Rock-salt-type lithium metal sulphides as novel positive-electrode materials

Atsushi Sakuda1, Tomonari Takeuchi1, Kazuhiro Okamura2, Hironori Kobayashi1, Hikari Sakaeb1, Kuniaki Tatsumi1 & Zempachi Ogumi2

1Research Institute for Ubiquitous Energy Devices, National Institute of Advanced Industrial Science and Technology (AIST), 1-8-31 Midorigaoka, Ikeda, Osaka 563-8577, Japan, 2Office of Society-Academia Collaboration for Innovation, Kyoto University, Gokasho, Uji, Kyoto 611-0011, Japan.

One way of increasing the energy density of lithium-ion batteries is to use electrode materials that exhibit high capacities owing to multielectron processes. Here, we report two novel materials, Li2TiS3 and Li3NbS4, which were mechanochemically synthesised at room temperature. When used as positive-electrode materials, Li2TiS3 and Li3NbS4 charged and discharged with high capacities of 425 mA h g\(^{-1}\) and 386 mA h g\(^{-1}\), respectively. These capacities correspond to those resulting from 2.5- and 3.5-electron processes. The average discharge voltage was approximately 2.2 V. It should be possible to prepare a number of high-capacity materials on the basis of the concept used to prepare Li2TiS3 and Li3NbS4.

Lithium-ion batteries with high energy densities are highly desirable as power sources for electric vehicles and electric power storage devices. The development of new high-capacity active materials for electrodes is essential for fabricating such batteries.

Positive electrodes, such as those made of layered and spinel-type lithium metal oxides and lithium metal phosphates, have been used in lithium-ion batteries. These electrodes usually have one equivalent of lithium per transition metal or less, and their capacities are less than 200 mA h g\(^{-1}\). Of late, layered lithium metal oxides with more than one equivalent of lithium per transition metal are being actively researched and developed as novel positive-electrode materials with capacities greater than 200 mA h g\(^{-1}\). However, it is still difficult to achieve reversible capacities greater than 300 mA h g\(^{-1}\) in layered lithium metal oxides. Transition metals act as the redox centre in many conventional active materials. In most cases, a single-electron reaction occurs during charging and discharging, and multielectron reactions, which are necessary for higher capacities, do not take place. This is partly because of (i) the instability of the active materials after the multielectron reactions, particularly in the charged state, where the higher valence state of transition metals is contained, and (ii) the irreversibility of the structures against larger changes in the valence state of the constituent metal ions. However, several exceptions have been reported. For instance, it had been reported that lithium vanadium oxides, \(v\)-Li\(_x\)V\(_2\)O\(_5\), show a capacity of more than 300 mA h g\(^{-1}\) and that approximately 3 lithiums per formula unit can be insert and removed from them; this corresponds to 1.5 electron processes per vanadium atom\(^2\). Although most positive-electrode materials charge and discharge mainly through the redox reaction of the transition metal, the redox reaction of anions as well as that of the transition metals should be exploited to achieve higher capacities. That is to say, it is essential that charge and discharge reactions involving more than two electrons should occur in the electrode materials. Therefore, the challenge is to develop new active materials that can charge and discharge through processes that involve more than two electrons.

Conversion electrodes, which involve the formation and decomposition of Li\(_2\)O, Li\(_2\)S, or LiF and the reduction and oxidation of metal nanoparticles, exhibit high capacities because their constituent materials undergo multi-electron reactions\(^3\). Most conversion electrodes show low potential and thus are usually employed as negative electrodes. A few conversion electrode materials, such as metal fluorides, show high capacities and voltages\(^4\). However, their reversibility is usually low because of the large structural changes that occur during charging and discharging.

Metal sulphides have also been studied as potential positive-electrode materials\(^5\). An advantage of metal sulphides is that their capacity is related to the sulphur redox reaction in addition to the redox reaction of the transition metal; this leads to a high capacity owing to the multielectron redox reaction. For example, crystalline TiS\(_2\) charges and discharges with reversible capacities greater than 300 mA h g\(^{-1}\), a value that corresponds to processes involving more than two electrons\(^6\). However, it has been reported that the reversibility of TiS\(_2\) is low,
probably owing to the transformation of its polyhedral structure from a trigonal prism to a more stable octahedron\cite{ref6}. It was recently reported that the amorphisation of TiS\textsubscript{3} via mechanical milling improves its performance as an electrode material\cite{ref12,ref13}. Amorphous TiS\textsubscript{3} exhibits a three-dimensional framework, which would be favourable for stabilising its structure against the large volume changes caused by the charge-discharge process. The development of electrode materials with structures that remain stable during multielectron processes is thus strongly desired.

