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FACILITY FORM 602

HYDROGEN-OXYGEN ELECTROLYTIC REGENERATIVE FUEL CELLS

Prepared for

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Contract NAS 3-2781

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1. INTRODUCTION

This report reviews the progress made on development of a regenerative hydrogen-oxygen fuel cell (NAS Contract 3-2781) during the period October 5--November 6, 1964. During the period covered, a number of single cell tests were conducted and the 6 cell 75-watt module was assembled and tested. The 75-watt unit was continually cycled for a 48-hour period, during which its performance was very satisfactory. After the continuous cycling period, additional tests were conducted on the unit to determine the effect of various parameters on performance characteristics. Data for these tests is presented within the report.

2. TECHNICAL DISCUSSION

2.1 Single Cell Tests Prior to Multi-Cell Tests

Severe reductions in KOH concentration, as a result of testing, were observed in previous cells. In order to decrease the effect of electrolyte loss, it was decided to increase the electrolyte concentration from 25 weight percent KOH to 40 weight percent in future cell tests. Assembly details and results obtained from cycling the additional cells constructed during this period are described in Table 1.

Cells # 19 and #20 contained excessive quantities of electrolyte. When the cell was assembled, electrolyte was squeezed out of the asbestos mat into the individual gas cavities. On attempting to cycle these cells, it was found that they exhibited poor performance on discharge and extremely large, i.e., 10-20 psi differential pressures at the start of charge and discharge. The excessive differential pressures were attributed to the wetting of the entire electrode and back-up screen forming NiO which took part in the reaction on both charge and discharge. Cell # 21 was constructed with the electrolyte quantity reduced to 29 grams of 40% KOH. This cell was cycled three times and allowed to sit in the open circuit condition overnight at

Cell #	O_2 Electrode #	O_2 Electrode Catalyst	H_2 Electrode #	H_2 Electrode Catalyst	Mat Thickness and Grade	Mat Dry Wt. Gms.	KOH %	KOH Wt. Gms.	Comments	Results
19		20 Mg.Pt.		20 Mg.Pt.	Pure .050	21.5	35	36.5		Cycled 2 times Cell flooded
20	9	20 Mg.Pt.	10	20 Mg.Pt.	Pure .050	22	40	35		Cell flooded.
21		10 Mg.Pt. 10 Mg.Pd.		20 Mg. Pt.	Pure .050	22	40	29		Cell cycled 3 times. Allowed to set over night, then [illegible] show no deterioration.
22		20 Mg.Pt.		20 Mg.Pt.	Pure .050	22	40	29		Cell used [illegible] new test set-up.
23		9 Mg.Pt.		9 Mg.Pt.	Pure .050	22	40	29	Cyanamid Electrodes Type AB-4	Cycled 7 times. High charge voltage [illegible] volts. Discharge voltage degraded with time. Final KOH 33
24		9 Mg.Pt.	27	20 Mg.Pt.	Pure .050	22	40	29	Used Type AB-4 as O_2 Electrode	Cycled 11 times High charge voltage 1.6-1.7 volts. Discharge degraded with time. Final KOH 27
25	46	20 Mg.Pt.	45	20 Mg.Pt.	Pure .050	22	40	29		Tested cell at 125°C. Tested cell at high current discharge

TABLE I. SUMMARY OF SINGLE CELL TESTS

70°C, and then cycled a fourth time. The cell exhibited no deterioration in performance during the period tested. Therefore it was decided to use this mat arrangement in the 75 watt unit.

2.2 Multi-Cell 75-Watt Unit Constructional Details

The 75 watt unit consisted of 6 series connected cells having 6-inch diameter electrodes. Both the hydrogen and oxygen electrodes were 20 mil nickel plaques containing 20 mg. of platinum per sq. cm. The mat consisted of 0.050 inch thick fuel cell millboard asbestos weighing 22 grams. The insulating spacers were 0.040 inch thick, thus, the mat was compressed 0.010 of an inch. They were soaked with 29 gms. of 40% KOH. The unit was assembled by stacking the individual electrodes, separator plates, and asbestos mats. A stainless steel bellows was attached to the oxygen end plate to balance the respective hydrogen and oxygen volumes. The entire cell assembly was then placed into the two halves of the outer tank that make up the oxygen and hydrogen storage compartments. The negative lead from the hydrogen end plate was brought through the tank by means of an insulated high pressure terminal.

2.3 75-Watt Cell Testing.

The assembled unit was installed in the test oven in the new fuel cell testing facility. Appropriate feed-throughs for electrical and hydraulic connections have been installed in the oven and test facility. The unit was flushed 10 times by pressurizing with hydrogen and oxygen to 50 psig and then venting the gases. A differential pressure transducer was used to measure the pressure difference between the oxygen and hydrogen compartment. An absolute pressure transducer was used to measure the pressure in the hydrogen compartment and a series of thermocouples around the periphery of the cell were used to determine temperature variations. The ambient temperature in the oven was raised to 70°C, and the cell was put on cycle. The cycle consisted of 65 minutes charge at 9.6 amps, and a discharge load of .33 ohms set to give 75-80 watts during discharge. In the initial cycles, the performance of the unit looked stable and satisfactory.

Therefore, it was decided to continue the cycling and conduct a 48-hour test. Data for cell voltage, cell pressure, and temperature during the continuous 48-hour test is shown in Figure 1.

Throughout the entire testing period, the differential pressure swing did not rise more than 0.2-0.3 psi. When the cell pressure reached 380-390 psi, the charger was shut off, and the cell was allowed to sit on open circuit until the cycling timer (set at a 65 minutes charge duration) switched the unit to discharge. After completion of the 48-hour test, the cell was vented and allowed to sit at temperature on open circuit. In the following days a number of other charge-discharge cycles were conducted to determine various performance capabilities, and if any deterioration in performance would occur. Figure 2 shows a series of discharge curves at different temperatures and loads. As can be seen, at a slightly higher temperature, the unit was capable of discharging continuously at 25 amps.

Figure 3 shows a test of cell capacity. The unit was charged until the cell pressure reached 450 psi, and then continually discharged at 15 amps until the cell voltage reached 3 volts. It should be noted that at the end of charge period, the cell voltage was still relatively low, indicating that the mats contained additional water that could have been utilized for additional capacity. Figure 4 shows a voltage vs. current curve for the unit, and the accompanying power output curve for this test. After an accumulation of a total of 39 cycles, the unit exhibited slightly deteriorated performance on both charge and discharge. Therefore, it was reasoned that all [illegible] information had been obtained, and the unit was disassembled and examined. The individual mats had gray to black discoloration adjacent to the hydrogen electrode. Electrolyte squeezed from [illegible] of two of the cells showed that the concentration had been reduced to approximately 13% KOH. Additional peripheral analytical tests are being conducted to determine the cause of this electrolyte consumption.

