

# Integrated Theoretical and Experimental Studies of Fuel Cell Electrocatalysts

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Significant progress has taken place over the past decade or so in understanding catalysis in electrochemical systems. Electrocatalysts used in fuel cells are a long-standing example of the application of nanotechnology in electrochemistry. In electrocatalysis in proton exchange membrane fuel cells (PEMFCs) and direct methanol fuel cells (DMFCs), the relatively low operating temperature and the use of reformed fuels or methanol put a premium on highly active, high surface area electrocatalysts.

The efforts of the past decade did not represent a complete departure from previous work. There was a substantial base of work that defined many critical aspects of the field. However, new tools are available that enable us to look in more detail at more complex interfaces than ever before. This includes first-principles quantum mechanical methods that begin to provide reliable descriptions of elementary processes occurring in complex environments such as the surface of real-world fuel cell catalysts. Stochastic and dynamic simulations are available that can follow the kinetic and temporal behavior of these systems.

For the past several years, the authors have collaborated in a U.S. Army Research Office-sponsored Multi-University Research Initiative (MURI) entitled, "Integrated Computational and Experimental Studies of Fuel Cell Electrocatalysts." We have focused on the development, refinement, and application of theoretical tools and experimental methods to interrogate the fundamental processes that control fuel cell systems. A theoretical framework for the robust description of electrode processes is also being developed. Experimental work is a critical adjunct to the theory, providing the validation as well as additional, targeted insight into features arising from the theory. We are gathering theory and experiment into a "toolkit" and this article provides a snapshot of the status of this effort.

## The Nature of the Beast: The Fuel Cell Electrode and Attendant Issues

Fuel cell electrodes in use today are composite materials consisting of a mixture of a high surface area electrocatalyst, typically Pt or Pt alloys, with an interpenetrating proton-conducting polymer phase. These components transport electrons, protons, and gas or solution phase reactants and products to and from the electrocatalyst site. The electrocatalyst is highly dispersed to maximize available surface area per weight and can be either supported on carbon (hydrogen-air fuel cells) or introduced as a metal "black." In either instance, the precious metal catalyst particles are nanoparticles, roughly 2 to 5 nm in diameter.

In Fig. 1, we illustrate the sandwich structure of a PEM fuel cell catalyst-coated membrane and the structure of the composite fuel cell electrode.

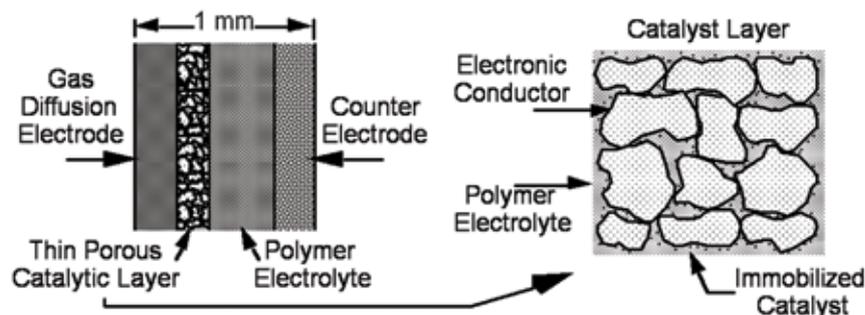


FIG. 1. Schematic of a PEM fuel cell catalyst-coated membrane and the structure of the composite fuel cell electrode.

This illustration provides a shorthand guide to issues that we can attack to deepen our understanding of the electrocatalysis issue in fuel cells, including

- the nature of the electrocatalyst (physical, electronic structure, alloying);
- the role of the support (catalyst-

- support interactions, support surface area, stability, conductivity);
- surface reactions (reaction pathways, adsorption processes, effect of potential);
- the solution side of the interface (polymer electrolyte, water); and
- long-range transport of all reagents.

## Theory Required for Describing Electrocatalysis Systems

The complexity of the electrocatalytic environment in fuel cells obscures the fundamental surface chemistry and physics. Simulation of these systems ultimately requires an integrated multiscale suite of theoretical and computational methods to traverse the disparate time and length scales that control the catalytic behavior of the materials and processes involved in real fuel cells. To this end, we have developed, validated, and applied a set of computational methods that

includes more accurate and universal quantum mechanical methods, new quantum mechanical embedding schemes to increase the speed of the calculations, coarse-grained clustering tools to model more realistic materials, and stochastic methods

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to simulate the particle structure morphology and kinetic behavior. We need appropriate methods to follow reaction pathways with reliable accuracy. This required capturing the complex behavior of the electrochemical interface including realistic materials such as metal alloys and nanoparticles and the environments in which they operate.

