

Preface

Electrocatalysts are the heart of power devices where electricity is produced via conversion of chemical into electrical energy. Impressive advances in surface science techniques and in first principles computational design are providing new avenues for significant improvement of the overall efficiencies of such power devices, especially because of an increase in the understanding of electrocatalytic materials and processes. For example, the development of high resolution instrumentation including various electron and ion-scattering and in-situ synchrotron spectroscopies, electrochemical scanning tunneling microscopy, and a plethora of new developments in analytical chemistry and electrochemical techniques, permits the detailed characterization of atomic distribution, before, during, and after a reaction takes place, giving unprecedented information about the status of the catalyst during the reaction, and most importantly the time evolution of the exposed catalytic surfaces at the atomistic level. These techniques are complemented by the use of *ab initio* methods which do not require input from experimental information, and are based on numerical solutions of the time-independent Schrödinger equation including electron-electron and electron-atom interactions. These first-principles computational methods have reached a degree of maturity such that their use to provide guidelines for interpretation of experiments and for materials design has become a routine practice in academic and industrial communities. The outcome of the *ab initio* methods includes thermodynamic and kinetic characterization of mechanistic reaction pathways, analysis of catalytic behavior of specific alloy compositions, stability of catalytic surfaces under certain gas or liquid environments, and more recently these sophisticated techniques have been extended to comprise the complexity of electrochemical phenomena. Further, as shown in this book, outcomes from *ab initio* methods can be used as input to model Hamiltonians where other essential effects as solvation are included thus giving a more realistic description of electrocatalytic systems. Beyond *ab initio* methods that give us the details of the chemistry of the process, classical molecular simulation techniques

where the electron-electron, electron-atom, and atom-atom interactions are represented by effective force fields permit the investigation of millions of atoms, and provide additional extremely important insights for physical phenomena that arise from collective interactions, and from environmental aspects such as temperature, pressure, and solvent effects. In addition, coarse-grained methods such as Kinetic Monte Carlo techniques have been developed to address many important catalytic and electrochemical processes involving time scales of the order of minutes and length scales in the order of microns. The outcomes of coarse-grained methods are linked and serve as input to continuum-based models.

This volume highlights advances in both theoretical and experimental techniques and points out both the progress made and the challenges remaining to be overcome in the near future to achieve further breakthroughs in electrocatalysis. The volume is organized by presenting the main thematic areas oriented towards specifics of electrodes, membranes and materials, experimental and computational design of proton-exchange membrane (PEM) and bio-fuel cells, along with recent developments in the synthesis and characterization of catalytic materials. In parallel, the occurrence of unwanted corrosion reactions and their subsequent effects on the lifetime of the electrocatalysts are analyzed both with the most advanced experimental techniques and with sophisticated computational methods.

Several chapters address various aspects related to electrocatalysis in PEM fuel cells, especially the oxygen reduction reaction (ORR), but also the anode oxidation reactions. Chapter 1 by Goodman, Soriaga, and collaborators presents a thorough investigation of alloy cathode electrocatalysts. Specifically, they investigate Pt-Co surface phase diagrams and provide an assessment of metal dissolution in acid medium, by combining low-energy ion scattering spectroscopy, X-Ray photoelectron spectroscopy, Auger electron spectroscopy, high resolution electron energy loss spectroscopy, low-energy electron diffraction, temperature-programmed desorption, and electrochemical methods. Chapters 2 to 6 deal with theoretical aspects of electrocatalytic reactions. In Chapter 2, Santos and Schmickler introduce a new approach to model an electrochemical system using a model Hamiltonian that incorporates the solvent effect to gas-phase density functional theory (DFT) calculations. The model is illustrated for H_2 oxida-

tion, and preliminary studies of electrocatalysis in nanostructures are also investigated with the same theory. Chapter 3 by Keith and Jacob presents a DFT-based theoretical analysis of ORR mechanisms, including solvent effects and incorporating the electrode potential in an effective way. Selvan and Keffer in Chapter 4 address the structure of the PEM polymer electrolyte membrane, transport through hydrophilic regions, and connectivity of the water clusters, and the interactions of the electrolyte medium with the electrocatalysts. All of these effects are relevant to the catalysis taken place at the membrane/catalyst/reactants interface. The ORR is also investigated by Sotelo and Seminario in Chapter 5, through a DFT-Green function analysis of small clusters that provide implications of local reactivity in the catalytic process. A different system is studied by Idupulapati and Mainardi in Chapter 6 that presents DFT modeling of the catalytic action of enzymes for the direct oxidation of methanol, focusing on understanding mechanisms with the goal of biomimetic design. Chapter 7 by Soria-ga and collaborators studies electrocatalytic oxidation and hydrogenation of chemisorbed aromatic compounds on palladium electrodes. Interfacial characterization using electron spectroscopy, low-energy electron diffraction, Auger electron spectroscopy, high resolution electron energy loss spectroscopy, scanning tunneling microscopy, and differential electrochemical mass spectrometry focus on benzene, hydroquinone, benzoquinone, and introduce an extensive analysis of the reaction mechanisms. Development of new models that connect the continuum descriptions with atomistic MonteCarlo simulations for the understanding of electrochemical systems is presented in Chapter 8 by Subramanian et al. In Chapter 9 by Balbuena and collaborators the ORR reaction in acid medium is revisited through DFT studies that address the complexity of Pt-based alloys in electrocatalytic processes, including surface segregation and metal dissolution processes. Chapter 10 by Coutanceau, Baranton, and Lamy gives a broad perspective of the use of surface science methods and electrochemical techniques to elucidate reaction mechanisms in electrocatalytic processes. Several modern techniques (spectroscopic and analytical) include infrared reflectance spectroscopy, electrochemical quartz crystal microbalance, differential electrochemical mass spectrometry, chemical radiotracers, and high performance liquid chromatography. Applications include analysis of reaction mechanisms of CO,

methanol, and ethanol oxidation on Pt-based electrocatalysts, and ORR on Fe-Phtalocyanine. In Chapter 11 Mukerjee and Arruda describe the use of in-situ synchrotron spectroscopy to analyze electrocatalysts dispersed on nanomaterials. Applications to ORR Pt-based alloy cathode nanocatalysts, anode reformat catalysts, and ORR in enzymatic centers illustrate the value of this technique to obtain a detailed in situ characterization of materials and mechanisms in electrocatalysis.

Perla B. Balbuena
Texas A&M University
College Station, TX, June 2010

Venkat R. Subramanian
Washington University
Saint Louis, Missouri

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