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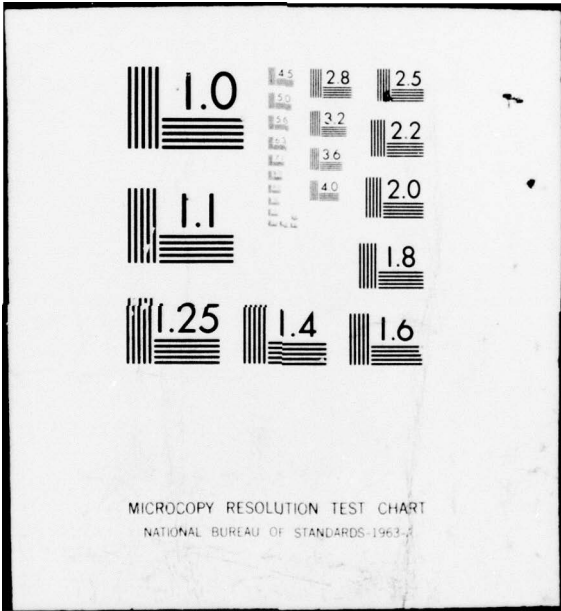
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Fuel Cell Session

METHANOL-AIR BATTERY

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Introduction

Efforts are continuing to develop a practical low power direct methanol-air battery for use in military equipment. This work is responsive to the requirement for light weight, low power, power sources for use in transistorized communication equipments that are or will be used by the Armed Forces. The methanol-air battery is especially attractive since methanol is an inexpensive, readily available fuel that presents no handling or transportation problems.

Experimental methanol-air cells have demonstrated long

term unattended operation with fuel utilization efficiencies as high as 82%. Single cells have operated for more than 8,000 hours, demonstrating the long life performance of cell electrode components. In addition, single cells exhibited the capability of operating at extremely cold temperatures. Experimental single cells, with methyl formate added to the electrolyte, have operated at temperatures down to -40°F with approximately a 30% drop in voltage during a pulse load of 2 A, superimposed on the steady state load of 40 mA. The long operating life of electrode components, plus the low

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temperature operating capability, make the methanol-air battery ideally suited for military use in remote areas where long unattended service is required. Nine-cell stacks have been evaluated and found capable of delivering 15 watts pulse power, under a practical test load cycle, with 40 milliwatts as the steady state output.

Discussion

Cell Design and Components

Single cell studies were conducted on cells with dual anodes and cathodes. Figure 1 shows a diagram of the cell design. An asbestos (fuel cell grade) separator is sandwiched between the cathode and anode to make an electrode pack.

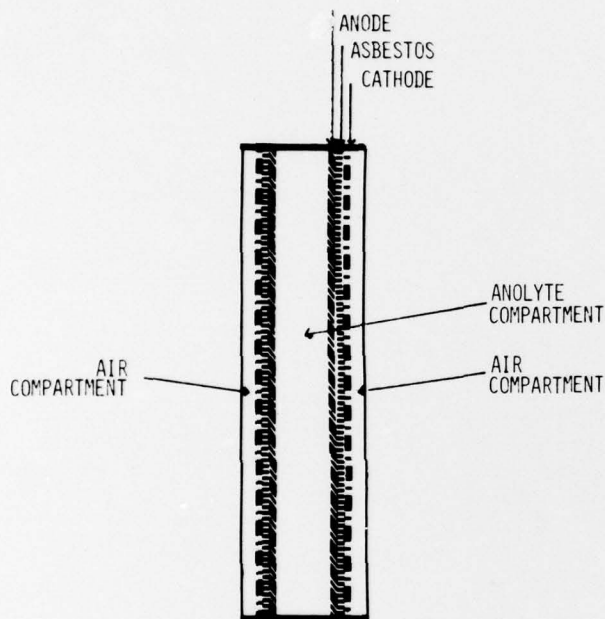


Figure 1. Single Cell With Dual Anodes and Cathodes.

One electrode pack is cemented to each side of an anolyte frame to form a complete cell. The cell's exterior dimensions are 3.5" x 9" x 0.375" with an active electrode area of 3.25" x 8.75". The air compartment serving the cathode is 1/8" in width with a 0.040" inlet air port in the top center edge of each air chamber. The small air ports are needed to minimize methanol losses during extended periods of operation. The asbestos separator serves a three-fold purpose: (1) electrical insulator between cathode and anode, (2) diffusion barrier to minimize methanol oxidation at the cathode, and (3) diffusion barrier to minimize methanol evaporation losses to the atmosphere.

