

Electrocatalysis of Hydrogen Oxidation and Oxygen Reduction

Electrocatalysts supporting the oxygen electrode reaction are commonly covered with thin oxide films that may have a profound influence over the kinetics of the reaction. Although a great deal of effort has been invested over many decades in studying the kinetics of the oxygen reduction reaction on platinum and on other noble metals and alloys, the reaction mechanism and the role of surface oxide films on the electrocatalytic properties of the substrate remain controversial and poorly understood. It has been known for many decades that the oxide films present on metals play critical roles in determining the rates of redox reactions at the interface, since charge carriers must quantum mechanically tunnel through the oxide layer for the reaction to occur. Thus, the film acts as a barrier and the extreme, inverse exponential dependence of the tunneling current on the film thickness is such that films of only a few monolayers thick may substantially inhibit the reaction. On the other hand, there exists the possibility that crystallographic defects in the surface of the oxide film (e.g., surface oxygen vacancies) may act as reaction sites in the catalytic sense and hence act to enhance the reaction rate. Substantial progress is unlikely to be made in designing new electrocatalysts at the fundamental level until these factors are understood.

The current project seeks to develop a fundamental understanding of the roles played by nanoscale passive oxide films on metal and alloy surfaces in the catalysis of the reduction of oxygen and the oxidation of hydrogen over a wide range of temperature (20°C - 220°C). The approach being explored is to combine electron transfer (tunneling) theory for redox reactions with the Point Defect Model (PDM) for the growth of thin, nanoscale passive oxide films on platinum electrocatalyst surfaces. The ultimate objective is to establish theory-based rules for designing new electrocatalysts.

During this work, the physical and defect structures of the oxide films that form on platinum in acid and alkaline solutions under steady state conditions have been investigated using Electrochemical Impedance Spectroscopy (EIS) and ARXPS (Angle-Resolved X-Ray Photoelectron Spectroscopy). The n-type electronic character of the passive films formed on platinum in both acid and alkaline solutions has been resolved by Mott-Schottky analysis and a bi-layer structure was observed for films formed at potentials greater than 1.3 V_{SHE} in acid solution by ARXPS analysis. Optimization of the PDM on the EIS data obtained in acid solution yields values for various kinetic parameters that are then used to predict the steady state film thickness and current. Good agreement with experiment is obtained.

The kinetics and mechanism of hydrogen electrode reaction on platinized nickel in alkaline solution has been explored at temperatures up to 220°C, using a controlled hydrodynamic reaction cell. Our study is expected to unveil the temperature dependencies of the kinetic parameters and to indicate the reaction mechanisms at elevated temperatures. The reaction rate is greatly inhibited upon the formation of a thin oxide layer, and the logarithmic of the oxidation current decreases linearly with the potential. Figure 2 shows the polarization curves of hydrogen reaction on platinum over a wide temperature range. A new method has been developed to measure the very thin film thickness *in-situ*, by combining the tunneling theory with the PDM. It

is demonstrated to be a very sensitive and convenient *in-situ* technique. However, at the current stage, the upper limit of the film thickness that can be determined is about 2nm, due to the passive current of platinum imposing a lower limit of the current that can be measured.

The oxygen reduction and evolution reactions on passive titanium in highly acidic solutions have also been studied in our laboratory (Figure 3). It is found that the rates of the reactions depend not only on the resistance of the oxide film, but also on the concentration of the surface oxygen vacancies ($V_{O,s}^{\bullet\bullet}$), which appear to act as catalytic reaction sites. Although oxygen vacancies have been implicated in the past in the oxygen evolution reactions on oxide electrocatalysts, to our knowledge this is the first time that vacancies have been implicated in the oxygen reduction reaction [3].

