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Discharge behaviour of copper(II) halide cathodes with molten nitrate electrolytes*

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This paper describes the discharge behaviour between 150 and 220 °C of cells using copper(II) halide as the cathode material and molten nitrate as the electrolyte for a reserve battery of high energy density running at medium temperatures. At these temperatures a lithium–aluminium alloy/copper(II) chloride cell can be discharged at a current density of $50\,\mathrm{mA\,cm^{-2}}$. The open-circuit potentials are 3.45 V (against 20 wt % lithium–aluminium alloy). Discharge results on the combination LiAl/$LiNO_3$–KNO_3/$CuCl_2$ cells show a capacity of $1343\,\mathrm{C\,g^{-1}}$ to zero voltage at a current density of $50\,\mathrm{mA\,cm^{-2}}$ at 230 °C. In practice, this is equivalent to a specific energy output of $356\,\mathrm{Wh\,kg^{-1}}$ of cathode to a 70% voltage cut-off. The compatibility of copper(II) chloride with nitrate electrolytes has been investigated. Copper(II) chloride appears to be compatible with nitrate up to about 260 °C. The performance of the LiAl/NO_3/CuF_2 cell was very poor giving a capacity of $50\,\mathrm{C\,g^{-1}}$.

Keywords: *reserve lithium cells*, *nitrate electrolytes*, *copper* (II) *chloride cathode*

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1. Introduction

In the last 12 years there has been an increased effort [1–5] aimed at investigating the performance of copper(II) chloride electrodes with various electrolytes for use in lithium rechargeable batteries. Despite the numerous advantageous characteristics of $CuCl_2$, particularly with respect to high energy density and high rate capability, its utilization as a cathode material has not yet been exploited commercially. The majority of these investigations were conducted in either organic electrolytes or in inorganic SO_2 electrolytes for use in rechargeable systems. The electrochemical behaviour of lithium–copper(II) chloride batteries based on sulphur dioxide electrolytes are complicated by the reduction of SO_2 and also the specific conductivity of organic based electrolytes is usually about one order of magnitude lower than that of aqueous sodium hydroxide or sulphuric acid, both of which are used in commercial batteries. It could probably be inferred that the development of the Li/$CuCl_2$ system is inhibited by the poor conductivity of electrolytes and also the reduction of sulphur dioxide based electrolytes. This problem could probably be solved by investigating the discharge performance of copper(II) chloride in a stable and highly conductive inorganic electrolyte. Thus, the objective of the present work was to investigate the discharge behaviour of cells containing lithium aluminium alloy anode, molten lithium nitrate–potassium nitrate electrolyte and copper(II) chloride cathode. The ultimate goal is to develop a medium-temperature high energy density reserve battery, running at a current density of 10 to $150\,\mathrm{mA\,cm^{-2}}$ and operating between 150 and 350 °C. The activation system of the proposed reserve medium-temperature battery is similar to that of a thermal battery in that an electrolyte which is solid under storage conditions would be melted to activate the battery. The nature of the cell discharge reactions and the compatibility of the cathode and the electrolytes will be discussed.

2. Experimental details

2.1. *Chemicals*

Potassium nitrate and lithium nitrate were used as the electrolyte materials. Copper(II) chloride was used as the cathode material. These reagents were obtained from Aldrich Chemical Company. The purities of potassium nitrate and lithium nitrate were declared as 99.99% and that of copper(II) chloride and copper(II) fluoride as 98%. The eutectic ratios of the electrolytes (33 mol % lithium nitrate, 67 mol % potassium nitrate) were weighed out and then mixed with silica binder (12%) and fused overnight at 160 °C. The resultant mixture was ground and passed through a $150\,\mu\mathrm{m}$ sieve before use. Portions of Ceylon fine flaked graphite (25%) were added to the cathode in order to improve the conductivity.

