Final Report

Small Fuel Cell to Eliminate Pressure Caused by Gassing in High Energy Density Batteries

(30 June 1965 - 30 June 1966)

Contract No. NAS 5-9594

Prepared by

Missile and Space Systems Division
Astropower Laboratory
Electrochemistry Department
Douglas Aircraft Company, Inc.
Newport Beach, California

for

Goddard Space Flight Center
Greenbelt, Maryland

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c/932

Figure 1. Ruptured 15 Ah Ag/Zn Cell

SUMMARY AND CONCLUSIONS

Silver-zinc batteries are known to evolve hydrogen and/or oxygen during operation and on stand.[1] Such gassing presents a severe problem in developing completely sealed batteries because gassing can result in high pressures and ultimately rupture the battery case.

This program was concerned with miniature hydrogen-oxygen fuel cells installed on the battery to consume evolved gases. In the process the fuel cells also deliver electrical energy that may be used for an auditory warning or telemetering response indicating battery gassing. It was demonstrated by the conclusion of this program that miniature fuel cells can be used successfully to relieve the pressure buildup in commercial silver-zinc cells.

The program was experimental and was devoted primarily to testing previously devised miniature fuel cells in both simulated and actual battery gassing environments. These tests included life tests in battery simulators, determining the effect of temperature and gas composition on performance, and evaluating water removal techniques. Performance tests of these miniature fuel cells in 100-amp-hour silver-zinc cells were also included. Fifteen miniature fuel cells were delivered to NASA Goddard.

A. Most Significant Results and Conclusions

1. Miniature fuel cells sealed into commercial silver-zinc cells consume evolved hydrogen and oxygen gases at a sufficiently rapid rate for maintenance of a minimal pressure level within the battery throughout its life without a significant increase in battery weight. The miniature fuel cell operates during charge, discharge and open circuit stand in the fully charged condition. Under similar battery operational conditions without an incorporated miniature fuel cell, rupture of the battery case can occur, as shown in Figure 1.
2. Miniature fuel cells can function effectively in the open-ended mode of gas flow for extended periods of time. Continuous operational life of as long as 8,000

hours was obtained and it appears that still longer life would be possible.

3. Accurate data on gassing behavior in commercial 100-ampere-hour silver-zinc cells can be obtained from installed miniature fuel cells. Both the nature and quantity of the gases evolved can be determined in a direct manner far more expeditiously than with any other method.

B. Other Noteworthy Results and Conclusions — Silver-Zinc Cell Gas Simulator Studies

1. Miniature fuel cells can function effectively in the open gas flow mode for extended periods of time. Eight cells with electrode areas ranging from 0.25 to 5.0 cm^2 functioned effectively in this manner under simulated battery gassing environments for operating times ranging from at least 4,000 to 8,000 hours. These miniature fuel cells would function over longer periods of time, if necessary.

2. Miniature fuel cells can function effectively in the dead end mode of gas flow for extended periods of time. Six cells with electrode areas ranging from 0.25 to 5.0 cm^2 functioned effectively in this manner under simulated battery gassing environments for operating times ranging from 1,900 to 6,000 hours.

3. The following relationship between miniature fuel cell size and its gas consumption capability was established. Fuel cells having cross sectional areas of 0.25 cm^2, 1.0 cm^2 and 5.0 cm^2 are capable of consuming hydrogen at rates of at least 1.6 cc/hr, 6.3 cc/hr and 10.6 cc/hr, respectively, over extended periods of time.

4. Functionality of miniature fuel cells was demonstrated for extended operating times (at least one month) on mixtures of hydrogen and oxygen in the anode, and pure oxygen in the cathode.

5. The effect of temperature on miniature fuel cell performance was determined. Electrical output at 40°C was approximately twice as high as at 25°C. Output at 0°C was approximately 80% of that at 25°C.

6. A relationship between miniature fuel cell open circuit voltage and hydrogen concentration in an anodic gas mixture of hydrogen and oxygen was determined experimentally. These results should be useful in determining internal cell (battery) gas composition by remote control or telemetering.

C. Commercial Silver-Zinc Cell Studies

1. Two miniature fuel cells are required for complete control of internal pressure in a sealed silver-zinc cell during all phases of its operation because both H_2 and O_2 are evolved. However, on open circuit stand or on limited, low level operation, only one miniature fuel cell is required (to consume hydrogen).

2. Two miniature fuel cells, both having 1.0 cm^2 cross sectional electrode areas, installed in 100 ampere-hour cells, limited the pressure rise to not more than 1.5 psig over the following cycling regime: 2-hour discharge at 20 amperes (40% depth of discharge) and 22-hour charge at 2 amperes. The ratio of evolved hydrogen to oxygen gases was approximately the same, i.e., 2.7 to 1 in one cell and 3.8 to 1 in another. The total gassing rates can vary between cells; total hydrogen and oxygen evolution rates in one silver-zinc cell were six times higher than those in another silver-zinc cell under identical operational conditions. Average gassing rates were 0.08 cc H_2/hour and 0.03 cc O_2/hour in one cell and 0.49 cc H_2/hour and 0.13 cc O_2/hour in another cell.

3. Similar gassing patterns were found for 15-ampere-hour commercial silver-zinc cells with two installed miniature fuel cells.

4. It would be possible to employ the product water derived from miniature fuel cells for life support purposes if the amount of battery gassing were large enough.

D. Recommended Future Effort

The findings of this program indicate that important applications of miniature fuel cells may be found in sealed silver-zinc batteries. Exploratory proprietary efforts have indicated that miniature fuel cells could be applied to sealed nickel-cadmium and lead-acid cells as well. The type of miniature fuel cells used in the current program could be effective in consuming and detecting the gases evolved in sealed nickel-cadmium and lead-acid cells. Other types of miniature fuel cells developed during a company sponsored program employed solid rather than gas type electrodes and manifested regenerative capability. These are

recommended for continued investigation, where external gas storage is either limited or undesirable.

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1.0 INTRODUCTION

Gassing in high energy density batteries involves the formation of hydrogen, oxygen or both within the batteries by any of several mechanisms. These include decomposition or dissolution of active electrode materials, liberation of absorbed gases, or internal electrolysis. Gassing may occur during all modes of operation including charge, discharge, and open circuit stand. The type of gas and the rate and extent to which it is evolved depend upon several factors including the type of battery, ambient temperature, and the charge-discharge regime to which the battery is subjected.

The phenomenon of gassing presents a serious problem in the development of completely sealed batteries. High pressures are developed that may lead to rupture of the cell case and to battery failure.

A unique method of dealing with this problem has been devised at Astropower Laboratory which consists of using miniature fuel cells to consume evolved battery gas. This concept had been tested on an earlier proprietary program.[2] The miniature fuel cells perform this function by electrochemically consuming the hydrogen or oxygen gases inside the battery to form water. Two fuel cells, one for consuming hydrogen and the other for oxygen, are usually required for this purpose as will be shown subsequently. One is supplied externally with hydrogen to consume the oxygen and the other is supplied externally with oxygen to consume the hydrogen. Of additional interest here is the use of alternative types of regenerable miniature fuel cells with solid rather than gas-type electrodes, i.e., silver or mercuric oxide in place of oxygen, and zinc or cadmium in place of hydrogen. Astropower has made considerable progress in developing these types of miniature fuel cells for this purpose.[3]

At the start of the current program it was not known how a miniature fuel cell could perform under gassing conditions in a silver-zinc cell. Such critical aspects as mode of installation into the battery,

stability of fuel cell performance and life and actual fuel cell dimensions for a particular silver-zinc battery type and size were to be determined. Although it was felt that a fuel cell designed around the KOH-asbestos membrane system was most appropriate for alkaline battery application, other membrane systems could offer advantages as well. The following program plan, based on the stipulations of the project work order, as well as on continuing discussions with technical personnel of NASA-Goddard Space Flight Center, was pursued. The type of batteries involved herein are of the silver-zinc type and the miniature fuel cells involved are of the hydrogen-oxygen gaseous diffusion type.

Outline of Program Plan

1. To select the optimum method of installing a miniature fuel cell on a silver-zinc cell. Three previously devised methods were considered here, including a "Jack" mounting, a "Screw" mounting, and a "Deep Insert" mounting.
2. To determine the long-term gas consumption capability of miniature fuel cells for as long as 5,000 hours.
3. To determine the relationship between miniature fuel cell size and gas consumption capability.
4. To design and fabricate the optimum type of miniature fuel cells based on the above for a given commercial silver-zinc cell.
5. To conduct performance tests on the miniature fuel cell in silver-zinc batteries at the 100 ampere-hour capacity level.
6. To deliver 15 miniature fuel cells to NASA-Goddard Space Flight Center at the conclusion of the program.

These objectives were achieved during the course of the program. Most significantly, it has been demonstrated that miniature fuel cells can be installed in commercial silver-zinc cells; and in an entirely reliable manner can consume the gases evolved within the cells. Therefore, the life of a battery can be prolonged with an added measure of safety.

The description of experimental procedures, results and discussions are given in the sections which follow.

2.0 TECHNICAL DISCUSSION

This section contains a complete description of the miniature fuel cells involved and results of all tests performed on them in both simulated and actual battery gassing environments.

2.1 Description of Miniature Fuel Cells

Basic elements of all miniature fuel cells employed on this program were essentially the same, and consisted of platinum electrocatalyst for both hydrogen and oxygen, and potassium hydroxide electrolyte at 30% concentration contained in an asbestos matrix having a thickness of one-eighth inch. The significant differences between cells were in the specific type or grade of platinum catalyst and overall cell configuration. Three general types of cell configurations were employed and were designated as the "initial," "modified," and "final" types. Overall sizes ranged from 0.25 cm diameter to 5.0 cm diameter. A brief description of each type is given below.

2.1.1 Initial Cell Type

Components of the initial miniature fuel cell are shown in Figure 2.

Both hydrogen and oxygen electrodes are identical and consist of platinum black, which has been bonded under pressure to a platinum-plated silver screen. A few strands of each screen pass through the cell frame and serve as external electrical leads. The electrodes in turn are bonded under pressure to a disc of sheet asbestos to form a rigid electrode-electrolyte assembly. A polyurethane rim is mounted on the outer periphery of the membrane by means of the jig designed for this purpose. The purpose of this rim is to provide internal gas seals both between compartments and external to the atmosphere. The electrode-electrolyte assembly, along with the gas distribution plates, are mounted in the cell housing to form the complete miniature fuel cell as shown in Figure 2. The housing is made of nylon, and the

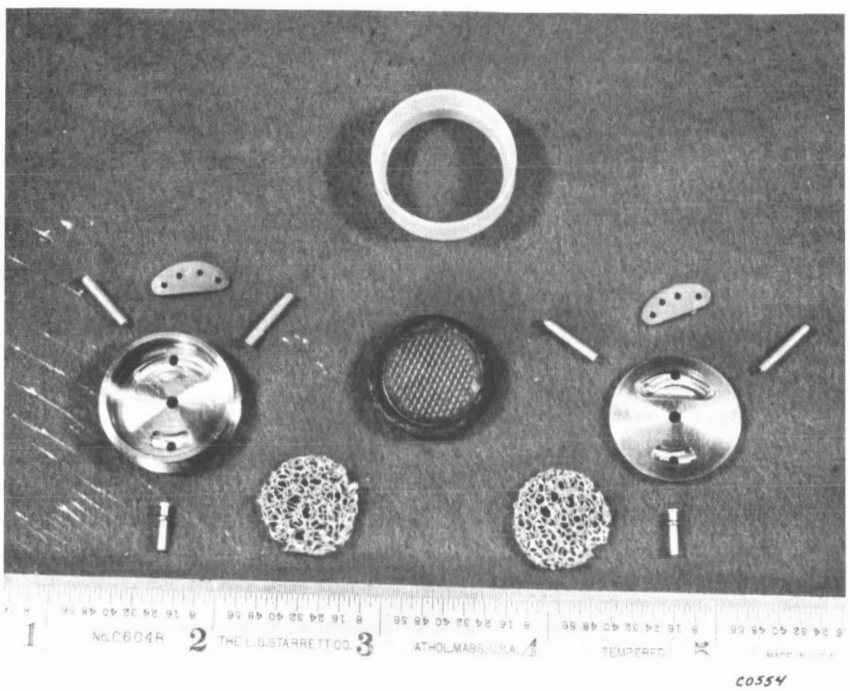

Figure 2. Initial Miniature Fuel Cell

distribution plates are made of stainless steel. One of the gas distribution plates contains inlet and outlet tubes for transmitting a gas (either hydrogen or oxygen) from an external supply tank. The other distribution plate has a machined center hole for transmitting gases to the electrode from either a silver-zinc battery or one of the battery simulators. The outside of this end plate is threaded for direct mounting onto either the battery or simulator.

2.1.2 Modified Type

Electrodes for this cell (Figure 3) were obtained from the American Cyanamid Company and included their Types A. B. -6, A. B. -40, and A. A. -1. Each of these was similar in that they consisted of platinum black catalyst deposited on a collector screen with the addition of a Teflon water-proofing agent. The only difference was in composition of the collector screens. Gold-plated nickel, nickel, and tantalum were the materials for Types A. B. -6, A. B. -40, and A. A. -1, respectively. The electrodes were cut to the desired dimension with specially prepared die punches. The same electrode material was employed for both hydrogen and oxygen electrodes in any given test.

The electrolyte again consisted of 30% KOH solution impregnated in a layer of 1/16-inch fuel-cell grade asbestos.

Electrodes were spot-welded to the gas distribution plates to provide good electrical contact. External electrical leads were then taken directly from external surfaces of these plates. Both plates were very similar to those described above; one contained inlet and outlet tubes for external gas supply and the other contained a hole for transmitting battery or simulator gases to the electrodes. The outside of the latter plate was threaded for mounting in a battery or simulator. Material of construction was stainless steel, as above.

Somewhat different types of gas seals were employed in this cell. Internal sealing between compartments was provided by compression of the outer periphery of the asbestos layer

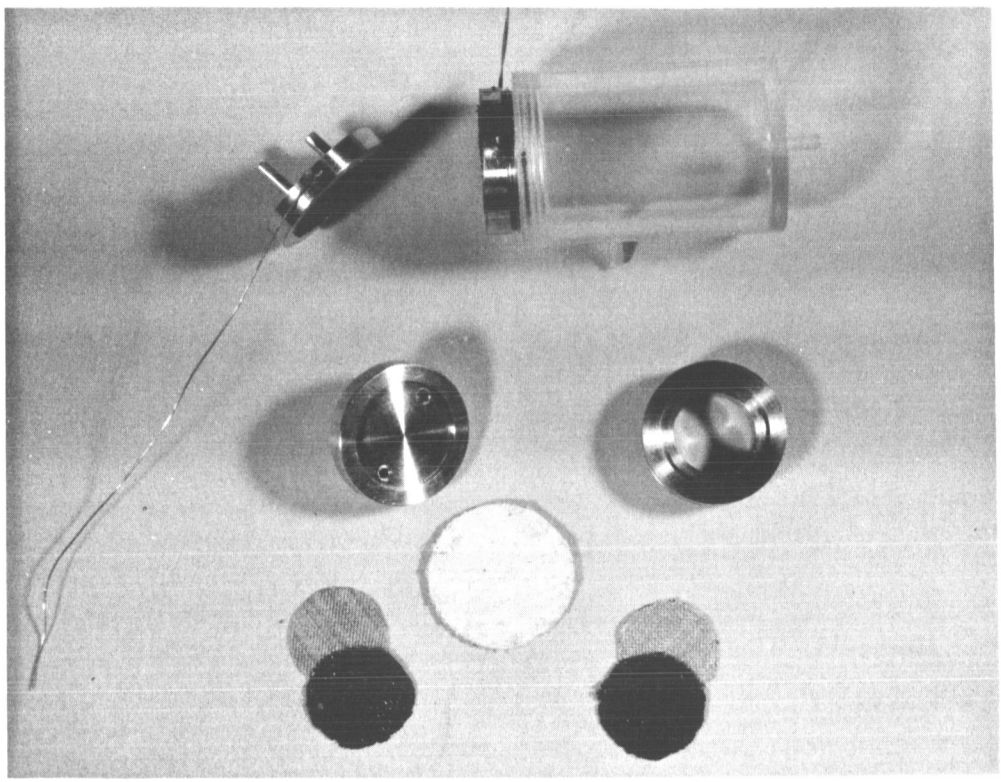

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Figure 3. Modified Miniature Fuel Cell

between the surfaces of the gas distribution plates. External sealing was provided by a bead of epoxy resin around the circumference where the cell halves meet.

Several sizes of these cells have been built with overall dimensions ranging from 0.25 inch in diameter to 5.0 inches in diameter.

2.1.3 Final Type

The final fuel cell configuration (Figure 4) is essentially the same as the modified type above with a few minor additions. The first was use of an internally-threaded plastic cover to hold the two cell halves together, instead of the bead of expoxy as above. The cover was machined in the form of a hexagonal nut so that it could be reproducibly torqued to the cell bottom. The second was addition of a special thread seal to provide insurance against gas leakage in the threads of the installed assembly. Detailed machine drawings of this type are given in Appendix A. Fifteen cells of this type were delivered to NASA-Goddard Space Flight Center.

2.1.4 Installation in Batteries

Three general methods of incorporating micro fuel cells into batteries were devised in a proprietary program.[3] The first of these is the "Jack" type arrangement shown in Figure 5. In this case the cell is designed for direct mounting on the battery vent tube. Battery gases must pass through this tube before entering the fuel cell. The second is the "Screw" type as shown in Figure 6. In this case the outer frame of the fuel cell is threaded into the battery case. Path length through which the gases must travel to reach the fuel cell is somewhat shortened in this case. (This is the type which has been delivered to NASA-Goddard.) The third is the "Deep Insert" type as shown in Figure 7. In this case the fuel cell is mounted deep inside the battery case and exposed directly to the gases evolved from the electrodes. A manifolding arrangement may also be employed as shown in Figure 8.

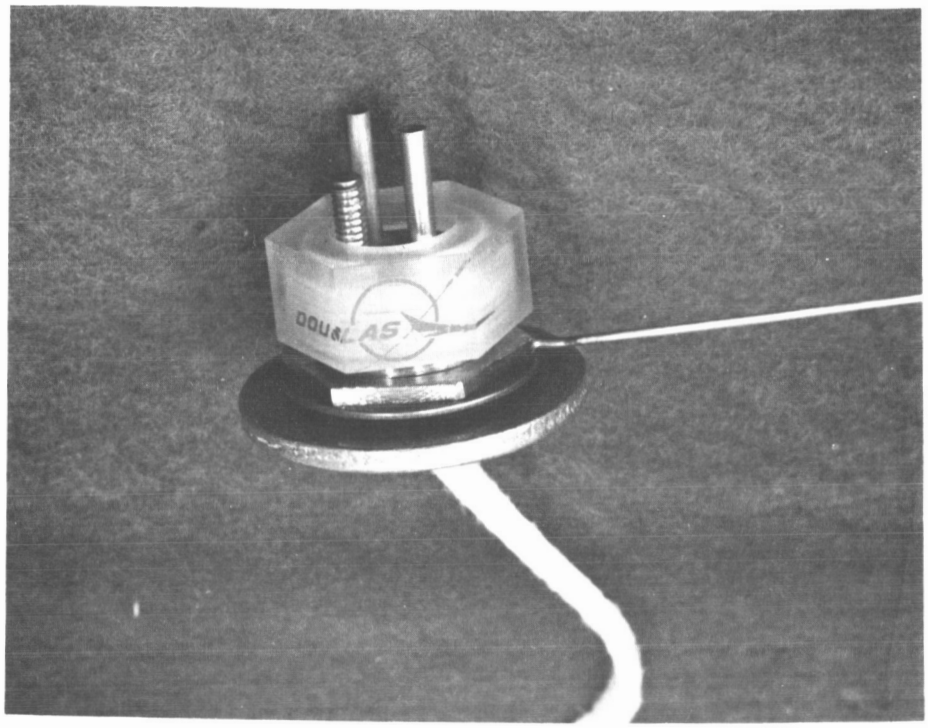

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Figure 4. Final Type of Miniature Fuel Cell

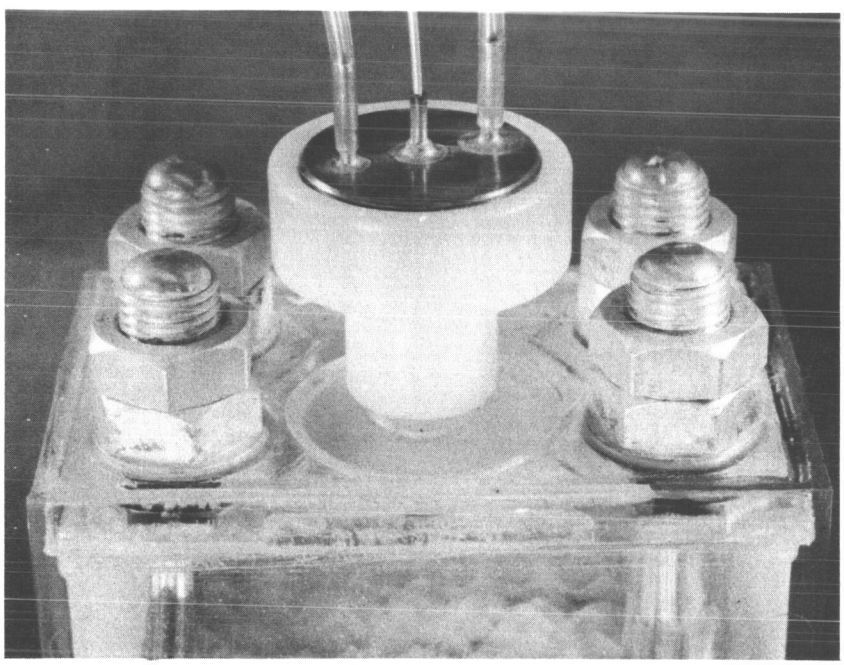

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Figure 5. Jack-Type (Press Fit Connection of Miniature Fuel Cell to Actual Ag/Zn Battery

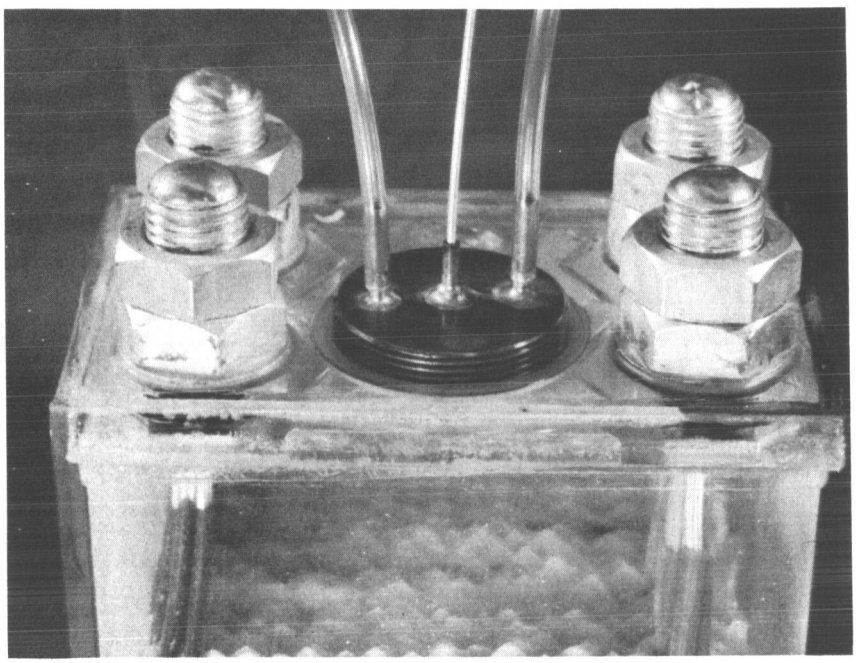

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Figure 6. Screw-Type Connection of Miniature Fuel Cell to Actual Ag/Zn Battery

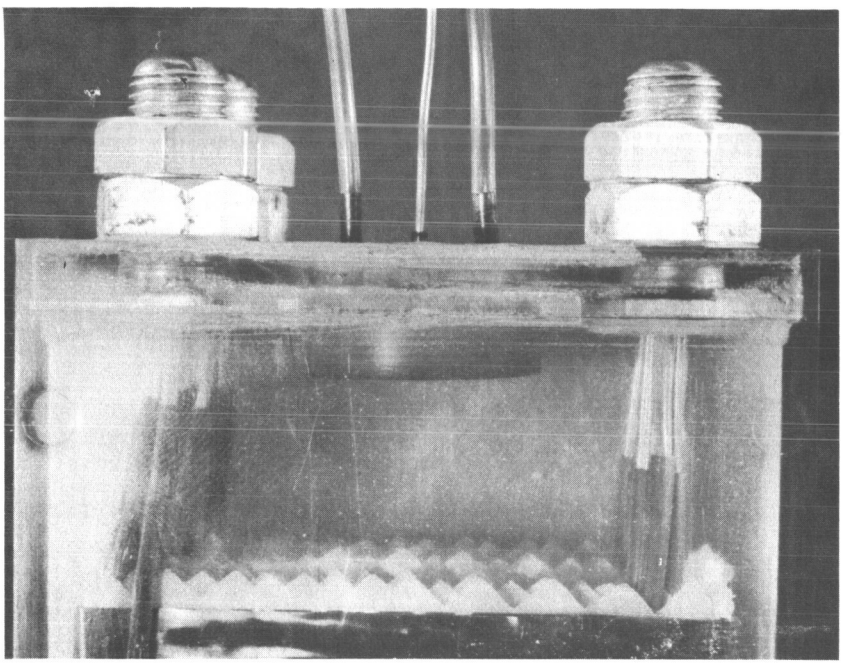

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Figure 7. Deep Insert Type of Miniature Fuel Cell Connection to Actual Ag/Zn Battery

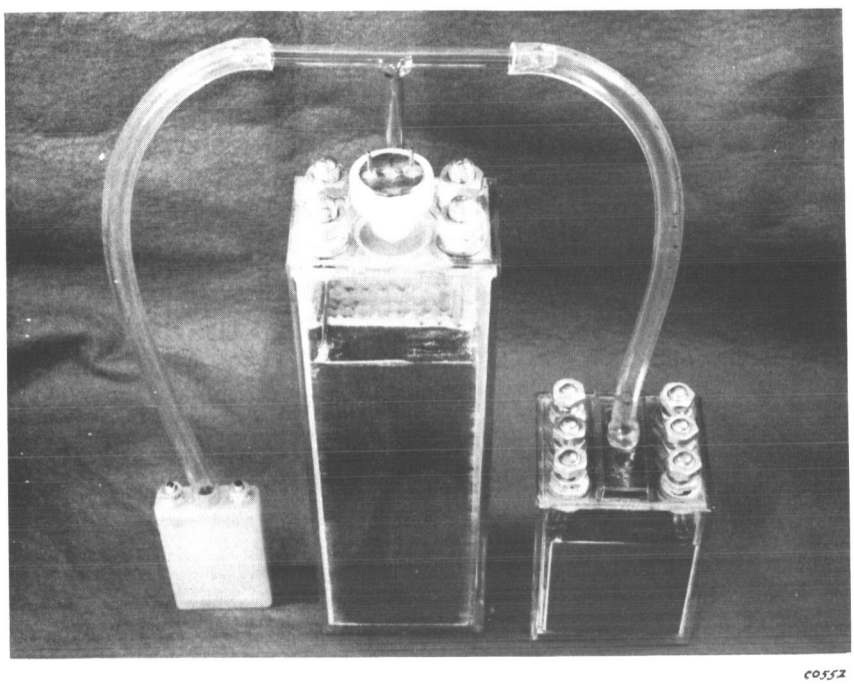


Figure 8. Application of Single Miniature Fuel Cell as Pressure Controller for Three Ag/Zn Batteries by Means of Manifolding Agreement

In this case the evolved gases from several batteries are manifolded to a single miniature fuel cell.

2.2 Tests in Battery Simulators

The purpose of this investigation was to determine the operational characteristics, including life, of miniature fuel cells employing the KOH-asbestos matrix type of electrolyte. Design goal was for 5,000 hours of continuous operation at 25°C. An integral part of this study was to derive a relationship between size of a miniature fuel cell and its gas consumption capability.

The tests were carried out in specially designed battery gassing simulators wherein gas compositions and flows could be closely controlled. Performance was determined as a function of gas composition, ambient temperature, and cell configuration. Methods of removing product water were also evaluated.

2.2.1 Life Tests Under Open Gas Flow Without Wicking

The purpose of these tests was to determine optimum components of the miniature fuel cells for long term continuous operation by the "open gas-flow mode" in the simulators shown in Figure 9. Pure hydrogen and oxygen were passed at flow rates of two cc/hour into the anode and cathode compartments of the miniature fuel cell. Excess gases that were not consumed were vented to the atmosphere. Water balance was maintained by adjustment of gas flow rates. Operating voltage under load as well as complete polarization data were measured periodically. Both the "initial" and "modified" cell types were employed in these tests.

Results of these tests are presented in Tables I, II, and III and are discussed in more detail below.

The cell in Test 1 employed the initial configuration and electrodes as described above in Section 2.1.1. Testing was initiated

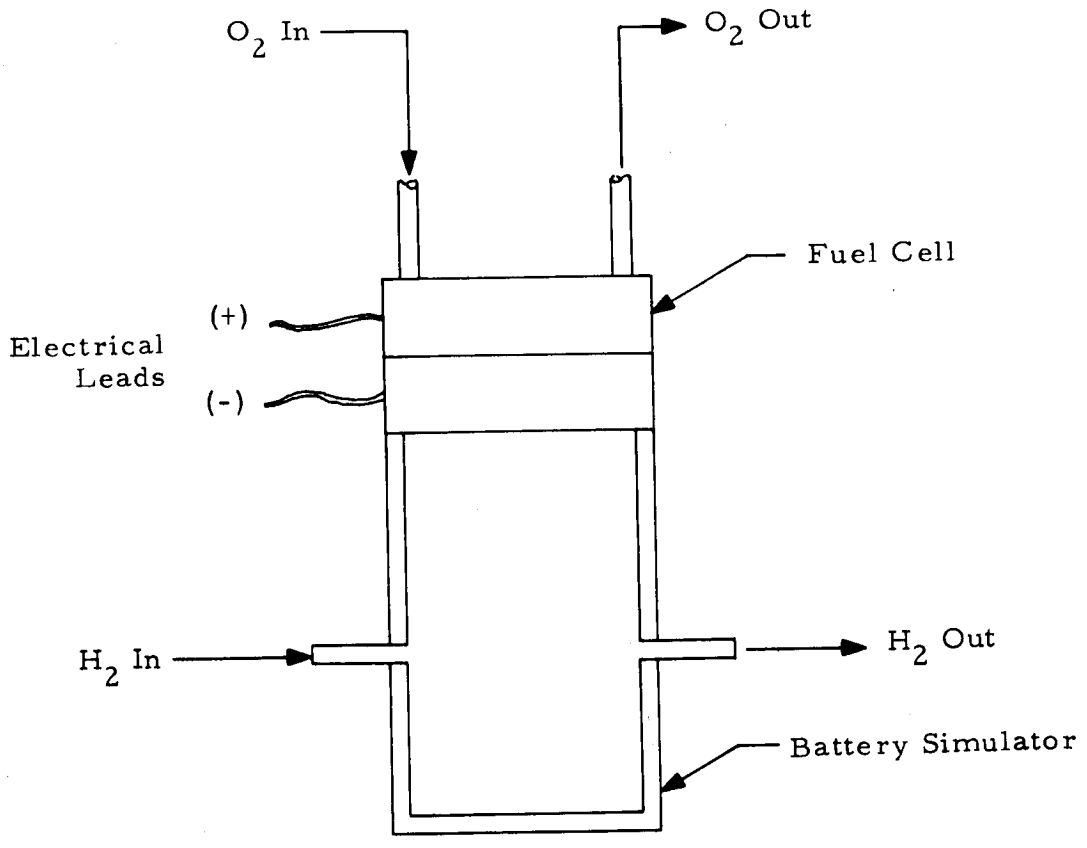


Figure 9. Schematic Diagram of Open Flow Tests

TABLE I

LIFE TESTS OF MINIATURE FUEL CELLS IN OPEN FLOW MODE OF OPERATION WITHOUT WICKS

Test No.	Cell Type	Electrode Type	Electrode Area (cm^2)	Load (ohms)	Time[a] (hrs)	Initial Voltage (volts)	Final Voltage (volts)
1	Initial	Proprietary	1.0	1000	7958	0.80	0.50
2	Modified	A. B. -6	1.0	1000	6105	0.90	0.80
3	Modified	A. B. -40	1.0	1000	5729	0.95	0.95
4	Modified	A. B. -6	1.0	100	5429	0.80	0.70
5	Modified	A. B. -40	1.0	100	5529	0.85	0.80
6	Modified	A. B. -40	0.25	4000	5049	0.95	0.92
7	Modified	A. B. -40	5.0	200	4899	0.95	0.60
8	Final	A. B. -40	1.0	1000	4233	0.88	.80

(a) All tests were terminated after the indicated number of hours. Longer operational life was possible.

