STUDIES OF HIGH RELIABILITY LONG-LIFE Li/SO_2 CELLS

CALVIN D. JAEGER, SAMUEL C. LEVY, EDWARD V. THOMAS and J. THOMAS CUTCHEN

Sandia National Laboratories, Albuquerque, NM 87185 (U.S.A.)

Summary

To satisfy the need for a 5-year battery, a long-term test of Li/SO_2 cells was initiated. Premature failures were observed and a program was undertaken to identify the cause of these failures. Based on the results of this program, changes in the cell design were made which gave rise to the Sandia modified Li/SO_2 cell having improved long-life performance.

Several batches of modified cells have been manufactured during the past five years. Acceptance testing of incoming cells from each batch revealed batch-to-batch variation in performance as well as a small proportion of cells with low capacity. A program to develop a non-destructive methodology for identifying cells with low inherent capacity was initiated. Several relevant non-destructive measurement parameters were identified. A decision tree screening technique, based on these parameters, was developed to identify those cells having low capacity.

Introduction

Sandia National Laboratories has a need for batteries capable of 5 years of continuous operation. To satisfy this need, a program was initiated to characterize high energy battery systems. Initial calculations indicated a lithium system was necessary to meet volume requirements. At the time, Li/SO_2 was the only lithium chemistry commercially available. There were no long-term test data, so cells were purchased from two manufacturers for testing under simulated operational conditions.

Background

Commercial Li/SO_2 D cells

Cells were placed on a test consisting of a resistive load corresponding to ~100 μA with a pulse load of ~10 mA superimposed at a 1% duty cycle (150 ms every 15 s). The cells were subjected to a temperature cycle ranging

0378-7753/87/$3.50

from −18 °C to +49 °C with a 1-day excursion to −40 °C and a 1-day excursion to +70 °C every six months.

After 18 months on test, cells started to fail (voltage <2.0 V during any portion of the test). A program was initiated to determine the cause of premature failure and to find a cure. Four distinct failure modes were found: corrosion of the glass in the glass-to-metal seal, corrosion of the tantalum positive pin, corrosion of the anode contact, and stress corrosion cracking of nickel-plated steel cans.

Sandia modified Li/SO_2 D cells

The above studies have resulted in a fix for each failure mode. Each has been incorporated into the commercial Li/SO_2 cells and has resulted in an improved version known as the Sandia modified cell [1]. Modifications include the use of a new corrosion-resistant glass (TA-23) in the glass-to-metal seal, and molybdenum as the positive-pin material. An arc-percussive weld is used to attach the aluminum tab from the cathode directly to the molybdenum pin. The anode has been redesigned to contain an expanded nickel grid between two sheets of lithium foil with connection to the can (negative terminal) via a nickel tab which is connected directly to the anode grid. The nickel-plated steel can is fully annealed and the radius of curvature at the bottom outer edge has been increased to reduce stress in that area. Real-time tests of these cells have been in progress for over 54 months with no failures to date.

Cell reproducibility

To date, 15 batches of modified cells have been manufactured by two suppliers. A summary of the batch acceptance data for one manufacturer is given in Fig. 1. There is significant batch-to-batch variation in capacity, and

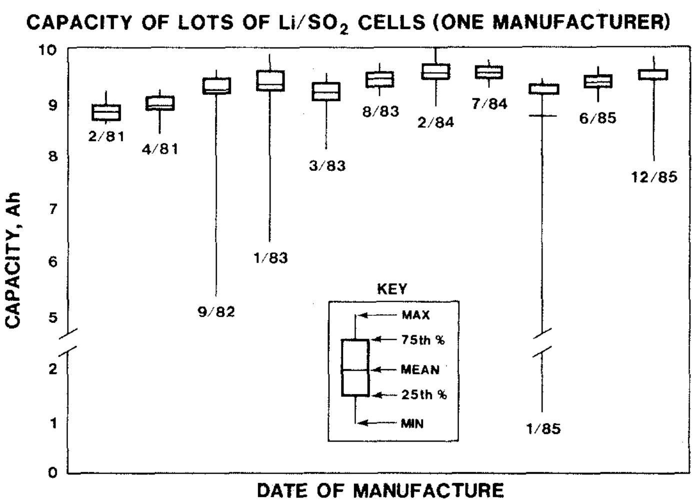

Fig. 1. Li/SO_2 cell acceptance data. Discharge at 6.25 Ω, 25 °C.

