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Oxygen Evolution at Platinum Electrodes in Alkaline Solutions

I. Dependence on Solution pH and Oxide Film Thickness

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ABSTRACT

The oxygen evolution reaction (OER) at platinum electrodes in alkaline solutions of various pH's is reexamined. The existence of two linear E -log i regions is confirmed, each having a different dependence on Pt oxide film thickness and the OH^- concentration. At low current densities (c.d.) $dE/d \log i = 60$ mV/decade, and, at high c.d., it is 120 mV/decade. While the rate of the OER is independent of the oxide film thickness at the electrodes at low c.d., it is strongly dependent on the film thickness at high c.d., as shown by the large decrease of the rates at a given potential with increasing film thickness. At low c.d., the reaction order with respect to OH^- is two, while, at high c.d., the order is 3/2. The fractional reaction order at high c.d., is unusual and cannot be accounted for by any standard mechanism proposed in the literature for the OER. These results show that the mechanism of the OER at platinum in alkaline solutions is complex and still not thoroughly understood.

It was reported previously (1, 2) and was recently confirmed (3) that the pH dependence of the oxygen evolution reaction (OER) at Pt electrodes in aqueous acid solutions is "anomalous," as it involves an apparent fractional reaction order of $-1/2$ with respect to H_3O^+ ions. This is seen in the change of the potential of the Pt electrode vs. a pH-independent reference electrode of -60 mV/pH unit, even though the Tafel slope is 120 mV/decade. It was also reported (2-5) that the rate of the OER in acid solutions depends on the thickness of the electronically insulating Pt oxide film that forms at the Pt electrode by the high field ionic migration of ions (5-10). The thickness of the film depends on the length of time the electrode is held at potentials above about 1.2V vs. RHE, or on the length of time that it is subjected to a constant anodic current density (c.d.) (2-5, 7, 11). It should be noted that the thickness of the Pt oxide film has not been determined in this work by any *in situ* or *ex situ* methods, but rather it is estimated from the charge passed during preanodization and from the subsequent application of the data treatment of the Mott-Cabrera model of film growth, which Pt oxide films appear to follow closely. It has also been demonstrated (2, 3, 10) that the

observed pH dependence in acid solutions— $\delta E/\delta \text{pH}$ equal to -60 mV/pH unit—is not an experimental artifact arising from different thicknesses of the surface films that may grow in solutions of different pH's. In fact, this anomalous pH dependence was consistently observed only when it had been ensured that the Pt oxide film thickness was the same in solutions of different pH.

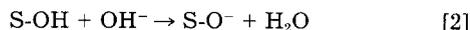
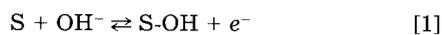
The fractional reaction order with respect to H_3O^+ , observed in acid solutions, cannot be understood in terms of a simple model of the electrode/solution interface, or in terms of any mechanism of the reaction based on such a model. To account for this reaction order, a model of a multiple barrier consisting of the barriers of the oxide film and the inner and the outer Helmholtz layers (IHL, OHL) was invoked (2-4, 10). According to this model, the first electron transfer step across the oxide film and the IHL is the slow and rate-determining process. The process of charge transfer across the OHL is fast and is not rate determining (3, 4, 10). In the proposed model, water molecules are the reactants in the rate-determining step (rds), producing protons, which are then transferred rapidly across the OHL, *i.e.*, there is a quasi equilibrium between the protons in the IHP and those in the bulk of the solution. Therefore, the potential difference across the

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oxide film and the IHL for a given rate of reaction must be independent of the pH of acid solutions (10), while the potential drop across the OHL is independent of pH. The observed pH dependence is then associated with the equilibrium process across the OHL. It should be noted here that the lack of dependence of the potential drop across the oxide film of pH indicates that the film conductivity is not changing with pH and, hence, is evidence for the unchanging nature of the film as a function of pH.

