

Photoelectrochemical Systems

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ABSTRACT: Photoelectrochemical systems encompass numerous applications involving semiconductor/electrolyte interfaces. A major goal has been solar energy conversion. Double-digit efficiencies have been reached with two different forms of semiconductor/electrolyte photojunction, directly excited or dye sensitized. Impressive performance with even polycrystalline semiconductor substrates is attainable in these devices and makes them promising in photovoltaics and photoelectrosynthesis for efficiency and cost. Achieving improved stability and further advances in output and economics depends on further progress in understanding and modifying solid/liquid interfaces. Related developments have produced numerous spin-offs of substantial importance to solid-state devices, processing technology, and surface chemistry. Further progress toward significant applications of interest to utility, electronics, and transportation industries, in energy conversion, and toward a host of specialized opportunities from sophisticated etching of microstructures to water purification requires a serious effort to support and strengthen the fundamental underpinnings of the field. These needs are categorized in the conclusion of this overview.

I. INTRODUCTION

Photoelectrochemistry, for our purposes, involves systems in which light excitation at a semiconductor/electrolyte junction causes charge separation and transfer to occur, with consequent chemical reaction at the interface. Light to electrical energy conversion may be one outcome when the junction is coupled into a cell to complete a circuit and has held the pivotal attraction. However, the chemical aspects lead to many other applications of increasing importance. Interest in phenomena at semiconductor/electrolyte junctions is historically coincident with the invention of the solid-state photovoltaic solar cell. Both areas have advanced from the base of understanding in solid-state physics. A junction coupled

to bulk phases exists in both solid-state and solid-liquid devices, and the study of these interfacial regions has been an important theme for physics and chemistry in the past 40 years.

In the 1970s, the experiments of Fujishima and Honda,¹ showing the feasibility of solar production of hydrogen fuel in a semiconductor-electrolyte cell, and Gerischer's basic concept² of a power-producing semiconductor-photoelectrochemical device led to rapid progress in the direction of energy conversion. With parallel growth in understanding of the active interface, the field has also evolved widely and there have been a multitude of imaginative extensions outside of energy problems. We will briefly outline the scope of these developments and summarize the research needs required for further translations into effective technology.

We treat the subject in five parts: Energy Conversion; Fabrication of Interfaces and Structures; Characterization; Synthesis, Detoxification, and Degradation; and Fundamental Issues. Funding of related research has been reduced since the early 1980s along with the diminished overall effort toward solar alternatives. Some of the promise for solar energy conversion has been dulled by generally unresolved long-term stability issues attributable to the chemistry at the solid-liquid junction. Yet, it is important to realize that the energy conversion research has been synergistic to the numerous other applications these efforts have spawned. We conclude with a list of needs for research, standards, and methodologies in this field that must be met to have substantial impact on surface processing and related technologies.

II. ENERGY CONVERSION

A. General Features

An illuminated photoelectrochemical (PEC) cell bears a formal resemblance to a traditional Schottky barrier photovoltaic (PV) device, with the metal layer contacting the semiconductor replaced by an electrolyte containing an appropriate redox couple. For both PEC and PV junction devices, light above bandgap energy excites carrier separation in the semiconductor, driving electronic charge (electron or hole, for p- or n-type, respectively) into the semiconductor bulk. Translating this into a current in a PEC requires charge transfer chemistry to occur both at the semiconductor electrode surface and at a second surface, or counterelectrode. The solid/liquid interface and the coupled chemistry impact cell function, design, and applications. Both striking opportunities and some inherent disadvantages for long-term energy conversion result when compared with the PV counterparts.

A semiconductor/electrolyte junction spontaneously forms and has continuous contact between the two phases. With excitation and charge collection at such junctions occurring close together, solid/liquid devices usually provide better performance with polycrystalline materials than do solid-state devices because a

more complete junction is formed by liquid wetting the polycrystalline grains. Because the PEC electrolyte is continuously available to the active junction, the interface may be modified to accomplish stability and enhance solar-to-electrical conversion. Many other useful aspects of the liquid junction system follow from these features. It is of considerable importance that the semiconductor may be in the form of discrete particles. Then the photocathodic (for p-type) or photoanodic (for n-type) reactions at the semiconductor surface are carried out vicinally to the respective anodic or cathodic reactions at an electronically coupled local counterelectrode. Fuel or other synthesis products may be generated in this mode rather than having direct power conversion through an external circuit.

Power conversion efficiencies comparable with those of solid-state cells have now been achieved in a variety of PEC cells. The knowledge base derived from these advances has furthered other applications such as microfabrication of solid-state devices, sensors, photocatalysis, and environmental improvement schemes, as elaborated in subsequent sections.

B. Light Absorption and Charge Transfer Schemes

In PEC systems, the absorption of photon energy yields electronic energy in the form of excess electron-hole pairs in semiconductors or in excited electronic states in molecules. Without a mechanism of charge separation, this initial electronic energy would be lost as heat through recombination. Two distinct mechanisms of converting an excitation process into charge separation (currents) have been applied in designing efficient photoelectrical systems. At semiconductor/liquid interfaces, an electric field (the space-charge layer) forms at the semiconductor surface with charge/ion redistribution at the liquid interface. If the photons are directly absorbed in the semiconductor to produce electron-hole pairs, this electric field impedes recombinative processes by oppositely accelerating and separating these charges, leading to minority-carrier injection into the electrolytic redox couple and photodiode behavior. This concept of carrier generation is illustrated in Figure 1A (for an n-type semiconductor).

