

## Dynamic Observation of Li-ion movement in a Solid-State Li-Ion Battery

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Rechargeable batteries with high power and high energy density are in great demand for various applications such as hybrid and electric vehicles. Solid-state Li-ion batteries are one of the most promising candidates because they have the potential to overcome some of the limitations of Li-ion batteries with organic liquid electrolytes. However, ion transport resistance at the interface between cathodes and solid electrolytes limits their electrochemical performance. To investigate the origin of interfacial resistance, we operated a solid-state Li-ion battery in a transmission electron microscope and visualized changes in Li-ion concentration and electrochemical reactions [1].

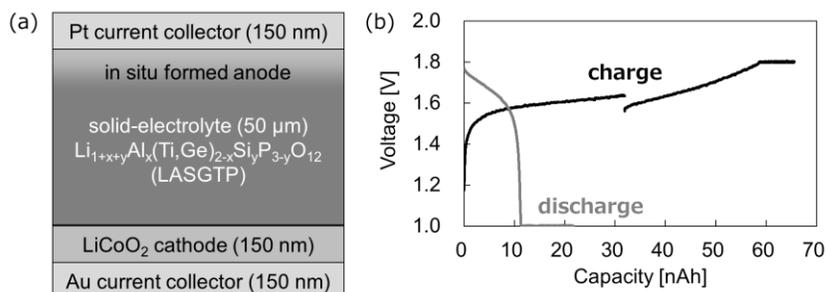
Figure 1(a) shows a schematic of the solid-state Li-ion battery used in this study. A 50  $\mu\text{m}$  thick  $\text{Li}_{1+x+y}\text{Al}_x(\text{Ti,Ge})_{2-x}\text{Si}_y\text{P}_{3-y}\text{O}_{12}$  (LASGTP) sheet was used as a solid electrolyte. A cathode of 150 nm thick  $\text{LiCoO}_2$  film was deposited onto the LASGTP sheet by pulsed laser deposition. Sputtering was used to deposit gold film onto the  $\text{LiCoO}_2$  film to function as a current collector. The other side of the Au film was covered with a platinum current collector. An in situ formed anode was prepared by electrochemical decomposition of the LASGTP solid electrolyte [2]. Figure 1(b) shows the charge and discharge curves of the solid-state Li-ion battery. A potential plateau is clear at around 1.65 V, indicating the electrochemical reaction between the reduction of Ti in the LASGTP sheet and the oxidization of Co in the  $\text{LiCoO}_2$  cathode.

ADF-STEM image and EEL spectrum image (SI) datasets were simultaneously acquired from the same region of the  $\text{LiCoO}_2$ /LASGTP interface during the charge and discharge reactions (0, 50, 100% charged and 33% discharged states). Figure 2(a) shows the change in Li-ion concentration in the  $\text{LiCoO}_2$  cathode film, visualizing Li-ion dynamics during the battery reaction. Li-ion in the  $\text{LiCoO}_2$  cathode was more concentrated near the Au current collector side than near the LASGTP solid electrolyte side in all the states. Figure 2(b) shows the change in Li-ion concentration at each point (A and B) indicated in Figs. 2(a). Points A and B have different Li-ion concentrations in the 0% charged state. A high Li-ion concentration is visible at point A near the Au current collector, and the changes in Li-ion concentration are larger than those at point B, where there is a low Li-ion concentration near the LASGTP solid-electrolyte. This result shows that the activity of the electrochemical reaction was not uniform, and it varied depending on the original Li-ion concentration. It is suggested that interfacial resistance originated from Li-poor region near the  $\text{LiCoO}_2$ /LASGTP interface.

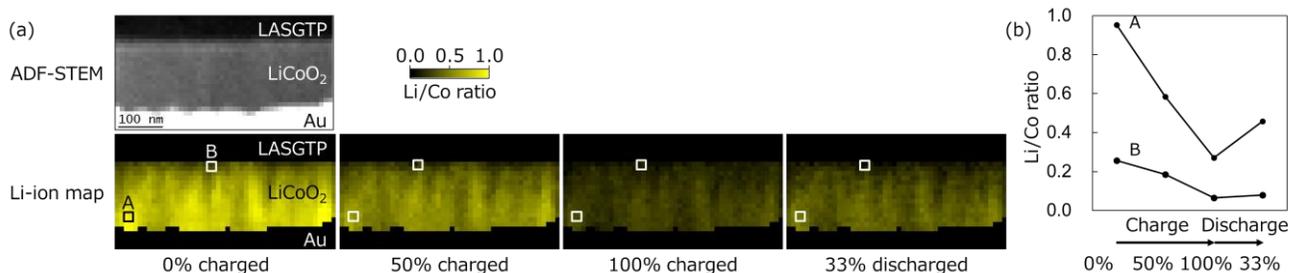
Figure 3 shows the selected-area electron diffraction pattern of the cathode film. Almost all diffraction spots were indexed to  $\text{LiCoO}_2$  with a layered rock-salt structure, the diffraction peaks of which are indicated by the rings. However, some weak diffraction spots indicated by gray arrows could not be indexed to  $\text{LiCoO}_2$  but could be indexed to spinel  $\text{Co}_3\text{O}_4$ . This result shows that the electrochemical inactive layer observed by in situ STEM-EELS was  $\text{Co}_3\text{O}_4$  [3].

## References:

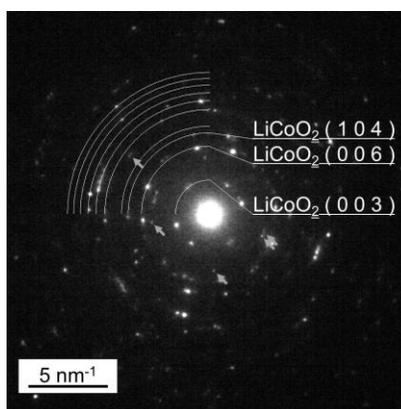
- [1] Y Nomura et al., *Nano Lett.* **18** (2018), p. 5892.  
 [2] Y Iriyama et al., *Electrochem. Commun.* **8** (2006), p. 1287.  
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**Figure 1.** Configuration and properties of solid-state Li-ion battery. (a) Schematic of solid-state Li-ion battery used in this study. (b) Charge and discharge curves.



**Figure 2.** In situ observation of Li-ion movement during electrochemical reactions. (a) ADF-STEM images and Li/Co ratio maps during the reaction. Same region was observed in each image. (b) Plots of Li/Co ratio at points A and B.



**Figure 3.** Selected-area electron diffraction pattern from the cathode film. White rings show diffraction spots of LiCoO<sub>2</sub>. Gray arrows show Co<sub>3</sub>O<sub>4</sub>.