Dynamic Measurements of Hydrogen and Lithium Distributions in Lithium-Cobalt-Oxide Films with Charging and Heating using Elastic Recoil Detection Techniques

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Abstract

The migrations of lithium (Li) as well as hydrogen (H) in multi-layers thin films of $Au/LiCoO_2$ (thickness: approximately 42 nm/80 nm), deposited onto one face of $Li_{1.4}Ti_2Si_{0.4}P_{2.6}O_{12}$–$AlPO_4$ (LATP) substrates, were dynamically observed with electric charging as well as isochronal annealing in vacuum by combining elastic recoil detection (ERD) analysis with Rutherford backscattering spectrometry (RBS) with 9.0-MeV O^{4+} ion-probe beams. The ERD spectra clearly revealed that Li atoms of approximately 9.4 at% migrated from the $LiCoO_2$ surface to the $LiCoO_2/LATP$ interface with H absorption by a charge of approximately 0.48 e/cm^2, which the acquired voltage was 1.65 V. In addition, the diffusion of Li atoms to the LATP bulk occurred with H release by isochronal annealing at only 323 K for 10 min. The presence of H significantly influences the Li^+ ion conduction for the Li-battery systems.

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1. Introduction

Lithium-cobalt oxide (LiCoO$_2$) thin films are the most commonly used cathode materials for rechargeable lithium-ion (Li$^+$) thin film batteries with smaller dimension and have found large scale potential applications in the commercial Li$^+$ ion batteries. The cathode is one of the critical components of the Li$^+$ ion thin film batteries and it determines the capacity, cyclic performance and thermal stability of the battery. In particular, the transport parameters relating to Li diffusion, trapping at trapping-sites, detrapping from the sites in the cathode materials, electrodes, and electrolyte are key factors that determines the rate at which a battery can be charged and discharged. So far, many diffusion measurements on LiCoO$_2$ have been performed on composite electrodes consisting of platinum (Pt), graphite, binders and other materials [1-4]. However, in particular, Pt electrodes, deposited onto the ceramics oxides as cathode materials to charge and discharge, play an important role in catalysis of the dissociation of water vapor. The large amounts of hydrogen (H) atoms and of water may be absorbed into the bulk [5, 6]. In the case of solid-state Li-batteries, it has been deduced that large amounts of H atoms are absorbed into the cathode materials which disturb Li$^+$ ion behavior. To clarify the relationship between trapped H atoms and Li$^+$ ion conduction in the LiCoO$_2$ thin films, it is essential to investigate the behaviors of both H and Li atoms at the same time, although there have been few direct Li-concentration analyses of materials [7, 8].

So far our group has studied effects of Pt catalyst for the production and storage of H from water in an all solid-state Li$^+$ ion batteries at the same time using the high-energy elastic recoil detection (ERD) technique with 9.0-MeV O^{4+} ion-probe beams [9]. The depth distributions obtained from ERD spectra enabled us to investigate *in situ* the behaviors of H and Li at the interfaces between the LiCoO$_2$ thin films and the Li$_{1.4}$Ti$_2$Si$_{0.4}$P$_{2.6}$O$_{12}$–AlPO$_4$ (LATP) substrates or the Pt electrodes in Li$^+$ ion batteries. The Li peak becomes broader than the H peak because of range straggling in the Al absorber film and the LiCoO$_2$ films. The measurement of the ERD 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. It is predicted that the presence of H in the LiCoO$_2$ thin films has a marked influence on Li$^+$ ion conduction in Li$^+$ ion battery systems.

In this present study, the dynamically measuring the depth profiles of H and Li at the surface and interface, and in the bulk of the LiCoO$_2$ thin films with approximately 80 nm thick, deposited on the LATP substrates using a pulsed laser deposition (PLD) device [10], has been carried out by combining ERD with RBS using 9.0-MeV O^{4+} ion probe beams, after electric charging and isochronal anealing conditions.

