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A Study of the Anomalous pH Dependence of the Oxygen Evolution Reaction at Platinum Electrodes in Acid Solutions

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ABSTRACT

Steady-state V -log i relationships have been determined for the oxygen evolution reaction at platinum electrodes in acid solutions of various pH's. At all pH's, Tafel slopes close to $2RT/F$ have been obtained after initially cathodically pretreating the electrode, polarizing it at a high anodic current density for a particular length of time, and then measuring the V -log i relationships at current densities lower than that used in the initial anodic electrode pretreatment. The order of the reaction with respect to hydrogen ions is then found to be one-half.

In other experiments, a rotating Pt ring disk electrode was used in solutions of various pH's in order to separate the currents due to Pt oxide film growth and those due to the oxygen evolution reaction and to accurately determine the charge density utilized for film growth. From this, it could be seen that the potential, at any constant charge density and pH, increases 120 mV for a tenfold increase of the current density, and that at a given current density and charge density, the potential decreases 60 mV as the pH increases one unit. These results confirm that the unusual fractional reaction order with respect to hydrogen ions is still obtained when the thickness of the oxide film remains constant. Further, it is reported here that the dependence of the oxygen evolution rates on pH can be attributed entirely to the dependence on the pH of the potential difference across the outer Helmholtz layer at the oxide film/solution interface. This simultaneous study of oxide film growth and the oxygen evolution reaction has led to a model for the potential distribution across the metal/oxide film/IHL/OHL/solution interface during the oxygen evolution reaction and to the conclusion that a fast quasi-equilibrium process exists across the outer Helmholtz layer.

The oxygen evolution reaction (OER) at platinum electrodes, in both acid and alkaline solutions, is a complex process that is still not satisfactorily understood. Evidence of this is shown by the great variance in the kinetic data of previous workers, even when apparently the same experimental conditions have been used, thus making any analysis of the reaction mechanism rather difficult. For example, in an early work, Hickling and Hill (1) reported a Tafel slope of $2RT/F$ (130 mV/decade) for the OER in 1N H_2SO_4 solutions at current densities from 10^{-5} to 10^{-3} A-cm⁻². On the other hand, Pushnograeva *et al.* reported two different Tafel slopes for the OER in this same solution (2). For current densities of about 10^{-5} - 10^{-3} A-cm⁻², the slope was close to $2RT/F$, while for current densities from about 10^{-3} - 5×10^{-2} A-cm⁻², the slope was close to $3RT/F$ (175-190 mV/decade). Shultze and Vetter, however, reported V -log i relationships with a slope of about 120 mV/decade at low current densities but a

slope of only 95 mV/decade at high current densities (3). Most other workers (4-11) have reported Tafel slopes close to $2RT/F$ in acid solutions, frequently for over five decades of current density (4, 6, 7).

Part of this variance in Tafel slope determinations can be related to the lack of control of electrode pretreatment and of the procedure of V -log i measurements. It is now well documented that a thin insulating oxide film, presumably Pt(OH)₂ (12), grows at a platinum surface at potentials more positive than about 1.0 V/RHE (13-16). The rate of growth depends on the potential and film thickness (13-16). It is also well known that the rate of the OER depends critically on the thickness of these films (3, 9, 17) so that the current density at a given potential decreases exponentially with increasing thickness of the oxide film (3, 17).

Due to the effect of the film thickness on the kinetics of the OER, it is essential that the determination of the Tafel lines, required for a mechanistic analysis of the OER, is carried out under strictly controlled conditions of film growth or film thickness. For example, meaningful Tafel lines have been obtained when the

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electrode was first anodically pretreated for a specified length of time at a higher current density, i_p , than those at which subsequent Tafel measurements were made (6, 9, 10). At current densities lower than i_p , and hence at the lower potentials, the field within the film that is the driving force for film growth (13-16) sufficiently decreases to render any further film growth negligible, as experimentally observed (12, 17-19). The Tafel lines can then be determined at an essentially constant film thickness. The film thickness itself will depend on the potential or the current density as well as the duration of electrode pretreatment. Irrespective of the film thickness, the Tafel lines obtained after this type of electrode pretreatment have a slope close to $2RT/F$ over a few decades of current density (6, 8-10, 17). However, they are shifted parallel to each other when different electrode pretreatment is used, i.e., the exchange current density changes (3, 9, 17).