TABLE II

INITIAL POLARIZATION DATA OF MINIATURE FUEL CELLS IN OPEN FLOW MODE WITHOUT WICKS

Current Density (ma/cm^2)	Potential (volts)							
	Test Number							
	1	2	3	4	5	6	7	8
0	0.91	1.01	1.02	1.02	0.94	1.01	1.05	1.00
1	0.75	0.95	1.00	0.96	.92	0.92	.97	1.00
2	0.63	0.92	0.90	0.92	.90	0.87	0.86	1.00
5	0.40	0.87	0.90	0.84	.86	0.75	0.78	.95
10	--	0.82	0.89	0.75	.80	0.61	0.63	.93
20	--	0.60	0.82	--	--	--	--	.90
50	--	--	--	--	--	--	--	.85
100	--	--	--	--	--	--	--	.75

TABLE III

FINAL POLARIZATION DATA OF MINIATURE FUEL CELLS IN OPEN FLOW MODE WITHOUT WICK

Current Density (ma/cm^2)	Potential (volts)							
	Test Number							
	1	2	3	4	5	6	7	8
0	0.85	0.95	0.99	0.98	0.95	0.98	1.00	0.98
1	0.73	0.94	0.98	0.96	0.92	0.89	0.98	0.95
2	0.50	0.90	0.95	0.90	0.90	0.82	0.80	0.90
5	0.29	0.80	0.89	0.80	0.82	0.70	0.75	0.84
10	--	0.75	0.85	0.50	0.75	--	0.55	0.80
20	--		0.79					0.70
50	--							--
100	--							--

in the early portion of the program and continued to the end for a total operating time of nearly 8,000 hours. Although this cell was found to exhibit relatively stable performance throughout this period, its current output or corresponding gas consumption capability was not optimal (see polarization data in Tables II and III). The limited output was attributed to inactive electrodes. This type of cell might be recommended for extremely long term operation in a silver-zinc battery in which very low but continuous gassing rates were anticipated.

The cells in Tests 2 and 3 contained American Cyanamid fuel cell electrodes Types A. B. -6 and A. B. -40, respectively, and were both discharged across a 1000-ohm load. Both were found to exhibit quite stable performance for operating times of approximately 6,000 hours. Longer operating lives were still possible. Operating voltage and polarization characteristics of the cell in Test 3 (with A. B. -40 electrodes), have remained exceptionally stable and slightly higher than the corresponding characteristics of the cell in Test 2 (with A. B. -6 electrodes). This trend was apparent earlier in the test program and on this basis it was decided to employ A. B. -40 electrodes in the battery tests near the end of the program.

The cells in Tests 4 and 5 also contained American Cyanamid fuel cell electrodes Types A. B. -6 and A. B. -40, respectively. These cells were each discharged across a lower resistance of 100 ohms, and therefore operated at higher currents than Tests 2 and 3 above. Performance of both of these cells remained relatively constant throughout the test period of over 5,000 hours but at somewhat lower voltages than corresponding Tests 2 and 3 above.

The significant parameter in Tests 6 and 7 was electrode area. Active area in Test 6 was 0.25 cm^2 or 1/4 of that employed in the preceding tests; the area in Test 7 was 5.0 cm^2 or 5 times that in the preceding tests. External loads on each were selected to give the same current densities as in Tests 1 through 3 inclusive,

i.e., 4000 ohms for Test 6 and 200 ohms for Test 7. Performance of the cell in Test 6 was found to remain quite constant for the indicated test period of slightly over 5,000 hours. Performance of the cell in Test 7, however, was found to decline appreciably during approximately the same test period. This decline was attributed to electrode flooding caused by inadequate gas flow for evaporating product water.

The distinguishing feature of the cell in Test 8 was its new case and cover design. These were modified to give more reliable gas seals and ease of assembly. Electrodes were of the American Cyanamid Type A. B. -40 with an electrode cross sectional area of 1.0 cm^2. Results have indicated that this cell can operate effectively and quite stably for at least the test period of over 4,000 hours, and most likely well beyond 5,000 hours. This cell type is essentially identical to the types employed in the battery tests (Sections 2.2.7 and 2.3) and delivered to NASA-Goddard.

Four additional tests employing American Cyanamid Type A. A. -1 electrodes were carried out earlier in the program. These were terminated after various intervals of 500 to 800 hours when performance had degraded to very low levels. The degradation was attributed to use of tantalum based A. A. -1 electrode material. Another test employing an organic anion exchange membrane (Ionics Type III EZL) in place of the KOH-asbestos electrolyte was also carried out during the early portion of the program. This test was terminated after 400 hours when cell performance had degraded to a very low level. This was attributed to oxidation of the membrane material.

2.2.2 Life Tests Under Dead-End Flow Without Wicking

In Tests 9 and 10 (Table IV) the gases were supplied to the cell in the dead end mode (without venting excess gases) and without wicks. Gases were stored in small containers and connected to each end of the cell with a short segment of tubing. For safety reasons,

TABLE IV

LIFE TESTS OF MINIATURE FUEL CELLS IN DEAD END MODE OF OPERATION AND WITHOUT WICKS

Test Cell Number	Cell Type	Electrode Type	Electrode Area (cm^2)	Load (ohms)	Time (hrs)	Notes
9	Modified	A. B. -6	1. 0	1000	1500	Voltage above 0. 8 v for majority of run
10	Modified	A. B. -6	1. 0	100	150	Terminated due to flooding, voltage above 0. 7 v for majority of run

the size and pressure of the gas containers was kept to a minimum and consisted of 250-ml Erlenmeyer flasks at atmospheric pressure or slightly below it. The flasks were refilled periodically to maintain the pressure level between atmospheric and approximately two inches of mercury vacuum. Electrodes were of the American Cyanamid Type A. B. -6 with an active area of 1.0 cm^2.

Stable performance was observed for Test 9 for over 1500 hours when discharged across a 100-ohm load with a corresponding current of approximately 1.0 ma. Hydrogen consumption rate in this case was approximately 0.4 cc/hour.

Test 10, which was discharged across a 100-ohm load with a corresponding current of approximately 10 ma, was terminated after 150 hours when performance began to decline rapidly. Hydrogen consumption rate in this case was approximately 4.0 cc/hour. The reason for the decline was attributed to electrode flooding as evidenced by an extremely wet condition upon disassembly.

These results signify that a miniature fuel cell without wicks and with 1.0 cm^2 area can consume approximately 630 cc of hydrogen at a rate of 4.0 cc/hour and at least this amount, if not more, at a rate of 0.4 cc/hour.

2.2.3 Life Tests Under Dead End Flow With Wicking

The purpose of these tests was to evaluate the use of wicks in transferring product water from the fuel cell to the battery electrolyte. Such water transfer is a necessity for long term operation of the fuel cell where electrode flooding could limit performance.

The tests were carried out in a simulated battery environment consisting simply of a small Erlenmeyer flask filled with hydrogen containing a small amount of potassium hydroxide solution (see Figure 10). The fuel cell was mounted in a rubber stopper and fitted into the mouth of the flask. One end of the wick was in contact

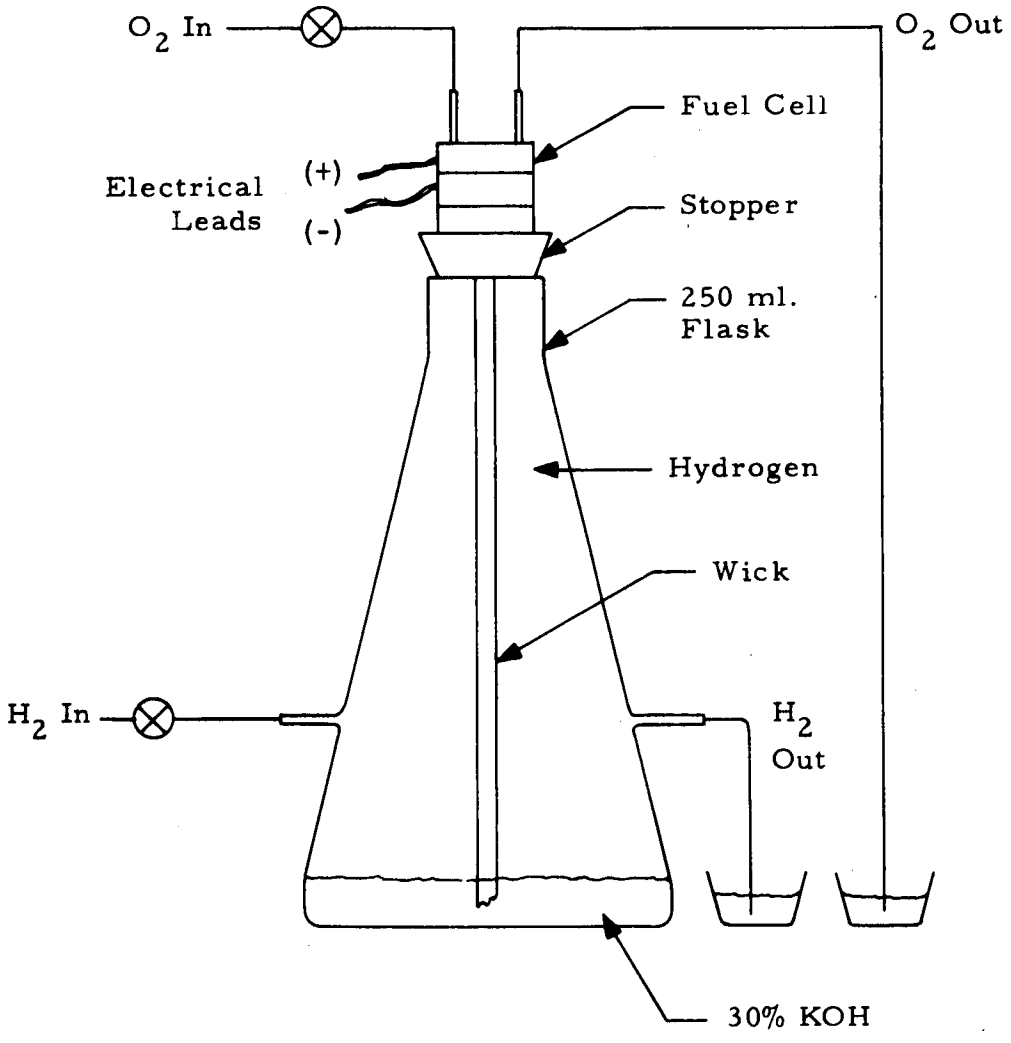


Figure 10. Schematic Diagram of Dead-End Flow Tests with Wicks

with the fuel cell electrolyte through a small hole cut in the middle of the hydrogen electrode and the other end was suspended in the simulated battery electrolyte, 30% KOH. Wick material was from the American Felt Company, Number 61NY185, and was cut in the form of a thin strip with dimension of approximately 1/16-inch by 1/8-inch by 6 inches. Electrodes were American Cyanamid Type A. B. -40 with active area of 1.0 cm^2.

Operation was carried out in a similar manner to that described in Section 2.2.2 but with some modifications. In this case the flask was filled with a small positive pressure of hydrogen from an externally located cylinder. Pressure was then finely adjusted so that there was essentially no flow through the bottle as evidenced by bubbling from a vent line immersed in water. Oxygen pressure and flow were set in the same manner to achieve this dead end mode of operation. The cells were run at constant current with daily adjustment of load on a decade resistance box.

The results obtained are given in Table V, and indicate that miniature fuel cells with 1.0 cm^2 cross-sectional electrode areas can operate for extended periods of time at current densities of 5 and 15 ma/cm^2 at voltages near 0.90 and 0.70 volts, respectively (see Tests 11 and 12). A cell with the same electrode area was unstable at a higher current density of 50 ma/cm^2 (see Test 13).

Performance of cells with both larger (5.0 cm^2) and smaller (0.25 cm^2) electrode areas were also found to be quite stable at current densities of 5 ma/cm^2 (see Tests 14 and 15). Performance of a cell with smaller electrode area (0.25 cm^2) was also found to be stable at a higher current density of 15 ma/cm^2 (see Test 17), whereas performance of a cell with larger electrode area (5.0 cm^2) was found to be unstable (see Test 14).

TABLE V

LIFE TESTS OF MINIATURE FUEL CELLS IN DEAD END MODE OF OPERATION WITH WICKS(a)

Test No.	Electrode Area (cm^2)	Current Density (ma/cm^2)	Time (hrs)	Notes
11	1.0	5	5720(b)	Stable for entire test near 0.9 volt
12	1.0	15	4511(b)	Stable for entire test near 0.7 volt
13	1.0	50	72	Unstable, voltage gradually declined
14	5.0	5	1900(b)	Stable for entire test near 0.9 volt
15	0.25	5	1900(b)	Stable for entire test near 0.9 volt
16	5.0	15	168	Unstable, voltage gradually declined
17	0.25	15	2592(b)	Stable for entire test near 0.6 volt

(a) All tests were conducted with the modified cell type and contained American Cyanamid Type A. B. -40 electrodes.

(b) Longer operational life was possible under stable conditions.

2.2.4 Hydrogen-Oxygen Mixture Tests

The object of these tests was to determine the effect of hydrogen-oxygen mixtures on miniature fuel cell performance. This is pertinent to their intended application in silver-zinc batteries wherein such mixtures are found. Contract work statement called only for examination of anodic H_2-O_2 mixtures versus a pure oxygen cathode. This was extended somewhat to include an examination of cathodic H_2-O_2 mixtures versus a pure hydrogen anode.

Two types of tests were carried out with these mixtures. The first was of the short-term, open-flow type wherein the gases were passed slowly across the fuel cell electrodes. A wide range of both anodic and cathodic mixtures was examined here. The second type was of longer duration in the dead-end mode. In this test a micro fuel cell was operated for an extended time on one anodic mixture. An additional investigation was also carried out on the effect of anodic composition on open circuit voltage. Results of these tests are given below.

2.2.4.1 Open End Gas Flow (Test Series No. 19)

These tests were carried out in the open end gas flow mode of operation. Hydrogen and oxygen were metered with flow meters through the anode compartment with pure oxygen in the cathode in one test series and then through the cathode compartment with pure hydrogen in the anode in another test series.

Results of these studies are given in Figures 11 through 14. Inspection of Figures 11 and 12 indicate that the fuel cell can function satisfactorily with mixtures on its anode side containing up to 30% oxygen. Performance in this mode of operation is noted to decline gradually with increasing oxygen content to a level of 30% oxygen and to fall rapidly with oxygen content increasing between 30 and 50%. Inspection of Figures 13 and 14 indicates that the fuel cell

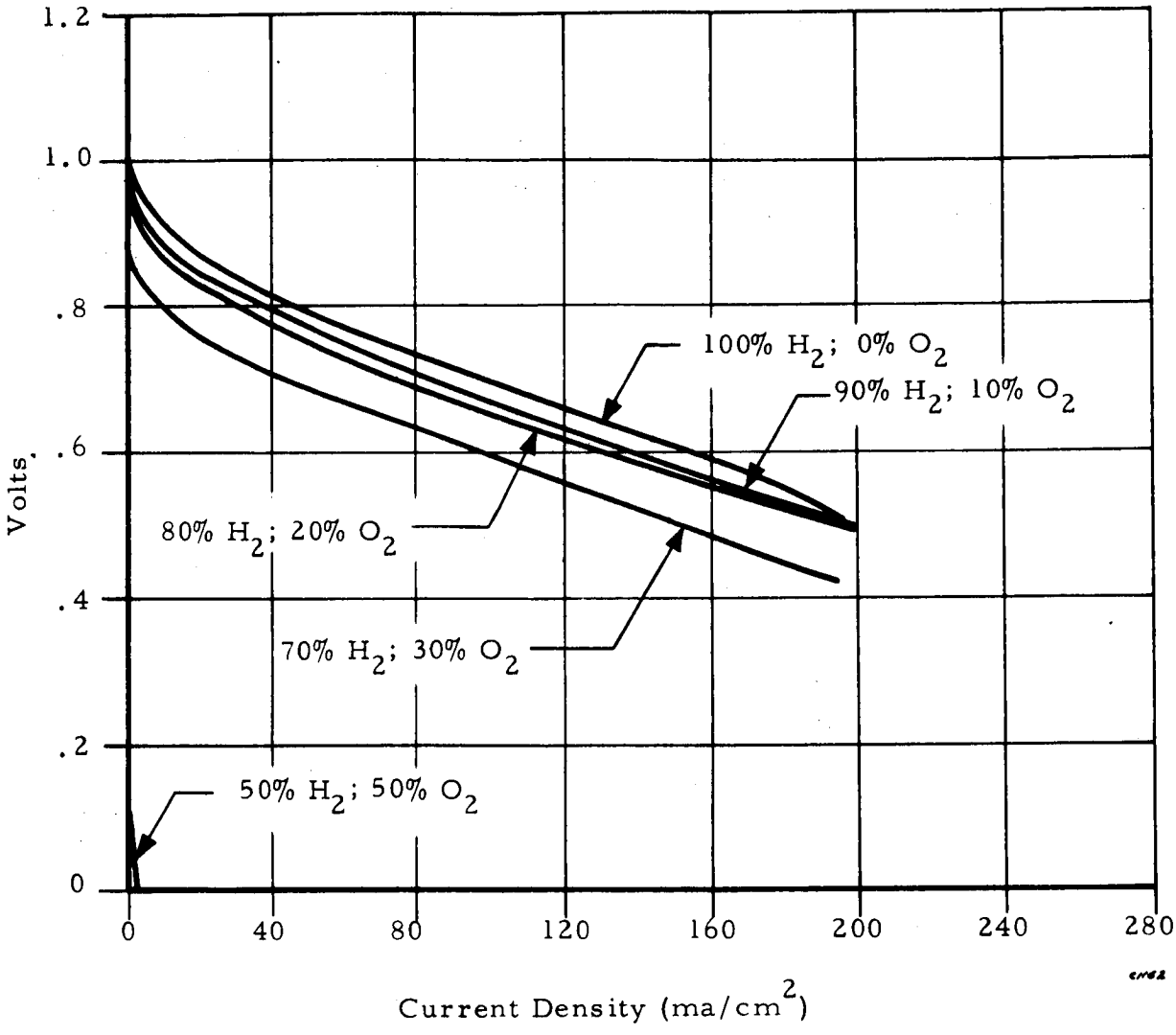


Figure 11. Performance of Miniature Fuel Cell With H_2-O_2 Mixtures in Anode After Several Hours of Operation

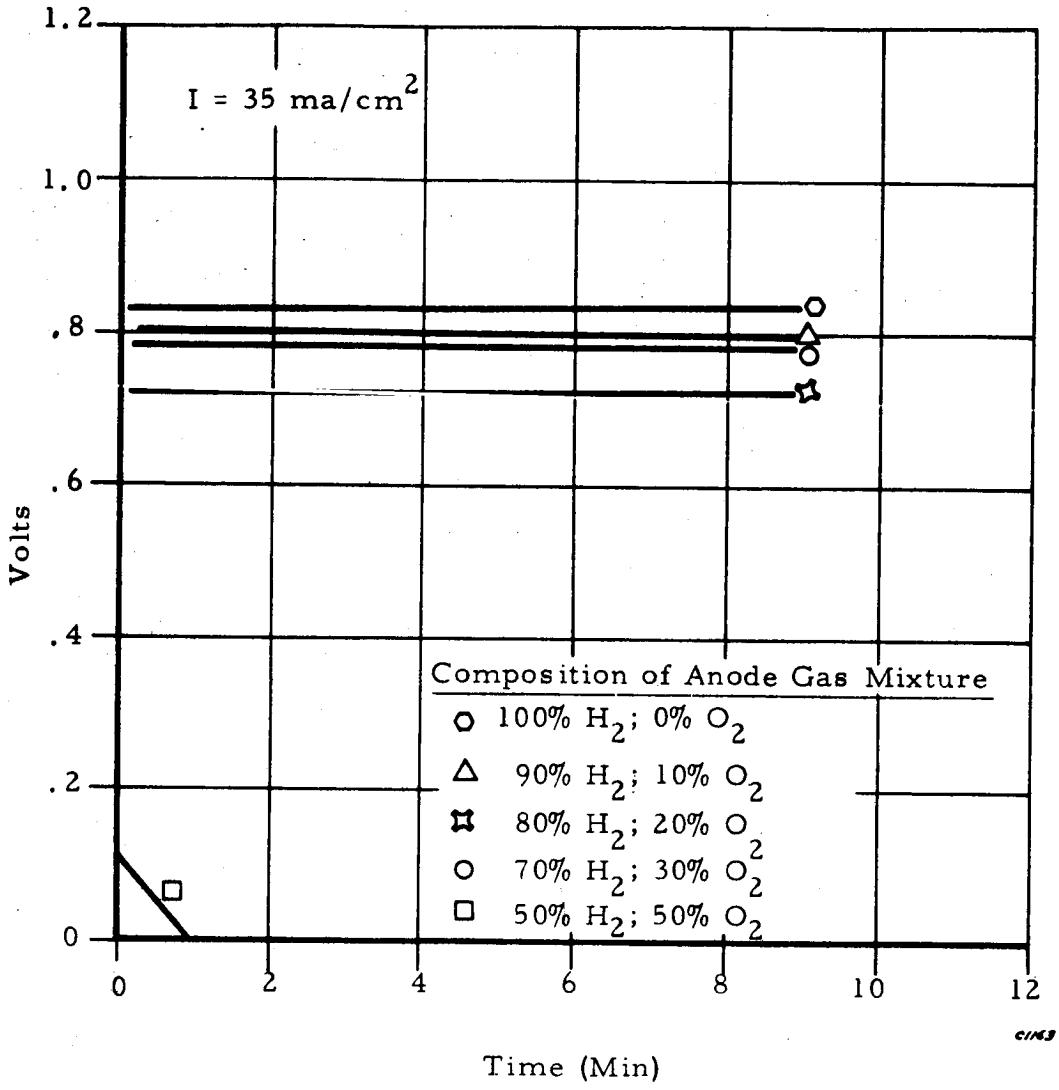


Figure 12. Performance of Miniature Fuel Cell With H_2-O_2 Mixtures in Anode After Several Hours of Operation

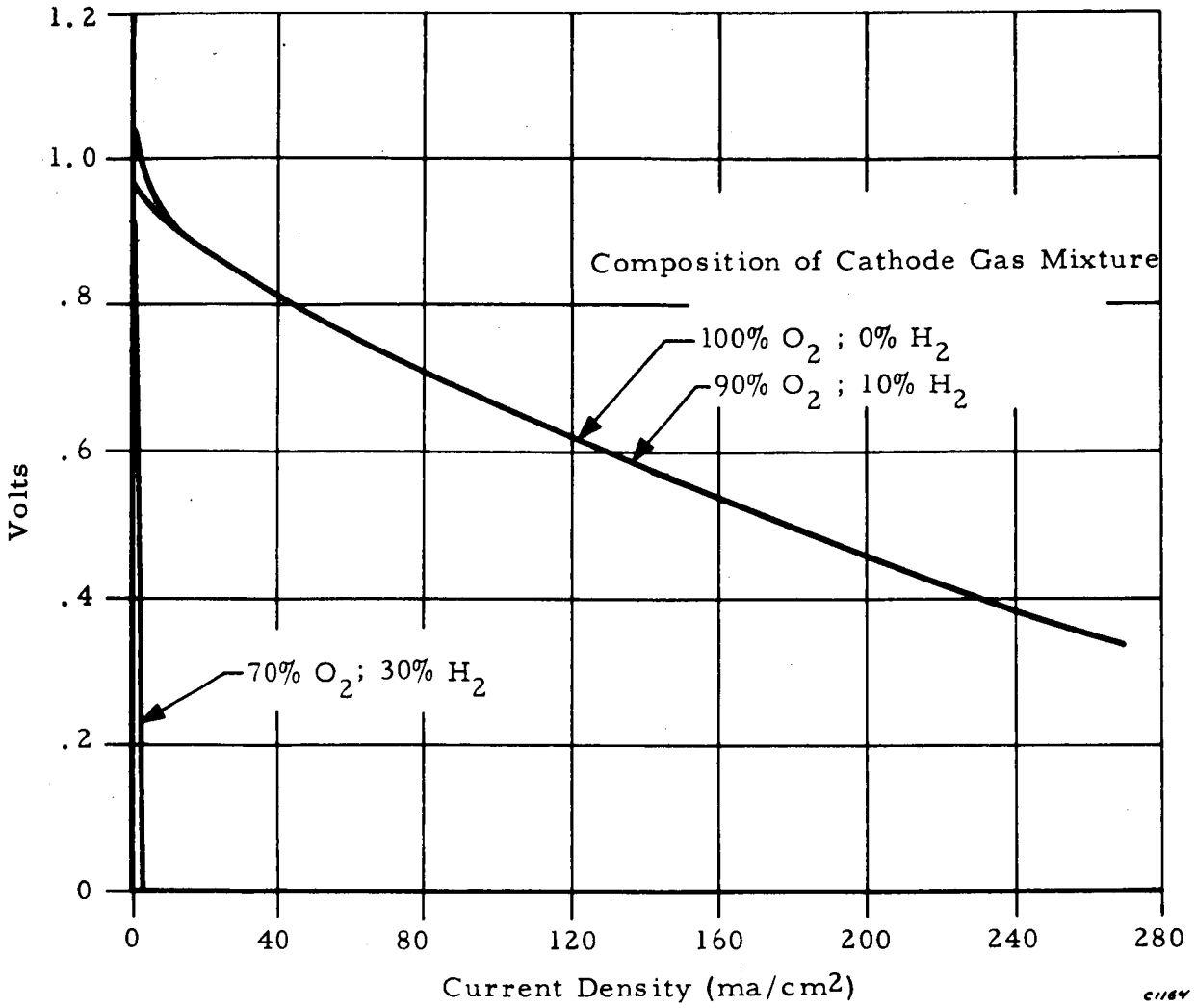


Figure 13. Performance of Miniature Fuel Cell With H_2-O_2 Mixtures in Cathode After Several Hours of Operation

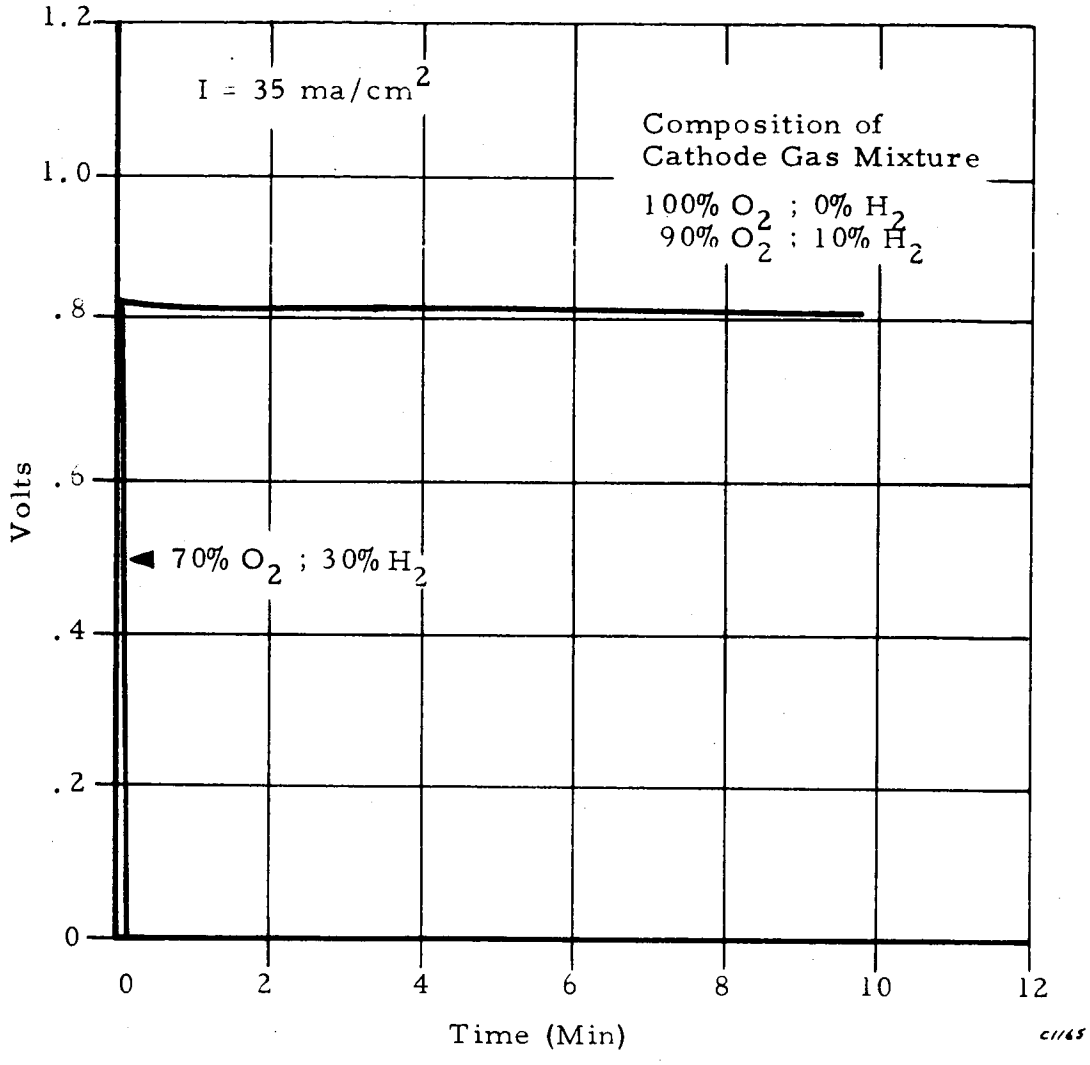


Figure 14. Performance of Miniature Fuel Cell With H_2-O_2 Mixtures in Cathode After Several Hours of Operation

can function satisfactorily with mixtures on its cathode side containing up to 10% hydrogen. Performance is noted to drop rapidly with hydrogen content at some level between 10 and 30%.

These results are directly applicable to the problem of estimating performance of miniature fuel cells when installed in commercial silver-zinc cells. Under normal operating conditions, including both stand and conventional cycling, internal battery gases consist of essentially pure hydrogen with little, if any, oxygen. Therefore, during normal conditions, a single miniature fuel cell, with its anode in contact with battery gases, should be capable of consuming essentially all internal gases.

During an overcharge period, oxygen is evolved and becomes mixed with the hydrogen. The miniature fuel cell would continue to function during this period until oxygen content reached 50%. At this point, the fuel cell would become inoperative and could not consume any more of the hydrogen. Internal pressure would continue to rise because of continued oxygen evolution. This pressure rise could be terminated, however, if the battery contained a second miniature fuel cell with its cathode in contact with internal gases. This cell would start and continue to consume oxygen when concentration of this gas had reached a level of 90%. Thus it may be shown that use of two miniature fuel cells would limit internal pressure rise in a silver-zinc cell during normal operation and also during overcharge. This matter will be discussed in greater detail in Section 2.3 of this report.

2.2.4.2 Dead-End Flow (Test Series No. 19)

In this test a miniature fuel cell was operated for an extended time on one anodic mixture consisting of 90% H_2 and 10% O_2. The tests were carried out in a "quasi" dead-end mode which was similar to the previously described dead-end tests (Section 2.2.2) but with one exception. In this case the simulator (a 250-ml

Erlenmeyer flask) was flushed briefly and refilled each day with the above mixture. This was necessary, since during operation the fuel cell would electrochemically consume the hydrogen and thereby change its concentration. The total volume was such that the calculated change was negligible for a one-day operation. In this manner it was possible to maintain an essentially constant composition for an extended period. The test was carried out over a period of one month at a current of 5 ma. Operating voltage was noted to decline somewhat each day from approximately 0.8 to 0.6 volts. Upon refilling, however, with the above mixture, the voltage again returned to the higher value. These results establish that the miniature fuel cell can operate effectively on mixtures of H_2 and O_2 in its anode for extended periods.

