Electron Transfer at Semiconductor Electrode–Liquid Electrolyte Interfaces

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Contents

I. Introduction/Organization

A. Photoelectrochemistry and Interfacial Electron Transfer

Even though the phenomena of electron transfer (ET) across semiconductor–liquid interfaces has been discussed in the literature for over 30 years, the early 1970s saw a dramatic growth in research in this area.[1–4] This growth was largely due to interest in solar energy conversion. During the past 20 years, research related to

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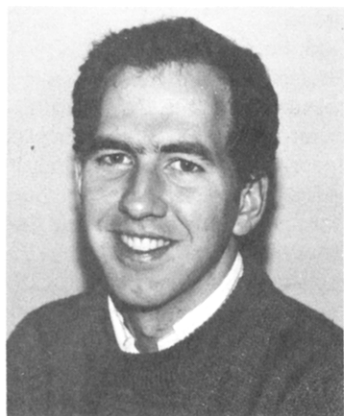
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liquid junction solar cells, often referred to as photoelectrochemistry, has diversified to include other applications including waste treatment, materials synthesis and processing, and sensors.

Interfacial electron transfer is fundamental to the operation of all devices based on photoelectrochemical cells. Understanding of ET processes between molecules in condensed phases has made enormous advances during the past 20 years,[5,6] and there has also been considerable progress in the area of ET at metal–electrolyte interfaces (MEI).[7,8] Despite the thousands of published papers on photoelectrochemistry, our understanding of ET at semiconductor–electrolyte interfaces (SEI) has not advanced as rapidly. Most experiments in this field are still interpreted within the context of a model developed in the 1960s by Gerischer[3,9–12] and many important questions pertaining to this model have remained unanswered or only partially answered.[13] One explanation for the slow development of fundamental principles lies in the large number of practical successes that have been achieved in photoelectrochemistry.

B. Basic Model for Electron Transfer at Semiconductor Electrodes

In order to facilitate discussion of the many topics covered in this review, it is necessary to present the basic picture and terminology associated with ET at the SEI.[14,15] This is most readily accomplished using the energy vs position (Gerischer) diagrams presented in Figure 1 for n-type (a) and p-type (b) doped semiconductor electrodes. Note that a second electrode immersed in the electrolyte solution must be assumed in Figure 1, if it is used to discuss the SEI in the context of an electrochemical cell. While these diagrams are similar to energy-level diagrams commonly used in spectroscopy, they contain a variety of subtle features which, if ignored, can result in confusion or misinterpretations.

The x axis on the semiconductor side of the SEI represents distance into the semiconductor perpendicular to the interface. The distances are on the order of 10^2 to 10^4 Å because at greater distances the properties of the semiconductor are assumed to be spatially uniform. This is not to say that processes occurring in the bulk of the semiconductor are not important in photoelectrochemical cells. Transport and recombination of electrons and holes in the bulk often affect the net current flow through the interface since these regions are in series. The x axis on the electrolyte solution side of the interface can be used to represent distance; however, this is generally not done for three reasons. First, the distance scales necessary to represent spatial inhomogeneity of properties such as potential in the solution are much smaller, i.e. on the order of 1–100 Å for double layers involving solutions of concentrated electrolytes. Second, the effects that strong electric fields present on the solution side of the SEI have on the properties of solvent and redox molecules in these regions are not well understood. Third, it is more useful to depict other features of the solution side of the SEI in these diagrams, namely, the density of electron states associated with oxidized and reduced redox molecules (see below).

Although the y axes in these diagrams primarily represent electron energies, the diagrams are used to describe phenomena occurring in electrochemical cells and also contain relevant electrostatic information in potential (V) and not energy (eV) units. Difficulty in distinguishing between thermodynamics (energies) and electrostatics (potentials) in electrochemical cells is common.[16] In this regard, it is useful to make a connection between cell potentials associated with the redox couple in the electrolyte and the energies of bands in the semiconductor. This can be accomplished by defining solution redox energies, E_{redox}, and formal re-
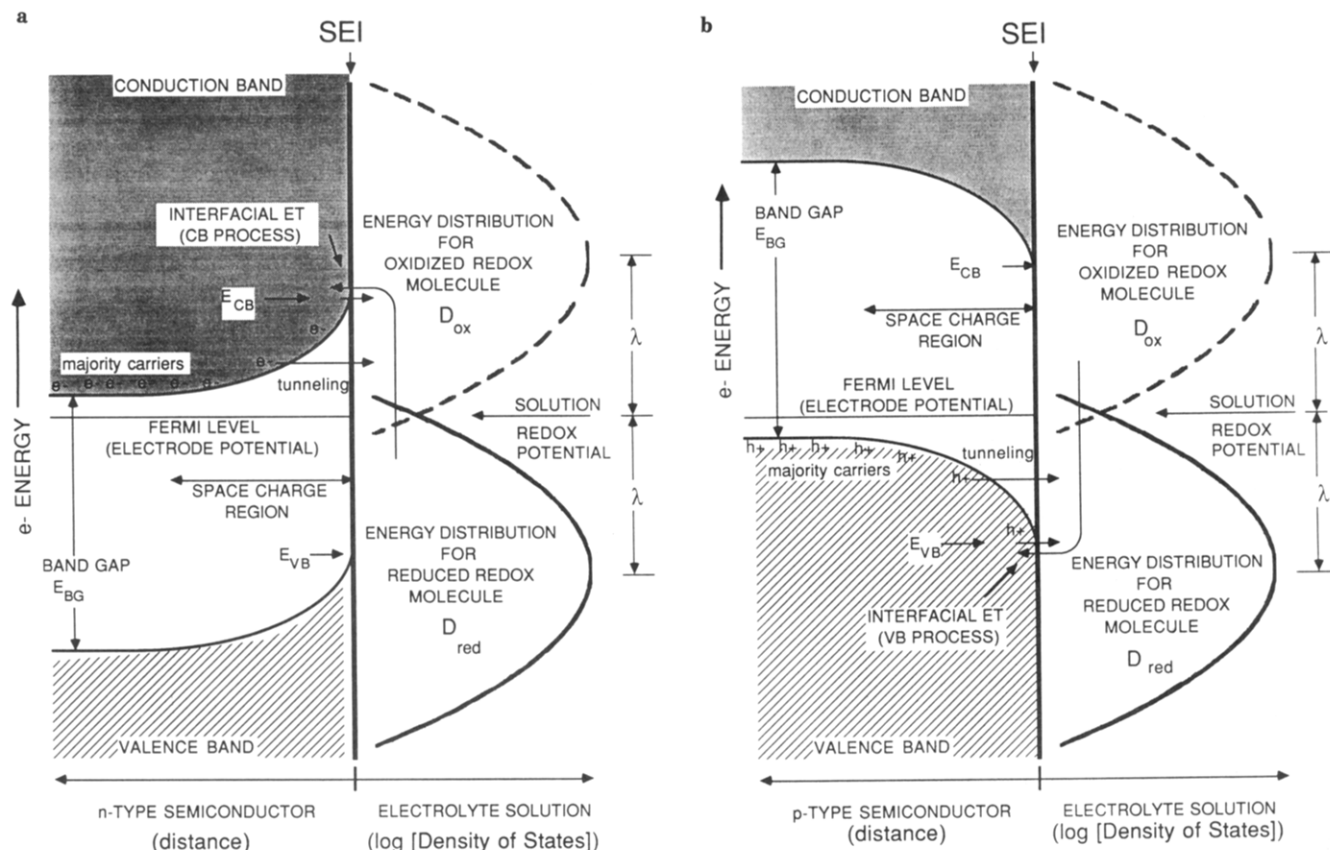
Figure 1. Energy level vs position representations of the SEI for n-type (a) and p-type (b) semiconductor electrodes in contact with an electrolyte solution containing equal concentrations of the oxidized and reduced forms of a redox molecule. This type diagram is used to introduce terminology common to models describing interfacial ET (see text).

duction energies, $E^{0\prime}$, associated with the potential quantities, E_{redox} and $E^{0\prime}$, which are related in the normal way via the Nernst equation. The potential quantities can be converted to energy units simply through multiplication by the elementary charge quantity, q. However, a quantitative relationship between energy and potential scales requires an assumed relationship between zero on each scale, e.g. the energy of an electron in vacuum and the potential of the normal hydrogen electrode, which cannot be done with thermodynamic rigor.[17] A second situation that involves both potentials and energies is the spatial dependence of an energy level or band within one phase, for example, calculating the energy of the conduction band at the interface, E_{CB}. The accuracy of such calculations depends on equations derived from an electrostatic model of the interface and various measured quantities including potential differences, properties of materials, etc.

With these caveats in mind, it is seen that the SEI's in Figure 1 parts a and b are in equilibrium (no net current flow) when the Fermi level (energy of a half-filled level) of the semiconductor electrode is equal to the solution redox energy. Various electronic circuits connecting the semiconductor electrode and a metal electrode in the electrolyte solution can be used to measure the potential across the entire cell or to impose a potential difference which results in net current flow. Certain experimental setups allow cell potentials to be measured or controlled with respect to a third, reference electrode and allow electrostatic measurements associated primarily with a single interface to be made.[17] In this sense, moving down the y axis of Gerischer di-

agrams represents more oxidizing or positive cell potentials (with respect to a reference electrode) and moving up represents reducing or negative potentials.

The position of the Fermi level energy, E_F, with respect to the solution redox energy (or to vacuum) depends on the work function and excess positive or negative charge associated with the semiconductor electrode. This relationship can be explained rigorously through the use of the electrochemical potential formalism.[17] For the n-type electrode, excess positive charge near the surface is accomplished by a depletion of conduction band electrons (e^-); negative surface charge for the p-type electrode is accomplished by a depletion of valence band holes (h^+). The electric fields associated with these charge distributions are represented by curvature of the bands and indicate the direction that free carriers will migrate in the field (electrons down, holes up). The region where this curvature exists in the electrode is often referred to as the space charge region. The depth of this region is related to the doping density (N_D), the dielectric properties of the semiconductor material and magnitude of the electric field. The condition where there is no excess charge associated with the semiconductor, and no associated electric field (no band bending), is referred to as the flat-band potential, E_{fb}. Measurement of E_{fb} is often used to calculate the conduction and valence band edge energies at the interface, E_{CB} and E_{VB} (see section IV).

The energy levels on the right-hand side of the interface are associated with the redox couple in the solution, in particular, the electrons to be transferred to the solid and the acceptors for electrons transferred to

the solution. In the same way that the levels in the valence band are filled, the levels for the reduced form of the redox couple (RED) are filled. Similarly, the levels for the oxidized form of the couple (OX) and the conduction band are empty states. These energy levels are represented as probability distributions due to oscillations in the electric fields experienced by the molecules in solution from movement of atoms in the solvent and the molecule itself. Although the distributions are Gaussian-shaped, they are depicted in logarithmic fashion by the parabolas in Figure 1 for clarity. The most probable energies for OX and RED are displaced from the formal reduction energy of the couple, $E^{0'}$, by the reorganization energy, λ. (These probabilities do not decay away to zero as might be erroneously concluded by the fact that the parabolic representations in Figure 1 terminate at the interface.) The absolute magnitudes for the probabilities in these distributions are also directly related to the concentrations of the oxidized and reduced forms of the redox couple in the solution near the interface. The fact that the oxidized and reduced distributions are symmetric in these figures indicate that [OX] = [RED]. The intersection point of the oxidized and reduced distributions represents the solution redox potential (or energy), i.e. the potential that a metal electrode would achieve if it were to equilibrate with the solution.

While electron transfer can involve both the valence and conduction bands, there are a variety of situations in which exchange with one band or the other is expected to dominate the current. In the dark, the high concentration of majority carriers with respect to minority carriers tend to cause the band containing the majority carriers (conduction band electrons at n-type interfaces and valence band holes at p-type) to dominate the current. Since Franck–Condon considerations require isoenergetic ET and assuming that only carriers near the surface react, most of the ET for the situation in Figure 1a will involve levels within a few kT of the conduction band edge, E_{CB}. If the material is highly doped ($N_D > 10^{18}$ cm^{-3}) and the space charge region is correspondingly thin, ET can involve a tunneling process. This consideration is ignored in many papers, even when highly-doped materials are employed. Minority band processes (h$^+$ at n-type and e$^-$ at p-type) become more likely as the formal reduction energy for the solution redox couple approaches the minority band edge. Of course, photocurrents reflect a combination of ET processes involving both minority and majority carriers.