It has also been recently demonstrated, with the use of a rotating ring disk electrode which can separate the two processes of oxygen evolution and oxide growth, that even when the oxide film is very thin and still growing, the V -log i relationships for oxygen evolution at any constant charge density representing the oxide film growth have a slope of 120 mV/decade (20).

As is customary in electrode kinetics, these slopes of 120 mV/decade have been associated with a mechanism in which a first charge transfer step is rate determining (4, 8, 10). A serious difficulty with this simple interpretation is that it cannot account for the observation that for the same electrode pretreatment (e.g., $i_p = \text{const.}$, $t = \text{const.}$) at any constant current density in the Tafel region, the potential decreases 60 mV as pH increases one unit (3, 9, 21). This leads to a fractional reaction order of one-half with respect to hydrogen ions (cf., Ref. 3 and 9).

The question can then be raised as to whether the observed fractional reaction order is related to different oxide film thicknesses existing in solutions of different pH's. In order to answer this, experiments have been carried out in which a solution of a given pH was rapidly replaced with a solution of a lower pH without interrupting the current flow during the Tafel measurements. These experiments showed that the fractional reaction order is real (9).

One explanation for this fractional reaction order has been that these thin oxide films are electronic insulators so that instead of having only a single barrier for charge transfer across the double layer at the oxide film/solution interface, a dual barrier comprised of both the oxide film and the oxide film/solution interface exists. If a chemical step following the first charge transfer step is then considered to be the rate-determining step, a Tafel slope of 120 mV/decade and a fractional reaction order of one-half with respect to hydrogen ions can be accounted for (9).

In recent studies of the growth of anodic oxide films at platinum, it has been suggested that the potential distribution across the metal/oxide film/solution interface is even more complex than suggested by the dual barrier model (14, 22) and is actually a distribution across three barriers, namely, the oxide film and the inner and outer Helmholtz layers. Under constant current conditions, the film initially grows without any significant oxygen evolution occurring, and the potential difference across the film increases linearly with increasing film thickness. The potential difference across the inner Helmholtz layer is considered to remain constant at a constant current density and increases as the current density for oxide growth increases. In contrast, the potential difference across the outer Helmholtz layer has been found to remain constant at all rates of oxide growth (22). Also, at any given film thickness and current density, the potential distribution across the film and the inner Helmholtz layer is independent of pH [in acid solutions only (22,

23)] while the potential difference across the outer Helmholtz layer decreases 60 mV as pH increases one unit. Even when both the OER and oxide growth occur concurrently, or when the OER is the major reaction, it has been shown by rotating ring disk experiments that oxide film growth continues according to the same rate equation as when only oxide film growth occurs (20). This indicates that when either oxide growth or oxygen evolution is the primary reaction, the potential distribution across the metal/oxide film/solution interface remains essentially unchanged. In particular, the potential difference across the outer Helmholtz layer remains independent of the rate of either oxide growth or of oxygen evolution and dependent on pH.

With the progress made in the studies of oxide growth at platinum anodes and with the development of a rational model for the potential distribution across the various interfaces, as well as with the success of the ring disk experiments in separating the rates of the individual processes, it has become warranted to examine the pH dependence of the OER and to analyze the fractional reaction order with respect to hydrogen ions by the rotating ring disk methods.

Experimental

Two types of experiments have been carried out. In the first, the steady-state V -log i relationships were determined for the OER in acid solutions of various pH's. A pre-reduced electrode was first subjected to an anodic current density of 3×10^{-3} A-cm $^{-2}$ for 1 hr, and then the V -log i relationships were determined at current densities less than this value.

In the second series of experiments, a Pt ring disk electrode was used in acid solutions of various pH's to separate and to follow individually the rates of oxide growth and the OER with time. The cell, electrode pretreatment, experimental procedures, and analysis of data were the same as described in a previous paper (20), and all measurements were made at room temperature.

