

## Thermodynamics and kinetics associated with semiconductor-based photoelectrochemical cells for the conversion of light to chemical energy

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**Abstract** -Semiconductor-based photoelectrochemical cells for the conversion of optical energy to chemical energy presently represent the best man-contrived systems for the direct conversion of solar energy to useful, storable chemical energy. The production of potent oxidants, such as  $\text{Cl}_2$ , and potent reductants, such as  $\text{H}_2$ , with high overall efficiency (>10%) is possible. The aim of this article is to summarize recent significant results and to illustrate the essential thermodynamic and kinetic factors associated with semiconductor-based photoelectrochemical cells.

### INTRODUCTION

Thermodynamics defines the world of chemical possibility, but kinetics control the rate of what happens in chemical systems. In recent years it has become evident that using light to drive otherwise unfavorable reactions is an endeavor where detailed understanding of both thermodynamics and kinetics is crucial to the development of viable systems for the conversion of solar energy to useful, storable chemical energy. The aim of this article is to present the state of the understanding of thermodynamics and kinetics of semiconductor-based cells for conversion of solar energy to chemical energy.

Semiconductor-based photoelectrochemical cells like that illustrated in Fig. 1 have been

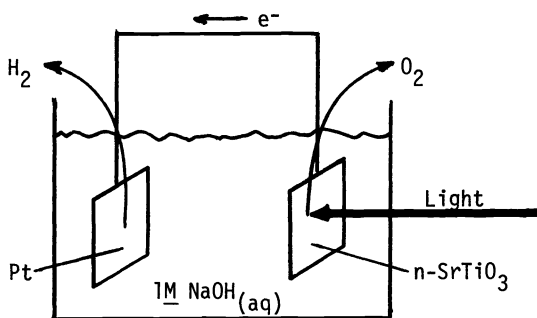


Fig. 1.  $\text{SrTiO}_3$ -based cell for the photoelectrolysis of  $\text{H}_2\text{O}$  according to equation (2).

demonstrated to be relatively efficient systems for solar conversion for three reasons (1). First, the semiconductor/liquid electrolyte interface, Fig. 2, is one which can be treated as a Schottky barrier (2). The barrier provides a mechanism for inhibiting the recombination of photogenerated charge carriers,  $e^-$  and  $h^+$ , with each other or with primary redox products derived from the photogenerated minority carrier ( $h^+$  for n-type semiconductor or  $e^-$  for p-type semiconductor). A large barrier height,  $E_B$ , gives rise to a large photo-voltage,  $E_y$ , and a good quantum yield for electron flow when  $E_y$  is large. A good quantum

yield for electron flow means that the photocurrent will be high. Photocurrent times  $E_y$  is the power delivered from the photoelectrode. The efficiency,  $\eta$ , for the photoelectrode is thus given by equation (1). Note that  $E_y$  is always defined relative to the electrochemical

$$\eta = \frac{(\text{Photocurrent})(\text{Photovoltage})}{(\text{Incident Optical Power})} \times 100\% \quad (1)$$

potential,  $E_{\text{redox}}$ , of the half-reaction occurring at the photoelectrode. At n-type semiconductors  $E_y$  is the extent to which an oxidation process can be effected at an

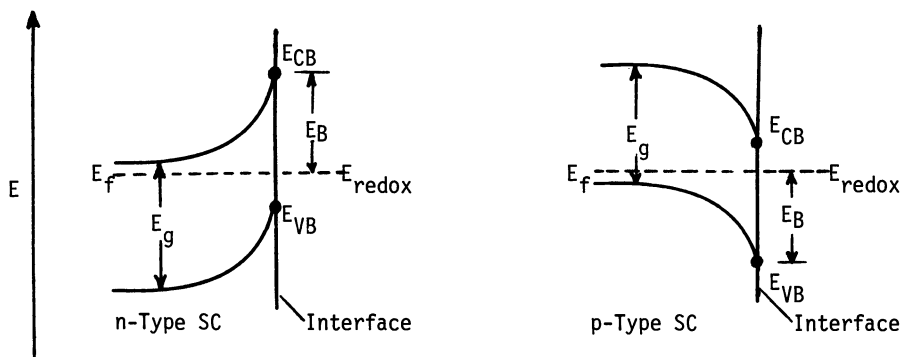


Fig. 2. Interface energetics for an n-type semiconductor (left) and a p-type semiconductor (right) at equilibrium with an electrolyte solution.

electrode potential,  $E_f$ , which is more negative than  $E_{\text{redox}}$  and at p-type semiconductors  $E_y$  is the extent to which a reduction can be effected positive of  $E_{\text{redox}}$ . Fig. 3 represents photocurrent-voltage curves for photoanodes (n-type) and photocathodes (p-type).

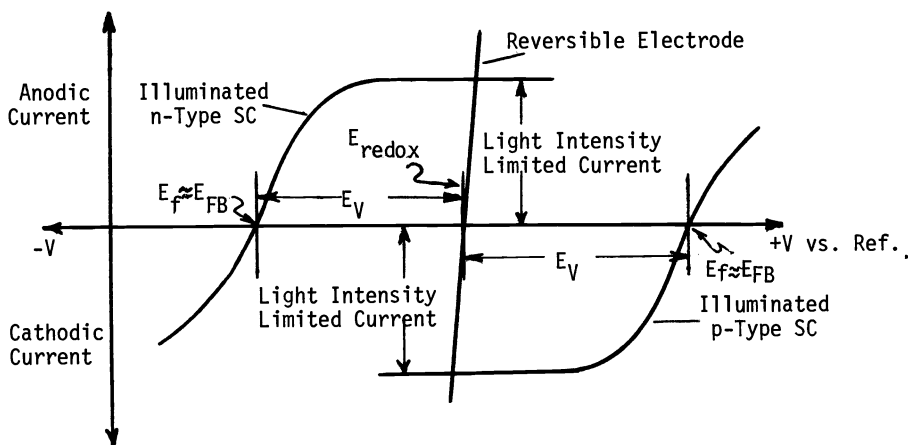
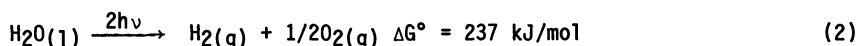


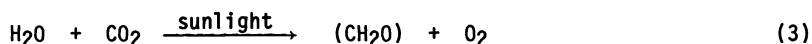
Fig. 3. Comparison of current-potential curves for a reversible electrode and illuminated semiconductor electrodes immersed in a solution containing both halves of a redox couple to poise the solution at  $E_{\text{redox}}$ .

