Growth and Properties of Oxide Films on Platinum II. pH Dependence in Alkaline Solutions

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The kinetics of growth of the oxide film on platinum has been studied in alkaline solutions as a function of pH. The experimental data confirm the existence of steady states in the current and thickness. Diagnostic criteria for the dependence of the steady state current and thickness on applied potential and pH are derived from the PDM, in which the point defects in the barrier layer are postulated to be cation vacancies, cation interstitials, and oxygen vacancies. The steady state thickness is then predicted to vary linearly with the applied potential and pH. These predictions are in good agreement with the experimental findings. The kinetic order of the barrier layer dissolution reaction with respect to the hydrogen ion concentration in the alkaline solution is found to be negative, which indicates that dissolution occurs via the formation of the platinate anion (\(\text{PtO}_2^{2-}\) and/or \(\text{PtO}_3^{2-}\)), the identity [Pt(II) versus Pt(IV)] depends upon the applied potential.

Introduction

Due to its noble metal properties, platinum metal dissolution apparently does not occur to any significant extent prior to anodic oxide formation. The investigation of initial oxide formation on platinum is therefore possible without interference from direct metal dissolution. Many aspects of the platinum oxide formation process have been studied, e.g., the irreversibility of oxide formation and the imbalance between the charge for oxide formation and reduction after double layer capacitance correction (1); the structure of oxide film on Pt, which has been found to be bilayer, with a thin \(\alpha\)-oxide as the inner (“barrier”) layer and a thick \(\beta\)-oxide” outer layer (2-7); the photo-electrochemical behavior of anodic platinum oxide film (8-10); capacitance measurements and the potential dependence of film capacity as analyzed by Mott-Schottky theory (11); the composition of the anodic oxide film (6, 7, 12, 13); and the surface structural changes at Pt during oxide film formation and reduction (14-16), to identify but a few of the previous studies.
A number of models, e.g. the Place Exchange Model (PEM) (3, 17, 18), the High Field Model (HFM) (19-23), the Nucleation and Growth Model (NGM) (24, 25), and the Point Defect Model (PDM) (11), have been proposed previously to describe anodic oxide film growth on platinum in aqueous environments. None of the models, except the PDM, predicts the existence of steady states in film thickness and current, because they fail to recognize that dissolution occurs at the barrier layer/solution interface. According to the PDM (26), the dependencies of the steady state thickness and passive current on the applied voltage and pH provide diagnostic criteria that may be used to identify the charge carrier in the film and thus the electronic character of the film (n-type or p-type), and to indicate the kinetic nature of the interfacial reactions (26). These criteria have been used to explore the fundamental nature of passivity on a number of metal (26) and the results are consistent with those obtained using other techniques, such as capacitance measurements analyzed in terms of Mott-Schottky theory and photo-electrochemistry. In the present study, the diagnostic criteria afforded by the PDM are used to characterize the anodic oxide film formed on platinum in alkaline environments.

Experimental

All electrochemical studies were carried out in a three-electrode glass electrochemical cell. The counter electrode was a Pt wire located in a separate compartment connected to the working electrode compartment via a glass frit. All potentials were measured against a Saturated Calomel Electrode (SCE) that was connected to the cell via a Luggin probe. The potentials have been converted to the Standard Hydrogen Electrode (SHE) scale by adding 0.24V to the measured values.

The working electrode was a pure platinum rod (Alfa, 99.99%) that was embedded in two-component epoxy resin. The working surface, of geometric area 0.32cm², was abraded with 800 and 1200 grit SiC paper, polished with 3µm diamond suspension (Leco), with 1µm, 0.3µm, and 0.05 µm Al₂O₃ powder, and was then rinsed with D.I. water (Resistivity = 18.2MΩ·cm). All experiments were performed at ambient temperature (20 ± 2 ºC) in KOH solution. The solution was deaerated with ultra pure Ar gas during the experiments.

The roughness factor of the working electrode surface was determined to be 1.82 (11) by comparing the charge for hydrogen adsorption with a reference value of 210µC per true unit area (3) in 0.5M H₂SO₄ solution. However, all of the experimental results are presented with respect to the geometric area. Evaluation of the charge for hydrogen adsorption was carried out by integrating the H-adsorption i-V profile in the cyclic voltammogram.

Electrochemical experiments were performed using a Solartron Model 1286 Electrochemical Interface. Electrochemical impedance data were recorded with a Solartron Model 1250 Frequency Response Analyzer (FRA), using an excitation voltage of 10mV rms and an applied frequency ranging from 50kHz to 0.03Hz. The capacitance of the interface was measured at frequencies of 10kHz, 5kHz, and 1kHz, while the
potential was being swept in the negative direction from the oxide formation potential. The voltage scan rate employed was 100mV/s.