**Method development.** At the most basic level (i.e., the electronic structure), Scuseria developed a more accurate and universal set of exchange-correlation functionals for first-principles density functional methods<sup>1</sup> that describe the overall thermodynamics and kinetics of processes that occur over metals, alloys, and oxide surfaces. Marzari developed a novel quantum mechanical embedding strategy to more rapidly determine the electronic properties of metals. Also, he established a novel *ab initio* Car-Parinello molecular dynamics approach that included a coarse-grained dielectric continuum model to more efficiently and accurately account for solvation effects.<sup>2</sup>

Neurock and Ceder<sup>3</sup> extended *ab initio* results from surfaces to the *in silico* synthesis of nanoparticle structures and the simulation of kinetics over these surfaces. Ceder developed a clustering strategy to model the complex behavior of alloy surfaces and nanometer alloy particles. Neurock used first-principles results to derive interatomic potentials in order to simulate the optimal particle, morphology, structure, and composition and developed an *ab initio* based kinetic Monte Carlo algorithm to simulate the electrocatalytic kinetics, and performance for nanoparticle alloys within more realistic electrochemical conditions.<sup>4</sup> These simulations have been used to follow the electrocatalytic behavior at operating conditions and to screen novel binary and ternary alloys for improved electrocatalytic performance. Neurock used these methods to suggest a novel set of ternary alloys comprised of Pt/Ru/Au that might be considerably more active than PtRu catalysts.

**Introducing potential.** What distinguishes electrochemistry from surface chemistry is the electrode potential. Because of the asymmetric nature of the electrode/solution interface, periodic boundary approaches which treat non-periodic fields and potentials were required and developed by Neurock.<sup>5,6</sup> *Ab initio* descriptions of electron and proton transfer were deployed for modeling charge transfer dependent activation energies. For

example, the transition state for the first reductive addition of H<sup>+</sup> to adsorbed oxygen at the electrified Pt/water interface at 0.7 V is shown in Fig. 2.

Despite the complexity of the interface, Nørskov<sup>7</sup> has shown that the polarization of the solution phase may cancel out in comparing overall reaction energies. Anderson<sup>8</sup> showed that the electrochemical behavior follows well defined linear free energy relationships whereby the reversible potentials can be determined using solution phase standard values ( $U$ ) and the adsorption bond strengths ( $E$ ) for the intermediates formed on the electrode surface

$$U_{\text{rev}}(\text{surface}) = U^{\circ} + \Delta E(\text{adsorption})/nF \quad (2)$$

where  $\Delta E(\text{adsorption})$  is the adsorption bond strength of the products minus that of the reactants. Figure 3 illustrates the example of hydroxyl

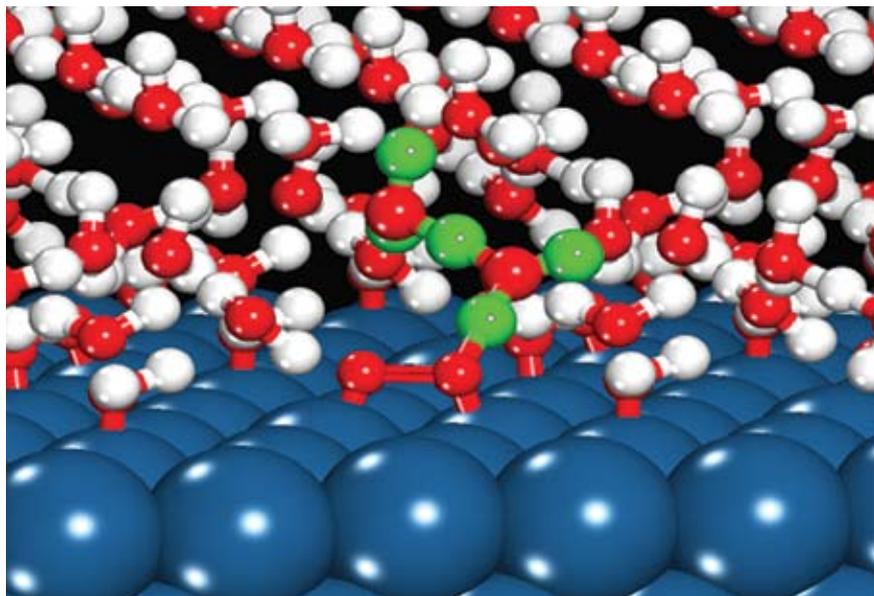


FIG. 2. *Ab initio* calculated transition state for the initial reduction of O<sub>2</sub> over Pt(111) at 0.7V.

group reduction to water. A key to low overpotentials is having weak interactions of the reactants and products with the catalyst sites, as well as low activation energy barriers for all reaction steps.

