A RECHARGEABLE LITHIUM BATTERY EMPLOYING A POROUS THIN FILM OF $Cu_{3+\delta}Mo_6S_{7.9}$

MASATAKA WAKIHARA, TAKASHI UCHIDA, TAKASHI MORISHITA, HIDEAKI WAKAMATSU and MASAO TANIGUCHI

Department of Chemical Engineering, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152 (Japan)

Summary

Porous, thin films of copper molybdenum sulfides ($Cu_{3+\delta}Mo_6S_{7.9}$), that have been prepared by the technique of painting and subsequent reaction with mixed H_2/H_2S gases at 500 °C, have been used as a cathode material for lithium secondary batteries. The test cell comprised: $Li/2$ M $LiClO_4$ in PC–THF (4:6)/$Cu_{3+\delta}Mo_6S_{7.9}$ (porous, thin film). The discharge reaction proceeded via the intercalation of lithium ions into the structural interstices of the cathode material.

The first discharge curve of the cell showed that the porous film could incorporate up to ~18 lithium ions per formula unit. The capacity of the thin film was four times higher than that previously reported for powder or pressed-pellet electrodes. The theoretical energy density was 675 W h kg^{-1}, *i.e.*, higher than that of TiS_2 (455 W h kg^{-1}) which is one of the best materials for high-energy lithium batteries. From X-ray diffraction studies of the lithium incorporated in the thin film at each discharge step, it is suggested that there are four incorporation reactions of lithium ions into the cathode. Finally, cycling tests have been conducted at room temperature.

Introduction

Factors determining the practicality of secondary electrochemical cells based on lithium intercalation systems include cell voltage, energy density, and cycle life. Recently, a large number of chalcogenides with three-dimensional frameworks, *e.g.*, molybdenum cluster sulfides, $M_xMo_6S_{8-y}$ (Chevrel phases), have been examined as the cathode material for secondary organic electrolyte lithium batteries [1 - 6]. The lithium ions are reversibly inserted in the structural vacant sites of these host materials. Copper molybdenum sulfide, $Cu_xMo_6S_{8-y}$ (CMS), is one of these intercalation host materials and is composed of nearly cubic Mo_6S_8 building blocks [7]. However, the application of CMS as the cathode in almost all secondary cells has been limited to the use of bulk specimens or pressed powders of the material. It is highly possible that a porous thin film of CMS, if capable of being prepared effectively, will serve as a suitable cathode when developing a

compact battery with a high energy capacity. Recently, our research group determined the non-stoichiometric ranges of CMS [8], and also succeeded in preparing porous and coherent thin films of CMS by the techniques of painting and subsequent reaction with mixed H_2S/H_2 gases [9].

In the present study, the CMS films were examined as cathode materials for lithium secondary batteries using organic liquid electrolytes. The mechanisms of lithium intercalation into the films were investigated by X-ray powder diffractometry.

Experimental

Powdered $Cu_3Mo_6S_{7.9}$ was prepared according to a method described previously [8]. Porous thin films of $Cu_{3+\delta}Mo_6S_{7.9}$ (CMS: $0 < \delta < 0.1$) were produced by painting the powder onto a Cu_2S layer followed by reaction with mixed H_2/H_2S gases. Full details of this procedure have been published elsewhere [9].

The porous CMS films were tested as the cathode material of lithium secondary batteries represented by the equation:

Li| LiClO$_4$ in organic solvent|CMS (porous thin film)   (I)

The cell design was similar to that reported in ref. 6. The electrolyte comprised 1 M LiClO$_4$ dissolved in propylene carbonate (PC) or tetrahydrofuran (THF). In addition, 2 M LiClO$_4$ dissolved in a 4:6 by volume mixture of PC and THF was used, according to the paper of Tobishima *et al.* [10]. These authors found that the ionic conductivity of this electrolyte is quite high (*i.e.*, 9.8×10^{-3} S cm^{-1}). The LiClO$_4$ was dried under vacuum at 150 °C for 12 h before use. The organic solvents were dehydrated with activated alumina powder. The prepared electrolytes were further purified by pre-electrolysis using a pair of lithium electrodes at a constant current of 5 μA. The discharge and discharge/charge cycling properties were measured galvanostatically at current densities (c.d.) of 0.3 - 7 mA cm^{-2}. The cell construction and all the measurements were carried out in an argon-filled dry box. The amount of lithium incorporated in the cathode was calculated from the charge transferred in the cell.

