

HYDROCARBON FUEL CELL ELECTRODES

Progress Report No. 2

July 16, 1965 - January 15, 1966

Prepared for

U. S. ARMY ENGINEER RESEARCH AND DEVELOPMENT LABORATORIES

FORT BELVOIR, VIRGINIA

April 22, 1966

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FOREWORD

This is Interim Progress Report Number 2 of a research program on hydrocarbon fuel cell electrodes conducted by the Central Research Division of American Cyanamid Company under contract with the U. S. Army Engineer Research and Development Laboratories (ERDL). The purpose of this program is to develop an electrode system which will produce 20 w/ft² at a minimum of 0.4 volt in a phosphoric acid matrix type cell utilizing a liquid hydrocarbon fuel (n-octane) and air, with a total platinum loading of not more than 20 g/ft². Dr. G. Frysinger and Mr. D. L. Beals of ERDL have been appointed technical representatives of the Contracting Officer.

TABLE OF CONTENTS

	<u>PAGE</u>
1. <u>SUMMARY</u>	1
2. <u>INTRODUCTION</u>	4
3. <u>EXPERIMENTAL</u>	5
4. <u>RESULTS AND DISCUSSION</u>	7
4.1 Fuel Electrodes	7
4.1.1 Variations in Type AA Electrodes	7
4.1.2 Platinum/Graphite Electrodes	12
4.1.3 Experimental Catalysts	12
4.1.4 Surface Area and Crystallite Size Measurements	15
4.2 Air Electrodes	18
4.3 Life-Testing	20
4.3.1 Octane Fuel	20
4.3.2 Propane Fuel	25
4.3.3 Hydrogen Fuel	28
4.3.4 Surface Area and Crystallite Size Measurements	28
4.4 Stability Studies	34
4.4.1 Type AA Electrodes	35
4.4.2 Platinum/Graphite Electrodes	40
5. <u>FUTURE WORK</u>	43
6. <u>PERSONNEL</u>	45
7. <u>REFERENCES</u>	46

LIST OF TABLES

<u>Table</u>	<u>Title</u>	<u>Page</u>
4-1	Performance Data: AA-1 Electrodes	8
4-2	Effect of Sintering on Type AA Fuel Electrodes	10
4-3	Performance Data: 14-17 mg Pt/cm ² Type AA Fuel Electrodes	11
4-4	Performance Data: Platinum/Graphite Fuel Electrodes	13
4-5	Performance Data: Experimental Catalyst Fuel Electrodes	16
4-6	Surface Area and Crystallite Size Measurements	17
4-7	Performance Data: Air Electrodes	19
4-8	Life Test Data	21
4-9	Surface Area and Crystallite Size Measurements - Life Test Electrodes	31
4-10	Surface Area and Crystallite Size Measurements - Material Stability Tests	39

LIST OF FIGURES

<u>Figure</u>	<u>Title</u>	<u>Page</u>
3-1	Test System	6
4-1	Octane-Air Life Test HCLT-22	23
4-2	Voltage Cycling, Octane-Air Life Test HCLT-22	24
4-3	Propane-Air Life Test HCLT-16	26
4-4	Voltage Cycling, Propane-Air Life Test HCLT-16	27
4-5	Hydrogen-Air Life Tests, Type AA Electrodes, 200°C	29
4-6	Hydrogen-Air Life Test HCLT-13, Platinum/Graphite Air Electrode, 175°C	30
4-7	Surface Area Data: Fuel Electrodes After Life-Testing	32
4-8	Surface Area Data: Air Electrodes After Life-Testing	33
4-9	Weight Loss Data: Type AA Electrodes, 100% H ₃ PO ₄ , 200°C	36
4-10	" " " : " " , " " , 175°C	37
4-11	" " " : " " ; " " , 150°C	38
4-12	" " " : Platinum/Graphite Electrodes 100% H ₃ PO ₄ , 150, 200°C	41

1. SUMMARY

Emphasis during the second period of the contract effort was placed on evaluating the performance of standard and experimental electrodes on normal octane and air at temperatures in the range 150 to 200°C. Treated polytetrafluoroethylene (PTFE) felt was used as the matrix in most of this work. The very low flows of octane and water required for operation in the small (2" x 2" active area) test cells were handled by special pumps.

Electrodes evaluated on the fuel side included:

- (1) Type AA electrodes, prepared from commercial platinum black with PTFE as a binder, at platinum loadings from 7 to 17 mg/cm².
- (2) Electrodes comprising physical mixes of platinum black with Cyanamid Graphite.
- (3) Electrodes containing various levels of platinum chemically deposited on Cyanamid Graphite.
- (4) Type RA (CO resistant) electrodes containing mixed noble metals and oxides of W, Mo, or both.
- (5) Electrodes containing platinum-ruthenium and platinum-gold alloy catalysts.

The effect of sintering the electrodes for a short time at elevated temperatures prior to testing was studied. Standard AA-1 electrodes, containing a nominal 9 mg Pt/cm², were used on the air side.

At 200°C, initial performance as high as 15-20 watts/ft² at 0.4 volt was achieved with electrodes containing 14 mg/cm² of commercial platinum black, with or without added graphite. For electrodes containing graphite, best performance was obtained when the electrodes were pre-sintered for ten minutes at 500°F.

Best performance at 175°C was 16 watts/ft², and at 150°C, 9-12 watts/ft², using in both cases electrodes containing 14 mg/cm² of commercial platinum black with no added graphite, and unsintered. The experimental catalysts [(3) through (5) above] were evaluated primarily at 150 and 175°C in the hope that higher catalyst activity might permit operating at these lower temperatures. In all cases, however, performance of these electrodes was poorer than that of electrodes containing an equivalent loading of commercial platinum black.

Modified air electrodes containing 5-7.5 mg Pt/cm² (either physically mixed with or chemically deposited on Cyanamid Graphite) were evaluated at 175°C. The best performance was somewhat poorer than that obtained with standard AA-1 electrodes.

A number of life tests were run with octane and air at temperatures of 175 to 200°C. These tests were generally characterized by severe voltage cycling (greater with octane than with propane) and a gradual deterioration in performance with time. Difficulties in maintaining stable operation during this period were due in part to mechanical problems with the pumps feeding water to the cells. These problems have now been largely overcome. The longest run with octane at 200°C was 300 hours, using a 40 mg Pt/cm² fuel electrode. Power density declined from 15 to 7 watts/ft² during this period. At 175°C, an electrode containing 14 mg Pt/cm² ran stably for 220 hours at 8 watts/ft² (approximately 0.4 volt at 20 ma/cm²), until the test was terminated because of crossleakage through the matrix. In other life tests, type AA electrodes operated relatively stably on hydrogen and air at 175 and 200°C for as long as 1000 hours. An air electrode

containing 25% Cyanamid Graphite showed no obvious deterioration after 1000 hours at 175°C. One test with propane as the fuel was run for 975 hours at 175°C. During most of this time a voltage of 0.4-0.45 v at 20 ma/cm² was maintained.

Surface area and crystallite size measurements were made on various types of electrodes before and after exposure to 100% phosphoric acid at 150-200°C in life tests and in oven stability tests. These measurements indicate that platinum loses surface area very rapidly under these conditions of exposure, particularly at 175-200°C.

2. INTRODUCTION

2.1 Objectives

The major objective of this contract is to develop an electrode system which will produce 20 watts/ft² with a hydrocarbon fuel and air in a fuel cell with a total platinum loading of not more than 20 g/ft². The fuel cell is to be a matrix type using phosphoric acid as the electrolyte. Originally the contract called for the use of propane as fuel at a temperature of 150°C. The program objectives were redirected, however, toward the use of n-octane as the test fuel at cell temperatures up to 200°C.

2.2 Scope

The scope of this program involves the fabrication and testing of experimental electrodes utilizing improved electrode structures, electrocatalysts, and/or fabrication techniques. These electrodes are to be tested in 2" x 2" phosphoric acid electrolyte matrix fuel cells. As a basis of comparison, standard Cyanamid AA-1 electrodes (9 mg Pt/cm²) are to be tested for uniformity and reproducibility. Finally, the life performance of selected electrodes which best achieve or exceed the characteristic goals outlined above will be investigated.

3. EXPERIMENTAL

Test system details, including design of the fuel cell and evaporator as well as general test techniques, were described in Progress Report No. 1. The only significant modifications introduced during this period involve (1) pumping of water and liquid hydrocarbon fuels rather than feeding from a pressurized tank, and (2) inclusion of a superheater following the evaporator to smooth out pulsations in the flow from the pumps. A syringe-type infusion pump (Harvard Apparatus Co., Model 975) was used to feed water, and an impulse-type pump (Harvard Apparatus Co., Lambda Pump, Model 1300-25) for octane. Figure 3-1 shows the test system, including the above-mentioned changes.

The n-octane used is Phillips 99.9% purity research grade. The procedures for obtaining the polarization curves and operating life tests are the same as those described previously in Progress Report No. 1.

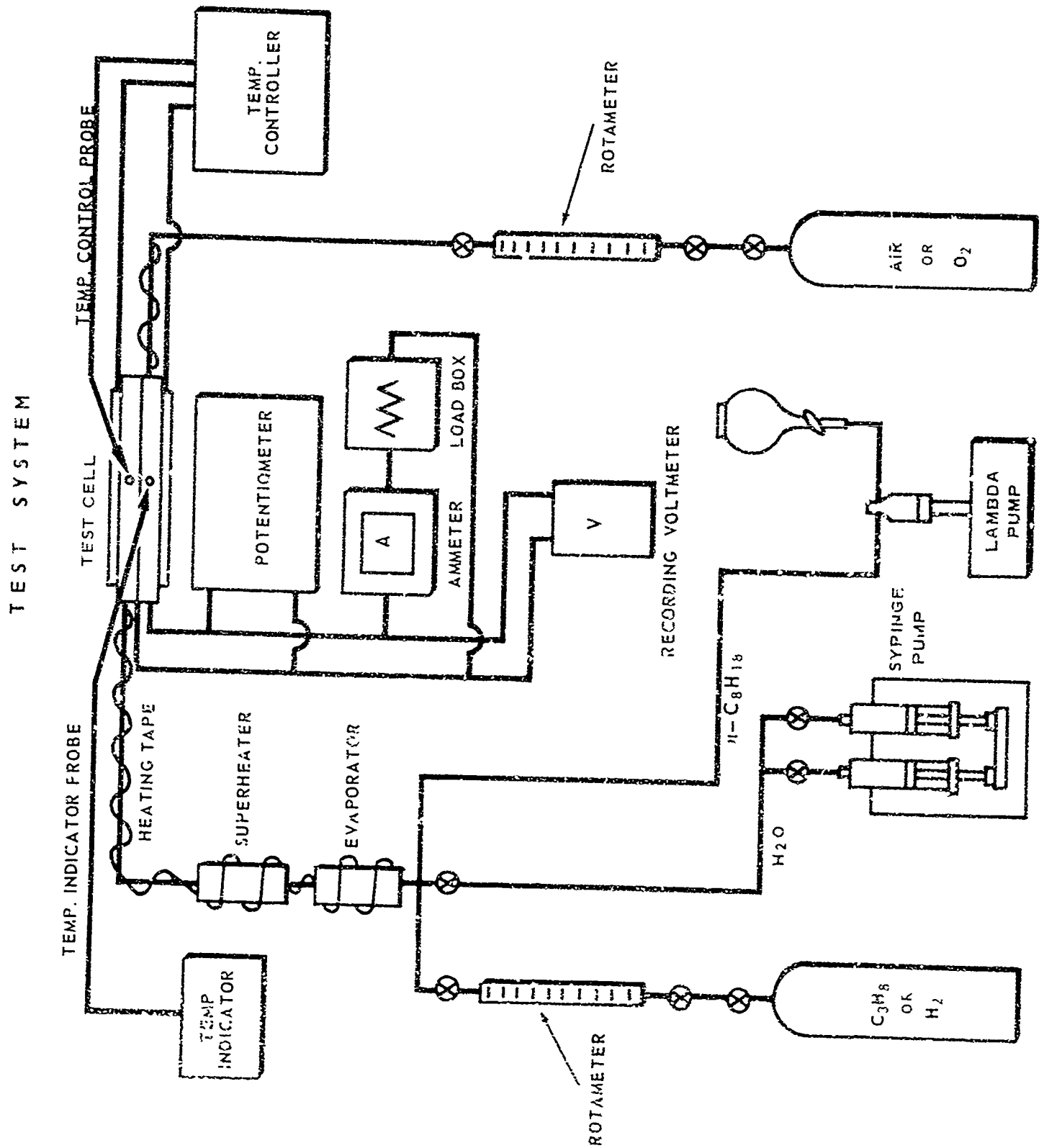


FIGURE 3-1

4. RESULTS AND DISCUSSION

4.1 Fuel Electrodes

Fuel electrodes were tested to determine the effect of the following modifications on performance:

1. Variations in Type AA electrodes
2. Incorporation of graphite into the electrode
3. Use of experimental catalysts

4.1.1 Variations in Type AA Electrodes

Type AA electrodes were prepared and tested to study the effects on performance of varying platinum loading, PTFE level and sintering temperature, with hydrogen and octane fuels. To provide a basis for comparison, standard AA-1 electrodes were also evaluated with hydrogen and octane fuels and air on the cathode side at 175-200°C.

