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1982-11-01



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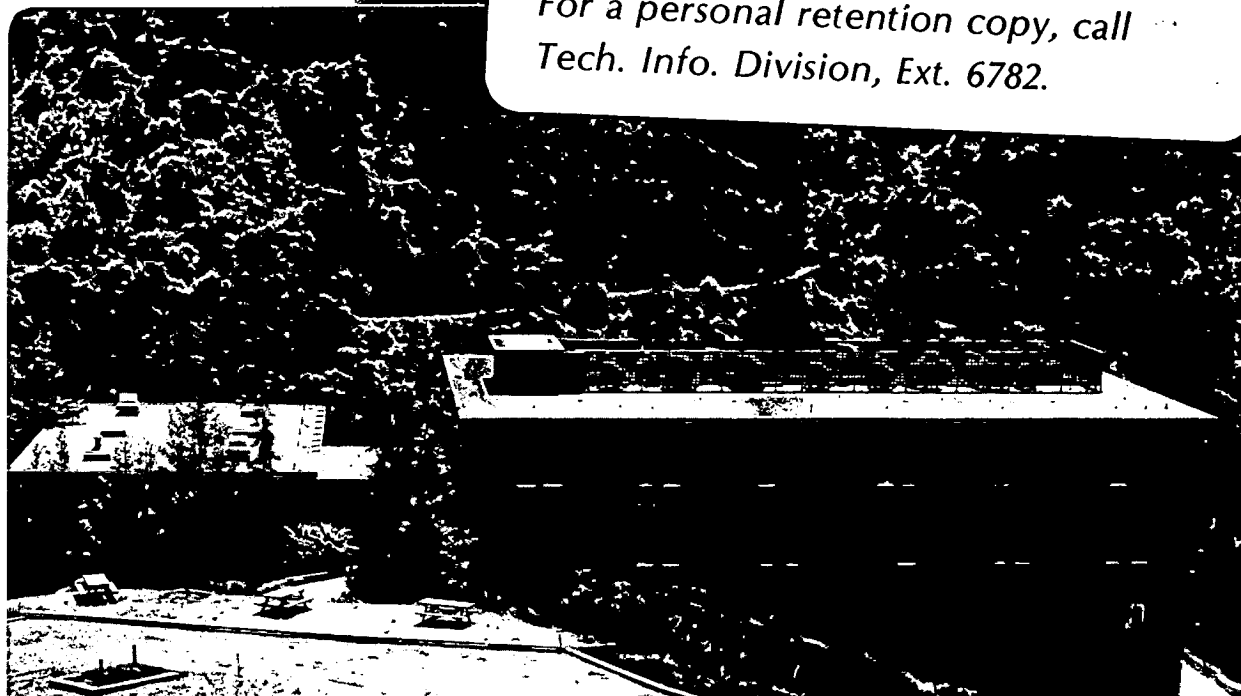
THE EFFECT OF  $\text{H}_2\text{PO}_4^-$  ANION ON THE KINETICS OF  
OXYGEN REDUCTION ON Pt

P.N. Ross and P.C. Andricacos

November 1982

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THE EFFECT OF  $\text{H}_2\text{PO}_4^-$  ANION  
ON THE KINETICS OF OXYGEN REDUCTION ON Pt

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ABSTRACT

Recent studies of anion adsorption on Pt have shown that trifluoromethane sulfonic acid (TFMSA) is a non-adsorbing electrolyte. Previous comparisons of the kinetics of oxygen reduction on Pt in TFMSA to the kinetics in  $\text{H}_3\text{PO}_4$  show qualitatively that better kinetics were obtained in TFMSA electrolyte, but these studies were not done in a manner in which the effect of specific adsorption by  $\text{H}_2\text{PO}_4^-$  anion was apparent. The effect is shown directly in this study by adding small aliquots of  $\text{H}_3\text{PO}_4$  to 0.1 M TFMSA while determining the oxygen reduction kinetics with a Pt rotating disc electrode. The range of  $\text{H}_2\text{PO}_4^-$  concentrations varied nearly four orders of magnitude, from  $2.9 \times 10^{-5}$  M to  $7.3 \times 10^{-2}$  M. The  $\text{H}_2\text{PO}_4^-$  had a dramatically negative effect on the kinetics. Based on  $\text{H}_2\text{PO}_4^-$  coverage data reported in the literature, the decrease in rate observed was greater than expected from just a site blocking effect. A small (<1 kcal/mol) increase in activation energy occurs in addition to the steric effect. Finite rates are observed even at saturation coverage due to either of two possible factors: i) a close-packed overlayer of very large ions leaves "holes" large enough for oxygen molecule penetration; ii) coulombic repulsion of like-ions prohibits the formation of a close-packed overlayer. The kinetic effect due to poisoning of the surface by specifically adsorbed  $\text{H}_2\text{PO}_4^-$  anion at saturation coverage is about a factor of 15 relative to the rate in a non-adsorbing electrolyte.

## Introduction

There are several reports in the literature from different laboratories [1-5] showing in a qualitative way that oxygen reduction kinetics on Pt were better in solutions of trifluoromethane sulfonic acid (TFMSA) than in phosphoric acid, the electrolyte currently in use in the major fuel cell development programs in the U.S. [6]. However, the relative comparisons were not made rigorously at the same temperature and at the same pH, nor were possible differences in oxygen solubility accounted for. Because it has been well established that there is specific adsorption of anions in  $H_3PO_4$  on Pt surfaces [7,8], it seems reasonable to suggest that the differences in kinetics may be due to reduced anion adsorption in the fluorinated alkane sulfonic acid electrolyte. Indeed, the recent study by Petrie, et al. [9] reports significantly lower coverages by  $CF_3SO_3^-$  than by  $SO_4^{2-}$  on Pt. Prior studies by Balachova and Kazarinov [10] showed that the adsorbability of some common anions was ranked in the order  $Cl^- > H_2PO_4^- > SO_4^{2-}$  (or  $HSO_4^-$ ). Combining these studies it would appear that the ranking of adsorbability would be  $Cl^- > H_2PO_4^- > SO_4^{2-} > CF_3SO_3^-$ .

The object of the present study was to determine in a more rigorous manner the effect of  $H_2PO_4^-$  anion on the kinetics of oxygen reduction. Because there is also a particular interest in the relative comparison of  $H_3PO_4$  and TFMSA electrolytes, and TFMSA appears to serve as an example of a non-adsorbing electrolyte, we have selected this acid as the baseline from which the anion effect can be observed.