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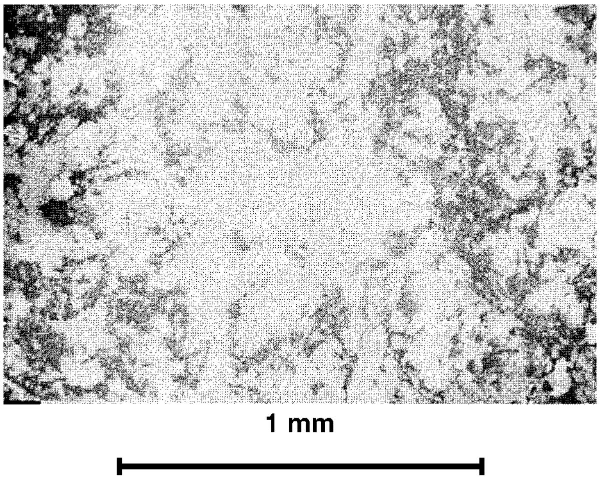

Fig. 1. SEM of cathode before discharge ($CuCl_2$).

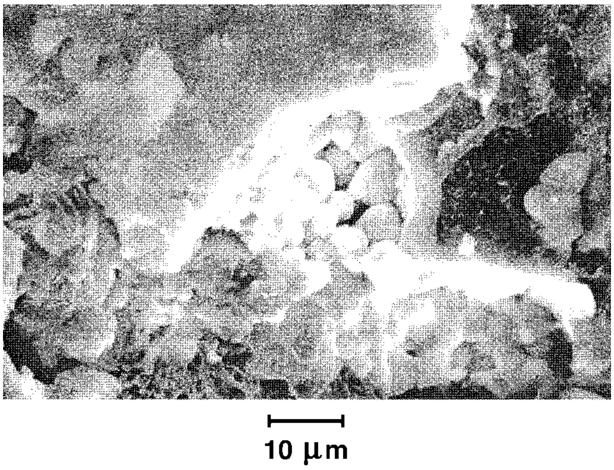

Fig. 2. SEM of discharged $CuCl_2$ pellet showing metallic copper.

2.2. *Analysis of materials*

The thermal analyses of materials used was carried out using combined thermogravimetric analysis (TGA) and differential thermal analysis (DTA). The heating rate was 10 °C min^{-1} and samples were heated in an atmosphere of helium. The thermogravimetric balance used was a Stanton Redcroft STA1000.

X-ray diffraction (XRD) analyses of selected discharged materials were carried out by the Microstructural Analysis Section, DRA Farnborough. The instrument used was a Siemens D500 diffractometer equipped with CuK_α radiation and a position sensitive detector to reduce data collection.

The surfaces of discharged $CuCl_2$-graphite pellets were observed by a scanning electron microscope (SEM) Phillips model 550 and the results are shown in Figs 1 and 2.

2.3. *Preparation of pellets for single cell tests*

Experimental single cells consisted of a separate 0.3 g 24% lithium aluminium alloy anode pellet pressed at about 5 tonnes cm^{-2} together with a bilayer pellet consisting of 0.3 g each of electrolyte binder (EB) and depolarizer–electrolyte layers pressed at 3 tonnes cm^{-2}. These cell components were sandwiched between flat iron current collectors, which in turn were sandwiched between mica insulators. Isothermal cell tests were then performed after the cells had been heated from both sides using electric heaters. A diagram of the single cell tester together with tests results are covered in Section 3. All powder handling, pelletization and subsequent discharge tests were carried out in an argon atmosphere of less than 10 ppm relative humidity. The proportions of electrolyte used in each test are shown in the individual discharge profile diagrams and the discharge results are discussed in Section 3.

3. Results and discussion compatibility of copper(II) chloride with nitrate

The thermograms obtained by the thermal analyses of lithium nitrate, copper(II) chloride and for a mixture of $CuCl_2$ and lithium nitrate are displayed in Figs 3 to 5. It can be seen in Fig. 3 that the lithium

