HETEROGENEOUS ELECTROCHEMICAL SYSTEMS FOR SOLAR ENERGY CONVERSION

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ABSTRACT

A survey is given on the various electrochemical systems which can be used for the conversion of solar light into electrical or chemical energy. They are compared with the similar processes in photosynthesis and their advantages or disadvantages are outlined.

Systems based on the photovoltages obtained at semiconductorelectrolyte junctions have reached the highest efficiencies and are discussed in more detail. The theoretically possible conversion efficiencies are outlined and the difficulties to reach them are explained. Photodecomposition of the semiconductor electrode is the most serious problem, for which the thermodynamic and kinetic conditions are discussed. Finally, a brief outline of the prospects for application is given.

INTRODUCTION

Redox reactions performed in an electronically excited state are the basis for all electrochemical processes in which light energy is converted into electrical or chemical energy. The redox properties of an excited molecule are represented in Figure 1 where the electronic energy terms are plotted on the left hand side in an "absolute" scale with the vacuum level as the reference zero and for comparison on the right hand side in the conventional electrochemical scale (ref. 1)
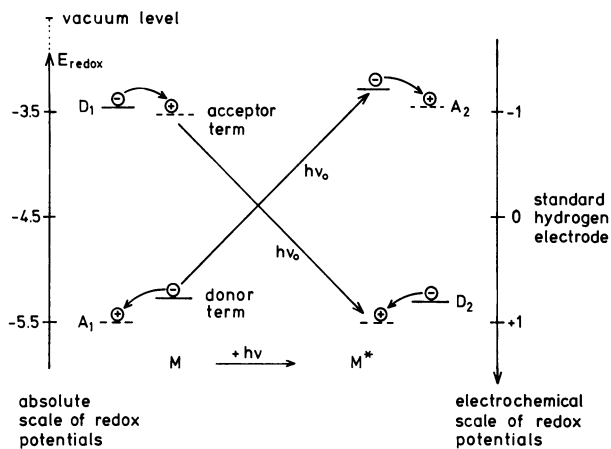

Fig. 1 Energy scheme of photoredox reactions

The difference between the respective redox potentials of the excited state and the ground state is the excitation energy left over in the longer living excited states after vibrational relaxation. This is the zero-zero transition in a molecule or the band gap in a semiconductor. The efficiency of energy conversion depends mainly on how much energy is lost by relaxation in the excited state and in the consecutive electron transfer reactions and how well the electron transfer steps can compete with the internal quenching processes of the excited state.

Nature has provided us in photosynthesis with a model for electrochemical light energy conversion. Figure 2 shows the energetics of the redox reactions in the thylacoid membrane performed by two excited chlorophyl molecules which are coupled by electron transfer chains through the membrane (ref. 2,3). The electric circuit is closed by a proton transport parallel to the electron transfer through the membrane. The result is a continuous performance of a reductive and an oxidative redox reaction on each side of the membrane in which 1.28 eV are optimally gained from two light quanta with together 3.6 eV minimum energy.
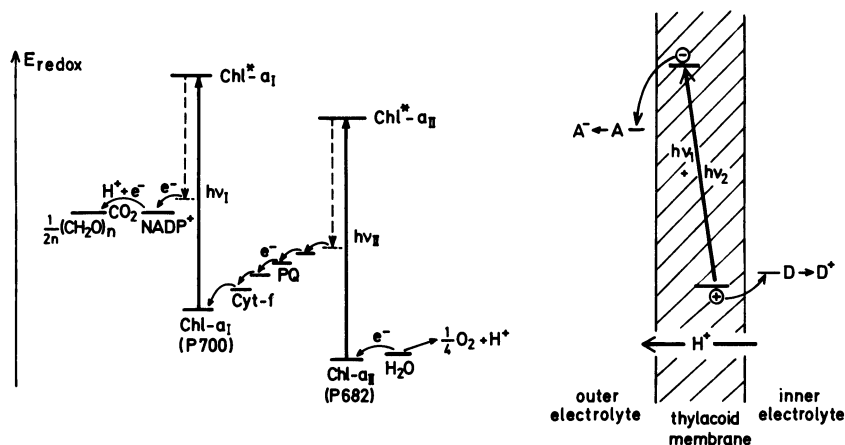

Fig. 2 Energy scheme of the electron transfer reaction in photosynthesis (left) and representation of photosynthesis as an internal photoelectrolysis cell (right)

The very complex photosynthetic system has been optimized during evolution to a perfection which hardly can be imitated by artificial systems on a similar molecular basis. However, we can learn from an analysis of this system which essential conditions must be fulfilled for efficient photoelectrochemical light energy conversion. These are the following ones:

Table 1: Essentials for efficient conversion of solar energy by photoelectrochemical systems

1) Fast charge separation after light absorption

2) separation of products in order to prevent reverse reactions

3) efficient absorption of solar light with minimal entropy production

4) adjustment of the redox potentials of the excited states to the redox reactions which store the energy

5) long term stability (or continuous reproduction)

Condition 1 and 2 can be derived from Figure 2. Condition 3 is fulfilled by the absorption spectrum of chlorophyl. However, to reach a minimal entropy production is in some contradiction to condition 1 since fast charge separation is necessarily connected with entropy production (cf the relatively large energy losses in the first electron transfer steps between the excited chlorophyl molecules and the primary acceptors in Figure 2). Condition 4 is excellently met in photosynthesis by the very low energy losses in the catalytically performed CO_2 reduction and H_2O oxidation by the final electron donors and acceptors in the photosynthetic electron transfer chains. The fifth condition is obtained by the selfregeneration of the energy converting system in nature. All artificial

systems must be judged according to how close they approach these essential conditions.

ARTIFICIAL SYSTEMS

The simplest system would be to use a homogeneous photoredox reaction which generates two products with a different redox potential in which the converted energy can be stored. The primary redox reaction can be either a photoreduction or a photooxidation as is shown in Figure 3. Intensive research is done in this field (ref. 4, 5, 6) where the most serious problem is to avoid the reverse redox reactions between the products and to separate them. These reactions are however not within the scope of this lecture.

$$M^* + A \longrightarrow M^+ + A^- \longrightarrow P_{ox} + P_{red} \qquad M^* + D \rightarrow M^- + D^+ \longrightarrow P_{red} + P_{ox}$$
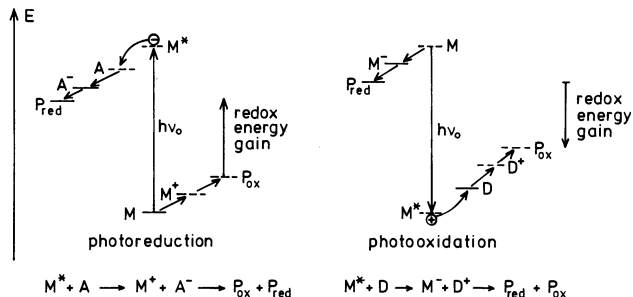
Fig. 3 Scheme for energy conversion by homogenous photoredox reactions with the stable products P_{red} and P_{ox}

