

## Copper oxide as a high temperature battery cathode material\*

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### Abstract

Copper oxide has been tested as a cathode material for high temperature primary reserve thermal batteries in single cells at 530 to 600 °C and at current densities of 0.1 to 0.25 A cm<sup>-2</sup> using lithium–aluminium alloy anodes and lithium fluoride–lithium chloride–lithium bromide molten salt electrolytes. Initial on-load voltages were around 2.3 V, falling to 1.5 V after about 0.5 F mol<sup>-1</sup> has been withdrawn. Lithium copper oxide, LiCu<sub>2</sub>O<sub>2</sub>, and cuprous oxide, Cu<sub>2</sub>O, were identified as discharge products.

### Introduction

Cathode materials for high temperature thermal reserve batteries must satisfy a number of requirements [1]. The existing cathode material, iron disulfide, has many advantages but has limited thermal stability and only a moderate voltage. Copper oxide is thermally stable and has a higher open-circuit voltage. It is a well-known battery cathode material in the lithium copper oxide ambient temperature cell and the discharge mechanism of these cells has been reviewed recently [2]. Previous work on high temperature discharges of lithium copper oxide cells using solid electrolytes has shown that copper oxide can be used as a high temperature battery cathode material [2]. As existing thermal batteries use molten salt electrolytes, either lithium chloride–potassium chloride ('binary') eutectic or lithium fluoride–lithium chloride–lithium bromide ('ternary') eutectic [3], copper oxide has been tested using a molten salt electrolyte. Ternary eutectic was used as the molten salt in the electrolyte. Pulsed discharges and powder X-ray diffraction (XRD) studies of partially discharged cathodes have been carried out to identify discharge intermediates and to establish the discharge mechanism.

### Experimental

Electrochemical discharges at 530 to 600 °C and at 0.1 to 0.25 A cm<sup>-2</sup> have been carried out using the single-cell tester described previously [1]. Discharges were carried

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out at constant current and the discharges are plotted as cell voltage versus capacity withdrawn. 0.3 g pellets of 19.9% lithium-aluminium alloy ('LiAl') (Lithco), pressed at 100 kN, were used as anodes. Two layer pellets consisting of a cathode layer and an electrolyte layer were pressed at 60 kN. The electrolyte layer (0.2 g) consisted of the ternary eutectic immobilized on magnesium oxide binder. The cathode layer consisted of either pure copper oxide or a mixture of copper oxide and ternary eutectic fused together at 475 °C. All cathode layers contained 0.1 g copper oxide. Pellets had a diameter of 1.6 cm with an area of 2.0 cm<sup>2</sup>.

Powder XRD patterns of cathodes that had been partially discharged to the beginning of the 1.4 V plateau were measured on a Siemens D500 diffractometer using Cu K $\alpha$  radiation. In order to reduce data collection time, a position sensitive detector was used, in case any phases present were air or moisture sensitive. Pulsed discharges were carried out on a regime of 54 s on load, 6 s open circuit.

## Results and discussion

Figure 1 shows discharges at 580 °C and 0.1 A cm<sup>-2</sup> of pure copper oxide and copper oxide/ternary eutectic mixtures in the ratios 2:1 and 4:1. The molten salt mixture was added to the cathode to improve the ionic conductivity. Both copper oxide/molten salt cathodes showed substantially better discharges than the pure copper oxide, with the 2:1 mixture giving the better results. This mixture was therefore used in all further experiments. The effect of current density on the discharge is shown in Fig. 2. Copper oxide could be discharged at both 0.1 and 0.25 A cm<sup>-2</sup> at 580 °C, though the voltage (*IR*) drop was significantly more at the higher current so 0.25 A cm<sup>-2</sup> is clearly near

