DESTRUCTIVE PHYSICAL ANALYSIS OF FLIGHT- AND GROUND-TESTED SODIUM-SULFUR CELLS

Margot L. Wasz and Boyd J. Carter
The Aerospace Corporation

Lt. Charles M. Donet
Air Force Research Laboratory

Richard S. Baldwin
NASA Lewis Research Center

Destructive physical analysis (DPA) was used to study the effects of microgravity on the sulfur electrode in sodium-sulfur cells. The cells examined in this work were provided by the Air Force Research Laboratory (AFRL) from their program on sodium-sulfur technology. The Naval Research Laboratory (NRL) provided electrical characterization of the flight-tested and ground-tested cells. The DPA was conducted by The Aerospace Corporation at the Technology Operations Division in El Segundo, California. This study was sponsored by the NASA-Lewis Research Center.

BACKGROUND

- The sodium-sulfur battery experiment (NaSBE) flew last November on Space Shuttle Columbia Mission, STS-87.

- Cells were heated to 350°C, cycled to verify capacity and simulate GEO and LEO profiles, then cooled down to ambient temperature from various states of charge (SOC)

- Ground tests duplicating the flight experiment were performed on four other sodium-sulfur cells from the same production lot last May

Last November, four sodium-sulfur cells were flown as a flight experiment on the Space Shuttle Columbia Mission, STS-87. This experiment was the third phase of an AFRL program (NaSTEC) to qualify sodium-sulfur cells for use in space. Earlier phases demonstrated cycle life and safe response under abuse conditions in ground tests.

The flight experiment, designed and executed by NRL, began by heating the cells to 350°C at a rate of about 18°C/hour. Two capacity verification cycles were performed, then two cycles at a simulated geosynchronus orbit (GEO) operation, and finally, 16 cycles at a simulated low earth orbit (LEO) operation. During the final discharge, individual cells were taken off line at different times, trapping them at nominal states of charge (SOC) of 100%, 80%, 60%, and 40%. Afterwards, the cells were cooled down to ambient temperature at a rate of about 14°C/hour. The same duty cycles were duplicated on four other cells on the ground to provide a direct comparison for better understanding the effects of microgravity on cell performance.
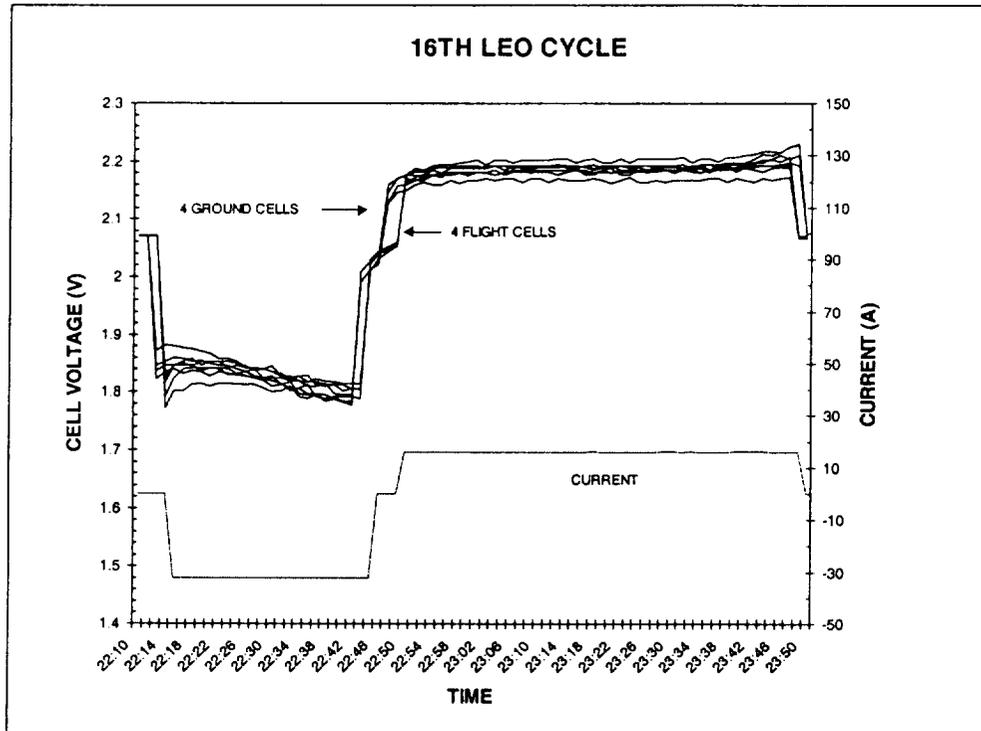
16TH LEO CYCLE

The above plot is an overlay of cell voltages from both the flight and ground-tested cells during the 16th LEO cycle. The simulated LEO orbit consisted of a thirty minute discharge at 32A (C/1.25) followed by a sixty minute charge at 16A (C/2.5). The total depth of discharge per cycle was about 40%. The cells were also maintained at open circuit for several minutes between charge and discharge and between each cycle.

