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

PROGRESS REPORT FOR PERIOD
30 JUNE TO 30 SEPTEMBER 1965
UNDER CONTRACT NAS 5-9594

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DOUGLAS

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SUMMARY

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

Scope of the program includes fabrication and testing of miniature fuel cells under simulated conditions of gassing. Sufficient tests are to be carried out to provide the necessary design data for specifying the appropriate size and configuration of miniature fuel cells to handle gassing rates that would be encountered in any size silver-zinc battery under anticipated operating conditions. In addition, prototype models are to be built and tested in a commercial 100 amp-hr silver-zinc battery and fifteen units are to be delivered to NASA Goddard.

Work performed during this first quarter consisted of fabrication and test of several experimental miniature fuel cells in specially designed battery simulators. Life tests indicate that the miniature fuel cells function satisfactorily in reduction of pressures in batteries for operating times of at least 1600 hours. Functionality of the miniature cells was shown for operation on mixtures of H_2 and O_2 containing up to 50% oxygen in the anode and up to 10% hydrogen in the cathode. The cells were also found to function satisfactorily at 40°C, where current output was 200% of that at 25°C, and also of that at 0°C, where current output was 80% of that at 25°C.

The experimental work has been carried out in accordance with the authorized statement of work. No major problems have arisen to date and work is proceeding on schedule. Plans for next period include continuation of existing life tests as well as initiation of new ones in the "dead end" mode of operation described herein.

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1.0 INTRODUCTION

The phenomena of gassing in silver-zinc cells and resultant pressure rise caused by gassing in sealed cells of this type are well known.[1,2] An uncontrolled pressure rise ultimately leads to rupture of the cell case and failure of the cell.

Several methods have been proposed for dealing with this problem in the past. These methods range from use of catalysts, to promote union of the gases (H_2 and O_2), absorbents for each of the gases such as pyrogallol for oxygen, to more recent methods based on stabistors, adhydrode and auxiliary electrodes. The adhydrode and auxiliary electrode techniques are based in part on the inherent electrochemical characteristics of high energy density batteries. In practice, these characteristics will vary under different modes of operation, including rate and degree of charge and discharge, and ambient temperature.

The objective of this program is to evaluate the use of a miniature fuel cell in solving the problem of gassing and pressure rise in sealed silver-zinc cells. Operation of such a miniature cell is not dependent upon electrochemical characteristics of the battery in which it is employed. Since it functions independently it therefore provides independent reliable control for the battery.

Illustrations of miniature fuel cells and methods in which they may be incorporated in silver-zinc batteries are shown in Figures 1 through 4. Several arrangements are illustrated, including a "Jack type," "Screw type," and "Deep Insert type." Sizes of these cells vary depending upon the anticipated gassing rates within the battery. Nominal overall dimensions of those shown are 2 cm dia. x 2 cm long. They may be mounted in any convenient place near the top of the battery without interferring with its normal operation.

Work performed during this period consisted of fabrication and test of experimental miniature cells in specially designed battery simulators. A detailed description of these cells and results of tests performed on them are given in the following sections.

2.0 TECHNICAL DISCUSSION

2.1 Description of Miniature Fuel Cells

Three general methods of incorporating the miniature fuel cells in a silver-zinc battery are shown in Figures 1 through 3. The first of these is the "Jack type" arrangement, as shown in Figure 1. In this case, the cell is designed for direct mounting on the battery vent tube. Battery gases must pass through the tube before entering the fuel cell. A Screw type arrangement is shown in Figure 2. In this case, the outer frame of the fuel cell is threaded so that it may be screwed into the top of the battery case. Path length through which the gases must travel to reach the fuel cell is somewhat shortened in this case. A Deep Insert type is shown in Figure 3. In this case, the fuel cell is mounted deep inside the battery case and exposed directly to the gases which are evolved from the electrodes.

Manifolding arrangements are also possible as shown in Figure 4. In this case, gases from several batteries are transmitted through tubing to one miniature cell.

In all of the cases described above, the cathode side of the fuel cell is supplied with pure oxygen from an appropriately small oxygen cylinder or tank.

Key components of all miniature fuel cells employed on this program have been the same for all tests. Potassium hydroxide solution has been employed as electrolyte. This solution is contained (immobilized) in an asbestos matrix. Platinum black has been employed as electrocatalyst for both hydrogen and oxygen.

Two basic types have been employed. A description of each of these is given below.

2.1.1 Initial Cell Type

Components of the initial miniature fuel cell are shown in Figure 5.

Both hydrogen and oxygen electrodes are identical and consist of platinum black, which has been bonded under a 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 gas seals both internal 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 4. The housing is made of nylon, and the 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 from either a silver-zinc battery or one of the battery simulators to the electrode. The outside of this end plate is threaded for direct mounting onto either the battery or simulator.

Several sizes of miniature cells have been built with overall dimensions ranging from 5 mm dia. x 5 mm long to 20 mm dia. x 10 mm long. Corresponding electrode diameters have ranged from 3 mm to 15 mm.

2.1.2 Modified Cell Configuration

This cell is shown in Figure 6.

Electrodes for this cell were obtained from the American Cyanamid Company. As in the cell described above both hydrogen and oxygen electrodes are identical and contain platinum black as the electrocatalyst, however, they do differ in some details. In this case, the collector screen is made of nickel or tantalum and a Teflon waterproofing agent has been admixed with the platinum black. Potassium hydroxide impregnated asbestos is again employed as electrolyte.

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

Somewhat different types of gas seals are employed in this cell. Internal seal between compartments is provided by compression of the outer periphery of the asbestos layer between the surfaces of the gas distribution plates. External seal is provided by a bead of epoxy resin around the circumference where the cell halves meet.

Several sizes of these cells have also been built with the same range in overall dimensions as the initial cell (Section 2.1.1).

2.2 Life Tests

Objective of these tests is to establish functionality of the miniature fuel cell for extended operating times to 5,000 hours. The tests are being carried out in the battery simulators described in Section 2.1. Pure hydrogen is fed to the simulator which communicates with the fuel cell anode and pure oxygen is fed to the fuel cell cathode. The cell is discharged continuously across a fixed load and daily record is made of voltage and current and other operational parameters.

