

ELECTROCHEMICAL SOLAR ENERGY CONVERSION

L. M. PETER

Department of Chemistry, The University, Southampton SO9 5NH (Gt. Britain)

(Received December 23, 1983)

1. Historical perspective

The ability of electrodes to generate voltage and current under illumination was first recognized by Becquerel [1] during the first half of the nineteenth century, but a proper understanding of the "Becquerel effect" had to wait until the 1950s, when Brattain and Garrett [2] performed their now classical experiments with germanium. A clearer understanding of the semiconductor-electrolyte junction emerged 5 years later with the work of Dewald [3] on ZnO, and at about the same time Tyagai [4] and Williams [5] showed that another wide band gap compound semiconductor, CdS, was also free of the surface states which had made work with the elemental semiconductors so difficult. Although semiconductor electrochemistry remained an academic concern during the 1960s, experimental progress was steady as new, mostly wide band gap, semiconductors became available and a proper theoretical foundation was established by Gerischer [6]. The majority of the work was carried out by a handful of research groups, most of them in Europe. A change of emphasis came in the early part of the 1970s, when Fujishima and Honda [7, 8] proposed that photoelectrochemical systems could be used for solar energy conversion. Unlike ZnO and CdS, TiO₂ appeared to be stable under illumination, and Fujishima and Honda suggested that it could be used as the photoactive electrode in a cell designed to use light energy to split water in a process now known as "photoelectrolysis" (Fujishima and Honda used the term "photosensitized electrolytic oxidation", which was more appropriate to the circumstances of their experiments). The appearance of the work of Fujishima and Honda coincided with the energy crisis and a new concern for alternative and renewable energy sources, and soon many electrochemists, particularly in the U.S.A., began to abandon their preoccupation with instrumental aspects of electroanalysis and electrode kinetics in favour of research aimed at achieving photoelectrochemical solar energy conversion. In 1974, however, Archer [9], reviewing electrochemical aspects of solar energy conversion, could still state that "no device of practical value has yet been made, and there is very little research work being carried out on photoelectrochemical cells today". In the 10 years which have followed, the scientific literature on all aspects

of photoelectrochemistry and the task of adequately reviewing it have grown enormously[†].

It soon became evident that two strategies could be followed. As an alternative to driving one-half of the water splitting reaction, the semiconductor electrode could be used to promote a redox reaction to produce electrical power rather than hydrogen fuel. The second option formed the basis of the regenerative photoelectrochemical cell, first discussed in depth by Gerischer [10]. Progress was now rapid, and by 1977 the Electrochemical Society was able to hold a meeting [11] which reflected the explosion in research effort. Heller and his colleagues at Bell Laboratories announced that they had already achieved a 9% solar-to-electrical power conversion efficiency with a cell using n-GaAs in a polyselenide electrolyte [12], and the race to devise cells with efficiencies above 10% was on.

2. Developments in cell performance: stability problems

The competitive spirit engendered by the desire to catch up with the performance of solid state cells led to dramatic improvements in photoelectrode response as new techniques of surface preparation were introduced. Early CdSe and CdTe cells attained solar efficiencies of around 8% [13] and, by 1979, the group at Bell Laboratories had reached efficiencies of 12% by "adsorbing" ruthenium(III) on a single-crystal n-GaAs photoanode which was subsequently used in a polyselenide electrolyte [14]; thin film cells were not far behind with an efficiency of 7.8% [15]. These efficiencies were already high enough to exclude serious consideration of alternative, but less efficient, photoelectrochemical systems such as photogalvanic cells (see for example ref. 16). At the same time, however, it became increasingly evident that the stability of semiconductor photoelectrodes was limited by thermodynamic and kinetic factors. The thermodynamic limitations are conveniently expressed in terms of the photodecomposition potential introduced and discussed by Gerischer [17], and more recently detailed Pourbaix diagrams for semiconductor decomposition reactions have been calculated which show clearly the conditions under which semiconductor electrodes are thermodynamically stable [18]. Fortunately, lattice decomposition reactions involve intermediate steps which may have rather high activation energies. Kinetic stabilization of the semiconductor is therefore possible if rapid electron transfer to a solution redox species scavenges minority carriers effectively from the surface of the semiconductor or if the solution redox species can react with intermediates (or "surface-trapped" minority carriers) formed during the initial steps of the photodecomposition reaction. Closer examination of many systems that were thought to be stable has

