

Lawrence Berkeley National Laboratory

LBL Publications

Title

KINETIC STUDIES USING A ROTATING CYLINDER ELECTRODE. I. ELECTRON TRANSFER RATES IN FERROUS/FERRIC SULFATE ON PLATINUM

Permalink

<https://escholarship.org/uc/item/9v32z74x>

Author

Morrison, B.

Publication Date

1985-10-01



Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

Materials & Molecular Research Division

RECEIVED
LAWRENCE
BERKELEY LABORATORY

OCT 14 1985

LIBRARY AND
DOCUMENTS SECTION

Submitted to Journal of Electroanalytical
Chemistry and Interfacial Electrochemistry

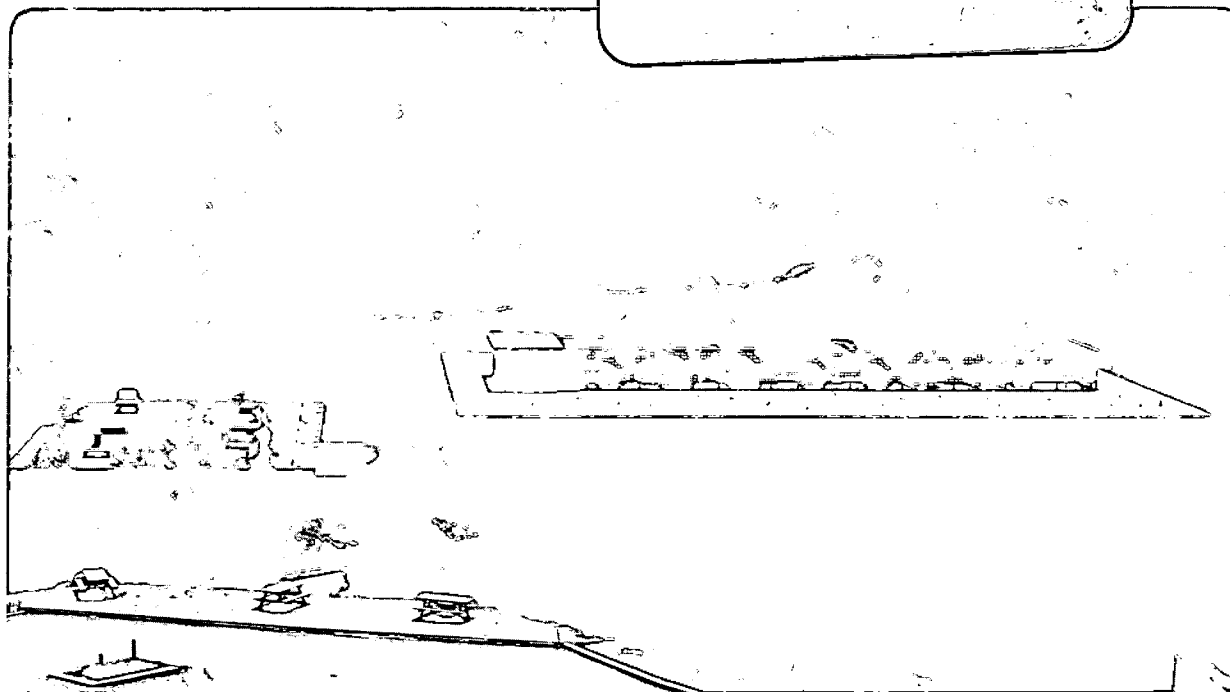
KINETIC STUDIES USING A ROTATING CYLINDER ELECTRODE.
I. ELECTRON TRANSFER RATES IN FERROUS/FERRIC SULFATE
ON PLATINUM

B. Morrison, K. Striebel, P.N. Ross, Jr.,
and P.C. Andricacos

October 1985

For Reference

Not to be taken from this room



LBL-20311
c.1

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

KINETIC STUDIES USING A ROTATING CYLINDER ELECTRODE

I. ELECTRON TRANSFER RATES IN FERROUS/FERRIC SULFATE ON PLATINUM*

B. Morrison, K. Striebel, P.N. Ross Jr.

Materials and Molecular Research Division
Lawrence Berkeley Laboratory
University of California
Berkeley, CA, 94720

and

P.C. Andricacos

IBM Thomas J. Watson Research Center
P.O. Box 218, Yorktown Heights, NY, 10598

*This work was supported by the U.S. Department of Energy
under Contract No. DE-AC03-76SF00098.

KINETIC STUDIES USING A ROTATING CYLINDER ELECTRODE

I. ELECTRON TRANSFER RATES IN FERROUS/FERRIC SULFATE ON PLATINUM*

B. Morrison, K. Striebel, P.N. Ross Jr.
Materials and Molecular Research Division
Lawrence Berkeley Laboratory
University of California, Berkeley, CA, 94720

and P.C. Andricacos
IBM Thomas J. Watson Research Center
P.O. Box 218, Yorktown Heights, NY, 10598

Abstract

A Pt rotating cylinder electrode has been used to study the mass transfer and kinetic characteristics of the $\text{Fe}^{+3}/\text{Fe}^{+2}$ redox reaction in a sulfate electrolyte. Mass transfer data indicate that limiting currents depend on the cylinder rotation speed to the 0.70 power. A model has been developed to extract kinetic parameters from mixed diffusion-kinetic data; according to this model, diffusion corrected kinetic currents at each potential are obtained by plotting inverse measured currents vs cylinder rotation speed to the -0.70 power and extrapolating the resulting straight lines to infinite rotation speed. Kinetic parameters for the $\text{Fe}^{+3}/\text{Fe}^{+2}$ reaction obtained on the cylinder electrode using this model coincided with values obtained for the same reaction on a rotating disk electrode using the Jahn-Vielstich model. It was thus concluded that rotating cylinders yield kinetic results which are equally satisfactory with those obtained from rotating disks.

