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 October 1 through November 1, 1965.

During this period, primary emphasis was placed on processing and testing single cells with various electrode structures in order to improve the cycle life capabilities of the oxygen electrode. Work was initiated on the determination and evaluation of the effects on the asbestos mat as a result of reactions with potassium hydroxide, and or changes that occur due to cycling in the regenerative fuel cell.

2. TECHNICAL DISCUSSION

2.1 Single Cell Tests

Seven single cell tests were conducted during this period to evaluate the performance of various electrode structures. Test results and construction variables of these cells are summarized in Table 1. Cell number 98 consisted of the same electrodes utilized in cells number 92 and 97, the results of which reported in the fifth quarterly report. The oxygen electrode was American Cyanamid type electrode employing 9 mgs. of platinum per sq. cm. with the nickel subscreen gold plated. The electrodes were washed after the use in previous tests, and a new asbestos mat was employed. The cell was cycled 30 times on a standard test cycle of 65 minutes charge at 9-10 amps, and 35 minutes of discharge at 15-18 amp. During the discharge, the voltage fell off after approximately 20 minutes of discharge indicating a flooding of the electrode. This performance was consistant throughout the first 30 cycles. Thereafter, the charge and discharge currents were reduced to 5 amps on charge, and 7.5--8 amps during discharge to avoid the fall-off in performance previously observed. The cell was cycled continuously fo an additional 95 cycles for a total of 125 cycles. During the reduced current cycling, the voltage during discharge reduced slightly. The final electrolyte concentration of the asbestos mat was analyzed to be 33.4 percent. Figure 1 shows the voltage performance of the cell at various cycles.

Cell number 99 consisted of oxygen and hydrogen electrodes of the EOS type fabricated of platinized porous nickel plaques. The cell was assembled and put on a standard test cycle of 65 minutes charge, 35 minutes discharge as a control. It was cycled continuously for 100 times during which the discharge performance showed a very slight degradation.

TABLE I

SUMMARY OF SINGLE CELL TESTS

Cell No.	O_2 Electrode No.	O_2 Electrode Catalyst	H_2 Electrode No.	H_2 Electrode Catalyst	Mat Thick. Inches	Mat Dry Wt. Gms.	Electrolyte % KOH	Electrolyte Wt. Gms.	Comments	Results
98		9 Mg.Pt./	215	20 Mg.Pt./	0.060	27.1	39.9	31	Oxygen electrode Cyanamid	125 cycles 30 @ high rate, 95 @ low rate
99	216	20 Mg./ cm^2	206	20 Mg.Pt./ cm^2	0.060	27.2	39.9	31.1		100 cycles. Showed good performance
100	2 ea.	9 Mg.Pt./ cm^2	215	20 Mg.Pt./ cm^2	0.060	27.0	39.9	31.1		60 cycles sensitive to water content.
101	2 ea.	9 Mg.Pt./ cm^2	215	20 Mg.Pt./ cm^2	0.060	27.1	39.9	31.0		15 cycles. Same performance as cell 100.
102		20 Mg.Pt./ cm^2	210	20 Mg.Pt./ cm^2	0.060	26.2	39.7	31	O_2 electrode Ni plaque gold coated and platinized	Cells shorted out after 5 cycles.
103		20 Mg.Pt./ cm^2	210	20 Mg.Pt./ cm^2	0.060	28.0	39.7	31	Repeat of cell No. 102	Still cycling, achieved 120 cycles.
104		9 Mg.Pt./ cm^2		9 Mg.Pt./ cm^2	0.060	27.5	39.7		Used rewashed Cyanamid AB 6.	Still cycling Achieved 100 cycles.

