In situ STEM-EELS observation in an all-solid-state lithium-ion battery

Nomura, Y.[1], Yamamoto, K.[2], Hirayama, T.[2] and Saitoh, K.[3]

[1] Panasonic Corporation, Japan, [2] Japan Fine Ceramics Center, Japan, [3] Nagoya University, Japan

All-solid-state lithium-ion batteries (LIBs) are expected to be the next generation batteries. One of the major drawback for the practical use is a charge transfer resistance at interfaces between cathodes and solid-electrolytes. This study presents the change of Li-ion distribution around a $LiCoO_2$/solid-electrolyte interface using scanning transmission electron microscopy (STEM) coupled with electron energy-loss spectroscopy (EELS) to identify the origin of interfacial resistance.

A 50 m thick $Li_{1+x+y}Al_x(Ti,Ge)_{2-x}Si_yP_{3-y}O_{12}$ (LASGTP, OHARA Inc.) was used as a solid-electrolyte. A 150 nm thick $LiCoO_2$ cathode film was deposited on one side of the LASGTP sheet by a pulse layer deposition. Au current collector was then deposited on top of the $LiCoO_2$ cathode by a sputtering deposition. The other side of the LASGTP sheet was covered with Pt. An anode was prepared by the partial decomposition of LASGTP during charge discharge reaction. The electrochemical cell was cycled at a current of 50 nA in a transmission electron microscope. Cutoff voltage was set to 1.8 V vs. Li/Li^+. Figure 1(a)-(d) show annular dark field (ADF) STEM image series around an interface between the $LiCoO_2$ cathode and the LASGTP solid-electrolyte during charge and discharge reaction. Figure 1(e)-(h) display Li-ion distribution series measured by EELS. The Li-ion maps show that the Li-ion concentration is not uniform in the $LiCoO_2$ film at all states. The region near the $LiCoO_2$/Au interface has higher Li-ion concentration than the region near the LASGTP/$LiCoO_2$ interface. Electronic state of Co-ion was also investigated by EELS. The result showed that the region with higher Li-ion concentration was electrochemically active and the region with lower Li-ion concentration was inactive. From the results of electron diffraction and Raman spectroscopy, we concluded that the Li-depleted region near the LASGTP/$LiCoO_2$ interface was Co_3O_4, which may cause interfacial resistance.

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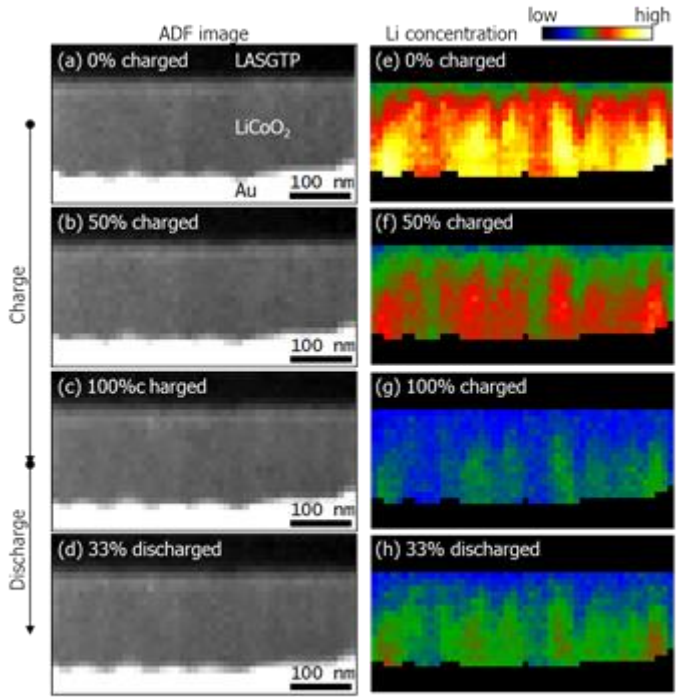

Fig. 1(a)-(d) ADF-STEM image series (e)-(h) Li-ion distribution series at 0%, 50%, 100% charged states and 33% discharged state.