AN UNUSUAL SELF-DISCHARGE OF A FIELD LITHIUM-THIONYL CHLORIDE BATTERY SUBMODULE

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Abstract
A lithium thionyl chloride submodule in a Peacekeeper site in May 1992 was found to be bulging to a considerable extent. When an attempt was made to discharge the submodule in place, the battery voltage was about 6.1V in two hours, vs. the expected 10.2V. Thus, it appeared that at least one cell had experienced self-discharge.

A subsequent discharge and dissection of the submodule conducted at NAVSURFWARCENDIV Crane showed that one cell in the submodule had indeed self-discharged, but no overt reason could be determined. A number of unusual observations did indicate however that the self-discharge had occurred very slowly, and was therefore a probable consequence of a soft short through a high resistance path.

This paper will discuss the discharge and dissection processes and the failure analysis findings, along with the unusual attributes of this particular failure.

Introduction
The backup MINUTEMAN lithium power source once consisted of lithium-thionyl chloride cells rated at 10K Ahr at a current density of 1mA/cm² and an open circuit voltage of 3.69V. The cells are arranged in three-cell submodules and a full module contains nine cells with an OCV of 33.1V.

In February 1992 a battery at a Peacekeeper site was found to be bulging. An attempt was made to discharge the battery in place, but when placed on load, this submodule attained only 6.07V, vs. the minimum 10.2V expected. It appeared that at least one cell had experienced self-discharge, so the submodule was frozen in LN₂ and shipped to NAVSURFWARCENDIV Crane for testing and dissection to determine the cause of the self-discharge.

At Crane, electrical tests were performed on the submodule before it was discharged. After discharge, additional electrical tests were performed, cells 2 and 3 were frozen and dissected, while cell 1 was dissected at ambient temperature. Material analyses were performed on several samples obtained from the dissections.

Experimental Results and Discussion

a. Cell Discharge
Each cell of the submodule was wired to a fixed 0.08 ohm resistance for discharge. Initial current readings were: cell 1 - 42A, cell 2 - 41A, and cell 3 - 8A. After 24hr discharge, the cell terminal to cell case voltages were (Table 1):

<table>
<thead>
<tr>
<th>Cell 1</th>
<th>Cell 2</th>
<th>Cell 3</th>
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<tbody>
<tr>
<td>41.3</td>
<td>0.172</td>
<td>3.56</td>
</tr>
<tr>
<td>40.5</td>
<td>0.152</td>
<td>3.59</td>
</tr>
<tr>
<td>3.1V</td>
<td>3.1V</td>
<td>3.1V</td>
</tr>
</tbody>
</table>

The maximum current provided by cell 3 was 10A throughout discharge, and at all times during discharge the cell behaved like a nearly discharged cell.

b. Pre-Dissection Testing
Each cell in the submodule contained a pressure relief valve; when tested, cracking pressures varied from 28.5-34.5psig and seating pressures varied from 26.5-34psig. All three valves performed reasonably close to standard values, and in fact, previous submodule tests had shown wider variances than these.

During dissection, there was no indication of electrolyte leakage from any of the three cells, or of any corrosion on the cells, and no evidence for an electrical path for discharge.

The three cells were x-rayed for anomalies; none were found, although no electrolyte level was observed in cell 3. Each cell was also pressurized with 10psig He for leak tests of the cell terminals and undisturbed positive fill ports. The leak test values for all three cells were consistent with those performed on past cells in prior dissections.

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The three cells were also weighed and compared to three bare discharged cells from another submodule. The weights were essentially identical, indicating that all six cells had been filled with the same amount of electrolyte during manufacture, so the problems with cell 3 of the submodule in question did not result from a low electrolyte fill.

c. Dissection

Cell 3 was frozen in LN₂ prior to dissection to provide an extra safety margin. When its top was removed, there were a large number of yellow-white powdery crystals lying on top of the cell stack. No such crystals had ever been found in previous dissections in the Service Life Analysis (SLA) program. Photographs of the crystals are reproduced in Figures 1 and 2 as they appeared in the cell stack. A small sample of frozen electrolyte was removed from the bottom of the cell can, though very little was available. The outside cell anodes were found to be completely free of lithium, showing that the cell was completely discharged. There were no crystals of any sort on the sides or bottom of the cell stack. All Tefzel® rails were in place and appeared normal, there were no missing plates, and cell can walls showed no corrosion.

After sitting overnight in a dryroom at 2%RH to thaw, the cell stack from Cell 3 appeared as in Figure 3. As the plates of the cell stack were separated, no additional crystalline material was found, but there was a substantial amount of black material on each negative plate (Figure 4). During normal SLA dissections the anode screen is about 99% empty with only small amounts of a black deposit. Overall, no obvious self-discharge mechanism was found during the dissection.

Cell 1 was dissected at ambient temperature. A total of 1.3l of free electrolyte was drained from this cell, which seemed unusually high compared to the average of 0.5l found in previous SLA dissections. However, no other anomalies were found, and the anode screens were essentially free of black material.

