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Oxygen reduction on platinum in mixtures of phosphoric and trifluoromethane sulphonic acids

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A rotating disk electrode study of O_2 reduction on platinum has been carried out in mixtures of concentrated H_3PO_4 and CF_3SO_3H at room temperature. The diffusion limiting current was found to increase with increasing amounts of CF_3SO_3H added to the H_3PO_4. The apparent first-order rate constant defined in terms of O_2 concentration (M) is lower in the mixed acids than in H_3PO_4 (86% by weight), but the concentration of O_2 increases by a much larger factor, with the result that the kinetics are faster in the mixed acids.

1. Introduction

The kinetics of O_2 reduction in such acid electrolytes as perfluoroalkane sulfonic acids [1–3] are of interest from the standpoint of identifying alternative electrolytes to H_3PO_4 presently used in acid fuel cells. The possibility of adding another electrolyte component to concentrated H_3PO_4, however, also is an interesting concept which merits investigation. The addition of strong acids such as the perfluorinated sulfonic acids offers the possibility of modifying the acid properties of this electrolyte system and increasing the solubility of O_2. The solubility of O_2 is known to be high in fluorinated organic solvents. A rotating disk electrode study of O_2 reduction on smooth platinum has been carried out at room temperature in a wide range of mixtures of concentrated phosphoric acid and trifluoromethane sulfonic acid (CF_3SO_3H: TFMSA) and will be summarized in this paper. It was demonstrated earlier [4], using Raman spectroscopy, that in the CF_3SO_3H–H_3PO_4–H_2O system, the CF_3SO_3H is fully ionized and protonates both H_2O and H_3PO_4 for mole fractions of the sulfonic acid less than 0.4.

2. Experimental details

Mallinckrodt 86% H_3PO_4 was purified as described previously [5]. Trifluoromethane sulfonic acid was carefully purified by multiple fractional distillation of the monohydrate at reduced pressure. Since the data for the vapor pressure of water over the CF_3SO_3H–H_3PO_4–H_2O ternary system is not available, it was arbitrarily decided to use mixtures with a constant concentration of water, i.e. 50 mol %. Therefore, in all compositions one H_2O molecule was present for each TFMSA and H_3PO_4 molecule. The activity of water, however, is likely to decrease somewhat due to protonation by CF_3SO_3H on going from 86% H_3PO_4 to CF_3SO_3H–H_3PO_4–H_2O systems of relatively high concentrations of TFMSA. No indication of Teflon wetting was observed for the mixture range investigated in this study, i.e. up to 25 mol % CF_3SO_3H–25 mol % H_3PO_4–50 mol % H_2O. The electrochemical measurements were carried out essentially as described earlier [5]. All potential values are quoted with respect to reversible H_2/H^+ with the pressure of H_2 = 1.0 atm.

3. Results and discussion

Voltammograms of smooth platinum were recorded in each electrolyte mixture prior to the O_2 reduction measurements to check electrolyte purity as well as to look for any differences in the intrinsic voltammetry of platinum between phosphoric acid and the mixtures.

A voltammogram of platinum recorded in a mixture consisting of 30 mol % H_3PO_4–20 mol % CF_3SO_3H–50 mol % H_2O is shown in Fig. 1. Also shown is a voltammogram of platinum for 86% H_3PO_4. In general, both voltammograms do not exhibit any significant impurity distortion. There are some differences in the hydrogen regions. Hydrogen gas evolution is seen to commence at more anodic potentials in the mixed acid electrolyte relative to phosphoric acid alone. The similarity in the charge values of the oxide regions of both curves indicates that perhaps the activity of water is not significantly different between the two electrolytes. This assumption has to be regarded with caution, however, since CF_3SO_3H is a very strong acid and will convert H_2O to H_3O^+ in the mixtures (along with protonating H_3PO_4).

