Journal of Power Sources, 5 (1980) 73 - 82

ABUSIVE TESTING OF LARGE $Li/SOCl_2$ CELLS

NIKOLA MARINCIC* and FRANZ GOEBEL
GTE Sylvania, 250 Winter St., Waltham, Mass 02154 (U.S.A.)

Summary

Results are reported of various abuse tests conducted with lithium–thionyl chloride primary batteries of 2 000 A h and 10 000 A h capacity. The mechanical abuse tests, such as shock and vibration, showed that the large prismatic cells can now be built to satisfy typical military requirements. The thermal abuse tests showed that the cells can withstand a considerable overheating or a thermal shock treatment, as long as provisions were made for the thermal expansion of the electrolyte. The electrochemical abuse tests showed that the cells could be overdischarged (driven in reverse beyond discharge) to an equivalent of up to 50% of the discharge capacity with no adverse effects. The short circuit test, as a combination of the electrochemical and thermal abuse, was performed with no rupture, explosion or any other adverse effects on the surroundings.

1. Introduction

The development of the $Li/SOCl_2$ battery system has passed through several characteristic stages since its discovery in the late 1960's [1]. In early 1970, studies were characterized by an intense research and development activity [2 - 4], sponsored in the United States by both the U.S. Government and private industry. The chemistry of the $Li/SOCl_2$ power source was well described during that phase of development and a possible hazardous behavior of the system was recognized.

The next interesting stage of development started with the implantation of $Li/SOCl_2$ cells into human patients in 1974, as power sources for cardiac pacemakers [5]. The continued successful use of the small, low rate batteries in this application has proven that, with proper engineering and hermetic packaging, $Li/SOCl_2$ cells could be made quite safe. This development also settled some of the early arguments regarding possible self-discharge, corro-

---

*Consultant.

sion of battery hardware, leakage after a prolonged storage, etc. All these possible modes of failure have been successfully prevented in the pacemaker power sources, judging by the performance of these devices over the last five years.

The concept of a very large cell was developed at the GTE Laboratories in 1975 [6]. A large battery, made of twenty 10 000 A h cells, was sucessfully tested in powering a military installation, and with this test a new era has begun in the development of the Li/$SOCl_2$ battery system. While the high energy density (600 W h/kg) has been proven, many deficiencies of the system have been uncovered, mostly in the area of hazardous behavior of the system under abusive conditions. As a result, the late 1970's are being dedicated to identifying possible hazards associated with the electrochemical system and also with the size, design and construction of cells and batteries.

The present program at GTE Sylvania is directed towards the development of a specific military power source. However, the findings regarding the hazardous behavior are of general importance in all other applications. Only a part of the large body of data accumulated in the past two years is presented in this paper. The results of specific tests conducted are presented here in an attempt to illustrate the present state of the art without reaching deeper into the origin of various hazards anticipated or experienced in the course of this development.

2. Design and performance of large cells

2.1. Mechanical design

The design of the early, large, rectangular Li/$SOCl_2$ cell has been briefly described previously [6, 7]. The cell design is schematically presented in Fig. 1. The same design principle has been maintained throughout this program, although many minor but significant changes have been introduced for the purpose of improving the safety characteristics of the cell.

The present 2 000 A h and 10 000 A h cells are made in welded, rectangular, stainless steel containers and with the covers incorporating hermetic feedthrough terminals. The electrode structure, consisting of flat, rectangular carbon cathodes, lithium anodes and glass separators, is situated in the container along with the plate interconnectors and various other components designed to reduce the probability of short circuit in the cell under severe mechanical or thermal abuse. Welds and feedthrough are routinely tested for hermeticity prior to installation in the cell as well as after the final step of mechanical assembly. The assembly procedure is conducted in a dry room atmosphere, with a maximum of 4% relative humidity, to assure a minimal presence of water in various components of the cell. The final step of assembly, the introduction of electrolyte, is conducted under carefully controlled conditions, designed to prevent the introduction of humidity and also to avoid hazardous situations that might develop as a result of human errors in the quality control and assembly procedures. A proper open circuit