The second reason for high efficiency is that the solid, semiconductor electrode can allow the use of lower energy light than would be absorbed by important reactants such as  $\text{H}_2\text{O}$ . Thus, the electrode is a photosensitizer and allows good response to a large fraction of the light energy available from the Sun. And the third reason for high efficiency is that the semiconductor provides an inherent multi-photon mechanism for reactions that could lead to useful fuel mixtures. The point is that one photon can excite one electron; thus, two moles of photons are required to split a mole of  $\text{H}_2\text{O}$ , equation (2). This fact is important



because thermodynamics for the reaction and a knowledge of the solar spectrum establish that a one photon mechanism would lead to such a low overall efficiency, much less than 10%, that the solar splitting of  $\text{H}_2\text{O}$  would be economically unattractive (3). Many of the important fuel-forming reactions will require sensitization and the use of multi-photon mechanisms, in order to achieve efficient solar conversion processes.

Natural photosynthesis is also an interfacial system involving a multi-photon mechanism for the chemistry represented by equation (3) employing a photosensitizer (chlorophyll) that



involves a unidirectional electron transfer sequence (4). Thus, the natural system for solar to chemical energy conversion and semiconductor-based photoelectrochemical devices have some important features in common, but, of course, the mechanisms of the energy transduction in the two systems differ considerably. An obvious difference is that the natural system is one based on relatively small molecules, while semiconductor-based devices depend on the properties of a semiconductor in contact with an electrolyte solution. In the sections below the essential thermodynamic and kinetic features of semiconductor-based devices will be presented and where possible molecular-based systems for effecting energy storing redox reactions will be compared.

#### ABSORPTION OF LIGHT: OPTIMIZING EFFICIENCY

Wavelength response of semiconductor photoelectrodes is controlled by the band gap,  $E_g$ , of the semiconductor. The value of  $E_g$  is taken to be the minimum energy necessary to raise an electron from the top of the valence band to the bottom of the conduction band (5). In this case, the molecular analogue is the minimum energy necessary to raise an electron from the HOMO to the LUMO in one-electron terms. Thus, whether a semiconductor responds to visible light depends on the value of  $E_g$ . It is known that the optimum value of  $E_g$  is -1.4 eV for semiconductor-based solar devices, where there is one semiconductor absorber in the system (5).

That there is an optimum value for  $E_g$  follows from the spectral distribution of the solar energy and a consideration of what optimizes the available electrical power from the input solar power. Sunlight is roughly a 6000 K black body emitter filtered by the Earth's atmosphere. The net result is that about one-half the energy is above and below 700 nm in wavelength. If  $E_g$  is large much of the incident light will not be absorbed and the efficiency would be low. Low efficiency is obtained, despite the fact that a larger  $E_g$  can give a larger photovoltage,  $E_V$ , because the photocurrent will be low, equation (1). While a very small value of  $E_g$  would lead to good light absorption, a very small value of  $E_g$  does not lead to highly efficient devices either, because the high photocurrent would be offset by a low photovoltage. The problem is that photons of higher energy than  $E_g$  are partially "wasted" in that the excess energy beyond the  $E_g$  is degraded to heat. In molecules, a similar problem exists in that upper excited states generally undergo such rapid nonradiative decay to the lowest excited state that the high energy of an upper excited state cannot be exploited in energy conversion processes that depend on bimolecular redox processes. Calculations show that the overall conversion efficiency for any solar conversion based on a single light absorber for promotion of an electron optimizes to ~30% for an  $E_g$  near 1.4 eV (5).

When two light absorbers are used the maximum efficiency is higher because two different values of  $E_g$  can be used to obtain a better match to the solar spectrum (6). Electrochemical cells would appear to be ideal systems in which to employ two light absorbers since there are two electrodes, both of which could be semiconductor photoelectrodes. Interestingly, the natural photosynthetic apparatus involves two photosystems (4), but the absorption properties and structural arrangement do not allow the higher efficiency that would be possible for a two absorber system. In principle, the highest efficiency for a device would be one where the solar spectrum is dispersed and an infinite number of light absorbers are used to match each wavelength to an  $E_g$ . While this is impractical, this situation gives a thermodynamic limit of ~70% conversion efficiency (6).

To turn to practical matters, it is possible to find many semiconductors and many molecules that could give rise to efficient solar energy conversion systems from the standpoint of absorption properties. It is thus no accident that photoelectrochemical devices employing one photoelectrode based on p-InP ( $E_g = 1.3 \text{ eV}$ ) (7) or n-GaAs ( $E_g = 1.4 \text{ eV}$ ) (8) are among

the most efficient devices. Further, these two materials have a very high absorptivity allowing the use of very thin absorbers compared to weaker absorbers such as Si with an  $E_g$  of 1.1 eV that is also close to the optimum  $E_g$  of 1.4 eV (5). However, while good absorption properties are necessary for high efficiency, other factors must be considered.

#### ENERGETICS FOR PHOTOREDOX PROCESSES

Optical properties of photosensitizers for redox reactions alone do not establish which redox reactions can actually be driven with light. The point is that the reducing power of photogenerated electrons or oxidizing power of photogenerated holes depends on the position, on the electrochemical scale, of the bottom of the conduction band,  $E_{CB}$ , and top of the valence band,  $E_{VB}$ , Fig. 2. Thus, two semiconductors having the same value of  $E_g$  may differ in the positions of  $E_{CB}$  and  $E_{VB}$  in the same sense that two molecules having the same HOMO-LUMO separation may differ markedly with respect to redox properties. Interestingly, however, the range of redox reactions that can be driven at a semiconductor electrode is much wider than when using a molecule where the semiconductor and molecule have the same wavelength response. The following paragraphs elaborate the energetic considerations for light-driven photoredox reactions.

An excited molecule,  $M^*$ , is a more potent oxidant and a more potent reductant than the ground state species,  $M$ . Thus, Fig. 4 represents the order of one-electron redox potentials for an  $M/M^*$  system. The extra oxidizing and reducing power of the excited species compared to the ground state is approximately given by the energy of the excited state compared to the ground state. Whether some species A can be oxidized to  $A^+$  or reduced to  $A^-$  is predictable by knowing  $E^\circ(A^+/A^-)$  and  $E^\circ(A/A^-)$  relative to  $E^\circ(M^*/M^-)$  and  $E^\circ(M^+/M)$ . To take a specific system, consider  $Ru(bpy)_3^{2+}$  as a photoredox sensitizer (9).