[†]Photochemical aspects of solar energy are reviewed annually in the *Specialist Periodical Report on Photochemistry*, Royal Society of Chemistry, London.

shown that photocorrosion does proceed at a finite rate, and even the polychalcogenide solutions evidently fail to provide complete stabilization. In the case of photoelectrolysis cells, the photoelectrodes must also resist attack by the photogenerated product. If a p-type semiconductor is used, the diffusion of hydrogen into the surface of the photocathode may create "near-surface" states that seriously degrade the cell efficiency even if decomposition does not occur [19].

3. New materials, and old materials rediscovered

Two important developments have tended to draw attention away from the polychalcogenide cells. Firstly Tributsch [20] suggested that layer-type transition metal dichalcogenides such as MoS_2 and MoSe_2 were very resistant to photocorrosion, and secondly Heller and coworkers began work on p-type semiconductors, particularly InP. Soon efficient and stable cells were constructed using MoSe_2 photoanodes in an iodide-triiodide redox electrolyte, and the extraordinary stability of the layer-type materials was confirmed by experiments which showed that it is possible to evolve chlorine and bromine at illuminated MoSe_2 photoanodes [21]. The layer-type compounds appeared, at least initially, to offer a way of avoiding the problems of photocorrosion. However, more detailed studies of the photoelectrochemistry of these materials showed that some of the early optimism was misplaced. The behaviour of the crystalline photoelectrodes is extraordinarily sensitive to surface morphology; steps in the van der Waals surface of the crystal act as sites for recombination and photocorrosion, so that good fill factors and stability are only obtained with crystals that have a low density of steps on the surface. An elegant demonstration of recombination at steps on MoSe_2 has been given by Parkinson *et al.* [22], who used the scanning laser spot technique to map the photocurrent generation efficiency on the crystal surface. These observations exclude the use of layer-type compounds in practice for electrochemical solar energy conversion since large-area polycrystalline electrodes would necessarily have a high density of step sites. Attempts to deactivate the steps by adsorption or electropolymerization have met with limited success. In 1980 Heller and coworkers announced that they had achieved a 9.4% solar efficiency with a p-InP/ VCl_3 - VCl_2 - HCl /C cell [23], and this efficiency was subsequently increased to 11.5% by surface treatment of the photocathode. Unlike the layer-type materials, InP appears to work reasonably well as a polycrystalline photoelectrode when the surface is treated with $\text{Ag}(\text{CN})_3^{2-}$. The success of the Bell group came as a surprise to many other workers since InP was known to be unstable in the absence of redox systems and, in non-aqueous solutions at least, it appeared to show Fermi level pinning consistent with a high density of surface states. The properties of the InP-solution interface are still not well understood, but it is possible that a thin oxide film is responsible for the absence of surface states in the InP/ V^{II} , V^{III} cell. p-InP and n- MoSe_2 are clearly top performers

in their class, and the two materials have been used together in an efficient photoelectrolysis cell utilizing an HBr or HI electrolyte [24].