In alkaline solutions, there are still some ambiguities concerning not only the mechanism of the reaction but the kinetic data for the OER as well. Hoar (12) reported a linear E -log i relationship with a Tafel slope of 60 mV/decade of c.d. Other workers reported E -log i relationships with a slope close to 120 mV/decade (13). Two linear E -log i relationships—one in the low c.d. regions with $\delta E/\delta \log i = 60$ mV/decade, the other in the high c.d. region with $\delta E/\delta \log i = 120$ mV/decade—have also been reported (14, 15). According to Iwakura and co-workers (15), in both the high and low c.d. regions $\delta E/\delta \text{pH}$ is close to -120 mV/pH unit, while, according to Dey and co-workers (14), at least in the very narrow pH region of 12-13, $\delta E/\delta \text{pH}$ is -120 mV/pH unit in the low c.d. region but is probably -180 mV/pH unit in the high c.d. region. This -180 mV pH dependence is equivalent to a fractional reaction order of 3/2 with respect to the OH^- ion for the OER in the high c.d. region in alkaline solutions.

A Tafel slope of 60 mV/decade and a pH dependence of -120 mV/pH unit in the low c.d. regions, as reported by Iwakura and co-workers, can formally be accounted for by the classical Krasilshchikov alkaline path (16), in which a chemical step, following a rapid electron-transfer step, is rate determining, e.g.



where S stands for a surface site. At high c.d., the first electron-transfer step in this reaction path would be rate determining and the pH dependence could be expected to be -120 mV/pH unit. However, if the pH dependence at high c.d. is -180 mV/pH unit, as reported by Dey *et al.* (14), then the mechanism given in [1] and [2] cannot be valid. Moreover, none of the reaction paths and the rds suggested in the literature [e.g., Ref. (17)] is successful in explaining the kinetic data if the pH dependence at high c.d. is indeed -180 mV/pH.

It should be noted that, in early work, little or no attention was paid to the presence of Pt oxide surface films, and, hence, it is possible that the above difficulties regarding the reaction order and the reaction mechanism might be an artifact caused by differing oxide film thicknesses in experiments performed in solutions of different pH's (18). It should also be noted that there is no guarantee that the thickness of the anodic Pt oxide film grown in alkaline solutions of different pH's is the same as when formed in acid solutions (3, 10), even when using the same electrode pretreatment consisting of the prepolarization of the electrode for a given length of time at a constant c.d., i_p , or at a constant potential, E_p . However, the applicability of the Mott-Cabrera growth law over the pH range of 11-14 (18) and over five decades of applied c.d. implies that λ , W , and V_o —and hence the entire potential distribution—remain essentially unchanged, despite large changes in solution pH and the film thickness. This is good evidence for the formation of oxide films of uniform structure and composition in alkaline solutions.

Therefore, the object of this paper is to determine and discuss the pH dependence of the OER at Pt electrodes in alkaline solutions in relation to the thickness of the underlying Pt oxide film. Also, we shall attempt to compare the pH dependence of this reaction in alkaline solutions with that observed in acid solutions.

Experimental

A Pt disk electrode (surface area = 0.46 cm^2) was used in an electrochemical cell that has been described previously (3, 10). A SCE in a separate compartment served as

the reference electrode. Solutions were prepared from analytical grade chemicals and conductivity water. For each measurement of the steady-state E -log i relationship, the Pt electrode was first polarized at a potential close to that of the hydrogen evolution reaction, so that any oxide film present at the electrode surface would be reduced. Then, the electrode was allowed to reach its rest potential in oxygen-saturated solutions (1-2 min) before a constant anodic current, i_p , was applied to it for a specified length of time, t_p , ranging from 60 to 3000s. After this pretreatment, the E -log i relationship was determined at $i < i_p$. This procedure ensures that the E -log i relationships are being determined at a constant thickness of the Pt oxide film (2, 10). Occasionally, after an E -log i relationship had been determined at $i < i_p$, the measurements were extended to $i > i_p$ by stepping the applied current from $i < i_p$ to $i > i_p$ for a length of time that was sufficient for reading the electrode potential. During this short excursion to higher c.d. and, hence, higher potentials, the thickness of the oxide film does not increase significantly enough to affect the kinetics of the OER, particularly when $t_p > 500$ s.

In another series of experiments, a wire electrode of about 0.5 cm^2 area was used in a cell that allowed the rapid exchange of solution in the test and the reference electrode compartments, without interrupting the current flow. E -log i relationships were obtained before and after the solutions were exchanged, so that the relationship between potential and solution pH at a constant c.d. and constant thickness of the oxide film could be unambiguously determined.