Rotating disk electrode polarization curves for O_2 reduction on platinum in various mixtures are shown in Fig. 2 for an electrode rotation rate of 1600 rpm. These curves were recorded in the cathodic direction, i.e. from high to low potentials. Prior to recording each curve the platinum surface was pretreated by first subjecting it to a potential of 1.45 V (RHE) in order to desorb or oxidize off any adsorbed impurities. The

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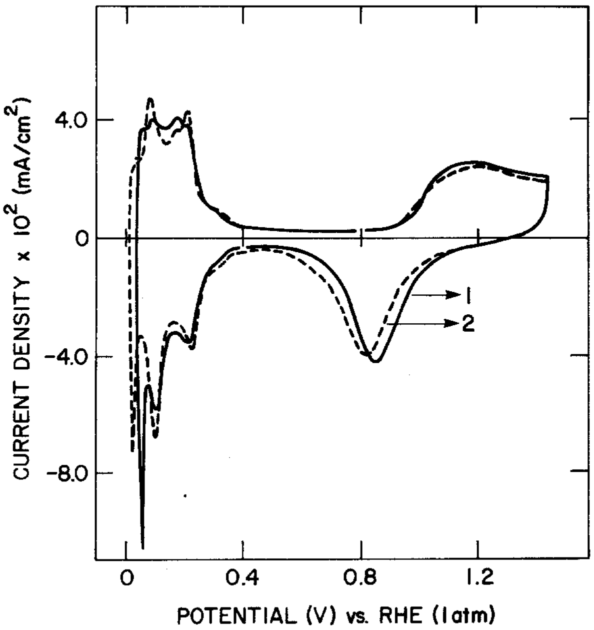

Fig. 1. Voltammograms of Pt in a solution consisting of 20 mol % CF_3SO_3H–30 mol % H_3PO_4–50 mol % H_2O solution (1) and in 85% H_3PO_4 (2). Sweep rate = 20 mV s^{-1}. T = 24°C.

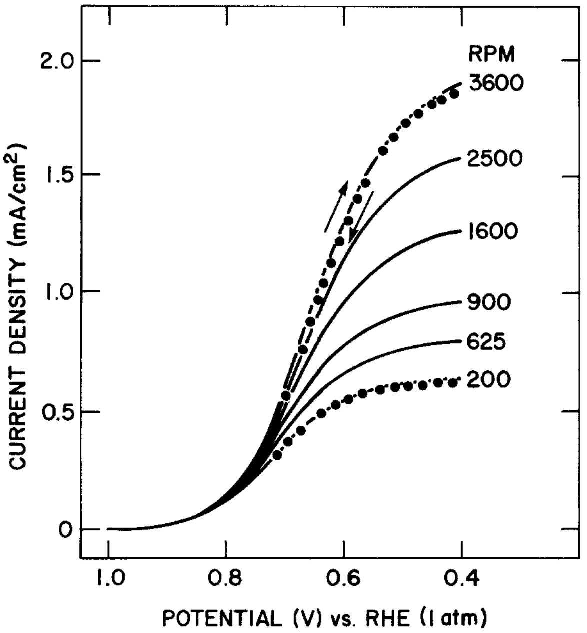

Fig. 3. Polarization curves for O_2 reduction on Pt in a solution consisting of 20 mol % CF_3SO_3H–30 mol % H_3PO_4–50 mol % H_2O. Sweep rate = 5 mV s^{-1}. T = 24°C.

surface was then reduced at 0.3 V (RHE). The diffusion limiting current, i_d, increases from a value of 0.117 mA cm^{-2} at 1600 rpm for 86% H_3PO_4 to 2.075 mA cm^{-2} at the same rotation rate for a mixture composition of 25 mol % H_3PO_4–25 mol % TFMSA–50 mol % H_2O, which is an increase of ~ 18 fold.

Polarization curves for O_2 reduction recorded at different rotation rates in a mixture of composition 30 mol % H_3PO_4–20 mol % CF_3SO_3H–50 mol % H_2O are shown in Fig. 3. A relatively small amount of hysteresis is present between the cathodic and anodic scans. Koutecky–Levich plots of $1/i$ vs $\omega^{-1/2}$ are shown in Fig. 4 for this electrolyte. Reasonably parallel straight lines are obtained. The inverse of the slope of these lines yields a value for the constant B of 3.38×10^{-2} mA cm^{-2} $(rpm)^{-1/2}$ where

$$B = 0.62nFD^{2/3}\nu^{-1/6}C_0 \qquad (1)$$

Here D is the diffusion coefficient of O_2, C_0 is the bulk electrolyte concentration of O_2 and ν is the kinematic viscosity. The other quantities in Equation 1 have their usual meaning. Using the value of B, the diffusion limiting current density may be calculated, i.e. $i_d = B\omega^{1/2}$. A series of parallel, straight-line, Levich plots was obtained for all the mixture compositions investigated in this study. This is fairly indicative that the kinetics of O_2 reduction on platinum in the mix-

