


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. 2014B0176 実験課題名 Title of experiment Depth profile measurement of Li concentrate 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 Masayasu Takeda 装置名 Name of Instrument/(BL No.) BL17 SHARAKU 実施日 Date of Experiment 10 <sup>th</sup> Nov. 2015 – 12 <sup>th</sup> Nov. 2015

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.

Our purpose is to measure lithium ion distributions in a solid electrolyte under applied voltage. For this purpose, we prepared a solid electrolyte sandwiched with metal electrodes. Amorphous  $\text{Li}_{1.5}\text{Al}_{0.5}\text{Ge}_{1.5}\text{P}_3\text{O}_{12}$  (LAGP) is selected as a model solid electrolyte. Both side of the 10 mm × 10 mm × 0.5 mm LAGP substrates are hand polished with polishing papers, and then Ni electrodes, with thickness of 200 nm, were deposited on both sides of the LAGP substrate by using DC magnetron sputtering. The schematic of the sample is shown in Fig. 1.

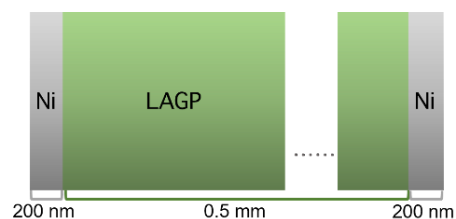


Fig. 1 A schematic of sample. Ni is deposited for 200 nm on both side of LAGP substrate.

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.

Solid electrolytes have wide applications ranging from all-solid lithium ion batteries (LIBs) to fuel cells. Conducting ions, lithium in the case of LIBs, distribute heterogeneously in the solid electrolytes. However, few researches have addressed the quantitative investigation of the spatial distribution of conducting ions. Therefore, it is quite important to reveal the ion distributions in solid electrolytes under applied voltage. In this study, we have tried to reveal applied-voltage-dependent Li ion distributions in a solid electrolyte by using neutron reflectivity measurements. The concept of this study is summarized in Fig. 2.

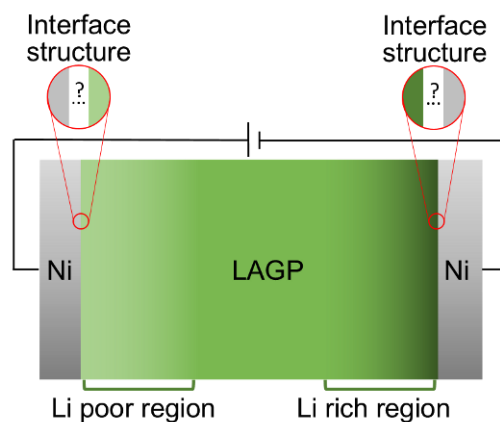


Fig. 2 Concept of this study. Lithium ion distribution around electrode/electrolyte interface is measured.

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

The experimental setup is shown in Fig. 3. The neutron beam incident direction is almost parallel to the Ni electrode surface. We measured the depth profile of Li ion distribution in the LAGP solid electrolyte. Voltage is applied with an electrochemical measurement system (SL-150, Biologic). Neutron reflectivity is measured in situ under applying 0, +5 and -5 V to the top Ni electrode. AC impedance spectra were also obtained before and after the neutron reflectivity measurements, to compare the insights from electrochemical measurements and the actual Li ion distribution.

The reflectivity profile at 0, +5 and -5 V are compared in Fig. 4. These results show that the ionic distribution have negligible dependence to the applied voltages. The simulated lines are also shown on Fig. 4, and the parameters for the simulation are summarized in Table 1. For the simulation, backing layer is presumed to be bulk LAGP, and the layers between Ni electrode and bulk LAGP is adjusted so that the simulation fits the experimental results. The simulation results clearly show that the interface layer is completely different from the bulk LAGP and Ni electrode. This layer exists regardless of the applied voltage, so the voltage dependence on the lithium ion distribution is not observed from the present results.

The lithium ion distribution should depend on the applying bias voltages, because it is well known that the lithium ion migrates from one electrode to the other electrode by applying bias voltages. However, we could not observe such phenomena in the neutron reflectivity measurements. We speculate that following points are the reasons of negligible dependence:

- i) The surface roughness was not good ( $R_a \sim 5$  nm).
- ii) The sample size (10 mm  $\times$  10 mm) was too small for the neutron reflectivity measurement.
- iii) LAGP was damaged by hand polishing and the Ni electrode/LAGP interface is not formed well.
- iv) The reflectivity of Ni electrode was too high and fine structures of LAGP was buried.

To overcome these possible reasons, we are now preparing new samples with Cr electrodes on the machine-polished solid electrolytes. Then, we plan to measure *in-situ* neutron reflectivity again in the next beam time.

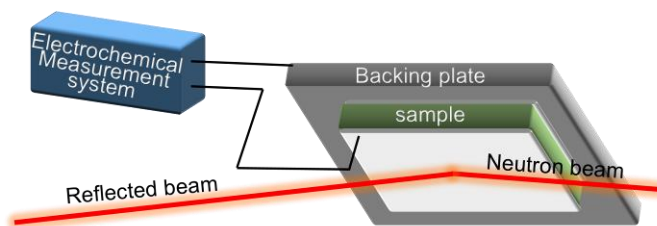


Fig. 3 A schematic of experimental setup. Neutron reflectivity measurement was carried out with in-situ voltage application and AC impedance measurement.

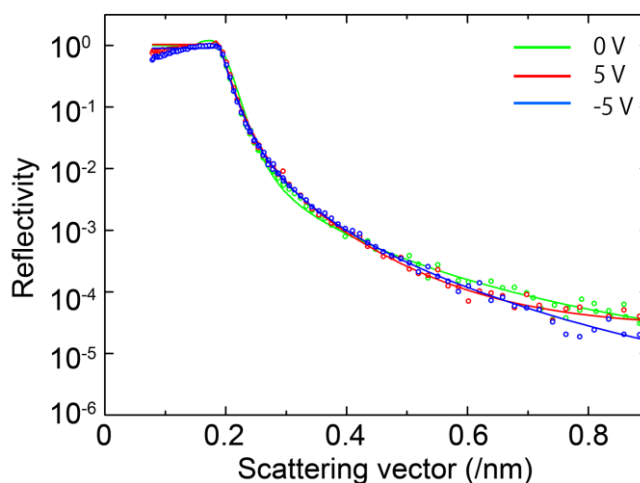


Fig. 4 Neutron reflectivity at 0 V (green), 5 V (red) and -5 V (blue). Circles are experimental data and lines are simulation results.

Table 1 Parameters for the simulation in Fig. 4.

	Thickness(nm)	SLD	Roughness(nm)
0 V			
Ni electrode	16.6	9.4141	14.4
LAGP bulk	Infinite	4.5762	7.27
5 V			
Ni electrode	9.68	9.4141	14.4
Interface layer	52.6	6.5000	2.23
LAGP bulk	Infinite	4.5762	0.02
-5 V			
Ni electrode	9.66	9.4141	14.6
Interface layer	15.4	6.5274	1.28
LAGP bulk	Infinite	4.5762	0.37