A PRELIMINARY EVALUATION OF LITHIUM BATTERIES FOR EXTENDED-LIFE CONTINUOUS-OPERATION APPLICATIONS

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Summary

A test program of several ambient temperature lithium battery systems has been initiated. Its purpose is to provide both real-time and accelerated data to determine the suitability of these systems to operate continuously for extended periods of up to 10 years. The Li/CuO and Li/$(CF_x)_n$ systems are compared with the Sandia-modified Li/SO_2 system that is currently being used in applications requiring operation for up to five years.

Preliminary results show the Li/CuO system to be stable over a wide range of temperatures (−40 to +70 °C) with a narrow performance band. Cell capacities ranged from 17 to 21 A h for spirally-wound D cells over the entire temperature range studied, for current drains up to several hundred milliamperes. The major drawback of the Li/CuO system is its low operating voltage coupled with a large voltage drop at the beginning of discharge.

The Li/$(CF_x)_n$ system has a substantial temperature effect. At 70 °C, cells vented at currents above 100 mA due to the buildup of internal pressure, while at −40 °C, cells operated only at 20 mA or less. At all conditions evaluated, a voltage step occurred near the end of life. This step occurred after complete utilization of the carbon monofluoride in the cathode-limited cells, when electrolyte reduction began. Further development is needed to make this system a viable candidate for long-life applications. Specifically, a new electrolyte solvent and an anode-limited design are required.

The modified Li/SO_2 cells gave a very consistent performance over the current and temperature range studied. Due to the large data base available for this system and the modifications to improve long-life capability (elimination of premature failure due to materials corrosion), Li/SO_2 remains the primary system for use in extended-life applications pending further developments in the evolution of the Li/CuO and Li/$(CF_x)_n$ designs.

Introduction

Several applications at Sandia National Laboratories require continuous power for periods exceeding five years. To meet these requirements, the

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Exploratory Batteries Division has initiated both real-time and accelerated tests of three lithium ambient temperature (LAMB) electrochemistries; Li/CuO, Li/$(CF_x)_n$ and Sandia-modified Li/SO_2.

The Sandia-modified Li/SO_2 cells are presently used in applications requiring continuous operation for up to five years. Real-time data have been obtained for 3.0 years with no failures to date. In other tests, conventional Li/SO_2 cells have been stored in a simulated real-world temperature cycle environment for up to 5.5 years. For those cells not failing due to corrosion effects, a 5.25%/year loss in capacity was observed.

For extended-life applications of greater than five years, it was decided to evaluate additional LAMB systems. Since a very stable system is necessary for these lifetimes, solid cathodes seemed appropriate. Also, a low-voltage system, with its inherently greater thermodynamic stability, may prove to be more desirable. Based on data in the literature [1, 2], two lithium chemistries, Li/CuO and Li/$(CF_x)_n$, were chosen for evaluation.

Experimental

Cells

All cells tested in this program were D-size with a spirally-wound internal configuration. The Li/CuO cells were manufactured by SAFT and are their standard commercial design. The cells have a dioxolane/$LiClO_4$ electrolyte and utilize a non-hermetic, crimp seal. The Li/$(CF_x)_n$ cells were obtained from Eagle-Picher Industries. A dimethylsulfite/$LiAsF_6$ electrolyte was used in these hermetically-sealed cells. The Li/SO_2 cells are a special Sandia-modified design built by both Duracell USA and Honeywell, Inc. The modifications include a new Sandia-developed (Type TA-23) glass in the glass-to-metal seal, molybdenum as the positive terminal, an arc–percussion weld of the aluminum cathode tab to the Mo pin, a nickel grid in the anode with connective tab from the grid to the can, double tabbing the cathode, increasing the radius of curvature at the bottom of the can, and annealing those cans made of nickel-plated, cold-rolled steel. Standard acetonitrile/LiBr was used in these Li/SO_2 cells.

Tester

All cells were tested at constant temperature in controlled-temperature chambers. The cells were discharged through standard 1% resistors. The test was controlled by a Hewlett-Packard 9836 Computer in conjunction with a Hewlett-Packard 6940B multiprogrammer.

