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Electron Holographic Li-ion Profiling in an All-solid-state Li-ion Battery

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Electron holography is a powerful technique for observing electromagnetic nano-fields. It has been used to study properties of magnetic materials and semiconductor devices that are vital for today's technological society [1, 2]. Lithium ion batteries (LIBs) are one of the most promising devices for reducing CO_2 emissions and creating a sustainable future because they can efficiently store and release large amounts of electricity [3]. However, the distribution and diffusion of Li ions within the device, which control its performance, are not yet sufficiently well understood. Here we report in-situ Li-ion profiling experiments of an all-solid-state LIB.

A 90 μm thick ceramic sheet with ionic conductivity of 10^{-4} S cm^{-1} at room temperature (OHARA Inc., Japan) was used as the solid electrolyte. A positive electrode of crystalline $LiCoO_2$ was deposited on one side of the sheet by pulsed laser deposition and the other side was coated to form a negative electrode. Next, the cathode and anode sides were coated with gold and platinum, respectively. An electron-beam transparent thin region was prepared from this sample by focused ion beam (FIB) milling. Finally, the specimen was loaded on a transmission electron microscope (TEM) specimen holder equipped with two electrodes for applying a voltage.

Figure 1 shows a schematic of the experiment and a typical phase map obtained by electron holography after charging the battery. The yellow region in Fig. 1(b) indicates that a high electric potential is formed at the negative electrode by positive Li ions which have migrated to it. Figure 2 shows a schematic of the experiment and a phase map when the two electrodes of the sample were connected via an external circuit. The electric potential across the electrolyte in this figure is essentially flat in the observed region, implying that excess Li ions at the negative electrode have returned to the positive electrode, as expected.

In summary, we have succeeded in profiling the Li-ion distribution in an all-solid-state lithium ion battery. This technique has the potential to reveal essential features of electrochemical reactions in Li-ion batteries on the nano-scale, and thereby contribute to research and development of these important devices.

References

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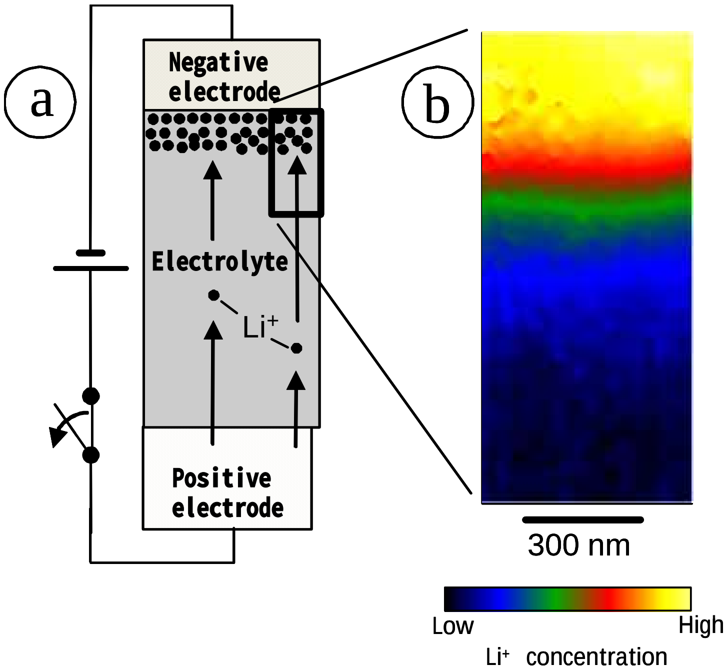

FIG. 1. In-situ measurement of Li-ion distribution after charging; (a) schematic of the experimental setup, and (b) phase map. The yellow region in (b) indicates high electric potential from positive Li ions in the vicinity of the negative electrode.

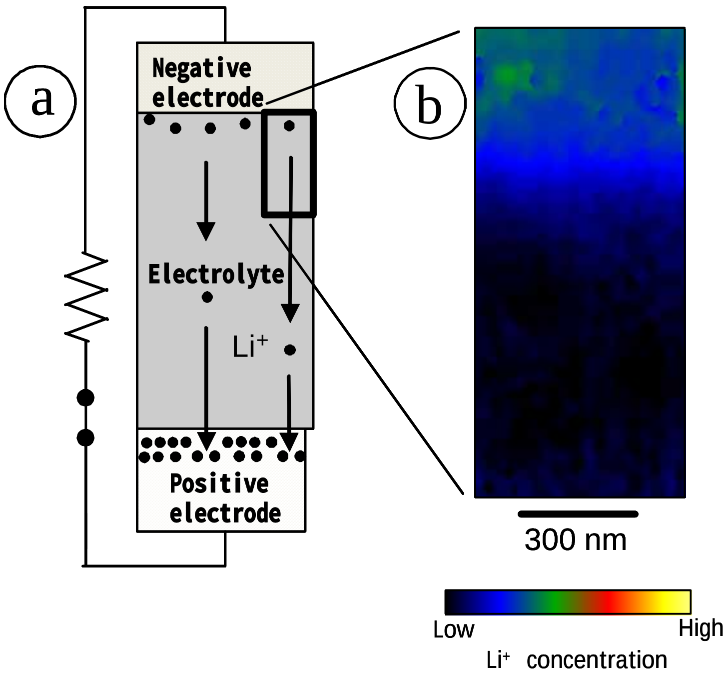

FIG. 2. In-situ measurement of Li-ion distribution when the two electrodes were connected; (a) schematic of the experimental setup, and (b) phase map. The electric potential in (b) is almost flat in the vicinity of the negative electrode.