Results and Discussion

Steady-state V-log i determination for the oxygen evolution reaction on Pt at a given pH.—As discussed above, steady-state V -log i relationships have been determined after first cathodically reducing the Pt electrode and then subjecting it to a constant anodic current density, i_p , in a 2N H $_2$ SO $_4$ solution for various periods of time. Some typical Tafel lines, which were obtained by the stepwise decrease of current density after the electrodes were charged at $i_p = 10^{-3}$ A-cm $^{-2}$ for 10 2 , 10 3 , and 10 4 sec, are shown in Fig. 1. After recording the potentials at the lowest current density, the V -log i relationships could be retraced by increas-

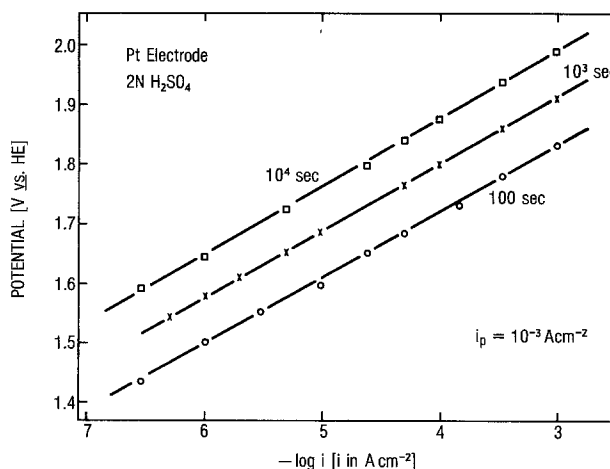


Fig. 1. V -log i relationships at Pt electrodes after various times at 10^{-3} A-cm $^{-2}$ in 2N H $_2$ SO $_4$. Note a decrease in the catalytic activity of the electrodes with time of pretreatment at 10^{-3} A-cm $^{-2}$.

ing current densities up to the current density of the initial anodic pretreatment. The electrode could remain at this current density for only a short time, such as 20-50 sec for the initial polarization time of 10^3 sec, as otherwise the potential would slowly increase further with time as the film thickness begins to increase again.

It can be seen in Fig. 1 that the Tafel lines for 3.5 decades of current density all have a slope close to 120 mV, independent of the length of time of anodic pretreatment at 10^{-3} A-cm $^{-2}$, as given in Eq. [1]

$$\frac{\partial V}{\partial \ln i} = \frac{2RT}{F} \neq f(d, V) \quad [1]$$

where d is the oxide film thickness, which is known to increase with time of polarization at the current density of electrode pretreatment (9, 16, 24).

It can also be seen in Fig. 1 that a tenfold increase of the polarization time at any particular current density increases the potential by about 75 mV

$$\frac{\partial V}{\partial \log t} = d \approx 75 \text{ mV} \quad [2]$$

This increase of the potential with time is indicative of the increasing oxide film thickness with time.

It is clear that a linear V -log i relationship would not have been observed if the electrode had been brought from a potential of about 1.0 V/RHE to a higher potential by gradually increasing either the potential or the anodic current density. This has been well documented by various workers (4, 6, 7, 10). Also, a linear V -log i relationship would not have been obtained if the measurements had been made first at low current densities, or potentials, and then at higher current densities, or potentials, as the films would have thickened during the course of these measurements.

It is clear, therefore, that linear Tafel lines with the slope of 120 mV can be obtained only when the thickness of the oxide film remains constant during Tafel line determinations² and that for a meaningful mechanistic analysis, the thickness of the oxide film should be known.

The pH dependence of the OER from steady-state measurements.—In order to determine the pH dependence of the OER under these steady-state conditions, a constant current density of $i_p = 3 \times 10^{-3}$ A-cm $^{-2}$ was applied to a prerduced electrode for 1 hr in all of the solutions studied. The Tafel lines were then determined by decreasing the current density in steps. Figure 2 shows that at any constant current density in the Tafel region, the potential has decreased 60 mV as the pH increased one unit. This potential-pH relationship is also shown in Fig. 3 for all of the solutions studied in this work. Significantly, it can be seen that an addition of neutral salts does not affect the kinetics of oxygen evolution. Further, it is seen that the same V -log i relationship is obtained in both H $_2$ SO $_4$ and HClO $_4$ solutions of the same pH.

