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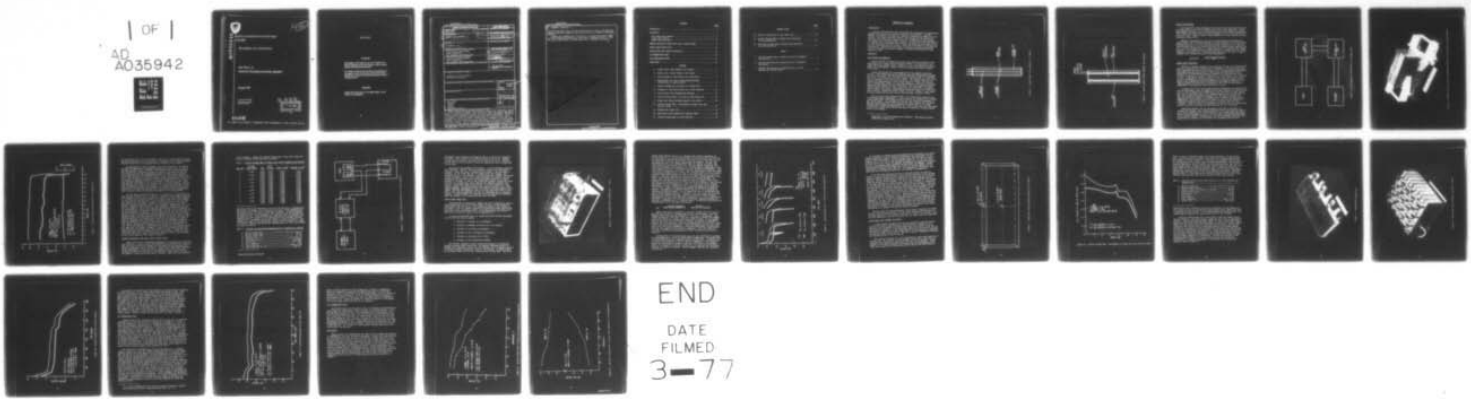

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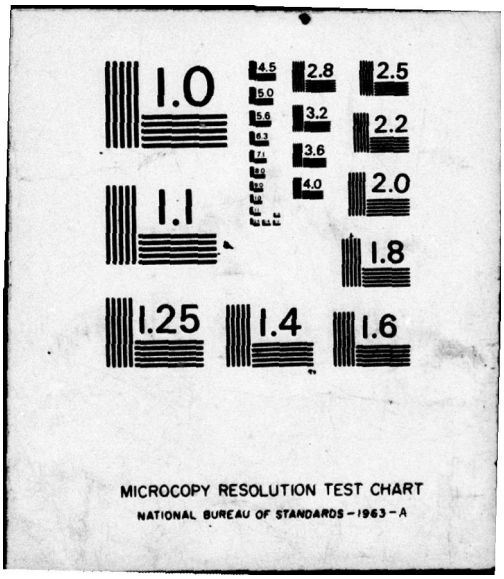
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Research and Development Technical Report

ECOM-4457

METHANOL-AIR BATTERIES

John Perry, Jr.

Electronics Technology and Devices Laboratory

January 1977

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The methanol-air battery shows promise of meeting the operational requirements of low power equipments, such as sensors, mines, and similar equipments. While primarily designed to satisfy low level output requirements, the system is capable of supporting transient peak loads on a cyclical basis. Cells charged with 120 ml of anolyte, consisting of 6 M methanol in 11 M KOH, have operated for 2,230 hours under cyclic load drains of 50 mA for 13 minutes and 2 A for 1 second. One cell operated for more than 8,000 hours with periodic refilling of fresh anolyte, demonstrating the long serviceable life of the

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electrode components. Fuel utilization efficiencies as high as 84% have been obtained from cells charged with an anolyte solution of methanol in potassium hydroxide.

Single cells charged with a fuel mixture of methanol and methyl formate in 5 M KOH operated satisfactorily under load at temperatures down to -40°C, with only a 30% decrease in voltage during the 2 A period of the cycle.

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METHANOL-AIR BATTERIES

INTRODUCTION

Previous investigations have established the feasibility of fabricating methanol-air batteries to operate on selected load profiles. However, methanol utilization efficiency was limited by evaporation losses at the air cathode. This report describes various cell designs and new fabrication techniques investigated to minimize the loss of methanol during prolonged cell operation on a single anolyte filling. Selected cells were life tested to evaluate their performance and determine the operating life capability of the cell components and cell design. Cells were also tested at low and high temperatures. Efforts are continuing to develop a practical lightweight, low power methanol-air battery, capable of operating unattended for long periods of time.

DISCUSSION

Cell Design and Component

Initial studies of methanol-air cells were conducted at ECOM on cells fabricated with a single anode and double cathode.[1] In addition to the single anode cell design, shown in Figure 1, a new cell design with double anodes was investigated. Figure 2 shows the double anode-double cathode cell design.

Anodes used during this investigation were the palladium-platinum (Pd-Pt) teflon bonded type and the cathodes were the silver-mercury (Ag-Hg) air type. The anodes were fabricated by mixing Pd-Pt 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 electrode 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 dried. The oxide powder was mixed with the teflon solution to form a paste that was rolled onto an expanded silver screen. The screen, containing the oxide paste mix, was fired in an oven at 260°C to reduce the silver oxide to silver. Finally, a thin teflon film was pressed onto the air side of the electrode at 4.137×10^8 Pa.

All test cells were fabricated with lucite frames which served as the electrolyte/anolyte compartment. A major problem was encountered in finding a good cement that would permanently bond the cell electrode components to the lucite frames. Lucite cement and several epoxy cements were evaluated. The best cement among the group evaluated was Delta Bond 152, an epoxy manufactured by Wakefield Engineering, Inc. Most of the test cells developed a leak at the cement joints after 1000 hours of operation, forcing termination of life testing.

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[1] John Perry, "Low Power Methanol-Air Battery," R&D Technical Report ECOM-3365, November 1970.