As the search for new materials with smaller band gaps has continued, it is perhaps inevitable that silicon should be "rediscovered". The poor chemical stability of silicon might appear to exclude its use in liquid junction cells, but it is a measure of the determination which characterizes much of the recent work on electrochemical solar cells that several groups have managed to operate aqueous silicon liquid junction cells. Bocarsly *et al.* [25], for example, have used ferrocene-derivatized n-Si in aqueous solution, and Heller *et al.* [26] have constructed a p-Si/VCl₃-VCl₂-HCl/C cell with a 2.8% efficiency. Some of the chemistry involved in these attempts is particularly elegant. Dominey *et al.* [27], for example, have derivatized p-Si with viologen units, and with the help of an attached platinum catalyst the photocathode generates hydrogen with high efficiency under illumination. In general, however, attempts to devise efficient photoelectrolysis cells have been less successful. Although Heller *et al.* [28] have demonstrated that p-InP coated with platinum islands can be used at high light intensities for the photoassisted electrolysis of water, and Nozik [29] has shown that "photochemical diodes" constructed from back-to-back n- and p-type semiconductors might allow light energy to be used to drive both halves of the water splitting reaction, it appears that the efficient photoelectrolysis of water without external bias is less likely to be realized than an efficient low cost liquid junction cell. In spite of this conclusion, many alternative strategies are being actively pursued. Storage systems have been discussed [30] which utilize photo-intercalation [31], and particulate semiconductor systems also offer certain advantages (see for example ref. 32). Although comparisons on the basis of efficiency and cost are inevitable, enthusiasm for a range of alternative systems remains, leading to a great deal of exciting new photochemistry. As the search for new materials goes on, experimental techniques become more sophisticated. Rather less emphasis is now being placed on cell performance; there is more concern for the physical chemistry of the semiconductor-electrolyte interface, and methods such as electroreflectance [33], photoacoustic spectroscopy [34], pulsed laser measurements [35], luminescence spectroscopy [36] and impedance analysis [37] are being used. At the same time, the importance of bulk and surface recombination and Fermi level pinning is now recognized, and more detailed theoretical descriptions of charge transfer kinetics have appeared in the literature [36]. Nevertheless, there is still a pressing need to compare these theories with carefully controlled experiments.

4. Outlook

The aims of current research in photoelectrochemical solar energy conversion are well established. The absolute requirements of low cost and long lifetime are inescapable in the final analysis, but at present no detailed com-

parisons with solid state systems appear to have been made. Unless the active element of the system is inexpensive, the cells will have to be used with concentrators and this may lead to problems of increased photocorrosion at higher temperatures. Photoelectrolysis cells must combine efficient charge carrier generation and separation with good catalytic performance, whereas the alternative approach of using an optimized solid state photovoltaic array in tandem with a conventional electrolyser involves the matching of two well-established technologies. A realistic analysis must conclude that the chances of using photoelectrochemical cells for large-area terrestrial solar energy conversion in the near future look slim, but less ambitious applications appear to be more feasible. Cells using solid or polymeric electrolytes could prove useful in small-scale applications if they can compete successfully with conventional silicon cells. Disperse systems, although they may not be economically viable for hydrogen generation, could be used for photoelectrosynthesis or for selective reactions in pollution control. The future development of many of these ideas should ensure that interesting new research will continue even if emphasis shifts away from solar energy conversion as the immediate objective. Meanwhile, future progress towards direct practical application of the great range of new ideas in photoelectrochemistry may have to wait alongside similar developments in heterogeneous catalysis for the next oil crisis. Research in photoelectrochemistry remains an investment in the future.

