# ERDA for depth analysis of Li in thin all-solid-state Li batteries

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Ion beam analysis is a powerful method to observe the depth profiles of various elements in materials. We performed elastic recoil detection analysis (ERDA) for analyzing light elements including Li. The depth profiles of Li were obtained during charging and discharging of the all-solid state Li-ion battery (ASSLB). We observed variation of the Li density in the solid electrolyte.

## 1. Introduction

Ion beam analysis is a powerful method for depth profiling and analysis of elemental composition of solid samples near the surface. Especially, Elastic Recoil Detection Analysis (ERDA) is a suitable method for the analysis of light elements.[1] One of the needs for light element analysis is the development of all-solid-state Li-ion batteries (ASSLB). Recently, the mechanism of Li ion transport and accumulation in ASSLBs has attracted attention. The ion distribution around the interface of ASSLBs is one of the most important factor to investigate the mechanism.[2] In this study, we introduce the depth profiling of Li near the surface of an ASSLB and a Half-cell during charging and discharging as one of the examples of light elemental analysis.

## 2. Experiment

The experiment was performed at Quantum Science and Engineering Center, Kyoto University. A schematic diagram of the experimental setup is shown in Fig.1. The experimental chamber has been installed in former RBS-line of the 1.7MV Cockcroft–Walton type tandem accelerator. It has Si semiconductor detectors (SSDs) for Rutherford backscattering spectrometry (RBS) and ERDA. The sample holder can be moved in the three dimensions and rotated 360°.

A stopper foil is fixed in front of the detector for ERDA so that unwanted scattered ions are stopped. The sample used in this experiment is an ASSLB and a Half-cell. The structure of ASSLB is Pt/LCO/LATP/$Fe_2(MoO_4)_3$/Pt. LCO indicates $LiCoO_2$ and LATP is $Li_{1+x}Al_xTi_{2-x}P_3O_{12}$. Note that the Pt at the top surface is partially stacked. Also, the structure of a Half-cell is Pt/LATP/ $Fe_2(MoO_4)_3$/Pt. Each sample was set at the angle of 75° to the plane where the ion beam was incident vertically. Particles recoiled forward of 30° and backscattered to 150°are detected by SSDs for ERDA and RBS, respectively. We used 9-MeV $O^{5+}$ beam and 7.5-MeV $O^{4+}$ for the present experiment. A thin Al foil of 6-μm or 5-μm thickness was used as the absorber of the SSD for ERDA. The samples were charged and discharged at a

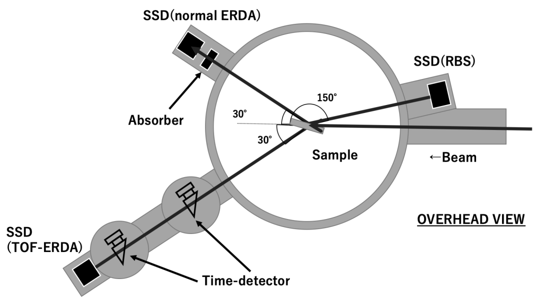


Fig.1 Schematic diagram of the experimental setup

constant current (± 1 $\mu$ A/cm$^2$) using a potentiostat. The experiment was started at the open circuit voltage (OCV) and the voltage was changed in the following order: 1.2V→0.0V→1.2V→1.4V→1.6V→1.8V, and 0.0V with ASSLB. On the other hand, 1.2V→1.4V→1.6V, and 0.0V with Half-cell.

## 3. Results

Figures 2 and 3 show the ERDA and RBS spectra of the ASSLB for different voltages. The normal ERDA spectrum in Fig.2 has a broad Li profiles and a sharp H peak. The Li distribution in the LCO cathode has maximum at OCV or 0V. As the voltage increases, the Li distribution on the higher channel side than the H peak decreases and reaches a minimum at 1.8V. After charging to 1.8V, the battery was discharged to 0V. In this case, the Li ion distribution on the cathode side increased again and was similar to the original profile. In the RBS spectra in Fig.3, the peak found around 700 to 800 channels is assigned to Co in the LCO cathode.

Figure 4 show the ERDA spectra of the Half-cell for different voltages. To investigate whether the change in the Li distribution in Half-cell is derived from the LCO, we measured the Li depth distribution while applying voltage to a half-cell without LCO layer. As shown in Fig.4, we observed the decrease of Li distribution at the channels higher than the H peak. From this result, we found that Li concentration on LATP interface decrease by changing voltage even without LCO layer.

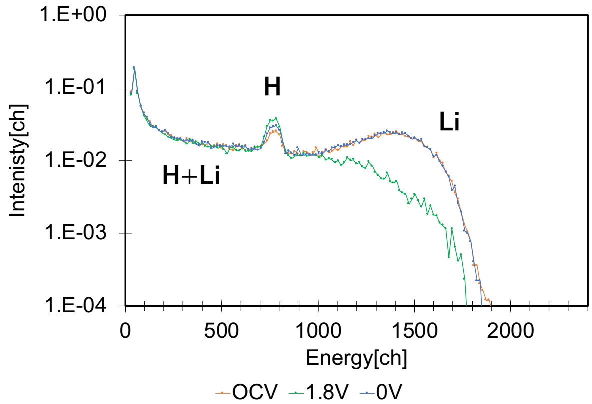


Fig.2 ERDA spectra.(ASSLB)

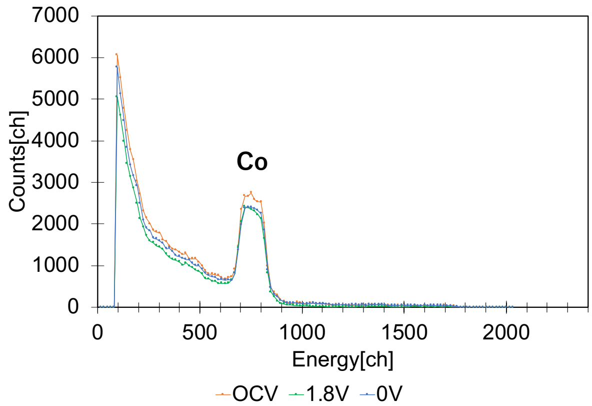


Fig.3 RBS spectra.(ASSLB)

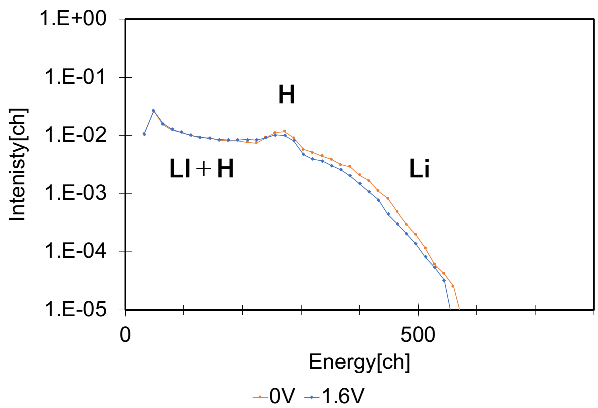


Fig4.ERDA spectra. (Half-cell)

## 4. Summary

In this study, we have succeeded in analyzing the depth profile of Li ions during charging and discharging of ASSLBs with ERDA. We also found that the Li concentration on LATP interface changes even without LCO layer.

Reference

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