REDUCTION OF OXYGEN ON PLATINUM BLACK AT FUEL CELL ELECTRODES

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Introduction

A problem common to the development of fuel cell electrodes and to the evaluation of catalysts has always been the difficulty of separating the effects of the electrode structure from the more fundamental limitations imposed by the intrinsic activity of the particular catalyst. In the past the problem has been attacked theoretically by assuming a model. The current-potential curves for certain porous electrodes can be predicted if the kinetics of the electrode process, the diffusion coefficients and ionic mobilities are known. Thus theories have been developed[1,2] for the Teflon bonded gas diffusion electrode.[3] There can be little doubt about the basic validity of the model used in these treatments.[4]

The usefulness of such theories, however, is severely limited if, as is often the case, the kinetics of the electrode process is not well known. To calculate the kinetic parameters from the overall polarization curve of a porous electrode has been apparently beyond previous capabilities.[5] As a result, in many instances neither the intrinsic electrocatalytic activity of the catalyst nor the structural details of a given electrode could be determined from experiments with such porous electrodes. This was especially true for the reduction of oxygen at Teflon bonded electrodes catalyzed with platinum black. The kinetic parameters for this reaction are poorly known, with the reported data applying mostly to smooth platinum and depending strongly on pretreatment and trace impurities in the electrolyte.

We have studied the reduction of oxygen at platinum catalyzed Teflon bonded porous electrodes in aqueous solutions of KOH, H_2SO_4 and H_3PO_4. A procedure was used which produced current potential curves essentially free of internal iR losses so that kinetic parameters for the electrochemical reaction could be obtained.

Experimental

Methods

The internal iR loss of a porous electrode should become negligible for low catalyst loadings L, i.e., for thin electrodes. A plot of I, the current per 1 cm^2 of electrode area at constant potential, versus the loading should, at low values of L, yield almost straight lines. The initial slope of these curves $i \equiv (dI/dL)_{L=0}$ (ma/mg) represents the current per 1 mg of catalyst loading without internal iR loss. The gas concentration overvoltage within the catalyst agglomerates is not excluded.

These iR-free data were then replotted as log i versus the potential. At small values of i the concentration overvoltage now becomes negligible and the plots yield the exchange current (per 1 mg of catalyst) and the Tafel slope for the electrochemical reaction.

As an independent check the oscillographic potential decay curves were analyzed in a few instances where the internal iR loss could be assumed to be negligible.

Electrodes

It is essential for the procedure just outlined that electrodes be made in such a way that a change in the loading does not produce a qualitatively different structure. Ideally only the electrode thickness should vary. The experimental results indicate clearly whether one is successful in this undertaking. However, we know of no method which will predictably produce the desired results.

It was found that a number of different methods produce satisfactory electrodes. The kind used in this work were the easiest to make and the most reliable.

A layer of Teflon (TFE 30, approximately 1 mg/cm^2) was sprayed on aluminum foil. This layer was air dried, vacuum dried and subsequently sintered to produce a thin porous sheet of Teflon. Upon this layer was sprayed catalyst containing Pt black and 30 W% TFE 30. At this Teflon content the maximum performance was obtained, falling off at higher and lower values. (Different Pt blacks sometimes require different Teflon contents to give maximum performance.) The Pt black was a product of Engelhard Industries and had a specific surface area of 24 m^2/g. The catalyst/Teflon layer was air dried and then lightly compacted with a roller pressed down by hand. Subsequently the electrode was vacuum dried and sintered. A current collector screen was pressed lightly into the catalyst layer. The screen material was pure nickel (for experiments in KOH) or gold plated tantalum (for acids). Finally the aluminum foil was dissolved by treatment with the respective electrolyte to be used. The electrode was washed with distilled water and dried at 120°C.

Apparatus

The measurements were made with the apparatus depicted in Figure 1. The test electrodes were mounted in a screw cap holder and current pick up was made via a platinum ring in contact with the current collector screen of the electrode. The electrode holder was made of Plexiglas [a] for use in KOH or of Lexan [b] for use in the acids.

The reference was a hydrogen electrode used in conjunction with a Luggin capillary of the design shown in Figure 2. Other designs than that in Figure 2 were tried but, at high current densities, gave poor results.

The cell was a 500 ml jacketed glass reaction kettle. The temperature was controlled by means of an external circulating constant temperature bath. Reagent grade chemicals were used without further purification.

