AD-A119 305 MASSACHUSETTS INST OF TECH CAMBRIDGE DEPT OF CHEMISTRY F/G 7/2
FUEL AND ELECTRICITY GENERATION FROM ILLUMINATION OF INORGANIC --ETC(U)
AUG 82 M S WRIGHTON N00014-75-C-0880
UNCLASSIFIED TR-34 NL

1 of 1
[illegible]

END
DATE
FILMED
10-82
DTIC

(12)

~~UNCLASSIFIED~~
SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE	READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER ONR TR-34 — 2. GOVT ACCESSION NO. AN9305	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) "FUEL AND ELECTRICITY GENERATION FROM ILLUMINATION OF INORGANIC INTERFACES"	5. TYPE OF REPORT & PERIOD COVERED INTERIM TECHNICAL REPORT 6. PERFORMING ORG. REPORT NUMBER N00014-75-C-0880
7. AUTHOR(s) MARK S. WRIGHTON	8. CONTRACT OR GRANT NUMBER(s) NR 051-579
9. PERFORMING ORGANIZATION NAME AND ADDRESS DEPARTMENT OF CHEMISTRY MASSACHUSETTS INSTITUTE OF TECHNOLOGY CAMBRIDGE, MASSACHUSETTS 02139	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
11. CONTROLLING OFFICE NAME AND ADDRESS OFFICE OF NAVAL RESEARCH DEPARTMENT OF THE NAVY ARLINGTON, VIRGINIA 22217	12. REPORT DATE AUGUST 27, 1982 13. NUMBER OF PAGES 39
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)	15. SECURITY CLASS. (of this report) UNCLASSIFIED 15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

DISTRIBUTION UNLIMITED; APPROVED FOR PUBLIC RELEASE; REPRODUCTION IS PERMITTED FOR ANY PURPOSE OF THE UNITED STATES GOVERNMENT

DTIC
ELECTE
SEP 16 1982
S D
E

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

18. SUPPLEMENTARY NOTES

PREPARED FOR PUBLICATION IN ACS SYMPOSIUM SERIES "INORGANIC CHEMISTRY: TOWARD THE 21st CENTURY"

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

photoelectrochemistry, light conversion, semiconductors, interfaces, photoelectrochemical cells

82 09 16 006

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Semiconductor-based photoelectrochemical devices represent good systems for the sustained, direct conversion of light to chemical or electrical energy. The interfacial structure, energetics, and and redox kinetics control the overall performance of such systems. Examples of improvements in efficiency and durability of photoelectrochemical cells stemming from chemical manipulations at semiconductor/liquid electrolyte interfaces illustrate the critical importance of understanding interface properties.

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE
S/N 0102-014-6601

UNCLASSIFIED
SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

OFFICE OF NAVAL RESEARCH

CONTRACT N00014-75-C-0880

Task No. NR 051-579

TECHNICAL REPORT NO. 34

"FUEL AND ELECTRICITY GENERATION FROM ILLUMINATION OF INORGANIC INTERFACES"

by

Mark S. Wrighton

Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

Prepared for publication in the ACS Symposium Series

"INORGANIC CHEMISTRY: TOWARD THE 21st CENTURY"

August 27, 1982

Fuel and Electricity Generation from Illumination of Inorganic Interfaces

Mark S. Wrighton
Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

Prepared for Publication in ACS Symposium Series
"INORGANIC CHEMISTRY: TOWARD THE 21st CENTURY"

FUEL AND ELECTRICITY GENERATION FROM ILLUMINATION OF INORGANIC INTERFACES

Mark S. Wrighton

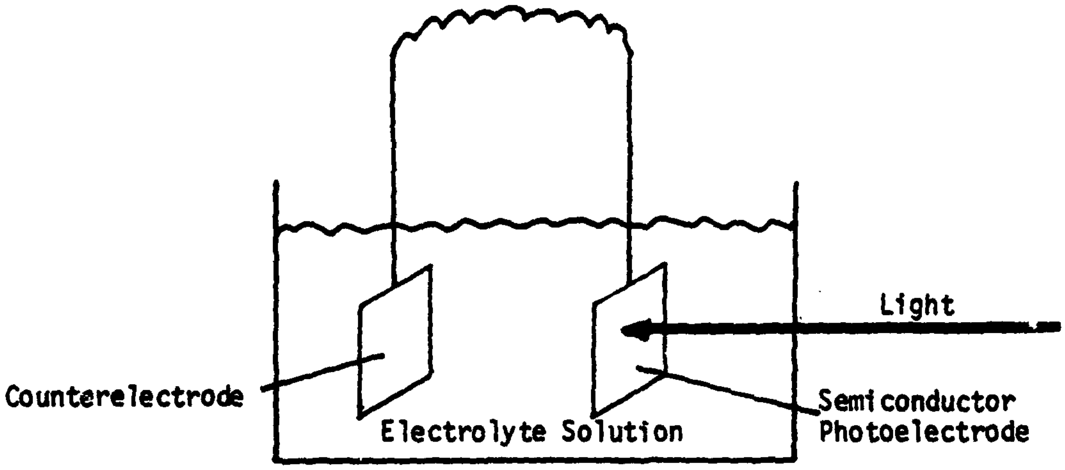
Department of Chemistry, Massachusetts Institute of Technology,
Cambridge, Massachusetts 02139

Abstract: Semiconductor-based photoelectrochemical devices represent good systems for the sustained, direct conversion of light to chemical or electrical energy. The interfacial structure, energetics, and redox kinetics control the overall performance of such systems. Examples of improvements in efficiency and durability of photoelectrochemical cells stemming from chemical manipulations at semiconductor/liquid electrolyte interfaces illustrate the critical importance of understanding interface properties.

Introduction

Inorganic chemistry at interfaces is crucial to a large number of processes, systems, and devices that have practical consequence now and into the 21st century. Heterogeneous catalyst systems, batteries, fuel cells, field effect transistors, optical and acoustical recorders, sensors, solar cells, and even natural plant photosynthesis are all dependent on interfaces. It is becoming evident that characterization, synthesis, manipulation, and understanding of interfacial properties will comprise a significant fraction of the fundamental effort undergirding many practical applications of inorganic chemistry. With the advent of an arsenal of new spectroscopic probes it is apparent that chemically complex interfaces can be characterized with good resolution. The impact of the structural characterization of interfaces is likely to be as great as from the structural characterization that is commonplace for relatively small molecular entities. Elucidation of molecular structure plays a central role in the understanding of reactions and leads to insight into details of mechanism and electronic structure. Exploitation of interfaces in inorganic-based systems can continue with no new insights. However, as the 21st century approaches inorganic chemists have the opportunity to contribute heavily to the understanding of interfaces and rational application of basic knowledge to better use interfaces.

One current basic research endeavor involves the use of illuminated interfacial chemical systems to bring about the sustained conversion of optical energy to chemical or electrical energy. In fact, semiconductor-based photoelectrochemical cells like that in Scheme I represent the best chemical systems for the direct conversion of optical energy to electrical energy or to chemical energy in the form of high energy redox products.[1] In such devices the light-absorbing semiconductor electrode immersed in an electrolyte solution comprises a photosensitive interface where thermodynamically uphill redox processes can be driven with optical energy. Depending on the nature of the photoelectrode, either a reduction or an oxidation half-reaction can be light-driven with the counterelectrode being the site of the accompanying half-reaction. N-type semiconductors are photoanodes, p-type semiconductors are photocathodes,[2-4] and intrinsic materials[5] can be either a photoanode or a photocathode depending on the nature of the contact by both the liquid and the wire of the external circuit. Within the past decade remarkable progress has emerged from conscious efforts to understand and improve semiconductor-based photoelectrochemical cells. Systems based on n-type GaAs,[6,7] n-type WSe_2,[8,9]



Scheme I Semiconductor-based photoelectrochemical cell. Energy output may be in the form of electricity by putting a load in series in the external circuit or the output can be in the form of chemical energy as redox products formed at the electrodes. N-type semiconductors effect uphill oxidations upon illumination and p-type semiconductors effect uphill reductions under illumination. Either or both electrodes in the cell can be a photoelectrode.

and p-type InP[10,11] have been shown to be able to convert sunlight with greater efficiency than the widely regarded minimum useful efficiency of 10% for large scale energy generation from sunlight in the United States.[12]

The aim of this presentation is to highlight both recent advances and to identify problems associated with illuminated semiconductor electrodes for optical energy conversion. Results from this laboratory will be highlighted. Practical applications, if they come at all, will be important in the 21st century and beyond. However, though the prospects for large scale energy generation from sunlight may appear dim, it is clear that existing fossil fuel reserves are finite, fission nuclear power has an uncertain future, and fusion does not work now and may not work in the future. Solar chemical conversion schemes do work on a large scale as evidenced by the natural photosynthetic apparatus. Existing solar insolation is far greater than man's needs. The research effort required to fully investigate interfacial solar conversion schemes is worth expending when viewed against the possible return and the prospect that other alternatives may prove unacceptable from a technical, social, political, economic, or safety standpoint.

Semiconductor/Liquid Electrolyte Interface Energetics

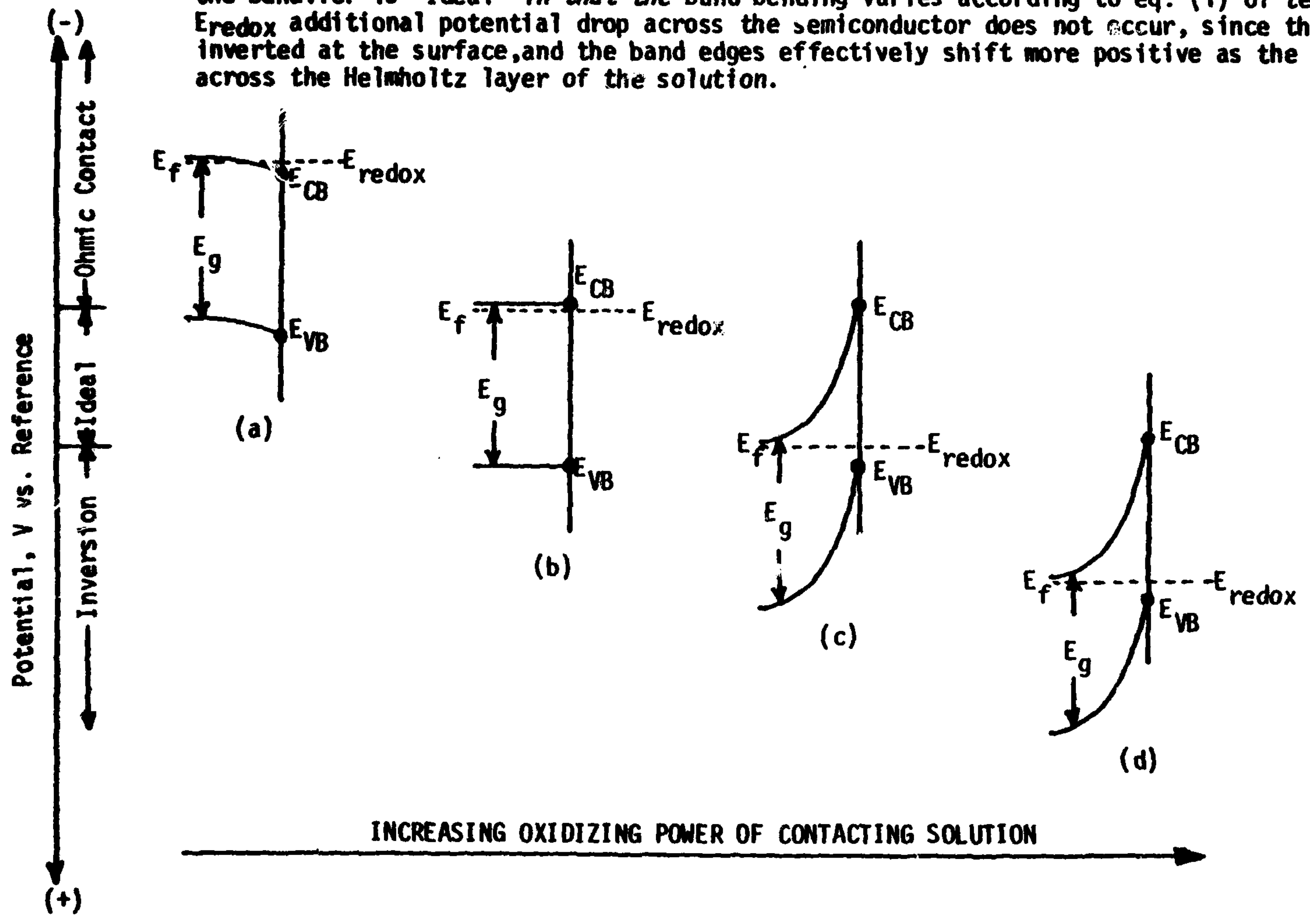
Schemes II and III represent the equilibrium interface energetics for ideal n- and p-type semiconductors, respectively, for contact by electrolyte solutions containing different redox reagents that vary in electrochemical potential, E_{redox}.[2-4,13] For E_{redox} sufficiently negative for n-, or sufficiently positive for p-type, semiconductors the electrode behaves as a metallic electrode, not blocking the flow of electrons in either direction. This situation is analogous to the criteria for forming an ohmic contact to an n- or p-type semiconductor.[14] When E_{redox} is between the top of the valence band, E_{VB}, and the bottom of the conduction band, E_{CB}, the p-type semiconductor is blocking to reductions and the n-type semiconductor is blocking to oxidations in the dark. The minority carrier (e^- or h^+ for p- or n-type semiconductors, respectively) is only available upon photoexcitation with $>E_g$ light and is driven to the interface, owing to the field in the semiconductor near the surface. The availability of the minority carrier at the interface upon photoexcitation allows oxidation with h^+ or reduction with e^-, and importantly the oxidizing power of the h^+ for n- and the reducing power for p-type semiconductors can be greater than that associated with the electrochemical potential (Fermi level), E_f, in the bulk of the semiconductor. This means that light can be used to drive thermodynamically non-spontaneous redox processes. The extent to which a process can be driven in an uphill sense is the photovoltage, E_V, that is given by equation (1) for ideal

