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SMALL FUEL CELL TO ELIMINATE PRESSURE CAUSED BY GASSING IN HIGH ENERGY DENSITY BATTERIES

PROGRESS REPORT FOR PERIOD
30 DECEMBER 1965 TO 31 MARCH 1966
UNDER CONTRACT NAS 5-9594

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MISSILE & SPACE SYSTEMS DIVISION
DOUGLAS AIRCRAFT COMPANY, INC.
SANTA MONICA/CALIFORNIA

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SMALL FUEL CELL TO ELIMINATE PRESSURE CAUSED BY GASSING IN HIGH ENERGY DENSITY BATTERIES

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SUMMARY AND CONCLUSIONS

This program is concerned with evaluating miniature fuel cells for preventing the build up of high pressures in sealed silver-zinc batteries. Astropower miniature fuel cells perform this function by electrochemically consuming the gases generated within these batteries during operation and stand. In the process, the miniature cells also deliver electrical energy that may be used for an auditory warning or telemetering response indicating battery gassing.

The experimental program during this report period consisted of initiating pressure relief tests on miniature fuel cells in 15-Ah silver-zinc batteries as well as continuing life tests of miniature fuel cells in battery simulators. The most significant results obtained during this period were finding that miniature fuel cells can effectively limit pressure rise in the 15-Ah batteries tested under various cycle regimes and that the miniature cells exhibit long continuous operational life (over 5500 hours to date). There is evidence that these same miniature fuel cells can be used effectively in still larger silver-zinc batteries and that they exhibit significantly long life capability.

Progress and significant results obtained during this quarter are summarized below.

1. Miniature fuel cells can effectively limit pressure rise in commercially available silver-zinc batteries and extend useful battery life.

2. Two miniature fuel cells are required for complete control of internal pressure in a sealed silver-zinc battery. One must be available to consume hydrogen and the other to consume oxygen; both gases are generated in appreciable quantities in these batteries during cycling. Two miniature fuel cells with 1.0 cm^2 active electrode areas have been demonstrated to be capable of consuming all the hydrogen by one fuel cell and all of the oxygen by the other fuel cell generated in a Yardney 15-Ah high rate battery under various discharge and charge regimes and also on stand.

3. Functionally of miniature fuel cells with active electrode areas ranging from 0.25 to 5.0 cm^2 has been demonstrated for extended operating times in the open gas flow mode without wicking of product water. Eight miniature cells have been in continuous operation in this mode in battery simulators with operating times

ranging from 1800 to over 5500 hours. Since this manner of operation is more severe than would be encountered in a battery application, even longer life may be expected in batteries.

4. Functionality of miniature fuel cells with active electrode areas ranging from 0.25 to 5.0 cm^2 has been demonstrated for extended operating times in the dead end gas flow mode with product water wicked to a simulated battery electrolyte. Six miniature cells have been in continuous operation in this mode with operating times ranging from 300 to over 3000 hours.

5. A relationship has been established between miniature fuel cell open circuit voltage and hydrogen concentration in an anodic gas mixture of hydrogen and oxygen. This relationship should be very useful in determining internal gas composition. As might be expected, open circuit voltage increased gradually with increasing hydrogen concentration from 0 to 86% H_2. At this concentration level, the open circuit voltage was found to increase sharply (a five-fold increase) with increasing hydrogen concentration to 1.0 volt. From 86 to 100% hydrogen, the open circuit voltage again increased gradually with increasing hydrogen concentration.

6. Functionality of miniature fuel cells has been demonstrated for extended operating times (at least one month) on mixtures of hydrogen and oxygen in the anode and pure oxygen in the cathode. As anticipated, electrical output is lower for decreasing anodic hydrogen concentrations.

7. A relationship between size of miniature fuel cell electrode and its capability of consuming evolved battery gases is being authenticated through longer duration tests. Cells with cross sectional electrode areas of 0.25, 1.0, and 5.0 cm^2 have been shown to be capable of consuming hydrogen continuously at rates of 0.5, 2.1 and 10.6 cc/hr respectively for at least 3000 hours continuously. Furthermore, significantly higher gas consumption rates are possible over shorter periods of time.

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1.0 INTRODUCTION

Most high energy density batteries are known to be subject to the phenomena of gassing.[1] This involves the formation of hydrogen, oxygen or both within the batteries by any of several mechanisms. These include decomposition of active electrode materials, liberation of adsorbed or absorbed gases, or internal electrolysis. Gassing may occur during all modes of operation including charge, discharge, and 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.

This program is concerned with evaluating miniature hydrogen-oxygen fuel cells as devices to control pressure rise in one special type of battery, i.e., the silver-zinc type. However, the results will be applicable to controlling pressure in other high energy batteries including the silver-cadmium and nickel-cadmium types. The miniature fuel cells perform this function by electrochemically consuming the hydrogen and oxygen gases inside the battery to form water. Two fuel cells are 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 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.[2]

The ultimate goal of this program is to develop miniature H_2-O_2 fuel cells to control internal pressure and also to monitor internal gassing in silver-zinc batteries. These objectives are being met by a two-phase experimental effort. These include tests of miniature fuel cells in commercial silver-zinc batteries as well as in specially designed battery simulators where their performance can be examined under closely controlled conditions.

2.0 TECHNICAL DISCUSSION

2.1 Description of Miniature Fuel Cells

This section contains a brief description of miniature fuel cells and methods in which they are incorporated in silver-zinc batteries.

All of the cells now under test are referred to as the "modified" type and have the following features. Each contains identical platinized fuel cell electrodes for both anode and cathode and 30% KOH as electrolyte impregnated in a layer of fuel cell grade asbestos. Cell frames are cylindrical and are made from stainless steel. Electrodes are spot welded to these frames so that external electrical contacts may be taken directly from the frames. The cell in Test 1 of Section 2.3.1 is referred to as the "initial" type and was described in the Second Quarterly Report.[3]

Several methods of incorporating the ministure fuel cells in batteries have been employed, including the screw type, jack type, and deep insert type (Figures 1 through 3). A manifold arrangement has also been employed for pressure relief in more than one battery as shown in Figure 4.

