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ERD measurement of depth profiles of H and Li in Pt-coated $LiCoO_2$ thin films

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ABSTRACT

By combining elastic recoil detection (ERD) analysis with Rutherford backscattering spectrometry (RBS) using 9.0-MeV oxygen-ion (O^{4+}) probe beams from a tandem accelerator, we simultaneously investigated the distributions of lithium (Li), hydrogen (H), cobalt (Co), and platinum (Pt) in 20 nm Pt/260 nm $LiCoO_2$ multi-layer thin films acting as the positive electrode in a solid-state Li^+ ion battery and, deposited on $Li_{1.4}Ti_2Si_{0.4}P_{2.6}O_{12}$–$AlPO_4$ (LATP) substrates by using pulsed laser deposition. Measurement of the ERD and RBS spectra revealed the effects of Pt deposition on the hydrogen absorption characteristics of the $LiCoO_2$ thin films, with segregation of Co to the surface as a catalyst. We speculate from the results that the presence of H in the $LiCoO_2$ thin films has a marked influence on Li^+ ion conduction in Li-battery systems.

1. Introduction

To protect the global environment, a variety of technologies have been developed for energy production and storage without CO_2 emission and in safer, more energy-efficient, and cheaper ways. It is likely that a catalyst for the production and storage of hydrogen from water and an all solid-state Li-battery will be developed. To realize these products, it is essential that we have information on the transport behavior of H and Li in hydrogen storage systems and in solid-state Li-batteries. So far, our group has developed Pt-coated Li_2ZrO_3 (or Li_4SiO_4) ceramics as hydrogen storage materials. We have also investigated the characteristics associated with hydrogen migration, such as the dissociation of water vapor on the top-most surfaces of materials, the surface and bulk diffusion of hydrogen, and the trapping and detrapping of hydrogen at trap sites. For these purposes we have used an elastic recoil detection (ERD) technique with 2.8 MeV He^{2+} ion beams from a tandem accelerator, installed at Tohoku University's Institute for Materials Research [1,2]. In the case of Pt-coated Li_2ZrO_3 materials, we have found that a gain in mass of more than about 22 wt.%, occurs upon exposure to an air atmosphere at room temperature after annealing at 623 K in a vacuum, because Pt plays an important role in catalysis of the dissociation of water vapor, and large amounts of hydrogen atoms and of water are absorbed into the bulk. In the case of solid-state Li-batteries, it has been speculated by our group that large amounts of hydrogen atoms are absorbed into the solid-state materials and then disturb Li^+ ion behavior. To clarify the relationship between hydrogen atoms and Li^+ ion conduction, we need to establish ways of investigating the behaviors of both hydrogen and lithium atoms at the same time, although there have been few direct Li-concentration analyses of materials [3,4].

Our aim here was to demonstrate the possibility of dynamically measuring the depth profiles of H and Li at the surface and interface, and in the bulk, of solid-state Li-battery systems of Pt/$LiCoO_2$/$Li_{1.4}Ti_2Si_{0.4}P_{2.6}O_{12}$–$AlPO_4$ (LATP) under heating and charging conditions by combining ERD with Rutherford backscattering spectrometry (RBS) using 9.0-MeV O^{4+} ion-probe beams.

2. Experiments

As standard samples for the investigation of Li distribution by using ion beam analysis, lithium-zirconium oxides (Li_2ZrO_3) were fabricated by means of a conventional solid-state reaction between two kinds of powders, Li_2CO_3 and ZrO_2, at 1373 K in an air atmosphere [1]. In addition, ytterbium-doped strontium-cerium oxides ($SrCe_{0.95}Yb_{0.05}O_{3-\delta}$) were also prepared by sintering powders of

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$SrCO_3$, CeO_2, and Yb_2O_3 at high temperature in an air atmosphere to yield standard samples including large amounts of residual hydrogen atoms [5,6]. A single-layer of lithium–cobalt oxide ($LiCoO_2$) and multi-layers of platinum/lithium–cobalt oxide (Pt/$LiCoO_2$) thin films were deposited onto one face of the SiO_2 or LATP [7] substrates by using a pulsed laser deposition device [8]. The $LiCoO_2$, Pt, and LATP materials act as anode electrode, electrode, and lithium conductor, respectively, on the solid state Li ion batteries. Therefore, we selected them as substrates for fabricating thin film solid-state Li^+ ion batteries. To prepare $LiCoO_2$ thin films, the temperature of the substrates, which were heated in a vacuum chamber, evacuated under a pressure of 5×10^{-3} Pa, was maintained at approximately 873 K during the deposition, and the pressure of the oxygen (O_2) gas introduced into the vacuum chamber was kept at approximately 23 Pa. The $LiCoO_2$ thin films prepared on each SiO_2 or LATP substrate were approximately 10 mm in diameter and 260–300 nm-thick. The thickness of Pt deposition on the $LiCoO_2$ thin film was approximately 20 nm. The thickness values were evaluated by RBS measurement (as shown in the RBS spectra in Figs. 3(a), 4(a) and (c)) at the same time as the depth profiles of Li and H in several specimens were analyzed by high-energy ERD with 2.8-MeV He^{2+} and 9.0-MeV O^{4+} ion-probe beams from the tandem accelerator at the Department of Nuclear Engineering, Kyoto University. Various specimens were irradiated with He^{2+} and O^{4+} ions at an incident angle of 75° to the surface normal of the films at room temperature. Forward-recoiled hydrogen ions (H^+) from elastic collisions with He^{2+} ions were detected at a scattering angle of 30° to the incident He^{2+} ion direction by using a solid-state detector (SSD) for ERD that was equipped with an absorber composed of 12 μm-thick Al film [9]. Forward-recoiled lithium ions (Li^+) and H^+ ions from collisions with O^{4+} ions were detected at a scattering angle of 30° to the incident O^{4+} ion direction by using a SSD for ERD that was equipped with an absorber composed of 6.0 μm-thick Al film [9]. Simultaneously, He^+ and O^+ ions back-scattered from elastic collisions with the constituent atoms of several specimens—including O, Al, Si, P, Ti, Co, Ge, and Zr atoms—were detected at an angle of 165° to the incident He^{2+} and O^{4+} ion directions by using a SSD for RBS. No temperature increase due to ion irradiations occurred, because the He^{2+} and O^{4+} ion fluxes were approximately 3.2×10^{13} ions/cm^2 s during the measurements, which took approximately 30 min.