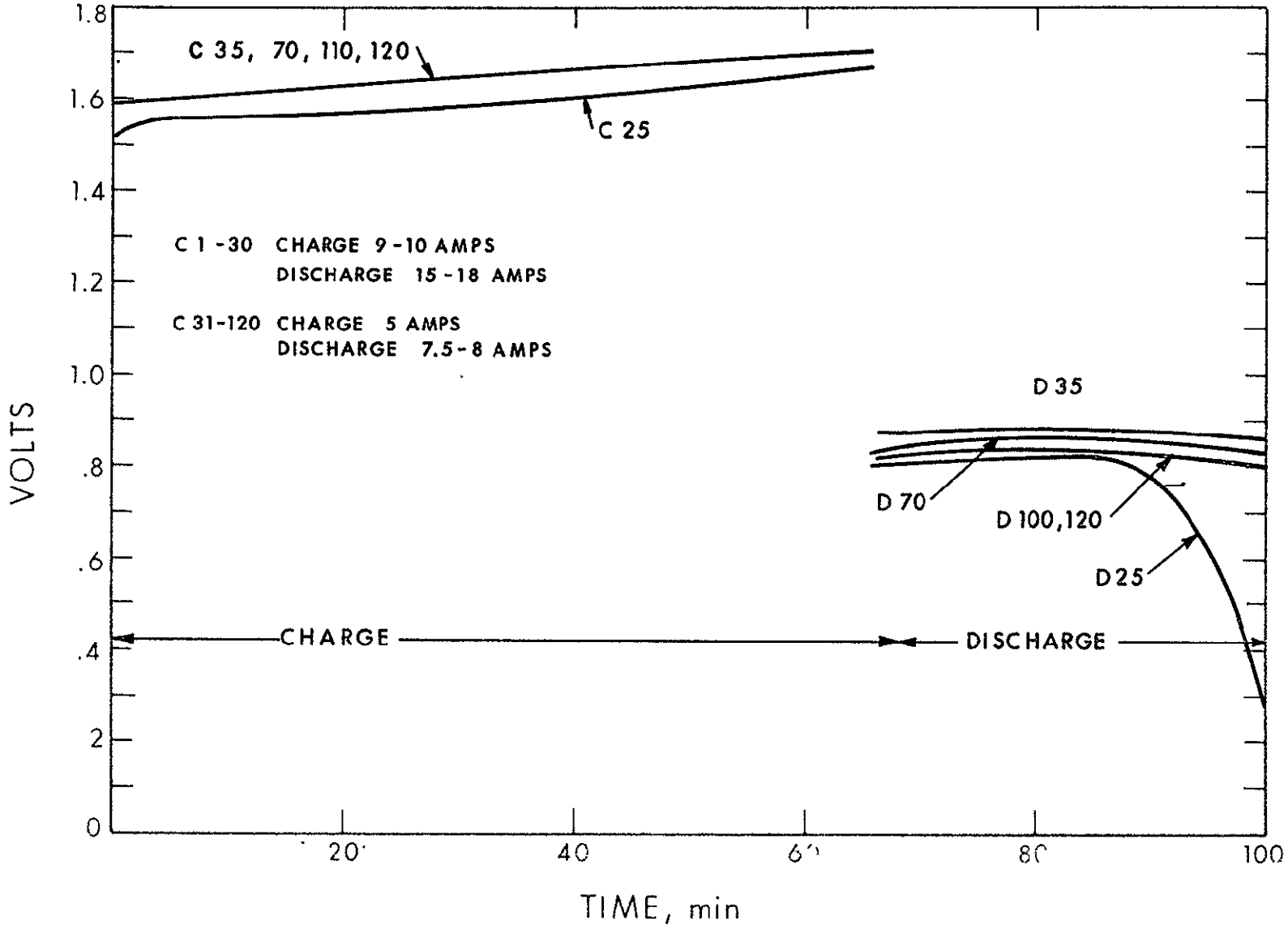

FIG. 1 CYCLING PERFORMANCE OF CELL NO. 98

The mat from this cell was removed, and saved for the purpose of determining effects in the asbestos. The performance data is shown on Fig. 2.

