Temperature dependence of the Tafel slope for oxygen reduction on platinum in concentrated phosphoric acid*

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Oxygen reduction on bright platinum in concentrated H_3PO_4 has been investigated with the rotating disc electrochemical technique at temperatures from 25 to 250° C and oxygen pressures up to 1.77 MPa. Cyclic voltammetry has been employed to study the anodic film formed on platinum in concentrated H_3PO_4 and the possible electroreduction of H_3PO_4 on platinum. The apparent transfer coefficient for the oxygen reduction has been found to be approximately proportional to temperature rather than independent of temperature. Such behaviour is difficult to reconcile with accepted theories for the effect of electrode potential on the energy barriers for electrode processes. It is of importance to establish an understanding of this phenomenon. Possible factors which can contribute to the temperature dependence of the transfer coefficient but which would not necessarily result in a direct proportionality to temperature include potential dependent adsorption of solution phase species, restructuring of the solution in the compact layer, proton and electron tunnelling, a shift in rate-determining step, changes in the symmetry of the potential energy barrier, penetration of the electric field into the electrode phase, insufficient correction for ohmic losses, and impurity effects.

Nomenclature

α transfer coefficient
β symmetry factor
β' temperature independent component of β
ν stoichiometric number
ω rotation rate (r.p.m.)
a, c constant and temperature coefficient in Equation 4 (no unit and K^{-1}, respectively)
B slope of Koutecky–Levich plot (mA cm^{-2} (r.p.m.)$^{-1/2}$)
b Tafel slope (V dec.$^{-1}$)
E potential (V)
F Faraday (C mol^{-1})

i current density (A cm^{-2})
i_L diffusion limiting current density (A cm^{-2})
K temperature independent component of Tafel slope (V dec^{-1}.)
R gas constant (J mol^{-1} K^{-1})
T temperature (K)
n number of electrons
$(\Delta \overrightarrow{G^{\ddagger}})°$ standard free energy of activation for forward process (J mol^{-1})
$(\Delta \overrightarrow{H^{\ddagger}})°$ standard enthalpy of activation for forward process (J mol^{-1})
$(\Delta \overrightarrow{S^{\ddagger}})°$ standard entropy of activation for forward process (J mol^{-1} K^{-1})

1. Introduction

As part of a continuing study of the oxygen reduction kinetics the present authors have amassed considerable data on the temperature dependence of the transfer coefficient for oxygen reduction on platinum in concentrated phosphoric acid over a wide range of temperatures (25 to 250° C). This paper presents these data and compares them to those in the literature.

Electrochemists usually consider the Tafel slope, b, to be directly proportional to the temperature with the transfer coefficient, α, a temperature-independent

constant. That is,

$$\left[\frac{\partial E}{\partial \ln (i)} \right]_T = b = -\frac{RT}{\alpha F} \qquad (1)$$

where α is a function of the symmetry coefficient, β, and the stoichiometric number, ν, for the rate controlling step in the overall reaction. For a one-electron single step reaction $\alpha = \beta$, although for more complex multiple step reaction mechanisms α is a function of β for the rate-determining step, but the specific relation between α and β depends on the mechanism. For a given rate determining step the Tafel slope b is then considered

to be directly proportional to the absolute temperature.

In the instance of the hydrogen generation reaction on mercury in aqueous solutions and several other electrocatalytic processes on various electrode surfaces, the temperature dependence of the Tafel slope has been found to deviate from the direct proportion expected from Equation 1 if α is a constant [1–4]. Conway lists, in his review paper [3], systems which deviate from α being a constant. These include hydrogen evolution on mercury and nickel in aqueous HCl, Ni–Mo alloys in aqueous KOH, anodic oxygen evolution and cathodic oxygen reduction on platinum in aqueous acid solutions, anodic bromine evolution on carbon in CH_3CN, and anodic nitrogen evolution on platinum in aqueous solution. Conway plotted the Tafel slope for hydrogen evolution on mercury in acid solution (methanol–water) against temperature over the range 180 to 340° K and found the Tafel slope to fit the following equation:

$$-b = \frac{RT}{\beta F} \equiv \frac{RT}{\beta'F} + K \qquad (2)$$

where α has been set equal to β for the rate-determining step (discharge).

Agar [4], Roiter and Jampolskaja [5], and Scharifker et al. [6] have reported experimental studies relating to the temperature dependence of the transfer coefficient for oxygen reduction. Agar and also Roiter and Jampolskaja have reported a temperature-dependent α, with α approximately directly proportional to temperature. On the other hand Scharifker et al. have reported an essentially temperature-independent transfer coefficient for oxygen reduction in 98% H_3PO_4.

In a very thorough study of the kinetics of the reduction of hydroxylamine over a temperature range of 1–94° C with the dropping mercury electrode Kirowa–Eisner, Schwarz, and Gileadi [7] have examined the temperature dependence of the Tafel slope and found that the Tafel slope is proportional to the absolute temperature with a transfer coefficient and symmetry factor independent of potential over the range 0.35 to 0.45 V vs RHE and $\alpha = 0.619 \pm 0.004$.