The fact that Figure 1 represents an ideal and simplified picture of the SEI cannot be overstressed. Solid-state physics provides a much more rigorous view of the semiconductor side of the interface[18] and every aspect of the depiction of the redox solution is disputed. Nevertheless, these diagrams are widely used and do provide a reasonable, qualitative explanation for current flow at the SEI both in the absence and presence of bandgap illumination.

C. Organization of the Review

This review attempts to cover the literature on ET at SEI's published since 1985; key references to earlier literature is provided for some topics. The emphasis is on papers relating to fundamental issues as opposed

to applications. Application advances will be mentioned in order to provide the reader with a context for the interest in a particular subfield. Rather than attempting to examine specific questions in detail, the goal of this review is to educate the reader with respect to the breadth of systems encountered in photoelectrochemistry and to indicate how these systems can be used to examine fundamental ET issues.

There is no shortage of reviews on photoelectrochemistry; therefore, we begin in section II by commenting on the ones published prior to 1986 and additional recent reviews. Section III is an attempt to categorize the many types of SEI's with respect to the semiconductor and the solution. After reading section III, it should be apparent that interpretation of ET experiments is critically dependent on an ability to characterize the SEI being studied. The inherent complexities of the SEI have been studied by a wide variety of techniques ranging from well-established methods (impedance analysis) to recent and potentially powerful developments (scanning tunneling microscopy). In section IV, an overview of these methods are described together with examples of recent work. Issues related to the energetics of the SEI and other factors influencing the interpretation of current flow are presented in section V. Section VI examines types of interfacial ET processes. Since Lewis has recently written an excellent review examining experiments relating to rates of ET reaction at the SEI, his approach and conclusions are described in section VII. Section VIII looks at recent theoretical treatment of the SEI. Some general comments are included in section IX.

II. Other Review Articles

The purpose of this section is to direct the reader to other general review articles on the subject of semiconductor electrochemistry. Post-1985 reviews that emphasize specific topics are discussed in sections III–VIII; many of these reviews also contain background material. Before proceeding, two materials that are virtually indispensable deserve mention. First, the textbook by Sze provides an in-depth description of the physics of semiconductors.[18] While this book deals solely with solid-state junctions, it provides a sound background for understanding interfacial ET from the semiconductor's point of view. The second key set of papers are those by Gerischer which describe the theoretical framework used by virtually everyone in the field. This framework is initially described in the early 1960s,[9] but a newcomer to the field will be more comfortable with one of Gerischer's more recent reviews.[3,12]

A. Pre-1980

The latter portion of the 1970s saw a virtual explosion of publications on photoelectrochemistry. This body of work is adequately reviewed in several books and monographs that appeared around 1980. In particular, the book by Morrison[14] and the monograph by Wilson[15] provide excellent descriptions of the models used to describe ET at the SEI. Both of these works examine relevant experimental data within the context of Gerischer's model and comment on the difficulties in obtaining unambiguous proof that the model is correct. Many of the questions that were unanswered at the

time of these reviews remain so today. Also appearing at this time were several reviews of general principles[2,3] along with those more oriented toward photoelectrochemical applications.[4,19–21]

Finally, Bard and Faulkner's textbook provides a brief description of photoelectrochemical phenomena, but it is especially useful because it is within the broader context of all electrochemistry.[17] In order to maintain continuity within this review, we have attempted to use abbreviations and symbols identical to those used by Bard and Faulkner.

B. 1980–1985

A set of reviews in a single issue of *The Journal of Chemical Education* provides an excellent, if somewhat dated, introduction to the field of photoelectrochemistry that is especially useful to students.[22–27] Other useful reviews from this period include the proceedings volumes edited by Nozik[28] and Schiavello,[29] a review of classic papers by Khan and Bockris,[30] and a general research review by Peter.[31]

C. 1986 to the Present

The book edited by Finklea provides in-depth reviews of several important chemical classes of semiconductor electrodes.[32] General reviews by Hamnett,[33] Memming,[34] and Uosaki and Kita[35] appeared at this time. Books edited by Pelizzetti and Serpone,[36] Schiavello,[37] and Fox and Chanon[38] contain discussions of a variety of topics related to the SEI and photoelectrochemistry. Reviews oriented toward solar energy conversion include those by Orazem and Newman[39] and Memming.[40] Fox[41,42] and Tributsch[43] have reviewed aspects of photoelectrolysis. Archer presented a historical perspective of photoelectrochemistry.[44]

III. Types of Semiconductor–Electrolyte Interfaces

Figure 1 represents an idealized picture of the SEI in several senses and it is important to keep the assumptions inherent in this picture in mind when attempting to relate experimental data to interfacial electron transfer rates. Figure 1 does not indicate that the interface when viewed in a perpendicular direction, as opposed to cross section, may be spatially inhomogeneous. This inhomogeneity may be of several forms. Polycrystalline semiconductor electrodes will have different crystal faces exposed to the electrolyte and this will effect the diagram if the material is anisotropic. Also, the semiconductor electrode may have structural defects and surface states which will effect the mechanism of ET (see section VI). If a photoelectrochemical process is being considered, the intensity and spatial inhomogeneity of the illumination has a dramatic effect on the energy vs position profile within the semiconductor. A quantity that is often critical to the interpretation of data is the energies of the valence and conduction band edges at the interface, E_{VB} and E_{CB}. Use of diagrams like Figure 1 often assumes that these energies, which are shown for an equilibrium situation, do not change when light or an applied potential is used to cause current flow across the interface. Such stability is the exception rather than the rule (see section V).

TYPES OF SEMICONDUCTOR ELECTRODES
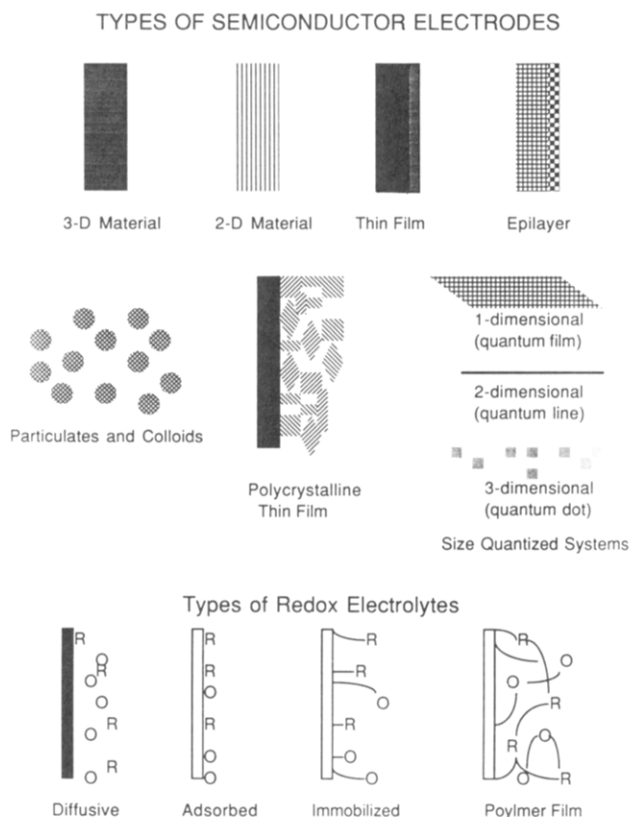
Figure 2. Classes of semiconductor electrodes and liquid redox electrolytes that can be contacted to form an SEI. Rates of electron transfer across each type of interface depends on the properties of the electrode and the electrolyte.

The situation is no less complicated on the electrolyte side of the interface. The only easily verifiable quantity in the electrolyte is the redox potential (Nernst potential) of the solution in the bulk. One often assumes that this is also the potential of solution at the interface, but this assumption is dependent on the magnitude of the current flow and the mass transfer characteristics of the interface. A more highly debated issue is the depiction of the density of electronic states associated with the redox couple. Uncertainties about the mechanism of electron transfer, the shape of the distributions, and the spatial dependence perpendicular to the interface all affect the ability to relate observables such as current flow to fundamental properties and interfacial ET rate constants.

The purpose of this section is to introduce the many types of SEI interfaces currently under investigation. In many cases, construction of a certain type of interface is undertaken with a practical (i.e. photoconversion) as opposed to fundamental purpose in mind. Nevertheless, a basic familiarity with these types of interfaces, diagrammed in Figure 2, is useful.

A. Types of Semiconductor Electrodes

1. Single Crystals and Epilayers

Single crystal semiconductor electrode materials[32] are, by far, most likely to conform to the ideal interfacial picture in Figure 1. The interfacial and bulk properties are spatially uniform and many equations describing the physics of charge transport in the solid state can be applied with accuracy.[18] Not surprisingly, conversion efficiencies for liquid junction solar cells constructed

from these materials can be quite high, often limited only by the quality of the individual crystal.[45] In some cases, thin films or epilayers of material with single crystal quality can be grown on a substrate by techniques such as molecular beam epitaxy (MBE)[46] or metal organic chemical vapor deposition (MOCVD).[47] Techniques are also available for the preparation of single-crystal semiconductor membranes ranging in thickness from 10 nm to microns; these techniques have been reviewed by Lee.[48] In general, single-crystal, epilayer, or membrane electrodes are quite expensive due to manufacturing costs. The availability of a specific material usually relates to use in the electronics industries, i.e. samples of materials such as Si, GaAs, and InP are relatively easy to obtain. Unfortunately, the bulk properties of single-crystal materials do not necessarily imply anything about the chemical nature of the electrode at the interface. The implications of this uncertainty are discussed in sections IV–VI.

When using single-crystal materials, the orientation is important,[49] especially if the solid-state or surface properties are anisotropic. This is especially true with so called two-dimensional materials of which layered metal dichalcogenides (LMD, e.g. MoS_2, WSe_2, SnSSe, etc.) are an important class.[50] The molecularly smooth and chemically inert van der Waals surfaces of LMD's often result in nearly ideal SEI's[51] which have been particularly useful for investigating ET processes.[52–55] Papers describing growth and doping methodology,[56,57] bulk and interfacial properties,[58,59] back-contacts,[60,61] and photoelectrochemical properties[55,62–64] have appeared recently.

Orientation can be important for other semiconductors as well. InP ⟨111⟩ has an indium-rich face and a phosphorous-rich face. The different faces have been shown to have unique properties which may influence the SEI behavior.[49]

2. Polycrystalline Electrodes and Thin Films

It is often a relatively simple matter to prepare electrodes of many semiconducting materials in which the size of individual crystals are small with respect to key properties associated with charge transport, e.g. minority carrier diffusion length. Photoconversion efficiencies with such electrodes are often limited by processes occurring at grain boundaries and other imperfections and are often smaller than those observed at single crystals. Due to the gross inhomogeneities associated with both the bulk and the interface, it is extremely difficult to apply an idealized model of ET to these materials in a quantitative way.

Several imaginative procedures for the preparation and surface modification of polycrystalline samples have been reported recently. Considerable excitement has been generated by Grätzel's group with regard to fabrication of polycrystalline TiO_2 films with surface roughness factors of several hundred.[65] Cabrera and Abruna prepared and characterized polycrystalline thin films of the 2-D material, WSe_2.[66]

Despite the problems mentioned above, preparation and characterization of photoelectrochemical properties for polycrystalline and thin-film electrodes has been intensely investigated. The rationale for this interest is easily understood. Polycrystalline materials with large surface areas are far less expensive to manufacture than are single crystals. Since single-crystal materials can achieve high conversion efficiencies, one hopes to be able to impart these useful interfacial ET properties to polycrystalline samples. Hodes et al. reviewed the use of polycrystalline films in photoelectrochemical cells in the mid-1980s.[67]

3. Suspensions of Semiconductor Particles and Colloids

The electrodes described above have overall macroscopic dimensions and can be contacted electrically; therefore, known potential differences can be applied across the interface. In many cases, sustained photoelectrochemical processes can be observed at individual particles of semiconductors, the best known example being TiO_2. In this type of system, conservation of charge requires that equal amounts of oxidation and reduction occur at the interface of each particle. While a relationship between ET at particles and macroscopic electrodes must exist (the concepts associated with Figure 1 must apply), it is virtually impossible to determine the relevant features of the interface quantitatively.

