

EFFECTS OF AN ADDITIVE MATERIAL, CuFeS_2 , ON Li/CuO BATTERY PERFORMANCE

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Summary

The discharge characteristics of the Li/CuO system have been improved by adding chalcopyrite (CuFeS_x , $1.6 < x \leq 2$) to the cathode.

The chalcopyrite was thermally prepared from iron disulfide and cuprous sulfide. The open-circuit voltage of synthetic chalcopyrite was ~ 0.2 V lower than that of cupric oxide. Chalcopyrite shows no voltage depression when discharged and only causes a relatively small increase in the cell thickness on its discharge. Both chalcopyrite and cupric oxide have a low solubility in the organic electrolyte.

In summary, a cathode system composed of cupric oxide and chalcopyrite has the following properties: a brief excursion to the plateau voltage, no voltage depression at the beginning of discharge, only a small increase in the cell thickness, and a good storage life. Button cells using this system have been successfully developed for electronic devices.

Introduction

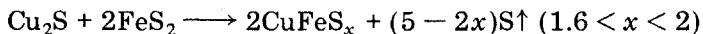
Several lithium battery systems with voltages of 1.5 have been developed throughout the world. These batteries have the advantage of voltage compatibility with conventional cells, as well as the regular features of 3 V lithium batteries.

Although CuO is a promising cathode material for 1.5 V lithium batteries [1], the Li/CuO system still has several disadvantages, namely: a high voltage excursion followed by a voltage depression, and a relatively large increase in cell thickness after discharge. Such characteristics cause certain practical problems, especially when the batteries are used with precise electronic devices. In the studies reported here, however, the noted disadvantages have been almost completely overcome by adding chalcopyrite to the CuO cathode. Details are given of the synthesis of chalcopyrite and the effects of its addition on the performance of button cells (GR920, 927).

Experimental

Synthesis of chalcopyrite

Synthetic chalcopyrite was thermally prepared from cuprous sulfide (Cu_2S) and iron disulfide (FeS_2) under a stream of nitrogen, *i.e.*,



The chalcopyrite was identified qualitatively by X-ray diffraction (XRD) analysis in a model RAD-3A diffractometer (Rigaku Denki Co., Ltd.) using copper $\text{K}\alpha_1$ radiation monochromized by graphite; the composition was determined quantitatively by chemical analysis. The specific gravity was measured in carbon tetrachloride (CCl_4) at 20 °C using a picnometer.

Addition to CuO and cell performance

The discharge characteristics of both natural and synthetic chalcopyrite and the effects of adding them to the CuO cathode were evaluated in a cell with a coin housing. The increase in the cell thickness was also measured during discharge.

Cathodes were subjected to XRD analysis at different depths of discharge. An X-ray photoelectron spectroscope (XPS), model ESCA LABO-5 (VG Instrument Ltd.) was used to determine the discharge products.

The solubilities of both synthetic chalcopyrite and CuO in various organic electrolytes were obtained using an atomic absorption and flame emission spectrophotometer, model AA-860 (NIPPON Jarrell-Ash Co., Ltd.).

The button cells were discharged at different rates and temperatures. Cell storage characteristics were examined under accelerated test conditions.

Results and discussion

Properties of synthetic chalcopyrite

The sulfur content of synthetic chalcopyrite at various temperatures and times of reaction is shown in Fig. 1 (a) and (b). The content, calculated from the weight of the products, ranged from 1.68 to 1.90; these values were in good agreement with those obtained by chemical analysis.

A reaction time of 6 h was required to produce synthetic chalcopyrite at 560 °C, but this period was reduced to 1.5 h when the temperature was increased to 590 °C. Synthetic chalcopyrite was found to be a mixture of the tetragonal and cubic crystal systems, as identified by XRD analysis (Fig. 2), isothermal phase relations of the Cu-Fe-S system [2], and other data on chalcopyrite [3, 4]. The specific gravity of the synthetic chalcopyrite increases proportionally with decrease in the sulphur content.

