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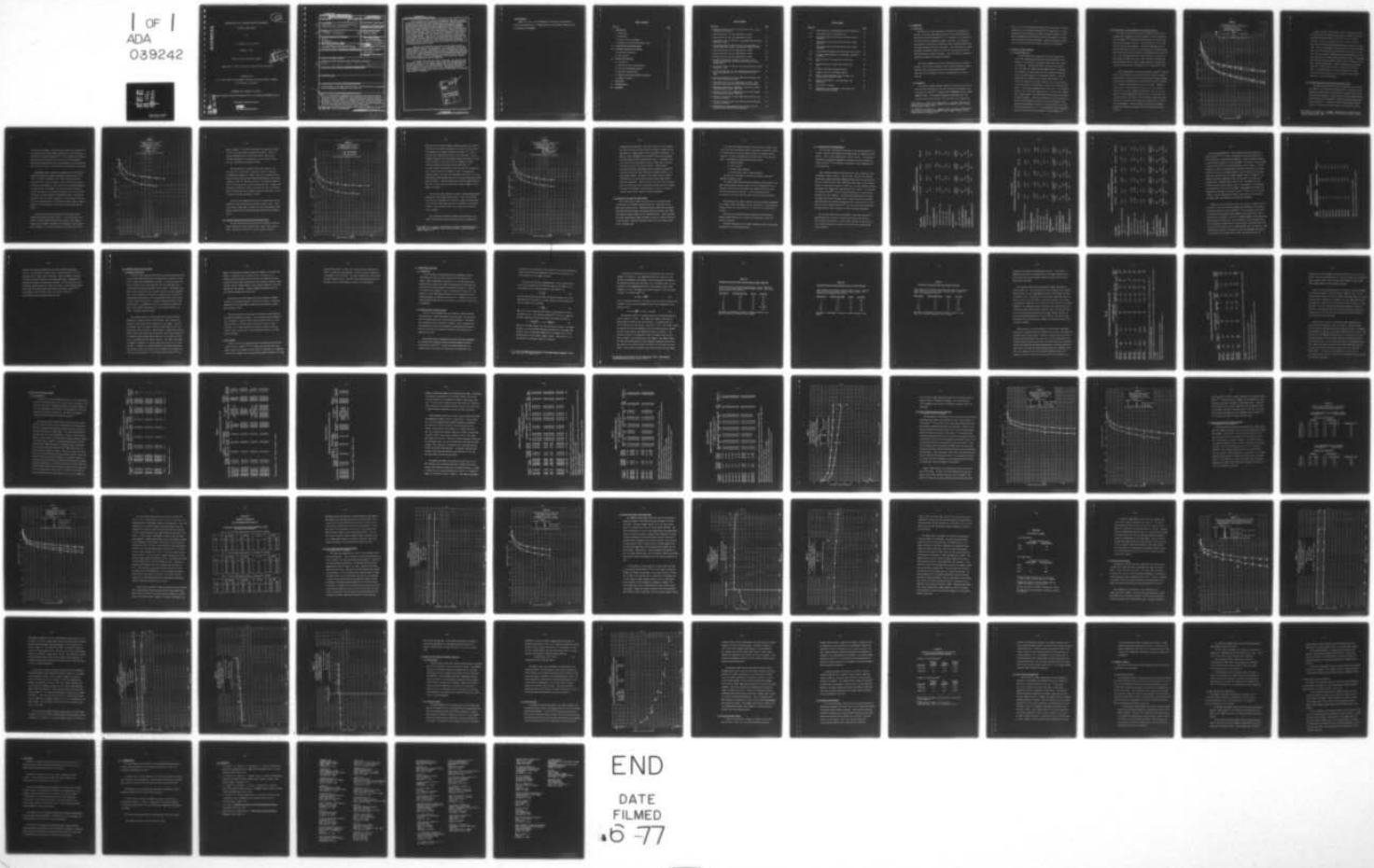

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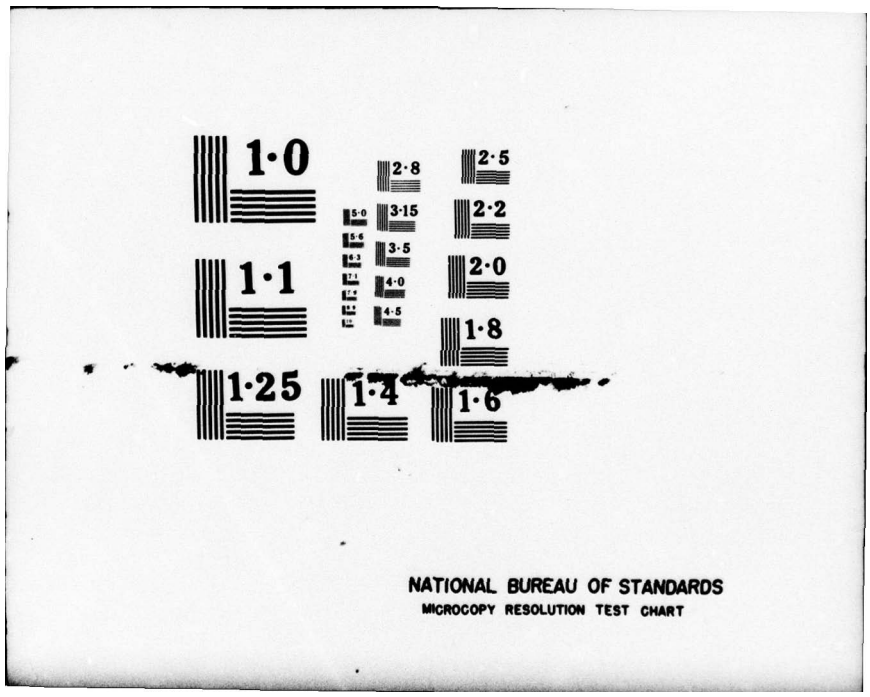
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OPTIMIZATION OF PT-DOPED KOCITE^{R} ELECTRODES IN H_3PO_4 FUEL CELLS

by

L. B. Welsh, R. W. Leyerle

January, 1977

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The use of UOP platinum impregnated Kocite materials as low-cost air and/or fuel electrocatalysts in phosphoric acid electrolyte fuel cells has been optimized with respect to some of the electrocatalyst and electrode structure parameters. Kocite materials are composite structures consisting of pyropolymers chemically bonded to refractory substrates. Fuel cell electrodes were fabricated from these materials and tested as anodes or cathodes in model fuel cells with Teflon-bonded platinum-black counter electrodes.

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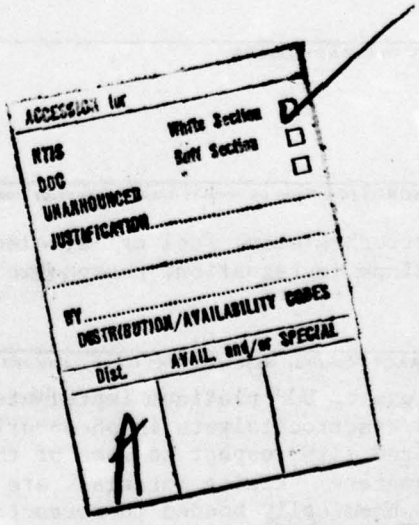
Kocite materials were produced in 200-400 gram quantities from high-surface-area aluminas with a particle size of ~500 nm. From the platinum-impregnated Kocite electrocatalyst, Teflon-bonded electrodes with porous, graphite-paper backing were fabricated by machine-calendering techniques. These electrodes had platinum loadings ranging from 0.22 to 0.58 mg/cm^2. When tested in model phosphoric acid fuel cells with 2 mg/cm^2 platinum black counter electrodes, full-cell IR-free performances of 0.70 and 0.77 volts as air and oxygen cathodes, respectively, have been obtained at 100 ma/cm^2 and 180°C using a 0.54 mg/cm^2 platinum electrode as a cathode in a cell with a silicon carbide matrix. Full cell IR-free performance of 0.67 and 0.74 as air and oxygen cathodes, respectively, have been obtained at 100 ma/cm^2 and 180°C using a 0.42 mg/cm^2 platinum loaded electrode as the cathode in a cell with a Kynol matrix. Lifetime testing of Kocite electrodes as cathodes indicates no catalyst deterioration occurs for periods in excess of 500 hours for temperatures from 150 to 180°C.

Under fuel cell operating conditions the electrolyte leaches the alumina substrate from the electrocatalysts, but no instability in cell performance appears to result. Measurements of the platinum particle sintering rate indicate a lower sintering rate for platinum on leached Kocite electrocatalysts than on platinum-doped carbon-black electrocatalysts having similar Pt/C ratios. Anodes incorporating Kocite electrocatalysts have shown better short term tolerance to a 5% CO contamination in the H_2 gas than 2 mg/cm^2 platinum black anodes when operated comparably.

To optimize the structure of Kocite electrodes, the platinum loading, Teflon content, and the catalyst layer density and thickness have been systematically varied. Test results indicate that the cell performance is directly proportional to the platinum loading. The optimal value for the Teflon loading is a weight ratio of ~1:1 to the leached electrocatalyst. The performance does not change substantially with variations of the catalyst layer density or thickness.



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I. INTRODUCTION

1.1 Objectives

The objective of this program was to optimize the performance of low-cost air and fuel electrodes fabricated from platinum-impregnated proprietary UOP Kocite[R] materials for use in phosphoric acid electrolyte fuel cells within the temperature range of 140-180°C. To accomplish this objective, various Kocite formulations were produced and fabricated into state-of-the-art fuel cell electrodes. These electrodes were tested as anodes or cathodes in model fuel cells with conventional platinum black electrodes as counter electrodes. Long term (500 hour) endurance testing was completed on promising electrodes.

This report summarizes the results obtained during this 15 month program. The fuel cell performance levels achieved during this period using fuel cell electrodes fabricated from platinum-doped Kocite[R] materials will be discussed, along with recommendations for future research.

1.2 Background

The current research program followed an evaluation of the performance of Kocite[R] materials in fuel cell electrodes for phosphoric acid electrolyte fuel cells[1,2] completed under USA/MERADCOM contract number DAAK02-75-C-0011. The program organization established under this previous contract was continued. This involved a joint program with

[1] L. B. Welsh, G. L. Hervert, D. H. Spielberg, K. J. Youtsey, "Carbonaceous Catalysts for H_3PO_4 Fuel Cells", MERDC Contract DAAK02-75-C-0011, Interim Technical Report, March, 1975.

[2] L. B. Welsh, R. W. Leyerle, G. L. Hervert, and K. J. Youtsey, "Carbonaceous Catalysts for H_3PO_4 Fuel Cells", MERDC Contract DAAK02-72-C-0011, Final Technical Report, September, 1975.

UOP Inc. as the prime contractor and Energy Research Corporation (ERC, a subsidiary of St. Joe Minerals Corporation) as subcontractor. A broad division of effort was made on the basis of the UOP capability to produce Pt-impregnated Kocite^{R} materials and the ERC capability to fabricate and optimize electrode structures. Testing and diagnostic evaluation of these electrodes were carried out jointly by UOP and ERC.

1.3 Review of Previous Results

1.3.1 Kocite^{R} Materials

Kocite^{R} materials are composite structures consisting of a thin film, semiconducting pyropolymer chemically bonded to the surface of an electrically insulating, high surface area, refractory substrate. The materials used to produce Kocite powders can vary widely but commonly include gamma alumina as the refractory substrate and hydrocarbons such as cyclohexane and benzene as the pyrolyzable material or pyropolymer precursor. Pyrolysis temperatures are commonly in the range of 400 to 900°C. The electrical conductivity of Kocite materials can be varied widely in a controlled manner by adjusting one or more of the following parameters: (a) substrate composition and surface area, (b) pyrolyzable material, and (c) reaction conditions (e.g., reaction time, temperature, ambient gases). The electrochemical behavior may also depend on these parameters. The current application of Kocite materials to fuel cell electrocatalysts consists of their utilization as high surface area extenders and supports for catalytically active materials (transition metals, etc.). The preparation of Kocite materials and their analysis have been discussed in earlier reports.[1,2]

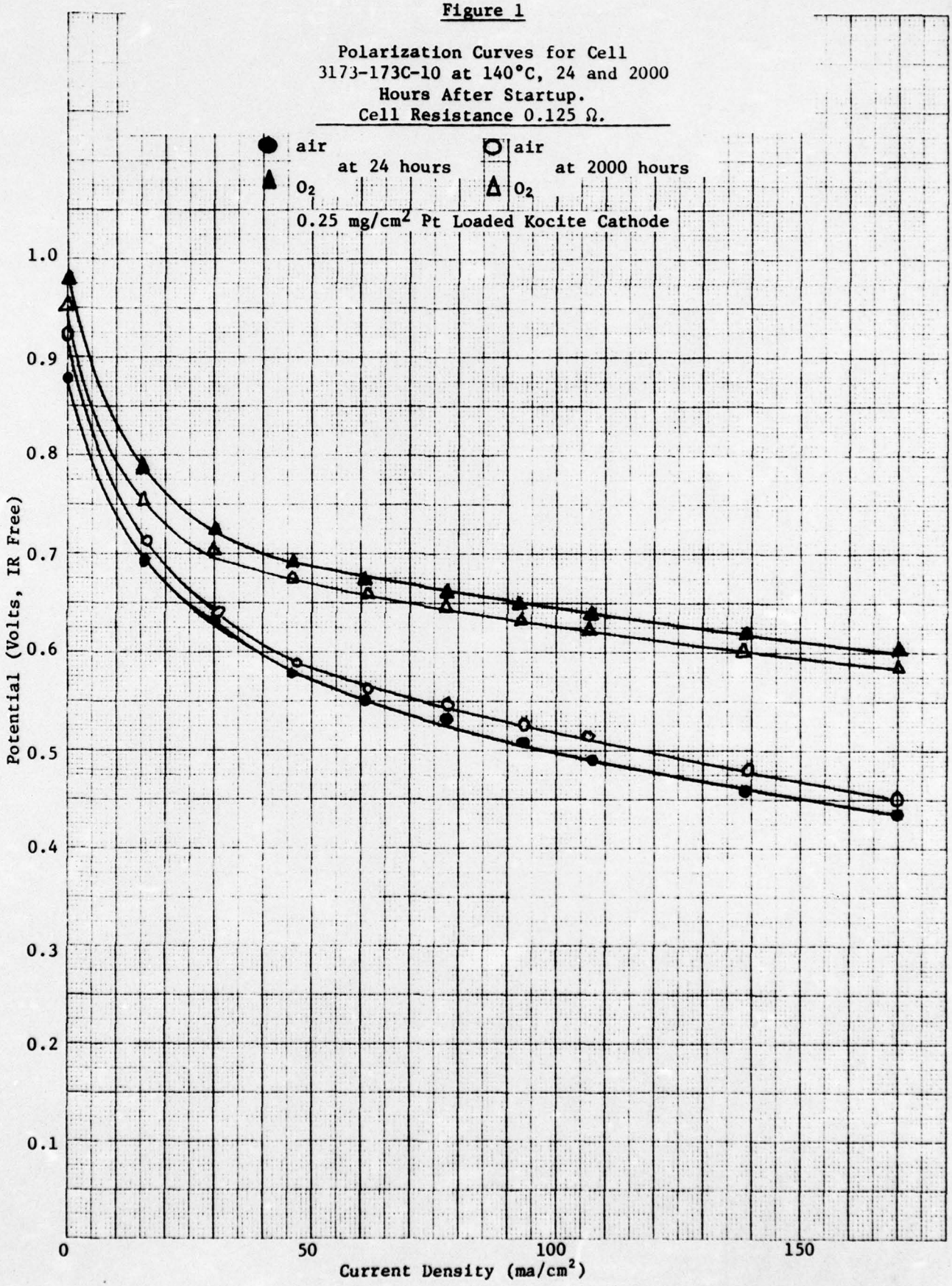
1.3.2 Program Status at the Inception of the Present Contract

The intent of the previous contract (DAAK02-75-C-0011) was to evaluate Kocite materials as electrocatalysts for use in H_3PO_4 fuel cell electrodes.[1,2] However, Kocite materials were found to have little electrocatalytic activity. Kocite materials were then evaluated as catalyst metal supports. During the remaining period of the previous contract, fuel cell electrocatalysts were produced from small particle size Kocite materials by impregnating them with platinum. These electrocatalysts were then fabricated into electrodes and evaluated in model fuel cells. This evaluation indicated that Kocite materials could be used as stable extenders or supports for catalytically-active metals in H_3PO_4 fuel cell electrodes at 140°C.

The best performance of a Kocite-containing electrode[2] achieved prior to the inception of the present contract is shown in Figure 1. In this figure, IR corrected full cell polarization curves are shown. The data were obtained using a Kocite cathode with 0.25 mg/cm^2 Pt loading and a 2 mg/cm^2 platinum black electrode as the anode. Comparison of the curves at 24 and 2000 hours shows the full cell stability achieved at that time. Though the performance of the cell at 100 ma/cm^2 on oxygen dropped after 2000 hours, the air performance increased by 25 mV. The cause of this performance change was unclear, but was not a result of any obvious deterioration of the electrode or cell components. The cell voltage of 518 mV was the highest performance obtained at 100 ma/cm^2 and 140°C during the previous contract.

Figure 1

Polarization Curves for Cell 3173-173C-10 at 140°C, 24 and 2000 Hours After Startup.
Cell Resistance 0.125 Ω.



Before the start of the present contract, sufficient lifetime testing (500 hours) at 140°C had been done to indicate that Kocite electrodes performed without deterioration as air or oxygen cathodes. However, the oxygen gain of the cells at 100 ma/cm^2 was larger than desired, indicating gas diffusion losses in the electrode. From cell performance results obtained with electrocatalysts made with Kocite materials having different particle sizes, it was clear that use of smaller alumina particles and optimization of electrode structure would reduce these gas diffusion losses. Preliminary cell testing was also performed at 180°C, where air cathode performance improved substantially. Limited lifetime testing indicated that Kocite cathodes perform stably at temperatures as high as 180°C. As hydrogen anodes, the initial performance of Kocite electrodes was encouraging, but the performance decayed quickly, possibly as a result of poisoning.