2. Experiments

Multi-layers of gold/lithium-cobalt oxide (Au/LiCoO$_2$) thin films were deposited onto one face of the LATP [11] substrates with approximatell 1 mm thick and 20 mm diameter using the PLD device [10]. The layered structure of LiCoO$_2$, a nearly cubic close-packed arrangement of oxygen ions (O^{2-}) with Li$^+$ and cobalt ions (Co^{3+}) occupying alternate layers of octahedral sites, is well suitable for the rapid deintercalation and intercalation of Li [12]. Subsequently, a single-layer of Pt was deposited onto opposite side of the LATP one. The LiCoO$_2$, Au, Pt, and LATP materials act as cathode which forms one electrode, with lithium conductor as another electrode in solid state Li ion batteries. Generally Pt electrodes on both faces of the LATP substrates should be selected for fabricating thin film solid-state Li$^+$ ion batteries. However, previous measurements using ERD revealed that Pt thin films actually act as catalysis for water dissociation and H absorption [9]. Therefore it was decided to make Au electrode deposited onto one face, to eliminate the influence of water dissociation during measurements. The thickness of Au and Pt deposition on the LiCoO$_2$ thin film was approximately 42 and 40 nm, respectively. The LiCoO$_2$ thin films prepared on LATP substrates were approximately 10 mm in diameter and 80 nm-thick. The thickness values were evaluated by RBS measurement (as shown in the RBS spectrum in Fig. 1(a)) at the same time as the depth profiles of Li and H in several specimens were analyzed in vacuum chamber, evacuated under a pressure of 1.3×10^{-5} Pa, by high-energy ERD with 9.0-MeV O^{4+} ion-probe beams from the tandem accelerator at the Department of Nuclear Engineering, Kyoto University. The Au/LiCoO$_2$ thin films side of the specimens were irradiated with O^{4+} ions at an incident angle of 75° to the surface normal of the films at room temperature. Forward-recoiled 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 using a SSD for ERD that was

equipped with an absorber composed of 6.0 μm-thick Al film [13]. Simultaneously, O^+ ions back-scattered from elastic collisions with the constituent atoms of several specimens were detected at an angle of 165° to the incident and O^{4+} ion directions by using a SSD for RBS. No temperature increase due to ion irradiations occurred, because the O^{4+} ion flux was approximately 3.2×10^{13} ions/cm^{2}s during the measurements, which took approximately 30 min.

After charging at the conditions at each applied currents of 1 A (three rounds), 3 A (one round), and 5 A (one round) for 1 min at room temperaure at approximatelly 301 K in vacuum and then leaving for 20 min without charging to obtain the steady states of activated Li$^+$ ions, the Li and H distributions on the only Au electrode side were *in situ* measured by combining ERD with RBS techniques. Similar Li and H *in situ* measurements were made on the Au only electrode side after isochronal annealing at various temperatures of 323, 373, and 423 K for 10 min in vacuum.

3. Experimental results and discussion

Fig. 1(a) shows a typical RBS spectra of backscattered O^{4+} ions, and Fig. 1(b) shows a typical ERD spectra of recoiled H$^+$ and Li$^+$ ions, from the deposition of 42 nm Au and 80 nm LiCoO$_2$ on LATP (Au/LiCoO$_2$/LATP) without and with charging up to 5.28 e/cm^2, as measured using 9.0-MeV O^{4+} ion-probe beams from a tandem accelerator.
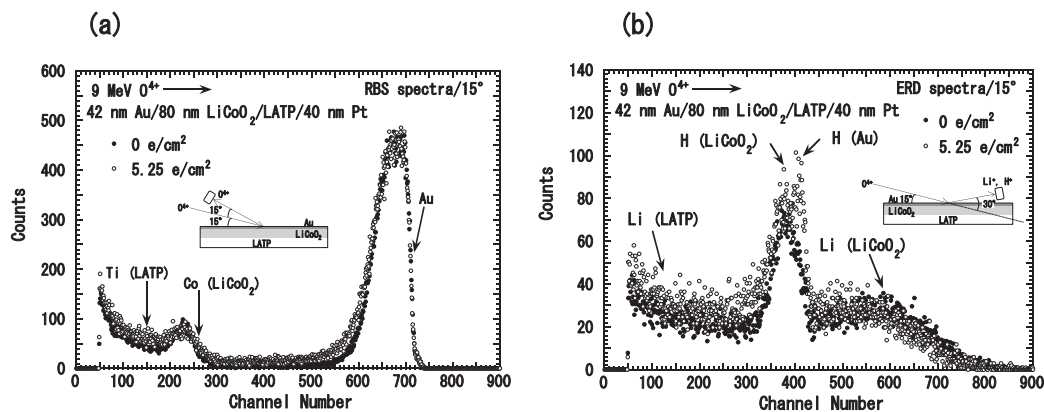

