

PHOTOELECTROCHEMISTRY AND SOLAR ENERGY: PROGRESS, PROMISE AND PROBLEMS*

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ABSTRACT

Progress in the development of photoelectrochemical (PEC) systems and improvements in stability and efficiency of semiconductor electrodes are described. Strategies for studying the semiconductor/solution interface and new structures for PEC devices to yield higher photovoltages and less expensive systems are suggested.

INTRODUCTION

During the last thirteen years, there has been much progress in understanding the semiconductor/solution interface and in developing photoelectrochemical (PEC) cells for the conversion of solar energy to electricity and useful chemicals. Modern studies in this field originated in the reports of Honda and Fujishima [1], who described current production and oxygen evolution at illuminated n-type TiO_2 electrodes. Research in this field was also spurred on by the "oil crisis" and the desire to develop energy systems involving renewable resources. A number of reviews are available which discuss the history and principles of semiconductor electrode systems, and describe the PEC systems that have been studied [2-9]. Even in the earliest work, it was clear that TiO_2 , which is a very stable and still an intensively investigated material, had too large a band-gap (E_g) to be useful in efficient solar energy systems. Many of the smaller band gap materials (with E_g 's of 1.1 to 1.5 eV) were often unstable when immersed in solution under illumination, were inefficient, or were too expensive for use in PEC cells. Moreover, the available photopotential generated at these materials was usually ≤ 0.6 V, so that PEC cells with a single photoelectrode produced relatively low output voltages and could only be employed for the production

*The Bruno Brever Memorial Lecture

of chemical species in reactions of low energy. Much of the research in the intervening years has been concerned with the stability, efficiency, and low output voltages of PEC cells and different approaches for solving these problems. In this paper we discuss some of the methods used by our group and others in attempting to overcome these problems and describe some of our recent PEC systems.

STABILITY

The earliest approaches to the stabilization of n-type semiconductor electrodes involved manipulation of the solution conditions (solvent or redox couple) to promote rapid reactions of solution species at potentials where the oxidative decomposition reaction of the semiconductor itself was slow or would not occur [10,11]. Thus n-GaAs was shown to be stable either in aqueous solutions containing selenide ion [12-21] or in non-aqueous solvents [22-25]. Numerous other studies have dealt with redox couples and solvents for stabilization of semiconductor electrodes. However, manipulation of the solution of necessity limits the range of potential and scope of reactions available. An alternative approach has involved modification of the electrode surface with transparent films which would conduct charge from the underlying semiconductor to solution species, but would isolate the semiconductor surface from the solution and thus prevent its oxidation. Different types of films have been tried, including polymers [26-29], metals [30-32] and semiconductors [33-36]. We have recently been investigating the behavior of silicide films on n-type silicon electrodes [37-39]. These films are formed by deposition of a thin ($\sim 40 \text{ \AA}$) layer of metal (e.g., Pt or Ir) on the Si surface followed by annealing. Thus n-Si*/PtSi/Fe²⁺, Fe³⁺/Pt cells are stable and show open circuit photovoltages of 0.4 V. Studies of the n-Si/PtSi electrode with a number of different redox couples spanning a potential range of more than 1.5 V [38,40] demonstrate that these cells always have photopotentials of 0.4 V; this suggests that the photoactive junction (which is indicated by an *) is the one between the Pt and PtSi. The PtSi-covered electrode is not stable,

however, during photoevolution of chlorine. The n-Si/IrSi electrode is more stable under these conditions, but the photocurrent at this electrode slowly decays during Cl_2 evolution (Fig. 1) [38]. However, the addition of an RuO_2 layer, which catalyzes chloride oxidation and apparently promotes more rapid removal of holes from the IrSi layer, permits stable operation for at least 7 days (Fig. 1).