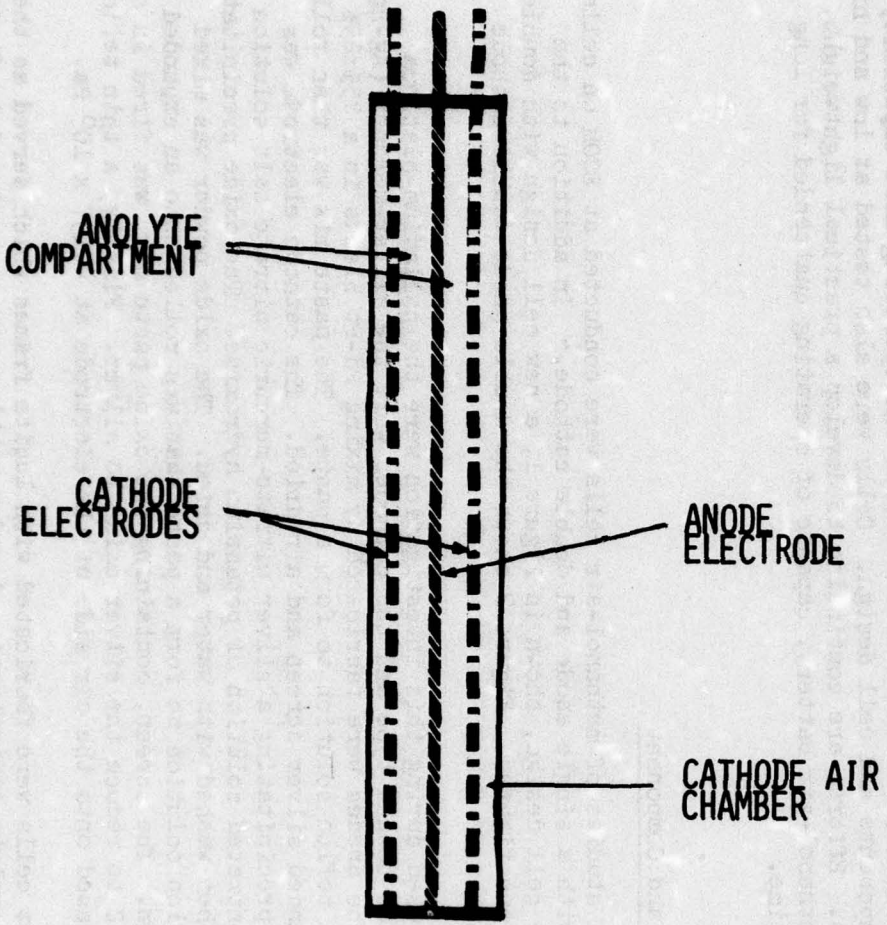

Figure 1. Single Anode, Dual Cathode, Cell Design

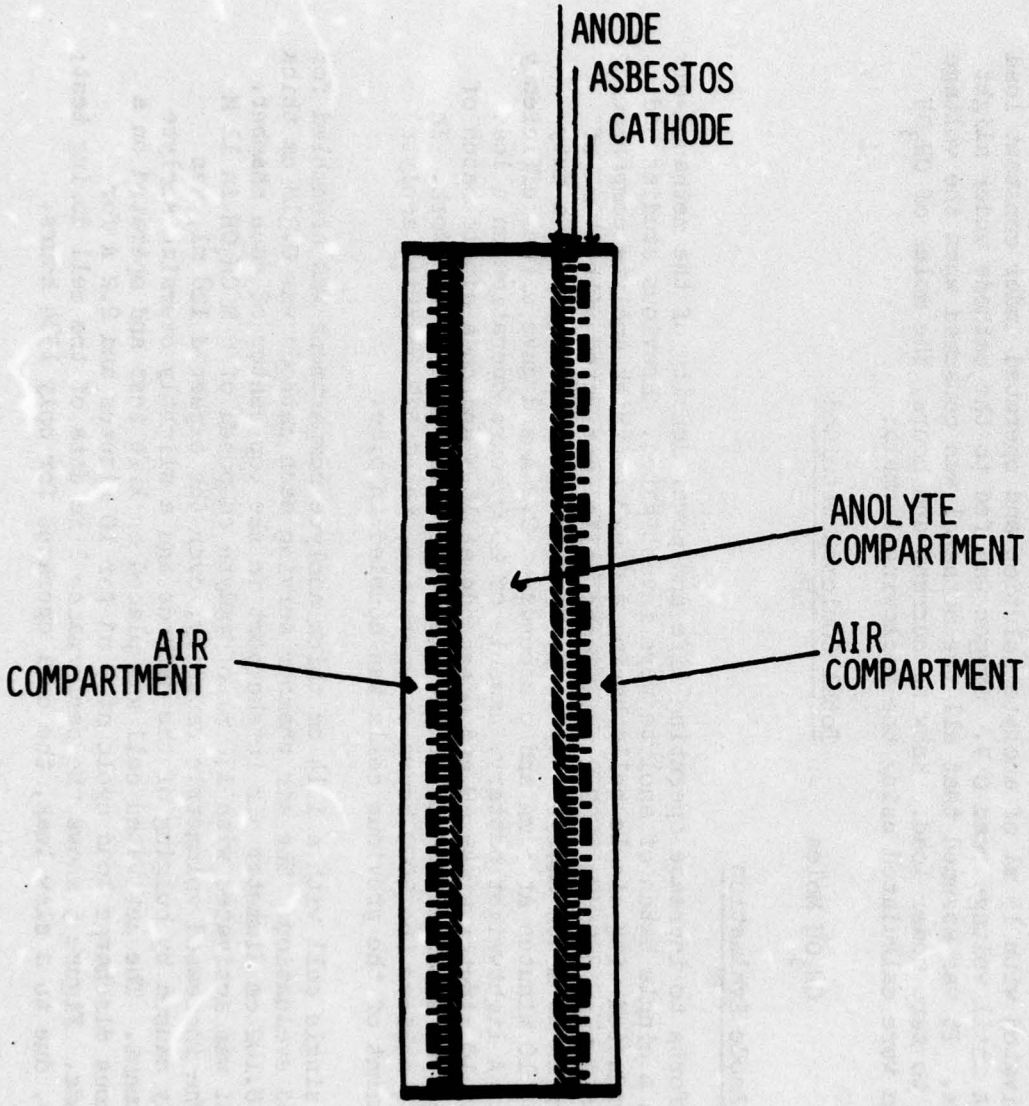

Figure 2. Double Anode, Double Cathode, Cell Design

Single Cell Testing

All single cells were discharged under cyclic loads using variable resistors and operated to a cutoff voltage of 0.60 VDC on the high pulse. Load requirements were based on a 9-cell methanol-air battery capable of operating with a DC-DC converter having an input requirement of 5-10 volts and an output of 24 volts. Figure 3 shows a block diagram of the test fixture used for evaluating single cells.

Methanol concentration in the cell after discharge was determined by using a small test cell measuring 8.89 cm x 8.89 cm (Figure 4) with an active electrode area of 5.1 cm x 5.1 cm and an anolyte volume of 15 ml. The cell was activated with 15 ml of anolyte solution and operated under constant load of 0.5 A until voltage read 0 V. Oxygen was fed to the cathode under slight pressure. It was assumed that all the methanol was consumed when the voltage dropped to zero under load. Knowing current and hours, the moles of CH_3OH consumed were calculated using the following formula:

$$CH_3OH \text{ Moles} = \frac{\text{Total Coulombs Obtained}}{nF}$$

Single Anode Evaluation

Efforts to increase operating life and power density of the methanol-air cell on a single batch of anolyte were investigated. Previous studies had been conducted with single cells having a 0.572 cm thick anolyte compartment; electrodes were 8.26 cm x 22.2 cm. These cells, activated with 64 ml of 6M CH_3OH in 11 M KOH anolyte solution, operated for 1000 hours on a duty cycle of 10 minutes at 5 mA and 6 seconds at 2.2 A and gave a fuel efficiency of 45%. A lightweight battery, capable of 2000 hours operation on a load cycle of 10 minutes at 45 mW and 6 seconds at 15 W and on a single batch of anolyte, was selected as one of the goals for this phase of the work. In order to achieve the 2000 hours of operation, the 0.572 cm thick anolyte compartment of the previous cells was doubled in size.

A single cell with a 1.14 cm thick anolyte compartment was assembled for test and evaluation. The air chamber serving each cathode was 0.318 cm thick with a 0.102 cm diameter air intake port in the top center of each chamber. The cell was activated with 170 ml of anolyte composed of 6 M CH_3OH in 11 M KOH. The increased volumetric capacity, over the expected 128 ml, was probably caused by bulging of the cathode and a slightly oversize anolyte compartment. The activated cell was placed on life test and operated on a continuous discharge load cycle of 5 mA for 10 minutes and 2.2 A for 6 seconds. Figure 5 shows the performance life data of the cell during test; however, due to a slow leak, the cell operated for only 1584 hours.

Additional methanol (40 ml) was added to the cell in an effort to increase the voltage. The voltage increased to 0.80 V on the pulse load of 2.2 A for 6 seconds and the cell remained on test an additional 1200 hours before voltage decreased to 0.60 V. At this time, testing was discontinued due to serious leakage. Theoretically, the cell contained enough fuel and electrolyte to operate for 6,088 hours on a discharge cycle of 5 mA

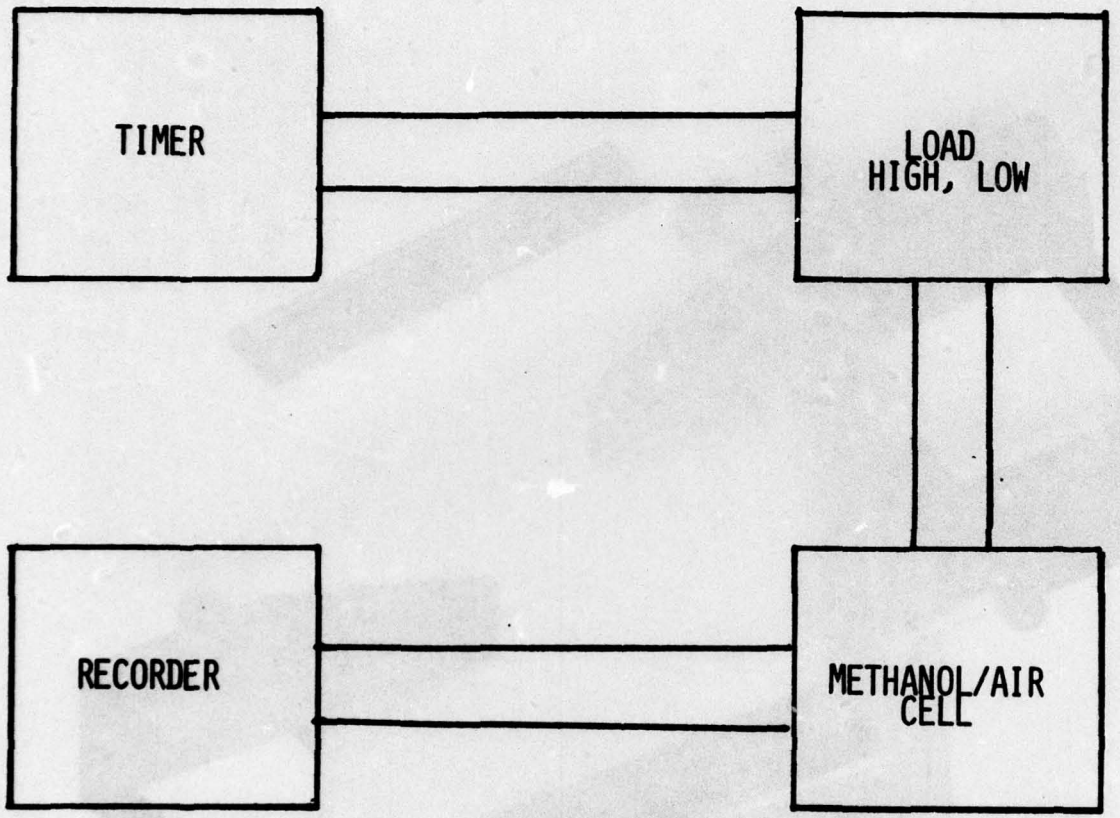

Figure 3. Block Diagram of Test Fixture for Single Cells

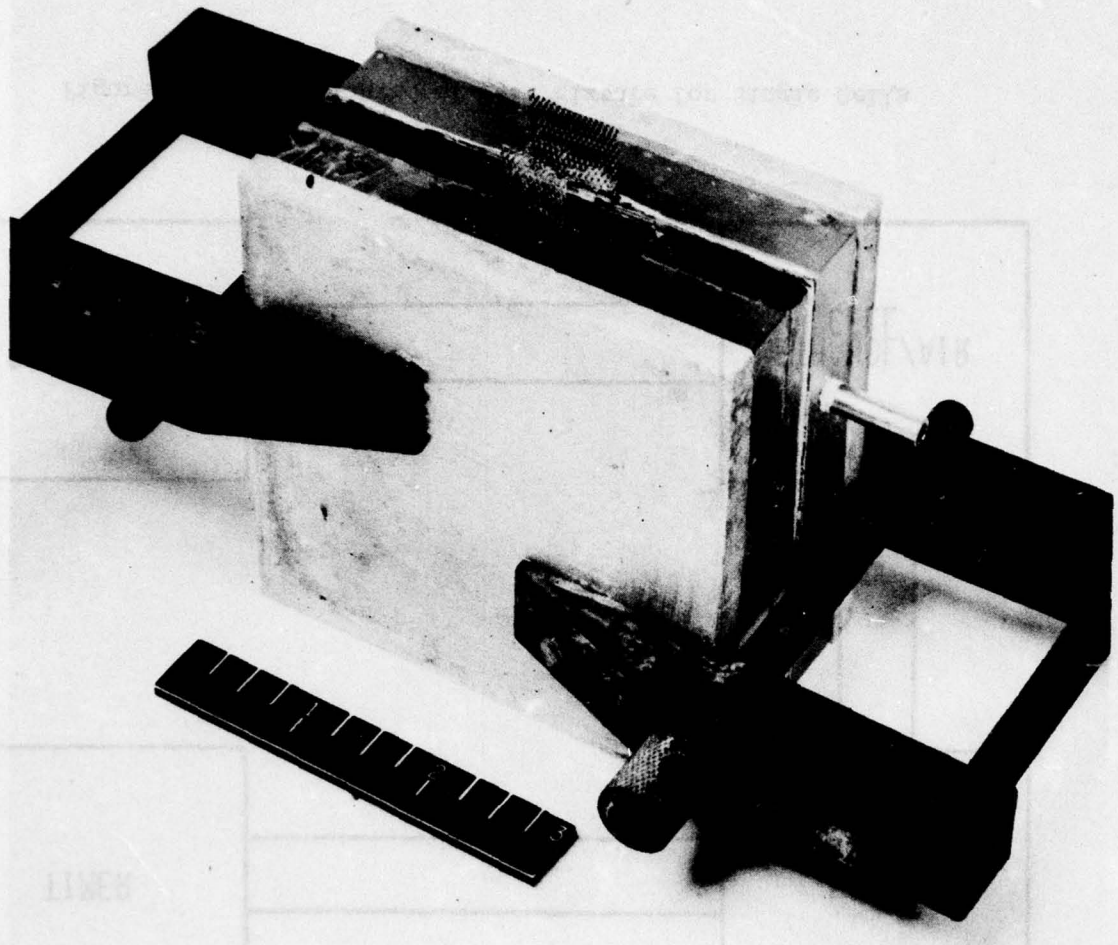

Figure 4. Methanol-Air Cell Used in Determining Methanol Concentration in Spent Anolyte