1.3.3 Results Obtained During the First Five Month Period

The major effort during the first five months of this contract was devoted to electrocatalyst development.[3] In particular, comparisons were made between electrocatalysts prepared using two different alumina substrates. Several batches of Kaiser Medium Alumina were ground and size classified to obtain base material having mean particle sizes of $1 - 2.5 \times 10^3$ nm. This is the same base that was used at the end of the previous contract for the 3173-173 series

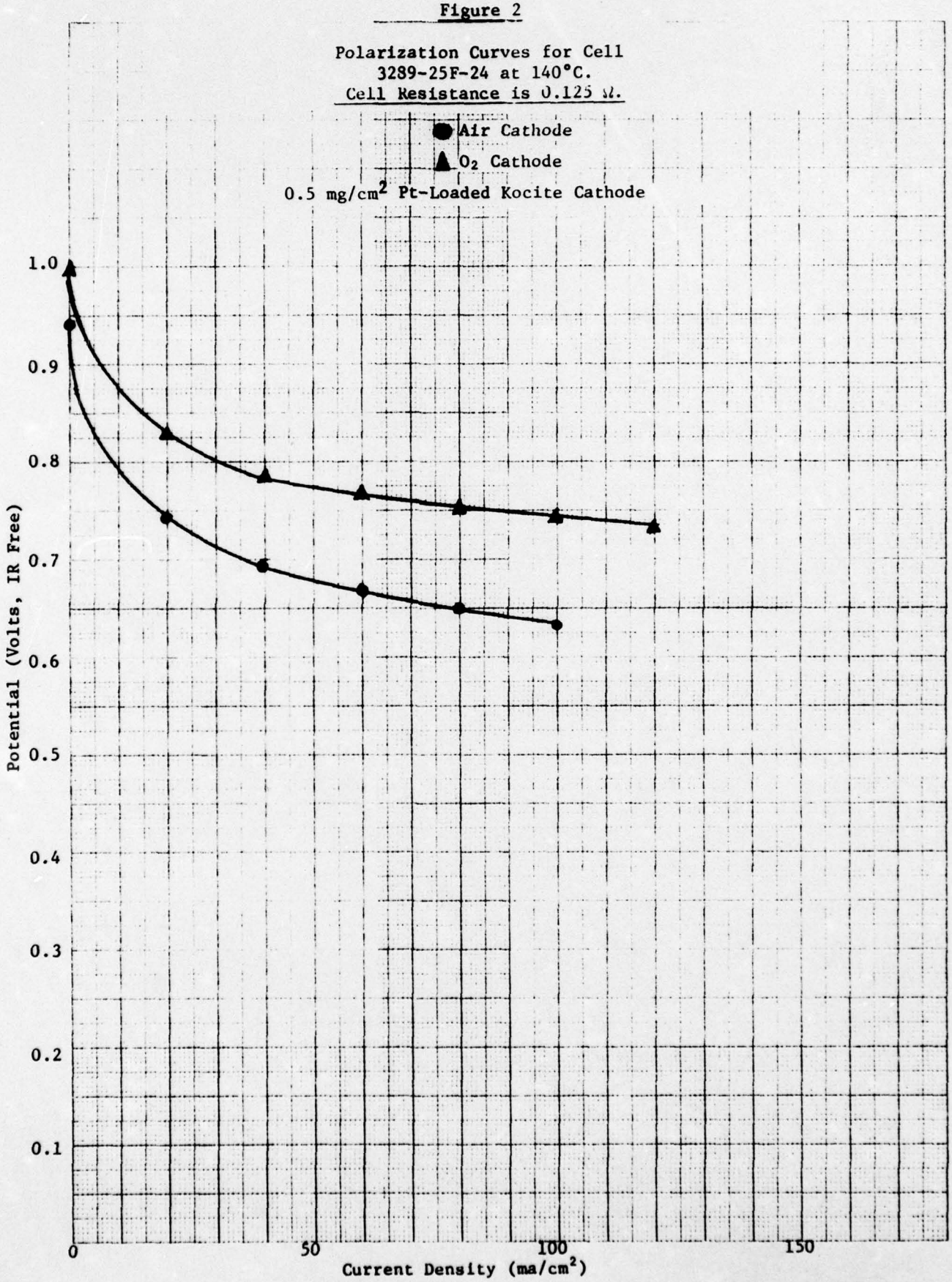
[3] L. B. Welsh, R. W. Leyerle, G. L. Hervert, "Optimization of Pt-Doped Kocite® Electrodes in H_3PO_4 Fuel Cells", MERADCOM Contract DAAG53-76-C-0014, Interim Technical Report, March, 1976.

electrocatalyst batches. The other base material, Alcoa's Hydral 705, was tested because it had a smaller mean particle size (~500 nm), a different pore volume distribution[3], and was commercially available. Both the particle size and the pore size of the resulting Kocite materials can substantially effect the performance of the electrocatalyst, particularly due to losses resulting from diffusion limitations.

Improvements made in production techniques and electrocatalyst structure resulted in increased performance levels of Kocite electrodes. The best performance level achieved during this period was obtained with a cell containing a cathode fabricated from electrocatalyst batch 3289-25F. This electrode had a platinum loading of 0.5 mg/cm^2, twice the loading of any previously tested electrode. The cell operated at an IR corrected voltage of 0.63 on air and 0.74 on oxygen at a current density of 100 ma/cm^2 at 140°C. Results obtained with this cell, shown in Figure 2, are 100 mV better than the best results obtained prior to this contract period, shown in Figure 1. However, the 110 mV O_2 gain of this cell was still larger than desirable.

The first Kocite material produced from the smaller Hydral alumina base material was batch 3380-31. A cell containing a 0.25 mg/cm^2 Pt-loaded cathode fabricated from catalyst batch 3380-31B operated at the highest performance level measured at that time for that Pt-loading. Full cell polarization curves for this cell are

Figure 2


Polarization Curves for Cell
3289-25F-24 at 140°C.
Cell Resistance is 0.125 Ω.
Air Cathode
O2 Cathode
0.5 mg/cm2 Pt-Loaded Kocite Cathode
Potential (Volts, IR Free)
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
50
100
150
Current Density (ma/cm2)

shown in Figure 3. At 140°C and 100 ma/cm^2, IR corrected voltages of 0.55 V on air and 0.66 V on oxygen were obtained. This air cathode performance level is about 30 mV better than the best electrode performance at the inception of this contract for the same cell temperature and platinum loading.

Cells with Kocite air cathodes were proved stable at current densities of 100 ma/cm^2 for periods in excess of 500 hours at temperatures ranging up to 180°C. One cell, containing an electrode from electrocatalyst batch 3289-25F, maintained an IR corrected voltage of 0.585 V for 500 hours at 160°C. The terminal voltage of this cell rose from 0.515 to 0.520 V during that time. Another cell, operating at 180°C with a similar electrode used as an air cathode, had a 25 mV decrease in its terminal voltage over 500 hours, but its IR corrected voltage was steady at 0.640 V.

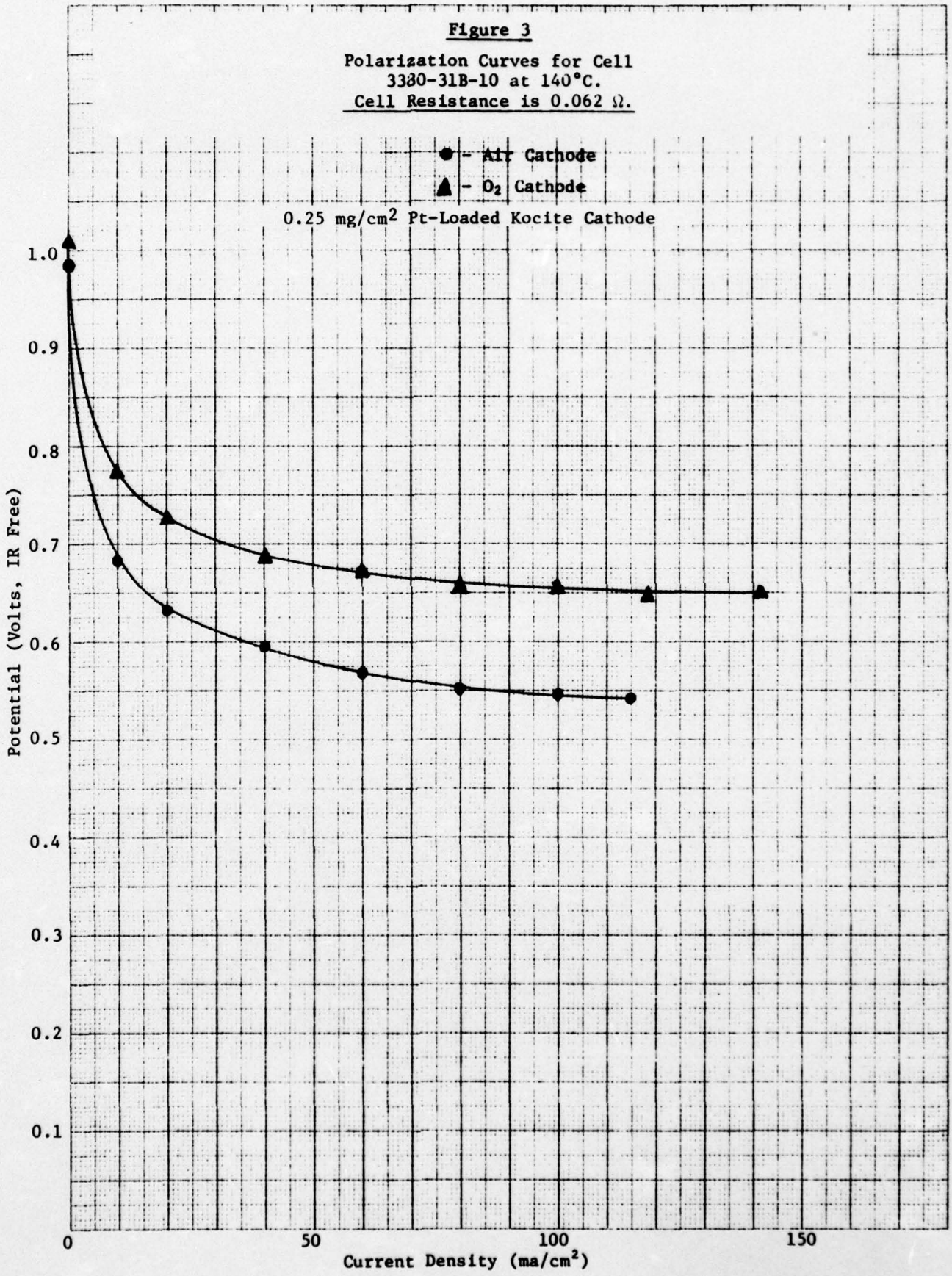
Facilities were completed during this five month period for the production of Kocite materials in batches of 300 g or more. These large batches allowed ERC to prepare electrodes using machine calendering techniques which improve electrode uniformity and reproducibility.

1.3.4 Results Obtained During the Second Five Month Period

The main effort during this period was to optimize the performance of Kocite electrodes produced from a single electrocatalyst batch. Systematic variations of certain electrode structure

Figure 3

Polarization Curves for Cell
3380-31B-10 at 140°C.
Cell Resistance is 0.062 Ω.



parameters such as teflon loading, catalyst loading, and catalyst layer density were made to determine the optimum electrode production parameters for machine calendered electrodes.[4] Electrocatalyst batch 3380-125B was used for these electrodes. The improvement achieved in cell performance during this period is illustrated in Figure 4, for a cell with a 0.22 mg/cm^2 Pt-loaded cathode containing electrocatalyst batch 3380-125B. At a current density of 100 ma/cm^2, the IR corrected cell voltage was 0.62 V on air and 0.71 V on oxygen at 149°C. The O_2 gain decreased to 90 mV. At 149°C, the performance of this cell on air at 100 ma/cm^2 was 100 mV higher than that of the cell operating at 140°C shown in Figure 1. This performance was also 80 mV higher than the best cell of the first five month period, shown in Figure 3 (0.25 mg/cm^2 Pt loading).

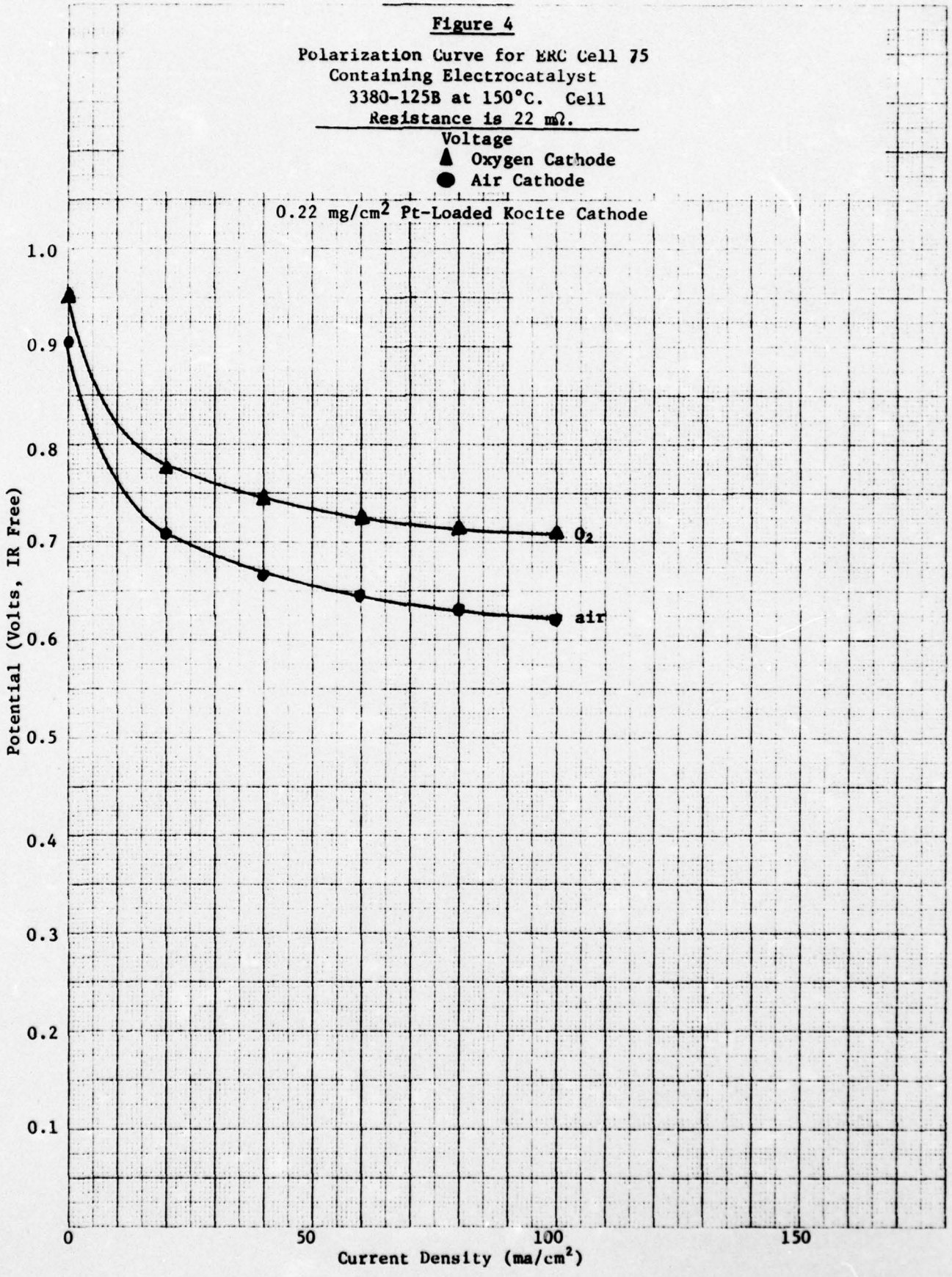
For the first time, during this period a stable performance was achieved by a cell having a Kocite anode. A cell, with an anode containing electrocatalyst batch 3289-25F, showed no deterioration of its IR free voltage after 500 hours of operation at 100 ma/cm^2 at 180°C. This cell had a 2 mg/cm^2 platinum black electrode as its air cathode.

The performance of Kocite electrodes having different electrode structures was studied during this period to determine the

[4] L. B. Welsh, R. W. Leyerle, "Optimization of Pt-Doped Kocite^R Electrodes in H_3PO_4 Fuel Cells", MERADCOM Contract DAAG53-76-C-0014, Interim Technical Report, August, 1976.

Figure 4

Polarization Curve for ERC Cell 75 Containing Electrocatalyst 3380-125B at 150°C. Cell Resistance is 22 mΩ.



optimum electrode structure. The teflon content of the electrodes was varied from 20 to 50 wt.% (based on the Kocite loading) and the performance of a large number of these electrodes was measured. In general, better performance was obtained[4] from cells containing electrodes having teflon contents below 40 wt.%. In addition, the cells achieved peak performance much more rapidly when electrodes were used having the lower teflon loading. Medium density electrodes gave better performance than low density electrodes[4], for which the catalyst layer often did not properly adhere to the carbon-paper backing. Variation of the catalyst layer thickness indicated that the use of thinner catalyst layers might improve electrode performance. Results obtained during the third five month period confirmed that lower teflon-loaded, medium density electrodes had superior performance characteristics, but the use of thinner catalyst layers did not improve electrode performance.

1.4 Program for the Last Five Month Period

The primary effort during this period was the continued testing of electrodes with differing electrode structure, fabricated from the same electrocatalyst batch. Experimentation was completed with catalyst batch 3380-125B and extensive testing was done with catalyst batch 3380-156G using electrodes loaded with $\sim$0.5 mg/cm^2 platinum. These electrodes have shown significantly higher performance and better stability than previous electrodes. Work was performed during the last five month period in the following areas.

(A) Using large batches of Kocite electrocatalysts, numerous electrodes have been fabricated by machine calendering to assess the effects of electrode structure variation and determine the optimum electrode structure. Cathode performance data have been taken at 150, 160, and 180°C. The parameters which have been varied include,

1) platinum loading

2) teflon content

3) catalyst layer thickness

4) catalyst layer density (bonding pressure)

(B) Tests were conducted to determine the extent of substrate leaching by phosphoric acid.

(C) Limited anode testing has been performed at 160 and 180°C. The short term tolerance of Kocite anodes to a 5% CO contamination in the hydrogen fuel gas has been determined and compared with the CO tolerance of platinum black electrodes. A cell consisting of Kocite electrodes as both the cathode and anode was also tested successfully.

(D) Substantial air cathode lifetime test data have been accumulated. As an example, stable performance has been obtained for cells with Kocite cathodes operated for over 4000 hours at 150°C and for over 2500 hours at 180°C.

(E) The rates of platinum particle sintering on Kocite electrocatalyst powders and Kocite electrodes were determined by X-ray diffraction techniques.

A detailed discussion of the results obtained in each of these areas is presented in the following sections.

II. PT-DOPED KOCITE^{R} ELECTROCATALYSTS

The preparation and physical properties of the platinum-doped Kocite batches, from which electrodes have been fabricated, are discussed in this section. Some of these properties are listed in Table I. As the general preparation and platinum impregnation techniques have been discussed in earlier reports[1-4], only specific alterations of these techniques will be discussed here.

Three different alumina base materials were used to prepare the electrocatalysts listed in Table I. The 3173-173B, 3173-173C, and 3289-25F batches were prepared from Kaiser Medium Alumina ground to a mean particle size of $\sim 2.2 \times 10^3$ nm, while batch 3380-104B is made using the same alumina ground to a mean particle size of $\sim 1.2 \times 10^3$ nm. The other batches were made from Hydral 705 alumina with a mean particle size of 500 nm. As discussed in an earlier report[3], the pore volume distributions of these electrocatalysts are quite different. The Kaiser based materials have a broad, two peaked distribution with peaks near 4.0 and 8.0 nm, while the Hydral based materials have a narrow distribution with a single peak near 4.0 nm. From the results reported earlier[1-4], both the pore volume distribution and mean particle size are expected to affect electrode performance.

For the same surface area and resistivity, the carbon content of a Hydral-based Kocite material is substantially smaller than that of a Kaiser-based Kocite material. Typical carbon contents are about 35 wt.% for the Kaiser-based Kocite materials and 24 wt.% for the Hydral-based Kocite materials.