The performance data obtained for standard AA-1 electrodes are given in Table 4-1. A polarization curve was obtained initially with hydrogen followed by the octane polarization curve. With octane, some voltage cycling (as much as 20-40 mv) was observed. The voltages reported for octane are, therefore, average values.

The performance obtained at 200° and 175°C shows wide variability. Data obtained on octane at 175°C were approximately the same as those obtained at 200°C, ranging from 0.28 to 0.35 volt at 40 ma/cm². To attain the objective of 20 watts/ft², a voltage of 0.54 v at a current density of 40 ma/cm², or 0.4 v at 54 ma/cm² is required. Best performance for standard AA-1 electrodes was 8-9 watts/ft² at 0.4 v.

TABLE 4-1

Performance Data - AA-1 Electrodes

Electrolyte: 100% H₃PO₄
 Matrix : Treated PTFE Felt
 Reactants : Hydrogen/Air, n-Octane/Air

	<u>H₂/Air</u>			<u>C₈H₁₈/Air</u>			<u>Cell Resistance (ohms)</u>
	<u>Working Voltage</u>			<u>Working Voltage</u>			
<u>Current Density, ma/cm²:</u>	<u>10</u>	<u>40</u>	<u>100</u>	<u>10</u>	<u>20</u>	<u>40</u>	<u>60</u>
200	.90	.76	.54	.55	.42	-	.05
"	.90	.82	.70	.51	.42	.29	.04
"	.89	.74	.48	.59	.49	.35	.06
"	-	-	-	.57	.42	-	.05
175	.87	.69	.43	.49	.39	.28	.05
"	.92	.84	.71	.54	.44	.28	.04
"	.88	.73	.51	.54	.38	.32	.04

Table 4-2 shows the effect on performance at 200°C of variations in PTFE level and sintering temperature (400-700°F) for electrodes containing 7-15 mg Pt/cm². The polarization curves were obtained at 200°C using 100% phosphoric acid as the electrolyte and a standard AA-1 air electrode. Data are reported only for hydrogen as the fuel; performance on octane was very poor. It appears from the data in Table 4-2 that sintering at temperatures above 500°F is detrimental to the performance of type AA electrodes.

Data given in Table 4-3 show the effects on performance at 150-175°C of PTFE level and of sintering for electrodes containing 14 and 17 mg Pt/cm². The electrodes were tested unsintered, or sintered for 10 minutes at 500°F. Octane/air performance data were obtained at both 150° and 175°C; hydrogen/air data were obtained only at 150°C. The air electrode again was a standard AA-1.

Good performance was obtained on octane with modified type AA electrodes containing either 14 or 17 mg Pt/cm². Maximum initial performance at 175°C with these modified electrodes was about 0.4 v at a current density of 40 ma/cm², or approximately 16 watts/ft². Performance at 150°C was appreciably lower, about 9-12 watts/ft² at 0.4 v. Varying the PTFE level did not appear to affect performance. Sintering at 500°F does not appear to affect performance on hydrogen, but may be detrimental to performance on octane, particularly at 150°C.

TABLE 4-2

Effect of Sintering on Type AA Fuel Electrodes

Temperature: 200°C
Electrolyte: 100% H₃PO₄
Matrix: Treated PTFE Felt
Air Electrode: AA-1

Fuel Electrode No. S7242-	Platinum Loading (mg/cm ²)	PTFE Level (%)	Sintering ⁽¹⁾ Temperature (°F)	Hydrogen/Air Performance Working Voltage			Cell Resistance (Ohms)
				10	40	100 ma/cm ²	
113-1	7	10	700	.735	-	-	.15
114-1	7	15	"	.81	-	-	.05
114-2	7	15	"	-	-	-	.09
114-2	7	15	"	.84	.65	.28	.04
113-4	7	15	"	-	-	-	.03
113-4	7	15	"	-	-	-	.03
113-3	10	10	"	.727	.70	.57	.03
113-3	10	10	"	-	-	-	.06
113-3	10	10	"	-	-	-	.08
113-3	10	10	"	-	-	-	.09
113-3	10	10	"	.44	-	-	.04
114-3	10	15	"	.79	.41	-	.04
114-3	10	15	"	.86	.83	-	.07
114-3	10	15	"	-	-	-	.05
114-3	10	15	"	.61	.57	-	.07
114-3	10	15	"	.64	~.3	-	.02
113-4	7	15	600	.91	~.2	-	.02
113-4	7	15	"	.57	-	-	.04
113-3	10	10	"	.48	-	-	.04
113-3	10	10	"	.79	-	-	.03
114-3	10	15	"	.67	-	-	.02
114-6	15	15	"	.56	-	-	.05
114-6	15	15	"	.66	-	-	.04
114-4	10	15	500	.89	.77	.59	.04
112-1	10	15	"	.87	.62	~.3	.05
114-6	15	15	"	.90	.79	.64	.05
114-6	15	15	"	.80	-	-	.06
125-2	10	20	400	.78	.67	.53	.05
122-1	10	15	-	.86	.63	-	.05

(1) Sintering Time: 10 Minutes

TABLE 4-3

Performance Data: 14-17 mg Pt/cm² Type AA Fuel Electrodes
Electrolyte: 100% H₃PO₄
Matrix: Treated PTFE Felt
Air Electrode: AA-1

Test Temperature °C	Electrode S-7242-	Platinum Loading (mg/cm ²)	PTFE Level (1) (%)	Working Voltage						Cell Resistance (Ohms)		
				H ₂ /Air								
				10	40	100	ma/cm ²	10	20		40	60
150	147-1	14	Unsintered	25	.91	.79	.66	.48	.39	.33	.30	.04
"	"	"	Sintered	"	.93	.83	.69	.52	.39	.14	-	.04
"	147-2	"	Unsintered	15	.89	.77	.65	.52	.43	.30	-	.04
"	"	"	Sintered	"	.93	.81	.71	.54	.41	.26	-	.04
150	147-3	17	Unsintered	25	.89	.80	.68	.52	.42	.32	.22	.04
"	"	"	Sintered	"	.92	.81	.70	.43	.27	-	-	.04
"	147-4	"	Unsintered	15	.88	.82	.68	.58	.47	.34	.22	.04
"	"	"	Sintered	"	.91	.91	.68	.37	.23	-	-	.04
175	147-1	14	Unsintered	25				.58	.46	.40	.32	.04
"	"	"	Sintered	"				.54	.47	.34	.26	.04
"	147-2	"	Unsintered	15				.59	.51	.42	.35	.04
"	"	"	Sintered	"				.58	.50	.38	.30	.04
175	147-3	17	Unsintered	25				.58	.49	.39	.32	.04
"	"	"	Sintered	"				.49	.37	.30	-	.04
"	147-4	"	Unsintered	15				.53	.44	.35	.27	.04
"	"	"	Sintered	"				.47	.38	.25	-	.04
200	131-1	14	Unsintered	10	.89	.69	.30	.43-.53	-	-	-	.04
"	"	"	Sintered	"	.90	.78	.64	.25	-	-	-	.07
"	131-2	"	Unsintered	15	-	N.D.	-	-	N.D.	-	-	-
"	"	"	Sintered	"	.91	.79	.64	.53	.40	-	-	.04
"	131-3	"	Unsintered	20	.92	.84	.73	.64	.55	.42	.37	.03
"	"	"	Sintered	"	.87	.79	.64	.51	.42	-	-	.04

(1) Sintered 10 minutes at 500°F

(2) Not Determined

4.1.2 Platinum/Graphite Electrodes

Preliminary life-testing of type AA electrodes had indicated a tendency for the catalyst material to shrink away from the screen. It was felt that incorporation of an inert filler material such as graphite might stabilize the structure. Table 4-4 shows data obtained with catalysts comprising physical mixtures of Cyanamid Graphite and platinum black. For the most part the data were obtained at 200°C, although a few tests were run at 150° and 175°C with several electrodes which gave good performance at 200°C.

With electrodes containing 10 mg Pt/cm², very poor performance on both hydrogen and octane was obtained with graphite levels above 25%. With graphite levels below 25%, performance was at best approximately equivalent to that of AA-1 electrodes.

In tests with 14 mg Pt/cm² loadings, performance showed little sensitivity to graphite levels in the range 7.5 to 25%. Performance at 10% PTFE was considerably poorer than at 15-20%. Good performance at 200°C (17-20 watts/ft² at 0.4 v) was achieved with sintered electrodes. While more data would be required to draw a firm conclusion, it appears that with platinum/graphite electrodes, better performance (at least at 200°C) may be achieved with sintered electrodes.

4.1.3 Experimental Catalysts

It was felt that the experimental catalysts might exhibit greater activity than the commercial platinum black catalysts, and therefore they might be used at lower cell temperatures. For this reason, most of the testing was conducted at 150-175°C. The catalysts tested included the following:

TABLE 4-4

Performance Data: Platinum/Graphite Electrodes-Fuel Electrodes
 Electrolyte: 100% H₃PO₄
 Matrix: Treated PTFE Felt
 Air Electrode: AA-1

A: Platinum Loading: 10 mg/cm²

Temperature °C	Electrode No.	% Graphite	% PTFE	Sintering Temp. °F	Voltage--Working					Cell Resistance (Ohms)
					H ₂ /Air 10	100	10	Octane/Air 20	40 mg/cm ²	
200	7242-125-1	50	20	Unsintered	.74	-	-	-	-	.05
200	7242-125-1	50	20	400	.38	-	-	-	-	.06
200	7242-125-1	50	20	500	.49	-(1) (60)	-	-	-	.07
200	7242-121-4	50	15	Unsintered	.85	.53	-	-	-	-
200	7242-125-3	33	20	Unsintered	.90	-	-	-	-	.03
200	7242-125-3	33	20	400	-	-	-	-	-	.06
200	7242-125-3	33	20	500	.51	-	-	-	-	.05
200	7242-126-2	25	20	Unsintered	.86	.38	.41	.29	.15 (1) (30)	.03
200	7242-126-2	25	20	400	.83	.50	-	.32	.18	.04
200	7242-126-2	25	20	500	.85	(80)(1) .15	.16	-	-	.04
200	7242-121-1	25	15	Unsintered	.78	.22	-	-	-	.06
200	7242-126-1	16.7	20	Unsintered	.88	.3	-	.40	.25	.05
200	7242-126-1	16.7	20	400	.87	.54	.37	.27	-	.05
200	7242-126-1	16.7	20	500	.87	.57	.48	.45	(35)(1) .34	.04

(1) At indicated current density.

(Continued)

1. Type RA catalysts (Pt and Rh blacks, together with oxides of tungsten and/or molybdenum) were developed under separate programs. At lower temperatures (70-80°C) this type of catalyst has been shown to be more resistant to poisoning by carbon monoxide than platinum alone.

