

PROBLEMS AND POTENTIAL IN THE SEMICONDUCTOR/ ELECTROLYTE APPROACH TO SOLAR CONVERSION*

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Summary

A general comparison of photoelectrochemical and solid state solar cells is made. It is concluded that although photoelectrochemical cells have problems, including corrosion and film formation, they have potential advantages over solid state cells for photovoltaic operation in the possibility of a lower cost. In a photosynthesis mode of operation, when the solar energy is stored as chemical energy, the use of a photoelectrochemical approach for direct conversion has potentially significant advantages over a combined solid state cell and metal electrolysis cell. The most interesting potential advantages arise in selectivity, where more desirable products can be generated, and in the use of suspended powders, where particularly low cost conversion could be realized.

1. Introduction

Extensive studies of semiconductors in electrolyte solutions with the objective of converting solar energy either to electrical energy directly or to stored chemical energy have been in progress since the report of Fujishima and Honda [1]. They demonstrated with TiO_2 that a photoproduced hole-electron pair could be used to dissociate water, storing the energy as hydrogen. The key property of semiconductors in solar energy conversion is the ability to separate the photoproduced hole from the photoproduced electron, thereby stabilizing the photoproduced hole until its energy can be converted to a useful form. This ability has been used since in many forms of photoelectrochemical solar energy conversion which generally can be classified as photovoltaic photoelectrochemical cells and photosynthesis photoelectrochemical cells (where for simplicity in description we shall include all reac-

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tions where the photon energy is used to stimulate net chemical changes in the latter category).

A great amount of effort has been expended in research to develop a practical solar conversion device based on photoelectrochemical cells. Although such cells have not yet reached the market-place, a substantial amount of valuable scientific information has been generated by this research. The purpose of this contribution, however, is to discuss the potential of photoelectrochemical devices in practical solar energy conversion, emphasizing the practicality of the development while not minimizing its contribution to basic knowledge. Thus, in the present discussion, we shall discuss some of the features of photoelectrochemical devices which bear on the practicality of their future use as photovoltaic devices, where they must compete with solid state photovoltaic devices, and features of photoelectrosynthesis devices, where they must compete with a combination of solid state photovoltaic solar cells and electrosynthesis using metal electrodes. As the solid state solar cell, we shall emphasize the metal/insulator/semiconductor (MIS) Schottky barrier cell; it is analogous to the photoelectrochemical Schottky barrier cell, and so the comparison can be readily made. The MIS cell has about 20 Å of insulating oxide between the metal and the semiconductor.

The hoped-for current-voltage characteristics and the band model for an MIS or a photoelectrochemical Schottky barrier cell are shown in Fig. 1. In the n-type semiconductor used for illustration the double layer at the surface (the Schottky barrier) forces the holes to the surface and, under ideal conditions, is adjusted to force most of the photoproduced electrons to the back contact. The model represents an MIS solid state cell if a metal layer is

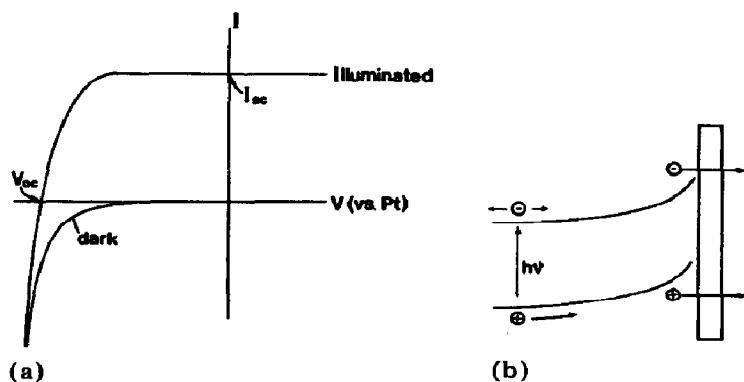


Fig. 1. Ideal solar cell characteristics for an n-type semiconductor: (a) current-voltage characteristics, where with an illuminated sample a high photocurrent is maintained to a voltage cathodic enough that electrons flow to the surface in appreciable quantities (the optimum operating conditions are such that IV is maximum, with the voltage near the open-circuit voltage V_{oc}); (b) band model under optimum operating conditions, with some electrons reaching the surface (the semiconductor is shown with a wide band gap (insulating) film on the surface).

deposited onto the insulator to collect the holes (and the low electron current) and represents a photoelectrochemical cell with a thin insulating film if an electrolyte is used to collect the holes and electrons arriving at the surface. In the discussion, we shall first describe the characteristics of photoelectrochemical cells that bear on their practical utilization. Specifically, we shall discuss corrosion and film formation because they may be the most serious problems associated with the practical utilization of photoelectrochemical devices. With this background, we can then discuss in more detail the advantages and disadvantages of the photoelectrochemical approach to solar energy conversion, compared with those of solid state cells.