Methods for the preparation of colloidal semiconductors and a description of their relevance to solar energy conversion have recently been reviewed by Kamat and Dimitrijevic.[68] They categorize the techniques used to prepare semiconductor colloids into three groups: precipitation from homogeneous solution, phase transformations, and reactions with aerosols.

4. Size-Quantized Systems

When the size of semiconductor electrodes becomes comparable to the de Broglie wavelength of the charge carriers (25–250 Å), the band structure model breaks down and the energy of electrons becomes quantized.[69] Size quantization can occur in one, two, and three dimensions leading to quantum dots, quantum wires, and quantum layers, respectively. Since relaxation of photoinduced electron–hole pairs, e^-/h^+, should be slower in quantized semiconductors, enhanced photoconversion efficiencies are theoretically possible. If differences in ET rates or products can be observed for the individual electronic states, these systems also have considerable potential for improved understanding of interfacial ET.

Many important contributions to this area have come from the laboratories of Henglein, Nozik, and Brus. Henglein's research involves small metal as well as semiconductor particles.[70] Nozik's studies have emphasized possible applications of size quantization to photoelectrochemistry;[71] therefore, most of the systems investigated have been quantum layers on the surfaces of 3-D electrodes. Quantization in these systems is achieved via fabrication of thin (<200 Å) alternating layers of semiconducting materials with different bandgaps creating superlattices or multiple quantum wells. Brus has investigated a variety of novel synthetic procedures for controlling the growth of II–VI semiconductor crystallites.[72]

To date, a majority of the research on size-quantized semiconductor systems has related to preparation and characterization. Since many semiconductors are insoluble salts (II–VI materials, silver halides, etc.), quantum particles are produced by mixing reagents that

lead to precipitation. The difficulties lie in achieving narrow particle size distributions and preventing subsequent aggregation. In some systems, controlled growth can be achieved by organic materials such as alkanethiols which effect growth and dissolution rates by adsorbing to the surface of growing particles. Micic, Meisel, and co-workers have shown that these growth processes can be followed by optical and radiation spectroscopies.[73-77] A second widely used preparation technique involves the use of membranes as a matrix for the precipitation reaction.[78] In order to obtain especially thin films of quantized particles, Fendler[79-81] and others[82] have explored the use of surfactant aggregates such as micelles, vesticles, bilayer lipid membranes, and Langmuir–Blodgett films as organizing media.

B. Types of Redox Electrolytes

Any discussion of interfacial ET is highly dependent on the assumed mechanism. The various mechanisms that have been proposed for ET at the SEI are presented in section VI; however, straightforward comparisons to theory[5,6] requires one-electron, outer-sphere ET. Certain classes of molecules, such as substitutionally-inert transition metal complexes (metallocenes and tris-1,10-phenanthroline or tris-2,2'-bipyridine complexes) and highly-conjugated organics (substituted PAH's), are likely to react by this mechanism. Both classes of molecules contain one-electron redox couples with a wide range of formal reduction potentials, $E^{0'}$, in which the oxidized and reduced forms of the couple are similar in structure and are chemically stable in certain electrolyte solutions. These features result in couples with relatively low intrinsic (Franck–Condon) barriers to ET; in some cases the barriers reflect only solvent activation. Unfortunately, many of these molecules, unless derivatized with charged groups, are soluble only in nonaqueous solvents. Much of the literature related to ET at semiconductor–aqueous interfaces is dominated by couples such as $Fe^{3+,2+}$, $Fe(CN)_6^{3-,4-}$, $Ce^{4+,3+}$, etc. It is doubtful whether these couples react via a simple outer-sphere mechanism.

It should be noted that many useful and stable photoelectrochemical processes do not occur by one-electron, outer-sphere ET mechanisms. These include virtually all cells that produce fuels, stable aqueous electrolyte cells (eg. cells involving polysulfide or I_3^-/I^- redox couples[14,32]), photooxidation of organics, and photoetching. Nevertheless, efficient and stable light to electricity conversion has been achieved in nonaqueous solvents by an outer-sphere mechanism.[45]

1. Diffusive Redox Systems

Cases in which the redox couple can diffuse freely in the electrolyte solution requires little discussion because this situation is common to most electrochemical cells and is described in depth in many texts.[17] Only a few key points need to be emphasized here. First, at all solid–liquid junctions the solvent is stagnant and the only forms of mass transport involve migration and diffusion. Since mass transport of molecular species must balance the interfacial current density via Faraday's law, processes at the MEI or SEI in which the interfacial current density is high often become limited by mass transport. Convection in the solution has a

dramatic effect on mass transport; a simple view of this effect is that higher degrees of convection result in thinner layers of stagnant solution next to the electrode. Of course, higher concentrations of redox couples result in proportionately higher rates of mass transport.

With respect to the types of semiconductor electrodes mentioned above, it is important to remember that solutions to convective–diffusive equations are dependent on the electrode geometry. These solutions are quite different for flat surfaces and particles. One simplifying feature of mass transport at the SEI is that migration terms can often be ignored since in many instances the potential drop across the interface occurs mostly in the electrode. This is not the case at the MEI where correction for double-layer effects greatly complicates the interpretation of ET rates.[7]

There are a number of ways in which mass transport effects can be minimized at the SEI. For photoinduced processes, the interfacial charge flux is easily controlled via the light intensity. For dark processes, current densities observed near equilibrium when the semiconductor is in depletion are low due to the low concentration of majority carriers at the surface. In these situations, solution convection may not be necessary. When studies at relatively high current densities are necessary, high concentrations of redox couple and convection are necessary to obtain useful rate data. Examples of the use of concentrated redox electrolytes are illustrated in Lewis' papers[45] while an interesting method for obtaining very high convection by using a jet electrode is provided by Olson.[83] Santangelo et al. have reported useful methods for analyzing voltammetric data obtained at SEI's involving diffusing redox couples[84] as well as surface attached couples.[85]

2. Adsorbed Redox Systems

Many highly conjugated organic molecules adsorb strongly to semiconductor surfaces. In many cases, this adsorption is sufficiently strong that a high surface coverage can be maintained in the absence of the redox species in solution. The practical objective in many of these systems is utilization of the optical properties of the adsorbed molecules, which are often dyes, to improve (red shift) the spectral response of the semiconductor.[86] From the fundamental ET perspective, many elegant experiments involving dye adsorption and ultrafast spectroscopic methods have been reported (see section VII). Even though adsorbed redox species provide quite high surface concentrations of solution redox species, these molecules are rapidly depleted as current flows across the interface. This is not a problem for experiments involving short illumination times or low intensities. For sustained currents, the ground state of the dye is repopulated by a second redox species in solution and all of the mass transport considerations mentioned above apply.

Adsorption of redox species to oxide semiconductors continues to be an active area highlighted by the work in Grätzel's laboratory on TiO_2; surface modification with Ru complex ions, metal cyanide complexes,[87] and dyes have been reported. In some instances, surface modification involves reaction with the surface.[88] A light-induced surface modification that is stable up to 1 year has been reported by Ryan and Spitler for rodamine dyes on oxide semiconductors.[89] Parkinson has

TABLE I. Techniques for Characterizing the Semiconductor–Electrolyte Interface

technique	primary use	other uses	refs
i-E curves	surface stability; estimate of IE	kinetics	14, 15, 17, 34, 54
impedance analysis	E_{fb} measurement	surface state characterization; N_D	14, 15, 17, 31, 33, 96, 99
RRDE	analysis of redox products	corrosion studies; reaction kinetics at disk	17, 55, 104, 105, 107, 108
photocurrent	PEC device evaluation	E_{fb} estimate; ET rates	14, 15, 17, 31, 34, 96
photovoltage	PEC device efficiency	recombination rates; E_{fb} estimate	3, 4, 14, 15, 28, 31, 33, 45, 96, 100, 101
illumination wavelength dependance	surface state energies	charge carrier collection velocities	97, 98
photoluminescence	recombination processes	surface state or quantum-well energies	109, 111–121
electroluminescence	recombination processes	surface state energies	109, 113, 119, 122–124
transient measurements	ET rate measurements	surface state relaxation rates	52, 96, 125–133
IMPS	photocurrent kinetics; recombination rates	surface state influence on ET	126, 134–136
EER	E_{fb} measurement	surface state characterization	137–144
IR	characterization of surface species		146–148
Raman	characterization of surface species		149, 150
Ellipsometry	characterization of surface films		151, 152
laser-spot scanning	spatially-resolved studies		153–155
STM	surface imaging	IE, etching small features	156–173
SECM	surface imaging	etching small features	174–176
UHV methods	chemical analysis of surface	surface morphology	150, 177–187

shown that dyes adsorbed on surfaces of 2-D materials such as SnS_2 produce remarkably efficient photosensitization.[53,90]

3. Immobilized Redox Systems

For molecules with useful redox properties that do not spontaneously adsorb to the semiconductor, very high surface concentrations can be achieved by synthetically bonding molecules to the surface. This type of system received considerable attention in the early 1980s because it resulted in lower corrosion rates in some systems.[26] Strategies for surface bonding of molecules to surfaces has been extensively reviewed; the review by Murray contains a specific discussion of the modification of semiconductor surfaces.[91]

Possibly the best example of achieving high concentrations of immobilized redox species is Bocarsly's work involving formation of $Cd(Fe(CN)_6{}^{2-,-})$ overlayers on n-CdS and n-CdSe electrodes.[92,93] These layers have been shown to enhance the stability of these n-type materials with respect to corrosion and result in electrocatalysis for reactions in solution.

4. Redox Polymer Films

Another approach to achieving high concentrations of redox couples at electrode surfaces involves coating the surface with a polymer and introducing the redox couple into the film via chemical bonding or electrostatic attraction. These methodologies are well established in the electrochemical literature.[91] Noufi et al.[94] were the first to utilize redox polymers for the stabilization of semiconductor electrodes. A recent example of this approach is found in work by Yildiz et al. who investigated polypyrrole-coated colloidal semiconductors.[95]

While concentrations of redox couples in polymer films can be quite high, the ability to supply high current densities at an interface is not a certainty. Charge transport in polymer films can be quite low due to hindered diffusion or weak electronic coupling.

IV. Techniques for Investigating the Semiconductor–Electrolyte Interface

A wide variety of techniques have been applied to characterize the SEI. Some of these methods are described below and summarized in Table I.

A. Classical Techniques

A number of electrochemical techniques have been applied to investigating the SEI since the 1950s. They are still frequently applied to SEI research to provide initial information about a system and for comparison with more elaborate techniques.

1. Current–Potential Curves

Basic characterization of the SEI with respect to ET involves obtaining current–potential curves either in a two- or three-electrode cell configuration. A variety of electrochemical techniques involving either static or flowing solution conditions are used for this purpose.[17] Current–potential (i-E) curves provide estimates of band-edge positions and evidence for chemical processes such as surface corrosion. Since the generation of minority carriers at the illuminated SEI leads to additional faradaic current, i-E curves under illumination are distinct from the nonilluminated case. Besides the obvious importance of large photocurrents to solar power applications, the illuminated i-E curve also provides clues about the nature of the SEI and the kinetics of charge transfer. These methods have been thoroughly reviewed.[14,15,31,34,96]

In addition to the potential dependence of photocurrent, some systems show interesting excitation wavelength dependence. Investigations with subbandgap light at ruthenium modified n-GaAs show the presence of Ru-induced surface states.[97] The use of variable suprabandgap wavelengths with different, shallow penetration allows measurements of majority carrier collection velocities.[98] More sophisticated photocurrent experiments involving the use of chopped or

pulsed light, measurement of transients, or modulation of illuminating wavelength are discussed later.

