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REVIEW

Electrochemical aspects of solar energy conversion

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Current research and development work in solar energy utilization is very briefly reviewed. Attention is drawn to the possible use of photoelectrochemical effects to convert solar energy directly to electric power or synthetic fuel. Photoelectrochemical cells that have been proposed for this purpose are classified into three types, and a detailed description of their mode of action is given. The solar spectrum at the earth's surface and terrestrial receipts of solar energy are discussed. The factors that limit the power conversion efficiency of photoelectrochemical cells are described, and a brief reference is made to the thermodynamics of photoelectric transducers. Some work that, although not directly related to solar energy conversion, is of possible relevance, is summarized: the topics covered are the photosensitization of processes at semiconductor electrodes, pigment films on metal electrodes, and the primary processes of energy and charge transfer in natural and artificial photosynthetic membranes.

1. Introduction

We receive an enormous amount of radiant energy from the Sun: the solar energy falling on the Earth's surface in a fortnight is equivalent to the energy contained in the world's initial supply of fossil fuels [1]. About one third of this energy maintains the hydrological cycle, and two thirds goes to heat the surface of land and oceans [2]. Only about 0·03% of the solar input is stored as chemical energy by the photosynthetic growth of green plants, yet this process provides all our food and the fossil fuels we are now so rapidly consuming. In the long term, if we are not to rely solely on nuclear power, we shall have to develop large scale methods for harnessing solar power. Solar energy may in principle be used to provide chemical fuel and electric power, as well as useful heat for various purposes. Systematic research work on solar energy utilization started in the 1950s and, thanks to the energy crisis, it has now become rather popular: the interested reader can refer to a number of general publications on the subject [3–8].

Solar energy may be used simply as heat, captured by absorbing black surfaces exposed to the sun to provide comfort heating and hot water for buildings, or (with focussing collectors) to raise steam to provide mechanical power. There are also a number of ways of converting solar energy directly into electric power or chemical fuel, by quantum processes that generally use only the more energetic photons in the solar spectrum. The silicon solar cell is the most highly developed of these direct conversion devices, and this and other photovoltaic devices now appear more promising for terrestrial use than photoemissive or thermoelectric transducers.

Any endothermic photochemical reaction represents a conversion of light energy to chemical energy. Provided the product is sufficiently stable, it can be sorted as a 'fuel' and reconverted to its original form, with evolution of energy, at will. The characteristics required of a photochemical process to be used on a massive scale to store solar energy are extremely demanding, and suffice it to say here that no suitable reaction has yet been discovered [9].

From time to time, efforts have been made to use photoelectrochemical (PEC) effects in devices for the direct conversion of solar energy to electric power or chemical fuel. No such device of practical value has yet been made, and there is very little research work being carried out on PEC cells today. This review presents a summary of some of the published work in this and related areas, and attempts to pinpoint the reasons for the prevailing gross inefficiency of PEC devices.

2. Photoelectrochemical energy conversion

2.1. *PEC effects and PEC cells*

A photoelectrochemical effect is defined as one in which the irradiation of an electrode/electrolyte system produces a change in the electrode potential (on open circuit) or in the current flowing (on closed circuit). The cause of this may be a photochemical reaction in bulk solution, the products of which are electroactive, or it may be that the cell contains a photosensitive membrane or electrode. Effects of this sort are very common: indeed, it would probably be hard to find an electrode/electrolyte system that was completely insensitive to absorbed light. Generally, PEC effects at clean metal electrodes are very small, being measured in mV or nA, and are due to phenomena such as electron emission from the metal surface, photolysis of solute species adsorbed on the electrode, or simply the thermal effect of the absorbed radiation [10]. More pronounced PEC effects are often found with semiconductor electrodes which may or may not be coated with sensitizing dye. These effects are generally due either to photosensitised charge injection into the electrode, or to decomposition of the electrode itself. Similar effects at a photosensitive membrane in the cell can transmit a PEC effect to the electrodes by alteration of the concentration of electroactive ions in solution. Finally, a PEC effect is likely to be observed at more or less any electrode immersed in a solution undergoing photolysis, since the photoinduced changes in concentration will probably affect the electrode potential. Several reviews of these phenomena exist [11–14].

It is clear that the photoelectrochemical effect, as defined above, may have a number of causes. It also has two common alternative names: the Becquerel effect, in honour of its discoverer [15] and the photogalvanic effect. The latter term implies that the photoinduced current flow is associated with a Faradaic process at the electrode (which must necessarily be the case if a direct current flows across the electrode/electrolyte interface). In contrast, a photovoltaic effect usually means one due simply to the photo-production of electrons and holes, unaccompanied by a chemical change. This term is perhaps best reserved for purely solid state electronic devices, although it is sometimes used to imply a photoelectrochemical effect due to a photoreaction occurring heterogeneously on the electrode surface rather than homogeneously in the bulk electrolyte.

A PEC cell is defined as one in which one or both half cells exhibit a PEC effect. In any PEC cell to be used for the conversion of solar to useful electrical or chemical energy, the net cell reaction occurring during illumination must be endoenergetic, and it would be advantageous in any practical device if both half cells exhibited a PEC effect. However, most work has been done either on cells composed of one PEC half cell and one conventional half cell, or simply on the potentiostatic investigation of PEC half cells.

Most of the PEC cells so far proposed for solar energy utilization can be classified as one of the following types:

2.1.1. *Chemical consuming PEC cells.* Such a cell at first sight seems to offer no advantage over conventional galvanic cells, which also consume chemicals during their operation. However, a PEC cell of this type is intended to convert freely available chemicals into useful products: particular interest centres on the PEC decomposition of water to hydrogen and oxygen. Although such a cell only operates on illumination, energy storage is achieved by collection of the cell product.

2.1.2. *Continuously operated photoregenerative cells.* Illumination produces a photochemical reaction in solution or at a photosensitive membrane which is the reverse of the spontaneous electrode reaction. The overall composition of the cell is invariant, and the cell functions only on illumination and has no storage capacity. This type of cell is really a variant of type 2.1.3.(a) below, and it is employed when the products of the photochemical reaction are not sufficiently stable to separate and store.

2.1.3. *Cyclically operated photoregenerative cells.* These cells are storage batteries in which the products of cell discharge, on illumination, regenerate the original cell fuels: the cell discharge is of course thermodynamically spontaneous, and it follows that the recharge by light must be endoenergetic. These cells can be subdivided on the basis of the nature of the recharge step.

(a) Open circuit recharge: the regeneration of the cell fuels from the products of discharge is a purely photochemical reaction. The cell converts light energy to chemical energy on recharge, and chemical energy to electrical energy on discharge.

(b) Closed circuit recharge: the action of light causes the net cell polarity to reverse, and the cell reaction is hence reversed, so that during recharge light energy is converted partly to electric energy, and partly to chemical energy.

Before describing PEC cells in detail, some consideration will be given to the thermodynamic and kinetic factors which limit the efficiency of PEC conversion of solar energy.

2.2. *The solar spectrum and terrestial receipt of solar energy*

The mean solar irradiance at normal incidence just outside the Earth's atmosphere is 1353 W m^{-2} [16] and the solar spectrum approximates fairly closely to that of blackbody radiation at 6000 K. The spectral distribution of sunlight reaching the Earth's surface is modified by scattering by aerosol, and by absorption by ozone (in the u.v.) and by water vapour and CO_2 (in the i.r.). The extent of these effects depends mainly on the air mass ratio, which is the ratio of the optical path length of sunlight through the atmosphere to the path length when the sun is at the zenith. Thus AMO sunlight means extra-terrestrial sunlight, AM1 means the sun is overhead and the maximum value, AM25, refers to a setting or rising sun. Fig. 1, adapted from Moon's data [17], illustrates the solar spectrum at normal incidence for *AM*0, *AM*2 and *AM*5 sunlight in a cloudless sky. The higher the air mass ratio, the greater the extent to which i.r. and u.v. are absorbed in the atmosphere, and so the higher is the proportion of visible wavelengths in sunlight. The energy distribution in the spectrum of *AM*2 sunlight (solar altitude = 30°) is given in Table 1. Table 2 gives the solar irradiance (at normal incidence), the total photon flux and the average photon energy for various values of m, the air mass ratio, and w, the numbers of cm of precipitable water vapour in the atmosphere.

The amount of solar energy received at any particular location depends mainly on the latitude and the average cloud cover. Fig. 2 gives mean insolation data for the world [18]: in cloudy areas, a substantial portion of the total radiation is diffuse, rather than direct from the sun, due to scattering by clouds. In such areas, the use of focussing collectors to concentrate direct sunlight is unlikely to be economic, and flat collectors capable of using diffuse as well as direct radiation must be employed. It is clear that to collect a substantial amount of energy, large areas must be covered with collection devices, and it follows that the cost per unit area and lifetime of the device are critical. As insolation varies both diurnally and seasonally, an inbuilt capacity for energy storage is highly desirable.

Storage capacity exists in most PEC cells, as pointed out in the previous section, and a solar PEC cell can thus accomplish in one stage what the photovoltaic cell/storage battery combination accomplishes in two. Moreover, most photovoltaic cells require scrupulous manufacture, and are expensive. It is possible that a PEC cells could be relatively cheap devices: however, whether they will ever compete with photovoltaic cells on grounds of efficiency and reliability cannot be predicted.

2.3. *Factors affecting the efficiency of PEC devices*

The following treatment of loss factors in PEC cells is based partly upon analogous treatments of the efficiency of photovoltaic cells [20, 21] and of purely photochemical energy storage [9]. Some of the loss processes to be described are determined by basic physical principles, and some by alterable parameters such as cell geometry.

