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METHODOLOGY FOR PREDICTING LONG-TERM FUEL CELL PERFORMANCE FROM SHORT-TERM TESTING

Final Technical Report

By
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August 1981

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Energy Research Corporation
Danbury, Connecticut

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**FINAL TECHNICAL REPORT
CONTRACT NO. DE-AC05-79ET15381**

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EXECUTIVE SUMMARY

The objective of this program was to develop a methodology for predicting long-term fuel cell performance from short-term testing, utilizing a perturbation testing technique. The technique applies small changes of predetermined levels in a predetermined sequence to the operating variables such that the decay mechanisms are not altered. This technique was tested on the phosphoric acid fuel cell (PAFC), because this technology is approaching a mature stage. The initial series of perturbation tests appear to be reasonably successful and a methodology is now available for further refinements. The progress made during the study is outlined below.

- Temperature, cathode potential and water partial pressure were selected as the operating variables for the study. Catalyst loading and Teflon content were selected as the cell component variables. A Balanced Incomplete Block Design (BIBD) was selected for the perturbation experiments.

- A test facility consisting of 22 high quality test stands was designed and constructed specially for the predictive testing. Test cell specifications were firmed after the initial pretesting. An excellent reproducibility and satisfactory performance levels were established in the test cell. A total of 18 perturbation cells, consisting of four build types, were assembled. A cell-to-cell variation in the IR-free performance was within ± 5 mV for each build type. Four baseline cells were also operated for approximately 5500 hours under unperturbed conditions to generate long-term baseline data for evaluation of the model. All of the planned 21 perturbations were completed in about 3000 hours.

- The data obtained in the perturbation experiments were analyzed using multiple regression technique and the parameters for a linear decay model were estimated along with their confidence intervals. However, during the analysis it was observed that the perturbation data of the first six periods were more meaningful with respect to the operating conditions, than the remaining data. Analysis of these data yielded reasonable estimates of the model parameters (95% confidence intervals were smaller than the estimates) and a good fit was obtained. The dependence on catalyst utilization, limiting current density and water partial pressure was eliminated from the model because of the lack of significance of these variables during previous analyses.

- A reasonable agreement was observed when the performance predicted by the aging model derived from perturbation testing technique was compared with the experimental data of unperturbed cells. Thus the perturbation testing technique was validated. A reasonable match was also obtained between the perturbation data (at center point conditions) and the baseline data, suggesting that the perturbation testing did not introduce any undue effects.

- Finally, it can be stated that the perturbation testing technique may be gainfully employed for predictive life testing of phosphoric acid fuel cells. The methodology developed and demonstrated by the study can be further refined and applied to other fuel cell systems. Some of the further refinements may include:

- a. extending the perturbation period to determine whether the catalyst utilization and the limiting current density vary linearly or nonlinearly with respect to time.

b. expanding the range of water partial pressures to reduce uncertainty in the parameters to be estimated.

c. implimenting higher precision in the control of water partial pressure levels during the experiments.

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INTRODUCTION

Considerable progress has been made in improving the performance, life and cost of fuel cell systems. The system costs can be estimated using a combination of prototype cost data and standard cost analysis techniques. The initial performance can be easily estimated using the models developed to date. However, no models are available at present to predict long-term performance or life of a fuel cell, with a given set of components. Some predictive life testing is, therefore, necessary. Predictive testing is also needed for optimization of design parameters (e.g., operating conditions) to minimize life cycle costs. Evaluation of new components also requires predictive testing, so that the behavior of these components can be estimated in a reasonable amount of time.

A new approach, based on the "perturbation technique", has been proposed in this study for such predictive testing. The approach involves small changes in the operating variables such that the decay mechanisms are not altered. The perturbation approach is an adaptation of "Evolutionary Operation" (EVOP)^{1,2} originally applied to plant operations. Changes are made in the operating conditions of an industrial plant to find the condition that would yield higher performance and the direction for further improvement. The changes are kept small so that the plant can continue to operate and to produce an acceptable product. In deactivation modeling for fuel cells, it is more important to understand the effects of the variables than to find improved conditions. The latter can be selected when the model is used to simulate commercial cell performance. An illustration of the perturbation technique is given in Figure 1. The operating variable being perturbed is temperature. As can be seen, the cell is operated initially at normal

1. Box, G.E.P., and Draper, N.R., Evolutionary Operation: a Statistical Method for Process Improvement, Wiley, New York 1969.
2. Box, G.E.P., Hunter, W.G., and Hunter, J.S., Statistics for Experimenters PP.362-367, Wiley, New York 1978.

FIGURE 1. ILLUSTRATION OF PERTURBATION TECHNIQUE
FOR A SINGLE VARIABLE

temperature after which the temperature is increased by a small amount so increasing the decay rate without changing the decay mechanism. The higher temperature is maintained for a predetermined time, and it is then reduced so that it is less than normal (a small change again) and the decay rate is less than that under normal conditions. The cell is then returned to normal temperature to check whether the system is behaving normally and the whole sequence is repeated. The experiments are short term and results are extrapolated for an estimate of long-term performance or life.

The perturbation technique has several advantages: perturbation on the same cell gives results that are free of cell-to-cell variation effects. Thus it provides us with statistical confidence. Since fewer cells are required than in accelerated testing, perturbation testing is more efficient and cost-effective. Also, because the perturbations are small, the results should be directly applicable to design conditions.

The phosphoric acid fuel cell has been selected for application of this technique because a considerable technical background is available and most of the cell components are well defined.

The approach used in this study was to fit a model of the rate of decay of fuel cell performance to laboratory data and then to use that model to predict the long-term performance. The specific decay model used was derived from the physical and chemical processes causing cell performance decay. The plan for the experiments - including experimental design, operating variable levels and other details - was prepared and testing was conducted accordingly. Test cells were operated under conditions that varied in a controlled manner. Performance data and the operating conditions were correlated by regression analysis technique to obtain model parameters. Data generated by baseline cells operating at constant operating conditions were

then used to test the model developed.

The experimental data obtained from testing indicated that the cells of the same build type had identical performance and decay characteristics. Estimated coefficients showed that the effects of voltage and temperature on catalyst utilization decay were more significant than any other variable. It appears that the initial series of perturbation tests was reasonably successful.

TASK I. AGING MODEL DEVELOPMENT

The objectives of this task were to:

- Develop a model of the rate of performance decay by utilizing the perturbation testing data.
- Verify the model with laboratory data of unperturbed cells.

I.1. Performance Decay Modes in the Phosphoric Acid Fuel Cell

Although prior assumptions on decay modes are not essential, a knowledge of possible decay modes and important parameters affecting the decay is desirable to perform a cost effective and efficient predictive testing. A primary decay mode limiting PAFC life appears to be related to cathode performance decay.³ A brief discussion of various decay modes based on available information is presented below.

A. Diffusion Limitation

A progressive increase in diffusion loss occurs with time which may be caused by two processes: carbon corrosion and Teflon degradation.

● Carbon Corrosion

Present PAFC electrodes consist of platinum, carbon, and Teflon. The carbon support is used to provide a conductive and highly dispersive base for the Pt catalyst crystallites and the Teflon mainly to impart hydrophobicity to the structure. Although the exact interaction between carbon, Pt, and Teflon is not fully understood, it is believed that the corrosion of carbon ($C + 2H_2O \rightarrow CO_2 + 4H^+ + 4e^-$) takes place especially at high potentials on the cathode side. This may result in separation of the carbon support from the Teflon, thereby losing the hydrophobicity provided by the Teflon. This may in turn allow acid to encroach upon and eventually fill the pores of the catalyst, causing a liquid phase diffusion pro-

3. Maru, H.C., Christner, L., "Phosphoric Acid Fuel Cell Cathode," in National Fuel Cell Seminar Abstracts, San Francisco, CA, July 11-13, 1978.

blem in an aged cell. It is also possible that carbon corrosion may result in Pt surface area loss and thus in an increased activation polarization.*

- Acid Attack on Teflon

Although Teflon is quite stable and resistant to phosphoric acid at room temperature, it may be subject to attack in a highly concentrated H_3PO_4 environment at a high temperature. This condition could result in a further loss of hydrophobicity, creating additional diffusional problems.

B. Platinum Deactivation (Crystallite Growth and Dissolution in Acid)

Current PAFC electrodes contain approximately 10% weight Pt with a Pt surface area of 50 to 100 m^2/g . Stability of this high surface area is important to minimize electrode polarization, especially at the cathode. There is, however, some controversy as to the nature of the roles of long-term platinum stability and its activity under load or open circuit operating conditions, long-term carbon stability under similar conditions, interfacial stability, and the role of Teflon Type. It is believed, however, that as the catalyst ages, Pt crystallites grow causing a reduction in active area, and this growth may be enhanced at high potentials. It is also believed that Pt may dissolve in the acid at high potentials. Thus the crystallite growth may lower the extent of Pt activity and the dissolution results in a net loss of catalyst.

The above decay modes relate to the cathode side. Other decay modes (such as anode poisoning, matrix bubble pressure loss or bipolar plate corrosion) appear to be only secondary modes and were omitted from this study.

* A further discussion of this is presented in Section IV.

I.2 Form of the Aging Model

A simple form of the aging model is the decay rate expressed as a function of variables affecting the decay. These can be called experimental variables and can be classified into two types: cell component and operating variables. Table I.1 lists important variables from each type and these are discussed below.

Because the changes in carbon properties can lead to difficulties with wetting and diffusion polarizations, a study of carbon support type was postponed. With the rising price of platinum, catalyst loadings on the electrodes have been reduced considerably, although the effect of loading on decay rate has not been studied. It is important, therefore, to study this variable. The degree of wetproofing can be controlled by varying the Teflon content or the degree of sintering. For this program, the wetproofing was varied by the Teflon content in the electrode because this is easily accomplished without involving any other complications.

The decay modes considered for this program are directly affected by the following operating variables:

<u>Decay Mode</u>	<u>Variables Affecting the Mode</u>
1. Carbon Corrosion	Temperature (T) Cathode Voltage (V_C) Acid Concentration, hence P_{H_2O}
<u>Decay Mode</u>	<u>Variables Affecting the Mode</u>
2. Platinum crystallite growth and dissolution ⁴	V_C , T, P_{H_2O}
3. Acid attack on Teflon	T, acid concentration

4. Bindra, P., Clouser, S. and Yeager, E., "Platinum Dissolution in Concentrated Phosphoric Acid", Journal of the Electrochemical Society Vo. 126, No. 9, September 1979.

TABLE I.1
EXPERIMENTAL VARIABLES

CELL COMPONENT VARIABLES

- Carbon Support Type
 - Carbon Type
 - Heat Treatment
- Platinum Loading
- Degree of Wetproofing
 - Teflon Content
 - Degree of Sintering

OPERATING VARIABLES

- Temperature (T)
- Cathode Voltage (V_C)
- Partial Pressure of Water Vapor (P_{H_2O})
- Pressure (P)
- Partial Pressure of Oxygen (P_{O_2})

Since acid concentration depends primarily on temperature and partial pressure of water vapor (P_{H_2O}), the independent operating variables that affect the decay rate directly are T , V_C , and P_{H_2O} . Variables such as total pressure (P) and P_{O_2} may or may not directly affect decay rates. To evaluate the effect of pressure, a pressurized test was also planned. This would provide information on the effect, if any, of pressure on the decay rate. To achieve the desired voltage levels, pure O_2 was used as a cathode gas. The partial pressure of water vapor in the cathode gas was varied by controlling the humidification of O_2 . Since P_{H_2O} was selected as the independent variable, P_{O_2} could not be an independent variable but would depend on P_{H_2O} . For this program it was assumed that there is no significant effect of P_{O_2} on decay rate, over the range considered (59-72 kPa).

Representation of decay rate requires measures of decay. Catalyst utilization was used as a measure of decay by the platinum deactivation mode. This was estimated from measured fuel cell performance and limiting current using the performance model.⁵ The limiting current was used as a measure of decay by the diffusion limitation mode.

Using the recommended variables and measures of decay as specified above, a simple decay rate model was formulated:

5. Baker, B., Maru, H., and Patel, D., "Fuel Cell Power Configurations," Final Report Prepared by Energy Research Corporation for Science Applications Inc. under Contract No. 04-117-01, August 1978.

20

A. Rate of Change of Catalyst Utilization

$$\frac{dCU}{dt} = k_{u_0} \exp(-E_u/RT) CU^{\alpha_u} V_C^{\beta_u} P_{H_2O}^{\gamma_u} \quad (I.1)$$

where,

CU = catalyst utilization

t = time

k_{u_0} = decay rate constant as a function of Teflon content and platinum loading

E_u = activation energy for decay mode A

R = universal gas constant

$\alpha_u, \beta_u, \gamma_u$ = statistical parameters

B. Rate of Change of Limiting Current Density:

$$\frac{di_L}{dt} = k_{i_0} \exp(-E_i/RT) i_L^{\alpha_i} V_C^{\beta_i} P_{H_2O}^{\gamma_i} \quad (I.2)$$

where,

E_i = activation energy for decay mode B

i_L = limiting current density

k_{i_0} = decay rate constant as a function of Teflon content, platinum loading

$\alpha_u, \beta_u, \gamma_u$ = statistical parameters

Model A gives CU and model B give i_L as a function of time. Using values of CU and i_L , the performance at time t can be estimated. The above simple form was used with existing data to develop the preliminary aging model.

