In Situ XAFS studies of the oxygen reduction reaction on carbon supported Pt and PtNi(1:1) catalysts

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Abstract. Platinum-nickel alloys have been considered one of the promising alternative catalysts for replacement of Pt since they show higher reactivity with less usage of Pt. To elucidate the role of Ni in the various stages of the oxygen reduction reaction and the corresponding changes to Pt in comparison with pure Pt clusters, we have conducted Pt L₃ and Ni K edge in situ XAFS measurements on carbon supported Pt and PtNi(1:1) nanoparticle catalysts under a wide range of operating potentials. We observe that in PtNi alloys the Pt-Pt bond distance is shorter and the distribution of Pt and Ni is non-uniform: Pt has a tendency to be found on the surface while Ni is mostly in the interior of the catalyst nanoparticles. In addition, while a change in oxidation of the pure Pt nanoparticles is clearly observed at different potentials, the Pt in the PtNi alloy remains nearly oxygen-free at all potentials but an accompanying oxidation change of Ni has been observed instead. This phenomenon suggests that the presence of Ni in the nanoparticle inhibits the coverage of oxygen adsorbate on Pt surface, resulting in more active sites on the Pt surface.

1. Introduction
Pt bimetallic alloys have received considerable attention since they show better oxygen reduction reaction (ORR) reactivity than pure Pt with relatively lower Pt loading [1]. However, in general the explanation of the improvement relevant to ORR mechanics due to Pt-M alloy is still a matter of controversy. The dissociation of oxygen molecules has long been considered the rate determining step for ORR. Recently, however, the removal of adsorbed oxygen species has come under equivalent scrutiny to help understand the electroactive properties of ORR catalysts [2,3]. Specifically, the accumulation of oxygen-containing adsorbates on the platinum surface during operation reduces the number of Pt active sites, thus impeding further dissociation of oxygen molecules. As a result, the overall rate of ORR is slowed and accompanied with an increase in the overpotential, which reduces the performance of PEMFCs with Pt cathode catalysts [2].

We report, here, a comparative study of PtNi(1:1)/C alloy and Pt/C nanoparticle cathode catalysts under different potentials, using an operando fuel cell and realistic catalyst loading. X-ray Absorption Spectroscopy (XAS) measurements taken at both Pt L₃ and Ni K edges provide potential-dependent local structural information about the oxygen adsorbates during ORR. The
results indicate that the Ni attracts oxygen more strongly than Pt, leaving the active platinum surface cleaner than in pure Pt clusters during the entire process, especially in the high potential region. Accordingly, a higher open circuit voltage has also been observed for PtNi(1:1)/C alloy catalysts. These results indicate a promising direction toward understanding why the inclusion of transition metals result in enhanced ORR activity relative to pure Pt.

2. Experimental Procedure
The Membrane Electrode Assembly (MEA) was prepared with standard procedures described elsewhere [4]. Nafion 117 was used as the membrane material with two kinds of carbon-supported electrocatalysts utilized on the cathode: 20Pt/C (Alfa Aesar, HiSpec 3000 stock #35849, lot #A305023) and PtNi(1:1)/C (30% acid washed, special made by E-Tek E1030523). The corresponding electrocatalysts loading were ca. 1.2mg/cm$^2$ and 1mg/cm$^2$ individually. In order to avoid interference with the desired Pt signal, the electrocatalyst utilized on the anode side was Pd/C (Alfa Aesar stock #38309, lot #C02R014) with a loading ca. 1.2mg/cm$^2$. The MEA was loaded into a newly designed fuel cell system with an open electrode as an air-breathing cathode [5]. The open circuit voltages were measured to be 780 mV and 860 mV for the cells with Pt/C and PtNi/C cathodes, respectively.