Homogeneous, photodriven, molecular redox reactions are conceptually an alternative conduit for PEC energy conversion, leading to photoexcited products that migrate and inject their charges into separate anodic and cathodic electrodes. However, such coupled charge separation and transport processes are too slow to inhibit recombination or other efficiency-destroying events, unless the excited molecules are directly adsorbed on the semiconductor to act as a charge mediator. In this latter dye-sensitization mode, light absorption occurs in the dye and the photogenerated majority carrier is then injected into a wide bandgap semiconductor, as illustrated in Figure 1B.

Development of dye-sensitized semiconductors was slow because of the limited fraction of light that could be harvested by a monolayer of dye and by competitive chemical-degradation pathways for the excited dye, considering the

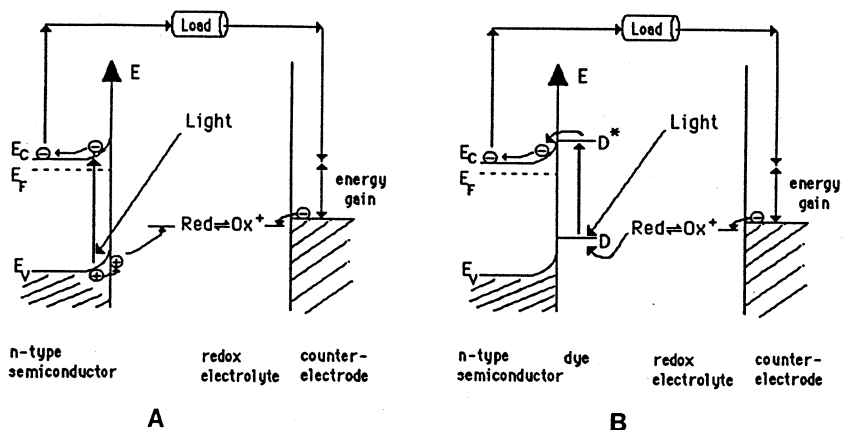


FIGURE 1. Carrier generation under illumination arising at (A) the semiconductor/electrolyte interface and (B) the semiconductor/dye sensitizer/liquid interfaces.

large number of turnovers of the injection process required for long-term stability. The first example of a dye-sensitized device with efficiency comparable with those achieved by direct excitation (Figure 1A scheme) was recently demonstrated through the use of a novel high-surface area, thin-film nanostructure of n-TiO₂ (produced by sol-gel routes), which is coated with an energetically matched trimeric ruthenium complex of high photostability and immersed in an iodide/iodine-containing electrolyte. The unusually high surface area of the transparent semiconductor, coupled to the spectral characteristics of the dye, harvests a high proportion of the incident insolation.³

Surface stability severely limits the life of electrolytically immersed semiconductors, and photocorrosion is of particular concern. A semiconductor or dye thermodynamically well matched to the solar spectrum may be intrinsically reactive in the PEC electrolyte. These factors restrict the choice of suitable electrolytes and require inventive chemistry.

C. PEC Developments

PEC energy conversion is thus a hybrid field encompassing electrochemistry, spectroscopy, and solid-state physics. Solar energy incident onto a variety of semiconductors can drive electrochemical reactions and result in the production of not only electrical but also chemical or electrochemical energy. In both Figures 1A and 1B, the photoelectrode is coupled to a metallic counterelectrode to generate electricity regeneratively, that is, with no net chemical change. Examples of cells with high solar to electrical conversion efficiencies are summarized in Table 1.

TABLE 1
Regenerative PEC Solar to Electrical
Conversion Efficiencies

Year	Solid/reacting ion	Efficiency (%)	Ref.
1991	nano n-TiO ₂ (dye)/I ⁻	~8	3
1990	n-CdSe/[KFe(CN) ₆] ³⁻	~16	4
1987	n-GaAs(Os ³⁺)/Se ²⁻	~15	5
1985	n-Cd(Se,Te)/S ²⁻	~13	6
1982	n-CdInSe ₂ /I ⁻	~9	7
1982	n-WSe ₂ /I ⁻	~10	8
1981	n-MoSe ₂ /I ⁻	~9	9
1981	p-InP/V ³⁺	~12	10
1978	n-GaAs(Ru ³⁺)/Se ²⁻	~12	11

These efficiencies approach those of more mature solid-state PV devices. Efficiency may also be expressed in terms of the power saved in carrying out chemical-fuel production. In one such cell, power savings for hydrogen generation at platinized p-InP have been realized by using up to 12% of the incident sunlight.¹²

