

Photo electrochemical Production of Hydrogen – a Dream or Reality?

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Intoduction

In the quest for new energy sources, hydrogen is one of the attractive secondary energy carriers. There seems to be convergence of opinion that in the future hydrogen will turn out to be the main energy carrier for mobile applications though doubts still persist and also possibly for stationary power generation in the stand alone mode. The transformation to hydrogen based economy is based on various fundamental and organizational factors mainly concerning production, storage and distribution. Among these three essential components of hydrogen economy, the production of hydrogen has received considerable attention. There are various methods and technologies that have been developed and a few of them have already been practiced. These technologies can be broadly classified as:

1. Thermo-chemical routes for hydrogen production
2. Electrolytic generation of hydrogen
3. Photolytic means of hydrogen formation
4. Biochemical pathways for hydrogen evolution and
5. Chemical (steam) reformation of naphtha

Each of these technologies can be coupled with one another and one can generate further production methods, and among them photo-electrochemical and photo-microbiological electrochemical methods have been receiving considerable attention in the last few decades. The purpose of this presentation is to examine the option of Photo electrochemical method, the problems faced and the opportunities that are available to make this a commercially viable process. It is therefore necessary to realize that the coverage may not be exhaustive.

Photo electrolysis of Water-Holy Grail of Electrochemistry

Direct photo electrolysis of water is normally considered as the holy grail of electrochemistry. The indirect photo electrolysis implies generation of electricity using a solar cell and utilizing the same for the electrolysis of water. This aspect will also be

not considered in this presentation. Historically, the discovery of photo electrolysis of water directly into oxygen at a TiO_2 electrode and hydrogen at a Pt electrode by the illumination of light greater than the band gap of TiO_2 [3.1 eV] is attributed to Fujishima and Honda [1] though photo catalysis by ZnO and TiO_2 has been reported much earlier by Markham in 1955 [2]. In the photo electrochemical cell, the photoelectro process involves the generation of charge carriers in the semi conducting electrodes and the transfer of these charge carriers across the electrode/electrolyte interface.[3] For the direct photo electrochemical decomposition of water to occur, several key criteria have to be met with. These can be stated at the first level as follows:

1. The band edges of the electrode must overlap with the acceptor and donor states of water decomposition reaction, thus necessitating that the electrodes should at least have a band gap of 1.23 V, the reversible thermodynamic decomposition potential of water. This situation necessarily means that appropriate semiconductors alone are acceptable as electrode materials for water decomposition. [4, 5].The situation is shown pictorially in Fig.1.
2. The charge transfer from the surface of the semiconductor must be fast enough to prevent photo corrosion and shift of the band edges resulting in loss of photon energy.

Employing these two essential criteria and considering the physics of semiconductor solution interface, various materials have been examined as anodes for direct photo electrochemical decomposition of water [6]. The efficiency of this process is still a point of contention, even though double digit efficiencies upto 18.3% has been reported using complex electrodes in an electrolytic cell. [7]. However, realizing this level of efficiency routinely and cheaply and sustaining it appear to be still eluding [8].

In the last three decades, a large number of semiconductor materials have been investigated for photo electrochemical applications. The semiconductor electrode system in efficient solar energy converters should have optimized band gap so as to be able to make maximum utilization of solar radiation, and should also have sufficient chemical stability against photo or other corrosion processes. Unfortunately most of the materials that satisfy the first criterion, namely

semiconductor materials with band gap around 1.4 eV are susceptible for photo corrosion, while stable materials with a wider band gap absorb light only in the UV region. In order to match these two opposing factors, various conceptual principles have been incorporated into typical TiO_2 system so as to make this system responsive to longer wavelength radiations. These efforts can be classified as follows:

- Dye sensitization [9]
- Surface modification of the semiconductor to improve the stability [10]
- Multi layer systems (coupled semiconductors)[11]
- Doping of wide band gap semiconductors like TiO_2 by nitrogen, carbon and Sulphur [12]
- New semiconductors with metal 3d valence band instead of Oxide 2p contribution [13]
- Sensitization by doping.

All these attempts can be understood in terms of some kind sensitization and hence the route of charge transfer has been extended and hence the efficiency could not be increased considerably. In spite of these options being elucidated, success appears to be eluding the researchers. The aim of this presentation is therefore to examine how this frustration has set in. Are there any other options available to wade away this frustration?