Comparisons of the electrical performance from the tests show good agreement. For the cycle shown above, cell temperatures are lower in the flight cells (329-347°C) than in the ground cells (343-355°C).

SCHEMATIC OF SODIUM-SULFUR CELL
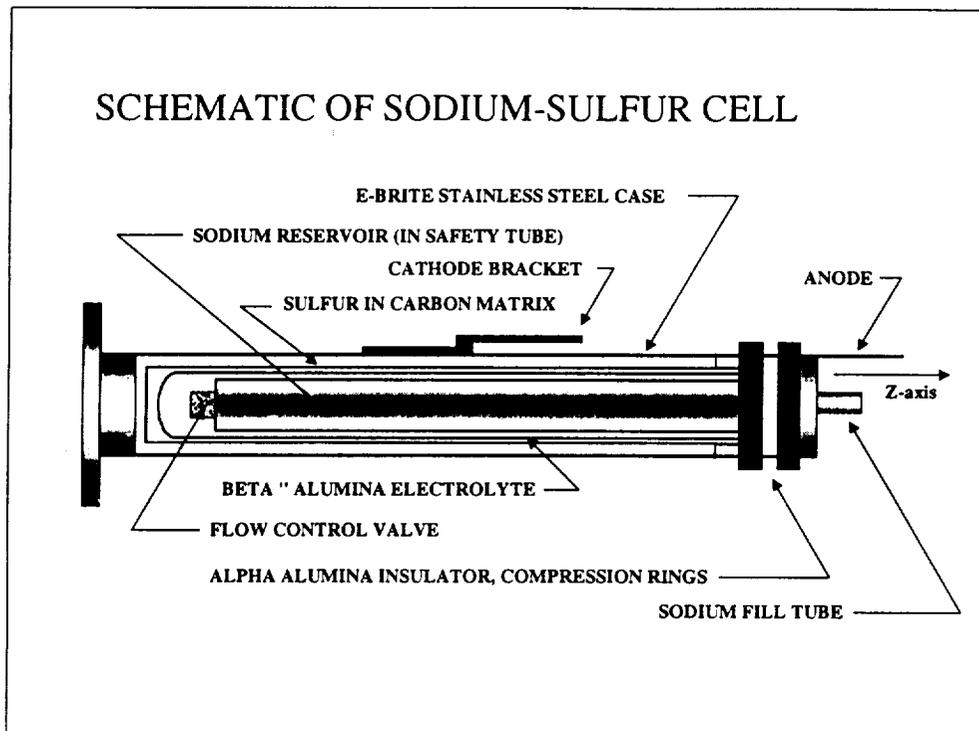
Twenty, 40 ampere-hour, sodium-sulfur cells were built by Eagle-Picher (EP) for the program in June, 1996. Each cell had a stainless steel safety tube which contained the sodium. A flow control valve made of porous nickel frit placed at the bottom of the safety tube moderated the flow of sodium to the inner diameter of the β" alumina electrolyte. The sulfur active material surrounded the ceramic electrolyte and was itself embedded in a carbon fiber matrix for conductivity. The cell case, whose inside surface was plated with chromium, was in electrical contact with the sulfur. The cathode terminal was welded on the outside of the case. The anode terminal, which passed through the top of the cell, was in electrical contact with the safety tube. The cathode and the anode were electrically isolated by an α-alumina insulator which was diffusion-bonded to an aluminum piece which was, in turn, diffusion -bonded to the stainless steel. Two compression rings protected the diffusion-bonded areas against external stresses. The length of each cell was about 9.44 inches. The average cell weight, including a flange piece welded to the bottom of the cell for connecting to an external support, was 580 grams.

During acceptance testing and in the ground experiment, cells were placed in an "anodes up" orientation.

TEST PLAN

- The program goals were to determine the effects of microgravity and to look for any signs of wear-out modes that could shorten life

- Preliminary work utilized visual inspection, ac impedance testing, and radiographic analysis to look for signs of electrolyte failure and to examine the structure of the sulfur electrode

- The core DPA effort focused on the sulfur electrode including composition analysis and elemental mapping

- Additional analysis examined the case and seals when signs of corrosion were found

The purpose of this study was to search for differences between the flight and ground-tested cells that could affect electrical performance or reveal any unanticipated response to the microgravity environment. In particular, the sulfur electrode would be analyzed to look for the effect of microgravity on mass transport and interfacial reactions at the β'' alumina interface. Also, signs of electrolyte cracking and any wear-out mode such as corrosion that would threaten cycle life would be investigated.