*This work was supported by the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

Introduction

Electrochemical kinetic information is occasionally required from electrolytes available only in small quantities. Purification of these electrolytes is an additional problem, especially when extraction of meaningful kinetic parameters is impossible in impure environments. A typical example is the reduction of O_2 in newly synthesized superacids for possible use in acid fuel cells. Due to the low solubility of the reactant, kinetic information must be extracted from data reflecting partial diffusion control and as a result these studies are usually conducted on rotating disk electrodes (RDE's). In order to minimize the effect of impurities the ratio of electrolyte surface area to electrolyte volume should be made as large as possible. In a typical RDE arrangement one is confronted with a small electrode in a relatively large electrolyte volume, a configuration that accentuates the role of impurities. To circumvent the problem we investigated the use of a rotating cylinder electrode (RCE) in which the electrode rotates in a concentric cylinder cell. Since the cylinder electrode area can be made 10 times larger than that of a disk electrode and the electrolyte volume 10 times smaller, the surface-to-volume ratio can be increased by two orders of magnitude (these numbers refer to experimental setups used before (1,2) for O_2 reduction studies in which the RDE area was 0.46 cm^2 and the electrolyte volume was not less than 100 cm^3 .)

The RDE has enjoyed wide popularity because its flow regime is stable over a wide range of rotation speeds and establishes a uniform

diffusion layer which is accurately computed via the Levich theory. By comparison, the hydrodynamics of the RCE are not accurately known and consequently the thickness of the diffusion layer must be determined empirically. A mass transfer correlation was first proposed by Eisenberg, Tobias, and Wilke (ETW correlation) (3). Subsequent investigators confirmed the validity of the ETW correlation and their results have been reviewed by Gabe and co-workers (4,5). However, to our knowledge the RCE has not been used to extract kinetic information for electrochemical reactions.

In this communication we describe the use of a rotating cylinder electrode assembly of our own construction to study the $\text{Fe}^{+3}/\text{Fe}^{+2}$ couple in sulfate solution. A parallel study with an RDE was made to compare mass transfer and kinetic results. Based on limiting current measurements we first established the mass transfer correlation. We then developed a model for extracting kinetic currents from mixed diffusion-kinetic values assuming a uniform diffusion layer and making use of the mass transfer correlation. Using standard methods we then extracted values for the Tafel slope and the exchange current density for the reaction. By comparing RCE and RDE results we conclude that kinetic parameters obtained from the cylinder electrode are in close agreement with those obtained from the RDE.

Experimental

The all-PTFE RCE assembly is shown in Figure 1. It consisted of a Pine Instruments Model DDC 32 Pt cylinder working electrode (geo. area = 6.8 cm^2 diameter = 0.85 cm) rotating in the center of a

cylindrical cell (ID = 2.54 cm). The graphite counter electrode was a ring concentric to the cylinder embedded in the walls of the cell providing a continuous surface. A small hole drilled through the ring provided communication with the separate reference electrode compartment ($\text{Hg}/\text{Hg}_2\text{SO}_4$). A PTFE capillary penetrated the hole ending exactly at the surface of the counter electrode.

In designing the RCE assembly several considerations were kept in mind: i) the dimensions of the gap between cell wall and cylinder electrode were chosen so as to minimize the volume of electrolyte without running into the danger of appreciably decreasing the bulk concentration of the reactant during the measurement (in the experiments reported here this was not a problem since the reactant was the product of the counter electrode reaction); ii) since one of our goals was to keep the volume of the electrolyte at a minimum no external circulation of the electrolyte was incorporated into the design; iii) non-conducting boundaries perpendicular to the electrode surface were not included at the expense of primary current distribution non-uniformity (however, we do not expect edge effects to affect our data significantly); iv) the specifications on the anode and the reference electrode probe design were chosen to avoid flow obstructions in the gap and to effect a constant electrolyte resistance configuration.

Parallel RDE experiments were performed in a glass cell with the same $\text{Hg}/\text{Hg}_2\text{S}_4$ reference electrode and a Pt foil counter electrode. Both Pt working electrodes were polished by 6 μm and then 1 μm diamond paste. They were degreased and then cleaned by soaking in a mixture

of nitric and sulfuric acids followed by rinsing and soaking in freshly distilled water at least 3 times. Roughness factors were estimated for each electrode (disk 1.7, cylinder 1.8) from the charge associated with hydrogen desorption in 0.5 M H_2SO_4 . However, this was used only as a check.

Experiments were performed in solutions containing x M Fe^{+2} , x M Fe^{+3} , and 0.5 M H_2SO_4 (prepared from AR grade chemicals and doubly distilled water) where $x = 0.010, 0.030, 0.050$. We chose this system because we did not want to contaminate our electrode assembly with anions hard to remove such as Cl^- , CN^- etc. The electrolytes were deaerated with Ar prior to the experiments.