Table I

Characteristics of Pt-Impregnated Kocite^{R} Preparations

Batch Number	3173-173B	3173-173C	3289-25A	3289-25F
Analysis, Wt.%				
Carbon Content of Kocite Material	34.7	33.20	36.80	36.80
Pt/(Pt + C)	5.50	13.1	8.96	22.9
Physical Characteristics				
ρ @ 25°C, Ω-cm	0.017	0.014	0.083	0.051
Apparent Bulk Density, g/ml	0.343	0.375	0.30	0.30
Surface Area, M/g	69	81	70	70
Pore Volume, ml/g	0.18	0.19	0.18	0.18
Average Pore Diameter, nm	10.4	9.4	10.3	10.3
Kocite^{R} Substrate				
Type	γ-Al_2O_3 (Kaiser)	γ-Al_2O_3 (Kaiser)	γ-Al_2O_3 (Kaiser)	γ-Al_2O_3 (Kaiser)
Size Range, 10^3 nm	2.2	2.2	1.2	1.2
Pyrolysis Temperature (°C)	900	900	900	900
Pyropolymer Precursor	C_6H_6	C_6H_6	C_6H_6	C_6H_6
Pt Addition	To Product	To Product	To Product	To Product
Pt Reduction Temperature (°C)	260	260	260	260

Table I (Cont'd)

Characteristics of Pt-Impregnated Kocite[R] Preparations

Batch Number	3380-31B	3380-31E	3380-31F	3380-31K	3380-65A
Analysis, Wt.%					
Carbon Content of Kocite Material	25.09	24.09	24.09	24.09	42.20
Pt/(Pt + C)	17.1	35.7	17.7	17.9	28.7
Physical Characteristics					
ρ @ 25°C, Ω-cm	0.0365	0.036	0.0365	0.036	0.006
Apparent Bulk Density, g/ml	0.28	0.28	0.28	0.28	0.85
Surface Area, M/g	69	69	69	69	59
Pore Volume, ml/g	0.09	0.09	0.09	0.09	0.15
Average Pore Diameter, nm	5.2	5.2	5.2	5.2	9.9
Kocite[R] Substrate					
Type	$\gamma + \chi Al_2O_3$ (Hydral)	$\gamma + \chi Al_2O_3$ (Hydral)	$\gamma + \chi Al_2O_3$ (Hydral)	$\gamma + \chi$-Al_2O_3 (Hydral)	γ-Al_2O_3 (Kaiser)
Size Range, 10^3 nm	0.5	0.5	0.5	0.5	2.2
Pyrolysis Temperature (°C)	850	850	850	850	900
Pyropolymer Precursor	C_6H_6	C_6H_6	C_6H_6	C_6H_6	C_6H_6
Pt Addition	To Product	To Product	To Product	To Product	To Product
Pt Reduction Temperature (°C)	260	260	250	260	250

Table I (Cont'd)

Characteristics of Pt-Impregnated Kocite® Preparations

Batch Number	3380-104B	3380-104H	3380-125B	3380-156E	3380-156G	3380-180F
Analysis, Wt.%						
Carbon Content of Kocite Material	37.3	37.3	19.08	21.31	21.31	22.24
Pt/(Pt + C)	11.7	12.4	21.1	33.6	34.8	52.9
Physical Characteristics						
ρ @ 25°C, Ω-cm	0.032	0.032	0.13	0.11	0.11	0.13
Apparent Bulk Density, g/ml	0.398	0.398	0.30	0.29	0.29	0.25
Surface Area, M/g	79	79	80	81	81	78
Pore Volume, ml/g	0.17	0.17	0.11	0.11	0.11	0.11
Average Pore Diameter, nm	8.6	8.6	5.5	5.4	5.4	5.6
Kocite® Substrate						
Type	γ-Al_2O_3 (Kaiser)	γ-Al_2O_3 (Kaiser)	$\gamma+\chi$-Al_2O_3 (Hydral)	$\gamma+\chi$-Al_2O_3 (Hydral)	$\gamma+\chi$-Al_2O_3 (Hydral)	$\gamma+\chi$-Al_2O_3 (Hydral)
Size Range, 10^3 nm	1.2	1.2	0.5	0.5	0.5	0.5
Pyrolysis Temperature (°C)	860	860	800	800	800	800
Pyropolymer Precursor	C_6H_6	C_6H_6	C_6H_6	C_6H_6	C_6H_6	C_6H_6
Pt Addition	To Product	To Product	To Product	To Product	To Product	To Product
Pt Reduction Temperature (°C)	260	260	260	260	260	260

The platinum impregnation of Kocite materials has been described in earlier reports.[1-4] In order to determine if each electrocatalyst has been prepared with a high platinum dispersion, an X-ray linewidth analysis of the platinum crystallite size was performed. The results of this analysis are given in Table II for the electrocatalysts listed in Table I. The percentage of Pt particles having diameters between 2.5 and 100 nm can be determined, as well as the average diameter of the Pt particles in this size range, when the X-ray data are compared against those of a standard. The numbers listed under agglomeration give the fraction of Pt atoms in Pt particles with a diameter greater than ∿2.5 nm. The numbers are only relative because particles smaller than ∿2.5 nm diameter are not measured as contributing to the Pt X-ray linewidth. The agglomeration numbers are normalized as discussed in an earlier report.[2] With a 5 wt.% Pt concentration, a typical agglomeration number is about 10% for both the Kaiser and Hydral based electrocatalysts with good Pt dispersion.

During the third five month period of the contract, evidence has been found that at fuel cell operating temperatures, phosphoric acid dissolves the alumina substrate of Kocite materials. For one material tested, only the carbonaceous pyropolymer layer remained after leaching and it had a surface area of ∿700 m^2/g. The rate of leaching depends on the temperature, Kocite material particle size, and the thickness of the pyropolymer layer. All the alumina is leached from the electrocatalysts used during this contract period when they are used in operating fuel cells for 500 hours. This leaching does not appear to degrade the fuel cell performance since many cells increase their voltage over the first few hundred hours in the

Table II

X-ray Analysis of Pt Crystallite Size

Kocite Batch	Crystallize Size[a] Nominal Diameter (nm)	Agglomeration[b]	Pt/(Pt + C)
3173-173B	13.0	0.02	5.50
3173-173C	6.0	0.10	13.1
3289-25F	3.4	0.03	22.9
3380-31B	3.2	0.22	17.1
3380-104B	5.1	0.10	11.7
3380-104H	6.0	0.26	12.4
3380-125B	4.4	0.12	21.1
3380-156E	7.5	0.31	33.6
3380-156G	6.6	0.22	34.6
3380-180F	12.2	0.39	52.9

[a]Mean size of crystallites over 2.5 nm diameter.

[b]These results are standardized as discussed in Reference 2.

same way that platinum impregnated carbon black electrode-containing cells do. This increase is probably due to increased wetting of the electrocatalyst layer, rather than the leaching. When the alumina is removed, the effective platinum loading of the resulting platinum impregnated carbonaceous pyropolymer electrocatalyst increases. For this reason all electrocatalyst platinum levels are listed on the basis of the Pt-Carbon content rather than the Pt-Carbon-Al_2O_3 basis used in the earlier reports.[1-4] This change is noted in Table I and in the tables in Section 4. The electrode platinum loadings remain the same.

III. ELECTRODE FABRICATION AND TESTING

3.1 Electrode Fabrication

The fabrication techniques used by ERC to prepare gas diffusion fuel cell electrodes containing Kocite electrocatalysts are similar to those used to prepare ERC platinum black electrodes. The process begins with the wet blending of the electrocatalyst with a dry PTFE powder and a filler within a petroleum distillate type of medium. Considerable care must be taken during this step to prevent any Kocite particle agglomeration. After filtration of the solids, a catalyst layer is formed by a calendering operation which can be accomplished either by hand rolling or with a machine rolling mill. To improve handling during the calendering process, a decomposable filler such as ammonium bicarbonate is used. After complete vaporization of the petroleum distillate, the filler is removed by gentle heating.

The remaining steps of electrode fabrication involve pressing, mounting on a current collector, and sintering. Some variation has occurred in these steps over the duration of this program. Initially the catalyst layer was pressed at 2000 psi (high density) onto a tantalum screen current collector. More recently, a highly porous and conductive carbon fiber paper such as produced by Union Carbide Corporation or Stackpole Carbon Company has been used as a less expensive alternative to the tantalum screen current collector. The carbon fiber paper is generally wetproofed to a certain degree prior to use, by treatment with FEP, a copolymer of tetrafluoroethylene and hexafluoropropylene. The pressure at which the catalyst layer is bonded to the current collector has also been varied. In the first five month period[3] low,

medium, and high density catalyst layers were prepared at 100, 500, and 2000 psi. During the later ten month period a different set of bonding pressures has been used for the machine calendered electrodes. During this period these electrodes have been prepared at 2000 psi (high density), 100 psi (medium density), and by using a different filler processing step (low density). Machine calendered electrodes have only been used with medium and low densities.

Following the electrode bonding step, the electrode is normally sintered in a nitrogen atmosphere at 345°C for 15 minutes. Electrodes prepared before the 3380-104B and 3380-125B electrocatalysts batches were sintered at 335°C.

The final thickness of the Kocite electrocatalyst layer depends on the bonding technique and pressure. For electrodes prepared during the last ten months, a 5 mg/cm^2 loading of Kocite powder and 50 wt.% PTFE content resulted in catalyst layer thicknesses of 0.004", 0.006", and 0.010" for the high, medium, and low density machine calendered catalyst layers, respectively. This thickness decreases as the PTFE content decreases.

3.2 Cell Testing

Details of the cell testing techniques and apparatus have been discussed in earlier reports.[1-4] No changes have been made during the present period, but attempts have been made to standardize cell components. A typical cell assembly now uses pooling type graphite hardware and a high

porosity Kynol matrix. At ERC, cell testing has been standardized at 149°C, the temperature ERC considers to be their baseline temperature for phosphoric acid fuel cells. Fuel cell performance at 160 and 180°C has been measured at UOP. A few cells were tested by ERC using an experimental silicon carbide matrix in place of the Kynol matrix.

IV. RESULTS AND DISCUSSION

4.1 Introduction

In this section, the characteristics and performance of platinum-impregnated Kocite electrodes tested at UOP and ERC are presented. After a discussion, in Section 4.2, of the platinum crystal sintering tests carried out by UOP, the performance of electrodes from various electrocatalyst batches is discussed in Section 4.3. Data on the stability and endurance of cells are presented in Section 4.4. The effects of various fabrication parameters on the optimization of electrode performance are discussed in Section 4.5. In Section 4.6 the results obtained during the third five months of the present contract will be summarized.

4.2 Platinum Particle Sintering Rates

As part of the determination of the stability of Kocite-derived electrocatalysts, initial measurements have been made of the sintering rates of platinum particles on Kocite-derived materials. The results were obtained by X-ray diffraction techniques. After a discussion of the methodology, results are presented for platinum sintering rates of both the electrocatalyst powders and the Kocite electrodes used in operating fuel cells.

The platinum particle agglomeration and size have been determined by the same X-ray diffraction methods previously applied to Kocite electrocatalyst powders.[2] To make this method quantitative for samples having widely differing compositions and thicknesses, cor-

rections have been made for both the change in the X-ray mass absorption coefficients arising from composition variations and the effects of a finite thickness of the sample to X-rays.

Previously the fraction of agglomerated Pt, Ag, was taken as the ratio of the intensity of the diffracted beam for the sample, I_s, to the intensity of the diffracted beam for the standard, I_{st},

$$Ag = \frac{I_s}{I_{st}} . \qquad (1)$$

This has been adjusted by dividing the measured intensity, I_m, by the beam attenuation expected for a certain composition and thickness for both the sample and the standard,

$$I = \frac{I_m}{D\ \sigma pt} , \qquad (2)$$

where σ pt is the scattering cross-section for platinum and D is the attenuation factor. The standard formulation[5] for D for a sample of variable composition and less than infinite thickness to X-rays is

$$D = \frac{\cos\ \theta\ C_{Pt}}{2\ \mu_m} \left[1 - \exp\left(\frac{-2\ \mu_m\ \rho_s}{\cos\ \theta}\right)\right] \qquad (3)$$

where θ is the angle between the X-ray beam and the normal to the sample surface, μ_m is the mean mass absorption coefficient for the sample composition, C_{Pt} is the platinum composition of the sample and ρ_s is the surface density of the catalyst sample in g/cm^2. (Note that $\rho_s = \rho\ t$, the density of the material times its thickness.)

[5] E. P. Bertin, Principles and Practice of X-ray Spectrometric Analysis, Plenum Press, New York 1970, pages 416-417.

To estimate the surface area of the platinum particles, they were assumed to be spherical. The agglomerated particles, which the X-ray analysis could measure, were assumed to have the measured mean diameter. The platinum particles with less than 2.0 to 2.5 nm diameter, which are the particles in the unagglomerated fraction, were assumed to have a mean diameter of 2.0 nm. For spherical particles of diameter d (nm) and density ρ (g/cm^3), the surface area[6] is

$$SA\ (m^2/g) = \frac{6000}{d\ \rho}\ . \qquad (4)$$

For 2.0 nm diameter particles, the surface area is 140 m^2/g. Therefore, the estimated surface area of the samples with the above assumptions of the particle size is,

$$SA = Ag\ \frac{6000}{d\ \rho} + (1-Ag)\ \cdot\ 140\ m^2/g. \qquad (5)$$

The sintering results for platinum particles on electrocatalysts are given in Tables 3, 4, and 5. The powders were soaked in 96% H_3PO_4 in pyrex beakers at 180°C for the time indicated. The samples were filtered, washed with deionized water, and dried at 110°C. With samples soaked for 340 and 505 hours, pyrophosphoric acid had formed during the soaking and the filtered samples were washed with caustic to remove it. The Al_2O_3 was assumed to be completely leached for samples soaked for one hour or longer; a fact verified with other samples. The samples soaked for 340 hours were analyzed for their elemental composition and the surface areas of the analyzed samples are indicated in the tables in parentheses. These values are slightly lower than the values for the assumed

[6] In agreement with Exxon Research and Engineering Company, EPRI Catalyst Sintering Program, RF 583-1, Monthly Report #1.

Table III

Platinum Sintering of Kocite Electrocatalyst Powder 3380-104H

X-ray analysis of Pt particle size and surface area for 3380-104H Kocite electrocatalyst powder soaked in H_3PO_4 at 180°C. The leached electrocatalyst is 12.3 wt.% Pt.

Time (hours)	Particle Size (nm)	Ag (%)	SA (m^2/g)
0	6.0	26	116
1	5.9	20	121
24	5.6	28	115
170	6.3	37	105
340	6.5	34	107 (105)
505	5.8	29	113

The number in parenthesis is based on chemical analysis of the sample and should be considered more reliable.

Table IV

Platinum Sintering of Kocite Electrocatalyst Powder 3380-156E

X-ray analysis of Pt particle size and surface area for 3380-156E Kocite electrocatalyst powder soaked in H_3PO_4 at 180°C. The leached electrocatalyst is 34 wt.% Pt.

Time (hours)	Particle Size (nm)	Ag (%)	SA (m^2/g)
0	7.5	31	108
1	6.4	50	92
24	7.3	57	82
170	14.8	100	20
340	14.5	94	(27)

The number in parenthesis is based on chemical analysis of the sample.

Table V

Platinum Sintering on Carbon Black Powder 3310-200E

X-ray analysis of Pt particle size and surface area for 3310-200E carbon black electrocatalyst powder from ERC soaked in H_3PO_4 at 180°C. The catalyst is 10 wt.%.

Time (hours)	Particle Size (nm)	Ag (%)	SA (m^2/g)
0	4.5	10	132
1	4.3	34	115
24	4.9	42	105
170	5.5	30	113
340	6.5	49	93 (87)

The number in parenthesis is based on chemical analysis of that sample and should be considered as more reliable.

composition and should be considered more accurate. Only traces of phosphate were found in the composition of the samples soaked for 340 hours, indicating that the caustic washing did remove the solid phosphates which had formed.

The sintering results for electrocatalyst powder 3380-104H are given in Table III. The catalyst with 12.3 wt.% platinum in the leached catalyst shows a loss of approximately 10 m^2/g in the surface area over the 500 hour test. The results for electrocatalyst 3380-156E, given in Table IV, show a loss of 80 m^2/g. The platinum loading of the leached electrocatalyst 3380-156E is 34 wt.% which is three times that of catalyst 3380-104H. For comparison, Table V lists the Pt sintering results for a carbon black based electrocatalyst prepared by ERC. The catalyst with a 10 wt.% platinum loading initially has a higher surface area than the two Kocite-containing powders, but loses 40 m^2/g of that surface area, retaining after the sintering test slightly less surface area than electrocatalyst 3380-104.

Tables VI and VII list the results for the sintering of platinum particles in electrodes which were operated in fuel cells. Electrodes are listed by pairs in these tables. The first listing of the pair is for a reference electrode which has not been run in a cell and the second (or third) listing is for the test electrode. The last two pairs of cells listed in Table VI were operated at two different temperatures in succession and this is indicated by the respective slash-separated numbers for temperature and time. For example, the cell with electrode 3380-125B-16 was first operated at 140°C for 425 hours and then at 160°C for 270 hours. The

Table VI

Platinum Sintering Results for Electrodes, 140 to 180°C

Electrodes	Time (hours)[a]	Temperature (°C)[a]	Platinum Concentration $\frac{Pt}{Pt + C}$ (wt.%)	Voltage (V)[b] air	Voltage (V)[b] O_2	Particle[d] Size (nm)	Ag (%)[e]	Surface Area (m^2/g)
3380-31B	-	-	18	-	-	6.4	10.5	130
3380-31B-16	1000	140	18	0.54	0.63	4.9	29	116
3380-31K	-	-	18	-	-	5.4	13	129
3380-31K-1	500	140	18	0.52	0.63	5.5	13	129
3380-125B	-	-	23	-	-	6.6	7.4	133
3380-125B-1	820	140	23	0.55	0.62	7.8	17	122
3380-125B	-	-	23	-	-	8.6	17	122
3380-125B-8	475	140	23	0.57	0.68	12.5	23	113
3380-125B	-	-	23	-	-	7.0	17	123
3380-125B-16	425/270	140/160	23	0.54	0.65	5.4	37	107
3380-156G	-	-	34	-	-	9.8	30	107
3380-156G-2	100/350	160/180	34	0.63[c]	0.71[c]	10.1	64	68

[a] Two cells had their operating temperature changed during cell operation. The times indicated refer to intervals at the respective temperatures.

[b] IR corrected voltage for the cells operating with the listed electrode as an air or oxygen cathode at 100 ma/cm^2 at 140°C.

[c] At 160°C.

[d] Mean size of crystallites over 2.5 nm diameter.

[e] These results are standardized as discussed in Section 4.2.

Table VII

Platinum Sintering Results for Electrodes, 500 Hours at 180°C

Electrodes	Time (Hours)	Temperature (°C)	Platinum Concentration $\frac{Pt}{Pt + C}$ (wt.%)	Voltages (V)[a] air	Voltages (V)[a] O_2	Particle Size[b] (nm)	Agglomeration[c] Ag (%)	Surface Area (m^2/g)
3289-25F	-	-	23	-	-	-	0	140
3289-25F-31	500	180	23	-	-	7.0	30	110
3380-156G	-	-	34	-	-	7.0	53	87
3380-156G-6	500	180	34	0.61	0.69	9.1	50	85
3380-156G	-	-	34	-	-	7.1	43	97
3380-156G-8	500	180	34	0.62	0.70	9.2	79	53
3310-200C[d]	-	-	10	-	-	4.7	12	130
3310-200C-1	500	180	10	0.61	0.68	5.8	35	108
3310-200C-3	500	180	10	-	-	7.3	49	90

[a] IR corrected voltages for cells operating with the listed electrode as an air or oxygen cathode at 100 ma/cm^2 at 140°C.

[b] Mean size of crystallites over 2.5 nm diameter.

[c] These results are standardized as discussed in Section 4.2.

[d] A set of electrodes containing an ERC Carbon-Black-based electrocatalyst.

voltage listed is the maximum IR corrected voltage for the cell at 100 ma/cm^2. After the electrodes were run, they were washed in hot deionized water, dried at 110°C, and the catalyst layer removed from the carbon paper backing before the X-ray analysis was made.

Table VI lists the sintering data for electrodes in high performance cells operating mostly at 140°C for various lengths of time. For the cells operated at 140°C, the loss of surface area ranges from 0 to 16 m^2/g and stays above 105 m^2/g for all samples. The only severe surface area loss measured was with the last electrode pair listed in Table VI. This electrode lost 1/3 of its surface area through operation at 180°C for 350 hours. These data indicate that platinum sintering is probably not a major factor in activity loss for low platinum loaded electrodes at 140°C for periods up to 1000 hours.

Electrodes run in cells for 500 hours at 180°C specifically to study platinum sintering are listed in Table VII. The three carbon black electrodes (3310-200C series) were obtained from ERC. The 3289-25F and 3310-200C electrode sets show loses ranging from 20 to 40 m^2/g. Data obtained with the 3380-156G electrode sets are contradictory, with one electrode showing no loss in surface area and the other having a 50% loss of surface area. The zero loss result may be an experimental artifact, however the surface area loss for the other 3380-156G electrode is still not as severe as the surface area loss for the 3380-156E powder sample. No drop in cell performance due to the loss in the platinum surface area was observed in the electrode lifetime tests for the 3380-156G electrodes.

