

Short Communication

Discharge Characteristics of Solid-state Cells Incorporating Thin Films of a Cuprous Halide Mixed Phase

M. A. K. L. DISSANAYAKE* and J. KARUNAMUNI

Department of Physics, University of Peradeniya, Peradeniya (Sri Lanka)

(Received May 25, 1988; in revised form July 19, 1988)

Summary

Thin, solid films of a CuCl:CuBr:CuI mixed phase are formed on copper substrates by an electrolytic deposition technique. The films are incorporated in solid-state cells with the configuration Mg/CuCl:CuBr:CuI/Cu. A typical cell gives an open-circuit voltage of ~ 1.3 V, a short-circuit current of ~ 10 mA, and a capacity of ~ 5 mA h.

Introduction

Low-energy-density, thin-film, solid-state cells based on Cu⁺-ion conductors are promising candidates for microwatt batteries in miniature electronic devices [1]. Although several copper(I) halide/organic-substituted ammonium halide systems and copper(I) halide/alkali halide systems with high Cu⁺-ion conductivity have been reported [2, 3], it has not been possible to prepare stable thin films of the Cu⁺-ion conducting materials by vacuum evaporation techniques; the compounds tend to decompose during evaporation. Electrolytic deposition is a more effective means of producing such films. Thin-film cells using a single cuprous halide (*i.e.*, CuCl, CuBr or CuI) have high internal resistances due to low ionic conductivities, $\leq 10^{-9}$ ohm⁻¹ cm⁻¹ at room temperature [4, 5]. It is possible, however, to reduce the internal resistance of such cells by employing a thin film consisting of a mixed phase of all three halides. This communication discusses the constant-load discharge characteristics of an Mg/CuCl:CuBr:CuI/Cu cell in which the electrolyte comprises a thin film of a mixed phase of three cuprous halides that is electrolytically deposited on a copper substrate.

Experimental

Thin films of CuCl:CuBr:CuI mixed phase were deposited on a copper substrate by the following method: the electrolytic solution was prepared by dissolving 5 "drops" of 45% HI solution, 15 ml of 0.1 M NH₄Cl, and 10 ml of 0.1 M NH₄Br in 100 ml of distilled water. Two, clean copper plates (dimensions: 4 cm \times 5 cm) were placed opposite each other in an electrolytic bath at a separation of ~ 5 cm. The current was maintained at 5 mA

* Author to whom correspondence should be addressed.

cm^{-2} for several minutes. During the electrodeposition process, NH_4^+ and H^+ cations migrated towards the cathode and were liberated as gaseous NH_3 and H_2 . The Cl^- , Br^- and I^- anions migrated towards the anode and reacted with Cu^+ ions to form a thin film of a mixed phase consisting of CuCl , CuBr and CuI . After deposition, the coated copper substrate was washed with ethanol and ether and then allowed to dry in a vacuum desiccator. The thickness of the film (estimated from current density and deposition time) was $\sim 50 \mu\text{m}$. Although chemical analysis revealed the presence of all three halides in the thin film, it has not been possible to determine the exact composition of the mixed phase.

Cells of configuration $\text{Mg/CuCl:CuBr:CuI/Cu}$ were fabricated by mechanically pressing a thin magnesium foil against the electrolyte film. Currents and voltages during discharge through various load resistors were measured using the method described previously [1].

Results and discussion

The open-circuit voltage of a typical $\text{Mg/CuCl:CuBr:CuI/Cu}$ cell was $\sim 1.3 \text{ V}$ and the short-circuit current was $\sim 10 \text{ mA}$. Constant-load discharge curves for $15 \text{ k}\Omega$, $5 \text{ k}\Omega$ and $1 \text{ k}\Omega$ resistors are shown in Fig. 1. The discharge curve for a $15 \text{ k}\Omega$ load shows a constant-voltage plateau at $\sim 900 \text{ mV}$ over a period of $\sim 90 \text{ h}$ and the average current drawn was $\sim 60 \mu\text{A}$. This cor-