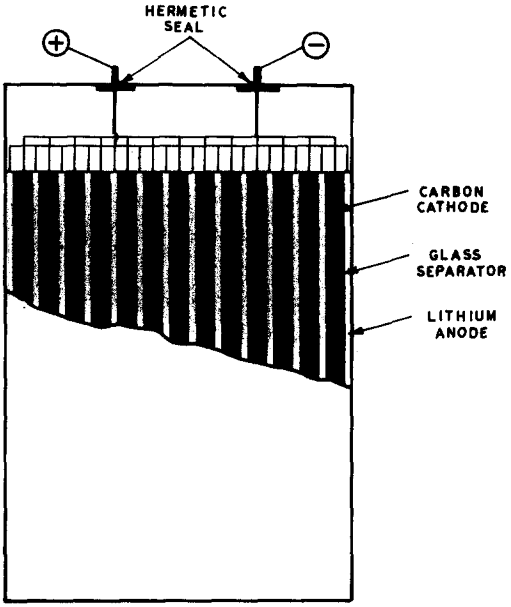

Fig. 1. Schematic presentation of prismatic cell design.

voltage of 3.67 V is the final proof that no internal short or partial short (bridging with less conductive materials such as carbon) is present. A lengthy quality control procedure is applied to these cells before they are released for any sort of testing or application.

2.2. *Electrical performance*

The state of the art in performance of the rectangular cells is represented in Figs. 2 and 3 for 2 000 and 10 000 A h cells, respectively. These data are incorporated into the paper as an illustration of the performance of cells used in all abuse tests described here. An energy density of 250 W h/lb or 550 W h/kg was realized with the 10 000 A h cell discharged at the 300 h rate to a 3.0 V cutoff voltage, even when this cell was designed as a lithium limited device. The discharge under constant load conditions proceeded with a minimal increase in the temperature, mostly at the very beginning of discharge. A slight pressure increase is observed only by the end of discharge, a phenomenon described earlier [8] resulting from an increase in the cell impedance at the end of discharge. The operating voltage of both cells remained unchanged throughout most of the discharge period and maintained a high value for these low rate cells discharged at a current density of about 1 mA/cm^2.

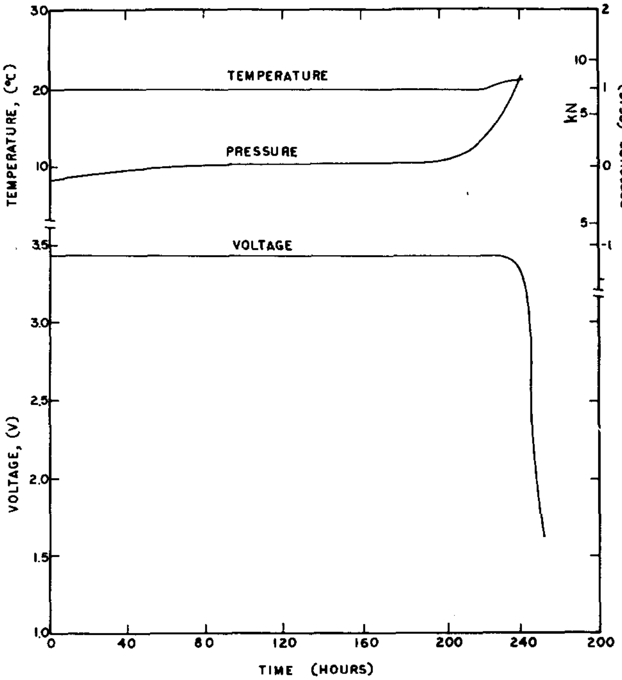

Fig. 2. Constant load discharge of a 2 000 A h cell.

3. Abusive tests

3.1. *Mechanical abuse*

Large prismatic cells were subjected to various means of mechanical abuse in order to verify their capability to withstand handling and transport. The cells were subjected to a partial discharge prior to the mechanical abuse, so that the initial operating characteristics of each cell could be established. Most of the tests, such as drops and 100 g shocks along any of the 3 axes, were uneventful, since the vital signs of the cell (voltage, pressure, and temperature) did not change during and after the abuse test. An example of such a test is given in Fig. 4, representing the results of the vibration tests. A 2 000 A h cell was subjected to vibration over the range of 50 - 2 000 Hz at a peak of 2 g.

The frequency was changed at the rate of 1 octave per minute, in both ascending and descending direction. The procedure was applied sequentially along all 3 axes. Figure 3 represents the vibration test results obtained for the vertical axis in the non-operating condition (at open circuit voltage). As the diagram shows, no changes were observed during the test in either the voltage, the pressure or the temperature of the cell.