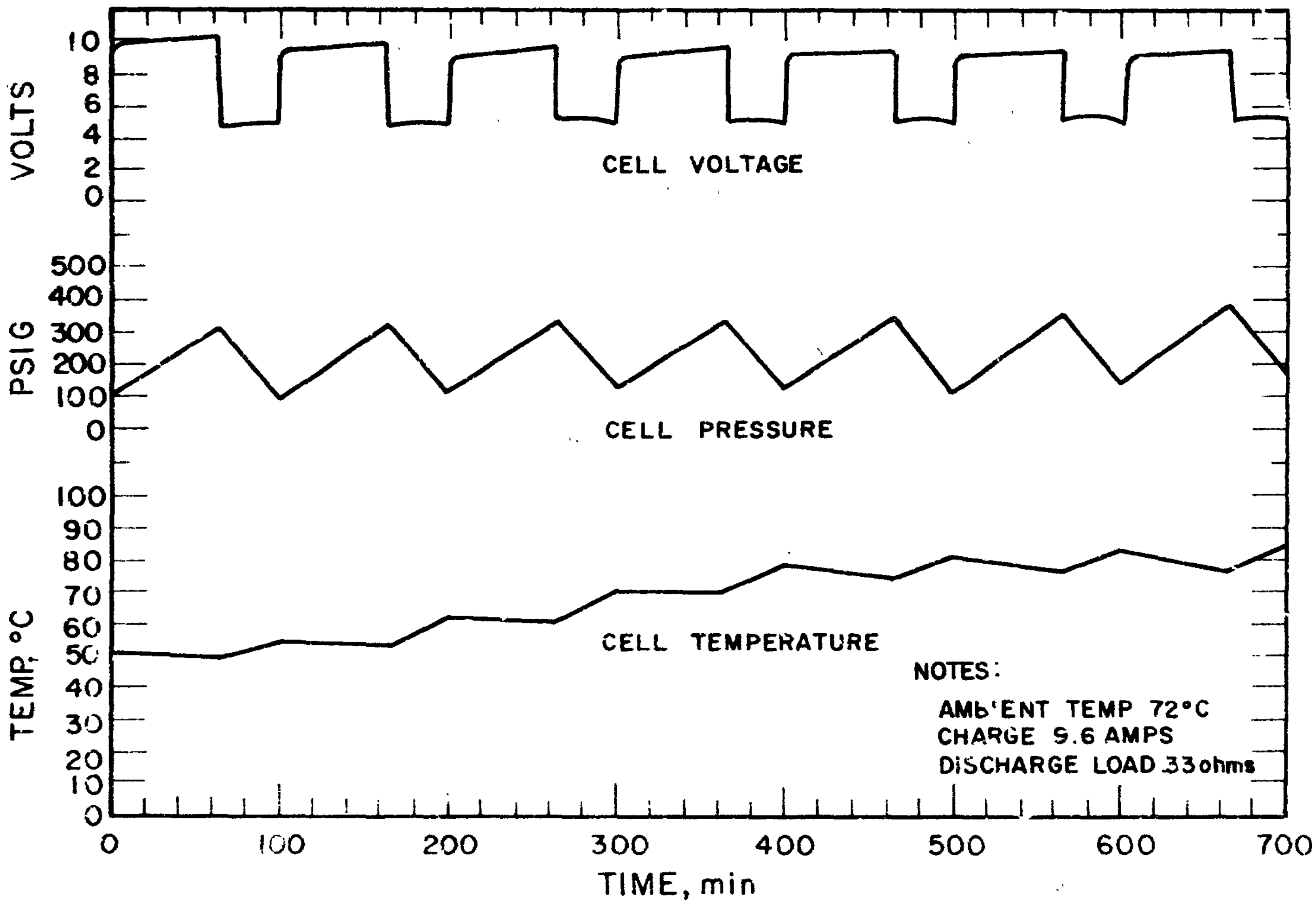

FIG. 1A CONTINUOUS 48-HOUR CYCLING OF 75-WATT ELECTROLYTIC REGENERATIVE H_2-O_2 CELL

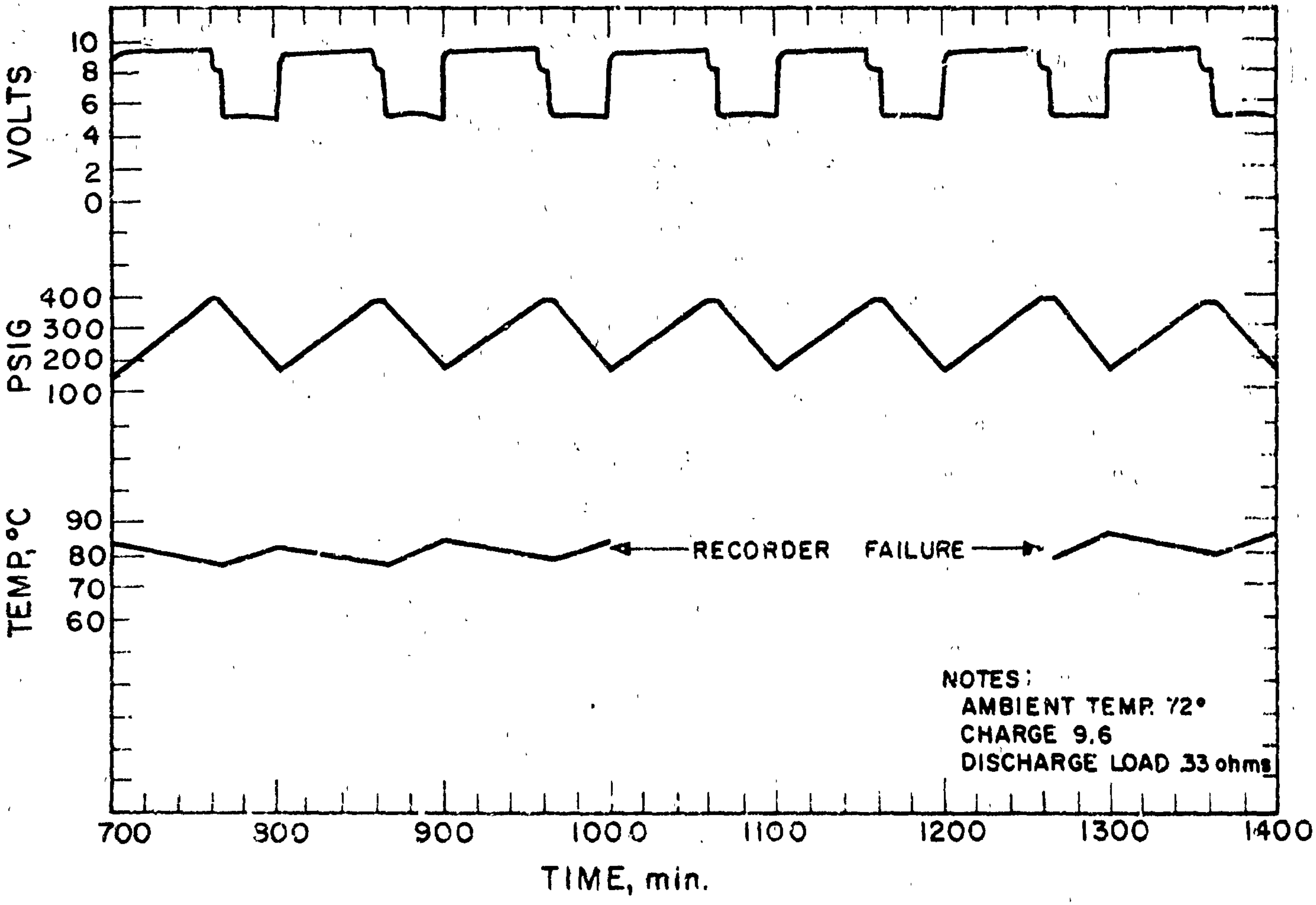

FIG. 1B CONTINUOUS 48-HOUR CYCLING