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HYDROGEN-OXYGEN ELECTROLYTIC REGENERATIVE FUEL CELLS

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16. Abstract The objectives of this program were to evaluate the processes, materials, and components that limit the cycle life of regenerative hydrogen-oxygen fuel cells. A composite capillary matrix was developed, tested, and demonstrated to be superior to fuel-cell-grade asbestos and other more commonly used matrix materials. Matrix materials manufactured and submitted by TRW were evaluated in this phase of the work. Extended cycle testing, followed by examination of the components of several cells, demonstrated that platinum metal migrates from the oxygen electrode into the matrix. X-ray diffraction analyses of several matrices showed changes in both the crystalline form and the uniformity of composition after extended cycling. For the electrode and matrix combination found to be best for the regenerative fuel cells, operation at 80° C exhibited considerably better cycle life than cells cycled at 50° C.			
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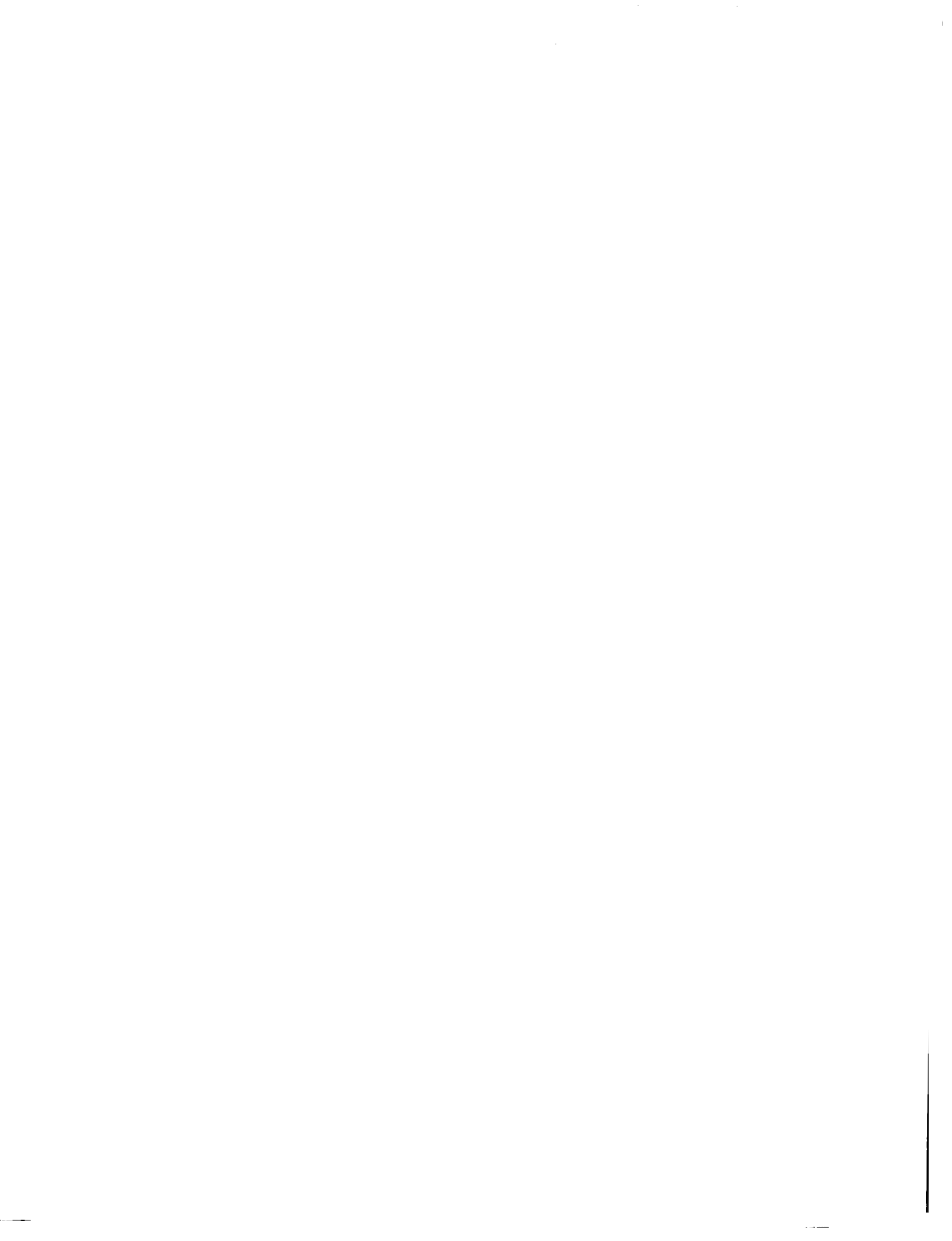
FOREWORD

The work described in this report was performed by Electro-Optical Systems under NASA contract NAS 3-10948 with Mr. Daniel G. Soltis, Direct Energy Conversion Division, NASA Lewis Research Center, as the Project Manager. The report was originally issued as Electro-Optical Systems report EOS-4007.



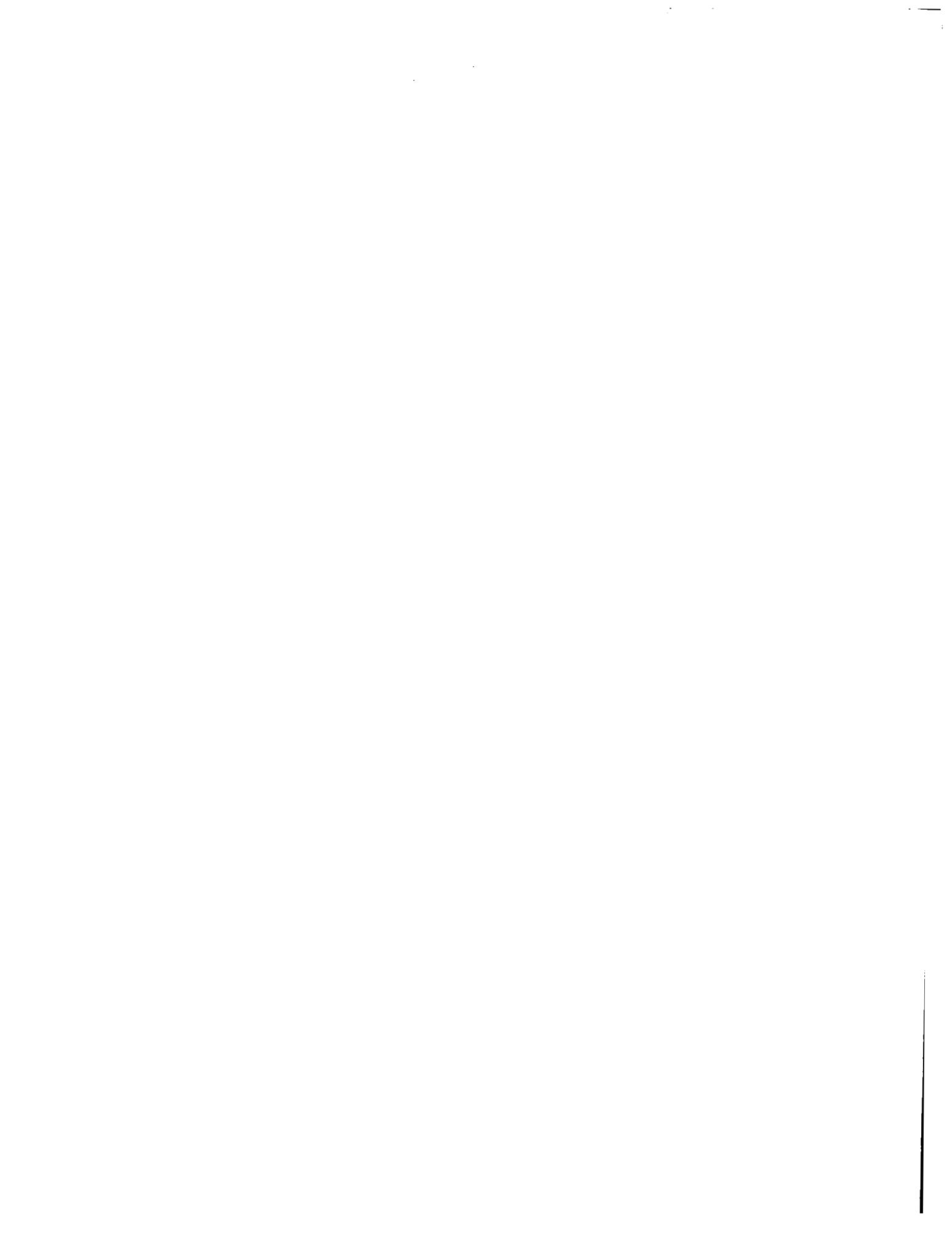
CONTENTS

1.	INTRODUCTION	2
2.	TECHNICAL DISCUSSION	4
2.1	Test Cell	4
2.2	Matrix Comparison Tests	5
2.2.1	Pressed Composite Matrix	5
2.2.2	Layered Pasted Membrane Matrix	14
2.2.3	Rolled Potassium Titanate and Teflon Matrices	19
2.2.4	Other Types of Matrices	21
2.3	Materials Studies	21
2.3.1	Cells with Polysulfone Backup Plates	27
2.3.2	Cells without Gold on Backup Plates and Screens	27
2.3.3	Special Tests for X-ray Diffraction Analysis	30
2.3.4	KOH Concentration Loss	34
2.3.5	Stability of Potassium Titanate	34
2.3.6	Catalyst Migration Tests	37
2.3.7	PT Migration in Electrolyte	42
2.3.8	Gold and Platinum Analysis in Fuel Cell Matrixes	42
2.4	Life Testing	47
2.4.1	90-Minute Cycle at 80°C	47
2.4.2	90-Minute Cycle at 50°C	52
2.4.3	24-Hr Cycle at 80°C	55
2.4.4	Modified 24-Hr Cycle at 80°C	55
2.4.5	Modified 24-Hr Cycle at 50°C	58
2.4.6	3.5 Hr Cycle at 50°C	58
2.4.7	Repeat of 90 Min Cycle at 80°C	62
2.5	TRW Matrices	75
2.5.1	CeO Matrices	75
2.5.2	ZrO Matrices	75
2.5.3	KT Matrices	79



CONTENTS (contd)

3. DISCUSSION OF RESULTS	81
4. CONCLUSIONS	85
ADDENDUM	87



ILLUSTRATIONS

1	Single Test Cell in Oven	6
2	Single Cell - Test Assembly	7
3	Single Fuel Cell Test Station	8
4	Bubble Cell Cross Section	12
5	Performance of Cell No. 3-A	15
6	Performance of Cell No. 8-A	20
7	Cycle Performance of Cell 28-A	28
8	Cycle Performance of Cell 39-A	29
9	Cycling Performance of Cell 21-A	31
10	Electrolyte Concentration Drop versus Cell Cycles	35
11	Cycle Performance of Cell 67-A	40
12	Charge and Discharge Polarization of Cell 67-A	41
13	Pt Migration in 30% KOH	44
14	Cycle Performance of Cell No. 29-A	53
15	Cycle Performance of Cell No. 33-A	54
16	Cycle Performance of Cell No. 53-A	56
17	Cycle Performance of Cell No. 63-A	57
18	Cycle Performance of Cell No. 64-A	59
19	Cycling Performance of Cell No. 65-A	60
20	Charge and Discharge Polarization of Cell No. 65-A	61
21	Cycle Performance of Cell No. 74-A	63
22	Cycle Performance of Cell No. 72-A	65
23	Charge and Discharge Polarization of Cell No. 72-A	66
24	Cycle Performance of Cell No. 73-A	67
25	Cycle Performance of Cell No. 75-A	68
26	Performance of Cell No. 76-A	69
27	Cycle Performance of Cell No. 77-A	71
28	Charge and Discharge Polarization of Cell 77-A	72
29	Cycle Performance of Cell No. 78-A	73
30	Cycle Performance of Cell 79-A	74
31	Cycle Performance of Cell No. 80-A	76
32	Charge/Discharge Characteristics of Cell No. 63-A	80

SUMMARY

The object of this program was to determine what processes and/or components limit the cycle life of the Electro-Optical Systems (EOS) hydrogen-oxygen regenerative fuel cell. The cell concept employed uses a capillary electrolyte matrix, located between two fuel cell electrodes, which serves as the medium for water storage during the charge and discharge processes. The gases are stored integrally under pressure.

Tests were performed to determine the most suitable type of matrix to be used as a standard. The matrix selected was a composite of 80% potassium titanate (KT), 10% asbestos, and 10% Teflon. These materials were formed into a mat and pressed.

Material study tests were conducted to determine the effects of component materials on the cycle life of the cells, and to determine what changes occurred in the cell components with cycle life. These tests revealed migration of gold and platinum metals as well as structural and other changes in the electrolyte matrix. It was demonstrated that the source of the migrating catalyst was the O_2 electrode. It was shown that the concentration of the KOH electrolyte became lower as cycle life increased.

Life testing consisted of cycling regenerative fuel cells using a 90-min cycle at $80^{\circ}C$ and at $50^{\circ}C$. Twenty-four-hour cycles were performed at $80^{\circ}C$ and $50^{\circ}C$. It became apparent from these tests that the cycle life of a cell is reduced when operating at $50^{\circ}C$ as opposed to $80^{\circ}C$.

Three types of electrolyte matrices manufactured by TRW have been tested. These matrices appear to be unsuitable for use in the regenerative fuel cell.

SECTION 1

INTRODUCTION

This report reviews the progress made on the development of the regenerative hydrogen-oxygen fuel cell under Contract NAS3-10948 during the period 1 April 1968 through 30 January 1970.

The electrolytic regenerative hydrogen-oxygen fuel cell is an energy storage concept that can provide high energy density, light weight, and reasonably long life.

To develop this concept into usable hardware for orbital and interplanetary space applications, Electro-Optical Systems, a Xerox Company, conducted a research and development program to define the design and operational parameters and the problem areas involved. This effort has been conducted under the sponsorship and technical direction of the Space Power Systems Office, Lewis Research Center, National Aeronautics and Space Administration.

The cell concept employed uses a capillary electrolyte matrix which is located between two fuel cell electrodes. The matrix serves as the medium for water storage during the charge and discharge processes. As a result of previous research and development, a set of electrodes and a unique matrix material have been developed that are capable of achieving lives up to 2500 hrs in a 90-min cycle regime. The scope of this program is to determine what processes and/or components limit the cycle life and how they may be altered to further extend cycle life. The specific work fell under four categories:

- a. Matrix comparison tests
- b. Material study tests

- c. Life tests
- d. TRW matrix tests

The matrix comparison tests were a screening process to select the most suitable matrix to be used in the other cell tests. The types of matrices tested fell into three categories. The first was a composite made from a mixture of potassium titanate (KT), Teflon and asbestos formed into a mat and pressed. The second type was made by sandwiching a pasted Teflon and potassium titanate barrier between two thin pressed KT and Teflon mats. The third type of matrix was made by forming a potassium titanate and Teflon composite with rollers. The latter two contained no asbestos.

The material study tests were to determine the effect of the metals present in the cell components on cell operation. Cell matrices were examined by X-ray diffraction to determine if metals were migrating through, and if there were any structural or other changes. Cells were cycled with and without gold-plated backup plate and screens. A cell was cycled with no metallic backup plate or screens. Catalyst migration tests were conducted using Pd as a tracer.

The life testing consisted of cycling a cell using a 90-min, a 24-hr, or a 3- to 5-hr cycle at 50°C and 80°C. The test was discontinued when the average cell voltage fell below 0.7V on discharge.

Three types of matrices manufactured by TRW were tested. The matrices were made of Teflon and potassium titanate, Teflon and zirconia, and Teflon and cerium oxide.

SECTION 2

TECHNICAL DISCUSSION

2.1 TEST CELL

A single, flat plate test cell was used to conduct the experimental evaluations of the various electrodes - matrix types.

The single cell unit consisted of two circular plates of Monel containing gas cavities in an approximate 2 to 1 volume ratio. Machined into these cavities were grooves for electrode backup plates and electrodes of 6-in. diameter. The two halves were joined together by a series of bolts along the periphery. Sealing was accomplished by the use of O-rings. A glass-reinforced epoxy spacer was used between the two plates to provide electrical insulation between the positive and negative sides of the cell. The insulating spacer thus provided the spacing between the two plates and also fixed the compression on the matrix. Since the diameter of the matrix was somewhat larger than the 6-in. electrodes, the peripheral edge of the matrix was compressed against the cell halves inside the insulating spacer, effectively preventing leakage around the matrix. Assembly was accomplished by stacking one end plate, backup screen, electrode, matrix, second electrode, second backup screen, and end plate, and then bolting the entire assembly together.

Certain fittings, valves, and instrumentation were attached to each of the chambers for pressure measurement and for flushing the unit. Major cell components were fabricated out of Monel to minimize corrosion problems. Since the cell did not contain a volume balancing mechanism to assure a 2 to 1 volume ratio, it was necessary to adjust the volumes by adding external tubing. The entire cell was set up in an oven that contained lead-ins for electrical and flushing gas connections.

Figure 1 is a photo of the assembled single cell, and Figure 2 is an assembly drawing of the unit giving details of the internal construction.

Each cell was provided with both a total and a differential pressure transducer. A pressure switch, which removed the cell from the charge circuit when the pressure reached a pre-set level, was also used in each cell. Figure 3 shows the fuel cell test station.

2.2 MATRIX COMPARISON TESTS

In order to determine the best methods of fabrication, three types of potassium titanate matrices were fabricated and cycle tested on a 60-min charge 30-min discharge at 55 and 100 mA/cm², respectively at 80°C. The charge capacity of the cells was limited by a pressure switch activated at 350 psi. Bubble-through tests were conducted in the laboratory on each type of matrix to determine their relative ability to hold pressure differentials. Table I is a summary of the cells cycled for matrix comparison tests.

2.2.1 PRESSED COMPOSITE MATRIX

A composite was made by forming a 80% potassium titanate, 10% Teflon, and 10% asbestos mixture into a mat and pressing it.

Fifteen matrices composed of 80% KT, 10% Teflon, and 10% asbestos were fabricated. To insure uniformity of these matrices, five were bubble-through tested. Figure 4 shows a diagram of the bubble-through apparatus. Table II shows a fair reproducibility in bubble-through pressure, the lowest being 6.6 psig. The remaining matrices were cycle tested.

Cells 2A, 3A, 4A, 5A and 6A in Table I contained the pressed matrices. Cell No. 4A can be eliminated from the results because of obvious internal damage. As can be seen from Table I, over 1000 cycles were achieved