Post flight analysis began with nondestructive evaluation by visual and radiographic inspection of all cells. Based on these results, DPA activities were selected with primary focus on the characterization of the sulfur electrode to determine the composition of phases present and their distribution throughout the cell.

TEST METHODS

- Fein Focus Radiography
- Optical Microscopy
- X-ray Diffraction (XRD)
- Raman Spectroscopy
- Scanning Electron Microscopy
- Energy Dispersive X-ray Analysis (EDX)

NOTE: Because of the reactivity of the active material to air, DPA was performed in a dry box, and all of the above methods were done using environmental cells

A variety of analytical techniques were used to examine material from the cells in this program. Nondestructive analysis utilized impedance measurements, stereo and x-ray microscopes to search for signs of leakage, thermal anomalies ("hot spots"), and electrolyte cracking, as well as to begin examination of the cathode material.

Sodium and sulfur are reactive in air, therefore all DPA activities were performed in an inert environment. Cell were dissected in an argon-filled glove box monitored with a residual gas analyzer and an oxygen sensor. Water concentration was typically less than 1 ppm. Environmental cells held powder samples permitting the collection of x-ray diffraction (XRD) patterns without exposure to air. Similarly, a transfer container was used to carry samples from the glove box to the JEOL JSM-840 scanning electron microscope (SEM) without exposure to air. Optical images and Raman spectra were also collected through the glass lid of an environmental cell. Of the material analyzed, only the cell cases were exposed to air prior to imaging and SEM/EDX.

RADIOGRAPHY

- Fein Focus and still x-ray radiography were used to look for signs of cracking in the electrolyte and to examine the structure of the sulfur electrode

- Results
  - No signs of electrolyte cracking
  - More change along the z-axis in the ground-tested cell at 100% SOC
  - Low density region identified under the sodium flow control valve

Real time x-ray radiography was performed on all four flight and ground cells using a Fein Focus model 160.52 x-ray camera. Seals at the top of the cell were examined closely for signs of leakage. Next, the sulfur-electrolyte interface was examined while slowly rotating the cell, beginning at the top, to look for signs of cracking. None were found.

X-ray radiography generates images where light and dark contrast correspond to relative changes in the type and density of material present. Contrary to expectation, the bottom of the sulfur region of ground-tested cell at 100% SOC was lighter than the top suggesting voids or low density material at the bottom of the cell. The flight-tested cell at 100% SOC was more homogeneous, and showed signs of a higher density phase along its entire length. The structure of the sulfur electrode at 40% SOC was about the same between flight and ground cells with signs of mixed low and high density material along the length of the cell. In all eight cells, a round light area directly under the flow control valve was observed.

The largest differences between flight and ground-tested cells were found for the nominal 100% SOC condition. Therefore, these cells were selected for DPA. Flight and ground cells at 40% SOC were also selected for DPA to bracket the range of possible effects.

MACROSCOPIC OBSERVATIONS
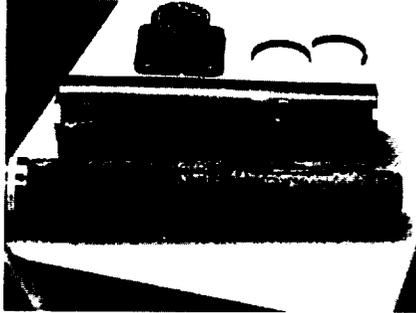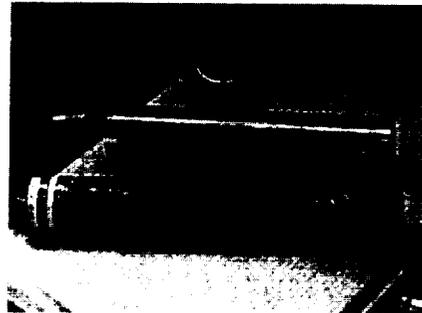
FLIGHT CELL #1   GROUND CELL #1

- Flight Cell - Voids concentrated at top
- Ground Cell - Voids concentrated at bottom

The above images of the sulfur electrode were taken through the window of the glove box within minutes of removal of the cell case during the DPA process and show the flight and ground-tested cells at 100% SOC. The top of the flight cell was composed of mostly voids in the carbon matrix. A small amount of sulfur was found in the top area at the surface of the electrolyte. This trend was reversed in the ground cell where the low density, low sulfur, region was concentrated at the bottom of the cell. This finding was unexpected because two cells from the same lot which had passed acceptance testing in the same "anodes up" orientation had large voids concentrated at the top, similar to the flight cell. Therefore, it is likely that some other factor than gravity is responsible for where the voids are concentrated.