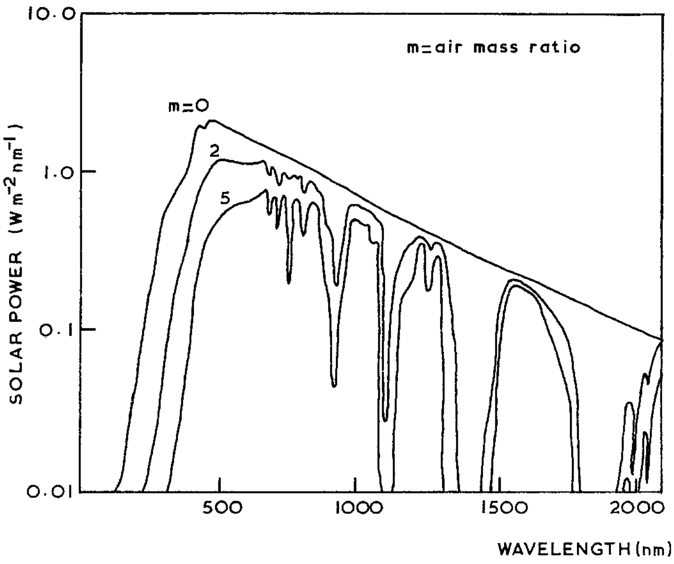

Fig. 1. Solar irradiance at normal incidence for *AM*0, *AM*2 and *AM*5 sunlight. Atmospheric pressure = 760 mm; precipitable water = 20 mm; dust = 300 particles cm^{-3}, ozone = 2.8 mm.

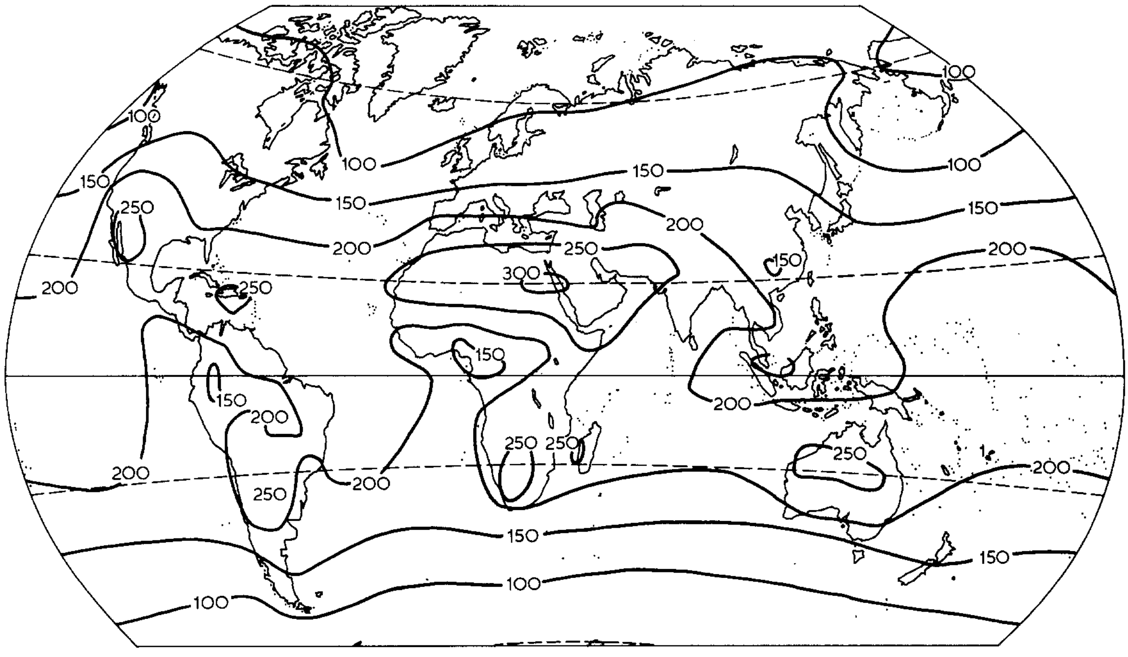

Fig. 2. Mean annual intensity of total solar radiation on a horizontal plane at the surface of the Earth (W m^{-2} averaged over 24 h. day).

*Table 1. Energy distribution in the terrestrial (AM2) solar spectrum**

Spectral region	*Interval boundaries*		*Solar irradiance*	
	Wavelength (nm)	*Wave number (cm^{-1})*	*$W\,m^{-2}$*	*Percentage of total*
Ultraviolet	0– 315	∞ –31,746	0	0
Near u.v.	315– 400	31,746–25,000	20·0	2·7
Blue	400– 510	25,000–19,608	108·0	14·6
Green/yellow	510– 610	19,608–16,393	118·0	16·0
Red	610– 700	16,383–14,286	102·0	13·8
Near i.r.	700– 920	14,286–10,870	174·0	23·5
Infrared	920–1400	10,870– 7,143	160·0	21·6
	1400– ∞	7,143– 0	58·0	7·8
			740·0	100·0

* From data given by Moon [17].

*Table 2. Parameters of the solar spectrum as a function of absorption conditions**

Air mass (m)	*cm precipitable water* (w)	*Comments*	*Irradiance, ($W\,m^{-2}$)*	*Photon flux, (No. $s^{-1}\,m^{-2}$)*	*Average photon energy (eV)*
0	0	Outside atmosphere	1350	$5{\cdot}8 \times 10^{21}$	1·48
1	0	Solar altitude = 90°	1060	$5{\cdot}0 \times 10^{21}$	1·32
2	0	Solar altitude = 30°	880	$4{\cdot}3 \times 10^{21}$	1·28
3	0	Solar altitude = 20°	750	$3{\cdot}9 \times 10^{21}$	1·21
3	5		590	$3{\cdot}2 \times 10^{21}$	1·18
1	0	Cloudy day	120	$5{\cdot}2 \times 10^{20}$	1·14

* From data given by Loferski [19]

2.3.1. *Ultimate efficiency.* All quantum converters of light are threshold devices: there is a certain threshold photon energy, E_g (which might be a semiconductor band gap, the work function of a metal surface or the energy of the first excited singlet state of a molecule) below which photons are not absorbed, or if they are, they do not produce the desired effect. Photons of energy $E > E_g$ are not entirely efficient even if they are completely absorbed, since vibrational relaxation almost inevitably occurs in the upper excited state before the charge transfer process can take place: the fraction $(E - E_g)/E$ of the photon energy is therefore dissipated as heat, and only the fraction E_g/E can be converted to useful work. If such a quantum converter is irradiated with white light the spectral irradiance of which is described by the function $P(E)$ and the flux density of photons by the function $N(E)$, then the fraction of the incident radiant energy available for conversion, η_{ult}, is given by

$$\eta_{ult} = \frac{E_g \int_{E_g}^{\infty} P(E)\, \mathrm{d}\ln E}{\int_0^{\infty} P(E)\, \mathrm{d}E} \tag{1}$$

$$= \frac{E_g \int_{E_g}^{\infty} N(E)\, \mathrm{d}E}{\int_0^{\infty} E N(E)\, \mathrm{d}E} \tag{2}$$

This factor is a function both of the irradiating spectrum and of E_g. The value of η_{ult} as a function of E_g is shown in Fig. 3 for *AM*0 and *AM*1 sunlight: η_{ult} has a maximum value of ~ 0·45 and the optimal value of E_g shifts from 1·1 eV to slightly higher values as the air mass increases. E_g values of most PEC devices are well above the optimum 1·1 eV (equivalent to light of wavelength 1127 nm). Many proposed devices operate only at blue or even shorter wavelengths ($E_g > 3$ eV).

2.3.2. *Light absorption efficiency.* The above calculation of ultimate efficiency assumed that the system was perfectly absorbing for all photons of $E > E_g$. This is somewhat unrealistic, and Equations

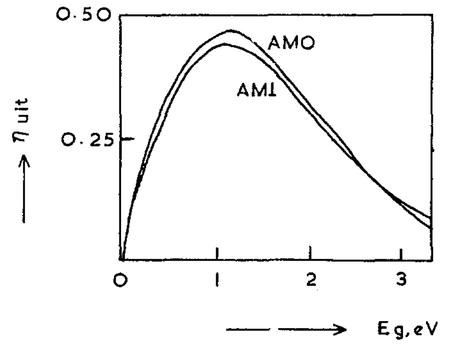

Fig. 3. Dependence of the ultimate efficiency η_{ult} on the threshold energy E_g for $AM0$ and $AM1$ sunlight.

1 and 2 should be modified by the factor A_E, the optical absorbance of the device for photons of energy E, giving a modified efficiency factor η'_{ult}:

$$\eta'_{ult} = \frac{E_g \int_{E_g}^{\infty} A_E P(E)\, \mathrm{d}lnE}{\int_0^{\infty} P(E)\, \mathrm{d}E} \tag{3}$$

$$= \frac{E_g \int_{E_g}^{\infty} A_E N(E)\, \mathrm{d}E}{\int_0^{\infty} EN(E)\, \mathrm{d}E} . \tag{4}$$

η'_{ult} may be made to approach η_{ult} by making the device sufficiently optically dense; this may however increase other loss factors considerably.

2.3.3 *Open Circuit voltage efficiency.* Let the change in open circuit potential that occurs on illumination of the PEC half cell be ΔV_0. The open circuit voltage efficiency factor, η_{V_0}, is defined by Equation 5:

$$\eta_{V_0} = \frac{e\Delta V_0}{E_g} . \tag{5}$$

The open circuit potential of the illuminated PEC electrode is determined by the requirement that hole-electron pairs are eliminated as rapidly as they are produced, there being no net current flow in the circuit. The generation rate depends on the light intensity and on the optical density of the half cell; thermal generation can normally be ignored by the comparison. The recombination rate is the sum of the rates of radiative recombination and of such non-radiative physical and chemical quenching processes as may occur in the system. The factor η_{V_0} is therefore only partly determined by unalterable properties, and is not a fundamental parameter of the system, but simply an indication of the extent to which light absorption produces charge transfer in the system. The value of η_{V_0} is generally less than unity although effects such as the liberation of trapped space charge in semiconducting solids may give rise to anomalously high values [22], which are not however reproducible.

The dependence of ΔV_0, and hence η_{V_0}, upon light intensity depends upon the nature of the particular PEC device, but a relationship of the form $\Delta V_0 = klnI$ not uncommonly holds for moderate light intensities. Similar behaviour is found in *p-n* junction photovoltaic devices and is predicted by theoretical considerations [21, 23].

