HYDROGEN-OXYGEN ELECTROLYTIC REGENERATIVE FUEL CELLS

Prepared for
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Contract NAS 3-2781

EOS Report 4110-ML-24 10 March 1966

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FACILITY FORM 602

(ACCESSION NUMBER)	(THRU)
24	1
(PAGES)	(CODE)
CR-75515	03
(NASA CR OR TMX OR AD NUMBER)	(CATEGORY)

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A Subsidiary of Xerox Corporation

CONTENTS

1. INTRODUCTION

This report reviews the progress made on the development of a regenerative hydrogen oxygen (RHO) fuel cell (secondary battery) under NASA Contract 3-2781 during the period of 1 February through 1 March, 1966. During this period, the testing of single cells was continued in order to improve cycle life capabilities and to obtain a better understanding of modes of deterioration in performance during cycling. A six cell (nominal 75-watt) unit was also assembled and subjected to test, employing gold-coated platinized electrodes that indicated improved life in single cell tests.

2. TECHNICAL DISCUSSION

2.1 Single Cell Test

Nineteen single cell tests were conducted during this period to evaluate the performance of various electrode structures. Test results and construction variables of these tests are summarized in Table 1. Cell No. 140 consisted of oxygen and hydrogen electrodes of the American Cyanamid type AB-6 that had been previously used in Cell 136, results of which were reported in the 23rd monthly report dated 10 February, 1966. During the initial flushing of this cell, in the normal checkout procedure, a gas leak was observed and the cell was never subjected to test due to this gas leakage.

Cell No. 141 consisted of gold-coated and platinized porous nickel plaques containing 14 milligrams of platinum per cm^2. These electrodes have previously been used in Cell No. 139 showing good initial performance but a fall-off towards the end of discharge, indicating flooding. In the assembly of this cell, a smaller quantity of electrolyte than normally used was employed. The cell was subjected to the standard test cycle of 65 minutes charge and 35 minutes discharge and has been cycled continuously for 380 cycles. It is still on test at this time. Performance of this cell is shown in Figure 1. There has been a gradual deterioration in voltage with cycle life, but at a considerably slower rate than with previous cells. Performance degradation in all previous cells has resulted in a fall-off in voltage at the beginning and end of discharge. In the case of this cell, degradation has shown up as an effect of a gradual lowering, but still maintaining a flat discharge voltage.

Cell No. 142 consisted of American Cyanamid type AB-6 electrodes that have been previously used in Cell 134. The electrodes were washed and reassembled with a new asbestos mat. The cell was cycled 46 times at which time an internal reaction and short developed within the cell. During the cycling period gradual degradation in the performance was observed.

