

Recent trends in photoelectrochemical cells

G V SUBBA RAO

Materials Science Research Centre, Indian Institute of Technology, Madras 600 036, India

Abstract. A brief survey is presented of the recent developments and emerging trends in research in photoelectrochemical cell for solar energy conversion utilizing semiconductor electrodes.

Keywords. Photoelectrochemical cell; semiconductor electrodes.

1. Introduction

Solar energy as received on the earth's surface constitutes less than 3% ultraviolet, about 44% visible region, about 52% near infrared and the rest in the far-infrared regions. Sunlight can be usefully harnessed in several ways. Semiconductor (SC)-based photoelectrochemical (PEC) cell forms one of the chemical routes for trapping solar energy (ChemTrapse). PEC cells can be classified into two types. When sunlight energy is converted into electrical energy, the device is called liquid junction solar cells (LJSC). In the second type, light energy is converted into chemical energy in the form of fuels and is known as photo-electrosynthesis (PES) cells. An example of the latter is the production of hydrogen by the photo-assisted electrolysis (PAE) of water. In PEC cells, the junction formation is easier (mere dipping of the semiconductor in the electrolyte) compared to the p-n junction formation in solid state photovoltaic cells (e.g. silicon). Energy conversion efficiencies (η) as high as 13% have been realized in PAE cells and $\sim 20\%$ in PEC cells. A large number of semiconductors of the mixed oxide and chalcogenide types have been studied for their PEC performance. However, practical solar cells based on these PEC and PAE cells have not been made so far because of the stringent materials requirement. Long-term stability of these SC electrodes under irradiation in the presence of aqueous electrolytes is a lingering problem. There is therefore a need to look for new materials as well as improve the characteristics of known SC materials for use in PEC and PAE cells. Several reviews have appeared in the literature about the state-of-the art of PEC cells (Kalyanasundaram 1985; Rajeshwar 1985; Wrighton 1985; Tributsch 1986).

2. PEC, PAE and PES cells

A PEC cell consists of a photoresponsive n-type SC electrode and a counterelectrode dipped in a suitable electrolyte (aqueous or nonaqueous). The counterelectrode can also be a photoresponsive p-type SC electrode. When the SC/electrolyte junction is illuminated by light of energy $h\nu \geq E_g$, the band gap of the SC electrode, photons are absorbed by the SC electrode producing electron-hole pairs. The electrons are excited into the conduction band (CB), while holes will be left behind in the valence band (VB) of the semiconductor. Because of the potential barrier (space-charge region) created in the SC after the SC/electrolyte junction formation, electrons and

holes are separated and their recombination inhibited. The majority carriers (electrons in the case of n-type SC electrode) flow to the counterelectrode while the minority carriers (holes in the case of n-type electrode) reach the surface and effect an electrochemical reaction (oxidation at the n-type SC electrode and reduction at the counterelectrode).

In an LJSC, a redox electrolyte system (e.g. polysulphide or iodine/iodide (aq.)) is employed where the oxidation reaction at the anode is counterbalanced by the reduction reaction at the cathode and hence there is no net change in the chemical composition of the redox electrolyte ($\Delta G = 0$) and light is converted to dc-electricity. In PAE and PES cells, the electrochemical reactions lead to stable and recoverable products ($\Delta G \neq 0$). High efficiency LJSC's and PAE cells that have been established over the years are listed in tables 1 and 2. The maximum theoretical values of η obtainable for LJSC's are 25–30% and 20–30% for PAE cells (Memming 1980). For oxidic materials in PAE cells, $\eta_{\text{theor.}}$ is $\sim 7\%$ when $E_g \geq 3.0$ eV (Weber and Dignam 1986).

Table 1. High conversion efficiency liquid junction solar cells.

