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Safety and reliability studies of primary lithium batteries

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Abstract

The safety and reliability of batteries are closely related. Examples are given to demonstrate how changes made in battery materials and design parameters to improve either safety or reliability may also enhance other characteristics. In one example, replacement of the glass in the glass-to-metal seal of Li/SO_2 cells to improve reliability also eliminated a serious safety problem associated with discharged cells. The second example relates to design parameters in Li/$SOCl_2$ cells for increased safety. A Taguchi analysis indicated several parameters affected safety upon reversal. The indicated levels of these parameters for improved safety also suggest improved reliability, although the long-term reliability studies have not yet been completed.

Introduction

Battery safety and reliability are intimately related. In terms of a battery's overall reliability, safety is one component that must be considered. Therefore, one may use the same tools and techniques to evaluate both aspects of a battery. In many cases, material or design changes made to improve either reliability or safety will also result in improvements to the other.

Both safety and reliability are affected by the battery's environment; during transportation, storage and use, as well as by its mode or rate of discharge. These parameters may be included in some evaluation techniques, e.g., fault-free analysis or Taguchi-type matrices, when assessing either reliability or safety.

Additional steps must be taken to assure both reliability and safety when fabricating multicell-battery packs. Use of safety devices, proper design and careful attention to thermal management are necessary to attain equivalent levels of safety and reliability in battery packs as are attained in single cells.

Examples of the close relationship between safety and reliability are given in the discussion section below.

Discussion

Li/SO_2 cell reliability and shock sensitivity

Tests of commercial Li/SO_2 cells were conducted at Sandia National Laboratories for use in a 5-year application. Results indicated poor reliability for long-term discharge. Failures began occurring at 18 months and most of the cells had failed by 36 months. A program was initiated to determine the cause of premature failures in Li/SO_2 cells.

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Several faults were found in the commercial cells, but the major cause was corrosion of the glass in the glass-to-metal seal. This resulted in a conductive product that coated the glass and allowed the cells to self-discharge across the seal.

A program was initiated to correct the faults leading to premature failure. One of the solutions evolving from this program was a corrosion-resistant glass, TA-23, for use in the glass-to-metal seal [1]. Cells built with this glass in the header plus some other material and design changes, demonstrated a >0.9999 reliability in the 5-year application.

A second benefit was derived from use of the TA-23 glass: improved safety. A serious problem with the earlier Li/SO_2 cells was shock sensitivity after discharge. Studies were conducted at Sandia National Laboratories to identify the cause of this problem [2]. It was found that shock sensitivity occurred in cells that were cathode (carbon) limited, either by design or by inefficient discharge. In either case, the SO_2 remaining in the cell maintained a passivating layer of lithium dithionite, $Li_2S_2O_4$, on the remaining lithium, which prevented it from reacting with the acetonitrile in the electrolyte. It had been shown earlier by Dey [3] that lithium metal in the same electrolyte with, and electrically connected to, another metal with which it alloys, e.g., aluminum, would undergo a process called spontaneous electrochemical alloying (SEA). In the cells described above, lithium metal is in the same electrolyte with the aluminum grid of the discharged cathode collector. Electrical connection may occur as a result of glass corrosion. Depending on the age and temperature history of the cell, the conductive product of the corrosion reaction may bridge the glass-to-metal seal and complete the circuit. As SEA occurs, a high surface area lithium–aluminum alloy forms inside the discharged cathode collector which is saturated with the product of the electrochemical reaction, lithium dithionite. The Sandia study showed that this finely-divided alloy, in the presence of dithionite, is very shock sensitive [2]. Use of the corrosion-resistant glass TA-23, developed for improved reliability, prevented the SEA from occurring by maintaining an open circuit between the lithium anode and aluminum cathode grid, and thus eliminated the shock-sensitive problem for Li/SO_2 cells.

Safety studies of $Li/SOCl_2$ *cells*

A lithium thionyl chloride battery was designed for an application in which there is a small probability that certain abusive conditions (e.g., reversal, charge) may occur. To insure safety of the system, even under the abusive conditions, a study was conducted to identify design parameters related to the safe operation of the D-size cells to be used in the battery [4]. A Taguchi L_8 orthogonal array was used to study seven design variables that may affect safety (Table 1). The variables chosen were: electrolyte concentration (1.0 versus 1.8 M $LiAlCl_4$), SO_2 additive (Yes, No), electrode surface (moderate-rate design [345 cm^2] versus low-rate design [145 cm^2]), free volume (standard (5 cm^3) versus excess (9 cm^3) with the same electrochemical balance), type of carbon in the cathode (single carbon (Shawinigan Black) versus blended carbons (Black Pearls-Shawinigan Black)), cathode drying method (vacuum oven versus vacuum oven followed by exposure to $SOCl_2$ vapor), and release pressure of the vent placed in the can bottom (1.4 versus 2.1 MPa). Special cells were constructed having a pressure transducer built into the header. A thermocouple was mounted on the sidewall of the cells.