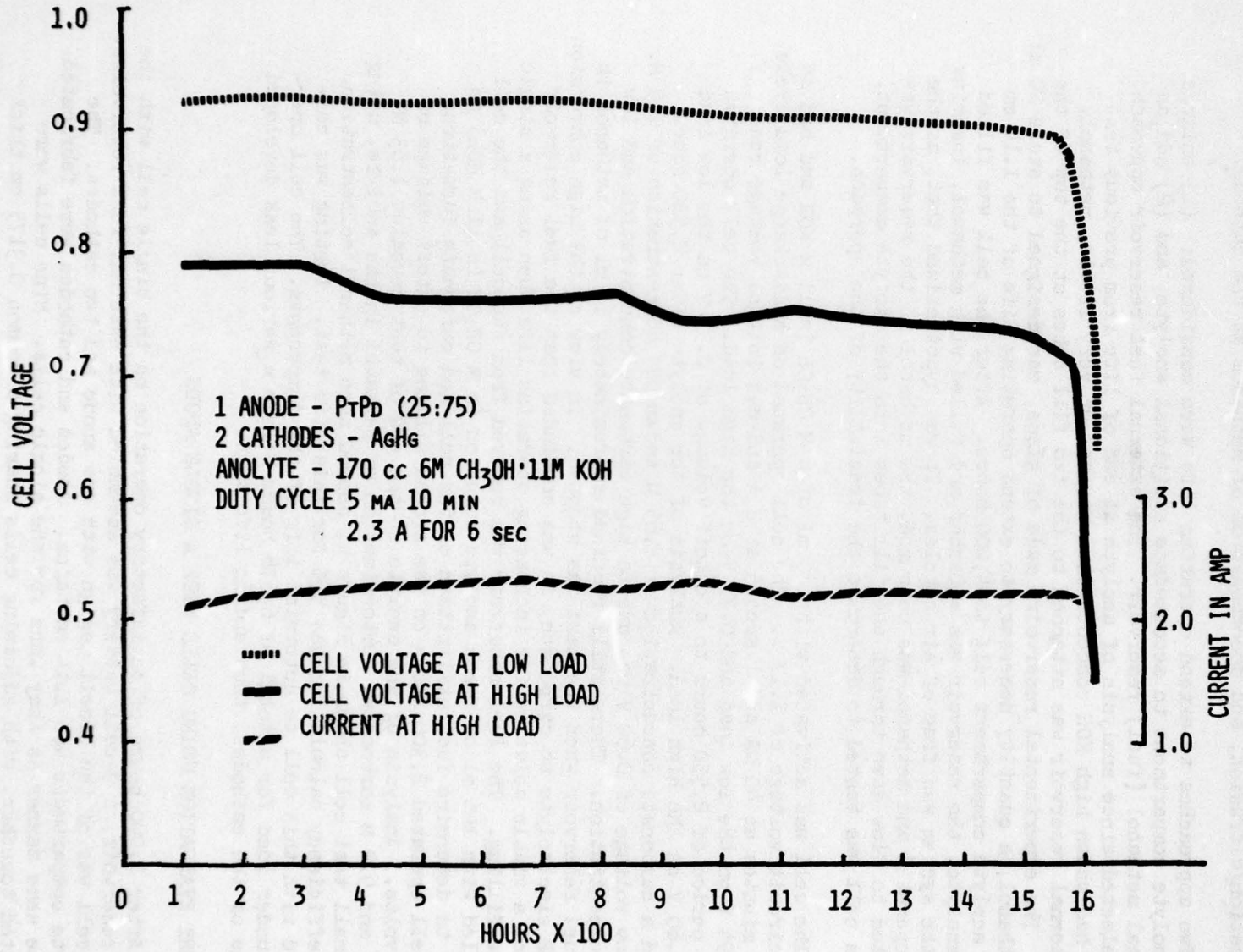

Figure 5. Current Voltage and Life Data of a Single Cell

for 10 minutes and 2.2 A for 6 seconds. The low fuel utilization efficiency and short operating life were attributed to methanol losses through leakage, evaporation/diffusion, and decomposition of methanol at the cathode.

Two approaches to extend operating life were considered: (1) enlarge the anolyte compartment to accommodate additional anolyte, and (2) add an external methanol (fuel) reservoir. The external fuel reservoir approach was selected since analysis of anolyte at end of life from previous test cells had shown high KOH concentration and no, or very little, methanol. An external reservoir was attached to the two fill tubes at the top of the cell. The experimental reservoir, made of glass, was designed to store 20 ml of methanol, a quantity necessary to extend operating life of the 1.14 cm thick anolyte compartment cell to 4,000 hours. After the cell was filled with anolyte, the reservoir was attached and filled with methanol, insuring that the system was free of air bubbles. It was hypothesized that, as the cell operated and methanol was consumed, the methanol in the reservoir was expected to flow down through the fill tubes into the anolyte compartment. Such a cell was tested to determine the feasibility of the approach.

The cell was activated with 180 ml of 6 M CH_3OH in 11 M KOH and had an open circuit voltage of 1.17 V. The cell operated on a discharge load cycle of 13 minutes at 40 mA and 1 second at 2 A and had initial voltage readings of 0.94 V on the low load and 0.78 V on the high load. The cell operated for a period of 2,550 hours to a cutoff voltage of 0.91 V on the low load and 0.60 V on the high load. Analysis of the anolyte after 2,520 hours showed a carbonate concentration of 7.65 M and an OH^- concentration of 1.9 M. The low voltage of 0.60 V was due to high carbonate concentration and low OH^- concentration. There still remained approximately 10 ml of methanol in the fuel reservoir when the test was stopped. In view of the high conversion of KOH electrolyte to carbonate, it was concluded that the fuel reservoir was not a viable solution for increasing operation life when using a single charge filling. The fuel reservoir was removed from the cell and the cell refilled with 166 ml of fresh anolyte solution (6 M CH_3OH in 11 M KOH) in order to determine fuel utilization of the cell and carbonate formation. The cell operated 2,300 hours on the second filling to cutoff voltage of 0.60 volts. Analysis of the anolyte at the end of test revealed 1.63 M OH^- and 9.2 M carbonate. Determination of methanol in the anolyte, using the small test cell shown in Figure 4, showed zero methanol concentration. Fuel efficiency calculation was 56% for this life test. Testing was continued with this cell to determine life of the components. The cell operated under load for a total of 6,678 hours before a serious leak developed at one of the cathodes, thus ending life test.

BATTERY EVALUATION USING CELLS WITH A SINGLE ANODE

After 1,000 hours of satisfactory operation on the single cell with the fuel reservoir, a 9-cell battery was assembled with external fuel reservoirs. Each cell was of the bicell design with one anode and two cathodes. The anolyte compartment was 1.14 cm thick. Anodes and cathodes were fabricated in the same manner as they were for the single cells. Nine cells were cemented together, with adjoining cells sharing a common 0.3175 cm thick air chamber. Single cells were series connected. Each cell was pre-tested

before assembly. Single cell current voltage data, taken after stabilization at indicated current, are shown in Table 1.

Table 1. Current Voltage Data of Single Cells Before Assembly Into Battery

Cell No.	Voltage Open Circuit	Amp.	Cell Voltage	Anode vs SCE*	Cathode vs SCE*
1	1.130	3.000	0.820	0.970	0.150
		0.005	1.150	1.100	0.050
2	1.175	3.000	0.870	1.030	0.045
		0.005	1.175	1.110	0.103
3	1.150	3.000	0.880	0.990	0.025
		0.005	1.130	1.075	0.100
4	1.130	3.000	0.890	0.970	0.090
		0.005	1.120	1.090	0.035
5	1.190	3.000	0.890	0.990	0.140
		0.005	1.150	1.120	0.030
6	1.180	3.000	0.890	0.970	0.090
		0.005	1.175	1.120	0.035
7	1.210	3.000	0.930	0.980	0.080
		0.005	1.190	1.100	0.070
8	1.130	3.000	0.920	1.090	0.180
		0.005	1.120	1.020	0.060
9	1.200	3.000	0.930	0.980	0.080
		0.005	1.190	1.100	0.070

The 9-cell battery was designed to deliver 12.24 watts on a 1 second pulse and 240 mW, on standby, for 13 minutes at 24 volts. Total operating time was projected as 4,000 hours of continuous operation. A DC-DC converter was used to deliver 24 volts output. The converter used was manufactured by Honeywell, Inc., Model G-2802A1 S/N 1, and was used in conjunction with external resistors to deliver 12.24 watt/240 mW for 1 second/13 minutes, respectively. A schematic of the test fixture is shown in Figure 6. The overall dry weight of the battery was 1.88 kg, with an average cell weight of 0.208 kg. Physical and electrical characteristics of the 9-cell battery are shown in Table 2.

Table 2. Physical and Electrical Characteristics of Methanol-Air Battery

1.	Exterior Dimensions	10.2 cm x 22.9 cm x 22.9 cm
2.	Battery Weight (Dry)	1.88 kg
3.	Battery Weight (Wet)	3.7 kg
4.	Electrode Size	8.3 cm x 22.2 cm
5.	Steady-State Power	0.24 Watts
6.	Pulse Power	12.24 Watts
7.	Pulse Duration	1 Sec
8.	Pulse Frequency	1 Every 13 Min
9.	Theoretical Service Life	4380 Hr +

