

## Semiconductor materials for liquid electrolyte solar cells

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**Abstract** - The general principles of operation of photoelectrochemical cells are briefly reviewed.

Particular attention is dedicated to the semiconductor materials which are presently considered as the most suitable for assuring high conversion efficiency and long stability to practical photoelectrochemical cells.

### PRINCIPLES OF OPERATION OF PHOTOELECTROCHEMICAL CELLS

A photoelectrochemical cell (PEC) is based on the junction between a semiconductor (either n or p type) and an electrolyte, generally liquid, containing a suitable redox couple. The energy schemes for n-type and p-type semiconductors in junction with a redox couple in solutions are illustrated in Figure 1. At equilibrium, the Fermi level of the semiconductor (which is the electrochemical potential of electrons) equalizes the Fermi level of the redox couple (which is the Nernst potential). This induces band bending with formation of a depletion layer at the interface. (1-5)

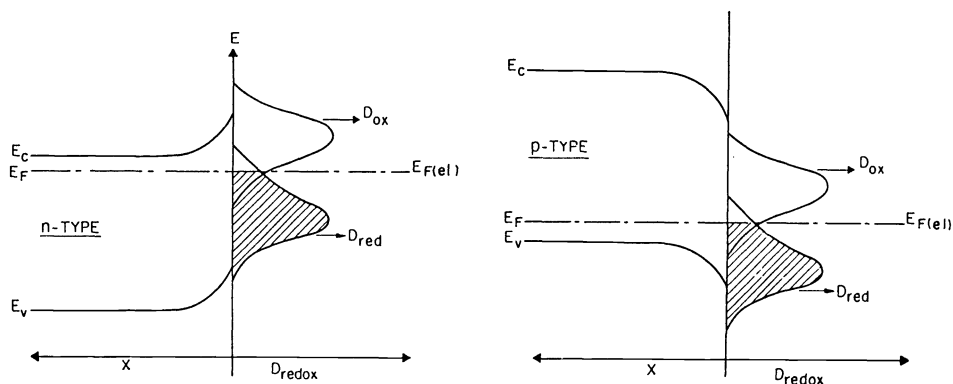


Fig. 1. The energy scheme of a n-type and a p-type semiconductor in junction with a redox couples.  $E_c$  = conduction band;  $E_v$  = valence band;  $E_F$  = Fermi level of the semiconductor;  $E_{F(e)}$  = Fermi level of the redox couple (Nernst potential).

Let us now consider a sequence formed by a semiconductor (supposedly n-type), immersed in an electrolyte containing a redox couple (schematized as Ox/Red, e.g.  $Fe^{3+}/Fe^{2+}$ ) and a metal (e.g. platinum or carbon). At equilibrium in the dark the Fermi levels of the three components equilibrate, as shown in Figure 2. When the semiconductor is illuminated with an energy  $h\nu$  equal or greater than the bandgap,  $E_{bg}$ , electron-hole couples are generated with a decrease in band-bending and a rise in the Fermi level (Figure 2). This situation gives rise to photopotential,  $eU_{ph}$ , equal to the difference between the Fermi level of the illuminated semiconductor and that of the redox couple in solution.

Under these circumstances, the maximum photovoltage corresponds to the condition where the bands are totally unbended. Therefore, the corresponding value of potential, called flat-band potential,  $U_{fb}$ , is of obvious relevance in PEC characterization. Furthermore, the photogenerated couples are readily separated by the field in the depletion layer. The minority carriers are injected into the solution where they drive the following oxidation process:



The majority carriers move toward the bulk of the semiconductor and, via an external load, can travel to the counter electrode, from which they are injected into the solution to drive the following reduction process which is just the opposite of process /1/.



In this fashion, it is possible to obtain a photovoltage and a photocurrent, and thus electric power through the system, without changes in the electrolyte composition.

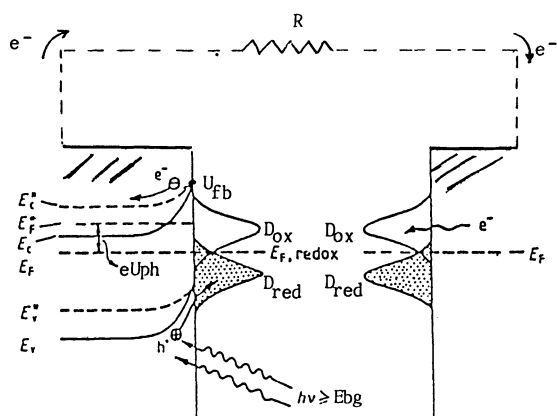


Fig. 2. Energy scheme of a regenerative photoelectrochemical cell (PEC) using a n-type semiconductor electrode at equilibrium and under illumination (the position of the bands under illumination is indicated by an asterisk).

