Interfacial Reaction between Electrode and Glass Electrolyte of All-Solid-State Lithium Ion Battery

T. Arai, T. Kumagai, J. Shirakawa, Y. Uchimoto, and M. Wakihara
Department of Applied Chemistry, Tokyo Institute of Technology
2-12-1 Ookayama, Meguro-ku, Tokyo, 152-8552, Japan

Application of solid electrolytes for lithium ion batteries is desirable because of their excellent properties such as safety, high energy density and so on, compared to those of batteries using organic liquid electrolytes. Among solid electrolytes, Li_2S-SiS_2- Li_4SiO_4 glass electrolytes are known to show high lithium ion conductivity (~10^{-3} S cm^{-1}) [1]. In the case of usual batteries using liquid electrolyte, SEI (solid electrolyte interface) layer forms at the interface between electrode and electrolyte and acts an important role for reversible cycles. However, the interfacial reaction between electrode and glass electrolyte has not been clarified yet.

In the present work, we investigated the interfacial reaction from the viewpoints of interfacial product and charge transfer reaction, especially, the product at the interface was measured by using soft X-ray absorption spectroscopy (XAS).

Li foil and In foil were used as the anode and $LiCoO_2$ and $LiMn_2O_4$ were used as the cathode. The glass electrolyte used in this study was $95(0.6Li_2S0.4SiS_2)$ $5Li_4SiO_4$, which was supplied at Minami-Tatsumisago group in Osaka Prefecture University [2-4].

From charge-discharge measurement, it was found that the cell which consists of In anode and $LiCoO_2$ cathode shows reversible charge and discharge capacity. However, for $LiMn_2O_4$ cathode, we could obtain only 1st charge capacity. In order to clarify these phenomena, we examined the interface between $LiCoO_2$ or $LiMn_2O_4$ cathode and glass electrolyte of the cell which had been kept charged after 10th charge-discharge cycle. S *K*-edge and Co L_2 and L_3-edge spectra were measured using synchrotron radiation at the beam lines BL-1A and BL-8B1, respectively, at UVSOR, Okazaki. The absorption was determined by the total-electron-yield method.

Fig. 1 shows S *K*-edge XANES spectra. Glass electrolyte shows broadened peak compared to its component, SiS_2 and Li_2S, which indicates that atoms around sulfur have various electron state in the glass electrolyte. The peak position of the spectra of glass electrolyte is almost the same as that of Li_2S indicating the chemical state of S is similar. As shown by an arrow in Fig.1, spectrum of the interface has shoulder at the same position with CoS though it has similar configuration and peak position to those of glass electrolyte. This indicates that CoS or some compound whose electron state is similar to that of CoS had been produced at the interface. Also, we present Co L_2 and Co L_3-edge XANES spectra in Fig.2. Peak positions of three samples sift toward positive energy in order of CoS, $LiCoO_2$ and the interface. Moreover, we calculated the ratio of peak intensity of L_2 to that of L_3. The ratio of $LiCoO_2$ was 2.04 while that of the interface was 2.17, which is larger than $LiCoO_2$. These phenomena indicate that Co ion in $LiCoO_2$ at the interfacial region was oxidized through charging. Then, we could confirm that lithium ion transferred from $LiCoO_2$. In addition, spectrum of $LiCoO_2$ has shoulder at the same position of CoS as shown by an arrow in Fig.2. This behavior is correspondent with the result of S *K*-edge XANES spectrum. On the other hand, after 1st cycle, we could not confirm the existence of product at the interface of the cell in which In anode and $LiMn_2O_4$ cathode were used. As a result, we suggest that what makes it possible for all-solid-state lithium ion batteries to conduct lithium ion at the interface is SEI which stabilize interface between electrode and glass electrolyte.

The investigation on charge transfer reaction will also be presented.

References

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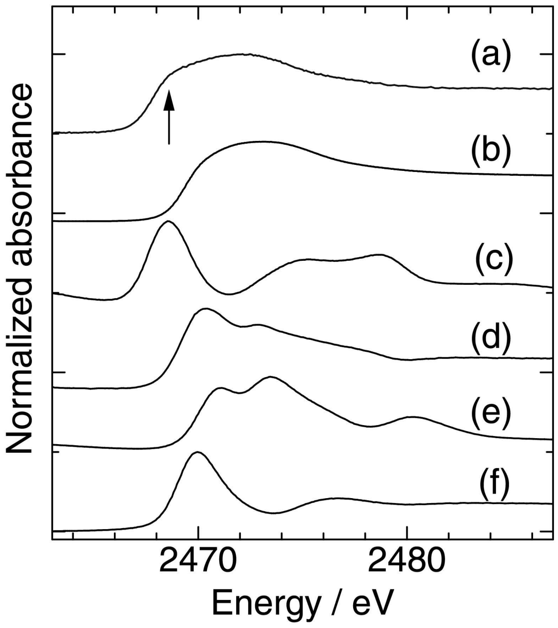

Fig.1 S *K*-edge XANES spectra and (a): interface of $LiCoO_2$/glass electrolyte (kept charged after 10th charge-discharge cycle), (b): glass electrolyte, (c): CoS, (d): SiS_2, (e): Li_2S, (f): S

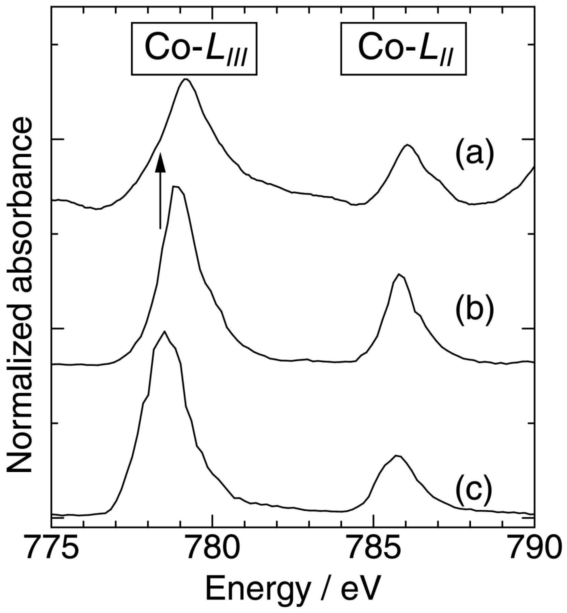

Fig.2 Co L_2 and Co L_3-edge XANES spectra and (a): interface of $LiCoO_2$/glass electrolyte (kept charged after 10th charge-discharge cycle), (b): $LiCoO_2$, (c): CoS