I.3 Preliminary Aging Model

A preliminary aging model was developed to help the design of experiments. Parameters in the model were estimated by fitting the simple form of the aging model to the existing data. Since the existing data was not specifically obtained for this type of analysis, reduced forms of the aging model were fitted to the data where applicable. As a result, various parameters were estimated separately rather than simultaneously. The parameters estimated were α_u , α_i , E_i . The aging model was adapted for data analysis as follows:

$$\frac{dCU}{dt} = r_u = k_{u_0} \exp(-E_u/RT) CU^{\alpha_u} V_C^{\beta_u} P_{H_2O}^{\gamma_u} \quad (I.3)$$

Taking logarithm on both sides,

$$\ln r_u = \ln k_{u_0} - E_u/RT + \alpha_u \ln CU + \beta_u \ln V_C + \gamma_u \ln P_{H_2O} \quad (I.4)$$

Expanding $\ln r_u$ into a Taylor's series about the center points of the independent variables⁶ gives:

$$\begin{aligned} \ln r_u = & (\ln r_u)_0 + a_1 \left[\frac{1}{T} - \frac{1}{T} \right] + a_2 [\ln CU - \ln \overline{CU}] + a_3 [\ln V_C \\ & - \ln \overline{V_C}] + a_4 [\ln P_{H_2O} - \ln \overline{P_{H_2O}}] + \frac{1}{2} a_{11} \left[\frac{1}{T} - \frac{1}{T} \right]^2 + \frac{1}{2} a_{22} \\ & [\ln CU - \ln \overline{CU}]^2 + \frac{1}{2} a_{33} [\ln V_C - \ln \overline{V_C}]^2 + \frac{1}{2} a_{44} [\ln P_{H_2O} - \ln \overline{P_{H_2O}}]^2 \\ & + a_{12} \left[\frac{1}{T} - \frac{1}{T} \right] [\ln CU - \ln \overline{CU}] + a_{13} \left[\frac{1}{T} - \frac{1}{T} \right] [\ln V_C - \ln \overline{V_C}] + a_{14} \\ & \left[\frac{1}{T} - \frac{1}{T} \right] [\ln P_{H_2O} - \ln \overline{P_{H_2O}}] + a_{24} [\ln CU - \ln \overline{CU}] [\ln P_{H_2O} - \ln \overline{P_{H_2O}}] \\ & + a_{34} [\ln V_C - \ln \overline{V_C}] [\ln P_{H_2O} - \ln \overline{P_{H_2O}}] + \text{higher order terms} \quad (I.5) \end{aligned}$$

6. Ware, C.H. Jr., "Chemical Reaction Rate Equations from Experimental Data," Proceedings of the 1975 Summer Computer Simulation Conference, p. 368.

For a simple linear model, $a_{ij} = 0$. Therefore, $\ln r_u = \ln r_{u_0}$

$$+ a_1 \left[\frac{1}{T} - \frac{1}{T_0} \right] + a_2 \left[\ln CU - \ln CU_0 \right] + a_3 \left[\ln V_C - \ln V_{C_0} \right] + a_4 \left[\ln P_{H_2O} - \ln P_{H_2O_0} \right] \quad (I.6)$$

Comparing (I.4) and (I.6)

$$a_1 = -E_u/R$$

$$a_2 = \alpha_u$$

$$a_3 = \beta_u$$

$$a_4 = \gamma_u$$

Similarly for model B.

$$a_1 = -E_i/R$$

$$a_2 = \alpha_i$$

$$a_3 = \beta_i$$

$$a_4 = \gamma_i$$

The model parameters E , α , β , and γ were estimated using the previous fuel cell data, to obtain a preliminary aging model for guiding the experimental design. The estimation of the parameters is discussed below.

Estimation of α_u

Performance data⁷ of cells (1230, 1258) were analyzed to estimate α_u . Data collected at constant temperature, relatively constant cathode voltage and water partial pressure were used to calculate CU decay rate. The decay rates and CU values were computed for each constant temperature interval (normal, 177°C, 7. Christner, L., George, M., "Electrode Optimization for Phosphoric Acid Fuel Cells," Monthly Technical Status Report No. 7, Contract ET-78-C-03-1873, Prepared for U.S. Department of Energy by Energy Research Corporation, Danbury, CT., December 1978.

and relatively higher temperatures, 191 and 204°C) at which the cells were operated. Under the stated operating conditions the model was further reduced to

$$\ln r_u = \ln r_{u_0} + \alpha_u (\ln CU - \overline{\ln CU}) \quad (I.7)$$

Plots of $\ln r_u$ against $(\ln CU - \overline{\ln CU})$ at each temperature indicated a slope (which represented α_u) of 1.01. The plot for Cell 1230 is presented in Figure I.1. It was also noted that r_u increased with temperature.

Estimation of α_i

The decay rate equation for limiting current Eqn. (I.2) was analyzed for this purpose. The data from the same cells (numbers 1230 and 1258) were fitted to the equation. In the analysis, each constant temperature period was treated separately, assuming the voltage and P_{H_2O} constant. An equation similar to (I.6) will be:

$$\begin{aligned} \ln r_i = \ln r_{i_0} + a'_1 \left(\frac{1}{T} - \overline{\frac{1}{T}} \right) + a'_2 (\ln i_L - \overline{\ln i_L}) + a'_3 \\ (\ln V_C - \overline{\ln V_C}) + a'_4 (\ln P_{H_2O} - \overline{\ln P_{H_2O}}) \end{aligned} \quad (I.8)$$

Under the conditions stated above, (I.8) can be reduced to

$$\ln r_i = \ln r_{i_0} + \alpha_i (\ln i_L - \overline{\ln i_L}) \quad (I.9)$$

The least square fit of the data to the linear equation (I.9) above yielded an estimate of α_i . The results are presented in Table I.2.

FIGURE I.1 PLOT OF $\ln r_u$ AGAINST $(\ln CU - \overline{\ln CU})$ FOR CELL 1230

TABLE I.2

ESTIMATES OF α_i FROM HIGH TEMPERATURE CELL DATA

Cell No.	Temperature During the Period, °C	α_i
1230	177	2.1
	191	2.2
1258	191	2.0
	204	2.7

It can be observed that estimated values of α_i are consistent within the cell and also from cell to cell. The deviation in the case of Cell 1258 at 204°C may be due to a large voltage variation within the constant temperature period. (In the analysis, voltage was assumed to be constant.) For the preliminary aging model, therefore, a value to $\alpha_i = 2$ was used.

Estimation of E_i

The parameter E_i , activation energy for the diffusion limitation decay mode, was estimated using data from Cell 1230. An average of $\ln i_L$ values at various temperatures was obtained, and substituted in equation (I.9). Decay rate r_i was calculated at each temperature as follows:

$$\ln r_i = \ln r_{i_0} + \alpha_i (\ln i_L - \ln i_{L_{\text{overall}}})$$

where,

$\ln i_{L_{\text{overall}}}$ is the mean of $\ln i_L$ values at various temperatures and $\ln i_L$ is at a constant temperature.

$\ln r_i$ was plotted against $1/T$ and the slope of the straight line obtained was assumed to be E_i/R . The estimated value of E_i was 25,150 cal/g mol. The positive value of E_i implies that the decay rate due to the diffusion mode increased with temperature.

Data from cell 1258 were not analysed because of a large voltage variation during the 204°C operating period.

Other Parameters

The parameter k_{u_0} was approximated by taking the exponent of $\ln r_{u_0}$ which is the same as the intercept in Figure I.1. An estimate of k_{i_0} was obtained similarly by plotting $\ln r_i$ against $(\ln i_L - \ln i_L)^0$. The parameter β was not estimated as the data available were at open circuit voltage (which was varying) and not at a particular voltage. It was not possible to estimate other parameters, as appropriate data were not available. For the sake of experimental design, the values of the remaining parameters were selected as listed in Table I.3.

TABLE I.3
PARAMETERS USED IN PRELIMINARY AGING MODEL

PARAMETER	VALUE
k_{u_0}	$2.4 \times 10^{-5} \text{ hr}^{-1}$
E_u	26,000 cal/gmol
α_u	1
β_u	1
γ_u	1
k_{i_0}	0.48 hr^{-1}
E_i	26,000 cal/gmol
α_i	2
β_i	1
γ_i	1

The preliminary aging model was used in the computation of the range of operating variables. The details are given in Task II.2. The final aging model obtained from the perturbation testing is discussed in Section IV.

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TASK II. DESIGN OF EXPERIMENTS

The objectives of this task were to

- Select a statistical design for the experiments;
- Select experimental parameters and operating conditions to yield necessary information in the shortest possible time with reasonable reliability.

II.1 Statistical Design

II.1.1 Operating Variable Design

For the perturbation experiments (based on operating variables), two types of designs were considered: a factorial design and a balanced incomplete block design (BIBD)⁸.

A complete cycle for factorial design is presented in Table II.1. All three operating variables are perturbed in each cell. It can be observed that in one cycle there are two periods (9 and 11) when all variables are at low levels. The lower decay rate at these conditions will require a longer constant condition period for measurement. A center point in the design is desirable because:

- Testing at the center point provides a check on the system behavior;
- It helps estimate the sum of coefficients of the squared terms in the regression equation;
- It provides information on experimental error in operation.

8. Hicks, C., Fundamental Concepts in the Design of Experiments, Second Edition, Holt, Rinehard and Winston, New York 1973.

TABLE II.1

A COMPLETE CYCLE FOR FACTORIAL DESIGN
(Based on Operating Variables)

Time Period	T	V _C	P _{H₂O}
1	O	O	O
2	H	H	H
3	H	H	L
4	H	L	H
5	H	L	L
6	L	H	H
7	L	H	L
8	L	L	H
9	L	L	L
10	O	O	O
11	L	L	L
12	L	L	H
13	L	H	L
14	L	H	H
15	H	L	L
16	H	L	H
17	H	H	L
18	H	H	H
19	O	O	O

Variable Levels: H-High, O-Center, L-Low

Factorial experiments with center points give an estimate of the sum of the coefficients of the squared terms in the regression analysis. Thus, it may or may not detect non-linearity in the decay model.

A complete cycle for BIBD is presented in Table II.2. In this design, only two of the three variables are perturbed in each cell. To get information on the main effects and on two factor interactions, three identical cells of each type are required which will include all three possible pairs of perturbed variables. This design has some advantages over the factorial design. BIBD gives an estimate of the coefficient of each squared term which enables detection of any nonlinearity in the model. Also a measurable decay can be attained in a reasonable period since there is always at least one variable at center level. Consequently, BIBD is preferred to the factorial design.

The BIBD presented above was modified to provide for orthogonal blocking. In the absence of orthogonal blocking, the cell to cell variability will be reflected in biased estimates of the coefficients to be evaluated. This bias means that the numerical values of the coefficients will be too high or too low depending on how the operating variables are assigned to the cells. The orthogonal blocking is not available, however, for three variable BIBDs. It was, therefore, achieved by selecting an orthogonal design in four variables and eliminating the fourth variable by treating it as a "dummy".

A complete cycle of BIBD with four variables is shown in Table II.3. The operating sequence consists of a 2×2 factorial in T and V_C , followed by one variable perturbation in P_{H_2O} (since the fourth variable is a dummy). Since all three operating variables are perturbed in each cell, the design provides for orthogonal blocking. However, in this study only one combination

TABLE II.2

A COMPLETE CYCLE FOR BIBD WITH THREE OPERATING VARIABLES

Time Period	T	V _C	P _{H₂O}
1	O	O	O
2	H	H	O
3	H	L	O
4	L	L	O
5	L	H	O
6	O	O	O
7	L	H	O
8	L	L	O
9	H	L	O
10	H	H	O
11	O	O	O
Variable Levels: H-High, O-Center, L-Low			

Note: At least three cells are required of each build type to execute the three combinations:

- T and V_C factorial and P_{H₂O} at center level (shown above)
- V_C and P_{H₂O} factorial and T at center level
- P_{H₂O} and T factorial and V_C at center level

TABLE II.3

A COMPLETE CYCLE OF BIBD WITH FOUR VARIABLES
(including one dummy variable)

Constant Condition Period	T	V_{C-}	P_{H_2O}
1	O	O	O
2	H	H	O
3	L	H	O
4	L	L	O
5	H	L	O
6	O	O	O
7	O	O	H
8	O	O	L
9	O	O	L
10	O	O	H
11	O	O	O
12	O	O	H
13	O	O	L
14	O	O	L
15	O	O	H
16	O	O	O
17	H	L	O
18	L	L	O
19	L	H	O
20	H	H	O
21	O	O	O

Levels: H - High; O - Center; L - Low

NOTE: The above design is symmetrical with respect to
Period 11.

was used instead of three combinations listed at the bottom of Table II.2, because of limited test stations. Thus more information was obtained on replication instead of getting information about P_{H_2O} interactions.