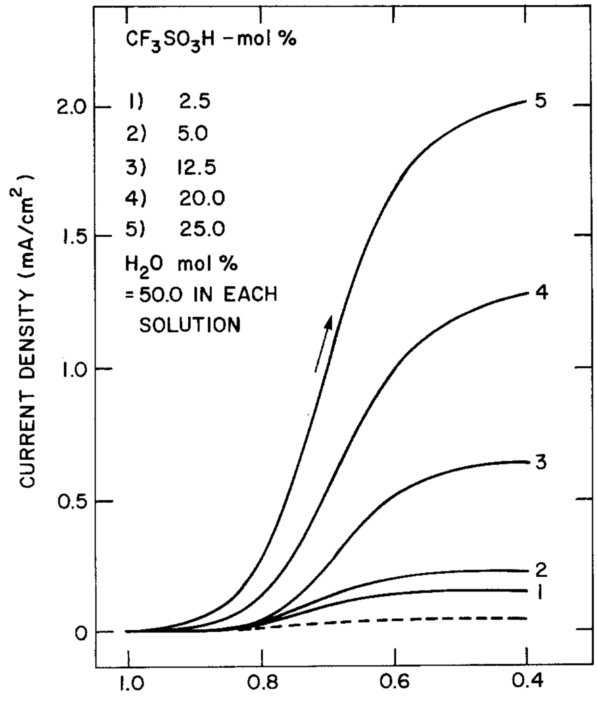

Fig. 2. Polarization curves for O_2 reduction on Pt at 1600 rpm in CF_3SO_3H–H_3PO_4–H_2O mixtures of different compositions. Dashed curve at the bottom is for 86% H_3PO_4. Sweep rate = 5 mV s^{-1}. T = 24°C.

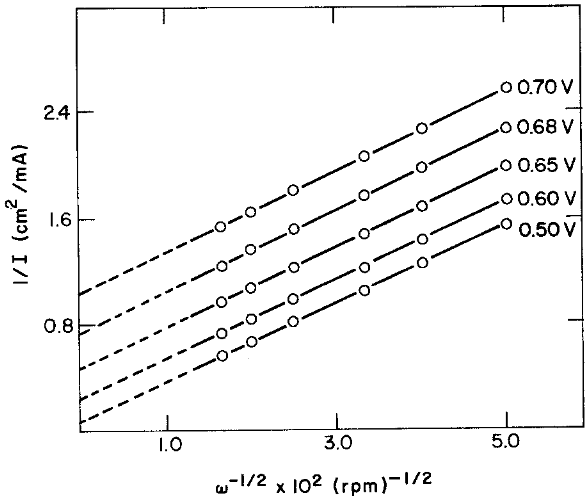

Fig. 4. Plots of $1/i$ vs $\omega^{-1/2}$ for O_2 reduction in a solution consisting of 20 mol % CF_3SO_3H–30 mol % H_3PO_4–50 mol % H_2O at 24°C.

Table 1. Comparison of different kinetic parameters for O_2 reduction in CF_3SO_3H–H_3PO_4–H_2O mixtures

