NONLEAKING BATTERY TERMINALS

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ABSTRACT

The potassium hydroxide (KOH) electrolyte used in conventional alkaline batteries is contained in a metal case and cover with ceramic insulators around the terminals. The silver zinc or silver cadmium batteries using a potassium hydroxide (KOH) electrolyte require a plastic battery case and cover to prevent internal shorting of the battery. Covering of the interior of a metal case and cover with plastic has not been satisfactory. The previous terminal seals on silver zinc battery cases and covers have not been successful for extended periods of time. The use of silver zinc or silver cadmium batteries for space vehicles or satellites require an extended life up to five years with a 100 percent reliability. Previous designs have failed at as low as nine months.

Three different terminals were designed for usage in a 40 ampere/hour silver zinc battery which has a 45 percent KOH by weight electrolyte in a plastic battery case.

Life tests, including thermal cycling, electrical charge and discharge for up to three years duration, were conducted on these three different terminal designs.

Tests for creep rate and tensile strength were conducted on the polyphenylene oxide (PPO) plastic battery cases. Some cases were unused and others containing KOH electrolyte were placed on life tests.

The design and testing of nonleaking battery terminals for use with a potassium hydroxide (KOH) electrolyte in a plastic case are covered in this presentation.

RECENT IMPROVEMENTS in the separator life of silver-zinc battery cells (1)* have made it possible to consider using silver-zinc cells for long-life applications in synchronous orbit. Use of the silver-zinc systems will at least double the energy density (watt-hour/kg) of the normal nickel-cadmium battery. This greater energy density will greatly decrease battery weight for the same energy capacity of the satellite.

The nickel-cadmium batteries presently in use for synchronous-orbit applications are constructed with stainless steel cases using metal sprayed ceramic insulators welded to the case. This construction forms a hermetic seal around the terminal posts. In the case of a silver-zinc cell, a stainless-steel case is incompatible with the electrodes of the cell and would thus form a gasing couple. Plastic coating of the stainless steel cases is not acceptable because the plastic coating is not 100 percent reliable. As a consequence, the silver-zinc system has always been housed in a plastic case.

A second-generation terminal seal designed for the 40-ampere-hour heat-sterilizable silver-zinc cell development is described in reference (1). This terminal is called the standard throughout this report. It consists of three O-ring seals, epoxy potting at both ends of the terminal and throughout the internal structure of the terminal O-ring assembly. A tabulation of 153 cells with this terminal design showed that 0.5 percent leaked at the positive terminal and 4 percent leaked at the negative terminal at an average age of 8 months.

Where silver-zinc batteries have been used for space applications, the complete battery was overpotted with an epoxy resin. This overpotting can keep a silver-zinc battery in operation up to a year before a cell leakage becomes detrimental.

For longer life, it is of vital importance to contain the KOH electrolyte within the cell case to maintain the balance of electrical charge and discharge capacity of all cells in the battery. One low-capacity cell in a battery can be charged and discharged to a condition where it gases. This gasing cell can explode and destroy the battery and possibly the mission.

This paper describes the design and test results of three terminal seals. Only one design, the two-piece design, has successfully contained the concen-
trated potassium-hydroxide electrolyte of a silver-zinc battery cell in a plastic case for 23 months of accelerated testing to date.

APPARATUS AND PROCEDURE

DESCRIPTION OF TERMINALS. Standard Terminal - The original terminal is shown in figure 1. It consists of a triple O-ring assembly with epoxy potting at both interior and exterior ends of the terminal and with potting throughout the O-ring assembly. After 12 months of testing, it became apparent that the standard terminal would not be 100 percent reliable for a 5-year service life.

Modified Terminal - The standard terminal was modified (fig. 2) to eliminate the interior epoxy potting and to place the top O-ring in compression by squeezing it around the terminal top by the compression of the slanted top washer. The terminal of this modified type was made of 304 stainless steel in place of the coin silver used on the standard terminal.

Two-Piece Terminal - A third terminal (fig. 3) was designed to incorporate a new basis for sealing. It was also made of 304 stainless steel. The basic principle for sealing off the KOH capillary leakage was to use resilient compression gaskets in addition to epoxy seals at the interior and exterior ends of the metal terminal with space between each seal so there would be no continuity of propagation of a leakage path.

The two-piece terminal incorporates two epoxy seals, one flat gasket and one O-ring gasket. The O-ring gasket was specified in place of a flat gasket for the upper gasket seal; it was felt the O-ring would assemble better than a flat gasket since the top piece of the two-piece terminal rotates against the top cover upon assembly of the terminal. Both gaskets were compressed 20 percent upon assembly. Ethylene propylene was specified for the gasket material since it was highly resistant to the concentrated KOH electrolyte (2).

DESCRIPTION OF TESTS. Voltage Impressed - The initial tests consisted of assembling the terminals in the battery cases without battery plates. These terminals were the standard design with and without internal potting, standard terminals with special cleaning, modified terminal design and the two-piece terminal design. The cells were heated to 135° C to simulate heat sterilization and then held at 320° C with a 1.2-volt potential impressed across the terminals for the duration of the test. Half of the cases were inverted.