Cell 2 was frozen in LN₂ and dissected like Cell 3 had been. When the cell top was removed, no crystals were found. A sample of frozen electrolyte was removed and then the cell stack was thawed in the same manner as for Cell 3. After 24hr in 2%RH, there was a buildup of corrosion just as found on Cell 3, with a white-yellow film on the top and sides of the cell stack. However, the cell stack was not as dry as Cell 3 had been. Also, when the plates were disassembled, they came apart easily and did not have separator paper stuck to the plates. Very little black material was found on the anode screens (Figure 5).

d. Material Analysis

Cathode analysis for Li, Al, and Fe was performed by plasma spectroscopy (ICPS). Levels found were in the same range as observed in previous SLA analyses. Electrolyte samples from all three cells were also analyzed by ICPS for Fe, Mg, Ni, Mo, Mn, and Cr. Results for Fe and Mg are in Table 2; the other four elements had zero concentrations. The Fe and Mg concentrations from Cell 3 were significantly higher than for Cells 1 & 2, but this was probably a concentration effect, given the electrolyte quantity found in Cell 3. The electrolyte samples were also analyzed by IR spectroscopy. The only difference among the spectra was in the HCl band for the Cell 3 sample, which was split with a sharp band in the spectral region attributed to S-H bond vibrations.

The yellow-white crystals found on the top of the Cell 3 stack were sealed in plastic jars in the dry dissection room and transferred to an inert atmosphere chamber. Figure 6 shows a selection of these crystals retained for analysis at Crane. In the inert atmosphere environment, through-crystal and surface electrical conductance measurements were performed. These were all >15-20 megohms, and many were >32 megohms. Crystals were then removed from the inert atmosphere and placed in a drying oven at 30°C and 10³ Torr for 16hr. When conductivity measurements were repeated in the inert atmosphere, all values were >32 megohms, even for surface measurements which were 15-20 megohms for the "damp" crystals.

Samples were prepared in the inert atmosphere for x-ray diffraction (XRD) and emission spectroscopy (ES). The XRD results indicated that the primary constituent of composition was orthorhombic sulfur,

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>IRON - ppm</th>
<th>MAGNESIUM - ppm</th>
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<tbody>
<tr>
<td>Cell 1A</td>
<td>1.572 ± 0.014</td>
<td>0</td>
</tr>
<tr>
<td>Cell 1B</td>
<td>0.881 ± 0.039</td>
<td>0</td>
</tr>
<tr>
<td>Cell 2A</td>
<td>0.981 ± 0.027</td>
<td>0</td>
</tr>
<tr>
<td>Cell 2B</td>
<td>1.062 ± 0.020</td>
<td>0</td>
</tr>
<tr>
<td>Cell 3A</td>
<td>8.079 ± 0.094</td>
<td>0.176 ± 0.015</td>
</tr>
<tr>
<td>Cell 3B</td>
<td>9.058 ± 0.113</td>
<td>0.418 ± 0.018</td>
</tr>
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FIGURE 1
CELL 3 PLATE STACK AFTER REMOVAL FROM CELL CAN

FIGURE 2
CLOSE-UP VIEW OF CELL 3 SULFUR CRYSTALS

FIGURE 3
CELL 3 STACK AFTER SITTING IN DRY ROOM OVERNIGHT

FIGURE 4
CELL 3 ANODE PLATE AND BLACK MATERIAL DISCOVERED DURING DISSECTION

FIGURE 5
CELL 2 ANODE SHOWING SMALL AMOUNT OF BLACK POWDER ON PLATES

FIGURE 6
SULFUR CRYSTALS IN DRY BOX
which is the most stable form thermodynamically. Crystals can be easily grown from solutions and this form of sulfur converts to monoclinic only at temperatures in excess of 96°C. In ES, the samples showed only Li and Al, at moderate levels, and ICPS confirmed this.

A gravimetric analysis was performed on two samples used for ICPS analysis, and the sulfur contents compared well for the two methods, viz. 87.61 and 93.13% by ICPS, 90.73 and 95.78% by gravimetry.

A sample of the black material found on Cell 3 anodes was analyzed by emission spectroscopy (ES). This showed moderate to large levels of Mg, B, Cr, and Ca, and large levels of Li, Al, and Ni. X-ray diffraction (XRD) data showed LiCl in those samples which contained white and grey components, while those which were black contained LiCl, Li₂O₂, and LiAlOCl₂. The black material was also examined under a microscope and a probe was used to separate the black material. When the probe was pushed into this material, a clear film shattered, exposing the black substructure. As soon as it was exposed to air, it turned to a liquid drop. This liquid tested alkaline to pH paper. XRD on the shattered film material showed it to be LiCl. When fragments of the black substructure were added to a drop of water on a spot plate under a microscope, a violent bubbling was observed, the dark material disappeared, and only a floating "scum" of bubbles and separator material remained on the water drop. These observations indicated that the black material was unreacted lithium metal, protected by a film of LiCl.

Conclusions

A lithium-thionyl chloride battery submodule from a Peacekeeper site which was found to be severely bulged was frozen and shipped to NAVSURFWARDCEN-DIV Crane for evaluation. During predissection testing, Cell 3 of the three-cell pack was found to be practically discharged. The electrolyte level in Cell 3 was also found to be very low, indicating self discharge. Polarization tests on Cell 3 during completion of discharge indicated that Cell 3 was in an advanced state of discharge, as well.

During dissection of all three cells, no significant differences in Cell 3 were observed in its physical structure in comparison to the other two cells. However, a substantial mass of yellow-white crystals were found on the top of the cell stack, and the anode plates were covered with a black residue. No yellow-white crystals were found in any other part of the Cell 3 stack.

Since no obvious self-discharge pathway was found during dissection of cell 3, the reasons for the discharge remain unknown. However, the existence of such large orthorhombic sulfur crystals with no entrapped impurities, and only on the top of the cell stack, indicates that a very gradual equilibrium process was responsible for their formation. Sulfur crystals of this size could be formed from a trickle discharge process, with the temperature remaining below 95°C (where monoclinic sulfur would form), and condensation from the vapor state of a sulfur species which was then reduced to free sulfur. Like the discharge process itself, the mechanism of the crystal formation is unknown.

Acknowledgments

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