**Surface composition.** Nanoparticles are dynamic systems. Alloy electrocatalysts such as Pt-Ru (anodes) or Pt-Co or Pt-Cr (cathodes) exhibit composition changes over time in the cell due to oxidation of base components coupled to surface segregation phenomena. Surface "islands" or "skins" of one catalyst component (e.g., Pt) on another, perhaps more base, metal (e.g., Ru, Co, Cr) can be formed naturally or synthetically, with significant implications in catalysis. Thus, it is essential to address the formation, structure and reactivity of such materials.

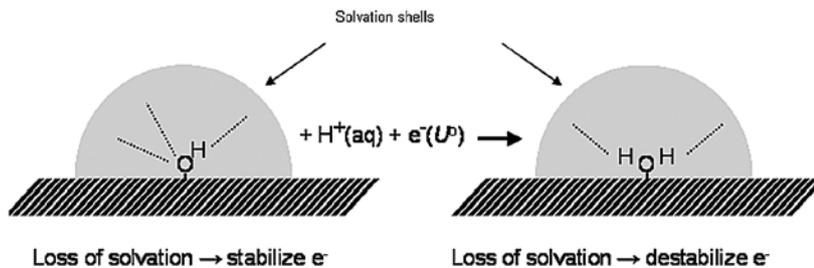
Ceder<sup>3</sup> developed a methodology to predict the equilibrated simultaneous surface segregation of alloy elements and adsorbates, using a coupled cluster expansion theory to write the state of the system in terms of adsorbate and surface layer occupation variables. Simulation of the surface ordering and segregation at a (111) surface of Pt<sub>(1-x)</sub>Ru<sub>x</sub> alloys in the presence of adsorbing oxygen showed (Fig. 4) that oxygen can induce Ru surface segregation. Under oxidation potential, Ru segregates to the surface and forms an island structure. Pt-Ru-O boundaries are important sites for CO oxidation.

## Experimental Studies

**Electronic states of electrocatalysts.** Until recently, X-ray absorption spectroscopy (XAS) was limited to providing geometric information on systems with short-range order,

i.e., the EXAFS technique. Ramaker and coworkers recently showed that electron scattering which produces the Pt L<sub>3</sub> XANES signal is very sensitive to the adsorption of O(H), H and CO. One disadvantage of XAS is the complex theoretical analysis required to obtain information from the data. However, XANES data can now be interpreted utilizing full multiple-scattering theoretical results from the FEFF8.0 code.<sup>9</sup> Mukerjee applied these techniques to obtain unprecedented detail on the nature of the interaction of O<sub>2</sub>, OH, CO, H<sub>upd'</sub> and H<sub>opd'</sub> and even OOH with Pt<sup>upd'</sup> and PtM (M = Ru, Sn, and Mo) electrodes.<sup>10</sup> This technique also can elucidate surface adsorbate reactions on non-Pt chalcogenide electrocatalyst and porphyrin moieties.

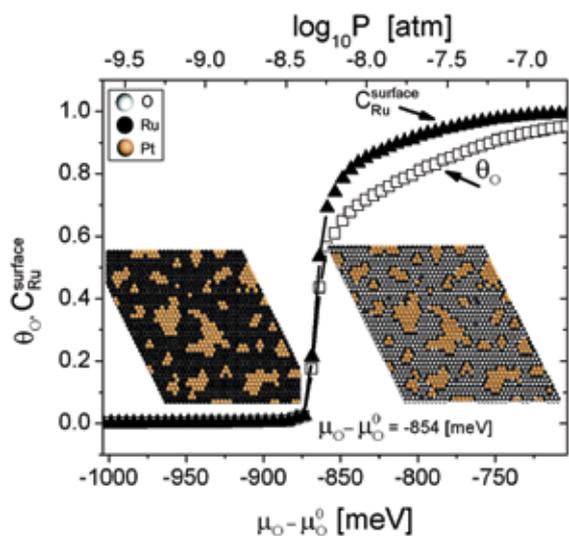
Studying the interplay of water



**FIG. 3.** Replacement of part of the bulk solvation shells with bonds to the catalyst using hydroxyl group electroreduction as a model. (see Ref. 10.)

