

## Photoelectrochemical devices—a multipurpose system

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**Abstract.** Various types of photoelectrochemical devices for solar energy conversion are reviewed and the future areas of research delineated.

**Keywords.** Photoelectrochemical devices; solar energy conversion.

### 1. Introduction

The study of photoelectrochemical (PEC) devices has aroused considerable interest and activity in solar energy research. The basic phenomena involved in these devices have long been studied (Brattain and Garrett 1955; Dewald 1960; Gerischer 1960, 1966, 1975; Williams 1960; Fujishima and Honda 1972). PEC devices are similar to the Schottky barrier type of solid state solar cells and have four possible advantages: (i) Insensitivity to gross defects: the PEC cell is less sensitive compared to the Schottky barrier solar cells to grain boundaries in the material. A good rectifying metal contact is needed for a Schottky barrier cell because on a badly defective semiconductor, a metal contact will be much more ohmic than an electrolytic contact. Thus the use of a defective polycrystalline material in PEC cells is their main advantage. (ii) Lower cost of manufacture as the costly diffusion process is avoided as compared to the p-n junction. (iii) Direct chemical storage. (iv) Use of a powder rather than an electrochemical cell so that both the reduction and the oxidation processes occur on the same particle. Thus although one may arrange for a second material deposited on the powder grains reduction occurs on one material and the oxidation on the other.

### 2. Application of PEC devices

Based on various applications, photoelectrochemical devices can be classified into: (i) photoelectrolytic cell; (ii) electrochemical-photovoltaic cell; (iii) rechargeable photoelectrochemical cell; (iv) photogalvanic cell and (v) photoelectrocatalysis cell. The basic principle involved in all these types is almost similar except for small variations in their operational mechanism.

#### 2.1 Photoelectrolytic cell

Here the optical energy is converted into chemical energy. The photogenerated hole is used to oxidize one species and the electron is used to reduce another. The reaction is chosen such that the products can be stored so that when they are subsequently reacted, the energy can be recovered. Water decomposition by the photoproduced carriers is one example. The photogenerated holes oxidize  $\text{OH}^-$  ions to give  $\text{O}_2$  whereas the electron reduces  $\text{H}^+$  ions to give  $\text{H}_2$  (figure 1). In this case the external

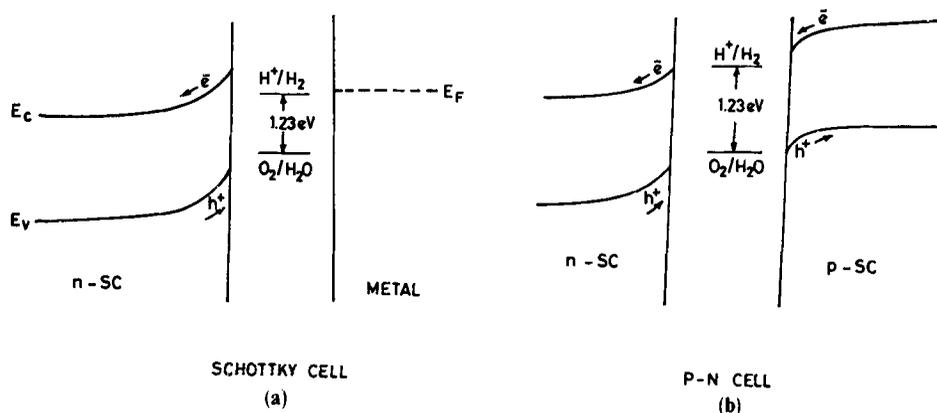


Figure 1. Sequence of energy level diagram for Schottky type and P-N type photoelectrolysis cell.

circuit is short-circuited to ensure free flow of the current. The solar energy is stored as the fuel hydrogen.