The data in Fig. 2 and 3 result in the following rate equation for oxygen evolution, where the reaction order with respect to hydrogen ions is one-half

$$i_{O_2} = K [H_3O^+]^{1/2} \exp \left[\frac{FV}{2RT} \right] \quad [3]$$

This fractional reaction order has been previously obtained from measurements in sulfuric acid solutions of two pH's in the absence of a neutral salt (9). It is now confirmed over a wide pH range in both H $_2$ SO $_4$ and HClO $_4$ solutions, with and without salt.

The separation of the rates of oxide growth and oxygen evolution in solutions of different pH's with a ring

²In the older data showing the slope of 120 mV/decade, the pretreatments of electrodes, which were frequently very extensive, appear to have led to the required condition for the constant slope.

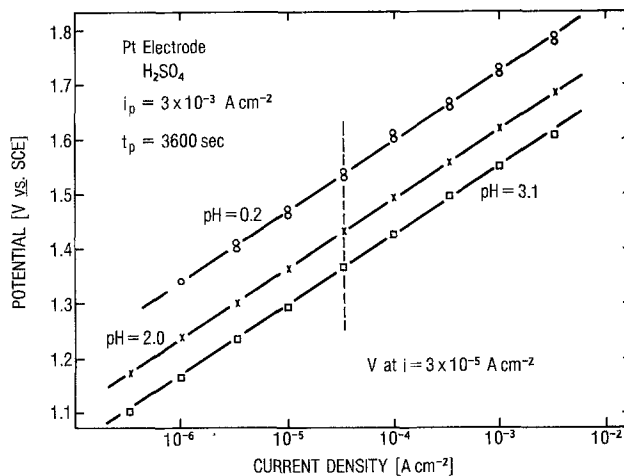


Fig. 2. V -log i relationships at electrodes after 1 hr at 3×10^{-3} A-cm $^{-2}$ prior to measurements in solutions of various pH's.

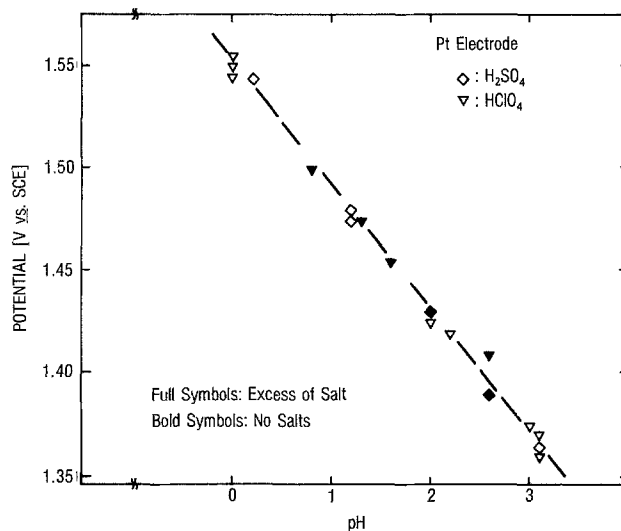


Fig. 3. Potentials at 3×10^{-5} A-cm $^{-2}$ at electrodes after 1 hr at 3×10^{-3} A-cm $^{-2}$ prior to V -log i measurements at $i < 3 \times 10^{-3}$ A-cm $^{-2}$. Potentials are recorded vs. SCE. Full symbols: an addition of the corresponding K^+ salt up to 1M.

disk electrode.—Rotating ring disk electrode experiments simultaneously provide the electrode potential, V , the current due to oxide growth, i_{og} , the current due to oxygen evolution, i_{O_2} , and the charge density, q , which is equivalent to the thickness of the oxide film, at all times of polarization by a constant anodic current, where q can be obtained by Eq. [4]

$$q = \int_0^t i_{og} dt \quad [4]$$

Thus, as has been shown previously (20), when a constant current is applied to a prerduced disk electrode, the potential initially increases linearly with time, starting at about 1.0 V/RHE. In this linear potential region, essentially all of the current is utilized for oxide film growth, and the ring current is essentially zero. This oxide film grows by the high field mechanism (13, 15) according to the following rate equation (25, 26)

$$i_{og} = i_{og,0} \exp \left[\frac{V - V_0}{cq} \right] \quad [5]$$

where c is a constant (≈ 57 VC $^{-1}$ cm 2) independent of pH, and V_0 is a parameter which depends on pH. The field within the oxide film is proportional to $(V - V_0)/q$.