All test cells were fabricated with lucite frame holders for the electrolyte/anolyte reservoir. A major problem was encountered in finding a good cement that would permanently bond the cell electrode components to the lucite frame holder. Lucite cement and several epoxy cements were evaluated for bonding adequacy and the best of these was used in cell construction. However, many of the test cells developed leaks at

the cement joints after 1,000 hours of operation, forcing termination of life test.

Electrode Fabrication

The anodes used during this investigation were of the Pd-Pt, teflon bonded type and the cathodes were of the Ag-Hg air type. Anodes were fabricated by mixing palladium-platinum blacks in a 75%:25% ratio with a teflon solution to form a paste. The paste mix was then rolled onto an expanded silver screen and air dried. The cathode was prepared by precipitating a silver nitrate/mercuric nitrate salt solution with a concentrated solution of potassium hydroxide. The oxide precipitate formed was then washed with water and air dried. The oxide powder was mixed with a teflon solution to form a paste that was rolled onto an expanded silver screen. The screen containing the paste mix was dried in an oven at 500°F until the Ag₂O was reduced to metallic silver. Finally, a thin 7 mil thick teflon film was pressed onto the air breathing side of the electrode at 60,000 psi.

Single cells were evaluated under practical load duty cycles to a cutoff voltage of 0.6 V on the high pulse. Figure 2 shows

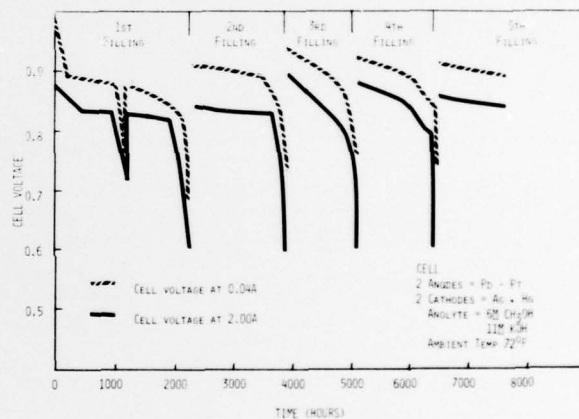


Figure 2. Current-Voltage and Life Data of a Single Cell.

the current-voltage and life data of a cell operating on a continuous discharge duty cycle of .040 A for 15 minutes and 2.0 A for 1 second. This load duty cycle was set for the single cell in order to simulate operation in a 9 cell battery that was required to deliver 0.24 watts stand-by and 12.24 watts pulse for 110 cycles per day. The cell was activated with 120 ml of anolyte containing 6 M CH₃OH in 11 M KOH and operated for 1200 hours before the voltage dropped to 0.7 volts on the high pulse load. This voltage drop was attributed to air starved cathodes. An additional 0.040" air port was opened in the chamber to permit more air flow. When testing was resumed, the cell operated for a total of 2,232 hours before voltage decreased to a cutoff voltage of 0.6 V. At the end of test, the anolyte was drained and analyzed for methanol content. The quantity of methanol present was too low to be detected. It was assumed that all methanol had been consumed through oxidation to CO₂ with some losses due to evaporation at the cathode. Analysis of anolyte showed carbonate concentration of 9.72 N and OH⁻ of 1.78 N. Calculations were

made to determine fuel utilization efficiency, assuming complete oxidation of methanol to CO_2 with a 6 electron change. A 82% fuel utilization efficiency was obtained based on the following calculation:

$$\%F = \frac{\text{coulombs obtained}}{(\text{total moles consumed}) \cdot nF} = \frac{341875.4}{(.72) \cdot 6 \cdot 96,500} = 0.82$$

After 2,232 hours of operation to the cutoff voltage of 0.6 V, the cell was refilled with 96 ml of anolyte of the same concentration and life testing resumed to determine operating life of components. Cell voltage was comparable to the first test. Open circuit voltage was 1.06 V. The cell operated for 1,560 hours on the second filling before voltage went below cutoff voltage. A methanol determination indicated that fuel had been exhausted. The cell operated for a total of more than 8,000 hours on three subsequent refills before serious external leakage problems developed which forced termination of life testing.

Single cell data demonstrated the long life capability of electrode materials and the capability of achieving high fuel utilization efficiencies. However, the energy density (Wh/lb) was low. This was attributed to the small amount of fuel stored in the cell as compared to the overall weight of the complete cell. The 120 ml of anolyte in the above cell contained 23.06 g of fuel. The electrolyte weighed 136.5 g, and the electrodes and frames weighed 218 g. The Wh/lb based on 2,232 hours was 111.96 Wh/lb.

