

## RECENT RESULTS REGARDING THE STORAGE CAPABILITIES OF LITHIUM ORGANIC CELLS USING LITHIUM PERCHLORATE-ETHER SOLUTIONS AS ELECTROLYTE\*

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### Introduction

Research carried out at SAFT over the past 18 years on lithium cells using solid cathodes and an organic electrolyte has resulted in the design of a variety of Li high energy primary batteries based on lithium perchlorate-ether solutions as electrolyte which were generally found to be quite compatible with the lithium anode. As far as the cathode is concerned, a number of possible materials were investigated, the selection of which was determined either by the decomposition potential of the electrolyte or more often by the direct or indirect solubility (through complexation with associated discharge products) at the cathode.

Among the potential candidates for the cathode, metal sulfides and oxides were studied: some of them were found to provide cell voltages within the electrochemical window of the above electrolytes and their solubility in the latter was found to be quite low. Moreover, they were able to deliver impressive figures as far as cell volumetric energy density was concerned, taking into account the high specific capacity for most of them, resulting from their electrochemical reduction to the metallic state.

Through this approach, copper sulfide then copper oxide, and later lead-bismuth oxides were successfully selected as cathode materials in Li cells using  $\text{LiClO}_4$ -ether solutions as electrolyte. This paper will discuss the performance and properties of these various battery systems after storage for extended periods of time.

### The lithium-copper sulfide cell

The use of metallic sulfides as cathodic materials in lithium cells was first mentioned as a patent claim [1] in the early 1960s, with an electrolyte consisting of a solution of lithium perchlorate in isopropylamine. Long term incompatibility of lithium with aliphatic amines limited the development of

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these systems until SAFT introduced the ether based electrolytes, which were found to be compatible with these battery systems [2].

Among the various sulfides studied for the cathode, CuS was found to be the most interesting, because of its good electronic conductivity and its low overpotential on discharge in the above electrolytes, particularly when 1M LiClO<sub>4</sub> in 70% THF-30% 1,2-DME\* was used as electrolyte. Large capacity, 30 A h Li/CuS cells using such an electrolyte were made by SAFT in the late sixties. These early cells contained thick cathodes (1.5 mm) made by direct thermal combination of copper and sulfur on a nickel-plated steel grid and shaped as rectangular, porous plates, the corresponding anode being made of laminated lithium on stainless steel grids. An interleaved assembly of cathodes and anodes, separated from each other by 0.3 mm non-woven polypropylene separators, was wrapped in a plastic bag and contained in a tin-plated steel casing. A "pop rivet" electrode feedthrough with a plastic insulation was used for both polarity terminals as shown in Fig. 1. Cell total volume was about 100 cm<sup>3</sup> with a corresponding weight of about 160 g.

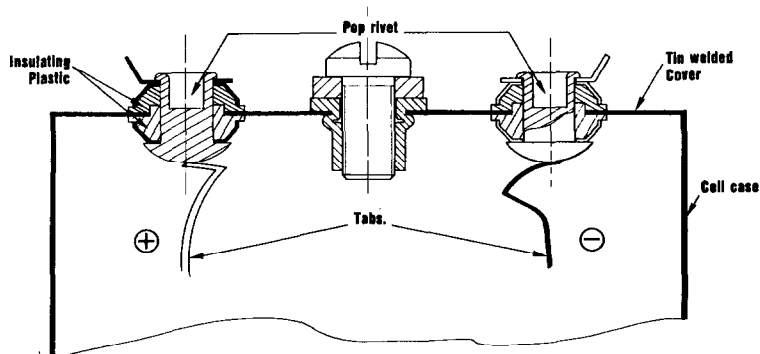


Fig. 1. Cross section of a plastic-to-metal seal positive and negative feedthrough used 15 years ago in Li/CuS prismatic cells.

Typical discharge characteristics corresponding to these cells are reported in Fig. 2 (continuous line) for various discharge loads to a cut off voltage of 1 V per cell. As can be seen, we obtained two discharge steps, as these early cells were balanced for the two electron reduction of copper sulfide (e.g., CuS/Cu<sub>2</sub>S, Cu<sub>2</sub>S/Cu)

In Fig. 2. we have also reported the discharge characteristics of these cells after 15 years storage (dashed line). Moreover, Table 1 compares recovered capacities before and after this long storage period.