2.2.4.3 Effect of Anode Gas Composition on Open End Circuit Voltage (Test No. 20)

A third test with gas mixtures involved measurement of the effect of anodic gas composition on open circuit voltage. The tests were carried out in the open gas-flow mode by passing mixtures of hydrogen and oxygen slowly across the anode compartment and pure oxygen across the cathode compartment. Flowmeters were employed to set approximate gas compositions which were checked with a gas chromatograph. Open circuit voltages were measured with a vacuum tube voltmeter.

Results of several runs are given in Figure 15. The shaded area gives the range of values obtained for several different tests. The following trend is evident. The voltage increases gradually with increasing hydrogen concentration in the range of zero to approximately 50%. At a concentration of hydrogen of about 70% there is a sharp increase in voltage. From 70 to 100% hydrogen there was again observed to be a low rate of increase of voltage with increasing hydrogen concentration.

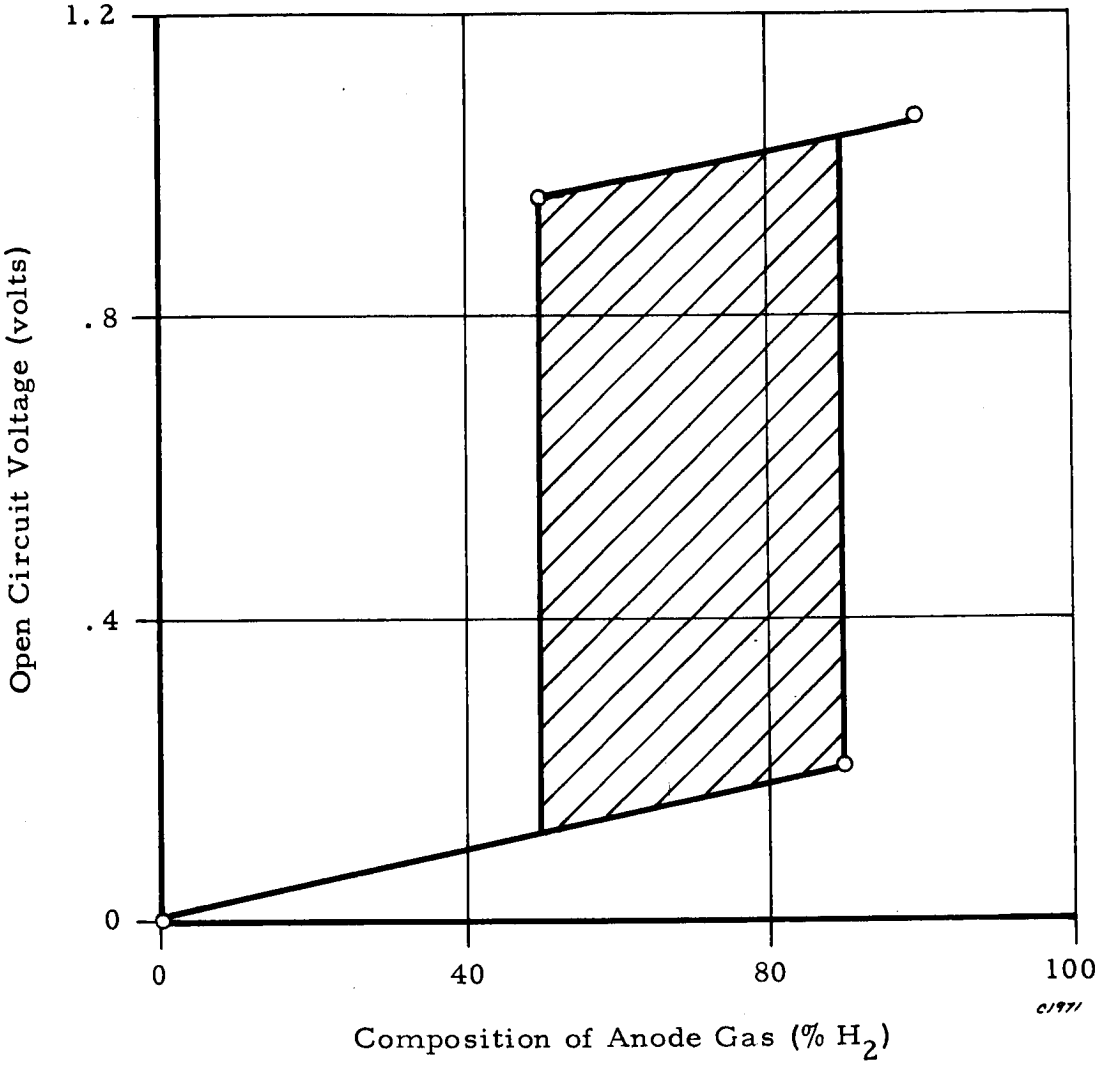


Figure 15. Effect of Composition of Anode Gas On Open Circuit Voltage of H_2-O_2 Fuel Cell

An explanation that can be offered for this phenomenon is that there is a critical concentration of hydrogen below which the anode ceases to be a true hydrogen electrode. At these low hydrogen concentrations the oxygen may block most of the active sites on the electrode.

2.2.5 Effect of Temperature on Performance (Test Series No. 21)

The effect of temperature on performance of both the original and modified cell types is given in Figures 16 and 17. The high temperature tests (40°C) were carried out in an oven and the low temperature tests (0°C) were carried out in an ice bath.

Results indicate a marked effect of temperature on performance of both the original and modified miniature cells. In each case, performance was noted to improve appreciably with temperature within the given range of 0 to 40°C. Typical results for the modified cell are given below after three to five hours of continuous operation.

Temperature (°C)	Operating Current at 0.6 V (ma/cm^2)
0	50
25	60
40	130

Operating current at 40°C is noted to be more than double that at room temperature. At 0°C, operating current is approximately 80% of that at room temperature.

This variation in performance of the miniature fuel cell with temperature fortuitously matches that of its intended application in a silver-zinc battery. At elevated temperatures, battery gassing rates are higher and the fuel cell would be required to operate at higher currents. Results establish this capability. At lower

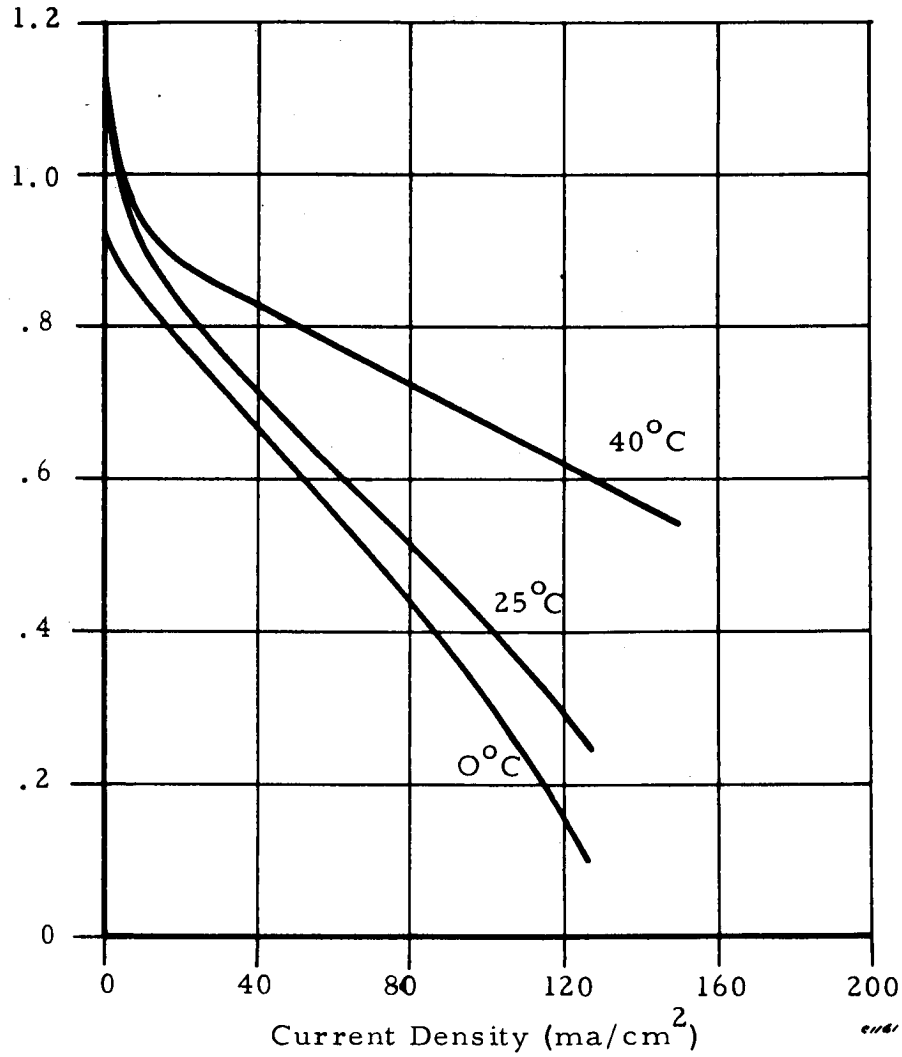


Figure 16. Effect of Temperature on Performance of Miniature Fuel Cell (Modified Cell Configuration) After Three to Five Hours of Continuous Operation

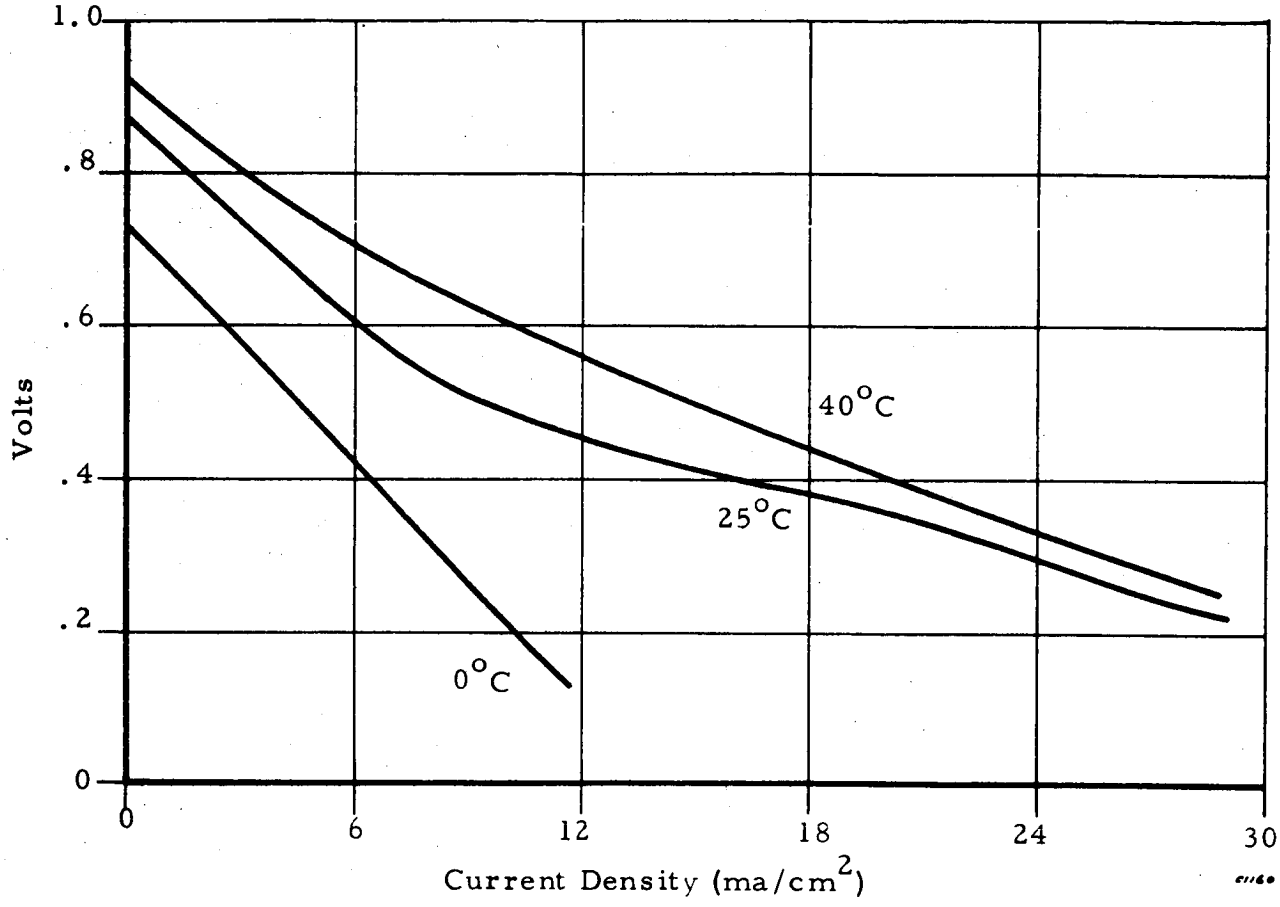


Figure 17. Effect of Temperature on Performance of Miniature Fuel Cell (Initial Cell Configuration) After Three to Five Hours of Continuous Operation

temperatures, gassing rates are lower as are corresponding required fuel cell current requirements. Results show only a small reduction in fuel cell current at lower temperatures and indicate that it should be capable of eliminating cell gassing problems at temperatures at least as low as $0^{\circ}C$.

2.2.6 Fuel Cell Size Versus Gas Consumption Capability

An important goal of this program was to establish a relationship between the size of a miniature fuel cell and its gas consumption capability. This will permit accurate sizing of the miniature fuel cell to accommodate the gassing rates that may be encountered in a particular battery under any mode of operation.

Results obtained with the modified type of miniature fuel cell indicate that during the initial stages of operation (the first 100 hours) the voltage-current characteristics of the miniature cells are independent of electrode size in the range of 0.25 to 5.0 cm^2. During this time, it may be shown that the gas consumption capability is directly proportional to fuel cell electrode area. This relationship may be expressed by the following equation:

$$R = 0.42\, i A$$

R = hydrogen consumption capability, cc H_2/hr

i = current density, ma/cm^2

A = electrode area, cm^2

This follows from the principles of electrochemical equivalence. The above relationship then gives the desired correlation between fuel cell size and gas consumption capability at least for the initial phases of operation and at relatively low current densities.

For extended operating times at low currents or for shorter operating times at high currents the above relationship must be modified because of the problem of removing product water. This has a pronounced effect on the voltage-current characteristics of the cell and

its corresponding gas consumption capability. This problem was solved at least in part by the use of wicks to transfer product water to the battery electrolyte. Results have indicated that miniature cells with electrode cross-sectional areas of 0.25 to 5.0 cm^2 can operate effectively with wicks at current densities of at least 15 ma/cm^2 continuously for extended periods. This corresponds to hydrogen consumption capabilities of 1.6 cc H_2/hour, 6.3 cc H_2/hour and 10.6 cc H_2/hour for cells with electrode areas of 0.25, 1.0 and 5.0 cm^2, respectively.

Finally it should be pointed out that the short term gas consumption capabilities are exceedingly high with respect to anticipated battery gassing rates. A cell with a cross-sectional electrode area of 1.0 cm^2, for example, has been shown to be capable of operating at currents up to 300 ma, which is equivalent to a corresponding hydrogen consumption rate of 126 cc H_2/hour.

2.2.7 Selection of Miniature Fuel Cell for Performance Tests in Silver-Zinc Cells

The miniature fuel cell selected for performance tests in silver-zinc cells was of the modified type with American Cyanamid Type A.B.-40 electrodes. The reasons for this choice were that this cell type was found to exhibit higher current and corresponding gas consumption capabilities than the initial type and that the A.B.-40 electrodes appeared to give the most stable output among those examined in this cell type. The operational mode selected was the "dead-end" gas flow with wicking of product water, as described in Section 2.2.3. Although the results had indicated that the miniature fuel cells had less than optimum output under this mode, it was believed to be the most practical with regard to sealing of the silver-zinc cell. The screw type installation was selected on the basis that it was found to be reliable and adequate in the simulator tests and that it would provide a convenient method of installing two fuel cells on a silver-zinc battery. Results of performance tests with this cell in this mode are given in the following sections.

2.3 Performance Tests in Silver-Zinc Cells

The purpose of these tests was to establish capability of the miniature fuel cells in consuming gases and limiting pressure rise in sealed silver-zinc batteries. The most extensive and thorough tests were conducted during the latter portion of the program on two 100-amp-hour, low-rate silver-zinc cells. Results of these tests are presented first in Section 2.3.1 below. Preceding these tests were a number of preliminary runs with commercial 15-amp-hour, high-rate silver-zinc cells. The purpose of the latter was merely to perfect the miniature fuel cell installation and operational techniques. Despite the limited intent, some significant results were obtained on this size and type of cell. Results are given in Section 2.3.2.

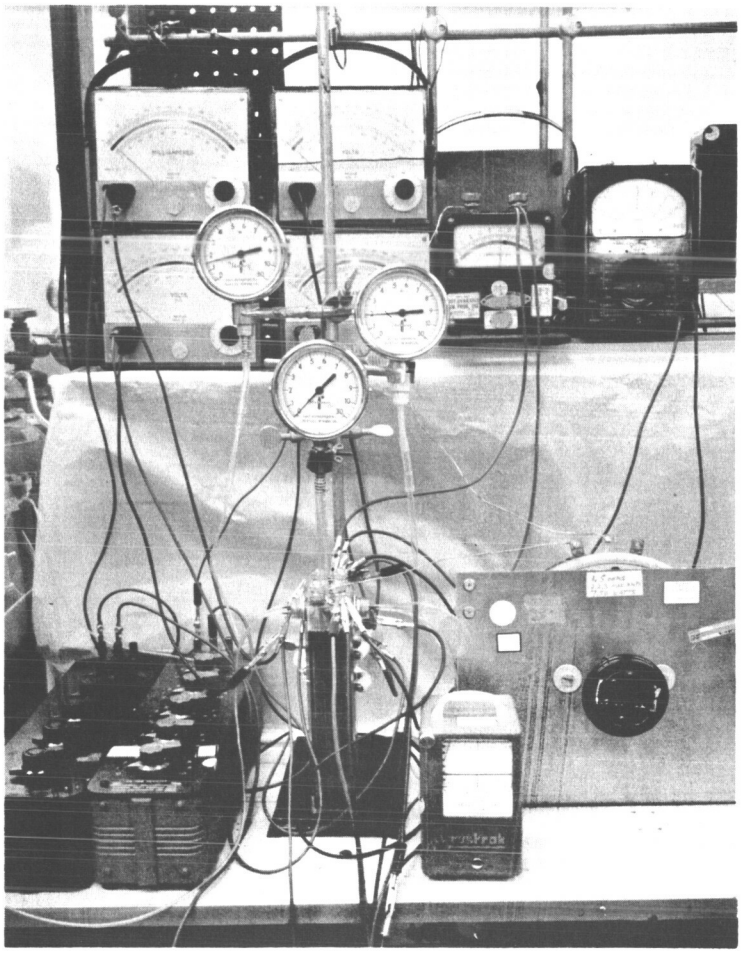
2.3.1 100-Amp-Hour Silver-Zinc Cycling Tests

Extensive cycle tests were carried out on two commercial 100-amp-hour silver-zinc cells each of which contained two miniature fuel cells as described below. These are designated as Tests 22 and 23, respectively. Cycle conditions for both tests were identical and were specified by the contract monitor as a 2-hour discharge at 20 amps (40% depth) and a 22-hour charge at 2 amps. Experimental details and results are given below.

2.3.1.1 Experimental

The silver-zinc cells were from Yardney Electric Corporation. They were shipped in the dry unformed state. Rated capacity was listed as 85 amp-hour but actual capacity was 120 to 140 amp-hours. For the purpose of this test they were therefore rated as nominal 100 amp-hour cells.

The miniature fuel cells were installed near the top of battery cases in accordance with the procedures outlined in Appendix A. An illustration of the test assembly is given in Figure 18.



c/931

Figure 18. Installation of Miniature Fuel Cell in a Commercial 100 Ampere-Hour Silver-Zinc Battery

Before initiation of cycling, the silver-zinc cells were carried through two formation cycles as recommended in the Yardney Instruction Sheet accompanying the cells. The following steps were involved:

1. Activation with electrolyte
2. Three-day stand
3. First formation charge at 3 amps to 2.05 volts
4. Discharge at 50 amps to 1.0 volt
5. Second formation charge at 3 amps to 2.05 volts

These formation cycles were carried out in the vented condition.

Upon initiation of cycling, the silver-zinc cells were sealed off by connecting the vent plugs directly to a pressure gage with a short segment of plastic tubing. The assembly was then leak tested by filling with 5 psig of nitrogen and checking all of the possible leakage joints with a special detergent. A further check on leakage was carried out by sealing the system off at 5 psig and observing any change in pressure while on stand. The detergent leak test was also performed periodically during each test.

The fuel cells were purged with their respective gases at the start of the test and a small positive pressure of 1.5 psig was applied to each in the dead-end mode.

Each of the miniature fuel cells was discharged continuously across a fixed load of 1.0 ohm throughout the test. Operating voltages and currents of both the silver-zinc cells and the miniature fuel cells as well as internal pressure were recorded continuously throughout the test.

Battery discharge was carried out through a variable ohmite resistor. Current was adjusted manually at 20 amperes. Battery charge was carried out with a conventional 12-volt battery charger in series with a variable resistor to adjust current to

2 amperes. Weston precision voltmeters and ammeters (± 1/4% accuracy) were employed on both the battery and fuel cells.

2.3.1.2 Results

Results of cycle tests on the two 100 A.H. silver-zinc cells are given in Tables VI and VII. These outline the performance of both the silver-zinc cells and their associated miniature fuel cells on a cycle-to-cycle basis. The first two columns give the end of charge and discharge voltages of the silver-zinc cell during each cycle. Charge and discharge currents and times are not listed as these were held constant as described above. The next column lists the maximum pressure developed during each cycle. The last eight columns give the currents and corresponding gas consumption rates of each of the miniature fuel cells. These are subdivided into the maximum and average rates during each cycle.

Inspection of Tables VI and VII reveals several significant points. First it should be noted that the maximum pressure developed in either cell is less than 1.5 psig throughout the indicated test periods. This established the fact that the miniature fuel cells are effective in limiting pressure rise to very moderate levels. Without the miniature fuel cells, it is estimated that internal pressures would increase at rates of at least 0.35 and 2.34 psi per day for Tests 22 and 23 respectively. This is based on the measured hydrogen evolution rates and cell volume. On this basis, the internal pressures would have reached levels of 10.5 and 50 psig, respectively, in Tests 22 and 23 by the end of the test period.

The miniature fuel cells were effective not only in consuming evolved gases at low rates that were encountered throughout most of these tests, but also at the high rates encountered from time to time. During Cycles 4 and 5 in Test 23, for example, there was an apparently sharp increase in the rate of hydrogen evolution, as evidenced by the increase in pressure and there was a simultaneous

TABLE VI

SUMMARY OF TEST NO. 22 ON 100 A. H. SILVER-ZINC CELL CONTAINING DUAL MICRO FUEL CELL ARRANGEMENT

Cycle No.	End Charge Voltage (volts)	End Discharge Voltage (volts)	Maximum Pressure (psig)	Maximum Current From H_2 Fuel Cell (ma)	Maximum O_2 Consumption Rate By H_2 Fuel Cell (c.c. O_2/hr)	Average Current From H_2 Fuel Cell (ma)	Average O_2 Consumption Rate By H_2 Fuel Cell (c.c. O_2/hr)	Maximum Current From O_2 Fuel Cell (ma)	Maximum H_2 Consumption Rate By O_2 Fuel Cell (c.c. H_2/hr)	Average Current From O_2 Fuel Cell (ma)	Average H_2 Consumption Rate By O_2 Fuel Cell (c.c. H_2/hr)
1	2.10	1.50	3.7*	40.0	8.0	.10	.02	.50	.21	.20	.08
2	1.87	1.50	0.3	.15	.03	.10	.02	.22	.08	.20	.08
3	1.88	1.51	0.4	.15	.03	.10	.02	.30	.12	.22	.08
4	1.89	1.52	0.5	.30	.06	.30	.06	.05	.02	.05	.02
5	1.88	1.54	0.2	.50	.06	.30	.06	.05	.02	.05	.02
6	1.94	1.54	0.8	.50	.10	.40	.08	.25	.10	.20	.08
7	1.93	1.52	0.6	.20	.10	.30	.06	.25	.10	.20	.08
8	1.94	1.53	0.5	.10	.04	.15	.03	.20	.10	.20	.08
9	1.94	1.53	0.4	.10	.02	.10	.02	.15	.06	.15	.06
10	1.94	1.54	0.5	.15	.02	.10	.02	.15	.06	.15	.06
11	1.94	1.53	0.6	.15	.03	.15	.03	.70	.29	.20	.08
12	1.95	1.54	0.3	.20	.03	.15	.03	.30	.12	.20	.08
13	1.95	1.52	0.5	.20	.04	.10	.02	.20	.08	.20	.08
14	1.94	1.52	0.5	.50	.04	.10	.02	.20	.08	.15	.06
15	1.94	1.52	0.8	.20	.10	.30	.06	.20	.08	.20	.08
16	1.95	1.52	0.8	.20	.04	.20	.04	.20	.08	.10	.04
17	1.94	1.52	0.6	.20	.04	.10	.02	.20	.08	.20	.08
18	1.93	1.53	0.9	.15	0	0	0	.20	.08	.20	.08
19	1.92	1.52	0.9	.15	0	0	0	.20	.08	.20	.08
20	1.94	1.51	0.5	0	0	0	0	.15	.08	.20	.06
21	1.94	1.51	0.6	0	0	0	0	.20	.08	.20	.08
22	1.94	1.51	0.9	0	0	0	0	.20	.08	.20	.08
23	1.95	1.50	0.9	0	0	0	0	.25	.10	.20	.07
24	1.95	1.52	0.9	0	0	0	0	.20	.08	.15	.06
25	1.87	1.50	1.3	0	0	0	0	.30	.12	.20	.08
26	1.96	1.52	1.4	0	0	0	0	.40	.16	.30	.12
27	1.95	1.52	1.2	.6	.12	.50	.10	.30	.12	.25	.10
28	1.95	1.50	1.5	.5	.10	.30	.06	.45	.18	.30	.12
29	1.95	1.50	1.5	.47	.10	.40	.08	.40	.18	.40	.16
30	1.95	1.52	1.2	.45	.10	.40	.09	.45	.18	.40	.16
							Avg .03				Avg .08

*Note: The voltage cutoff device failed to operate during this cycle and the cell was therefore overcharged somewhat. This resulted in oxygen evolution as evidenced by the increased output of the cell supplied with H_2. Internal pressure reached the maximum indicated and then gradually declined during the next discharge.

TABLE VII

SUMMARY OF TEST NO. 23 ON 100 A. H. SILVER-ZINC CELL CONTAINING DUAL MICRO FUEL CELL ARRANGEMENT

Cycle No.	End Charge Voltage (volts)	End Discharge Voltage (volts)	Maximum Pressure (psig)	Maximum Current From H_2 Fuel Cell (ma)	Maximum O_2 Consumption Rate By H_2 Fuel Cell (c.c. O_2/hr)	Average Current From H_2 Fuel Cell (ma)	Average O_2 Consumption Rate By H_2 Fuel Cell (c.c. O_2/hr)	Maximum Current From O_2 Fuel Cell (ma)	Maximum H_2 Consumption Rate By O_2 Fuel Cell (c.c. H_2/hr)	Average Current From O_2 Fuel Cell (ma)	Average H_2 Consumption Rate By O_2 Fuel Cell (c.c. H_2/hr)
1	1.95	1.52	0	.70	.14	.70	.14	.50	.21	.40	.16
2	1.96	1.51	0	.95	.20	.70	.14	.20	.08	.20	.08
3	1.95	1.52	1.0	1.0	.21	.10	.02	10	.04	.10	.04
4	2.10	1.53	1.2	.95	.20	.45	.10	15	.06	.10	.04
5	1.90	1.52	1.5	1.0	.21	1.0	.21	42 5	17.9	3.0	1.26
6	1.77	1.52	0	1.3	.27	1.3	.27	24.0	10.0	3.91	1.60
7	1.73	1.51	0	1.2	.25	.45	.10	2.1	.88	.70	.30
8	2.10	1.46	0	.35	.07	.20	.04	20	.04	.20	.08
9	1.65	1.54	0	.40	.08	.20	.04	5.2	2.2	1.1	.46
10	1.65	1.22	0	1.20	.25	.80	.16	2.4	.96	2.0	.80
11	1.72	1.45	0	.70	.14	.60	.12	1.6	.67	1.4	.59
12	1.94	1.50	0	1.0	.21	.50	.10	1.3	.55	0.9	.38
13	1.92	1.50	0	1.2	.24	.40	.08	.40	.17	0.3	.12
14	1.95	1.52	0	.25	.05	.20	.04	2.1	.80	0.7	.28
15	1.95	1.37	0	1.0	.20	.40	.08	300.0	120.0	2.0	.80
16	1.65	1.54	0	.15	.03	.15	.03	.45	.19	0.1	.04
17	1.92	1.54	0	.15	.03	.15	.03	.45	.19	0.1	.04
18	1.92	1.54	0	.15	.03	.10	.02	.10	.04	0.1	.04
19	1.65	1.33	0	.10	.02	.05	.01	.50	.20	0.1	.04
20	1.66	1.57	0	1.8	.38	.10	.02	0	0	0.0	0
21	1.92	1.53	0	.10	.02	.10	.02	.30	.12	0.0	0
							Avg .09				Avg .34

increase in output of the miniature fuel cell supplied with oxygen. Output of the miniature fuel cell increased to a sufficient rate (17.9 cc H_2 per hour maximum and 3 cc H_2 per hour average) to limit the pressure rise to only 1.5 psig.

Based on the indicated fuel cell response data, it is possible to draw several other conclusions in regard to the gassing characteristics of this type of silver-zinc cell. Hydrogen is evolved under these cycling conditions at average rates ranging from 0.1 to 0.5 cc H_2/hour. Oxygen is evolved during most of the cycles but at much lower rates of 0.03 to 0.10 cc O_2/minute. During some periods there was no measurable oxygen evolution.

It is difficult to draw a more detailed quantitative analysis of gassing characteristics, since the results show that gassing is not reproducible among silver-zinc cells of this type and also from cycle to cycle within a given cell. The only consistent trend was in Test 22 wherein internal pressure was noted to rise slightly during each discharge period and to decline to zero psig by the end of the first hour of each charge period. Output of the fuel cell supplied with oxygen was noted to increase slightly during these periods and indicated that the rise was due mainly to hydrogen evolution. One possible explanation is that there is an increase in temperature on discharge which causes an increase in the dissolution rate of zinc and a corresponding increase in hydrogen evolution rate. This phenomenon was not observed in Test 23. Aside from the possible trend of slightly increased hydrogen evolution rate during discharge, there did not appear to be any other consistent variation in gassing rate of either H_2 or O_2 throughout each cycle. If the cells had been overcharged, there would have undoubtedly been an increase in oxygen evolution; however, this was not the case, as the charge was terminated at 2.05 volts maximum by means of a voltage cut-off.

The average gassing rates of both H_2 and O_2 are significantly greater in Test 23 than in Test 22. Relative

rates are approximately 6/1 for H_2 and 4/1 for O_2 for the two tests. This can be explained only on the basis of differences in the silver-zinc cells themselves, as all other conditions are identical.

One similarity between the gassing phenomena of the two cells is in the ratio of evolved H_2 to O_2. These ratios are of the same order of magnitude in both tests, i.e., 2.7 H_2/1.0 O_2 in Test 22 and 3.8 H_2/1.0 O_2 in Test 23.

Finally, it is to be noted that there is very little weight penalty associated with the use of miniature fuel cells. In these tests, for example, the combined weight of the two fuel cells in each battery is under 50 grams and the combined battery-fuel cell weight is 1240 grams. These miniature fuel cells were not designed for minimum weight under this program; it is expected that under optimum design considerations, the contribution of two miniature fuel cells to the overall battery weight should not be more than one percent.

2.3.2 15 Amp-Hr Silver-Zinc Cycle Tests

As mentioned in the preceding section, the purpose of tests with the 15 amp-hr, high-rate silver-zinc cells was to develop reliable installation and test procedures for the miniature fuel cells in batteries. This was to be in preparation for the tests in 100 amp-hr cells already described. Several short term cycle tests were carried out with these batteries both with and without miniature fuel cells. Results are given below.