The rotating disc electrode technique was utilized to determine the possible effect of the  $H_2PO_4^-$  anion on solubility and to extract the

kinetic components of the current-potential behavior. Kinetic measurements were made holding pH constant by using additions of  $\text{H}_3\text{PO}_4$  to 0.1 M TFMSA solution (pH=1) in the mM range as well as making a detailed comparison of the kinetics in a pure  $\text{H}_3\text{PO}_4$  solution of the same pH (0.7 M). Because  $\text{H}_3\text{PO}_4$  is a weak acid ( $K_1 = 7.6 \times 10^{-3}$ ), the addition to a strong acid does not change the pH, and the  $\text{H}_2\text{PO}_4^-$  concentration will be lower than in pure  $\text{H}_3\text{PO}_4$  of the same molarity. This fact helps one to study the effect of anion at very low concentration levels in the bulk electrolyte.

### Experimental

Experiments were performed in all glass cell equipped with a separate compartment for a DHE reference electrode [11] connected to the central compartment via a Luggin capillary.\* The working electrode was a Pt rotating disc electrode (RDE) polished to a mirror finish using a succession of alumina pastes [12]. Electrode rotation was controlled by a Pine Instruments Analytical Rotator and the disc potentials were controlled using a Pine RD3 Potentiostat. The counter electrode was a thick Pt foil immersed directly in the electrolyte.

Malincrodt 85%  $\text{H}_3\text{PO}_4$  was purified by a standard  $\text{H}_2\text{O}_2$  treatment (13) then diluted to 0.7 M (pH = 1). TFMSA from 3M Corporation was first distilled in  $\text{N}_2$  as received and then refluxed with  $\text{H}_2\text{O}_2$ ; a second distillation of the TFMSA -  $\text{H}_2\text{O}_2$  mixture yielded a product which separated into a liquid (TFMSA) and a solid ( $\text{TFMSA}\cdot\text{H}_2\text{O}$ ) phase upon standing at room temperature after crystallization at  $-0^\circ\text{C}$ . 0.1 M TFMSA solution was prepared from the anhydrous acid diluted with purified  $\text{H}_2\text{O}$ . Both 0.7 M  $\text{H}_3\text{PO}_4$  and 0.1 M TFMSA were pretreated in the cell by electrolysis with a Pt gauge anode for approximately 72 hrs.  $\text{H}_2\text{PO}_4^-$  ions were added to 0.1 M

\*The DHE was 15 mV below an RHE in these acids. All potentials are with respect to the DHE.

TFMSA using the 0.7 M  $\text{H}_3\text{PO}_4$  solution in an all-Teflon syringe and/or pipette.

Cyclic voltammograms (CV) were recorded in  $\text{N}_2$ -saturated electrolyte on the stationary RDE. Before CV recording, the disc electrode surface was cleaned by an anodic pulse (1.7 v; 30 sec; 1000 rpm) followed by a cathodic pulse (0.25 v; 15 sec; 0 rpm) to reduce all surface oxide. After cathodic pretreatment, the electrode potential was stepped to 0.8 v and the CV recorded (at 0 rpm) by potential sweeping at  $100 \text{ mV}\cdot\text{sec}^{-1}$  first in the anodic direction. Following the completion of CV (typically 3 cycles 0-1.5V), the electrolyte was saturated with  $\text{O}_2$  and the oxygen reduction kinetic measurements were initiated. At each rotation rate, the disc electrode treatment procedure was repeated. At the end of the cathodic pulse, the current passing through the oxide-free Pt RDE was taken to be the diffusion limiting current corresponding to the chosen rotation speed. The disc current-potential (i-E) curve was then recorded in the anodic direction at a sweep rate of  $10 \text{ mV}\cdot\text{sec}^{-1}$ .

### Results and Discussion

In. Fig. 1 are cyclic voltammograms obtained in the 0.7 M  $\text{H}_3\text{PO}_4$  and 0.1 M TFMSA solutions. The resolution of the H-region and the flatness of the double layer region of the  $\text{H}_3\text{PO}_4$  CV indicate satisfactory purity [14]. However, the TFMSA purification was apparently not as successful as the resolution of the H-region was degraded with increasing rotation rate. Consequently, RDE measurements have been conducted in the rotation speed range of 100-900 rpm to minimize convective transport of impurities to the electrode surface.

Such measurements are shown in Fig. 2 for  $\omega = 400$  rpm. Curve D indicates that the diffusion limiting current density in 0.7 M  $H_3PO_4$  is lower than in 0.1 M TFMSA (curve A). Successive additions of  $H_3PO_4$  to 0.1 M TFMSA (curves B and C) do not affect the limiting current. On the contrary, they have a significant effect on the kinetics as witnessed by the decrease in the current in the potential region of mixed diffusion-kinetic control. A similar effect is observed in the potential region of pure kinetic control ( $>0.9V$ )

If it is assumed that the  $i$ - $E$  curves recorded potentiodynamically at 10 mV/s are equivalent to steady-state curves for a clean surface, and that the overall kinetics are first order in oxygen concentration at the surface, currents in the potential region of mixed diffusion-kinetic control can be analyzed with the  $i^{-1}$  vs.  $\omega^{-1/2}$  correlation [15], given by:

$$\frac{1}{i} = \frac{1}{i_k} + \frac{1}{B\sqrt{\omega}} \quad (1)$$

where  $i$  is the observed current,  $i_k$  is the kinetically controlled current,  $\omega$  the rotation rate, and  $B$ , for aqueous solutions simplified [16] to:

$$B = 0.62 nF C_o D^{2/3} \nu^{-1/6} \quad (2)$$

for  $\omega$  in radius per second,  $F$  is the Faraday,  $C_o$  the solubility of oxygen, and  $\nu$  the kinematic viscosity. In principle, the diffusion limiting current density should be given by the simple relation,

$$i_L = B\sqrt{\omega} \quad (3)$$



Plots of  $i^{-1}$  vs.  $\omega^{-1/2}$  and/or  $i_L$  vs  $\omega^{1/2}$  should be linear with slopes that are either  $B^{-1}$  or  $B$ . The intercept of the  $i^{-1}$  vs  $\omega^{1/2}$  fixed-potential lines for  $\omega^{-1/2} \rightarrow 0$  should give the value of the kinetically controlled current,  $i_k$ , for that potential. In a self-consistent way, the kinetic current can also be calculated directly from the observed current at the potential of interest and the limiting current density for that rotation rate from the relation