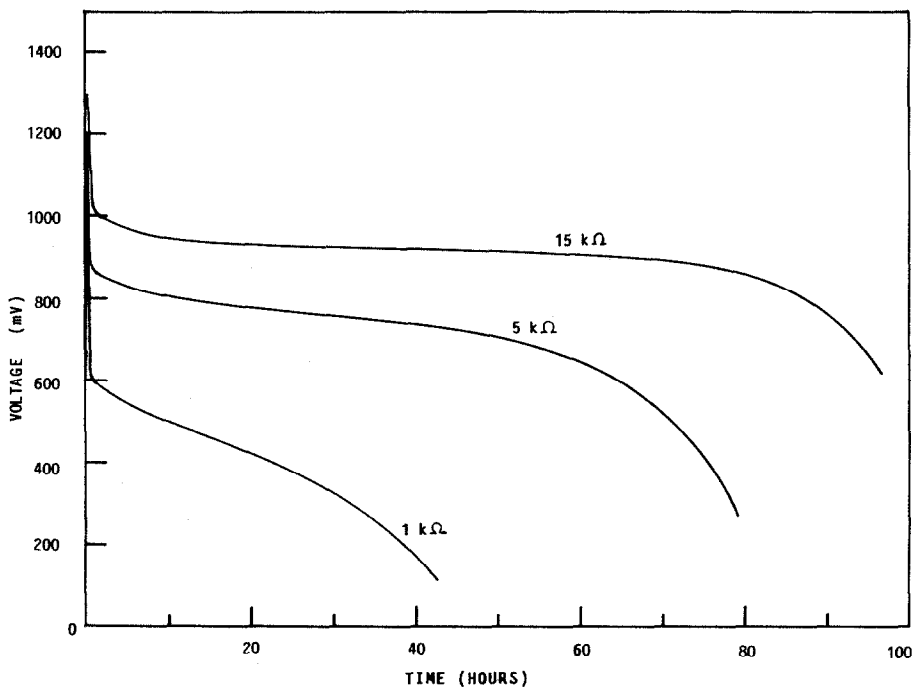


Fig. 1. Constant-load discharge curves for $\text{Mg/CuCl:CuBr:CuI/Cu}$ cell. Loads as indicated. Average current during discharge through $15 \text{ k}\Omega$ resistor was $\sim 60 \mu\text{A}$.

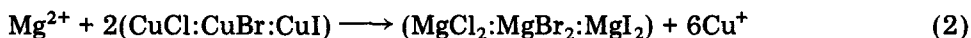
responds to a cell capacity of ~ 5 mA h; this value is comparable with that for an Li/LiI+40 mol% $\text{Al}_2\text{O}_3/\text{PbI}_2, \text{Pb}$ cell first reported by Liang [6] and then later developed into a commercial low-drain battery for miniature electronic devices.

The internal resistance of thin-film cells made with only one cuprous halide electrolyte and Mg/Cu electrodes was found to be $>10 \text{ M}\Omega \text{ cm}^{-2}$. This high value is due to the low ionic conductivities of cuprous halides at room temperature. On the other hand, the internal resistance of the cells with mixed cuprous halide phases was $\sim 600 \Omega \text{ cm}^{-2}$. It should be noted, however, that the latter value increased with discharge time. The relatively low value of the internal resistance of mixed-phase cells indicates a possible enhancement of ionic conductivity from a synergistic effect in the mixed-phase ionic solid. Such a phenomenon has been demonstrated for several multi-phase systems consisting of low-conducting ionic solids [7 - 9]. In these systems, the interfacial conduction between grains of different phases raises the overall ionic conductivity above that of the individual phases.

During discharge of the cell, magnesium is oxidized at the anode; *i.e.*,



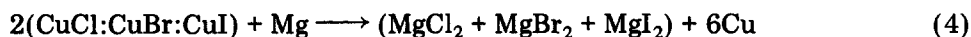
The Mg^{2+} ions react with the electrolyte to form a mixed phase of magnesium halides at the electrolyte/magnesium interface, *i.e.*,



The Cu^+ ions migrate to the copper cathode and are there reduced to copper metal, *i.e.*,



In summary, the overall discharge results in a depletion of the electrolyte, formation of a magnesium halide mixture at the electrolyte/magnesium interface, and a deposition of metallic copper at the cathode. Increase in the internal resistance during cell discharge is due to the formation of the thin layer of the magnesium halide mixture. A metallic copper layer has also been observed to form at the anode/electrolyte interface. This is probably caused by the following chemical reaction:



These reaction products also contribute to the internal resistance of the cell.

References

- 1 M. A. K. L. Dissanayake, J. Karunamuni and H. M. N. Bandara, *J. Power Sources*, 24 (1988) 165.
- 2 S. Chandra, *Superionic Solids*, North-Holland, Amsterdam, 1981, p. 84.
- 3 O. Yamamoto, Y. Takeda and R. Kano, in B. V. R. Chowdari and S. Radhakrishna (eds.), *Materials for Solid State Batteries*, World Scientific, Singapore, 1986, p. 275.
- 4 J. B. Wagner and C. Wagner, *J. Chem. Phys.*, 26 (1957) 1597.
- 5 T. Matsui and J. B. Wagner, *J. Electrochem. Soc.*, 124 (1977) 610.
- 6 C. C. Liang, *Appl. Solid State Sci.*, 4 (1974) 95.

- 7 C. C. Liang, *J. Electrochem. Soc.*, 120 (1973) 1289.
- 8 F. W. Poulsen, in F. W. Poulsen, N. H. Andersen, K. Clausen, S. Skaarup and O. T. Sørensen (eds.), *Transport-Structure Relations in Fast Ion and Mixed Conductors*, Risø National Laboratory, Denmark, 1985, p. 67.
- 9 M. A. K. L. Dissanayake and B.-E. Mellander, *Solid State Ionics*, 21 (1986) 279.