A nine-cell battery, containing single cells of the dual anode-dual cathode design, was assembled for test and evaluation. The anolyte volume of the single cell was increased from 9 in³ to 18.05 in³ to extend operating life and increase energy density of the overall battery system. Figure 3 shows a

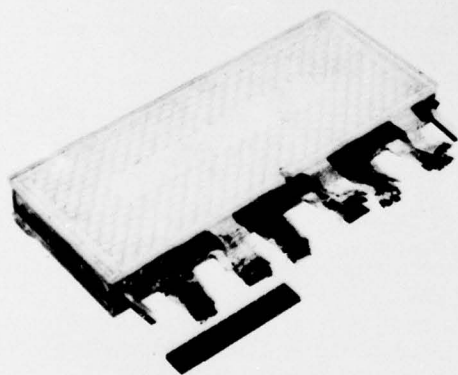


Figure 3. Experimental Single Cell.

complete single cell. In order to preclude internal leakage between cells, each cell was assembled individually with its own air chamber. Consequently, if one cell developed an electrolyte leak, the performance of the adjacent cells would not be affected as was the case with previous batteries tested. Figure 4 shows the complete methanol-air battery. Physical

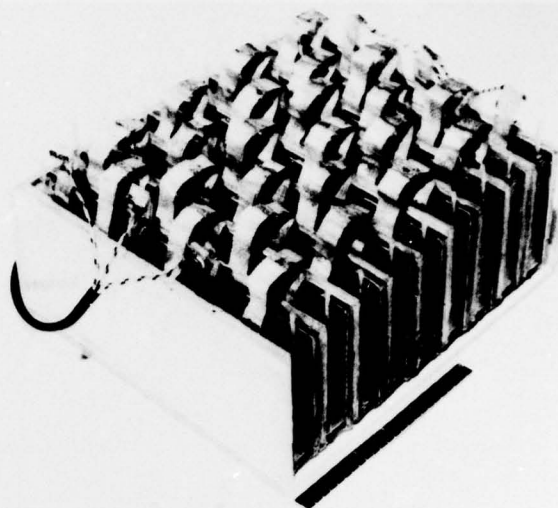


Figure 4. Methanol-Air Battery (Experimental).

and electrical characteristics are shown in Table 1.

The battery was activated with 2670 ml of 8 M CH_3OH in 13 M KOH. Each cell contained an average of 296 ml of

TABLE I
PHYSICAL AND ELECTRICAL CHARACTERISTICS OF
9 CELL METHANOL-AIR BATTERY STACKS

1. EXTERIOR DIMENSIONS	4" X 8" X 10"
2. BATTERY WEIGHT (DRY)	4.7 LBS
3. ANOLYTE VOLUME (8M CH_3OH IN 13M KOH)	2670 ML
4. BATTERY WEIGHT (WET)	12.95 LBS
5. INITIAL OPEN CIRCUIT VOLTAGE	9.63 V
6. INITIAL CLOSED CIRCUIT VOLTAGES	
A. WITH 0.04 A LOAD	9.40 V
B. WITH 2.00 A LOAD	8.50 V
7. STEADY-STATE POWER	0.40 WATTS
8. PULSE POWER	15 WATTS
9. PULSE DURATION	1 SEC
10. PULSE FREQUENCY	1 EVERY 15 MIN
11. SERVICE LIFE (THEORETICAL)	7159 HRS
12. ENERGY DENSITY	232 Wh/Lb

anolyte. Calculations, made to determine theoretical operating life and energy density based on the 2 A/1 second and 40 mA/13 minute load cycle, show 7159 hours of operation and 232 Wh/lb, respectively. If the battery operated at 83% efficiency, the calculated energy density would be 192.6 Wh/lb.

Open circuit voltage of the battery was 9.63 V at the beginning of test. Current-voltage data are shown in Figure 5. The battery stack operated under a load cycle of 2 A/1 second and 50 mA/10 minutes for 500 hours before problems began. At this time, cell #9 had a reverse reading under the 2 amp load and had to be removed from the stack. Cell failure was attributed to the cathodes and half-cell measure-