Equation 5 is not directly applicable to PEC cells of type III a, in which the photochemical and electrochemical processes occur consecutively rather than rather than simultaneously. An analogous factor can be defined in terms of the (positive) free energy change of the photochemical reaction involved [9]:

$$\eta_{V_0} = \frac{\Delta G}{nF} \frac{e}{E_g} . \tag{6}$$

2.3.4. *Photon efficiency.* This factor, and the following one, describe the behaviour of a PEC half cell under closed circuit conditions. Again, this definition is not applicable to cells of type III a. The photocurrent-voltage characteristic of other types of PEC half cell is usually of the form shown in Figure 4: a limiting photocurrent, i_{lim}

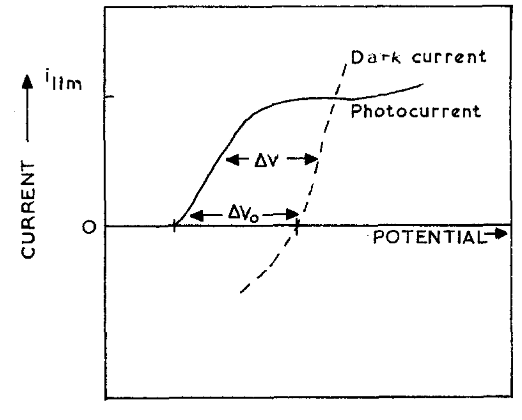

Fig. 4. Characteristic form of dark and photo-current/voltage curves for PEC half cell. The limiting photocurrent, i_{lim}, is proportional to light intensity.

appears, which is independent of potential and proportional to the light intensity. In this case, the photon efficiency, η_ϕ, is defined as the ratio of the number of electrons flowing per photon absorbed:

$$\eta_\phi = \frac{i_{\text{lim}}/e'}{\int_{E_g}^{\infty} A_E N(E)\,\mathrm{d}E} \tag{7}$$

where e' is the electronic charge in coulombs. This factor has low values if the energy of the optically excited states is quenched before charge separation occurs, or if the electroactive species is produced by photolysis in solution and is so unstable that only a small proportion survives long enough to diffuse to the electrode; even if the electroactive species is stable, concentration polarisation may severely limit i_{lim}. The value of η_ϕ is therefore dependent on solution concentrations, cell geometry and other factors that affect mass transfer within the cell.

2.3.5. *Current-voltage efficiency.* The nominal power that a PEC half cell delivers by transducing light of irradiance P into a flow of electrons is $\eta'_{ult}\eta_{V_0}\eta_\phi P$, and the nominal power conversion efficiency is $\eta'_{ult}\eta_{V_0}\eta_\phi$. The actual power conversion efficiency depends upon the photocurrent-voltage characteristic of the half cell. If this were rectangular, the half cell would deliver the nominal power; if the characteristic were linear, implying an ohmic internal resistance, the maximum deliverable power would be one quarter of the nominal power. In general, the ratio of the power delivered to the nominal power is given by

$$\eta_{iV} = \frac{i\Delta V}{i_{\text{lim}}\Delta V_0} \tag{8}$$

and the actual power conversion efficiency is thus

$$\eta = \eta'_{ult}\,\eta_{V_0}\eta_\phi\eta_{iV}. \tag{9}$$

η_{iV} is not constant, and its variation with V is determined by the sum of the internal losses due to ohmic resistance, charge transfer overpotential and concentration polarisation in the half cell, as in a conventional half cell. Equation 9 is directly applicable to the whole PEC cell only if the counter half cell is non-polarizable so that no power loss occurs in it.

The ohmic resistance of a PEC half cell is substantial if semiconducting electrodes of poor conductivity are employed. From Table 2 it is seen that the maximum photon flux that a PEC cell has to handle in unconcentrated sunlight $15 \times 10^{21}\eta_{ult} \leqslant 2\cdot5 \times 10^{21}$ photons $s^{-1}\,m^{-2}$. (This corresponds to a maximum photocurrent density of 40 mA cm^{-2}.) The scale-up of a resistive device which has good efficiency when small may result in an unacceptable increase in the resistive loss.

2.4. *Thermodynamics of photoelectric transducers*

The above treatment implies that a photoelectric device can in principle convert monochromatic light of frequency E_g/h to useful work with perfect efficiency, and this applies rigorously only to a photoelectric transducer maintained at 0 K. At any higher temperature, T, the device emits the thermal radiation characteristic of that temperature and in this case, the Carnot limiting efficiency of the device is $(T_s - T)/T_s$ where T_s is the 'temperature' of the incident radiation [24]. This second law limitation, which also applies to the upper limit on the conversion of radiant energy to chemical free energy [25–27], often puzzles chemists, who tend to think of photochemistry purely in terms of isolated molecular events. However, it may be helpful to point out that if this limitation did not apply, the device would produce useful power from the radiation incident upon it even when 'in the dark' in isothermal surroundings.

If the incident radiation emanates from a black body, then T_s is the temperature of the body. For solar radiation, $T_s \simeq 6000$ K so if $T = 300$ K, the Carnot limiting efficiency is $\sim 0\cdot95$.

3. Photosensitized decomposition of water: an example of cells of type I

In the next four Sections, a few examples drawn from the older literature of the various types of PEC devices will be given.

The decomposition of water to hydrogen and oxygen is a highly endothermic process:

$$H_2O(l) \rightarrow H_2 + \tfrac{1}{2}O_2\text{: } \Delta H^\circ = +295\,\text{kJ},$$
$$\Delta G^\circ = +237\,\text{kJ}. \tag{10}$$

Hydrogen burns cleanly in air, yielding water once more, and could be a valuable fuel if only a suitable method of bring about the decomposition of water could be found. Various thermal methods have been suggested [28], but reaction [10] is so endothermic that even at elevated temperatures, the equilibrium lies well on the left hand side. The decomposition can in principle be more elegantly achieved by some sort of photocatalysis. The decomposition of 1 mol of water requires the input of at least 237 kJ; this is equivalent to 2·46 eV per molecule, and so only light of wavelength shorter than 500 nm could be effective in a single quantum photocatalytic process. A stepwise process that proceeded at a photocatalytic surface and required two (or more) quanta per molecule of water decomposed would use the solar spectrum more efficiently. Since the electrochemical decomposition of water to hydrogen and oxygen is a two electron stepwise process, it might be possible to find an electrode at which a two quantum photoelectrochemical breakdown of water could occur.

Fujishima and Honda [29, 30] have reported behaviour of this sort at an *n*-type semiconducting TiO_2 electrode in aqueous electrolyte. Current-voltage curves obtained in the dark and on irradiation with light of wavelength below 415 nm (corresponding to the band gap, 3·0 eV) are shown in Figure 5a. The authors showed that the anodic photocurrent was due to the evolution of oxygen, and concluded that the PEC reaction shown in Fig. 5b occurs. Photon absorption excites an electron from the valence band of TiO_2 to the conduction band, and the hole in the valence band is filled by transfer of an electron from a water molecule, yielding OH and finally, in a four quantum process, molecular oxygen. The plateau region in the photocurrent corresponds to the limiting efficiency of electron injection in the conduction band under anodic bias, which causes electrons to migrate to the electrode interior as illustrated in Fig. 5b. Fujishima and Honda noted that the anodic photocurrent commenced at −0·5 V, a more negative potential than the hydrogen evolution potential at this pH: they therefore constructed the electrochemical cell [Pt(platinised)/aqueous electrolyte/TiO_2], and observed current to flow in the same sense when the TiO_2 electrode was irradiated. They concluded that hydrogen was evolved at the cathode according to the following net reaction scheme:

$$TiO_2 + 2h\nu \rightarrow 2e^- + 2p^+ \qquad (11)$$

$$2p^+ + H_2O \rightarrow \tfrac{1}{2}O_2 + 2H^+ \text{ (at } TiO_2 \text{ electrode)} \qquad (12)$$

$$2e^- + 2H^+ \rightarrow H_2 \qquad \text{(at Pt electrode).} \qquad (13)$$

A photon efficiency of 0·1 is quoted without experimental details [30]. No titanium was detected in solution [29] so it appears that TiO_2 does not decompose on illumination under anodic bias, unlike ZnO [31] and CdS [32]; this may perhaps be due to the strong covalent bonding in the TiO_2 lattice. The counter electrode, platinised platinum, used in this work, is of course reversible for hydrogen evolution. Were it not, the photon efficiency might well be reduced by charge transfer resistance at this electrode.

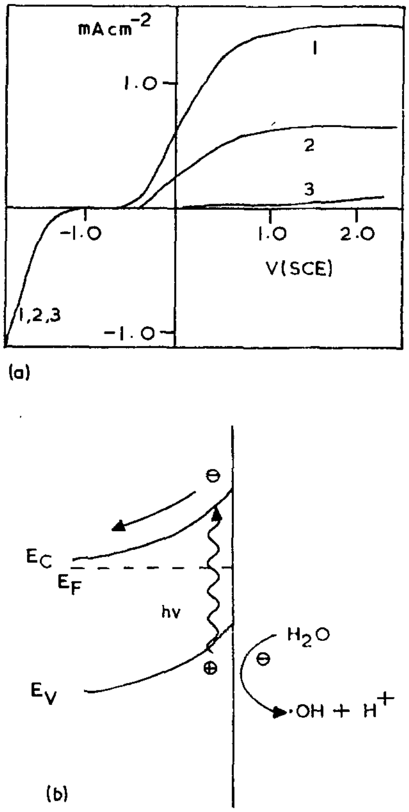

Fig. 5. (a) Current-voltage curves for *n*-TiO_2 electrode [29]. Illumination by 500 W xenon lamp, pH = 4·7, curve 1 = light intensity 2*I*, curve 2 = light intensity *I*, curve 3 = dark current. (b) Photoelectrochemical oxidation of water at *n*-TiO_2 electrode under anodic bias. E_C = conduction band edge, E_V = valence band edge, E_F = Fermi level.

Memming *et al.* [33] have discussed the evolution of oxygen from irradiated TiO_2 in another context. They located the flat band potential of TiO_2 at −0·3 V versus SCE at pH = 1. They showed that illumination of the TiO_2/electrolyte interface on open circuit leads of itself to slow photolysis of water; holes created by the light are consumed for formation of oxygen, and simultaneously an equal number of electrons are consumed in reducing H^+. The nature of the TiO_2 electrode surface is also discussed. In aqueous solutions, the TiO_2 surface consists of acidic and alkaline Ti–OH groups in equal amounts, and the first step in the photoelectrochemical evolution of oxygen is described as

$$\geqslant \mathrm{Ti{-}OH} + p^+ \longrightarrow \geqslant \mathrm{Ti}^{\cdot +}\ {}^{\cdot}\mathrm{OH}. \qquad (14)$$

Kallmann and Pope [34, 35] observed that water was decomposed on illumination with 365 nm light of a thin anthracene crystal separating two identical 0·01 M NaCl solutions. The crystal absorbs the light strongly so that the optical excitation is inhomogeneous and a Dember voltage (due to the differing mobilities of electrons and holes) is created across the crystal. Holes are injected at the illuminated face by the reduction of water to hydrogen, while oxygen is produced at the dark crystal face. Light of intensity of 0·3 mW cm^{-2} produces an open circuit photovoltage of 100–200 mV, but the photocurrent is drastically limited by the resistance of the membrane, and the maximum power conversion efficiency is only 2×10^{-6}.