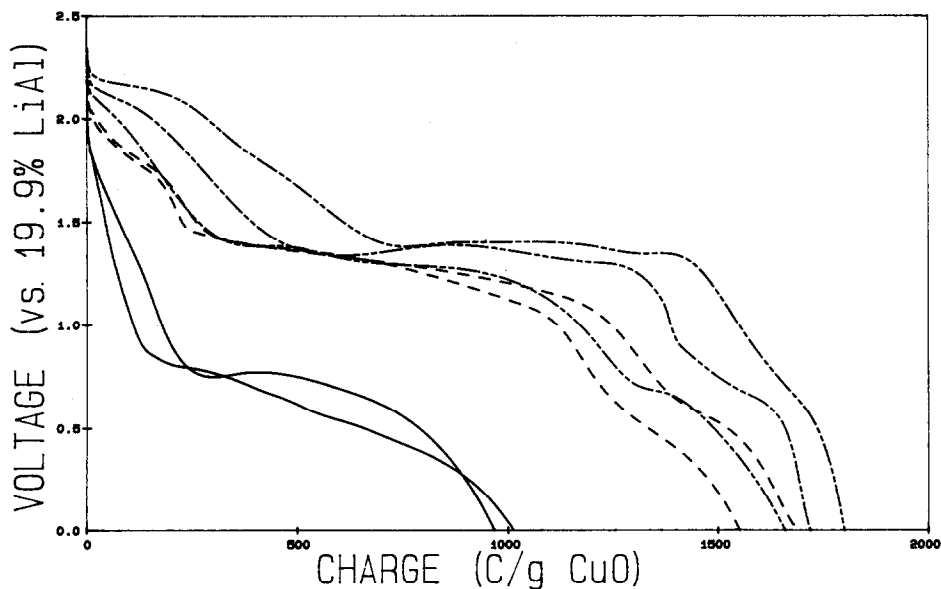


Fig. 1. CuO discharges at 580 °C and 0.1 A cm<sup>-2</sup> of (—) CuO only and (---) CuO/ternary eutectic mixture, ratio 4:1, and (- · - · -) CuO/ternary eutectic mixture, ratio 2:1.

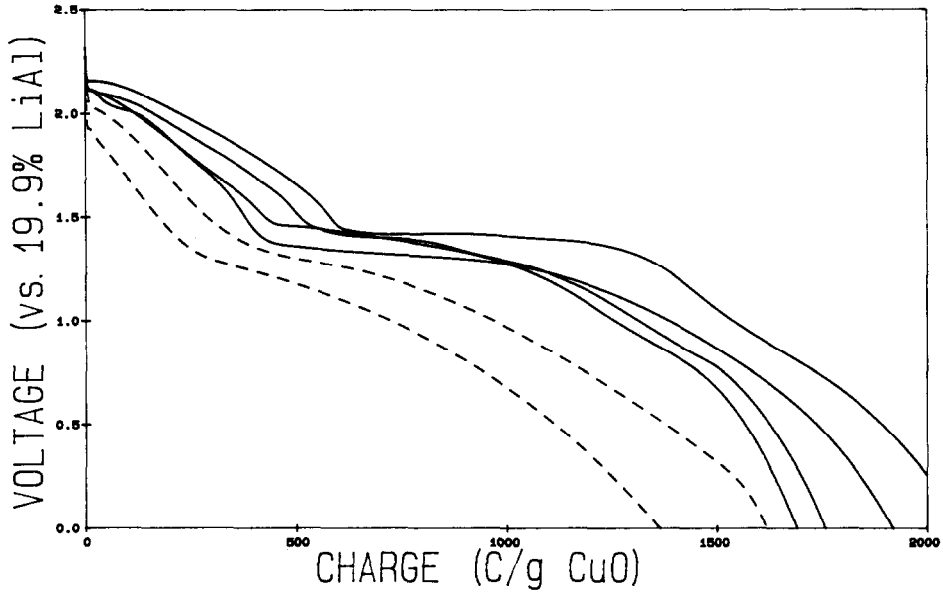


Fig. 2. Effect of current density on CuO discharges at 580 °C: (—) 0.1 A cm<sup>-2</sup>, and (---) 0.25 A cm<sup>-2</sup>.