Since the lithium-incorporated CMS films produced in the electrochemical cells were sensitive to air and moisture, the X-ray diffraction (XRD) analysis of the Li_xCMS films of various lithium compositions was accomplished by covering the sample with a polyethylene film, each end of which was sealed with silicone grease (Dow Corning Co.). In order to obtain a clear diffraction pattern through the polyethylene film, a high power X-ray generator (50 kV, 100 mA: Rotaflex RU-200, Rigaku Co.) was employed.

Results and discussion

The XRD pattern showed that the prepared thin film consisted of a pure copper Chevrel phase with hexagonal lattice parameters of $a = 9.770$ Å

and $c = 10.22$ Å; these values are in good agreement with those reported in the literature [4]. An electron micrograph of the CMS film (Fig. 1(a)) revealed that the painted CMS particles sintered to form an uneven layer on the substrate. An electron micrograph of the cross-section (Fig. 1(b)) clearly demonstrated the porous nature of the CMS film. The thickness of the film was 70 - 80 μm.

Figure 2 shows a typical first discharge curve of cell (I) using 2 M LiClO$_4$ in 4:6 PC:THF as the electrolyte at a c.d. of 1.0 mA cm^{-2}. For comparison, the literature data obtained by using powdered Chevrel phase compounds as cathode materials [4 - 6] are also given. It should be noted that before the cell voltage dropped to 1 V, as many as 18 lithium ions per formula unit of CMS (Li/CMS) were incorporated in the film used in this study. This value is about four times higher than those reported in the literature. The discharge curve is quite flat with a cell voltage of 1.83 - 1.58 V in the range $x < 15$, where x represents the composition of lithium in the cathode material with the formula $Li_x Cu_{3+\delta} Mo_6 S_{7.9}$. The discharge curves
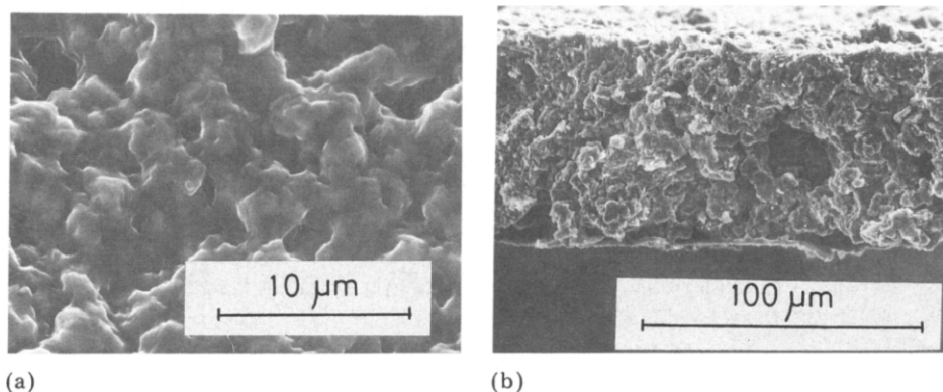

(a)   (b)