Electrode (E_g , eV)	Electrolyte (aq.)	Efficiency η^*	Remarks	Reference
<i>n</i> -CdSe _{0.65} Te _{0.35} (1.47)	CsS _x + 0.5 mM CuSO ₄	12.7%	Single crystal electrode	Levy-Clement <i>et al</i> (1985)
<i>n</i> -CdSe (1.7)	Ferri/ferro cyanide	12.4%	Single crystal electrode	Frese Jr (1982)
<i>n</i> -CuInSe ₂ (1.01)	2MHI + 2MKI + 0.02M In ₂ + 0.02MCuI + 0.02M In ₂ (SO ₄) ₃	12.0%	Surface modified with In ₂ O ₃ layer	Cahen and Chen (1984); Menezes (1984)
<i>p</i> -InP (1.35)	VCl ₃ -VCl ₂ -HCl	13.0%	Surface modified with In ₂ O ₃ layer	Heller <i>et al</i> (1981)
<i>n</i> -WSe ₂ (1.35)	2MKI + 0.02MI ₂	19.8%	SeCl ₄ -used as the transporting agent	Azaiez <i>et al</i> (1986)
<i>n</i> -GaAs (1.42)	Ferrocene-ferrocenium in LiClO ₄ methanol solution	15.5%	Similar to high efficiency solar cell (Si/methanol)	Gabouze and Gorochov (1986)

$\eta^* = \{(I \times V)_{\text{max}} / (\text{optical power input})\} \times 100$; where $(I \times V)_{\text{max}}$ is the maximum output power of the cell.

Table 2. Photoassisted electrolysis cells.

Electrodes	Electrolyte	Efficiency η^*	Remarks	Reference
<i>n</i> -SrTiO ₃ /Pt	1 M NaOH	< 1%	requires no applied bias; stable; uv light used	Wrighton (1979)
<i>n</i> -Fe ₂ O ₃ / <i>p</i> -Fe ₂ O ₃	1 M NaOH	0.05%	requires no applied bias; visible light used	Leygraf <i>et al</i> (1982)
<i>n</i> -TiO ₂ / <i>p</i> -LuRhO ₃	K ₂ SO ₄ (pH = 7)	0.12%	requires no applied bias; visible and uv lights used	Jarrett <i>et al</i> (1980)
<i>p</i> -InP/graphite	1 M HClO ₄	13.3%	applied bias; surface modified with hydrogen-saturated Rh islands	Heller (1984)

*Conversion efficiency, $\eta = \frac{(\text{energy stored as fuel}) - (\text{electrical energy input})}{(\text{incident solar energy})}$

3. Recent studies

Considerable effort has been put in worldwide research in PEC cells during the last two years (Abstracts 1986). The most significant achievement has been the improvement in η of LJSC. Thus, η values of 20% with n-WSe₂ and of 15.5% with n-GaAs semiconductor electrodes have been reported (Azaiez *et al* 1986; Gabouze and Gorochov 1986). Both these SC's have been investigated by many workers but the improvement in η has been effected only through a better crystal growth technique (n-WSe₂, using SeCl₄ as the transporting agent in the CVT technique) (Azaiez *et al* 1986), or by the use of a new non-aqueous redox electrolyte (for n-GaAs) (Gibbons *et al* 1984; Gabouze and Gorochov 1986) (see table 1).

Other recent studies carried out on PEC cells can be classified as: (i) new materials—new semiconductors and new growth methods of known materials; (ii) surface modification/protection of known SC materials for PEC studies; (iii) rechargeable batteries and photogalvanic cells; (iv) new experimental techniques for the study of PEC behaviour of semiconductors; (v) theory, models and mechanisms and (vi) devices.

3.1a *New materials*: A wide variety of pure and mixed oxides, chalcogenides and pnictides have been examined for their PEC behaviour (table 3). Only some of them were found to be photoactive with good stability. It is expected that more materials will be tested for possible breakthroughs.

Table 3. New and novel SC electrodes studied in recent years.