*Saturated Calomel Electrode

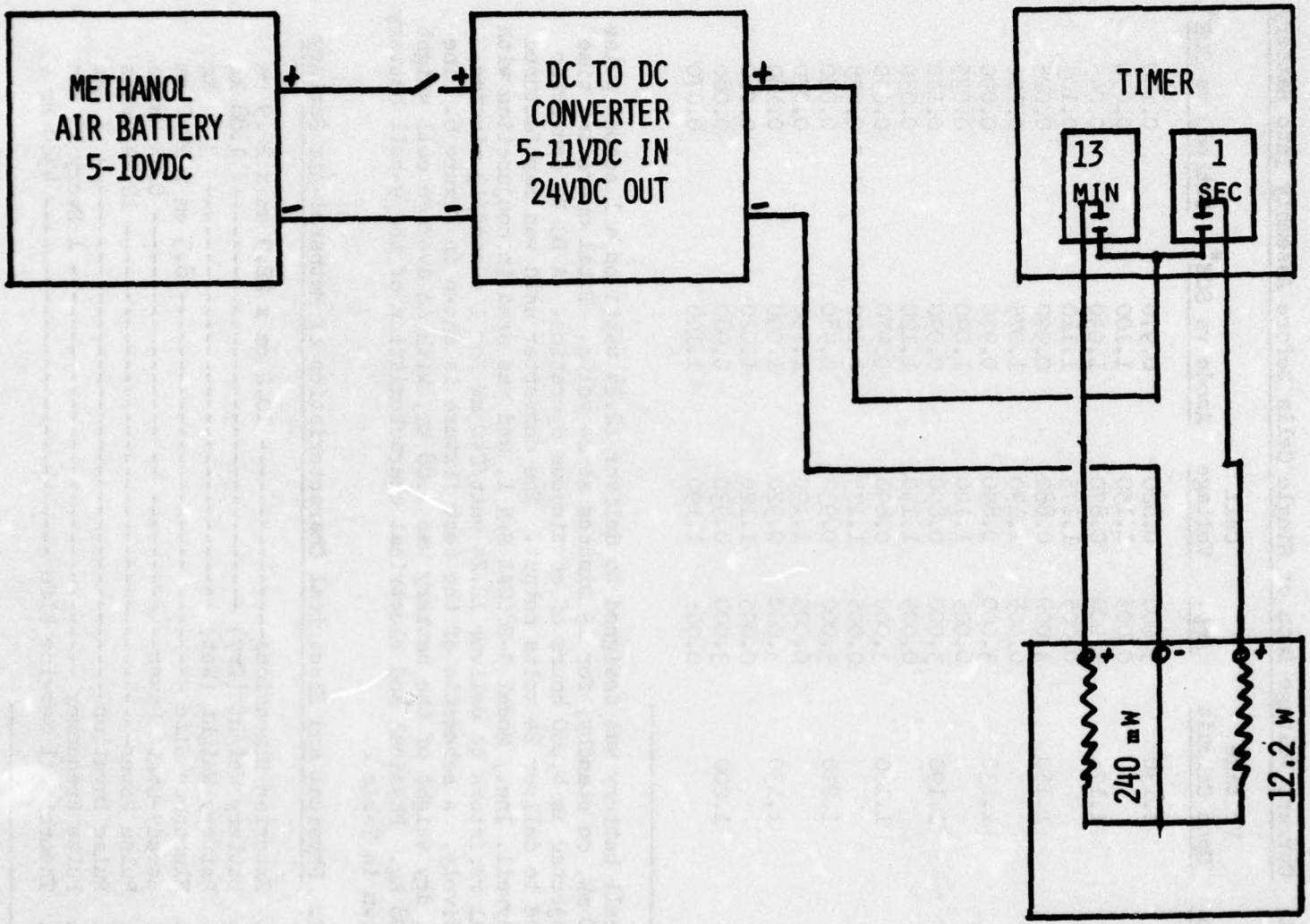

Figure 6. Schematic of the Test Fixture for a 9-Cell Battery

Individual cells contained an average of 180 ml of anolyte (6 M CH_3OH in 11 M KOH). Total weight of the activated battery was 3.7 kg. Battery voltage (open circuit) at the start of the test was 10.13 V. Initially, one air port at the top center of each air chamber was used to supply air to the cells.

The battery was operated for 200 hours before the external reservoirs were installed. Figure 7 shows the completed battery with reservoirs attached. After 500 hours of operation the voltage of Cell #6 began to decrease. It was found that the air intake holes were clogged, thus shutting off air to the cathodes. Once the holes were cleared, the battery voltage increased. After 1,000 hours of operation, an anolyte leak was observed at the cemented joints of Cell #9, which resulted in a sharp decrease in voltage. It was at this point that internal leakage was noted with most of the cells and, also, that the air chambers contained free anolyte. Holes were placed in the bottom of the air chambers to allow liquid to drain. The fuel reservoirs were removed from the cells, since leakage prevented replacement of fuel in relation to electrochemical utilization. The test was continued, with fuel being added from time to time. After 1,600 hours of operation, the test was terminated due to excessive leakage. As noted earlier, the external reservoir approach was abandoned after the results of the single cell test were reviewed.

DOUBLE ANODE SINGLE CELL

Investigations on methanol-air single cells were continued in order to extend operational life on a single anolyte filling. It was decided to investigate a new cell design; a two anode-two cathode bicell (Figure 2). An asbestos (fuel cell grade) separator was sandwiched between the cathode and anode to make an electrode pack. One electrode pack was cemented to each side of an anolyte frame to form a completed cell.

It was postulated that this cell design would have several advantages over the previous designs; namely:

1. Decrease in internal cell resistance.
2. Decrease in methanol diffusion out of the cathode.
3. Increase in electrical performance.
4. Increase in fuel utilization (efficiency).
5. Increase in operating life of cell.
6. Increase in cell mechanical strength.

The asbestos separator served a three-fold purpose: (1) electrical insulator between cathode and anode, (2) physical diffusion barrier to minimize fuel (methanol) contact with the cathode, and (3) physical barrier to minimize methanol evaporation losses at the cathode. An added feature of the double anode cell was the increased anode surface area. The first

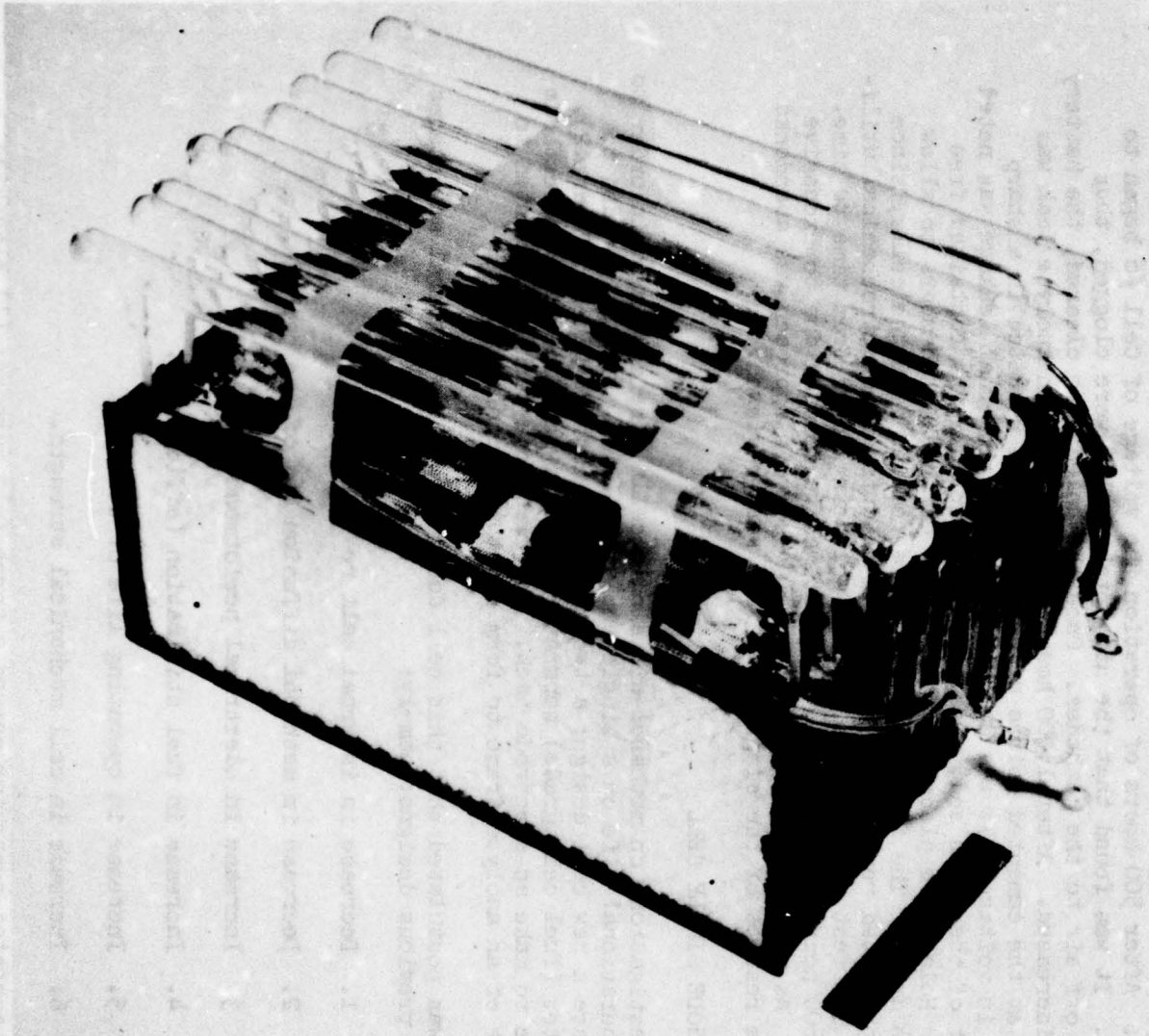

Figure 7. Single Anode 9-Cell Methanol-Air tery

double anode-cathode bicell to be evaluated had exterior dimensions of 8.9 cm x 22.9 cm x 1.3 cm and an electrode active area of 8.3 cm x 22.2 cm. Air compartments serving the cathodes were 0.3175 cm in width with a 0.102 cm inlet port in the top center edge of each air chamber. The cell was activated with 120 cc of anolyte containing 6 M CH_3OH in 11 M KOH. The total weight of the cell was 449.46 g. The cell anolyte volume was less than that contained in the earlier 1.14 cm thick anolyte compartment of the single anode cell, due to differences in cell assembly and components. Cell open circuit voltage was 1.05 volts. The cell was placed on life test under a continuous discharge cycle of 40 mA for 13 minutes and 2.0 A for 1 second. Current voltage data for the life test of the dual anode cell is shown in Figure 8. The cell operated for 1,200 hours before voltage dropped to 0.70 volts. This voltage drop was attributed to air starved cathodes. An additional 0.102 cm air port was opened in each air chamber close to the existing hole allowing more air to flow into the air chambers. When testing was resumed the cell operated for a total of 2,232 hours before voltage decreased to a cutoff voltage of 0.60 V. The cell achieved an energy density of 184.9 W·h/kg. The anolyte was drained and analyzed for methanol content. The quantity of methanol present was too low to be detected by laboratory detection methods. It was assumed that all of the methanol had been consumed through oxidation to carbonate with some losses due to evaporation at the cathode electrode. Analysis of anolyte showed carbonate concentration of 9.72 M and hydroxide concentration of 1.78 M. Calculations were made to determine fuel utilization efficiency, assuming methanol was oxidized to carbonate with a 6 electron change. An 82% fuel utilization was obtained based on the following calculation:

$$\eta_F = \frac{\text{coulombs obtained}}{\text{total moles consumed} \cdot nF} = \frac{341,875.4}{0.12 \times 6 \times 6 \times 96,500}$$

After 2,232 hours of operation to a cutoff voltage of 0.6 V, the cell was refilled with 96 ml of anolyte and the life test resumed. Cell performance after refilling was comparable to the initial performance. Open circuit voltage was 1.06 volts. The cell continued to operate for another 1,560 hours before the voltage went below cutoff voltage. It was assumed that the cell was out of fuel after a methanol determination indicated no methanol was in the anolyte. The cell was drained and refilled for a third, fourth, and fifth time, thereafter. The cell operated for more than 8,000 hours with very little degradation in electrode performance, demonstrating the long life capability of electrode components. This cell, with the 5 refills, achieved an energy density of 340.5 W·h/kg for 8,300 hours of operation.

Investigation of the double anode type cell was continued to determine the performance with a 0.572 cm thick anolyte compartment. The anodes were of Pt-Pd (25%:75%) and the cathodes were of the Ag-Hg type. Seventy-six ml of anolyte were required to fill the anolyte compartment. This volume of anolyte was sufficient to operate a cell for 1,375 hours on a discharge cycle of 10 minutes at 50 mA and 1 second at 2 A, based on the theoretical oxidation of CH_3OH to carbonate. The air chamber thickness was increased to 0.635 cm.