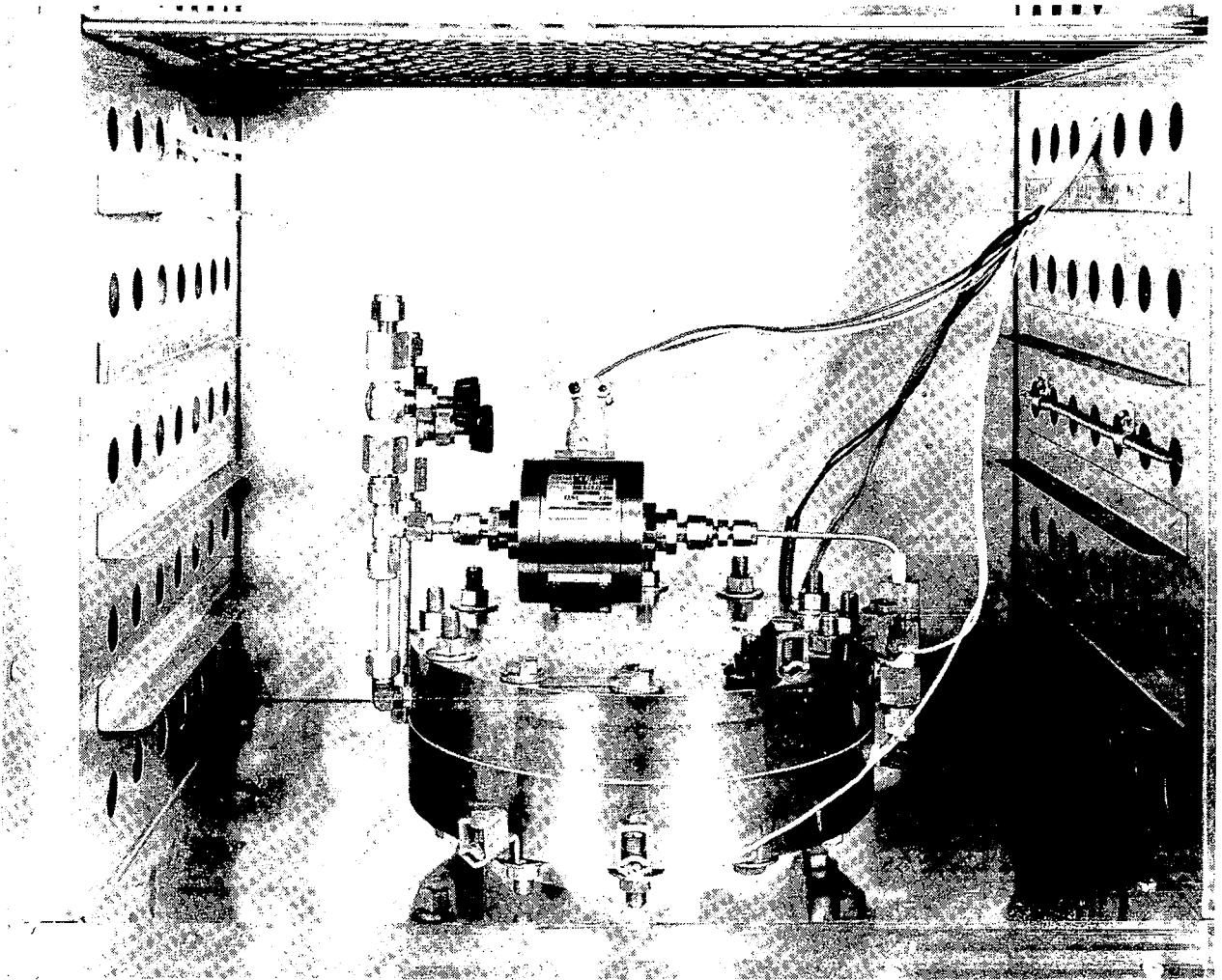


Figure 1. Single Test Cell in Oven

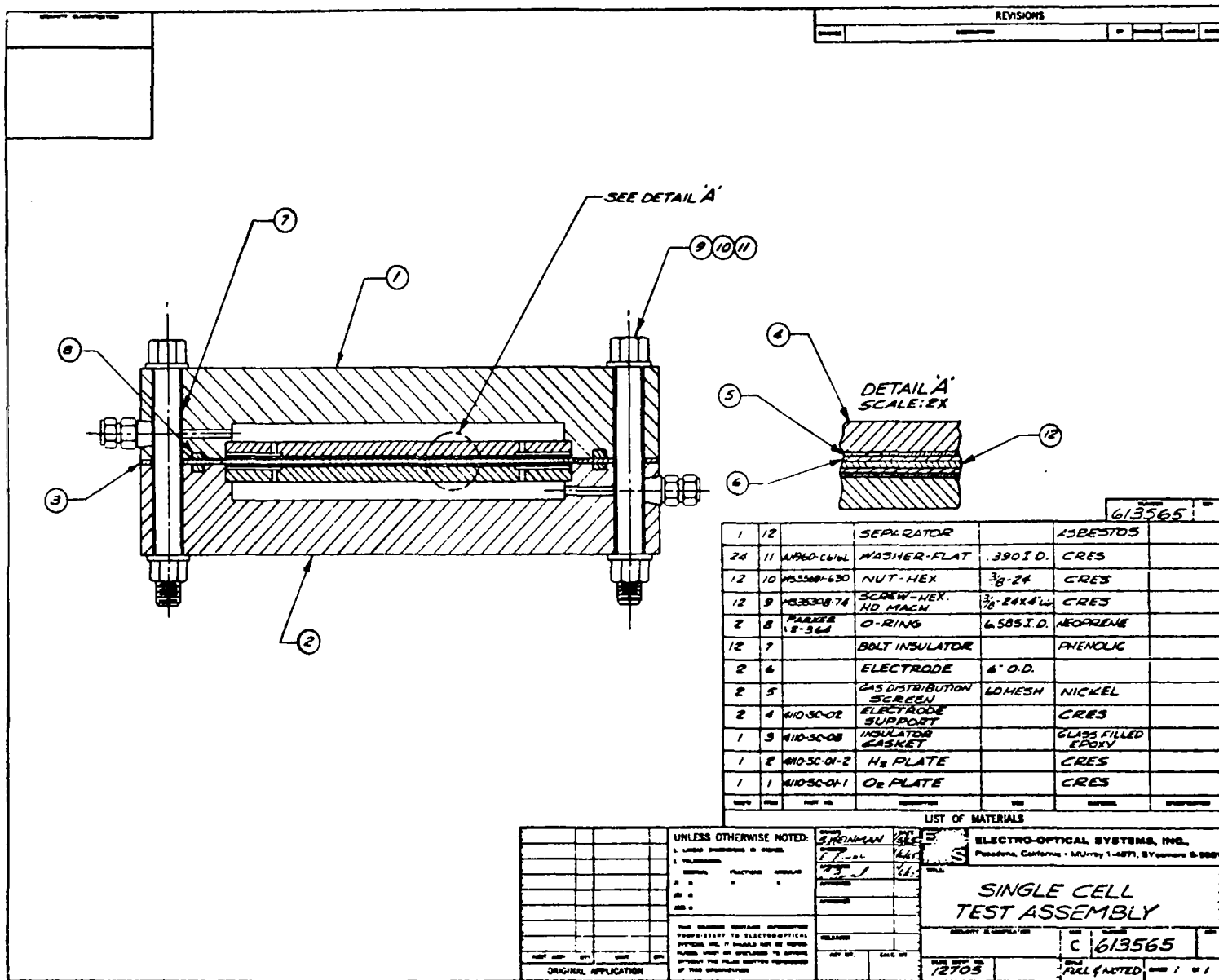


Figure 2. Single Cell - Test Assembly

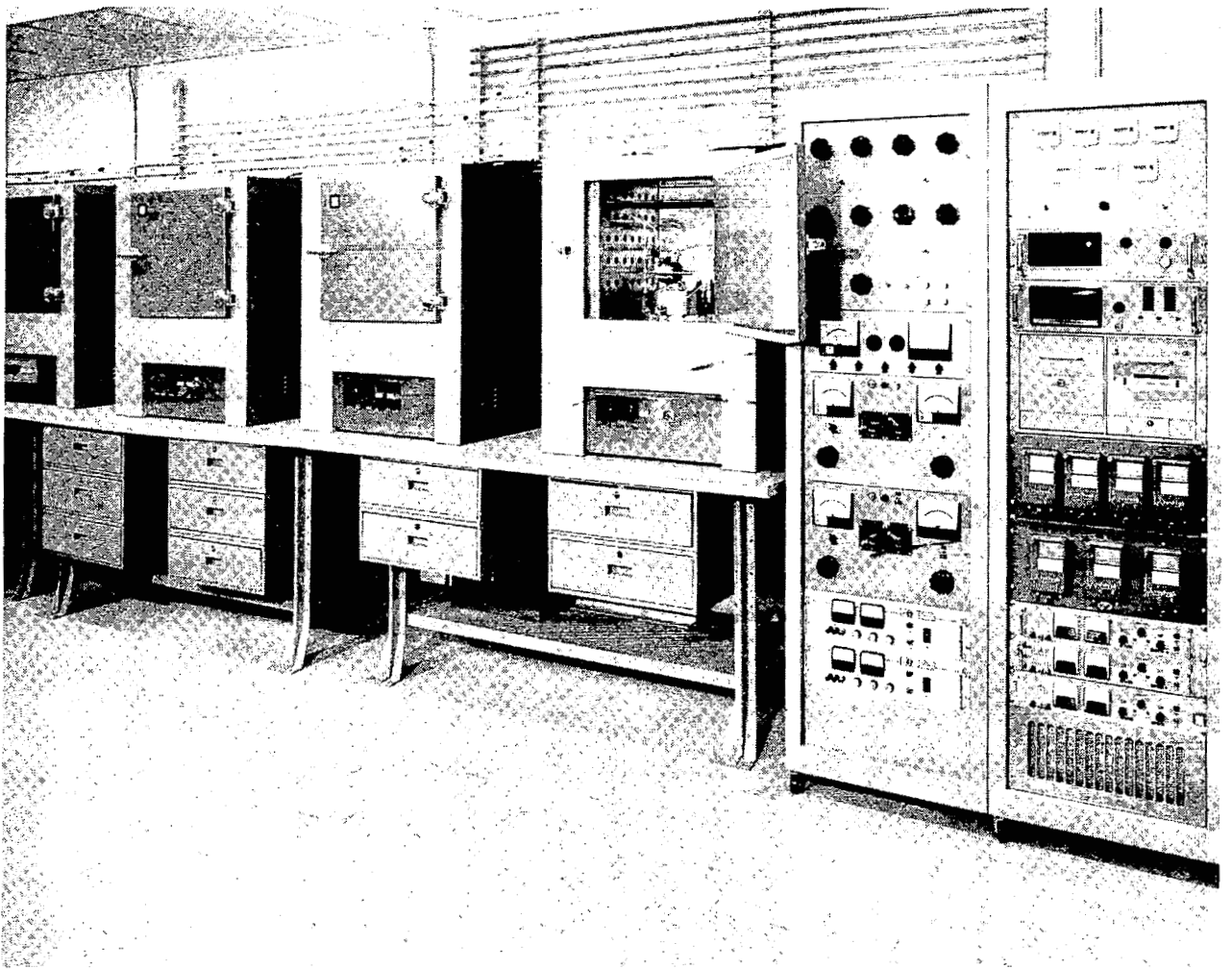


Figure 3. Single Fuel Cell Test Station

TABLE I
SUMMARY OF CELLS
MATRIX COMPARISON TESTS AT 80°C

Cell No.	Matrix	No. of Cycles	Type of Cycle	Electrodes	Electrolyte	Final KOH	Impedance at 80°C		Comments
							Initial	Final	
2A	Pressed composite	1067	60/30 min 10/17.5A	EOS/Cyanamid AB-6	45 g of 30.0%	19.3%	0.001Ω	0.006Ω	Sample sent for X-ray diffraction Normal failure.
3A	Pressed composite	1802	60/30 min 10/17.5A	EOS/Cyanamid AB-6	45 g of 30.0%	19.1%	0.001Ω	0.005Ω	
4A	Pressed composite	152	60/30 min 10/17.5A	EOS/Cyanamid AB-6	45 g of 30.0%		0.006Ω	0.007Ω	Upon disassembly, a burnt spot was observed
5A	Pressed composite	1460	60/30 min 10/17.5A	EOS/Cyanamid AB-6	45 g of 30.0%	16.5%	0.002Ω	0.005Ω	Normal failure.
6A	Pressed composite	805	60/30 min 10/17.5A	EOS/Cyanamid AB-6	45 g of 30.0%	20.3%	0.001Ω	0.005Ω	Normal failure.
7A	Pasted 50% KT/ 50% Teflon mem- brane sandwiched between 90% KT/ 10% Teflon mats	455	60/30 min 10/17.5A	EOS/Cyanamid AB-6	45 g of 30.0%	23.5%	0.007Ω	0.007Ω	Normal failure.
8A	Pasted 50% KT/ 50% Teflon mem- brane sand- wiched between mats	762	60/30 min 10/17.5A	EOS/Cyanamid AB-6	50 g of 30%	24.15%	0.001Ω	0.009Ω	Normal failure.

TABLE I
SUMMARY OF CELLS (contd)
MATRIX COMPARISON TESTS AT 80°C

Cell No.	Matrix	No. of Cycles	Type of Cycle	Electrodes	Electrolyte	Final KOH	Impedance at 80°C		Comments
							Initial	Final	
11A	Pasted 50% KT/ 50% Teflon membrane sandwiched between two mats	6	60/30 min 10/17.5A	EOS/Cyanamid AB-6	50 g of 30%				Test discontinued due to faulty transducer
12A	Pasted 50% KT/ 50% Teflon membrane sandwiched between two mats	290	60/30 min 10/17.5A	EOS/Cyanamid AB-6	47.5 g of 30%	26.35%	0.006Ω	0.006Ω	Discontinued because of gas recombination - self-discharge
14A	Pasted 50% KT/ 50% Teflon membrane sandwiched between two mats	115	60/30 min 10/17.5A	EOS/Cyanamid AB-6	47.5 g of 30%	28.6%	0.006Ω	0.016Ω	Discontinued after cell subjected to 30 psig differential
15A	Pasted 50% KT/ 50% Teflon membrane sandwiched between two mats	130	60/30 min 10/17.5A	EOS/Cyanamid AB-6	47.5 g of 30%	26.7%	0.007Ω		Normal failure
18A	Pasted 50% KT/ 50% Teflon membrane sandwiched between two mats	896	60/30 min 10/17.5A	EOS/Cyanamid AB-6	47.5 g of 30%	25.4%	0.004Ω	0.011Ω	Discontinued when charge voltage exceeded 2.0 volts

TABLE I
SUMMARY OF CELLS (contd)
MATRIX COMPARISON TESTS AT 80°C

Cell No.	Matrix	No. of Cycles	Type of Cycle	Electrodes	Electrolyte	Final KOH	Impedance at 80°C		Comments
							Initial	Final	
20A	Pasted 50% KT/ 50% Teflon mem- brane sand- wiched between two mats	34	60/30 min 10/17.5A	EOS/Cyanamid AB-6	47.5 g of 30%	26.7%	0.065Ω	0.036Ω	Discontinued be- cause of gas recombination - self discharge
9A	80% KT and 20% Teflon rolled	0	60/30 min 10/17.5A	EOS/Cyanamid AB-6	45 g of 30%				Gas recombination self discharge
10A	80% KT and 20% Teflon	0	60/30 min 10/17.5A	EOS/Cyanamid AB-6	45 g of 30%				Gas recombination self discharge
13A	80% KT and 20% Teflon	0	60/30 min 10/17.5A	EOS/Cyanamid AB-6	45 g of 30%				Gas recombination self discharge

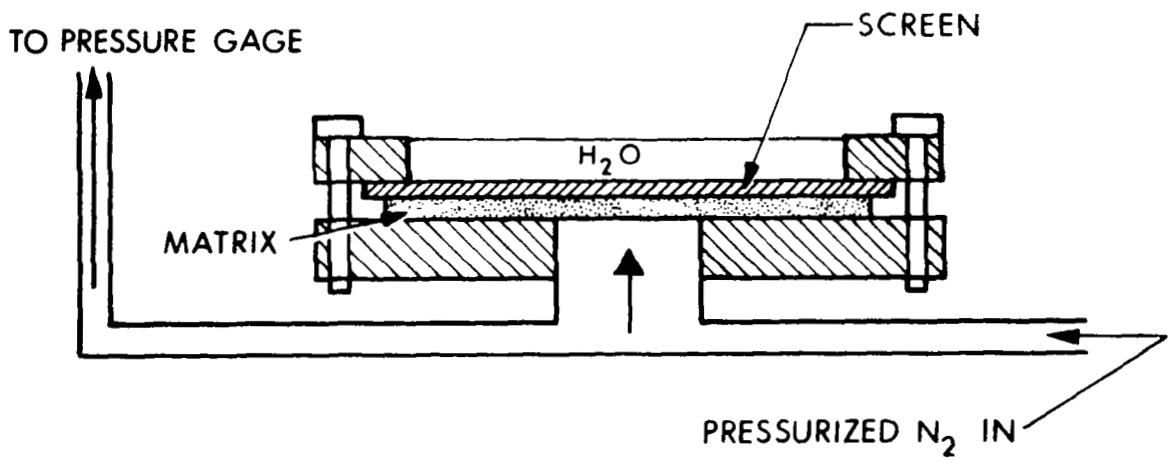


Figure 4. Bubble Cell Cross Section

TABLE II

BUBBLE-THROUGH TESTS
80% KT, 10% Teflon, 10% Asbestos,
0.060-In. Separator

<u>No.</u>	<u>Thickness (inches)</u>	<u>Dry Wt. (grams)</u>	<u>KOH, grams of Approx. 40% soln.</u>	<u>Pressure (psig)</u>
1	0.067	26.9	45.0	10.8
2	0.068	27.3	45.0	8.8
3	0.070	27.2	45.0	6.6
4	0.068	26.5	45.0	7.0
5	0.068	26.6	45.0	9.5

using this type of matrix. Figure 5 shows the cycling performance of cell 3-A. The 1802 cycles represent 2700 hours of continuous testing. As can be seen in Figure 5, the most extreme degradation in performance occurred during the last 100 cycles. When these cells were disassembled it was observed that much of the gold was gone from the O₂ backup screens and plates. The H₂ backup screen and plate were clean, exactly as originally installed.

The matrix contained three distinct layers. In general, the layer on the O₂ side was soft and light in color. The layer on the H₂ side was gray and brittle. The middle layer was black. Samples of these matrices were examined using spectrographic and X-ray diffraction techniques. It was determined that the black middle layer contained platinum and gold and that other changes were occurring in the matrix. This phenomena will be discussed in more detail in Subsection 2.3, Materials Studies.

2.2.2 LAYERED PASTED MEMBRANE MATRIX

The matrix was fabricated by pasting a 50% potassium titanate and 50% Teflon mixture on a Teflon screen. This pasted membrane was sandwiched between two thin mats made from 90% potassium titanate and 10% Teflon.

The bubble-through testing was done in a single cell with standard screens, electrodes, and spacer in order to duplicate cycle test conditions. To allow a comparison using the same test fixture, pressed matrices were bubble-through tested also. Table III is a summary of the bubble-through tests. All the matrices contained 45 g of 30% KOH. Ten pressed composite matrices were tested in this new fixture. Table III shows the bubble-through pressures to be higher than those tested in the old fixture. An average of 24.5 psig bubble-through was demonstrated. The lowest pressure was 5 psig. Better support of the matrices in the test cell than in the other test fixture probably accounted for the difference in results.

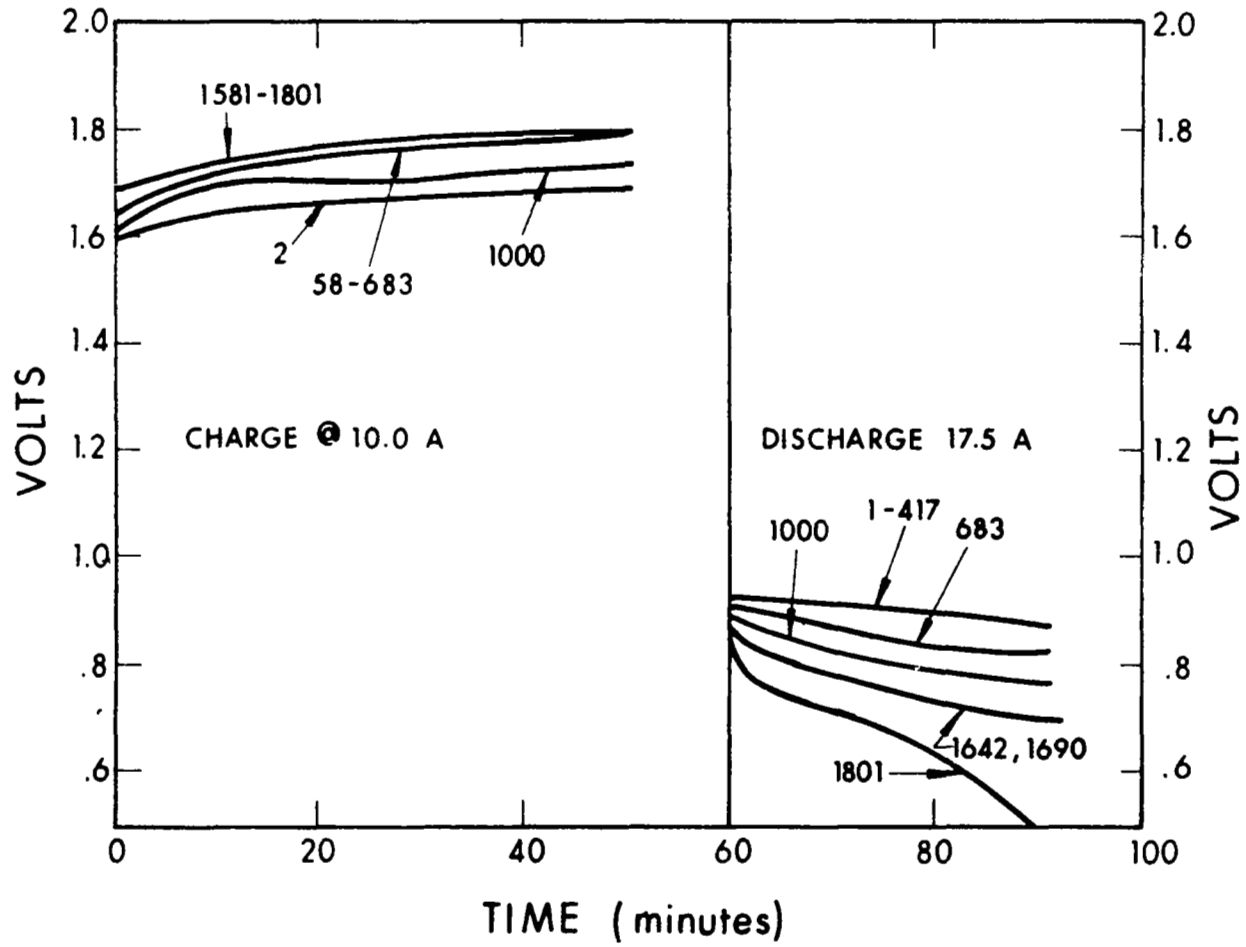


Figure 5. Performance of Cell No. 3-A

TABLE III
BUBBLE-THROUGH TESTS

No.	Thickness (inch)	Dry Wt. (grams)	Wt. of 30% KOH (grams)	Test Temp. (°C)	Composition	Bubble- Through Pressure (psig)
6	0.066	28.0	45	25	Pressed Composite, 80% KT/10% Teflon/ 10% asbestos	50
7	0.067	28.1	45	25	Pressed Composite, 80% KT/10% Teflon/ 10% asbestos	42
8	0.064	28.2	45	25	Pressed Composite, 80% KT/10% Teflon/ 10% asbestos	35.0
9	0.067	28.0	45	25	Pressed Composite, 80% KT/10% Teflon/ 10% asbestos	28.0
10	0.067	27.8	45	25	Pressed Composite, 80% KT/10% Teflon/ 10% asbestos	5.0
11	0.065	27.7	45	25	Pressed Composite, 80% KT/10% Teflon/ 10% asbestos	20.0
12	0.030 0.029	10.7 10.8	45 45	25 25	Pasted 90% KT/10% asbestos membrane sand- wiched between two 90% KT/10% asbestos mats	3.0
13	0.033 0.033	11.0 11.0	45 45	25 25	Pasted 90% KT/10% asbestos membrane sand- wiched between two 90% KT/10% asbestos mats	66.0
14	0.033 0.033	11.0 11.0	45 45	25 25	Pasted 90% KT/10% asbestos membrane sand- wiched between two 90% KT/10% asbestos mats	68.0

TABLE III
BUBBLE-THROUGH TESTS (contd)

No.	Thickness (inch)	Dry Wt. (grams)	Wt. of 30% KOH (grams)	Test Temp. (°C)	Composition	Bubble-Through Pressure (psig)
15	0.033	10.9	45	25	Pasted 90% KT/10% asbestos membrane sandwiched between two 90% KT/10% asbestos mats	61.0
	0.033	10.9	45	25		
16	0.31	10.8	45	25	Pasted 90% KT/10% asbestos membrane sandwiched between two 90% KT/10% asbestos mats	32.5
17	0.063	27.4	45	25	Pressed Composite, 80% KT/10% Teflon/10% asbestos	13.0
18	0.065	28.3	45	25	Pressed Composite, 80% KT/10% Teflon/10% asbestos	23.0
19	0.064	27.1	45	25	Pressed Composite, 80% KT/10% Teflon/10% asbestos	5.0
20	0.064	27.2	45	25	Pressed Composite, 80% KT/10% Teflon/10% asbestos	24.0
23	-	-	45	80	80% KT and 20% Teflon rolled on 60 mesh screen	2.0
24	-	-	45	80	80% KT/10% Teflon/10% asbestos standard mix rolled into a matrix	3.5
25	0.072	27.1	45	25	80% KT/10% cotton/10% Teflon pressed into a matrix	5.0
26	0.070	26.2	45	25	80% KT/10% cotton/10% Teflon pressed into a matrix	3.0

TABLE III
BUBBLE-THROUGH TESTS (contd)

No.	Thickness (inch)	Dry Wt. (grams)	Wt. of 30% KOH (grams)	Test Temp (°C)	Composition	Bubble- Through Pressure (psig)
27	0.085	30.1	63	80	80% KT and 20% Teflon rolled into a matrix	10.0
28	0.085	26.9	51	80	79% KT/20% Teflon, and 1% cotton rolled into a matrix	6.5
29	0.087	25.3	42	80	80% KT and 20% Teflon rolled into a matrix	11.5
30	0.070	23.0	40	80	80% KT and 20% Teflon rolled into a matrix then pressed at 300 psig	5.0
31	0.087	27.3	45	80	70% KT and 30% Teflon rolled into a matrix	4.0
32	0.054	21.5	35	80	80% KT and 20% Teflon rolled into a matrix and pressed at 450 psig	3.5
33	0.087	25.1	41	80	80% KT/20% Teflon rolled into a matrix	10.0
34	0.060	22.3	37	80	80% KT/20% Teflon rolled into a matrix then pressed at 770 psig	3.5
35	0.087	26.9	40	80	70% KT/30% Teflon rolled into a matrix	3.0

Fifteen layered, pasted-membrane matrices were fabricated. The matrices were made by sandwiching a 50% KT/50% Teflon pasted membrane in between two pressed 90% KT/10% asbestos mats. Five of the matrices were bubble-through tested. Table III shows an average bubble-through of about 57 psig, if test no. 7 showing 3 psig is thrown out. Eight of the remaining layered, pasted-membrane matrices were cycle tested.

Cells 7A, 8A, 11A, 12A, 14A, 15A, 18A and 20A in Table I contained layered pasted membrane matrices. Cells 11 and 14 were discontinued because of inadvertent mechanical difficulties. Two other cell tests, nos. 12 and 20, were discontinued when the gases recombined by passing through the matrix. The remaining four cells demonstrated cycle lives under 1000 cycles. Figure 6 shows the cycle life characteristics for cell 8-A, which was one of the longer cycling cells. If the test results of the pressed composite matrix are compared to those of the layered pasted membrane type, it can be seen that the pressed composite matrix is more reliable and more nearly reproducible.

It was observed that after cycling, the layered matrices contained a black layer in the pasted membrane similar to that found in the pressed matrix.

2.2.3 ROLLED POTASSIUM TITANATE AND TEFLON MATRICES

Various rolled matrices were fabricated using Teflon powder. Table III shows that the 80% potassium titanate (KT) and 20% Teflon showed the most promise. Some 80% KT and 20% Teflon-rolled matrices were pressed at pressures between 300 and 800 psig; then they were bubble-through tested. Table III shows that the pressing weakened the structure since the bubble-through pressures were lower. Table III also shows that an increase of Teflon to 30% of the matrix weight decreased the resulting bubble-through pressure.

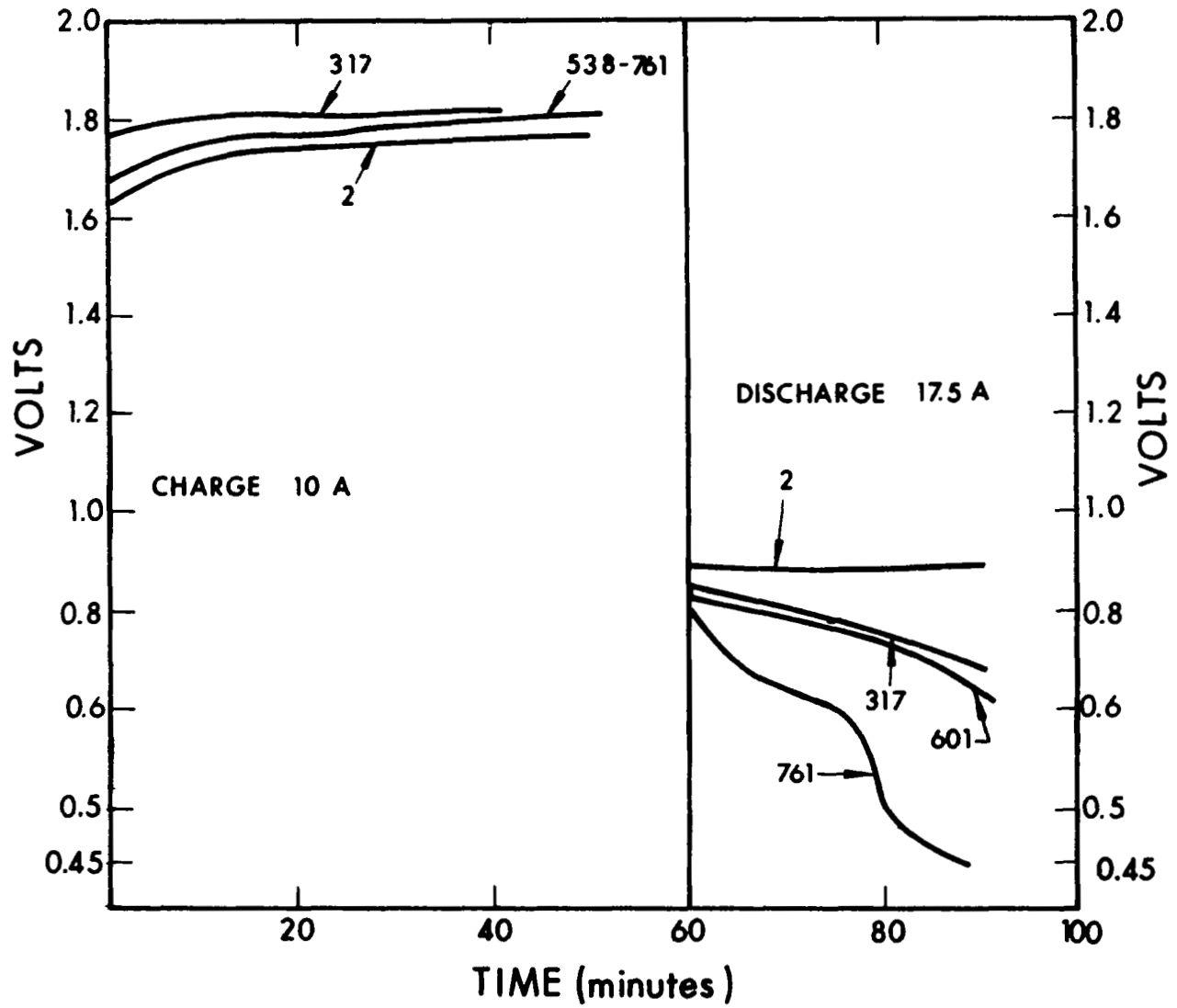


Figure 6. Performance of Cell No. 8-A

Two other variations of matrix fabrication were tried. An 80% KT and 20% Teflon mixture was rolled onto a 60-mesh Teflon screen. This matrix gave a bubble-through of 2.0 psig. The other matrix was a standard mixture of 80% KT, 10% Teflon, and 10% asbestos rolled into a matrix. This sample gave a bubble-through of 2.0 psig.

Cycling tests were tried using the 80% KT and 20% Teflon rolled matrices. Table I shows that cells 9A, 10A and 13A, containing these rolled matrices, did not function as fuel cells at 80°C.

2.2.4 OTHER TYPES OF MATRICES

Two samples of cotton were tested for 8 days in 30% KOH at 70°C. Sample 1 showed an 8.71% loss in weight, and sample 2, a 7.28% loss. Two pressed matrices were made using cotton in place of asbestos. Tests nos. 25 and 26 in Table III show the bubble-through pressure of this type of matrix to be low. Another matrix was made by rolling 79% KT, 20% Teflon and 1% cotton. Test 28 of Table III shows a 6.5 psig bubble-through. No cycle tests were attempted using this type of matrix.

Matrices were fabricated using Kel-F No. 630 in place of Teflon. Both the rolled and pressed types of matrices made with Kel-F proved to be too brittle for use in a fuel cell.

2.3 MATERIALS STUDIES

To study the effect of electrode and structural materials, a series of experiments was conducted. The materials studies cells fell into five categories:

- a. Cells with polysulfone backup plates
- b. Cells without gold on backup plates and screens
- c. Special cycle tests for X-ray diffraction and spectrographic analysis of electrolyte matrix

- d. Tests to trace catalyst migration
- e. Tests with varied electrode configurations.

Table IV presents a summary of the cells cycled for the material study tests.