Cell number 100 consisted of two Cyanamid 9 mg. platinum per sq. cm. (gold plated nickel screen) electrodes back to back on the oxygen side, and a standard EOS platinized nickel plaque on the hydrogen side. Purpose of the test was to determine if the back to back oxygen electrodes would reduce the sensitivity to water content, i.e., flooding out and drying observed with American Cyanamid Electrodes when used in the regenerative fuel cell. The cell was cycled continuously for 60 times on the standard cycle. A typical cycle is shown in Figure 3. As can be seen, even with the back to back oxygen electrodes, the cell exhibited a gradual rise in voltage at the end of charge (indicating drying out) and a dip in the voltage initially during discharge, and rapid fall-off in voltage toward the end of discharge (indicating flooding). However, during the middle of discharge, the performance of these electrodes was excellent.

Cell number 101 was a repeat of the previous cell number 100 utilizing the same electrodes after they had been washed and employing a new asbestos mat. The performance of the cell was virtually identical to the previous cell, and the test was stopped after 15 cycles.

Cell number 102 consisted of a standard porous nickel plaque 20 mg. platinum per sq. cm. hydrogen electrode, and a new type oxygen electrode. This oxygen electrode was fabricated at EOS by gold plating then platinizing a standard porous nickel plaque.

The procedure used in preparing these new electrodes is similar to that used in fabricating our standard type. The steps are as follows:

1. Plaques are washed and degreased.
2. A hot (190-200°F) electroless gold plating solution is
   ntinuously recycled through the plaque. The plating
   lution is a commercial material designated Aurolectroless-N,
   nufactured by Lee Ronal Inc. It contains 1 troy ounce of
   ld per gallon. The average plating thickness obtained is
   50 micro inches.