4.3 Fuel Cell Performance Results

4.3.1 Introduction

In this section the performance results for cells tested during the third five month period of the contract will be presented. Lifetime test data will be discussed in Section 4.4 and the analysis of the cell performances as they bear on the optimization of the electrodes will be given in Section 4.5. The fuel cell design and testing procedures have been discussed in Section 3.

The characteristics of the Kocite electrodes and cell builds tested at ERC and UOP are listed in Tables VIII and IX respectively. The cells included in the review of previous results in Section 1.3 have also been listed in these tables. Cell build characteristics are given for cells that performed well or that are otherwise noteworthy. In most cases the electrodes had a nominal platinum loading of either 0.25 or 0.5 mg/cm^2. Electrodes fabricated from electrocatalyst batch 3380-156G having a 0.25 mg/cm^2 platinum loading and the electrodes from electrocatalyst batch 3380-180F had half the normal catalyst loading of 5 mg/cm^2. The teflon content was varied from 18 to 50 wt.% with most electrodes having a teflon content of 20 or 30 wt.% relative to the Kocite loading prior to leaching. Almost all electrodes fabricated during this period were machine-rolled with medium catalyst layer densities. The exceptions are the low teflon content electrodes of catalyst batches tested previously which were made in small quantities for preliminary testing by ERC. All ERC cells and most UOP cells are operated with an electrolyte pool in the cell hardware to

Table VIII

Characteristics of Pt-Doped Kocite Electrodes - ERC

Cell Build Number	Kocite Electrocatalyst Batch	Platinum Loading (mg/cm^2)	Platinum Concentration $\frac{Pt}{Pt + C}$ (wt.%)	Teflon Content		Fabrication Method	Relative Catalyst Layer Density[a]	Electrode Prewetted (day)
				Nominal (wt.%)	After Leaching (wt.%)			
ERC 75	3380-125B	0.22	21	30	65	Machine	Medium	1
ERC 83	3380-125B	0.22	21	30	65	Machine	Medium	None
ERC 85	3380-156G	0.26	35	40	70	Machine	Medium	1
ERC 86	3380-156G	0.28	35	50	78	Machine	Medium	1
ERC 87	3380-156G	0.26	35	30	61	Machine	Medium	1
ERC 89	3380-156G	0.56	35	30	61	Machine	Medium	1
ERC 91	3380-156G	0.27	35	30	61	Machine	Medium	1
ERC 95	3380-156G	0.54	35	20	46	Machine	Medium	1
ERC 96	3380-180F	0.56	53	30	53	Machine	Medium	1
ERC 97	3380-180F	0.33	53	40	64	Machine	Medium	1
ERC 99	3380-156G	0.54	35	20	46	Machine	Medium	1
ERC 100	3380-156G	0.42	35	30	61	Machine	Medium	1
ERC 101	3380-156G	0.54	35	20	46	Machine	Medium	1
ERC 102	3380-156G	0.58	35	20	46	Machine	Medium	1
ERC 105	3289-25F	0.47	23	20	36	Hand	Medium	7
ERC 107	3380-125B	0.48	21	18	50	Hand	Medium	3
SiC-3	3380-156G	0.54	35	20	46	Machine	Medium	1

[a]Medium bonding pressure = 100 psi.

Table IX

Characteristics of Pt-Doped Kocite Electrodes - UOP

Cell Build No.	Platinum Loading (mg/cm^2)	Platinum Concentration $\frac{Pt}{Pt + C}$ (wt.%)	Teflon Content		Fabrication Method	Test Hardware and Electrode Substrate	Relative Catalyst Layer Density[a]	Electrode Prewetted
			Nominal (wt.%)	After Leaching (wt.%)				
3173-173C-10	0.24	13	30	65	Hand-Rolled	Tantalum	High	1 hour
3173-173C-16	0.24	13	30	65	Hand	Tantalum	High	1 hour
3289-25F-24	0.50	23	30	50	Hand	Graphite Pooling	High	1 day
3289-25F-30	0.50	23	30	50	Hand	Tantalum	High	1 day
3380-31B-10	0.25	17	30	61	Hand	Graphite	High	1 hour
3380-125B-21	0.22	21	30	65	Machine	Graphite	Medium	1 day
3380-125B-24	0.22	21	30	65	Machine	Graphite	Medium	1 day
3380-125B-25	0.22	21	30	65	Machine	Graphite	Medium	1 day
3380-125B-26	0.24	21	20	52	Machine	Graphite	Medium	1 day
3380-125B-28	0.24	21	20	52	Machine	Graphite	Medium	1 day
3380-156G-1	0.26	35	40	70	Machine	Graphite	Medium	None
3380-156G-2	0.26	35	40	70	Machine	Graphite Pooling	Medium	1 day
3380-156G-4	0.26	35	40	70	Machine	Graphite	Medium	1 day
3380-156G-7	0.56	35	30	61	Machine	Graphite Pooling	Medium	1 day
3380-156G-8	0.56	35	30	61	Machine	Graphite Pooling	Medium	1 day
3380-156G-9	0.56	35	30	61	Machine	Graphite Pooling	Medium	1 day
3380-156G-11	0.56	35	30	61	Machine	Graphite Pooling	Medium	1 day
3380-156G-13	0.54	35	20	46	Machine	Graphite Pooling	Medium	1 day
3380-156G-14	0.54	35	20	46	Machine	Graphite Pooling	Medium	1 day
3380-156G-15	0.54	35	20	46	Machine	Graphite Pooling	Medium	1 day
3380-156G-16	0.54	35	20	46	Machine	Graphite Pooling	Medium	1 day

[a]Bonding pressure - High = 2000 psi, Medium = 100 psi.

Table IX (Cont'd)

Characteristics of Pt-Doped Kocite Electrodes - UOP

Cell Build No.	Platinum Loading (mg/cm^2)	Platinum Concentration $\frac{Pt}{Pt + C}$ (wt.%)	Teflon Content		Fabrication Method	Test Hardware and Electrode Substrate	Relative Catalyst Layer Density[a]	Electrode Prewetted
			Nominal (wt.%)	After Leaching (wt.%)				
3380-156G-17	0.58	35	20	46	Machine	Graphite	Medium	1 day
3380-156G-18	0.58	35	20	46	Machine	Graphite Pooling	Medium	1 day
3380-156G-19	0.42	35	30	61	Machine	Graphite Pooling	Medium	1 day
3380-156G-21	0.54	35	20	46	Machine	Graphite Pooling	Medium	1 day
3380-156G-22	0.58	35	20	46	Machine	Graphite	Medium	1 day
3380-156G-23	0.58	25	20	46	Machine	Graphite Pooling	Medium	2 days

[a]Bonding pressure - High = 2000 psi, Medium = 100 psi.

improve lifetime performance by preventing matrix dryout. Prewetting of the Kocite electrodes by float filling in H_3PO_4 at 140°C was continued because cells assembled dry tended to develop gas crossover. All cells were assembled using an ERC fabricated 2 mg/cm^2 Pt black electrode as the counter electrode except for cell 3380-156G-23 which had Kocite electrodes for both the anode and cathode.

The performance levels of the cells listed in Tables VIII and IX are summarized in Tables X and XI, respectively. In these tables the full cell terminal and IR corrected voltages at 100 ma/cm^2 are listed for cells with the Kocite electrode used as an air cathode, oxygen cathode, and hydrogen (vs. standard air) anode. Fuel cell operation was normally conducted at 150°C at ERC and 160 and 180°C at UOP. Also listed in Tables X and XI is the oxygen gain number for each cell. ERC did not report resistance corrections for individual cells, so a ~40 mV correction at 100 ma/cm^2 has been assumed. This correction is consistent with corrections measured at UOP, and previous ERC experience. In general, comparable performance levels have been measured at ERC and UOP on cells with electrodes from the same electrode batch.

The highest performance level obtained by ERC was with cell SiC-3 having a silicon carbide matrix and a cathode from electrocatalyst batch 3380-156G loaded with 0.54 mg/cm^2 platinum. At 180°C it produced 0.66 V terminal operating on air and 0.73 V terminal on oxygen at 100 ma/cm^2 as shown in Figure 5. The highest performance

Table X

Summary of ERC Cell Performance Results

Cell Build Number	Kocite Batch	Platinum Loading (mg/cm^2)	Teflon Loading[b] (wt.%)	Cell Voltages[a] (volts) at 100 ma/cm^2 with Kocite Electrode On: Terminal Voltage[c] Air	Terminal Voltage[c] O_2	Terminal Voltage[c] H_2 (vs air)	IR Corrected Voltage[d] Air	IR Corrected Voltage[d] O_2	IR Corrected Voltage[d] H_2 (vs air)	O_2 Gain (mV)[d]	Temp. (°C)
ERC 83	3380-125B	0.22	30 (65)	0.49	0.60	0.54	0.53	0.64	0.58	110	150
ERC 85	3380-156G	0.26	40 (70)	0.54	0.62	0.59	0.58	0.66	0.63	80	150
ERC 86	3380-156G	0.28	50 (78)	0.49	0.56	0.56	0.53	0.60	0.60	70	150
ERC 87	3380-156G	0.26	30 (61)	0.56	0.64	0.60	0.60	0.68	0.64	80	150
ERC 89	3380-156G	0.56	30 (61)	0.60	0.68	0.62	0.64	0.72	0.66	80	150
				0.62	0.69	-	0.66	0.73	-	70	180
ERC 91	3380-156G	0.27	30 (61)	0.54	0.62	0.61	0.58	0.66	0.65	80	150
ERC 95	3380-156G	0.54	20 (46)	0.59	0.67	0.60	0.63	0.71	0.64	80	150
ERC 96	3380-180F	0.57	30 (53)	0.58	0.66	0.63	0.62	0.70	0.67	80	150
				0.56	0.65	0.60	0.60	0.69	0.64	90	180
ERC 97	3380-180F	0.33	40 (64)	0.53	0.62	0.60	0.57	0.66	0.60	90	150
ERC 99	3380-156G	0.54	20 (46)	0.56	0.66	0.60	0.60	0.70	0.64	100	150
				0.56	0.67	0.61	0.61	0.71	0.65	100	180
ERC 100	3380-156G	0.42	30 (61)	0.55	0.65	0.63	0.59	0.69	0.67	100	150
ERC 101	3380-156G	0.54	20 (46)	0.58	0.66	0.63	0.62	0.70	0.67	80	150
ERC 102	3380-156G	0.58	20 (46)	0.56	0.66	0.60	0.61	0.70	0.64	90	150
ERC 105	3289-25F	0.47	20 (37)	0.48	0.62	0.60	0.52	0.66	0.64	140	150
ERC 107	3380-125B	0.48	18 (50)	0.56	0.64	0.60	0.60	0.69	0.64	90	150
SiC-3	3380-156G	0.54	20 (46)	0.66	0.73	-	0.70	0.77	-	70	180

[a]Cell voltage obtained with a 2 mg/cm^2 Pt-black counter electrode.

[b]Nominal teflon loading - figures in parenthesis are values for the leached electrodes.

[c]Measured at the current collector plates.

[d]Though no resistance correction has been reported by ERC, a 40 mV IR correction has been assumed for consistancy with the UOP data.

[e]Voltage difference between air and oxygen performance at 100 ma/cm^2.

Table XI

Summary of UOP Cell Performance Results

Cell Build Number	Platinum Loading (mg/cm^2)	Teflon Loading[a] (wt.%)	Cell Voltages[b] (volts) at 100 ma/cm^2 with Kocite Electrode On: Terminal Voltage (V)[c] Air	O_2	H_2	IR Connected Voltage (V)[d] Air	O_2	H_2	O_2 Gain[e] (mV)	Temperature °C
3380-125B-21	0.22	30 (65)	0.43	0.55	0.53	0.54	0.66	0.64	120	140
			0.51	0.60	0.60	0.59	0.68	0.68	90	160
3380-125B-24	0.22	30 (65)	0.47	0.58	0.58	0.57	0.68	0.68	110	160
3380-125B-25	0.22	30 (65)	0.52	0.63	0.59	0.61	0.69	0.65	80	160
3380-125B-26	0.24	20 (52)	0.55	0.68	0.64	0.59	0.71	0.67	120	160
			0.57	0.67	-	0.62	0.72	-	100	180
3380-125B-28	0.24	20 (42)	0.56	0.65	-	0.61	0.69	-	80	160
			0.60	0.67	-	0.63	0.70	-	70	180
3380-156G-1	0.26	40 (70)	0.54	0.61	0.55	0.58	0.71	0.65	130	160
3380-156G-2	0.26	40 (70)	0.58	0.66	0.65	0.63	0.71	0.69	80	160
			0.59	0.66	0.65	0.62	0.69	0.68	70	180
3380-156G-4	0.26	40 (70)	0.54	0.64	0.63	0.59	0.69	0.68	100	160
			0.59	0.66	0.64	0.63	0.70	0.68	70	180
3380-156G-7	0.56	30 (61)	0.57	0.66	0.59	0.60	0.69	0.62	90	160
3380-156G-8	0.56	30 (61)	0.58	0.68	0.67	0.62	0.72	0.71	100	160
			0.58	0.66	-	0.62	0.70	-	80	180

[a] Nominal teflon loading - figures in parentheses are values for the leach electrodes.

[b] Cell voltage obtained with a 2 mg/cm^2 Pt black counter electrode (see f) for cell 3380-156G-23.

[c] Measured at the current collector plates.

[d] Resistance measured with a 1 KHz Resistance Bridge.

[e] Voltage difference between air and oxygen performance at 100 ma/cm^2.

[f] The cell had Kocite electrodes as both the anode and cathode.

Table XI (Cont'd)

Summary of UOP Cell Performance Results

Cell Build Number	Platinum Loading (mg/cm^2)	Teflon Loading[a] (wt.%)	Cell Voltages[b] (volts) at 100 ma/cm^2 with Kocite Electrode On: Terminal Voltage (V)[c] Air	O_2	H_2	IR Connected Voltage (V)[d] Air	O_2	H_2	O_2 Gain[e] (mV)	Temperature °C
3380-156G-9	0.56	30 (61)	0.58	0.67	0.52	0.61	0.70	0.55	90	160
			0.61	0.69	0.59	0.64	0.72	0.62	80	180
3380-156G-11	0.56	30 (61)	0.61	0.68	0.70	0.63	0.70	0.72	70	160
			0.63	0.69	0.63	0.66	0.72	0.66	60	180
3380-156G-13	0.54	20 (46)	0.61	0.69	0.64	0.64	0.72	0.68	80	160
			0.62	0.70	0.66	0.65	0.73	0.69	80	180
3380-156G-14	0.54	20 (46)	0.60	0.69	0.62	0.64	0.72	0.65	90	160
			0.62	0.69	0.64	0.66	0.74	0.68	70	180
3380-156G-15	0.54	20 (46)	0.61	0.70	0.67	0.65	0.74	0.67	90	160
			0.62	0.70	0.66	0.66	0.74	0.70	80	180
3380-156G-16	0.54	20 (46)	0.52	0.59	0.52	0.65	0.72	0.64	70	160
3380-156G-17	0.58	20 (46)	0.59	0.68	0.63	0.63	0.72	0.66	90	160
3380-156G-18	0.58	20 (46)	0.56	0.66	0.60	0.60	0.70	0.65	100	160
3380-156G-19	0.42	30 (61)	0.64	0.70	0.63	0.67	0.73	0.65	60	160
			0.65	0.71	0.65	0.68	0.74	0.67	60	180
3380-156G-21	0.54	20 (46)	0.61	0.70	0.65	0.65	0.72	0.67	90	160
			0.63	0.70	0.67	0.67	0.74	0.71	70	180
3380-156G-22[f]	0.58	20 (46)	0.56	0.66	0.62	0.60	0.70	0.66	100	160
3380-156G-23[f]	0.58	20 (46)	0.56	0.64	-	0.63	0.70	-	70	160
			0.57	0.64	-	0.63	0.70	-	70	160

[a] Nominal teflon loading - figures in parentheses are values for the leached electrodes.

[b] Cell voltage obtained with a 2 mg/cm^2 Pt black counter electrode (see f) for cell 3380-156G-23.

[c] Measured at the current collector plates.

[d] Resistance measured with a 1 KHz Resistance Bridge.

[e] Voltage difference between air and oxygen performance at 100 ma/cm^2.

[f] The cell had Kocite electrodes as both the anode and cathode.

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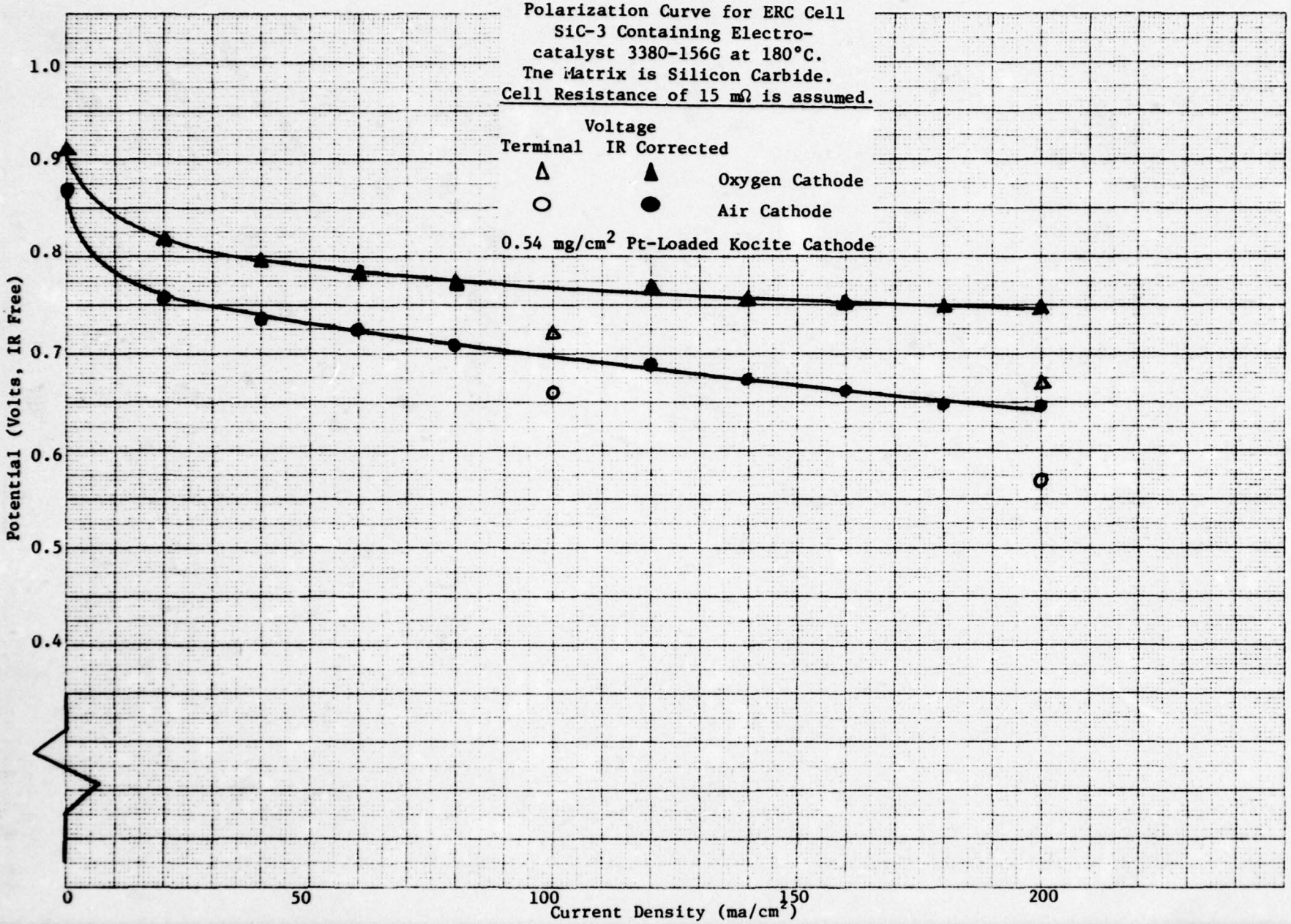
Figure 5

Polarization Curve for ERC Cell SiC-3 Containing Electrocatalyst 3380-156G at 180°C. The Matrix is Silicon Carbide. Cell Resistance of 15 mΩ is assumed.



of a cell with a Kynol matrix was achieved by the UOP cell shown in Figure 6 with a 0.42 mg/cm^2 Pt loading. This cell operated at 0.65 V terminal on air and 0.71 V terminal on oxygen at 180°C and 100 ma/cm^2.