$$i_k = \frac{i \cdot i_L}{i_L - i} \quad (4)$$

The  $i^{-1}$  vs  $\omega^{-1/2}$  plots for 0.7 M  $H_3PO_4$ , 0.1 M TFMSA and the acid mixtures are shown in Fig. 3. Linear plots were obtained in every case except that for pure TFMSA, which shows an upward curvature for increasing  $\omega$ . We attribute this curvature to impurity effects in the pure TFMSA solution; the kinetic effect of the impurity is apparently not first order in impurity concentration. However, this curvature essentially vanishes when the pure TFMSA is made 11.4 mM in  $H_3PO_4$ . The explanation for this effect of  $H_3PO_4$  on the curvature of  $i^{-1}$  vs  $\omega^{-1/2}$  plots is probably related to the preferential adsorption of phosphate anion to be discussed subsequently. The  $B$  coefficients measured from the limiting currents (so-called Levich plots) are summarized in Table 1, and as noted before, these data show that the additions of mM quantities of  $H_3PO_4$  to 0.1 M TFMSA solution had no significant effect on the physical properties of the solution, e.g. viscosity, oxygen diffusivity, oxygen solubility, in agreement with intuition. Furthermore, the value of  $B$  calculated using the physical constants for dilute phosphoric acid solution [17] is 0.385, in better

agreement with the value measured from the limiting currents. The limiting current data as illustrated by the one example in Fig. 2, clearly indicate that the solubility of oxygen is higher in 0.1 M TFMSA than in 0.7 M  $\text{H}_3\text{PO}_4$ , and the B values of Table 1 suggest a solubility about 10% higher. Therefore, we have chosen to extrapolate the  $i_k$  from eq. (4) rather than use intercepts of the  $i^{-1}$  vs  $\omega^{-1/2}$  plots. The extrapolated  $i_k$  vs E relations are shown in Fig. 4, with a further summary of these curves in Table 2. Although  $i_k$  should be independent of  $\omega$ , different  $i_k$  values were obtained for each rotation rate. This is easily explained in terms of impurity effects. The impurity has little or no effect on the limiting current, but a major effect on the kinetic current. With increasing rotation rate, the impurity has a proportionately greater effect on the kinetic current relative to the diffusion controlled current. Equivalently, the dependence of the kinetic current on the impurity concentration is probably not first order and eq. (4) is valid only if the kinetics were first order in both oxygen and the impurity concentrations. In spite of this impurity effect, it is clear that even mM concentrations of  $\text{H}_3\text{PO}_4$  produced a dramatic reduction in the rate of oxygen reduction.

The effect of  $\text{H}_3\text{PO}_4$  on the kinetics of oxygen reduction in TFMSA are summarized using primarily the 400 rpm data. The effect was essentially independent of potential in the potential region explored, i.e. the ratio of  $i_k$  in  $\text{H}_3\text{PO}_4$  solutions to the  $i_k$  for 0.1 M TFMSA solution was independent of potential. In the presence of a strong acid like TFMSA, and in relatively dilute solutions we are using here,  $\text{H}_3\text{PO}_4$  behaves as a very weak acid since the first dissociation constant is  $7.6 \times 10^{-3}$  [18]. The  $\text{H}_2\text{PO}_4^-$  anion concentrations for the TFMSA solutions in Table 2 can be

computed from the weak acid approximation,

$$\begin{aligned} [\text{H}_2\text{PO}_4^-] &\approx K_1 [\text{H}_3\text{PO}_4]/[\text{TFMSA}] \\ &\approx 7.6 \times 10^{-2} [\text{H}_3\text{PO}_4] \end{aligned} \quad (5)$$

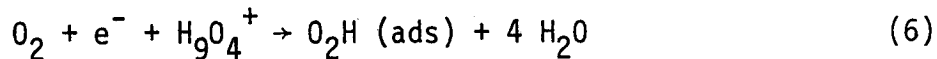
which yields  $2.9 \times 10^{-5}$  M and  $8.7 \times 10^{-4}$  M for the 0.38 mM and 11.4 mM solutions, respectively. Clearly, the largest effect was observed when the anion was introduced to TFMSA at the lowest concentration used; increasing the concentration by four orders of magnitude decreased the rate only a factor of four beyond the initial decrease. A more thorough quantitative analysis of the poisoning effect of  $\text{H}_2\text{PO}_4^-$  anions is, unfortunately, not possible at this time due to the lack of sufficiently complete adsorption data. However, it would appear, both on the basis of the existing  $\text{H}_2\text{PO}_4^-$  adsorption and the present kinetic data, that the anion coverage is near saturation in 0.7 M  $\text{H}_3\text{PO}_4$ .

The most recent review of phosphate anion adsorption studies is by Horanyi [19]. Work prior to 1970 was reviewed by Balashova and Kazarinov [10]. The adsorption isotherm data obtained by the radio-tracer technique used by Horanyi, et al. [20] are mostly at lower concentrations ( $<10^{-5}$  M) of anion than used here. Although, we have conducted experiments in the range of concentrations below  $10^{-5}$  M, the impurity effect in the pure TFMSA solution masks to a large extent the anion effect in this range of concentrations. However, there appears to be both accurate kinetic measurements here and appropriate coverage data reported in the literature [20] for  $2.9 \times 10^{-5}$  M  $\text{H}_2\text{PO}_4^-$  anion concentration. The adsorption data indicate a surface coverage of  $9 \times 10^{13}$  ions/cm<sup>2</sup>, essentially independent of potential between 0.8 - 1.0 V. To use this data to interpret the kinetic effect requires knowledge of the number of Pt sites blocked per adsorbed anion. If the  $\text{H}_2\text{PO}_4^-$  ion on

the surface has the same structure as in crystals [21], then one anion would block three Pt sites. If the anion on the surface is hydrated, and one uses the ionic radius of the ion in solution [22], as many as eight Pt sites would be blocked per adsorbed anion. The lower number appears to be more consistent with the saturation coverage of  $\text{H}_2\text{PO}_4^-$  reported by Bagotzky et al. [23] of  $3.6 \times 10^{14}$  ions/cm<sup>2</sup>, and three Pt sites blocked per anion would mean that  $2.7 \times 10^{14}$  Pt sites/cm<sup>2</sup> are blocked at the  $2.5 \times 10^{-5}$  M  $\text{H}_2\text{PO}_4^-$  concentration. Since  $1.2 \times 10^{15}$  sites/cm<sup>2</sup> is a typical site density for a polycrystalline Pt surface, the fractional number of Pt sites blocked at this concentration is about 25%. If oxygen reduction proceeds by a single-site rate-determining step, then the effect of blocking about 25% of the sites would reduce the rate by less than the observed factor of 2.5, indicating an effect beyond site blocking. The kinetic data and the coverage data of Bagotzky, et al. [23] are consistent with the conclusion that the surface is near saturation coverage by  $\text{H}_2\text{PO}_4^-$  anion in 0.7 M  $\text{H}_3\text{PO}_4$ . The reaction can proceed at a finite rate even at saturation coverage due to either of two factors: i) even in a close-packed structure of anions, the large size of anion leaves "holes" large enough for the oxygen molecule to fit through; ii) coulombic repulsion of the like-ions prohibits the formation of a close-packed structure.