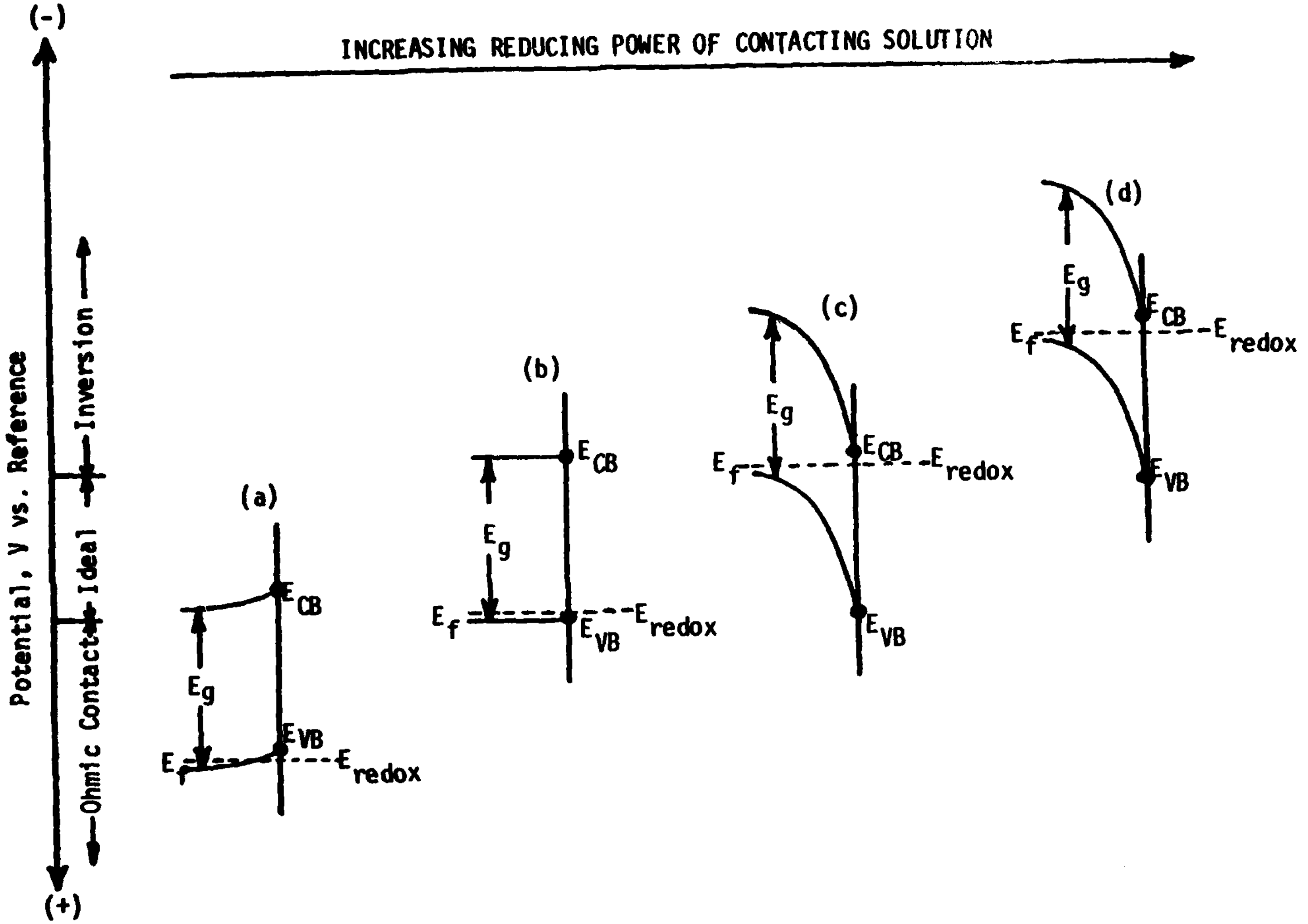
$$E_V = |E_{FB} - E_{redox}| \qquad (1)$$

(For E_{redox} between E_{CB} and E_{VB})

semiconductors where E_{FB} is the flat-band potential, i.e. the value of E_f where the bands are not bent. For commonly used carrier concentrations E_{FB} is within 0.1 V of E_{VB} for p-type semiconductors, and for n-type semiconductors E_{FB} is within 0.1 V of E_{CB}. Thus, $>E_g$ illumination of a semiconductor electrode at open-circuit tends to drive E_f to E_{FB}, more positive for p-type

Scheme II Representation of the interface energetics for an ideal n-type semiconductor in contact with electrolyte solutions of differing E_{redox}. For E_{redox} more negative than the flat band potential, shown in (b), there is little band bending (no barrier) and the electrode is reversible with respect to the redox couple and is said to be in ohmic contact, (a). For E_{redox} between the flat band potential and some positive potential represented in (c) the drop in potential occurs across the semiconductor and the behavior is "Ideal" in that the band bending varies according to eq. (1) of text. For more positive E_{redox} additional potential drop across the semiconductor does not occur, since the semiconductor is inverted at the surface, and the band edges effectively shift more positive as the potential drop occurs across the Helmholtz layer of the solution.





Scheme III Representation of the interface energetics for an ideal p-type semiconductor in contact with electrolyte solutions of differing E_{redox}. The situation is analogous to the n-type semiconductor except that the more postive E_{redox} gives an ohmic contact and the most negative E_{redox} gives inversion. For E_{redox} between the flat band potential, (b), and some negative potential the behavior is "Ideal" in that the band bending varies according to eq. (1) of the text.

electrodes and more negative for n-type electrodes compared to dark equilibrium where $E_f = E_{redox}$.

Ideally, the maximum value of E_V approaches the band gap, E_g, of the semiconductor. However, $\sim$0.3 V of band bending is required to efficiently separate the e^- - h^+ pairs created by light. The separation of e^- - h^+ pairs is essential to obtain a high quantum yield for net electron flow, Φ_e. In any energy conversion application the efficiency, η, for the photoelectrode is given by equation (2), and since i is proportional to Φ_e it is desirable to

$$\eta = \frac{E_V \times i}{\text{Input Optical Power}} \tag{2}$$

i = photocurrent

obtain a large value of Φ_e. Good E_V at $i = 0$ (illuminated, open-circuit) or good i at $E_V = 0$ (illuminated, short-circuit) are both situations that give $\eta = 0$. The objective is to optimize the product of E_V and i in order to achieve the maximum efficiency. Figure 1 shows a steady-state photocurrent-voltage curve[15] for an n-type WS_2 (E_g = 1.4 eV) photoanode-based cell for conversion of light to electricity employing the Br_2/Br^- redox couple and the inset shows the full cell energetics for operation at the maximum power point, the value of E_f when $E_V \times i$ is maximum. Figure 2 shows a similar curve for a cell based on p-type WS_2 employing $Fe(\eta^5\text{-}C_5Me_5)_2^{+/0}$ as the redox couple.[16] In solar energy applications an E_g in the range 1.1-1.7 eV is desirable, since a single photoelectrode based device would have optimum solar efficiency, exceeding 20, for such band gaps.[12]

The WS_2 electrodes represent n- and p-type semiconductors that behave relatively ideally[15,16] with respect to interface energetics in that the value of E_V does vary with E_{redox} according to equation (1) for E_{redox} within $\sim$0.8 V of E_{FB}. However, for many electrode materials the variation in E_V does not follow equation (1).[17] For example, n-type CdTe (E_g = 1.4 eV) can give either a constant value of E_V (independent of E_{redox}) or a nearly ideal variation in E_V, Figure 3, depending on the pretreatment of the surface prior to use.[18] The ability to improve the value of E_V from the constant value of $\sim$0.5 V to $\sim$0.9 V using a reducing surface pretreatment is clearly desirable, but at the same time certain oxidation reactions can be driven in an uphill sense using the oxidizing pretreatment that could not be done with the CdTe pretreated with the reducing reagent.

For CdTe it is evident that the surface pretreatment chemistry is related to the value of E_V. In fact, Auger and X-ray photoelectron spectroscopy reveal a correlation of the E_V vs. E_{redox} behavior related to the composition of the surface of CdTe.[18] The oxidizing surface etch leaves a Te-rich overlayer that causes the CdTe to behave as if it is coated with a metal having a work function that gives a Schottky barrier height of $\sim$0.6 V. In the liquid junction system the analogue of Schottky barrier height is the $E_{redox} - E_{CB}$ or $E_{redox} - E_{VB}$ separation for p- or n-type semiconductors. If a Schottky barrier is immersed into a liquid electrolyte solution the value of E_V should be independent of E_{redox}, as found from n-type CdTe after an oxidizing pretreatment.

Generally, when E_V is fixed for a wide range of E_{redox} the semiconductor is said to be "Fermi level pinned".[17] Fermi level pinning simply means that the value of E_f at the surface of the semiconductor is pinned to some value relative to the band edge positions, independent of the electrochemical potential of a contacting solution or work function of a contacting metal. The pinning of the E_f is due to surface states of sufficient density and distribution. Thus, the presence of surface states can alter the behavior of a semiconductor photoelectrode with respect to output efficiency vs. E_{redox} owing to a limitation on E_V. The degree of alteration in behavior depends on the surface state distribution. For n-type CdTe the value of E_V is fixed to ~0.5 V, a relatively small fraction of the band gap. For p-type InP (E_g = 1.3 eV) it would appear that the surface state distribution is such that the value of E_V is fixed to ~0.8 V,[11] a much larger fraction of the band gap. Understanding and controlling surface states is thus crucial to development of efficient semiconductor-based devices.

Even for ideal (surface-state free) semiconductors the behavior with respect to E_V vs. E_{redox} can be confusing. For the ideal p- or n-type semiconductor sufficiently negative or positive E_{redox}, respectively, will result in carrier inversion at the surface of the semiocnductor, Schemes *II* and III.[14,19] In the region of E_{redox} where there is inversion the semiconductor photoelectrode can still effect uphill redox processes upon illumination and E_V can be independent of E_{redox}. The Fermi level, relative to the band edge positions, simply cannot be driven significantly more negative than E_{CB} or more positive than E_{VB}. Thus, for a range of E_{redox} the band edge positions vary with E_{redox} in a manner similar to when surface states between E_{CB} and E_{VB} pin the Fermi level. In the ideal case it is the high density of states from the valence or conduction band that eventually gives an E_V that is independent of E_{redox}.

When the observed value of E_V is a large fraction of E_g it is not easy to determine whether surface states pin E_f or whether a tailing density of valence or conduction band states effect pinning. Whenever the E_V exceeds $1/2E_g$ there is a measure of carrier inversion at the surface at dark equilibrium, but this does not mean that strong inversion is possible. Strong inversion can only occur when the region between E_{CB} and E_{VB} is sufficiently free of states that E_V can approach E_g. Generally, it is difficult to effect strong inversion when the semiconductor is in contact with any conductor, including liquid electrolyte solutions. The metal chalcogenides, MoS_2, $MoSe_2$, WS_2, and WSe_2, seem to be closest to ideal of the semiconductors studied, though there still seems to be a role for surface states.[15,16,20] A material such as n-type CdTe that gives a fixed E_V at $<1/2E_g$ must be one that is Fermi level pinned by states between E_{CB} and E_{VB} . Fermi level pinning would also appear to apply to photoelectrode materials such as $SrTiO_3$,[21] TiO_2,[21] InP,[11] GaAs,[22] and Si.[23]

Manipulating surface states of semiconductors for energy conversion applications is one problem area common to electronic devices as well. The problem of Fermi level pinning by surface states with GaAs, for example, raises difficulties in the development of field effect transistors that depend on the ability to move the Fermi level at the surface. Interface electronic states need to be understood in all semiconductor-based devices and will continue to be the object of study for the foreseeable future.

The conclusions from these considerations are that semiconductor photoelectrodes can be used to effect either reductions (p-type semiconductors) or oxidations (n-type semiconductors) in an uphill fashion. The extent to which reaction can be driven uphill, E_V, is no greater than E_g, but may be lower than E_g owing to surface states between E_{CB} and E_{VB} or to an inappropriate value of E_{redox}. Both E_g and E_{FB} are properties that depend on the semiconductor bulk and surface properties. Interestingly, E_V can be independent of E_{redox} meaning that the choice of E_{redox} and the associated redox reagents can be made on the basis of factors other than theoretical efficiency, for a given semiconductor. Thus, the important reduction processes represented by the half-reactions (3)-(5) could, in principle, be effected with the same efficiency at a Fermi level pinned (or carrier inverted) p-type semiconductor photocathode. However, as is usual in chemical systems, thermodynamics relates what is possible, but kinetics rule whether a thermodynamically spontaneous process will occur at a practically useful rate.

$$N_2 + 6H^+ + 6e^- \longrightarrow 2NH_3 \qquad (3)$$

$$CO_2 + 2H^+ + 2e^- \longrightarrow HCOOH \qquad (4)$$

$$2H^+ + 2e^- \longrightarrow H_2 \qquad (5)$$

Each of the reduction processes represented in (3)-(5) has great potential practical significance if it could be done efficiently using solar energy. However, each is a multi-electron process having poor heterogeneous kinetics at illuminated p-type semiconductors. Thus, the ability to exploit the available driving force from illumination of a semiconductor will depend on improvements in heterogeneous kinetics for these and other multi-electron redox processes. Success in this particular area will have practical consequence in the future even if semiconductor-based photoelectrochemical devices fail to prove useful. Development of better fuel cells depends on the improvement of heterogeneous redox kinetics of multi-electron processes. If fusion works and provides inexpensive electricity, chemical fuel formation via electrolytic processes may be useful. Again, heterogeneous kientics must be improved. And clearly, heterogeneous catalytic chemistry will continue to be the key to efficient chemical production. The problem of poor heterogeneous kinetics for most fuel-forming reactions is thus one facet of a generic problem pervading much of chemistry.

One additional problem at semiconductor/liquid electrolyte interfaces is the redox decomposition of the semiconductor itself.[24] Upon illumination to create e^- - h^+ pairs, for example, all n-type semiconductor photoanodes are thermodynamically unstable with respect to anodic decomposition when immersed in the liquid electrolyte. This means that the oxidizing power of the photogenerated oxidizing equivalents (h^+'s) is sufficiently great that the semiconductor can be destroyed. This thermodynamic instability is obviously a practical concern for photoanodes, since the kinetics for the anodic decomposition are often quite good. Indeed, no non-oxide n-type semiconductor has been demonstrated to be capable of evolving O_2 from H_2O (without surface modification), the anodic decomposition always dominates as in equations (6) and (7) for n-type CdS[25] and Si,[26] respectively. Protecting visible light

$$CdS + 2h^+ \longrightarrow Cd^{2+}_{(aq)} + S \qquad (6)$$

$$Si + 4h^+ + 2H_2O \longrightarrow SiO_2 + 4H^+_{(aq)} \qquad (7)$$

responsive n-type semiconductors from photoanodic decomposition has been a major activity in the past half dozen years and will continue to be an issue of concern. The p-type semiconductors have not been plagued by gross durability problems, but thermodynamic instability can be a problem in some cases.[24,27] Interestingly, the redox decomposition processes of semiconductors are multi-electron processes that can be sufficiently slow that kinetic competition with desired redox processes can be successful to bring about sustained generation of energy-rich products or electricity from photoexcitation of a photoanode.