Electrolyte H_3PO_4–CF_3SO_3H–H_2O *(mol%)*			i_D *at 1600 rpm (mA cm^{-2})*	B *(mA cm^{-2} (rpm)$^{1/2}$)*	$\frac{i}{i_d - i}$ *(mA cm^{-2})*	$\frac{i\,(i_d)}{i_d - i}$ *(mA cm^{-2})*	k_2/k_1 *at 0.8 V*	k_2'/k_1' *at 0.8 V*	*Kinematic viscosity (cp)*
50	0	50	0.117	2.9×10^{-3}	45.7×10^{-2}	5.3×10^{-2}	–	–	30.42
47.5	2.5	50	0.181	4.53×10^{-3}	22.3×10^{-2}	4.04×10^{-2}	0.76	0.49	24.54
45.0	5.0	50	0.224	6.1×10^{-3}	21.5×10^{-2}	4.50×10^{-2}	0.87	0.47	22.63
40.0	10.0	50	0.481	1.20×10^{-2}	10.83×10^{-2}	5.21×10^{-2}	0.98	0.24	17.30
37.5	12.5	50	0.728	1.82×10^{-2}	7.39×10^{-2}	5.38×10^{-2}	1.02	0.16	16.46
30.0	20.0	50	1.350	3.38×10^{-2}	11.16×10^{-2}	15.06×10^{-2}	2.84	0.24	11.75
25.0	25.0	50	2.075	5.2×10^{-2}	15.12×10^{-2}	31.37×10^{-2}	5.92	0.33	11.37

k_1, k_1': rate constants for 50 mol% H_3PO_4–50 mol% H_2O (~86% H_3PO_4).
k_2, k_2': rate constants for mixed acids.

tures is first order with respect to dissolved O_2 in all cases. Values of B and i_d are listed in Table 1 for the various mixtures. Further confirmation of the reaction order of the reduction of O_2 on platinum in the mixture electrolytes may be obtained from reaction order plots. The O_2 reduction current i may be written as follows for a specified potential:

$$i = kC_0^m \left[\frac{i_d - i}{i_d}\right]^m \qquad (2)$$

where k is the rate constant and m the reaction order. A plot of log i vs log $[(i_d - i)/i_d]$ should yield a straight line with a slope of m. Plots of this type are shown in Fig. 5 for the mixture of composition 30 mol % H_3PO_4–20 mol % CF_3SO_3H–50 mol % H_2O. The slopes of these straight plots vary from 1.06 at 0.70 V to 1.11 at 0.55 V. This provides further confirmation that the reaction order is essentially 1 for O_2 reduction in the mixed phosphoric/sulfonic acid electrolyte system. The reaction order for O_2 reduction on platinum in concentrated phosphoric acid is generally accepted as being unity [5, 6].

Tafel plots for O_2 reduction on platinum in several mixtures are shown in Fig. 6. For clarity of presentation, the Tafel plots of some of the mixtures have not been included. The value of i_d used in the construction of these plots was obtained using the B values of the Koutecky–Levich plots for each mixture. The slopes of the linear regions of the various Tafel plots are listed in Table 1. No change in Tafel slope was observed on going from 86% H_3PO_4 to the mixture of highest CF_3SO_3H content. The Tafel slope value of $-2RT/F$ observed here for O_2 reduction on platinum is usually taken to indicate that the first electron transfer step is rate determining. Recent results, however, which show that experimentally measured Tafel slopes for O_2 reduction on platinum do not show the expected dependence on temperature, suggest that Tafel slopes should be used with caution as a mechanistic indicator [7]. The bending of the Tafel plots in Fig. 6 at the higher potentials is due to the initial stages of anodic oxide film formation on the platinum surface (see voltammetry curves in Fig. 1). The deviations from linearity in the Tafel plots at low potential may be due to a slight error in the i_d values used in

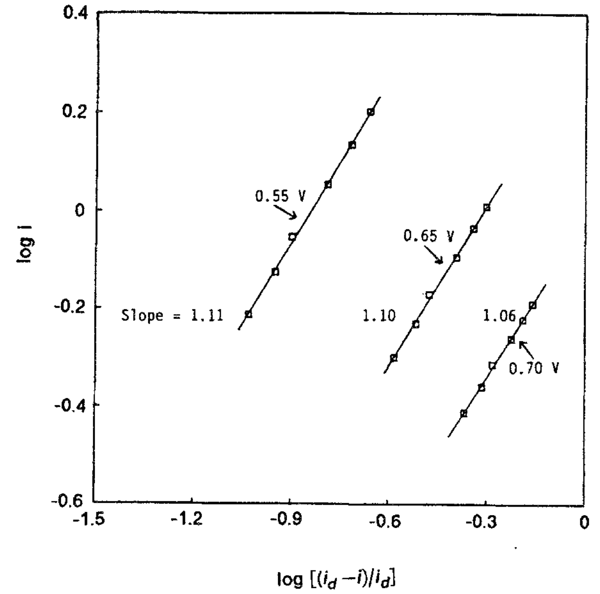

Fig. 5. Reaction order plots for O_2 reduction on Pt in 30 mol % H_3PO_4–20 mol % CF_3SO_3H–50 mol % H_2O at 25°C.