2.2 Performance Tests on Batteries

The object of this phase of the program was to determine capability of miniature fuel cells in controlling pressure rise in normally vented type silver-zinc batteries when cycled in the sealed condition. This was to be determined by comparing the pressure rise in these batteries when cycled both with and without miniature fuel cells.

Initially it was anticipated that the internal battery gases would be essentially pure hydrogen. Therefore, the first tests were carried out with one miniature fuel cell installed on the battery and supplied externally with oxygen. It was subsequently found however, that there were appreciable quantities of oxygen evolved, especially during the initial discharge. Thereafter, tests were carried out with two miniature fuel cells, one for consuming hydrogen and the other for consuming oxygen.

The batteries that were used for this purpose were from Yardney Electric Company (Yardney 15-AH-HR). These were the dry charged type filled with electrolyte prior to use.

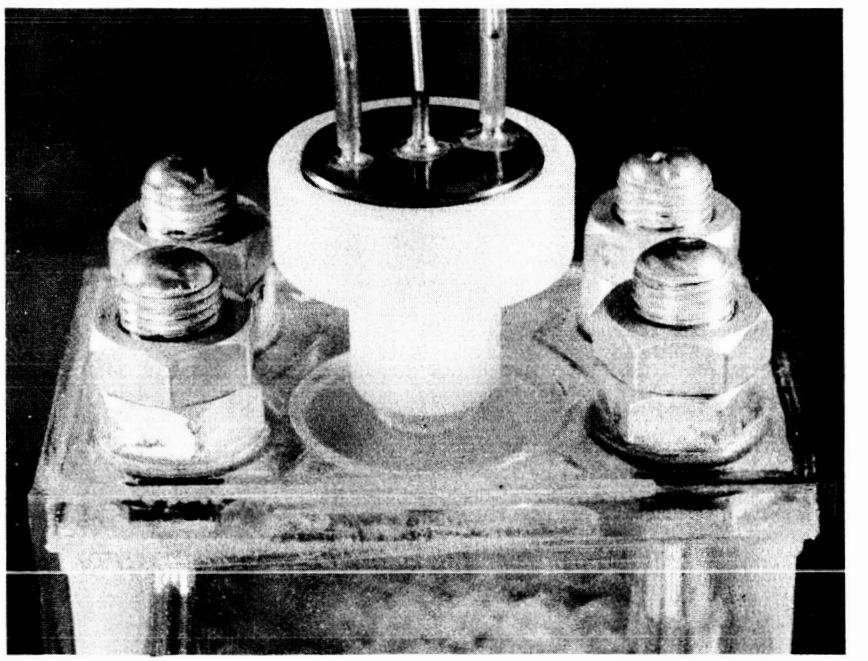

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Figure 1. Jack-Type (Press Fit) Connection of Miniature Fuel Cell to Actual Ag/Zn Battery

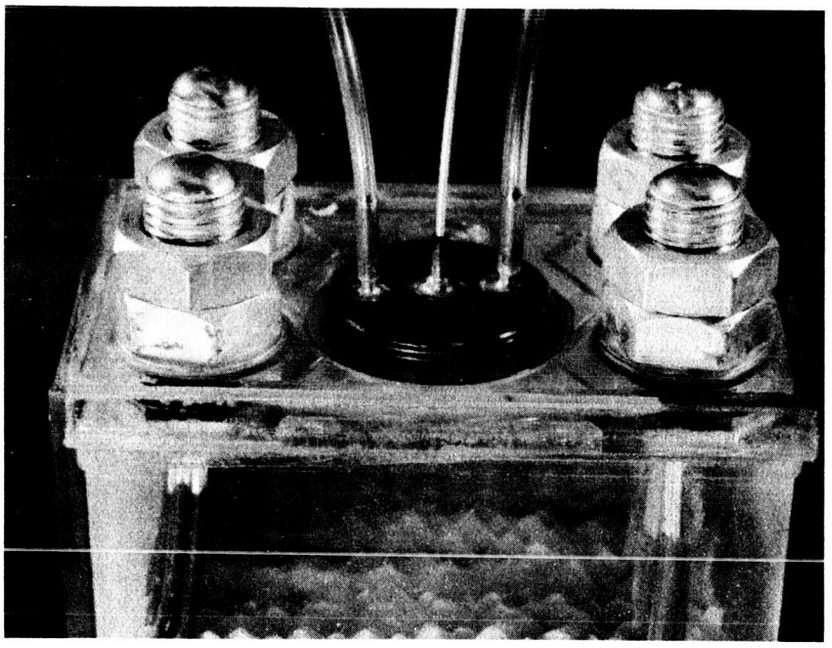

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Figure 2. Screw-Type Connection of Miniature Fuel Cell to Actual Ag/Zn Battery

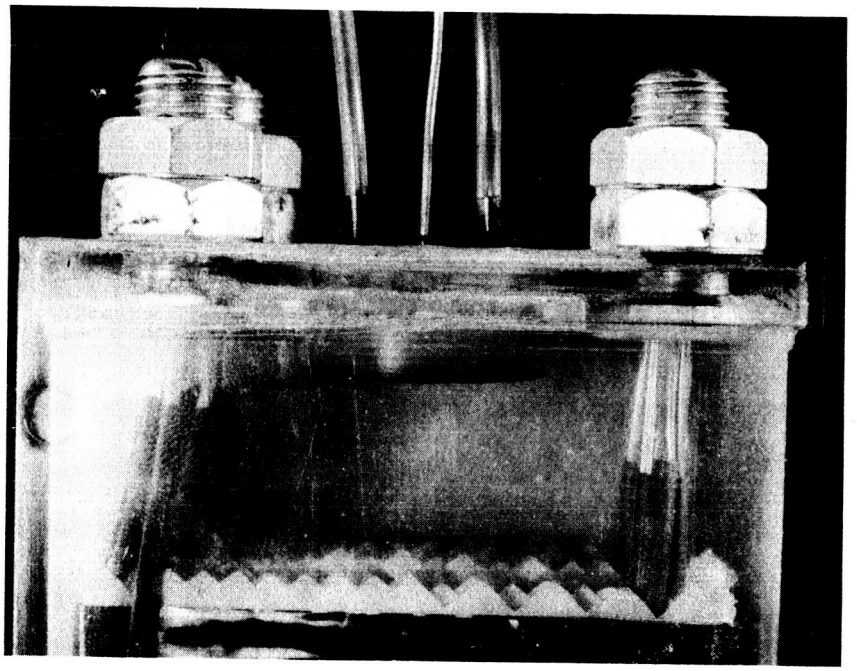

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Figure 3. Deep Insert Type of Miniature Fuel Cell Connection to Actual Ag/Zn Battery

