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Re-examination of copper Chevrel-phase sulfides as cathode in lithium secondary batteries

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Abstract

As cathode of lithium secondary batteries, copper Chevrel-phase sulfide $\text{Cu}_x\text{Mo}_6\text{S}_8$ (CMS) and its host cluster Mo_6S_8 (MS) were re-examined. These cells could be galvanostatically discharged up to $x=4.2\text{--}5.0$ (Li_xCMS) when the current density was 0.1 mA/cm^2 with a cutoff voltage at 1.5 V. In a deep cycling test in MS and CMS carried out between 1.5 and 2.6 V at 0.5 mA/cm^2 , the cell discharge capacity remained fairly constant up to at least 250 cycles, except decreasing during a few initial cycles.

Keywords: Secondary lithium batteries; Copper; Molybdenum sulfide

1. Introduction

A large number of chalcogenides with three-dimensional frameworks, e.g., molybdenum cluster sulfides, $\text{M}_x\text{Mo}_6\text{S}_{8-z}$ (Chevrel phase, M = metal) with a hexagonal or rhombohedral unit cell have been examined as cathode in organic electrolyte lithium secondary batteries at room temperature [1–6]. These host materials ($\text{Mo}_6\text{S}_{8-z}$) contain two kinds of tetrahedrally coordinated M sites which can accept lithium ions by an intercalation reaction [7].

In our earlier work of phase diagrams of the Cu–Mo–S system, copper Chevrel-phase sulfides $\text{Cu}_x\text{Mo}_6\text{S}_{8-z}$ had rather wide non-stoichiometric compositions both for copper and sulfur [8]. For the stoichiometric sulfur atoms which occupy eight corners of a cluster Mo_6S_8 (MS), the $\text{Cu}_4\text{Mo}_6\text{S}_8$ (CMS) was only a stable compound at 1000 °C. Copper atoms in the M site can be easily leached out by an acid solution [8] or by a mixed solution of iodine and acetonitrile [9]. The substitution of protons in the M sites takes place when any acid solution is used, whereas only bare Mo_6S_8 , stabilized by Mo–S Coulomb forces among neighbouring clusters, is obtained when the latter solution is used. Some investigators [10] have pointed out that the cathode with copper Chevrel-phase sulfides can be recharged for only a limited number of cycles because of the

deposition of metallic copper occurring with the intercalation of lithium ions.

Tarascon et al. [1] have only tried 10 cycles with Mo_6S_8 . It was reported by Mulhern et al. [11] that the capacity of the Li/MS cell decayed with the increasing of cycle numbers. It was pointed out that the long cycle life was obtained only at shallow cycling [12]. However, the deposited copper from the cluster may act as a current corrector for long cycle life when a suitable potential range is selected. The cycling of CMS results in a discharge/charge cycling of MS after several cycles. So far, a generalized evaluation of the cathode properties for CMS and MS has not yet been made.

In the present paper, the cycling behaviour of well-characterized $\text{Cu}_4\text{Mo}_6\text{S}_8$ and Mo_6S_8 has been re-examined, and it is suggested that these materials are one of the promising cathode materials in the lithium secondary cells.

2. Experimental

CMS was synthesized by the high-temperature solid-state reaction as previously published [10]. The powders by mixing Cu, Mo and S in stoichiometric ratio were sealed in evacuated quartz ampoules. At first, the ampoule was preheated at 400 °C for 12 h and then heated to 1000 °C for two days followed by rapid quenching. After regrinding, the resultant compound was heated at the same temperature for another three

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days followed by quenching. The phase identification of the product and the evaluation of the hexagonal lattice parameters were carried out by powder X-ray diffractometry (XRD) using Cu $K\alpha$ radiation. MS was prepared by leaching out the copper from CMS using iodine in an acetonitrile medium. No decomposition of CMS was observed during leaching.

The MS or CMS powder was mixed with 8 wt.% of acetylene black and 7 wt.% of Teflon powder and then pressed into a film. A disc was cut from the film and used as the cathode. Lithium foil was used as the anode. 1 M LiClO_4 in propylene carbonate (PC) was used as the electrolyte. The galvanostatic measurement of a lithium rechargeable cell is almost the same as described earlier [4,5].

3. Results and discussion

The hexagonal lattice parameters of CMS and MS were $a_H = 9.75$, $c_H = 10.26$ Å and $a_H = 9.19$, $c_H = 10.88$ Å, respectively. XRD shows that single-phase products were obtained.

Fig. 1 shows the deep cycling behaviour of $\text{Li}/\text{Cu}_4\text{Mo}_6\text{S}_8$ cell for the first two cycles in the voltage range from 1.5 to 2.6 V at a current density of 0.1 mA/cm^2 . The cell voltage drops abruptly at the beginning of the first discharge corresponding to $0 < x < 0.1$. There exists a second voltage drop at around 1.7 V. After this, the cell voltage plateaued until discharging to $x \approx 4$. The cell voltage of the second cycle increases to 2.2 V compared with the first cycle near at $x = 1$. The cycling behaviour of $\text{Li}/\text{Mo}_6\text{S}_8$ cell for first two cycles is shown in Fig. 2. There exist three intermediate phases of Li_xCMS . There is no doubt about the non-existence of protons in Mo_6S_8 obtained in our laboratory, which is different from other reports [8,13] indicating that Mo_6S_8 was obtained by removing Cu using inorganic acid. When Mo_6S_8 is discharged at 0.1 mA/cm^2 , as much as 4.2. Li ions per formula unit of Mo_6S_8 were incorporated at the cutoff voltage of 1.5 V (Fig. 2).

