Preparation of Novel Electrode Materials Based on Lithium Niobium Sulfides
Atsushi SAKUDA, a,b* Tomonari TAKEUCHI, a Hironori KOBAYASHI, a
Hikari SAKAEBE, a Kuniaki TATSUMI, a and Zempachi OGUMI b

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

* Corresponding author: a.sakuda@aist.go.jp

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ABSTRACT
Novel lithium niobium sulfide electrode materials, xLi2S-NbS2-(2-x)S (x = 1/2–2), were mechanochemically synthesized using Li2S, NbS2, and S8 as starting materials, and their electrochemical performance was investigated. The electrodes with x = 1/2 were in amorphous phase, while those with x = 1 and 3/2 are assigned as cubic phase. Cells prepared with these electrodes charge and discharge reversibly, with a capacity of ca. 400 mA h g\(^{-1}\). Within the wide operational voltage range 1.0–3.0 V, Li3NbS4 charges and discharges with ca. 4.5-electron processes between Li8.4NbS4 and Li9.5NbS4, Li3NbS4 discharges even at a high current density of 2000 mA g\(^{-1}\) at 30°C.

Keywords : Lithium Secondary Battery, Niobium Sulfide, Mechanical Milling, Electrode Material

1. Introduction
Rechargeable batteries with high energy densities are required for developing high-performance electric vehicles (EVs). Commercially produced lithium-ion batteries usually use lithium transition metal oxides or phosphates such as LiCoO2, Li(Ni,Co,Mn)O2, LiMn2O4, and LiFePO4 as positive electrode materials. These electrodes exhibit well-balanced electrode performance, a very high energy density, and charge-discharge characteristics of the cells using the lithium niobium sulfide electrode in the wide cutoff voltages and under high current densities.

In this paper, we report on the preparation of some novel lithium niobium sulfides, xLi2S-NbS2-(2-x)S (Li1.5NbS4, Li2NbS4, and Li3NbS4, where the x = 3/2 sample was previously reported as Li1.5NbS4, and their electrochemical performance. We also report the charge-discharge characteristics of the cells using the lithium niobium sulfide electrode in the wide cutoff voltages and under high current densities.

2. Experimental
Lithium niobium sulfides, Li1.5S-NbS2-Sx, were mechanochemically synthesized at room temperature using a planetary ball mill apparatus (P-7, Fritsch GmbH). In an argon-filled glove box, the mixture of lithium sulfide (LiS, 99.9%, Mitsuwa Pure Chemicals), niobium disulfide (NbS2, 99%, High Purity Chemicals), and sulfur (S8, 99.9%, Wako Pure Chemical Industries) was placed into a zirconia pot (45 mL) along with zirconia balls (4 mm in diameter, 90 g). The total weight of the mixture was fixed to 1 g. A stainless steel cover was fixed to avoid exposure to air. The rotation speed and time of ball milling were fixed at 510 rpm and 60 h (60 min × 60), respectively. Powder XRD measurements were performed at room temperature over the 2θ range angle 25° < 2θ < 80°, with a step size of 0.1° using a NEW D8 ADVANCE (Bruker AXS) diffractometer operating with CuKα radiation. The calculated powder X-ray data of rock-salt-type Li8.4NbS4 were obtained using the software program Powder Cell. The electrochemical cells were also constructed in an argon-filled glove box. The working electrodes were prepared from Li1.5S-NbS2-S (10 mg), acetylene black (AB, 1 or 2 mg), and polytetrafluoroethylene (PTFE) powder (0.7 mg). A mixture of Li1.5S-NbS2-S, AB, and PTFE was ground using agate mortar and attached to an Al mesh current collector. A 1-M solution of LiPF6 in a 50:50 (by volume) mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (Tomiyama Pure Chemical Industries Ltd.) was used as the electrolyte, and a lithium foil disk was used as the counter electrode. Electrochemical measurements were performed at 30°C using a charge-discharge unit (TOSCAT-3100, Toyo System) at various current densities between 5 and 2000 mA g\(^{-1}\). The cell was cycled between 1.5 and 3.0 V, or between 1.0 and 3.0 V.