TABLE IV
SUMMARY OF CELLS
MATERIALS STUDIES

Cell No.	Matrix	No. of Cycles	Type of Cycle	Electrodes	Electrolyte	Final KOH	Impedance at 80°C		Comments
							Initial	Final	
17A	Pressed composite	16	60/30 min 10/17.5A	EOS/Cyanamid AB-6	45 g of 30%		0.007Ω	0.013Ω	Standard AB-6 O ₂ electrode. Teflon screens, polysulfone backup plates. Test terminated by ignition
22A	Pressed composite	418	60/30 min 10/17.5A	EOS/Cyanamid AB-6	45 g of 30%	11.9%	0.007Ω	0.010Ω	Standard AB-6 O ₂ electrode. Ni screens, no gold, polysulfone backup plates. Normal failure.
28A	Pressed composite	724	60/30 min 10/17.5A	EOS/Cyanamid AB-6	45 g of 30%	25.15%	0.004Ω	0.014Ω	Standard AB-6 O ₂ electrode. Ni screens, no gold, polysulfone backup plates. Normal failure.
39A	Pressed composite	150	60/30 min 10/17.5A	EOS/Cyanamid AB-6	45 g of 30%	26.95%	0.008Ω	0.006Ω	This is Cell 28 with a new matrix. Normal failure.
25A	Pressed composite	116	60/30 min 10/17.5A	Special	45 g of 30%	13.95%	0.008Ω	0.011Ω	Teflon backup screens. Polysulfone backup plates. All Pt electrodes. Test terminated by ignition.
50A	Pressed composite	50	60/30 min 10/17.5A	EOS/Cyanamid AB-4	45 g of 30%	23.6%	0.004Ω	0.014Ω	No gold on backup screens. AB-4 O ₂ electrode without gold polysulfone backup plate. Test terminated by gas recombination

TABLE IV
SUMMARY OF CELLS (contd)
MATERIALS STUDIES

Cell No.	Matrix	No. of Cycles	Type of Cycle	Electrodes	Electrolyte	Final KOH	Impedance at 80°C		Comments
							Initial	Final	
16A	Pressed composite	322	60/30 min 10/17.5A	EOS/Cyanamid AB-6	45 g of 30%	24.3%	0.004Ω	0.009Ω	No gold on backup plates and screens Normal failure. No gold on backup plates and screens Normal failure. No gold on backup plates and screens. Test terminated by ignition
21A	Pressed composite	555	60/30 min 10/17.5A	EOS/Cyanamid AB-6	45 g of 30%	24.3%	0.004Ω	0.011Ω	
23A	Pressed composite	62	60/30 min 10/17.5A	EOS/Cyanamid AB-6	45 g of 30%	13.4%	0.005Ω	0.005Ω	
26A	Pressed composite	407	60/30 min 10/17.5A	EOS/Cyanamid AB-6	45 g of 30%	13.0%	0.003Ω	0.011Ω	
30A	Pressed composite	50	60/30 min 10/17.5A	EOS/Cyanamid AB-6	45 g of 30%	26.45%	0.003Ω	0.025Ω	50 cycle cell for X-ray diffraction test
34A	Pressed composite	100	60/30 min 10/17.5A	EOS/Cyanamid AB-6	45 g of 30%	25.45%	0.007Ω	0.004Ω	100 cycle cell for X-ray diffraction test
37A	Pressed composite	200	60/30 min 10/17.5A	EOS/Cyanamid AB-6	45 g of 30%	23.2%	0.007Ω	0.004Ω	200 cycle cell for X-ray diffraction test
38A	Pressed composite	400	60/30 min 10/17.5A	EOS/Cyanamid AB-6	45 g of 30%	21.9%	0.002Ω	0.009Ω	400 cycle cell for X-ray diffraction test
35A	Pressed composite	1240	60/30 min 10/17.5A	EOS/Cyanamid AB-6	45 g of 30%	24.1%	0.003Ω	0.013Ω	This is cell 34 with a new matrix. X-ray diffraction test performed. Normal failure.

TABLE IV
SUMMARY OF CELLS (contd)
MATERIALS STUDIES

Cell No.	Matrix	No. of Cycles	Type of Cycle	Electrodes	Electrolyte	Final KOH	Impedance at 80°C		Comments
							Initial	Final	
54-A	Pressed composite	41	60/30 min 10/17.5A	Pd on Ni plaque for O ₂ electrode EOS H ₂ electr.	45 g of 30.1% KOH		0.005Ω	--	Catalyst migration test. Cell internally shorted.
61-A	Pressed composite	0		Pd on Ni screen with Teflon binder for O ₂ electrode EOS H ₂ electr.	45 g 30.4% KOH	--	--	--	Pd catalyst on O ₂ electrode too coarse
67-A	Pressed composite	639	60/30 min 10/17-5A	Pd on Ni screen with Teflon binder for O ₂ electrode EOS H ₂ electr.	45 g of 30.4% KOH	20.1%	0.004Ω	0.008Ω	Catalyst migration test. Cell self discharged at 49 cycles. New matrix installed. Normal failure at 639 cycles.
66-A	Pressed composite	395	60/30 min 10/17.5A	O ₂ double zone electrode EOS H ₂ electrode	45 g of 30.4% KOH	24.7%	0.009Ω	0.008Ω	O ₂ electrode with dc double catalyst loading. Normal failure.
71-A	Pressed composite	372	60/30 min 10/17.5A	O ₂ double zone electrode EOS H ₂ electrode	45 g of 30.4 KOH	19.5%	0.007Ω	0.007Ω	O ₂ electrode with double zone double catalyst loading. Normal failure.

TABLE IV
SUMMARY OF CELLS (contd)
MATERIALS STUDIES

Cell No.	Matrix	No. of Cycles	Type of Cycle	Electrodes	Electrolyte	Final KOH	Impedance at 80°C		Comments
							Initial	Final	
68-A	Pressed composite	200	60/30 min 10/17.5A	0.035-in-thick H ₂ electrode Cyanamid AB-6 O ₂ electrode	45 g of 30.4% KOH	27.1%	0.006Ω	0.008Ω	Test discontinued at 200 cycles
70-A	Pressed composite	200	60/30 min 10/17.5A	0.050-in-thick H ₂ electrode Cyanamide AB-6 O ₂ electrode	45 g of 30.4% KOH	19.65%	0.007Ω	0.009Ω	Test discontinued at 200 cycles.

2.3.1 CELLS WITH POLYSULFONE BACKUP PLATES

Cells 17A, 22A, 25A, 28A, 39A, and 50A listed in Table IV has polysulfone backup plates. The cells were tested at 80°C using the 90-minute cycle. Cells 17A and 25A had Teflon backup screens. In both tests an attempt was made to remove all metals outside of the electrodes. Cell 17A contained an AB-6 O₂ electrode and standard EOS H₂ electrode. Cell 25A had special platinum electrodes on both sides. Both tests were short-lived and inconclusive. Since it was felt that the Teflon screen probably flowed while the cell was in operation, some tests were performed using nickel screens. Both cells 22A and 28A were cycled with polysulfone backup plates and nickel screens without gold. The only gold present was in the Cyanamid AB-6 O₂ electrodes. It can be seen that the cycle life of these cells are limited when compared to the series of pressed matrix cells shown in Table IV. Cell 28A was run out to 724 cycles where the degradation was quite extreme, which is shown in Figure 7. In order to determine if the matrix was limiting the life of the cell, a new matrix was put in cell 28A. This modified assembly was numbered cell 39A. As can be seen in figure 8, this cell performance degraded rapidly thus indicating that other factors besides the matrix are limiting cell life. Cell 50A was an attempt to run a cell with no gold at all. The Cyanamid AB-4 electrode is made without gold plate on the screen. The test was terminated after 50 cycles when the gases recombined. After viewing the tests run with polysulfone backup plates, it was decided that the mechanical irregularities introduced in the cell assembly with the polysulfone plates added uncertainty to the validity of the test results. Therefore, the use of polysulfone was discontinued.

2.3.2 CELLS WITHOUT GOLD ON BACKUP PLATES AND SCREENS

Cycle tests were run at 80°C using the 90-minute cycle. The cells contained the standard Cyanamid AB-6 O₂ electrode and EOS H₂ electrodes, and a pressed electrolyte matrix. The backup plates and screens contained

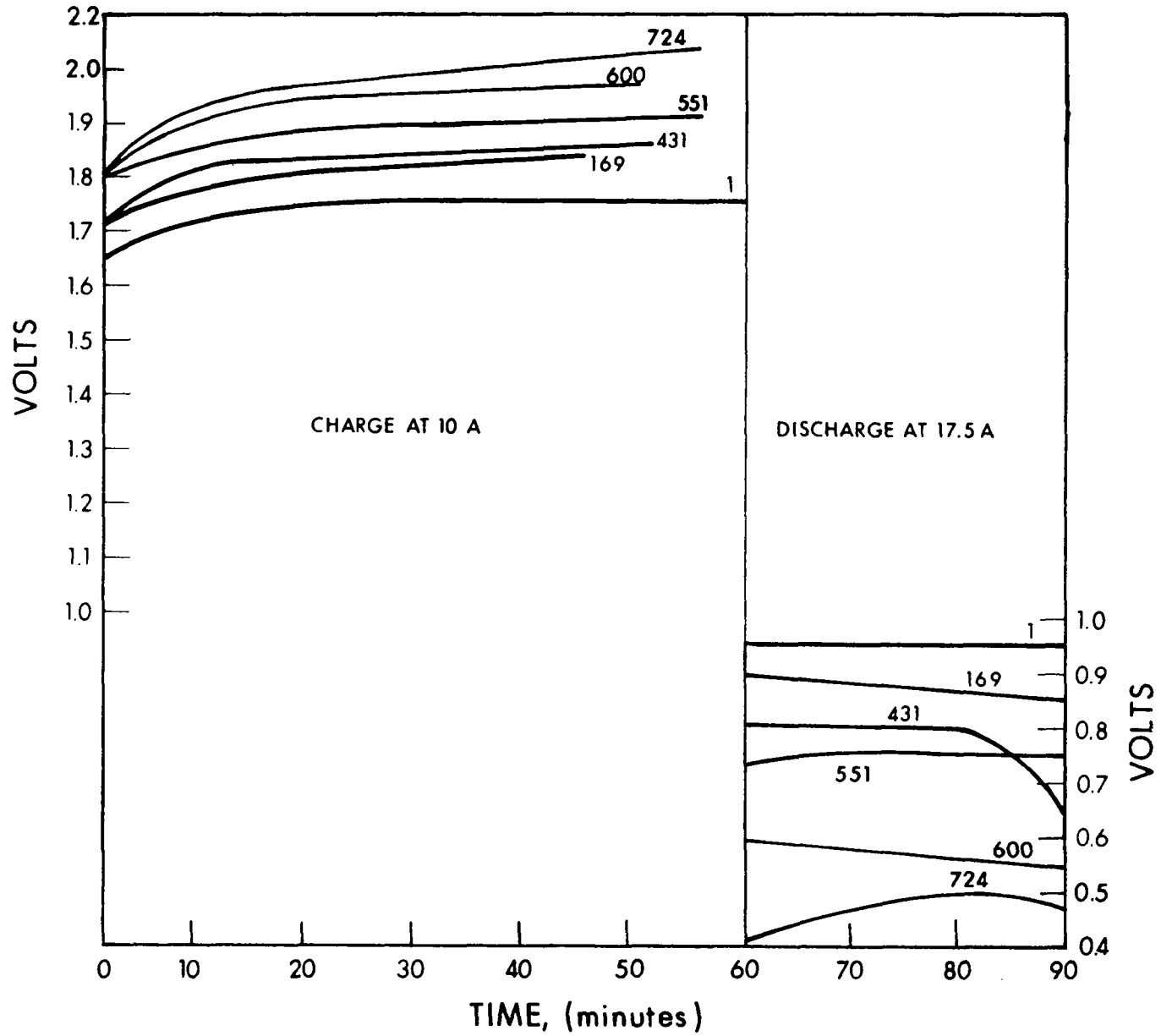


Figure 7. Cycle Performance of Cell 28-A

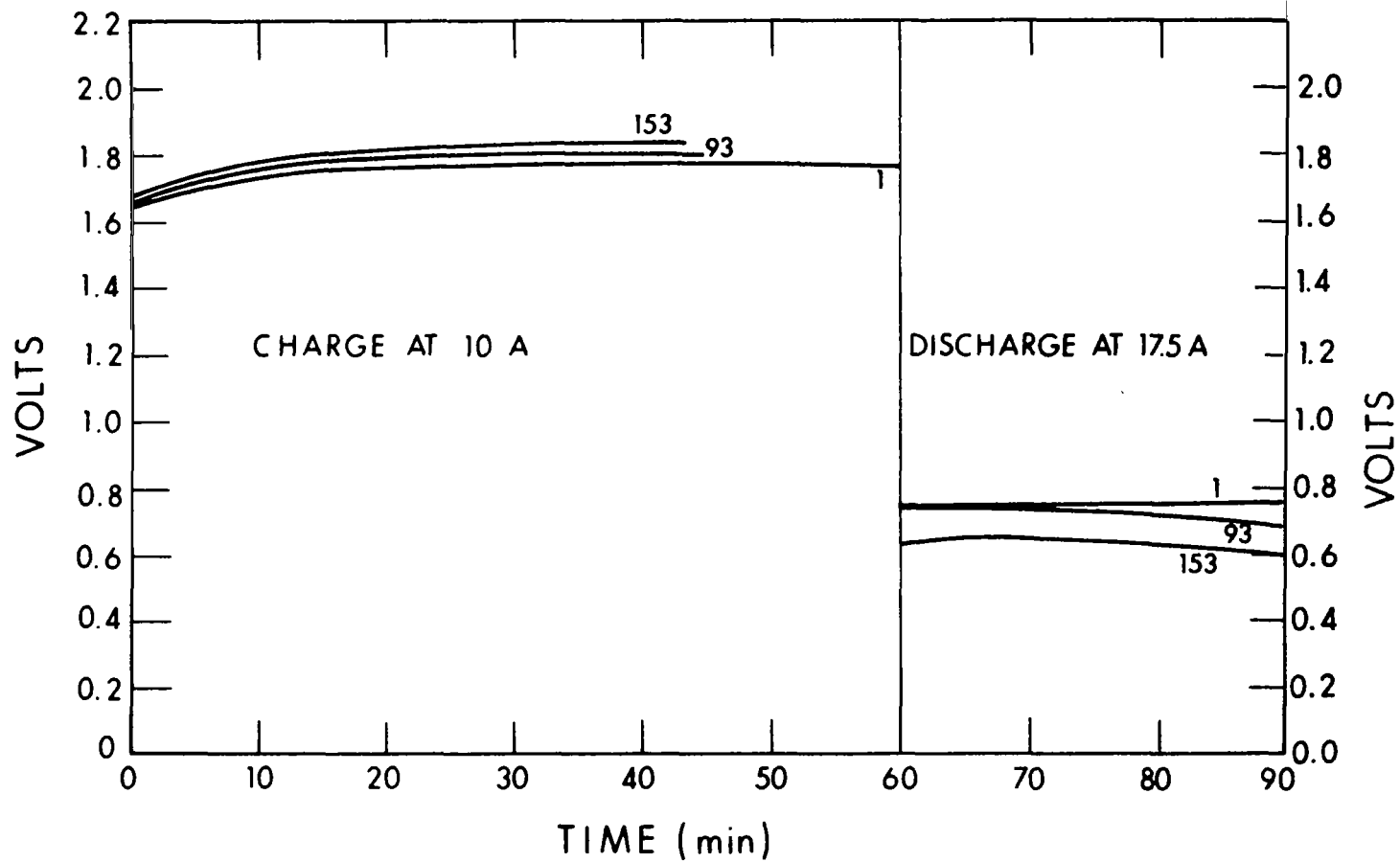


Figure 8. Cycle Performance of Cell 39-A

no gold. Cell nos. 16A, 21A, 23A, and 26A in Table IV (also without gold screens) show similar cycle lives when compared with the polysulfone cells mentioned previously. No cell ran over 600 cycles. Figure 9 shows the cycle life characteristics for cell 21A, which demonstrated the longest cycle life in this series.

When these cells were disassembled it was observed that the O₂ backup screens and plate contained a loose black discoloration. The H₂ screens and backup plates were clean. The matrices had the same distinct black middle layer observed in the previous cells. On cell 21A, gold was detected on the H₂ backup screen. The gold must have come across from the Cyanamid AB-6 O₂ electrode, since there is no other source. It can be concluded from these tests that cell life is shortened if the backup plates and screens are not gold plated.

2.3.3 SPECIAL TESTS FOR X-RAY DIFFRACTION ANALYSIS

In order to learn what changes occur in the electrolyte matrix, X-ray diffraction studies were done. Unused matrices with and without KOH were examined. It appears that the "as received" fibers are composed of a major phase of potassium titanate, probably of the formula (K₂Ti₄O₉). Examination of both sides and the middle of an unused matrix revealed that the potassium titanate is of the same crystallographic composition as the "as received" fibers, and that the Teflon and asbestos is uniformly distributed throughout the matrix. When the matrix was wet with 30% KOH, the potassium titanate changed into a crystallographically unidentified complex.

To determine if the presence of KOH without electrical cycling causes phase changes in potassium titanate, the following samples were prepared and submitted for X-ray diffraction analysis.

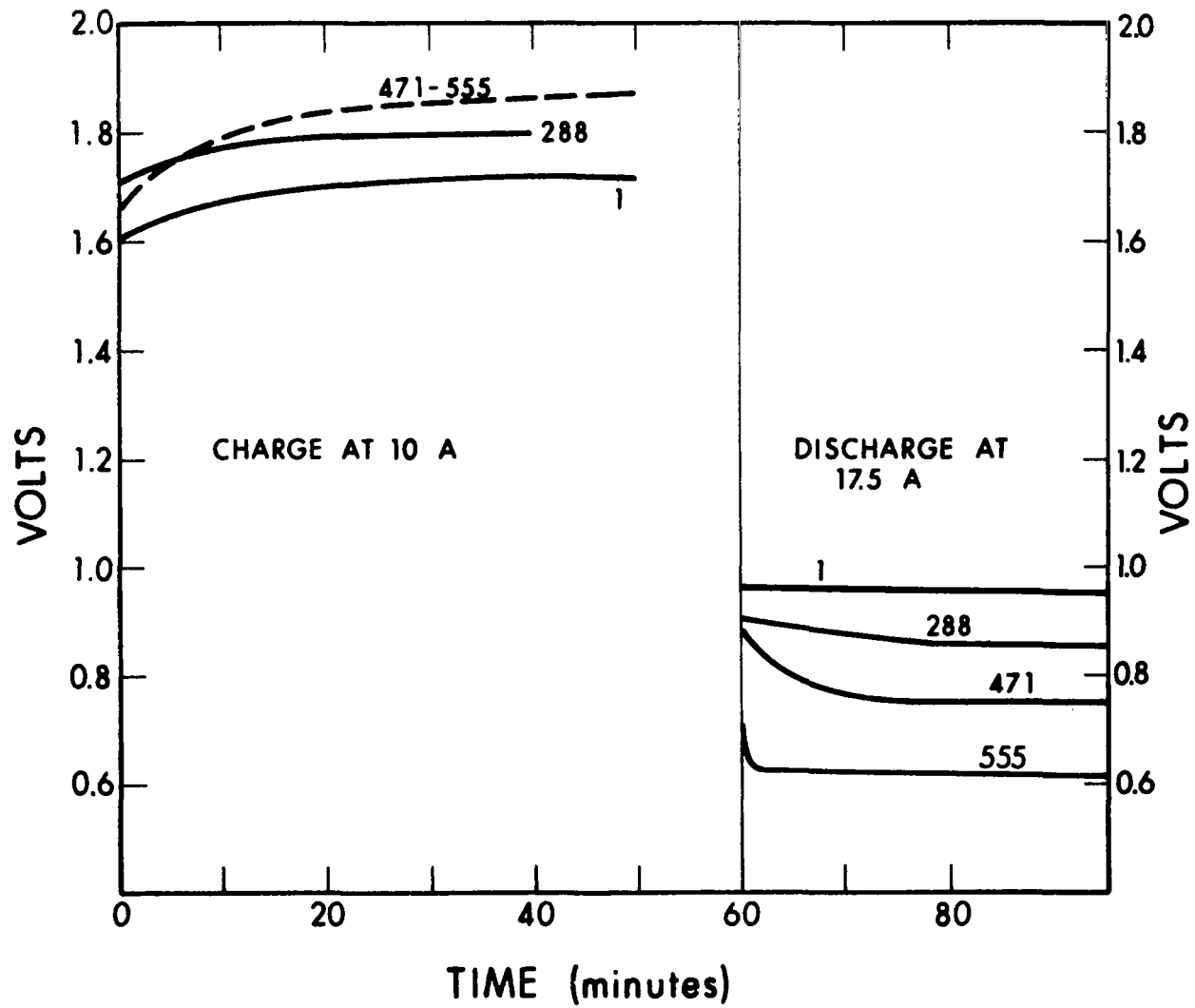


Figure 9. Cycling Performance of Cell 21-A

- AX-2 untreated potassium titanate
- AX-3 potassium titanate soaked in 30% KOH for 5 days at 25°C
- AX-4 potassium titanate soaked in 30% KOH for 5 days at 50°C
- AX-5 potassium titanate soaked in 30% KOH for 5 days at 80°C

All the samples treated in KOH showed poor crystallinity unless they were dried. Pressing the sample gave various unidentified phases not matching that of the untreated raw material. Oven drying gave an even different pattern. A portion of sample AX-5 was water washed and filtered, this caused the crystallographic pattern to change and match that of the untreated fibers.

Table IV lists the cell matrices that were submitted for X-ray analysis. The first matrix submitted was from cell no. 2A of the matrix comparison tests. This cell ran 1067 cycles. Table V gives a summary of the results from the X-ray diffraction tests. As can be seen from the summary, the middle black layer contains elemental platinum and gold. The H₂ side contains mostly potassium titanate and the O₂ side has major phases of Teflon and asbestos.

As Table IV shows, tests were conducted where cells were cycled 50, 100, 200, 400 and 1200 cycles at 80°C using the 90-minute cycle regime. The matrices were submitted for X-ray diffraction analysis. The results are summarized in Table V. It can be seen from the summary that the results obtained from the analysis of the matrix from cell 2A are verified. As the cycle life increases, it is evident that Teflon and asbestos become concentrated on the O₂ side. This can mean that the Teflon and asbestos are moving to the O₂ side or the potassium titanate away from it toward the H₂ side. It also can be seen from Table V that platinum moves into the matrix immediately, since it is detected after only 50 cycles.

TABLE V

SUMMARY OF X-RAY DIFFRACTION

80°C 50 Cycle Cell 30	80°C 100 Cycle Cell 34	80°C 200 Cycle Cell 37	80°C 400 Cycle Cell 38	80°C 1240 Cycle Cell 35	80°C 1067 Cycle Cell 2	50°C 105 Cycle Cell 29
Middle black layer. No Pt.	Middle black layer. Small Pt in the side of layer. No Au.	Middle black layer. Same structure as H ₂ side. Same amount of Teflon and asbestos. Some Pt, no Au.	Middle black layer. Major phase of Au intermediate phase of Pt several phases of KT.	Middle black layer. Pt, no Au. Teflon and asbestos in moderate amounts. Mixed types of KT.	Middle black layer. Major phase Au intermediate phase of H ₂ Ti ₄ O ₉ , strong phase Pt and trace Teflon.	No black layer observed. No Pt or Au. No Teflon or asbestos.
H ₂ side very little Teflon. No asbestos.	H ₂ side low in Teflon and asbestos.	H ₂ side major phase K ₂ Ti ₄ O ₉ . Slightly more Teflon and asbestos than 50 and 100-cycle cells.	H ₂ side major phase K ₂ Ti ₄ O ₉ . Minor amounts of Teflon and asbestos.	H ₂ side trace of Teflon. No asbestos. Minor Au strong phase of unidentified KT.	H ₂ side of Teflon. Minor phase asbestos, major phase mixed KT.	H ₂ side, very little Teflon - 1/2 as much as 50 cycle at 80°C. No asbestos.
O ₂ side high in Teflon; low in asbestos.	O ₂ side moderate concentration of Teflon and asbestos. Titante phases H ₂ and O ₂ side similar but lack crystal- linity on H ₂ side. Are not identified.	O ₂ side major phase is Teflon. Asbestos phase in greater concentration than titanate.	O ₂ side major phases Teflon and asbestos.	O ₂ side major phases of Teflon and asbestos.	O ₂ side major phases of Teflon and asbestos.	O ₂ side low in Teflon and low in asbestos, but twice as much as 50 cycle of 80°C.

A matrix from cell 29A cycled at 50°C for the life test series was submitted for X-ray diffraction analysis. The cell had only 100 cycles. It can be seen from the summary, Table V, that the asbestos and Teflon did not concentrate at the O₂ side as shown for 100 cycles at 80°C.

2.3.4 KOH CONCENTRATION LOSS

Table IV shows that the series of cells (nos. 30A, 34A, 37A, and 38A) used for X-ray diffraction testing revealed a relationship between cycle life and KOH electrolyte concentration. Figure 10 shows that, after the first 200 cycles, the concentration loss of KOH becomes smaller as a plateau on the curve is approached. Cells 2A, 3A, and 6A from Table V are also plotted in Figure 10 and show the plateau to be about 19%.

2.3.5 STABILITY OF POTASSIUM TITANATE

The Dupont patent describes two stable species of potassium titanate. The first is a tetratitanate given the formula $K_2Ti_4O_9$; the second is a hexatitanate with the formula $K_2Ti_6O_{13}$. It was claimed that the extracted tetratitanate has superior flexibility and fiber lengths, as much as 40% of the potassium content can be removed by water washing, and the tetratitanate can be converted to the more stable hexatitanate by heating to temperatures above 1100°C. However, there is conflicting evidence that the KT converts to rutile at the high temperature.

Samples 1, 2 and 3 in Table VI were untreated samples of potassium titanate. The first two samples were simply water washed; one with cold water, the second with hot water. The third sample was treated with KOH then water washed. As can be seen, approximately a 5% loss in weight occurred in all three samples. This indicates a soluble fraction in the untreated potassium titanate. Sample 4 was a portion

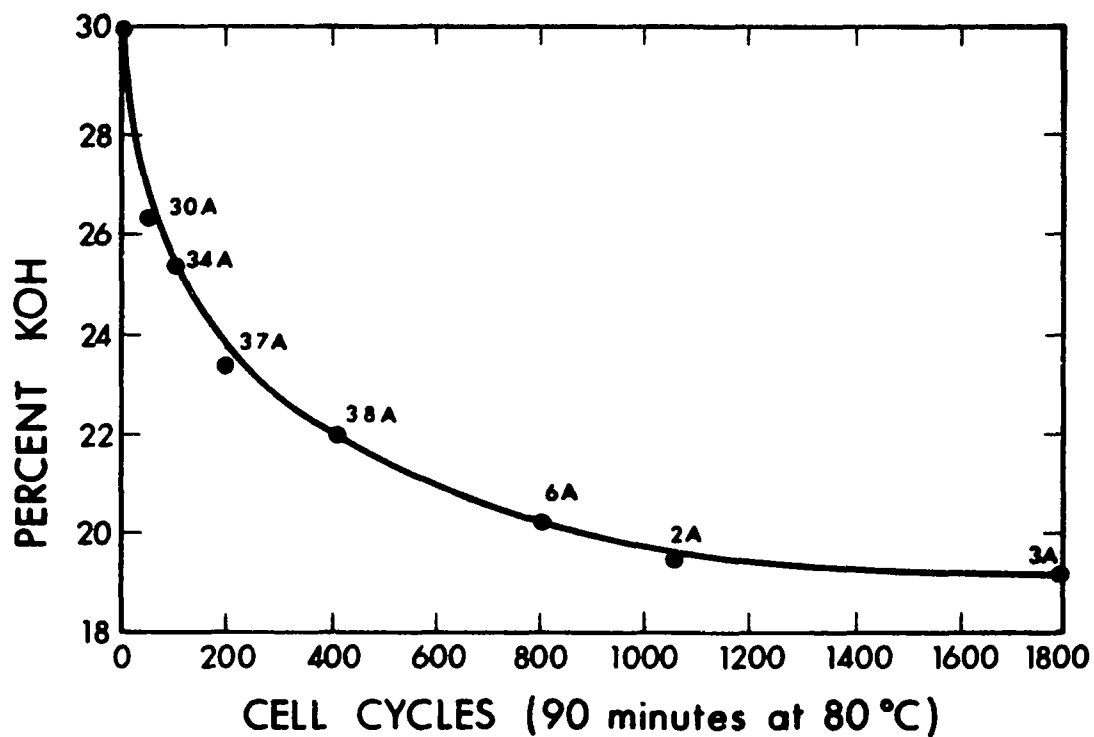


Figure 10. Electrolyte Concentration Drop versus Cell Cycles

TABLE VI

POTASSIUM TITANATE STABILITY TESTS

No.	Sample	Treatment	Loss
1	10.0000g of untreated potassium titanate.	Soak for 48 hours in distilled water at room temperature.	0.2473g (2.5%)
1A	Same sample above.	Wash through büchner funnel for 6 hours with distilled water at room temperature.	0.4218g (4.2%)
2	5.0305g of untreated potassium titanate.	Wash through büchner funnel for 6 hours with distilled water at 90 to 100°C.	0.2201g (5.0%)
3	2.5125g of untreated potassium titanate.	Boiled in 300 cc of 30% KOH for 6 hours. Wash through büchner funnel until pH is same as wash water.	0.1308g (5.2%)
4	0.8570g of untreated potassium titanate.	Fired at 1200°C.	0.0580g (6.6%)
5	1.0912g of potassium titanate fired at 1200°C.	Washed through büchner funnel for 6 hours with distilled water at 90 to 100°C.	0.0038g (0.35%)
6	2.4386g of potassium titanate fired at 1200°C.	Boiled in 300 cc of 30% KOH for 6 hours. Washed through a büchner until pH is same as wash water.	0.0210g (0.87%)
7	4.2330g of Baker Reagent grade TiO ₂	Boiled in 400 cc of 30% KOH for 6 hours. Washed through a büchner funnel until pH is same as wash water.	0.0145g (0.34%)

of untreated potassium titanate that was fired at 1200°C. As can be seen, a 6.6% loss of weight occurred. A sample of fired potassium titanate was submitted for X-ray diffraction tests. A major phase was identified as TiO_2 (rutile), an intermediate phase was identified as the hexatitanate ($K_2Ti_6O_{13}$). A few other low-intensity reflections were observed that do not fit the pattern for rutile or hexatitanate. The occurrence of the large amount of rutile present in this sample indicates that the prolonged high temperature environment has initiated disassociation of the titanate. As the decomposition and vaporization temperatures of potassium oxide occur much below 1,000°C, this compound disappears as fast as disassociation of the titanate phase occurs. Stabilization of the hexatitanate phase should be possible at a lower temperature, with perhaps not so much degradation of the fiber structure. Samples 5 and 6 are fired potassium titanate, a mixture of hexatitanate and rutile. As can be seen in Table VI, there was small loss in weight from either water washing or treatment with hot KOH. This indicates that the fired potassium titanate has a smaller fraction of soluble material.