The flat, gray material located on the surface of the active material on some of the areas is $CrNaS_2$ that has separated from the case.

MACROSCOPIC OBSERVATIONS
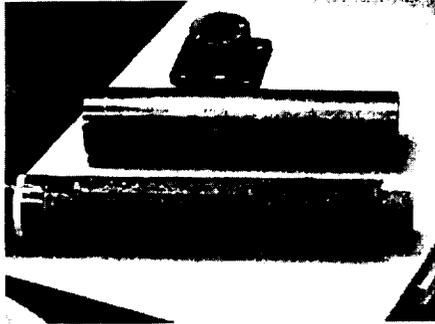
FLIGHT CELL #4   GROUND CELL #4

- Flight Cell - Voids concentrated along edges of carbon mats
- Ground Cell - Voids concentrated at bottom

The images above show the flight and ground cells at the nominal 40% SOC condition. Voids, along with orange and rich yellow regions are evident. Voids in the flight cell concentrated along the length of the cell at the interface between carbon mats. This trend was less evident in the ground cell where voids also concentrated at the bottom of the cell. A large amount of the orange phase was found on top of the carbon mat at the top of the ground cell.

Again, as seen in the other two cells at 100% SOC, $CrNaS_2$ adhered to some parts of the the sulfur electrode in both cells.

MACROSCOPIC OBSERVATIONS

CELLS AT 100% SOC (FLIGHT CELL ON TOP)

- Orange phase found at the sulfur/electrolyte interface on both cells (Na_2S_5)

These images show the interface of the sulfur electrode and the electrolyte after the sulfur matrix was peeled away on cells at 100% SOC. Removal of the active material was difficult in both cells. The flight cell (top) showed an orange phase at the interface along 70% of its length. At the top, the interface was light yellow, characteristic of sulfur. In the ground cell (bottom), the orange phase was found along the entire length of the cell. In both cells, the orange phase appeared to be situated only at the electrolyte interface, and the region on the outer diameter of the active material appeared only gray or yellow.

MACROSCOPIC OBSERVATIONS
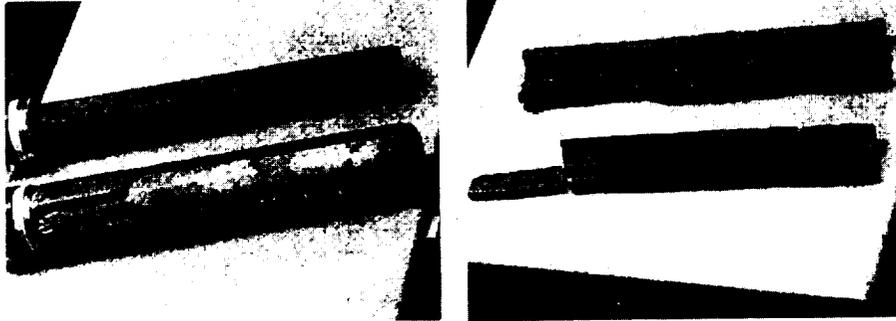
CELLS AT 40% SOC (FLIGHT CELL ON TOP)

- Flight cell - Uniformly orange throughout cathode material (Na_2S_5)
- Ground cell - Orange and yellow (Na_2S_5 and Na_2S_4)

The above images show the interface of the sulfur electrode and the electrolyte after the sulfur matrix was peeled away on cells at 40% SOC. Removal of the active material was much easier, particularly in the flight cell (top). The interface on the flight cell was uniformly orange along its entire length. However, the interface on the ground cells (bottom) showed both orange and yellow regions. The white patches on the electrolyte correspond with the orange and region in the sulfur electrode. Note that, unlike cells at 100% SOC, the colored regions found at the electrolyte interface extend to the outer diameter of the sulfur electrode.

MACROSCOPIC OBSERVATIONS
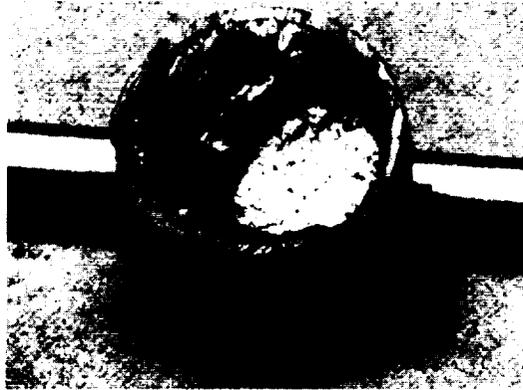
CROSS SECTION OF BOTTOM OF FLIGHT CELL #4

- Large void found directly under the flow control valve inside the electrolyte

The bottom of the ceramic electrolyte on flight cell #4 (40% SOC) was removed using a diamond wafering saw. The low density region under the flow control valve identified with the x-ray camera was found to be a large void. Although this feature was found on all flight and ground cells, it could represent non-optimal performance for the cell design.

