

THE INFLUENCE OF PREPARATION CONDITIONS ON THE ELECTROCHEMICAL BEHAVIOUR OF CuO IN A Li/CuO CELL

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(Received August 6, 1984)

Summary

A dozen CuO samples prepared under various conditions and from different starting materials were evaluated as cathode materials for a primary Li/CuO cell. The "thin electrode" method was used for rapid evaluation of the samples. Both coulombic efficiency and discharge voltage depend considerably on the method of synthesis. No correlation was found between the specific surface area and the resistivity of the samples on the one hand and the cathode performance on the other. Best results were obtained from CuO prepared by the oxidation of Cu₂O under controlled temperature and time of oxidation.

Introduction

With its high specific capacity per unit weight and volume and its discharge voltage close to that of the Leclanché cell, the Li/CuO cell is one of the nonaqueous power sources which has asserted itself in the market place [1, 2]. It is known that in commercial Li/CuO cells the copper oxide used for the cathode is obtained "by the controlled oxidation of a special copper powder to provide optimum purity together with correct particle size and shape" [2].

There are practically no published data on the performance of CuO cathodes produced by other methods. By contrast, numerous methods for the preparation of CuO are known. Neither are there any data available on the effect some of the relevant physical and electrical properties of the CuO powders have on their performance as cathodes in Li/CuO cells. The present paper is a preliminary attempt to evaluate the electrochemical performances of CuO cathodes made from CuO prepared by several methods, and to find a correlation between cathodic efficiency and discharge voltage on the one hand and the specific surface area and resistivity on the other.

Experimental

Materials

All reagents used for the synthesis of CuO were of reagent grade (Lachema, Czechoslovakia) The cell electrolyte was 1M LiClO₄ (Merck) in propylene carbonate (Merck) containing less than 50 ppm of water. The conducting additive was Teflonized acetylene black, P 1042 (Stickstoffwerk, Priestentz, GDR) [3]

Methods of synthesis

The following methods were used for the preparation of the CuO powders.

(i) Thermal decomposition of copper hydroxycarbonate, obtained by precipitation from a copper sulphate solution with a solution of Na₂CO₃. The precipitate, CuCO₃·Cu(OH)₂·1/2H₂O was washed, dried, and heated for 15 h at 530 °C to obtain CuO

(ii) CuO was precipitated by the slow addition of 1M CuSO₄ to boiling 1M Na₂CO₃. The precipitate was washed and dried at 105 °C

(iii) Thermal decomposition of CuCO₃·Cu(OH)₂·1/2H₂O at 300 °C for 6 h, obtained by precipitating from a Cu(NO₃)₂ solution with NH₄HCO₃.

(iv) Thermal decomposition of Cu(NO₃)₂. After drying to remove the water of crystallization, the salt was heated for 10 h at 320 °C in air.

(v) A solution of CuSO₄ was reacted with NaHPO₂ to obtain copper hydride [4]. The latter was washed, dried, oxidized in air at 100 °C for 1 h, and finally oxidized at 360 °C for 20 h in an oxygen atmosphere

(vi) Copper powder, prepared by cementation of a CuSO₄ solution with Zn, was washed, dried, and oxidized in air for 1 h at 400 °C

(vii) The sample obtained by the gradual heating of copper (method (vi)) under controlled air atmosphere in the range 200 - 400 °C for 3 h was additionally oxidized for 0.5 h at 400 °C in a pure oxygen atmosphere.

(viii) Thermal oxidation in air of metallic copper powder (Merck) for 10 h at 400 °C.

(ix) Oxidation of Cu₂O (POCH, Poland) in air at 400 °C for 0.5 h

(x) The sample obtained by the preceding method was additionally oxidized in air at 400 °C for 16 h

(xi) The sample obtained by method (ix) was further oxidized in oxygen at 400 °C for 0.5 h.

(xii) Commercial CuO (Lachema, Czechoslovakia).

Physical properties and chemical analysis

The specific surface area of all the samples was determined by the BET method. The d.c. resistivity was measured using powder samples pressed at 1 ton/cm² between two Al disc electrodes (1 cm²). The CuO content was determined by chemical analysis [5]. The data are presented in Table 1.

TABLE 1

Characteristics of CuO samples

No	CuO (%)	BET (m ² /g)	ρ (ohm cm)
1	97	0.66	1.7×10^5
2	98	16.2	1.6×10^4
3	100	15.2	2.6×10^5
4	96	0.69	3.9×10^3
5	100	1.39	2.9×10^4
6	85	1.42	1.1×10^3
7	89	1.87	5.4×10^3
8	87	0.61	2.5×10^3
9	70	2.52	4.5×10^4
10	93	1.14	3.9×10^4
11	94	1.24	4.6×10^4
12	70	1.26	9.7×10^3

Cathode preparation

Thin test electrodes, described earlier [6, 7], were used for rapid electrochemical evaluation. About 20 mg per cm² of the cathode mix (50 wt.% CuO, 33 wt.% acetylene black, 17 wt.% Teflon) was spread by rolling onto a Ni gauze (1.5 cm² one side). A four-compartment glass cell housed the test electrode, two large Li counter electrodes, and a Li reference electrode. The test cathodes were discharged galvanostatically at a 10 h rate.