The XAS experiments were carried out at the Materials Research Collaborative Access Team (MRCAT) beamline, Sector 10ID [6], at the Advanced Photon Source at Argonne National Laboratory. The liquid nitrogen cooled Si (111) monochromator was operated in continuous scan mode with an entire spectrum collected in 2 minutes. The gas mixture in the 30 cm Io chamber were tuned to 10% absorption and the 5 cm fluorescence chamber was filled with 100% Ar. An appropriate metal foil (Ni, Pt metal) was used for energy calibration. The fuel cell was initially conditioned by operating at 50°C with humidified H$_2$ flowing on the anode and air flowing over the cathode. The in situ XAS measurements were performed at the Pt L$_3$ and Ni K absorption edges. Measurements were made at different electrode potentials from 0 mV (short circuit) to 900 mV (in the overpotential region) using an EZStat (NuVant Systems, Inc.). Data were collected for at least one hour at each potential to ensure that any time varying effects could be removed during the analysis. The data were processed and fitted using the Iffeffit-based Athena and Artemis programs [7,8]. Multiple scans were rebinned, merged and normalized with background removed using the AUTOBK algorithm. The $\chi(R)$ were modeled using single scattering paths calculated by FEFF6L [9].

3. Results and Discussion
Since the white line of the Pt L$_3$ edge arises from $2p_3/2$ to empty 5d electronic transitions, the variation of white line intensity is correlated with and provides a sensitive probe of the abundance of oxygen adsorbates around Pt [10,11]. Figure 1 shows the Pt L$_3$ edges for Pt/C and PtNi/C at 0 mV and the difference spectra around the Pt white line for both the Pt and the PtNi catalysts at selected potentials using the 0 mV data as the reference. Strikingly, the Pt catalyst shows a significant variation with potential while the PtNi exhibits virtually no change at the Pt edge.

In order to provide a more quantitative assessment of the potential dependent effects, we performed fits of the EXAFS spectra for both electrocatalysts to extract the structural parameters of the metal clusters and the average number of absorbed oxygen around Pt (and Ni). In all cases, we fit $\chi(R)$ in the range 1.3Å<R<3.3Åwith multiple k-weighting ($k^1$, $k^2$, $k^3$). After the initial individual fits were completed, it was evident that many of the fitting parameters of the metallic core of the catalyst nanoparticles remained unchanged as the potential varies. Therefore, all the data were fitted simultaneously across all potentials, with a common set of parameters for the metal-metal scattering paths. Additionally, for the PtNi/C catalyst, the Pt and Ni spectra were fit simultaneously, with a restriction that the Pt-Ni and Ni-Pt distances and
Figure 1. Pt L3 absorption edge (a) for Pt/C (black) and PtNi/C (light grey) at 0 mV and difference in normalized absorption for 530 mV (black), 780 mV (light grey) and 900 mV (dark grey) potentials in (b) Pt/C, and (c) PtNi(1:1)/C catalyst. The Pt spectra at 0 mV were used as reference.

$\sigma^2$ be the same. Metal-oxygen paths were included for each potential with a common path length and $\sigma^2$ fixed to 0.01 in order to stabilize the fits and extract an average number of metal-oxygen bonds. The results of the metal core fits and the metal-oxygen distances are reported in Table 1 and representative fits to the 900 mV potential data, showing the magnitude of $\chi(R)$ and the Fourier filtered $\chi(k)$ are presented in Figure 2. The average number of metal-oxygen bonds as a function of potential for both catalysts is shown in Figure 3. The data taken at 0 mV and the Pt edge of the PtNi catalyst, when fit independently showed no evidence of significant Pt-O or Ni-O bonds and therefore, we applied additional constraints. For the Pt edge path in PtNi/C, the effective number of Pt-O bonds was refined as a single parameter across all potentials. This resulted in an upper limit of detectability represented in Figure 3 by the horizontal line. The Ni-O path for the 0 mV data yielded a value of $N_{Ni-O} = 0.52 \pm 0.75$, effectively zero. This is shown in light grey in Figure 3.

The results of the metal core fits shown in Table 1 indicate that the total number of metal neighbors of Pt in PtNi/C is the same as for the Pt/C catalyst, while the total metal neighbors of Ni is close to the nominal value expected for a bulk FCC structure. This indicates that the PtNi/C catalyst has an outer layer primarily composed of Pt with most of the Ni below the surface, supporting the theory that Pt will segregate to the surface of a PtNi alloy, driven by negative segregation energies [12,13]. The 1.8:1 and 2.4:1 ratios of $N_{Pt}/N_{Ni}$ near neighbors around Pt and Ni, respectively indicate that the nominal composition of the PtNi/C catalyst is less than 1:1 in the metal core. This is partially a result of the acid wash performed during preparation of the membrane electrode assembly which removes the surface nickel oxide, however it may also indicate that some of the nickel is outside the cluster in an oxidized environment. The Pt-Pt bond length in Pt/C is only slightly shorter than that in bulk platinum (2.775 Å) but in PtNi/C it is significantly reduced. This is in agreement with previous reports and results in tensile force between Pt atoms which acts to modify its electronic properties [14-17]. The Ni-Ni bond length is significantly expanded compared to that in Ni metal (2.492 Å) and the Pt-Ni length is intermediate between those of Pt-Pt and Ni-Ni.