2.3.2.1 Operation Without Miniature Fuel Cells (Test No. 24)

In this test the battery was cycled in the sealed condition without miniature fuel cells. This was accomplished by connecting the battery vent cap directly to a pressure gage via plastic tubing. Conditions and results of this test are given in Table VIII.

TABLE VIII

CYCLE TESTS ON 15 AMP-HR SILVER-ZINC BATTERIES CONTAINING MINIATURE FUEL CELLS*

Test No.	Number of Fuel Cells Installed	Battery Cycle Regime	Number of Cycles	Pressure Range (psig)	Range of Fuel Cells Output (ma and mv)
25	1	1/2 hr discharge at 10 amps and 1 hr charge at 5 amps	20	0-10	0 to 300 ma at 0.2 volt with H_2 and 0 to 200 at 0.1 volt with O_2
26	2	1 hr discharge at 5 amps and 5 hr charge at 1 amp	5	0-.08	0 to 1 ma at 1 mv for H_2 cell and 0 to 1 ma at 1 mv for O_2 cell
27	2	1/2 hr discharge at 5 amps and 1 hr charge at 2.5 amps	14	0-10	0 to 60 ma at 0.1 volt for H_2 cell and 0 to 85 ma at 0.1 volt to O_2 cell
28	0	1/2 hr discharge at	3	> 15	--

*Note: 1. Electrode areas of all fuel cells were 1.0 cm^2

2. Battery is Yardney 15 AH-HR

3. Tests performed at ambient temperature

Internal pressure was noted to rise very rapidly during the initial discharge to 8.5 psig and to continue to rise during subsequent cycles. At the end of the second charge period, with pressure in excess of 15 psig, a rupture of cell components occurred and resulted in slow leakage of internal gases.

These results show that rapid rise in internal pressure occurs when the battery is cycled in the sealed condition. The rise in pressure was found to increase progressively with cycle time and might have increased much beyond 15 psig, had not the rupture occurred (as shown in Figure 1). This indicates that substantial gassing rates in this type of battery are possible. Much of this gassing, at least at the early stages of cycling, was found to be due to evolving oxygen (see Section 2.3.2.5).

2.3.2.2 Operation With One Miniature Fuel Cell (Test No. 25)

This test was initiated with one miniature fuel cell installed in the battery. The fuel cell was supplied with oxygen initially and then alternatively with hydrogen and oxygen. Results are given in Table VIII (see Test 25).

Internal pressure was noted to rise very rapidly during the initial discharge to approximately 10 psig. The fuel cell gave essentially no response during this period while it was supplied with oxygen. When the external gas supply was switched from oxygen to hydrogen, however, its open circuit voltage increased to 1.0 volt. Upon placing the cell on load midway in the discharge period at 100 ma at 0.7 volt, the rate of pressure increase was diminished and the pressure began to decline throughout the following charge period.

During the course of subsequent cycling, the following observations were made.

1. With hydrogen supplied to the fuel cell, its response was generally negligible except near the end of each

charge period. At this point its output increased to a maximum of nearly 300 ma and 0.2 volt. A simultaneous increase in internal pressure was observed during the end of the charge period. In some instances this rise in pressure was in excess of 10 psig. Pressure was observed to decline after the end of charge with the fuel cell on load. Output of the fuel cell decreased gradually as pressure was reduced to atmospheric.

2. With oxygen supplied to the fuel cell, its output was in the range of 0.0 to 3.0 ma at 0.0 to 3.0 mv throughout all portions of the cycles, except during start-time after a few days of stand. Under these conditions the output of the fuel cell increased rapidly to a level of between 100 to 200 ma and 0.1 volt. Output decreased gradually after a few minutes as internal pressure was reduced from approximately 1.0 psig to atmospheric.

Based on these observations, the following conclusions may be drawn.

1. The high rate batteries generate oxygen quite rapidly near the end of charge. A miniature fuel cell with 1.0 cm^2 electrode area and supplied with hydrogen can effectively consume this oxygen at rates up to 1.0 cc O_2/min (this is based on the observed current of 200 ma). Use of such miniature fuel cells can effectively limit pressure rise to a reasonable level near 10 psig under these conditions.
2. The batteries generate hydrogen continuously at very low rates. A miniature fuel cell with 1 cm^2 cross sectional electrode area and supplied with oxygen is more than adequate to consume all of this amount of hydrogen. Such a cell can also consume the hydrogen which collects during a three-day stand within a few minutes.

2.3.2.3 Operation With Two Miniature Fuel Cells (Test No. 26)

In this test two miniature fuel cells were installed in a previously used battery (two cycles). One cell was supplied externally with oxygen to consume internal hydrogen. Longer cycle times and lower currents were employed in this test than in previous tests (see Table VIII, Test 26).

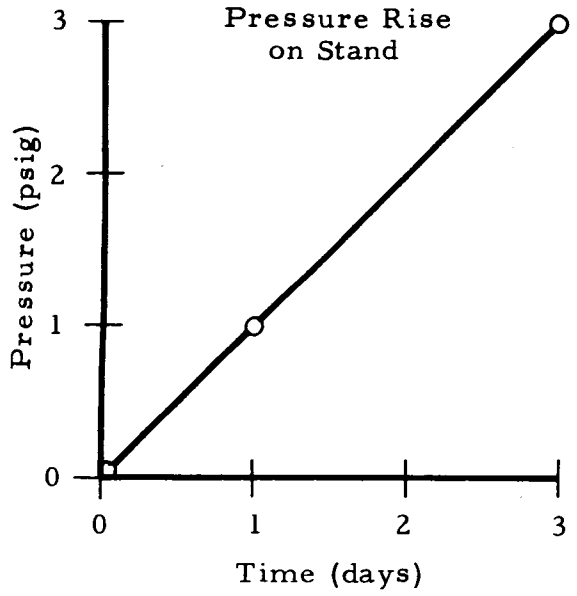
Very low pressures were developed within the battery during the course of five of the indicated cycles (a maximum of only 0.08 psig). Response of the fuel cell supplied with oxygen was within the range of 0.0 to 1.0 ma throughout all of the cycles, whereas response of the fuel cell supplied with hydrogen was somewhat less than the above value.

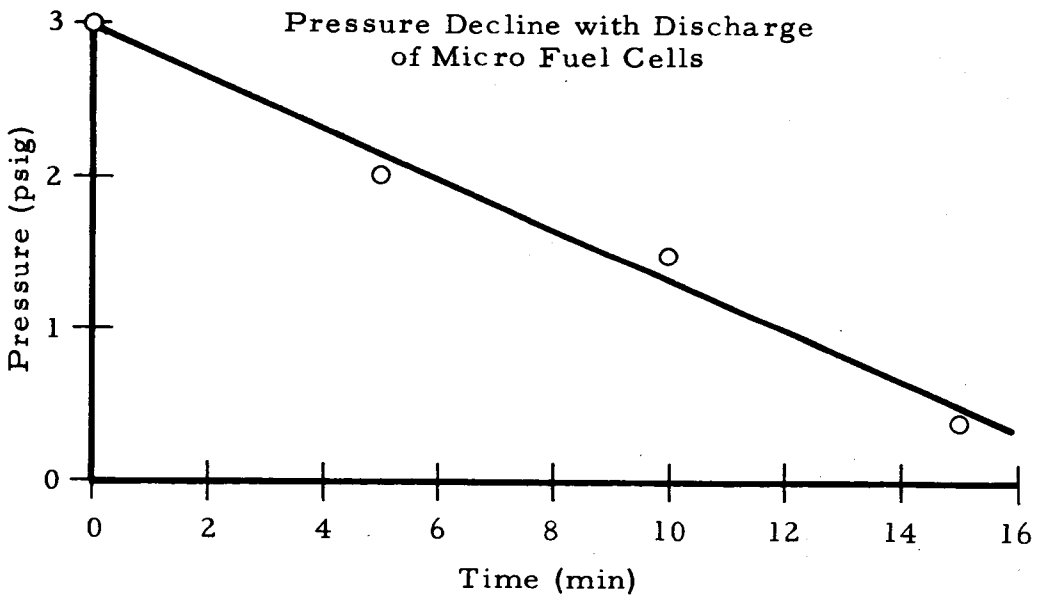
These results indicate that the silver-zinc cell generates very small quantities of gases under the above cycle regime and that two miniature fuel cells, each with 1.0 cm^2 electrode areas, are more than adequate to limit pressure rise.

2.3.2.4 Operation With Two Miniature Fuel Cells (Test No. 27)

A new 15-Ah silver-zinc battery was employed in this second cycle test with a dual fuel cell arrangement as described above. The 1/2 hour-1 hour cycle was again employed as in Test 25 but at lower currents (see Table VIII, Test 27).

Observed phenomena during this test were similar to those in Test 25. Internal pressure was again noted to increase during initial discharge but to a lower level than in Test 25. Response of the fuel cell supplied with hydrogen was higher during initial discharge and also at the end of each charge cycle than at other times throughout the cycles. Output of this fuel cell during initial discharge was effective in limiting pressure rise to 4.5 psig. Response of the fuel cell supplied with oxygen was within the range of 0.0 to 2.0 ma at 0.0 to 2.0 mv at all times during the cycles except at the point of start-up after a three-day stand. Fuel cell and battery performance during this period are given in Figure 19. For the case described here the battery had been charged prior to stand and is therefore indicated to be on discharge at the indicated start time. As shown in Figure 19, the response of the fuel cell supplied with O_2 increased rapidly to and maintained a current level of 83 ma at 0.16 volts throughout the discharge





Fuel Cell Modes of Operation	H_2 Cell on OCV	H_2 Cell on 1 Ω load, 83 ma @ 0.16 volt
	O_2 Cell on OCV	O_2 Cell on 1 Ω load, 1 ma @ 0.01 volt
Battery Mode of Operation	Stand in Charged State	Discharge @ 5 amps @ 1.5 volts

Figure 19. Relief of Pressure in Silver-Zinc Battery with the Use of Micro Fuel Cells

period. Internal pressure was simultaneously observed to decrease from 3.0 psig to atmospheric during this period. Response of the cell supplied with H_2 was at a level of 1.0 ma and 1.0 mv throughout this period. As before, these results indicate that hydrogen is the predominant gas formed on stand and that the fuel cells can effectively consume this hydrogen as well as a small amount of oxygen in a relatively short time.

2.3.2.5 Gassing During Initial Discharge (Test No. 28)

As mentioned previously, internal battery pressure was noted to increase very rapidly during the initial discharge. Fuel cell response indicated that the rise in pressure was due mainly to oxygen evolution. In order to reaffirm this conclusion, a new 15 Ah cell was placed on discharge and the evolved gases were collected by displacement of water. Samples of this gas were then analyzed chromatographically and gave the following results.

Component	Volume %
H_2	13.3
O_2	45.0
N_2	41.7

These results reaffirm that oxygen is the predominant species evolved on initial discharge. A small amount of hydrogen is also noted. The presence of nitrogen is explained of course by the fact that the cell is filled with air at the start of the test. An estimated oxygen evolution rate during this test was 2 cc O_2/min.

2.4 Product Water for Life Support

Removal of product water from the miniature fuel cells for life support purposes does not appear feasible because of the limited quantities which have been found. At best the rate of product water formation would be .01 gms H_2O/day for a 100 amp-hr cell. This corresponds to

an average hydrogen evolution rate of 0.5 cc H_2/hour in Test 23, Section 2.3.1.2. Although the gassing rates might be much greater under other cycle regimes or ambient temperature, the corresponding water formation rates would remain quite small.

3.0 PROJECT PERSONNEL

The following Astropower staff members are associated with this program at this time.

Dr. C. Berger, Principal Investigator

Dr. M. P. Strier

Mr. H. Frank

Mr. C. Brygger

4.0 NEW TECHNOLOGY

A reliable method of sealing a miniature fuel cell in a silver-zinc battery was found with the use of a special thread seal as shown in Figure 18 and described in Appendix A and Figure A-5.

REFERENCES

1. Francis, Howard T., Space Battery Handbook, pp. 42-47 15 April 1963).

2. Douglas Proprietary Program S. O. 81367-002.

3. Douglas Proprietary Program S. O. 81367-005.

APPENDIX A

DESCRIPTION AND OPERATION OF MINIATURE FUEL CELLS DELIVERED TO NASA GODDARD SPACE FLIGHT CENTER

A. 1 DETAILS OF FINAL UNITS

Detailed drawings and descriptions of the final miniature fuel cells delivered to NASA Goddard are given below.

A. 1. 1 Miniature Fuel Cell Base

The miniature fuel cell base (see Figure A-1) is machined from 304 stainless steel bar stock. The outside diameter of the base is threaded along its entire length with 5/8 - 32 threads for attachment to the battery case on one end and the cover on the other end. The base contains a 0. 375-inch diameter through-hole for transmitting battery gases, and a recessed area with 0. 453 inch diameter to accommodate the electrode and gas distribution screen. The base also contains a serrated edge on its electrode face to provide a gas tight seal against the adjacent asbestos layer.

A. 1. 2 Miniature Fuel Cell Top

The miniature fuel cell top (see Figure A-2) is also machined from 304 stainless steel bar stock. The top contains a recessed area with . 450-inch diameter to accommodate an electrode and gas distribution screen, and also contains a serrated edge to provide a second gas tight seal on the adjacent asbestos. The top is drilled in two locations to accommodate two gas manifolds with . 090 inch diameters. These manifolds, also of 304 stainless, are silver brazed into the respective holes with "Easy Flow" Alloy 45. The top is also drilled and tapped in one location to accommodate a threaded terminal post with . 093-inch diameter.

A. 1. 3 Miniature Fuel Cell Cover

The miniature fuel cell cover (see Figure A-3) is machined from plexiglass bar stock. The external surface is machined in the form of a standard 0. 750-inch hex nut to accommodate a standard torque wrench. The internal surface is drilled and tapped with 5/8 - 32 threads to a depth of 0. 280 inch to correspond to the threads on the

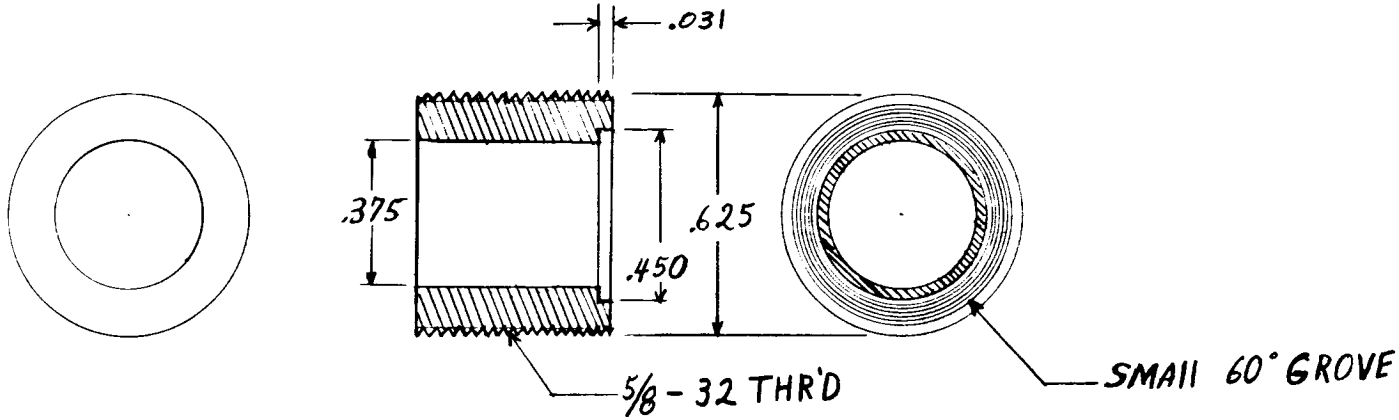


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Figure A-1. Micro Fuel Cell Base

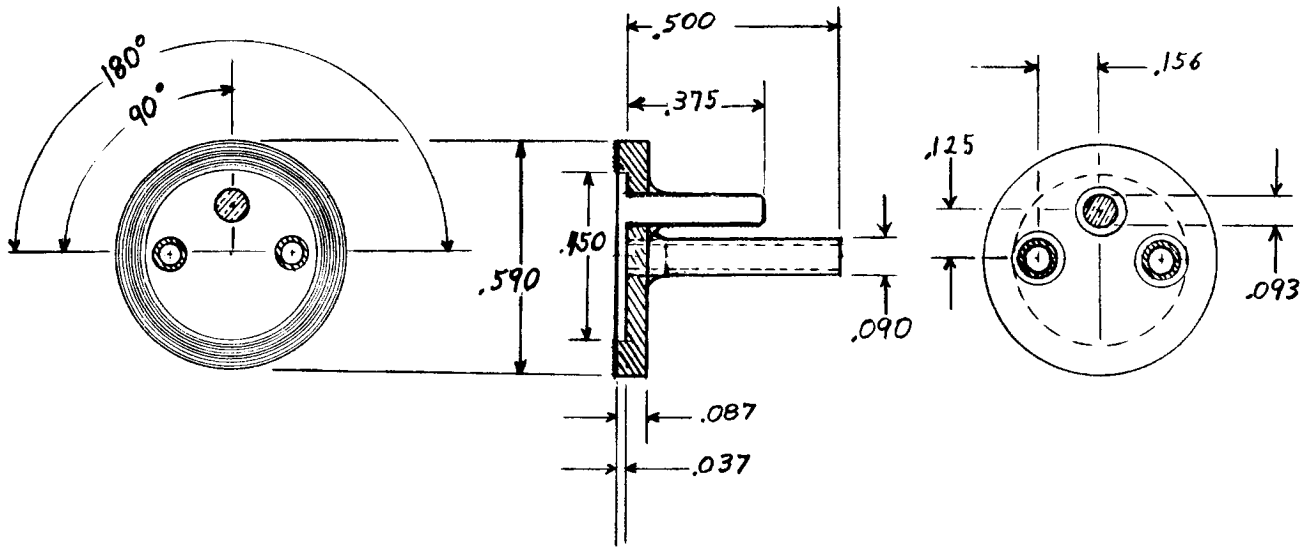

Figure A-2. Micro Fuel Cell Top

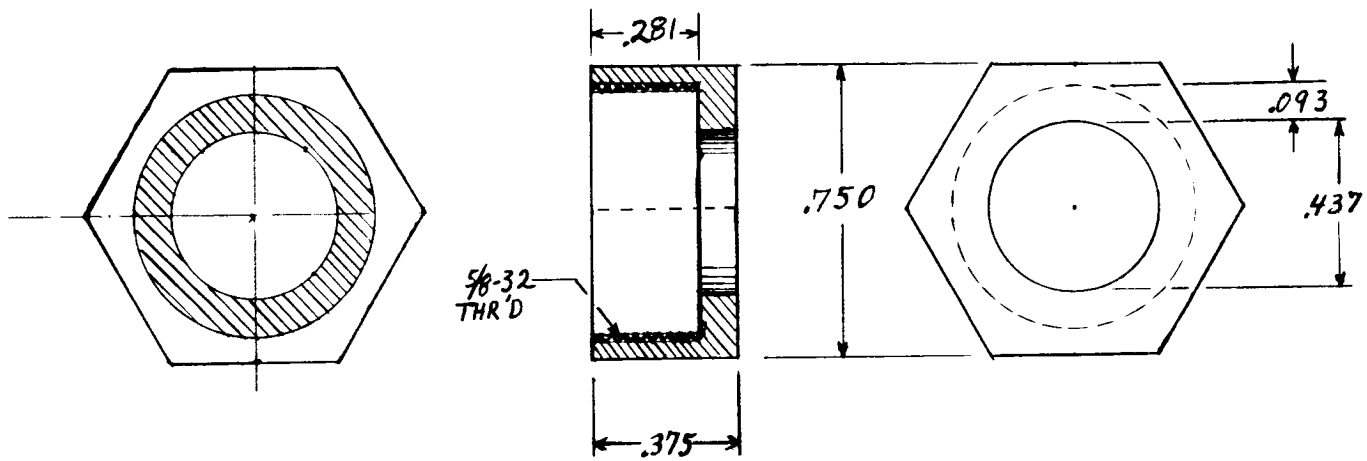

Figure A-3. Micro Fuel Cell Cover

miniature fuel-cell base. The cover also contains a 0.437-inch diameter through-hole to accommodate the gas manifolds and terminal of the miniature fuel cell top.

A.1.4 Miniature Fuel Cell Lock Nut

The miniature fuel cell lock nut (Figure A-4) is machined from 304 stainless steel bar stock. Its external surface is machined in the form of a standard 0.750-inch hex nut to accommodate a standard wrench. The internal surface is drilled and tapped with 5/8 - 32 threads for mounting on the fuel cell base. A thin piece of stainless steel wire 0.035-inch diameter is silver brazed to one of the external hexagonal surfaces to provide the second terminal.

A.1.5 Thread Seal

The thread seal (see Figure A-5) was purchased from the Parker O-Ring Company. The part consists essentially of a metal washer with a moulded-in rubber seal.

A.1.6 Electrodes and Screens

A special punch was machined and hardened for cutting electrodes with the desired diameter of 0.450 inch. The electrodes were then prepared simply by punching them from a sheet of the electrode material supplied by American Cyanamid Co. The material was designated as "American Cyanamid Fuel Cell Electrode Type A.B.-40." The same punch was also used to cut the gas distribution screen from a stock material of 200-mesh nickel with thickness of 0.010 inch.

A.1.7 Asbestos

Another punch was machined and hardened for cutting asbestos matrix discs with the desired diameter of 0.562 inch. The matrices were then prepared by simply punching them from a sheet of asbestos stock material. This material was obtained from Johns Manville Corporation and was 1/16 inch thick. It was designated as "Fuel-Cell Grade Asbestos."

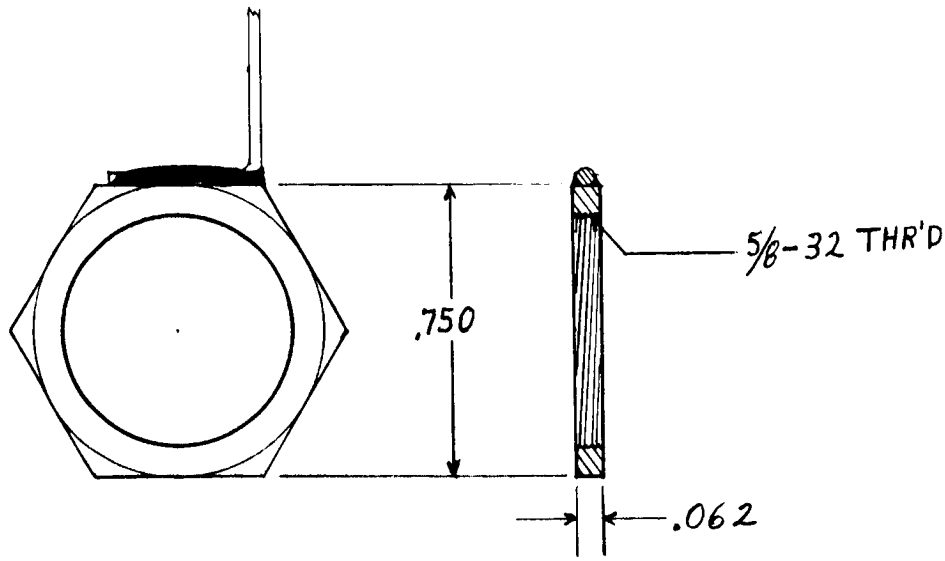

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Figure A-4. Micro Fuel Cell Lock Nut

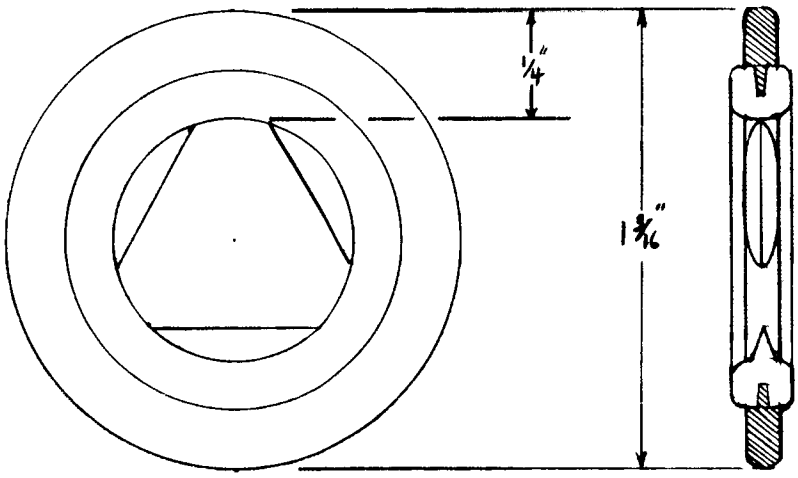

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Figure A-5. Thread Seal

A.2 DETAILED ASSEMBLY AND OPERATIONAL INSTRUCTIONS

This section contains detailed instructions on the assembly and disassembly of the miniature fuel cells as well as instructions on installation in batteries and start-up procedures. Also included are sample evaluation tests.

A.2.1 Assembly

The micro fuel cells have been completely assembled at Astropower Laboratory and are ready for installation and test in a battery or simulator. In the event that the cells are taken apart for inspection, they may be reassembled in the following manner.

1. Fasten thread seal to bottom portion of miniature fuel cell base. This may be accomplished by passing the wick through the center of the thread seal and then twisting the thread seal onto the base until approximately 1/16 inch of the threads extends through the thread seal.
2. Apply washer to top side of base and let fall in place on the thread seal.
3. Apply lock nut to top side of base and screw it firmly (finger tight at this point) against the washer.
4. Position electrolyte matrix in center of fuel cell top.
5. Position top portion of fuel cell on top of electrolyte matrix.
6. Position cover over top and screw into base firmly (finger tight again at this point).

A.2.2 Activation and Installation

The fuel cell may be activated by two alternative methods depending upon the time requirements for initiation of testing.

1. Quick Activation – In this method the cell is activated by adding electrolyte directly to the matrix. This requires disassembly of the top portion of the cell. The asbestos matrix is taken out and

placed on a clean surface. Three drops (or approximately 0.1 gm) of 30% KOH solution are then applied to the upper surface and let saturate for about one minute. The matrix is then turned over and three more drops are applied to the other surface and let saturate for another minute. The matrix is then replaced in the cell and the unit is reassembled as described in Section 3.0.

2. Slow Activation – The cell may also be activated without disassembly by merely immersing the wick in the battery electrolyte or a solution of 30% KOH and waiting for a sufficient time until the electrolyte has been wicked and saturated the matrix. It has been found that a stand time of at least three hours is required for complete activation by this method for a wick length of 1-1/2 inches.

A.2.3 Installation

The miniature fuel cell is installed in a battery or battery simulator in accordance with the following procedures.

1. The case of the battery or simulator is first drilled with a standard 5/8-inch drill.
2. The hole is then tapped with a 5/8 - 32 thread drill.
3. The fuel cell is then inserted in the tapped hole starting with the wick first and followed by the threaded fuel cell base. The cell is screwed in by hand to a depth of at least 1/16 inch.
4. The wick is then suspended in the electrolyte in the case of a simulator, or wedged between the plates in the case of a battery, with a thin screwdriver or tool which has also been supplied. The screwdriver or tool may be inserted through the battery vent cap.
5. The lock nut is then tightened against the washer and thread seal with a special thin wrench. Applied torque should be finger tight or approximately 10 inch-lbs.
6. The two halves of the micro fuel cell are then tightened by applying a torque wrench to the hexagonal cell cover. Applied torque is quite critical in order to provide a good seal. The recommended value is 10 inch-pounds.

7. Electrical contacts are made to the screw terminal on the top and the extended steel wire attached to the lock nut. This wire is made extra-long and may be cut to any desired length.

A.2.4 Start-Up Procedures

In the case of simulator tests the following start up procedures are recommended.

1. Flush the top fuel-cell electrode with either hydrogen or oxygen (depending on the gas to be employed in the simulator) for a period of at least five minutes at a flow rate of at least 20 cc/minute.

The gas may be introduced at either of the two gas ports and should be vented from the other to a well-ventilated area.

2. Flush the simulator with either H_2 or O_2 (depending on the gas employed in the top fuel cell electrode) in a similar manner to that described above. Flushing time will depend upon the size of the simulator. For a nominal simulator size of 50 to 100 cc, a flushing time of at least one hour at 20 cc/minute is recommended. Inlets and outlets to the simulator should be arranged to promote good circulation within.

3. Leak Test – Apply a positive pressure of 1 to 2 psig in the simulator and check for leaks on the top side of the micro fuel cell with a good detergent. If leaks are found then retighten fuel cell cap.

In the case of an actual battery test the top electrodes of each fuel cell are flushed with their respective gases (either H_2 or O_2) for the recommended times above. The battery tests can also be carried out in either the open end or dead end mode of operation described below. The cells should also be leak tested as described above by applying a pressure inside the battery. This is most readily applied through the battery vent cap.

A.2.5 Testing Miniature Fuel Cells

The miniature fuel cells can be tested under a variety of modes of gas flow listed below.

1. Open-End in Both Top Electrode and Simulator – In this case the gases are passed slowly into and out of the simulator and top electrode at very low rates, i.e., a fraction of a cc/minute. This mode permits the highest fuel cell output and corresponding gas consumption capability for long term continuous operation.

2. Open-End in Top Electrode and Dead-End in Simulator – In this case the top electrode is fed with a slow flow of gas as above and the simulator is fed one-way, or dead-end. This more closely resembles the mode which would be encountered in an actual battery test. Output of the micro fuel cell is almost as high as that with open end flow in both electrodes as above.

Recommended pressure in the simulator in this mode is 1 to 2 psig. This can be maintained adequately with a dual stage regulator. The micro fuel cell can withstand higher pressure differential pressures to 10 psig but the lower values are recommended.

3. Dead-End in Both Top Electrode and Simulator – In this case the gases are fed one way or dead end to both simulator and top electrode. There is no limit to the pressures employed here but the pressure differential should be kept to a minimum as described above. This mode does not permit as high an output for long term operation as in the above modes. Maximum currents are in the range of 1 to 10 ma in this case.

4. Battery Tests – There are only two alternative modes of gas flow in the battery tests, i.e., open flow or dead end in the top fuel cell electrodes. The battery gases of course are restricted to dead-end flow in this case. Two fuel cells are employed, one supplied with H_2 and the other with O_2.

In the open flow mode the gases are passed slowly across the cell at the rates described above. In the dead end mode the gas vent lines are merely connected to a pressure gage. Operating pressures of both gases in this case should be approximately the same and in the range of 1 to 2 psig.

A.2.6 Performance Testing

The following tests may be employed to evaluate micro fuel-cell performance.

1. Gas Consumption Capability – The ability of a micro fuel cell to consume H_2 or O_2 can be determined directly or indirectly. In the direct method one measures the pressure decline in a battery or simulator in which the fuel cell is installed and operating. In the indirect method one merely measures the current and calculates the corresponding gas consumption rates based on Faraday's laws.

2. Polarization Characteristics – The polarization or voltage-current characteristics define the electrochemical performance and also give the gas consumption capability in a precise manner. These characteristics may be determined simply by recording the voltage and current output of the cell when operated over a range of external loads.

3. Stability – Stability of electrochemical performance and corresponding gas consumption capability may be determined by continuous long term operation. This may be carried out in any of the three following methods.

   a. By running at constant load and recording operating voltage and current at various intervals of time.

   b. By running at constant current and recording operating voltage versus time. This requires either a constant current supply or manual adjustment of load.

c. By running at constant voltage and recording operating current versus time. This requires a constant voltage supply or manual adjustment of load.

A.2.7 Sample Evaluation Test

Suggestions for an initial evaluation test in a simulator are given below.

1. Assembly micro fuel cell in a simulator which could be any small (50-100 cc) plastic container which is resistant to KOH. Add a small amount of 30% KOH to bottom and immerse wick.
2. Flush simulator with H_2 and top electrode with O_2 as described in Section A.2.4.
3. Apply 2 psig or approximately 4 inches mercury pressure of H_2 in simulator and seal off.
4. Pass oxygen slowly across top electrode.
5. Place micro fuel cell on discharge across fixed load of about 200 ohms and measure voltage, current, and pressure versus time.

