Interface characterization of cathode electrode in lithium-ion battery by operand neutron reflectometry

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1. Introduction

Lithium-ion batteries (LIBs) are used in consumer mobile electronics and are expected to be widely applied in products, such as energy-storage systems and electric vehicles, that demand high current/power, high capacity, long-life, improved safety, and low cost. The high current/power operation of LIBs requires knowledge of lithium-ion transport properties in the cathode material or at the electrode/electrolyte interface during the battery operation. Operand neutron or X-ray reflectometry is enable us to analyze the density profile in the cathode material and the interface width at the electrode/electrolyte interface. Previous studies using the reflectometry were based on in-situ cells in which the electrolyte was fully filled [1, 2]. Since the surface of the thin film cathode was fully soaked in the electrolyte, it was difficult to form the solid electrolyte interface (SEI) on the thin film. Therefore, we newly designed an in-situ aluminum-laminated cell, which is composed of the cathode thin film, a separator filled by the electrolyte and Li metal.

Previous studies have reported results of the neutron and X-ray reflectometry measured at several state of charge (SOC) based on the in-situ cells filled by the electrolyte [1-3]. In this report, we successively measured the neutron reflectivity of the newly designed in-situ cell during the battery operation because of MLF operation in 2017B from 150 kW to 400 kW to clarify lithium-ion transport properties in the $LiCoO_2$ cathode and at the electrode/electrolyte interface during the battery operation.

2. Experiment

The cathode film was $LiCoO_2$/Pt/Cr on the Si substrate. The newly designed in-situ cell laminated by aluminum was composed of the $LiCoO_2$ thin film as cathode, lithium metal as anode and separator filled by the electrolyte of 1.0 mol dm^{-3} $LiClO_4$ in a 1:1 volumetric mixture of ethylene carbonate (EC) and diethyl carbonate (DEC). The in-situ cell was operated with cyclic voltammetry (CV) mode (0.1 mV/s) from OCV (Open Circuit Voltage) to 4.2 V. The neutron reflectivities were measured at BL17 in MLF during the battery operation. Neutron beams were incident on the substrate side of the film and reflect at the $LiCoO_2$ film/electrolyte interface. Three neutron reflectivities are measured for ~ 6 hours with $\theta/2\theta$ = 0.3/0.6, 0.9/1.8 and 2.0/4.0 degree at OCV, 4.2 V. Moreover, successive neutron reflectivities were measured with $\theta/2\theta$ = 0.3/0.6 from OCV to 4.2 V and time-sliced every 20 minute. We analyzed the measured neutron reflectivities using Motofit analysis code [4].

3. Results

Figure 1(a) shows the measured and calculated neutron reflectivities at OCV and 4.2 V. The OCV (4.2 V) corresponded to SOC of 0 % (100 %) before (after) the battery operation. Figure 1(b) shows the scattering length density (SLD) profiles after the analysis of the neutron reflectivities. The SLD and interface width of $LiCoO_2$ increased from OCV to 4.2 V because of the lithium de-intercalation

from the cathode ($LiCoO_2$) to the anode (Li metal) due to the minus value of the lithium SLD. The time-sliced reflectivities from OCV to 4.2 V are shown in Fig. 2(a) and were different each other. Figure 2(b) shows the CV curve (red line) and the SLD of $LiCoO_2$ (blue marked line) vs. voltage. The CV curve shows the 3.65 V unknown peak and 3.9 V peak due to the lithium de-intercalation. The SLD of $LiCoO_2$ was increased over 3.65 V, i.e. the analysis of the lithium-ion transport at the electrode/electrolyte interface during the battery operation by the operand neutron reflectometry based on the newly designed in-situ cell has been realized.

References

[1] M. Hirayama et al., J. Power Sources 168 (2007) 493-500.

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[3] M. Hirayama, et al. Electrochemistry, 78, 413-415 (2010).

