All-solid-state sodium batteries using amorphous TiS_3 electrode with high capacity

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Abstract

All-solid-state sodium cells ($\text{Na}_{15}\text{Sn}_4$ / Na_3PS_4 glass-ceramic / $\alpha\text{-TiS}_3$) showed a high capacity of over 300 mAh per gram of TiS_3 at the 1st discharge-charge cycle. The capacity was gradually decreased to 100 mAh g^{-1} at the 10th cycle. Nyquist plots of the cell showed that the resistance of the $\alpha\text{-TiS}_3$ composite electrode became larger with the discharge-charge cycles. The XRD patterns of the $\alpha\text{-TiS}_3$ composite electrode before and after the 1st cycle indicated that the $\alpha\text{-TiS}_3$ was still amorphous during discharge-charge process. The Raman bands attributable to $\alpha\text{-TiS}_3$ were also observed after the 1st cycle. The SEM images and EDX mapping indicated that the $\alpha\text{-TiS}_3$ particles aggregated in the electrode after the 10th cycle. The all-solid-state sodium cell using $\alpha\text{-TiS}_3$ composite electrode with acetylene black as a conductive additive showed the high capacity of over 300 mAh g^{-1} for 5 cycles.

Keywords

all-solid-state battery, sodium battery, amorphous electrode, TiS_3 , sulfide

1. Introduction

Rechargeable batteries with high energy density and high safety using low-cost materials are desired as large-sized batteries for application to eco-cars and smart grids. Sodium is a negative metal comparable to lithium and an abundance source [1]. All-solid-state batteries are known as highly safe batteries because of leak-proof and non-flammability [2-4]. All-solid-state sodium batteries are thus expected to be next-generation batteries with high energy density, high safety and low cost. Solid electrolytes are a key material to fabricate solid-state batteries. We have recently found that Na_3PS_4 glass-ceramics, where cubic- Na_3PS_4 was precipitated, showed a high Na^+ ion conductivity [5,6]. All-solid-state cells Na-Sn / crystalline TiS_2 (*c*- TiS_2) using the Na_3PS_4 glass-ceramic electrolyte successfully operated as a rechargeable battery at 25°C. However, the capacity of the cell was still low, *ca.* 100 mAh per gram of TiS_2 . Increasing capacity of the cell is a next issue to be solved. Titanium trisulfide, TiS_3 is a positive electrode with high theoretical capacity of 558 mAh g⁻¹, which is larger than that of 240 mAh g⁻¹ for TiS_2 [7-9]. A sodium cell using crystalline TiS_3 (*c*- TiS_3) has been reported and it shows a larger capacity than the theoretical capacity of TiS_2 [10]. However, the capacity drastically decreased at the 2nd cycle because the *c*- TiS_3 was deteriorated. On the other hand, we have applied amorphous TiS_3 (*a*- TiS_3) electrode to

all-solid-state lithium cells [11,12]. The solid-state cell with α -TiS₃ exhibited better cycle performance than that with crystalline TiS₃ in lithium-ion liquid-type cells [12]. Thus, α -TiS₃ is also attractive as a positive electrode for all-solid-state sodium cells because amorphous electrode materials with structural flexibility and free volume would be effective in intercalation of sodium ions as well as lithium ions.

In this study, all-solid-state sodium cells using α -TiS₃ electrode were fabricated and the cell performances were investigated. Structure and morphology of the electrode were examined for the cells before and after charge-discharge processes. Effects of the addition of carbon additives to the electrode on cycle performance of the cells were also discussed.

2. Experimental

Na₃PS₄ glass-ceramic powders for a solid electrolyte were prepared by ball milling and consecutive heat treatment [5,13]. Na₁₅Sn₄ alloy was used as a negative electrode because the alloy showed a low potential vs. Na⁺/Na and good cyclability in the cells using liquid and solid electrolytes [13,14]. Na₁₅Sn₄ powders were prepared by ball milling of stoichiometric amounts of Na and Sn using a planetary ball milling apparatus with a zirconia pot (45 ml) and 500 zirconia balls (4 mm diameter) [13]. The mechanochemical alloying was performed for 5 h at a fixed rotation speed of the base

disk of 510 rpm. The α -TiS₃ as a positive active material was prepared by ball milling of c -TiS₂ and sulfur [10]. The composite electrodes were prepared by hand mixing of α -TiS₃ and the Na₃PS₄ glass-ceramic with or without acetylene black (AB) with the weight ratio of 40 : 60 : 0 or 6. The all-solid-state cells were fabricated as follows. The Na₁₅Sn₄ powders (100 mg) as a negative electrode and the Na₃PS₄ glass-ceramics (80mg) as a separator, the obtained α -TiS₃ composites (7.5 mg) as a positive electrode were set in a polycarbonate tube (10 mm in diameter) and pressed together under 360 MPa. Finally, the three-layered pellet was sandwiched between two stainless-steel disks as a current collector. The electrochemical tests of the cells were carried out at a constant current density of 0.013 mA cm⁻² (3.3 mA g⁻¹) at 25 °C in an Ar atmosphere using a charge-discharge measuring device (VMP3, Bio-Logic Co.). All the processes of the cell fabrication and the electrochemical tests were performed in a dry Ar-filled glove box.

3. Results and discussions

Discharge-charge curves of an all-solid-state cell Na₁₅Sn₄ / Na₃PS₄ glass-ceramics / α -TiS₃ without AB are shown in Fig.1. The cell worked as a secondary battery. The initial discharge capacity was over 300 mAh per gram of TiS₃, which was larger than the capacity of the cells using c -TiS₂ [5]. However, the initial irreversible capacity

appeared and the capacity of the cell was gradually decreased with discharge-charge cycles.