Oxides	References	Binary chalcogenides (x = S, Se)	References
Pb ₃ O ₄	Sharon <i>et al</i> (1984)	SnS ₂ , ZrS ₂	Fotouhi <i>et al</i> (1986)
CuMO ₂ (M = Y, Al, Cr)	Benko and Koffyberg (1986); Doumerc <i>et al</i> (1986)	FeS ₂ , RuS ₂	Ennaoui <i>et al</i> (1986); Piazza and Tributsch (1987)
TiNb ₂ O ₇	Subba Rao <i>et al</i> (1984)	InSe, ZnSe	Roy <i>et al</i> (1986); Singh and Rai (1987)
Sr ₂ TiO ₄	Paranthaman <i>et al</i> (1986a, b)	Sb ₂ Se ₃	Roy <i>et al</i> (1986)
Sr ₃ Ti ₂ O ₇			
Zn ₂ TiO ₄	Matsumoto <i>et al</i> (1986)	Sb ₂ S ₃ , In ₂ S ₃	Becker <i>et al</i> (1986a)
Zn ₂ Mo ₃ O ₈	Paranthaman <i>et al</i> (1986a)		
Pnictides (x = P)	References	Ternary compounds and miscellaneous	References
ZnP ₂	Ryan and Parkinson (1986)	CdBi ₂ S ₄	Pawar <i>et al</i> (1986)
Zn ₃ P ₂	Turner <i>et al</i> (1986)	CdCr ₂ Se ₄	Manivannan <i>et al</i> (1987)
MP _x (M = V, Fe, Co, Ni) (0 < x < 2)	Sharon and Tamizhmani (1986)	HgCr ₂ Se ₄ CdIn ₂ Te ₄	Becker <i>et al</i> (1985) Becker <i>et al</i> (1986b)
Cu ₄ SnP ₁₀	Tributsch (1986)	HgIn ₂ Te ₄	Becker <i>et al</i> (1986b)
CdSnP ₂	Folmer <i>et al</i> (1985)	AgIn ₅ Se ₈	Razzini <i>et al</i> (1986)

3.1b *New growth methods:* Selenium tetrachloride (SeCl_4) was found to be the best transporting agent as compared to Br_2 or I_2 for the growth of WSe_2 single crystals and to achieve high efficiencies (Azaiez *et al* 1986). Selective doping enhanced the grain size of the crystallites in CuInSe_2 , another well-known PEC material (Ram Janam 1986). Tellurium-substituted cadmium selenide, $\text{CdSe}_{0.65}\text{Te}_{0.35}$ was earlier found to give $\eta \sim 7\text{--}8\%$ in polysulphide electrolyte (Hodes 1980). Levy-Clement *et al* (1985) found that an η value of 12% can be achieved by modifying the crystal growth technique (vertical Bridgmann under controlled Se pressure).

3.2 *Surface modification/protection of known materials*

GaAs and CuInSe_2 electrodes can be suitably modified by coating with thin oxide layers to give enhanced stability and better PEC performance (Kohl *et al* 1977). GaAs was stabilized in a new electrolyte (Gabouze and Gorochoy 1986) (see table 1). Cesium polysulphide electrolyte (as compared to Na_2S or K_2S) gives long term stability to the $\text{CdSe}_{0.65}\text{Te}_{0.35}$ (Levy-Clement *et al* 1985). Photoetching also seems to increase the PEC performances of various materials. CdTe surface was modified with Ru and Pt to give better PEC performances (Mandel *et al* 1986; Bose and Holz 1987).

3.3 *Rechargeable batteries and photogalvanic cells*

Photogalvanic cells use metal electrodes and produce electricity as a result of irradiation of light-absorbing molecules in solution. Albery (1982) set a practical upper limit of about 4% solar energy conversion efficiency for photogalvanic cells. The best photogalvanic cell so far constructed has an efficiency of only 0.03% (viz Pt (or SnO_2)/ $\text{Fe}^{2+/3+}$, thionine, leucothionine/Pt).