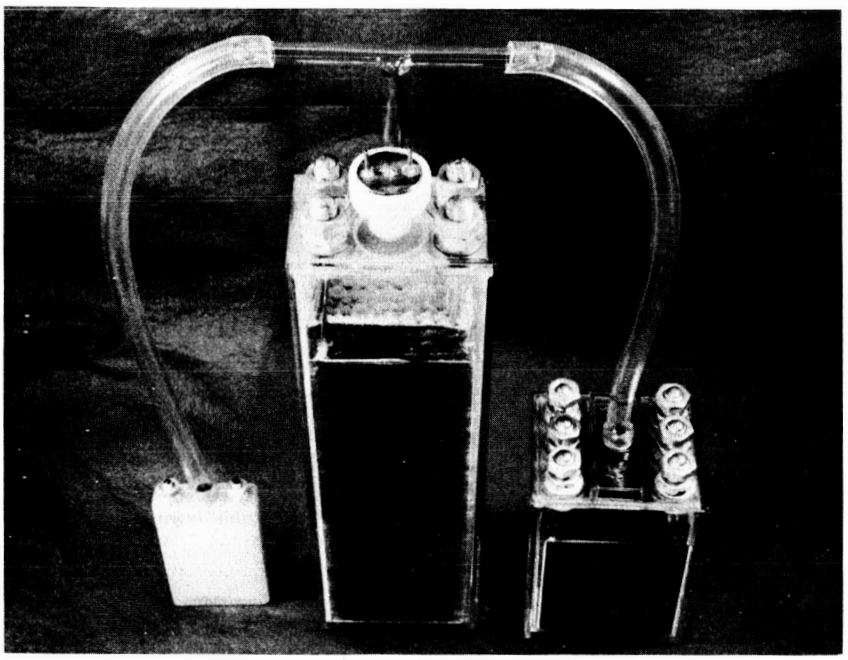


Figure 4. Application of Single Miniature Fuel Cell as Pressure Controller for Three Ag/Zn Batteries by Means of Manifolding Arrangement

The fuel cells were mounted near the top of the battery case with one electrode exposed to the battery gas head space and the other electrode outside the case and connected by tubing to either a hydrogen or oxygen supply.

2.2.1 Operation without Miniature Fuel Cells

In this test the battery was cycled in the sealed condition without miniature fuel cells. Sealing 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 I (See Test 4).

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 a rapid rise in internal pressure when the battery is cycled in the sealed condition. The rise in pressure was found in increase progressively with cycle time and might have increased much beyond 15 psig, had not the rupture occurred. This indicates substantial gassing rates in this type of battery. Much of this gassing, at least at the early stages of cycling, was found to be due to evolving oxygen (See Section 2.2.3).

2.2.2 Operation with Miniature Fuel Cells

Results of three cycle tests on silver-zinc batteries containing miniature fuel cells are given in Table I and are discussed more fully below.

2.2.2.1 Test 1

This test was initiated with one miniature fuel cell installed on the battery. The fuel cell was supplied with oxygen initially and then alternatively hydrogen and oxygen.

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,

TABLE I

CYCLE TESTS ON 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)
1	1	1/2 hr discharge at 10 amps and 1 hr charge at 5 amps	16	0-10	0 to 300 ma at 0.2 volt with H_2 0 to 200 at 0.1 volt with O_2
2	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 0 to 1 ma at 1 mv for O_2 cell
3	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 0 to 85 ma at 0.1 volt to O_2 cell
4	0	1/2 hr discharge at 10 amps	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

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 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-up 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 of up to 0.7 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 electrode areas 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.

2.2.2.2 Test 2

In this test a previously used battery (two cycles) was installed with two miniature fuel cells. One cell was supplied externally with hydrogen to consume internal oxygen and the other 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 I).

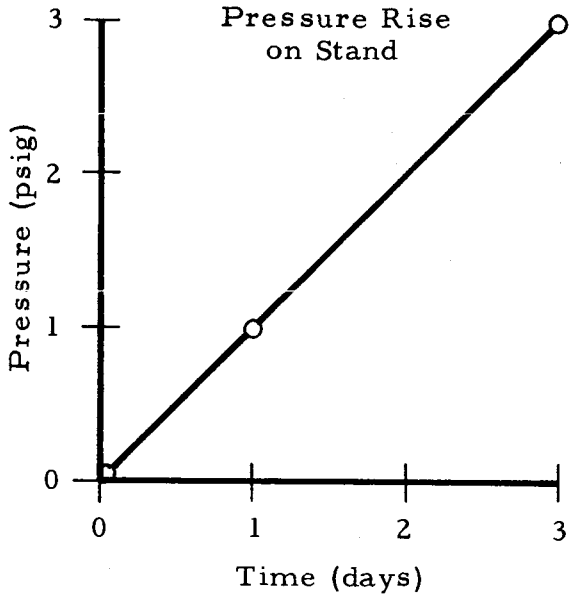
Very low pressures were developed within the battery during the course of five of the indicated cycles (a maximum of only 0.08 psig). Response of the fuel cell supplied with oxygen was within the range of 0.0 to 1.0 ma throughout all of the cycles, whereas response of the fuel cell supplied with hydrogen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