In further experiments, we used "practical" 0.6 - 0.7 mm-thick test CuO cathodes with 0.1 g per cm² of the cathode mix (80 wt.% CuO + 13 wt % acetylene black + 7 wt % Teflon) pressed onto an expanded Ni grid (1 cm²). The galvanostatic discharge was performed in laboratory glass cells with the cathode sandwiched between two Li foil electrodes and two layers of non-woven polypropylene separator (Kendal, USA) In this case the discharge was at the 100 h rate

Results and discussion

(i) Thin test electrodes

All discharge curves (Figs 1 - 5) start at a voltage exceeding 2.24 V (a reversible potential of a Li/CuO cell [2]). It is known that CuO powders contain adsorbed oxygen and water [8] and oxygen is also dissolved in the electrolyte. It was found [9] that this oxygen and water were responsible for the initial high discharge voltage between 2.5 and 3 V (Theoretical, reversible potentials of Li-O₂ and Li-H₂O systems are close to this value.) Experiments to investigate this influence further are in progress. The preliminary results show a decrease in initial voltage if dry argon gas is bubbled through the cell to remove oxygen.

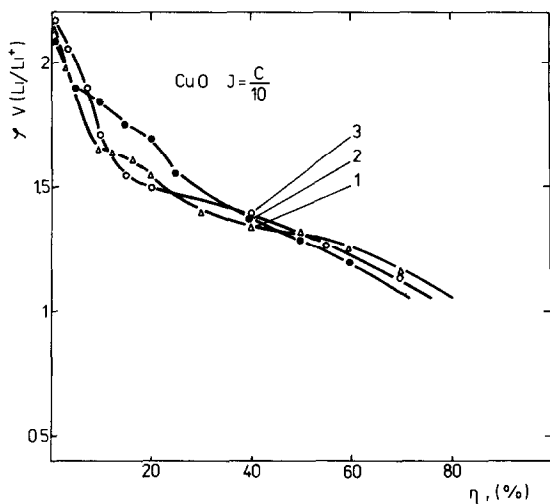


Fig 1 Discharge curves of samples 1, 2 and 3. Thin test electrodes, $C/10$ rate

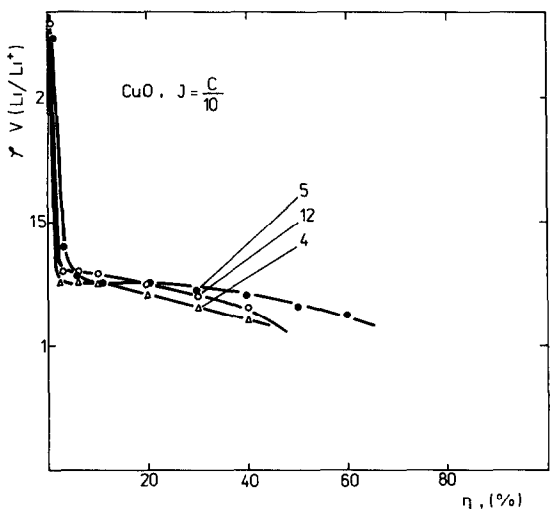


Fig 2 Discharge curves of samples 4, 5 and 12 Thin test electrodes, $C/10$ rate

The discharge curves for test cathodes from samples 1, 2, and 3 are presented in Fig. 1. (The faradaic charge as a percentage of theoretical capacity is denoted as η) The coulombic efficiencies are satisfactory, but the persistence of a higher cell voltage, above 1.5 V, well into discharge, makes these samples inappropriate for 1.5 V cells.

It was found by X-ray diffraction analysis that samples 1 and 2 contained $\text{Cu}_4(\text{OH})_6 \cdot \text{SO}_4$ as an impurity, which could not be removed by washing. Neither chemical nor X-ray analysis revealed the presence of other compounds in sample 3. On the other hand, oxides 1, 2, and 3 all pass through the hydroxycarbonate intermediate. A number of factors contribute

and it is therefore difficult, from the available information, to assess which one is responsible for the initial high voltage portion of the discharge curve

The discharge curves for test cathodes prepared from samples 4, 5 and 12 are shown in Fig 2. All these have lower coulombic efficiencies and lower discharge voltages. In the case of sample 12 this could be assigned to the reduced content of CuO (70% CuO, 30% Cu₂O, see Table 1). Samples 4 and 5 were prepared under long-term (several hours) heating conditions. A better electrochemical performance was obtained with sample 6 (short-term oxidation of copper powder) (Fig. 3). Long-term oxidation causes a drop in the electrochemical performance (samples 7, 8), but the influence of the starting material is also detectable

The deleterious effect of prolonged heating on the electrochemical activity is also apparent from Fig 4, the discharge curve of sample 11 shows an appreciably higher capacity than that of sample 10. The very low capacity of sample 9 may be attributed to incomplete oxidation of Cu₂O after 0.5 h heating in air. The changes in electrochemical activity caused by thermal treatment of the electrode material cannot be related to the surface areas which are practically identical for most of the samples. The different electrochemical activities might be explained by different solid-phase reaction kinetics caused by changes in the crystallographic structure, and non-stoichiometry during thermal treatment.

