

***In-situ* Optical Microscopy for Graphite Negative Electrode Layers in All-Solid-State Lithium Batteries**

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Recently, all-solid-state lithium batteries have attracted global attentions because of their higher safety due to the use of nonflammable inorganic solid electrolytes. Bulk-type all-solid-state batteries employ composite electrodes consisted of electrode active materials and solid electrolytes, and thus a lot of solid-solid interfaces are in composite electrode layers. In order to achieve higher battery performance, it is important to clarify electrochemical reaction mechanisms at the solid-solid interfaces and evaluate reaction distributions in the electrode layer.

A LiCoO₂ positive electrode and a graphite negative electrode are generally used in commercial lithium batteries with organic liquid electrolytes. However, there are few papers regarding all-solid-state batteries using graphite composite electrodes.^[1] It is worth studying charge-discharge properties and reaction mechanisms of graphite composite electrodes in all-solid-state lithium batteries for practical use in the near future. Colors of graphite particles change from black *via* dark blue and red to gold during a lithiation process.^[2] Observation of color changes enables us to evaluate reaction distributions in a graphite electrode layer during a charge-discharge process. In this study, *in-situ* optical microscopy was conducted for a graphite electrode layer in solid-state cells to examine local reaction distributions in the electrode during charge-discharge cycles.

Composite graphite working electrodes were prepared by mixing graphite and 75Li₂S·25P₂S₅ (mol%) glass electrolyte particles with weight ratios of $x : 100-x$ ($x = 50, 60$ and 70). 75Li₂S·25P₂S₅ glass and lithium-indium alloy were used as a solid electrolyte separator and a counter electrode, respectively. The cells (Graphite/75Li₂S·25P₂S₅ glass/Li-In) operated at 25°C under a current density of 0.13 mA cm⁻² with a cut-off voltage of -0.62~1.0 V (vs. Li-In). A cell with the $x = 50$ electrode was cut to obtain flat cross-sectional observation areas. *In-situ* optical microscopic observation was conducted for the cross-section of the graphite electrode layer at room temperature under a current density of 0.068 mA cm⁻².

The cell using the $x = 50$ electrode showed the highest reversible capacities of more than 250 mAh g⁻¹. During the initial lithiation process, *in-situ* optical micrographs exhibited that almost all graphite particles in the electrode layer changed their colors from black to gold. However, during the 3rd lithiation process, only graphite particles near the electrolyte separator layer showed color changes, suggesting that degradation of cycle performances caused and inhomogeneous reaction distributions were formed in the graphite electrode layer. In addition, the color changes in graphite particles were quantitatively evaluated.

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References:

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