Thermal cycle, Voltage Impressed - In subsequent testing cases were given a thermal cycle of 12 hours at 135° F and 12 hours at ambient temperature in addition to the impressed voltage. The ovens used and the test setup used is shown in figure 4.

Electric Cycling - Electrical cycling, charge-discharge, of the standard cells had many terminal failures in a short time of testing. It was known that these particular cells had been overcharged and had been gassing, thus becoming overpressurized. Therefore, it was apparent that pressure had some effect on the leak rate of these cells.

Pressure Testing - A quick test to find differences in terminal seals was conducted by pressurizing cases made with the different types of terminals. The covers of all the cells separated from their cases at 150 psig pressure before any terminal leakage could be observed.

Discharged stand - A quantity of 236 cells (472 terminals, 2 per cell) were made to be used for future electrical testing. These cells were cycled electrically for two cycles then stored discharged waiting future tests.

Plastic Testing - Material testing was conducted on new and year old, KOH-soaked plastic battery cases. These cases were 30 percent glass-filled polyphenylene oxide. Tensile-strength and modulus-of-elasticity tests were run at room temperature and at 275° F.

Leakage Path - A program was developed to determine the actual capillary leakage path of the KOH electrolyte. This KOH leakage is termed electrophoresis or ion migration. Since the path would be of a minute size, a method of marking the path with a dye would greatly help in determining this leakage fault. The path, at the terminal epoxy interface, had to be in the metal or epoxy or both.

Six batteries of the standard and modified terminal designs, which were previously removed from testing due to terminal leakage, were used for this test. These six batteries were unsealed and a fluorescein dye was introduced into their electrolyte. The dye-doped batteries were resealed, inverted, and pressurized to 40 psig. Discolored potassium carbonate was observed on several of the terminals within a few days of the pressurization (fig. 5).

The leaking terminal battery covers were sepa-
rated from the cases (fig. 6) and the terminals cut out of the covers. Leaking and nonleaking terminals were sectioned (fig. 7) longitudinally. These half sections of the terminal-cover epoxy assemblies were immersed in liquid nitrogen to render the plastic and epoxy brittle and to put the metal terminals and surrounding plastic into a differential contraction stress. The terminals were then pulled from the plastic epoxy cover, and the mating sections were then examined under a 20-power viewing microscope. The metal terminal half sections broke cleanly from the epoxy potting thus exposing the KOH leakage pattern.

TEST RESULTS

TERMINAL TESTS - The original work on seals was done at the Astropower facility of the McDonnell Douglas Corp. Subsequently, the work was taken over by the Stanford Research Institute and the 32° C, voltage-impressed tests continued there. The first lots (table 1, item A) of seals tested, consisted 12 cases of the standard configuration as made in cells and six cells (12 terminals) with special cleaning of all surfaces. As shown in table 1 the first leaks appeared at 6 months.

The next set of seal assemblies consisted of standard assemblies without epoxy around the O-rings, a modified design (fig. 2) and the two-piece design (fig. 3). All the assemblies were put together at the Astropower Laboratory but the parts for the modified and the two-piece design were supplied by Lewis Research Center. Twelve seals of each type were tested at Astropower on the voltage impressed, 32° C test (table 1, item A). The first leaks appeared on the standard type at 9 months and on the modified type at 11 months, which was after the tests had been transferred to Stanford Research Institute.

These same three types of terminals, 18 of the standard design and 16 each of the modified and the two-piece design, were brought back to the Lewis Research Center for additional testing. The test consisted of impressed voltage plus a 12-hour thermal cycle that should have accelerated the leakage (table 1, item B). However, despite the extra stress of thermal cycling, the first leak on the standard, no epoxy, design did not appear until 15 months of testing and no leaks have occurred on the modified and the two-piece design.

A backlog of 236 cells (172 standard terminals) were made and stored for future use. Sixty-four of the cells (table 1, item C) were charged and discharged through two cycles, and 21 leaking terminals were found. These cells were overcharged, causing an internal pressure build up. Therefore, pressure has to be a factor, though it was not found on the quick pressure test.

Inspection of the 236 cells (table 1, item D) in the discharge stand backlog found the first leaking terminals at 10 months.

A fluorescein dye was added to the electrolyte of several leaking batteries. These batteries were resealed and pressurized in an inverted position until further leakage was evidenced by the dye on the leaking terminals (fig. 5).

The leakage path through the standard and modified terminal assemblies (figs. 1 and 2) was found to be primarily an epoxy-metal interface failure. The sealing epoxy starts to separate from the metal terminal at the interior face (electrolyte side) and the separation continues until the inner seal is finally penetrated.

Leaking and nonleaking terminals from the same battery cell were sectioned and examined under a 20-power viewing microscope. In nonleaking terminals, the epoxy seal had started separation from the internal end of the terminal but had not progressed through to the lower O-ring assembly. This was evidenced by the fluorescein dye discoloration on the partially separated section of the epoxy seal.