Discharge characteristics and addition rate

The discharge characteristics of cupric oxide (CuO) and synthetic chalcopyrite ($\text{CuFeS}_{1.8}$) are shown in Fig. 3 (a). It can be seen that whereas

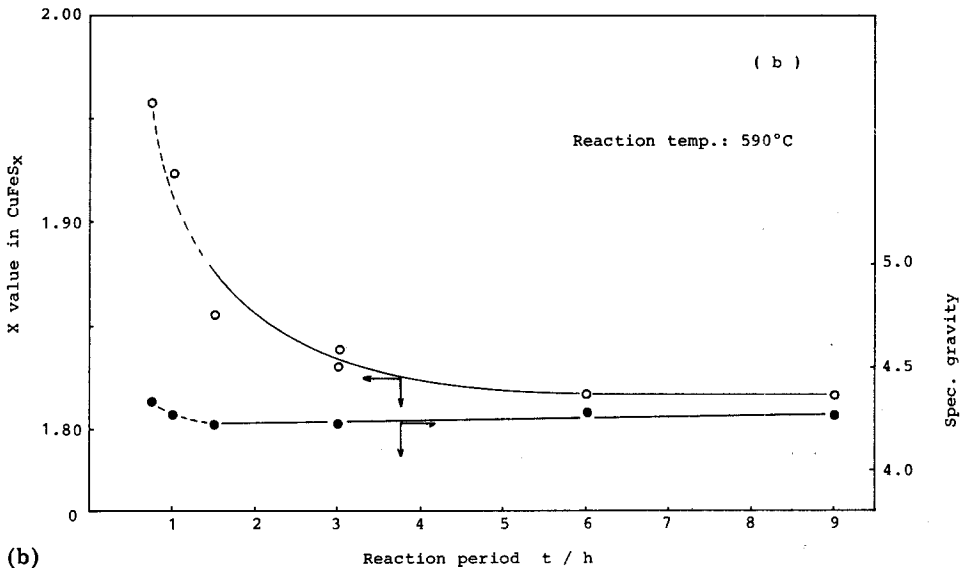
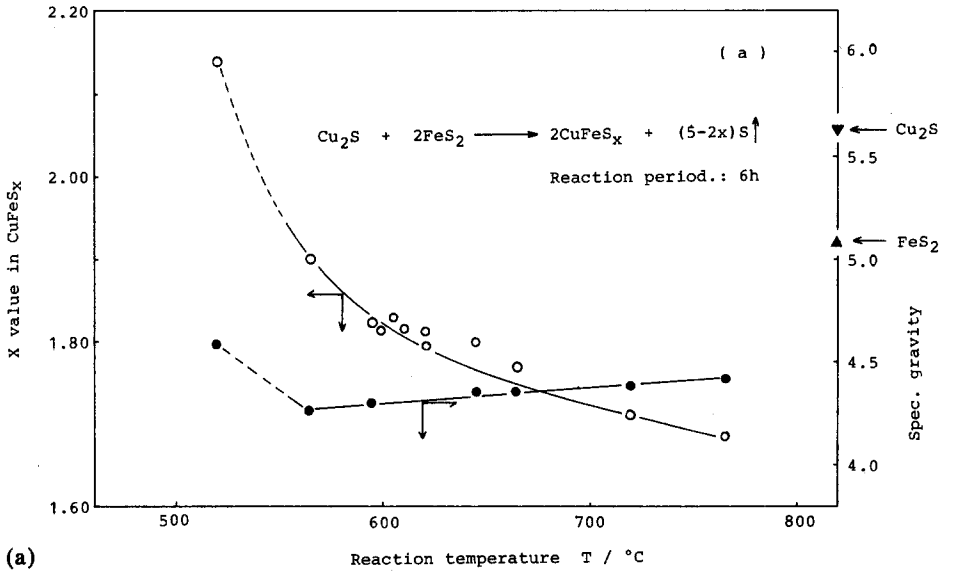


Fig. 1. Synthesis of chalcopyrite: (a) temperature effect; (b) period effect.

the Li/CuO system exhibits a voltage depression upon discharge, the $\text{Li}/\text{CuFeS}_{1.8}$ system does not. In addition, CuO has a larger discharge capacity than $\text{CuFeS}_{1.8}$. However, the $\text{Li}/\text{CuFeS}_{1.8}$ system shows a smaller increase in cell thickness after discharge, *i.e.*, about half that of the Li/CuO system. These characteristics were also exhibited by cells containing natural chalcopyrite (CuFeS_2).