Suppression of Photocorrosion of Photoanodes and Manipulation of Kinetics for Anodic Processes

In 1976 the first sustained conversion of visible light to electricity using an n-type semiconductor-based cell (CdS (E_g = 2.4 eV) or CdSe (E_g = 1.7 eV)) was reported.[25,27] In the ensuing six years remarkable progress has been realized in this area. The key has been to find reducing reagents, A, that can capture photogenerated oxidizing equivalents, h^+, at a rate that precludes decomposition of the semiconductor, equation (8). The reverse process, equation (9), can then be effected at the counterelectrode to complete

$$A + h^+ \longrightarrow A^+ \qquad (8)$$

$$A^+ + e^- \longrightarrow A \qquad (9)$$

a chemical cycle involving no net chemical change, but yield significant efficiency for electricity generation. Now, a variety of n-type semiconductor/solvent/electrolyte/A^+/A/counterelectrode systems are known to comprise efficient, durable visible light energy to electrical energy.[6-9,15,25,27,28]

Often, there is a potential regime where the process represented by (8) is completely dominant compared to the anodic decomposition of the semiconductor. In some cases, e.g. CdS/S_n^{2-},[29] CdTe/Te_n^{2-},[29] and $MoSe_2/I_3^-$,[30] the redox species interact strongly with the electrode material resulting in changes in E_{FB}. Such strong interactions can be useful in protecting the semiconductor. In the examples cited above, E_{FB} shifts more negative reducing the tendency for anodic decomposition and opening a wider potential regime where the desired oxidation process can be effected without completion from anodic decomposition.

The unique interactions of a semiconductor with solution species, such as $MoSe_2$ with I_3^-,[30] are very likely the sorts of situations that will lead to the first applications of semiconductor photoelectrochemical devices for photochemical synthesis of redox products. Generally, the practical competition will come from conventional, including electrochemical, methods for producing redox reagents. When the semiconductor electrode has unique surface chemistry this can change the product distribution and in some cases it may be that the semiconductor may be the only surface at which a desired reaction will occur efficiently. However, even when a semiconductor is the electrode material of choice it is not clear that light would be used. The desirable interactions that exist for a p-type photocathode, for example, would likely exist as well for the oppositely doped, n-type, material. The reductions that require light at the p-type electrode can be effected in the dark at the n-type material. Also, degenerately doped semiconductors often behave well in the dark and are not blocking to any redox processes. However, the unique chemistry of semiconductor surfaces needs to be elucidated before a verdict can be reached regarding the practical consequences.

The strong interaction of the I_3^-/I^- redox system with the metal dichalcogenide materials was recently exploited[31] to bring about the visible light-driven process represented by equation (10). In 50% by weight H_2SO_4 the reaction as written requires ~0.3 V or driving force, a good match to the

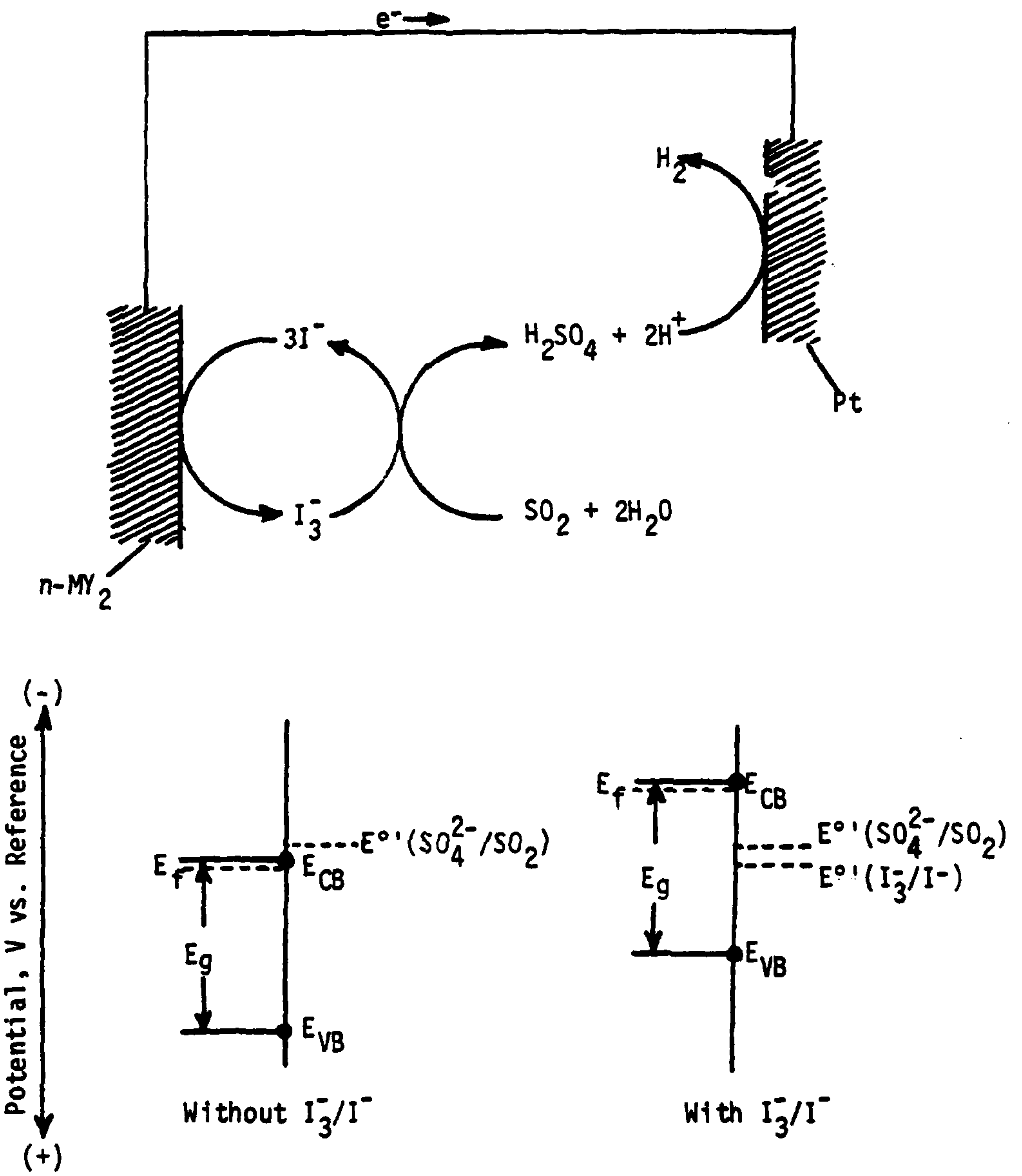
$$SO_2 + H_2O \xrightarrow[\substack{\sim 50\%\ H_2SO_4, \\ \sim 10^{-3}\ \underline{M}\ I^-}]{h\nu} H_2SO_4 + H_2 \qquad (10)$$

photovoltage at the maximum power point for n-type WS_2-based cells for the oxidation of I^-.[15] But the oxidation of SO_2 to SO_4^{2-} in H_2SO_4 has poor kinetics[32] and does not compete with photoanodic decomposition of the electrode. Further, $E_{redox}(SO_4^{2-}/SO_2)$ is such that equation (1) predicts a very small photovoltage.[32] The I_3^-/I^-, though, interacts to shift E_{FB} of WS_2 favorably to give a good E_V with respect to $E_{redox}(SO^{4-}/SO_2)$ and simultaneously provides a mechanism for the oxidation of SO_2, since the I_3^- rapidly oxidizes SO_2 to SO_4^{2-}, Scheme IV. Thus, the I_3^-/I^- serves as a redox mediator and favorably alters the interface energetics to give a good E_V and a potential window of durability. The visible light-driven reaction represented by equation (10) is one of the most efficient optical to chemical energy conversions (up to ~14% from 632.8 nm light) known. The system illustrates the complex relationships that must be understood in order to efficiently drive multi-electron redox processes.

The suppression of photoanodic corrosion is not always difficult. For example, metal dichalcogenides are not durable in aqueous 0.1 M KCl; equation (11) represents the photoanodic decomposition process for MoS_2.[33] However, the

$$MoS_2 + 18h^+ + 8H_2O \longrightarrow 16H^+ + 2SO_4^{2-} + Mo^{6+} \qquad (11)$$

oxidation of low concentrations of Cl^- occurs in CH_3CN solution with 100% current efficiency.[34] Even in aqueous solution the oxidation of Cl^- can be effected at sufficiently high Cl^- activity.[15,35] In aqueous 15 M LiCl the oxidation of Cl^- has 100% current efficiency. The high LiCl concentration yields very high Cl^- activity and lower activity of H_2O, both contributing to the improved durability of illuminated n-type MoS_2.[35] Thus, these experiments show, not surprisingly,[24] that the medium in contact with the semiconductor can alter the overall interfacial chemistry, even though Cl^- is available as a reductant in each case. The ability to effect the sustained generation of Cl_2 at an illuminated interface shows that potent oxidants can be made

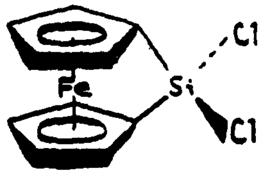


Scheme IV Representation of the I_3^-/I^- mediated oxidation of SO_2 at illuminated metal dichalcogenide photoanodes (top) and interface energetics witho and with I_3^-/I^- in 6M H_2SO_4/1M SO_2 for MoS_2 after ref. 31. Note that in the absence of the mediator system the photovoltage for the SO_2 oxidation would be expected to be negligible. The adsorption of the I_3^-/I^- is unaffected by the SO_2 so the negative shift of the flat band potential can be exploited to give a photovolatge for the desired process with the I_3^-/I^- system simultaneously providing an acceleratio of the SO_2 oxidation.

photochemically; Cl_2 is thermodynamically more potent, and kinetically more agressive, than O_2.

The ability to manipulate the anodic corrosion problem using high concentrations of redox active electrolyte also makes possible the sustained oxidation of Br^- at illuminated metal dichalcogenide-based cells, Figure 1.[15] The use of high concentrations of electrolyte has proven valuable in situations involving other photoanode materials, notably n-type Si.[36,37]

Reducing photoanodic corrosion with high concentrations of redox active materials led to the conclusion that redox reagents covalently anchored to the photoelectrode might prove useful.[38] For example, research showed that n-type Si could be a durable photoanode in EtOH/0.1 M $[n\text{-}Bu_4N]ClO_4/Fe(\eta^5\text{-}C_5H_5)_2{}^{+/0}$ for the generation of electricity.[26] The $Fe(\eta^5\text{-}C_5H_5)_2$ is a fast, one-electron reductant that is durable and gives a durable oxidation product. Subsequent study showed that the reagent represented by I can be polymerized and



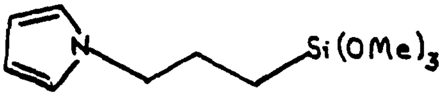
I

attached to the surface of n-type Si to protect it from photoanodic corrosion.[38-40] The important result is that once the electrode is made durable using the surface-confined redox system, $[A^+/A]_{surf.}$, then the photo-electrode can be used to sustain many oxidation processes, say $B \rightarrow B^+$, where B itself is not successful in competing with the anodic corrosion of the electrode. The ability to photooxidize B would then depend on the thermodynamics and kinetics for the interfacial process represented by equation (12) and not the kinetics for h^+ capture by B. It has been shown that

$$[A^+]_{surf.} + B \longrightarrow B^+ + [A]_{surf.} \qquad (12)$$

n-type Si derivatized with I is capable of effecting the photoassisted oxidation of a variety of reagents in H_2O solvent, where the decomposition (7) is most severe.[40] In several cases it has been established that the process represented by (12) represents the dominant path for production of B^+. Thus, in principle, the molecular properties of the surface-confined reagent could be exploited to effect specific reactions. For the surface species derived from I the oxidizing power is fixed to ~+0.45 V vs. SCE, the formal potential, $E^{\circ\prime}$, of the surface reagent.[41] However, the $Fe(\eta^5\text{-}C_5H_5)_2{}^{+/0}$ systems are outer-sphere reagents and do not offer any basis for selectivity other than the potential. However, such species may prove useful in facilitating the redox reactions of biological reagents, vide infra.

Several groups have recently shown[36,42-44] that photoanode materials can be protected from photoanodic corrosion by an anodically formed film of "polypyrrole".[45] The work has been extended[46] to photoanode surfaces first treated with reagent II that covalently anchors initiation sites for the



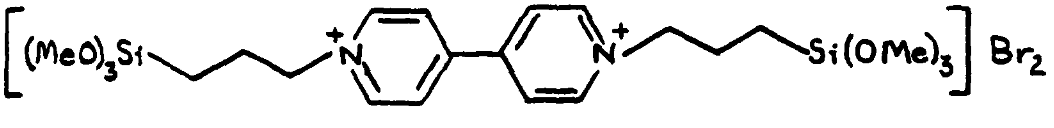
II

formation of polypyrrole. The result is a more adherent polypyrrole film that better protects n-type Si from photocorrosion. Unlike the material derived from polymerization of I, the anodically formed polypyrrole is an electronic conductor.[45] This may prove ultimately important in that the rate of ion transport of redox polymers may prove to be too slow to be useful in attaining useful photoccurrent densities. For the electronically conducting polymer the rate would not be limited by ion transport.

At this point it is evident that there are many approaches to the sustained conversion of visible light using photoanodes. The approaches based on strong interaction, e.g. $WS_2/I_3^-/I^-$,[15] or modified surfaces, e.g. derivatized n-type Si,[38-40] seem most interesting since the unique properties of the interface can be exploited at the molecular level. Significantly, the generation of potent oxidants such as Br_2 or Cl_2 can be effected using visible light and with reasonably good efficiency but without electrode deterioration.