Results

E-log i relationship of the OER in alkaline solutions.—In Fig. 1 and 2, E -log i relationships are shown for the OER for $i_p = 10^{-4} \text{ A}$ and after various t_p in a solution of $\text{pH} = 13.7$, without the addition of a K_2SO_4 supporting electrolyte, and in a solution of $\text{pH} = 12.9$, with the addition of K_2SO_4 , respectively. In both cases, two linear E -log i relationships are observed. At low c.d. $\delta E/\delta \log i = 60$ mV/decade, while at high c.d. it is close to 120 mV/decade, as had been observed previously (14, 15).

It should be noted in Fig. 1 and 2 that in the high c.d. region, where the Tafel slope is 120 mV/decade, the potentials at any given c.d. are higher after a long t_p than after a short t_p . This increase of the electrode potential with t_p at high c.d., reported here for the first time for alkaline solutions, is attributed to the presence of a Pt oxide film on the electrode surface, which increases in thickness with the time of anodic pretreatment. It is important to note that different electrode pretreatments and, hence, the presence of oxide films with different thicknesses influence the kinetics of the OER only in the high c.d. region. In the low c.d. region, the E/i relation-

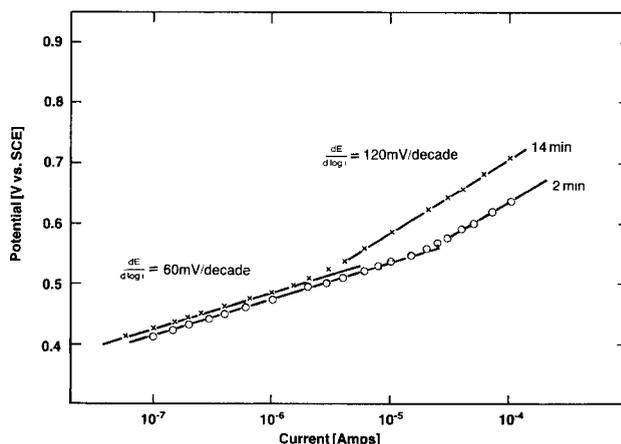


Fig. 1. E -log i relationships in $\text{pH} 13.7$ KOH solution with no supporting electrolyte. Times of prepolarization at $i_p = 10^{-4} \text{ A}$ are given in the figure. Electrode area ($\sim 0.46 \text{ cm}^2$) is not corrected for surface roughness ($\text{RF} \approx 1.5$).

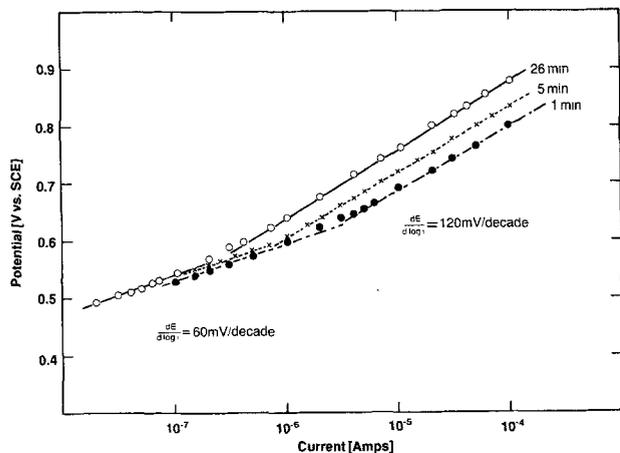


Fig. 2. The same as in Fig. 1, but pH = 12.9, and K₂SO₄ supporting electrolyte is now present.

ship is independent of the electrode pretreatment and the oxide film thickness.

E-pH relationship of the OER in alkaline solutions.—In Fig. 3, *E-log i* relationships for $i_p = 10^{-4}$ A and $t_p = 300$ s are shown in KOH solutions of pH = 12.2 and 13.1, both without any supporting electrolyte. Similarly, in Fig. 4, *E-log i* data that were obtained in KOH solutions of pH = 12.8 and 13.6 in excess K₂SO₄ are shown. In Fig. 4, i_p is 10^{-4} A and t_p is 26 min. It is clear from these figures that a very strong pH dependence is present in alkaline solutions in both c.d. regions. No effect of the diffuse double layer is evident in these experiments.

In Fig. 5, the potentials from Fig. 3 at 10^{-4} A and $t_p = 300$ s, where the Tafel slope is 120 mV/decade, are plotted against the solution pH along with data obtained in numerous other experiments, but at the same c.d. and t_p . $\delta E/\delta \text{pH}$ is seen to be -180 mV, which agrees with the data of Dey and co-workers (14). This is an unusually high and “anomalous” pH dependence, in that it leads once again to a fractional reaction order of 3/2 with respect to the OH⁻ ion.