activation and oxygen reduction overpotentials reveals the effect of transition metal alloys on OH poisoning of Pt-based electrocatalysts. Analysis

workers are developing techniques that provide unique insights into the nature of adsorbates on electrodes. Electrochemical nuclear magnetic



**FIG. 4.** Monte Carlo simulation of the surface structure evolution as a function of oxygen chemical potential,  $T$  and bulk Ru composition ( $C_{Ru}$ ).<sup>3</sup>

of water activation at the respective K edges of the alloyed transition metals in addition to the  $I_{Pt}$  edge studies of the Pt portion of the alloy showed the extent to which different metals perform the “bi-functional effect,” selectively adsorbing  $OH_{ads}$  to leave the Pt free for molecular O adsorption. Until the Pt-M  $\Delta\mu$  study, such conclusions were based on theoretical DFT calculations and indirect evidence provided by the electrochemical studies.

**Chalcogenide electrocatalysts.** Pt-based electrocatalysts are ideally suited to the  $\Delta\mu$  analysis primarily because of previous extensive morphological characterizations. In contrast, chalcogenide electrocatalysts are comprised of nanoscale amorphous clusters making a detailed analysis of the structure/property relationships inherently difficult. We have applied the  $\Delta\mu$  technique to a mixed-phase chalcogenide electrocatalyst,  $Rh_xS_y$ , showing that the canted octahedral  $Rh_6$  eaves on the  $Rh_3S_4$  phase were the active site (Fig. 5).

**Adsorbed intermediates: EC-NMR and SFG studies.** Wieckowski and co-

resonance spectroscopy (EC-NMR) is a relatively new technique in electrochemistry and in fuel cell catalysis that permits a detailed study of (i) electronic structure of both anode and cathode electrodes, (ii) adsorbates on metal/alloy surfaces, and (iii) surface motions on the electrodes.<sup>11</sup> The NMR parameters (spectra and relaxation rates) can be readily interpreted in terms of the Fermi level local density of states ( $E_f$ -LDOS) Fig. 6 and diffusion constants. Experiments can be

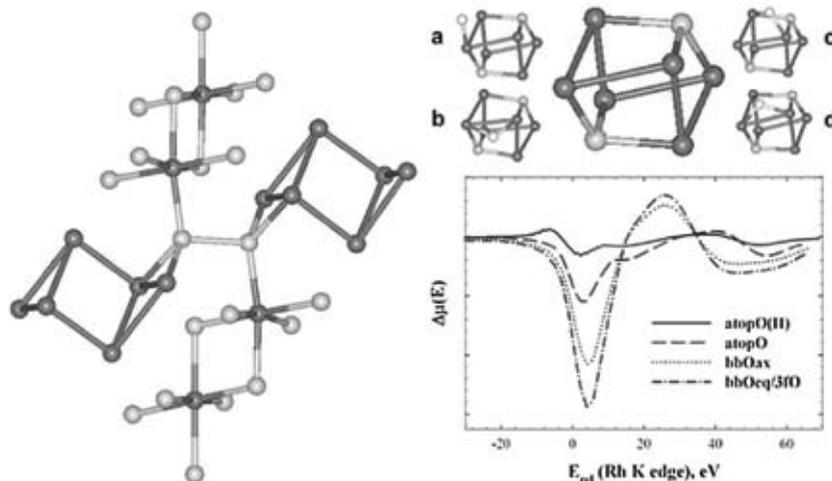
performed either under direct potentiostatic control or with samples prepared in a separate electrochemical cell and transferred to an NMR cell. The EC-NMR derived parameters show a direct correlation with the electronegativity of different

adsorbates and on the substrate surface  $E_f$ -LDOS. Such correlations can explain the improved methanol tolerance of Pt/Ru in methanol oxidation and the enhanced catalytic activity of Pt/Pd in formic acid oxidation. EC-NMR studies suggest invariance of the surface electronic properties of Pt nanoparticles with respect to the particle size and provide the first direct measurement of surface diffusion parameters of CO adsorbed on nanoparticle Pt-black electrodes. CO coverage dependence of surface diffusion parameters (Fig. 7) shows that the lateral interactions exert a stronger influence on surface diffusion and that free-site hopping is the major mechanism for CO surface diffusion on partial CO coverages.