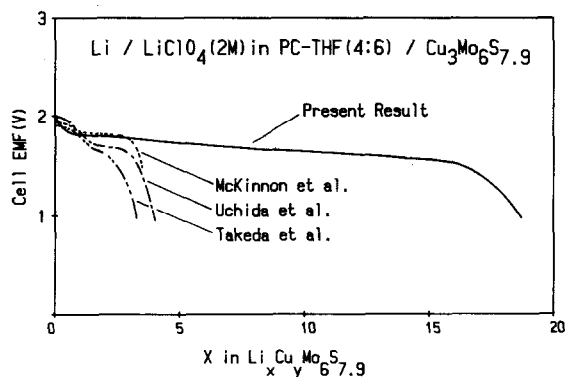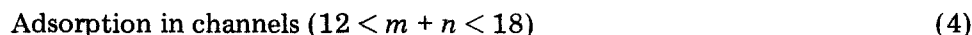Fig. 1. Electron micrographs of (a) surface and (b) cross-section of porous $Cu_3 Mo_6 S_{7.9}$ thin film.

Fig. 2. Discharge curve of Li/$Cu_3 Mo_6 S_{7.9}$ cell in 2 M LiClO$_4$/PC–THF (4:6); c.d. = 1.0 mA cm^{-2}.

were fairly reproducible and, in every run, incorporation of 18 ± 1 Li/CMS was observed (cut-off voltage: 1 V). Based on the discharge curve shown in Fig. 2, the theoretical energy density was calculated to be 675 W h kg^{-1}. This value is higher than that of TiS$_2$ (455 W h kg^{-1}) which is one of the most promising cathode materials for lithium secondary batteries.

Discharge of cell (I) using 2 M LiClO$_4$ in 4:6 PC:THF was also carried out at various c.d., *i.e.*, 3, 5, 6 and 7 mA cm^{-2}. When the c.d. was increased to 7 mA cm^{-2}, the amount of incorporated lithium decreased abruptly to 4 Li/CMS (cut-off voltage: 1 V), whereas more than 10 Li/CMS were incorporated at a c.d. below 6 mA cm^{-2}.

The following four cell reactions are proposed for the mechanism of lithium incorporation into the cathode:

$$x\text{Li}^+ + xe^- + \text{Cu}_3\text{Mo}_6\text{S}_{7.9} \longrightarrow \text{Li}_x\text{Cu}_3\text{Mo}_6\text{S}_{7.9}\ (x < 2) \tag{1}$$

$$\text{Li}_x\text{Cu}_3\text{Mo}_6\text{S}_{7.9} + y\text{Li}^+ + ye^- \longrightarrow \text{Li}_{x+y}\text{Cu}_{3-y}\text{Mo}_6\text{S}_{7.9} +$$
$$+ y\text{Cu}\quad (2 \leqslant x + y < 5) \tag{2}$$

$$\text{Li}_m\text{Mo}_6\text{S}_{7.9} + n\text{Li}^+ + ne^- \longrightarrow \text{Li}_{m+n}\text{Mo}_6\text{S}_{7.9}\ (5 \leqslant m + n \leqslant 12, m \geqslant 5) \tag{3}$$