We focused on the lithium predoping of metal sulphide electrodes because (i) it might stabilise the structure and (ii) lithium-containing positive-electrode material is highly desirable; commercial negative electrodes usually do not contain lithium. In contrast to lithium metal oxides and metal sulphones, lithium-containing metal sulphides have not been widely studied; a few exceptions are Li\textsubscript{2}FeS\textsubscript{2} and LiTi\textsubscript{1}M\textsubscript{1}S\textsubscript{2} (M = V, Cr, or Fe), etc.\cite{ref14,ref15}. The development of new lithium-containing metal sulphones (Li\textsubscript{x}MS\textsubscript{y}) has been a challenge. However, it should be possible to fabricate new crystalline-phase materials with high capacities and good structural reversibility by extracting/inserting Li in lithium-containing metal sulphides.

Here, we report the development of two novel lithium transition metal sulphides, Li\textsubscript{2}TiS\textsubscript{3} and Li\textsubscript{2}NbS\textsubscript{4}, which were fabricated via mechanochemical synthesis. The structures and electrode performances of the sulphones were investigated. We found that Li\textsubscript{2}TiS\textsubscript{3} and Li\textsubscript{2}NbS\textsubscript{4} exhibited reversible charging and discharging with high capacities of 425 and 386 mA h g\textsuperscript{-1}, respectively; these values correspond to processes involving 2.5 and 3.5 electrons, respectively.

**Results**

Figure 1a shows the X-Ray diffraction (XRD) patterns of TiS\textsubscript{2}, Li\textsubscript{2}S, a mixture of TiS\textsubscript{2} and Li\textsubscript{2}S that was not mechanically milled (0 h), and Li\textsubscript{2}TiS\textsubscript{3} samples prepared by mechanical milling (MM) for 20, 40, 60, and 100 h. Diffraction peaks corresponding to TiS\textsubscript{2} and Li\textsubscript{2}S were not evident after the milling process; however, several new peaks appeared. The XRD patterns of Li\textsubscript{2}TiS\textsubscript{3} after MM for 40, 60, and 100 h were similar. The broad peak observed at 2θ = 10–25° was owing to the Kapton\textsuperscript{®} film.

Figure 1b shows the XRD pattern of Li\textsubscript{2}TiS\textsubscript{3} prepared by MM for 40 h and the simulated XRD pattern of Li\textsubscript{2}TiS\textsubscript{3} with a rock-salt-type structure (Fm–3m). It was assumed that its unit cell contains four formula units (Li\textsubscript{2}S\textsubscript{2}/Ti\textsubscript{1/3}I\textsubscript{1/3}4S\textsubscript{4b}), and the cell parameter is a = 5.06 Å. Table 1 shows the simulated powder X-ray data obtained using the software program PowderCell\textsuperscript{®}. The peak positions of the prepared Li\textsubscript{2}TiS\textsubscript{3} sample were consistent with those of the simulated rock-salt-type Li\textsubscript{2}TiS\textsubscript{3}. This suggests that the synthesised Li\textsubscript{2}TiS\textsubscript{3} sample had a rock-salt-type structure. Furthermore, the intensity ratios of the XRD peaks of the prepared Li\textsubscript{2}TiS\textsubscript{3} sample were in good agreement with the simulated ones for Li\textsubscript{2}TiS\textsubscript{3}, indicating that the Ti occupancy in the 4a sites was approximately 0.33. Pattern fitting, performed using the program RIETAN-2000\textsuperscript{®}, also indicated that the Li and Ti occupancies in the 4a sites were approximately 0.665(4) and 0.335(4), respectively. To the best of our knowledge, this is the first report of a lithium titanium sulphide with a rock-salt-type structure.