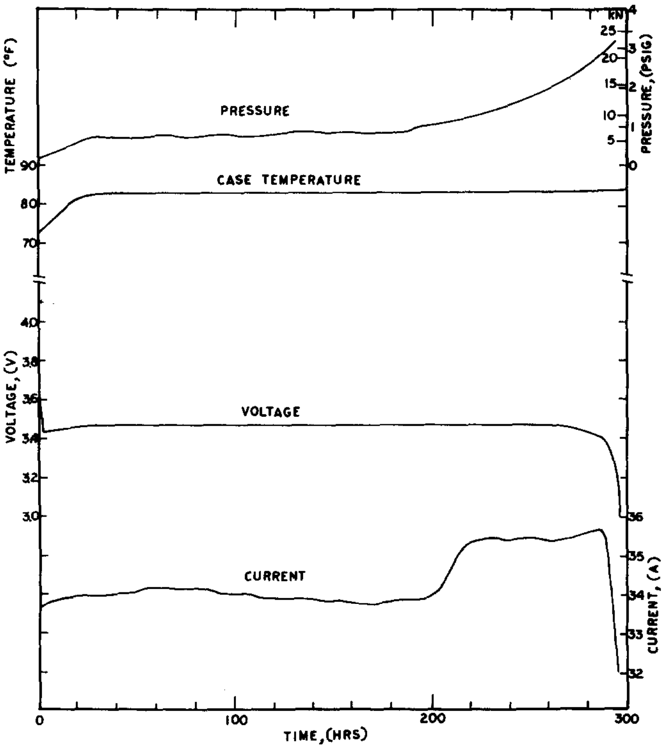

Fig. 3. Constant load discharge of a 10 000 A h cell.

3.2. Thermal abuse

The thermal shock was performed on a 2 000 A h cell between the temperatures -- 54 and 63 °C. The cell was held in each of the two temperature chambers for 4 h and the cycle was repeated three times. The open circuit voltage, the temperature of the cell's case, and the internal pressure were monitored for the entire period of the test. Following the thermal shock test, the cell was allowed to equilibrate at room temperature before the 1 hour discharge was performed at 8 A to determine the effect, if any, of the thermal shock on the performance characteristics of the cell. The operating characteristics were not found different from those established in the 1 hour discharge preceding the thermal shock tests, except for the variation in the internal pressure (between — 48 kN and 48 kN (-- 7 psig and 7 psig)), and the variation in the cell voltage (between 3.56 and 3.76 V), depending upon whether the cell was at the lowest or at the highest temperature. No leakage, rupture or venting were observed in the course of this test.

The overheating test was conducted on a 2 000 A h cell in a silicone oil bath which reached a temperature of 121 °C over a period of two hours and remained at approximately that temperature for an additional 5 hours. The test results are shown in Fig. 5.

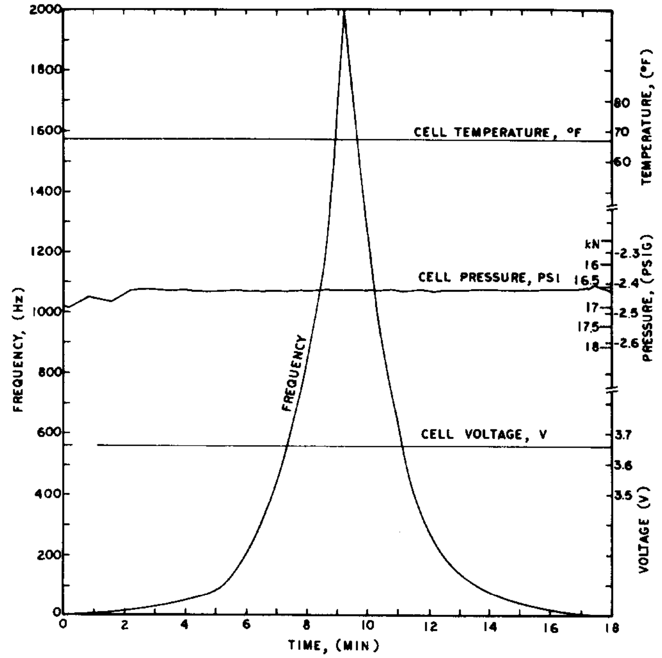

Fig. 4. Vibration test of a 2 000 A h cell.