Aqueous suspensions of semiconducting materials not uncommonly exhibit photocatalytic behaviour towards solution-phase redox reactions. Aerosols of powdered semiconductors sometimes act analogously towards gas-phase redox reactions. This behaviour is, like metallic corrosion, electrochemical in nature. Illumination produces holes and electrons in the catalyst, and these react with electron donors and acceptors in solution:

$$h\nu \rightarrow h^+ + e^- \quad \text{(in solid)} \qquad (15)$$

$$h^+ + D \rightarrow D^+ \qquad (16)$$

$$e^- + A \rightarrow A^-. \qquad (17)$$

It appears that water can act as both electron donor and acceptor in such systems. Kuznetsov [36, 37] has reported that water vapour is decomposed to hydrogen and oxygen on u.v. irradiation of powdered HfO_2 and BeO. The quantum yield is low (0·003 on HfO_2 at $\lambda = 254$ nm, 0·02 on BeO at $\lambda = 206$ nm). Moreover, the back reaction seems also to be photocatalyzed. Mamming's work on TiO_2 has been reported above.

It has long been known [38] that aqueous suspensions of silver chloride and other silver salts produce oxygen on illumination. The overall stoichiometry is given by Equation 18:

$$\mathrm{AgCl(s)} + H_2O + h\nu \rightarrow \mathrm{Ag(s)} + \mathrm{HCl} + \tfrac{1}{4}O_2. \qquad (18)$$

This endothermic reaction can be sensitised to wavelengths longer than 405 nm by adsorbed dyes such as chlorophyll [39]. Although a PEC cell based upon a similar reaction is described later, it does not appear possible to devise a practical energy converter based upon this reaction, since the silver halide cannot be completely regenerated (by for example the addition of Fe^{3+}) and so it is subject to ageing.

Hydrogen peroxide is produced when oxygenated aqueous suspensions of ZnO, CdS and CdSe are illuminated, though the steady state concentration is low because peroxide decomposition is also photosensitised [40]. Early workers [9, 40, 41] suggested that the reaction was due to the photoformation of charge carriers in the solid, followed by Reactions 19–25.

$$\begin{aligned}
&\mathrm{ZnO(s)} && + h\nu && \rightarrow e^- + h^+ \text{ (in crystal)} && (19)\\
&O_2\mathrm{(ads)} && + e^- && \rightarrow {}^{\cdot}O_2^- \text{ (ads)} && (20)\\
&{}^{\cdot}O_2^-\mathrm{(ads)} && + H^+ && \rightarrow HO_2^{\cdot} && (21)\\
& && 2HO_2^{\cdot} && \rightarrow H_2O_2 + O_2 && (22)\\
&H_2O\mathrm{(ads)} && + h^+ && \rightarrow OH^{\cdot} + H^+ && (23)\\
& && 2OH^{\cdot} && \rightarrow \tfrac{1}{2}O_2 + H_2O && (24)\\
&\text{Net: } H_2O && + \tfrac{1}{2}O_2 && \rightarrow H_2O_2 \quad (\Delta G^\circ = 106\ \mathrm{kJ}). && (25)
\end{aligned}$$

Thus the zinc oxide was thought to have a purely catalytic role in the endothermic formation of hydrogen peroxide. However, more recent work [42] indicates that the reaction is photocorrosion rather than photocatalysis. On irradiation, Reactions 19–22 occur but the light-generated holes in the semiconductor cause, not the photooxidation of water, but the hydrolysis of the solid. The pH is observed to decrease during the course of the reaction. Dixon and Healy [42] suggested that this reaction involved interstitial Zn^+ ions, formed by ionisation of interstitial Zn atoms in the *n*-type semiconductor:

$$\text{Formation of} \quad ZnO \rightarrow Zn(i) + \tfrac{1}{2}O_2 \qquad (26)$$

$$Zn^{+}(i) \qquad Zn(i) \rightarrow Zn^{+}(i) + e^{-} \qquad (27)$$

$$\begin{matrix}\text{On} \\ \text{irradiation}\end{matrix} \begin{cases} Zn^{+}(i) + h\nu + h^{+} \rightarrow Zn^{2+} & (28) \\ Zn^{2+} + nOH^{-} \rightarrow Zn(OH)_n^{(n-2)-} & (29) \end{cases}$$

4. The iron/thiazine dye cell: an example of cells of type II

The reversible photobleaching reaction between the thiazine dyes thionine or methylene blue and ferrous ions, reaction [30], is well known.

$$\tfrac{1}{2}Th + Fe^{2+} \underset{\text{dark}}{\overset{h\nu}{\rightleftarrows}} \tfrac{1}{2}\text{Leu-Th} + Fe^{3+} \qquad (30)$$

The forward reaction is fairly endoenergetic ($\Delta G^{\circ} = 40$ kJ at pH = 2), and the products, leuco-dye and Fe^{3+}, are virtually colourless. The dyes adsorbs in the region 500–700 nm which is reasonably compatible with the solar spectrum. Equation 30 seems an appealing reaction on which to base a PEC energy converter, since the Leu-Th/Th couple is electrochemically reversible and Fe^{3+}/Fe^{2+} is moderately reversible [43]. Moreover, the photochemical reaction is free of unwanted side products. The rapidity of the back reaction is, however, a grave disadvantage.

The kinetics of Equation 30 have been established by Hatchard and Parker [44]. Omitting protonation of the dye and leuco-dye, which is pH-dependent, the important reactions are:

Forward reactions

$$Th + h\nu \rightarrow Th^{*} \qquad (31)$$

$$Th^{*} + Fe^{2+} \rightarrow Th^{\cdot -} + Fe^{3+} \qquad (32)$$

$$2Th^{\cdot -} \rightarrow Th + \text{Leu-Th} \qquad (33)$$

Back reactions:

$$\text{Leu-Th} + Fe^{3+} \rightarrow Th^{\cdot -} + Fe^{2+} \qquad (34)$$

$$2Th^{\cdot -} \rightarrow Th + \text{Leu-Th} \qquad (35)$$

$$Th^{\cdot -} + Fe^{3+} \rightarrow Th + Fe^{2+}. \qquad (36)$$

Th^{*} is the triplet state of the dye, and $Th^{\cdot -}$ is the semithionine half-reduced form.

Hatchard and Parker [44] determined the rate of this series of reactions in 0·1 N H_2SO_4 and found that back reaction [36] was very rapid; concentrations of Fe^{3+} as low as 10^{-4} M had a noticeable effect on the composition of the photostationary state. This observation is crucial to the photogalvanic behaviour of the system and traces of air which produce Fe^{3+} from Fe^{2+} are doubtless responsible for the gradual deterioration in performance that is usually noted.

The photogalvanic behaviour of the system has been the subject of a number of studies [45–48]. Attempts have been made to prevent the occurrence of the back reactions by use of an ethereal emulsion, leuco-dye accumulating in the ethereal phase [49, 50]. However, the establishment of the phase equilibrium is too slow to be genuinely competitive.

Some electric power can be drawn without separation of the reaction products by photolysing the solution near one of two inert electrodes. The illuminated electrode becomes negative with respect to the dark one, typically by 100–200 mV and on closing the circuit, current can be drawn continuously. Despite the number of reports on this phenomenon, the reasons for it seem never to have been set out in simple electrochemical terms. The photolysed solution, which is partially bleached in the photostationary state, contains a low concentration of leuco-dye and an increased concentration of Fe^{3+}, according to Equation 30. This results in a substantial lowering of the electrode potential because the dye couple has a lower standard electrode potential and is more reversible than the iron couple, and the former reaches limiting current conditions at lower overpotentials than the latter. (The whole effect is hence readily suppressed by using a dirty electrode.) Under closed circuit conditions, the net process at the illuminated electrode is therefore anodic. Fig. 6 gives, schematically, the current-voltage curves of the two redox couples for typical solution concentrations ((Fe^{2+}) ~ 10^{-2} M, (Fe^{3+}) ~ 5×10^{-5} M, (Th) ~ 10^{-5} M). The open circuit dark potential, E_D, is controlled mainly by the iron couple. The open circuit potential of the illuminated electrode, E_L, is the potential at which Leu-Th is oxidized, and Fe^{3+} reduced, at equal rates. Under closed circuit conditions, the following sequence of reactions occurs:

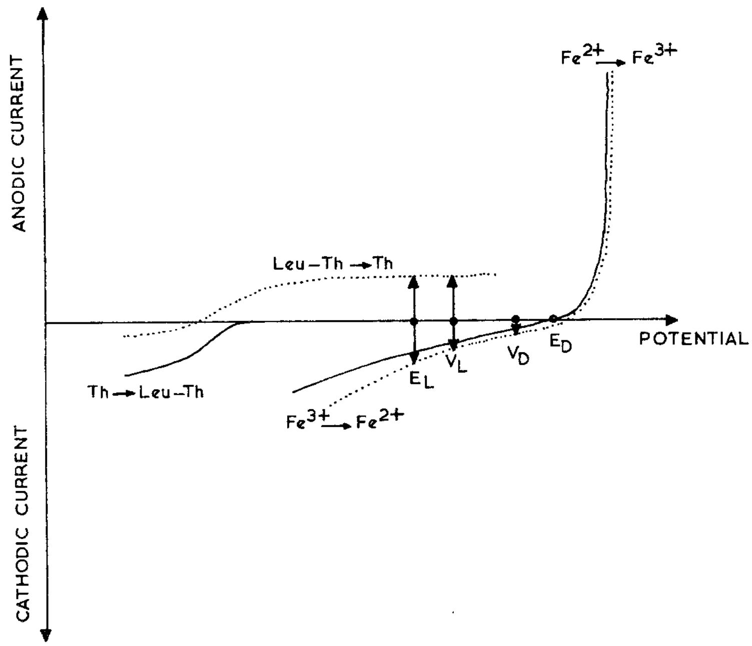

Fig. 6. Electrode processes in the iron-thiazine dye cell. ——— = dark current, ... = photoinduced current, E_D = open circuit potential of dark and illuminated electrodes respectively. $E^\circ_{\text{Fe}^{3+}/\text{Fe}^{2+}} = 0{\cdot}770$ V, $E^\circ_{\text{Th/Leu-Th}} = 0{\cdot}534 - 0{\cdot}09$ pH.