2. Experimental details

2.1. Electrochemical apparatus and RDE procedures

The oxygen reduction measurements were carried out in all Teflon cells using the rotating ring disc technique, in some instances in a high pressure vessel. This technique provides control of mass transport. The oxygen reduction polarization curves on a bright platinum disc were obtained with a Pine potentiostat together with an X–Y recorder using both scanning and point-by-point measurements. The scanning measurements were carried out by switching the gain settings on the X–Y recorder during the voltage sweep so that very low current densities could be accu-

rately measured. This enabled the currents used to obtain the Tafel plots to be recorded over a dynamic range of 10^4 and the Tafel slope to be evaluated with partial significance in third figure. Oxygen reduction on platinum under these conditions normally proceeds by a parallel mechanism. In the present research the maximum amount of peroxide produced in the potential region, where the Tafel slope was evaluated, corresponded to less than 5% of the oxygen consumed at the electrode at room temperature and less than 1% above 100° C. The peroxide was measured with the platinum-ring electrode potentiostated at 1.3 V vs RHE. This potential is in the diffusion limited region for peroxide oxidation. The ring was subjected to reducing conditions (0.3 V) between each measurement to keep the anodic film from growing sufficiently thick to inhibit the peroxide oxidation.

The high pressure vessel consisted of two chambers (Fig. 1). The motor was isolated in one chamber with the electrochemical cell in the other chamber. Nitrogen was fed into a shroud around the motor and oxygen into the electrochemical cell. This pressurized system was operated with the rotating ring-disc electrode at temperatures up to 100° C during oxygen reduction measurements and with platinum flag electrodes up to 218° C during cyclic voltammetry measurements. The temperature was measured with a thermocouple with the reference junction in
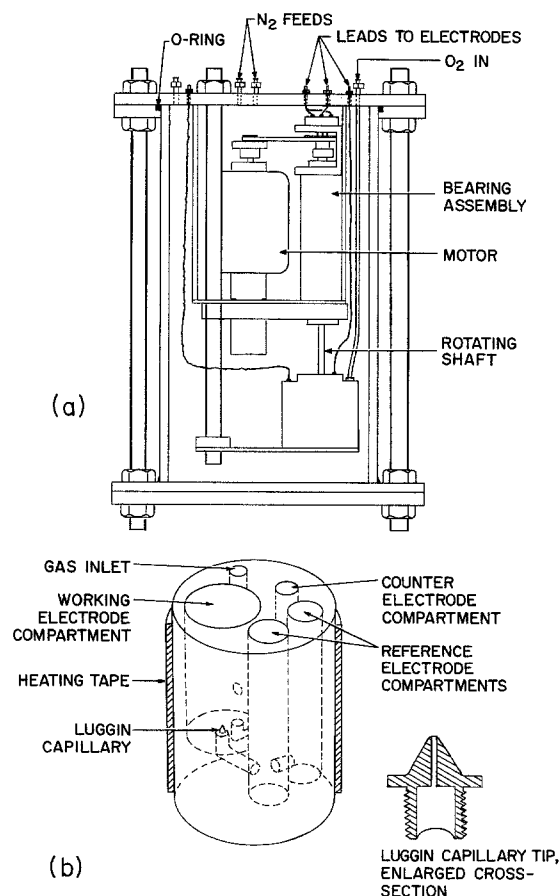

Fig. 1. Pressurized system for rotating ring-disk electrode measurements at elevated temperatures in concentrated H_3PO_4. (a) detail view of electrochemical cell (b).
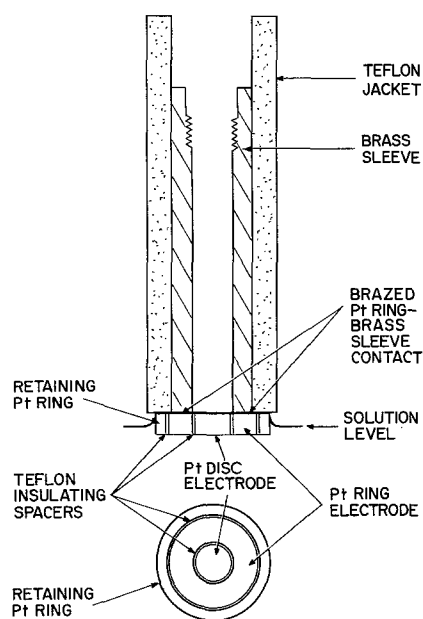
Fig. 2. Rotating ring-disc electrode for use at high temperatures (not to scale.)

an ice–water bath with an accuracy of the order of 1° C.

The Teflon insulating the disc electrode was surrounded by the platinum-ring electrode (Fig. 2). The platinum-ring electrode was brazed onto the brass shaft and then machined in place. The disc electrode was pressure fitted into the ring with a Teflon spacer between the disc and ring. The Teflon insulating the outer diameter of the platinum-ring electrode was likewise surrounded by an outer platinum-retaining ring. The outer retaining platinum-ring was pressure fitted onto the Teflon surrounding the platinum-inner ring electrode. The inner platinum-ring electrode and the outer retaining platinum-ring, by virtue of having a coefficient of thermal expansion about one-tenth that of Teflon, restrained the Teflon from irreversible expansion. This arrangement maintained a tight seal at higher temperatures (up to 250° C). The counter electrode was platinum foil and the reference electrode was a dynamic hydrogen electrode, both in separate compartments.

2.2. Purification

The 85% phosphoric acid (Mallinckrodt) was purified by procedures described in [8] involving treatment with H_2O_2 followed by platinum-catalyzed peroxide decomposition. Concentrations higher than 85% were obtained by heating to volatilize off water. The concentrations were determined by titration with NaOH. Concentrations higher than 100% corresponded to condensation of H_3PO_4 to form polyphosphates. The solutions were saturated with purified oxygen or air during the polarization measurements. The oxygen and air were purified by passing them through a series of traps. The traps were silica gel to adsorb H_2O, Hopcalite (Mine Safety Company) to oxidize CO to CO_2, rutile at dry ice/ethanol tempera-

ture to adsorb organics, and tightly compacted glass wool to remove dust.