4.3.2 Kocite Electrocatalyst Batch 3380-125B
Pt Loading 0.125 to 0.25 mg/cm^2

The performance of the majority of the cells built with electrodes containing this catalyst were reported in detail in the previous Interim Report.[4] This was the first large electrocatalyst batch from which machine calendered electrodes were fabricated. Details of the results obtained by varying the structure of the electrodes prepared from this batch are discussed in that report.[4] Testing has been completed during this period on two electrode batches prepared from this electrocatalyst batch, one with loadings of 0.22 mg/cm^2 Pt and 30 wt.% teflon and the other with 0.25 mg/cm^2 Pt and 20 wt.% teflon. Cells with electrodes from these batches performed better than cells with electrodes from other electrode batches fabricated from the 3380-125B electrocatalyst. These electrodes, along with an electrode fabricated from the 3380-156G electrocatalyst batch, to be discussed in Section 4.3.3, gave the best performance of any Kocite-containing electrodes to date having a platinum loading of ∿0.25 mg/cm^2.

Figure 7 shows the full cell polarization curves for the best cell of this group. At 180°C, the cell produced IR corrected voltages of 0.63 V when operated on air and 0.70 V on oxygen at 100 ma/cm^2. The best cell using an electrode from the other electrode

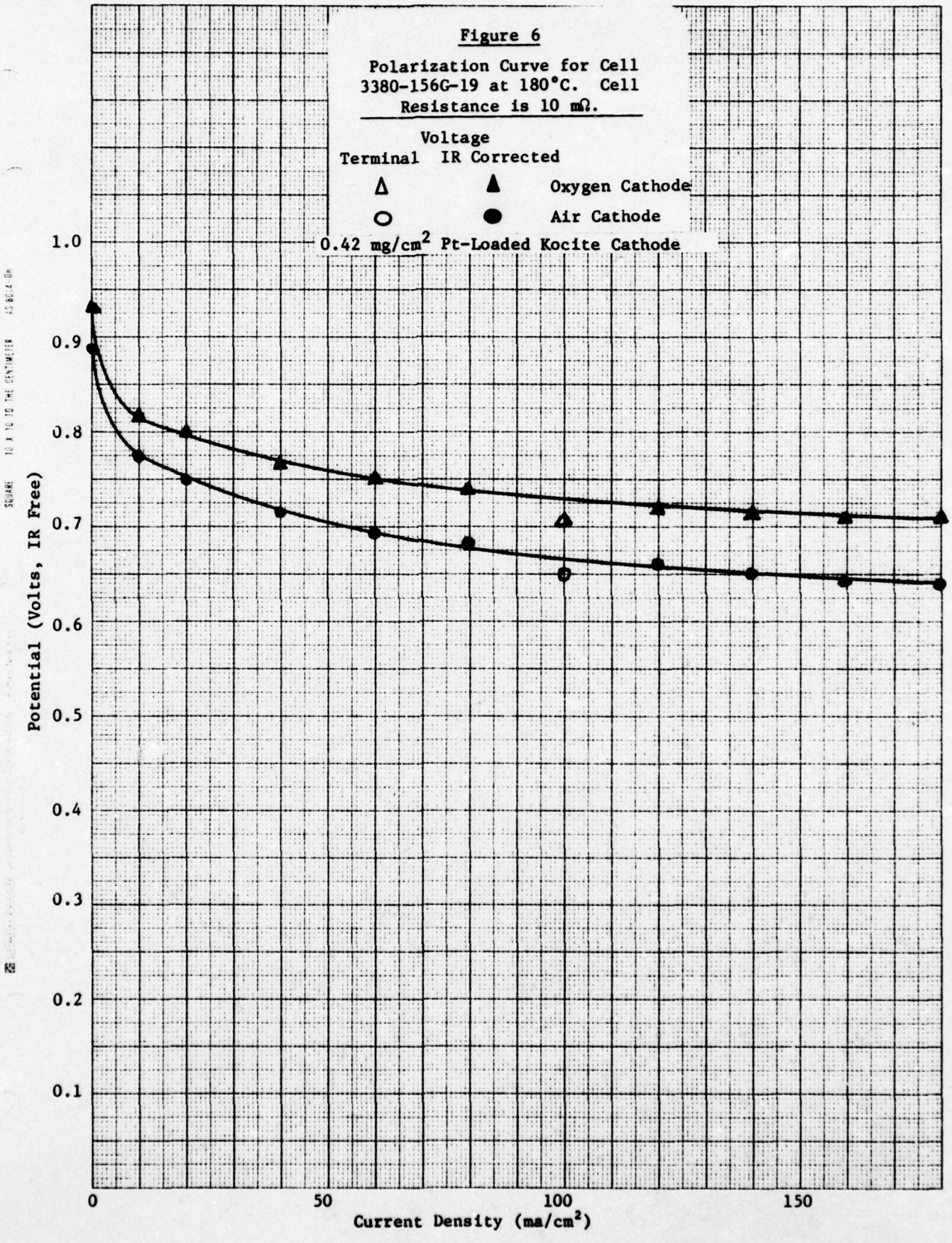
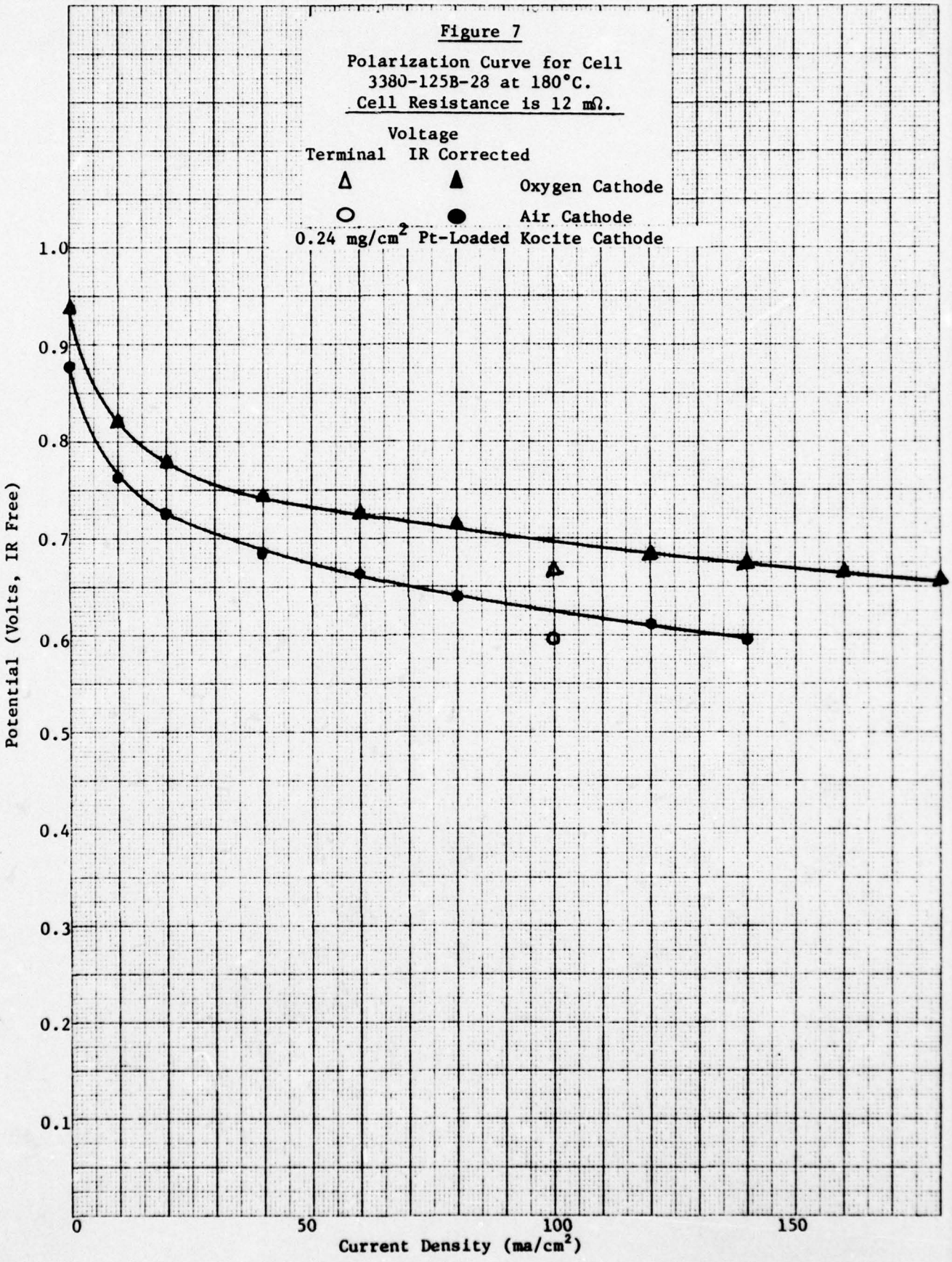


Figure 6

Polarization Curve for Cell 3380-156G-19 at 180°C. Cell Resistance is 10 mΩ.

Figure 7

Polarization Curve for Cell 3380-125B-28 at 180°C.
Cell Resistance is 12 mΩ.



batch was shown in Figure 4 and was reported in the previous Interim Report.[4] Table XII contains a summary of the performance of cells containing electrodes from these two electrode batches. (ERC Cell 83 was started with no float filling and never attained the level of performance achieved by the other cells.) The rest of the cells had an oxygen performance that was comparable, with a variation in the O_2 gain at 100 ma/cm^2 of between 70 and 110 mV.

4.3.3 Kocite Electrocatalyst Batch 3380-156G
Pt Loading 0.26 to 0.58 mg/cm^2

Electrodes fabricated from electrocatalyst batch 3380-156G produced the highest performance levels of any electrodes tested during this program. The best full cell polarization curves for a cell containing an electrode incorporating this electrocatalyst batch, with a Kynol matrix, are shown in Figure 6. At 180°C and with a 0.42 mg/cm^2 Pt-loaded electrode, this cell maintained IR corrected voltages of 0.67 V when operated on air and 0.73 V on oxygen at 100 ma/cm^2. The internal resistance of the cell was very low, with the terminal voltages being 0.65 V on air and 0.71 V on oxygen. Comparable performance was obtained with another cell as shown in Figure 8. This second cell, with an electrode having a platinum loading of 0.54 mg/cm^2, had IR corrected voltages of 0.66 on air and 0.73 on oxygen at 100 ma/cm^2.

Table XII

Summary of Best Performance for Electrodes from Electrocatalyst Batch 3380-125B

Cells 3380-125B-21, 24, 25 and ERC 75 and 83
0.22 mg/cm^2 Pt 30 wt.% Teflon

Voltage (V) at 100 ma/cm^2

	Terminal		IR Corrected		
Cell	Air	Oxygen	Air	O_2 Cathode (V)	Temperature (°C)
UOP 21	0.51	0.60	0.59	0.68	160
UOP 24	0.47	0.58	0.57	0.68	160
UOP 25	0.52	0.63	0.61	0.69	160
ERC 75	0.56	0.65	0.62	0.71	150
ERC 83	0.49	0.60	0.53	0.64	150

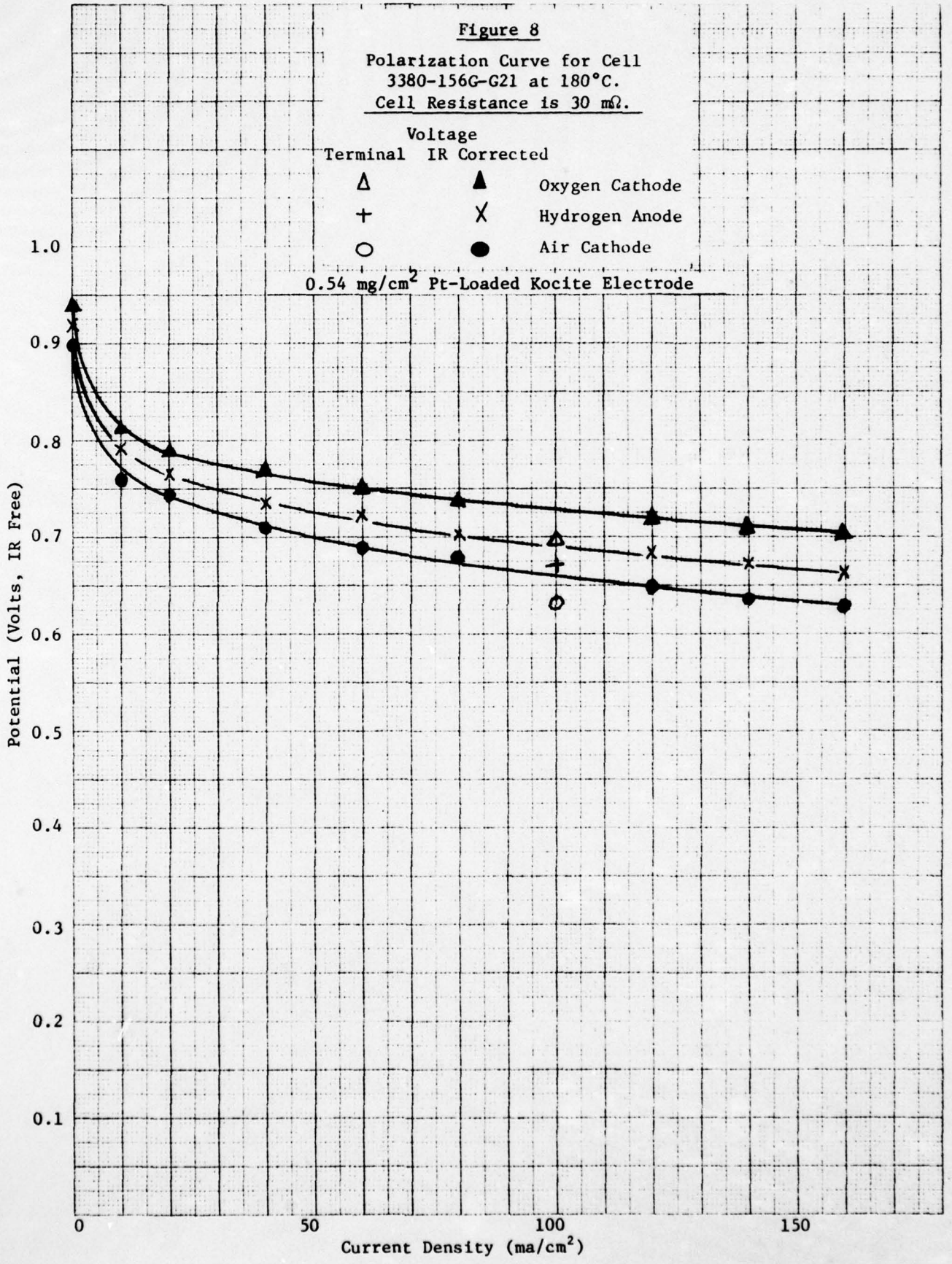
Cells 3380-125B-26 and 28 and ERC 89
0.24 mg/cm^2 Pt 20 wt.% Teflon

Voltage (V) at 100 ma/cm^2

	Terminal		IR Corrected		
Cell	Air	Oxygen	Air	O_2 Cathode (V)	Temperature (°C)
UOP 26	0.57	0.67	0.62	0.70	180
UOP 28	0.60	0.67	0.63	0.70	180
ERC 82	0.54	0.62	0.57	0.67	150

Figure 8

Polarization Curve for Cell
3380-156G-G21 at 180°C.
Cell Resistance is 30 mΩ.



Electrodes fabricated from electrocatalyst batch 3380-156G were run in cells operated under the same conditions to determine the reproducibility of performance within an electrode batch. Table XIII tabulates the air cathode, oxygen cathode and hydrogen anode (vs. standard air) results at 160°C for electrodes from three different electrode batches prepared with slightly different fabrication techniques. In each case the performance of three or more electrodes was determined. Though large spreads occur in the terminal voltages due to differing cell resistances, the values of the IR corrected voltages are close. For Set 1, the IR corrected air cathode values differ by 19 mV and the oxygen cathode values by 23 mV. For Set 2, the air cathode voltages vary by only 11 mV and the oxygen cathode values by 18 mV. For Set 3, the air cathode differences are 33 mV and the oxygen cathode differences are 20 mV. The oxygen gain values at 100 ma/cm^2 differ by 10 to 20 mV among the sets. The most reproducible performance levels were obtained using electrodes in Set 2. More electrodes from this batch were tested and in each case where the cell performed well, the cell voltage was within a few mV's of its peak value in 24 hours. The results achieved using the Set 2 electrodes indicate that reproducible performance should be obtainable using Kocite electrodes.

