Fabrication of hard carbon/NASICON composite anodes for all-solid-state batteries.

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Introduction

All-solid-state batteries are attracting attention for their superior safety compared to lithium-ion batteries, which use flammable organic electrolytes. In particular, all-solid-state batteries that use oxide solid electrolytes offer extremely high safety, but it is difficult to form a good interface between the electrode active material and the solid electrolyte, and they have not yet been put into practical use. In this study, we have fabricated composite negative electrodes for all-solid-state sodium-ion batteries (ASS-SIBs) from NASICON solid electrolyte powder and hard carbon spherical particles via a sol-gel process.

Experimental Procedures

Resorcinol was dissolved in a mixed solvent of distilled water, ethanol, and ammonia aqueous solution. Subsequently, formaldehyde was added and the mixture was stirred at room temperature for 24 hours, then subjected to still standing at 60 °C for 24 hours. The product was recovered by centrifugation, washed with distilled water, and dried at 60 °C for 24 hours. The dried sample was pre-calcined at 800 ºC under a nitrogen gas flow, then calcined at 1600 ºC to obtain carbon particles (RF-CS). RF-CS and NASICON powder were mixed, and pellets were formed by uniaxial compression and cold isostatic pressing (CIP). Subsequently, RF sol was impregnated, which was subjected to still standing at 60 ºC for 24 hours followed by drying at 60 ºC to obtain a RF/NASICON composite. Afterward, the hard carbon/NASICON composite was prepared by calcination at 900 °C under a nitrogen atmosphere. The obtained samples were subjected to powder X-ray diffraction (XRD), scanning electron microscope with an energy dispersive X-ray spectrometer (SEM-EDX), thermogravimety (TG) and differential thermal analysis (DTA), and Galvanostatic charge-discharge tests.

Results and Discussion

Fig. 1 (a) shows the SEM image of RF-CS. Spherical particles with a particle size of approximately 0.9–2 μm were found to have been produced. Fig. 1 (b) shows the SEM image of the hard carbon/NASICON composite. It was observed that RF-CS was partially agglomerated and incorporated. Furthermore, TG-DTA measurements (Fig. 2) confirmed the incorporation of two types of carbon into the composite, totaling 19 wt.%. This composite was assembled with a Na foil into a Na | NASICON | hard carbon/NASICON ASS half-cell, and the results of charge-discharge testing are shown in Fig. 3. At 60 °C and 5 mA g^{-1}, it exhibited a reversible capacity of 66 mAh g^{-1} and an initial coulombic efficiency of 75.6%.

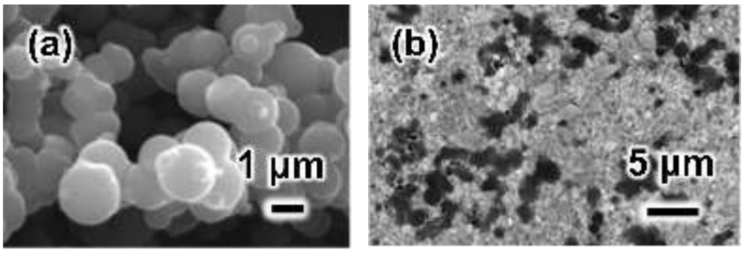

Fig. 1 SEM images of (a) RF-CS and (b) hard carbon/NASICON composite.

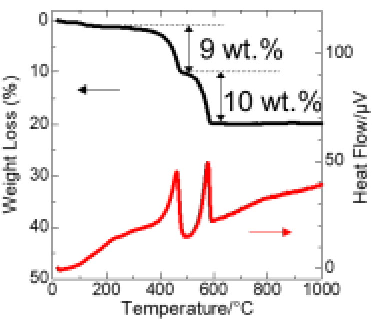

Fig. 2 TG-DTA curves of hard carbon/NASICON composite.

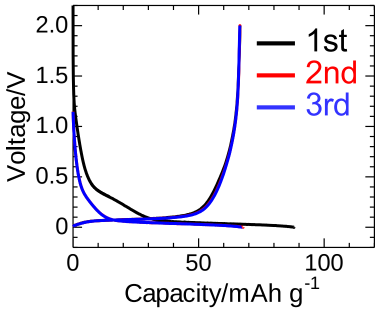

Fig. 3 Charge-discharge curves of hard carbon /NASICON electrolyte at 60 ºC, 5 mA g-1.

References

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