Improving the Kinetics for Hydrogen Generation from P-Type Semiconductors

No naked semiconductor photocathode has been demonstrated to have good kinetics for the evolution of H_2, despite the fact that the position of E_{CB} in many cases has been demonstrated to be more negative than $E°'(H_2O/H_2)$. This means that electrons excited to the conduction band have the reducing power to effect H_2 evolution, but the kinetics are too poor to compete with $e^- - h^+$ recombination. The demonstration that N,N'-dimethyl-4,4'-bipyridinium, MV^{2+}, could be efficiently photoreduced at illuminated p-type Si to form MV^+ in aqueous solution under conditions where $E°'(MV^{2+/+}) = E°'(H_2O/H_2)$ when no H_2 evolution occurs establishes directly that the thermodynamics are good, but the kinetics are poor, for H_2 evolution.[23,47] The ability to efficiently reduce MV^{2+} to MV^+ at illuminated p-type Si led to studies of the surface derivatizing reagent III for use as an electron acceptor on photocathode surfaces.[48]



III

Subsequent deposition of Pd(0) by electrochemical reduction of low concentrations of aqueous $PdCl_4^{2-}$ leads to the interface represented in Scheme V.[49] The Pd(0) is crucial to bring about equilibration of the surface-confined viologen reagent, $[(PQ^{2+/+})_n]_{surf.}$, with the H_2O/H_2 couple. The $[(PQ^{2+/+})_n]_{surf.}$/Pd(0) catalyst system can, in principle, be used on any photocathode surface to improve H_2 evolution kinetics.

The improvement in photoelectrochemical H_2 evolution efficiency using the $[(PQ^{2+/+})_n]_{surf.}/Pd(0)$ system is reflected by the data in Figure 4. For the naked surface, H_2 evolution barely onsets at $E°'(H_2O/H_2)$. For the photoelectrode bearing $[(PQ^{2+/+})_n]_{surf.}/Pd(0)$ the onset for H_2 evolution is up to ~500 mV more positive than $E°'(H_2O/H_2)$. The extent to which the onset is more positive than $E°'(H_2O/H_2)$ is E_V. It is obvious that the modified photoelectrode gives superior performance.

The mechanism of the catalysis for the $p\text{-}Si/[(PQ^{2+/+})_n]_{surf.}/Pd(0)$ system is represented by equations (13) and (14). The $E°'[(PQ^{2+/+})_n]_{surf.} = -0.55 \pm 0.5$ V vs. SCE,[50] independent of pH, whereas $E°'(H_2O/H_2)$ varies with pH.

$$[(PQ^{2+})_n]_{surf.} \xrightarrow{ne^-} [(PQ^+)_n]_{surf.} \qquad (13)$$

$$nH^+ + [(PQ^+)_n]_{surf.} \xrightarrow{Pd(0)} [(PQ^{2+})_n]_{surf.} + 1/2nH_2 \qquad (14)$$

Thus, the catalyzed process represented by (14) is only downhill for sufficiently low pH; at the lower pH's the driving force is greater and the rate is faster. However, as the pH is lowered E_V becomes smaller. This leads to an optimum in overall energy conversion efficiency at pH = 4. For monochromatic 632.8 nm light the efficiency for photoassisted H_2 evolution is up to ~5% whereas naked electrodes have negligible efficiency.[49,50]

The $[(PQ^{2+/+})_n]_{surf.}$ system can also be employed with Pt(0)[50] as the catalyst instead of Pd(0). Both Pt(0) and Pd(0) have excellent H_2 evolution kinetics. One virtue of Pd(0) is that it is much more easily detected by Auger electron spectroscopy than is Pt(0).[49] Auger electron spectra taken while sputtering the surface with Ar^+ ions have led to the establishment of interface structures like that represented in Scheme V. Typically, 10^{-8} mol/cm^2 of PQ^{2+} centers and ~10^{-8} mol/cm^2 of Pd(0) are used to give an overlayer of ~2000 A in dimension. A key feature of the interface represented by Scheme V is that there is no Pd(0) at the p-type Si/SiO_x surface. This means that the only mechanism for equilibrating H_2O/H_2 with the photogenerated reducing equivalents is via the $[(PQ^{2+/+})_n]_{surf.}$ system. Studies have also been done with Pt(0) or Pd(0) dispersed throughout the polymer from III via the sequence represented by equations (15) and (16) for Pd(0).[49] In such cases there is at least a small

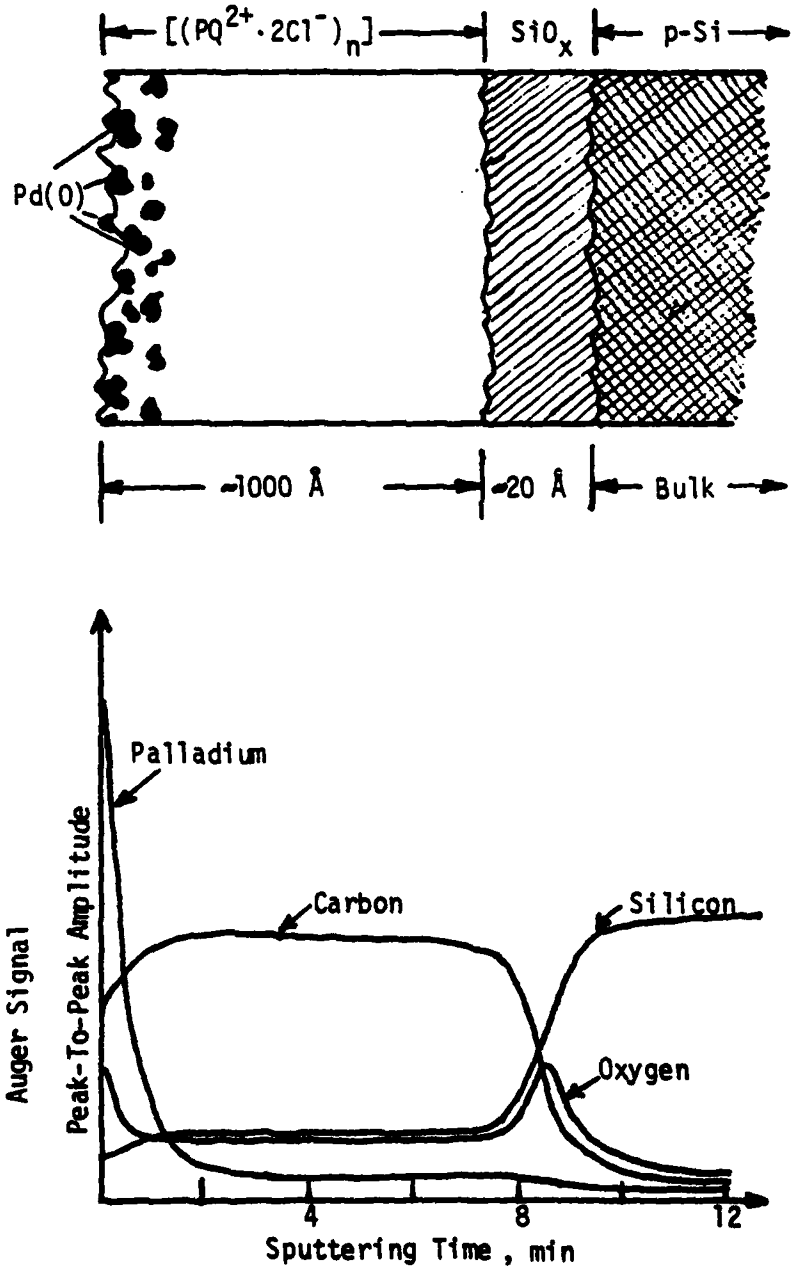
$$[(PQ^{2+}\cdot 2Br^-)_n]_{surf.} + nPdCl_4^{2-} \longrightarrow [(PQ^{2+} \cdot PdCl_4^{2-})_n] + 2nBr^- \qquad (15)$$

$$[(PQ^{2+} \cdot PdCl_4^{2-})_n]_{surf.} \xrightarrow{\text{reduce}} \xrightarrow{\text{oxidize}} [(PQ^{2+} \cdot 2Cl \,.\, Pd(0))_n]_{surf.} \qquad (16)$$

amount of Pd(0) at the p-type Si/SiO_x surface. The Pd(0) at the p-type Si/SiO_x surface should be responsible for some H_2 evolution current density, since the direct deposition of Pd(0) or Pt(0) (without III) onto p-type Si/SiO_x does improve H_2 evolution dramatically.[50,51] Indeed, the direct deposition of catalytic metals onto p-type InP has led to a demonstration of ~12% efficiency for the solar-assisted production of H_2.[52]

The ability to efficiently catalyze the H_2 evolution with a metal deposited onto the p-type semiconductor raises the legitimate question of why

Scheme V Representation of the catalytic p-type Si photocathode for H_2 evolution prepared by derivatizing the surface first with the reagent III in the text followed by deposition of approximately an equimolar amount of Pd(0) by electrochemical deposition. The Auger/depth profile analysis for Pd, Si, C, and O is typical of such interfaces, ref. 49, for coverages of approximately 10^{-8} mol of PQ^{2+} per cm^2.



use III at all, let alone attempt to prepare and exploit the more ordered interface represented by Scheme V. In theory, the efficiency of all devices based on a given semiconductor would be the same. The direct deposition of Pt(0) or the use of $[(PQ^{2+/+})_n]_{surf.}$/Pd(0) are both ways of catalyzing the H_2 evolution. A problem with the redox polymers, as already mentioned, is that rate is likely to be ion transport limited. A problem with Pt(0) and Pd(0) is that they often give an ohmic contact, rather than a Schottky barrier, with p-type semiconductors. For example, in attempting to catalyze H_2 evolution from illuminated p-type WS_2 by electrochemically depositing Pt(0) or Pd(0) a large percentage of the electrodes give an ohmic contact.[16] This results in no photoeffects from the electrode. A uniform coating with the redox polymer from III gives a reproducible, photosensitive surface that can be used to generate H_2 via Pd(0) or Pt(0) deposited on the outermost surface. Neither of the approaches has led to sufficiently durable catalysts that practical devices are at hand; the Pt(0) or Pd(0) is very easily poisoned. Surprisingly, the $[(PQ^{2+/+})_n]_{surf.}$ polymer does not suffer deterioration on the timescale of loss of activity of the Pd(0) or Pt(0) catalyst.

The synthesis of catalytic photocathodes for H_2 evolution provides evidence that deliberate surface modification can significantly improve the overall efficiency. However, the synthesis of rugged, very active catalytic surfaces remains a challenge. The results so far establish that it is possible, by rational means, to synthesize a desired photosensitive interface and to prove the gross structure. Continued improvements in photoelectrochemical H_2 evolution efficiently can be expected, while new surface catalysts are needed for N_2 and CO_2 reduction processes.

A Role for Biological Redox Catalysts?

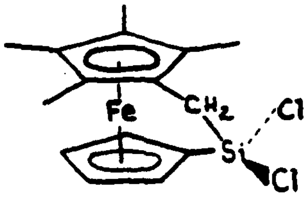
The enzymes hydrogenase, nitrogenase, and formate dehydrogenase can be used to equilibrate reducing reagents with H_2O/H_2, N_2NH_3, and $CO_2/HCOOH$, respectively.[53] In no case do the enzymes involve expensive noble metals as catalysts. Practical considerations aside, the multi-electron transfer catalysis effected by enzymes provides an existence proof for desired photoelectrode catalysts. One of the major difficulties is that large biological redox reagents are often unresponsive at electrode surfaces. For a variety of reasons the heterogeneous electron transfer kinetics for large biological reagents are poor. However, small redox reagents dissolved in solution do equilibrate rapidly with the large biological reagents.[54] Interestingly, MV^+, for example, will effect reduction of H_2O, N_2, or CO_2 when the proper enzyme is present as a catalyst.[53] The use of surface-confined, fast, one-electron, outer-sphere redox reagents like those derived from I or III as redox mediators for biological reagents would seem to represent an excellent approach to the equilibration of the electrode with the biological reagents.

Experiments relating to the oxidation and reduction of ferro- and ferricytochrome c, cyt c(red) and cyt $c_{(ox)}$ from horse heart, establish that photoelectrodes derivatized with molecular reagents can give significantly improved response to biological redox reagents.[55,56] The cyt c provides an example of a readily accessible biomolecule that generally has poor kinetics at electrode surfaces.[57] The first experiments concerned electrodes derivatized with III.[55] The fact that MV^+ rapidly reduces cyt $\underline{c}_{(ox)}$ to cyt $\underline{c}_{(red)}$ led to the use of the $[(PQ^{2+/+})_n]_{surf.}$ for this purpose.[58] The $E°'$(cyt $\underline{c}_{(ox)}$/cyt $\underline{c}_{(red)}$) is ~+0.02 V vs. SCE[59] and the reaction represented by equation (17) is

$$[(PQ^+)_n]_{surf.} + n\ \text{cyt}\ \underline{c}_{(ox)} \longrightarrow [(PQ^{2+})_n]_{surf.} + n\ \text{cyt}\ \underline{c}_{(red)} \qquad (17)$$

thus downhill by ~0.5 V. Interestingly, the process represented by (17) was shown to account for the reduction of cyt c at illuminated p-type Si functionalized with III.[55] The reduction of cyt $\underline{c}_{(ox)}$ at electrodes derivatized with III is mass transport limited and independent of coverage of PQ^{2+} centers on the electrode from ~10^{-10} to 10^{-8} mol/cm^2. Naked electrodes do not respond to the cyt $\underline{c}_{(ox)}$ in the same potential range. Inasmuch as adsorption of cyt c, or impurities contained in it, onto most electrodes leads to overall poor kinetics, it is particularly noteworthy that high concentrations of cyt $\underline{c}_{(ox)}$ can be reduced with good kinetics via the $[(PQ^+)_n]_{surf.}$. Thus, the modification of electrode surfaces with III brings about improvement in response with respect to reduction of cyt $\underline{c}_{(ox)}$.