Keywords : Lithium Secondary Battery, Niobium Sulfide, Mechanical Milling, Electrode Material
A XRD pattern of rock-salt-type Li₃NbS₄ is also shown in Fig. 1, prepared Li₂S·NbS₂·S₈. The composition in the starting materials varied from 1 to 4. Figure 1 shows the XRD patterns of the prepared sample was amorphous. The initial powder (Li₂S, NbS₂, and S₈) for the present samples (Li₃NbS₄ composition), and molar ratio of starting materials.

### Table 1. Composition of prepared lithium niobium sulfides, xLi₂S·NbS₂·(2–x)S₈ (Li₃ NbS₄ composition), and molar ratio of starting materials.

<table>
<thead>
<tr>
<th>x</th>
<th>Li₂S</th>
<th>NbS₂</th>
<th>S₈</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>1/2</td>
<td>0.5</td>
<td>1</td>
<td>1.5</td>
<td>LiNbS₄</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>Li₂NbS₄</td>
</tr>
<tr>
<td>3/2</td>
<td>1.5</td>
<td>1</td>
<td>0.5</td>
<td>Li₃NbS₄</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>1</td>
<td>0</td>
<td>Li₂NbS₄</td>
</tr>
</tbody>
</table>

3. Results and Discussion

Table 1 summarizes the composition and molar ratios of the initial powder (Li₂S, NbS₂, and S₈) for the present samples (x = 1/2–2). The S/Nb ratio was fixed to 4, and the lithium composition was varied from 1 to 4. Figure 1 shows the XRD patterns of the prepared Li₂S·NbS₂·S₈. The x = 3/2 samples (Li₃NbS₄) were assigned as the rock-salt-type cubic phase (Fm3m).

The simulated XRD pattern of rock-salt-type Li₃NbS₄ is also shown in Fig. 1, assuming that the unit cell contains four formula units of [Li₃/4Nb₁/4S₇] with the cell parameter of 5.13 Å. The simulated data are listed in Table 2. The pattern of the x = 1 sample was similar to that of the Li₃NbS₄ (x = 3/2 sample). The XRD patterns of the x = 1/2 sample showed no obvious peaks, indicating that the prepared sample was amorphous. The x = 2 sample mainly consisted of Li₂S with minor impurities and an unknown phase. Small impurity peaks were observed, such as those of zirconia-based materials, which were contaminated by the zirconia pot and balls during the ball milling process. The amount of contamination seemed to depend on the hardness of both the starting and obtained materials. The contamination tended to increase with increasing Li₂S composition in the starting materials.

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**Figure 2.** SEM image of Li₃NbS₄ particles.

Figure 2 shows an SEM image of the x = 3/2 sample (Li₃NbS₄). Although the particle size was not uniform, 0.1–10 μm particles were observed in the SEM image. There were some large particles with size more than 10 μm.