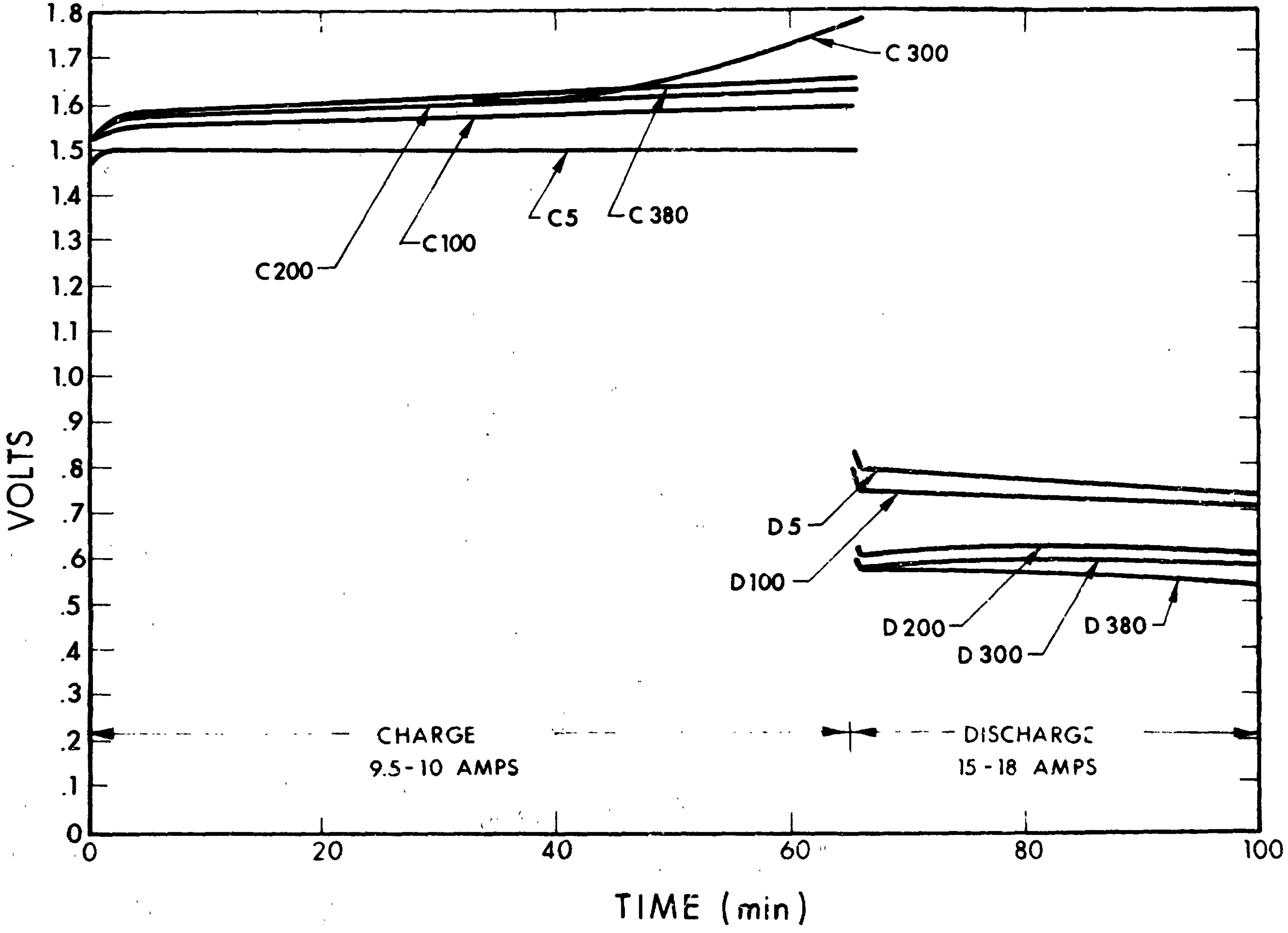

FIG. 1 CYCLING PERFORMANCE OF CELL SERIAL NO. 141

TABLE 1

SUMMARY OF SINGLE-CELL TESTS

Cell No.	O_2 Electrode		H_2 Electrode		Mat Thick (In.)	Mat Dry Wt (gm)	Electrolyte		Comments	Results
	No.	Catalyst	No.	Catalyst			KOH	Wt (gm)		
140	Am.Cy.	9 mg Pt/cm^2	Am.Cy.	9 mg Pt/cm^2	0.060	27.0	40	31.0	Electrodes from Cell 136	Not subjected to test due to gas leakage.
141	A_u 14	15 mg Pt/cm^2	A_u 18	15 mg Pt/cm^2	0.060	27.5	40	29	Electrodes from Cell 139	Still cycling.
142	Am.Cy.	9 mg Pt/cm^2	Am.Cy.	9 mg Pt/cm^2	0.060	27.5	40	31.0	Electrodes from Cell 134	Cycled 46 times. Developed internal reaction & short. Gradual degradation.
143	Am.Cy.	9 mg Pt/cm^2	Am.Cy.	9 mg Pt/cm^2	0.060	27.0	40	31.0	Electrodes from Cell 135	Shorted out during 12th cycle.
144	Am.Cy.	9 mg Pt/cm^2	Am.Cy.	9 mg Pt/cm^2	0.060	27.5	40	31.0	Electrodes from Cell 140	9 cycles. Fair performance.
145	Am.Cy.	9 mg Pt/cm^2	Am.Cy.	Nickel Plaque	0.060	27.3	40	31.0	-	Charged for 1-1/2 hrs.
146	Am.Cy.	Nickel Plaque	Am.Cy.	9 mg Pt/cm^2	0.060	26.8	40	31.0	-	Charged for 1-1/2 hrs.
147	Mod. Am.Cy.	9 mg Pt/cm^2+ 7 mg Pt/cm^2	Am.Cy.	9 mg Pt/cm^2	0.060	27.5	40	31.0	Electrodeposited Pt on top of Am. Cy. electrode	Flat good initial performance. 53 cycles, gradual degradation.