The rotating ring-disc electrode was polished progressively down to $0.05 \mu m$ alumina and cleaned with distilled water in preparation for the experiments [8]. The rotating ring disc electrode was lowered into the cell until it just contacted the solution. The gases introduced into the cell were presaturated with water vapour in order to have the same water vapour partial pressure as the phosphoric acid solution. The gases were introduced into the working electrode compartment by bubbling them through the solution for more than 1 h prior to commencing measurements. The measurements were principally at 101 kPa (1 atm) pressure although a number were also carried out with a rotating disc electrode at oxygen pressures up to 1.7 MPa in the high pressure vessel.

2.3. Voltammetry

Cyclic voltammetry measurements in the absence of oxygen were used to check on the presence of impurities in the electrolyte. The cyclic voltammetry measurements were conducted using platinum foil flag electrodes spot welded to platinum wires which extended out of the cell. The area of the working electrode was $10.95 \, cm^2$ unless otherwise stated. Prior to use for electrochemical measurements the foils were rinsed with distilled water, dried, heated to red heat in a hydrogen–air flame, cooled and then placed in solution. The solutions were saturated with purified argon or nitrogen gases which were presaturated with water vapor to have the same water vapour partial pressure as the phosphoric acid solution. The counter electrode was platinum foil. The reference electrode was a high surface area platinum black standard hydrogen electrode during measurements at atmospheric and a dynamic hydrogen reference electrode at elevated pressures.

3. Results and discussion

3.1. Cyclic voltammetry

Cyclic voltammetry was used to test for the presence of adsorbed foreign species on the platinum surface in the oxygen reduction potential region and to examine the purity of the H_3PO_4 solutions. Figures 3–6 indicate the presence of an anodic film at potentials positive to 0.9 V at ambient temperatures in 88 and 100% H_3PO_4. Figures 3 and 4 indicate these H_3PO_4 solutions to be of reasonable purity. These curves were obtained after 5–20 potential cycles. Impurity effects show up at slow sweep rates as loss of symmetry in the hydrogen adsorption–desorption region. The peak structure in this region is sensitive to the particular crystal planes which are present on the platinum surface, and thus it is difficult to compare the hydrogen peaks on polycrystalline platinum with literature data. Such anionic species as Cl^-, HSO_4^-, $H_2PO_4^-$ can be strongly adsorbed on plati-
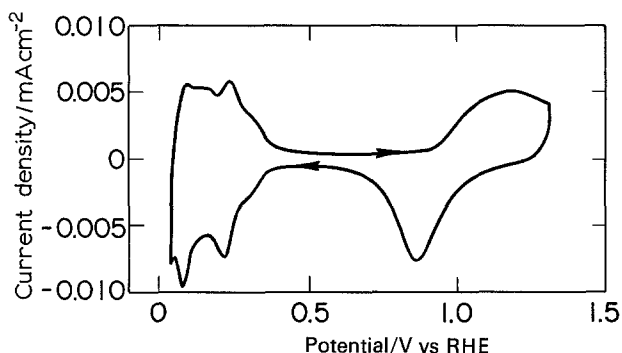
Fig. 3. Voltammetry at a 10.95 cm^2 geometric area platinum foil electrode in purified 88% H_3PO_4 at 22° C, argon saturated. Sweep rate: 5 mV s^{-1}.

num in acid electrolytes and can contribute directly to the peak structure in the hydrogen adsorption region as well as modify the hydrogen adsorption–desorption peaks.

At higher temperatures the voltammetry curves were more complex and included well defined H adsorption–desorption peaks and additional oxidation peaks showing the presence of electroactive species on the anodic sweep in the double layer region, peaks I and II in Fig. 5. These peaks were observed only at temperatures higher than 60° C in concentrated phosphoric acid. Such peaks in the double layer region have also been observed in the voltammetry curves on platinum in 98% H_3PO_4 at 25 to 150° C by Scharifker et al. [6] and at 160° C in 90 and 106% H_3PO_4 by Vogel and Baris [9]. The cathodic window opening curves in Fig. 6 demonstrate that these species result from potential excursions negative to 0.4 V. Separate experiments provide evidence that these peaks represent the oxidation of lower valence state phosphorous compounds [8, 9]. The lower valence species are produced on the electrode surface at high temperatures by the reduction of phosphate at potentials in the hydrogen region in concentrated phosphoric acid solutions. Additional observations are the stirring rate did not influence the charge under these peaks in the anodic sweep, the peak position shifted toward more negative potentials as the temperature was increased (became more reversible), and the charge under the oxidation peak increased with the logarithm of the
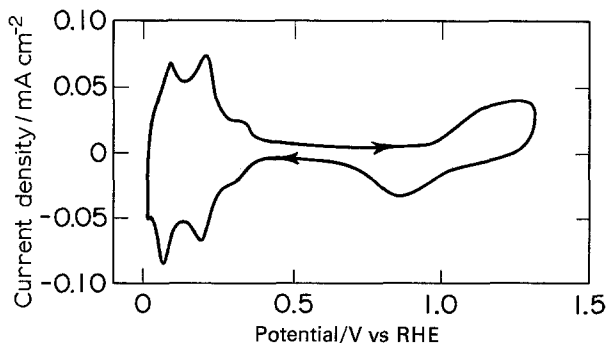