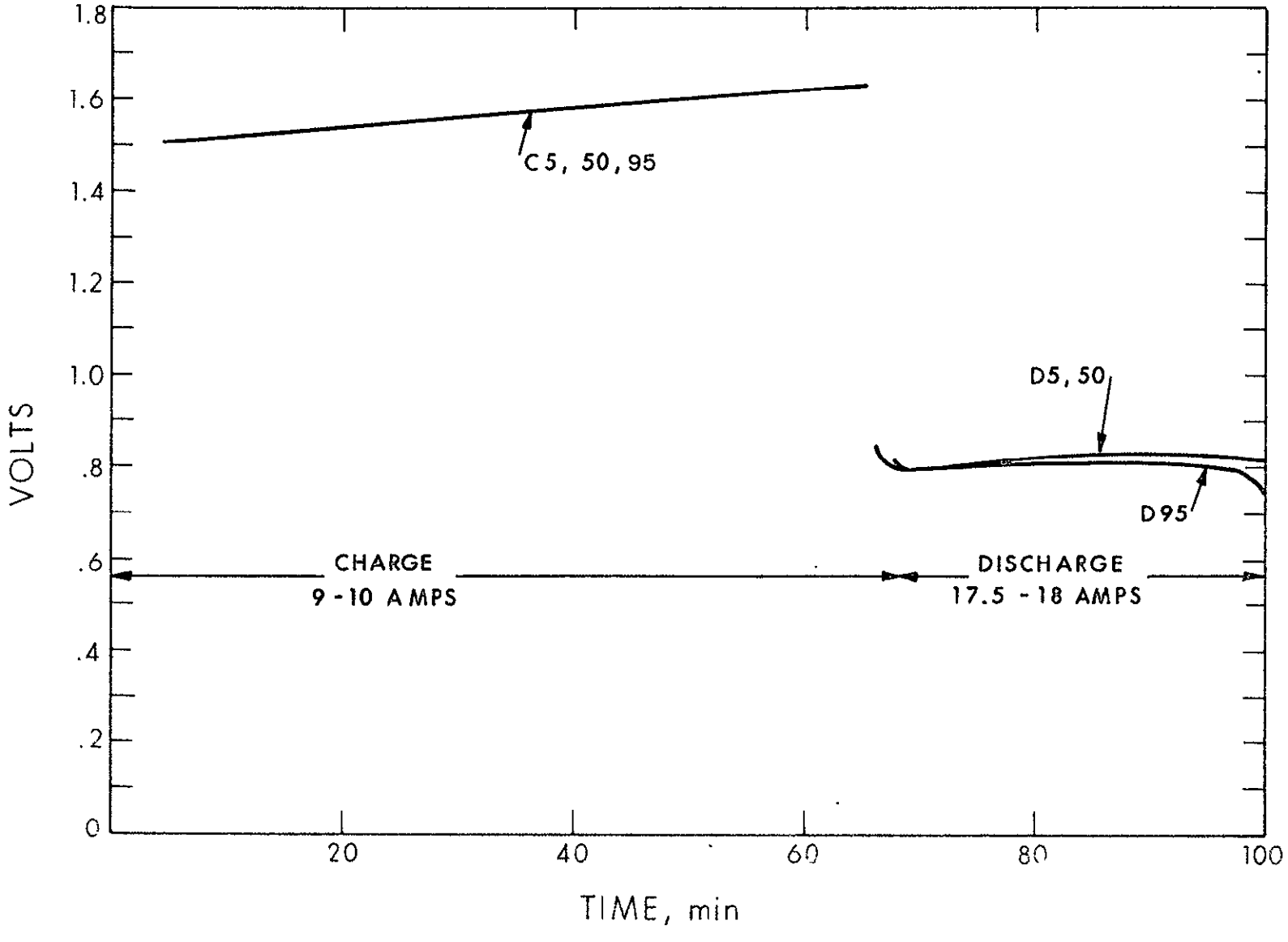

FIG. 2 CYCLING PERFORMANCE OF CELL NO. 99

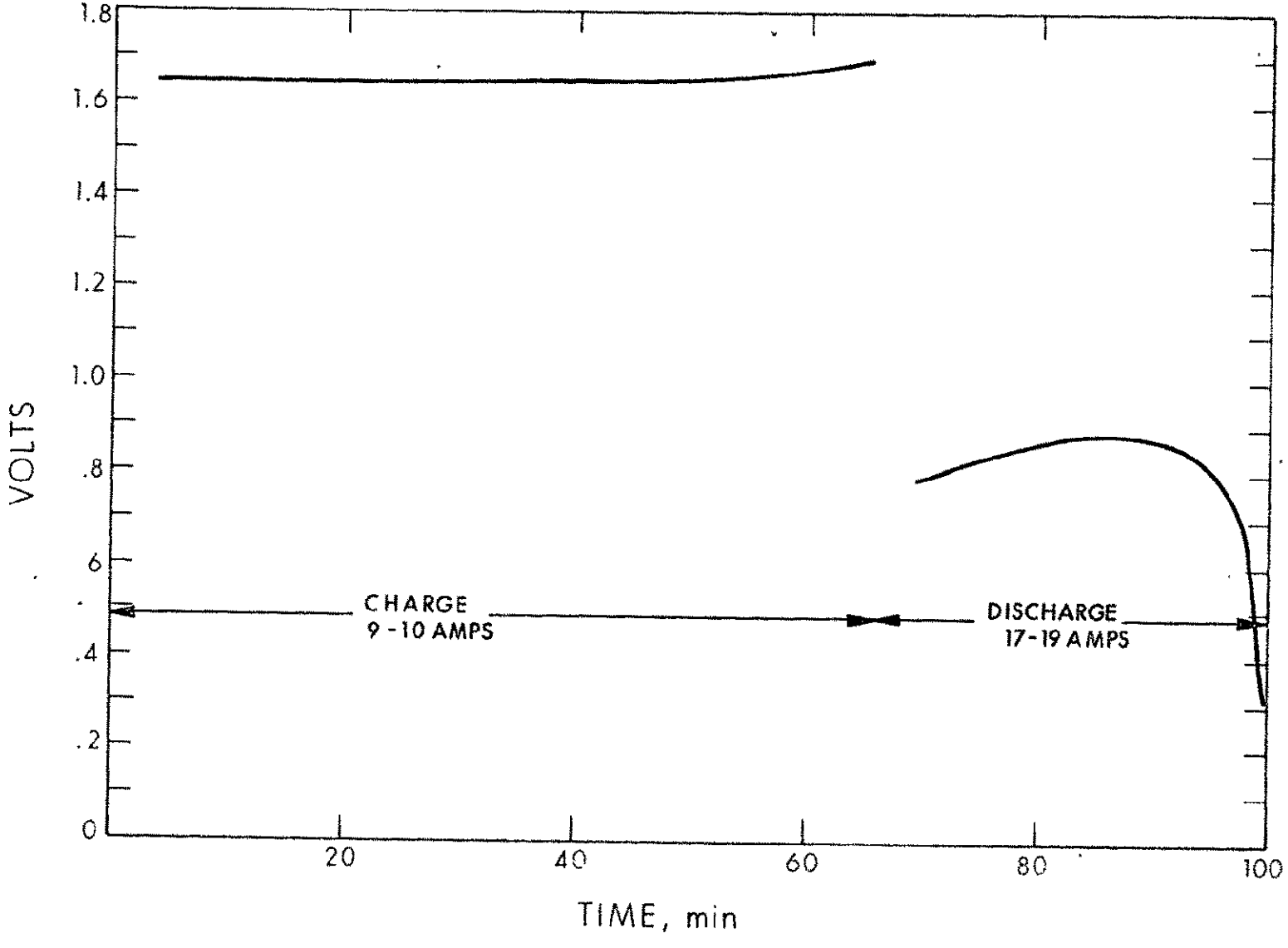

FIG. 3 PERFORMANCE DATA OF TWO CYANAMID ELECTRODE BACK TO BACK AS OXYGEN ELECTRODES

3. After removal from the electroless bath, the electrodes are washed then immersed in a gold cyanide electroplating bath. An electroplating thickness of an additional 50 micro inches is then put on the electrodes.
4. After removal from the gold electroplating bath, the electrodes are washed and immersed in a chloroplatinic acid plating bath. Platinum is plated on the electrode to an equivalent of 20 mg/cm^2.

Cell number 102 was cycled 5 times and then developed an internal short. It was disassembled and examined. The short was found on the edge of the electrodes due most probably to poor assembly. The electrodes were washed, assembled with a new asbestos mat and designated cell number 103.

Cell 103 has achieved 120 cycles, and is still on cycle. Results obtained thus far are shown in Figure 4. No substantial degradation has occurred as yet. This gold plating approach appears to be a promising technique for improving the life of the oxygen electrode.

Cell number 104 was installed with American Cyanamid H_2 and O_2 electrodes having 9 mg. platinum per sq. centimeter on gold plated nickel screens. This test was set up to determine effects that occur in the asbestos without "free" nickel being present in the electrodes. The cell was cycled continuously for 100 cycles. It showed a gradual degradation in performance with cycling. It is intended to disassemble the cell, wash the electrodes, reinsert them, and then, utilizing the same asbestos mat, see if this will improve performance. If performance improves, it can be surmised that some water soluble coating on the electrodes causes degradation. If performance remains degraded, it can be surmised that the asbestos is the cause of degradation.

2.2 Asbestos Studies

Asbestos samples taken from multicell unit serial number 1003-34 (the test results of which were reported in the fifth quarterly report) was submitted to an outside testing laboratory for a semi-quantitative spectrographic analysis. Two samples of used mats were