II.1.2 Cell Component Variable Design

The factorial experiments based on cell component variables with selected variable levels are listed in Table II.4. This required four different types of cells. The experiments will evaluate the effect of platinum loading and Teflon content along with their interactions.

A summary of all cells of different build types is presented in Table II.5. Eighteen perturbation cells were assembled as indicated. Four more cells of Build Type IV were operated without perturbations to establish baseline performance and generate long-term data for model verification. These cells were operated at center point conditions. This means a total of 22 cells operating at atmospheric pressure. In addition, as mentioned in the table, one cell of Build Type IV was operated at 50 psia to study the effect of total pressure on performance decay.

TABLE II.4
FACTORIAL EXPERIMENTS
(Based on Cell Component Variables)

Build Type	Cathode Pt Loading, mg/cm ²	Teflon Content, w/o
I	0.3	40
II	0.6	40
III	0.3	45
IV	0.6	45

II.2 Selection and Testing of Operating Variable Levels

The difference in levels (range) of operating variables affects the standard deviation (SD) of parameters. The SD of the parameters and hence the precision of predicted fuel cell life are inversely proportional to this difference. The levels should be selected, therefore, so that the life can be estimated with a reasonable precision.

TABLE II.5 SUMMARY OF TEST CELLS

Build Type	No. of Cells	Operation Mode
I	6	Perturbations
II	3	Perturbations
III	3	Perturbations
IV	6	Perturbations
IV	4	Baseline
IV	1	Pressurized

A computer program was prepared to estimate appropriate ranges of operating variables for a given precision in the estimate of life. The logic of the program is outlined in Figure II.1. It was found that the ranges estimated were too large to be practical.

A new approach, therefore, was tried. Practical levels were selected and tested in the fuel cell to see if measurable decay can be obtained in a reasonable period of time. The selected levels are as in Table II.6. The performance decay observed as a result of the primary decay modes is pre-

FIGURE II.1

LOGIC OF COMPUTER PROGRAM TO AID IN DESIGN OF EXPERIMENTS

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sented in Table II.7. It can be seen that the levels chosen for perturbation experiments do provide measurable decay in a reasonable period of one week. The voltage levels were revised to obtain better precision and stability in the measured current. The following factors were considered in the selection of the new voltage levels:

- The 'high' voltage level should produce current densities greater than 40 mA/cm^2 since, at lower current densities, the sensitivity of current to a voltage change is considerably lower.

- The 'low' voltage level should produce current densities lower than 200 mA/cm^2 since, at higher current densities, the ability to control current and hence cathode voltage is not satisfactory.

The revised voltage levels are presented below:

High	0.810V
Center	0.770V
Low	0.730V

From the results of the pre-testing experiments, durations of the constant condition periods were estimated and are shown in Table II.8. With these durations, after allowing for a stabilization time between perturbation periods, the entire perturbation cycle was estimated to be complete in approximately 3600 hours.

TABLE II.6
LEVELS OF OPERATING VARIABLES

VARIABLE	LEVEL		
	High H	Center O	Low L
T, °C	191	184	177
V _C , Volts	0.86	0.81	0.76
P _{H₂O} , kPa	42	35	29

TABLE II.7
CELL DECAY AT DIFFERENT LEVELS OF OPERATING VARIABLES

CONSTANT CONDITION PERIOD NO.	VARIABLES			PERIOD, HOURS	CURRENT, A		CATALYST UT., %	
	T, °C	V _C , V	P _{H₂O} , kPa		Initial	Final	Initial	Final
1	177	0.760	25	90	1.90	1.80	20.7	17.5
2	191	0.760	39	72	2.24	2.06	28.9	24.5
3	184	0.760	27	48	1.77	1.69	17.6	16.3
4	184	0.780	32	48	1.39	1.30	25.0	22.8
5	177	0.700	40	144	4.26	3.71	15.1	12.5
6	177	0.740	34	144	2.01	1.51	15.9	12.0

Cell Components:

Anode: 0.6 mg Pt/cm², 40% TFEFuel: H₂

Cathode: Same as Anode

Oxidant: O₂

Matrix: SiC

TABLE II.8

SELECTED DURATIONS OF PERTURBATION PERIODS

Constant Condition Period	T	V _{IR}	P _{H₂O}	Duration of Period, Days
1	O	O	O	5
2	H	H	O	4
3	L	H	O	5
4	L	L	O	7
5	H	L	O	5
6	O	O	O	5
7	O	O	H	4
8	O	O	L	7
9	O	O	L	7
10	O	O	H	4
11	O	O	O	5
12	O	O	H	4
13	O	O	L	7
14	O	O	L	7
15	O	O	H	4
16	O	O	O	5
17	H	L	O	5
18	L	L	O	7
19	L	H	O	5
20	H	H	O	4
21	O	O	O	5

TASK III. TESTING

The objectives of this task were to:

- Generate data at center point conditions (Baseline cells)
- Generate data under perturbed conditions (Perturbation cells)
- Post-test evaluation of cell components to rationalize the cell behavior.

III.1 Test Stations

A test facility was designed and constructed for a total of 22 atmospheric pressure cells. Figure III.1 shows the details of a test stand. The important features of these test stands are listed in Table III.1.

All the meters were digital and calibrated. A precision of 10 mA was attained in ammeter to measure the decay in current precisely. Temperature controller for the cell had a dual set-point. One set-point was to control cell temperature; the other was to shut off heating system and remove the load from fuel cell circuit to prevent cell damage when cell temperature increased beyond the set upper limit. Cathode gas flexibility made it possible to use air during break-in period, O_2 during perturbation or baseline testing and an O_2 - N_2 mixture during i_L measurements. To vary humidification level in oxidant, a humidifier with capacity of humidifying up to 20% water vapour level was also included. The complete test facility is shown in Figure III.2.

Proper settings were established in the temperature controller and Variacs for the oxidant humidifier, corresponding to 100% saturation of O_2 at 46 and 50°C. These levels correspond to center and high levels of P_{H_2O} . Initially an effort was made to control the temperature of the exit gas (from the humidifier) at the saturation temperature by controlling the heating of humidifier

FIGURE III.1 TEST-STANDS FOR PREDICTIVE TESTING

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TABLE III.1
SPECIAL FEATURES OF TEST STANDS

Voltmeter	Digital, Precision 1 mV
Ammeter	Digital, Precision 10 mA
Temperature Controller	
For Cell	Precision - 2°C, Dual Set Point
For Humidifier	Precision - 1°C
Pyrometer	Digital, Precision 1°C, Multiswitch
Cathode Gas Flexibility	O ₂ , Air, O ₂ -N ₂ Mixture,
	Humidification up to 20% Humidity

FIGURE III.2 TEST FACILITY FOR PREDICTIVE TESTING

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water. However, the lag in the system caused large variations in exit gas temperature, so this method was discarded. Finally the water temperature in the humidifier was controlled by the temperature controller at a certain level (higher than saturation temperature) so that the exit gas (from the humidifier) was saturated at the required temperature. The humidifier exit gas temperature was maintained the same or slightly higher than the saturation temperature, by wrapping heater tape around the exit tube (going to fuel cell cathode inlet), to prevent condensation of water vapor.

III.2 Test Cell For Predictive Testing

Statistical testing in this program imposed stringent requirements on test cell performance in terms of performance level and reproducibility. Also, because perturbation testing was required at several temperatures, water vapor concentrations and voltage levels, some component changes were made based on available data. Candidate test cell configurations were pre-tested to ensure reproducibility and performance levels required for this study. Additional changes implemented in the test cell configuration and assembly procedure as a result of this testing are discussed below.

III.2.1 Reduced Resistance of Test Cells

Resistance of the test cells was observed in the range of 15 to 20 m Ω which was higher than the normally expected range of 10 to 15 m Ω . An effort was made to reduce the resistance. Resistance of test cells was decreased by achieving improved plate to backing paper contact. Contact resistance decreased with increased compression on the backing paper. The test cell schematic shown in Figure III.3 suggests that higher compression on the backing paper can be achieved by lowering the shim thickness. Experimental results summarized in Table III.2 suggest

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FIGURE III.3 PLATE TO BACKING PAPER CONTACT HAS BEEN IMPROVED BY REDUCING SHIM THICKNESS

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TABLE III.2

AVERAGE RESISTANCE OF 25 cm² TEST CELLS

No. of Cells Studied	Shim to Electrode Clearance (each side), mil	Test Cell Resistance mΩ	
		Mean	Std. Dev.
11	5-7	20	2.94
		15	1.84
11	8-10	15	1.84

TABLE III.3

REPRODUCIBILITY AND STABILITY OF INITIAL TEST CELLS

NO. OF TEST CELLS STUDIED	PLATES USED	STARTING PERFORMANCE, V _{IR} , mV		PERFORMANCE DECAY WITHIN FIRST 24 Hrs, mV		
		At 100 mA/cm ²	At 200 mA/cm ²	At 100 mA/cm ²	At 200 mA/cm ²	OCV
10	"Thick" 25% Varcum Plates	685-707	638-658	26-55*	25-60*	20-54
4	"Thin" 25% Varcum Plates	710-720	660-670	12-15	10-12	10-12

* Decay process continued even after 24 hours but at a slower rate.

that increasing the shim to electrode clearance from 5 - 7 mils to 8 - 10 mils lowered the contact resistance and, as a result, cell resistance dropped by about 5 m Ω . No ill effect was observed on the performance and stability of the test cells due to higher compression on the electrode and on the backing.

III.2.2 Improved Stability and Reproducibility of Test Cells

Most 25 cm² test cells initially built for this program were not sufficiently stable or identical in performance to fulfill the stringent conditions required for a meaningful statistical analysis under this program. Some results of Table III.3 and polarization experiments performed at different time intervals on a decaying test cell suggested loss of effective area of the cathode and/or anode. The plausible reasons were: irreversible drying of electrodes, major obstruction to gas flow pattern, and poisoning of the electrodes. The following attempts were undertaken to identify and eliminate the factor causing the secondary decay.

To check whether the electrodes were dry, electrolyte content (extent of wetting) of electrodes was measured for a post-test cell which had exhibited significant decay (53 mV in 96 hours). Electrolyte content was fairly acceptable: 1.15 and 1.08 $\mu\text{l}/\text{mg}$ of carbon for the anode and cathode, respectively. Electrolyte content of the Mat-1 matrix from another cell was also within acceptable limits.

While searching for major obstructions to gas flow, some engineering problems were detected, such as: asymmetry in the anode and the cathode rib areas, and different dimensions of the two end channels compared to other channels. Corrections were implemented. Some modification was performed on the gas flow channels to improve the uniformity in gas flow pattern. These modifications did not significantly improve test cell performance.

Electrode poisoning, the third possible factor, might be caused by the corrosion products from acid attack on the plates. In order to find which plates' corrosion products caused this poisoning, a comparison was made of "thick" and "thin" (molded ~6 months earlier) Varcum plates. Four test cells built with "thin" plates exhibited better performance than the cells with thick plates. Still an improvement was necessary. Most of the decay, which was very small, occurred in the first 24 hours. Initial performance and the performance decay of these test cells are compared with test cells built from "thick" plates in Table III.3. The decay of test cells built from "thick" plates continued even after 24 hours. This indicated that the corrosion products of the "thick" plates might be causing electrode poisoning.

As an effort to solve the above problem, the "thick" Varcum plates were heat treated. The details are discussed below:

- Improved Resin/Graphite Plates

Three cells were built using resin-bonded graphite plates with the following treatments;

- a) Reused plates - used in a cell operated for 700 hours at 177°C
- b) "Leached" plates - leached in 100% H_3PO_4 at 170°C for 48 hours.
- c) PES-coated plates - coated with polyether sulphone on channel side except in the rib area.

It was observed that the decay rate was slower in these cells than in cells built with fresh, "thick" Varcum plates; however, additional improvement was necessary.

- Heat Treated Plates

Three cells (Nos. 60, 61, and 62) were built with identical cell components to study the reproducibility and stability of performance. The specifications of cell components are presented below:

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Anode: Catalyst Loading 0.6 mg/cm^2
Teflon Content 40%
Cathode: Catalyst Loading 0.5 mg/cm^2
Matrix: SiC

In all cells a 10 mil compression was applied to each electrode. Plates used in cells were heat treated according to the procedure being developed under ERC's DOE Contract DEN3-67. The results obtained during testing are summarized in Table III.4. The three cells were almost identical in performance. The variation of IR-free voltage at 200 mA/cm^2 was within $\pm 2 \text{ mV}$. The OCV for Cell 60 was lower than that for Cells 61 and 62. Decay in IR-free performance during the first 8 hours was very small (9 to 12 mV). Total initial decay for all three cells was within 12 to 15 mV. The performance after 330 hours yielded a catalyst utilization of 20 to 21%.

