HYDROGEN-OXYGEN ELECTROLYTIC REGENERATIVE FUEL CELLS

Prepared for

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1. INTRODUCTION

This report reviews the progress made on the development of a hydrogen-oxygen regenerative fuel cell (secondary battery) under NASA contract 3-2781 during the period August 1 through September 1,1965.

During this period, primary emphasis was placed on the testing of single cells with various electrode structures in order to obtain a better understanding of cell performance controlling factors, and methods of improving the oxygen-electrode. The first 500 watt, 34 series cell prototype was assembled and subjected to preliminary electrical tests.

2. TECHNICAL DISCUSSION

2.1 Single Cell Tests

Six single cell tests were conducted during this period to evaluate the performance of various electrode structures. Test results and the construction variables of these cells is summarized in Table 1. Cells number 92 and 93 were assembled utilizing oxygen electrodes purchased from American Cyanamid Corporation. These were the standard AB-4 type containing 9 milligrams of platinum per square centimeter, with the exception that the nickel substrate screen had been gold plated to minimize oxidation and corrosion. Cell number 92 was cycled 130 times on the standard 65 minute charge, 35 minute discharge test cycle. Figure 1 shows voltage performance of the cell at various cycles. As can be seen there was a gradual increase of the charging voltage, and a decrease in the discharge voltage as the cycling continued. The final electrolyte concentration within the asbestos mat was found to be between 26.2 and 26.9 percent. Examination of the cell components after the cell was disassembled revealed no obvious changes in the electrodes. The gold plating on the nickel subscreen, wherever visible, looked impervious and firmly attached to the screen.

Cell number 93 was similar to 92 with the exception that one layer of .060 asbestos was used and cycled only 38 times. This cell showed good discharge performance (0.80-0.84 volts), but the voltage during charge rose very rapidly to values as high as 2.0 volts. As cycling continued, the voltage on charge got progressively higher, and the discharge voltage fell off rapidly towards the end of discharge. The test was therefore discontinued. KOH concentration in the mat was found to be 27.8, and 28.4 percent on two samples extracted from the asbestos mat.

TABLE 1
SUMMARY OF SINGLE CELL TESTS

Cell No.	O_2 Electrode #	O_2 Electrode Catalyst	H_2 Electrode #	H_2 Electrode Catalyst	Mat Thickness and Grade	Mat Dry Wt.	KOH %	KOH Wt. (gms.)	Comments	Results
92		9 Mg Pt/ cm^2	215	20 Mg.Pt/ cm^2	2 x .030	27	40.3	31	Cyanamid Oxygen electrode with gold plated screen.	Final KOH 26.2% 26.9% 130 cycles Cell should show gradual degradation in performance.
93		"	213	"	.060	27.5	40.3	31	"	Final KOH 27.8%, 28.1% 38 cycles. Cell showed initial poor performance on charge.
94		20 Mg Pt/ cm^2		"	.060	27.1	40.3	31	Bishop platinized oxygen electrode	Final KOH 35.3% 35.6% 21 cycles. Showed initial good performance, but degraded slowly.
95		40 Mg.Pt/ cm^2	213	"	.060	26.0	40.3	31	"	Final KOH 29.4%, 48 cycles.Increased catalyst did not improve performance.
96		9 Mg.Pt/ cm^2	213	"	.060	27.3	40.3	31	Same electrodes as cell No. 93	Final KOH 29.6% 29.7% Cycled 37 poor initial performance.
97		"	215	"	.060	27.0	40.3	31	Same electrodes as cell No. 92	Final KOH 25.7, 25.8% Cycled 95 times.Initial good performance. Gradual degradation with cycling.