OF 25 WATT ELECTROLYTIC REGENERATIVE H_2-O_2 FUEL CELL (contd)

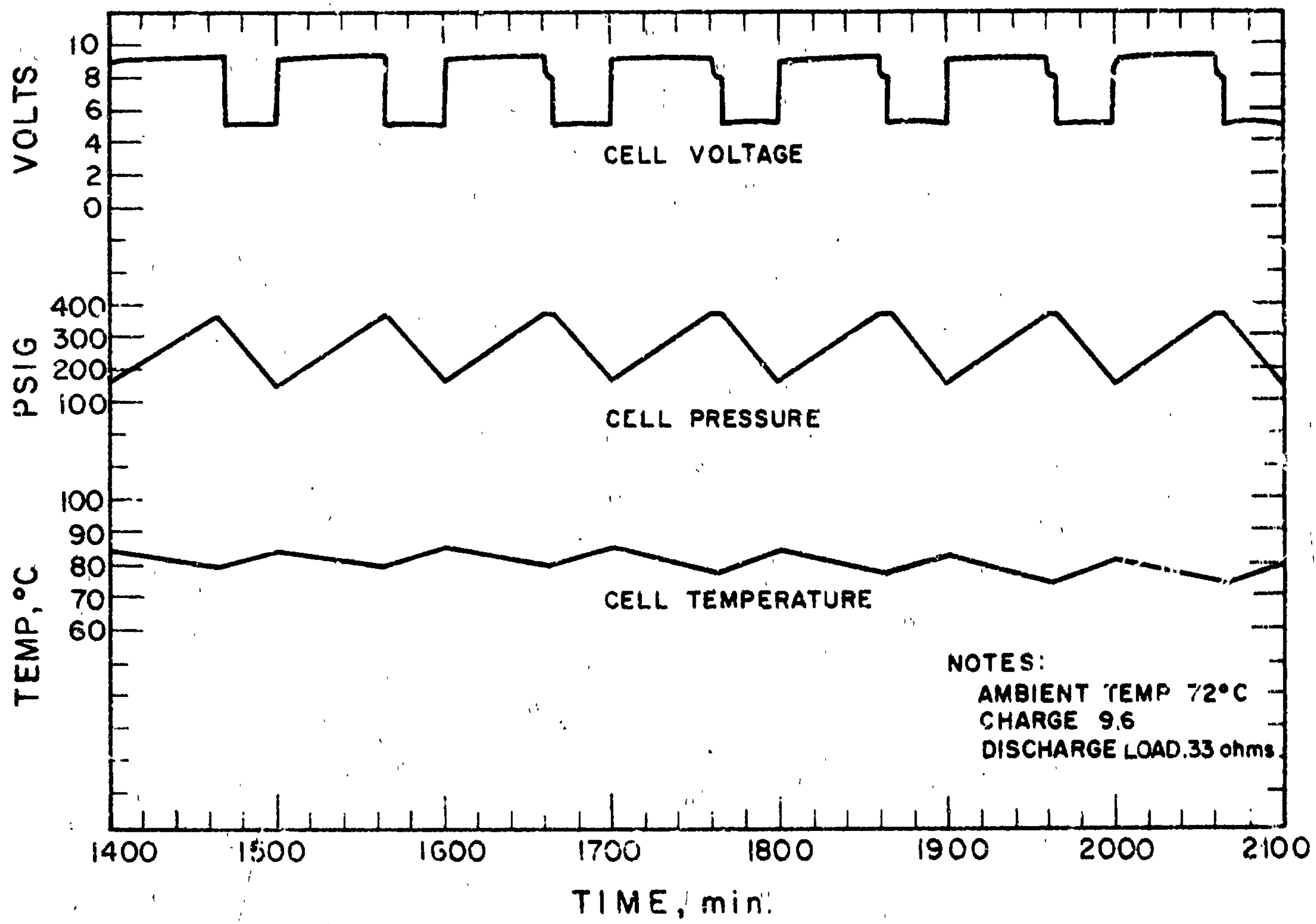

FIG. 1C CONTINUOUS 48-HOUR CYCLES OF 75-WATT ELECTROLYTIC REGENERATIVE H_2-O_2 FUEL CELL (contd)

