CHAPTER 11

PHOTOASSISTED DECOMPOSITION OF WATER USING

MOLYBDENUM DISULPHIDES

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11.1 Photoelectrolysis

Solar energy appears attractive as a means of meeting many of future energy needs. Although it is a non-polluting renewable source, sunlight has two major "defects" it has a low energy density (~ 1 KW/m^2) and it is intermittent. Thus a useful system for utilizing solar energy should be efficient, inexpensive and have a means of storage. Solar photovoltaic cells can have good efficiencies ~ 20 % for converting solar energy to electrical energy but they are too expensive at the present time and they require a bank of batteries for energy storage. Thus there is room for other solar alternatives. About 14 years ago Fujishima and Honda[1] published a letter in "Nature" suggesting that an electro-chemical cell consisting of an n-type single crystal TiO$_2$ anode and platinum black electrode could be used with visible light to decompose water into H$_2$ and O$_2$. Their report stimulated considerable interest and research because of possibility of utilizing this effect to obtain H$_2$ from solar energy. Because H$_2$ as a fuel has many attracting features, a case has been made for a "Hydrogen Economy"[2]. However, an efficient photoelectrolysis system which operates with sunlight, although very attractive, is not available at the present time because of electrode material limitations.
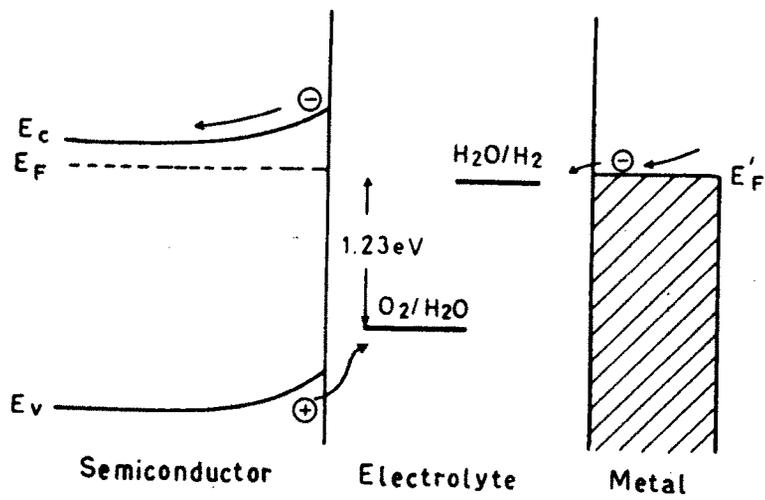
Fig. 11.1

Relative positions of semiconductors
bandedges, Fermi and redox energy levels
for photoelectrolysis cell.

In determining the material requirements for such electrodes
let us begin by considering the principle of operation of a
photoelectrolysis cell.

Principle of Photoelectrolysis

In its simplest form, a photoelectrolysis
system consists of an electrochemical cell with two electrodes,
one of which is a semiconductor, connected together externally
and immersed in an electrolyte. The electron energy diagram
of a cell with an n-type semiconductor, an electrolyte and a
Pt counter electrode is given in Fig. 11.1. In the electrolyte
are shown the mean free energy for the H_2 reaction,
$E(H_2/H_2O)$ and 1.23 eV below, that of the O_2 reaction,
$E(H_2O/O_2)$. The solar energy conversion takes place near the
semiconductor-electrolyte interface where the energy bands
in the semiconductor are bent because of the lining up of
the semiconductor Fermi level or electrochemical potential,
E_F, with that of the solution $E(H_2/H_2O)$. For the case shown
here, the work function of the semiconductor is less than
that of the solution and equilibrium is achieved by
electrons leaving the semiconductor and flowing into the
solution ions. The semiconductor surface is thus depleted
of electrons and becomes less n-type than bulk. The positive
charge of the depletion region is balanced by the ionic

counter charge in the solution and the solution counter charge can be represented to a good approximation by a sharp plane of charge located at a definite distance from the surface i.e. by a Helmholtz layer.