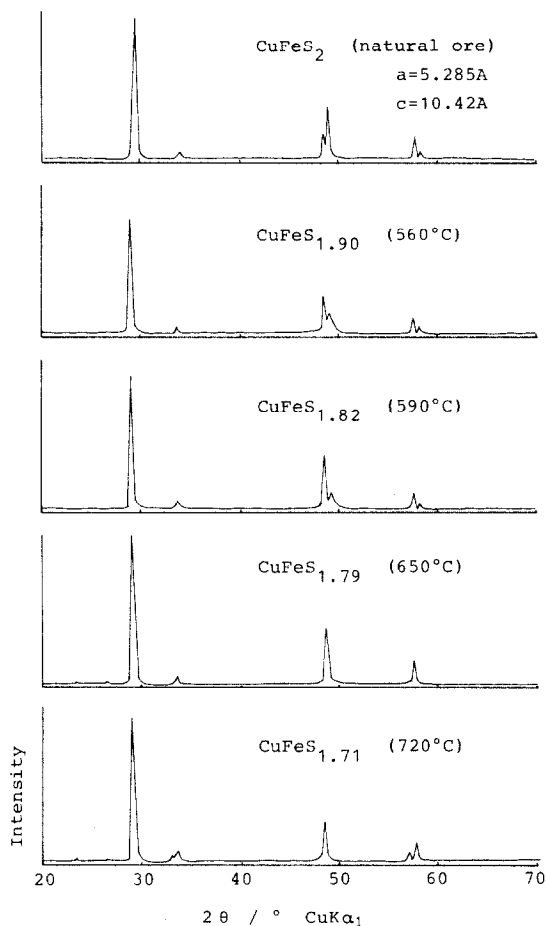
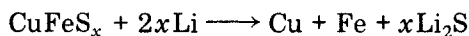
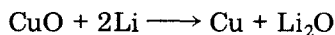


Fig. 2. XRD patterns of natural chalcopyrite and chalcopyrite synthesized at various temperatures.

Natural chalcopyrite was found to have a ZnS (zinc blende) structure [5] with the c -axis doubled and a strongly covalent configuration [6]. Thus, this material has a lower degree of lattice filling than the synthetic variety. It is therefore concluded that the observed small increase in the cell thickness and the absence of a voltage depression upon discharge are related to the crystal configuration of synthetic chalcopyrite.

The discharge characteristics obtained for different addition rates of synthetic chalcopyrite to the CuO cathode are shown in curves (b) to (f) of Fig. 3. It is seen that the optimum addition rate lies between 30 and 40 wt. %.

From XRD and XPS analyses of cathodes subjected to various depths of discharge, the overall cell reactions are considered to be:



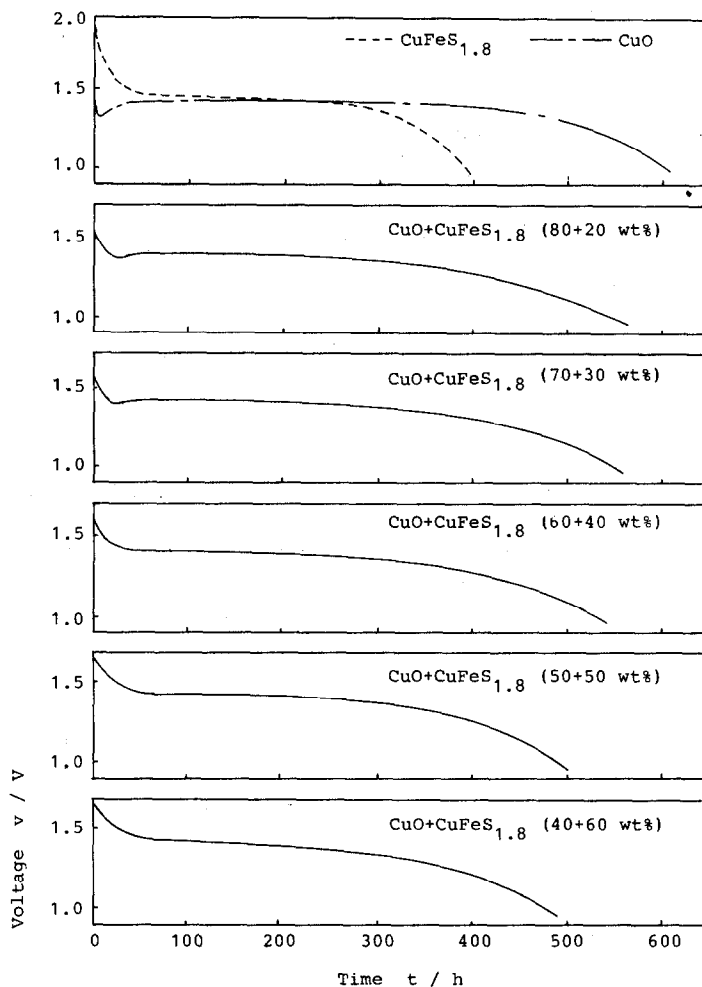


Fig. 3. Discharge characteristics of CuO, $\text{CuFeS}_{1.8}$ and their mixtures (R2320 size, 20°C , $5\text{ k}\Omega$).