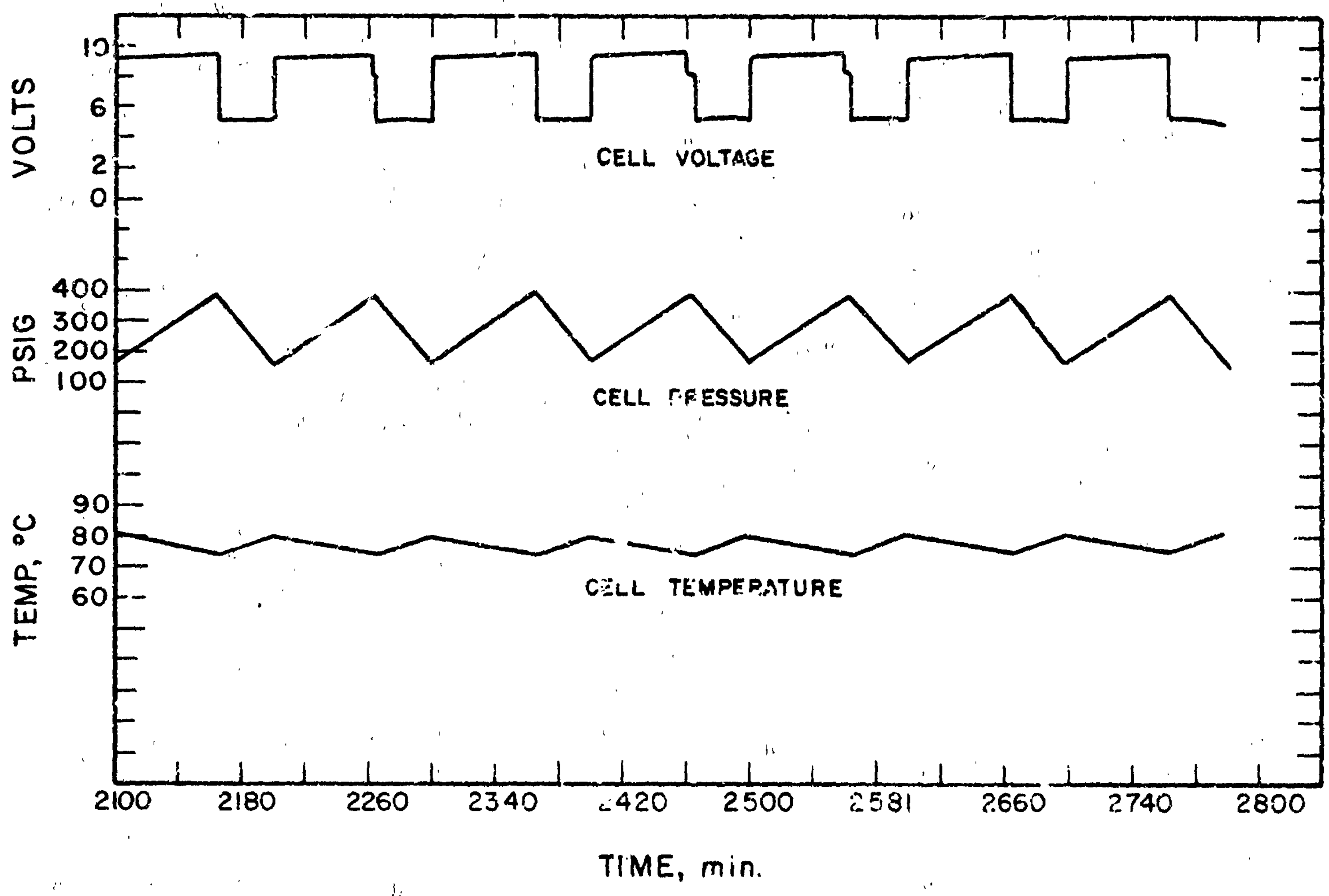

FIG. 3D CONTINUOUS 48-HOUR CYCLING OF 75-WATT ELECTROLYTIC REGENERATIVE H_2-O_2 FUEL CELL (contd)

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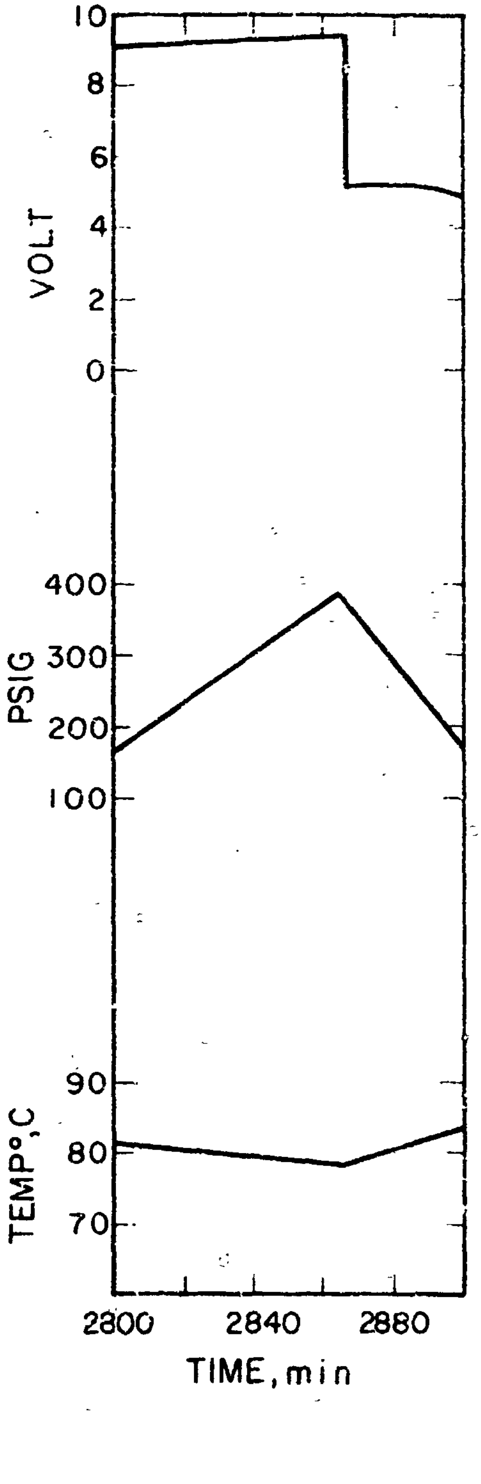

FIG. 1E CONTINUOUS 48-HOUR CYCLING OF 75-WATT ELECTROLYTIC REGENERATIVE H_2-O_2 FUEL CELL (contd)