Finally, the components of a PEC cell are analogous to those in a conventional battery and, in principle, the charge produced by the cell can also be electrochemically stored by the addition of a third electrode and an appropriate separator, instead of being stored in a product fuel. Figure 2 shows one configuration of a PEC cell combining such *in situ* electrochemical storage with solar conversion capability to yield a continuous output that is insensitive to daily variations in illumination. The practical system shown combines a Cd(Se,Te)/S²⁻ based conversion half cell and a Sn/SnS storage electrode to give a single cell operating at an

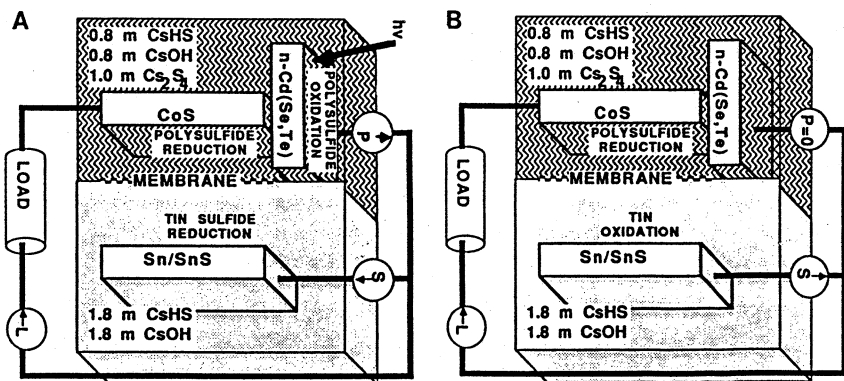


FIGURE 2. A PEC cell in a system combining both solar conversion and storage capabilities: (A) under illumination and (B) in darkness or low light.

overall efficiency of 11.4%.¹³ Under illumination (Figure 2A), photocurrent is used partly to drive an external load and partly to reduce metal cations in the storage electrode. Then, in darkness or at low light levels, the storage compartment can take over power delivery (Figure 2B) by metal oxidation.

D. Economic Considerations

Practical terrestrial-energy conversion requires inexpensive, efficient, and stable devices. Inexpensive systems require low-cost materials, ease of fabrication, simple chemical steps, and a means of handling the chemical fuel produced, if the latter is the desired product. For any kind of PV device, synthesis of single-crystal material is often time and energy intensive, and the process will normally be limited to forming smaller cross-sectional area cells at high cost. A variety of techniques can provide cheaper forms of polycrystalline or amorphous thin-film semiconductors to consume relatively small amounts of material while covering large surface areas. Modes of film preparation include slurry techniques, chemical vapor deposition, casting of polycrystals, radio frequency (RF) sputtering, vacuum coevaporation, sol-gel processing, chemical bath deposition, hot pressing, and electrodeposition among others. These techniques have been variously used to prepare thin-film electrodes of n-CdS, n-CdSe, n-CdTe, n-GaAs, p-InP, n-Si and p-Si, and n-TiO₂ for PEC cells.^{3,14}

A particular advantage of electrodeposition (plating) techniques is the possibility of a one-step chemical synthesis of a semiconductor without using a great deal of heat energy to form the eventual electrode, thus reducing the energy payback time, as well as initial cost, compared with virtually every other scheme of synthesis. Future developments in both solid-state and liquid junction photovoltaics will benefit from a variety of commercial thin-film techniques being developed for materials such as a-Si:H, CuInSe₂, CdS, CdTe, and GaAs.

The performance of PEC solar cells can degrade with time, typically significantly faster than is observed for solid-state cells. Corrosion and passivation of the solid/liquid interface and degradation of the electrolyte can occur. Countering the degradation processes requires controlling kinetics through the PEC interface and developing alternative stable combinations of semiconductor and electrolyte. A loss of efficiency is generally observed for polycrystalline materials compared with single-crystal forms. These losses are generally attributed to kinetic origins, for example, recombination at grain boundaries. It is of interest that thin-film PEC structures have sometimes exhibited greater stability than single-crystal counterparts, which have better initial efficiencies. This phenomenon has been attributed to lower microscopic photocurrent density. The longest lifetime PEC device demonstrated to date, slurry-deposited thin-film n-Cd(Se,Te) electrodes immersed in modified polysulfide solutions, has operated outdoors for approximately 1 year. In this system, photoelectrode and electrolyte stability was achieved by systematic optimization of the solution composition.¹⁵ Efficient dye-sensitized devices, with

a 2-month-equivalent sunlight lifetime, have been demonstrated. This advance reflects a substantial reduction in the quantum yield to degradation reactions with Ru-based dye complexes compared with previous all-organic light absorbers.

III. FABRICATION OF INTERFACES AND STRUCTURES

Many fabrication procedures developed for PEC cells apply to other areas. Exploitation of light-induced chemistry of the semiconductor at an electrolyte junction includes surface tailoring, etching, and other manipulations of the morphology and surface composition of semiconductors. Because all of these efforts relate to the surface processing of semiconductors and to the same underlying theory implicit in our discussion of PEC cells, they will also benefit from better understanding of the fundamentals of this technology.

