Synthesis of novel 1-dimensional structure from Mo$_6$S$_8$ Chevrel phase of electrode for Mg batteries

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Abstract

The Chevrel phase (CP) (Mo$_6$S$_8$), which is used as an electrode material in Mg rechargeable batteries, has a capacity limit owing to ion insertion and trapping. To address this problem, we modify the wire structure of the CP. Mo$_6$S$_3$I$_6$ nanowires, in which iodine is substituted for Mo$_6$S$_8$ nanowires as infinite CP structures, can be synthesized in various ways. When synthesizing stoichiometrically, an unwanted secondary phase may appear. We solved these problems by reducing the synthesis time. Electrochemical analysis was performed using these nanowires as an active material in Mg batteries.

1. Introduction

Mo$_6$S$_8$ Chevrel phase (CP) structures are widely used as Mg electrode materials. Mg ions enter the cavities of each Mo$_6$S$_8$ unit cell and form a ring structure weak Mg bonds. This formation reduces the diffusion rate of Mg ions in the active material during charging and discharging and limits their capacity [1–4]. As is clear from figure 1(a), the more Mo$_6$S$_8$ unit cells are connected, the more M ions (Cr, Cu, Fe, Co, Sn, or Pb) can enter. Thus, increase in the trapping phenomenon and diffusion rate owing to the transformation to 1-dimensional (1D) Mo$_6$S$_8$ in the structure of the Mo$_6$S$_8$ CP (figure 1(b)) was expected [5]. 1D Mo$_6$S$_8$, can be synthesized through M ion removal from M$_2$Mo$_6$S$_8$ as it is obtained by removing metals from metal–compounds such as M$_2$–CP. However, there are several synthesis mechanisms for this material. First, it was known as a method for synthesizing M$_2$Mo$_6$S$_8$ by initially forming M$_2$MoS$_4$ and then obtained after several sulfur addition steps. Recently, a Mg battery method for synthesizing 1D Mo$_6$S$_8$ at high temperatures was reported [7]. However, this method is complicated and time consuming.

To address this problem, we focused on Mo$_6$S$_8$–I$_x$, a 1D material with the same structure as Mo$_6$S$_8$ that can control the electrical properties of semiconductor metals based on the availability of X [8–10]. Various studies on the synthesis of Mo$_6$S$_8$–I$_x$ are being conducted; among them, Mo$_6$S$_3$I$_6$ wires (figure 1(c)) were synthesized in a manner similar to the CP synthesis of Mo$_6$S$_8$; that is, the wires were synthesized from Mo$_6$S$_3$I$_2$ CP material that replaced iodine in Mo$_6$S$_8$ CP [8, 9]. Typically, Mo$_6$S$_3$I$_6$ nanowires (NWs) are in the stoichiometric ratio shown in the following ideal reaction:

$$6Mo(s) + 3S(s) + 3I_2(s) \rightarrow Mo_6S_3I_6(s)$$

However, for realistic synthesis, $6Mo(s) + 3S(s) + 3I_2(s) \rightarrow xMo_6S_3I_x(s) + yMoI_2(g) + \text{various intermediate phase}$. Thus, in the study on the synthesis of Mo$_6$S$_3$I$_x$ NWs, MoI$_2$ and Mo$_6$S$_3$I$_2$ act as seeds for the synthesis of Mo$_6$S$_3$I$_x$ NWs [7]. In addition, to prevent the explosion of the quartz ampoule owing to the high vapor pressure of iodine at high temperatures during synthesis, the precursor ratio was modified to the following reaction formula:
In the above reaction, Mo₆S₆I₂ acts as a seed, and the final material was used to synthesize Mo₆S₃I₆ NWs. In addition, the most commonly used substrates have been synthesized using Mo foil, Mo wire, and quartz \[11\text{–}13\]. However, synthesis can be performed without them, and the synthesis time could be reduced. This method is expected to be applicable to various Mo₆S₃I₆ synthesis methods.