● Conclusion

The satisfactory result obtained with heat treated plates indicated that the corrosion products of "thick" Varcum plates may have poisoned the electrodes, causing a high initial performance decay and that heat treating is the solution.

III.2.3 Compatibility Testing of Mat-1 Matrix

Since the Mat-1 matrix has shown promising results in PAFC tests at ERC, it was selected for the perturbation testing. Its compatibility with the present test cell configuration needed to be tested, however.

Cell 63 was assembled with a Mat-1 matrix and heat-treated plates. Cell component specifications and performance data are summarized in Table III.5. The initial IR-free performance at 5A (200 mA/cm^2) was 0.630V. Total initial decay in performance was only 2 mV. The peak performance attained by the cell was satisfactory for the perturbation testing.

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TABLE III.4 STABILITY AND REPRODUCIBILITY OF CELLS WITH HEAT TREATED PLATES

PERFORMANCE CHARACTERISTIC	Cell 60	Cell 61	Cell 62
Initial V_{IR} @ 5A, V	0.659	0.660	0.656
Peak V_{IR} @ 5A, V (Before first decay)	0.659	0.663	0.659
Decay in V_{IR} @ 5A during first 8 hrs, mV	12	9	9
Lowest V_{IR} @ 5A, V (Total Decay = Peak V_{IR} - Lowest V_{IR})	0.644 ($\Delta_T=15mV$)	0.648 ($\Delta_T=15mV$)	0.647 ($\Delta_T=12mV$)
Peak IR Free Performance @ 200 mA/cm ² , V	0.669	0.666	0.668
Initial OCV, V	0.891	0.946	0.945
OCV at Peak Performance, V	0.946	0.940	0.950
Ohmic Resistance, m Ω	10	10	11.5

Operating Conditions: 177°C, air, 5A. (= 200 mA/cm²)

TABLE III.5
PERFORMANCE CHARACTERISTICS OF MAT-1 MATRIX CELLS

CELL NO.	63	64	65	66
TEST OBJECTIVE	Mat-1	Mat-1	Mat-1	Mat-1
ANODE				
Catalyst Loading, mg/cm ²	0.6	0.6	0.6	0.6
Teflon Content, %	40	40	40	40
CATHODE				
Catalyst Loading, mg/cm ²	0.6	0.6	0.6	0.6
Teflon Content, %	40	40	40	40
MATRIX	Mat-1	Mat-1	Mat-1	Mat-1
PEAK IR-free PERFORMANCE, V	0.665 432 hrs.	0.656 288 hrs.	0.654 480 hrs.	0.661 288 hrs.

Operating Conditions: 177°C, 5A, air.

Three more cells (Nos. 64, 65, and 66) with Mat-1 matrix were assembled with identical components to check the reproducibility of performance. The variation of IR-free performance between the cells was within ± 5 mV which was reasonable (cf. Table III.5).

After testing the compatibility of the Mat-1 matrix, a decision was made to go ahead with the building of perturbation test cells.

III.3 Perturbation Test Cells

All plates for perturbation test cells were heat treated and the current collectors were gold plated. Nine perturbation test cells: 6 (No. 101-106) of Build Type IV and 3 (No. 107-109) of Build Type III were assembled on the same day. This was to minimize any effect of external, uncontrolled factors. The other 9 perturbation test cells: 6 (No. 110-115) of Build Type I and 3 (No. 116-118) of Build Type II were assembled together on another day, a week later. Baseline cells 119 and 120, 121 and 122 were also built on same day. Testing was initiated soon after the cells reached peak performance. The performance reproducibility of test cells, testing and results obtained are discussed in the following subsections.

● Performance Reproducibility of Test Cells

Cell components and performance characteristics of the test cells are summarized in Tables III.6 and III.7. Cathodes of the cells represented four build types with respect to catalyst loading and Teflon content. Reproducibility of various performance parameters within each build type is summarized in Table III.8. The performance variability (IR-free) within each of the four build types was within ± 5 mV. This demonstrates a very good performance reproducibility. Other characteristics such as ohmic resistance (r), open circuit voltage (OCV) and

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TABLE III.6 PERFORMANCE REPRODUCIBILITY OF PERTURBATION CELLS

CELL NO.	101	102	103	104	105	106	107	108	109
CATHODE Catalyst Loading, mg/cm ²	0.6	0.6	0.6	0.6	0.6	0.6	0.3	0.3	0.3
Teflon Content, %	45	45	45	45	45	45	45	45	45
PEAK PERFORMANCE ^a IR-Free, V @ hours	0.655 336	0.655 288	0.651 288	0.655 288	0.652 288	0.658 288	0.643 336	0.634 456 ^b	0.644 336
Catalyst Utilization, %	17.3	17.3	15.6	17.3	16.0	18.7	21.9	17.4	22.5
O ₂ gain @ 200 mA/cm ² , mV C	68	66	68	64	67	67	64	68	59
OHMIC RESISTANCE, mΩ	8.5	9.3	9.2	8.5	8.4	8.4	8.9	9.3	9.4
OCV, V C	0.920	0.920	0.925	0.925	0.930	0.930	0.920	0.920	0.925

CELL NO.	110	111	112	113	114	115	116	117	118
CATHODE Catalyst Loading, mg/cm ²	0.3	0.3	0.3	0.3	0.3	0.3	0.6	0.6	0.6
Teflon Content, %	40	40	40	40	40	40	40	40	40
PEAK PERFORMANCE ^a IR-free, V @ 216 hours	0.624	0.632	0.630	0.624	0.630	0.625	0.670 ^d	0.667	0.668
Catalyst Utilization, %	16.4	20.1	19.2	16.4	19.2	16.9	22.7	21.0	21.5
O ₂ gain @ 200 mA/cm ² , mV C	68	64	68	66	66	66	65	66	69
OHMIC RESISTANCE, mΩ	11.6	10.5	9.4	9.8	9.9	10.5	9.0	9.8	8.3
OCV, V C	0.920	0.925	0.920	0.920	0.920	0.920	0.930	0.930	0.930

- a. Operating Conditions: 177°C, 5A, Air
b. 0.632V @ 336 hrs.
c. @ 216 hrs.
d. @ 142 hrs.

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TABLE III.7 PERFORMANCE REPRODUCIBILITY OF BASELINE CELLS

CELL NO.	119	120	121	122	Avg.	Range
CATHODE						
Catalyst Loading, mg/cm ²	0.6	0.6	0.6	0.6		
Teflon Content, %	45	45	45	45		
PEAK PERFORMANCE*						
IR-free, V	0.667	0.667	0.667	0.660	0.665	± 0.004
@ hours	312	312	288	288		
Catalyst Utilization, %	23.5	23.5	23.5	19.7	22.6	± 1.900
OHMIC RESISTANCE, m Ω	9.2	9.2	10.0	10.6	9.8	± 0.700
OCV, V †	0.920	0.920	0.925	0.925	0.923	± 0.003

* Operating Conditions: 177°C, 5A, Air.

† @ 312 hours

TABLE III.8 REPRODUCIBILITY WITHIN A BUILD TYPE

	BUILD TYPE			
	I	II	III	IV
Performance Characteristics	0.3 mg/cm ² 40% TFE Cells 110-115	0.6 mg/cm ² 40% TFE Cells 116-118	0.3 mg/cm ² 45% TFE Cells 107-109	0.6 mg/cm ² 45% TFE Cells 101-106
Peak Performance (IR-free) @ 5A, mV	628 $\pm$ 4.0	668 $\pm$ 1.5	640 $\pm$ 5.0	654 $\pm$ 3.5
OCV, mV	921 $\pm$ 2.5	930 $\pm$ 0.0	922 $\pm$ 2.5	925 $\pm$ 5.0
O ₂ gain, mV	66 $\pm$ 2.0	67 $\pm$ 2.0	64 $\pm$ 4.5	67 $\pm$ 2.0
Ohmic Resistance, m Ω	10.3 $\pm$ 1.1	9.0 $\pm$ 0.8	9.2 $\pm$ 0.3	8.7 $\pm$ 0.5

* $\pm$ numbers represent range of quantities

oxygen gain also showed a good reproducibility. Cell resistance for each build type varied within $\pm 0.8 \text{ m}\Omega$ except for Cell 110, whose resistance increased by $0.5 \text{ m}\Omega$ from a previous measurement of $11.0 \text{ m}\Omega$. OCV for all the cells showed the same reproducibility as the IR-free performance. Oxygen gain ranged from 74 to 69 mV, except for Cell 109 which had 59 mV. This excellent reproducibility in performance parameters established excellent reproducibility of components and build procedures, and imparted confidence in the statistical testing. The accuracy of measuring performance and O_2 gain was within $\pm 1 \text{ mV}$; measurement accuracy of ohmic resistance was also excellent.

III.4 Perturbation Testing

After achieving peak performance in the test cells, perturbation testing was initiated. The cycle of perturbation was completed on all 18 cells*.

During each constant condition period, measurements of r , current (I) and terminal cell voltage (V) at operating conditions and limiting current at low O_2 concentration were conducted at the beginning and at the end of the period. Measurements of r , I and V were taken every day during each period. The experimental data was then processed by a computer program which estimated catalyst utilization, CU , and limiting current density, i_L , for data analysis. The program mainly consisted of the cell performance model.

During Period 16, Cell 102 showed a large increase in resistance (from 31 to $120 \text{ m}\Omega$ during a weekend). The cell was terminated since the desirable voltage level was not attainable. Elimination of this cell from the test data did not affect the data analysis, because 5 other cells of this build type provided

* Cell 102 terminated after Period 16 because of large increase in ohmic loss. Cell 106 terminated after Period 19 and Cell 117 terminated after Period 10 because of increased ohmic loss after power failure.

the replicates. During Period 20 for Cells 101 and 103 thru 109 and Period 18 for Cells 110 thru 116 and 118, testing was interrupted twice: first due to power shutdown and second due to H_2 supply cut-off. Cell performance was affected because of these interruptions: ohmic resistance increased and cell performance decreased. Soon after the cell performance stabilized, the perturbation conditions were re-established, and testing was resumed. Cell 106 was terminated since the desired voltage level was not achievable.

At the completion of perturbations, all eighteen cells were terminated. The post-test findings from the disassembly of these cells are reported in Section III.8.

III.5 CU and i_L Decay

Computational methods for calculation of CU and estimation of i_L were finalized. (Appendices A and B). Using these methods, i_L and CU data were computed. The CU and i_L decay plots for Cell 101 (Build Type IV, 0.6 mg/cm^2 Pt loading, 45% TFE) and Cell 107 (Build Type III, 0.3 mg/cm^2 Pt loading, 45% TFE) are shown in Figures III.4 and III.5, respectively. The decay rates in all 21 periods of these cells are listed in Table III.9. The decay plots for Cell 110 (Build Type I, 0.3 mg/cm^2 , 40% TFE) and Cell 116 (Build Type II, 0.6 mg/cm^2 , 40% TFE) are presented in Figures III.6 and III.7, respectively. The decay rates are summarized in Table III.10. Test conditions of Periods 1 and 6 represent the center levels of the variables; conditions of Periods 2 and 4 correspond to high and low levels of temperature and cathode potential, respectively. As expected, the observed catalyst utilization decay rate is higher in Period 2 and lower in Period 4 compared to Periods 1 and 6. It can also be observed that CU varies linearly with time during a perturbation period. The comparison of decay rates between Periods 2 and 3 and between Periods 4 and 5 showed temperature effect. Comparison between Periods

FIGURE III.4 CU AND i_L DECAY OF CELL 101

D1389

FIGURE III.5 CU AND i_L DECAY OF CELL 107

D1390

TABLE III.9

CU AND i_L DECAY RATES OF
TYPICAL CELLS OF BUILD TYPES IV AND III

	CELL 101		CELL 107	
PERIODS	$-\frac{dCU}{dt}$	$-\frac{di_L}{dt}$	$-\frac{dCU}{dt}$	$-\frac{di_L}{dt}$
	$10^{-2}\%/hr$	$10^{-2}A/cm^2.hr$	$10^{-2}\%/hr$	$10^{-2}A/cm^2.hr$
1	1.0394	0.5597	1.8643	0.1063
2	3.4691	0.4614	4.5839	1.1578
3	3.8449	0.2749	4.0806	0.5736
4	0.5702	0.1937	1.2343	0.7034
5	0.4770	0.3196	1.6553	0.0833
6	1.6839	0.3159	0.9120	1.9100
7	1.9301	0.7830	1.0384	0.3674
8	1.5884	0.3703	2.8301	0.3392
9	1.6453	0.3454	1.9175	0.0366
10	2.2644	0.4338	2.9465	0.3732
11	1.8723	0.3061	3.3036	0.3488
12	0.7907	0.2748	4.8510	1.2924
13	-0.0875	0.3568	-0.0553	1.0767
14	1.0367	0.1806	7.0112	0.3669
15	0.9591	0.2231	1.4497	0.4629
16	1.7665	0.3977	3.2367	0.0301
17	0.5322	0.3376	1.4625	0.7301
18	0.4836	0.3403	0.8953	1.1314
19	1.1916	0.1326	1.9464	0.6555
20	2.5558	0.2805	8.2506	0.3627
21	1.9300	0.2812	3.0638	0.3544