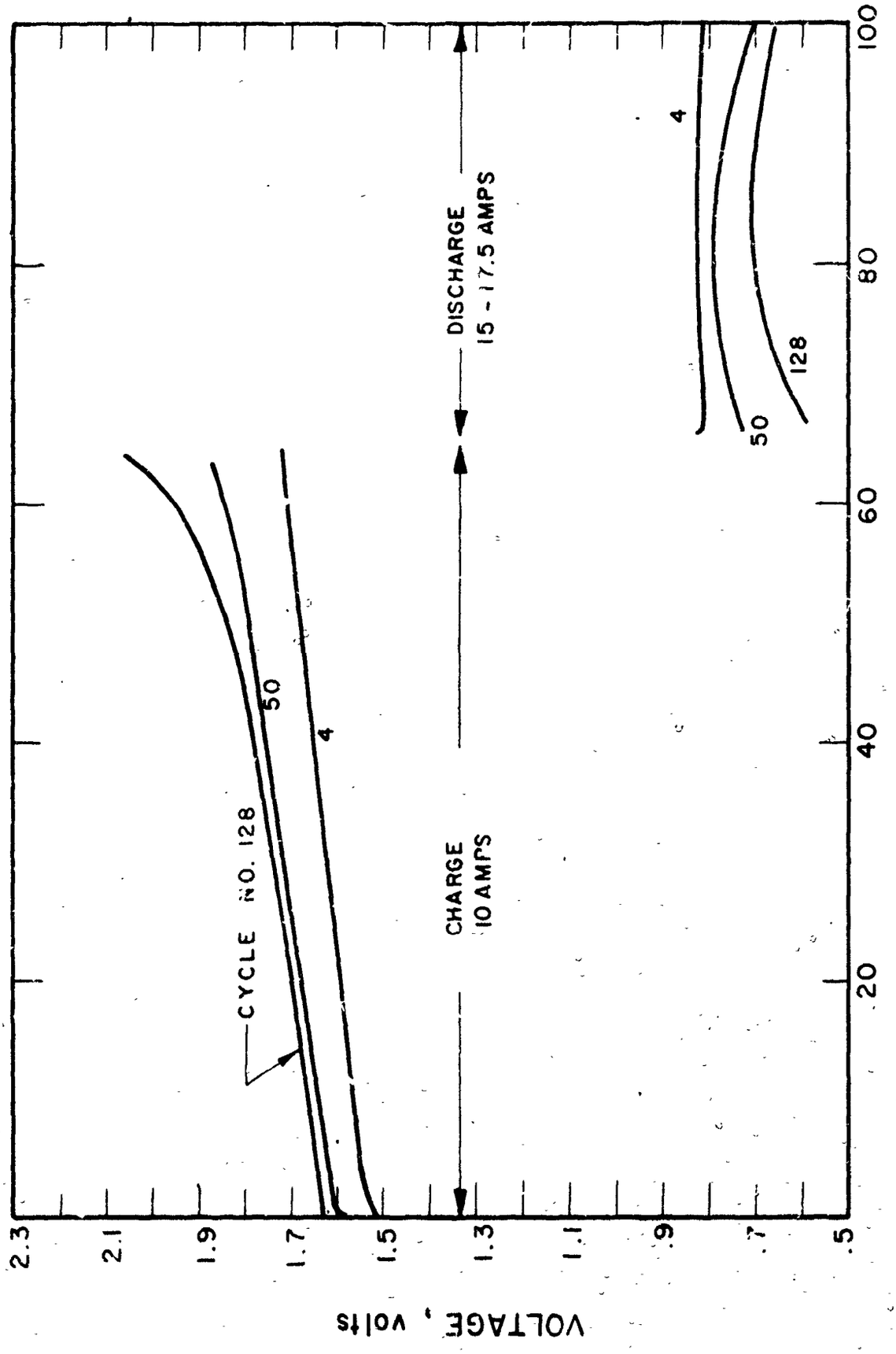

FIG. 1 CYCLING PERFORMANCE OF CELL NO. 92

Cell number 94 consisted of an oxygen electrode that had been platinized to 20 mg. of platinum per sq. cm. by a proprietary process of the Bishop Company. The substrate of these electrodes consisted of porous sintered carbonyl nickel plaques of the type used in standard EOS electrodes. This cell was cycled 21 times. The initial performance of the cell was good, discharge voltage being approximately 0.82 volts, and charge voltage approximately 1.6--1.75 volts. However, as the cycling continued a gradual increase in the charging voltage, and a decrease in the discharge voltage accompanied with a substantial fall-off in discharge voltage at the end of discharge was observed.

Cell number 95 consisted of an oxygen electrode that had been platinized by the Bishop Company to 40 mg. of platinum per sq. cm. This cell also exhibited good initial performance, and showed a gradual degradation of both charge and discharge voltage. However, the increased catalyst loading of the electrode did not improve performance above that obtained with the 20 mg. platinum per sq. cm. loading, as used in cell number 94.