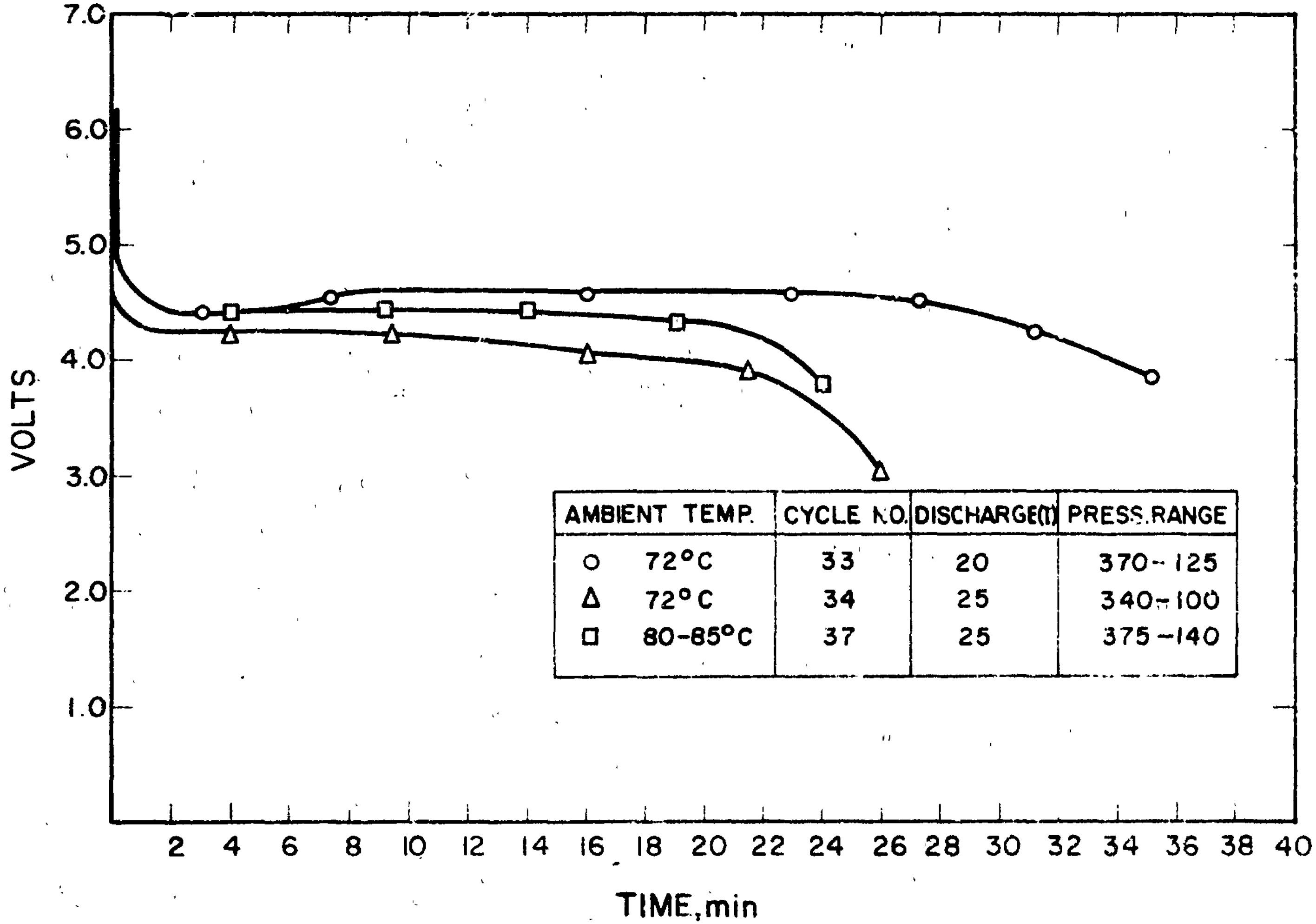

FIG. 2 DISCHARGE DATA 75-CELL ELECTROLYTIC REGENERATIVE H_2-O_2 FUEL CELL

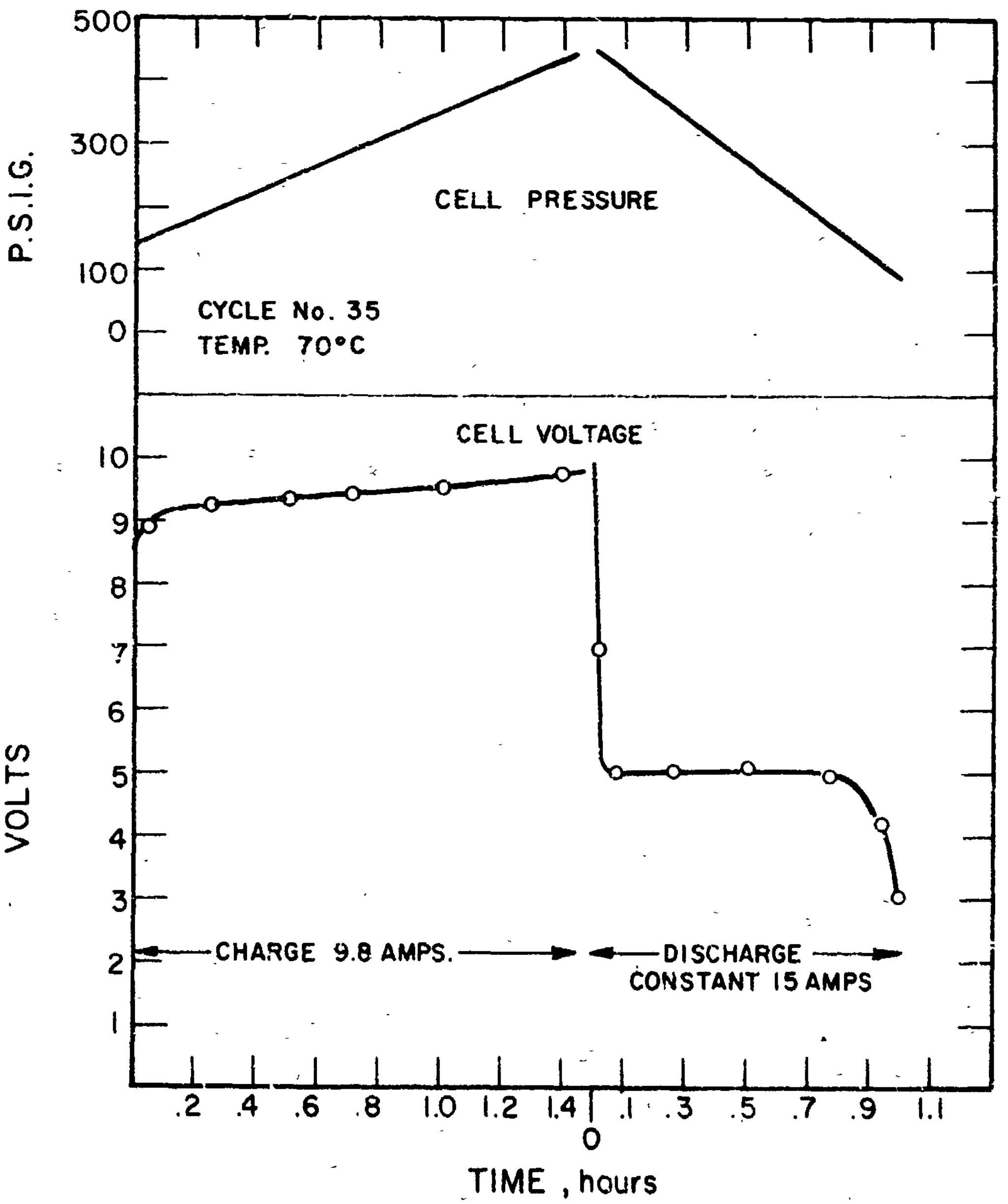

FIG. 3 CAPACITY TEST CYCLING DATA H_2-O_2 ELECTROLYTIC REGENERATIVE FUEL CELL

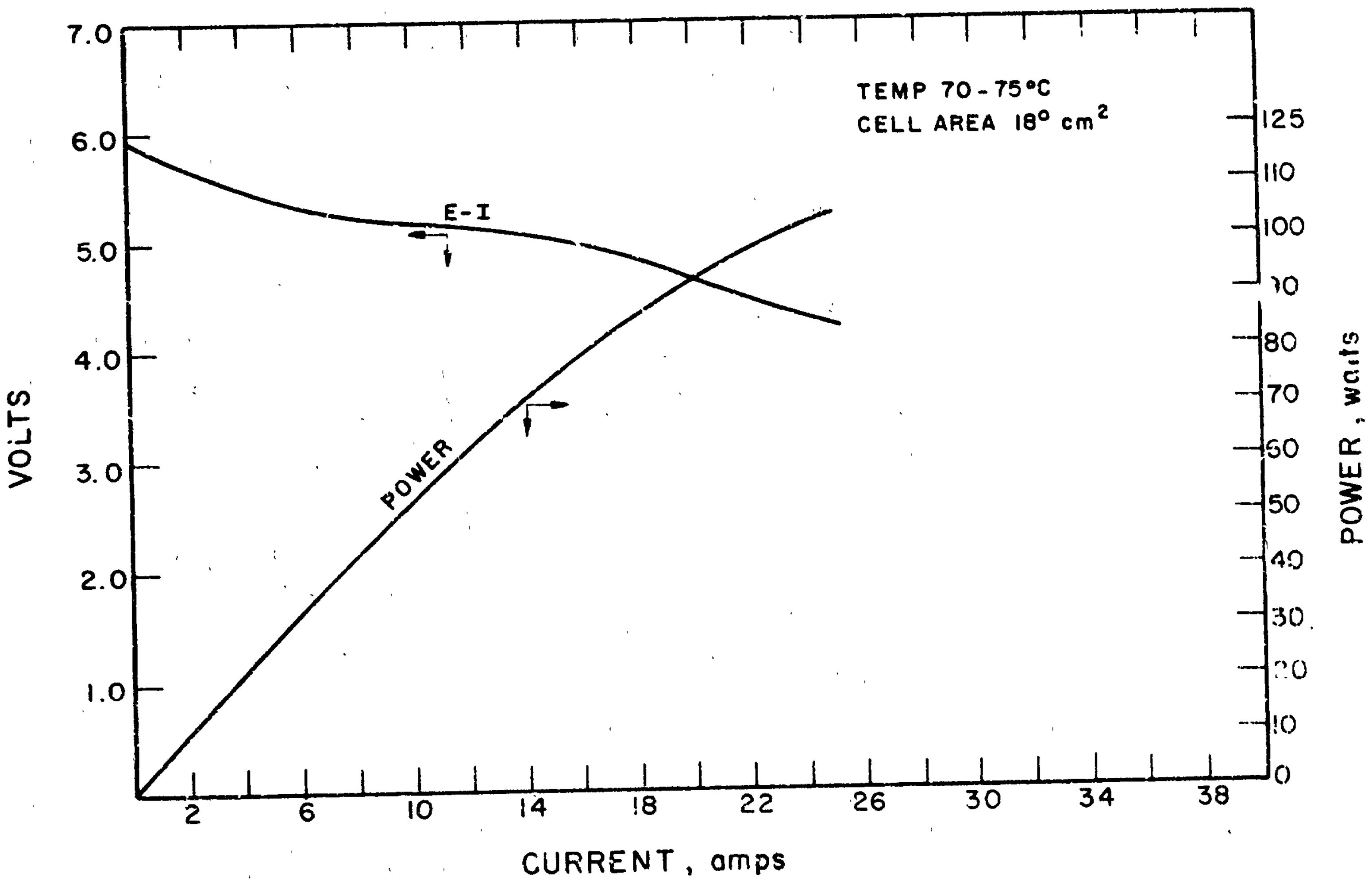

FIG. 4. PERFORMANCE DATA 75-WATT (6 CELL) ELECTROLYTIC REGENERATIVE H_2-O_2 FUEL CELL

2.4 Single Cell Tests After Multi-Cell Tests

After completion of the 75 watt cell testing, the single cell test oven was rearranged and another series of cells were assembled and tested. Cell # 22 was used to check out the new set up. Cell # 23 employed Cyanamid Type AB-4 fuel cell electrodes. The initial discharge voltage at 16 amps was 0.8--0.82 volts, but the charge voltage ranged between 1.7--1.9 volts. After 7 cycles, the discharge voltage dropped to 0.76--0.78 volts. At this point the cell was disassembled and the electrolyte concentration in the mat measured. It was found to be 33%.

Cell #24 utilized a Type AB-4 electrode on the oxygen side, and a standard EOS (20 mg/cm^2 platinum) hydrogen electrode. The discharge voltage at 16 amps initially was between 0.80 and 0.82. The charge voltage ranged between 1.7 and 1.8 volts. After 11 cycles, the discharge voltage dropped to 0.78 volts. Again the cell was dissassembled and the electrolyte concentration measured. This time it had dropped from 40% to 33%.

Cell #25 was assembled to test capabilities of the cell at elevated temperatures. Figure 5 shows E-I data for the cell at 125°C. This cell is still on cycle.

The data obtained at 125° is quite remarkable in that currents approaching 100 amperes were obtained at 0.55 volts. Due to overheating of the load bank and associated electrical hardware, the high current levels were only measured for periods of time less than 30 seconds. However, the values obtained are indicative of the high pulse power the unit is capable of.

2.5 Preliminary 500 Watt Cell Design Weights

As a result of the recent series of tests indicating the excellent performance achievable with the new cell design and improved electrodes, preliminary weight calculations of a 500 watt, 35 cell