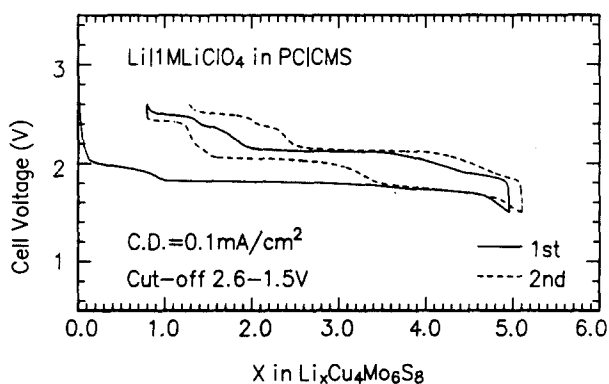


Fig. 1. Cell voltage vs. lithium concentration x in $\text{Li}_x\text{Cu}_4\text{Mo}_6\text{S}_8$ for the first two cycles.

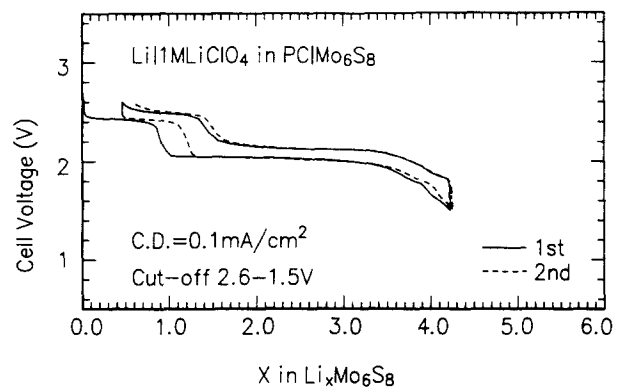


Fig. 2. Cell voltage vs. lithium concentration x in $\text{Li}_x\text{Mo}_6\text{S}_8$ for the first two cycles.

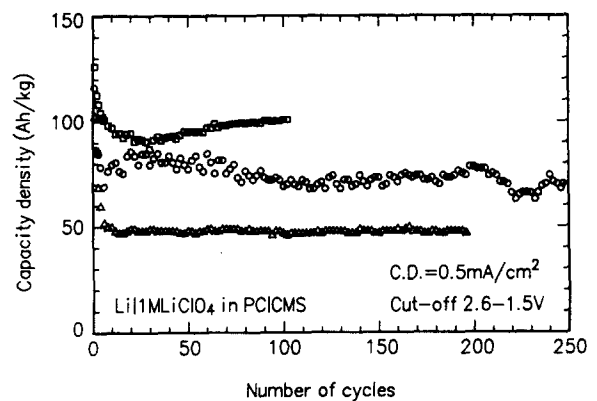


Fig. 3. Capacity density vs. cycle number for Mo_6S_8 and $\text{Cu}_4\text{Mo}_6\text{S}_8$ at a current density of 0.5 mA/cm^2 , and for Mo_6S_8 at 0.2 mA/cm^2 .

The existence of two intermediate phases in Li_xMS was suggested. The discharge/charge profile of MS, in the present study, agreed well with that of Tarascon et al. [1].

The relationship between capacity and cycles of Mo_6S_8 and $\text{Cu}_4\text{Mo}_6\text{S}_8$ at a current density of 0.5 mA/cm^2 is shown in Fig. 3. Both MS and CMS show good cycling characteristics. The cell capacity plateaued up to at least 250 cycles, except it decreased during the first cycles. It shows that CMS does not behave completely as MS because Cu ions cannot completely be deposited even in deep cycling at a cutoff voltage of 1.5 V because, after the 100th cycle, the existence of CMS can be still suggested from the XRD patterns. The capacity density of MS which includes no Cu in the cluster is great compared with that of CMS. Thus, MS without protons in the structure seems to be a promising cathode material in lithium secondary cells.

Fig. 3 also shows the relationship between capacity density and cycle number of Mo_6S_8 at a current density of 0.2 mA/cm^2 . The theoretical energy density of the cathode at 20th, 50th and 100th cycle were 189.5, 193.9 and 207.1 Wh/kg, respectively.

4. Conclusions

The cathode properties of Chevrel-phase sulfides, $\text{Cu}_4\text{Mo}_6\text{S}_8$ and Mo_6S_8 in lithium secondary batteries were re-examined and their promising properties were recognized at room temperature. Especially Mo_6S_8 that does not contain any proton in the structure showed a long cycle life with an energy density of almost 200 Wh/kg in the potential range between 2.6 and 1.5 V.

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