Geometric (steric) blocking of Pt sites by itself does not appear to account for the kinetic effect of  $\text{H}_2\text{PO}_4^-$  anions. It is, however, possible to account for the magnitude of the observed effect if the activation barrier is raised by the specifically adsorbed anions. The rate-determining step for oxygen reduction is generally considered [24] to be the addition of the first electron to molecular oxygen in the

double layer to form the adsorbed  $O_2H$  species,



The effect of anions on the monomolecular chemical rate constant can be represented by a Bronsted relation,

$$k = k_0 (1-\theta_A) \exp [-\beta \Delta\Delta G_{ads} (\Gamma_A)/RT] \quad (7)$$

where  $k_0$  is the rate constant in the  $H_2PO_4^-$  free electrolyte,  $\theta_A$  is the fraction of Pt sites blocked by anions,  $\Gamma_A$  is the coverage by anions,  $\Delta\Delta G_{ads}$  is the change in the adsorption free energy of  $O_2H$  in the presence of anions, and  $\beta$  is the Bronsted coefficient. Assuming  $\beta = 0.5$ , and using  $\theta_A = 0.25$  at  $2.9 \times 10^{-4}$  M  $H_2PO_4^-$ , the observed factor of 2.5 for  $k/k_0$  can be accounted for in eq.(7) by a  $\Delta\Delta G_{ads}$  of about 0.75 kcal/mol, (an increase in activation energy of only 0.4 kcal/mol). We have not been able to obtain the temperature dependence of the i-E curves with sufficient precision to determine whether or not  $H_2PO_4^-$  adsorption does increase the activation energy by amount this small. There is, however, some supporting evidence for the decrease in adsorption energy from the voltammetry curves in Figure 1. Following Damjanovic and co-workers [24], we assume that the adsorption energies for all oxygenated species that constitute the water dissociation products are equally affected by  $H_2PO_4^-$  ions, then the shift in the anodic wave observed when  $H_2PO_4^-$  is added to TFMSA can be used to derive a value for  $\Delta\Delta G_{ads}$ , i.e.  $\Delta\Delta G_{ads} = nF\Delta E_{\frac{1}{2}} \approx 1.2$  kcal/mole for a shift of 50 mV in the half-wave potential (and  $n = 1$ ). As seen from Figure 1, the observed shift in the "oxide" anodic wave was about 50 mV at  $7.3 \times 10^{-2}$  M  $H_2PO_4^-$  and was virtually the same even when the  $H_3PO_4$  concentration was as low as 25 mM. There is at least a qualitative indication that the adsorption energy for  $O_2H$  is probably

decreased by  $\text{H}_2\text{PO}_4^-$  adsorption by an amount consistent with the kinetic data.

The addition of  $\text{H}_2\text{PO}_4^-$  to TFMSA did not have a significant effect on the observed Tafel slopes of the  $i_k$  vs. E data, as indicated in Table 2. For all the solutions, the observed Tafel slope was  $120 \pm 10$  mV per decade in the 0.7 - 0.8 V potential region, which is nominally  $2 \text{ RT/F}$  at room temperature. This is the same Tafel slope reported by others [12, 25] for oxygen reduction on Pt in concentrated (85%)  $\text{H}_3\text{PO}_4$ , and by Damjanovic and Genshaw [26] in 0.1 M  $\text{HClO}_4$  at potentials below 0.8 V. In the solutions containing  $\text{H}_3\text{PO}_4$ , there was not a well-defined Tafel region above 0.8 V. However, in 0.1 M TFMSA, there were two well-defined Tafel regions with a transition at ca. 0.85 V, similar to the transition reported by Damjanovic and Genshaw [26] for 0.1 M  $\text{HClO}_4$ . According to Damjanovic and co-workers [24], this transition is correlated to the onset of anodic film formation, which can be seen in the voltammetry curve of Figure 1 to occur at ca. 0.8 - 0.85 V. The addition of  $\text{H}_2\text{PO}_4^-$  anions to TFMSA caused this onset to shift in the anodic direction, and at 0.7 M it is shown in Figure 1 that the shift is about 50 mV. This shift is reflected, to a lesser extent, in the  $i_k$  vs. E data, but the combined effect of the reduced current and the anodic shift moves the expected transition to a region where the potentiodynamic  $i - E$  curves (Figure 2) require correction for adsorption pseudocapacitance. We have not made these corrections, nor analyzed this region of the  $i_k - E$  curves in sufficient detail to determine whether or not the expected transition in Tafel slope occurs in  $\text{H}_2\text{PO}_4^-$  containing solution.

#### Acknowledgements

This work was supported jointly by the Electric Power Research Institute under contract RP-1676-2 and the Assistant Secretary for Fossil Energy, Office of Fuel Cells, Advanced Research Concepts Div. of the U.S. Department of Energy under contract DE-AC03-76SF00098

Table 1. Values of the B coefficient for O<sub>2</sub> reduction in TFMSA, H<sub>3</sub>PO<sub>4</sub>, and their mixtures.

ELECTROLYTE	B, mA·cm <sup>-2</sup> sec <sup>1/2</sup>	
	from: $i_L$ vs $\omega^{1/2}$	from: $i^{-1}$ vs $\omega^{-1/2}$
0.1 M TFMSA	0.459	0.499*
0.1 M TFMSA + 0.38 mM H <sub>3</sub> PO <sub>4</sub>	0.459	0.505
0.1 M TFMSA + 11.4 mM H <sub>3</sub> PO <sub>4</sub>	0.459	0.496
0.7 M H <sub>3</sub> PO <sub>4</sub>	0.382	0.423

\* Calculated from straight lines at 0.725, 0.775, and 0.800 V.

Table 2. Kinetic parameters of  $O_2$  reduction on Pt in TFMSA,  $H_3PO_4$  and their mixtures.

