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## Lower Activation Overpotential for Oxygen Reduction Reaction (ORR) at a Proton Exchange Membrane Fuel Cell Interface: An Electrochemical and *In Situ* XAS Investigation

S. Mukerjee and R. C. Urian (Northeastern U.)

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**Introduction:** The principle causes of the poor kinetics of the four-electron oxygen reduction reaction can be attributed mainly to the low exchange current density of the oxygen reduction reaction<sup>1, 2</sup>. The high cathodic overpotential loss of  $\sim 220$  mV, at potentials close to the open circuit with the current state of the art low Pt loading electrocatalysts is attributed to a mixed potential that is set up at the oxygen electrode. The mixed potential is due to a combination of slow O<sub>2</sub>-reduction kinetics and competing anodic process such as Pt-oxide formation and/or impurity oxidation<sup>3</sup>. Further, the low exchange current density of the O<sub>2</sub>-reduction reaction results in a semi-exponential Tafel like behavior, indicating that the reaction is activation controlled over three orders of magnitude in current density. It has been determined that the exchange current density of O<sub>2</sub>-reduction is 5-6 orders of magnitude lower than that of H<sub>2</sub>-oxidation reaction<sup>1,4</sup>.

Further breakthrough in performance therefore requires changing to an alternative electrocatalyst system. A review of the solid state electrochemistry of materials available for interface with proton exchange membrane fuel cells clearly shows that the Pt based alloy electrocatalysts offer the best prospect for achieving the highest possible performance levels with long term stability. Significant improvement of ORR electrocatalysis on Pt based alloy systems therefore requires a two fold effort. Firstly, inhibiting the formation of adsorbed oxygenated species (primarily Pt-OH) beyond 0.8 V, a known surface poison and secondly, change the electronic and short range atomic order around Pt to induce alternative lower energy pathways for improved ORR kinetics.

**Methods and Materials:** Binary alloy electrocatalysts (such as PtCo and PtNi) were prepared in-house using a colloidal 'sol', approach with co-reduction of precursor salt solution in an aqueous solution. This was followed by incorporation onto specially modified carbon supports (Vulcan XC-72R) to enable 30% metal loading. Electrodes were prepared in-house with electrocatalyst loading of 0.4 mg/cm<sup>2</sup>. All the binary alloy electrocatalysts were evaluated relative to commercially available state of the art Pt/C electrodes (E TEK, Denora N.A., Somerset, NJ) with 0.4 mg/cm<sup>2</sup> and metal loading in electrocatalysts at 20 %. Standard steady state polarization measurements were conducted at 85°C in a 5 cm<sup>2</sup> fuel cell test set up capable of simultaneous single and half cell measurements. In addition a variety of methods were used to characterize the electrocatalysts, which included, TEM, XRD, and *in situ* x-ray absorption measurements (XAS) at the National Synchrotron Light Source (NSLS) in Brookhaven National Laboratory (BNL). Table 1 lists the results of some of these measurements. Further, insights into the lower overpotential losses with binary alloys and the possible formation of a skin effect where an outer skin of Pt is formed on the alloy metal clusters was also conducted using a specially constructed *in situ* spectro-electrochemical cell using synchrotron based XAS. Details of this approach is given elsewhere<sup>5</sup>

**Results:** The results of these investigations have shown that the alloy electrocatalysts such as the PtCo/C, PtCr/C and the ternary alloy PtCoCr/C exhibit up to 50 mV lowering of the activation overpotential which translates to approximately five fold enhancement in current density at a potential such as 0.5 V. These higher activity for ORR has been the subject of our present investigation. The motivation was to build up on the wealth of previous data<sup>5</sup>, and specifically investigate the following: (A) The role of surface OH species created as result of anodic activation of water in the aqueous environment of the hydrated membrane, on the overpotential. This was based on the original premise that the surface adsorbed OH species is poisonous to ORR. Our current data using *in situ* XAS at the Pt L edge (L<sub>3</sub> and L<sub>2</sub>) shows unambiguously that the alloying of Pt with first two transition elements such as Co and Cr, results in a shift in the onset of Pt-OH formation. This is evident from comparison of the Fourier transforms of EXAFS measured at 0.54 and 0.84 V vs. RHE. The Pt L<sub>3</sub> edge spectra at 0.54 V, conducted in a sealed electrochemical cell, implied that the measured response both for XANES and EXAFS was devoid of influence any anionic adsorbed species on the Pt surface. This is because the potential of 0.54 V is close to the potential of zero charge and well within the double layer region. However 0.84 V is beyond the onset potential for Pt-OH formation. Therefore, as expected Pt-O interactions are evident from the Fourier transforms of the Pt L<sub>3</sub> edge EXAFS (figure 1). This is not evident from the corresponding comparison of the 0.54 and 0.84 V Fourier transforms (figure 1), which shows the spectra for a PtCr/C. This is a direct spectroscopic evidence of a shift in PtOH formation. This is corroborated with electrochemical evidence. These include lower charge for CO stripping on the alloys as compared to Pt/C. A lower CO stripping charge indicates that OH species on the surface are present at a lower level. In addition comparison of the cyclic voltammograms show that the peak for Pt-OH formation is absent for the alloys as compared to Pt/C (figure 2). In addition, *in situ* XAS spectra was taken at the K edge of the alloying element with the electrode polarized at 0.9V vs. RHE. Comparison of the spectra for period up to 10 hours show no evidence of dissolution or corrosion of the alloying element.