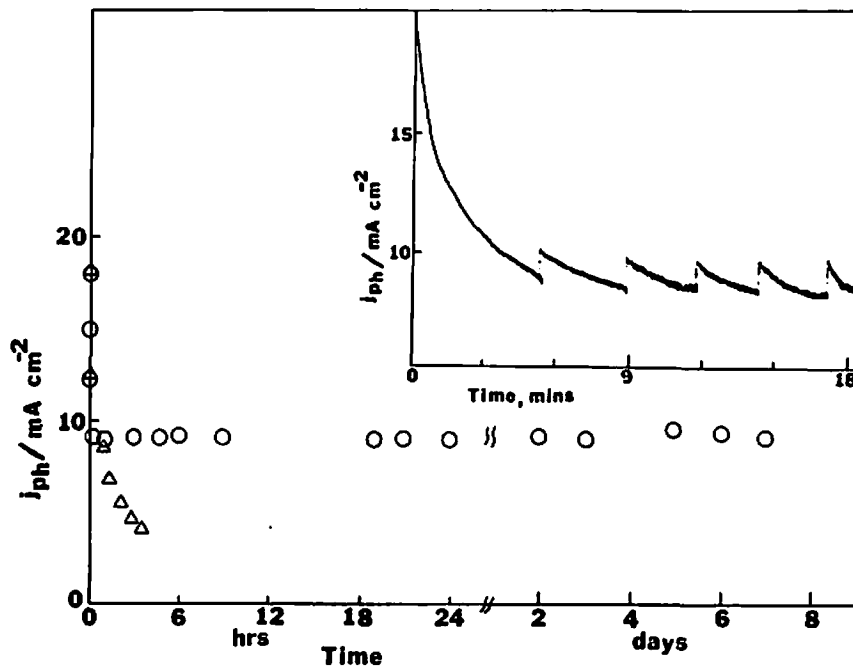


Fig. 1 Stability of n-Si/IrSi electrode during evolution of chlorine. Photocurrent density j_{ph} (at bias of 1.0 V vs SCE) vs time is shown for irradiation at 65 mW cm^{-2} (tungsten-halogen lamp), for 11 M LiCl at pH 5 Δ = n-Si/IrSi; \circ = n-Si/IrSi/ RuO_2 . The insert shows the fluctuation of photocurrent at early times because of Cl_2 gas bubbles on the electrode surface. [38].

Although p-type materials tend to be more stable in aqueous solutions, since they are cathodically protected from oxidative degradation by the photoreaction [41,42], catalysis of desired reactions, such as hydrogen evolution, is still important. For example, reduction of protons does not occur very readily on an illuminated p-GaAs (or p-Si) electrode, even though the potential of photogenerated electrons, corresponding to the energy of the conduction band edge, is several tenths of a volt more negative than that required thermodynamically for this reaction. Hydrogen evolution is promoted by suitable redox couples (e.g., the viologens), either in solution or immobilized on the electrode surface, in the presence of Pt [43-47] or by suitable metal deposits on the electrode surface [48,49].

Much progress has been made in the purposeful modification of semiconductor surfaces for the purposes of stabilization and catalysis. We call these multicomponent electrodes and solutions "integrated chemical systems" [50,51], which we define as designed heterogeneous systems consisting of several components (e.g., semiconductor, polymer film, catalyst, solution) acting together in a synergistic way to carry out a particular process.

EFFICIENCY

The efficiency of semiconductor PEC cells (best defined as the electrical or chemical energy produced divided by the light energy input) is governed by a number of factors. The *ideal* maximum efficiency is a function of the match between the incident radiation and the semiconductor band gap and the maximum photovoltage that is possible, as governed by the Fermi level in the semiconductor (usually represented as the flat band potential, V_{fb}) and the redox level in solution. In actual cells, kinetic factors also play a role in decreasing the efficiency. These factors can involve the bulk semiconductor (e.g., loss of photogenerated minority carrier through recombination, as expressed by the diffusion length, L) and the interfaces. Electron-hole recombination at the solution interface, often probably involving surface or

interface states [52], as well as the finite rate of charge transfer to solution species, are also important. An important contribution to improvements in the efficiency of PEC cells has been the passivation of recombination centers and modification of surface states by chemical treatment of the semiconductor surface [53,54]. Such treatments may be especially important in the passivation of grain boundaries and exposed edges in polycrystalline semiconductor electrodes [55-58]. Improvements in performance by greater attention to the surface and bulk semiconductor properties has recently been stressed [59].