While experiments with the cyt $\underline{c}_{(ox)}$ at $[(PQ^{2+/+})_n]_{surf.}$ do establish a point, the disparity $E°'$ of the reagent and the mediator precludes the claims that electrodes can in fact equilibrate with the biological reagent. The synthesis of IV has led to the demonstration that derivatized electrodes can be



IV

equilibrated with biological redox reagents.[56] Representing the surface species from IV by $[PMFc^{+/0}]_{surf.}$, the $E°'[PMFc^{+/0}]_{surf.}$ = +0.04 V vs. SCE, that is very close to the $E°'$ for cyt c. Conventional Pt electrodes derivatized with IV can be used to oxidize cyt $\underline{c}_{(red)}$, or reduce cyt $\underline{c}_{(ox)}$ near the $E°'$ of cyt c, via the equilibrium process represented by equation (18).

$$[PMFc^+]_{surf.} + \text{cyt}\ \underline{c}_{(red)} \rightleftharpoons [PMFc^0]_{surf.} + \text{cyt}\ \underline{c}_{(ox)} \qquad (18)$$

Importantly, n-type Si electrodes derivatized with IV can be used in aqueous electrolyte solution at pH = 7 and the process represented by equation (19) can

$$[PMFc^0]_{surf.} + h^+ \longrightarrow [PMFc^+]_{surf.} \qquad (19)$$

be effected in an uphill sense, Ey ~ 300 mV. As on the Pt surface, the $[PMFc^+]_{surf.}$ on n-type Si is capable of effecting the oxidation of cyt $\underline{c}_{(red)}$. Thus, the n-type Si/$[PMFc^{+/0}]_{surf.}$ electrode can be used to effect the uphill oxidation of cyt $\underline{c}_{(red)}$. The rate constant for reaction represented by equation (20) is >7 x 10^3 $M^{-1}s^{-1}$. The observed heterogeneous electron rate constant is >1 x 10^{-4} cm/s for a variety of electrodes independently prepared,

$$[\mathrm{PMFc}^{+}]_{\mathrm{surf.}} + \mathrm{cyt}\ \underline{c}_{(\mathrm{red})} \longrightarrow [\mathrm{PMFc}^{0}]_{\mathrm{surf.}} + \mathrm{cyt}\ \underline{c}_{(\mathrm{ox})} \qquad (20)$$

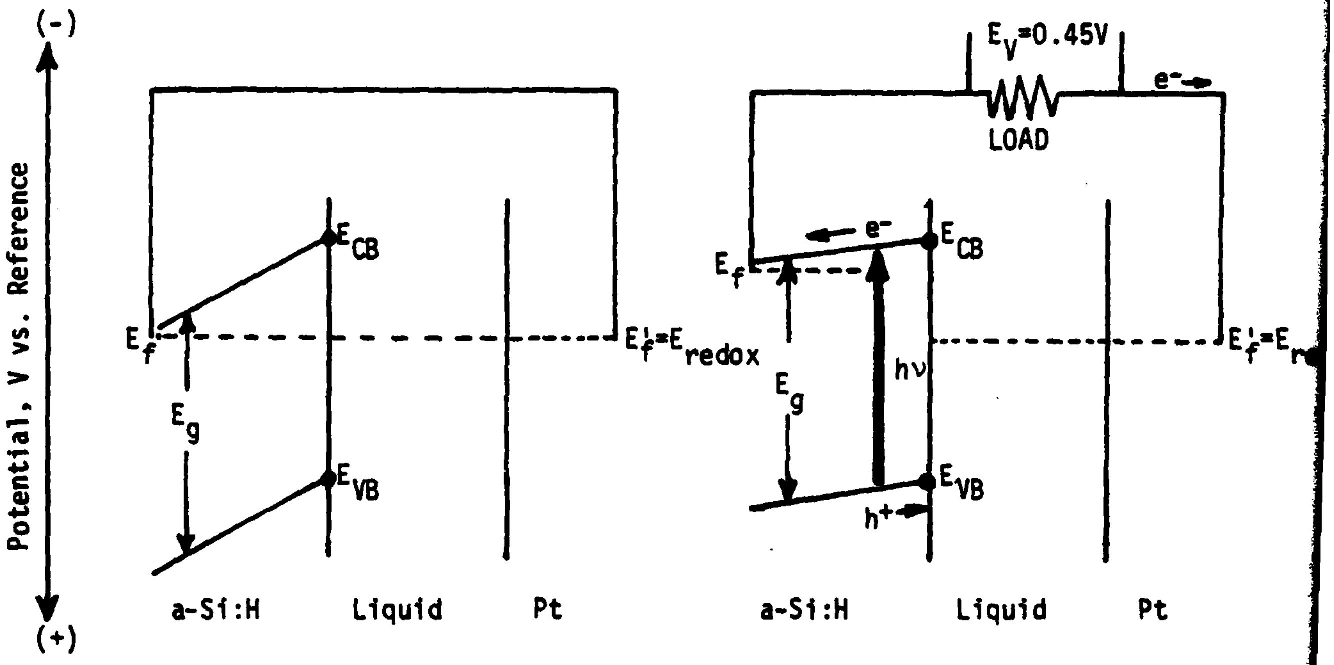
representing substantial improvement compared to naked electrodes that give negligible rates under the same conditions.[56] *Significantly*, as for $[(PQ^{2+/+})_n]_{surf.}$, the $[PMFc^{+/0}]_{surf.}$ is useful at high concentrations of cyt c. Very pure, low concentration cyt c apparently responds well at conventional electrodes, but small amounts of decomposition or impurities cause severe problems from adsorption.[60] The surface reagents from III or IV apparently minimize the adsorption problems, while providing a mechanism for exchanging electrons with the electrode.[55,56] Preliminary results have established that hydrogenase can equilibrate with the polymer derived from III, suggesting that the one-electron polymers from III and IV can in fact come into redox equilibrium with multi-electron transfer catalysts for reactions of possible importance in energy conversion.

Large Area Photosensitive Materials

The studies described so far have concerned relatively small, ~0.1-1 cm^2, single-crystal photoelectrode materials. Promising results have been obtained in that there are a variety of durable, efficient paths to generation of high energy chemicals or electricity. However, single-crystal photoelectrode materials are likely to remain too expensive for significant practical development. The question is whether the basic results from single-crystal systems can be applied to large area photosensitive materials not necessarily fabricated from single crystals. In this area as well some promising results have been obtained. Thin film and/or polycrystalline GaAS[61] and CdX[62] photoanodes have been shown to have relatively good efficiency compared to their single-crystal analogues.

Recently, results from amorphous hydrogenated silicon, a-Si:H, $E_g = 1.7$ eV, obtained in a glow discharge of SiH_4 show significant promise. Solid state devices from solar to electrical energy conversion based on absorption of light by a-Si:H have been shown to have almost 10% efficiency[63] and it is believed that a-Si:H can be produced inexpensively and uniformly in large areas.

In principle, intrinsic photoconductors such as a-Si:H can be good photoelectrodes.[5,64] Scheme VI shows the approximate interface situation for a recently reported a-Si:H-based cell for the generation of electricity.[64] Critically, the intrinsic thin film (1-4 μ) of a-Si:H was deposited onto a very thin (~200 A) heavily n-doped a-Si:H layer on stainless steel in order to assure that the Fermi level contacts the bottom of the conduction band. This means that E_{redox} positions of E_{CB} will result in a field across the photoconductor such that photogenerated h^+'s will be driven toward the electrolyte/redox couple solution. For E_{redox} close to E_{VB} the E_V would be expected to approach E_g as for an n-type semiconductor photoanode. As for any other photoanode the a-Si:H is susceptible to photoanodic decomposition, but the corrosion can be completely suppressed by using the 0.1 M $[n\text{-}Bu_4N]ClO_4/EtOH/Fe(\eta^5\text{-}C_5H_5)_2^{+/0}$ electrolyte/redox couple solution, Figure 5. Interestingly, the sustained conversion of 632.8 nm light is just as efficient for the intrinsic a-Si:H photoanode as for single-crystal n-type Si electrodes under the same conditions.[5]



Scheme VI Representation for the interface energetics for intrinsic a-Si:H at short-circuit, dark equilibrium with ferricenium/ferrocene in EtOH/electrolyte solution (left) and under illumination with 632.8 nm light with a load in series in the external circuit (right). The diagrams are adapted from data in ref. 65 for intrinsic a-Si:H (1-4μ thick) on stainless steel first coated with heavily n-doped a-Si:H (200 Å thick) to insure an ohmic contact near the bottom of the conduction band. In typical experiments E_{redox} is +0.4 V vs. SCE.

The surface of a-Si:H can also be derivatized with reagent I and the E_V is ~750 mV compared to $E_V \approx 500$ mV on single crystal n-type Si.[5] This result suggests that a-Si:H could be durable in aqueous solutions via protection by the surface reagent. As for n-type Si this would allow the use of large area, efficient a-Si:H to effect a variety of light-driven oxidation processes.

Summary

Semiconductor-based photoelectrochemical cells can effect the sustained, direct conversion of light to chemical or electrical energy with good efficiency. There are several approaches to suppressing the photocorrosion of n-type semiconductor photoanodic materials, all depending on the manipulation of interface properties such as structure, energetics, and kinetics. The visible light-driven generation of Cl_2 from photoanodes represents the most potent oxidant generated from non-oxide electrodes. Output parameters depend on surface properties as reflected in experiments with reducing vs. oxidizing pretreatments for n-type CdTe. Interfacial redox kinetics can be modified by rational means as illustrated with results for photocathodes modified to improve H_2 evolution kinetics. However, much more work remains to be done on multi-electron processes to bring about improvements in kinetics. Certain enzymes may prove useful in N_2, CO_2, or H_2O reduction. Progress in relatively efficient, large area, inexpensive photoelectrode materials has been made, with a-Si:H being one example. At this point the performance of interfacial inorganic chemistry systems for energy conversion is sufficiently good that they cannot be ruled out as contenders for large scale energy generation. The near-term, pre-2000 charter is to fully elaborate the basic science underlying the interfacial systems with a conscious effort directed toward efficient (>10%) durable, and inexpensive systems for the direct production of energy-rich redox products from abundant, inexpensive resources such as H_2O and CO_2. It is too early to focus on fuel vs. electricity generation as the ultimate objective. Many of the requirements for both outputs are the same but fuel generation poses the greatest challenge, since useful fuel generation will require new multi-electron transfer catalysts.

Acknowledgements

Research support from the United States Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences is gratefully acknowledged. Support from GTE Laboratories, Inc. and Dow Chemical Company, U.S.A. for aspects of this work is also acknowledged. Partial support from the Office of Naval Research for work on the surface chemistry of CdTe is appreciated.

Literature Cited

1. Wrighton, M.S., Chem. Eng. News, 1979, 57, Sept. 3, p. 29.

2. (a) Wrighton, M.S., Acc. Chem. Rev., 1979, 12, 303;
   (b) Nozik, A.J., Ann. Rev. Phys. Chem, 1978, 29, 189.

3. Gerischer, H., J. Electroanal. Chem., 1975, 68, 263 and in "Physical Chemistry: An Advanced Treatise", Eyring, H., Henderson, D., and Jost, W., eds., Academic Press: New York, 1970, Vol. 9A, Chapter 5.

4. Bard, A.J., Science, 1980, 207, 139 and J. Phys. Chem., 1982, 86, 0000.

5. (a) Rose, A., Phys. Stat. Sol., 1979, 56, 11,
(b) Calabrese, G.S.; Lin, M.S.; Dresner, J.; Wrighton, M.S., J. Am. Chem. Soc. 1982, 104, 0000.

6. (a) Heller, A.; Parkinson, B.A.; Miller, B., Appl. Phys. Lett, 1978, 33, 521;
(b) Heller, A.; Lewerenz, H.J.; Miller, B., Ber. Bunsenges. Phys. Chem., 1980, 84, 592.

7. Ellis, A.B.; Bolts, J.M.; Kaiser, S.W.; Wrighton, M.S., J. Am. Chem. Soc., 1977, 99, 2848.

8. Kline, G.; Kam, K.; Canfield, D.; Parkinson, B.A., Solar Energy Mtls., 1981, 4, 301.

9. Fan, F.R.F.; White, H.S.; Wheeler, H.S.; Bard, A.J., J. Electrochem. Soc., 1980, 127, 518.

10. Heller, A.; Miller, B.; Lewerenz, H.J.; Bachman, K.J., J. Am. Chem. Soc., 1980, 102, 6555.

11. Dominey, R.N.; Lewis, N.S.; Wrighton, M.S., J. Am. Chem. Soc., 1981, 103, 1261.

12. "Solar Photovoltaic Energy Conversion", Ehrenreich, H., ed., The American Physical Society, 335 East 45th Street, New York, New York 10017, 1979.

13. Jaeger, C.D.; Gerischer, H.; Kautek, W.; Ber. Bunsenges. Phys. Chem., 1982, 86, 20.

14. Sze, S.N.,"Physics of Semiconductor Devices", Wiley: New York, 1969.

15. Baglio, J.A.; Calabrese, G.S.; Kamieniecki, E.; Kershaw, R.; Kubiak, C.P.; Ricco, A.J.; Wold, A.; Wrighton, M.S.; Zoski, G.D., J. Electrochem. Soc., 1982, 129, 0000.

16. Baglio, J.A.; Calabrese, G.S.; Harrison, D.J.; Kamieniecki, E.; Ricco, A.J.; Wrighton, M.S.; Zoski, G.D., submitted for publication.

17. Bard, A.J.; Bocarsly, A.B.; Fan, F.R.F.; Walton, E.G.; Wrighton, M.S., J. Am. Chem. Soc., 1980, 102, 3671.

18. (a) Tanaka, S.; Bruce, J.A.; Wrighton, M.S., J. Phys. Chem., 1981, 85, 3778;
(b) Aruchamy, A.; Wrighton, M.S., J. Phys. Chem., 1980, 84, 2848.

19. (a) Turner, J.A.; Manassen, J.; Nozik, A.J., Appl. Phys. Lett., 1980, 37, 488 and ACS Symposium Ser., 1981, 146, 253;
(b) Kautek, W.; Gerischer, H., Ber. Bunsenges. Phys. Chem., 1980, 84, 645;
(c) Nagasubramanian, G.; Bard, A.J., J. Electrochem. Soc., 1981, 128, 1055.

20. (a) Schneemeyer, L.F.; Wrighton, M.S., J. Am. Chem. Soc., 1980, 102, 6964;
(b) White, H.S.; Fan, F.R.F.; Bard, A.J., J. Electrochem. Soc., 1981, 128, 1045.