TABLE 1 (Cont.)

SUMMARY OF SINGLE-CELL TESTS

Cell No.	O_2 Electrode		H_2 Electrode		Mat Thick (In.)	Mat Dry Wt (gm)	Electrolyte		Comments	Results
	No.	Catalyst	No.	Catalyst			KOH	Wt (gm)		
148	Am.Cy.	9 mg Pt/cm^2	Am.Cy.	Nickel Plaque	0.060	27.4	40	33.0	-	Charged for 2 hours.
149	-	Nickel Plaque	Am.Cy.	9 mg Pt/cm^2	0.060	28.0	40	33.0	-	Charged for 2 hours.
150	Mod. Am.Cy.	9 mg Pt/cm^2 + 15 mg Pt/cm^2	Am.Cy.	9 mg Pt/cm^2	0.060	27.0	40	31.0	Electrodeposited Pt on top of Am. Cy. electrode	Cycled 11 times. Fair performance.
151	Mod. Am.Cy.	9 mg Pt/cm^2 + 7 mg Pt/cm^2	Am.Cy.	9 mg Pt/cm^2	0.060	27.0	40	31.0	Electrodes from Cell 147	-
152	Am.Cy.	9 "	"	"	0.060	27.0	40	31.0	Electrodes from Cell 150	Cycled 7 times. Fair performance.
153	A_u26	14 mg Pt/cm^2	A_u36	14 mg Pt/cm^2	0.060	27.0	40	30.0	-	2 cycles. Poor performance.
154	"	"	"	"	0.060	27.0	40	30.0	Electrodes from Cell 153	2 cycles. Slight improvement.
155	Mod. Am.Cy.	9 mg Pt/cm^2 + 14 mg Pt/cm^2	A_u40	14 mg Pt/cm^2	0.060	26.5	40	31.0	Pt Am. Cy. O_2 electrode. Nickel plaque hydrogen	2 cycles. Poor performance.
156	A_u26	14 mg Pt/cm^2	A_u36	14 mg Pt/cm^2	0.060	27.0	40	31.0	Electrodes from Cell 154	2 cycles. Poor performance.

TABLE 1 (Cont.)

SUMMARY OF SINGLE-CELL TESTS

Cell No.	O_2 Electrode		H_2 Electrode		Mat Thick (In.)	Mat Dry Wt (gm)	Electrolyte		Comments	Results
	No.	Catalyst	No.	Catalyst			% KOH	Wt (gm)		
157	Mod. Am.Cy.	9 mg Pt/ cm^2 + 15 mg Pt/ cm^2	A_u 40	14 mg Pt/ cm^2	0.060	27.0	40	31.0	Electrodes from Cell 155	1 cycle. Poor performance.
158	Bishop	7 mg + 15 mg pt/ cm^2	-	15 mg Pt/ cm^2	0.060	27.5	40	31.0	Electroplated Bishop O_2 electrode.	8 cycles. Good performance.
159	Mod. Am.Cy.	9 + 15 mg Pt/cm^2	A_u Cy.	9 mg Pt/ cm^2	0.060	27.0	40	31.0	O_2 Electrode from Cell 157	17 cycles. Poor performance.

Cell 143 consisted of American Cyanamid type AB-6 electrodes that have been previously used for Cell 135. These electrodes were also washed prior to use and assembled in the cell with new asbestos mat. This cell showed fair initial performance, but developed an internal short during the 12th cycle and the test was discontinued.

Cell No. 144 consisted of American Cyanamid type AB-6 electrodes that have been previously used in Cell 140. This cell did not exhibit any unusual performance characteristics and was shut down after 9 cycles.

Cells 145 and 146 were assembled in an attempt to determine the source of discoloration and platinum migration observed in previous cells. Cell 145 consisted of an American Cyanamid type electrode on the oxygen side and a porous carbonyl nickel plaque, uncatalyzed, on the hydrogen side. Cell 146 consisted of a nickel plaque on the oxygen side and an American Cyanamid type electrode on the hydrogen side. Both of these cells were charged continuously for 1-1/2 hours. It was difficult to remove the asbestos mats from the electrodes (due to loss of water during electrolysis), and no conclusions were reached from the test.