SM-48457-F

Final Report

Small Fuel Cell to Eliminate Pressure Caused by Gassing in High Energy Density Batteries

(30 June 1965 - 30 June 1966)

Contract No. NAS 5-9594

Prepared by

Missile and Space Systems Division
Astropower Laboratory
Electrochemistry Department
Douglas Aircraft Company, Inc.
Newport Beach, California

for

Goddard Space Flight Center
Greenbelt, Maryland

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C/932

Figure 1. Ruptured 15 Ah Ag/Zn Cell

SUMMARY AND CONCLUSIONS

Silver-zinc batteries are known to evolve hydrogen and/or oxygen during operation and on stand.[1] Such gassing presents a severe problem in developing completely sealed batteries because gassing can result in high pressures and ultimately rupture the battery case.

This program was concerned with miniature hydrogen-oxygen fuel cells installed on the battery to consume evolved gases. In the process the fuel cells also deliver electrical energy that may be used for an auditory warning or telemetering response indicating battery gassing. It was demonstrated by the conclusion of this program that miniature fuel cells can be used successfully to relieve the pressure buildup in commercial silver-zinc cells.

The program was experimental and was devoted primarily to testing previously devised miniature fuel cells in both simulated and actual battery gassing environments. These tests included life tests in battery simulators, determining the effect of temperature and gas composition on performance, and evaluating water removal techniques. Performance tests of these miniature fuel cells in 100-amp-hour silver-zinc cells were also included. Fifteen miniature fuel cells were delivered to NASA Goddard.

A. Most Significant Results and Conclusions

1. Miniature fuel cells sealed into commercial silver-zinc cells consume evolved hydrogen and oxygen gases at a sufficiently rapid rate for maintenance of a minimal pressure level within the battery throughout its life without a significant increase in battery weight. The miniature fuel cell operates during charge, discharge and open circuit stand in the fully charged condition. Under similar battery operational conditions without an incorporated miniature fuel cell, rupture of the battery case can occur, as shown in Figure 1.
2. Miniature fuel cells can function effectively in the open-ended mode of gas flow for extended periods of time. Continuous operational life of as long as 8,000

hours was obtained and it appears that still longer life would be possible.

3. Accurate data on gassing behavior in commercial 100-ampere-hour silver-zinc cells can be obtained from installed miniature fuel cells. Both the nature and quantity of the gases evolved can be determined in a direct manner far more expeditiously than with any other method.

B. Other Noteworthy Results and Conclusions – Silver-Zinc Cell Gas Simulator Studies

1. Miniature fuel cells can function effectively in the open gas flow mode for extended periods of time. Eight cells with electrode areas ranging from 0.25 to 5.0 cm^2 functioned effectively in this manner under simulated battery gassing environments for operating times ranging from at least 4,000 to 8,000 hours. These miniature fuel cells would function over longer periods of time, if necessary.

2. Miniature fuel cells can function effectively in the dead end mode of gas flow for extended periods of time. Six cells with electrode areas ranging from 0.25 to 5.0 cm^2 functioned effectively in this manner under simulated battery gassing environments for operating times ranging from 1,900 to 6,000 hours.

3. The following relationship between miniature fuel cell size and its gas consumption capability was established. Fuel cells having cross sectional areas of 0.25 cm^2, 1.0 cm^2 and 5.0 cm^2 are capable of consuming hydrogen at rates of at least 1.6 cc/hr, 6.3 cc/hr and 10.6 cc/hr, respectively, over extended periods of time.

4. Functionality of miniature fuel cells was demonstrated for extended operating times (at least one month) on mixtures of hydrogen and oxygen in the anode, and pure oxygen in the cathode.

5. The effect of temperature on miniature fuel cell performance was determined. Electrical output at 40°C was approximately twice as high as at 25°C. Output at 0°C was approximately 80% of that at 25°C.

6. A relationship between miniature fuel cell open circuit voltage and hydrogen concentration in an anodic gas mixture of hydrogen and oxygen was determined experimentally. These results should be useful in determining internal cell (battery) gas composition by remote control or telemetering.

C. Commercial Silver-Zinc Cell Studies

1. Two miniature fuel cells are required for complete control of internal pressure in a sealed silver-zinc cell during all phases of its operation because both H_2 and O_2 are evolved. However, on open circuit stand or on limited, low level operation, only one miniature fuel cell is required (to consume hydrogen).

2. Two miniature fuel cells, both having 1.0 cm^2 cross sectional electrode areas, installed in 100 ampere-hour cells, limited the pressure rise to not more than 1.5 psig over the following cycling regime: 2-hour discharge at 20 amperes (40% depth of discharge) and 22-hour charge at 2 amperes. The ratio of evolved hydrogen to oxygen gases was approximately the same, i.e., 2.7 to 1 in one cell and 3.8 to 1 in another. The total gassing rates can vary between cells; total hydrogen and oxygen evolution rates in one silver-zinc cell were six times higher than those in another silver-zinc cell under identical operational conditions. Average gassing rates were 0.08 cc H_2/hour and 0.03 cc O_2/hour in one cell and 0.49 cc H_2/hour and 0.13 cc O_2/hour in another cell.

3. Similar gassing patterns were found for 15-ampere-hour commercial silver-zinc cells with two installed miniature fuel cells.

4. It would be possible to employ the product water derived from miniature fuel cells for life support purposes if the amount of battery gassing were large enough.

D. Recommended Future Effort

The findings of this program indicate that important applications of miniature fuel cells may be found in sealed silver-zinc batteries. Exploratory proprietary efforts have indicated that miniature fuel cells could be applied to sealed nickel-cadmium and lead-acid cells as well. The type of miniature fuel cells used in the current program could be effective in consuming and detecting the gases evolved in sealed nickel-cadmium and lead-acid cells. Other types of miniature fuel cells developed during a company sponsored program employed solid rather than gas type electrodes and manifested regenerative capability. These are

recommended for continued investigation, where external gas storage is either limited or undesirable.

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1.0 INTRODUCTION

Gassing in high energy density batteries involves the formation of hydrogen, oxygen or both within the batteries by any of several mechanisms. These include decomposition or dissolution of active electrode materials, liberation of absorbed gases, or internal electrolysis. Gassing may occur during all modes of operation including charge, discharge, and open circuit stand. The type of gas and the rate and extent to which it is evolved depend upon several factors including the type of battery, ambient temperature, and the charge-discharge regime to which the battery is subjected.

The phenomenon of gassing presents a serious problem in the development of completely sealed batteries. High pressures are developed that may lead to rupture of the cell case and to battery failure.

A unique method of dealing with this problem has been devised at Astropower Laboratory which consists of using miniature fuel cells to consume evolved battery gas. This concept had been tested on an earlier proprietary program.[2] The miniature fuel cells perform this function by electrochemically consuming the hydrogen or oxygen gases inside the battery to form water. Two fuel cells, one for consuming hydrogen and the other for oxygen, are usually required for this purpose as will be shown subsequently. One is supplied externally with hydrogen to consume the oxygen and the other is supplied externally with oxygen to consume the hydrogen. Of additional interest here is the use of alternative types of regenerable miniature fuel cells with solid rather than gas-type electrodes, i.e., silver or mercuric oxide in place of oxygen, and zinc or cadmium in place of hydrogen. Astropower has made considerable progress in developing these types of miniature fuel cells for this purpose.[3]

At the start of the current program it was not known how a miniature fuel cell could perform under gassing conditions in a silver-zinc cell. Such critical aspects as mode of installation into the battery,

stability of fuel cell performance and life and actual fuel cell dimensions for a particular silver-zinc battery type and size were to be determined. Although it was felt that a fuel cell designed around the KOH-asbestos membrane system was most appropriate for alkaline battery application, other membrane systems could offer advantages as well. The following program plan, based on the stipulations of the project work order, as well as on continuing discussions with technical personnel of NASA-Goddard Space Flight Center, was pursued. The type of batteries involved herein are of the silver-zinc type and the miniature fuel cells involved are of the hydrogen-oxygen gaseous diffusion type.

Outline of Program Plan

1. To select the optimum method of installing a miniature fuel cell on a silver-zinc cell. Three previously devised methods were considered here, including a "Jack" mounting, a "Screw" mounting, and a "Deep Insert" mounting.
2. To determine the long-term gas consumption capability of miniature fuel cells for as long as 5,000 hours.
3. To determine the relationship between miniature fuel cell size and gas consumption capability.
4. To design and fabricate the optimum type of miniature fuel cells based on the above for a given commercial silver-zinc cell.
5. To conduct performance tests on the miniature fuel cell in silver-zinc batteries at the 100 ampere-hour capacity level.
6. To deliver 15 miniature fuel cells to NASA-Goddard Space Flight Center at the conclusion of the program.

These objectives were achieved during the course of the program. Most significantly, it has been demonstrated that miniature fuel cells can be installed in commercial silver-zinc cells; and in an entirely reliable manner can consume the gases evolved within the cells. Therefore, the life of a battery can be prolonged with an added measure of safety.

The description of experimental procedures, results and discussions are given in the sections which follow.

2.0 TECHNICAL DISCUSSION

This section contains a complete description of the miniature fuel cells involved and results of all tests performed on them in both simulated and actual battery gassing environments.

2.1 Description of Miniature Fuel Cells

Basic elements of all miniature fuel cells employed on this program were essentially the same, and consisted of platinum electrocatalyst for both hydrogen and oxygen, and potassium hydroxide electrolyte at 30% concentration contained in an asbestos matrix having a thickness of one-eighth inch. The significant differences between cells were in the specific type or grade of platinum catalyst and overall cell configuration. Three general types of cell configurations were employed and were designated as the "initial," "modified," and "final" types. Overall sizes ranged from 0.25 cm diameter to 5.0 cm diameter. A brief description of each type is given below.

2.1.1 Initial Cell Type

Components of the initial miniature fuel cell are shown in Figure 2.

Both hydrogen and oxygen electrodes are identical and consist of platinum black, which has been bonded under pressure to a platinum-plated silver screen. A few strands of each screen pass through the cell frame and serve as external electrical leads. The electrodes in turn are bonded under pressure to a disc of sheet asbestos to form a rigid electrode-electrolyte assembly. A polyurethane rim is mounted on the outer periphery of the membrane by means of the jig designed for this purpose. The purpose of this rim is to provide internal gas seals both between compartments and external to the atmosphere. The electrode-electrolyte assembly, along with the gas distribution plates, are mounted in the cell housing to form the complete miniature fuel cell as shown in Figure 2. The housing is made of nylon, and the

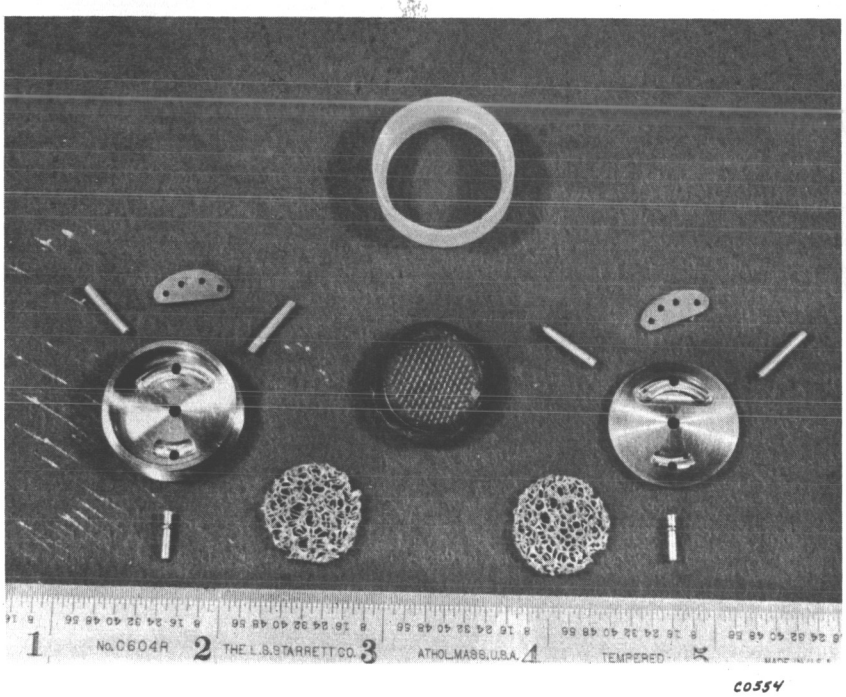

Figure 2. Initial Miniature Fuel Cell

distribution plates are made of stainless steel. One of the gas distribution plates contains inlet and outlet tubes for transmitting a gas (either hydrogen or oxygen) from an external supply tank. The other distribution plate has a machined center hole for transmitting gases to the electrode from either a silver-zinc battery or one of the battery simulators. The outside of this end plate is threaded for direct mounting onto either the battery or simulator.

2.1.2 Modified Type

Electrodes for this cell (Figure 3) were obtained from the American Cyanamid Company and included their Types A. B. -6, A. B. -40, and A. A. -1. Each of these was similar in that they consisted of platinum black catalyst deposited on a collector screen with the addition of a Teflon water-proofing agent. The only difference was in composition of the collector screens. Gold-plated nickel, nickel, and tantalum were the materials for Types A. B. -6, A. B. -40, and A. A. -1, respectively. The electrodes were cut to the desired dimension with specially prepared die punches. The same electrode material was employed for both hydrogen and oxygen electrodes in any given test.

The electrolyte again consisted of 30% KOH solution impregnated in a layer of 1/16-inch fuel-cell grade asbestos.

Electrodes were spot-welded to the gas distribution plates to provide good electrical contact. External electrical leads were then taken directly from external surfaces of these plates. Both plates were very similar to those described above; one contained inlet and outlet tubes for external gas supply and the other contained a hole for transmitting battery or simulator gases to the electrodes. The outside of the latter plate was threaded for mounting in a battery or simulator. Material of construction was stainless steel, as above.

Somewhat different types of gas seals were employed in this cell. Internal sealing between compartments was provided by compression of the outer periphery of the asbestos layer

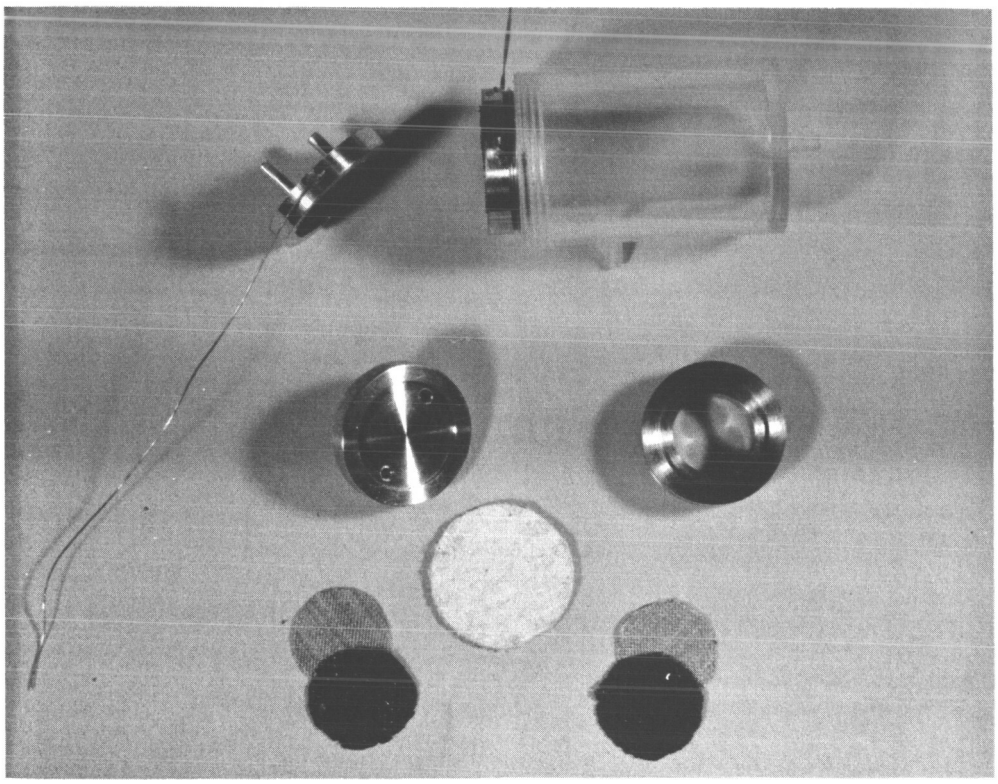

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Figure 3. Modified Miniature Fuel Cell

between the surfaces of the gas distribution plates. External sealing was provided by a bead of epoxy resin around the circumference where the cell halves meet.

Several sizes of these cells have been built with overall dimensions ranging from 0.25 inch in diameter to 5.0 inches in diameter.

2.1.3 Final Type

The final fuel cell configuration (Figure 4) is essentially the same as the modified type above with a few minor additions. The first was use of an internally-threaded plastic cover to hold the two cell halves together, instead of the bead of expoxy as above. The cover was machined in the form of a hexagonal nut so that it could be reproducibly torqued to the cell bottom. The second was addition of a special thread seal to provide insurance against gas leakage in the threads of the installed assembly. Detailed machine drawings of this type are given in Appendix A. Fifteen cells of this type were delivered to NASA-Goddard Space Flight Center.

2.1.4 Installation in Batteries

Three general methods of incorporating micro fuel cells into batteries were devised in a proprietary program.[3] The first of these is the "Jack" type arrangement shown in Figure 5. In this case the cell is designed for direct mounting on the battery vent tube. Battery gases must pass through this tube before entering the fuel cell. The second is the "Screw" type as shown in Figure 6. In this case the outer frame of the fuel cell is threaded into the battery case. Path length through which the gases must travel to reach the fuel cell is somewhat shortened in this case. (This is the type which has been delivered to NASA-Goddard.) The third is the "Deep Insert" type as shown in Figure 7. In this case the fuel cell is mounted deep inside the battery case and exposed directly to the gases evolved from the electrodes. A manifolding arrangement may also be employed as shown in Figure 8.

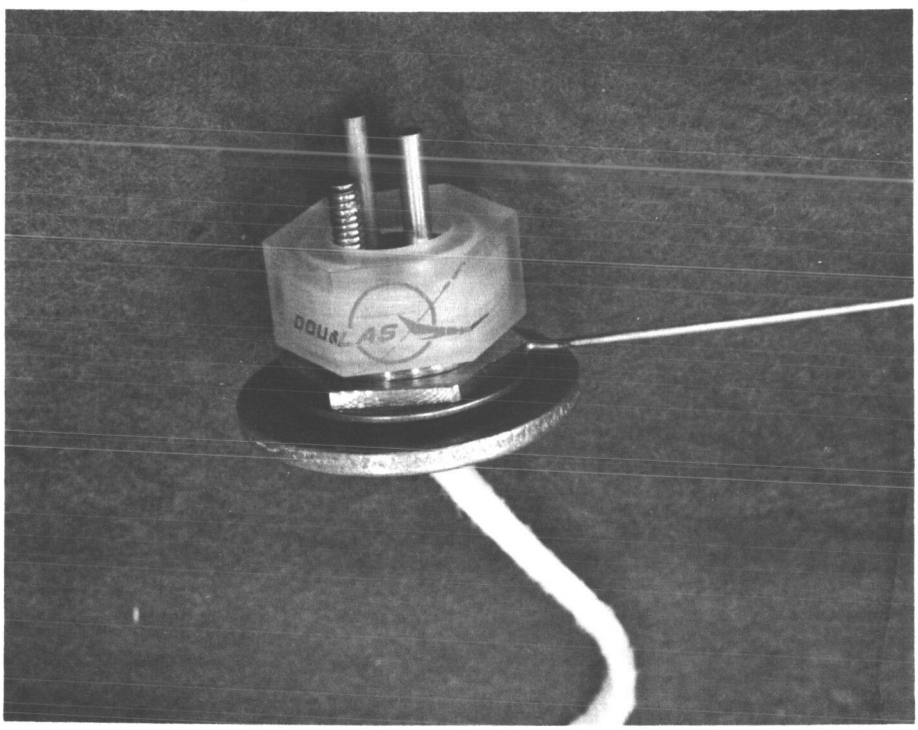

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Figure 4. Final Type of Miniature Fuel Cell

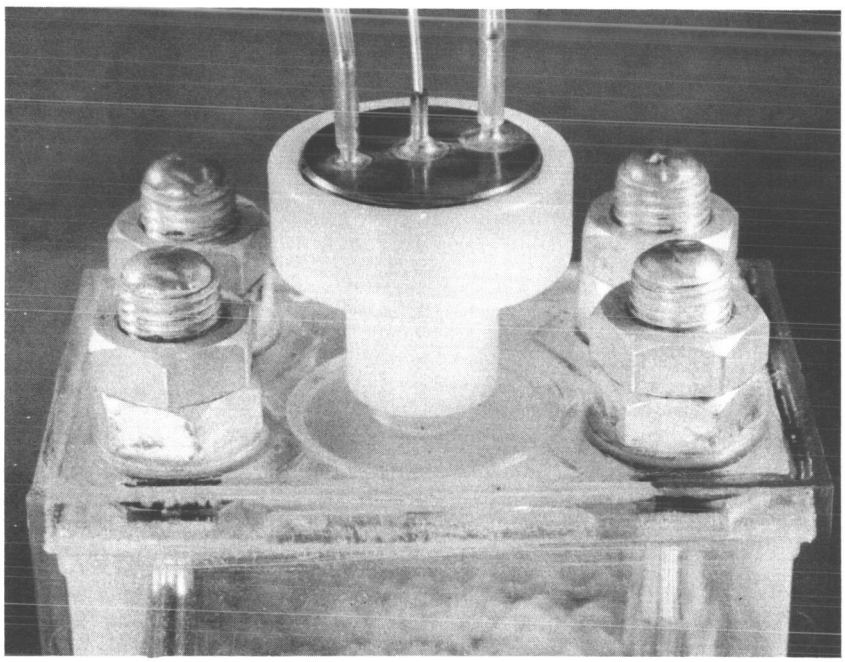

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Figure 5. Jack-Type (Press Fit Connection of Miniature Fuel Cell to Actual Ag/Zn Battery

Figure 6. Screw-Type Connection of Miniature Fuel Cell to Actual Ag/Zn Battery

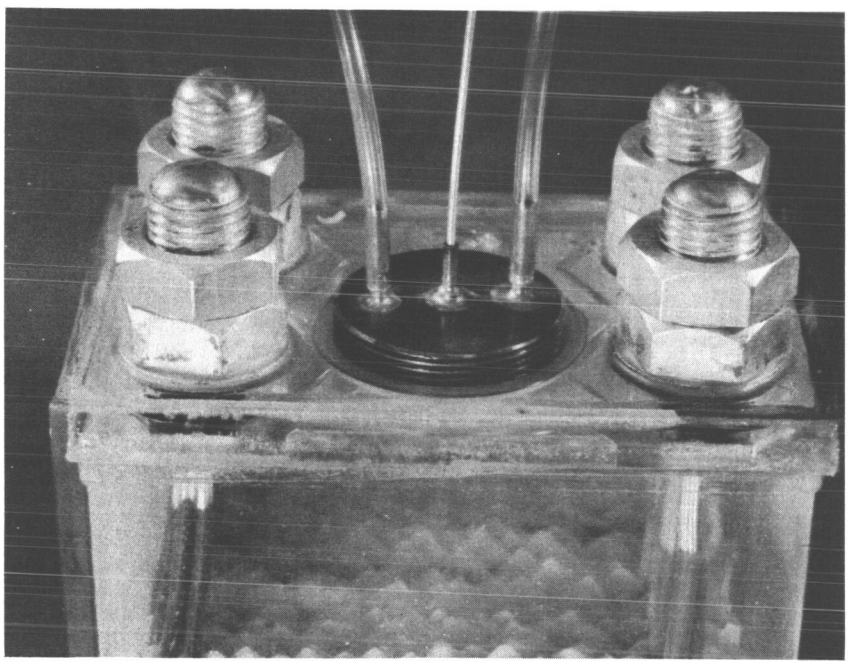

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Figure 6. Screw-Type Connection of Miniature Fuel Cell to Actual Ag/Zn Battery

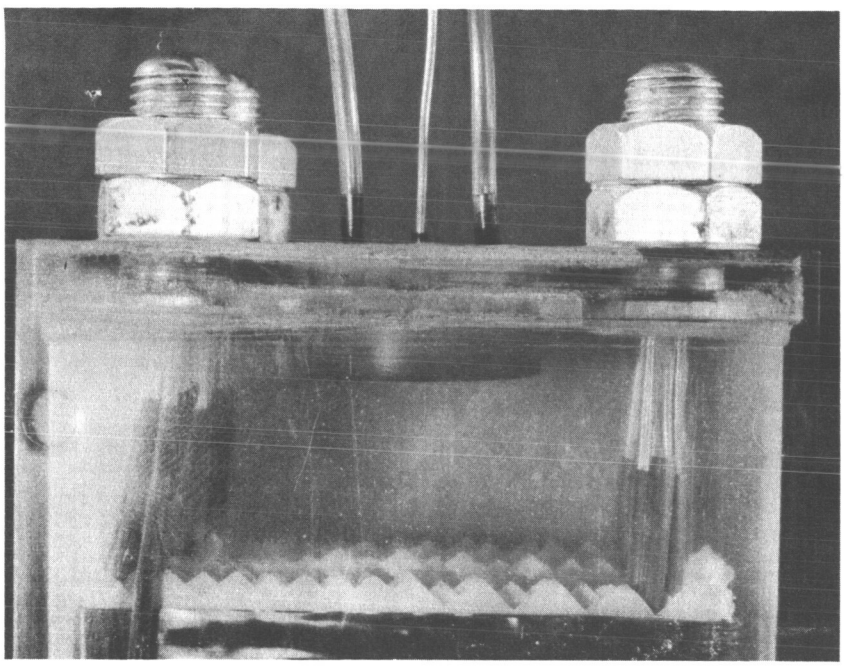

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Figure 7. Deep Insert Type of Miniature Fuel Cell Connection to Actual Ag/Zn Battery

Figure 8. Application of Single Miniature Fuel Cell as Pressure Controller for Three Ag/Zn Batteries by Means of Manifolding Agreement

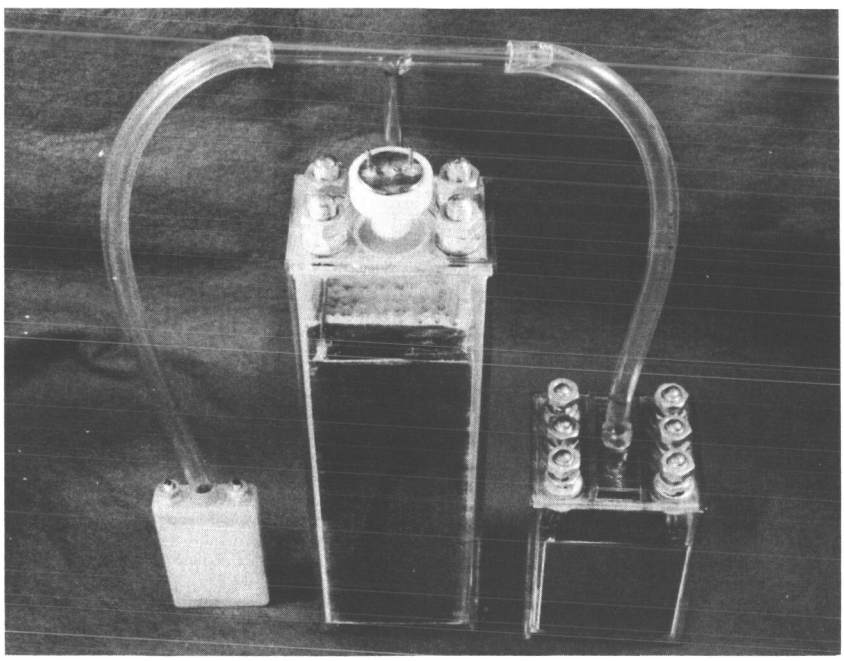

Figure 8. Application of Single Miniature Fuel Cell as Pressure Controller for Three Ag/Zn Batteries by Means of Manifolding Agreement

In this case the evolved gases from several batteries are manifolded to a single miniature fuel cell.

2.2 Tests in Battery Simulators

The purpose of this investigation was to determine the operational characteristics, including life, of miniature fuel cells employing the KOH-asbestos matrix type of electrolyte. Design goal was for 5,000 hours of continuous operation at 25°C. An integral part of this study was to derive a relationship between size of a miniature fuel cell and its gas consumption capability.

The tests were carried out in specially designed battery gassing simulators wherein gas compositions and flows could be closely controlled. Performance was determined as a function of gas composition, ambient temperature, and cell configuration. Methods of removing product water were also evaluated.

2.2.1 Life Tests Under Open Gas Flow Without Wicking

The purpose of these tests was to determine optimum components of the miniature fuel cells for long term continuous operation by the "open gas-flow mode" in the simulators shown in Figure 9. Pure hydrogen and oxygen were passed at flow rates of two cc/hour into the anode and cathode compartments of the miniature fuel cell. Excess gases that were not consumed were vented to the atmosphere. Water balance was maintained by adjustment of gas flow rates. Operating voltage under load as well as complete polarization data were measured periodically. Both the "initial" and "modified" cell types were employed in these tests.

Results of these tests are presented in Tables I, II, and III and are discussed in more detail below.

The cell in Test 1 employed the initial configuration and electrodes as described above in Section 2.1.1. Testing was initiated

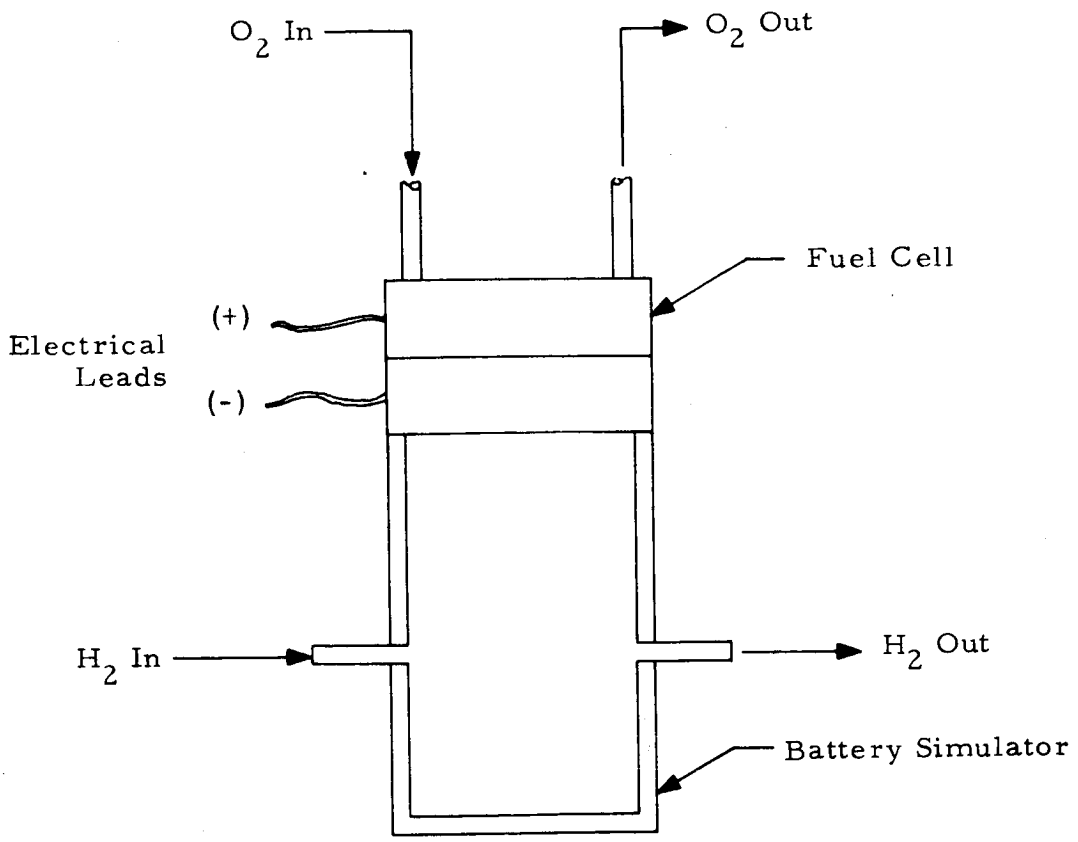

Figure 9. Schematic Diagram of Open Flow Tests

TABLE I

LIFE TESTS OF MINIATURE FUEL CELLS IN OPEN FLOW MODE OF OPERATION WITHOUT WICKS

Test No.	Cell Type	Electrode Type	Electrode Area (cm^2)	Load (ohms)	Time[a] (hrs)	Initial Voltage (volts)	Final Voltage (volts)
1	Initial	Proprietary	1.0	1000	7958	0.80	0.50
2	Modified	A. B. -6	1.0	1000	6105	0.90	0.80
3	Modified	A. B. -40	1.0	1000	5729	0.95	0.95
4	Modified	A. B. -6	1.0	100	5429	0.80	0.70
5	Modified	A. B. -40	1.0	100	5529	0.85	0.80
6	Modified	A. B. -40	0.25	4000	5049	0.95	0.92
7	Modified	A. B. -40	5.0	200	4899	0.95	0.60
8	Final	A. B. -40	1.0	1000	4233	0.88	.80

(a) All tests were terminated after the indicated number of hours. Longer operational life was possible.