Cell numbers 96 and 97 were repeats of cells 92 and 93, utilizing the same electrodes with fresh asbestos mats. Before the test each of the electrodes was washed with hot distilled water and dried. Performance obtained with cell 96 was similar to that obtained with cell number 93, i.e., the charge voltage would rise rapidly to levels as high as 2.2 volts. Discharge performance was low, ranging between 0.5 and 0.7 volts. The cell was cycled 37 times. Cell number 97 showed good initial performance, but gradually degraded with cycling. Voltage performance at various cycles is shown in Figure 2. The final KOH concentration in the mat was found to be 25.7 percent.

Test results, using American Cyanamid electrodes, indicate that performance degradation can occur even though nickel is not present in the electrochemical reaction zone. Since these electrodes can apparently be rejuvenated by a simple washing process, this indicates that either the asbestos/electrolyte interface is the cause of performance degradation, or some water soluble catalyst poison is

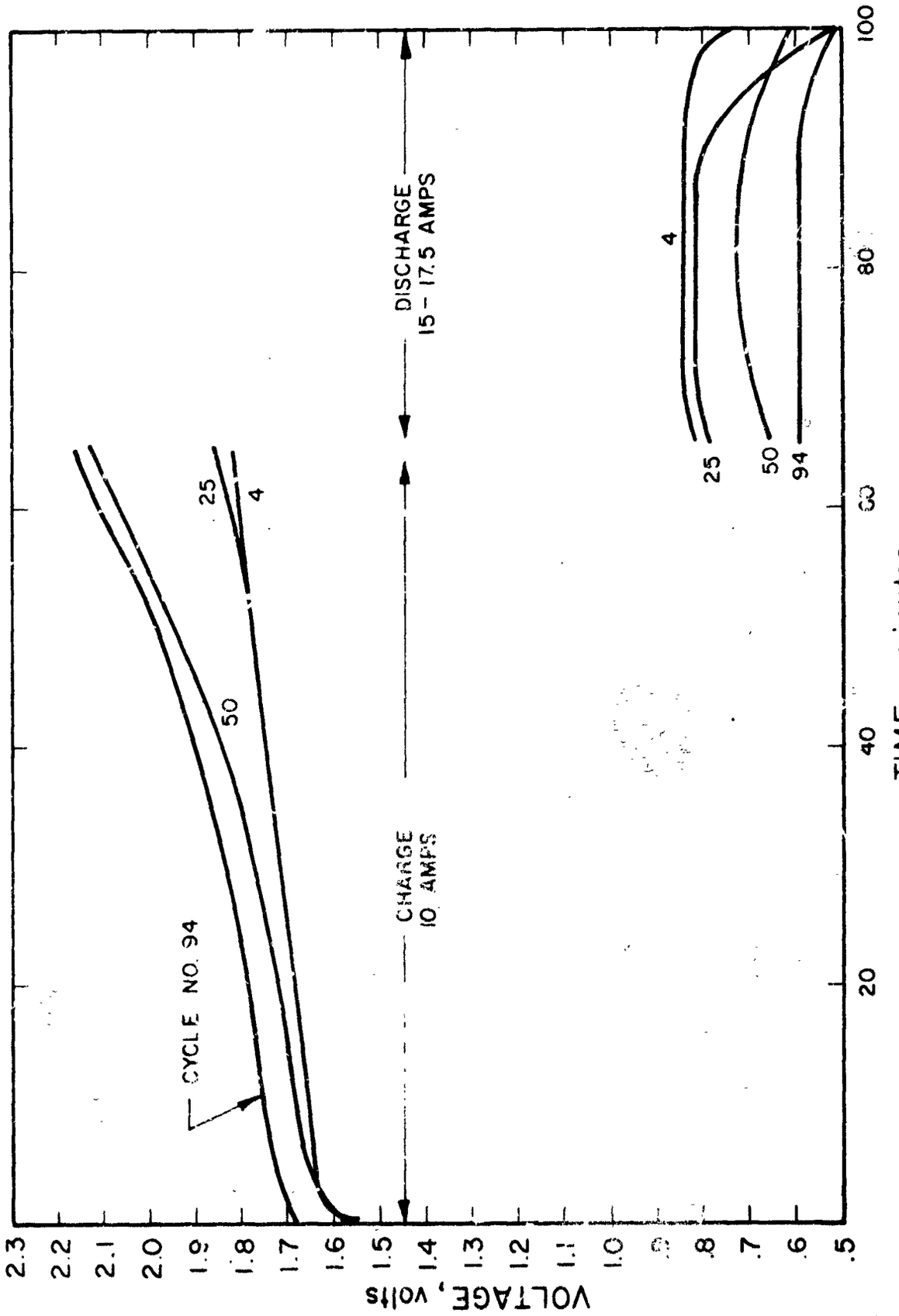

FIG. 2 CYCLING PERFORMANCE OF CELL NO. 97

formed which is removed by washing. Since KOH is lost during cycling, the initial premise appears to be more likely. This KOH loss factor is definitely accelerated by cyclical operation and indications are that increasing temperature also accelerates the loss. This loss factor will be investigated in depth in the near future.

2.2 Multicell Testing