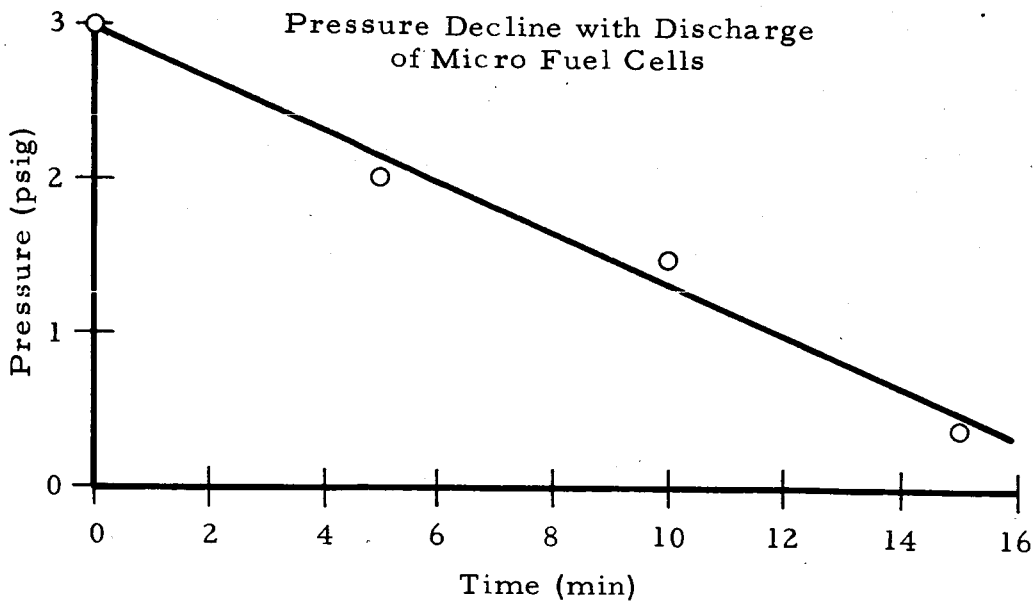
These results indicate that the silver-zinc battery generates very small quantities of gases under the above cycle regime and that two miniature fuel cells, each with 1.0 cm^2 electrode areas, are more than adequate to limit pressure rise.

2.2.2.3 Test 3

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 hr - 1 hr cycle was again employed as in Test 1 but at lower currents (See Table I).

Observed phenomena during this test were similar to those in Test 1. Internal pressure was again noted to increase during initial discharge but to a lower level than in Test 1. 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 5. 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 5, the response of the fuel cell supplied with O_2 increased rapidly to and maintained





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

a current level of 83 ma at 0.6 volts throughout the discharge 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.

2.2.3 Gassing During Initial Discharge

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.

2.3 Life Tests

The object of these tests is to determine operational life of miniature fuel cells as a function of both cell configuration and operational parameters. Design goals call for a miniature fuel cell with a life of 5000 hours of continuous operation.

The tests are run in specially designed battery simulators described in the previous Quarterly Report 2.[3] The tests are divided into two groups, depending upon the mode of gas flow. These are the open flow mode and the dead end mode. Test results obtained during the current report period are presented in Tables II, III, and IV.

TABLE II

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 (hours)	Average Voltage (volts)	Average Current (ma)
1	Initial	Proprietary	1.0	1000	5525	0.50	0.50
2	Modified	A.A.-1	1.0	1000	794	***	***
3	"	A.A.-1	1.0	1000	587	***	***
4	"	A.A.-1	1.0	1000	982	***	***
5	"	A.A.-1	1.0	1000	834	***	***
6	"	A.B.-6	1.0	1000	3672	0.90	0.90
9	"	A.B.-40	1.0	1000	3296	0.95	0.95
14	"	A.B.-40	1.0	100	3096	0.88	8.80
18	"	A.B.-6	1.0	100	2857	0.90	9.0
20	"	A.B.-40	0.25	4000	2616	0.95	0.25
21	"	A.B.-40	5.0	200	2648	0.60	3.0
24	Organic Membrane	A.B.-40	1.0	1000	456	***	***
27	Modified No. 2	A.B.-40	1.0	1000	1800	0.88	0.88

*The electrode type in Tests 2-27 inclusive refers to American Cyanamid Company designation
**These test numbers correspond to those listed in the second Quarterly Report
***Terminated at indicated time

TABLE III

POLARIZATION DATA OF MINIATURE FUEL CELLS ON LIFE TEST AT END OF THIRD QUARTER

Current Density (ma/cm^2)	Potential* (volts) TEST NUMBER							
	1	6	9	14	18	20	21	27
0	0.80	0.98	1.00	0.99	0.95	0.98	0.95	0.95
1	0.75	0.94	0.97	0.98	0.92	0.93	0.85	0.95
2	0.65	0.87	0.95	0.95	0.87	0.87	0.83	0.94
5	0.45	0.78	0.92	0.91	0.77	0.74	0.82	0.93
10	—	0.60	0.86	0.83	0.65	0.55	0.80	0.90
20	—	—	0.80	0.70	0.35	0.30	0.75	0.86
50	—	—	0.60	0.50	—	—	0.60	0.75
100	—	—	0.40	—	—	—	0.40	0.55

*Note: It may be noted that the voltages listed here are somewhat higher than the corresponding ones in Table II. The reason for this is that the above measurements are taken after the cells have been on open circuit for a short time during which voltage recovers to a higher level.

TABLE IV

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

Test No.	Fuel Cell Type	Electrode Area (cm^2)	Current Density (ma/cm^2)	Potential (volts)	Time (hrs)
1	Modified	1.0	5	0.90	3011
2	"	1.0	15	0.75	2387
3	"	5.0	5	0.90	1900
4	"	0.25	5	0.74	1900
5	"	5.0	15	0.65	336
6	"	0.25	15	0.52	336

2.3.1 Open End Flow without Wicks

These tests have been carried out in the plastic battery simulators shown schematically in Figure 6. Hydrogen and oxygen are passed slowly and continuously into the anode and cathode compartments. Excess gases that are not consumed are vented to the atmosphere. The cells are run continuously across a fixed load resistance. Operating voltage as well as a complete polarization curve are measured periodically.

The cell in Test 1 has continued to function satisfactorily, but at a slightly reduced output throughout this quarter. Total operating time to date is 5525 hours, which is somewhat more than the design goal of 5000 hours. The test will be continued.

Tests 2 through 5 inclusive, were terminated during the last quarter due to slow degradation. This was attributed to the use of the American Cyanamid A.A.-1 electrodes as described in the last quarterly report.

Tests 6 and 9 contain American Cyanamid electrodes Types A.B.-6 and A.B.-40, respectively, and are both operated across 1000-ohm loads. Both cells have continued to exhibit stable performance throughout this quarter (over 3300 hours) with operating voltage in Test 9 being slightly higher (0.05 volt) than that of Test 6.

