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"Dioxygen Reduction in Various Acid Electrolytes"

by

E.B. Yeager, M. Razaq, D. Gervasio, A. Razaq and D. Tryk

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Department of Chemistry
Case Western Reserve University
Cleveland, Ohio 44106-7078

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Dioxygen reduction has been examined in several new acid electrolytes and mixtures of these electrolytes with concentrated phosphoric acid (used in present acid H₂-O₂ fuel cells). The polarization curves have been determined on smooth platinum with the rotating disk and ring-disk electrodes and on high-area platinum with gas-fed electrodes of the semi-hydrophobic-type. The polarization is less than with concentrated H₃PO₄ in some of these alternative electrolytes. Possible explanations are discussed.
Dioxygen reduction in various acid electrolytes
E. Yaeger, M. Razaq, D. Gervasio, A. Razaq and D. Tryk

Case Center for Electrochemical Sciences and the Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106, U.S.A.
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1 INTRODUCTION

The performance of the phosphoric acid fuel cell is limited principally by the irreversibility of the O2 reduction reaction and the severe voltage losses at the air cathode. This irreversibility is in part caused by the strong adsorption of the electrolyte (particularly H2PO4-) on platinum catalyst. This has prompted the examination of alternative electrolytes to concentrated H3PO4.

O2 reduction has been examined by the authors in a number of purified acid electrolytes including perfluorosulfonic, phosphoric, sulfonamide and carbonic acids. These have been synthesized by Prof. D. Des Marteau of Clemson University and Prof. D. Burton of the University of Iowa. The polarization for O2 reduction on smooth Pt as well as highly dispersed Pt of gas-fed O2 cathodes is substantially lower in some of these electrolytes as well as their mixtures compared to concentrated H3PO4.

Several factors may be responsible for these differences in the polarization curves for O2 reduction on smooth platinum as well as highly dispersed platinum. These include the following:

- differences in acidity
- specific ionic adsorption of the electrolyte
- differences in the compact layer structure at the interface
- differences in the solubility of O2
- differences in the diffusion coefficient of O2
- impurity effects.

These factors will be considered later in this paper in the discussion of the polarization data in these various acid electrolytes. In addition large changes in the conductivity may result in changes in the apparent polarization curves because of the difficulties in taking into account ohmic losses in the porous active catalyst layer. Differences in the wettability properties of the electrolyte can also have a major effect on the accessibility of the electrolyte to the electrocatalysts (e.g. Pt) in this active layer and produce major adverse effects on the voltage-current curves.

Of the various strong acids, CF3SO3H-H2O would normally be among the most attractive in terms of low overpotential, lack of specific adsorption on Pt, high O2 solubility and the knowledge how to clean this acid up with respect to adsorptive impurities.

Unfortunately, the perfluorosulfonic acids have much lower ionic conductivity than H3PO4 at high concentrations and this leads to excessive ohmic loss that may more than offset the lower polarization at the air cathodes in fuel cells using this electrolyte. A further complication is that CF3SO3H at high concentration (6 M) wets Teflon and this causes boiling of the Teflon bonded gas diffusion electrodes.

II MIXTURES OF CONCENTRATED PHOSPHORIC AND TRIFLUOROMETHANE-
SULFONIC ACID

An alternative approach is the use of a mixture of H3PO4 with a strong acid such as CF3SO3H with both acids at high concentrations, e.g., 25 mol% each acid and 50 mol% H2O. The adsorption of the phosphate anion on the Pt surface can still occur but the activity of the phosphoric acid should be significantly depressed and this should reduce the adsorption of the phosphate anion on the Pt surface. The solubility of O2 would be still increased although not by as much as with the pure CF3SO3H. The presence of the H3PO4 is expected to keep the conductivity of the electrolyte still quite high because of the Grothius-type conduction mechanism.

