

LITHIUM-COPPER MOLYBDATE AND LITHIUM-COPPER TUNGSTATE ORGANIC SOLVENT BATTERIES

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Summary

The characteristics and performances of the Li/CuMoO₄ and Li/CuWO₄ couples in LiAsF₆- γ -butyrolactone are reported in terms of discharge mechanism, polarization and cathode efficiency. On the basis of the energetic properties, these copper oxysalts may be regarded as very promising cathodes for the development of high energy lithium power sources.

Introduction

In previous work [1], the electrochemical properties of lithium-silver molybdate and lithium-silver tungstate couples in various organic electrolytes were investigated. The results showed the excellent cathodic behaviour of the two silver oxysalts in terms of stability and discharge characteristics in the LiAsF₆- γ -butyrolactone electrolyte.

It therefore appeared of interest to extend the study to the analogous copper salts which have the considerable advantage of being of lower weight and cost. This study has been directed to the investigation of the discharge mechanism and to the analysis of the characteristics and performance of copper molybdate and copper tungstate coupled with lithium in various organic electrolytes.

Experimental

The preparation of the two copper salts has required particular care. First, a precipitation procedure, analogous to that adopted for the preparation of the silver salts [1], was attempted. The addition of a solution of copper nitrate to one of sodium molybdate or sodium tungstate, respectively, formed products other than those desired. In one case a mixture of copper oxymolybdates was obtained, as shown by X-ray analysis. In the other case, the result of the precipitation procedure was an amorphous material of un-

known nature. This procedure was then discarded in favour of solid-state syntheses. Following this method CuMoO_4 was prepared by pelletizing an intimate mixture of CuO and MoO_3 and annealing it at 500°C for 8 hours. The mixture was then again powdered, pelletized and annealed at 500°C for 16 hours. Finally, the reaction was completed by a further powdering, pelletizing and annealing at 650°C for 14 hours. After these treatments, the X-ray analysis did not reveal any traces of the starting components, thus showing the purity of the final compound. CuWO_4 was prepared by annealing at 750°C for 10 hours an intimate mixture of CuO and WO_3 . Also in this case, the purity of the final compound was controlled by X-ray analysis.

Lithium ribbon (Foote Mineral Co.) and lithium hexafluoroarsenate (Alfa Ventron) were used as received. Lithium perchlorate (Merck) was dried at 250°C under vacuum. High purity γ -butyrolactone (BL) and propylene carbonate (PC) were obtained by vacuum distillation of the commercial products.

The electrolyte solutions, *i.e.* $1.5\text{ M LiAsF}_6\text{-BL}$ and $1\text{ M LiClO}_4\text{-PC}$, prepared following the general procedure described by Campanella and Pistoia [2], were kept in a dry-box where the electrochemical cells were also assembled and tested. The latter were of the "button type" formed by placing in contact a lithium disc (anode), three glass wool separator discs soaked with the electrolyte solution and a pellet of the cathodic material. This pellet was obtained by pressing a thin layer of a mixture of the copper oxysalt with graphite (10 wt.% of graphite) on a substrate of inert supporting metal (copper or, in the case of X-ray analyses, silver). The cells, of average total thickness 0.3 cm and surface area 1.2 cm^2 , were then housed in a plastic container having stainless-steel terminals.

The chemical, electrochemical and X-ray analyses were carried out using standard procedures and equipment.

Results and discussion

Lithium-copper molybdate system

The applicability of CuMoO_4 as cathodic material coupled with lithium in organic electrolytes was tested by assembling the cell



This cell had an open circuit voltage (OCV) of 3.2 V at room temperature. A typical polarization curve of the cell is shown in Fig. 1. This curve indicates the good behaviour of the system which is able to sustain relatively high current densities before undergoing serious polarizations. Having ascertained the discharge capabilities of the Li/CuMoO_4 couple, the influence of the electrolyte on its performance was next considered by using $\text{LiClO}_4\text{-PC}$ as alternative electrolyte solution. The polarization curve of the cell