A few of the 0.54 mg/cm^2 Pt-loaded electrodes were tested by ERC with an experimental SiC matrix rather than the usual Kynol matrix. While several of these cells had gas crossover problems, the performance of cell SiC-3, shown in Figure 5, is about 40 mV higher than

Table XIII

Summary of UOP Results

Cell Performance and Reliability

Electrodes from Electrocatalyst Batch 3380-156G - 160°C
Voltage (mV) at 100 ma/cm^2

Set 1 - 30 wt.% PTFE, medium density, 0.56 mg/cm^2 Pt loading

Cell	Air Cathode		O_2 Cathode		O_2 Gain	H_2 Anode	
	Term	IRC	Term	IRC		Term	IRC
7	570	605	656	691	86	585	620
8	582	617	679	714	97	675	710
9	583	615	675	700	92	523	555
11	609	624	687	703	78	703	720

Set 2 - 20 wt.% PTFE, medium density, 0.54 mg/cm^2 Pt loading

Cell	Air Cathode		O_2 Cathode		O_2 Gain	H_2 Anode	
	Term	IRC	Term	IRC		Term	IRC
13	614	646	688	717	74	650	680
14	602	638	688	721	86	622	655
15	609	645	698	735	89	673	670
16	523	649	592	718	69	517	643
21	614	643	700	741	93	653	668

Set 3 - 20 wt.% PTFE, medium density, 0.58 mg/cm^2 Pt loading

Cell	Air Cathode		O_2 Cathode		O_2 Gain	H_2 Anode	
	Term	IRC	Term	IRC		Term	IRC
17	592	631	682	716	90	630	663
18	558	598	657	696	99	602	645
22	557	600	657	699	100	616	655

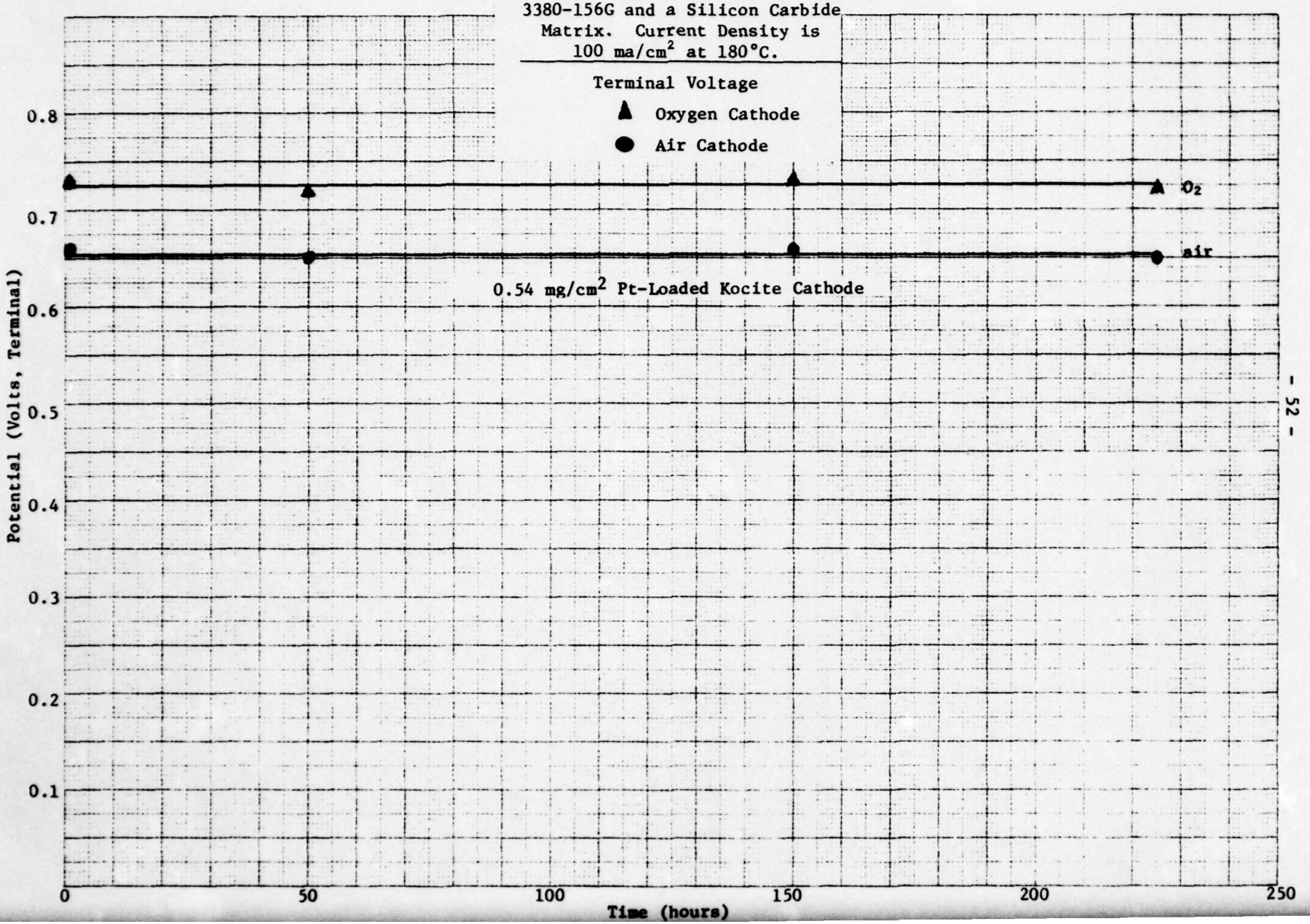
ERC obtained with the same type of electrode using a Kynol matrix. The reason for the performance increase is not known, however the internal resistance is not substantially different for the cells, indicating that the increase is not an internal resistance effect. The primary value of the SiC matrix is that it will allow operation at 180°C and above without a matrix degradation problem. The 225 hour life test shown in Figure 9 shows the basic stability of the cell, however gas crossover in the matrix occurred at that time. Further development of the matrix should improve cell life.

4.3.4 Kocite Electrocatalyst Batch 3380-180F Pt Loading 0.33 to 0.57 mg/cm^2

This batch was impregnated at a level of 20 wt.% based on the Kocite base material. After leaching, the platinum concentration is 52 wt.% based on the remaining carbonaceous pyropolymer. Because of this high platinum concentration, the platinum particle size and agglomeration listed in Table 2, are high. Because of the large platinum particle size, testing of this electrocatalyst was limited. The performance of a cell containing this electrocatalyst is shown in Figure 10 and is not as good as that for the cells containing electrodes from electrocatalyst batch 3380-156G having a similar Pt-loading. The high platinum agglomeration of this batch makes it difficult to compare results obtained using electrodes from this electrocatalyst batch with results obtained using electrodes from other electrocatalyst batches because the platinum particle size distribution differs substantially from that of other batches.

Figure 9

225 Hour Lifetime Test for ERC Cell SiC-3 With an Air Cathode Containing Electrocatalyst 3380-156G and a Silicon Carbide Matrix. Current Density is 100 ma/cm^2 at 180°C.



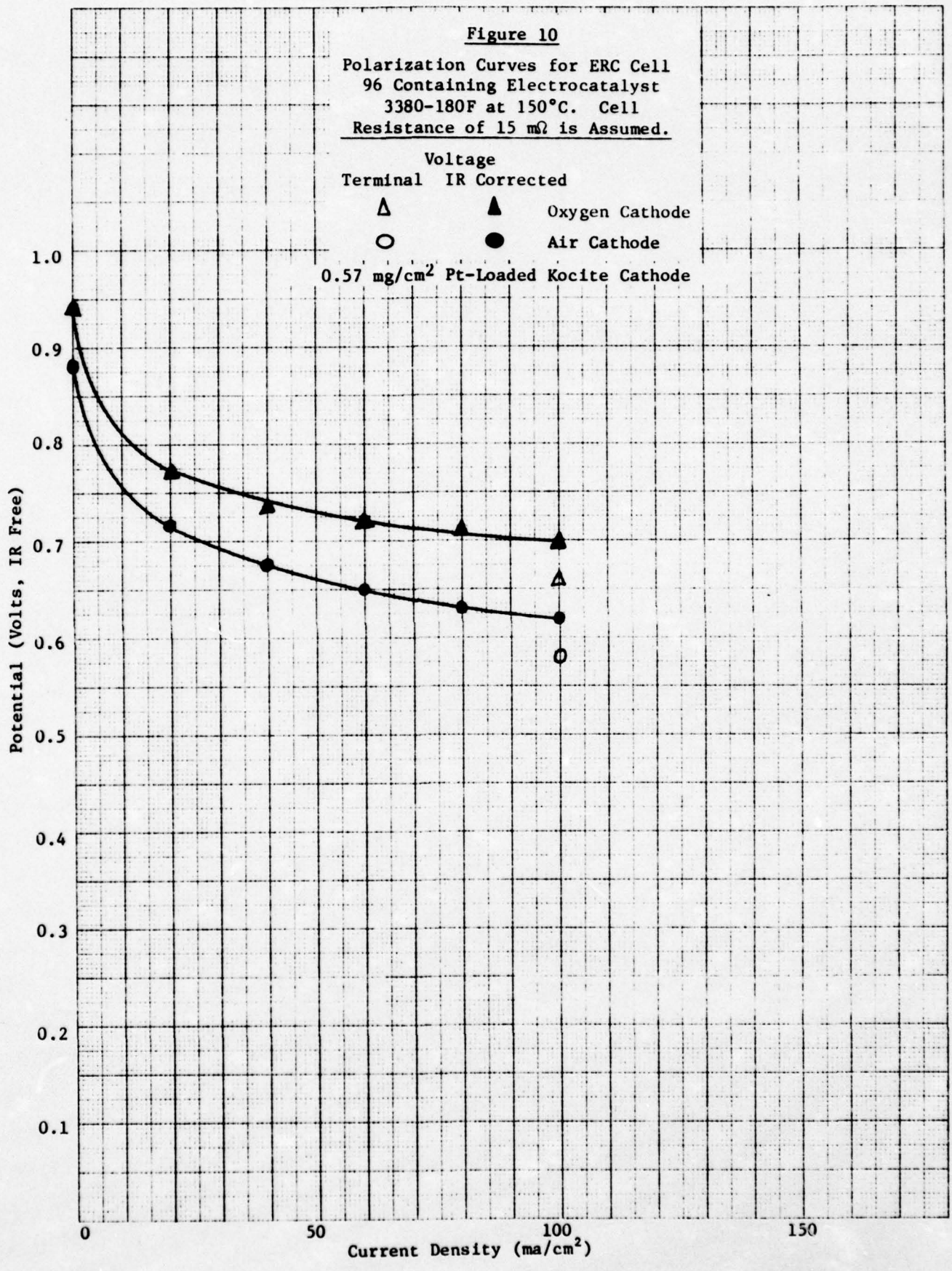


Figure 10
Polarization Curves for ERC Cell 96 Containing Electrocatalyst 3380-180F at 150°C. Cell Resistance of 15 mΩ is Assumed.
Voltage
Terminal IR Corrected
Oxygen Cathode
Air Cathode
0.57 mg/cm² Pt-Loaded Kocite Cathode
Potential (Volts, IR Free)
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
50
100
150
Current Density (ma/cm²)

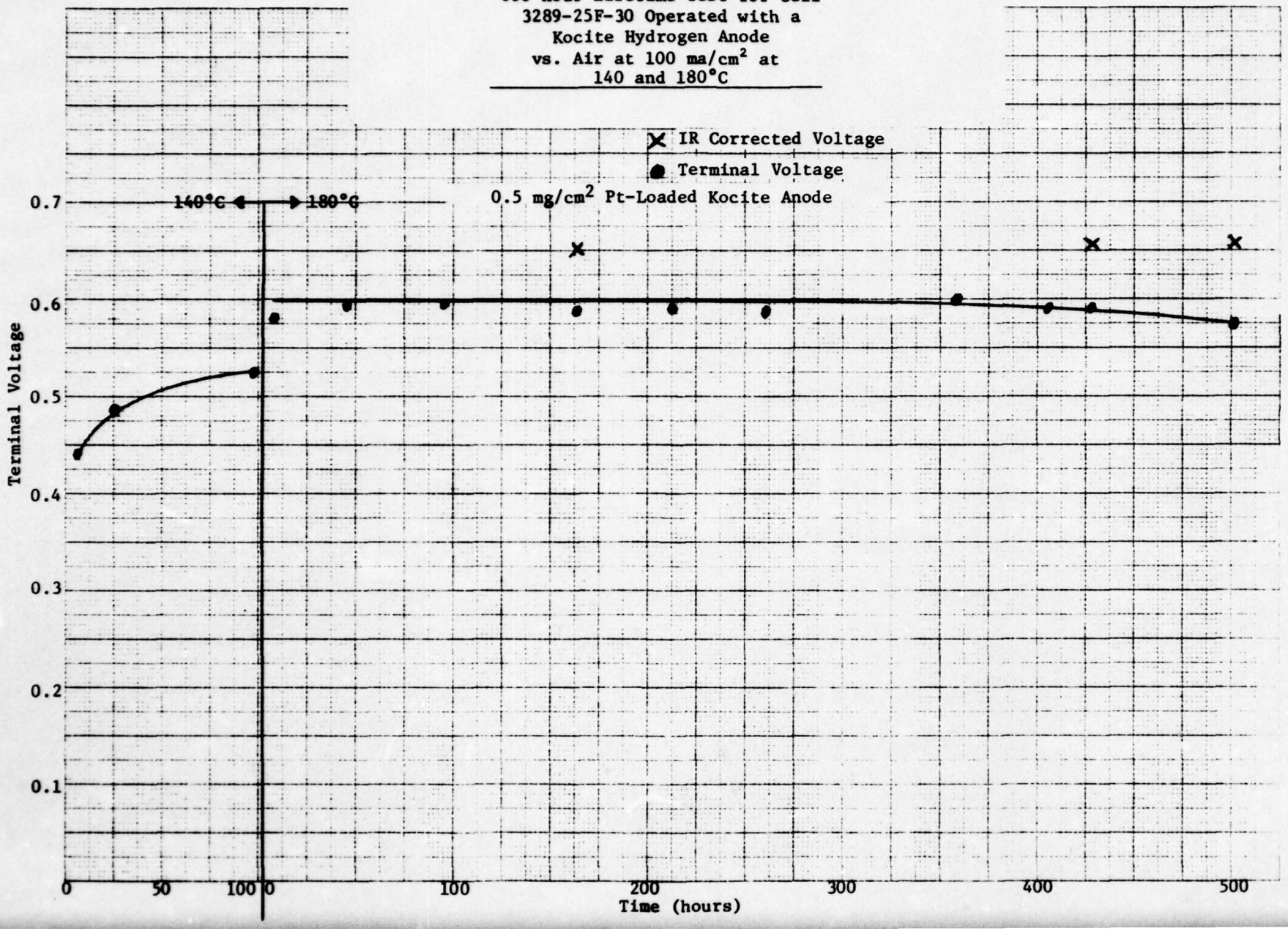
4.3.5 Anode Performance and CO Tolerance

The emphasis during this contract has been on evaluating the cathode performance rather than the anode performance of Kocite electrodes. The best voltage obtained for a cell with a Kocite anode is a terminal value of 0.70 V at 100 ma/cm^2 and 160°C. The anode polarization of a cell is low compared with the cathode polarization, so that this terminal voltage is more indicative of a good cathode performance by the platinum black electrode rather than a superior anode performance by the Kocite electrode. The variation of anode results listed in Tables X and XI further suggests that the values may depend more on the platinum black cathode than the Kocite anode. Three areas of anode performance are discussed below, (A) anode lifetime tests, (B) CO tolerance of Kocite electrodes, and (C) use of Kocite electrodes as both the anode and cathode in a cell.

(A) The ability of Kocite anodes to operate stably was shown in the previous Interim Report[4] for the cell shown in Figure 11. Though the terminal voltage began to drop after 300 hours of operation at 180°C, this drop was due to increased cell resistance and the IR corrected voltage remained fixed at 0.66 V at 100 ma/cm^2. Another example of this stability is displayed in Figure 12 by the lifetime test for cell 3380-156G-23 with both a Kocite anode and cathode. Though the terminal voltage at 160°C and 100 ma/cm^2 has decreased 30 mV in 1200 hours, the IR corrected voltage has been

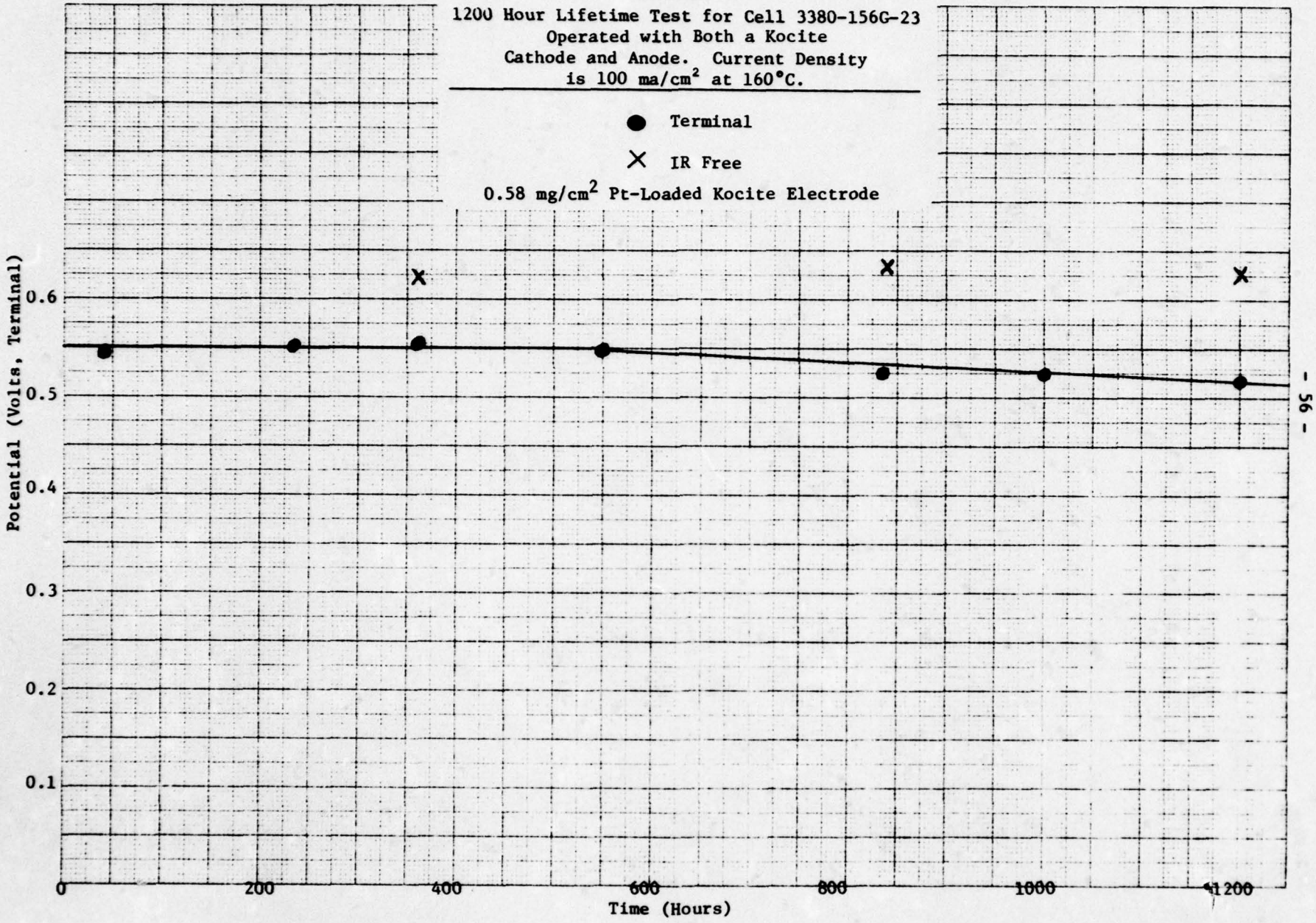
Figure 11

600 Hour Lifetime Test for Cell 3289-25F-30 Operated with a Kocite Hydrogen Anode vs. Air at 100 ma/cm^2 at 140 and 180°C



SQUARE 10 X 10 TO THE CENTIMETER

Figure 12



0.625 ± 0.005 V over that time. Since the IR corrected voltage is comparable to other cells with the same cathode and 2 mg/cm^2 platinum black anodes, listed in Table XIII, these data indicate that the anode as well as the cathode gives stable performance at 160°C for over 1200 hours.

(B) Initial data are available on the short term resistance of Kocite anodes to CO poisoning. Two cells were tested with a mixture of 5% CO in the H_2 fuel gas. The results for 5 to 10 minute exposures for the Kocite anodes and the 2 mg/cm^2 Pt black anodes are shown in Table XIV. The cell listed first had been operated for 1700 hours at 160°C while the cell listed second had been operated for 800 hours at 160°C and 1000 hours at 180°C. The values given in the table are the voltage changes of the cell on switching from pure H_2 to the CO-H_2 mixture for 5 minutes. In the first cell, the Kocite electrode shows only half the change at 180°C that the Pt black electrode does. For the second cell, the Kocite electrode has 1/5 the change that the Pt black electrode has. At lower temperatures the performance differential favors the Kocite electrode even more noticeably. The poor performance of the second cell using the Pt black electrode may be due to sintering of the platinum in the Pt black electrode at 180°C. Though more deterioration could be expected for longer exposures to the CO, the short term resistance of the Kocite electrodes compared to Pt black electrodes is very good.

Table XIV

CO Tolerance of Anodes

Cell 3380-156G-19

	Voltage Difference[a] (mV)	
	Kocite Anode	Pt-Black Anode
180°C	5	10
160°C	6	20

Cell 3380-156G-11

	Voltage Difference[a] (mV)	
	Kocite Anode	Pt-Black Anode[b]
180°C	5	25
160°C	8	60[c]
140°C	25	300[d]

[a]Voltage difference between the cell operating on pure H_2 and a 5% CO-H_2 mixture for 5 minutes.

[b]Commercial 2 mg/cm^2 Pt-black electrodes used as counter electrodes in all test cells.

[c]Initial decline was ∿3 mV/min, continued for >30 min.