The rock-salt-type Li\textsubscript{2}TiS\textsubscript{3} was employed as an electrode active material for lithium secondary batteries. Figure 2a shows the charge-discharge curves for the first 5 cycles of the cells fabricated using Li\textsubscript{2}TiS\textsubscript{3}. The initial charge and discharge capacities were 273 and 425 mA h g\textsuperscript{-1}, respectively. Figure 2b shows the charge-discharge characteristics as a function of the lithium content. It was found that approximately 1.6 lithium atoms per formula unit could be inserted into the structure during the initial charging process and 2.5 lithium atoms could be inserted into the structure during the initial discharging process. The extraction and insertion of 2.5 lithium atoms into the structure of Li\textsubscript{2}TiS\textsubscript{3} was reversible during repeated cycling. Thus, this electrode active material could contain more than 2 lithium atoms in its structure; the structure could be charged and discharged such that it ranged from Li\textsubscript{0.4}TiS\textsubscript{3} to Li\textsubscript{2.9}TiS\textsubscript{3} over voltages of 1.5–3.0 V. The initial charging and discharging curve exhibited significant overlap with the second and third curves for the structure ranging from Li\textsubscript{0.4}TiS\textsubscript{3} to Li\textsubscript{2.9}TiS\textsubscript{3}, suggesting that the charge-discharge mechanism remained unchanged. Figure 2c shows the cycle performance of the cell fabricated using Li\textsubscript{2}TiS\textsubscript{3}. The discharge profiles did not change drastically over 5 cycles; however, the capacity of the cell faded after the 10th cycle.

**Table 1 | Simulated powder X-ray data for Li\textsubscript{2}TiS\textsubscript{3} for a = 5.06 Å**

(The data were obtained using Cu-K\textsubscript{α} radiation.)

| h | k | l | 2θ (deg) | d (Å) | Intensity |
|---|---|---|---------|------|-----------|
| 1 | 1 | 1 | 30.58   | 2.92 | 16 |
| 2 | 0 | 0 | 35.45   | 2.53 | 100 |
| 2 | 2 | 0 | 51.01   | 1.79 | 61 |
| 3 | 1 | 1 | 60.65   | 1.53 | 5 |
| 2 | 2 | 2 | 63.65   | 1.46 | 19 |
| 4 | 0 | 0 | 75.03   | 1.27 | 8 |
| 3 | 1 | 1 | 83.15   | 1.16 | 2 |
| 4 | 2 | 0 | 85.81   | 1.13 | 23 |
| 4 | 2 | 2 | 96.45   | 1.03 | 18 |
To further investigate the electrochemical reactions occurring during the charge-discharge processes, ex situ XRD measurements were performed for Li$_x$TiS$_3$ with $x = 2.0, 1.0, 0.4, 1.4$, and $2.6$ (Figure 3). The peaks became broad after a 1.0-electron charge, as shown in Figure 3b. Further, the peaks became even broader and decreased in intensity after the charge to Li$_{0.4}$TiS$_3$ (Figure 3c). Some of these broader, lower-intensity peaks in Figure 3c were identified as being attributable to ZrO$_2$, which could have contaminated the test samples during the ball-milling process. Finally, after the discharge to Li$_{1.4}$TiS$_3$ (Figure 3d) and Li$_{2.6}$TiS$_3$ (Figure 3e), the peaks became sharper and increased in intensity. These results indicate that the extraction of lithium atoms from Li$_2$TiS$_3$ results in amorphisation and that reverse reactions occur during the discharge process. It should be noted that the XRD pattern corresponding to the rocksalt-type sample was observed after discharging to Li$_{2.6}$TiS$_3$. This suggests that the volume change during charge and discharge can be expected to occur in a three-dimensional manner.

To evaluate the cyclability of Li$_2$TiS$_3$, an all-solid-state cell was constructed using Li$_2$TiS$_3$ as the electrode material. It is known that a number of electrode materials show high cyclability when used in all-solid-state cells. Figure 4a shows the charge-discharge curves of the all-solid-state cell at 50°C. Figure 4b shows the cycling performance of the all-solid-state cell. The cell exhibited high capacity retention, retaining 97% of its capacity from the 5th to the 50th cycle.

**Figure 3** XRD patterns of Li$_x$TiS$_3$ before and after the charge-discharge measurements. The patterns correspond to $x = (a) 2.0$, (b) $1.0$, (c) $0.4$, (d) $1.4$, and (e) $2.6$.

