

## THE Li/Cu<sub>4</sub>O(PO<sub>4</sub>)<sub>2</sub> COUPLE: A NEW VERSION FOR LONG-LIFE LOW-RATE APPLICATIONS

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### Summary

The performance of lithium copper oxyphosphate, a 2.4 V operating voltage battery system using 2 M LiClO<sub>4</sub>/dioxolane, is presented. The cells have excellent discharge characteristics and shelf life, and also demonstrate some advantage in capacity over Li/MnO<sub>2</sub> cells of the same size at the 2 V cut-off voltage.

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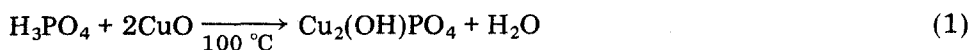
### Introduction

The Li/Cu<sub>4</sub>O(PO<sub>4</sub>)<sub>2</sub> battery system has evolved from recent research carried out by SAFT on the use of copper oxysalts as cathode materials in order to provide lithium cells with higher voltages than the Li/CuO cell, but still with a fairly good specific capacity due to electrochemical reduction of these compounds to the metallic state. Copper oxyphosphate has been selected as one of the most promising materials on account of its complete compatibility with a number of organic electrolytes over a wide range of environmental conditions. This has led to the development of a lithium battery system for high temperature applications up to 175 °C [1, 2]. Other versions have been researched for operation at low to fairly high temperatures and studies in this area are reported in this paper.

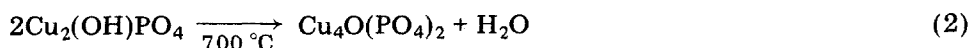
### Cell chemistry

#### *Preparation of copper oxyphosphate*

Various methods have been investigated for the preparation of Cu<sub>4</sub>O(PO<sub>4</sub>)<sub>2</sub>. One method involves [1] the dehydration of synthetic copper hydroxyphosphate at elevated temperature. The latter compound is obtained by reaction of phosphoric acid with copper at 100 °C, *i.e.*,



Dehydration is conducted at 700 °C, *i.e.*,



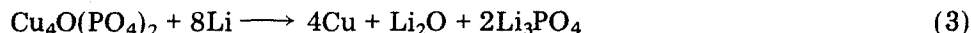
The resulting product is then ground to the grain size required for making the cathode mix.

### *Product characteristics*

Copper oxyphosphate powder has a bright-green colour. The material is non-hygroscopic and has a structure that is derived from a cubic close-packed arrangement of oxygen atoms with one tenth of the oxygen atom missing. Such an arrangement can promote lithium ion diffusion inside the lattice during electrochemical reduction. The specific gravity (by pycnometry) is 4.4 g cm<sup>-3</sup>. Using the latter figure, and considering that the electrochemical reduction of the compound proceeds to the formation of copper metal, the specific capacity is 2 A h cm<sup>-3</sup>.

### *Discharge mechanism*

The discharge mechanism of an Li/Cu<sub>4</sub>O(PO<sub>4</sub>)<sub>2</sub> cell involves a charge of 8 Faradays per mole according to the following reaction:



Although X-ray diffraction phase analysis has confirmed that copper metal is produced during the discharge process, neither Li<sub>2</sub>O nor Li<sub>3</sub>PO<sub>4</sub> has been clearly identified. The open-circuit voltage (OCV) of this system is 2.7 V at ambient temperature; useful voltages lie in the range 2 - 2.6 V, depending on the load conditions. Furthermore, only 70 - 75% of the theoretical capacity calculated from the overall process may be recovered at a cell voltage of greater than 2 V at low rates.

### **Cell construction**

Data were obtained on AA- and C-size cells using a bobbin-type construction. The latter comprised a central anode of lithium and a surrounding cathode made from a compacted mixture of Cu<sub>4</sub>O(PO<sub>4</sub>)<sub>2</sub> and graphite; the cathode was in contact with the cell case. The cells were filled with 2 M LiClO<sub>4</sub>-dioxolane electrolyte (note, this has been used for the Li/CuO system). The cells were of the crimped-seal type, but in order to evaluate the ability of these cells to be stored and to operate at temperatures up to 100 °C or to support severe thermal cycling conditions, a glass-to-metal seal instead of the crimped seal design was also tested; this used the corrosion-resistant glass material (TA 23) recently introduced by Sandia National Laboratories [3].