The importance of the nature of the semiconductor surface, either because of recombination or Fermi level pinning [52], has led to increased interest in methods of studying the semiconductor/solution interface. We have recently discussed the usefulness of the in-phase component (ac conductance) of the interfacial impedance in studying surface states [60,61]; this work followed from earlier studies at semiconductor/metal interfaces [62]. Although capacitance (out-of-phase impedance) measurements are widely used to determine the flat-band potential of semiconductor electrodes, they are of only limited value in studying surface states. For example, with metal-oxide semiconductor (MOS) devices, the capacitance method for the determination of surface state properties is said to suffer [62] from the fact that the variation in the total observed capacitance values required to find the surface capacitance, even for frequency changes over a large range, is very small; this leads to errors in calculating the density of surface states and their time constants. However, the parallel equivalent conductance (G_p) (the in-phase component of the total admittance corrected for the space-charge resistance) is more useful in characterizing interface states, since one can measure directly the properties related to the capture and emission rates of charge carriers by surface states. Even in those cases where the quadrature signal gives a frequency independent C-V plot, the location of surface states and their time constants can be determined from the in-phase component [61]. G_p is usually

expressed as:

$$G_p = C_{ss} \frac{\omega^2 \tau / (1 + \omega^2 \tau^2) + G_D}{\omega^2 \tau^2} + G_D = G_{ss} + G_D \quad (1)$$

where $\tau = R_{ss} C_{ss}$; $G_D = 1/R_D$ (R_D is the space charge layer resistance); R_{ss} and C_{ss} are the resistance and capacitance, respectively, associated with the surface states; $\omega = 2\pi f$ is the frequency.