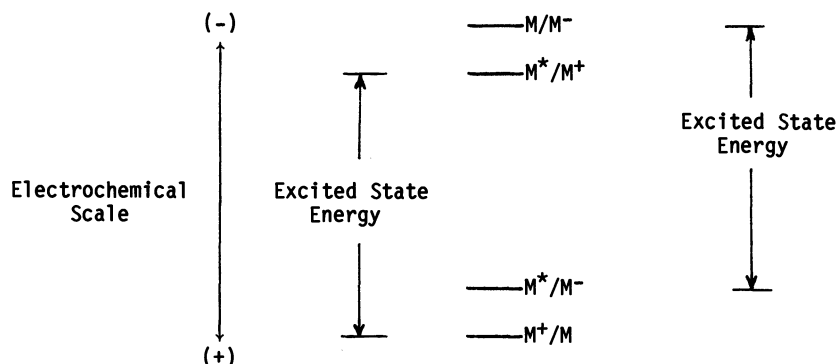
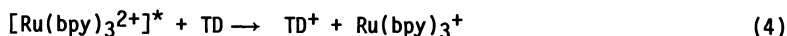


Fig. 4. Ordering of one-electron redox levels for a molecular photosensitizer.

*N,N,N',N'*-tetramethyl-*p*-phenylenediamine (TMPD) and *N,N*-dimethyl-*p*-toluidine (TD) can both be oxidized by the photoexcited  $Ru(bpy)_3^{2+}$ , equations (4) and (5), based on a



consideration of redox potentials. However, the redox process represented by equation (4) would give rise to greater efficiency, since it is thermodynamically more difficult to oxidize TD than TMPD. The point is that the energetics for these one-electron, outer-sphere processes lead to clear-cut, unambiguous predictions regarding which excited state redox processes will occur and which will give the highest efficiency. The key is that the  $E^\circ(M^*/M^-)$  and  $E^\circ(M^+/M)$  potentials are fixed and can be known.

For semiconductor photoelectrodes the prediction of which redox reactions can be effected on energetic grounds and which will give the highest efficiency is also possible. However, the properties of the semiconductor/liquid electrolyte interface give rise to the prediction that a given semiconductor photoelectrode can give the same conversion efficiency for redox couples having very redox different potentials (10). The semiconductor analogue of the excited state redox potentials of molecules are the positions of the bottom of the conduction band,  $E_{CB}$ , and top of the valence band,  $E_{VB}$ , at the interface. When the electrochemical potential,  $E_{redox}$ , of the contacting solution is situated between  $E_{CB}$  and  $E_{VB}$  it is possible to drive a redox reaction in an uphill sense. The extent to which the reaction can be driven in an uphill sense is the photovoltage,  $E_y$ , which can approach the

barrier height,  $E_B$ , at infinitely high light intensity. For an n-type semiconductor  $E_B$  is the difference between  $E_{CB}$  and  $E_{redox}$ , and for a p-type semiconductor the value of  $E_B$  is the difference between  $E_{VB}$  and  $E_{redox}$ . Obviously,  $E_y$  can be maximized when  $E_{redox}$  is as close as possible to  $E_{VB}$  or  $E_{CB}$  for n- or p-type semiconductors, respectively. A good situation is shown in Fig. 2. The essential features are to have as large a value of  $E_B$  as possible and to retain the thermodynamic power to oxidize the redox species with photo-generated  $h^+$  at n-type semiconductors or to reduce the redox species with photo-generated  $e^-$  at p-type semiconductors. The positions of  $E_{CB}$  and  $E_{VB}$  define the maximum reducing power of  $e^-$ 's and  $h^+$ 's, respectively. Thus, the maximum value of  $E_y$  from a semiconductor is  $E_g$ , the separation of  $E_{CB}$  and  $E_{VB}$ . In the same sense, for molecules the maximum energy storable using the excited species is the energy of the excited state, the separation between the ground and excited electronic states.

The seemingly simple energetic criteria that lead to a maximum value of  $E_y$  are somewhat confusing when actually choosing redox systems. The first impression is that very negative or very positive redox couples would not be useful inasmuch as it would seem that the light driven reactions would not be thermodynamically possible. However, for "ideal" semiconductors a wider range of  $E_{redox}$  than spanned by the separation of  $E_{CB}$  and  $E_{VB}$  can, in principle, be useful. "Ideal" semiconductors are those having no surface states between  $E_{CB}$  and  $E_{VB}$ . Fig. 5 illustrates the semiconductor/liquid electrolyte interface situation

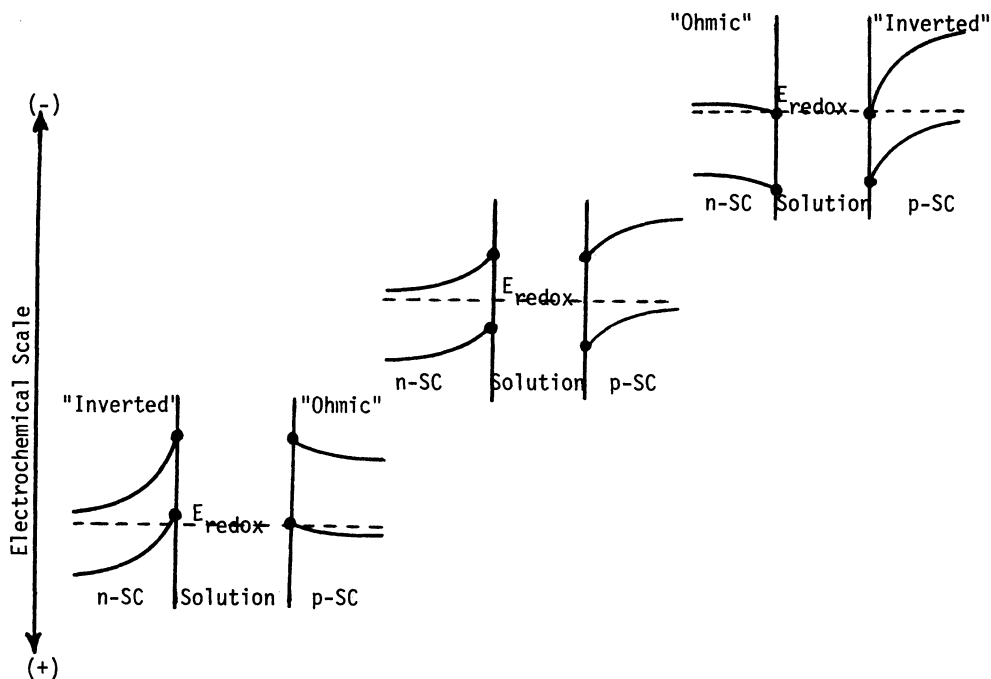


Fig 5. Interface energetics for ideal n- and p-type semiconductors in contact with electrolyte solutions of differing  $E_{redox}$ .