2. Impedance Analysis

The capacitance dependence on applied potential is an important means of characterizing the SEI. A plot of $1/C_{sc}^2$ vs E ("Mott–Schottky" plots) should be linear with a slope proportional to the bulk doping density and an intercept corresponding to the flat-band potential. Clearly, if one hopes to apply models based on the picture of the SEI in Figure 1, determining these important interfacial energetic parameters is crucial. Unfortunately, various complications may limit this technique such as assumptions about the equivalent circuit or imperfections in the SEI. Many reviews discuss Mott–Schottky plots in more detail.[14,15,17,31,33,96] More complicated impedance analysis involving multiple frequencies and a variety of equivalent circuits may provide information about surface states; this topic is further discussed in section V. A review of impedance analysis at the SEI has been published by Chazalviel.[99]

3. Photovoltage

An illuminated semiconductor electrode in contact with a redox solution will attain a potential difference vs an auxiliary metal electrode, which is in equilibrium with the solution. This potential difference is called the photovoltage. Theoretically, the maximum obtainable photovoltage should equal the difference between the majority carrier band edge and the solution redox energy. However, this theoretical limit is rarely obtained due to band-edge movement and recombination effects. Again, this topic has been previously reviewed, particularly with respect to solar energy applications.[3,4,14,15,28,31,33,96,100,101] Recent work by Lewis and co-workers provides a good example of fundamental investigations of the SEI with photovoltage measurements.[45]

4. Electrochemical Product Analysis

Identification of the products of redox reactions at the SEI is especially important with respect to evaluating the stability of photoconversion systems. A recent example is the high efficiency n-CdSe/Fe(CN)$_6^{3-,4-}$ cell reported by Licht[102] which has been questioned by Bocarsly.[103]

Rotating-ring disk electrodes (RRDE) provide a powerful method for evaluating electrochemical products. In a typical experiment, products formed at the SEI disk are swept past the metallic ring where they can be detected. By varying the rotation rate, the mass transfer can be precisely controlled allowing insights into the kinetics and mechanisms of reactions at the disk.[17] This technique has been applied to many SEI systems in the past two decades. Recent examples include investigations of the electroreduction of oxygen[104] and the photooxidation of water[105] at n-TiO$_2$ and studies of corrosion products under different conditions at n-WSe$_2$,[55] p-GaP,[106] and p-/n-InP[107,108] electrodes.

B. Optical Techniques Specific to Semiconductors

The ability to photogenerate e$^-$/h$^+$ pairs at the SEI has led to the development of a wide variety of tech-

niques other than photocurrent involving photoeffects at semiconductors. The experimental complexity ranges from fairly simple and routine (photocurrent measurements) to rather complex (electrolyte electroreflectance).

1. Photoluminescence

Photogenerated e$^-$/h$^+$ pairs at the SEI may radiatively recombine to yield photoluminescence (PL). PL is the main competing process to photocurrent and therefore often behaves as the complement to photocurrent, producing a "mirror-image" potential dependence. Ellis has published a detailed review of PL.[109]

Smandek et al. have presented a discussion of the basic "dead-layer" theory along with critical comparisons of photocurrent and PL of several common semiconductors.[110] Several researchers have investigated PL changes following surface modifications in accord with the "dead-layer" model. PL intensity was shown to be reduced at n-CdSe treated with lanthanide β-diketonates[111] and n-GaAs coated with a 10-nm cobalt film.[112] Also, whereas Mn-doped ZnS modified with polyvinylferrocene exhibited identical PL as the bare crystal, I$_2$ treatment of the PVF coating quenched the PL.[113] Conversely, PL is enhanced at n-CdSe treated with mono- or diamines[114] or mono- or diphosphines.[115]

Studies of interfacial energetics with PL have also been done. Ellis' group investigated both n- and p-GaAs interfaces and determined the space-charge width and surface minority carrier-capture velocities.[116,117] Uosaki et al. employed PL to demonstrate increased surface recombination velocities at Pt-treated p-GaAs during hydrogen evolution. Their results also suggested shifts in flat-band potentials.[118] The luminescence spectrum has been used to describe the types of surface states present at the SEI. For example, PL at the n-TiO$_2$–aqueous interface suggested various oxidized and reduced species adsorbed on the surface.[119]

A final example is the work of Nozik, Parsons, and co-workers who used PL measurements to determine the cooling rates of "hot electrons" in GaAs/AlGaAs superlattice, multiple-quantum well, and single-quantum well structures.[120,121]

2. Electroluminescence

Electroluminescence (EL) is a similar technique in which the e$^-$/h$^+$ pair recombine from the biased electrode and a solution-generated donor or acceptor. Ellis' review also covers EL.[109] The mechanism leading to EL is generally more complex than PL since, for example, a hole must be injected from the solution into the valence band to combine with a conduction band electron. For this reason, EL is limited to specific systems and has low quantum yields (10^{-4}–10^{-5}).[96]

EL studies are often done in conjunction with PL.[113,119] Studies of Mn-doped ZnS showed identical PL and EL peaks suggesting that the same luminescent center was involved.[113] Shifts in EL peaks with different dopant metals in CVD-grown ZnS suggested unique mechanisms among the materials.[113] Nogami et al. have studied the influence of surface states on the EL of polycrystalline n-TiO$_2$.[122,123]

Although normally confined to n-type SEI's, EL has recently been observed at p-GaAs and p-InP.[124]

3. Transient and Time-Resolved Measurements

The optical measurements described so far are often done under constant illumination. However, additional information is available by using pulsed or chopped illumination and following the transients in either the photovoltage, photocurrent, or luminescence. Reviews of transient techniques as related to the SEI have recently been published.[96,125,126]

An approach related to PL was used by Willig et al. to investigate electron transfer at the SEI. By exciting adsorbed dyes on n-SnS$_2$ and following the fluorescence decay, the rate of electron injection into the conduction band was studied.[52]

It is also possible to follow changes in the conductivity of the semiconductor following pulsed illumination by monitoring microwave reflectivity or radio frequency changes. This technique has been used to investigate charge transfer at Si–methanol redox solution interfaces,[127] the effects of H$_2$ evolution at n-Si,[128] and the interfacial energetics of n-WSe$_2$.[129]

The transient grating method involves creating an optical interference pattern of photoinduced charge carriers at the semiconductor surface and then probing this "gradient" with a separate optical probe. Since the gradient is due to e$^-$/h$^+$ pairs in the semiconductor, the gradient lifetime can be related to charge transfer kinetics at the SEI. This technique was used by Nakabayashi et al. to study the photoelectrochemical oxidation of 2-propanol on TiO$_2$.[130] Miller and co-workers have extended this technique to the picosecond time scale in studies of charge transfer at TiO$_2$–H$_2$O interfaces.[131]

A related technique, known as electrooptic sampling, has also been employed by Miller's group. In this experiment, the photogenerated charge carriers produce a phase change in polarization components of the optical probe. The rate of longitudinal separation of e$^-$/h$^+$ pairs in the space–charge region can be monitored on a subpicosecond scale.[132] Miller has used this technique to show that nonthermalized charge carriers reach the surface in a GaAs/oxide/CH$_3$CN system.[133]

4. Intensity-Modulated Photocurrent Spectroscopy

Intensity-modulated photocurrent spectroscopy, described as the optical equivalent of ac electrical techniques,[126] measures the photocurrent response to modulation of the excitation intensity. Details are available in other reviews.[126,134]

Peter and co-workers have used this technique to investigate several systems. Experiments with n-GaAs/alkaline selenide solutions analyzed recombination processes, surface-state relaxation times, band-edge shifts, and effects of Ru treatment.[135] IMPS was also used to investigate the mechanism of the photocurrent multiplication effect of the photodissolution of n-Si in ammonium fluoride.[136]

5. Reflectance Methods

The most common of these is electrolyte electroreflectance (EER). By modulating the electric field in the semiconductor (through a small applied ac potential) the dielectric constant and thus the reflectivity of the SEI is varied. The corresponding ratio of ac and dc components of the reflected light, $\Delta R/R$, at different wavelengths produces the EER spectrum. This spec-

provides information about the potential distribution across the SEI. A review of the theory and interpretation of EER spectra has recently been published by Hammett.[137]

n-GaAs in various electrolytes shows differences in the potential distribution across the depletion layer. About 70% of the potential drop occurred in the semiconductor for the n-GaAs–0.1 M NaOH interface.[138] Lemasson and VanHuong investigated n-InP, GaAs, Ga$_{0.47}$In$_{0.53}$As in aqueous and nonaqueous solution with EER to determine densities of surface states.[139]

The complex TiO$_2$–H$_2$O interface has been investigated with EER. Tafalla et al. obtained direct measurements of flat-band shifts of illuminated TiO$_2$.[140] Also, EER detected reversible shifts in flat-band potential due to local pH effects at TiO$_2$ during H$_2$ formation.[141] Changes in the EER spectrum at TiO$_2$ treated with hydrogen peroxide suggest formation of surface states due to adsorbed HO$_2$$^-$ species.[142]

Other studies with EER include monitoring potential distribution changes at polycrystalline n-CdS during photoetching[143] and demonstration of the removal of Fermi-level pinning in CuInSe$_2$ after bromine/methanol etching.[144]

A technique related to EER is photoreflectance (PR). In this experiment the electric field of the SEI is modulated with a pulsed or chopped laser beam while measuring the reflected light from a second illumination source. Again, the dependence of $\Delta R/R$ vs wavelength of the secondary source gives the PR spectrum. This method has been employed by Peterson et al. to obtain some excellent data from GaAs/AlGaAs superlattices. In these experiments, they were able to observe 32 theoretically predicted optical transitions corresponding to discreet quantum levels in the superlattice.[145]

C. General Spectroscopic Techniques Applied to the SEI

Several widely-used analytical techniques, such as IR spectroscopy, have been applied to investigations of the SEI. A few examples are presented below.

1. IR Techniques

IR techniques can provide information about adsorbed chemical species at the SEI. An IR reflection technique used to investigate photooxidation of Fe(CN)$_6$$^{4-}$ at n-GaAs showed the formation of several gallium/iron cyanide complexes.[146] A study of illuminated n-Si/NH$_4$F showed a steady increase in the intensity of the Si–H stretching band, apparently due to the formation of a porous Si layer.[147] The adsorption of ferrocyanide on TiO$_2$ has been investigated with IR methods.[148]

2. Raman Spectroscopy

Raman spectroscopy combined with IR reflectance measurements were used to determine that the oxide formed on p-InP in tartaric acid was mainly indium dihydrogen phosphate.[149] Raman scattering was used to identify surface oxidation species of FeS$_2$ as polysulfides and sulfur.[150]

3. Ellipsometry

Ellipsometry is a powerful method for studies of thin films on solids. Gottesfeld has reviewed the electro-

chemical applications of this technique recently.[151] As an example, ellipsometry has been used to study etching of the SiO_2 layer with HF.[152]

D. Scanning Probe Methods

1. Laser-Spot Scanning

Probing the SEI with a focused spot of light can provide spatial resolution of the optical properties of the system. Although originally employed to monitor the spatial dependence of photocurrent,[153] this technique has been applied to other optical semiconductor measurements. For example, this technique has been adapted for EER measurements.[154] A modified laser spot microscope that allows monitoring of reflected light and photocurrent simultaneously was used to study InSe and Pt-treated InSe.[155]

2. Scanning Tunneling Microscopy

Since the invention of scanning tunneling microscopy STM by Binnig and Röhrer, this technique has been shown to be exceedingly useful for investigating interfaces. This technique involves a small "tunneling" current between the tip of a sharp probe and the surface of interest. By scanning the tip across the surface, atomically-resolved images can be obtained. Besides the imaging ability, the various parameters involved can yield other important information about the interface; some examples of this are described below.

Several STM technical advances have increased its potential applications to electrochemistry and analysis of semiconductor–solution interfaces. Sonnefeld et al. were the first researchers to obtain atomic resolution of a substrate immersed in electrolyte,[156,157] thus expanding STM to an in situ technique. Potential control of the substrate vs a reference potential has been demonstrated.[158,159] Specially-prepared tips have been developed that minimize faradaic current at the tip such that images in redox solutions can be obtained.[160] Such developments are sure to increase the use of STM for investigations of electrode–solution interfaces. Recent reviews of STM and electrochemical applications of STM have been published.[161–164]

Two types of STM applications to semiconductor-solution interfaces are (1) in situ monitoring and/or induction of surface changes and (2) determination of interfacial energetics of the SEI. Examples of these two classes of experiments are presented.