[d]Initial decline was ∿100 mV/min, eventually declined by >400 mV.

(C) UOP Cell 3380-156G-23 is the first cell assembled with both a Kocite cathode and anode in the same cell. The performance compares quite well with the other Set 3 group of cells in Table XIII, which have the same electrode for a cathode. Figure 13 shows the polarization curve for the cell. As shown in this figure, the curves for the cell with the anode and cathode electrodes reversed is superimposable on the curves shown. The IR corrected voltages with either direction of gas flow were 0.62 V on air and 0.70 V on oxygen at 160°C and 100 ma/cm^2. These data indicate that with pure H_2, the polarization contributed by Kocite anodes is not significantly greater than that of the standard 2 mg/cm^2 platinum black anodes.

4.4 Electrode Lifetime Tests

Although only 500 hour tests were required by the contract, substantial efforts have been made to determine the longer term performance of cells with Kocite electrodes. Cells with these electrodes are stable with no loss in the IR corrected performance over periods of several thousand hours at temperatures up to 180°C. The use of graphite cell hardware with an electrolyte reservoir has helped minimize cell dryout and stabilize the terminal voltage performance of the cells.

As an example of the stability of cells with Kocite electrodes used as air cathodes, cell ERC 75 was still operating at 150°C after 4000 hours of operation (6 months). In this case an electrode from electrocatalyst batch 3380-125B was used. As shown in Figure 14,

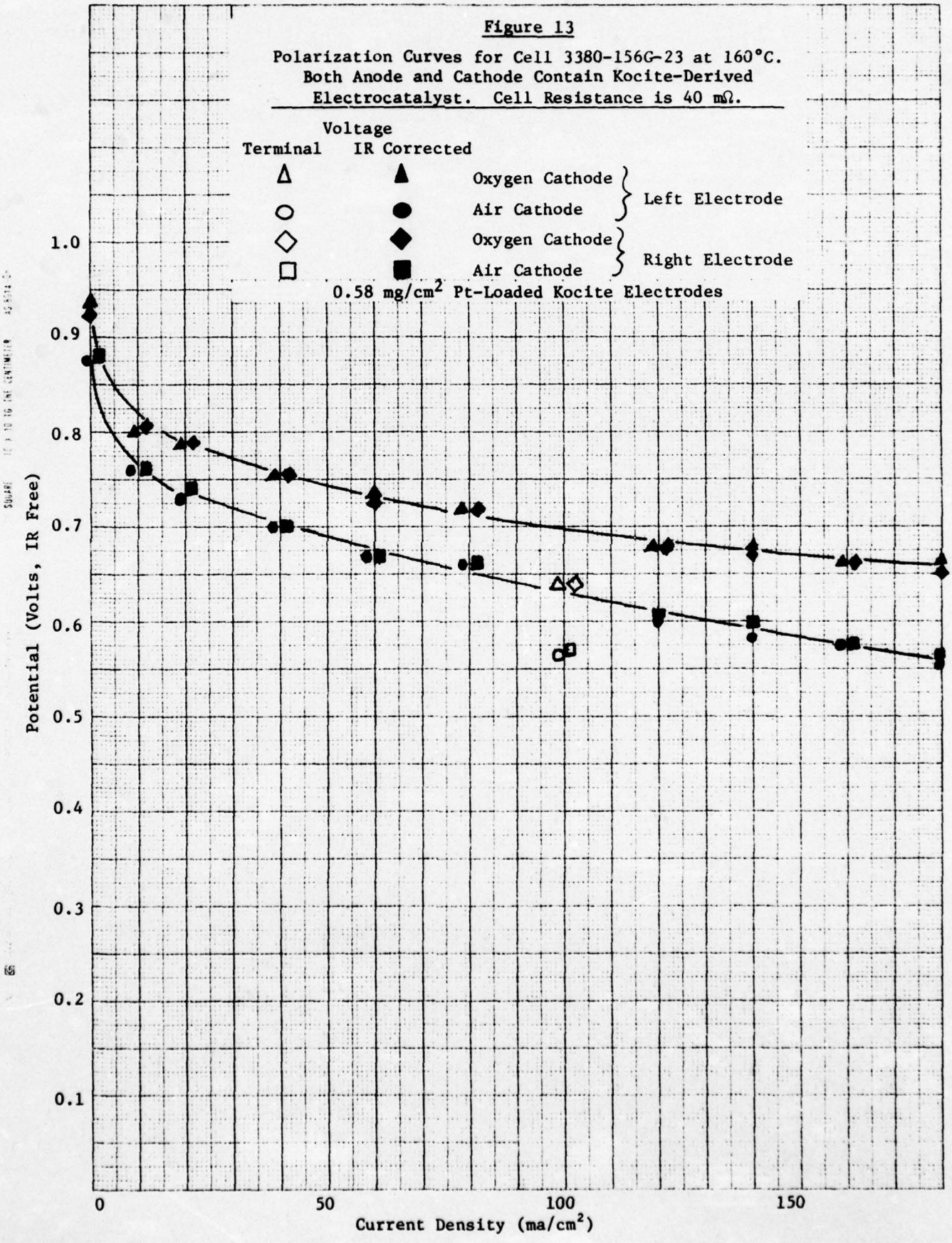
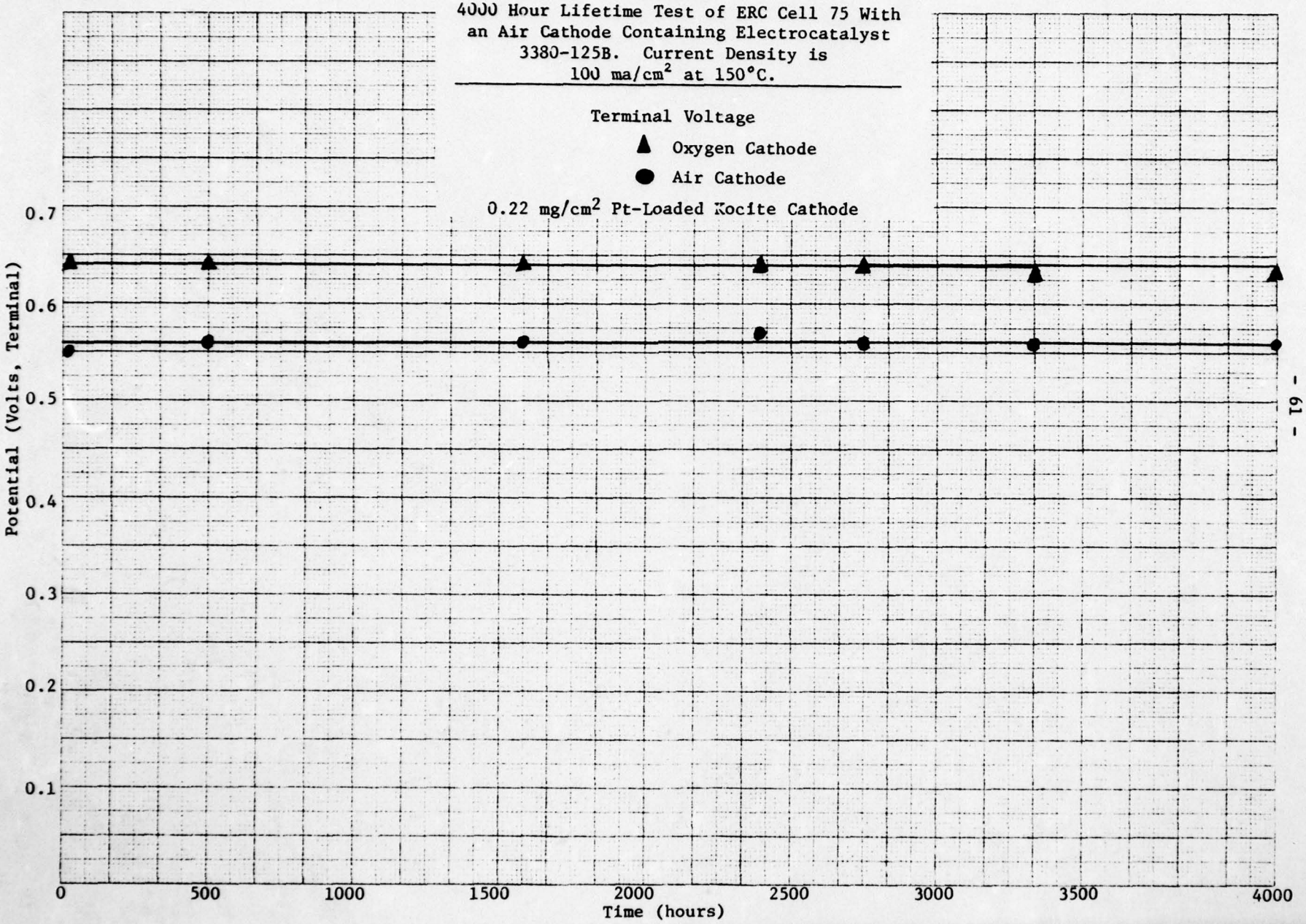


Figure 13

Polarization Curves for Cell 3380-156G-23 at 160°C. Both Anode and Cathode Contain Kocite-Derived Electrocatalyst. Cell Resistance is 40 mΩ.

Figure 14

4000 Hour Lifetime Test of ERC Cell 75 With an Air Cathode Containing Electrocatalyst 3380-125B. Current Density is 100 ma/cm^2 at 150°C.



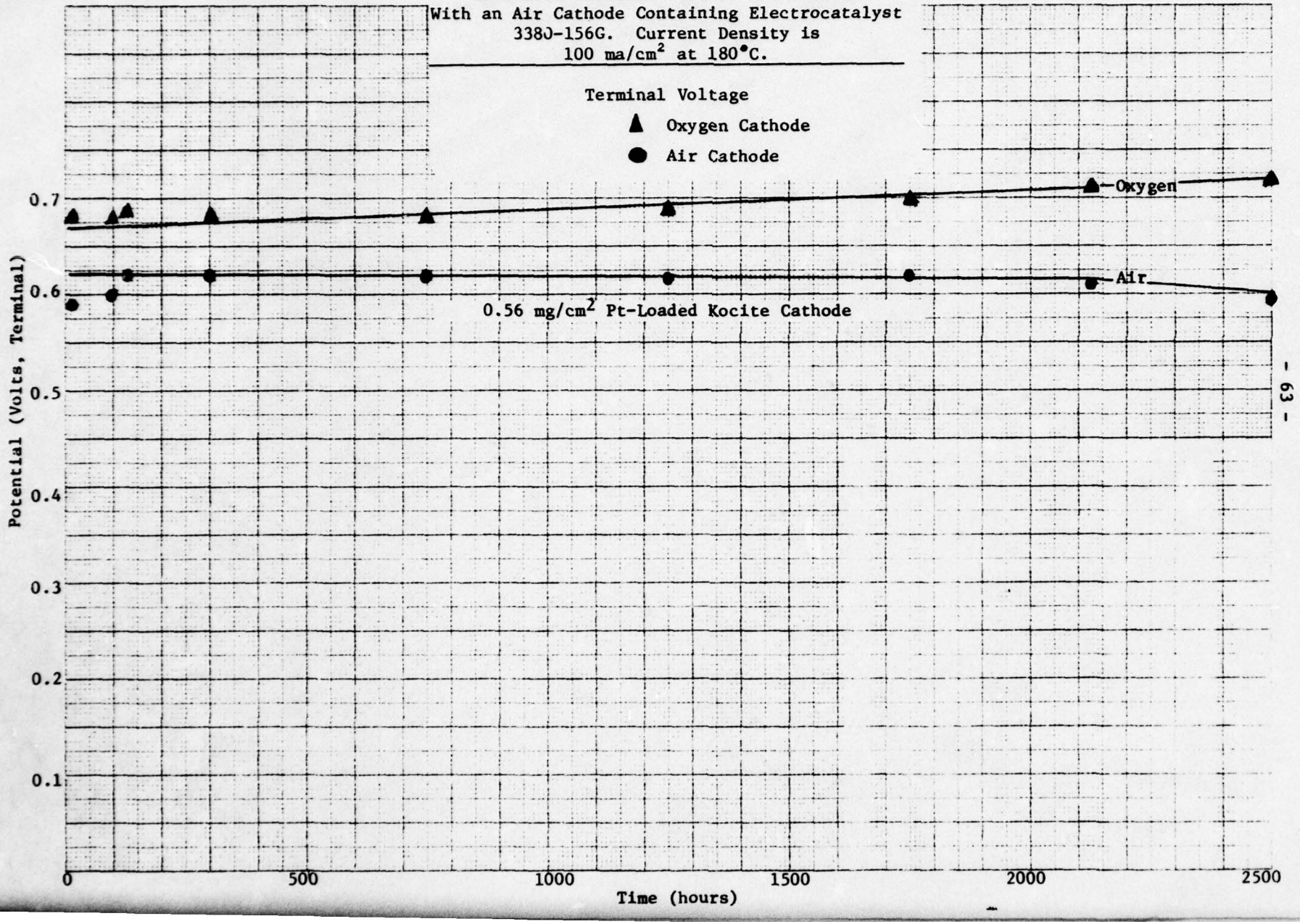
the terminal voltage of the cell at 100 ma/cm^2 has been stable at 0.56 V. At 180°C, a cell with a cathode made from electrocatalyst batch 3380-156G has had increasing oxygen cathode performance for over 2500 hours, as shown in Figure 15. At 100 ma/cm^2 and 180°C, the terminal voltage of the cell on oxygen reached 0.72 V, while on air the cell voltage dropped below 0.60 V, giving an oxygen gain of 120 mV. This indicates the growth of some diffusion related loss, possibly catalyst layer flooding. No resistance corrections are available for these cells to allow evaluation of the IR corrected performance.

At UOP, cells containing cathodes fabricated from electrocatalyst batch 3380-156G have been running with excellent stability. An example of the performance of such a cell is shown in Figure 16. With the Kocite electrode used as an air cathode, a steadily increasing performance was obtained at 160°C for 1700 hours. After 1700 hours this cell had the best terminal voltage of any cell with a Kynol matrix at 160°C, 0.638 V at 100 ma/cm^2. (Polarization curves for this cell were shown in Figure 6.) The long term performance of another cell is shown in Figure 17. This cell has run for 800 hours at 160°C and then 1500 hours at 180°C with a terminal voltage over 0.61 V at 100 ma/cm^2 for the time at 180°C. All of the above cells were still in operation at the time of this report.

The cell with the highest terminal voltage, ERC's SiC-3 was stable at 180°C for 225 hours at 0.66 V with 100 ma/cm^2 current density as shown in Figure 10. At that time cross gas leakage occurred in the matrix

Figure 15

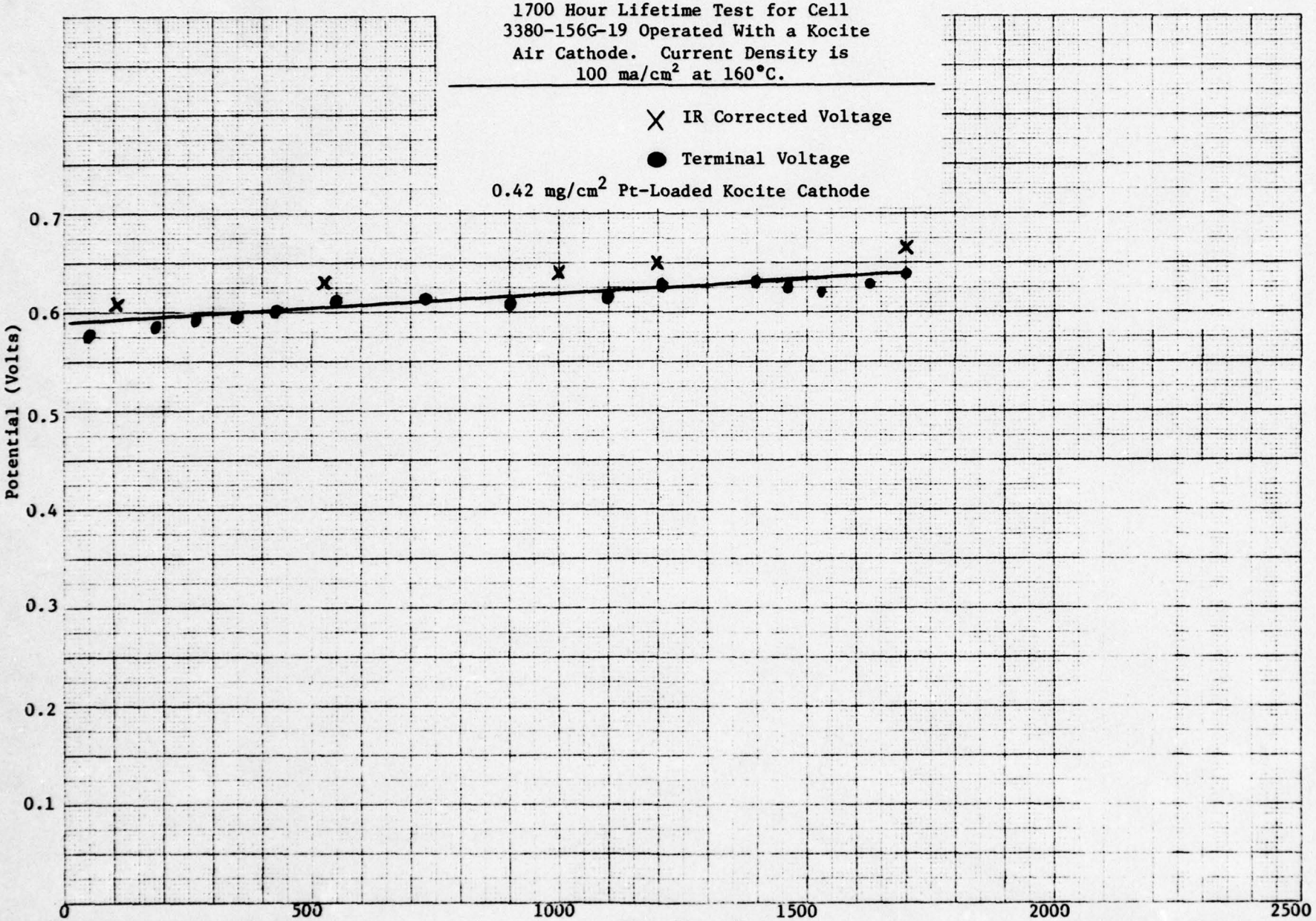
2500 Hour Lifetime Test of ERC Cell 89
With an Air Cathode Containing Electrocatalyst
3380-156G. Current Density is
100 ma/cm^2 at 180°C.