as a function of  $E_{redox}$  for "ideal" n- and p-type semiconductors. The so-called flat band potential,  $E_{FB}$ , is the electrode potential,  $E_f$  where there is no band bending, and for a given solvent/electrolyte/combination is a characteristic of the semiconductor. The value of  $E_{FB}$  can be experimentally determined and is useful in making predictions regarding useful redox couples, since  $E_{FB} \approx E_{CB}$  for n-type semiconductors and  $E_{FB} \approx E_{VB}$  for p-type semiconductors. Often, the onset of photocurrent corresponds to  $E_{FB}$ , Fig. 3. Knowing  $E_{FB}$  allows a prediction of  $E_B$ . When  $E_{redox}$  is more negative than  $E_{CB}$  for n-type semiconductors or more positive than  $E_{VB}$  for p-type semiconductors there is no space-charge layer in the semiconductors,  $E_B \approx 0$ , and no photovoltage is expected. In fact, the semiconductor should respond as would a metallic electrode. In solid state language this is the analogue of an ohmic contact where current can pass in either direction in the dark.

Photovoltage is expected when  $E_{redox}$  is more positive than  $E_{CB}$  for n- or more negative than  $E_{VB}$  for p-type semiconductors, and  $E_B$  can approach the value of  $E_g$ . The minority carrier

process does not occur in the dark. The interesting feature is that  $E_{redox}$  greater than  $E_g$  more positive than  $E_{CB}$  or  $E_g$  more negative than  $E_{VB}$  for n- or p-type semiconductors, respectively, can still be useful. In such cases, the surface of the semiconductor is said to be "inverted". The point is that when the surface undergoes strong inversion of the carrier distribution, the effective positions of  $E_{CB}$  and  $E_{VB}$  change as  $E_{redox}$  is changed, because the potential drop occurs across the Helmholtz layer in the solution and not in the semiconductor. Thus, for the ideal semiconductors the prediction is that photovoltage,  $E_y$ , will go from zero to  $E_y \approx E_B \approx E_g$  as  $E_{redox}$  is varied and that a wide range of positive redox couples at n- or negative redox couples at p-type semiconductors could be useful in achieving as large an  $E_y$  as theoretically possible. Change in the  $E_{CB}$ ,  $E_{VB}$  positions would be analogous to changing the excited state redox potentials of a molecule. For molecules, however, there is no analogue of carrier inversion leading to movement of the excited state redox potentials. Accordingly, the range of useful  $E_{redox}$  values for molecules is narrower than for semiconductors.

The "ideal" model is one where the semiconductor is essentially free of electronic levels between  $E_{CB}$  and  $E_{VB}$ . So-called surface states, of sufficient density and distribution, between  $E_{CB}$  and  $E_{VB}$  lead to different expectations (10). The semiconductors p- and n- $WS_2$  are relatively free of such surface states and do give more or less good agreement with theory with respect to  $E_y$  vs.  $E_{redox}$ , Fig. 6 (11). The lack of  $E_y \approx E_g = 1.4$  V is due to

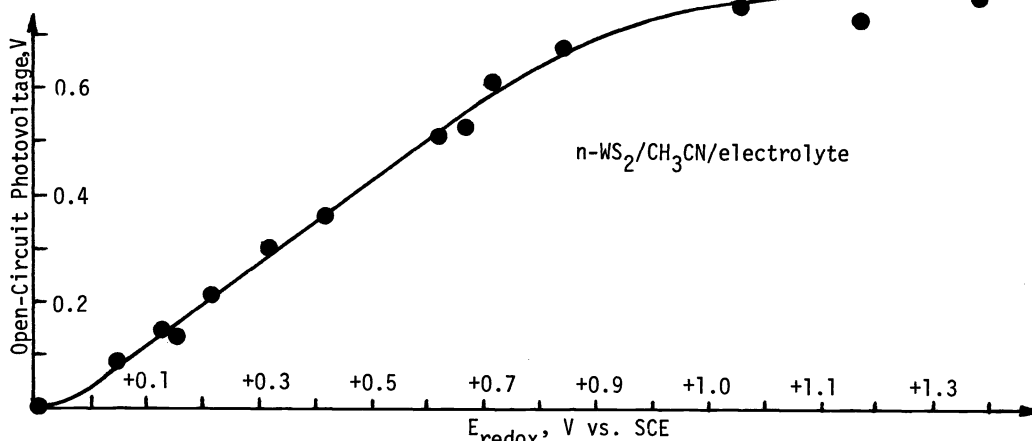


Fig 6. Open-circuit photovoltage vs.  $E_{redox}$  for n- $WS_2$  in  $CH_3CN$ /electrolyte solution (11a).

$e^- - h^+$  recombination and the use of less than infinite excitation rate (light intensity). However, some semiconductors have intrinsic or extrinsic surface states such that  $E_f$  at the surface is fixed relative to  $E_{CB}$  and  $E_{VB}$  (10). In this situation the system is said to be "Fermi level pinned" and there is constant band bending in the semiconductor, independent of  $E_{redox}$ , giving rise to an  $E_y$  that is independent of  $E_{redox}$ . An example of an extrinsically pinned semiconductor is n-CdTe, Fig. 7 (12). The data in Fig. 7 illustrate the

