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PERSPECTIVES

Inner-Sphere Heterogeneous Electrode Reactions. Electrocatalysis and Photocatalysis: The Challenge

Allen J. Bard

Center for Electrochemistry and Department of Chemistry and Biochemistry, The University of Texas at Austin, Austin, Texas 78712

Received February 23, 2010; E-mail: ajbard@mail.utexas.edu

Abstract: This paper offers a perspective on inner-sphere heterogeneous electron-transfer reactions and electrocatalysis as it is applied to electrochemical energy conversion systems. Fundamental concepts and an overview of past approaches to studies of these types of reactions are discussed. A method for the discovery of new electrocatalysts (for example, ones for the oxygen reduction reaction) and photocatalysts (for solar energy conversion to fuels) based on scanning electrochemical microscopy is briefly described, as well as new surface interrogation techniques for quantifying intermediates.

It is probably presumptuous to take on the field of heterogeneous electrocatalysis after so much experimental and theoretical work on this subject has been carried out over many years. However, long-standing and important problems of both a fundamental and applied nature remain to be solved, and perhaps it is worthwhile to look at the current state and possible new directions. Hence I offer my Perspective to a general audience. Let me emphasize that, in a field in which such an enormous amount of work has been done, this is not at all a review, and only a few references to prior work (including some reviews) are given. In the important field of energy, electrochemistry provides a bridge for the efficient interconversion of chemical energy and electrical energy. Thus, the main sources of portable electrical energy in a myriad of electronic devices and in hybrid and electrical vehicles are batteries. Other types of rechargeable batteries are needed for electricity storage from intermittent sources like wind turbines or solar photovoltaic cells. The conversion of renewable fuels, like hydrogen, to electrical energy is more efficient in electrochemical systems (fuel cells), which are not Carnot cycle limited, and may play a role in vehicles and stationary electrical sources. The production of hydrogen by water electrolysis or the conversion of carbon dioxide to useful fuels using electricity from renewable sources, such as sunlight, is also of interest, especially in light of the environmental cost and finite availability of fossil fuels.

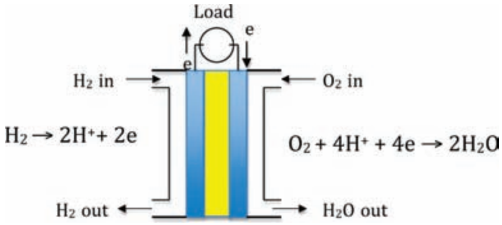

Figure 1. Schematic of polymer membrane electrolyte hydrogen−oxygen fuel cell.

However, in many applications, the lack of efficient, stable, and inexpensive electrocatalysts for such systems remains a major problem. Consider, for example, fuel cells based on the oxidation of H_2 at an anode and the reduction of O_2 at a cathode (Figure 1). As discussed below, these are not simple electrode reactions, and electrocatalysts are needed at both electrodes to carry them out at a reasonable rate. For room-temperature fuel cells, platinum has been the mainstay for this purpose for over 100 years, but it is expensive, in limited supply, and suffers from performance limitations. For example, Pt (perhaps alloyed with other metals) is the only electrocatalyst considered for the oxygen reduction reaction (ORR). However, kinetic limitations in the ORR are the major source of efficiency loss in a fuel cell. Will it be possible to find alternative materials, and what approaches are available to understand the electrode reactions?

The problem of solar energy conversion through photoelectrochemical systems presents similar problems. In such systems, radiant energy is added to the electrochemical system to promote chemical reactions, for example, the production of hydrogen or the oxidation of wastes. Photoelectrochemical systems might ultimately play a role in CO_2 remediation via the production of base or by reduction of carbon dioxide to a fuel. Although this field is a mature one, inexpensive, efficient, and stable materials for the capture of light (photocatalysts) and the promotion of the electron-transfer reactions (electrocatalysts, e.g., for H_2 and O_2 production in so-called water splitting) have yet to be discovered. Consideration of electrocatalysis (or, as discussed further, inner-sphere electron transfer) is also important in understanding corrosion phenomena (e.g., O_2 reduction on the surface of the corroding material) and in many electrochemical syntheses (e.g., H_2 and Cl_2 evolution in the chloralkali process).

I was asked to give my perspective on a field of interest, and I have chosen this one. I hope the comments will be useful, or at least thought-provoking.

Inner- and Outer-Sphere Reactions

It is often thought that the first act that occurs in an electrochemical reaction is the transfer of an electron, but this is frequently not the case for inner-sphere heterogeneous electron transfers. The concept of *inner-sphere* and *outer-sphere* electron-transfer reactions was introduced by Taube[1] to deal with redox

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reactions of coordination complexes in solution. In outer-sphere reactions, the electron transfer occurs between two species with no bonding between them, with the electron tunneling from one to the other, probably across a solvation layer. In inner-sphere reactions, the electron transfer occurs in an activated complex where a ligand is shared between the donor and acceptor molecules (and where the bridging ligand may or may not be transferred during the reaction).[1,2] This concept can also be extended to heterogeneous electrode reactions, where in an outer-sphere reaction the reactants, products, and intermediates do not interact strongly with the electrode material and electron transfer occurs by tunneling across at least a monolayer of solvent, while in an inner-sphere reaction there is a strong interaction of reactant or product with the electrode surface.[3] Thus, in a heterogeneous inner-sphere reactions, the reactants, intermediates, or products are often specifically adsorbed on the electrode surface. Heterogeneous inner-sphere reactions are often called *electrocatalytic* reactions (although this term is sometimes applied in the literature to some homogeneous solution-phase electron-transfer reactions as well). One can typically distinguish experimentally between inner- and outer-sphere electrode reactions because outer-sphere reactions are generally rather insensitive to the nature of the electrode material (except for small double-layer and metal electronic effects or the presence of films that block tunneling),[3] whereas inner-sphere reactions depend very strongly on the electrode material. For example, outer-sphere reactions, like the oxidation of ferrocene methanol or the reduction of $Ru(NH_3)_6^{3+}$, show very similar electrochemical behavior with Pt, Au, or C electrodes. However, the reduction of oxygen or of protons is very different with these same materials. Another way to distinguish between inner- and outer-sphere reactions is to adsorb a monolayer of a small molecule, for example, a short-chain thiol $[HS(CH_2)_2COOH]$, on an electrode (Au). While long-chain thiols affect outer-sphere reactions, since they affect the ability of an electron to tunnel from the electrode to the solution species, a short chain has only a small effect. Thus, the oxidation of ferrocene methanol looks very much the same on bare or the C3-thiol-modified Au (Figure 2B). However, for a reaction like the oxidation of hydrazine, this adsorbed layer has a very large effect, because the active surface atoms needed to carry out the oxidation reaction are largely blocked (Figure 2A). Similar effects are found when a thin oxide film forms on an electrode: outer-sphere reactions are relatively unperturbed, while inner-sphere reactions can be turned off.

The treatment of outer-sphere electrode reactions, coupled with preceding or following homogeneous chemical reactions and multiple electron steps (so-called CE, EC, and ECE reactions), has been extensively developed over the past 50 years.[3] The development of cyclic voltammetric and other electroanalytical methods that are useful over a wide temporal range and the use of nonaqueous solvents with wide potential windows, as well as powerful theoretical and simulation methods for rigorously treating complex reaction schemes, have led to the field now sometimes called *molecular electrochemistry*.[4,5] Important insights into the behavior of materials and reactions in both organic and inorganic chemistry have resulted. However, there has not been similar progress in heterogeneous inner-sphere electrochemistry, which is an older but significantly more complex field, despite extensive studies with powerful analytical tools and theory.