XRD RESULTS

- Three samples per cell
- Flight and ground cells at 100% SOC indexed to sulfur, although other minor peaks were recorded
- Both cells at 40% SOC contained unidentifiable peaks which relaxed to either Na_2S_5 or Na_2S_4
  - Flight cells showed mostly Na_2S_5 (relaxed)
  - Ground cells showed Na_2S_5 and Na_2S_4 (relaxed)
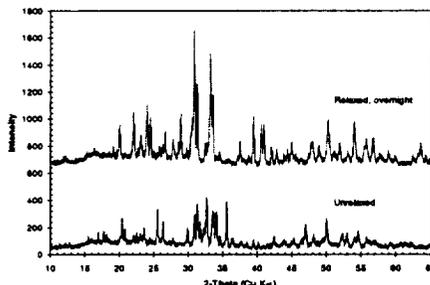
Relaxation in a powder sample from the bottom of ground cell #4. Peaks in the upper spectra index to Na_2S_5.

Three powder diffraction samples were prepared in the glove box from the cathode material located at 20%, 50% and 80% along the axis of the cell. Care was taken to insure that all of the active material from the inner diameter to the outer diameter would be present. The sample was then ground to a fine powder with a mortar and pestle and placed in an environmental XRD sample holder. XRD spectra were collected using a Philips diffractometer and Cu K_α generator operating at 45kV/30mA. A monochromator was used to suppress Cu K_β peaks.

XRD spectra for both flight and ground cells at 100% SOC indexed to sulfur for all three regions. Minor peaks belonging to a metastable sodium polysulfide phase were also found in all samples. These peaks were strongest in the middle sample of the flight cell and the bottom sample of the ground cell.

XRD spectra from the cells at 40% SOC contained metastable peaks which relaxed to Na_2S_5 and Na_2S_4 upon repeated exposure to the x-rays. Relaxation only occurred with exposure to the x-ray radiation. The flight cells relaxed to mostly Na_2S_5 with little change along the length of the cell, whereas the ground cells relaxed to both Na_2S_5 and Na_2S_4 phases. A higher concentration of Na_2S_4 was found at the middle and bottom of the ground cell.

RAMAN SPECTROSCOPY

- Orange and yellow regions seen during DPA on ground cell #4 identified
  - Deep yellow region is mostly Na_2S_4
  - Orange region is mostly different phases of Na_2S_5
  - Crystallites of both Na_2S_5 and Na_2S_4 could be found in either region
- Other findings from Raman analysis
  - Three phases of Na_2S_5 found, β- and γ-phases seemed to be less stable than the α-phase
  - No free sulfur in samples from ground cell #4
  - Possible preferred orientation of phases

Quantification of the sodium and sulfur present in the sulfur electrode by SEM/EDX was unable to identify the source of the yellow and orange phases seen macroscopically. Therefore, Raman spectroscopy was used to analyze the material.

Reference Raman spectra for Na_2S_2, Na_2S_3, Na_2S_4, α-Na_2S_5, β-Na_2S_5, γ-Na_2S_5 and sulfur were found from a review of the published literature. A sample containing both the orange and yellow regions from the ground cell left at 40% SOC was examined. Spectra from all three phases of Na_2S_5 were found in the orange grains in the orange region. Yellow grains in the orange region were Na_2S_4. Likewise, orange grains in the yellow region were found to be Na_2S_5 and the yellow grains Na_2S_4. The β and γ-phases found, however, seemed to be less stable than the α-phase of Na_2S_5. Also, the peak intensities recorded suggest possible preferred crystal orientation for the Na_2S_5 phases.

SEM/EDX - SULFUR ELECTRODE

- Three samples from each cell examined
- Na, S, Cr, Al, C and O mapped from the inner to the outer diameter of the active material
- Quantification - the table below shows the ratio of atomic % Na to atomic %S found in the sodium-rich phases of the sulfur electrode

Flight #1	Region	Ground #1
0.086	top	0.072
0.123	middle	0.146
0.117	bottom	0.092
Flight #4	**Region**	**Ground #4**
0.142	top	0.140
0.117	middle	0.155
0.114	bottom	0.206

Three samples from each cell were examined by SEM/EDX. The samples were cut from cathode material located at 20%, 50%, and 80% along the cell axis. Care was taken to insure that material from both the electrolyte interface and the case interface was included in each sample. After cutting, the samples were smoothed with fine grit sandpaper to remove contamination and to create a flat surface for analysis. Debris from the sanding process was removed with a brush. Samples were transferred from the glovebox to the SEM in an airtight holder preventing exposure to air. During the SEM/EDX analysis, regions were imaged and mapped for the x-ray spectra of Na, S, Cr, Al, C and O from the inner to outer diameter. When a sodium-rich phase was found, a ZAF quantification routine was used to calculate the atomic percents of sodium to sulfur present.