After some time of constant current polarization, the linear V/t behavior ceases and the potential increases

more slowly and nonlinearly at a rate which decreases with time. The current at the ring electrode then increases due to the reduction of oxygen which is being evolved at the disk electrode, but the current soon levels off and rather slowly approaches the current expected for essentially 100% oxygen evolution at the disk electrode (20).

When the current at the ring electrode, i_{ring} , is scaled to the current at the disk electrode, i_{disk} , the current due to Pt oxide growth can be obtained as in Eq. [6] (20)

$$i_{og} = i_{disk} - i_{ring} \quad [6]$$

These ring disk data show that the oxide film continues to grow even when oxygen evolution is the main reaction at the disk electrode. This has previously been observed by coulometry (24) and ellipsometry (16).

It can be seen in Fig. 4 that, as in the case when only oxide growth occurs and Eq. [5] is obeyed, the observed V/q relationship is also linear even when the OER is the primary reaction at the disk. Further, when V is calculated from Eq. [5] by utilizing the integrated value of q (Eq. [4]) and the current due to oxide growth (Eq. [6]) and is then compared to the observed potential at the disk electrode, these two V/q relationships match very closely as shown in Fig. 4 for two pH's. Consequently, the oxide films continue to grow at all pH's in acid solutions with the same mechanism even during vigorous oxygen evolution as when no significant oxygen evolution occurs.

At any constant charge density and a given pH, the potential increases 120 mV for a tenfold increase of the current density (not shown in Fig. 4). It follows that the rate of the OER in a solution of a given pH can be expressed by the following equation (20)

$$i_{o2} = k' \exp \left[\frac{-mFq}{2RT} \right] \exp \left[\frac{FV}{2RT} \right] \quad [7]$$

where $m (= \partial V / \partial q)$ is a constant which has been determined to be 270-330 $\text{VC}^{-1} \text{cm}^2$ (20), and where other symbols have their usual significance. Equation [7] shows that the rate of the OER depends critically on the thickness of the oxide film.

It is also seen in Fig. 4 that in both linear $V-q$ regions, the potential at any constant thickness of the oxide film has decreased 60 mV as the pH has increased by one unit. As essentially all of the current in the second linear V/q region is utilized for the OER, the following relationships can be established for the OER

$$\frac{\partial V}{\partial \text{pH}} = - \frac{2.3RT}{F} \neq F(q, i_p) \quad [8]$$

and

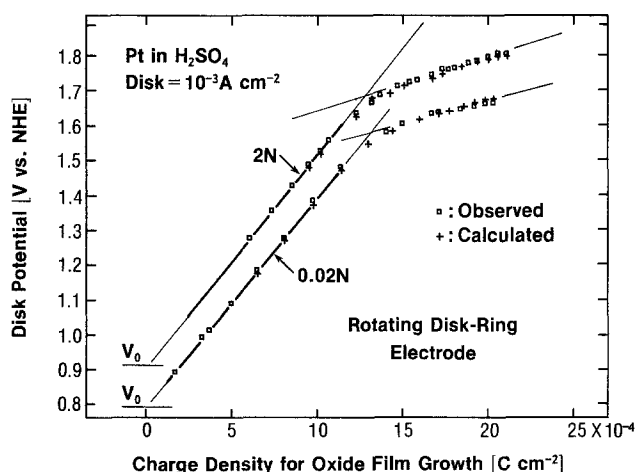


Fig. 4. $V-q$ relationships at two pH's. Note two regions in which $V-q$ lines in solutions of different pH's are parallel. Note also the close match of the calculated and observed potentials.

$$\frac{\partial V}{\partial q} = m \neq f(\text{pH}, i_p) \quad [9]$$

By combining these equations with Eq. [7], the following rate equation for the OER is obtained

$$i_{o2} = K[\text{H}_3\text{O}^+]^{1/2} \exp \left[\frac{-mFq}{2RT} \right] \exp \left[\frac{FV}{2RT} \right] \quad [10]$$

Since Eq. [10] is determined from simultaneous measurements of V , i , and q in solutions of different pH's, the fractional reaction order with respect to H_3O^+ is confirmed at all thicknesses of the oxide film, even at the earliest stages of oxygen evolution when the films are very thin and still growing. This fractional reaction order cannot be ignored and must be considered in any mechanistic analysis.