Electrode polarizations were measured galvanostatically employing two 12 volt batteries of high capacity (automobile type) in series and variable resistances in series with cell and batteries. The external iR loss between electrode surface and opening of Luggin capillary was determined from oscilloscopic potential-time traces on turning the current on and off. A relay with mercury wetted contacts [c] was used for this purpose. The highest currents used were established with this setup in less than approximately 1 μ second. The time traces were measured with an oscilloscope [d] in conjunction with a camera.

Experimental Procedure

In Figure 3 the external iR-losses measured when the current is turned on (η_Ω)

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[a] Product of Rohm and Haas.
[b] Product of General Electric Company.
[c] Potter and Brumfield, JMP 8120 12.
[d] Tektronix, Model 561A with plug-in units 3A7 and 3B3.

and on turning it off (η_Ω') are plotted as a function of the current. Approximately 5 minutes elapsed between the two measurements. The plot of η_Ω is linear and the slope equals that calculated from the electrolyte conductance for this particular geometry.

The plot is not linear for η_Ω' values of which fall below the line at high currents. This deviation is due to the changes in temperature and electrolyte concentration in front of the electrode.

By the time the electrode polarization is established the external iR-loss has changed. By using the final value (η_Ω') this effect is eliminated. However, another one is introduced: the concentration change also results in a liquid junction potential ϵ_D and a pH drop between capillary tip and electrode. Both effects decay slowly and are, therefore, not eliminated with the iR measurement. In order to eliminate these external non-ohmic potential drops one would use the initial value η_Ω rather than the value on current interruption (η_Ω'). Based on past experience(6) we believe that the error due to these sources is considerably smaller than the error caused by the temperature change. We therefore used the final value η_Ω' to correct for the external iR loss.

The compromise necessary for correcting the polarization data introduces an unavoidable error which, however, becomes significant only at very high current densities.

The electrodes were prepolarized at low potentials to remove the initial oxygen coverage from the platinum surface. The electrode was then allowed to drift back to 1000 mV after which the measurement was made.

Results and Discussion

The experimental results obtained for 85% H_3PO_4 at 120°C are presented in Figure 4 and Figure 5 for air (1 atm) and Figures 6 and 7 for oxygen (1 atm). Within the experimental reproducibility the curves are linear below certain loadings.

Similar data were measured for 30% KOH at 70°C, for 20% H_2SO_4 at 70°C and for 50% H_3PO_4 at 70°C, all for air (1 atm) and for oxygen (1 atm). The data follow the same general pattern as those in Figures 4 to 7.

Within the initial approximately linear portion of these curves the internal iR loss is very small, certainly smaller than the reproducibility of the results. This means that the potential was the same for every catalyst particle in the electrode and it is physically meaningful to normalize the data by dividing the observed currents by the catalyst loading. The resulting specific current (per mg of catalyst) is proportional to the true current density at the Pt-electrolyte interphase if the concentration overvoltage is negligible, i.e., at low currents and especially on pure oxygen.

Plots of specific currents versus the potential are presented in Figures 8 and 9. This method of plotting the data has the advantage that the difficulties encountered in eliminating the external iR drop at high current densities (I) (per unit electrode area) are largely avoided: quite large specific currents (i) can be obtained at low overall current densities I if the catalyst loading is low. At the other end of the scale problems sometimes occur stemming largely from the increasing influence of impurities in the electrolyte on the performance of very lowly loaded electrodes. This problem is eliminated by measuring the small specific currents at highly loaded electrodes and consequently fairly large external currents. Under these conditions impurities in the electrolyte are ineffective because of the very large ratio of platinum surface to electrolyte in the electrode pores.

The semi-logarithmic plots for pure oxygen in H_2SO_4 and in KOH are linear over such a wide current range that we feel justified in calculating specific exchange currents and Tafel slopes from the curves in Figure 8. The results are given in Table I.

Table I

Values for i_o and b at P_{O_2} = 1 atm obtained from steady state data.