2. Platinum deposited on Cyanamid Graphite. The platinum in these catalysts has a crystallite size on the order of 30-50 Å.

3. Platinum-noble metal alloys.

Data obtained in tests with electrodes containing the above catalysts are tabulated in Table 4-5. In most cases, the electrodes were sintered before testing. In general, performance on octane was significantly poorer than was obtained with equivalent loadings of commercial platinum black. The test which gave the best performance (0.37 v at 40 ma/cm²) used an unsintered electrode containing 75% platinum deposited on Cyanamid Graphite. Further work with unsintered electrodes of this type is warranted.

4.1.4 Surface Area and Crystallite Size Measurements

Catalyst surface area (BET-N₂) and crystallite size measurements were made on various electrode samples in an effort to gain some insight into the relationship between these variables and catalyst activity. Listed in Table 4-6 are data for type AA electrodes and for electrodes containing platinum deposited on or physically mixed with Cyanamid Graphite. Sample size was 2" x 2" in all cases.

TABLE 4-5

Performance Data: Experimental Catalyst Fuel Electrodes (14 mg noble metal/cm²)
Electrolyte: 100% H₂PO₄
Matrix: Treated PTFE Felt
Air Electrode: AA-1

Electrode	Catalyst	Graphite Level (%)	PTFE Level (%)	Sintering Temp. (°F)	Test Temp. (°C)	H ₂ /Air Performance Working Voltage at 100 ma/cm ²	Oxygen Performance Working Voltage at 100 ma/cm ²	Cell Resistance (ohms)
Type RA Catalysts								
7242-138-1	Pt + W, Mo oxides	25	15	500	150	.91	.47	.04
7242-137-4	Pt + Rh + W, Mo oxides	"	"	"	175	N.D.	.21	"
7242-137-3	"	"	"	"	"	.88	.48	.07
7242-138-2	Pt + Rh + W oxide	"	"	"	150	.87	.46	.06
7546-5/	"	"	"	"	175	.84	.57	.05
7242-138-3	Pt + Rh + Mo oxide	25	15	500	175	.89	.45	.03
	"	"	"	"	150	N.D.	.67	.03
	"	"	"	"	175	N.D.	"	"
Platinum Catalyst Preparations								
7242-137-1	85% Pt	15	15	500	150	.85	.33	"
7242-137-2	"	"	"	"	175	N.D.	"	"
7242-139-2	75% Pt, Chemically Deposited	25	"	"	150	.89	N.D.	"
"	"	"	"	Unsintered	"	.86	.54	.04
"	"	"	"	500	175	.85	.36	.04
7242-139-1	50% Pt,	50	"	500	200	N.D.	.59	"
7242-121-4	"	"	"	"	150	.88	.49	"
7242-122-5	"	"	"	"	175	N.D.	.20	.03
	"	"	"	"	200	.68	.46	.04
	"	"	"	"	200	.83	.43	.07
Noble Metal Alloys								
7242-136-1	95% Pt, 5% Ru	15	15	500	150	.89	.49	.05
7242-136-2	"	"	"	"	175	N.D.	.31	.05
7242-148-1	"	0	25	"	150	.89	"	"
"	"	"	"	Unsintered	150	"	N.D.	"
7242-148-2	75% Pt, 25% Ru	0	"	500	175	.86	.57	.04
7242-136-3	50% Pt, 50% Au	15	15	"	150	.86	.48	.04
	"	"	"	"	175	N.D.	.26	.06

(1) Graphite physically mixed except where noted.

TABLE 4-6

Surface Area and Crystallite Size Measurements

Sample Size: 2" x 2"

<u>Electrode</u>	<u>Nominal Pt Loading mg/cm²</u>	<u>Graphite Level (%)</u>	<u>Sintering Temp. (°F)</u>	<u>Surface Area⁽¹⁾ (m²)</u>	<u>Crystallite Size Å (Å)</u>
<u>Type AA Electrodes</u>					
AA-1	8-10	--	unsintered	5.0 ⁽³⁾	(2)
"	"	--	"	4.3	(2)
"	"	--	"	4.6	(2)
S7242-125-2	10	--	400	3.7	--
S7242-122-1	"	--	500	3.4	--
"	"	--	"	3.1 ⁽³⁾	--
S7242-114-4	"	--	"	5.3	110
S7242-113-5	"	--	700	3.0	110
<u>Platinum/Graphite Electrodes</u>					
S7242-125-3	10	33	unsintered	7.2	--
"	"	"	500	2.6	--
S7242-121-1	"	25	"	4.0	210
"	"	"	"	2.0 ⁽³⁾	170
S7242-121-4	"	50	"	3.9	120
"	"	"	"	1.0 ⁽³⁾	120

(1) Measured area for 2" x 2" sample.

(2) 80-100 Å for commercial Platinum Black.

(3) Electrode used to obtain polarization data @ 20°C.

If all its surface were available, a 2" x 2" AA-1 electrode containing approximately 10 mg Pt/cm² should have an area of 7-8 m², based on a surface area of 27-31 m²/g for commercial platinum black. As indicated in Table 4-6, the surface area measurements obtained on fresh, unsintered AA-1 electrodes ranged from 4-5 m² or somewhat below the calculated value. The data indicate that, in general, sintering tends to decrease the surface area and increase crystallite size to some extent. Table 4-6 also lists data for electrodes which have been used in obtaining polarization data at 200°C. It is apparent that significant decreases in surface area are associated with even these short tests.

4.2 Air Electrodes

As discussed in Progress Report No. 1, it would be desirable to decrease the catalyst loading on the cathode side of the fuel cell system. Catalyst loading on the fuel side then may be increased to as high a level as possible consistent with a total loading of 20 g/ft² for the system.

Performance data for air electrodes are given in Table 4-7. Two types of electrodes were tested. One was commercial platinum black catalyst at a loading of 7.5 mg/cm² admixed with 12-25% Cyanamid Graphite, with PTFE levels of 10-20%. These electrodes were unsintered or sintered at 500°F, as indicated. The second type of electrode studied contained 5 mg/cm² of platinum chemically deposited at levels of 25, 50 or 75% on Cyanamid Graphite. PTFE level was 20%. The electrodes were not sintered. Performance data were obtained at 175°C using 100% phosphoric acid, glass fiber matrix and an AA-1 hydrogen electrode.

TABLE 4-7

Performance Date: Air Electrodes
 Temperature: 175°C
 Electrolyte: 100% H₃PO₄
 Matrix: Glass Fiber
 H₂ Electrode: AA-1

Electrode No.	Pt Loading mg/cm ²	Graphite Level (%)	PTFE Level (%)	Sintering Temp. (°F)	H ₂ /Air Performance:			H ₂ /O ₂ Performance:			Cell Resistance (ohms)
					Working Voltage	100 ms/cm ²	10	40	100 ms/cm ²	Working Voltage	100 ms/cm ²
7510-37-1	7.5 ⁽¹⁾	25	10	500	-	-	-	-	-	-	.05
7510-37-2	"	"	"	Unsintered	-	-	-	-	-	-	-
7510-37-3	"	"	15	500	.745	.609	.735				.02
"	"	"	"	Unsintered	.639	-	-				.02
"	"	"	20	500	.812	.627	.731				.03
"	"	"	"	Unsintered	.887	.567	.784				.02
7510-45-1	7.5 ⁽¹⁾	12	10	500	.915	.667	.816				.02
7510-44-1	"	"	"	Unsintered	-	-	-				-
7510-45-2	"	"	15	500	.926	.536	.699				.03
7510-44-2	"	"	"	Unsintered	.726	-	-				.02
7510-45-3	"	"	20	500	.829	.597	.715				.03
7510-44-3	"	"	"	Unsintered	.815	.243	.665				.02
7510-86-1	5.2 ⁽²⁾	25	20	Unsintered	.82	.21	.51	.93	.85	.77	.03
7510-86-2	"	50	"	"	.82	.18	.59	.93	.80	.64	.01
7510-86-3	"	75	"	"	.86	.62	.74	.93	.82	.73	-
AA-1 (Ave.)	7-9	0	25	Unsintered	.91	.69	.80	.906	.83	.735	.04 (ave.)

(4)

- 19 -

- (1) Commercial platinum black, physically mixed with Cyanamid Graphite
 (2) Platinum deposited on Cyanamid Graphite
 (3) Data on 150°C, 85% H₃PO₄
 (4) Not determined.

For the physical mixes of commercial platinum black with graphite, better results were obtained at 12% than at 25% graphite, and in general, with sintered than unsintered electrodes. The effect of PTFE level is not clear. The best performance was somewhat poorer than that obtained with standard AA-1 electrodes.

Although all three of the chemically deposited samples (all deposited by the same method, but at different levels) performed well on oxygen, only one (75% Pt on Cyanamid Graphite) gave good performance on air. Best performance was, again, poorer than with AA-1 electrodes.

Further work with this type of catalyst is planned, with emphasis on modifying the structure of the electrode to obtain better performance on air.

4.3 Life-Testing

A total of 20 life tests were run at temperatures of 175-200°C, 15 with octane, two with propane, and three with hydrogen as fuel. Data for all the life tests are tabulated in Table 4-8. The longest test with octane lasted 465 hours at 175°C using an electrode containing 40 mg Pt/cm².

4.3.1 Octane Fuel

With octane as fuel, six life tests were conducted using AA-40 (40 mg Pt/cm²) fuel electrodes. Six tests were run with electrodes containing 14 mg/cm² platinum black with and without added Cyanamid Graphite. Single tests were also run with an RA type catalyst, a platinum-ruthenium alloy, and with a chemically deposited platinum on graphite catalyst. All of these latter tests were run with a noble metal loading of 14 mg/cm² on the fuel side.

TABLE 4-8

Life Test Data

Electrolyte: 100% H₂PO₄
Matrix: Treated PTFE Felt

Anode		Cathode		Test Temp. (°C)	Test Duration (hours)	Fuel Rate \times Stoich.	H ₂ O/Fuel Mole Ratio	Current Density (mA/cm ²)		Working Voltage		Cell Resistance	
Electrode No.	Type	Graphite Level (%)	Pt Loading (mg/cm ²)					Initial	Final	Initial	Max.	Initial (ohm)	Final (ohm)
A. Hydrogen-Air Tests													
HE12-4	AA	-	20	200	800	1	0	40	40	.71	.77	.71	.039
HE12-5	AA-1	-	9	200	200	1	0.1-0.4	60	60	.63	.63	.62	.034
HE12-11	AA-1	-	7.5	175	770	1	0	40	40	.75	.79	.69	.034
					1000	1		60	60	.67	.69	.68	.038
B. Propane-Air Tests													
HE12-6	AA	-	20	200	330	~15	~6	40	40	.52	-	.43	.037
HE12-16	AA-1	-	9	175	975	~35	.08-1.6	20	20	.40	-	.28	.040
C. Octane-Air Tests													
HE12-7A	AA	-	40	200	125	~40	~6	40	40	.34	-	0	.028
HE12-7B	AA	-	20	200	300	~40	~4	40	40	.40	-	.36	.025
HE12-9	AA	-	20	200	250	15	1.5-5	40	28	.55	-	.33	.020
HE12-19	AA	-	9	175-200	160	15-30	~5	30	16	.40	-	.40	.038
HE12-20	AA	-	9	175	380	15-30	3-8	40	30	.32	-	.35	.040
HE12-21	AA	-	9	175	136	12-30	6	20	30	.47	-	.30	.070
HE12-22A	AA	-	40	175	465	12-30	6-9	20	30	.30	-	.40	.032
HE12-8	Pt/Graphite (2)	15	9	200	90	15	3-5	40	0	.43	-	.00	.040
7242-130-3	Pt/Graphite (2)	25	9	175-200	150	30	2-3	20	10	.46	-	.47	.017
7242-128-2	Pt/Graphite (2)	25	9	150	40	30	1-5	20	20	.53	-	.40	.033
7242-131-1	AA	-	9	175-200	140	30	4	20	12	.35	-	.40	.040
7242-129-2	Pt/Graphite (2)	15	9	175	-	-	-	No Performance	No Performance	-	-	-	.033
7242-147-2	AA	-	9	175	-	-	-	No Performance	No Performance	-	-	-	.047
HE12-15	AA	-	9	175	220	30	6-9	20	20	.43	-	.40	.040
HE12-22B	95 Pt/3 Pt (2)	15	9	175	240	30	~5	20	0	.40	-	.037	.035
HE12-17A	HE12-17B	14 Pt/Ru	9	175	-	-	-	No Performance	No Performance	-	-	-	.040
HE12-17B	HE12-17C	14 Pt/Ru	9	175	-	-	-	No Performance	No Performance	-	-	-	.037
HE12-18	7242-139-2	25	9	175	-	-	-	No Performance	No Performance	-	-	-	-

(1) Air electrode 87510-59, containing 2% Cyanamid Graphite.
(2) Catalyst physically mixed with graphite, electrode sintered 10 minutes at 500°C.