Results

Current-potential curves were recorded at several rotation speeds in each cell by first pulsing the working electrode between 0.05 and 1.5 V vs RHE to obtain a reproducible surface, followed by sweeping at 10 mV/sec from the oxidation limiting current to the reduction limiting current. As shown in Figure 2 for the RCE, at potentials anodic to the equilibrium potential Fe^{+2} oxidizes, whereas at potentials cathodic to the equilibrium potential Fe^{+3} reduces. The amounts of Fe^{+2} and Fe^{+3} added or removed during a measurement are insignificant compared to the total amounts originally present in the electrolyte. The set of curves exhibits common features: a diffusion limited current plateau at high overpotentials and a current region near the equilibrium potential where the current is under mixed diffusion-kinetic control. Diffusion limited currents for the RDE can be analyzed with the Levich theory; mixed diffusion-kinetic currents for the

RDE can be analyzed with the Jahn-Vielstich model (6) in which both anodic and cathodic reactions are assumed to be first order with respect to the reactant concentrations. The RDE Jahn-Vielstich model is more appropriate than the Frumkin-Tedoradse model (7) for extracting kinetic parameters for fast reactions since it takes into account both forward and backward reactions. A similar type of analysis can be done for the RCE and will be outlined in the following sections.

a. Mass Transfer Analysis

Following Eisenberg et al (3), measured limiting current densities on the RCE, i_L , can be correlated to the Reynolds number as shown in Figure 3, where the quantity

$$j_d = \frac{i_L}{nFc^b} Sc^{0.644} \quad [1]$$

is plotted against the Reynolds number,

$$Re = \frac{vd}{\nu} = \frac{\omega d^2}{2\nu} \quad [2]$$

on a log-log scale. In equations [1] and [2], v is the peripheral velocity of the cylinder electrode, ω is the angular velocity, d is the cylinder diameter, c^b is the bulk concentration of the reactant, ν is the kinematic viscosity of the electrolyte, n is the number of transferred electrons (equal to 1 in this case), and F is Faradays constant. The Schmidt number, $Sc (= \nu/D)$ has been computed using diffusivity values obtained from the RDE limiting current values and the Levich equation:

$$D_{\text{Fe}^{+2}} = 3.89 \times 10^{-6} \text{ cm}^2/\text{s} \text{ and } D_{\text{Fe}^{+3}} = 3.34 \times 10^{-6} \text{ cm}^2/\text{s} \quad [3]$$

Figure 3 indicates that for both anodic and cathodic reactions,

$$j_d = 0.0964 \text{ Re}^{-0.30} \quad [4]$$

Equation [4] can be rearranged to yield several equivalent forms

$$i_L = 0.0593nFc_d^{0.40} v^{-0.344} D^{0.644} \omega^{0.70} \quad [5]$$

$$\text{Sh} = 0.0964 \text{ Re}^{0.70} \text{ Sc}^{0.356} \quad [6]$$

The dependence of the limiting current density on all dimensional variables characterising the cylinder electrode is clearly outlined in Equation [5]. Most notably, i_L varies with 0.70 power of the angular rotation speed. Equation [6] is the dimensionless form of eq. [5]. Sh is the Sherwood number defined by

$$\text{Sh} = \frac{i_L d}{nFDc_b} \quad [7]$$

Although the exponent dependence of Sh on Re is in excellent agreement with the ETW correlation, the value of the numerical constant in eq. [6] is ca. 18% higher (0.0964 here, compared with 0.0791 in the ETW correlation). There is some confusion in the literature as to the exact reasons for this type of discrepancy and these have been discussed elsewhere (4,5). However, as we shall see later, the value of this coefficient does not enter into the kinetic analysis.

An expression for the Nernst diffusion layer thickness, δ , can be extracted from eq. [5]

$$\delta = \frac{nFDc^b}{i_L} = 16.86d^{-0.40}v^{0.344}D^{0.356}\omega^{-0.70} \quad [8]$$

Introducing

$$B = 16.86d^{-0.40}v^{0.344}D^{0.356} \quad [9]$$

we can rewrite eqs. [5] and [8] as follows

$$i_L = nFDc^b \frac{\omega^{0.70}}{B} \quad [10]$$

$$\delta = B\omega^{-0.70} \quad [11]$$

Since the value of B depends on the diffusivity of the reactant (cf. eq. [3]), one should distinguish B_O for the oxidized species (Fe^{+3}) from B_R for the reduced species (Fe^{+2}).

b. Kinetic Analysis

For a first order reaction $O + ne^- = R$ the relation between the current density, i , and the surface concentrations of the reactant and product, C_O^S and C_R^S respectively, is given by

$$i = nF(k_f C_O^S - k_b C_R^S) \quad [12]$$

where k_f and k_b are rate constants related to the standard rate constant, k^0 , and the overpotential, η , by Tafel's equation

$$k_f = k^0 \exp(-\alpha f \eta) \quad [13a]$$

$$k_b = k^0 \exp((1-\alpha) f \eta) \quad [13b]$$

Partial diffusion control is reflected in eq. [12] for the case when surface concentrations are not equal to the bulk concentrations, c_0^b and c_R^b . When these are equal, the resultant current density, i_K , is the purely kinetic current density and is described by the following equation

$$i_K = nF(k_f c_0^b - k_b c_R^b) \quad [14]$$

In the steady state and for a uniformly thick diffusion layer, surface and bulk concentrations for the RCE are simply related to the diffusion limited current densities of the reduction and oxidation reactions, i_L^0 and i_L^R respectively

$$c_0^s = c_0^b \left(1 - \frac{i}{i_L^0}\right) = c_0^b - i \frac{B_0}{nFD_0} \omega^{-0.70} \quad [15a]$$

$$c_R^s = c_R^b \left(1 + \frac{i}{i_L^R}\right) = c_R^b + i \frac{B_R}{nFD_R} \omega^{-0.70} \quad [15b]$$

where use of eq. [10] for the limiting current densities has been made. Combination of eqs. [12], [14], and [15] for the RCE yields

$$i^{-1} = i_K^{-1} + i_K^{-1} (B_O D_O^{-1} k_f + B_R D_R^{-1} k_b) \omega^{-0.70} \quad [16]$$

