perspectives
on physical electrochemistry

The study of electrochemistry is the study of systems. Whether the system is divided into the three domains of mass transport, electron transfer, and homogeneous kinetics or visualized as a thermodynamic expectation restricted by kinetics and dynamics, the conceptualization remains that of a physical electrochemist. The domain of physical electrochemistry extends from the traditional elegance of thermodynamics through new materials, and efficient power sources, to sophisticated modeling and experimental protocols. In what follows, several areas of physical electrochemistry are highlighted, and are ordered from the substantially theoretical through to the more practical. The sequence is as follows: double layer studies, electron transfer theory, molecular dynamics modeling, spectroscopic investigations, electroanalysis, and modified electrodes. These topics and the content of the following reviews are by no means an exhaustive representation of the diverse components and research activities that constitute physical electrochemistry. Nonetheless, they do highlight the critical coupling between theory and experiment that is the hallmark of sophisticated research in physical electrochemistry. ∎

Recent Developments in Double Layer Studies

by W. Ronald Fawcett

David Grahame established double layer studies in the United States. At the time of his famous review[1] in 1947, experimental work was limited to thermodynamic studies at liquid mercury. In 1997, Grahame's pioneering work was honored by a symposium of The Electrochemical Society[2], where three distinct advances over the last 50 years became apparent. First, experimental techniques for studying double layer phenomena at well-characterized solid metal electrodes are well established. Second, a battery of spectroscopic techniques allows characterization of the metal/solution interface at a molecular level. Third— and perhaps the one most easily overlooked advance—is the availability of high speed, powerful computers. Grahame's only tool for analyzing his capacity data was an adding machine, 1940 version.

Here, some of the major advances in this field are outlined: thermodynamic aspects of double layer studies, spectroscopy and scanning tunneling microscopy for atomic and molecular level investigations, and major theoretical advances. Reviews of some of these topics are found in Ref. 3.

Single crystals are needed to study the double layer at solid electrodes. From the pioneering work of Frumkin, both the work function and the point of zero charge of a single crystal metal depend on the crystallographic orientation exposed to solution. Hamelin and Clavilier carried out pioneering work in this area and on the preparation of single crystal metal surfaces. Lipkowski[4] later obtained reproducible thermodynamic data for adsorption at single crystal gold surfaces.

Double layer studies at solid metal electrodes are plagued by the frequency dispersion of interfacial capacity because single crystal surfaces are not atomically smooth, but have microscopic imperfections such as steps. Surface reconstruction is induced by surface preparation techniques such as flame annealing, and by the experimental perturbations of adsorption and change in electrode potential. These problems are overcome when electrodes are carefully prepared in the working solution, and thermodynamic data are collected chronoamperometrically.[4] Questions about the interpretation of thermodynamic data at solid electrodes raised at the Montréal symposium[2] are now resolved.[5]

High quality data are important in the interpretation of double layer effects in electrode kinetics.[6] Double layer data should be obtained by the same technique used to obtain the kinetic data.[7] Potential sweep voltammetry for the reduction of $[Co(NH_3)_6]^{3+}$ at various gold single crystal (Au(111), Au(110), and Au(210)) electrodes leads to the conclusion that the species transported through the diffuse double layer is an ion pair with a net charge of +2. These experiments confirm ideas traceable to

Frumkin that outer sphere electron transfer kinetics at electrodes depend on the point of zero charge of the metal electrode.

A variety of spectroscopic techniques is now available to study the structure of the electrical double layer.[3] A particularly powerful technique is subtractively normalized interfacial FTIR spectroscopy (SNIFTIRS). Faguy and Marinkovic[18] described a hemispherical window for greatly enhanced sensitivity. To study the adsorption of organic molecules on single crystal gold electrodes, Lipkowski, *et al.*[8] used SNIFTIRS with polarized infrared radiation to track the orientation of pyridine at the electrode/solution interface. SNIFTIRS also tracked the reorientation of solvent molecules at the interface as the sign of the electrode potential was reversed.[9] Other important spectroscopic techniques include X-ray scattering experiments, sum-difference frequency generation, and second harmonic generation.[3]

Scanning tunneling microscopy (STM) is an invaluable tool for surface analysis.[10] A related technique used in interfacial electrochemistry is scanning electrochemical microscopy (SECM).[11] Kolb studied reconstruction of gold electrodes using STM[3] to map the spatial arrangement of adsorbed atoms. The work function depends strongly on the atomic structure of the surface. This, in turn, affects the point of zero charge and therefore double layer composition.

Significant advances have been made recently in double layer theory. Schmickler[12] emphasized the role of the metal in improving the model of the double layer. Introduction of pseudo-potentials into the simple jellium model accounts for effects of surface crystallinity on derived double layer properties. Another area of research involves Monte Carlo (MC) and molecular dynamics (MD) calculations. In early work, MC simulations of the diffuse layer were carried out at the primitive level, where ion distribution functions were determined assuming a dielectric continuum for the solvent. These calculations showed that classical Gouy-Chapman (GC) theory overestimates the potential drop across the diffuse layer for 1-1, 2-1, and 2-2 electrolytes.[17]

Recently, in non-primitive level MD simulations for aqueous 1-1 electrolytes,[13,14] solvent molecules are included as discrete components; water molecules are described using the rigid SPC/E model with partial charges on each atom; and ions are charged Lennard-Jones spheres. The electrode is modeled as a conducting wall with no specific chemical interactions with either ions or water molecules, but image interactions important in determining the electrostatic energy of individual ions are considered. Results were obtained for concentrated solutions of NaCl and CsF, where specific adsorption is absent for the smaller cation Na^+ but is present for Cs^+ at negative charge densities. Correspondingly for anions, Cl^- is specifically adsorbed at positive charge densities but the smaller, more strongly hydrated F^- anion is not (Fig. 1). MD calculations yield valuable information about double layer structure. However, the model must be improved by incorporation of specific chemical interactions between the metal electrode and solution components.

In spite of the impressive advances made in double layer simulation, there is still a critical need for an analytical model of the diffuse layer. All analyses of experimental data rely on the GC model in spite of its well-known imperfections. In the early 1980s, attempts were made to develop an improved diffuse layer model based on the integral equation approach.[15] However, the equations could not be solved analytically and reasonable results over a wide range of electrode charge densities are only available using the hypernetted chain approximation (HNC). Important double layer parameters such as the potential drop across the diffuse layer ϕ^d are only obtained after lengthy iterative computer calculations. More recently, Fawcett and Henderson[16] used a generalized mean spherical approximation (GMSA). With the HNC equations as a guide, an analytical expression for the potential drop ϕ^d was derived. For 1-1 electrolytes, exact agreement with the earlier MC results of Torrie and Valleau[17] is found
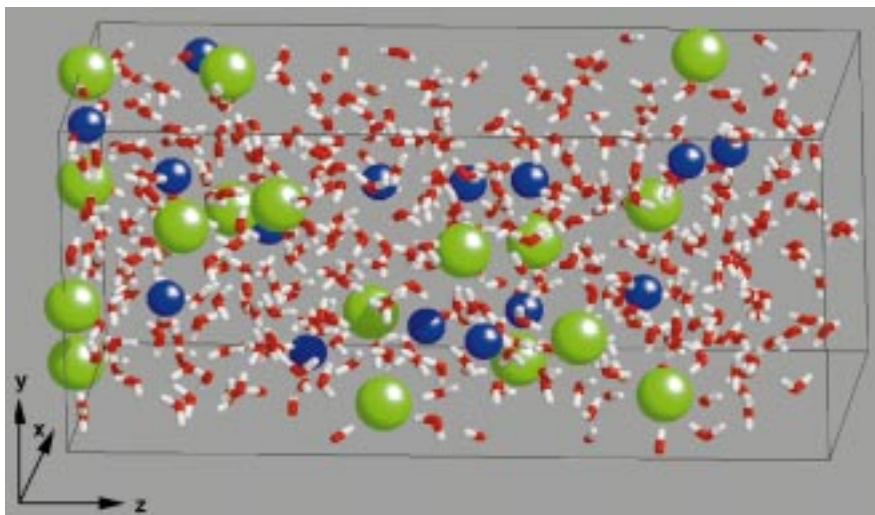

Fig. 1. Snapshot of the simulation of 2.2 M NaCl at a surface charge density of 9.9 $\mu C\ cm^{-2}$. The small spheres are Na^+ ions and the larger ones, Cl^- ions. The electrode is on the left. Reprinted from J. Electroanal. Chem., **450**, 327 (1998) with permission from Elsevier Science.
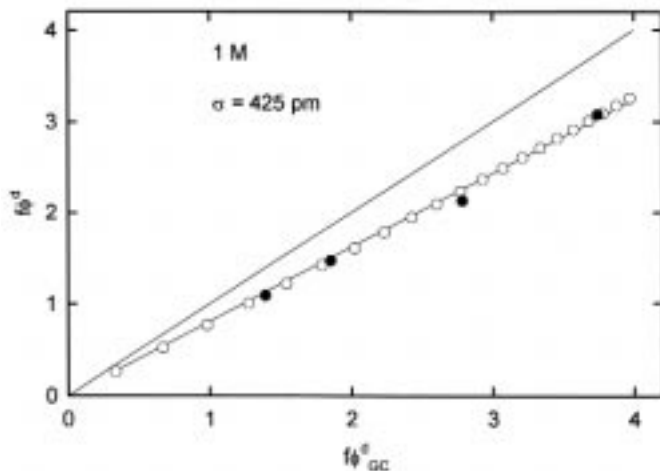

Fig 2. Plot of $f\phi^d$ estimated at 1 M by the GMSA (○) against the GC estimate $f\phi^d_{GC}$ where $f = F/RT$. The MC results are shown (●). The upper solid line gives the GC results. Data from J. Phys. Chem., **104**, 6837 (2000). Reproduced by permission of the American Chemical Society.

(Fig. 2). Further advances of the GMSA model will include detailed examination of the effects of ionic size, derivation of ion-electrode correlation functions within the diffuse layer, and extension to more complex electrolytes including 2-1, 2-2, and 3-1 systems. Improved estimates of ϕ^d will enhance the interpretation of double layer effects in electrode kinetics.