(In solution near anode) $\frac{1}{2}\text{Th} + \text{Fe}^{2+} \underset{\text{dark}}{\overset{h\nu}{\rightleftarrows}} \frac{1}{2}\text{leu-Th} + \text{Fe}^{3+}$

(At illuminated anode) $\left\{\begin{array}{l} \frac{1}{2}\text{Leu-Th} \rightarrow \frac{1}{2}\text{Th} + e^- \\ \text{Fe}^{3+} + e^- \rightarrow \text{Fe}^{2+} \end{array}\right.$ at greater rate than

(At dark cathode) $\text{Fe}^{3+} + e^- \rightarrow \text{Fe}^{2+}$

There is no net chemical reaction, and the device should operate indefinately without replenishment of materials. However, it is obvious from Fig. 6 that the short circuit current of the cell will be extremely low since it must be less than the limiting current due to leuco-dye oxidation, and the photostationary state concentration of leuco-dye is very small. Moreover, the leuco-dye is produced in bulk solution and diffusion to the electrode surface and back reactions [34–36] are competitive. Unfortunately, as Potter and Thaler point out [46] there is no effective means of gaining a favourable balance in this competition. All that can be done is to make the ratio of electrode area to solution volume as large as possible.

The maximum power conversion efficiency of the iron-thiazine dye cell is therefore mainly limited by the low value of η_ϕ, and a variety of low values have been quoted (Rabinowitch, < 1% [45]; Miller, 0·12% [47]; Potter and Thaler, 0·0003% [46]).

The efficiency of this device might possibly be improved by modifying the dye or the $\text{Fe}^{3+}/\text{Fe}^{2+}$ couple (e.g. by complexation) so that the back reaction was not so fast. However, according to the Marcus theory, this could only be achieved by making one or both of the redox couples substantially less reversible at the electrode, and that would also reduce efficiency. Alternatively, it might be possible to increase the yield of the photochemical reaction by the sort of catalytic effect reported by Hafner *et al.* [51]. They found that the photoreduction of dyes such as thionine and toluidine blue by ascorbic acid or allylthiourea (ATU) was increased by the addition of organic substances such as azulene, which are themselves unchanged. Apparently the dye triplet reacts with azulene (to give the radical cation $\text{Az}^{\cdot+}$) faster than it does with ATU, but ATU is nonetheless oxidised via the subsequent reaction:

$$\text{Az}^{\cdot+} + \text{ATU} \rightarrow \text{Az} + \text{ATU}^{\cdot+}. \qquad (37)$$

5. Cells of type IIIa

5.1. *The nitrosyl chloride cell*

Nitrosyl chloride decomposes endothermically to nitric oxide and chlorine on irradiation with visible light:

$$\mathrm{NOCl} + h\nu \rightarrow \mathrm{NO} + \mathrm{Cl} \tag{38}$$

$$\cdot\mathrm{Cl} + \mathrm{NOCl} \rightarrow \mathrm{NO} + \mathrm{Cl_2} \tag{39}$$

$$\text{Net: } 2\mathrm{NOCl} + h\nu \rightarrow 2\mathrm{NO} + \mathrm{Cl_2}: \Delta G^\circ = +40\,\mathrm{kJ}. \tag{40}$$

The primary quantum yield for the production of NO is 2·0 (for $\lambda < 640\,\mathrm{nm}$) in the gas phase and in carbon tetrachloride solution it is 0·75–1·00. This high quantum yield and long threshold wavelength seem promising, and the reaction has been the subject of a number of studies [52–55]. The photochemical reaction products, once separated, can act as the fuels in a battery [54, 55] in which the cell reaction is the regeneration of nitrosyl chloride:

$$\mathrm{NO} + \tfrac{1}{2}\mathrm{Cl_2} \rightarrow \mathrm{NOCl}: E^\circ = 0{\cdot}21\,\mathrm{V}, i_{sc} = 8.1 \times 10^3\,\mathrm{A\,cm^{-2}} \tag{41}$$

Chlorine and nitrosyl chloride are soluble in carbon tetrachloride while nitric oxide is insoluble, and Neuwirth [52] therefore used this solvent to separate the two. Unfortunately, though the back reaction between the two is slow in the gas phase, it is rapid in carbon tetrachloride, and the effective quantum yield of reaction [40] is reduced to an unacceptably low value, even in a flow system [52].

5.2. *The cis/trans acid cell*

One way to overcome the problems associated with the NOCl cell is to employ an endothermic photochemical reaction for which the thermal back reaction is slow, despite the fact that it must be thermodynamically spontaneous. The photochemical isomerisation of fumaric acid to maleic acid is such a reaction, although the threshold wavelength is impractically short and the reverse reaction is also a photochemical process [56].

$$\text{Trans } \mathrm{HO_2CCH = CHCO_2H} \rightarrow \text{Cis } \mathrm{HO_2CCH = CHCO_2H}: \Delta G^\circ = +29\,\mathrm{kJ}. \tag{42}$$

At 313 nm, the quantum yield of the forward reaction is 0·12 and that of the reverse reaction 0·048.

In a patented cell described by Clampitt and German [57], solid trans-acid gradually dissolved in one half cell as the saturated solution is irradiated to produce more soluble cis-acid. The other half-cell contains unirradiated, unchanged trans-acid. After a time, the cell can act as a hydrogen ion concentration cell, since maleic acid ($\mathrm{p}K_{\mathrm{a1}} = 1{\cdot}9$) is more acidic than fumaric acid ($\mathrm{p}K_{\mathrm{a1}} = 3{\cdot}0$). On subsequent discharge of the cell cis-acid is transported across the liquid junction from the irradiated to the dark side. (It seems unlikely that this discharge could be maintained at a reasonable rate without upsetting the liquid junction.) The dark side must contain a catalyst to reconvert the cis to the trans isomer, which then will precipitate in the dark side. Irradiation of the latter charges up the cell again.

As the dissolution of a solid phase is involved, the coulombic capacity of the battery should be reasonable. However, the cell voltage, depending solely on an ionic concentration difference, is low, as shown in Table 3. The theoretical cell voltage was calculated by Clampitt and German from equation [43]:

$$E = \frac{RT}{F} ln \frac{[\mathrm{H^+}]_{\mathrm{trans}}}{[\mathrm{H^+}]_{\mathrm{cis}}} \cong \frac{RT}{2F} ln\, K_{\mathrm{cis}}c_{\mathrm{cis}}/K_{\mathrm{trans}}c_{\mathrm{trans}} \tag{43}$$

in which K_{cis}, K_{trans} are the acid dissociation constants of maleic and fumaric acids respectively. (This expression appears to be in error by omission of the factor $2t^-$ for a concentration cell with transport.)

5.3. *The cyclic photogalvanic silver halide cell*

Zaromb *et al.* [58, 59] have described a cell based on the endothermic photochemical decomposition of a silver chloride electrode or membrane. The principle of the cell is illustrated in Fig. 7. Electrode *A* is AgCl-coated platinum, and electrode *B* is porous carbon or platinum. The discharged cell contains $10^{-2}\,\mathrm{M}\ \mathrm{FeCl_2}$ in 0·2 M HCl. On

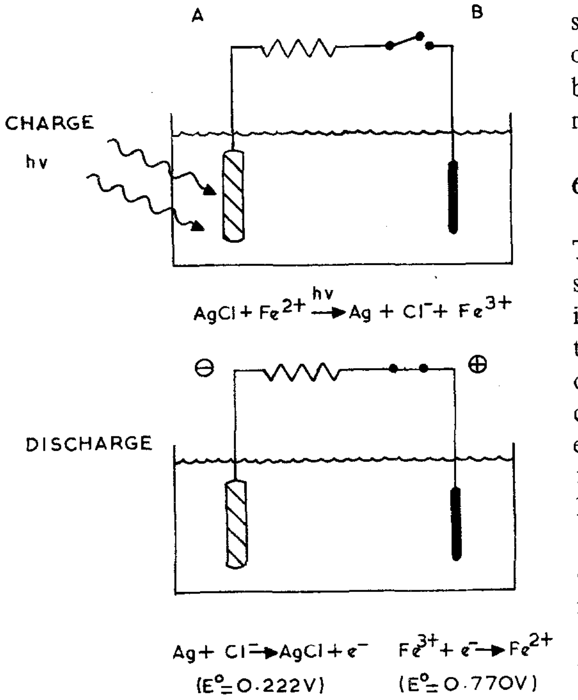

Fig. 7. Cyclic photogalvanic silver chloride cell.

irradiating electrode A with light of wavelength <405 nm, Fe^{3+} is formed in solution:

$$AgCl + h\nu \rightarrow Ag + \tfrac{1}{2}Cl_2 \qquad (44)$$

$$\tfrac{1}{2}Cl_2 + Fe^{2+} \rightarrow Cl^- + Fe^{3+} \qquad (45)$$

$$\text{Net: } AgCl + Fe^{2+} + h\nu \xrightarrow[\phi \sim 0{\cdot}02]{h\nu} Ag + Cl^- + Fe^{3+}. \qquad (46)$$

The cell is therefore photochemically charged (on open circuit), Fe^{3+} building up in solution and electrode A being reduced. On discharging the cell, these reactions are reversed, as shown in Fig. 7.

Unfortunately, as Zaromb *et al.* pointed out, this cell is not a practical device, since the silver chloride electrode deteriorates in days, and, worse, the charge stored by illumination vanishes within an hour, the presumed self-discharge reaction being the reverse of Reaction 46. The extent of recharge achievable by light is also severely limited by this reaction, which is significant at $[Fe^{3+}] > 10^{-3}$ M.

In an alternative version of the cell [59], the silver halide is present as a membrane. On irradiation, chlorine accumulates on one side of the membrane, and Fe^{3+} is reduced to Fe^{2+} on the other side by the silver. The intention is presumably to avoid the occurrence of back reactions by separating reactants, but details of cell resistance and the effect of repeated cycling on the membrane are not given.

