

AN INVESTIGATION ON VARIOUS CATHODIC MATERIALS IN COPPER SOLID-STATE POWER SOURCES

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Summary

The electrochemical behaviour, in terms of stability, polarization and cycling capability, of a series of electrode materials in a copper solid electrolyte is reported. The results indicate that, among the various materials examined, TiS_2 and $\text{Cu}_{1.8}\text{S}$ may be considered as very promising cathodes for reversible copper solid-state cells. Eventual failures of these cells have to be ascribed mainly to the anode (the copper electrode) owing to its poor reversibility in the solid electrolyte examined.

Introduction

The recent discovery by Takahashi and coworkers [1, 2] of a series of highly conductive copper solid electrolytes has stimulated interest in the practical applications of these materials. Copper solid-state devices would have in fact considerable advantages in terms of cost and weight with respect to the most common ones based on silver solid conductors.

Attention has mainly been focused on the most conductive compounds of the series and, in particular on the one obtained by combining 0.94 mol of CuBr with 0.06 mol of N, N' -dimethyl triethylene diamine dibromide. In Table 1 are summarized the properties of this electrolyte, as determined by various authors. While there is fair agreement on the total and electronic conductivity, a substantial discrepancy appears in the reported activation energy values. A possible reason for this could be the presence of a different concentration of unreacted starting materials in the samples examined by the various authors. It has in fact been ascertained [3 - 5] that the reaction between the two components, *i.e.*, CuBr and N, N' -dimethyl triethylene diamine dibromide, could proceed to completion only after indefinitely long periods of annealing. Under practical conditions, the X-ray analyses of the final product always show the diffractions of cuprous bromide.

Despite this, the material, if prepared and kept under dry conditions, has an exceptionally high conductivity which is prevalently ionic in character.

TABLE 1

Properties of DTDBr₂-CuBr at 25 °C

Total conductivity (ohm cm) ⁻¹	Electronic conductivity (ohm cm) ⁻¹	Activation energy (kcal/mol)	Copper transport number	Decompos. potential (V)	Reference
3.5×10^{-2}	$2 \times 10^{-12*}$	2.7	1		[2]
2.0×10^{-2}	4×10^{-13}	4.1	1.01 ± 0.03	0.7	[3]
3.1×10^{-2}					[4]
6.5×10^{-3}		5.7			[5]

* At 100 °C.

In principle this property would make the electrolyte of great interest for practical applications. However, preliminary work in our laboratories [3] has indicated the incompatibility of the most common halogen electrodes with the electrolyte and recent results reported by Armstrong *et al.* [4] have shown a very low value of exchange current for the Cu/Cu⁺ electrode. However, because of the potential importance related to copper solid-state power sources in general, we felt it to be of interest to extend the electrochemical investigation, in terms of stability, polarization and cycling capability, to a series of electrode materials. The results of this investigation are reported in this work.

Experimental

The electrolyte preparation procedure, which basically follows that reported by Takahashi *et al.* [2], has been already described [3].

Cu_{1.8}S was obtained by synthesis from the elements (99.999% purity). The synthesis was carried out for two days in a two section Pyrex tube sealed under vacuum. The section containing copper was kept at 475 °C while that containing sulphur in stoichiometric excess was maintained at 350 °C. The X-ray diffraction powder patterns of the product so obtained agreed with those reported in the literature [6].

TiS₂ was also prepared by synthesis from the elements, following the procedure indicated by Winn [7]. CuBr₂ and WO₃ were reagent grade products and used without further purification.

The cells for the stability and charge-discharge tests were assembled by pressing the electrolyte and a thin layer of the electrode material under examination into a single pellet of 1.26 cm² surface area. This pellet was placed in a plastic container, having gold plated terminals, to which was then added the counter electrode (generally copper or a mixture of copper and the electrolyte) also in the form of a pressed pellet. The polarization studies were carried out using a copper wire inserted into the electrolyte, which acted as reference electrode.

The polarization and charge-discharge curves were obtained and recorded using standard equipment.

Results and discussion

In a previous paper [3] it has been shown that the *N, N'*-dimethyl triethylene diamine dibromide (DTDBr₂)-cuprous bromide electrolyte has a decomposition potential of 0.7 V at 25 °C, possibly related to the reaction:



Therefore the selection of the electrode materials to use in connection with DTDBr₂-CuBr is restricted to those couples whose e.m.f. is less than 0.7 V at 25 °C.

Using copper as the negative electrode, we have then considered Cu_{1.8}S, WO₃ and TiS₂ as possible candidates for the development of stable copper solid-state cells. This choice was determined by the following reasons.