TABLE II

INITIAL POLARIZATION DATA OF MINIATURE FUEL CELLS IN OPEN FLOW MODE WITHOUT WICKS

Current Density, (ma/cm^2)	Potential (volts) Test Number							
	1	2	3	4	5	6	7	8
0	0.91	1.01	1.02	1.02	0.94	1.01	1.05	1.00
1	0.75	0.95	1.00	0.96	.92	0.92	.97	1.00
2	0.63	0.92	0.90	0.92	.90	0.87	0.86	1.00
5	0.40	0.87	0.90	0.84	.86	0.75	0.78	.95
10	--	0.82	0.89	0.75	.80	0.61	0.63	.93
20	--	0.60	0.82	--	--	--	--	.90
50	--	--	--	--	--	--	--	.85
100	--	--	--	--	--	--	--	.75

TABLE III

FINAL POLARIZATION DATA OF MINIATURE FUEL CELLS IN OPEN FLOW MODE WITHOUT WICK

Current Density (ma/cm^2)	Potential (volts) Test Number							
	1	2	3	4	5	6	7	8
0	0.85	0.95	0.99	0.98	0.95	0.98	1.00	0.98
1	0.73	0.94	0.98	0.96	0.92	0.89	0.98	0.95
2	0.50	0.90	0.95	0.90	0.90	0.82	0.80	0.90
5	0.29	0.80	0.89	0.80	0.82	0.70	0.75	0.84
10	--	0.75	0.85	0.50	0.75	--	0.55	0.80
20	--		0.79					0.70
50	--							--
100	--							--

in the early portion of the program and continued to the end for a total operating time of nearly 8,000 hours. Although this cell was found to exhibit relatively stable performance throughout this period, its current output or corresponding gas consumption capability was not optimal (see polarization data in Tables II and III). The limited output was attributed to inactive electrodes. This type of cell might be recommended for extremely long term operation in a silver-zinc battery in which very low but continuous gassing rates were anticipated.

The cells in Tests 2 and 3 contained American Cyanamid fuel cell electrodes Types A.B.-6 and A.B.-40, respectively, and were both discharged across a 1000-ohm load. Both were found to exhibit quite stable performance for operating times of approximately 6,000 hours. Longer operating lives were still possible. Operating voltage and polarization characteristics of the cell in Test 3 (with A.B.-40 electrodes), have remained exceptionally stable and slightly higher than the corresponding characteristics of the cell in Test 2 (with A.B.-6 electrodes). This trend was apparent earlier in the test program and on this basis it was decided to employ A.B.-40 electrodes in the battery tests near the end of the program.

The cells in Tests 4 and 5 also contained American Cyanamid fuel cell electrodes Types A.B.-6 and A.B.-40, respectively. These cells were each discharged across a lower resistance of 100 ohms, and therefore operated at higher currents than Tests 2 and 3 above. Performance of both of these cells remained relatively constant throughout the test period of over 5,000 hours but at somewhat lower voltages than corresponding Tests 2 and 3 above.

The significant parameter in Tests 6 and 7 was electrode area. Active area in Test 6 was 0.25 cm^2 or 1/4 of that employed in the preceding tests; the area in Test 7 was 5.0 cm^2 or 5 times that in the preceding tests. External loads on each were selected to give the same current densities as in Tests 1 through 3 inclusive,

i.e., 4000 ohms for Test 6 and 200 ohms for Test 7. Performance of the cell in Test 6 was found to remain quite constant for the indicated test period of slightly over 5,000 hours. Performance of the cell in Test 7, however, was found to decline appreciably during approximately the same test period. This decline was attributed to electrode flooding caused by inadequate gas flow for evaporating product water.

The distinguishing feature of the cell in Test 8 was its new case and cover design. These were modified to give more reliable gas seals and ease of assembly. Electrodes were of the American Cyanamid Type A. B. -40 with an electrode cross sectional area of 1.0 cm^2. Results have indicated that this cell can operate effectively and quite stably for at least the test period of over 4,000 hours, and most likely well beyond 5,000 hours. This cell type is essentially identical to the types employed in the battery tests (Sections 2.2.7 and 2.3) and delivered to NASA-Goddard.

Four additional tests employing American Cyanamid Type A. A. -1 electrodes were carried out earlier in the program. These were terminated after various intervals of 500 to 800 hours when performance had degraded to very low levels. The degradation was attributed to use of tantalum based A. A. -1 electrode material. Another test employing an organic anion exchange membrane (Ionics Type III EZL) in place of the KOH-asbestos electrolyte was also carried out during the early portion of the program. This test was terminated after 400 hours when cell performance had degraded to a very low level. This was attributed to oxidation of the membrane material.

2.2.2 Life Tests Under Dead-End Flow Without Wicking

In Tests 9 and 10 (Table IV) the gases were supplied to the cell in the dead end mode (without venting excess gases) and without wicks. Gases were stored in small containers and connected to each end of the cell with a short segment of tubing. For safety reasons,

TABLE IV

LIFE TESTS OF MINIATURE FUEL CELLS IN DEAD END MODE OF OPERATION AND WITHOUT WICKS

Test Cell Number	Cell Type	Electrode Type	Electrode Area (cm^2)	Load (ohms)	Time (hrs)	Notes
9	Modified	A. B. -6	1.0	1000	1500	Voltage above 0.8 v for majority of run
10	Modified	A. B. -6	1.0	100	150	Terminated due to flooding, voltage above 0.7 v for majority of run

the size and pressure of the gas containers was kept to a minimum and consisted of 250-ml Erlenmeyer flasks at atmospheric pressure or slightly below it. The flasks were refilled periodically to maintain the pressure level between atmospheric and approximately two inches of mercury vacuum. Electrodes were of the American Cyanamid Type A. B. -6 with an active area of 1.0 cm^2.

Stable performance was observed for Test 9 for over 1500 hours when discharged across a 100-ohm load with a corresponding current of approximately 1.0 ma. Hydrogen consumption rate in this case was approximately 0.4 cc/hour.

Test 10, which was discharged across a 100-ohm load with a corresponding current of approximately 10 ma, was terminated after 150 hours when performance began to decline rapidly. Hydrogen consumption rate in this case was approximately 4.0 cc/hour. The reason for the decline was attributed to electrode flooding as evidenced by an extremely wet condition upon disassembly.

These results signify that a miniature fuel cell without wicks and with 1.0 cm^2 area can consume approximately 630 cc of hydrogen at a rate of 4.0 cc/hour and at least this amount, if not more, at a rate of 0.4 cc/hour.

2.2.3 Life Tests Under Dead End Flow With Wicking

The purpose of these tests was to evaluate the use of wicks in transferring product water from the fuel cell to the battery electrolyte. Such water transfer is a necessity for long term operation of the fuel cell where electrode flooding could limit performance.

The tests were carried out in a simulated battery environment consisting simply of a small Erlenmeyer flask filled with hydrogen containing a small amount of potassium hydroxide solution (see Figure 10). The fuel cell was mounted in a rubber stopper and fitted into the mouth of the flask. One end of the wick was in contact

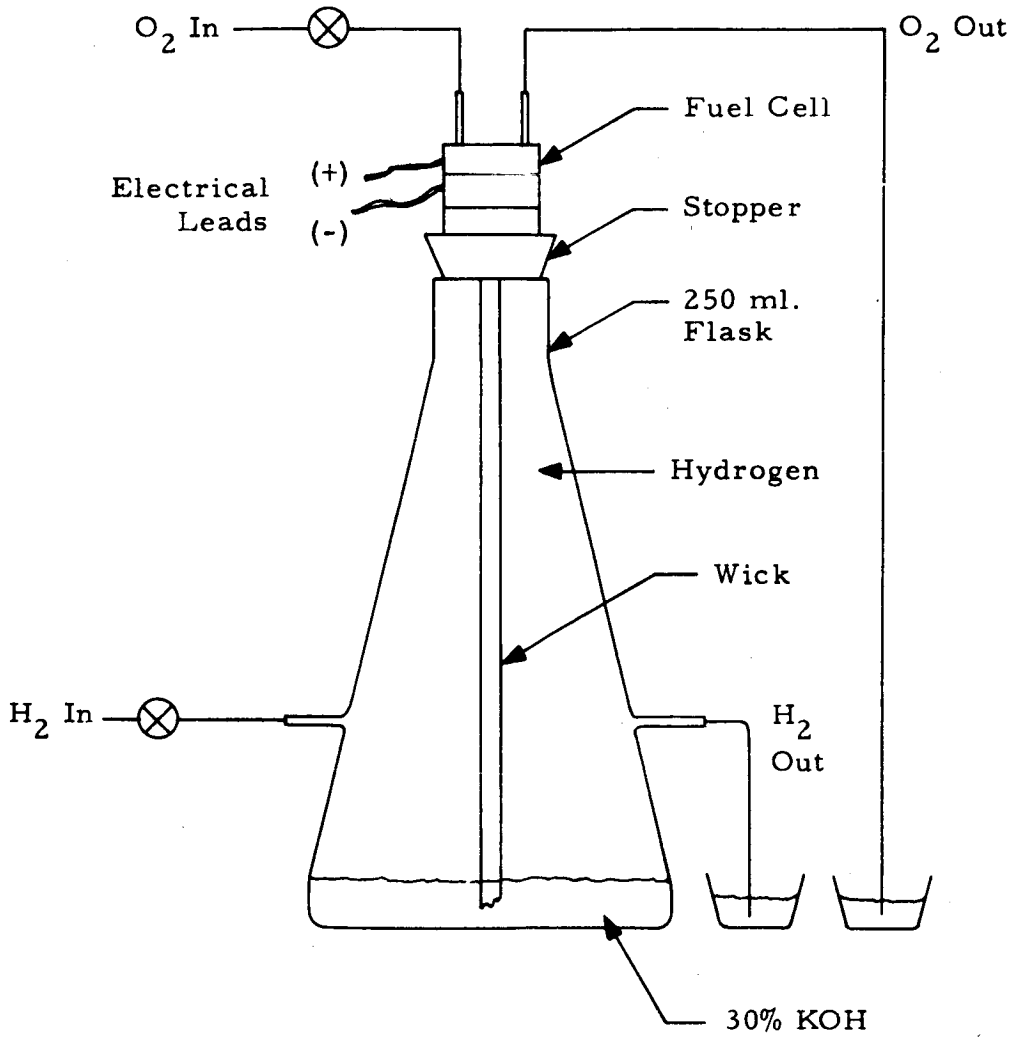

Figure 10. Schematic Diagram of Dead-End Flow Tests with Wicks

with the fuel cell electrolyte through a small hole cut in the middle of the hydrogen electrode and the other end was suspended in the simulated battery electrolyte, 30% KOH. Wick material was from the American Felt Company, Number 61NY185, and was cut in the form of a thin strip with dimension of approximately 1/16-inch by 1/8-inch by 6 inches. Electrodes were American Cyanamid Type A. B. -40 with active area of 1.0 cm^2.

Operation was carried out in a similar manner to that described in Section 2.2.2 but with some modifications. In this case the flask was filled with a small positive pressure of hydrogen from an externally located cylinder. Pressure was then finely adjusted so that there was essentially no flow through the bottle as evidenced by bubbling from a vent line immersed in water. Oxygen pressure and flow were set in the same manner to achieve this dead end mode of operation. The cells were run at constant current with daily adjustment of load on a decade resistance box.

The results obtained are given in Table V, and indicate that miniature fuel cells with 1.0 cm^2 cross-sectional electrode areas can operate for extended periods of time at current densities of 5 and 15 ma/cm^2 at voltages near 0.90 and 0.70 volts, respectively (see Tests 11 and 12). A cell with the same electrode area was unstable at a higher current density of 50 ma/cm^2 (see Test 13).

Performance of cells with both larger (5.0 cm^2) and smaller (0.25 cm^2) electrode areas were also found to be quite stable at current densities of 5 ma/cm^2 (see Tests 14 and 15). Performance of a cell with smaller electrode area (0.25 cm^2) was also found to be stable at a higher current density of 15 ma/cm^2 (see Test 17), whereas performance of a cell with larger electrode area (5.0 cm^2) was found to be unstable (see Test 14).

TABLE V

LIFE TESTS OF MINIATURE FUEL CELLS IN DEAD END MODE OF OPERATION WITH WICKS(a)

Test No.	Electrode Area (cm^2)	Current Density (ma/cm^2)	Time (hrs)	Notes
11	1.0	5	5720(b)	Stable for entire test near 0.9 volt
12	1.0	15	4511(b)	Stable for entire test near 0.7 volt
13	1.0	50	72	Unstable, voltage gradually declined
14	5.0	5	1900(b)	Stable for entire test near 0.9 volt
15	0.25	5	1900(b)	Stable for entire test near 0.9 volt
16	5.0	15	168	Unstable, voltage gradually declined
17	0.25	15	2592(b)	Stable for entire test near 0.6 volt

(a) All tests were conducted with the modified cell type and contained American Cyanamid Type A. B. -40 electrodes.

(b) Longer operational life was possible under stable conditions.

2.2.4 Hydrogen-Oxygen Mixture Tests

The object of these tests was to determine the effect of hydrogen-oxygen mixtures on miniature fuel cell performance. This is pertinent to their intended application in silver-zinc batteries wherein such mixtures are found. Contract work statement called only for examination of anodic H_2-O_2 mixtures versus a pure oxygen cathode. This was extended somewhat to include an examination of cathodic H_2-O_2 mixtures versus a pure hydrogen anode.

Two types of tests were carried out with these mixtures. The first was of the short-term, open-flow type wherein the gases were passed slowly across the fuel cell electrodes. A wide range of both anodic and cathodic mixtures was examined here. The second type was of longer duration in the dead-end mode. In this test a micro fuel cell was operated for an extended time on one anodic mixture. An additional investigation was also carried out on the effect of anodic composition on open circuit voltage. Results of these tests are given below.

2.2.4.1 Open End Gas Flow (Test Series No. 19)

These tests were carried out in the open end gas flow mode of operation. Hydrogen and oxygen were metered with flow meters through the anode compartment with pure oxygen in the cathode in one test series and then through the cathode compartment with pure hydrogen in the anode in another test series.

Results of these studies are given in Figures 11 through 14. Inspection of Figures 11 and 12 indicate that the fuel cell can function satisfactorily with mixtures on its anode side containing up to 30% oxygen. Performance in this mode of operation is noted to decline gradually with increasing oxygen content to a level of 30% oxygen and to fall rapidly with oxygen content increasing between 30 and 50%. Inspection of Figures 13 and 14 indicates that the fuel cell

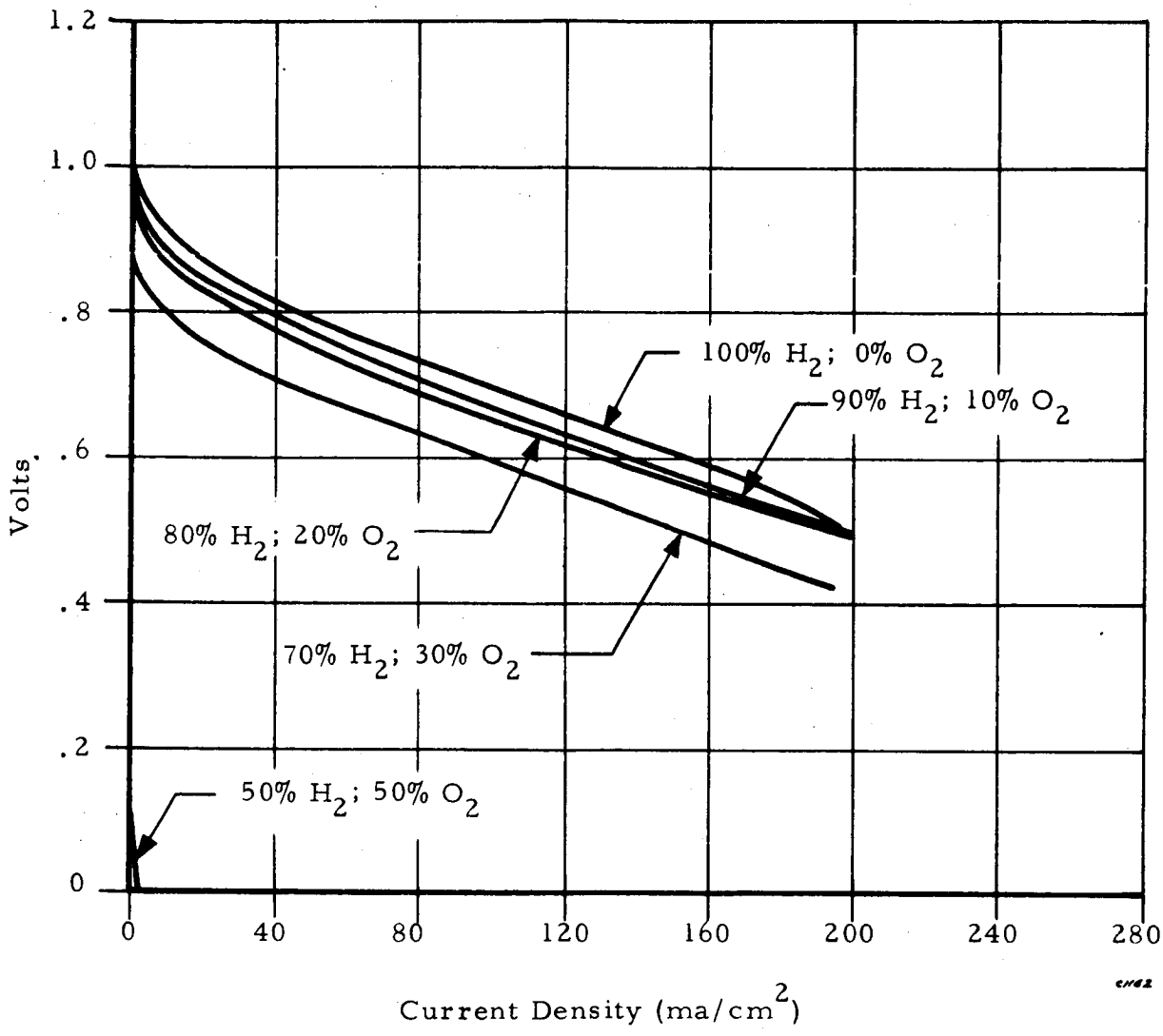

Figure 11. Performance of Miniature Fuel Cell With H_2-O_2 Mixtures in Anode After Several Hours of Operation

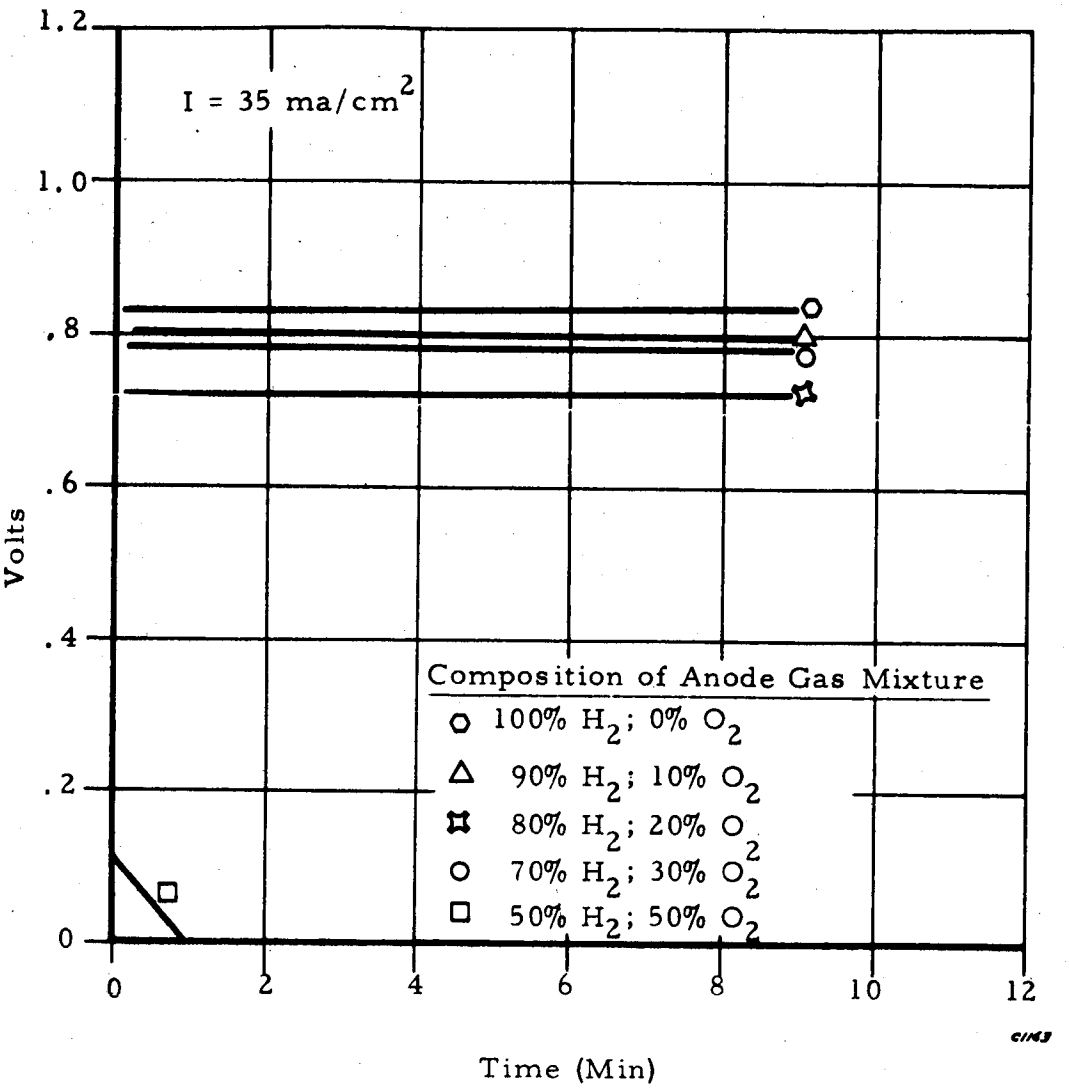

Figure 12. Performance of Miniature Fuel Cell With H_2-O_2 Mixtures in Anode After Several Hours of Operation

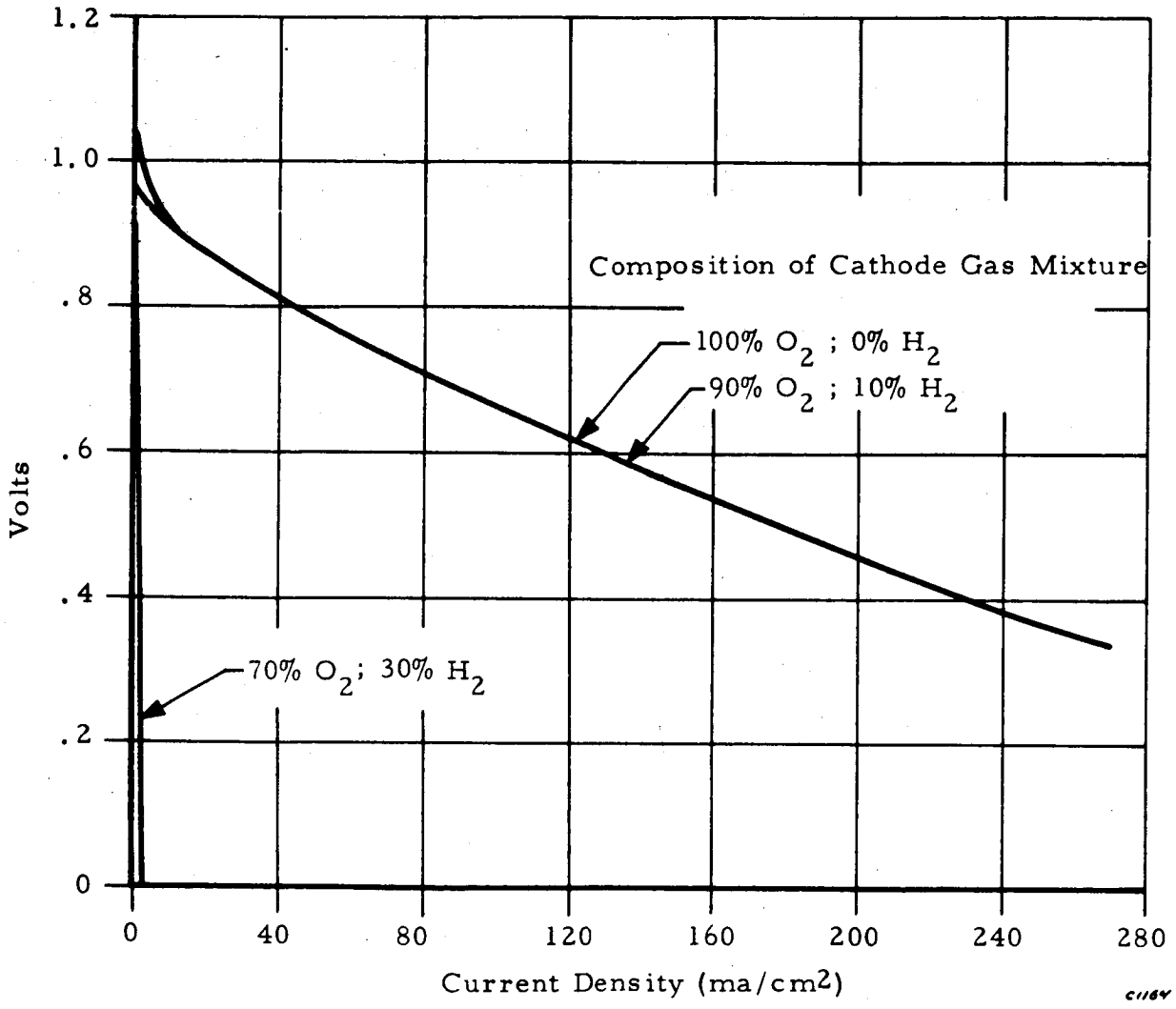

Figure 13. Performance of Miniature Fuel Cell With H_2-O_2 Mixtures in Cathode After Several Hours of Operation

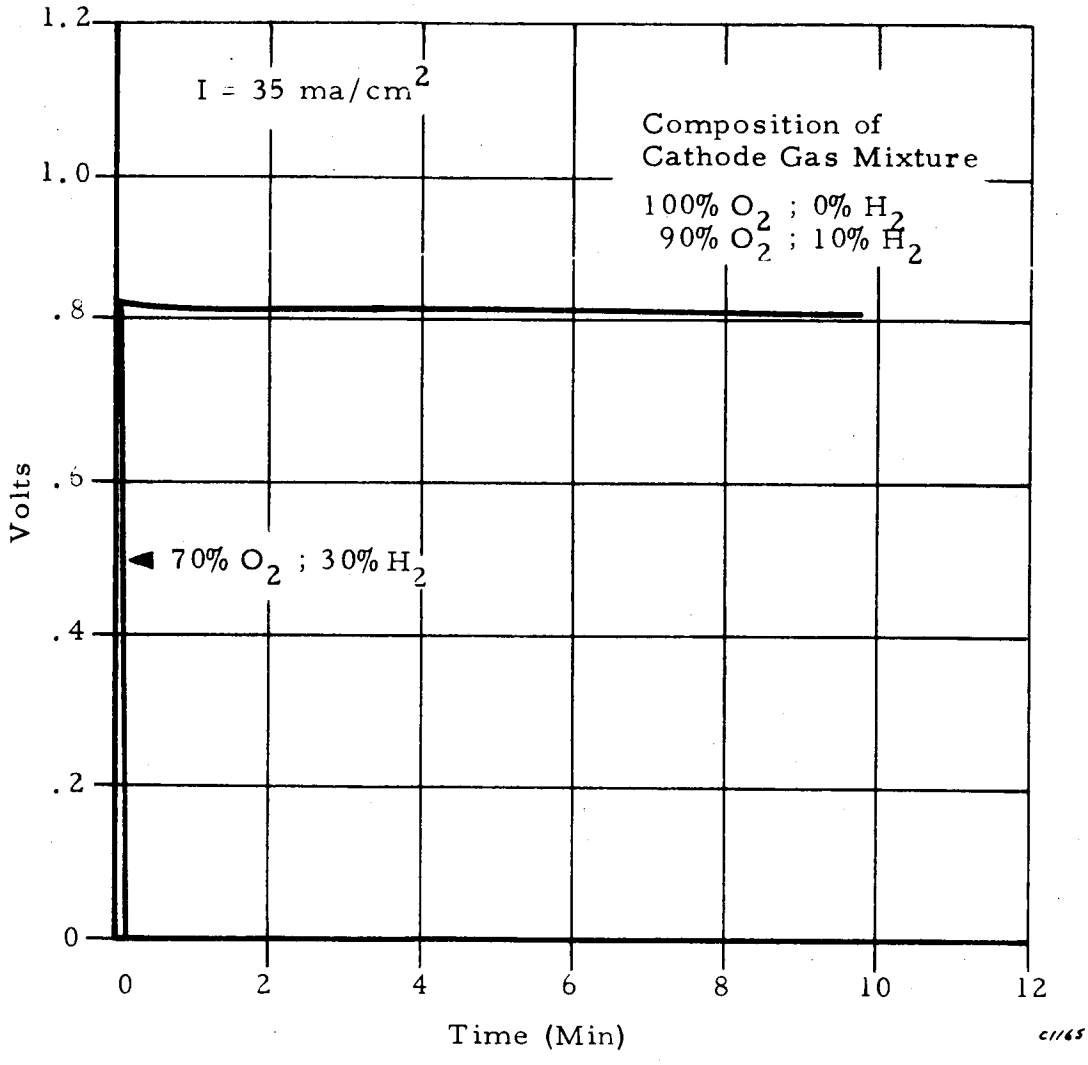

Figure 14. Performance of Miniature Fuel Cell With H_2-O_2 Mixtures in Cathode After Several Hours of Operation

can function satisfactorily with mixtures on its cathode side containing up to 10% hydrogen. Performance is noted to drop rapidly with hydrogen content at some level between 10 and 30%.

These results are directly applicable to the problem of estimating performance of miniature fuel cells when installed in commercial silver-zinc cells. Under normal operating conditions, including both stand and conventional cycling, internal battery gases consist of essentially pure hydrogen with little, if any, oxygen. Therefore, during normal conditions, a single miniature fuel cell, with its anode in contact with battery gases, should be capable of consuming essentially all internal gases.

During an overcharge period, oxygen is evolved and becomes mixed with the hydrogen. The miniature fuel cell would continue to function during this period until oxygen content reached 50%. At this point, the fuel cell would become inoperative and could not consume any more of the hydrogen. Internal pressure would continue to rise because of continued oxygen evolution. This pressure rise could be terminated, however, if the battery contained a second miniature fuel cell with its cathode in contact with internal gases. This cell would start and continue to consume oxygen when concentration of this gas had reached a level of 90%. Thus it may be shown that use of two miniature fuel cells would limit internal pressure rise in a silver-zinc cell during normal operation and also during overcharge. This matter will be discussed in greater detail in Section 2.3 of this report.

2.2.4.2 Dead-End Flow (Test Series No. 19)

In this test a miniature fuel cell was operated for an extended time on one anodic mixture consisting of 90% H_2 and 10% O_2. The tests were carried out in a "quasi" dead-end mode which was similar to the previously described dead-end tests (Section 2.2.2) but with one exception. In this case the simulator (a 250-ml

Erlenmeyer flask) was flushed briefly and refilled each day with the above mixture. This was necessary, since during operation the fuel cell would electrochemically consume the hydrogen and thereby change its concentration. The total volume was such that the calculated change was negligible for a one-day operation. In this manner it was possible to maintain an essentially constant composition for an extended period. The test was carried out over a period of one month at a current of 5 ma. Operating voltage was noted to decline somewhat each day from approximately 0.8 to 0.6 volts. Upon refilling, however, with the above mixture, the voltage again returned to the higher value. These results establish that the miniature fuel cell can operate effectively on mixtures of H_2 and O_2 in its anode for extended periods.