Sample 7 is Baker Reagent grade TiO_2 . It was subjected to hot KOH and water washed. As can be seen, the weight loss was small, showing that TiO_2 is stable in KOH for this test condition.

2.3.6 CATALYST MIGRATION TESTS

In order to determine whether the Pt found in the black layer of the matrix was transferred from one or both electrodes, a test was run using a Pt electrode on the H_2 side and a Pd electrode on the O_2 side. Cell 54-A contained a standard EOS H_2 electrode and a nickel plaque with palladium on the O_2 side. The standard pressed component matrix with 45 g of KOH was used with a 0.060-in. spacer. The cell built up large differential pressures because the Pd electrode on the O_2 side had excess nickel which would oxidize on charge and be reduced on

discharge. Despite the differentials, the cell ran 41 cycles. A sample of the matrix was submitted for a semiquantitative analysis, as can be seen from Table VII. The black layer contains palladium and no platinum. This result indicates that the metal is removed from only the O₂ electrode.

To eliminate the differential pressures, an electrode was fabricated by forming Pd powder on an 0.010-in.-thick, gold-plated, expanded nickel screen. This electrode was used in cell 61-A with a standard EOS electrode on the H₂ side. The matrix was the standard pressed composite type, and it contained 45 g of 30.4% KOH. The spacer was 0.060-in. thick. The cell was charged to 350 psig. On discharge it was found that the cell could not sustain any current. Upon reexamining the Pd powder, it appeared to be a grey color, probably too coarse to act as a catalyst.

Some Pd black was purchased from Engelhart Company and another O₂ electrode was fabricated in the same manner as above and assembled in cell 67-A. Cell 67-A contained the standard EOS H₂ electrode, a pressed composite matrix with 45 g of 30.4% KOH, and a 60-mil spacer. The cell ran 49 cycles and then began to self-discharge because of internal gas leakage. The cell was taken apart and a new matrix was inserted. The cell was run for 639 cycles. The test was discontinued when the average discharge voltage fell below 0.7V. Figure 11 shows a fast degradation in cycle performance after 300 cycles. Figure 12 shows the initial and final polarization curves for the second matrix cell. The initial and final impedances of the cell with the second matrix were 0.004Ω and 0.008Ω at 80°C. The final concentration of the KOH was 20.1%. Upon disassembly it was observed that the H₂ backup plates and screen were clean. The O₂ screens and backup plate had a black discoloration.

TABLE VII

SEMIQUANTITATIVE SPECTROGRAPHIC ANALYSIS OF
MIDDLE SECTION OF FUEL CELL MATRIX NO. 54-A

<u>Element</u>	<u>%</u>
Potassium	35.0
Titanium	23.0
Silicon	5.1
Magnesium	3.4
Calcium	0.36
Boron	0.025
Manganese	0.033
Iron	0.012
Aluminum	trace
Copper	0.0047
Nickel	trace
Palladium	1.1
Platinum	not detected less than 0.05
Other elements	nil

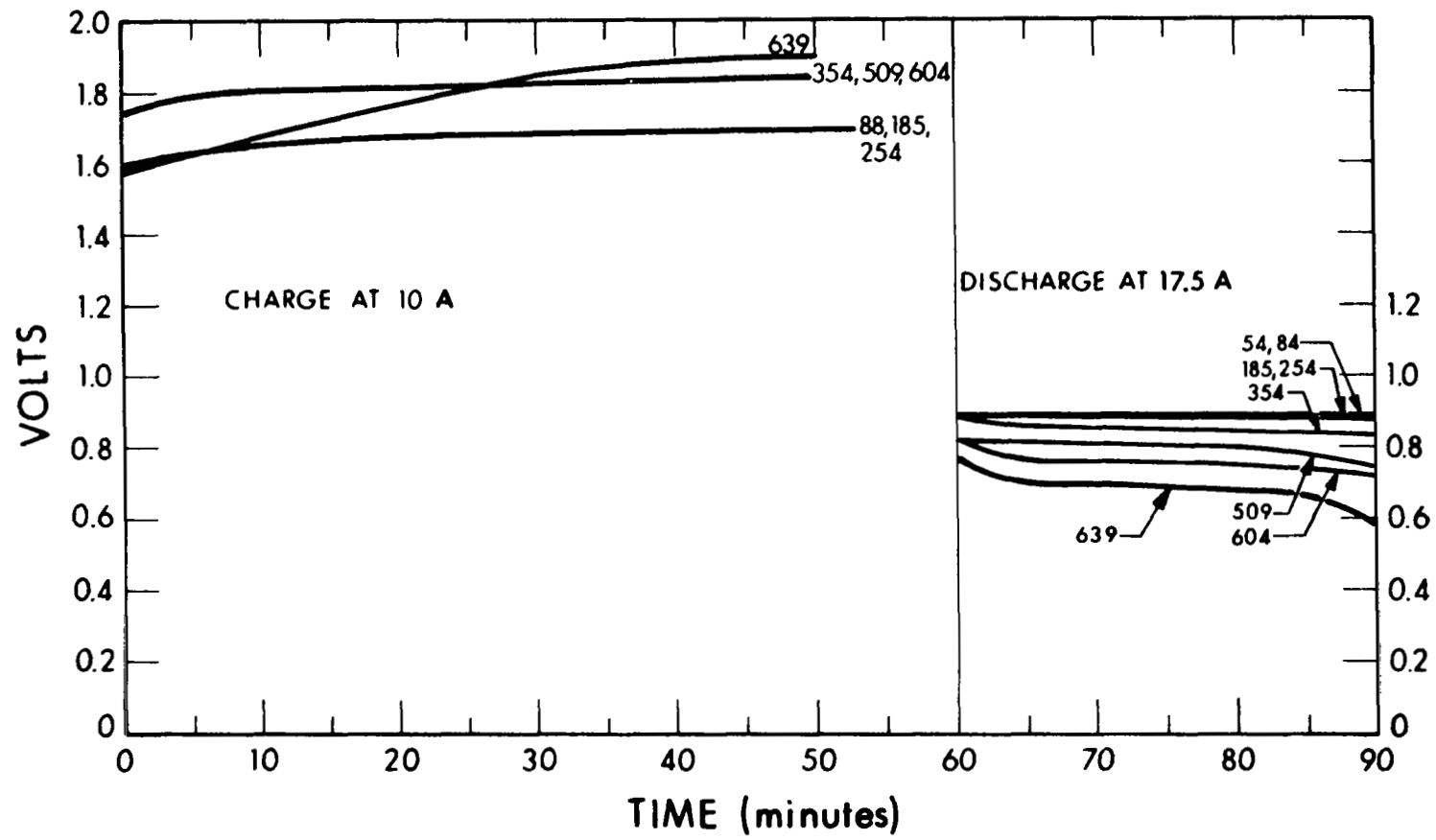


Figure 11. Cycle Performance of Cell 67-A

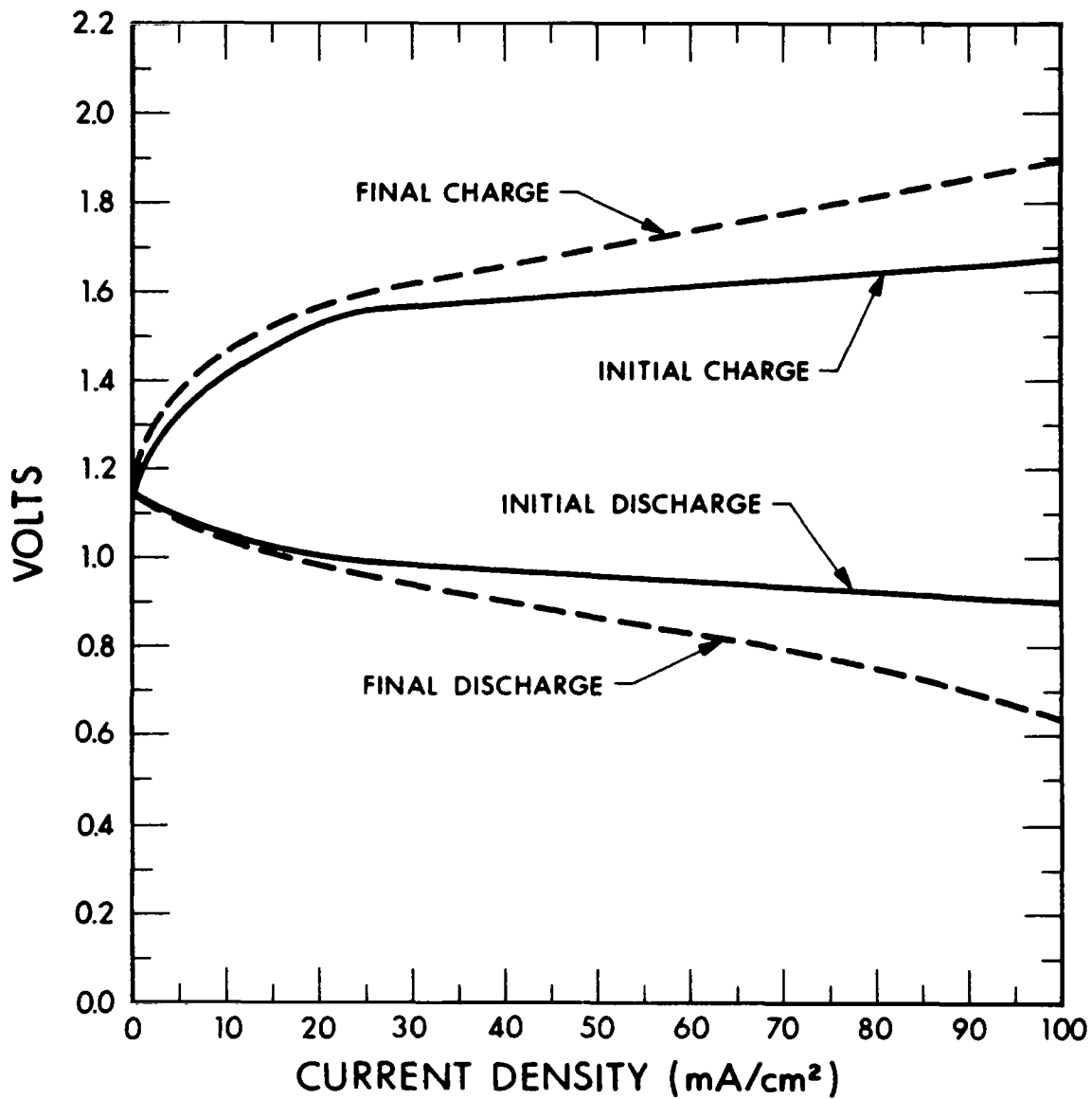


Figure 12. Charge and Discharge Polarization of Cell 67-A

Table VIII shows the results of a spectrographic analysis of the matrix from cell 67-A. As shown, the matrix contains only palladium, confirming the results of cell 54. The migration occurs only from the O₂ electrode.

2.3.7 PT MIGRATION IN ELECTROLYTE

A 2-in.² Cyanamid AB-6 electrode was run as a cathode in 750 cc of 30% KOH for 400 hrs. A current density of 27.8 mA/cm² was used. Water was replaced as it was electrolyzed, keeping the concentration constant. A platinum crucible lid (2.5 in.²) was used as the anode and weighed periodically. Figure 13 shows a weight gain during the first 72 hours, then a constant weight, and a loss in weight. The Cyanamid electrode was weighed at the beginning and end of the test and showed no change in weight. The conclusion is that no Pt was removed from the O₂ electrode under the above conditions. Some impurities were removed from the electrolyte during the first 72 hours. The migration of Pt in the fuel cell is apparently not simple electrodeposition.

2.3.8 GOLD AND PLATINUM ANALYSIS IN FUEL CELL MATRIXES

Table IX lists the analytical results obtained using 1-in.² samples of fuel cell matrixes. The gold was analyzed gravimetrically, and the Pt was analyzed using a spectrophotometer. Blank matrixes were run and showed no gold or platinum. A 1-in.² matrix sample from cell 5-A was submitted to an outside testing laboratory, Truesdail Laboratories, for analysis. Table X shows the results to be in line with those obtained at EOS.

This analysis represents the minimum amount of Pt removed from the electrode or electrodes, since some may be deposited outside of the matrix. If all the migrating platinum comes from the O₂ electrode, as the Pd electrode cell test indicated, the analysis shows that at least

TABLE VIII

SEMIQUANTITATIVE SPECTROGRAPHIC ANALYSIS OF
MIDDLE SECTION OF FUEL CELL MATRIX NO. 67-A

<u>Element</u>	<u>%</u>
Potassium	16.0
Titanium	42.0
Palladium	1.0
Silicon	2.4
Magnesium	3.7
Iron	0.037
Boron	0.014
Manganese	0.037
Gold	0.084
Aluminum	0.084
Copper	0.0019
Chromium	0.0061
Calcium	0.061
Other elements	nil

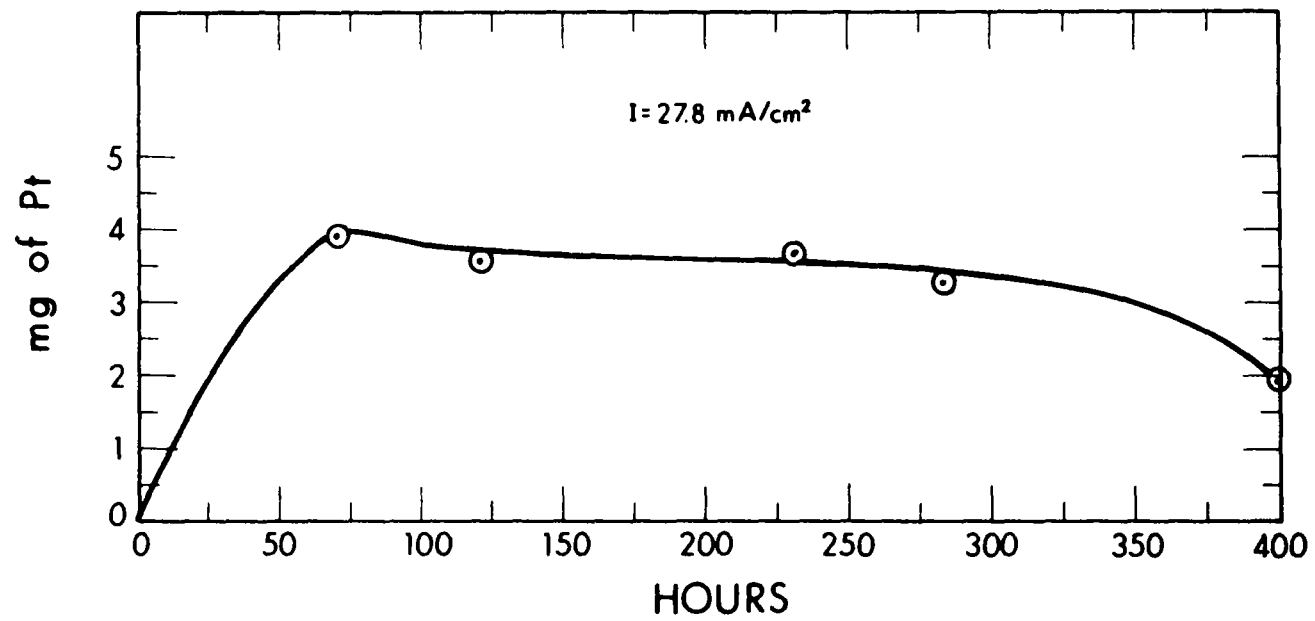


Figure 13. Pt Migration in 30% KOH

TABLE IX

A_μ AND Pt ANALYSIS OF FUEL CELL MATRIX

Cell No.	Cycles	mg/in. ²		Based on 27.2 in. ² Area		Comments
		A _μ (mg)	Pt (mg)	A _μ (mg)	Pt (mg)	
30-A	50	4.9	0.833	133	22.6	90-minute cycle at 80°C
34-A	100	1.45	3.75	31.2	102	90-minute cycle at 80°C
37-A	200	9.6	2.25	262	61.2	90-minute cycle at 80°C
38-A	400	22.8	2.75	620	75	90-minute cycle at 80°C
35-A	1240	9.85	14.75	268	401	90-minute cycle at 80°C
5-A	1460	14.8	12.25	402	333	90-minute cycle at 80°C
3-A	1802	7.6	11.25	207	306	90-minute cycle at 80°C
29-A	105	2.4	0.583	65.2	15.85	Cycled at 50°C

TABLE X

DETERMINATION OF GOLD AND PLATINUM
SAMPLE OF MATRIX FROM CELL 5A

	<u>Milligrams/in.²</u>
Gold	11.21
Platinum	14.19

Note: Analysis by Truesdail Laboratories

25% of the catalyst can be removed from the electrode under these conditions. The resulting change in the O₂ electrode (loss of catalyst) most probably is a large factor in degradation of performance with cycle life.

2.4 LIFE TESTING

Using the pressed matrix selected in the matrix comparison tests, an EOS H₂ electrode, Cyanamid AB-6 O₂ electrode, and a 0.060-in. spacer, fuel cells were built and life cycled under various cycle regimes. The cells had an electrode area of 180 cm².

The cycle regimes that were used are as follows:

- a. One-hr charge at 10A, 1/2-hr discharge at 17.5A, 80°C
- b. One-hr charge at 10A, 1/2-hr discharge at 17.5A, 50°C
- c. 22.8-hr charge at 0.850A, 1.2-hr discharge at 14.4A, 80°C
- d. 22.8-hr charge at 0.65A, 1.2-hr discharge at 10.0A, 80°C
- e. 22.8-hr charge at 0.65A, 1.2-hr discharge at 10.0A, 50°C
- f. 2.5-hr charge at 3.5A, 1.0-hr discharge at 8.0A, 50°C
- g. A repeat of cycle "a" above.

Table XI is a summary of the life tests performed during the program.

2.4.1 90-MINUTE CYCLE AT 80°C

The pressed matrix cells from the matrix comparison tests are included in this subsection to cover cycle regime "a" from the previous list. This series of cells provides a baseline of over 2000 hrs operation for comparison with the other cycle regimes.

TABLE XI

SUMMARY OF CELLS LIFE TESTS

Cell No.	Matrix	No. of Cycles	Type of Cycle	Test Temp. (°C)	Electrodes	Electrolyte	Final KOH (%)	Impedance at same (°C) as "Test Temp."		Comments
								Initial	Final	
2-A	Pressed composite	1067	60/30 min 10/17.5A	80	EOS/Cyanamid AB-6	45 g of 30.0%	19.3	0.001Ω	0.006Ω	Sample sent for X-ray diffraction Normal failure.
3-A	Pressed composite	1802	60/30 min 10/17.5A	80	EOS/Cyanamid AB-6	45 g of 30.0%	19.1	0.001Ω	0.005Ω	Normal failure.
4-A	Pressed composite	152	60/30 min 10/17.5A	80	EOS/Cyanamid AB-6	45 g of 30.0%		0.006Ω	0.007Ω	Upon disassembly, a burnt spot was observed
5-A	Pressed composite	1460	60/30 min 10/17.5A	80	EOS/Cyanamid AB-6	45 g of 30.0%	16.5	0.002Ω	0.005Ω	Normal failure.
6-A	Pressed composite	805	60/30 min 10/17.5A	80	EOS/Cyanamid AB-6	45 g of 30.0%	20.3	0.001Ω	0.005Ω	Normal failure.
29-A	Pressed composite	105	60/30 min 10/17.5A	50	EOS/Cyanamid AB-6	45 g of 30.0%	29.4	0.004Ω	0.016Ω	Sent sample for X-ray diffraction test Normal failure.
31-A	Pressed composite	104	60/30 min 10/17.5A	50	EOS/Cyanamid AB-6	45 g of 30.0%	26.25	0.004Ω	0.005Ω	Had ignition hole that resealed
32-A	Pressed composite	200	60/30 min 10/17.5A	50	EOS/Cyanamid AB-6	45 g of 30.0%				Ignition terminated test
33-A	Pressed composite	399	60/30 min 10/17.5A	60	EOS/Cyanamid AB-6	45 g of 30.0%	26.25	0.004Ω	0.008Ω	Normal failure.
60-A	Pressed composite	63	60/30 min 10/17.5A	50	EOS/Cyanamid AB-6	45 g of 30.0%	26.55	0.011Ω	0.12Ω	Normal failure.

TABLE XI

SUMMARY OF CELLS LIFE TESTS (contd.)

Cell No.	Matrix	No. of Cycles	Type of Cycles	Test Temp. (°C)	Electrodes	Electrolyte	Final KOH (%)	Impedance at same (°C) as "Test Temp."		Comments
								Initial	Final	
19-A	Pressed composite	10	22.8-hr charge, 1.2-hr discharge, 0.850 to 0.900A charge, 14.4A discharge	80	EOS/Cyanamid AB-6	45 g of 30.0%				24-hr cycles terminated by ignition at 625 psig
24-A	Pressed composite	78	22.8-hr charge, 1.2-hr discharge, 0.850 to 0.900A charge, 14.4A discharge	80	EOS/Cyanamid AB-6	45 g of 17.0%	10.7	0.007Ω	0.007Ω	24-hr cycles Normal failure.
36-A	Pressed composite	41	22.8-hr charge, 1.2-hr discharge, 0.850 to 0.900A charge, 14.4A discharge	80	EOS/Cyanamid AB-6	45 g of 30.0%	21.35			24-hr cycle Cell shorted out
49-A	Pressed composite	31	22.8-hr charge, 1.2-hr discharge, 0.850 to 0.900A charge, 14.4A discharge	80	EOS/Cyanamid AB-6	45 g of 30.0%	21.3			24-hr cycle terminated by gas recombination - self discharge
53-A	Pressed composite	48	22.8-hr charge, 1.2-hr discharge, 0.65A charge, 10.0A discharge	80	EOS/Cyanamid AB-6	45 g of 30.0%		0.005Ω		24-hr cycle terminated by gas recombination - self discharge.

TABLE XI

SUMMARY OF CELLS LIFE TESTS (contd.)

Cell No.	Matrix	No. of Cycles	Type of Cycles	Test Temp. (°C)	Electrodes	Electrolyte	Final KOH (%)	Impedance at same (°C) as "Test Temp."		Comments
								Initial	Final	
57-A	Pressed composite	0	22.8-hr charge, 1.2-hr discharge, 0.65A charge, 10.0A discharge	80	EOS/Cyanamid AB-6	45 g of 30.1% KOH				shorted on initial cycle
59-A	Pressed composite	10	22.8-hr charge, 1.2-hr discharge, 0.65A charge, 10.0A discharge	80	EOS/Cyanamid AB-6	45 g of 30.1% KOH				24-hr cycles failed after being reverse-charged
63-A	Pressed composite	30	22.8-hr charge, 1.2-hr discharge, 0.65A charge, 10.0A discharge	80	EOS/Cyanamid AB-6	45 g of 30.4% KOH	21.9			24-hr cycle discontinued because of faulty transducer
64-A	Pressed composite	32	22.8-hr charge, 1.2-hr discharge, 0.65A charge, 10.0A discharge	50	EOS/Cyanamid AB-6	45 g of 30.0% KOH	27.9			24-hr cycle discontinued because of gas recombination
65-A	Pressed composite	111	2.5-hr charge, 1.0-hr discharge, 3.5A charge, 8.0A discharge	50	EOS/Cyanamid AB-6	45 g of 30.4% KOH		0.006 Ω	0.009 Ω	3.5-hr cycle Normal failure.
72-A	Pressed composite	314	60/30 min 10/17.5A	80	EOS/Cyanamid AB-6	45 g of 29.8% KOH		0.007 Ω		Normal failure.

TABLE XI

SUMMARY OF CELLS LIFE TESTS (contd.)

Cell No.	Matrix	No. of Cycles	Type of Cycle	Test Temp. (°C)	Electrodes	Electrolyte	Final KOH (%)	Impedance at same (°C) as "Test Temp."		Comments
								Initial	Final	
73-A	Pressed composite	758	60/30 min 10/17.5A	80	EOS/Cyanamid AB-6	45 g of 29.8% KOH		0.004Ω		Removed from test because of faulty transducer
74-A	Pressed composite	17	60/30 min 10/17.5A	80	EOS/Cyanamid AB-6	37.6 g of 29.8% KOH		0.009Ω		Matrix made from special DuPont hexatitronate; 0.050-in. spacer used
75-A	Pressed composite	444	60/30 min 10/17.5A	80	EOS/Cyanamid AB-6	45 g of 29.8% KOH		0.006Ω		Removed from test because of faulty transducer. Put back on test.
76-A	Pressed composite		60/30 min 10/17.5A	80	EOS/Cyanamid AB-6	45 g of 29.8% KOH				On test.
77-A	Pressed composite	226	60/30 min 10/17.5A	80	EOS/Cyanamid AB-6	45 g of 29.8% KOH		0.005Ω	0.011Ω	Power supply failed. Discharge voltage fell below 0.70 volts.
78-A	Pressed composite	492	60/30 min 10/17.5A	80	EOS/Cyanamid AB-6	45 g of 29.8% KOH		0.003Ω		On test.
79-A	Pressed composite	375	60/30 min 10/17.5A	80	EOS/Cyanamid AB-6	45 g of 29.8% KOH		0.005Ω		On test.
80-A	Pressed composite	236	60/30 min 10/17.5A	80	EOS/Cyanamid AB-6	45 g of 29.8% KOH		0.003Ω		On test.