A combination of a homogeneous photoredox reaction with a heterogeneous electrode reaction is the so-called photogalvanic cell (ref. 7, 8, 9). The principle is shown in Figure 4.
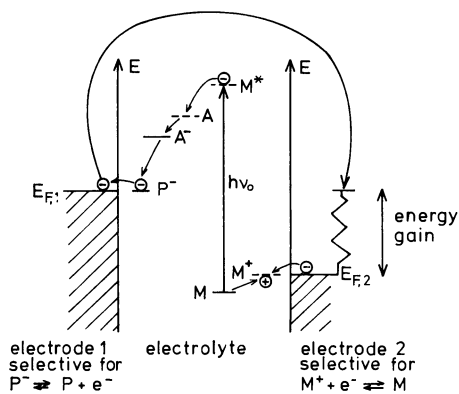

Fig. 4 Reaction scheme of a photogalvanic cell with the process:

The essential condition is that the products (P^- and M^+ in Figure 4) have a long enough life time to reach the respective electrode before they react with each other. Besides this, the electrodes must be fully selective for only one of the redox reactions. The first condition can apparently only be met if consecutive reactions stabilise one of the products what reduces the energy gain. The second condition seems to be even more difficult to fulfill for both systems simultaneously. The systems which have been studied have one selective electrode (ref. 9, 10) and tolerate a mixed potential at the other which is not illuminated. The result is a much smaller voltage output than theoretically possible.
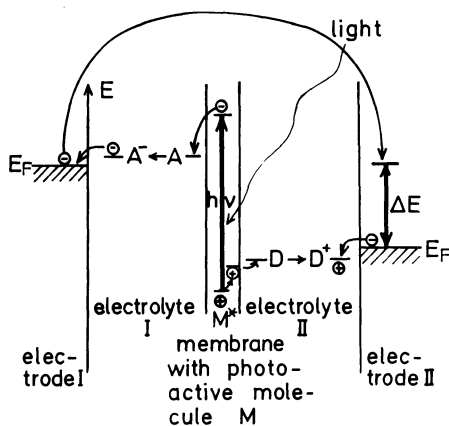
Fig. 5 Photoelectrolysis cell with an asymmetric membrane as the energy converter

A device which comes closest to the photosynthetic system is shown in Figure 5. It contains a thin membrane with a sensitizer for redox reactions. The membrane separates two compartments containing different redox couples and the sensitizer must have such redox properties that it can photoreduce one couple and oxidise the other afterwards or photooxidise one couple and reduce the other thereafter.

The difficulty with such systems is to meet the necessary redox properties and to avoid quenching and other losses. In addition to this, only very thin membranes can be employed in this way since otherwise the internal resistance would become too high. (The device acts as a power generator!) This condition limits the light absorption which can be reached by a single membrane so that one would need many membranes in series in order to get an efficient use of the light. Conversion efficiencies with such arrangements have by these reasons remained extremely low up to now (ref. 11-13).

Systems where the photoeffects occur in a solid electrode differ much more from the model of photosynthesis. They have however the advantage that light can be completely absorbed in a thin layer and the excited state still is efficiently active at the interface between the electrode and the electrolyte. Only semiconducting materials are applicable for this purpose since the life time of excited states in metals is by far too short.

Light absorption in a semiconductor leads to the generation of electron hole pairs which can undergo redox reactions with suitable electron acceptors or donors at a contact with an electrolyte as shown in Figure 6.
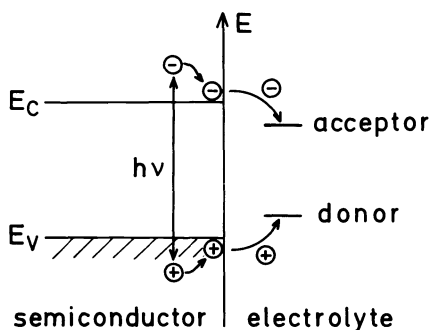
Fig. 6 Photoredox reactions at the semiconductor-electrolyte interface

Such photoreduction or photooxidation processes provide an energy gain as in the homogeneous case discussed before. If both types of redox reactions proceed at the same interface simultaneously, the yield will be very low because most electron hole pairs will be lost by recombination or the products react with each other in the reverse direction. In order to obtain a reasonable efficiency one needs therefore a mechanism which separates the electrons and holes and lets only one type of electronic charge carriers reach the interface.

Solid state photovoltaic devices are based on such a charge separation in semiconductors with p-n-junctions or Schottky barriers (ref. 14, 15). A contact between a semiconductor and an electrolyte easily forms a Schottky barrier if the electrolyte contains a suitable redox couple (ref. 16). The electric field present in the depletion layer of the Schottky barrier drives photogenerated electrons and holes in opposite directions what is explained in the next section (cf Fig. 8).

The principle of a cell in which the energy conversion occurs in a Schottky barrier is depicted in Fig 7 for a n-type semiconductor. The electric field in the space charge layer drives the holes to the surface where they can oxidise a redox system while the electrons remain on a higher energy level in the bulk of the semiconductor. They can be transferred from there to a counter electrode where they can reduce another redox couple. Light energy is transferred in this way into a difference in redox energies between the two redox couples as shown in the energy diagram of Figure 7.
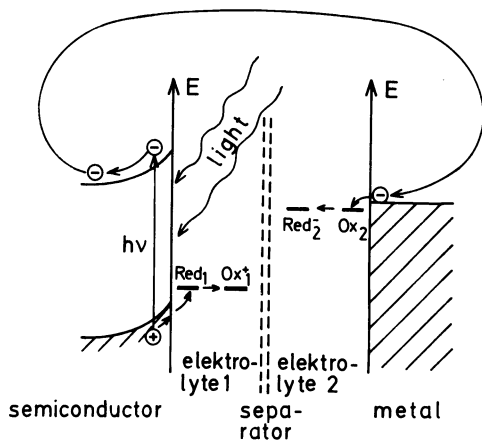

Fig. 7 Photoelectrolytic cell with a n-type semiconductor electrode for the conversion of light energy into redox energy

The final result is very similar to that one of photosynthesis. While the electrolysis circuit in the latter system is closed internally through the thylacoid membrane by a parallel transport of electrons and ions this circuit is here closed externally via an electronic conductor. Both systems provide easy separation of the products. The high mobility of the excited electronic states in the semiconductor is a particular advantage since one does not need many active interfaces in series as in photosynthesis in order to obtain complete light absorption. On the other hand, the lower variability of solid state properties compared to the flexibility of the redox properties of molecules is a disadvantage regarding the adjustment to particular redox reactions in the electrolyte. However, the simplicity of such devices makes them quite attractive for technical development. We shall discuss in the following only their state of development and their problems in more detail for they are the most promising electrochemical systems at present.