Fig. 1 Typical (a) RBS spectra of back-scattered O^{4+} ions and (b) ERD spectra of recoiled H$^+$ and Li$^+$ ions from 42 nm Au/20 nm LiCoO$_2$/LATP/40 nm Pt (●) without and (○) with charging at 5.28 e/cm^2, obtained by using 9.0-MeV O^{4+} ion-probe beams.

The horizontal axes (Channel Number) for the RBS and ERD spectra correspond to energies of the backscattered O^{4+} ions and recoiled H$^+$ and Li$^+$ ions, respectively, and represent the depth from the surface. On the vertical axes, the counts / energy in the RBS and ERD spectra correspond to the concentrations of constituent elements such as $_1$H, $_3$Li, $_8$O, $_{14}$Si, $_{15}$P $_{22}$Ti, and $_{27}$Co in Au/LiCoO$_2$/LATP. The thickness of each Au and LiCoO$_2$ thin film was determined from approximately 628-711 and 195-255 channels of Fig. 1(a), taking into account the Rutherford backscattering cross-sections of O^+ ions in the case of constituent elements in Au/LiCoO$_2$/LATP, the stopping cross-sections for O^+ ions, and the solid angle of detection [13]. There is no significant change in the spectra between before and after charging, except for the a little diffusion of Au atoms into LiCoO$_2$ perhaps initiated by elastic collisions due to ion probe-beam, as seen approximately in 450-615 channels of Fig. 1(a). On the other hand, the sharp and broad peaks at approximately 320-419 and 450-849 channels in ERD of Fig. 1(b) correspond to the H and Li concentrations in LiCoO$_2$ thin films. The Li peak becomes broader than the H peak, because the range straggling due to the stopping power of Li is larger than that of H in the Au, LiCoO$_2$ film and the Al absorber [13]. It is assumed by the basis of our previous experimental
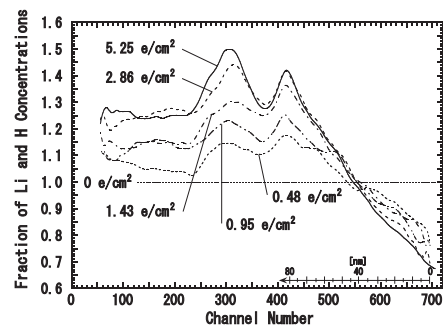

Fig. 2 Electric charge dependence of Li and H distributions in Au/LiCoO$_2$/LATP, normalized to the ERD spectrum for the uncharged-sample in Fig. 1 (b).

results [9] that the H peak ranging from approximately 320-419 channels in ERD spectrum for the uncharged-sample may probably correspond to H atoms absorbed by the $LiCoO_2$ film, as the H concentration in the Au film was quite low. The each peak at around 370 and 410 channels in ERD spectrum for the charged-sample up to 5.28 e/cm^2 may probably indicate H or water (H_2O) retained in the $LiCoO_2$ films and H_2O adsorbed only onto the surface of the Au thin film, respectively. Also, it is assumed in this present study that each area at approximately 450-549 and 550-849 channels indicates Li concentrations at the interface between $LiCoO_2$ thin films and LATP, and at the surface of the thin films, respectively. It appears from Fig. 1(b) that the Li concentrations at the interface and the surface increase and decrease, respectively, after charging up to 5.28 e/cm^2. The gradual degradation of Li distribution is from the $LiCoO_2$ film.