Several life tests were initiated on models of the initial cell design during the early stages of this program. All but one of these tests were discontinued, however, shortly thereafter. The reason for terminating these tests was not due to degradation in performance (each was functioning well at the time), but was related to evaluation of other Astropower miniature cells with new electrodes. As pointed out in Section 2.3, electrical performance of miniature cells with new electrodes and slightly modified configuration was found to be significantly greater than those with old electrodes and configuration. It was therefore decided to place more emphasis on testing of the new cell type, rather than the old type, which would most likely be discarded.

Several of these new cells were subsequently assembled and placed on life test.

A summary of all life tests is given in Table I. Results indicate no degradation in performance with time to 1,600 hours for cells of the initial design, and to 600 hours for cells of the modified design. Stability of operation has been found to be independent of external load (or fuel cell current) within the given range. Voltage of each cell has remained relatively constant throughout the test period, except for minor fluctuations within the given ranges. Cause for these flctuations was attributed to variations in gas flows. These variations in flow were, in turn, caused by faulty needle valves. Cleaning of these valves has improved their performance and minimized the fluctuations in voltage.

A final point should be made here in regard to operating conditions for the above life tests and plans for additional tests. As indicated above, the chosen operating condition simulated those in an actual silver-zinc cell, but differed slightly in regard to gas flow. In an actual cell, the battery gases would be "dead ended" at one side of the fuel cell, whereas, in these tests, gases were passed across one side of the fuel cell and vented to the atmosphere. Although the gas flows employed were very low (1cc/minute) this mode of operation may be significantly different than the "dead end" mode. Therefore, additional life tests in other latter mode of operation will be initiated during the next quarter. A few exploratory runs were recently carried out in this mode in preparation for these tests.

2.3 Effect of Cell Configuration on Performance

Amongst the various types of miniature fuel cells which Astropower had examined for this program was one that contained electrodes from the American Cyanamid Co. Electrical performance of miniature cells with these electrodes was noted to be significantly greater than the type which employed internally prepared electrodes. Comparative performance is given below.

Current Density (ma/cm^2)	Voltage of Initial Cell (Volts)	Voltage of Modified Cell* (Volts)
1	.83	1.00
10	.49	.90
100	0	.60

*Containing American Cyanamid Fuel Cell Electrodes

TABLE I

SUMMARY OF LIFE TESTS

Test (No.)	Configuration	Total Time (Hrs.)	Load (ohms)	Voltage Range (Volts)	Current Range (ma)
1	Initial	1,600	1,000	.5 - .8	.5 - .8
2	Modified	600	1,000	.7 - .9	.7 - .9
3	"	300	1,000	.7 - .9	.7 - .9
4	"	100	500	.7 - .9	1.4 - 1.8
5	"	100	100	.7 - .9	1.0 - 9.0

H_2 and O_2 flow nominally at 1cc/min.

Ambient temperature 24 to 26^{o}C

More reliable gas sealing properties were also noted for the modified cell. This was established in routine check out tests in which leaks were frequently found on cells of the initial type, but never on cells of the modified type.

2.4 Effect of Temperature on Performance

The effect of temperature on performance of both the original and modified cell types is given in Figures 7 and 8. 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.

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 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 to at least 0°C.

2.5 Operation with H_2 - O_2 Mixtures

The objective of these studies was to establish functionality of the miniature fuel cell when operated on mixtures of hydrogen and oxygen. Two cases were examined here. In the first case, hydrogen-oxygen mixtures were fed to the anode side of the fuel cell, while pure oxygen was fed to the cathode side. In the second case, hydrogen-oxygen mixtures were fed to the cathode side of the cell, while pure hydrogen was fed to the anode side.

Results of these studies are given in Figures 9 through 12. Inspection of Figures 9 and 10 indicate that the fuel cell can function satisfactorily with mixtures on its anode side containing up to 50% oxygen. Performance in this mode of operation is noted to decline gradually with oxygen content to a level of 50% oxygen and to fall rapidly with oxygen content between 50 and 70% oxygen. Inspection of Figures 11 and 12 indicate that the fuel cell 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% hydrogen.

These results are directly applicable to the problem of estimating performance of miniature cells when installed in commercial silver-zinc batteries. 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 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 reaches 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 due to 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 has 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 battery during normal operation and also during overcharge.

2.6 Fuel Cell Sizing

Pressure rise in a sealed silver-zinc battery will be dependent upon the relative rates of gas evolution within the battery and consumption by the fuel cell. In order to limit pressure rise, it is necessary that the consumption rate be at least equal to the evolution rate. Matching of these rates can be carried out by selecting the proper sized fuel cell.

From the data which has been accumulated to date, it is possible to predict rate of gas consumption by a given size fuel cell. For example, if the fuel cell is run at a current of 100 ma/cm^2, the following relationship would apply:

(1) $$d = .17\sqrt{R}$$

Where:

d = diameter of fuel cell electrode, cm,

R = hydrogen consumption rate, (cc/hr)

Overall diameter of the fuel cell is approximately 1/2 cm more than that of the electrode. Overall thickness is nominally 1 cm.

A typical gassing rate in a silver-zinc battery may be estimated on the basis of data supplied by NASA Goddard personnel.[3]

Gas Evolved	H_2
Battery Void Space	1/2" x 1/2" x 1-3/4"
Duration	1/2 hr. discharge
Performance Cycles (2 weeks)	224
Pressure Build up over 2 weeks	60 psig

From this data the rate of hydrogen evolution is calculated to be 8.4×10^{-3} cc/hr. The corresponding fuel cell diameter from Equation (1) above is 0.016 cm. In this case, the minimum size fuel cell would be sufficient to handle this gassing rate (nominally 1/2 cm dia.).

Another example might consider the unlikely, but possible, case of excessive overcharge. Let us assume that the battery is placed on a continuous light charge of 100 ma. In this case, the gases consist of essentially pure hydrogen and oxygen. Evolution rates correspond to overcharge current of ma. Two fuel cells must be employed here; one to consume H_2 and another to consume O_2. Each cell must consume the equivalent of 100 ma of these gases to limit pressure rise. If operating fuel cell current is 100 ma/cm^2, as above, then each cell must have electrode area of 1 cm^2. Correspondingly, electrode diameter is therefore 1.13 cm and overall fuel cell diameter is approximately 1.6 cm.