Model of the metal oxide film solution interface and dependence on pH.—The growth of the anodic oxide film at Pt electrodes has been found to obey Eq. [5], which also expresses the rate of the high field migration of ions through an insulating film (25). In this equation, V_o is the only pH dependent parameter, decreasing 60 mV as pH increases one unit (15, 23). V_o is considered to be the potential in the inner Helmholtz plane with respect to a pH independent reference electrode, and therefore, it gives a measure of the potential difference across the outer Helmholtz layer, ΔV_{OHL} . ($V - V_o$) is then the potential difference across the growing oxide film and the inner Helmholtz layer (22). A simple model suggested for the potential distribution across the complex interface, comprised of the oxide film and the inner and outer Helmholtz layers, is shown in Fig. 5, for two current densities and two pH's.

The close match between the calculated and observed potentials (Fig. 4) in the ring disk experiments has shown that even when oxygen evolution becomes the major reaction, the potential difference across the outer Helmholtz layer, ΔV_{OHL} , remains constant at a given pH, irrespective of the rate at which the oxide is still growing (22). In other words, ΔV_{OHL} has the same value in the predominantly oxygen evolution region as in the predominantly oxide growth region. This implies that as the rate of oxide growth decreases and the OER becomes more predominant, the observed increasing potential must be a result of an increased potential difference across the oxide film and the IHL, rather than across the OHL. Since Eq. [5] also holds in the oxygen evolution region, and since i_{og} continuously decreases with the thickness of the oxide film,

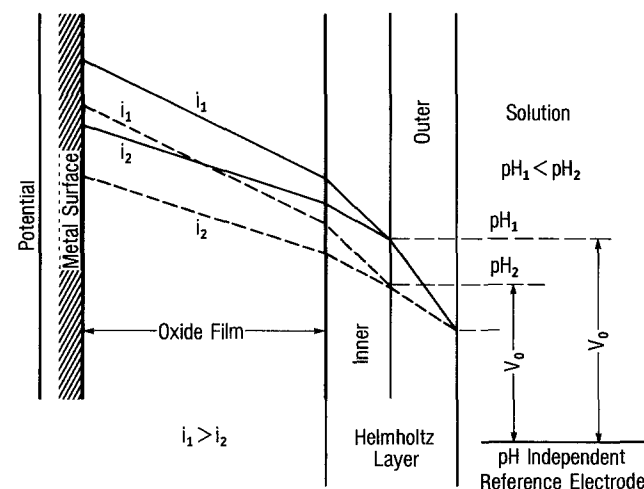


Fig. 5. Model of the potential distribution across the oxide film and the inner and outer Helmholtz layer at two current densities and two pH's. The same model holds both when oxide growth process and the oxygen evolution reaction predominate. Note that potential difference across the OHL is independent of the applied current density but decreases as pH increases.

the field within the film and the IHL must also decrease. This is possible only because the thickness of the film increases at a faster rate than the potential difference across the oxide film (Fig. 6).

When the solution pH increases one unit, V_0 decreases 60 mV and the potential of the inner Helmholtz plane, with respect to a pH independent reference electrode, also decreases 60 mV (22, 23). Therefore, in solutions of different pH's, the potential difference across the film and the inner Helmholtz layer is the same for the same current density of oxide growth and the thickness of the oxide film, independent of pH, as is illustrated in Fig. 5. As a consequence, the V - q lines in the first linear V - q region, when essentially only oxide growth occurs, and in the second V - q region, when oxygen evolution is the major reaction, are parallel but shifted along the V axis by 60 mV per pH unit (cf. Fig. 4). The shift is due entirely to the dependence of ΔV_{OHL} on pH.

