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HYDROGEN-OXYGEN ELECTROLYTIC REGENERATIVE FUEL CELLS

by

M. Klein and E. Findl

prepared for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

CONTRACT NAS3-2781

EOS ELECTRO-OPTICAL SYSTEMS, INC., PASADENA, CALIFORNIA
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QUARTERLY REPORT

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TABLE OF CONTENTS

LIST OF ILLUSTRATIONS

1. INTRODUCTION

This report reviews the progress made on development of a regenerative hydrogen-oxygen fuel cell under NASA Contract 3-2781 during the period of 1 April through 30 June 1965. The program objective is the development of an electrolytically regenerative hydrogen oxygen fuel cell that will be superior in performance to currently available rechargeable batteries. The device under development consists of a cell stack that is utilized as an electrolyzer during charge periods, and as a fuel cell during discharge periods. Integral gas storage tanks are used to contain the hydrogen and oxygen gas generated during charge. Such a device offers advantages in the area of watt hours per lb., high ambient temperature operation, and greater cycle life than that which can be obtained from existing secondary batteries. A two phase program is being conducted. Phase 1 consisted of the design, development and testing of a nominal 75 watt, 44 watt hour, 6 cell unit to demonstrate the feasibility of a multi-cell regenerative device. This phase has been completed. Phase 2 consists of the design and development of a 500 watt 600 watt hour, 34 cell unit of minimum weight for evaluation as a flight prototype.

2. SUMMARY

During the period covered, the design for the first prototype, 500 watt multicell unit was completed. All components were fabricated, and a check out model was assembled. Due to gas leakage in the insulating spacers of the cell stack, the unit was not subjected to electrical test. Performance testing has been postponed until a new type of spacer is received, and incorporated in the stack. A six-cell 75 watt unit was continuously cycled for 353 cycles, at $\approx 90^{\circ}C$, at which time the test was discontinued due to performance degradation. This test pointed out areas for future improvements. Single cell tests were continued to obtain additional information on electrode structures, electrolyte-asbestos combinations, and test conditions.

It was firmly established that the major cause of cell performance degradation is the oxidation of nickel in the cathode plaques.

3. TECHNICAL DISCUSSION

3.1 Single Cell Tests

During this period, single cell tests of the type described in the previous quarterly report[1] were continued. Table I summarizes the single cell tests initiated and describes cell construction and results obtained. Cell number 55 was set up with the objective of increasing cell capacity to the desired 21 ampere hour level. The approach taken was to include electrolyte soaked KOH mats in the respective hydrogen and oxygen gas compartments behind the electrodes to provide additional water. The mat arrangement, between the electrodes, was of the standard type used on previous tests. Theoretically, as the electrolyte concentration is increased within the cell mat, due to the removal of water, a partial pressure driving force would occur for transfer of water from that stored in the mats behind the electrodes to the separator matrix. Likewise on discharge as water is formed, there is a partial pressure driving force to transfer the water in the cell mats to the storage mats in the gas compartments. However, the major question involved is the rate at which water is transferred by diffusion compared to the rates of water formation and removal during the cycling of the cells. The results of cell number 55 were inconclusive, and generally speaking the cell performance was poor throughout all portions of the normal cycles. This could possibly be attributed to the old electrodes that had been used in the assembly of the cell.

Cell number 56 was assembled and essentially was a repeat of the construction of the previous cell. The oxygen compartment contained one layer of 0.015" asbestos (dry weight 6.5 grams), impregnated with 6.5 grams of 40.7 percent KOH. The hydrogen gas compartment contained two layers of 0.015" asbestos (12.9 grams dry

TABLE I

SUMMARY OF SINGLE CELL TESTS

Cell #	O_2 Electrode		H_2 Electrode		Mat Thickness and Grade	Mat Dry Wt.	KOH		Comments	Results
	#	Catalyst	#	Catalyst			%	Wt. (gms.)		
55	96	20 Mg Pt/cm^2	95	20 Mg Pt/cm^2	0.060	26.5	40.7	31.0	Wet Asbestos placed in gas compartments.	Cell performed poorly on charge and discharge
56	110	10 mg$_2$Pt/cm^2 10 mg$_2$Pd/cm^2	102	10 mg Pt/cm^2 10 mg Pd/cm^2	0.060	26.5	40.7	31.0	"	Wet mat in gas compartments did not transfer water to the cell to improve performance.
57	123	20 Mg$_2$Pt/cm	122	20 Mg$_2$Pt/cm	0.060	27	40.7	31.6	Electrodes made on new automatic process.	Performances poorer than with manual processed electrodes.
58	123	"	124	"	0.060	26.5	41.7	31.0	Automatic electrode on O_2 side only	Performance better than cell No. 57 but still worse than the standard cell.
59	126	"	125	"	0.060 0.015	33.1	40.7	41	No gas distribution screen behind electrodes.	Cell developed leakage, test discontinued
60	123	"	129	"	0.060	27	40.7	32.5	Subjected cell to storage at 150°C	After the 150°C storage, cell performance slightly degraded.

TABLE I (con.)

61	125	20 Mg_2Pt/cm	126	20 Mg_2Pt/cm	0.030 0.015 0.030	32.5	40.7	42	No gas distribution behind electrodes	Improved capacity slightly.
62	125	"	126	"	0.030 0.015 0.015	32.5	40.7	40	"	"
63	-	"	-	"	0.060	27.5	40.7	31.2	Bishop electrodes	High voltage on charge. Fair on discharge
64	124	"	123	"	0.060 0.015	33.0	40.7	40	Automatic electrode on H_2 side.	Cell used to check out new setup
65	125	"	126	"	0.060	26.5	40.7	35	Used second set of electrodes behind the standard electrodes.	Cell developed leakage. Test discontinued

Cell No.	O_2 Electrode		H_2 Electrode		Mat Thickness	Mat Dry Weight	KOH		Comments	Results
	No.	Catalyst	No.	Catalyst			%	Wt. (gms.)		
66	124	20 mg. Pt/cm2	123	20 mg. Pt/cm2	0.060 0.015	40.9	40.7	48	Capacity improvement test	Attained >18AH on discharge, current efficiency <80%.
67	Bish.	20 mg. Pt/cm2	Bsh.	20 mg. Pt/cm2	0.060	27.35	40.7	31.9	Retest of Bishop electrode	Attained >21AH on discharge, current efficiency >85%.
68	125 + old	20 mg. Pt/cm2	126 + old	20 mg. Pt/cm2	0.060	27.29	40.7	35	Capacity improvement test No back-up screen -.045 spacer	No improvement in capacity
69	125	20 mg. Pt/cm2	126 + old	20 mg. Pt/cm2	0.060	25.9	40.7	35	Repeat of 68 with 2 electrodes on H_2 only	No improvement in capacity.
70	139	20 mg. Pt/cm2	151	20 mg. Pt/cm2	0.060	26.1	40.7	30.5	First attempt at thermal sterilization cycle	KOH loss accelerated-Performance poor after sterilization-O_2 Electrode mechanically degraded. Other cell components OK.
71	125	20 mg. Pt/cm2	126 + old	20 Mg. Pt/cm2	0.060	26.2	40.7	35	Repeat of 69	No improvement in capacity.

TABLE I (con.)