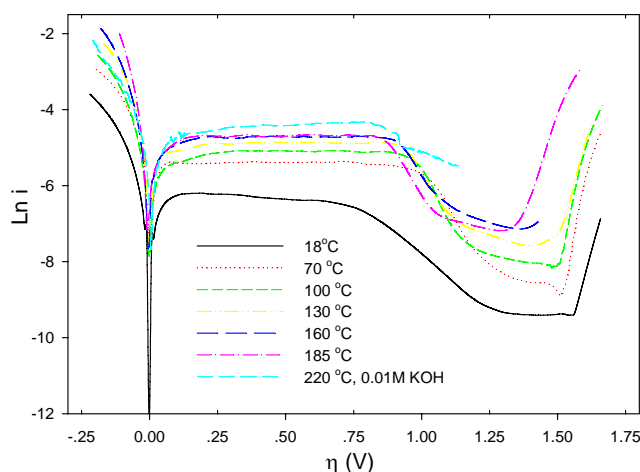


Figure 2. Quasi-steady polarization curves for hydrogen reaction on platinum over a wide temperature range in 0.1M KOH, with the impeller rotating at 400rpm, and hydrogen pressure 2.61bar (equivalent to $[H_2] = 1.824 \times 10^{-3} \text{m}$). Sweep rate: 0.5mV/s.

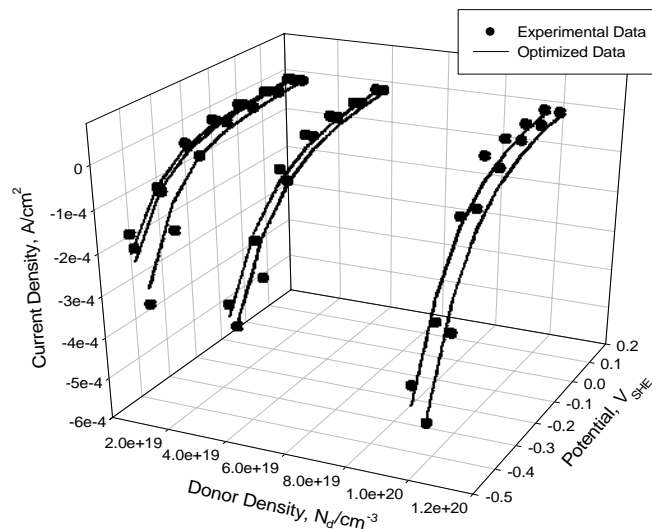


Figure 3. Experimental and optimized potentiodynamic polarization data (i versus E) for the oxygen reduction reaction on oxide films formed anodically on titanium in 0.5 M H_2SO_4 solution. The polarization behavior is adequately described by the transcendental equation $i \approx \pm ke^{\pm b(E_0 + vt - |i|\lambda L / C_{V_o}^b)} (C_{V_o}^b)^{n'}$, where the negative sign is taken for oxygen reduction, E_0 is the initial potential, v is the voltage sweep rate, λ is a constant, $C_{V_o}^b$ is the concentration of oxygen vacancies in the bulk of the film, $n' = 0.66n$, and n is the kinetic order. For the oxygen reduction reaction, $n = 0.676$, demonstrating the involvement of oxygen vacancies in the reaction [3].

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Papers:

1. Adan Sun, Janyce Franc, and Digby Macdonald. "Growth and Properties of Oxide Films on Platinum I. EIS and XPS Studies", *Journal of Electrochemical Society*, in press (2006)
2. JianEr Bao, Digby D. Macdonald. "Hydrogen Oxidation on Oxidized Platinum at Elevated Temperatures, Part I. The Tunneling Current", *Journal of Electroanalytical Chemistry in Honor of Dr. Boris Grafov*, in press (2006).
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4. M. Kamrunnahar, JianEr Bao, and Digby D. Macdonald, "Challenges in the Theory of Electron Transfer at Passive Interfaces", *Corrosion Science.*, 47, p3111 (2005).
5. JianEr Bao, Cheng-Lung Liao, Rodrigo E. Vilar Martinez, and Digby D. Macdonald, "Kinetics and Mechanism of Hydrogen Electrode Reaction on Platinum at Elevated Temperatures", *Electrochemical Society Transactions*, 209th ECS meeting, Denver, CO, in press (2006)
6. Adan Sun and Digby Macdonald. "Growth and Properties of Oxide Films on Platinum II. pH Dependence", *Electrochemical Society Transactions*, 209th ECS meeting, Denver, CO, in press (2006).

7. Adan Sun and Digby Macdonald. "Growth and Properties of Oxide Films on Platinum I. EIS and XPS Studies", *207th ECS meeting*, Quebec City, Canada, May 2005
8. JianEr Bao and Digby D. Macdonald, "Oxidation of Hydrogen on Oxidized Platinum and Film Thickness Measurements by Tunneling Spectroscopy", *Proceedings of 207th ECS Meeting, Electrocatalysis Symposium*, Quebec City, Canada, to be published (2005).

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