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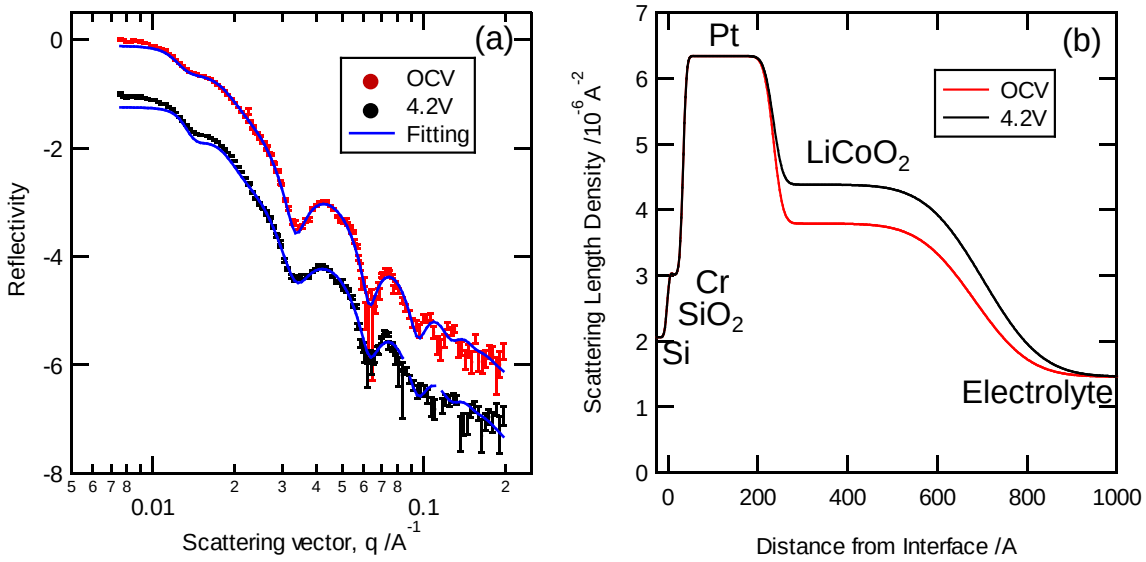

Fig. 1 (a) Measured and calculated neutron reflectivities at OCV and 4.2 V, (b) scattering length density (SLD) profiles of OCV and 4.2 V.

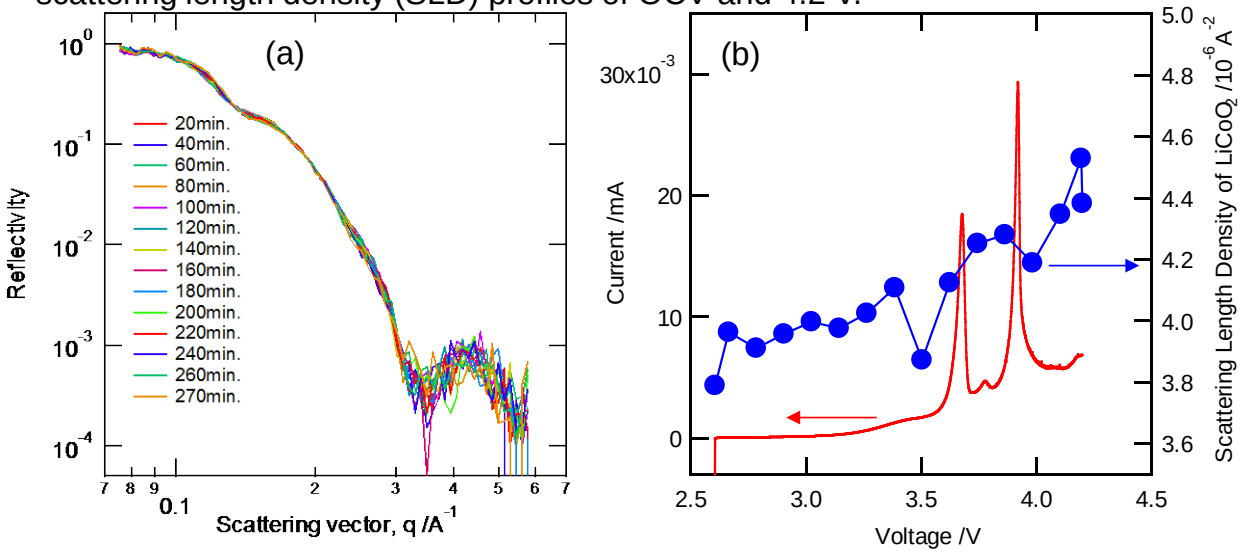

Fig. 2 (a) Measured reflectivities from OCV to 4.2 V, (b) cyclic voltammetry curve (red line) and SLD of $LiCoO_2$ (blue marked line) vs. voltage.