**Results and Discussion**

**Electrochemical Properties**

Cyclic voltammograms (Figure 1) were first recorded in 0.01M, 0.1M, and 1M KOH solutions at a scan rate 100mV/s. Similar to the voltammograms measured in acidic solutions, the cyclic voltammograms obtained in alkaline solutions of different pH show also three regions: the hydrogen adsorption and desorption region at lower potentials (-0.8V_{SHE} - -0.4V_{SHE}); the double layer capacitance region at intermediate potentials (-0.4V_{SHE} - -0.2V_{SHE}); and the formation and reduction of platinum oxide(s) region at higher potentials (-0.2V_{SHE} – 1.0V_{SHE}). The passive (oxide formation) potential region in Figure 1 is observed to shift in the negative direction with increasing pH, as expected from the Pourbaix diagram, and the film formation potentiodynamic current density increases with increasing pH, as does the steady state current density, a finding that is predicted by the PDM (26).

In Figure 2, Mott-Schottky plots obtained in alkaline solutions display positive slopes, which are characteristic of n-type semiconductors (11). The capacitance measurements in acid solution (11) also show that the anodic film on platinum is n-type in electronic character although a small region of negative slope exists in the Mott-Schottky plots at high potentials. The Mott-Schottky studies therefore show that the dominant defects in the oxide films formed anodically on platinum in both alkaline and acid solutions are oxygen vacancies and/or platinum interstitials, as postulated in the Point Defect Model (PDM) (27).

The regions of negative slope in Mott-Schottky plots observed at high potentials in acidic solutions are not found for the films formed in alkaline solutions, although a tendency toward a change in slope is indicated in Figure 3 for the data measured for the highest formation potential. In this regard, it is important to note that the Mott-Schottky plots presented in Figures 2 and 3 are “unconventional”, in that the film was grown at the formation potential for a period of 24h and then the potential was swept in the negative direction at a sweep rate of 100mV/s while simultaneously measuring the capacitance at
1kHz. This procedure was adopted, in order to “freeze-in” the defect concentration and the film thickness, so as to comply more closely with Mott-Schottky theory. The origin of the tendency toward a negative slope (and hence toward p-type character) at high potentials is controversial and it may indicate that cation vacancies become the dominant defect or it may arise from anion adsorption or some other process. This issue will be explored in greater depth in a subsequent paper.

Figure 2: Mott-Schottky plots of platinum at oxide formation potential of 0.44V$_{SHE}$ as a function of KOH concentration. Voltage sweep rate is 100mV/s.

Steady state is usually defined as being a state of a system in which the conditions do not change with time. Accordingly, a true steady state during film growth arises only from a balance between the rate of film growth and the rate of film dissolution (28). Transient experiments were then designed to examine whether the anodic film grown on platinum attains a true steady state. In Figure 4, the change in film thickness is plotted as a function of time as the potential is stepped from a higher value to a lower value in the passive potential region. At each potential, the system is allowed to evolve by holding the potential constant for 24h. The formation potentials were selected from Figure 1 to be in the passive potential range in order that the electroreduction of the passive film at the metal/film interface can be discounted as the reason for film thinning on stepping the passive potential from a high to a low value. The film thickness was then determined from the imaginary component of electrochemical impedance measured at a fixed frequency of 1kHz. It is noted from Figure 4, that the film thicknesses immediately decreases after stepping the potential in the negative direction for all three pH values but, then, after a few seconds, the thickness increases until a new steady state thickness is attained. Of particular importance is that the film thickness decreases as the formation potential decreases. As we have summarized in the previous paper (11),

Figure 3: Mott-Schottky plots for the platinum oxide film formed in 0.1M KOH solution as a function of film formation potential.

Figure 4: The reduction in thickness of the passive film on platinum as a function of pH upon stepping the potential from the high to low values.
PDM predict that the oxide film should grow to infinite thickness instead of reaching steady state within finite time, and regardless of whether $\Delta V$ is positive or negative, and irrespective of the magnitude of the step in voltage, the film will continue to grow (29). In this regard, it is apparent that these predictions are contrary to the results in Figure 4. The PDM explains this behavior by noting that, when the potential is stepped in the negative direction, the rate of the film formation becomes smaller than the rate of dissolution and, accordingly, the film thickness decreases until the steady state for lower potential at same pH is reached (28).

**Diagnostic Criteria of the PDM**

The steady state of the passive film has been extensively studied and explained according to the PDM, in which the dominant defects are cation vacancies, anion vacancies, and cation interstitials. The analytical relationships between the steady state film thickness and the passive current and the applied potential and solution pH gives rise to the diagnostic criteria. These analytical diagnostic criteria predict that the passive films on nickel (30) and tungsten (28) are p-type and n-type, respectively, which have been demonstrated by capacitance measurements analyzed according to Mott-Schottky theory.