As can be seen from these various results, no significant cell voltage deterioration was observed during this storage period and capacity loss was less than 1% per year, irrespective of the rate of discharge. In addition to the above, for the highest discharge rate tested (3 Ω), which corresponds to a current density of 1.3 mA/cm<sup>2</sup>, the initial on load voltage of cells stored for

\*On a volume basis.

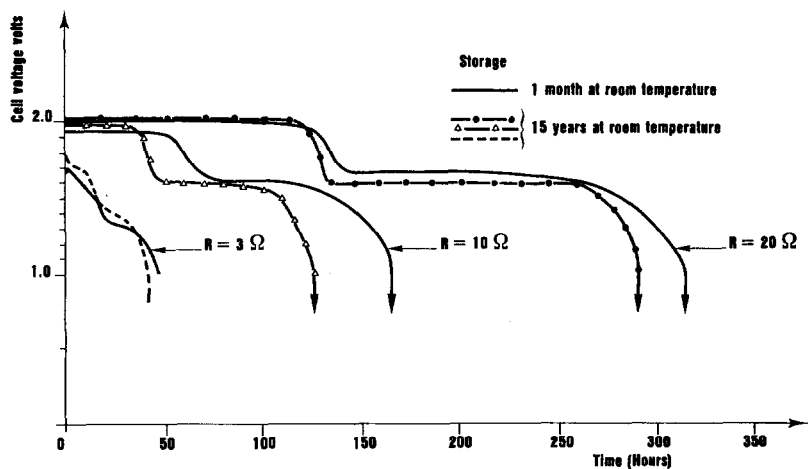


Fig. 2. Performance of Li/CuS prismatic cells after 15 years room temperature storage.

TABLE 1

Discharge load ( $\Omega$ )	Cell capacity (A h)	
	Fresh cells	15 year storage at room temperature
20	27.6	26.6
10	26.2	21.2
3	21.3	20.3

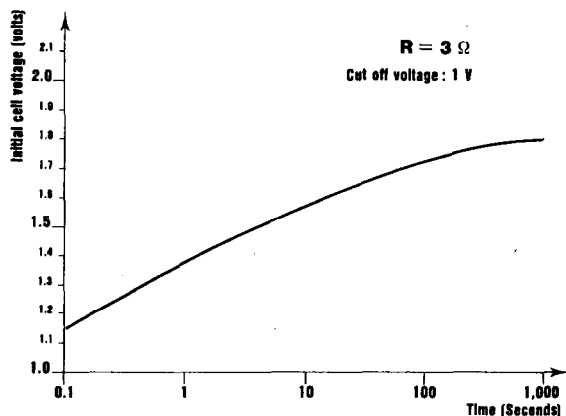


Fig. 3. Starting voltage of Li/CuS prismatic cells on a  $3 \Omega$  load after 15 years room temperature storage.

15 years was recorded on an oscilloscope to determine if such stability was due to a protective film on the anode formed by a slow reaction between lithium and THF. Figure 3 shows such a voltage-time curve which seems to

demonstrate the correctness of our hypothesis; nevertheless, it is interesting to note the fast recovery of this initial voltage which already reached 1.4 V within one second, well above the cut-off voltage of 1 V selected for this battery system. Moreover, it must also be remembered that the Li/CuS/THF based electrolyte was unable to withstand storage at 70 °C even for short periods, a fast reaction occurring between Li and THF under these conditions leading to the formation of ring opened products with a severe deterioration of the Li/electrolyte interface.

### The lithium-copper oxide cell

Copper oxide as cathode material for Li cells was progressively substituted for CuS by SAFT in the early seventies. First, as far as cell manufacturing was concerned, it was easier to produce as a pure material than CuS; then it was found to provide a similar working voltage to that of conventional existing Leclanché and alkaline MnO<sub>2</sub> primary cells, with quite high associated figures for the volumetric energy density (in excess of 600 W h/dm<sup>3</sup>), taking into account its very high specific capacity (4.30 A h/cm<sup>3</sup>). In addition to the above, the simultaneous replacement of the 1M LiClO<sub>4</sub>-THF (70)-1,2-DME (30) mixture by the 2M LiClO<sub>4</sub>-dioxolane solutions as electrolyte was also found to extend the performance of such a battery system, both in terms of rate capability at any temperature and improved shelf life properties at temperatures up to 70 °C for extended periods of time.

