All-Solid-State Lithium Secondary Batteries with High Capacity

Using Black Phosphorus Negative Electrode

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Introduction

Rechargeable lithium-ion batteries with higher energy density are required for eco-cars such as EV and HEV. At present, carbonaceous materials are used as a negative electrode in lithium-ion batteries, but great efforts have been made to find alternative negative electrodes with higher capacity. Among the various candidates for negative electrode materials, transition metal phosphides have recently attracted attention. These materials show relatively high capacity and low intercalation potential in a cell using a conventional liquid electrolyte. It was reported that all-solid-state lithium batteries using NiP₂ exhibited the initial reversible capacity of 1000 mAh g⁻¹ and a good cycle performance [1].

Among phosphorus allotropes, black phosphorus (black P) is an attractive electrode material because black P has a layered structure and relatively high electronic conductivity. Black P is prepared traditionally by high-pressure routes from white or red P, but it was recently reported that black P was synthesized by a mechanical milling technique at ambient pressure and temperature. In addition, it was reported that black P had high capacity in an electrochemical cell using a conventional liquid electrolyte [2].

In the present study, black P was prepared by mechanical milling of red P. The all-solid-state cells using black P as an active material and Li₂S-P₂S₅ glass-ceramics as a solid electrolyte were fabricated. In addition, to improve electrochemical performance, black P-acetylene black (AB) composites were prepared and were applied to the all-solid-state cells. The performance of the cells was investigated.

Experimental

Black P was prepared by mechanical milling with the SPEX 8000D mixer/mill apparatus. Red P was used as a starting material. Black P-AB composite was prepared by mechanical milling of the mixture of black P and AB with the weight ratio of black P/AB = 4/1. Black P-AB composite was applied to all-solid-state cells. The all-solid-state Li-In/P cells were fabricated with the 80Li₂S·20P₂S₅ glass-ceramic electrolyte [3]. The cells were charged and discharged under several current densities from 0.064 to 3.8 mA cm⁻² at room temperature in an Ar atmosphere.

Results and discussion

Figure 1 shows the SEM images of black P-AB composites. The particle size of black P-AB composite was between 1 and 5 μm. The particle size of the original black P was about 30 μm, indicating that the mechanical milling of black P and AB brought about a decrease of the particle size of the composite.

Figure 2 shows the charge-discharge curves of the Li-In / 80Li₂S·20P₂S₅ glass-ceramic / black P-AB cell at the current density of 0.064 mA cm⁻². Numerals indicate cycle number.

References


Fig. 1  SEM image of black P-AB composite.

Fig. 2  Charge-discharge curves of Li-In / 80Li₂S·20P₂S₅ glass-ceramic / black P-AB cell at the current density of 0.064 mA cm⁻². Numerals indicate cycle number.