2. Experimental section

2.1. Synthesis of Mo₆S₃I₆

Focusing on the synthesis method of the CP, we recognized that the heat treatment time and temperature of the ternary molybdenum compound \(M_xMo_6X_8\), depended on the properties of the M and chalcogen (X) elements and the nature of the ternary molybdenum chalcogenide. The synthesis temperature was modified \[14\]. The elemental 12M Mo (99.9%, \(\approx 3 \mu m\) Avention, 234.48 mg), 9M S (99.98%, Sigma–Aldrich, 58.76 mg), and 4M I₂ (> 99.99%, Sigma–Aldrich, 206.76 mg) were mixed with mortar and sealed in an evacuated quartz tube. First, the heat was increased from 900 to 1100 °C for 48 h in a tube furnace, and fixed at 1100 °C, where the NWs clearly formed. Next, heat treatment was performed starting at 72 h, and then cooled down to room temperature at 5 °C min⁻¹, gradually reducing the heating time. The experiment was concluded by mechanically opening the ampoule (figure 2), removing the source, and peeling off the Mo₆S₃I₆ NWs from the quartz using pouring.

\[
12Mo (s) + 9S (s) + 4I_2 (s) \rightarrow Mo_6S_3I_6 (s) + Mo_6S_6I_2 (s)
\]

In the above reaction, Mo₆S₆I₂ acts as a seed, and the final material was used to synthesize Mo₆S₃I₆ NWs. In addition, the most commonly used substrates have been synthesized using Mo foil, Mo wire, and quartz \[11\text{–}13\]. However, synthesis can be performed without them, and the synthesis time could be reduced. This method is expected to be applicable to various Mo₆S₃I₆ synthesis methods.
ethanol along the quartz wall. We dispersed 50 mg of Mo6S3I6 NWs for 10 min (2s on/2s off) at 400 W in 100 ml of isopropyl alcohol (IPA) by tip sonication. Finally, bath sonication was carried out for 3 h [7, 15, 16].

2.2. Electrochemical measurement
Coin–cell was prepared for the electrochemical characterization of the Mo6S3I6 NWs. The electrode as a current collector was prepared by coating a copper foil with mixing 50 wt% Mo6S3I6 NWs powder of the active material, 30 wt% super–P carbon of the conducting agent, and 20 wt% polyvinylidene fluoride (PVDF) of binder dissolved in N–methyl–2–pyrrolidone (NMP). After coating, the cathodes were dried at 60 °C for 12 h in a vacuum oven. The diameter and loading mass of the electrodes were 12 π and approximately 0.49 mg·cm−2, respectively. We assembled 2032 coin–cells in an Ar–filled glovebox using Mg foil (0.25 mm thick) as the counter electrode with native MgO removed by polishing and the PE–PP membrane as the separator. 0.4M (PhMgCl)2–AlCl3/tetrahydrofuran (THF) solvent as a APC electrolyte and stirred it for 1 day. A coin–cell consisting of electrodes and a spaper was filled with electorlyte (S1).

2.3. Characterization of active materials
We used a field emission scanning electron microscope (FE–SEM, Hitachi and JEOL) to observe the morphologies and sizes of the synthesized Mo6S3I6 NWs. X–ray powder diffraction (XRD, Bruker) patterns were characteristic Cu Kα radiation sources. The vibration mode of Mo and S characterization was performed using Raman spectroscopy at λ = 532 nm (WITec Project). Further, dispersions of Mo6S3I6 bundles were prepared and measurement were performed with high–resolution transmission electron microscopy (HR–TEM, JEOL),

Figure 2. Schematic of synthesis growth for Mo6S3I6 nanowires. After synthesis of Mo6S3I6 NWs, the reaction materials were divided between the source and transport zones in the quartz ampule.
and electrochemical tests (WonATech) were conducted in the voltage range of 0.05 to 1.30 V at room temperature.