Fig. 4. Voltammetry at a 10.95 cm^2 geometric area platinum foil electrode in purified 100% H_3PO_4 at 19° C, argon saturated at 101 kPa (1 atm). Sweep rate: 50 mV s^{-1}.
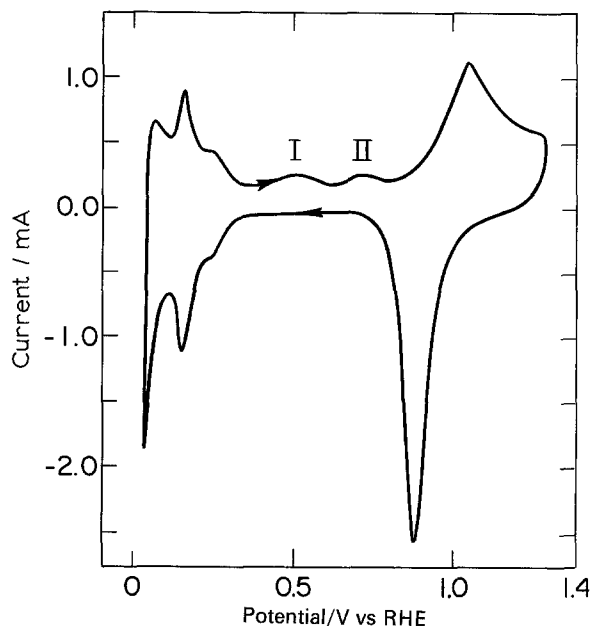

Fig. 5. Voltammetry curve for platinum foil (10.95 cm^2 geometric area) in 94% H_3PO_4 at 150° C. Sweep rate: 50 mV s^{-1}. Argon saturation at 101 kPa (1 atm).

holding time at 0.10 V. The lack of an effect of solution agitation and the increase in oxidation peak charges with the logarithm of holding time indicate the species is not a trace impurity. The rate of reduction of a trace impurity in the solution phase should exhibit sensitivity to solution agitation and a linear increase in charge with holding time. All of these experiments point to the oxidation of the products of the reduction of H_3PO_4 itself as giving rise to the extraneous oxidation peaks observed in the double layer charging region of platinum. The Mott–Cabrerra and place exchange treatments of anodic film formation lead to such logarithmic dependence of film growth on time. Vogel and Baris observed similar film formation. The platinum electrode sur-
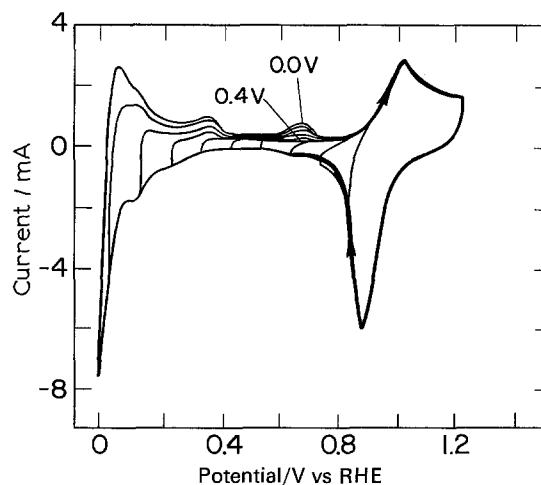

Fig. 6. Voltammetry curves for platinum in purified 86% H_3PO_4 at 208° C as the cathodic sweep limit is decreased. Nitrogen saturation in a pressure vessel. Sweep rate: 100 mV s^{-1}. Electrode area: 9 cm^2. H_2O vapour pressure is 330 kPa. Voltages indicated on the figure correspond to the cathodic limit of the previous sweep.

face was maintained free of these species by taking care to restrict the electrode to potentials positive to 0.3 V at all times at high temperatures.

3.2. Oxygen reduction

Figure 7 indicates the polarization curve for oxygen reduction at platinum in 85.5% H_3PO_4 at 1.76 MPa oxygen pressure at 100° C as a function of disc rotation rate up to 2 500 r.p.m. Figure 8 indicates a typical Tafel plot observed in the present study with the factor $i_L/(i_L - i)$ used to obtain the current under kinetic control. Since the diffusion limiting current density i_L is a constant for a given rotation rate, this factor was omitted from the plot. This analysis technique procedure is equivalent to calculating the steady-state kinetic current from a Koutecky–Levich analysis and then plotting the kinetic current as a function of potential. The Tafel slope at more negative potentials (< 0.9 V) is -0.122 V dec.$^{-1}$ while at more positive potentials at 100° C the slope is numerically less but without any extended linear Tafel range. Prior studies of platinum in acid electrolytes, including the present study, have found Tafel slopes of -0.12 to -0.15 V dec^{-1} at higher polarization (< 0.7 V vs RHE at ambient temperature) with the value dependent on the direction of the potential sweep and the potential to which the platinum was exposed immediately before the polarization measurements. The lower slopes at more positive potential have also been observed by various workers in aqueous H_2SO_4 at 25° C [6, 10]. The lower slope region corresponds to that where anodic film formation begins and hence this lower Tafel slope is
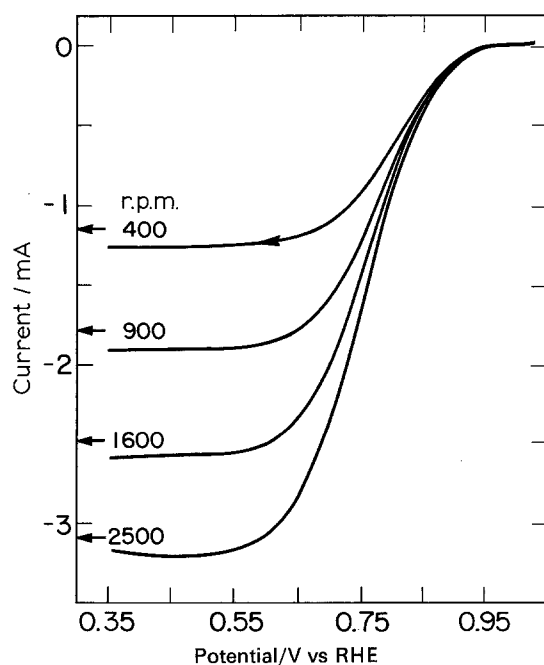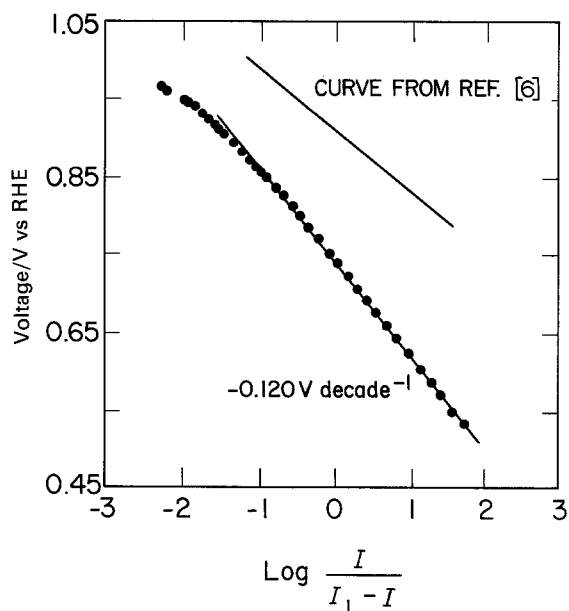

