

In situ neutron reflectometry analysis of electrode/electrolyte interface for lithium batteries

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1. Introduction

Neutron reflectometry is a powerful technique that can provide an atomistic understanding of solid/liquid interfaces as a function of the depth, since neutrons have a sufficiently small absorption cross-section for penetrating electrochemical cells so that electrochemical interfaces can be probed. As a light element, lithium has a relatively high neutron scattering power compared to that of X-rays, and the depth profile of the neutron scattering length density (SLD) obtained by curve fitting can reveal the surface structure changes of lithium battery electrode films during electrochemical processes. Nanosizing of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ has recently been the focus for improving the rates of lithium deintercalation by reducing the path lengths for electronic and lithium ion transport in the electrode. We have been investigating the interfacial reactions of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ using an epitaxial-film model electrode the discharge-charge measurements. The discharge-charge measurements, which were conducted with 1 mol dm^{-3} LiPF_6 containing propylene carbonate (PC), revealed that a 23.8-nm-thick $\text{Li}_4\text{Ti}_5\text{O}_{12}$ film exhibited a small capacity of 115 mAh g^{-1} compared to the theoretical value of 175 mAh g^{-1} . Recently, the neutron reflectometry analyses revealed that the phase change occurs in the 10 nm surface region from the $\text{Li}_4\text{Ti}_5\text{O}_{12}/1 \text{ mol dm}^{-3}$ LiPF_6 PC interfaces during the initial reaction processes. This implies that the surface-reconstructed phase formed in the LiPF_6 containing PC electrolytes limits the lithium intercalation. on this proposal, we analyzed the interfacial reactions of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ with the 1 mol dm^{-3} LiPF_6 ethylene carbonate–diethyl carbonate (EC:DEC/3:7 vol.%) electrolyte to clarify the effects of the electrolyte species on the surface structure and the electrochemical properties of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ electrolyte.

2. Experiment

Epitaxial $\text{Li}_4\text{Ti}_5\text{O}_{12}(111)$ thin films were grown on 0.5%Nb-doped $\text{SrTiO}_3(111)$ substrates ($20 \times 20 \times 5 \text{ mm}$, Crystal Base Co., Ltd.) using a KrF excimer laser with a wavelength of 248 nm and pulsed laser deposition (PLD) apparatus (PLAD131, AOV Inc.). The following optimal synthetic conditions were selected based on results of our previous studies : oxygen pressure, $p\text{O}_2 = 6.6 \text{ Pa}$; distance between substrate and target, $d = 60 \text{ mm}$; laser frequency, $f = 10 \text{ Hz}$; deposition time, $t_d = 5\text{-}25 \text{ min}$; energy density, $E = 0.3\text{-}0.4 \text{ J cm}^{-2}$; temperature, $t = 650 \text{ }^\circ\text{C}$. In situ NR measurements were performed on SOFIA (BL-16), which is a time-of-flight reflectometer. An electrochemical cell was composed of a $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{SrTiO}_3$ cathode, a Li anode and deuterated EC/DEC electrolytes containing 1 mol dm^{-3} LiPF_6 as a supporting electrolyte, with the purpose of the deuterated electrolytes being to prevent incoherent scattering (80.27 and 2.05 for ^1H and ^2H , respectively). Deintercalation and intercalation were performed via the potentiostatic method using a potentiostat/galvanostat (Ivium Tech., Compactstat). The NR spectra were collected using the single-frame mode at 0.3, 0.6, and 1.2 $^\circ$, and the individual data points were combined. The cell conditions were monitored after the cell construction (OCV), at 1.6, 1.4, and 1.2 V (vs. Li/Li⁺) at the first discharge, 3.0 V at the first charge, and after discharging and charging in the fifth cycle.