FIGURE III.6 CU AND i_L DELAY OF CELL 110

D1409

FIGURE III.7 CU AND i_L DECAY OF CDLL 110

n1410

TABLE III.10

CU AND i_L DECAY RATES OF
TYPICAL CELLS OF BUILD TYPES I AND II

	CELL 110		CELL 116	
PERIODS	$-\frac{dCU}{dt}$	$-\frac{di_L}{dt}$	$-\frac{dCU}{dt}$	$-\frac{di_L}{dt}$
	$10^{-2}\%/hr$	$10^{-2}A/cm^2.hr$	$10^{-2}\%/hr$	$10^{-2}A/cm^2.hr$
1	2.4569	0.2673	3.1459	0.3764
2	6.0563	0.1641	2.7224	0.1767
3	2.2675	0.0225	5.6562	0.1367
4	0.7982	0.4457	1.1718	0.9340
5	1.9053	0.1771	1.2716	0.7491
6	3.5092	0.3873	8.6489	0.2101
7	2.9577	0.0683	1.8136	0.5427
8	4.0825	0.3557	1.9351	0.1633
9	3.1029	0.3190	2.2011	1.1112
10	0.7499	0.3012	8.0260	0.6631
11	3.0453	0.6440	0.7878	0.1432
12	2.4434	0.3499	1.1857	0.2793
13	-0.0095	0.2945	1.4310	0.4911
14	2.4130	0.2565	1.5718	0.5503
15	2.4623	0.7683	0.3492	0.1685
16	4.0856	0.2685	1.4639	0.3730
17	1.8953	1.0623	0.3267	-0.0122
18	0.6768	0.5991	0.3646	0.2549
19	4.1433	0.4263	1.5516	0.0135
20	7.4744	0.2731	3.0909	0.0724
21	2.5758	0.1635	0.7472	0.2199

3 and 4 and between Periods 5 and 2 showed cathode potential effect on decay rates. It was observed that, for the selected levels of VC and T, the effect of cathode potential variations on CU decay rate was more pronounced than that of temperature variations.

The other cells behaving similarly except for Cells 102, 106, 109, and 117. These cells showed significant increases in r . The increase in r in these cells was also accompanied by a decrease in performance (i.e., I , i_L , CU). Cell 117 ultimately showed a sudden large increase in r (to 72 m Ω), causing cell failure; the cell was terminated. To minimize any cell failure by unexpected increases in r , the duration of constant condition periods was reduced from 4, 5 and 7 days to 3, 4 and 5 days, respectively.

After the completion of all 21 perturbations, testing was terminated. Most of the data obtained during perturbation testing was acceptable and was used in regression analysis. The data of Periods 20 and 21 for Build Types III and IV and Periods 18 thru 21 for Build Types I and II were not used in analysis because of disturbance in testing. This should not affect our data analysis because the lost data only represents 15% of the total data. The results are discussed under Data Analysis.

III.6 Baseline Cells

Four baseline cells were operated at center point conditions. The cells completed ~5600 hours. The long-term data was used to verify the aging model. The details are presented in Task IV. Performance decay of Cell 121 is shown in Figure III.8. The small discontinuities in performance was observed mostly at acid additions. Ohmic resistance of the cell is also included in the plot. As can be seen, interruptions due to power failure and H₂ shut-off caused a substantial increase in

FIGURE III-8 LIFE GRAPH OF BASELINE CELL (NO. 121)

D1643

resistance. A correlation of this with the performance loss and resistance increase due to electrolyte loss are noticeable. Addition of electrolyte recovered the performance completely and reduced the resistance to some extent.

The operating temperature of Cells 119 and 120 was increased to 191°C after 2400 hours to determine whether the gradual cell resistance increase in perturbation cells was caused by the severe operating conditions or just the perturbations. The plot of r against time for these cells indicated that the resistance did not increase at a faster rate after the increase in temperature. This suggests that the rate of increase in ohmic resistance does not depend on operating conditions.

III.7 Pressurized Cell

Cell 125 with a cathode Pt loading of 0.6 mg/cm² and a Teflon content of 40% was pressurized to 345 kPa (50 psia) and operated at center point conditions. After ~1000 hours, the cell was depressurized by the safety system during a power failure. Since this affected cell performance, the test was terminated. The measured performance (in terms of current), is plotted against time in Figure III.9. The decay at 184°C was not continuous, which may be due to the inaccuracies in resistance measurements of the pressurized cell (long terminals). To visualize a continuous decay, temperature and voltage were increased to 191°C and 0.810V. The decay was fast but a cell failure was suspected based on very high decay rate. The cell had operated for about 72 hours at these elevated conditions when the power failure occurred. Effect of pressure on performance decay is examined in Task IV.

III.8 Post-Test Analysis

III.8.1 Disassembly of Test Cells

All 18 cells were disassembled for post-test analysis at

FIGURE III.9 PRESSURIZED CELL DECAY

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the end of perturbation testing. Components of Cells 101, 103, 104, 105, 107, 108, 110, 112, 114, and 115 were found in normal conditions, except for cells 105 and 108. In some cells, backings were crushed but no acid leaked through. Cells 105 and 108 had acid wet backings. Cell 110 had a cracked anode plate but no acid leakage. The remaining cells are discussed below.

Cell 102: Disassembly of Cell 102 revealed that a portion of the cathode backing (facing the acid channel) was wet and had disintegrated; the cathode plate was also corroded in the lower half of the channel area.

Cell 106: Cell 106 had a hole in the cathode backing along the exhaust channel. The hole which developed during testing was sealed with Viton. The plate surface opposite the acid channel and 1/4 of the channel area were found to be soft.

Cell 109: During disassembly of Cell 109, the anode backing and plate were found to be cracked, but no acid had leaked through. The cathode backing was cracked along inlet and exhaust channels and was wet. The cathode plate was dry but softened in the area opposite the wet backing. A crack was observed in the center of the plate.

Cell 111: Anode plate was broken at lower left corner. Cathode backing was cracked across bottom and up along right side. It was wet along lower crack. The cathode-SiC was disintegrated over cracked area of backing. Some softening was observed on cathode plate inner surface, around surface facing acid channel and lower left channel area. Plate was cracked across exhaust channel.

Cell 113: Cathode backing was wet in lower left corner. SiC layer was broken down under wet area of backing. Cathode plate inner surface facing the acid channel and lower right channel area were soft.

Cell 116: Cathode backing was wet in right lower corner.

Cathode plate inner surface was soft under acid channel and upper right side.

Cell 117: Cathode backing was wet and disintegrated. Cathode plate was corroded. The highest corrosion was near exhaust channel.

Cell 118: Cathode backing was wet along exhaust channel. Cathode plate inner surface was soft under acid channel and upper right side.

Pre and post-test ECA (Electrochemical area) measurements of the electrodes are discussed next.

III.8.2 ECA Measurements

• Pre-Test ECA's

The catalyst used in the fabrication of the electrodes was 10% Pt supported on carbon black (Vulcan XC-72). In calculating catalyst utilization values, it was assumed that after the break-in period, i.e., when the actual testing period started, the catalyst possessed an actual surface area of 50 m²/g. It should be noted that the initial true Pt area is expected to be much higher. An attempt was made to measure the initially available true area of the catalyst used via electrochemical area measurement technique (ERA*).

The ECA of two fresh samples from an electrode[†] (0.6 mg/cm², 40% TFE) was measured using a floating electrode cell set-up. A typical voltammogram (showing well defined and literature reported hydrogen absorption and desorption peaks) obtained from the first samples is shown in Figure III.10. The hydrogen absorption charge estimated from this figure provided a Pt area

* Area related to the hydrogen absorption/desorption charge.

[†] The cathode of Cells 116 thru 118 came from this 5x15 in. electrode.

D1412

FIGURE III.10 POTENTIODYNAMIC CURRENT/POTENTIAL
 PROFILE FOR VULCAN SUPPORTED CATALYST

of $106 \text{ m}^2/\text{g}$. A catalyst area of $102 \text{ m}^2/\text{g}$ was estimated from the second sample. The values are in agreement with the known ECA's of this type of catalyst.

Pretest ECA's for cathodes from four cells each representing a build type, were measured for comparison with post-test ECA's to see the extent of decay. ECA's ranged from 90 to $100 \text{ m}^2/\text{g}$ which is fairly reasonable for Vulcan XC-72 type catalyst. Cathode of Cell 110 had ECA of $50 \text{ m}^2/\text{g}$ which is considerably low. This may be attributed to the comparatively small sample size and/or insufficient wetting.

- Post-Test ECA

ECA's of Cells 103, 107, 110 and 117 (cathodes) were also measured at the end of perturbation testing (~ 3000 hours). A loss of $60\text{--}85 \text{ m}^2/\text{g}$ was observed in ECA during the testing, which seemed reasonable. The values obtained were compared with catalyst utilization computed at the end of perturbation testing. It was observed that the ECA and CU did not correlate well. The question of this correlation is, however, beyond the scope of this study.

TASK IV. DATA ANALYSIS AND MODEL VERIFICATION

Objectives of this task were:

- Interpretation of Results -
 - a) Elimination of "unimportant" parameters.
 - b) Incorporation of new parameters, if necessary.
 - c) Modification of mathematical form when needed.
- Verification of aging model by fitting the experimental data of unperturbed tests.

IV.1 Data Analysis

A multiple regression analysis program was prepared to test the experimental data. Data analysis was initiated to estimate the model parameters by fitting average cell data to the simple aging model. The coefficients, the standard deviations and 95% confidence intervals obtained by processing data of good cells (101, 103, 104, 105) from Build Type IV are listed in Table IV.1. To determine whether the model equation satisfactorily agrees with the data, the following standard techniques for an F Test were applied.

1. Fit the equation to the data, calculating the residual sum of squares.
2. Where there are repeat observations, at a single set of conditions, construct an error sum of squares. Do this for each set of repeat observations.
3. Subtract the error sum of squares determined in Step 2 from the residual sum of squares. Call this a lack of fit sum of squares.
4. The null-hypothesis will be that the equation does in fact fit the data. Under the null-hypothesis the only reason that the predicted values differ from the observed values is experimental error.
5. Calculate an error variance and a lack of fit variance by dividing the respective sums of squares by their corresponding degrees of freedom, thus obtaining an error variance and a

TABLE IV.1

PARAMETERS OBTAINED USING $\beta (\ln V_C - \overline{\ln V_C})$ AS A VOLTAGE TERM*
(Build Type IV)

Fit by Average Cell

<u>CU</u>	<u>i_L</u>
$\ln r_{u_0} = -4.282 \pm 0.064$	$\ln r_{i_0} = -5.684 \pm 0.086$
$E_u = 2700 \pm 6100$	$E_i = 2100 \pm 8300$
$\alpha_u = 0.1634 \pm 0.2366$	$\alpha_i = 1.155 \pm 0.413$
$\beta_u = 11.33 \pm 2.18$	$\beta_i = 1.120 \pm 2.699$
$\gamma_u = 0.5604 \pm 0.5483$	$\gamma_i = 0.5673 \pm 0.7418$

Fit by Cells

<u>CU</u>	<u>i_L</u>
$E_u = 2700 \pm 4300$	$E_i = 700 \pm 7200$
$\alpha_u = 0.0201 \pm 0.1565$	$\alpha_i = 0.2371 \pm 0.4284$
$\beta_u = 11.96 \pm 1.37$	$\beta_i = 0.1298 \pm 2.326$
$\gamma_u = 0.3568 \pm 0.3987$	$\gamma_i = 0.2172 \pm 0.6786$
$\ln r_{u_{01}} = -4.3637 \pm 0.0967$	$\ln r_{i_{01}} = -5.7142 \pm 0.1808$
$\ln r_{u_{02}} = -4.4296 \pm 0.0896$	$\ln r_{i_{02}} = -5.8391 \pm 0.1500$
$\ln r_{u_{03}} = -4.2019 \pm 0.0879$	$\ln r_{i_{03}} = -5.4299 \pm 0.1497$
$\ln r_{u_{04}} = -4.1978 \pm 0.1073$	$\ln r_{i_{04}} = -5.8298 \pm 0.1898$

* $\pm$ Numbers are the standard deviations of the estimates

- lack of fit variance.
6. Under the null-hypothesis each of these is an independent estimate of the error variance and their ratio will be distributed as the F statistic. If the lack of fit variance is smaller than the error variance, conclude that there is no lack of fit. If it is larger, form the ratio of lack of fit to error variance.
 7. Compare the variance ratio obtained in Step 6 with the value in an F table. If the calculated value is smaller than the tabulated value, conclude that there is no lack of fit. If it is greater than the tabulated value, conclude that there is a lack of fit (reject the null-hypothesis).

