


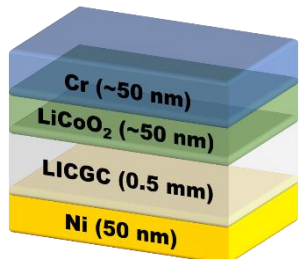
実験報告書様式(一般利用課題・成果公開利用)

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	承認日 Date of Approval 2017/1/13 承認者 Approver Kazuhiko Soyama 提出日 Date of Report 2017/1/13
課題番号 Project No. 2016A0225 実験課題名 In-situ Li concentration at electrolyte/electrode interfaces in solid state lithium ion battery under battery operation 実験責任者名 Name of principal investigator Taro Hitosugi 所属 Affiliation Tohoku University	装置責任者 Name of Instrument scientist 曾山 和彦 装置名 Name of Instrument/(BL No.) BL-17 実施日 Date of Experiment Jun. 16 <sup>th</sup> 2016 – Jun. 19 <sup>th</sup> 2016 Nov. 9 <sup>th</sup> 2017 – Nov. 12 <sup>th</sup> 2017

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.

<p>1. 試料 Name of sample(s) and chemical formula, or compositions including physical form.</p> <p>Our purpose is to measure the distribution of Li at an interface of an electrode and a solid electrolyte (solid-electrolyte/electrode interface) under applied voltage. For this purpose, we prepared an all-solid battery device. The device consists of a <math>\text{Li}_2\text{Al}_{0.5}\text{Ti}_{0.75}\text{Ge}_{0.75}\text{Si}_{0.5}\text{P}_{2.5}\text{O}_{12}</math>(LICGC) solid-electrolyte substrate with a Ni blocking electrode (50 nm) on one side and a <math>\text{LiCoO}_2</math> positive electrode (50 nm) on the other side. The <math>\text{LiCoO}_2</math> electrode was covered with a Cr current collector (50 nm). The Ni blocking electrode and the Cr current collector were deposited by using DC and RF magnetron sputtering method, respectively, and the <math>\text{LiCoO}_2</math> positive electrode was deposited by using pulsed laser deposition (PLD) method. The dimensions of the LICGC solid electrolyte is 10 mm x 10 mm x 0.5 mm. A schematic of the device is shown in Fig. 1.</p>
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<p>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.</p>	
<p>The Li distribution at a solid-electrolyte/electrode interface is of crucial concern because the distribution has great influence on the charge transfer reaction at the interface; the charge transfer reaction often determine the charge/discharge speed of solid-state Li batteries (ss-LB). However, few studies have reported the Li distribution in solid electrolytes under battery operations. This is because of nothing but the difficulty in measuring the Li distribution inside a ss-LB device in a non-destructive manner. Recently, we have demonstrated that a neutron reflectivity method can clearly resolve the Li distribution at a solid-electrolyte/electrode interface in nano-meter scale spatial resolution. The results showed that, when a Li blocking electrode is used, a Li distribution in a solid electrolyte do not show abrupt change near the solid-electrolyte/electrode interface under applied bias voltage. In this study, we aimed to reveal the role of Li-non blocking electrode, that is, <math>\text{LiCoO}_2</math> positive electrode in the formation of Li distribution at the interface.</p>	 <p><b>Fig. 1</b> A schematic of model Li battery device used for neutron reflectivity measurements.</p>

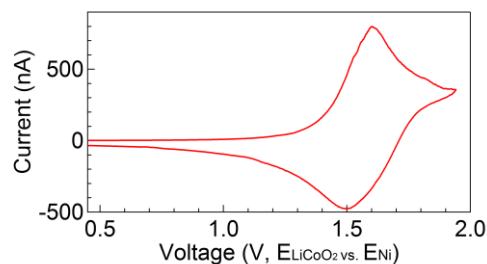
## 2. 実験方法及び結果(つづき) Experimental method and results (continued)

Using neutron reflectivity measurements, we tried to determine the depth profile of the density of Li in ss-LB devices. Neutron reflectivity was measured *in-situ* for three-types of states, initial (as-prepared,  $\sim 0.5$  V), charged (1.8 V) and discharged (0.3 V) states, using BL-17 SHARAKU. A typical cyclic-voltammetry profile of the device is shown in Fig. 2. AC impedance spectra (SP-150, Biologic) were also measured before and after the neutron reflectivity measurements, to compare the insights from electrochemical measurements and the actual Li distributions.

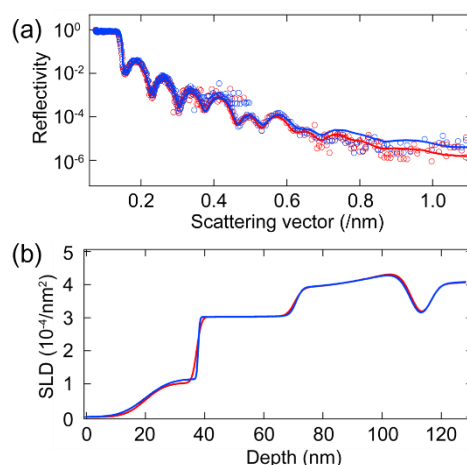
The reflectivity profiles and neutron scattering length density (SLD) profiles at charged and discharged states are compared in Fig. 3. These profiles show that there is only very small difference between charged and discharged state. Although the Li concentration *inside* the electrode at discharged state must be different from that at charged state, the difference in the Li composition at the positive-electrode/electrolyte *interface* was hardly observed in charged and discharged states.

On the other hand, the Li composition of the interface at initial state was much different from that of charged or discharged states. We have measured neutron reflectivity of as-prepared sample (initial state, *i.e.*, no voltage is applied after depositing Ni, LiCoO<sub>2</sub> and Cr electrodes). The reflectivity profiles and SLD profiles at initial and charged states are compared in Fig. 4. The profiles at the initial state is completely different from that at the charged state. The difference is pronounced at the interface of the positive electrode and the solid electrolyte (depth of  $\sim 120$  nm in Fig. 4(b)). This result indicates the formation of an interphase layer. The possible origin of the layer is two-fold; one is the reaction between the positive electrode and the solid electrolyte, and the other is a damage by the deposition of positive electrode. This intermediate layer disappeared on charging.

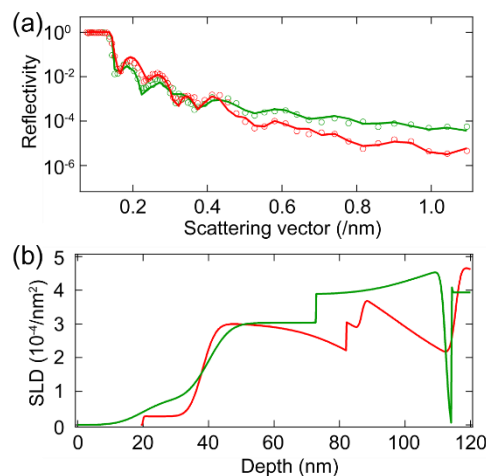
Our finding on the intermediate layer at the interface of the positive electrode and the solid electrolyte in the initial state is quite important for designing ss-LB devices. The investigation of the role of this intermediate layer to the ionic conductivity across this interface is the next crucial step to realize solid-state Li batteries.



**Fig. 2** Cyclic-voltammetry profile of the Li battery device used for neutron reflectivity measurements.



**Fig. 3** (a) Reflectivity profiles and (b) neutron scattering length density profiles at charged (red) and discharged (blue) state.



**Fig. 4** (a) Reflectivity profiles and (b) neutron scattering length density profiles at initial (green) and charged (red) state.