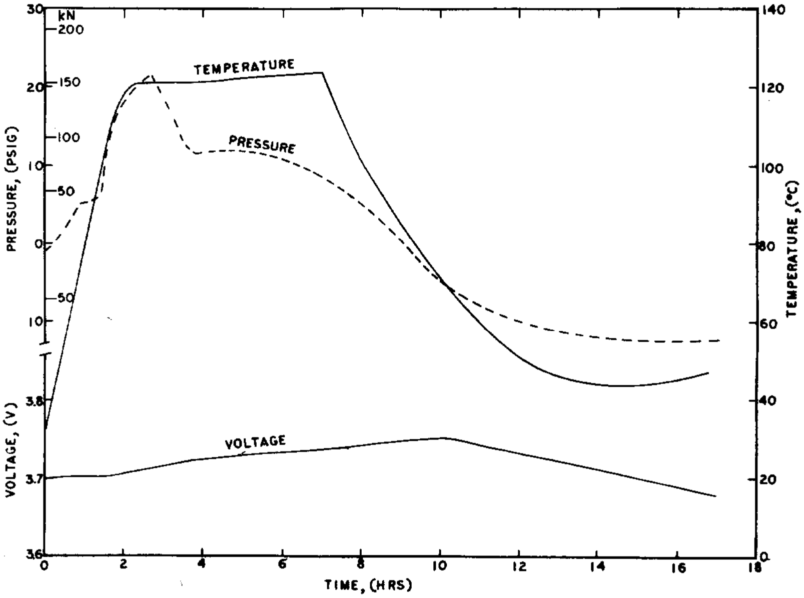

Fig. 5. Overheating test of a 2 000 A h cell.

The open circuit voltage remained within the range expected for the change in temperature, while the temperature at the surface of the container did not appear different from that measured in the bulk of the oil. The cell was connected to a scrubber *via* a check valve which opened only for a brief period at the pressure maximum of 159 kN (23 psi). The lack of any further increase in pressure following the venting and reclosing of the check valve is evident from the diagram and suggests that a uniform heating was achieved throughout the cell. The drop in pressure below normal upon cooling indicates almost a complete removal of entrapped air from the cell at the point of venting. No leakage or rupture was observed during this test.

3.3. Electrochemical abuse

Overdischarge and the short circuit discharge are the most common means of electrochemical abuse of cells and batteries. The ability to withstand overdischarge is an important characteristic of the system whenever it is used to build batteries with cells in series, as has been discussed on many occasions [9, 10]. The hazardous behavior, or lack of it, during the short circuit discharge is another important characteristic, particularly when one is working with cells of a very large capacity. A few examples of the numerous tests conducted are shown here to demonstrate the state of the art in the design and construction of single cells as well as to show, in general, the potential for other applications of batteries made with the $Li/SOCl_2$ system.

The results of overdischarge are represented in Fig. 6 for a 2 000 A h cell. A constant discharge current of approximately 8 A was maintained throughout the discharge and overdischarge period of the test. The cell voltage, its internal pressure, the cell temperature and the chamber temperature were all monitored continuously for the duration of the test. The voltage drop at the end of discharge was accompanied by a slight increase in both the pressure and the cell temperature. The overdischarge was continued for over 50% of the discharge time. The negative cell voltage of approximately − 1.75 V was established and remained unchanged until the end of the test. A remarkable ability of the cell to withstand the overdischarge is sufficiently illustrated by the diagram in Fig. 6. No leakage, rupture or venting was observed during this test.

The short circuit test with the 2 000 A h cell has been discussed previously [7]. It was repeated here with a slightly modified cell construction, showing, essentially, the same good characteristics of the cell. With a 12 mΩ load across the cell terminals a current of approximately 200 A was maintained throughout 90 min, at a voltage around 2.5 V, before a gradual decrease of voltage and current was observed. The cell vented only briefly at around 69 kN (10 psig), before the steady increase in the pressure and temperature was completed and a gradual decrease in both of these parameters ensued. No leakage or rupture, other than the controlled venting, was observed during this test. These results are shown in Fig. 7.

The experience with the 2 000 A h cell on short circuits enabled us properly to prepare for tests with the larger 10 000 A h cell. Hardly any change in the experimental procedure appeared necessary as a result of the work with the 2 000 A h cell, except for different ranges on instrumentation

