Lowering Activation Overpotential for Oxygen Reduction Reaction (ORR) in a PEM Fuel Cell: New Insights and Directions

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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[1, 2]. The high cathodic overpotential loss of ~ 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_2-reduction kinetics and competing anodic process such as Pt-oxide formation and/or impurity oxidation[3]. Further, the low exchange current density of the O_2-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_2-reduction is 5-6 orders of magnitude lower than that of H_2-oxidation reaction[1,4].

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.

Experimental

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^2. All the binary alloy electrocatalysts were evaluated relative to commercially available state of the art Pt/C electrodes (ETEK, Denora N.A., Somerset, NJ) with 0.4 mg/cm^2 and metal loading in electrocatalysts at 20 %. Standard steady state polarization measurements were conducted at 85°C in a 5 cm^2 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[5]

Results

Table 1 shows the results in *ex-situ* XRD and *in situ* XAS measurements to determine (a) the particle size, (b) Pt *d-band* vacancies and (c) the Pt-Pt bond distance & lattice parameters. The results on the particle size and lattice parameters are in good agreement. A remarkable degree of crystallinity is exhibited by the clusters so prepared by the colloidal sol methods. In addition, alloy formation is evident from the changes afforded to the Pt electronic states and the Pt-Pt bond distances. Figure 1 shows the *i*R corrected Tafel slopes showing a clear enhancement of ORR activity. These results will be presented in detail during the symposium as well as the results of the *in situ* XAS measurement and analysis.

Table 1

Electro catalyst	Lattice Parameter (Å)		Pt *d-band* vacancy	Particle Size (Å)	
	XRD Lattice Param. (Pt-Pt bond distance)	EXAFS Pt-Pt bond distance		XRD	EXAFS
Pt/C	3.927 (2.77)	2.77	0.33	28	35
PtNi/C	3.812 (2.695)	2.71	0.368	35	35
PtCo/C	3.854 (2.725)	2.72	0.409	31	31

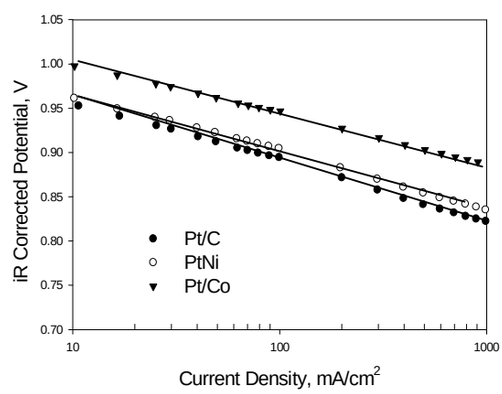

Figure 1. *i*R corrected Tafel plots for Pt/C, PtNi/C and PtCo/C for oxygen reduction at 85°C in H_2/O_2 with 16/11 psig back pressure.

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