Test matrix

All cells were discharged through fixed resistors corresponding to currents of approximately 10, 30, 100, 200, 500 and 1000 mA at −40, −20, 20 and 70 °C. Three cells were discharged at each current and temperature combination for a total of 72 cells of each chemistry.

Results

Li/CuO

Typical discharge profiles of Li/CuO cells for a nominal 10 mA drain are shown in Fig. 1. An initial drop in voltage from 2.35 to 1.35 V during the first 5 - 10% of life was characteristic for the Li/CuO cell discharges. After reaching the steady-state voltage, the profile was flat and reasonably reproducible from cell to cell. Figures 2 and 3 illustrate the change in voltage profile over the temperature range studied. As can be seen, there is relatively little change in performance over the temperature range −40 to +70 °C for the 10 mA drain rate. At higher currents, the effect of temperature was more pronounced, and the initial voltage drop was less evident.

Li/$(CF_x)_n$

Typical discharge profiles of Li/$(CF_x)_n$ cells are shown in Fig. 4 for a nominal 10 mA drain rate. The sloping discharge and voltage step near end of life was observed under all test conditions. The abrupt voltage drop occurred upon total utilization of the CF_x cathode in the cathode-limited cells. The subsequent reduction of the dimethylsulfite electrolyte solvent produced the second voltage plateau.

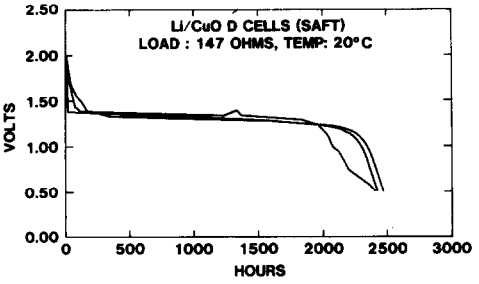


Fig. 1. Discharge of Li/CuO cells at nominal 10 mA drain.

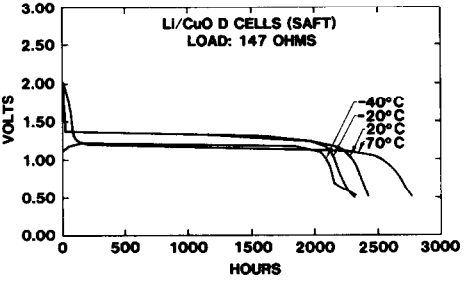


Fig. 2. Effect of temperature on Li/CuO discharge profile, nominal 10 mA drain.

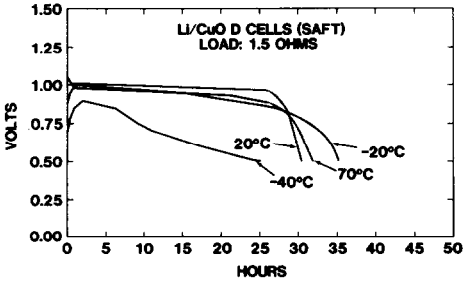


Fig. 3. Effect of temperature on Li/CuO discharge profile, high drain rate.

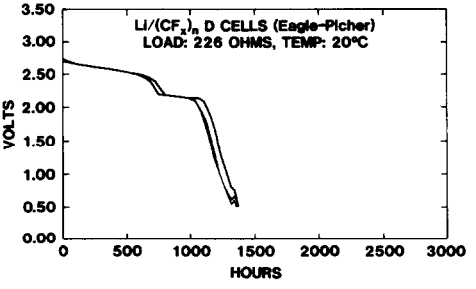
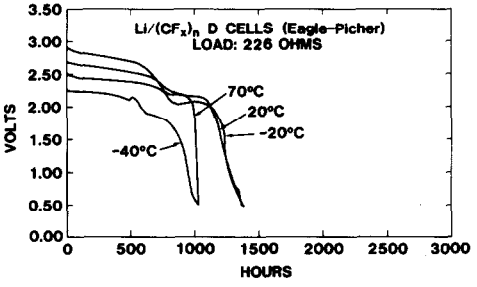


Fig. 4. Discharge of Li/$(CF_x)_n$ cells at nominal 10 mA drain.

