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XPS Analysis of Surface State on Grass Ceramics

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Oxide-based grass ceramics solid electrolyte $Li_{1+x+y}Al_x(Ti_{2-y}Ge_y)P_{3-z}Si_zO_{12}$ (LATP) exhibits superior chemical stability in air compared to sulfide-based solid electrolytes (e.g., $Li_{10}GeP_2S_{12}$, Li_6PS_5Cl) and is easier to handle. Therefore, it is expected to be applied to solid-liquid coexisting semi-solid batteries. However, at the interface between the solid electrolyte and the liquid electrolyte, the energy barrier to lithium-ion transfer is significant, which is known to affect battery performance [1]. In particular, the chemical state of the solid electrolyte surface is considered to be an important factor influencing the interface resistance; however, studies on the surface chemical state are limited compared to those on bulk properties. In this study, we investigated how differences in surface chemical states obtained by polishing LATP surfaces in air and argon atmospheres affect lithium-ion transfer resistance between the solid and liquid electrolytes using electrochemical impedance spectroscopy (EIS) and X-ray photoelectron spectroscopy (XPS).

This study investigated samples obtained after electrochemical measurements as shown in the literature [1] using commercially available LATP (AG-01, thickness 150 μm, Ohara Co., Ltd.). The samples were first washed with ethanol, followed by polishing in two different atmospheres: atmospheric air and an argon glove box. After polishing, each sample was washed with an organic electrolyte (LE) containing 1 M LiTFSI dissolved in ethylene carbonate:ethyl methyl carbonate (3:7 v/v%, Kishida Chemical) in a glove box, and then a Li|LE|LATP|LE|Li two-electrode cell was assembled. Electrochemical impedance measurements were performed at 25°C at the open circuit voltage to estimate the lithium-ion transport resistance at the solid-liquid interface.

XPS measurements of the polished samples without liquid electrolyte treatment were performed using PHI Quantes (ULVAC-PHI) with an Al K_α radiation (SR center, SA-1). Si-2p, Ti-2p, and C-1s core-level spectra were obtained. The binding energy was calibrated using the C-1s peak top (284.6 eV), and the spectra intensity was normalized using the Si-2p peak.

The EIS results revealed that the solid-liquid interface resistance of atmospheric polishing LATP was significantly increased compared to that of sample polished in an Ar atmosphere. This suggests that surface resistance layer formed by atmospheric polishing impedes ion transport.

Fig. 1 shows the core-level XPS spectra of the LATP polished in air and Ar atmospheres. No significant differences in the binding energies of the Si-2p and Ti-2p spectra were observed depending on the atmospheres. However, the C-1s spectrum of air polished sample shows higher peak attributed to organic carbon species. These organic carbon species seem to be organic impurities formed or adsorbed on the LATP surface during polishing. It is speculated that these organic carbon species form a thin organic layer at the solid-liquid interface, impeding the lithium-ion transfer, resulting the increased resistance observed in the EIS.

Based on the above results, it was demonstrated that the organic carbon layer formed by atmospheric polishing inhibits lithium-ion transfer at the liquid/solid interface. This study Therefore, grinding in an argon atmosphere is concluded to be an effective pretreatment method as it suppresses the adsorption of organic impurities and reduces interface resistance.

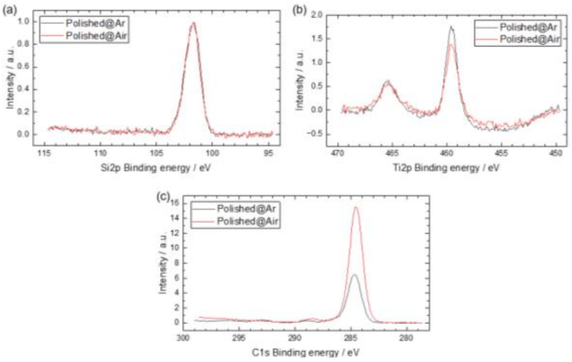

Fig. 1 Core-level XPS spectra of the LATP polished in air and Ar atmospheres (a) Si-2p, (b) Ti-2p, (c) C-1s.

References

[1] T. Suzuki, Y. Miyaura, K. Okazaki, C. Zhong, K. Shimoda, F. Kondo, M. Fujii, H. Kinoshita, Y. Orikasa, *Chem. Commun.*, **2025**, *61*, 2953.