Cell capacities were measured to a 2 V cut-off for different discharge loads and storage conditions. The low-rate, continuous discharge capabilities of cells using glass-to-metal seals were also investigated for temperatures up to 100 °C.

## Cell performance

### Cells with crimped seals

Typical discharge curves for  $\text{Li}/\text{Cu}_4\text{O}(\text{PO}_4)_2$  cylindrical AA bobbin cells at 20 °C are shown in Fig. 1. For comparison, curves are also included for an  $\text{Li}/\text{CuO}$  system using the same electrolyte chemistry and cell technology. It can be seen that in terms of battery configuration, two  $\text{Li}/\text{CuO}$  cells can be replaced by only one  $\text{Li}/\text{Cu}_4\text{O}(\text{PO}_4)_2$  cell. Figure 2 compares the optimal energy and capacity density of some of the well-known 1.5 and 3 V lithium solid cathode systems, as well as the state-of-the-art performance of conventional cells of the same specific battery size and technology (AA bobbin). The data clearly demonstrate the superior volumetric energy density of the  $\text{Li}/\text{Cu}_4\text{O}(\text{PO}_4)_2$  cell. Indeed, this latter cell is one of the most energetic lithium solid cathode systems currently available.

A further interesting characteristic of the  $\text{Li}/\text{Cu}_4\text{O}(\text{PO}_4)_2$  system is the absence of a voltage spike at the beginning of discharge, as exhibited by the  $\text{Li}/\text{CuO}$  cell. This feature is clearly illustrated in Fig. 3 which shows the

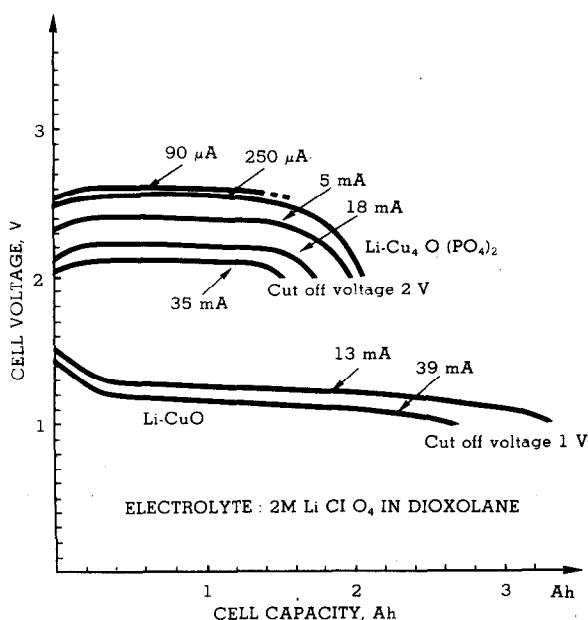


Fig. 1. Discharge curves of  $\text{Li}/\text{Cu}_4\text{O}(\text{PO}_4)_2$  and  $\text{Li}/\text{CuO}$  AA-size bobbin cells for various discharge loads at 20 °C.

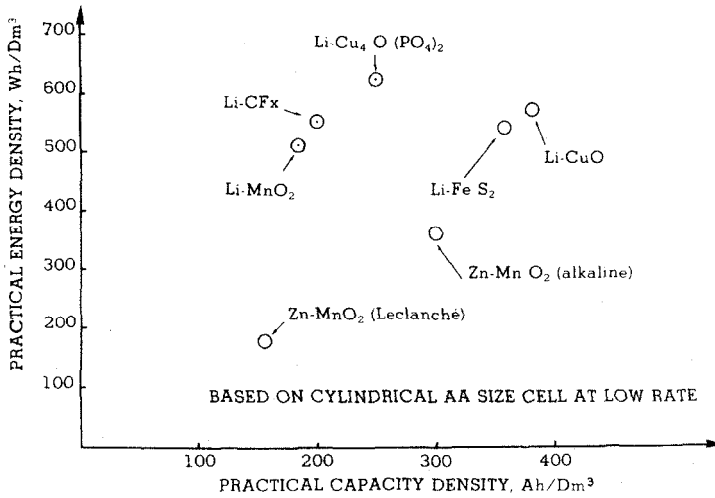


Fig. 2. Energy density us. capacity density for various battery systems.