## 2.2 Electrochemical-photovoltaic cell

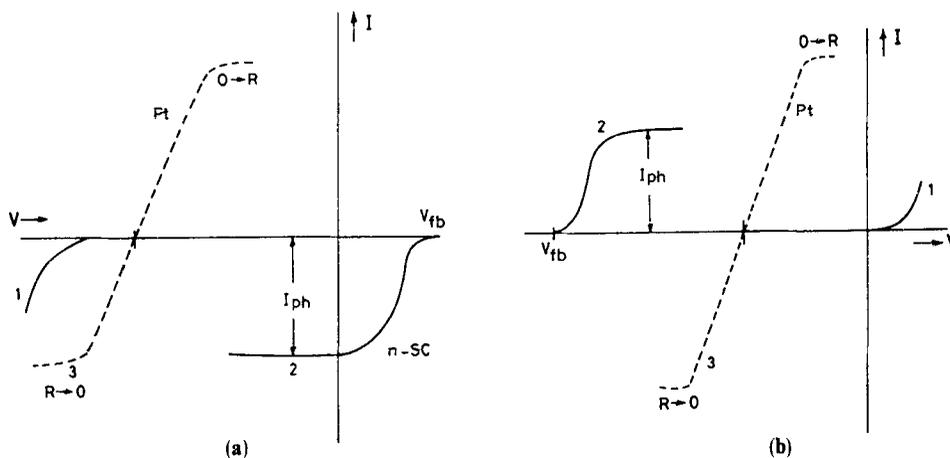
In this case, the photo-produced hole-electron pair is used to directly generate electricity in the same way as in the solid state solar cells. The reaction that occurs at the counter-electrode is simply the reverse of the photo-assisted process at the semiconductor. Ideally the cell operates with conversion of light to electricity and with no change in the solution composition or the electrode materials. The operating characteristics of such a cell can be deduced from I-V curves such as those in figure 2.

## 2.3 Rechargeable PEC cell

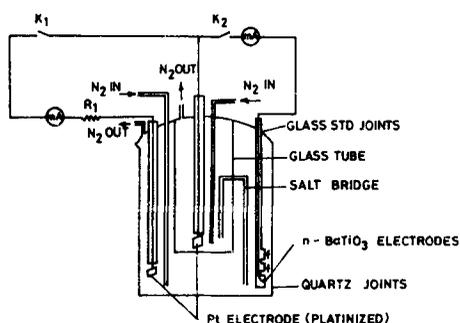
Recently efforts have been made to produce a rechargeable photoelectrochemical cell (Manassen *et al* 1977; Memming 1978; Sinha and Sharon 1982). Such a cell resembles a storage battery, except that charging is carried out by the light rather than by an external power supply. In this system two redox electrolytes are used in two cell compartments separated by a salt-bridge or by an ion-selective membrane (figure 3). On illumination, one redox system is oxidized at the n-type semiconductor electrode and the second redox system gets reduced in the next compartment at the platinum electrode or on p-type semiconducting electrode. When the cell is kept in dark, the reverse reaction takes place electrochemically generating power during its operation.

## 2.4 Photogalvanic cell

In the photogalvanic cell, optical energy is also converted into electrical energy (Clark and Eckart 1975; Gomer 1975). However, the incident light is absorbed by the molecular species in solution, and the electrical power is generated by charge transfer from excited molecular species to electrodes in contact with the light-absorbing system. Photogalvanic effect is due to the change in the current-potential charac-



**Figure 2.** I-V curves for solution containing couple O/R (a) n-type semiconductor in the dark (curve-1) and under illumination (curve-2) (b) P-type semiconductor in the dark (curve-1) and under illumination (curve-2). Curve-3 is I-V curve at Pt-electrode.



**Figure 3.** Schematic diagram of a rechargeable photo-electrochemical cell. Compartment I contains the  $Ce^{3+}/Ce^{4+}$  redox system, compartment II contains the  $Fe^{2+}/Fe^{3+}$  redox system.  $K_1$  and  $K_2$  keys;  $R_1 =$  load resistor of  $100 \Omega$ .