The results of the metal-oxygen bond fits shown in Table 1 show that the Pt-O distance is lengthened in PtNi/C compared to Pt/C. The Ni-O distance is significantly shorter than both of the other distances. The increase in the Pt-O distance in the PtNi/C catalyst by 0.07 Å is indicative of a Ni-induced change in the Pt electronic structure which results in a weakened
**Figure 2.** Representative data for 900 mV potential (solid grey) and corresponding fit (black dashed) in both R space magnitude (left) and imaginary component (center) and Fourier-filtered q space with Hanning window (right), (a) Pt/C; (b) Pt in PtNi(1:1)/C; (c) Ni in PtNi(1:1)/C. The solid black lines in the χ(q) figures correspond to the contribution from the metal-oxygen path.

**Table 1.** Fitting results for the metal cores and the metal-oxygen distances of Pt/C and PtNi/C nanoparticle catalysts (bond lengths in Å).

|                  | Pt/C          | PtNi/C        |
|------------------|---------------|---------------|
|                  | Pt            | Pt            |
|                  | Ni            | Ni            |
| N_{Pt}           | 8.7 ± 0.2     | 6.1 ± 0.3     | 3.7 ± 0.2     |
| r_{Pt-Pt}        | 2.479 ± 0.001 | 2.692 ± 0.003 | 2.572 ± 0.006 |
| σ_{Pt-Pt}²       | 0.0061 ± 0.0001 | 0.0061 ± 0.0007 | 0.009 ± 0.001 |
| N_{Ni}           | 3.4 ± 0.1     |               |               |
| r_{Pt-Ni}        |               | 2.635 ± 0.004 |
| σ_{Pt-Ni}²       |               | 0.009 ± 0.001 |
| N                | 9.5 ± 0.4     | 12.6 ± 0.7    |
| r_{Pt-O}         | 2.02 ± 0.01   | 2.09 ± 0.03   | 1.90 ± 0.01   |
| σ_{Pt-O}         |               |               |
| σ_{Pt-Ni}²       |               |               |
Figure 3. Number of oxygen near neighbors for Pt in Pt/C (squares) and for Ni in PtNi/C (circles) as a function of applied potential. The Ni value at 0 mV, in grey with error bars extending outside the range of the figure, is shown for completeness. The horizontal line represents the upper bound for oxygen near neighbors of Pt in PtNi.

Pt-O bond [18]. The number of Pt-O bonds at 0 mV in the Pt/C catalyst is consistent with the detectability limit and indicates that at 0 mV when the cathode is operating at maximum current, the Pt surface is essentially clear of any blocking oxygen species. As the potential is raised to the operating regime of 400-600 mV and then to the overpotential region at 900 mV, $N_{\text{Pt}-\text{O}}$ is found to be an average of 0.51, 0.14 above the detectability limit. Despite the proximity to the detectability limit and the size of the estimated standard deviations, the variation in $N_{\text{Pt}-\text{O}}$ may be considered significant, since it tracks the trends shown in the Pt/C $\Delta\mu(E)$ (Figure 1a). In the PtNi/C-containing cell, the Pt-O bonds all but disappear, leaving only a variation in the number of Ni-O bonds. This absence of Pt-O bonds is reflected in the PtNi/C $\Delta\mu(E)$ difference spectra (Figure 1b) where the potential variation is negligible for PtNi/C compared to Pt/C. At 0 mV, the Ni shows no presence of oxygen neighbors, however at higher potentials this stabilizes at an average 0.84, 0.47 above the detectibility limit and significantly more than seen in the Pt/C catalyst. While the error bars are still quite large, $N_{\text{Ni}-\text{O}}$ shows an upward trend as potential is increased. This is consistent with a slowing of the ORR and the expectation that the catalyst surface becomes saturated with oxygen adsorbates. Since the number of metal neighbors for nickel were not found to vary appreciably from 12 with potential, one may conclude that the Ni-O bonds are primarily on the small fraction of Ni which remains on the surface of the catalyst nanoparticles and that these Ni atoms have a significant amount of adsorbed oxygen.