A. Etching

The etching of semiconductors, with and without the action of light, is critical to the cleaning and texturing of surfaces for device fabrication and formation of geometric shapes and interconnects in integrated circuit and wafer-level technology. Covering the range from preparing uniform, smooth surfaces with low recombination velocities, through anisotropic processes for patterned pits or holes, to light-assisted drilling of vias, these applications of semiconductor/electrolyte interfaces have become familiar to modern processing. The net chemical reaction generated at any local area of a semiconductor surface by a flux of light is usually proportional to the local intensity of absorbed light. Some of the most interesting applications have been those in which the incident light has been spatially patterned in electrolytes compatible to the accompanying dissolution chemistry and kinetics. The following sampling of some of the more sophisticated light-assisted etching techniques that have had impact on semiconductor technology illustrates the versatility of PEC processing.

Symmetrically graded intensity has been used to fabricate lenses directly on emitting surfaces of semiconductor lasers,¹⁶ diffraction patterns from a pair of light beams have inscribed holograms,¹⁷ and laser beams of ultraviolet (UV) frequency have drilled holes in semiconductors,¹⁸ all through photochemical processes. Gratings can be made with v-grooves etched through resist patterns,¹⁹ and surfaces can be textured to be matte and nonreflective for photothermal methods as well as for PEC or PV efficiency improvement.¹¹ Etching can be controlled, either through light generation of carriers or through charge injection by the redox system, under circumstances appropriate to the redox potentials and the substrate band edges in the redox medium. Many open questions remain in these areas that have to do with chemical processes (dissolution mechanisms, passivation), light channeling, and solid-state diffusion lengths, charge transfer kinetics, and crystal face faceting and

etch-stopping phenomena. The interactions between chemistry and solid-state transport that lead to structures of extreme anisotropy and phenomena of high contemporary interest, such as luminescent processes in porous silicon, are not yet understood. Many improvements in the efficiency and reproducibility of PEC and PV converters have resulted from etching processes that provide more ideal surfaces with fewer surface states and reduced recombination.

Forming complex wafer-level structures requires demanding processing steps to carry out either anisotropic or isotropic material removal, as necessary. Both "wet" and "dry" (chemical solution and plasma etching) methodologies are required for the full range of problems, although the plasma methods are more adaptable to the anisotropic etch needs of fine line patterns. Mechanistic understanding of the wet chemical processes has lagged. Kinetic interpretation has advanced further in the study of the competitive substrate corrosion processes in PEC cells than in the area of understanding purposeful etching itself.

Commonly achieved submicron dimensions are placing greater demands on the quality of substrates as dielectric layers become thinner and breakdown mechanisms are more severely tested. This requires interpreting surface roughening from chemical treatment in much more detail than earlier technology required. Development progresses, but generally through empirical studies. The selectivity of dissolution rates for different semiconductors or alloys, as in III-V laser fabrication, is an example. Considerably less effort has been expended on systematic studies of differences between related materials or of different crystal faces in the same pure (or alloy) semiconductor.

Significant accomplishments have been made through these sophisticated means of what amounts to micromachining of surfaces. Modeling here is difficult because of the complex interactions. Better mechanistic understanding is needed because of the diversity and attraction of the applications and the dependence of semiconductor and laser-device fabrication on the control of many such techniques.

B. Deposition

Reference has already been made to the deposition of thin films by a variety of means to form semiconductor substrates for energy conversion devices. Electrochemical techniques have long been attractive for such substrate synthesis, that is, additive processing schemes as opposed to the subtractive ones of the etching section. Large-area devices can be formed electrochemically and economically with an energy expense that is readily recoverable because the current densities and voltages of solar conversion cells in outdoor exposure and in electroplating are very much alike. Nonelectrolytic immersion chemistries are similarly attractive for economic manufacturing.

Examples of both chemical and electrochemical synthesis are plentiful, especially for II-VI compounds, but there are limitations in the device quality of

materials formed. Crystallinity is sometimes achieved only with postannealing, not in the as-deposited product. The epitaxy or crystalline order that can be achieved with chemical vapor or molecular beam deposition is a problem for the solvent systems of electrochemistry. Whether efforts to improve electrochemical morphology (by such techniques as underpotential deposition to introduce epitaxy) will have broad impact is a research question. These studies can now be supported by the proliferation of surface structure and *in situ* techniques such as scanning tunneling and atomic force microscopies, which have only recently been made available.

C. Specialized Surfaces and Sensors

Because of the need in a PEC cell to improve the kinetics of the desired charge-transfer step while inhibiting photocorrosion, much effort has gone into modifying surfaces by chemical or electrochemical means to enhance efficiency and stability. Modification can range from using submonolayer additions of metal ions^{5,11} or depositing thin, electron-tunnelable films of surface oxides,¹⁰ all the way to forming a buried junction of a discrete metal or polymer interphase to which the solution phase is only a contact, not barrier determining. The chemical lessons learned in improving these surfaces have also been applied to solid-state PV junction devices of higher efficiency and to new sensors, as examples of interesting spin-offs.

Sensors dependent on surface interaction of liquid or gas phases with a semiconductor that alters the potential distribution or work function of the surface have been developed for a wide range of species. Work-function devices with metallized semiconductors are used as hydrogen sensors, for example. The field of electrolytic sensing through changing potentials in the gate region of a field effect transistor has grown strongly during the period common to work on PEC interfaces.²⁰ Light-addressable PEC sensors (LAPS)²¹ have been shown to be versatile and sensitive devices for a wide variety of species.