Tests 14 and 19 containing American Cyanamid electrodes Type A.B.-40 and A.B.-6, respectively, were both operated across 100-ohm loads. Cells in both of the above tests have continued to exhibit stable performance under the above conditions for over 2800 hours.

The significant parameter for Tests 20 and 21 is electrode area. Active electrode area in Test 20 is 0.25 cm^2, or 1/4 of that employed in the above tests; active area in Test 21 is 5.0 cm^2, or five times that employed in the above test.

Electrodes in both of these tests are American Cyanamid Type A.B.-40. Performance of the cell in Test 20 (with smaller area) has remained constant throughout this period, near 0.95 volt, for over 2600 hours.

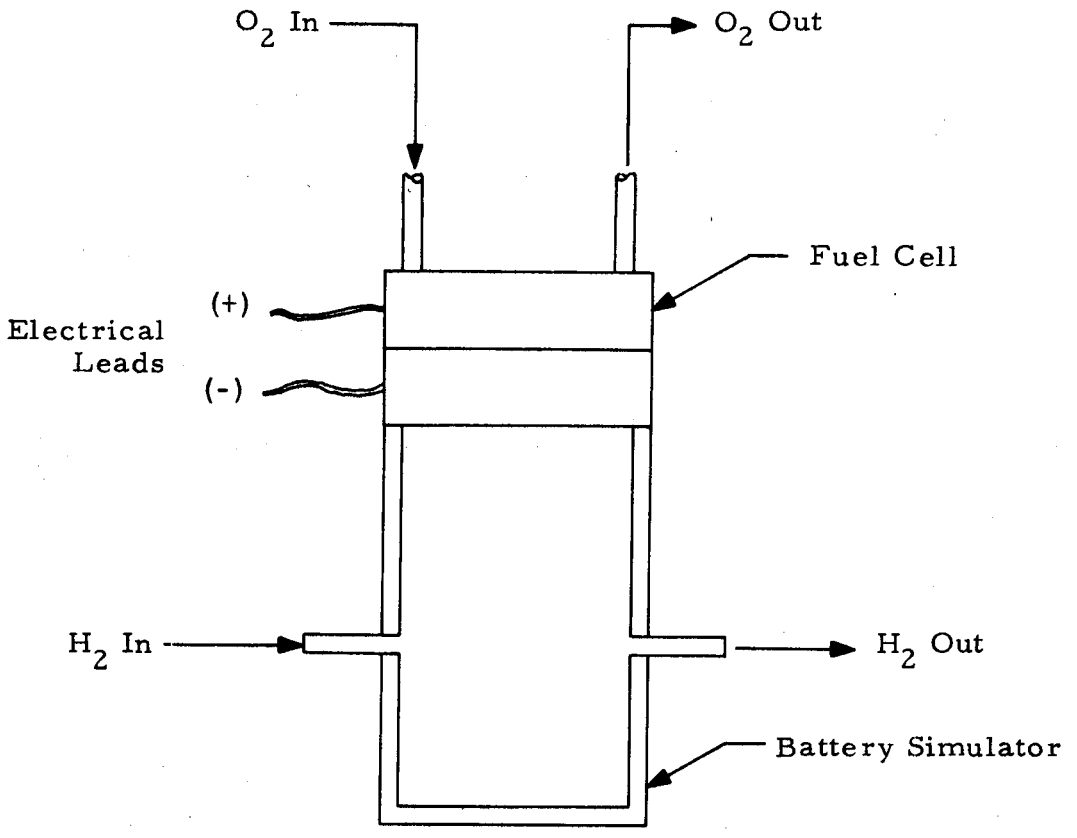


Figure 6. Schematic Diagram of Open Flow Tests

Performance of the cell in Test 21 (with larger electrodes) has dropped somewhat during the quarter from 0.95 volt to 0.60 volt. This may possibly be explained by flooding due to inadequate flow of gas for evaporating product water. In a battery application this problem would be resolved by wicking product water to the battery electrolyte.

The only new life test initiated in this group during the quarter is Test 27. The distinguishing feature of this cell is its new case and cover design. These components have been slightly modified to give more reliable gas seals and easier method of assembly. The cell has exhibited stable performance near 0.88 volt while discharging across a 1000-ohm load for 1800 hours. This cell design is being employed in the pressure relief tests in batteries described in Section 2.4.

2.3.2 Dead End Flow with Wicks

The purpose of these tests is 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 have been carried out in a simulated battery environment consisting simply of a small Ehrlenmeyer flask filled with hydrogen and containing a small amount of potassium hydroxide solution (See Figure 7). The fuel cell is mounted in a rubber stopper and fitted into the mouth of the flask. The fuel cells are the modified type described in Section 2.1 with the addition of a wick. One end of the wick is in contact with the fuel cell electrolyte through a small hole cut in the middle of the hydrogen electrode and the other end is suspended in the simulated battery electrolyte which is 30% KOH. Wick material is from the American Felt Company, Number 61NY185, and is cut in the form of a thin strip approximately 1/16 inch x 1/8 inch x 6 inches. Electrodes are American Cyanamid Type A.B.-40 with active area of 1.0 cm^2.

Operating methods to achieve the dead end mode were given previously.[2] The cells have been run at constant current with daily adjustment of load on a decade resistance box. The results are given in Table II.