Electrolyte	Temperature	b (mv)	i_o (A/mg)	i_o (mA/cm^2)[a]	E* (mV)[7]
30 W% KOH	70°C	50 ± 5	0.9×10^{-4}	4×10^{-10}	1195
20 W% H_2SO_4	70°C	64 ± 5	1×10^{-4}	4×10^{-10}	1186
50 W% H_3PO_4	70°C	60 ± 5	$\sim 1 \times 10^{-4}$	$\sim 4 \times 10^{-10}$	1175
85 W% H_3PO_4	120°C	60 ± 5	$\sim 1 \times 10^{-4}$	$\sim 4 \times 10^{-10}$	1191

[a] Using 24 m^2/g for specific surface area of the Pt black. This value based on BET and hydrogen stripping experiments.

Included in Table I are values for H_3PO_4 although the data in Figure 8 are not sufficient to accurately extrapolate to equilibrium potential. In H_3PO_4 the concentration overvoltage becomes noticeable at relatively low currents even on pure oxygen. The kinetic data in this case were obtained by determining the Tafel slope b from the oscilloscopic traces and then extrapolating the low current end of the curve in Figure 8 with this value for b.

The Tafel slope was determined by assuming that the electrode capacity C* is potential independent below approximately 800 to 850 mV. We further assumed that at not too large currents the concentration of oxygen at the catalyst surface is approximately constant for a short time after the polarizing current is interrupted. With these assumptions we can integrate the equation for the current after interruption.

$$(1) \qquad 0 = i = i_c + i_F = C^* \frac{dE}{dt} - kce^{-\frac{2.3}{b}E} .$$

In (1) i, i_c and i_F are the total, the charging and the Faradaic currents respectively, E is the electrode potential (iR free since experiment is done within linear range of curves in Figures 4 to 7), k is a constant and b the Tafel slope.

The integration of (1) yields

$$(2) \qquad E = K_1 + b \log (K_2 + t)$$

$$K_1 \equiv b \log \frac{2.3\ kc}{b\ C^*}$$

$$K_2 \equiv \frac{b\ C^*}{2.3\ kc} \exp \frac{2.3\ E\ (t=0)}{b}$$

By varying K_2 until the plot of log $(K_2 + t)$ versus E is a straight line we can determine the Tafel slope b as the slope of this linear plot.

Furthermore we have

$$(3) \qquad \frac{dE}{dt} = \frac{b}{2.303\ (K_2 + t)}$$

$$(4) \qquad \left(\frac{dE}{dt}\right)_{t\ =\ 0} = \frac{b}{2.303\ K_2} .$$

The capacity C^* is then given by

$$(5) \qquad C^* = \left(\frac{i_F}{dE/dt}\right)_{t=0}$$

$(i_F)_{t=0}$ is equal to the external current before interruption. We can therefore determine the product k·c from the value of K_1 (or K_2). In Figure 10 plots of log (K_2 + t) versus E are given for the following two cases:

(I)	(II)
20% H_2SO_4	85% H_3PO_4
P_{O_2} = 1 atm	P_{O_2} = 1 atm
70°C	120°C
L = 4.9 mg Pt/cm^2	L = 4.9 mg Pt/cm^2
i = 300 ma/cm^2	i = 300 ma/cm^2

The parameters of these curves (Figure 10) are presented in Table II.

Table II

Determination of Tafel parameters from oscilloscopic E-t traces after current interruption for experiments I and II above.

	K_1 (mv)	K_2 (m sec)	b (mV)	$(dE/dt)_{t=0}$ (Volt/sec)	C^* (μF/cm^2)	kc (ma/cm^2)	i_o (A/cm^2)
I (H_2SO_4)	766	8.0	66	3.56	84.3	9.77×10^{13}	1.1×10^{-4}
II (H_3PO_4)	760	2.5	57	9.90	30.3	1.6×10^{16}	4.3×10^{-5}

The data in Table II are referred to 1 cm^2 external electrode area. The value for the exchange current in H_2SO_4 is for saturation concentration at P_{O_2} = 1 atm since the concentration overvoltage in this case was negligible (see Figure 8). Using the value 24 m^2/g for the specific surface area of the catalyst black we have for the true exchange c.d. $i_o = 1 \times 10^{-10}$ A/cm^2. The agreement with the steady state data (Table I) is satisfactory.

The value for i_o in Table II for H_3PO_4 is of little value because it refers to an unknown value for the oxygen concentration which, however, by evidence of the curve in Figure 8 was less than the solubility at P_{O_2} = 1 atm.

Additional data, also obtained from oscilloscope traces, are listed in Table III. The agreement with the steady state results again is satisfactory.

