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Embedded cluster Δ-XANES modeling of adsorption processes on Pt

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ABSTRACT

Full multiple scattering models of X-ray absorption near edge spectra of Pt Janin clusters, with atop and bridge bound oxygen, were systematically improved by increasing the number of cluster atoms contributing X-ray photoelectrons from unity (limited-absorber model), to all six Janin cluster Pt atoms, and finally embedding the Janin cluster into a larger Pt reservoir with photoelectron contributions from all atoms. The simulated XANES of the adsorbate modified clusters were subtractively normalized to their respective clean clusters to yield Δ-XANES signatures. The sequential analysis of previously published limited-absorber model, and the isolated and embedded all atoms models provide insights concerning the relative contribution of surface vs. subsurface atoms to adsorbate induced ligand effects and charge compensation provided by the bulk lattice. Limitations to the application of Δ-XANES signatures to interpretation of Δ-XANES data obtained from an air-breathing fuel cell are discussed.

1. Introduction

Adsorbate coverage potential-dependencies on distributions of sites are key factors in electrocatalysis. For example, during the oxygen reduction reaction (ORR) at cathode surfaces, diffusing dioxygen must compete with mobile anions from the electrolyte and tenaciously adsorbed oxygen for free Pt sites. While competition with mobile anions for active sites is mitigated by use of ionomer electrolytes with anchored anions (e.g., Nafion) [1], tenaciously adsorbed oxygen is more problematic. A strategy for improving ORR kinetics is alteration of the Pt electronic band structure (by alloying) to shift the oxidation potential to higher values [2–7]. A number of mixed metal catalysts have been studied as alloys and more recently as core shell structures. Model systems such as Pt skin alloys suggest that the key issue is electronic structure, with no need for alloying components on the surface [8–10]. De-alloying of Pt alloys is another strategy [11–16]. Experimental ORR studies have been complemented with computational modeling based primarily on cluster or periodic density functional theory (DFT) [17–30].

At the anode, oxygen adsorption is a key step in direct methanol fuel cell (DMFC) methanol oxidation, which occurs by a bifunctional methanol oxidation mechanism [31–33]. Although Pt oxidatively adsorbs methanol to yield adsorbed CO with ease, it cannot provide the oxygen containing species required to convert CO to CO_2 within practical DMFC anode potentials (200–350 mV vs. NHE): Practical DMFC anode catalysts are binary or ternary alloy systems where the alloying components chemisorb oxygen at lower potentials (e.g., Os, Ru, W, etc.) [31–38].

In spite of decades of sustained effort, improvements in both anode and cathode kinetics have been incremental and likely due to better preparative methods for membrane and electrode assemblies.

The ability to measure adsorption site coverage dependencies and correlate those dependencies to catalyst structure is essential if successful strategies for design of better catalysts are to evolve. Thus, subtractively normalized X-ray absorption near edge spectroscopy (Δ-XANES) has been under development for analysis of site-specific adsorption in a variety of electrochemical systems [39–45]. The XANES of the substrate under adsorbate-free conditions is used as a subtraction standard for XANES obtained under conditions conducive to adsorption (e.g., by altering the potential or chemical environment). The challenge is interpretation of the experimental Δ-XANES ($\Delta\mu$ fingerprints). Ramaker has used theoretical XANES of model clusters such as the Pt_6 Janin cluster [46] (Fig. 1), with and without adsorbates, to calculate theoretical $\Delta\mu$ fingerprints ($\Delta\mu$ signatures) [39–45]. The 6-atom Janin cluster accommodates four important oxygen absorption site configurations: atop, bridged, fcc, and hcp [46]. The clusters of Fig. 1 have been used for calculations of $\Delta\mu$ signatures using FEFF8, a full multiple scattering code that employs self-consistent-field calculations of local electronic structure [47,48]. To date, the Ramaker $\Delta\mu$ signatures for oxygen adsorption have been limited to the scatter-

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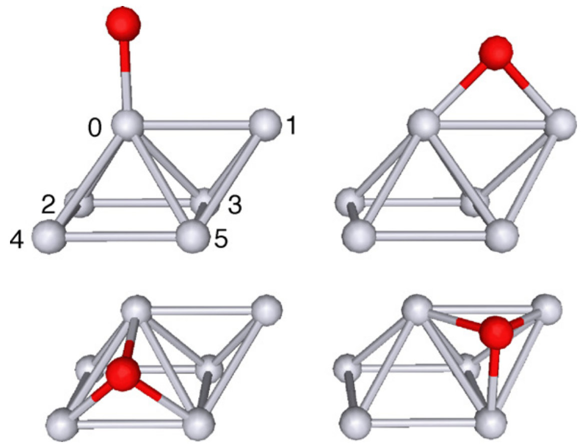

Fig. 1. Janin cluster with adsorbed oxygen. Clockwise from top left: atop adsorption, bridged adsorption, hexagonal close-packed (hcp) adsorption, and face-centered cubic (fcc) adsorption.

ing of photoelectrons originating from only one adsorbing Pt atom (atom-0 in Fig. 1) [40–42]. However, Ankudinov et al. [49] showed that changes in the near neighbor Pt-scattering potentials due to adsorbate-Pt bonds (i.e., changes in the Pt electronic structure) can be more important than the effect of Pt-adsorbate photoelectron multiple scattering. For example, the Pauling electronegativity value for oxygen is 1.3 units larger than for Pt: charge transfer from the Pt lattice to the adsorbate oxygen is expected. The withdrawal of electrons from near neighbor Pt atoms should cause a blue shift in their respective XANES spectra. Such blue shifts would be manifested as a negative dip at the low-energy side of the $\Delta\mu$ fingerprint. Fig. 2 schematizes charge transfer from neighboring Pt atoms upon adsorption of atop oxygen.