Before we do this, we compare the properties of the different systems we have presented in this section under the view of the essentials of Table 1. This is represented in Table 2.

Table 2: Comparison of the properties

Photoelectrochemical Devices for Solar Energy Conversion					
Systems	efficient charge separation	product separation	efficient light absorption	performance of redox reactions	long term stability
Homogeneous Photo-redox Reaction	difficult	difficult	good	good or modest	questionable
Photogalvanic Cell	difficult	difficult	good	modest, poor selecti-vity of electrodes	good
Membrane Cell with Sensitizer	poor	good	poor	modest	poor
Semiconductor Cell with Redox Electrolyte	good	good	good	limited by corrosion	limited or poor

FUNCTION OF SEMICONDUCTOR BASED CELLS

The charge separation step in a semiconductor which corresponds to the electron transfer in a homo-geneous photoredox reaction is the separation of electron hole pairs. This occurs in the depletion layer of a Schottky barrier and is shown for a n-type semiconductor in Figure 8. The upper part of this figure gives a picture of the charge distribution. The lower part shows the energy of the elec-trons at the band edges in the Schottky barrier.
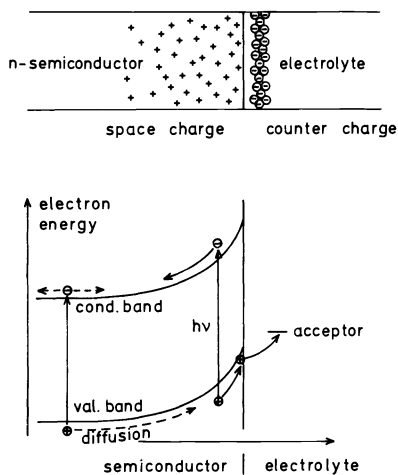

Fig. 8 Formation of a depletion layer at the contact between an electrolyte and a n-type semiconductor

Such a depletion layer is formed if the electrolyte contains a redox system which can extract the majority carriers form the semiconductor until equilibrium is achieved. An excess charge of opposite sign is then left in the space charge layer (formed by immobile donors or acceptors) which is compensated by a counter charge in the electrolyte. If the ion concentration is high enough in the electrolyte, the latter charge is highly concentrated at the interface.

Whether a Schottky barrier is formed at a semiconductor-redox electrolyte contact or not, depends on the differences of the free energy of electrons between both systems in the uncharged state. The free energy of electrons in a semiconductor can be described by the Fermi level, E_F^o , of the un-charged semiconductor and in a redox electrolyte by the redox potential of the equivalent redox Fermi level, E_{redox}. If both coincide, we have no charge transfer and equilibrium. This is shown in

Figure 9a for a n-type and a p-type semiconductor. If E_{redox} is below E_F^o, a depletion layer is

formed at a n-type semiconductor and an accumulation layer at a p-type one as shown in Figure 9b.
If E_{redox} is above E_F^o, as shown in Fig. 9c, an accumulation layer is formed at the n-type semi-

conductor and a deplation layer at the p-type semiconductor. Knowing the values of E_F^o and E_{redox},

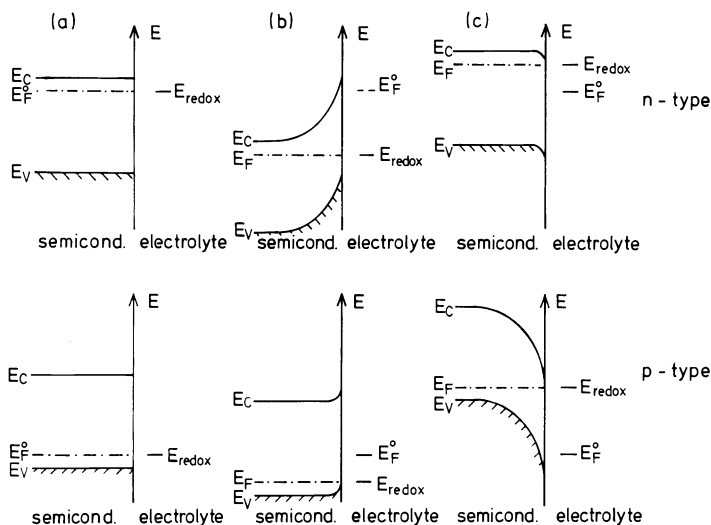one can predict what kind of boundary layer will be found.

Fig. 9 Energy diagrams of typical situations at a semiconductor-electrolyte contact:
flat band situation, depletion layer, accumulation layer

There are experimental techniques available which allow to measure the position of E_F^o of a semi-
conductor, being in contact with a particular electrolyte, in the electrochemical scale of redox
potentials (ref. 17-20). We shall use the results here but not discuss these methods.

At equilibrium. E_F and E_{redox} must be equal which is obtained by a difference of the electric poten-

tial, $\Delta\Psi$, in the electric double layer formed at the contact. We shall use E_{redox} in the electrolyte

as the reference system for the free energy and therefore is in Fig. 9 the Fermi level in the semi-
conductor shifted to this position.

$$E_F = E_F^o - e_o \Delta\Psi = E_{redox} \text{ at equilibrium.} \tag{1}$$

The position of the band edges follows the local electric potential, $\Psi(x)$, according to,

$$E_c = E_c^o - e_o \Psi(x): \quad E_v = E_v^o - e_o \Psi(x) \tag{2}$$

Therefore a bending is obtained if (x) varies.

The free energy of the electronic charge carriers in the semiconductor is decisive for the equi-
librium with redox systems and for their reactivity. At thermal equilibrium in the semiconductor,
there is no difference between the free energy of electrons and holes. Under illumination, however,
we can expect such a difference which will increase with the light intensity and gives the driving
force for recombination and for the electrochemical reactions at the interface. Because electrons
and holes can be treated as individual entities being in statistical equilibrium within their respective
energy bands although equilibrium is not established between themselves, their energetics can be
described under illumination in quasi-thermodynamic terms (ref. 21). The Fermi level is split then
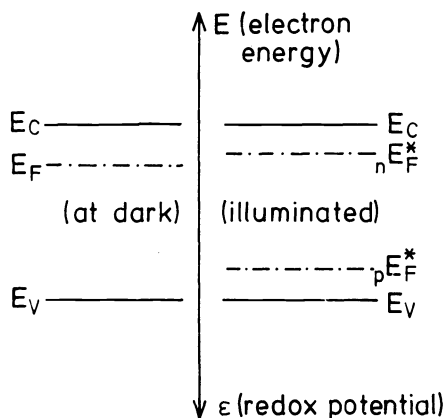into two quasi-Fermi levels, for the electrons $_nE_F^*$, and for the holes $_pE_F^*$, as shown in Figure 10.