A note of clarification is necessary. In the treatment of homogeneous reactions coupled to an electron-transfer reaction at an electrode, for example, an EC reaction, the following chemical reaction is usually outer-sphere, but it could be a *homogeneous* inner-sphere reaction. In the discussion here, we are only considering *heterogeneous* inner-sphere reactions on an electrode surface. Moreover, one could have a heterogeneous molecular reaction by immobilizing a homogeneous reactant on an electrode surface, although such "heterogenized" homogeneous catalysts are rarely used in comparison to electocatalytic reactions involving "materials" as electrodes. Finally in the Marcus treatment of outer-sphere reactions (both homogeneous and heterogeneous), the energetic effects caused by changes in the nuclear coordinates (the reorganization energy or λ value) are separated into inner (λ_i, related to changes in molecular bond lengths) and outer (λ_o, related to solvation effects) factors. These terms are unrelated to inner- and outer-*sphere* effects.[3]

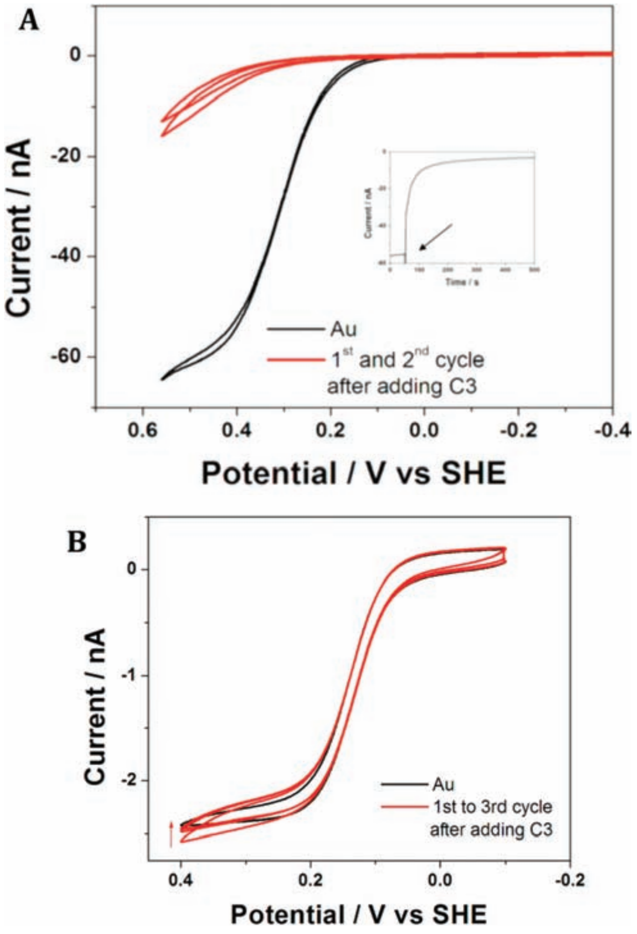

Figure 2. Effect of surfactant on cyclic voltammograms of a Au ultramicroelectrode. (A) Inner-sphere: 12 mM hydrazine + 50 mM phosphate buffer before and after addition of 50 μM 3-mercaptopropionic acid (C3). The inset shows the current transient before and after injection. (B) Outer-sphere: 1 mM ferrocene methanol + 50 $NaClO_4$ before and after addition of 50 μM C3. Adapted with permission from Xiao, X.; Pan, S.; Jang, J. S.; Fan, F.-R. F.; Bard, A. J. *J. Phys. Chem. C* **2009**, *113*, 14978. Copyright 2009 American Chemical Society.

An alternative way of comparing these two types of reactions is suggested by considerations of the energy needed for an electron transfer, as shown in Figure 3. Outer-sphere single-electron transfers carried out electrochemically in an aprotic solvent, for example, the oxidation of aromatic hydrocarbons in acetonitrile, can be correlated with the ionization of these molecules in the gas phase by plotting the electrochemical half-wave potential, $E_{1/2}$, or standard potential, $E°$, vs the vertical

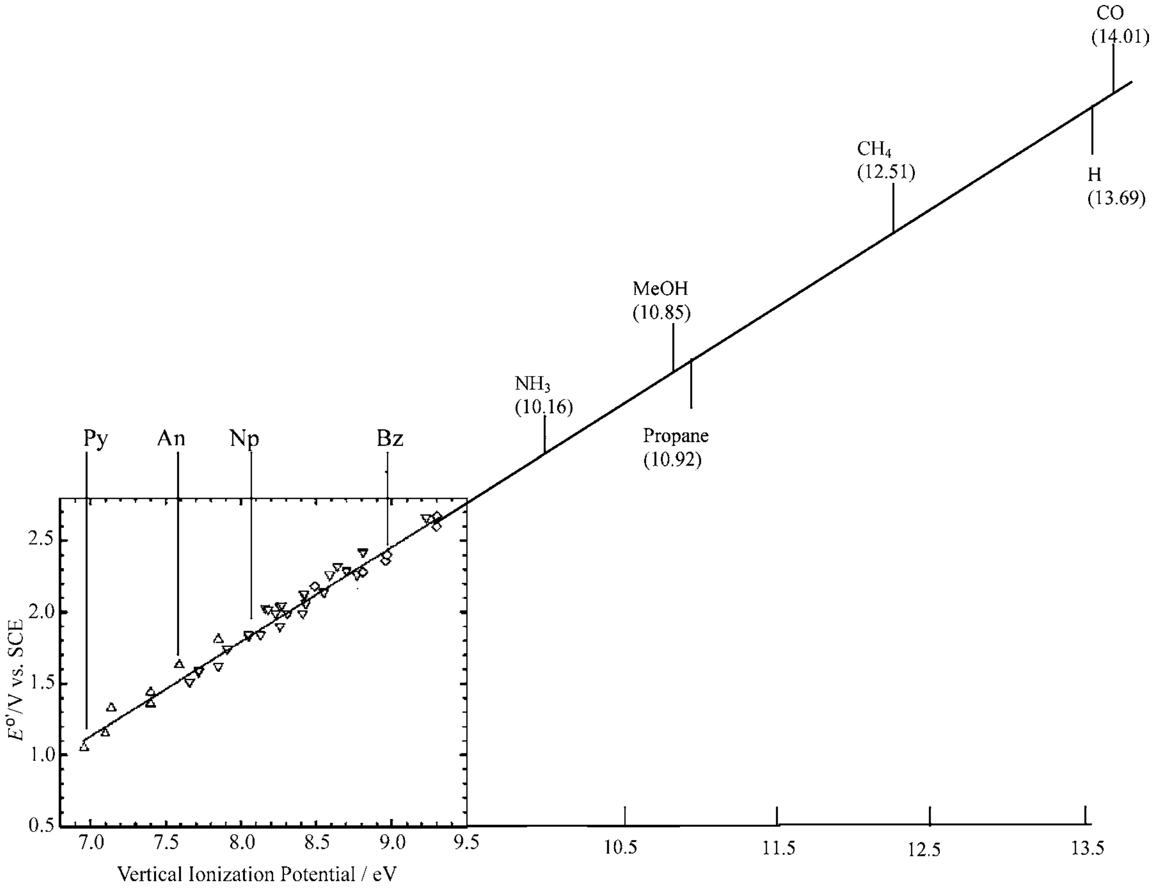

Figure 3. Electrochemical standard potentials ($E^{\circ\prime}$) versus vertical ionization potential for a series of solution species (within a box defined by the axes of available potentials) and ionization potentials of other molecules at values >10 eV. E (V vs SCE) = 0.68 × IP (eV) − 3.46. Abbreviations: Py, perylene; An, anthracene; Np, naphthalene; Bz, benzene. The points shown are taken from Nelsen, S. F.; Thompson-Colon, J. A.; Kirste, B.; Rosenhouse, A.; Kaftory, M. *J. Am. Chem. Soc.* **1987**, *109*, 7128−7136 for fused-ring aromatic hydrocarbons and alkylated benzenes.