Cell No. 147 consisted of an American Cyanamid type AB-6 oxygen electrode that was modified at EOS by electrodepositing an additional 7 mg/cm^2 black platinum layer on one surface that was subsequently assembled in the cell adjacent to the asbestos mat. The hydrogen electrode employed was a standard American Cyanamid type AB-6 electrode. This modification of the electrode was an attempt to increase the thickness of the electrode structure and make the electrodes less sensitive to matrix water content. As shown in Figure 2, this electrode structure initially showed good flat performance, but as cycling continued, gradual degradation in the performance was observed. Previous tests with American Cyanamid electrodes showed considerably higher charging voltages, presumably due to a lack of availability of water in the electrode during the charge mode. Since the outer layer of electrodeposited platinum was not wet-proofed, this section of the electrode probably contributed considerably to the lowering of the charge voltage. This type of electrode structure indicates a possible technique for increasing the performance

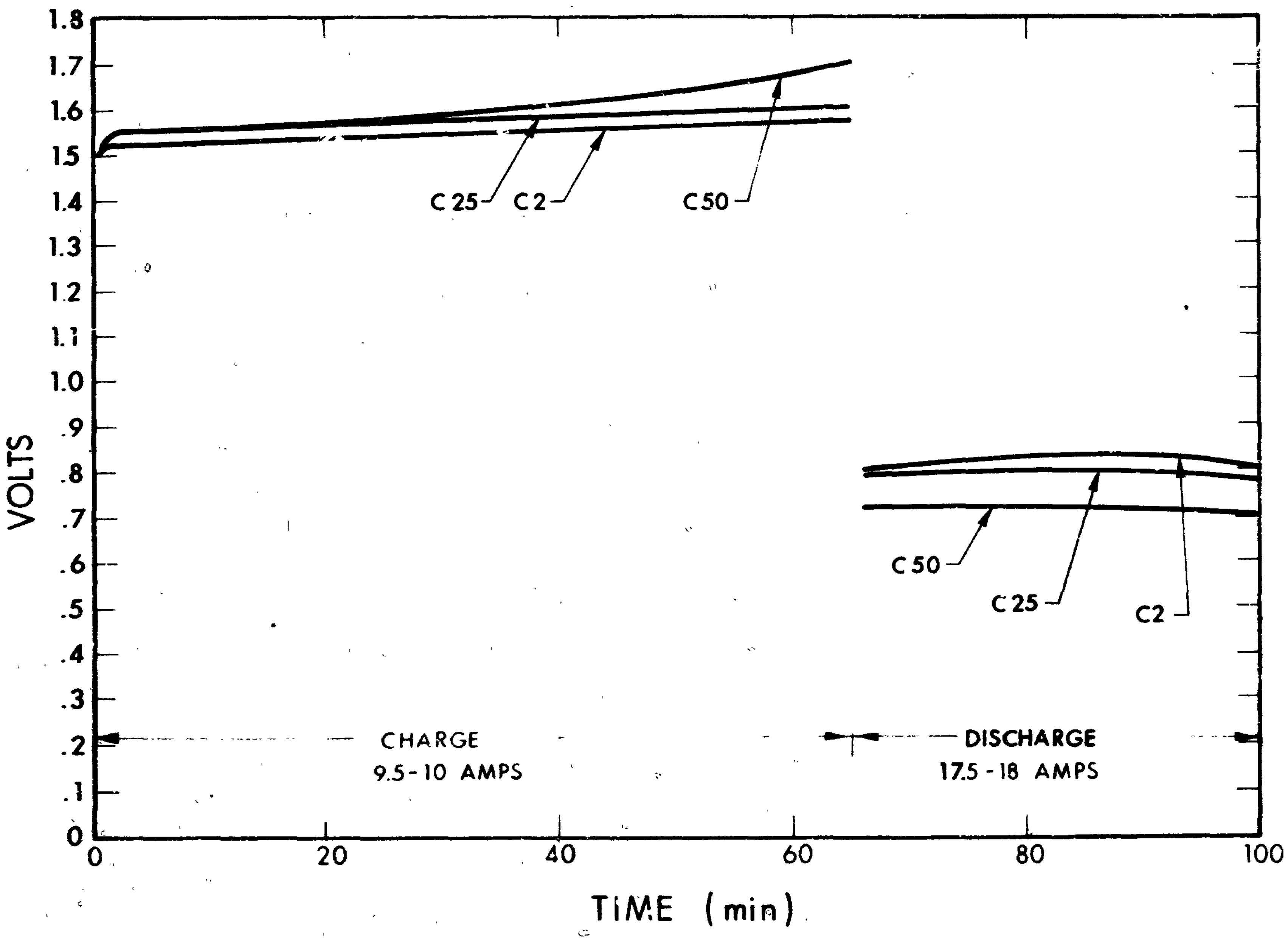

FIG. 2 CYCLING PERFORMANCE OF MODIFIED PLATINIZED AMERICAN CYANAMID ELECTRODE CELL SERIAL NO. 147

capabilities of American Cyanamid type electrodes, if the gradual deterioration in performance problem can be overcome.

Since the results of cells Nos. 145 and 146 were inconclusive, the repeat of this type test was conducted with cells 148 and 149. Cell 148 consisted of an American Cyanamid oxygen electrode and a nickel plaque hydrogen electrode. Cell 149 consisted of a nickel plaque oxygen electrode and American Cyanamid hydrogen electrode. In this case, the asbestos mats initially were impregnated with an additional two grams of electrolyte above that normally used in order to prevent sticking of the mats to the electrodes. The cells were charged continuously for two hours at 10 amps. and then disassembled. There were no obvious discolorations observed on either of the asbestos mats. The only conclusion that can be drawn is that it is necessary to run the cells for a longer period of time to encounter meaningful changes in the asbestos mat.

Cell No. 150 consisted of a modified American Cyanamid type AB-6 electrode of the type used in Cell No. 147 with the exception that instead of 7 milligrams of platinum being electrodeposited on the electrode, 15 milligrams of platinum per cm^2 were electrodeposited. Performance of this cell was mediocre, and cycling was stopped after the eleventh cycle. It was hypothesized that the additional platinum possibly was blocking the lower active material and was not accomplishing any useful purpose.