In order to estimate the dependence of Li and H migrations in $Au/LiCoO_2/LATP$ on the electric charge more clearly, the ERD spectra for the various charged-samples were normalized to the ERD spectrum for the uncharged-sample, as shown in Fig. 2. It can be seen clearly at approximately 450-700 channels in Fig. 2 that the migration of Li atoms from the surface to the interface between $LiCoO_2$ thin films and LATP dramatically occurs in the beginning of the charge of 0.48 e/cm^2. Subsequently, the gradual degradation of the Li distribution proceeds with an increase of the charge. In addition, it can be seen below approximately 230 channels in Fig. 2 that diffusion of Li atoms from $LiCoO_2$ thin films leads to the gradual increase of Li concentration in LATP uniformly against the depth. The two peaks at around 300-310 and 410 channels may be associated with H absorption from the vacuum or H segregation from the $LiCoO_2$ film and LATP bulk by charging and ion irradiation during the ion beam analysis.

Fig. 3 shows the correlation between the fraction of Li moved to initial Li concentration in $Au/LiCoO_2/LATP$ and the gained voltage as a function of electric charge, which have been normalized to the ERD spectrum for the uncharged-sample in Fig. 1(b). The gained voltages were 1.19, 1.65, 1.76, 1.84, 2.76, and 6.23 V for each supplied charges of approximately 0.048, 0.48, 0.95, 1.43, 2.86, 5.25 e/cm^2, respectively. It can be seen in Fig. 3 that rapid increase (fraction of Li moved : approximately -6.6 % and -1.7 %) and decrease (approximately +9.4 %) of Li concentrations at the $LiCoO_2/LATP$ interface (450-549 channels) and in the LATP bulk (150-249 channels) and at the $LiCoO_2$ surface (550-849 channels), respectively, occurred with a charge of approximately 0.48 e/cm^2, obtained at voltage of approximately 1.65 V. Subsequently, the fraction of Li moved gradually changed up to approximately -12.2 % at the $LiCoO_2/LATP$ interface, -22.5 % in LATP, and +18.4 % at the $LiCoO_2$ surface with an increase in the number of charge supplied up to approximately 5.25 e/cm^2 and the voltage of 6.23 V. The values at 450-849 channels which

Fig. 3 Correlation between the fraction of Li moved in $Au/LiCoO_2/LATP$ and the voltage as a function of electric charge.

correspond to the change in concentration of Li in the whole $LiCoO_2$ film, as shown in Fig. 1(b), gradually increase in an increase of the electric charge. The result indicates the migration of Li from the $LiCoO_2$ film to LATP bulk. However, the higher increase of Li at 150-249 channels may be attributed to the diffusion from the $LiCoO_2$ thin film as well as segregation from the LATP bulk.