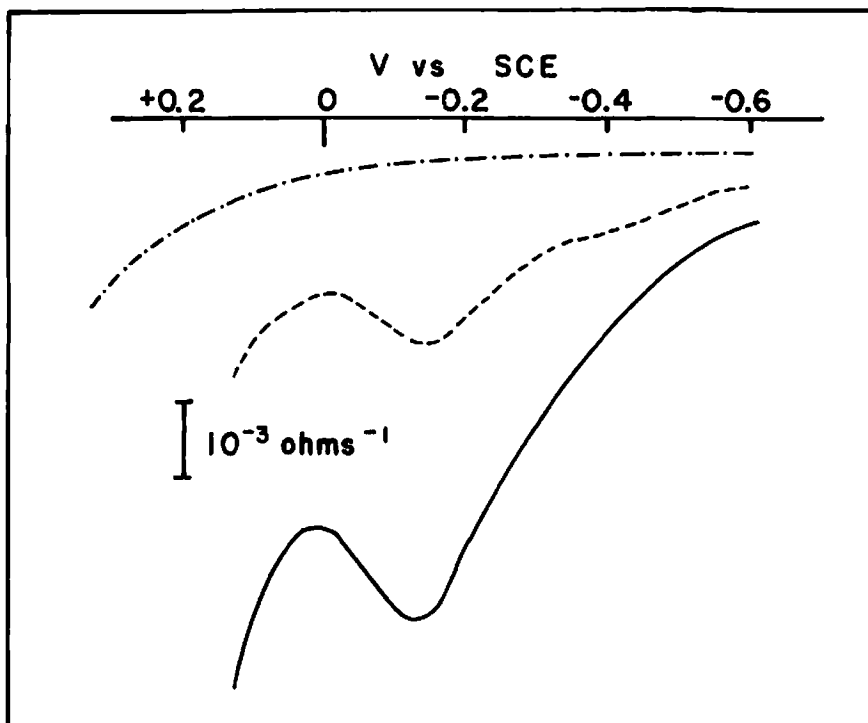


Fig. 2 Effect of pretreatment of p-InP electrode on the equivalent parallel conductance (G_p) in 0.1 M EuCl_3 , 1 M HClO_4 . (a) etched electrode (5% Br_2 , MeOH) at (—) 1 kHz and (---) 5 kHz; (b) after dipping the electrode in 0.01 M RuCl_3 , 0.1 M HNO_3 solution for 2 min (-·-·-) 1 kHz. [63]

Studies in our laboratory by Magasubramanian and Wheeler have shown [63] that the in-phase component can be used to locate the surface states of semiconductors contacting liquid electrolytes. For example, a plot of the in-phase component (G_p) as a function of potential for two frequencies for an etched p-InP (100) contacting an aqueous solution containing 0.1 M EuCl_3 , 1 M HClO_4 (Fig. 2) shows a peak at -0.15 V that is characteristic of surface states located at the equivalent energy level. When the p-InP is dipped into a solution of 0.01 M RuCl_3 and 0.1 M HNO_3 , smooth plots are obtained which are characteristic of surface-state-free surfaces (Fig. 2). We ascribe the absence of the peak in the case of the Ru^{3+} dip treatment to the blocking or splitting of the surface states by Ru^{3+} , as has been invoked to explain the beneficial effects of Ru and Pb ions on n-GaAs [53], La ions on polycrystalline WSe_2 [64], and Zn ions on n-CdSe photoelectrodes [65].

DEVICE PHOTOVOLTAGE

The maximum driving force for a PEC device with a single photoactive junction (e.g., semiconductor/solution or Si/PtSi) is rarely more than 0.8 V and is often below 0.6 V. Similarly, the p-Si/n-Si junction in the Texas Instruments Solar Energy System (TISES) [66], which is separated from the solution by a suitable noble-metal overlayer, develops about 0.55 V. If more energetic reactions (such as the decomposition of HCl to H_2 and Cl_2) are to be driven in PEC cells without an external bias, multiple photoactive junctions must be employed [67]. For example, cells with both photoactive anodes and cathodes, carefully matched to maximize efficiency, can be used to obtain higher voltages. This strategy is employed in the TISES system, where two different types of small (0.25 mm) silicon spheres (n-Si on p-Si photocathodes and p-Si on n-Si photoanodes) embedded in a glass matrix and connected by a conductive backing are used to photodecompose HBr to H_2 and Br_2 . This system is illustrated in Fig. 3.

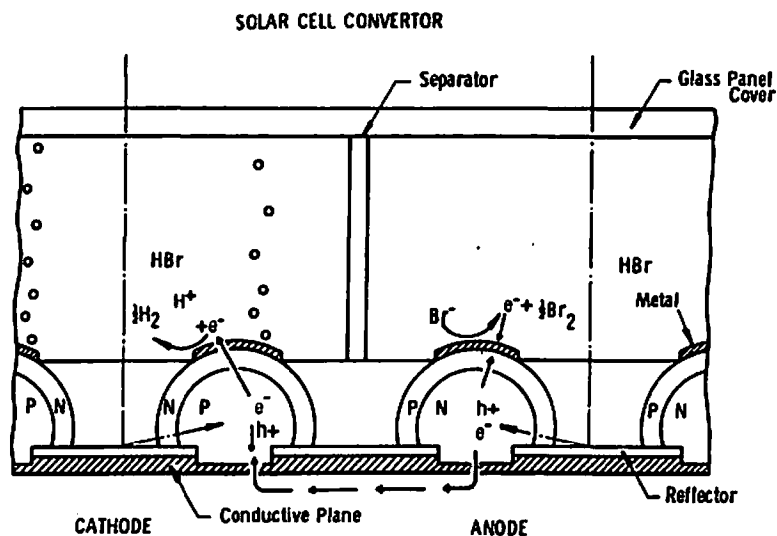


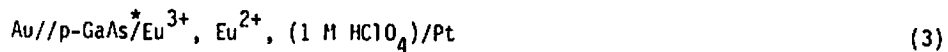
Fig. 3 Texas Instruments solar array based on p-Si/n-Si spheres for photodecomposition of HBr to H₂ and Br₂. [66]