**Figure 4** Electrode performance of Li$_2$TiS$_3$ in an all-solid-state cell. (a) Charge-discharge curves of the all-solid-state cell fabricated using Li$_2$TiS$_3$ at 50°C. Cut-off voltages were 0.9–2.4 V (versus a Li-In counter electrode). The cell was precycled at 30°C. Current densities were 0.1 mA cm$^{-2}$ for the 1st–4th cycles and 0.5 mA cm$^{-2}$ after the 5th cycle. (b) Cycling performance of the all-solid-state cell fabricated using Li$_2$TiS$_3$ at 50°C.
Thus, Li₂TiS₃ exhibits high reversibility when subjected to charge-discharge cycling.

A number of novel lithium metal sulphides can be developed through mecha­nochemical synthesis on the basis of the concept employed for altering the structure of Li₂TiS₃. Here, we show an example of one such material, Li₃NbS₄, which has a structure similar to that of Li₂TiS₃ and was prepared by mecha­nochemical synthesis from Li₂S, NbS₂, and S₈. Figure 5a shows the XRD pattern of Li₃NbS₄. The XRD pattern is similar to that of Li₂TiS₃. Therefore, Li₃NbS₄ should also have a cubic structure, with the cell parameter a = 5.13 Å.

Figure 5b shows the charge-discharge curves of the cell fabricated using Li₃NbS₄ and a liquid-based electrolyte. Cut-off voltages were 1.5–3.0 V (versus a Li counter electrode). (c) Cycling performance of the cell fabricated using Li₃NbS₄.

Figure 5 | Characterisation of Li₃NbS₄. (a) XRD pattern of Li₃NbS₄ prepared by MM for 40 h and the simulated XRD pattern of Li₃NbS₄ with a rock-salt-type structure (Fm–3m) obtained using the cell parameter a = 5.13. (b) Charge-discharge curves of the cell fabricated using Li₃NbS₄ and a liquid-based electrolyte. Cut-off voltages were 1.5–3.0 V (versus a Li counter electrode). (c) Cycling performance of the cell fabricated using Li₃NbS₄.

The XRD patterns of the synthesised samples were recorded using an X-ray diffractometer (Rotaflex RU-200B/RINT, Rigaku). Prior to the measurements, the samples were covered with Kapton® film in an argon-filled glove box to prevent exposure to air. The electrochemical cells used to test the samples were also constructed in an argon-filled glove box. The working electrodes were prepared from LiₓTiS₃ (10 mg), acetylene black (2 mg), and polytetrafluoroethylene (PTFE) powder (0.7 mg). A 1 M solution of LiPF₆ in a 50:50 (by volume) mixture of EC and DMC (Tomiyama Pure Chemical Industries Ltd.) was used as the electrolyte. The counter electrode consisted of a Li foil disk (15 mm diameter, 0.2 mm thickness). The electrochemical measurements were performed at 30 °C using a charge-discharge unit (TOSCAT-3100, Toyo System) at a current density of 10 mA g⁻¹ between 1.5 and 3.0 V. The all-solid-state cells were constructed as follows. LiₓTiS₃, the glass electrolyte 70(0.75Li₂S₀.25P₂S₅)·30LiI, and acetylene black (AB) were mixed in a weight ratio of 60:30:10 in an agate mortar, and the mixture was used to prepare the positive-electrode material. The glass electrolyte LiₓS·P₂S₅·LiI, which has an ionic conductivity of more than 10⁻⁴ S cm⁻¹, was used as the solid electrolyte. A lithium-indium alloy was used to make the counter electrode. Bilayered pellets consisting of the positive-electrode material (10 mg) and the glass electrolyte (70 mg) were pressed under a pressure of 360 MPa (diameter = 10 mm). Pieces of indium foil (thickness = 0.3 mm, diameter = 9 mm) and lithium foil (thickness = 0.1 mm, diameter = 8 mm) were then placed on top of the bilayer pellets by pressing them all together under a pressure of 100 MPa. The pellets were pressed using two stainless steel rods, which were used as current collectors for both the positive electrode and the negative.
electrode. All the processes for preparing the electrochemical cells were performed in a dry Ar-filled glove box ([H$_2$O] < 1 ppm).

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\section*{Author contributions}
A.S. synthesised the materials and wrote the paper. A.S., T.T., K.O., H.K. and H.S. characterised the synthesised materials. K.T. and Z.O. designed and supervised the project.

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