The variance ratios obtained of 1.67 for CU and 0.73 for the i_L case were lower than the value of 2.16 in the F table implying that there was no lack of fit. There was still, however, a high uncertainty in the estimated coefficients. This was interpreted as experimental error embedded in the numbers needed to be separated.

To separate the experimental error from the coefficient and include it in the rate constants, the data were fitted by the cells. In this method, the constant term was dropped from the regression equation. A number of independent variables equal to the number of cells being processed were added as shown in Table IV.2. This gave the unique parameters E , α , β , γ for each build type, whereas the decay rate constant k_0 ($=e^{\ln r_{u_0}}$) varied from cell to cell.

The results obtained using the fit-by-cells method are presented in Table IV.1. It was observed that the standard deviation of coefficients decreased significantly after fitting data by cells. It was also seen that the effect of V on CU decay was more significant than any other variable. The strong effect of V on CU decay was indicated by a value of β_u equal to 11. An effort was made to explain this value of β_u in the light of theory.

TABLE IV.2
MATRIX OF VARIABLES FOR USE IN "FIT-BY-CELLS" ANALYSIS

PERIODS OR OBSERVATIONS	Y $(\ln r_u - \overline{\ln r_u})$	X ₁ $(\frac{1}{T} - \overline{\frac{1}{T}})$	X ₂ $(\ln CU - \overline{\ln CU})$	X ₃ $(\ln v_{IR} - \overline{\ln v_{IR}})$	X ₄ $(\ln P_{H_2O} - \overline{\ln P_{H_2O}})$	X ₅	X ₆	X ₇	X ₈
1	.	.	.	.	.	1	0	0	0
.	.	.	.	.	.	1	0	0	0
.	.	.	.	.	.	.	.	.	.
21	.	.	.	.	.	1	0	.	.
22	.	.	.	.	.	0	1	.	.
.	.	.	.	.	.	0	1	.	.
.	.	.	.	.	.	.	.	.	.
.	.	.	.	.	.	.	.	.	.
42	.	.	.	.	.	.	1	0	.
43	.	.	.	.	.	.	0	1	.
.	.	.	.	.	.	.	.	1	.
.	.	.	.	.	.	.	.	.	.
.	.	.	.	.	.	.	.	.	.
63	.	.	.	.	.	.	.	1	0
64	.	.	.	.	.	.	.	0	1
.	.	.	.	.	.	.	.	0	1
.	.	.	.	.	.	.	.	.	.
84	.	.	.	.	.	0	0	0	1

For an electrochemical reaction, the rate constant k can be written as:

$$k = k'_0 e^{-E/RT + f(\eta)/RT}$$

where E is activation energy and η is polarization.

$$f(\eta) = \beta'\eta \quad (\text{linear with } \eta)$$

$$\begin{aligned} k &= k'_0 e^{-E/RT + \beta'\eta/RT} \\ &= k'_0 e^{-E/RT + \beta'(V-E)/RT} \quad (\text{For anodic reaction}) \end{aligned}$$

E = The Nernst potential

Including the E term in k'_0 , as it is almost constant, gives

$$\begin{aligned} k &= k'_0 e^{-E/RT} \cdot e^{\beta'V/RT} \\ &= k'_0 e^{-E/RT} \cdot e^{\beta V/T} \quad \text{Where } \beta = \beta'/R \end{aligned}$$

The voltage term was thus made similar to the temperature term. ($e^{\beta V/T}$ instead of V^β). The coefficients obtained with this new voltage term are summarized in Table IV.3.

A value of 7100 K/V for β_u and 14,100 cal/gmol volt for β'_u , were obtained. This meant a contribution by the voltage term of 10900 cal/g mol (at 0.77V) to the activation energy. To verify the above values, the terms $\frac{\beta'V}{RT}$ and $\frac{\alpha FV}{RT}$ (from the Tafel equation) were compared:

$$\begin{aligned} \beta' &= \alpha F \\ \alpha &= \frac{\beta'}{F} \quad \alpha = \text{Transfer coefficient} \end{aligned}$$

From the value of β' obtained, α was estimated to be 0.61.

TABLE IV.3

PARAMETERS OBTAINED USING $\beta(\frac{V}{T} - \frac{\bar{V}}{T})$ AS A VOLTAGE TERM *

(BUILD TYPE IV)

Fit by Cells

<u>CU</u>	<u>i_L</u>
$E_u = 13600 \pm 4400$	$E_i = 900 \pm 3800$
$\alpha_u = 0.0263 \pm 0.1567$	$\alpha_i = 0.2873 \pm 0.4284$
$\beta_u = 7100 \pm 800$	$\beta_i = 100 \pm 1400$
$(\beta'_u = 14100 \pm 1600)$	$(\beta'_i = 200 \pm 2700)$
$\gamma_u = 0.3596 \pm 0.3993$	$\gamma_i = 0.2171 \pm 0.6786$
$\ln r_{u_{O_1}} = -4.3654 \pm 0.0970$	$\ln r_{i_{O_1}} = -5.7141 \pm 0.1809$
$\ln r_{u_{O_2}} = -4.4301 \pm 0.0897$	$\ln r_{i_{O_2}} = -5.8391 \pm 0.1500$
$\ln r_{u_{O_3}} = -4.2016 \pm 0.0881$	$\ln r_{i_{O_3}} = -5.4299 \pm 0.1497$
$\ln r_{u_{O_4}} = -4.1962 \pm 0.1074$	$\ln r_{i_{O_4}} = -5.8299 \pm 0.1897$

* ± Numbers are the standard deviations of the estimates

This agrees with α values obtained from the corrosion study of carbon. It is an interesting result, because it suggests that the activity (i.e., catalyst surface area) of the cathode catalyst is significantly affected by voltage probably through carbon support corrosion.

The F-test was performed on results obtained from the fit-by-cell method. The computed variance ratios for CU and i_L decay modes were 3.393 and 2.440, respectively. The F ratio from the statistical tables was 1.983. As the calculated variance ratios were higher than the table value, it was interpreted that the interaction and/or quadratic terms were required to get a good fit.

To test whether quadratic terms are required in the model, $\ln r_u$ and $\ln r_i$ residuals were plotted against t , T , V and P_{H_2O} for Build Types I and IV (from individual cell data). No systematic curvature trend was observed in the plots. The random nature of the points indicated that no quadratic term for any of the variables is necessary in the model to fit the data. Typical plots of $\ln r_u$ residual against V_C and $\ln r_i$ residual against P_{H_2O} are presented in Figures IV.1 and IV.2. As a result only the interaction terms were added to the model.

According to the nature of the model, only the possible interaction terms were selected. The interaction terms added were: $T-V_C$, $CU-T$, $CU-V_C$, $CU-P_{H_2O}$, for CU and similar terms for i_L . The same fit-by-cell method was used. The results are listed in Table IV.4. The calculated F ratios (5.33 for CU, 8.34 for i_L decay) in this case also were higher than the F ratio from the F Table (2.120).

FIGURE IV.1 $\ln r_u$ RESIDUAL AGAINST V_C PLOT FOR BUILD TYPE I

FIGURE IV.2 $\ln r_i$ RESIDUAL AGAINST P_{H_2O} PLOT FOR BUILD TYPE I

TABLE IV.4
PARAMETERS ESTIMATED FOR MODEL
WITH INTERACTION TERMS*
(BUILD TYPE IV)

<u>CU</u>	<u>i_L</u>
$E_u = 19300 \pm 5400$	$E_i = 8000 \pm 8200$
$\alpha_u = 0.2540 \pm 0.2575$	$\alpha_i = 0.2038 \pm 0.9195$
$\beta_u = 14700 \pm 900$	$\beta_i = 1100 \pm 1500$
$\beta'_u = 29200 \pm 1900$	$\beta'_i = 2200 \pm 2900$
$\gamma_u = 0.3993 \pm 0.4078$	$\gamma_i = 0.3612 \pm 0.6459$
$\ln r_{u_{O_1}} = -4.0971 \pm 0.1066$	$\ln r_{i_{O_1}} = -4.5220 \pm 0.2190$
$\ln r_{u_{O_2}} = -4.0691 \pm 0.0947$	$\ln r_{i_{O_2}} = -4.0100 \pm 0.1496$
$\ln r_{u_{O_3}} = -3.8960 \pm 0.0950$	$\ln r_{i_{O_3}} = -4.9362 \pm 0.1675$
$\ln r_{u_{O_4}} = -3.8210 \pm 0.1131$	$\ln r_{i_{O_4}} = -4.6593 \pm 0.1774$
$(T-CU) \rightarrow \theta_u = 3071 \pm 6172$	$\theta_i = -7324 \pm 7990$
$(T-V) \rightarrow \zeta_u = -2.7763 \times 10^7 \pm 2.5777 \times 10^7$	$\zeta_i = 2.9383 \times 10^7 \pm 4.093 \times 10^7$
$(CU-V) \rightarrow \psi_u = 8522 \pm 6532$	$\psi_i = -2120 \pm 9421$
$(CU-P_{H_2O}) \rightarrow \xi_u = -0.5634 \pm 1.5522$	$\xi_i = 7.0383 \pm 5.4568$

* $\pm$ Numbers are the standard deviations of the estimates

The lack of fit meant that the equation did not fit as well as could have been expected from the knowledge of experimental error. That is, there was a greater difference between the predicted values of the model and the experimental data than could be explained by variations in the measurements, the operation, and the cells. For cells 101, 103, 104 and 105, it did not appear that the problem lay with the model (with all of the main variables plus the available interactions included). Instead, the more probable explanation was that the system had undergone some kind of rapid or step change which had disrupted the agreement between the data and the model. This is illustrated qualitatively in Figure IV.3, in which the data are assumed to have been generated by the solid line with the indicated small amount of scatter around the true value. If an attempt is made to fit all these data by the best exponential decay, the dashed line is obtained. The difference between the data points and the dashed line (which is representative of the lack of fit) is much greater than the differences between the solid line and the data points which are representative of the error variance. The ratio of the two variances would be much larger than expected by chance alone and it would be concluded as a lack of fit between the dash line model and the data. There certainly is such a lack of fit.

For the particular situation depicted in Figure IV.3, it could be expected that the observed and calculated residuals will start by being positive, then become increasingly positive, and then suddenly switch to negative to remain essentially negative for the remainder of the observations. This was especially so for the results obtained from Cell 101; the first 11 periods had residuals which, apart from the first and the fourth (the fourth being essentially zero), were all positive, and periods 12-18 had residuals which were all negative except for number 15. In the break between 11 and 12, the residuals changed from a large positive value to a large negative value in a single step. However, none of the other cells in Build Type IV exhibited this behavior.

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FIGURE IV.3 SYSTEM UNDERGOING RAPID OR STEP CHANGE

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The data for Build Type III (Cells 107, 108, 109), Build Type I (Cells 110-115) and Build Type II (Cells 116, 118) were processed to check if any other cell exhibited similar behavior. It was observed that Cells 108, 109 and 116 exhibited behavior similar to Cell 101.

The other possible failure in the experiment could be a divergence in the performance at longer operating times. This possibility is depicted in Figure IV.4. In such a situation, the error variance would increase with time. This was tested by comparing the error variance estimated for the first six periods with the error variance estimated for the remaining 13 periods (the last two periods, 20 and 21, were eliminated from the analysis because of disturbance in testing). The comparison for Build Type IV is presented in Table IV.5. It can be observed that, for Cell 101, 103, 104 and 105, the error variance for the first six periods is almost identical to that for the remaining 13 periods. This was also the case for other build types except Build Type I. (For Build Type I error variance for CU increased with time.) This is an important result, since throughout the experiment most of the cells had the same basic performance and therefore, had the same life characteristics.

In view of the possibility that the model's lack of agreement with the data is the result of a step change, a correlation of the data from the first six periods was attempted. This was permitted since performance in the first six periods was representative of the performance over the remainder of the test. In addition, the CU, i_L , and P_{H_2O} terms were omitted from the regression equation because of their small magnitude and higher uncertainty. When the data from Cells 101, 103, 104 and 105 were used, there was no lack of fit. The results are given in Table IV.6. The right column is the overall activation energy which is a function of V_C .