The cells at the nominal 100% SOC showed separate phases of sulfur and sodium polysulfide. The distribution of the phases was similar, and the concentration of sodium in each cell was highest at the middle of the cell. The sodium distribution of the cells at 40% SOC appeared homogeneous and little difference was found between the two cells. Overall, the sodium concentration was higher in the ground cell, particularly in the bottom sample. The following two pages show the sodium maps of the three samples for each cell. The white areas evident in the cells at 40% SOC are voids in the material.

EDX MAPPING OF FLIGHT (LEFT) AND GROUND (RIGHT) CELLS AT 100% SOC (NOMINAL)
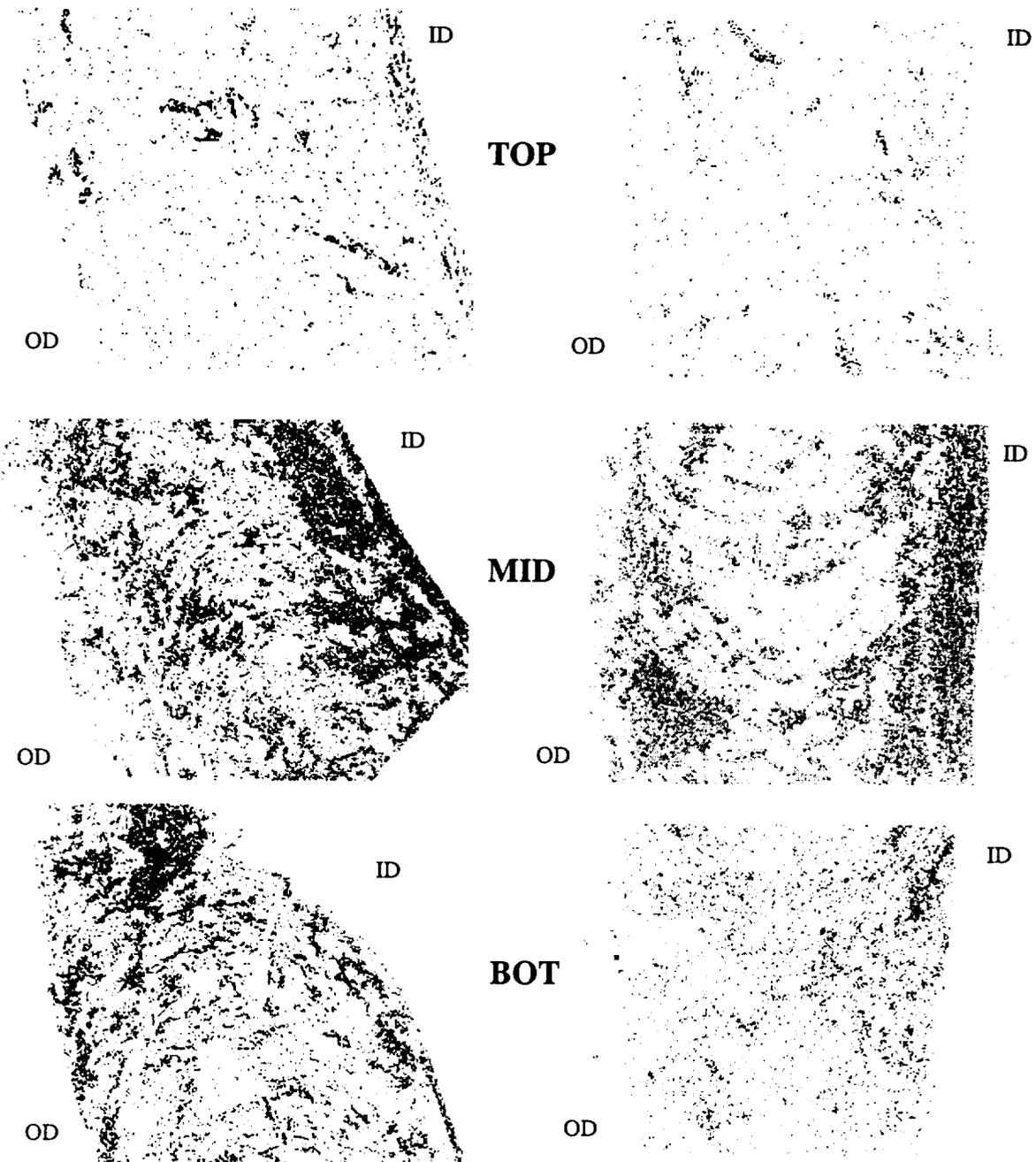
Bands of sodium-rich phases were found in the middle samples of each cell