Cell No. 151 consisted of the original modified American Cyanamid electrode that was used in cell 147. The electrodes were washed and reassembled with a new asbestos mat. Initial performance of this cell indicated some performance improvement over that obtained from the latter cycle performance of cell 147. The cell was cycled intermittently for an additional 53 cycles with gradual degradation.

Cell 152 consisted of the modified American Cyanamid oxygen and hydrogen electrodes that were previously used in cell 150. The electrodes were washed and then assembled with a new asbestos mat. The cell exhibited fair performance very similar to what was obtained with cell 150. After 7 cycles, the test was discontinued.

Cell No. 153 consisted of a new set of electrodes containing 14 milligrams of platinum per cm^2 electrodeposited on porous nickel plaques that had been gold-coated. The cell was put on the test and subjected to two cycles. Performance of the cell was extremely poor, operating at about 0.5 volt at 10 amps. Therefore, the cell was disassembled, the electrodes were washed, and reassembled with a new asbestos mat, in a new cell designated Cell No. 154. This cell showed only a slight improvement in performance over the results of the previous cell. After two cycles, this test was also discontinued.

Cell No. 155 consisted of an oxygen electrode of the American Cyanamid type that had 15 milligrams of platinum electrodeposited on the surface assembled adjacent to the asbestos mat. The hydrogen electrode was a porous nickel plaque that contained 15 milligrams of platinum electrodeposited on the surface assembled adjacent to the asbestos mat. This nickel plaque contained no gold-coating. The cell was subjected to test, exhibited poor performance and after two cycles, the test was discontinued.

Cell No. 156 consisted of the gold-coated platinized electrodes previously used in Cell No. 154. The electrodes were washed and assembled in the cell with a new asbestos mat. This cell showed poor performance and after two cycles, the test was discontinued.

One conclusion to be drawn from this series of tests is that after three successive washings and test attempts, the electrodes always exhibit extremely poor performance. This can be attributed to one or more of the following causes:

(a) Chemical poisoning of the catalyst,
(b) Coating of the catalyst by substances from the matrix or electrolyte,
(c) Reduction of catalyst surface area,
(d) Physical loss of catalyst from the electrode to the mat.

