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Short Communication

Discharge Characteristics of Solid-state Cells with Magnesium and Copper Electrodes and Thin-film, Solid Electrolyte of Cuprous Sulphate

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Summary

Thin, solid films of cuprous sulphate have been formed on copper substrates by a chemical deposition technique. Solid–state cells of configuration $Mg(-)/Cu_2SO_4/Cu(+)$ have been fabricated and their constant-load discharge characteristics have been investigated. A typical cell exhibits an open-circuit voltage of ~1.8 V and a capacity of ~10 mA h.

Introduction

Solid-state cells based on Cu^+-ion conductors are promising electrochemical power sources because of their low cost compared with cells based on Ag^+- and Li^+-ion conductors. Such cells also have the advantage of using copper metal as one of the electrodes. Low energy-density, thin-film cells with Cu^+-ion conductors are potential candidates for microwatt batteries for use in miniature electronic devices.

Many of the reported stable inorganic Cu^+-ion conductors have rather low ionic conductivities at ambient temperature, while most of the high conducting copper(I) halide/organic substituted ammonium halide systems and copper(I) halide/alkali halide systems are either unstable or difficult to obtain in the form of thin films [1 - 3]. Cu_2SO_4 is found to be a good Cu^+-ion conductor having, at room temperature, a conductivity of 5.56×10^{-4} $(ohm\ cm)^{-1}$ [4]. In this paper, we report the constant-load discharge characteristics of an $Mg(-)/Cu_2SO_4/Cu(+)$ cell in which the electrolyte comprises a thin film of Cu_2SO_4 chemically deposited on a copper substrate.

Experimental

Thin films of cuprous oxide were formed on copper substrates by the anodic oxidation method described in ref. 5. A pair of rectangular copper sheets, each of dimensions 4 cm × 5 cm, was placed in an electrolytic bath with the faces parallel and at a separation of about 2.5 mm. The bath consisted of reagent grade $CuSO_4$ (0.01 M), NaCl (0.005 M) and LiCl(0.005 M)

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at pH 4.5. Oxidation was carried out for 50 min at a constant current density of 3 mA cm^{-2} and at 86 °C.

The copper sheet containing the thin film of Cu_2O was subsequently immersed in a hot solution of dimethyl sulphate (120 °C) for ~15 min. The resulting thin film of Cu_2SO_4 was washed successively with ethyl alcohol and diethyl ether, and then allowed to dry in a vacuum desiccator. The film was not characterized, but Cu_2SO_4 powder samples, prepared by an identical chemical reaction using reagent grade Cu_2O powder, were tested and confirmed as Cu_2SO_4. Solid-state cells of configuration Mg(−)/Cu_2SO_4/Cu(+) were fabricated by mechanically pressing a thin magnesium foil against the Cu_2SO_4 electrolyte film.

Currents and voltages during discharge through various load resistors were measured using TRIO digital multimeters with 0.1 μA and 0.1 mV sensitivities. The data were also recorded with a Kipp and Zonen chart recorder of 0.1 mV sensitivity. Throughout the measurements, the cells were enclosed in a dry desiccator.

Results and discussion

A typical cell of configuration Mg(−)/Cu_2SO_4/Cu(+) had an open circuit voltage of ~1.8 V and a short-circuit current of ~3.2 mA. Constant-load discharge curves for 20 kΩ, 10 kΩ and 2 kΩ resistors are shown in Fig. 1. The discharge curve for a 20-kΩ load shows a constant-voltage plateau of about 650 mV over a period of about 150 h. The average current drawn through the resistor during the 200-h discharge period was ~50 μA.

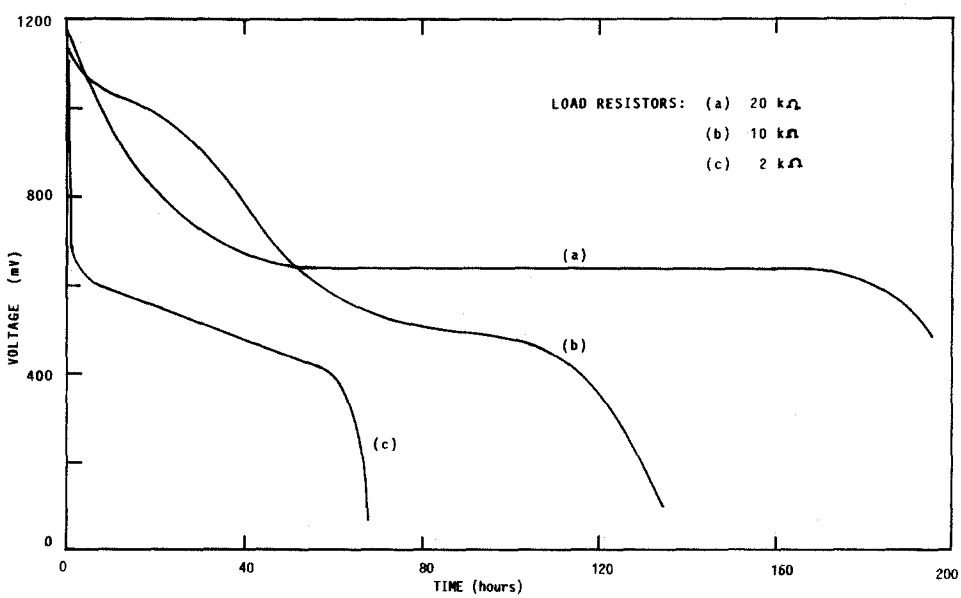

Fig. 1. Constant-load discharge curves for Mg/Cu_2SO_4/Cu cell. Average current during discharge through 20 kΩ ~50 μA.

This corresponds to a cell capacity of ~10 mA h. The internal resistance of the cell was ~600 Ω, initially, but then increased with discharge time.

During the cell discharge process, the charge-transfer reactions at the respective electrodes can be represented as follows:
At the Mg anode, oxidation takes place via the reaction:

$$Mg \longrightarrow Mg^{++} + 2e^- \quad (1)$$

The Mg^{++} ions react with the electrolyte to form the product $MgSO_4$ at the electrolyte/Mg interface, *i.e.*,

$$Mg^{++} + Cu_2SO_4 \longrightarrow MgSO_4 + 2Cu^+ \quad (2)$$

The Cu^+ ions migrate through the electrolyte to the copper cathode.

The charge-transfer reaction at the cathode is:

$$Cu^+ + e^- \longrightarrow Cu \quad (3)$$

As a result, metallic copper is deposited on the surface of the copper cathode.

In summary, the overall discharge reaction gives rise, therefore, to a depletion of Cu_2SO_4 electrolyte, formation of $MgSO_4$ at the electrolyte/Mg interface, and deposition of metallic copper on the cathode. The increase in the internal resistance of the cell observed during the discharge process is possibly due to the formation of the $MgSO_4$ layer at the electrolyte/Mg interface.

Conclusions

The discharge characteristics of solid-state cells with chemically prepared Cu_2SO_4 thin films and copper and magnesium electrodes have been investigated. The open-circuit voltage of a typical cell is ~1.8 V and the capacity is ~10 mA h. These types of cells may be developed as cheaper, low-energy-density power sources for miniature electronic devices.

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