2. Corrosion and film formation on semiconductor electrodes

2.1. Corrosion

Photo-induced corrosion, a ubiquitous problem in photoelectrochemical cells [2], is almost always associated with holes [3]. In Fig. 2 we indicate a model for a hole, a missing valence electron in a reasonably covalent semiconductor lattice. Such a hole is produced as the first step in solar conversion, the absorption of the photon. The valence electron is excited to the next excited state (the conduction band), leaving the hole in the valence bond structure. The double bond is converted to a one-electron bond where the hole is localized. The hole is free to move through the crystal; other valence electrons jump into the empty bond that is the hole and the hole thus moves. Corrosion can occur if the hole reaches the surface.

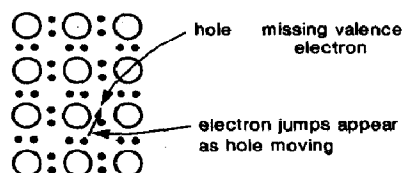


Fig. 2. Schematic molecular model for a covalent semiconductor missing one valence electron, where the missing electron is a hole. The hole can move to the surface by successive neighbouring valence electrons moving into the unoccupied position, causing apparent movement of the hole.

The “back bond” between the surface atom and the crystal is converted from a two-electron bond to a one-electron bond. If two holes occupy the same back bond of the surface atom, the bond is completely broken; there are no bonding electrons. Analysis suggests [4, 5] that the capture of one hole at a back bond of a surface atom is reversible, but that if two holes are captured on the same back bond the process is irreversible [4, 5] and corrosion results. Presumably the surface atom becomes hydrolysed (in an aqueous solution) and, once the surface atom coordinates to an OH^- group or its equivalent, the corrosion process is irreversible.

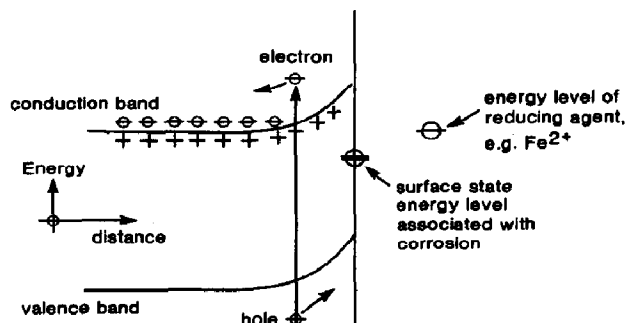


Fig. 3. Band model for corrosion: when a hole is captured on a back bond (energy level not shown), the remaining unpaired electron is at a higher energy level than a normal valence bonding electron. The higher energy level is shown as a surface state associated with corrosion. The energy level of a reducing agent ion in solution is also indicated.

The energy band model for the same process on an n-type semiconductor is shown in Fig. 3. Here a photon excites the valence electron from the energy levels in the valence band to the conduction band. Again, if one hole is captured on a back bond, the process is reversible, but the hole capture leaves the surface atom in the form of a radical (an atom with an unpaired electron). This unpaired electron has an energy level different from that of the normal valence electrons in the material and is expected to be at a substantially higher energy. Thus the surface state shown in Fig. 3, associated with corrosion, is in the midgap position. If a hole is captured on that surface state, as described above, the back bond is completely broken and corrosion results.

The most straightforward way to avoid photocorrosion is to use a strong reducing agent in solution, as indicated on the energy level diagram of Fig. 3. The electron from the reducing agent (say Fe^{2+}) transfers to the lower energy associated with the hole on the back bond of the surface atom, thus restoring the bonding electron to the surface atom and preventing corrosion. The competition for the photoproduced holes between the reducing agent in solution and corrosion can be monitored by observing the rate of generation of the oxidized form of the reducing agent in solution using a rotating ring disc electrode. Such a measurement permits corrosion by holes to be studied and the models to be analysed in some detail.

Figure 4 shows the results of such a measurement [6] where the "stabilization efficiency" (the ratio of hole capture by the reducing agent to the total hole current to the surface) is plotted as a function of the concentration of the reducing agent. Figure 4, curve a, shows the results for well-etched GaAs; curves b and c show the results for increasing mechanical damage (scratching with alumina powder). It is observed in Fig. 4 that the stabilization efficiency increases rapidly, but not linearly, as the concentration of the reducing agent increases. It is the analysis of such rate laws that leads to the model [4, 5] described briefly above, where the first hole capture at the back bond is reversible and the second hole capture is irreversible.