The data for H_3PO_4 in Table I agree with those determined[8] from experiments on smooth platinum surfaces in highly purified electrolyte.

Table III

Tafel slopes determined from oscilloscope traces for P_{O_2} = 1 atm.

Electrolyte	Temp. (°C)	L (mg Pt/cm^2)	i (ma/cm^2)	b (mV)
30% KOH	70	6.0	840	50
30% KOH	70	3.9	840	51
20% H_2SO_4	70	6.0	1000	67
20% H_2SO_4	70	3.9	1000	70

Curves such as those in Figures 8 and 9 have proven very useful in comparing different catalysts. For this purpose one has to make electrodes which yield curves like II in Figure 8. Other possible applications exist in such development work as reduction in catalyst loading or agglomerate size where progress can be seen clearly by comparing suitably reduced data with those in Figures 8 or 9. The data also indicate how far any structural improvements can possibly be carried.

The shape of the curves for KOH is of particular interest. Curves of this shape, with a sharp bend into a limiting current are not observed for electrodes which do not have porous Teflon backing at the gas side. The present curves have the general form usually expected for a flat sheet electrode with a Nernst diffusion layer. We believe that this behavior is the result, at least in part, of internal flooding of the electrode caused by the same process which, in the absence of a Teflon backing forces electrolytes out the back of the electrode. This force on the electrolyte increases with the current density and produces an increased thickness of the electrolyte film which covers the porous catalyst agglomerates. Thus this electrolyte film depends on the current density and, at high currents, sharply limits the current.

References

(1) R. Brown and L. A. Horve, Abstract No. 203, ECS Meeting, May 1967.

(2) J. Giner and C. Hunter, Abstract No. 327, ECS Meeting, October 1968.

(3) L. W. Niedrach and H. R. Alford, J. Electrochem. Soc., 112 (1965) 117.

(4) J. Giner, J. M. Parry, S. Smith, and M. Turchan, Abstract No. 328, ECS Meeting, October 1968.

(5) E. Yeager, "The Study of the Kinetics of Electrode Processes," Contract No. Nonr. 2391(00), Office of Naval Research, June 30, 1967, AD 673 096.

(6) J. Lundquist and W. Vogel, Abstract No. 335, ECS Meeting, October 1968.

(7) Measured against the hydrogen electrode (P = 1 atm) in the same medium. Standard potentials from: J. Llopis and J. Giner, Quimica, L(B) (1954) 921.

(8) A. J. Appleby and A. Borucka, Abstract No. 338, ECS Meeting, October 1968.