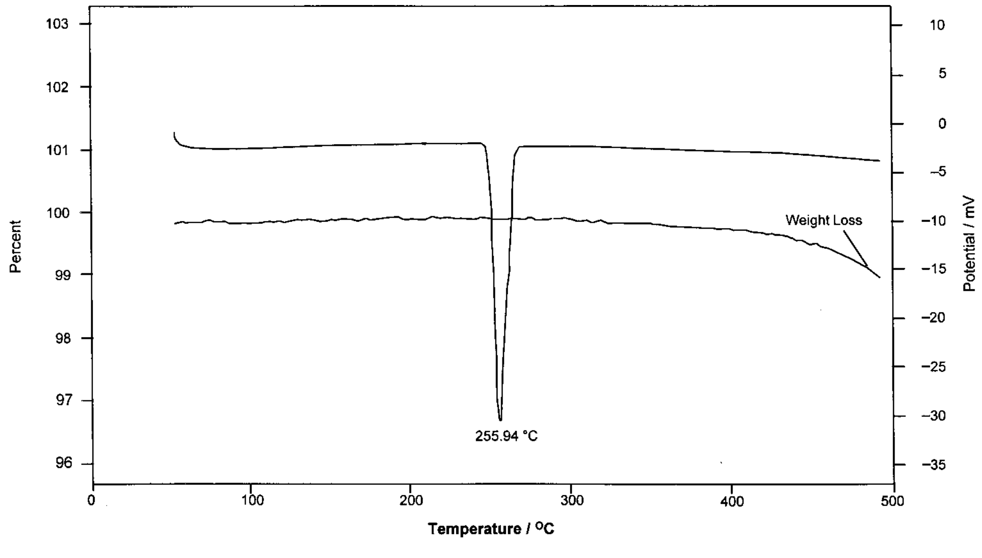

Fig. 3. Thermal analysis of lithium nitrate.

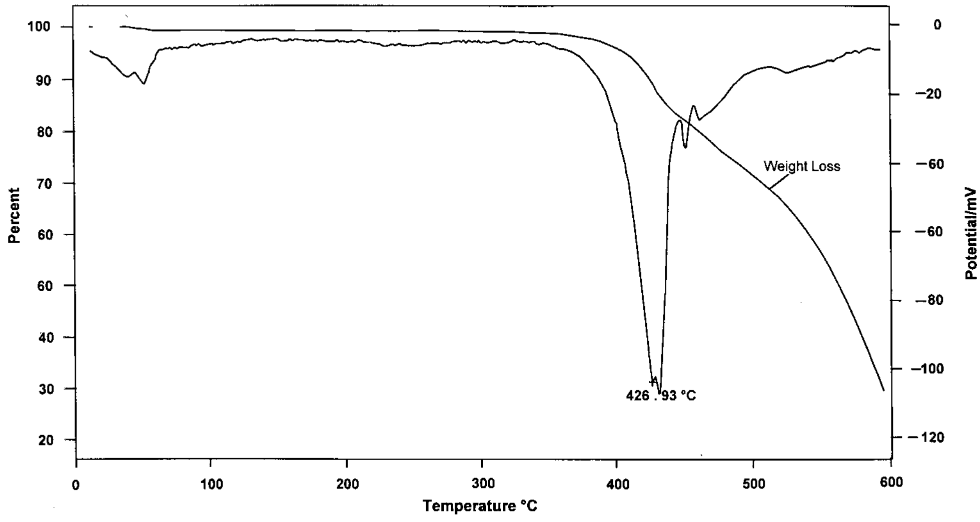

Fig. 4. Thermal analysis of lithium nitrate.

nitrate melted at 252 °C and the liquid on its own appears to be thermally stable up to at least 500 °C, indicating no self-decomposition within the operating temperature of the cell. Decomposition of nitrate occurred above 500 °C but this appears to be an endothermic process [6]. Therefore, any decomposition in the cell would probably be less hazardous than that of molten perchlorates which are known to degrade exothermally.