3.0 CONCLUSIONS

A miniature fuel cell used for pressure reduction in batteries exhibits stable performance for operating times of at least 1,600 hours. Functionality of these miniature cells has been ascertained for operation on mixtures of battery gases (H_2 and O_2) containing up to 50% oxygen in the anode and up to 10% hydrogen in the cathode. The cells can also operate effectively at 40°C, where current output is approximately 200% that at 25°C, and 0°C where current output is 80% that at 25°C.

4.0 PROGRAM FOR SECOND QUARTER

Life tests of the five cells in the battery simulators will be continued. Additional life tests will be initiated in the "dead end" mode of operation. These latter tests will be run at various loads and with different mixtures of hydrogen and oxygen in the anode.

Analyses of experimental data will be made to obtain correlation data between size of miniature fuel cell and rate and capacity of gas consumption in batteries.

5.0 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

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1. Francis, Howard T., "Space Battery Handbook," pp. 42-47 (15 April 1963).
2. "Silver-Zinc Secondary Battery Investigation," Technical Documentary Report, RTD-TDR-63-4029, pp. 60-66, (31 October 1963).
3. Personal Communication, Mr. Thomas Hennigan, NASA-Goddard (17 July 1964).

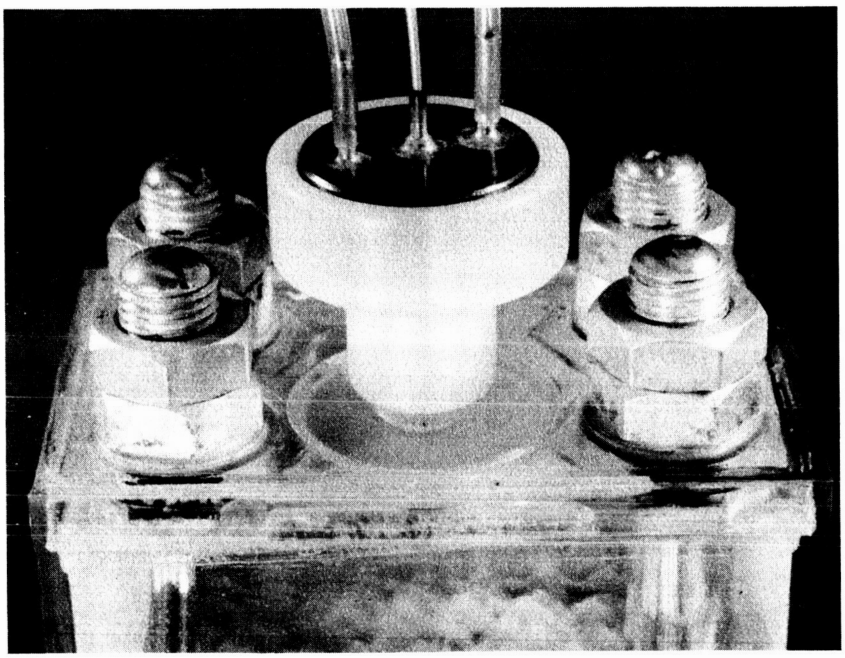

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Figure 1. Jack-Type (Press-Fit) Connection of Miniature Fuel Cell to Actual Ag/Zn Battery

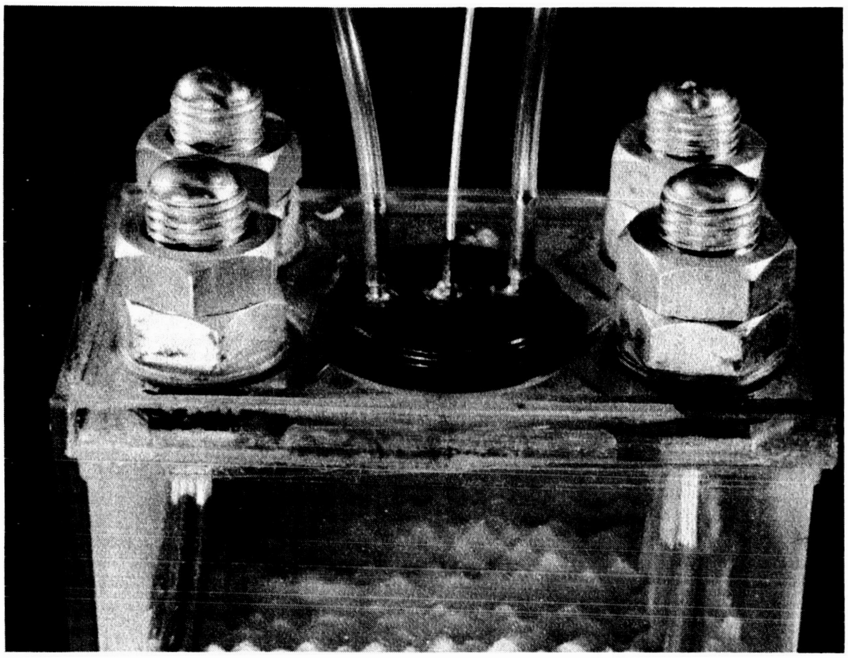

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Figure 2. Screw-Type Connection of Miniature Fuel Cell to Actual Ag/Zn Battery