Prior work using laser Raman spectroscopy has demonstrated that in the CF3SO3H-H3PO4-H2O system, the sulfonic acid is almost fully ionized and protonates both H3PO4 and CF3SO3H for mole fractions of the sulfonic acid less than 0.4. Furthermore, these spectroscopic studies indicate that the formation of either the proton monohydrate (H2O+CF3SO3H) or the phosphonium ion [P(OH)3]+ is sufficient to promote the ionization of the CF3SO3H, i.e.,

CF3SO3H + H2O → CF3SO2+ + H2O+ (a)

CF3SO3H + OH- = P(OH)3+ → CF3SO2+ + P(OH)3+ (b)

Figure 1 indicates the Tafel plots for O2 reduction on smooth polycrystalline Pt in the CF3SO3H-H3PO4-H2O four mixtures and in 86% H3PO4 at 25°C. The measurements were made with the rotating disk technique; details are given elsewhere. The abscissa corresponds to the current density, i corrected for mass transport by multiplication with the factor i/i, where i is the diffusion limiting current density. For Fig. 1, the rotation rate was 1000 rpm. The Tafel slope in the potential region 0.7 to 0.7 V was 0.012 V decade which at 25°C corresponds to 0.14 F. The bending of the Tafel plot at more positive potentials is due to the initial stages of the anodic film.
(PtOH) formation on Pt. 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 constructing this figure. These were obtained from the slopes of the Koutecky-Levich plots of \( 1/i \) vs. \( 1/\sqrt{v} \). As \( i \) approaches \( i_d \), any error in \( i_d \) is greatly magnified. Another possibility is a kinetic limiting current associated with a step which is potential independent or which has only a very small potential dependence, e.g., the dissociative desorption of \( O_2 \).

The reaction order with respect to \( O_2 \) has been confirmed as first order from the slope of plots of \( \log i \) vs. \( \log [(i_d - i)/i_d] \) obtained with the rotating disk electrode. For example, for the 30 mol% \( H_3PO_4 \) - 20 mol% TFMSA - 50% \( H_2O \) solution, the slopes of these linear plots varied from 1.06 at 0.70 V to 1.10 at 0.55 V. No change in Tafel slope was obtained in going from 86% \( H_3PO_4 \) to 25% mol% TFMSA - 25% \( H_3PO_4 \) - 50% \( H_2O \) at 25 °C.

Measurements in the authors' laboratory, however, indicate that the Tafel slope on bright polycrystalline Pt in the double layer region is almost independent of temperature over the range 25 to 250 °C in concentrated \( H_3PO_4 \) and hence the apparent transfer coefficient is approximately proportional to the absolute temperature over this range (see Fig. 2).

The Tafel slope of 0.12 V/decade would ordinarily be taken as evidence that the rate-determining step for \( O_2 \) reduction on Pt is the first electron transfer step. This raises questions concerning the significance of the Tafel slopes for multistep electrode reactions involving adsorbed intermediates.

![Fig. 1. Tafel plot for \( O_2 \) reduction in \( CH_3COOH-H_3PO_4 \) mixture and 86 mol% \( H_3PO_4 \) at 25 °C. Values (mV/cm) were: (1) 0.116, (2) 0.726, (3) 1.35, (4) 2.08. Rotation rate = 1600 rpm².](image1)

![Fig. 2. Temperature dependence of apparent transfer coefficient for \( O_2 \) reduction in concentrated \( H_3PO_4 \).](image2)

The first order rate constant is defined by the rate equation written in the form

\[
i = 4k_2P_{O_2} \cdot (i_d - i)/i_d
\]

where \( P_{O_2} \) is the partial pressure (atm) of \( O_2 \) gas in equilibrium with the electrolytic solution. In Table I are listed the ratios of the rate constants \((k_2)\) for the mixed acids to that \((k_1)\) of the 86% \( H_3PO_4 \) both at 0.80 V vs. RHE. The ratios of the rate constants were calculated using the following equation:

\[
k_2/k_1 = (i_d - i)/i_d, \quad (i_d - i)/i_d
\]

with the condition that \( P_{O_2} \) and the potential are the same for both electrolytes. In Eq. (2), the subscripts 1 and 2 correspond to the measurement in \( H_3PO_4 \) and the mixed electrolytes, respectively.