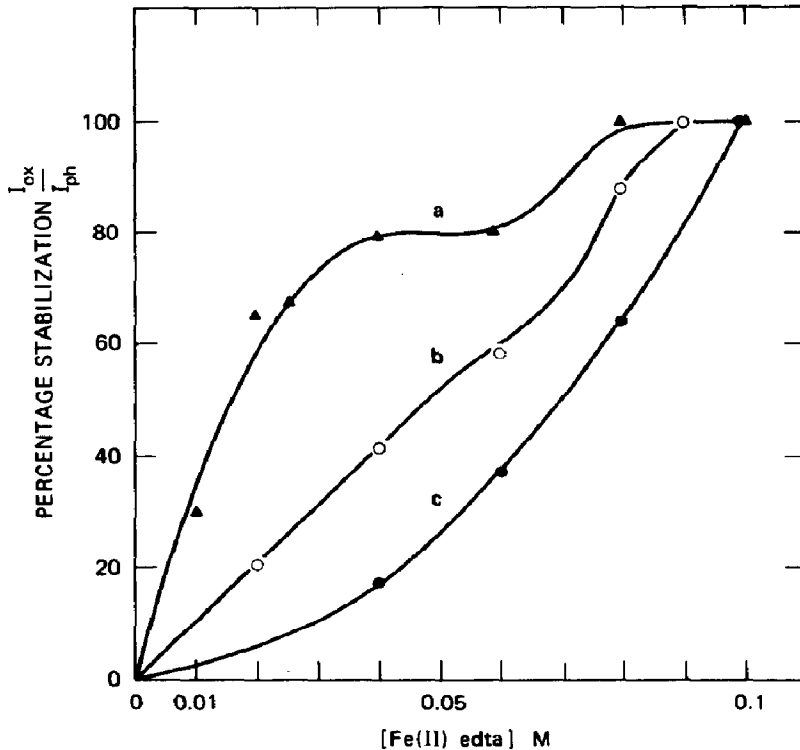


Fig. 4. Stabilization efficiency S vs. concentration of the stabilizing agent ($S = I_{ox}/I_{ph}$ where I_{ox} is the hole current oxidizing the reducing agent and I_{ph} is the total photocurrent): curve a, surface well etched; curve b, mechanical damage to the surface; curve c, more mechanical damage to the surface.

Because mechanical damage has such a strong effect, the rate-limiting step in corrosion can be associated with defects. Through a study of the rate constants associated with the corrosion [4] it is suggested that the rate-limiting step in corrosion is hole capture at the back bond of an atom on a surface step.

We have discussed (Fig. 4) the use of stabilizing agents to prevent corrosion, but many other techniques have been used to induce stability and thus to make photoelectrochemical devices more practical. Such methods include the deposition of polymer films [7 - 12], the deposition of metal [13, 14] or tin oxide [15, 16] films onto the semiconductor (see Section 3.3), the use of insulators [17] or corrosion products [16], the use of layer compounds where the valence band electrons are in non-bonding orbitals [7, 12] and the use of intrinsically stable semiconductors such as titanates or iron oxide [18 - 20]. None of these has been completely satisfactory. For example, the layer compounds will corrode on edge planes although they are stable on the basal plane. Titanates are intrinsically quite stable but their band gap is large so that a small portion of the solar energy is adsorbed. Iron oxide is basically a low efficiency semiconductor in solar conversion, presumably because of defects in the material.

2.2. Surface films

The uncontrolled formation of surface films during operation is another serious problem in photoelectrochemical devices. The controlled use of surface films can be beneficial if they do not degrade the characteristics but passivate the surface. In some cases, such as for CdSe and InP, naturally conducting films which enhance the stability appear to form. In the case of InP, an In_2O_3 conducting film resulting from corrosion appears to passivate the surface [16]. However, if the conducting film does not prevent further corrosion it is not helpful.

Usually, however, films are undesirable. A "thick" insulating or semi-insulating film will substantially lower or even eliminate [21, 22] the solar energy conversion efficiency because it acts as a resistor in series with the device, and with any modest resistance very quickly the voltage output of the solar device is lost. If the film could be made thin enough (of the order of 20 Å) the film would be desirable. A thin insulating film has been shown to be beneficial both with solid state [23, 24] and with photoelectrochemical Schottky barrier cells [21], where in both cases improved conversion efficiency results and in the photoelectrochemical case improved corrosion resistance results. For example, it has been shown [21] that the stabilization efficiency is highest with an insulating film about 20 Å thick on the surface. This improved stabilization efficiency arises because a voltage appears across this insulating film due to the hole storage at the surface, and this voltage enhances the hole capture rate by the stabilizing agent. Improved conversion efficiency results because the thin film blocks the undesirable electron current to the surface, while permitting the desired hole current to the surface. Unfortunately, with photoelectrochemical cells it is difficult to maintain the film thickness at 20 Å; usually the film will either corrode or grow. Thus, with photoelectrochemical cells, surface films are in general undesirable, and the problem is to avoid surface film formation while still avoiding dissolution of the semiconductor electrodes.