In Fig. 6, the potentials obtained from Fig. 3 at the lower c.d. of 10^{-5} A, where $\delta E/\delta \log i = 60$ mV/decade, or the potentials obtained by extrapolating the plot from the low c.d. region to 10^{-5} A, are plotted against the solution pH. All other available data obtained at 10^{-5} A in solutions of different pH's are also included in the figure. In this low c.d. region, $\delta E/\delta \text{pH} = -120$ mV, which can be considered as “usual,” and leads to a reaction order of two with respect to the OH⁻ ion. The same $\delta E/\delta \text{pH}$ dependence is obtained when the experiments are carried out with varying i_p and t_p .

To confirm the pH dependence obtained from these steady-state *E-log i* experiments, the *E-log i* relationships were also determined in solution exchange experi-

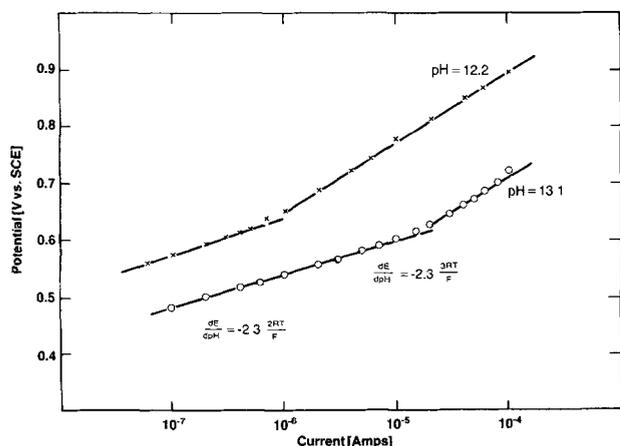


Fig. 3. *E-log i* relationships at pH of 12.2 and 13.1. $i_p = 10^{-4}$ A, $t_p = 300$ s.

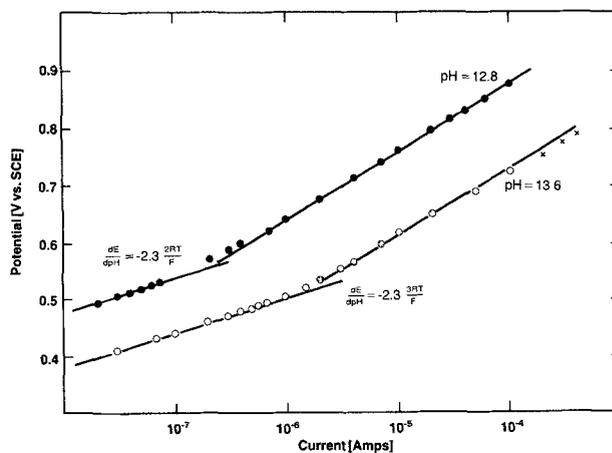


Fig. 4. *E-log i* relationships in pH 13.6 and 12.8 solutions with excess K₂SO₄. $i_p = 10^{-4}$ A, $t_p = 26$ min. x: Points determined at the end of the experiment by jumping the current from $i < i_p$ to $i > i_p$.

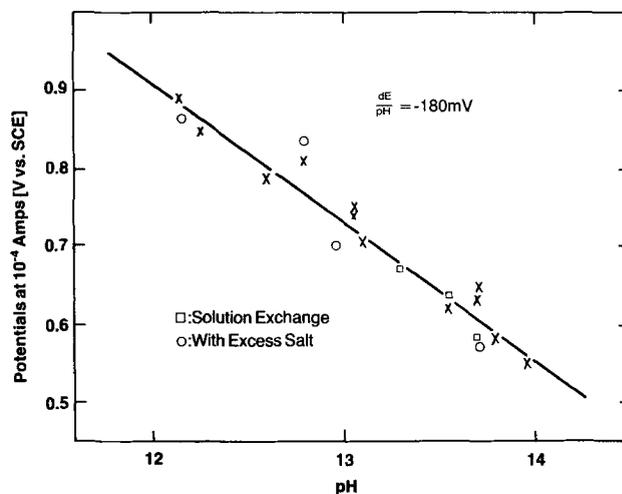


Fig. 5. Potentials at 10^{-4} A (the high current-density region) in solutions of different pH's. x: No excess salt. Data from the solution exchange experiments (see Fig. 7) are also included. $t_p = 300$ s, $i_p = 10^{-4}$ A.