**Conclusions:** The conclusions of this work are as follows:

- (A) Alloying of Pt with first row transition elements results in enhanced ORR activity, due to a lowering of the activation overpotential. In this present work a lowering of about 50 mV for PtCr/C was realized.
- (B) The lowering of the activation overpotential is at least partly due to the shift in the onset potential of Pt-OH formation on the alloy surface.
- (C) The in situ XAS at the K edge of the alloying element clearly indicates that the more oxidizable element in the binary and ternary alloys are stable even at high potentials such as 0.9 V.

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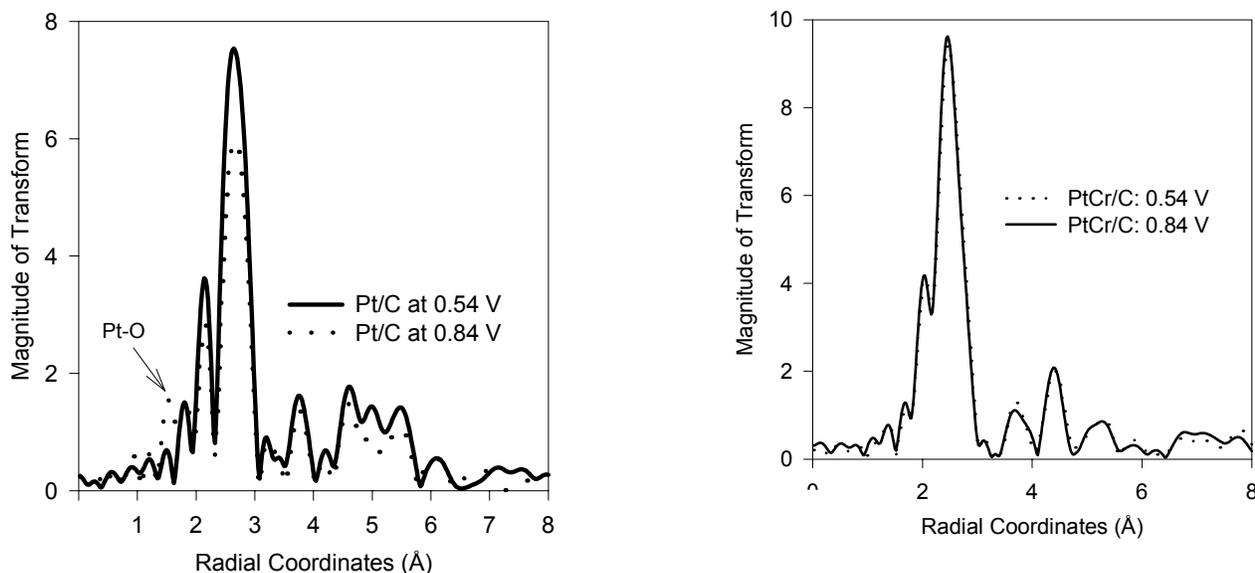


Figure 1. Comparison of the EXAFS at Pt L<sub>3</sub> edge for (a) Pt/C and (b) PtCr/C at 0.54 and 0.84 V vs. RHE.

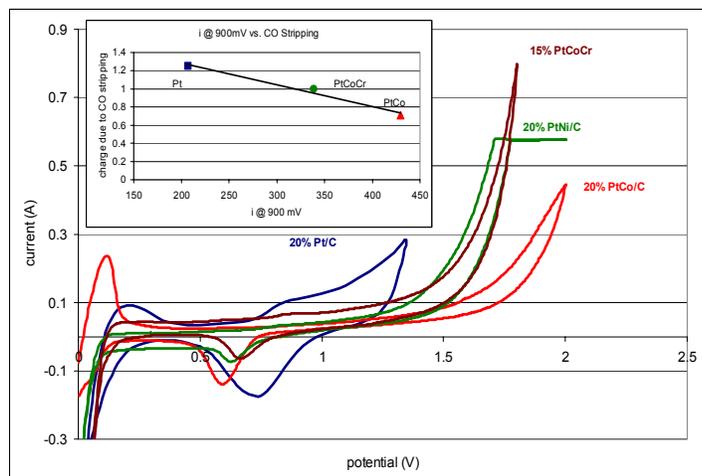


Figure 2. Cyclic voltammograms of binary and ternary Pt alloy electro-catalysts [PtCo/C, PtNi/C] compared with Pt/C. Inset shows the charge for CO stripping on the same electrocatalysts.