ELECTROLYTE	$H_2PO_4$ conc./ $mol\ dm^{-3}$	$i_k^* / mA \cdot cm^{-2}$			Tafel slope $b / V \cdot dec^{-1}$	
		E/V			E/V	
		0.700	0.800	0.900	>0.800	0.700-0.800
0.1 M TFMSA	-	52	9.4	1	0.085	0.117-0.135 <sup>†</sup>
0.1 M TFMSA + 0.38 mM $H_3PO_4$	$2.9 \times 10^{-5}$	22	4.2	0.4	N.D.	0.114-0.140
0.1 M TFMSA + 11.4 mM $H_3PO_4$	$8.7 \times 10^{-4}$	10	1.8	0.2	N.D.	0.127-0.137
0.7 M $H_3PO_4$	$7.3 \times 10^{-2}$	5	0.7	0.06	N.D.	0.113-0.135

<sup>†</sup>Variations in the Tafel slope originate from the dependence of  $i_k$  on  $\omega$  (see text).

\*From i-E data at 400 rpm.

N.D.  $\equiv$  not a well-defined Tafel slope in this potential region.



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Figure Captions

Fig. 1. Cyclic voltammogram of a Pt stationary RDE in 1: 0.1 M TFMSA; 2: 0.1 M TFMSA + 25 mM  $\text{H}_3\text{PO}_4$ ; 3: 0.7 M  $\text{H}_3\text{PO}_4$  ( $\text{N}_2$  saturated) obtained at  $100 \text{ mV}\cdot\text{sec}^{-1}$ .

Fig. 2. Potentiodynamic current/potential curves for  $\text{O}_2$  reduction on a Pt RDE obtained at  $10 \text{ mV}/\text{sec}$  (see text for details). All curves are for  $\omega = 400 \text{ rpm}$ .

A: 0.1 M TFMSA

B: 0.1 M TFMSA + 0.38 mM  $\text{H}_3\text{PO}_4$

C: 0.1 M TFMSA + 11.4 mM  $\text{H}_3\text{PO}_4$

D: 0.7 M  $\text{H}_3\text{PO}_4$

Fig. 3.  $i^{-1}$  vs.  $\omega^{-1/2}$  plots for  $\text{O}_2$  reduction on a Pt RDE: a) 0.1 M TFMSA; b) 0.1 M TFMSA + 0.38 mM  $\text{H}_3\text{PO}_4$ ; c) 0.1 M TFMSA + 11.4 mM  $\text{H}_3\text{PO}_4$ ; d) 0.7 M  $\text{H}_3\text{PO}_4$ .

Fig. 4. Tafel plots for  $\text{O}_2$  reduction on a Pt RDE;  $i_k$  is in  $\text{mA}\cdot\text{cm}^{-2}$  (geo.)

A: 0.1 M TFMSA

B: 0.1 M TFMSA + 0.38 mM  $\text{H}_3\text{PO}_4$

C: 0.1 M TFMSA + 11.4 mM  $\text{H}_3\text{PO}_4$

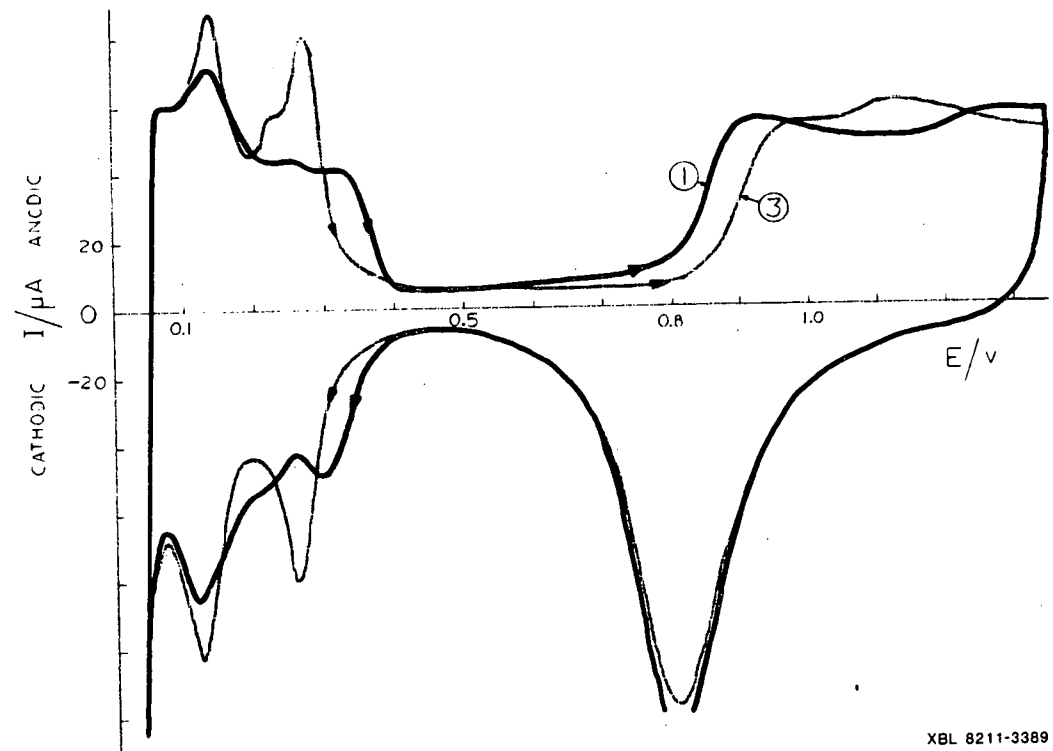
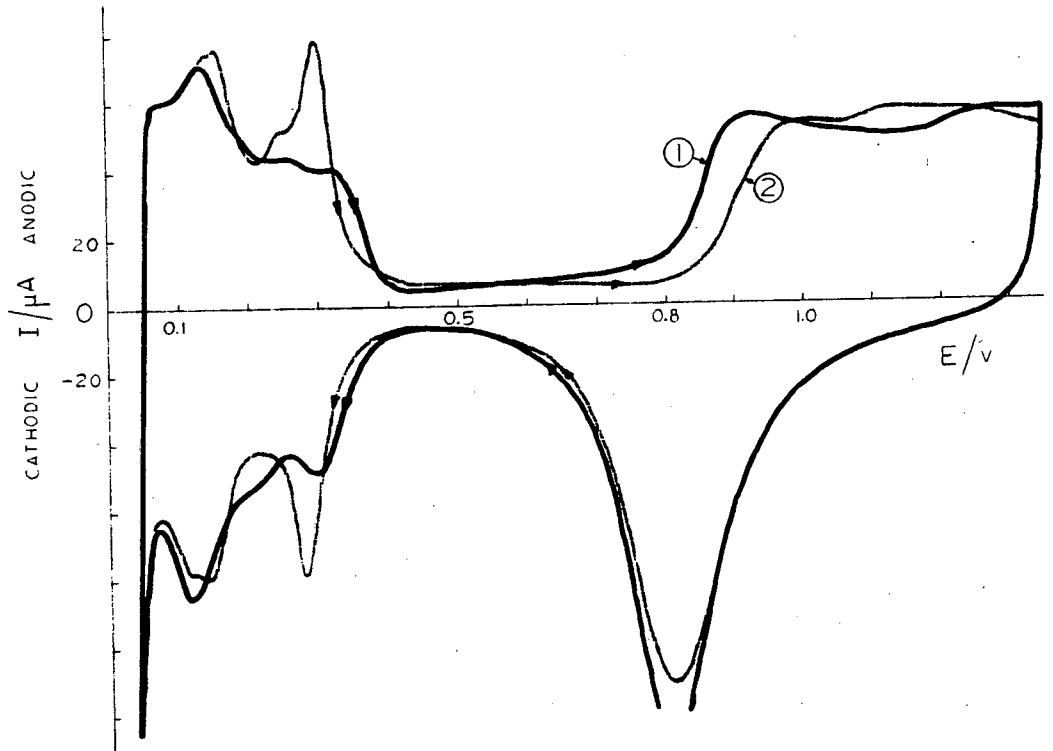
D: 0.7 M  $\text{H}_3\text{PO}_4$