It should also be possible to produce multilayer devices with several photoactive junctions, e.g., an internal Schottky barrier involving a metal/semiconductor junction in series with a semiconductor/solution junction. It is also of interest to consider methods of coupling individual devices in series to produce larger voltages. A useful analogy perhaps is the electric eel; in this animal individual nerve cells, which normally produce only 100 mV, are coupled to produce hundreds of volts. The following discussion concerns the operation of multijunction devices and describes several reactions carried out with the Texas Instruments silicon solar arrays. Details of these experiments will be published elsewhere [68].

We use the following notation for multilayer semiconductor devices:



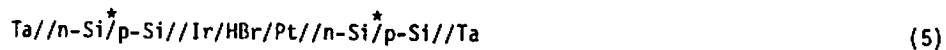
where CM represents the contacting metal to phase A, SM is a surface layer contacting the solution phase, S. A double slash (//) indicates an ohmic contact between phases, and implies a negligible potential drop at this boundary. Thus, a typical PEC cell [41] might be represented as



A cell with an internal photoactive junction, e. g., n-Si/PtSi [37], would be represented as



and the TISES system, made up of a p on n photoanode (TIA) and an n on p photocathode (TIC), shown in Fig. 3, as



The electrochemical behavior for these devices, either in the dark or under illumination, can be described phenomenologically by considering the i - V behavior of each junction independently. The cell behavior is derived by realizing that the junctions are in series, so that the same current passes through all junctions, and the cell voltage, V_{cell} , is given by the sum of the potential drops across the junctions plus any resistive (iR) drops within the phases. Although analytical expressions can be written for these junctions (diode equations for semiconductor/semiconductor or Schottky junctions and the usual electrochemical expressions involving kinetics and mass transport for the metal/solution junctions), graphical determination of the cell characteristics from experimental or derived i - V curves is also possible. Such an analysis for the cells (4) and (5) above is given in Figs. 4 and 5.

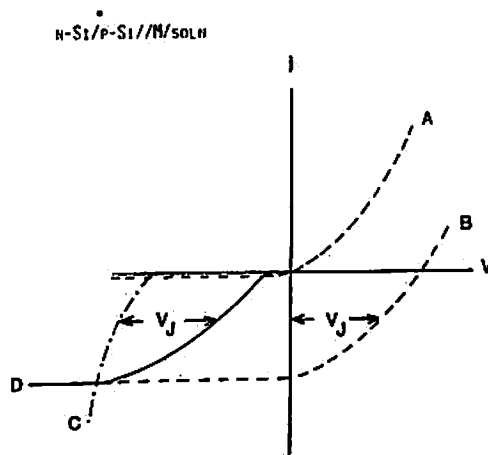


Fig. 4 Representative j - V curves for system $\text{InGa/n-Si}^*/\text{PtSi}/\text{Fe}^{3+}, \text{Fe}^{2+}$. (A) voltage drop ($\Delta V = V_J$) at $n\text{-Si}/\text{PtSi}$ junction in the dark; (B) as A, under illumination; (C) j - V curves (V_{ref} SCE) at $\text{PtSi}/\text{solution}$ junction alone; (D) as C, under bias from illuminated junction in B. [68]