2.2.4.3 Effect of Anode Gas Composition on Open End Circuit Voltage (Test No. 20)

A third test with gas mixtures involved measurement of the effect of anodic gas composition on open circuit voltage. The tests were carried out in the open gas-flow mode by passing mixtures of hydrogen and oxygen slowly across the anode compartment and pure oxygen across the cathode compartment. Flowmeters were employed to set approximate gas compositions which were checked with a gas chromatograph. Open circuit voltages were measured with a vacuum tube voltmeter.

Results of several runs are given in Figure 15. The shaded area gives the range of values obtained for several different tests. The following trend is evident. The voltage increases gradually with increasing hydrogen concentration in the range of zero to approximately 50%. At a concentration of hydrogen of about 70% there is a sharp increase in voltage. From 70 to 100% hydrogen there was again observed to be a low rate of increase of voltage with increasing hydrogen concentration.

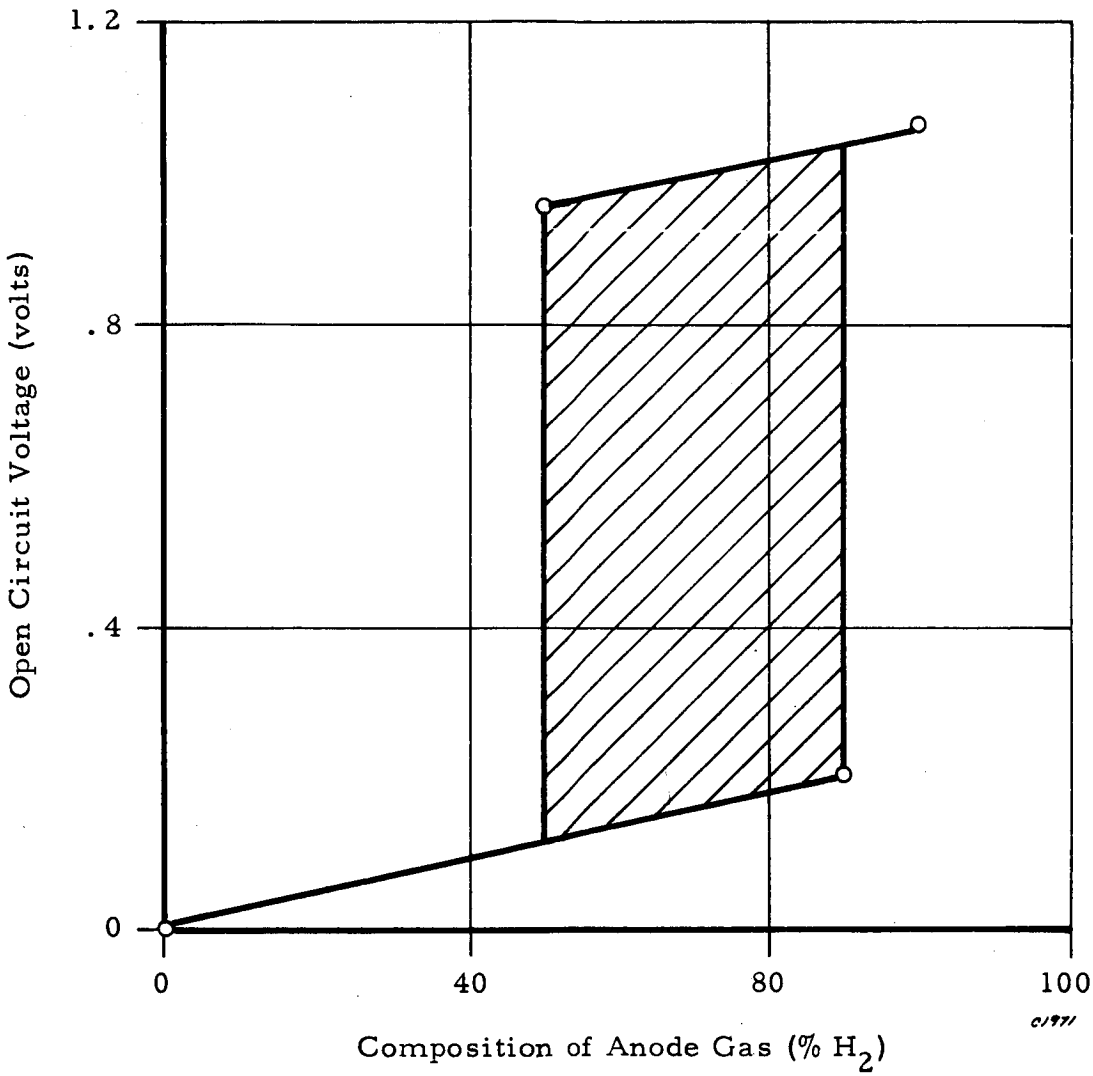

Figure 15. Effect of Composition of Anode Gas On Open Circuit Voltage of H_2-O_2 Fuel Cell

An explanation that can be offered for this phenomenon is that there is a critical concentration of hydrogen below which the anode ceases to be a true hydrogen electrode. At these low hydrogen concentrations the oxygen may block most of the active sites on the electrode.

2.2.5 Effect of Temperature on Performance (Test Series No. 21)

The effect of temperature on performance of both the original and modified cell types is given in Figures 16 and 17. The high temperature tests (40°C) were carried out in an oven and the low temperature tests (0°C) were carried out in an ice bath.

Results indicate a marked effect of temperature on performance of both the original and modified miniature cells. In each case, performance was noted to improve appreciably with temperature within the given range of 0 to 40°C. Typical results for the modified cell are given below after three to five hours of continuous operation.

Temperature (°C)	Operating Current at 0.6 V (ma/cm^2)
0	50
25	60
40	130

Operating current at 40°C is noted to be more than double that at room temperature. At 0°C, operating current is approximately 80% of that at room temperature.

This variation in performance of the miniature fuel cell with temperature fortuitously matches that of its intended application in a silver-zinc battery. At elevated temperatures, battery gassing rates are higher and the fuel cell would be required to operate at higher currents. Results establish this capability. At lower

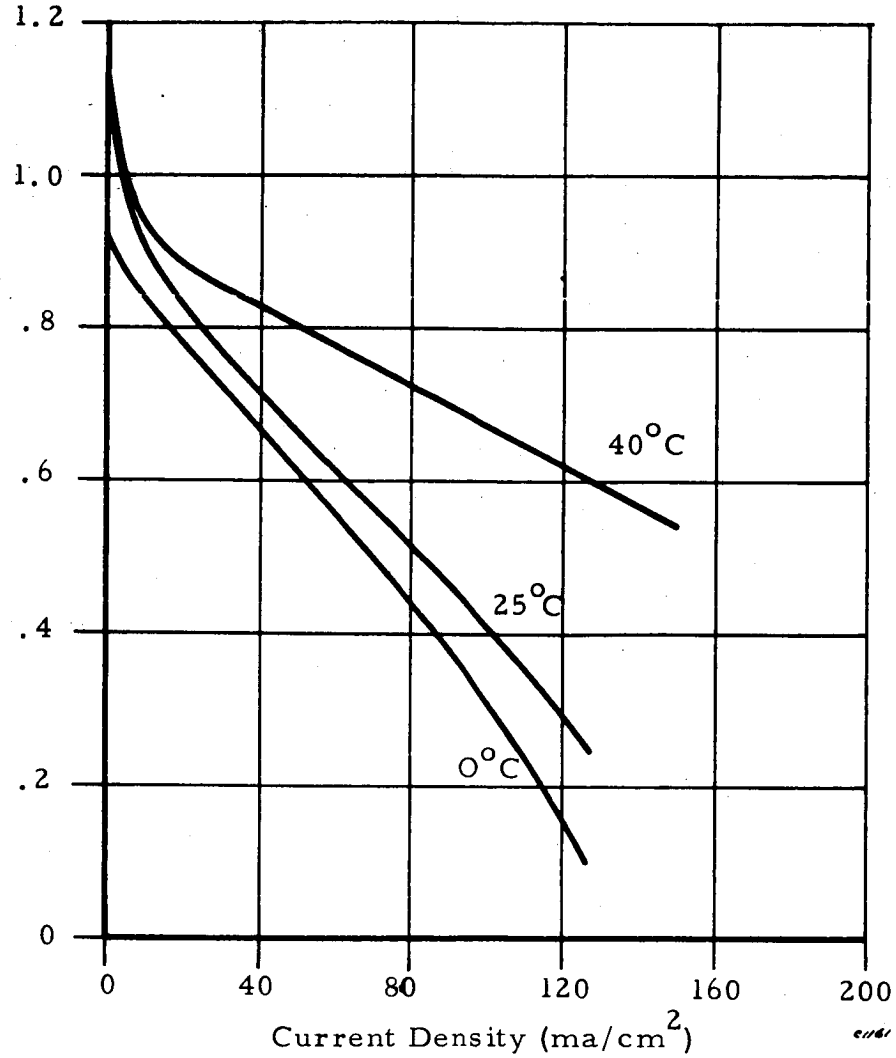

Figure 16. Effect of Temperature on Performance of Miniature Fuel Cell (Modified Cell Configuration) After Three to Five Hours of Continuous Operation

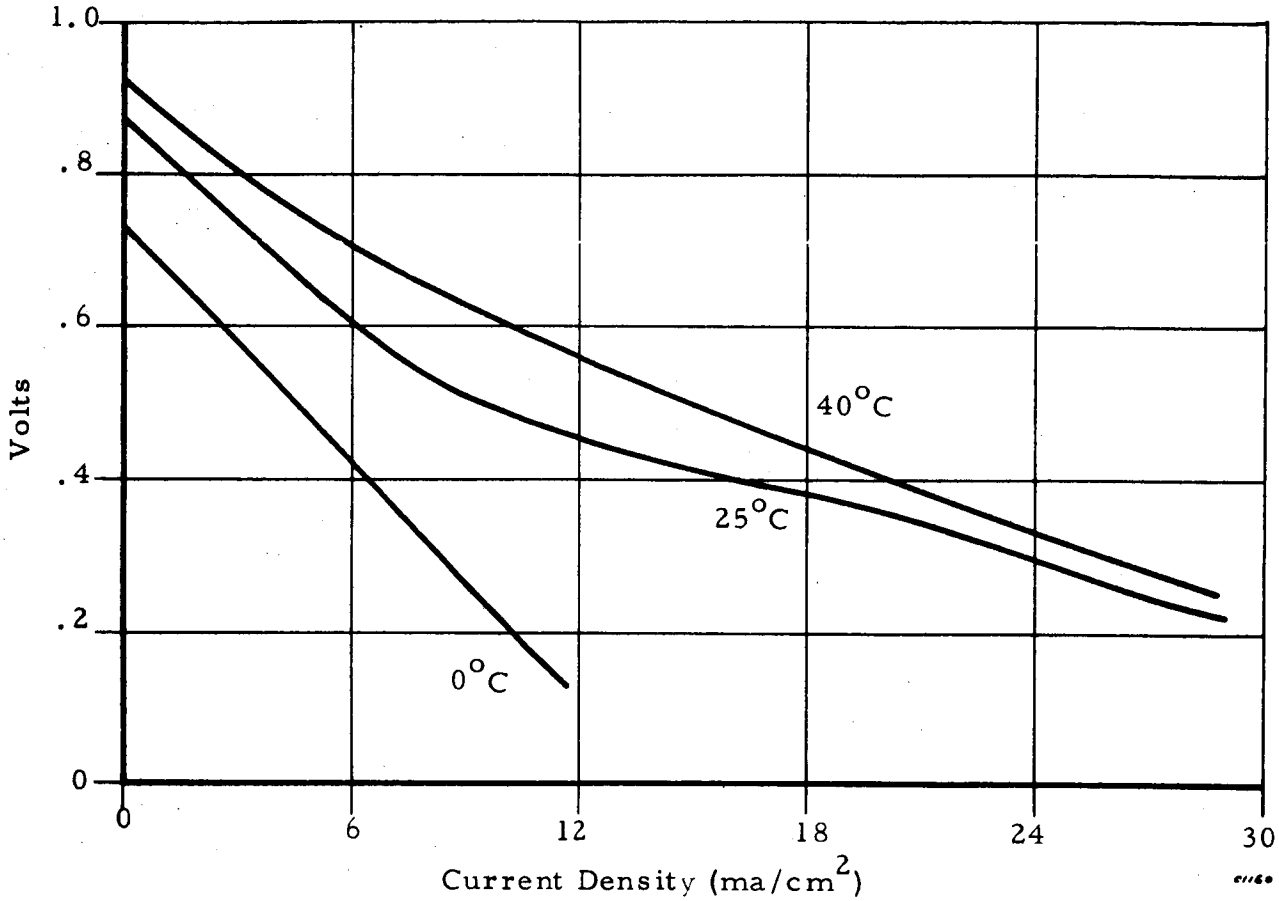

Figure 17. Effect of Temperature on Performance of Miniature Fuel Cell (Initial Cell Configuration) After Three to Five Hours of Continuous Operation

temperatures, gassing rates are lower as are corresponding required fuel cell current requirements. Results show only a small reduction in fuel cell current at lower temperatures and indicate that it should be capable of eliminating cell gassing problems at temperatures at least as low as $0^{o}C$.

2.2.6 Fuel Cell Size Versus Gas Consumption Capability

An important goal of this program was to establish a relationship between the size of a miniature fuel cell and its gas consumption capability. This will permit accurate sizing of the miniature fuel cell to accommodate the gassing rates that may be encountered in a particular battery under any mode of operation.

Results obtained with the modified type of miniature fuel cell indicate that during the initial stages of operation (the first 100 hours) the voltage-current characteristics of the miniature cells are independent of electrode size in the range of 0.25 to 5.0 cm^2. During this time, it may be shown that the gas consumption capability is directly proportional to fuel cell electrode area. This relationship may be expressed by the following equation:

$$R = 0.42\, i A$$

R = hydrogen consumption capability, cc H_2/hr

i = current density, ma/cm^2

A = electrode area, cm^2

This follows from the principles of electrochemical equivalence. The above relationship then gives the desired correlation between fuel cell size and gas consumption capability at least for the initial phases of operation and at relatively low current densities.

For extended operating times at low currents or for shorter operating times at high currents the above relationship must be modified because of the problem of removing product water. This has a pronounced effect on the voltage-current characteristics of the cell and

its corresponding gas consumption capability. This problem was solved at least in part by the use of wicks to transfer product water to the battery electrolyte. Results have indicated that miniature cells with electrode cross-sectional areas of 0.25 to 5.0 cm^2 can operate effectively with wicks at current densities of at least 15 ma/cm^2 continuously for extended periods. This corresponds to hydrogen consumption capabilities of 1.6 cc H_2/hour, 6.3 cc H_2/hour and 10.6 cc H_2/hour for cells with electrode areas of 0.25, 1.0 and 5.0 cm^2, respectively.

Finally it should be pointed out that the short term gas consumption capabilities are exceedingly high with respect to anticipated battery gassing rates. A cell with a cross-sectional electrode area of 1.0 cm^2, for example, has been shown to be capable of operating at currents up to 300 ma, which is equivalent to a corresponding hydrogen consumption rate of 126 cc H_2/hour.

2.2.7 Selection of Miniature Fuel Cell for Performance Tests in Silver-Zinc Cells

The miniature fuel cell selected for performance tests in silver-zinc cells was of the modified type with American Cyanamid Type A.B.-40 electrodes. The reasons for this choice were that this cell type was found to exhibit higher current and corresponding gas consumption capabilities than the initial type and that the A.B.-40 electrodes appeared to give the most stable output among those examined in this cell type. The operational mode selected was the "dead-end" gas flow with wicking of product water, as described in Section 2.2.3. Although the results had indicated that the miniature fuel cells had less than optimum output under this mode, it was believed to be the most practical with regard to sealing of the silver-zinc cell. The screw type installation was selected on the basis that it was found to be reliable and adequate in the simulator tests and that it would provide a convenient method of installing two fuel cells on a silver-zinc battery. Results of performance tests with this cell in this mode are given in the following sections.

2.3 Performance Tests in Silver-Zinc Cells

The purpose of these tests was to establish capability of the miniature fuel cells in consuming gases and limiting pressure rise in sealed silver-zinc batteries. The most extensive and thorough tests were conducted during the latter portion of the program on two 100-amp-hour, low-rate silver-zinc cells. Results of these tests are presented first in Section 2.3.1 below. Preceding these tests were a number of preliminary runs with commercial 15-amp-hour, high-rate silver-zinc cells. The purpose of the latter was merely to perfect the miniature fuel cell installation and operational techniques. Despite the limited intent, some significant results were obtained on this size and type of cell. Results are given in Section 2.3.2.

2.3.1 100-Amp-Hour Silver-Zinc Cycling Tests

Extensive cycle tests were carried out on two commercial 100-amp-hour silver-zinc cells each of which contained two miniature fuel cells as described below. These are designated as Tests 22 and 23, respectively. Cycle conditions for both tests were identical and were specified by the contract monitor as a 2-hour discharge at 20 amps (40% depth) and a 22-hour charge at 2 amps. Experimental details and results are given below.

2.3.1.1 Experimental

The silver-zinc cells were from Yardney Electric Corporation. They were shipped in the dry unformed state. Rated capacity was listed as 85 amp-hour but actual capacity was 120 to 140 amp-hours. For the purpose of this test they were therefore rated as nominal 100 amp-hour cells.

The miniature fuel cells were installed near the top of battery cases in accordance with the procedures outlined in Appendix A. An illustration of the test assembly is given in Figure 18.

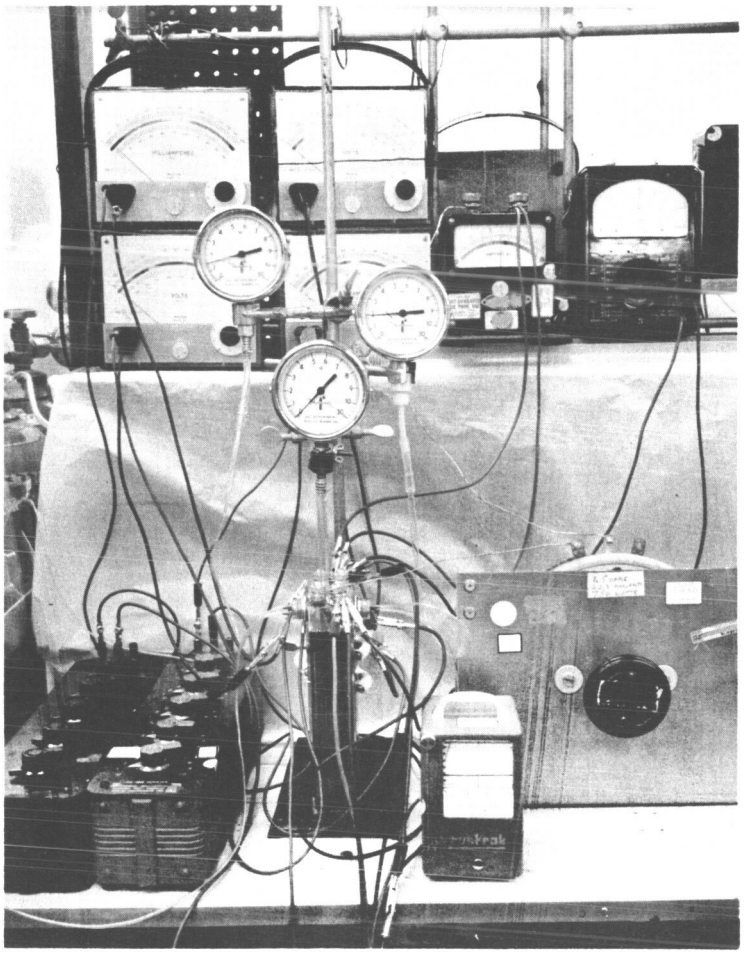

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Figure 18. Installation of Miniature Fuel Cell in a Commercial 100 Ampere-Hour Silver-Zinc Battery

Before initiation of cycling, the silver-zinc cells were carried through two formation cycles as recommended in the Yardney Instruction Sheet accompanying the cells. The following steps were involved:

1. Activation with electrolyte
2. Three-day stand
3. First formation charge at 3 amps to 2.05 volts
4. Discharge at 50 amps to 1.0 volt
5. Second formation charge at 3 amps to 2.05 volts

These formation cycles were carried out in the vented condition.

Upon initiation of cycling, the silver-zinc cells were sealed off by connecting the vent plugs directly to a pressure gage with a short segment of plastic tubing. The assembly was then leak tested by filling with 5 psig of nitrogen and checking all of the possible leakage joints with a special detergent. A further check on leakage was carried out by sealing the system off at 5 psig and observing any change in pressure while on stand. The detergent leak test was also performed periodically during each test.

The fuel cells were purged with their respective gases at the start of the test and a small positive pressure of 1.5 psig was applied to each in the dead-end mode.

Each of the miniature fuel cells was discharged continuously across a fixed load of 1.0 ohm throughout the test. Operating voltages and currents of both the silver-zinc cells and the miniature fuel cells as well as internal pressure were recorded continuously throughout the test.

Battery discharge was carried out through a variable ohmite resistor. Current was adjusted manually at 20 amperes. Battery charge was carried out with a conventional 12-volt battery charger in series with a variable resistor to adjust current to

2 amperes. Weston precision voltmeters and ammeters (± 1/4% accuracy) were employed on both the battery and fuel cells.

2.3.1.2 Results

Results of cycle tests on the two 100 A.H. silver-zinc cells are given in Tables VI and VII. These outline the performance of both the silver-zinc cells and their associated miniature fuel cells on a cycle-to-cycle basis. The first two columns give the end of charge and discharge voltages of the silver-zinc cell during each cycle. Charge and discharge currents and times are not listed as these were held constant as described above. The next column lists the maximum pressure developed during each cycle. The last eight columns give the currents and corresponding gas consumption rates of each of the miniature fuel cells. These are subdivided into the maximum and average rates during each cycle.

Inspection of Tables VI and VII reveals several significant points. First it should be noted that the maximum pressure developed in either cell is less than 1.5 psig throughout the indicated test periods. This established the fact that the miniature fuel cells are effective in limiting pressure rise to very moderate levels. Without the miniature fuel cells, it is estimated that internal pressures would increase at rates of at least 0.35 and 2.34 psi per day for Tests 22 and 23 respectively. This is based on the measured hydrogen evolution rates and cell volume. On this basis, the internal pressures would have reached levels of 10.5 and 50 psig, respectively, in Tests 22 and 23 by the end of the test period.

The miniature fuel cells were effective not only in consuming evolved gases at low rates that were encountered throughout most of these tests, but also at the high rates encountered from time to time. During Cycles 4 and 5 in Test 23, for example, there was an apparently sharp increase in the rate of hydrogen evolution, as evidenced by the increase in pressure and there was a simultaneous

TABLE VI

SUMMARY OF TEST NO. 22 ON 100 A.H. SILVER-ZINC CELL CONTAINING DUAL MICRO FUEL CELL ARRANGEMENT

Cycle No.	End Charge Voltage (volts)	End Discharge Voltage (volts)	Maximum Pressure (psig)	Maximum Current From H_2 Fuel Cell (ma)	Maximum O_2 Consumption Rate By H_2 Fuel Cell (c.c. O_2/hr)	Average Current From H_2 Fuel Cell (ma)	Average O_2 Consumption Rate By H_2 Fuel Cell (c.c. O_2/hr)	Maximum Current From O_2 Fuel Cell (ma)	Maximum H_2 Consumption Rate By O_2 Fuel Cell (c.c. H_2/hr)	Average Current From O_2 Fuel Cell (ma)	Average H_2 Consumption Rate By O_2 Fuel Cell (c.c. H_2/hr)
1	2.10	1.50	3.7*	40.0	8.0	.10	.02	.50	.21	.20	.08
2	1.87	1.50	0.3	.15	.03	.10	.02	.22	.08	.20	.08
3	1.88	1.51	0.4	.15	.03	.10	.02	.30	.12	.22	.08
4	1.89	1.52	0.5	.30	.06	.30	.06	.05	.02	.05	.02
5	1.88	1.54	0.2	.50	.06	.30	.06	.05	.02	.05	.02
6	1.94	1.54	0.8	.50	.10	.40	.08	.25	.10	.20	.08
7	1.93	1.52	0.6	.20	.10	.30	.06	.25	.10	.20	.08
8	1.94	1.53	0.5	.10	.04	.15	.03	.20	.10	.20	.08
9	1.94	1.53	0.4	.10	.02	.10	.02	.15	.06	.15	.06
10	1.94	1.54	0.5	.15	.02	.10	.02	.15	.06	.15	.06
11	1.94	1.53	0.6	.15	.03	.15	.03	.70	.29	.20	.08
12	1.95	1.54	0.3	.20	.03	.15	.03	.30	.12	.20	.08
13	1.95	1.52	0.5	.20	.04	.10	.02	.20	.08	.20	.08
14	1.94	1.52	0.5	.50	.04	.10	.02	.20	.08	.15	.06
15	1.94	1.52	0.8	.20	.10	.30	.06	.20	.08	.20	.08
16	1.95	1.52	0.8	.20	.04	.20	.04	.20	.08	.10	.04
17	1.94	1.52	0.6	.20	.04	.10	.02	.20	.08	.20	.08
18	1.93	1.53	0.9	.15	0	0	0	.20	.08	.20	.08
19	1.92	1.52	0.9	.15	0	0	0	.20	.08	.20	.08
20	1.94	1.51	0.5	0	0	0	0	.15	.08	.20	.06
21	1.94	1.51	0.6	0	0	0	0	.20	.08	.20	.08
22	1.94	1.51	0.9	0	0	0	0	.20	.08	.20	.08
23	1.95	1.50	0.9	0	0	0	0	.25	.10	.20	.07
24	1.95	1.52	0.9	0	0	0	0	.20	.08	.15	.06
25	1.87	1.50	1.3	0	0	0	0	.30	.12	.20	.08
26	1.96	1.52	1.4	0	0	0	0	.40	.16	.30	.12
27	1.95	1.52	1.2	.6	.12	.50	.10	.30	.12	.25	.10
28	1.95	1.50	1.5	.5	.10	.30	.06	.45	.18	.30	.12
29	1.95	1.50	1.5	.47	.10	.40	.08	.40	.18	.40	.16
30	1.95	1.52	1.2	.45	.10	.40	.09	.45	.18	.40	.16
							Avg .03				Avg .08

*Note: The voltage cutoff device failed to operate during this cycle and the cell was therefore overcharged somewhat. This resulted in oxygen evolution as evidenced by the increased output of the cell supplied with H_2. Internal pressure reached the maximum indicated and then gradually declined during the next discharge.

TABLE VII

SUMMARY OF TEST NO. 23 ON 100 A. H. SILVER-ZINC CELL CONTAINING DUAL MICRO FUEL CELL ARRANGEMENT

Cycle No.	End Charge Voltage (volts)	End Discharge Voltage (volts)	Maximum Pressure (psig)	Maximum Current From H_2 Fuel Cell (ma)	Maximum O_2 Consumption Rate By H_2 Fuel Cell (c.c. O_2/hr)	Average Current From H_2 Fuel Cell (ma)	Average O_2 Consumption Rate By H_2 Fuel Cell (c.c. O_2/hr)	Maximum Current From O_2 Fuel Cell (ma)	Maximum H_2 Consumption Rate By O_2 Fuel Cell (c.c. H_2/hr)	Average Current From O_2 Fuel Cell (ma)	Average H_2 Consumption Rate By O_2 Fuel Cell (c.c. H_2/hr)
1	1.95	1.52	0	.70	.14	.70	.14	.50	.21	.40	.16
2	1.96	1.51	0	.95	.20	.70	.14	.20	.08	.20	.08
3	1.95	1.52	1.0	1.0	.21	.10	.02	.10	.04	.10	.04
4	2.10	1.53	1.2	.95	.20	.45	.10	.15	.06	.10	.04
5	1.90	1.52	1.5	1.0	.21	1.0	.21	42.5	17.9	3.0	1.26
6	1.77	1.52	0	1.3	.27	1.3	.27	24.0	10.0	3.91	1.60
7	1.73	1.51	0	1.2	.25	.45	.10	2.1	.88	.70	.30
8	2.10	1.46	0	.35	.07	.20	.04	.20	.04	.20	.08
9	1.65	1.54	0	.40	.08	.20	.04	5.2	2.2	1.1	.46
10	1.65	1.22	0	1.20	.25	.80	.16	2.4	.96	2.0	.80
11	1.72	1.45	0	.70	.14	.60	.12	1.6	.67	1.4	.59
12	1.94	1.50	0	1.0	.21	.50	.10	1.3	.55	0.9	.38
13	1.92	1.50	0	1.2	.24	.40	.08	.40	.17	0.3	.12
14	1.95	1.52	0	.25	.05	.20	.04	2.1	.80	0.7	.28
15	1.95	1.37	0	1.0	.20	.40	.08	300.0	120.0	2.0	.80
16	1.65	1.54	0	.15	.03	.15	.03	.45	.19	0.1	.04
17	1.92	1.54	0	.15	.03	.15	.03	.45	.19	0.1	.04
18	1.92	1.54	0	.15	.03	.10	.02	.10	.04	0.1	.04
19	1.65	1.33	0	.10	.02	.05	.01	.50	.20	0.1	.04
20	1.66	1.57	0	1.8	.38	.10	.02	0	0	0.0	0
21	1.92	1.53	0	.10	.02	.10	.02	.30	.12	0.0	0
							Avg .09				Avg .34

increase in output of the miniature fuel cell supplied with oxygen. Output of the miniature fuel cell increased to a sufficient rate (17.9 cc H_2 per hour maximum and 3 cc H_2 per hour average) to limit the pressure rise to only 1.5 psig.

Based on the indicated fuel cell response data, it is possible to draw several other conclusions in regard to the gassing characteristics of this type of silver-zinc cell. Hydrogen is evolved under these cycling conditions at average rates ranging from 0.1 to 0.5 cc H_2/hour. Oxygen is evolved during most of the cycles but at much lower rates of 0.03 to 0.10 cc O_2/minute. During some periods there was no measurable oxygen evolution.

It is difficult to draw a more detailed quantitative analysis of gassing characteristics, since the results show that gassing is not reproducible among silver-zinc cells of this type and also from cycle to cycle within a given cell. The only consistent trend was in Test 22 wherein internal pressure was noted to rise slightly during each discharge period and to decline to zero psig by the end of the first hour of each charge period. Output of the fuel cell supplied with oxygen was noted to increase slightly during these periods and indicated that the rise was due mainly to hydrogen evolution. One possible explanation is that there is an increase in temperature on discharge which causes an increase in the dissolution rate of zinc and a corresponding increase in hydrogen evolution rate. This phenomenon was not observed in Test 23. Aside from the possible trend of slightly increased hydrogen evolution rate during discharge, there did not appear to be any other consistent variation in gassing rate of either H_2 or O_2 throughout each cycle. If the cells had been overcharged, there would have undoubtedly been an increase in oxygen evolution; however, this was not the case, as the charge was terminated at 2.05 volts maximum by means of a voltage cut-off.

The average gassing rates of both H_2 and O_2 are significantly greater in Test 23 than in Test 22. Relative

rates are approximately 6/1 for H_2 and 4/1 for O_2 for the two tests. This can be explained only on the basis of differences in the silver-zinc cells themselves, as all other conditions are identical.

One similarity between the gassing phenomena of the two cells is in the ratio of evolved H_2 to O_2. These ratios are of the same order of magnitude in both tests, i.e., 2.7 H_2/1.0 O_2 in Test 22 and 3.8 H_2/1.0 O_2 in Test 23.

Finally, it is to be noted that there is very little weight penalty associated with the use of miniature fuel cells. In these tests, for example, the combined weight of the two fuel cells in each battery is under 50 grams and the combined battery-fuel cell weight is 1240 grams. These miniature fuel cells were not designed for minimum weight under this program; it is expected that under optimum design considerations, the contribution of two miniature fuel cells to the overall battery weight should not be more than one percent.