ionization potential, IP[6,7] (or the computed energy of the highest occupied molecular orbital). Although such plots depend upon the solvation energies of the parent and the radical cation, within a given class of compounds, they often show remarkably linear correlations, suggesting that solvation effects are functions of ion size in a way that tracks the IP. The slope in the plot of Figure 3 is ~0.7 (compared to 1 expected in the absence of solvation effects).[8] The intercept depends upon the reference electrode used and its potential on an absolute scale. The axes drawn to form a box around the data points roughly represents the available potentials for the solvent window of acetonitrile. At more positive potentials, the solvent or supporting electrolyte oxidizes. This line is then extended beyond the box to roughly predict potentials needed for the one-electron oxidation of other species indicated by their known IP values (assuming a similar solvation effect holds, as addressed below). These include many species that are considered as fuels that can be oxidized to CO_2 and water, for example, carbon monoxide and methanol:

$$H_2CO_3 + 6H^+ + 6e \rightleftarrows CH_3OH + 2H_2O \qquad E^\circ = 0.044\ \text{V} \tag{1}$$

$$CO_2 + 2H^+ + 2e \rightleftarrows CO + H_2O \qquad E^\circ = -0.106\ \text{V} \tag{2}$$

where the E° values are given in tables of potentials reported versus the normal or standard hydrogen electrode.[9] However, such oxidations involve multielectron transfers and coupled chemical reactions in complex reaction schemes. Clearly, the potential predicted from the IP for the transfer of one electron for the formation of the methanol radical cation is much more positive than the potential of the overall six-electron reaction. This strongly implies that a heterogeneous outer-sphere reaction of species outside the box is not generally possible with available solvents, and certainly not in water, which has a much smaller potential window than acetonitrile. Thus, to carry out the oxidation of such species, one must deal with inner-sphere reactions and think about completely different routes than one considers in the outer-sphere box.

It is only fair to emphasize that this picture is at best approximate. Solvation effects can be very important, especially for small molecules. Consider the hydrogen atom, where the huge solvation energy of the proton (e.g., a hydration energy of about 11 eV)[10] moves the potential to much less positive values than would be suggested by the well-known IP of 13.69 eV. Such effects are less important with other species, like methanol, however. It is also possible that strong specific adsorption of the product of the electron-transfer reaction, for example, the radical cation, can shift the potential to less positive values (to result in inner-sphere single-electron transfer). However, again it is unlikely that the adsorption free energies of the needed several electronvolts exist for most of these cases to move these reactions inside the box (Figure 3).

A similar treatment holds for reduction reactions. Correlations of potentials for reductions with gas-phase electron affinities (EA) (and the lowest unoccupied molecular orbital energies)

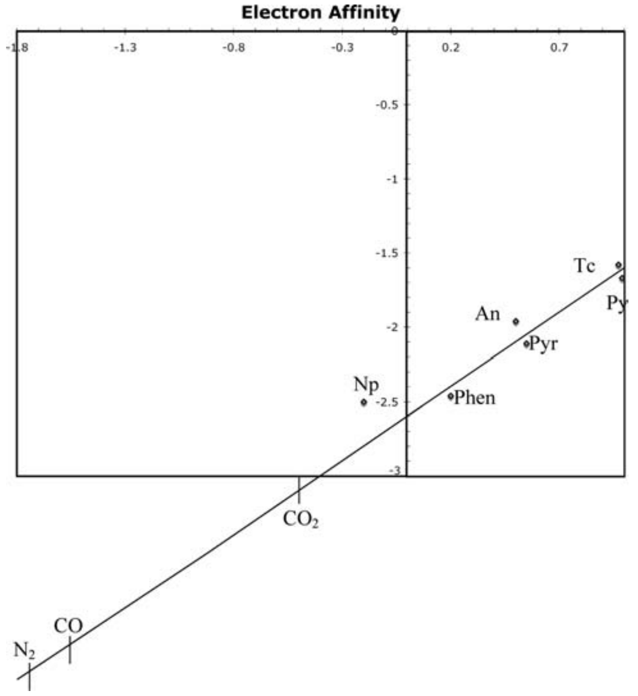

Figure 4. Half-wave potentials in 75% dioxane−water versus electron affinity for some aromatic hydrocarbons. Abbreviations: An, anthracene; Np, naphthalene; Phen, phenanthrene; Py, perylene; Pyr, pyrene; Tc, tetracene. As electron affinities become less positive, more energy is needed to add the electron to the molecule, and negative values denote molecules that spontaneously lose an electron in the gas phase (and have considerable uncertainties in their values shown). The point for Np was not used in drawing the line because the radical anion is unstable, which caused a shift in the measured half-wave potential to less negative values. Half-wave potential data are taken from ref 6, Table 7.1.

can be given.[6−8] A fairly simple one is shown in Figure 4. Note that a more positive EA indicates an easier addition of an electron to the neutral parent molecule and a negative EA indicates spontaneous loss of an electron from the radical anion in the gas phase. Again, solvation effects of the radical anions are important, however, so the reduction of naphthalene or CO_2 to radical anions can occur electrochemically in aprotic solvents, even though their EAs are negative and their gas-phase counterparts are not stable. In a manner analogous to the IP plot, the reactions within the solvent potential window can occur by outer-sphere electron transfer, while many of those outside of the box cannot. Thus, if one is interested in the reduction of dinitrogen to ammonia and considers the EA, it is extremely unlikely that the reaction proceeds by an initial one-electron electron transfer to N_2. Note, however, that inner-sphere reactions can and do occur inside the boxes (i.e., within the available potential ranges for 1e transfers), especially when multielectron transfers are considered. A case in point is O_2 reduction, where EA = 0.45. In an aprotic solvent, one-electron reduction to superoxide ($O_2^{\bullet-}$) occurs. Because of strong solvation effects, the potential for this reduction is considerably less negative than suggested by the plot of Figure 4, probably around −0.9 V for this solvent and potential scale. This reaction also occurs in very alkaline aqueous solutions with the indicated potential of the reaction,

$$O_2 + e \rightarrow O_2^{\bullet-} \qquad E^\circ = -0.284 \text{ V vs NHE} \tag{3}$$

However, the 4e reduction of oxygen to water,

$$O_2 + 4H^+ + 4e \rightarrow 2H_2O \qquad E^\circ = +1.23 \text{ V vs NHE} \tag{4}$$

that takes place at a much more positive potential undoubtedly occurs via an inner-sphere reaction in a complex process that involves the addition of $4H^+$ and the breaking of the O−O bond in the overall reaction scheme. As mentioned, this ORR is often the limiting factor in low-temperature fuel cells.