Preliminary results obtained in our laboratories [3] on the discharge behaviour of substoichiometric copper sulphides were encouraging and indicated that these materials deserve further investigation. As pointed out by various authors [8 - 10] tungsten trioxide is capable of reacting with sodium and hydrogen to form bronzes of the Na_xWO₃ and H_xWO₃ type. If a similar reaction takes place with copper too, WO₃ could act as a satisfactory electrode.

Finally, Whittingham [11] has shown how copper may be electrochemically intercalated into layered transition-metal disulphides, and in particular into TiS₂ to form a compound indicated as Cu_xTiS₂. Titanium disulphide appeared therefore as a very suitable electrode material for copper solid-state cells.

The determination of the stability of these materials was considered of priority in the investigation of their behaviour as electrodes in connection with the DTDBr₂-CuBr electrolyte. Cells of the type:



where the cathode was in turn Cu_{1.8}S, WO₃ and TiS₂, were then assembled and the values of the related open circuit voltage (*OCV*) followed with time.

The results reported in Fig. 1 show that the *OCV* of the cells using WO₃ and TiS₂, after a period of stabilization, reached a constant value. Also when Cu_{1.8}S was used, the cell showed a stable and reproducible voltage.

In Fig. 1 is also reported the time dependence of the *OCV* of a cell using cupric bromide, a typical unstable material in DTDBr₂-CuBr. The comparison shows how the behaviour of the three materials here investigated may be considered satisfactory in terms of stability.

The *OCV* values for the WO₃, TiS₂ and Cu_{1.8}S cells are summarized in Table 2. The electrochemical processes of the cells are difficult to interpret but may be tentatively indicated as follows:

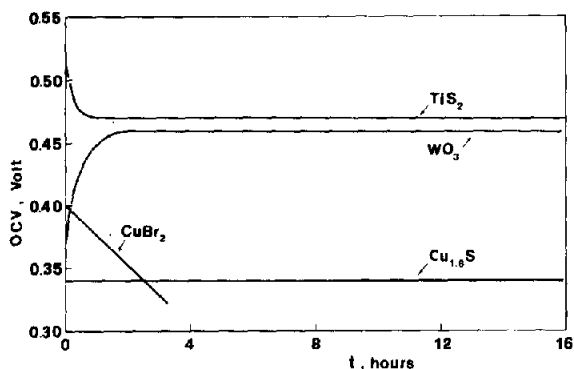


Fig. 1. Time dependence at 25 °C of the open circuit voltage (OCV) of cells similar to (2) having TiS_2 , WO_3 , $\text{Cu}_{1.8}\text{S}$ and CuBr_2 , respectively, as cathodes.

TABLE 2

Open circuit voltages at 25 °C of cells similar to (2) having various cathodic materials

Cathodic material	OCV (V)
$\text{Cu}_{1.8}\text{S}$	0.337
WO_3	0.460
TiS_2	0.470

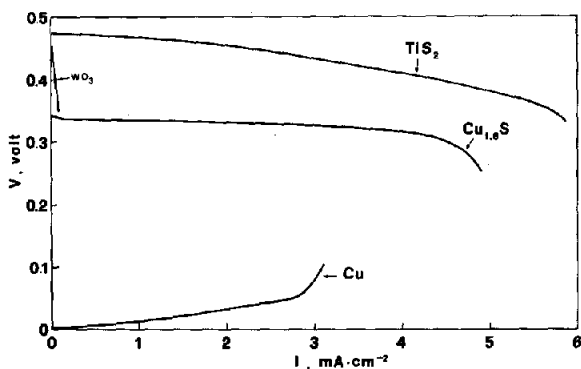


Fig. 2. Polarization sweeps (0.2 mA/min) of various electrodes in solid-state cells similar to (2) at 25 °C.



The polarization curves of the three electrodes have been determined with cells similar to (2), where the electrolyte was added to the electrode materials

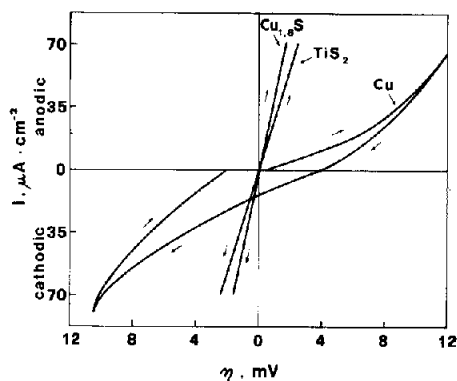


Fig. 3. Micropolarization test for the Cu, TiS_2 and $\text{Cu}_{1.8}\text{S}$ electrodes in the $\text{DTDBr}_2\text{-CuBr}$ electrolyte at 25°C .