3. Experimental results and discussion

We examined typical RBS spectra of backscattered He^{2+} ions (Fig. 1(a)) and O^{4+} ions (Fig. 2(a)) and ERD spectra of recoiled H^+ ions (Fig. 1(b)) and H^+ and Li^+ ions (Fig. 2(b)) from $SrCe_{0.95}Yb_{0.05}O_{3-\delta}$ and Li_2ZrO_3, as measured at room temperature in a vacuum by using 2.8-MeV He^{2+} and 9.0-MeV O^{4+} ion probe beams from a tandem accelerator. The horizontal axes for the RBS and ERD spectra correspond to several energies of the back-scattered He^{2+} and O^{4+} ions and recoiled H^+ and Li^+ ions, respectively, and represent the depth from the surface. On the vertical axes, the counts per an energy in the RBS and ERD spectra correspond to the concentrations of constituent elements such as $_{70}Yb$, $_{58}Ce$, $_{40}Zr$, $_{38}Sr$, $_{8}O$, $_{3}Li$, and $_{1}H$ in $SrCe_{0.95}Yb_{0.05}O_{3-\delta}$ and Li_2ZrO_3. However, the Yb peak is not apparent in the RBS spectra

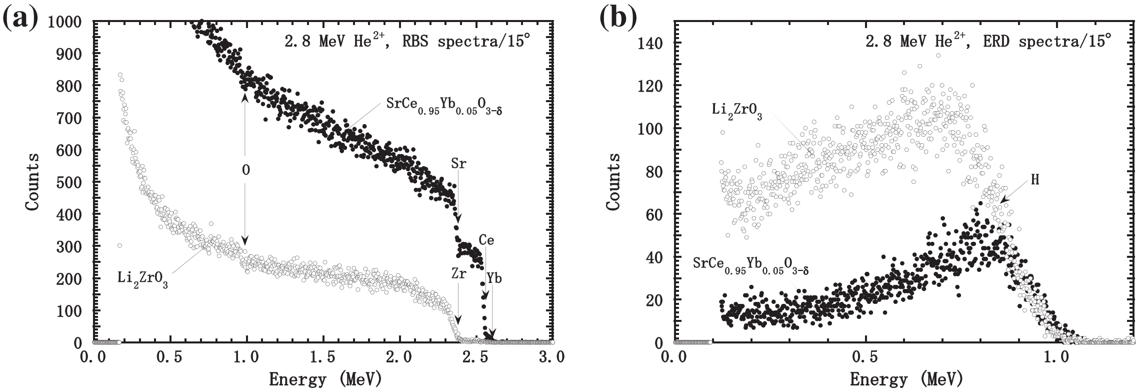

Fig. 1. Typical (a) RBS spectra of back-scattered He^{2+} ions and (b) ERD spectra of recoiled H^+ ions from $SrCe_{0.95}Yb_{0.05}O_{3-\delta}$ and Li_2ZrO_3, obtained by using 2.8-MeV He^{2+} ion-probe beams.

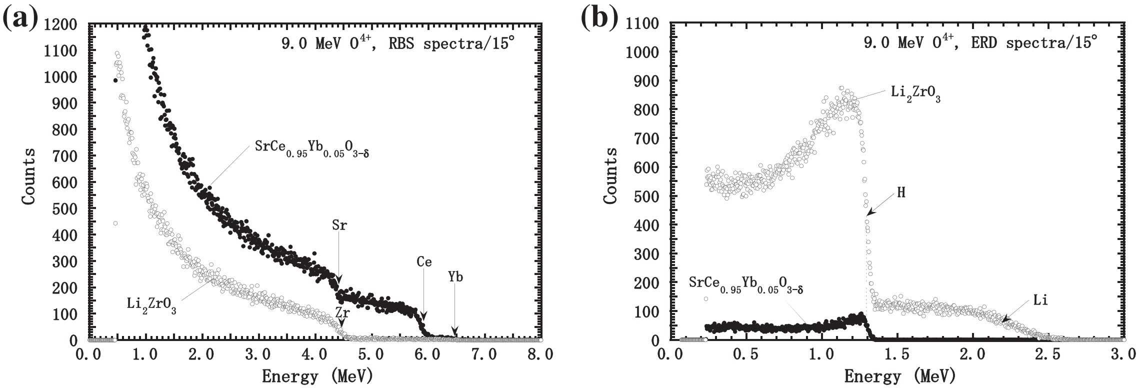

Fig. 2. Typical (a) RBS spectra of back-scattered O^{4+} ions and (b) ERD spectra of recoiled H^+ and Li^+ ions from $SrCe_{0.95}Yb_{0.05}O_{3-\delta}$ and Li_2ZrO_3, obtained by using 9.0-MeV O^{4+} ion-probe beams.