Fig. 4 shows typical ERD spectra of recoiled H^+ and Li^+ ions from 42 nm Au/80 nm $LiCoO_2$/LATP/40 nm Pt without and with heating at 423 K for 10 min, measured at room temperature of 301 K using 9.0-MeV O^{4+} ion-probe beams. Intensities of both the sharp and broad peaks at approximately 320-419 and 450-849 channels in ERD of Fig. 4 decrease by heating at 423 K for 10 min. In contrast, the intensity of the broad peaks at approximately 120-249 channels seems to show a slight increase. Fig. 5 shows dependence of Li and H distributions in $Au/LiCoO_2/LATP$ on several annealing temperatures up to 423 K, normalized to the ERD spectrum at 301 K in Fig. 4. The reduction of H and Li atoms was observed by annealing even at 323 K at the Au surface, in $LiCoO_2$ bulk (320-419 channels), at the $LiCoO_2/LATP$ interface (450-549 channels) at the $LiCoO_2$ surface (550-849 channels) and the $LiCoO_2$ bulk (450-849 channels), regions respectively, while slight increase of Li atoms was observed in the LATP bulk (150-249 channels). The fraction of the both Li as well as H in the $LiCoO_2$ thin films reached to approximately 0.7-0.8 at 423 K. The thermally activated Li atoms were able to diffuse into the LATP bulk with the release of H absorbed in the $LiCoO_2$ thin films. It is deduced from the results that the vapor in air should not be absorbed into the $LiCoO_2$ film
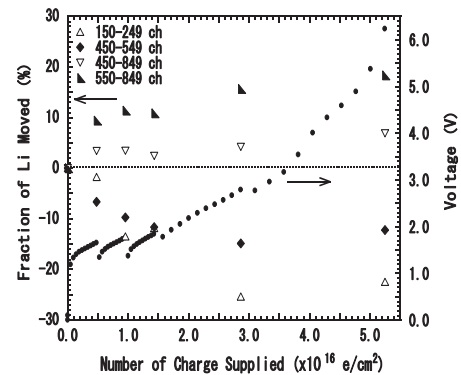
and LATP bulk during the fabrication, in order to gain the higher rate at which a battery can be charged and discharged and to extend the life of the battery.
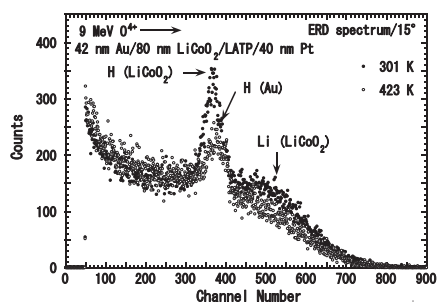

Fig. 4 Typical ERD spectra of recoiled H^+ and Li^+ ions from 42 nm Au/80 nm $LiCoO_2$/LATP/40 nm Pt (●) before and (○) after isochronal annealing at 423 K for 10 min, measured using 9.0-MeV O^{4+} ion-probe beams.
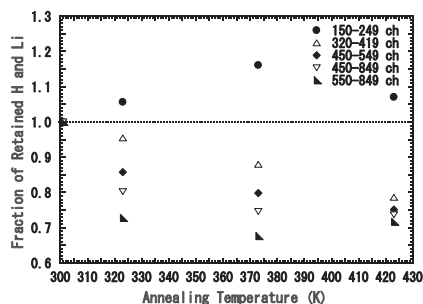
Fig.5 Temperature dependence of Li and H distributions in Au/$LiCoO_2$/LATP with heating up to 423 K, normalized to the ERD spectrum at 301 K in Fig. 4.

4. Summary

The behaviors of the constituent Li atoms, as well as the residual H atoms, in multi-layers of 42 nm Au/80 nm $LiCoO_2$ films, deposited onto one face of LATP substrates using the pulsed laser deposition, were investigated *in situ* using the high-energy ERD technique with 9.0-MeV O^{4+} ion-probe beams, after charging up to 5.25 e/cm^2 at room temperature and heating up to 423 K in vacuum. The ERD spectra clearly revealed the sharp peak for the residual H atoms and a broad peak for the Li atoms, because of its higher depth resolution, although some peaks from H and Li were overlapping. It was dynamically found in ERD spectra that the Li atoms of approximately 9.4-18.4 at% migrated from the surface to the $LiCoO_2$/LATP interface with H absorption with a charge of approximately 0.48-5.25 e/cm^2, which the acquired voltage was 1.65-6.23 V. In addition, the gradual reduction of the residual H atoms as well as the constituent Li atoms and the slight increase of Li in the LATP bulk were observed *in situ* after isochronal annealing up to 423 K for 10 min. The fraction of the both Li and H in the $LiCoO_2$ thin films reached to a value of approximately 0.7-0.8 at 423 K. The results allow us to conclude that the presence of H significantly influences the Li^+ ion conduction for the Li-battery systems.

Acknowledgements

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