1: 100 rpm

2: 200 rpm

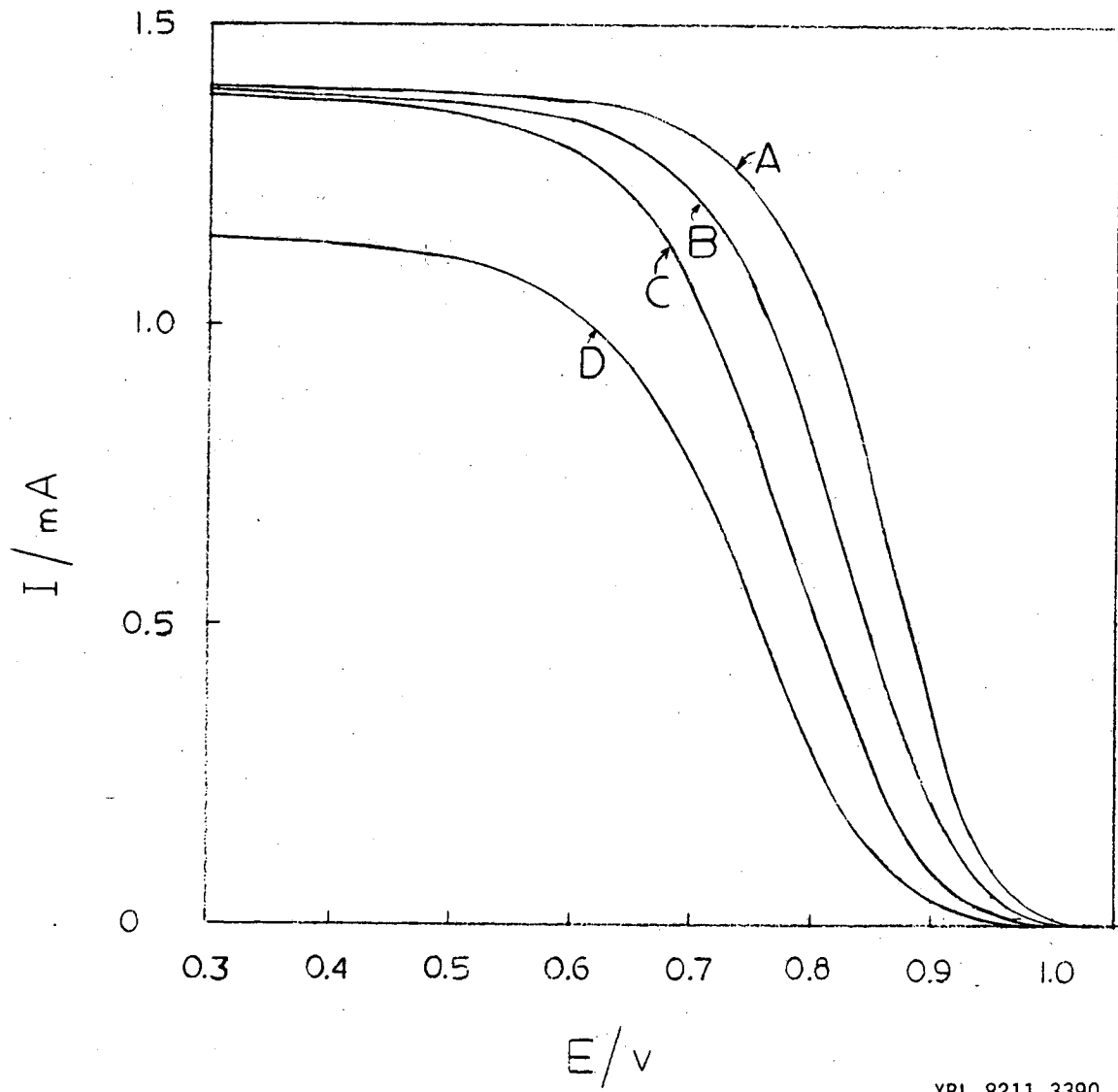
3: 400 rpm

4: 900 rpm



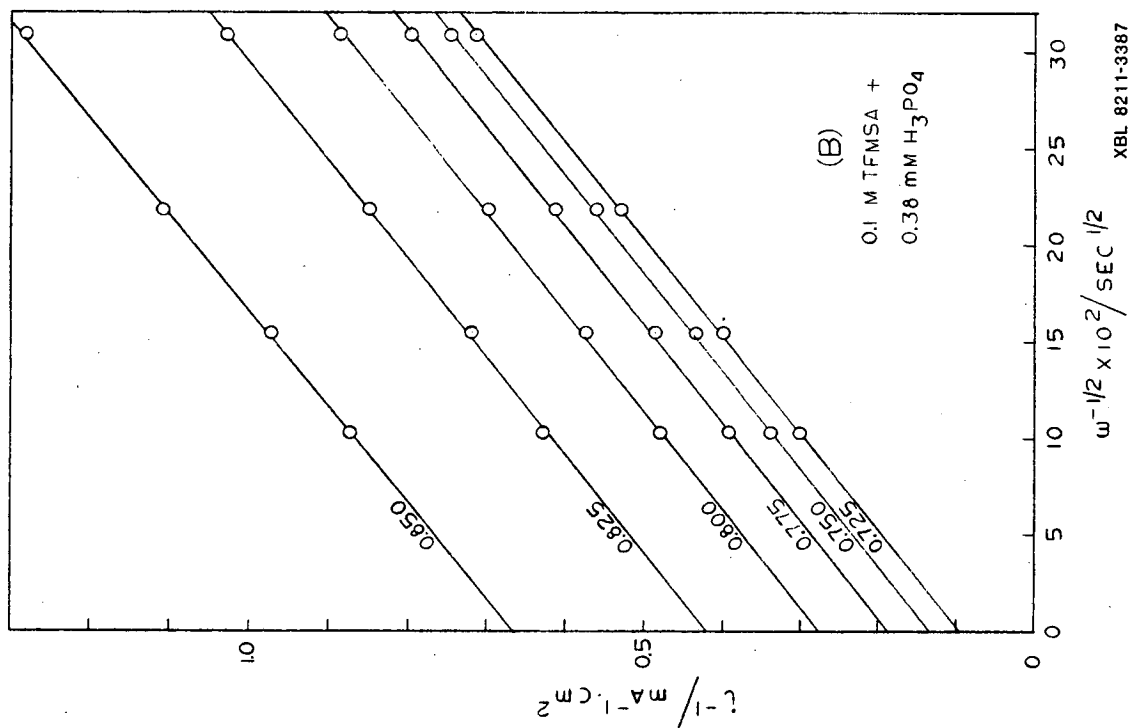
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Fig. 1



