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Primary solid-state batteries constructed from copper and indium sulphides

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Copper and indium sulphides were prepared by a chemical precipitation method and further characterized. Low-cost, easily fabricated dry cells were constructed by gluing the metal sulphides on a magnesium foil using a polymer electrolyte. The efficiency, energy densities and cell voltage values of the cells were in the range 8.1–6.2 mWh cm^{-3}, 150–77 mWh g^{-1} and 1.58–1.21 V, respectively.

1. Introduction

Solid-state batteries have been in use for a long time. (This denomination has been used in many cases when the separator between the electrodes of the cell is a solid fast-ion conductor.) The potential applications of polymer electrolyte solid-state batteries span the entire range of battery products, from smart credit cards to standby power in telecommunications, including Polaroid instant film packs and batteries built into printed-circuit boards in laptop personal computers. Their combination of high-energy density and mechanical rigidity make them particularly attractive for application in space [1–4].

A solid-state battery has three components. The first is an electron source (anode), a metal, the second is a fast-ion conductor, polymer electrolyte for example, and the third component is an electron exchanger (cathode). The aim of this work was the preparation of conducting materials consisting of copper sulphides, the investigation of electrical properties of these preparations and their application as cathods for the development of new dry cells.

2. Experimental procedure

2.1. Sulphides preparation

The metal sulphides (CuS, In_2S_3, $CuCdS_2$ and $CuZnS_2$) were prepared at pH 2.5, 25 °C using the appropriate volumes from 10^{-2} M stock solutions. The stock solutions were prepared from reagents $CdCl_2$, $InCl_3$, $ZnCl_2$, $CuCl_2$ and $(NH_4)_2S$ which were purchased from Merck (*pro analysi*) and standardized by atomic absorption spectroscopy (Varian 1200) (for the metal chloride solutions) and by a titrimetric iodine method [5] (for the amonium sulphide solution). The precipitated solids were characterized by elemental analysis, X-ray diffraction (Phillips 1300/00) using aluminium as internal standard, by infrared spectroscopy (Perkin Elmer 477) and by scanning electron microscopy (Jeol JSM-35).

2.2. Electrical measurements and construction of the cells

The metal sulphides were subsequently made into pellets using an infrared KBr pellet die. The pellets (= 1 mm thick, 13 mm diameter) were made by applying a pressure of 1400 MPa. For the conductivity measurements, a centred square four-probe array of the electrical contacts was made by pressing tungsten wires against the specimen [6]. The conducting materials obtained and their properties are summarized in Table I. Then the pellets were stuck on a magnesium foil (Merck 99.9%) using as gluing material a thin film of 10% wt/wt PVA, PEO or PVP in 2 M KCl aqueous solution as shown schematically in Fig. 1. The reagents polyethylene oxide (PEO) MW = 600 000, polyvinyl alcohol (PVA) MW = 140 000 and polyvinyl pyrolidone (PVP) MW = 44 000 were purchased from Aldrich. The cell voltage was measured by a high-input impedance voltmeter (10^{11} Ω). The electrical properties of the preparation are summarized in Table II.

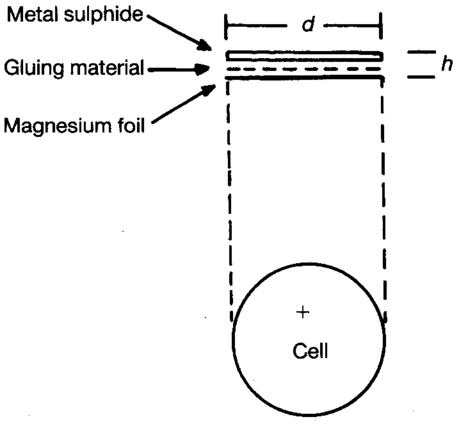

Figure 1 Construction of the cells presented in Table II, weight 0.5 g, $d = 1.3$ cm, $h = 0.12$ cm.