Another conclusion to be drawn is that the loss of KOH (noted in most runs) is not a primary mode of cell deterioration, since mat replacement does not improve performance of deteriorated cells to any appreciable extent. This facet was again verified in Cell No. 157. This cell consisted of the modified American Cyanamid electrode and the platinized nickel electrode previously used in Cell 155. These electrodes were washed and assembled with a new asbestos mat to see if the washing process would improve the performance. The cell showed very poor performance and after one cycle, the test was discontinued.

Cell No. 158 consisted of a porous nickel plaque oxygen electrode that was gold-coated at EOS and platinized by Bishop Metals to half the depth of the electrode with 7 milligrams of platinum per cm^2. An additional 15 milligrams of platinum per cm^2 was electrodeposited at EOS on the heavy platinum side which was assembled adjacent to the asbestos mat. The hydrogen electrode employed was a standard gold-coated platinized nickel plaque containing 15 milligrams of platinum per cm^2. The cell showed good initial performance, however, the cell developed a leak and the test was discontiued after 8 cycles. These electrodes will be retested in a new cell setup.

Cell No. 159 consisted of the modified American Cyanamid electrode employed in Cell No. 157 on the oxygen side, an American Cyanamid electrode on the hydrogen side, plus a new asbestos mat. Performance was poor again, and the test was stopped after 17 cycles.

A considerable number of tests have been made with Cyanamid and EOS electrodes. Table 2 compares these based upon an overall observation of performance. It is our belief that the ideal regenerative electrode would combine certain aspects of the EOS and Cyanamid electrodes. Desirable electrode features are as follows:

(1) No nickel content,

(2) Relatively thick (20 mil) porous substrate catalyzed uniformly in depth,

(3) Catalyst loading of 10 - 20 mg/cm^2,

(4) Catalyst mechanically bonded to substrate.

The desirability of wet-proofing is not well defined as yet, but indications are that it is not required.

TABLE 2

ELECTRODE PERFORMANCE COMPARISON

Performance Test	Std. EOS 20 mg/cm^2	Am. Cya. AB4, AB6, 9 mg/cm^2	Gold-Plated EOS, 7-14 mg/cm^2
Charge Performance	Very good	Fair to Poor	Very good
Discharge Performance	Good	Excellent at peak. Poor to Fair at beginning and end of cycle.	Fair
Cycle life	Fair	Poor	Fair
Oxidation resistance of substrate	Poor	Excellent	Initially fair, gradually changing to poor.

2.2 Multicell Testing

In accordance with the program work statement, any single cell electrode type having a cycle life capability of > 100 hours at a satisfactory performance level is to be evaluated in a 6-cell test assembly. The gold-coated, electro-platinized nickel substrate electrodes exceed this criterion. Therefore, a 6-cell, 75-watt nominal battery was assembled. The 6-cell unit, designated serial No. 108, was similar in construction to the multicell unit serial No. 107, described in the 4th Quarterly Report dated 18 July 1965, with the following exceptions:

1. The electrodes on both the hydrogen and oxygen sides were gold-plated nickel plaques platinized to 14 mg/cm^2.
2. The backup gas distribution screens behind the electrodes and the bipolar plates were gold-plated to prevent possible oxidation of the nickel surfaces.
3. The hydrogen and oxygen end plates employed were of the type used in the 34 multicell design that allows for the incorporation of the end stack electrodes directly on the end plate.
4. A bellows with a modified flange to accommodate the 34 cell end plate.
5. A new teflon bellows stop to compensate for stack length changes caused by (3) and (4).

The cell was operated for 10 cycles at which time a short developed that fully discharged the unit to 0 volts. The short was traced to a failure of the insulation on the main feed-thru terminal through the stack. This terminal consisted of a 1/4 inch copper rod that is sealed and insulated from the tank by means of a teflon ring. Apparently this ring of teflon gradually flowed allowing the copper rod shank to short out. Difficulties with this fitting have been encountered in the past, and it was decided to replace this with a different feed-thru that employs a 1/8 inch copper rod and allows for a much thicker teflon insulation ring.

