

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

Yuki Nomura^{1,2*}, Kazuo Yamamoto³, Tsukasa Hirayama³, Emiko Igaki¹, and Koh Saitoh⁴

¹. Technology Innovation Division, Panasonic Corporation, Moriguchi, Osaka, Japan.

². Department of Crystalline Materials Science, Nagoya University, Nagoya, Aichi, Japan.

³. Nanostructures Research Laboratory, Japan Fine Ceramics Center, Nagoya, Aichi, Japan.

⁴. Institute of Materials and Systems for Sustainability, Nagoya University, Nagoya, Aichi, Japan.

* Corresponding author: nomura.yuki001@jp.panasonic.com

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 μm 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 LiCoO_2 film was deposited onto the LASGTP sheet by pulsed laser deposition. Sputtering was used to deposit gold film onto the 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 LiCoO_2 cathode.

ADF-STEM image and EEL spectrum image (SI) datasets were simultaneously acquired from the same region of the 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 LiCoO_2 cathode film, visualizing Li-ion dynamics during the battery reaction. Li-ion in the 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 LiCoO_2 /LASGTP interface.

Figure 3 shows the selected-area electron diffraction pattern of the cathode film. Almost all diffraction spots were indexed to 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 LiCoO_2 but could be indexed to spinel Co_3O_4 . This result shows that the electrochemical inactive layer observed by in situ STEM-EELS was Co_3O_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.
 [3] This work was partly supported by the Japan Society for the Promotion of Science, Grant-in-Aid for Scientific Research KAKENHI (JP 17H02792) and Nagoya University microstructural characterization platform as a program of the “Nanotechnology Platform”. We are grateful to Prof. Shunsuke Muto and Dr. Jun Kikkawa for their valuable discussion on STEM-EELS analysis.

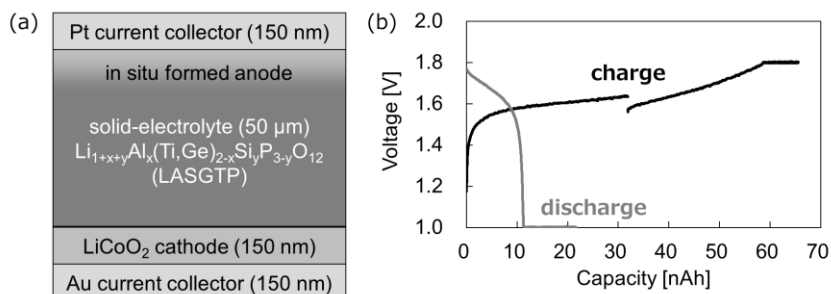


Figure 1. Configuration and properties of solid-state Li-ion battery. (a) Schematic of solid-state Li-ion battery used in this study. (b) Charge and discharge curves.

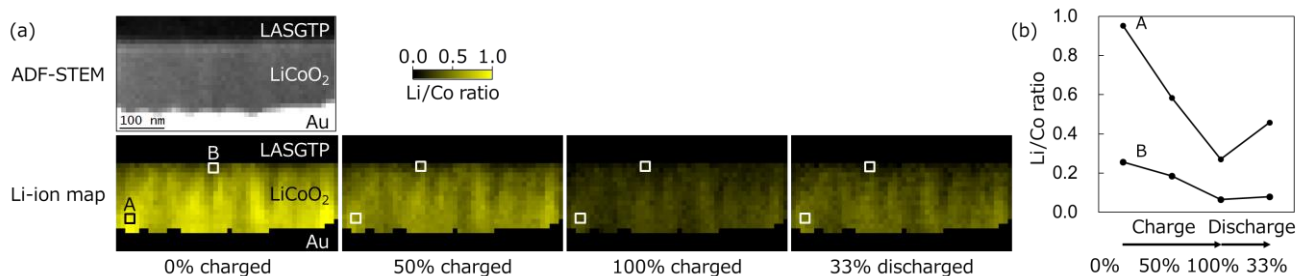


Figure 2. In situ observation of Li-ion movement during electrochemical reactions. (a) ADF-STEM images and Li/Co ratio maps during the reaction. Same region was observed in each image. (b) Plots of Li/Co ratio at points A and B.

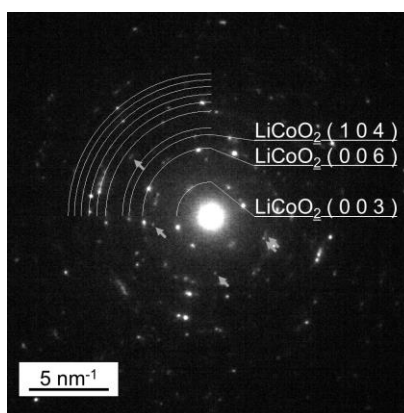


Figure 3. Selected-area electron diffraction pattern from the cathode film. White rings show diffraction spots of LiCoO_2 . Gray arrows show Co_3O_4 .