The Status Today

The major advances in photo electrolysis of water and photo catalysis for the decontamination of water have centered on TiO_2 based systems probably fabricated in various forms, like sputtered films, nanocrystalline state or with appropriate dopants and charge transfer agents. All these attempts have not yet led to the desired levels of efficiency even though in a recent communication, Licht et al [7] claimed that a combination of photo potential matched semiconductors with effective water electrolysis catalysts like RuO_2 and Pt(black) can form a photo electrolysis cell which can sustain water splitting at 18.3% conversion efficiencies. They have also proposed that alternate dual band gap systems may provide 30% solar photo electrolysis conversion efficiency. In spite of all these achievements photo electrolysis of water is still a challenging commercial proposition. The major stumbling block in this endeavour is the formulation

of a suitable photo anode with appropriate band gap (for maximum utilization of available solar radiation) and suitable band edge positions so that the hydrogen and oxygen evolving reaction potentials lie between the valence and conduction band edges. The available and known semiconductors with a few exceptions can satisfy the second criterion as seen from the data presented in Fig.2. Reverting back to the appropriate value of band gap, a semiconductor with a band gap of 2.2 eV or less, will be reasonable for solar efficiencies but most semiconductors with band gaps in this range are photochemically unstable in water. In addition to this, the technical challenges faced by scientists include obtaining suitable catalyst systems for oxygen and hydrogen evolution reactions without any energy loss by the so called over voltages. The known catalyst systems are highly energy loss systems and hence yield low efficiencies.

The attempts that have been pursued so far are mainly directed towards the band edge engineering and also to generate new designs of semiconductor hybrid combinations. In this area, a variety of metal oxides (single and mixed) has been examined. Even though this route has thrown open the largest possibility of materials unfortunately none of these materials to date has shown any desirable efficiency. New materials based on photovoltaic devices have also been examined. Though these materials have shown considerable efficiencies in the photovoltaic mode, they were found to be unsuitable for PEC applications. There are also attempts to bring in new concepts like tandem cells, triple junctions, p-n combinations and specialty designs, but till date no remarkable success has been reported.

The opportunities that are obviously available as such now include the following:

1. Identifying and designing new semiconductor materials with considerable conversion efficiency and stability
2. Constructing multilayer systems or using sensitizing dyes so as to increase absorption of solar radiation.
3. Formulating multi-junction systems or coupled systems so as to optimize and utilize the possible regions of solar radiation.
4. Developing catalytic systems which can efficiently dissociate water.

The other opportunities evolved

However unsuccessful this effort can be, it has still thrown open some opportunities for us. Some of them are:

1. Deposition techniques have been considerably perfected and hence can be exploited in various other applications like in thin film technology especially for various devices and sensory applications.
2. The knowledge of the defect chemistry has been considerably improved and developed.
3. Optical collectors, mirrors and all optical analysis capability have increased which can be exploited in many other future optical devices.
4. The understanding of the electronic structure of materials has been advanced and this has helped to our background in materials chemistry.
5. Many electrodes have been developed, which can be a useful for all other kinds of electrochemical devices.

These are some of the spin offs of the sustained research in the photo electrolysis of water.

Limited success – Why?

The main reasons for this limited success in all these directions are due to:

1. The electronic structure of the semiconductor controls the reaction and engineering these electronic structures without deterioration of the stability of the resulting system appears to be a difficult proposition.
2. The most obvious thermodynamic barriers to the reaction and the thermodynamic balances that can be achieved in these processes give little scope for remarkable improvements in the efficiency of the systems as they have been conceived and operated. Totally new formulations which can still satisfy the existing thermodynamic barriers have to be devised.
3. The charge transfer processes at the interface, even though a well studied subject in electrochemistry has to be understood more explicitly, in terms of interfacial energetics as well as kinetics. Till such an explicit knowledge is available, designing systems will have to be based on trial and error rather than based on sound logical scientific reasoning.

The Possibilities

One can adjust the energy levels of the photo anode or can alter the energy levels of the substrate but since water is the substrate in this endeavour and hence this possibility is limited. If it were to be any other substrate one can excite the substrate and alter its redox values and then manipulate the life time of the excited states in some trapped condition inside the cavities of the semiconductor by using porous materials. This will be based on the excited state chemistry of the substrate. Therefore exploitation of the excited state of the substrate is not possible in the case of photo electrolysis of water to adjust the energy levels.