Cell No.	O_2 Electrode No.	O_2 Electrode Catalyst	H_2 Electrode No.	H_2 Electrode Catalyst	Mat Thickness	Mat Dry Weight	KOH %	KOH Wt. (gms.)	Comments	Results
72	AA-1	9 mg. Pt/cm^2	214	20 mg. Pt/cm2	0.060	27.0	40.5	31	Cyanamid Electrode on O_2 side.	Cell leaked through worn spacer.
73	AA-1	"	217	"	0.060	27.0	40.5	31.1	"	Tantalum screen dissolved in electrolyte
74	AA-1	"	214	"	0.060		40.5	31	"	"
75	AA-1	"	217	"	0.060	27.5	40.5	31	"	"
76	AB-4	"	217	"	0.060	27.2	40.5	36	"	Cell cycled showed gradual deterioration Final KOH 31.4,30.5
77	AB-40	40 mg. Pt/cm^2	214	20 mg. Pt/cm^2	0.060	2	40.5	31	"	Showed good peak performance but water sensitive, 31.6, 31.4
78	AB-40	40 mg. Pt/cm2	112	20 mg. Pt/cm2	0.060	27.1	40.5	31	"	Final "KOH
79	217	20 mg. Pt/cm2	214	20 mg. Pt/cm^2	0.060	27.2	40.3	31	KOH washed mat	Cell not cycled 35.2 35.2 Final KOH
80	AB-4	9 mg/ Pt/cm^2	211	"	0.060	27.0	40.3	33		Cell showed rapid deterioration
81	217	20 mg/ Pt/cm2	214	"	0.060	27.1	40.3	31	Mat KOH washed	Still cycling
82	235	"	234	"	0.060	27.2	40.3	31	Ref. electrode	Ref. electrode shorted out.
83	108	"	118	"	0.060	27.1	40.3	31	Used electrodes from S/N 107	Poor performance
84	216	"	118	"	0.060	27.1	40.3	31	Used Hydrogen electrode New Oxygen electrode	Good performance

TABLE I (con.)

weight) impregnated with 14 grams of 40.7 KOH. The 2-1 mat ratio within the gas compartments was utilized in order to maintain the gas volume balance in the cell. The cell performed similar to other cells when subjected to the standard cycle, 35 minutes discharge, 65 minutes charge. However, when the charge was continued beyond the standard 65 minute period to increase the cell capacity, the voltage rose, and reached two volts, after 19.6 ampere hours was supplied to the cell. At this point, the cell pressure was 487 psig. On the subsequent discharge, the voltage dipped initially, rose to a reasonable level, and then fell off drastically at the end of discharge, after only 13.7 ampere hours had been removed from the cell. The cell pressure at this point was 180 psig. On the third charge, when the cell pressure reached 450 psi, there was a sharp drop in pressure, indicating internal cell recombination. The test was therefore discontinued. From the results it can be concluded that the diffusion rates to and from the cell mat to the storage mats behind the electrodes were not sufficient to alter the cell performance. The type of performance obtained was essentially similar to cells without storage mats in the respective gas compartments.

Cell number 57 was assembled to check out a new set of electrodes processed in a new automatic electrode technique. This procedure is described in the third quarterly report[1]. A rapid cycle time was employed, and from visual observations, it appeared that the catalyst was uniformly dispersed through the porous nickel plaques . The cell was cycled on the standard 65 minutes charge, 35 minutes discharge. Performance, as shown in Figure 1, is slightly worse than obtained with electrodes prepared in the manual process with the exception that there is a rapid drop off at the end of discharge. The structural aspects of the electrodes were good. It is apparently very critical where the catalyst is located within the porous nickel plaques . Visually it appears that in our manual process, a heavier catalyst loading exists on the top of the electrode, the surface adjacent to the asbestos mat, with a decreasing catalyst loading out to the backside. These electrodes

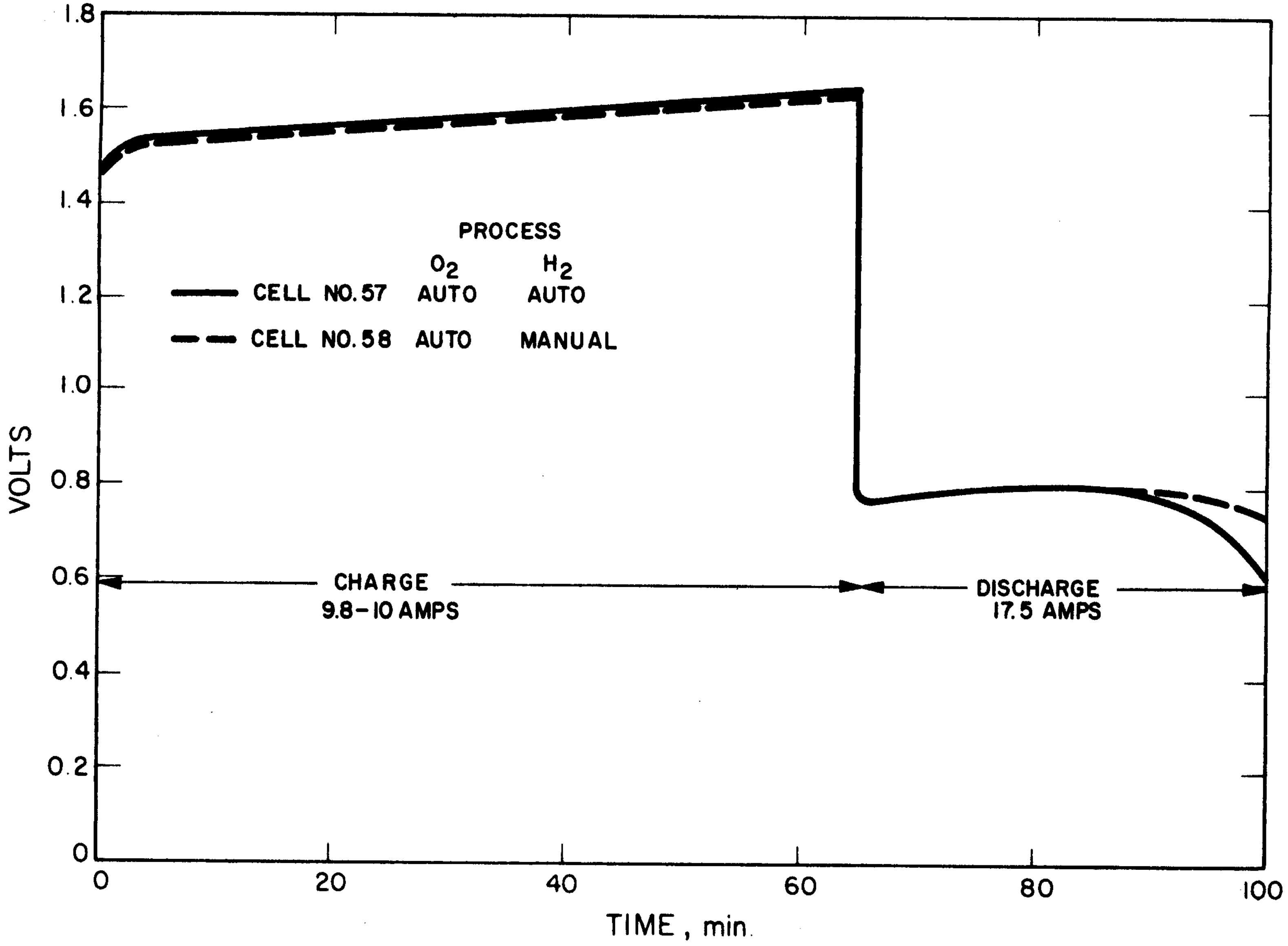

FIG. 1 PERFORMANCE DATA OF AUTOMATIC PROCESSED ELECTRODES

appeared to have a more uniform distribution of loading, and possibly the actual reaction zone had a relatively low catalyst loading. The location of the catalyst in the automatic process can be somewhat adjusted by the cycle used in applying the catalyst.

Cell number 58 was assembled with one of the automatic electrodes on the oxygen side to see the relative comparison between normal cells and the cell containing two automatic processed electrodes. The performance of this cell was improved above the previous cell, but did not reach the levels of cells employing electrodes made by the manual process. Performance of this cell is also shown in Figure 1.

Cell number 59 was an increased capacity test with a mat consisting of one layer of 0.060" asbestos, and one layer of 0.015" asbestos. In addition, the liquid content in the mat was increased to 41 grams of KOH. The cell was initially cycled over the normal cycle 35 minutes discharge, 65 minutes charge. However, during cycling, the cell developed leakage through a valve on the hydrogen side, resulting in excessive differential pressures. Due to the gas leakage, and apparently a loss of water via gas leakage, it was decided to discontinue the test.

Cell number 60 was assembled to determine if any deteriorating effects occur after cell storage at 150°C. The cell was assembled, cycled in the normal manner at 70°C, discharged to 0 pressures, and allowed to sit at 150°C over the week-end for a period of 67 hours. At the end of this time, the cell temperature was reduced to 70°C and cycled in the normal manner. As shown in Figure 2, the performance of the cell had degraded slightly, possibly as a result of the high temperature storage. The type of degradation shown indicated a possible loss of water in the cell. When the cell was disassembled, it was found that the epoxy-glass fiber spacer ring that insulates cell halves, and provides the desired cell compression, had deteriorated in the area where it was in contact with electrolyte from the mat.