Insight into modulated structures such as quantum wells and possible new functions for them have been obtained by PEC techniques.²² The formation of porous nanostructures with high bandgap materials such as n-TiO₂ was earlier mentioned as critical to improving the efficiency of dye-sensitized cells.³ Self-assembled monolayers may also be used to modify semiconductor substrate surfaces. All of these areas of surface morphology manipulation are subjects of recent interest and will continue to have synergistic interaction with PEC studies.

Further credence to the need for fundamental studies is evident from the brief mention in this section of the inventive interface engineering already used on PEC cell surfaces. There are also numerous key issues in catalysis, spatial control, selectivity, kinetics, and environmental compatibility that underlie application and should be pursued.

IV. SYNTHESIS, DETOXIFICATION, AND DEGRADATION

As we have discussed, PEC systems may facilitate not only solar-to-electrical-energy conversion but may also drive electrochemical and chemical energy processes. This concept has been productive in PEC synthesis, production of fuels, and detoxification of pollutants in water systems. It has also contributed to our understanding of natural solar processes occurring where there are semiconductors in contact with reactable substrates.

The classic system exemplifying PEC synthesis is water photoelectrolysis to generate hydrogen. Fujishima and Honda¹ showed that n-TiO₂ can be used to split water at about 0.1% solar-to-chemical-energy conversion efficiency. This semiconductor has a bandgap of 3.0 eV and absorbs about 4% of the incident insolation. Other wide bandgap materials can absorb photons energetic enough for this reaction (Table 2), but they have similar efficiency constraints.

Materials with a bandgap of less than 2.0 eV are much more capable of excitation with a substantial fraction of the incident sunlight in which 1.4 eV for a single absorber yields an optimum solar efficiency by balancing the overlap with the solar spectrum and photon energy. Materials with bandgaps near 1.4 eV may be used for hydrogen generation with concurrent electrical bias (Table 2).

PEC generation of products can result from photocatalysis when the reaction is thermodynamically favored but kinetically inhibited (the synthesis of ammonia from the elements). Product formation may be driven energetically by light excitation when the reaction is uphill thermodynamically, as in most fuel-generating reactions (water splitting or various carbon dioxide reduction schemes). Goals for both types of processes include obtaining valuable products, energy savings, environmental advantage, novel routes, useful fuels, remote generation on demand, and modeling of biological pathways.

A variety of PEC synthetic processes have been studied. Carbon dioxide or simple organics have been converted to molecules such as methanol, formalde-

TABLE 2
Photoelectrolysis of Water

Year	Semiconductor ^a	Bandgap (eV)	Counterelectrode	Ref.
1972	n-TiO ₂ (c)	3.0	Pt	1
1976	n-TiO ₂ (c)	3.0	p-GaP (2.4 eV)	23
1979	n-Fe ₂ O ₃ (f)	2.2	Pt	24
1981	p-InP(Ru)(c)	1.35	Pt	12
1986	n-SrTiO ₃ (doped)	~3.0	Pt	25
1986	p-Si(c)/polypyrrole	1.1	RuO ₂ (p)	26
1986	p-CdTe(f)	1.4	Pt	27
1986	p-InP(c)	1.35	n-GaAs	28
1988	n-CdSe(c)	1.7	—	29

^a c = single crystal; f = film; p = powder.

hyde, formic acid, or methane on substrates such as TiO_2 ,³⁰ GaAs and GaP,^{31,32} SiO_2 -doped Fe_2O_3 ,³³ and BaTiO_3 ,³⁴⁻³⁷ Hydrogen and carbon dioxide have been generated from sugar, starch, and cellulose at RuO_2 and TiO_2 interfaces.³⁸ The conversion of Cl⁻ and Br⁻ to halogens at MoS_2 or MoSe_2 junctions has also been reported.³⁹ Numerous other examples could be cited.

PEC systems have been suggested for decontaminating environmental pollution or other detoxification processes. A model system has even been suggested for saline demineralization combining photoredox and membrane processes.⁴⁰ The photoassisted oxidation of oil slicks on sea water is being pursued and modeled on TiO_2 particles.^{41,42} Certain noxious inorganics can be broken down on semiconductor particles. Practical developments in these areas could lead to large-scale applications.

Thus, PEC systems have value not only as energy conversion devices, but also in electrosynthesis, detoxification, and understanding and preventing light-driven degradation reactions such as those that might occur in illuminated paints containing semiconductor pigments. We stress that the underlying kinetics and thermodynamics of particles have a close relationship to the photoelectrochemistry already discussed. There are many special circumstances to be considered, however, among which are catalyzing the surfaces of small particles for both anodic and cathodic reactions, the consequences of generating products in close proximity, and quantum confinement effects, in small enough particles, that shift bandgaps, band edges, and light-absorption characteristics. These generate theoretical problems for the underlying science above and beyond those of macrosized semiconductor electrodes.

V. CHARACTERIZATION

A. Introduction

The characterization of PEC cells must serve at least the significant functions of

- Developing standards and testing procedures for PEC devices
- Establishing the surface, interface, and bulk properties of semiconductor materials
- Developing general techniques that can be used to analyze other related systems.