2.4.2 90-MINUTE CYCLE AT 50°C

Cells 29A, 31A, 32A, 33A, and 60A in Table IV were cycled using regime "b". Two of the cells, nos. 31-A and 32-A, were terminated when an internal ignition occurred.

Cell 29-A was terminated at 105 cycles when the discharge fell below 0.7V. Figure 14 shows that the charge voltage was quite high near 1.9V for the first 100 cycles, then it abruptly began to rise above 2.0V. The discharge at 104 cycles began quite low, then it recovered half way through the cycle. This phenomenon is an indication that the cell may have become too dry. Upon disassembly of the cell, it was observed that H₂ and O₂ screens were clean. The H₂ electrode looked good. The matrix adhered to the O₂ electrode and appeared drier than usual. A black layer extended slightly into the matrix from the H₂ side. There was no distinct dark middle layer.

Cell 60-A was terminated after 63 cycles when the discharge fell below 0.7V. The inside of the cell appeared identical to 29-A discussed above. There was no distinct dark middle layer in the matrix.

Cell 33-A was a standard cell constructed in the same manner as cells 29A, 31A, and 32A. This cell was run at 60°C instead of 50°C to determine if a slightly higher temperature would lead to longer cycle lives. The cell ran 399 cycles and was removed from test. Figure 15 shows a final average discharge voltage of 0.65. The initial and final impedances at 60°C were 0.004Ω and 0.008Ω. The final KOH analysis gave a concentration of 26.25%. Upon disassembly, it was observed that the electrodes, screens, and plates on both sides of the cell were in good condition. The H₂ side of the matrix was gray and hard. The gray layer extended into the middle of the matrix. The O₂ side was gray on the surface and white immediately under the surface. The matrix appeared to be softer on this side. As was observed in the 50°C cells, no distinct middle

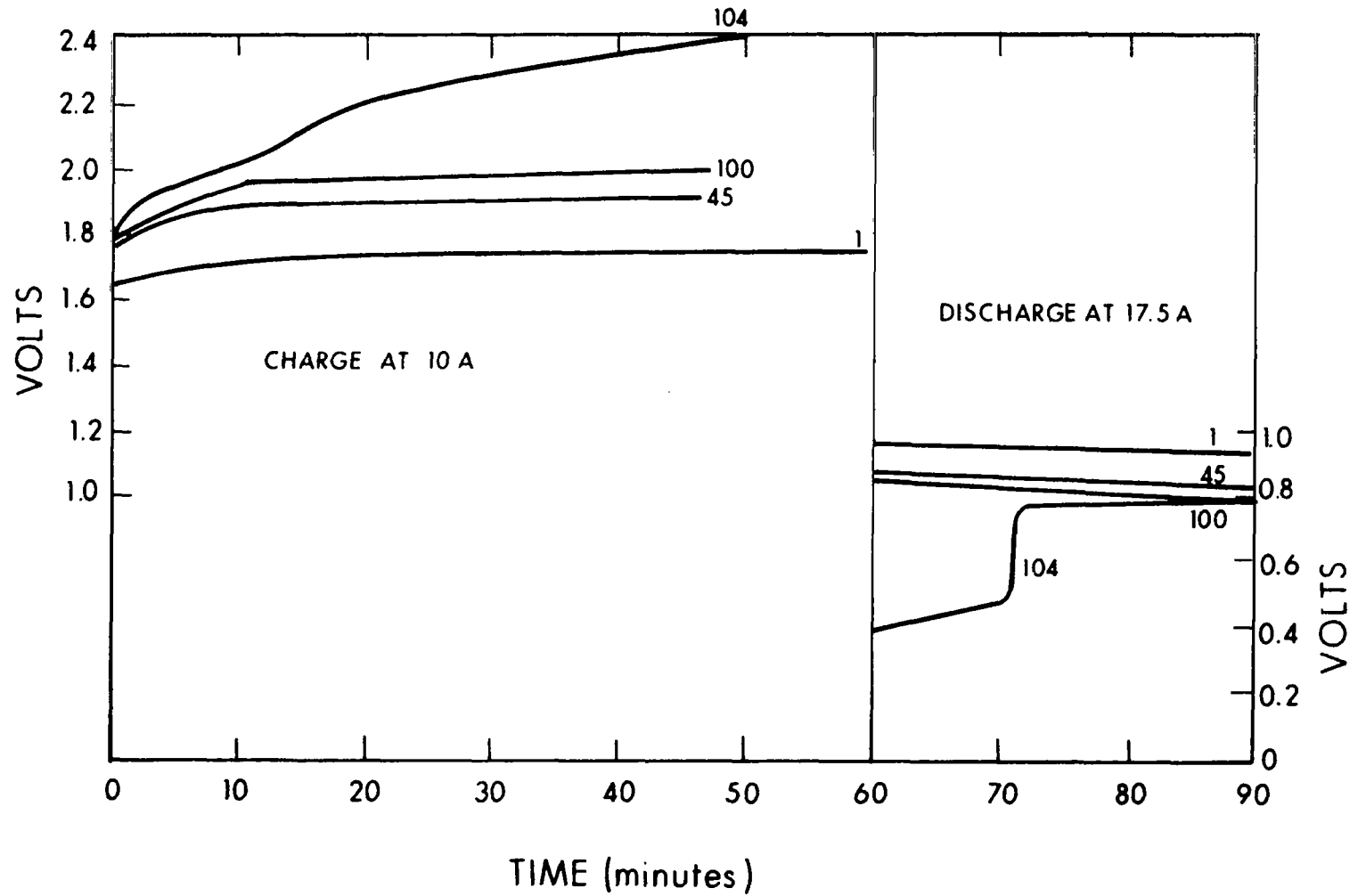


Figure 14. Cycle Performance of Cell No. 29-A

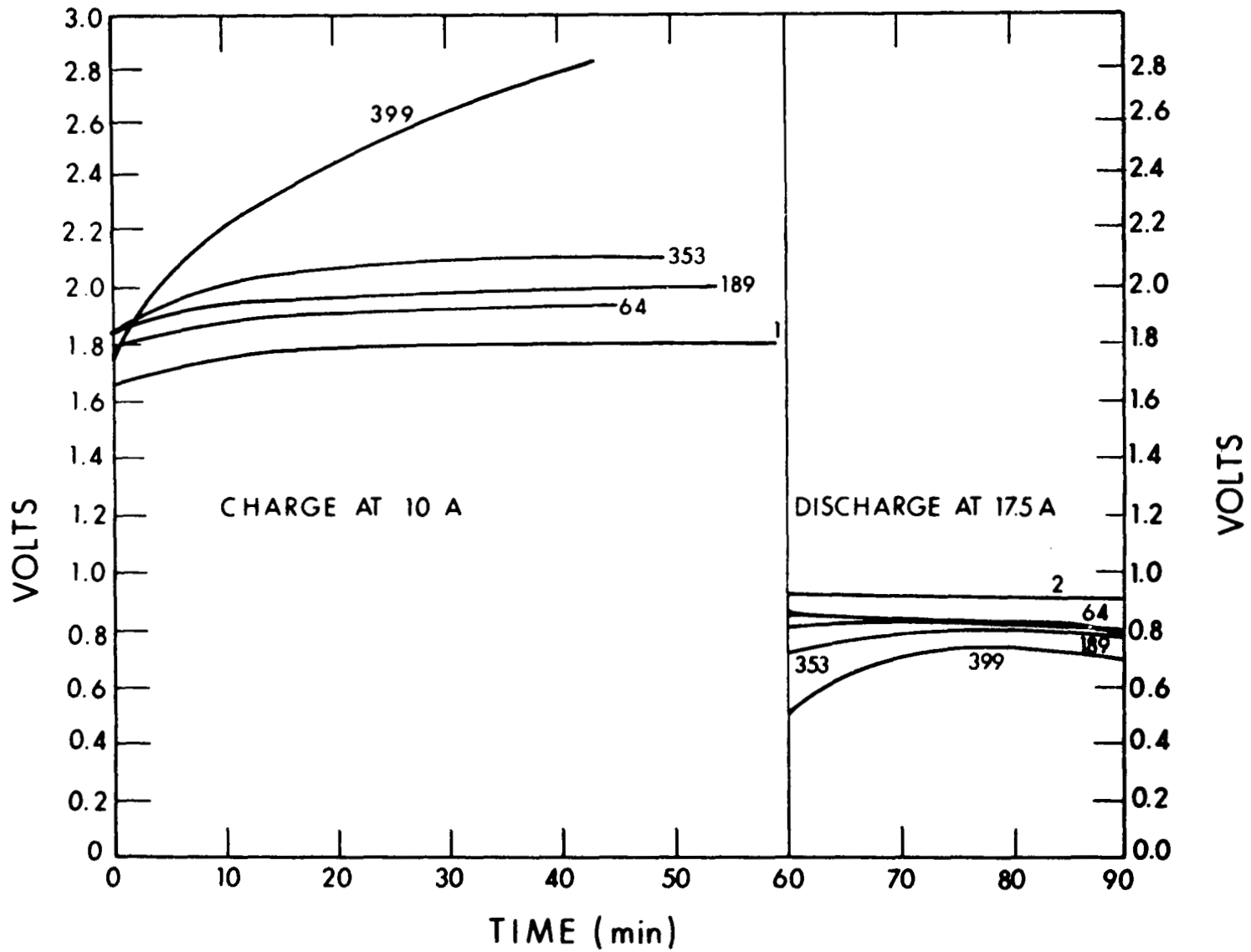


Figure 15. Cycle Performance of Cell No. 33-A

layer can be identified. This cell ran at 60°C and demonstrated a little better cycle life than any of the 50°C cells, but did not approach the cycle life demonstrated by the 80°C cells. The high charge voltages obtained at the lower temperatures may adversely affect the low-temperature cells. A 24-hr test at 50°C might give different results since the charging current density will be lower with a corresponding lower voltage.

2.4.3 24-HR CYCLE AT 80°C

Cells 19A, 24A, 36A, 49A, and 53A were cycled using regime "c". The cells were charged to 500 psig using a limiting pressure switch. All of the tests except one were terminated by ignition, gas recombination, or internal cell shorts. The conclusion was reached that the cells were being overcharged beyond the capacity inherent in the cell configuration. It was decided that the 24-hr test regime be changed, limiting the charge pressure to 400 psig. This means discharging at about 10A instead of 14.4A.

2.4.4 MODIFIED 24-HR CYCLE AT 80°C

Cell 53-A was changed to cycle regime "d" after running 7 cycles on cycle regime "c". The cell ran 48 cycles before it failed because of internal gas recombination. Figure 16 shows that the cell had a tendency to flood toward the end of discharge. Cell 57-A shorted out on its initial cycle. Cell 59-A ran 10 cycles then was accidentally charged in reverse, after which it failed. Cell 63-A ran 30 cycles when it was subjected to high differential pressures because its transducer failed. Figure 17 shows the performance characteristics of cell 63-A. As can be seen, the discharge voltage remained above 0.9V until near the end, when flooding occurred.

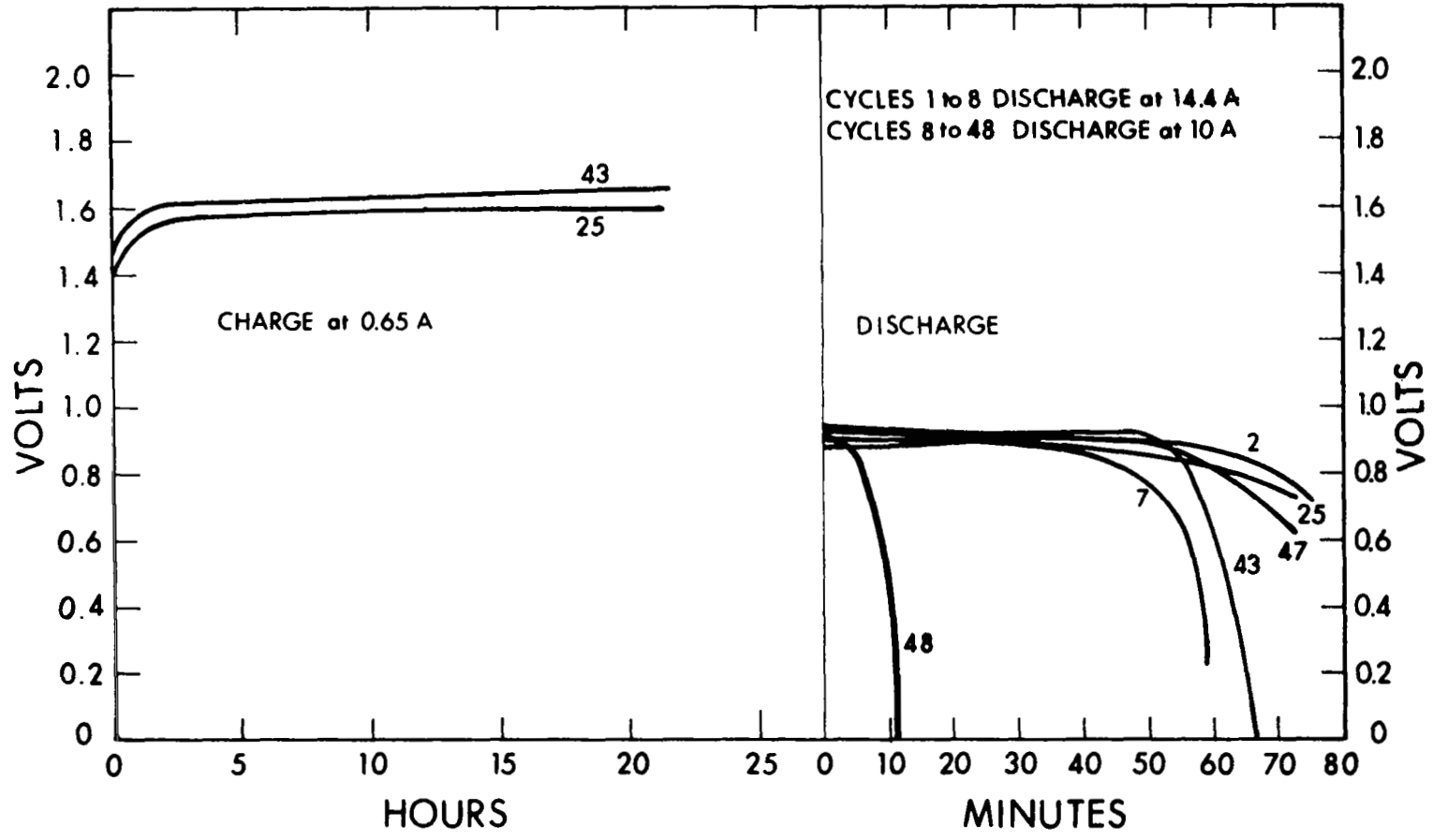


Figure 16. Cycle Performance of Cell No. 53-A

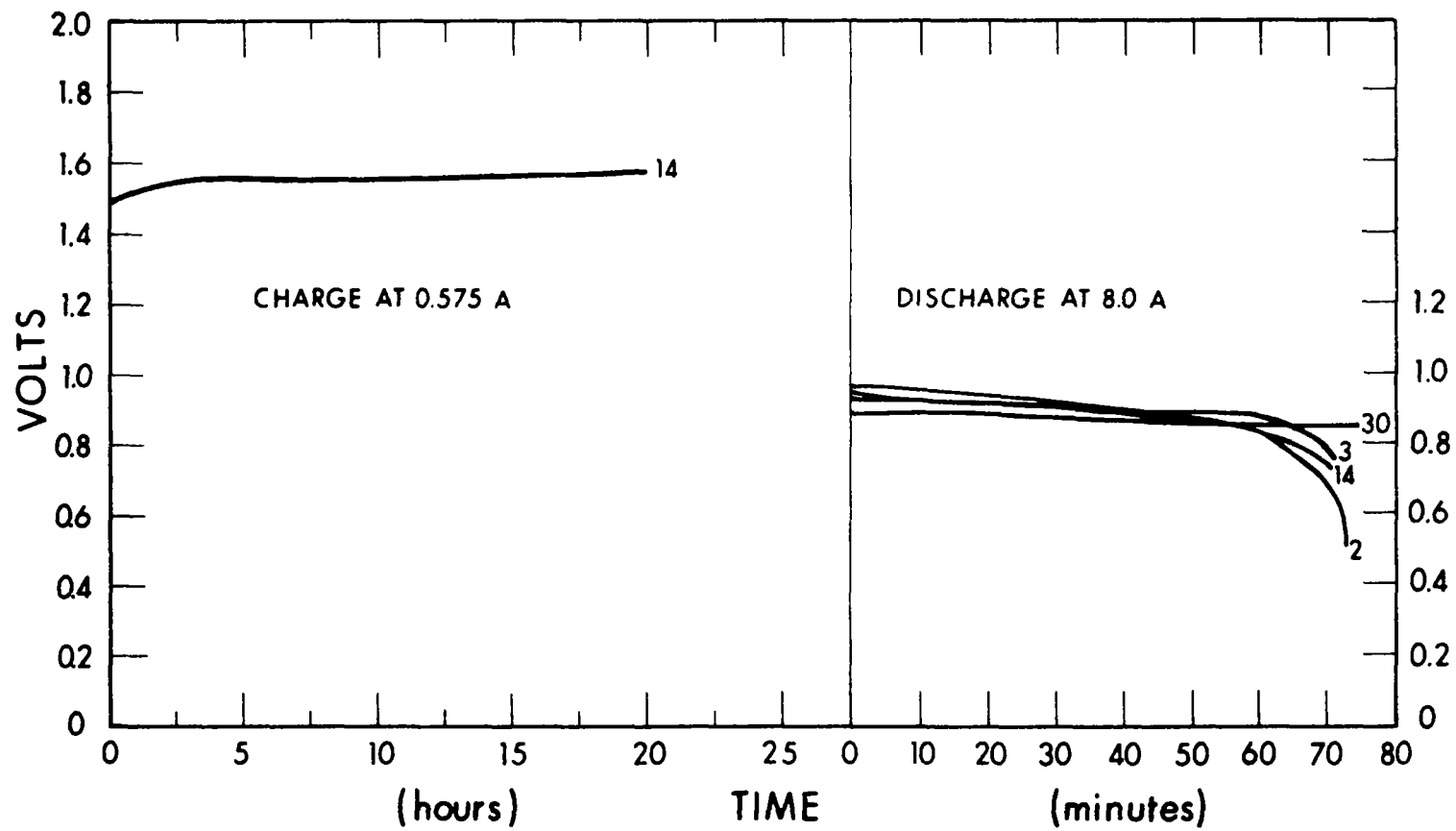


Figure 17. Cycle Performance of Cell No. 63-A

2.4.5 MODIFIED 24-HR CYCLE AT 50°C

Cell 64-A was cycled using regime "e". The cell is a duplicate in construction of all the life test cells. As Figure 18 shows, the cell averaged above 0.9V for 30 cycles. The cell began to self-discharge after the 31st cycle. No external short circuits could be found. The test was terminated and the cell was taken apart. Nothing was found that could account for the self discharge. Both the H₂ and O₂ backup screens and electrodes were clean. The matrix was slightly gray on the O₂ side and a darker gray on the H₂ side. There was no dark layer in the middle of the matrix. This is consistent with other cells cycled at 50°C. The final KOH concentration was 27.9%.

2.4.6 3.5 HR CYCLE AT 50°C

Cell 65-A had a pressed composite matrix containing 45g of 30.4% KOH. The standard EOS/Cyanamid electrodes were used. The spacer was 0.060 in. thick. The cell was put on a time cycle of 2.5 hrs charge and 1 hr discharge. A pressure switch limited the charge to 350 psig. The charge current was 3.5A and the discharge was 8.0A. The ambient temperature was 50°C. The test was run for 111 cycles and then discontinued because of performance degradation. Figure 19 shows a voltage drop at the end of discharge. The drop was small for the first 50 cycles and became extreme after 90 cycles. Figure 20 shows the initial and final polarization curves.

Upon disassembly, it was observed that the electrodes and screens on both sides were clean. The matrix had no discoloration, and platinum adhered to the matrix on the H₂ side. The O₂ side was white and soft. No middle dark layer was observed. This is consistent with other cells cycled at 50°C.

