Special Topic on Interfacial Electrochemistry and Photo(electro)catalysis

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Special Topic on Interfacial Electrochemistry and Photo(electro)catalysis

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ABSTRACT

Interfacial electrochemistry and photo(electro)catalysis are key processes that convert the energy of photons or electrons to chemical bonds in many energy conversion and storage technologies. Achieving a molecular level understanding of the fundamental interfacial structure, energetics, dynamics, and reaction mechanisms that govern these processes represents a broad frontier for chemical physics and physical chemistry. This Special Topic contains a collection of articles that range from the development of new experimental and computational techniques to the novel application of those techniques for mechanistic studies, as the principal investigators seek a fundamental molecular understanding of both electrode/electrolyte interfaces and the relevant electrocatalytic, photocatalytic, and photoelectrochemical reactions taking place thereabout. Altogether, this collection of articles captures the current state of this very active, frontier research field and highlights the current and remaining key scientific challenges and opportunities.

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Providing sustainable clean energy for human activities is one of the major scientific challenges of the 21st century. Addressing this challenge will likely require novel energy harvesting, conversion, and storage concepts and technologies, and many of these technologies will involve molecular level electrochemical and photo(electro)catalytic processes at electrified solid/liquid interfaces–the study of which necessarily involves both experimental and theoretical/modeling difficulties. For example, (i) selective probing of the interfacial region, which is much smaller compared to the bulk electrodes and electrolytes, requires *in situ* interface specific or sensitive spectroscopic techniques. (ii) Many important energy conversion processes involve multiple-step interfacial reactions of multiple electrons and protons, where new rate theories may have to be developed. (iii) Electrochemical processes are strongly influenced by the large interfacial electric field, as well as strong interactions between reactants and

electrodes, ions and solvents. Thus, theoretical and computational models of these interfacial processes will likely require both an atomistic level description of bond formation/breaking processes and an accurate description of the interfacial solvent/electrolyte/electric field environment. (iv) In photocatalytic and photoelectrochemical conversions, these processes are coupled to optical fields, which generate electrons and holes in semiconductor electrodes to drive the reactions. Altogether, achieving a microscopic molecular level understanding of interfacial electrochemical and photo(electro)catalytical processes represents a broad frontier field of chemical physics and physical chemistry.

In recent years, this frontier field has attracted intense interest within the chemical physics and physical chemistry communities. Facilitated by recent advances in experimental and computational techniques, and driven by the societal need of a more sustainable energy infrastructure,

important progress has been made. Thus, there is a need to publish a special topic on interfacial electrochemistry and photo(electro)catalysis, to highlight these advances, and to assess the status of this field: what are the best models that describe energy conversion processes (from electrons/photons to chemical bonds) that occur at the solid/liquid interfaces? Can these processes be optimized on the basis of our microscopic understanding? Can one identify, quantify, and ultimately control the elementary processes that govern macroscopic efficiencies (turnover rates), reaction pathways (selectivity), and electrode/catalyst stabilities (degradation)? A particular goal of this special topic is to merge both theoretical and experimental articles, as we feel that there is still a significant gap between these two subfields within this large area of frontier research.

This special topic contains 33 articles ranging from the development of new characterization and computational techniques to novel applications that explore the current state of the field. Many articles focus on improving our fundamental, molecular understanding of the electrode/electrolyte interfaces. Others focus on improving our molecular understanding of important electrocatalytic, photocatalytic, and photoelectrochemical reactions, including water oxidation, hydrogen evolution, oxygen reduction reactions (ORR), oxygen evolution reactions (OER), and N_2 and CO_2 reduction reactions. Altogether, this collection of articles provides a terse and deep introduction for the scientist interested in a fundamental understanding of a wide range of energy conversion and storage technologies, including solar-to-fuel and electron-to-fuel conversion, fuel cells, and batteries. Let us now briefly summarize the articles herein.

An accurate description of the electrode/electrolyte interface is one of the key issues in understanding electro- and photoelectro-chemical processes and is the focus of several articles. Sakong *et al.* study the structure of the electric double layer at the water/metal electrode interface using *ab initio* molecular dynamics (AIMD) simulations, aiming at improving the description of the interfacial charge and potential distribution using a polarization scheme instead of point charges.[1] Piccinin *et al.* investigate the double layer structure at the hematite/water interface also using AIMD simulations and focus on the interactions of water molecules and ions with different hematite surfaces to decipher how these interactions affect the water structure and electrostatic potential profile.[2] Gaigeot *et al.* examine the structure of water at the water/Co_3O_4 (111) (water oxidation catalyst) interface using AIMD simulations and compute sum-frequency generation (SFG) spectra of the interfacial water molecules.[3] Sayer *et al.* develop a AIMD simulation method for describing polar-ionic solid/electrolyte interfaces.[4]

