

## A high-temperature lithium–copper oxide cell with a solid polymer electrolyte

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### Abstract

The electrochemical behaviour of lithium cells with a solid polymer electrolyte,  $\text{P}(\text{EO})_8 \cdot \text{LiClO}_4$  and a composite cathode with CuO as the active substance was studied at a temperature of 120 °C. The utilization of the CuO increases significantly with increasing content of acetylene black in pressed composite electrodes; the best results were obtained using 40 wt.% CuO + 40 wt.% C + 20 wt.%  $\text{P}(\text{EO})_8 \cdot \text{LiClO}_4$ . The CuO composite cathode can be cycled in the potential range 1.5–3.0 V (versus  $\text{Li}/\text{Li}^+$ ); the first cycle of the electrode yields about 135 mA h/g CuO but the capacity decreases rapidly in further cycles. The discharge of fresh Li/CuO cells occurs in two steps; however, a short heating period of unloaded cells leads to the conversion of CuO to a material that is discharged in a single step but with retention of the original coulombic capacity, which is close to the theoretical value of 674 mA h/g CuO. Because of the high initial potential of CuO (3.2 V versus  $\text{Li}/\text{Li}^+$ ), the heating of fresh cells results in the degradation of the properties of the solid electrolyte, leading to rapid self-discharge of the cell. This can be avoided by decreasing the cathode potential to about 2.7 V either potentiostatically or by galvanostatic removal of charge corresponding to about 0.3%  $C_r$ .

### Introduction

The Li/CuO system is of great importance among lithium cells now produced, especially because of its applicability in a very broad temperature range [1–3]. A large number of laboratories [4–12] has studied electrochemical processes in Li/CuO cells, resulting in a considerable amount of knowledge. The effect of the method of preparing the CuO on the cathode properties was elucidated in refs. 13 and 14, including the effects of various additives [15], and relationships were found between the morphology and structure of CuO and its utilization in real electrodes [16, 17]. The mechanism of the reduction of CuO was clarified in refs. 18–20 and the kinetics of the discharge reaction has been studied [21].

The stoichiometry of the discharge reaction in the Li/CuO cell can be described [2] by the summary equation



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The anodic reaction obeys the simple equation



Under normal function of Li/CuO cells, the polarization of the lithium electrode is only several tens of mV [2, 19]; consequently, the cell behaviour during discharge is affected primarily by the cathode [21]. The discharge of the cathode occurs through insertion of  $\text{Li}^+$  ions [18–20] into the monoclinic [22] CuO lattice



However, under normal conditions and realistic current densities, this reaction occurs with sufficient velocity only on the surface of the CuO particles, while the diffusion of  $\text{Li}^+$  into the bulk of these particles is slow. Consequently, cells should be constructed using either CuO with a large BET surface area or CuO prepared by thermal oxidation under controlled conditions, where a mosaic texture of the individual CuO grains is formed, facilitating faster diffusion of  $\text{Li}^+$  into the bulk of the particles [17].

The insertion compound in eqn. (3) is only an intermediate, yielding Cu and  $\text{Li}_2\text{O}$  in a subsequent electrochemical reduction or decomposing to CuO,  $\text{Cu}_2\text{O}$  and  $\text{Li}_2\text{O}$  [19–21]. The CuO and  $\text{Cu}_2\text{O}$  formed again enter the electrochemical reactions so that the reduction can be described formally by summary eqn. (1). In practice, almost 100% utilization of CuO can be attained [14] (100%  $C_t = 674$  mA h/g CuO). The theoretical voltage of the cell, 2.24 V under standard conditions, can be attained only in the absence of current after a prolonged storage period; when the cell is loaded by even very small current densities of the order of units of  $\mu\text{A cm}^{-2}$ , the cell voltage at 25 °C decreases to a stable value of about 1.5 V, given by the discharge according to eqn. (3) [21].

In addition to common applications, Li/CuO cells with liquid electrolytes are also employed at elevated temperatures; for example, AA-size cells from the SAFT company can be used up to 150 °C [3], permitting high-temperature applications, such as oil well data logging. The need for cells working in this temperature region has led to further research; for example, Tranchant *et al.* [20] studied the electrochemical behaviour of copper oxide in molten dimethyl sulfone at 150 °C. The elevated working temperature leads to changes in the mechanism of the discharge reaction; two plateaux at higher potentials than for discharge at room temperature usually appear on the discharge curves [2, 3, 20].