ments. Here, an *E-log i* relationship was initially determined in a solution of low pH for a given i_p and t_p , and then the solution was rapidly exchanged in less than 1 min with a solution of a higher pH, without interrupting the current flow, and then a second set of *E-log i* measurements was made (Fig. 7). The electrode was then again reduced, anodically pretreated with the same i_p and t_p as in the low pH solution, and the *E-log i* relationship was redetermined in the high pH solution. The results of this last measurement are also shown in Fig. 7.

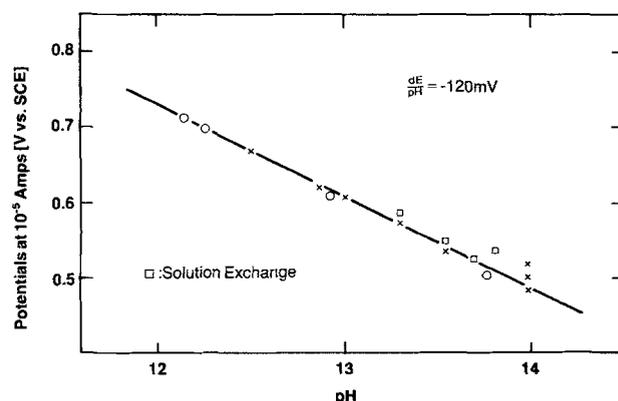


Fig. 6. Potentials at 10^{-5} A (the low current-density region) in solutions of different pH's. Symbols have the same significance as in Fig. 5. $t_p = 300$ s, $i_p = 10^{-4}$ A.

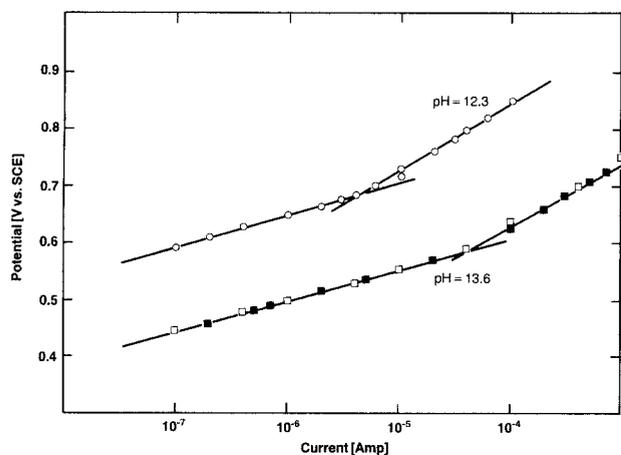


Fig. 7. E -log i relationships in solution exchange experiments. Circles: pH = 12.3. Open squares: Measurements after the solution exchange without current interruption. Filled squares: Electrode reduced, anodically pretreated, and measurement taken in the exchanged solution. Data at $i > i_p$ are taken by jumping the current from $i < i_p$ to $i > i_p$ for a short time (a few seconds). $i_p = 10^{-4}$ A, $t_p = 300$ s.

The close match between the latter data with the data obtained in the high pH solution immediately after the solution exchange validates the unusually high pH dependence observed in both c.d. regions. The results of these experiments show that the fractional reaction order in the high c.d. region cannot be due to variations in the thickness of the underlying Pt oxide films grown in solutions of differing pH. They also show that, for a given i_p and t_p , the thickness of the oxide film is the same in solutions of different pH and that the thickness does not change as the solutions are exchanged. Potentials observed in these solutions exchange experiments at 10^{-4} and 10^{-5} A are plotted also in Fig. 5 and 6, respectively.

It should be noted here that in acid solutions, the Tafel slope for the OER at Pt electrodes is equal to 120 mV/decade and $\delta E/\delta \text{pH}$ is equal to -60 mV/pH unit over the entire range of c.d. (2, 3). These results in acid solutions also imply a fractional reaction order with respect to the H_3O^+ ion, but of $-1/2$, rather than of $3/2$, as for OH^- at high c.d. in alkaline solutions.