Because ΔV_{OHL} does not change with a change in current density when a Tafel line is determined by decreasing current density over a range of current densities, it is the potential difference across the oxide film and the inner Helmholtz layers which changes 120 mV for each decade of current density (Fig. 7). It follows that it is the potential difference across the oxide film and the inner Helmholtz layer which controls the rate of the OER. The observed 60 mV dependence of the rate of the OER on pH and the observed fractional reaction order with respect to hydrogen ions reflects only the change of ΔV_{OHL} with pH, while the potential differences across the oxide film and the inner Helmholtz layer at a given current density, $(V - V_0)$, do not change, i.e., $(V - V_0)$ at any constant current density is independent of pH. The explanation of the observed pH dependence of the OER and the fractional reaction order with respect to hydrogen ions is, therefore, an explanation of the pH dependence of ΔV_{OHL} .

The fact that ΔV_{OHL} remains constant over a large range of current densities must mean that the charge transfer process occurring across the outer Helmholtz layer is fast and in quasi equilibrium. The most likely process for this would be the rapid transfer of a proton from a water molecule at the inner Helmholtz plane across the outer Helmholtz layer to a water molecule in the outer Helmholtz plane, according to

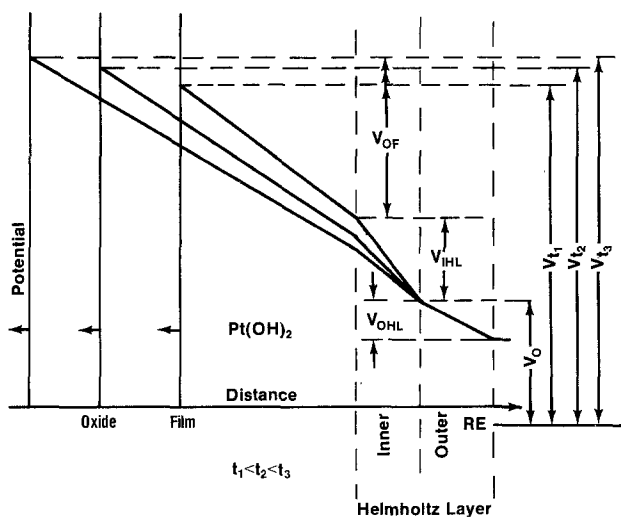


Fig. 6. Model for the potential distribution across the oxide film and the inner and outer Helmholtz layer in the transition from predominantly oxide growth to predominantly oxygen evolution. As current density for oxide growth and the fields in the oxide film and IHL decrease, the potential still increases because the film thickness increases faster than the field decreases. Note that ΔV_{OHL} is not affected in the transition.

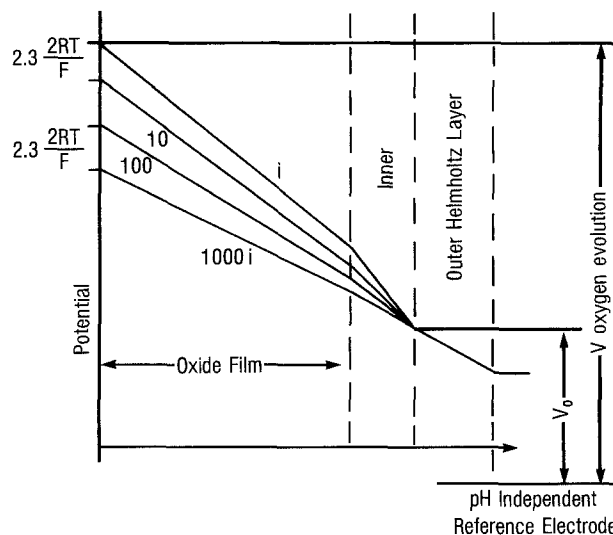
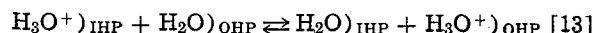
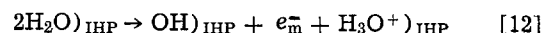


Fig. 7. When the Tafel lines are determined by decreasing the current density incrementally, the potential distribution across the oxide film and the inner and outer Helmholtz layer adjusts so that ΔV across the oxide film and the IHL decreases 120 mV for a tenfold decrease of current density. Note that ΔV_{OHL} remains constant.



