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Interface analysis of $LiCoO_2$ positive electrode/$Li_7La_3Zr_2O_{12}$ solid electrolyte

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A lithium ion conducting ceramic, $Li_7La_3Zr_2O_{12}$ (LLZ), is a promising solid-electrolyte for advanced all-solid-state lithium ion batteries, in terms of fast ion conductivity (> 1 x 10^{-4} S cm^{-1} at room temperature) and good chemical stability against Li metal (or Li-alloys) as negative electrodes [1]. However, electrodes/LLZ interface have not been investigated at all and then its basic properties for reducing the interfacial resistance should be clarified.

In this work, thin films of $LiCoO_2$ were deposited on well-crystallized LLZ pellet, and its interface was investigated by transmission electron microscopy (TEM). Finally, we will show the fundamental problems on interface for developing all-solid-state battery system using LLZ as the solid electrolyte. Although there are several kinds of electrode active materials, $LiCoO_2$ is the most famous one and have been already investigated in other solid state battery systems. Thus, this work focuses on this electrode active material.

The cross-sectional TEM image of the $LiCoO_2$ /$Li_7La_3Zr_2O_{12}$ interface region is presented in Fig. 1(a). All layers of Pt current collector, $LiCoO_2$ thin film, and $Li_7La_3Zr_2O_{12}$ are observed with different contrast. However, the interface region between $LiCoO_2$ and $Li_7La_3Zr_2O_{12}$ is not sharp. In the enlarged TEM image shown in Fig. 1(b), anomalous–contrast is observed in ～50 nm in the vicinity of the $LiCoO_2$/$Li_7La_3Zr_2O_{12}$ interface (indicated by a yellow arrow), and the contrast is almost parallel to the each layer. The intensity profile along A-B clearly shows that the anomalous contrast layer exists in the vicinity of $LiCoO_2$/$Li_7La_3Zr_2O_{12}$ interface. In general, the intensity tendency of each layer is caused by the transmission ability related to atomic weight of solids. In this profile, the flat profile is observed in $LiCoO_2$ and $Li_7La_3Zr_2O_{12}$ regions. However, in anomalous contrast region, the intensity gradually decreases. Presumably, it is considered that some elements diffused in the region.

The TEM image and EDS profile near $LiCoO_2$/$Li_7La_3Zr_2O_{12}$ interface are shown in Fig. 2. As shown in Fig. 2(a), the layer (indicated by yellow arrow) was clearly observed in the interface. The EDS line profile was obtained along the yellow arrow indicated in the TEM image of Fig. 2(a). We did an EDS analysis with an electron nanoprobe of ~5 nm in diameter. In the EDS line profile shown in Fig. 2(b), the distribution of each element in all layers is shown. Here, we have focused on the diffusion layer region of $LiCoO_2$ and $Li_7La_3Zr_2O_{12}$ interface, indicated by red dotted lines. From the result of the EDS line profile, we found that the elements Co, La, and Zr coexisted in the reaction layer, and did not crystallize. In particular, a small amount of Co in $LiCoO_2$ positive electrode diffused toward the $Li_7La_3Zr_2O_{12}$ electrolyte. Thus, we attribute that the formation of the reaction layer to the mutual diffusion between the $LiCoO_2$ and $Li_7La_3Zr_2O_{12}$ during the deposition of $LiCoO_2$ at high temperature. These results indicate that the electrochemical performance of $LiCoO_2$/$Li_7La_3Zr_2O_{12}$ is strongly affected by the reaction layer generated by diffusion in the interface.

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References

[1] R. Murugan et al., Angew. Chem. Int. Ed. 46 (2007) 7778.