The feed-thru terminal was replaced and the cell was once again subjected to test. The cell was operated for an additional 70 cycles on an intermittent basis due to gradual differential pressure buildups that indicated possible gas leakage. The voltage performance of the unit is presented in Figure 3. As can be seen, there is a gradual degradation in performance as the cycling continues. The unit is still under test and additional cycling will be conducted.

2.3 Analytical Tests

An analytical test of a gold-coated carbonyl nickel plaque was conducted to determine the quantity of gold that is actually deposited in the plaque. The electroless process employs 400 cc per electrode of a solution that contains one ounce of gold per gallon. This results in the theoretical deposition of 3.29 grams of gold per plaque. Next, the plaque is electroplated with gold at a half an ampere per hour, resulting in a theoretical yield of 3.66 grams of gold. Therefore, the total theoretical yield is 6.95 grams of gold per electrode. In the analytical test, a standard gold-coated plaque was dissolved in acid, yielding 6.64 grams of gold. This represents slightly better than 95 percent of the theoretical gold employed. The test was conducted as a check of our processing, to assure that we were obtaining the gold coverage intended.

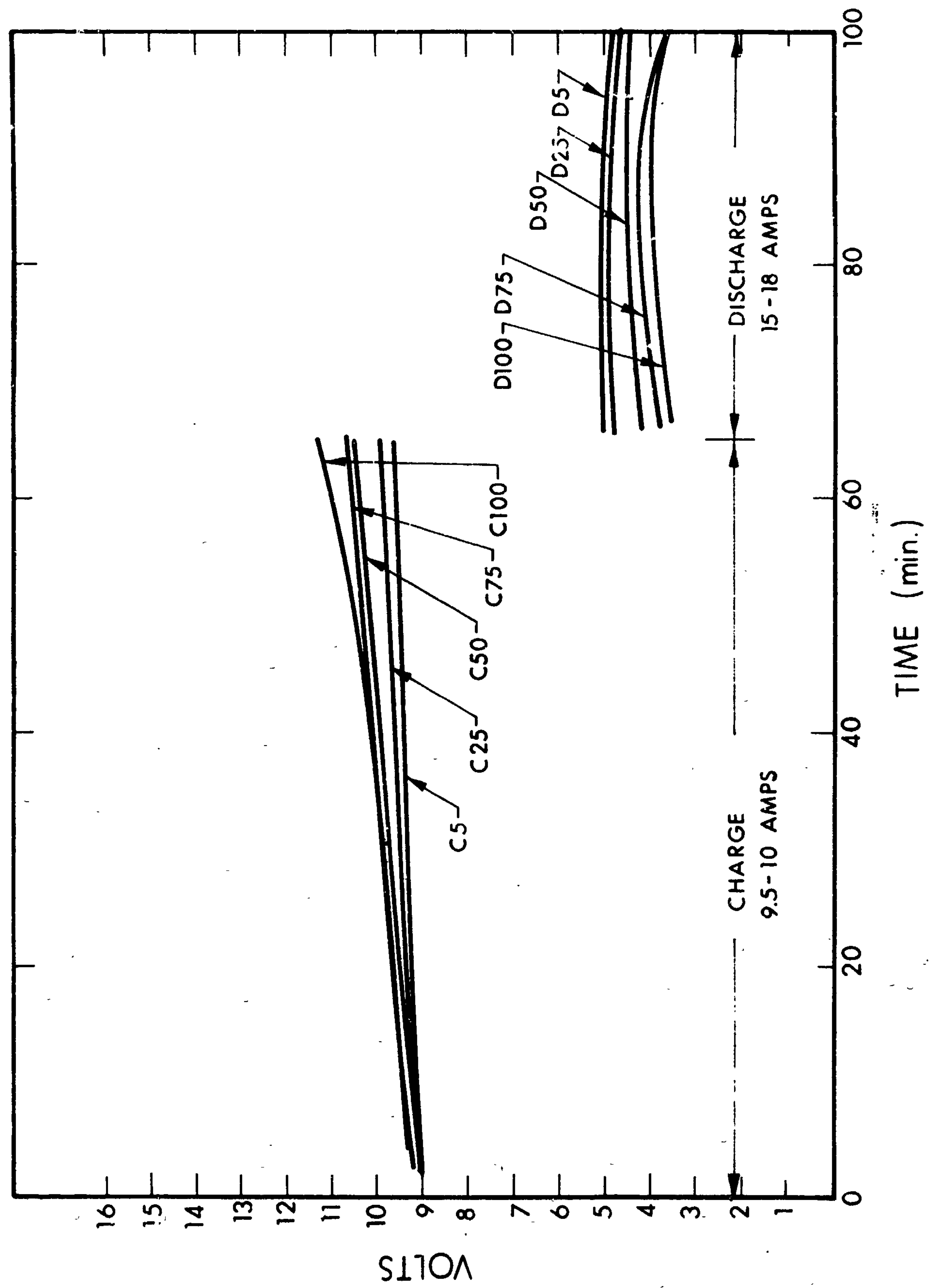

FIG. 3 CYCLING PERFORMANCE OF 6-CELL REGENERATIVE FUEL CELL SERIAL NO. 108

3. PLANS FOR THE NEXT PERIOD

At the end of this test period, a technical meeting was held with Messrs. H. Schwartz, D. Soltis and P. Pomerantz of NASA, and Messrs. M. Klein and E. Findl of EOS in attendance. The discussions included a review of past test results and conclusions to be drawn from some plus tests and test methods to uncover the primary mode of cycle life failure. In addition, a priority status was given to each test. The new tests are given in Table 3.

Tests already in progress will be continued. A second six-cell battery will be assembled using components identical to battery SN-108 to evaluate duplicability of test results. Certain modifications of Pt catalyst loading and Aμ corrosion plating to improve performance will be made using the porous nickel plaques.

TABLE 3

REVISED TEST PLAN

First Priority Tests

1. Assemble a single cell and operate same as an O_2 concentration cell at ≈ 150 PSIG in a continuous mode at 100 ma/cm^2. Parameters to be evaluated are:
   - (a) effect of charge and discharge on cell performance;
   - (b) Pt migration into matrix.

   This test is to be conducted to eliminate high voltage i.e., $>$ 1.5 volts, effects on the matrix and to see if long term performance can be achieved if cycling is eliminated.
2. Assemble a single cell and operate same as an O_2 concentration cell at ≈ 150 PSIG in a cyclic mode at 100 ma/cm^2. Parameters to be evaluated are:
   - (a) effect of cyclic operation;
   - (b) Pt migration into matrix.

   This test complements Test 1 to determine if it is low voltage cycling that causes degradation.
3. Set up asbestos quality control procedure. Two criteria are to be investigated, using 50 mats as the test samples. The criteria are: (a) gas porosity of the dry mat, and (b) weight.
4. Pretreat electrolyte to eliminate any possible contaminants. Two procedures are to be employed, namely triple distillation of the water solvent and pre-electrolysis of the KOH electrolyte.

Second Priority Tests

5. Study possible changes in Pt catalyst characteristics by (a) measurement of electrode surface area before and after cycling; and (b) measure crystalographic properties of catalyst before and after cycling.
6. Evaluate matrices other than fuel cell grade asbestos. Initial suggested materials included potassium titananate paper, acid leached fuel cell grade asbestos and non-reactive porous plastics.

7. Evaluate the chemical purity of the fuel cell grade matrix by electrolyzing an asbestos pulp in pre-purified electrolyte after a 24 hour soak at ~ 80°C The electrolyzed asbestos pulp is to be reconstituted and formed into a mat for testing in a single cell.
8. Evaluate the performance of Chem Cell Corp. electrodes in single cells.

<u>Third Priority Tests</u>

9. Purchase and test Cyanamid type AB-6 electrodes having pure gold backup screens to eliminate any possibility of nickel contamination.
10. Evaluate cell performance using optimum electrodes, optimum mat and high purity pre-electrolyzed electrolyte.
11. Set up a single cell using two multicell end plates plus a 6-cell bellows in the six-cell tankage to eliminate ΔP effects.

4. FINANCIAL STATEMENT

Man hours and dollar expenditure for the period 28 January 1966 through 4 March 1966 were as follows:

Direct Labor Hours	1,193.50
Direct Labor Dollars	$5,292.09
Purchases and Commitments	$5,404.21
Total Dollar Expenditure	$20,601.15