3. Results and discussion

3.1. Analysis of Mo$_6$S$_3$I$_6$ nanowire

The photographic and SEM images of the synthesized material source and transport zones are shown in figure 2. Knowing that ternary molybdenum chalcogenide reacts at 800 to 1100 °C, [17] we synthesized it from 900 to 1100 °C. First, we confirmed the wire growth by SEM (figure 3(a)), and nanowires seem to be highly dense, and the Mo$_6$S$_3$I$_6$ NWs and MoS$_2$ were synthesized at 900 °C. Above 1000 °C, the torsional mode of Mo as Mo$_6$ octahedron can be observed at 94.27 cm$^{-1}$ in figure 3(c) [18–22]. In addition, at 1000 °C, the crystallinity of Mo$_6$S$_3$I$_6$ NWs were improved and characterized by XRD, SEM, and Raman spectroscopy. MoS$_2$ and Mo$_2$S$_3$ phases were observed at 2$\theta$ = 14.44 (MoS$_2$, ICCD number: 98–002–6622) and 2$\theta$ = 16.24 (Mo$_2$S$_3$, ICCD number: 01–081–2031), respectively, in XRD, [18, 19] and 310, 378, and 407 cm$^{-1}$ in Raman spectroscopy [18, 20]. At 1050 °C, the MoS$_2$ disappeared, the nanowire crystallinity improved, and the Mo$_6$S$_3$I$_6$ phase acting as a Mo$_6$S$_3$I$_6$ NW seed was observed. The Mo$_6$S$_3$I$_6$ and Mo$_6$S$_3$I$_6$ phases were synthesized only when the temperature was raised to 1100 °C. In the XRD results shown in figure 3(b), unlike the Mo$_6$S$_3$I$_6$ (ICDD number: 00–038–0540) seeds in the source zone, the Mo$_6$S$_3$I$_6$ seed in the transport zone was expected to remain as several hundred nanometers in size. However, the particles were small and wire synthesis was not achieved. It was later confirmed that the Mo$_6$S$_3$I$_6$ with decreasing and Mo$_6$S$_3$I$_6$ phases were synthesized only when the temperature increased to 1100 °C.

Figure 3. Analysis of synthesized Mo–S–I NWs based on the temperature for 48 h. (a) SEM images of wire growth with increasing temperature. (b) XRD patterns at 900 to 1100 °C. (c) Raman spectroscopy results.
To investigate the Mo$_6$S$_3$I$_6$ NWs synthesized at 1100 °C, the synthesis time was varied and observed. Typically, synthesis takes approximately 72 h [7, 12]. Hence, we determined whether to increase or decrease the starting time at 72 h. First, SEM was used (figure 4(a)) to confirm the shapes of the wire after synthesis based on the time. We observed that an area resembling seeds were confirmed at the end of the wire after 72 h. The thickness of the wires was an average of 300 nm. The XRD data indicated that various phases, such as Mo$_6$S$_3$I$_6$, Mo$_6$S$_6$I$_2$, Mo$_2$S$_5$I$_3$ (ICCD number: 00-039-0717), and Mo$_2$S$_3$ occurred after 72 h (green color). After 60 h, wires were synthesized. However, their thickness varied. The SEM image in figure 4(a) shows that an area resembling seeds were confirmed at the end of wires, and Mo$_6$S$_3$I$_6$ (wire phase) and Mo$_6$S$_6$I$_2$ (seed phase) occurred, which corresponds with the XRD results (figure 4(b)). After 48 h, the average wire thickness was 200 nm (∼20 nm after

Figure 4. Analysis of synthesized Mo–S–I NWs heat–treated at 1100 °C. (a) SEM images of wire growth with decreasing time. (b) XRD patterns from 24 to 72 h. (c) Mo$_6$S$_3$I$_6$ NWs by Raman spectroscopy (d) TEM images of wire growth after 48 h.
dispersion), and XRD data showed that the Mo$_6$S$_3$I$_6$ wire was synthesized. Therefore, it was confirmed that the change in the wire composition occurred within 48 h. Mo$_2$S$_3$ and Mo$_2$S$_5$I$_3$ were observed after 24 h, but decreased after 36 h, and the structural change to Mo$_6$S$_6$I$_2$ was confirmed. After 42 and 48 h, the Mo$_6$S$_3$I$_6$ phase was dominant, and it was observed that Mo$_6$S$_6$I$_2$ decreased and the crystallinity of the Mo$_6$S$_3$I$_6$ phase peaked after 48 h. In the Raman spectroscopy results, the peaks did not change. However, the peak intensities and S-breathing modes gradually decreased, contrasting the results depended on temperature. Thus, if the synthesis time is insufficient, the phase change is incomplete, whereas if it is excessive, bonds cannot be formed owing to the loss of iodine (energy instability). In the formed Mo$_6$S$_3$I$_6$ NWs, TEM showed a microstructure with an interatomic gap (0.932 nm), which is shown in figure 4(d) and S2[7, 23]. It was confirmed that MoI$_2$ material formed by the synthesis of Mo$_6$S$_3$I$_6$ did not appear, and that the mechanism was similar to that of CP synthesis. However, it was confirmed that Mo$_6$S$_3$I$_6$ NWs were synthesized by the new reaction formula.