The exchange current densities varied from \( 1.7 \times 10^{-8} \) A/cm² for 86% \( H_3PO_4 \) to \( 7.5 \times 10^{-8} \) A/cm² for the mixture with the highest TFMSA concentration, 25 mol% \( H_3PO_4 \) - 25 mol% TFMSA - 50 mol% \( H_2O \) at 25 °C. The corresponding change in the ratio of the rate constants is \( k_2/k_1 = 5.9 \) at \( E = 0.80 \) V vs. RHE (see Table 1). In this comparison, the number of electrons per \( O_2 \) molecule has been taken to be 4 and to be the same for all of the measurements corresponding to the linear region in the Tafel plots.

<table>
<thead>
<tr>
<th>Transfer Coefficient</th>
<th>Temperature (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.80</td>
<td>600</td>
</tr>
<tr>
<td>0.50</td>
<td>400</td>
</tr>
</tbody>
</table>
TABLE 1. Comparison of kinetic parameters for O2 reduction in CF3SO3H-11H3PO4-H2O mixture at 25°C<sup>20</sup>

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>H3PO4-CF3SO3H-H2O (mol%)</th>
<th>(i_a) (mA/cm&lt;sup&gt;2&lt;/sup&gt;)</th>
<th>(B) (mA/cm&lt;sup&gt;2&lt;/sup&gt;)(rpm)&lt;sup&gt;3/2&lt;/sup&gt;</th>
<th>(\eta_f) (mbar)</th>
<th>(k_f) (at 0.8 V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>0</td>
<td>50</td>
<td>0.117</td>
<td>2.9 \times 10&lt;sup&gt;-2&lt;/sup&gt;</td>
<td>5.3 \times 10&lt;sup&gt;-2&lt;/sup&gt;</td>
</tr>
<tr>
<td>37.5</td>
<td>12.5</td>
<td>50</td>
<td>0.728</td>
<td>1.82 \times 10&lt;sup&gt;-2&lt;/sup&gt;</td>
<td>5.38 \times 10&lt;sup&gt;-2&lt;/sup&gt;</td>
</tr>
<tr>
<td>30.0</td>
<td>20.0</td>
<td>50</td>
<td>1.35</td>
<td>3.38 \times 10&lt;sup&gt;-2&lt;/sup&gt;</td>
<td>15.1 \times 10&lt;sup&gt;-2&lt;/sup&gt;</td>
</tr>
<tr>
<td>25.0</td>
<td>25.0</td>
<td>50</td>
<td>2.08</td>
<td>5.2 \times 10&lt;sup&gt;-2&lt;/sup&gt;</td>
<td>31.4 \times 10&lt;sup&gt;-2&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

\(k_1\) = rate constant for 50 mol % H11PO4 - 50 mol % H2O (= 86 % H11PO4)
\(k_2\) = rate constant for mixed acids
\(B = 0.62 \cdot D^2 \cdot \eta_0\), obtained from惬 uptake-Levich plots
\(i_a\) = diffusion limiting current density

The k/f ratios are close to unity for the acid mixtures with up to 12.5 mol% TFMSA but deviate substantially from unity for higher mol% of TFMSA (see Table 1). Several factors can contribute to the change of the k/f ratio including changes in the activity coefficient in the transition state, the activity of H2O and the partially solvated protons and the adsorption of phosphate species on the Pt surface. Impurity effects cannot be discarded as a possible factor contributing to the change of the k/f ratio at high H2PO4 and TFMSA concentration since these acids are difficult to purify to the extent that the Pt surface is completely free of impurities. The faster kinetics in the concentrated CF3SO3H solution in Table 1 and Fig. 1 may be caused by a decrease in the adsorption of the H2HPO4<sup>-</sup> on the Pt surface and/or the higher solubility of O2 in the concentrated CF3SO3H compared with 86% H11PO4.

