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Electron Holographic Li-ion Profiling of an Inorganic Solid-state Electrolyte

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Lithium ion batteries (LIBs) can efficiently store and release large amount of electricity, and are considered the most promising devices for reducing CO_2 emissions [1]. However, the distribution and diffusion of Li ions which control the performance of the batteries have not yet been studied sufficiently. These days we are trying to observe lithium ion distributions in all-solid-state LIBs, and here we report our first in-situ Li-ion profiling experiment for an inorganic solid-state electrolyte.

A 90 μm thick ceramic sheet of composition $Li_{1+x+y}Al_yTi_{2-y}Si_xP_{3-x}O_{12}$ (ionic conductivity of 10^{-4} S cm^{-1} at room temperature; OHARA Inc., Japan) was used as the solid electrolyte. Electrodes of crystalline $LiCoO_2$ were deposited on both sides of the sheet by pulsed laser deposition. Then, one side was coated with gold and the other side with platinum. This sample, with an electron-beam transparent thin region prepared by focused ion beam (FIB) milling, was loaded on a purpose-built TEM holder equipped with two fixed electrodes for applying voltage.

Figure 1 shows a schematic of the experiment and a typical phase map when a voltage of 3.8 V was applied to the sample. The bright contrast in Fig. 1(b) shows the high electric potential formed by the positive Li ions. Figure 2 displays a schematic of the experiment and a phase map when two electrodes of the sample were connected without a potential difference applied, showing that the electric potential in the electrolyte is almost flat in the observed region.

In conclusion, we have succeeded in clearly profiling the Li-ion distribution in a solid-state electrolyte. We believe that this technique will enable us to reveal essential features of electrochemical reactions in Li-ion batteries and contribute to the development of superior Li-ion batteries.

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Reference

[1] M. Armand and J.-M. Tarascon, Nature **451**, (2008) 652.

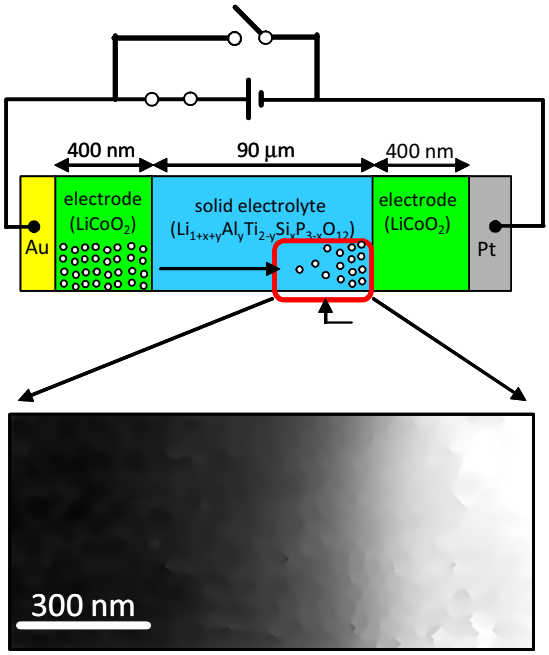

FIG. 1. In-situ measurement of Li-ion distribution when a voltage of 3.8 V was applied between Au and Pt electrodes: (a) schematic of the experiment, and (b) phase map. The bright contrast in (b) indicates high electric potential from positive Li ions.

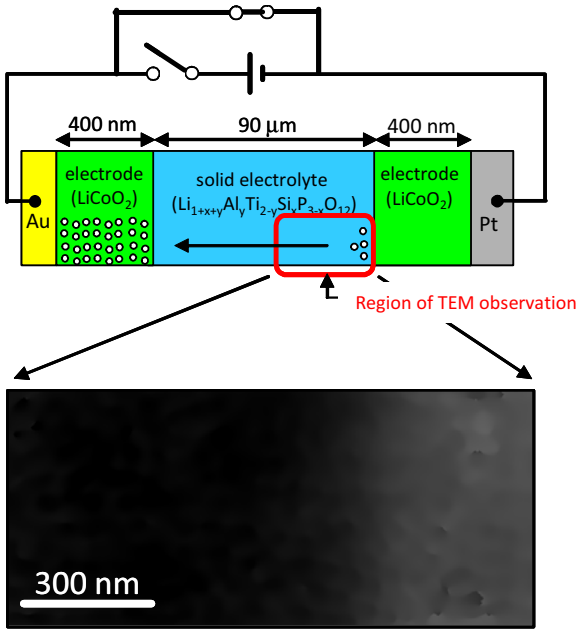

FIG. 2. In-situ measurement of Li-ion distribution when the two electrodes were short-circuited: (a) schematic of the experiment, and (b) phase map. The electric potential in (b) is almost flat across the observed region.