EXPRESS LETTER

Mechanochemical synthesis of cubic rocksalt Na₂TiS₃ as novel active materials for all-solid-state sodium secondary batteries

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An all-solid-state sodium secondary battery is a candidate for the next generation batteries for the ubiquitous smart grid systems.¹⁻⁴ Inorganic solid electrolytes and economical sodium resources provide the advantages of high reliability, high energy density, and low cost to all-solid-state sodium batteries.⁵⁻⁷ One of the bottlenecks in the next step towards the practical use of all-solid-state sodium batteries is the development of long-life and high capacity electrode active materials. For instance, the intercalation materials of sodium transition metal oxides have been widely known as active materials with a high voltage; however, they have a few limitations such as capacity fading.⁸⁻¹¹ Many candidate next generation materials have been reported in literature and new active materials that withstand practical use are desired.

Mechanochemical (MC) process is an effective technique to synthesis glass and glass-ceramics. For instance, cubic Na₃PS₄ glass-ceramics prepared by the process and a subsequent heat treatment⁷ have been applied as a solid electrolyte with a high conductivity of over 10⁻⁴ S cm⁻¹. The MC process has also been employed to produce advanced amorphous active materials with enhanced electrochemical properties. The amorphization of V₂O₅,¹⁰ TiS₂,¹²,¹³ and MoS₂¹⁴ via MC process has induced a high capacity and suppressed the structural degradation. In the past years, cation disordered active materials have attracted attention for facilitating Li diffusion¹⁵ and utilizing an anion redox in Li-rich oxide.¹⁶,¹⁷ Sato et al. reported that MC process produced cation disordered active materials, namely, metastable LiMnO₂ and NaMnO₂, and suppressed the phase transition and volume change in the charge/discharge test.¹⁸ Transition metal sulfides have also been reported to form cation disordered structures, such as cubic rocksalt Li₂TiS₃ and Li₃NbS₄ via the MC process. The active materials have high capacity and good structural reversibility.¹⁹ In transition metal sulfides with disordered structures, the covalent bonds between the transition metal and sulfur formed the network structure and therefore suppressed the capacity fading derived from the structure deterioration.²⁰,²¹ Recently, we reported a sodium containing transition metal sulfide, amorphous Na₂TiS₃, which showed higher ionic conductivity than ordered monoclinic Na₂TiS₃ due to the presence of free volume owing to the amorphous structure.²² The increment in the ionic conductivity facilitated the increase in its reversible capacity to 250 mAh g⁻¹ from 140 mAh g⁻¹ of the ordered monoclinic Na₂TiS₃, which suggested that crystal polymorphisms intensely affected the electrochemical property of transition metal sulfides. The MC process affords various useful polymorphisms and is promising for the creation of novel phases with high capacity and high reversibility in the Na₂TiS₃ active material.

In this work, we synthesized cation disordered cubic rocksalt Na₂TiS₃ as a new electrode material using a MC process. The structure of cubic rocksalt Na₂TiS₃ is verified, and the thermodynamic changes and its correlation with
amorphous Na$_2$TiS$_3$ are investigated. The electrode performance in all-solid-state cells is also examined.

Amorphous and cubic rocksalt Na$_2$TiS$_3$ were produced by the MC process utilizing Na$_2$S (Nagao Co. Ltd., 99.1%) and TiS$_2$ (Kojundo Kagaku, 99%) as starting materials. These were mixed at a 1:1 molar ratio and 1.0 g of the mixture was placed into a 45 mL zirconia pot with 500 zirconia balls (4 mm in diameter, 90 g). The pots were rotated in a planetary ball milling apparatus (Fritsch, P-7) for 10 hours, and different rotation speeds of 360–510 rpm afforded the different structures of the prepared samples. Powder X-ray diffraction (XRD; Cu Kα) patterns were obtained by a diffractometer (SmartLab, Rigaku). The combination of differential thermal analysis (DTA) and high temperature XRD (Cu Kα) was employed to observe the thermodynamic properties of the samples. DTA was performed at 10 °C min$^{-1}$ under N$_2$ gas flow using a differential thermogravimetric analyzer (Thermo plus EVO02, Rigaku). High temperature XRD analysis were also performed using a diffractometer (UltimaIV, Rigaku). After holding the samples for 15 min at each temperature, XRD patterns were recorded.

A Na$_{1.5}$Sn$_4$ counter electrode was prepared using mechanical alloying with Ketjen Black, without the addition of an ionic conductor. A Na$_3$PS$_4$ glass-ceramic was used as a separator, and the solid electrolyte was prepared via the MC process and subsequent heat treatment. The all-solid-state cells with active materials were fabricated to investigate the electrode performances. Two types of composite positive electrodes were prepared by mixing in an agate mortar. The first one for the charge/discharge tests, and the second for the ex-situ XRD measurement to observe the structural change in the active materials with a redox reaction. The compounding ratio of the first electrode is Na$_2$TiS$_3$ (37.7 wt%), Na$_3$PS$_4$ (56.6 wt%), and acetylene black (5.7 wt%), whereas that of the second electrode is Na$_2$TiS$_3$ (66.0 wt%), Na$_3$PS$_4$ (28.3 wt%), and acetylene black (5.7 wt%). The all-solid-state cells were charged and discharged using a charge–discharge measuring device (VMP-3, Biologic) under dry Ar atmosphere. The cells were disassembled, and the positive electrodes were retrieved and analyzed using the XRD diffractometer (SmartLab, Rigaku).