Fig. 8. Tafel plot for oxygen reduction on a platinum disc in purified 85.5% H_3PO_4 at 101° C. Oxygen pressure 1.76 MPa. Rotation rate: 1600 r.p.m.

probably the result of simultaneous changes in the nature of the electrode surface with potential, together with changes in the symmetry of the potential energy barrier for the rate controlling step.

The Tafel slope of -0.122 V dec^{-1} at higher overpotentials at ambient temperature (22° C) suggests that the first electron transfer is rate controlling but such reasoning is now open to question due to the unexpected temperature independence for the Tafel slope as discussed later. A Tafel slope of -0.148 V dec^{-1} is expected at 100° C from Equation 1 using the traditional kinetic implications associated with an α value of 0.5. The temperature dependence of the Tafel slope was further examined in the range 25 to 250° C. The polarization curves for oxygen reduction in 100.3% H_3PO_4 at 206° C are shown in Fig. 9 and the Tafel plot extracted from these data in Fig. 10. The Tafel slope calculated from the plot is -0.125 V dec^{-1} in the anodic film free potential region, shifting to a lower value at potentials positive to 0.9 V. A Tafel slope of -190 mV^{-1} at 206° C is expected from Equation 1 with an α value of 0.5. The potential was restricted to values positive to 0.5 V at all times so as not to adsorb impurities onto the surface as demonstrated by the cyclic voltammetry curves in Figs 5 and 6. This procedure was successful but did not permit direct measurements of the diffusion limited current density in the potential region negative to 0.5 V where the currents are expected to approach a diffusion limiting value. When the rotating disk electrode potential was extended to 0.3 V, there was a large hysteresis between the cathodic and anodic sweeps at a sweep rate of 5 mV s^{-1} with the anodic sweep exhibiting quite low current densities for the reduction of oxygen. The currents at higher rotation rates are possibly still under partial kinetic control at 0.5 V. Koutecky–Levich plots of $1/i$ against $\omega^{-1/2}$ from the

Fig. 7. Polarization curve for oxygen reduction on platinum in purified 85.5% H_3PO_4 at 100° C. Rotating electrode area: 0.196 cm². Rotation rates are indicated in r.p.m. Scan rate (negative direction): 5 mV s^{-1}. Oxygen pressure: 1.76 MPa. Arrows indicate diffusion limited current densities obtained using the Levich–Koutecky plot.
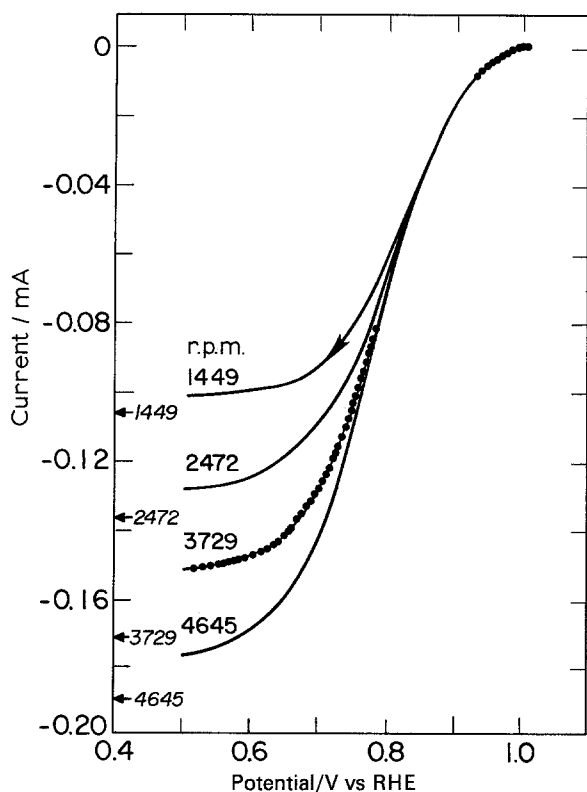
Fig. 9. Oxygen reduction polarization curves on a platinum disc $(0.196\,cm^2$ in purified 100.3% H_3PO_4 at 206°C and 101 kPa (1 atm) pressure. Rotation rates are indicated in r.p.m. Scan rate (negative): $5\,mV\,s^{-1}$. Sweep in opposite direct indicated by the dots on the 3 729 r.p.m. curve. Reference electrode is a reversible hydrogen electrode in the same solution. Arrows indicate limiting currents extracted from Koutecky–Levich plots.
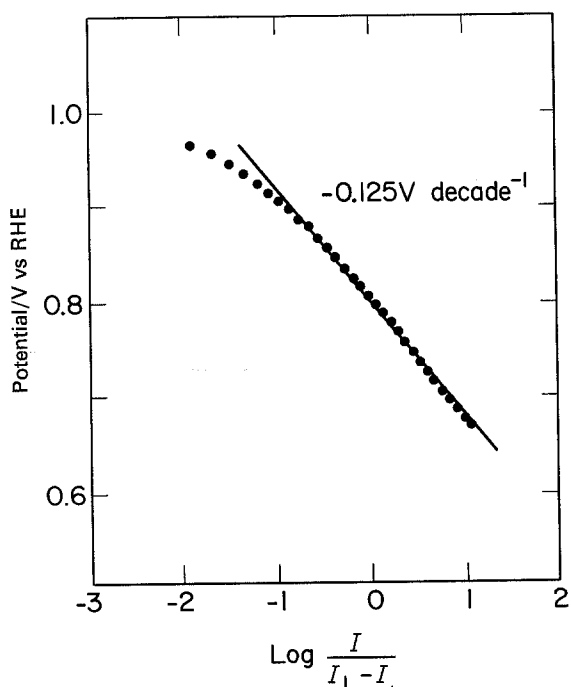