One of the ways of simplifying the technology of cell production involves the use of solid electrolytes instead of liquid electrolytes. A great deal of effort is being expended at present on research on lithium cells containing solid polymer electrolytes based on poly(ethylene) oxide (PEO) [23]. The working temperature of 70–150 °C is a disadvantage in common applications; at this lower temperature limit, the conductivities of normal solid polymer electrolytes rapidly decrease [24].

The industrial applications of Li/CuO cells at elevated temperatures [3] has led us to consider the utilization of our experience with CuO and solid polymer electrolytes in the construction of a high-temperature cell consisting of the Li/CuO system with a solid polymer electrolyte. This work was thus carried out to characterize this type of cell and to study changes in the mechanism of the discharge reaction at elevated temperatures.

## Experimental

All experiments on cells utilizing solid polymer electrolytes were carried out in a two-electrode arrangement at a temperature of 120 °C. The poly(ethylene) oxide (Aldrich, *MW* 5 000 000; used as received)-based solid electrolyte foils were prepared [25] by casting a 1 vol.% solution of PEO, containing the appropriate amount of the salt in acetonitrile, onto a PTFE foil. The solvent was allowed to evaporate slowly at 25 °C. The resulting films, usually about 100  $\mu\text{m}$  thick, were dried for one day at 120 °C under vacuum and then left for at least one month in a dry argon environment in the glove box (less than 20 ppm of  $\text{H}_2\text{O}$ ). The composition  $\text{P}(\text{EO})_8 \cdot \text{LiClO}_4$  was selected for all the experiments because it yields the highest ionic conductivity in the temperature interval 70–150 °C [23].

The cathode was prepared using pure, very fine CuO powder, prepared by thermal decomposition of  $\text{Cu}(\text{OH})_2$  by a previously described method [14]. CuO was mixed with an appropriate amount of acetylene black P1042 (Stickstoffwerke, Piesteritz, F.R.G.) and the mixture was then wetted under ultrasonics with pure acetonitrile; the appropriate amount of 1 vol.% acetonitrile solution of solid electrolyte  $\text{P}(\text{EO})_8 \cdot \text{LiClO}_4$  was then added. The slurry formed was stirred for 8 h by a magnetic stirrer, with short ultrasonic treatment for periods of 5 min (repeated).

The slurry was then poured onto a PTFE support and the acetonitrile was slowly evaporated at 25 °C. The foil of the cathode composite formed was dried under vacuum at 60 °C (3 h) and then at 120 °C (8 h), and finally stored in a dry box. Prior to use in the cells, the foil was pressed under a pressure of about 10 MPa and then circular cathodes were cut out, with a geometric area of 1.77  $\text{cm}^2$ . These cathodes, with a thickness of about 100  $\mu\text{m}$ , are denoted in the subsequent text as 'foil' cathodes. The method of their preparation is similar to procedures that are widely used in the preparation of composite cathodes from other inorganic materials [23, 26].

Cathodes prepared by the following procedure will be termed 'pressed' cathodes. An acetonitrile slurry of CuO, C and  $\text{P}(\text{EO})_8 \cdot \text{LiClO}_4$  was evaporated to dryness and freed of traces of acetonitrile by heating to 120 °C under vacuum for 3 h. The residue was ground and homogenized on a rotary mill. The mixture was then pressed under a pressure of 6  $\text{t}/\text{cm}^2$  to form circular pellets with a geometric area of 1.77  $\text{cm}^2$  and thickness of 100–180  $\mu\text{m}$  (depending on the carbon content). The pressed cathodes were then dried

by heating under vacuum as for the foil cathodes. The amount of CuO in both types of cathodes was selected so that 100%  $C_t$  corresponded to approx. 10 mA h.

The electrochemical cells were assembled according to the button cell design [27]. Freshly scraped lithium metal was pressed into a stainless steel die, the circular lithium surface was usually covered with one 100  $\mu\text{m}$  thick sheet of the solid electrolyte, and the composite CuO cathode was then attached to the top of the structure. The electrode assembly, spring-loaded between stainless current collectors to  $\sim 0.2$  MPa, was hermetically sealed with a PTFE foil and taken out of the glove box for electrochemical measurements.

For the sake of comparison, several discharge curves were measured for CuO at 25  $^{\circ}\text{C}$  in 1 M  $\text{LiClO}_4$ /propylene carbonate (PC) [19]. The measuring electrode was prepared by rolling a 1:1 mixture of CuO and PTFE-containing acetylene black [28] (75% acetylene black P1042 and 25% Teflon GP-1, ICI, U.K.) on a stainless steel grid, and was discharged in a four-compartment glass cell. Two large Li counter electrodes were placed on each side of the working electrode. The potential of the working electrode was measured against a Li reference electrode immersed in the electrolyte used.