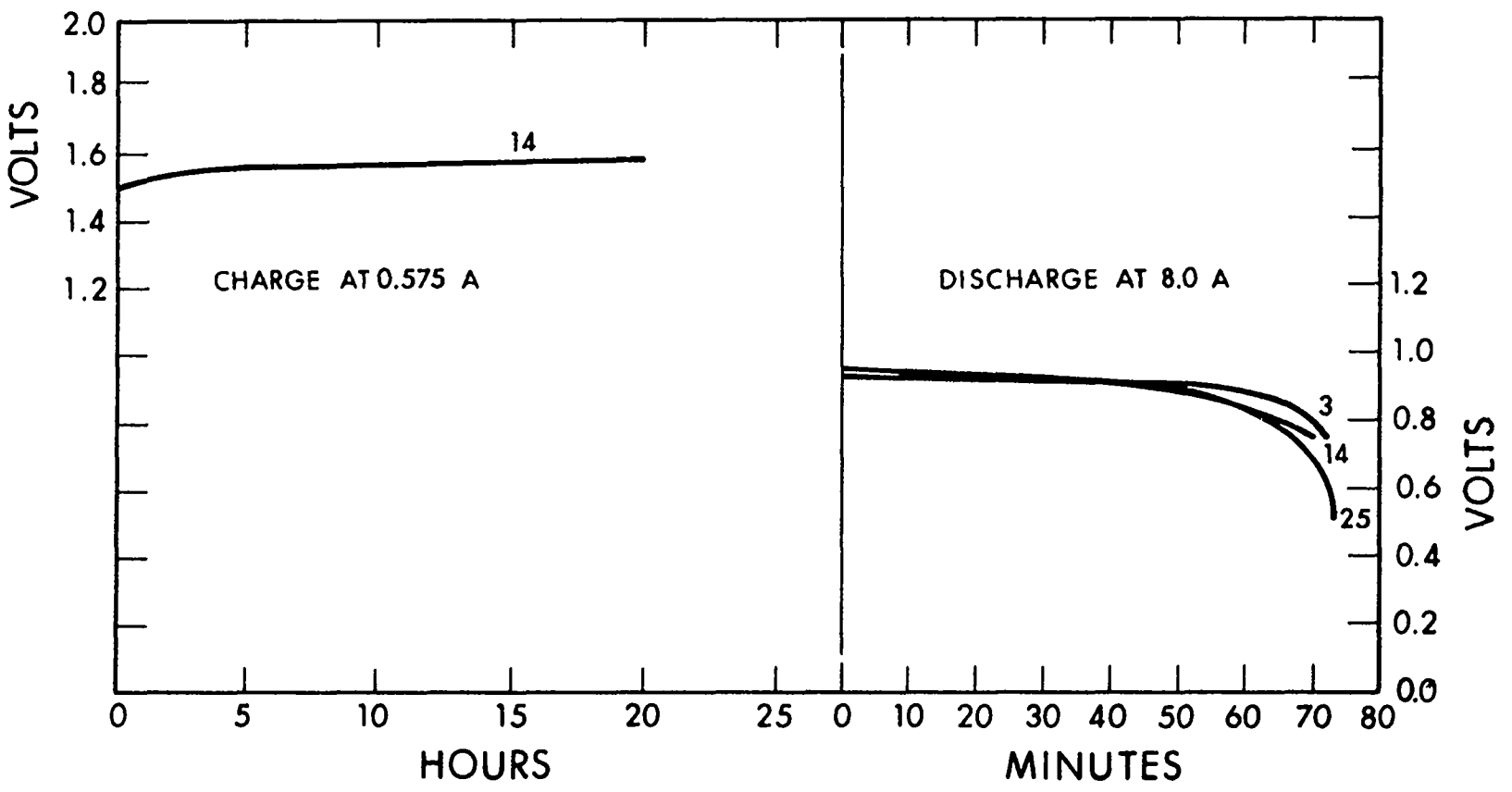


Figure 18. Cycle Performance of Cell No. 64-A

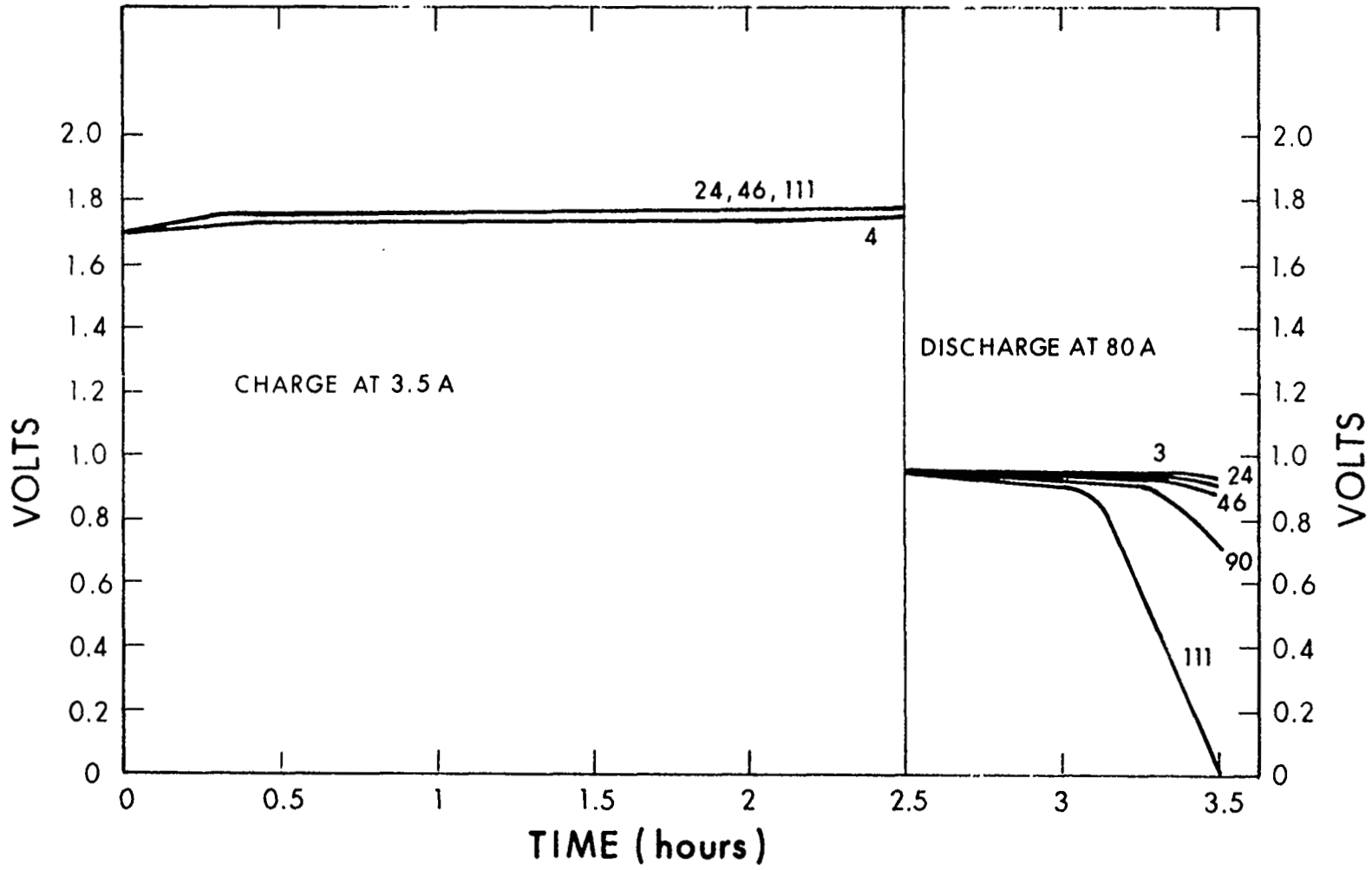


Figure 19. Cycling Performance of Cell No. 65-A

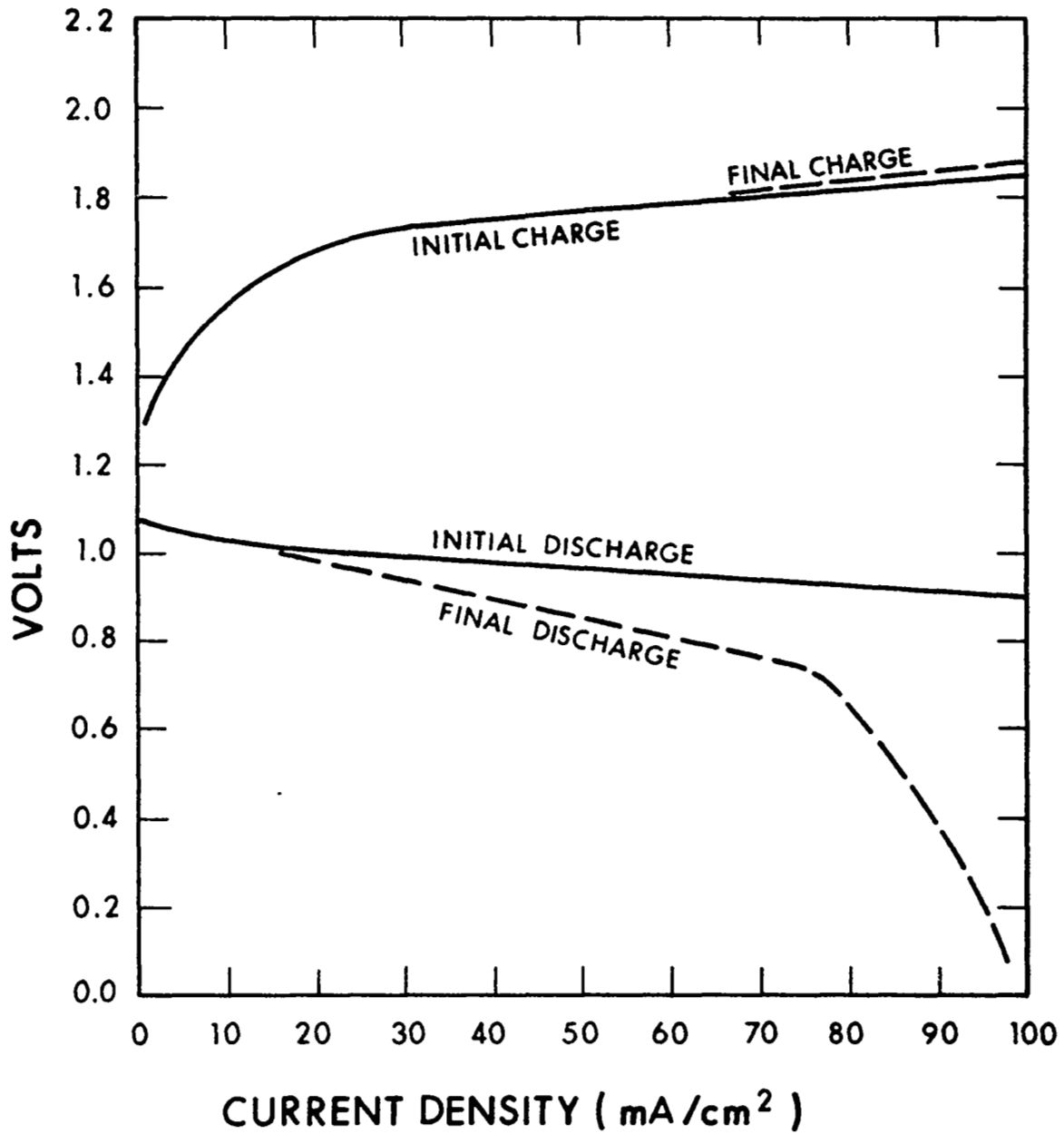


Figure 20. Charge and Discharge Polarization of Cell No. 65-A

2.4.7 REPEAT OF 90 MIN CYCLE AT 80°C

In order to reevaluate the DuPont potassium titanate material, cells 72-A through 80-A were life-cycled using the 90-min regime at 80°C. Cell 74-A contained a special hexatitanate matrix. The other cells contained matrices fabricated from washed DuPont potassium titanate.

2.4.7.1 DuPont Hexatitanate Matrix Cell

Cell 74-A was a trial cell with a matrix fabricated with the special DuPont hexatitanate supplied by NASA Lewis. The cell contained the standard EOS and Cyanamid AB-6 electrodes. The composition of the matrix was 80% KT, 10% Teflon and 10% asbestos. It weighed 29.2 g but was only 0.052 in. thick, whereas the ordinary titanate matrices are over 0.060 in. thick. A 0.050-in. spacer was used to insure compression of the matrix. Because of the spacing, only 37.6 g of KOH was used. The hexatitanate matrix was difficult to handle because of its high specific gravity and lack of tensile strength when wet. It was torn at the edge during assembly. The tear was pushed together and appeared to seal. The cell ran 6 cycles and began to self discharge. Figure 21 shows the performance was good while it ran. When the cell was disassembled, it was observed that all the components were clean. There was no dark middle layer in the matrix. Due to the limits of the program, the hexatitanate was not pursued further.

2.4.7.2 Regular DuPont Potassium Titanate Matrix Cells

Cell 72-A was the first of this life test series. It contained the standard EOS and Cyanamid AB-6 electrodes. The matrix was fabricated from the ordinary DuPont potassium titanate. The composition was 80% KT, 10% Teflon and 10% asbestos. It weighed 27.2 g and contained 45 g of 29.8% KOH. The spacer was 0.060 in. thick. The cell ran 314 cycles and the test was discontinued when the discharge dropped below 0.7V.

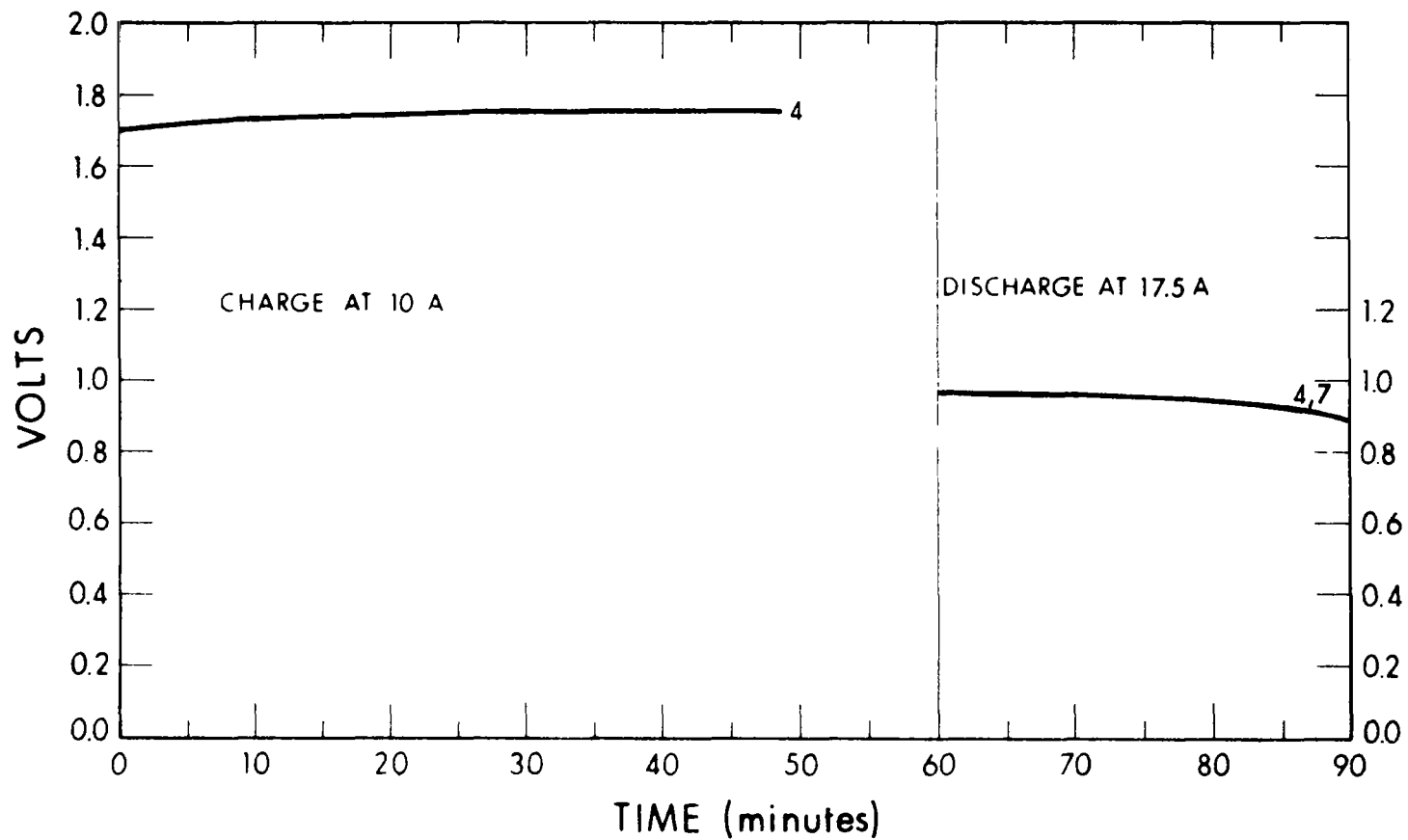


Figure 21. Cycle Performance of Cell No. 74-A

Figure 22 shows a large degradation in cycle performance after 270 cycles. Figure 23 shows the initial and final polarization curves for this cell. Upon disassembly, it was observed that the screens and backup plates on the O₂ side were extremely corroded. The H₂ screens and backup plate were clean. The matrix on the O₂ side was discolored and had a distinct dark middle layer.

Cell 73-A was a life test cell; it contained standard EOS and Cyanamid AB-6 electrodes. The matrix was fabricated from the ordinary DuPont potassium titanate. The composition was 80% KT, 10% Teflon and 10% asbestos. It weighed 27.4 g and contained 45 g of 29.8% KOH. The spacer was 0.060 in. thick. The cell operated 758 cycles and was removed from test because of a faulty transducer. Figure 24 shows the cycle life performance of this cell. The extreme degradation of performance was probably a result of overpressurization caused by the faulty differential transducer.

Cell 75-A was a life test cell; it contained standard EOS and Cyanamid AB-6 electrodes. The matrix was fabricated from the ordinary DuPont potassium titanate. The composition was 80% KT, 10% Teflon and 10% asbestos. It weighed 27.6 g and contained 45 g of 29.8% KOH. The spacer was 0.060 in. thick. The cell operated 444 cycles and was removed from test because of a faulty transducer. Figure 25 shows the average discharge voltage to be 0.76V.

Cell 76-A was a life test cell; it contained standard EOS and Cyanamid AB-6 electrodes. The matrix was fabricated from the ordinary DuPont potassium titanate. The composition was 80% KT, 10% Teflon and 10% asbestos. It weighed 27.3 g and contained 45 g of 29.8% KOH. The spacer was 0.060 in. thick. The cell operated 321 cycles. Figure 26 shows the average discharge voltage to be 0.74V.