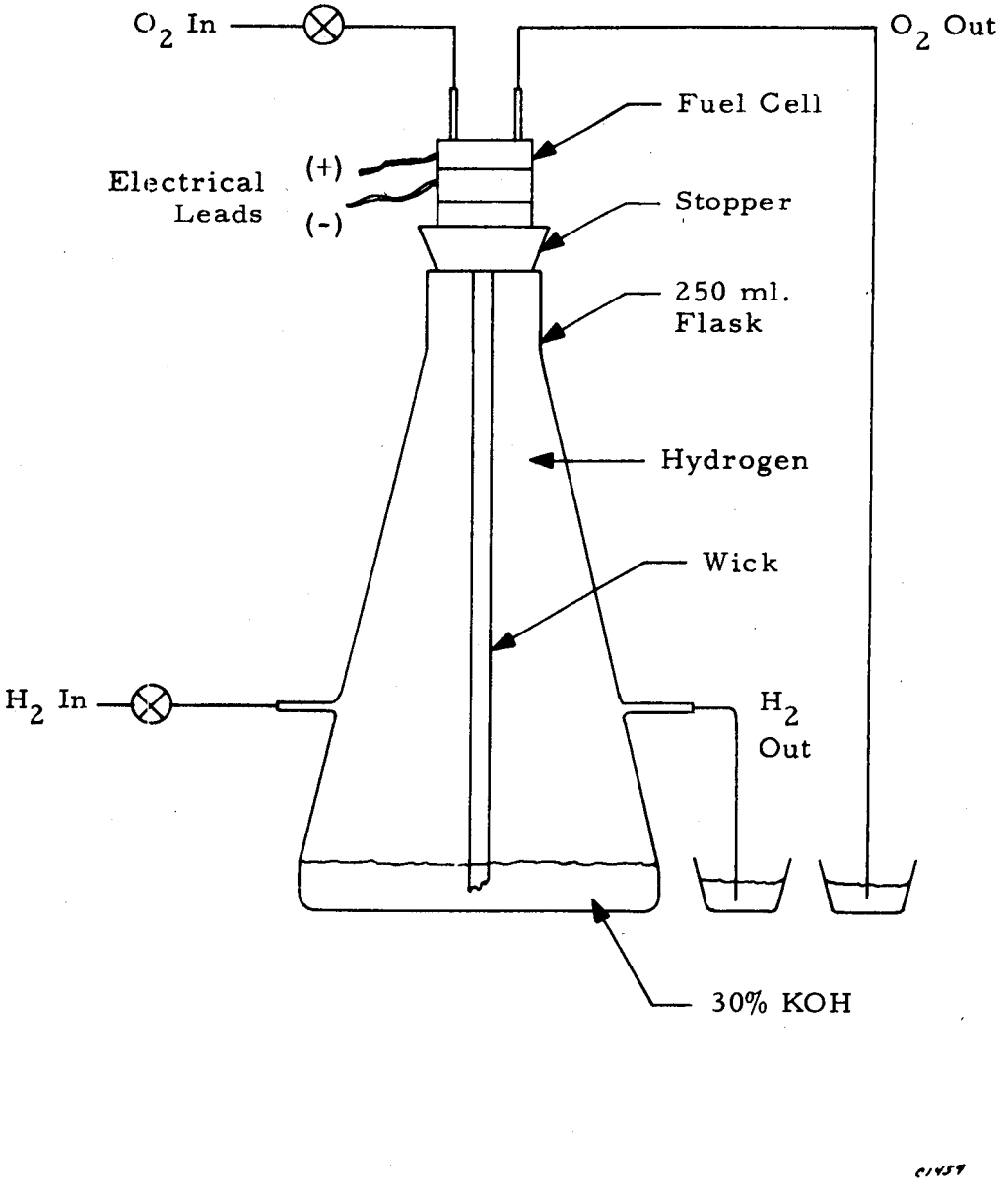


Figure 7. Schematic Diagram of Dead End Flow Tests with Wicks

The results indicate that a miniature fuel cell with 1.0 cm^2 electrode area (Test 2) can operate effectively in this manner at current densities of at least 15 ma/cm^2 for at least 2300 hours. Product water is effectively wicked at this rate to maintain stable cell performance. At the lower current density of 5 ma/cm^2 (Test 1) performance has been found to be very stable for a still longer operating time of over 3000 hours.

Performance of cells with both larger (Test 3) and smaller (Test 4) cross sectional electrode areas is noted to be quite stable for at least 1900 hours. Therefore, product water is effectively wicked from cells with electrode areas at 5.0 cm^2 and 0.25 cm^2 in this manner.

At a higher current density of 15 ma/cm^2 the operating voltages of cells with 0.25 and 5.0 cm^2 electrode areas are relatively stable for over 300 hours but at somewhat lower voltage levels than was observed at lower current densities.

2.3.3 Fuel Cell Size Versus Gas Consumption Capability

An important goal of this program is 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 accomodate the gassing rates that may be encountered in any size battery under any mode of operation.

Results to date 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 then 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:

$$R = 0.42\, i\, A \qquad (1)$$

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 shown to be applicable here. 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 due to 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 is being resolved by the use of wicks to transfer product water to the battery electrolyte. Results to date indicate that miniature cells with electrode cross-sectional areas of 0.25 to 5.0 cm^2 can operate effectively with wicks at currents of at least 5 ma/cm^2 for extended periods. This corresponds to hydrogen consumption capabilities of 0.53 cc H_2/hr and 1.6 cc H_2/hr for cells with electrode areas of 0.25 and 5.0 cm^2, respectively. Additional tests are in progress to determine capabilities at higher rates, for extended times.

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/hr.

2.4 Hydrogen Oxygen Mixture Studies

It has been shown in previous sections that both hydrogen and oxygen are formed in a silver-zinc battery during normal operating conditions. Therefore, in a battery application, the miniature fuel cell will be exposed to mixtures of these gases. Since very little is known about performance of miniature cells with these gas mixtures, a series of tests was carried out with miniature fuel cells in battery simulators. Three significant points were established in these tests during the quarter as described below.

1. It was found that a miniature cell can operate effectively on mixtures of H_2 and O_2 in its anode for extended times.

2. It was found that a miniature fuel cell consumes H_2 in a mixture mainly by electrochemical action.

3. A relationship was established between open circuit voltage and gas composition.

2.4.1 Operation with Mixtures in Anode

These tests have been carried out in an assembly similar to that shown in Figure 7. The fuel cell is mounted on a rubber stopper which in turn is inserted into a 250-ml Ehrlenmeyer flask. Oxygen is passed slowly across the externally located fuel cell cathode while the internal anode is in contact with H_2-O_2 mixtures inside the flask. These mixtures are prepared by flushing the flask with these gases at pre-set flow rates. After flushing, the flask is sealed off on the inlet and exit so that the anode is operating in a dead-end mode of operation. The fuel cell is of the modified type described in Section 2.1 and contains American Cyanamid electrodes Type A.B.-40 for both anode and cathode. A wick is employed to transfer product water from the fuel cell to a simulated battery electrolyte (a small amount of 30% KOH solution in the bottom of the flask). During operation, the fuel cell consumes hydrogen and therefore changes the composition of the gases within the flask with time. The extent of this change is minimized by periodic flushing with the H_2 and O_2 gases to give the initial composition. In this manner each run is carried out with an essentially constant gas composition.