## Results and discussion

### *Measurements in a liquid electrolyte*

Prior to measurements on CuO in composite electrodes, its electrochemical properties were studied in a liquid electrolyte at 25  $^{\circ}\text{C}$ . The discharge curves (Fig. 1) are smooth, with a single voltage plateau at about 1.35–1.45 V, where the difference between the curves for discharge currents  $C_t/20$  and  $C_t/100$  was only about 0.1 V. The utilization of CuO approached 100%  $C_t$ , which (in agreement with published results [14]) indicates a two-electron reduction of each CuO molecule.

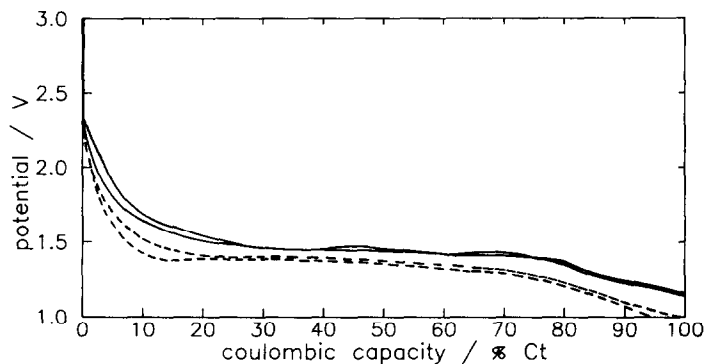


Fig. 1. Galvanostatic discharge curves for a CuO cathode in 1 M  $\text{LiClO}_4$  + PC liquid electrolyte. Temperature 25  $^{\circ}\text{C}$ ; 100%  $C_t \approx 5$  mA h; discharge currents: (—)  $C_t/100$ , (---)  $C_t/20$ .

### Pressed cathodes

Commonly used composite electrodes usually [23] contain about 50% solid polymer electrolyte and only about 5% carbon. Our experience indicates that the reason for the low carbon content is an attempt to increase the energy density of composite electrodes and also technological difficulties connected with commonly employed foil electrodes. No problems were associated with the preparation of electrodes containing 5–10 wt.% C in our laboratory; however, foils with higher C content cracked and could not be used. The good properties of pressed composite positive electrodes for secondary cells,  $\text{Li}/\text{P}(\text{EO})_8 \cdot \text{LiClO}_4 / \text{Na}_x\text{V}_y\text{CrS}_2$  [29], led us to study pressed composite CuO cathodes. This type of cathode permits measurements of the dependence of the electrochemical behaviour of composites on the content of acetylene black and solid polymer electrolyte in the cathode.

Typical results are depicted in Fig. 2(a)–(c), giving the galvanostatic discharge curves for cathodes containing the same amount of CuO (corresponding to the theoretical coulombic capacity  $C_t \approx 10$  mA h) and various C: $\text{P}(\text{EO})_8 \cdot \text{LiClO}_4$  ratios, discharged at a temperature of 120 °C and currents of  $C_t/20$  and  $C_t/100$ . As the acetylene black content increases, the utilization of the CuO rapidly increases, indicating that the current loading of relatively thick cathodes (100–180  $\mu\text{m}$ ) is not limited by the ionic conductivity of the solid electrolyte filling the void space between the individual CuO and C particles, but that the main limiting factor is apparently the insufficient electronic conductivity of the cathode limiting electron transfer from the current collector to the individual CuO particles. A carbon content of 40% is necessary for satisfactory electrode functioning (Fig. 2(c)); this is a relatively high value and limits especially the maximal attainable volume energy density of composite cathodes. It is not clear whether this amount of conducting additive is actually essential or whether the preparation of the cathodic composite mixture causes complete coverage of some of the CuO or C particles by the polymer electrolyte film, with consequent electronic insulation from the current collector. However, modifications of the preparation procedure for composite electrodes (by shortening or omitting some operations ensuring complete wetting of CuO and C by the solid electrolyte solution) always led to lower utilization of CuO and greater scattering of the results; consequently, the best pressed cathode composition would appear to be 40 wt.% CuO + 40 wt.% C + 20 wt.%  $\text{P}(\text{EO})_8 \cdot \text{LiClO}_4$ .