cells with low capacity (<8 A h) have been observed in several cases. The cause of poor performance has been found to be manufacturing related (*e.g.*, improper weld schedules) in each instance. Therefore, a 100% screening of cells appears necessary to insure a reproducible, reliable product, even though all the identified cell defects leading to premature failure and poor reliability have been corrected.

Reliability and methodology program

A program has been underway at Sandia to develop a methodology for screening individual Li/SO_2 cells used in long-life applications on the basis of expected performance. The reliability of these cells (measured by performance) is affected by deleterious chemical and electrochemical processes taking place within the cell. These processes occur continuously from the time of manufacture, and their rates are affected by the environments experienced by the cells. Certain features of this cell deterioration should be measureable if a relevant and sensitive non-destructive technique is used. Three such candidate techniques have been evaluated in this program: microcalorimetry, open-circuit voltage measurements, and complex impedance analysis.

Test matrix

In order to support this program, a test matrix was designed. The test matrix, consisting of 140 fresh, spirally-wound Sandia-modified D cells from a single batch, stored under various conditions and discharged at various rates, is outlined in Table 1. All cells were stored at a mildly accelerated-ageing temperature of 40 °C, half at open circuit (OC) and half under a light load of 7500 ohms (LL), except for 20 cells which were discharged immediately (baseline cells, BL). Prior to discharge, non-destructive tests were

TABLE 1

Test matrix

Load final discharge (Ω)	0 yr	0.5 yr		1.0 yr		1.5 yr	
		OC	LL	OC	LL	OC	LL
57		X	X	X	X	X	X
11							
5.5							
3							
0.8		X	X	X	X	X	X

Note: 4 cells tested at each condition. Microcalorimetric measurements are indicated by X.
OC = Open circuit, LL = Light load.

performed on all cells. The cells were then discharged at one of the five rates called for by the test matrix.

Non-destructive measurements

Cell voltage. Cell voltage measurement is the easiest of the non-destructive techniques that can be applied to a cell. In our study, we identified a number of anomalous factors which affect the cell voltage, *e.g.*, electrolyte decomposition, storage at elevated temperatures, and discharge through an external load. Although the influence of some of these factors was readily apparent, open-circuit voltage did not prove to be a reliable predictor of the residual cell capacity.

Microcalorimetry. Microcalorimetry is a very sensitive technique which enables one to measure heat flux in the microwatt range. Although microcalorimetry has been used quite satisfactorily with certain heart pacemaker batteries, we were unable to relate the measured heat output to the residual cell capacity.

Complex impedance analysis. The complex impedance spectrum for Li/SO_2 D-cells consists of contributions from three different elements [2]: the ohmic component; the lithium anode impedance; and the porous carbon cathode-collector impedance. Figure 2 shows a typical complex-impedance spectrum for the cells being studied in this program, as well as ten impedance parameters which characterize the spectrum. The ohmic component is given by the high frequency intercept, R1. It is related to the bulk electrolyte

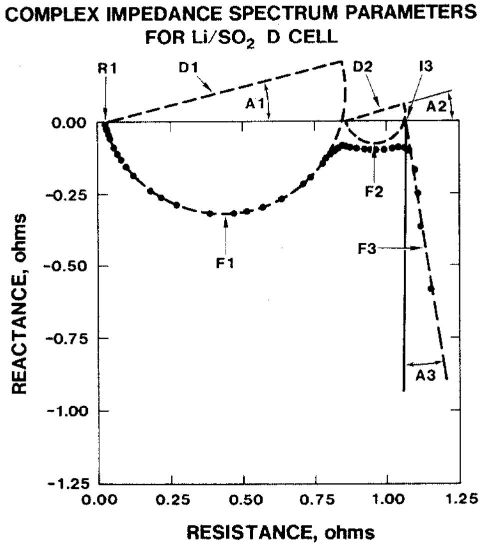

Fig. 2. Typical complex impedance spectrum for an Li/SO_2 cell. Points represent actual data at each frequency, dashed lines represent estimated spectrum from regression analysis.