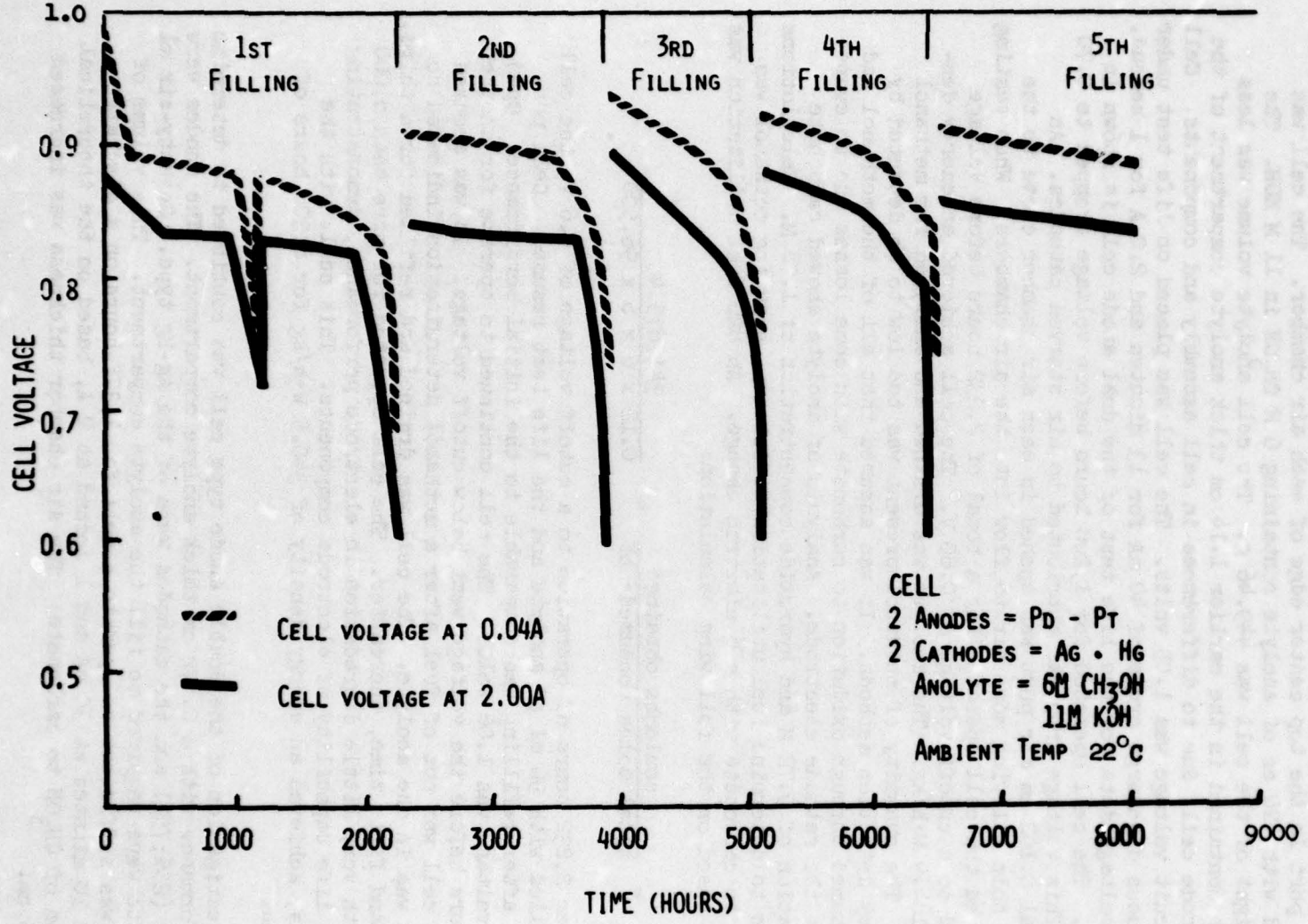

Figure 8. Current Voltage Data - Life Test of Dual Anode Cell

In an effort to achieve long term operation and to minimize fuel losses through evaporation, a 0.178 cm hole was placed in the side-center of the 0.635 cm thick air chamber. Previous single cells were run with a 0.102 cm diameter hole in the top of the air chamber (Figure 9). It was felt that, with the air hole on top of the chamber, incoming air was partially restricted due to the methanol vapor pressure buildup within the chamber. Another problem encountered with the small hole on top of the air chamber was the condensation of vapors around the hole. The condensation eventually evaporated and the salt deposits sealed off the openings to incoming air.

It was felt that with the air hole in the side center, as shown in Figure 9, a more even distribution of air over the full face of the cathode would be achieved, minimizing the clogging of the intake air hole with salt deposits. The air holes located in the side of the air chambers did not solve the problem of salt buildup. As can be seen in Figure 10, the voltage on the high load shows a steady decrease, and after 670 hours of operation, it was observed that the air hole was clogged with salt deposits. Once the hole was cleared the voltage increased indicating that the cathode had been air starved. It was also observed that the voltage curve showed a steady decrease with time indicating a possible fuel limiting problem and/or reaction product buildup. After 1,100 hours of operation, the voltage had reached the cutoff voltage of 0.60 V. Calculation showed that the cell had a fuel utilization efficiency of 84%. Fuel utilization efficiency on the cells with the 0.57 cm anolyte compartment and the 1.14 cm compartment were comparable. As can be seen, an increase in fuel utilization was achieved with the double anode cell over the single anode cell tested with the same size anolyte compartment. This was attributed to the use of the asbestos barrier at the cathode, which reduced the oxidation of fuel at the cathode and diffusion of methanol through the cathode electrode.

The next phase of the program deals with efforts to improve the energy density of the existing system. The low energy density was attributed to the small amount of fuel (methanol) that can be stored in the system. Also, the cell components, such as electrodes and cell frame, were not optimized.

DOUBLE ANODE CELL BATTERY EVALUATION

A second battery assembled for test and evaluation contained single cells of the double anode and double cathode design. Because of the increased fuel efficiency obtained during single cell studies using the dual physical separator, it was considered feasible at this time to try and increase the operating life and energy density of the battery by increasing the anolyte volume of the system. The cell's anolyte compartment thickness was increased from 1.14 cm to 1.58 cm.

This battery consisted of 9 cells connected in series and stacked in a battery case. To preclude internal leakage between cells, each cell was assembled individually and completely, with its own air chamber. Consequently, if one cell developed an internal leak, the performance of the other cells would not be affected as was the case of the first battery.