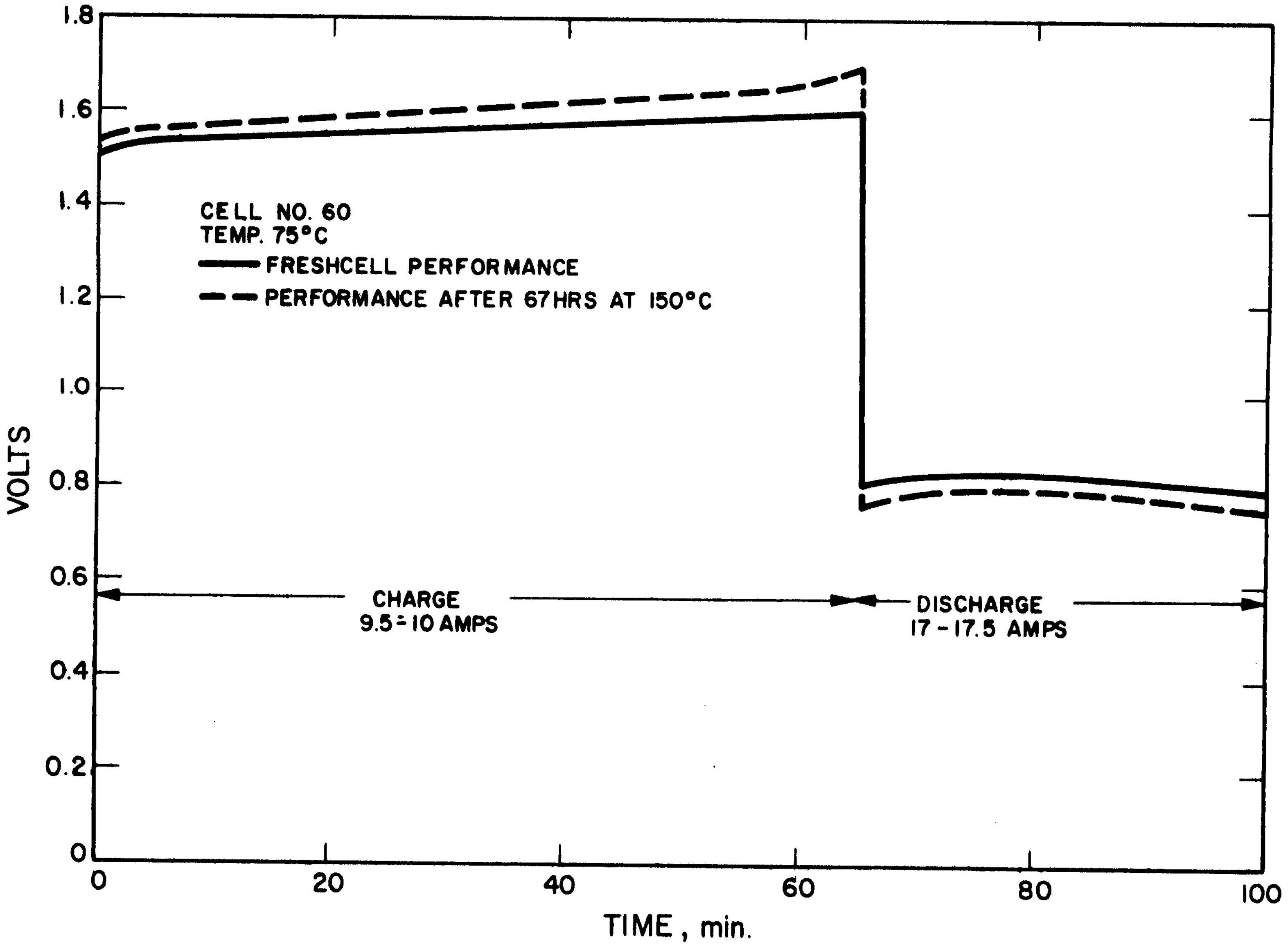

FIG. 2 EFFECT OF HIGH TEMPERATURE STORAGE ON CELL PERFORMANCE

In addition, there was a greenish color on the mat adjacent to this deteriorated area. Therefore, it could not be concluded whether the deterioration was actually caused by some change in the cell electrodes, water loss, or contamination.

Cells number 61 and 62 were attempts at increasing capacity by using an asbestos matrix consisting of one layer of 0.030", one layer of 0.015", and a second layer of 0.030" in that order, with reduced compression and relative high quantity of electrolyte. This geometry provided increased capacity over the standard cells, but still did not achieve the desired 21 ampere hour level.

Electrodes, supplied as samples by Bishop Metals were used in cell number 63. These electrodes were standard porous nickel plaques (the type used in EOS electrodes) that had been platinized by a Bishop proprietary process that impregnates the catalyst in half the electrode adjacent to the mat. The platinum catalyst loading of these electrodes was 20 mg. per square cm. On charge, the cell voltage rose rapidly to as high as 3 volts. However, on discharge, the performance was fair and an average plateau voltage of 0.75 volts was obtained. Measurements of the cell impedance indicated that the cell resistance was slightly higher than normal cells. Therefore, it was decided to discontinue the test, reassemble the cell, and re-run to assure performance obtained was reproducible.

To check out the possibility of increasing cell performance by utilizing thicker electrodes that are uniformly catalyzed, cell number 65 was assembled with two of our standard (manual) platinized porous nickel electrodes on both the hydrogen and oxygen side of the asbestos mat. In addition, the mat electrolyte was increased slightly. The initial cell performance looked promising. However, on the second discharge, the cell developed a leak through one of the O rings that seal the periphery of the cell. Therefore, the test was discontinued.

Cell number 66 was set up using two layers of asbestos, i.e., 0.060" + 0.015", using no back up screens and a 0.045" spacer. A large amount of electrolyte (48 grams) was added on the premise that additional water would increase capacity. The maximum capacity attained was in excess of 18 AH. However, voltage performance on discharge indicated flooding near the end of the cycle. In addition, current efficiencies of somewhat less than 80 percent were noted.

Cell number 67 was assembled to re-evaluate the Bishop platinum electrodes. These electrodes were loaded (20 mg./cm^2)with the platinum located principally in the front half of the electrode. As initially received, the electrodes contained what we believe to be acetic acid. In this condition, as described for cell number 63, performance was not satisfactory. Prior to re-use, the electrodes were thoroughly washed to eliminate reaction products between the KOH electrolyte and the "acetic acid". Performance was vastly improved in cell number 67 as compared to the prior test. In addition, and more important, the goal of 21 amp. hour capacity was achieved as shown in Figure 3. This single cell test indicates that the location of the catalyst and electrolyte within the electrodes is critical for high capacity. Theory indicates that the hydrogen electrode (where water is consumed and formed) should be the critical electrode. (There is some experimental evidence for this based on our test results using American Cyanamid electrodes.) During the charge process, it is apparently desirable to have the H_2 electrode partially saturated with water. During discharge, however, this is not as desirable. Test results indicate that capacity is limited by electrode flooding at the end of discharge, and electrode drying out at the end of charge. Apparently the Bishop electrodes permit rapid transfer of water between the mat and the electrode, thus effectively limiting the flooding and drying out processes. Additional samples of Bishop electrodes will be tested to further evaluate this effect. These electrodes will include different catalyst loadings and the locations of the loading.

