
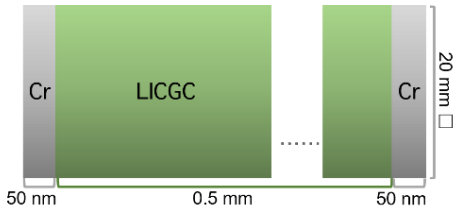


実験報告書様式(一般利用課題・成果公開利用)

(※本報告書は英語で記述してください。ただし、産業利用課題として採択されている方は日本語で記述していただいても結構です。)

	承認日 Date of Approval 承認者 Approver 提出日 Date of Report
課題番号 Project No. 2015A0272 実験課題名 Title of experiment Bias-voltage-dependent depth profile measurement of Li concentration at electrolyte/electrode interfaces 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 山崎 大 装置名 Name of Instrument/(BL No.) BL-17 実施日 Date of Experiment Mar. 3rd, 2016 – Mar. 7th 2016

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 distribution of Li ions in a solid electrolyte under applied voltage. For this purpose, we prepared a solid electrolyte sandwiched with metal electrodes. Amorphous $\text{Li}_{1+x+y}\text{Al}_x(\text{Ti},\text{Ge})_{2-x}\text{Si}_y\text{P}_{3-y}\text{O}_{12}$ (LICGC) is selected as a model solid electrolyte. Chromium (Cr) electrodes, with thickness of 50 nm, were deposited on both sides of the mirror polished 20 mm × 20 mm × 0.18 mm LICGC substrate by using DC magnetron sputtering. A schematic of the sample is shown in Fig. 1.</p>	 <p>Fig. 1 A schematic of sample. Chromium is deposited on both sides of a $\text{Li}_{1+x+y}\text{Al}_x(\text{Ti},\text{Ge})_{2-x}\text{Si}_y\text{P}_{3-y}\text{O}_{12}$ (LICGC) surface.</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。)</p> <p>Experimental method and results. If you failed to conduct experiment as planned, please describe reasons.</p> <p>Distribution of Li ions in solid electrolytes is key information for revealing the mechanism of all-solid-state Li-ion battery operations. However, few studies have reported the Li-ion distribution in solid electrolytes. Recently, we have succeeded in unveiling the distribution of Li ions at electrode/electrolyte interfaces under voltage application, using Rutherford backward scattering (RBS) and nuclear reaction analysis (NRA) methods. The results clearly show that, when 5 V is applied to a positive electrode, a Li composition decreases for more than 40% within 8 μm from the positive-electrode/electrolyte interface (Fig. 2). This is quite surprising because it is widely believed that the Li-ion-density depression layer, namely, space-charge layer, is a nano-meter scale in solid electrolytes. Although the distribution of Li ions in micrometer scale became clear, investigations of the depletion of Li in a nano-meter scale at the interface is still unsatisfactory. To answer this question, we carried out neutron reflectivity measurements of LICGC solid electrolyte with applying various voltages. The concept of this study is summarized in Fig. 3.</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-ions in a LICGC solid electrolyte. Neutron reflectivity is measured *in-situ* under applying 0, +2.5, +5, -2.5 and -5 V to the top Cr electrode. AC impedance spectra (SL-150, Biologic) were also obtained before and after the neutron reflectivity measurements, to compare the insights from electrochemical measurements and the actual Li-ion distributions.

The reflectivity profiles at 0, +5 and -5 V are compared in Fig. 4. The circles show the experimental profiles and the solid lines are simulation results. The profiles show clear difference depending on voltages, especially in the region of large scattering vector.

The scattering length density (SLD) profiles used for the simulated lines in Fig. 4 are shown in Fig. 5. The SLD profile at +5 V is larger than that at 0 V in deep region over 50 nm. These results can be interpreted as following. The difference in SLD between +5 V and 0 V is according to the difference in Li-ion compositions because active ions in LICGC is only Li. Since the SLD value of Li is quite small (about -9), the SLD value is increased when the Li composition is decreased. Hence, the result at +5 V indicates that the Li composition around positive electrode/electrolyte interface is decreased. The decrease of Li composition is consistent with the RBS and NRA result in Fig. 2. Here, we note that there is no steep peak of SLD value in the profile at +5 V; this means that there is no abrupt change of Li density near the positive electrode/electrolyte interface.

In contrast to the SLD profile at +5V, the SLD profile at -5 V is smaller than that at 0 V in the deep region over 50 nm. This is because the Li ions concentrate around negative-electrode/electrolyte interface. At 0 to 50 nm, the SLD value is very small because Li appears on top side of negative Cr electrode by applying -5 V; a phenomenon well known as “Li stripping” reactions [1]. These results show that the SLD values have a good correspondence with profiles obtained using RBS and NRA (Fig. 2). Furthermore, the results indicate that there is no abrupt change in SLD value in nm scale. Therefore, we conclude that there is no steep Li depression or accumulation around the electrode/electrolyte interfaces.

To conclude, the RBS, NRA and neutron reflectivity measurements revealed that the density of Li-ions in solid electrolytes changes in μm scale, depending on applied voltages.

[1] F. Sagane, *et al.*, *J. Pow. Sources*, **225** (2013) 245-250.

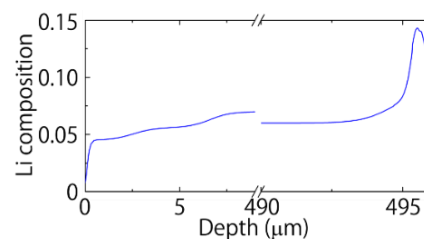


Fig. 2 Li-ion distribution measured using Rutherford backward scattering and nuclear reaction analysis. The measured sample is $\text{Li}_{1+x}\text{Ge}_{2-y}\text{Al}_y\text{P}_3\text{O}_{12}$ sandwiched with Ni

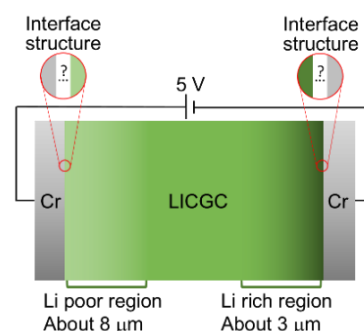


Fig. 3 Concept of this study. Lithium-ion distribution near electrode/electrolyte interface is measured.

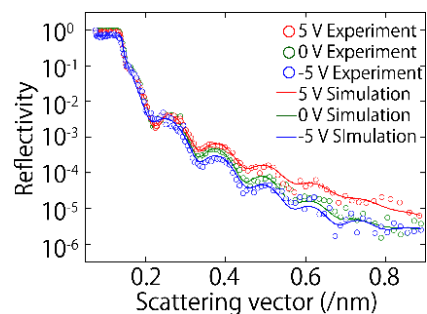


Fig. 4 Neutron reflectivity obtained at 0 V (green), 5 V (red) and -5 V (blue). Circles are experimental data and lines are simulation results.

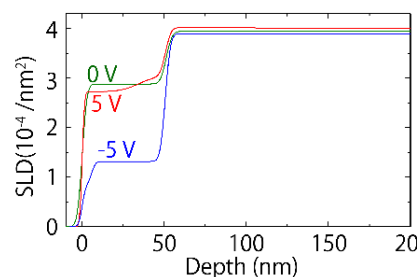


Fig. 5 SLD depth profile at 5 V (red), 0 V (green) and -5 V (blue) used for the simulation in Fig. 4.