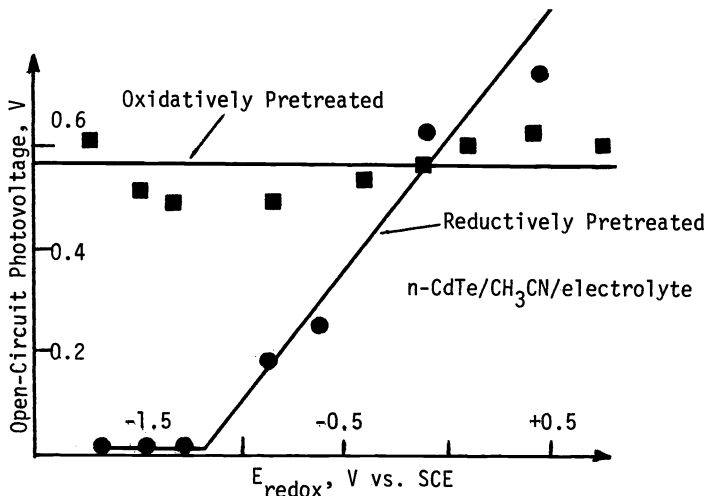


Fig 7. Comparison of photovoltage vs.  $E_{redox}$  for reduced and oxidized n-CdTe (12).

consequence of Fermi level pinning; constant  $E_y$  as a function of  $E_{redox}$ . That the pinning is an extrinsic property is illustrated by  $E_y$  vs.  $E_{redox}$  for n-CdTe that is treated with a reducing etch rather than an oxidizing etch, Fig. 7. The reducing etch gives a nearly stoichiometric, Cd/Te = 1/1, surface and  $E_{redox}$  varies as would be expected for a surface free of surface states (12,13). The oxidizing pretreatments typically used for CdTe give rise to Te-rich overlayers that can be regarded as extrinsic states between  $E_{CB}$  and  $E_{VB}$  of the CdTe (12,13). The interesting finding regarding the pinned n-CdTe is that negative redox couples, that give an ohmic contact to the intrinsic n-CdTe, can give rise to a significant value of  $E_y$ . Thus, the complication of surface states between  $E_{CB}$  and  $E_{VB}$  need not be deleterious, but Fermi level pinned systems do have a maximum value of  $E_y$  that may or may not be as large as for a non-pinned, ideal system. Molecules have no analogue of Fermi level pinning; the excited state redox reactions that are thermodynamically possible are well-defined by knowing the ground state redox potentials and the energy of the excited state.

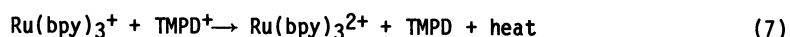
In some instances the distribution and density of surface states of semiconductor leads to neither a completely Fermi level pinned surface nor an "ideal" response to change in  $E_{redox}$ . Interfaces involving Si semiconductors, for example, are sometimes ill-defined owing to the irreproducibility in forming an oxide on the Si surface (14). A pure n- or p-Si (intrinsic surface) would be pinned, but an oxide of the proper stoichiometry can lead to interfaces that behave ideally, and if the oxide is also sufficiently thin, <20 Å, to not be too resistive efficient liquid junction devices can be devised (14). Interfaces involving InP have also been difficult to characterize in solid state and liquid junction devices (7,15). In any event, full characterization of semiconductor interface energetics requires insight into the nature of intrinsic and extrinsic surface properties.

It was indicated above that  $E_{FB}$  for a semiconductor is measured for a given solvent/electrolyte combination. In general, the value of  $E_{FB}$  varies depending on the interaction of solution species with the surface of the semiconductor. For oxide semiconductors  $E_{FB}$  typically varies in aqueous solution as pH is varied, 59 mV/pH (16). This shift in  $E_{FB}$  is due to the acid-base chemistry of the surface with the negative surface charge giving rise to a more negative value of  $E_{FB}$ . Such a shift does have an analogy in molecular systems where redox potentials are pH dependent. However, many molecules have pH independent redox potentials, and many semiconductor surfaces are not influenced by pH. For example, excited  $Ru(bpy)_3^{2+}$  is expected to have pH-independent redox potentials and  $E_{FB}$  of n-CdS appears to be essentially independent of pH (17). The semiconductors having pH dependent  $E_{FB}$  values can, in principle, give different photovoltages for driving pH independent redox reactions. Another interesting fact is that certain solution species can interact strongly with semiconductor surfaces to change  $E_{FB}$ . Perhaps the best example is the interaction of  $I_3^-/I^-$  with n-MoS<sub>2</sub> to effect a negative shift of  $E_{FB}$  of -0.5 V (18). Such specific interactions can, likewise, give rise to a larger than expected photovoltage and provide examples of especially efficient semiconductor/electrolyte/redox couple combinations (18).

#### INHIBITION OF BACK REACTION

The formation of the space-charge layer of the semiconductor, the region of band bending, is what makes it possible to inhibit back electron transfer. Light absorption in the band bending region results in  $e^- - h^+$  generation in a strong field that efficiently brings the minority carrier to the interface available for reaction. The transfer of the minority carrier to a solution species can occur at an electrode potential  $E_f$  where the reverse process should occur in the dark. However, the back electron transfer is inhibited because the majority carrier would have to go over the barrier or tunnel through it, both of which can be slow relative to the rate of some redox process at the counterelectrode. Generally, a barrier (band bending) of -0.4 V can be effective in inhibiting back electron transfer to an extent sufficient to achieve a quantum yield for electron flow of the order of unity (5). The point is that good photocurrent can be obtained when  $E_y$  is good allowing efficient transduction of optical energy to electrical or chemical energy, depending on the nature of the chemical reactions. When the electrode reactions are the reverse of each other the electrical power from the device is just photocurrent times  $E_y$ .

Molecular systems in homogeneous solution do not provide a mechanism for inhibiting back electron transfer. For example, the efficient energy storing redox chemistry represented by equations (4) and (5) is not useful because the back reactions given by equations (6) and (7) waste the stored energy into heat at essentially a diffusion controlled rate. This



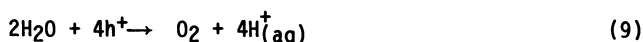
problem plagues homogeneous photoredox systems for optical energy conversion. Thus, despite very efficient light absorption and primary charge transfer, molecular systems have proven to be very inefficient overall. The buildup of the space-charge layer of the semiconductor upon immersion into a solution/electrolyte/redox couple combination is a fundamental advantage that can lead to high efficiency.