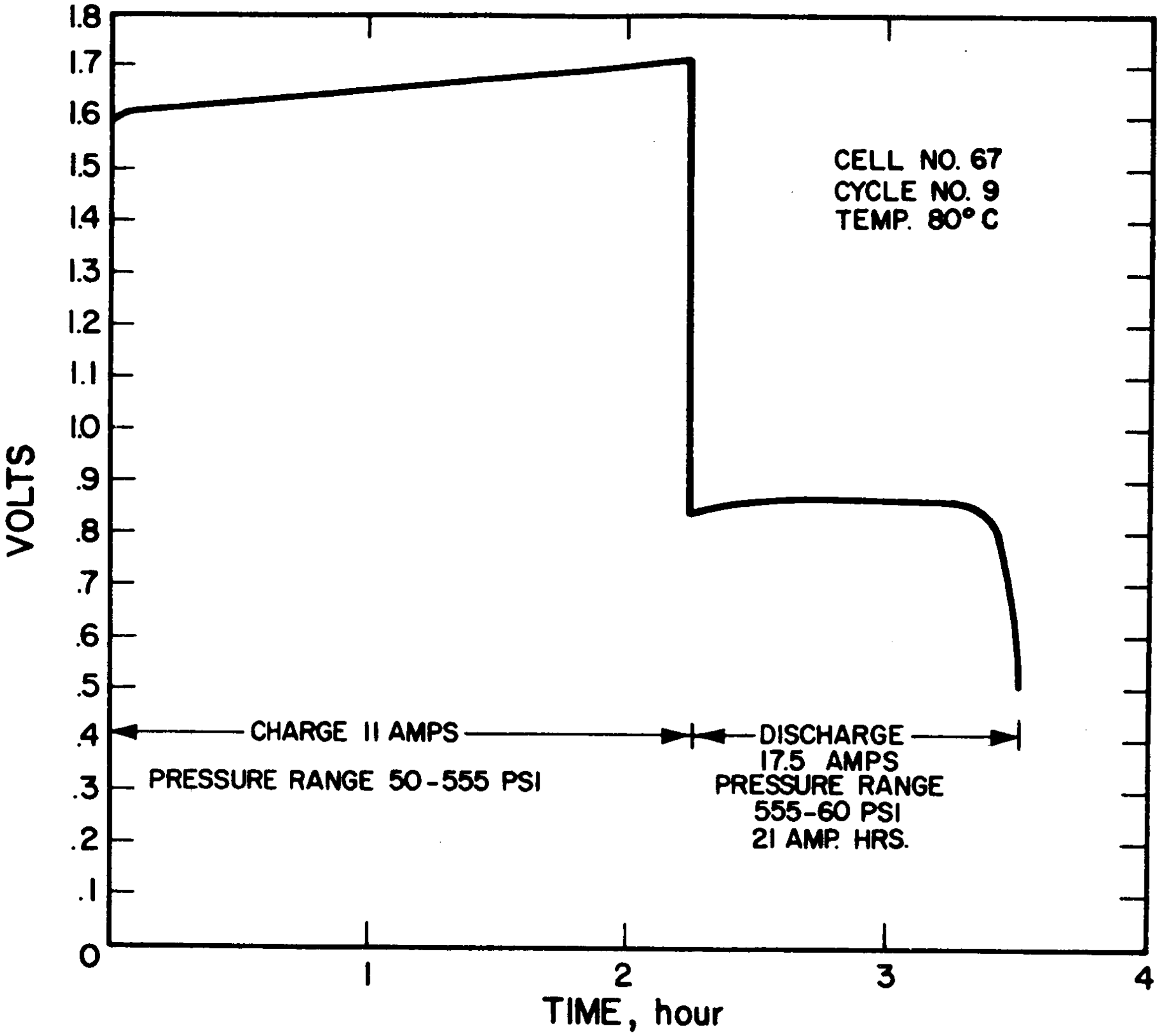

FIG. 3 HIGH CAPACITY TEST

Cell number 68 was assembled to evaluate the effect of doubling the electrode thickness on improving capacity. In this case water would be stored within the electrodes, thus improving capacity without increasing internal IR losses. A 0.045" spacer was utilized in conjunction with a 0.060" asbestos mat. Two cycles were run during which it was noted that appreciable recombination was occurring at elevated pressures.

It was surmised that the inter-electrode leakage was due to the electrolyte being squeezed out of the mat due to the high compression caused by the use of dual electrodes.

In order to prevent this high compression loading, the second 0_2 electrode was eliminated in cell number 69. Electrical performance on this cell was very poor, and after 5 cycles the run was terminated.

Cell number 70 was assembled to evaluate the effects of thermal sterilization on cell performance. The sterilization test consisted of three initial cell electrical performance cycles, to provide a datum, followed by the three thermal cycles specified by NASA, followed by three additional electrical performance cycles. Results of the test were mixed. Electrical performance deteriorated somewhat after thermal cycling. Upon dissassembly, it was noted that the oxygen electrode had visually changed from a black catalyst surface to a dull gray surface material. Electrolyte concentration within the asbestos dropped from 40 percent to 29 percent. The asbestos mat was blackened on the oxygen side and contained black particles dispersed throughout the matrix, gradually decreasing in concentration from the 0_2 to H_2 electrode. These were the only visually deteriorated components. No corrosion was evidenced, the ethylene propylene rubber "0" rings showed no signs of deterioration, the glass epoxy spacer was undamaged, and the H_2 electrode was apparently unchanged.

Cell number 71 was a repeat of cell 69 using the same electrodes as number 69. Performance was very poor indicating the electrodes were somehow damaged in prior use. After 7 cycles the test was terminated.

Single cells number 72, 73, 74, and 75 were set up to evaluate American Cyanamid type AA-1 electrodes. These electrodes consist of a platinum, teflon mix that is coated on a tantalum wire screen. The catalyst loading is 9 mg. per sq. cm., and the electrode thickness is 0.015". In all the cell tests, the Cyanamid electrode was used on the oxygen side, and an EOS 20 mg. platinum per sq. cm. porous nickel plaque electrode was used on the hydrogen side. In cell number 72, a leak developed through a worn out spacer in the cell, and the cell was never subjected to test.

Cells number 73, 74, 75 were cycled a limited number of times. Performance was very poor on both charge and discharge. Disassembly of the cells revealed that the tantalum screen within the electrode had been entirely dissolved in the alkaline electrolyte.

Cell number 76 incorporated an American Cyanamid AB4 type electrode on the oxygen side. This is a 9 mg. per sq. cm. platinum catalyst load electrode on a nickel screen. The cell was set up to determine long term cycling effects on this type of oxygen electrode. The cell was cycled on the standard 65 minute charge at 9.5 to 10 amps., and 35 minutes discharge at 17-18 amps. The cell initially contained a higher quantity of electrolyte. Throughout the first 45 cycles, performance showed a gradual deterioration, as indicated by higher charging voltage and lower discharge voltage. In addition, during the latter cycles, discharge voltage showed a more pronounced dip at the beginning and end of discharge. From the 46-49th cycles, which occurred overnight, the charging current apparently drifted upwards tending to overcharge the cell. The following morning, during the 50th cycle, the current was readjusted to bring the cell back to normal operating pressures. However, from the 50-54th cycle, performance had dropped considerably from that of the previous day.

The cell was therefore disassembled. One edge of the asbestos mat was found pushed inward. Apparently when the cell overcharged, the asbestos mat dried out to a point where gas mixing had occurred within the cell. This internal leakage and subsequent reaction is believed to have caused the sharp degradation in performance that occurred after the 50th cycle. Other aspects of the internal cell components look clean. The gold plating that was used on the gas distribution screen and back-up plate behind the oxygen electrode had a tendency to peel off, as opposed to the hydrogen side where the gold-plating was still very adherent. Analysis of the KOH concentration in the asbestos mat revealed a final KOH in the range of 31.4 to 31.5 percent.

Cells number 77 and 78 were assembled to determine if performance improvements could be obtained by using higher catalysts loaded oxygen electrodes. The oxygen electrodes employed were American Cyanamids' type AB40, which consists of a nickel screen coated with a platinum teflon mix with 40 mg. of platinum per sq. cm. The cells were cycled on a normal 100 minute cycle. Typical performance is shown in Figure 4. As can be seen, the voltage of the cell took an initial dip when the discharge was started, rose to a high level, and then dipped off once again at the end of discharge. During the cycle, cell discharge voltages as high as 0.9 of a volt at 17.5 amps were obtained. This performance exceeded all previous test results. However, this high performance level only occurs during a short portion of the discharge. Apparently the AB40 electrode performance is very sensitive to water content. During the middle of the discharge, the optimum liquid quantity occurs, and peak performance is obtained. For the rechargeable type fuel cell, where water is stored in the asbestos mats, this sensitivity to liquid quantity is not desirable. Possibly different initial electrolyte quantities and compression ratios could alter the water sensitivity of type AB40 electrodes. This approach will be evaluated at a later time.