The lithium-copper oxide primary system has now been in quantity production for a number of years using bobbin technology to produce cylindrical AA and 1/2 AA cells, and the performance of such cells stored in various environmental conditions has been reported in many papers [3, 4]. For example, results for 9 1/4 years storage tests were recently presented for these bobbin cells [5] as shown in Fig. 4, illustrating their excellent storage capability at room temperature for extended periods of time both in terms of O.C.V., cell impedance, average voltage, and cell capacity (less than 0.5% loss per year). It is particularly interesting to note the absence of impedance rise, the latter also being confirmed by some initial cell voltage measurements performed at the beginning of 1984 on 11.5-year old cells which were submitted to different loads ranging from 10 to 40 Ω, corresponding to current densities varying from about 10 - 3 mA/cm<sup>2</sup>, for short periods to check the absence of any voltage delay (Fig. 5) after such long storage. In contrast with THF based electrolytes, this means that the lithium-solvent reaction does not occur or is not impeded by any film on the surface of the lithium. This remarkable behaviour is also in agreement with the findings of other investigators who demonstrated that LiClO<sub>4</sub>-dioxolane electrolytes have shown the best Li cycling efficiency of any solution to date [6].

Based on its potential capabilities as a long life battery system, the Li/CuO bobbin cell was also considered in the early seventies as a possible candidate for powering some medical devices, in spite of its low working voltage

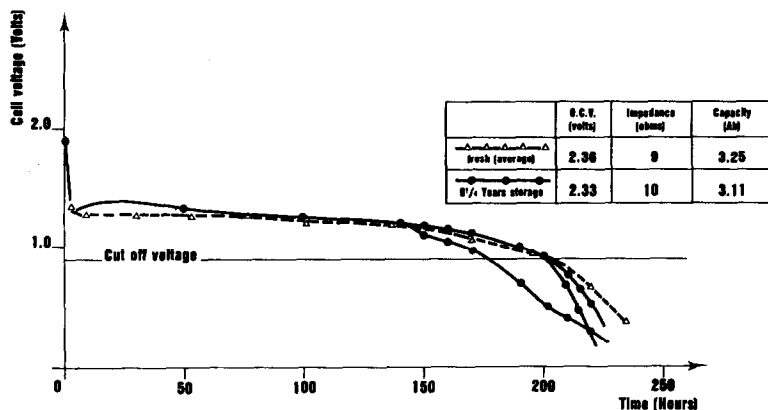


Fig. 4. Performance of Li/CuO cylindrical AA cells on a  $75 \Omega$  load after 9  $\frac{1}{4}$  years room temperature storage.

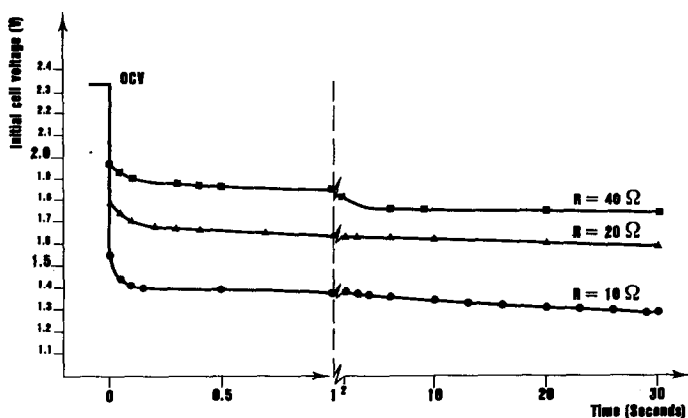


Fig. 5. Starting voltages of Li/CuO cylindrical AA cells on various loads after 11.5 years room temperature storage.

but taking into account its quite high volumetric specific energy and expected reliability.

Two types of experiments were conducted at that time; some of them are still continuing.

In one series of experiments the Li/CuO bobbin AA cells were stored initially for 3 months at  $60^\circ\text{C}$ , and were then discharged at  $37^\circ\text{C}$  on a  $75 \text{ k}\Omega$  load which corresponds roughly to the twenty years rate.