The development of effective dielectric continuum-based models of the electric double layer has attracted considerable interest due to their high computational efficiency. Andreussi *et al.* present a study of double layer capacitance using such a continuum model that can be coupled to a first-principle description of the charged metal surface to show a large effect of dielectric cavity parameterization.[5] Baskin *et al.* develop a local free-energy functional-based continuum model for accurate modeling of chemical speciation at electrified solid/liquid interfaces.[6] Ringe *et al.* develop a generalized molecular solvation model for non-aqueous solutions, which are often involved in batteries and other energy storage devices.[7] Hybrid *ab initio*-continuum methodologies represent an attractive approach for simulating molecular processes at the electrode/electrolyte interfaces at an accuracy level intermediate to pure continuum or fully explicit solvation. Hoermann and co-workers discuss such a grand canonical simulation study of the electrical interface that treats the metal electrode at the density functional theory (DFT) level, the water with a self-consistent solvation model and the double layer using a phenomenological continuum model.[8] This method allows us to merge a computational description of the hydrogen electrode with a general grand canonical description of the electrified interface, and the method is used to study the electro-adsorption of H and Cl on metallic electrodes. Melander *et al.* present a separate grand canonical approach with a DFT description of the electrified electrode/liquid interface, in which systematic coarse-graining is employed to allow a rigorous treatment of the electric double layer at a reduced computational cost.[9]

In addition to accurate double layer structure models, theoretical methods for calculating the rates of dynamical processes on metal electrodes remain a challenge. Subotnik and co-workers report a comparison of two surface hopping algorithms for describing electron transfer at metal/adsorbate interfaces.[10] Advances in experimental techniques have enabled the direct probes of surface structure and dynamics. Domke *et al.* investigate the potential-dependent vibrational spectral shift of sulfate on Au (111) using electrochemical surface enhanced IR reflection spectroscopy (SC-SEIRAS), delineating the contributions of potential-dependent coverage and interfacial field strength (through the vibrational Stark effect).[11] King and co-workers study the dynamics of electrons at a DMSO/Cu(111) interface using time- and angle-resolved two-photon photoemission spectroscopy, directly following the processes of electron localization and polaron formation at the interface.[12] Meyer and co-workers investigate the temperature dependence of forward and backward electron transfer rates at the interface of molecular sensitizers and oxide nanoparticles.[13]

Designing catalytic systems for efficient and selective electrocatalytic transformation, such as water reduction, O_2 reduction and evolution, and CO_2 and N_2 reduction, remains an unsolved challenge. These reactions are essential for the development of a range of energy conversion and storage technologies, including electrolyzers, fuel cells, or batteries (especially metal-air batteries). Many papers in this Special Topic focus on elucidating the mechanisms of electrocatalytic reactions, in an effort to provide insights for rational improvement of catalytic activities. Suntivich *et al.* study the mechanisms of electrocatalytic chlorine evolution reactions on RuO_2(110) and IrO_2(110) surfaces, relying on insights provided by electrochemical kinetics.[14] Further insight can be gained by using *in situ* spectroscopy and computational modelling. Tong and co-workers examine the effect of surface-bound

sulfide on the oxygen evolution reaction on Pt using combined *in situ* electrochemical attenuated total internal reflection-surface enhanced IR absorption spectroscopy, microkinetic simulation, and DFT calculations.[15] Their result suggests that sulfide adsorption may break the scaling relationship of pure metal electrodes and can be used to alter reaction pathways. Klingan et al. examine the mechanism of CO_2 reduction on Cu using *in situ* surface enhanced Raman spectroscopy (SERS), leading to the identification of key intermediates, including two distinct types of adsorbed CO molecules.[16] Carter and co-workers study the mechanism of CO_2 reduction on Cu by combined experiment (low temperature scanning tunneling microscopy and atomic force microscopy) and computational (DFT) techniques, focusing on the adsorption configuration of formic acid (HCOOH) and the effect of CuO formation.[17] Janik et al. study the mechanism of electrocatalytic N_2 reduction on low index Fe surfaces in an aqueous environment by DFT, reporting a larger than expected overpotential for this reaction.[18] Jacob et al. study the self-diffusion mechanism on perfect and imperfect Li(100) surfaces, a process that is essential for the mechanism of Li metal batteries.[19] Behm and co-workers reveal that Mg^{2+} ions have a pronounced effect on O_2 evolution and reduction reactions at a Au electrode in ionic liquids using combined differential electrochemical mass spectrometry (DEMS) and *in situ* infrared spectroscopy.[20] This work provides important mechanistic insights into the design of Mg-air batteries.