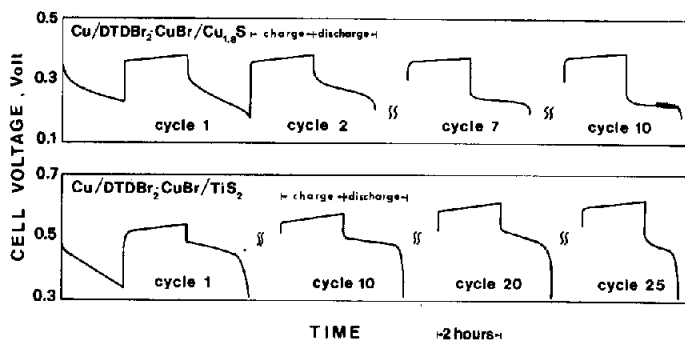


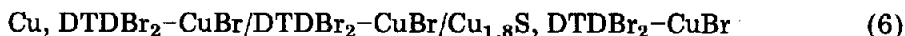
Fig. 4. Charge-discharge cycles at 0.2 mA h and 25°C of cells (6) and (7).

to reduce interfacial contact effects. A copper wire was inserted into the electrolyte to serve as reference electrode. The results corrected for the i.r. drops, are reported in Fig. 2, and show that while WO_3 suffers severe polarization, TiS_2 and $\text{Cu}_{1.8}\text{S}$ may withstand relatively high current drains. Attention has therefore been focused on the latter materials, and their reversibility has been tested with micropolarization runs using cells similar to those adopted for the polarization studies.

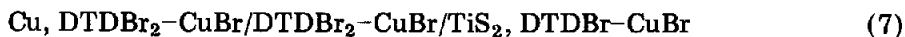
The results are shown in Fig. 3. In the case of TiS_2 and $\text{Cu}_{1.8}\text{S}$ the anodic straight lines lie on the prolongation of the cathodic ones, thus showing their reversibility. This is not the case for the copper electrode (also reported in Fig. 3) where the micropolarization traces show definite effects of hysteresis. These effects, even if to a lesser extent, also take place in the case of an electrode made of freshly electrodeposited copper. This lack of reversibility may be explained on the basis of the work of Armstrong *et al.* [4] in which the slow charge transfer reaction of the Cu/Cu^+ electrode was pointed out.

From the above discussion, it appears that $\text{Cu}_{1.8}\text{S}$ and TiS_2 may be considered as very promising cathodic materials for reversible copper solid-state cells. Eventual failures in these cells may be ascribed to the anode (the copper

electrode) owing to its poor reversibility. To ascertain this, the two following cells:



and



were assembled and submitted to charge-discharge cycles at 0.2 mA h.

The results are shown in Fig. 4 for cells (6) and (7) respectively. In both cases it may be noted how the discharge curves improve after the first charge. This is related to the fact that freshly electrodeposited copper has a much lower overpotential than the starting copper metal, as also reported by Armstrong *et al.* [4]. The first cycles are also very satisfactory in terms of efficiency which is of the order of 90%.

For cell (6) this satisfactory behaviour proceeds up to the tenth cycle when some deterioration takes place, evidenced by the poor discharge curve. The performance of cell (7), which sustained 25 cycles before showing detectable breakdown, is decidedly better.

As already mentioned, the reason for the failure of the cells is likely to be ascribable to the copper electrode. The poor reversibility of this electrode may possibly originate dendritic deposition, which is a cumulative process cycle after cycle thus producing a progressive increase in the internal resistance of the cell.

Conclusions

The results of this work indicate that titanium disulphide and substoichiometric copper sulphide may be considered as efficient electrode materials in rechargeable solid copper cells. Their practical use is at the moment hindered by the poor kinetic properties of the copper electrode in the DTDBr₂-CuBr electrolyte. It seems therefore very important to search for new copper solid electrolytes and/or to develop alternative copper electrodes. It must be mentioned that recently Sammels *et al.* [5] have reported the synthesis of highly conductive electrolytes based mainly on the combination of cuprous bromide with quinuclidine hydrobromide, 3-quinuclidone hydrobromide and pyridinium hydrobromide. No studies on the kinetics of the electrodes used in connection with these electrolytes are reported. Nevertheless the cycling test of the cell:



studied by the authors, shows a progressive deterioration in terms of charge-discharge efficiency. It is therefore reasonable to suppose that also in this electrolyte the copper electrode has a poor reversibility. Future work on solid-state copper devices should then be mainly directed towards the optimization of this electrode.

Acknowledgement

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