Because X-rays probe all atoms in the cluster, a first order improvement to the 1-atom (limited-absorber) $\Delta\mu$ signatures results from inclusion of absorption events from all Pt atoms (adsorbate-free and adsorbing) of the Janin cluster [50–53]. Although these all-atoms signatures, derived from isolated Janin clusters, enabled consideration of charge transfer, or ligand effects, the extent of charge depletion is overemphasized because the Janin cluster atoms are artificially under-coordinated [51,52]. The importance of metal atom coordination numbers in adsorption processes has been emphasized by Greenler [54]. A second order improvement over the limited-absorber model, that addresses the above problem involves embedding the Janin cluster into a larger reservoir of X-ray absorbing Pt atoms.

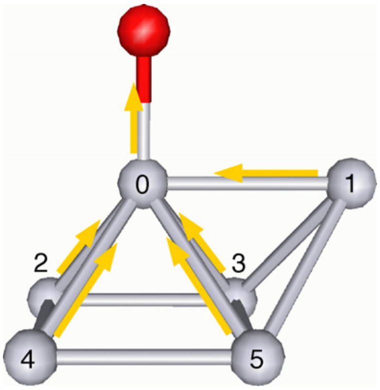

Fig. 2. A Janin cluster with atop-adsorbed oxygen. The orange arrows represent the direction of charge transfer from near neighbor atoms.

This work shows how progressive improvement of $\Delta\mu$ signature models (i.e., from the limited-absorber model of Ramaker, to the isolated Janin cluster all-atoms model, and finally to the embedded Janin cluster all-atoms model) elucidates the importance of both charge transfer effects (e.g., charge depletion and XANES blue shifts) induced by the adsorbate, *and* charge compensation by bulk Pt atoms. Moreover the isolated Janin cluster all-atoms model highlights the relative contributions to charge transfer from each Janin cluster atom. The charge depletion that results from charge transfer in the isolated cluster models is masked by charge compensation when the isolated cluster is embedded in a larger Pt reservoir (i.e., embedded all-atoms models). Thus observations extracted from progressively and systematically increasing the number of photoelectron contributors (i.e., from limited-absorber Janin cluster model to the embedded all-atoms model) contributes to the understanding of the ligand effect and charge compensation by electron density from the bulk.

2. Theory

2.1. Janin all-atoms signatures: first order adjustment

All-atoms signatures were computed for the atop and bridged adsorption configurations, modeling the Pt (1 0 0) surface. The calculations were performed using FEFF8, a full multiple scattering code [55], with the Pt–O distance fixed at 2.0 Å. The XANES for the adsorbate-free cluster and adsorption configurations were computed on a per-atom basis (0–5, Fig. 1). These simulated XANES were used to calculate per-atom $\Delta\mu$ signatures, which could be averaged without weighting or configurationally averaged to yield isolated all-atoms signatures. The criteria for the method of averaging will be discussed later.

2.2. Embedded all-atoms signatures: second order adjustment

When the atop-adsorbed Janin cluster is embedded into a 32-atom fcc Pt reservoir, the Janin cluster symmetry is increased to C_{4v} with the Pt–O bond as the C_4 axis [56]. The C_4 operation creates four equivalent atom-1 sites about atom-0. Further, atom-2, -3, -4, and -5 (the subsurface atoms) become equivalent. The increased symmetry allows for reassignment of the six available FEFF8 potentials to accommodate atoms of the Pt reservoir. Four unique potentials are distributed between the oxygen, atom-0, the atom-1s, and the subsurface atoms. The final two potentials are assigned to the reservoir. Each of the four non-reservoir (Janin atoms) potentials yields a per-atom signature. The per-atom signatures of a cluster configuration are configurationally averaged to yield an embedded all-atom signature. The configurational average weights the per-atom signatures by the multiplicity generated by relevant symmetry operations (i.e., the atom-1 per-atom signature and the subsurface atom signatures are both weighted by four because their rotation about the C_4 axis).

The bridged adsorption configuration yields C_{2v} symmetry upon insertion into the Pt reservoir. The σ_v plane bisects the oxygen, atom-3, and atom-5. The σ_v reflection makes atom-1 and -0 equivalent. Additionally, atom-2 and -4 have equal counterparts opposite of the plane. The σ_v' plane bisects the oxygen, atom-1, and atom-0. Reflection through the σ_v' plane equates the atom-2s to the atom-4s, and atom-3 to atom-5. As before, per-atom signatures are generated from the unique potentials of atom-0/1s, atom-2/4s, and atom-3/5s. Configurational-averaging weights atoms-2/4 by four, atoms-3/5 by two, and atoms-1/0 by two as per the relevant symmetry operations.