The band bending in the depletion region (Fig. 11.1) indicates a gradient of electron energy, or an electric field. Thus if light of energy $h\nu$ greater than the band gap energy E_g is incident on the semiconductor electrolyte interface and absorbed in the depletion region, electrons will be excited from the top of the filled valence band, E_v, to the bottom of the conduction band, E_c, leaving positive holes behind. The natural tendency of the photon-excited electrons and holes to recombine is prevented by the electric field due to the bent bands. Under the influence of this electric field the electrons move away from the surface into the bulk of the semiconductor and then to the Pt counter electrode (since the two electrodes are connected together through the external circuit) where they discharge H_2 according to the reaction

$$2e^- + 2H^+ \longrightarrow H_2 \qquad (11.1)$$

The holes, on the other hand, move in the depletion region

electric field to the semiconductor-electrolyte interface and tunnel from the semiconductor surface to the (H_2O/O_2) solution level to discharge O_2 according to the equation

$$2p^+ + H_2O \longrightarrow \tfrac{1}{2}O_2 + 2H^+ \qquad (11.2)$$
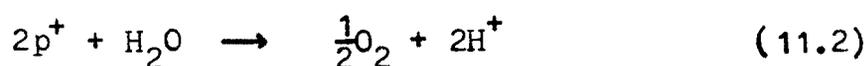
The overall reaction is thus the decomposition of water with light i.e.,

$$H_2O \xrightarrow{h\nu} H_2 + \tfrac{1}{2}O_2 \qquad (11.3)$$

This brief description of the operation of photoelectrolysis indicates that the following material parameters are important for efficient photocatalytic electrodes :

(1)   The flat band potential of the semiconductor must be "more negative" than the potential of H_2O/H_2 couple. In other words, conduction band energy must lie above the $E(H_2O/H_2)$ level.

(2)   The valence band should lie below the $E(H_2O/O_2)$ couple, otherwise no transfer of holes from the valence band is possible.

Both conditions can be fulfilled simultaneously if :

$$E_g = E_c - E_v > E(H_2O/H_2) - E(H_2O/O_2) = 1.23 \text{ eV} \quad (11.4)$$

Free energy involved in the decomposition of water is 1.23 eV. Hence for photoelectrolysis cell $\Delta G > 0$ as against $\Delta G = 0$ for electrochemical photovoltaic cells. The energy consumed by photogenerated electrons to move from the conduction band edge via the external circuit to counter electrode is

$(E_c - E_f) + e V_b$, where V_b is the band bending. So, the net energy available for photoelectrolysis reaction would be:

$E_g - [(E_c - E_f) + e V_b]$ This energy available must be equal to or greater than the combined energy necessary for:

(a)   Photoelectrolysis

(b)   Ohmic loss (iR)

(c)   Photoelectrode overpotential (η_a) associated with the evolution of O_2 which is the difference between the valence band edge and the H_2O/O_2 level

(d)   Counter electrode overpotential (η_c) associated with the evolution of H_2 which is the difference between the conduction band edge and H_2/H_2O level

atom of the semiconductor thereby breaking a semiconductor
bond. The former reaction is what is desired since the
latter reaction results in the dissolution of the electrode.
Gerischer[4] has suggested that semiconductor electrodes in
which phototransitions do not involve bonding orbitals
would be more stable to photodissolution. In this respect
"transition metal chalcogenides" emerge as very promising
material where the phototransitions involve non-bonding
d-d orbitals of Mo atoms. Keeping all this in view author
has selected molybdenum disulphide, MoS_2 photoelectrode for
photoelectrolysis. The experimental results of photoelectro-
lysis cell with n-MoS_2 have been discussed in the present
chapter.

11.2   Experimental Results and Discussions

The homogeneous photoelectrolysis cells
with n-MoS_2 have been set up, by using spiral of platinum
wire of length 25 cm and 0.05 cm in diameter as cathode and
iodide/iodine electrolyte of concentrations 2 M NaI, 0.025 M
I_2, 0.5 M Na_2SO_4, 0.5 M H_2SO_4, in the cylindrical compartment
7 cm in diameter and 4 cm in height. The cell (semiconductor
area $\simeq$ 0.2 cm^2) has been illuminated by incandescent bulb
with illumination intensity 100 mw/cm^2. The gases evolved

have been collected using two inverted funnels held over
anode and cathode.