Inner-Sphere Heterogeneous Electrode Reactions (ISERs)

If direct electron-transfer reactions are not possible because of high IP values, how do processes in which the overall multielectron reaction is thermodynamically feasible proceed at an electrode? How does the oxidation of MeOH and CO to CO_2 (reactions 1 and 2) occur? For inner-sphere reactions, we are now more in the regime related to heterogeneous catalysis on metals that has been extensively studied, especially for gas-phase reactions,[11,12] but also for electrocatalysts in solution.[13,14] Two key factors dominate: (1) Specific adsorption of reactant, product, or intermediate must be considered. For reactants, an important factor is dissociative adsorption of the molecule on the electrode surface. The adsorbed reactant molecule can strongly interact with metal atoms to an extent that bonds are broken and new fragments are formed. For example, H_2, with an IP of 15.4 eV, which is well outside the box in Figure 2, dissociates on Pt to adsorbed hydrogen atoms, which are readily oxidized to protons. The same is true of formic acid, which dissociates at open circuit to CO_2 and H atoms on Pt[15] and also produces CO during its oxidation. As indicated above, the strong adsorption of an intermediate can shift the potential by the free energy of adsorption. (2) Species that adsorb but do not dissociate can also be oxidized (or reduced) by mechanisms that do not involve direct electron transfers to the electrode. For example, in the oxidation of CO, strongly adsorbed CO on Pt remains intact because of the strength of the CO triple bond. In this case, the production of surface species that can carry out the oxidation is important. For example, on Pt, depending on the potential and the solution conditions, different oxidizing species (like OH radicals and adsorbed O atoms) can form by oxidation of water. These are capable of reacting directly with adsorbed surface species via reactions that do not depend directly upon the IP. Thus, the oxidation, or stripping, of CO on Pt occurs via its reaction with OH radicals in a Langmuir−Hinshelwood reaction mechanism (where two different adsorbed species react). This is analogously true for reductions of some adsorbed species (like olefins) in aqueous solutions, where the reduction occurs via adsorbed hydrogen atoms, not by direct electron addition. Such a model is actually a throwback to much older proposed mechanisms of electrochemical reactions, where “nascent oxygen” (e.g., OH or O) or “nascent hydrogen” (e.g., H) was invoked to interpret the reaction paths (even for reactions that we now classify as outer-sphere reactions).[16]

Past Approaches to Electrocatalyst Discovery

In finding new electrocatalysts, both the chemical composition and the structure of the material can be important. As one considers, for example, bi- or trimetallic alloys or mixtures, one must deal with huge numbers of possibilities, both in the identity of the elements and in their relative amounts. This is further complicated by the fact that structural considerations can be important, so even with single-crystal metals, the different faces show different activities (e.g., for face-centered cubic Pt, the

(111), (100), and (110) faces). Special sites on a surface, for example, edges or corner sites, may also behave differently and indeed may be the key active sites in a reaction. In addition to these effects, the composition and the structure of the support on which the catalytic material is placed, for example, carbon or a metal oxide, can also play a role in catalyst performance. Moreover, other species in solution, certainly the solvent but also ions and adventitious impurities, can compete for adsorption sites and, if they are strongly adsorbed, "poison" the electrode surface for the reaction of interest. Indeed, even intermediates in an electrode reaction of interest, for example, CO in the oxidation of methanol, can poison (or greatly decrease the rate of) the electrode reaction. All of these considerations make study and theoretical treatments of ISERs difficult.

Detailed reaction mechanisms of ISERs, although the subject of many studies, are difficult to establish with the same confidence as that of outer-sphere ones because of all of these additional factors. There have been many, often very challenging studies with so-called "well-defined electrode surfaces", where single-crystal metals are prepared, characterized in a vacuum, for example, by low-energy electron diffraction (LEED) and scanning tunneling microscopy (STM), brought into highly purified solutions in electrochemical cells, and then returned to vacuum for characterization.[14] Powerful spectrometric methods, including synchrotron radiation-based techniques and mass spectrometry on well-characterized surfaces, are also becoming more widely used for studying intermediates and products.[14] These studies are closely related to similar catalysis studies for gas-phase reactions. An additional complication is that the surface may change during the course of an electrode reaction. For example, the catalyst may sinter, with growth of the catalyst particles, undergo reorganization to a different surface crystal form, or oxidize.

Electrochemical reactions are unique in that the rate of the reaction can be measured directly, since the rate is i/nF, where i is the current, n the number of electrons transferred, and F Faraday's constant. Typical mechanistic studies, for example, by a reaction order approach where the rate (current density) is studied as a function of potential and solution composition, are complicated by the large number of parameters needed to describe the reaction (e.g., electron-transfer and chemical rate constants, adsorption energies of reactants, intermediates, products and adsorbed solvent and ions). A classical approach, employed extensively, for example, for the hydrogen evolution reaction (HER), involves making general assumptions about adsorption energies (or adsorption isotherms) and the rate-determining step and predicting the variation of the current density with potential to obtain the transmission coefficient (symmetry factor), α, or equivalently, the "Tafel slope" (the slope of the plot of $\log(i)$ vs potential), which is then compared to experimental values. However, while this approach can be used to eliminate suggested reaction mechanisms, it has not proven very useful for even a qualitative evaluation of slightly complex ISERs. There are many examples in the literature that suggest mechanisms based on this approach that conflict with other studies that have identified intermediates.[17] Generally, it appears that one cannot elucidate complex multistep reactions on the basis of only a few parameters like a Tafel slope and reaction order. This is illustrated by the fact that, even after extensive study, there is no general agreement on the reaction mechanism, or even the rate-determining step, for the ORR on platinum.[18]

Theoretical tools and computing power have greatly advanced. For example, density functional theory (DFT) can be employed with reasonable size metal clusters to estimate the energies of intermediates on particular sites. This leads to estimates of energies of activation and predictions of preferred reaction paths. A difficulty with this approach involves the large number of surface structures that are possible, especially as one turns to multimetallic electrocatalysts, and while good estimates can be made when experimentally known compositions and structures are used, the predictive power for new electrode materials has been limited. Moreover, there is considerable uncertainty in dealing with the effect of potential on the reaction rate and with charged intermediates.[19] With ab initio methods it has also been difficult to deal with realistically large metal assemblies and do temporal simulations over experimentally interesting time ranges. Thus, the long-sought goal of using theory to discover new electrocatalyst compositions and design catalyst structures has, so far, remained largely unfulfilled.

There is clearly a need for models that can provide qualitative or semiquantitative guidelines to predict electrocatalytic behavior. For example, catalytic activity is often correlated with the metal lattice distances, and, via the Pauling theory of metals, the metal radius correlates with the percentage d-character of the metallic bond.[20] More recent models relate the d-bands to the strength of chemisorption of a species, which can affect the electrocatalytic activity of metals.[21] Another approach is through volcano curves,[22] which show a plot of activity (e.g., reaction rate) against some parameter, for example, the free energy of adsorption, that, in principle, leads one to useful materials. However, these well-established approaches have largely not yet led to the ability to select, on the basis of available physical or chemical data, metal alloys or other compositions that have proved to be efficient electrocatalysts. We have proposed thermodynamic guidelines for selecting catalysts which do not, however, have a firm theoretical backing but have helped us in finding catalysts for the ORR.[24]

Approaches Based on Scanning Electrochemical Microscopy

Discovery of new electrocatalysts with better performance, higher stability, and lower cost is not easy, and only the brave stray far from Pt. In fact, new compositions and structures are often found through intuitive approaches and experimental testing of different materials. What is needed, in addition to guidelines for predicting compositions and structures worth synthesizing and investigating, are automated methods of synthesizing and characterizing new materials and rapid methods of screening these for the desired electrode reactions under realistic conditions.