Since films as little as 30 Å in thickness can be highly deleterious, such undesirable films can be invisible. Many reported cases of poor solar cell characteristics could be due to the presence of invisible and undetected films; tests with intentionally deposited insulating films present show characteristics [21] similar to those obtained in many cases of inefficient photoelectrochemical systems.

3. Potential advantages and remaining problems with photoelectrochemical photovoltaic cells

3.1. The use of imperfect semiconductors

One potential advantage of the photoelectrochemical photovoltaic cell is the relative insensitivity to poor material, *i.e.* to flaws in the crystal structure. A flaw in the semiconductor can effectively short out the solar cell with a metal/semiconductor cell. As indicated with Fig. 1, under ideal operating conditions a low flow of electrons to the metal should occur.

Because of the bulk levels associated with a scratch, dislocation or grain boundary, electrons can readily flow to the surface in the region of such flaws [25], while the flow is low (at the optimum level) elsewhere. A high electron flow of course counters the desired hole flow, and the conversion efficiency is reduced [26].

With a photoelectrochemical cell, such current through flaws would also occur but is limited by the electrolyte. First, whereas in the metal there is essentially an infinite density of states for the electrons to flow to, with the electrolyte the density of states is the ion density, and the flow is limited. Secondly, because the flaws are normally of limited area, diffusion limitations associated with the rate of diffusion of the ions to the flaw restrict the current to the flaw. Thus the photoelectrochemical cells can operate reasonably well [26] with flawed material.

With semiconductors where a suitable oxide can be formed to make an MIS cell as discussed in Section 1, the electrochemical cell no longer shows such an advantage. Specifically, with silicon and with GaAs [24], a thin oxide layer is intentionally formed on the surface of a Schottky barrier solar cell. This oxide effectively blocks the current of electrons to the surface while still permitting the holes to tunnel through to the metal. For this purpose the oxide should be of the order of 20 Å in thickness. As mentioned in Section 2.2, a similar oxide could also be very helpful in improving the efficiency of a photoelectrochemical solar cell, but in this case it is extremely difficult to maintain the oxide thickness at exactly the right value.

Thus, for some semiconductors, but not all, it can be anticipated that the photoelectrochemical photovoltaic cells will have an advantage in that in general poorer quality material can be used.

3.2. Simplicity of design

The major potential advantage of the photoelectrochemical photovoltaic solar cell over the solid state solar cell is its simplicity of design. In principle at least, a layer of semiconductor can be deposited in the bottom of a tray, the tray filled with a solvent, electrical contacts attached to the semiconductor and to a counterelectrode and electrical power collected when the semiconductor is exposed to the Sun.

Obviously the above is a gross simplification and in practice, for an efficient photoelectrochemical solar energy converter, the unit must be carefully designed [27] both with respect to the active components in the cells such as the semiconductor and the electrolyte [28] and with respect to hermetic sealing to avoid evaporation of solvent. To date, the "well-designed system" which has the conversion efficiency optimized to compete with solid state solar cells has not been lower in cost.

However, the cost of the photovoltaic systems is still the major problem in the general use of solar energy-to-electricity conversion for solid state cells. Thus, photoelectrochemical photovoltaic cells are still a serious candidate on the basis of their potentially low cost of production, if a suitable system is found.

3.3. Electrolyte/metal/insulator/semiconductor cells

By use of an electrolyte/metal/insulator/semiconductor (EMIS) configuration, the corrosion problem can be avoided somewhat while still retaining some of the design simplifications of the photoelectrochemical solar cells and thus perhaps a cell lower in cost than the straightforward MIS cell can be produced. An EMIS cell is a cell with an MIS Schottky barrier and where the electrolyte is only used to make electrical contact to the metal. Alternatively, a conducting oxide, such as In_2O_3 or SnO_2 , can be used in place of the metal.

3.4. Remaining problems of photoelectrochemical photovoltaic cells

The corrosion problem is still a general problem. Cases of electrodes which have been stable over many years have been reported, specifically in work on CdSe at the Weizmann Institute, but the stability seems to be at the expense of conversion efficiency. Other cells, such as the EMIS cell, have not been tested over the many years necessary.

The efficiency of photoelectrochemical cells in general is lower than that observed with MIS cells. There are several causes for lower efficiency that must be overcome. Usually the optimum electrolyte for high efficiency is not the same as the optimum electrolyte for corrosion resistance, and so a compromise must be made. Thus research must continue on corrosion (and on optimized electrolytes for efficiency) to reduce the need for corrosion control and to permit the high efficiencies possible. There are other sources of efficiency loss that must be minimized system by system. The electrolyte is often highly coloured, and so absorption loss in the electrolyte can lead to low efficiency. Alternatively, the electrode processes can have a significant overvoltage, leading to energy loss.