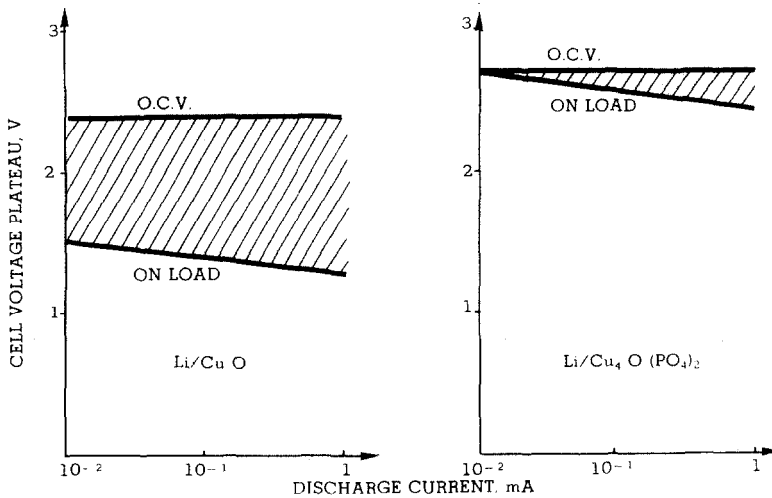


Fig. 3. Cell working voltage us. open-circuit voltage of Li/CuO and Li/Cu<sub>4</sub>O(PO<sub>4</sub>)<sub>2</sub> AA-size bobbin cells for various discharge currents at 20 °C.

working voltage for the two systems at various current drains when the steady state is reached *versus* the corresponding initial OCV.

The Li/Cu<sub>4</sub>O(PO<sub>4</sub>)<sub>2</sub> system can also be compared with the 3 V Li/MnO<sub>2</sub> battery, especially when the cut-off voltage required can reach values as low as 2 V/cell. Figure 4 presents the comparative discharge characteristics for AA-size low-rate cells of each battery system. It is interesting to note the superior voltage regulation and the 30 - 60% improvement in cell capacity of the Li/Cu<sub>4</sub>O(PO<sub>4</sub>)<sub>2</sub> cell for both the loads investigated.

As is the case with the Li/CuO battery, the Li/Cu<sub>4</sub>O(PO<sub>4</sub>)<sub>2</sub> battery is noted for its excellent long-term storage characteristics, even at temper-

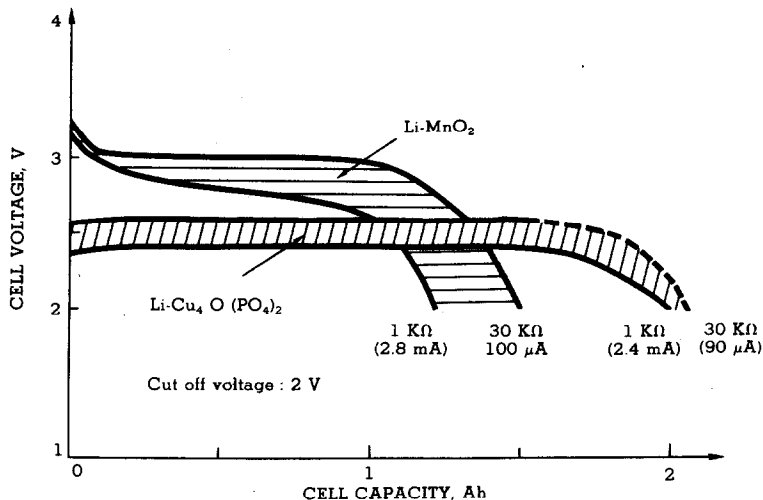


Fig. 4. Discharge curves of  $\text{Li/Cu}_4\text{O(PO}_4)_2$  and  $\text{Li/MnO}_2$  AA-size bobbin cells for various discharge loads at  $20^\circ\text{C}$ .

atures as high as  $70^\circ\text{C}$ , which is the limiting temperature for crimped-seal cells. Some recent results obtained from crimped-seal AA cells stored for one year at  $70^\circ\text{C}$ , and then discharged at the one-year rate at room temperature, are given in Fig. 5. The data show that there is no significant degradation in cell performance compared with that for cells discharged at the same rate and stored at ambient temperature.