21. Lin, M.S.; Hung, N.; Wrighton, M.S., J. Electroanal. Chem., 1982, 000, 0000.

22. Fan, F.R.F.; Bard, A.J., J. Am. Chem. Soc., 1980, 3677.

23. Bocarsly, A.B.; Bookbinder, D.C.; Dominey, R.N.; Lewis, N.S.; Wrighton, M.S., J. Am. Chem. Soc., 1980, 102, 3683.

24. Bard, A.J.; Wrighton, M.S., J. Electrochem. Soc., 1977, 124, 1706.

25. Ellis, A.B.; Kaiser, S.W.; Wrighton, M.S., J. Am. Chem. Soc., 1976, 98, 1635.

26. Legg, K.D.; Ellis, A.B.; Bolts, J.M.; Wrighton, M.S., Proc. Natl. Acad. Sci. USA, 1977, 74, 4116.

27. (a) Gerischer, H., J. Electroanal. Chem., 1977, 82, 133;
(b) Park, S.M.; Barber, M.E., J. Electroanal. Chem., 1979, 99, 67.

28. Wrighton, M.S., in "Chemistry in Energy Production", Wymer, R.G. and Keller, O.L., eds., National Technical Information Service, U.S. Department of Commerce, 5285 Port Royal Road, Springfield, Virginia 22161.

29. Ellis, A.B.; Kaiser, S.W.; Bolts, J.M.; Wrighton, M.S., J. Am. Chem. Soc., 1977, 99, 2839.

30. (a) Tributsch, H., J. Electrochem. Soc., 1978, 125, 1086;
(b) Gobrecht, J.; Tributsch, H.; Gerischer, H., J. Electrochem. Soc., 1978, 125, 2085.

31. Calabrese, G.S.; Wrighton, M.S., J. Am. Chem. Soc., 1981, 103, 6273.

32. Lu, P.W.T.; Ammon, R.L.; J. Electrochem. Soc., 1980, 127, 2610.

33. Tributsch, H.; Bennet, J.C., J. Electroanal. Chem., 1977, 81, 97.

34. Schneemeyer, L.F.; Wrighton, M.S.; J. Am. Chem. Soc., 1979, 101, 6496.

35. Kubiak, C.P.; Schneemeyer, L.F.; Wrighton, M.S., J. Am. Chem. Soc., 1980, 102, 6898.

36. Fan, F.R.F.; Wheeler, B.L.; Bard, A.J., J. Electrochem. Soc., 1981, 128, 2042.

37. Results for platinum silicide/Si photoanodes appear very promising in combination with high concentration electrolytes; Bard, A.J., private communication.

38. Wrighton, M.S.; Austin, R.G.; Bocarsly, A.B.; Bolts, J.M.; Haas, O.; Legg, K.D.; Nadjo, L.; Palazzotto, M.C., J. Am. Chem. Soc., 1978, 100, 1602.

39. Bolts, J.M.; Bocarsly, A.B.; Palazzotto, M.C.; Walton, E.G.; Lewis, N.S.; Wrighton, M.S., J. Am. Chem. Soc., 1977, 101, 1378.

40. Bocarsly, A.B.; Walton, E.G.; Wrighton, M.S., J. Am. Chem. Soc., 1980, 102, 3390.

41. Wrighton, M.S.; Palazzotto, M.C.; Bocarsly, A.B.; Bolts, J.M.; Fischer, A.B.; Nadjo, L., J. Am. Chem. Soc., 1978, 100, 7264.

42. Noufi, R.; Tench, D.; Warren, L.F., J. Electrochem. Soc., 1980, 127, 2310 and 1981, 128, 2596.

43. Skotheim, T.; Lundstrom, I.; Prejza, J., J. Electrochem. Soc., 1981, 128, 1625.

44. Noufi, R.; Frank, A.J.; Nozik, A.J., J. Am. Chem. Soc., 1981, 103, 1849.

45. (a) Kanazawa, K.K.; Diaz, A.F.; Geiss, R.H.; Gill, W.D.; Kwak, J.F.; Logan, J.A.; Rabolt, J.; Street, G.B., J. Chem. Soc., Chem. Commun., 1979, 854;
(b) Diaz, A.F.; Castillo, J.J., J. Chem. Soc., Chem. Commun., 1980, 397;
(c) Kanazawa, K.K.; Diaz, A.F.; Gill, W.D.; Grant, P.M.; Street, G.B.; Gardini, G.P. Kwak, J.F., Synth. Met. 1979/1980, 2, 329;
(d) Diaz, A.F.; Vasquez Vallejo, J.M.; Martinez Duran, A, IBM J. Res. Dev. 1981, 25, 42.

46. Simon, R.A.; Ricco, A.J.; Wrighton, M.S.; J. Am. Chem. Soc., 1982, 104, 2031.

47. Bookbinder, D.C.; Lewis, N.S.; Bradley, M.G.; Bocarsly, A.B.; Wrighton, M.S., J. Am. Chem. Soc., 1979, 101, 7721.

48. Bookbinder, D.C.; Wrighton, M.S., J. Am. Chem. Soc., 1980, 103, 5123.

49. Bruce, J.S.; Murahashi, T.; Wrighton, M.S., J. Phys. Chem., 1982, 86, 0000.

50. Dominey, R.N.; Lewis, N.S.; Bruce, J.A.; Bookbinder, D.C.; Wrighton, M.S., J. Am. Chem. Soc., 1982, 104, 467.

51. Nakato, Y.; Abe, K.; Tsubomura, H., Ber. Bunsenges. Phys. Chem., 1976, 80, 1002.

52. Heller, A.; Vadimsky, R.G., Phys. Rev. Lett., 1981, 46, 1153.

53. Summers, L.S., "The Bipyridinium Herbicides", Academic Press: London, 1980, pp. 122-124.

54. (a) Szentrimay, R.; Yeh, P.; Kuwana, T., ACS Symposium Series, 1977, 38, 143;
(b) Heineman, W.R.; Meckstroth, M.L.; Norris, B.J.; Su. C.-H. Bioelectrochem. Bioenerg., 1979, 6, 577;
(c) Kuwana, T.; Heiniman, W.R., Acc. Chem. Res., 1976, 9, 241.

55. Lewis, N.S.; Wrighton, M.S., Science, 1981, 241, 944.

56. Chao, S.; Robbins, J.L.; Wrighton, M.S., J. Am. Chem. Soc., 1982, 104, 0000.

57. Margoliash, E.; Schejtor, A., in "Advances in Protein Chemistry", Anfinsen, C.B.; Anson, M.L.; Edsall, J.T.; Richards, F.M., eds, Academic Press: New York, 1969, vol. 21, chapter 2.

58. Land, E.J.; Swallow, A.J., Ber. Bunsenges. Phys. Chem., 1975, 79, 436.

59. Margalit, R.; Schejter, A., Eur. J. Biochem., 1973. 32, 492.

60. Bowden, E.F.; Hawkridge, F.M.; Chlebowski, J.F.; Bancroft, E.E.; Thorpe, C.; Blount, H.N., submitted for publication and private communication.

61. Heller, A.; Miller, B.I.; Chu, S.S.; Lee, Y.T., J. Am. Chem. Soc., 1979, 101. 7632.

62. Hodes, G., Nature, 1980, 285, 29.

63. Dresner, J., private communication.

64. Cahen, D.; Hodes, G.; Manassen, J.; Vainas, B.; Gibson, R.A.G., J. Electrochem. Soc., 1980, 127, 1209.

Figure Captions

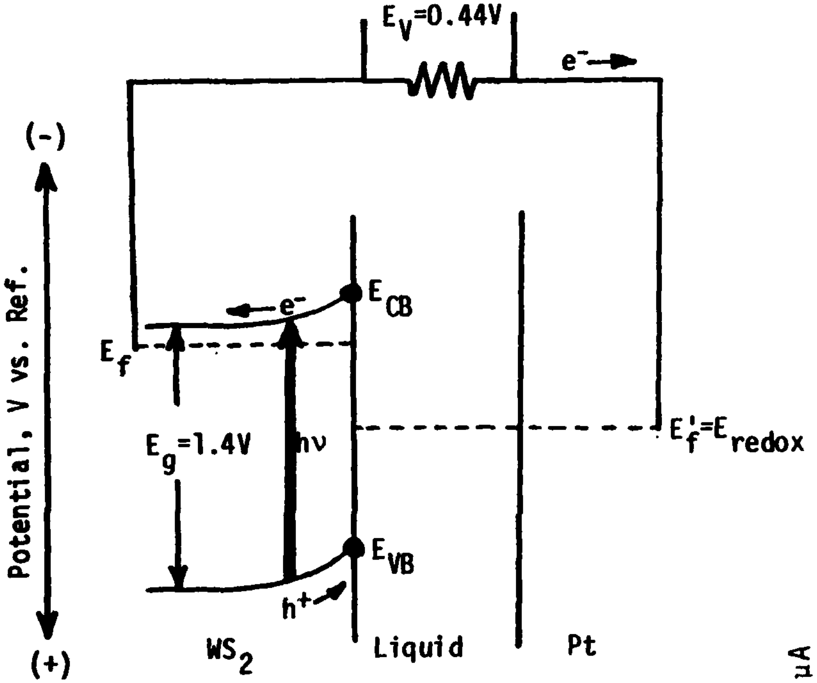
Figure 1. Cell (lower left), cell energetics at maximum power point (upper left) and output characteristics (right) for an n-type WS_2-based photoelectrochemical cell. The electrolyte is 12 M LiBr and E_{redox} = +0.64 V vs. SCE; for current density multiply current shown times 32 cm^{-2}, ref. 15.

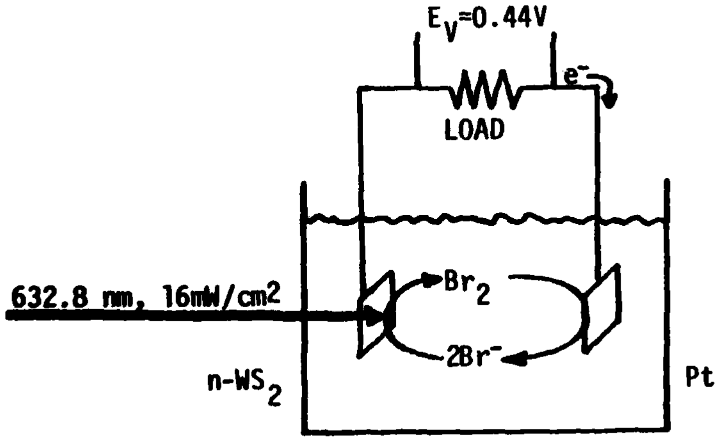
Figure 2. Cell (lower left), cell energetics at maximum power point (upper left) and output characteristics (right) for a p-type WS_2-based photoelectrochemical cell. The Eredox is -0.38 V vs. Ag^+/Ag; for current density multiply current shown by 32 cm^{-2}, ref. 16.

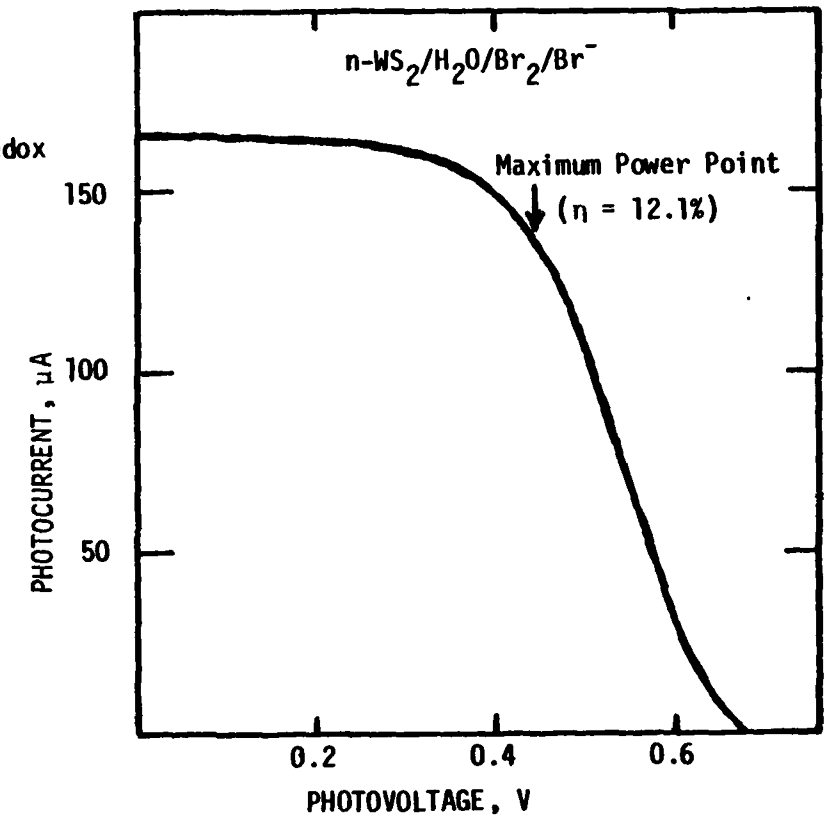
Figure 3. Photovoltage from n-CdTe etched with an oxidizing etch (●) or an oxidizing etch followed by a reducing treatment ($NaOH/S_2O_4{}^{2-}$) (■) is a function of $E_{1/2}$ of a contacting couple. The numbers refer to redox couples: 1-$Ru(bipy)_3{}^{0/-}$; 2-$Ru(bipy)_3{}^{+/0}$; 3-$Ru(bipy)_3{}^{2+/+}$; 4-$TQ^{+/0}$; 5-$TQ^{2+/+}$; 6-$Fe(\eta^5\text{-}C_5Me_5)_2{}^{+/0}$; 7-$Fe(\eta^5\text{-}C_5H_5)_2{}^{+/0}$; 8-$TMPD^{2+/+}$; 9-$TMPD^{+/0}$; 10-$MV^{2+/+}$; 11-$MV^{+/0}$; see ref. 18.