Acetylene black and other carbonaceous materials can be electrochemically reduced at potentials close to, or even higher than, 1 V ( $\text{Li}/\text{Li}^+$ ) [30]. Consequently, the contribution of the acetylene black to the discharge curves of CuO in Fig. 2 was estimated by preparing a number of composite electrodes with the composition 50% C + 50%  $\text{P}(\text{EO})_8 \cdot \text{LiClO}_4$ . The cells with these electrodes were discharged with a current of only 20  $\mu\text{A}$ , which is far less than in measurements on the composite cathodes containing CuO. Even under these conditions, the electrochemical reduction of the carbon black was negligible compared with CuO, as can be seen in Fig. 2(b) and (c), where the results for carbon black alone are denoted by the dotted lines.

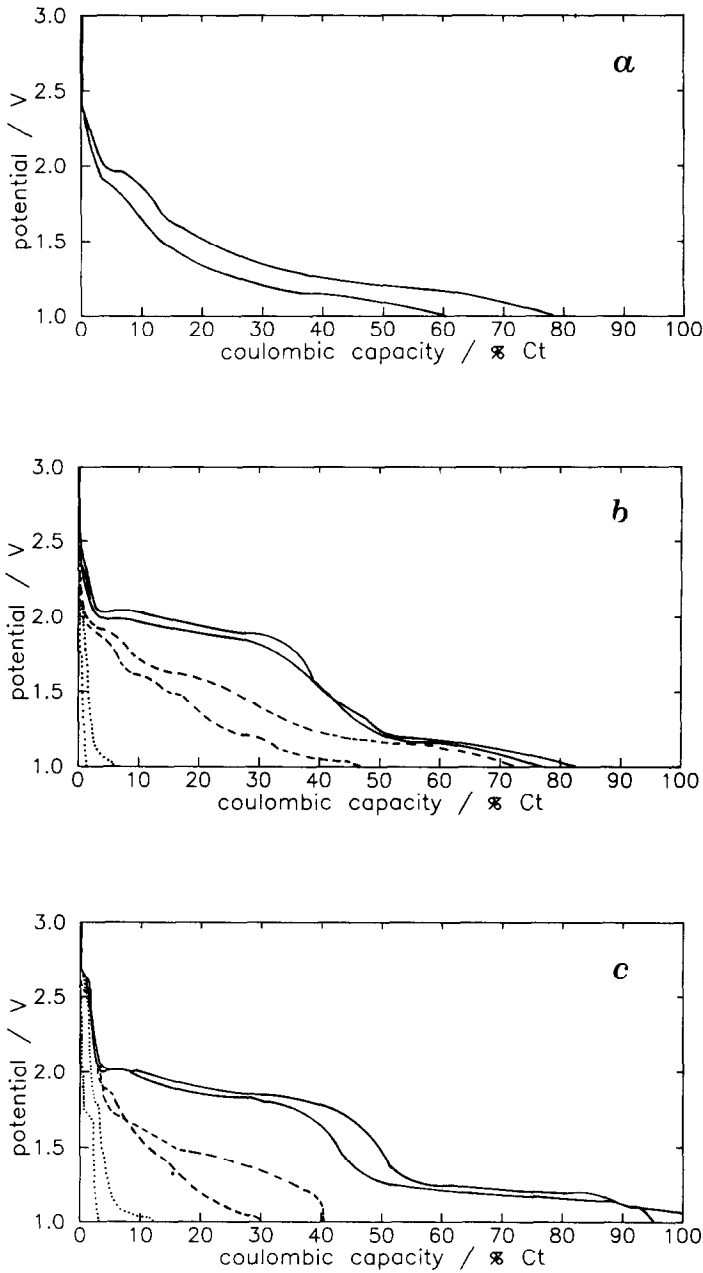
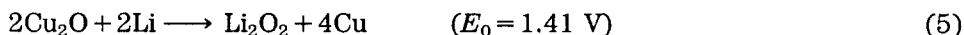
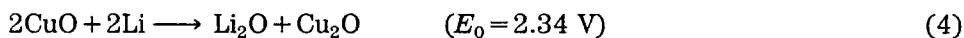


Fig. 2. Galvanostatic discharge curves of  $\text{Li/P(EO)}_8\cdot\text{LiClO}_4$ /pressed composite cathode cells. Temperature  $120^\circ\text{C}$ ;  $100\% C_t \approx 10 \text{ mA h}$ ; discharge currents: (—)  $C_t/100$ , (---)  $C_t/20$ ; discharge commenced 1 h after heating the cell to the working temperature. For comparison, curves are given (dotted lines) for electrodes containing  $50\% \text{ C} + 50\% \text{ P(EO)}_8\cdot\text{LiClO}_4$  discharged by a current of  $20 \mu\text{A}$ . (a)  $40\% \text{ CuO} + 10\% \text{ C} + 50\% \text{ P(EO)}_8\cdot\text{LiClO}_4$ , (b)  $40\% \text{ CuO} + 20\% \text{ C} + 40\% \text{ P(EO)}_8\cdot\text{LiClO}_4$ , (c)  $40\% \text{ CuO} + 40\% \text{ C} + 20\% \text{ P(EO)}_8\cdot\text{LiClO}_4$ .