The above is a brief introduction to some new, exciting developments in double layer research, but it is by no means exhaustive. For example, considerable effort has been expended to understand the properties of polarizable interfaces modified by self-assembled monolayers (SAMS).[19] Finally, it has been my experience that quite a few electrochemists find the double layer a source of frustration that they wish would disappear. Unfortunately, double layers are present at all boundaries between phases that contain free charges such as ions. Thus, the ultimate irony is that brain activity, whether it involves love or contempt for the double layer, is a manifestation of double layer phenomena. Hopefully, the work being carried out at the metal/solution interface will also find application in biological systems. ∎

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Hopping Across Interfaces: Heterogeneous Electron Transfer Dynamics

by Robert J. Forster

From molecular electronic devices to catalysis and corrosion, the dynamics of heterogeneous electron transfer underpin key scientific and technological advances. Microelectrodes and high performance instrumentation enable the study of heterogeneous electron transfer reactions under unusual conditions and at short timescales. Localized, even atomically resolved, measurements of electron transfer dynamics allow construction of precise maps of surface reactivity. Adsorbed monolayers continue to revolutionize our understanding of the effects of distance, molecular structure, solvent reorganization, and microenvironment on electron transfer dynamics. Sophisticated theoretical models allow general conclusions to be drawn from specific chemical systems. The advantages of electrochemistry over spectroscopy are increasingly recognized, particularly for providing direct information and probing interactions with tremendous sensitivity. Investigations into heterogeneous electron transfer have come of age, providing powerful new insights with importance far outside the realm of electrochemistry. The future will see increasingly detailed studies and implementations in diverse areas including biochemistry, sensors, molecular electronics, and advanced materials.

The Elementary Steps

Figure 1 illustrates the elementary steps in the overall electron transfer process for a solution phase reactant: transport, nuclear activation, electronic coupling of the redox center with the electrode, and the instantaneous elementary electron transfer event. In this ideal case, specific surface interactions between the redox centers and the electrode surface are not considered.

Transport—Transient electrochemical measurements with a solution phase redox probe establish a competition between electron transfer at the surface and diffusion to and from the electrode.[1] For successful measurement of electron transfer rates, the mass transport rate must exceed the electron transfer rate. Mass transport limitations are eliminated by controlling the experimental timescale, using stirred and flowing solutions, rotating the electrode or, more conveniently, using microelectrodes, *i.e.,* electrodes with critical dimension ≲ 10 µm.

Thermal Activation—In solution, the energy of the donor Highest Occupied Molecular Orbital (HOMO) or acceptor Lowest Unoccupied Molecular Orbital (LUMO) vary continuously. Random thermal fluctuations and the ingress and egress of solvent dipoles from the solvation shell cause donor and acceptor levels to fluctuate about some mean value, which may facilitate or hinder electrolysis at any particular instant. Electron transfer only occurs when the energy of electrode and molecular states are identical, that is, resonance is achieved. Typically, only an extremely small fraction of species adjacent to the electrode to have sufficient energy to allow electron transfer to resonance because the free energy required to create these activated states is typically many times higher than the average thermal energy.

Electronic Coupling—Once resonance is achieved, donor and acceptor orbitals must couple electronically. The extent of electronic coupling between the redox centers and electrode typically increases exponentially with decreasing separation.

What about the timescale for elementary electron transfer? Because of the huge difference in the mass of electrons and nuclei, electron transfer occurs instantaneously relative to nuclear motion (*i.e.*, the Franck-Condon principle applies). At the instant of electron transfer, the redox center switches from the oxidized to reduced form while maintaining its internal structure and solvation shell. Given instantaneous electron transfer, energy is not exchanged with the surrounding medium. Therefore, as discussed above, the internal energy of the reactants and products must be identical.

Butler-Volmer Model—The Butler-Volmer formulation is the oldest and least complicated model for heterogeneous electron transfer kinetics, but, as a macroscopic model, it does not explicitly consider the individual steps described above. However, this empirical formulation does provide an experimentally accessible description of electrode kinetics. From a semi-log plot of the overpotential (η) versus current density, the symmetry factor (α) and the standard heterogeneous rate constant ($k°$) are obtained. However, the Butler-Volmer formulation is deficient in a number of respects. First, the prediction that rate constants will increase exponentially with electrical driving force agrees with experiment only over a limited range of overpotentials. Microelectrodes allow the rate constant (k) to be measured over very wide ranges of η, where k initially depends exponentially on η but becomes independent of η for more extreme values. Second, the Butler-Volmer formulation fails to account for the known distance dependence of heterogeneous electron transfer rates. Third, it cannot predict how changes in either redox center structure or solvent will affect $k°$. Marcus theory addresses these issues directly and is widely accepted as the most powerful and complete description of electron transfer reactions.

Marcus Theory—We concentrate first on the standard heterogenous electron transfer rate constant, $k°$, when the electrochemical driving force is zero. Transition state theory focuses on the intersection of the free energy surfaces. The reaction rate depends on the product of the number of molecules with sufficient energy to reach the transition state at a particular instant in time and the probability that they cross over the transition state. The number of molecules at the transition state depends on the free energy of activation, $\Delta G°$.

Marcus assumes that the dependence of $\Delta G°$ on the reaction coordinate is described as a simple parabola. That is, each vibration involved in redox center activation behaves as a harmonic oscillator and the solvent energy depends quadratically on the charge density of the molecule. The free energies of both outer sphere solvent reorganization, ΔG_{os}, and inner-sphere vibrations, ΔG_{is}, contribute to the total free energy of activation, ΔG_{Total}. The inner sphere free energy of activation represents the minimum energy required to change the internal structure of the redox center to its nuclear transition state configuration. The outer sphere, or solvent, component arises because the redox center charge typically changes significantly during electron transfer. ΔG_{os} is dependent on the static (ε_s) and optical (ε_{op}) dielectric constants of the solvent. Unlike the empirical Butler-Volmer model, the Marcus formulation yields a heterogeneous electron transfer rate constant sensitive to both the structure of the redox center and the solvent.

The frequency factor, υ, describes the success rate of transition state crossings. Thus, υ is the product of the rate of motion along the reaction coordinate, υ_n, and the probability of crossing over from the reactant to product hypersurfaces once the transition state has been reached, κ_{el}.

If electron transfer significantly distorts the bond lengths and angles of the molecule, *i.e.*, $\Delta G_{is} \gg \Delta G_{os}$, υ is typically 10^{13} to 10^{14} s^{-1}. If the molecular structure is largely unperturbed by redox switching, then υ_n is dictated by the dynamics of solvent reorganization and for typical electrochemical solvents is 10^{11} to 10^{12} s^{-1}.

The magnitude of κ_{el} varies from zero to unity, dependent on whether the electronic coupling is weak or strong. For strong electronic (adiabatic) coupling, there is significant flattening of the reaction hypersurface close to the transition state. The rate of crossing the barrier region is reduced but the probability of electron transfer actually occurring once the transition state has been achieved is close to unity. Adiabatic reaction rates are sensitive to the dynamics of solvent relaxation. Heterogeneous electron transfers are often assumed to be adiabatic because it simplifies the kinetic analysis, but this assumption is often not justified. In contrast, non-adiabatic reactions involve weak coupling and the transition state appears as a sharp cusp.

Potential Dependence of the Rate Constant—The sensitivity of heterogeneous electron transfer rates to overpotential depends on the extent of electronic coupling between the reactant and the electrode.[2] For strongly coupled reactants, electron transfer occurs predominantly through states near the Fermi level of the electrode and the adiabatic potential dependent rate con-
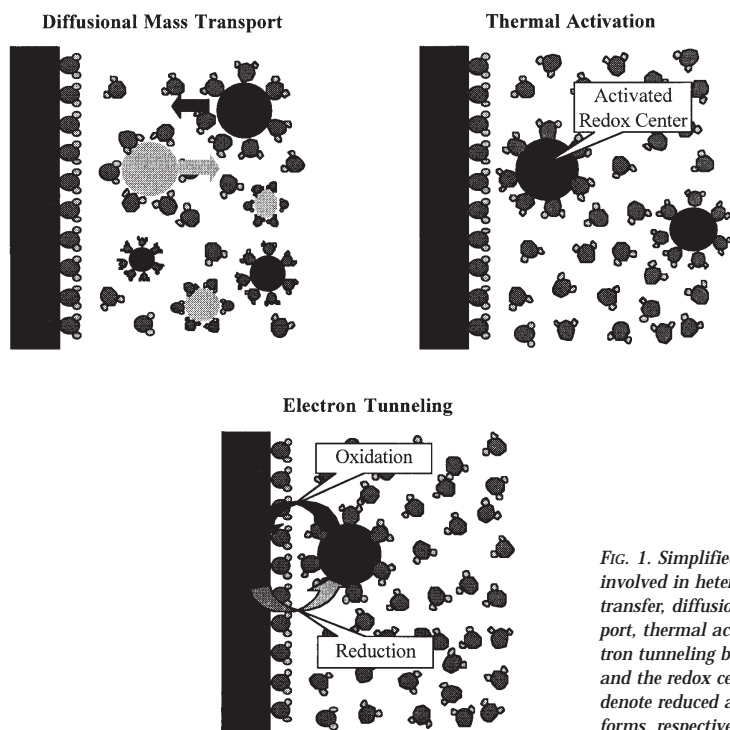
Diffusional Mass Transport

Thermal Activation

Activated Redox Center

Electron Tunneling

Oxidation

Reduction

FIG. 1. *Simplified elementary steps involved in heterogeneous electron transfer, diffusional charge transport, thermal activation, and electron tunneling between electrode and the redox center.* ● *and* ● *denote reduced and oxidized forms, respectively.*

stant is given by the product of the frequency factor, υ_n, and the density of acceptor states in the molecule, D_{ox}.

For non-adiabatic systems, electrons with energies below the Fermi level can be transferred and it is necessary to sum over all electron energies, not just at the Fermi level, E_f. The effects of electronic coupling on $k(E)$ only become apparent at high driving forces. Perhaps the most significant consequence of the Marcus formalism is that, unlike Butler-Volmer theory, it predicts a curvature in plots of ln k $vs.$ η in both the adiabatic and non-adiabatic cases. For extremely large driving forces, k no longer depends on η and reaches a maximum when $\eta \simeq \lambda$. This is the famous Marcus inverted region.

Electron Transfer Dynamics of Solution Phase Reactants—Heterogeneous electron transfer rate constants are conveniently measured using transient electrochemical techniques with microelectrodes being used in the majority of studies. At short times, the diffusion layer thickness is much smaller than the microelectrode radius and planar diffusion dominates. Under these conditions, classical theories, *e.g.*, that of Nicholson and Shain,[3] can be used to extract kinetic parameters from the scan rate (v) dependence of the separation between the anodic and cathodic peak potentials (ΔE_p). Two complexities must be considered. First, Faradaic and charging currents must be separated. In cyclic voltammetry, the charging current increases proportionally to v, whereas the Faradaic current for a diffusive species is proportional $v^{1/2}$. Therefore, the ratio of Faradaic to charging current decreases with increasing scan rate. One strategy is to measure the charging current in blank electrolyte and to subtract it from the current observed in the presence of the analyte. Second, ohmic drop can distort the wave shape when heterogeneous electron transfer rates are determined from the scan rate dependence of ΔE_p. Ohmic effects not only contribute significantly to ΔE_P independent of heterogeneous electron transfer, but also vary with scan rate. Several strategies are used to decrease ohmic effects. Faradaic information can be extracted either by means of convolution of the voltammograms with the diffusion operator $(\pi t)^{-1/2}$, or by simulation of the experimental voltammogram using a model that incorporates ohmic and capacitive factors. Ohmic drops can be largely compensated using positive feedback circuitry during measurements.