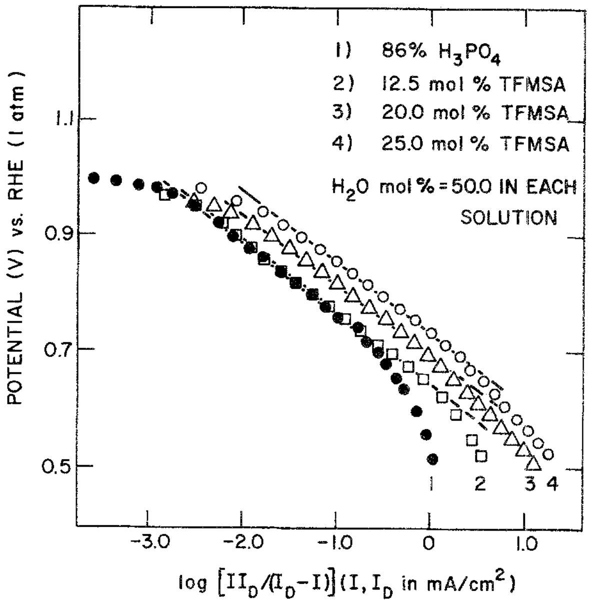

Fig. 6. Tafel plots for O_2 reduction in CF_3SO_3H–H_3PO_4–H_2O mixtures and in 86% H_2PO_4 at 25°C. i_d values (mA cm^{-2}) are: (1) 0.116; (2) 0.728; (3) 1.35; (4) 2.075. Rotation rate = 1600 rpm.

construction of the Tafel plots. As i approaches i_d in value, appreciable inaccuracy can develop in the value of $i_d i/(i_d - i)$ if some uncertainty is associated with the value of i_d. A possible reason for observing very high slope values or a tendency to approach limiting kinetic currents at low potentials is that a step, which is essentially potential independent, is involved in the O_2 reduction process which becomes rate controlling. Such a step could be, for instance, dissociative adsorption of O_2 on the platinum surface. There is, however, insufficient experimental evidence for this step in the O_2 reduction reaction.

The apparent exchange current densities obtained by extrapolation of the linear regions of the Tafel plots for the various mixtures to $E = 1.23\,\mathrm{V}$ (RHE) vary from $1.7 \times 10^{-8}\,\mathrm{A\,cm^{-2}}$ for 86% H_3PO_4 to $7.5 \times 10^{-8}\,\mathrm{A\,cm^{-2}}$ for the mixture of highest TFMSA content, 25 mol % H_3PO_4–25 mol % TFMSA–50 mol % H_2O. A comparison of the mass transport-corrected current densities at 0.8 V (RHE), which is a potential in the Tafel linear region, has also been carried out as follows.

(a) Expressing the kinetics of O_2 reduction in terms of the partial pressure of O_2:

$$i_k = kP_{O_2} \tag{3}$$

where k is the first order rate constant.
Since

$$kP_{O_2} = \frac{i(i_d)}{i_d - i} \tag{4}$$

$$\left[\frac{i(i_d)}{i_d - i}\right]_2 \Big/ \left[\frac{i(i_d)}{i_d - i}\right]_1 = k_2(P_{O_2})_2/k_1(P_{O_2})_1 \tag{5}$$

In the present study, the subscript 2 stands for the mixture electrolyte and 1 for 86% H_3PO_4. The comparison of $i(i_d)/(i_d - i)$ value is, therefore, equivalent to comparing the first order rate constant (k).