The results on smooth Pt suggest that the addition of a strong acid to concentrated H3PO4 will lower the polarization for O2 reduction at high performance gas-fed O2 cathodes using highly dispersed Pt as the catalyst in phosphoric acid fuel cells. TFMSA, however, is not as attractive as an additive in fuel cells operating at temperatures of ≈190 °C because of its volatility. The addition of TFMSA to concentrated H3PO4 also decreases the conductivity. In concentrated H3PO4, extensive hydrogen bonding occurs and the reduction is principally by a Grotthuss-type conduction mechanism involving protons hopping between adjacent H3PO4 molecules. The TFMSA reduces the intermolecular hydrogen bonding and thus reduces the conductivity. The increased ohmic loss is likely to offset much of the gain in cell voltage associated with the decrease in polarization of the O2 cathode.

III. O. REDUCTION WITH PERFLUORINATED SULFON IMIDE AS AN ADDITIVE TO CONCENTRATED H11PO4

Some of the perfluorinated phosphoric, phosphonic, sulfonimide and carbonyl electrolytes have substantial effects on the O2 electrode polarization even when added at relatively low concentrations to 85% H11PO4<sup>6,7</sup> (see Table II).

Of particular interest are the perfluorosulfonimides (PFSI), such as the strong acid CF3SO2N(H)SO2CF<sub>3</sub>F<sub>9</sub>. The voltammetry curves for Pt in N2 saturated 85% H11PO4 with and without 4% (0.16 M) of this PFSI are shown in Fig. 1. The addition of the PFSI has relatively little effect on the voltammetry curve for Pt in 85% H11PO4 without O2 present. This voltammogram plus others for more dilute solutions of PFSI in H11PO4 provide evidence that the PFSI is not strongly adsorbed on Pt while H2PO4 is strongly adsorbed. Figure 4 presents the polarization curve recorded with the rotating disk electrode technique. The polarization curves for the 85% H11PO4 with and without 4% PFSI (Fig. 4) indicate that PFSI lowers the half wave potential \(E_{1/2}\) by ≈90 mV while the limiting current is increased by ≈64%.

Table II: Oxygen reduction at high surface area electrodes in sulfonamidic and hypophosphonic acid solutions

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Temperature [°C]</th>
<th>(E_{1/2}) (mV)</th>
<th>(\eta_f) (mbar)</th>
<th>(k_f) (at 0.8 V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>84 % (FSO3N&lt;sub&gt;2&lt;/sub&gt;)NH&lt;sub&gt;1&lt;/sub&gt;</td>
<td>70</td>
<td>-55</td>
<td>105</td>
<td>180</td>
</tr>
<tr>
<td>84 % (CF3SO2)NH&lt;sub&gt;1&lt;/sub&gt;</td>
<td>70</td>
<td>50</td>
<td>50</td>
<td>30</td>
</tr>
<tr>
<td>85 % (PO(OH)&lt;sub&gt;1&lt;/sub&gt;CF&lt;sub&gt;3&lt;/sub&gt;)</td>
<td>100</td>
<td>50</td>
<td>70</td>
<td>50</td>
</tr>
<tr>
<td>85 % H11PO4 plus less than 0.1 % (CF3SO2)N(H)SO2CF&lt;sub&gt;3&lt;/sub&gt;F&lt;sub&gt;9&lt;/sub&gt;</td>
<td>100</td>
<td>45</td>
<td>0</td>
<td>20</td>
</tr>
<tr>
<td>85 % H11PO4 plus 0.5 % CF3SO2N(H)SO2CF&lt;sub&gt;3&lt;/sub&gt;F&lt;sub&gt;9&lt;/sub&gt;</td>
<td>70</td>
<td>70</td>
<td>70</td>
<td>70</td>
</tr>
</tbody>
</table>

The mixture of 85% H11PO4 and 4% PFSI has the milky appearance of an emulsion. High concentrations H11PO4 solutions involves a three dimensional strongly hydrogen bonded structure and the PFSI tends to be squeezed out of the bulk...
H\textsubscript{3}PO\textsubscript{4} solution forming a physically adsorbed layer at the electrode surface with the hydrocarbon C\textsubscript{2}F\textsubscript{6} tail probably oriented towards the electrode surface and the polar end towards the bulk solution. The structure of this layer including its thickness needs to be established. In-situ spectroscopic techniques such as infrared reflectance (SNIF-TIRS, EMIRS) and Raman (SERS) should be able to provide such information.