In other words, each cathode material is reduced to its metallic elements. The amounts of dissolved metallic ions (Cu^{2+} and/or Fe^{3+}) are found to be of the order of ppm.

Button cells

In the button cell design, the cathode consisted of the mixed active materials described above, a carbon black conductor and a fluoride resin binder. Microporous polyolefin separators were used. These components were selected on account of their discharge performance, cell impedance, and the storage characteristics. The cathode system was compatible with a nickel-plated steel collector (can). The electrolyte was lithium perchlorate dissolved in a mixture of propylene carbonate and dimethoxyethane

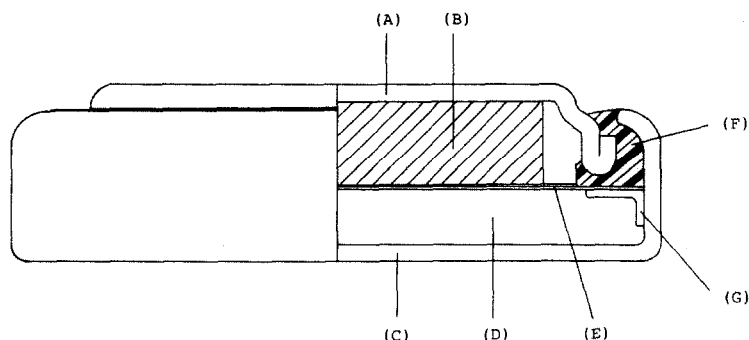


Fig. 4. Cross-sectional view of button cell. (A), top (-); (B), lithium anode; (C), can (+); (D), cathode; (E), separator; (F) gasket; (G), ring.

TABLE 1

Specifications of button cells

Model no.	GR920	GR927
Nominal voltage (V)	1.55	1.55
Nominal capacity (mA h)	40	60
Dimension dia. (mm)	9.5	9.5
height (mm)	2.05	2.70
Approx. weight (g)	0.5	0.6

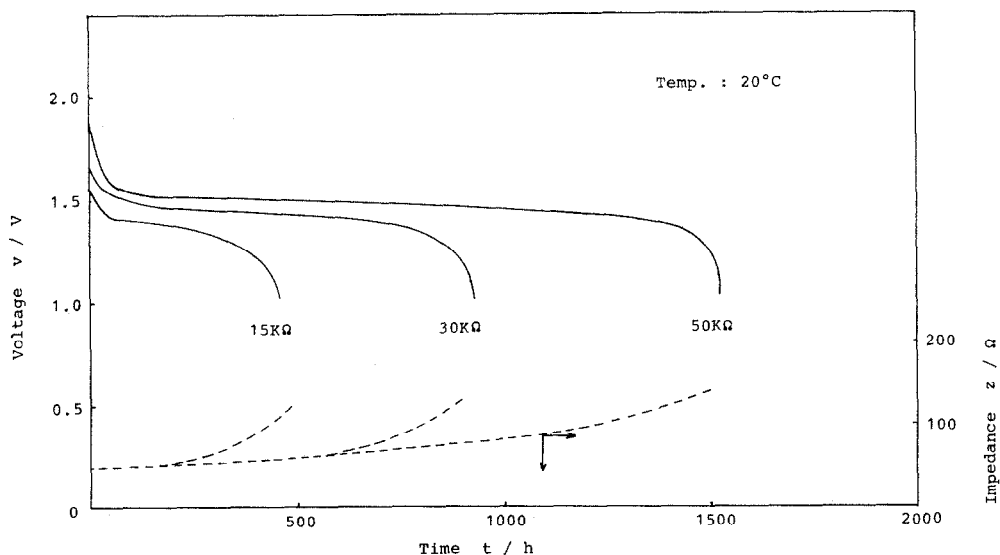


Fig. 5. Discharge characteristics of a GR920 cell.

solvents. A cross-sectional view and the specifications of the button cells (GR920, 927) are given in Fig. 4 and Table 1, respectively.