Equation 16 can be used to analyze results of RCE experiments. If the reaction is first order, a plot of i^{-1} vs $\omega^{-0.70}$, at constant potential, should yield a straight line. The inverse of the diffusion corrected purely kinetic current at the particular value of the overpotential is obtained from the intercept. The slope depends on both transport and kinetic parameters and changes for each value of the overpotential. It should be noted that eq. [16] resembles the Jahn-Vielstich model for the rotating disk electrode; however, the B's and the exponents of ω are different in the two systems. Furthermore, it is obvious that a model of similar architecture can be developed to describe the behavior of a first-order reaction on any convective electrode, e.g. the recent work by Alberly with the impinging-jet electrode (8). For the case of very high overpotentials and/or slow kinetics the backward reaction can be neglected. Letting $k_b \gg 0$ in eqs. [14] and [16] we obtain

$$i^{-1} = i_K^{-1} + (nFD_O c_O^b B_O^{-1})^{-1} \omega^{-0.70} \quad [17]$$

where now

$$i_K = nFk_f c_O^b \quad [18]$$

and k_f is defined by eq. [13a]. For the analysis of eq. [17], the same type of plot (i^{-1} vs $\omega^{-0.70}$) as before can be used. However, the slope is now independent of the overpotential and as a result

i^{-1} vs $\omega^{-0.70}$ lines should be parallel to each other yielding a value for D_0 . It should be noted that eq. [17] is also a limiting case of eq. [16] for high overpotentials; in other words, i^{-1} vs. $\omega^{-0.70}$ plots for a fast reaction (eq. [16]) should eventually be parallel for high values of the overpotential; however, observation of this effect will depend on the value of the overpotential at which the reaction becomes totally diffusion limited.

Inverse current plots for the $\text{Fe}^{+3}/\text{Fe}^{+2}$ redox reaction are shown in Figure 4 for both cylinder and disk electrodes with the concentrations of both reactants equal to 0.05 M. In Figure 4A, i^{-1} is plotted against $\omega^{-0.70}$ for various values of the potential according to eq. [16]. A similar equation for the disk has been provided by the Jahn-Vielstich model and it dictates that inverse currents should be plotted against $\omega^{-0.50}$, as shown in Figure 4B. Since the $\text{Fe}^{+3}/\text{Fe}^{+2}$ reaction is fairly fast the straight lines obtained are not parallel and both forward and backward reactions have to be taken into account when analyzing data. Extrapolation of the straight lines to infinite rotation speed for each potential yields values for the inverse of the purely kinetic currents which can then be used to construct Tafel plots, such as the one appearing in Figure 5. Extraction of kinetic parameters is straightforward and a summary of kinetic results appears in Table I.

It is seen that Tafel slopes obtained from both disk and cylinder data are nearly identical, i.e. within the accuracy normally expected for this type of measurement. The Tafel slope for the redox reaction is nominally $2RT/F$ imparting a value for the transfer coefficient equal

to 0.5. Nearly identical exchange current densities were derived from the cylinder and disk data, yielding a value for the concentration-independent standard rate constant of ca. 10^{-3} cm/s. Table I indicates that a kinetic study can be performed with a rotating cylinder electrode and yield results which are as valid as those obtained from an RDE.

As mentioned above the slopes of the inverse current curves are not equal since most of the current variation before total diffusion control occurs near the equilibrium potential. According to eq. [16] knowledge of the kinetic and transport parameters makes it possible to compute these slopes and compare with the experimentally determined values. For slow reactions advance knowledge of the kinetic parameters is not required and as indicated by eq. [17] transport parameters alone are sufficient for the slope computation. An equation analogous to eq. [17] is routinely used for the analysis of the slow O_2 reduction on RDEs and has been useful in determining solubility, O_2 diffusivity, or even number of transferred electrons if the other two values can be independently determined. In the case of Fe^{+3}/Fe^{+2} the situation is sufficiently straightforward to allow a comparison between experimental and computed inverse slopes. In eq. [16] we have used the values

$$k^0 = 1.23 \times 10^{-3} \text{ cm/s} \quad \text{and} \quad \alpha = 0.5 \quad [19]$$

in conjunction with eqs. [13] and [14] to compute values for k_f , k_b , and i_K , respectively, for each overpotential of Fe^{+2} oxidation. For

the transport parameters D_0 , D_R , and B_0 , B_R we have used eqs. [3] and [9] respectively. The results are reported in Table II and it can be seen that the agreement between computed and experimental values is very good. It should be noted that this is a check for consistency rather than an independent determination.

Conclusions

A Pt electrode rotating in a concentric cylindrical cell has been used to study the $\text{Fe}^{+3}/\text{Fe}^{+2}$ redox reaction in a sulfate electrolyte. In a parallel experiment the same system was studied with a rotating disk electrode. Mass transfer analysis for the RCE indicated that diffusion limited current densities vary with the 0.70 power of the angular rotation speed. By plotting inverse currents vs the -0.70 power of the rotation speed, diffusion corrected data were obtained for the kinetic parameters of the reaction. We found that both rotating cylinder and rotating disk electrodes yield nearly identical results for the Tafel slope and the standard rate constant of the reaction. We therefore conclude that despite the empirical nature of the RCE mass transfer characterization equally reliable kinetic data can be obtained as with the RDE. The RCE may offer additional advantages such as uniform current distribution and an improved electrode area to electrolyte volume ratio.

References

1. P.N. Ross and P.C. Andricacos, J. Electroanal. Chem., 154, 205(1983).
2. K. Striebel, P.C. Andricacos, E.J. Cairns, P.N. Ross, and F.R. McLarnon, J. Electrochem. Soc., 132, 2381(1985).
3. M. Eisenberg, C.W. Tobias, and C.R. Wilke, J. Electrochem. Soc., 101, 306(1954).
4. D.R. Gabe, J. Appl. Electrochem., 4, 91(1974).
5. D.R. Gabe and F.C. Walsh, J. Appl. Electrochem., 13, 3(1983).
6. D. Jahn and W. Vielstich, J. Electrochem. Soc., 109, 894(1962).
7. A.N. Frumkin and G. Tedoradse, Z. Elektrochem., 62, 251(1958).
8. W.J. Albery, J. Electroanal. Chem., 191, 1(1985).