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FIGURE IV.4 : PERFORMANCE DIVERGING AT LONGER OPERATING TIMES

TABLE IV.5
COMPARISON OF ERROR ESTIMATES
AT TWO DIFFERENT TIME PERIODS

BUILD TYPE IV (Cells 101, 103, 104, 105)		CU	i_L
Sum of squares for error for first 6 periods	=	1.9653	4.9712
Degrees of freedom for error for first 6 periods	=	18	18
Sum of squares for error for last 13 periods	=	3.9541	12.5754
Degrees of freedom for error for last 13 periods	=	36	36
Error variance for first 6 periods	=	0.1092	0.1762
Error variance for last 13 periods	=	0.1098	0.3493
Variance Ratio	=	1.00	1.26
$F_{0.05, 18, 36}$			1.91
BUILD TYPE III (Cells 107, 108, 109)		CU	i_L
Error Variance			
First 6 Periods	=	0.1642	0.6700
Last 13 Periods	=	0.3263	1.0969
Variance Ratio	=	1.9880	1.6371
$F_{0.05, 12, 22}$			2.23
BUILD TYPE I (Cells 110-115)		CU	i_L
Error Variance			
First 6 Periods	=	0.0872	1.0802
Last 13 Periods	=	0.2244	0.7928
Variance Ratio	=	2.5745	0.7339
$F_{0.05, 30, 59}$			1.65
BUILD TYPE II (Cells 116, 118)		CU	i_L
Error Variance			
First 6 Periods	=	0.1656	0.4397
Last 13 Periods	=	0.1783	1.0336
Variance Ratio	=	1.0767	2.3505
$F_{0.05, 6, 12}$			3.00

TABLE IV.6

PARAMETERS ESTIMATED AFTER EXCLUDING CU , i_L AND
 P_{H_2O} TERMS FROM REGRESSION EQUATION

BUILD TYPE IV (Cells 101, 103, 104, 105)				
Parameter	$\ln r_{u_o}$	E_u	β_u	$E_{overall} = E_u - 0.77R\beta_u$
Estimate	-4.309	16900	8100	4500
Std. Error	0.078	5900	1100	6100
95% Conf. Interval Based upon $t_{0.025, 18} = 2.1$	± 0.164	± 12400	± 2300	± 12900
Parameter	$\ln r_{i_o}$	E_i	β_i	$E_{overall} = E_i - 0.77R\beta_i$
Estimate	-5.551	18700	2900	5700
Std. Error	0.087	6600	1200	6900
95% Conf. Interval	± 0.183	± 13900	± 2600	± 14400
BUILD TYPE III (Cells 107, 108, 109)				
Parameter	$\ln r_{u_o}$	E_u	β_u	$E_{overall}$
Estimate	-3.848	18800	5900	2800
Std. Error	0.078	5900	1100	6100
95% Conf. Interval Based upon $t_{0.025, 18} = 2.1$	± 0.164	± 12400	± 2300	± 12900
Parameter	$\ln r_{i_o}$	E_i	β_i	$E_{overall}$
Estimate	-5.375	6900	-1100	8583
Std. Error	0.366	28000	5000	29000
95% Conf. Interval	± 0.769	± 58800	± 10500	± 60900

TABLE IV.6 (Con't)

PARAMETERS ESTIMATED AFTER EXCLUDING CU, i_L AND P_{H_2O} TERMS FROM REGRESSION EQUATION

BUILD TYPE I (Cells 110, 111, 112, 113, 114, 115)				
Parameter	$\ln r_{u_o}$	E_u	β_u	$E_{overall}$
Estimate	-3.765	21400	6200	11900
Std. Error	0.110	8300	1500	8600
95% Conf. Interval $\pm$ based upon $t_{0.025,18} = 2.1$	0.231	± 17400	± 3150	± 18100
Parameter	$\ln r_{l_o}$	E_l	β_l	$E_{overall}$
Estimate	-5.851	-14900	-6800	- 4500
Std. Error	0.199	15000	2800	15600
95% Conf. Interval $\pm$	0.418	± 31500	± 5900	± 32800
BUILD TYPE II (Cells 116, 118)				
Parameter	$\ln r_{u_o}$	E_u	β_u	$E_{overall}$
Estimate	-3.752	7000	7400	-4300
Std. Error	0.197	14900	2800	15500
95% Conf. Interval Based upon $t_{0.025,18} = 2.1$	± 0.414	± 31300	± 5900	± 32600
Parameter	$\ln r_{i_o}$	E_i	β_i	$E_{overall}$
Estimate	-5.470	-22500	-8700	-9200
Std. Error	0.167	12600	2300	13100
95% Conf. Interval	± 0.351	± 24500	± 4500	± 27500

Although E_u , β_u , E_i , and β_i are statistically significant (as can be seen from the fact that their estimates are greater than the 95% confidence limits), when they are combined in an overall or apparent activation energy, the two factors tend to cancel each other out leaving a number which is smaller than its confidence interval. This result, however, does not diminish the significance of the two factors in any way. Since activation energies of rate processes cannot be negative, the conclusion is that the E_{overall} lies between 0 and 17,400, although the best estimate is 4500 cal/g mol.

The estimated parameters for Build Types I, II, and III are also presented in Table IV.6. The F-test indicated there was no lack of fit apart from the i_L case in Build Type III. The lack of fit here may be due to less data (only two good cells out of three) and fewer i_L measurements taken during each perturbation. Therefore a few spurious values could have relatively large effects and lead to a false conclusion that there is a lack of fit.

IV.2 Comparison of Parameters Between Different Build Types

The model parameters E (activation energy for decay reactions - temperature term), E_v (activation energy for decay reactions - voltage term), and E_{overall} (overall activation energy - T and V terms) varied significantly from one build type to the other. However, the variation of decay rate constant ($\ln r_0$) from one build type to the other was negligible. The activation energy had negative values for Build Types I, II and III in the diffusion limitation mode. Since the activation energies of rate processes cannot be negative, E_{overall} must lie on the positive side of the confidence interval. The 95% confidence level intervals for the parameters overlapped considerably from one build type to the other.

IV.3 Final Form of the Aging Model

The final form of the aging model obtained by substituting the estimated parameters in the decay rate equation representing platinum deactivation is presented below for each build type. The decay rate equation accounting for diffusion loss was discarded, because the limiting current density remained sufficiently high and consequently the diffusion polarization was negligible for the entire test duration.

- Build Type IV (0.6 mg/cm², 45% TFE)

$$r_u = - \frac{dCU}{dt} = 0.0134 \cdot \exp \left(-8505 \left(\frac{1}{T} - 0.0022 \right) \right) \cdot \exp \left(8100 \left(\frac{V_C}{T} - 0.0017 \right) \right)$$

where,

r_u is the rate of decrease in catalyst utilization with time, %/hour.

T is absolute temperature, K

V_C is cathode potential, V

- Build Type III (0.3 mg/cm², 45% TFE)

$$r_u = - \frac{dCU}{dt} = 0.0213 \cdot \exp \left(-9461 \left(\frac{1}{T} - 0.0022 \right) \right) \cdot \exp \left(5900 \left(\frac{V_C}{T} - 0.0017 \right) \right)$$

- Build Type I (0.3 mg/cm², 40% TFE)

$$r_u = - \frac{dCU}{dt} = 0.0232 \cdot \exp \left(-10770 \left(\frac{1}{T} - 0.0022 \right) \right) \cdot \exp \left(6200 \left(\frac{V_C}{T} - 0.0017 \right) \right)$$

- Build Type II (0.6 mg/cm², 40% TFE)

$$r_u = - \frac{dCU}{dt} = 0.0285 \cdot \exp \left(-3523 \left(\frac{1}{T} - 0.0022 \right) \right) \cdot \exp \left(7400 \left(\frac{V_C}{T} - 0.0017 \right) \right)$$

IV.4 Model Verification

Once the model parameters were estimated, the only task remaining was to evaluate the model by utilizing baseline cell data. Observation of the baseline cell lifegraph revealed that the decay was exponential (faster decay in the beginning and flattening at the end), rather than linear. It was recognized that it is necessary to have CU and i_L terms in the model to make it represent the baseline cells.

Estimates of the parameters and the 95% confidence intervals obtained after adding CU and i_L terms back in the regression equation are presented in Table IV.7. Parameters were estimated only for Build Type IV (Cells 101, 103, 104, 105) since baseline cells were also of the same build type. On observation of the results, a high uncertainty in the parameters was found even though a good fit was obtained. This can be attributed to the limited amount of data. With data from just six perturbations, it is difficult to get a good estimate of α 's and the uncertainty in α 's made the estimates of other parameters (E, β) worse compared to the results of Table IV.6. Finally different values of α 's and decay rate constants were attempted to match the predicted and the experimental lifegraphs. The details are presented below.

To evaluate the aging model developed, cell performance was predicted at different times and compared with the experimental performance data of the baseline cells. Since the baseline cells were operated at center point conditions (184°C, 0.770V), the model equation was simplified as shown below.

For CU

$$\ln r_u = \ln r_{u_0} - \frac{E_u}{R} \left(\frac{1}{T} - \frac{1}{\bar{T}} \right) + \alpha_u (\ln CU - \overline{\ln CU}) + \beta_u \left(\frac{V}{T} - \frac{\bar{V}}{\bar{T}} \right)$$

At center point conditions $\frac{1}{T} = \frac{1}{\bar{T}}$ and $\frac{V}{T} \approx \frac{\bar{V}}{\bar{T}}$ hence $\ln r_u = \ln r_{u_0} + \alpha_u (\ln CU - \overline{\ln CU})$ or $r_u = - \frac{dCU}{dt} = k_{u_0} \cdot (CU/\bar{CU})^{\alpha_u}$ (IV.1)

TABLE IV.7

PARAMETERS ESTIMATED AFTER INCLUDING P_{H_2O} TERM BACK
IN REGRESSION EQUATION

BUILD TYPE IV (Cells 101, 103, 104, 105)

Parameter	$\ln r_{u_o}$	E_u	α_u	β_u	E_{overall}
Estimate	-4.309	18000	-0.1005	8400	5100
Std. Error	0.095	16200	1.374	4600	17700
95% Conf. Interval Based on $t_{0.025, 18} = 2.1$	± 0.200	± 34000	± 2.885	± 9700	± 37200

Parameter	$\ln r_{i_o}$	E_i	α_i	β_i	E_{overall}
Estimate	-5.551	18900	-0.1282	2900	14500
Std. Error	0.106	9000	0.9995	1500	9300
95% Conf. Interval	± 0.223	± 18900	± 2.099	± 3200	± 19500

where, $\tilde{CU} = e^{\overline{\ln CU}}$

Similarly for i_L $r_i = -\frac{di_L}{dt} = k_{i_0} (i_L/\tilde{i}_L)^{\alpha_i}$ (IV.2)

where, $\tilde{i}_L = e^{\overline{\ln i_L}}$

The resulting equation (IV.2) no longer contains any of experimental design variables. Integration of equations (IV.1) and (IV.2) gives $\tilde{CU}$ and i_L as a function of time. By substituting $\tilde{CU}$ and i_L in the performance model⁵, the current density at any time t can be estimated, which represented performance at $V_C = 0.770V$ and time, t .

Different values of the decay rate constants (k_{u_0} , k_{i_0}) and α 's, within the 95% confidence interval were used to predict the performance and compare with the baseline performance. Finally the minimum values of decay rate constants and the maximum values of α 's were used to predict the lifegraph up to 5600 hours. As shown in Figure IV.5, the lifegraph was in a very good agreement with the experimental data for baseline cells except for the higher experimental performance towards the end of the testing. To some extent this is a result of an increase in cell performance (current density) due to acid additions. The overall performance decay of baseline cells is slowed down by these performance gains, which are difficult to eliminate. Since the model does not account for acid additions, the predicted performance is free from their effects, and experimental performance is higher. The fact that there are parametric values which lie within the 95% confidence limits of the estimates, that bring the perturbation results in agreement with the baseline data provides support for this approach. Because of a large uncertainty in the parameteric values, however, it is a weak test.

5. Baker, B., Maru, H., and Patel, D., "Fuel Cell Power Configurations", Final Report Prepared by Energy Research Corporation for Science Applications, Inc., Under Contract No. 04-117-01, August 1978.

The performance decay of a pressurized cell at 50 psia pressure is shown in Figure IV.6. The partial pressure of water and O_2 in the pressurized cell were maintained at the same level as in the baseline cells at atmospheric pressure to study any effect of total pressure on cell performance decay. Based on the decay at $184^\circ C$ temperature it can be stated that an effect on cell decay was observed. The rate of decrease of current density is only about one fourth as great for the high pressure cell as it is for the baseline cell. The sudden and severe decay at $191^\circ C$ may have been caused by severe corrosion or by a cell failure. No conclusion was made about decay at higher temperature.

FIGURE IV.5 COMPARISON OF AGING MODEL DERIVED FROM PERTURBATION EXPERIMENTS, WITH UNPERTURBED TEST DATA

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FIGURE IV.6 PERFORMANCE DECAY OF PRESSURIZED CELL

Overall Conclusions:

The following overall conclusions were made.

