 1:1 volumetric mixture of ethylene carbonate and diethyl carbonate.
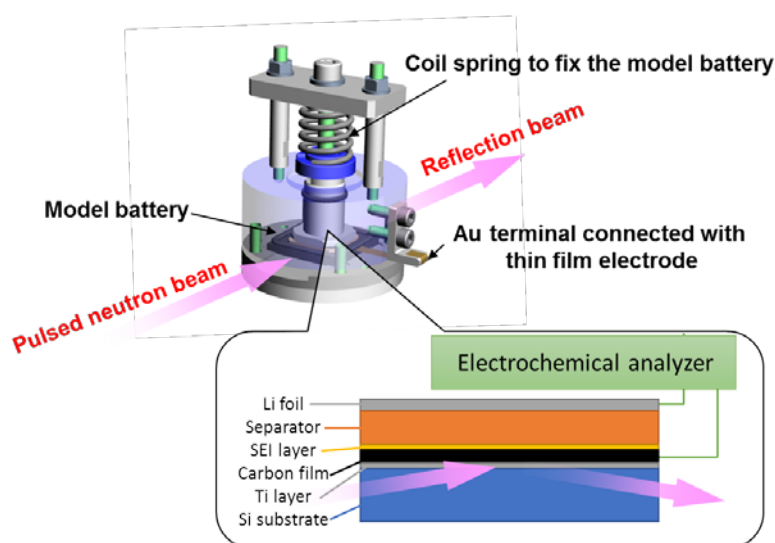

Figure 1. Schematic illustration of the electrochemical cell and cross-section of the model battery system for *in situ* NR measurements.

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. The electrochemical reaction at the carbon electrode was controlled potentiostatically with an electrochemical analyzer with a scan rate of 0.2 mV/s in the potential E range from the open circuit voltage (OCV; ca. 3.1 V) to 0.05 V (*vs.* Li/Li$^+$) during the NR measurement. The NR data was acquired every 10 minutes with 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 0.09 to 0.33 nm^{-1}.

Figure 2 shows a voltammogram of the carbon electrode during the *in situ* NR experiment. First, the current I, was weak from OCV (3.1 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 1.2 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 reduction peak in the E range between 0.6 and 1.5 V with a peak around 1.2 V.

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

A large reductive I was observed at potentials lower than 0.6 V in each solution, which may be assigned partly to lithium intercalation, because the presence of the corresponding oxidation peak assigned to lithium deintercalation at around 1.5 V. This reductive current is presumably due to decomposition of the electrolyte and/or organic solvent, which contributes to SEI formation. I decreased again with an increase in the dI/dE slope below 0.6 V, which mainly indicates the intercalation of Li ions. However, the charge consumed for the reductive current was much larger than that for the oxidation peak in each solution, and hence, a substantial fraction of the reduction current at potentials < 0.6 V was consumed by irreversible processes such as direct decomposition of solvent molecules on the carbon surface.
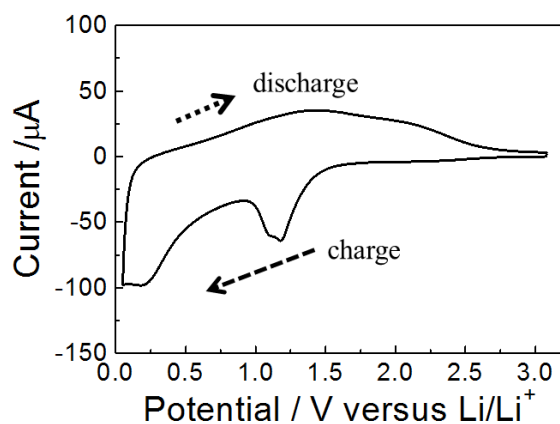

Figure 2. Voltammogram of the carbon thin film electrode in 1 mol dm^{-3} LiPF$_6$ dissolved in a 1:1 volumetric mixture of ethylene carbonate and diethyl carbonate.

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, ρ, of the interfacial layers, respectively. In contrast to the lack of change from OCV (=3.1 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 charge reaction. The change of R in the period and critical value were observed at E from 0.05 V to 2.5 V, and the change of R may be small at E from 2.5 V to 3.1 V during 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, OCV (3.1 V), charge 0.05 V, and 1cycled 3.1 V (*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 shows the dependence of ρ_C, ρ_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.
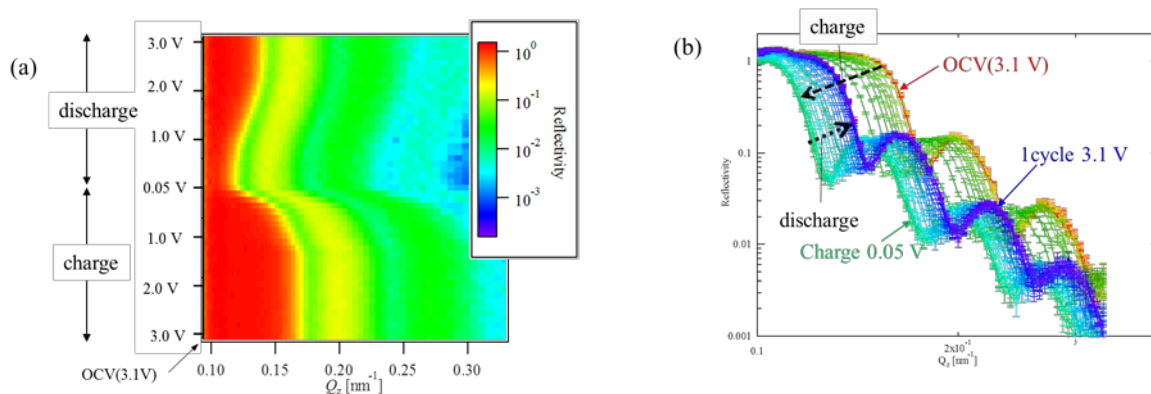