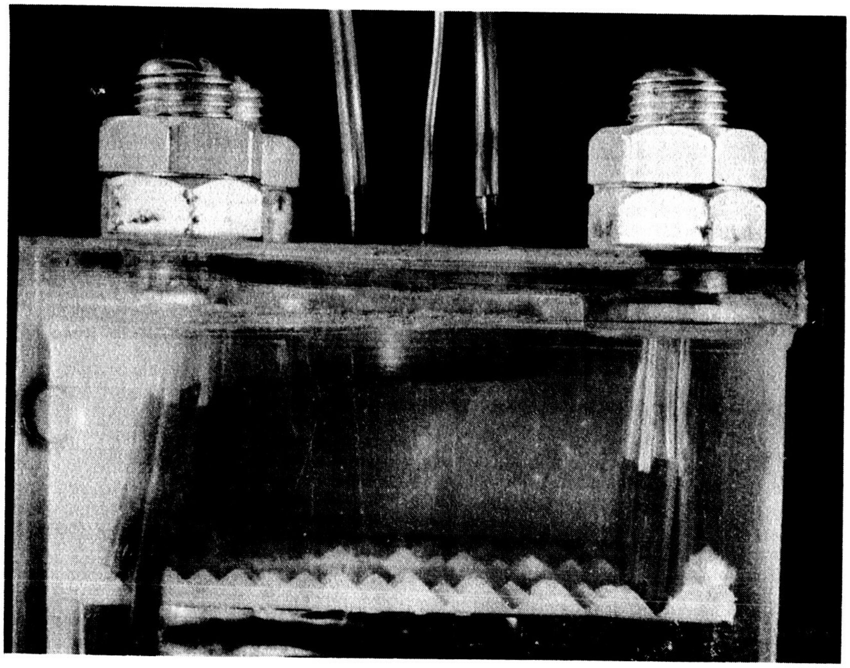

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Figure 3. Deep Insert Type of Miniature Fuel Cell Connection to Actual Ag/Zn Battery

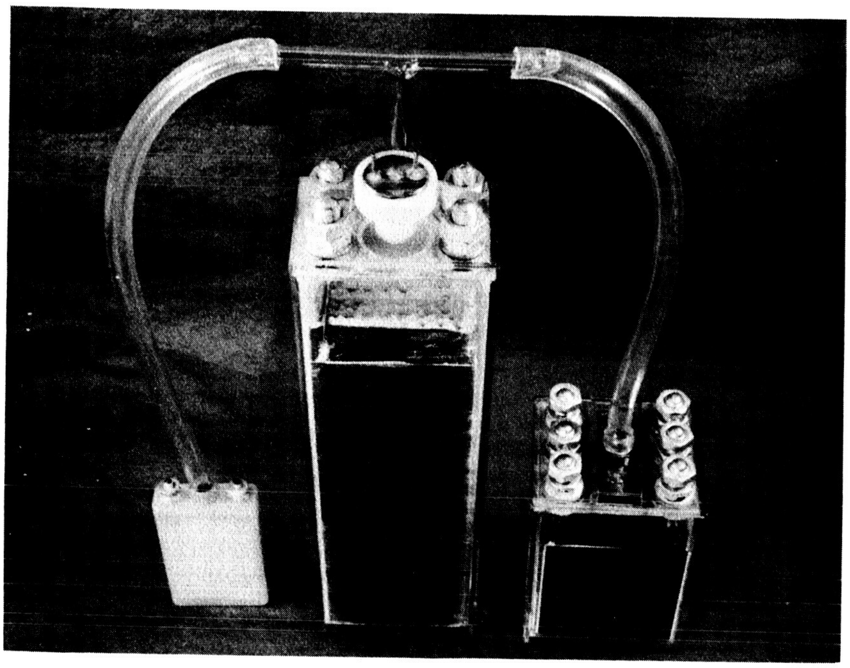

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Figure 4. Application of Single Miniature Fuel Cell as Pressure Controller for Three Ag/Zn Batteries by Means of Manifolding Arrangement

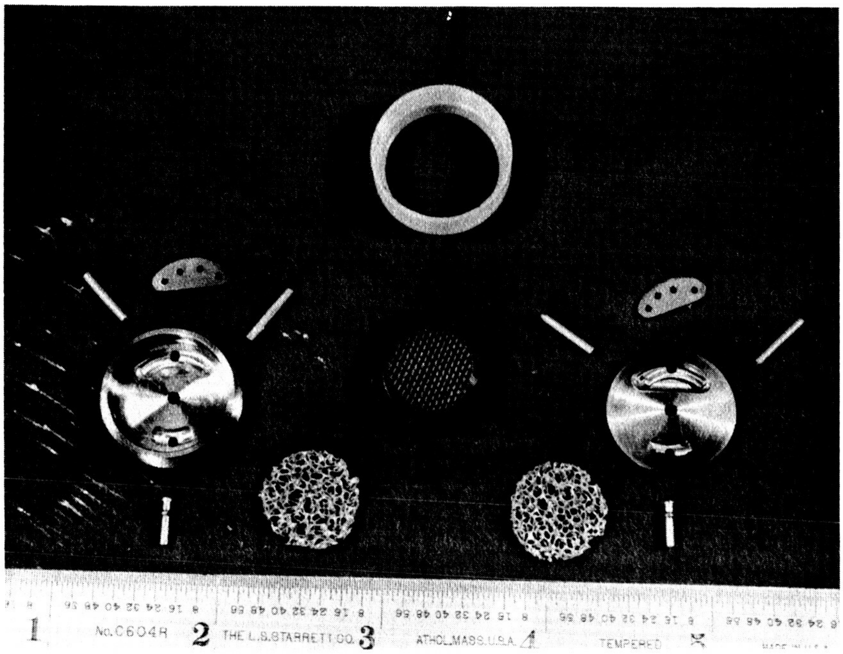

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Figure 5. Initial Miniature Fuel Cell