Rapid synthesis and screening has been used for finding active catalyst compositions by several approaches.[23] For example, a Pd−Co catalyst for oxygen reduction with a performance near to that of Pt in acidic solution and with a lower sensitivity to methanol was found by this approach.[24] Rapid preparation of an array of Pd−Co spots on glassy carbon (GC) was carried out with a simple robotic dispenser, with compositions Pd_xCo_{1-x} ranging from $x = 0$ to 1 in steps of 0.1 (Figure 5). The array was screened in deaerated 0.5 M H_2SO_4 by scanning electrochemical microscopy (SECM),[25] where a tip electrode that was generating oxygen was scanned in close proximity to the array and the current passing through the GC was measured (Figure 6). Only the electrocatalyst spot immediately under the tip saw an appreciable flux of oxygen and was addressed. The resulting

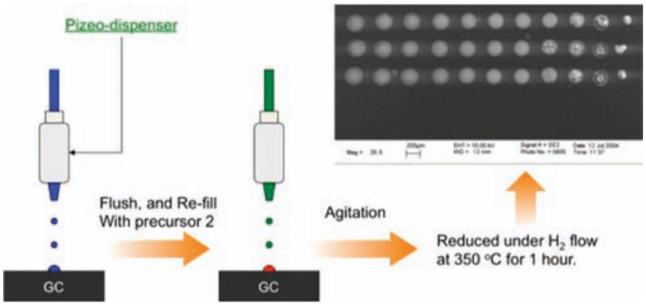

Figure 5. Method of array preparation using a dispenser. The piezo-dispenser is moved with a stepping motor under computer control and dispenses a designated number of drops of different solutions on substrate (e.g., glassy carbon); this is then subjected to an appropriate treatment (e.g., precipitation, reduction, oxidation) to produce the desired multicomponent array.

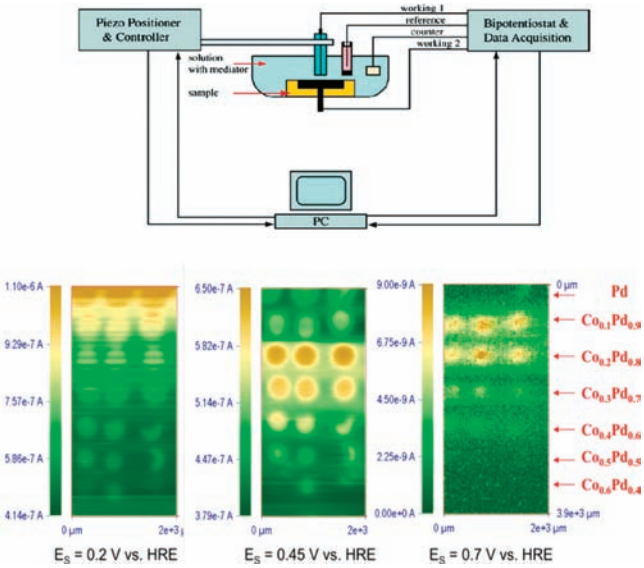

Figure 6. Top: Schematic diagram of a scanning electrochemical microscope and tip (working electrode 1) scanning above the array (sample) (working electrode 2). Bottom: Results for scanning an array of Pd−Co spots (indicated at right) in a solution of deaerated 0.5 M H_2SO_4 held at different potentials, where the tip generates O_2 as it scans across the array. Each row is a replicate of three spots to indicate reproducibility in spot preparation. Adapted with permission from ref 24. Copyright 2005 American Chemical Society.

image showed the best catalyst compositions. Of course, a problem with this approach is that the synthesis methods for the catalyst spots are limited, and the materials are not well characterized before the screening. However, once good possibilities are uncovered in the screening, alternative methods of preparation, more careful characterization, and studies with larger electrodes and with fuel cell membrane electrode assemblies are undertaken.[26,27] Of course, key issues of catalyst stability under long-term operating conditions, such as particle sintering, segregation, and corrosion, also have to be addressed.

Another aspect of electrocatalysis involves experimental approaches to determining the electrode reaction mechanism from electrochemical studies. As discussed above, the “classical” approach to this, trying to use the overall steady-state current−potential behavior as a function of reactant concentration, has not been very fruitful. What is needed is a transient approach analogous to that used for electrode reactions with coupled homogeneous reactions that has proved to be very useful in elucidating reaction mechanisms and measuring the rates of coupled reactions. The greater complexity of surface reactions will require following adsorbed species as functions of time and potential. This has been attempted by looking at cyclic voltammetric surface waves, but identification of the species producing the waves is difficult, as is separation of species generation from species consumption. For example, it is difficult to measure the species formed by dissociation on the electrode at open circuit electrochemically. However, spectroscopic methods like infrared and Raman have been used in many studies and, where they are sensitive enough, for example, in the detection of CO, have provided valuable information. Electrochemical impedance spectroscopy (EIS) can also supply information about adsorbed species in some cases.[28]

A SECM-based surface interrogation technique shows considerable promise.[29] In this approach a tip is held in close proximity to an electrode of equal size (e.g., each 25 μm diameter). A mediator in solution allows one to generate a reactant at the tip that can “titrate” the surface intermediate at the electrode below, taken to a potential of interest and then held at open circuit. For example, to determine adsorbed oxygen species on Pt or Au, the species $Ru(NH_3)_6^{2+}$ is generated at the tip (from $Ru(NH_3)_6^{3+}$), and this coulometrically titrates the oxidizing oxygen species on the surface. Adsorbed hydrogen[15] and CO[30] have also been determined by this approach. While SECM cannot identify the nature of the surface species with the same power as spectroscopic methods, selectivity is based on the nature of the “titrant” generated at the SECM tip, just as in conventional or coulometric titrations. It remains to be seen whether this technique will be able to measure short-lived intermediates or those with a low surface concentration that may decay at open circuit. Understanding the kinetic details of the tip response also needs to be addressed.

An important consideration about nanoparticle (NP) electrocatalysts is how the size, shape, structure, and support affect the activity. There have been many studies of this at the ensemble level, where the effect of a large number of particles is examined, but these inevitably involve a distribution of properties, and it is difficult to separate the effects of the different variables, especially if some NPs are much more active than others. Electrochemical studies with a single NP, although challenging, can be carried out.[31−34] Spectroscopic methods, like the fluorescence methods used in single-molecule detection experiments, can also play an important role in such studies.[35] An alternative approach is to study collisions of single NP electrocatalysts (e.g., Pt) from a low-concentration ensemble in solution with an inactive electrode material (e.g., C, Au), using the amplification effect from the electrocatalyzed reaction to generate sufficient (∼pA) currents to allow detection with good signal-to-noise.[36]

Photocatalyst Discovery

The widespread interest in the utilization of sunlight as an energy source has led to increased activity in the area of photoelectrochemistry (PEC).[37] Of particular interest is the use of sunlight to generate fuels like hydrogen, or, combined with CO_2 mitigation, carbonaceous fuels. There is less interest in photovoltaic devices based on PEC, with the possible exception of dye-sensitized solar cells (DSSCs), because of perceived difficulties with liquid-based devices compared to all-solid-state ones that are now commercially available. PEC is based on an electrochemical cell where at least one electrode is a semiconductor, which when irradiated generates electron−hole pairs that can be used to produce a current and drive redox reactions