![Graph](image)

The physically adsorbed PFSI layer at the electrode surface perturbs the structure of the double layer and lowers the effective dielectric constant adjacent to the electrode surface. The chemical potentials of adsorbed ionic species as well as H\textsubscript{3}PO\textsubscript{4} and water molecules are dependent on the dielectric properties in the electrolyte phase immediately adjacent the Pt electrode. The O\textsubscript{2} molecule is relatively non-polar and the decrease in dielectric constant is expected to favor O\textsubscript{2} adsorption, not so much because of a direct interaction with the (O\textsubscript{2})\textsubscript{ads} but rather through the destabilization of adsorbed more polar species and the freeing up of more adsorption sites for O\textsubscript{2}. The PFSI layer is probably only a single molecule thick and does not seem to interfere with O\textsubscript{2} and water/proton transport at this interface. This layer resembles a self-ordered Langmuir-Blodgett film with the fluorocarbon end towards the platinum. In this layer O\textsubscript{2} has a higher concentration than in the bulk H\textsubscript{3}PO\textsubscript{4} and H\textsubscript{2}O has a lower concentration than in the bulk solution.

The PFSI is a relatively strong acid (pK\textsubscript{a} = 0.91) compared to the first ionization of H\textsubscript{3}PO\textsubscript{4} (pK\textsubscript{a1} = 2.15). The solubility of the PFSI in 85% H\textsubscript{3}PO\textsubscript{4}, however, is slightly less than 0.5% and the PFSI in excess of 0.5% forms an emulsion. The addition of 4% PFSI would suppress the ionization of the H\textsubscript{3}PO\textsubscript{4} but the hydrogen ion concentration would change by only a small amount (less than 1%).

The generation of H\textsubscript{2}O\textsubscript{2} was monitored with the rotating ring-disk technique with a potential of 1.1 V vs. RHE applied to the ring while scanning the disk potential form 0 to 0.4 V. The ratio of the peroxide oxidation current on the ring electrode to the O\textsubscript{2} reduction current on the disk was very small and essentially the same with and without the 4% PFSI. In Fig. 4 the increase in the diffusion limiting current density in the rotating disk experiment with 4% PFSI added to 85% H\textsubscript{3}PO\textsubscript{4} is relatively large (64% at 2500 rpm) and depends on the change in O\textsubscript{2} solubility and diffusion coefficients of the O\textsubscript{2} in the electrolytic solution. These were determined using microelectrode technique. The solubility and diffusion coefficients are given in Table III. Both O\textsubscript{2} solubility and diffusion coefficients are much larger in the 84% PFSI than the 85% H\textsubscript{3}PO\textsubscript{4}. The difference in the CD\textsubscript{3}O\textsubscript{2} product for the 85% H\textsubscript{3}PO\textsubscript{4} and 84% PFSI is sufficient to account for the 64% increase in limiting current density with 4% PFSI added to 85% H\textsubscript{3}PO\textsubscript{4}.

![Graph](image)

Table III. The solubility and diffusion of O\textsubscript{2} determined using a Pt microdisk electrode at 20 °C in various electrolytes.

<table>
<thead>
<tr>
<th>Electrolytes</th>
<th>Solubility mol\textsuperscript{-1}</th>
<th>Diffusion coefficient cm\textsuperscript{2}s\textsuperscript{-1}</th>
</tr>
</thead>
<tbody>
<tr>
<td>85% H\textsubscript{3}PO\textsubscript{4}</td>
<td>4.4 × 10\textsuperscript{-4}</td>
<td>1.27 × 10\textsuperscript{-6}</td>
</tr>
<tr>
<td>85% (CH\textsubscript{3}SO\textsubscript{2})\textsubscript{2}NH</td>
<td>4.7 × 10\textsuperscript{-4}</td>
<td>1.64 × 10\textsuperscript{-6}</td>
</tr>
<tr>
<td>8% (CH\textsubscript{3}SO\textsubscript{2})\textsubscript{2}NH</td>
<td>6.0 × 10\textsuperscript{-4}</td>
<td>1.6 × 10\textsuperscript{-6}</td>
</tr>
<tr>
<td>84% (CH\textsubscript{3}SO\textsubscript{2})\textsubscript{2}NH</td>
<td>6.0 × 10\textsuperscript{-4}</td>
<td>1.6 × 10\textsuperscript{-6}</td>
</tr>
</tbody>
</table>