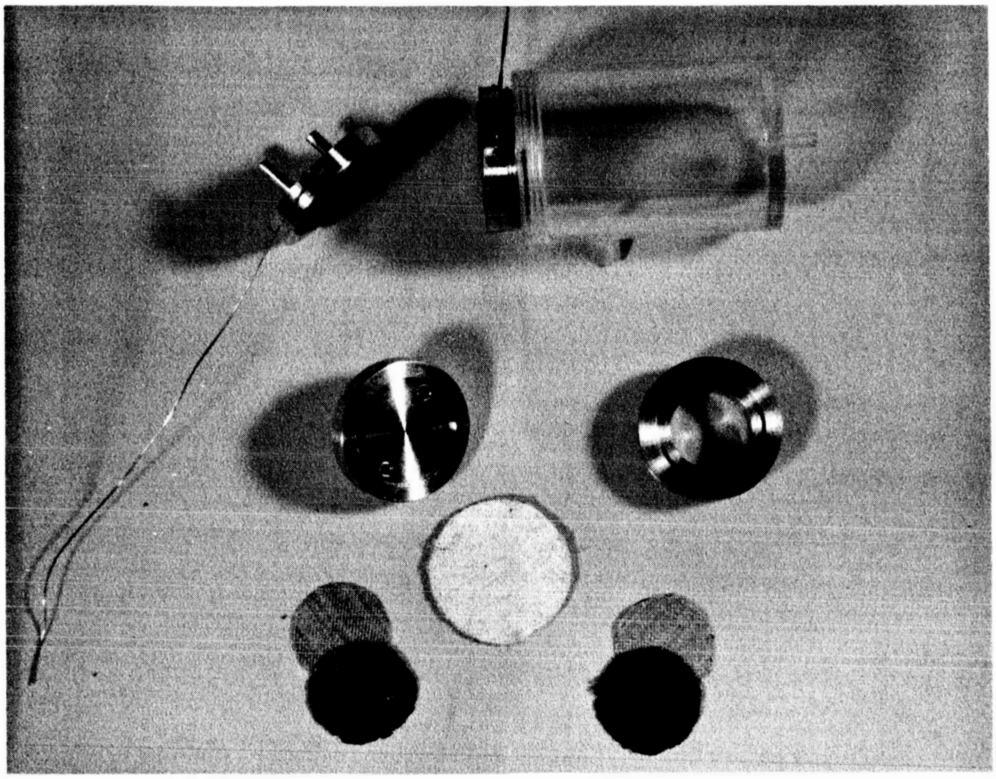

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Figure 6. Modified Miniature Fuel Cell

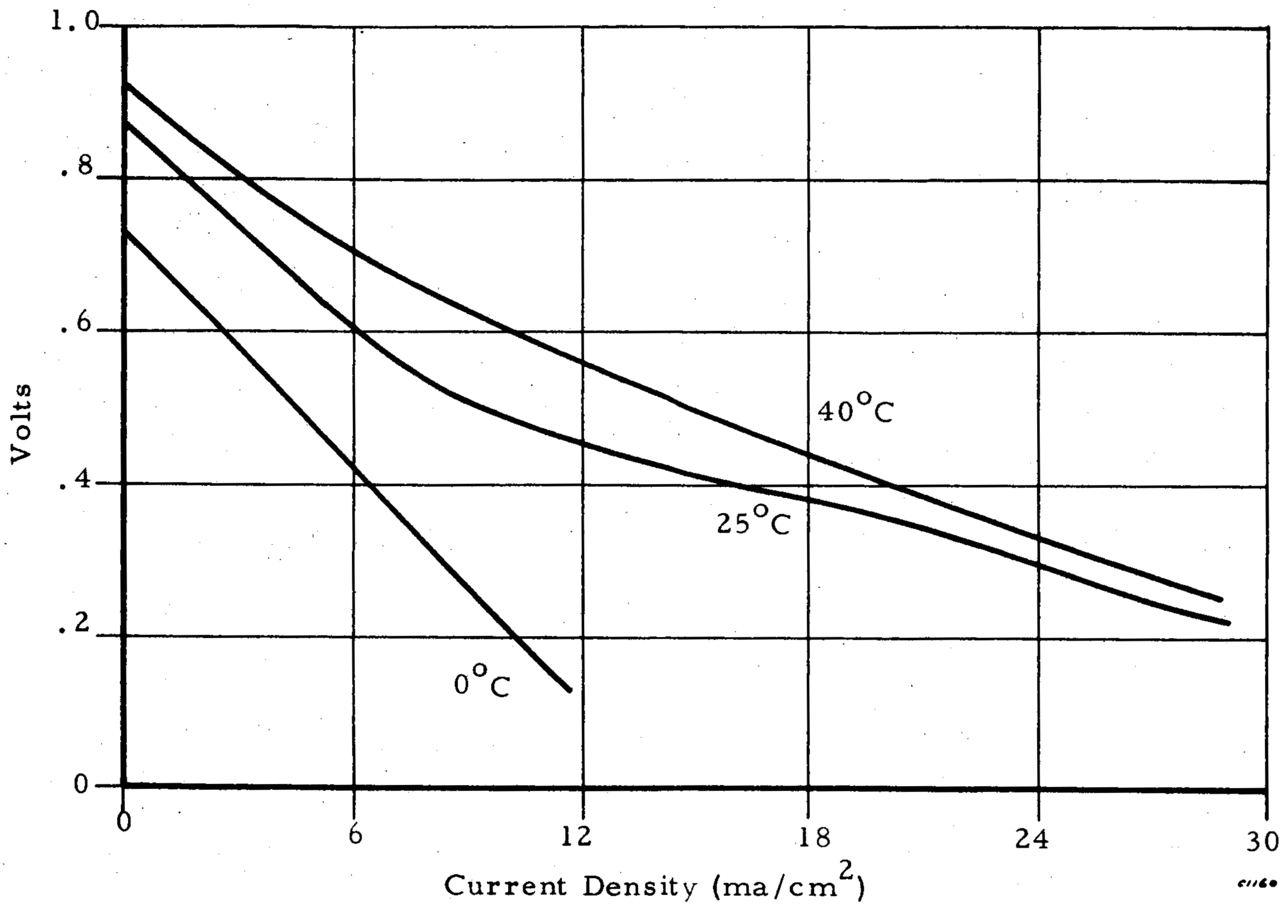

Figure 7. Effect of Temperature on Performance of Miniature Fuel Cell (Initial Cell Configuration)