#### DURABILITY OF SEMICONDUCTOR ELECTRODES

The most unfortunate difficulties encountered with semiconductor photoelectrodes are problems associated with durability. Photoanodes, n-type semiconductors, especially have been regarded as generally susceptible to degradation. In fact, it has been argued that all n-type semiconductors immersed in an electrolyte solution are thermodynamically unstable when illuminated with  $>E_g$  photons (19). The point is that it is always possible to find an oxidative decomposition process that can occur with holes having the oxidizing power of the top of the valence band,  $E_{VB}$ . For example, CdS undergoes oxidative decomposition in aqueous electrolyte according to equation (8) and the potential for this



decomposition,  $E_p^\circ$ , is  $\sim +0.08$  V vs. SCE (19). The position of  $E_{VB}$  is  $\sim +1.6$  V vs. SCE. Thus, the process represented by equation (8) is downhill by a great deal. The maximum oxidizing power of the  $h^+$  of 1.6 V vs. SCE reflects considerable potency. Oxidation of  $\text{H}_2\text{O}$  to  $\text{O}_2$  according to equation (9) is also thermodynamically possible and in strongly alkaline



media has nearly the same driving force as for oxidative decomposition of CdS. However, kinetics favor the decomposition process to a degree that completely favors irreversible degradation according to equation (8) at any pH. For n-type semiconductors procedures for improving durability have been developed, however, that have yielded durable, efficient devices for conversion of optical energy. Generally, the key to such procedures is to retard the rate of degradation while improving the rate of the desired process.

While no non-oxide photoanodes have been shown to be durable when used to effect  $\text{O}_2$  evolution, some oxide electrodes do give sustained formation of  $\text{O}_2$  at the expense of  $\text{H}_2\text{O}$  according to equation (9). The n-SrTiO<sub>3</sub>-based cell for water splitting is especially durable and has been shown to be capable of effecting  $\text{O}_2$  at a high rate without degradation (20). The oxide photoanodes are susceptible to photoanodic decomposition (19), but the  $\text{H}_2\text{O}$  oxidation process is also thermodynamically viable and is kinetically competitive. Unfortunately, the oxides suffer from too large a value of  $E_g$ , for n-SrTiO<sub>3</sub>  $E_g = 3.2$  V (20), or too small a photovoltage for  $\text{O}_2$  evolution, as for n-Fe<sub>2</sub>O<sub>3</sub> (21), or both a large  $E_g$  and a small  $E_v$ , as for n-SnO<sub>2</sub> (22). In general, small band gap,  $E_g \approx 1.4$  V, non-oxide n-type semiconductors require one of several procedures to suppress degradation.

The durability of p-type semiconductors is also a matter of concern, but the situation is not as severe as with n-type semiconductors. While reductive degradation of p-type semiconductors is possible with electrons having the reducing power of  $E_{CB}$ , some semiconductors are thermodynamically stable with respect to reductive degradation under  $>E_g$  illumination in electrolyte solution (19).

#### KINETICS FOR FUEL-FORMING REDOX REACTIONS

Another problem with semiconductor photoelectrodes is that most of the reactions of interest from the standpoint of forming fuels are multi-electron processes which are kinetically sluggish at most electrodes, e.g. oxidation and reduction of  $\text{H}_2\text{O}$ . In some cases a desired reaction does not occur to any extent, e.g.  $\text{CO}_2 + 8\text{H}^+ + 8e^- \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$ . When the desired photoanodic process is kinetically slow this means that the suppression of oxidative decomposition of the electrode may be difficult. When degradation is not a problem, poor redox kinetics can lead to poor performance because the desired redox reaction cannot be effected at a value of  $E_f$  where the maximum value of  $E_y$  can be achieved.

To illustrate that kinetics, not thermodynamics, can limit the efficiency of a semiconductor photocathode-based cell, consider the light-driven reduction of  $\text{H}_2\text{O}$  to  $\text{H}_2$  vs. the one-electron reduction of N,N'-dimethyl-4,4'-bipyridinium,  $\text{MV}^{2+}$ , to  $\text{MV}^+$  using a p-InP



( $E_g = 1.3$  V) photocathode (23). The  $MV^{2+}/+$  redox couple is a one-electron, outer-sphere redox system that is known to have good heterogeneous electron transfer kinetics and at  $pH \approx 7$  has the same  $E^\circ$  as the  $H_2O/H_2$  redox couple which is regarded as a redox couple with sluggish kinetics at most electrodes (24). The point is that reduction of  $H_2O$  to  $H_2$  or  $MV^{2+}$  to  $MV^+$  requires the same thermodynamic reducing power, but the rate of reduction at an electrode can be very different. At illuminated p-InP the reduction of  $MV^{2+}$  occurs with an  $E_f$  of up to  $-0.8$  V and with very high overall efficiency, but under the same conditions the reduction of  $H_2O$  to  $H_2$  has negligible efficiency (23). This sort of behavior is typical for p-type semiconductors that have been investigated to date. Improving the performance of photocathodes for  $H_2$  evolution requires catalysis of the reaction. In the absence of catalysis the rate for  $H_2$  generation is insignificant at  $E_f$  where  $E_f$  would be high. In some cases the use of photocathodes requires more electrical energy, in addition to the optical energy, than does a conventional reversible electrode!

Kinetics for oxidation processes at illuminated n-type semiconductors are also a problem, but as discussed above, the situation is typically complicated further by the anodic decomposition of the electrode. Much emphasis has been placed on producing  $O_2$  from  $H_2O$ , owing to the fact that a chemical cycle could be completed by combustion of the photo-generated reductant. The oxidation of  $H_2O$  to  $O_2$  is a 4  $e^-$  process and the  $O_2/H_2O$  redox couple is known to have poor kinetics (24). Catalysis of the reaction is again required in order to achieve high efficiency for generation of solar fuel mixtures of a reduced compound, e.g.  $H_2$ , and  $O_2$  from photooxidation of  $H_2O$ .

#### SEMICONDUCTOR-BASED PHOTOELECTROCHEMICAL CELLS: SOME EXAMPLES

n-SrTiO<sub>3</sub>-Based Cells for Photoelectrolysis of H<sub>2</sub>O. The device represented in Fig. 1 is one where the water splitting reaction, equation (1), can be driven with light as the only input energy. The n-SrTiO<sub>3</sub> has the important property that the position of  $E_{VB}$  is more positive than  $E^\circ(O_2/H_2O)$  and the position of  $E_{CB}$  is more negative than  $E^\circ(H_2O/H_2)$ . Thus, photoexcited electrons (majority carriers driven to the bulk) can effect the desired reduction process and the reaction occurs with good kinetics and negligible overvoltage at a Pt cathode connected to the n-SrTiO<sub>3</sub>. The photogenerated holes (minority carriers driven to the interface) have the oxidizing power to oxidize water and the reaction occurs at the SrTiO<sub>3</sub> surface without degradation of the SrTiO<sub>3</sub> even at extraordinarily high light intensity giving  $>5$  A/cm<sup>2</sup> current density (20).