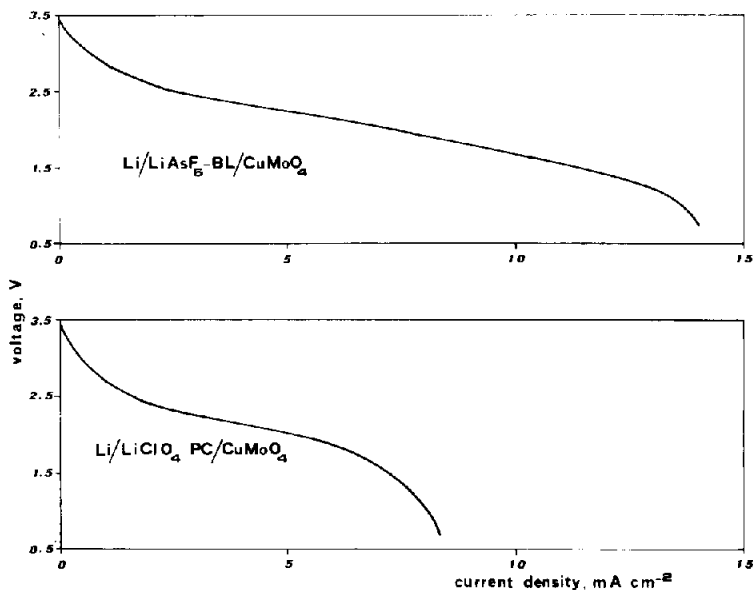


Fig. 1. Typical polarization curves of the Li/CuMoO₄ couple in LiAsF₆-BL and LiClO₄-PC electrolytes at room temperature.

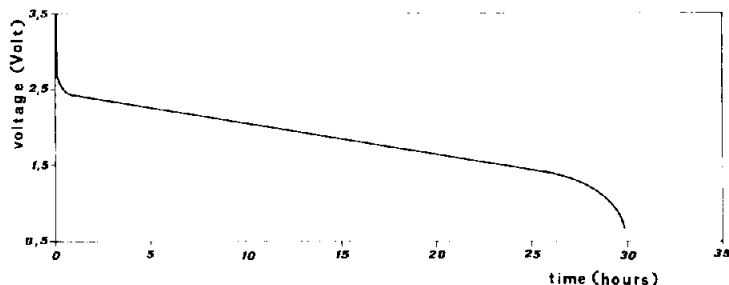
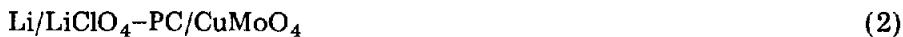


Fig. 2. Typical discharge curve of the Li/LiAsF₆-BL/CuMoO₄ cell at 0.5 mA cm⁻² and at room temperature (cathode weight: 80 mg).



which utilizes this electrolyte, is also shown in Fig. 1. The comparison indicates that cell (1) remains the most effective in terms of voltage and discharge characteristics. Attention was therefore focused on this cell and in Fig. 2 is shown a typical discharge curve at a low rate (0.5 mA/cm²). From the shape of the curve, the discharge process seems to be characterized by only one plateau. In order to determine the number of electrons involved in this process, a coulometric analysis was carried out. Cells containing a known amount of cathodic material (typically around 50 mg) and lithium in excess, were discharged at low rates (typically 0.25 mA/cm²) and the voltage was