(3) Water/fuel ratio varied to study effect on performance.

(4) Current densities as high as 60 mA/cm² using O₂ in place of air were attained during portions of this test (see Figures 4-1, 4-2).

(5) Test terminated by cross leakage of reactants through the matrix.

(6) Sintered 10 minutes at 500°C.

(7) Platinum chemically deposited on graphite, electrode sintered 10 minutes at 500°C.

In most of the octane life tests, a water-to-octane mole ratio in the range 3-9 was maintained. Difficulties were experienced with the pumps feeding water into the evaporators. Performance in most of these tests suffered because of periodic water-pump failures.

Performance of the AA-40 electrodes was disappointing in that while a current density of 40 ma/cm^2 could be obtained at the beginning of some life tests, it could not be maintained. Figure 4-1 shows that in life test HCLT-22, conducted at 175°C , current densities as high as 60 ma/cm^2 could be obtained for short periods of time by using oxygen rather than air at the cathode.

The voltages indicated in Figure 4-1 are the average values over a period of time. The voltages for all the life tests using octane as the fuel cycled from about 0.2 to about 0.5 volt. Typical voltage cycling is shown in Figure 4-2, a reproduction of the strip chart taken from the voltage recorder during life test HCLT-22. The strip chart reveals two types of voltage cycling: a periodic sharp drop-off to about 0.2 v, and a constant cycling of about 20 mv. The periodicity of the sharp drop-off depended on the current density at which the cell was operated. The interval between drop-offs was as long as $1 \frac{1}{2}$ hours at low current densities or as short as 10-15 minutes at high current densities (60 ma/cm^2).

The life tests with 14 mg Pt/cm^2 fuel electrodes were run at current densities of 20 ma/cm^2 or less, since higher current densities proved difficult to maintain for any appreciable length of time. Voltage cycling was similar to that described in tests with AA-40 electrodes. In most cases, average performance decreased substantially with time.

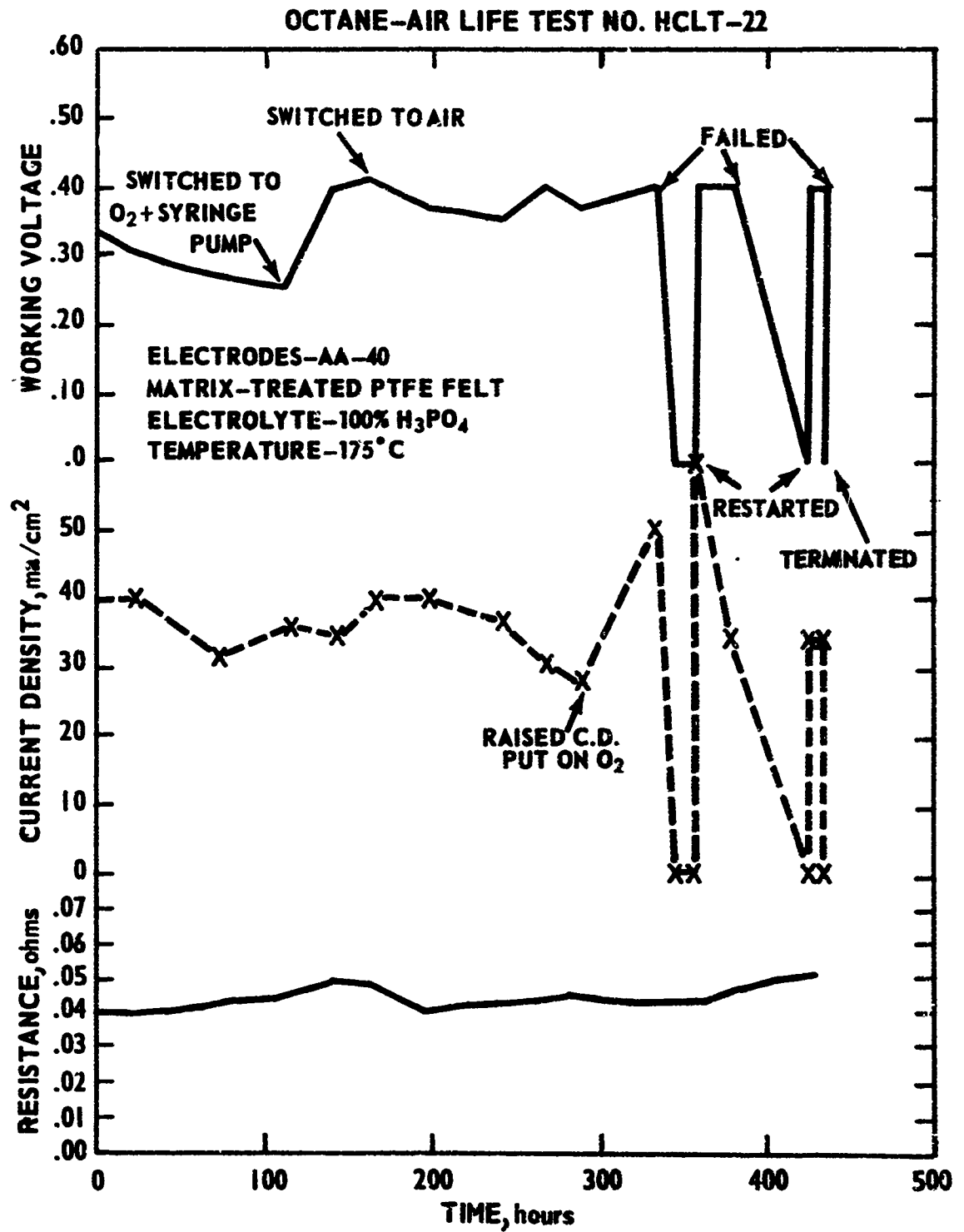
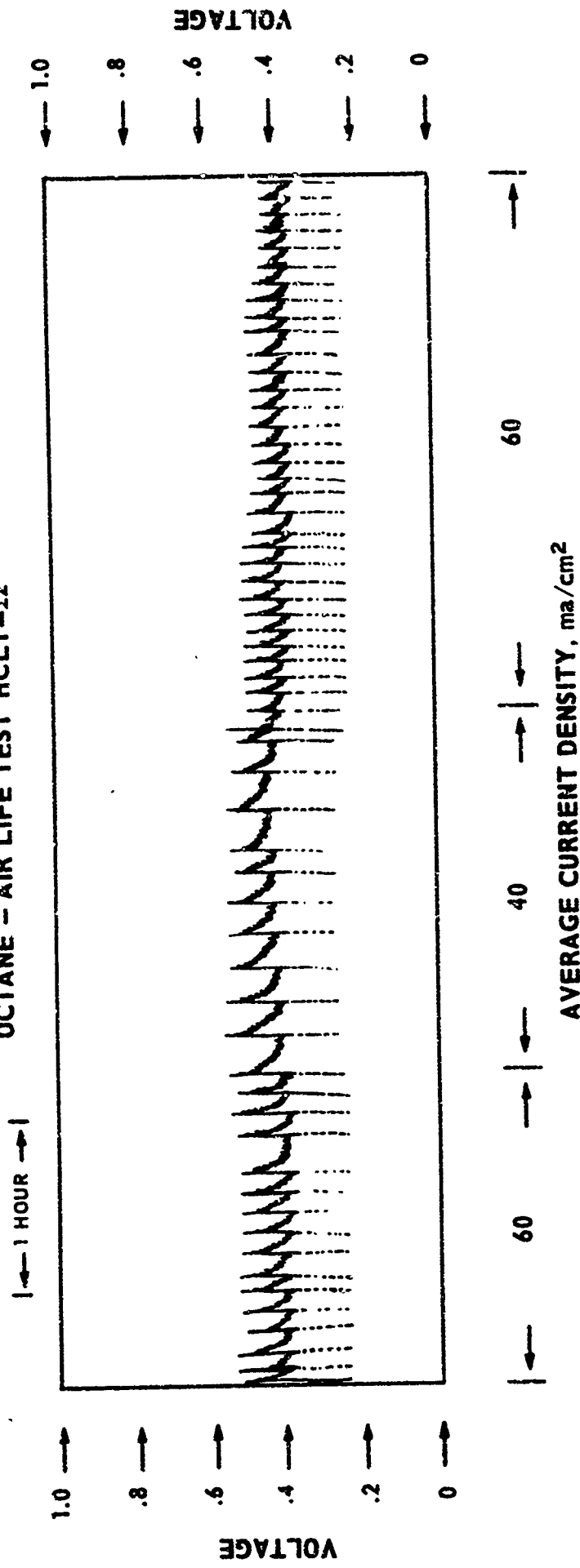


FIGURE 4-1

VOLTAGE CYCLING
OCTANE - AIR LIFE TEST HCLT-22



ELAPSED TIME : ABOUT 300 HOURS

FIGURE 4-2

In one run, however, (HCLT-23) an average voltage of about 0.4 v at 20 ma/cm² was maintained for 220 hours until the run was terminated because of leakage of octane through the matrix. An unsintered fuel electrode containing no graphite was used in this test.

4.3.2 Propane Fuel

Two life tests on propane were run during this period. In life test HCLT-6, using an AA-40 anode, performance decreased from approximately 19 to 12 watts/ft² during 330 hours at 200°C. In life test HCLT-16, using standard AA-1 electrodes on both sides, a current density of 20 ma/cm² was maintained for 975 hours at 175°C. This test was conducted to determine the effect of very low values of the water-to-fuel ratio on performance. The life history of this test is shown in Figure 4-3. Water-to-propane mole ratios of 0.08 to 1.6 were studied over the course of the test. The ratio of water to propane was controlled by the temperature of a water saturator for the propane gas. Several failures occurred during this life test because of drying out of the saturator. After 800 hours, the cell suffered an irreversible increase in resistance after such a failure. Thereafter, performance was very poor. It appears from the data obtained in this test that performance increased with increasing water content of the fuel.

The voltage indicated in Figure 4-3 is the average voltage. The actual cycling of the voltage is illustrated in Figure 4-4. Although the cycling is less severe with propane than with octane, the same two modes of cycling, a periodic sharp drop of about 0.2 volts and a constant cycling of about 20 mv, were observed.