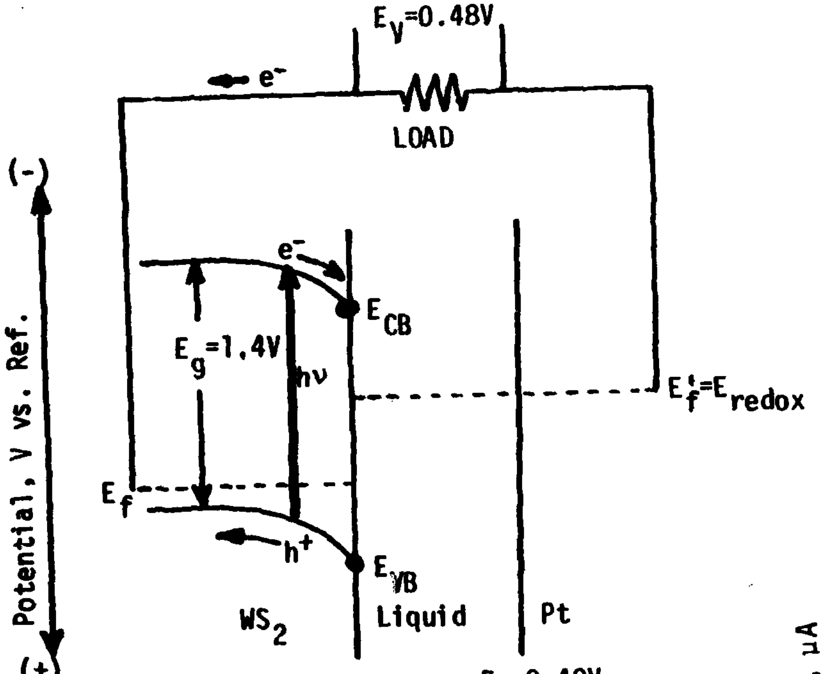
Figure 4. Comparison of photocathodic current (632.8 nm; ~6 mW/cm^2) for naked p-type Si (----), p-type Si bearing $[(PQ^{2+})_n]_{surf.}$, p-type Si bearing $[(PQ^{2+})_n]_{surf.}$ (——), and p-type Si bearing $[(PQ^{2+})_n]_{surf.}/Pd(0)$ (-•-•) at pH = 4. The photocathodic current in the latter case is associated with H_2 evolution that occurs more positive than $E^{0'}(H_2O/H_2)$. For current density multiply values shown by 10 cm^{-2}. The current peak for the smooth curve is associated with the uphill reduction $[(PQ^{2+})_n]_{surf.} \rightarrow [(PQ^{+})_n]_{surf.}$, see ref. 49.

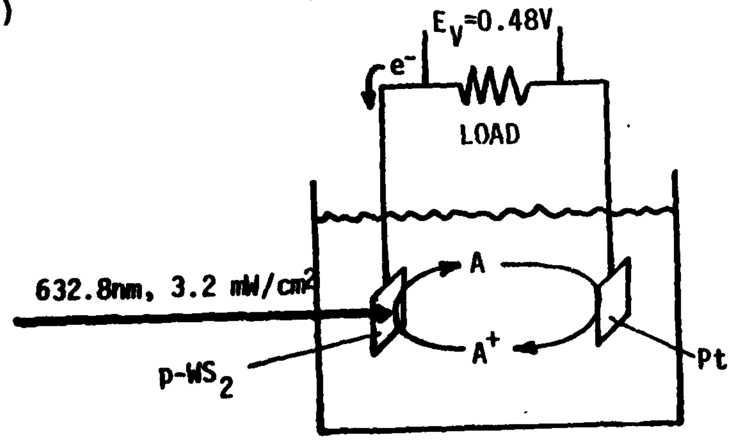
Figure 5. Output characteristics and photocurrent density at maximum power point against time (inset) for an intrinsic a-Si:H photoanode based cell, see ref. 5.

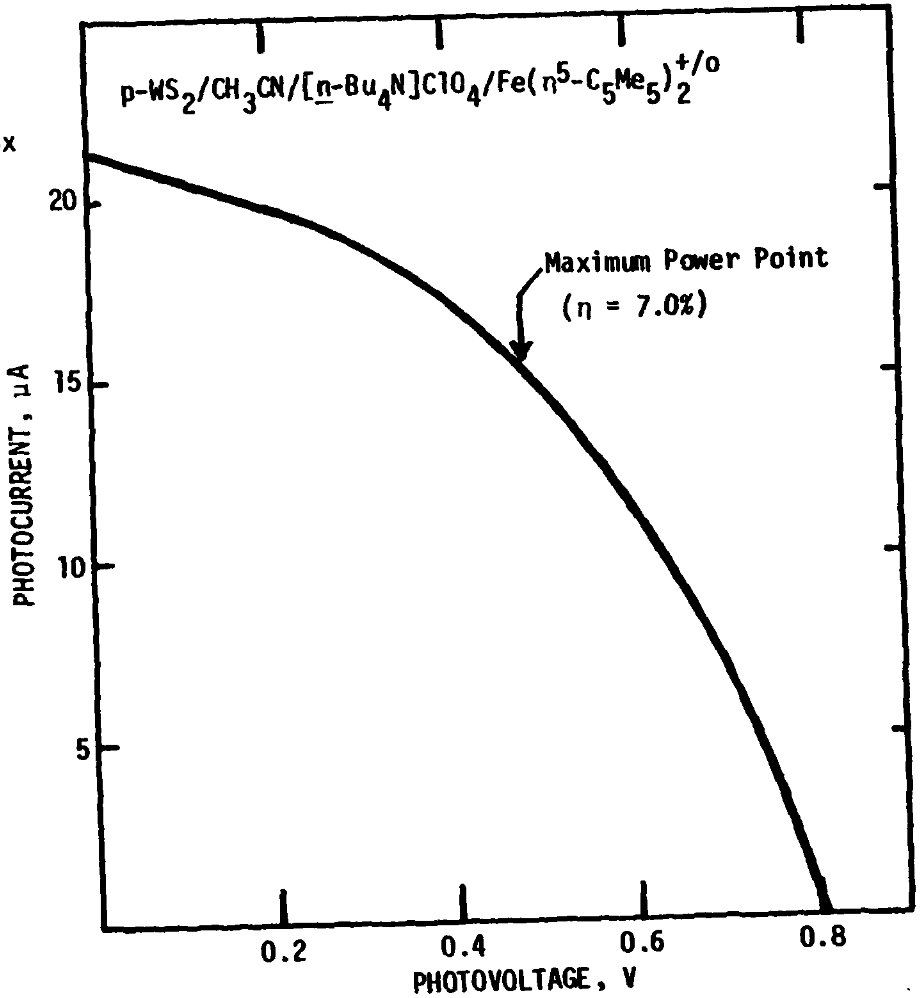

E_V=0.44V
e⁻
(-)
Potential, V vs. Ref.
(+)
E_{CB}
e⁻
E_f
E_g=1.4V
hν
E_f'=E_{redox}
E_{VB}
h⁺
WS_2
Liquid
Pt

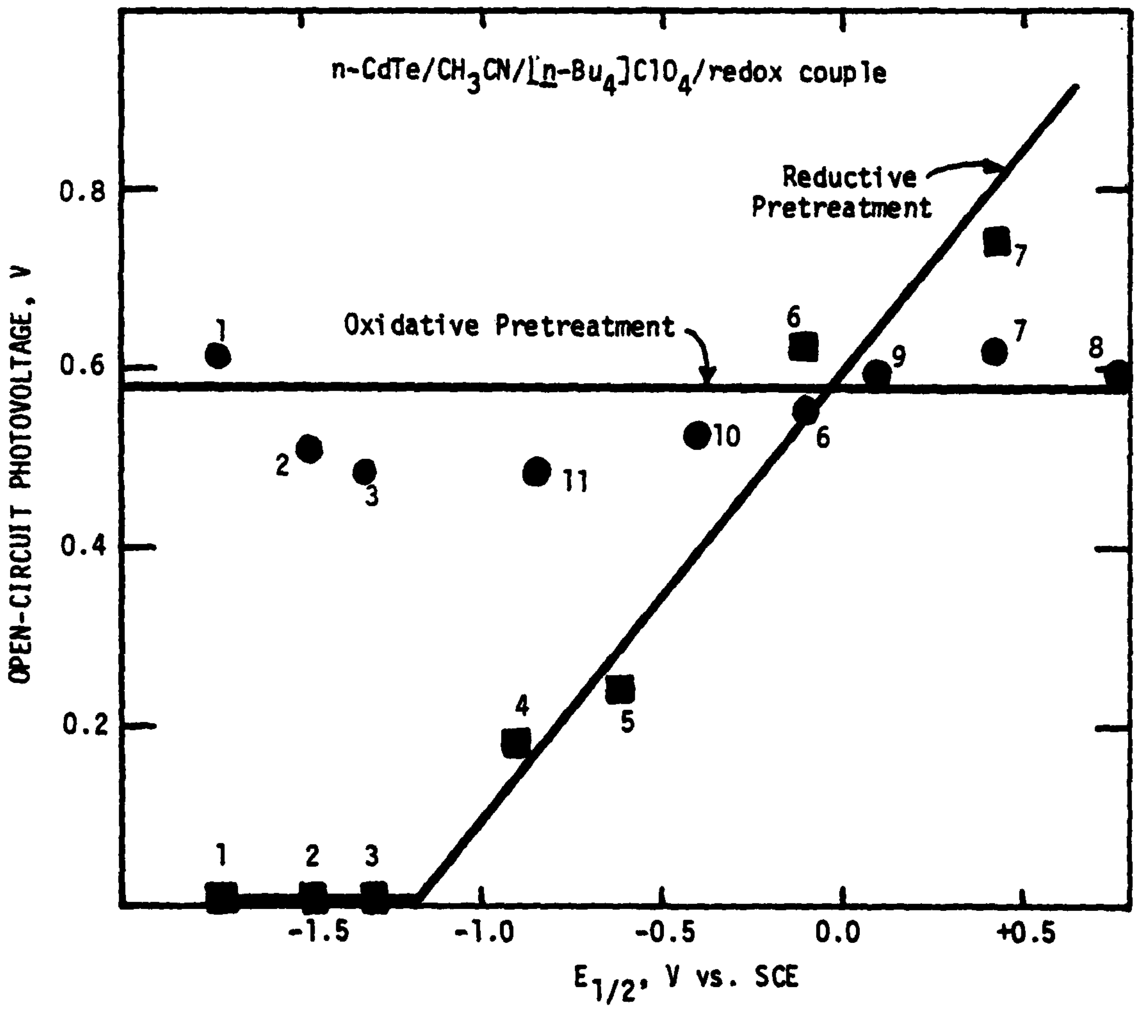

E_V=0.44V
e⁻
LOAD
632.8 nm, 16mW/cm2
Br_2
$2Br^-$
n-WS_2
Pt

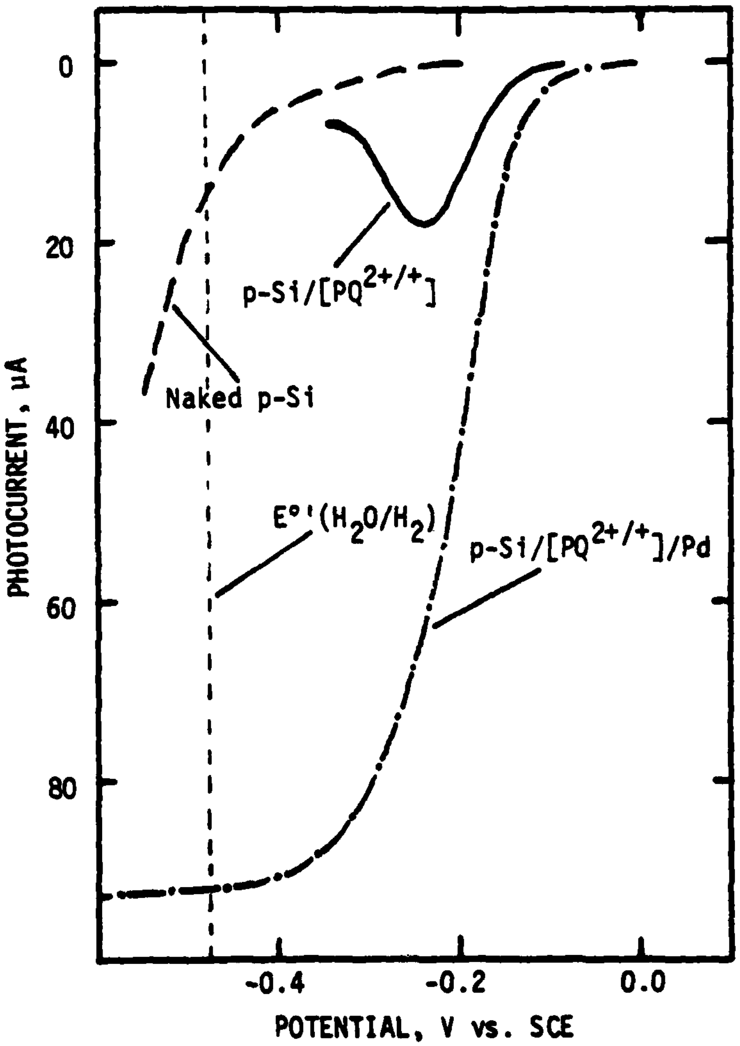

n-$WS_2/H_2O/Br_2/Br^-$
Maximum Power Point
(η = 12.1%)
150
100
50
PHOTOCURRENT, μA
0.2
0.4
0.6
PHOTOVOLTAGE, V

