International Journal of Chemistry Research

ISSN- 0976-5689 Vol 2, Issue 2, 2011

Review Article

STUDIES ON PHOTOELECTROCHEMICAL CELLS – A BRIEF REVIEW

P.K.MAHAPATRA[1]*, B.B.PANDA[1] AND M.K.GHOSH[2]

[1] Post graduate Department of Chemistry, G.M. (Auto.) college, Sambalpur-768004 Orissa, India; [1] Department of Chemistry, Govt. College of Engineering, Kalahandi, Orissa India

Received: 16 July 2010, Revised and Accepted: 22 Aug 2010

ABSTRACT

The present review on renewable energy is directed to the development of photoelectrochemical cells based on thin film compound semiconductor electrodes. Attempts have been made to include the valuable work done so far on energy conversion starting from the work of Becquerel. The review paper has been presented briefly and systematically.

Keywords: Liquid junction, Thin film, Photoelectrochemical cell.

INTODUCTION

the present commercial energies are based on the fossil and nuclear fuels which have dangerous consequences on our environment. In order to avoid that, research is going on to find clean and renewable energies to meet the present energy crisis. The main efforts of research workers have been focused in very recent years to the development of photoelectrochemical cells of regenerative type otherwise called photovoltaic cells which convert solar energy directly into electrical energy involving a redox reaction($\Delta G=0$). This is also called Liquid-junction solar cells.

The field of photoelectrochemistry is originated from the work of Becquerel[1] in the year 1839. A little further work was done on this topic for the next hundred years and the origin of this photovoltaic phenomenon (Becquerel Effect) was not well understood. Extensive investigation of semiconductor-liquid electrolyte junction PEC cells was carried out in the 1950's and 1960's.In the year 1954–55. Brettain and Garrett[2-3] made a classical investigation of the effect of light on Germanium (Ge) electrode in contact with electrolyte.

Their experiment offered evidence as to the distinct roles played by holes and conduction electrons in the discharge of cations & in the anodic dissolution.

In the year 1959 Gobrecht et al[4] observed photovoltaic effects in metal electrolyte and elemental semiconductor-electrolyte system. Richard William, in the year 1960 studied[5] the photovoltaic effect with a number of compound semiconductors like CdS, CdSe, CuI, ZnO, ZnS, ZnTe, GaAs. He has classified two distinct types of electrode reactions on the semiconductor-electrolyte interface. First type is the reaction of the photoelectrode material itself with eventual destruction (photoanodic dissolution) and the second type is the reaction at a chemically inert electrode material by the exchange of electrons with an oxidation –reduction (redox) couple consisting of two different ionic species dissolved in the electrolytic solution. Studies on photoelectrochemical cells using semiconducting materials like Si, CdS, ZnS, CdSe, ZnSe, ZnTe, GaAs, GaP, ZnO, $KtaO_3$, Ta_2S, $SrTiO_3$ and TiO_2 have been extensively conducted by several researchers[6-13]. Basic understanding of photoelectrochemical phenomenon and important observation on the kinetics and energetic of electron transfer across the semiconductor-electrolyte junction were made by Gerischer, Morrison,Memming and others in early seventies[14-38].

Whatever works done in photoelectrochemistry before 1970 were of fundamental nature. At the beginning of 1970, renewed efforts were directed at these systems and many combinations of semiconductors and liquid were discovered that could affect the stable conversion of light into electricity. The work of Honda and coworkers[39-42] on photosensitized electrolytic oxidation using n-TiO_2 semiconductor electrode was not found to be suitable for practical application of solar energy conversion. In the same year 1971, Fujishima et al[43] attempted to quench the semiconductor electrode decomposition process by using suitable redox couples. H.Gerischer reviewed the well known photoeffects observed at semiconductor electrode in a PEC cell[44] using CdS, CdSe and GaP electrode in the form of single crystal stated that such effects are based on the formation of schottky barrier at the solid semiconductor-redox electrolyte junction. A.B.Ellis, M.S.Wrighton et al and many workers have carried out extensive series of investigations on stabilization of photoelectrodes using redox aqueous electrolyte[45-50]. In all the cases mentioned above experiments were conducted mostly with single crystal. From the year 1976 onwards polycrystalline semiconducting materials were used in PEC cells[51-57]. In the year 1980 A.Heller and B. Miller[58] reported a 12% solar to electrical conversion efficiency with the n-GaAs electrode in polysulphide electrolyte. A.J.Bard etal observed[59] that Fermi level pinning is brought about by semiconductor surface states resulting the band bending across the semiconductor. Then the illumination of the semiconductor can result an output photovoltage which is independent of solution potential. If a change in the surface states can be brought about, the output photovoltage can be improved. The flat bend potential can be determined from the photocurrent and photovoltage values, the method been employed by Butler and Ginley[60]. A good piece of work has been done by K.L.Chopra et al on thin film semiconductor electrode in photoelectrochemical cells[61].