Comparison of Figs. 1 and 2(c) reveals the differences between the discharge curves at 25 and 120 °C. Two discharge plateaux (at approx. 1.9 and 1.2 V, Fig. 2(c)) appear on the discharge curve for the discharge of cells containing solid electrolyte at 120 °C. These two plateaux are clearly a result of the higher temperature, as they have also been observed for Li/CuO cells with liquid electrolytes at temperatures above 70 °C [2, 3, 20]. The length of each discharge plateau corresponds to almost exactly  $1 e^- / \text{CuO}$ , i.e., 50%  $C_t$  (Fig. 2(c)). This could indicate that the reduction of CuO at 120 °C does not occur through the insertion of  $\text{Li}^+$  into the crystal lattice but that it rather occurs stepwise through the subsequent one-electron reduction steps, e.g., according to the following scheme (the standard potentials of these reactions are closest to the observed potential plateaux)



It is probable that, similarly to the reaction(s) at 25 °C in liquid electrolyte [21], the reduction mechanism in a solid electrolyte at 120 °C is affected primarily by the kinetics of the individual reactions and that two reaction mechanisms compete—the stepwise discharge according to eqns. (4) and (5) and the insertion mechanism according to eqn. (3).

#### *Foil cathodes*

The first experiments with foil cathodes, prepared analogously to secondary systems with solid polymer electrolytes [23], were not very successful. It was found to be impossible to prepare a cathodic composite foil containing more than 10% acetylene black as the substance cracked and completely crumbled at higher C contents. The reproducibility of the galvanostatic discharge curves was very poor; coulombic capacities scattering between 50 and 100%  $C_t$  were attained for a discharge current of  $C_t/100$ . These results are apparently a consequence of poor contact between the CuO and C particles in the cathode, as the electrode behaviour was greatly improved after pressing the evaporated cathode foil.

The rate of sedimentation of the individual components is apparently an important factor in the preparation of foil cathodes—it was found that the underside of the cathode should be mounted in the direction towards the current collector. It would thus appear that the slow solvent evaporation produces an inhomogeneous foil whose lower side has a relatively higher content of C and CuO (because of the relatively rapid sedimentation of the solid phase). The differences between the two sides of the cathode are visible to the naked eye. The formation of these inhomogeneities can obviously be suppressed by the use of far more concentrated, and thus more viscous solutions of the polymer electrolyte to prepare the composites. However, the cathode foil then contains a large number of bubbles that are retained in the composite as a result of the high viscosity of the mixture.

Figure 3 depicts typical discharge curves for foil cathodes prepared by the optimum procedure. The character of the curve is the same as for the

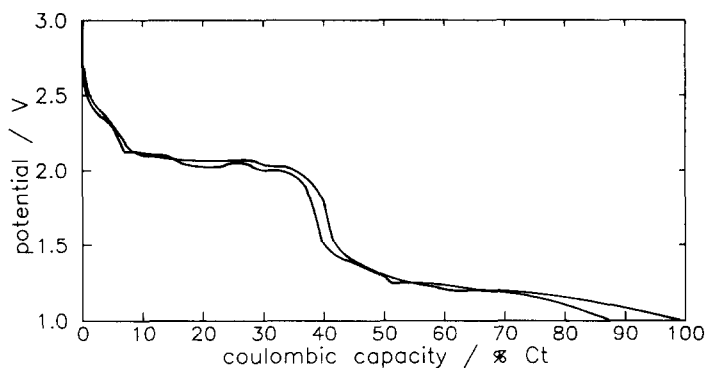


Fig. 3. Galvanostatic discharge curves for Li/P(EO)<sub>8</sub>·LiClO<sub>4</sub>/foil composite cathode (45%CuO + 5%C + 50%P(EO)<sub>8</sub>·LiClO<sub>4</sub>) cells. Temperature 120 °C; 100%  $C_t$  = 10 mA h; discharge current  $C_t/100$ ; discharge commenced 1 h after heating the cell to the working temperature.

pressed cathodes in Fig. 2(c). Comparison of the two types of cathodes clearly reveals that the discharge curves are not affected by the reduction of the acetylene black present, as large differences in its content (5 and 40%) yield practically identical results.