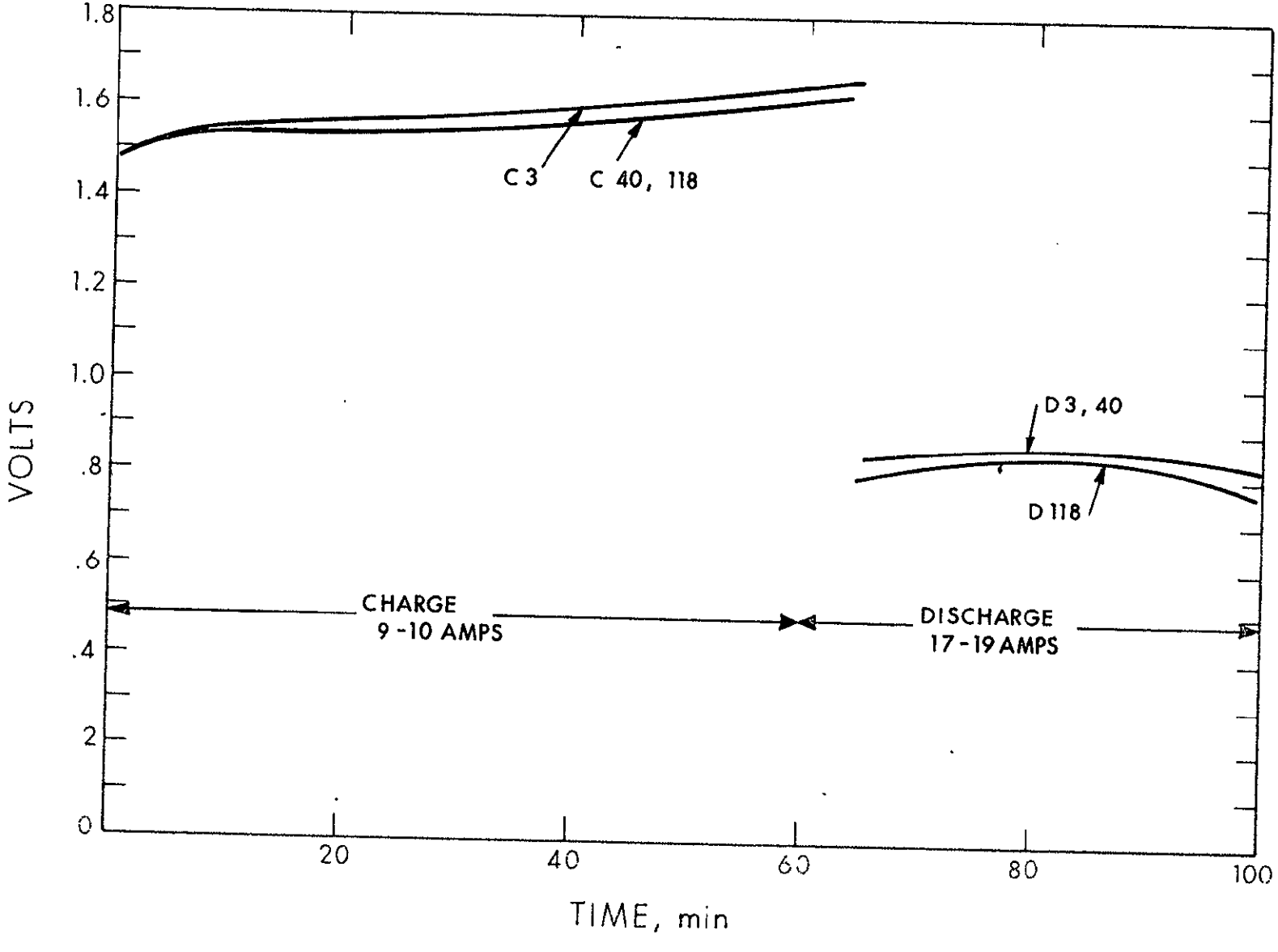

FIG. 4 CYCLING PERFORMANCE OF CELL NO. 103

prepared by mixing fuel cell grade asbestos in a blender to obtain a homogeneous mixture. A third sample was prepared utilizing a fresh asbestos mat by homogenizing it with distilled water. The results of the analysis are presented in Table II. The major difference between these and previous test results was the large percentage of calcium found in the asbestos mats Prior spectrographic analyses showed calcium concentrations in the tenths of a percent range. However, the asbestos material used in these tests represents a new lot of material recently received from Johns Manville. Possibly there is this variation in the raw material. Two samples of dry asbestos, one from the previous shipment, and one from the new lot have been submitted to an analytical testing laboratory to confirm this point.

The semi-quantitative spectrographic analysis method is not suitable for the measurement of major constituents, accurately. Therefore, a wet analytical procedure will be utilized to determine the actual elemental composition of the asbestos material.

An additional spectrographic analysis was made on reaction products scrapped from certain bipolar plates in cell assembly 1003-34. In appearance, this material was black and gummy containing a quantity of moisture. The analysis showed it to be principally nickel, with a quantity of potassium (from the KOH electrolyte) and a small percentage of platinum (from the electrodes). Here again is a demonstration of the conversion of nickel (from the O_2 electrode and bipolar plate) to the hydroxide as a function of cycling.