Resistivity has no obvious relation to the electrochemical parameters of the tested samples (Table 1)

The optimum oxidation temperature (see samples 5 - 11) lies in the range 300 - 500 °C since heating of our samples to 600 °C leads to a decrease in the capacity and voltage of the cells.

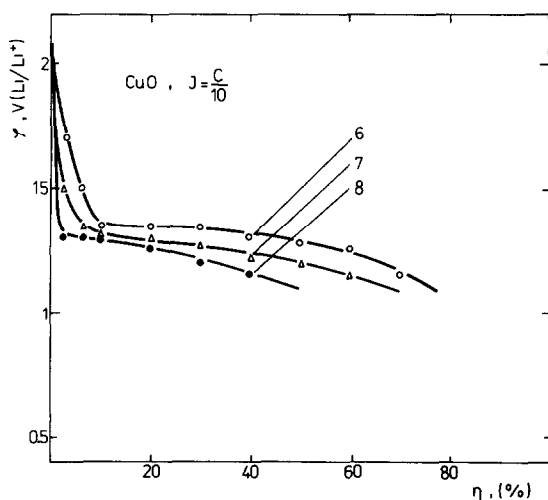


Fig 3 Discharge curves of samples 6, 7 and 8 Thin test electrodes, C/10 rate

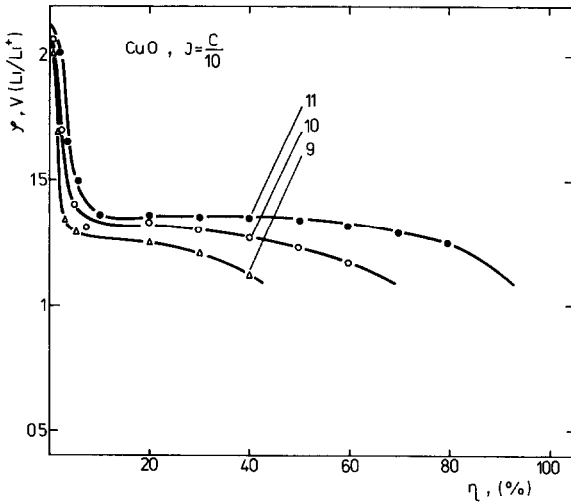


Fig 4 Discharge curves of samples 9, 10 and 11 Thin test electrodes, $C/10$ rate

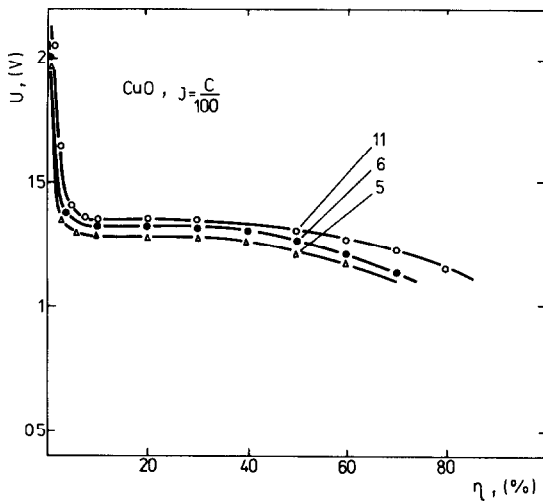


Fig 5 Discharge curves of samples 5, 6 and 11 Practical test electrodes, $C/10$ rate

(u) Practical test electrodes

A survey of the results obtained with the thin test electrodes reveals that the best performance is achieved with samples 5, 6, and 11. These were used for the preparation of practical test electrodes, and their discharge curves are shown in Fig 5. The curves correlate very well with those obtained with the thin test electrodes, illustrating the suitability of thin electrodes for rapid evaluation of solid cathode materials.

Conclusion

The method of preparation of CuO has a considerable impact on its performance as a cathode for Li cells. Of the starting materials, Cu₂O seems to be the most promising. Neither the CuO content, the specific surface area nor the resistivity can serve as guidelines in selecting the best material. More experimental work is necessary to correlate physical, structural and/or compositional features with the electrochemical performance. Prolonged heating of the CuO samples has, in all cases, a negative effect on their electrochemical activity.

References

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