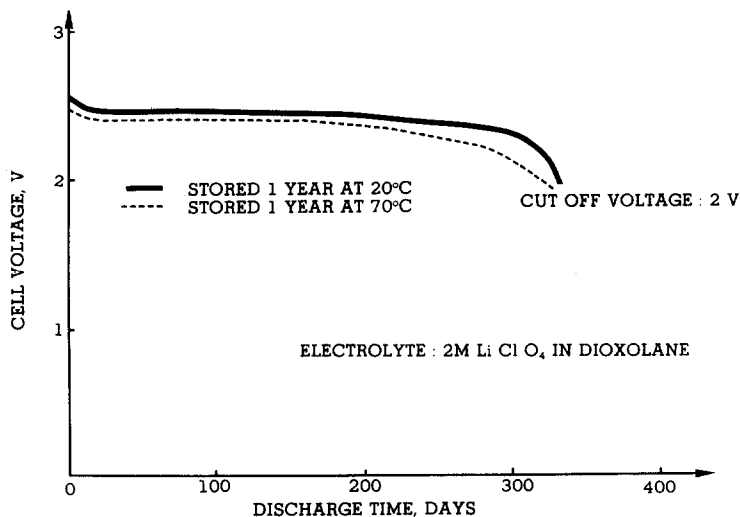


Fig. 5. Effect of high temperature storage on performance of  $\text{Li/Cu}_4\text{O(PO}_4)_2$  AA-size bobbin cells discharged at  $20^\circ\text{C}$  under  $10\text{ k}\Omega$ .

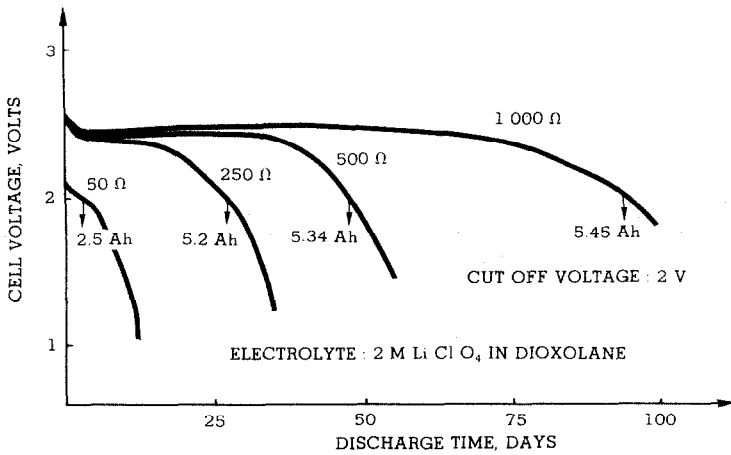


Fig. 6. Effect of discharge load on performance of Li/Cu<sub>4</sub>O(PO<sub>4</sub>)<sub>2</sub> C-size bobbin cells at 20 °C.

The performance characteristics of C-size bobbin cells are given in Fig. 6 for discharge rates ranging from a few days to 100 days. The findings demonstrate that these cells are essentially designed for low-rate discharges.

#### Cells with glass-to-metal seals

In order to assess the ability of Li/Cu<sub>4</sub>O(PO<sub>4</sub>)<sub>2</sub> cells to deliver continuous low levels of power for extended periods under extreme environmental conditions, hermetically-sealed AA cells have been discharged at the one-year rate at various temperatures ranging from ambient to 100 °C. The data obtained are shown in Fig. 7 in the form of discharge curves. No differ-

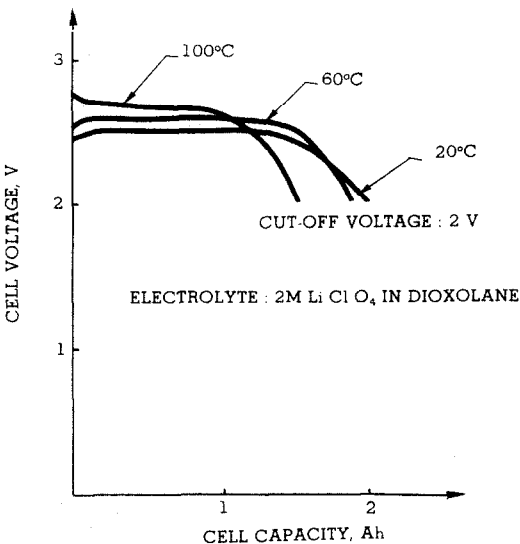


Fig. 7. Effect of discharge temperature on performance of hermetically-sealed, AA-size bobbin cells under 10 k $\Omega$ .