The data presented in Figure 3 provide direct evidence that Ni inhibits the formation of blocking Pt-O bonds at all potentials by preferentially binding to oxygen species produced from the initial dissociation of oxygen molecules. Additional insight can be gained from the data taken at 900 mV, which is higher than the open circuit voltage for both Pt/C and PtNi(1:1)/C clusters. At this potential, the ORR has ceased and water activation occurs instead, re-oxidizing
the surface. This phenomenon is observed for Pt/C in both the difference spectra where the 900 mV curve is larger than at 780 mV and the number of Pt-O bonds, which trends upward at 900 mV. In PtNi/C, however, this effect is absent, indicating that even under these harsh conditions the presence of Ni is able to keep the active sites of the Pt surface free from oxygen adsorbates.

4. Summary
Pt L3 and Ni K edge in situ XAFS measurements on carbon supported Pt and PtNi(1:1) nanoparticles in an operando fuel cell have been carried over a wide range of potentials. By structural modeling of the catalyst’s metal core, we find that the Pt-Pt bond distance is shorter in PtNi/C than in Pt/C and the distribution of Pt and Ni is non-uniform: platinum preferentially occupying the surface with nickel mostly buried inside the metal core. Analysis of the metal-oxygen bonds show that in comparison to the Pt/C the platinum in PtNi/C is maintained virtually free from adsorbed oxygen at all potentials by a reduced Pt-O bond strength caused by the nickel in the metal core and the action of the surface nickel which bonds more strongly to oxygen species. The mostly platinum surface of the PtNi/C catalyst, thus has more active sites than the corresponding surface of Pt/C and this is reflected in the higher open circuit voltage observed in our experiments: 860 mV versus 780 mV. These results provide insight into the mechanism of enhanced ORR performance in a mixed metal catalyst.

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References
[1] Mukerjee S, Srinivasan S, J. Electroanal. Chem. 357, 201 (1993).
[2] Nørskov J K, Rosmeisl J, Logadottir A, and Lindqvist L, J. Phys. Chem. B 108, 17886 (2004).
[3] Zhang J, Mo Y, Vukmirovic M B, Klie R, Sasaki K, and Adzic R R, J. Phys. Chem. B 108, 10955 (2004).
[4] Stoupin S, Rivera H, Li Z, Segre C U, Korzeniewski C, Casadonte D J, Inoue H and Smotkin E S, Phys. Chem. Chem. Phys. 10, 6430 (2008).
[5] Lewis E A, Jia Q, Rivera H, Grice C, Segre C U, and Smotkin E S, manuscript in preparation.
[6] Segre C U et al., J. Synchr. Rad. Instrum.: Eleventh U.S. Conference CP521 419-422 (2000).
[7] Newville M, J. Synchrotron Rad. 8, 322 (2001).
[8] Ravel B, Newville M, Phys. Scr. T115, 1007 (2005).
[9] Rehr J J, Mustre de Leon J, Zabinsky S I, and Albers R C, J. Am. Chem. Soc. 113, 5135 (1991).
[10] Teliska M, O’Grady W E, and Ramaker D E, J. Phys. Chem. B 108 2333 (2004).
[11] Lewis E A, Segre C U and Smotkin E S, Electrochimica Acta, doi:10.1016/j.electacta.2009.06.067 (2009).
[12] Abrikosov I A, Ruban A V, Skriver H L, and Johansson B, Phys. Rev. B 50, 2039 (1994).
[13] Hammer B and Nørskov J K, Adv. Catal. 45, 71 (2000).
[14] Mukerjee S, Srinivasan S, Soriaga M, McBreen J, J. Electrochem. Soc. 142, 1409 (1995).
[15] Mavrikakis M, Hammer B, and Nørskov J K, Phys. Rev. Lett. 81, 2819 (1998).
[16] Nørskov J K et al., J. Catal., 209, 275 (2002).
[17] Kitchin J R, Nørskov J K, Barbeau M A and Chen J G, Phys. Rev. Lett. 93, 156801 (2004).
[18] Kim H J, Choi S M, Nam S H, Seo M H, Kim W B, Catal. Today, 146, 9 (2009).