Fig. 2 shows (a) XRD patterns and (b) Raman spectra of the α -TiS₃ electrode before and after the initial discharge-charge process. In the XRD patterns, only cubic-Na₃PS₄ peaks as the electrode were observed in the XRD patterns before and after discharge-charge cycle, suggesting that α -TiS₃ maintained amorphous structure even after discharging and charging. In the all Raman spectra, Raman bands attributed to PS₄³⁻ of the solid electrolyte were observed. Raman bands attributable to TiS₃ [10] were observed before the discharging process. These Raman bands were also observed after the first charge process; the α -TiS₃ after the first cycle had a local structure similar to that of before the cycle. These structural analyses indicated that the α -TiS₃ were not crystallized and decomposed at the initial discharge-charge process.

Nyquist plots of the cells after the 1st and 5th discharge-charge processes are shown in Fig. 3. The bottom one is the Nyquist plots of the symmetric cell Na₁₅Sn₄ / Na₃PS₄ glass-ceramics / Na₁₅Sn₄ for comparison. The Nyquist plots of the symmetric cell suggested a distorted semicircle (labeled as “R1”) with the characteristic frequency of 0.1 MHz was attributed to the components of the Na₁₅Sn₄ electrode and the Na₃PS₄ electrolyte separator; these two components were not able to be separated. Another

semicircle (labeled as “R2”) with the characteristic frequency of 1 kHz was observed in the Nyquist plots of the cells after the discharge and charge process. It is probably attributed to the component of α -TiS₃ electrode, suggesting that the component resistance of the α -TiS₃ composite electrode was increased with cycling.

Fig.4 shows SEM images and EDX mapping of the α -TiS₃ composite electrode (a) before and (b) after the 10th discharge-charge process. EDX mapping of the Ti element indicated that α -TiS₃ particles were aggregated after discharge-charge process. The aggregations of α -TiS₃ would result in shutoff of electron conductive paths in the α -TiS₃ electrode. The aggregation of the α -TiS₃ particles would be caused by the volume change of the α -TiS₃ particles during the discharge-charge processes. The Na⁺ ion insertion would bring larger volume expansion of the particles than Li⁺ ion insertion because the size of Na⁺ ions is larger than that of Li⁺ ions. This is one of factors for the initial irreversible capacity and severe degradation on cycling of the all-solid-state sodium cells, comparing with the all-solid-state lithium cells [12].

The effects of the addition of AB as a conductive additive to α -TiS₃ composite electrode were examined. The discharge-charge curves of the cell using α -TiS₃ electrode with AB are shown in Fig. 5. The profiles of the curves almost overlapped from the 2nd to 5th cycle, and the cell showed a reversible capacity of over 300 mAh g⁻¹ for 5 cycles.

The good cyclability of the cell suggested that the added AB prevented shutoff of electron conduction paths in the α -TiS₃ composite electrode during cycling. In addition, AB particles may give a space for the volume change of α -TiS₃ particles, and the buffer space for the volume change may be effective in preserving adhesion among the particles.

4. Conclusion

The all-solid-state sodium cells using α -TiS₃ showed a high capacity over 300 mA h g⁻¹ at the first discharge process. The capacity of the cells gradually decreased with the discharge-charge process. XRD measurement and Raman spectroscopy of the α -TiS₃ electrode indicated the α -TiS₃ maintained amorphous and local structure after discharge-charge process. The SEM images and EDX mapping suggested the α -TiS₃ particle aggregated after the cycles, which would increase the resistance in the α -TiS₃ composite electrode with the discharge-charge cycles. Therefore, the nano-carbon material AB was added to the α -TiS₃ composite electrode. The all-solid-state sodium cells using α -TiS₃ electrode with AB showed a reversible capacity of over 300 mAh g⁻¹ for the 5 cycles. The capacity of the cell using α -TiS₃ was three times higher than that of the cell using TiS₂ crystal. Thus, α -TiS₃ is an attractive positive electrode material with high capacity for all-solid-state sodium batteries.

Acknowledgements

The present work was partially supported by JST “Advanced Low Carbon Technology Research and Development Program” and MEXT program “Elements Strategy Initiative to Form Core Research Center”.

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Figure captions

Fig. 1. Discharge-charge curves of the cell $\text{Na}_{15}\text{Sn}_4$ / Na_3PS_4 glass-ceramic / $\alpha\text{-TiS}_3$.

Fig. 2. (a) XRD patterns and (b) Raman spectra of the $\alpha\text{-TiS}_3$ composite electrode before and after discharge-charge process.

Fig. 3. Nyquist plots of the cell $\text{Na}_{15}\text{Sn}_4$ / Na_3PS_4 glass-ceramic / $\alpha\text{-TiS}_3$ after the 1st and 5th discharge-charge process. The bottom one shows the Nyquist plots of the symmetric cell $\text{Na}_{15}\text{Sn}_4$ / Na_3PS_4 glass-ceramic / $\text{Na}_{15}\text{Sn}_4$. R1 and R2 in the figure denote the resistances of “ $\text{Na}_{15}\text{Sn}_4$ electrode and Na_3PS_4 electrode separator” and “ $\alpha\text{-TiS}_3$ electrode”, respectively.

Fig. 4. SEM images and EDX mappings of the $\alpha\text{-TiS}_3$ electrode (a) before and (b) after the 10th discharge-charge process.

Fig. 5. Discharge-charge curves of the cell $\text{Na}_{15}\text{Sn}_4$ / Na_3PS_4 glass-ceramics / $\alpha\text{-TiS}_3$ with AB.

Figure(s)

Fig. 1

Fig. 2 (a)

Fig. 2 (b)

Fig. 3

(a)

(b)

Fig. 4

Fig. 5