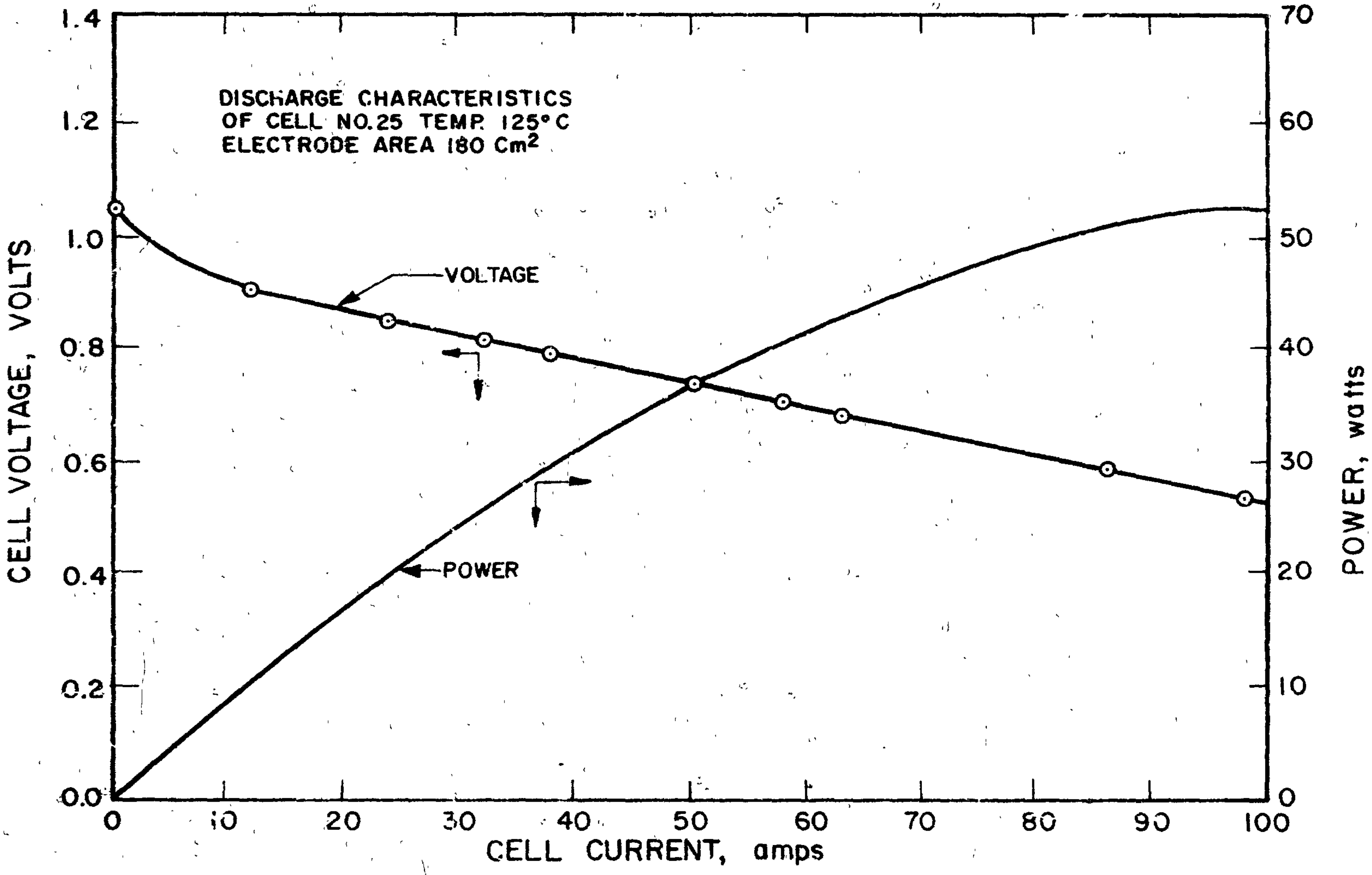

FIG. 5 CELL NO. 25 DISCHARGE CHARACTERISTICS

unit were undertaken. Two sets of calculations were made, one using existing components, and the second using improved lower weight components which we feel are well within the current state of the art. Table 2 shows the itemized component weights used in the calculated cell weights. Details of the tank weight calculations are given in Appendix I. Further weight reductions are possible, using advanced materials and design considerations. Details of such reductions are given in the next section.

2.6 Potential Improvements in Regenerative Fuel Cell Design Using Advanced Light Weight Materials.

The purpose of this discussion is to review the results of a preliminary analysis which was performed to determine the potential reduction in weight of a regenerative fuel cell which may be possible by utilizing advanced light weight materials. A review of the existing design concept scaled up to the 500 watt nominal power rating indicates that with relatively few and simple improvements, the weight of such a system could be reduced to the 35-40 lb. level. Such a unit would utilize magnesium cell separators, and 6061-T6 aluminum alloy gas tankage. The unit would be capable of an energy capacity of 600 watt hours at a 500 psi peak storage pressure, at a temperature of 100°C and power drains of either 500 watts or 1000 watts. The cell stack assembly would have an estimated weight of about 20-25 lbs., and the gas tankage assembly would have an estimated weight of about 10-15 lbs. The best estimate of the energy to weight ratio of such a unit would be 15-17 watt hours per lb. The unit would be essentially identical to the present design with minor modifications to reduce weight in non-critical areas. The principle change in operation would be achieved by raising the operating temperature to the 100°C level to allow a drain of 1000 watts at the short duration discharge.

To examine the feasibility of further reductions in weight, several advanced materials were considered for use in the present design. The existing cell stack assembly uses nickel plated magnesium separators with a density of about .065 lbs. per cubic inch. If one of the new light weight aircraft structural materials such as the

	35 Cell Unit Existing Design Wt. (gms)		35 Cell Improved Design Estimated Achievable Wt. (gms)		
1. Separator Plate	Each	Total	Each	Total	How Weight Reduction Accomplished
1. Separator Plate	159.5	5750	140	5040	Additional gas grooves.
2. Insulating Spacers	21.9	767	20	700	Use epoxy instead of teflon
3. Electrodes	21.0	1470	15	1050	Use AC electrode on O_2
4. Asbestos Mat	22.0	770	21	735	Use .050" instead of .054"
5. Gas Distribution Screens	12.1	846	0	0	Eliminate Screens
6. Pressure Balancing Bellows	1328	1328	800	800	Use thinner flange.
7. H_2 end plate	1139	1139	360	360	Use Mg instead of Al and reduce to 1/4"
8. O_2 end plate	1375	1375	480	480	Use Mg instead of Al and reduce to 1/4"
9. Stack bolt assembly	65	780	65	780	No change
10. Bellows "O" ring	20	20	15	15	Reduce thickness.
11. Flange "O" ring	28.1	56	20	40	Reduce thickness.
12. Flange Bolt Assembly	31.5	378	30	360	Use smaller washers
13. Electrical connector	200	200	200	200	No change
14. Electrolyte	29	960	28	360	Reduce KOH to 30%
15. Tankage*	6400	6400	5270	5270	Reduce flange diameter and use 50K psi alloy.
TOTAL		22,390 gms or 49.3 lbs.		16,690 gms. or 36.5 lbs.	

*Estimated for 500 W model

TABLE 2. COMPONENT WEIGHTS FOR 500 W MODEL

magnesium-lithium alloy LA141A can be used, with a density of .049 lbs. per cubic inch, an immediate reduction of the cell stack of about 4-5 lbs. is possible. The use of this and other similar magnesium-lithium alloys is gaining rapidly, and in this particular application would depend on the development of a suitable nickel plating process for protection against electrochemical attack. Other design improvements in the cell stack bolts and end caps are certainly possible with improved high strength, light weight materials, thereby making another 2-3 lb. reduction in weight feasible. Therefore, the minimum weight of a 600 watt hour capacity cell stack is probably on the order of 16-18 lbs., as compared to the present average of about 25 lbs.

The gas tankage is the other most critical weight element of the system. The existing tank design for a 500 watt unit would utilize the 6061-T6 aluminum alloy with a working yield stress of 33,000 psi, and a density of 0.1 lbs./cu. inches. There appear to be several alternative materials which could make significant reductions in the present tank configuration, which appears to weigh about 12-15 lbs. If one of the structural titanium alloys could be nickel plated, or coated with an inert material such as teflon, to protect against spontaneous reaction in the pure oxygen environment, then a design working stress of 100,000 psi can be used with material density of 0.160 lbs./cu in.; thereby resulting in a tank wall thickness of approximately .030". The weight of the gas storage tankage utilizing titanium would therefore be about 7-8 lbs. including flanges.