$$\text{Adsorption in channels } (12 < m + n < 18) \tag{4}$$
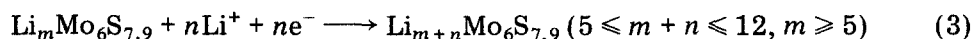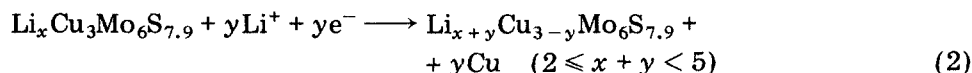
According to Takeda *et al.* [5], lithium ions in the range $0 < x < 2$ intercalate into the CMS film (reaction (1)) without any sub-reaction, and when the x value exceeds 2, the lithium intercalation is accompanied by copper deposition (reaction (2)). In the latter reaction, the amount of copper deposited is expressed by y. We also identified metallic copper in the range of $x > 2$. On the other hand, the XRD pattern of Li$_x$CMS revealed that a pure lithium Chevrel phase, Li$_x$Mo$_6$S$_{7.9}$, having different lattice parameters from those of the copper Chevrel phase (the crystal structure is the same), formed when $x + y \geqslant 5$. Therefore, the range of $x + y$ in which reaction (2) occurs would be $2 \leqslant x + y < 5$. For $x \geqslant 5$ (*i.e.*, $m + n \geqslant 5$ in reaction (3)), the intercalation of lithium into the lithium Chevrel phase proceeds according to reaction (3). The findings of Yvon *et al.* [7] show that lithium ions are intercalated in two possible locations in the crystal structure, each of which comprises 6 sites. On the other hand, the compositional variation of the lattice parameters of Li$_x$Mo$_6$S$_{7.9}$ (Fig. 3) shows that the hexagonal lattice parameters a and c change continuously up to x ($= m + n$) $\simeq 12$ and then become constant in the range x ($= m + n$) > 12. On the basis of the above discussion, lithium intercalation in Li$_x$Mo$_6$S$_{7.9}$ (reaction (3)) is assumed to occur when $5 \leqslant x$ ($= m + n$) $\leqslant 12$. For $x(= m + n) > 12$, adsorption of lithium ions takes place in channels that exist in the porous CMS film (reaction (4)).

Pure PC and THF were also employed as the organic solvent of the electrolyte. The first discharge curves are given in Fig. 4 and Fig. 5, respectively. The amount of lithium incorporation at a c.d. of 1.0 mA cm^{-2} was about 14 and 13 Li/CMS when 1 M LiClO$_4$ was dissolved in PC and THF, respectively. The THF-based electrolyte was found to react gradually with the cathode material.
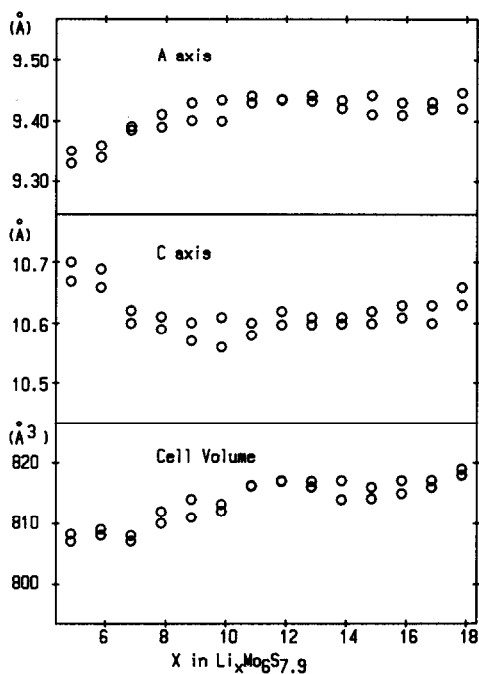
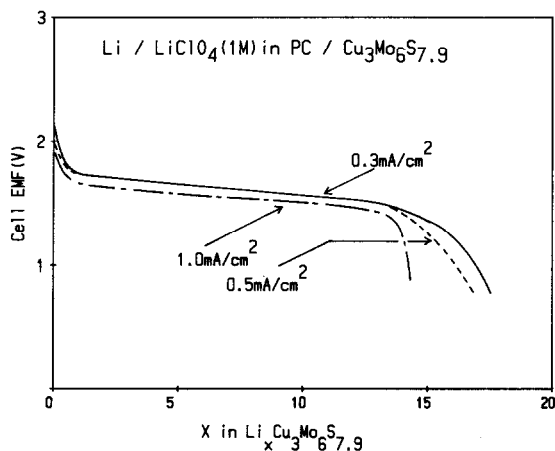Fig. 3. Plot of lattice parameters and cell volume *vs.* x in $Li_xMo_6S_{7.9}$.

Fig. 4. Discharge curves of $Li/Cu_3Mo_6S_{7.9}$ cell in 1 M $LiClO_4/PC$; c.d. = 0.3, 0.5 and 1.0 mA cm^{-2}.