Fig. 10. Tafel plot obtained for oxygen reduction on a platinum disc electrode $(0.196\,cm^2)$ in purified 100.3% H_3PO_4 at 206°C and 101 kPa (1 atm) oxygen pressure. Scan rate (positive): $5\,mV\,s^{-1}$. The rotation rate: 3 729 r.p.m. The reference electrode is a reversible hydrogen electrode in the same solution. Tafel slope is $-125\,mV\,dec.^{-1}$.
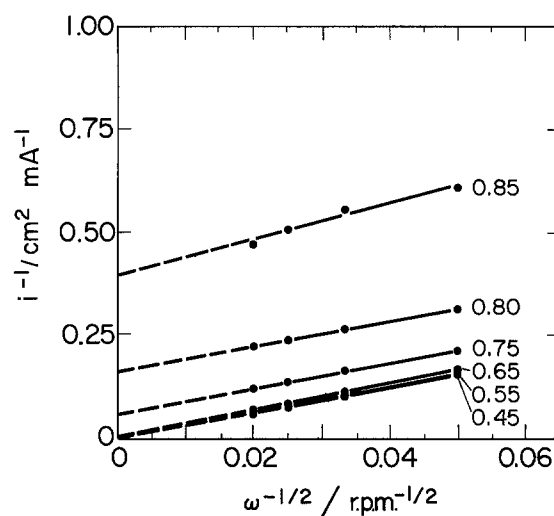

Fig. 11. Koutecky–Levich plot from rotating disc data for oxygen reduction on platinum in purified 85.5% H_3PO_4 at 101°C. Based on data in Fig. 7. Scan rate: $5\,mV\,s^{-1}$. Oxygen pressure is 1.76 MPa. The B value at potentials $< 0.8\,V$ is $0.318\,mA\,cm^{-2}\,(r.p.m.)^{-1/2}$.

data in Figs 7 and 9 were constructed to calculate the diffusion limited current density at each r.p.m., see Fig. 11. The slopes are parallel to one another as is to be expected when the back reaction is negligible. The calculated values are indicated by the horizontal arrows in Figs 7 and 9 and indicate that diffusion limited current densities were not directly measured at the most cathodic potential. Possibly the n value, assumed to be constant in the Koutecky–Levich plots, depends on potential mechanistically. The i_L values from the Koutecky–Levich plots were used to construct the Tafel plots in this study.

A compilation of the Tafel slopes observed as a function of temperature and phosphoric acid concentration is given in Table 1. Various electrode pretreatments were tested and their effects on the resulting Tafel slopes indicated in Table 1. All electrodes were stored in distilled water between uses. At elevated temperatures no electrode pretreatment was necessary in a particular solution if the electrode had previously been cycled about thirty times from 0.05 to 1.3 V at room temperature in a separate solution of purified H_3PO_4. At 100°C and above, the electrode was removed from the room temperature solution after cycling and inserted into the solution in the cell. The voltage was then swept at $5\,mV\,s^{-1}$ from 1.0 to 0.5 V with stirring. This procedure resulted in almost no hysteresis between the anodic and cathodic sweeps. The dots on the curve at 3 729 r.p.m. in Fig. 10 are the anodic sweep curve and fall quite precisely upon the cathodic sweep curve.

