

# Stability of Pt-3d-Pt Bimetallic Cathode Electrocatalysts for PEMFC

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## Introduction

Proton exchange membrane fuel cells (PEMFC) have the potential to be a commercially viable next generation portable or stationary power source. However, currently the cost of such a device is still prohibitively high due partially to the expensive raw materials used for the cathode and anode electrocatalyst [1]. This study focuses on the cathode electrocatalyst. The industrial standard for the cathode for many years has been pure platinum, which has the highest activity for a pure electrocatalyst for the oxygen reduction reaction (ORR) [2]. However, due to the cost of platinum, it is necessary to reduce the amount of platinum loading while keeping at least the same activity as platinum to allow PEMFC to become competitive in the consumer market.

One method of reducing the amount of platinum loading and still retain the same or even better activity of pure platinum is to substitute in a transition metal from the 4<sup>th</sup> row of the periodic table (hereon referred to as a 3d group transition metal). Even more, it has been shown in literature that these Pt-3d bimetallic electrocatalysts have shown enhanced activity for the ORR. However, this increased activity occurs only for the subsurface configuration in which the 3d transition metal layer resides under a layer of epitaxial platinum [3]. If the 3d transition metal segregates to the surface, the activity for the ORR will decrease even below that of Pt. Since this enhanced activity occurs only for a specific configuration, this study focuses on quantifying the stability of the 3d transition metal (Ti, V, Cr, Mn, Fe, Co, and Ni) to remain in the 2<sup>nd</sup> layer of the substrate when exposed to cathode-like environments (O<sub>2</sub>, O, H<sub>2</sub>, H, OH, and H<sub>2</sub>O<sub>2</sub>) [4].

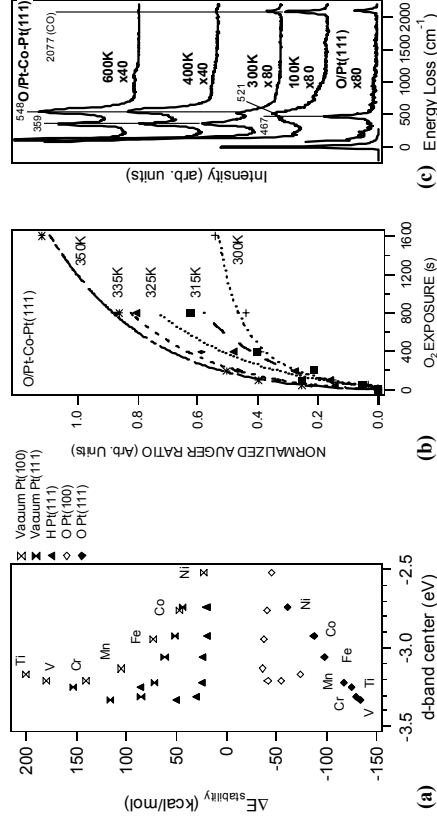
## Materials and Methods

Pt-Ni and Pt-Co bimetallic systems were studied on Pt(111) single crystals and also polycrystalline Pt films using Auger electron spectroscopy (AES) and high-resolution electron energy loss spectroscopy (HREELS). Density functional theory (DFT) modeling of Pt-3d-Pt(111) and Pt-3d-Pt(100) bimetallic systems (Ti through Ni) were performed using Dacapo v2.7 total energy program with various adsorbates (O<sub>2</sub>, O, H<sub>2</sub>, H, OH, and H<sub>2</sub>O<sub>2</sub>).

## Results and Discussion

The thermodynamic stability of the Pt-3d-Pt(111) and Pt-3d-Pt(100) bimetallic systems were predicted using DFT shown in Figure 1(a). DFT predicts that while all of the Pt-3d-Pt systems are thermodynamically stable in vacuum and with a 0.5 ML hydrogen, all of these systems are unstable with a 0.5 ML oxygen layer adsorbed. For Pt(111), it is predicted that the Pt-Ni-Pt(111) is the most stable Pt-3d-Pt(111) system. For the Pt(100) face, however, the Pt-Mn-Pt(100) is predicted to be the most stable subsurface configuration in oxygen. These predictions agree well with the kinetic and vibrational experiments conducted in UHV for Pt-Co and Pt-Ni on Pt(111) and polycrystalline Pt foil. Figure 1(b) demonstrates the instability of subsurface Co in Pt(111) when exposed to O<sub>2</sub>. Pt-Ni-Pt(111) was found to have a higher

activation barrier to surface segregation than Pt-Co-Pt(111) as predicted by DFT. Figure 1(c) shows the vibrational spectrum of O<sub>2</sub> dosed onto Pt-Co-Pt(111) and the resulting surface segregation of Co with increasing temperature.



**Figure 1.** (a) DFT predictions of the thermodynamic stability of the Pt-3d-Pt(111) and Pt-3d-Pt(100) bimetallic systems when exposed to vacuum, O, and H. ( $\Delta E = E_{\text{Pt-3d-Pt}} - E_{\text{3d-Pt-H}}$ ). (b) Normalized Co/Pt Auger ratio as a function of oxygen exposure at various exposure temperatures. 0 corresponds to all of the Co in the subsurface and 1 corresponds to all of the Co on the surface of Pt(111). (c) HREELS vibrational scan of 200 L of O<sub>2</sub> dosed onto Pt-Co-Pt(111) at various temperatures.

## Significance

While the subsurface Pt-3d-Pt(111) configuration has demonstrated increased activity for the ORR over pure Pt, the instability of these bimetallic surfaces will hinder the durability of this type of electrocatalyst. This study demonstrates the need to stabilize the subsurface 3d transition metal in order to take full advantage of the increased activity. Bimetallic catalysts could potentially reduce the amount of platinum loading by up to 85% if the platinum nanoparticle is replaced with a stable platinum coated 3d transition metal nanoparticle and thus reduce the raw material cost of this technology.

## References

1. H. Tsuchiya and O. Kobayashi, International Journal of Hydrogen Energy 29, 985 (2004).
2. K. Kinoshita, *Electrochemical Oxygen Technology*. (John Wiley & Sons, Inc., Pennington, 1992).
3. V. Stamenković, T.J. Schmidt, P.N. Ross, and N.M. Marković, Journal of Electroanalytical Chemistry 554-555, 191 (2003).
4. C.A. Menning, H.H. Hwu, and J.G. Chen, J. Phys. Chem. B. 110, 15471 (2006)