Figures 4 and 5 show the thermal analyses of copper(II) chloride and that of a copper(II) chloride/lithium nitrate mixture. It can be seen in Fig. 4 that $CuCl_2$ is thermally stable up to about 375 °C but beyond this temperature copper(II) chloride decomposed, probably to copper(I) chloride and evaporated almost completely by 600 °C. The thermogram in Fig. 5 ($LiNO_3/CuCl_2$ mixture) showed that lithium nitrate melted at 251 °C as expected, but four endotherms were also seen, which means that the compound decomposes in the presence of nitrate. It is possible that the molten nitrate has reacted with $CuCl_2$ to form copper nitrate which is less stable than copper(II) chloride at about 340 °C. This process could be represented by the equation shown below:

$$CuCl_2 + 2\,LiNO_3 \longrightarrow Cu(NO_3)_2 + 2\,LiCl \quad (1)$$

A small melting point peak was seen at 588 °C; this is probably a depressed melting point for lithium chloride since the expected melting point for LiCl is 605 °C [7]. The equation above indicates how the electrolyte could react with the cathode. However, the energy output from the $LiAl/LiNO_3$–$KNO_3/CuCl_2$ cell indicates that these materials are good enough for a one shot reserve battery system.

The thermal analysis of copper(II) fluoride was not carried out because it appears to decompose readily.

3.1. *$LiAl/LiNO_3$–$KNO_3/CuCl_2$–NO_3 cells at 150–200 °C*

A diagram of the single cell tester and completion of energy for some nitrate cells are shown in Fig. 6 and Table 1, respectively.

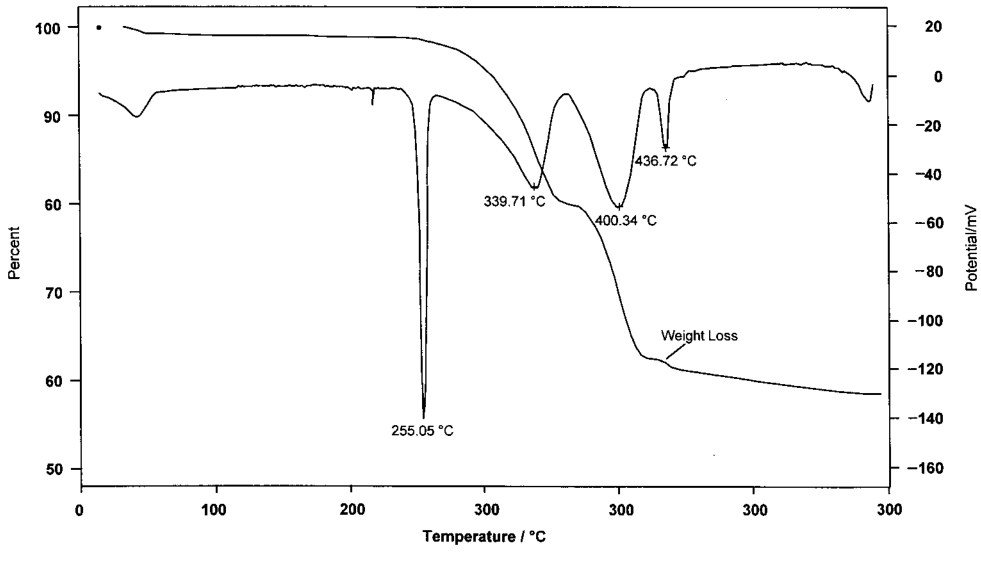

Fig. 5. Compatibility of copper chloride with lithium nitrate.