Fig. 10 Fermi energy E_F and quasi-Fermi energies E_F in a n-type semiconductor

The definitions are as follows (ref. 21):

At equilibrium:

$$E_F = E_c + kT \ln \frac{n}{N_c} = E_v - kT \ln \frac{P}{N_v} \tag{3}$$

$$n \cdot p = N_c \cdot N_v \cdot \exp\left(-\frac{E_{gap}}{kT}\right) \tag{4}$$

$$E_{gap} = E_c - E_v \tag{5}$$

At illumination:

$$_n E_F^* = E_c + kT \ln \frac{n^*}{N} \ , \ \ n^* = n + \Delta n^* \tag{6}$$

$$_p E_F^* = E_v - kT \ln \frac{p^*}{N_v} \ , \ \ p^* = p + \Delta p^* \tag{7}$$

The difference between E_F^* and $_p E_F^*$ is the maximum free energy available from the illuminated semi-

conductor, i.e. the maximal driving force for photoelectrolysis.

In reality, the useful driving force is smaller since electron hole pair separation causes energy losses and light absorption cannot be uniform in the material. In order to get a better idea of the efficiency which can be obtained we shall consider now the energetics of an illuminated Schottky barrier. This is depicted in Figure 11 for a n-type semiconductor (part a) and a p-type one (part b).

The equilibrium situation at dark is compared there with the illuminated case. The electron hole pair separation in the space charge layer leads to a loss of positive excess charge in the semiconductor and therefore to a reduction of the band bending. In the bulk of the n-type semiconductor, E_F is shif-

ted upwards, in the p-type semiconductor downwards. The result is a difference between E_F in the

bulk and E_{redox} in the electrolyte which corresponds to a photovoltage V_{photo} and can be used as the

driving force, $\Delta E = - e_o V_{photo}$, for electrolysis. The illuminated cases show also the course of the

quasi-Fermi levels in the boundary layer. If the semiconductor is kept isolated, a steady state will be reached in which all generated electron hole pairs disappear by recombination in the bulk or on the surface and partially by a mutual redox reaction in opposite direction at the interface. If it is

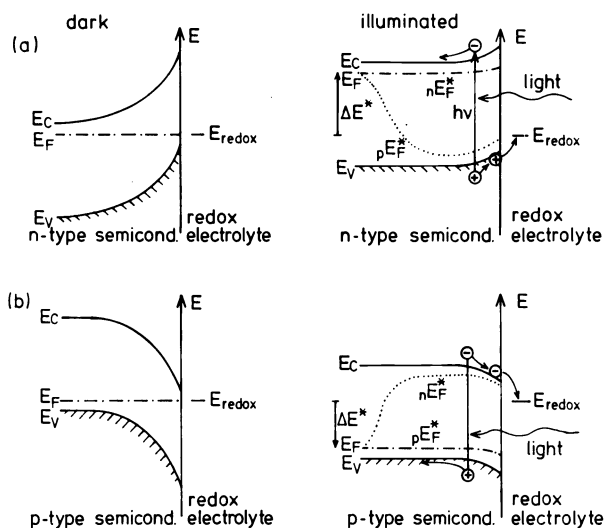connected with a counterelectrode electrons are driven to this electrode and we obtain photoelectrolysis.

Fig. 11 Energy diagrams of Schottky barriers in the dark and under illumination with course of quasi-Fermi energies

EFFICIENCY OF ENERGY CONVERSION

Before we shall consider the various devices of this type, we shall discuss the possible yield of solar energy conversion with semiconductor Schottky barriers. Although solar light has a very high content of free energy, its conversion into electrical or chemical energy is unavoidably connected with a great loss of entropy production (ref. 22-24). The reason is the width of the solar spectrum which is shown in its intensity versus quantum energy in Figure 12.
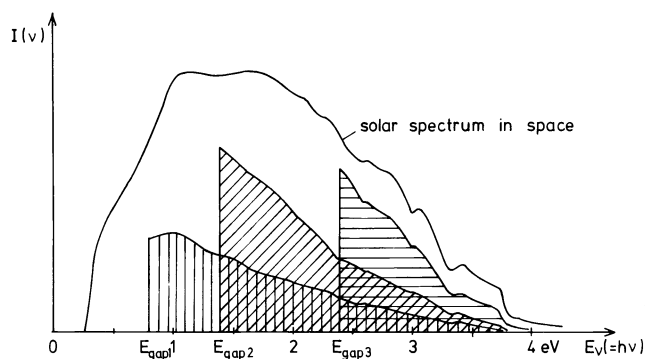

Fig. 12 Solar spectrum and converted energy in dependance of the light quantum energy for ideal threshold absorbers

A semiconductor has a threshold for light absorption which is ideally given by the band gap. All light below this threshold is lost. Since electrons and holes on energy levels far away from the band edges very quickly dissipate their excess energy into heat, all light quanta with larger energy than E_{gap}

contribute only the band gap energy to the conversion. The remaining free energy is even smaller due to the statistical distribution of the electrons and holes over the available energy states (the concentration term in equations (3, 6, 7)). The conversion efficiency is therefore depending on the band gaps and given by

$$(8) \qquad \Phi \approx \frac{(E_{gap}-C) \cdot E_{gap} \int\limits_{E_{gap}}^{\infty} I(v) \, \frac{dE_v}{E_v}}{\int\limits_{0}^{\infty} I(v) \, dE_v}$$

The term C in the calculator is a measure for the statistical entropy term which depends on the light intensity. It is further assumed that the absorption above the threshold leads to a quantum yield of one for the generation of electron-hole pairs, which certainly will not be found in real systems. With a value of C = 0.4 eV, the integrals of the calculator of equation (8) are depicted in Figure 12 for 3 different thresholds. One sees clearly that the conversion efficiency varies with E_g and passes a maximum between 1 and 2 eV.
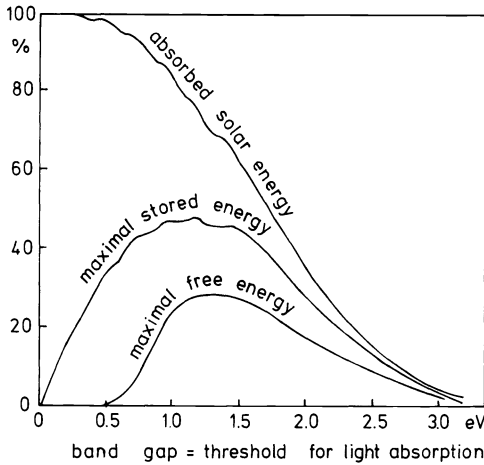

Fig. 13 Solar energy absorption and conversion efficiency of a threshold absorber in dependence of the threshold energy