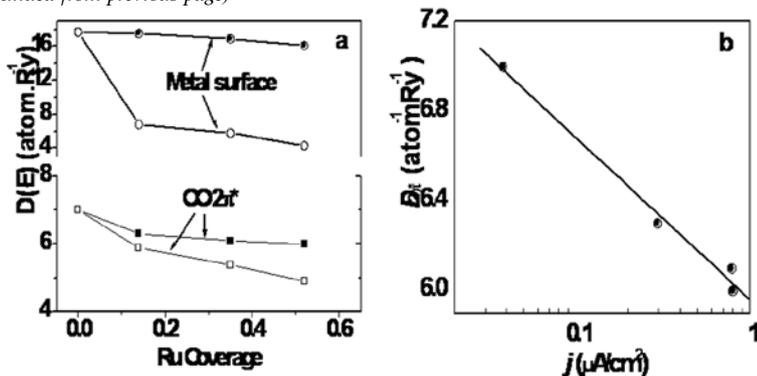
Femtosecond broadband multiplex sum frequency generation spectroscopy (BB-SFG), combined with thin layer electrochemistry, provides the ability to probe the vibrational behavior of adsorbed molecules without the IR drop penalty.<sup>12</sup> Recent work concerns adsorbed CO phase transformations and multiple bonding on Pt and Pt/Ru electrodes, and extension of BB-SFG to study catalytic reactions of fuel cell molecules such as methanol and formic acid in acidic media. Linear and multiple bonded CO are molecular electronic sensors that probe the geometric and electronic state of the electrode surface. The studies reveal the nature of reactive intermediates, and how surface dynamics affect surface electrochemical reactivity.

**HRTEM studies: What you see is not necessarily what you get.** The reactions occurring in fuel cells take place on nanoparticles. Thus, it is critical that we begin to understand the impact of the particle size and structure on reactivity. Ernst and Zawodzinski have deployed HRTEM in an effort to ascertain the structure of such particles and to determine the strain relative

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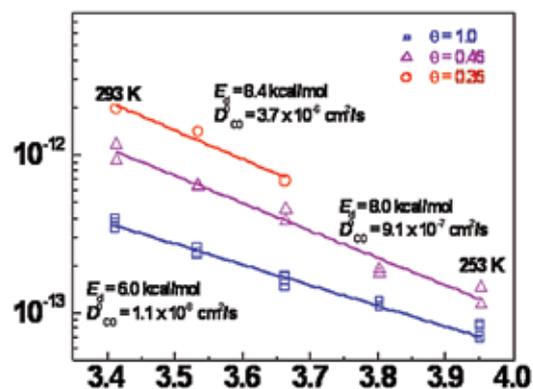


**FIG. 5.** A unit cell (left) of the monoclinic  $Rh_3S_4$ , FEFF models (top right) of the  $Rh_6$  octahedra. The theoretical  $\Delta\mu$  signatures (bottom right) generated by FEFF8 from the above models.

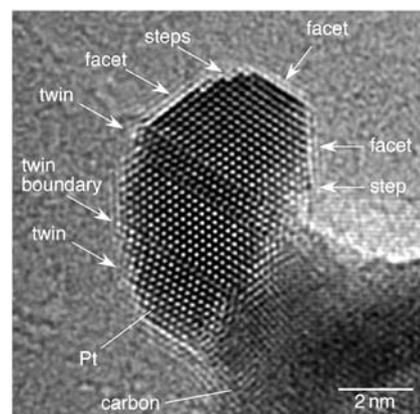


**FIG. 6.** (a) Variation of the Ef-LODS for surface Pt atoms and the 2p\* Ef-LODS of adsorbed CO in Pt/Ru catalysts as a function of the surface Ru coverage. Open symbols correspond to Pt atoms directly affected by the Ru islands, and closed symbols represent those away from the Ru islands. (b) Linear correlation between the 2p\* Ef-LODS of adsorbed CO and the steady-state methanol oxidation current densities with the Pt/Ru catalyst.<sup>3</sup>

to reference structures. An illustration of the type of detail that can be obtained from HRTEM is shown in Fig. 8. Steps, facets, twin boundaries, and so on are clearly visible from such studies. HRTEM images of catalysts such as those shown in Fig. 8 are common in the literature. However, for quantitative interpretation, (e.g., for developing a map of lattice strain in the particle), they are inadequate.



**FIG. 7.** Coverage dependence of CO surface diffusion (Kobayashi, Babu, Chung, Oldfield, and Wieckowski, *in press*).



**FIG. 8.** HRTEM of a supported Pt nanoparticle.

To remedy this, we are calculating accurate surface electron densities by exit-wave reconstruction, using a series of stepped-focus images to obtain the necessary information.