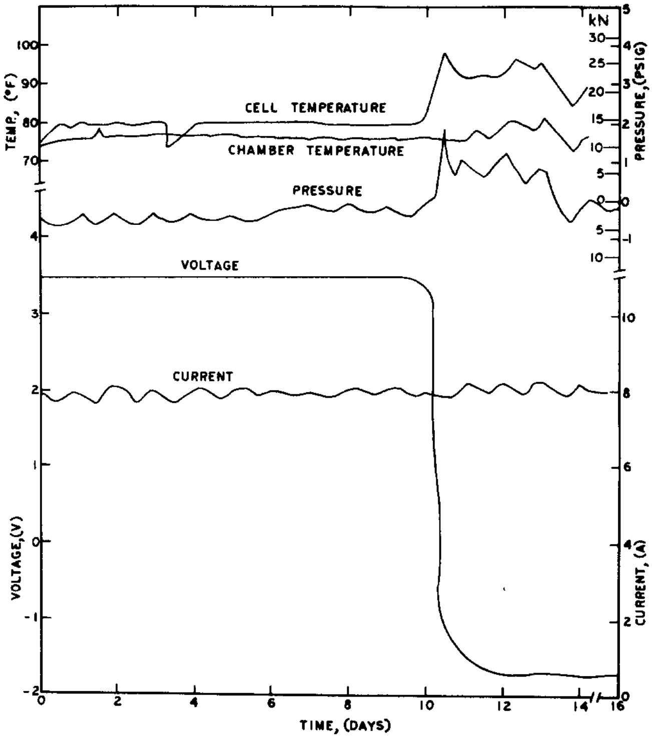

Fig. 6. Overdischarge test of a 2 000 A h cell.

and a lower load across the cell terminal. The current, the voltage, the pressure, and the temperature were monitored continuously throughout the test, the results of which are shown in Fig. 8. A current of approximately 700 A was maintained for almost two hours above 2 V before a gradual and then a sudden drop in both the current and the voltage was observed. A steady increase in the temperature to a maximum of 60 °C was followed by a steady cooling after the discharge was completed. A pressure increase to slightly above 138 kN (20 psig) occurred in the first hour of test, followed by a decrease after a brief venting through a pre-set check valve into the scrubber at the temperature maximum. The removal of the load after the sudden drop of voltage showed a full recovery of the open circuit voltage, but no capability of the cell to deliver any appreciable current. No leakage or rupture was experienced during this test.

4. Discussion

The energy density obtained in recent tests with the large cells appears to be the same as that reported previously [7] in spite of the progress of the last two years in the efficiency of cathode discharge and the overall improvement of the electrode structure. The emphasis on the safety of the structure has forced us to introduce additional inactive components and that, combined

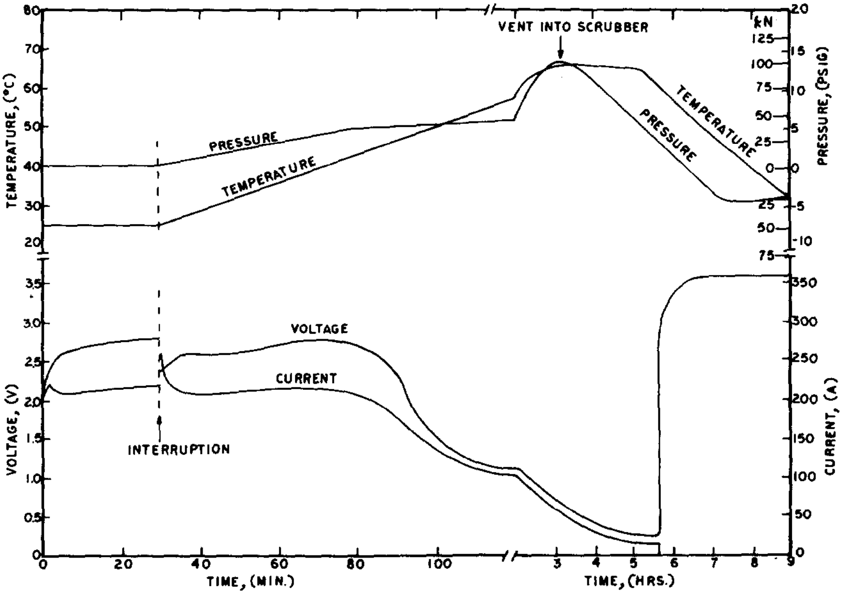

Fig. 7. Short circuit discharge of a 2 000 A h cell.