Studies to optimize the selectivity of carrier reactions should be emphasized to try to eliminate side reactions. The use of catalysts, the better understanding of selectivity on semiconductor electrodes and the choice of electrolytes must be studied with a view to preventing undesirable film formation, minimizing corrosion and minimizing electrolyte changes with time.

4. Advantages and remaining problems of photoelectrochemical photosynthesis

4.1. Introduction

Here we wish to assess photoelectrochemical photosynthesis cells where the solar energy is either stored in the form of chemical energy or it is used in a photoelectrosynthesis or photoelectrocatalytic process to synthesize valuable chemicals. The potential of this approach should be compared with the potential for development of effective photoelectrochemical photovoltaic cells. It should also be compared with a series arrangement combining a solid state photovoltaic cell and a metal electrochemical cell.

4.2. *Selectivity*

The semiconductor electrode seems to show a potential selectivity for certain chemical reactions and products which differs from the selectivity on a metal electrode and which could give the semiconductor electrode an advantage [29, 30]. This is illustrated by the reduction of CO₂ selectively to methanol [31, 32], a process that can occur with 100% efficiency on GaAs [32] (while in a saturated CO₂ solution reduction on metal electrodes yields only formic acid, a product of less interest in energy conversion). Unfortunately, little is known regarding the reasons for this difference in selectivity. The problems of determining whether the difference between metals and semiconductors is real and, if real, how to optimize the selectivity, are probably of paramount importance in the successful development of photosynthesis cells. More details are discussed in Section 4.5.

4.3. *The use of suspended powder*

What may be the greatest potential advantage of the photoelectrochemical photosynthesis approach over either solid state cells or photoelectrochemical photovoltaic cells is the possibility of using the semiconductor as a suspended powder rather than as an electrode of an electrochemical cell in converting solar energy [33 - 38]. In comparison with the photoelectrochemical photovoltaic cell described in Section 3, the cost of solar energy conversion using suspended powders and a synthesis reaction could be very low because the system (in principle) is simpler: a powder is suspended in an appropriate electrolyte solution, it is exposed to the Sun and the product is collected. This is design simplicity in its extreme. It also avoids to a great extent the photocorrosion problem because if the powder does corrode it is easily replaced when its activity declines.

To date, high efficiency with this approach has not been attained. The system is difficult to optimize. The photon striking the surface of the powder particle produces the photoproduced hole and the photoproduced electron in the semiconductor particle. The holes and electrons must be physically separated to avoid recombination (the return of the excited electron to the valence band). The photoproduced electron must reduce a species A at the surface; the photoproduced hole must not reoxidize A⁻ but must oxidize a different species B at the surface. The two products thus generated must be useful and must be collected. Workers in this area have attempted to separate the hole reaction and the electron reaction by depositing catalysts on two sides of the powder particle. The approach has been moderately successful. For example, Graetzel and coworkers [37, 38] have reported the dissociation of hydrogen sulphide into hydrogen and sulphur. This approach seems to be the most promising for the successful low cost conversion of solar energy using a semiconductor/electrolyte system.

4.4. *Electrolyte/metal/insulator/semiconductor cells*

Metal overlayers have been used to avoid the corrosion problem in photoelectrosynthesis as in photovoltaic systems. With this approach the

possible advantage of improved selectivity is not realized, and thus, for example, such systems are not used for CO₂ reduction to methanol. However, many other energy storage reactions that are appropriate to metal electrodes are feasible.

4.5. Combination systems

Work is in progress on the combination of a photoelectrochemical photovoltaic cell and chemical storage in the same cell.

The system is designed so that when the solar energy is converted to the energy of the hole–electron pair this energy can be directly extracted as electrical energy (photovoltaic mode), or when the electrical energy is not immediately needed the energy can be stored by a suitable electrode reaction (photoelectrosynthesis mode, *i.e.* a battery [39]). The potential advantage of this particular system of solar energy conversion as opposed to a solid state cell–battery combination is the fact that the chemical storage capacity, being a part of the solar cell, is distributed over a wide area. Separate storage facilities are not required, and the biggest problem in the conversion of solar energy to electricity, namely the storage of the electrical energy until night-fall when the electrical energy is needed, is very simply overcome. However, there is no evidence to date that this approach would be lower cost than the solid state cell–battery combination.

Another combination that is feasible with the conversion of solar energy to chemical energy by a photoelectrochemical cell is the possibility of adding a small applied voltage when necessary. An example of this would be the photoelectrocatalysis of water on a TiO₂ photoelectrochemical cell, where the conduction band edge of the TiO₂ is just not quite energetic enough to reduce protons. A small applied voltage makes the overall reaction feasible. This is a poor example, of course, because the use of TiO₂ for solar energy conversion cannot be efficient because of the low absorption of solar energy by TiO₂. However, the example illustrates the principle.