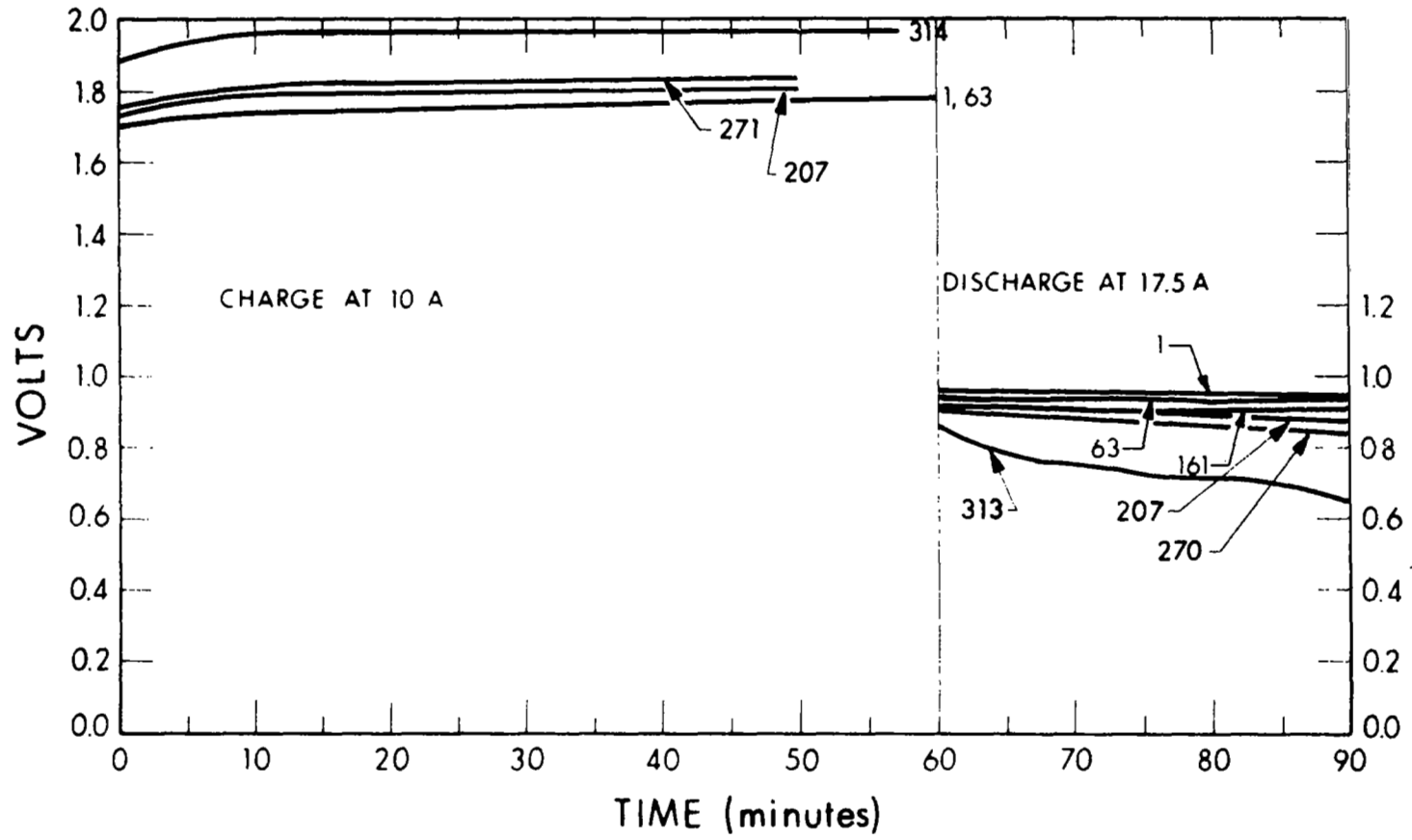


Figure 22. Cycle Performance of Cell No. 72-A

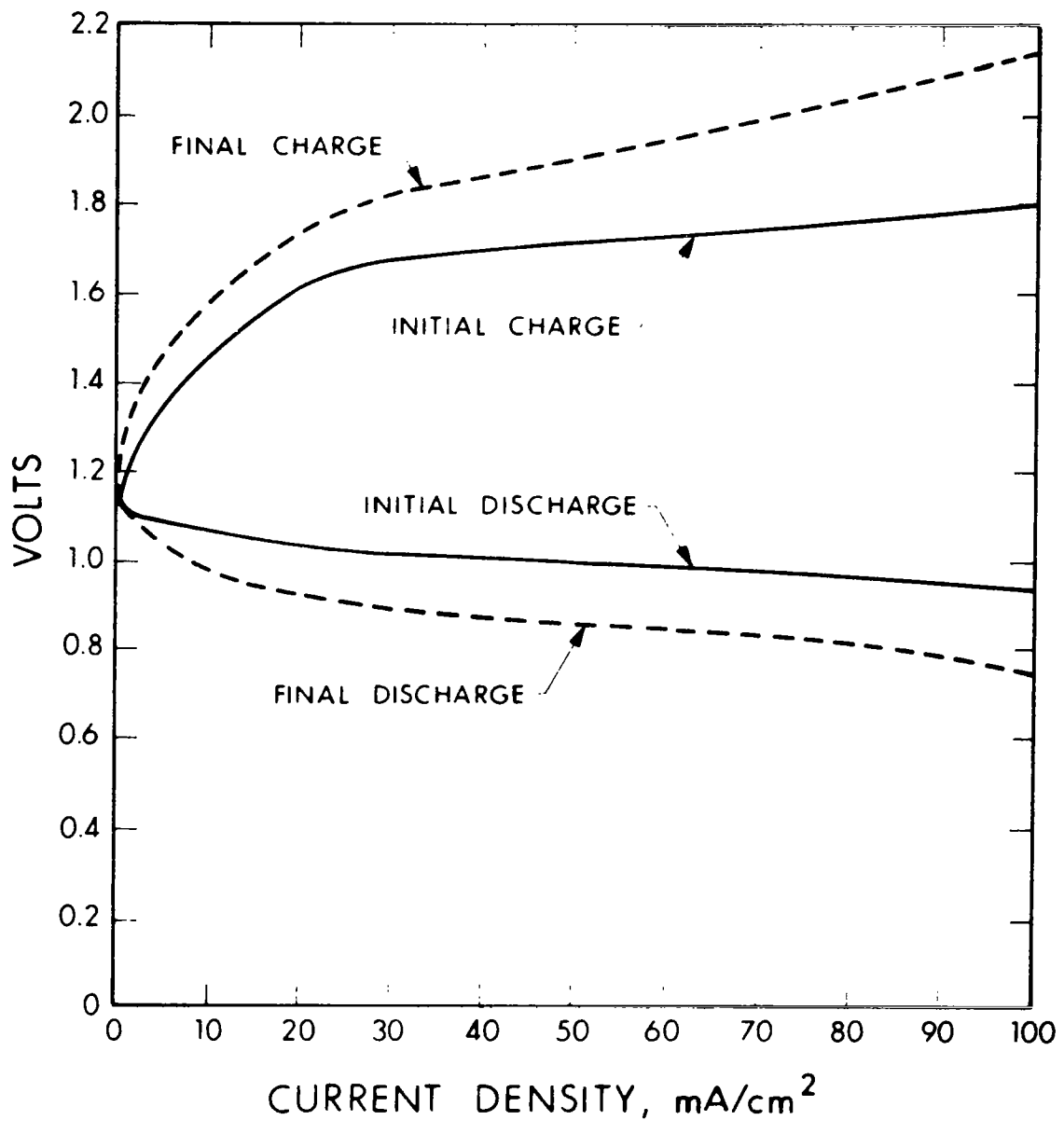


Figure 23. Charge and Discharge Polarization of Cell No. 72-A

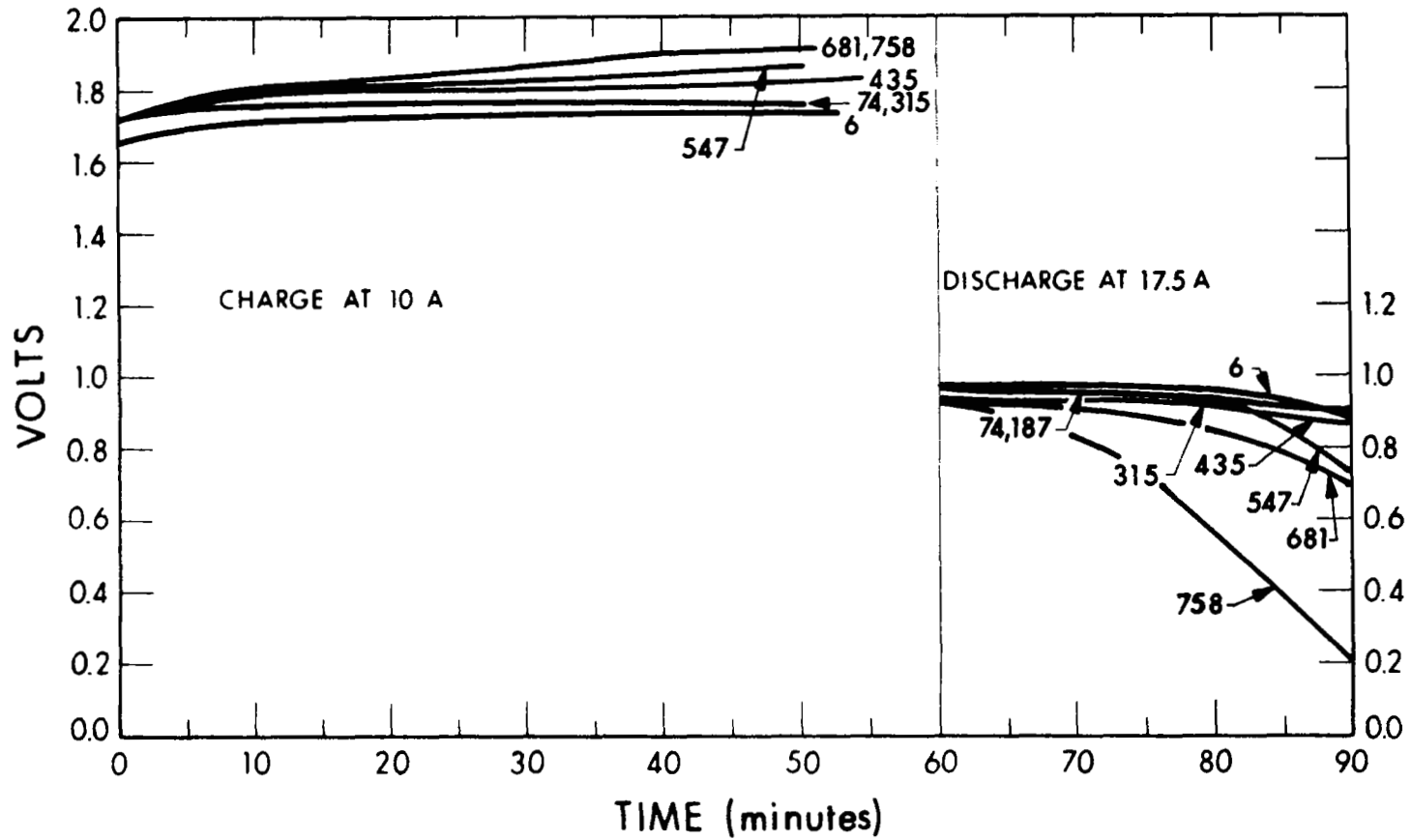


Figure 24. Cycle Performance of Cell No. 73-A

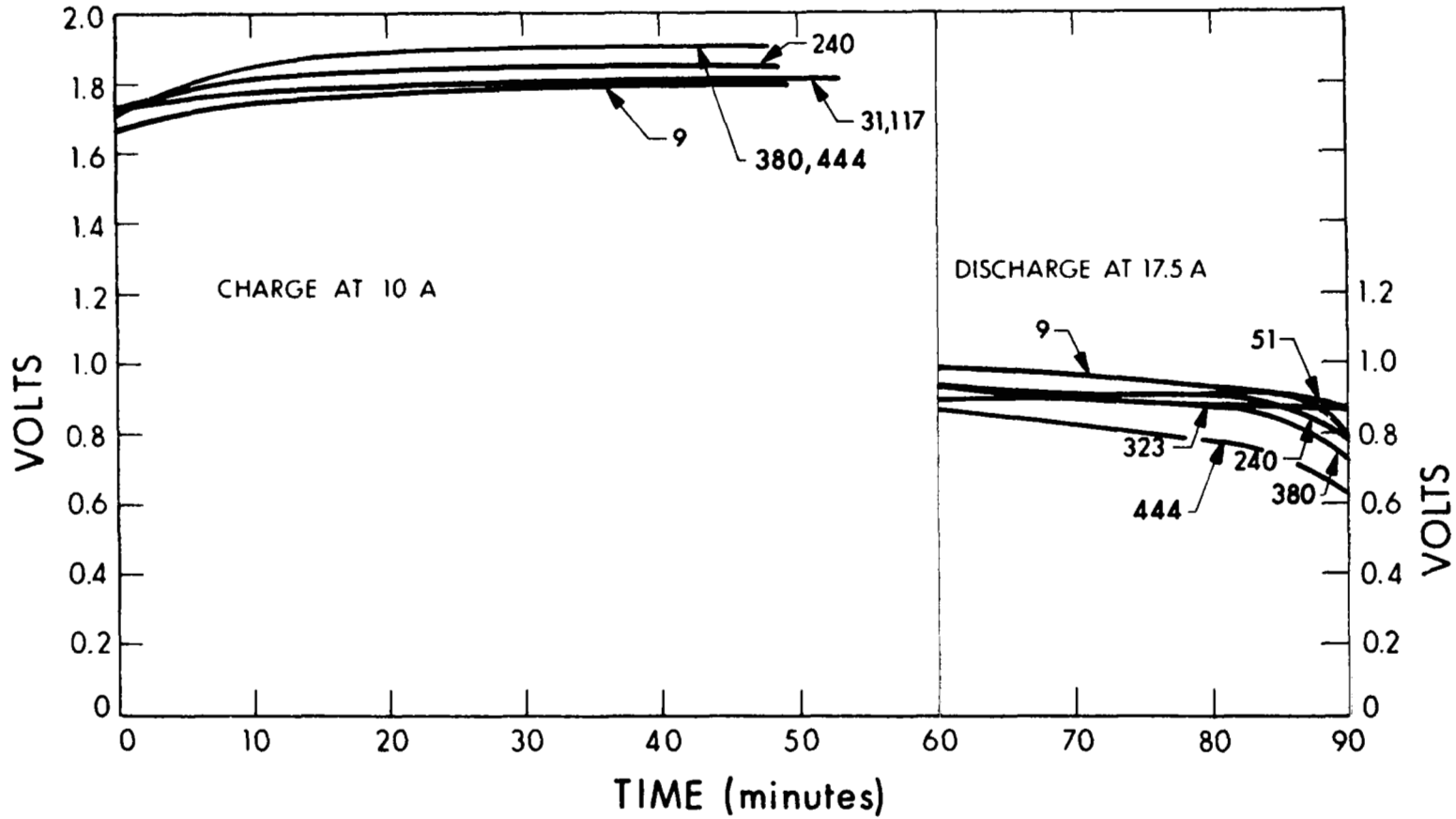


Figure 25. Cycle Performance of Cell No. 75-A

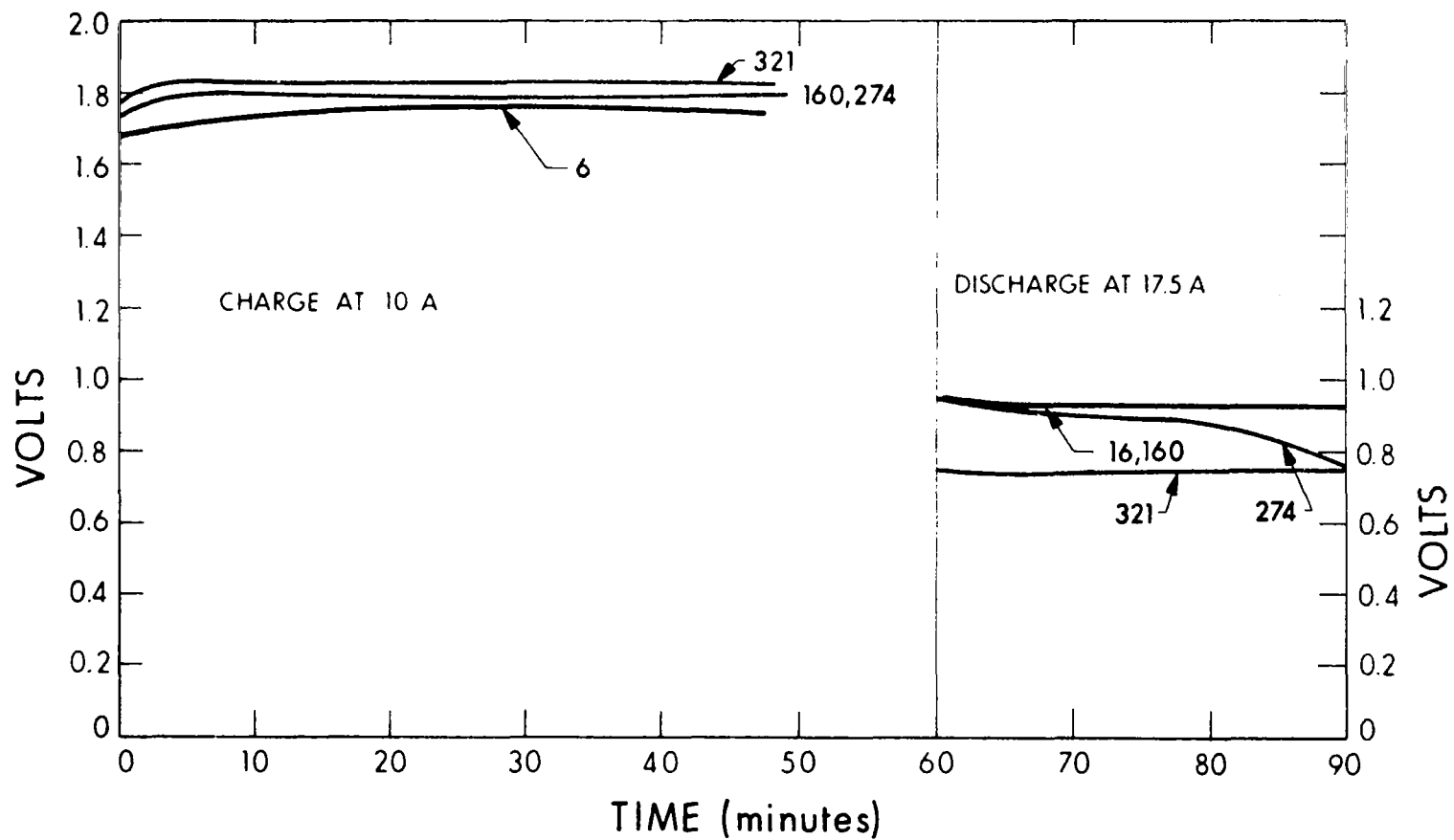


Figure 26. Performance of Cell No. 76-A

Cell 77-A was a life test cell; it contained standard EOS and Cyanamid AB-6 electrodes. The matrix was fabricated from the ordinary DuPont potassium titanate. The composition was 80% KT, 10% Teflon and 10% asbestos. It weighed 27.3 g and contained 45 g of 29.8 KOH. The spacer was 0.060 in. thick. The cell operated 226 cycles and the test was discontinued because the discharge voltage fell below 0.7V. Prior to the voltage degradation, the cell was reverse-charged by a Ni-Cd battery in series with it. The power supply that charges the cells inadvertently quit functioning during the weekend. Figure 27 shows the cycle performance of the cell. Figure 28 shows the polarization curves for cell 77-A. The cell was disassembled and it was found that the H₂ electrode and screens and backup plate were clean. However, the O₂ screens and backup plate were slightly corroded. The matrix had the typical dark middle layer.

Cell 78-A was a life test cell; it contained standard EOS and Cyanamid AB-6 electrodes. The matrix was fabricated from the ordinary DuPont potassium titanate. The composition was 80% KT, 10% Teflon and 10% asbestos. It weighed 27.3 g and contained 45 g of 29.8% KOH. The spacer was 0.060 in. thick. The cell operated 492 cycles. Figure 29 shows the average discharge voltage to be 0.8V.

Cell 79-A was a life test cell; it contained standard EOS and Cyanamid AB-6 electrodes. The matrix was fabricated from the ordinary DuPont potassium titanate. The composition was 80% KT, 10% Teflon and 10% asbestos. It weighed 27.6 g and contained 45 g of 29.8% KOH. The spacer was 0.060 in. thick. The cell operated 375 cycles and is still on test. Figure 30 shows the average discharge voltage to be above 0.77V. After cycle 320 the cell remained on discharge over a weekend because a cycle switch became faulty. Cycle 375 indicates the cell performance degraded.

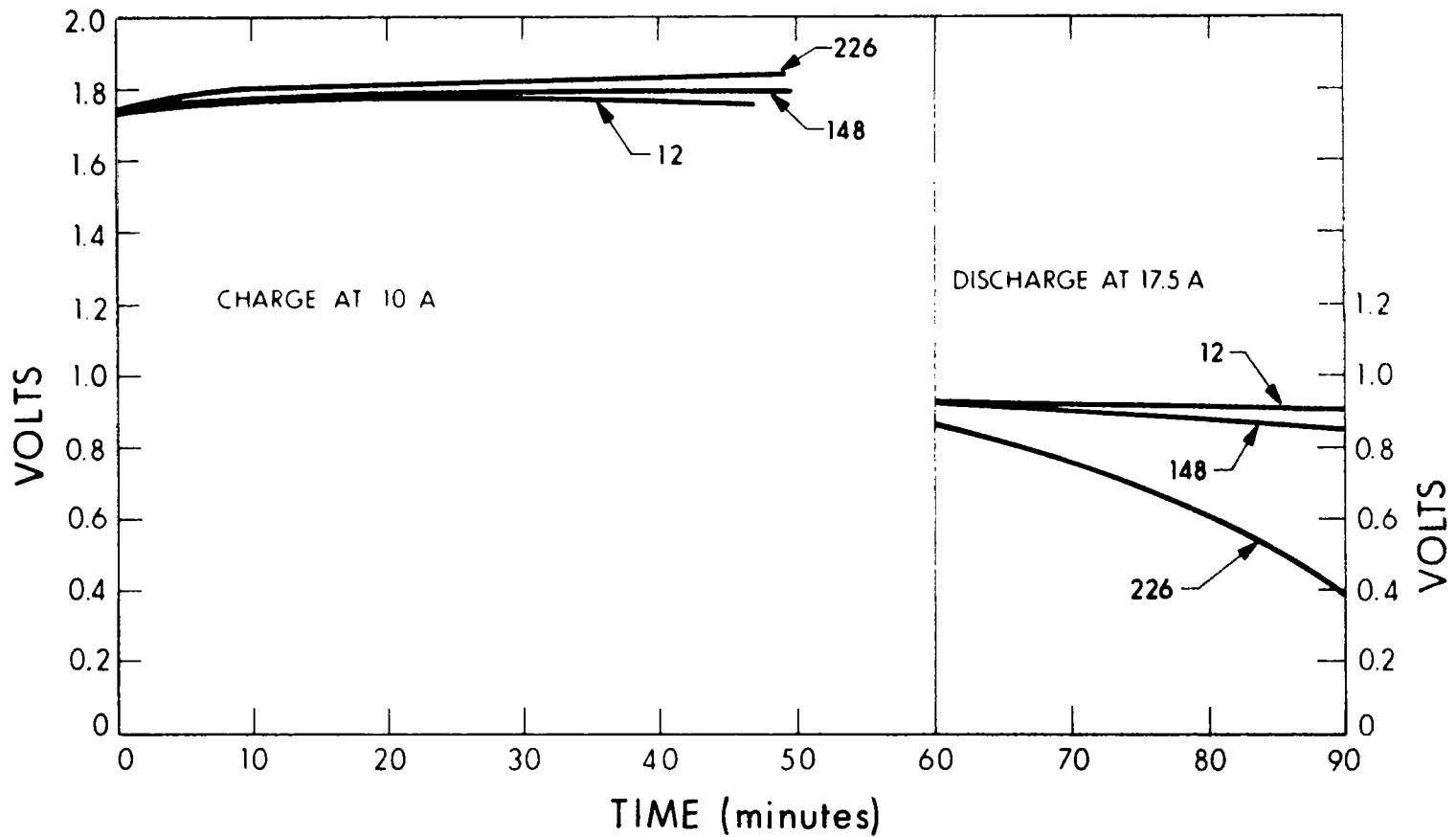


Figure 27. Cycle Performance of Cell No. 77-A

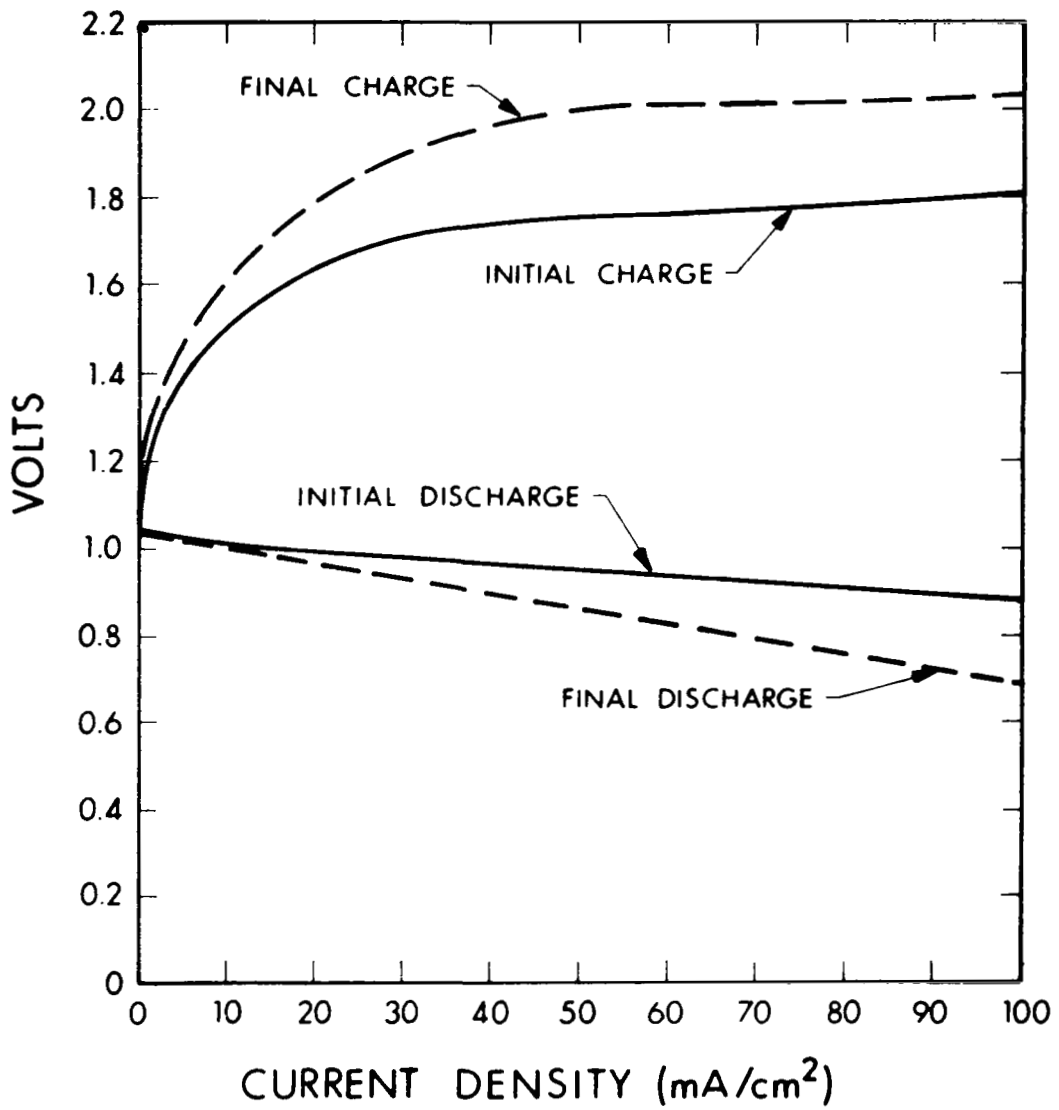


Figure 28. Charge and Discharge Polarization of Cell 77-A

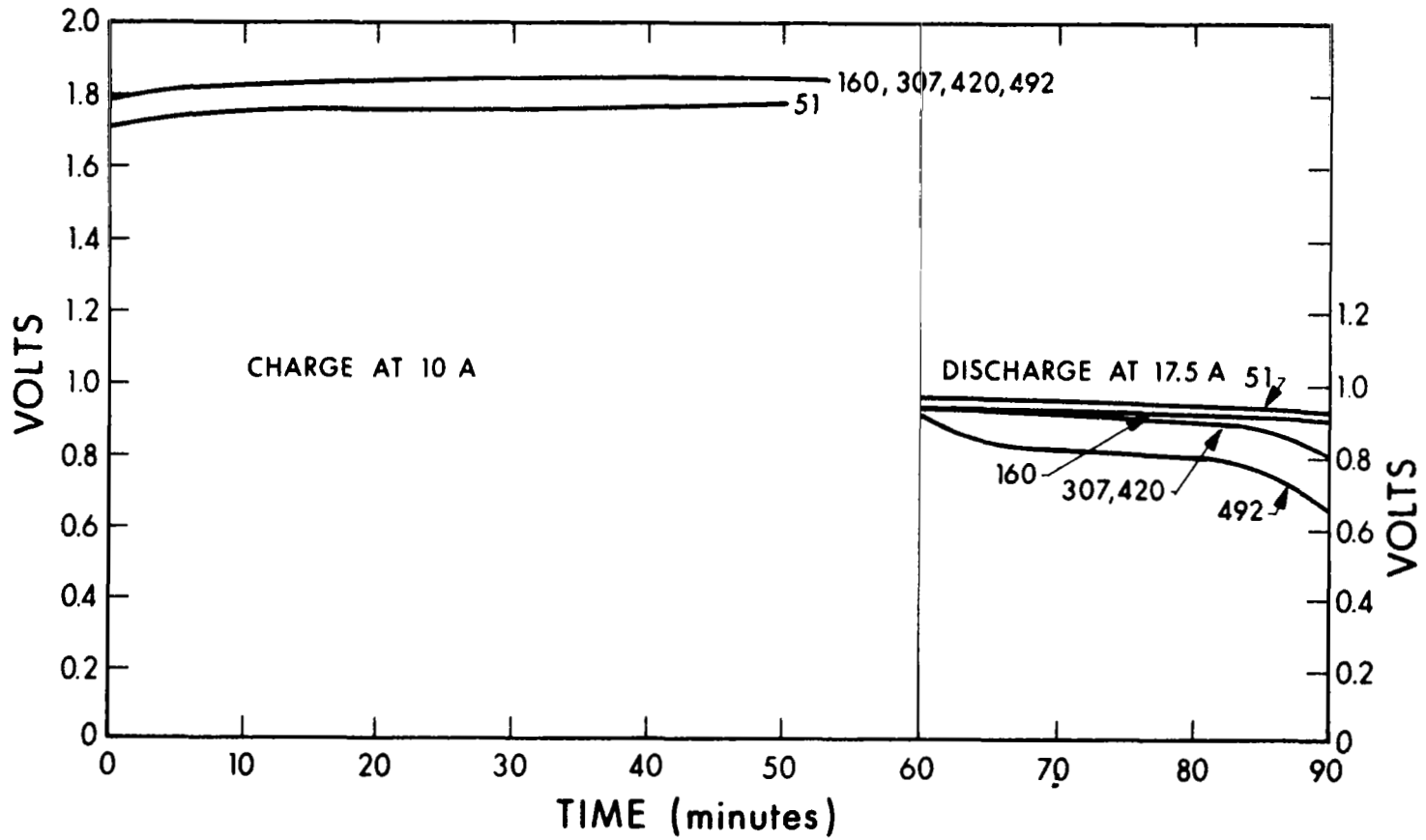


Figure 29. Cycle Performance of Cell No. 78-A

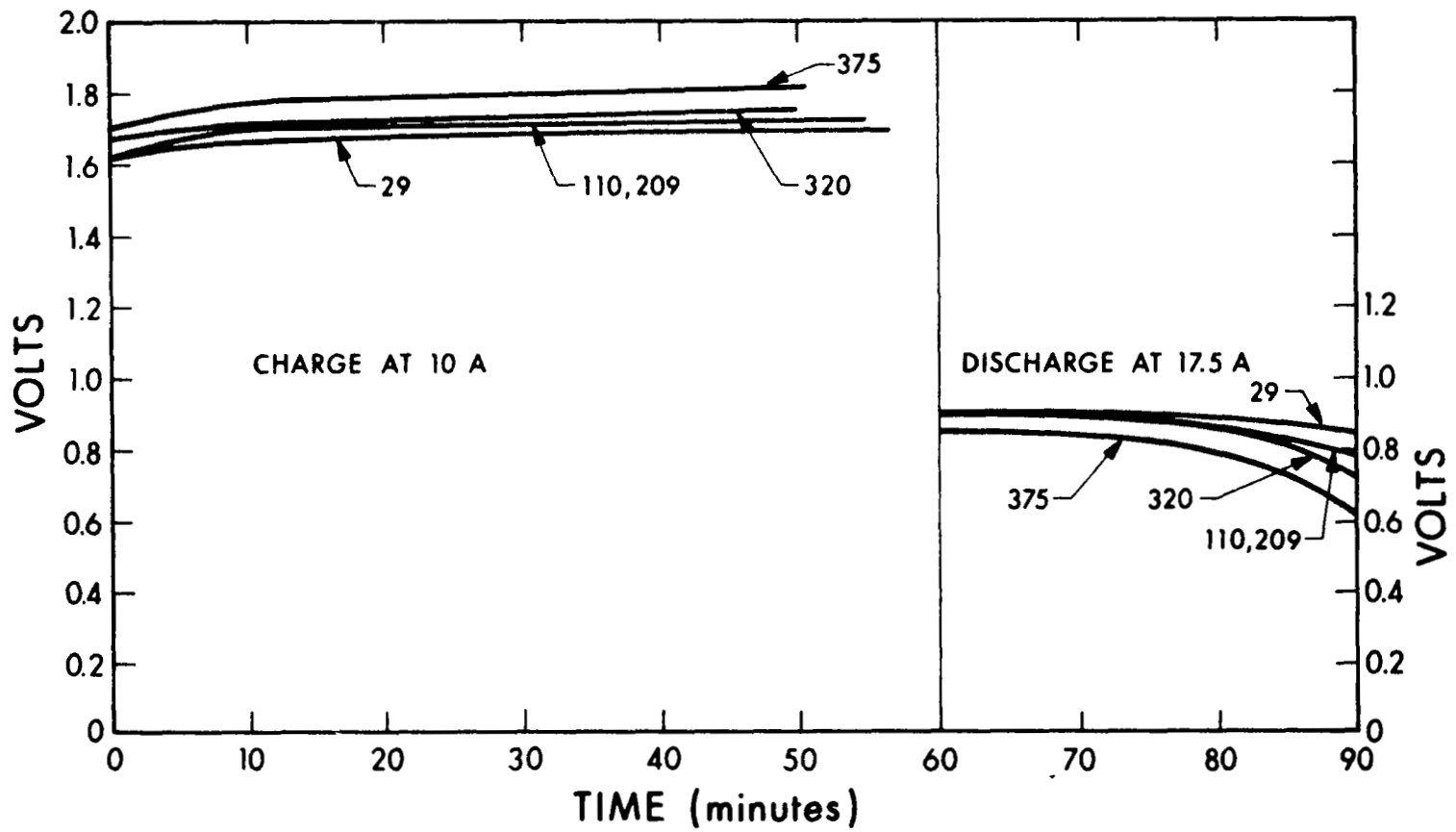


Figure 30. Cycle Performance of Cell 79-A

Cell 80-A was a life test cell; it contained standard EOS and Cyanamid AB-6 electrodes. The matrix was fabricated from the ordinary DuPont potassium titanate. The composition was 80% KT, 10% Teflon and 10% asbestos. It weighed 28.1 g and contained 45 g of 29.8% KOH. The spacer was 0.060 in. thick. The cell operated 256 cycles and was removed from test because of a faulty transducer. Figure 31 shows the average discharge voltage to be above 0.7V. After cycle 200, the power supply inadvertently failed leaving this cell fully discharged over a weekend. This may account for the drop in cycle performance after cycle 200.

2.5 TRW MATRICES

Three types of electrolyte matrices were manufactured at TRW for testing in the EOS regenerative fuel cell. Table XII is a summary of the cell tests using these matrices. The matrices were all 0.060 in. thick. A 0.050-in. spacer was used in all the tests to ensure that the edges were properly sealed. The test cells contained standard EOS H₂ electrodes and Cyanamid O₂ electrodes.

2.5.1 CeO MATRICES

The matrices were fabricated from cerium oxide held together with a Teflon binder. Table XII shows that this type of matrix is unsuitable for the regenerative fuel cell since the gases recombine readily through the matrix at 80°C. One cycle was achieved at 25°C.

2.5.2 ZrO MATRICES

The matrices were fabricated from zirconia held together with a Teflon binder. Table XII shows that this type of matrix is also unsuitable for the regenerative fuel cell since the gases readily recombine through the matrix. No cycles were achieved at 25°C.

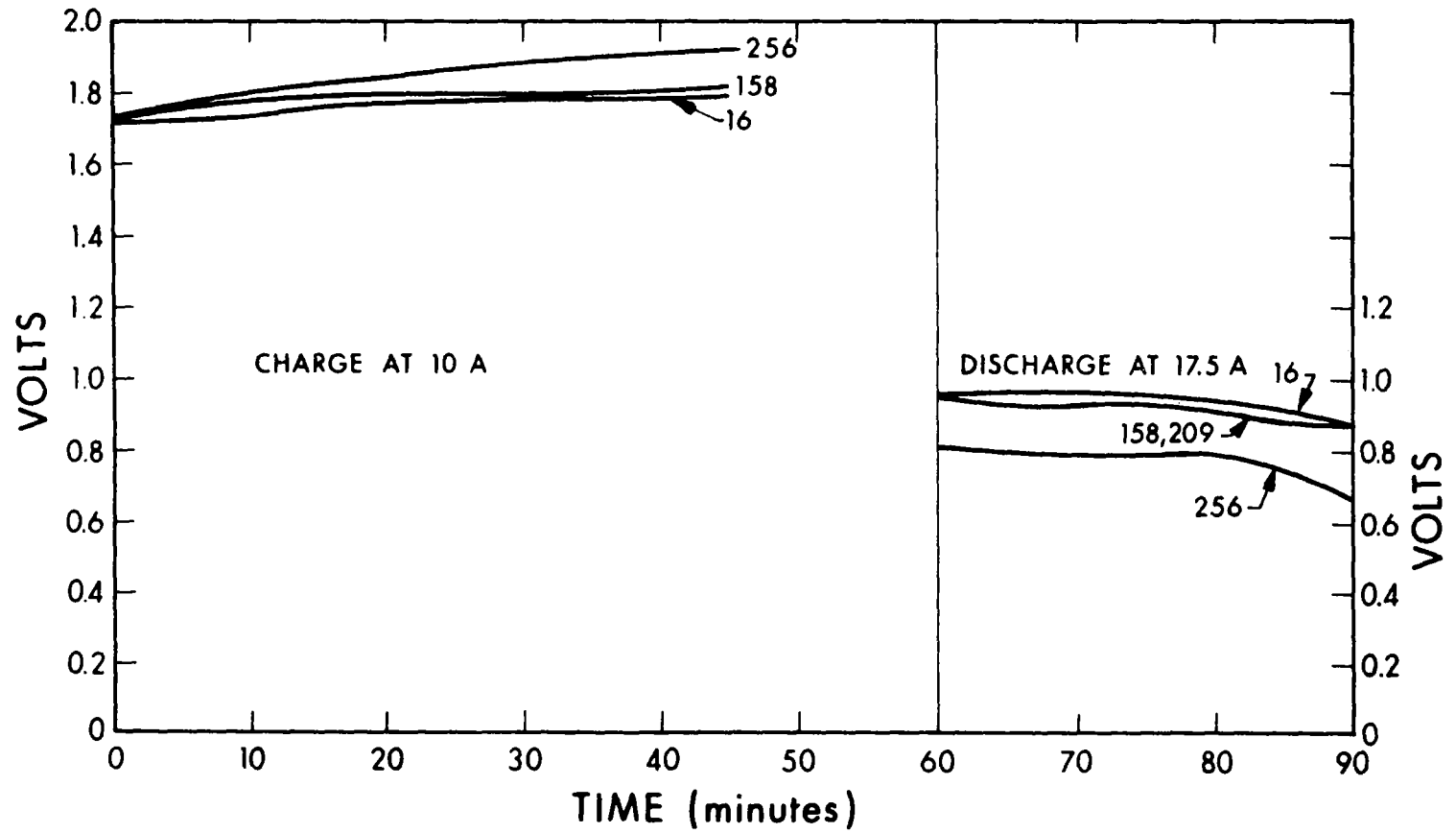


Figure 31. Cycle Performance of Cell No. 80-A

TABLE XII

SUMMARY OF CELLS
TRW MATRIXES

Cell No.	Matrix	No. of Cycles	Test Temp. (°C)	Electrodes	Electrolyte	Impedance at 80°C		Comments
						Initial	Final	
42-A	TRW CeO No. 161	1	25 & 80	EOS/Cyanamid AB-6	39.7 g of 30.4%	0.008Ω	0.007Ω	One cycle at 25°. Self discharged at 80°C; 0.050 in. spacer
43-A	TRW CeO No. 160	0	80	EOS/Cyanamid AB-6	40.4 g of 30.4%	0.008Ω		Recombination of gases* through matrix; 0.050 in. spacer
44-A	TRW CeO No. 167	0	80	EOS/Cyanamid AB-6	40.5 g of 30.4%	0.008Ω		Recombination of gases* through matrix; 0.050 in. spacer
45-A	TRW CeO No. 165	0	80	EOS/Cyanamid AB-6	40.5 g of 30.4%	0.004Ω		Recombination of gases* through matrix; 0.050 in. spacer
55-A	TRW CeO No. 164	0	80	EOS/Cyanamid AB-6	40. g of 30%	0.004Ω		Recombination of gases* through matrix; 0.050 in. spacer
46-A	TRW ZrO No. 258	0	25	EOS/Cyanamid AB-6	29.4 g of 30.1%	0.013Ω at 25°C		Recombination of gases* at 25°C; 0.050 in. spacer
47-A	TRW ZrO No. 262	0	80	EOS/Cyanamid AB-6	26.2 g of 30.4%	0.008Ω		Recombination of gases* at 80°C; 0.050 in. spacer
48-A	TRW ZrO No. 263	0	80	EOS/Cyanamid AB-6	27.3 g of 30.1%	0.012Ω at 25°C		Recombination of gases* at 80°C; 0.050 in. spacer

* Self Discharge

TABLE XII
SUMMARY OF CELLS (contd)
TRW MATRIXES

Cell No.	Matrix	No. of Cycles	Test Temp. (°C)	Electrodes	Electrolyte	Impedance at 80°C		Comments
						Initial	Final	
51-A	TRW ZrO No. 266	0	80	EOS/Cyanamid AB-6	34.0 g of 29.5%	0.013Ω at 25°C		Recombination of gases* at 80°C; 0.050 in. spacer
52-A	TRW ZrO No. 267	0	80	EOS/Cyanamid AB-6	23.0 g of 29.5%	0.008Ω		Recombination of gases* at 80°C; 0.050 in. spacer
40-A	TRW KT No. 86	2	25 & 80	EOS/Cyanamid AB-6	53.9 g of 29.5%	0.001Ω		2 cycles at 25°C. Gases recombined at 80°C; 0.050 in. spacer
41-A	TRW KT No. 87	0	80	EOS/Cyanamid AB-6	40.0 g of 30.4%	0.003Ω		Gases recombined* through matrix; 0.050 in. spacer
56-A	TRW KT No. 67	0	80	EOS/Cyanamid AB-6	40.0 g of 30.1%	0.004Ω		Gases recombined* through matrix; 0.050 in. spacer
58-A	TRW KT No. 68	0	80	EOS/Cyanamid AB-6	40.0 g of 30.1% KOH			Gases recombined* through matrix; 0.050 in. spacer
62-A	TRW KT Nos. 74, 75, and 76	1	80	EOS/Cyanamid AB-6	42.0 g of 30.1% KOH			Gases recombined* through matrix; 0.050 in. spacer

* Self Discharge

2.5.3 KT MATRICES

The matrices were fabricated from potassium titanate and a Teflon binder. Table XII shows that two cycles were achieved at 25°C, none at 80°C with cell No. 40. Three TRW potassium titanate matrices were pressed at 740 psig. The final thickness of each matrix was approximately 0.002 in. The weight of the three matrices stacked together was 20.5 g. The matrices were wet down with 42 g of 30.4% KOH and put in cell 64-A. The standard EOS/Cyanamid electrodes and an 0.050-in. spacer were used. The cell was tested at 80°C. Figure 32 shows that on charge the voltage rose about 2.0V, and on discharge a current greater than 10A could not be sustained. Because of the limits of the program, this approach was not pursued further.