Discharge/charge cycling studies were also performed. Figure 6 shows the results obtained when using 2 M $LiClO_4$ dissolved in 4:6 PC:THF at a c.d. of 1.0 mA cm^{-2}. The cycling test was carried out in the short range of $1 < x < 2$ (x in Li_xCMS). Stable discharge/charge profiles were maintained until about the 300th cycle, but a severe decline in the cell voltage was observed after the 350th cycle.
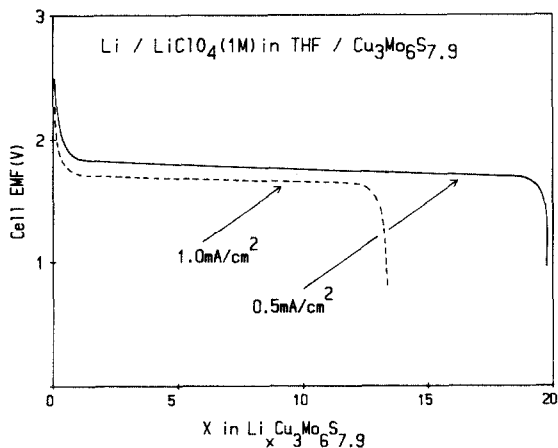
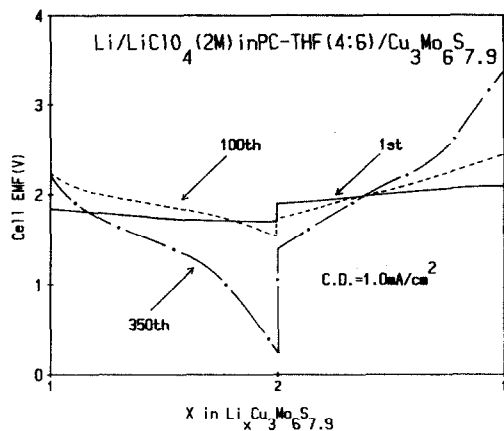Fig. 5. Discharge curves of Li/Cu$_3$Mo$_6$S$_{7.9}$ cell in 1 M LiClO$_4$/THF; c.d. = 0.5 and 1.0 mA cm^{-2}.

Fig. 6. Cycling behaviour of Li/Cu$_3$Mo$_6$S$_{7.9}$ cell in 2 M LiClO$_4$/PC–THF (4:6); c.d. = 1.0 mA cm^{-2}.

References

1 R. Schöllhorn, M. Kümpers and J. O. Besenhard, *Mater. Res. Bull.*, *12* (1977) 781.

2 J. M. Tarascon, F. J. Disalvo, D. W. Murphy, G. W. Hull, E. A. Rietman and J. V. Waszczak, *J. Solid State Chem.*, *54* (1984) 204.

3 S. T. Coleman, W. R. Mckinnon and J. R. Dahn, *Phys. Rev. B*, *29* (1984) 4147.

4 W. R. Mckinnon and J. R. Dahn, *Solid State Commun.*, *52* (1984) 245.

5 Y. Takeda, R. Kanno, M. Noda and O. Yamamoto, *Mater. Res. Bull.*, *20* (1985) 71.

6 T. Uchida, K. Watanabe, M. Wakihara and M. Taniguchi, *Chem. Lett.*, (1985) 1095.

7 K. Yvon and A. Paoli, *Solid State Commun.*, *24* (1976) 41; K. Yvon, A. Paoli, R. Flükiger and R. Chevrel, *Acta Crystallogr.*, *B33* (1977) 3066.

8 S. Yamamoto, K. Matsui, M. Wakihara and M. Taniguchi, *Mater. Res. Bull.*, *18* (1983) 1311.

9 M. Wakihara and T. Morishita, *J. Electrochem. Soc.*, *133* (1986) 2104.

10 S. Tobishima and A. Yamaki, *Electrochim. Acta*, *28* (1983) 1067.