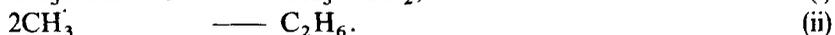
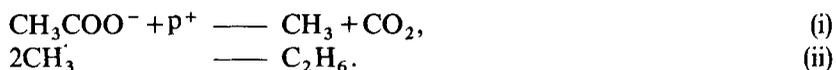
teristics of an electrode/solution half-cell produced by photolysis of the solution. Such an effect is to be expected in any photochemical reaction which alters the concentration of any component of the solution to which the electrode is responsive.

### 2.5 Photoelectrocatalysis cell

When a semiconductor is illuminated and the electrons and holes move to the surface, the electrons will reduce the species at the surface; the holes will oxidize the species at the surface. The two processes can be the same reaction. If not, however, permanent chemical changes will occur in the medium in which the semiconductor is immersed. Such photo-induced chemical changes are termed photocatalytic effects (Hauffe 1968; Frewd and Gomes 1969; Morrisson 1971, 1977; Bard 1979; The Volkenstein 1973). The important concept in photocatalysis is that the flow of electrons and holes to the surface must be equal at the steady state. If they are not, either (i) the surface becomes electrostatically charged stopping the process or

(ii) another electrode must be present to complete the electrical circuit and the process is termed "Photoelectrocatalysis", not photocatalysis. A practical difference between photocatalysis and photo-electrocatalysis is that the former can occur on powders, as no counter-electrode is required. Both desirable and undesirable reactions can occur, either in photocatalysis or photoelectrocatalysis. Recently much of the interest has been in desirable reaction, specifically photocatalytic or photoelectrocatalytic conversion of solar to chemical energy. However, to date, electrochemical solar energy conversion has not been found attractive from a practical point of view because of the low efficiency and/or corrosion problems. On the other hand, there has been a substantial interest in undesirable photocatalysis in particular on  $\text{TiO}_2$ , specifically the cases of undesirable photocatalytic oxidation of resin and polymers in paints and plastics. In such cases one is interested in preventing photocatalysis with  $\text{TiO}_2$ . It is generally accepted that  $\text{OH}^-$  ions at the surface are oxidized by the photoproduced holes to the radicals  $\text{OH}$  and these latter can oxidize a whole spectrum of organics or other reducing agents. However, Miyake *et al* (1977) suggest that photocatalysis may never be as practical as photo-electrocatalysis because with photocatalytic reactions one always has the competition of direct recombination, whereas in photoelectrocatalysis the applied voltage can be used to keep the majority carriers away from the surface and avoid surface recombination.

One of the interesting examples of photoelectrocatalysis is the photoassisted oxidation of acetate ion to ethane in acetonitrile solution at n-type  $\text{TiO}_2$  electrodes. Light energy greater than  $E_g$  causes formation of electron-hole pair when the potential of the semiconductor is positive of the flat-band potential, the bands are bent upward and the photogenerated holes migrate to the electrode surface while the electrons drift to the bulk of the electrode, thus preventing recombination. The holes at energies characteristic of the valence band or low lying surface states are effectively strong oxidizing agents and can abstract electrons from acetate ion initiating the cascade of steps in the Kolbe reaction.



The potential for the photo-oxidation of acetate is negative of that for the onset of hydrogen ion reduction in the acetate/acetic acid mixture ( $-0.8$  V vs Ag, reference electrode) suggesting that photoelectrocatalysis, with little or no external applied voltage, leading to a mixture of ethane and hydrogen is possible.

It is thus obvious that electrocatalysis using semiconductor electrodes without special characteristics has great promise for controlled chemical synthesis. We should, therefore, design in principle the band edges of semiconductor such that a suitable catalytic reaction could take place. This is a promising field where photoelectrochemical devices can prove useful. A major breakthrough is also required in preventing the corrosion of semiconductor.

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