

# ***In Situ* NMR/IR/Raman and *ab initio* DFT Investigations of Pt-Based Mono- and Bi-metallic Nanoscale Electrocatalysts: from Sulfur-Poisoning to Polymer Promoters to Surface Activity Indexes**

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membrane fuel cells and high temperature solid oxide fuel cells, systematic mechanistic investigations of sulfur-poisoning of Pt-based electrocatalysts in an electrochemical environment and its possible remedies have been surprisingly rare as compared to what has been done on heterogeneous catalysts in the gas phase in general. As asserted in the Feb. 2004 OBES report “Basic Research Needs for the Hydrogen Economy”, *detailed mechanistic studies of the sulfur poisoning and tolerance of anode and cathode materials in general have yet to be undertaken*. Consequently, our current insufficient electronic-level understanding of the problem represents one of the most important contemporary challenges for the development of technologically viable fuel cells. Overcoming such a hurdle is urgently needed in the basic energy science research because it is a central issue underlying the practical durability and performance of fuel cells and also determining the fuel specifications.

## **Objectives**

The proposal targets two primary objectives:

1. Significantly advance our fundamental understanding of sulfur poisoning of Pt-based mono- and bi-metallic nanoscale electrocatalysts through careful interrogation of long and short range electronic effects caused by the poisonous sulfur-metal bonding.
2. Investigate and establish correlations among the surface  $d$  band center, the frontier orbitals of the metal surface as represented by the surface local density of states at the Fermi level ( $E_f$ -LDOS), and the associated electrochemical reactivity.

Achieving these objectives will lead one step closer to achieving the long-term goal of the PI. That is, by firmly establishing fundamentally-justified and experimentally-proved detailed electronic structure – surface reactivity relationships based on crosscutting *in situ* investigations of (real-world) nanoscale electrocatalysts, like these proposed in this project (*vide infra*), the PI strives to make substantial intellectual contributions to the development of unified predictive descriptions and concepts of heterogeneous catalysts (electronic) structure and activity by which new catalytic materials with desired functionalities (e.g., activity, selectivity, sustainability, and durability) can be rationally designed and developed

## **Technical Barriers**

Although of great practical and fundamental importance in improving impurity tolerance of anode and cathode materials for both low temperature proton-exchanged

## **Abstract**

Over the current funding period (08/15/10 – present), we have achieved the following results: (1) identified the chemical state of adsorbed sulfur species on a Pt surface; (2) discovered that adsorbed sulfur species at low coverage can substantially enhance the oxygen reduction reaction (ORR), methanol oxidation reaction (MOR), and CO monolayer oxidation reaction (CMOR); (3) discovered that adsorption of PVP (polyvinylpyrrolidone) on commercial Pt black and carbon-supported Pt electrocatalysts can substantially enhance MOR and formic acid oxidation reaction (FAOR) activity. In addition, the adsorbed heavy PVP (360k) shows molecular switch-like behavior that can be used for freeing active sites for reactions at low potentials where the reactions take place and protecting and stabilizing the surface at high potentials where the bare Pt surface is most susceptible to corrosion; (4) demonstrated that the widely-used but unjustified current ratio criterion for CO tolerance in MOR is largely inadequate; (5) identified the most active surface water species in the MOR; (6) Studied the electronic properties of Pt shells in Au@Pt and Ru@Pt; and (7) Application of the condensed Fukui function to predict reactivity in core-shell transition metal nanoparticles (NPs).

## Progress Report

### 1. The chemical state of adsorbed sulfur species on a Pt surface

The chemical state of adsorbed sulfur on a Pt surface was identified and investigated by a combination of detailed electrochemical (EC) measurements, in situ surface enhanced Raman scattering (SERS) and ab initio density functional theory (DFT) calculations. The SERS data coupled with the DFT calculations provide the first convincing evidence showing that the adsorbed sulfur is in a sulfide ( $S^{2-}$ ) state.

### 2. ORR, MOR, and CMOR enhanced by sulfur adsorption

We have reported a remarkable observation that robust activity enhancement in ORR (65 mV positive shift of the half-wave potential and 133% increase in kinetic current density at 0.6 V vs. Ag/AgCl) on commercial Pt electrocatalyst (Pt/C, 40 wt. %, d ~ 4.1 nm) could be achieved by adsorbing sulfide at low coverage ( $\theta_{S,H} \sim 0.16$ ), although the strong poisoning effect did prevail at high sulfide coverage as frequently observed. This unexpected activity enhancement was ascribed to a combination of an increase of the potential of surface oxidation and weakened surface bonding. Additionally, the effect of sulfide adsorption on the reactivity of core-shell (M@Pt, M=Au and Pd) NPs in the ORR was also investigated and compared with that of Pt/C so that possible remedies to the sulfur-poisoning of a pure Pt surface at high sulfide coverage may be identified. The results showed that the Pd@Pt NPs appeared to be the most tolerant electrocatalyst towards sulfur poisoning in ORR among the samples studied.