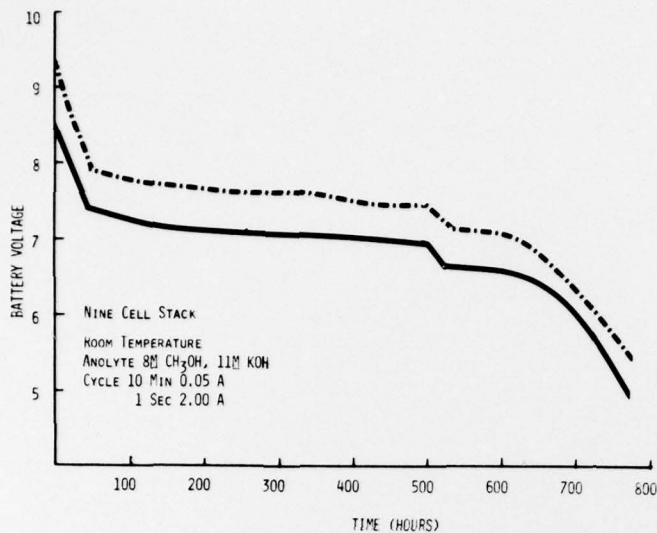


Figure 5. Current-Voltage and Life Data of a Battery Stack.

ments showed very high polarization. The test was continued for an additional 250 hours before voltage dropped for a second time. Cell #8 was removed due to low voltage. By this time the battery had developed serious leaks in all of the cells.

Low Temperature Study

Low temperature studies were conducted using 3 M HCOOCH_3 (methyl formate) in 5.5 M KOH as the anolyte. Methyl formate was used as fuel since previous studies had shown that the addition of potassium formate to the methanol cell improved the performance at low temperatures. A 5.5 M KOH electrolyte solution was used to ensure that the electrolyte would remain in the liquid state at -40°F to permit maximum ion transport. Low temperature testing was conducted by first soaking the cell for 24 hours on open circuit, at a given temperature, and then operating cell on a continuous discharge load cycle of 13 minutes at 40 mA and 1 second at 2.0 A for at least 24 hours at each temperature level. Since the goal was to achieve satisfactory cell performance at -40°F , the test was started at -40°F and increased sequentially in 10 degree increments. The open circuit voltage of the cell at the end of the 24 hour soak at -40°F was 0.95 V. Cell voltage after 24 hours on discharge cycle was 0.82 V at 40 mA load and 0.62 V at 2.0 A load, showing a 34% decrease in voltage from room temperature performance at the high load. This performance was maintained for 72 hours which demonstrated the capability of the cell to operate in a -40°F environment. Low temperature performance data are shown in Figure 6.

After test at -40°F , the cell was soaked for 24 hours and

operated for at least 24 hours at temperature steps in the -30°F to $+72^\circ\text{F}$ range. Figure 6 shows increase in cell voltage with increase in temperature. During low temperature operation, the cathode was found to be the most limiting of the two electrodes, as shown from performance curves in Figure 6. When cell was operating at -40°F , the cathode showed an increase in polarization of 0.275 V while the

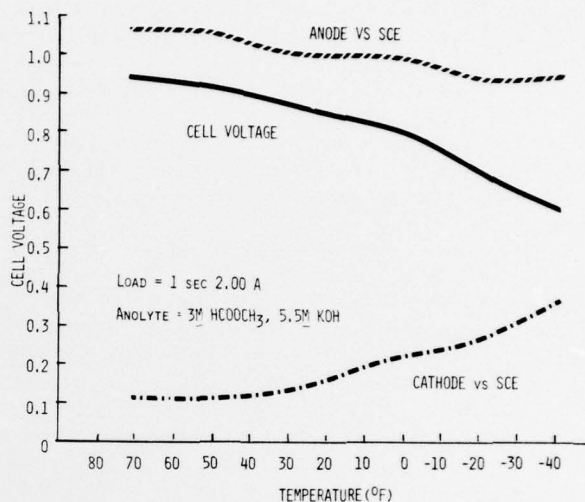


Figure 6. Low Temperature Performance Data of a Single Cell.

anode showed an increase of only 0.115 V. when compared to room temperature voltages. Visual observation of anolyte solution at -40°F showed it to be in a liquid state, and free of ice crystals.

Conclusions

These investigations have demonstrated the feasibility of long-term operation of methanol-air battery components through life testing of more than 8000 hours. Fuel utilization efficiency, using bulk or single charge fuel/electrolyte storage techniques, has increased to 82% with changes in cell design and fabrication techniques. Each attempt to get long-term operation from multicell stacks and batteries resulted in short operational life caused by mechanical leakage, forcing termination of test. A continued investigation will be directed toward improving fabrication techniques, selecting better bonding cements, or alternatively, changing cell frame materials. Studies showed that these methanol-air batteries can operate at extremely low temperatures with anolyte solutions containing 3 M HCOOCH_3 (methyl formate) in 5.5 M KOH.

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