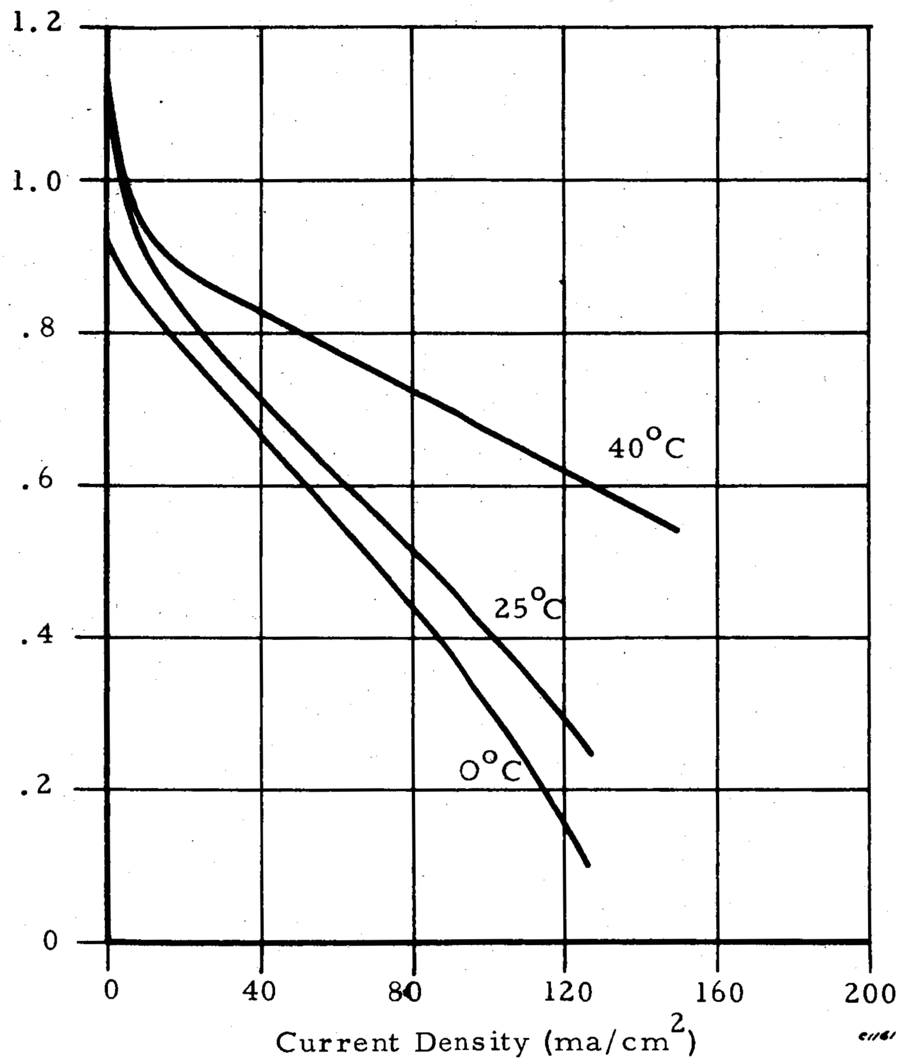

Figure 8. Effect of Temperature on Performance of Miniature Fuel Cell (Modified Cell Configuration)

