MLF−Experimental Report	提出日 Date of Report 2011/6/30
課題番号 Project No. 2010A0057 実験課題名 Title of experiment Interface structure analysis of lithium battery electrodes using neutron reflectometry 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.） ARISA-II, SOFIA (BL No.16) 実施日 Date of Experiment 2010/6/23 - 6/26 2010/11/19-11/20

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 $Li_4Ti_5O_{12}$ (111) thin-films were synthesized on $SrTiO_3$(111) substrate by a pulsed laser deposition method using a KrF laser (247 nm) and a $Li_{5.2}Ti_5O_{12}$ target. The crystal structure, thickness, density, and roughness were characterized by X-ray diffraction and reflectivity measurements. The $Li_4Ti_5O_{12}$ (111) thin-film is described as cubic system with a space group of *Fd-3m*, which structure is the spinel structures. The film thickness was about 30 nm.

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.

We used an in-situ spectro-electrochemical cell with an electrolyte, $CD_3CN+LiPF_6$, and a counter Li electrode. In our in-situ cell, neutron beam passes through the substrate which situates below the electrode and the electrolyte. 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. The reflectivity was measured as a function of the momentum transfer, $Q_z = (4\pi\sin\theta)/\lambda$, in a Q_z range of 0.005 to about 0.20 $Å^{-1}$. The spectra obtained were analyzed using the fitting software, Parratt32.

Fig. 1 neutron reflectivity spectra and scattering length density profiles of epitaxial $Li_4Ti_5O_{12}$ (111) thin-film electrode during the first charge/discharge processes. We can refine the neutron reflectivity spectrum at open circuit voltage (OCV) condition with a structural model, electrolyte/

$Li_4Ti_5O_{12}$ / $SrTiO_3$. However, this model did not provide good fitting results for the neutron reflectivity spectra at the charge/discharge reactions. We then used another model, electrolyte/ interfacial layer/ $Li_4Ti_5O_{12}$ / $SrTiO_3$, and the lower values of residual sum of squares were obtained. This result indicates that an interfacial layer with a similar density to the electrolyte was formed at the $Li_4Ti_5O_{12}$/electrolyte interface during the first charge/discharge reaction. The thickness of the interfacial layer is about 30 nm, and the scattering length density changes with reaction voltages. On battery operation, lithium ions intercalate and deintercalate to the $Li_4Ti_5O_{12}$ electrode at dischargeing and charging process, respectively. As lithium ions have a negative coherent scattering length (−1.9 fm for ^{7}Li:^{6}Li=92.5:7.5), the scattering length density of $Li_4Ti_5O_{12}$ increased with lithium deintercalation. Furthermore, the scattering length density of the interfacial layer also changes with voltages, indicating concentration gradients of diffusing lithium ions in the electrode/electrolyte interface. This might be the first experimental evidence of forming electric double layer at the practical electrode/electrolyte interface in lithium batteries. The neutron reflectivity gives a better understanding of the interfacial reactions at the electrode/electrolyte interface that determine the stability and power characteristics of lithium batteries.

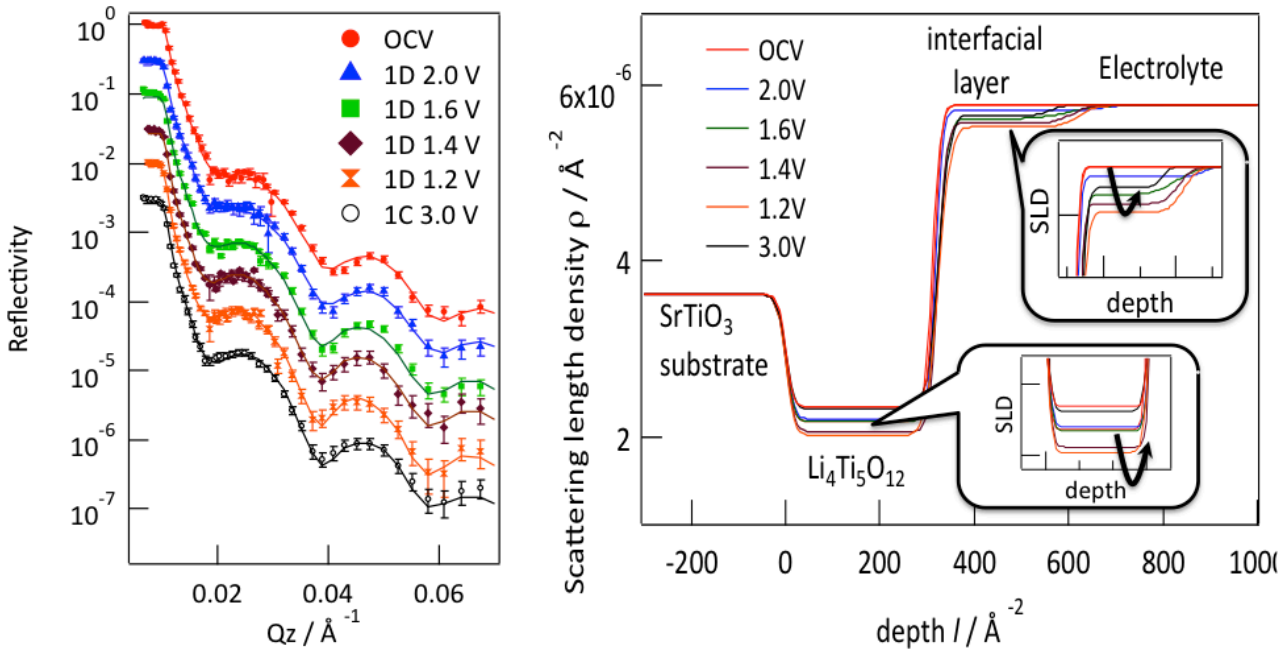

Fig. 1 Neutron reflectivity spectra and scattering length density profiles of epitaxial $Li_4Ti_5O_{12}$ (111) thin-film electrode during the first charge/discharge processes.