KS SQUARE 10 X 10 TO THE CENTIMETER AS 6014-0M

Figure 16

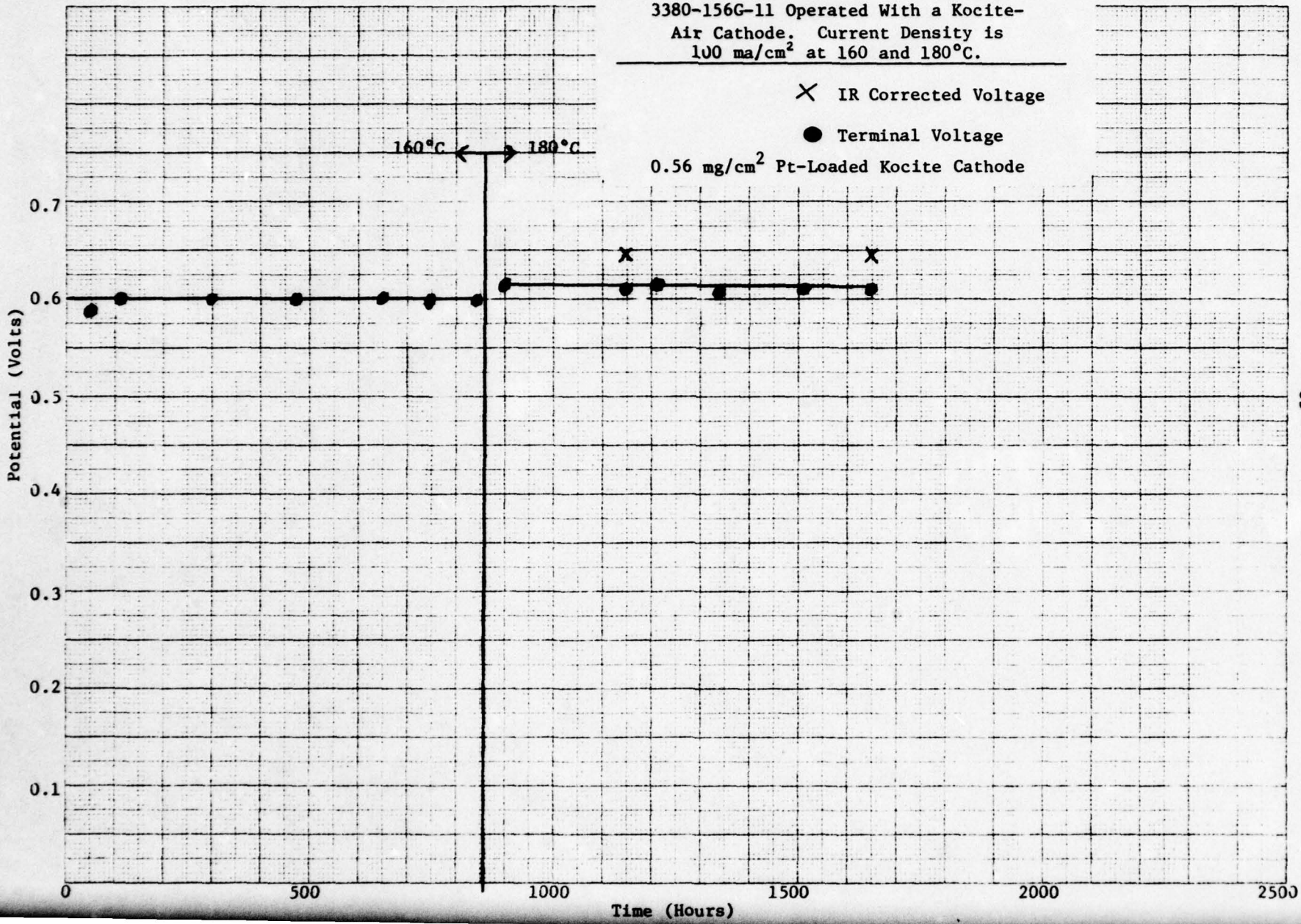
1700 Hour Lifetime Test for Cell 3380-156G-19 Operated With a Kocite Air Cathode. Current Density is 100 ma/cm^2 at 160°C.



SQUARE 10 X 10 TO THE CENTIMETER AS 6214 OH

Figure 17

1700 Hour Lifetime Test of Cell 3380-156G-11 Operated With a Kocite-Air Cathode. Current Density is 100 ma/cm^2 at 160 and 180°C.



and the cell was shut down. No electrode instability was evident in the cell and improvements in the matrix should allow Kocite electrodes to operate stably at high performance levels for much longer times.

4.5 Results of the Structure Parameter Variation

4.5.1 Introduction

The main effort during this contract period has been to optimize both the electrocatalyst and the electrode structure. The emphasis has been on obtaining systematic performance data of electrodes fabricated from the two large electrocatalyst batches, 3380-125B and 3380-156G. Five parameters have been systematically varied during the course of the optimization program; platinum loading, teflon content, catalyst layer thickness, catalyst layer density, and cell operation temperature. The effect of varying these parameters on cell performance will be discussed in this section. Where possible, the optimum value or range of values will be identified for these parameters.

4.5.2 Platinum Loading

Platinum loadings of the electrodes used in this program have been in the range from 0.22 to 0.58 mg/cm^2 for electrodes made from both electrocatalyst batches 3380-125B and 3380-156G. Normally, electrodes had a nominal Pt loading of either 0.25 or 0.50 mg/cm^2. Within this range electrode performance is nearly proportional to Pt loading. At 100 ma/cm^2 current density and 160°C, the average

difference in the IR corrected voltage between cells with air cathodes having either a 0.25 or a 0.5 mg/cm^2 Pt loading was ∿40 mV. The Tafel slope of these cells was 120 to 140 mV/decade. If the current is proportional to the platinum loading, then the voltage increase for doubling the platinum loading should be

$$130 \text{ mV/decade} \times \log 2 \simeq 40 \text{ mV}, \qquad (6)$$

in agreement with the measured value.

The degree to which cell performance is proportional to Pt loading is shown in the polarization curves plotted in Figure 18. In this figure, cell voltage has been plotted as a function of the current per gram of platinum or the platinum-specific current. If the performance was proportional to the platinum loading, all the curves should be superimposed. For the best cells at each Pt loading, the relation holds very well. The platinum specific polarization points fall within a zone about 10 mV wide for cells having electrodes loaded between 0.22 and 0.56 mg/cm^2 Pt.

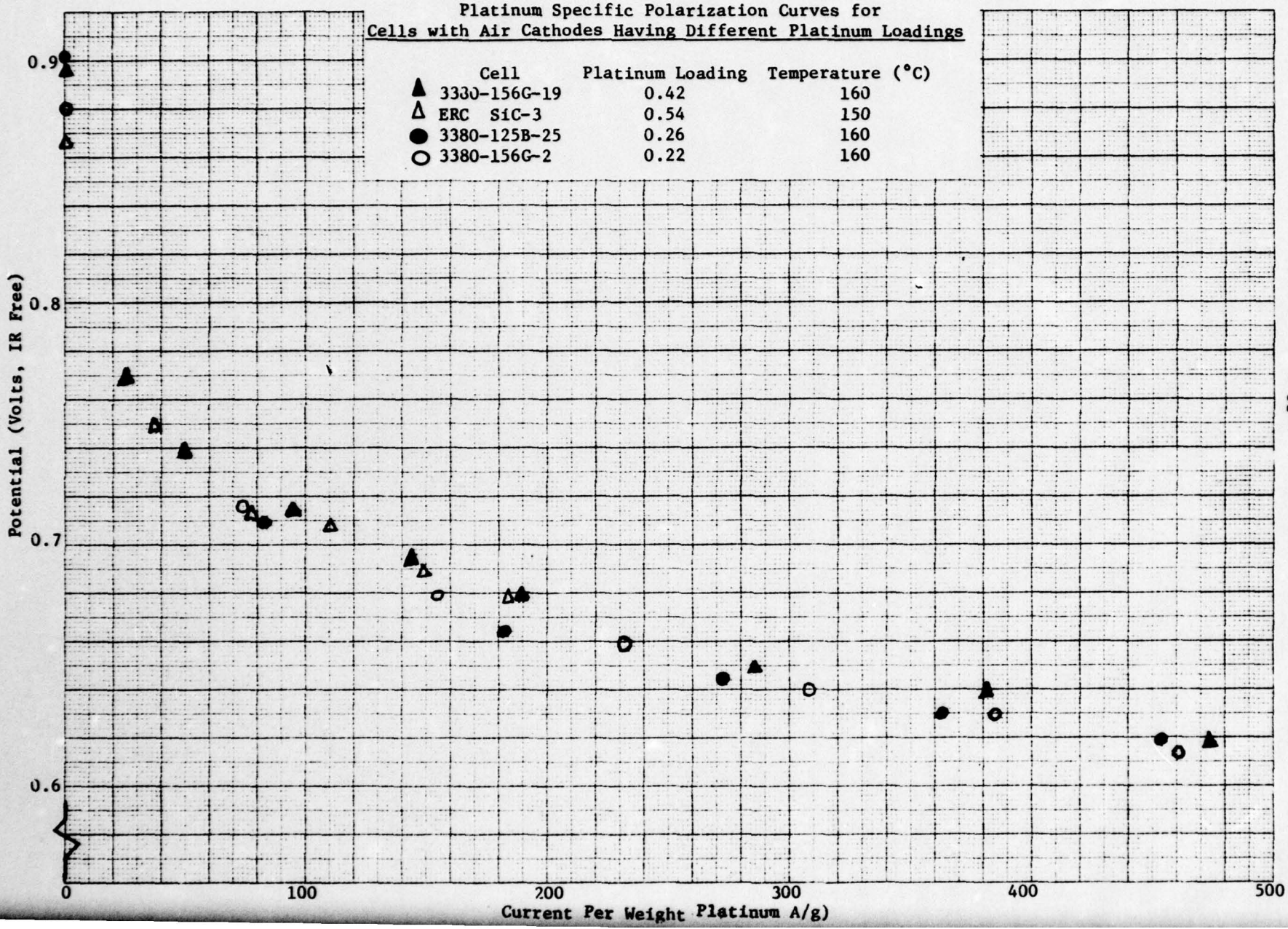
4.5.3 Teflon Content

To optimize the electrode structure, the teflon content of the electrodes has been varied in this study from ∿15 to 50 wt.% of the unleached Kocite material. The results[4] indicate that electrodes with lower teflon loadings have higher performance levels and reach their maximum performance more quickly than electrodes having higher teflon loadings. For electrodes made from either the 3380-125B or the 3380-156G electro-

Figure 18

Platinum Specific Polarization Curves for
Cells with Air Cathodes Having Different Platinum Loadings

Cell	Platinum Loading	Temperature (°C)
▲ 3330-156G-19	0.42	160
△ ERC SiC-3	0.54	150
● 3380-125B-25	0.26	160
○ 3380-156G-2	0.22	160



catalyst batches, the best performance was obtained with electrodes having a 20 or 30 wt.% teflon content. Attempts to operate at still lower teflon loadings failed because of flooding between the catalyst layer and the carbon paper support. This flooding caused the detachment of the catalyst layer from the support. This problem can probably be reduced by using a higher bonding pressure during electrode fabrication.

One possible reason that the electrodes with lower teflon loadings operate better than ones with higher loading is that with leaching, the weight percentage of teflon drastically increases. For an electrode containing electrocatalyst 3380-156G, a 50 wt.% teflon content becomes a 78 wt.% teflon content after leaching. 20 and 30 wt.% teflon loads become respectively 46 and 61 wt.% after leaching. (The teflon contents of electrodes after leaching are listed in Tables VIII and IX.) Thus the electrodes with the better performance have teflon contents which have a weight ratio of about 1:1 teflon to leached electrocatalyst. This is consistent with ERC's practice of using 50 wt.% teflon in their platinum-impregnated carbon-black electrodes. The optimum teflon content appears to be the loading which has about equal weights of teflon and electrocatalyst after the leaching process.

4.5.4 Electrocatalyst Loading

A Kocite electrocatalyst loading of 5 mg/cm^2 has been standard for most of the Kocite electrodes fabricated during the

present contract period. Though this loading is relatively large in comparison with platinum black or platinum-doped carbon-black electrodes, there is no indication that a thinner catalyst layer with a higher platinum concentration produces any performance improvement. The proportionality of performance to platinum loading discussed in Section 4.5.2 indicates that the same percentage of platinum is being utilized in all electrodes for which performance data are plotted in Figure 18.

A comparison between electrodes with 5 mg/cm^2 of electrocatalyst 3380-125B and 2.5 mg/cm^2 of electrocatalyst 3380-156G is given in Table XV. Each electrode has about the same platinum loading, $\sim$0.25 mg/cm^2. The average IR-free voltage at 100 ma/cm^2 of each group of electrodes is listed for both air and oxygen performance. The small differences between the average (<5 mV) indicates that the same percentage of the catalyst layer contributes to the performance of each cell.

4.5.5 Catalyst Layer Density

For the cells listed in Tables VIII and IX the electrodes were fabricated by bonding the catalyst layer to the carbon paper backing at "medium" density (100 psi pressure). ERC found this procedure suitable for machine-rolled platinum-doped carbon-black electrodes and it was used with little variation for the Kocite electrodes. Earlier in the program, some of the electrodes made from electrocatalyst 3380-125B were fabricated by a different

Table XV

Comparison of the Performance of Electrodes with Differing Catalyst Loadings

Average Air Cathode Voltages[a]

Electrode[b]	Catalyst Loading (mg/cm^2)	Pt Loading (mg/cm^2)	Average Voltage (V)
3380-125B	4.4	0.22	0.594
3380-156G	2.6	0.26	0.596

Average O_2 Cathode Voltages[a]

Electrode[b]	Catalyst Loading (mg/cm^2)	Pt Loading (mg/cm^2)	Average Voltage (V)
3380-125B	4.4	0.22	0.690
3380-156G	2.6	0.26	0.685

[a] IR Corrected voltages at 150°C and 160°C at 100 ma/cm^2 current density.

[b] 3380-125B Cells - UOP 21, 24, 25, 26, 28
3380-156G Cells - UOP 1, 2, 4 and ERC 85, 87, 91

process that produced a less dense (low density) catalyst layer. These electrodes however tended to separate from the backing material during prewetting. A similar problem was encountered with the low teflon content (∿15 wt.%), medium density electrodes and was discussed in Section 4.5.3. The adherence of the catalyst layer to the backing material was insufficient to prevent electrolyte from getting between them. The electrolyte floods the back of the electrode rather than the catalyst layer itself. Use of higher bonding pressures should eliminate the problem.

4.5.6 Cell Operating Temperature

Cell operation at higher temperatures has the advantage of improved cell performance and substantially greater tolerance of the anode to poisoning from CO in the fuel. In cells with Kocite air cathodes, the average improvement in performance approaches 1 mV/°C at 100 ma/cm^2 current density. The increase results from faster diffusion and a higher oxygen reaction rate. For pure oxygen the gain is somewhat less because there is a minimal diffusion penalty to overcome. While no problems are seen in operating cells at 150 to 160°C, ERC makes no representation as to the stability of its cell components, particularly the Kynol matrix, at 180°C or above. With careful control of the water balance and electrolyte replacement, cells do appear to operate quite stably at 180°C as shown by Figure 15 in which the cell ran for 2500 hours as an air cathode. With the proper silicon carbide matrix, these

cells should operate stably at temperatures of 180°C or higher. Although platinum sintering should be more of a problem at the higher temperatures, there has been no indication from the 180°C lifetime tests completed to date that sintering is limiting cell performance.

4.6 Summary of Results

Over this contract period, several important results have been obtained which are listed below.

(A) Electrode Performance

The performance levels of cells using Kocite electrodes as cathodes have been dramatically improved during this contract period. The best cell used an experimental SiC matrix and operated stably on air with terminal and IR corrected voltages of 0.66 and 0.70 V, respectively, at 100 ma/cm^2 and 180°C. The Pt-loading of this cathode was 0.54 mg/cm^2. At this current density O_2 gains have been reduced to 70 to 80 mV routinely and in some cases to 60 mV. The performance levels obtained with Kocite electrodes are comparable to the levels obtained by ERC using their Pt-impregnated carbon-black electrodes.

(1) According to ERC experience, the use of a silicon carbide rather than Kynol matrix improves cell performance ∿40 mV at 100 ma/cm^2 and 150°C. The best cell to date with a Kynol matrix used a 0.42 mg/cm^2 Pt-loaded Kocite cathode and had a terminal voltage of 0.646 V on air at 100 ma/cm^2 and 180°C. This indicates that still higher air cathode performance may be expected from Kocite electrodes in cells with a SiC matrix.

(2) Cells with cathodes from the same electrode batch have given highly reproducible results.

(3) Cells have run stably as air cathodes at 100 ma/cm^2 for periods up to 2500 hours at 180°C and 4000 hours at 150°C. At the time of this report, these cells were still operating.

(4) A cell with a Kocite anode has run stably for over 500 hours at 180°C with a current density of 100 ma/cm^2. A cell with Kocite electrodes as both the anode and cathode has operated stably for over 1200 hours.

(5) Kocite anodes have shown greater short term resistance to CO poisoning than 2 mg/cm^2 platinum black anodes when used with 5% CO in H_2 fuel gas. At 180°C, the platinum black electrode had 2 to 5 times the voltage loss of the Kocite-electrode. This difference was more pronounced at lower temperatures.

(b) Electrode Structure Optimization

The program to optimize the structure of the Kocite electrodes has yielded significant improvements in both the stability and performance levels of these electrodes. The results of this program indicate the following:

(1) The best performance results were obtained with electrodes having a teflon content of 20 to 30 wt.% of the fabricated electrode or ∿1:1 weight ratio with the leached Kocite-derived electrocatalyst.

(2) Electrodes with medium density (100 psi bonding pressure) catalyst layers have better performance characteristics than electrodes with low density layers. For electrodes with the lowest

teflon contents, higher pressure must be used during electrode fabrication to bond the catalyst layer to the carbon paper backing.

(3) The Al_2O_3 substrate is leached from the electrocatalyst leaving a carbonaceous pyropolymer material with a surface area as high as 750 m^2/g. The leaching does not appear to impair the lifetime performance of electrodes containing the leached electrocatalyst.

(4) The cell performance levels are proportional to the platinum loading in the range 0.2 to 0.6 mg/cm^2 platinum. Thicker layers of a less heavily platinum loaded catalyst may give comparable results.

(C) Platinum Crystallite Sintering

The amount of Pt crystalline growth at 180°C has been determined by X-ray diffraction techniques for both electrocatalyst powders soaked in H_3PO_4 and Kocite electrodes operated in fuel cells.

(1) For catalyst powders with no applied potential the sintering rate appears to depend on the platinum to carbon ratio of the catalyst with higher Pt-loaded powders sintering more rapidly. For the same value of Pt/C, the rate of sintering was less for Kocite electrocatalyst powders than for ERC Pt-doped carbon black powders.

(2) For catalysts in electrodes operated as air cathodes in fuel cells, the sintering was not significant at 160°C or below. At 180°C the results were similar to the results for the powders with the catalysts having a higher value of Pt/C showing greater sintering. Pt sintering did not appear to limit electrode performance, since the lifetime tests did not show performance loses matching the rate of platinum sintering.

V. CONCLUSIONS

Based on the improved results obtained during the latter part of the contract period, several conclusions concerning low cost fuel cell electrodes using Kocite-derived materials can be stated.

(A) Kocite electrodes can be used as stable cathodes and anodes at 180°C. Cells with both a Kocite anode and cathode operate comparably with those containing a Pt black anode.

(B) Electrode optimization has progressed to the point where terminal voltages of 0.66 V at 100 ma/cm^2 and 180°C have been achieved with a cell having 0.5 mg/cm^2 Pt-loaded Kocite air cathode. Electrode performance is proportional to the platinum loading and varies with temperature at the rate of ∿1 mV/°C from 140 to 180°C. The teflon content of the catalyst layer should be in the ratio of ∿1:1 with the carbonaceous pyropolymer component of the electrocatalyst.

(C) A number of cells containing cathodes from the best electrode batch were run under the same conditions. The similarity of cell performance indicated that Kocite electrodes can perform reproducibly.

(D) The rate of sintering of platinum particles on Kocite-derived electrocatalysts was determined by X-ray diffraction techniques. Sintering rates for the Kocite-derived electrocatalysts were found to be lower than on carbon-black electrocatalysts of the same platinum loading.

VI. RECOMMENDATIONS

To further improve the performance of Kocite-containing electrodes and continue their development for use in H_3PO_4 electrolyte fuel cells, the following recommendations are made:

(A) Prepare and test electrocatalysts in which the Al_2O_3 has been leached either before or after impregnation. Electrocatalysts with high Pt dispersion should then be fabricated into electrodes and tested in model fuel cells.

(B) Determine if the electrode structure should be modified to obtain maximum performance from the leached electrocatalysts.

(C) Test Kocite electrodes as anodes and cathodes at 180°C for extended periods (5000 hr. or more). Continue the Pt sintering experiments to relate the sintering rate to the electrocatalyst composition and preparation method.

(D) Produce and test electrodes of the size used in fuel cell stacks.

(E) Fabricate and test a full size fuel cell stack.

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