We have investigated the effect of adsorbed sulfide ( $S^{2-}_{ads}$ ) on MOR taking place on Pt/C NPs using EC and attenuated total reflection-surface enhanced IR absorption spectroscopy (ATR-SEIRAS) techniques. The observed substantial enhancement in MOR activity per active site was rationalized by an enhanced parallel reaction pathway by the  $S^{2-}$  adsorption that did not lead to poisonous CO. Moreover, there was delayed/suppressed adsorption of electrolyte anions and oxygen-containing species and increased amounts of isolated free water monomers caused by the sulfide adsorption-induced more negatively charged Pt sites, which led to more available active sites, weakened bonding interaction between the Pt NPs and oxygen-containing species, and more active water species for MOR along the parallel reaction pathway.

We have also investigated the influence of adsorbed sulfide ( $S^{2-}_{ads}$ ) on CMOR on carbon-supported Pt/C NPs using electrochemical and in situ ATR-SEIRAS techniques. An enhanced kinetics of CMOR on the  $S^{2-}_{ads}$ -Pt/C was observed by potentiodynamic CO stripping and potentiostatic

CO oxidation analyses. EC impedance measurements revealed a weakened bonding of oxygen-containing species with the  $S^{2-}_{ads}$ -Pt/C surface as compared with the clean Pt/C surface, which we believe was the main reason for the observed enhanced CMOR by the  $S^{2-}_{ads}$ . The in situ SEIRAS data showed the existence of both linear- and bridge-bonded CO in all samples and that the sulfide adsorption substantially increased the fraction of the former on the available Pt sites and facilitated the conversion between them. Our results also indicate that the frequently observed pre-CMOR current most likely arises from oxidation of weakly-bonded CO rather than from reactions taking place at defect sites.

### 3. PVP Effects

We have discovered unexpected yet highly remarkable and intriguing observations of the PVP-enhanced electrocatalytic activity of the Pt nanoparticles for MOR and FAOR. In situ FTIR investigation suggests strongly that the observed activity enhancements are likely due to the PVP-induced additional reaction pathways. These observations may open up a new paradigm of research in which the protecting/stabilizing organic ligands can now be incorporated as an advantageous part of a nanocatalytic system.

We have also studied the effect of the commonly used 55k MW and a heavier chain of 360k MW PVP on commercial 40 wt% Pt/C using electrochemical methods and in situ SEIRAS experiments during the MOR and related gaseous CO oxidation. The PVP-modified samples exhibited an enhanced long-term CO tolerance with a small hindrance to the intrinsic activity of Pt/C. Increased water adsorption in the presence of polymer was observed to coincide with the oxidation of adsorbed CO and was related to the desorption of the surface-bound carbonyl of PVP via in situ SEIRAS. The notable differences between the adsorbate trends are indicative of adsorbed polymer interactions with the surface. Interestingly it is the strong dependence of the polymer molecular weight (Mw) that led to qualitatively different behavior. Understanding the effects of adsorbed PVP on electrocatalytic reactions is of fundamental and practical importance due to its widespread use in synthesized NPs targeted for fuel cell applications.

### 4. An unjustified current ratio criterion for CO tolerance in MOR

We have revisited a popular criterion that uses the ratio between the peak currents of the respective positive (anodic) and negative (cathodic) potential scans,  $I_f/I_b$ , in the cyclic voltammetry of methanol electro-oxidation to gauge CO-tolerance and catalytic activity of Pt-based electro-catalysts and its inadequacy was revealed by an in situ SERAIS study.