PROPANE - AIR LIFE TEST NO. HCLT-16

ELECTRODES - AA-1
 MATRIX - TREATED PTFE FELT
 ELECTROLYTE - 100% H_3PO_4
 TEMPERATURE - 175°C.
 CURRENT DENSITY - 20 ma/cm²

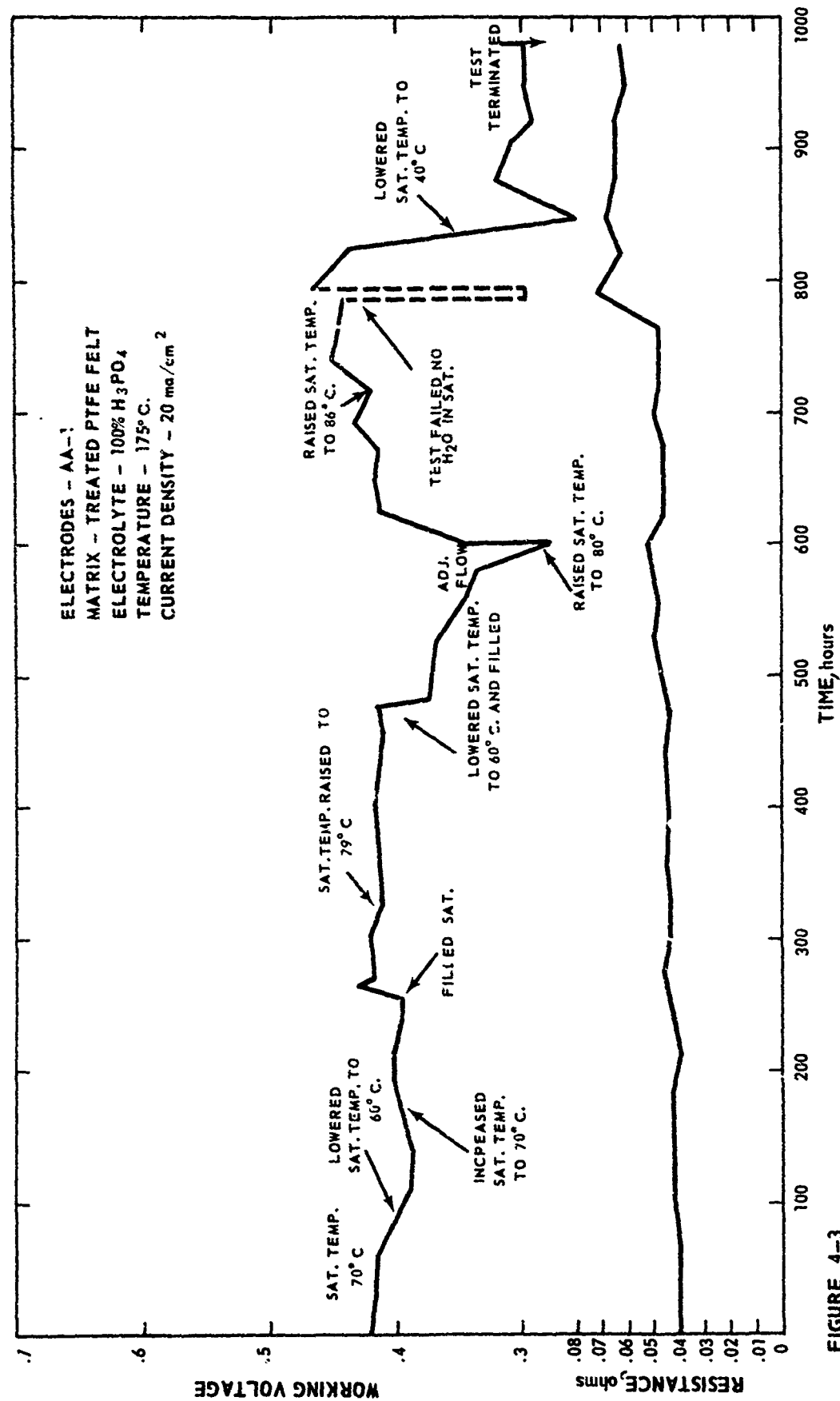
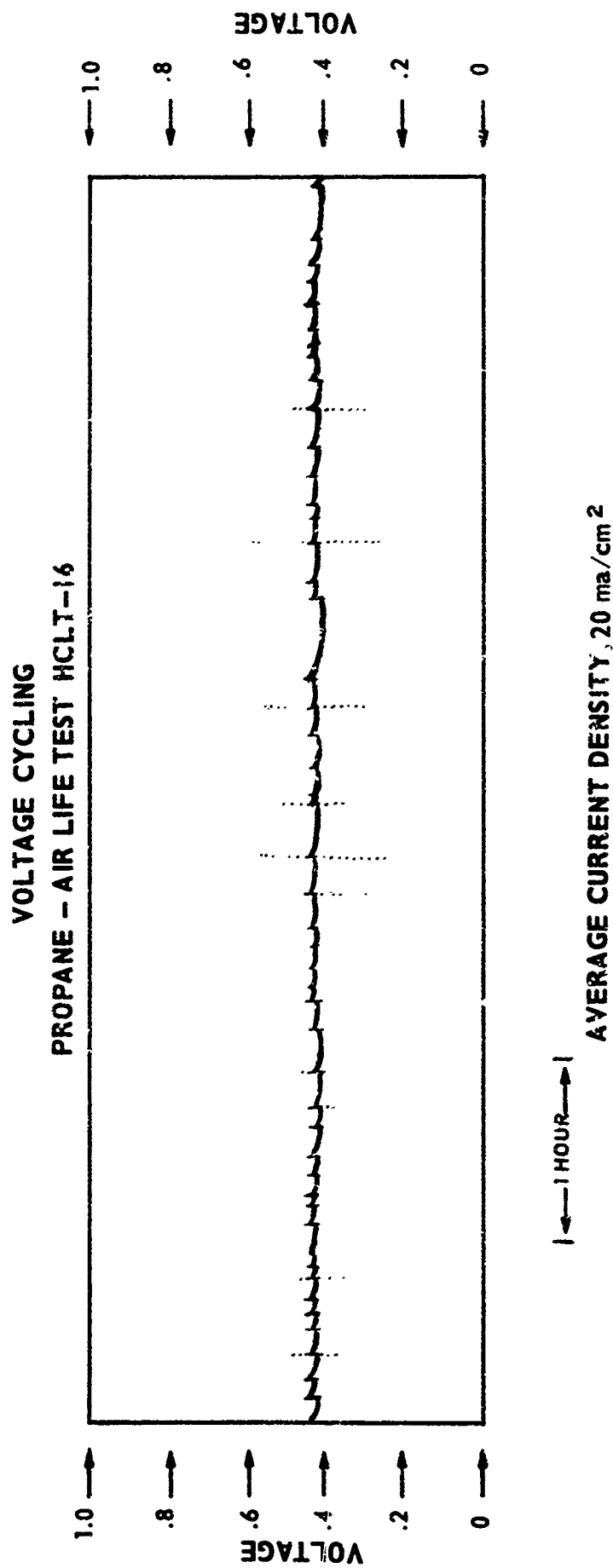


FIGURE 4-3



ELAPSED TIME : ABOUT 200 HOURS

FIGURE 4-4

4.3.3 Hydrogen Fuel

Three life tests using hydrogen as fuel were conducted mainly to determine the stability of the fuel cell system. Tests HCLT-4 and 5 were run at 200°C to evaluate treated PTFE felt as the matrix. In both tests type AA electrodes were used, but in one test the platinum loading was 10 mg/cm² and in the other 20 mg/cm². Life test No. 4 was run at 40 ma/cm² for approximately 800 hours, then at 60 ma/cm² for an additional 200 hours (see Figure 4-5). Voltages were fairly steady over this period of time.

In life test No. 13, conducted at 175°C, an experimental air electrode containing Cyanamid Graphite was used. This electrode contained 7.5 mg Pt/cm² physically mixed with 25% Cyanamid Graphite. The electrode was sintered at 500°F and contained 20% PTFE. Performance was stable over the entire 1000 hours of the test. An overall drop in voltage of approximately 30 mv and a negligible increase in internal resistance were observed (see Figure 4-6).

4.3.4 Surface Area and Crystallite Size Measurements

Electrodes from a number of the life tests reported in Table 4-8, as well as from several previously reported tests⁽¹⁾ were submitted for surface area and crystallite size measurements. The data are presented in Table 4-9 and in Figures 4-7 and 4-8. The data shown in the figures were normalized by dividing the measured surface area by the nominal platinum loading of the electrode neglecting any weight losses which may have occurred during the tests. Actual weight loss measurements for life-tested electrodes were not felt to be meaningful because of mechanical losses and sticking of the matrix to the electrodes on disassembly of the cell.