Figures 5 and 6 show the effect of temperature on performance. A considerable spread in load voltage and capacity was observed over the temperature range, particularly at the higher current drains. At 70 °C, cells vented for currents of 100 mA or greater, resulting in the termination of these tests. At the nominal 1 A rate, cells tested below room temperature failed to yield any capacity above 2.0 volts.

Li/SO_2

Performance data for the Li/SO_2 system have been reported previously [3]. Typical low-rate (~ 10 mA) performance as a function of temperature is illustrated in Fig. 7. The flat discharge profile and consistent performance are typical of this chemistry. The voltage delay phenomenon at the low temperature is evident at the beginning of discharge.



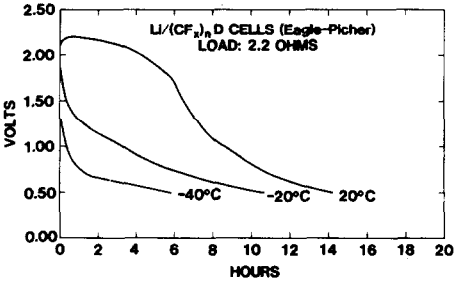


Fig. 5. Effect of temperature on $Li/(CF_x)_n$ discharge profile, nominal 10 mA drain.

Fig. 6. Effect of temperature on $Li/(CF_x)_n$ discharge profile, high drain rate.

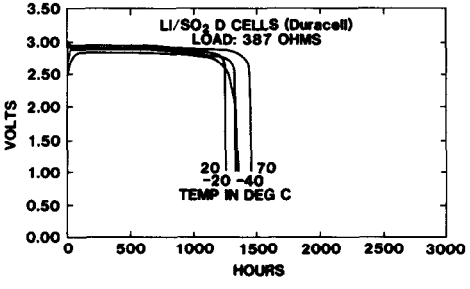


Fig. 7. Discharge of Li/SO_2 cells at nominal 10 mA drain.

Discussion

Results of these initial characterization tests indicate that the Li/CuO system shows promise as a long-life battery. At the low current drain used in long-life applications, the Li/CuO cells exhibited consistent performance

over a wide temperature range. The initial drop in voltage at the beginning of discharge could be a problem for some applications, but in many cases this phenomenon can be accommodated. The low operating voltage (as compared with other lithium systems) might also cause problems, particularly for high-voltage applications. This is partly compensated for by the high cell capacity. Another plus factor is the excellent storage data reported for this chemistry [2], which supports the Li/CuO system as a prime candidate for long-life, continuous-operation applications.

The $Li/(CF_x)_n$ system is basically a very stable electrochemistry and should be suitable for extended-life use. However, the results obtained in this study indicate that more work needs to be done to improve the performance characteristics of these cells. Use of an anode-limited design should eliminate the voltage step which occurs near the end of life. To improve performance at the temperature extremes, other electrolyte solvents need to be examined. Good low-temperature conductivity and the absence of gas-producing side reactions are important criteria for any electrolyte chosen.

The Li/SO_2 system with the Sandia-developed modifications still appears to be the system of choice for long-life applications. However, with only 3.0 years of real-time data and a measured capacity loss of 5.25%/year, a second LAMB system is desirable. Also, the high internal pressure of the Li/SO_2 system is of some concern for safety reasons.

Conclusions

Preliminary characterization tests of Li/CuO and $Li/(CF_x)_n$ cells have been carried out and results compared with Sandia-modified Li/SO_2 cells. The Li/CuO system with its consistent performance over the temperature range of −40 °C to +70 °C, high capacity, and thermal stability, is a prime candidate for long-life requirements. Low operating voltage and an initial voltage drop are the main drawbacks.

The $Li/(CF_x)_n$ system needs further improvements to become a viable candidate for extended life use. Improvements in the electrolyte, and an anode limited design, should make this chemistry more attractive.

The Sandia-modified Li/SO_2 system, with the large data base available and our greater understanding of its failure mechanisms, remains the primary choice for extended-life, continuous-operation applications.

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