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## Activation Energies for Oxygen Reduction on Platinum Alloys: Theory and Experiment

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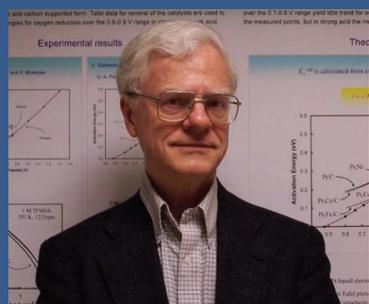
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*We present a quantum chemical and experimental analysis of the electrode-potential dependencies of activation energies for the first step in oxygen reduction over platinum and platinum-alloy catalysts in both polycrystalline and carbon-supported form. Tafel data for several of the catalysts are used to predict potential-dependent activation energies for oxygen reduction over the 0.6-0.9 V range in acid. Comparisons with the theoretical curve show good agreement above 0.8 V, suggesting a fairly constant pre-exponential factor. Arrhenius determinations of activation energies over the 0.7-0.9 V range for strong acid trend with the potential, as predicted by theory. These combined results provide strong support that, during the four-electron reduction of O<sub>2</sub> to H<sub>2</sub>O on fuel-cell platinum cathodes, the first electron-transfer step has the highest activation energy.*

Determining the compositions and structures of electrocatalyst surfaces and the mechanisms and kinetic parameters of reactions occurring on them are goals at the frontier of the field of electrochemistry. In this study, we found that measured kinetic results for oxygen reduction on unsupported polycrystalline platinum and platinum alloy (Pt<sub>3</sub>M) electrodes and on carbon-supported nanoclusters are quite similar. The similarity is justified theoretically with a simple local reaction center model for the first reduction step, which involves just two Pt atoms.

For the unsupported electrodes studied by the Lawrence Berkeley National Laboratory (LBL) group, surface compositions were determined using low-energy ion-scattering (LEIS) spectroscopy. The group found that the annealed electrodes were covered with a Pt skin. Supported nanoclusters studied by the Northeastern University group were characterized using x-ray diffraction (XDS), x-ray absorption near edge fine structure (XANES), and extended x-ray absorption fine structure (EXAFS) spectroscopies at beamline X11A. That group determined, respectively, nanocatalyst particle sizes, atomic ratio, and atom-coordination and nearest-neighbor distances. They found that the particles have average sizes of 2.5 nm for Pt/C, 3.6 nm for PtCo/C, and 3.9 nm for PtFe/C. The XANES and EXAFS results were consistent with Pt<sub>3</sub>M alloy composition and the presence of a Pt skin on their surfaces.

Rotating disc electrodes were used to ensure accurate current density measurements at the chosen electrode potentials, and the temperature dependencies yielded Arrhenius activation energies. For all the unsupported polycrystalline electrodes (Pt, sputtered Pt<sub>3</sub>Ni and Pt<sub>3</sub>Co, and annealed Pt<sub>3</sub>Co), activation energies centered on 0.24 eV ± 0.025 eV and did not demonstrate a dependence on potential, the results being the same as earlier studies of supported nanoparticles at LBL. In its measurements of supported nanoclusters, the Northeastern group was able to reduce the uncertainties in activation energies to about 0.02 eV for Pt/C and 0.005 eV for PtCo/C. For PtFe/C the uncertainties were the same as in the LBL measurements. The Northeastern activation energies for Pt/C and PtCo/C displayed the same trend as the theoretically



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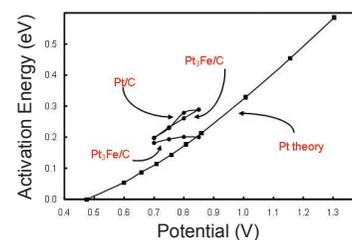
predicted electrode potential values, as shown in **Figure 1**. The theoretical values determined using the local reaction center model electron transfer theory developed at Case Western Reserve University (Case) are systematically about 0.1 eV smaller than the Arrhenius values, for unknown reasons.

We then took the Arrhenius/Tafel expression

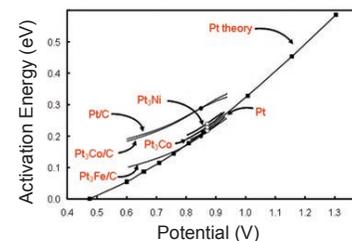
$$\log[i(U)] = \log(A) - E_a(U)/(2.3026RT)$$

where  $i$  is the kinetic current density,  $A$  is the preexponential factor,  $U$  is the potential, and  $E_a$  is the activation energy, and determined the  $A$  values by fitting one of the experimental  $E_a$  values. With the  $A$  values, we used the above equation to calculate activation energies, as shown in **Figure 2**. The trends in  $E_a$  vs.  $U$  over the 0.8 V – 0.95 V range are in good agreement with the trend predicted at Case.

The overall agreement between the theoretical predictions and the measured current densities suggest that (i) the first electroreduction step, forming adsorbed OOH, is the rate-limiting step; and (ii) the active catalyst sites for the various catalyst systems are similar, and the presence of alloying atoms adjacent to the active site does not dramatically affect the activation energy. The ability to calculate qualitative apparent activation energies as functions of electrode potential from the Tafel plot data suggests that the surface density of active sites may remain fairly constant over the 0.8 to 0.95 V range on each of the catalysts.



**Figure 1.** Experimental activation energies at different electrode potentials (SHE) for carbon-supported Pt, Pt<sub>3</sub>Co, and Pt<sub>3</sub>Fe in 1M CF<sub>3</sub>SO<sub>3</sub>H.



**Figure 2.** Calculated activation energies at different electrode potentials (SHE) determined from Tafel plots data. Open circles are for unsupported electrodes at LBL and filled circles are for supported nanoparticles at Northeastern.