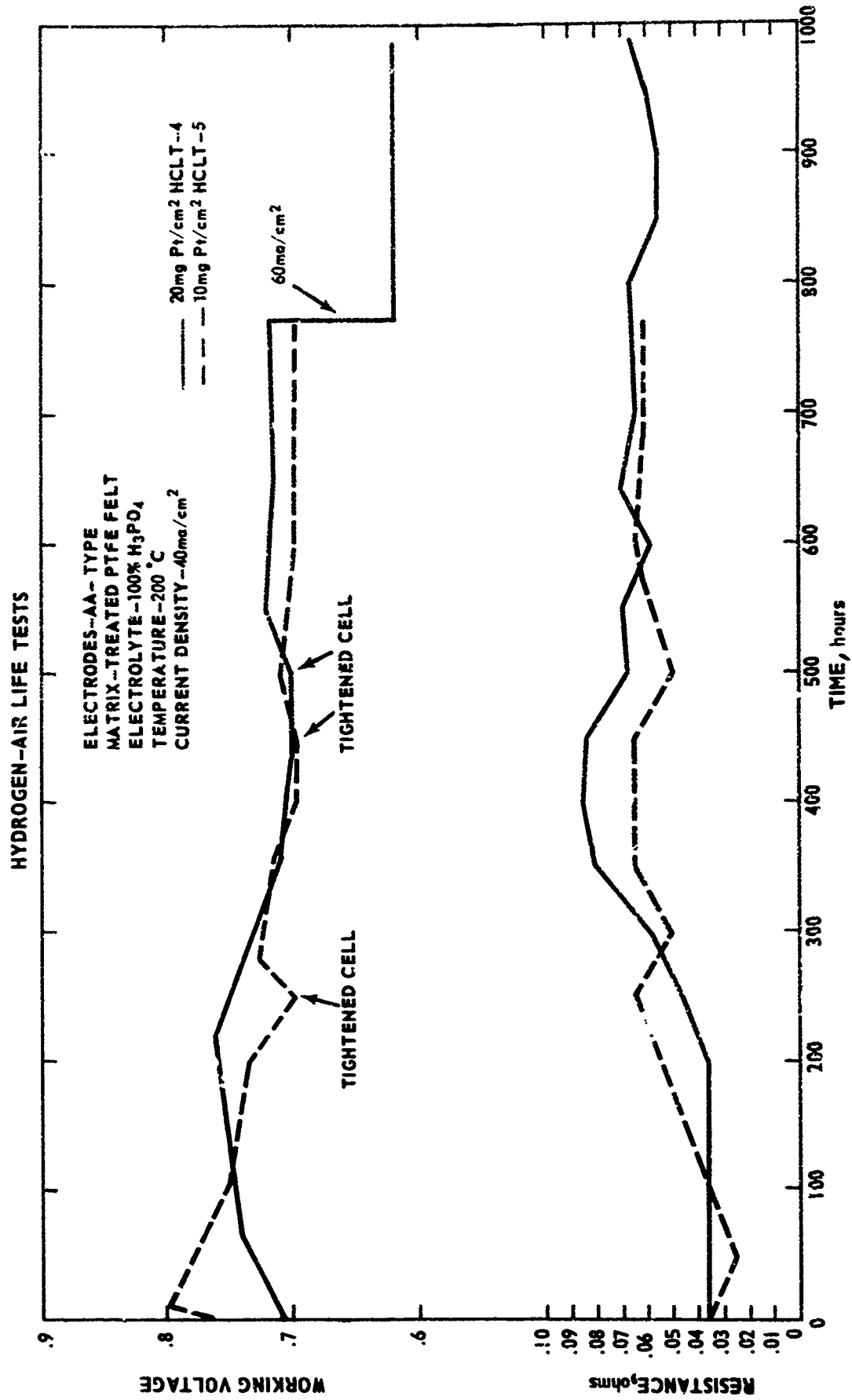


FIGURE 4-5

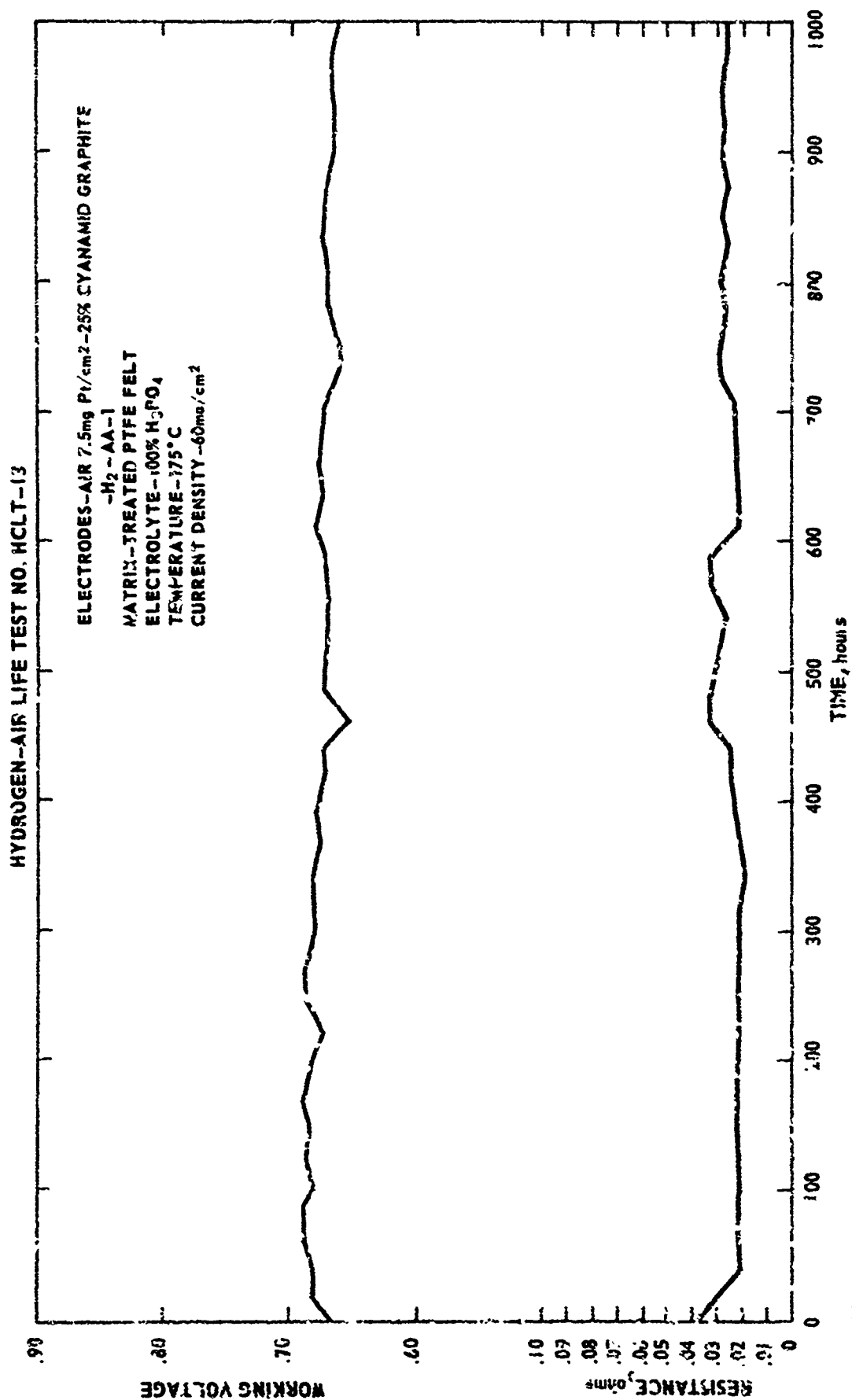


FIGURE 4-6

TABLE 4-9

Surface Area and Crystallite Size Measurements-

Life Test Electrodes

Matrix: Treated PTFE Felt - 100% H₃PO₄

Size: 2" x 2"

Life Test No.	Test Temp. °C	Condition hrs.	Electrode	Loading mg Pt/cm ²	Surface Area		Crystallite Size Å (X-ray) ⁽¹⁾
					(m ²)	(m ² /g Pt) ⁽¹⁾	
BT3C3-13	200	82 ⁽²⁾	Hydrogen/Heptane AA-1	10	2.9	12.5	-
"	"	"	Air "	"	1.7	7.3	-
FCUS-7.	"	125	Octane AA-40	40	3.0	2.9	-
"	"	"	Air "	"	2.7	2.6	-
HCUS-1	"	125	Hydrogen AA-1	10	1.9	8.2	210
"	"	"	Air "	"	1.4	6.0	170
HCUT-4	"	1000	Hydrogen AA	20	1.0	1.9	-
"	"	"	Air "	"	2.2	4.3	220
HCUT-5	"	705	Hydrogen AA-1	10	0.5	2.1	-
"	"	"	Air "	"	0.8	3.4	-
HCUT-3	175	300	Hydrogen "	"	3.0	12.9	-
"	"	"	Air "	"	1.4	6.0	-
HCUT-15	"	1000	Hydrogen "	"	2.6	11.2	-
"	"	"	Air Pt + Graphite ⁽³⁾	7.5	1.5	-	-
HCUT-16	"	975	Propane AA-1	10	1.4	6.0	-
"	"	"	Air "	"	2.7	12.8	-
HCUT-20	"	300	Octane AA-40	40	8.2	8.0	-
"	"	"	Air AA-1	10	3.1	13.3	-

(1) Based on nominal platinum loading, neglecting weight losses during life test

(2) 10 hours with heptane followed by 72 hours with hydrogen

(3) 2% Cyranid Graphite Physically mixed with Pt black

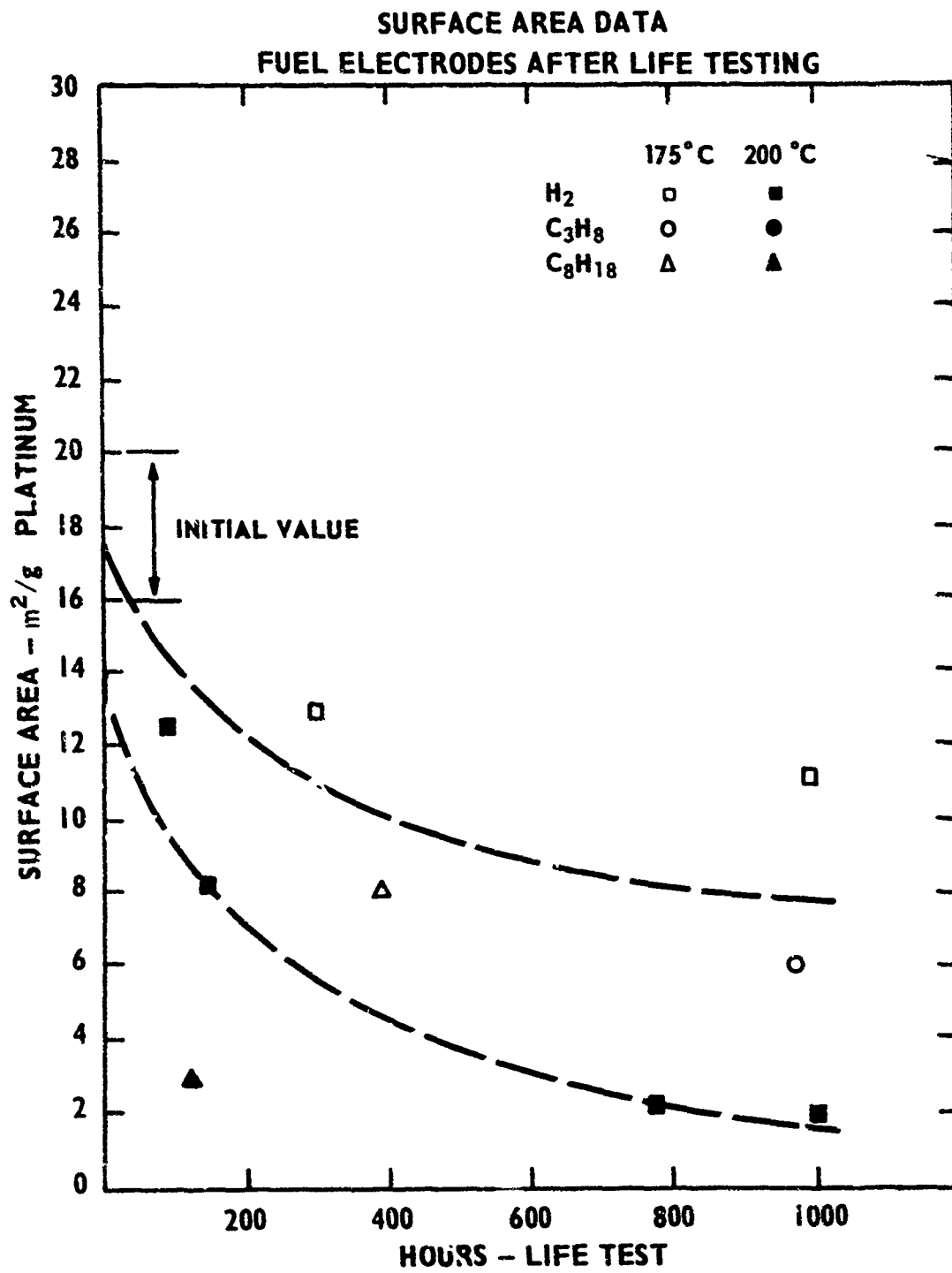
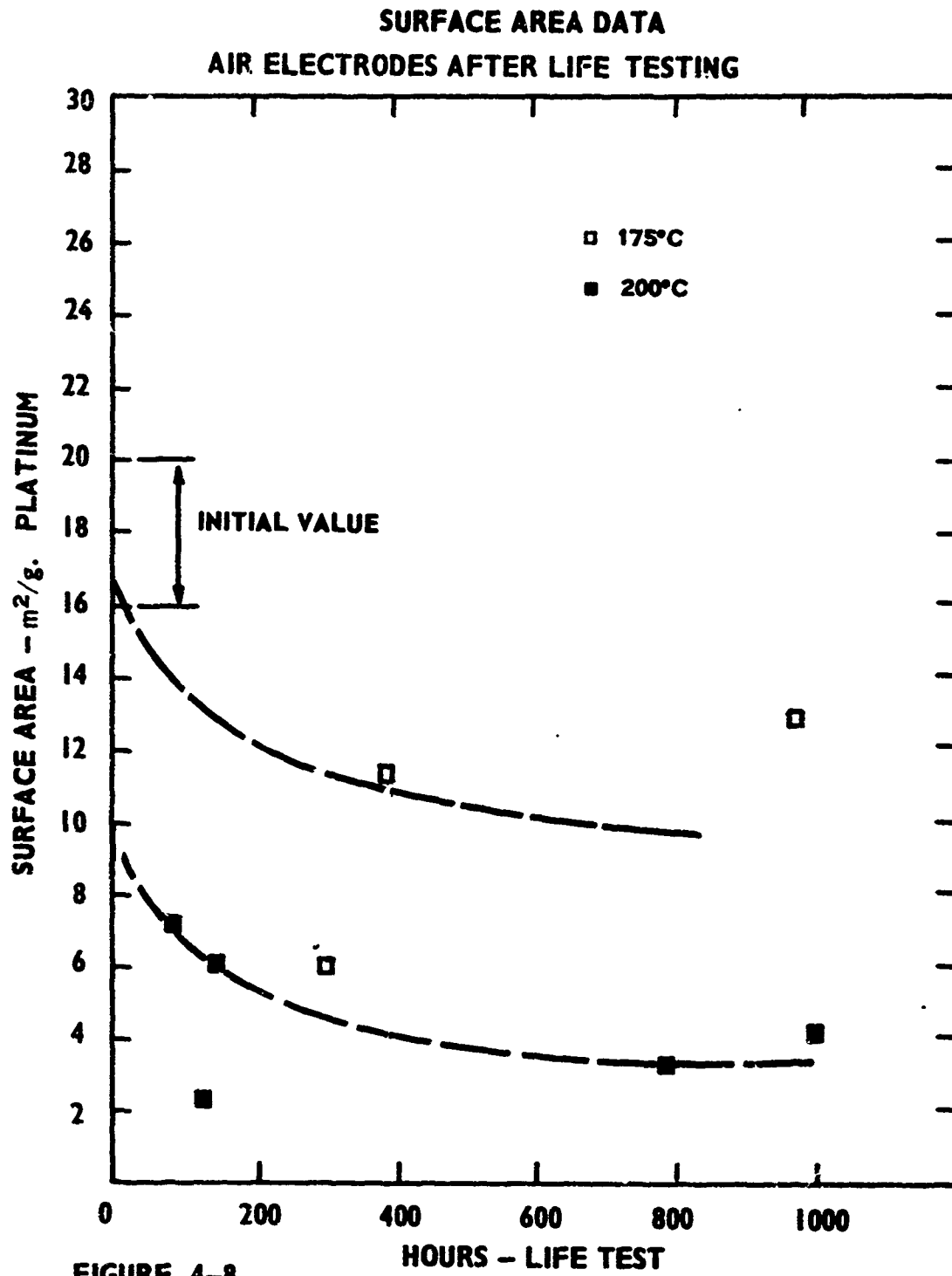


FIGURE 4-7



It is apparent from the data that substantial losses in surface area occurred during these tests at both fuel and air electrodes, and at both 175° and 200°C. In these tests, surface area losses at 175°C appear to be less severe than at 200°C. Measurements made on three of these electrodes tested at 200°C also indicate a substantial growth in crystallite size.

