MLF Experimental Report	提出日 Date of Report
課題番号 Project No. 2013B0166 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.) SOFIA (BL No.16) 実施日 Date of Experiment (2014/03/22 09:00 ～ 2014/03/25 07:00)

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_2MnO_3 (001) thin film was synthesized on $SrTiO_3$(111) substrate by a pulsed laser deposition method using a KrF excimer laser (248 nm) and $Li_{3.2}MnO_3$ target. Crystal orientation, thickness, density and roughness were evaluated by X-ray diffraction and reflectivity measurements. The Li_2MnO_3 (001) thin film is described as monoclinic system with a space group of $C2/m$, which structure is the lithium excess layered rocksalt structures. Thickness of the Li_2MnO_3 (001) film about 45 nm. Electric conductive $SrRuO_3$ buffer layer was introduced between the substrate and the Li_2MnO_3 (001) epitaxial film to compensate poor electric conductivity of the sample.

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 $LiPF_6$ 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 were measured as a function of the momentum transfer, $Q_z = (4\pi\sin\theta)/\lambda$, in the Q_z range of 0.07 to 1.1 nm^{-1}. The Parratt32 program that uses Parratt's method was used for reflectivity data analysis.

Figure 1 shows neutron reflectivity spectrum of the Li_2MnO_3 (001) film on $SrRuO_3$(111)/$SrTiO_3$(111) at as-deposited state. A three-layer model composed of the $SrTiO_3$ substrate, the $SrRuO_3$ film, and the Li_2MnO_3 (001) film provided the best fitting of the reflectivity curve. Table 1 summarizes the fitting results of thickness, scattering length density (SLD), and interfacical roughness of each layer. The film thickness and surface roughness of the Li_2MnO_3 (001) film were 45.1 nm and 5.4 nm, respectively. The scattering length density ρ was 1.97 x 10^{-4} nm^{-2}, which is related to the film density d with the following equation.

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

where M is the molecular weight, b overall scattering length in the unit cell, and N_A the Avogadro's number. As natural lithium has a negative coherent scattering length (-1.9 fm for ^{7}Li:^{6}Li = 92.5:7.5), the lithium deficient phase should have a higher SLD value than Li_2MnO_3. In contrast, the SLD value decreases with increasing the deficiency of oxygen atoms with positive coherent scattering length (5.8 fm). Here we estimated the deficiencies of lithium and oxygen in the film using the SLD value, the composition of $Li_{2-2x}Mn(IV)O_{3-x}$ and the lattice volume of 200.9(14) Å^3 based on the results of X-ray diffraction, hard X-ray photoelectron spectroscopy, and neutron reflectometry. The x value was calculated to 0.05. The Li/Mn ratio of 1.90 is consistent to the result from the ICP analysis (1.86(7)). Hence, we concluded that the obtained film has the chemical composition of $Li_{1.90}Mn(IV)O_{2.95}$. This result demonstrates that oxygen deficiency occurs to compensate the charge valance for the lithium loss in the film. Based on the obtained fitting results, neutron reflectivity spectra during the electrochemical process will be analyzed.

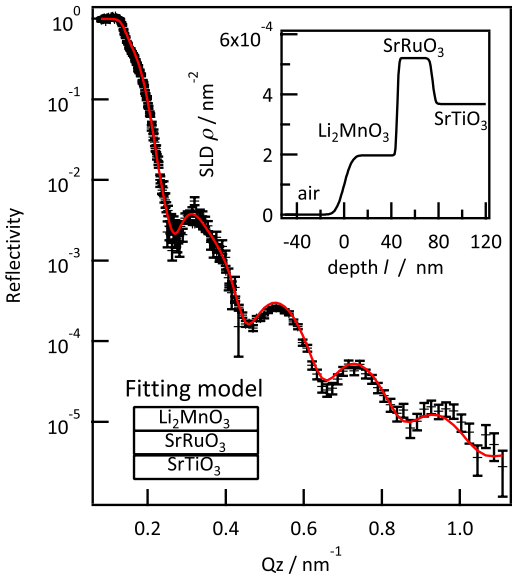

Figure 1 Neutron reflectometry analysis result of an epitaxial Li_2MnO_3(001) film. Inset depicts the SLD profile calculated using the fitting parameters summarized in Table 1.

Table 1 Refined thickness, SLD and roughness of Li_2MnO_3(001)/ $SrRuO_3$(111)/$SrTiO_3$(111) film.

Component	Thickness l / nm	SLD ρ / nm^{-2}	Roughness r_s / nm
Li_2MnO_3	45.1	1.93 x 10^{-4}	5.4
$SrRuO_3$	29.9	5.20 x 10^{-4}	1.1
$SrTiO_3$	-	3.53 x 10^{-4} (fixed)	1.8