ence in cell capacity is observed up to 60 °C and even for 200 days of continuous operation at 100 °C, 75% of the capacity delivered at ambient temperature is retained. The capacities recovered to the 2 V cut-off voltage at the one-year rate *versus* operating temperature are given in Fig. 8. Also included are some results obtained previously with a propylene carbonate-tetraglyme-LiCF<sub>3</sub>SO<sub>3</sub> electrolyte at >100 °C, together with capacities delivered by hermetically-sealed AA Li/SOCl<sub>2</sub> cells under similar conditions. It is interesting to note the relatively small amount of self discharge exhibited by the Li/Cu<sub>4</sub>O(PO<sub>4</sub>)<sub>2</sub> system compared with the Li/SOCl<sub>2</sub> system, especially when the operating temperature is increased.

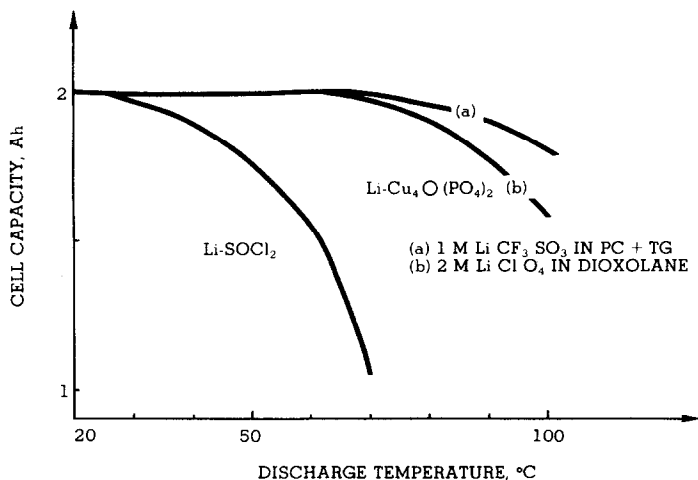


Fig. 8. Comparative performance of Li/Cu<sub>4</sub>O(PO<sub>4</sub>)<sub>2</sub> and Li/SOCl<sub>2</sub> hermetically-sealed AA-size bobbin cells discharged at the one-year rate as a function of temperature and for the 2 V cut-off voltage.

As a result of the above studies, it is concluded that the Li/Cu<sub>4</sub>O(PO<sub>4</sub>)<sub>2</sub> cell, with most of the lithium solid cathode couples, is better suited to applications requiring low-current drains (such as memory back-up) than liquid cathode systems. Further, the Li/SOCl<sub>2</sub> and Li/Cu<sub>4</sub>O(PO<sub>4</sub>)<sub>2</sub> systems yield similar capacities at ambient temperature to the 2 V cut-off limit.

## Conclusion

The Li/Cu<sub>4</sub>O(PO<sub>4</sub>)<sub>2</sub> system, using the LiClO<sub>4</sub>-dioxolane electrolyte, appears to have very good storage characteristics, not only in the active state but also under continuous low-rate discharge at fairly elevated temperatures. This conclusion especially holds when a hermetic construction is used.

The Li/Cu<sub>4</sub>O(PO<sub>4</sub>)<sub>2</sub> system, a so called "3 V lithium system" may also provide some other advantages over its Li/MnO<sub>2</sub> counterpart, in terms of

both cell capacity and voltage regulation when a 2 V cut-off is specified. Thus, the  $\text{Li/Cu}_4\text{O}(\text{PO}_4)_2$  system may be an alternative power source in applications associated with new-generation memory back-up facilities that can accept low operating voltages and can be used in fairly severe environments.

## References

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- 2 M. Broussely and P. Terrien, in A. Kozawa and K. Kordesh (eds.), *Progress in Batteries and Solar Cells*, Vol. 5, JEC Press Inc., 1984, pp. 91 - 94.
- 3 J. P. Gabano, *Proc. 26th Battery Symp., Kyoto, Japan, November 1985*, pp. 125 - 133.