If the semiconductor electrode and the counter electrode are separated by a suitable membrane and two different redox electrolytes are used in each half cell, it would be possible to oxidize one set of redox electrolytes in one half cell and reduce the other set of redox electrolytes in the other half cell. Here solar energy is used to perform these reactions to charge the cell. The possible use of transition metal phosphide and other semiconductors for the solar chargeable battery has been discussed by Sharon and Tamizhmani (1986).

3.4 *New experimental techniques*

Various new experimental techniques have been developed/applied to study the PEC behaviour. Some of them are: (i) time domain spectroscopy (TDS) for capacitance measurements (Braun *et al* 1986), (ii) double beam illumination ($h\nu \geq E_g$; $h\nu \lesssim E_g$) to study intrinsic semiconductors (von Kanel *et al* 1984), (iii) electromodulated infrared spectroscopy for *in situ* measurements (Venkateswara Rao *et al* 1986), (iv) laser spot scanning for correlation of grain boundaries and defects at the SC surface (Carlsson and Holmstrom 1986), (v) photothermal beam depletion technique for *in situ* observation and detection of unstable species during cell reaction (Dortche-Merle *et al* 1986), (vi) electrochemical photocapacitance spectroscopy (EPS) for identification of energy levels and concentrations before and after surface modifica-

tion of the semiconductors (Mandel *et al* 1986), and (vii) Raman spectroscopy to identify composition of modified surface (Bose and Holz 1987).

3.5 Theory, models and mechanisms

A Schottky barrier theoretical model was developed by Chandra *et al* (1986) to explain the I-V characteristics and the Fermi-level pinning observed in GaAs PEC cells. Mechanistic studies of etchpit formation by PEC etching were reported by Marcu and Tenne (1986), whereas a kinetic model for the quantized electron transfer from superlattice photoelectrodes (GaAs/GaAs_{0.5}P_{0.5}) was proposed by Nozik *et al* (1986).

3.6 Devices

An engineering design for the PEC cell was suggested by Gerischer (1980) (figure 1). This is a modified version of an earlier type.

4. Emerging trends for PAE and PES cells

Stable oxides (e.g. TiO₂ and SrTiO₃) possess large bandgaps ($E_g \geq 3.0$ eV) and hence cannot utilize sufficient portion of the solar energy for PEC conversion. In order to reduce E_g and induce visible-light response, doping with transition metal oxides and thin-film metal coatings have been tried without much success (Kalyanasundaram 1985; Rajeshwar 1985; Tributsch 1986; Wrighton 1985). The strategy of the so-called *d*-band oxides and chalcogenides seems to offer good promise. In these compounds (e.g. MoS₂, RuS₂, Mo₂Re₄Se₈, LuRhO₃, Zn₂Mo₃O₈), both the VB and CB arise out of the *d*-electrons and the photoresponse is attributed to the electronic *d*→*d* (band) transitions. According to Tributsch (1986), these *d*-band chalcogenides can act as excellent photocatalytic materials for PAF of water (figure 2).

More detailed studies can throw further light on the PEC behaviour of the *d*-band materials.

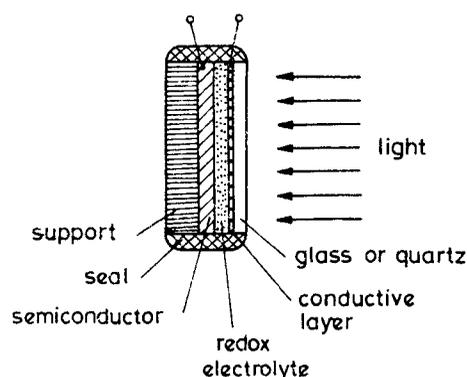


Figure 1. An engineering design of a practical PEC cell for solar energy conversion (Gerischer 1980).