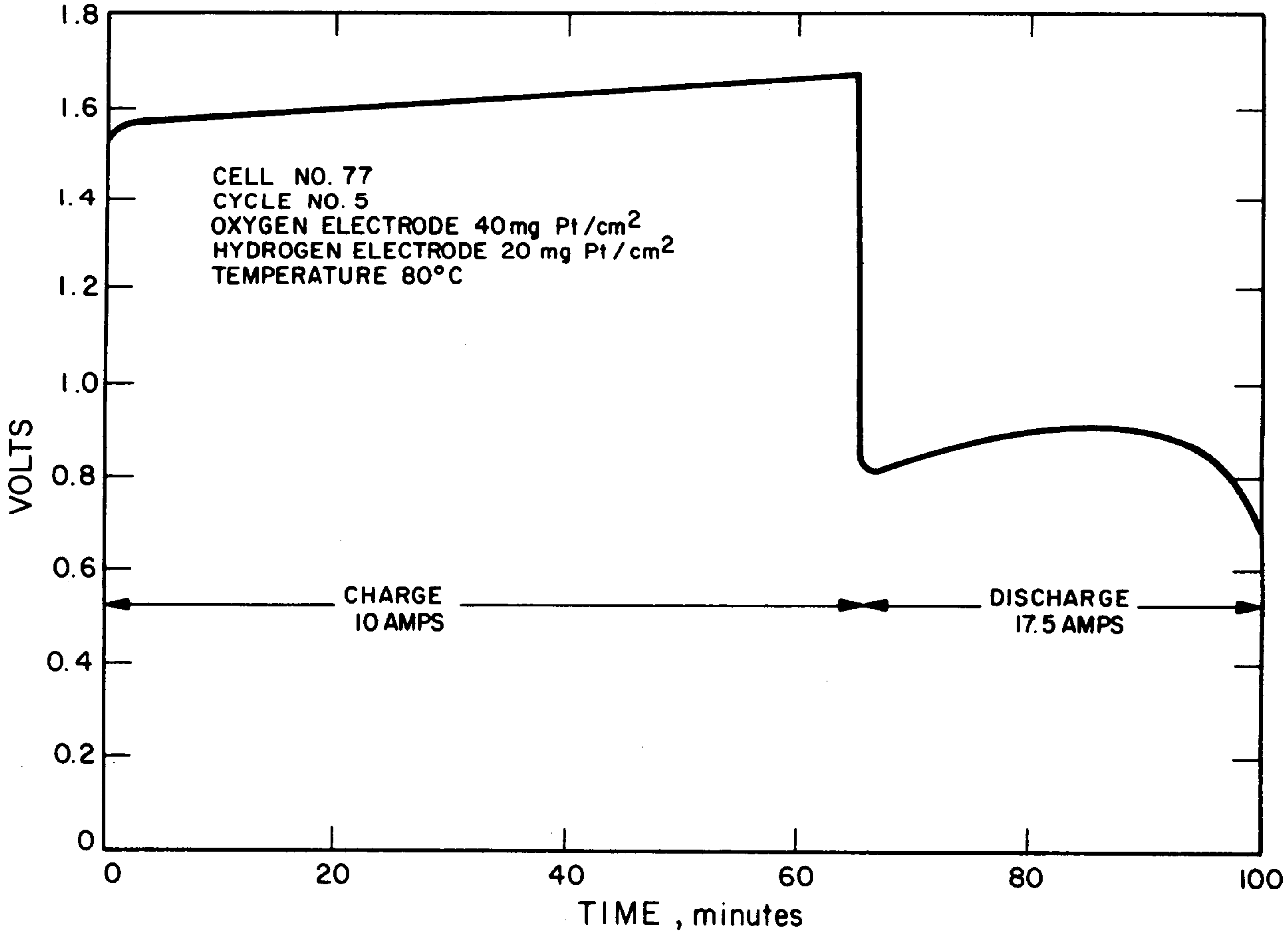

FIG. 4 PERFORMANCE DATA OF HIGH CATALYST LOADED OXYGEN ELECTRODE

To obtain a better understanding of the cause of KOH depletion that has been encountered in previous tests, two asbestos mats of a pure fuel cell grade were pre-washed with one liter of hot 38 percent KOH. The potassium hydroxide solution was sucked through the asbestos mats by means of a Buckner funnel-vacuum set up. The same liter of KOH was sucked through each mat four times. The mats were then washed with approximately 8 gallons of distilled water, and dried overnight in an air oven. Cell number 79 was assembled with one of these mats and two standard 20 mg. platinum per sq. cm. electrodes in a single cell housing, and allowed to sit overnight. Without subjecting it to electrical test, the cell was dissassembled, and the sample of electrolyte from the mat was analyzed. This resulted in a final electrolyte concentration of 35.2 percent. The mat had been initially impregnated with 40.3 percent KOH. This drop in electrolyte concentration indicates the possibility that (a) during the washing process, the reacting substance in the mat did not have sufficient time to react, (b) the handling of the asbestos mat when it is wet down and disassembled, causes an electrolyte loss, or (c) our test method and analysis has a 12 percent error. These possibilities and the results determined will be further investigated.

Cell number 81 contained the second electrolyte washed mat. It was put on cycle, and is still cycling, the results of which will be reported in the next quarterly report.

Cell number 80 was to be a repeat of cell number 76 which contained a standard American Cyanamid AB4 type oxygen electrode. A smaller quantity of electrolyte was used in this cell than in cell number 76. When cell 76 was disassembled, free liquid was found in the oxygen gas compartment indicating that it had been squeezed out of the mat during assembly. Cell number 80 rapidly deteriorated in performance. After 9 cycles, the voltage on discharge rose to 2 volts. On discharge, a substantial initial dip was encountered, and a rapid fall off in voltage towards the end of discharge was also observed.

In discussions with NASA Lewis, and American Cyanamid technical personnel, it was revealed that gradual performance deteriorations with these type of electrodes has been encountered in primary hydrogen oxygen fuel cells. In that case, it was reasoned that a gradual oxidation of the nickel screen caused the degradation in performance. To overcome this deficiency, American Cyanamid has fabricated experimental electrodes in which the nickel screen is gold plated, and they have found that this considerably reduced performance deterioration. The phenomena of the nickel substrate being oxidized would be greatly accelerated in a regenerative device, since oxidation occurs much more readily during the charge portion of the cycle. This mode of deterioration is in agreement with our thinking and was a primary reason for evaluating American Cyanamid electrodes as a method of eliminating porous nickel plaques such as EOS electrodes. However, the high porosity nickel porous plaque electrode remains the best electrode from the standpoint of overall performance. Gold plated nickel screen Cyanamid electrodes will be evaluated in single cell tests during the next quarter.

In order to determine which electrode causes fall-off in performance due to drying out and flooding, cell number 82 was assembled with a reference electrode in the asbestos mat. The reference, an activated Raney nickel powder on a nickel screen, was placed between two layers of 0.030" asbestos mat. During the second cycle, the reference electrode shorted to the oxygen side of the cell, due to poor insulation on the feed through wire. Therefore, the test was discontinued and the cell disassembled. Refinements of this reference electrode technique will be made, and additional tests of this type will be undertaken.

Cell number 83 consisted of a set of electrodes that had been used in the multi-cell unit, serial number 107. The electrodes were washed with the distilled water after removal from the multi-cell unit, and assembled in a single cell test set up with a fresh asbestos mat. Typical performance of this cell is shown in Figure 5. The charge voltage did not show any significant difference than performance obtained with fresh electrodes. However, upon switching to discharge, a substantial shift in differential pressure was noted, and a higher voltage level was obtained for a short period of time indicating a substantial quantity of nickel oxide in the oxygen electrode. The voltage then fell to approximately 0.7 volt. It then fell off sharply toward the end of discharge. This performance represents a considerable deterioration when compared to performance of a fresh set of electrodes.

Cell number 84 was a single cell that utilized the same hydrogen electrode as cell 83 with a fresh oxygen electrode and asbestos mat. The performance of this cell is also shown on Figure 5. The discharge voltage is considerably better, indicating the deteriorated performance was caused by changes in the oxygen electrode.

The substantial differential pressures and the nickel oxide hydroxide plateau voltage of cell number 83 is strongly indicative that the mode of deterioration is the conversion of the nickel in the oxygen electrode to a nickel oxide or hydroxide form.

