

Self-forming mechanism of a protection layer on the interface between LiFePO₄ and sulfide solid electrolyte in all-solid-state batteries.

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Oxide coating layer such as LiNbO₃ is generally used to reduce the interfacial resistance between cathode active materials and sulfide solid electrolytes for all-solid-state lithium secondary batteries. It was reported that the interfacial resistance is caused by the space-charge layer and atomic inter-diffusion at the interface between oxide active materials and sulfide solid electrolyte without oxide coating layer^{1, 2}. Meanwhile, we developed the low resistance interface using LiFePO₄/sulfide electrolyte, which presents theoretical capacity of LiFePO₄ with no coating layer³. The batteries indicate low capacity and high resistance in the first few cycles, then their capacity increases and their resistance significantly decreases after several charge-discharge cycles. It is suggested that self-forming protection layer is produced at the interface by some interfacial reactions. In this work, the discussion centers on understanding the self-forming mechanism of the protection layer.

At a first step, the existence of self-forming layer was investigated by STEM-EDS. LiFePO₄ coated with carbon partially, sulfide solid electrolyte and carbon additive were mixed as a positive electrode. The pellets consisting of the positive electrode/sulfide solid electrolyte/a negative electrode of Li₄Ti₅O₁₂ were pressed under RT. The charge/discharge cycles were performed for the cell between 1.6~2.3 V and 4.1 V vs. Li/Li⁺ under 60°C. In addition, the cross-section surface of positive electrode was analyzed by STEM-EDS. In case of cut-off voltage: 2.1/2.3V vs. Li/Li⁺, the capacities decreased with number of cycles. However in case of cut-off voltage: 1.6 V vs. Li/Li⁺, the capacity gradually increased with cycles (Figure 1). According to STEM-EDS, O, S, P and only a few atomic percent Fe were observed at the interface layer between LiFePO₄ and sulfide solid electrolyte in the cell of 1.6 V vs. Li/Li⁺.

To clarify the chemical compounds forming at the interface by XAS study, the battery cell composed of LiFePO₄ thin film, sulfide electrolyte and Li-In was also prepared. After charge/discharge cycles at 1.6-4.1 V vs. Li/Li⁺, the LiFePO₄ film and electrolyte were separated from the electrolyte pellet. The surface of LiFePO₄ film was analyzed by XAS. Sulfites, sulfates and Phosphoric acid were detected at the interface layer. Additionally, Fe amount in the interface decreases with cycles, and Fe ions were widely detected inside sulfide electrolyte after more cycles. This result corresponds to STEM-EDS analysis. It is supposed that Fe ions of the interface diffuse into the bulk of sulfide electrolyte and disappear from interface layer. Therefore, the self-forming interface layer finally composes of the compounds including PO_x and SO_x without Fe. It could stably function as a protection layer with Li ion conductivity.

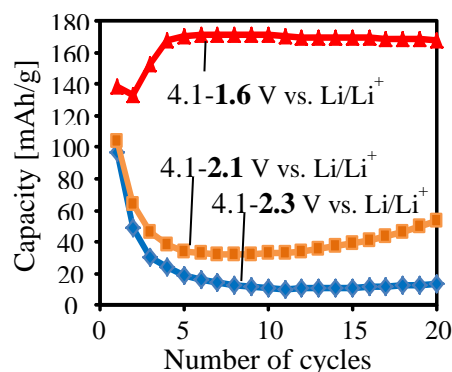


Figure 1 Cycling performances of LiFePO₄/Li₄Ti₅O₁₂ cells at 0.1 C.

References:

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