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DISCHARGE PROPERTIES OF $Mo_6S_{8.0}$ AND $Cu_yMo_6S_{7.75}$ (y=1.05 AND 2.0) IN LITHIUM SECONDARY CELLS

Takashi UCHIDA, Kazuo WATANABE, Masataka WAKIHARA,
and Masao TANIGUCHI
Department of Chemical Engineering, Tokyo Institute of Technology,
Ookayama, Meguro-ku, Tokyo 152

The discharge properties of stoichiometric $Mo_6S_{8.0}$, a mixture of $Mo_6S_{7.75}$ and $Cu_{2.0}Mo_6S_{7.75}$ having the chemical formula on average of $Cu_{1.05}Mo_6S_{7.75}$, and $Cu_{2.0}Mo_6S_{7.75}$ in lithium secondary cells were examined in the first cycle. When stoichiometric $Mo_6S_{8.0}$ was discharged at a current density of 0.5 mA cm^{-2}, as much as 3.9 lithium ions per formula unit of $Mo_6S_{8.0}$ were incorporated at a cut-off voltage down to 1 V.

The binary cluster compound Mo_6S_8 is expected to be a potential cathode material of lithium secondary batteries.[1)] Several authors[1-4)] have reported the behavior of Mo_6S_8 as a cathode material of lithium secondary cells. Since Mo_6S_8 is thermally unstable,[2)] it has been prepared indirectly from ternary molybdenum sulfides, $M_yMo_6S_8$ (M=Cu,Ni,...), by removing the third element M. The ternary molybdenum sulfides are usually found as sulfur deficient compounds $M_yMo_6S_{8-z}$. In the case of copper molybdenum sulfide, $Cu_yMo_6S_{8-z}$, the relationship between y and 8-z at 1000 °C have been investigated by Yamamoto et al.[5)] in our laboratory. They reported that the stoichiometric compound was obtained when y=4, i.e. $Cu_4Mo_6S_{8.0}$, while a deficiency of sulfur was observed in the compounds in the range of $2 \leqq y \leqq 3$. Tarascon et al.[6)] reported that stoichiometric $Cu_2Mo_6S_8$ was prepared at 1250 °C, which was not obtained at 1000 °C by Yamamoto et al.[5)] We have tried in the preliminary experiments to prepare stoichiometric $Cu_2Mo_6S_8$ at 1200 and 1250 °C. It was found that at 1200 °C a single phase of $Cu_2Mo_6S_{8.0}$ could not be obtained, and that at 1250 °C the quartz tube used as the container of the reaction severely reacted with the sample, and pure copper molybdenum sulfide could not be obtained. Accordingly, it would be difficult to prepare stoichiometric $Cu_2Mo_6S_8$ even at higher temperatures around 1200 °C. The Mo_6S_8 compounds tested to date as the cathode material of lithium secondary cells were prepared from $Cu_2Mo_6S_{8-z}$,[1-3)] $Cu_3Mo_6S_{8-z}$,[4)] or $NiMo_3S_4$.[2)] Though the exact composition of the last compound was not reported, it seems that well characterized stoichiometric Mo_6S_8 has not been studied yet as a cathode material of the lithium secondary cells.

In this study, stoichiometric $Mo_6S_{8.0}$, $CuMo_6S_{7.75}$, and $Cu_2Mo_6S_{7.75}$ were tested as cathode materials of a lithium secondary battery.

$Cu_4Mo_6S_{8.0}$ and $Cu_2Mo_6S_{7.75}$ were prepared in the same method as that reported in the previous paper.[5] Stoichiometric Mo_6S_8 was obtained by leaching out copper from $Cu_4Mo_6S_{8.0}$ with 6 mol dm^{-3} hydrochloric acid for 10 d. $CuMo_6S_{7.75}$ was prepared by a partial leaching of $Cu_2Mo_6S_{7.75}$ with the same acid for 1 h. The composition of Mo_6S_8 was determined by oxidizing the sample (≈60 mg) in air at 500 °C for 45 min to get stoichiometric MoO_3. From the weight change before and after the oxidation, it was estimated to be $Mo_6S_{8.03(\pm 0.05)}$. This compound is considered to be stoichiometric within the experimental limitations and is expressed as $Mo_6S_{8.0}$ in this paper. The residual amount of copper in $Mo_6S_{8.0}$ and y value in $Cu_yMo_6S_{7.75}$ were determined by atomic absorption. The amount of the residual copper in $Mo_6S_{8.0}$ was less than 0.02 per the formula unit of $Mo_6S_{8.0}$. The copper content of $CuMo_6S_{7.75}$ was found to be $Cu_{1.05}Mo_6S_{7.75}$. The X-ray diffraction pattern showed that $Cu_{1.05}Mo_6S_{7.75}$ was a mixture of $Mo_6S_{7.75}$ and $Cu_{2.0}Mo_6S_{7.75}$, but, we designate this mixture as $Cu_{1.05}Mo_6S_{7.75}$. The electrochemical cell used in this study is shown in Fig.1. A mixture of 8 mg of the cluster compound and 20 wt% of teflon powder was pressed onto a nickel mesh at a pressure of 5×10^8 Pa and used as the cathode. Lithium metal (Wako pure chemicals, 99%) was used as the anode. On the basis of a study of Tobishima and Yamaji,[6] 2 mol dm^{-3} $LiClO_4$ solution of propylene carbonate(PC)-tetrahydrofuran(THF) mixture with the mixing ratio of PC/THF = 4/6 was used as the electrolyte. The solution was dehydrated with activated alumina powder. It was further purified by preelectrolysis using a pair of lithium electrodes at a constant current (≈5μA) until just before use. All the cell construction and measurements were carried out in an argon-filled dry box.