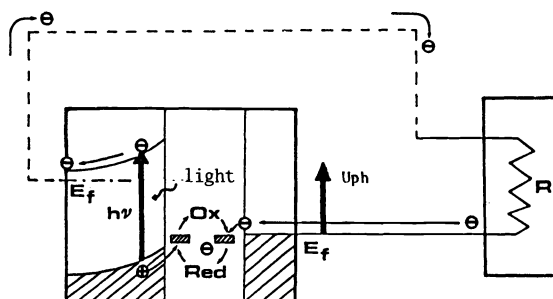


Fig. 3. Operational scheme of a PEC

Hereunder described is the operation of so called 'regenerative' PEC, where, as again schematized in Figure 3, the light (solar) energy can be directly transformed into electric energy. In fact, under load, a photovoltage,  $U_{ph}$ , established between the semiconductor and the counterelectrode and a corresponding photocurrent density,  $J_{ph}$ , flows. The properties of a PEC are characterized by a current-voltage plot. The  $J_{ph} \times U_{ph}$  product is the power output at any point and its highest value  $P_m$  represents the maximum output power available. The ratio between  $P_m$  and the sunlight power incident on the electrode area,  $P_o$ , is the maximum solar energy efficiency,  $\eta_m$ , of the PEC. The limiting power of a PEC is obviously the product between the open circuit voltage,  $U_{oc}$ , and the short circuit current,  $J_{sc}$ . The ratio  $P_m / (U_{oc} / J_{sc})$  is defined as the fill factor,  $FF$ , of the PEC.

### SEMICONDUCTOR MATERIALS FOR PECs

The concept of operation of a PEC is technologically appealing since the solid/liquid junction is easily obtained (simply by immersion of the semiconductor electrode into the liquid electrolyte) and by the selection of semiconductors having suitable bandgap values, reasonable high efficiencies may in principle be foreseen. However, the photogenerated minority carriers, rather than drive the desired electrochemical reaction in solution, may oxidize (n-type) or reduce (p-type) the semiconductor itself, this leading to photocorrosion processes which rapidly degrade the life of PEC.

To prevent this photocorrosion effect, two main routes can be followed, one based on a kinetic approach and the other based on a material selection approach.

The first route is pursued with the choice of suitable electrolyte compositions in order to make the rate of transport of the photogenerated minority carriers to the redox couple much faster than that of photocorrosion. In such a way, even if the photocorrosion process is thermodynamically favoured, its rate is made negligibly small so that effectively the semiconductor electrode becomes kinetically stable.

The material approach is directed to the selection of semiconductor materials whose optical transitions do not involve bonding orbitals, thus, in principle, having promise of good stability against photocorrosion. This condition appears to be fulfilled by layered semiconductors (e.g. molybdenum and tungsten chalcogenides) and by ternary semiconductors (e.g. copper indium selenide).

### LAYERED SEMICONDUCTORS

Figure 4 compares the band scheme of a 'classical' semiconductor, i.e. CdS, with that of a layered semiconductor, i.e. MoS<sub>2</sub>. It may be noticed that while in the former the transition effectively involves p-s bonding orbitals, in the latter only the metal d-orbitals are separated by the gap. A similar situation applies for MoSe<sub>2</sub> and WSe<sub>2</sub>, where also the optical transitions concern d-d Mo or W orbitals. Pec cells using tungsten and molybdenum dichalcogenides in junction with the I<sup>-</sup>/I<sub>2</sub> couple in aqueous solutions, have been developed and good stability experimentally confirmed (6,7).

Furthermore, some of the molybdenum and tungsten dichalcogenides, and MoSe<sub>2</sub> and WSe<sub>2</sub> in particular, have favourable band-gap values (i.e. around 1.5 eV) for the solar spectrum, so that reasonably high efficiencies may be obtained with PEC cells based on these semiconductors (B).

However one of the major problems of PECs, and in general, of solar cells, is related to the recombination of the photogenerated carriers which may lead to severe decay in efficiency. As is well known in semiconductor technology, recombination may be largely induced by surface states. Figure 5 illustrates the effect of surface states  $E_{ss}$  on the operation of a PEC: rather than oxidize the redox species in solution a fraction of the photogenerated holes are trapped in their surface state  $E_{ss}$  where they recombine with electrons tunneling from the conduction band. Obviously, this fraction is not available for the photoelectrochemical reaction and thus the efficiency of the overall process drops.