The n-SrTiO<sub>3</sub> photoanode for  $H_2O$  oxidation to  $O_2$ , equation (9), gives an efficiency up to 25-30% for monochromatic near-UV light (25). However, as mentioned above,  $E_g = 3.2$  eV and the solar efficiency is low,  $\sim 1\%$ , because  $<5\%$  of the energy from the Sun is not effective in exciting electrons in SrTiO<sub>3</sub>. It is noteworthy that the SrTiO<sub>3</sub>-based cell at  $\sim 1\%$  is about the same efficiency of natural plant photosynthesis under the best circumstances. Further, the SrTiO<sub>3</sub> works as a polycrystalline material (26). But the low solar efficiency makes SrTiO<sub>3</sub> economically unattractive at any device cost. It is widely believed that a solar efficiency of  $\sim 10\%$  is needed to be economically viable, owing to high and relatively fixed systems costs. The virtue of the SrTiO<sub>3</sub> system is that it establishes that a durable, high efficiency, inexpensive system is possible if the Sun were a good near-UV source! This system has stimulated much research to find photoanodes having a smaller  $E_g$ .

The large rate ( $>5$  A/cm<sup>2</sup>) for  $O_2$  evolution from SrTiO<sub>3</sub> is at first surprisingly given that  $O_2$  evolution is regarded as kinetically sluggish. However, the separation of  $E_{VB}$  and  $E^\circ(O_2/H_2O)$  is very large ( $\sim 1.7$  V) and can be regarded as the driving force for  $O_2$  evolution. Many conventional electrodes will give good  $O_2$  evolution rates at an electrode potential that is 1.7 V positive of  $E^\circ(O_2/H_2O)$ . For SrTiO<sub>3</sub>,  $O_2$  evolution onsets  $\sim 1.5$  V negative of  $E^\circ(O_2/H_2O)$ , because  $E_B$  for the  $O_2/H_2O$  couple is  $>1.5$  V. But the oxidizing power of the holes,  $E_{VB}$ , is much greater than thermodynamically required. The objective in finding a photoanode for  $H_2O$  oxidation with a smaller gap is to minimize the loss in effecting  $O_2$  evolution, while retaining a large  $E_g$ .

n-WS<sub>2</sub> for the Photooxidation of Cl<sup>-</sup>. The metal dichalcogenides  $MY_2$  ( $M = Mo, W; Y = S, Se$ ) have been extensively investigated. One of the more remarkable findings is the photooxidation of  $Cl^-$  to  $Cl_2$  demonstrated with n-type MoSe<sub>2</sub>, MoS<sub>2</sub>, and WS<sub>2</sub> (11a,27). These photoanodes have  $E_g$  values close to 1.3 eV and have been shown to be durable, even though  $Cl_2$  is a more potent oxidant than  $O_2$ . The durability has been achieved by using extraordinary concentrations of  $Cl^-$ , namely  $\sim 15$  M LiCl in  $H_2O$ . The activity of  $Cl^-$  is of the order of 500 M! Perhaps equally important is the fact that the activity of  $H_2O$  is diminished considerably when such a high electrolyte concentration is used. The high activity of  $Cl^-$  is important in achieving a high rate for  $h^+$  capture leading to the desired product. Lower  $H_2O$  activity should suppress the rate of oxidative decomposition of the semiconductor, since the products are species that contain oxygen, e.g.  $SO_4^{2-}$ .

The photogeneration of  $\text{Cl}_2$  at a non-oxide  $\text{MY}_2$  semiconductor having a nearly optimum value of  $E_g$  establishes that very potent oxidants can, in principle, be generated with high solar efficiency. Surprisingly, the conversion efficiency for the oxidation of  $\text{Cl}^-$  to  $\text{Cl}_2$  is lower than for the oxidation of  $\text{I}^-$  to  $\text{I}_3^-$ . The result is surprising because a priori one would expect a larger  $E_y$  for the  $\text{Cl}_2/\text{Cl}^-$  redox at an n-type semiconductor. Part of the puzzle is clarified by the fact that the efficiency for the  $\text{I}_3^-/\text{I}^-$  redox couple is higher than expected, owing to a strong interaction of  $\text{I}_3^-/\text{I}^-$  with  $\text{MY}_2$  giving a larger than expected value of  $E_y$  (18). However, the  $\text{Cl}_2/\text{Cl}^-$  suffers from poor kinetics at the  $\text{WS}_2$  electrode. This fact is easily established by comparing the overvoltage for  $\text{Cl}_2$  generation in 15 M  $\text{LiCl}$  at p- $\text{WS}_2$  and at Pt, regarded as having good kinetics for the  $\text{Cl}_2/\text{Cl}^-$  redox couple (28). Study of  $\text{Cl}_2$  generation at p- $\text{WS}_2$  in the dark is possible because oxidation of  $\text{Cl}^-$  is a majority carrier process and  $E^\circ(\text{Cl}_2/\text{Cl}^-)$  is positive of  $E_{\text{FB}}$ . The result is that at  $\sim 20 \text{ mA/cm}^2$  the overvoltage for  $\text{Cl}_2$  generation is 300-400 mV larger for p- $\text{WS}_2$  than for Pt. The conclusion is that while 15 M  $\text{LiCl}$  effectively suppresses degradation of the, n- $\text{WS}_2$  the kinetics for  $\text{Cl}_2$  production are not optimum and lower than expected  $E_y$  is the result.