Bard and co-workers were able to etch nanometer-scale features on illuminated GaAs while immersed in solution.[165] Small features were inscribed on the surface by moving the tip across the surface. In a similar study, Nagahara et al. etched Si and GaAs near the tip without illumination by using an HF solution.[166] This group has also monitored nickel deposition at Ge and concluded that the Ni initially deposited uniformly and then began to deposit as islands. The same paper also describes monitoring the in situ photocorrosion of GaAs.[167] Another interesting corrosion study was performed by Sakamaki et al. Again using STM in situ, they observed a negligible rate of photocorrosion at the van der Waals plane of n-MoS_2 immersed in CH_3CN electrolyte. However, after adding 4% water to the CH_3CN solution, photocorrosion initiated at defects in the MoS_2 and

propagated along the van der Waals plane of the semiconductor.[168]

Very small, well-controlled modifications have been demonstrated on layered metal dichalcogenides. Parkinson has shown "layer-by-layer" etching of these compounds[169] while Schimmel et al. have shown created small distortions in WSe_2 with preserved atomic order.[170] Although neither of these experiments was done in solution, it may be possible to later extend these advances to in situ conditions.

The second class of experiments involves the interfacial energetics of the SEI. Itaya and Tomita noted that good images of n-TiO_2 could not be obtained with the semiconductor in depletion.[171] They were most successful with the sample biased negative of E_{fb} with the tip held positive of E_{fb}. In studies of n-ZnO by these same authors, a similar effect is observed and they note that the tunneling current drops drastically when the semiconductor is in depletion.[158] Carlsson et al. performed similar experiments at GaAs and GaP and again found imaging dependent on the interfacial energetics of the semiconductor/solution/metallic tip.[172] Bockris and co-workers, following their work on p-Si, suggest that the STM imaging dependence of their system indicates surface states at the Si–solution interface.[173]

3. Scanning Electrochemical Microscopy

Scanning electrochemical microscopy (SECM), developed by Bard and co-workers,[174] is somewhat related to STM. An ultramicroelectrode (UME) is held very close to a surface immersed in a redox solution. The proximity of the surface influences the diffusion of redox species to the electrode, and thus, by monitoring the current as the electrode is scanned across the surface, structural information can be obtained. The resolution is limited by the size of the UME and is thus several orders of magnitude less than STM (μm vs Å). Improved UME's may lead to higher resolution.

The advantages in SECM derive from the electrochemical information available. Bard's group has used this approach for studies of SEI's. Well-defined, small structures can be etched on several III–V and II–VI semiconductor electrodes using the SECM to electrogenerate bromine or other strong oxidants.[175] More in-depth studies of GaAs using the SECM identified hole injection into the valence band as the etching mechanism. Other aspects of this SEI system were also investigated including valence band energy and differences between n- and p-type GaAs.[176]

E. Ex Situ Ultrahigh Vacuum Techniques

By transferring the semiconductor electrode to ultrahigh vacuum (UHV), the vast array of well-known surface analysis techniques become available. No comparable in situ techniques currently exist that can provide the information available from such methods as X-ray photoelectron spectroscopy (XPS). It can be argued that the semiconductor surface will be altered or contaminated during the transfer from solution to UHV. However, equipment and procedures have been designed to facilitate the transfer from electrolyte to UHV.[177] The use of such apparatus and a little caution allows real information about semiconductor electrodes to be obtained with these ex situ methods. An extensive review of the many UHV experiments is beyond the

scope of this paper. Therefore, a few studies of semi-conductor electrodes using UHV techniques will be presented to indicate the type of information available.

1. Effects of Surface Preparation

In an investigation of n-GaAs, Solomun et al. used LEED to differentiate an ordered, annealed surface from a damaged, Ar^+ sputtered surface. Both surfaces were found to be more electrochemically active than one etched with Br_2/methanol. Also, XPS analysis showed that a surface layer enriched with As^0 formed in acidic solutions.[178]

Scanning electron microscopy (SEM) and XPS were used to physically and chemically characterize the surface of p-InP prepared with an HCl or $Br_2/NH_3(aq)$ etch. The results clearly showed improved surface characteristics with the bromine etch. This cleaner surface also demonstrated significantly better photoe-lectrochemical properties.[179] A similar study was performed with n-GaAs electrodes. Three different etches were shown by XPS to produce surfaces that were either oxide free, enriched in As^0, or oxide covered. The electrochemistry of the three surfaces was compared in aqueous and nonaqueous electrolytes.[180]

2. Adsorbed Species on Semiconductor Surfaces

CdSe electrodes specially treated with silver were analyzed with Auger electron spectroscopy (AES) and XPS to show that the Ag diffused as Ag^0 several tens of nanometers into the CdSe. Combined with PL measurements, a band model for this unique material was suggested.[181] Sander et al., using XPS and ultra-violet photoelectron spectroscopy (UPS), found that chlorine reacts chemically with $CuInS_2$ and $CuInSe_2$ surfaces while water adsorbs simply.[182] XPS and extended X-ray absorption fine-structure spectroscopy (EXAFS) were applied to an investigation of adsorbed cobalt complexes on GaAs.[183] Secondary-ion mass spectroscopy (SIMS) was used to investigate chloro-carbon adsorption on Cs/MoS_2.[184]

3. Corrosion and Oxidation Products

XPS was used to characterize n-GaAs before and after electrochemical treatment. Whereas cathodic polarization of the sample produced no changes, anodic polarization led to a variety of changes in the surface characteristics.[185] A study of the photocorrosion of CdS by AES and XPS identified the products as sulfur (no oxygen present) or sulfate (oxygen present).[186] The oxidation products of FeS_2 were identified by using XPS in conjunction with SEM/energy dispersion X-ray analysis.[150] Surface oxides and the influence of chloride on photocorrosion of InP were investigated with X-ray diffraction (XRD) by Hsieh and Shih.[187]

V. Aspects of Interfacial Energetics

A. Description

The interfacial energetics for an SEI are defined by the spatial dependence of the potential drop at the SEI and the relative positions of energy states among the semiconductor bulk, surface states, and solution species. In almost any experiment at the SEI where quantitative

interpretations are desired, determination of the interfacial energetics (IE) is necessary in order to relate current flow to kinetic and thermodynamic models; this is often not a straightforward procedure.

The potential drop at an interface is related to the spatial distribution of charge. For the ideal SEI this charge distribution is dominated by the space-charge region (SCR). When the electrode is biased, the bands are bent representing an electric field while the band-edge energies (the energies of the bands at the inter-facial plane) remain constant. Real systems can have charged states located within angstroms of the inter-facial plane that can accommodate some of the potential drop. The nature of these "surface states" determines to what extent the system deviates from ideal behavior. This influence may be quite large creating a condition known as "Fermi-level pinning" where virtually all of the electric field occurs near the interfacial plane.[188] More commonly, the IE reflects the charge distribution across both the SCR and the surface states. It follows from this description that modifications of the SEI that perturb the semiconductor surface can change the IE.

B. Surface Preparation

The pretreatment afforded the semiconductor surface will amost always affect the behavior of the SEI. Considerable effort has been devoted to developing etching, polishing, and cleaning procedures to repro-ducibly provide surfaces free from defects and contam-inants. Although this is an important topic, it is thoroughly presented in other sources. Finklea's book discusses surface treatments for many semiconductors and provides an overview of the approaches taken to-ward surface preparation.[32] Also, specific procedures are generally provided in the experimental section of many of the papers cited in this review.

C. Measurements of Interfacial Energetics

Measurement of the flat-band potential, E_{fb}, and the doping density, N_D, allows calculation of band-edge energies, space-charge widths, and density of holes and electrons as a function of potential.[14] Methods for determining E_{fb} and N_D were discussed in section IV. Mott–Schottky measurements are clearly the most common but should be verified by a complimentary technique where possible.

Numerous experiments have shown that even seem-ingly innocuous changes in the conditions of the SEI can induce significant shifts in the E_{fb}. It is therefore essential that the IE be treated as dynamic parameters that must be evaluated for a given set of experimental conditions.

1. Systems with Constant IE

Systems that have highly stable IE under a variety of conditions are rare. An example of a system that contradicts this trend is the n-WSe_2/CH_3CN interface. The E_{fb} of a given n-WSe_2 electrode has been shown to be nearly identical in blank electrolyte and metallocene redox solutions of differing concentrations and rest potentials.[54] Apparently this behavior arises from the inertness of the van der Waals surface of the layered

metal dichalcogenide crystal which yields a low density of surface states.

2. Systems with Variable IE

The IE of most SEI systems are dependent on one or more experimental conditions. Although such shifts may be a nuisance, the trick is to ensure that variations are controlled and predictable. Many systems show highly stable and reproducible IE within a specific set of experimental parameters. Systematic changes in IE may provide some information about the properties of the SEI. Examples of several factors known to induce shifts in IE are presented below.

pH. The effects of pH on the E_{fb} have been studied extensively. Two types of pH dependence have been observed. First, the E_{fb} often shifts systematically with pH changes. If H^+ or OH^- ions are adsorbed at the interface, the measured interfacial capacitance will vary as a function of pH. It can be shown that the expected relationship should be 59 mV/pH unit.[14] Finklea has recently compiled a large number of E_{fb} measurements for TiO_2 and shown that the pH dependence is close to the theoretical 59 mV/pH.[189]

However, pH effects may not be manifested in a systematic change in the E_{fb}. Large pH changes may induce effects more related to chemical changes induced by the acidic or basic electrolyte rather than a simple electrostatic variance of the Helmholtz capacitance. Such a situation is often associated with changes in the corrosion potential of the semiconductor. An example of this behavior has been described for an n-WSe$_2$ system.[55]

Redox Couple. By changing the redox couple, the energies of solution donor/acceptor states is varied. This can lead to systematic E_{fb} shifts with the solution rest potential as demonstrated for n-GaAs[190] and p-InP[179] in CH_3CN solutions. Memming and co-workers showed that certain redox couples could eliminate the illumination-induced E_{fb} shift at n-WSe$_2$ in acidic electrolyte.[55] Explanations for such effects can be based on the relative energies of the different redox couples.

Redox couples can influence the SEI through chemical interactions as well. E_{fb} shifts in WSe$_2$/aqueous solutions of I_3^-/I^- have been attributed to adsorption of the triiodide ion to the surface.[51,191]

Illumination. Illumination of the SEI leads to a flux of minority carriers to the surface. Unless these carriers are quickly and completely removed, they can induce perturbations in the IE. Shifts in E_{fb} are observed for many illuminated SEI systems from trapping of charge carriers at the surface. However, reduction in the number of trapped charged species may remove the shift. For example, Etman has shown that E_{fb} of n-WSe$_2$ is dependent on illumination intensity, with no detectable shift from dark conditions at low intensities.[192] The addition of redox couples capable of accepting minority carriers can eliminate E_{fb} shifts.[55,192,193] Reduced E_{fb} shifts in p-InP following platinum treatment was explained by enhanced photoreduction of hydrogen thus reducing trapped carriers.[194]

Surface Character. Obviously changes in the physical of chemical properties of the semiconductor surface can influence the behavior of the SEI. Alterations in the surface character are readily apparent in IE changes. Tomkiewicz et al. found significant improvement in the

characteristics of $CuInSe_2$ after etching with $Br_2/$ methanol.[144] Segar et al. compared the effects of a HCl etch to a Br_2/methanol etch of InP and found only the latter treatment suitable for providing predictable and reproducible IE.[179] Chongyang et al. showed that the interfacial characteristics of FeS_2 improved following photooxidation of chloride which apparently modifies the density and energies of surface states.[195]

D. Surface States

1. Origin and Significance

The solid-state properties of a semiconductor are generally modeled by the band theory where a valence and conduction band are separated by a forbidden region, the bandgap. At the interface of this solid state with a solution, the crystal structure is physically and chemically different than within the bulk. These differences can produce discreet energy levels within the bandgap known as "surface states". Surface states may be derived from the "dangling bonds" of unfilled valencies on surface atoms, defects in the crystal structure, formation of oxide layers, or adsorbed chemical species. More in-depth descriptions of surface states are available in many reviews.[3,14,15,33]

In any case, the existence of energy levels within the "forbidden layer" can greatly complicate theoretical treatments of the SEI. Charge transfer, recombination processes, and impedance analysis theories were developed for the "ideal" interface where electrons and holes can exist only in the valence or conduction band. Surface states may mediate charge transfer, provide recombination centers, and allow applied potential drop to occur at the surface rather than the space–charge region. Unfortunately, quantitative determination of the energies, distribution, and precise nature of surface states is complicated and the data is usually open to various interpretations. This limits theoretical treatments of systems with significant contributions from surface state processes. It is therefore desirable to avoid surface states within the system for fundamental analysis of the SEI.[51]

2. Characterization

Eliminating surface states is not feasible at many SEI systems of interest. Therefore considerable effort has been devoted to characterization. The two classes of experiments utilized are optical methods and impedance analysis; some examples from recent literature follow.