(b) When the kinetics are expressed in terms of the concentration of dissolved O_2:

$$i_k = k'C_{O_2} \tag{6}$$

where k' is the first order rate constant in this case. Rearranging Equation 6 and combining it with Equation 5

$$\left[\frac{i}{i_d - i}\right]_2 \Big/ \left[\frac{i}{i_d - i}\right]_1 = \frac{(i_d)_1 k_2'(C_{O_2})_2}{(i_d)_2 k_1'(C_{O_2})_1} \tag{7}$$

Since $i_d = 0.62nFACD^{2/3}\nu^{-1/6}\omega^{1/2}$,

$$\left[\frac{i}{i_d - i}\right]_2 \Big/ \left[\frac{i}{i_d - i}\right]_1 = \frac{k_2'}{k_1'}\left[\frac{D_1}{D_2}\right]^{2/3}\left[\frac{\nu_2}{\nu_1}\right]^{1/6}$$

$$\simeq \frac{k_2'}{k_1'}\left[\frac{\nu_2}{\nu_1}\right]^{5/6} \tag{8}$$

The comparison of $i/(i_d - i)$ values is seen to be equivalent to comparing the kinetics at the same concentration of O_2 in the electrolytes with a correction for the kinematic viscosity ratio.

Values of $i(i_d)/(i_d - i)$ and $i/(i_d - i)$ for the various electrolytes are listed in Table 1 for 0.8 V (RHE). The number of electrons per O_2 molecule (n) has been assumed to be constant. In pure solutions n is close to 4. In order to determine k_2'/k_1' ratios, the viscosities of the various electrolytes were measured (Table 1).

The rate constant ratio k_2/k_1 (Equation 5) increases with increasing amount of CF_3SO_3H in the electrolyte for mixture containing > 20 mol % of CF_3SO_3H. At lower concentrations of CF_3SO_3H, the values of k_2/k_1 are slightly less than 1. This, however, does not necessarily mean that the kinetics are intrinsically slower in these mixtures. The enhancement in the kinetics in these electrolytes is probably more than offset by impurity effects, that is, impurites introduced along with the trifluoromethane sulfonic acid. At higher concentrations the impurity effect is being offset by the enhanced kinetics due to the increase in O_2 solubility, and to a certain extent the increased diffusivity, accompanying the addition of CF_3SO_3H to the concentrated phosphoric acid.

The comparison of k_1' and k_2' (Equation 8) indicates that the kinetics are slower in the mixtures when the concentration of O_2 is used for the activity of O_2 (Table 1). The deviations in the k_2'/k_1' values for different mixtures from a simple monotonic behaviour may be due in part to the difference in the degree of purity of the mixed electrolytes. Differences in water and proton activity, and electrolyte adsorption behavior on platinum may also account for some of the difference between the electrolytes. However, because of the concentrated nature of the electrolytes used in the study the effects of these factors cannot be readily calculated.

The present investigation highlights the fact that the differences in the kinetics of O_2 reduction between concentrated electrolytes can be due to differences in O_2 concentration, whereas the rate constant obtained upon correcting for differences in O_2 concentration may not change, or may in fact decrease somewhat in the case of the solution of higher concentration of O_2. On the other hand, in dilute acid solutions the solubility of O_2 does not normally differ significantly from acid to acid. In this case the influence of factors such as adsorption in the O_2 reduction kinetics on platinum can often be seen, as for example in the study of Ross and Andricacos [8] in dilute solutions of CF_3SO_3H to which small amounts of H_3PO_4 were added. High O_2 solubility is desirable for fuel cell electrolytes since it results in more effective transport of O_2 to the cathode. In principle, an electrolyte exhibiting high O_2 solubility may be more attractive for fuel cell application than other electrolytes with, for example, more favorable adsorption properties.

The present study suggests that the addition of another component to concentrated phosphoric acid can lead to significant improvements in O_2 electrode kinetics. Trifluoromethane sulphonic acid is probably not a suitable acid to add to phosphoric acid for practical fuel cell operation at e.g. 190° C because of its volatility. Furthermore, we have observed that the addition of CF_3SO_3H to H_3PO_4 is accompanied by a decrease in conductivity [9]. Other mixture systems may warrant investigation, e.g. $H_3PO_4/(CF_2SO_3H)_2$, and possibly mixtures of phosphoric acid and perfluoroalkane phosphoric acids, e.g. $(CF_2PO(OH)_2)_2$.

Acknowledgement

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