

Sn₄P₃ Negative Electrode in Ionic Liquid Electrolyte for Na-Ion Battery

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As negative electrode materials of Na-ion battery, elemental phosphorus (P) and tin (Sn) are promising because of much higher theoretical capacities of 2596 mA h g⁻¹ for P and 847 mA h g⁻¹ for Sn compared with that of *ca.* 300 mA h g⁻¹ for a conventional hard carbon. The disintegration of active material layers is, however, induced by their significant volume expansions of 490% and 525% for the formation of Na₃P and Na₁₅Sn₄, and by a tin's aggregation during charge–discharge. In addition, Na₃P has a poor electronic conductivity. The disintegration and the low conductivity lead to an electrical isolation of the active material layer and the resulting rapid capacity decays of P electrode¹ and Sn electrode^{2,3}. In this study, we developed a high-capacity negative electrode material based on Sn–P compounds, and tried to improve the electrode performance by applying an ionic liquid electrolyte.

Figure 1 shows performances of Sn–P compound electrodes cycled in an ionic liquid electrolyte comprised of *N*-methyl-*N*-propylpyrrolidinium bis(fluorosulfonyl)amide (Py13-FSA or C₃C₁pyrrFSA) and NaFSA. The Sn electrode showed a rapid capacity decay by the 10th cycle, resulting in an inferior performance to hard carbon. Although a high initial capacity of 1160 mA h g⁻¹ was observed for the P electrode, the capacity drastically decreased in a few cycles. The capacity of the SnP₃ electrode also steeply dropped in the initial several cycles. On the other hand, the Sn₄P₃ electrode showed a gradual increase in the capacity for the initial 10 cycles, and maintained high capacities of 800 mA h g⁻¹ until the 150th cycle⁴. Our nanostructure observations for Sn₄P₃ electrode revealed that elemental Sn and elemental P are formed after the initial charge–discharge, and that crystalline Sn nanoparticles are uniformly dispersed in amorphous-like P matrix⁴. From these results, we demonstrated that there are two important factors to improve the performance: i) utilization of Sn–P compound, and ii) its higher volume fraction of Sn than P.

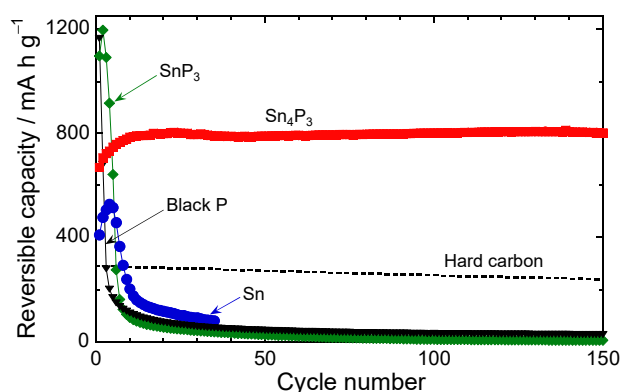


Figure 1. Cycling performances of Sn₄P₃ and SnP₃ electrodes at 50 mA g⁻¹ in ionic liquid electrolytes.

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