In Fig. 6 we have reported the cell voltage recorded during the first ten years; the test is still continuing, with over 1.5 A h capacity recovered so far. In another series of experiments, the Li/CuO bobbin AA cells were first initially pre-discharged to 50% depth of discharge through a  $75 \text{ k}\Omega$  load, (20 years rate) at  $37^\circ\text{C}$  to check the influence of discharge products on cell life. As can be seen from Fig. 7, the maximum capacity recovered (3.2 A h) was

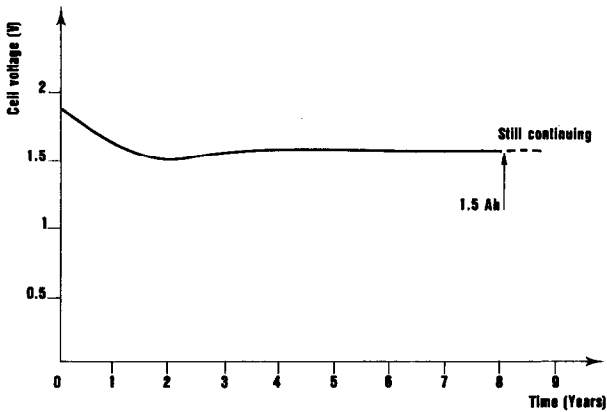


Fig. 6. Discharge characteristics of Li/CuO cylindrical AA cells discharged at 37 °C on a 75 k $\Omega$  load (twenty year rate) after initial storage for 3 months at 60 °C.

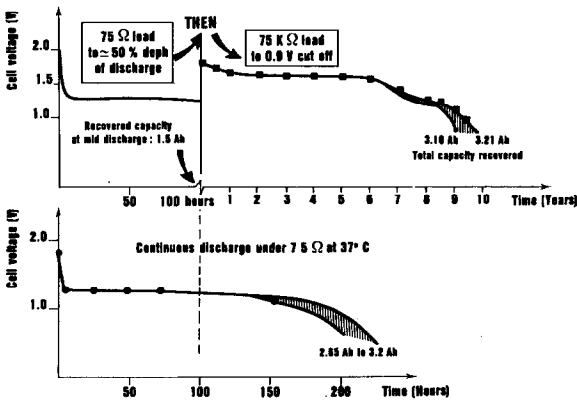


Fig. 7. Some performance characteristics of Li/CuO cylindrical AA cells.

similar to the total capacity accessible through discharge measured through 75  $\Omega$ .

On the other hand, in the context of higher power, larger cylindrical cells, SAFT have introduced in the last few years C and D Li/CuO cells using spirally wound electrodes, the performances of which have been described in a recent paper [7] and which demonstrated excellent storage capabilities over a wide range of temperatures. This feature has now been confirmed for extended periods of time with D cells stored at room temperature. The longest storage period for which results are available for this new generation of cells is 27 months. This is shown in Fig. 8 where we have reported some statistical data on the capacity recovered for a number of such stored cells discharged on a 2.2  $\Omega$  load to a cut-off voltage of 0.9 V. Compared with fresh cells the capacity so obtained differs only by 1%, corresponding to a loss of capacity of less than 0.5% per year. In Table 2, we have also reported average capacities recovered under the various loads investigated. Compared

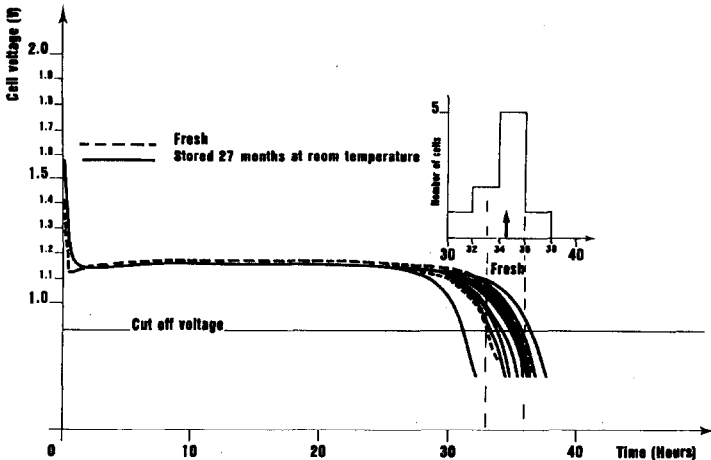


Fig. 8. Performance of Li/CuO cylindrical, D wound cells on  $2.2 \Omega$  after 27 months storage at room temperature.