Under these conditions, the micro fuel cell has been able to perform for over 720 hours without any apparent degradation in performance. The performance level is proportional to the concentration of hydrogen in the anodic mixture.

2.4.2 Chemical and Electrochemical Reaction

A second gas mixture study was initiated on the apparatus shown schematically in Figure 8. The object here was to test functionality of a dual fuel cell arrangement, one for consuming O_2 and the other for consuming H_2. The external electrodes of each of the cells were supplied with H_2 and O_2, respectively, and the internal electrodes were exposed to gas mixtures inside the simulator (actually, a small plastic container with volume of approximately 50 cc). Operation was carried out in a similar manner to that described above, i.e., the simulator was filled with a given mixture of H_2 and O_2 by flushing with these gases at pre-set flow rates and the simulator was then sealed off

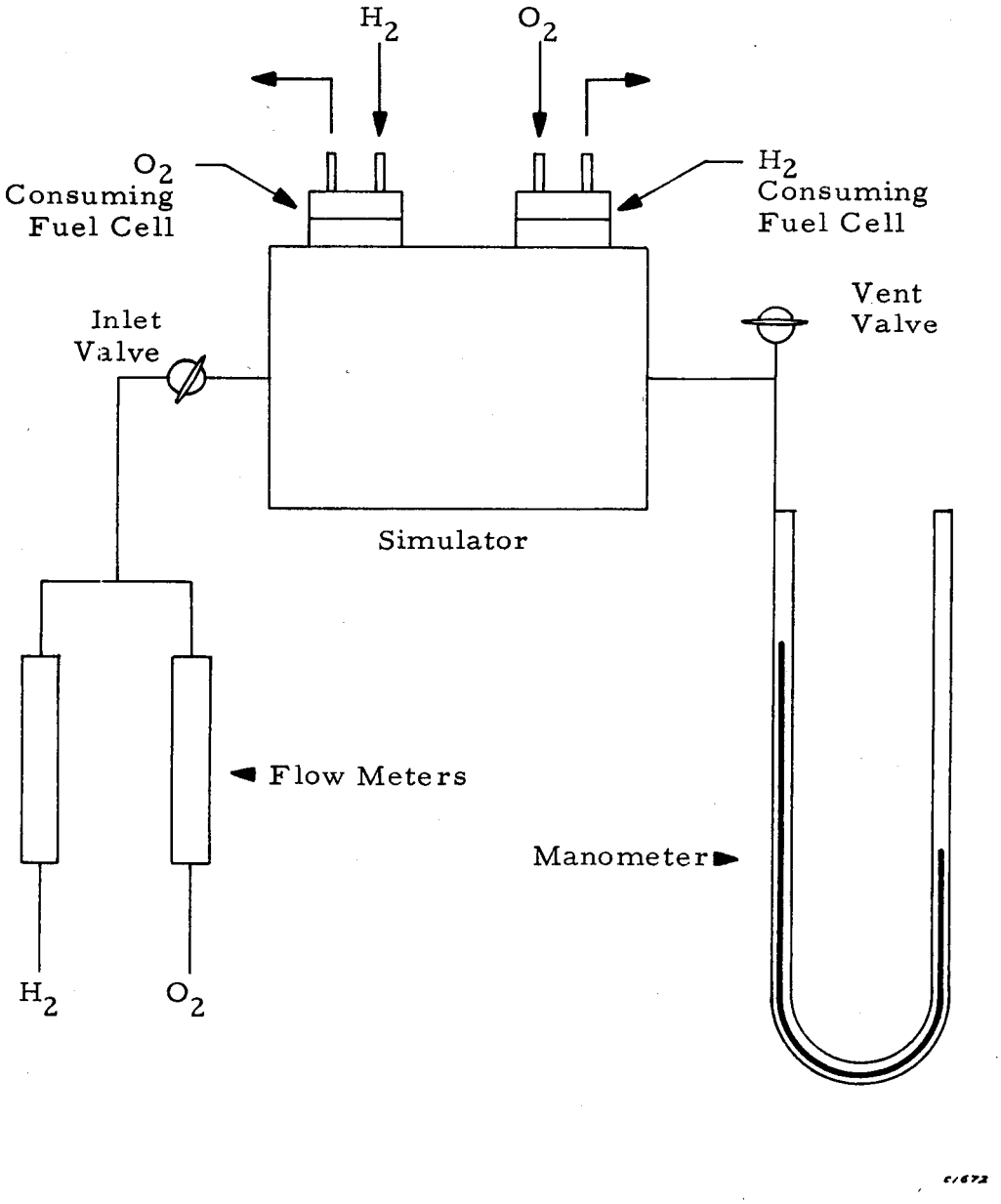


Figure 8. Dual Fuel Cell Arrangement in Battery Simulator

with one pressure tap to a manometer. The fuel cells contained electrodes with 1.0 cm^2 active electrode and were run at constant current.

Results of these tests are as follows:

1. With a stoichiometric mixture of H_2 and O_2 in the simulator (66-2/3% H_2 and 33-1/3% O_2) the output of the fuel cell supplied with O_2 was near 5.0 ma at 0.8 volt, whereas output of the fuel cell supplied with H_2 was a fraction of a milliampere at a fraction of a millivolt. Pressure was noted to decline quite rapidly within the simulator under these conditions from atmospheric to nearly 200 mm Hg above atmospheric in a few minutes.

2. With an oxygen rich mixture (66-2/3% O_2 and 33-1/3% H_2), the output of the fuel cell supplied with H_2 was near 5.0 ma at 0.8 volt, whereas the output of the fuel cell supplied with O_2 was a fraction of a milliampere at a fraction of a millivolt. The pressure was noted to decline but at a somewhat lower rate than the prior run with a stoichiometric mixture. The rate of pressure decline decreased with time and the pressure ultimately reached a plateau.

It appears from the work that the rate of pressure decline can be governed by the composition of gas mixture involved. However, this matter would require further investigation as the rate of gas consumption by each fuel cell is regulated by various pertinent fuel cell operational parameters such as its external resistance.