3.2. Electrochemical test of Mo$_6$S$_3$I$_6$ nanowire
The cells were charged and discharged in a voltage range from 0.05 to 1.30 V versus Mg/Mg$^{2+}$, and the constant current was set at 15 mA g$^{-1}$ (1/5 C). Then, the battery characteristics were investigated. In figure 5(a), the Mo$_6$S$_8$ CP, which was used as a cathode in Mg batteries, exhibits two plateaus owing to the change in the mechanism of divalent Mg and does not confirm the change in mechanism. In addition, although the theoretical specific capacity per unit weight of the active Mo$_6$S$_3$I$_6$ material was $\sim$75 mAh g$^{-1}$, the specific capacity confirmed in the initial discharge was 219.4 mAh g$^{-1}$, which is double the improved electrical conduction of Mo$_6$S$_3$I$_6$ NW discharge capacity when using a Mo$_6$S$_8$ CP ($\sim$100 mAh g$^{-1}$). The specific capacity of typical insertion anode materials is lower than 100 mAh g$^{-1}$,[24] which is smaller than the specific capacity ($>300$ mAh g$^{-1}$) of metal alloy anodes. Nanowire materials were first studied a lot as an anode material in lithium–ion batteries. Among them, various materials such as CNT[25] and Si[26] are used, and the potential of Mo–S–I nanowires has also been shown through simulations[27]. However, despite the high theoretical capacity of MBs, insertion–type anode materials, such as layered–Na$_2$Ti$_3$O$_7$[28] and Li$_x$Ti$_3$O$_7$[29, 30] have been experimentally identified as alternatives. Nevertheless, they have a low diffusion kinetic energy owing to the strong electrostatic interaction between divalent Mg$^{2+}$ and their anions/cations[31]. Hence, in figure 5(b), a voltage of 0.14 V was obtained in

Figure 5. (a) Galvanostatic charge and discharge profiles at a constant current of 0.2 C (15 mAh g$^{-1}$) and (b) dQ/dV profile within a discharging range of 0.05 to 1.30 V versus Mg/Mg$^{2+}$ (c) Cycle performance of Mo$_6$S$_3$I$_6$ NWs and coulombic efficiency, and (d) the rate of capability at current densities in the range of 1/15 to 2 C (1C = 75 mA g$^{-1}$).
the first cycle and that of 0.07 V in the second cycle. As shown in figure 5(c), the capacity rapidly decreased from the second cycle, theoretical values at the 10th cycles, and capacity of ~44.5 mAh g⁻¹ is maintained without loss after 25 cycles. The coulombic efficiency remained above 90%. Further, these capacities were confirmed by varying current density, as shown in figure 5(d). In the insertion mechanism of Mo₆S₉, ions interact with both the surface of the CP and the electrolyte salt (MgCl₂) and solvent (THF). Cations such as solvated MgCl⁺ and Mg₆Cl₄⁻ are attracted to the negatively charged surface of the CP, which in turn weakens their interactions with solvent molecules, promoting the Mg dissolution process. Here, Mg ions bind to sulfur ions, and Cl⁻ bonds move to the Mo surface. Moreover, it does not interfere with Mg insertion because the solvated MgCl⁺ and Mg₆Cl₄⁻ interact [32]. Based on this principle, we used a suitable electrolyte (0.4 M APC), and expected more Mg intercalation because sulfur and iodine ions have negative charge. Therefore, the capacity of Mo₆S₇I₆ NWs is similar to that of insertion cathode materials (Na₂Ti₅O₁₂, Li₄Ti₅O₁₂), even though their potentials are widely different. To improve the electrochemical properties of NW, further investigation is required.

4. Conclusions

We synthesized and analyzed Mo₆S₇I₆ NWs and found that second phases such as MoI₂ appear at 900 °C, and synthesis was performed under various conditions. Mo₆S₉I₆ NWs were synthesized with MoS₂ and Mo₂S₃ phases below 1000 °C, and the Mo₂S₉I₆ seed phase remained up to 1050 °C. We employed SEM, XRD, and Raman spectroscopy to confirm that the crystallinity of the nanowires improved at 1100 °C. At 1100 °C, various compounds were formed before Mo₆S₇I₆ NWs formed. The synthesis of Mo₆S₇I₆ NWs was optimized at 1100 °C for 48 h. The nanowire was used as an active material and the electrochemical test showed a specific capacity of 219.4 mAh g⁻¹ at 0.07 V. We showed that Mo₆S₇I₆ NWs are suitable as MIB anodes and can be used with high–voltage cathode materials (MoS₂ [33], WSe₂ [34], and Ti₃C₂Tₓ [35–38]) in APC electrolytes. Mo₆S₇I₆ are expected to be utilized in various applications [39–44].

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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