Deposition of a small amount of Pt onto n- $\text{WS}_2$  improves the optical to chemical energy conversion efficiency significantly. A comparison of photocurrent-voltage curves with and without deposited Pt reveals improvement in efficiency. Further, equivalent platinization of p- $\text{WS}_2$  reduces its overvoltage to a value close to that for a Pt electrode. These results are in accord with the conclusion that Pt is a catalyst for the evolution of  $\text{Cl}_2$ . However, the improvement in efficiency for the photoanode is difficult to interpret quantitatively from knowing the reduction in overvoltage upon platinization of p- $\text{WS}_2$ . The reason for this difficulty is that the improvement in photoconversion efficiency may be partially due to suppression of  $e^- - h^+$  recombination, a problem not present for the p- $\text{WS}_2$  anode used in the dark. The possibility that  $e^- - h^+$  recombination is suppressed by the deposited metal and results in efficiency improvement is realistic because low coverage of Pt deposited electrochemically accumulates along steps and defects on the single crystal surface. The steps and defects have been identified as recombination sites on  $\text{MY}_2$  electrodes (11a). Finally, improvement of the efficiency of naturally occurring n-MoS<sub>2</sub> single crystal photoelectrodes can be much more dramatic, from <1% to ~10% for  $\text{Cl}_2$  production using 632.8 nm light. The order of magnitude improvement presumably comes about by both suppressing  $e^- - h^+$  recombination on the low quality surface and by catalyzing the desired process of  $\text{Cl}_2$  generation.

Unfortunately, the n- $\text{MY}_2$  photoanodes for  $\text{Cl}_2$  generation using visible light are not practical. There are at least three reasons for this: (1) the durability of the  $\text{MY}_2$  has only been demonstrated in ~15 M  $\text{LiCl}$ ; durable operation in concentrated  $\text{NaCl}$ , a typical  $\text{Cl}_2$  source, has not been demonstrated; (2) only high quality single crystals of  $\text{MY}_2$  have been demonstrated to be highly efficient and procedures for growing large area, high efficiency material have not been found; and (3) the Pt used to achieve high efficiency is rapidly oxidatively dissolved by the  $\text{Cl}_2$  evolved from the surface. Despite these practical deficiencies, the generation of  $\text{Cl}_2$  with ~10% solar efficiency is an achievement of note inasmuch as  $\text{Cl}_2$  is a genuinely useful chemical oxidant (28). In comparison,  $\text{O}_2$  generation is easier thermodynamically but more difficult kinetically and substantially lower overall efficiency has been demonstrated.

Photoreduction of Water to  $\text{H}_2$ . As indicated above, the light-driven reduction of  $\text{H}_2\text{O}$  to  $\text{H}_2$  at p-type semiconductors generally requires catalysis. One method has involved the deposition of noble metals such as Pt, Pd, or Rh directly onto the semiconductor surface. This method has proven to give the highest efficiencies for photoelectrolysis. Catalysis of  $\text{H}_2$  evolution from illuminated p-InP (7),  $\text{WS}_2$  (11b), and Si (29) has been well-studied. Each of these semiconductors has a value of  $E_g$  near the optimum for solar conversion. For p-InP (7) and  $\text{WS}_2$  (11b) the maximum photovoltage for the generation of  $\text{H}_2$  is ~0.8 V, a good fraction of their ~1.3 eV band gap. The p-InP-based devices have been demonstrated to significantly exceed 10% solar to  $\text{H}_2$  chemical energy conversion.

Another approach to the catalysis problem has involved the modification of the photocathode surface with a viologen-based redox polymer into which is dispersed a noble metal such as Pd or Pt. This approach has been best illustrated with single crystal p-Si (30) and thin film a-Si:H (31) photocathodes. In principle, the redox polymer/noble metal approach could prove more efficient than the approach involving direct deposition of the noble metal onto the semiconductor, since the dispersed catalyst could have more real surface area per unit of geometric photocathode surface area. So far, the redox polymer/noble metal catalysts have yielded less efficient devices. Absorption of light by the polymer, slow charge transport through the polymer, and deactivation of the noble metal in an organic matrix contribute to the lower efficiencies for the redox polymer/noble metal catalyst systems.

Modification of the surface of photocathodes with viologen-based polymers, without noble metals, offers the prospect of using redox enzymes as the electron transfer catalyst. Generally, large redox enzymes do not equilibrate directly with conducting surfaces; the

surface-confined polymers can thus serve as mediators for the enzymes. Proof-of-concept experiments have been demonstrated with viologen-modified p-Si to effect the reduction of horse heart ferricytochrome c (32).

Reduction of Aqueous Bicarbonate to Formate. Natural photosynthesis involves the photogeneration of reduced carbon compounds from  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . Accordingly, there is intense interest in effecting the light-driven reduction of aqueous  $\text{CO}_2$  with man-contrived systems. The problem is that the reduction of  $\text{CO}_2$  to any reduced compound is kinetically sluggish and generally requires large overvoltage. From the natural world, the enzyme formate dehydrogenase has been demonstrated to be capable of catalyzing the reaction of  $\text{H}_2$  with bicarbonate,  $\text{CO}_3\text{H}^-$ , an aqueous  $\text{CO}_2$  equivalent, to form formate,  $\text{HCO}_2^-$  (33). The mediated reduction of  $\text{CO}_3\text{H}^-$  to  $\text{HCO}_2^-$  has been effected at illuminated p-InP in aqueous solution using formate dehydrogenase as the catalyst and  $\text{MV}^{2+}$  in solution as the mediator (34). The enzyme/mediator catalyst system thus allows the reduction to proceed at a good theoretical efficiency.

Recently, the reduction of  $\text{CO}_3\text{H}^-$  has been demonstrated to be catalyzed at Pd surfaces (35). In fact, electrodes modified with a viologen-based polymer into which Pd is dispersed will serve as cathodes for the reduction of  $\text{CO}_3\text{H}^-$  to  $\text{HCO}_2^-$  (35). The reduction can be effected close to the thermodynamic potential (<80 mV overvoltage) with high current efficiency (>80%) to produce significant  $\text{HCO}_2^-$  (>0.2 M), but the rate is too low to give practical efficiencies for a solar driven process where the Sun can give  $\sim 25 \text{ mA/cm}^2$ . Interestingly, however, the high surface area for the Pd dispersed in the polymer gives far superior performance compared to a direct Pd deposition procedure. Further, the catalyzed  $\text{CO}_3\text{H}^-$  to  $\text{HCO}_2^-$  process is one that works for Pd, and not Pt, despite the similar activity of these two metals toward the  $\text{H}_2\text{O}/\text{H}_2$  couple. An ultimate objective is to generate liquid fuels such as  $\text{CH}_3\text{OH}$ . The thermodynamics for  $\text{H}_2$ ,  $\text{HCO}_2^-$ ,  $\text{CH}_4$ ,  $\text{CH}_3\text{OH}$ , etc. are all fairly similar---the key is to find catalysts that will be useful for photocathode-driven processes.

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