Direct evidence of surface-state presence can be obtained from optical methods using subbandgap light. Adsorption or emission of photons with energies less than the bandgap must be associated with transitions to or from bandgap surface states. Salvador has used photocurrent transients from subbandgap illumination and concluded that surface states due to Ti^{3+} and oxygen deficiencies are present near the conduction band edge.[196] Jung and Kolb associated the subbandgap photocurrent of Ru treated n-GaAs with hole formation in a Ru-induced surface state.[97] Luminescence experiments at TiO_2 show several peaks with subbandgap wavelengths. These peaks were assigned to several surface states associated with species formed during the photooxidation of water.[119,122,123]

EER has become an increasingly popular technique for characterizing surface states. Siripala and Tomkiewicz showed that changes in the magnitude of $\Delta R/R$ can be related to surface states.[197] This approach has been used by Ferrer et al. to study the interaction of H_2O_2 with TiO_2.[142] Also, Lemasson and Van Huong have used EER to study surface states on InP, GaAs, and $Ga_xIn_{1-x}As$.[139] Details of this method can be found in Hamnett's recent review of EER.[137]

In another type of optical experiment, electromodulated IR reflectance technique was used by Chazalviel and Venkateswara Rao to investigate different types of surface states on a n-Si-CH_3CN interface.[198] They concluded that charging/decharging of oxidation-induced surface states has significant atomic reorganization effects.

Impedance measurements are still the most common method for characterization of surface states. These experiments are critically dependent on the equivalent circuit used to evaluate the impedance components. Whether or not the chosen circuit adequately describes the true SEI can be debated (see part D). Impedance measurements have been used by Gibb and Scholz to analyze Ag and I_3^- induced surface states on p-WSe_2.[59] Goosens et al. investigated electrochemically created surface states on p-GaP/hypobromite.[199] Bockris has investigated surface states at several illuminated systems and discussed the difficulties with impedance measurements under these conditions.[200,201]

E. Equivalent Circuits

The long standing use of impedance analysis has placed considerable attention on equivalent circuits of the SEI. The reader is referred to Morrison's book for further discussion.[14] Hamnett's review presents details and equivalent circuits for a number of different situations.[33]

Since impedance measurements reflect the entire electrochemical cell, separating individual interfacial components from the data requires some careful analysis. In practice it is desirable to eliminate contributions to the impedance from as many sources as possible. Some experimental considerations, such as cell construction and minimization of uncompensated resistance, generally will leave the impedance controlled by interfacial effects (space–charge region, surface states, Helmholtz region, etc.).

In some situations, the interfacial impedance may be successfully modeled as a simple, two-element RC circuit. Surface states can be ignored if the surface state density is low or their time constant for charging is slow with respect to the measurement frequency. It can be shown that the Helmholtz capacitance, C_H, can be neglected since it is generally much larger than the space–charge capacitance, C_{sc}. The controlling capacitance is then simply C_{sc} allowing straightforward determination of Mott–Schottky plots.

Commonly observed anomalies in Mott–Schottky plots, such as nonlinearities or frequency dispersion, are indications of inadequacies in the assumed circuit. To account for the presence of surface states, a resistor and capacitor in parallel with the space–charge capacitance is often added to the model. Determining the values of the circuit elements then requires impedance measurements over a range of frequencies. Additional

complications are introduced when faradaic current is flowing across the interface; circuits may then need to consider Warburg impedance in parallel with the surface state and space–charge elements.

Equivalent circuits for the illuminated SEI are somewhat controversial. Bockris and co-workers discussed the inadequacies of conventional model circuits for characterizing the illuminated interface and proposed new equivalent circuits consistent with experimental data.[200,201] Conversely, Goossens and Schoonman show that the impedance of surface recombination can generally be modeled by a simple series RC circuit.[202]

It must be emphasized that the equivalent circuit model may not necessarily reflect the true SEI. Considering things like surface states as simple capacitors can be misleading since these states are much more dynamic, i.e. they can "cross talk" with the solution and the semiconductor bulk. Also, several competing circuits may fit the same impedance data making determination of the individual circuit elements ambiguous.

The discussion on equivalent circuit considerations to this point has focused on impedance measurements. Equivalent circuits are also an important aspect of interpreting transient measurements such as laser-pulsed photocurrents. The limiting resolution of the transient will be determined by the controlling RC time constant of the electrochemical cell. Willig has discussed the importance of distinguishing RC-response artifacts from interfacial charge transfer processes.[203]

VI. Mechanisms of Interfacial Electron Transfer Reactions

The literature describing ET processes at semiconductor electrodes contains a host of terms used to differentiate between mechanisms. Although discussions of these mechanisms can be found elsewhere,[14,15] this section begins with brief definitions of the common terms and conventions. In the latter portion of the section, several instances in which ET mechanisms have played an important role in the recent photoelectrochemistry literature are discussed.

A. Processes Related to the Semiconductor Electrode

1. Dark Processes

Figure 1 depicts p- and n-type semiconductors in equilibrium with a solution redox couple. There is no net current flow across the interface in this situation; however, anodic (oxidation of solution species) and cathodic (reduction of solution species) current of equal magnitudes produce a so-called exchange current density, j_o. The value of j_o is of great fundamental importance as discussed in section VII and in detail by Lewis.[13] Figure 3 depicts the four possible current flow situations that occur when an external bias is used to change the potential of the semiconductor electrode to positive (parts b and d) or negative (parts a and c) values with respect to the solution resulting in net anodic (parts b and d) and cathodic (parts a and c) currents, respectively. When the applied potential results in decreased band bending and a greater density of majority carriers available for ET at the surface, the interface is in forward bias (parts a and d). The op-
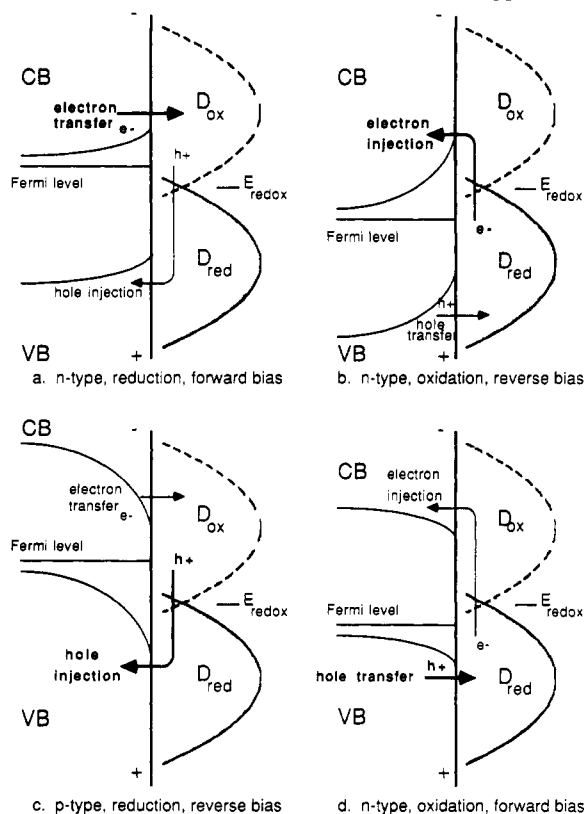
ELECTRON TRANSFER PROCESSES AT THE DARK SEI

a. n-type, reduction, forward bias

b. n-type, oxidation, reverse bias

c. p-type, reduction, reverse bias

d. n-type, oxidation, forward bias

Figure 3. Electron transfer processes involved in anodic and cathodic current flow at nonilluminated n-type (a and b) and p-type (c and d) SEI's. Dark arrows indicate processes involving majority carriers in the semiconductor which would be expected to dominate current flow for interfacial energetic situations like those depicted.

posite situations produce interfaces in reverse bias (parts b and c) and are characterized by more band bending and fewer majority carriers.

In principle, electron (or hole) exchange with solution species will have contributions from both the valence and conduction bands and this issue is often critical from a mechanistic viewpoint. For semiconductors with large bandgaps (>2 eV), current flow is dominated by the band that has an energy closest to the redox couple, at least at potentials near equilibrium. Significant current contributions from both bands are more likely for small bandgap materials and at large applied potential biases. The terms electron and hole transfer are used to distinguishing between conduction and valence band processes, respectively. For example, the net cathodic current in Figure 3a can result from electron transfer from the conduction band to an oxidized molecule or by injection of a hole from the molecule into the valence band.

The interfaces shown in Figure 3 are in a depletion condition,[25] i.e. the E_F of the semiconductor electrode lies between E_{VB} and E_{CB}. This condition is by far the most important for photoelectrochemistry or measurements related to ET. At more negative applied potentials for n-type semiconductors (positive potentials for p-type), majority carriers accumulate at the surface and current flow resembles processes observed at metal electrodes. When E_F is positive of E_{VB} for n-type electrodes (negative of E_{CB} for p-type), conditions of extreme depletion or carrier inversion exist. Current flow is usually irreproducible in these situations and

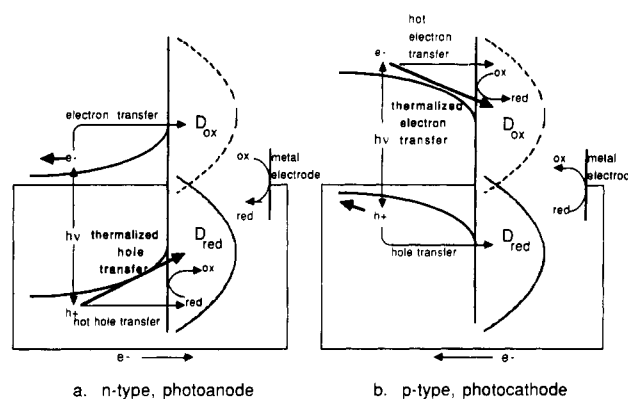ELECTRON TRANSFER PROCESSES AT THE ILLUMINATED SEI

a. n-type, photoanode

b. p-type, photocathode

Figure 4. Photoinduced electron transfer processes at the n-type (a) and p-type (b) SEI's contacted to metal counter electrodes. Dark arrows indicate the processes primarily responsible for the observed photocurrent.

likely to be dominated by tunneling processes or band-edge movement as is illustrated in the work by Koval et al. on the redox reactions of metallocenes at p-InP.[204]

2. Photoinduced Processes

Figure 4 depicts illuminated n-type (a) and p-type (b) semiconductor solution interfaces in which the potential of the electrode in the bulk is the same as redox potential of the solution. This situation can be achieved by connecting the semiconductor to a metal electrode in the solution; the observed net current being referred to as the short circuit photocurrent. This current will be anodic for n-type materials since it is caused by valence band holes that are driven to the interface by the field in the space charge region. Cathodic photocurrents resulting from conduction band electrons are observed at p-type semiconductors. As in the case with dark currents, the interface can also be biased with respect to the solution potential which will effect the magnitude and sign of the current. The dark arrows in Figure 4 represent the charge separation event, interfacial ET reaction and collection of majority carriers at the back contact that are usually considered in photoelectrochemical processes. The lighter arrows indicate other processes which can also be important at the SEI, namely back-reaction of majority carriers and hot electron or hole transfer. The significance of these processes to photoelectrochemistry have been the subject of a number of recent investigations.