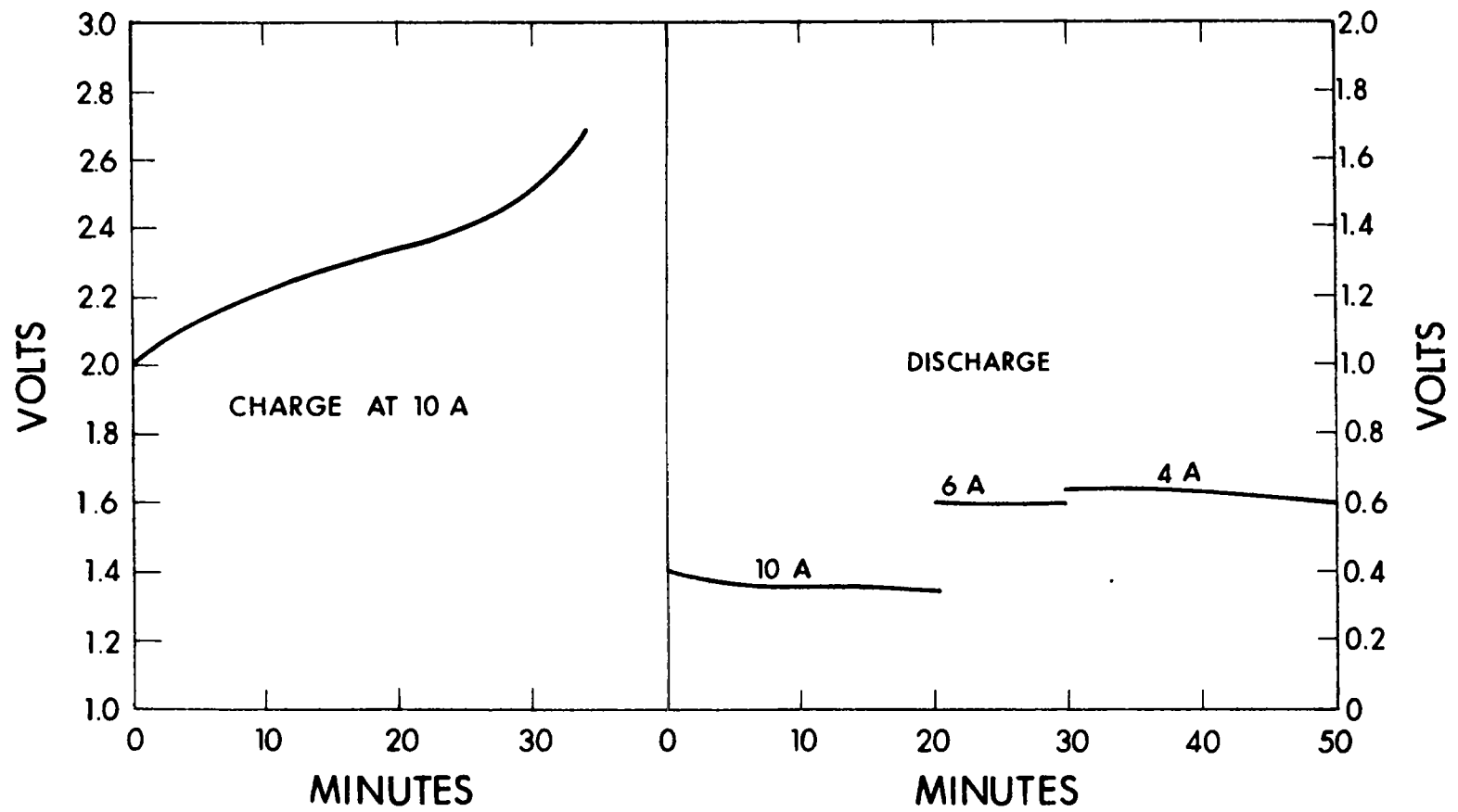


Figure 32. Charge/Discharge Characteristics of Cell No. 63-A

SECTION 3

DISCUSSION OF RESULTS

The three types of electrolyte matrices screened in the matrix comparison tests were as follows:

- a. Pressed composite matrix
- b. Layered pasted membrane matrix
- c. Rolled potassium titanate and Teflon matrices

Only the first two types of matrices were successfully used in a fuel cell. The Teflon in the rolled type of matrix probably flows readily as the pressure increases during charge when the temperature is up to 80°C.

The results from the bubble-through tests, Table III, showed the layered matrix could hold higher pressure differentials. The cycling tests proved the pressed type of matrix to be superior. Most of the pressed composite matrix cells ran over 1000 cycles. None of the layered type reached 1000 cycles. Furthermore, as can be seen in Table I, some of the layered type of matrix cells failed from gas leakage through the matrix. The pressed type of matrix is simpler to fabricate; because of this, a more uniform product can be expected. A component in the layered matrix is a hand-pasted membrane which could vary considerably. The mats, another component, are made from pressed potassium titanate and Teflon, and are thin. The absence of asbestos makes the mats fragile, and they could be damaged while handling. The pressed composite matrix appears to be superior to the other types tested for use in the regenerative fuel cell.

The material studies tests revealed that changes were taking place in the matrix, and that metals and other material were moving through the matrix. The polysulfone backup plate cells did not reveal much, other than to verify the results obtained by cycling fuel cells without gold-plated backup plates and screens. The results indicate that the cycle life is shortened when the gold plating is not present. Another observation made was that gold can be transferred from the O_2 side to the H_2 side while cycling the fuel cell.

The cycle tests using Pd O_2 electrodes revealed that the catalyst found in the matrix comes only from the O_2 electrode. The Pt analysis tests demonstrated that 25% of the Pt from the O_2 electrode can be deposited in the matrix.

The most revealing materials tests were the X-ray diffraction series. Three distinct phenomena are seen to be occurring within the electrolyte matrix:

- a. A layer where migrating gold and platinum concentrate is formed
- b. Teflon and asbestos concentrate on the O_2 side of the matrix
- c. Crystallographically, there are phase changes in the potassium titanate.

The mechanism for the migration of the platinum and gold is not understood at the present time. One suggested mechanism is that concentration gradients created in the KOH during charge and discharge of the fuel cell allows Pt in solution to precipitate out in one area of the matrix. Another suggested mechanism is that a dendrite growth from the H_2 electrode may be partially dissolved. Future investigation should be done to determine the solubility of Pt in KOH, and to find the extent of the Pt loss from the electrodes.

As has been discussed in the materials testing section, the X-ray diffraction tests indicate that as cycle life increases, both the Teflon and asbestos become more concentrated at the O_2 side of the matrix. Either the Teflon and asbestos are migrating toward the O_2 side or the potassium titanate is moving toward the H_2 side. The mechanism of this phenomenon is not apparent. Future investigation should look into the solubility of the matrix components. Tests could be devised in which Teflon and asbestos could be introduced at one side of a cell containing electrolyte or KT and electrolyte, and an electric current could be introduced to see if the material migrates. The same test could be run introducing potassium titanate at one side of a cell with KOH electrolyte. It has been suggested that the use of membrane barriers might change or slow down the migration of Teflon and asbestos or potassium titanate.

The X-ray diffraction tests indicate that, by adding KOH, crystallographic phase changes occur in the potassium titanate. Further changes may be caused by the electrical cycling of the cell. It was shown that the change caused by adding KOH is reversible by washing out the KOH. This test was performed on sample AX-5 which was "as received" potassium titanate soaked in KOH for 5 days at $80^{\circ}C$. This result indicated that it may not be possible to crystallographically stabilize the potassium titanate merely by soaking it in KOH. However, investigations should be conducted to determine if the potassium titanate could be electrically stabilized into an irreversible crystallographic phase.

Throughout the cell testing phase of the program, random failures occurred that could be attributed to mechanical difficulties with the test cell and cyclic equipment. The test cell had many seal areas and instrumentation fittings which developed gas leaks occasionally. An external gas leak of one of the gases results in a buildup of a differential pressure and the ultimate cell failure. Test equipment failures were also encountered which would cause the over charge or over discharge of a cell

and damage the cell. Considerable difficulties were encountered with differential transducer failures. It is therefore necessary to discount these types of failures to draw meaningful conclusions from the test data.

The life cycle tests revealed that, using the 90-min cycle regime, cycle life is decreased when the temperature is lowered to 50°C. The one test conducted at 60°C indicated that there may be an improvement in cycle life with increased temperature. Further investigation of this effect of temperature should be carried out.

The capacity requirements for the 24-hr test regime were too severe for cells of the current configuration. Tests using a 12 to 13A-hr cell capacity instead of 17.3A-hr were inconclusive. One 3.5-hr cycle was run at 50°C and demonstrated short cycle life. This result is in line with the other 50°C tests.

The rerun of the 90-min cycle regime at 80°C was inconclusive because of transducer and equipment failures.

The TRW matrices proved to be unsuitable for use in the regenerative fuel cell since the gases readily recombine through the matrix. A test was run using three matrices pressed together to provide a denser material. The cell ran at a low current density for 1 cycle.

SECTION 4

CONCLUSIONS

The best electrolyte matrix for use in regenerative fuel cells is a composite of 80% potassium titanate, 10% Teflon, and 10% asbestos. X-ray diffraction studies of this matrix material, after extensive cycling of the fuel cell, indicate that the asbestos and Teflon tend to migrate toward the oxygen electrode; this phenomenon is more pronounced with increasing cycle life. The X-ray diffraction studies also indicate that crystallographic changes take place within the potassium titanate, and that this change is due to some action of the KOH electrolyte.

The matrix materials supplied by TRW, including potassium titanate, cerium oxide, and zirconium oxide, each using Teflon as a binder, were all found to be unsuitable for regenerative fuel cell application. All of the TRW matrices allowed combination of the reactant gases through the matrix.

The platinum catalyst on the oxygen electrode tends to migrate into the electrolyte matrix, with as much as 25% of the original platinum content of the electrode being lost into the matrix. This may be one of the major causes of degradation of performance with extended cycle life of regenerable fuel cells. No loss of platinum catalyst from the hydrogen electrode was observed.

Gold, from the gold plating of the screens on which platinum is deposited in the manufacture of the oxygen electrodes, tends to migrate into the matrix. In some instances, this gold has been found deposited on the hydrogen side backup screens. Tests run without gold plating

of the components has demonstrated that cycle life is reduced when the gold is not present.

In cells that were subjected to the most extensive cyclic operation, corrosion of the backup screens and plates was observed.

The concentration of the KOH electrolyte was shown to decrease as the cycle life of cells increased.

For the electrode and matrix combination found to be best for the regenerative fuel cells, operation at 80°C exhibited considerably better cycle life than cells cycled at 50°C.

ADDENDUM

This addendum consists of the observations from the extended life tests on Cells Nos. 73A through 80A. These cells were still under test at the time the Final Report was initially submitted.

Subsection 2.4.7 of the Final Report covers the work on these cells up to the time the Report was prepared. That data is summarized in Table XI.

Table XI-A of this addendum summarizes the test results of the extended work. Platinum and gold analyses were performed on selected matrices from this series of tests. The data and discussion of the results are included.

TABLE XI-A
SUMMARY OF EXTENDED LIFE TESTS
(Continuation of Table XI)

Cell No.	Matrix	No. of Cycles (orig. report)	Type of Cycle	Test Temp. (°C)	Electrodes	Electrolyte Initial	Final KOH (%)	Impedance at same (°C) as "Test Temp."		Comments
								Initial	Final	
73-A	Pressed composite	758	60/30 min 10/17.5A	80	EOS/Cyanamid AB-6	45 g of 29.8% KOH	26.1	0.004Ω		Removed from test because of faulty transducer
75-A	Pressed composite	(444) 633	60/30 min 10/17.5A	80	EOS/Cyanamid AB-6	45 g of 29.8% KOH	21.0	0.006Ω		Removed from test because of faulty transducer after 444 cycles. Put back on test. Removed from test at 633 cycles, performance degradation
76-A	Pressed composite	489	60/30 min 10/17.5A	80	EOS/Cyanamid AB-6	45 g of 29.8% KOH	23.1	0.007Ω	0.012Ω	Removed from test because of faulty transducer after 321 cycles. Put back on test. Removed after 489 cycles, voltage below 0.70 volts.
78-A	Pressed composite	(492) 672	60/30 min 10/17.5A	80	EOS/Cyanamid AB-6	45 g of 29.8% KOH	19.4	0.003Ω		Pressure transducer failed. Removed from test at 672 cycles when voltage dropped to below 0.70 volts.

TABLE XI-A

SUMMARY OF EXTENDED LIFE TESTS (contd)
(Continuation of Table XI)

Cell No.	Matrix	No. of Cycles (orig. report)	Type of Cycle	Test Temp. (°C)	Electrodes	Electrolyte Initial	Final KOH (%)	Impedance at same (°C) as "Test Temp."		Comments
								Initial	Final	
79-A	Pressed composite	(375) 390	60/30 min 10/17.5A	80	EOS/Cyanamid AB-6	45 g of 29.8% KOH	20.2	0.005Ω	0.015Ω	Cell reverse charged at 375 cycles, failed circuit breaker left cell on discharge over weekend. After 15 additional cycles, discharge below 0.70 volts.
80-A	Pressed composite	(236) 318	60/30 min 10/17.5A	80	EOS/Cyanamid AB-6	45 g of 29.8% KOH	21.5	0.003Ω		Cell reverse charged at 200 cycles, failed circuit breaker left cell on discharge over weekend. After 118 additional cycles, below 0.70 volts.

CELL 73-A

As has been reported this cell operated a total of 758 cycles, being removed from test because of a faulty differential transducer which caused overpressurization of the cell.

The cell was disassembled and the following observations noted: O_2 side; oxidation of the screens, plate, and electrode were observed along with the removal of approximately 85 percent of the gold plating; H_2 side; no apparent degradation: Matrix: O_2 side was yellow in color with gray spots around the outer edge and a few dark yellow spots near the center. H_2 side was dark gray all over in a uniform pattern. Center was typically dark gray in the immediate center, lightening out as it approached the H_2 electrode.

CELL 75

After 444 cycles the cell was removed from test to replace a faulty transducer. After the transducer was replaced, the cell ran an additional 189 cycles giving a total number of 633 cycles. The last cycle would not discharge at higher than 0.50V at 17.5 amps.

When the cell was disassembled the matrix appeared to be extremely wet. The O_2 side of the cell: the backup plate and screens still had some gold left and were covered with a blue-white material that looked like a teflon coating. H_2 side: the backup plate and screens were clean with no apparent signs of Au removal; the electrode, screen, and plate were totally soaked with electrolyte. The matrix was wet on the surface and brittle, showing little or no KOH in the center. The center of the matrix contained the typical dark deposition.

CELL 76-A

After 321 cycles the cell was taken off the test because of a faulty pressure transducer. The transducer was replaced and the cell ran an additional 168 cycles with an average discharge voltage of 0.74V. The total number of completed cycles was 489. The cell was taken off test when the discharge voltage fell below 0.70V.

The cell was disassembled and the following observations were made:
O₂ side: the plate lost an estimated 50 percent of the Au coating, with one spot being extremely oxidized directly across from the backup plate screw. The H₂ side was clean. The matrix was typical in appearance with the usual grayish color on the H₂ side and dark central layer.

CELL 78-A

The cell operated for an additional 180 cycles with a faulty, or totally nonfunctional pressure transducer until the discharge voltage fell below 0.70V; total cycles 672.

The cell was then disassembled and the following observations noted;
O₂ side: the backup place and screens had Au plating in the center with an oxidized band 1.5 inches wide on the periphery. Black material (probably E.P.) was in a band on the outer edges of the plate H₂ side; plate and backup screen had no apparent change. The matrix was gray in surface coloring with the typical middle layer.

CELL 79

At 375 cycles the cell was taken off test due to a blown circuit breaker which left the cell on discharge over a weekend. After the appropriate changes in the circuit were made, the cell test was continued for an additional 15 cycles, but the cell was damaged by the extensive discharge and the average voltage fell below 0.7V. Total cycles amounted to 390.

Upon disassembling the cell the following observations were made:

O₂ side: a black soot-like material covered the edges of the plate about 1 inch in width. The soot washed away with water. An estimated 90 percent of the gold was gone, leaving a Zn-like appearance to the surface of the plate. H₂ side: the backup plate and screens were in good shape. The matrix: the O₂ side of the matrix was brownish in color with a 2 inch white spot located one-third of the way across the matrix and opposite the backup plate screw. A brown spot was directly over the screw. H₂ side: the matrix was light gray in color with a greenish spot directly over the backup plate screw. The typical dark middle layer was observed.

CELL 80-A

Cell 80-A was the last of the life test series. It contained the standard EOS and Cyanamid AB-6 electrodes. The matrix was fabricated from the ordinary DuPont potassium titanate. The composite was 80 percent KT, 10 percent teflon and 10 percent asbestos. It weighed 28.1 gms. and contained 45.0 gms of 29.8 percent KOH. The spacer was 0.060 inch thick. As Fig. 33 shows, the cell ran a total of 318 cycles and the test was discontinued when cell performance dropped below 0.7V on discharge. The performance drop was due to equipment failures which allowed the cell to discharge to zero several times over a single weekend. It appears that a circuit breaker blew which turned off the power supply, disabling the cell from charge mode.

The cell was disassembled and the following observations noted: O₂ side; the screens, plate and electrode were covered with a black substance and green powder; the gold plating was still visible with about 50 percent having been removed from the plate. H₂ side: no apparent change, looks like new. Matrix: the O₂ side had a brownish coloring to it. The H₂ side was uniformly gray. The center had the usual dark layer.

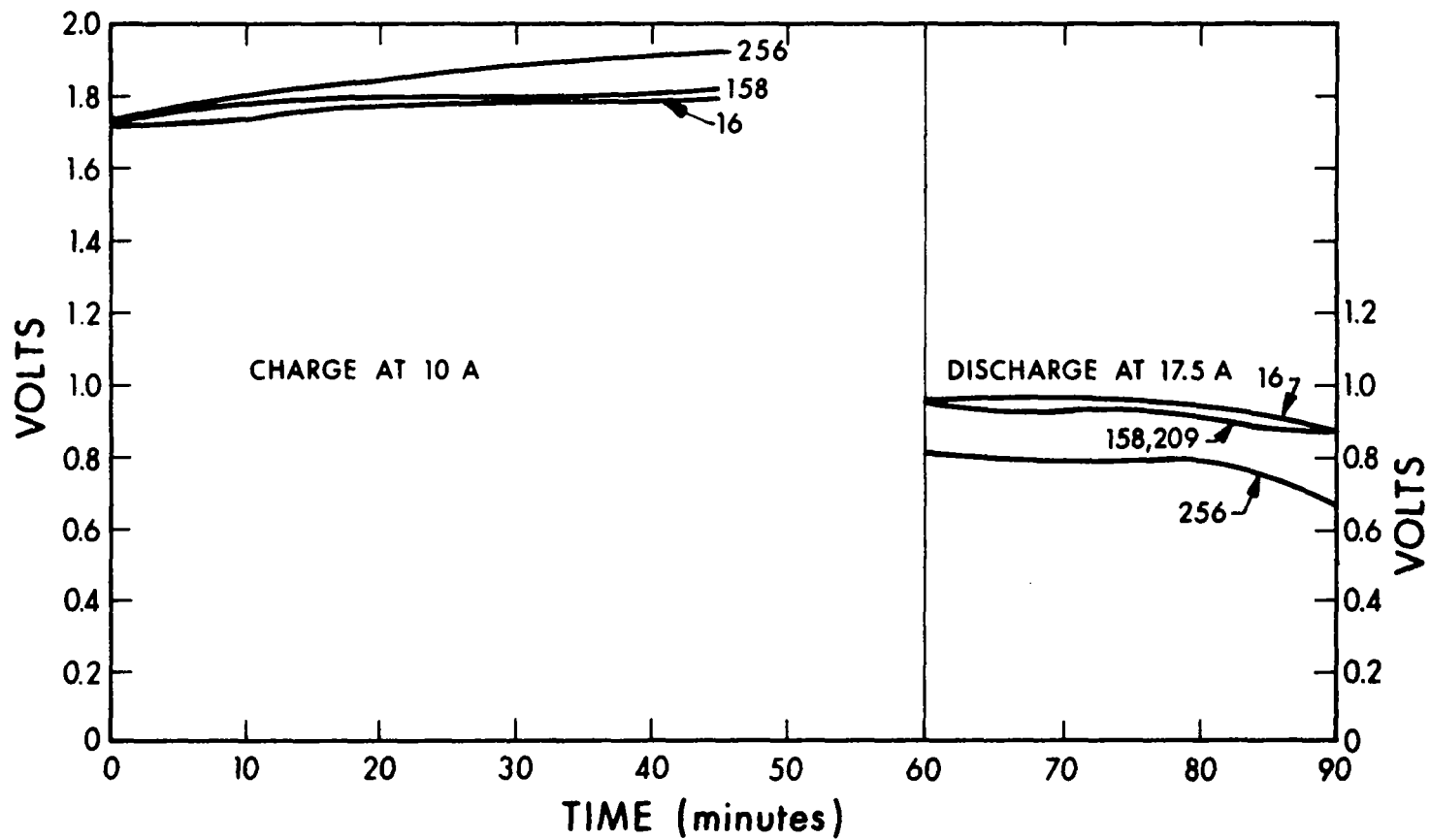


Figure 33. Cycle Performance of Cell No. 80-A, Contd.

The above results are in concurrence with those discussed in Section 3 of this report.

GOLD AND PLATINUM ANALYSIS IN FUEL CELL MATRICES

Analytical tests were run on the matrices from the life tests to determine the amount of gold and platinum deposited. Table XIII is a tabulation of these results:

TABLE XIII

GOLD AND PLATINUM ANALYSES OF FUEL CELL MATRICES

Cell No.	Cycles	mg/in ²		Based on 27.2 in ² area	
		Au	Pt	Au (mg)	Pt (mg)
73-A	758	3.5	14.22	95.2	386.2
75-A	633	4.1	10.75	111.5	291.0
76-A	489	6.9	11.90	187.7	323.7
77-A	226	1.6	5.0	43.5	136.0
78-A	672	5.1	2.06	138.7	56.0
79-A	390	5.2	15.35	141.4	417.5
80-A	318	2.6	15.39	70.7	417.6

The analytical results given in Table XIII along with those in Subsection 2.3.8 show there is no correlation between the number of cell cycles and concentrations of gold and platinum within the matrix. All the samples for analysis were obtained from near the center of the matrix to minimize local effects.

By previous observations it was determined that gold migrates from the oxygen toward the hydrogen side. Gold deposition on the hydrogen side resulting from migration from the oxygen side was visually observed, and is reported in Subsection 2.3.2. Platinum may also migrate across and deposit on the hydrogen electrode.

From previous observations, it appears that platinum and gold enter the matrix from the oxygen side during the cell cycles. The X-ray diffraction tests conducted during this program indicate that the gold and platinum are deposited in the matrix in the metallic state. The mechanisms that might occur could be the following:

- a. Dissolved metal ions enter the matrix on the oxygen side and reduce to the metallic state. The reduced metals redissolve in the electrolyte and deposit on the hydrogen electrode, backup plate, or screens.
- b. At the same time, another mechanism could be occurring that allows some of the dissolved metal ions to migrate from the O_2 side through the matrix and deposit directly on the hydrogen electrode, backup plate, or screens.
- c. Precipitation of the metal salts could be caused by transient KOH concentrations in the matrix. The change in concentration would depend upon the rate water is disassociated and formed during charge and discharge, as well as the rate of mechanical transport in the matrix. Reduction of the salts could be caused by hydrogen gas entering the matrix, the cyclic reversing of the electrochemical potential, or a combination of both.