4.6. Selectivity as the most important problem

With the exception of the case where a suspended powder is used, the ubiquitous photo-induced corrosion is a problem with the photoelectrosynthesis as with the photovoltaic approach to photoelectrochemical solar conversion. Continuing research into ways to avoid corrosion is needed in all photoelectrochemical device development. Other problems of Section 3.4 are also present in this case to a greater or lesser degree.

However, we feel that the most important problem to be analysed before successful photosynthesis devices can be developed is selectivity. Selectivity is even more important here than in the photovoltaic case. For powdered suspensions, highly selective hole and electron reactions must be developed to increase the efficiency of the energy conversion. In all cases, better models of selectivity on semiconductors must be developed to optimize the surface and thus the desired reactions.

Two possible origins of special selectivity with semiconductor electrodes as opposed to metal electrodes can be suggested. One is the selectivity in accordance with ionic energy levels, as suggested by the Marcus–Gerischer model. Only ions with energy levels isoenergetic with the band edges will be electroactive, according to this model. Unfortunately the selectivity fails in many experimental cases [40, 41] (although it is apparently valid in others [42, 43]) and it would be of value to determine whether the model is wrong or whether the model is incomplete in real cases.

Another possible origin of selectivity is surface states, intentional or otherwise. Special surface additives can provide surface states on the surface [43], *i.e.* energy levels to mediate the carrier transfer. With metals, such surface states would be less active because of the high density of electrons near the Fermi energy.

In our laboratory at Simon Fraser we are studying selectivity with surface treatments to stimulate preferred adsorption and to deposit active sites as well as carrying out experiments to study specific carrier reactions. Some early results obtained in our laboratory by Baofang Li, a visiting scientist from China, on specificity associated with electron transfer processes may be of interest, suggesting a possible reason for the failure of the Marcus–Gerischer model.

Figure 5 shows the Marcus–Gerischer model [44] for reduction by isoenergetic electron transfer from the conduction band of a semiconductor to two species, A and B, in solution. The gaussian curves on the right-hand side of Figs. 5(a) and 5(b) represent the distribution of energy levels for the ion according to the Marcus–Gerischer model. Now for an isoenergetic electron transfer it is clear that the electrons from the conduction band cannot

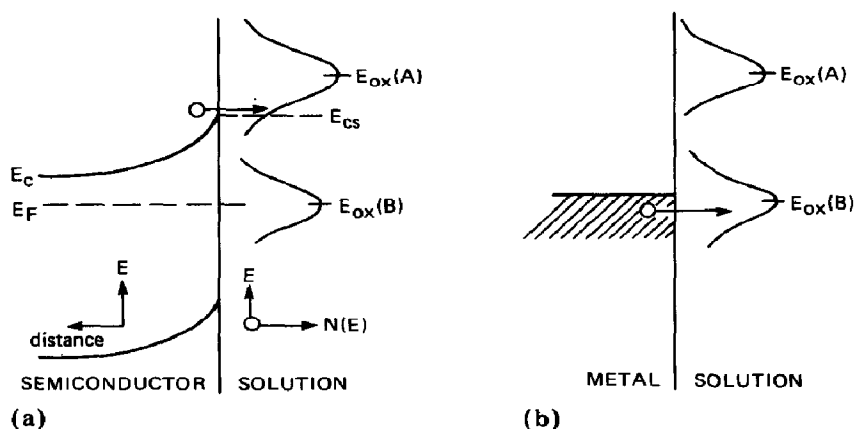


Fig. 5. A possible reason for semiconductor selectivity based on the Marcus–Gerischer model: (a) semiconductor band model with the “density of levels in solution” for two ions, A and B (with isoenergetic electron transfer the reduction of species A should be favoured); (b) equivalent model for a metal, with the Fermi energy in the metal determined by species B, but with a cathodic bias (with isoenergetic electron transfer the reduction of species B will always be favoured).

transfer to species B because the energy level for species B has negligible probability of being at the conduction band energy. The energy level of species A is better located for electron transfer, with E_{ox} approximately equal to the energy of the conduction band. This then should make the electrode highly selective for the reduction of species A. In contrast, with a metal electrode the reduction of species B should dominate, as in Fig. 5(b). However, experimentally, even with a semiconductor where the energy level of a species is well below the conduction band, such as ion B in Fig. 5, electron transfer is typically observed to occur at a high rate.

One possible reason suggested [44] for the preferred reduction of species B contrary to the Marcus–Gerischer model is described using Fig. 6. The reason is the presence of bulk energy levels associated with dislocations (imperfect crystal structure of the semiconductor). If enough energy levels are present in the band gap region, electrons from the conduction band could “trickle down” through these levels to the energy of $E_{ox}(B)$ and a high cathodic current will be observed. Other levels to mediate such electron transfer, such as surface states on the semiconductor [40 - 47], vibrational-rotational excited energy levels of the ion [48] or shifts in the ion energy level due to adsorption can be suggested. However, Baofang Li has emphasized the possible role of bulk states due to damage. Such damage has been shown to affect the electrode properties [49, 50], but the question here is whether it can remove the rate limitation imposed by the Marcus–Gerischer model.