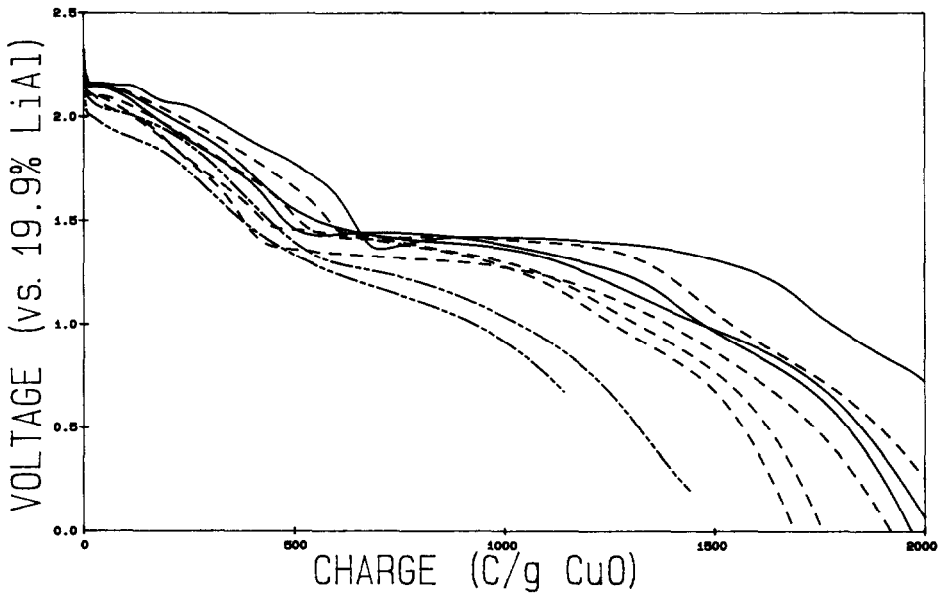
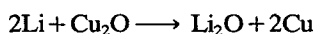
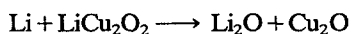
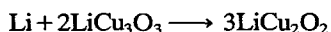
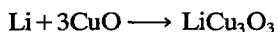


Fig. 3. Effect of temperature on CuO discharges at 0.1 A cm<sup>-2</sup>: (—) 600 °C; (---) 580 °C, and (-·-·-) 530 °C.

to the practical upper current limit for this system. At higher temperatures, the discharges were slightly better (see Fig. 3) though the effect was not large over the small temperature range investigated.



A pulsed discharge (Fig. 5, full line) showed a normal on-load discharge but the open-circuit pulses (plotted as circles in Fig. 5) showed a voltage of about 2.3 V up to about 200 C g<sup>-1</sup> CuO (0.15 F mol<sup>-1</sup>) then a fairly steady voltage at about 2.0 V up to around 600 C g<sup>-1</sup> CuO (0.5 F mol<sup>-1</sup>) then a sharp drop to the long plateau at around 1.5 V. The difference between the open-circuit voltage and the on-load voltage is the *IR* drop which is plotted in Fig. 5 as a dashed line. This shows that the internal resistance increases up to ~600 C g<sup>-1</sup> CuO (0.5 F mol<sup>-1</sup>) when it falls sharply and remains low until ~1500 C g<sup>-1</sup> CuO (1.25 F mol<sup>-1</sup>) when it starts to rise again. This suggests the formation of LiCu<sub>3</sub>O<sub>3</sub>, LiCu<sub>2</sub>O<sub>2</sub> and Cu<sub>2</sub>O in succession, the last two compounds having been identified by XRD, with LiCu<sub>3</sub>O<sub>3</sub> and LiCu<sub>2</sub>O<sub>2</sub> having a relatively high resistance and Cu<sub>2</sub>O having a lower one. The most probable mechanism for the high temperature discharge of lithium copper oxide cells is:



## Conclusions

Copper oxide can be used as a high temperature thermal battery cathode material using molten salt electrolytes. The discharge is likely to proceed through the formation of the intermediate compounds LiCu<sub>3</sub>O<sub>3</sub>, LiCu<sub>2</sub>O<sub>2</sub> and Cu<sub>2</sub>O.

## Acknowledgement

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