As indicated above, the general Point Defect Model (Figure 5) postulates that the point defects present in the barrier layer are cation vacancies, cation interstitials and oxygen vacancies as designated by the Kroger-Vink notation (31). The diagnostic criteria are predicted from the dependencies of $L_{ss}$ and $\ln I_{ss}$ on the formation potential and pH, and depend on whether a change in the oxidation state occurs upon ejection of a cation from the barrier layer/solution (outer layer) interface during dissolution of the film. For those cases where no change in oxidation state occurs upon ejection of a cation from the barrier layer ($I = \chi$) or upon dissolution of the film occurs, the diagnostic functions are summarized in Table 1.

![Figure 5: Schematic of physicochemical processes that are envisioned to occur within the barrier oxide (MO$_{\chi/2}$) layer on passive metal, according to the Point Defect Model.](image-url)
Table I: Diagnostic Criteria for Determining the Conductive Nature of the Barrier Layer ($\Gamma = \chi$).

<table>
<thead>
<tr>
<th>Criterion</th>
<th>Cation Vacancies Conducting (p-type)</th>
<th>Metal Interstitials Conducting (n-type)</th>
<th>Oxygen Vacancies Conducting (n-type)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\left( \frac{\partial \ln I_{\text{ss}}}{\partial V} \right)_{\text{pH}}$</td>
<td>$\alpha, \alpha \Gamma \gamma$</td>
<td>$0$</td>
<td>$0$</td>
</tr>
<tr>
<td>$\left( \frac{\partial L_{\text{ss}}}{\partial V} \right)_{\text{pH}}$</td>
<td>$\frac{1}{e} [1 - \alpha]$</td>
<td>$\frac{1}{e} [1 - \alpha]$</td>
<td>$\frac{1}{e} [1 - \alpha]$</td>
</tr>
<tr>
<td>$\left( \frac{\partial \ln I_{\text{ss}}}{\partial \text{pH}} \right)_{\gamma}$</td>
<td>$\alpha, \beta \gamma$</td>
<td>$2.303 n - \beta \gamma (\alpha + \alpha_\gamma)$</td>
<td>$\alpha, \beta \gamma (1 - \chi) - 2.303 n$</td>
</tr>
<tr>
<td>$\left( \frac{\partial L_{\text{ss}}}{\partial \text{pH}} \right)_{\gamma}$</td>
<td>$\frac{1}{e} \left( \frac{2.303 n}{\alpha, \gamma \gamma - \beta} \right)$</td>
<td>$\frac{1}{e} \left( \frac{2.303 n}{\alpha, \gamma \gamma - \beta} \right)$</td>
<td>$\frac{1}{e} \left( \frac{2.303 n}{\alpha, \gamma \gamma - \beta} \right)$</td>
</tr>
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Plots of $\ln(I_{\text{ss}})$ against potential for platinum in KOH solutions (pH 12-14) are shown in Figure 6. As predicted by the PDM, the logarithm of steady state current density is independent of applied voltage prior to the oxygen evolution region or perhaps prior to the region where Pt (II) is oxidized to Pt (IV). This behavior is consistent with the prediction of the PDM for an n-type oxide (Table 1). It is also noted that the current density obtained by stepping the potential in the positive direction followed by stabilization for 24 hours is in good agreement with the current density obtained by stepping the potential in the reverse direction. The system is thus demonstrated to be in the steady state and hence the diagnostic criteria apply.

Figure 6: Dependence of the steady state current density on applied potential and pH.

Figure 7: Dependence of steady state thickness of the platinum oxide film as a function of applied voltage and pH.