Typical voltage profiles of a GR920 cell are shown in Fig. 5; temperature characteristics are presented in Fig. 6; storage characteristics at 60 °C

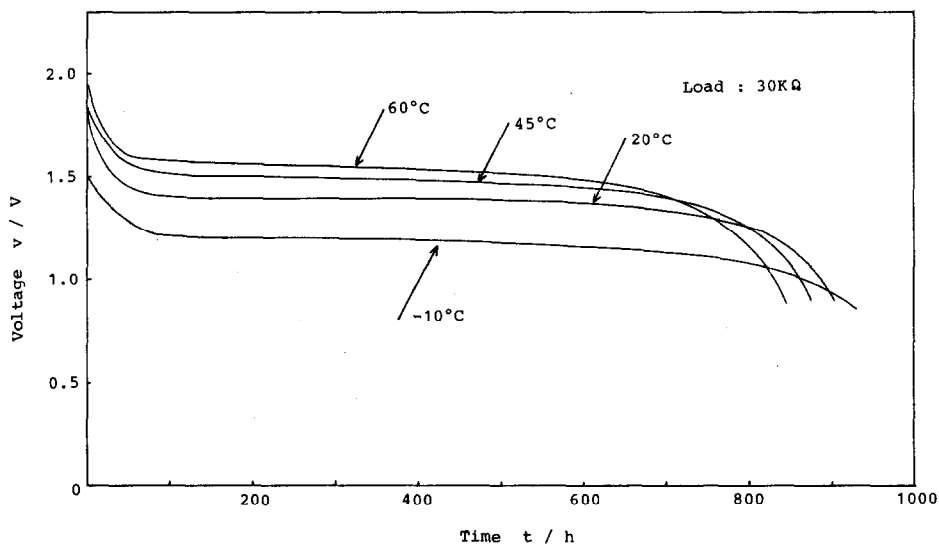


Fig. 6. Temperature characteristics of a GR920 cell.

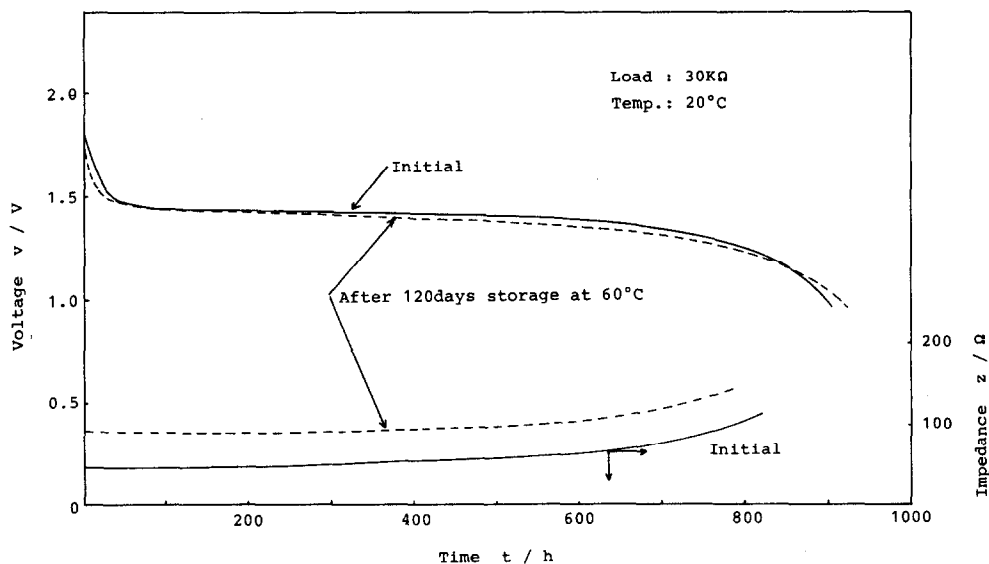


Fig. 7. Storage characteristics of a GR920 cell.

are shown in Fig. 7. The deterioration rate of the capacity is estimated to be $<1\%$ per year at room temperature. Further, storage for 20 days at 60°C is considered to be equivalent to a storage period of one year at room temperature. This conclusion is supported by the low solubilities mentioned above. These findings confirm the successful development of button cells using $\text{CuO}/\text{CuFeS}_2$ cathodes.

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