In Figure 13, the influence of the position of the threshold on the overall energy absorbed, the energy stored by charge carriers with the energy of the band edges and the free energy left over is represented for an ideal absorber (ref. 24, 25). One sees that the maximum conversion efficiency for normal solar light intensity is in order of 26-30 % for a threshold of 1.4 - 1.6 eV. The really obtainable values are lower for these values are derived under optimal assumptions.
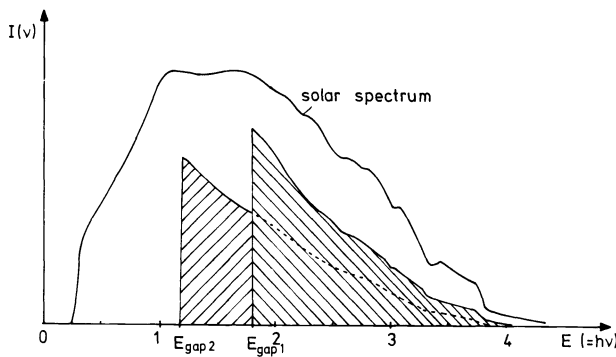

Fig. 14 Solar light conversion efficiency of a device with two threshold absorber in dependence of the threshold energy

There is one possibility for improvement by using several junctions with different thresholds in series which the light passes consecutively (ref. 26). The most energetic light quanta are absorbed in the first junction and the transmitted light in the following ones. The same can be reached by splitting

the sun light spectrally into two parts and absorbing each part with a different threshold device. The principle of such systems is shown in Figure 14 for a device with two thresholds. The conversion efficiency can reach there:

$$(9) \quad \Phi \approx \frac{(E_{gap,1} - C) E_{gap,1} \int_{E_{gap,1}}^{\infty} I(\nu) \frac{dE_\nu}{E_\nu} + (E_{gap,2} - C) E \int_{E_{gap,2}}^{E_{gap,1}} I(\nu) \frac{dE_\nu}{E_\nu}}{\int_0^{\infty} I(\nu) \, dE_\nu}$$

where the ideal assumptions are made as before in equation (8). Theoretically, efficiencies up to 43 % appear obtainable with such combinations. However, it is very unlikely that one can approach such an ideal situation. One condition, very difficult to meet in such an arrangement, is the adjustment of the two photocurrents generated in both parts of the system to equal size. Otherwise, the exceeding amount of the photocurrent in one of the junctions will be lost by recombination.

DEVICES WITH SEMICONDUCTOR ELECTRODES

The simplest photoelectrochemical device is the so-called 'regenerative cell' which just serves as a power source like solid state photovoltaic cells (ref. 16, 25, 29). The principle is shown in Figure 15 with a n-type semiconductor. The photoredox reaction at the semiconductor electrode is compensated at the metallic counter electrode by the reverse redox reaction. No chemical change occurs in the system as a whole. The photovoltage generated at the semiconductor electrode can be used for work.
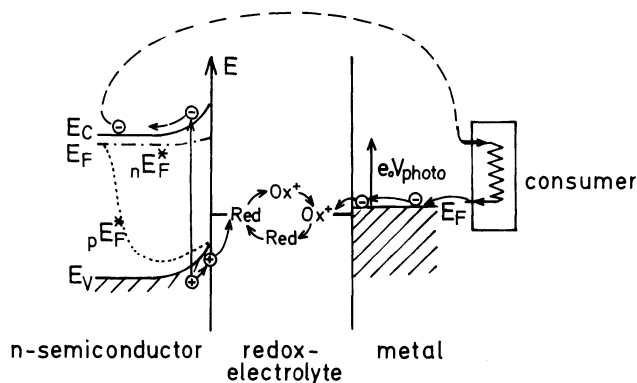

Fig. 15 Energy scheme of a regenerative photoelectrochemical cell

The internal resistance of such a cell must be minimised in order to obtain a maximal power output. Concentration polarisation at the electrodes can become a problem if the rate of diffusion and transport by convection is too low. The electrolyte must be transparant in order to illuminate the semiconductor from the front side. These are conditions which cause some restrictions for the materials and redox systems which can be employed. A design, which fulfills the geometric conditions optimally is depicted in Figure 16. It contains a transparent counter electrode because this gives an optimal exposition of the semiconductor electrode to the light source.

By a variation of R_{ext} one can measure the power output in form of current voltage characteristics.

Figure 17 gives typical examples for 3 systems which have been studied in this way. Semiconductors with a small band gap give high currents at short circuit, but low voltages, such with wider band gaps give lower currents but higher voltages. The theoretically possible output has been nearest approached with GaAs-electrodes (ref. 30, 31). The other systems are farther off from these efficiencies. The main reason is that redox systems which would in the dark provide the highest Schottky barriers or even form an inversion layer at the contact and therefore should generate the largest photovoltages cannot be employed because they cause corrosion. This problem will be discussed in the last section.
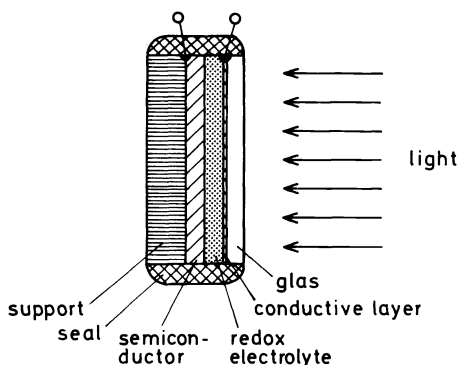
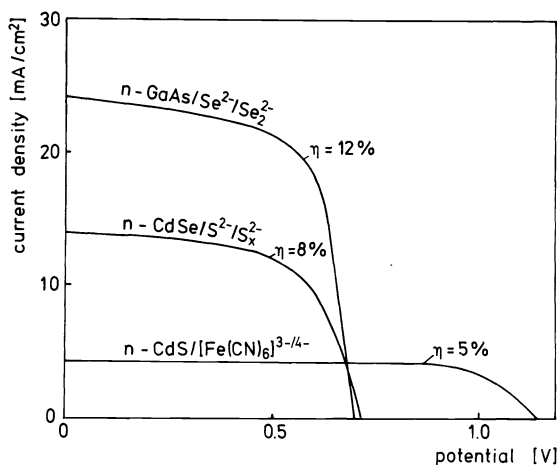Fig. 16   Model of a cell for photovoltaic application

Fig. 17   Power characteristics of 3 different regenerative solar cells

More attractive than the regenerative cell appears a device where the converted energy has not to be used immediately but can be stored directly. We have seen such a system already in Figure 7. The mechanism of energy conversion is the same as in the regenerative cell (ref. 25, 29). The photovoltage generated in the semiconductor electrode is however used now for driving two different redox reactions in opposite direction as in photosynthesis. The simplest cell of this type is a system with two redox couples in solution which are separated by a semipermeable membrane as was shown in Figure 7. For the charging process the solutions have to flow through such a cell while the sun is shining. The charged redox electrolytes can be stored outside in tanks. The stored energy can later be used in a redox battery into which the charged redox solutions have to be transferred.