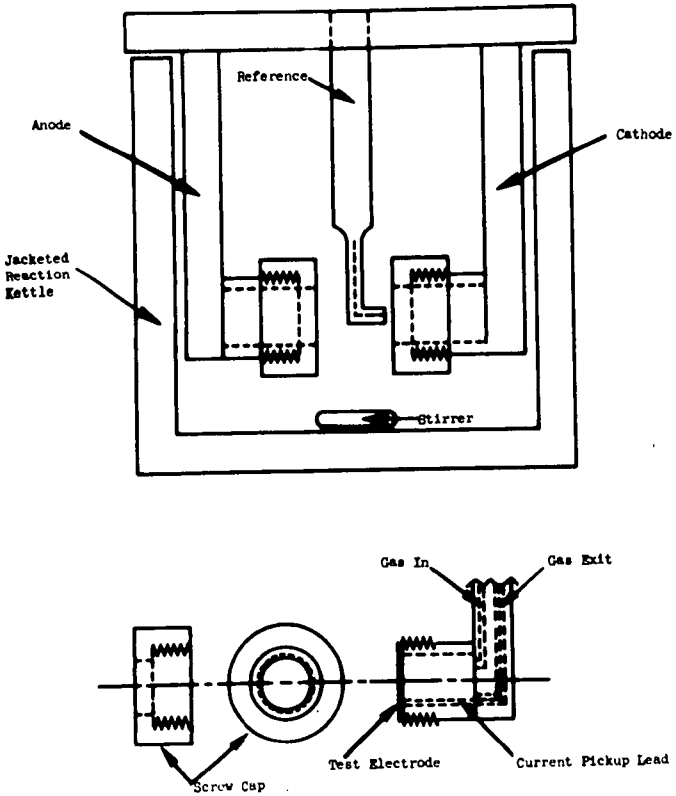

Figure 1. Cell Design

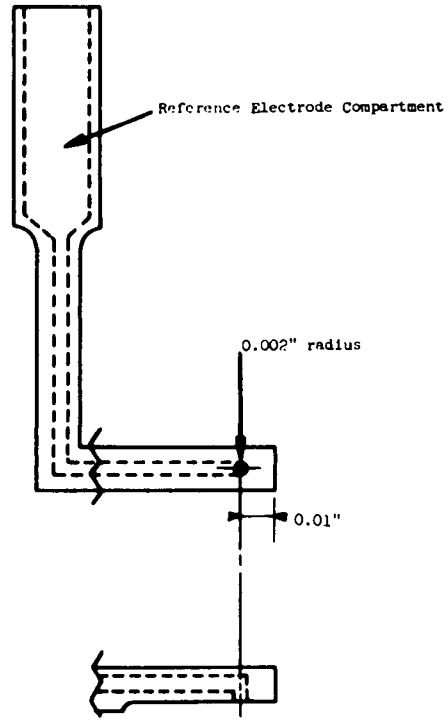

Figure 2. Reference Electrode Assembly

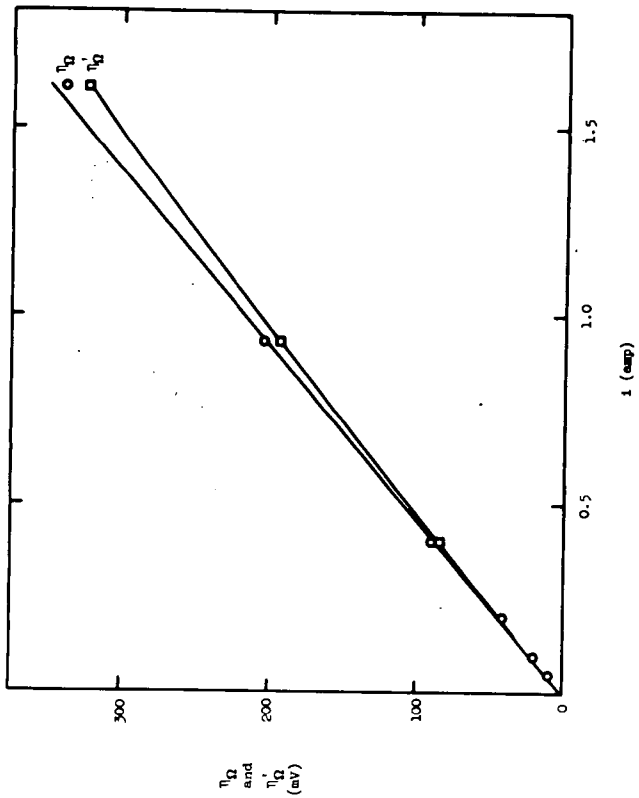

Figure 3. Variation of η_Ω and η'_Ω with Current. Electrode area was 2.81 cm^2.