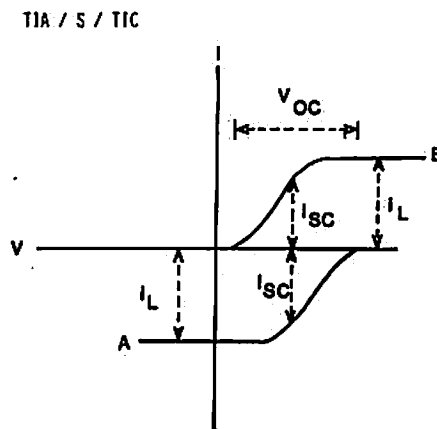


Fig. 5 Representative curves for TISES system (equation (5)). (A) TIA; (B) TIC. V_{OC} = open-circuit voltage, i_{sc} = short circuit current, i_L = limiting photocurrent. [68]

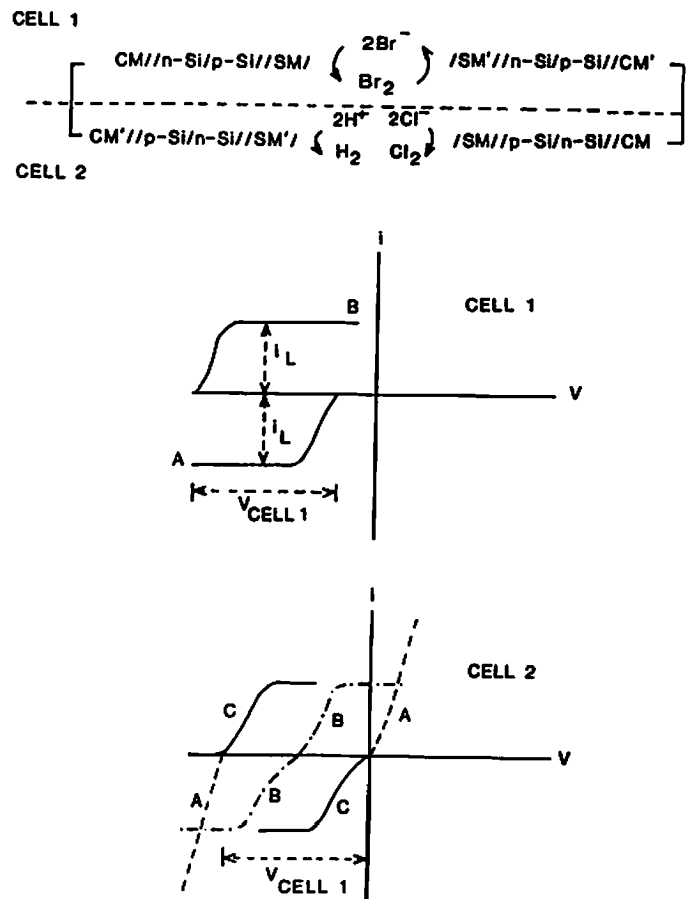


Fig. 6 Schematic representation of dual cell photoarray system.
 TOP: i - V curves for cell 1, (A) TIA; (B) TIC (see Fig. 5).
 BOTTOM: i - V curves for cell 2, (A) (---) Pt electrode in HCl; (B) (---) TIA and TIC in HCl under illumination; (C) (—) as in B, under bias from cell 1. [68]

To obtain photovoltages larger than 1.5 - 2 V, either multijunction electrodes with two (or more) photoactive junctions in each electrode must be employed or the PEC cells must be coupled together. An example of the latter arrangement is the coupling of two TISES arrays in two photocells: (a)