EDX MAPPING OF FLIGHT (LEFT) AND GROUND (RIGHT) CELLS AT 40% SOC (NOMINAL)
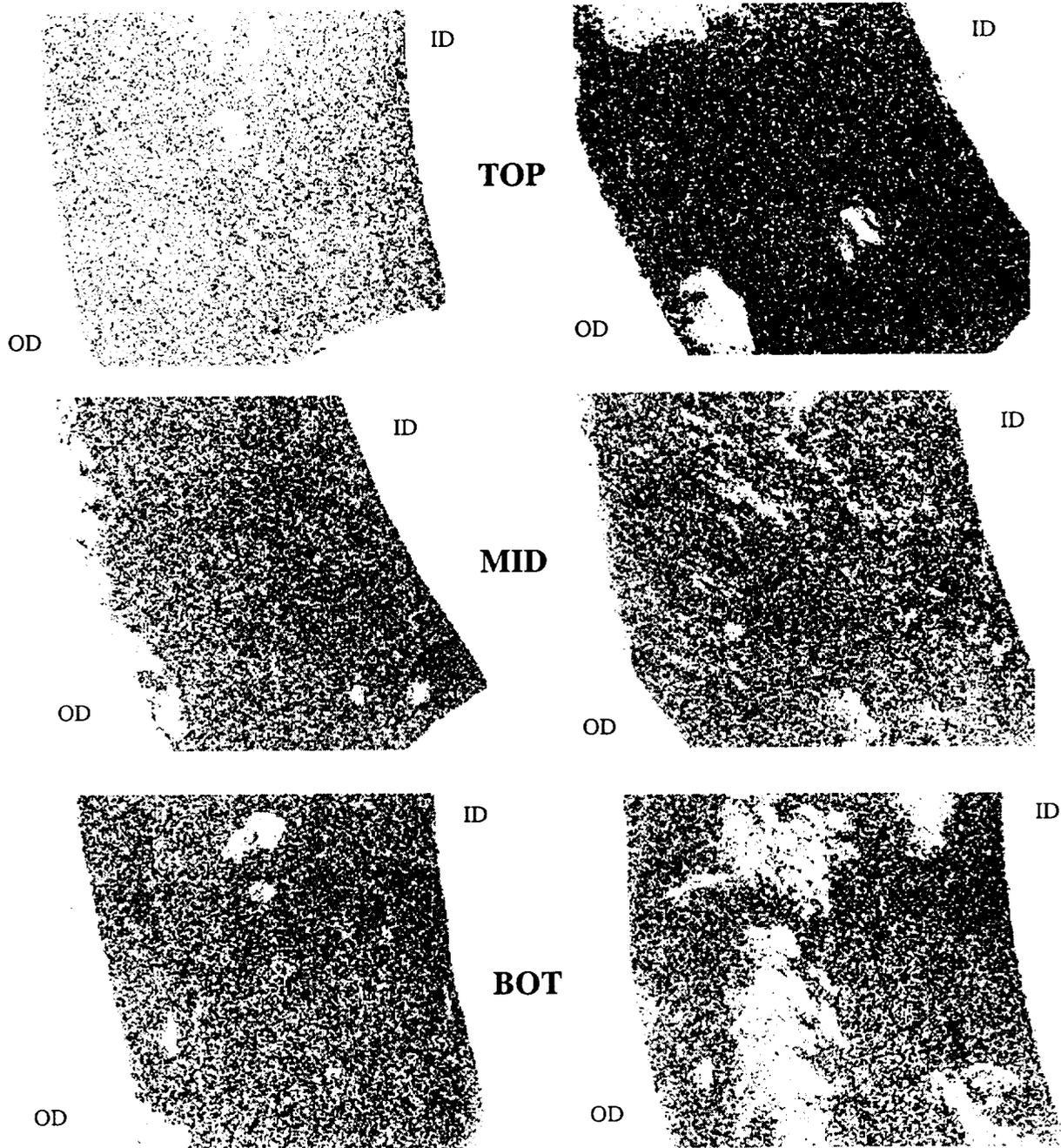
Sodium concentration is homogeneous along each cell (the white areas in the samples are voids)