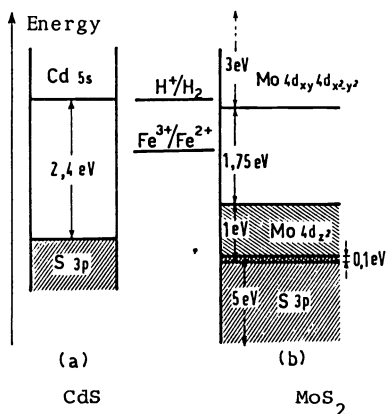


Fig. 4. Band Structures of CdS and of MoS<sub>2</sub>.

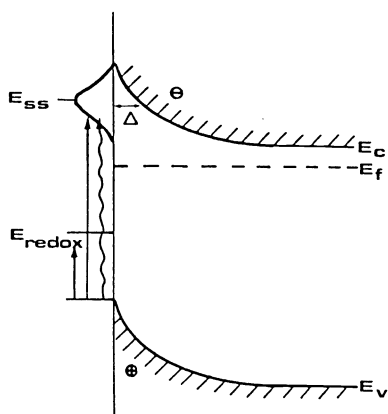


Fig. 5. Changes recombination by electron tunneling to a surface state ( $E_{ss}$ ).

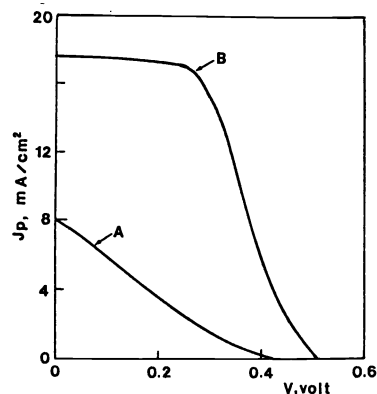


Fig. 6. Output characteristics of 'smooth' (B) and of 'structured' (A) MoS<sub>2</sub> photoanodes in junction with a  $I^-/I_2$  redox couple.

The transition metal dichalcogenides typically have a layered structure. The layers are loosely held by van der Waals bonds and thus steps or fractures may easily form on the crystal surface. These structural defects act as recombination sites and thus 'irregular' crystals have much poorer conversion efficiency than smooth crystals (Figure 6).

Practical applications of PEC based on the layered semiconductors would require polycrystalline electrodes which probably would have 'structured' rather than a 'smooth' surfaces. Therefore, recombination and corrosion at surface steps are serious problems and, consequently, various routes have been followed to overcome or, at least, to attenuate them.

For this purpose a treatment based on a selective passivation of the defect sites appears to be rather efficient. Since the conductivity of the carriers is much faster along the van der Waals layers than across them, there is a drift of charges to the step edge. Therefore, by polarizing a layered semiconductor in the dark in an electrolytic cell, it is possible to selectively electrodeposit a non-conductive material, such as a polymer (e.g. polyindole), and thus electrically isolate the defective sites from the solution. Figure 7 shows that this operation effectively improves the performance of a structured MoSe<sub>2</sub> crystal in a stable manner (9).

However, even after this treatment, the efficiency of layered semiconductor PEC remains basically too low to attract considerable attention in the practical sense, and thus alternative stable materials have to be considered.

**TERNARY SEMICONDUCTORS**

High electrochemical stability is basically offered by ternary chalcogenides (i.e. CuInSe<sub>2</sub>, CdIn<sub>2</sub>Se<sub>4</sub>...) in respect to the binary analogues (i.e. CdSe, CdS). The most promising material of the family is copper indium selenide, CuInSe<sub>2</sub>, which has a band gap of about 1 eV, i.e. an optimal value for solar applications.

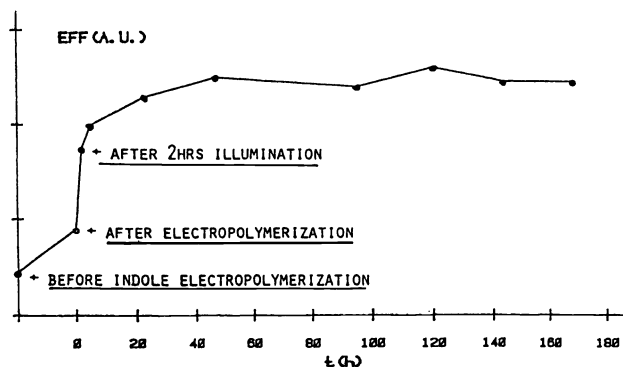


Fig. 7. Stability under illumination of a MoSe<sub>2</sub> crystal after selective electrodeposition of polyindole.