Standardizing the testing of PEC devices is necessary to provide a consistent means of comparing data on their efficiency and stability and on other quality measures. Accelerated test procedures would be preferable, although the complex nature of the total cell complicates such considerations. On a fundamental level, techniques are necessary to characterize the nature of surfaces, interfaces, and bulk

materials. Both electrochemical and nonelectrochemical techniques are required. An important consequence of progress in interfacial and bulk characterization is that these techniques can be applied to other systems. Methods that can be applied *in situ* have received increasing attention and have obviously great value in electrolyte systems.

B. Standardization of Testing Procedures

Although PEC engineering efficiency is nominally the straightforward measure of the ratio of electrical power out/light power in, there is, nonetheless, a strong need for standardization of testing procedures. Taking a maximum voltage-current product from a cell output is routine, but whether 2- or 3-electrode configurations are used (all or part of the resistive loss accounted for, respectively) and whether cell engineering and counterelectrode placement are realistic are two of the factors that impact on the final percent of efficiency claimed. The spectrum of the light source, as well as the absolute power level, is also critical and has effects varying with the semiconductor bandgap, action spectrum, and solution absorbance. There are typically more variables in the measurements of a PEC device than in those of a PV device. Measurement in actual sunlight or with solar simulators is desirable, but there are intensity and spectral effects to be considered for specific conditions and standardization is required for effective comparisons. For the most part, stability data can be obtained with laboratory light sources as long as there are no special wavelength-sensitive degradation mechanisms. In one such case, photon energies that can excite the wide bandgap semiconductor in dye-sensitized cells will lead to greatly increased dye degradation.

Accelerated testing is an important goal, especially to determine the long-term stability of PEC cells. Reasonable means of stressing the cells for this purpose need to be evaluated; for example, an enhanced level of light intensity may change the degradation mechanisms and, consequently, the lifetime estimation.

C. Analysis of Surfaces, Interfaces, and Bulk Properties

Many techniques have been used in the characterization of surface, interface, and bulk properties of PECs. Historically, the determination of bulk parameters such as minority-carrier lifetimes and carrier diffusion lengths have been well established from solid-state physics, and certain techniques such as Mott-Schottky plots were used initially for electrolyte junctions. During the past 10 years, a number of novel techniques have been developed for the characterization of electronic, electrochemical, and chemical processes at semiconductor/electrolyte interfaces. These can be grouped under electrochemical, solid-state, and nonelectrochemical methods.

Table 3 contains a summary of techniques currently available for the characterization of semiconductor surfaces, the interfacial region, and bulk properties of both phases. Further discussion is beyond the scope of this article. Combining the methods listed in Table 3 with the many forms of *in situ* optical spectroscopies and techniques such as scanning tunneling and atomic force microscopy gives the experimenter powerful tools for understanding the fundamental processes in PEC cells. The diversity of materials introduces the question of availability to individual investigators and the encouragement of cooperative work that compares different complementary techniques.

D. Needs

The dynamic nature of semiconductor/electrolyte interfaces requires characterization methods sensitive to kinetic parameters. The properties of PEC cells are such that techniques should be sensitive to bulk, interface, and surface processes arising from the potential drops in these regions. Although a wide range of analytical tools has been identified earlier, a need still remains for improved techniques to characterize many aspects of these interfaces, particularly those sensitive to interfacial dynamics. Processes related to passivation, surface damage, and surface stability are examples in which improved characterization techniques would be of considerable benefit.

The complications of electrode processes, however, can be reversed to advantage in many cases. The electrochemical interface can be used as a temporary contact to characterize bulk and interfacial properties of semiconductor materials. Such flexibility is unique to the semiconductor/electrolyte interface.

VI. FUNDAMENTAL ISSUES

The previous sections have covered a variety of applications of semiconductor/electrolyte interfaces and their characterization. The areas considered for enhanced support are investigation of the PEC conversion of light to electrical and chemical energy, investigation of electrochemical and PEC means for the fabrication of interfaces and structures, investigation of characterization techniques that use or pertain to semiconductor/electrolyte interfaces, and investigation of photoelectrochemically driven reactions such as chemical synthesis and detoxification of hazardous wastes. Success in these target areas requires a parallel effort for study of the theoretical underpinnings, termed here the supporting fundamental issues. An overall physical and chemical description for PEC systems already exists. Transferring this description to specific systems will require supporting further research in promising areas defined by these investigations.

