

## Mechanism of the Anodic Oxidation of Platinum

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The mechanism of the anodic oxidation of platinum in the oxygen electrode region of potential remains controversial. Thus, some workers adopt, somewhat uncritically, the High Field Model (HFM) [1] and others have used the Place Exchange Model (PEM) [2] to interpret their data. Recently, one of the present authors [3-5] employed the Point Defect Model (PDM) to interpret Electrochemical Impedance Spectroscopic (EIS) and Potentiodynamic Polarization Data (PPD). The reviewers of the latter paper were highly critical of the use of the PDM, even though they were unable to point to any data that favored the HFM or the PEM. In this paper, we apply an analytical analysis of the oxide film growth transient on platinum in 1 M H<sub>2</sub>SO<sub>4</sub> and demonstrate, unequivocally, that the PDM provides a superior theoretical framework than either the HFM or the PEM for interpreting oxide film growth on platinum.

The three models of interest, the HFM, the PDM, and the PEM yield the following rate laws for film growth under potentiostatic (potential step) conditions:

$$\frac{dL}{dt} = Ae^{B/L} \quad (1)$$

$$\frac{dL}{dt} = A'e^{-b_2L} - C \quad (2)$$

$$\frac{dL}{dt} = A''e^{-bL} \quad (3)$$

respectively, where L is the film thickness, and A, A', A'', b, and b<sub>2</sub> are constants, as defined elsewhere [6]. Because the film is observed to achieve a steady-state, which requires two terms to be present on the right side, the HFM and the PEM can be rejected upon that basis alone. However, a more analytic approach exists which makes use of the equations derived by Zhang, et.al. [6] to analyze the full transient according to the HFM, the PDM, and the PEM; viz:

$$\sqrt{\frac{-i'}{i(i-\delta)}} = \left[ \frac{1}{\chi^F} \sqrt{\frac{\Omega RT}{aV}} \right] \ln(i) - \left[ \frac{1}{\chi^F} \sqrt{\frac{\Omega RT}{aV}} \right] \ln(A) \quad (4)$$

$$\sqrt{\frac{-i'}{i(i-\delta)}} = \sqrt{\frac{\alpha_2 \varepsilon \Omega}{RT}} \quad (5)$$

and

$$\frac{\sqrt{-i'}}{i} = \sqrt{\frac{\alpha_2 \varepsilon \Omega}{RT}} \quad (6)$$

respectively. In these expressions, i' is the differential of

the current with respect to time during oxide film thickening, δ is the steady state current density, χ is the cation oxidation state in the oxide film, Ω is the mole volume of the film per cation, a is the half jump distance in the HFM, V is the over potential (magnitude of the voltage step), α<sub>2</sub> is the transfer coefficient for the film formation reaction at the metal/film interface, and ε is the electric field strength in the barrier layer. Comparing Equations (4) and (5) shows that the diagnostic value lies in the slope of the plot of the left sides of the equations, f(i), versus ln(i). Such a plot for the anodic oxidation of platinum in 1 M H<sub>2</sub>SO<sub>4</sub> upon stepping the potential from the double layer region to the oxide formation region after 50 hours had elapsed to achieve steady state, as indicated by the time invariance of the current density, is shown in Figure 1. with the associated parameter values being summarized in Table 1. Similar plots are obtained for different overpotentials, demonstrating that the PDM provides a superior account of the anodic oxidation of platinum than does either the HFM or the PEM, with the former not accounting for the slope and the latter not accounting for the finite steady-state current density.

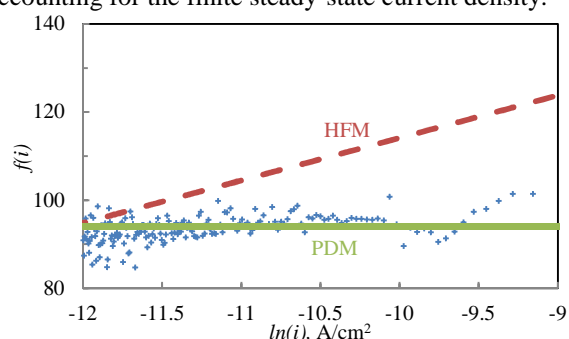


Figure 1. Potentiostatic current transient and mechanism diagnostic plot,  $f(i)$  vs.  $\ln(i)$  for platinum in 1 mol/m<sup>3</sup> H<sub>2</sub>SO<sub>4</sub> at 20 ± 2 °C. Potential stepped from 0.4V<sub>SCE</sub> to 1.1V<sub>SCE</sub>.

Table 1. Parameter values used in the computation of  $f(i)$  versus  $\ln(i)$ .

|          |   |                      |
|----------|---|----------------------|
| $\chi$   | Cation valence                                      | 2                    |
| $F$      | Faraday's constant, C/mol                           | 96485                |
| $\Omega$ | Molar volume per oxide cation, cm <sup>3</sup> /mol | 14.97                |
| $R$      | Gas constant, J/mol·K                               | 8.314                |
| $T$      | Temperature, K                                      | 293                  |
| $a$      | Half jump distance, cm                              | $1.5 \times 10^{-8}$ |
| $V$      | Overpotential, V                                    | 0.7                  |
| $\delta$ | Steady-state current density, A/cm <sup>2</sup>     | $5 \times 10^{-8}$   |

Feixiong Mao gratefully thanks the China Scholarship Council for supporting his stay in the United States.

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