### Fundamental Electrocatalytic Processes: Combined Theory and Experimental Studies of Reaction Pathways

Another facet of the team's work focuses on studies of reaction pathways for oxidation of various fuels and on the oxygen reduction reaction. Wieckowski and Neurock<sup>13</sup> integrated experimental probes of reaction paths together with theory to trace the methanol oxidation pathway. This reaction was chosen as a model because of the large body of previous work on the intermediates. The combined effort revealed that at lower potentials the reaction proceeds via a single pathway, the initial activation of C-H bonds to form hydroxymethyl, hydroxymethylene, formyl, and CO intermediates. Higher potentials open up secondary paths that proceed through O-H bond activation and lead to the production of formaldehyde and formic acid. These secondary pathways do not appear to proceed via the route involving CO production.

Anderson and Mukerjee<sup>10</sup> combine theory and experiment to elucidate the oxygen reduction reaction. Their approach uses a local reaction

center model for electron transfer studies and treats it as an open system with regard to electron transfer. Application to the first step in O<sub>2</sub> reduction on platinum electrodes yielded potential-dependent activation energies in good agreement with those from experimental Arrhenius plots, as shown in Fig. 9.

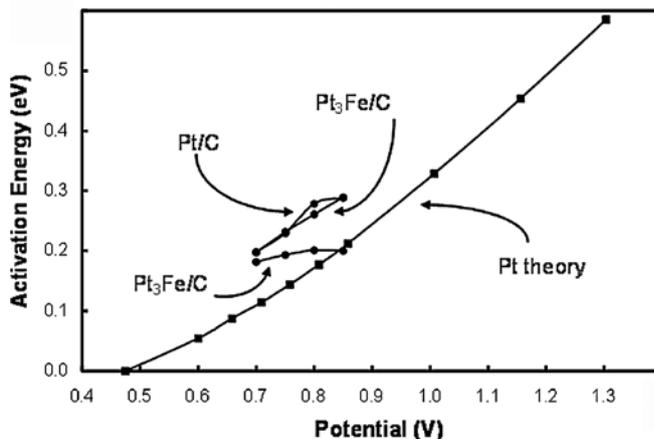
### Toward a Description of Composite Electrodes

In Fig. 10, we show a diagram that summarizes a stepwise heuristic for the build-up of electrode structure. In order to assimilate information from theory and fundamentals of reaction pathways and material structure to understand electrode performance in fuel cells, Mann and Zawodzinski<sup>14</sup> are constructing a multi-scale model of a thin film catalyst layer. This model considers a nested series of structures formed by well-defined interactions. For example, Pt nanoparticles interact with carbon support to form the catalyst particles typically used. These interact with each other and with the proton conducting binder.

A simple model of catalyst utilization for supported catalysts used in fuel cells was developed. The effects of catalyst loading, particle size, and support surface area on catalytic area loss were evaluated. The values obtained for catalytic area losses from the geometric model suggest the existence of optimum structures for fuel cell electrodes. Based on this, we developed a description of carbon-precious metal nanoparticle interactions, based on colloidal interaction theories that naturally provide a description of particle agglomeration and desorption phenomena. A description of percolation pathways for transport through the electrode also emerges from the work.

### Summary

Research in our collaborative activity was presented. This work provided a unique opportunity to



**FIG. 9.** Experimental vs. predicted activation energies for O<sub>2</sub> reduction to OOH.

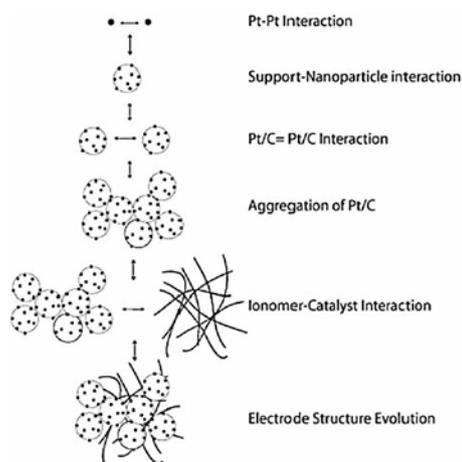


Fig. 10. Hierarchy of the electrode structure.

merge state-of-the-art theory and experiment applied to a practical target. In addition to providing unique insights into the underlying interfacial electrochemistry, the methods are beginning to identify more active electrocatalytic materials.

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