#### *Behaviour of the cells at 25 °C*

Although a working temperature of over 70 °C has been recommended for practical applications of solid polymer electrolyte P(EO)<sub>8</sub>·LiClO<sub>4</sub> [31], it was found that Li/P(EO)<sub>8</sub>·LiClO<sub>4</sub>/polypyrrole cells could be discharged at 25 °C at a current density below 0.1  $\mu\text{A}/\text{cm}^2$  with very good utilization of polypyrrole [25]. Consequently, several cells with CuO composite cathodes were tested at 25 °C.

A coulombic capacity of only 0.1%  $C_t$  was attained at room temperature with cell loading by a current density of 0.1  $\mu\text{A}/\text{cm}^2$ —the second day after switching the current on, the polarization of the cell reached several volts. However, after switching the current off, the OCV value was again more than 2 V after less than one second. A certain increase in the capacity could be attained by heating the cell to 120 °C for 3 h, apparently leading to recrystallization of the solid polymer electrolyte [31] and to improvement in the electrical contacts. Even then, however, the capacity after cooling was only 0.3%  $C_t$  for discharge with a current density of 0.1  $\mu\text{A}/\text{cm}^2$ .

#### *Cycling of CuO electrodes*

Deeper discharge of CuO cathodes in liquid electrolytes is irreversible [21]. However, the discharge of CuO at 120 °C in cells with solid polymer electrolytes apparently occurs through a different reaction mechanism and thus it might be possible to cycle CuO under certain conditions. It was found that the cell cannot be recharged after discharging to 100%  $C_t$ . This is also true for partial discharge when the final voltage of the cell is lower than 1.3 V, i.e., when the second plateau (Fig. 3) is attained in the discharge.



However, CuO can be cycled at 120 °C in the potential range 1.5–3.0 V. The utilization of CuO at cycling currents of  $\pm C_t/100$  is about 20%  $C_t$  in the first cycle, i.e., the coulombic capacity is about 135 mA h/g CuO. This capacity is comparable with the real capacities attained for other lithium systems [23, 26]. The attainable capacity decreases during the cycling: after 10 cycles a value of only about 3%  $C_t$  was found. This value then remains constant for subsequent cycles.

The cells after galvanostatic cycling can be discharged to lower voltages to obtain the remaining capacity. A typical result is depicted in Fig. 4. The cell underwent 30 cycles between 3.0 and 1.5 V, where the first discharge yielded a coulombic capacity of 20%  $C_t$ . Discharge of the cycled cell to 1.0 V yielded the remaining 80% capacity. It is interesting that the discharge plateau at about 1.2 V, corresponding to the second discharge step in Fig. 3, then covers the whole discharge curve in Fig. 4. Thus, cycling between 1.5 and 3.0 V converts all the CuO in the cathode to a substance that is discharged at 1.2 V. The same results were obtained for a cell cycled between 1.3 and 3.2 V; discharge to 1 V then yielded 40–60%  $C_t$ .

#### *Behaviour of unloaded cells*

The first question to be answered after the discovery that shallow cycling influences the properties of the CuO cathode is whether CuO is stable in the initial state or whether it spontaneously changes at a temperature of 120 °C or reacts with the polymer electrolyte. Consequently, an attempt was made to measure the discharge curves of cells heated to the given temperature for various periods of time under open circuit conditions. However, all the cells shorted after standing for several days—this was surprising, because both Li/P(EO)<sub>8</sub>·LiClO<sub>4</sub>/polypyrrole [25] and Li/P(EO)<sub>8</sub>·LiClO<sub>4</sub>/Na<sub>x</sub>V<sub>y</sub>CrS<sub>2</sub> [29] cells with the same solid electrolyte, and made in the same way in the same test vessels as the CuO cell, worked without shorting for up to several months. It was also interesting that the cells discharged with a current of