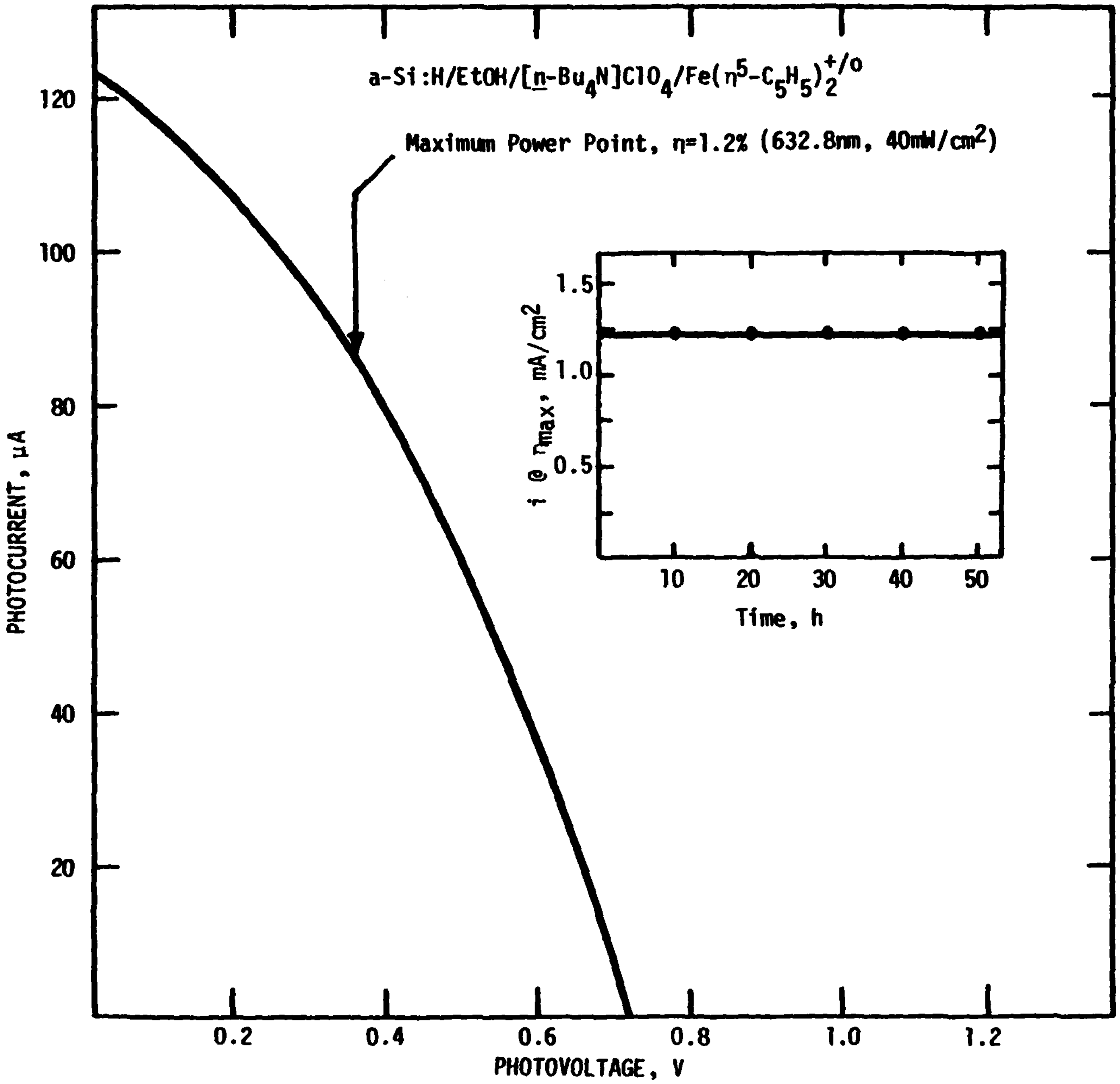

E_V=0.48V
e^-
LOAD
(-)
(+)
Potential, V vs. Ref.
e^-
E_{CB}
E_g=1.4V
$h\nu$
$E_f'=E_{redox}$
E_f
h^+
E_{VB}
WS_2
Liquid
Pt


E_V=0.48V
e^-
LOAD
632.8nm, 3.2 mW/cm^2
A
A^+
p-WS_2
Pt


p-WS_2/CH_3CN/[n-Bu_4N]ClO_4/Fe(η^5-C_5Me_5)$_2^{+/o}$
Maximum Power Point
(η = 7.0%)
PHOTOCURRENT, μA
20
15
10
5
0.2
0.4
0.6
0.8
PHOTOVOLTAGE, V


n-CdTe/CH3CN/[n-Bu4]ClO4/redox couple
Reductive Pretreatment
Oxidative Pretreatment
OPEN-CIRCUIT PHOTOVOLTAGE, V
0.8
0.6
0.4
0.2
-1.5
-1.0
-0.5
0.0
+0.5
E1/2, V vs. SCE
1
2
3
4
5
6
7
8
9
10
11


0
20
40
60
80
PHOTOCURRENT, μA
-0.4
-0.2
0.0
POTENTIAL, V vs. SCE
p-Si/[PQ$^{2+/+}$]
Naked p-Si
E°'(H_2O/H_2)
p-Si/[PQ$^{2+/+}$]/Pd


a-Si:H/EtOH/[n-Bu$_4$N]ClO$_4$/Fe(η^5-C$_5$H$_5$)$_2^{+/o}$
Maximum Power Point, η=1.2% (632.8nm, 40mW/cm^2)
PHOTOCURRENT, μA
120
100
80
60
40
20
0.2
0.4
0.6
0.8
1.0
1.2
PHOTOVOLTAGE, V
i @ η_{max}, mA/cm^2
1.5
1.0
0.5
10
20
30
40
50
Time, h

TECHNICAL REPORT DISTRIBUTION LIST, GEN

	No. Copies
Office of Naval Research Attn: Code 472 800 North Quincy Street Arlington, Virginia 22217	2
ONR Branch Office Attn: Dr. George Sandoz 536 S. Clark Street Chicago, Illinois 60605	1
~~ONR Area Office~~ Disestablished ~~715 Broadway~~ ~~New York, New York 10003~~	1
ONR Western Regional Office 1030 East Green Street Pasadena, California 91106	1
ONR Eastern/Central Regional Office Attn: Dr. L. H. Peebles Building 114, Section D 666 Summer Street Boston, Massachusetts 02210	1
Director, Naval Research Laboratory Attn: Code 6100 Washington, D.C. 20390	1
The Assistant Secretary of the Navy (RE&S) Department of the Navy Room 4E736, Pentagon Washington, D.C. 20350	1
Commander, Naval Air Systems Command Attn: Code 310C (H. Rosenwasser) Department of the Navy Washington, D.C. 20360	1
Defense Technical Information Center Building 5, Cameron Station Alexandria, Virginia 22314	12
Dr. Fred Saalfeld Chemistry Division, Code 6100 Naval Research Laboratory Washington, D.C. 20375	1

	No. Copies
U.S. Army Research Office Attn: CRD-AA-IP P.O. Box 1211 Research Triangle Park, N.C. 27709	1
Naval Ocean Systems Center Attn: Mr. Joe McCartney San Diego, California 92152	1
Naval Weapons Center Attn: Dr. A. B. Amster, Chemistry Division China Lake, California 93555	1
Naval Civil Engineering Laboratory Attn: Dr. R. W. Drisko Port Hueneme, California 93401	1
Department of Physics & Chemistry Naval Postgraduate School Monterey, California 93940	1
Dr. A. L. Slafkosky Scientific Advisor Commandant of the Marine Corps (Code RD-1) Washington, D.C. 20380	1
Office of Naval Research Attn: Dr. Richard S. Miller 800 N. Quincy Street Arlington, Virginia 22217	1
Naval Ship Research and Development Center Attn: Dr. G. Bosmajian, Applied Chemistry Division Annapolis, Maryland 21401	1
Naval Ocean Systems Center Attn: Dr. S. Yamamoto, Marine Sciences Division San Diego, California 91232	1
Mr. John Boyle Materials Branch Naval Ship Engineering Center Philadelphia, Pennsylvania 19112	1

TECHNICAL REPORT DISTRIBUTION LIST, GEN

	No. Copies
Dr. Rudolph J. Marcus Office of Naval Research Scientific Liaison Group American Embassy APO San Francisco 96503	1
Mr. James Kelley DTNSRDC Code 2803 Annapolis, Maryland 21402	1

TECHNICAL REPORT DISTRIBUTION LIST, 359

No. Copies

Dr. Paul Delahay
Department of Chemistry
New York University
New York, New York 10003 1

Dr. E. Yeager
Department of Chemistry
Case Western Reserve University
Cleveland, Ohio 41106 1

Dr. D. N. Bennion
Department of Chemical Engineering
Brigham Young University
Provo, Utah 84602 1

Dr. R. A. Marcus
Department of Chemistry
California Institute of Technology
Pasadena, California 91125 1

Dr. J. J. Auborn
Bell Laboratories
Murray Hill, New Jersey 07974 1

Dr. Adam Heller
Bell Laboratories
Murray Hill, New Jersey 07974 1

Dr. T. Katan
Lockheed Missiles & Space
Co, Inc.
P.O. Box 504
Sunnyvale, California 94088 1

Dr. Joseph Singer, Code 302-1
NASA-Lewis
21000 Brookpark Road
Cleveland, Ohio 44135 1

Dr. B. Brummer
EIC Incorporated
55 Chapel Street
Newton, Massachusetts 02158 1

Library
P. R. Mallory and Company, Inc.
Northwest Industrial Park
Burlington, Massachusetts 01803 1

No. Copies

Dr. P. J. Hendra
Department of Chemistry
University of Southhampton
Southhampton SO9 5NH
United Kingdom 1

Dr. Sam Perone
Department of Chemistry
Purdue University
West Lafayette, Indiana 47907 1

Dr. Royce W. Murray
Department of Chemistry
University of North Carolina
Chapel Hill, North Carolina 27514 1

Naval Ocean Systems Center
Attn: Technical Library
San Diego, California 92152 1

Dr. C. E. Mueller
The Electrochemistry Branch
Materials Division, Research
& Technology Department
Naval Surface Weapons Center
White Oak Laboratory
Silver Spring, Maryland 20910 1

Dr. G. Goodman
Globe-Union Incorporated
5757 North Green Bay Avenue
Milwaukee, Wisconsin 53201 1

Dr. J. Boechler
Electrochimica Corporation
Attention: Technical Library
2485 Charleston Road
Mountain View, California 94040 1

Dr. P. P. Schmidt
Department of Chemistry
Oakland University
Rochester, Michigan 48063 1

Dr. H. Richtol
Chemistry Department
Rensselaer Polytechnic Institute
Troy, New York 12181 1

TECHNICAL REPORT DISTRIBUTION LIST, 359

	No. Copies
Dr. A. B. Ellis Chemistry Department University of Wisconsin Madison, Wisconsin 53706	1
~~Dr. M. Wrighton~~ ~~Chemistry Department~~ ~~Massachusetts Institute~~ ~~of Technology~~ ~~Cambridge, Massachusetts 02139~~	1
Larry E. Plew Naval Weapons Support Center Code 30736, Building 2906 Crane, Indiana 47522	1
S. Ruby DOE (STOR) 600 E Street Washington, D.C. 20545	1
Dr. Aaron Wold Brown University Department of Chemistry Providence, Rhode Island 02192	1
Dr. R. C. Chudacek McGraw-Edison Company Edison Battery Division Post Office Box 28 Bloomfield, New Jersey 07003	1
Dr. A. J. Bard University of Texas Department of Chemistry Austin, Texas 78712	1
Dr. M. M. Nicholson Electronics Research Center Rockwell International 3370 Miraloma Avenue Anaheim, California	1
Dr. Donald W. Ernst Naval Surface Weapons Center Code R-33 White Oak Laboratory Silver Spring, Maryland 20910	1

	No. Copies
Dr. R. P. Van Duyne Department of Chemistry Northwestern University Evanston, Illinois 60201	1
Dr. B. Stanley Pons Department of Chemistry University of Alberta Edmonton, Alberta CANADA T6G 2G2	1
Dr. Michael J. Weaver Department of Chemistry Michigan State University East Lansing, Michigan 48824	1
Dr. R. David Rauh EIC Corporation 55 Chapel Street Newton, Massachusetts 02158	1
Dr. J. David Margerum Research Laboratories Division Hughes Aircraft Company 3011 Malibu Canyon Road Malibu, California 90265	1
Dr. Martin Fleischmann Department of Chemistry University of Southampton Southampton 509 5NH England	1
Dr. Janet Osteryoung Department of Chemistry State University of New York at Buffalo Buffalo, New York 14214	1
Dr. R. A. Osteryoung Department of Chemistry State University of New York at Buffalo Buffalo, New York 14214	1
Mr. James R. Moden Naval Underwater Systems Center Code 3632 Newport, Rhode Island 02840	1

TECHNICAL REPORT DISTRIBUTION LIST, 359

No. Copies

Dr. R. Nowak
Naval Research Laboratory
Code 6130
Washington, D.C. 20375 1

Dr. John F. Houlihan
Shenango Valley Campus
Pennsylvania State University
Sharon, Pennsylvania 16146 1

Dr. M. G. Sceats
Department of Chemistry
University of Rochester
Rochester, New York 14627 1

Dr. D. F. Shriver
Department of Chemistry
Northwestern University
Evanston, Illinois 60201 1

Dr. D. H. Whitmore
Department of Materials Science
Northwestern University
Evanston, Illinois 60201 1

Dr. Alan Bewick
Department of Chemistry
The University
Southampton, S09 5NH England 1

Dr. A. Himy
NAVSEA-5433
NC #4
2541 Jefferson Davis Highway
Arlington, Virginia 20362 1

No. Copies

Dr. John Kincaid 1
Department of the Navy
Stategic Systems Project Office
Room 901
Washington, DC 20376

M. L. Robertson
Manager, Electrochemical
Power Sonices Division
Naval Weapons Support Center
Crane, Indiana 47522 1

Dr. Elton Cairns
Energy & Environment Division
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720 1

Dr. Bernard Spielvogel
U.S. Army Research Office
P.O. Box 12211
Research Triangle Park, NC 27709 1

Dr. Denton Elliott
Air Force Office of
Scientific Research
Bldg. 104
Bolling AFB
Washington, DC 20332 1

TECHNICAL REPORT DISTRIBUTION LIST, 051A

	No. Copies
Dr. M. A. El-Sayed Department of Chemistry University of California, Los Angeles Los Angeles, California 90024	1
Dr. E. R. Bernstein Department of Chemistry Colorado State University Fort Collins, Colorado 80521	1
Dr. C. A. Heller Naval Weapons Center Code 6059 China Lake, California 93555	1
Dr. J. R. MacDonald Chemistry Division Naval Research Laboratory Code 6110 Washington, D.C. 20375	1
Dr. G. B. Schuster Chemistry Department University of Illinois Urbana, Illinois 61801	1
Dr. A. Adamson Department of Chemistry University of Southern California Los Angeles, California 90007	1
~~Dr. M. S. Wrighton~~ ~~Department of Chemistry~~ ~~Massachusetts Institute of Technology~~ ~~Cambridge, Massachusetts 02139~~	1
Dr. M. Rauhut Chemical Research Division American Cyanamid Company Bound Brook, New Jersey 08805	1
Dr. J. I. Zink Department of Chemistry University of California, Los Angeles Los Angeles, California 90024	1
Dr. D. Haarer IBM San Jose Research Center 5600 Cottle Road San Jose, California 95143	1
Dr. John Cooper Code 6130 Naval Research Laboratory Washington, D.C. 20375	1
Dr. William M. Jackson Department of Chemistry Howard University Washington, DC 20059	1
Dr. George E. Walraffen Department of Chemistry Howard University Washington, DC 20059	1

FILME

0-8