In Li's experiments, various ions were studied at various pH values to vary a parameter α , the energy difference between the conduction band and the redox potential E° of a species in solution, where the energy determined

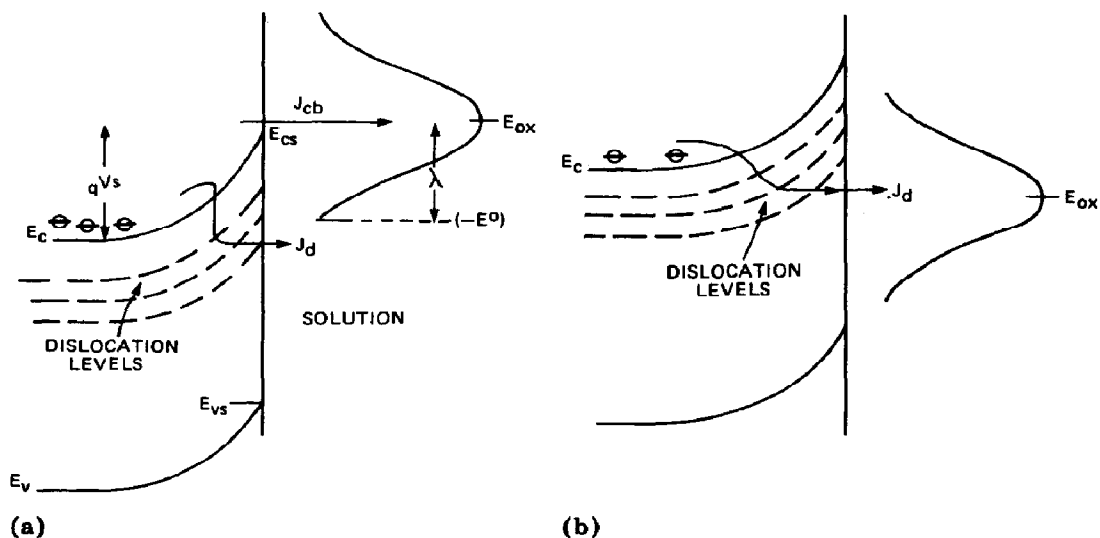


Fig. 6. The possible influence of bulk flaws (energy levels) on semiconductor selectivity: (a) E° is almost as negative as the flat-band potential (little isoenergetic electron transfer through flaws); (b) E° is much more positive than the flat-band potential (all electron transfer through flaws).

from the redox potential is an energy close to the bottom of the gaussian curve. Thus the value of x for an oxidizing agent such as species A in Fig. 5(a) would be just above zero. The value for species B would be of the order of 1 V. If the Marcus-Gerischer model holds, the current should be low at $x \leq 0$ (E° is more negative than V_{fb}), increase rapidly as x increases, pass through a maximum at $x \approx 1$ V ($E_{cs} \approx E_{ox}$), and decrease. If damage is destroying the selectivity, as suggested in Fig. 6(b), the current for the damaged surface should always be higher than that for the etched surface, with the difference increasing as x increases.

The experimental results for a series of oxidizing agents with various values of x on the abscissa as measured are shown in Fig. 7. On the ordinate we plot a parameter proportional to the logarithm of the current, namely the surface barrier potential V_s at the semiconductor surface at constant current. Plotting this is equivalent, as indicated, to plotting the logarithm of the current at constant surface barrier potential. Results similar to that anticipated are observed, although the scatter is very large. The scatter is expected to be