3.2 Multicell Testing

A 6 cell, 75 watt unit (S/N 107) was placed on cycle test near the end of the last report period, and operated during this period. The cell was cycled continuously on the standard 65 minute charge, 35 minute discharge regime for 353 cycles. Cycling was carried out overnight, and during week-ends. The test set-up contained a

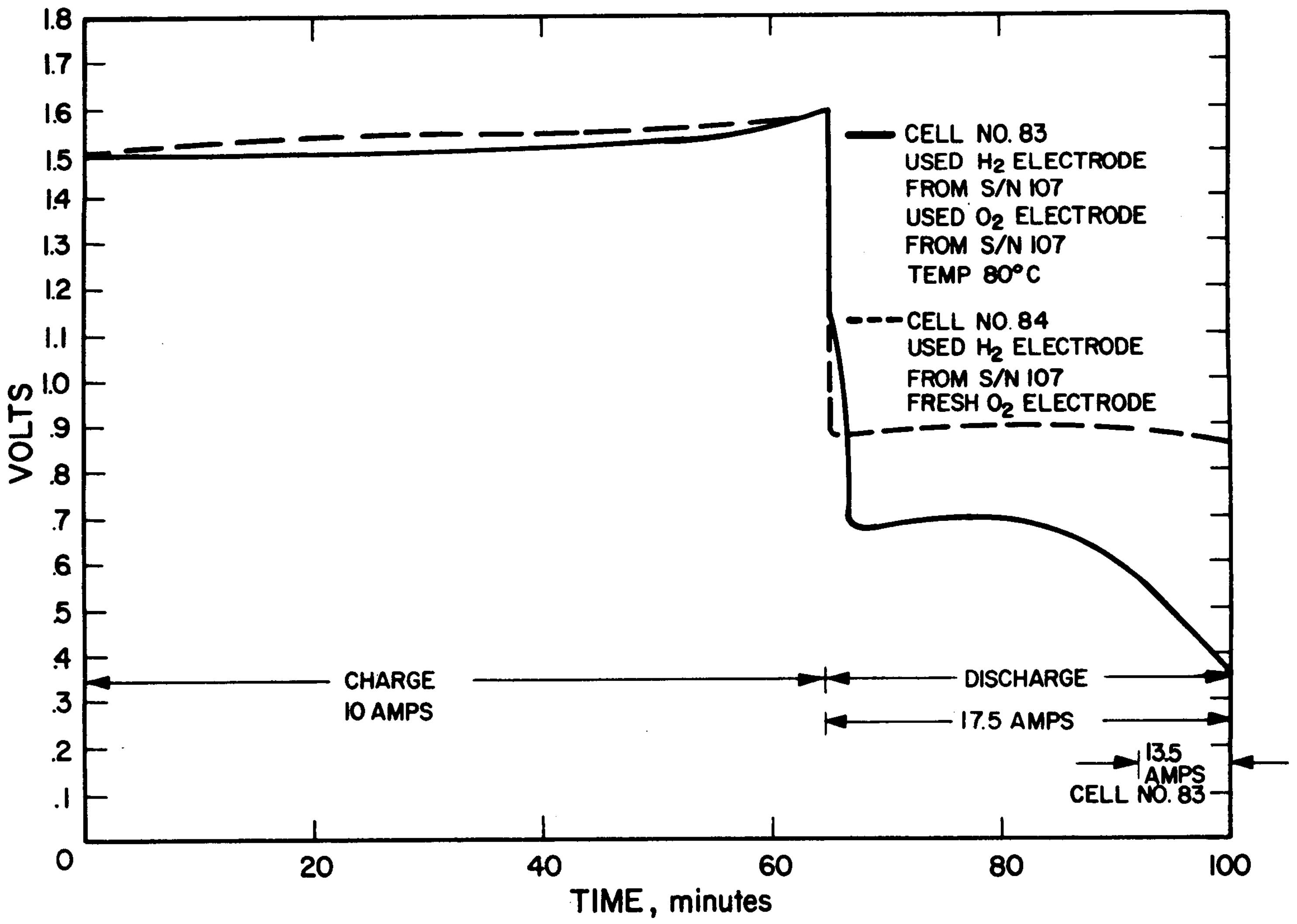

FIG. 5 PERFORMANCE OF ELECTRODES FOR MULTI-CELL S/N 107

pressure switch, which automatically shut down the cell charger when the cell pressure reached approximately 385 psi. Throughout the first 200 cycles, there was only a slight change in performance, with voltage on charge increasing slightly, and voltage at the end of discharge decreasing slightly. From the 200-342nd cycle, charge voltage increased gradually and discharge voltage decreased gradually. This change in voltage performance is shown in Figures 6 and 7. Figure 6 is a family of curves at various cycles. Figure 7 is a plot of the extreme voltage points to show the rate of deterioration as a function of cycles. As can be seen up to the first 200 cycles, the deterioration rate appears to be at one level. Beyond that cycle, there is a more rapid fall off in performance, with the slope for the end of discharge voltage being greater than the other deteriorating modes.

At the 343th cycle, which occurred in the middle of the night, data indicates that an internal reaction took place. From that point on, the performance was considerably worse, as shown in Figure 6. After 353 cycles, the cell test was discontinued, and an impedance measurement was made of the cell at operating temperature. It was found to be 0.034 ohms. The assembly was allowed to cool to room temperature, and another resistance measurement was made. In this case, it was found to be 0.098 ohms. This value is considerably larger than the initial resistance at room temperature which was 0.057 ohms.

Examination of the internal components revealed that the inside of the bellows, which contains hydrogen, had rusted on the surface, apparently due to long term contact with potassium hydroxide vapors. The outside of the bellows and the oxygen compartment showed a black to green discoloration, indicating the chemical reaction took place in that compartment. The stack bolts had residual torques of 25-30 inch pounds. Initially, these bolts were torqued to 70 inch pounds. The Belleville springs on the ends of the stack bolt still were fully compressed.

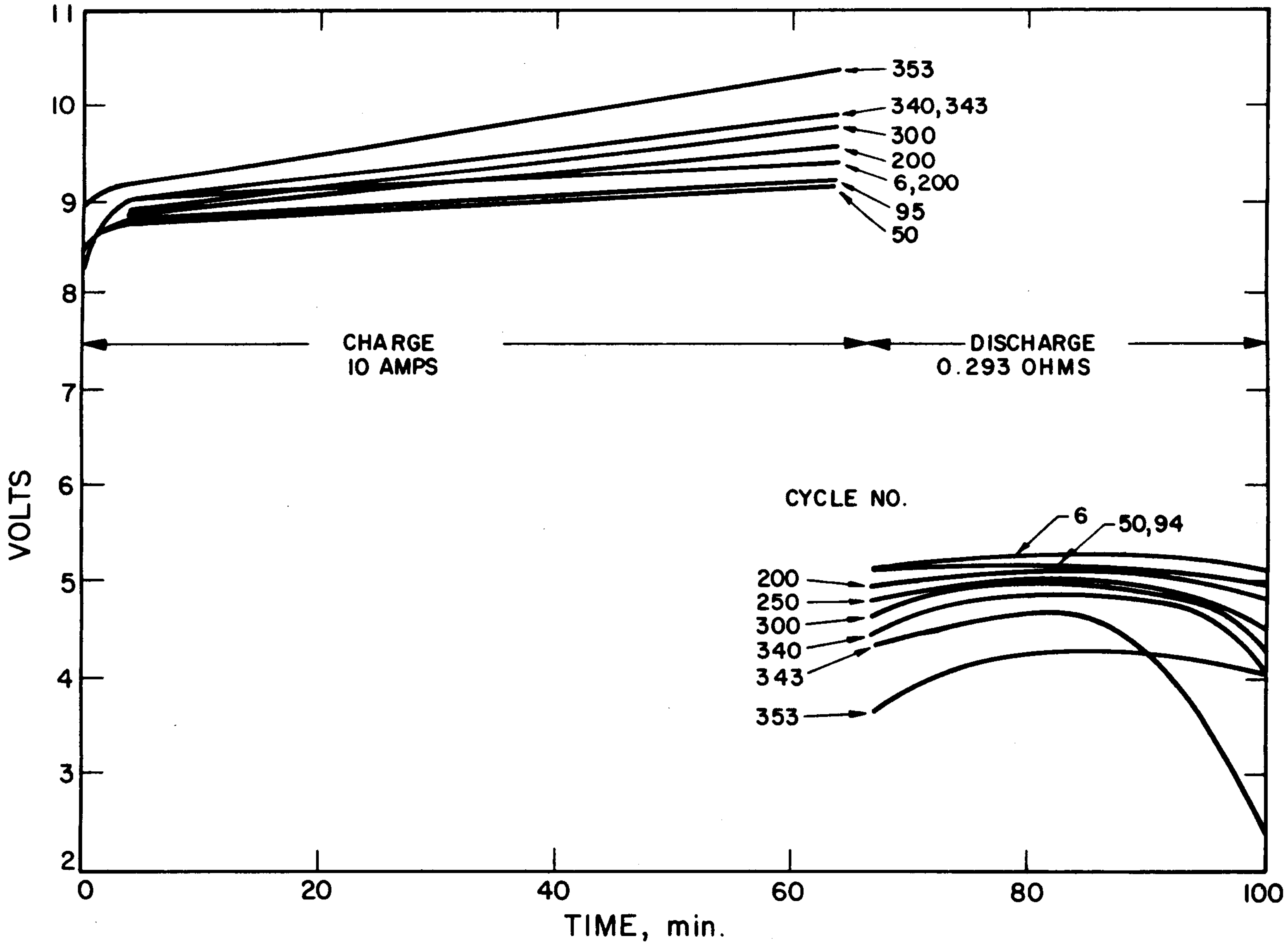

FIG. 6 VOLTAGE PERFORMANCE DATA AT DIFFERENT CYCLES OF REGENERATIVE FUEL CELL (S/N 107)