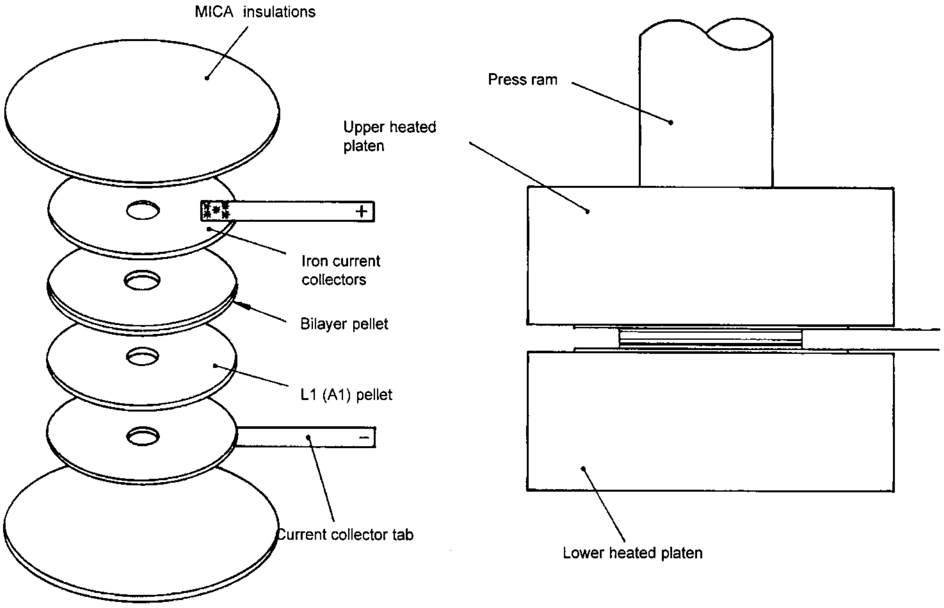

Fig. 6. Single cell tester.

Table 1. Computation of energy of some nitrate cells

Cathode	*Temp* /°C	*Current* /mA	*OCV* /V	*Duration to 0* V/min	*Energy Density to 0* V *cut-off* /Wh kg^{-1} *of cathode*
CuF_2	200	50	3.40	3.0	29
$CuCl_2$	200	50	3.40	12.0	110
$CuCl_2$	150	50	3.40	14.0	139

Typical discharge curves obtained for copper halides at 150 and 200 °C with a current density of 25 mA cm^{-2} are presented in Fig. 7. A LiAl/$CuCl_2$ cell with nitrate electrolyte had an o.c.v. of 3.4 V and exhibited two distinct voltage plateaux (see Fig. 7). The first plateau was between 2.0 and 1.7 V and the next one was a sloping plateau from about 1.5 to 0.5 V. In a previous report [5], it was claimed that copper(II) chloride in conjunction with SO_2 electrolytes did discharge with two voltage plateaux. The first occurred at 3.4–3.2 V and it is thought to represent the reduction of $CuCl_2$ to CuCl as shown by Equation 2:

$$CuCl_2 + Li^+ + e^- \longrightarrow CuCl + LiCl \qquad (3.4\text{–}3.2\,V) \tag{2}$$

The second plateau, around 2.5 V, is said to correspond to the reduction of CuCl to Cu:

$$CuCl + Li^+ + e^- \longrightarrow Cu + LiCl \qquad (2.5\,V) \tag{3}$$

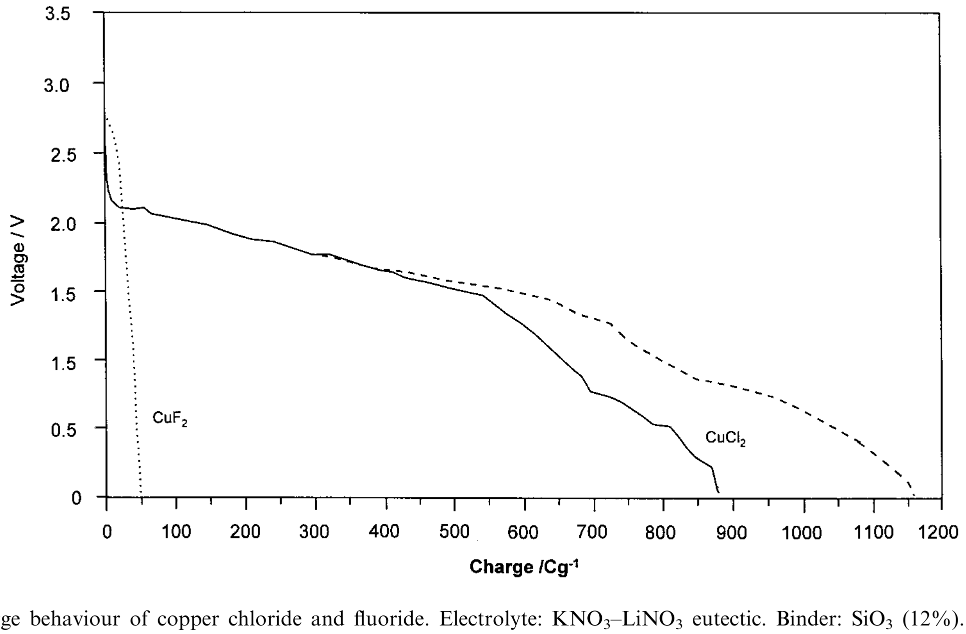

Fig. 7. Discharge behaviour of copper chloride and fluoride. Electrolyte: KNO_3–$LiNO_3$ eutectic. Binder: SiO_3 (12%). Anode: Li(Al). Cathode: $CuCl_2$ (70%), nitrate eutectic (30%). (—) 200 °C (- - -) 150 °C CuF_2 (70%), nitrate eutectic (30%). (. . . .) 200 °C. Current density: 25 mA cm^{-2}.

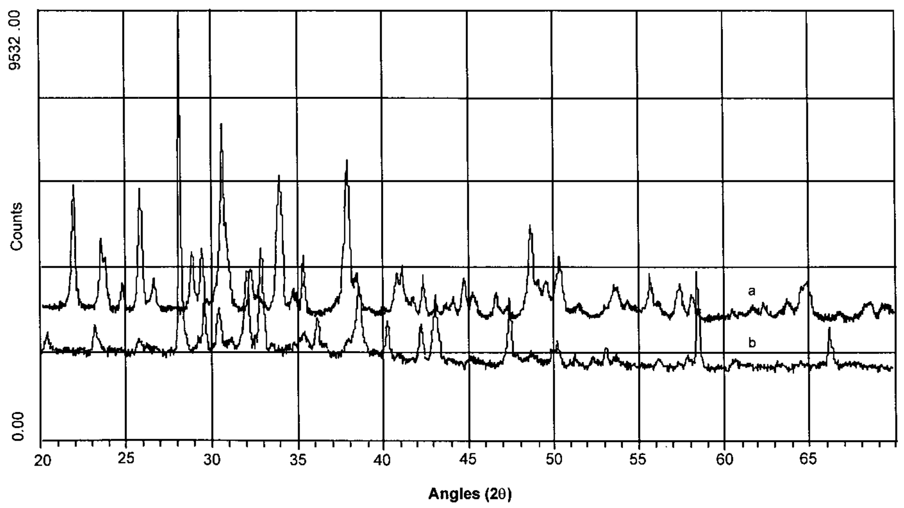

Fig. 8. Comparison of X-ray diffractograms of the starting (a) and final (b) discharged products. (a) $CuCl_2$ cathode pellet material before discharge. Principal components: $CuCl_2.2H_2O$ (eriochalcite), $CuCl_2$ (copper(II) chloride), $LiNO_3$ (lithium nitrate), KNO_3 (potassium nitrate), Al (aluminium) (b) $CuCl_2$ cathode pellet material after discharge. Principal components: $CuCl_2.2H_2O$ (eriochalcite), $CuCl_2$ (copper(II) chloride), $LiNO_3$ (lithium nitrate), KCl (sylvite), CuCl (nantokite), Cu_2O (cuprite).

To establish which reaction mechanism might prevail when copper(II) chloride is discharged in conjunction with the nitrate electrolyte at medium temperature (150–200 °C), X-ray diffraction patterns of $CuCl_2$ pellets were determined before and after discharge. The XRD powder patterns obtained are shown in Figs 8 and 9, together with assignments. A sample of the discharged cathode material was shown to contain a mixture of unreacted copper(II) chloride and some new compounds. It can be seen in Fig. 8, that CuCl was present in the discharged residue, it can therefore be inferred that $CuCl_2$ has been reduced as shown in Equation 2 above. Copper was not identified, and $CuCl_2$ was still present in the discharged pellet. It may therefore be said that the second electron reduction did not occur (Equation 3); hence the pellet has only been partially discharged. As a result of this the energy density obtained for $CuCl_2$ was very low (about 139 Wh kg^{-1}) because some portion of the cathode material did not react during discharge. Further optimization of the cathode composition gave better results and these will be discussed in Section 3.3.