6. Cells of type IIIb

The iron/thiazine dye cell described in a previous section and other similar photoredox reactions can in principle be made the basis of a storage battery that is rechargeable by light. Electric power can be drawn from the cell both on discharge and on recharge. In one half-cell there is a chemically inert electrode in a solution of dye and an oxidising or reducing agent. This is combined with a counter half-cell whose potential lies between the potential of the photosensitive half-cell in the light and in the dark. This approach has the merit of avoiding the mixing of reactants.

The following treatment is based on that of Tributsch [60]. Consider an ordinary redox Reaction 47.

$$D_I + A_{II} \rightarrow A_I + D_{II} \qquad (47)$$

which proceeds spontaneously if the free energy of reaction is negative. This redox reaction can be divided into partial reactions that proceed at separate electrodes in a galvanic cell, as shown in Fig. 8a. Discharge can continue until the cell reaction has reached equilibrium, which in any practical system will be well on the right hand side of Equation 47.

Now suppose a dye S which photo-oxidises D_{II} back to A_{II} is added to the RH half-cell, as in Fig. 8b. On irradiation, the following reaction occurs.

$$S^* + D_{II} \rightarrow S_{red} + A_{II}. \qquad (48)$$

'S_{red}' is a schematic representation of the semi-reduced or leuco-dye. On open circuit, the potential of the RH electrode becomes more negative (as explained for the iron/thiazine dye cell). If it becomes more negative than the LH electrode, then the cell is recharged, as shown in Fig. 8b, and the above reaction is reversed. The input of light energy in the excitation $S \rightarrow S^*$ has provided enough energy to drive the cell reaction thermodynamically uphill, and the action of the dye is catalytic in the sense that it is eventually converted to its original form. (One basic point that is usually overlooked is the *extent* to which the cell can be recharged by light.)

Table 3. Potential of cis/trans acid concentration cells

Concentration of maleic acid (M)	*Concentration of fumaric acid* (M)	*Background electrolyte* (M)	*Theoretical potential* (mV)	*Observed potential* (mV)
0·060	0·060	–	33	6
0·060	0·060	1 M KCl	33	35
0·060	0·060	2 M KCl	33	35
6·72	0·060	–	95	100
6·72	0·060	1 M KCl	95	111

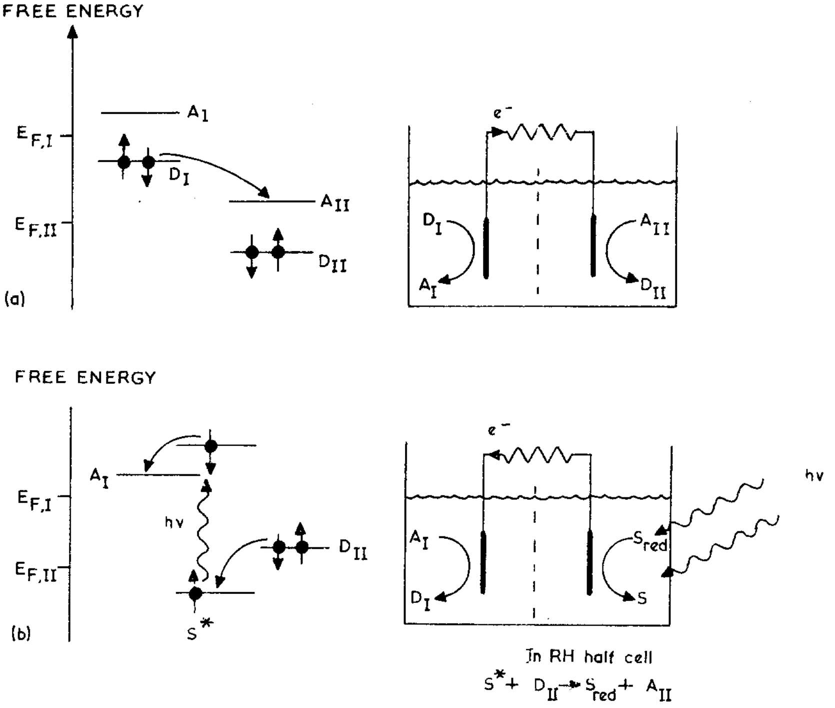

Fig. 8. Dye-sensitized photoregenerative storage battery. (a) Thermodynamically spontaneous cell discharge (in the dark); (b) Light induced recharge. A_I, D_I and A_{II}, D_{II} = redox couples, S = sensitizing dye, $E_{F,I}$ and $E_{F,II}$ = Fermi levels of the two redox couples. Adapted from [60].

A similar cell based on a dye-sensitised photoreduction can easily be imagined, since an electronically excited molecule has an increased capacity both for oxidation and reduction, as illustrated in Fig. 9.

In the early 1960s, several cells operating on these principles were investigated. Eisenberg *et al.* [61–63] used the dyes proflavine or phenosoafranine with ascorbic acid or EDTA as reducing agent. The counter electrode couple was SnF_6^{2-}/SnF_6^{4-} or $Fe^{III}(EDTA)/Fe^{II}(EDTA)$. The charge/discharge curves for the proflavine/ascorbic acid cell are shown in Figs. 10a and b. The change in open circuit potential of the dye electrode is quite encouraging (~ 0·4 V) but the maximum power developed during the recharge stage was only 20 μW at 0·2 V, a power conversion efficiency of 0·002. It is clear from Fig. 10a that polarization of the dye electrode limits the short circuit current to a very low value. The low dye concentration and the back reaction of S_{red} in solution are doubtless responsible for this. The cell discharge curve (Fig. 10b) is not really meaningful since the dye electrode under test was in a completely discharged state, i.e. no dehydroascorbic acid was added. However, as ascorbic acid is susceptible to oxidation, there may have been traces present.

In an attempt to overcome the problems

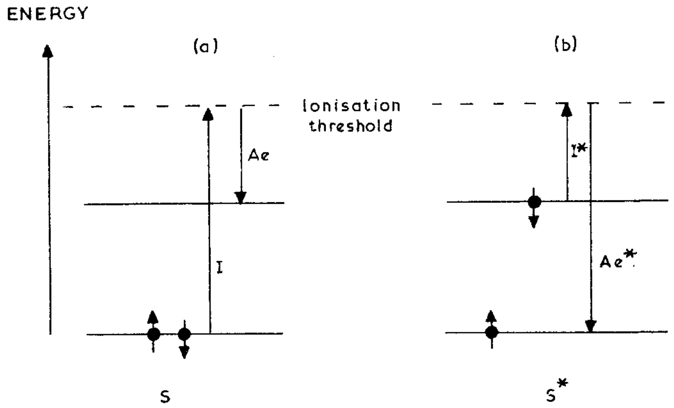

Fig. 9. The ionisation energy, *I*, and the electron affinity, *Ae*, of the ground state (*a*) and excited state (*b*) of molecule *S*.

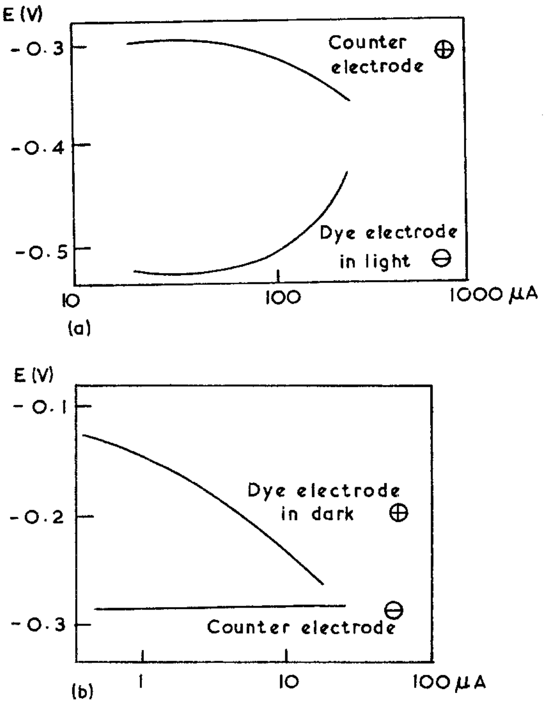

Fig. 10. Current-voltage curves for (a) charge and (b) discharge of the cell

Pt	4×10^{-4} M proflavine hydrochloride 10^{-2} M ascorbic acid 1 M KBr	4×10^{-2} M K_2SnF_6 4×10^{-2} M K_4SnF_6	Pt.

Potential versus Ag, AgCl electrode. Light intensity in (a) 900 W m^{-2}. From [62].

associated with use of a dye solution, Anderson *et al.* [64, 65] used a metal electrode coated with the triarylmethane dye Victoria Blue B, again with ascorbic acid, and a Ag/AgCl counter electrode. This cell worked in so far as the polarity of the cell was reversed on irradiation of the dye-coated electrode and yet the dye layer was essentially unchanged, since many thousands of times more coulombs could be drawn than were required to oxidise or reduce all the dye present. The optimal dye thickness was ~10 monolayers. Again, the maximum power conversion efficiency was extremely low, and the main reason for this is probably the very effective quenching of the excited dye S* at a metal electrode, either by Förster energy transfer or by a double electron transfer, as illustrated in Fig. 11. This is taken from an interesting paper by Memming and Kürsten [66] which discusses the photoelectrochemical behaviour at metal electrodes of the dyes rhodamine B, fluorescein and crystal violet in conjunction with various oxidising and reducing agents.

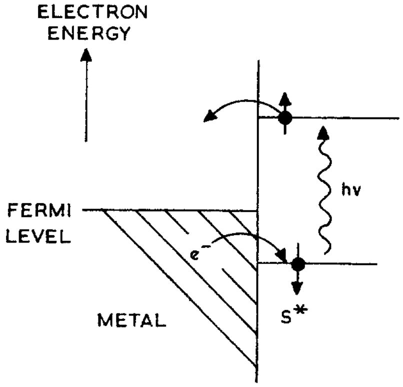

Fig. 11. Quenching of an electronically excited molecule S*, by 'double electron transfer' with a metal.