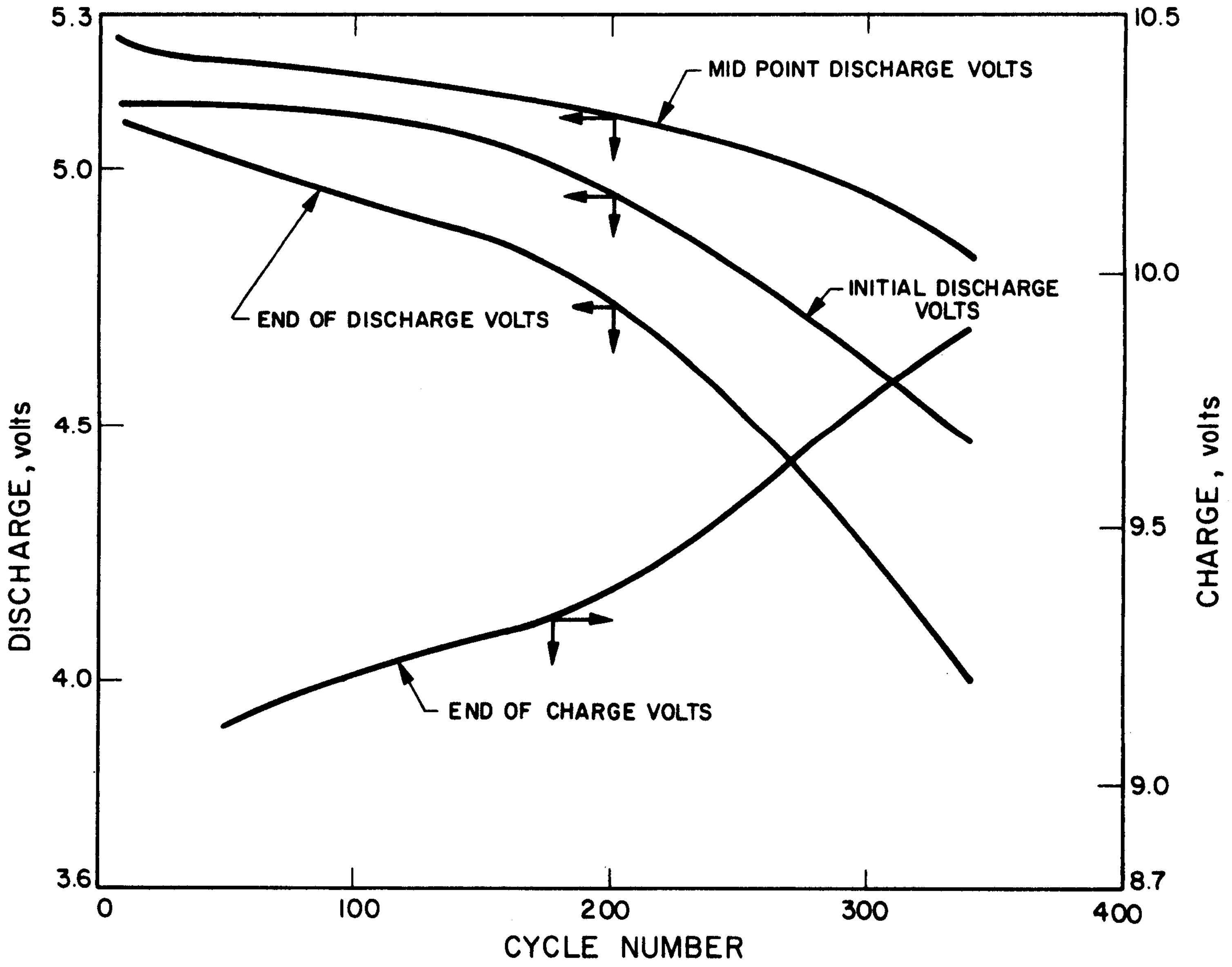

FIG. 7 EFFECT OF FUEL CELL VOLTAGE AS A FUNCTION OF CYCLING (S/N 107)

Taking apart the cell stack, it was found that the oxygen back-up screen and bipolar plate had a black discoloration. The bipolar plates and screen from the hydrogen electrodes looked perfectly clean. The oxygen electrodes in four of the cells had crumbled away along the edge, which probably was due to chemical deterioration. However, in other areas, the structure of the oxygen electrode appeared fine. The asbestos mats had a black discoloration adjacent to the hydrogen electrodes, and were relatively clean facing the oxygen electrodes. Analysis of all the mats in the cell stack revealed final KOH concentrations in the range of 23-25 percent KOH, as shown in Table II.

The performance data showed two problem areas: (a) gradual degradation in performance, and (b) long term gas mixing that lead to an internal reaction that further degraded performance. Gradual degradation in performance could be caused by a number of problems. Most probably degradation was caused by gas mixing, structural deterioration of the oxygen electrode, and/or gradual loss of KOH, due to a nickel hydroxide side reaction within the cell. The cause of the slow gas mixing that lead to the chemical reaction is believed due to leakage through the spacers as picked up in the 500 watt unit. (See Section 3.3).

Cycle life performance achieved is considered very encouraging, and has indicated certain modes of deterioration that occur which will be investigated further. It appears that additional studies on the asbestos mat are justified. For long term use, a nickel substrate for the oxygen electrode is not desirable, since it apparently gradually oxidizes with cycling and structurally deteriorates. It also can be related to the electrolyte consumption, since the formation of certain nickel oxides could tie up OH^- ions. These possibilities will be investigated further in single cell tests.

TABLE II

FINAL ELECTROLYTE CONCENTRATION OF FUEL CELL S/N 107

	Sample	
Cell #	A %	B %
1	22.9	22.7
2	22.9	22.9
3	21.5	21.2
4	22.9	22.7
5	24.8	24.9
6	25.6	25.1

3.3 Multicell 500 Watt Unit

During this report period, all the components for the P1-500 watt unit were received and inspected. The gas tanks were hydrostatically tested to 800 psig and found to be acceptable. The components and a stack assembly are shown in Figures 8 and 9.

A 500 watt, 34 cell battery was assembled during the later part of this period. No problems were encountered during the assembly. However, during a routine checkout for cell stack gas leakage, a number of very small leaks were noted on the external diameter of the stack. Attempts to stop the leakage by compressing the cell stack further were unsuccessful. Visually it appeared that the leaks were in the glass teflon insulating spacers. In order to evaluate this possibility, several tests were made using both new and used spacers. It was definitely established that certain of the spacers leak, probably due to poor glass-teflon bonding.

Due to this leakage problem, glass-teflon spacers will be eliminated. Instead, we will substitute the glass-epoxy material which we are using successfully in single cell tests. Electrical testing of the 500 watt unit has been postponed until new spacers can be received.

A weight breakdown of the prototype on the basis of aluminum tank is presented in Table III.