The polarization of the O\textsubscript{2} cathode (Fig. 5) has also been examined using high surface area Prutech gas-fed electrodes in 85% H\textsubscript{3}PO\textsubscript{4} without and with 0.5% PFSI at 70 °C in a micro H\textsubscript{2}/O\textsubscript{2} fuel cell (Fig. 6). The polarization is 70 mV less at a current density of 100 mA/cm\textsuperscript{2} in the 0.5% PFSI solution. The polarization curves in the 0.5% PFSI + 85% H\textsubscript{3}PO\textsubscript{4} solutions are independent of time over the 48 h time period of the experiments. This suggests that the mixed electrolyte concentration of PFSI is lower than the critical value which would promote flooding of the gas-fed electrodes. At lower concentrations (e.g., 0.12%) the PFSI still depresses the polarization at 70 °C but not by as much (≈ 30 mV or 100 mA/cm\textsuperscript{2}).

The volatility of the PFSI in 85% H\textsubscript{3}PO\textsubscript{4} at 150 °C was checked by heating the mixture in a beaker. After 5 h with 4% PFSI + 85% H\textsubscript{3}PO\textsubscript{4}, a substantial amount of the PFSI was lost by evaporation. Thus the intrinsic vapor pressure of the PFSI itself is
too high for operations under acid fuel cell conditions (190 °C). A condenser system could be used to recover the PFSI from the vapor phase.

Other electrolytes which have been investigated in the authors’ laboratory at both low and high concentrations with Prototech high area Pt electrodes are listed in Table II for either 70 or 100 °C together with polarization data. The relatively poor performance of the 84%-F(PSO₂)₂NH may be due to stability problems and/or impurities. The perfluorosulfonic carboxaid probably forms a self-assembled layer with the C₄F₉ tail closest to the interface.

IV. O₂ REDUCTION IN CONCENTRATED PERFLUOROBIS PHOSPHORIC ACID

The decrease in polarization for the Prototech Pt catalyzed O₂ cathode in 85% (H₂)PO₂CF₂CF₂PO(OH)₂ as compared with 85% H₃PO₄ is quite substantial at 100 °C (see Table II). These electrodes have been operated in this electrolyte at 200 °C with relatively little increase in polarization over 500 h. The bis phosphoric acids were synthesized by Prof. D. Burton and his research group.¹³

V. THE ROLE OF O₂ SOLUBILITY

One of the important differences between the perfluoro acids and H₃PO₄ is the much greater solubility of O₂. Higher solubility of O₂, however, does not necessarily mean lower polarization and faster kinetics.

To illustrate this, consider a reaction mechanism involving the following initial step as rate controlling.

\[
\text{Pt} + O₂ \rightarrow \text{Pt} + O
\]

With reaction (c) rate determining, the rate of the forward process can be given by¹⁵:

\[
\nu_1 = \frac{k_f}{\gamma_k} \cdot a_{O₂} \cdot a_{\text{Pt}}
\]

where \(k_f\) is the forward rate constant, \(\gamma_k\) is the activity coefficient for the transition state, \(a_{O₂}\) is the activity of O₂ in the electrolyte phase and \(a_{\text{Pt}}\) is the activity of bare Pt sites. The interaction of water with the Pt sites is assumed to be weak.