CELL CASE ANALYSIS
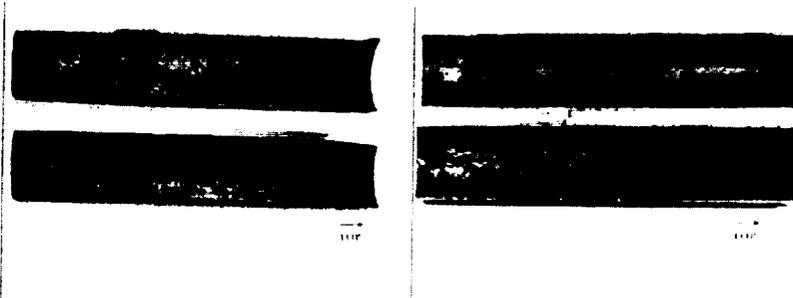
- The inside surface of the case from cells at 100% SOC (left) differed from cases from cells at 40% SOC (right)
- Both flight and ground cell cases looked about the same

Any corrosion of the cell case would have important implications for long duration use of the cell design. Therefore, the condition of the interior of the cell cases was examined. The general appearance of the cell cases varied with SOC, however, both flight and ground-tested cells appeared the same at the same SOC. The above images show the appearance of the inside of the cell cases for cells at 100% SOC (left) and 40% SOC (right). Cells at 100% SOC contained metallic bright areas and areas of gray/green black. The cells at 40% SOC also had some bright, metallic regions as well red and dark shiny black deposits.

The cell cases were cleaned in acetone and dried in air prior to imaging.

SEM/EDX - CELL CASE, INNER DIAMETER

- EDX of the different phases identified the following
  - metallic = Cr
  - gray/green phase, $CrNaS_2$
  - shiny black phase, $(Cr,Na)_2S_2$
  - red phase, 1.0Cr:2.3Na:2.8S
- No iron found in the EDX spectra
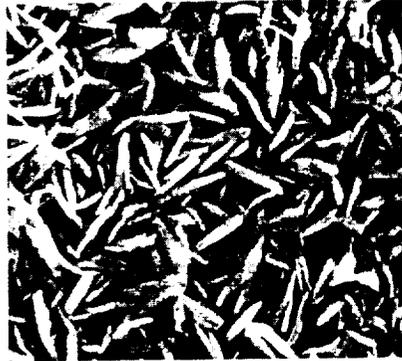
$CrNaS_2$ crystals found on case

The four different phases found on the cell cases were analyzed by SEM/EDX. The shiny metallic phase was chromium, and the other phases were all combinations of Cr, Na, and S. Quantification of the gray/green phase indicated that it was stoichiometric $CrNaS_2$.

No iron was found in any of the EDX spectra and no sign of corrosion past the chromium layer was found in this portion of the analysis.

SEM/EDX - CELL CASE, CROSS-SECTION

Pitting and cracks found on the inner diameter of the cell case. a) $CrNaS_2$ layer, b) chromium oxide (black spots), and c) chromium/stainless steel interface

The cell case of the ground cell left at 40% SOC was sectioned with a diamond wafering saw, mounted in metallographic epoxy resin, and polished.

Optical and SEM imaging found cracks in the chromium layer and signs of pitting attack. The above images show examples of these features, including cracks which appear to initiate from the $CrNaS_2$ layer. The region above the $CrNaS_2$ layer is the epoxy resin which has also reacted with the $CrNaS_2$. The darks spots at the chromium-$CrNaS_2$ interface on the image at the left are chromium oxide.

SUMMARY OF OBSERVATIONS

- Distribution of voids in the sulfur electrode was different between flight and ground cells at 100% and 40% SOC, different sodium polysulfide phases were found in flight and ground cells at 40% SOC
- No evidence for electrolyte cracking or leakage at seals, possible evidence for the non-passive formation of $CrNaS_2$

CONCLUSIONS

- Cell design appears to have worked well in microgravity
- The chemical composition of the sulfur electrodes in the flight cells were at least as uniform, if not more so, than the sulfur electrodes in the ground cells
- The ground test data base should provide a conservative life estimate for on-orbit life and performance

To summarize, some features were found in the sulfur electrode which could be the result of differing gravity environments. The distribution of voids was different between cells at both 100% and 40% SOC. Also, the sodium polysulfide phases found at 40% SOC were not the same between the flight and ground cells. No signs of sulfur leakage were found on any of the cells, nor were there any signs of cracking of the electrolyte in either the electrical or radiographic data. However, analysis of the cell case suggest that the $CrNaS_2$ compounds formed on the chromium liner are not passive. This could have implications for long term use of this design feature.

In conclusion, the cell design as a whole worked well in the microgravity environment. The chemical composition of the sulfur electrodes in the flight cells were at least as uniform, if not more so, than the sulfur electrodes in the ground cells. This finding implies that the ground test data base should provide a conservative life estimate for on-orbit life and performance for this chemistry.

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