3. Results

Fig. 1 shows neutron reflectometry analysis results of $\text{Li}_4\text{Ti}_5\text{O}_{12}(111)$ films in pristine condition and following soaking in the 1.0 mol dm^{-3} LiPF_6 EC/DEC (3:7 vol.). The reflectivity spectra were plotted as functions of the scattering vector, $Q_z = 4\pi\sin\theta/\lambda$ where λ is the neutron wavelength and θ is the glancing angle. A two-layer model consisting of surface impurity/ $\text{Li}_4\text{Ti}_5\text{O}_{12}$ / SrTiO_3 fitted closely with the reflectivity curve for the pristine film. The SLD value of the pristine $\text{Li}_4\text{Ti}_5\text{O}_{12}$ films was $2.03 \pm 0.04 \times 10^{-4} \text{ nm}^{-2}$, which is consistent with the theoretical value of $2.04 \times 10^{-4} \text{ nm}^{-2}$ as calculated with the ICSD data (#15787). The pristine film was covered with a surface impurity layer with a thickness of $2.0 \pm 0.3 \text{ nm}$, and the surface impurity had a higher neutron SLD value than the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ layer. Considering the SLD values of typical lithium containing oxides ($3.46 \times 10^{-4} \text{ nm}^{-2}$ for Li_2CO_3 , $8.15 \times 10^{-5} \text{ nm}^{-2}$ for Li_2O , and $6.02 \times 10^{-6} \text{ nm}^{-2}$ for LiOH), the surface layer consisted of Li_2CO_3 . NR spectra collected under the OCV condition were analyzed using the three-layer model ($\text{SrTiO}_3/\text{Li}_4\text{Ti}_5\text{O}_{12}$ -bulk/ $\text{Li}_4\text{Ti}_5\text{O}_{12}$ -surface/SEI/electrolyte), which was the same model used for the $\text{Li}_4\text{Ti}_5\text{O}_{12}(111)$ film in the 1.0 mol dm^{-3} LiPF_6 PC electrolyte. The $\text{Li}_4\text{Ti}_5\text{O}_{12}$ layer showed no significant changes in the SLD using 1.0 mol dm^{-3} LiPF_6 EC/DEC electrolyte. Furthermore, no surface reconstruction proceeded at the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ surface following soaking in the EC/DEC-based electrolyte. In the previous study, the film electrode was soaked in the 1.0 and 2.4 mol dm^{-3} LiPF_6 PC electrolyte, the SLD increased in the entire region of the 16 nm -thick $\text{Li}_4\text{Ti}_5\text{O}_{12}$ film. This result clarified that the surface reconstruction of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ was influenced by the solvent and the solute species in the organic electrolytes.

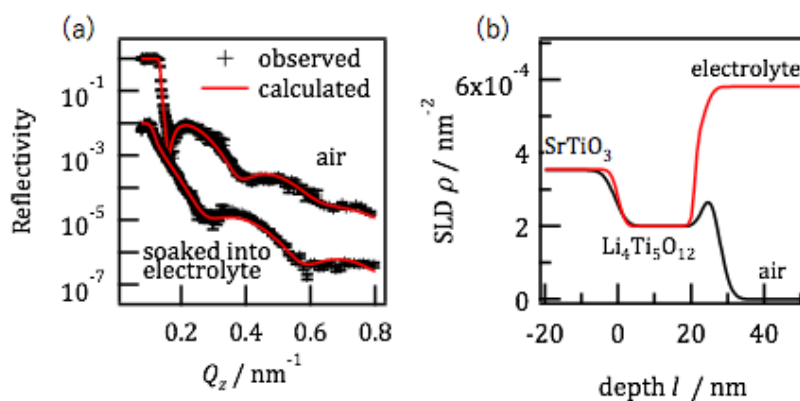


Fig. 1 (a) In situ reflectometry analysis results and (b) neutron SLD profiles of epitaxial $\text{Li}_4\text{Ti}_5\text{O}_{12}(111)$ films in pristine conditions and after soaking in an electrolyte of 1 mol/dm^3 LiPF_6 EC:DEC (3:7 vol.).

4. Conclusion

The neutron reflectometry analyses revealed that the phase change occurs in the 10 nm surface region from the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /organic electrolyte interfaces during the initial reaction processes. The surface-reconstructed phase formed in the LiPF_6 containing PC electrolytes limits the lithium intercalation although the surface-reconstruction behavior is highly influenced by the electrolyte composition. The $\text{Li}_4\text{Ti}_5\text{O}_{12}$ surface does not show transitions to the low-active phase in the EC/DEC based electrolytes, which leads to highly-reversible lithium intercalation. Our results have demonstrated the importance of surface reactions in the development of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anodes for lithium ion batteries of high power density. In future works, we will conduct further NR experiments to detect interfacial structures at the electrolyte-side which should also affect the electrochemical properties of intercalation electrodes.