resistance plus any other "bulk" effects such as solid resistances. The lithium anode contribution is represented by two semi-circular elements. The variables that characterize the first semi-circle are the diameter, D1; the skew angle, A1; and the frequency at the maximum reactance, F1. The second semi-circle has similar variables D2, A2 and F2. The porous carbon-collector contribution is represented by an inclined line, sometimes called a constant phase angle. Three variables characterize the impedance for this element: the intercept of the line with the resistance axis, I3; the angle between the line and a line normal to the resistance axis, A3; and the characteristic frequency for that line, F3. Values for these parameters are determined using non-linear, least-squares regression.

Shown in Fig. 3 are "box and whisker" plots for the impedance parameters R1 and A1. It is particularly interesting to note how the various storage regimes affect these parameters. As will be discussed in later sections, these parameters can be related to remaining cell capacity.

Data analysis — identification of relevant predictors

The purpose of the data analysis was to identify a subset of non-destructive measurement variables that related empirically with the capacity remaining at the time measurements were made. It is expected that this subset of variables will form the basis for a good predictor of remaining capacity.

The load applied during final discharge affects remaining capacity. Figure 4 graphically displays the observed relationships between the median remaining capacity (of each group of four cells) and discharge rate for the range of storage conditions. From Fig. 4, it is clear that the discharge rate effect is strongest for the LL-cells. It is also clear that there is a loss of capacity in the LL-cells over and above that due to the capacity removed during storage; this was approximately 0.28 A h per month. A non-parametric version of the product–moment correlation coefficient, Spearman's rho [3], was used to measure the pairwise association between remaining capacity and each non-destructive measurement variable. Because the residual capacity was affected by discharge rate, the correlation analyses were necessarily segregated by discharge rate. Measures of association between residual capacity and each non-destructive measurement variable, for each discharge rate, were computed.

R1 and A1 have statistically significant negative associations with the residual capacity for each discharge rate. This means that cells with relatively low values of R1 and A1 have better performance characteristics than cells with relatively high values. Similar results were noted for other Li/SO_2 cells [4]. Further analysis indicated that D1 may also have predictive relevance, in combinations with R1 and A1. Figure 5 illustrates how the residual capacity varies with each of the three parameters R1, A1, and D1. Each cell in the test matrix (excluding the 18-month cells) is grouped by storage regime and discharge rate and is represented by a glyph. The glyph consists of a circle with radius proportional to the measured capacity for the cell and has three