During the report period, the new insulator separators fabricated from glass epoxy sheet were received, and a 34 series cell, 500 watt prototype was assembled incorporating these separators. Platinized porous nickel plaque electrodes of the standard EOS type were utilized. The intent of the assembly was to use existing hardware to check out the mechanical, thermal and electrochemical characteristics of the 500 watt design, and to debug the readout instrumentation. This unit, designated cell number 1002-34, incorporated stainless steel gas tanks.

The cell was placed in the test chamber, and put on standard cycle, 65 minutes charge at 10 amps, and 35 minutes discharge at a nominal current of 17.5 amps. The cell performed satisfactorily during the initial cycles. However, during the 7th and 8th cycles a wiggle in the cell voltage was observed. In the middle of the 8th discharge, an internal short developed. It was later found that the short was between the positive terminal bus and the negative tank wall at the insulated feed through connector.

During cycling, substantial temperature gradients ($\Delta 40^{\circ}C$) were encountered between the cell stack and the end of the hydrogen tank where the feed through was located. Typical temperatures during discharge were $110^{\circ}C$ at the H_2 end of the cell stack and approximately 70° at the tank end. This temperature gradient apparently caused condensation of moisture in the cool end of the tank. The condensed water apparently caused the copper bus to corrode causing a metallic short from the bus to the grounded feed through connector. Figure 3 shows data for saturation pressure of KOH solutions vs. temperature and