TABLE I Semiconducting cathodes and their characteristics

Sample	Chemical composition	Conductivity (S cm^{-1})	Thermopower (μV K^{-1}) (charge carriers)
1	CuS	1125	15 (p)
2	In_2S_3	5×10^{-3}	100 (n)
3	$CuCdS_2$	25	17 (p)
4	$CuZnS_2$	400	73 (n)

TABLE II Dry cells containing polymer electrolytes and their characteristics. Magnesium foil thickness 0.02 cm, total cell thickness 0.12 cm, external load 2 MΩ, surface area 1.33 cm^2

Cell	Cell voltage (V)	Discharge time (h)	Polymer electrolyte	Metal sulphide cathode	Efficiency (mWh cm^{-3} or Wh kg^{-1})
1	1.580	600	PVA	In_2S_3	8.1 or 150
2	1.230	600	PVA	CuS	6.3 or 116
3	1.210	600	PVA	$CuZnS_2$	6.2 or 114
4	1.220	400	PVA	$CuCdS_2$	4.2 or 77
5	1.320	600	PEO	CuS	6.8 or 125
6	1.230	600	PVP	CuS	6.3 or 116

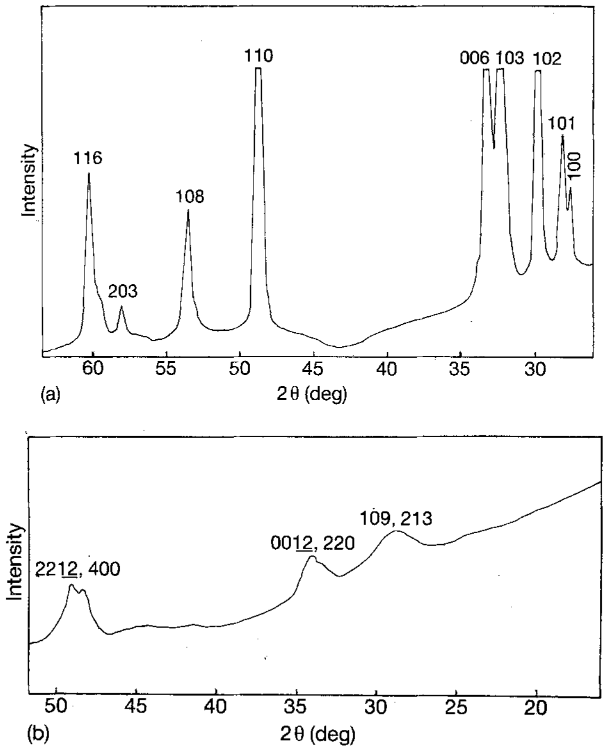

Figure 2 Powder X-ray diffraction of (a) CuS, (b) In_2S_3.

3. Results and discussion

Chemical analysis based on dissolution of precipitated metal sulphide specimens gave the stoichiometry CuS, In_2S_3, $CuCdS_2$ and $CuZnS_2$ (mean of twenty specimens). For the CuS and In_2S_3 specimens the stoichiometry was confirmed from the X-ray diffractogram pattern as shown in Fig. 2 [7, 8]. The solid phases $CuCdS_2$ and $CuZnS_2$ could not be confirmed by X-ray diffraction because of the microcystalline character of the precipitate. The scanning electron micrographs of the precipitated metal sulphides are shown in Fig. 3.

The electrochemical reaction which produces the energy, is the oxidation of the metal $Mg = Mg^2 + 2e$. If the oxidation reaction takes place spontaneously, the chemical energy of the metal is converted to thermal energy rather than electrical energy. This problem can be solved by the appropriate combination of the cathode (electron exchanger) and the solid electrolyte. The cathode allowing the reduction process, accepts electrons from the external circuit and positive ions through intercalation. From Table II, it may be concluded that the In_2S_3 was a cathodic material with better performance which yielded a magnesium cell with the best electrical characteristics. The above conclusion is valid when the electrolyte PVA/KCl is used between the anode and the cathode. For the CuS cathodic material, the solid electrolyte