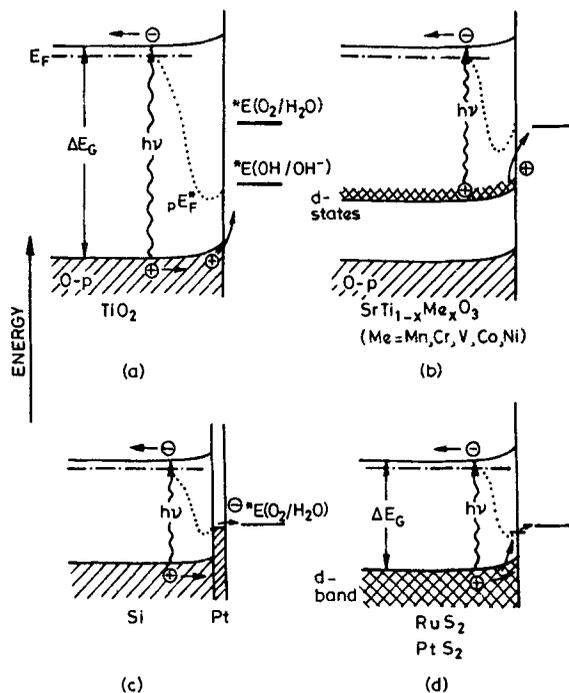


Figure 2. Different strategies for the development of photoelectrodes for the evolution of oxygen from water: (a) large-band gap oxides; (b) transition metal doped oxides; (c) metal coated low-band gap SC's; (d) d-band sulfides (after Tributsch 1986).

Acknowledgements

Thanks are due to Dr M Paranthaman for help in the preparation of the manuscript. Thanks are due to DNES, New Delhi for the award of a research grant.

References

- Abstracts 1986 *Proc. Sixth Int. Conf. on Photochem. Conv. and Storage of Solar Energy, Paris*
 Albery W J 1982 *Acc. Chem. Res.* **15** 142 (and references therein)
 Azaiez C, Levy F, Campet G and Claverie J 1986 Paper D-53 of Abstracts 1986
 Becker R S, Zhou G D and Elton J 1985 *Solar Energy Mater.* **12** 371
 Becker R S, Zheng T, Elton J and Saeki M 1986a *Solar Energy Mater.* **13** 97
 Becker R S, Zhou G D and Elton J 1986b *J. Phys. Chem.* **90** 5866
 Benko F A and Koffyberg F P 1986 *Mater. Res. Bull.* **21** 753
 Bose D N and Holtz M 1987 *Mater. Lett.* (in press)
 Braun C M, Fujishima A and Konda H 1986 paper D-21 of Abstracts 1986
 Cahen D and Chen Y W 1984 *Appl. Phys. Lett.* **45** 746
 Carlsson P and Holmstrom B 1986 Paper D-7 of Abstracts 1986
 Chandra S, Singh S L and Khare N 1986 *J. Appl. Phys.* **59** 1570
 Dorthé-Merle A M, Morand J P and Maurin E 1986 Paper H-15 of Abstracts 1986
 Doumerc J P, Ammar A, Wichainchai A and Pouchard M 1986 Paper D-57 of Abstracts 1986
 Ennaoui A, Fiechter S, Jaegermann W and Tributsch H 1986 *J. Electrochem. Soc.* **133** 97
 Folmer J C W, Tuttle J R, Turner J A and Parkinson B A 1985 *J. Electrochem. Soc.* **132** 1608
 Fotouhi B, Katty A and Gorochoy O 1986 *Compt. Rend. Paris, Ser. II, Mec. Phys.* **303** 1001
 Frese Jr. K W 1982 *Appl. Phys. Lett.* **40** 275