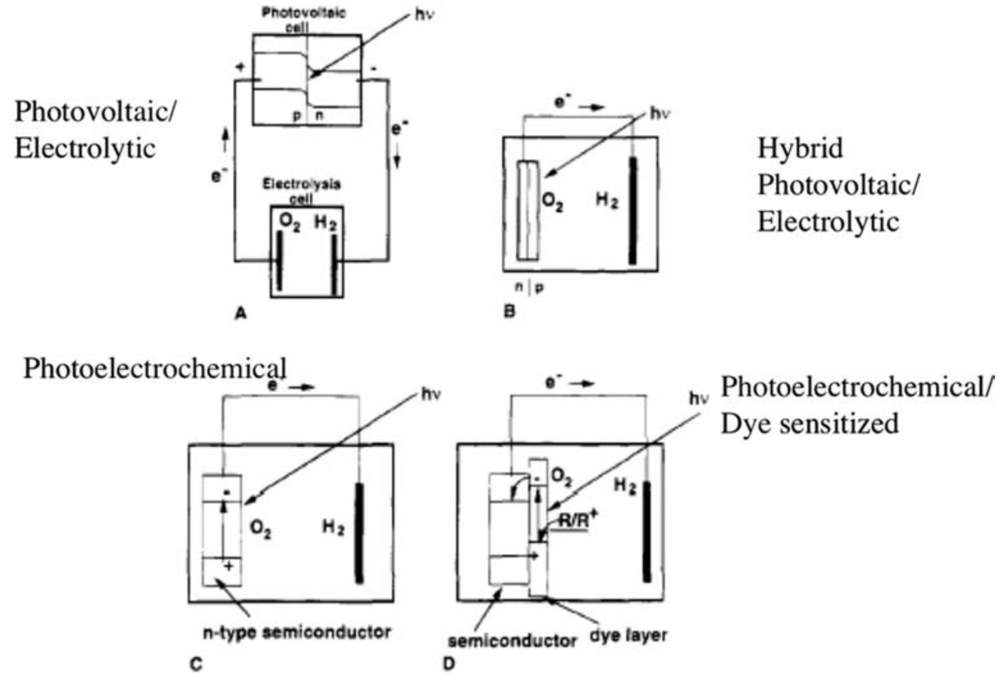

Figure 7. Schematic diagram of different types of photoelectrochemical cells. Adapted with permission from ref 38. Copyright 1995 American Chemical Society.

(Figure 7).[38] In the systems depicted, an oxidation reaction occurs at the n-type semiconductor and a reduction reaction at the counter electrode. Extensive research over about the past 40 years has led to the elucidation of the general principles of such systems and the discovery of many semiconductor materials that can be used, although none has so far been found with the needed efficiencies, costs, and stabilities for a practical, deployable system.

The energetics of the system is often given in terms of the band energies in the semiconductor and the energies of redox reactions in the liquid. For example, in illustrating the popular "water splitting" reaction involving the photoelectrolysis of water to produce H_2 and O_2, the system is often shown as in Figure 8. While this is correct in illustrating the thermodynamic requirements, it is misleading in suggesting the semiconductor electrode requirements in the absence of appropriate electrocatalysts at both semiconductor and metal cathode, for the very reasons discussed in the beginning about outer-sphere and inner-sphere heterogeneous electrode reactions. The absorption of a photon by the semiconductor generates a single electron and hole, so only one-electron reactions are available at water energy levels (orbitals) (as shown in Figure 9), and these are very different than the multielectron levels implied in Figure 8. Consider cells involving TiO_2, a widely investigated semiconductor material, which can carry out water splitting with an applied bias. The absorption of a photon produces an electron in the conduction band and a hole in the valence band. Chemically this corresponds to a charge transfer from a surface hydroxide to a Ti(IV) center to produce a hydroxyl radical and Ti(III). The hydroxyl radical production requires considerably more energy (a higher potential) than that implied in the 4e transfer to produce O_2. Thus, in a usual energy level diagram, available molecular orbitals rather than overall electrode half-reactions are more appropriate. Said in another way, the levels shown for water should at least be the one-electron ones describing an "effective band gap" of the solution, shown in Figure 9 and based on potentials for the formation of hydrogen atoms and hydroxyl radicals,[39] which is considerably larger than that implied by the multielectron thermodynamic ones.[40] Indeed, if the band gap of water were 1.23 eV, it would be black! The now classic paper by Fujishima and Honda[41] raised the possibility of photoelectrochemical water splitting with TiO_2 but, in fact, did not demonstrate it at any useful level, since the cell used had no additional external or internal bias and the conduction band edge of TiO_2 is not at a position where hydrogen evolution can occur at a reasonable rate. The existence of a photocurrent in a PEC cell is not proof of water splitting, since reduction of oxygen at the Pt cathode is a possibility. Only with a bias, provided externally or by having the TiO_2 in an

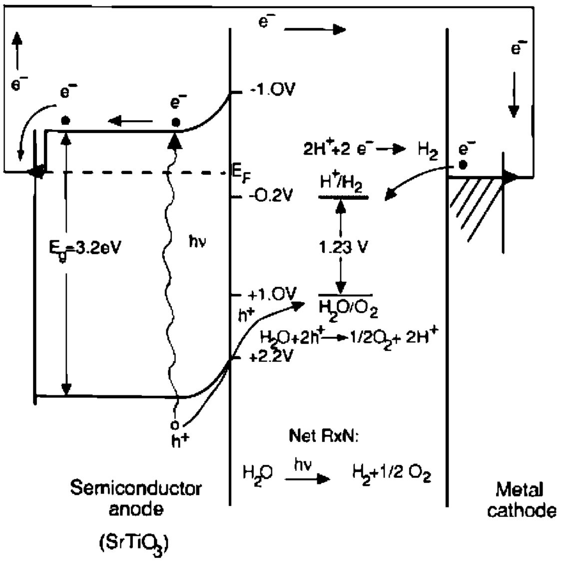

Figure 8. Typical semiconductor band diagram with respect to thermodynamic (multielectron transfer) half-reactions in solution for water splitting for $SrTiO_3$/solution/Pt photoeletrochemical cell. Adapted with permission from Nozik, A. J.; Memming, R. *J. Phys. Chem.* **1996**, *100*, 13061. Copyright 1996 American Chemical Society.

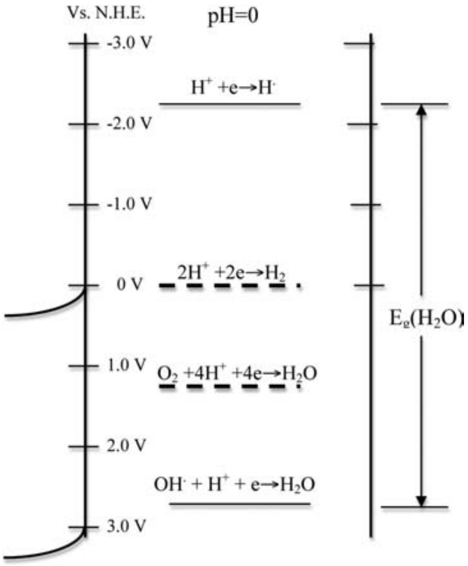

Figure 9. More realistic schematic of the bands in TiO_2 and water (solid lines). The dashed lines are the thermodynamics for the multielectron reactions that require electrocatalysts.

alkaline medium and the Pt electrode in an acidic one, is TiO_2 capable of generating O_2 and H_2, however.[42]