## 5. The most active surface water species in MOR

We have reported a detailed electrochemical in situ SEIRAS investigation of two different core-shell, Ru@Pt and Au@Pt/C, metal NPs. We were able to identify the most active sites and surface water species involved in the carbon monoxide oxidation reaction (COR) and MOR on these NPs. We discovered that exposing the as-synthesized Ru@Pt NPs to air could turn them into largely surface-ruthenated NPs whose structure was rather stable under multiple potential cycling between -0.2 and 0.7 V (vs. Ag/AgCl, 3 M) and reduction at -0.3 V but could be annealed by the COR. The SEIRAS data enabled the identification of the Ru coordinated to Ru, Ru coordinated to Pt, and Pt-islands on Ru -core sites on the COR-annealed Ru@Pt NPs among which the most active sites were the Pt-islands on Ru-core sites for the COR and MOR, as evidenced by an onset potential as low as -0.1 V for the COR. For the Au@Pt/C NPs, the SEIRAS data showed a much higher onset potential (0.45 V) for the COR that accounted for their much lower activity observed as compared to that of the Ru@Pt in terms of COR and MOR. Among the three different surface water species, namely the water monomer, the weakly hydrogen-bonded water, and the strongly hydrogen-bonded water, the SEIRAS data pointed to the weakly hydrogen-bonded water as the dominant source that provided oxygen for the COR and MOR. Furthermore, the SEIRAS data showed that the surface water structure was very different in reaction media, i.e., with pre-adsorbed CO or methanol, from that in pure supporting electrolyte, an observation that strongly cautions the practice of using the latter to identify the active water species.

## 6. $^{195}\text{Pt}$ and $^{13}\text{C}$ NMR study of Au@Pt and Ru@Pt core-shell electrocatalysts

Pt-based core-shell (M@Pt where M stands for core element) NPs have recently been under increasing scrutiny in the fields of fuel cell and lithium air battery electrocatalysis due to their promising prospects in optimizing catalytic activity, reducing Pt loading and consequently lowering its cost. To achieve the latter, delineating spatially resolved local (surface) elemental distribution and associated variations in electronic properties under working condition (i.e., in situ) is arguably a prerequisite of fundamental importance in investigating electrocatalysis but unfortunately is still sorely missing. In this regard, in situ  $^{195}\text{Pt}$  EC NMR of Pt-based NPs is unique in terms of accessing such information, particularly the spatially resolved partition between the s- and d-like Fermi level local density of states ( $E_F$ -LDOS) modified by the core elements. In this paper, we report a comparative in situ  $^{195}\text{Pt}$  EC-NMR investigation of Ru@Pt vs. Au@Pt NPs which was complemented by in situ  $^{13}\text{C}$  EC-NMR of the  $^{13}\text{CO}$  adsorbed on the respective NPs generated via dissociation of methanol and by ab initio DFT calculations. The results showed opposing electronic effects between Ru

vs. Au cores: the former substantially reduced the s-like but not the d-like  $E_F$ -LDOS of the Pt shell while the latter did the opposite. According to recent quantum calculations, a reduction in d-like partition would weaken the Pt–O bond while a reduction in s-like partition would weaken the Pt–H bond, which is largely in agreement with experimental observations.

## 7. The condensed Fukui function to predict reactivity in core-shell transition metal nanoparticles

Chemical reactivity descriptors are a powerful means for understanding reactivity in a wide variety of chemical compounds. These descriptors, rooted in density functional theory, have found broad application in organic chemical reactions, but have not been as widely applied for other classes of chemical species such as nanoparticles, which are the subject of this article. Specifically, we explore application of the Fukui function, the global hardness and softness, the local softness, and the dual descriptor to pure metallic and core-shell nanoparticles, with and without a CO molecule bound to the surface. We find that the Fukui function is useful in predicting and interpreting chemical reactivity, and that it correlates well with the results of the popular d-band center method. Differences in the Fukui function before and after bonding of a CO molecule to the surface of a nanoparticle reveal interesting information about the reactivity of the nanoparticle surface. The change in the Fukui function when an electric field is applied to the molecule is also considered. Though the results are generally good, some of the limitations of this approach become clear.

## Future Directions

While continuing to focus on unraveling the surface chemistry of sulfur and other conventional poisonous species on Pt-based electrocatalysts, we will explore a novel perspective of it, which was inspired by some very interesting observations made over the current grant period. Specifically, it was observed that traditionally undesirable species, such as sulfur, can actually promote, rather than poison, catalytic activity of Pt-based electrocatalysts. For instance, at relatively low coverage (<20%), adsorbed sulfur species can promote considerably COR, MOR, and ORR activity; adsorbed PVP can substantially enhance MOR and formic acid oxidation reaction (FAOR) activity; and adsorbed iodine can significantly improve the stability of PtCu alloy electrocatalyst for ORR. These observations are along the line of a new emerging area of research in which many traditional poisoning species have been observed to promote catalytic reactions. However, much of the surface chemistry that governs such behavior remains to be uncovered and their potential practical applications are largely unexplored.



**Publication list (including patents) acknowledging the DOE grant or contract<sup>1-24</sup>**

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