The activity of O₂ in the electrolyte phase is controlled by the condition that the chemical potential of the dissolved O₂ be equal to that of the O₂ in the gas phase in equilibrium with the electrolyte phase, i.e.

\[
\mu_{O₂} = \mu_{O₂}^\text{gas} + RT \ln(a_{O₂}) = \mu_{O₂}^\text{gas} + RT \ln(a_{O₂})
\]

where the \(\mu\) terms correspond to the chemical potentials of the sub-scripted species, the \(a\) terms are the activities and the \(\mu^\text{gas}\) terms correspond to the standard state values. Thus the chemical potential of the O₂ in the electrolyte phase is independent of the
particular electrolyte phase provided the O₂ in the electrolyte phase is in equilibrium with the O₂ in the gas phase. The O₂ solubility should not directly influence the kinetics unless the reaction is under O₂ transport control in the gas and/or electrolyte phases. This can be seen by recalling from absolute rate theory\(^\text{16}\) that the rate constant \(k_t\) in Eq. (3) is given by

\[
k_t = \frac{k k T}{h} K_* = \frac{k k T}{h} \exp \left( \frac{\mu_*^* - (\mu_{O_2}^{\infty}) - (\mu_{O_2}^{\infty})}{RT} \right) \tag{5}
\]

where \(k\) is the transmission factor, \(K_*\) is the apparent equilibrium constant for the (O--O)ads reactant in the transition state (\(\Phi\)), \(\mu_*^*\) is the chemical potential of the adsorbed oxygen in the transition state and the remaining symbols have their usual meaning. Recall that the equilibrium constant and chemical potential for the transition state are calculated from the partition functions with the vibration mode corresponding to transmission over the potential energy barrier omitted since it has already been used to derive the pre-exponential term \(k k T / h\). Combining Eqs. (3) and (5) yields

\[
v_t = \frac{k k T}{h} \exp \left( \frac{(\mu_*^* - (\mu_{O_2}^{\infty}) - (\mu_{O_2}^{\infty})_2)}{RT} \right) \tag{6}
\]

and

\[
v_t = \frac{k k T}{h} \exp \left( \frac{(\mu_*^* - (\mu_{O_2}^{\infty})_2)}{RT} \right) \exp \left( \frac{(\mu_{O_2}^{\infty})}{RT} \right) \tag{7}
\]

with \((\mu_{O_2}^{\infty})_2 = (\mu_{O_2}^{\infty})_3 = \text{constant}\). The dependence of the kinetics on the factor \((\mu_{O_2}^{\infty})_2\) is offset by then term \(\exp (\mu_{O_2}^{\infty})_2/RT\) since \((\mu_{O_2}^{\infty})_2\) is held constant. The solubility of O₂ in the particular electrolytic solution has no direct effect on any term in Eq. (5a) but in a sense it may have a small indirect effect on the standard state chemical potential \((\mu_*^*_{O_2})\) of the O--O species involved in the transition state. The interaction with the electrolytic solution in the transition state may have some similarity with the interaction of dissolved O₂ with the electrolytic solution. This effect would be expected to be quite small compared with that involving the change on the activity of the "bare" Pt \((\mu_{Pt})\) in Eq. (7), particularly when specific adsorption of the electrolyte occurs on Pt. In general O₂ solubility has a substantial effect on the polarization curve for O₂ electroreduction only when mass transport of O₂ is controlling. Thus, it is not surprising that the solubility of O₂ drops off by a factor of 10\(^{-2}\) between 0.1 and 10 M KOH without a corresponding drop-off in the rate of O₂ reduction on Pt electrodes in concentrated KOH. Of course, for a given electrolyte-solvent system, the rate of adsorption of O₂ (e.g., reaction c) is proportional to the O₂ concentration with \((\mu_{O_2}^{\infty})_2\) constant (see Eq. (5)).
VIII. COMPETITION OF O₂ WITH ELECTROLYTE COMPONENTS FOR ADSORPTION SITES

While water is important to the O₂ reduction reaction, the adsorption of H₂O or other polar species in the electrolytic solution may lead to a reduction in the accessibility of O₂ to the transition metal sites of the catalyst and hence a depression of the kinetics. There is little doubt that the adsorption of such species as HSO₄⁻, Cl⁻, and H₂PO₄⁻ depresses the kinetics of O₂ reduction on platinum.