TABLE 3
Characterization Techniques for PEC Cells and Components

Techniques at Semiconductor/Electrolyte Interfaces*

Technique	Application
Photocurrent Spectroscopy — measurement of photo current as a function of wavelength, intensity, electrode potential, and electrolyte composition	Determination of surface and bulk properties of semiconducting and insulating materials (e.g., quantum efficiency, bandgap, inter- and intraband transitions, structure, localized states, etc.), characterization of processes such as recombination, trapping, photocorrosion, tunneling, etc.
Photocurrent Imaging — measurement of the spatial distribution of photocurrent (or photovoltage) as a function of wavelength, intensity, electrode potential, and electrolyte composition. ⁴⁴ (resolution ~2 μm)	Identification of spatial distribution of defects, grain boundaries, secondary phases, surface damage, sub-bandgap states
Capacitance/Mott-Schottky Analysis — measurement of space-charge capacitance as a function of band bending (voltage) (usually a single-frequency measurement)	Determination of dopant concentration and flat band potential; in some cases, interband states may also be measured
Carrier Depth Profiling — sequential capacitance measurements and photoetching	Determination of dopant concentration as a function of depth into the material
Electrochemical Photocapacitance Spectroscopy (EPS) — measurement of capacitance or full frequency impedance response under sub-bandgap illumination ⁴⁵	Determination of density of deep-level states and rate of trapping
Electrochemical Impedance Spectroscopy — measurement of electrode impedance as a function of frequency (typically 10 kHz–1 mHz) under illumination as a function of wavelength, intensity, electrode potential, and electrolyte composition	Analysis of kinetics of photoprocesses in space-charge and double layer regions; electron transfer to electrolyte; bulk and surface recombination; trapping at surface states, etc.
Photoacoustic Spectroscopy (PAS) — measurement of acoustic signal generated by light absorption ⁴⁶	Characterization of processes such as radiationless recombination
Intensity Modulated Photocurrent Spectroscopy (IMPS) — measurement of the alternating current (AC) response to a modulated photon flux as a function of direct current (DC) intensity, wavelength, electrode potential, and electrolyte composition; alternatively, the frequency dependent quantum efficiency may be determined from photocurrent transient data ⁴⁷	Frequency domain analysis of relaxation of photoprocesses in terms of the frequency-dependent quantum efficiency; kinetic analysis of electron transfer, recombination, trapping, etc.
Time Domain Transient Analysis — measurement of the time-dependent photocurrent (or photovoltage) response to a short photon pulse (1 ps – 1 μs); measurements may be performed under open-circuit conditions across a load (two-electrode cell) or with constant band bending (three-electrode cell) ⁴⁸	Analysis of the kinetics of bulk and surface recombination, electron transfer via surface states, charging of the space-charge region, relaxation of the band edges (two-electrode cell); for ultrafast pulses, processes such as carrier generation may be investigated

TABLE 3 (continued)
Characterization Techniques for PEC Cells and Components

Techniques at Semiconductor/Electrolyte Interfaces^a

Technique	Application
Maximum Power Spectroscopy — the maximum power output of a PEC or PV device is measured from the cell response to a small amplitude AC voltage perturbation as a function of light intensity and wavelength; this technique can also be used for the spatial distribution of the maximum power output by scanning a focused laser beam ⁴⁹	Identification of regions of efficiency losses in PEC and PV devices (analysis of loss mechanisms)

Techniques at Solid-State Junctions^b

Electron Beam-Induced Current/Photon Beam-Induced Current (EBIC/PBIC) — measurement of current induced by focused electron or photon beam excitation as a function of distance from a junction; EBIC may be carried out in a scanning electron microscope with a resolution of ~0.1 μm	Determination of minority-carrier diffusion length as a function of position
Open-Circuit Voltage Decay — measurement of the rate of decay of the open-circuit voltage in response to minority-carrier injection	Determination of carrier lifetimes
Transient Capacitance Measurement — measurement of the capacitive time constant in response to a voltage step at a reversed biased semiconductor/insulator interface; spatial resolution obtained by deposition of metal dots on the insulating layer	Determination of carrier lifetimes

^a These techniques involve the use of an electrolyte as a means for voltage perturbation and current collection. Because the electrolyte phase is removable, these techniques may also be used for the characterization of solid-state structures and devices.⁴³

^b These techniques were developed for the characterization of solid-state structures and devices.

A. Introduction

The critical components of a PEC (see, for example, Figures 1A and 1B) are the semiconductor, the electrolyte, and a counterelectrode. Electrical connection is made to the semiconductor through an ohmic contact, and illumination can be provided through the electrolyte or the ohmic current collector. Developing comprehensive models for this system requires that the physics governing the optical and electronic processes within the semiconductor be coupled to the electrolytic processes that govern the electrolyte. A unique aspect for the development of comprehensive models for PEC cells is that the models must account for the coupling of processes that take place in regions of vastly different scale. The thickness of the electrically neutral region of a semiconductor depends on

the dimensions of the electrode and may be of the order of 100 μm . The space-charge region in the semiconductor may be of the order of 0.1 μm . The electrolytic analogy to the space-charge region is the diffuse part of the double layer, which may extend 0.002 μm , but is typically of the order of ionic dimensions in more concentrated electrolytic solutions. Concentrations vary in an electrically neutral region that may extend 100 μm , and, outside this region, current and potential are governed by Laplace's equation.