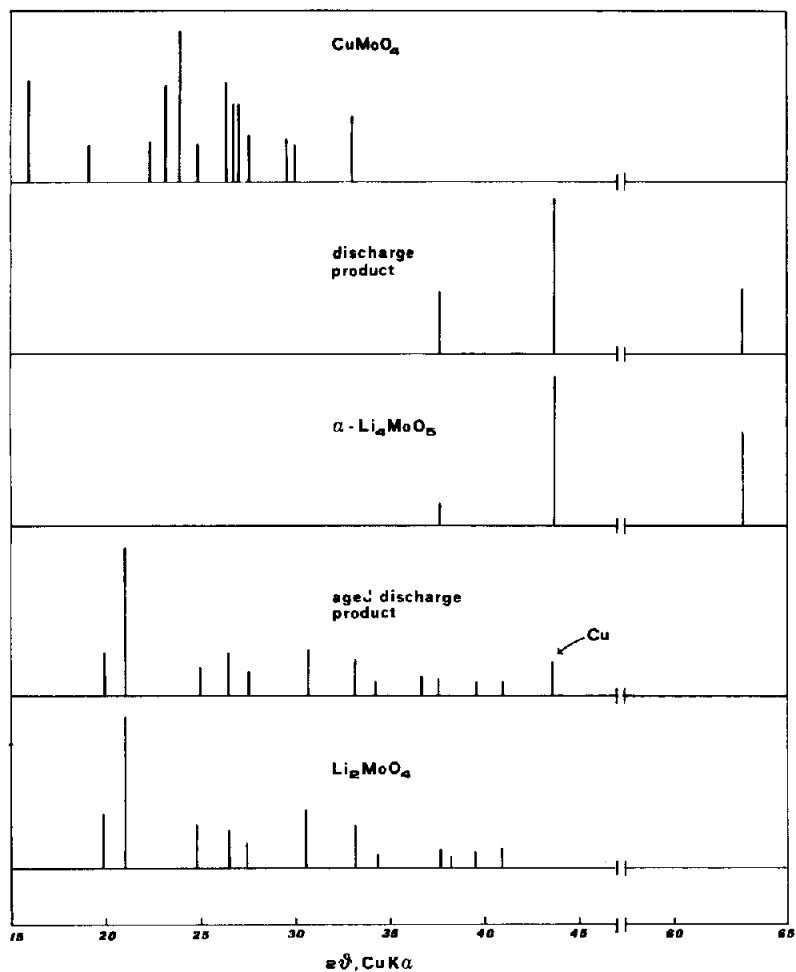


Fig. 3. X-ray diffraction patterns of the starting and discharged cathodic materials of the Li/LiAsF₆-BL/CuMoO₄ cell. Data for Cu, Li₄MoO₅ and Li₂MoO₄, have been obtained from ASTM card indexes.

followed as a function of time. When the voltage reached zero, the process was considered to be complete and from the coulombs consumed, the number of electrons was obtained. This number, as an average of various determinations, was found to be two per mole of CuMoO₄.

In an attempt to further characterize the electrochemical reaction, the cathodic mass of a cell similar to (1) was submitted to X-ray analysis immediately after a complete low rate discharge. The results of this analysis are schematically reported in Fig. 3, together with the diffraction pattern of the starting material, *i.e.* CuMoO₄. This Figure shows that in the X-ray diffraction pattern for the discharge product the majority of the lines of Li₄MoO₅ and of Cu are present. However, when the analysis was performed on a dis-

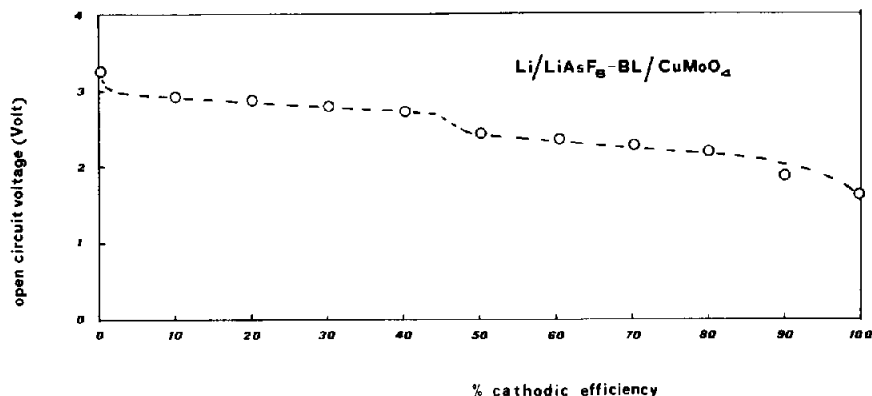


Fig. 4. OCV values as a function of the discharge depth for the Li/LiAsF₆-BL/CuMoO₄ cell at room temperature.

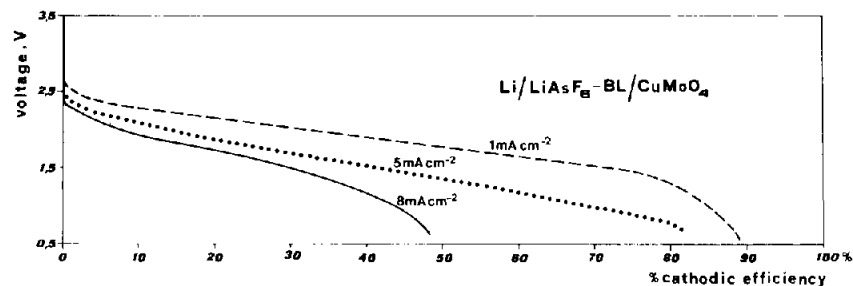


Fig. 5. Typical discharge curves of the Li/LiAsF₆-BL/CuMoO₄ cell at various rates at room temperature.

charge product which had been left standing for few hours, the lines of Li₄MoO₅ vanished and in turn those related to Li₂MoO₄ appeared.

On the basis of these results and those of the coulometric analysis, one may suggest that the discharge process of cell (1) is based on two electrons per CuMoO₄ mole with the formation of Cu, Li₄MoO₅ and possibly of MoO₃ (this latter has not been identified by X-ray analysis). Li₄MoO₅ then, on standing in the laboratory atmosphere and in the presence of MoO₃, readily transforms to a more stable phase which is Li₂MoO₄.