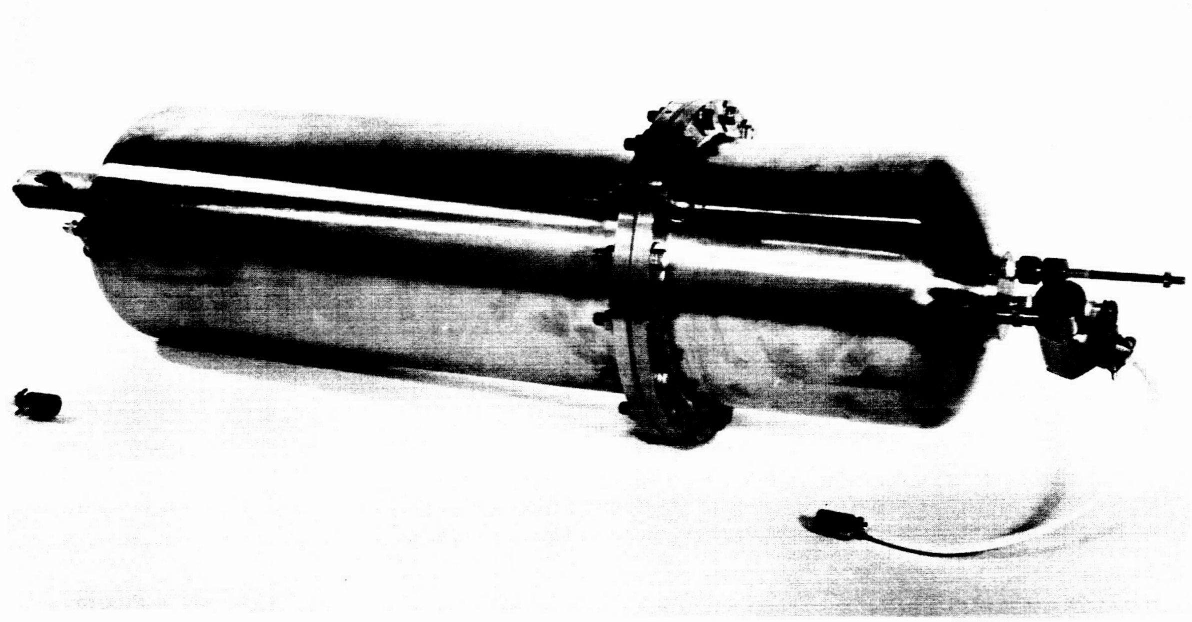

FIG. 8 500-WATT REGENERATIVE HYDROGEN-OXYGEN TANKS AND CELL STACK

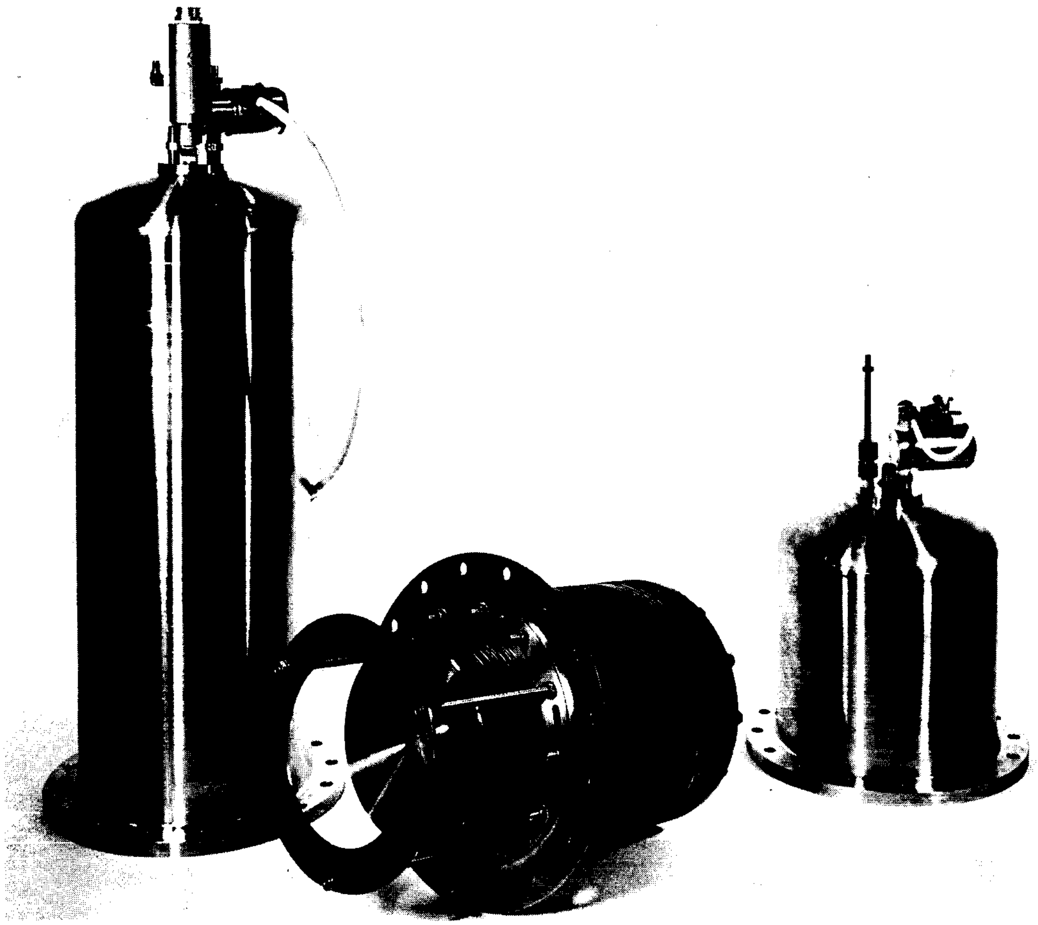

FIG. 9 500-WATT REGENERATIVE HYDROGEN-OXYGEN FUEL CELL ASSEMBLY

TABLE III

WEIGHT BREAKDOWN OF 500 WATT H_2-0_2 REGENERATIVE FUEL CELL

Item	Unit Weight-lbs.	Total Weight-lbs.
1 ea. H_2 end plate	1.68	1.68
1 ea. 0_2 end plate	0.89	0.89
33 ea. Bipolar plate	0.39	12.85
1 ea. Bellows	1.90	1.90
12 ea. Stack bolt assembly	0.17	2.04
1 ea. Anode lead	0.13	0.13
2 ea. Tank "O" ring	0.06	0.12
1 ea. Bellows "O" ring	0.04	0.04
1 ea. H_2 tank and bolts	8.75	8.75
1 ea. 0_2 tank	4.80	4.80
34 ea. Asbestos mat	0.06	2.04
34 ea. Gas distribution screen	0.01	0.34
34 ea. Electrolyte	0.07	2.38
34 ea. Electrodes	.05	1.70
		39.66
Stack Assembly		25.99 lbs.
Tank Assembly		13.67 lbs.

4. CONCLUSIONS

The cycling of the 6 cell,75 watt unit,for over 500 hours has demonstrated the potential of a regenerative hydrogen oxygen fuel cell for long term use. The modes of deterioration noted, plus other observations obtained from single cell tests, indicate that loss of electrolyte, loss of catalytic activity, and increased cell differential pressures may all be the result of the gradual oxidation of the nickel constituents within the oxygen electrode. The elimination of nickel that can be oxidized within the oxygen electrode should provide considerably increased life capabilities.

Single cell tests with various electrode structures have shown the importance and criticality of the location of the catalysts within the porous active electrodes to obtain peak performance and high cell capacities. The 21 ampere hour objective was achieved by using electrodes that had the catalyst within the half of the electrode. adjacent to the asbestos mat.

5. PLANS FOR THE NEXT PERIOD

Single cell tests will be continued to evaluate the following:

- a. Non nickel electrode structure for the oxygen electrode .
- b. Methods for reducing drying out and flooding effects.
- c. Capacity improvement factors.

Additional six cell units will be assembled and subjected to long term tests when promising electrode mat configurations are uncovered as a result of single cell testing.

The 500 watt, 34 cell unit will be reassembled upon receipt of the new insulator spacers. After check out, the unit will be cycled and performance tests made.

REFERENCES

(1) Klein M., "Hydrogen-Oxygen Electrolytic Regenerative Fuel Cells
EOS Report 4110-QL-3

FINANCIAL STATEMENT

Manhours and dollar expenditures for the period June 1 through July 2, 1965 were as follows:

Direct Labor Hours	642.25
Direct Labor Dollars	$3,487.22
Purchases and Commitments	82.69
Total Dollar Expenditure	$7,502.65