Such a system has not yet been developed practically since it is difficult to find the right combination of redox couples and to build a cell construction which exposes the semiconductor electrode to the sun light without getting a too high internal resistance. Research has concentrated more on the photoelectrolysis of water since the first sucessful attempt has been reported by Fujishima and Honda (ref. 34). No membrane is needed in this case because the products are so little soluble and so inert that they don't interact with the other electrode. The necessary photovoltage for water decomposition is theoretically 1.23 V. To generate such a photovoltage, the semiconductor must have a larger band gap in order to overcome the unavoidable losses by entropy production (ref. 35). One can expect that this will add at least 0.6 eV to the band gap. Besides this, the position of the band edges of a suitable semiconductor has to be rightly located relative to the redox Fermi levels of the water oxidation and the water reduction reactions respectively. A semiconductor with optimal properties for this purpose should therefore have the position of the band edges which are shown in Figure 18. This figure is designed for a n-type semiconductor and indicates also the course of the quasi-Fermi levels in the illuminated semiconductor electrode which is needed for the photoelectrolysis of water.
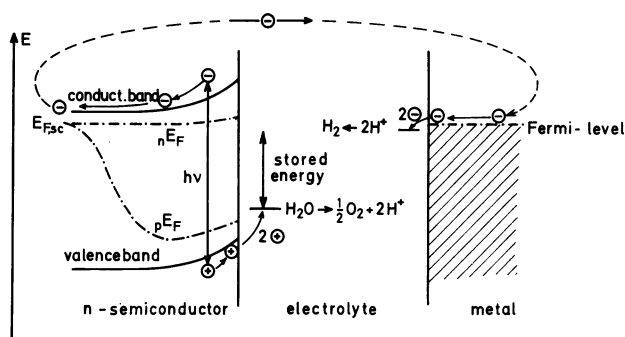
Fig. 18 Energy scheme of a cell with one n-type semiconductor electrode for the photoelectrolysis of water

This picture shows all the energy losses by charge separation (band bending) and by entropy production in the semiconductor (the distance between the quasi-Fermi levels and the respective band edges) and in the electrode reactions (the overvoltages are indicated by the distances between the Fermi levels at the surface of the electrodes and the respective redox Fermi levels in solution).

In reality the overvoltage of the water oxidation is known to be very large if the surface is not particularly active as a catalyst. One cannot expect that a semiconductor useful for the generation of the necessary photovoltage should just be such an exceptional catalyst. Therefore, the minimal band gap for this reaction will further increase to 2.2 eV or more (ref. 25). Consequently, we need a n-type semiconductor with a position of the conduction band at least 0.3 eV above the water reduction Fermi level and a position of the valence band at least 0.7 eV below the Fermi level for water oxidation.
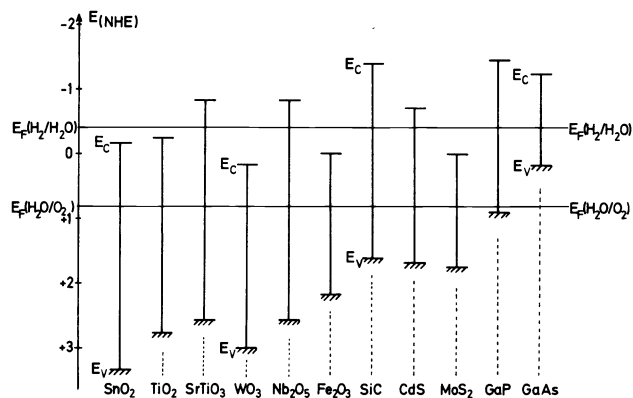

Fig. 19 Position of band edges of various semiconductors in aqueous electrolytes at pH 7

As mentioned before, the position of the band edges can be measured in suitable electrolytes. Figure 19 gives a survey of the results for an aqueous electrolyte at pH 7. This picture leads to the deplorable conclusion that very few semiconductors meet the conditions for water decomposition. Those which do it have either a too large band gap and absorb therefore too little sun light (like $SrTiO_3$, M_2O_5, Ta_2O_5, and SiC) or decompose under illumination (like CdS) as we shall discuss later.

With p-type semiconductors, which are much rarer in nature, the situation is not better. They usually have too small band gaps for this reaction besides serious stability problems. We must conclude that efficient water decomposition by direct photoelectrolysis with a single photoactive semiconductor electrode as the generator of the driving force appears to be impossible. One will need an assisting external voltage source which could be a photovoltaic cell or a second photovoltage generating junction in service with the first one. This corresponds to the two quanta consumption per equivalent of the redox reactions in photosynthesis and lets decrease the overall efficiency by a factor

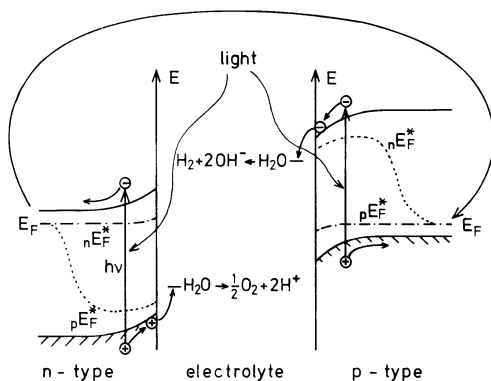of 0.5 if two equal semiconductors would be used.

Fig. 20 Photoelectrolysis cell with two power generating electrodes, one n-type and the other p-type.

Proposals of this kind have been made. Yoneyama (ref. 36) and Nozik (ref. 37) have proposed to combine a n-type and a p-type photoelectrode as the anode and the cathode in the same cell. The principle of such an arrangement is shown in Figure 20. The two photovoltages together have to provide here the necessary driving force and the semiconductors can therefore have smaller band gaps. The problem is to find the right combination of different semiconductors because the n-type specimen must have a position of the conduction band somewhat above the position of the valence band of the p-type semiconductor and both band edges must be located in between the two redox Fermi levels of the water decomposition reactions as shown in this figure. Otherwise the addition of the photovoltages would be wasted.
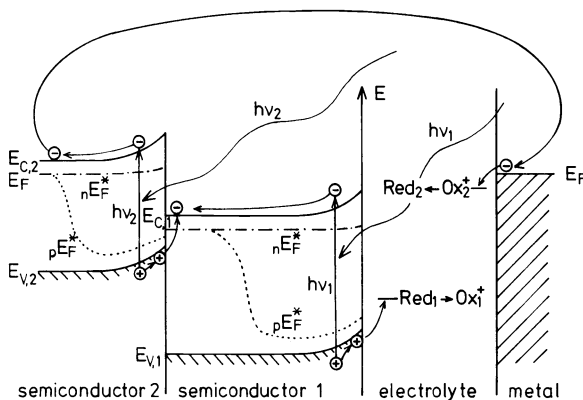