It has been observed that there is no gas
evolution with only light. So the external bias is applied
from a dry cell using potentiometric arrangement, where
positive terminal of battery is connected to the $n-MoS_2$
electrode. The dependence of rate of evolution of oxygen
on the applied bias under an illumination is shown in
Fig. 11.2. It is seen from Fig. 11.2 that the observable
evolution of oxygen begins at about 0.9 V and the rate of
evolution increases with the increasing external bias. The
results in Fig. 11.2 can be explained as follows :

In the case of those semiconductor electrodes
for which the conduction band edge is only slightly above the
Fermi level for water reduction, the quasi Fermi level of
the electrons can not reach a large enough driving force
for hydrogen evolution. An additional voltage is therefore
required. Moreover, by applying a bias a more effective
electron-hole separation can be brought about thereby
increasing the efficiency. The electron-energy correlations
for an unbiased and biased photoelectrolysis cells are shown
in Figs. 11.1 and 11.3. In the case of unbiased cell
$E_F \simeq E_F'$. Further, E_F' is not much higher than H_2O/H_2

Fig. 11.2   Dependence of oxygen evolution
            on bias voltage for a n-MoS$_2$
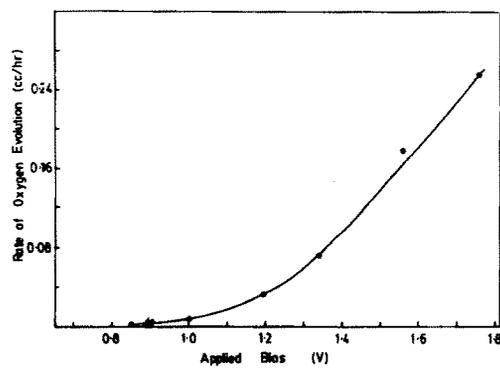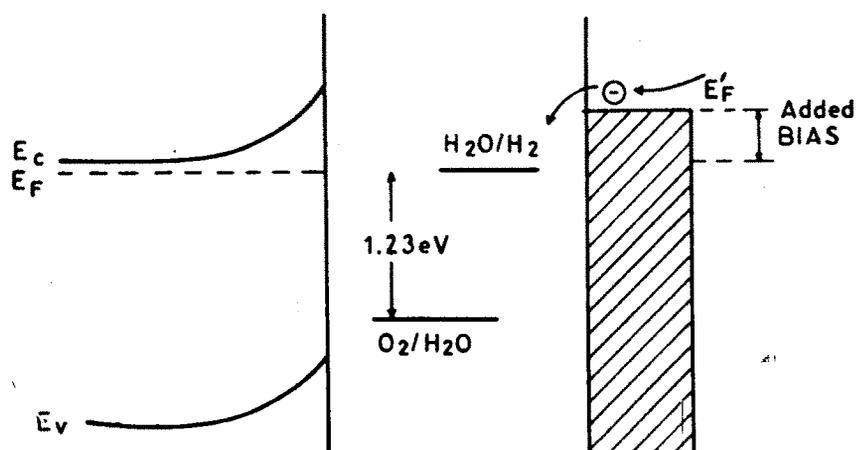   based photoelectrolysis cell.

Fig. 11.2

Fig. 11.3

Relative positions of semiconductor bandedges, Fermi level and redox energy for a bised photo-electrolysis cell.

couple energy and electron transfer is not efficient.
The application of an external bias $(E_F - E_F^!)/e$ ensures
that the Fermi level of electrons in the metal goes higher
than in the H_2O/H_2 redox system so that hydrogen evolution
occurs.

There are various methods of applying bias
such as :

(I)   External voltage source, an external source of
        d.c. voltage provides the bias.

(II)   Electrochemical photovoltaic cell as a bias,
        the external biasing could also be provided by
        an electrochemical photovoltaic cell. Thus, the
        biasing power is also derived from solar energy.

(III)   Concentration cell bias. The semiconductor is
        placed in a strong basic anolyte solution while
        the metal counter electrode is placed in strong
        acidic catholyte. The two compartments, separated
        by an agar bridge, have different ionic activity
        or concentrations and hence a voltage difference
        appears biasing the photoelectrolysis cell. However,
        the concentration cell type biasing is not suitable

for long term use since the pH difference between
the two compartments decreases as the neutralisation
proceeds with photoelectrolysis.

It has been observed by Tributsch[5] that
the rate of oxygen evolution for photoelectrolysis cell
with MoS_2 can be increased by means of a redox-catalyst,
tris (2,2-bipyridine)-ruthenium (II).

11.3   Conclusions

The PEC effect can be used for photoelectro-
lysis of water into oxygen and hydrogen. The molybdenum
disulphides electrodes used in homogeneous photoelectrolysis
cells indicate that for the evolution of oxygen and
hydrogen an external bias $\simeq$ 1 V is necessary.

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