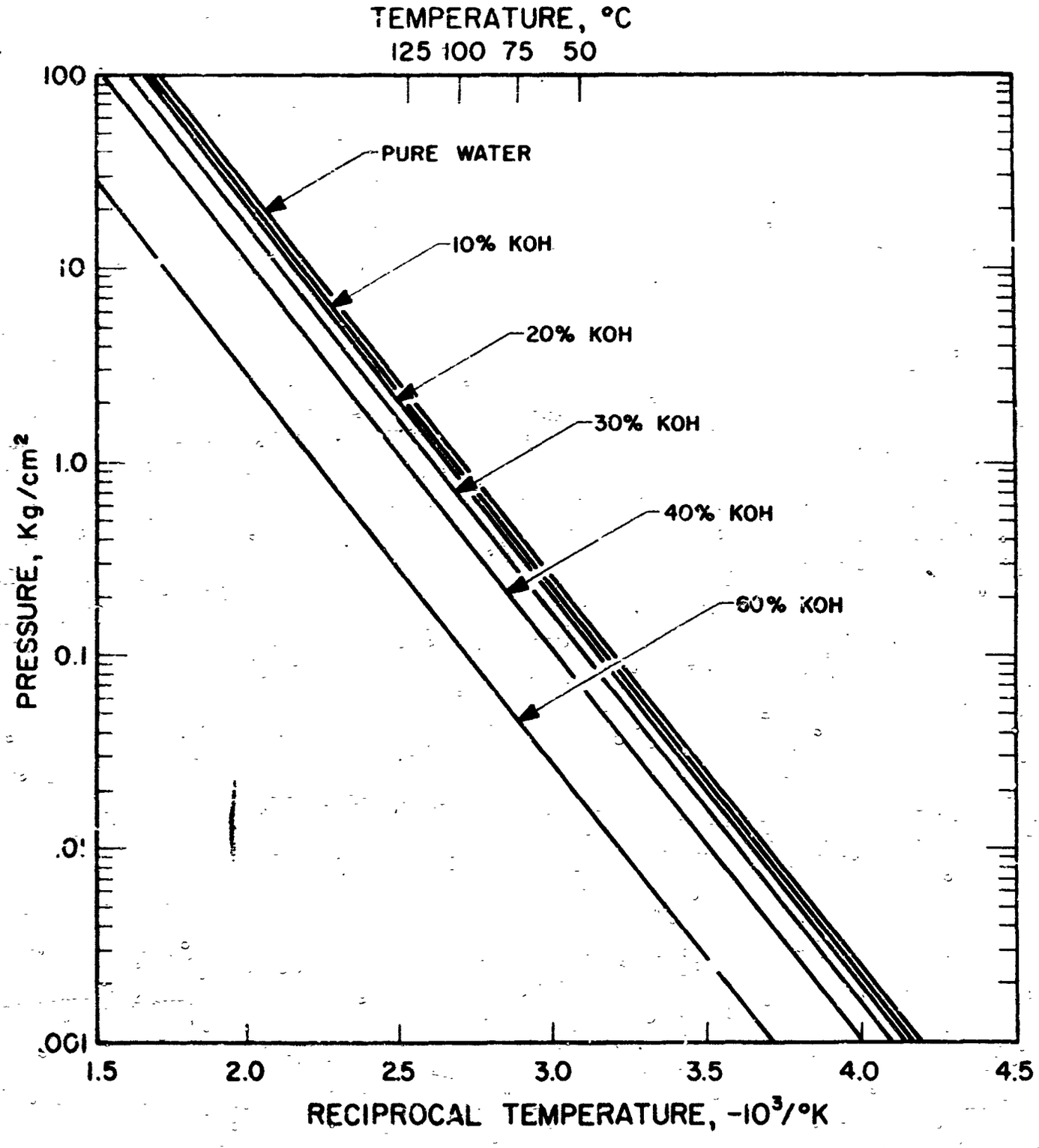

FIG. 3 SATURATION PRESSURE OF KOH SOLUTIONS VS TEMPERATURE AND CONCENTRATION

concentration. It shows that approximately 30°C temperature differences can be tolerated without exceeding the saturation pressure of the 40 percent KOH solution and water, and therefore avoiding condensation. However, since all the heat is generated by the cell stack, and the stainless steel tank is a poor conductor, the rate of heat transfer was such that the end of the hydrogen tank did not heat up sufficiently during discharge.

Figure 4 shows typical voltage performance of the unit during its initial cycles. Since the performance of the cell stack was quite good when the short developed, the tanks were disassembled and a new insulated feed through was installed. Asbestos insulation was wrapped around the hydrogen end of the tank in an attempt to keep the end hot enough to prevent additional condensation. The unit was subsequently cycled through the 26th discharge. During the second cycling period, a degradation in discharge voltage was observed similar to that recorded in previous single and 6 cell tests. The discharge voltage during the initial and end portions of discharge was 10-20 percent lower than at the mid point. This performance data is also shown in Figure 4. Large temperature gradients were again observed between the cell stack and the hydrogen tank end, and it was assumed that additional condensation within the unit was occurring due to this temperature gradient. Considering the gradual degradation of performance and the substantial temperature gradient encountered, it was decided to discontinue the test and make modifications on the unit to eliminate the temperature problem.

Examination of the disassembled unit showed all aspects of the internal components in good condition, and did reveal that additional condensation had taken place in the end of the hydrogen tank.

To determine overload capabilities of the unit during the 12th discharge, voltage vs current data was obtained, and is presented in Figure 5. This showed considerable overload capabilities with minimal polarizations. This data was also utilized in plotting power vs