As shown in Table I, the heterogeneous electron transfer dynamics of a diverse range of species have been investigated (anthracene[4], anthraquinone[4], benzoquinone[5], ferrocene[6], ferrcyanide[7], 9-fluorenone[8], and $[Ru(bpy)_3]^{2+}$ [6]). The magnitude of k° varies significantly. Large poly-aromatic hydrocarbons that can be reduced with very little change in bond lengths or angles exhibit very large standard rate constants, *e.g.*, k° for anthracene[9] is 3.5 cm s^{-1}. Where molecular structure is significantly distorted by the redox reaction, or where the reaction involves multiple steps, k°'s as small as 10^{-9} cm s^{-1} are observed. That is, k° spans ten orders of magnitude!

To extend the upper limit of measurable electron transfer rate constants, measurements can be made at lower temperatures, because even for heterogeneous electron transfers with negligible inner sphere reorganization energies, activation barriers of 20-25 kJ mol^{-1} are expected. Considerably slower rates are observed by decreasing the temperature by a few tens of degrees. Microelectrodes facilitate these measurements because solvents, such as alcohols and nitriles, that remain liquid over a wide temperature range, can be used without catastrophic ohmic effects. Weaver and co-workers[10] investigated ferrocene, *o*-nitrotoluene and nitrometisylene systems in acetonitrile, propionitrile, and butyronitrile at gold microdiscs using scan rates up to 10^4 V s^{-1} between 200 and 300 K. Experimental voltammograms were simulated, taking activation enthalpy, temperature-dependent diffusion coefficients, and double layer capacitance into account. For ferrocene, k° ranged from 0.083 cm s^{-1} at 198 K to ~5.5 cm s^{-1} at 298 K, and yields an activation enthalpy of 20 kJ mol^{-1}.

Adsorbed Monolayers—For solution phase reactants, the diffusion controlled current at short times ultimately limits the maximum rate constant that can be measured. For diffusive species, the thickness of the diffusion layer, δ, is defined as $\delta = (\pi Dt)^{1/2}$, where t is polarization time and D is the diffusion coefficient. For D = 1×10^{-5} cm^2 s^{-1} and t = 10 ns, the diffusion layer thickness is $\simeq 50$ Å. For a 1 mM bulk concentration of the electroactive species, only 10,000 molecules would be electrolyzed at a 1 µm radius microdisk. This yields an average current of 170 nA, which is too small to be detected with nanosecond time resolution.

Monolayers, self-assembled or spontaneously adsorbed on an electrode eliminate diffusion limitations and pre-concentrate the redox probe. Under the diffusive conditions above, there are $\approx 1.7\times10^{-20}$ mol of electroactive material within the diffusion layer; for a 1 µm disc this is an equivalent surface coverage of $\approx 5.4\times10^{-13}$ mol cm^{-2}. In contrast, the surface coverage, Γ, observed for dense monolayers is typically > 100-fold larger with coverages of the order of 10^{-10} mol cm^{-2}. This gives rise to much larger currents, easily detected at short timescales.

As exemplified by the work of Chidsey,[11] Abrûna,[12] and Finklea,[13] electroactive adsorbed monolayers have been developed that exhibit close to ideal reversible electrochemical behavior under widely varying experimental conditions of timescale, temperature, solvent, and electrolyte. These studies elucidated the effects of electron transfer distance, tunneling medium, molecular structure, electric fields, and ion pairing on heterogeneous electron transfer dynamics. Moreover, they have provided the detailed experimental data necessary to test contemporary models such as the Marcus theory. First, as shown in Fig. 2, a

Table I. Rate Constants for Heterogeneous Electron Transfer Determined by Transient Methods.		
Analyte	Electrode	k° / cm s^{-1}
Anthracene	Au, 6.5 µm	3.46±0.55
Anthraquinone	Pt cylinder, r = 25.4 µm, l < 0.25 cm	1.78±0.35
Benzoquinone	Au, 6.5 µm	0.39±0.1
Ferrocene	Au, 5 µm	3.1±1.1
Ferrocyanide	C cylinder, r = 15 µm, l = 500 µm	0.0114±0.0022
9-Fluorenone	Pt, 6 µm	3
$[Ru(bpy)_3]^{2+}$	Au, 5 µm	2.5

* Dimension given is the radius of a microdisc electrode unless otherwise stated.

plot of ln k° *vs.* the number of repeating units in the bridging ligand (typically the number of methylene units in an alkane chain) is linear. This result indicates that tunneling rates decay exponentially with distance. The slope of this plot yields the tunneling parameter, β, which for alkane-thiol systems is 1.0-1.1 Å^{-1}. Second, as illustrated in Fig. 3, ln k *vs.* η is not linear for all driving forces. Unlike the predictions of the Butler-Volmer model when η ≈ λ, curvature is observed and k eventually becomes independent of the driving force. This behavior is consistant with that predicted by the Marcus theory. Third, by using temperature dependent measurements of k and E°′, the activation enthalpy and reaction entropy are obtained. These values are used to calculate the free energy of activation and, provided k° is known, the pre-exponential factor can be determined.

Our group has assembled similar monolayers and probed the dynamics of both ground and electronically excited states.[14] Studies on metal centered oxidation and ligand based reduction processes reveal that matching the energy of states within the redox center and the bridge can significantly increase k°.[15] Few systems allow orientational effects on heterogeneous electron transfer to be probed, but we compared the heterogeneous electron transfer rates for spontaneously adsorbed and Langmuir monolayers of $[Os(dpp)_2 Qbpy](ClO_4)_2$ where dpp is 4,7-diphenyl-1,10-phenanthroline and Qbpy is 2,2′:4′,4″:4″4′-quarterpyridyl.[16] In spontaneously adsorbed monolayers, Qbpy acts as a bridge between the redox center and microelectrode surface. In horizontal touch experiments on Langmuir films, Qbpy was in the aqueous sub-phase and electrical contact occurred through the diphenyl-phenanthroline ligands. Heterogeneous electron transfer rate constants measured at an overpotential of 50 mV were $1.2 \pm 0.3 \times 10^6$ and $1.7 \pm 0.2 \times 10^5$ s^{-1} for the spontaneously

adsorbed and Langmuir monolayers, respectively. Given that the reorganization energies are indistinguishable for the two systems, this result suggests that molecular orientation can significantly affect k.

Conclusions and Future Directions

Novel Experimental Approaches— Models that describe heterogeneous electron transfer across the electrode/solution and electrode/film interfaces are now well developed and cast in forms that are amenable to experimental investigation. The most promising results are expected from applying experimental innovations, *e.g.*, nanometer dimensioned electrodes for ultrafast measurements and scanning probe microscopies for monitoring localized, even single electron events. The twin strengths of powerful new experimental approaches and accessible theory enable complex reactions to be meaningfully probed. Despite the success of the Marcus and related theories, ambiguities remain in determining some parameters even for mechanistically simple reactions. For example, the adiabaticity of the electron transfer primarily affects the pre-exponential term in the rate expression. To determine the pre-exponential term, the exponentially dependent free energy of activation must be accurately known. Moreover, the pre-exponential factor includes both κ_{el} and υ_n, which are often difficult to deconvolve. However, electrochemists are becoming increasingly aware that voltammetric experiments alone cannot provide accurate measurements of all the parameters necessary for a complete theoretical description.

Quantum Chemical Models—The next decade will see a shift away from phenomenological models toward microscopic (atomic level) descriptions of electrode kinetics. Novel approaches will benefit from interplay between quantum chemistry and modern theories of charge transfer. It is now almost 25 years since the cluster model of the metal surface was first used to describe the structure and composition of the electrical double layer. Now quantum chemical calculations of model supermolecules such as metal cluster plus reactants promise to provide truly elementary insights into heterogeneous electron transfer. In particular, *ab-initio* calculations, using the computationally less demanding density functional theory coupled with the Kohn-Stam formalism, would appear to be an especially attractive approach.
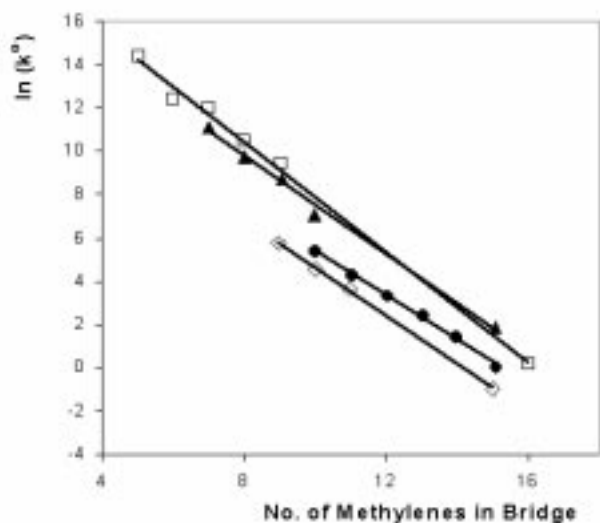

FIG. 2. Semi-log plots of the standard heterogeneous electron transfer rate constant, k°, versus the number of methylene units in the alkane-thiol bridge. The symbols ●, ▲, ▢, and ◇ denote $HS(CH_2)_n$ $CONHCH_2py\text{-}Ru(NH_3)_5^{2+}$, $HS(CH_2)_nNHCO\text{-}Ferrocene$, $HS(CH_2)_nOOC\text{-}Ferrocene$ and Cytochrome C electrostatically adsorbed on $HS(CH_2)_nCOOH$. (Reprinted, (abstracted/excerpted) with permission of Science, **251**, 919 (1991). American Association for the Advancement of Science).
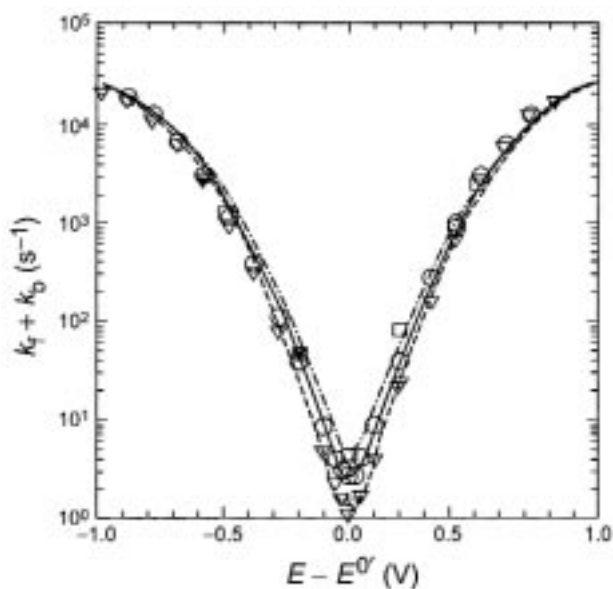

FIG. 3. Tafel plots of ln(k) vs. overpotential for a mixed self-assembled monolayer containing $HS(CH_2)_{16}OOC\text{-}Ferrocene$ and $HS(CH_2)_{15}CH_3$ in 1.0 M $HClO_4$ at three temperatures. The symbols, ▼, ○, and ▢ denote data obtained at 1, 25 and 47°C. The solid lines are the predictions of the Marcus theory for a standard heterogeneous electron transfer rate constant of 1.25 s^{-1} at 25°C and a reorganization energy of 0.85 eV (54.8 kJ mol^{-1}).