The discharge process was further investigated by determining OCV values as a function of the discharge depth. As shown in Fig. 4, on the basis of a two-electron change, the OCV slightly varied around 2.75 V for the discharge range from 10 to 40% and around 2.30 V from 50 to 80%. From this it may be assumed that the discharge process is really performed in two successive steps, each of which is related to the exchange of one electron. The two OCV values, *i.e.* 2.75 V and 2.30 V, represent the equilibrium voltages for the exchange of the first and the second electron, respectively. These values are relatively close to one another and this possibly explains the fact that in the continuous discharge curves, as for instance that of Fig. 2, the two steps are not easily distinguishable.

TABLE 1

Performance and energetic characteristics of the cathodic materials of cells 1 and 3 at room temperature. Data related to Ag_2WO_4 and Ag_2MoO_4 [1] are also reported for comparison purposes.

	Specific capacity (Ah/g)	Specific energy (Wh/g)	Efficiency (%)
Low rate: 0.5 mA/cm ²			
CuMoO_4	0.24	0.43	98
Ag_2MoO_4	0.14	0.41	98
CuWO_4	0.16	0.32	95
Ag_2WO_4	0.11	0.37	98
High rate: 8 mA/cm ²			
CuMoO_4	0.13	0.19	50
Ag_2MoO_4	0.07	0.15	50
CuWO_4	0.11	0.16	40
Ag_2WO_4	0.07	0.20	75

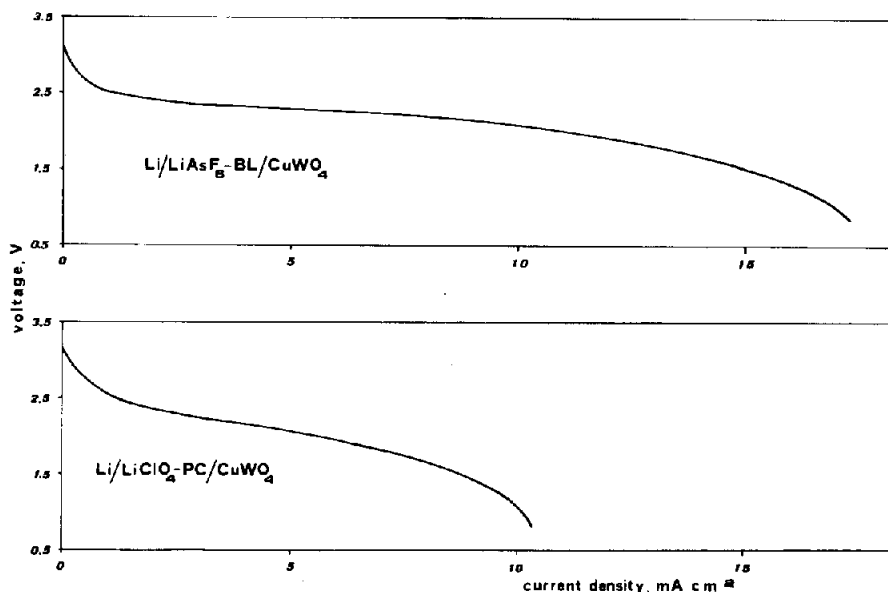


Fig. 6. Typical polarization curves of the Li/CuWO_4 couple in $\text{LiAsF}_6\text{-BL}$ and $\text{LiClO}_4\text{-PC}$ electrolytes at room temperature.

To complete the electrochemical investigation of copper molybdate coupled with lithium in $\text{LiAsF}_6\text{-BL}$, cell (1) was submitted to discharge at various rates. Typical results are reported in Fig. 5. The excellent behaviour of the cell is demonstrated by the fact that, even at discharge current densities of 8 mA/cm², the cathodic efficiency remains as high as 50%. This is further confirmed by the data shown in Table 1, where the performance and

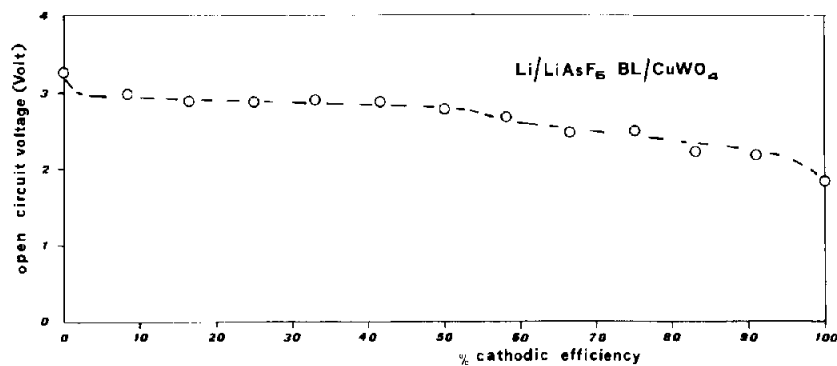


Fig. 7. OCV values as a function of the discharge depth for the Li/LiAsF₆-BL/CuWO₄ cell at room temperature.