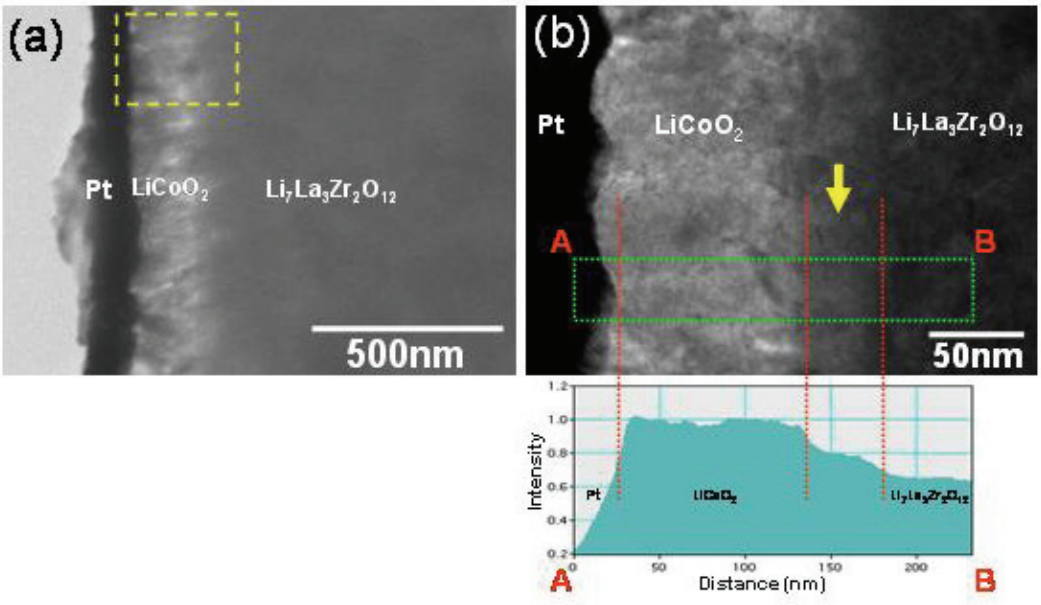

FIG 1. (a) Cross-sectional TEM image of a part of the $LiCoO_2$ positive electrode/$Li_7La_3Zr_2O_{12}$ solid electrolyte. (b) Enlarged image obtained for the rectangular region indicated by broken yellow lines shown in (a). In (b), intensity profile indicates the integrated rectangular region of the $LiCoO_2$/$Li_7La_3Zr_2O_{12}$ interface indicated by broken green. The broken red lines indicated the boundary of respective layers.

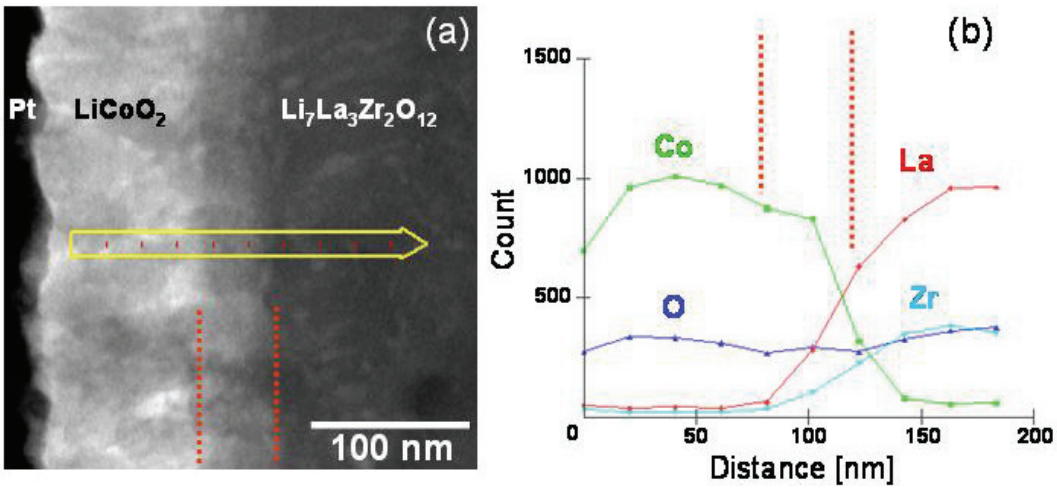

FIG 2. Cross-sectional TEM image of $LiCoO_2$/$Li_7La_3Zr_2O_{12}$ interface (a) and its EDS line profile for element analysis obtained from yellow arrow (b). Broken red lines indicate reaction layer in $LiCoO_2$/$Li_7La_3Zr_2O_{12}$ interface.