Analytical Applications—When attempting to determine the concentration of a particular redox active species in a complex mixture, typically the response of the target analyte is separated from redox active interferences on the basis of different formal potentials. There have been relatively few reports on using electrochemical reactivity, *i.e.,* electrode kinetics, to differentiate the concentration of a target analyte based on the difference between its time constants and those of the interferents. Because the width of the electrochemical response for any species is a sizeable fraction of the potential window, the potential axis alone provides very limited resolution. Coupling of the time and potential axes makes discrimination of the analyte considerably more likely. The time-resolved approach will benefit significantly from the dramatic expansion in time window provided by high speed instrumentation and microelectrodes.

A very positive outcome from the more widespread understanding of the factors that influence heterogeneous electron transfer is the rational design of modified surfaces for analytical applications. Understanding the dependence of k on distance and molecular structure allows monolayers with excellent blocking properties to be developed. Understanding electrostatically driven interfacial binding will lead to advanced chemical sensors tailored for interfacial reactivity and especially heterogeneous electron transfer. ∎

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Atomistic Modeling and Simulation

by Michael R. Philpott

Personal computers (PCs) are cheap, and Moore's law increases are still available in CPU speed (currently 1.3 GHz) and information storage density (about 40 Gb in^{-2}). In short, the combination of price, hardware advance, and user-friendly software has put advanced modeling capabilities firmly in the office and laboratory. Figure 1 depicts the main regimes of modeling. Each provides an important level of insight and ideas for new experiments. The atomic scale is concerned with electronic structure and atomic motion. In continuum modeling, the atomic details are averaged to simpler quantities at length and times scales that are larger than those of molecules. The third regime uses kinetics to follow changes in composition due to reactions, temperature, and pressure. Here, the main interest is on atomic scale modeling with a focus on molecular dynamics (MD).

Atomic Scale Modeling

The main tools for atomic scale modeling are electronic structure and MD codes. An impressive array of software for doing quantum electronic structure and geometry optimizations is available with friendly graphic user interfaces. You do not have to know any Fortran, C++, or even own a slide rule. A good account of MD and Monte Carlo (MC) methods in chemical modeling and simulation can be found in a recent book.[1] A lot of research is devoted to increasing system size (using parallel computers) and to increasing the simulation time scale. Voter at Los Alamos National Laboratory has described several schemes that give orders of magnitude increase in time span. In electrochemistry, the most important interactions are sums of electrostatic interactions. In three dimensions, these sums over q_1q_2/r_{12} are shape dependent. The best methods to compute these sums are the reaction field, Ewald method, plane-wise slab summation, fast multipole method, and the particle mesh method. The last two provide the fastest algorithms.

Newtonian MD and MC—In a MD simulation, Newton's equations of motion for the degrees of freedom of the atoms (or molecules) are solved subject to the boundary conditions on the entire system. Information about the trajectories is stored. The interaction potentials of the atoms must be known (usually an analytical formula) and a thermostat must be specified. For systems in equilibrium, the MC method is useful because only the potential energy function of the system is used to calculate time independent properties like molecular distribution functions. In practice, MC is often combined with MD in a hybrid scheme to improve the efficiency of the random moves of the MC part. Simulations of electrochemical phenomena have greatly increased our appreciation for how solvent and ions are distributed and how their motion is correlated near flat electrodes. The main drawbacks are the short simulation times and the low quality of the interatomic potentials. For water, there are about a dozen empirical models for simulating the properties of the bulk liquid at room temperature and pressure. These models are used in studies that range from clathrates to electric double layers. Attempts to improve on empirical potentials by fitting to the results of electric fields obtained from *ab initio* quantum chemistry calculations have not so far resulted in any superior models for condensed matter properties.

MD with Bond Order Potentials—Bond order potentials were introduced to describe solids like silicon, germanium, and diamond, which have directed covalent bonds.[2] Potentials specialized to hydrocarbon materials including two, three, and four atom terms[3] have been developed. In these potentials, the stretching of covalently bonded atomic pairs is described by a pair of exponentials as in the Morse potential for diatomic molecules. In the limit of large bond extensions, the potential describes homolytic bond fission. By these means some of the key aspects of chemical bond breaking and formation are included.

Car-Parrinello MD—In condensed phases, forces are intrinsically many bodied because they are dependent on the local environment around the atoms. The use of empirical potentials is avoided in this important molecular dynamics method that combines density functional theory (DFT) with MD.[4] The effective potentials determining the forces acting on individual atomic nuclei are found simultaneously using DFT for the electron density and classical mechanics for the atomic nuclei. Applications to all types of materials and their combinations have been reported. In electrochemistry, these include bulk water, ionic solutions, water on oxide surfaces, and water between metal electrodes. Because the electronic part of the simulation is very computationally intensive, the calculations have been performed on systems of small size and for short times.

Another strategy is to extend the time scale by placing some constraints on the nuclear or electronic motion to reduce the computational burden. Recently, our group in Singapore developed the notion of "chemistry in a box MD," a modification of the Car-

Three Modeling Regimes

Atomic scale modeling
Electrons, atoms, molecules, ions & polymers: metals, surface & interfaces, liquids, self & supra-molecular assemblies, soft matter, crack propagation, grain boundaries

Continuum modeling
Mechanical properties, field and current distribution, stream lines, concentration profiles, micro-electronics & packaging, composites

Kinetics modeling
Diffusion, migration, reaction rates & yields, concentration gradients

FIG. 1. Atomic scale, continuum scale, and kinetic modeling—the three regimes of modeling used in electrochemical materials science systems.
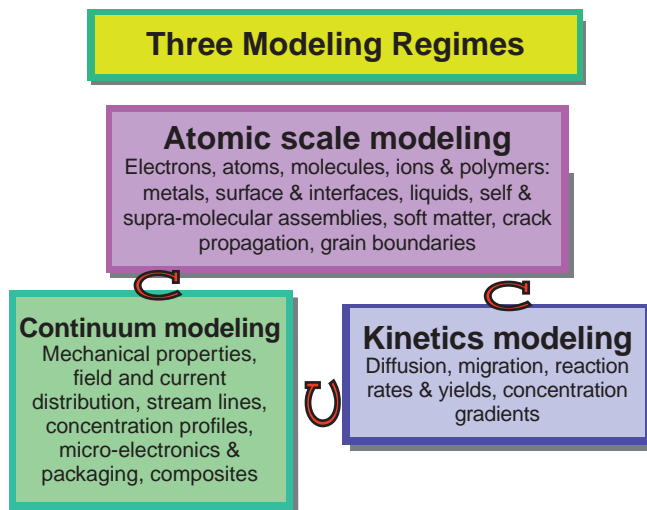
Parrinello MD scheme useful when all the electrons involved in the chemistry are localized, and when all the molecules of the surroundings not involved in the chemistry can be treated by classical MD using empirical potentials.[5] Though this is a departure from the spirit of the Car-Parrinello MD, it has a pragmatic twist in that simulation times of tens of picoseconds are accessible on a single processor workstation. Figure 2 shows a metal cluster immersed in concentrated approximately 2M salt solution. The snapshot of cluster and molecules illustrates two features of the method—a small box frame around the cluster connected with the electronic calculation and the larger box frame for the MD calculation. The Car-Parrinello method is applied to the metal cluster only and the species in solution are treated by classical mechanics with analytical potentials. Interactions between the cluster and solution species are proportional to cluster electron density as a factor in the otherwise analytical potential. The middle part of Fig. 2 shows an adatom slightly displaced from the cluster along with all water molecules in its first solvation shell. All other solution species are omitted for visual clarity. The key physics is the stabilization of the metal adatom as a monovalent cation by the presence of the polar solvent. If the atom were to be removed from the cluster in vacuum it would be uncharged. Figure 2 also shows, on the left side graph, a plot of the radial distribution function g(r) of water around the ion and the solvation number n(r) with a plateau at n = 4.

Some Fundamental Electrochemical Mechanisms

Fundamental mechanisms are those with a large conceptual impact. A prioritized list for electrochemistry could be the following: water > water and ions > electrons > protons > ions at interfaces >… . In water and its solutions, the hydrogen bond is poorly understood, because few experiments are able to probe the electron distribution.[6] Electron transfer processes pervade much of electrochemistry and the description by Marcus theory is very widely applied in interpreting experiments. In MD simulations, Heinzinger and coworkers have performed pioneering work on numerous aspects of electrolyte solutions.

Debye-Hückel Theory of Ion Solvation and Electric Charge Screening—Theory and computer simulation reveal details of the inner structure of the first solvation shell. For example, the distortion of the solvent geometry and electronic polarization of highly charged ions like Al^{3+} ions. The Car-Parrinello MD method has been applied to several charged cations and details of water geometric distortions examined. Exchange of molecules in solvation shells is experimentally measurable using NMR. The coupling of the hydration shell to the local solvent H bond network, and then to long-range correlations that determine the dielectric constant, is not understood. The analytical work of Henderson and coworkers on solutions using the Ornstein-Zernike equation has been of importance in establishing a platform of understanding.

Theory of Electric Double Layers and Structure of the Inner Layer—The Gouy-Chapman continuum theory of electric double layer screening of charged electrodes has been the basis for interpreting many of the seminal experimental findings in this field.[7] Extensions to include the molecular structure of the inner layer[8] have provided a comprehensive working model of the solution side. The complex problem of integrating into one theory the metal electrons, adsorbed ions, and water remains a very difficult task. There have been very beautiful experimental studies of adsorption of ions and neutrals on metal and semiconductor electrode surfaces. *In situ* STM and AFM have revolutionized the experimental field. There has been some progress using classical MD to study the transition from bulk to inner Helmholtz layer. An intact double layer comprising Stern layer and outer layer has been simulated in a system large enough that the bulk electrolyte region was clearly identifiable.[9] More calculations are needed to study the expansion of the double layer at lower salt levels.

Noble Metal Deposition and Dissolution—The continuing work of Kolb on metal underpotential deposition and deposition from probes exemplifies some of the fine experimental work in progress. A recent book summarizes the traditional viewpoint quite well.[10] Movement of adions from kink sites onto terraces and then into solution is a computational grand challenge by almost any measure. The solvent stabilizes the cation. However, the composition of the supporting electrolyte influences the reaction path as shown in the STM experiments of copper metal dissolution in halide and sulphate media.[11] These represent big challenges for theory and computer simulation.