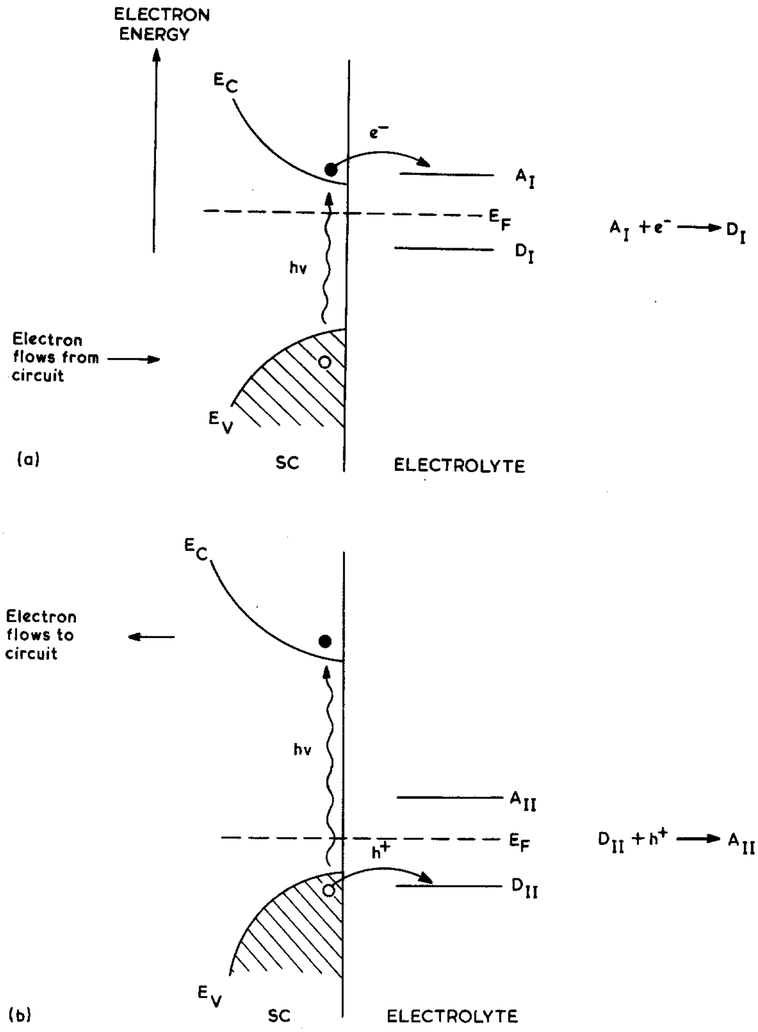

Fig. 12. Photoinjection of charge at a semiconductor (*SC*) electrode. E_v and E_c = valence and conduction band energies. (a) Photo reduction of A_I in solution; (b) Photo-oxidation of D_{II} in solution.

7. Photosensitization of charge transfer at semiconductor electrodes

The PEC devices discussed in the above sections have been characterised chiefly by very low photon efficiencies. In recent years, a considerable amount of work has been carried out, mainly in Germany, on semiconductor photoelectrochemistry and the photosensitization of processes at semiconductor electrodes [32, 67–70]. These processes can occur at much higher proton efficiencies (even at heavily doped electrodes which are sufficiently conducting to be used in a galvanic cell). Although most of this work has been fundamental in nature and in no way directed towards solar energy utilization, practical developments could ensue, and therefore a summary of the field will be given.

Charge injection phenomena are observed at semiconductor electrodes on absorption of photons of energy $E > E_g$, which promote electrons from the valence band to the conduction band. Electron transfer can then occur between the conduction band of the semiconductor and an oxidising agent in solution (Fig. 12a) or hole transfer between the valence band and a reducing agent (Fig. 12b). These effects can be observed in semiconductors of both large and small band gap. A wide band gap semiconductor ($E_g > 3$ eV) cannot, however, utilize the

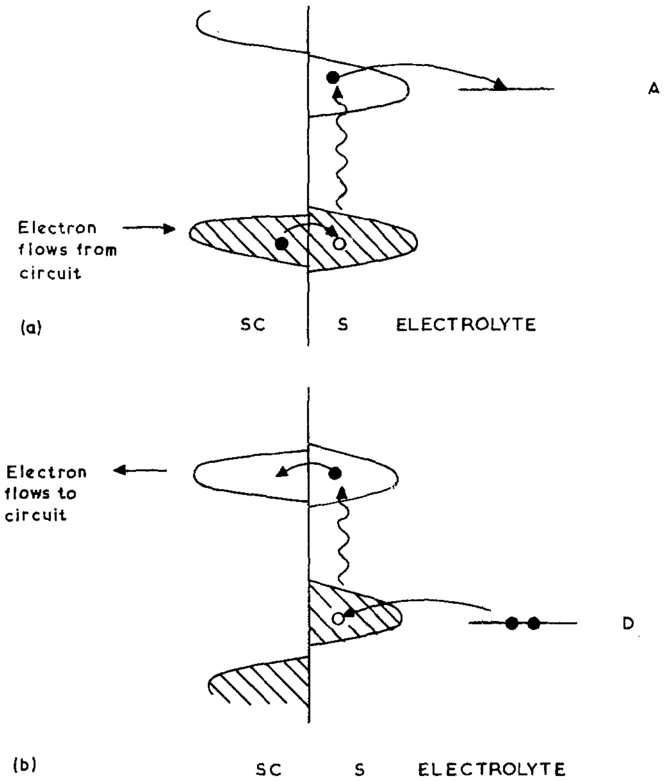

Fig. 13. Photosensitized charge injection at a semiconductor electrode. (a) Photoreduction of *A*; (b) Photo-oxidation of *D*. *S*, sensitizing dye.

solar spectrum efficiently and unfortunately smaller band gap semiconductors tend to be unstable in an electrochemical environment, particularly when irradiated. For example, electrodes of Ge, Si, GaAs, CdSe and GaP (and CdS and ZnO under illumination) are subject to oxidative destruction under anodic conditions, and Ge and Cu_2O are subject to reductive destruction [32, 71]. Thus the sensitization of chemically inert wide band gap semiconductor electrodes to visible light could be of practical, as well as fundamental, interest. Monolayers or multilayers of organic dyes (which are themselves semiconducting) can act as efficient sensitizers.

Suppose the valence bands of the sensitizing dye and the electrode overlap, but the conduction bands do not, as in Fig. 13a. On excitation of the dye, hole injection can occur into the valence band of the electrode, but a back transfer of an electron from the dye conduction band is impossible. If an electron acceptor of suitable redox potential is present in solution, then it can be reduced with high quantum efficiency. Similarly, if the conduction bands of the electrode and dye overlap, but the valence bands do not, then efficient photo-oxidation of a species in solution can occur, as shown in Fig. 13b. Dye molecules of high photochemical stability can sensitize many times.

This brief description of photosensitization is very much simplified. The effects of crystal imperfection and localized energy levels in the semiconductor surface, and of excited states and impurities in the semiconductor or dye, can be considerable. The geometric structure of the adsorbed dye film is a determining factor in its photochemical behaviour [67]. The dye may aggregate on the substratum resulting in displacement of the action spectrum from the absorption spectrum of the monomer [74]. The detailed crystal structure of multilayer films will greatly affect the effective charge carrier mobility. Increasing film thickness, though it increases the fraction of light absorbed, generally results in a lowering of the photon efficiency. Moreover, the relative role of charge transfer and energy transfer within the dye layer [75] and even the correct model of charge injection [73] are matters of controversy.

Many photosensitized processes have been reported. The chlorophyll-sensitized oxidation of hydroquinone and phenylhydrazine at zinc oxide electrodes [60, 67, 76] is typical, although a report [77] of its practical possibilities seems a little over-optimistic. The maximum photon efficiency (observed with phenylhydrazine) was ~0·125. Fig. 14 shows the spectral dependence of the photocurrent, after subtraction of the electrode background current. As compared with the chlorophyll absorption spectrum in benzene, the bands are red-shifted by about 10 nm, probably due to the polar environment at the electrode/water interface. Fig. 15 shows the dark and photo-current-voltage curves at 670 nm. The photocurrent reaches a limiting value under anodic bias, which facilitates electron injection into the interior of the semiconductor. (In a galvanic cell incorporating this half cell, the working anode potential would be between −1·0 and 0·0 V, and hence the photon efficiency would be lower than its limiting value).

Dye-sensitization of cathodic processes is exemplified by the work of Tributsch *et al.* on GaP electrodes [67, 74]. The photon efficiency of a monolayer of rhodamine B is of the order of 0·1–0·3. Hole injection at GaAs electrodes can be sensitized to infra-red wavelengths by benzthiazole-undecacyanine.

The relatively high photon efficiency of charge injection at sensitized semiconductor electrodes prompts one to ask whether such an electrode could be of any use in solar energy conversion. It is relatively easy to imagine a cell of type I, II or IIIb containing one, or preferably two, such sensitized electrodes which would convert some radiant to electric energy. Unfortunately, high photon efficiency is generally associated with only monolayer coverages of sensitizer, and a monolayer of even a very intensely absorbing dye absorbs less than 1% of the incident light. Thus the photon efficiency defined in practical terms, as the electrons flowing per incident photon, rather than per absorbed photon, could only be extremely low. One way to overcome this difficulty might be to use a transparent microporous conducting solid as the substrate to be sensitized. The solvent would have to be of the same refractive index as the substrate to prevent light scattering. This approach might also alleviate mass transfer problems, since the effective reaction surface of the electrode would be much greater than its geometric area.

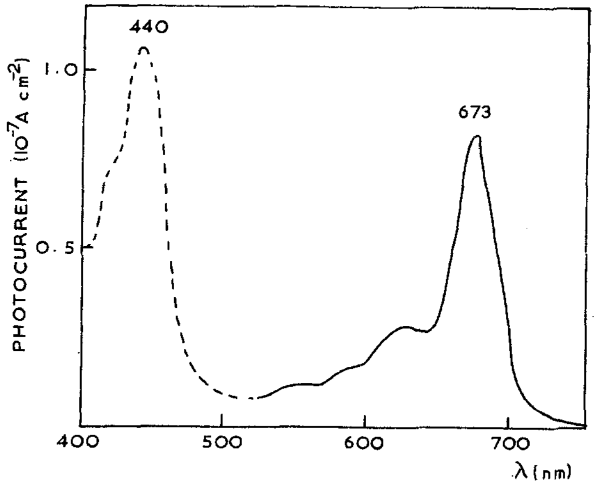

Fig. 14. Spectral dependence of photocurrent at ZnO electrode sensitized by a sub-monolayer deposit of Chl a, in 4 × 10^{-2} M hydroquinone plus 1 M KCl.