Furthermore, the steady state thickness shown in Figure 7 was calculated from specific capacitance data by assuming that the oxide is the dielectric of a parallel plate capacitor with a leaky, parallel resistance in analyzing EIS data measured at each formation potential. It is observed that the film thickness increases linearly with the formation potential, and the slope is independent of pH, within the experimental uncertainty. According to the diagnostic criteria of the PDM, this slope does not depend
on pH, and equals $(1 - \alpha)/\varepsilon$. The polarizability of the barrier layer/solution interface, $\alpha$, can have values between 0 and 1, with other work (26) indicating that for very thin films, the value lies toward the upper extreme of this range. Taking $\alpha = 0.8$ and $\varepsilon = 2 \times 10^6$ V/cm from a previous study (11), we have $\partial \ln(L_{ss})/\partial V = 1.0$ nm/V for all pH ranges, which is in satisfactory agreement with the experimental value of 0.92 nm/V (Figure 7). Alternatively, the electric field strength for passive metals having very thin passive films lies between $2 \times 10^6$ V/cm and $5 \times 10^6$ V/cm, which after assuming $\alpha = 0.5$ yields $\partial \ln(L_{ss})/\partial V = 2.5$ nm/V and 1.0 nm/V, respectively, again in reasonable agreement with experiment. As we have discussed elsewhere (11), due to the difficulty in measuring values for fundamental parameters in the PDM, these estimates must be viewed as being only semi-quantitative until the optimization of the PDM on high quality electrochemical impedance data can be completed. This work is now underway. In this regard, the value of $\partial \ln(L_{ss})/\partial V$ and the value of the steady-state current, $I_{ss}$, provide important constraints on the optimization process. It is also noteworthy that a pH dependence of $\partial V/\partial L$ of platinum oxide film formed in alkaline solutions was observed by Damjanovic et al. (32, 33) using galvanostatic measurements, which is contrary to our experimental result (Figure 7), but no dependence of $\partial V/\partial L$ in acid solution (23, 34) was reported. Damjanovic et al. (22) stated that only if the rate determining step occurs at the film/solution interface, the observed pH dependence in alkaline solution and independence in acid solution could be accounted for in terms of the HFM model, although they have also questioned if the change in the charge distribution within the oxide film affects the field in the double layer and consequently the rate of oxide growth if a process at the oxide film/solution interface is the rate determining step. However, we further note that, while the acid solution used by Damjanovic et al (22) was purged with argon, the alkaline solution was purged with oxygen. Accordingly, the oxygen reduction reaction presumably occurred on the platinum surface, with the result that the electrochemical response was not determined by the oxide film alone. Finally, under galvanostatic conditions, it is difficult to accept that a steady state may have been achieved, in which case the diagnostic criteria given in Table 1 for potentiostatic conditions do not apply.

![Figure 8: Dependence of the steady state current on pH for passive platinum at two formation voltages.](image)
As shown in Figure 6, the steady state current does not depend on the applied voltage prior to oxygen evolution for all three pH values investigated. A plot of the steady state current versus pH is shown in Figure 8. Here, we plot the current density measured at 0.34 and 0.44V_{SHE} for three pH values, since only these two applied voltages are in the passive potential range before oxygen evolution. It is noted from Figure 8 that the logarithm of steady state current density linearly increases with the pH, and the slope is equal to 0.58. From Table 1, we may then calculate \( \frac{\partial \ln(I_{ss})}{\partial pH} \). Note that the dominant defects in an n-type oxide could be either oxygen vacancies or metal interstitials, or both, and that the diagnostic criteria are the same for these two defects (Table 1). As we have stated elsewhere (11), this renders difficult differentiation between the oxygen vacancy and the cation interstitial being the dominant defect in an oxide on the basis of electrochemical studies alone (Table 1). However, recent work in this laboratory suggests that these cases may be differentiated by optimization of the PDM on high quality electrochemical impedance data through examination of the values for the rate constants obtained. The fact that \( \frac{\partial \ln(I_{ss})}{\partial pH} \) is independent of pH (Figure 8) is consistent with the diagnostic criteria listed in Table 1 and it is evident that this quantity, too, may become an important constraint in optimization.

It is also very interesting to note that the kinetic order of the dissolution reaction at the barrier layer/solution interface with respect to the \( (H^+) \) is negative, according to the experimentally-determined dependencies of \( L_{ss} \) and \( I_{ss} \) on pH. Since the dissolution reaction occurs in alkaline solution, the sign of the kinetic order is accounted for by assuming that the barrier layer dissolves to form platinate species is thus possible to be produced in the solution. The reaction (7) in Figure 5 in alkaline solutions could then be expressed as follows;

\[
PtO + 2OH^- \rightarrow PtO_2^{2-} + H_2O
\]

or possibly

\[
PtO + 4OH^- \rightarrow PtO_3^{2-} + 2H_2O + 2e^- 
\]

The first reaction would account for the passive state, in which the oxidation state of the cation in the barrier layer is identical to that in solution (\( PtO_2^{2-} \)), while the second reaction, in which a change in oxidation state occurs upon dissolution (not included in the diagnostic criteria listed in Table 1), may account for the Tafel behavior observed at higher potentials (Figure 6). However, the same Tafel behavior may be accounted for by oxygen evolution, so that a major task in future work will be to differentiate between these two possibilities.
Summary and Conclusions

The present experiments and analysis show that there is nothing different about the properties and growth of the anodic oxide film on platinum formed in both acid and alkaline solutions. The experimental data show that the oxide film is a highly defective n-type oxide and has a bi-layer structure. The experimental data confirm the existence of steady-states in the current and film thickness. Diagnostic criteria derived from the PDM account for the experimentally-determined dependencies of the steady state passive current and film thickness on voltage and pH in the passive region. The kinetic order for dissolution of the barrier layer with respect to hydrogen ion concentration is found to be negative, which indicates that the film may dissolve to form platinate Pt(II) or Pt(IV) species. In future work, the experimentally established diagnostic criteria derived from the PDM will be employed as constraints in the optimization of the PDM on EIS data.

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References