The Fermi level position of the counter electrode also is not a very suitable parameter to manipulate since the known hydrogen evolution metals have their Fermi levels almost at the same value. Therefore the limited options available have to fall within the limitation that the semiconductors used should have wide band gap greater than 1.23 V. If this is so, then one can exploit with less recombination rate and also longer stability and probably with higher absorption coefficient not in the whole spectrum but in the range where the semiconductor used absorbs. Under these circumstances the possibilities are:

1. one can exploit semiconductors with changed character of the valence band and conduction bands. In most oxides they are composed of oxygen 2p character for the valence band and metal d level for the conduction band. Instead of this if one had mixed bands like the valence band had mixed 2p character of oxide ions and d levels and in the same way the conduction band had a mixed d character and that of oxygen 2p level then recombination rates may be suitably altered. This can also considerably alter the dissolution potential of the semiconductor and hence give rise to different photochemical efficiencies.

This principle of mixing the orbital contribution to the valence band and conduction band in terms of the oxygen 2p and metal d orbitals is treated in a different language in terms of the covalency of the bond [5]. One another parameter relevant to the electrochemistry by semiconductor is the flat band potential which is a measure of the band bending that will be caused at the semiconductor as a result of the presence of semiconductor solution interface. The value of the flat band potential is also a measure of the difficulty with which the charge transfer takes place. This parameter if it were to be a function of

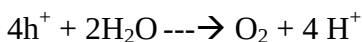
potential then manipulation and reduction of this flat band potential is possible. Essentially if one were to transform the flat band potential to the real system it reflects the allowed energy levels and their wave functions whose energies are altered due to band bending. So if these wave functions are easily perturbed or perturbable with respect to potential then one can modulate the flat band potential and can essentially reduce the barrier for charge transfer.

There are a variety of attempts for finding alternate configurations for the photo-anodes in photo electrochemical cells. These include:

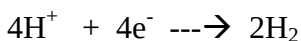
1. Nanocrystalline (mainly oxides like TiO_2 , ZnO , SnO and Nb_2O_5 or chalcogenides like CdSe) mesoscopic semiconductor materials with high internal surface area are examined wherein the pores of such systems are filled with semi-conducting or conducting medium[14]. If a dye were to be adsorbed as a monolayer, enough can be retained on a given area of the electrode so as to absorb the entire incident light. Since the particle sizes involved are small, there is no significant local electric field and hence the photo-response is mainly contributed by the charge transfer with the redox couple. In this configuration two factors essentially contribute to the photo-voltage observed, namely, the contact between the nano crystalline oxide and the back contact of these materials as well as the Fermi level shift of the semiconductor as a result of electron injection from the semiconductor. Another aspect of the nano crystalline state is the alteration of the band gap to larger values as compared to the bulk material which may facilitate both the oxidation/reduction reactions that cannot normally proceed on bulk semiconductors. The response of a single crystal anatase can be compared with that of the meso-porous TiO_2 film sensitized by ruthenium complex ($\text{cis RuL}_2 (\text{SCN})_2$, where L is 2-2'-bipyridyl-4-4'-dicarboxylate). The incident photon to current conversion efficiency (IPCE) is only 0.13% at 530 nm (the absorption maximum for the sensitizer) for the single crystal electrode while in the nano crystalline state the value is 88% showing nearly 600-700 times higher value [15]. This increase is due to better light harvesting capacity of the dye sensitized nano crystalline material but also due to mesoscopic film texture favouring photo-generation and collection of charge carriers [16]. It is clear therefore that the nano

crystalline state in combination with suitable sensitization is one another alternative which is worth investigating.

2. The second option is to promote water splitting in the visible range using Tandem cells. In this a thin film of a nanocrystalline WO_3 [17] or Fe_2O_3 [18] may serve as top electrode absorbing blue part of the solar spectrum. The positive holes generated oxidize water to oxygen



The electrons in the conduction band are fed to the second photo system consisting of the dye sensitized nano crystalline TiO_2 and since this is placed below the top layer it absorbs the green or red part of the solar spectrum that is transmitted through the top electrode. The photo voltage generated in the second photo system favours hydrogen generation by the reaction



The overall reaction is the splitting of water utilizing visible light. The situation is similar to what is obtained in photosynthesis.

Dye sensitized solid hetero-junctions and extremely thin absorber solar cells have also been designed with light absorber and charge transport material being selected independently so as to optimize solar energy harvesting and high photovoltaic output. However, the conversion efficiencies of these configurations have not been remarkably high [19].

Soft junctions, especially organic solar cells, based on interpenetrating polymer networks [20], polymer/fullerene blends [21], halogen doped organic crystals [22] and a variety of conducting polymers [23,24] have been examined. Though the conversion efficiency of incident photons is high [25], the performance of the cell declined rapidly. Long term stability will be a stumbling block for large scale application of polymer solar cells.