Analysis of the Results and Discussion

The present results confirm that there are indeed two linear E -log i regions for the OER at Pt electrodes in alkaline solutions. At low c.d., the Tafel slope is close to 60 mV/decade, while, at high c.d., the slope is close to 120 mV/decade. Also, these two Tafel regions have different pH dependences, with a $\delta E/\delta \text{pH}$ of -120 mV/pH unit at low c.d. and -180 mV/pH unit at high c.d. All of these data have been obtained over a relatively wide range of solution pH and with carefully controlled, although not accurately known, thicknesses of the underlying Pt oxide films.

The kinetics of the OER in the high c.d. region.—The kinetics in the high c.d. region are discussed first because of their similarity to the kinetics of the OER observed in acid solutions (2, 3, 10). In alkaline solutions, the high c.d. data lead to the following rate equation

$$i_{b,h} = k_h[\text{OH}^-]^{3/2} \exp\left[\frac{FE}{2RT}\right] \quad [3]$$

where the subscript "b" refers to alkaline (basic) solutions, "h" to the high c.d. region, k_h is the pre-exponential factor, and E is the potential of the Pt electrode with respect to the pH-independent SCE. The pre-exponential factor is considered to be independent of the solution pH. It does, however, depend on the choice of the pH-independent reference electrode, but this dependence does not affect the analysis of the data presented here. In addition, k_h has been found to decrease as t_p increases at a constant i_p , or as i_p increases at a constant t_p . This type of dependence on electrode

pretreatment was also observed in acid solutions (2, 3) and was attributed there to the effect of varying oxide film thickness with electrode pretreatment (time of preanodization). Hence, it is anticipated that k_h in alkaline solutions contains a parameter that depends on the thickness of the Pt oxide film.

Experiments carried out previously in acid solutions (2, 3, 5, 10) had been directed primarily towards determining the influence of the oxide film thickness on the OER kinetics, particularly in the case when the OER was the dominant reaction. By using a rotating ring-disk electrode to separate the current at a Pt disk into that due to the OER and that due to oxide film growth, it was established that the rate of the OER at any constant potential decreases exponentially with increasing thickness of the oxide film. Further, it was shown that the reaction order with respect to the H_3O^+ is $-1/2$. Thus, the following rate equation describes the kinetics of the OER in acid solutions

$$i = A[\text{H}_3\text{O}^+]^{-1/2} \exp\left[\frac{-mFq}{2RT}\right] \exp\left[\frac{FE}{2RT}\right] \quad [4]$$

Here, q is the charge density determined from these ring-disk experiments and is equivalent to the thickness of the oxide film, m is a constant that can be experimentally determined, and A contains the frequency factor, an exponential term with the reaction activation energy, and a term that depends on the choice of the pH-independent reference electrode.

Therefore, these ring-disk electrode experiments showed clearly that, in acid solutions, the OER depends on both the Pt oxide film thickness and on the solution pH, the latter dependence being fractional (Eq. [4]).

In the case of the OER at Pt in alkaline solutions, direct experimental evidence is not yet available to show whether the rate of the OER at high c.d. also depends exponentially on the thickness of the oxide film, as it does in acid solutions. However, in view of the fact that, in alkaline solutions, an insulating oxide film is known to grow by the same mechanism as it does in acid solutions (18), and because the oxide film continues to grow, as in acid solutions, even after the OER becomes the predominant reaction at long t_p and high potentials, as seen by the effect of electrode pretreatment, it seems justifiable to assume that the observed dependence of the rate of the OER on electrode pretreatment is also caused by its exponential dependence on the thickness of the oxide film in exactly the same way as was experimentally observed in acid solutions, *i.e.*

$$k_h = B \exp\left[\frac{-mFq}{2RT}\right] \quad [5]$$

Equation [3] can then be rewritten as

$$i_{b,h} = B[\text{OH}^-]^{3/2} \exp\left[\frac{-mFq}{2RT}\right] \exp\left[\frac{FE}{2RT}\right] \quad [6]$$

where the parameter " m " in Eq. [6] in alkaline solutions, a factor that converts q to film thickness, is not necessarily numerically equal to " m " in Eq. [4] in acid solutions, but has the same physical significance in both cases [*c.f.*, Ref. (3 and 10)].