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Fig. 2



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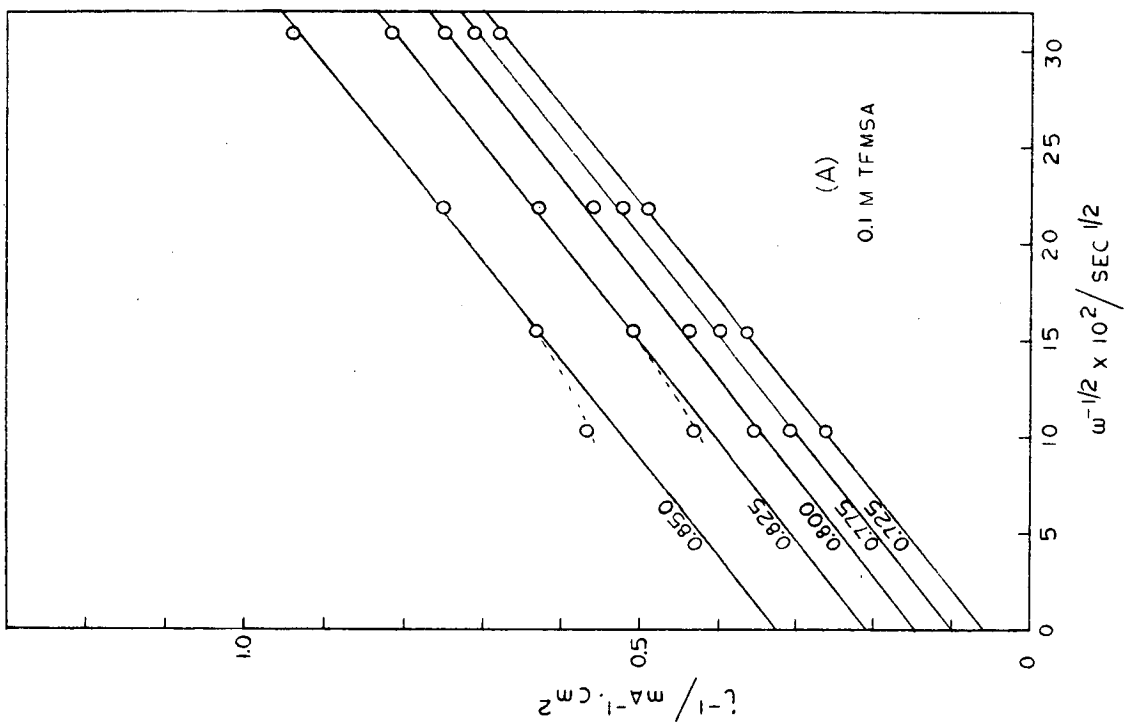