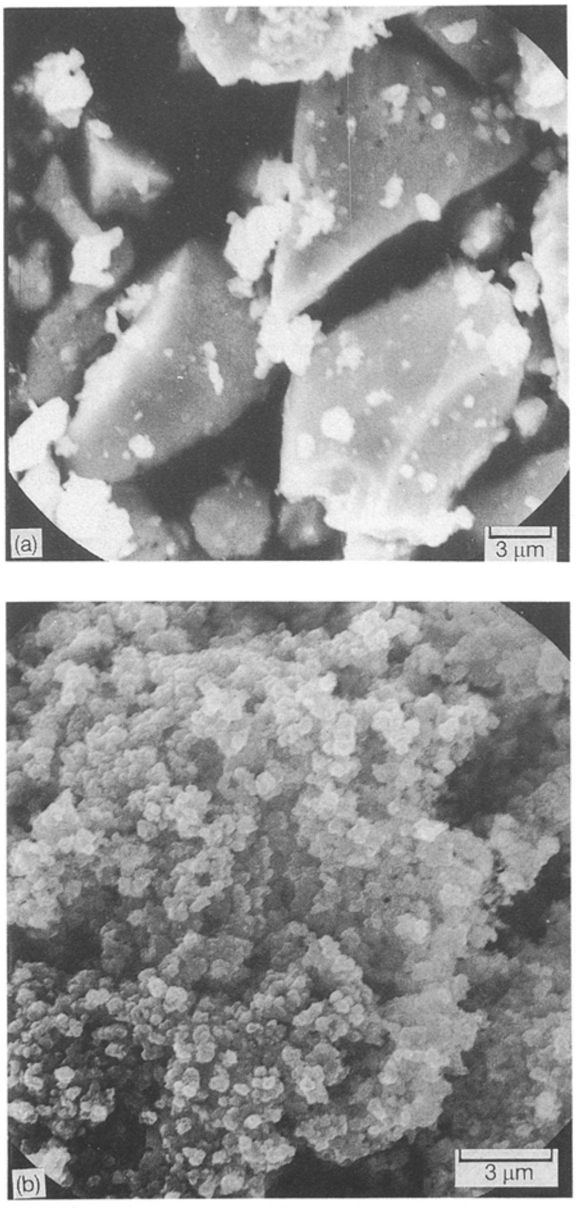

Figure 3 Continued

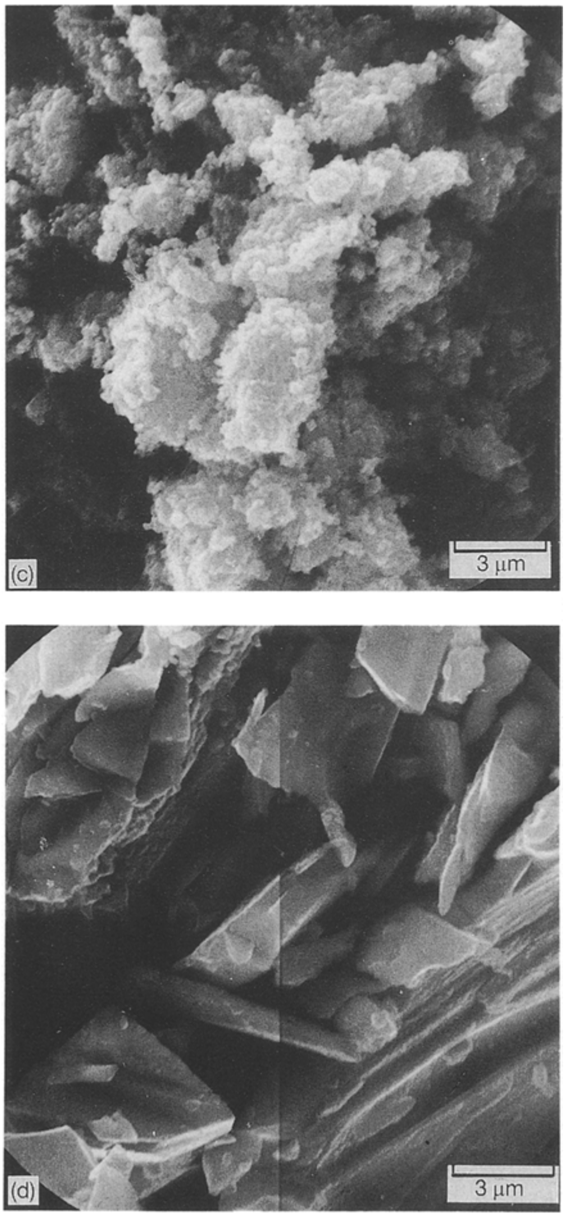

Figure 3 Scanning electron micrographs of (a) In_2S_3, (b) CuS, (c) $CuCdS_2$, and (d) $CuZnS_2$ crystallites.

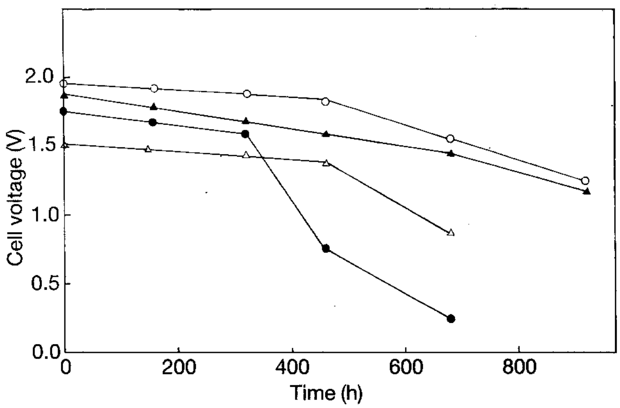

Figure 4 Discharge curves for the Mg/PVA–KCl/sulphides primary batteries, under a load resistance of 2 MΩ. Cell no: (○) 2, (●) 4, (△) 3, (▲) 1.

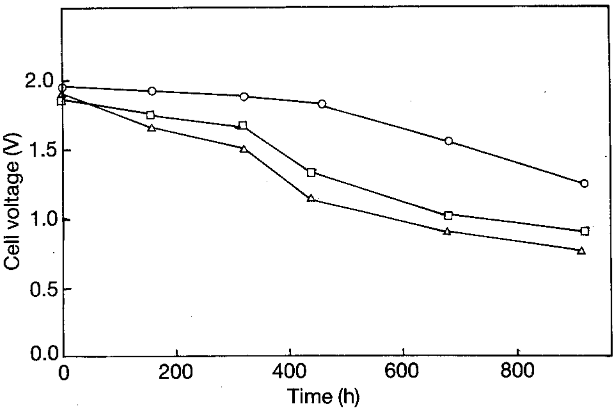

Figure 5 Discharge curves for the Mg/polymer electrolyte/CuS primary batteries, under a load resistance of 2 MΩ. Cell no: (○) 2, (△) 6, (□) 5.

PEO/KCl is preferable, leading to the construction of the most efficient cell (Table II).

Figs 4 and 5 show the discharge behaviour of the cells described in Table II under a load resistance of 2 MΩ. Dry cells using conducting polymers as cathodic material, were the most efficient in yielding the highest cell voltage values, between 1.9 and 1.4 V [4]. The dry cells presented here have lower cell voltage values, between 1.58 and 1.21 V, but are safer for health.

Finally, the efficiency of the cells ranging from 8.1–6.2 mWh cm^{-3}, is comparable to other commercial cells [9] constructed using polyaniline as a cathode and lithium aluminium as the anode (Bridgestone and Seiko) as well as to the AA-size BASF/VARTA commercial cells [10].

The energy densities of the cells shown in Table II were 77–150 mWh g^{-1}, three to seven times more than the energy density of the PbO_2–H_2SO_4–Pb multiple charge–discharge system (20 mWh g^{-1} [11]) and two to four times more than the energy density of the nickel/cadmium rechargeable cell.

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