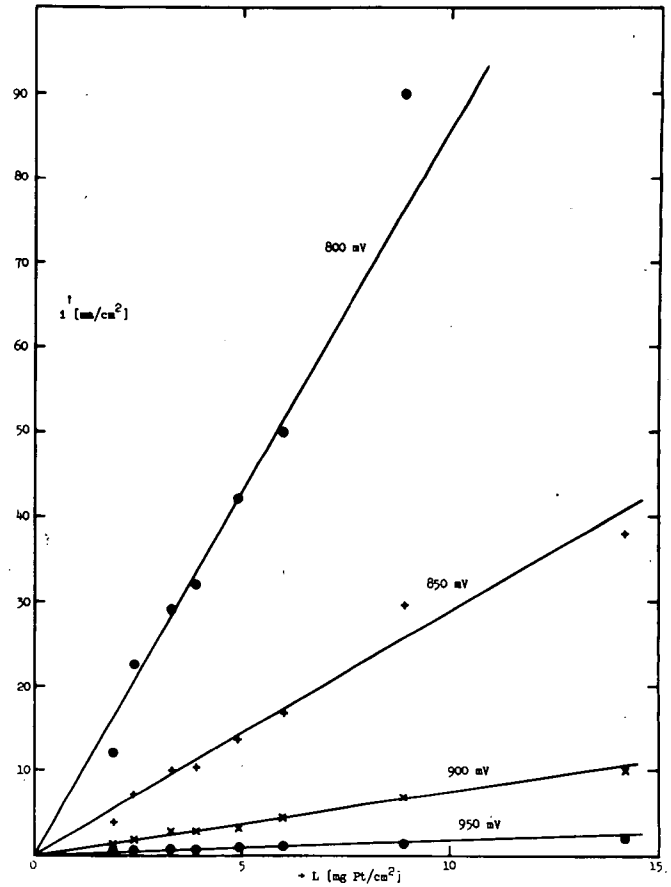

Figure 4. Performance on Air 120°C, 85 W% H_3PO_4

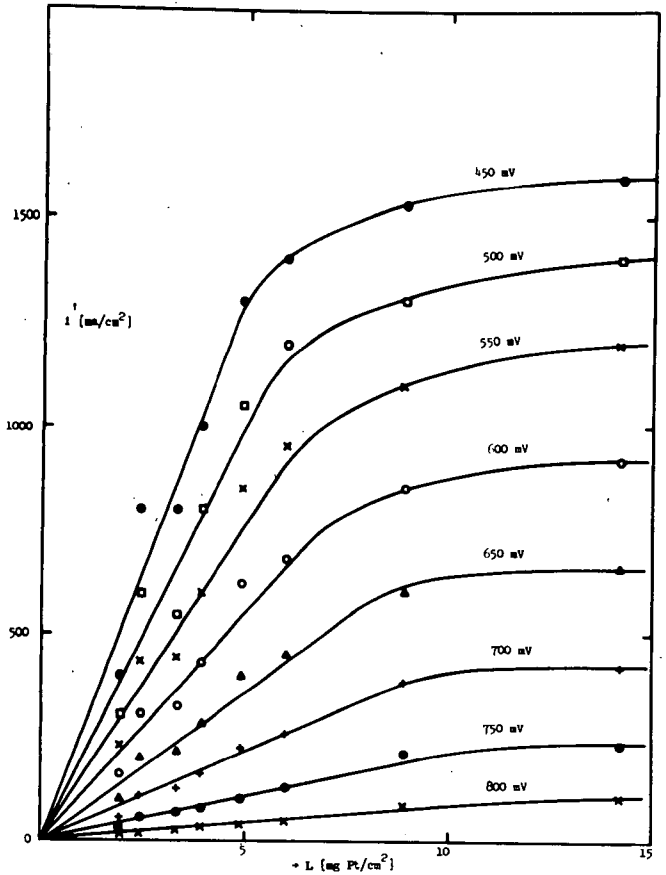

Figure 5. Performance on Air
120°C, 85 W% H_3PO_4

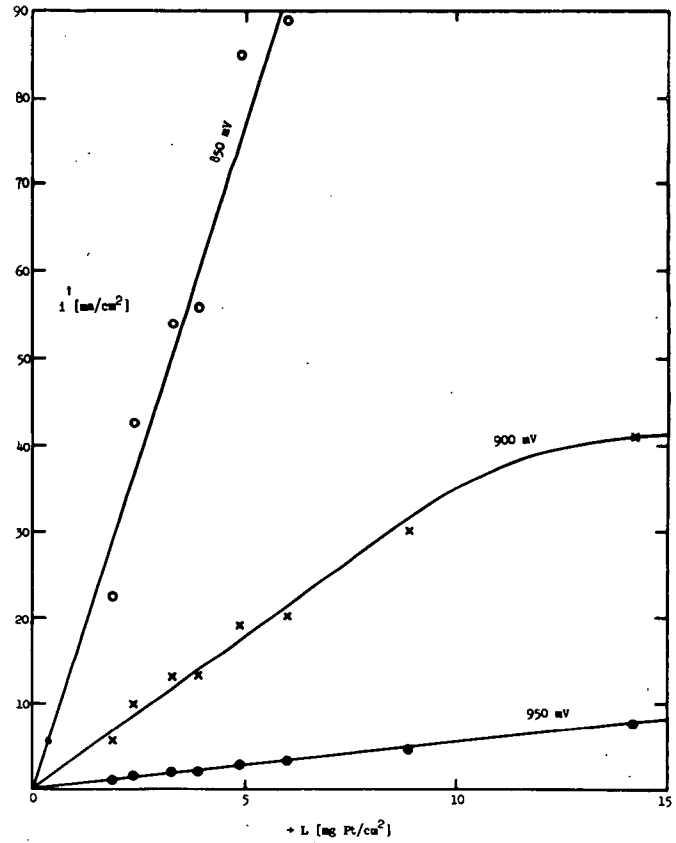

Figure 6. Performance on Oxygen