As another approach, if one of the new high strength weldable aluminum alloys such as Kaiser 7039, or Alcoa X-7106 proves to be satisfactory at operating temperatures of 250^{0}F, then a design yield stress of 45,000 psi would be available. These materials can be expected to have all of the desirable properties of the older aluminum alloys, and would result in a gas tankage weight of 10 lbs. Another alternative, and probably the most attractive, considers the use of the new beryllium-aluminum alloys developed by Lockheed Missiles and Space, and recently licensed to the Brush Beryllium Company. These alloys vary in percentage from 25-45 weight percent of aluminum with the remainder pure beryllium. They appear to have good ductility and corrosion resistance, and also are sufficiently weldable to be used for tank design. The main advantage of these alloys is a working yield stress of 70,000 psi with a density of .074 lbs./cu in. If this material becomes available and can be used in this application, it would result in a total tank weight of 6 lbs. including flanges. The last alternative considered, involves the use of glass filament wound tanks. Although the present technology has resulted in very high strength to weight ratio configurations, it is not believed that these tanks are practical for this application at this time. The two factors which influence this conclusion are the unpredictable effect of temperature cycling on the strength characteristics of the glass filament structure, and secondly, the heat transfer requirements of the fuel cell assembly whereby a high thermal conductivity, both axially and radially, on the tank structure are desirable for heat rejection purposes. However, it is likely that with current developments underway, a high temperature metallic filament wound tank will become feasible for this application in the near future, utilizing some of the high temperature resins and adhesives presently being developed.

The conclusions derived from this preliminary study of trends in performance are significant. The minimum weight of a 600 watt hour regenerative fuel cell assembly using the most practical advanced structural materials which could become available in the next 2-3 years, appears to be a lower limit of about 20 lbs., and a likely weight of about 25 lbs. This would result in a system energy to weight ratio of 24 watt hours per lb. If the capacity of the existing cell stack could be increased by improving the water storage capability, the energy to weight ratio of the system could probably be raised to at least 30 watt hours per lb. This appears to be a reasonable goal for a regenerative fuel cell battery operating at 100°C after a development prototype has been completed and reliable cyclic operation is achieved. For the foreseeable future, this system appears to be significantly superior to other secondary batteries on an energy/weight basis.

3. PLANS FOR THE NEXT PERIOD

During the next period, additional single cell tests will be run in order to determine the cause of KOH consumption and the related effect on cycling. Additional analytical tests will be conducted to determine the mode of KOH consumption. A new 6 cell unit will be assembled and subjected to testing to determine additional performance characteristics.

It is anticipated that preliminary design work on the 500 watt unit will be initiated and certain long delivery time items ordered. This, of course, assumes that approval will be obtained to start Phase II of the program.

4. FINANCIAL STATEMENT

Manhours and dollar expenditures for the period October 2 through October 30, 1964 were as follows:

Direct Labor Hours	563.50
Direct Labor Dollars	$ 2,617.12
Purchases and Commitments	$ 4,964.38
Total Dollar Expenditure	$15,000.68

APPENDIX I

I. TANK SIZE CALCULATIONS

A. Gas Volume

Electrochemical Equivalent of H_2 = 26.6 amp.hr./gm.

Amp. hr./cell = 600/28 = 21.4 amp. hr./cell required.

Total Wt. of H_2 generated = $\frac{21.4 \times 35}{26.6}$ = 28.2 gm.

Assume operating pressure (max.) = 450 psig $T = 100^{\circ}C = 672^{\circ}R$

H_2 volume = $\frac{28.2 \times 672 \times 10.73}{2 \times 454 \times 450}$ = 0.497 $ft.^3$

O_2 volume = 1/2 H_2 volume = 0.248 $ft.^3$

Gas volume = 0.745 $ft.^3$ required

B. Cell Volume Calculations

Cell stack gas ports = 0.375 $in.^3$ per cell

Separator plate distribution ports = 0.668 $in.^3$ per cell

~~End plate gas ports = 0.67 $in.^3$~~

Total cell stack gas volume = 36(0.375 + 0.668) + 0.67 = 38.3 $in.^3$

External gas volume required = (1728 x 0.745) -38.3 = 1248 $in.^3$

Stack length (excluding bellows)

L_s = (36 x 0.180) + (35 x 0.040) + (2 x 0.50) = 8.88 inches

Stack volume = $\frac{\pi D^2}{4}$ L = 0.785 $(7.875)^2$ · 8.88 = 433 $in.^3$

Bellows solid volume = $\frac{\pi(D_o^2 - D_i^2)}{4}$ x 0.525 = 0.785 (36-18.3) x 0.525

= 7.3 $in.^3$

Total cell volume = Gas volume + stack volume + bellows volume

= 1248 + 433 + 7.3 = 1688.3 $in.^3$

C. Tank Length

Assume tank ID = 8.0 inches.

End cap volumes = 1/6 πD^3 = 0.53 x $(8)^3$ = 271 $in.^3$

Cylindrical volume = $\frac{\pi D^2}{4} \cdot L$ = 1688.3 - 271 = 1417.3 in.^{3}

L Cylindrical portion = $\frac{1417.3 \times 4}{\pi \cdot 64}$ = 28.2 inches

Total tank internal length = 28.2 + (2 x 4) = 36.2 inches

II. TANK WEIGHT CALCULATIONS

A. Cylindrical Section Weight

S_y = 33 K psi for 6061-T6 aluminum at 100°C

P proof = 600 psig

Safety factor = 1.5

$S = \frac{Pd}{2t}$

$t = \frac{600 \times 1.5 \cdot 8}{2 \cdot 33 \times 10^3} = \frac{7,200}{66,000}$ = 0.109 inches or D_o = 8.22 inches

V Cylinder V End Caps

Tank Weight = $V \cdot \rho = \frac{\pi(D_o^2 - D_i^2)}{4} \cdot L_C + 1/6\ \pi\ (D_o^3 - D_i^3)\ \rho$

ρ_{Al} = 0.10 lb./in.^{2}

Tank Weight = 0.785 (3.46) · 28.2 + 0.53 x 42.6 x 0.1
(less flange)

= (76.6 + 22.6) x 0.1 = 9.9 lbs.

B. Flange Weight Calculation

Thickness = 0.608 inches (based upon present design)

OD = 10.5"

ID = 8.0"

$V_{Solid} = \frac{\pi(D_o^2 - D_i^2)}{4} \cdot t$ = 0.785 · (10.5^2 - 8.0)^2 · 0.608
= 0.785 x 46.25 x 0.608 = 22.1 in.^{3}

$V_{Bolt\ Holes} = 12\ \frac{\pi}{4}$ · (0.406)^2 (.608) = 0.94 in.^{3}

$V_{"O"\ ring\ groove} = \frac{\pi}{4}$ (8.6^2 - 8.4^2) x 0.14 + 0.785 x 3.4 x 0.14
= 0.37 in.^{2}

V_{Total} = 22.1 - 0.94 - 0.37 = 20.8 in.^{3}

$W_{Flanges}$ = 2 (20.8 · 0.1) = 4.2 lbs.

Total Tank Weight = 4.2 + 9.9 = 14.1 lbs. = 6400 gms.