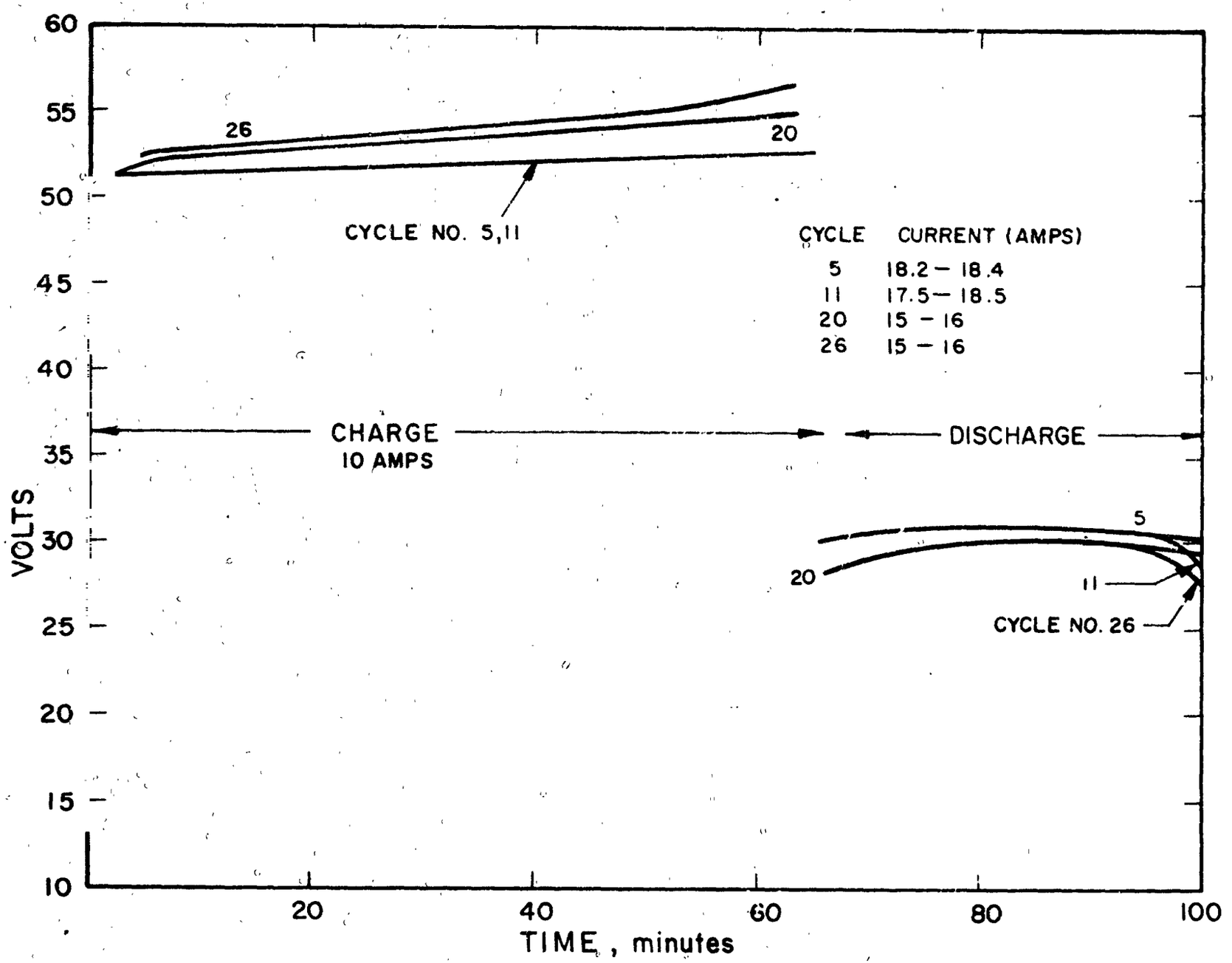

FIG. 4 CYCLING PERFORMANCE OF 500 WATT REGENERATIVE HYDROGEN-OXYGEN FUEL CELL S/N 1002-24

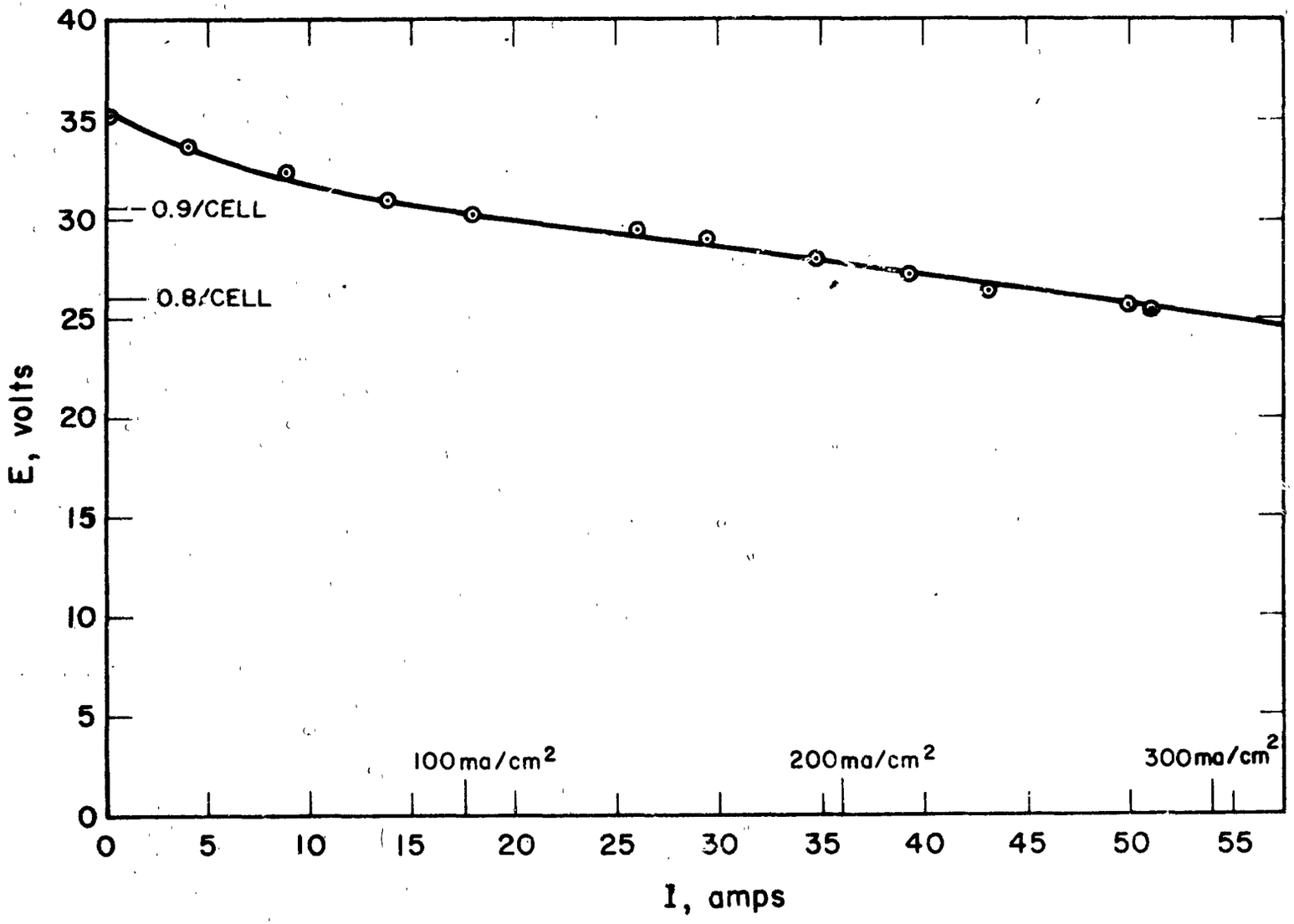

FIG. 5 VOLTAGE VS CURRENT DATA FOR 500 WATT REGENERATIVE HYDROGEN-OXYGEN FUEL CELL S/N 1002-34

current data which is presented in Figure 6. These tests of the 500 watt unit showed that the mechanical design, including compensating bellows, tank volumes, etc. was proper, and that the unit is capable of running continuously in excess of 500 watts, and has an overload capability > 2.5 times nominal.

The temperature gradient and condensation problem encountered can be attributed primarily to the poor thermal conductivity of the stainless steel tank used. It is believed that an aluminum tank such as will be used in the final design would have eliminated the problem. However, additional tests will be conducted to study and minimize the temperature gradient, and improve dissipation of heat from the stack.

