

# Reaction Mechanism of FePS<sub>3</sub> Electrodes in All-Solid-State Lithium Secondary Batteries Using Li<sub>2</sub>S-P<sub>2</sub>S<sub>5</sub> Solid Electrolytes

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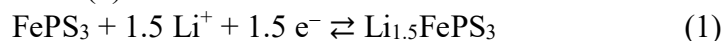
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In all-solid-state lithium secondary batteries using sulfde-based solid electrolytes, transition-metal sulfides have been considered as active materials with high capacity, based on the redox reaction of transition metals and sulfur [1]. Since these active materials and the sulfde-based solid electrolytes include sulfur, an interfacial layer with high resistance, which cause degradation of the batteries, is expected not to be formed at the interface between electrodes and electrolytes. Moreover, a study of the redox reaction of transition metal and sulfur is important for increasing the capacity of active materials. We have previously investigated FePS<sub>3</sub> as active materials in all-solid-state batteries using Li<sub>2</sub>S-P<sub>2</sub>S<sub>5</sub> solid electrolytes [2]. FePS<sub>3</sub> is reported to be intercalated with 1.5 mol of Li<sup>+</sup> per FePS<sub>3</sub> in batteries using liquid electrolytes [3], as shown in reaction (1).



In this reversible intercalation reaction, the theoretical capacity is 220 mAh g<sup>-1</sup>. However, the reaction mechanism of FePS<sub>3</sub> in all-solid-state batteries is unclear. In our previous report, with respect to the discharge-charge behavior, the discharge voltage of the batteries increased from the second cycle onwards [2]. The reason for the increase in the discharge voltage has not been investigated, and a study to clarify the reaction mechanism of FePS<sub>3</sub> should be useful to gain an understanding of layered transition-metal sulfide active materials in all-solid-state batteries. In this study, the reaction mechanism of FePS<sub>3</sub> electrodes in all-solid-state lithium secondary batteries using Li<sub>2</sub>S-P<sub>2</sub>S<sub>5</sub> solid electrolytes was investigated by using X-ray diffraction patterns, X-ray absorption spectra, Raman spectra, and density-functional theory (DFT). In discharge-charge measurements, the reversible discharge-charge reaction (FePS<sub>3</sub> + xLi<sup>+</sup> + xe<sup>-</sup> ⇌ Li<sub>x</sub>FePS<sub>3</sub>, 0 ≤ x ≤ 1.5) was confirmed. With this reaction, Li<sup>+</sup>-inserted FePS<sub>3</sub> with low crystallinity was formed with the reduction of iron during the discharge cycle, and crystalline FePS<sub>3</sub> appeared along with the oxidation of iron during the charge cycle. Raman spectra showed that this discharge-charge cycle does not destroy P<sub>2</sub>S<sub>6</sub><sup>4-</sup> structural units. The change of the crystalline phase, the redox reaction of iron as well as sulfur, and the increase in the discharge voltage were discussed using first-principle calculations assuming Li<sup>+</sup> insertion and the structural modification of FePS<sub>3</sub>. The results of DFT calculation can explain the experimental results of the change of crystalline phase and the increase in the discharge voltage. Further, the calculation shows that not only iron but also sulfur is oxidized and reduced upon discharge-charge cycle.

## References:

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