The discharge curves of $Mo_6S_{8.0}$, $Cu_{1.05}Mo_6S_{7.75}$, and $Cu_{2.0}Mo_6S_{7.75}$ measured under constant currents in the first cycle are given in Fig.2. It is shown that the cell voltage of $Cu_{1.05}Mo_6S_{7.75}$ during the discharge lies in between those of $Mo_6S_{8.0}$ and $Cu_{2.0}Mo_6S_{7.75}$. $Mo_6S_{8.0}$ exhibits the highest cell voltage among these three compounds before the cell voltage falls down sharply at the end of discharge. It should be noted that, when $Mo_6S_{8.0}$ is discharged at 0.5 mA cm^{-2}, as much as 3.9 lithium ions per the formula unit of $Mo_6S_{8.0}$ were incorporated at the cut-off voltage of 1 V. So far, following values have been reported for the incorporation of lithium per the formula unit of Mo_6S_8 measured by constant current discharge. 3.6 Li per Mo_6S_8 (Takeda et al.,[1] at 1 V cut-off, 0.2 mA cm^{-2}), 3.4 Li per Mo_6S_8 (Tarascon et al.,[3] at 1 V cut-off, 1 mA cm^{-2}), 3.4 Li per Mo_6S_8 (McKinnon et al.,[4] at 1.5 V cut-off, discharged at 3 h rate[4]). Incorporation of 3.9 Li per Mo_6S_8 observed in this study is the highest value

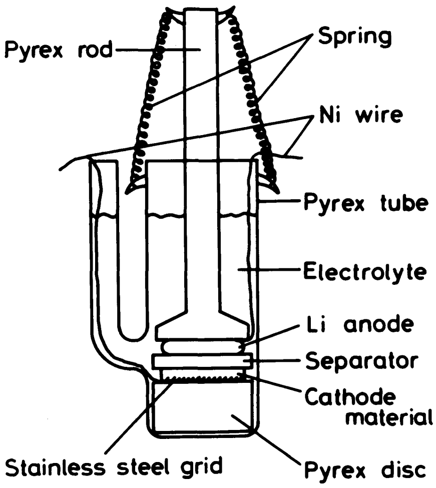

Fig. 1. Electrochemical cell.

ever reported. Accordingly, it could be concluded that the stoichiometric $Mo_6S_{8.0}$ obtained in this study exhibited the largest discharge capacity among Mo_6S_8 compounds investigated so far. Another characteristic feature of the discharge curves of $Mo_6S_{8.0}$ is that the curves are quite flat and exhibit considerably high cell voltage at relatively high current densities such as 1 mA cm^{-2}. Three different plateaus with approximate voltages of 2.4, 2.0 and 1.8 V are observed in Fig.2. The appearance of each plateau seems to correlate with total amount of lithium(x) and copper(y) when the compounds are represented by $Li_xCu_yMo_6S_{8-z}$. The relationship between the appearance of each plateau and the ranges of x, y, and (x+y) are tabulated in Table 1. Table 1 suggests that the EMF of the cell, $Li/Cu_yMo_6S_{8-z}$, is closely related to the total amount of metal ions which occupy the vacant metal sites among the three dimensionally arrayed Mo_6S_8 clusters of the Chevrel compounds.[8] Takeda et al.[1] reported a lithium-copper exchange reaction which would occur when $Cu_yMo_6S_{8-z}$ is discharged in lithium secondary cells. For example, for the discharge of $Cu_2Mo_6S_{7.8}$, the following equation is proposed by them.

$$2Li^+ + Li_2Cu_2Mo_6S_{7.8} + 2e^- = Li_4Cu_{2-y}Mo_6S_{7.8} + yCu$$

In this study, the presence of metallic copper was also observed when $Cu_2Mo_6S_{7.75}$ was discharged so as to give $x \simeq 4$. Accordingly, the ranges of (x+y) given in Table 1 are thought to be the highest limit and the actual values will be smaller than those given in this table.