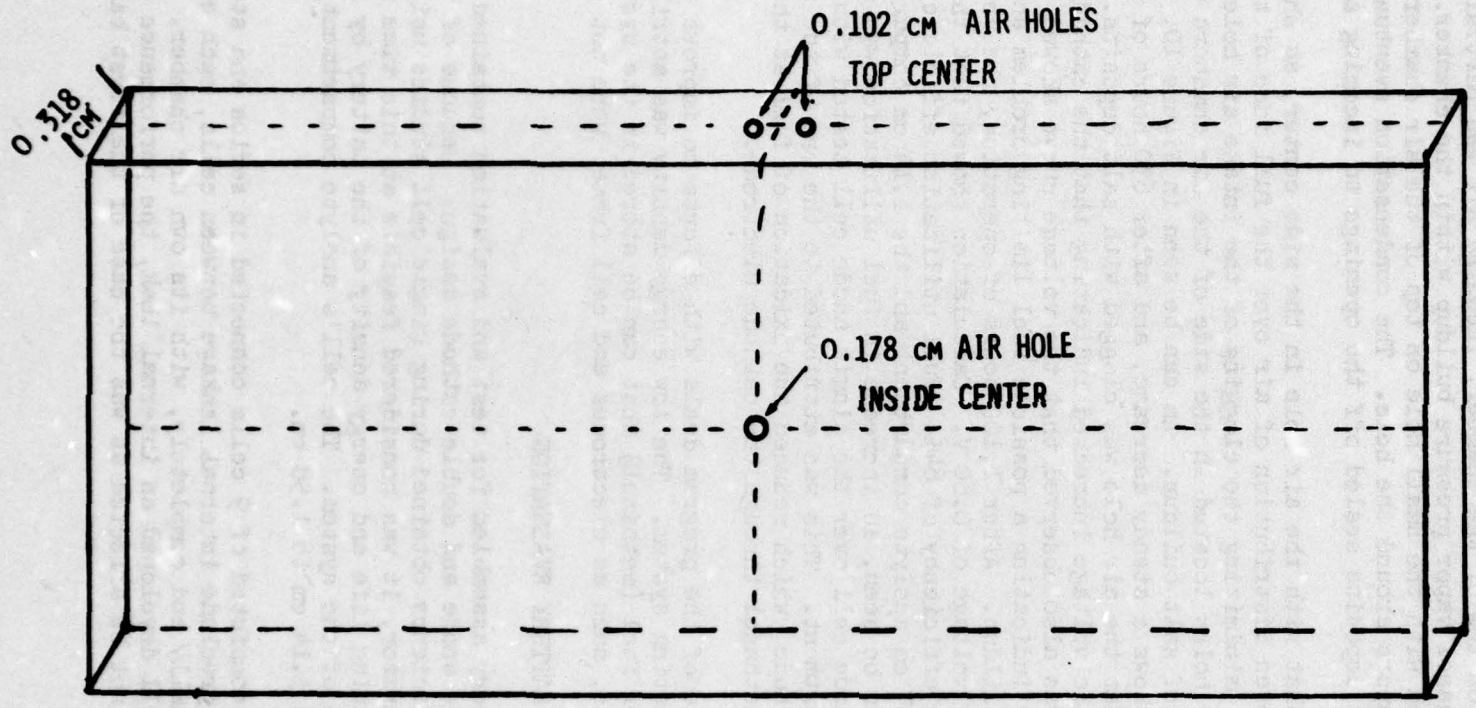

Figure 9. Single Cell Design Showing Location of Air Holes

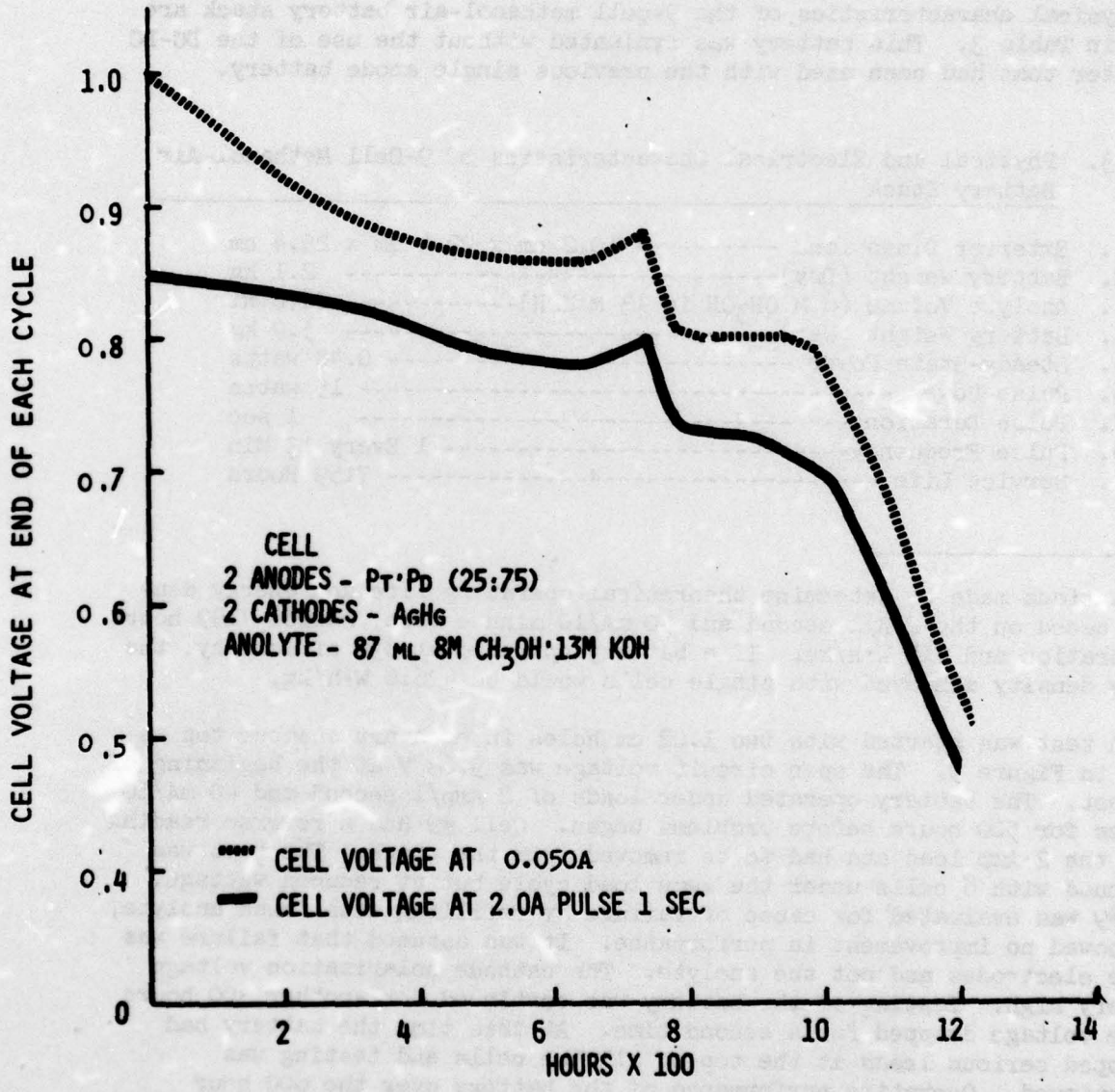

Figure 10. Current Voltage Data - Performance of Single Cell with Side Air Holes

Figure 11 shows a completed single cell before stacking it in the battery case. A one-inch slot was placed in the center of a screen spacer in each air chamber, as shown in Figure 11. This slot was intended to allow free air circulation in this area to improve cathode performance. The electrode's size and composition were the same as for the previous single cell of the double anode design. Figure 12 shows the complete battery in the case. The total weight of the dry battery excluding case, interior end plates, and spacers was 2.13 kg with an average cell weight of 0.24 kg lbs. Electrical and physical characteristics of the 9-cell methanol-air battery stack are shown in Table 3. This battery was evaluated without the use of the DC-DC converter that had been used with the previous single anode battery.

Table 3. Physical and Electrical Characteristics of 9-Cell Methanol-Air Battery Stack

1.	Exterior Dimensions	10.2 cm x 22.4 cm x 25.4 cm
2.	Battery Weight (Dry)	2.1 kg
3.	Anolyte Volume (8 M CH_3OH in 13 M KOH)	2670 ml
4.	Battery Weight (Wet)	5.9 kg
5.	Steady-State Power	0.40 watts
6.	Pulse Power	15 watts
7.	Pulse Duration	1 sec
8.	Pulse Frequency	1 Every 13 Min
9.	Service Life	7159 Hours

Calculations made to determine theoretical operating life and energy density, based on the 2 A/1 second and 40 mA/10 minute test, showed 7159 hours of operation and 514 W·h/kg. If a battery operated at 83% efficiency, the energy density achieved with single cells would be 426.6 W·h/kg.

A test was started with two 1.02 cm holes in each air chamber top as shown in Figure 9. The open circuit voltage was 9.63 V at the beginning of the test. The battery operated under loads of 2 Amp/1 second and 40 mA/10 minutes for 500 hours before problems began. Cell #9 had a reverse reading under the 2 Amp load and had to be removed from the stack. The test was continued with 8 cells under the same load cycle but at reduced wattage. Cell #9 was evaluated for cause of failure by refilling with fresh anolyte, but showed no improvement in performance. It was assumed that failure was in the electrodes and not the anolyte. The cathode polarization voltage was very high. Testing of the battery was continued for another 300 hours before voltage dropped for a second time. At this time the battery had developed serious leaks at the top of all the cells and testing was discontinued. Operating performance of the battery over the 800 hour period is shown in Figure 13.