Cells were discharged at either of two rates (15 or 500 mA) and then either driven into reversal at 500 mA or charged at 500 mA. Internal pressure, skin temperature and discharge capacity were monitored. Responses used in the analysis of the data were: maximum pressure, maximum temperature, rate of pressure increase, and vent

TABLE 1

Taguchi-L_8 orthogonal array used in Li/$SOCl_2$ safety study[a]

Cell No.	Electrolyte concentration (M)	SO_2 additive	Design	Free volume	Carbon	Cathode drying	Vent pressure (MPa)
1	1.0	No	MR	Standard	BP/SAB	Vac/TC	1.4
2	1.0	No	MR	Excess	SAB	Vac	2.1
3	1.0	Yes	LR	Standard	BP/SAB	Vac	2.1
4	1.0	Yes	LR	Excess	SAB	Vac/TC	1.4
5	1.8	No	LR	Standard	SAB	Vac/TC	2.1
6	1.8	No	LR	Excess	BP/SAB	Vac	1.4
7	1.8	Yes	MR	Standard	SAB	Vac	1.4
8	1.8	Yes	MR	Excess	BP/SAB	Vac/TC	2.1

[a] MR design = 345 cm^2, LR = 145 cm^2 electrode area.
Standard free volume = 5 cm^3, excess free volume = 9 cm^3.
Carbon type BP/SAB = blend of Cabot black pearls 2000, SAB = Shawinigan acetylene black.
Cathode drying method: Vac = vacuum-oven dried, Vac/TC = vacuum-oven dried plus exposure to $SOCl_2$ vapors.

severity. Cell capacity was also used as a response so the effect of the various parameters on performance could be defined.

Results were dependent on the test conditions experienced by the cells. For cells discharged at 15 mA and then driven into reversal at 500 mA, the following parameters resulted in cells with increased safety: free volume (standard (5 cm^3)), carbon in cathode (blended carbon), electrolyte concentration (1.0 M $LiAlCl_4$).

The parameters resulting in increased safety for cells discharged at 500 mA and then driven into reversal at 500 mA were: free volume (excess (9 cm^3)), carbon in cathode (single carbon), cell design (low rate (145 cm^2)), additives (no SO_2).

The third matrix, in which cells were discharged at 500 mA and then charged at 500 mA, resulted in one cell type venting violently while none of the other seven variations vented at all. This skewed the results sufficiently that this test was disqualified.

Results from the entire study were then combined and each parameter was ranked according to its relative effect on cell safety. Three variables were found to have a consistent effect: cell design (low rate (145 cm^2)), additives (no SO_2), electrolyte concentration (1.0 M $LiAlCl_4$).

Other parameters, e.g., free volume, type of carbon used in the cathode, show contradictory effects, depending on the discharge rate of the cells. This demonstrates the importance of designing cells for a specific application.

The effect of excess lithium in cells experiencing reversal was also observed in this test matrix. In the series discharged at 500 mA and driven into reversal at 500 mA, the low rate design did not discharge as efficiently as the moderate-rate design. Upon entering reversal, the low-rate cells had from 5 to 9 A h of lithium remaining while the moderate rate cells had only 2 to 2.5 A h in them. Upon entering reversal, the voltages of the moderate rate cells were more negative and very erratic compared with the voltages of the low-rate cells, which were less negative and stable. The maximum pressure reached in reversal is plotted versus the lithium remaining in the cell at the start of reversal (Fig. 1). These results indicate that an excess of lithium in Li/$SOCl_2$ cells leads to a safer cell in reversal.

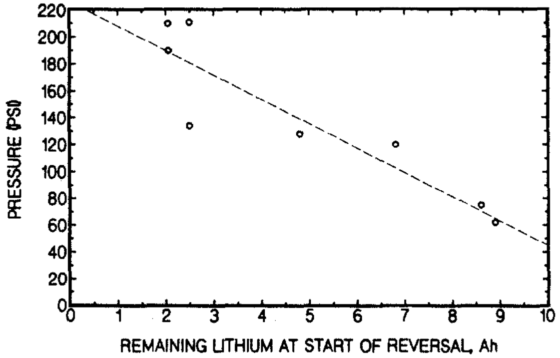

Fig. 1. Maximum pressure reached during reversal at 500 mA after discharge at 500 mA vs. amount of lithium in cell at start of reversal.

Although aging and reliability studies are not yet complete, it seems reasonable to assume that the lower surface area electrodes and lower electrolyte concentration that correlate with improved safety should also lead to a lower self-discharge rate and therefore, contribute to increased reliability.

Multicell-battery packs

Multicell-battery packs, if not properly designed, may have safety problems even if built from cells that have been proven safe for the particular application. Certain features need to be kept in mind when designing multicell-battery packs. If cells that are designed to vent are used (e.g., Li/SO_2, $Li/SOCl_2$, etc.), the battery pack must include a volume into which gasses may vent if necessary, and a path for the vented gasses to escape. Thermal management must be considered, especially in large batteries where some cells are surrounded by others, or in situations when a battery is to be located in an area where heat cannot be easily removed. Fuses or current-limiting resistors and thermal switches should be considered, depending on the battery design and/or use scenario.

Blocking diodes should be used to prevent charging of one string of cells by another string connected in parallel. In some instances, reversed bias diodes may be required on each cell in a series string to prevent individual cells from being driven into reversal.

Proper soldering or welding of all intercell connections and leads, to prevent intercell shorting during environmental stress that may occur during transportation, handling or use, is also an important consideration to the design of a safe battery pack.

The level of safety measures to be taken needs to be determined for each multicell-battery design. Abuse tests must be conducted on full battery packs to insure safe operation.

A number of these safety considerations will also result in a more reliable battery pack, e.g., appropriate thermal management and proper intercell connections.

Summary

Battery safety and reliability are closely related and many of the same techniques, e.g., fault-tree analysis and Taguchi methods, can be used to study both.

In many cases, changes made in the components or design of a cell to improve either safety or reliability, e.g., corrosion-resistant glass in Li/SO_2 cells, will also enhance the other characteristic.

Taguchi methods have been used to design safety into Li/$SOCl_2$ cells. However, safe designs are application dependent. If a cell is to be used for a different application than for which it was designed, safety studies should be repeated.

Safe, reliable cells do not insure a safe, reliable battery. Safety and reliability must be designed into multicell-battery packs and tests conducted on the complete package.

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