

## TEM analysis of thin film electrode/glass ceramic solid-electrolyte interfaces

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All-solid-state rechargeable lithium ion batteries (LIBs) are expected to be one of the main power sources for hybrid and fully electric vehicles. However, practical use of all-solid-state LIBs requires the high interfacial-resistance between the electrode and the solid electrolyte to be decreased. Analyzing the electrode/ electrolyte interface is thus important to clarify the causes of this interfacial resistance.

Thin film electrodes of  $\text{LiMn}_2\text{O}_4$  or  $\text{LiCoO}_2$  were deposited on a glass ceramic solid electrolyte sheet [ $1$ ]( $\text{Li}_{1+x+y}\text{Al}_x(\text{Ti,Ge})_{2-x}\text{Si}_y\text{P}_{3-y}\text{O}_{12}$ , manufactured by OHARA Inc.) by pulsed laser deposition. The electrolyte has an ion conductivity of  $1 \times 10^{-4} \text{ S cm}^{-1}$  at room temperature. The macroscopic properties of the battery were characterized by cyclic voltammetry (CV). CV results for the  $\text{LiCoO}_2$ /electrolyte sheet confirmed the lithium insertion-extraction reaction was just as reversible as when a liquid electrolyte is used, while the redox reactions were not clearly observed in the case of  $\text{LiMn}_2\text{O}_4$ .

To identify the reasons for the difference in electrochemical behavior, the region near the  $\text{LiMn}_2\text{O}_4$ /electrolyte interface was observed with a scanning transmission electron microscope (STEM). The region around the  $\text{LiMn}_2\text{O}_4$  negative-electrode/solid-electrolyte interface was thinned by using a focused ion beam. Fig. 1(a) shows a high-angle annular dark-field (HAADF)-STEM image for  $\text{LiMn}_2\text{O}_4$ /electrolyte. The brighter contrast indicates heavier atomic mass. The image reveals an 8 nm thick white layer in the interface. Fig. 1(b) shows an energy-dispersive X-ray spectroscopy (EDS) elemental line-profile across the interface. Ge, P, Mn, and Al can be identified in this reaction layer. It is clearly seen the pileup of Ge in the interface. Fig. 2 shows STEM-EDS elemental mapping images and TEM image around the interface. In particular the concentration of Ge is noticeably higher in the reaction layer. Such a composition should have poor conductivity, suggesting that the reaction layer formed during PLD is the cause of the high interfacial resistance. Results of detailed comparison from TEM analysis of the  $\text{LiCoO}_2$ /electrolyte system support this view.

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### References

- [1] J. Fu, J. Am. Ceram. So., 80(7), 1901 (1997)

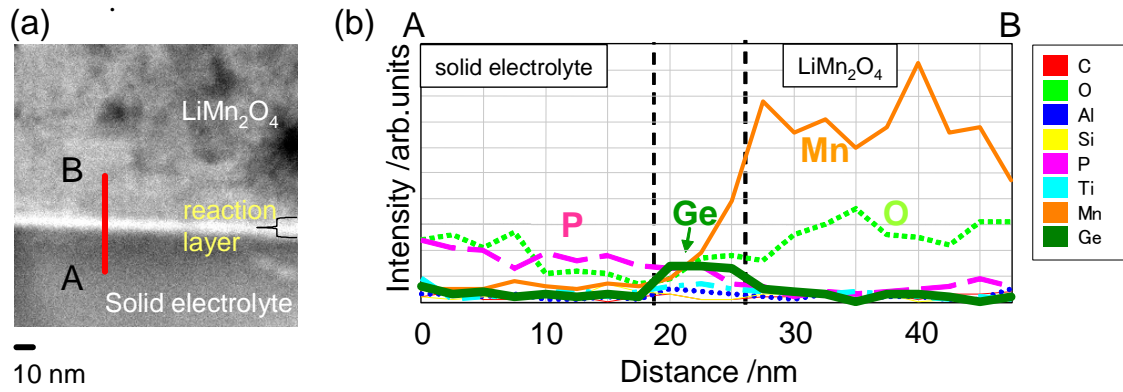


Fig. 1 (a) Cross-sectional HAADF-STEM image near the  $\text{LiMn}_2\text{O}_4$ / electrolyte interface. (b) STEM-EDS line profile near the electrode/electrolyte interface.

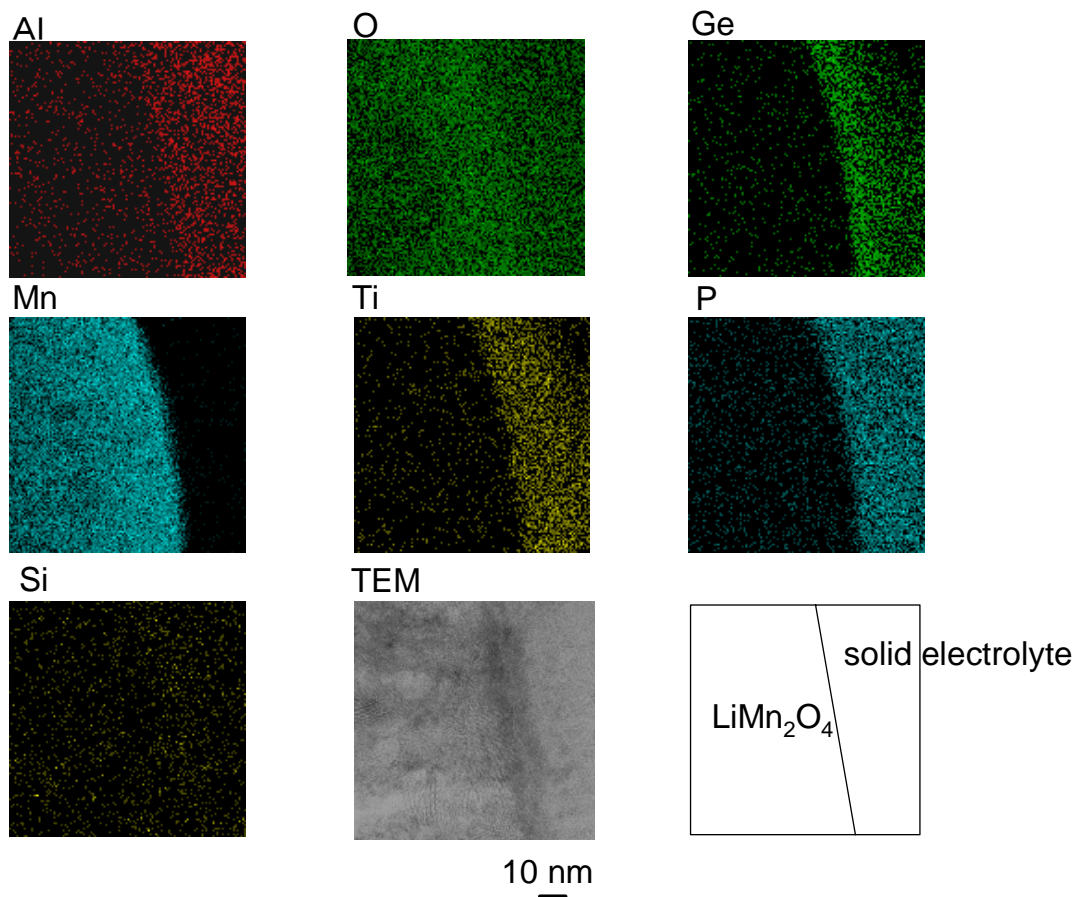


Fig. 2 STEM-EDS elemental mapping images and TEM image near the electrode/electrolyte interface.