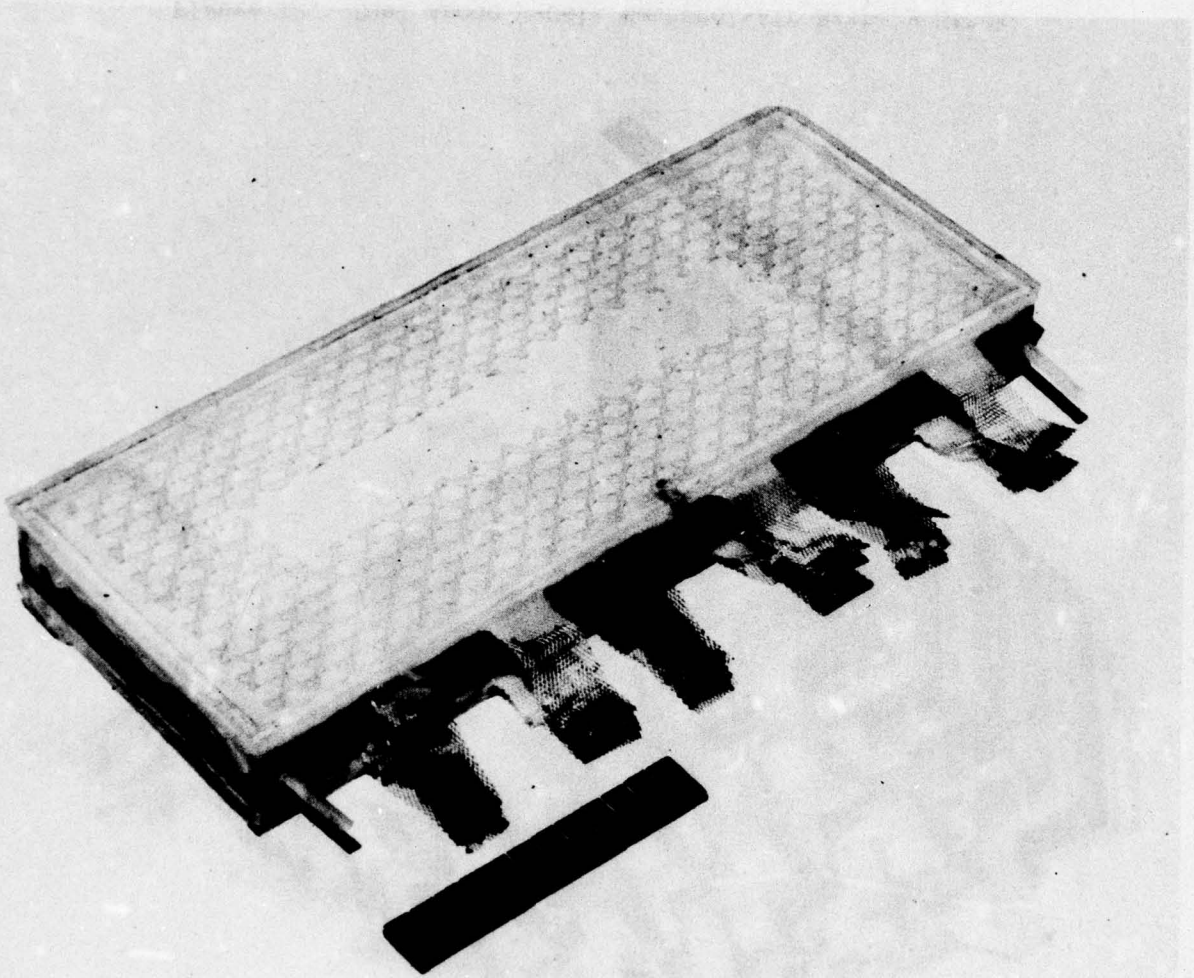

Figure 11. Methanol-Air Single Cell

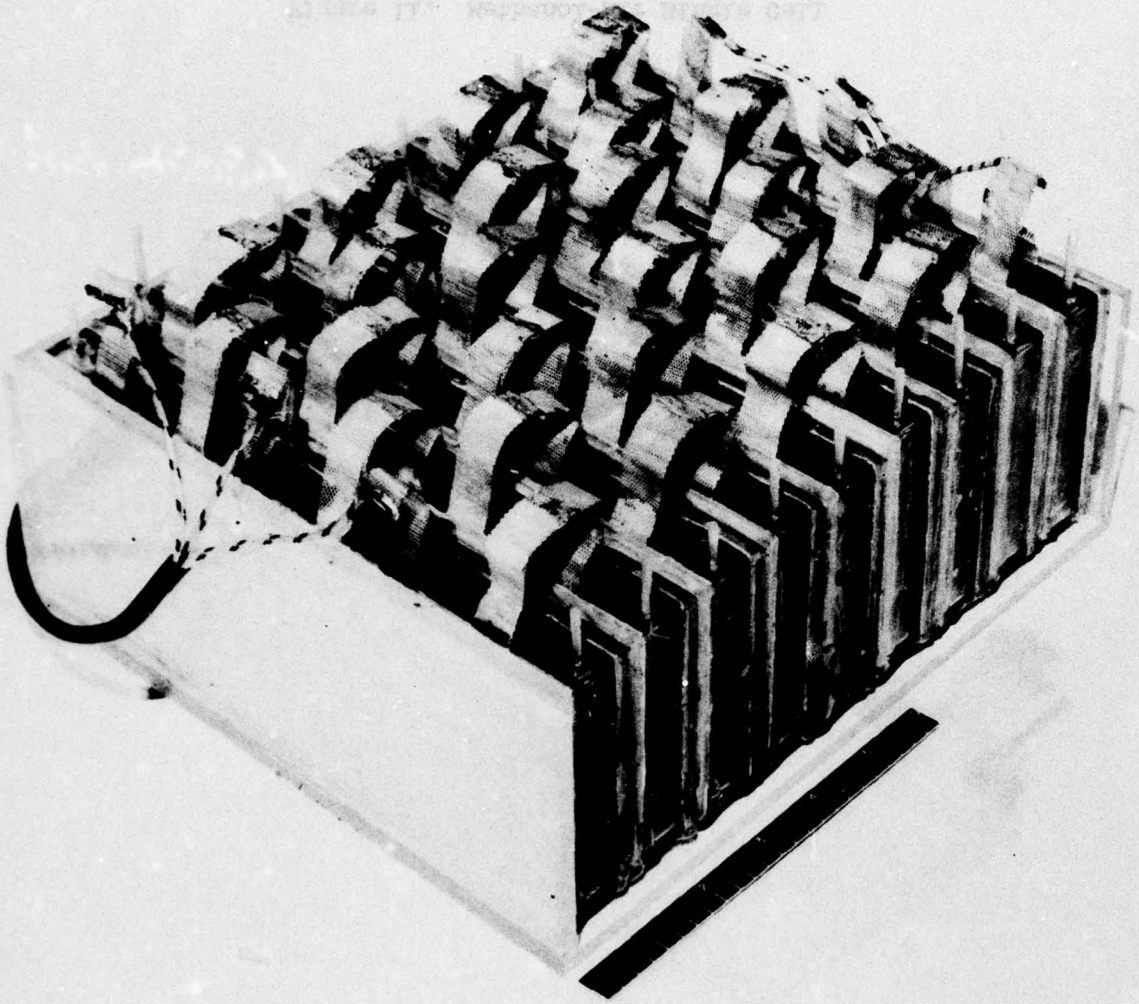

Figure 12. Dual Anode 9-Cell Methanol-Air Battery Stack

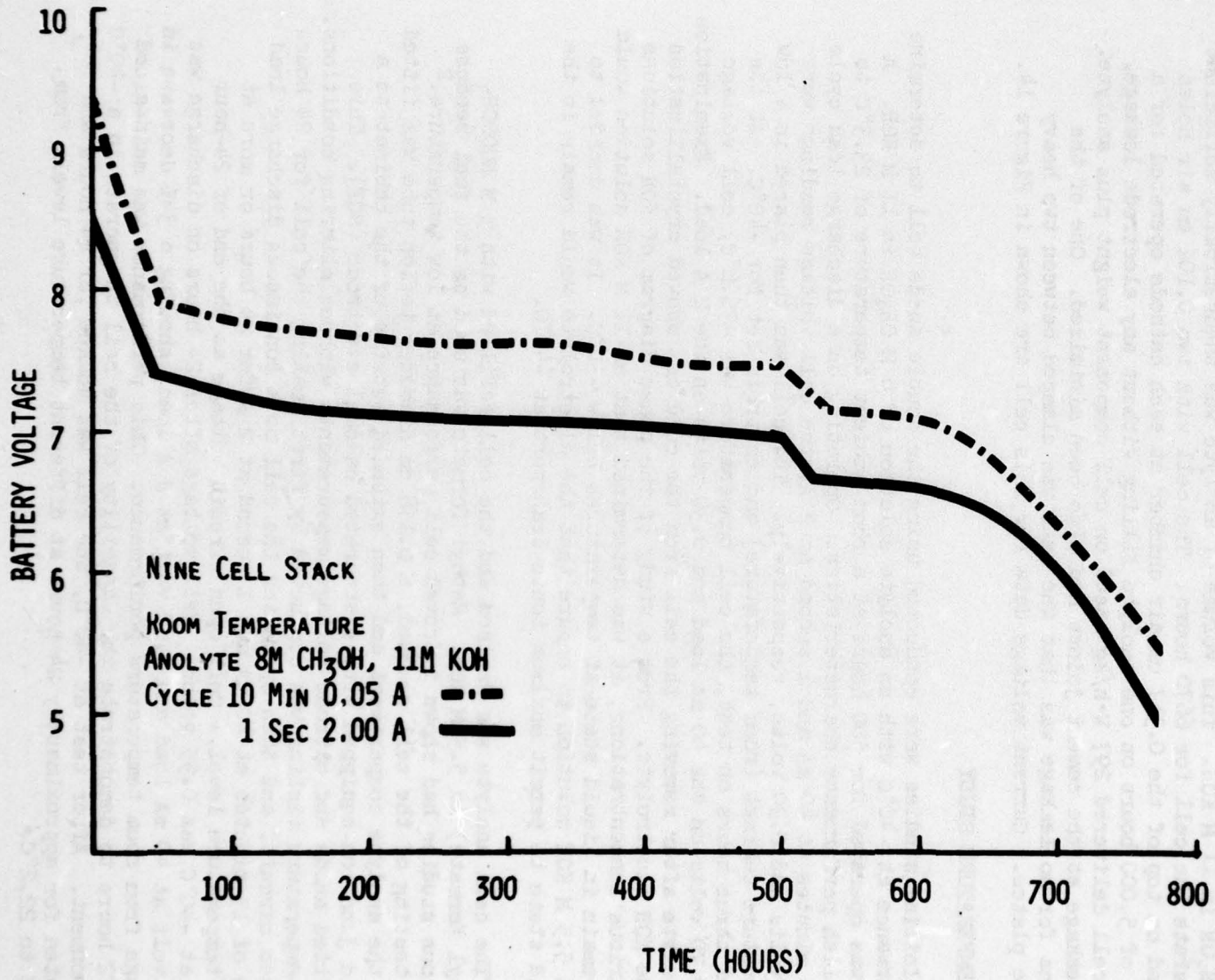

Figure 13. Current Voltage Data of 9-Cell Battery

In an effort to achieve long term operation on a single batch of anolyte, a second single cell of the double anode design was placed on test. This cell had the enlarged anolyte compartment (1.59 cm) and was assembled the same as previous cells. The cathode catalyst was silver-mercury and the anode catalyst was palladium platinum. The cell was filled with 300 ml of 6 M CH_3OH in 11 M KOH. This volume of anolyte was theoretically sufficient to operate the cell for 6670 hours. The cell with two 0.102 cm air holes located on top of the 0.317 cm air chamber at each cathode operated for a total of 5,000 hours on one anolyte filling without any electrode leakage. This cell delivered 297 W·h/kg based on cell component weight plus anolyte. The leakage at the cement joints had also been minimized. One of the reasons for no leakage was that the cell was clamped between two heavy lucite plates. Current voltage data for this cell are shown in Figure 14.

LOW TEMPERATURE STUDY

Initial studies were conducted using the double anode cell to determine performance at -40°C with an anolyte solution of 6 M CH_3OH in 11 M KOH. A cell was operated for 500 hours at a room ambient temperature of 23.3°C to establish performance characteristics. Operating on a discharge load cycle of 13 minutes at 40 mA and 1 second at 2 A, the cell voltage readings were 0.95 volts and 0.90 volts, respectively. The cell was then placed in a low temperature cabinet (room temperature) and controls set for -40°C. At the end of three hours on test, the cell temperature was -36.6°C, cell voltage was 0.70 volts on the 40 mA load and 0.30 volts on the 2 A load. Examination of anolyte after removing the cell from the cold box showed crystallization of the KOH electrolyte. From a study of the phase diagram of KOH solutions at various concentrations, it was determined that an 11 M KOH solution would not remain in liquid state at temperatures below -30°C. It was decided to use a 5.5 M KOH solution to ensure that the electrolyte would remain in the liquid state to permit maximum ionic transport at -40°C.

The cell anolyte was drained and the cell refilled with 3 M $HCOOCH_3$ (methyl formate) in 5.5 M KOH. Methyl formate was used as the fuel because previous studies had shown improved cell performance at low temperature.[2] When testing of the cell resumed, a 0.158 cm diameter teflon tube was fitted into the anolyte compartment and then extended outside of the cabinet to a liquid junction equipped with a saturated calomel electrode (SCE). This permitted anode and cathode voltage measurements without altering conditions. Low temperature testing was conducted by first soaking the cell for 24 hours on open circuit, and then operating the cell on a continuous discharge load cycle of 13 minutes at 40 mA and 1 second at 2 A for 24 hours or more at each temperature level. Cell open circuit voltage at the end of 24-hour soak at -40°C was 0.95 volts. Cell voltage after 24 hours on discharge was 0.82 volt at 40 mA load and 0.62 volt at 2 A load, showing a 34% decrease in voltage from room temperature performance. This performance was maintained for 72 hours to demonstrate the capability of the cell to operate in a -40°C environment. After test at -40°C, the cell was soaked for 24 hours and operated for approximately 24 hours at different temperature levels from -34°C to 22.2°C.

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[2] H. L. Plust "Methanol-Air Fuel Cells as Long-Life Sources of Energy," The Brown Boveri Review, January/February 1966, pp. 5-17.