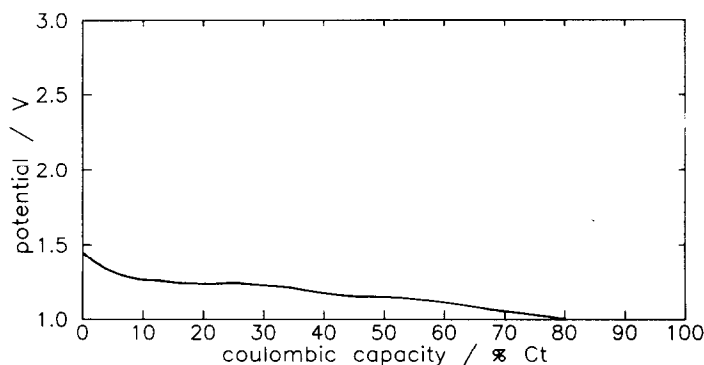


Fig. 4. Typical galvanostatic discharge curve for the Li/P(EO)<sub>8</sub>·LiClO<sub>4</sub>/foil composite cathode (45%CuO + 5%C + 50%P(EO)<sub>8</sub>·LiClO<sub>4</sub>) cell measured after 30 galvanostatic cycles ( $\pm C_t/100$ ) between 1.5 and 3.0 V. Temperature 120 °C; 100%  $C_t$  = 10 mA h; discharge current  $C_t/100$ .

$C_t/100$ , i.e., for 100 h, were not shorted. Thus, the system was investigated in greater detail, and the dependence on time of the OCV of the cells with CuO cathodes was measured at 120 °C.

It was found that the open circuit voltage of the cells decreases very rapidly with time (Fig. 5). Several plateaux with reproducible potentials can be seen on the curves. Complete spontaneous discharging of the cells occurred after 40–60 h; after 15 h the cell voltage was only slightly greater than 1 V. These results indicate that CuO interacts with the  $P(\text{EO})_8 \cdot \text{LiClO}_4$  solid electrolyte at elevated temperatures. The original only ionically conductive [31] material either attains partial electronic conductivity, leading to rapid spontaneous discharge, or the CuO is dissolved in the solid electrolyte. The change in the properties of the solid electrolyte is apparently caused by a very high initial potential of CuO (about 3.2 V versus  $\text{Li}/\text{Li}^+$ ), probably causing a partial electrolyte oxidation. The reduction products of CuO cannot

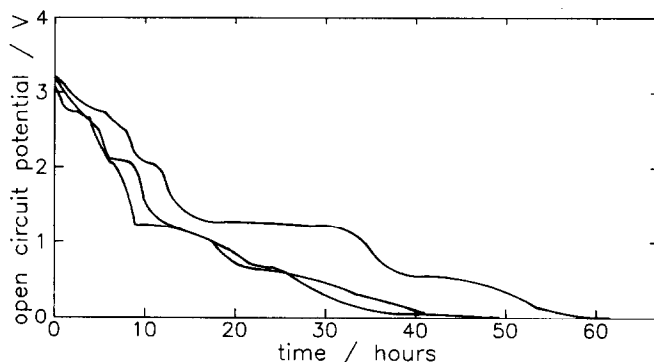


Fig. 5. Dependence of OCV on time for fresh  $\text{Li}/\text{P}(\text{EO})_8 \cdot \text{LiClO}_4/\text{foil}$  composite cathode (45%CuO+5%C+50% $\text{P}(\text{EO})_8 \cdot \text{LiClO}_4$ ) cells. Three nominally identical cells containing two solid electrolyte layers (100  $\mu\text{m}$ +15  $\mu\text{m}$ ); temperature 120 °C; 100%  $C_t \approx 10$  mA h.

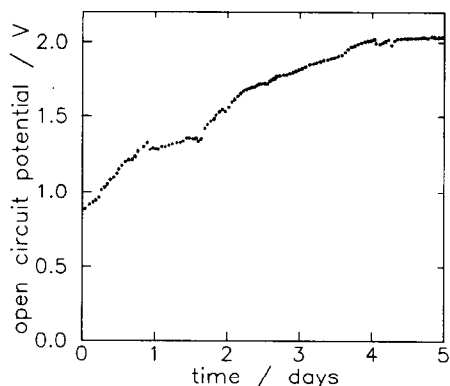


Fig. 6. Dependence of OCV on time for the  $\text{Li}/\text{P}(\text{EO})_8 \cdot \text{LiClO}_4/\text{foil}$  composite cathode (45%CuO+5%C+50% $\text{P}(\text{EO})_8 \cdot \text{LiClO}_4$ ) cell after potentiodynamic discharge (0.1 mV/s) to a voltage of 0.3 V. Temperature 120 °C.

cause modification of the solid electrolyte as shorts do not appear in the partly or completely discharged cell (Fig. 6). The hypothesis of the effect of the high potential is supported by the fact that electrolyte modification does not occur after potentiostatic (partial) cell discharge to 2.7 V (consuming about 0.3%  $C_0$ ).