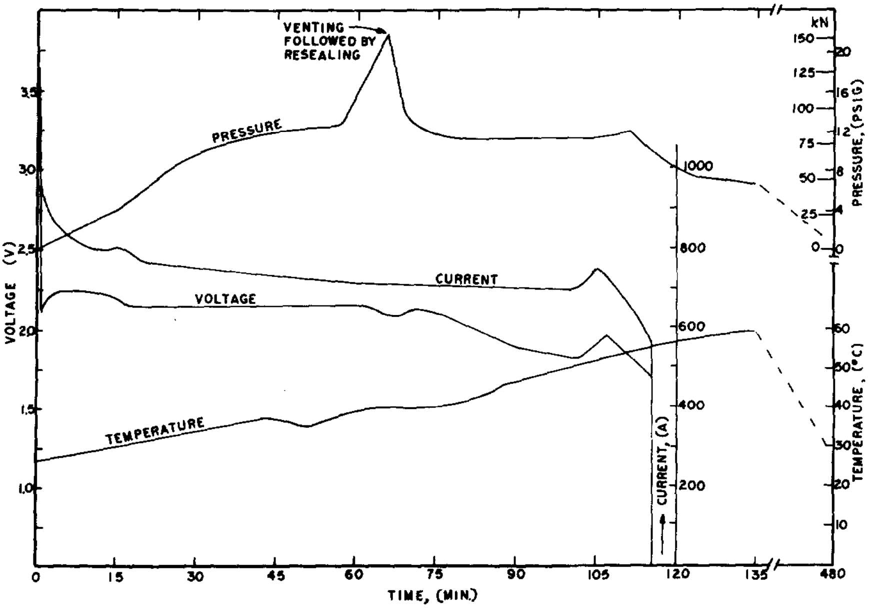

Fig. 8. Short circuit discharge of a 10 000 A h cell.

with the general acceptance of the lithium limited electrode configuration, is mostly responsible for this behavior. The discharge rate capability of the cells has been improved, however, since the operating voltage of these cells is somewhat higher than that of the cells discharged two years ago with the same current density.

The original concept of a safe, large cell has now been proven valid. The large cell, designed with a limited area of electrodes, can be discharged efficiently, while on short circuit it cannot deliver a current high enough to lead to the runaway reaction reported on several occasions in the last six years. Both of the experiments shown in Figs. 7 and 8, as well as the one reported earlier [7], demonstrated the validity of the concept.

The mechanical abuse has not really produced new evidence of hazardous behavior since the obvious origins of hazards were eliminated by the design of the cell, while those suspected to exist were not found to be present during the tests. The good stability in the electrolyte of an otherwise fragile carbon electrode was proven in the shock and vibration tests and is due, largely, to the similarity in densities of the electrolyte (1.70 g/cm^3) and bulk carbon (1.95 g/cm^3). The components with much larger density (current collectors, cell interconnectors) and those with much lower density (lithium) were also much easier to restrict as far as the relative motion of various components on shock and vibration is concerned.

The resistance to thermal abuse was greatly improved with the introduction of a venting check valve and a scrubber for the effluents. Only a brief venting was observed, and it involved inert gases trapped in the cell, before any significant losses of electrolyte were experienced. A uniform overheating, with the temperature remaining below the melting point of lithium, was found safe, whether carried out by an external source or with the cell's own energy. The overall prospects for the safe use of large cells have been greatly improved, as evidenced by the abuse tests presented here.

Acknowledgement

The authors are indebted to the U.S. Air Force for continuous support of this program and to GTE Sylvania, CSD for permission to publish this work.

References

1 J. P. Gabano, *French Patent No. 1 583 804*, December 5, 1969.
2 J. J. Auburn *et al.*, *J. Electrochem. Soc.*, *120* (1973) 1 613.
3 W. K. Behl *et al.*, *J. Electrochem. Soc.*, *120* (1973) 1 619.
4 J. J. Auborn and N. Marincic, in D. H. Collins (ed.), *Power Sources 5*, Academic Press, London, 1975, p. 683.
5 N. Marincic *et al.*, *Fall Meeting of Electrochemical Society*, The Electrochemical Society, Princeton, N.J., 1975, Extended Abstr. 72 - 2, p. 101.
6 N. Marincic and F. Goebel, *J. Appl. Electrochem.*, *8* (1978) 11.
7 N. Marincic and F. Goebel, *Proc. 28th Power Sources Symp., Atlantic City, June, 1978*, The Electrochemical Society, Princeton, N.J., p. 244.
8 C. R. Schlaikjer, F. Goebel and N. Marincic, *J. Electrochem. Soc.*, *126* (1979) 513.
9 D. L. Chua, J. O. Crabb and S. L. Deshpande, *Proc. 28th Power Sources Symp., Atlantic City, N.J., 1978*, The Electrochemical Society, Princeton, N.J., p. 247.
10 G. Younger, *NASA Conf. Publ. 2088*, Goddard Space Flight Center, Greenbelt, Md., 1978, p. 505.