2.4.3 Effect of Mixtures on Open Circuit Voltage

Another series of runs was carried out to determine the effect of anode gas composition on open circuit voltage. These tests were carried out in the apparatus shown schematically in Figure 7. Oxygen was fed slowly to the cathode side of the micro fuel cell in the open flow mode. Mixtures of hydrogen and oxygen were also fed in the open flow mode into the Erhlenmeyer flask in which the anode side of the fuel cell was immersed. Desired gas compositions were set by varying the flow rates of the H_2 and O_2. Exact compositions were determined periodically by chromatographic analysis of the exit gas stream. Open circuit voltages were measured with a Hewlett-Packard vaccum tube voltmeter.

Results of the tests are given in Figure 9. With pure hydrogen in the anode, open circuit voltage (OCV) is noted to be 1.07 volts. This is in accord with other H_2-O_2 fuel cell data in alkaline media.[4] As oxygen content was increased the OCV was noted to decrease gradually at first, and then very rapidly at a composition of approximately 86% H_2 and 14% O_2. At this composition, the OCV decreased from 1.03 volts to 0.25 volt. The OCV was then noted to decrease gradually with increasing O_2 content to zero volt for pure oxygen. The same OCV characteristics were obtained by varying the gas compositions, starting with pure oxygen and gradually increasing the hydrogen content.

Now, it appears that the micro fuel cell is capable of affording a quantitative measure of gas concentrations.

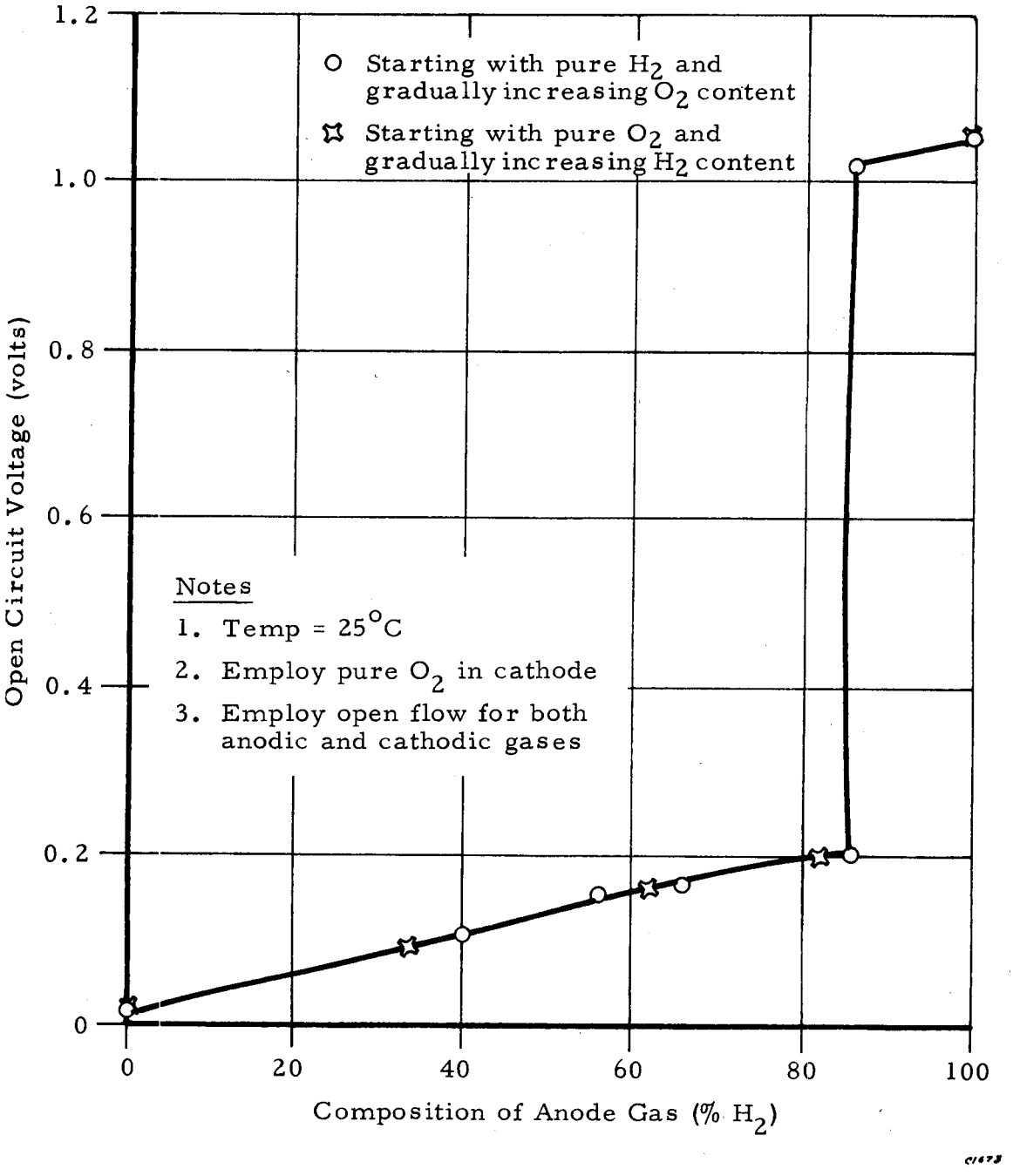


Figure 9. Effect of Composition of Anode Gas on Open Circuit Voltage of H_2-O_2 Fuel Cell

3.0 PROGRAM FOR FOURTH QUARTER

1. Performance tests of miniature cells in 15 Ah silver-zinc batteries will be continued under different cycle conditions for the battery.
2. Fifteen miniature fuel cells will be fabricated for delivery to NASA Goddard.
3. All existing life tests will be continued throughout the next quarter or until failure occurs.

4.0 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

5.0 NEW TECHNOLOGY

There were no new developments during this report period.

REFERENCES

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

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3. "Small Fuel Cell to Eliminate Pressure Caused by Gassing in High Energy Density Batteries," 2nd Quarterly Report, Contract NAS 3-9594, January 1966.

4. Fuel Cells, (W. Mitchell ed.) Academic Press Inc., New York, p. 333-35, (1963).