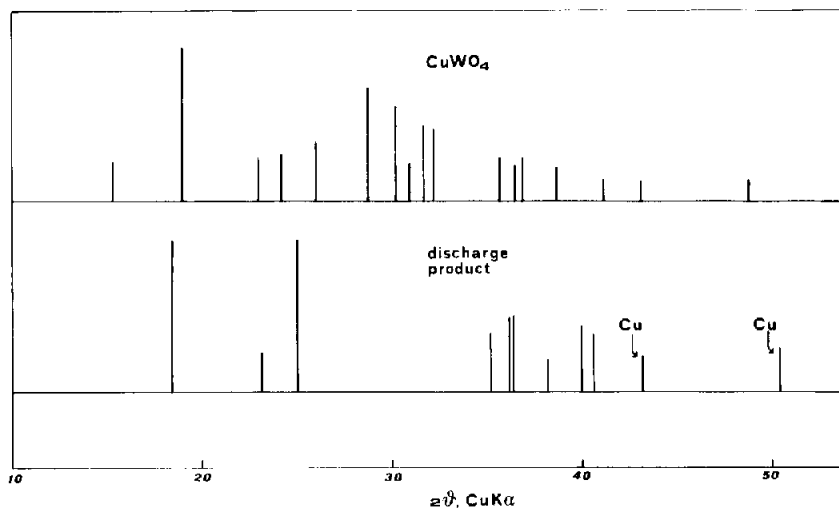


Fig. 8. X-ray diffraction patterns of the starting and discharged cathodic materials of the Li/LiAsF₆-BL/CuWO₄ cell.

the energetic characteristics of copper molybdate as cathodic material in type (1) cells are summarized.

Lithium-copper tungstate system

The electrochemical behaviour of the Li/CuWO₄ couple in organic electrolytes has been investigated by considering the cells:



and



Cells (3) and (4) showed OCV values around 3.1 V at room temperature and the typical polarization curves reported in Fig. 6. This Figure shows clearly

that cell (4) has a poorer performance than cell (3) and therefore attention was focused on the latter.

The investigation of the electrochemical process of cell (3), based on coulometric analysis, furnished a value of two electrons for the total discharge. A two-electron process is also indicated by the trend of the open circuit voltages as a function of the discharge depth, reported in Fig. 7. The identification of the discharge products seems in this case even more complicated than for the Li/CuMoO_4 couple. The X-ray analyses, both of fresh and aged samples of cathodic masses recovered after complete low rate discharges, show in fact identical results, schematically shown in Fig. 8. In the diffraction pattern, some of the most intensive lines of copper may be identified while those related to any known lithium tungstate are not present but rather a series of peaks not yet identified. Possibly these peaks may be related to an unknown solvated form of lithium tungstate. Further work is certainly necessary to clarify this point.

The electrochemical characterization of the Li/CuWO_4 couple in LiAsF_6 -BL has been extended with the investigation of the behaviour under various rates of discharge, as reported in Fig. 9. These results indicate that CuWO_4 as well as CuMoO_4 , may indeed be regarded as very interesting cathodic materials for the development of high energy lithium power sources.

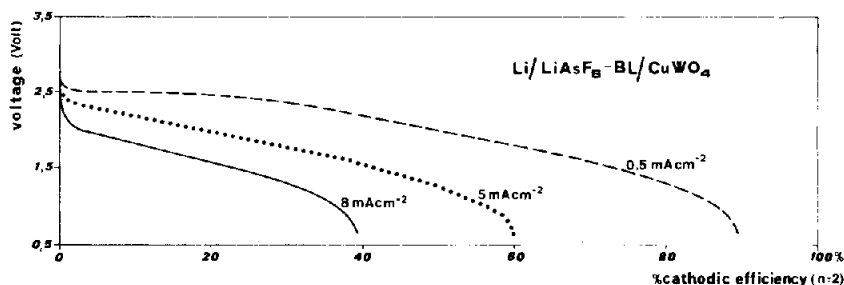


Fig. 9. Typical discharge curves of the $\text{Li}/\text{LiAsF}_6\text{-BL}/\text{CuWO}_4$ cell at various rates at room temperature.

Acknowledgements

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