The surface recombination rates of semiconductor-liquid junction based PEC cells can be successfully controlled by photoelectrode surface modification[62-63]. Mixed compound semiconductor electrodes were found to exhibit better photoresponse then simple photoelectrodes[64]. The power conversion efficiency of PEC cell based on n-GaAs photoelectrode in sulphide-polysulphide redox system has been significantly enhanced by surface modification of photoanode through Ruthenium and Osmium metal ions[65]. A good amount of work has been done using n-CdSe,n-CdS electrodes on Photoelectrochemical cells[66-70]. It has been observed[71] that the use of non-aqueous redox electrolytes is generally useful in enhancing the stability of PEC solar cells by suppressing the corrosion reaction at semiconductor-electrolyte interface.

It has been reported that[72] introduction of Antimony up to 0.075 W% to CdS thin film decreases the band gap of CdS and increases the photosensitivity. A variety of sensitizing dyes have been examined to improve the photoelectrochemical characteristics of semiconductor photoelectrode system[73]. A paper on dye sensitization of Antimony doped CdS Photoelectrochemical solar cells has been appeared[74], where it is reported that organic dyes Eosin, Thymol and Rhodamin 6G if used as sensitizer in PEC solar cells, the efficiency was found to increase by almost double, the increase in efficiency being attributed to increase in the density of majority free carriers (electron). Even application of dye in PEC solar cell increases the stability of the system. Further controlled chemical and thermal processing can lead to viable levels of photoconversion with high stability[75]. The possibility of tuning of band gap by gradual variation of proportion of elements of the same family of atoms practically advantageous in designing liquid electrolyte-solid semiconductor junction PEC cells for enhancing solar energy conversion efficiency[76]. The potential of the application of thin film prepared by simple two step method has been studied after optimization of different parameters and annealing for conversion of solar energy into electricity[77]. It has been reported that CdSe film grown by brush plated technique on substrates at high temperature, when used as photoanode in PEC cells increases the efficiency of the same as compared to those prepared at room temperature and post annealed[78]. In another paper the preparative parameters like deposition potential, solution concentration, bath temperature, pH of the electrolytic bath and deposition time have been optimized by using photoelectrochemical technique to obtain well adherent and uniform thin film and found that the material exhibits a direct optical transition having band gap energy 1.72eV[79]. The role of every layer of descending band gap energy on the performance of PEC cell has been demonstrated[80] where it has been found that the three layered electrode exhibits more photoresponse than bilayer. It has been experimented in the paper[81] that the efficiency and fill factor are maximum and lighted ideality factor is minimum in annealed photoanode. It has been examined[82] that the photoactivity and electrochemical corrosion of thin film are improved on inclusion of surfactant facilitated colloidal particulates. The cyclic voltametric method has been found to be an effective method for preparation of thin film. The film prepared by the said method have been found to have band gap energy in the range of 1.32eV-1.4eV[83] and found to be an effective method for demonstrating photo conversion efficiency up to the order of 4%. The effect of current density and deposition time on cell parameters has been studied[84] and it has been found that the cell parameters of cell having binary thin film increase with the increase of current density. Recently a paper has been appeared where it is stated that mixing lower band gap semiconducting material to wide band gap semiconductor as photo electrode and adding dye having absorption band energy lower than band gap of the semiconductor to the redox electrolyte of the PEC cell could enhance the efficiency and stability of cell using mixed CdS-CdSe[85].

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