Table 1. Kinetic Parameter for the $\text{Fe}^{+3}/\text{Fe}^{+2}$ Redox Reaction

Kinetic Parameter	RCE	RDE
Exchange Current Density $i_0(\text{A.cm}^{-2})$	5.95×10^{-3}	6.4×10^{-3}
Standard Rate Constant $k^0(\text{cm.s}^{-1})$	1.23×10^{-3}	1.32×10^{-3}
Tafel slope (mV.dec.^{-1})		
Cathodic	132	127
Anodic	125	124

Table 2. Slopes of Inverse Current Plots for the RCE

Overpotential (V)	Slopes ($\text{mA}^{-1}\text{rpm}^{-0.7}$)	
	Experimental	Computed
0.037	2.44	2.75
0.057	2.02	2.10
0.077	1.87	1.85
0.097	1.75	1.75
0.167	1.75	1.67

Figure Captions

- Fig. 1 Rotating cylinder electrochemical cell.
- Fig. 2 Current-potential sweeps at the RCE in 0.05 M FeSO_4 , 0.05 M $\text{Fe}_2(\text{SO}_4)_3$ and 0.5 M H_2SO_4 .
- Fig. 3 Mass-transfer correlation for the RCE including data for oxidation and reduction reactions; \circ : 0.01 M, \square : 0.03 M, \diamond : 0.05 M Fe^{+2} and Fe^{+3} .
- Fig. 4 Inverse current plots for A : RCE and B : RDE. 0.05 M Fe^{+2} and 0.05 Fe^{+3} in 0.5 M H_2SO_4 .
- Fig. 5 Tafel plot of data calculated from Fig. 4. X : RCE, O : RDE.