Fig. 3

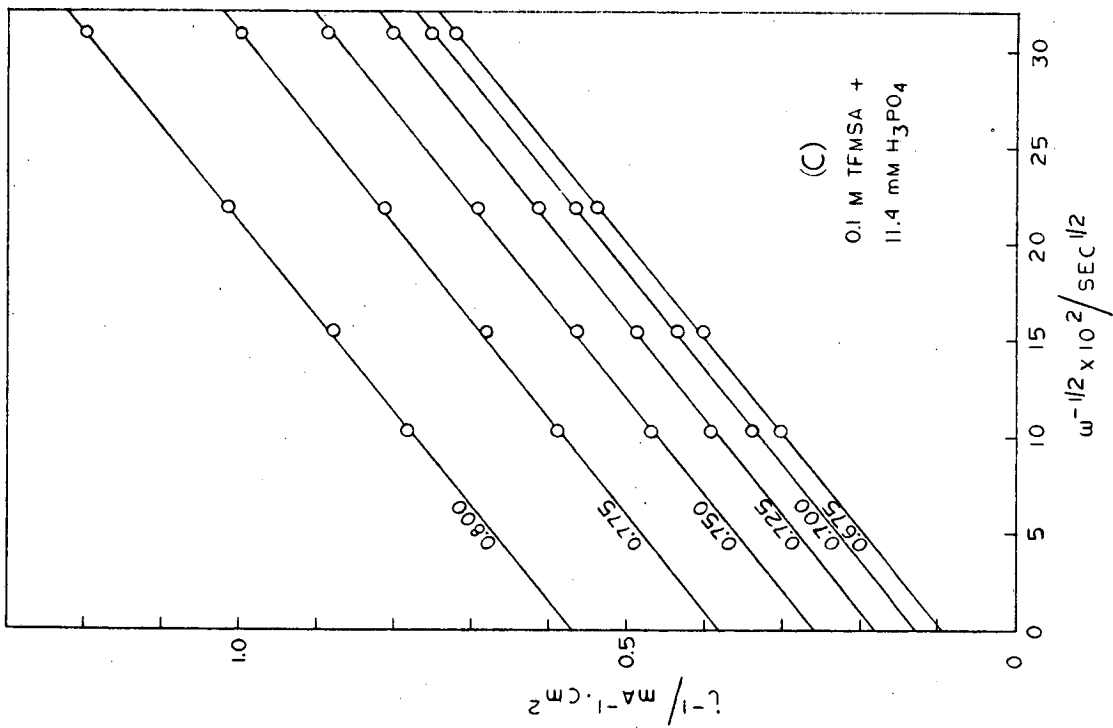
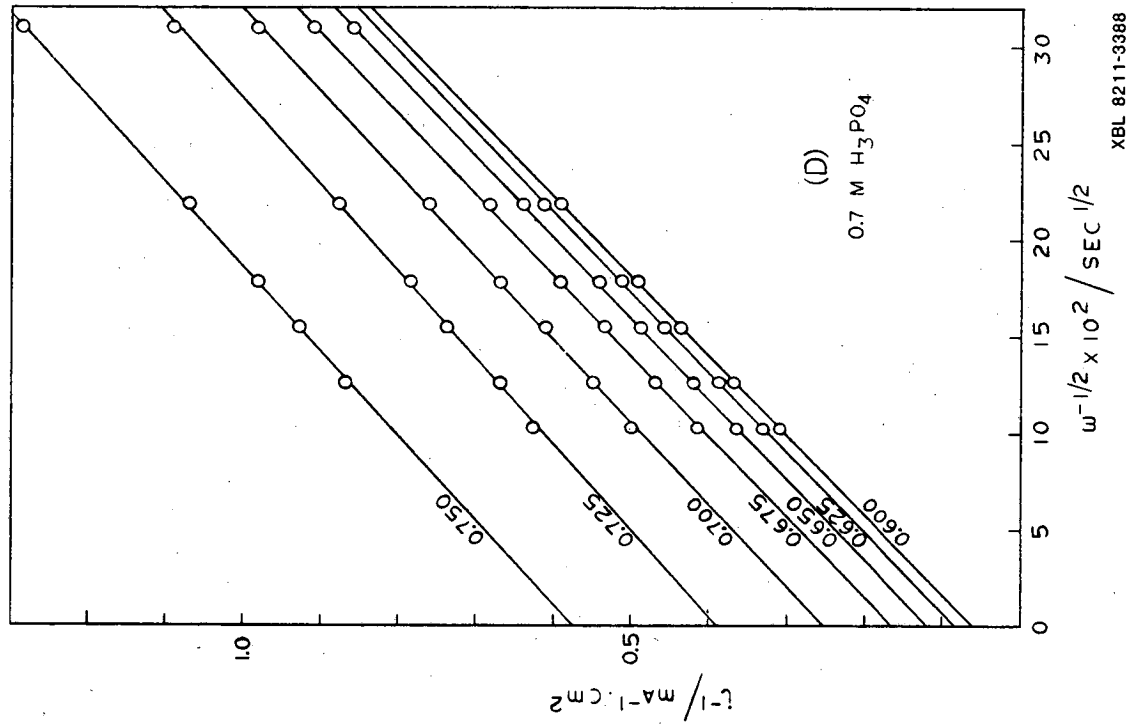
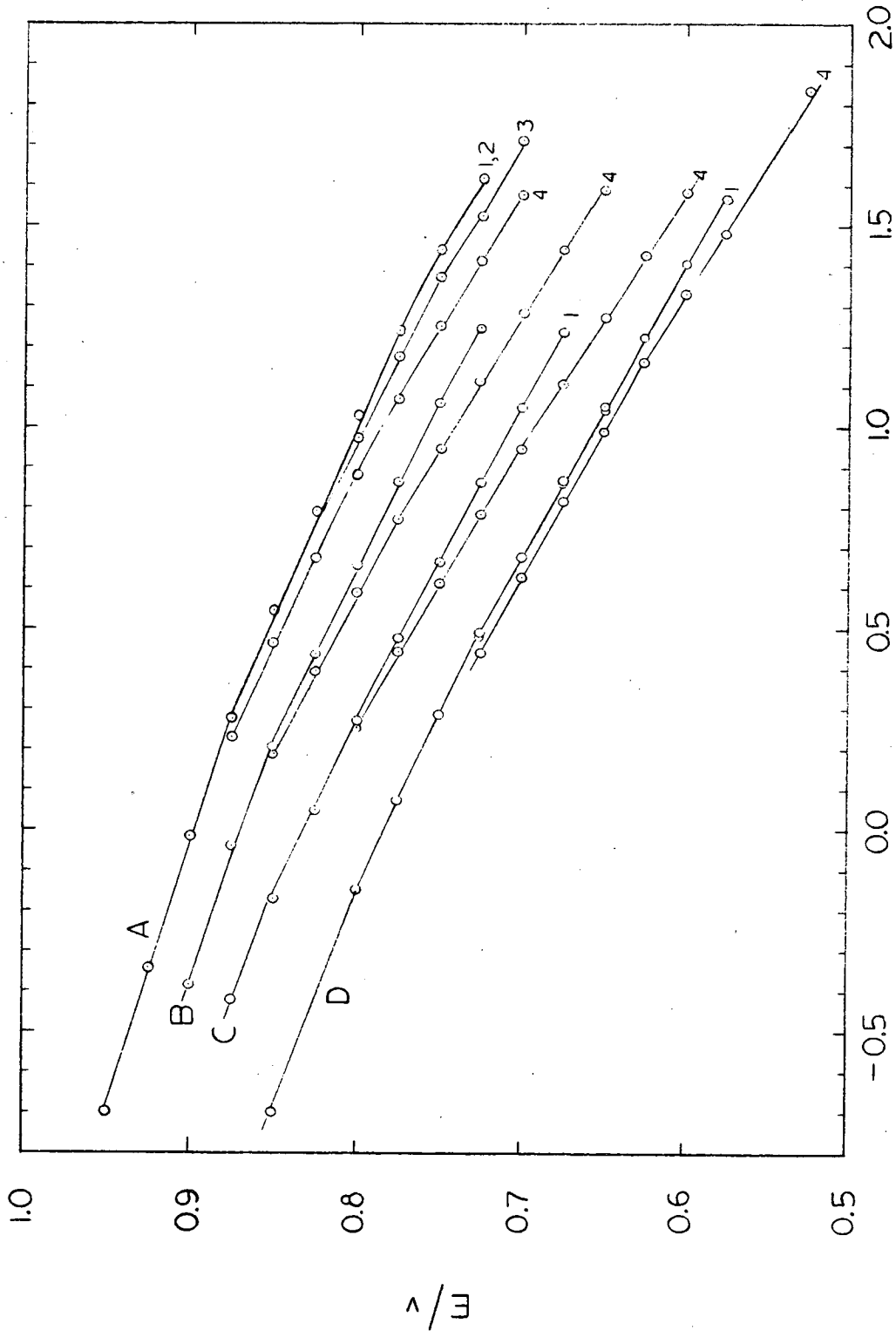


Fig. 3



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$\text{LOG}(\dot{L}_k)$

Fig. 4



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.

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