It was demonstrated quite early that the principles of PEC in cells could be carried over to particulate semiconductors, and TiO_2, sometimes platinized, could be used to carry the oxidative decomposition of CN^- and organic species.[43,44] This has recently become a quite active area, with numerous papers describing new materials tested for the decomposition of species like methylene blue or methyl orange. Such studies can indicate possible usefulness of the new material but are usually carried out under conditions where the reactions are photocatalytic ones, in the sense that the light enables an oxidation reaction, for example, of methylene blue with O_2, but without net conversion of radiant to chemical energy. The same is true with other reactions that investigate one-half of the water splitting reaction (e.g., O_2 evolution) but utilize a “sacrificial reagent” for the reduction reaction. In this case, the nature and redox potential of the sacrificial reagent govern how much, if any, radiant energy is captured as chemical energy. For example, if Ag^+ is used to capture the electrons in an acidic solution ($pH = 0$) where O_2 is evolved, then only about 0.43 eV is gained from the radiant energy, since the potential of the Ag^+/Ag couple is 0.80 V vs NHE. If peroxydisulfate is used as the sacrificial oxidant, then no energy is captured, since the $S_2O_8^{2-}/SO_4^{2-}$ couple has a potential near 2 V and is itself thermodynamically capable of oxidizing water. The same considerations apply when sacrificial reductants, like S^{2-} or organic molecules, are used in studies of particulate systems for H_2 evolution.

In the search for new photocatalysts with desirable band gaps, band energy locations, and stability, the SECM technique, as described above for electrocatalyst searches, can also be used with slight modification.[45,46] The array is prepared in a similar manner with fluorine-doped tin oxide (FTO) as the substrate. The scanning tip is replaced with a fiber optic connected to a xenon lamp light source. The fiber optic is surrounded by a gold ring electrode, so that electrochemical monitoring of the products of a photoreaction at a spot on the array can be monitored. Analogous approaches to laser scanning of photocatalyst arrays have also been reported.[47,48] This technique, as with electrocatalysts, sacrifices flexibility in the synthesis method but allows rapid screening of a large range of compositions. For example, additions of metal (dopants) to Fe_2O_3 have been shown to improve significantly the performance.

In the search for semiconductor photocatalysts for water splitting and fuel production, no single material has yet emerged that shows the efficiency and stability that suggest widespread applicability. A fundamental problem is that a semiconductor with a band gap that allows the needed oxidation and reduction reactions with required overpotentials to drive reactions at a reasonable rate with available electrocatalysts does not absorb a sufficient fraction of the solar spectrum to yield the needed efficiency. This is probably the evolutionary motivation for biological photosynthesis in green plants utilizing two photosystems in the so-called Z-scheme. Thus, multiple semiconductors and junctions will probably be needed to produce practical devices. Systems like this, for example, the photochemical diode with a p-(ohmic contact)-n structure, were suggested as early as 1976,[49] and for two n-type structures in a Z-scheme in 1979.[50] An example of a two n-semiconductor Z-scheme that showed water splitting with no bias has recently appeared.[51] Large-scale demonstrations with multiple semiconductor junctions have been described, and a system that was made in large areas for the solar splitting of HBr to H_2 and Br_2 with about an 8% efficiency, invented by Kilbey and produced by Texas Instruments, utilized two Si p-n junctions.[52] This could be incorporated in a more complex cell to carry out more energetic reactions, like H_2 and Cl_2 evolution,[53] and additional multijunction schemes were used to carry out water splitting and other reactions.[54] The record multijunction system for water splitting, for a p-$GaInP_2$ semiconductor connected by a tunnel junction to a p-n-GaAs photocell that provided an additional bias, was reported to show an efficiency of >11%.[55] Systems closer in overall structure to biological systems might be developed from “integrated chemical systems”, which are small (μm to mm) cells that can be inexpensively fabricated (and are perhaps self-organizing) and then assembled into a larger device.[56,57] The challenge is to make stable and inexpensive systems with practical electrocatalysts to make large-scale deployment practical.

Conclusions

Advances in electrochemical theory, instrumentation, and methodology over the past 60 years (unfortunately rarely recognized in most general and physical chemistry textbooks) have produced important insights into outer-sphere electron-transfer reactions in organic chemistry, inorganic chemistry, and biochemistry. The importance of electrocatalysts and photocatalysts in the development of practical sustainable energy systems should provide the needed impetus to bring our understanding and control of inner-sphere heterogeneous electron transfers to a similar level of development.

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References

(1) Taube, H. *Electron Transfer Reactions of Complex Ions in Solution*; Academic Press: New York, 1970; p 27.

(2) Haight, G. P., Jr. In *Encyclopedia of Physical Science and Technology*; Meyers, R. A., Ed.; Academic Press: New York, 2002; Vol. 5, p 352.

(3) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods—Fundamentals and Applications*; Wiley: New York, 2001; p 116.

(4) Saveant, J. M. *Elements of Molecular and Biomolecular Electrochemistry*; Wiley: New York, 2006.

(5) Saveant, J. M. *Chem. Rev.* **2008**, *108*, 2111–2112.

(6) Streitwieser, A., Jr. *Molecular Orbital Theory for Organic Chemists*; Wiley: New York, 1961; Chap. 7.

(7) Peover, M. E. In *Electroanalytical Chemistry*; Bard, A. J., Ed.; Marcel Dekker: New York, 1967; Vol. 2, p 41.

(8) Evans, D. H. *Chem. Rev.* **2008**, *108*, 2113–2144.

(9) Bard, A. J.; Jordan, J.; Parsons, R. *Standard Potentials in Aqueous Solution*; Marcel Dekker: New York, 1985.

(10) Tissandier, M. D.; Cowen, K. A.; Feng, W. Y.; Gundlach, E.; Cohen, M. H.; Earhart, A. D.; Coe, J. V.; Tuttle, T. R., Jr. *J. Phys. Chem. A* **1998**, *102*, 7787–7794.

(11) Somorjai, G. A. *Introduction to Surface Chemistry and Catalysis*; Wiley-Interscience: New York, 1994.

(12) Ponec, V.; Bond, G. C. *Catalysis by Metals and Alloys*; Elsevier: Amsterdam, 1995.

(13) Lipkowski, J., Ross, P. N., Eds. *Electrocatalysis*; Wiley-VCH: New York, 1998.

(14) Koper, M. T. M., Ed. *Fuel Cell Catalysis—A Surface Science Approach*; Wiley: New York, 2009.

(15) Rodríguez-López, J.; Bard, A. J. *J. Am. Chem. Soc.* **2010**, *132*, 5121–5129.

(16) Creighton, H. J. *Principles and Applications of Electrochemistry*, 2nd ed.; John Wiley & Sons: New York, 1928, Vol. 1, p 274.

(17) Johnson, J. W.; Wroblowa, H.; Bockris, J. O'M. *Electrochim. Acta* **1964**, *9*, 639.

(18) Gottesfeld, S. In ref 14, p 2.

(19) Janik, M. J.; Wasileski, S. A.; Taylor, C. D.; Neurock, M. In ref 14, pp 94−95.

(20) Boudart, M. *J. Am. Chem. Soc.* **1950**, *72*, 1040.

(21) Hammer, B.; Nørskov, J. K. In *Advances in Catalysis*, Vol. 45; Gates, B. C., Knözinger, H., Eds.; Academic Press: New York, 2000; p 71.

(22) Balandin, A. A. *Adv. Catal.* **1969**, *19*, 1.