4.4 Stability Studies

In Progress Report No. 1 we described material stability tests conducted on standard AA-1 electrodes to determine the ability of the electrodes to withstand the fuel cell environment for extended periods of time. In this period of investigation, similar tests were conducted with standard AA-1 electrodes and platinum/graphite electrodes at 150-200°C.

The test procedure as described in the previous report was as follows:

1. Electrode samples (2" x 2") were submerged completely in 200 cc of 100% phosphoric acid contained in a 600 cc PTFE Beaker.
2. The beaker was covered by a glass crystal and placed in the oven at the desired temperature.
3. At the desired length of time two or three electrodes were removed from the phosphoric acid, washed, dried and weighed. In several cases, the electrodes were returned to the beaker for additional exposure. Where the latter procedure was used, the data are denoted "returned."

4.4.1 Type AA Electrodes

Figure 4-9 summarizes the weight loss data obtained at 200°C with type AA electrodes, including data previously reported⁽¹⁾. It is obvious that there is wide variability in the experimental data. Part of this variability may be attributed to differences in procedure. For example, the greatest weight losses occurred with electrodes S7510-15B. In this case, only 40 cc of phosphoric acid was used, or just enough to cover the electrodes. In the tests in which the electrodes were weighed and returned for additional exposure, the weight loss curves show a tendency to level off, possibly due to reoxidation of the platinum surface between periods of exposure.

Weight loss data for AA-1 electrodes exposed to phosphoric acid at 175°C are shown in Figure 4-10. Here again there is a wide variability in the data. The overall range of the data is about the same as for the data at 200°C, indicating that corrosion may also be a serious problem at 175°C. Corrosion rates at 150°C, as indicated by the data in Figure 4-11, appear to be significantly lower than at 175-200°C.

Surface area and crystallite size measurements were made on many of the electrodes exposed to phosphoric acid in oven tests. The data are shown in Table 4-10. It is apparent from the data that type AA electrodes lose a considerable portion of their surface area during very short periods of exposure at all three temperature levels, 150, 175, and 200°C. Part of the loss in surface area can be attributed directly to loss of platinum, although the correlation between the weight loss data and the surface area data is not particularly good.