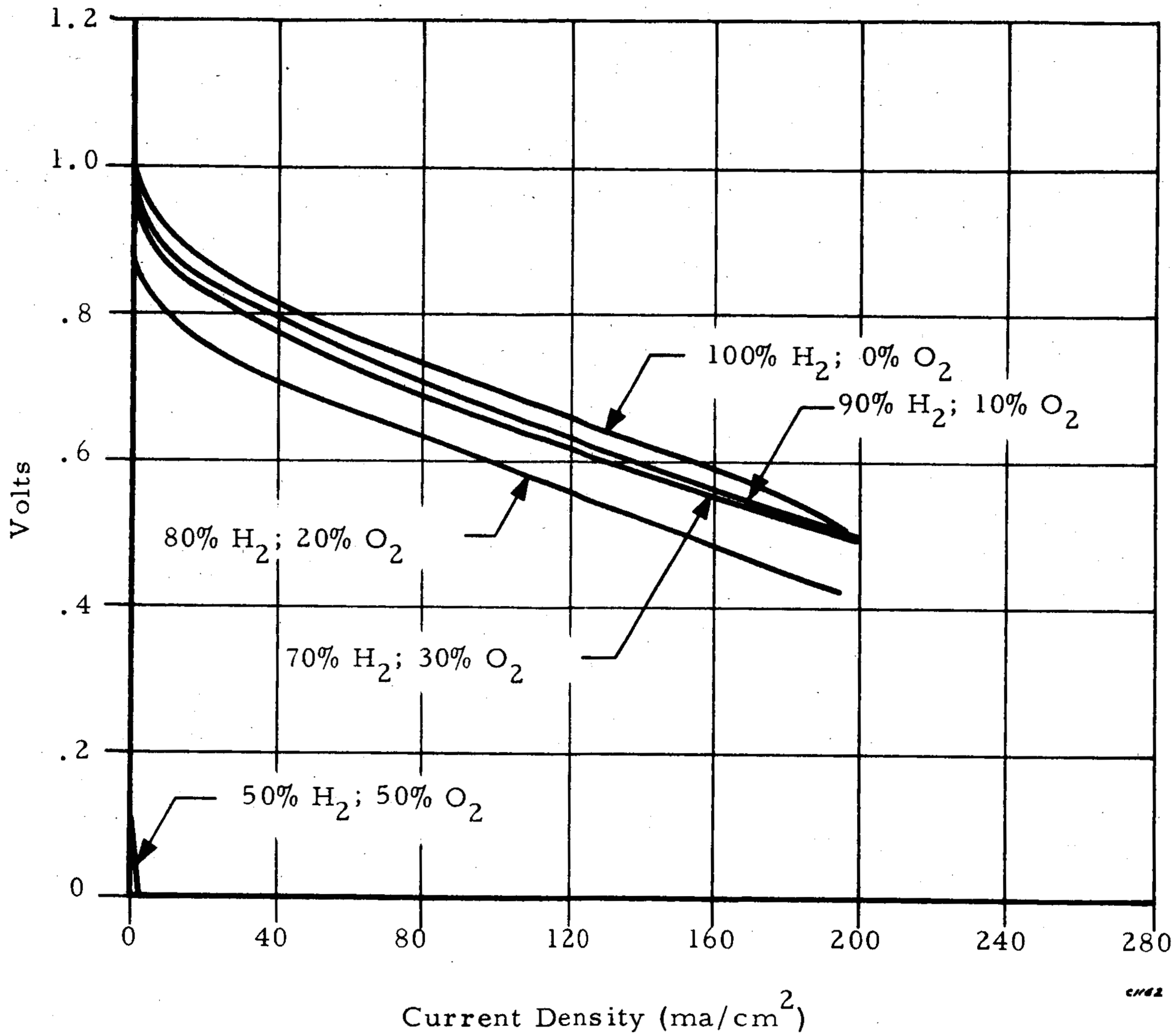

Figure 9. Performance of Miniature Fuel Cell With H_2-O_2 Mixtures in Anode

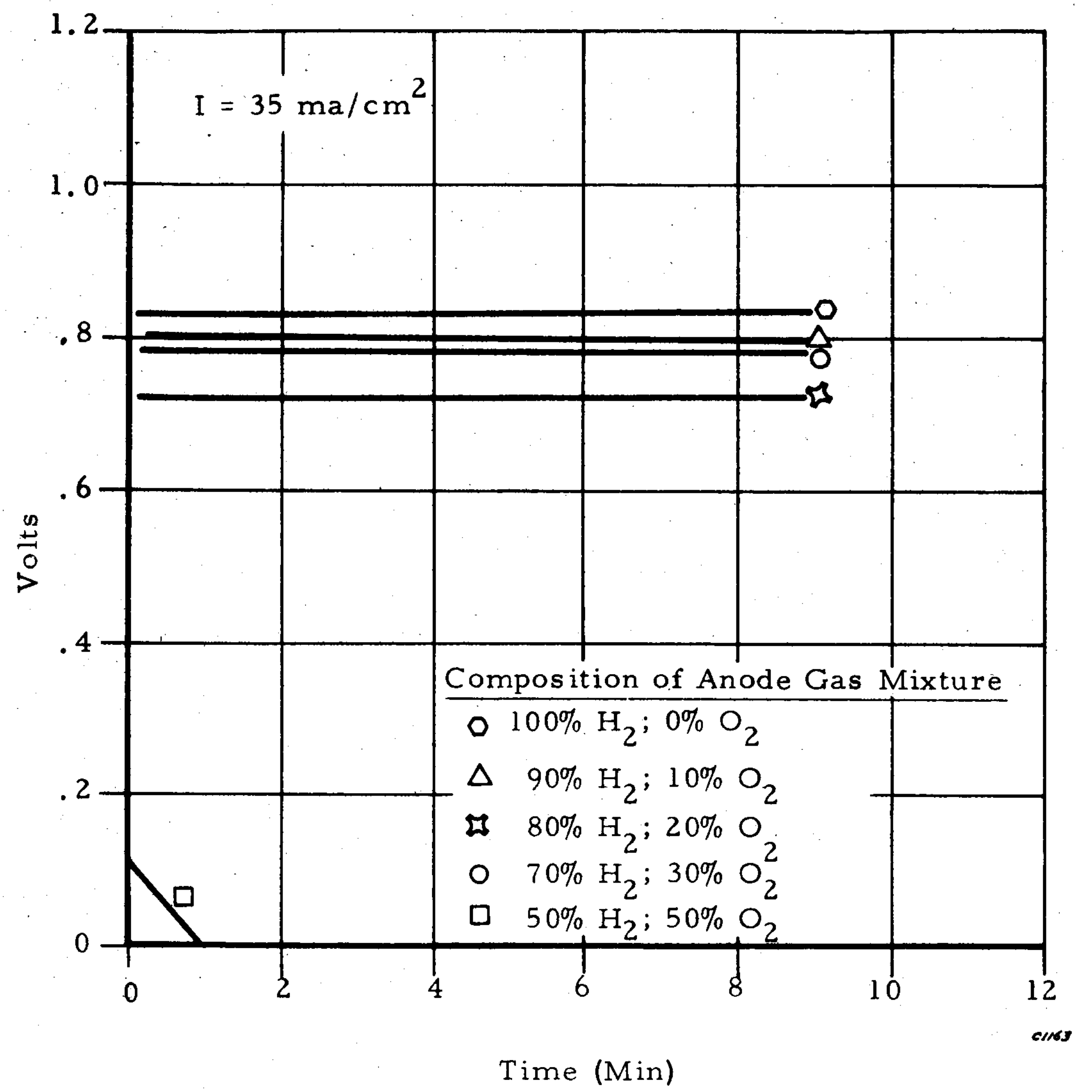

Figure 10. Performance of Miniature Fuel Cell With H_2-O_2 Mixtures in Anode