Frustration to Opportunity

It is possible that a variety of new configurations and new materials will be examined for photo electrochemical applications in future. However, the concept of separate light absorber and charge transport material as independent options has opened up a variety of new possibilities. Even though sensitized nano materials do not show the same

efficiencies as the conventional silicon based systems, they have certain specific advantages over the conventional systems. The cost of production of nano material based systems will be lower than that based on silicon cells. Secondly the light absorption efficiency (light from all angles can be absorbed) as well as the dependence of efficiency with temperature are the factors in favour of the dye sensitized nano structured materials for PEC applications.

Hydrogen Production – Research Opportunities

As has been pointed out earlier, one of the important aspects for the selection of suitable photo-anode, is the selection of appropriate semiconductor material which will show considerable absorption in the extended wavelength region, as well as satisfy the energetics for the water decomposition reaction. In this search various strategies have been adopted in the past, which include:

1. New semi-conducting materials with conversion efficiencies and stability have been identified. These are not only simple oxides, sulphides but also multi-component oxides based on perovskites and spinels.
2. Multilayer configurations have been proposed for absorption of different wavelength regions. In these systems the control of the thickness of each layer has been mainly focused on.
3. Sensitization by dyes and other anchored molecular species has been suggested as an alternative to extend the wavelength region of absorption.
4. The coupled systems, thus giving rise to multi-junctions is another approach which is being pursued in recent times with some success
5. Activation of semiconductors by suitable catalysts for water decomposition has always fascinated scientists and this has resulted in various metal or metal oxide (catalysts) loaded semi conductors being used as photo-anodes.
6. Recently a combinatorial electrochemical synthesis and characterization route has been considered for developing tungsten based mixed metal oxides and this has thrown open yet another opportunity to quickly screen and evaluate the performances of a variety of systems and to evolve suitable composition-function relationships which can be used to predict appropriate compositions for the desired manifestations of the functions[26].

It has been shown that each of these concepts, though has its own merits and innovations, has not yielded the desired levels of efficiency. The main reason for this failure appears to be that it is still not yet possible to modulate the electronic structure of the semiconductor in the required directions as well as control the electron transfer process in the desired direction.

This means that we are yet to learn how the protein structure in nature is capable of optimizing the water splitting process. How to generate such a structure in the synthetic photo anode material? It is also essential that we learn how the enzyme hydrogenase functions at the molecular level and how does it facilitate the hydrogen production.

In recent times there have been various attempts to mimic enzymes in protein mantles by encapsulating metal complexes in zeolites. These encapsulated metallic species have been shown to exhibit altered redox properties and the information available may sooner or later lead to postulate wherein *a priori* prediction of the behavior of the encapsulated systems may become possible. It is therefore hoped that such embedded systems will be able to replicate the biological mode of water splitting so as to make this process economically viable. The frustration that has set in for the formulation of new materials for PEC applications has been turned to an excitement in terms of the configurations in which these materials can be exploited for PEC applications. It is possible that an appropriate configuration may soon be available so as to make this route an attractive way for the production of hydrogen.

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Legend to the figures:

Fig.1. Schematic representation of a photo-electrochemical cell for the photo cleavage of water.

Fig.2. The positions of bands of semiconductors relative to the standard potentials of several redox couples (shown at the right hand side of the figure). The positions of the valence and conduction band of semiconductors appear favourable for one or the other of the redox reaction of the cleavage of water.