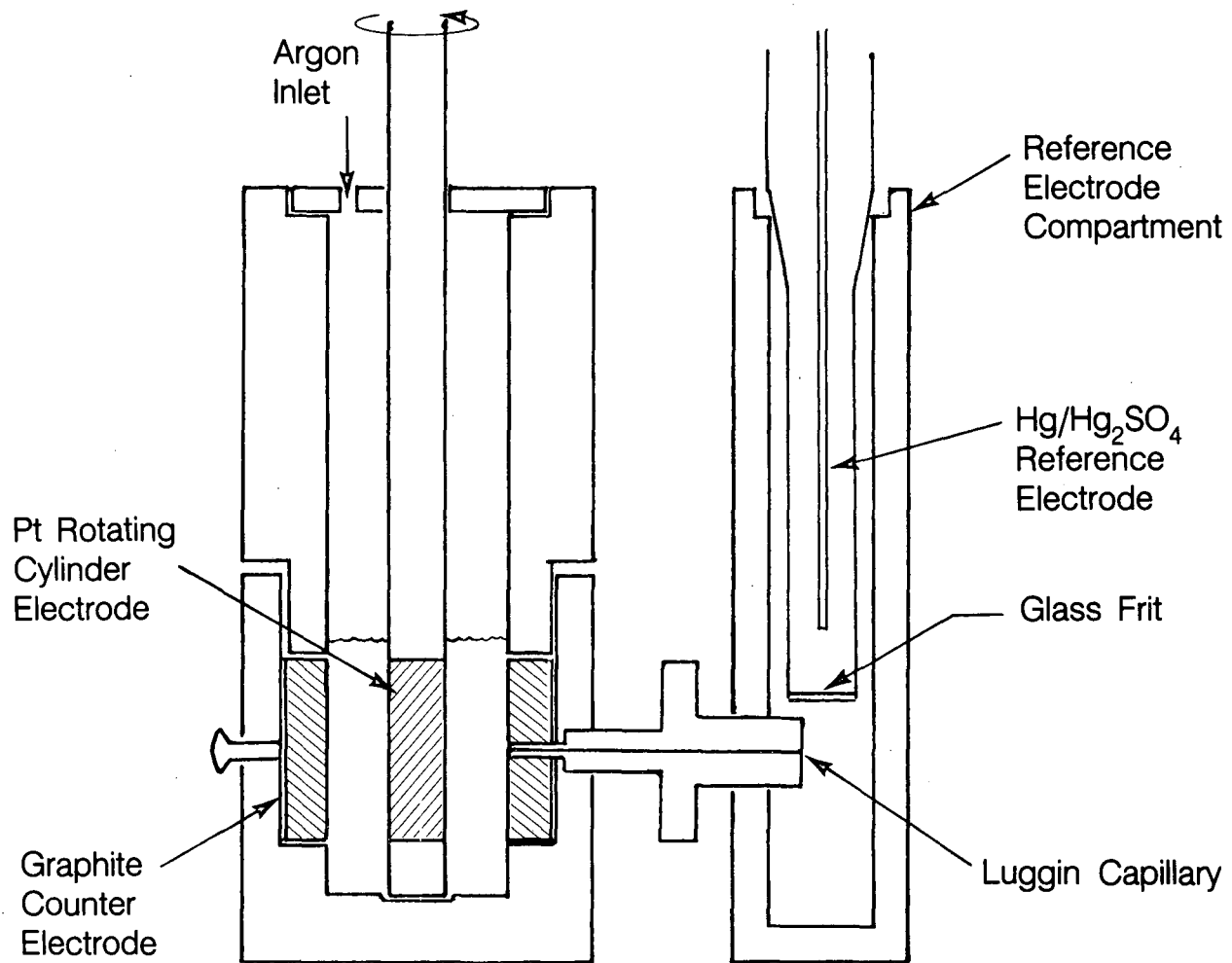
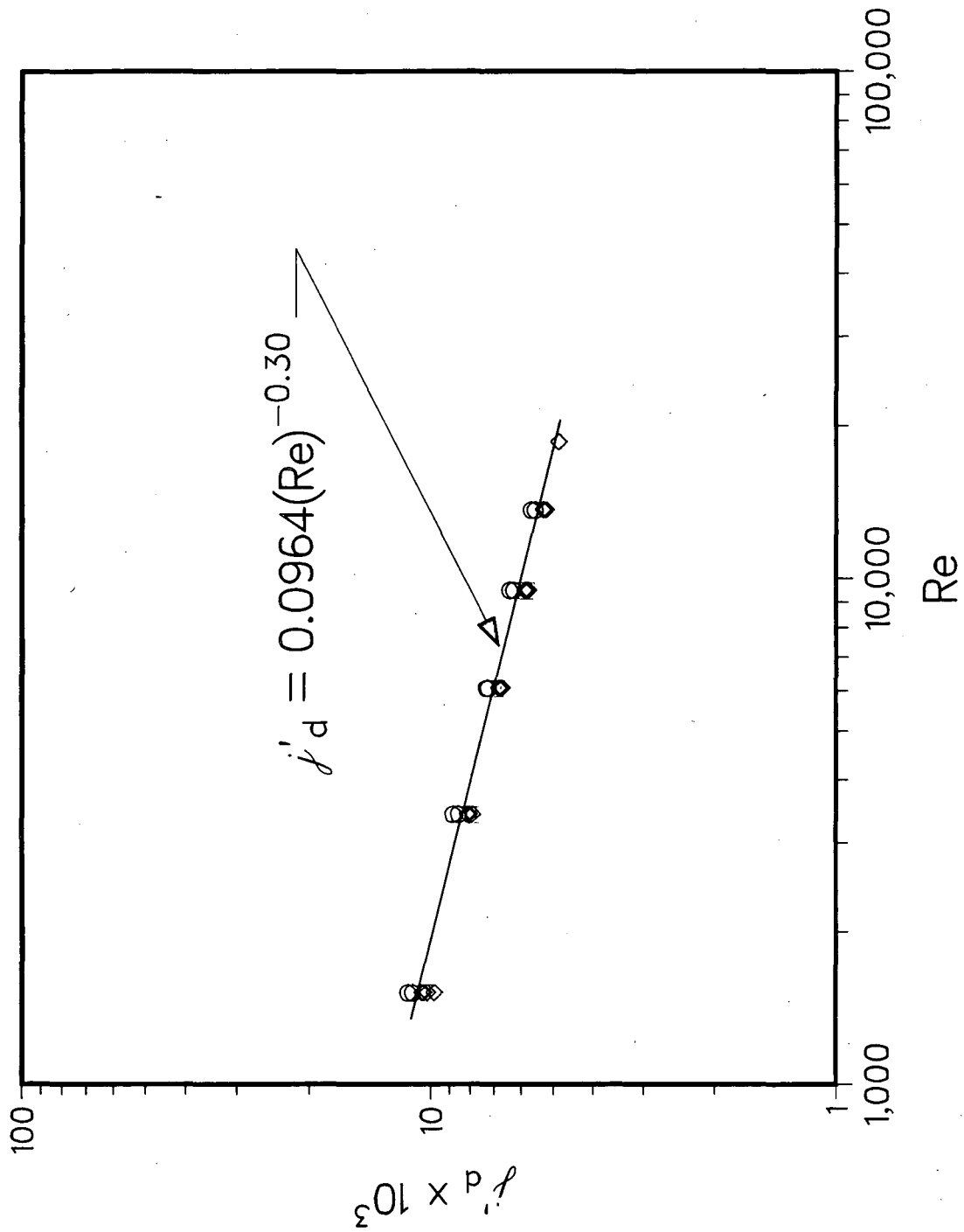
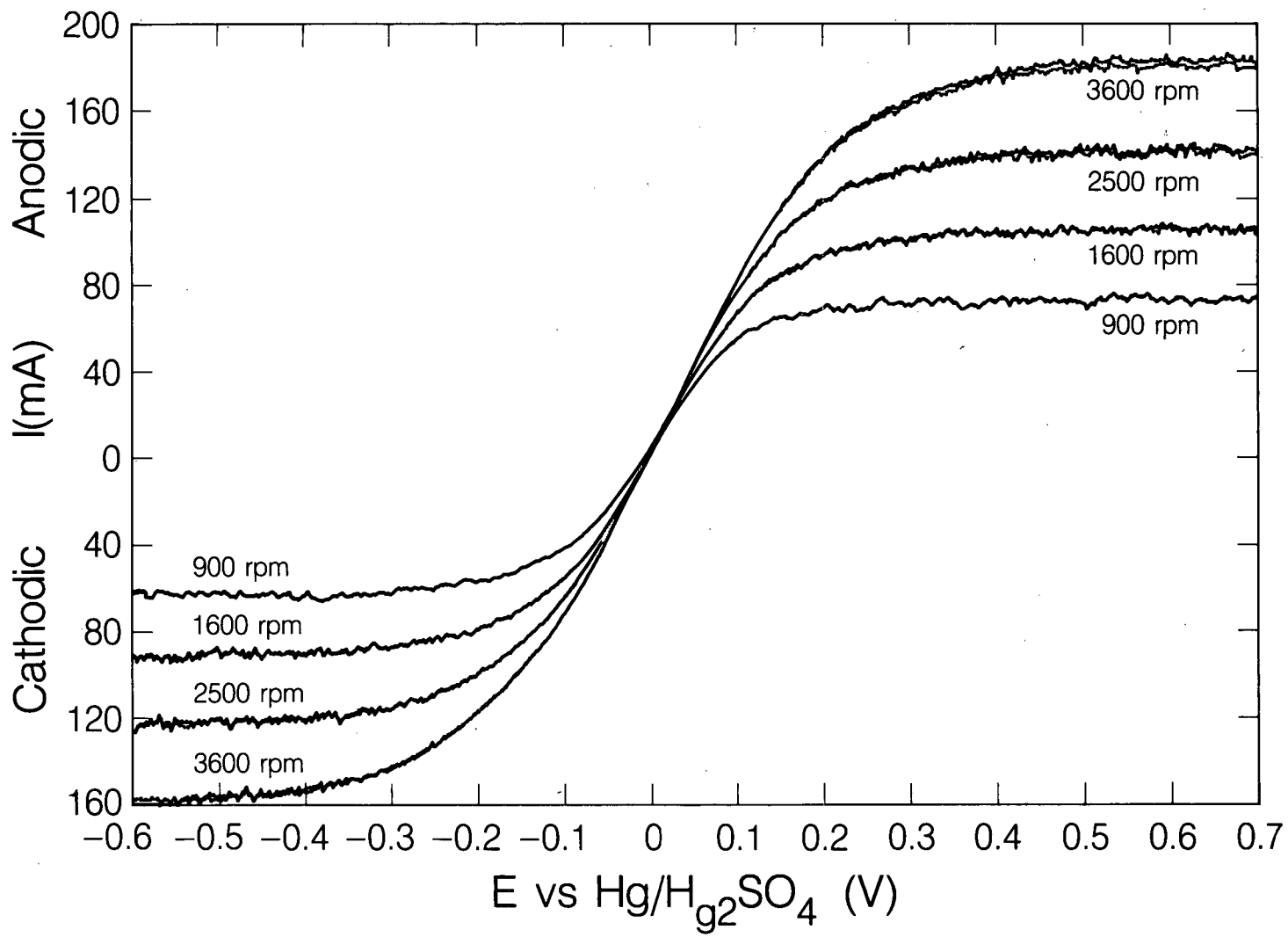