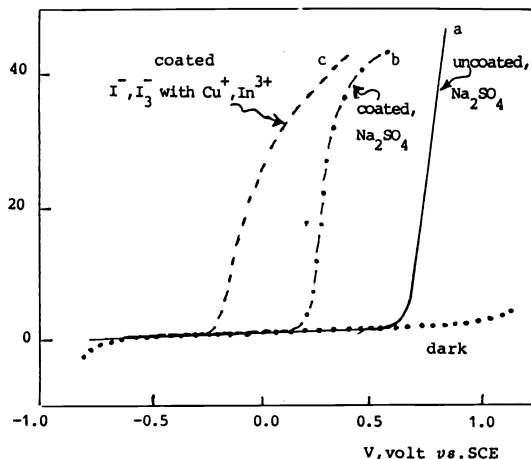


Fig. 8. Current-voltage curves for a n-CuInSe<sub>2</sub> polycrystalline electrodes under various conditions.

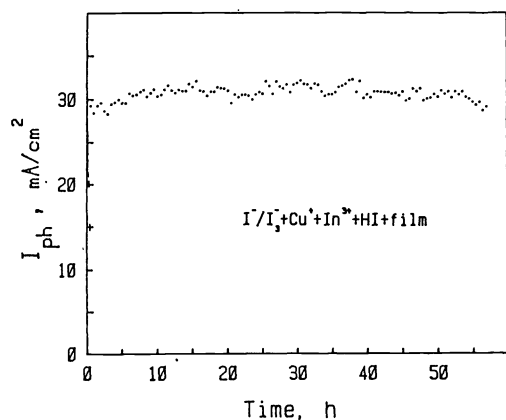


Fig. 9. Photocurrent of a CuInSe<sub>2</sub> PEC using a modified I<sup>-</sup>/I<sub>2</sub> electrolyte.

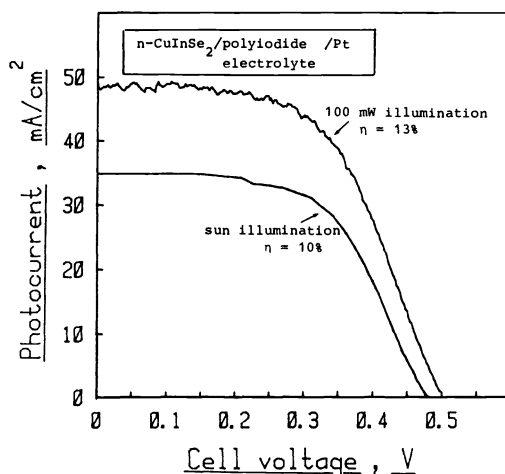


Fig. 10. Output characteristics of CuInSe<sub>2</sub> - based photoelectrochemical cells.

Indeed, by protecting the surface of this semiconductor by an indium oxide film and using a I<sup>-</sup>/I<sub>2</sub> aqueous electrolyte with suitable additions of Cu<sup>+</sup> and In<sup>3+</sup> ions, solar efficiencies around 12% have been reported for PECS using single (10, 11) and homogenous polycrystalline (12) n-CuInSe<sub>2</sub> photoelectrodes.

Figure 8 shows the current-voltage curves of a n-CuInSe<sub>2</sub> polycrystalline electrode (13). Curve a refers to the response in a Na<sub>2</sub>SO<sub>4</sub> aqueous solution. Since no redox couple is present, the large current flowing at about 0.6 V vs SCE (SCE = standard calomel electrode) must necessarily be related to a photocorrosion process, which is likely to be:



To protect the photoanode from this corrosion, one can deposit a layer (about 50 Å thick) of indium oxide on the electrode surface. This can be achieved by electrodepositing indium on CuInSe<sub>2</sub> and then thermally oxidizing it to indium oxide. However, curve b of Figure 8, which refers to an indium oxide coated CuInSe<sub>2</sub> electrode, shows that this treatment alone is not sufficient to protect the electrode since current is still flowing. This current is probably due to the dissolution of the indium oxide layer: in fact, repeating the voltage sweeps, the onset of current progressively shifts anodically to finally match that of curve a.

Only when the oxide-coated electrode is used in a solution containing the I<sup>-</sup>/I<sub>2</sub> couple plus Cu<sup>+</sup> and In<sup>3+</sup> ions, is total stabilization achieved, as shown by the cathodic onset of the related photocurrent (curve c of Figure 8). Effectively, Figure 9 shows that under these conditions, the photocurrent of a CuInSe<sub>2</sub> PEC remains constant upon prolonged illumination. Furthermore, the performance of this type of PEC is also very promising, since conversion efficiencies of 13% under simulated illumination and of 10% under direct sun illumination (Figure 10) have been obtained (13).

These values are encouraging and indicated that by proper selection of the semiconductor materials and of the nature and of the composition of the electrolyte solutions, photoelectrochemical cells of practical interest may eventually be developed.

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