Electron and Proton Transfer—Due to the exquisite control that experimentalists have over selective electron transfer, these reactions have been extensively studied. Marcus theory pro-
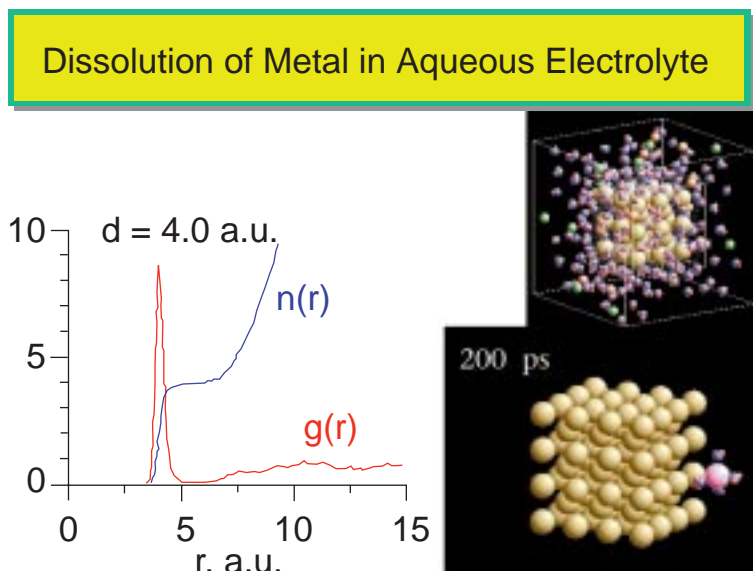

FIG. 2. *Chemistry in a box molecular dynamics simulation. Electrochemical example showing some aspects of a small metal cluster surrounded by aqueous electrolyte. (The figures are described moving clockwise from the right hand side.) First is a snapshot of an entire system consisting of the electronic box containing a 35 atom metal cluster and the molecular dynamics box containing aqueous electrolyte surrounding the cluster in the electronic box. Second is a graphic of a larger 91-atom cluster with an adion surrounded by four stabilizing water molecules belonging to the first hydration shell. All other water molecules and ions are omitted for clarity. Third is a plot of the radial distribution function g(r) for water around the adion depicted in second (middle) picture along with the water occupation number n(r) as a function of distance from the adion.*

vided a versatile theory at an early stage that has guided generations of experimentalists. Modern theoretical work involves exploring and expanding the early framework by explicitly including effects and features previously inaccessible without computers (metal band structure, molecular electronic structure). Next in importance is understanding the transfer of protons in solution, ice, and biomolecules. In water, the structure and dynamics of the hydrated proton continue to be hotly debated. The structure of H_3O^+ and H_5O^{2+} has been studied by Car-Parrinello MD as well as by purely quantum chemical cluster techniques. The reaction path and transition state for transfer is still under discussion.

STM and AFM Probes—Basic understanding of how STM works and how the images are interpreted quantitatively is a quantum scattering problem. The sensing fields involve spatially delocalized states with electric current entering or leaving a tip that ends in a small collection of atoms. However, because the experimentation is now so well advanced, it would be unusual for theory to overturn the way the instrument is used. Still the field is a long way from enjoying the sort of design and development that exists for TEM. AFM is conceptually simpler since the sensing fields and interactions are short range. Here the obstacles are lack of accurate interatomic potentials.

Batteries—In the last few years, there has been progress in the calculation of the electronic structure of Li ion battery materials and related rocking chair systems. Modern DFT codes that calculate the metal band structure have been used to predict the battery voltage. It is possible to make a survey of hypothetical new electrode materials without going in the laboratory. This may speed research for better materials.[12,13] There has also been exploratory work on mechanisms of phase transitions as Li ions are depleted or stored. Newman (UCB) has described kinetic modeling of the whole battery system. The intercalation of metal and other species into graphite has been studied using quantum chemistry cluster models. Issues concerning the electronic structure and possible phase transitions in the cathode materials like Li_xCoO_4 provide unprecedented insights and reinforce the conceptual foundation for materials development. Another area where theory has provided a deep level of understanding is in the transport of Li ions through liquid polymer electrolytes (MPI polymer). Finally, it is worth mentioning that the motion of Li ions in and out of the electrodes affects the kinetics and ability of the battery system to deliver current. This is a fertile field for theorists willing to work with experimental materials scientists. ■

Summary

Judicious use of simulation has provided important insight into numerous fundamentally important electrochemical mechanisms. However, it is always important to remember that the results of all our simulations have to be more than just pretty, expensive pictures. What are needed are clever theories and models to guide the computer simulations.

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Electrochemical Surface Spectroscopy

by Michael J. Weaver and Sally A. Wasileski

One of the most notable broad-based developments in surface electrochemical research in recent years involves the capability of probing molecular-level properties of electrode-solution interfaces by means of spectroscopic techniques. The original purview of surface spectroscopy lay almost exclusively in ultrahigh vacuum (UHV)-based systems. This is due to the lack of bulk-phase interferences, the applicability of electron as well as photon spectral probes, as well as the unique degree of surface cleanliness, compositional control, and structural order attainable in UHV environments. Triggered by the development of UHV technology, the rapid advances made in surface science, starting 30 to 40 years ago, encouraged the spectroscopic examination of electrode interfaces by controlled surface transfer between electrochemical and UHV environments. Such *ex situ* characterization strategies provided much of the original spectroscopic insight into chemisorbate structure at electrodes, using techniques such as X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES) for atomic structure, and electron energy-loss spectroscopy (EELS) for vibrational characterization.[1]

Starting in the 1970s, several coupled developments facilitated a detailed microscopic-level characterization of *in situ* electrochemical interfaces by means of optical spectroscopy. The first strategy to exert a major impact was based on the discovery and realization of surface-enhanced Raman scattering (SERS) in the mid-1970s.[2] While originally limited to coinage-metal surfaces (largely silver electrodes), SERS provided the first potential-dependent vibrational spectra for adsorbates at metal-solution interfaces. Although also requiring some degree of nanoscale surface roughness for the SERS effect, as outlined below, recent strategies expand the technique to encompass other interfacial materials. These developments, together with the dramatically improved sensitivity and flexibility of Raman instrumentation, now endow SERS with much promise for the vibrational characterization of diverse interfaces.[3]

Another important development initiated during the 1970s was the extraction of optical absorbance information for electrode-solution interfaces in the absence of surface enhancement by using potential-modulation strategies, especially in conjunction with electrochemical thin-layer cells so to minimize the solution optical path length.[4,5] The interfacial portion of the optical absorbance is sensitive to electrode potential via double-layer field and other effects, such that it can often be extracted from the dominant bulk-phase interferences by potential modulation with a lock-in amplifier.[4,5] While this strategy was initially applied to the UV/visible spectral region,[4] it was subsequently recognized that the infrared spectral region was also accessible, despite the strong light absorption by aqueous solvent.[5] Measurements with a grating spectrometer, dubbed "electrochemically modulated infrared spectroscopy" (EMIRS), yielded the first vibrational spectra for chemisorbates at transition-metal electrodes. The rapid commercialization of Fourier transform infrared (FTIR) spectrometers in the early 1980s, together with their adoption for infrared reflection-absorption spectroscopy (IRAS) at metal-UHV interfaces, led to the widespread use of FTIR at electrochemical interfaces. While potential-difference spectral strategies are required to eliminate bulk-phase solution interferences, these are more flexible than the modulation tactics required in EMIRS, enabling absolute infrared spectra to be obtained for chemisorbate species in many cases. Such EC-IRAS measurements have been used extensively to examine reactive as well as stable electrochemical systems.

Another seminal development encouraging the application of EC-IRAS and other *in situ* optical spectroscopies involved the recognition by Clavilier (1980) that ordered, monocrystalline metal electrodes could readily be prepared by annealing in an oxy-gas flame. While originally controversial, this and related tactics have become a standard means of preparing Pt-group and coinage-metal surfaces for electrochemical use. Furthermore, the emergence of *in situ* scanning tunneling microscopy (STM) a decade later enabled the spatial structure of such ordered electrodes to be scrutinized down to the atomic level. Taken together, the applicability of microscopic-level techniques to ordered monocrystalline metal electrodes has established multifaceted links between related electrochemical and UHV-based interfaces, thereby rendering electrochemical surface science as a coherent (and sophisticated) research discipline.

Electrochemical interfaces have also been investigated by other *in situ* spectroscopic methods in recent years. Nonlinear spectroscopies, especially visible-IR sum frequency generation (SFG) and second-harmonic generation (SHG), in principle share the advantage of SERS of

FIG. 1. Stretching frequencies for saturated CO and NO adlayers on Pt-group low-index surfaces in aqueous electrochemical compared with UHV environments at equivalent surface potentials. Data are taken from Ref. 10.
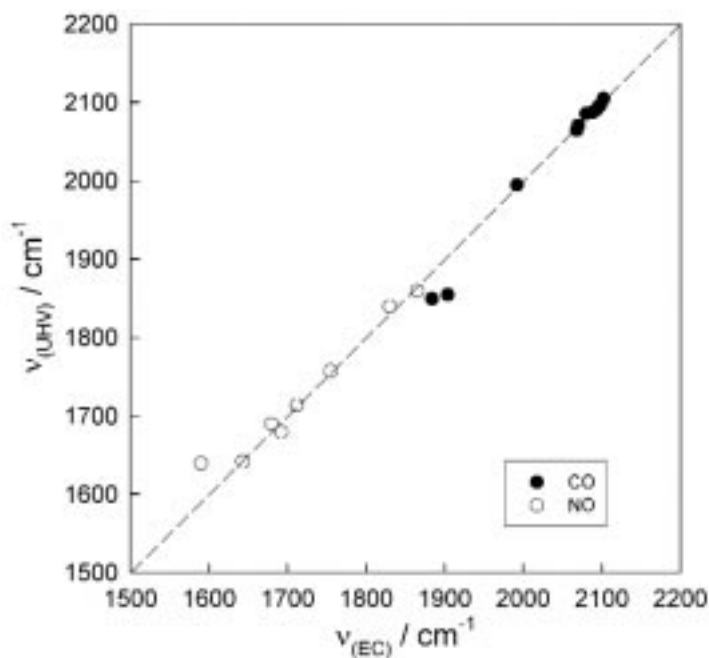
being based on phenomena occurring only at surfaces, therefore being intrinsically surface-sensitive methods.[6] The former provides molecular vibrational information, akin to IRAS and SERS. While hampered by sensitivity and bandwidth constraints, even NMR is now providing intriguing information on the electronic properties of metal-solution interfaces.[7] We now describe very briefly three examples of recent applications of vibrational spectral methods (each culled unabashedly from results in our laboratory) to fundamental structure and bonding issues in surface electrochemistry.