A test of fuel cell grade asbestos in excess concentrated potassium hydroxide at elevated temperatures was made to verify that the material dissolves. A sample of asbestos was enclosed in a nickel screen and hung in a metal beaker containing 70 percent KOH heated to 150°C. For a 70 percent concentration of KOH, the boiling point is slightly above 200°C.) After a period of 4 hours, the nickel screen was removed. The asbestos had entirely disappeared. This result confirms previously reported results by American Cyanamid. A similar test at

TABLE II

ASBESTOS SPECTROGRAPHIC ANALYSIS

	Pure Asbestos Sample	Samples Taken From Fuel Cell S/N 1003-34	
Ag	.0005%*	.0005%*	.0005%*
Al	.08%	.09%	.01%
As	.05%*	.05%*	.05%*
B	.01%	.01%	.01%
Ba	.08%*	.08%*	.08%*
Be	.0001%*	.0001%*	.0001%*
Bi	.001%*	.001%*	.001%*
Ca	8.5%	7.%	8.5%
Cd	.05%*	.05%*	.05%*
Co	.007%*	.007%*	.007%*
Cr	.008%*	.008%*	.008%*
Cu	.01%	.02%	.01%
Fe	.2%	.01%	.1%
K	Not Detected	Rem.△	Rem.△
Li	.1%*	.1%	.1%*
Mg	21.%	15.%	5.%
Mn	.04%	.005%	.001%
Mo	.01%*	.01%*	.01%*
Na	.07%*	.15%	.1%
Nb	.01%*	.01%*	.01%*
Ni	.005%*	.05%	.07%
Pb	.007%*	.007%*	.007%*
Sb	.02%*	.02%*	.02%*
Si	16.5%	8.5%	3.5%
Sn	.005%*	.005%*	.005%*
Sr	.01%	.005%	.005%
Ti	.003%*	.003%*	.003%*
V	.005%*	.005%*	.005%*
Zn	.1%*	.1%*	.1%*
Zr	.003%*	.003%*	.003%*
Pt	.01%*	.17%	.13%

*Less Than

Anion---Rem.

△ Plus Anion

150°C and 60 percent potassium hydroxide revealed some loss in the asbestos, but we were unable to determine the exact loss, due to shedding of the remaining material during washing after the test. These tests were conducted with a considerable excess of electrolyte. In a fuel cell, such a dissolution process is not necessarily significant because of the minimal quantity of electrolyte used.

2.3 Instrumentation

Detailed wiring diagrams and equipment procurements have been prepared to expand our testing capabilities. An instrumented set-up is being prepared having the capability of testing five single cells, two 6 cell units, and one 34 cell-unit simultaneously. The heart of the testing complex will consist of a data acquisition system that employs a digital volt meter, a scanner, (to automatically switch the DVM to one of 100 channels), and a printer for readout of the channel being monitored. With this system it will be possible to record continuously individual cell voltages, current, pressures, and temperatures for long term cycling tests. Some of the components of the instrumentation system have been received and assembly of the system has been initiated.

3. PLANS FOR THE NEXT PERIOD

Single cell tests will be continued to evaluate various oxygen electrode structures including porous nickel plaques and felt metal nickel plaques that have been gold coated at EOS and (a) platinized by Bishop Platinum using a proprietary process, and (b) at EOS by electroplating. Electrodes have also been ordered from American Cyanamid with nickel subscreens that have a minimum of 100 microns gold to assure pin and pore free coatings on the nickel subscreen.

Analytical tests will be conducted on samples of asbestos to determine lot variations, raw material constituents, and what effects occur in asbestos as a result of direct reaction with potassium hydroxide and or the effects of cycling in a regenerative cell. The new instrumentation set up will be assembled and utilized in single cell testing.

4. FINANCIAL STATEMENT

Manhours and dollar expenditure for the period October 1, 1965 through October 29, 1965 were as follows:

Direct Labor Hours	767
Direct Labor Dollars	$3,338.46
Purchases and Commitments	$22,255.84
Total Dollar Expenditure	$35,423.14