Alternatively, during oxygen evolution, a water molecule in the inner Helmholtz plane may discharge, ejecting a proton across the outer Helmholtz layer



Therefore, while the rate of proton transfer across the outer Helmholtz layer is fast and independent of ΔV_{OHL} , the slower electron transfer step across the anodic film and the inner Helmholtz layer are potential dependent and rate limiting. The mechanism of the electron transfer is another subject and will be dealt with in a subsequent paper.

The actual value of ΔV_{OHL} is not known. If it is assumed that at Pt the zero electrode potential coincides with the potential of zero charge (pzc) and that the pzc decreases 60 mV per unit of pH vs. a pH independent reference electrode, as reported (27), then ΔV_{OHL} can be considered to be constant at every pH. The rate of the OER could then be expressed with respect to the pzc as follows

$$i = C \exp \left[\frac{-mFq}{2RT} \right] \exp \left[\frac{V_{pzc}}{2RT} \right] \quad [14]$$

where V_{pzc} is the electrode potential against the pzc and C is a constant independent of the pH.

It is evident from this work and a previous paper (20) that the OER and the oxide growth reaction at a Pt electrode are closely interrelated. Substantial progress has been made in understanding the anomalous pH dependence of the OER and its fractional reaction order with respect to hydrogen ions by understanding the potential distribution at the metal/oxide film/solution interface. Further progress in the understanding of the OER and of the dependence of ΔV_{OHL} on pH is expected by extending these types of studies to alkaline solutions where the pH dependence of the oxide growth reaction (22) and of the OER (28) are more complex than in acid solutions.

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The Recombination of Photogenerated Minority Carriers in the Depletion Layer of Semiconductor Electrodes

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ABSTRACT

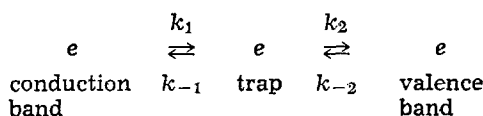
The problem of depletion layer recombination in illuminated semiconductor electrolyte systems, as used for solar energy conversion, is considered. It is shown that there can be four different kinetic cases. The conditions for the existence of these different cases as a function of the potential drop across the depletion layer, the irradiance, and the photocurrent are derived. Analytical solutions for current voltage curves for the different cases are derived and criteria for distinguishing between the different cases are given. The effects of concentration polarization of the majority carriers are considered and shown to be negligible for typical semiconductors.

In a previous paper (1), we extended the treatment by Gartner (2) and by Wilson (3) of the problem of the transport and kinetics of photogenerated minority carriers in semiconductor electrolyte cells to include the effect of the recombination of minority carriers in the depletion layer. In Ref. (1), we assumed that the kinetics of the recombination were first order throughout the depletion layer. This assumption may be contrasted with that made by Reichman (4) in his treatment of depletion layer recombination. He followed Sah, Noyce, and Shockley (5) and assumed that because of the repulsion of majority carriers from the surface, the recombination kinetics changed somewhere in the depletion layer from being first order in minority carriers to being first order in majority carriers. In this paper, we present a unified treatment of these two cases. We also consider two other new cases which can arise where the recombination kinetics are first order in both majority and minority carriers. We describe and discuss the conditions under which these four different cases are found. We present a simple general diagram which shows how the zones of dominance of the different cases depend upon experimental

variables such as irradiance and applied potential. We derive simple analytical expressions for the current-voltage curves and show how the different cases may be distinguished. Hitherto it has been assumed that the concentration of majority carriers is given by a Boltzmann distribution in the field of the depletion layer. Laser and Bard's simulation (6) showed that there could be a buildup of photogenerated majority carriers, while they are waiting to be transported out of the depletion layer. In our treatment, we consider the effect of transport on the concentration of majority carriers. We show that although there can indeed be a buildup, it is unlikely to effect the recombination kinetics of typical semiconductors. Throughout this paper, we will consider the case of a p-type semiconductor.

The Rate Limiting Step in Recombination

We assume that the recombination process is the same as that of Shockley and Read (7), but we will use the normal notation of chemical kinetics. With the following rate constants



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Key words: photoelectrochemistry, semiconductor kinetics, semiconductor/liquid electrolyte.