TIC/S/TIA and (b) TIC/S'/TIA to produce an open-circuit photovoltage of 2.2 V across solution S'. For example, solution S can be a single redox couple (Br_2/Br^-), so that this cell behaves as a photovoltaic cell and provides a bias to cell (b) which adds to the photovoltage developed there. The method of connection of these cells and the relevant i-V curves are shown in Fig. 6 for the reaction, $\text{HCl} \longrightarrow 1/2\text{H}_2 + 1/2\text{Cl}_2$, with a $\Delta G^\circ = 1.36 \text{ eV}$ ($\text{pH} = 0$). Note that the i-V curves for a single TIA and TIC in HCl show poor overlap, so that use of a single array in 11.6 M HCl gives no observable photocurrent. When this cell is biased by a second cell containing 1.0 M $\text{Br}_2/1.0 \text{ M KBr}$, a short-circuit current density of 7.3 mA cm^{-2} and an open circuit photovoltage of 2.0 V is obtained (a tungsten-halogen lamp illumination of 170 mW cm^{-2}) [68]. This represents an efficiency of about 5.8%, when the output power is taken as the power that would be obtained by consuming the products, H_2 and Cl_2 , in a fuel cell at the same current density as that found in their production.

NEW SYSTEMS AND STRUCTURES

While systems which show reasonable stabilities and efficiencies have been produced, practical PEC cells and devices will require less expensive materials and new structures. Thin-film semiconductor materials, especially if they can be produced economically on a large-scale, can replace single crystal or thick polycrystalline semiconductor electrodes. Semiconductor particulate systems have also been shown to be useful for a number of photoreactions [1-3] and are potentially very inexpensive. The major problems with current particulate systems are their rather low efficiencies, the production of both oxidation and reduction products without separation, and the difficulty of holding the particulate photocatalyst in place in large-scale flow systems. Improvements in performance will require new concepts in the design of these systems. For example, the particles can be formed and held in a polymer matrix [51,69]. To illustrate this approach, consider the CdS/Nafion system [51]. Nafion is a perfluorinated sulfonate polymer which

can readily incorporate cations [70]. If a Nafion membrane is immersed in a solution containing Cd^{2+} , this ion is incorporated into the membrane. Exposure of this membrane to H_2S causes CdS to precipitate in the membrane. By appropriate regulation of the precipitation conditions, the location of the CdS layer within the membrane can be controlled. It is also possible to incorporate redox couples (mediators or relays), such as methyl viologen (MV^{2+}), into the membrane to produce the system Nafion/ $\text{CdS}/\text{MV}^{2+}$. Irradiation of this initially yellow membrane causes it to turn blue, as photogenerated electrons cause the reduction of MV^{2+} to MV^+ . By incorporation of suitable catalysts, such as Pt, H_2 evolution is also possible. These membrane systems still have not shown vectorial electron transfer with product separation nor the needed efficiencies, however. Alternative configurations involving different types of supports are possible. For example, deposition of semiconductor layers on clays, zeolites, or silica substrates can be carried out. Especially with larger semiconductor particles, absorption of light in the bulk of the particle is probably not useful in carrying out photoreactions, since e^-h^+ recombination probably occurs in the bulk before the photogenerated carriers can reach the surface and react. When the semiconductor is deposited on the surface of a nonabsorbing (large band-gap) substrate, more efficient utilization of the light should be possible. Moreover, the substrate may be useful for incorporation of electron transfer catalysts and other catalyst/support interactions are possible.

CONCLUSIONS

A number of promising devices have emerged for the conversion of radiant energy to chemical energy or electricity, based on work at a number of laboratories. Stable and efficient systems have been demonstrated, but economically useful and practical systems have not yet been attained. Further development of such systems will require new materials and configurations, improvements in efficiencies with polycrystalline and amorphous materials, and fundamentally a better understanding of semiconductor materials and the nature

of the semiconductor/solution interface.

ACKNOWLEDGMENTS

The author is grateful to members of our laboratory, especially F. R. F. Fan, M. Krishnan, G. Nagasubramanian, T. Varco Shea, B. Wheeler, and J. White, for their contributions to this work. The support of the National Science and Robert A. Welch Foundations is gratefully acknowledged. I would also like to thank Texas Instruments and the TISES group for supplying Si arrays and their advice and assistance.

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