

Binder-Free Silicon-Based Composite Anodes in Ionic Liquid Electrolytes for Li-ion Battery

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INTRODUCTION

Silicon-based materials are highly anticipated to be applied to a high-capacity anode in the next-generation Li ion battery because Si has about ten times larger theoretical capacity in comparison with graphite anode in practical use. There are, however, serious disadvantages of Si as anode material: its high hardness and its high electrical resistivity. In addition, its drastic volume changes during charge–discharge generate a stress and degrade performances of Si-based electrodes. To improve the performances, we have studied various ionic liquid electrolytes for binder-free Si-based electrodes [1-3] because Li-ion transfer at the electrode/electrolyte interface directly affects the performances and it can be easily controlled by cation and anion structures of the ionic liquids. We have, moreover, revealed that forming a composite of Si and other active materials is effective to enhance the anode performances [3,4]. For instance, LaSi₂ is more deformable by an external force and has a much higher electronic conductivity in comparison with elemental Si. An electrode performance of LaSi₂/Si composite, therefore, is expected to enhance by using a suitable ionic liquid electrolyte.

In this study, we investigated the effect of the structures on the anode performances for binder-free LaSi₂/Si composite electrodes.

EXPERIMENTAL

Thick-film electrodes and LaSi₂/Si composite were prepared by a gas-deposition (GD) method [5]. An active material powder of LaSi₂/Si composite was synthesized by a mechanical alloying (MA) method [3]. Lanthanum chips and Si powder were mixed so that the weight ratio of LaSi₂:Si is 70:30. The weight ratio of MA balls to the mixture was set to be 15:1. The MA was performed using a high-energy planetary ball mill at 300 rpm at room temperature for 5 h. Thick-film electrodes of the LaSi₂/Si were prepared on Cu foils by GD. Electrodes of Si alone were also prepared for comparison.

Anions of ionic liquids used in this study are bis(trifluoromethanesulfonyl) amide [TFSA⁻] and bis(fluorosulfonyl)amide [FSA⁻]. A cation is *N*-methyl-*N*-propylpiperidinium [PP13⁺]. Electrolytes were prepared by dissolving a salt of Li-TFSA in these ionic liquids with a concentration of 1.0 M. For comparison, we used an electrolyte of 1.0 M LiClO₄-dissolved propylene carbonate (PC, C₄H₆O₃) as a conventional organic electrolyte. We assembled 2032-type coin cells consisted of the thick-film electrodes (working electrode), Li sheets (counter electrode), and the ionic liquids electrolyte. The charge–discharge tests were performed at 303K and under constant current densities of 0.420 A g⁻¹ (Si alone) or 0.315 A g⁻¹ (LaSi₂/Si composite), corresponding to current rates of 0.12C or 0.25C. A potential range was set to be 0.005–2.000 V vs. Li/Li⁺.

RESULTS AND DISCUSSION

Figure 1 shows a dependence of discharge (Li-extraction) capacities on charge–discharge cycle number for the electrodes of LaSi₂/Si composite and Si alone in the various electrolytes. The capacities of LaSi₂/Si electrodes have been converted to ones per mass of elemental Si. In the PC electrolyte, the capacity of the Si electrode rapidly decreased by the 100th cycle. In contrast, the capacity decay was suppressed in the ionic liquid electrolyte using [PP13⁺][TFSA⁻]. When the anion of the ionic liquid was changed to [FSA⁻], the Si electrode exhibited larger discharge capacities for 150 cycles. Our previous analysis have suggested that Li ions smoothly transfer at the electrode/electrolyte interface in FSA-based electrolytes because of their easier desolvation, which enables efficient electrode reactions of Li-insertion/extraction and improves the performances [2,3].

The composite electrode of LaSi₂/Si in the [PP13⁺][TFSA⁻] electrolyte showed an initial capacity of 1480 mA h g(Si)⁻¹ and a remarkably stable cyclability: a very high retention of 100% was attained at the 100th cycle. By changing from [TFSA⁻] to [FSA⁻], the composite electrode provided a drastic improvement in the performance. We found not only a large initial capacity of 3300 mA h g(Si)⁻¹ but also a high capacity retention of 91% at the 100th cycle. A ratio of the 100th cycle's capacity to silicon's theoretical capacity (3580 mA h g⁻¹) was as high as 84%. This result shows that elemental Si in the composite could be effectively used to Li-insertion/extraction even after a long-term charge–discharge by the promising applicability of [PP13⁺][FSA⁻] and by a benefit of LaSi₂ as conductive material and buffer material for the stress.

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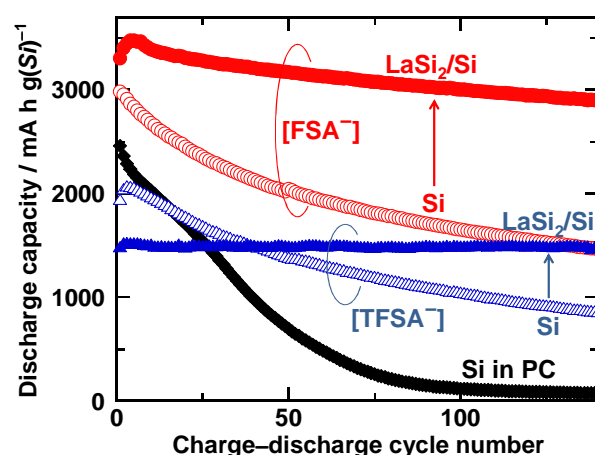


Fig.1 Cycling performances of LaSi₂/Si composite electrodes in two kinds of ionic liquid electrolytes using [PP13⁺][FSA⁻] and [PP13⁺][TFSA⁻], comparing electrodes of Si alone. The discharge capacities of LaSi₂/Si electrodes were converted to capacities per mass of elemental Si in composite.