Hot carriers are quite controversial and are discussed later in this section. The significance of interfacial majority carriers reactions at illuminated SEI's is clear from Gerischer's theoretical presentations[3,205] via the concept of quasi-Fermi levels. When an SEI is illuminated with light that causes generation of minority carriers, the populations of electrons and holes near the interface are changed. This change is often represented by a flattening of the semiconductor bands, but it is also useful to define a quasi-Fermi level near the surface that more accurately reflects the increased concentration of minority carriers. This quasi-Fermi level will be closer to the valence band for n-type materials and closer to the conduction band for p-type. In a variety of studies, Memming and co-workers have demonstrated the quasi-Fermi level concept by performing experiments

with p- and n-type electrodes of the same material and obtaining current potential curves in the dark and under illumination.[34,40] Pleskov and Gurevich have reviewed the concept of quasi-Fermi levels and how they relate to interfacial current flow.[206]

A second body of work that emphasized the understanding of the photostationary state achieved for carriers near the surface of illuminated semiconductors and back reaction of majority carriers emerged from Lewis' group.[45] This work involves a quantitative understanding of the factors which control open-circuit photovoltages, V_{OC}, observed at SEI's. In principle, the magnitude to V_{OC} can be controlled by bulk properties of the semiconductor electrode, ET reaction kinetics for majority or minority carriers, or the effects of surface states. Since it is an important device property, correct assignment of the factor(s) which limit V_{OC} is necessary for rational improvement of photoelectrochemical devices. By employing an appropriate model, utilizing p- and n-type materials with known bulk properties, and making measurements of V_{OC} as a function of temperature and wavelength, Lewis provided a high level of understanding for a variety of materials including Si, GaAs, and InP.[98,207-214]

B. Processes Related to the Solution

1. Outer-Sphere ET (Weak Coupling) and Inner-Sphere ET (Strong Coupling)

The terms were initially employed by Taube to distinguish limiting mechanisms for bimolecular reactions between complexed metal ions in solution.[215] Outer-sphere mechanisms refer to reactions in which the coordination spheres of the reacting ions remain intact throughout the ET event. Inner-sphere refers to reactions in which ligand substitution on at least one of the complex ions results in a lower energy pathway for ET; this substitution generally results in a molecular bridge between the reacting ions. The bridge, which remains intact through the activated complex, provides strong electronic coupling between the ions and can also serve to lower the activation energy. While inner-sphere pathways provide a mechanism for rapid ET, rates for such reactions are generally not amenable to simple theoretical treatment.

In contrast, Marcus theory[5,216,217] has enjoyed great success in quantitative treatment of outer-sphere processes. For this type of mechanism, a distinction is usually made between so-called adiabatic reactions, in which the electronic coupling in the activated complex is relatively small but sufficient to yield a transmission coefficient (κ) of unity, and nonadiabatic reactions in which the coupling is extremely weak and $\kappa < 1$.

These same mechanisms of ET have been investigated for heterogeneous reactions at the MEI.[7] At the SEI, outer-sphere reactions clearly take place when appropriate redox systems are utilized (see section III) while certain couples clearly proceed via an inner-sphere pathway (e.g. oxidation of halide ions).

2. Multielectron Processes

Many commercially important redox processes involve multielectron redox couples. This type of reaction is difficult to treat from a theoretical point of view and it is often experimentally difficult to define a rate-de-

termining, single-electron step. With respect to the SEI, one process that continues to attract attention is the oxidation of organics and water at TiO_2. This interest is clearly related to the potential commercialization of waste treatment processes.[218-221] Since the oxidation of water to oxygen or organic compounds to carbon dioxide involve many electrons, the issue centers around the mechanism for holes, which are one-electron oxidants, crossing the SEI. Some of the possibilities are direct hole transfer to a molecule in solution (Figure 4a) and the formations of intermediate species such as $\cdot OH$ radicals. There are several proposed mechanisms involving $\cdot OH$ radicals that are consistent with most of the data describing decomposition of organics in aqueous bulk reactions.[222] Fox et al.[42,223-225] have elegantly demonstrated that different oxidation products can be produced depending on the solvent and reaction conditions, which is consistent with several ET pathways.

In addition to arguments based on product analysis, evidence regarding the oxidative mechanism at n-TiO_2 has been obtained from optically-induced transients at single crystals,[226,227] in particulate slurry cells,[228-231] and for particles adsorbed on platinum electrodes.[232] At single crystals, Norton et al. concluded that water oxidation was occurring via an outer-sphere mechanism at pH < 12 and by an inner-sphere mechanism at higher pH. Tafalla et al. interpreted transients in basic solutions in terms of a kinetic model and concluded that evolution of oxygen proceeds through surface bound $\cdot OH$ and HO_2^-.[227] Most of the research on slurry cells invoke collection of the electrons remaining on TiO_2 particles after the holes have reacted from anodic transients seen at Pt electrodes immersed in the slurry.[228-231] Peterson and Nozik[229] also observed cathodic transients in the absence of hole scavengers which they attributed to freely diffusing hydroxyl radicals. In contrast, on the basis of evidence from pulse radiolysis studies, Lawless et al.[233] concluded that $\cdot OH$ rapidly reacts with particulate TiO_2 and was unlikely to exist as a solution species. Brown observed that all of the previous observations on transients in slurry cells could be duplicated with Pt electrodes coated with TiO_2 particles (none in solution).[232] He also observed that the transients were highly dependent on the illumination conditions prior to the pulse causing the electrochemical transient. These conflicting reports serve to illustrate the difficulties inherent in using the simple SEI picture to interpret complicated, multielectron processes.

Another commonly encountered example of multielectron processes at the SEI is the phenomena of current doubling, i.e. observed photocurrents that exceed one electron in the external circuit per incident photon. Current doubling is observed when an intermediate redox species, which is formed by reaction of a photogenerated minority carrier, injects a majority carrier into the semiconductor. For example, consider the species OX in Figure 4a produced from a photogenerated hole. If OX can be further oxidized, OX $\rightleftharpoons$ OX' + e$^-$, and if $E^{0'}$ for the OX'/OX couple is negative of (above) E_{CB}, OX' can inject an electron into the conduction band of the n-type semiconductor.

Peter's recent review contains many examples of current-doubling at the SEI.[126] Observed quantum

efficiencies for reduction of IO_3^- at p-GaAs can be as high as 3–6.[234] Bocarsly[103] has demonstrated that oxidation of CN^- contributes to the unusually large photovoltages that were reported by Licht[102] for n-CdSe/$Fe(CN)_6^{3-,4-}$ cells.

3. Normal and Inverted Energy Regimes

One of the most interesting predictions of the Marcus theory of ET is the existence of normal and inverted regimes.[5] The theory predicts that for small driving forces the rate constant will increase with increasing driving force (normal region) but, when the driving force exceeds the reorganization energy, the rate constant decreases with increasing driving force. The existence of the inverted region has been confirmed for bimolecular and intramolecular processes,[235,236] but observation of the inverted region at the SEI or MEI is experimentally difficult.

Observation of the inverted region at wide bandgap semiconductors should be possible if the $E^{0\prime}$ for the redox couple is more than the reorganization energy away from the band edge supplying the majority carriers. Memming and Mollers presented data of this effect prior to 1980,[237] but interpretation of these experiments contains some unlikely assumptions. Fujishima and Honda used n-ZnO to study highly exothermic ET processes, but the effects were much smaller than expected.[238–241] The relatively few attempts to study this phenomenon at the SEI is somewhat surprising given the theoretical importance of the normal and inverted regions.

4. Electrocatalysis

The kinetics of many multielectron reactions are quite slow at semiconductor electrodes (and metal electrodes) in the absence of species that can catalyze these reactions. The most commonly encountered type of electrocatalysis at the SEI is via deposited metals. The best known example is the effect of platinum deposition on the oxidation of organics at illuminated TiO_2.[225] Another landmark that illustrates the importance of metal catalysis to photoconversion is the work by Heller et al. on hydrogen reduction at p-InP which used noble metal deposits as catalysts.[242,243] Szklarczyk and Bockris showed that the magnitude of this catalysis was directly related to the exchange current density for the H^+/H_2 exhibited for the metal.[244]

While electrocatalysis at the SEI by deposited metals is an expected phenomena, a series of papers by Lewis' group demonstrated that electrocatalysis was also primarily responsible for the effect of adsorbed Ru^{3+} and Os^{3+} ion at the n-GaAs/KOH, $Se^{-,2-}$ interface.[180,245–247] This research effort has been recently summarized by Lewis.[45]

C. Corrosion and Photoetching

For many SEI's, especially those involving n-type materials in aqueous electrolytes, redox processes that involve decomposition of the electrode have standard potentials within the bandgap and occur rapidly upon illumination. The theory of such processes is well-developed and considerable effort has been made to prevent photocorrosion reactions which are generally deleterious with respect to photoconversion.[205,248–250]

Photocorrosion is usually a multielectron redox process and its relationship to fundamental ET models entails all of the problems discussed above in section VI.B.2. Nevertheless, there has been considerable recent interest in exploiting photocorrosion processes as a means of controlled semiconductor processing. This processing is often referred to as photoetching and has been applied to β-SiC,[251] Si,[136,147] and several III–V materials.[252–255]

D. Nonthermalized (Hot) Carriers

Matching the solar spectrum to the adsorption spectrum of a photoconversion device presents severe constraints on the efficiency of solar energy conversion. The conversion device (plant, homogeneous molecular system, semiconductor electrode) must absorb light at long wavelengths in order to collect a large fraction of solar photons; however, the extra energy in the short wavelength photons, relative to the absorption onset, tends to be inefficiently converted into electricity or chemical-free energy. One way to think about the excess energy in short wavelength photons is that, upon absorption, it creates "hot" charge carriers. By assuming that the excess energy results in carriers with increased kinetic energy of $(3/2)kT$, a photon with 0.5 eV of excess energy would create a carrier with an effective temperature of about 4000 K above the temperature of the lattice. In condensed phases, this excess energy will be dissipated as heat to the system unless the "hot carrier" can be trapped and utilized. Since currently available conversion devices are unable to prevent thermalization losses of this type, theoretical energy conversion efficiencies are near 30%. Devices that could utilize hot carriers could have efficiencies in excess of 60%.[256]

The chemistry and physics of hot carriers is currently under investigation in a variety of fields. A majority of these papers appear in the solid-state physics or surface-science literature (over 100 papers annually). Topics being addressed include experimental and theoretical investigations of hot electron transport in semiconductors,[257] especially III–V heterostructures,[258] and of emission of hot electrons into vacuum.[259] Of greater relevance to this review is the trapping of hot electrons in oxide layers on silicon.[260] Capture of hot electrons in SiO_2 produces traps which results in degradation of performance for a variety of MOS devices.[261] Reactions of hot carriers by molecules adsorbed on semiconductors and metals is receiving attention in UHV studies. For example, it has been shown that hot electron photoreduction of CH_3Cl through buffer layers of Ar and H_2O occurs on GaAs and Ni surfaces.[262]

Interest in how hot carriers might effect photoelectrochemical phenomena was provoked by theoretical studies by Williams and Nozik[263] and experimental work by Nozik and co-workers.[256,264] Recent papers by the SERI group (Solar Energy Research Institute) have emphasized hot carrier effects in quantized semiconductor systems such as superlattices and small particles.[69,75,77,121,265–275] Nozik and McClendon have recently reviewed the subject of ET from quantum confined states.[71]

As in other situations in which the ET mechanism is controversial, detection of appropriate products provides key evidence. Koval and Segar[276,277] have used

irreversible chemical reactions to trap hot electrons produced at the p-InP–acetonitrile interface using the couple $Cu(II,I)(trans-diene)^{2+,+}$. The Cu(II) form of the couple can be reduced by thermalized electrons at either low- or high-doped p-InP. Since $E^{0\prime}$ for the Cu(I,0) couple is negative of E_{CB} for InP, the Cu(I) complex can only be reduced by electrons above E_{CB}. This irreversible reaction results in plating of copper metal on the surface of the electrode. Anodically stripping this film is a sensitive means of determining the exact amount of Cu(0) product produced via reaction with hot electrons.

