V.G.8 Analysis of the Mechanisms of Electrochemical Oxygen Reduction and Development of Ag-alloy and Pt-alloy Electro-catalysis for Low Temperature Fuel Cells

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Program Scope

Electrochemical oxygen reduction reaction (ORR) is the major source of overpotential loss in low-temperature fuel cells. Expensive, Pt-based materials have been found to be the most effective catalysts. Exploration of alternatives has been hampered by stability constraints at the typical operating conditions of low pH and high potential.

I will discuss our studies of elementary mechanism of ORR on various metal electrodes using kinetic analysis of reaction pathways and quantum chemical calculations. These studies allowed us to identify the elementary steps and molecular descriptors that govern the rate of ORR. Using these performance descriptors we have been able to identify families of Pt and Ag-based alloys that exhibit superior ORR performance is acid and base respectively.

We have synthesized these alloys to demonstrate the superior ORR activity with rotating disk electrode experiments. We have also performed thorough structural characterization of the bulk and surface properties with a combination of cyclic voltammetry, X-ray diffraction, and electron microscopy with spatially resolved energy-dispersive X-ray spectroscopy and electron energy loss spectroscopy

Objectives: The broad objective of our research efforts is to employ combined experimental–theoretical approaches to study the impact of small perturbations in the structure of solid catalysts (for example, promotion by alkali promoters, poisoning, or alloying) on the outcome of chemical and catalytic surface reactions. Ultimately, we are interested

in developing predictive theories that would guide us in the design of new or improved solid catalysts and electro-catalysts [1,2].

FY 2016 Highlights

Accomplishments: So far we have focused on four central themes, (a) development of a general, physically transparent framework designed to shed light on underlying mechanisms associated with the impact of the perturbation of a metal surface on the chemical transformation on the surface, (b) the analysis of the impact of alkali promoters on chemical transformation on metals and, (c) the study of the effect of the perturbation in the chemical composition of active metal sites by formation of an alloy on the chemical activity of the site, and (d) applying the predictive models to identify promising alloy catalysts in a number of probe reactions, including electrochemical ORR. Concrete accomplishments include the following.

- We have developed a general and physically transparent model, based on density functional theory (DFT) methodology, which allows us to identify underlying physical mechanisms that govern the changes in the chemical activity of a metal surface site as the local chemical environment of the site is perturbed. This framework allows us to de-convolute and quantify various mechanisms by which the perturbation of a metal surface changes its chemical activity. These mechanisms induce (i) local electronic effect, (ii) electrostatic, and (iii) polarization effect. This framework can be used to study various perturbations, including chemical promotion, poisoning and alloying. The work has been accepted for publication in The Journal of Chemical Physics [3].

- This model was utilized in a case study of the effect of Cs adsorbates (promoters) on the O_2 dissociation reaction on Ag(111). These studies revealed that the main mode by which Cs affects the dissociation of O_2 on Ag(111) is a long-range electrostatic/polarization interaction between Cs and relevant reaction intermediates. These interactions stabilize the transition state involved in the dissociation of O_2, therefore lowering the activation barrier. We demonstrated that these findings are fairly universal for metal surfaces promoted with alkali promoters [3].

- We have also studied how a working state of an alkali promoter changes as a function of external conditions, i.e., pressure and temperature of reactants. In this

context, we have examined possible formation of Cs-oxide complexes as a function of the chemical potential of gas-phase O_2 (pressure and temperature). We employed ab initio statistical mechanics to account for the effect of finite temperature and pressure of reactants. We have investigated whether and how the underlying mechanism of promotion depends on the nature of the alkali complex.

- We have also employed the model, referenced in the first bullet, to analyze mechanisms associated with the changes in the chemical activity of metal surfaces in response to the formation of alloys. In this context, we developed a predictive framework that can relate the geometric structure of an active center in a metal alloy material to its chemical activity [3-5]. The model allows us to relate readily accessible physical properties of the metals that form the active site in the alloy (electronegativity and the geometric extend of d-orbitals) to various descriptors of catalytic activity (e.g., the adsorption energy of critical adsorbates). We performed a number of experimental studies verifying and validating the predictive capacity of the proposed framework [3-5].

- We have used this predictive model to screen through large libraries of alloy materials identifying the most optimal active sites for electrochemical ORR in acid and base [1,5,6].

- The screening process has led us to the discovery of a number of Ag-based alloys for ORR in base that could meet techno-economic targets [7]. We have synthesized and tested one of these alloys in the form of Ag-Co nanoparticles. Rigorous measurements demonstrated the superior activity and stability of this material in electrochemical ORR compared to pure Ag nanoparticles of equal size. In base, this material reaches approximately 50 % the rate of commercial Pt electro-catalysts which meets the techno-economic target [7,8].

- More recently, we have expanded our studies to the development of a new family of Pt-based ORR electro-catalysts for ORR in acid. This has led to the development of novel Pt-alloy compositions which include layered structures of Au-Co core, covered by layers of Au and one layer of Pt. Testing of these alloy materials showed that the materials are approximately four times more active that the commercial Pt standards for this reaction [9].

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