The discharge profile for copper(II) fluoride at a current density of 25 mA cm^{-2} and at 200 °C is shown in Fig. 7, a sloping discharge curve was observed and the performance of this cell was very poor. The capacity was 29 Wh kg^{-1}. It is possible that the cathode material (CuF_2) decomposed readily in the presence of nitrates. It was not possible to determine the stability of copper(II) fluoride by thermal analysis because it appeared to be very sensitive to moisture in the air. It is also likely that CuF_2 has a higher resistance, hence a poor discharge.

3.2. *LiAl/$LiNO_3$–KNO_3/$CuCl_2$–graphite cells at 150–245 °C*

Figure 10 shows the discharge curve for copper(II) chloride–graphite based cells while the corresponding

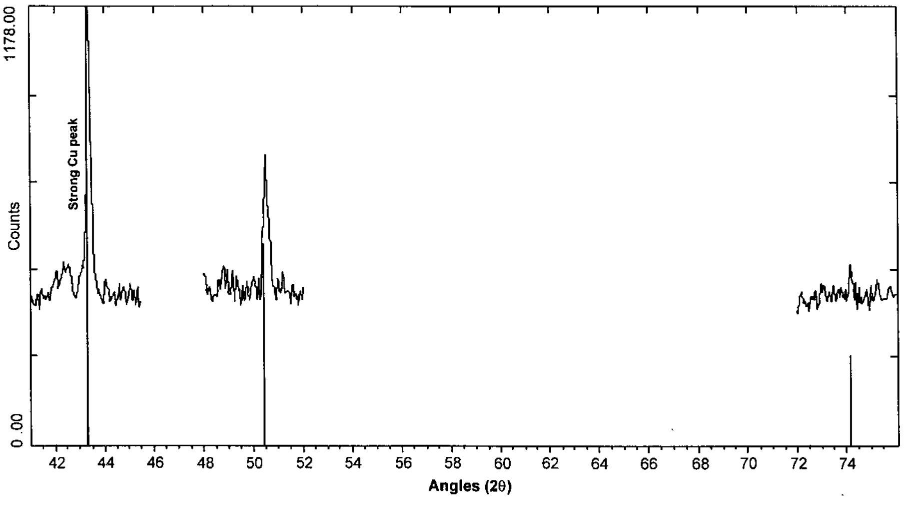

Fig. 9. X-ray diffraction pattern shows presence of metallic copper.

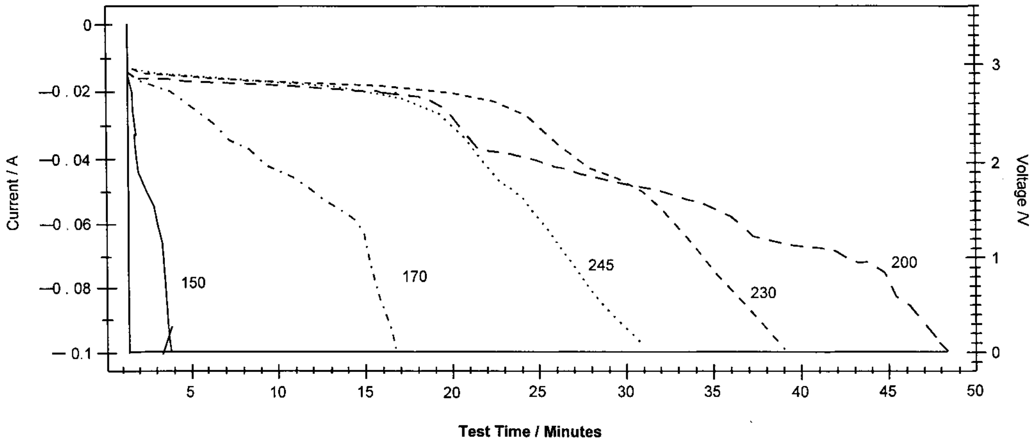

Fig. 10. Copper chloride single cell tests 150–245 °C. Temperatures: (———) 150 °C; (—·—·—) 170 °C; (— — —) 200 °C; (– – – –) 230 °C; (· · · ·) 245 °C.