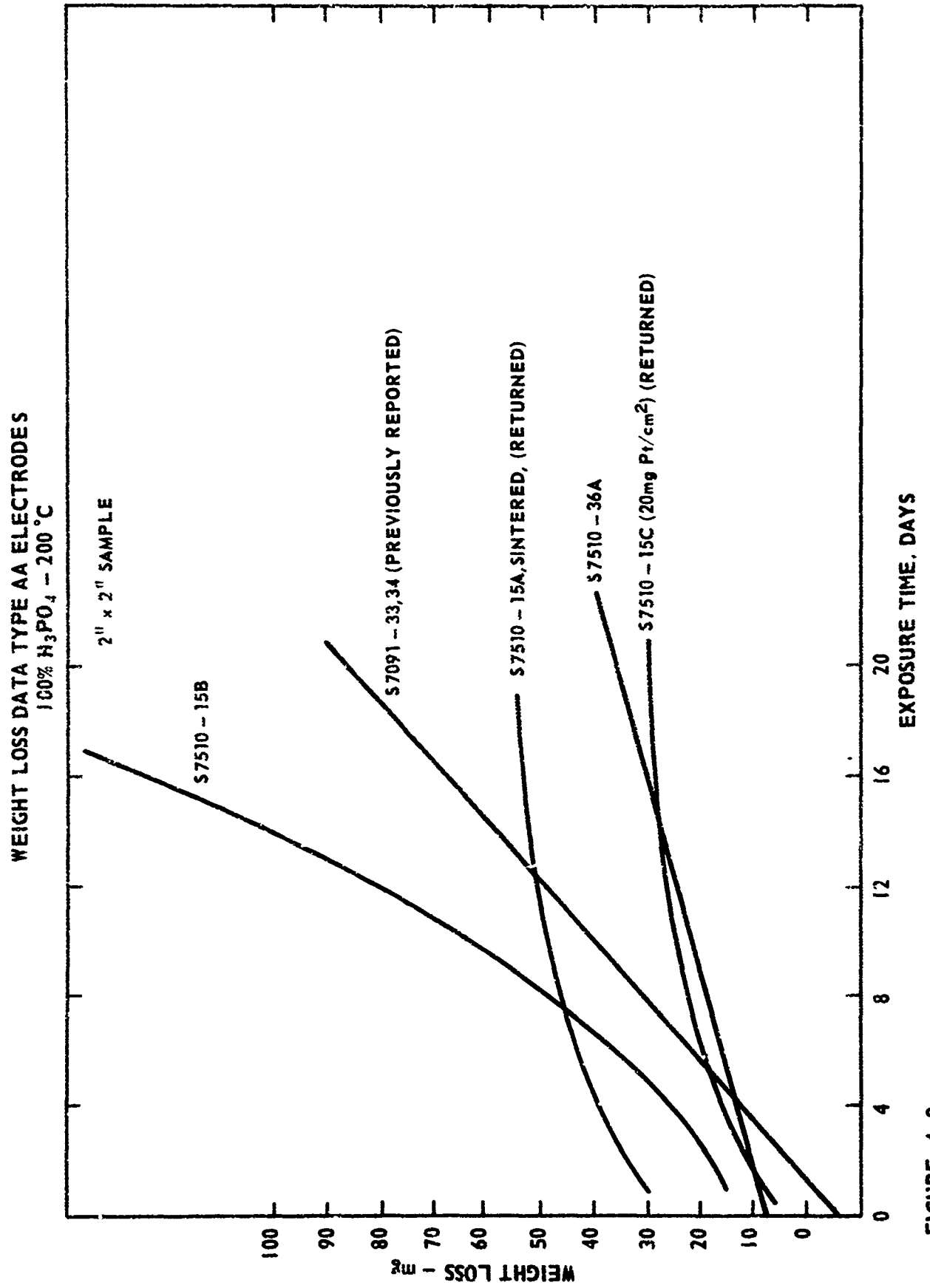


FIGURE 4-9

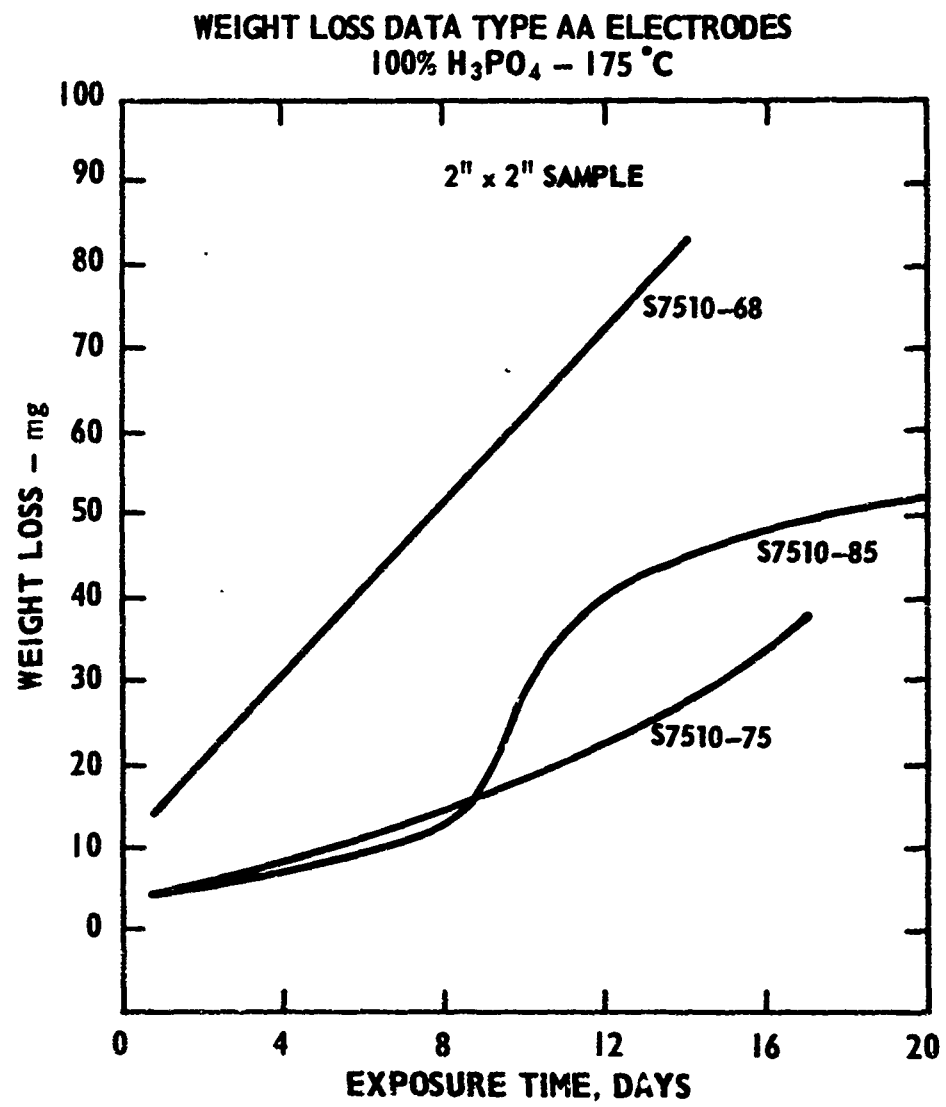


FIGURE 4-10

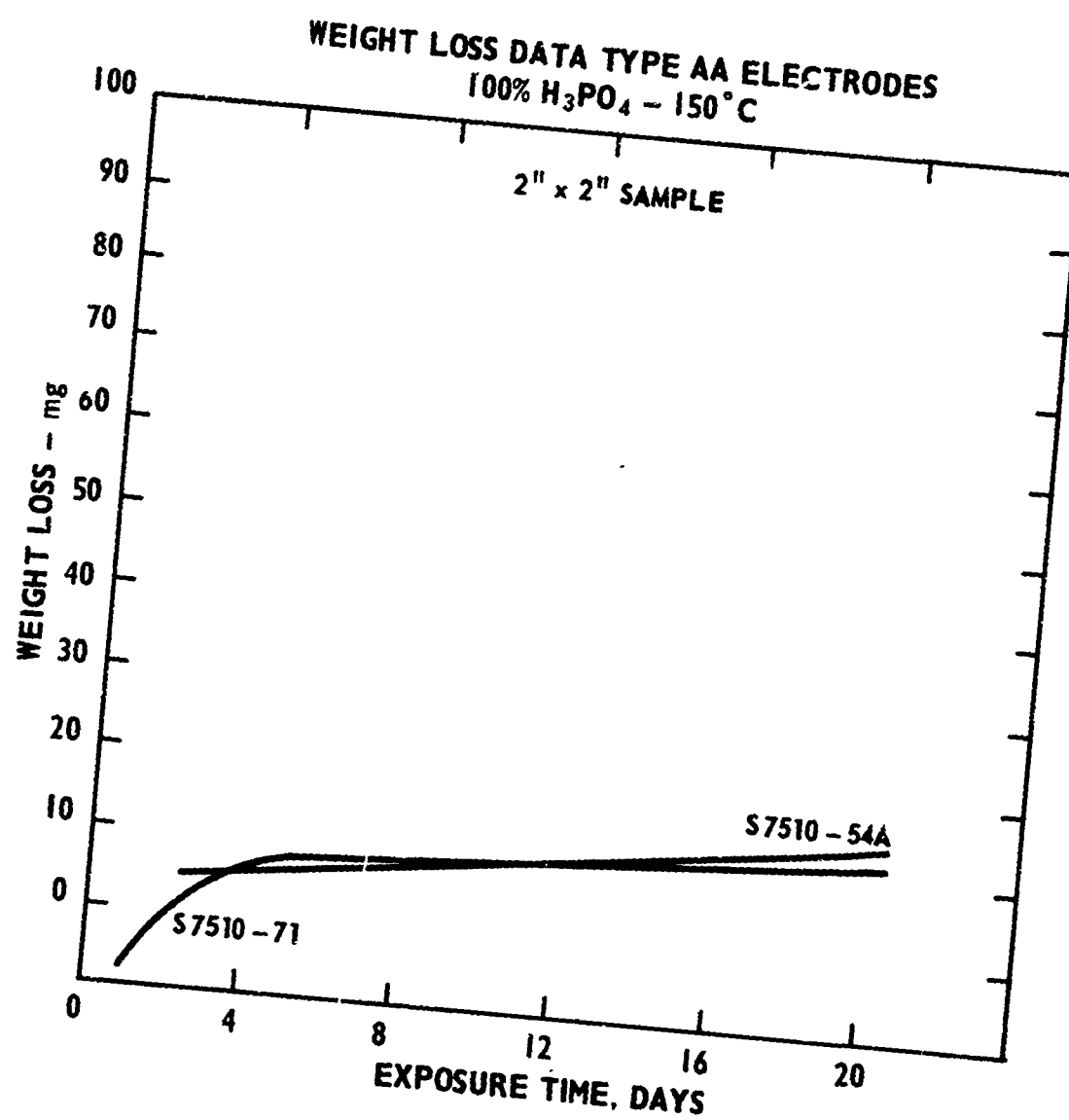


FIGURE 4-11

TABLE 4-10

Surface Area and Crystallite SizeMeasurements - Stability Studies

Exposure Temp: 150-200°C

Size: 2" x 2"

AA-1 Electrodes

<u>Test No.</u>	<u>Exposure Temp. °C</u>	<u>Exposure Conditions</u>	<u>Days</u>	<u>Surface Area m²/Sample</u>	<u>Crystallite Size Å</u>
S7510-54A	150	100% H ₃ PO ₄	3	2.2, 1.7	-
"	"	"	6	1.9, 1.8	-
"	"	"	19	1.7, 1.8	-
S7510-68A	175	"	1	5.3, 4.9	-
"	"	"	4	5.3, 3.3	-
"	"	"	12	2.3, 2.2	-
S7091-33, 34	200	"	1	1.2	240
"	"	"	4	1.0	210
"	"	"	10	1.6	190
"	"	"	20	1.8	210
S7510-15B	"	"	1	1.3	160
"	"	"	5	0.8	210
"	"	"	10	0.6	-
"	"	"	19	0.2	240
S7091-33B	"	Air	10	5.5, 4.2	-
S7510-15A	(Unexposed)		0	3.7, 3.4, 5.3	110
AA-1 Sintered(1)	200	100% H ₃ PO ₄	19	1.6, 1.8	210, 220

Platinum/Graphite Electrodes

S7510-36B	-	-	0	3.6, 2.8, 3.0	
BA-1 (2.5 mg Pt/cm ² , 75% Cyanamid Graphite)	200	100% H ₃ PO ₄	1	2.4, 2.4	
			5	1.9, 1.8	-
			10	1.8, 1.8, 2.0	
			23	2.0	
S7510-54B	150	"	3	4.9, 5.5	
14 mg Pt/cm ² 25% Cyanamid Graphite			19	3.6, 2.8	
S7510-54C	150	"	3	3.4, 2.2	-
7.5 mg Pt/cm ² 25% Cyanamid Graphite			19	1.8, 2.8	

(1) 500°F - 10 Minutes

The samples (S7510-15B) which showed the highest weight losses (Figure 4-9) also showed the greatest loss in surface area. On the other hand, the samples exposed at 150°C showed high losses in surface area even though weight losses were small.

Electrode samples exposed for ten days to air at 200°C in the absence of phosphoric acid showed no loss in surface area as compared to fresh electrodes. This is consistent with data reported previously⁽¹⁾ in which no loss in performance was noted for electrodes exposed only to air at 200°C.

Crystallite size measurements are available only for samples exposed at 200°C. A substantial growth in crystallite size, from an average of about 100 Å in unexposed electrodes to about 200 Å in the exposed samples, was observed.

4.4.2 Platinum/Graphite Electrodes

Several types of graphite-containing electrodes were exposed to phosphoric acid in oven tests. Weight loss data for these electrodes are shown in Figure 4-12. Type BA-1 electrodes (2.5 mg Pt/cm², chemically deposited at 25% Pt on Cyanamid Graphite) were tested at 200°C. For these electrodes, either sintered or unsintered, the weight losses were much lower (on the order of 0.02-0.04 mg/cm²/day) than in the corresponding tests with type AA electrodes. Electrodes containing 7.5 and 14 mg/cm² of platinum black physically mixed with 25% Cyanamid Graphite were exposed to phosphoric acid at 150°C. The weight loss rate for these electrodes was substantially the same as shown for AA-1 electrodes at 150°C in Figure 4-11.

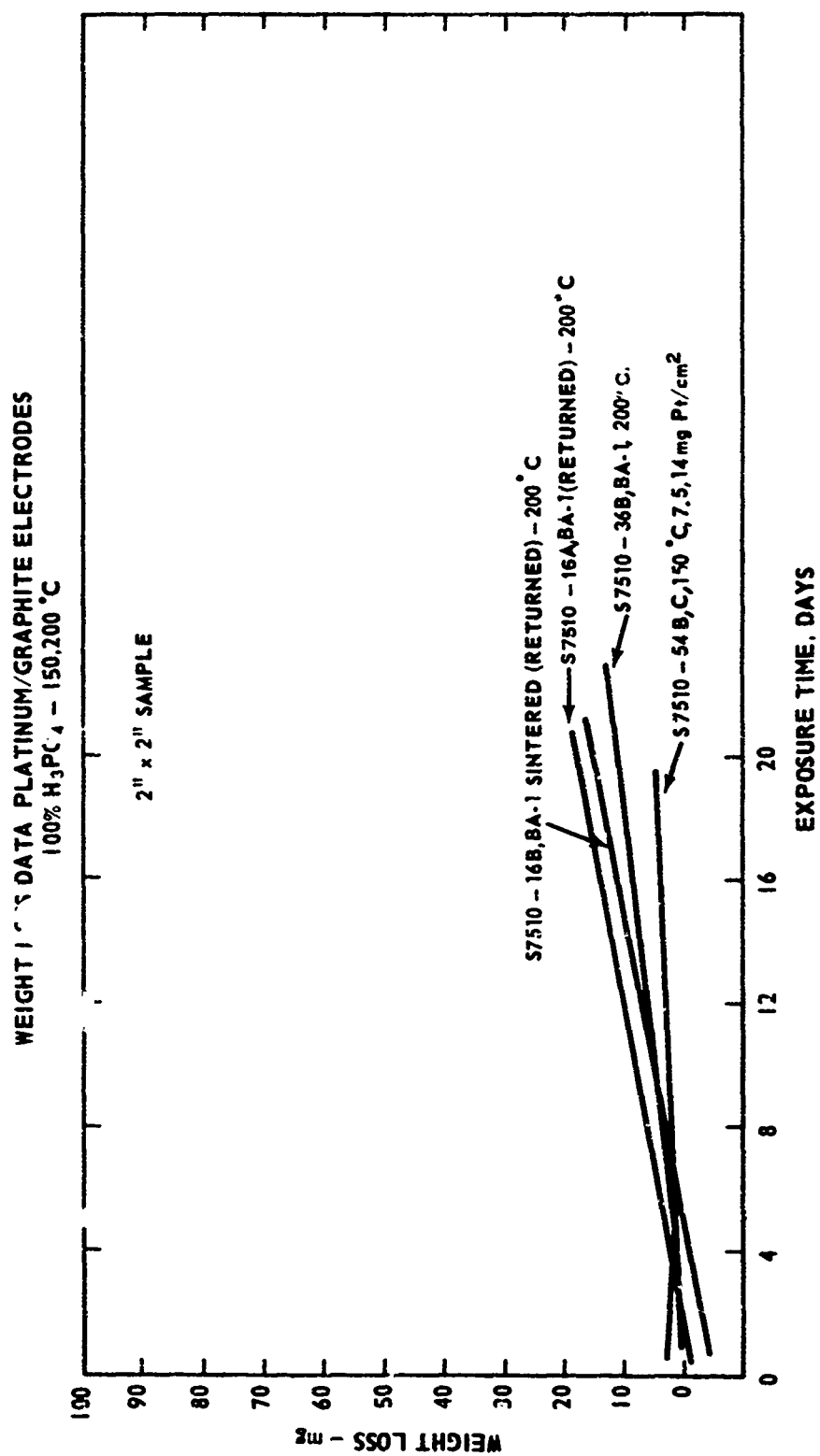


FIGURE 4-12

Surface area measurements obtained on the exposed platinum/graphite electrodes are shown in Table 4-10. Downward trends in surface area similar to those previously shown for type AA electrodes were observed. For the BA-1 electrodes, the surface area remaining after five days at 200°C corresponds approximately to that attributable to the graphite alone (Cyanamid Graphite has a surface area of about 12 m²/g).

5. FUTURE WORK

Electrode development work for both fuel and air electrodes will continue with the objective of maximizing performance on octane and air, using approximately 15 mg/cm² of noble metal on the fuel side and 5 mg/cm² on the air side. Emphasis will be placed on operating at 150-175°C in order to minimize catalyst stability problems.

During the present report period work with "high area" platinum catalysts chemically deposited on Cyanamid Graphite was initiated. This work will be continued and extended to incorporate other substrates such as metal carbides. New catalyst materials, such as Adams type noble metal preparations, will also be evaluated. Modifications in preparational techniques designed to increase the porosity of both fuel and air electrodes will be investigated. It is also planned to evaluate electrodes involving fabrication techniques and structural configurations differing significantly from those which have been employed in the preparation of type AA and other electrodes used thus far in the program.

Life testing on octane and air will continue with the objective of demonstrating long term performance stability. The test program will be designed to study the influence of operating variables such as temperature and fuel humidification, and of electrode variables such as PTFE level, incorporation of graphite, and sintering conditions. The long-term stability of promising new electrode formulations will also be investigated.

Exploratory work with impure hydrogen fuel will be initiated. This work, representing a new and secondary objective under the present contract, will be directed toward the development of technology for a hydrocarbon reformer-acid fuel cell system. Initial work will involve the evaluation of Type RA and AA electrodes at noble metal loadings of approximately 15 mg/cm² with hydrogen containing 10% CO in cells operating with phosphoric acid electrolyte at 150-175°C.

6. PERSONNEL

R. G. Haldeman	Project Manager
W. P. Colman	Project Leader
V. Corso, Jr.	Principal Investigator
A. Peruzzi	Assistant Scientist
D. Fletcher	Laboratory Assistant

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