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# Structure–property–activity correlations of Pt-bimetallic nanoparticles: A theoretical study

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ABSTRACT

A novel modeling approach based on FEFF8 calculations is developed to study the relationships between the atomic structure, electronic property, and oxygen reduction reaction (ORR) activity of $Pt_3M$ nanoparticles (NPs) in combination with experimental results. We have developed a representative cluster model of $Pt_3M$ (M = Cr, Mn, Fe, Co, Ni) NPs, namely $Pt_{19}M_6$, based on experimental X-ray absorption spectroscopy (XAS) data, and demonstrated that the calculated Pt surface *d-band* center $\varepsilon_d$ can be directly related to the ORR catalytic enhancement trends exhibited by $Pt_3M$ NPs in cathode catalysts. The correlations between $\varepsilon_d$ and cluster morphology parameters such as the Pt—Pt bond distance $d_{PtPt}$ (strain effects), the Pt—M bond distance $d_{PtM}$ (interlayer ligand effects), and the choice of specific element M (pure ligand effects) are established. The results show that strain effects play a dominant role in downshifting $\varepsilon_d$ for late 3d elements, and ligand (pure ligand plus interlayer strain) effects can either upshift or downshift $\varepsilon_d$ relative to Pt depending on the near-surface morphology. The implications of the complex nature of ligand effects are discussed. This modeling approach complements the XAS technique in understanding structure–property–activity relationships of PtM NPs, and the understanding established here can be used to provide a fundamental basis for the improvement of existing cathode catalysts.



## 1. Introduction

The structure–property–activity correlations of well-characterized Pt bimetallic alloys have been established by Stamenkovic's [1,2] (on ordered extended surfaces) and Norskov's [3,4] (theoretical calculations). Their work demonstrates the crucial role played by subsurface M atoms in shifting the Pt surface *d-band* center $\varepsilon_d$, and how this alters the oxygen binding energy $\Delta E_o$ of the modified Pt surface to accelerate the sluggish oxygen reduction reaction (ORR). Both $\varepsilon_d$ and $\Delta E_o$ have been directly correlated to ORR kinetics with a general consensus of a volcano type behavior based on choice of alloying element, and regarded as good descriptors of the activity of PtM alloys [4,5]. It has also been postulated that the ORR mechanism established for bulk Pt alloy surfaces is applicable to understand the activity of supported Pt-bimetallic NPs, which are known to exhibit specific ORR activities 2–5 times higher than that of Pt [6,7]. However, accurate structure–property–activity correlations of $Pt_xM$ NPs are stymied due to the more complex nature of such NP's, and the generally poor characterization of their physical and electronic structure.

X-ray absorption spectroscopy (XAS) has long been used to study supported $Pt_xM$ NP catalysts, since it offers unique insights into electrode processes by providing simultaneously, electronic and short-range (atomic scale) structural information on the catalysts under in situ and operando conditions including ORR [6,8–10]. By studying a series of $Pt_3M$ NP catalysts using in situ XAS, Mukerjee et al. stated that the enhanced ORR activities of $Pt_3M$ NPs were related to the modified Pt—Pt bond length and Pt *d-band* vacancies [6,8]. These studies and those reported later [9,11,12] correlated these parameters to (a) the onset potential of water activation for atop and sub-surface oxides, (b) affinity for molecular oxygen binding as a function of potential and presence of surface adsorbed moieties, and (c) the self-segregation of the alloying element as a function of potential and concomitant surface adsorbed species. Later, the $\Delta\mu$ XANES (X-ray absorption near edge structure) technique pioneered by Ramaker et al. extended the XAS technique from a bulk-averaging structural technique (e.g. extended X-ray absorption fine structure (EXAFS)) into a surface adsorbate sensitive technique [13,14]. They demonstrated that the $\Delta\mu$ technique

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