Fig. 1



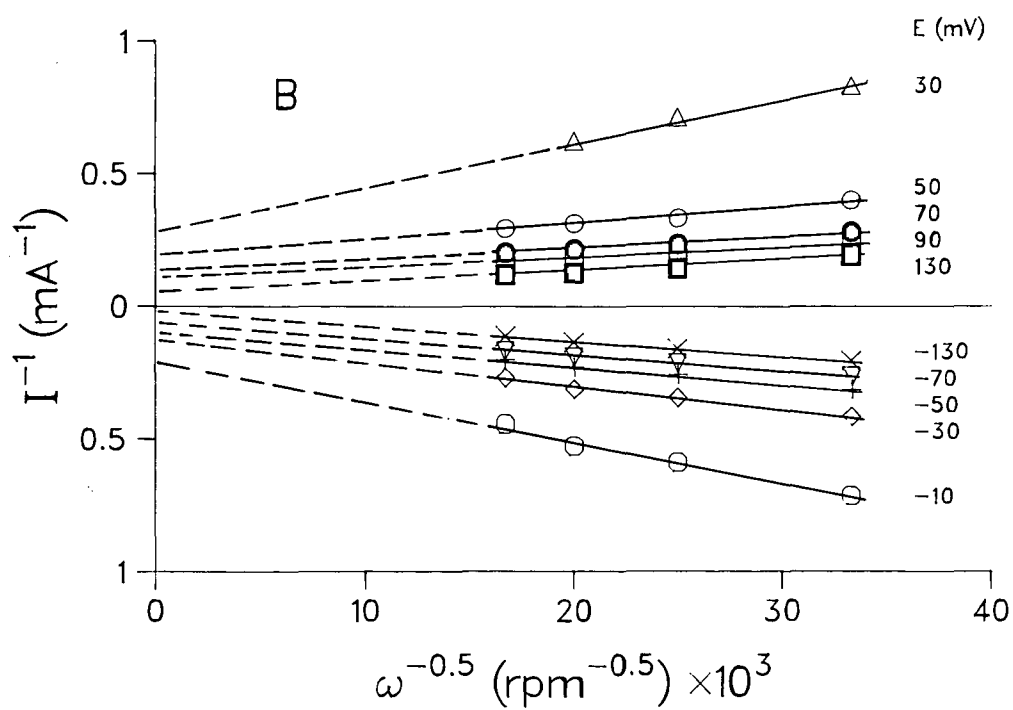
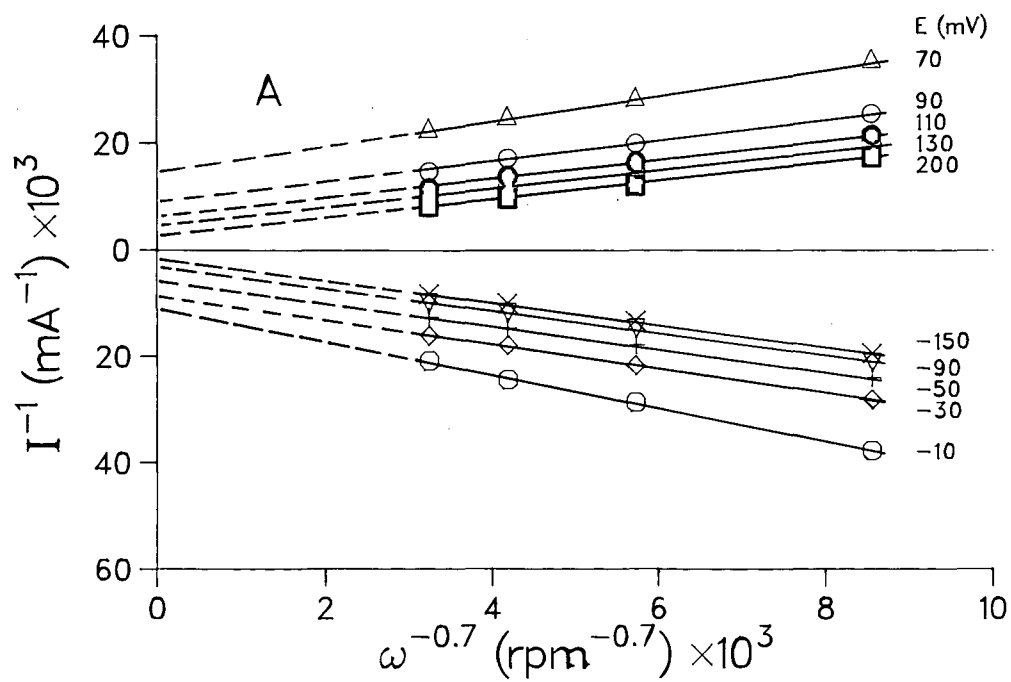
XBL 8511-4498