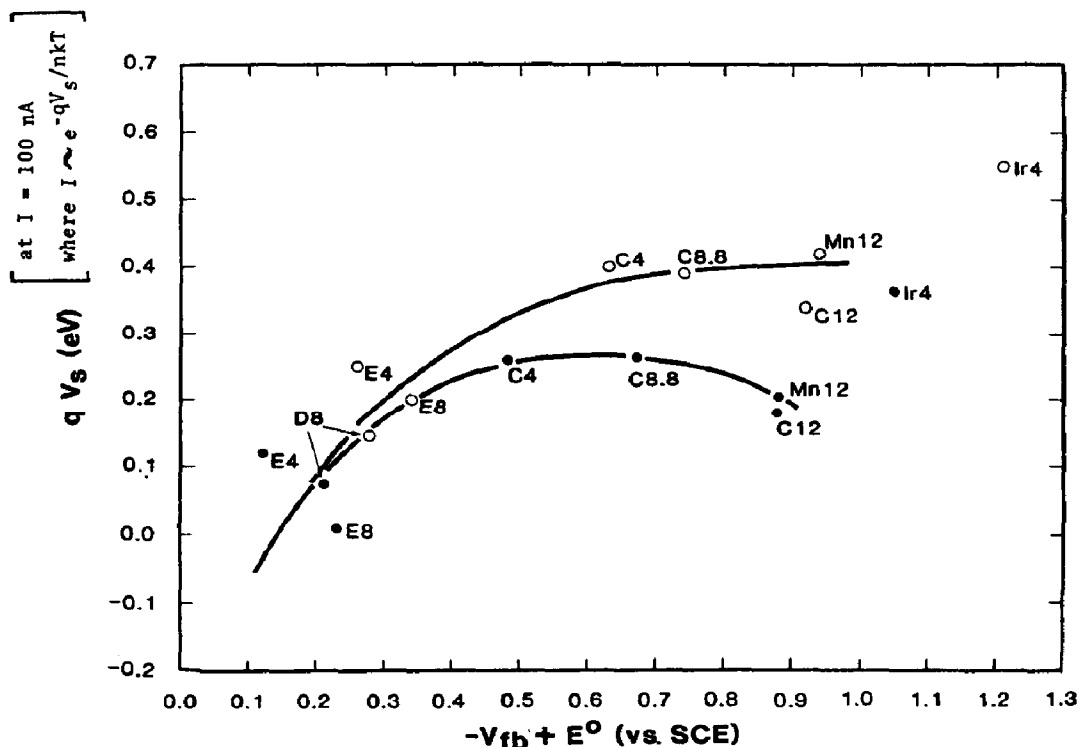


Fig. 7. Effect of surface damage on cathodic current from the (0001) plane of ZnO to various ions in solution (concentration, 10^{-4} M in 1 M KCl): \circ , measurements on the damaged surface; \bullet , measurements on the etched surface; points C, $[\text{Fe}^{\text{III}}(\text{CN})_6]^{3-}$; points D, $[\text{Fe}^{\text{III}}(\text{dtpa})_3]^{3-}$ (dtpa \equiv diethylenetriaminepentacetic acid); points E, $[\text{Fe}^{\text{III}}\text{edta}]^-$; points Ir, $[\text{Ir}^{\text{III}}\text{Cl}_6]^{3-}$; points Mn, MnO_4^- . The numerals indicate the pH in aqueous solution. (SCE, standard calomel electrode.)

large because of the variation in the cross section for hole capture of the various species which cannot be taken into account. However, increasingly high values on the abscissa suggest that the current to the damaged surface becomes larger than the current to the well-etched surface by an increasing amount as x increases. For example, for MnO_4^- the current at constant surface barrier potential is higher by almost three orders of magnitude with the surface damaged. This suggests that dislocations are indeed active in transferring electrons to solution, contrary to the Marcus-Gerischer predictions.

Further experiments along this line are in progress. If the results continue to support the proposed model they suggest that, in cases of photoelectrochemical solar energy conversion where selectivity is important, semiconductors with few crystalline flaws must be used. Unfortunately there are few such cases; satisfactory materials could be silicon, germanium, epitaxial GaAs and, most practical, powder semiconductors that have not been subjected to mechanical damage.

5. Conclusions

Throughout the discussion the words "has potential" have been used very liberally to describe the advantages of photoelectrochemical cells. The research over the past years, since the original Fujishima-Honda publication [1], has exposed many problems in what initially appeared to be a rather simple concept for the conversion of solar energy. We have described some of these and urged appropriate research. There is no doubt that other workers in the field could list others. Many advances have been made in solving these problems, but most of them are still with us to a greater or lesser extent.

However, this same research has also shown us the great potential of the semiconductor/electrolyte approach to solar conversion and to electrochemistry. Let us consider photoelectrochemical photovoltaic cells; workers have obtained photoelectrochemical photovoltaic cells almost as efficient as the best solid state photovoltaic cells. The photovoltaic approach is far from dismissed and much active research is continuing in this area. However, the photoelectrochemical photosynthesis approach, converting solar energy or electrical energy to chemical energy, seems to be even more exciting. Although to date the efficiency of photosynthesis has been low, the approach could be extremely rewarding.

As a final remark we might compare the effort invested in three categories: solid state solar energy conversion, photoelectrochemical photovoltaic conversion and photoelectrochemical photoelectrosynthesis. The amount of time, study and money devoted to these three developments varies by orders of magnitude; the effort on solid state devices has been very large compared with the effort on photoelectrochemical photovoltaic devices, which in turn has been large compared with the effort on photoelectrochemical synthesis devices. It appears that the interest in synthesis devices is increasing rapidly at the present time and hopefully with a substantial

effort in that area we shall soon see some practical systems for direct solar energy conversion from optical to chemical energy.

Acknowledgments

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