- Gabouze N and Gorochov O 1986 Paper D-91 of Abstracts 1986
- Gerischer H 1980 *Pure Appl. Chem.* **52** 2649
- Gibbons J F, Cogan G W, Gronet C M and Lewis N S 1984 *Appl. Phys. Lett.* **45** 1095
- Heller A, Miller B and Thiel F A 1981 *Appl. Phys. Lett.* **38** 282
- Heller A 1984 *Science* **223** 1141
- Hodes G 1980 *Nature (London)* **285** 29
- Jarrett H S, Sleight A W, Kung H H and Gillson J L 1980 *J. Appl. Phys.* **51** 3916
- Kalyanasundaram K 1985 *Solar Cells* **15** 93
- Kohl P A, Frank S N and Bard A J 1977 *J. Electrochem. Soc.* **124** 225
- Levy-Clement C, Triboulet R, Rioux J, Etcheberry A, Licht S and Tenne R 1985 *J. Appl. Phys.* **58** 4703
- Leygraf C, Hendewerk M and Somorjai G A 1982 *Proc. Natl. Acad. Sci.* **79** 5739
- Mandel K C, Basu S and Bose D N 1986 *Solar Cells* **18** 25
- Manivannan A, Aruchamy A, Aravamudan G and Subba Rao G V 1987 *Solar Energy Mater.* **15** 299
- Marcu V and Tenne R 1986 Paper D-1 of Abstracts 1986
- Matsumoto Y, Omae M, Watanabe I and Sato E 1986 *J. Electrochem. Soc.* **133** 711
- Memming R 1980 *Electrochim. Acta* **25** 77
- Menezes S 1984 *Appl. Phys. Lett.* **45** 148
- Nozik A J, Thacker B R, Turner J A and Olson J M 1986 Paper D-111 of Abstracts 1986
- Paranthaman M, Aravamudan G and Subba Rao G V 1986a *Indian J. Technol.* **24** 399
- Paranthaman M, Aruchamy A, Aravamudan G and Subba Rao G V 1986b *Mater. Chem. Phys.* **14** 349
- Pawar S H, Tamhankar S P and Lokhande C D 1986 *Solar Energy Mater.* **14** 71
- Piazza S and Tributsch H 1987 *J. Appl. Electrochem.* **17** 613
- Rajeshwar K 1985 *J. Appl. Electrochem.* **15** 1
- Ram Janam 1986 *Investigations on synthesis, growth and characterization of chalcopyrite semiconductor $CuInSe_2$ in relation to solar cell fabrication*, Ph.D. thesis, Banaras Hindu University, Varanasi
- Razzini G, Bicelli L P, Arfelli M and Scrosati B 1986 *Electrochim. Acta* **31** 1293
- Roy C B, Nandi P K and Mahapatra P K 1986 *Electrochim. Acta* **31** 1227
- Ryan M A and Parkinson B A 1986 *Appl. Phys. Lett.* **48** 1754
- Sharon M, Sudhir K and Sathe N P 1984 *Solar Cells* **12** 353
- Sharon M and Tamizhmani 1986 *J. Mater. Sci.* **21** 2193 (and references therein)
- Singh K and Rai J P 1987 *Phys. Status Solidi.* **A99** 529
- Subba Rao G V, Aruchamy A, Aravamudan G and Paranthaman M 1984 *Advances in Hydrogen Energy*, **4**, *Hydrogen energy progress V 3* (New York: Pergamon Press) Vol. 3, p. 1075
- Tributsch H 1986 in *Modern aspects of electrochemistry 7* (eds.) J O'M Bockris, B E Conway and R E White (New York: Plenum) No. 17, p. 303
- Turner J, Parkinson B A and Bhusan M 1986 *J. Electrochem. Soc.* **133** 536
- Venkateswara Rao A, Chazalviel J N and Ozanam F 1986 Paper D-33 of Abstracts 1986
- von Kanel H, Kaldis E, Wachter P and Gerischer H 1984 *J. Electrochem. Soc.* **131** 77
- Weber M F and Dignam M J 1986 *Int. J. Hyd. Energy* **11** 225
- Wrighton M S 1979 *Acc. Chem. Res.* **12** 303
- Wrighton M S 1985 *Pure Appl. Chem.* **57** 57