

Determination of Specific Site Adsorption on Pt and Pt Alloy Electrocatalysts using *in situ* X-ray Absorption Spectroscopy

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High cathodic overpotential losses are a common feature of low and medium temperature polymer electrolyte fuel cells (PEMFCs) which can be attributed in part to electrocatalyst surface poisoning by chemisorbed OH species. Further, other "directly" adsorbed species such as anions from the electrolyte can also poison Pt sites.^{1,2} Such directly adsorbed anions also lower the fuel cell current densities by altering the hydrogen oxidation and evolution reactions at the anode. The adsorption of anions are controlled not only by electronic and physical interactions, but also by the geometry of the anion-platinum complex.^{3,4}

Recently, it has been shown that the Pt adsorbate scattering, visible in the near edge XANES region, is very sensitive to the adsorbate site symmetry. Using a novel analysis technique allows isolation of this Pt-adsorbate scattering, combined with theoretical calculations, allows for the *in situ* determination of adsorption sites on platinum electrodes utilizing Pt L_{2,3} X-ray Absorption Near Edge Structure (XANES).^{5,6} This XANES data can be interpreted with full multiple scattering theoretical results from the FEFF 8.0e⁷ code. Comparison of theory with experimental data allow unique spectral signatures to be determined for H, OH, and O in atop, bridged, and/or 3-fold fcc absorption sites. Using this technique, Teliska *et al*^{5,6} have previously determined the adsorption sites and changes with coverage, of atomic H, OH, and O on a Pt/C electrode in aqueous HClO₄ or H₂SO₄ electrolyte.

The objective of this investigation is to examine the adsorption of (bi)sulfate and TFMSA anions on Pt and Pt based alloy electrodes using X-Ray Absorption Spectroscopy (XAS). The electrodes used are Pt clusters (1.5-3 nm) supported on carbon, and therefore have a wide variety of adsorption sites where the co-adsorption of anions and O, H and OH can occur. The dependence of adsorbed anion coverage on the Pt clusters as a function of potential, cluster morphology for site preference of adsorption by the anions, and the interdependence between O(H) and anion adsorption is studied.

As mentioned above, the adsorption of anions from the electrolyte plays a role in the kinetics of the ORR by either blocking or "crowding" available adsorption sites, and by changing the electronic and/or geometric properties of the Pt clusters. We have seen evidence for all of these effects. More specifically we have seen the following:

- Significant direct anion adsorption occurs in 0.1M H₂SO₄ and 6M TFMSA, while it does not in 0.1M HClO₄ and 1M TFMSA.
- Direct anion adsorption significantly hinders O(H) adsorption and the formation of subsurface O.
- Direct anion adsorption causes the Pt cluster to become more spherical to increase exposure to the electrolyte, which weakens the Pt-Pt bonding at the surface.

d) The direct anion adsorption becomes specific only after lateral interactions from other chemisorbed species at the surface force the anions to go into specific sites

e) The effect of alloying has a profound affect on the strength of the anion adsorption, and whether specific or non-specific adsorption occurs.

A representative example of these observations is shown in Figure 1 where a comparison of the Pt-Pt coordination numbers, N_{Pt-Pt}, obtained from an EXAFS analysis of Pt/C clusters in 0.1M H₂SO₄ and HClO₄ and 1 and 6 M TFMSA is made. Even though the Pt electrodes were the same in all cases, the measurements show enhanced coordination numbers for Pt/C clusters in the first pair with 0.1M H₂SO₄ > HClO₄. These results show that when anion adsorption such as bisulfate occurs, N_{Pt-Pt} increases suggesting that the clusters become more spherical (as mentioned previously in item c above). The direct scattering from the adsorbed anions is observed in the XANES only when the anions adsorb in specific sites, and this scattering is seen only when chemisorbed OH is on the surface (items d and e above).

This presentation will focus on determination of the nature of adsorbed species on Pt and Pt alloy electrocatalysts in terms of their specific adsorption sites, these will be correlated to measured oxygen reduction kinetics.

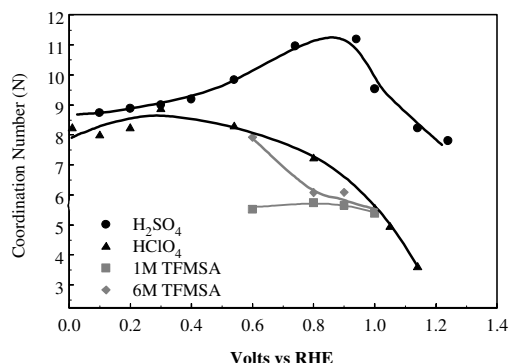


Figure 1: Comparison of the Pt-Pt coordination numbers, N_{Pt-Pt} obtained from the EXAFS analysis of Pt/C clusters in 0.1M H₂SO₄ and HClO₄ and 1 and 6 M TFMSA. The Pt electrodes were the same in the H₂SO₄/HClO₄ and 1/6 M TFMSA pairs.

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