- The effects of temperature and voltage on the platinum deactivation rate were significant. The analysis indicates that the effect may be through carbon corrosion. No conclusion was reached about the effect of water partial pressure, since the estimate of parameter γ , order of decay reaction with respect to P_{H_2O} , was small and had a high uncertainty.

- At center point conditions the temperature and the voltage terms reduce to unity and a relative comparison of decay rates from one build type to the other can be made based on k_u . At 45% Teflon content, the electrode with 0.6 mg/cm² platinum loading decayed slower than the 0.3 loaded electrode. However, at 40% Teflon content, change in platinum loading had no effect on decay.

- At 0.3 mg/cm² platinum loading, a 45% Teflon loaded electrode decayed at approximately the same rate as a 40% TFE electrode. However, at 0.6 loading, a 45% Teflon electrode decayed slower than 40% TFE electrode.

- The initial series of perturbation tests appeared to be reasonably successful. Although some mechanical problems were encountered in the last few perturbation periods, about 85% of the perturbation data obtained were useable.

- Since no divergence was observed in the performance decay characteristics of the identical cells, it is practical to study controlled variables which influence fuel cell life (such as temperature, cathode potential and water partial pressure) in experiments as short as one month.

- To determine the effects of uncontrolled variables (catalyst utilization and limiting current density) on the decay rates, somewhat longer tests are needed of about two months.

- A good agreement between the perturbation and baseline data was obtained. As a result we have validated the method for predictive testing of the phosphoric acid fuel cell via perturbation.

- The methodology for predictive testing established by this study can be further refined and can be applied to other fuel cell systems such as the molten carbonate fuel cell. The disturbances in the testing caused by power failure, reactant cut off, etc. should be minimized to prevent disruption of the test. The range of operating variables such as water partial pressure should be expanded to lower the uncertainty in parameters. A precise control of water partial pressure may also reduce the uncertainty. Some technique should be devised to take care of the performance gains by acid additions or acid loss decay mode should be included in the study.

APPENDIX A: METHOD FOR ESTIMATION OF i_L

The decay of oxygen reduction limiting current at the cathode is a measure of carbon support decay. Limiting current was measured at different stages of cell decay. Accurate measurement of limiting current was highly desirable for the accuracy of the model to be developed. Presently there is no universally accepted method of estimating the limiting current of an operating fuel cell cathode. ERC examined different possible methods of estimating i_L from the experimental data, and selected the following method.

Using 4% O_2 and 96% N_2 gas mixture, polarization data are obtained for constant flow (a typical plot is shown in Figure A.1). A portion of this V against I data (Section AB in the Figure), where diffusion polarization appears to be dominant, is processed by a computer program for the evaluation of limiting current. The algorithm used in the computer program is discussed below. For each experimental point, η_{dif} is estimated from equation (A.1).

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FIGURE A.1 POLARIZATION PLOT FOR ESTIMATION OF
LIMITING CURRENT

$$\eta_{dif} = E_o + \frac{RT}{2F} \ln \left(\frac{P_{O_2}^{1/2} \cdot P_{H_2}}{P_{H_2O}} \right) - V - Ir - \eta_a - \eta_{c,a} \quad (A.1)$$

Where,

E_o = Standard emf, V

P_{O_2} = Average O_2 partial pressure, atm.

P_{H_2} = Average H_2 partial pressure, atm.

P_{H_2O} = Average H_2O partial pressure, atm.

V = Terminal voltage, V

I = Total cell current, A

r = Ohmic resistance, Ω

η_a = Anode activation polarization, V

$\eta_{c,a}$ = Cathode activation polarization, V

Estimation of anode and cathode activation potential is discussed at the end of the appendix.

The well known relationship between i (cell current density), i_L (limiting current density) and η_{dif} is:

$$\eta_{dif} = \frac{RT}{2F} \ln \left[\frac{i_L}{i_L - i} \right] \quad (A.2)$$

This can be rearranged to:

$$i = k \times P_{O_2} \left[1 - \exp \left(- \frac{\eta_{dif} \times 2F}{RT} \right) \right] \quad (A.3)$$

where,

$k \cdot P_{O_2} = i_L$ and k is a proportionality constant.

It is apparent from Equation (A.3), that the least square estimate of k is obtained using experimentally observed i , and evaluated η_{dif} values. The limiting current corresponding to the experimental conditions is then readily estimated from the calculated P_{O_2} and estimated k value.

Estimation of Anode and Cathode Activation Polarizations

The Anode activation polarization is assumed to be

$$\eta_a = I \times 0.002$$

and the cathode activation polarization is calculated from

$$\eta_{c,a} = \frac{RT}{F} \ln \frac{i}{i_o \times A_o} \quad (A.4)$$

where,

$$i_o = 0.2327 \left(P_{O_2}^{3/4} \right) \left(P_{H_2O}^{0.4377} \right) \exp \left(\frac{-13,217}{RT} \right) A/cm^2 \quad (A.5)$$

and,

$$A_o = \frac{\text{True area, cm}^2}{\text{Geometric area, cm}^2}$$

The value of A_o for the electrode is estimated from an independent performance study at low current density employing pure oxygen as the oxidant.

In that case,

$$A_o = \left(i/i_o \right) \times e^{\left(\eta_{c,a} \frac{F}{RT} \right)} \quad (A.6)$$

where,

$$\eta_{c,a} = E_o + \frac{RT}{2F} \ln \left(\frac{P_{O_2}^{1/2} P_{H_2}}{P_{H_2O}} \right) - V - Ir - \eta_{dif} - \eta_a \quad (A.7)$$

With oxygen and at a low current density, η_{dif} is less than 1 mV and can be neglected in calculating $\eta_{c,a}$.

APPENDIX B: COMPUTATIONAL METHOD FOR CU

The method used to compute the catalyst utilization, CU, for data analysis is described here in detail, along with the sample calculation.

● Steps

1. Define CU, the catalyst utilization, as

$$CU = \frac{I_{\text{cell, expt.}}}{I_{\text{cell, theo.}}} \times 100, \%$$

where, $I_{\text{cell, expt.}}$ = experimental total cell current, amps.

$I_{\text{cell, theo.}}$ = theoretical total cell current, amps.

$$2. I_{\text{cell, theo.}} = (i_o) \times \frac{\text{real area}}{\text{geometric area}} \times A \times \exp \left(\eta_{c,a} \cdot \frac{F}{RT} \right)$$

where, i_o = exchange current density, A/cm² real area

A = cell geometric area, cm²

$\eta_{c,a}$ = cathode activation polarization, V

T = cell temperature, K

$$3. \eta_{a,a} = E_{\text{TOPC}} - V - Ir - \eta_a - \eta_{\text{dif}}$$

where, V = cell terminal voltage, V

Ir = cell potential drop due to ohmic resistance, V

r = cell resistance, Ω

η_a = anode polarization, V

η_{dif} = cathode diffusion polarization, V

E_{TOPC} = theoretical open circuit potential, V

$$4. E_{\text{TOPC}} = E_o + \frac{RT}{2F} \ln \frac{P_{\text{O}_2, \text{avg}}^{1/2} P_{\text{H}_2, \text{avg}}}{P_{\text{H}_2\text{O}, \text{avg}}}$$

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where, E_o = standard emf, $V = 1.2605 - 0.00025 \cdot T$

$P_{O_2,avg}$ = Average oxygen partial pressure in the cell, atm.

$$= \left(P_{O_2,in} \times P_{O_2,out} \right)^{\frac{1}{2}}$$

$P_{H_2,avg}$ = Average hydrogen partial pressure in the cell, atm.

$$= \left(P_{H_2,in} \times P_{H_2,out} \right)^{\frac{1}{2}}$$

$$P_{H_2O,avg} = \left(P_{H_2O,in} + P_{H_2O,out} \right) / 2$$

It can be shown that for fuel cells, the geometric averages for P_{O_2} and P_{H_2} , and the arithmetic average for P_{H_2O} closely approximate to the current density weighted, integrated average of each variable. Note that, in calculating $P_{H_2O,out}$, it will be assumed that the exit streams (both fuel and oxidant) are in equilibrium with the average acid concentration of the cell.

5. Assume that

$$\eta_a = 0.002 \times I$$

This is a reasonable assumption for pure H_2 , equivalent to 5 mV/ (100 mA/cm²)

$$6. \quad \eta_{dif} = \frac{RT}{2F} \ln \frac{I_L}{I_L - I}$$

The calculation for limiting current, I_L , has been described in Appendix A.

$$7. \quad i_o = 0.2327 \times (P_{O_2,avg})^{\frac{3}{4}} P_{H_2O,avg}^{0.4377} \times e^{\frac{-5652}{T}}, \text{ A/cm}^2$$

(least square fit of Kunz and Groover data).

$$8. \quad (\text{Real area/geometric area}) = CL \times SA$$

where,

CL = catalyst loading of the electrode, mg/cm² (geo.)

SA = catalyst specific surface area, cm² (true)/mg

Experimental Data

Experimental data from period 17, for cell 110 (performance at operating conditions) have been used.

Performance:

$$\begin{aligned} I_{\text{exp}} &= 1.72\text{A} \\ V &= 0.711\text{V} \end{aligned}$$

Independent Variables	
Variable	Value
$P_{\text{H}_2, \text{in}}$	1.00 atm.
H_2 utilization	85%
$P_{\text{O}_2, \text{in}}$	0.90 atm.
$P_{\text{H}_2\text{O}, \text{in}}$	0.10 atm.
Stoich O_2	2
T	(273 + 191) K
r, ohmic resistance	0.011 Ω
CL, catalyst loading	0.27 mg/cm ²
SA, catalyst specific surface area	50 m ² /g (assumed)

Sample Calculations

$$\begin{aligned} (1) \quad P_{\text{O}_2, \text{avg}} &= (P_{\text{O}_2, \text{in}} \times P_{\text{O}_2, \text{out}})^{\frac{1}{2}} \\ &= (0.90 \times 0.38)^{\frac{1}{2}} \\ &= 0.58 \text{ atm.} \end{aligned}$$

$$\begin{aligned} P_{\text{H}_2\text{O}, \text{avg}} &= (P_{\text{H}_2\text{O}, \text{in}} + P_{\text{H}_2\text{O}, \text{out}})/2 \\ &= (0.10 + 0.62)/2 \\ &= 0.36 \text{ atm.} \end{aligned}$$

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(The calculation of $P_{H_2O,out}$ is explained at the end of the appendix.)

$$\begin{aligned} P_{H_2,avg} &= (P_{H_2,in} \times P_{H_2,out})^{\frac{1}{2}} \\ &= (1 \times 0.38)^{\frac{1}{2}} \\ &= 0.62 \text{ atm.} \end{aligned}$$

$$\begin{aligned} (2) \quad E_{TOPC} &= 1.1445 + 0.0053 \\ &= 1.1498V \end{aligned}$$

$$\begin{aligned} (3) \quad I_L &= 121.12A \\ \eta_{dif} &= \frac{R(191 + 273)}{2F} \ln \frac{121.12}{121.12-1.72} \\ &= 0.00029V \quad (\text{negligible}) \end{aligned}$$

$$\begin{aligned} (4) \quad \eta_{ca} &= E_{TOPC} - \eta_a - \eta_{dif} - Ir - V \\ &= 1.1498 - 0.002 \times 1.72 - 0.00029 - 0.011 \times 1.72 - 0.711 \\ &= 0.416V \end{aligned}$$

$$\begin{aligned} (5) \quad i_o &= 0.2327 (0.58)^{\frac{3}{4}} (0.36)^{0.4377} \times e^{\frac{-0.6652}{273+191}} \\ &= 0.59 \times 10^{-7} \text{ A/cm}^2 \end{aligned}$$

$$\begin{aligned} (6) \quad I_{cell,theo.} &= 0.59 \times 10^{-7} \times (24.09 \times 0.27 \times 50 \times 10)e \\ &= 6.35 \text{ A} \end{aligned}$$

$$\begin{aligned} CU &= \frac{1.72}{6.36} \times 100 \\ &= 27\% \end{aligned}$$

$$\frac{0.416 \times F}{R(273+191)}$$

Calculation of H₂O Content in Exit Streams

Basis: H₂ in at 100 cm³/min

H₂ consumed at 85 cm³/min

H₂ out at 15 cm³/min

O₂ consumed at 42.5 cm³/min

O₂ in at 85 cm³/min

O₂ out at 42.5 cm³/min

H₂O in with O₂ stream at 9.4 cm³/min

H₂O produced at 85 cm³/min

H₂O out with H₂ stream at $(85 + 9.4) \times \frac{15}{15 + 42.5}$
 = at 24.6 cm³/min

H₂O in H₂ stream out = $\frac{24.6}{15 + 24.6} \times 100 = 62.1\%$

H₂O in O₂ stream out = $\frac{85 - 24.6}{(85 - 24.6 + 42.5)} \times 100$
 = 62.1 %