Fig. 21 Photoelectrolysis cell with a 'two-colour' semiconductor electrode as the power generator

  Another theoretically better combination is employing two Schottky barriers, or a Schottky barrier and a p-n-junction, with materials of different band gap in series as explained in the previous section (ref. 26-28), (compare Fig. 14). This combination has been used in a regenerative cell, however with poor adjustment of the two junctions to each other (ref. 38). The principle of such a device is shown in Figure 21. Such systems could be more suitable for the photodecomposition of water since the band gap of the first junction can be smaller and absorb more sun light than in a single junction device due to the additional voltage gained in the second junction. However, to find the right combinations with equal photocurrent yield and the right positions of the band edges is also a hitherto unsolved task.
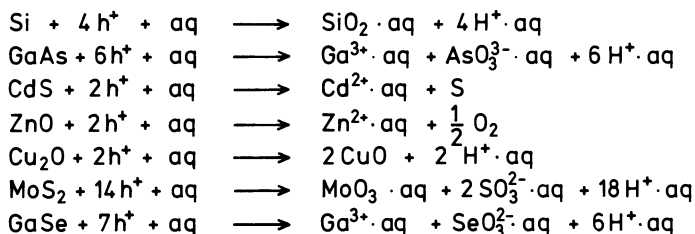
PHOTODECOMPOSITION

Besides the many problems regarding the position of the band edges and the width of the band gap which

we have already discussed, the most serious problem of photoelectrolysis is the photodecomposition of the semiconducting material. This can be caused by an accumulation of holes or of electrons in the surface (ref. 18,39). Table 3 gives a selection of typical decomposition reactions.

Table 3 Decomposition reactions of semiconductors

Electrolytic Decomposition of Semiconductors

Anodic processes (p - type specimen or photodecomposition of n - type materials)

$$Si + 4h^+ + aq \longrightarrow SiO_2 \cdot aq + 4H^+ \cdot aq$$
$$GaAs + 6h^+ + aq \longrightarrow Ga^{3+} \cdot aq + AsO_3^{3-} \cdot aq + 6H^+ \cdot aq$$
$$CdS + 2h^+ + aq \longrightarrow Cd^{2+} \cdot aq + S$$
$$ZnO + 2h^+ + aq \longrightarrow Zn^{2+} \cdot aq + \tfrac{1}{2} O_2$$
$$Cu_2O + 2h^+ + aq \longrightarrow 2CuO + 2H^+ \cdot aq$$
$$MoS_2 + 14h^+ + aq \longrightarrow MoO_3 \cdot aq + 2SO_3^{2-} \cdot aq + 18H^+ \cdot aq$$
$$GaSe + 7h^+ + aq \longrightarrow Ga^{3+} \cdot aq + SeO_3^{2-} \cdot aq + 6H^+ \cdot aq$$

Cathodic processes (n - type specimen or photodecomposition of p - type materials)

$$Si + 4e^- + aq \longrightarrow SiH_4 + 4OH^-$$
$$CdS + 2e^- + aq \longrightarrow Cd + S^{2-} \cdot aq$$
$$ZnO + 2e^- + aq \longrightarrow Zn + 2OH^- \cdot aq$$
$$Cu_2O + 2e^- + aq \longrightarrow 2Cu + 2OH^- \cdot aq$$
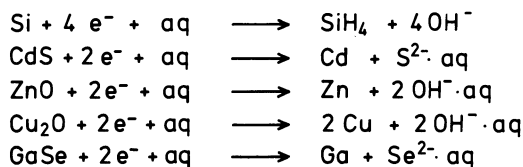$$GaSe + 2e^- + aq \longrightarrow Ga + Se^{2-} \cdot aq$$

Figure 22 shows the principle mechanism of such decomposition processes. Since the energy states of the valence band have usually bonding character, a hole in such a band means bond weakening. If the conduction band is formed by antibonding states, occupation of such a state means equally a bond weakening. Figure 22 describes how a bond can be broken by the reaction with two holes (oxidative decomposition) or two electrons (reductive decomposition). These reactions have to pass intermediates of radical character, which are more energetic than the final states and therefore often will form an activation barrier for the overall process.
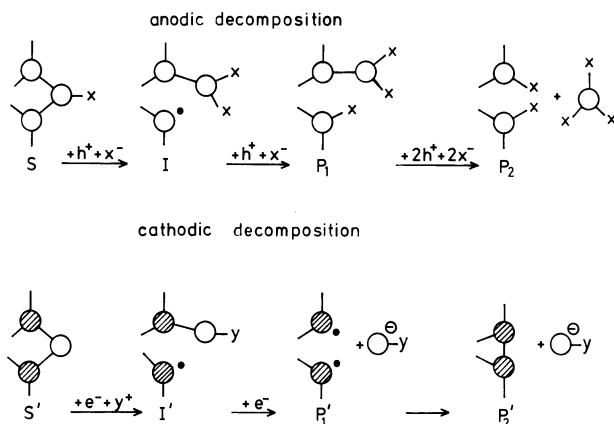

Fig. 22 Mechanism of anodic and cathodic decomposition of a semiconductor

The thermodynamics of photodecomposition have been discussed by two groups (ref. 40,41). The free energy of the minority carriers plays a decisive role in such a treatment because it varies with their concentration at the surface. In a Schottky barrier, the minority carriers are under illumination

accumulated at the surface and if this accumulation exceeds a critical value, decomposition will begin. This critical threshold will depend on the energy of the most energetic intermediate which has to be passed in the overall reaction path. By comparing the energy differences of each step in the reactions of Figure 22, one can distinguish three different situations which should indicate whether a semiconductor will photodecompose or not. These situations are shown in the energy diagrams of Figure 23
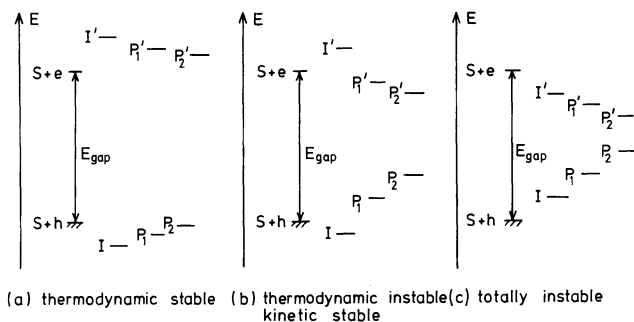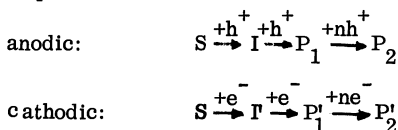

(a) thermodynamic stable (b) thermodynamic instable (c) totally instable
                              kinetic stable

Fig. 23 Energy diagram for anodic and cathodic decomposition reactions with the reaction sequences:

anodic: $S \xrightarrow{+h^+} I \xrightarrow{+h^+} P_1 \xrightarrow{+nh^+} P_2$

cathodic: $S \xrightarrow{+e^-} I' \xrightarrow{+e^-} P_1' \xrightarrow{+ne^-} P_2'$

The energy of the initial state of these processes in terms of redox reactions is either the electron at the conduction band edge or the hole at the valence band edge. If the energy of the most energetic intermediate (in the simplified model of Figure 22, I or I') is above the conduction band for the cathodic reaction or below the valence band for the anodic reaction, the semiconductor is stable. The stability is total if also the final product has an energy in these ranges (part a). The system is only relatively stable due to slow kinetics, if the energy of the final products is below or above the respective band edges (part b). If the energy of the intermediates is inside the band gap, the semiconductor is instable (part c).