Fig. 2



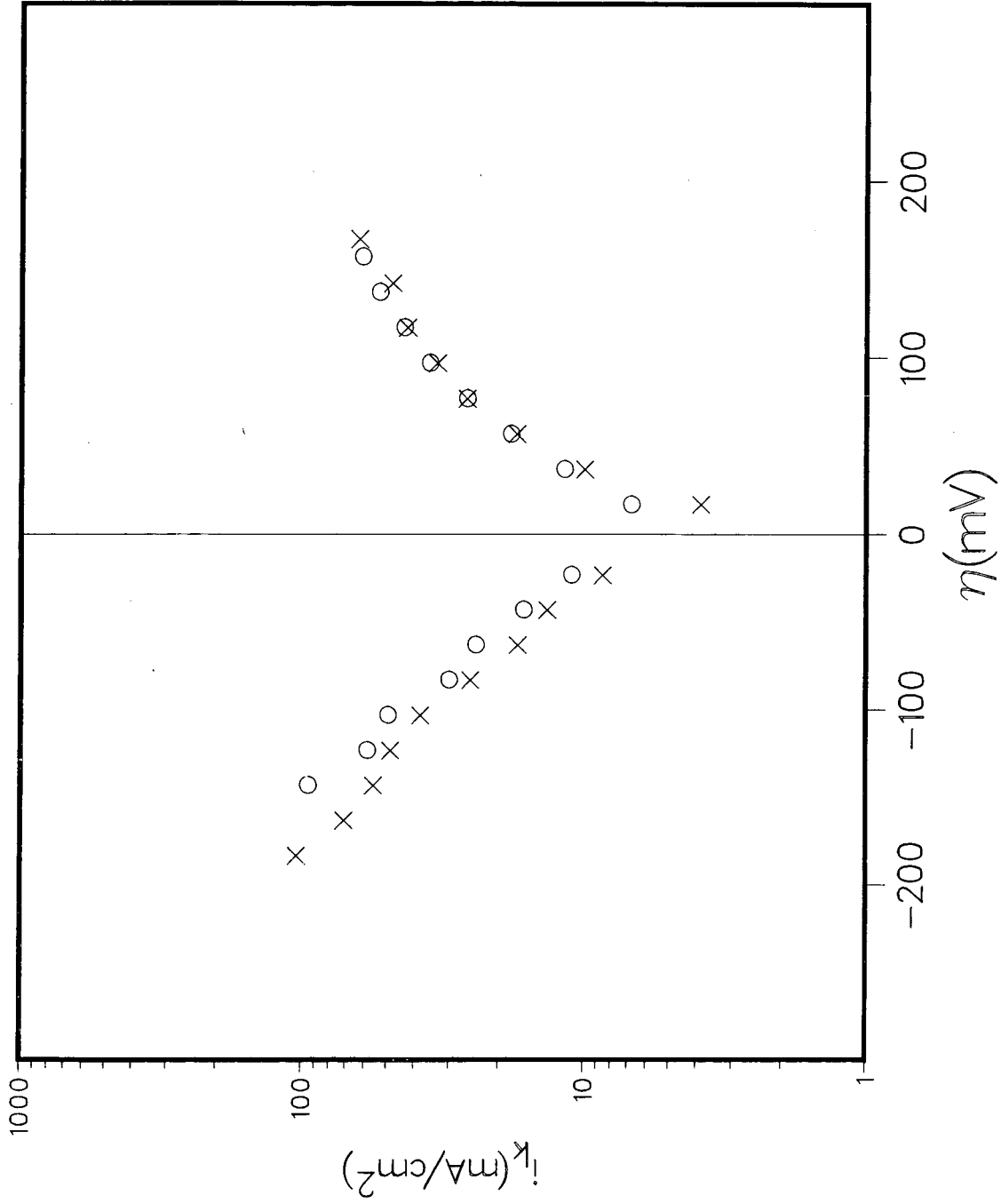
XBL 859-8986

Fig. 3



XCG 8510-441

Fig. 4



XBL 8511-4499

Fig. 5

This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U.S. Department of Energy to the exclusion of others that may be suitable.

*LAWRENCE BERKELEY LABORATORY
TECHNICAL INFORMATION DEPARTMENT
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720*