The kinetics of the OER in alkaline solutions in the low c.d. region.—The kinetics for the OER in the low c.d. region lead to the following rate equation for the OER

$$i_{b,l} = k_l[\text{OH}^-]^2 \exp\left[\frac{FE}{RT}\right] \quad [7]$$

where the subscript "l" indicates the low c.d. region. Now, $\delta E/\delta \log i = 60$ mV/decade and $\delta E/\delta \text{pH} = -120$ mV/pH unit. The pre-exponential factor, k_l , is independent of the solution pH, as was k_h at higher c.d. In contrast to the observations at high c.d., k_l has been shown to be independent of the electrode pretreatment conditions, and, hence, is independent of the thickness of the anodic oxide film.

Summary

Overall, this study of the kinetics of the OER at Pt electrodes in alkaline solutions has yielded some important and new observations. First, it has confirmed the existence of two Tafel regions. At low c.d., $\delta E/\delta \log i$ is 60 mV/decade, while at high c.d. the Tafel slope is 120 mV/decade. A second, and perhaps the most significant result has been that, at low c.d., the rate shows no dependence on the thickness of the underlying Pt oxide film, while, at high c.d., the rate depends on the oxide film thickness. This varying dependence on oxide film thickness is vital to the elucidation of the mechanism of the OER in alkaline solutions. The fact that the reaction rate at low c.d. is independent of oxide film thickness but is dependent on film thickness at high c.d. cannot be readily explained. This observation would imply that one step in the reaction path depends on oxide film thickness and that, as the c.d. changes, another step in the same reaction path is independent of film thickness. As far as we are aware, no behavior similar to this has been reported either for this or any other electrochemical reaction.

A third important result obtained from this work is that, at high c.d., the reaction order with respect to OH^- is fractional, being equal to 3/2. None of the standard mechanisms proposed in the literature can account for such a fractional reaction order. This once again shows that the mechanism of the OER at Pt electrodes is still not understood in spite of the widely held view to the contrary.

Therefore, any mechanism that is proposed for the OER in alkaline solutions must take into account the two different Tafel slopes obtained at high and low c.d., the dependence of the rate of the reaction on oxide film thickness at high c.d. but not at low c.d., and the fractional pH dependence at high c.d. This will be attempted in a subsequent paper.

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Anomalous Temperature Dependence of the Tafel Slope

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ABSTRACT

The anomalous temperature dependence of the Tafel slope b is discussed. Experimental evidence is sparse and in part unreliable, but it can be said with confidence that the classical relationship: $b = 2.3RT/\alpha F$ is not confirmed experimentally and appears to be the exception rather than the rule. It is shown that, contrary to common belief, an assumed potential dependence of the entropy of activation cannot give rise to the anomalous temperature dependence of the Tafel slope. The importance of the anomalous temperature dependence of b to the understanding of the theory of the elementary charge transfer process is emphasized. The types of experiments needed to determine the way in which the Tafel slope changes with temperature in different systems (the knowledge of which is essential for proper comparison with theory) are discussed.

The electrochemical rate equation for a simple charge transfer process, at potentials far removed from the reversible potential, is commonly written (1) as

$$i = i_0 \exp(-\beta n F/RT) \quad [1]$$

where β is the symmetry factor which, in the simple model, represents the fraction of the change in the electrochemical free energy of the reaction caused by the applied potential which affects the electrochemical free energy of activation of the reaction

$$\beta = (1/F)(\partial \Delta G^{\ddagger} / \partial \eta) \quad [2]$$

In complex electrode reactions involving several steps and adsorbed intermediates at quasi equilibrium in steps preceding the rate-determining step, the parameter β in Eq. [1] is replaced by α , which is related to the nature of the rate-determining step and its position in the reaction sequence, as well as to the type of adsorption isotherm

controlling the adsorption of intermediates (2, 3). In general it has the form

$$\alpha = \eta + \beta \quad [3]$$

in which n is zero or a small integer. When the rate-determining step does not involve charge transfer, α is not a function of β .

Equation [1] leads to the well-known Tafel slope

$$b = (\partial \eta / \partial \log i) = 2.3RT/\alpha F \quad [4]$$

in which $\alpha = \beta$ should be considered a special case.

In the classical treatment of electrode kinetics α and β are implicitly assumed to be independent of both overpotential and temperature. The constancy of β with potential has been questioned both experimentally and theoretically. Nevertheless, it can be stated with a high degree of confidence that there are many cases, notably hydrogen evolution on mercury and on other metals (4, 5), reduction of bromate and iodate on mercury (6),

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