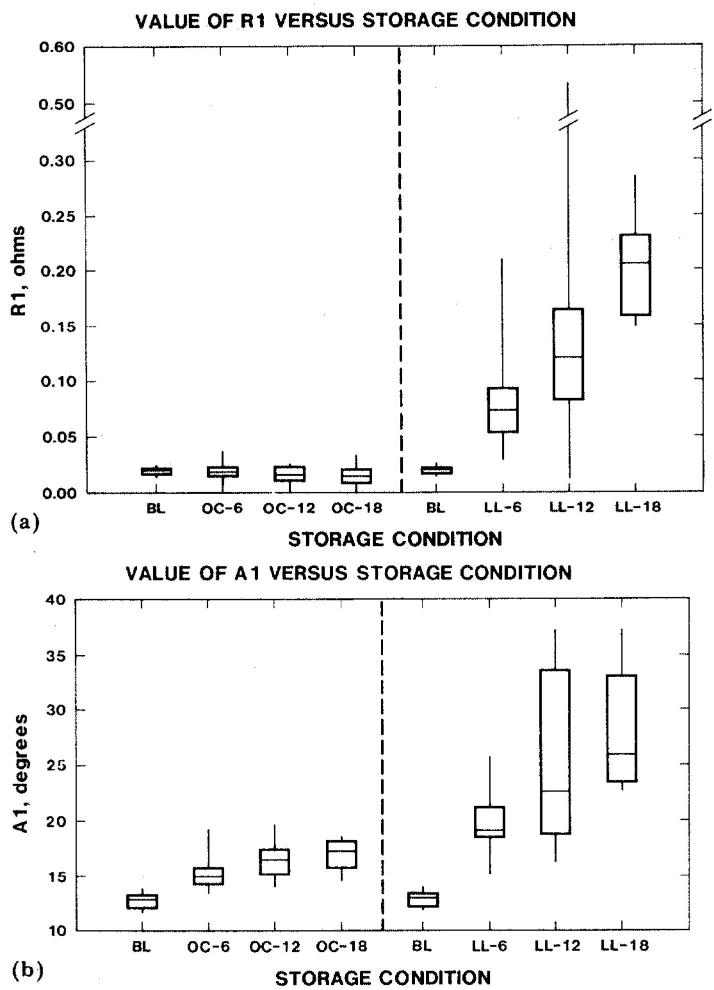

Fig. 3. Complex impedance parameters *vs.* storage condition (months at either OC or LL). (a) High frequency intercept; (b) skew angle.

legs radiating out from the center of the circle with lengths proportional to the three predictor variables. Note that variables R1, A1, and D1 generally increase with decreasing capacity.

Cell screening

Ideally, one would like to model residual capacity as a continuous response variable, dependent on a linear combination of independent variables (*i.e.*, multiple linear regression). However, the complex nature of the relationships between predictor variables and residual capacity makes this a difficult task. From an operational viewpoint, what we really need is to be able to identify those cells with serious capacity deficiency. A conceptually simple methodology that achieves this is a "decision tree". In the decision

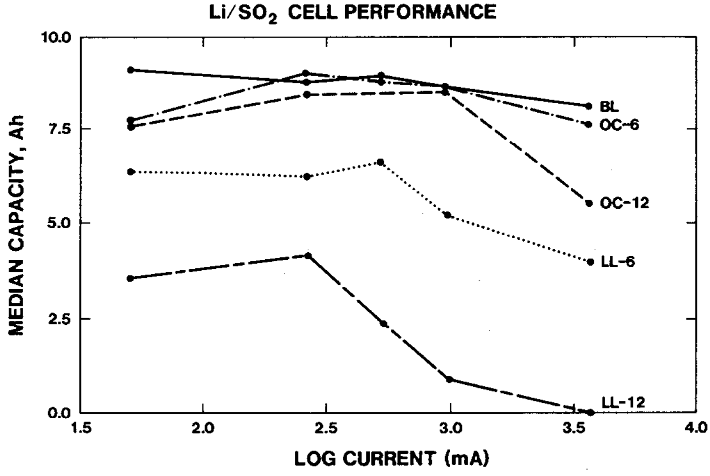

Fig. 4. Median capacity of Li/SO_2 cells *vs.* discharge rate for various storage conditions.

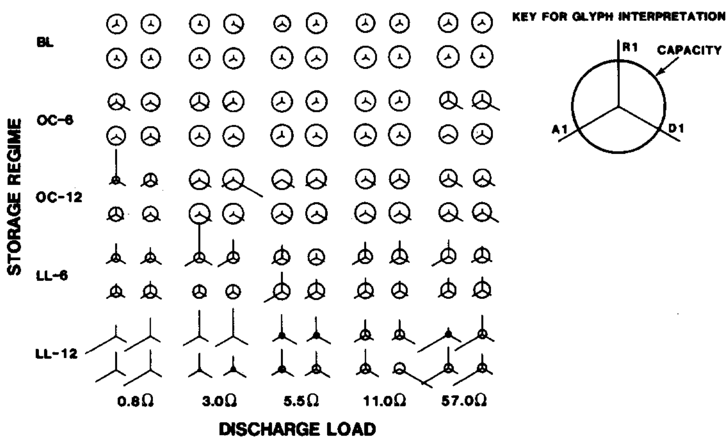

Fig. 5. Graphical representation of the relationship between cell capacity and three complex impedance parameters as a function of storage condition and discharge rate.