120°C, 85 W% H_3PO_4

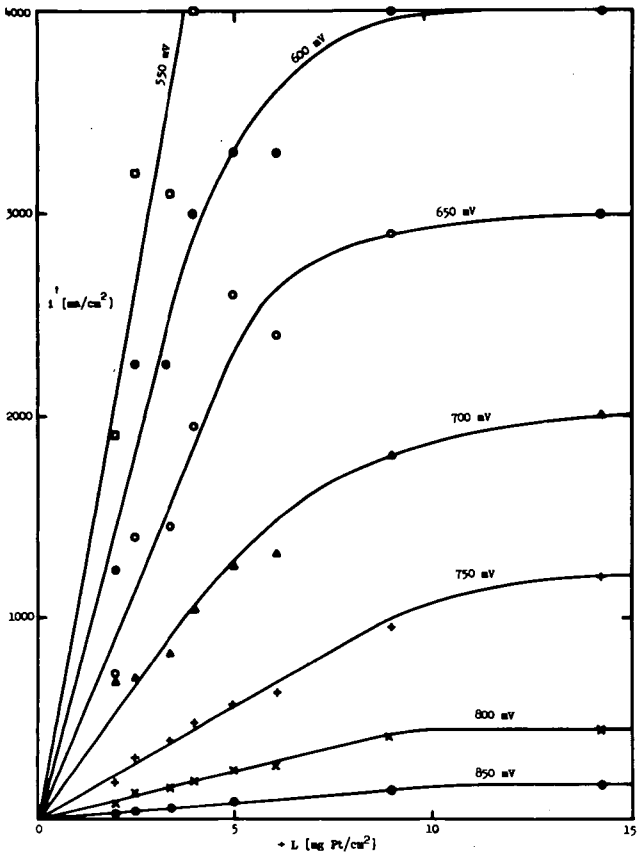

Figure 7. Performance on Oxygen
120°C, 85 W% H_3PO_4

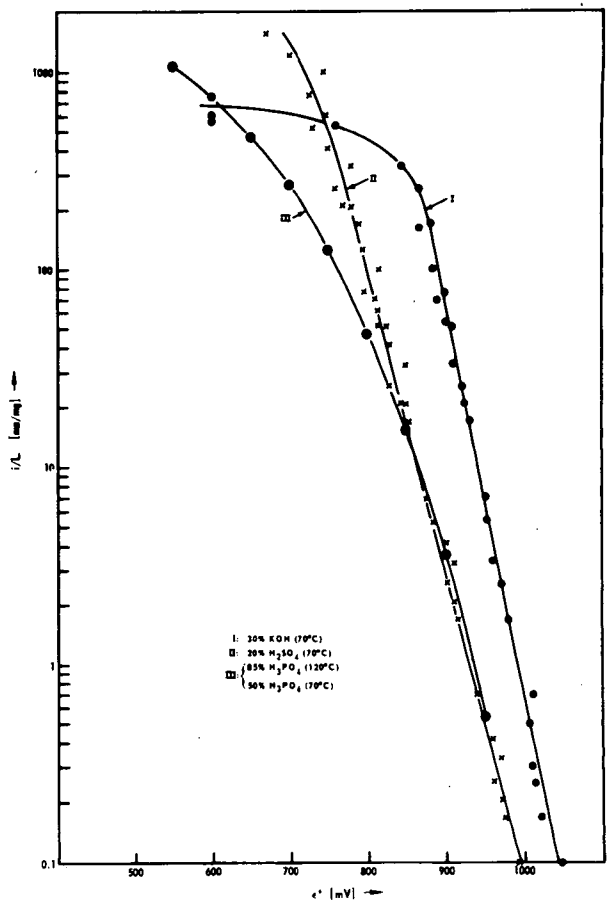

Figure 8. Polarization Curves for Oxygen
Normalized to 1 mg Pt/cm^2