The polarization measurements at 25°C in 85% and higher H_3PO_4 concentrations presented a serious problem because of the time dependence of the measurements and the large effect of prior potential treatments. The electrode pretreatment effects were manifested during conventional slow sweep measurements $(5\,mV\,s^{-1})$. The current density observed at a

Table 1. *Measured Tafel slopes and apparent transfer coefficients, and the theoretical Tafel slopes using Equation 1 based on $\alpha = 0.5$ with the first electron transfer rate controlling*

Temperature/° C	$[H_3PO_4]$/wt %	Oxygen pressure/MPa	Tafel slopes/mV $(dec.^{-1})$		α value
			Observed	Theoretical	observed
25	85	1.86	$-117^\dagger$, $-149*$	118	0.50, 0.40
25	96.6	1.81	$-144*$	118	0.41
25	105.4	1.51	$-150*$	118	0.40
100	92	0.101	$-117^\ddagger$	148	0.63
101	85.5	1.77	$-122^\ddagger$	149	0.61
104	103	0.101	$-121^\ddagger$	150	0.62
150	92	0.101	$-127^\ddagger$	168	0.66
206	103	0.101	$-126^\ddagger$	190	0.75
207	100.3	0.101	$-125^\ddagger$	191	0.76
251	106.7	0.101	$-128^\ddagger$	208	0.81

* Potential held at 0.05 V for 5 s; potential then stepped to 1.0 V and held at this value for 5 s followed by recording the cathodic sweep at $5\,mV\,s^{-1}$.

† Anodic sweep recorded at $5\,mV\,s^{-1}$ starting at 0.05 V

‡ No pretreatment.

particular potential depended upon the potential sweep direction and sweep rate and prior exposure of the electrode to potentials outside the 0.3 to 1.0 V potential range normally used for the oxygen reduction measurements. These effects may result from adsorption–desorption of impurities or from restructuring of the platinum surface, or from the slowness of reduction of the anodic film formed at more anodic potentials. The explanation that the hysteresis is due to residual impurities after the purification procedures is contradicted by the results at temperatures above 100° C. At these temperatures cycling to more anodic potentials was unnecessary and little hysteresis is observed between positive and negative sweeps whereas the same solution at room temperature exhibits a significant hysteresis. It is possible the platinum electrode surface becomes restructured during potential cycling. This restructuring could produce a facetted surface [11] which may have a different activity for oxygen reduction. A possible explanation for this lack of a time dependent effect and the small hysteresis at elevated temperatures, in light of the preceding discussion concerning room temperature phenomena, is that steady state is reached more rapidly between impurities adsorbed on the electrode and in the solution. Further, the surface structure of the platinum may reach an equilibrium state in much shorter times at elevated temperatures and consequently the residual anodic film is more readily reduced in the range of potentials where oxygen reduction was measured.

3.2.1. Effect of temperature on the Tafel slope for oxygen reduction. The Tafel slope *b* is essentially independent of temperature over the 25 to 250° C range as indicated in Table 1. The phosphoric acid concentration has not been held constant over this temperature range. There are, however, several groups of data at constant composition in Table 1, albeit some with only two points. Changes in the composition do not appear to produce a substantial change in the Tafel slope. At a temperature near

100° C phosphoric acid concentrations from 85.5 to 103% all yield a Tafel slope of approximately $-0.12\,V\,dec^{-1}$. Likewise near 205° C a Tafel slope of $-0.125\,V\,dec^{-1}$ is obtained. Although the conditions in Table 1 differ widely, the Tafel slope is essentially constant. This constancy of the Tafel slope as a function of temperature is wholly unexpected from present theories of electrochemistry. The difference between the measured Tafel slope and that expected from theory (Table 1) is not small and is well outside the experimental error.

Scharifker, Zelenay and Bockris [6] have proposed that the temperature independence of the Tafel slope for oxygen reduction at platinum in concentrated phosphoric acid is due to impurities. Although impurities certainly can affect Tafel slopes, it takes a remarkable coincidence for an impurity to produce an effect which yields an α value which is approximately proportional to temperature and equal to 0.5 at 25° C. We do not believe that the anomalous temperature independence of the Tafel slope in the present work is due to an impurity effect, but acknowledge that such may be possible.

The Tafel slopes in the present study have all been evaluated at the higher overpotentials where cyclic voltammetry curves indicate the electrode surface to be essentially anodic film free. Care was taken in the present work not to allow an anodic film of PtOH to form on the electrode surface by excursions of potential into the anodic film formation region prior to the oxygen reduction polarization measurements. The Tafel plots were linear over at least one order of magnitude of current in the potential region shown to be anodic film free by the voltammetry curves. This was generally not the case in the work reported in [6]. The Tafel slopes were evaluated by Scharifker *et al.* [6] in the potential range 0.8 to 1.0 V and thus included the effects of the start of anodic film formation. The Tafel slopes reported in the present paper were evaluated in the potential region 0.5 to 0.85 which is essentially free of the anodic film.
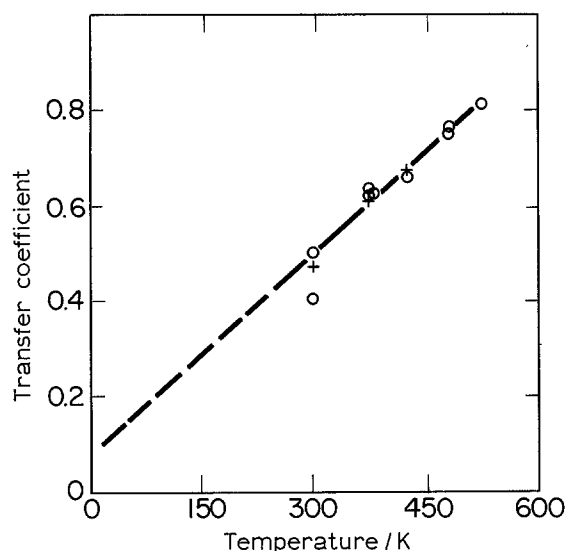
Fig. 12. Plot of values for the apparent transfer coefficient versus temperature for oxygen reduction in H_3PO_4 obtained in this work (○) and those from reference 12 (+). Note that at 298 K the lower point was obtained after procedure a in Table 1, whereas the circular point on the line was obtained after procedure b in Table 1.