Figure 3. NR profiles as a function of potential during the charge and discharge reaction obtained by *operando* measurement.
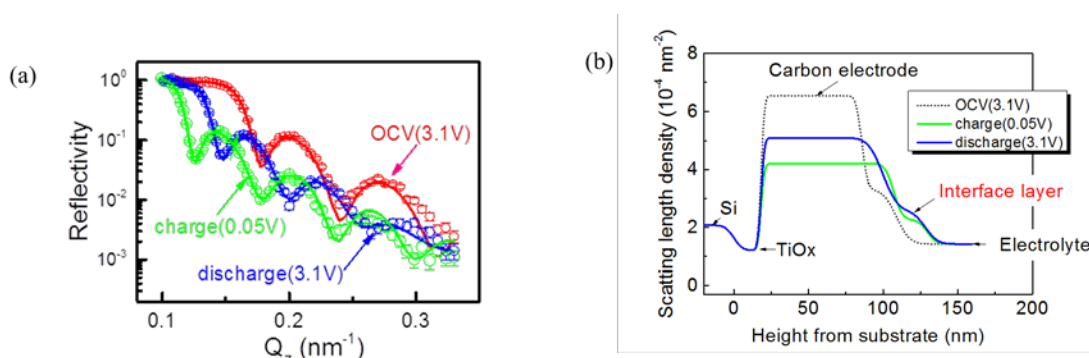

Figure 4. (a) Neutron reflectivity *vs.* Q_z and fitting results (solid line) at different potentials. (b) Evolution of scattering length profiles obtained by fitting for the electrochemical reaction at the model electrode.

The fitting result indicated the presence of an interfacial layer, even at the OCV, with $d_I = 20.6 \pm 0.7$ nm and $\rho_I = (2.88 \pm 0.08) \times 10^{-4}$ 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 SEI formation. Furthermore, the values of d_I and ρ_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 charge reaction up to 29.6 ± 4.3 nm at $E = 0.05$ V and thinned with discharge reaction down to 20.1 ± 0.7 nm at $E = 3.1$ V. On the other hand, ρ_I decreased with charge reaction down to $(2.16 \pm 0.04) \times 10^{-4}$ nm^{-2} at $E = 0.05$ V and increased up to $(2.95 \pm 0.05) \times 10^{-4}$ nm^{-2} at $E = 3.1$ V after discharged reaction.

Next, we focused on the intercalation of Li$^+$ ions into the electrode during the charge reaction; d_C was 67.2 ± 0.2 nm at OCV, increased monotonically up to 87.6 ± 0.3 nm at $E = 0.05$ V during charge reaction, and decreased 81.6 ± 0.3 nm at $E = 3.1$ V after discharge reaction, whereas ρ_C was $(6.46 \pm 0.02) \times 10^{-4}$ nm^{-2} at OCV, decreased monotonically down to $(4.15 \pm 0.01) \times 10^{-4}$ nm^{-2} at $E = 0.05$ V during charge reaction, and increased up to $(5.14 \pm 0.01) \times 10^{-4}$ nm^{-2} at $E = 3.1$ V after discharge reaction. The change in d_C is consistent with the volumetric change induced by Li$^+$ intercalation/deintercalation into carbon, because the *c*-axis length of Li$^+$-intercalated/deintercalated carbon is larger than that of carbon.
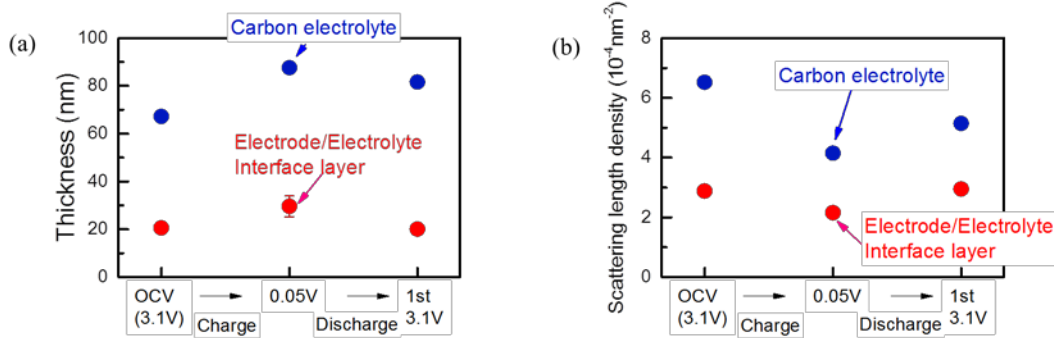

Figure 5. Evolution of the interfacial structure at the carbon electrode during electrochemical reaction: (a) thickness and (b) scattering length density as a function of potential for carbon electrode and interface layer between electrode and electrolyte.