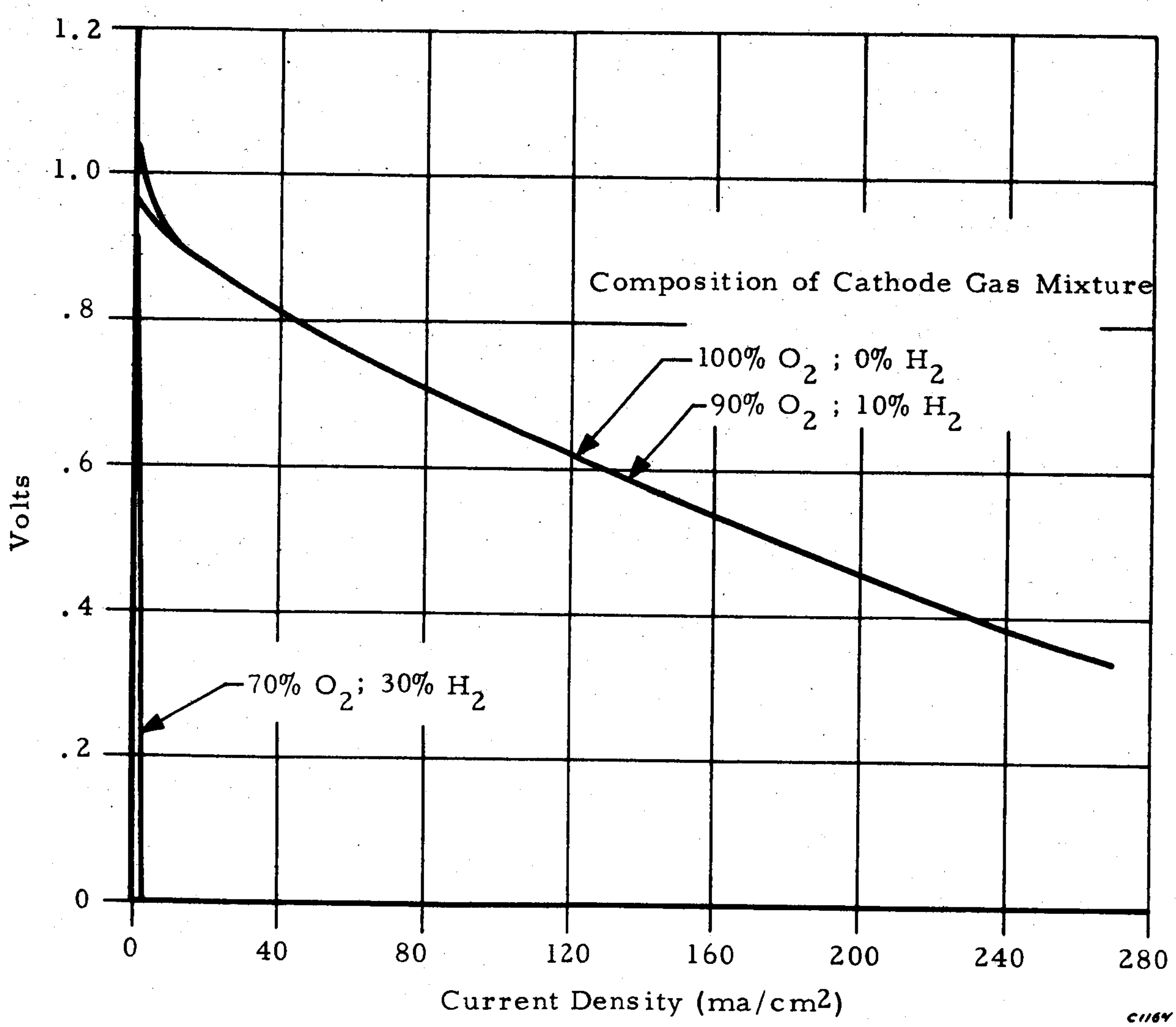

Figure 11. Performance of Miniature Fuel Cell With H_2-O_2 Mixtures in Cathode

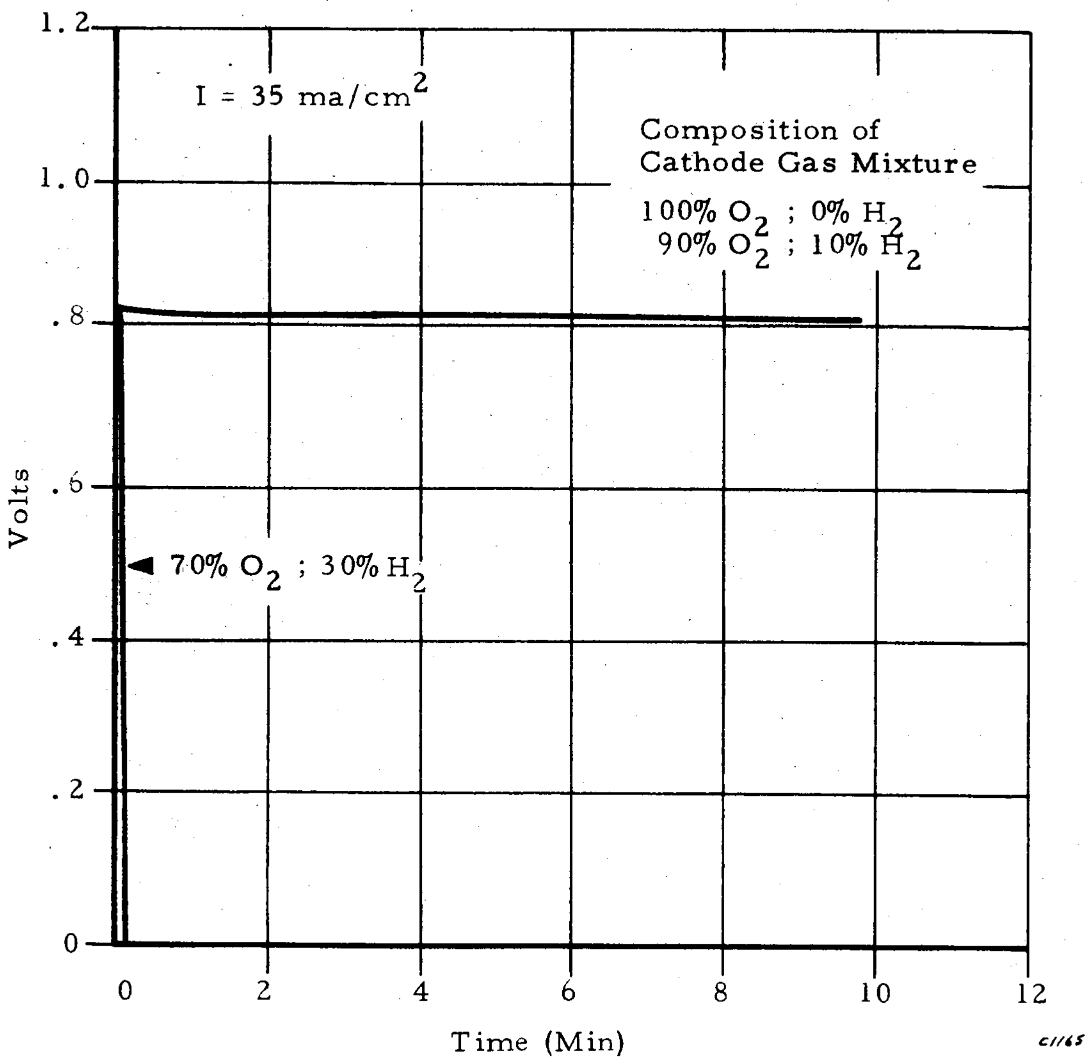

Figure 12. Performance of Miniature Fuel Cell With H_2-O_2 Mixtures in Cathode