3.2.2. Effect of temperature on the transfer coefficient for oxygen reduction.

The apparent transfer coefficients in the present work have been calculated from the Tafel slope with Equation 1 and are plotted in Fig. 12. The data of Huang et al. [12] is included in this plot for comparison and shows quite good agreement with the data from the present work. Over the temperature range investigated α is directly proportional to the absolute temperature rather than being a constant. In itself this is quite surprising since most kinetic treatments relate the transfer coefficient to a symmetry factor β, to which it is directly equal if the first electron transfer step is rate controlling. On the basis of α apparently being equal to 0.5 and the expectation of a symmetry factor of 0.5, various workers have proposed such a first electron transfer to be rate controlling for oxygen reduction. This is now in doubt. The temperature dependence of the transfer coefficient can also lead to complications in calculating the heat of activation for electrode processes as discussed by Bockris and Kahn [13].

The Tafel slope is related to the standard free energy of activation $(\Delta G^{\ddagger})^{\circ}$ by the equation [2]:

$$\frac{1}{b} = \left[\frac{\partial \ln i}{\delta E}\right]_T = -\left[\frac{\delta(\overrightarrow{\Delta G^{\ddagger}})^{\circ}/RT}{\delta E}\right]_T$$

$$= -\frac{\delta}{\delta E}\left[\frac{(\overrightarrow{\Delta H^{\ddagger}})^{\circ} - T(\overrightarrow{\Delta S^{\ddagger}})^{\circ} + \beta FE}{RT}\right]_T \quad (3)$$

where $(\overrightarrow{\Delta H^{\ddagger}})^{\circ}$ and $(\overrightarrow{\Delta S^{\ddagger}})^{\circ}$ are the standard enthalpy and entropy of activation. This equation reduces to

$$\left[\frac{\delta \ln i}{\delta E}\right]_T = -(a + cT)\frac{F}{RT} \quad (4)$$

where

$$a = \frac{\delta}{\delta E}\left[\frac{(\overrightarrow{\Delta H^{\ddagger}})^{\circ} + \beta FE}{RT}\right]_T \quad (5)$$

$$c = -\left[\frac{\delta(\overrightarrow{\Delta S^{\ddagger}})^{\circ}/F}{\delta E}\right]_T \quad (6)$$

or

$$\alpha = a + cT \quad (7)$$

From the data over the 225° C temperature range, $a = 0.08$ and $c = 0.0014\,K^{-1}$. Therefore, at room temperature and above,

$$\alpha \approx cT \quad (8)$$

Thus most of the potential dependence of the rate appears to be associated with the potential dependence of the entropy of activation rather than the simple change of the height of the potential energy barrier [4, 14].

Conway has discussed the various factors that can contribute to the temperature dependence of the transfer coefficient. These include [3]:

(i) tunnelling in reaction coordinate space;

(ii) potential dependent surface adsorption of the reactants;

(iii) dependence of the structure of the compact double layer (particularly solvent structure and thickness) on temperature and potential;

(iv) changes in the activity coefficient for the activated state with potential as a result of adsorption–desorption of various charged species such as anions of the supporting electrolyte [15];

(v) changes in the symmetry of the potential energy barrier with potential and temperature;

(vi) penetration of the electric field at the electrochemical interface into the electrode phase;

(vii) a shift in the rate determining step over a range of potentials and temperatures;

(viii) impurity effects.

Although these factors can result in a temperature dependent α, they do not necessarily result in a direct proportion. Tunnelling in reaction coordinate space seems unlikely, particular for the oxygen reduction reaction taking into account the masses of the reacting species and intermediates. Tunnelling might be a possibility if the rate determining step in oxygen reduction is a proton transfer step, protons being the only nuclei involved in the reaction light enough to tunnel significant distance. Examination of the oxygen reduction kinetics on platinum in deuterated phosphoric acid by Ghoneim et al. [16] did not find a kinetic isotope effect and thus proton tunnelling, if it is involved, must not occur until after the rate determining step in the oxygen reduction.

The other factors above are more likely. Even so, none of these factors appear capable of explaining

the temperature dependence of α for the oxygen reduction on platinum. For example, a shift in the rate determining step with temperature can produce changes in α. These changes usually result in non-linear Tafel plots.

Currently uncertainty exists as to the mechanism for the four-electron oxygen reduction on platinum. In the opinion of the authors, the most likely explanation is that oxygen reduction proceeds through the dissociative adsorption of the oxygen molecule on the platinum surface. This probably occurs with simultaneous electron transfer using the traditional analysis via Equation 1 and the observed Tafel slope of $-0.12\,\mathrm{V\,dec.}^{-1}$ at 25° C. Evidence in favour of the dissociative adsorption as rate controlling also includes the lack of a significant hydrogen–deuterium kinetic isotope effect and the marked suppression of the four-electron pathway by the other adsorbed species such as chloride in acid electrolytes.

The temperature dependence of the transfer coefficient is not unique to the oxygen reduction reaction as pointed out by Conway [1–3, 14]. In fact, it is questionable whether the Tafel slope has the expected proportionality to T for most electrode processes involving adsorbed species.

4. Conclusions

The most significant feature of these experiments on oxygen reduction on platinum in acid solutions has been the finding that the apparent transfer coefficient has an almost direct proportionality to temperature. It is of fundamental importance to electrochemistry that this dependence be explained.

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