Figure 1 shows the XRD patterns of Na$_2$TiS$_3$ prepared via the MC process. In contrast to amorphization of Na$_2$TiS$_3$ with ball milling at 360 rpm, broad diffraction peaks indexed to cation disordered cubic rocksalt structure (cubic, $a = 5.43$ Å) are observed in the XRD pattern of the Na$_2$TiS$_3$ prepared by ball milling at 510 rpm. Sodium and titanium randomly occupy the cation site of the rocksalt structure in cubic rocksalt Na$_2$TiS$_3$, although the ionic radii of sodium and titanium were significantly different than those of lithium and titanium. Figure 2(a) shows the DTA curves for the amorphous Na$_2$TiS$_3$ (α-Na$_2$TiS$_3$) and cubic rocksalt Na$_2$TiS$_3$, respectively. Two large exothermic peaks are observed at ~400 and ~475°C in DTA curves for α-Na$_2$TiS$_3$ as shown in Fig. 2(a). Figure 2(b) shows high temperature XRD patterns for α-Na$_2$TiS$_3$ at individual temperatures of 375, 450, and 475°C. At 375°C, for the first broad exothermic peak, the halo pattern...
becomes broad peaks indexed to cubic rocksalt Na$_2$TiS$_3$. At the second exothermic peak at $\approx 460^\circ$C, the broad diffraction peaks in the XRD pattern separate into increasing number of sharp peaks, suggesting that the stable phase of Na$_2$TiS$_3$ (monoclinic) is precipitated. Figure 2(c) shows the schematics for the thermodynamic change in crystal structures between the amorphous phase, cubic rocksalt phase, and monoclinic Na$_2$TiS$_3$. Cubic rocksalt Na$_2$TiS$_3$ with cation disordered phase is metastable and is gradually formed from the $\alpha$-Na$_2$TiS$_3$ during heating, with less thermodynamic stability. Upon further heating at higher temperatures, all constituent atoms are packed and ordered, and monoclinic Na$_2$TiS$_3$ as a stable phase is obtained.

Figure 3 shows the charge–discharge curves for the all-solid-state cells with (a) cation disordered cubic rocksalt Na$_2$TiS$_3$ and (b) $\alpha$-Na$_2$TiS$_3$ active materials. Both the cells operate reversibly. The reversible capacity of $\alpha$-Na$_2$TiS$_3$ at the 3rd cycle is 250 mAh g$^{-1}$ of Na$_2$TiS$_3$. The cell shows negligible irreversible capacity at the 1st charge–discharge cycle, although the expansion of the cut-off voltage causes capacity fading by insertion over 2 mol Na per TiS$_3$ (Fig. S1). The cell with cubic rocksalt Na$_2$TiS$_3$ shows a reversible capacity of 270 mAh g$^{-1}$, which is close to theoretical capacity of 282 mAh g$^{-1}$ of Na$_2$TiS$_3$. Figures 3(c) and 3(d), exhibit the rate capability and the cyclability of the cells, respectively, with cubic rocksalt Na$_2$TiS$_3$. The current density loading the cells increases gradually. At 0.13 mA cm$^{-2}$, the discharge capacity is held down through a capacity reduction of 70% of the initial capacity (at 0.013 mA cm$^{-2}$). On relaxation after exposure to harsh conditions at 0.64 mA cm$^{-2}$, the capacity is maintained, suggesting that cubic rocksalt Na$_2$TiS$_3$ shows stable structure change under a full charge and discharge; however, it should involve large structural changes. As shown in Fig. 3(d), the capacity retention of the cell is favorable for long term examination. For the 30th cycle at 0.13 mA cm$^{-2}$, the coulombic efficiency of the cell is above 99.5% and the capacity is maintained without any reduction. Figure 4 shows (a) charge–discharge curves for the all-solid-state cells using cubic rocksalt Na$_2$TiS$_3$ and (b) ex-situ XRD patterns for the pristine cell and the disassembled cells during the 1st charging or discharging. In the XRD patterns of cubic rocksalt Na$_2$TiS$_3$, the diffraction from the 200 plane broadens and shifts slightly shifted toward the higher angle after the 1st charge. A reversible peak shift is observed at the 1st discharge. The small shrinking of the unit cell should be favorable for suppressing a capacity fading. Conversely, the reduced intensity of diffraction peaks is observed for the specimen derived from cubic rocksalt Na$_2$TiS$_3$ during the 1st charging, sug-
Na2TiS3 active materials. Red circles show the point at which the Na15Sn4 were described by VESTA.25) KAKENHI, grant Number 17K14547. The crystal structures by the Japan Society for the Promotion of Science (JSPS) Na3PS4 electrolyte.

In summary, the cation disordered cubic rocksalt Na2TiS3 was synthesized as a novel metastable phase via a MC process. The phase transition was observed upon heating in the amorphous Na2TiS3 phase; it first crystallized into a metastable cubic rocksalt phase, and thereafter transformed into an ordered monoclinic phase at higher temperature. The cells with cubic rocksalt Na2TiS3 electrode operated as a secondary battery with excellent reversibility for 30 cycles. The cell showed a high capacity of 270 mAh g⁻¹, close to the theoretical capacity of 282 mAh g⁻¹. Further improvements in the rate capability and durability of cubic rocksalt Na2TiS3 are now being investigated.

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References