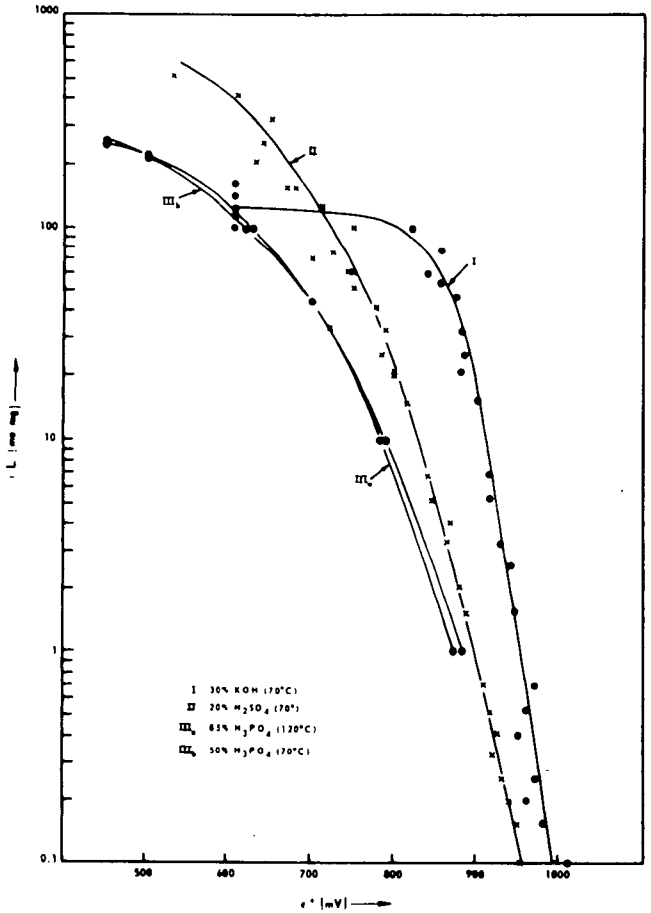

Figure 9. Polarization Curves for Air Normalized to 1 mg Pt/cm^2

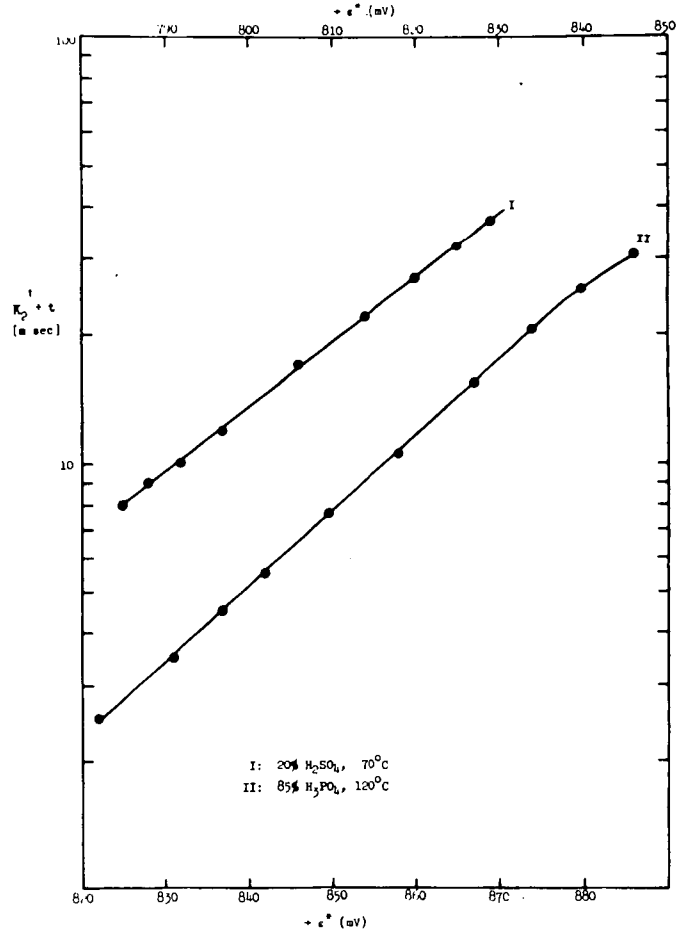

Figure 10. Determination of Tafel Parameters from Oscillographic ε-t Traces after Interrupting an External Current