The first concerns the archetypical case of carbon monoxide chemisorption on Pt-group metals. This chemisorbate is of broad-based interest in both electrochemistry and UHV-based surface science for several reasons, including its common presence as a poison in electrocatalytic oxidations, but (more positively) as a simple coordinating diatomic species with vibrational properties that are sensitive to the chemical and electrostatic environment. Partly for the latter reasons, CO (along with the related species NO) have been widely studied by vibrational spectroscopy, especially on oriented single-crystal electrodes by means of IRAS.[8,9] Given that related IRAS measurements have been widely pursued in UHV, the spectra can also provide a unique means of linking the chemisorbate properties of electrochemical and vacuum-based interfaces.

A basic property of chemisorbates in electrochemical systems is that their vibrational frequencies depend on the applied electrode potential. This effect, commonly termed Stark tuning, arises both from chemical and electrostatic effects on the surface bonding. Shifts in electrode potential can also alter the surface binding energetics, including the preferred binding geometries. These factors are important, and have been particularly well studied for CO and NO. It is of fundamental interest to compare potential-dependent C-O and N-O vibrational frequencies, ν_{CO} and ν_{NO}, at monocrystalline electrodes with corresponding data obtained at clean metal-UHV interfaces to ascertain the influence of double-layer solvation/charge effects on the former.[10]

Figure 1 shows a global comparison along these lines for saturated coverages of CO and NO on (111) and (100) surfaces of Pt, Rh, Ir, and Pd surfaces with the aqueous electrochemical and UHV-based frequencies forming the x- and y-axes, respectively. An essential point is that the former frequencies are all measured at electrode potentials, E_m, equivalent to the observed work function, Φ_m, for the (solvent/charge-free) metal-UHV interfaces. The best concordance, shown by the unit slope (x=y) line, was found

by matching the (adjustable) E_m and Φ_m values by taking the absolute potential of the standard hydrogen electrode to be 4.8 ($\pm$ 0.1) V, in harmony with independent estimates of this quantity.[10] Note that the Φ_m values vary by over 1 eV, and the Stark-tuning ($d\nu/dE_m$) slopes are sufficiently large (*ca.* 30-80 cm^{-1} V^{-1}), so that this near-uniform agreement is a clear indication of the dominant effect of the average interfacial potential (and hence field) in determining the chemisorbate vibrational properties. Consequently, the electrostatic, rather than more specific chemical (such as solvational), properties of the double layer are dominant here. Similar, although less quantitative, results along these lines are obtained for low chemisorbate coverages, suggestive in some cases of a more specific role of coadsorbed solvent under these conditions.[11]

The second brief illustration of the fundamental value of vibrational spectroscopy to electrochemistry involves the metal-chemisorbate modes (ν_{M-X}) themselves. While these vibrations occur at frequencies ($\leq$ 600 cm^{-1}), too low to be accessed in most cases by IRAS, they are readily observable with SERS. Although the SERS effect itself is limited chiefly to Group IB metals, coating such surfaces with ultrathin (nanoscale) films imparts comparable enhancement also to the overlayer and adsorbates found thereon.[3] In particular, we have examined transition metal, oxide, and compound semiconductor surfaces by this overlayer SERS approach.[3]

Figure 2 shows the effect of altering the electrode on the surface-halogen force constants, f_{M-X}, for chloride and bromide adlayers bound to Group VIII and IB substrate, extracted from SERS ν_{M-X} data.[12] The f_{M-X} values show a systematic correlation with the *d*-band occupancy; the stronger bonding (higher f_{M-X} values) seen with fewer *d*-electrons suggesting the increasing importance of halide-metal electron donation. Consistent trends are found for the Stark-tuning ($d\nu_{M-X}/dE$) slopes, indicating that the sensitivity of the bond frequency to the electrostatic field diminishes as the halide-metal bonding becomes less ionic.[12]

The third brief example also concerns harnessing SERS for examining chemisorption at Pt-group electrode-solution interfaces, but now for polyatomic adsorbates, specifically aromatic species. Figure 3 contains a pair of SER spectra obtained for benzonitrile (C_6H_5CN) and toluene ($C_6H_5CH_3$) on palladium. Their molecular structure
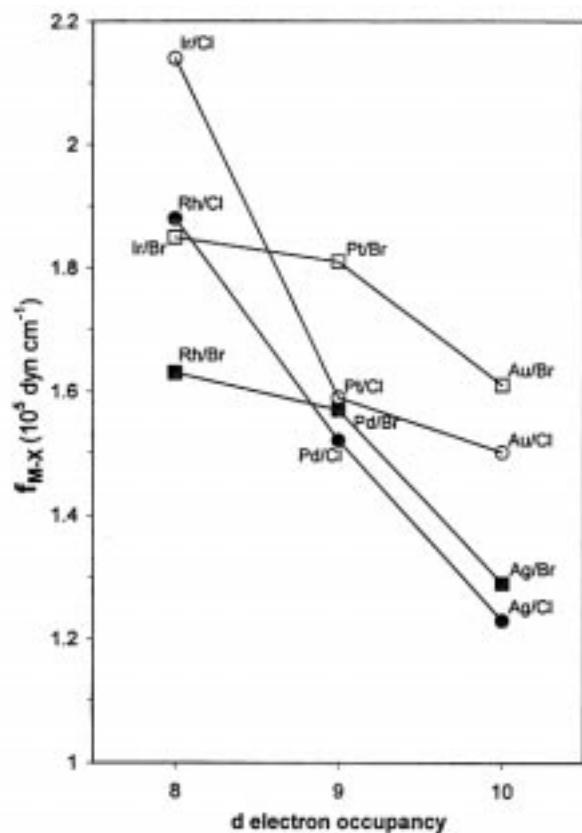
FIG. 2. Surface-adsorbate force constants for halides chemisorbed on Group VIII and IB metal electrodes in aqueous solution plotted versus d-electron occupancy. Data extracted from SERS data in Ref. 12.

(and thereby the bulk-phase Raman spectra) are similar, but the corresponding SER spectra are markedly different. There are numerous aromatic ring modes observable in the frequency region shown, reflecting the excellent sensitivity as well as liberal surface selection rules offered by SERS. (Very few of these modes appear, and only weakly, in corresponding IRAS data.) Note, however, that several ring modes (*e.g.,* the v_{12} mode at *ca.* 1000 cm^{-1}) are much broader in the toluene than the benzonitrile spectra, and are shifted significantly (in some cases up to 50-100 cm^{-1}) from their uncoordinated values. These and other spectral dissimilarities reflect differences in the chemisorbate coordination (and orientation) geometries of benzonitrile and toluene, being tethered to palladium via the nitrile and benzene moieties, respectively.[13] Similarly to the simple halogen cases mentioned above, a number of the intramolecular (as well as the metal-adsorbate) modes are dependent on the metal; altering the electrode material can therefore yield rich insight into the chemical nature of the surface bonding.

Overall then, our broad-based understanding of electrode-chemisorbate surface bonding can now be advanced substantially by the judicious use of *in situ* vibrational spectroscopy. Also worth mentioning in this context is the current emergence of Density Functional Theory (DFT) as a practical means of analyzing as well as predicting surface vibrational properties in terms of *ab initio* quantum chemistry. Although applications of DFT to electrochemical systems are still in their infancy,[14,15] it is clear that such approaches have much to offer in enhancing our understanding of surface vibrational spectroscopy in particular, as well as advancing greatly our quantum-chemical appreciation of electrochemical surface bonding on a broad front.

Finally, it should be emphasized that this brief summary is grossly incomplete, as well as strongly biased. Besides merely acknowledging the importance of spectroscopies beyond vibrational methods, we have scarcely mentioned the growing emphasis on utilizing such strategies to examine reactive as well as stable electrochemical systems. Indeed, the application of time-resolved spectral tactics (especially in conjunction with transient electrochemical information), to elucidate catalytic reaction pathways and other dynamical phenomena, clearly constitutes a crucial (and largely unsurmounted) challenge in electrochemical surface science. Overall, the future holds much for the expanding application of electrochemical spectroscopic methods to problems critical to emerging technologies as well as to fundamental science. ■

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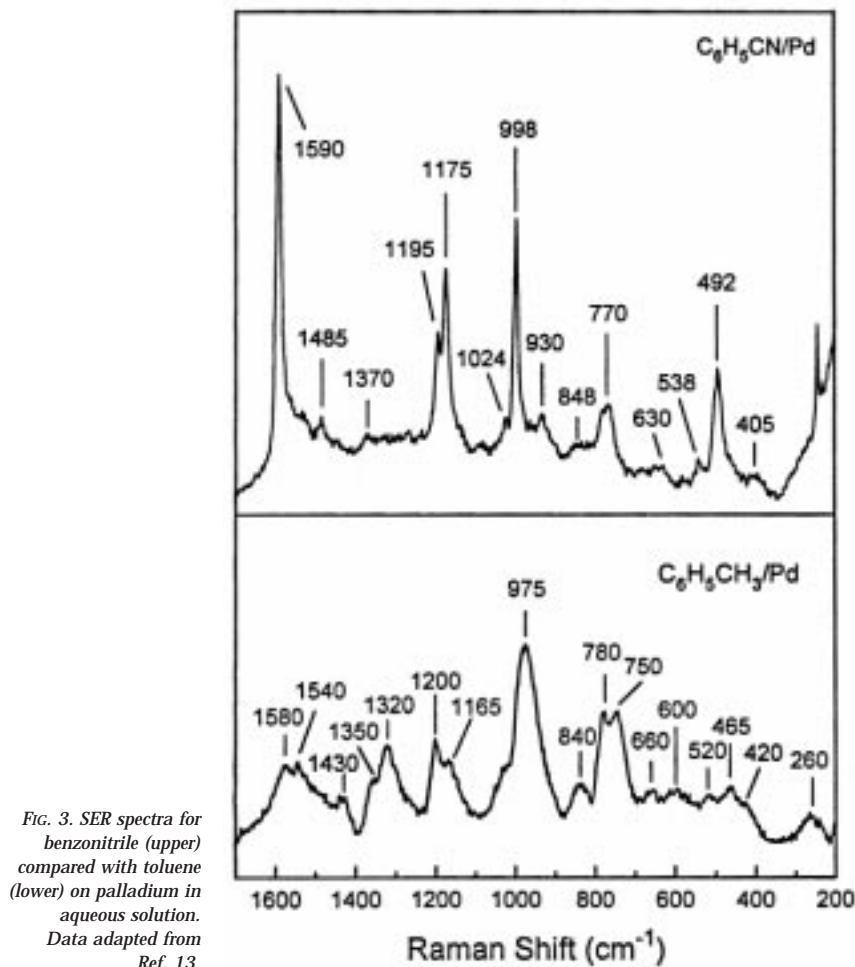
FIG. 3. SER spectra for benzonitrile (upper) compared with toluene (lower) on palladium in aqueous solution. Data adapted from Ref. 13.