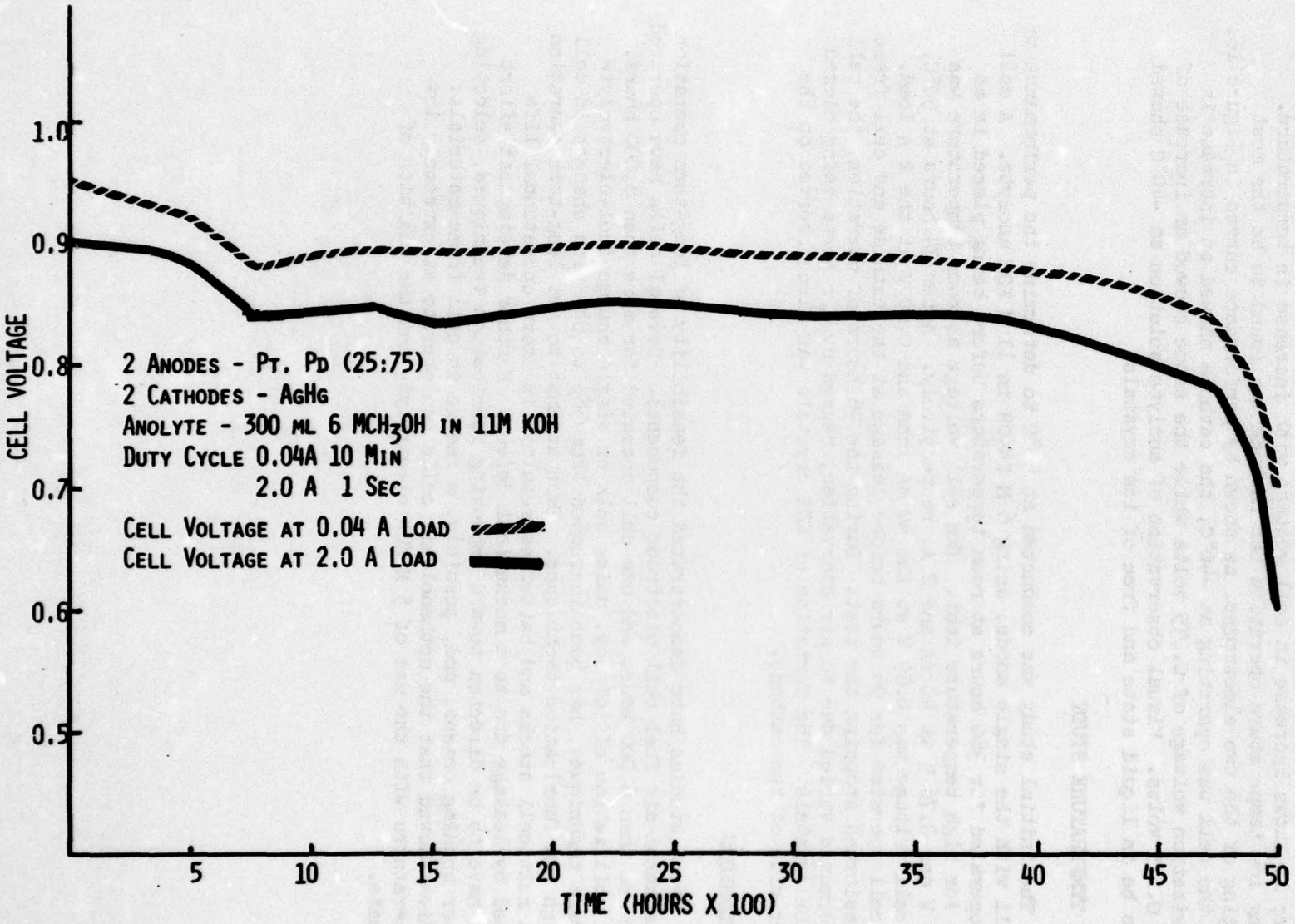

Figure 14. Current Voltage Data of Dual Anode Cell

Figure 15 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 by performance curves in Figure 16. When the cell was operating at -40°C, the cathode showed an increase in polarization voltage of 0.275 volts while the anode showed an increase of only 0.115 volts. Visual observation of anolyte solution at -40°C showed it to be in liquid state and free of ice crystals.

HIGH TEMPERATURE STUDY

The initial study was conducted at 50°C to determine the performance of a cell with the single anode, using 6 M CH_3OH in 11 M KOH anolyte. A cell was operated for 380 hours at room temperature before being placed in an oven for high temperature test. The cell voltage at room temperature was 0.90 V and 0.76 V at 40 mA and 2 A, respectively. After 24 hours at 50°C, the cell voltage was 0.89 V at the 40 mA load and 0.80 V at the 2 A load. The cell operated for 96 hours before leakage at the cathode and cell frame necessitated stopping the test. During the 96 hours of operation, the cell performance varied due to air starvation, caused by air ports being closed by KOH crystals. The formation of KOH crystals was also observed on the outer side of the cathode.

CONCLUSIONS

These studies have demonstrated the feasibility of long-term operation of methanol-air fuel cell electrode components. Several cells have operated for more than 6,000 hours and one cell operated for more than 8,000 hours. Fuel utilization efficiency, using bulk or single charge fuel-electrolyte storage techniques, has been increased from 56% to 84% 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 leakage due to a mechanical defect. Further development effort will have to be directed toward improving fabrication techniques, selecting better bonding cement, and, possibly, a change in cell frame materials. Studies showed that the methanol-air cells can operate at extremely low temperatures with the use of 5 M KOH electrolyte and the addition of formate.

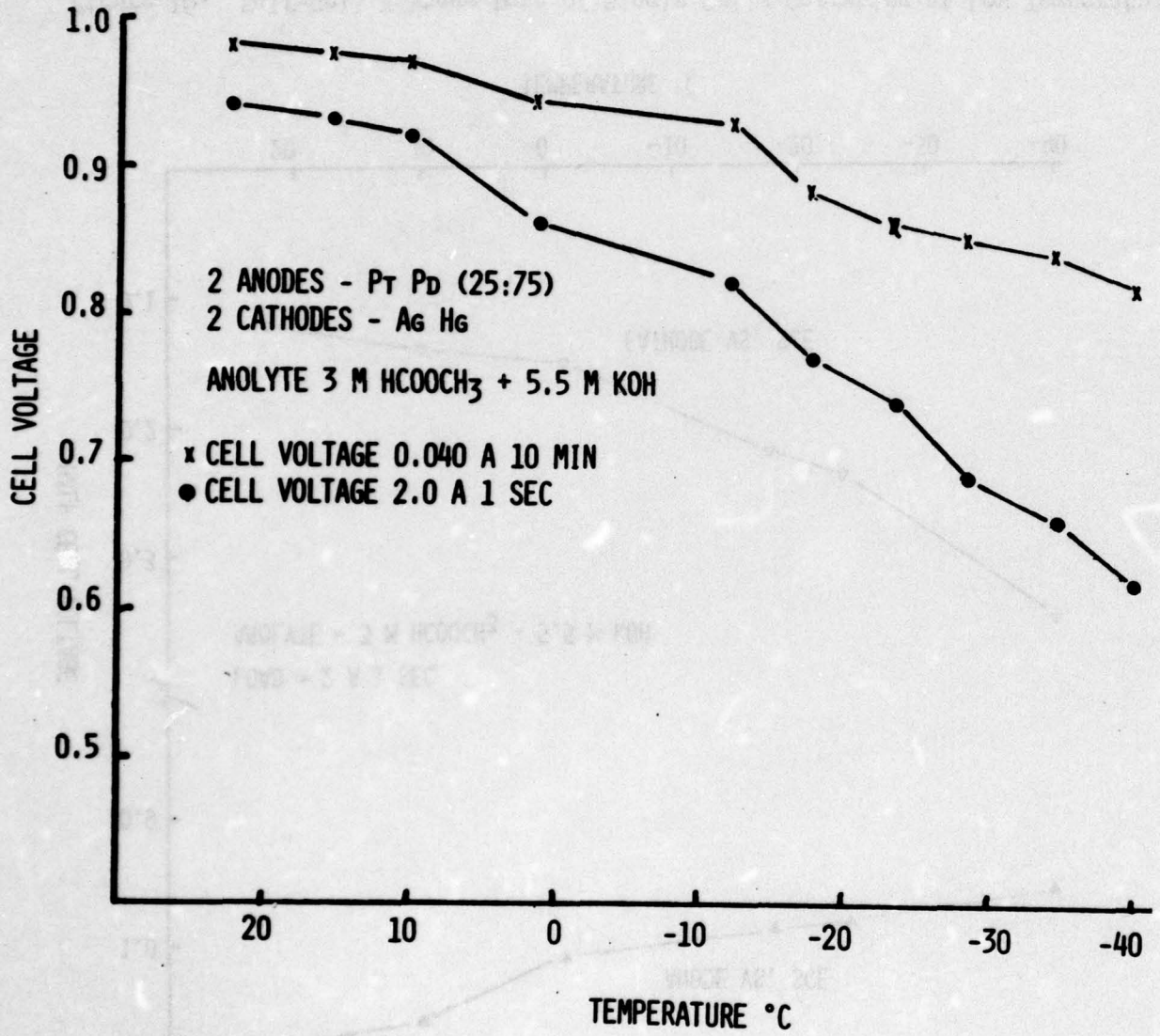

Figure 15. Current Voltage Data of Single Cells Operating at Low Temperatures

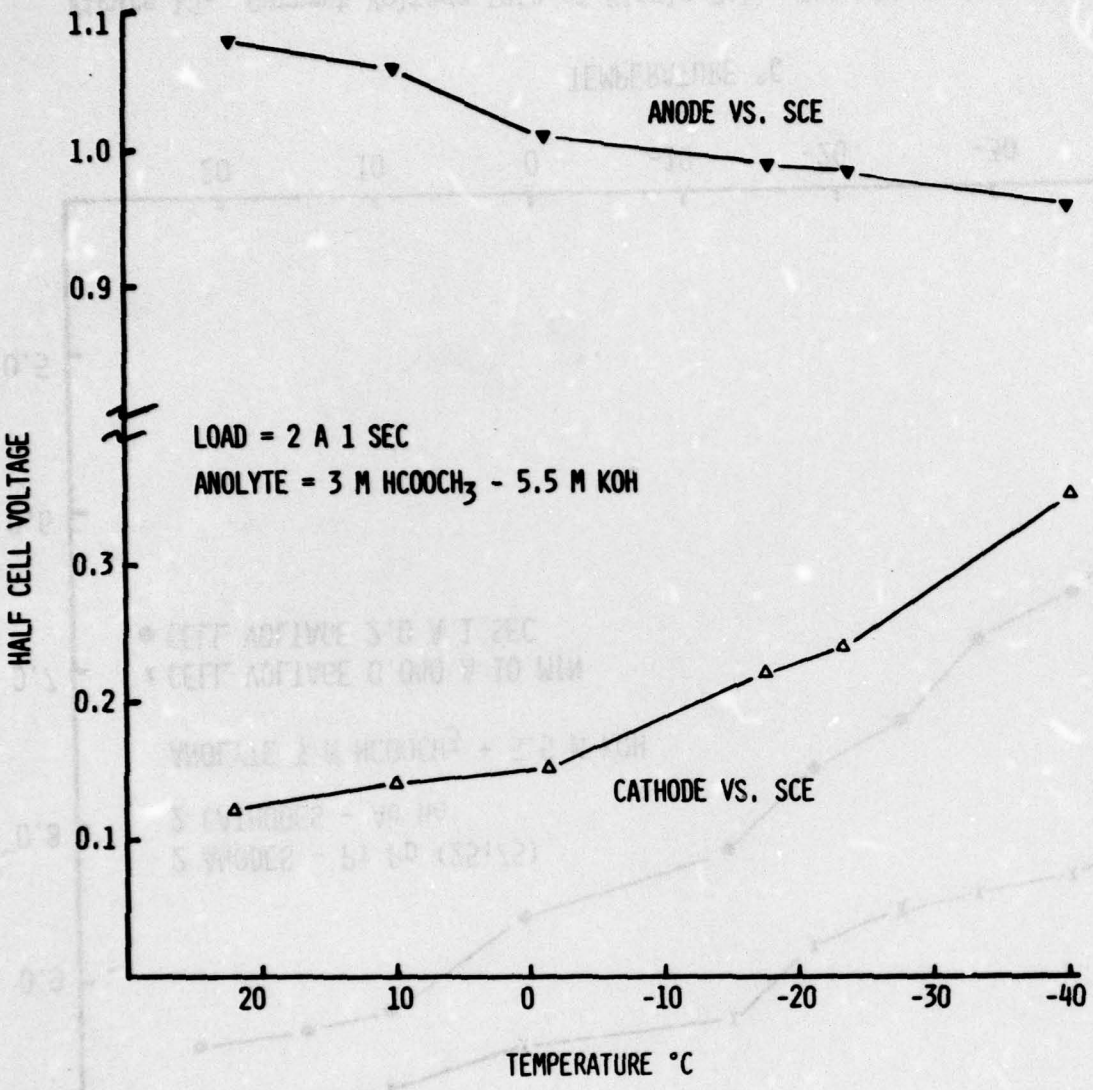

Figure 16. Half-Cell Voltage Data of Single Cells Operating at Low Temperatures