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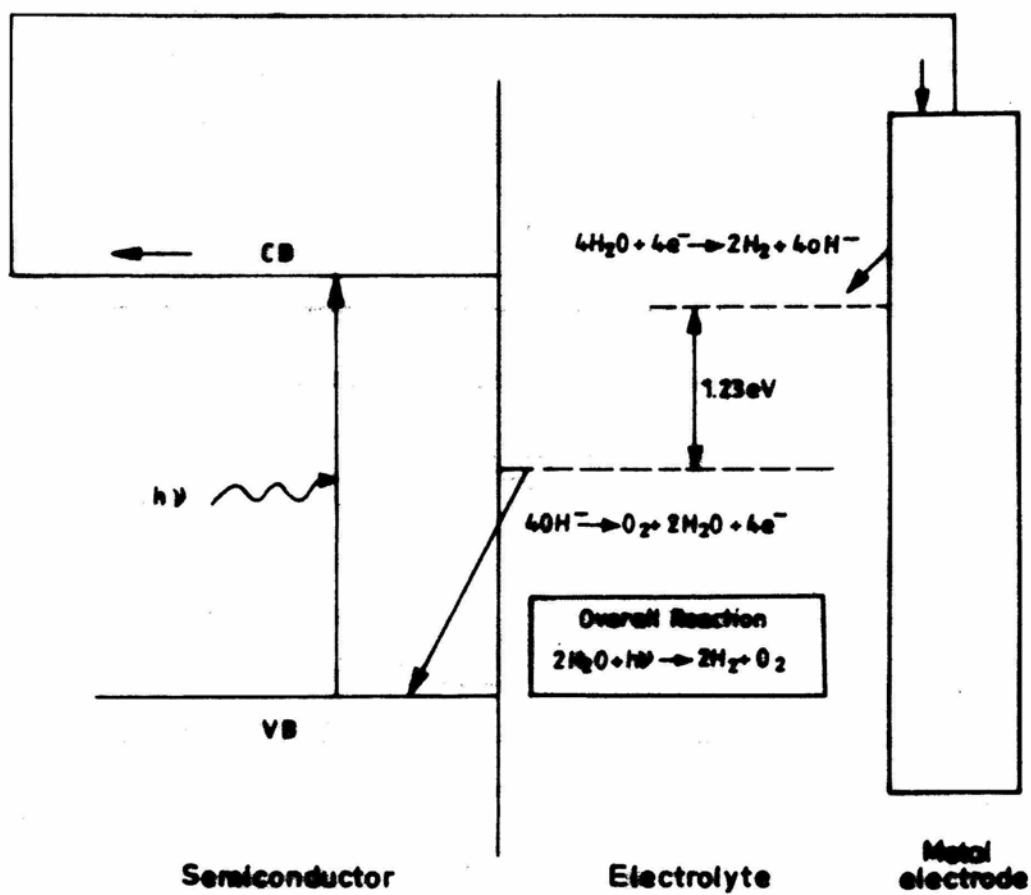


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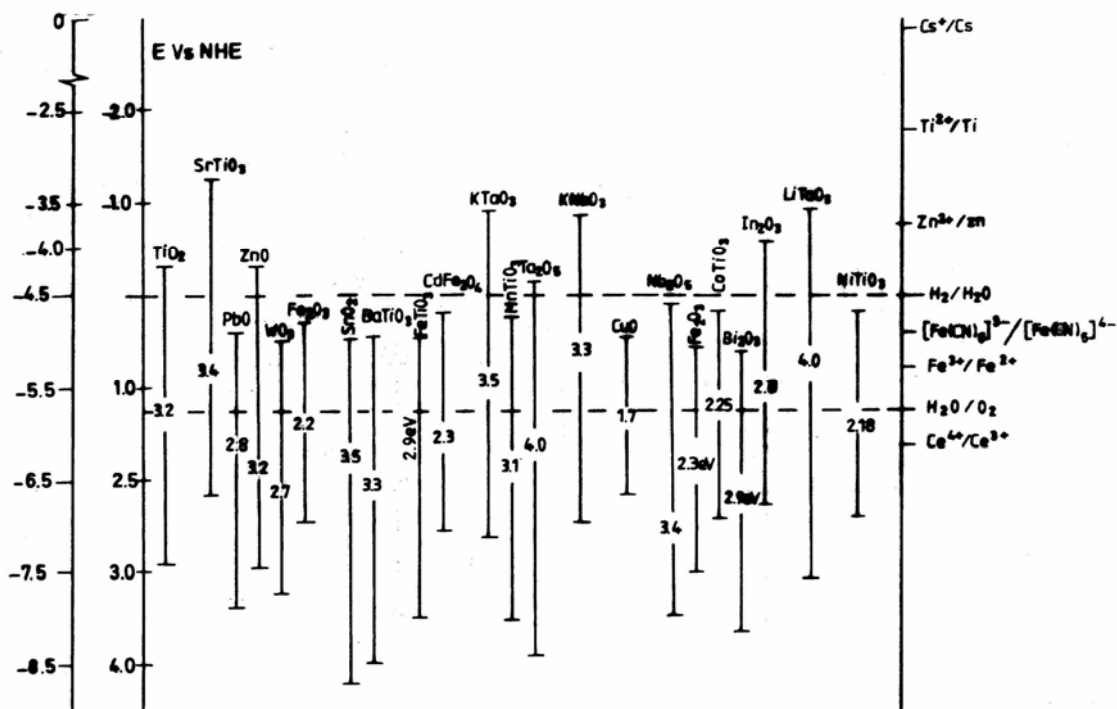


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