For simplicity, the situation for anodic and cathodic decomposition has been assumed as equal in Figure 23. Any combination of the different cases however is possible. It appears that the favourable situation of Figure 23a never exists for the anodic process (ref. 40). All semiconductors seem to be unstable against anodic photodecomposition while cathodic photodecomposition is much less common. It appears therefore that p-type semiconductors are better suitable for photoelectrochemical light energy conversion than n-type ones. However, p-type materials are much rarer and therefore the selection of properties regarding the energy position of band edges etc. is very limited. Besides this, at open circuit conditions or in the range of the highest photovoltages, the concentration of the majority carriers becomes relatively high at the surface and the anodic decomposition could go on then in the dark if the semiconductor is not stable in this direction.

In some cases, a kinetic stability has been observed for n-type materials, particularly at semiconducting compounds of transition metals having layer structures (ref. 42, 43). In these systems, the valence band states have little bonding character and the conduction band states are not much bond weakening neither that electronic excitation does not seriously affect the bond strength in the crystal. In addition to this, the wave functions of these states overlap little or not with the wave functions of possible reactants in the solution. This means a high activation barrier for decomposition exists although the overall reaction affinity for corrosion is thermodynamically large in these systems.

Such kinetic stability can also be reached by a competing redox reaction which consumes the electronic charge carriers at the interface quickly enough to prevent the decomposition reactions. This is the normal reason for stability in all systems which have been claimed as being stable (ref. 44-50). One example is the CdS-electrode in contact with the redox system S^{2-}/S^{2-} where the photooxidation of CdS (cf Table 3) competes with the reaction:

$$S_n^{2-} + S^{2-} + 2h^+ \longrightarrow S_{n+1}^{2-}$$
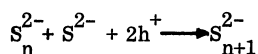
This different kind of kinetic stabilisation can be described in similar terms as case b in Figure 23 by a comparison of the energies of the various stages of the reactions. This is done in Figure 24 following the kinetics of the simplified reaction schemes in Figure 22.
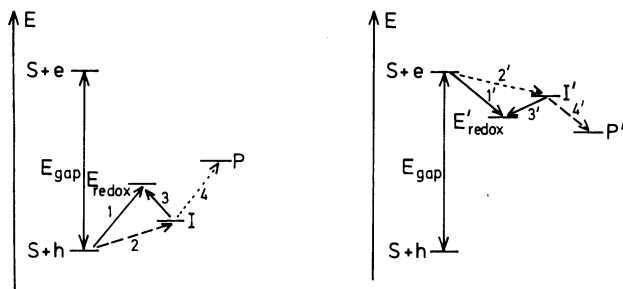
Fig. 24 Stabilisation by redox reactions:
energy diagram for the competition between decomposition reactions and redox reactions with the reaction schemes:

anodic: (1) $S + h + Red \longrightarrow S + Ox$ (fast)
          (2) $S + h \longrightarrow I$ (slow)
          (3) $I + Red \longrightarrow S + Ox$ (fast)
          (4) $I + h \longrightarrow P$ (slow)

cathodic: (1 ') $S + e + Ox \longrightarrow S + Red$ (fast)
          (2 ') $S + e \longrightarrow I'$ (slow)
          (3 ') $I' + Ox \longrightarrow S + Red$ (fast)
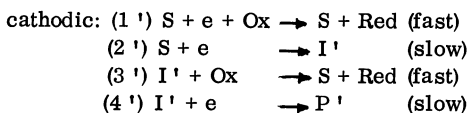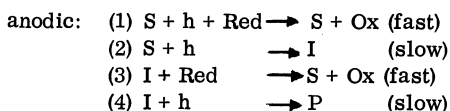   (4 ') $I' + e \longrightarrow P'$ (slow)

Figure 24 shows the competing processes and their energies in the scale of redox reactions. Stabilisation is obtained if the redox reaction is energetically much more favourable than the formation of the intermediate and the first intermediate interacts fast enough with the redox system in order to reconstitute the original state of the semiconductor surface. How efficient the competition is, depends on the kinetic parameters and cannot be derived from such energy comparison. However, the larger the differences in driving force are, the better are the chances for stabilisation. This is particularly so if the competing redox reaction is a one-electron transfer process without kinetic complications and has therefore a large rate constant while the decomposition reaction has always a very complex mechanism with at least one slow reaction step involved. The scheme of Figure 24 can give only a qualitative guide-line for a judgement of the stability. The processes involved are by far too complicated and depend to a large extent also on the electrolyte composition. It needs therefore an experimental check-up from case to case.

CONCLUSIONS

The critical review of the problems involved in solar energy conversion by photoelectrolysis has shown that some very serious difficulties have to be overcome in order to make such systems technically applicable and economically compatible. The cells based on semiconductor-electrolyte junctions as the energy converters are the most efficient systems. However, they suffer primarily of the corrosion problem. The question is whether such interfaces can be stabilised without too much loss in conversion efficiency. Another serious problem is the limited availability of materials with an optimal band gap for solar light conversion, which at the same time should have the right position of the band edges in order to perform the redox reactions wanted. This appears to exclude the chance that direct water photoelectrolysis can efficiently be performed in such cells. A separation of the power generation in photovoltaic devices and the water decomposition in an electrolysis cell with electrodes of high catalytic activity and metallic character seems to be more promising since these functions can then be optimised separately.

One can be somewhat more optimistic with regard to the development of a photoredox battery in which two different redox systems are used for energy storage. The principle of such a system was depicted in Figure 7. In such a device the redox potentials can be adjusted to the position of the band edges by a suitable selection of the redox couples and corrosion is less likely if the competing redox reaction is a fast one-electron transfer process. More emphasis should therefore put on such developme-

nts. The best chances have un doubtedly regenerative cells which are also less complicated with respect to cell construction. These are however photovoltaic systems which have to compete with solid-state devices of the same type. The disadvantage of the photoelectrochemical cells is the necessity to seal them tightly in order to avoid electrolyte losses. Their advantage lies in the simplicity,

Therefore much more research is needed on the formation of thin semiconducting layers with suitable photoelectric properties for electrolysis. Hydrogen from water for energy storage might then be obtained in a second step by classical techniques.

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