tree approach, observed values of important variables, such as R1, A1, and D1, are compared with some threshold values. Each comparison yields a binary response (accept/reject) which corresponds to predicting relatively high or low capacity for the cell. In order for a cell to be accepted, each comparison must yield an "accept" response, Fig. 6. The selected threshold values, X1 - X3, would depend upon our previous empirical observations, desired capacity, and the specification of one of two types of risk. Type I risk is defined as the probability of rejecting a cell that, if discharged, would meet the capacity requirements. Type II risk is defined as the probability that a cell that has been accepted will not meet the capacity requirements.

For high-reliability applications, one would select a relatively low target value for Type II risk. This implies the selection of relatively stringent threshold values which generally imply relatively large Type I risk. So, as we

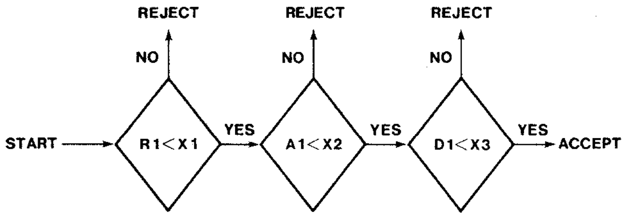

Fig. 6. Decision tree diagram for cell acceptance.

require higher reliability, we would generally reject more "good" cells. Therefore, the problem is to find relevant variables and a set of threshold values that both minimize Type II risk yet do not make the Type I risk unacceptably large. Using a decision-tree rule with these properties would constitute an effective screening technique. As an example of how this method might work in a high-reliability Li/SO_2 application, consider the following: assume that the minimum acceptable capacity is dependent on the load (8.5, 8.25, 8.0, 7.75, and 7.5 A h for loads of 57, 11, 5.5, 3, and 0.8 ohms, respectively). Then apply the multiple decision rule as illustrated in Fig. 6 to all the cells using the illustrative set of threshold values indicated in Table 2. As shown in Table 2, reliability is significantly increased without rejecting an unreasonable number of "good" cells. Because we have purposely chosen threshold values that work well with the available data, our estimates of risk are lower than what one would have in practice with other cells. A better way to estimate those risks would be to apply the rule to cells not used in selecting the threshold values.

TABLE 2

Results of decision-tree screening*

	Total	Number rejected	Number accepted
'Good' cells	44	6	38
'Bad' cells	56	52	4
Total cells	100	58	42
Reliability	0.44	—	0.90

*Threshold values: R1 $<$ 0.026; A1 $<$ 16.0; D1 $<$ 4.0.

A new methodology, Classification and Regression Trees (CART), that extends the simple decision tree to a much more complicated structure, allowing for interactions between variables, has recently been developed [5]. CART selects the optimal set of prediction variables and threshold values, given an existing data set and a specification of relative risk (Type I/Type II). In addition, CART provides accurate estimates of the risks associated with the set of prediction variables and threshold values. This methodology will soon be used in order to develop an operational predictor.

Conclusions

Elimination of the parasitic reactions leading to premature failure of Li/SO_2 cells does not guarantee a reliable product. Variations in manufacturing processes can lead to both within-batch and between-batch variation in cell performance, resulting in a reduction of overall reliability. To improve the reliability of batches of Li/SO_2 cells a study of sensitive, non-destructive measurements was undertaken. Use of just three complex impedance parameters in a decision-tree approach shows promise in improving batch reliability. However, to achieve the increased reliability, a number of "good" cells are rejected. A new technique, Classification and Regression Trees (CART), will soon be used to develop an operational predictor that will achieve an optimal balance between accepting bad cells and rejecting good cells.

References

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