The leaking terminals had the lower epoxy seal separated as evidenced by the staining from the terminal lower section. The dyed electrolyte leaked into the O-ring assembly and through it to the exterior.

The O-rings as used in the standard and modified terminals were not effective in sealing off the KOH seepage. The lack of pressure inside the cells would not allow the O-rings to act as the pressure seals they are normally designed for.

The exterior potting of the standard and modified terminal assemblies would only seal off the seepage between the outside of the nut and the plastic cover and not the flow along the threads of the terminals through the hold-down nut.

There was no evidence of any corrosion path or chemical action on either the standard coin-silver terminal or the modified or two-piece stainless-steel terminals. Thus, it appears the KOH leakage is not a crevice corrosion or an electrochemical problem.

PLASTIC TESTS - Tensile strength tests and modulus of elasticity tests were conducted on sections...
of new and on used polyphenelyne oxide battery cases. The used case had contained the 45 percent KOH electrolyte for 18 months.

Both tensile strength and modules of elasticity drop off approximately 30 percent for both the higher sterilization temperature and for exposure to the 45 percent electrolyte. The drop in values due to the higher temperature is expected for a plastic; however, the drop in strength due to KOH exposure was unanticipated. This drop might be some of reason for the leaking on the older cells which were pressurized because of faulty testing procedures.

SUMMARY OF RESULTS

The two-piece battery terminal design is the only successful nonleaking silver-zinc battery terminal tested to date. Accelerated life tests have been run on these two-piece terminals for 23 months to date without failure. Other terminals, both the standard design and the modified design, have had initial failures in as low as 8 months of testing.

The KOH leakage through the terminal assemblies of the standard and modified terminals is due to a gradual failure of the epoxy-metal terminal interface bond coupled with a misapplication of the O-ring used in the terminal assembly.

There is no evidence of any corrosion on either of the coin-silver or stainless-steel terminals or of any crevice corrosion in the terminal assemblies. There is also no evidence of any plastic failure due to chemical or electrochemical action; however, there is a weakening of about 30 percent in tensile strength and modulus of elasticity of the polyphenylene oxide plastic when it is immersed in 45-percent KOH for 18 months.

The two-piece terminal, which uses compression gaskets of ethylene propylene plus epoxy seals on the inner and outer surfaces and spaces between the seals, appears to be the best design to date for a nonleaking battery terminal.

REFERENCES

Table 1 - Test Results

<table>
<thead>
<tr>
<th>Item</th>
<th>Test</th>
<th>Type of seals on first test leak</th>
<th>Months to present age, month</th>
<th>Number of leaks</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Voltage</td>
<td>1</td>
<td>6</td>
<td>24</td>
</tr>
<tr>
<td></td>
<td>Impressed,</td>
<td>12</td>
<td>6</td>
<td>24</td>
</tr>
<tr>
<td></td>
<td>$32^\circ$ C</td>
<td>$c_1$</td>
<td>9</td>
<td>23</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2</td>
<td>11</td>
<td>23</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3</td>
<td>---</td>
<td>23</td>
</tr>
<tr>
<td>B</td>
<td>Thermal Cycle; Voltage</td>
<td>$a_1$</td>
<td>18</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>Impressed</td>
<td>2</td>
<td>---</td>
<td>23</td>
</tr>
<tr>
<td>C</td>
<td>Electric Cycling</td>
<td>1</td>
<td>128</td>
<td>NA</td>
</tr>
<tr>
<td>D</td>
<td>Discharge Stand</td>
<td>1</td>
<td>472</td>
<td>10</td>
</tr>
</tbody>
</table>

$^a$Standard second-generation design is represented by 1; modified standard design by 2; and two-piece design by 3.
$^b$Specially cleaned.
$^c$Without epoxy on O-rings.

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Table 2 - Plastic Case Properties

Tensile Strength

<table>
<thead>
<tr>
<th>Material</th>
<th>Temperature, $^\circ$F</th>
<th>Stress, psi</th>
<th>Modulus of elasticity, psi</th>
</tr>
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<tbody>
<tr>
<td>New Case</td>
<td>75</td>
<td>10200</td>
<td>$0.85 \times 10^6$</td>
</tr>
<tr>
<td></td>
<td>75</td>
<td>10900</td>
<td>.85</td>
</tr>
<tr>
<td></td>
<td>275</td>
<td>6570</td>
<td>.65</td>
</tr>
<tr>
<td></td>
<td>275</td>
<td>5960</td>
<td>--------</td>
</tr>
<tr>
<td>Used Case</td>
<td>75</td>
<td>7060</td>
<td>.58</td>
</tr>
<tr>
<td></td>
<td>275</td>
<td>4500</td>
<td>.45</td>
</tr>
</tbody>
</table>
Figure 1. - Standard battery terminal.

Figure 2. - Modified battery terminal.
Figure 3. - Two-piece battery terminal.

Figure 4. - Thermal cycling test apparatus.
Figure 5. - Leaking standard battery terminals.
Figure 6. - Internal ends of standard terminals.
Figure 7. - Sectioned standard terminal assembly.