8. Metal electrodes with relatively thick dye coatings

Although monolayer amounts of dye cannot sensitize a metal electrode, it is possible that a thicker coating of a suitably coloured substance could act as its own semiconducting electrode, the metal beneath serving simply as a back contact. The light absorption profile in a thick highly absorbing film will be non-uniform, according to the Beer–Lambert Law, so that optical

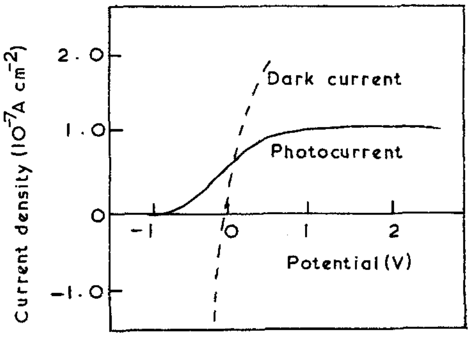

Fig. 15. Dark and photo-current/voltage curves for Chl a – sensitized ZnO.

excitation must be followed by charge or energy transfer through the bulk of the film to the metal. Meier [73] has quoted several examples of efficient sensitization effects in dye films up to 1 μm thick.

Wang [78] has reported light-driven transfer of electric charge across more than 70 molecular layers of pigment molecules in the cell

$$\mathrm{Al}\left|\begin{array}{l}\text{Multilayered zinc}\\ \text{tetraphenylporphyrin}\end{array}\right|\begin{array}{l}0{\cdot}1\ \mathrm{M}\ K_3Fe(CN)_6\\ 0{\cdot}1\ \mathrm{M}\ K_4Fe(CN)_6\end{array}\Bigg|\ \mathrm{Pt.}$$

On irradiation with amber light of unspecified intensity, the coated electrode exhibits a photopotential of the order of −1·1 to −1·3 V and photocurrents of the order of microamps can be drawn. (Wang demonstrated that two such cells in series can electrolyze water, and drew an analogy with the behaviour of photosystems I and II, the pigment multilayer being likened to chlorophyll antennae in the chloroplast.) Smaller but similar effects have been reported in 0·2–0·5 μm films of chlorophyll on platinum [79] and in 1 μm films of copper phthalocyanine on platinum [80].

In the case of such thick films on metal or semiconductor substrates, the model of charge injection given in the previous section should be modified by recognition of the fact that a *p-n* contact potential will exist between the substrate and the pigment film, due to the difference in work function of the two materials. As in purely solid state photovoltaic cells, this contact potential impedes the flow of majority carriers across the junction, but allows light-generated minority carriers to pass freely [69, 73].

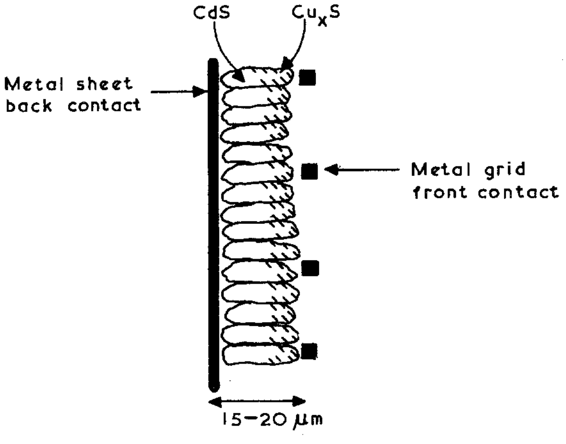

Fig. 16. Schematic representation of the CdS/Cu$_2$S solar cell.

There are several problems posed by the use of relatively thick pigment films. Firstly, charge and energy transfer mobilities even within a single crystal of an organic material are generally poor because of weak coupling in molecular organic crystals, which leads to narrow conduction bands compared with inorganic semiconductors such as silicon. It is possible to enhance the dark and photoconductivity of dyes by doping or by minor structural modifications [81] but the resistance of most thick dye films is still extremely high. Furthermore, if a polycrystalline film is used then grain boundaries will act as efficient traps for charge carriers. However, provided the crystallites are sufficiently large to extend from the back to the front surface of the film, efficiency might not be too much reduced. CdS/Cu$_2$S solar cells have a working efficiency of about 6%, despite their polycrystalline nature, because of this. Moreover, the junction is formed not between separate crystals but within each crystallite by substitution of Cu for Cd, as shown in Fig. 16.

9. Biological photosynthesis and model photosynthetic systems

In photosynthetic units *in vivo* it appears that the initial, probably highly unstable, products of chlorophyll-sensitized oxidation and reduction are separated and thus they do not wastefully recombine but carry on through the reaction chain, converting light to chemical free energy with high efficiency. Harmful indiscriminate reactions with the surroundings are avoided. The process has electrochemical characteristics in that electron transport across biological membranes is involved. There may therefore be useful lessons about photoelectrochemical energy conversion to be learnt from the study of the primary processes of photosynthesis.

A compact summary of the salient points of these processes is given in a review by Clayton [82]: 'Photosynthetic tissues are organized functionally into aggregates of light harvesting pigments associated with reaction centres. The pigments absorb light and deliver energy to the reaction centres, where an oxo-reductive photochemistry ensues. The primary photoproducts, oxidising and reducing entities, serve as starting points for electron transfer that is coupled to phosphorylation. In known cases the primary photochemical electron donor is chlorophyll'. About 200–400 chlorophyll molecules are

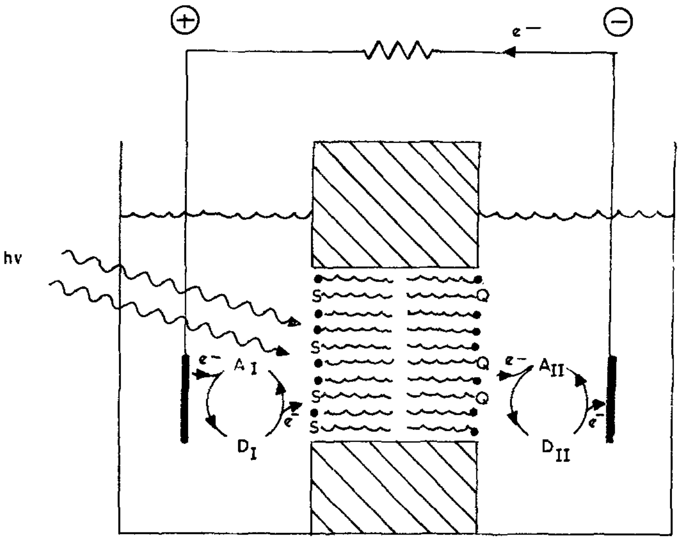

Fig. 17. Photoelectrochemical cell containing bilayer membrane. The sensitizer molecule, *S*, and the electron acceptor, *Q*, must have hydrophilic heads and hydrophobic tails.

associated with each reaction centre in higher plants and algae. There has been some disagreement as to whether each group of chlorophyll molecules can transfer energy only to its own reaction centre, or whether each photosynthetic unit is really a much larger group of collector molecules among which are scattered a suitable number of reaction centres which compete with one another for the common supply of excited states. The weight of the evidence seems to support the latter view [83, 84].

The purpose of the light gathering antennae of chlorophyll and carotenoids is to increase the efficiency of light energy utilization and to broaden the spectral range of light absorption. Much effort has been devoted to determining the nature of the coupling between the chlorophyll molecules in the chloroplast, and whether energy is transferred by a singlet or triplet state of chlorophyll or by charge transfer. Borisov and Godik [85] have recently reviewed this field. They conclude that a charge transfer mechanism is impossible on the grounds that the photoconductivity of chlorophyll organizates prepared in a variety of ways (some from chloroplasts) always shows an activation energy of 0·1–0·3 eV, whereas according to data available on reaction centres in chromatophores, transfer efficiency is not much decreased even at 1 K. Experiments on the increase in chlorophyll fluorescence yield, as reaction centres are inactivated, show that singlet, not triplet, energy transfer is involved. Estimates of the strength of coupling between chlorophyll molecules differ according to whether it is assumed that energy transfer per se or the trapping of energy by reaction centres is the slow step which determines fluorescence lifetimes. It seems likely that the coupling is moderately strong ($\sim 100\,\text{cm}^{-1}$) and that energy transfer by delocalised singlet excitons is the slow step.

The orientation of chlorophyll molecules in the antenna cannot be quasi-crystalline, because fluorescence from chlorophyll *in vivo* is strongly depolarised. Ancillary pigments such as carotenoids play an important part in the chloroplast both by protecting chlorophyll from oxidative destruction and by transferring energy of wavelengths not directly absorbed by chlorophyll itself to the antenna. It follows that experiments on energy and charge transfer in single crystals or multilayer organizates of pure pigments do not really imitate nature.

Increased understanding of photosynthetic processes *in vivo* has prompted study of energy transfer in thin films and electrochemical processes associated with synthetic membranes [86–90]. Sineshchekov *et al.* [86] have found evidence for the formation of various types of molecular aggregates in monolayers and thin films containing chlorophyll and carotenoids and of energy transfer between them down a 'step-by-step' descent involving aggregates with absorption maxima at increasing wavelengths, terminating with chlorophyll aggregates with absorption maxima at 700–730 nm. Some of these effects disappear on ageing, presumably because crystallization within the films gives rise to aggregates incapable of energy transfer. This work suggests the possibility of using mixed dye films, which absorb a large portion of the visible spectrum, in solar PEC cells.

It is well established that electronic conduction can occur through bilayer membranes of lipids. (BLM are ultrathin membranes containing only two molecular layers of long-tailed molecules.) Photoelectric effects can be observed if pigments are incorporated into the membrane. This has suggested [89, 91] the design of a PEC cell of the type shown in Fig. 17, in which electron tunelling through two lipid layers occurs. With a suitable electron donor on one side of the membrane, and an acceptor on the other side, the quantum efficiency of charge injection can be high. BLM made of natural lipids are fragile and can only be made in small areas. Valenty [92] is using ultrathin polymeric membranes of high mechanical strength. Calvin [91] has suggested that more stable asymmetric membranes could be made by inclusion of carotenoids in the membrane interior to thicken and stiffen it, and concludes that such a system, which emulates the chloroplast activity of the green plant may well, in the more distant future, be a means of capturing the energy of the sun and producing electricity directly from it.

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