In Situ Electron Holography and Spatially Resolved Electron Energy Loss Spectroscopy for Studying Electrochemical Reactions at Electrode/Electrolyte Interfaces in an All-Solid-State Lithium-Ion Battery

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Rechargeable batteries are considered an essential technology for future sustainable societies [1]. Nevertheless, the electrochemical reactions in batteries that control their performance are not yet fully understood. It is essential that detailed knowledge about the electrochemical reactions be obtained to find clues for the development of more efficient batteries. For this purpose, direct observation of ion distributions and measure electric potential distributions, in particular, near the interface between electrodes and electrolyte during charge-discharge cycling, is of fundamental importance. In this paper we report our latest results of observations of such phenomena in all-solid-state lithium-ion batteries.

In situ electron holography is a powerful technique to map electric potential distributions in working batteries [2,3], while electron energy loss spectroscopy (EELS) is an effective technique to directly detect lithium distributions. A combination of the two methods provides a powerful means of revealing the electrochemical reactions that occur at electrode/electrolyte interfaces.

Figure 1 shows a schematic of the model battery used in our experiments. Figure 2(a) shows an electric potential distribution measured at the negative side by electron holography after the first charge-discharge cycle. The negative potential indicates that a negative electrode region was formed *in situ* during this cycle [1]. Figure 2(b) shows the lithium-ion distribution measured by spatially resolved electron energy loss spectroscopy (SR-EELS) obtained from a specimen after 50 charge-discharge cycles. This figure indicates that the *in situ* negative electrode contains excess lithium. In this talk the relationship between the electric potential distribution and the lithium-ion concentration will be discussed.

In summary, we have successfully observed distributions of electric potential and lithium ions at the negative electrode side of an all-solid-state lithium-ion battery. These microscopy techniques provide useful insights into the electrochemical reactions that take place in all-solid-state batteries during cycling, and should aid the design of high-performance devices.

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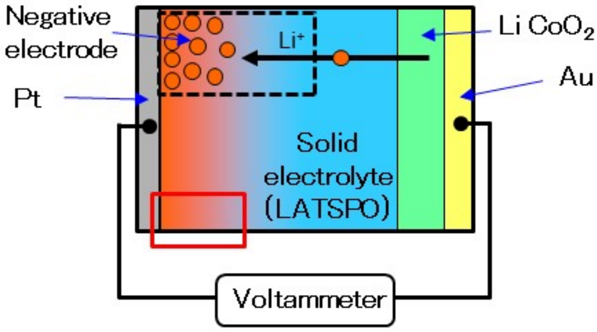

FIG. 1. Schematic of the model battery sample used in the experiments. An area corresponding to that enclosed by the red rectangle was observed by electron holography and SR-EELS.

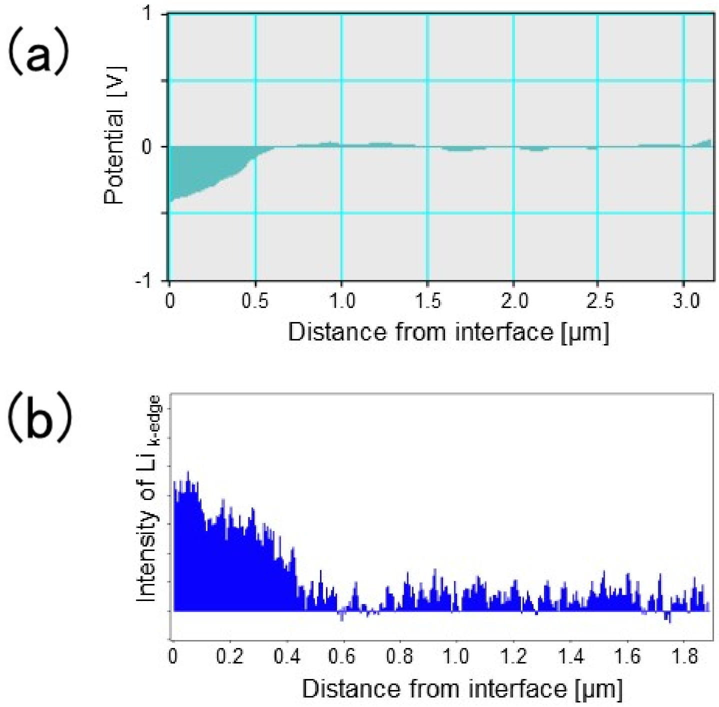

FIG. 2. Results from (a) *in situ* electron holography and (b) SR-EELS at the negative electrode side, showing the electric potential distribution and lithium concentration, respectively, as a function of distance. The negative electric potential on the left-hand side in (a) is consistent with the excess Li content in (b) in the *in situ* formed negative electrode even after different numbers of cycles.