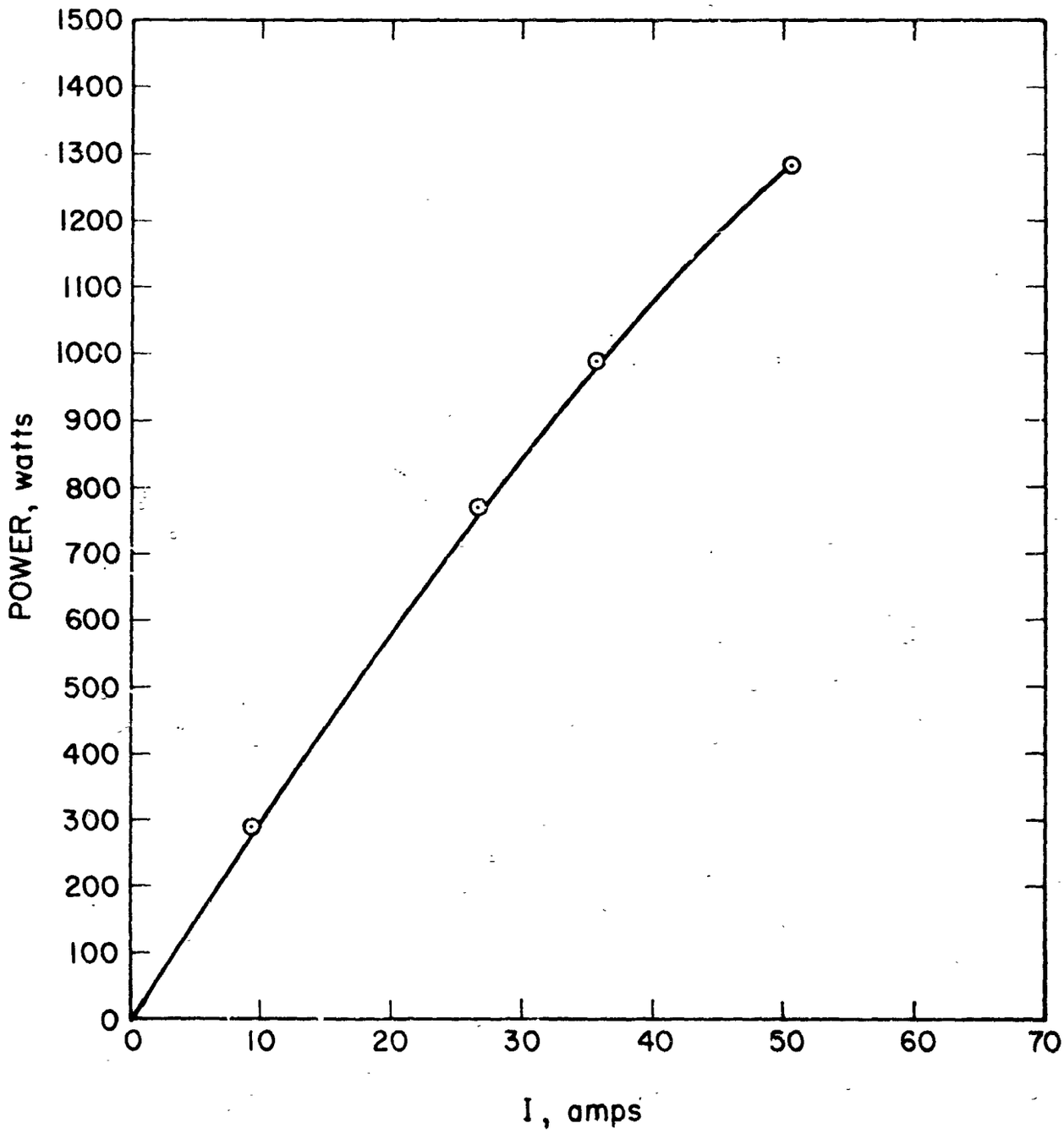

FIG. 6 POWER VS CURRENT FOR 500 WATT REGENERATIVE HYDROGEN-OXYGEN FUEL CELL S/N 1002-34

3. PLANS FOR THE NEXT PERIOD

The 500 watt multicell unit will be rebuilt with a strip heater placed around the hydrogen tank end, such that the heating of this portion of the tank can be controlled manually during the testing of the cell. In addition the rebuilt stack will utilize a 50 percent potassium hydroxide electrolyte to reduce the condensation problem. After these changes have been incorporated in the unit, it will be subjected to additional electrical cycling tests. Single cell tests will be continued on various electrode structures to obtain a better understanding of the cause of degradation encountered in cycling, and to improve the oxygen electrode structure.

4. FINANCIAL STATEMENT

Manhours and dollar expenditures for the period July 31 through August 27, 1965 were as follows:

Direct Labor Hours	618.5
Direct Labor Dollars	$3,003.42
Purchases and Commitments	348.71
Total Dollar Expenditure	$8,531.38