

Rock-salt type Li_2TiS_3 as New Positive Electrode Materials for Lithium-Metal Sulfides Secondary Batteries

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Enhancement of energy density of lithium-ion batteries is strongly desired for the power sources for electric vehicles. Development of new electrode materials with high capacity is essential to achieve the lithium-ion batteries with high energy density. Positive electrode materials of oxide families have been practically used in lithium-ion batteries. These electrodes usually show a capacity of less than 300 mAh g⁻¹. Metal sulfides are a promising candidate of a positive electrode material because of their high theoretical capacities although their working voltages are lower than oxide-based electrodes. Furthermore, the lithium-containing metal sulfides have not widely studied, except for a few examples such as Li_2FeS_2 and $\text{LiTi}_y\text{M}_{1-y}\text{S}_2$ (M=V, Cr, Fe) [1, 2]. Metal sulfide electrodes usually do not contain lithium; thus, lithium-containing negative electrodes are required to construct secondary cells. Lithium-containing metal sulfides will expand the choice of the negative electrode.

In this study, we developed a new sulfide positive electrode Li_2TiS_3 with rock-salt structure by the mechanochemical synthesis. The structure and electrode performance of Li_2TiS_3 were investigated.

Li_2TiS_3 was mechanochemically synthesized at room temperature using a planetary ball mill apparatus (P-7, Fritsch). Lithium sulfide (Li_2S) and titanium disulfide (TiS_2) were used as starting materials. Li_2S (9.5 mmol) and TiS_2 (9.5 mmol) were weighed and the mixture was put into a zirconia pot (45 mL) with 500 zirconia balls (4mm in diameter). The rotation speed was 510 rpm; the ball mill duration was 40 h. The samples for the X-ray diffraction (XRD) measurements were covered with Kapton® film to avoid the exposure to air. The electrochemical cells were constructed in an argon-filled glove box. The working electrodes were prepared using 10 mg Li_2TiS_3 , 2 mg acetylene black, and 0.7 mg polytetrafluoroethylene (PTFE) powder. The solution of 1 M LiPF_6 in a 50 : 50 mixture of EC and DMC by volume was used as an electrolyte. The counter electrode was Li foil. The electrochemical measurements were carried out at 30°C at a current density of 10 mA g⁻¹ between 1.7 and 3.0 V.

Figure 1 shows the XRD pattern of Li_2TiS_3 prepared by ball milling for 40 h. By the ball milling, the diffraction peaks attributable to TiS_2 and Li_2S disappeared; several new diffraction peaks appeared. The new peaks were identified by rock-salt structure ($Fm-3m$). Figure 1 also shows the simulated pattern of Li_2TiS_3 with rock-salt structure, assuming that its unit cell contains 4 formula units of $[\text{Li}_{2/3}/\text{Ti}_{1/3}]^{4a} \text{S}^{4b}$ and the cell parameter is $a=5.057$

Å. The cell parameter was obtained by the pattern fitting using RIETAN-2000 [3]; the pattern fitting indicated that the Li and Ti occupancies in 4a sites are ca. 0.665(4) and 0.335(4), respectively. The simulated powder X-ray data was calculated using Powder Cell program [4].

Figure 2 shows charge-discharge curves of the cells using Li_2TiS_3 for initial 5 cycles. The measurement was conducted from charging process. The 1st charge and discharge capacities were 275 mAh g⁻¹ and 370 mAh g⁻¹, respectively. The capacity of ca. 360 mAh g⁻¹ was kept after the 5th cycle. The capacity of 370 mAh g⁻¹ corresponds to 2.2-electron process. The average discharge voltage was ca. 2.2 V.

The rock-salt type Li_2TiS_3 is a candidate for the positive electrode materials for lithium-metal sulfides secondary batteries. We are now examining the charge/discharge mechanism; the results will be presented in the meeting.

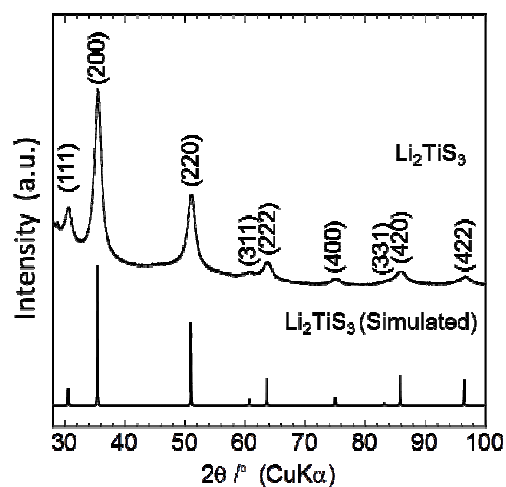


Figure 1. XRD patterns of Li_2TiS_3 prepared by ball milling for 40 h and Li_2TiS_3 simulated with rock-salt structure ($Fm-3m$).

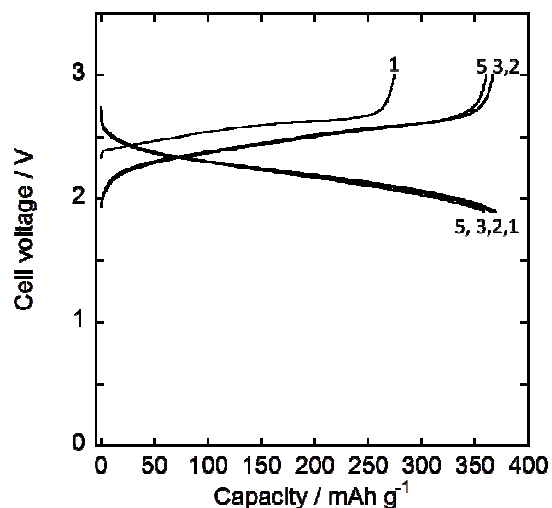


Figure 2. Charge-discharge curves of the cell using Li_2TiS_3 . The cutoff voltages were 1.9 - 3.0 V vs. Li counter electrode.

References

- [1] J. M. Tarascon *et al*, *Phys. Rev. B*, **28** (1983) 6397.
- [2] L. Blandeau *et al*, *J. Phys. C*, **20** (1987) 4271.
- [3] F. Izumi *et al*, *Mater. Sci. Forum*, **321-324** (2000) 198.
- [4] W. Kraus *et al*, *J. Appl. Crystallogr.* **29** (1996) 301.

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