The equations for convective and diffusive transport of species through the electrolyte are well established, as are those that govern the solid-state behavior of the semiconductor. The interface between the semiconductor and electrolyte, however, is not as well understood. Although the semiconductor characteristics play a significant role in determining the performance of PEC cells, further success will require a mechanistic understanding of the role of electrolytic species. The unresolved issues tend to center on physical properties that determine the interaction is between the electrons and holes in the semiconductor and the ionic species of the electrolyte. Because certain aspects of this system are well understood, careful experimental design can be used to isolate the unknown features. For example, use of a rotating ring-disk electrode for which the fluid mechanics and mass-transfer characteristics are well defined can be combined with concomitant control of the light flux. The influence of interactive variables can be individually distinguished through experimental designs that allow application of mathematical models for interpretation of results.

B. Areas for Research

Fundamental research in the area of energy conversion should improve the understanding of the semiconductor/electrolyte interface and provide a data base for electrolyte modification. Work is needed in several coupled areas.

Heterogeneous reaction mechanisms — The sequence of bond breaking is critical to understanding the way facets are formed, for example, in the PEC fabrication of small devices. Passivation phenomena and charge transfer kinetics are important in energy conversion and chemical synthesis as well as in fabrication. The understanding of the manner in which the surface may be stabilized against corrosion and the manner in which self-healing can occur will also depend on knowledge of kinetic mechanisms.

Polycrystalline surfaces — We have mentioned that a significant difference between solid-state and PEC solar cells lies in the relative ease of forming an interface with both crystalline and polycrystalline materials that is accessible for characterization by external probes. Although some empirical rules have been established to relate the PEC performance of polycrystalline materials to single-crystal counterparts, development of a better understanding of morphological effects is critical. Grain boundaries are associated with increased recombination

losses, reduced current densities, and increased effective surface area. Solid-state diffusion is enhanced in grain boundaries.

Double layer structure — Many of the techniques used to characterize the electronic structure of semiconductors rely on measurements of capacitance at the semiconductor/electrolyte interface. Anomalous changes in the space-charge capacity with applied potential have been attributed to the influence of deep-level electronic states within or at the surface of the semiconductor. Surface states can limit the photopotential obtained in PEC cells by “Fermi-level pinning” and can reduce the power efficiency by providing pathways for enhanced recombination. Although models for the semiconductor/electrolyte interface have traditionally been based on solid-state descriptions, the influence of ionic species, either through specific adsorption onto the surface or through adsorption in a diffuse double layer, needs further study. Even the applicability of traditional models for the diffuse double layer is questionable for the ionic concentrations typically used in PEC processes. A better understanding of the electrolytic contribution to the semiconductor/electrolyte interface may be needed, for example, to explain the unexpectedly high photopotentials that have recently been reported.

Homogeneous reactions in electrolytic solutions — Electrolyte modification has been pursued intensively as a means of providing high power efficiencies with low rates of photocorrosion by matching electrolyte and semiconductor properties. A fundamental need exists for creating a thermodynamic data base for ionic species in a variety of solvents. The issues include the rate and equilibrium constants for electrochemically active species and the influence of electrochemically inert counterions (through adsorption or homogeneous interactions). Efforts in this area can also support the study of the kinetics and equilibrium constants for (heterogeneous) adsorption of ionic species that can lead to shifts in the flat band potential.

Microscale processes — The application of models to PEC fabrication of submicron-scale structures requires consideration of different phenomena than those treated in models of larger scale systems. Surface roughening, tunneling, and double-layer processes can play major roles on current (or reaction) distribution and selectivity; whereas, in contrast to large-scale systems, convective transport of electrolytic species may be comparatively unimportant. To be applicable, models must therefore account for the interactions between potential and concentration in the electrolyte close to the semiconductor surface as well as in solid-state processes.

These research areas require that experimental studies be coupled with the parallel development and use of comprehensive mathematical models. Further development of PEC energy conversion, fabrication of interfaces and structures, synthesis and detoxification, and characterization will be served with mathematical models that can be used to extract relevant physical properties, to guide experimental design, and to predict the response of the system based on well-founded hypotheses. Although the fundamental theory to be used is not new, the models must account for the complicated interactions among coupled physical phenom-

ena. Interpretation based on simplistic models is often inadequate and can lead to misleading or incorrect conclusions.

VII. RESEARCH NEEDS AND OPPORTUNITIES IN PEC SYSTEMS

Research in PEC systems primarily aimed at energy conversion has achieved notable milestones and produced a variety of valuable spin-offs both to other technologies and to the understanding of the underlying science. We conclude that the field deserves strong consideration for support within the broader context of PV systems. To accelerate this progress, a number of specific needs should be addressed, given in priority order:

1. Cross-fertilization between developments in photochemical and PV technologies
2. Comprehensive studies of solution phase and surface chemistry and modification
3. Increased level of characterization of the bulk-, interfacial-, and liquid-phase properties of these systems, with stress on techniques capable of following the dynamics of the system
4. Synergistic correlations of characterization and theoretical modeling
5. Application of novel nanostructures that can amplify energy-conversion schemes and other solar applications
6. Development of more efficient and stable photoelectrodes to support substantive efforts for hydrogen production from solar energy
7. Exploration of opportunities in electrochemical deposition and processing that can lead to low-cost cells
8. Integral storage schemes
9. Fundamental understanding of etching processes and structurally sensitive control
10. Development of PEC strategies for enhancement of the environment (detoxification and synthesis)
11. Standardization of efficiency and stability measurements and testing procedures

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