Electrochemistry as an Analytical Technique

by Lou Coury

A ttempting to define the boundaries of electroanalytical chemistry would be a difficult exercise, and any result would be subject to constant revision anyway. For the purposes of this brief overview, electroanalysis will be characterized as involving the application of one or more electrochemical techniques for measuring some quantity of interest. This quantity of interest is as likely to be a rate constant as a concentration, for example.

Textbooks credit Michael Faraday as being the father of electroanalytical chemistry through the formulation of his laws of electrolysis. Although the experimental techniques he used were in large part developed by his mentor Humphry Davy during his discovery of many of the alkali and alkaline earth metals, it was Faraday who related a measurable parameter (weight of a plated metal) to other numerical quantities (charge passed through a solution and elemental equivalent weight). Hence, Faraday rather than Davy is credited with realizing that electrochemical methods may be used for analytical purposes. This article will consider a few representative examples of things that can be measured using electrochemistry.

Why Electrochemistry?

The use of electrochemistry in the service of measurement science is likely to be taken for granted by members of ECS, given our backgrounds and biases. However, it is appropriate to list the characteristics that make electrochemistry especially useful to analytical chemists. First, techniques such as coulometry and electrogravimetry are, at least in theory, absolute methods. They may therefore be used in certain situations where a suitable standard is unobtainable. This is in contrast to calibration-based analyses that require the generation of standard curves using a reference standard.

Second, electrochemical methods give signals that vary with the activities of analyte species rather than their concentrations. For solution phase reactions, the former are relevant for understanding, *e.g.*, thermodynamic behavior. Similarly, electrochemical methods are useful for speciation studies. Elements present as ions having different oxidation states may be distin-guished from one another, which may not be the case if an atomic spectrometric approach is used.

Third, electrochemical methods yield an electrical signal directly; no primary signal transduction step is necessary (*e.g.*, photomultiplier tube or ion collector). This situation has several benefits including straightforward generation of real-time signals, useful for sensors and flow stream monitoring. Also, the lack of this transduction stage results in ease of miniaturization. Micro-electrodes are used in neuroscience for this reason, in addition to the fact that their small size results in high spatial resolution.

Fourth, electrochemical detectors are selective, not universal. Some analytes do not undergo redox reactions at an appreciable rate within commonly accessible solvent windows. Thus, in some cases, electrochemical sensors and detectors are used without a prior separation step. To illustrate this point, if all the species present in human blood gave a signal at the potential used for enzymatic glucose detection, the prospects for making direct determination of glucose in a drop of whole blood would be (at best) remote.

Fifth, electrochemical signals result from processes occurring at a surface. Whereas there are some clear drawbacks to this, there are also advantages. Because surfaces may naturally (or can be made to) accumulate ions and molecules from solution (*e.g.*, adsorption, ion exchange, electrodeposition), preconcentration strategies are often coupled with electrochemical detection steps. Anodic and cathodic stripping voltammetry are common examples. Such techniques are capable of giving very low limits of detection (sub-nanoMolar, in some cases).

What Can Be Measured?

The remainder of this report summarizes a few examples of unusual parameters and phenomena measured using electrochemical techniques. No attempt is made to provide a comprehensive list. Rather, the focus is on a relatively small number of studies that illustrate the diversity of electroanalytical measurements.

Concentration Measurements at the Cellular Level—The quantity most fre-quently measured using electrochemistry is concentration (or more precisely, as noted above, activity). Measurement of solution pH, ion activities using an ISE, solution conductance by laboratory water purifiers, water content of organic solvents by Karl Fischer titration, glucose in whole blood with hand-held meters, oxygen in blood by clinical blood gas analyzers, and oxygen in automotive exhaust gases with solid electrolyte-based sensors are all economically important examples of electroanalytical measurements falling into this category.

An example from the research realm of how sophisticated this class of measurements has become is shown by work by Wightman and colleagues.[1] In their work, release of the neurotransmitter dopamine from intracellular vesicles in single neurons isolated from mouse retinas was described. Their experimental protocol involved a combination of optimized electronics and data acquisition, high-precision positioning of carbon fiber microelectrodes, and the ability to evoke dopamine release through delivery of specific reagents via a pressure ejection micropipet. In this way, they were able to show that individual secretion events result in the release of between 8 and 170 zeptomoles of dopamine, with an average value of 52 zmol or about 32,000 dopamine molecules.

Measurement of Kinetic Rate Constants to Elucidate Charge Transport in DNA Strands—Kinetic measurements are frequently performed using electrochemical methods. Because current is a derivative signal, it is inherently indicative of rate. Using various electroanalytical techniques and measurement time scales, heterogeneous electron transfer, solution electron transfer or solution atom (group) transfer rates may be probed. Classic papers in this area were published by Nicholson and Shain,[2,3] and Savéant.[4] More recently, the development of efficient computational algorithms and the rise of powerful yet inexpensive personal computers have resulted in the widespread use of digital simulation techniques for the extraction of kinetic parameters from voltammetric data.[5]

An interesting example of electrochemical rate measurements used to probe an issue of fundamental import-

ance, *viz.*, the charge transport characteristics of double-stranded (ds) DNA, is provided in recent work by Heller, *et al.*[6] By comparing current densities for the electroreduction of H_2O_2 at soybean peroxidase-modified electrodes electrically wired with either ds-DNA or a hydrophilic Os redox polymer, they were able to determine that the diffusivity of electrons in unaligned and unstretched calf thymus DNA is less than 10^{-11} cm^2 s^{-1}. This result led the authors to conclude that, in the absence of chain alignment, ds-DNA is not an electrical conductor.

Heller *et al.*, conclude that ds-DNA may undergo an insulator-to-semiconductor transition upon parallel alignment. The organization of ds-DNA into aligned arrays is further discussed in the context of an evolutionary strategy for preserving genetic information. Because addition of a hole or electron to the semiconducting form of DNA has the effect of dispersing the charge over a large number of atoms, this situation prevents any particular atom in the assembly from being particularly reactive, which could result in genetic damage. The fact that such an important concept could be developed by examining peak separations in cyclic voltammograms[3] (along with the other measurements used by these authors) provides an interesting example of the power of electroanalytical measurement techniques.

Spatially-Resolved Kinetic Measurements for Probing Differences Between Cancerous and Normal Biological Cells—The technique known as scanning electrochemical microscopy (SECM) allows many types of electrochemical measurements to be made as a precise function of position.[7] In one implementation of this experiment, an ultramicroelectrode is scanned with respect to position over a surface, and amperometric or voltammetric data may be obtained as a function of x, y, and z-coordinates.

In an upcoming paper, Mirkin and colleagues demonstrate the use of SECM to distinguish differences between non-motile, non-transformed human breast epithelial cells; breast cells with a high level of motility; and highly metastatic breast cancer cells.[8] In their work, they demonstrate that effective rate constants can be measured for bimolecular reactions between small diffusing molecules (*i.e.*, redox mediators) and intracellular redox moieties. Significantly, different redox activities are shown for the three different types of breast cells. Because SECM generates a map of transmembrane charge transfer rates, the authors point out the possibility of using the technique to detect aberrant responses in large arrays of cells and tumor specimens.

Measurement of Mass Transport-Limited Currents to Understand Transdermal Transport—The administration of some pharmaceutical compounds poses a challenge either because the drugs may be metabolized in the gastrointestinal tract before they can be absorbed, or because the compounds are simply poorly absorbed into the bloodstream. One alternative strategy that is receiving increasing attention is called iontophoretic transdermal drug delivery. This technique uses an applied current on the order of a few hundred microamps per square cm to force molecules across layers of skin. Both charged species (ions) as well as neutral compounds may be delivered in this way.

White and collaborators at the University of Utah and ALZA Corporation have recently investigated the mechanism of transport of neutral

molecules using SECM.[9] In their experiments, the flux of hydroquinone across samples of skin taken from hairless mice was monitored as a function of the applied transdermal current. Both voltammograms and amperometric data were collected with an SECM, and the signal recorded was due to the oxidation of hydroquinone that traversed the mouse skin sample at various sites. By altering the polarity of the current, its magnitude and the pH of the bathing solution, the authors were able to show that neutral molecules are carried through hair follicles in the skin via electro-osmotic flow. Furthermore, they were able to determine that the isoelectric point of the follicles occurs at pH 3.5. Hence, the authors could change the direction of transdermal fluid flow by changing the solution pH from below to above pH 3.5. The latter observation is important in applications such as non-invasive glucose monitoring, where movement of analyte from below the surface of the skin to an external sensor is required.

A Nanoscopic Coulter Counter—The final example highlighted in this brief report concerns the construction by Sun and Crooks[10] of a Coulter counter for nanometer-sized particles. Coulter counters are commercially-available instruments used to determine the volume of particles suspended in a conductive liquid. The electrical quantity that is actually measured is the change in resistance (*e.g.*, change in current at constant potential, or vice versa) across a small aperture as particles pass through the opening. The change in resistance recorded is related to the volume of liquid displaced by the particles. Also, the number of particles in a defined volume can be counted. In addition to particle analytes, measurements on cell suspensions are commonly performed.

Commercial implementations of this technology are usually restricted to examination of particles with mean diameters in the micrometer range. Sun and Crooks have recently extended the range of such measurements to nanometer-size polystyrene particles through construction of a single pore in a gold membrane.[10] One advantage to the use of gold as the membrane in their device is that the surface chemistry of the interior of the pore can be controlled by thiolate self-assembly chemistry. More recently, the same researchers are focusing on the use of single carbon nanotubes to form the pores in their Coulter counters. Thus, it is conceivable that this work may soon lead to the ability to count individual (macro-) molecules as they pass through such well-defined orifices. ■

Acknowledgments

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Architecture on Electrodes – Modeling Meets Materials

by Johna Leddy

Modified electrodes developed as a natural consequence of paradigm changes for physical electrochemical measurements. In the first half of the twentieth century, measurements were made at mercury electrodes in aqueous electrolytes; pristine electrode surfaces were the rigor of the day. Solid electrodes came into use in the 1950s. This in turn led to the use of nonaqueous solvents. The emphasis in electrochemical measurements shifted from the thermodynamic to the dynamic. The expectation of rigorously clean surfaces diminished, and evolved into an interest in intentionally modified electrode surfaces. Merz and Bard[1] reported the first polymer modified electrode in 1978.

Evolution of Modified Electrodes

Polymers were the first materials used to build matrices on electrode surfaces. Electroactive or redox polymers such as polyvinyl ferrocene and polymers of bipyridyl transition metal complexes were among the first evaluated. Ion exchange matrices such as Nafion provided the flexibility of easily coating an electrode and intercalating a redox species. Polyaniline, polythiophene, and polypyrrole were among the electron conducting polymers investigated next. Inorganic polymer-like materials such as clays, zeolites, and sol gels were also studied.

Polymer films were largely viewed as a bulk, homogeneous matrix, and their properties were discussed in terms of either macroscopic or molecular length scales. Experimental studies focused on mass transport effects and the design of matrices for optimized cross exchange and mediated reactions. Polymers provide a versatile method for surface modification and high material loading of electroactive moieties. However, polymer structures tend to form randomly, and true architectures are difficult to orchestrate.