TABLE 2

Discharge load ( $\Omega$ )	Cell capacity (A h)		Number of cells
	Fresh cells	27 month storage at room temperature	
2.2	18.00	17.8	9
5.11	17.81	17.15	3
6.66		18.58	3
20		18.68	3
40	18.00	19.26	3

with cells using bobbin technology, it must be concluded from these early experiments that cylindrical, spirally wound cells do not have a significantly higher rate of self-discharge than bobbin cells, in spite of their extended electrode surface area.

### The lithium-lead bismuthate cell

This battery was developed by SAFT in the mid seventies as a miniature power source to replace the silver oxide-zinc cell in the watch application, as it was found to fit the 1.5 - 1.6 cell voltage required with a comparable volumetric energy density and improved shelf-life. This battery system is based on lithium perchlorate-dioxolane electrolyte (2M) which, as already reported, has been found to be of interest both in terms of cell performance and storage capability. Several button cell types have been developed, the features of which have been given in a number of papers [8].

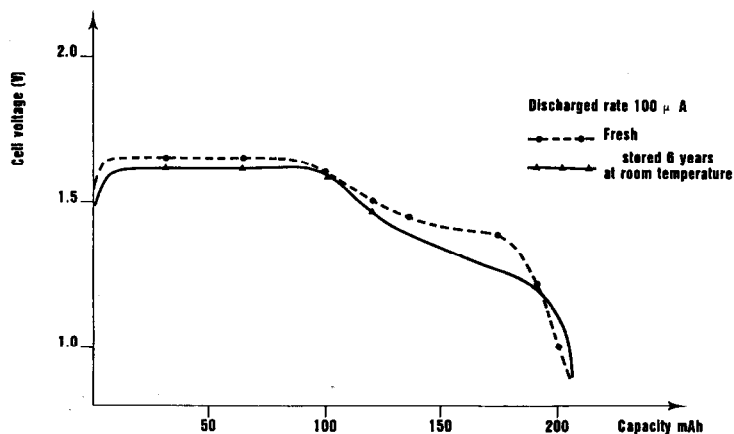


Fig. 9. Performance of  $\text{Li}/\text{Bi}_2\text{Pb}_2\text{O}_5$  button cells after 6 years storage at room temperature.

Present storage data after 6 years at room temperature are presented in Fig. 9 in which we have reported cell discharge characteristics of LP 1154 cells (dia.: 11.4 mm; height: 5.4 mm) discharged on a 13 k $\Omega$  load for both fresh and stored cells. As indicated in this Figure, no significant loss of capacity has been observed under these conditions, thus demonstrating the very good storage capability of this system, despite the fact that some limited solubility of the cathodic compounds was noticed in the dioxolane electrolyte.

## Conclusions

The fifteen-year storage test of the  $\text{Li}/\text{CuS}$  cells, a SAFT pioneering lithium solid cathode battery system, using a lithium perchlorate-ether solution as electrolyte (1M  $\text{LiClO}_4$  in THF-1,2-DME), has demonstrated in real time the ability of Li systems to be stored for extended periods of time.

The use of  $\text{LiClO}_4$ -dioxolane electrolyte which, in contrast to the other ether-based solutions, is believed to be stable in the presence of lithium (no film formation, no delay effect), allowing in addition high current drain for solid cathodes such as  $\text{CuO}$ ,  $\text{Pb}_2\text{Bi}_2\text{O}_5$  ..., has led us to define a unique  $\text{Li}/\text{CuO}$  battery system which still exhibits highly reproducible performances for cells which have been stored in excess of ten years.

To our knowledge, it has been found that such properties may be extended to the  $\text{Li}/\text{LiClO}_4$ -dioxolane battery systems, using insoluble depolarizers in such electrolytes to give cell O.C.V. not exceeding 2.6 - 2.7 V maximum. This precludes the use of highly oxidizing materials such as  $\text{CF}_x$  or  $\text{MnO}_2$ , but allows the possibility of selecting new, moderate oxidizers such as  $\text{Cu}_4\text{O}(\text{PO}_4)_2$ , which was found to operate at twice the working voltage of the  $\text{Li}/\text{CuO}$  battery system with comparable volumetric energy density.



## References

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