VII. Rates of Interfacial Electron Transfer Reactions

Rates of interfacial ET reactions are readily measured as current densities, j (Å cm^{-2}) and are also related to rates of concentration change for molecular species in solution near the surface of the electrode via Faraday's law. At semiconductor electrodes, rates can also be determined, in principle, by measuring the lifetimes of photogenerated reactants. These reactants can be electrons/holes in the semiconductor or excited state molecules near the interface. Unfortunately, the overall rate of interfacial ET at semiconductor electrodes is often limited by processes other than ET itself, e.g. molecular or ion transport, nonfaradaic reactions, or chemical reactions associated with ET. Therefore, while an enormous amount of data describing interfacial currents and carrier lifetimes are available for many of the interfaces described in section III, surprisingly little of this data relates to questions concerning the fundamental aspects of interfacial ET in a straightforward manner.

This situation has been recently reviewed by Lewis;[13] his findings are summarized below. The first part of Lewis' review consists of developing a mathematical framework for relating rate expressions commonly used to describe interfacial ET to a detailed equation used to describe intramolecular electron transfer.[5] One problem with conceptualizing these relationships is in understanding the different rate constants and expressions used to describe various situations, as indicated in Table II. Lewis also provides estimates or limits for many of the parameters contained in these equations that are not easily obtained experimentally.

In the latter part of the review, experimental data that might be used to verify various aspects of the theoretical model are separated into four groups: concentration decay experiments for carriers in the semiconductor,[127,131,278–281] transient photocurrent measurements,[125,226,227,282,283] rate constants (lifetimes) from dye sensitization experiments,[52,53,65,86,90,284,285] and steady-state photocurrent yields.[98,116,264,277] The review also discusses the few attempts to measure heterogeneous rate constants directly at dark SEI's.[14,54,204] The conclusion is that few, if any, of these experiments can be related to the model. First, for couples with reduction potentials located within the bandgap of the semiconductor, exchange current densities are so low that they tend to be dominated by artifacts. Low current densities are primarily a result of low concentrations of majority carriers near the surface of the semiconductor electrode. Second, interfacial energetics at many SEI's cannot be determined accurately (see section V). Third,

TABLE II. Rates Constants Used To Interrelate Homogeneous and Heterogeneous Electron Transfer (from Lewis[13])

ET rate constant	definition and use
k_{D-A}, s^{-1}	for intramolecular ET between a donor (D) and an acceptor (A); product of vibration frequency, electronic coupling, and Franck–Condon factors, $k_{D-A} = \nu_n \kappa_{el} \kappa_n$
k^0_{metal} and k^0_{sc}, cm s^{-1}	standard rate constants for ET at the MEI and SEI; defined at electrode potential equal to $E^{0\prime}$ for solution redox couple; often used in rate equations assuming reaction order of 1 for solution redox species and limitless carriers in electrode
k_{et}, cm^4 s^{-1}	ET rate constant at SEI; assumes interfacial rate depends on concentrations of carriers in semiconductor and solution redox species
k_n, cm s^{-1}	ET rate constant at SEI; similar to k^0_{sc} used for rate expressions in which carriers in semiconductor electrode react with constant surface concentration of solution species

for systems studied in water the mechanism and/or reorganization energies associated with ET are ambiguous.

Many experimental results from concentration decay measurements are also difficult to interpret due to varying assumptions concerning the appropriate equivalent circuit. Nevertheless, Lewis points out that at least some of these experiments are consistent with calculations derived from the theoretical model. For systems in which the solution redox species are adsorbed leading to high surface concentrations, capture of photogenerated minority carriers via interfacial ET effectively competes with other decay processes. For outer-sphere, diffusing redox couples, which produce low surface concentrations, neither photogenerated minority carriers or majority carriers created close to the surface at short excitation wavelengths are captured effectively. The data that is most at odds with these conclusions are reports of hot carrier ET by diffusing species which would have to occur in subpicosecond timescales.

Reliable lifetimes for quenching of excited state dyes adsorbed on semiconductors by interfacial ET range from less than 10 ps to hundreds of picoseconds. Lewis concludes that these values are consistent with the model, i.e ET rates for this type of system can be extremely rapid and unidirectional if the driving force is large and if nuclear and electronic terms are near their optimal values.

Steady-state current–voltage curves obtained at illuminated SEI's are reported in most papers dealing with energy conversion. They contain information which is directly related to device performance and also to rates of ET reactions of majority and minority carriers with solution species. Observation of high photovoltages, V_{OC}, at an SEI is consistent with low reaction rates for majority carriers, which is the dominate ET process in the dark. As noted above, these rates are low for diffusing solution species but under certain experimental conditions (low temperature and high light intensity) can control V_{OC}. Lewis discusses several cases in which attempts to vary the ET rate for majority carriers by

changing the reduction potential or concentration for the redox couple have failed to produce the predicted effects.[45] Of course, efficient photoconversion requires that minority carriers produced by illumination undergo interfacial ET. Lewis uses his mathematical framework to show that efficient collection of minorities does not require extremely rapid interfacial ET. The rate of this process only has to exceed the flux of minorities arriving at the surface and be faster than recombination processes.

VIII. Theory of Interfacial Electron Transfer Reactions

A. Difficulties and Theoretical Approaches

As indicated in the previous section, it is possible to separate rate constants for ET at the SEI into a product of vibrational frequency (ν_n), electronic coupling (κ_{el}) and nuclear (κ_n) (Franck–Condon) terms. Of these three terms, ν_n, which represents a vibrational frequency along the reaction coordinate, is most readily calculated from first principles and has a value of about 10^{13} s^{-1}. The electronic coupling term varies from unity for adiabatic reactions to very small values for nonadiabatic reactions and decreases exponentially with distance. The nuclear factor contains the reorganization energy, λ, associated with ET and a driving force term. Even if one assumes that ν_n can be calculated, there is considerable difficulty associated with separating the effects of κ_{el} and κ_n on measured rate constants. In cases where this has been attempted, the approach involves either assuming the reaction is adiabatic ($\kappa_{el} = 1$) and calculating the reorganization energy or assuming knowledge of λ and calculating κ_{el}. Neither approach is very satisfying or insightful. Insight into the separation of these terms can often be obtained for homogeneous ET reactions by measuring the temperature dependence of the rate constant. Unfortunately, the interpretation of activation parameters for electrochemical ET reactions is quite complicated and model dependent.[7]

Exacting theories for charged species near an interface are exceedingly complex[286] and a discussion of them is beyond the scope of this review. In general, interfaces tend to be approached with an emphasis on either liquid- or solid-state physics. While such a simplification may be appropriate for either the MEI or semiconductor–metal junctions,[18] descriptions of the SEI that do not treat both sides of the interface with equal rigor are unlikely to provide accurate insight into ET processes. Smith has recently shown that there are close relationships between solid-state and fluid statistical mechanical theories for electrostatics in the weak-coupling limit which may lead to a more even and unified description of the SEI.[287]

B. Calculation of Reorganization Energies

A common assumption that has been used when comparing theory with experiment for ET at the SEI or MEI is that λ for the heterogeneous reaction is one-half of the value for a homogeneous process involving the same solution redox couple. This idea was proposed by Marcus[217] many years ago for the MEI and is a consequence of the dielectric continuum model by

assuming the static dielectric constant, ϵ_{met}, for the metal electrode is infinite. How this approximation was extended to ET at the SEI is quite curious (it was never suggested by Marcus) given that ϵ's for semiconductors are not infinite, in fact, values of ϵ_{semi} are often less than appropriate values for the solution. In any case, recent theoretical papers clearly indicate that this approximation may not hold at the MEI and almost certainly not with respect to the SEI.

One recent approach to the problem of calculating reorganization energies at interfaces has involved the use of dielectric functions as calculated from nonlocal electrostatic theory. Kornyshev and co-workers used this approach to calculate solvent reorganization terms for the MEI and found behavior that was significantly different from the classical electrostatic model.[288] Smith and Koval extended this approach to the SEI by presenting a method for calculating image potential for an ion near this interface. In opposition to a classical approach assuming an infinite ϵ_{semi}, they calculated repulsive image potentials for many SEI situations.[289] Simple calculations of λ using this approach led them to conclude that optimum distances of ET at the SEI would not necessarily be the distance of closest approach. If this conclusion is correct, it further complicates attempts to calculate and separate κ_n and κ_{el}.

Marcus has also examined the question of reorganizations energies for ET across interfaces with dissimilar dielectric properties.[290] He concludes that λ for ET at a typical SEI could be twice that for the same molecule at an MEI.

C. Promising Experimental Approaches

Comparisons between theory and experiment have been essential in understanding ET processes. Clearly, types of experiments that directly relate to values of κ_n or κ_{el} for ET at the SEI would be most valuable. McManis et al. have utilized solvent-induced changes in self-exchange rate constants for metallocene couples in order to calculate electronic coupling for these reactions.[291] The implications for studying ET using so-called dynamical solvent effects has been reviewed by Weaver.[8] This approach could be valuable if applied to the SEI; however, other effects on the SEI brought about by changing the solvent could mask kinetic effects due to electronic coupling. Mallouk et al. are studying ET-quenching reactions for redox species irreversibly adsorbed to a series of oxide semiconductors.[292] These experiments may also provide information about electronic coupling at the SEI.

A direct experimental approach to measuring reorganization energies may be available through resonance Raman studies. Hupp et al. have used this technique to obtain mode-by-mode assessments of the Franck–Condon barrier to intramolecular ET.[293,294] Extension of this technique to molecules adsorbed on semiconductors are in progress.

IX. Concluding Remarks

Although the field of photoelectrochemistry is now mature, new and exciting discoveries about redox processes at the SEI continue to be made. There are several reasons to be optimistic about the future of this field especially with regard to fundamental ET issues.

The SEI is distinct from the MEI in that specific properties (bulk and surface) for semiconductor electrode materials vary more than for metal electrodes. In this sense, SEI's more closely resemble molecular donor/acceptor systems because the properties of both donor and acceptor, and their electronic interactions, influence ET. Experimentalists and theorists show an increasing willingness to treat ET at the SEI in a manner that considers the properties of both phases more equally.

While this review has illustrated the complexity of the SEI, this should not be regarded as a disadvantage of these systems. Rather, the wide variety of SEI types and processes represent a particularly rich research area. The review also described experimental techniques that are being developed to investigate and understand SEI's. It is not unrealistic to believe that in the next 5–10 years, STM and other spectroscopic techniques will allow measurement of ET rates over very small, possibly even molecular, electrode areas. This should mitigate the problems associated with inhomogeneity of the interface, allowing ET across SEI's with known and controllable properties to be studied. The results should provide new insight into interfacial charge transport, improved performance of photoconversion devices, and entirely new practical uses for semiconductor liquid junction cells.

X. Abbreviations and Symbols

Abbreviations

e^-/h^+	electron–hole pair, produced thermally at low energies, by light at high energies
EER	electrolyte electroreflectance
ET	electron transfer
EL	electroluminescence
IMPS	intensity modulated photocurrent spectroscopy
i-E	current–potential
IE	interfacial energetics
LMD	layered metal dichalcogenides
MBE	molecular beam epitaxy
MEI	metal electrode–liquid electrolyte interface
MOCVD	metal organic chemical vapor deposition
PEC	photoelectrochemical cell
PL	photoluminescence
RRDE	rotating-ring disk electrode
SCR	space–charge region
SEI	semiconductor electrode–liquid electrolyte interface
STM	scanning tunneling microscopy
SECM	scanning electrochemical microscopy
V_{OC}	open-circuit photovoltage

Symbols

C_{sc}	space–charge capacitance
C_H	Helmholtz capacitance
$E^{0\prime}$	formal reduction potential for a solution redox couple ($OX + ne^- = RED$)
E_{redox}	rest potential of the redox solution
$\mathcal{E}^{0\prime}$	formal reduction energy for a redox couple in solution
$\mathcal{E}_{redox}$	redox energy of a solution

E_{VB} and E_{CB}	energy of the valence and conduction band edges at the interface [These energies can be expressed with respect to an electron in vacuum or, more commonly, with respect to a reference half-cell (reference electrode).]
E_{BG}	bandgap energy
E_F	Fermi level energy
E_{fb}	Flat-band potential of the semiconductor
N_D	doping density (cm^{-3})
ϵ	dielectric constant
λ	reorganization energy
κ_{el}	electronic coupling
κ_n	nuclear factor
ν_n	vibrational frequency

XI. Acknowledgments

XII. References

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