Monolayer modified electrodes were formed as Langmuir Blodgette films, self assembled monolayers (SAMs), and covalently attached layers such as alkanethiols on gold. Monolayers on electrodes allowed detailed investigation of electron transfer effects. Because the redox probes are held immediately at the electrode surface, measurements are not complicated by mass transport. The properties of monolayers are described not in terms of bulk and macroscopic extent, but rather in terms of molecular and nanoscopic length scales. Monolayers provide for versatile surface modification and excellent control of structure across a two-dimensional surface, but introduce little electroactive material.

Composites are multi-component, heterogeneous matrices usually formed either by self-assembly or layering of components. Detailed architectures are achievable in three dimensions. Composites can provide greater architec-

tural flexibility than monolayers and the high material loading of polymer films. With composites, order is induced over several length scales, ranging from the molecular, through the nanoscopic, microscopic, and macroscopic. Microscopic components can be used to create a nanoscopic interface that controls the characteristics of the system. For example, self-assembly at the interface between a microscopic particle and ion exchange polymer can create an ordered nanoscopic interface that facilitates flux of permeants through the composite several fold.[2]

Composites provide a promising route to devices on electrodes, including mechanical actuators and switches. Materials can be graded for enhanced mass and electron transfer. Templates on a microscopic level can be used to form new composite materials. On a molecular scale, Makote and Collinson[3] templated dopamine in an inorganic-organic hybrid sol-gel matrix by co-casting dopamine in the sol-gel, and then extracting the dopamine from the dried film. The resulting sol-gel modified electrode has enhanced affinity for dopamine as compared with other structurally similar neurotransmitters and compounds.

Fundamentals for All Modified Electrodes

As in all electrochemical systems, three effects must be considered: mass transport, electron transfer, and homogeneous kinetics. These effects must be designed into the matrix of a successfully modified electrode. Transport can be sustained through either electrolyte filled porous structures or a viscous but liquid-like modifying layer. Electron transfer must be charge compensated by ion motion throughout the films. Homogeneous kinetics are introduced when films contain mediators and catalysts. Selectivity can be introduced by structure-based restrictions on size, charge, and hydrophobicity.

The correct balance between mass transport, electron transfer, and homogeneous kinetics provides the basis for building many elegant structures on electrodes. Among the most impressive systems are those that wire biologically significant molecules (*e.g.*, proteins and enzymes) to the electrode such that there is direct electronic communication as well as electrocatalyzed consumption of substrates. Armstrong and coworkers recently studied intramolecular electron transfer relays in an electroactive enzyme, fumarate reductase, and identified individual electron transfer steps.[4] Rusling and coworkers[5] incorporated the individual components of the photosynthetic reaction center of bacteriochlorophyll into a phosphatidylcholine film, and demonstrated electroactivity. In another study, this group[6] demonstrated electrochemical and electrocatalytic activity in a layered structure of myoglobin and cytochrome $P450_{cam}$. In these successfully engineered systems, a balance of mass transport of substrates and counter ions as well as electron transfer and homogeneous reaction kinetics must be achieved.

Evaluating Modified Electrodes

In the realm of physical electrochemistry, modified electrodes are evaluated through a combination of experiments and modeling. Experimental studies are largely voltammetric with three main classes of investigation: evaluation of electron transfer across and through monolayers; assessment of the electrochemical properties of electroactive and electron conducting moieties in films; and determination of the flux of permeants from solution through the modifying layer to the electrode surface. Imaging and spectroscopy often augment electrochemical studies.

The experimental evaluation of polymers, monolayers, and composites follow very similar protocols. The assessment bifurcates in the modeling of the physical systems. Polymers and monolayers are traditionally treated as homogeneous matrices, whereas composites, by their very nature, are heterogeneous micro- and nano-structures.

Traditional models for polymers treat the layer as a homogeneous matrix where only flux in the coordinate normal to the electrode is considered. For electroactive films, systems are evaluated under one of two limiting conditions. For diffusion length less than film thickness, voltammetric results are analogous to those for redox probes in solution, provided there are no strong inter-moiety interactions in the film. In the second limiting case, diffusion length far exceeds film thickness, and the response is evaluated under thin layer conditions. Models for permeation of redox probes through electrochemically inert layers were first presented by Gough and Leypold[7] for steady state, rotating disk voltammetry. For transient methods, data are collected either at early times when the diffusion length of the permeant is less than the film thickness or under conditions where the diffusion length far exceeds the film thickness. Whether for steady state or transient models, the polymer is treated as a homogeneous matrix. That is, if the diffusion length is larger than either the diameter of or the distance between pin-holes in the film, the homogeneous model is applicable. Amatore, Savéant, and Tessier[8] presented a model for cyclic voltammetry that allowed assessment of pinhole dimensions based on the peak splitting. Andrieux and coworkers[9] presented steady state models for homogeneous films on electrodes wherein diffusion of substrates, exchange of electrons, and mediation reactions were considered. The commercial simulation program DigiSim allows modeling of homogeneous thin layers where diffusion from solution is precluded.

Models for composites differ in that they must allow for the heterogeneous structure. Heterogeneity introduces complexities of mixed length scales, interfaces, multi-dimensionality, and porosity. Voltammetric studies of composites often register effects over a range of length scales such that the system response is governed by several parameters in addition to the film thickness. To the extent that effects depend on length scales microscopic and smaller, composites are sometimes governed by rules different from those for macroscopic materials. Composite properties are often dominated by interfaces. By their microscopic and nanoscopic nature, composites have a very high ratio of internal surface area to volume. From classical physical chemistry, strong forces and gradients are often established at interfaces, and such forces can impact composite characteristics.

The protocol to appreciate the role of structure in composite behavior is to evaluate composites as a function of an appropriate characteristic dimension. For example, in composites formed of spherical microparticles embedded in an ion exchange polymer, vary microparticle radius at fixed particle volume fraction and measure flux of a redox probe through the composites. Such characterization of composites will usually demonstrate a variation of properties with characteristic length. Often, the relationship between properties and characteristic length is fractal. Fractal systems have three characteristics. First, the images (*e.g.*, SEM) often appear visually self-similar over different length scales. Second, a noninteger power law characterizes the mathematical relationship between the measured property and the characteristic dimension.

Property α [Characteristic Length]$^{-\mu}$

Third, for a system to be fractal, the power law must apply over at least an order of magnitude in characteristic length. It has been shown that for microspheres embedded in Nafion, the flux of redox probes through the composite increases with

decreasing microsphere radius. A power law characterizes the relationship between flux and radius with an exponent of 0.78.[2] The same power law characterizes the increase in ion exchange capacity with decreasing particle radius.[10] The exponent of 0.78 is consistent with transport along the two dimensional surface of the microspheres. While fractal exponents are not intuitively transparent, they do provide information about what is dominating system responses. Guidance in the form of a fractal relationship enables tailoring and optimizing composites for specific electrochemical activity. It should be noted that when assessing the role of structure in composites formed of permeable and non-permeable material, it is necessary to normalize measured parameters such as flux by the fraction of permeable material.

Current Trends

Some recent trends point to the development of device components and switches on electrodes. Electrodes modified with a monolayer containing cis-azobenzene precludes direct electron transfer to a redox species in solution, but upon photoconversion to trans-azobenzene, direct electron transfer occurs because the trans configuration generates a more porous film.[11] Coating liquid crystals on the electrode forms an electrochemically activated switch, where the electronic conductivity changes by 10^5 under electrochemical perturbations.[12] An electrochemically actuated mechanical system relies on the flux of lithium ions in and out of a 3.5 cm long carbon nanotube to generate displacements of several centimeters.[13] Size selectivity has been engineered into a film by exploiting pores that occur naturally in the crystal structure of a rhenium complex.[14] The orientation of peptide nanotubes perpendicular to the electrode surface provides size selectivity for small redox probes.[15] Such structures lead one to conjure plumbing and electrical wiring of devices on electrodes.

Scaffolding has been built on scales from the molecular to the nanoscopic. Savéant and coworkers build a highly ordered, multilayer enzyme modified electrode by exploiting antigen-antibody and avidin-biotin binding.[16] Alternating layers of polyoxometalates and cations have formed multilayer structures.[17] Such structures have order on the molecular to nanometer length scale normal to the electrode and longer length scales in the plane parallel to the electrode.

Dendrimer structures on electrodes provide the opportunity to design three-dimensional matrices; spherical dendrimers form monolayers with higher dimensionality than the two dimensional structures provided by alkane based self assembled monolayers.[18] Here, on the electrode normal, the length scale is higher than molecular. Scaffolds of nanometer length scales are formed of nanometer sized gold nanoparticles linked with organic binders.[19,20] Microscopic scaffolding is formed by microparticles bound to an electrode by a matrix such as an ion exchange polymer.[2]

Thus, new tools are evolving for the construction of true three-dimensional architectures on electrode surfaces. These structures hold the promise of actuation by external stimuli, as well as the design of graded materials. Devices, reactors, transducers, and switches on a molecular to microscopic length scale are possible constructs on electrodes.

Future Directions

We can expect a greater variety of nano- and microscopic structures on electrodes, with design ideas drawn from the macroscopic world. Surprises will arise as behavior at submacroscopic length scales

often differs from that at the macroscopic. Successful developments will require advances in modeling, experimentation, and design paradigms.

The modeling of homogeneous films would be advanced by models for cyclic voltammetry of permeants through inert and ion exchanging films. Ion exchange models have the added complexity of electroneutrality requirements. No voltammetric models account for the changes that occur when ions of charge $n+$ initially loaded into an ion exchanging film undergo electrolysis. More sophisticated models will be developed as composite structures become more complex. Experimentally, nondestructive imaging methods that view the interior of composites with molecular to microscopic resolution would allow a better appreciation of the role of the interface.

A greater variety of design schemes will evolve including templates on all length scales, lost wax processes for microscopic structures and intercalating components into interfaces, and more robust as well as switchable scaffolding. Formation has thus far relied on self assembly to a large extent; more elaborate chemistries will evolve. Composites will serve as microscopic transducers. If composite matrices are to find techno-logical applications, more robust materials will be needed. Rapid response sensors will depend on enhancing transport through composites. Composite arrays with addressable sites in three dimensions would have applications in sensors and information storage; photoelectrochemical methods might be appropriate. As submacroscopic systems often yield fractal (*i.e.*, nonlinear) responses, it is conceivable that amplification schemes may be developed. In general, design paradigms will evolve that will allow composites to be tailored for specific applications. Such paradigms would find application in the design of heterogeneous structures such as fuel cell catalyst layers. Designing architectures on electrodes can be viewed as plumbing, wiring, constructing, engineering, modeling, or nonlinear optimization, but the rich complexity of the domain leaves the researcher with opportunities on many length scales and ample room to play. ∎

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