On the other hand, the formation of physically adsorbed layer of a surfactant type molecule such as C₄F₉-SO₂-NH-SO₂-CF₃ on the platinum surface promotes the O₂ reduction kinetics (see Section IV). This may be explained on the basis that the adsorbed perfluoromide renders the interfacial region less polar and hence favors O₂ adsorption in competition with polar components of the electrolyte for adsorption sites on the Pt. It may not be so much that the surfactant reduces the free energy of adsorption of the O₂ but rather it increases the free energy of adsorption of H₂O and ionic components because of the lower effective dielectric constant in the electrolyte phase immediately adjacent to the catalyst surface.

CONCLUSIONS CONCERNING THE ROLE OF THE ELECTROLYTE IN O₂ REDUCTION

The following are some of the conclusions reached by the authors concerning the role of the electrolyte in the kinetics of O₂ reduction in concentrated acid solutions.

1. Proton transfer is not involved in the rate determining step and is not an important factor in O₂ reduction kinetics in concentrated H₃PO₄.

2. The O₂ competes with various species in the electrolyte for adsorption sites on platinum catalyst and this in turn results in the depression of the kinetics. Anionic species such as Cl⁻, H₂PO₄⁻, HSO₄⁻ are particularly detrimental. In seeking new acid electrolytes, species which strongly adsorb on Pt and similar catalysts should be avoided.

3. Additives which form self assembled ordered films on Pt may lower the O₂ reduction overpotential significantly. The decrease may be explained on the basis of a decrease in the dielectric constant in the interfacial region caused by the additive. This increases the adsorption of O₂ as a non-polar species and decreases the adsorption of polar species such as the various phosphate species and even water itself.

4. Thermodynamic and kinetic considerations indicate that the O₂ solubility in the electrolytic solution should not have a direct effect on the rate of O₂ reduction at a fixed potential and fixed O₂ partial pressure in equilibrium with the electrolytic solution provided mass transport of O₂ in the electrolyte phase is not controlling.

Two mechanisms which meet this criteria are the following:

**Mechanism I for O₂ Reduction**

```
\[
\begin{align*}
\text{Pt} + \text{H}^+ & \rightarrow \text{Pt}^+ + \text{H}^+ \\
\text{Pt}^+ + \text{e}^- & \rightarrow \text{Pt} \\
\text{II} & \rightarrow \text{III} \\
\text{IV} & \rightarrow \text{V} \\
\text{VI} & \rightarrow \text{VII} \\
\text{VIII} & \rightarrow \text{IX}
\end{align*}
\]
```

**Mechanism II for O₂ Reduction (dual site)**

```
\[
\begin{align*}
\text{Pt} + \text{O} & \rightarrow \text{Pt} - \text{O} \\
\text{Pt} - \text{O} & \rightarrow \text{Pt} - \text{O} \\
\text{e}^- & \rightarrow \text{Pt} - \text{O} \\
\text{Pt} - \text{O} & \rightarrow \text{Pt} - \text{O} \\
\text{Pt} - \text{O} & \rightarrow \text{Pt} - \text{O} \\
\text{e}^- & \rightarrow \text{Pt} - \text{O} \\
\end{align*}
\]
```
In each case the rate determining step is the adsorption of O₂ on the Pt surface and the reaction is first order in O₂ concentration for a given electrolyte, as has been observed in rotating disk electrode studies. The differences between mechanism I and II is that mechanism I involves a single Pt surface atom while mechanism II involves two adjacent sites on two different Pt surface atoms.

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ИЗВОД

РЕДУКЦИЯ КИСЛОРОДА У РАЗЛИЧИМ КИСЛОРОДИМ ЕЛЕКТРОЛИТАМ


Case Center for Electrochemical Sciences and the Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106, U.S.A.

Прукавина је електрохемијска реакција кисеоника у неким кисеонидим електролитима у коме се кисеоник редукује ниском фосфорном кисеонидом у води. Користи се у ниским концентрацијама извора извора. Опредељено је да је у њиховом случају повлијано дифузивним електролитом. У неким од ових извора, редукују се два атома платине у фосфорном кисеониду. Резултати су моделацијом овог ефекта.

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3. S. Towner, Ph.D. Thesis, Chemistry Department, Case Western Reserve University, Cleveland, Ohio 44106