### Voltammetric measurements

Figure 7 depicts a typical voltammogram for the reduction of CuO in the composite cathode at 120 °C. There are two marked peaks (1.94 and 0.99 V versus Li/Li<sup>+</sup>) corresponding to the first and second galvanostatic discharge plateaux (at 1.9 and 1.2 V) in Fig. 3. There is a clear change in the shape of the voltammogram for the cell held potentiostatically at 2.7 V for 15 h. For the fresh cell, the charge collected in the potential range 2.7–1.4 V (i.e., the first peak) is practically equal to the charge collected in the potential range 1.4–1.0 V (the final discharge voltage of real cells); for cells left to stand for 15 h at 2.7 V, the charge corresponding to the region 2.7–1.4 V is roughly one third of that corresponding to the region 1.4–1.0 V. After the cell is left to stand for a prolonged period of time at 2.7 V, the peak at 1.94 V completely disappears, while that at 0.99 V increases. However, the overall charge delivered from the cell does not change and is independent of the cell heating time prior to discharging,

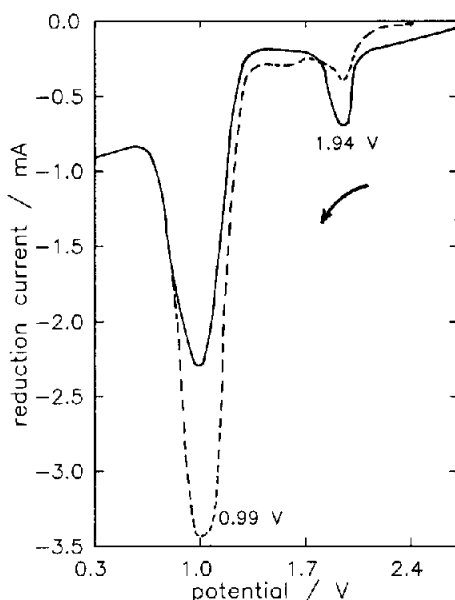


Fig. 7. Voltammetric discharge curves for the Li/P(EO)<sub>8</sub>·LiClO<sub>4</sub>/foil composite cathode (45%CuO+5%C+50%P(EO)<sub>8</sub>·LiClO<sub>4</sub>) cell. Temperature 120 °C; potential scan rate 0.1 mV/s; 100%  $C_0$  = 10 mA h. (—) Fresh cell; (---) cell maintained at 120 °C potentiostatically at 2.7 V for 15 h.

indicating relatively rapid conversion of the initial CuO to a material that is discharged at lower potentials.

It should be pointed out that voltammetric discharge of the cell at a rate of 0.1 mV/s results in much higher polarization than galvanostatic discharge by a current of  $C_t/100$ . The cathode is loaded by a current density of up to 2 mA/cm<sup>2</sup>, which naturally leads to a considerable shift of the peak potentials from the equilibrium values, which can be up to several hundreds of millivolts higher.

## Conclusions

(i) The utilization of CuO in pressed composite cathodes greatly increases with increasing content of acetylene black, while a relatively small amount of solid electrolyte in the composite is sufficient. The best results were obtained using composites containing 40 wt.% CuO + 40 wt.% C + 20 wt.% P(EO)<sub>8</sub>·LiClO<sub>4</sub>.

(ii) The discharge of freshly prepared Li/P(EO)<sub>8</sub>·LiClO<sub>4</sub>/CuO cells occurs in two steps at 1.9 and 1.2 V, each of which corresponds to one-electron reduction of CuO.

(iii) Heating of freshly prepared cells leads to a degradation of the solid electrolyte, resulting in fast spontaneous discharge, probably as a result of the high initial potential of CuO (3.2 V versus Li/Li<sup>+</sup>). This phenomenon can be avoided by removal of a capacity corresponding to about 0.3%  $C_t$  or partial potentiostatic discharge to a voltage of about 2.7 V.

(iv) The composite CuO cathode can be cycled in the potential range 1.5–3.0 V. In the first cycle, the coulombic capacity of the cathode is about 135 mA h/g CuO; this value rapidly decreases in subsequent cycles.

(v) CuO is changed relatively rapidly in the cell to a material that discharges in a single step at a lower potential (1.2 V); however, the overall coulombic capacity of the cell is retained within experimental error.

(vi) The cells can be loaded by a current density of up to 2 mA/cm<sup>2</sup> at 120 °C.

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