(23) (a) Liu, R.; Smotkin, E. S. *J. Electroanal. Chem.* **2002**, *535*, 49. (b) Strasser, P.; Fan, Q.; Devenney, M.; Weinberg, W. H.; Liu, P.; Nørskov, J. K. *J. Phys. Chem. B* **2003**, *107*, 11013. (c) Guerin, S.; Hayden, B. E.; Lee, C. E.; Mormiche, C.; Owen, J. R.; Russell, A. E. *J. Comb. Chem.* **2004**, *6*, 149. (d) Jayaraman, S.; Hillier, A. C. *J. Comb. Chem.* **2004**, *6*, 27. (e) Jambunathan, K.; Jayaraman, S.; Hillier, A. C. *Langmuir* **2004**, *20*, 1856. (f) Jayaraman, S.; Hillier, A. C. *J. Phys. Chem. B* **2003**, *107*, 5221. (g) Jambunathan, K.; Hillier, A. C. *J. Electrochem. Soc.* **2003**, *150*, E312.

(24) Fernandez, J. L.; Walsh, D. A.; Bard, A. J. *J. Am. Chem. Soc.* **2005**, *127*, 357.

(25) Bard, A. J., Mirkin, M. V., Eds. *Scanning Electrochemical Microscopy*; Marcel Dekker: New York, 2001.

(26) Fernandez, J. L.; Raghuveer, V.; Manthiram, A.; Bard, A. J. *J. Am. Chem. Soc.* **2005**, *127*, 13100.

(27) Fernandez, J. L.; White, J. M.; Sun, Y.; Tang, W.; Henkelman, G.; Bard, A. J. *Langmuir* **2006**, *22*, 10426.

(28) Lasia, A. In *Modern Aspects of Electrochemistry*; Conway, B. E., Bockris, J., White, R. E., Eds.; Kluwer Academic/Plenum Publishers: New York, 1999; Vol. 32, pp 143−248.

(29) Rodríguez-López, J.; Alpuche-Avilés, M. A.; Bard, A. J. *J. Am. Chem. Soc.* **2008**, *130*, 16985.

(30) Wang, Q.; Rodríguez-López, J.; Bard, A. J. *J. Am. Chem. Soc.* **2009**, *131*, 17046.

(31) Meier, J.; Friedrich, K. A.; Stimming, U. *Faraday Discuss.* **2002**, *121*, 365.

(32) Meier, J.; Schiotz, J.; Liu, P.; Norskov, J. K.; Stimming, U. *Chem. Phys. Lett.* **2004**, *390*, 440.

(33) Chen, S. L.; Kucernak, A. *J. Phys. Chem. B* **2004**, *108*, 13984.

(34) Tel-Vered, R.; Bard, A. J. *J. Phys. Chem. B* **2006**, *110*, 25279.

(35) (a) Novo, C.; Funston, A. M.; Mulvaney, P. *Nat. Nanotechnol.* **2008**, *3*, 598. (b) Xu, W.; Kong, J. S.; Yeh, Y.-T. E.; Chen, P. *Nat. Mater.* **2008**, *7*, 992. (c) Xu, W.; Kong, J. S.; Chen, P. *J. Phys. Chem. C* **2009**, *113*, 2393. (d) Xu, W.; Kong, J. S.; Chen, P. *Phys. Chem. Chem. Phys.* **2009**, *11*, 2767. (e) Chen, P.; Xu, W.; Zhou, X. C.; Panda, D.; Kalininskiy, A. *Chem. Phys. Lett.* **2009**, *470*, 151.

(36) (a) Xiao, X. Y.; Bard, A. J. *J. Am. Chem. Soc.* **2007**, *129*, 9610. (b) Xiao, X.; Fan, F.-R. F.; Zhou, J.; Bard, A. J. *J. Am. Chem. Soc.* **2008**, *130*, 16669.

(37) Archer, M. D.; Nozik, A. J. *Nanostructured and Photoelectrochemical Systems for Solar Photon Conversion*; Imperial College Press: London, 2008.

(38) Bard, A. J.; Fox, M. A. *Acc. Chem. Res.* **1995**, *28*, 141.

(39) Bard, A. J.; Parsons, R.; Jordan, J. *Standard Potentials in Aqueous Solution*; Dekker: New York, 1985.

(40) do Couto, P. C.; Cabral, B. J. C. *J. Chem. Phys.* **2007**, *126*, 014509.

(41) Fujishima, A.; Honda, K. *Nature* **1971**, *238*, 37.

(42) Fujishima, A.; Kohayakawa, K.; Honda, K. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 1041.

(43) Frank, S. N.; Bard, A. J. *J. Am. Chem. Soc.* **1977**, *99*, 303.

(44) Kraeutler, B.; Bard, A. J. *J. Am. Chem. Soc.* **1978**, *100*, 2239.

(45) Lee, J.; Ye, H.; Pan, S.; Bard, A. J. *Anal. Chem.* **2008**, *80*, 7445.

(46) Jang, J. S.; Lee, J.; Ye, H.; Fan, F.-R. F.; Bard, A. J. *J. Phys. Chem. C* **2009**, *113*, 6719.

(47) (a) Woodhouse, M.; Herman, G. S.; Parkinson, B. A. *Chem. Mater.* **2005**, *17*, 4318. (b) Woodhouse, M.; Parkinson, B. A. *Chem. Mater.* **2008**, *20*, 2495.

(48) (a) Baeck, S. H.; Jaramillo, T. F.; Brändli, C.; McFarland, E. W. *J. Comb. Chem.* **2002**, *4*, 563. (b) Jaramilo, T. F.; Baeck, S. H.; Kleiman-Schwarsctein, A.; Choi, K. S.; Stucky, G. D.; McFarland, E. W. *J. Comb. Chem.* **2005**, *7*, 264.

(49) Nozik, A. J. *Appl. Phys. Lett.* **1976**, *29*, 150.

(50) Bard, A. J. *J. Photochem.* **1979**, *10*, 59.

(51) Maeda, K.; Higashi, M.; Lu, D.; Abe, R.; Domen, K. *J. Am. Chem. Soc.* **2010**, *132*, 5858–5868.

(52) (a) Kilby, J. S.; Lathrop, J. W.; Porter, W. A. Solar Energy Conversion. U.S. Patent 4,021,323, May 3, 1977. (b) McKee, W. R. *IEEE Trans. Compon., Hybrids, Manuf. Technol.* **1998**, *CHMT-5*, 425.

(53) White, J. R.; Fan, F.-R. F.; Bard, A. J. *J. Electrochem. Soc.* **1985**, *132*, 544.

(54) (a) Smotkin, E.; Bard, A. J.; Campion, A.; Fox, M. A.; Mallouk, T.; Webber, S. E.; White, J. M. *J. Phys. Chem.* **1986**, *90*, 4604. (b) Smotkin, E.; Cervera-March, S.; Bard, A. J.; Campion, A.; Fox, M. A.; Mallouk, T.; Webber, S. E.; White, J. M. *J. Phys. Chem.* **1987**, *91*, 6. (c) Cervera-March, S.; Smotkin, E.; Bard, A. J.; Campion, A.; Fox, M. A.; Mallouk, T.; Webber, S. E.; White, J. M. *J. Electrochem. Soc.* **1988**, *135*, 567.

(55) Khaselev, O.; Turner, J. A. *Science* **1998**, *280*, 425.

(56) Krishnan, M.; White, J. M.; Fox, M. A; Bard, A. J. *J. Am. Chem. Soc.* **1983**, *105*, 7002.

(57) Bard, A. J. *Integrated Chemical Systems*; Wiley: New York, 1994.

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