The variation of the lattice parameters of $Li_xMo_6S_{8.0}$ as a function of the lithium composition x is shown in Fig.3. $Li_2Mo_6S_{8.0}$ and $Li_{2.5}Mo_6S_{8.0}$ were found to be the mixtures of two kinds of cluster compounds having different lattice parameters, as shown in Fig. 3. These results agree well with those of Tarascon et al.[3] who reported the existence of the same two phase mixtures in the range of $1<x<2.6$. On the other hand,

Table 1. Relationship between the appearance of each plateau and the ranges of x, y, and (x+y).

	plateau 1 (≃2.4 V)	plateau 2 (≃2.0 V)	plateau 3 (≃1.8 V)
$Mo_6S_{8.0}$ (y=0.02)	x<0.7	x>1	---
$Cu_{1.05}Mo_6S_{7.75}$ (y=1.05)	---	x<2	x>2.5
$Cu_{2.0}Mo_6S_{7.75}$ (y=2.0)	---	x<1	x>3.5
	(x+y)<0.7	1<(x+y)<3	(x+y)>3.5

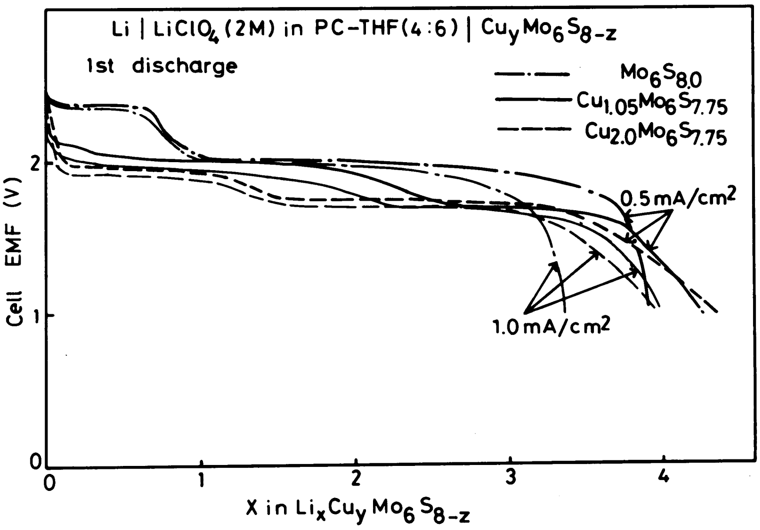

Fig. 2. First discharge curves of $Mo_6S_{8.0}$, $Cu_{1.05}Mo_6S_{7.75}$ and $Cu_{2.0}Mo_6S_{7.75}$ at the current densities of 0.5 and 1 mA/cm^2.

Cheung and Steele[7)] reported the existence of a single phase, $Li_{2.3}Mo_6S_{7.7}$, which they prepared by reacting $Mo_6S_{7.7}$ with n-butyl lithium. In this study, the discharge of $Mo_6S_{8.0}$ was continued up to x=2, and then the cathode was left under open circuit conditions for 40 h. No significant homogenization was observed, however, by the X-ray diffraction analysis. Accordingly, $Li_xMo_6S_8$ would behave as a two phase mixture in the range of $1<x<2.6$, in practical cells.

The discharge curves of $Cu_{1.05}Mo_6S_{7.75}$ and $Cu_{2.0}Mo_6S_{7.75}$ in Fig.2 extend to larger x than those of $Mo_6S_{8.0}$. Similar phenomenon is also observed in the discharge curves between $Mo_6S_{7.8}$ and $Cu_xMo_6S_{8-z}$ reported by Takeda et al.[1)] This would suggest the occurrence of some side reactions during the discharge of copper Chevrel compounds, although details are not clear at present.

Tarascon et al.[5)] suggested that ion exchange of the cation by protons might also take place as a side reaction when $M_yMo_6S_8$ was leached with mineral acids. It is difficult to say whether or not this exchange reaction occured in the present cell. However, the present results show that this reaction if any has no significant influence on the cathode properties of Mo_6S_8, because $Mo_6S_{8.0}$ prepared in this study ehxibited rather high discharge capacity compared to the Mo_6S_8 compounds prepared by different methods.[1,3,4)]

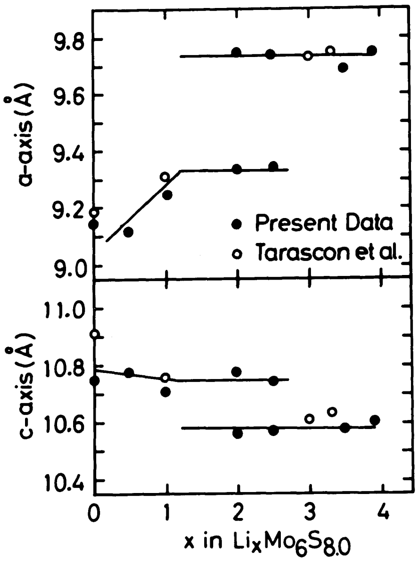

Fig. 3. The compositional variation of lattice parameters of $Li_xMo_6S_{8.0}$ as a function of lithium composition x.

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