2.3.2 15 Amp-Hr Silver-Zinc Cycle Tests

As mentioned in the preceding section, the purpose of tests with the 15 amp-hr, high-rate silver-zinc cells was to develop reliable installation and test procedures for the miniature fuel cells in batteries. This was to be in preparation for the tests in 100 amp-hr cells already described. Several short term cycle tests were carried out with these batteries both with and without miniature fuel cells. Results are given below.

2.3.2.1 Operation Without Miniature Fuel Cells (Test No. 24)

In this test the battery was cycled in the sealed condition without miniature fuel cells. This was accomplished by connecting the battery vent cap directly to a pressure gage via plastic tubing. Conditions and results of this test are given in Table VIII.

TABLE VIII

CYCLE TESTS ON 15 AMP-HR SILVER-ZINC BATTERIES CONTAINING MINIATURE FUEL CELLS*

Test No.	Number of Fuel Cells Installed	Battery Cycle Regime	Number of Cycles	Pressure Range (psig)	Range of Fuel Cells Output (ma and mv)
25	1	1/2 hr discharge at 10 amps and 1 hr charge at 5 amps	20	0-10	0 to 300 ma at 0.2 volt with H_2 and 0 to 200 at 0.1 volt with O_2
26	2	1 hr discharge at 5 amps and 5 hr charge at 1 amp	5	0-.08	0 to 1 ma at 1 mv for H_2 cell and 0 to 1 ma at 1 mv for O_2 cell
27	2	1/2 hr discharge at 5 amps and 1 hr charge at 2.5 amps	14	0-10	0 to 60 ma at 0.1 volt for H_2 cell and 0 to 85 ma at 0.1 volt to O_2 cell
28	0	1/2 hr discharge at	3	> 15	--

*Note: 1. Electrode areas of all fuel cells were 1.0 cm^2

2. Battery is Yardney 15 AH-HR

3. Tests performed at ambient temperature

Internal pressure was noted to rise very rapidly during the initial discharge to 8.5 psig and to continue to rise during subsequent cycles. At the end of the second charge period, with pressure in excess of 15 psig, a rupture of cell components occurred and resulted in slow leakage of internal gases.

These results show that rapid rise in internal pressure occurs when the battery is cycled in the sealed condition. The rise in pressure was found to increase progressively with cycle time and might have increased much beyond 15 psig, had not the rupture occurred (as shown in Figure 1). This indicates that substantial gassing rates in this type of battery are possible. Much of this gassing, at least at the early stages of cycling, was found to be due to evolving oxygen (see Section 2.3.2.5).

2.3.2.2 Operation With One Miniature Fuel Cell (Test No. 25)

This test was initiated with one miniature fuel cell installed in the battery. The fuel cell was supplied with oxygen initially and then alternatively with hydrogen and oxygen. Results are given in Table VIII (see Test 25).

Internal pressure was noted to rise very rapidly during the initial discharge to approximately 10 psig. The fuel cell gave essentially no response during this period while it was supplied with oxygen. When the external gas supply was switched from oxygen to hydrogen, however, its open circuit voltage increased to 1.0 volt. Upon placing the cell on load midway in the discharge period at 100 ma at 0.7 volt, the rate of pressure increase was diminished and the pressure began to decline throughout the following charge period.

During the course of subsequent cycling, the following observations were made.

1. With hydrogen supplied to the fuel cell, its response was generally negligible except near the end of each

charge period. At this point its output increased to a maximum of nearly 300 ma and 0.2 volt. A simultaneous increase in internal pressure was observed during the end of the charge period. In some instances this rise in pressure was in excess of 10 psig. Pressure was observed to decline after the end of charge with the fuel cell on load. Output of the fuel cell decreased gradually as pressure was reduced to atmospheric.

2. With oxygen supplied to the fuel cell, its output was in the range of 0.0 to 3.0 ma at 0.0 to 3.0 mv throughout all portions of the cycles, except during start-time after a few days of stand. Under these conditions the output of the fuel cell increased rapidly to a level of between 100 to 200 ma and 0.1 volt. Output decreased gradually after a few minutes as internal pressure was reduced from approximately 1.0 psig to atmospheric.

Based on these observations, the following conclusions may be drawn.

1. The high rate batteries generate oxygen quite rapidly near the end of charge. A miniature fuel cell with 1.0 cm^2 electrode area and supplied with hydrogen can effectively consume this oxygen at rates up to 1.0 cc O_2/min (this is based on the observed current of 200 ma). Use of such miniature fuel cells can effectively limit pressure rise to a reasonable level near 10 psig under these conditions.

2. The batteries generate hydrogen continuously at very low rates. A miniature fuel cell with 1 cm^2 cross sectional electrode area and supplied with oxygen is more than adequate to consume all of this amount of hydrogen. Such a cell can also consume the hydrogen which collects during a three-day stand within a few minutes.

2.3.2.3 Operation With Two Miniature Fuel Cells (Test No. 26)

In this test two miniature fuel cells were installed in a previously used battery (two cycles). One cell was supplied externally with oxygen to consume internal hydrogen. Longer cycle times and lower currents were employed in this test than in previous tests (see Table VIII, Test 26).

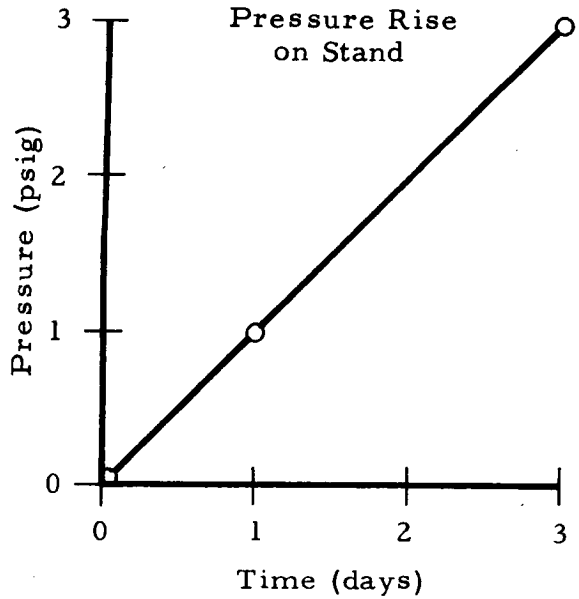
Very low pressures were developed within the battery during the course of five of the indicated cycles (a maximum of only 0.08 psig). Response of the fuel cell supplied with oxygen was within the range of 0.0 to 1.0 ma throughout all of the cycles, whereas response of the fuel cell supplied with hydrogen was somewhat less than the above value.

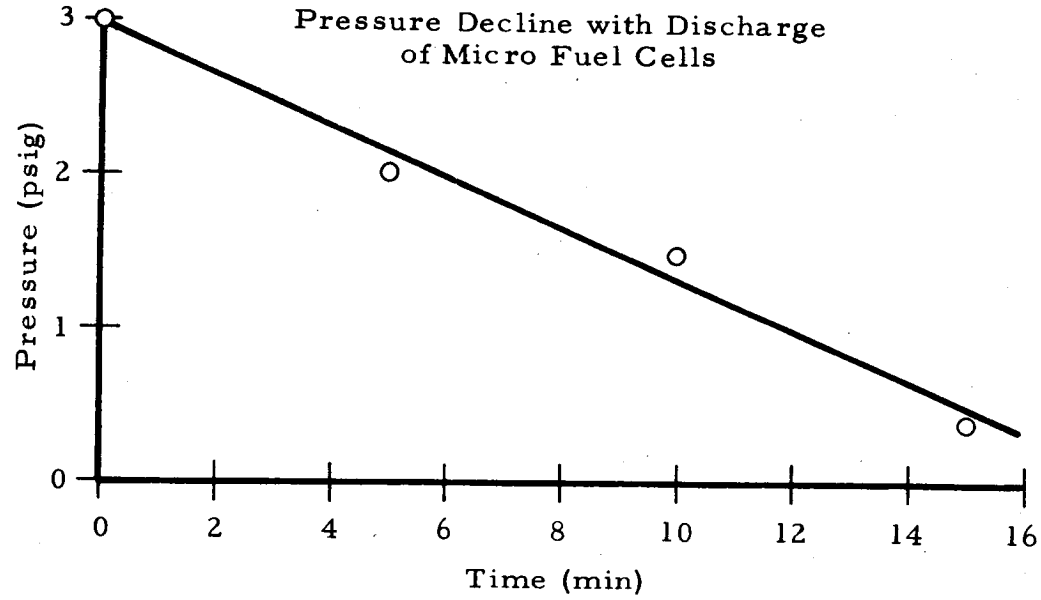
These results indicate that the silver-zinc cell generates very small quantities of gases under the above cycle regime and that two miniature fuel cells, each with 1.0 cm^2 electrode areas, are more than adequate to limit pressure rise.

2.3.2.4 Operation With Two Miniature Fuel Cells (Test No. 27)

A new 15-Ah silver-zinc battery was employed in this second cycle test with a dual fuel cell arrangement as described above. The 1/2 hour-1 hour cycle was again employed as in Test 25 but at lower currents (see Table VIII, Test 27).

Observed phenomena during this test were similar to those in Test 25. Internal pressure was again noted to increase during initial discharge but to a lower level than in Test 25. Response of the fuel cell supplied with hydrogen was higher during initial discharge and also at the end of each charge cycle than at other times throughout the cycles. Output of this fuel cell during initial discharge was effective in limiting pressure rise to 4.5 psig. Response of the fuel cell supplied with oxygen was within the range of 0.0 to 2.0 ma at 0.0 to 2.0 mv at all times during the cycles except at the point of start-up after a three-day stand. Fuel cell and battery performance during this period are given in Figure 19. For the case described here the battery had been charged prior to stand and is therefore indicated to be on discharge at the indicated start time. As shown in Figure 19, the response of the fuel cell supplied with O_2 increased rapidly to and maintained a current level of 83 ma at 0.16 volts throughout the discharge





Fuel Cell Modes of Operation	H_2 Cell on OCV	H_2 Cell on 1 Ω load, 83 ma @ 0.16 volt
	O_2 Cell on OCV	O_2 Cell on 1 Ω load, 1 ma @ 0.01 volt
Battery Mode of Operation	Stand in Charged State	Discharge @ 5 amps @ 1.5 volts

Figure 19. Relief of Pressure in Silver-Zinc Battery with the Use of Micro Fuel Cells

period. Internal pressure was simultaneously observed to decrease from 3.0 psig to atmospheric during this period. Response of the cell supplied with H_2 was at a level of 1.0 ma and 1.0 mv throughout this period. As before, these results indicate that hydrogen is the predominant gas formed on stand and that the fuel cells can effectively consume this hydrogen as well as a small amount of oxygen in a relatively short time.

2.3.2.5 Gassing During Initial Discharge (Test No. 28)

As mentioned previously, internal battery pressure was noted to increase very rapidly during the initial discharge. Fuel cell response indicated that the rise in pressure was due mainly to oxygen evolution. In order to reaffirm this conclusion, a new 15 Ah cell was placed on discharge and the evolved gases were collected by displacement of water. Samples of this gas were then analyzed chromatographically and gave the following results.

Component	Volume %
H_2	13.3
O_2	45.0
N_2	41.7

These results reaffirm that oxygen is the predominant species evolved on initial discharge. A small amount of hydrogen is also noted. The presence of nitrogen is explained of course by the fact that the cell is filled with air at the start of the test. An estimated oxygen evolution rate during this test was 2 cc O_2/min.

2.4 Product Water for Life Support

Removal of product water from the miniature fuel cells for life support purposes does not appear feasible because of the limited quantities which have been found. At best the rate of product water formation would be .01 gms H_2O/day for a 100 amp-hr cell. This corresponds to

an average hydrogen evolution rate of 0.5 cc H_2/hour in Test 23, Section 2.3.1.2. Although the gassing rates might be much greater under other cycle regimes or ambient temperature, the corresponding water formation rates would remain quite small.

3.0 PROJECT PERSONNEL

The following Astropower staff members are associated with this program at this time.

Dr. C. Berger, Principal Investigator

Dr. M. P. Strier

Mr. H. Frank

Mr. C. Brygger

4.0 NEW TECHNOLOGY

A reliable method of sealing a miniature fuel cell in a silver-zinc battery was found with the use of a special thread seal as shown in Figure 18 and described in Appendix A and Figure A-5.

REFERENCES

1. Francis, Howard T., Space Battery Handbook, pp. 42-47 15 April 1963).

2. Douglas Proprietary Program S. O. 81367-002.

3. Douglas Proprietary Program S. O. 81367-005.

APPENDIX A

DESCRIPTION AND OPERATION OF MINIATURE FUEL CELLS DELIVERED TO NASA GODDARD SPACE FLIGHT CENTER

A. 1 DETAILS OF FINAL UNITS

Detailed drawings and descriptions of the final miniature fuel cells delivered to NASA Goddard are given below.

A. 1. 1 Miniature Fuel Cell Base

The miniature fuel cell base (see Figure A-1) is machined from 304 stainless steel bar stock. The outside diameter of the base is threaded along its entire length with 5/8 - 32 threads for attachment to the battery case on one end and the cover on the other end. The base contains a 0. 375-inch diameter through-hole for transmitting battery gases, and a recessed area with 0. 453 inch diameter to accommodate the electrode and gas distribution screen. The base also contains a serrated edge on its electrode face to provide a gas tight seal against the adjacent asbestos layer.

A. 1. 2 Miniature Fuel Cell Top

The miniature fuel cell top (see Figure A-2) is also machined from 304 stainless steel bar stock. The top contains a recessed area with . 450-inch diameter to accommodate an electrode and gas distribution screen, and also contains a serrated edge to provide a second gas tight seal on the adjacent asbestos. The top is drilled in two locations to accommodate two gas manifolds with . 090 inch diameters. These manifolds, also of 304 stainless, are silver brazed into the respective holes with "Easy Flow" Alloy 45. The top is also drilled and tapped in one location to accommodate a threaded terminal post with . 093-inch diameter.

A. 1. 3 Miniature Fuel Cell Cover

The miniature fuel cell cover (see Figure A-3) is machined from plexiglass bar stock. The external surface is machined in the form of a standard 0. 750-inch hex nut to accommodate a standard torque wrench. The internal surface is drilled and tapped with 5/8 - 32 threads to a depth of 0. 280 inch to correspond to the threads on the

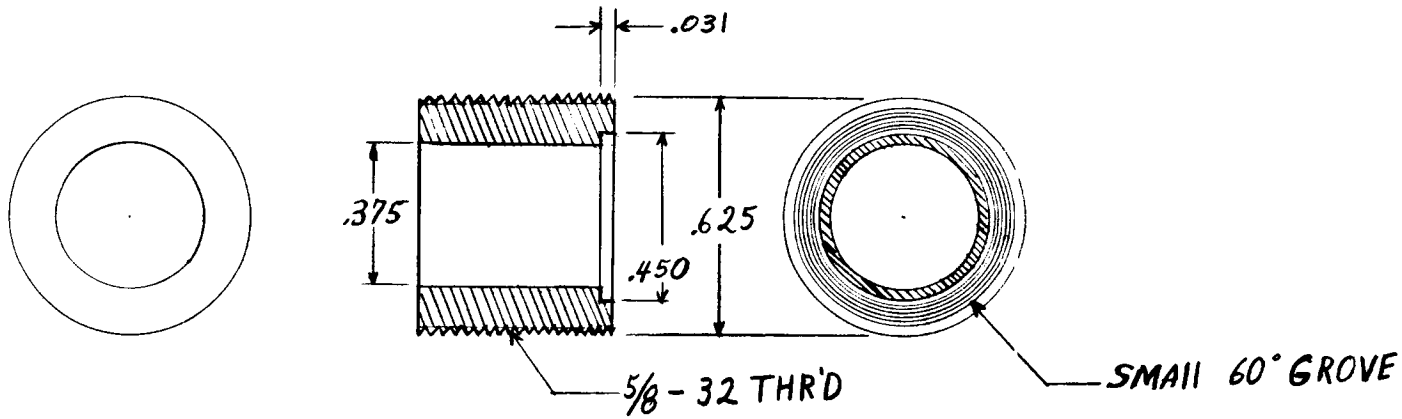


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Figure A-1. Micro Fuel Cell Base

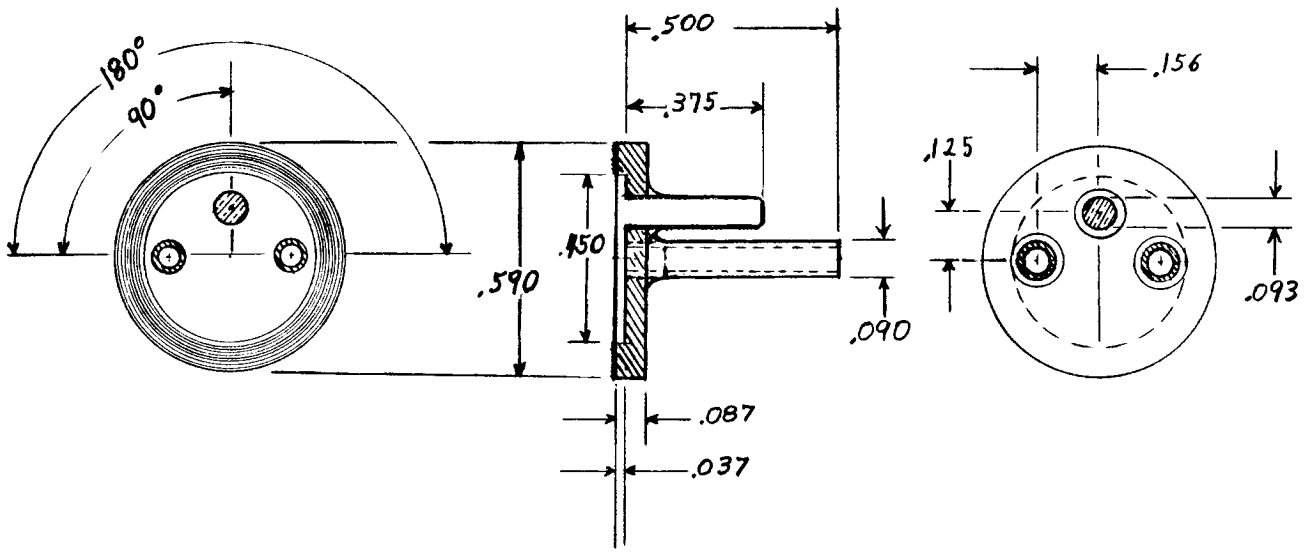

Figure A-2. Micro Fuel Cell Top

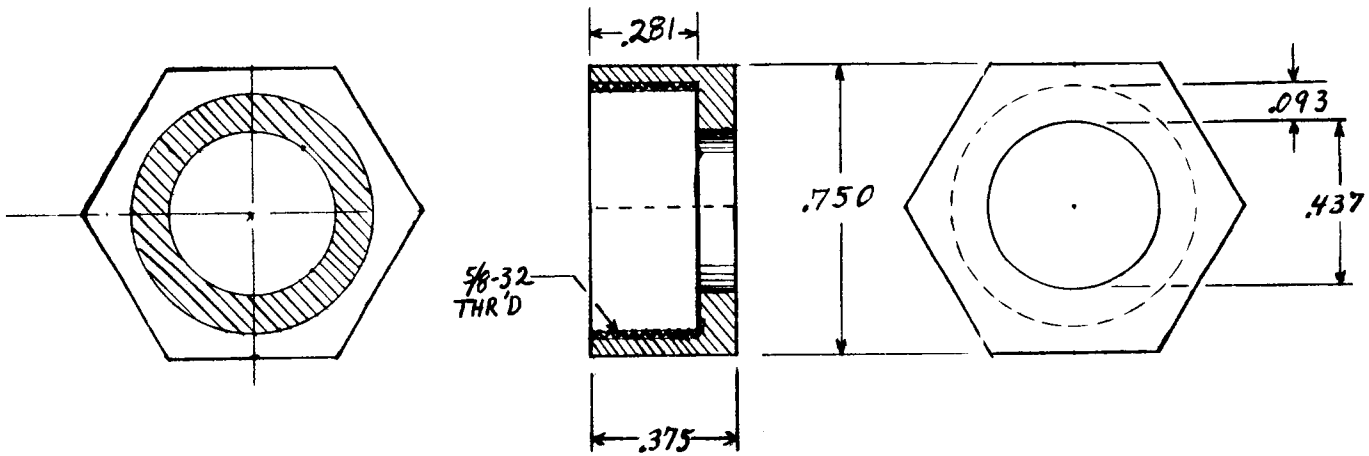

Figure A-3. Micro Fuel Cell Cover

miniature fuel-cell base. The cover also contains a 0.437-inch diameter through-hole to accommodate the gas manifolds and terminal of the miniature fuel cell top.

A.1.4 Miniature Fuel Cell Lock Nut

The miniature fuel cell lock nut (Figure A-4) is machined from 304 stainless steel bar stock. Its external surface is machined in the form of a standard 0.750-inch hex nut to accommodate a standard wrench. The internal surface is drilled and tapped with 5/8 - 32 threads for mounting on the fuel cell base. A thin piece of stainless steel wire 0.035-inch diameter is silver brazed to one of the external hexagonal surfaces to provide the second terminal.

A.1.5 Thread Seal

The thread seal (see Figure A-5) was purchased from the Parker O-Ring Company. The part consists essentially of a metal washer with a moulded-in rubber seal.

A.1.6 Electrodes and Screens

A special punch was machined and hardened for cutting electrodes with the desired diameter of 0.450 inch. The electrodes were then prepared simply by punching them from a sheet of the electrode material supplied by American Cyanamid Co. The material was designated as "American Cyanamid Fuel Cell Electrode Type A.B.-40." The same punch was also used to cut the gas distribution screen from a stock material of 200-mesh nickel with thickness of 0.010 inch.

A.1.7 Asbestos

Another punch was machined and hardened for cutting asbestos matrix discs with the desired diameter of 0.562 inch. The matrices were then prepared by simply punching them from a sheet of asbestos stock material. This material was obtained from Johns Manville Corporation and was 1/16 inch thick. It was designated as "Fuel-Cell Grade Asbestos."

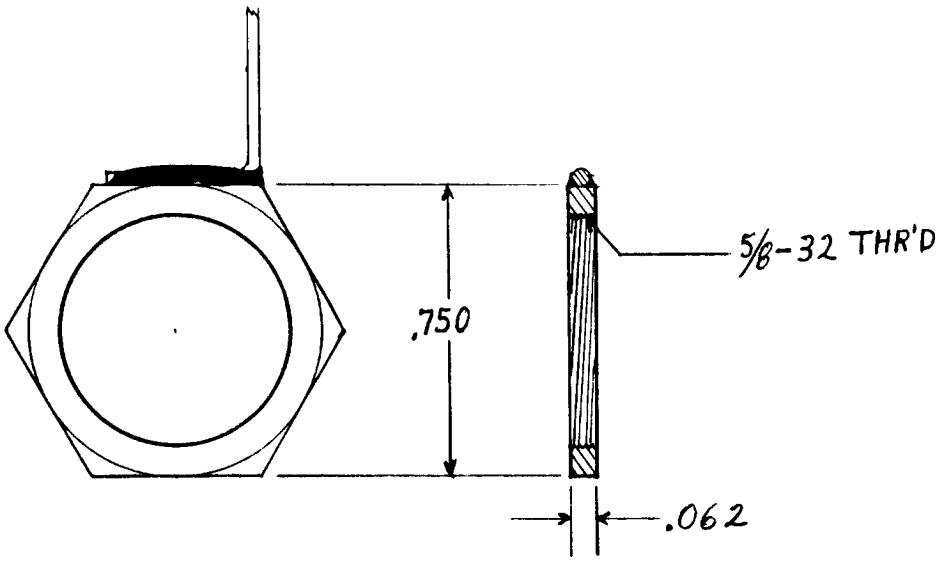

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Figure A-4. Micro Fuel Cell Lock Nut

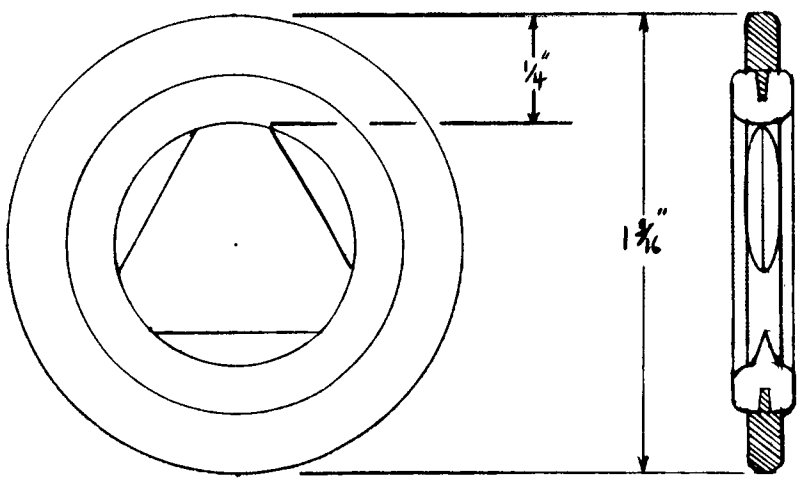

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Figure A-5. Thread Seal

A. 2 DETAILED ASSEMBLY AND OPERATIONAL INSTRUCTIONS

This section contains detailed instructions on the assembly and disassembly of the miniature fuel cells as well as instructions on installation in batteries and start-up procedures. Also included are sample evaluation tests.

A. 2. 1 Assembly

The micro fuel cells have been completely assembled at Astropower Laboratory and are ready for installation and test in a battery or simulator. In the event that the cells are taken apart for inspection, they may be reassembled in the following manner.

1. Fasten thread seal to bottom portion of miniature fuel cell base. This may be accomplished by passing the wick through the center of the thread seal and then twisting the thread seal onto the base until approximately 1/16 inch of the threads extends through the thread seal.
2. Apply washer to top side of base and let fall in place on the thread seal.
3. Apply lock nut to top side of base and screw it firmly (finger tight at this point) against the washer.
4. Position electrolyte matrix in center of fuel cell top.
5. Position top portion of fuel cell on top of electrolyte matrix.
6. Position cover over top and screw into base firmly (finger tight again at this point).

A. 2. 2 Activation and Installation

The fuel cell may be activated by two alternative methods depending upon the time requirements for initiation of testing.

1. Quick Activation – In this method the cell is activated by adding electrolyte directly to the matrix. This requires disassembly of the top portion of the cell. The asbestos matrix is taken out and

placed on a clean surface. Three drops (or approximately 0.1 gm) of 30% KOH solution are then applied to the upper surface and let saturate for about one minute. The matrix is then turned over and three more drops are applied to the other surface and let saturate for another minute. The matrix is then replaced in the cell and the unit is reassembled as described in Section 3.0.

2. Slow Activation – The cell may also be activated without disassembly by merely immersing the wick in the battery electrolyte or a solution of 30% KOH and waiting for a sufficient time until the electrolyte has been wicked and saturated the matrix. It has been found that a stand time of at least three hours is required for complete activation by this method for a wick length of 1-1/2 inches.

A.2.3 Installation

The miniature fuel cell is installed in a battery or battery simulator in accordance with the following procedures.

1. The case of the battery or simulator is first drilled with a standard 5/8-inch drill.
2. The hole is then tapped with a 5/8 - 32 thread drill.
3. The fuel cell is then inserted in the tapped hole starting with the wick first and followed by the threaded fuel cell base. The cell is screwed in by hand to a depth of at least 1/16 inch.
4. The wick is then suspended in the electrolyte in the case of a simulator, or wedged between the plates in the case of a battery, with a thin screwdriver or tool which has also been supplied. The screwdriver or tool may be inserted through the battery vent cap.
5. The lock nut is then tightened against the washer and thread seal with a special thin wrench. Applied torque should be finger tight or approximately 10 inch-lbs.
6. The two halves of the micro fuel cell are then tightened by applying a torque wrench to the hexagonal cell cover. Applied torque is quite critical in order to provide a good seal. The recommended value is 10 inch-pounds.

7. Electrical contacts are made to the screw terminal on the top and the extended steel wire attached to the lock nut. This wire is made extra-long and may be cut to any desired length.

A. 2. 4 Start-Up Procedures

In the case of simulator tests the following start up procedures are recommended.

1. Flush the top fuel-cell electrode with either hydrogen or oxygen (depending on the gas to be employed in the simulator) for a period of at least five minutes at a flow rate of at least 20 cc/minute.

The gas may be introduced at either of the two gas ports and should be vented from the other to a well-ventilated area.

2. Flush the simulator with either H_2 or O_2 (depending on the gas employed in the top fuel cell electrode) in a similar manner to that described above. Flushing time will depend upon the size of the simulator. For a nominal simulator size of 50 to 100 cc, a flushing time of at least one hour at 20 cc/minute is recommended. Inlets and outlets to the simulator should be arranged to promote good circulation within.

3. Leak Test – Apply a positive pressure of 1 to 2 psig in the simulator and check for leaks on the top side of the micro fuel cell with a good detergent. If leaks are found then retighten fuel cell cap.

In the case of an actual battery test the top electrodes of each fuel cell are flushed with their respective gases (either H_2 or O_2) for the recommended times above. The battery tests can also be carried out in either the open end or dead end mode of operation described below. The cells should also be leak tested as described above by applying a pressure inside the battery. This is most readily applied through the battery vent cap.

A. 2. 5 Testing Miniature Fuel Cells

The miniature fuel cells can be tested under a variety of modes of gas flow listed below.

1. Open-End in Both Top Electrode and Simulator – In this case the gases are passed slowly into and out of the simulator and top electrode at very low rates, i. e., a fraction of a cc/minute. This mode permits the highest fuel cell output and corresponding gas consumption capability for long term continuous operation.

2. Open-End in Top Electrode and Dead-End in Simulator – In this case the top electrode is fed with a slow flow of gas as above and the simulator is fed one-way, or dead-end. This more closely resembles the mode which would be encountered in an actual battery test. Output of the micro fuel cell is almost as high as that with open end flow in both electrodes as above.

Recommended pressure in the simulator in this mode is 1 to 2 psig. This can be maintained adequately with a dual stage regulator. The micro fuel cell can withstand higher pressure differential pressures to 10 psig but the lower values are recommended.

3. Dead-End in Both Top Electrode and Simulator – In this case the gases are fed one way or dead end to both simulator and top electrode. There is no limit to the pressures employed here but the pressure differential should be kept to a minimum as described above. This mode does not permit as high an output for long term operation as in the above modes. Maximum currents are in the range of 1 to 10 ma in this case.

4. Battery Tests – There are only two alternative modes of gas flow in the battery tests, i. e., open flow or dead end in the top fuel cell electrodes. The battery gases of course are restricted to dead-end flow in this case. Two fuel cells are employed, one supplied with H_2 and the other with O_2.

In the open flow mode the gases are passed slowly across the cell at the rates described above. In the dead end mode the gas vent lines are merely connected to a pressure gage. Operating pressures of both gases in this case should be approximately the same and in the range of 1 to 2 psig.

A.2.6 Performance Testing

The following tests may be employed to evaluate micro fuel-cell performance.

1. Gas Consumption Capability – The ability of a micro fuel cell to consume H_2 or O_2 can be determined directly or indirectly. In the direct method one measures the pressure decline in a battery or simulator in which the fuel cell is installed and operating. In the indirect method one merely measures the current and calculates the corresponding gas consumption rates based on Faraday's laws.

2. Polarization Characteristics – The polarization or voltage-current characteristics define the electrochemical performance and also give the gas consumption capability in a precise manner. These characteristics may be determined simply by recording the voltage and current output of the cell when operated over a range of external loads.

3. Stability – Stability of electrochemical performance and corresponding gas consumption capability may be determined by continuous long term operation. This may be carried out in any of the three following methods.

   a. By running at constant load and recording operating voltage and current at various intervals of time.

   b. By running at constant current and recording operating voltage versus time. This requires either a constant current supply or manual adjustment of load.

c. By running at constant voltage and recording operating current versus time. This requires a constant voltage supply or manual adjustment of load.

A.2.7 Sample Evaluation Test

Suggestions for an initial evaluation test in a simulator are given below.

1. Assembly micro fuel cell in a simulator which could be any small (50-100 cc) plastic container which is resistant to KOH. Add a small amount of 30% KOH to bottom and immerse wick.
2. Flush simulator with H_2 and top electrode with O_2 as described in Section A.2.4.
3. Apply 2 psig or approximately 4 inches mercury pressure of H_2 in simulator and seal off.
4. Pass oxygen slowly across top electrode.
5. Place micro fuel cell on discharge across fixed load of about 200 ohms and measure voltage, current, and pressure versus time.