results are summarized in Table 2. As shown in Table 2 and Fig. 10 the energy densities obtained from the LiAl/CuCl$_2$ cells increased with temperature between 150 and 230 °C but at 245 °C the energy output fell slightly; the reason for this is not quite clear but one explanation could be that the silicon binder is beginning to lose its ability to immobilize the electrolytes at higher temperature. It is however important to report that cells (LiAl/NO$_3$/CuCl$_2$–graphite) which contained graphite in the cathode performed better than those cells (LiAl/NO$_3$/CuCl$_2$–nitrate) that used nitrates salts to enhance the conductivity of their cathodes. Furthermore the capacity of the graphite-based cell at 200 °C was 1343 C g^{-1}, since the theoretical capacity CuCl$_2$ is 1400 C g^{-1} for a two electron reduction, it can therefore be said that the graphite–copper(II) chloride has followed the reaction steps shown in Equations 2 and 3. Evidence for the reduction of CuCl to Cu was obtained from X-ray diffraction pattern and scanning electron microscopy (SEM); these results are shown in Figs 9,1 and 2. Pellets were examined before and after discharge. In Fig. 9 the X-ray powder pattern shows a strong metallic copper peak. The results from SEM showed no copper in the starting materials however strong evidence for the presence of copper metal was obtained for discharged samples. The SEM results (Fig. 1) before discharge tests indicate that no copper crystals were present, but after the discharge tests (Fig. 2) copper crystals were observed. These results and the X-ray results (Fig. 9) support the notion that CuCl$_2$ had been reduced to Cu. The theoretical efficiency attained for the graphite-based cell (LiAl/NO$_3$/CuCl$_2$–graphite) was about 96% based on the active cathode material only, it must be emphasized that because the electrolyte used is a strong oxidant, therefore , some side reactions are likely to occur. For example, a portion of the nitrate electrolyte will be reduced to nitrite.

Table 2. Energy densities for CuCl$_2$–graphite cathode

Cathode	*Temp /°C*	*OCV /V*	*Duration to 0 V/min*	*Energy Density to 0 V cut-off /Wh kg^{-1} of cathode*
CuCl$_2$	150	3.407	2.48	8.50
CuCl$_2$	170	3.423	15.47	98.10
CuCl$_2$	200	3.306	47.00	355.67
CuCl$_2$	230	3.247	37.75	436.88
CuCl$_2$	245	3.208	30.07	348.21

4. Conclusions

A medium temperature reserve battery has been investigated to provide moderate currents (up to 50 mA cm^{-2}) at temperatures between 150 and 245 °C. Two composite cathode materials, that is, (copper(II) chloride–lithium nitrate/potassium nitrate and copper(II) chloride–graphite) were evaluated as possible candidates for use as cathode in medium temperature reserve lithium battery. The most promising cell combination appeared to be lithium–aluminium alloy/lithium/potassium nitrate eutectic–12% silica/copper(II) chloride–graphite. The above mentioned cell out performed the copper(II) chloride–nitrate based cell because (i) it yielded more energy within a defined voltage band, and (ii) the internal resistance of its cells was lower than those of the copper(II) chloride–eutectic nitrate-based cells and their rate capability was higher.

The coulombic efficiency of LiAl/nitrate–silica/CuCl$_2$–graphite approaches 96% at temperatures above 200 °C and high electric efficiencies (watt hours removed on discharge) were very promising.

Evidence from X-ray diffraction pattern and scanning electron microscopy (SEM) has shown that two electron reduction of copper(II) chloride had occurred when graphite was used to enhance the conductivity of the cathode material (see Equations 2 and 3). Furthermore, the results obtained from simultaneous thermogravimetric and differential analysis have shown that copper(II) chloride is thermally stable on its own (up to about 380 °C) and when mixed with the electrolyte it is stable up to 240 °C, which is good enough in the presence of nitrate for a one shot reserve cell system.

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