Metal alloys and doping of metal oxides have been shown to enhance electrocatalytic activities. Vojvodic and co-workers investigate the structure and electronic properties of the Fe dopant in cobalt oxide nanoislands on Au(111) using a combination of scanning tunneling microscopy, x-ray photoemission spectroscopy, and DFT calculations.[21] Weitzner et al. study the effect of an applied bias on Pd–Au surface alloys on Au(111) via Metropolis Monte Carlo simulation within an extended grand canonical ensemble, showing that the relative surface fractions of Pd monomer, dimer, and trimer are in good agreement with *in situ* scanning tunneling microscopy measurements.[22] Peterson et al. study ORR reactions of Fe/Pt(111) and Co/Pt(111) alloys by DFT calculations, elucidating the effect of doping induced strain on intermediate binding and ORR activities.[23] Auer and co-workers examine the size, shape, and interfacial structure of Pt clusters on carbon-supports using high-resolution transmission electron microscopy and rationalize their observations with quantum chemical calculation of the electronic interactions between the Pt and the supporting carbon materials.[24] Herrero et al. study the effect of electrode preparation methods on the activities of glycerol oxidation on Pd modified Au electrodes in alkaline media.[25] DFT calculations have found increasing applications in elucidating reaction mechanisms and screening of catalysts, and Viswanathan et al. examine the robustness of DFT based catalyst screening methods, identifying effective descriptors for electrocatalytic oxygen evolution and reduction reactions.[26]

Photocatalysis and photoeletrocatalysis offer a way to directly drive catalytic transformation reactions using the energy of photons. These processes require materials or material combinations that can absorb sun light, separate and transport charges, drive catalytic reactions, and be stable under catalytic turnover conditions. These more stringent requirements have limited the choice of materials to small bandgap oxides (such as $BiVO_4$, a-Fe_2O_3, and WO_3). Water oxidation can proceed through the formation of H_2O_2 *or* O_2 and Wang et al. study the competition of these pathways on $BiVO_4$ and WO_3 photoanodes, proposing that the ease or difficulty of (de) protonation of the M-OOH intermediates is a key factor determining the branching ratio of these pathways.[27] Coating the surface of oxide electrodes by catalytic layers such as Ni hydroxide (NiOOH) has been shown to increase the catalytic activities, although the mechanism remains unclear. Bieberle-Huetter et al. study how NiOOH enhances the catalytic activities of hematite using DFT + U calculations, showing that Ni atoms at the edge sites of the NiOOH layer are more active than the Ni atoms at the basal plane.[28] Because of highly oxidative conditions involved in water oxidation, the stability of photoanodes (by ion dissolution) and resulting poisoning of photocathodes (by ion deposition) remain a key challenge even for oxide materials. Domen and co-workers show that $BiVO_4$ photoanodes can be stabilized by dispersing a chelating resin (for Bi^{3+} ions) in the electrolyte and coating the photoanode surface by anion-conducting ionomers.[29] One way to utilize wide bandgap materials as photocatalysts is to reduce their effective bandgap by doping. Kenmoe et al. examine the electronic structure and optical properties of N- and S- doped TiO_2 nanotubes.[30] Truhlar et al. examine the effect of Ti and Zr doping on the optical, electronic, and catalytic activities of cerium metal-organic frameworks (MOFs).[31] Another way to utilize wide bandgap oxides as photoanodes is through sensitization by molecular chromophores. Meyer et al. study light-driven water oxidation by dye-sensitized photoanodes consisting of a molecular chromophore/catalyst assembly on a mesoporous double shell ZnO/TiO_2 electrode (prepared by atomic layer deposition).[32] High photocurrents on the double shell electrode are attributed to a built-in barrier for charge recombination at the ZnO/TiO_2 interface. In recent years, coating thin oxide layers by atomic layer deposition has been investigated as an effective strategy for the protection of low bandgap semiconductor electrodes and sensitizers, fabrication of heterojunctions, and interfacing light absorbers and catalysts at the nanoscale. In their perspective article, Frei et al. summarize recent advances and key future scientific challenges and research opportunities in these areas.[33]

In summary, a fundamental molecular level understanding of interfacial electrochemistry and photo(electro)catalysis is essential for the rational improvement and development of energy conversion and storage technologies. This Special Topic highlights some recent advances in these areas. These papers demonstrate both the need and power of combined electrochemical, *in situ* spectroscopic and computational approaches in addressing these problems. Significant advances in experimental, theoretical, and computational tools are still needed, and interfacial electrochemistry and photo(electro)catalysis remains frontier research areas in chemical physics and physical chemistry.

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