Figures 3(a)–3(d) shows the charge-discharge curves of the cells using the prepared samples. The initial charging capacities of the samples of x = 1/2, 1, 3/2, and 2 were 88, 187, 289, and 343 mAh g⁻¹, respectively. The initial discharging capacities were 446, 413, 386, and 357, respectively, for the same samples. The initial charging capacity increased with increasing initial lithium content, and values were close to those calculated assuming that all of the contained lithium ions can be extracted during charge. In contrast, discharging capacity decreased with increasing initial lithium content; the discharge capacities of around 400 mAh g⁻¹ were larger than the initial charging capacity. The cells can be reversibly charged and discharged with the capacity corresponding to the initial discharging capacity after the 2nd cycle. Figures 3(e)–3(h) show charge-discharge characteristics as a function of lithium content. The prepared samples of x = 1/2–3/2 can be charged and discharged approximately between Li₂S·NbS₄ and Li₃NbS₄. The discharge voltages were almost identical, although the charging voltage of the x = 3/2 sample was higher than those of x = 1/2 and 1. The charge-discharge profile of the x = 2 sample differed slightly from those of the others, and the x = 2 sample showed a lower capacity than the other samples. This may be related to the residual Li₂S, which is an electronic insulator and is reported to be electrochemically inactive in carbonate-based electrolytes. The electrode performance of Li₂S·NbS₄ of lower discharge cutoff was also investigated. Figure 4(a) shows the charge-discharge curves of Li₂S·NbS₄ cycled between 1.0 and 3.0 V. The initial discharging capacity largely increased from 386 to 486 mAh g⁻¹ when the cutoff voltage was lowered from 1.5 to 1.0 V. Figure 4(b) also shows...
charge-discharge characteristics as a function of lithium content. The capacity of 486 mAh g\(^{-1}\) corresponds to ca. 4.5-electron processes, and the reaction was reversible during repeated cycling. Li\(_3\)NbS\(_4\) could be charged and discharged such that it ranged from Li\(_{0.4}\)NbS\(_4\) to Li\(_{4.9}\)NbS\(_4\) over the voltages 1.0–3.0 V. The estimated energy density of Li/Li\(_3\)NbS\(_4\) was 923 Wh kg\(^{-1}\). This value is higher than those of commercially available lithium-ion batteries such as Li/Li\(_{1-x}\)CoO\(_2\) and Li/Li\(_{1-x}\)(Ni,Mn,Co)O\(_2\) (600–800 Wh kg\(^{-1}\)). Thus, it can be concluded that Li\(_3\)NbS\(_4\) shows a relatively high energy density. The charge-discharge mechanisms of the electrode materials reported in this study are unclear at the present stage. A better understanding of the redox mechanism is needed for the improvement of electrode performance and further development of related electrode materials. We will continue to investigate this charge-discharge mechanism in the future.

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Figure 3. Charge-discharge curves of samples of (a) \(x = 1/2\), (b) \(x = 1\), (c) \(x = 3/2\) (Li\(_3\)NbS\(_4\)), and (d) \(x = 2\), and charge-discharge characteristics described as a function of lithium content: (e) \(x = 1/2\), (f) \(x = 1\), (g) \(x = 3/2\) (Li\(_3\)NbS\(_4\)), and (h) \(x = 2\).

Figure 4. (a) Charge-discharge curves of the cell using Li\(_3\)NbS\(_4\) cycled between 1.0 and 3.0 V vs. the Li counter electrode and (b) the charge-discharge characteristics described as a function of lithium content.

Figure 5. (Color online) Charge-discharge curves of the cell using Li\(_3\)NbS\(_4\) at various discharge current densities from 5 to 2000 mA g\(^{-1}\).
mA g\(^{-1}\). The cells were charged at a current density of 100 mA g\(^{-1}\) with the CC-CV mode. Even at high current densities of more than 1000 mA g\(^{-1}\), the cell can be sufficiently discharged, indicating that Li\(_3\)NbS\(_4\) essentially exhibits a superior rate capability. The powder-compressed pellet of the prepared Li\(_3\)NbS\(_4\) showed a high electronic conductivity of \(2.0 \times 10^{-3}\) Sc m\(^{-1}\). This would relate to a favorable rate capability of Li\(_3\)NbS\(_4\).

4. Conclusion

Novel lithium niobium sulfides \(x\text{Li}_2\text{S} \cdot \text{NbS}_2 \cdot (2-x)\text{S} (x = 1/2, 1, 3/2, \text{ and } 2)\) were mechanochemically prepared as positive electrode materials for lithium/metal sulfide secondary batteries. All cells using prepared lithium niobium sulfides reversibly charged and discharged. The initial charging capacity increased with increasing lithium content (\(x\)), while the discharge capacities were approximately similar, irrespective of the \(x\) value. The cell with the \(x = 3/2\) sample (Li\(_3\)NbS\(_4\)) can be reversibly charged and discharged with a high capacity of 486 mAh g\(^{-1}\), which corresponds to 4.5-electron processes when the cell was cycled between 1.0 and 3.0 V. Li\(_3\)NbS\(_4\) can be discharged even at the current density 2000 mA g\(^{-1}\) at 30°C. It shows a large capacity and superior rate capability; it is a suitable candidate for positive electrode materials for lithium/metal sulfide secondary batteries. We need to further investigate the fundamental redox mechanism for further developing high-performance novel electrode materials.

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