 <b>MLF Experimental Report</b>	提出日 Date of Report 2014, 10/10
課題番号 Project No. 2012A0108 実験課題名 Title of experiment In situ neutron reflectometry analysis of electrode / electrolyte interface for lithium batteries 実験責任者名 Name of principal investigator Ryoji Kanno 所属 Affiliation Tokyo institute of technology	装置責任者 Name of responsible person Norifumi Yamada 装置名 Name of Instrument/(BL No.) BL16 実施日 Date of Experiment 2012/10/26-29

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.

Epitaxial  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  (111) thin films were synthesized on  $\text{SrTiO}_3$  (111) substrate by a pulsed laser deposition (PLD) method using a KrF excimer laser (248 nm) and  $\text{Li}_{5.2}\text{TiO}_{12}$  target. Crystal orientation, thickness, density and roughness were evaluated by X-ray diffraction and reflectivity measurements. On the top of the  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  epitaxial film, a solid electrolyte of  $\text{Li}_3\text{PO}_4$  was deposited by the PLD method. Thicknesses of the  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  epitaxial film and  $\text{Li}_3\text{PO}_4$  layer were about 24 and 5 nm, respectively. Structures of the  $\text{Li}_3\text{PO}_4/\text{Li}_4\text{Ti}_5\text{O}_{12}$  and  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  film electrodes were investigated by neutron reflectometry analysis.

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.

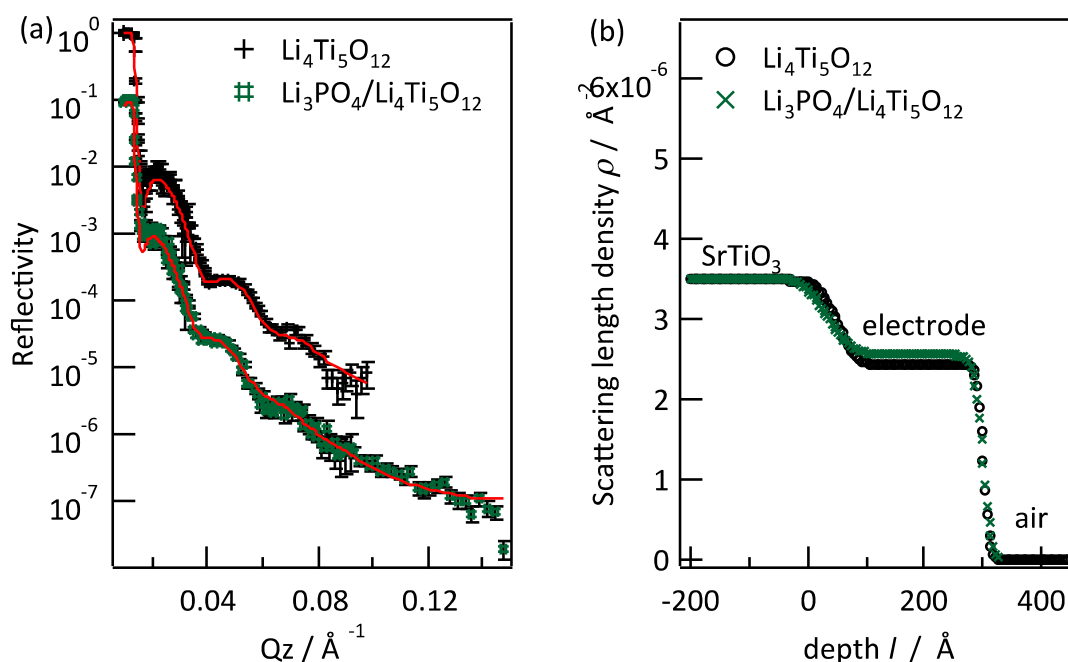
An *in situ* spectro-electrochemical cell was used for the neutron reflectivity measurements. Deuterated propylene carbonate (PC), which contains 1M  $\text{LiPF}_6$  and lithium metal were used as the electrolyte and the counter electrode, respectively. De-intercalation and intercalation were performed by the potentiostatic method with a potentiostat/galvanostat (Ivium Tech., Compactstat). Structural changes were observed by the potentiostatic method during electrochemical (de)intercalation. Reflectivity spectra of the thin film electrodes were measured as a function of the momentum transfer,  $Q_z = (4\pi\sin\theta)/\lambda$ , in the  $Q_z$  range of 0.01 to  $0.14 \text{ \AA}^{-1}$ . The Parratt32 program that uses Parratt's method was used for reflectivity data analysis. Figure 1 (a) shows neutron reflectivity spectrum of the  $\text{Li}_3\text{PO}_4/\text{Li}_4\text{Ti}_5\text{O}_{12}$  and  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  epitaxial films on  $\text{SrTiO}_3$  (111) at as-deposited state.

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

Three-layer and two-layer models of  $\text{Li}_3\text{PO}_4/\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{SrTiO}_3$  and  $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{SrTiO}_3$  provided best fitting of the reflectivity spectra. Figure 1 (b) illustrates the scattering length density (SLD) profiles from the analysis results for both film electrodes. The  $\text{Li}_3\text{PO}_4$  film stacking increased the SLD of the  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  region. The scattering length density  $\rho$  was  $2.42 \times 10^{-6} \text{ \AA}^{-2}$ , which is related to the film density  $d$  with the following equation.

$$\rho = \frac{b \cdot N_A}{M} d \quad (1)$$

where  $M$  is the molecular weight,  $b$  overall scattering length in the unit cell, and  $N_A$  the Avogadro's number. Therefore, the  $\text{Li}_3\text{PO}_4$  stacking changed the density of the  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ . As natural lithium has a negative coherent scattering length ( $\square 1.9 \text{ fm}$  for  ${}^7\text{Li} : {}^6\text{Li} = 92.5 : 7.5$ ), the increase in the SLD indicates a lithium deficient phase formation, which could be described as  $\text{Li}_{4-x}\text{Ti}_5\text{O}_{12}$ . Structural information at the as-deposited states is an important indicator for further structural analysis. Based on the obtained results, *in situ* structural analysis during the charge-discharge process will be demonstrated.



**Figure 1** Neutron reflectometry spectra with fitting curves (a) and the SLD profiles calculated using analysis results (b) for the  $\text{Li}_3\text{PO}_4/\text{Li}_4\text{Ti}_5\text{O}_{12}$  and  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  thin film electrodes.