References

- 1 E. Becquerel, *C.R. Acad. Sci.*, 9 (1839) 561.
- 2 W. H. Brattain and C. G. B. Garrett, *Bell Syst. Tech. J.*, 34 (1955) 129.
- 3 J. F. Dewald, in N. B. Hannay (ed.), *Semiconductors*, Reinhold, New York, 1959, pp. 727 - 752.
- 4 V. A. Tyagai, *Izv. Akad. Nauk S.S.S.R., Ser. Khim.*, (1963) 1556.
- 5 R. Williams, *J. Chem. Phys.*, 32 (1960) 1505.
- 6 H. Gerischer, *Z. Phys. Chem. N.F.*, 26 (1960) 223; 27 (1961) 48.
- 7 A. Fujishima and K. Honda, *Bull. Chem. Soc. Jpn.*, 44 (1971) 1148.
- 8 A. Fujishima and K. Honda, *Nature (London)*, 238 (1972) 37.
- 9 M. A. Archer, *J. Appl. Electrochem.*, 5 (1975) 17.
- 10 H. Gerischer, *J. Electroanal. Chem.*, 58 (1975) 263.
- 11 A. Heller (ed.), *Proc. Meet. on Semiconductor Liquid-junction Solar Cells*, Electrochemical Society, Princeton, NJ, 1977.
- 12 K.-C. Chang, A. Heller, B. Schwartz, S. Menezes and B. Miller, *Proc. Meet. on Semiconductor Liquid-junction Solar Cells*, Electrochemical Society, Princeton, NJ, 1977, p. 132.
- 13 A. Heller, K.-C. Chang and B. Miller, *J. Electrochem. Soc.*, 124 (1977) 697.
- 14 B. A. Parkinson, A. Heller and B. Miller, *J. Electrochem. Soc.*, 126 (1979) 954.
- 15 A. Heller, H. J. Lewerenz and B. Miller, *Ber. Bunsenges. Phys. Chem.*, 84 (1980) 592.
- 16 W. J. Albery, in F. Cardon, W. P. Gomes and W. Dekeyser (eds.), *Photovoltaic and Photoelectrochemical Solar Energy Conversion*, Plenum, New York, 1981, p. 313.
- 17 H. Gerischer, *J. Electroanal. Chem.*, 82 (1977) 133.
- 18 S. Park and M. E. Barber, *J. Electroanal. Chem. Interfacial Electrochem.*, 99 (1979) 67.

- 19 J. Li, R. Peat and L. M. Peter, *J. Electroanal. Chem. Interfacial Electrochem.*, to be published.
- 20 H. Tributsch, *Faraday Discuss. Chem. Soc.*, 70 (1980) 189.
- 21 L. F. Schneemeyer, M. S. Wrighton, A. Stacy and M. J. Sieriko, *Appl. Phys. Lett.*, 36 (1980) 701.
- 22 B. A. Parkinson, T. E. Furtak, D. Canfield, K. K. Kamand and G. Kline, *Faraday Discuss. Chem. Soc.*, 70 (1980) 234.
- 23 A. Heller, B. Miller, H. J. Lewerenz and K. J. Bachman, *J. Am. Chem. Soc.*, 102 (1980) 6555.
- 24 B. A. Parkinson, K. K. Kam, G. Kline and C. Levey, *Energy Res. Abstracts*, 7 (1982), no. 29429.
- 25 A. B. Bocarsly, E. G. Walton and M. S. Wrighton, *J. Am. Chem. Soc.*, 102 (1980) 3390.
- 26 A. Heller, H. J. Lewerenz and B. Miller, *J. Am. Chem. Soc.*, 103 (1981) 200.
- 27 R. N. Dominey, N. S. Lewis, J. A. Bruce, D. C. Bookbinder and M. S. Wrighton, *J. Am. Chem. Soc.*, 104 (1982) 467.
- 28 A. Heller, E. Aharon-Shalom, W. A. Bonner and B. Miller, *J. Am. Chem. Soc.*, 104 (1982) 6942.
- 29 A. J. Nozik, *Appl. Phys. Lett.*, 30 (1977) 567.
- 30 H. Tributsch, *Appl. Phys.*, 23 (1980) 61.
- 31 M. Abramovich and H. Tributsch, *J. Electroanal. Chem. Interfacial Electrochem.*, 138 (1982) 121.
- 32 B. Reichman and C. E. Byvik, *J. Phys. Chem.*, 85 (1981) 2255.
- 33 M. Tomkiewicz, J. K. Lyden, R. P. Silberstein and F. H. Pollack, *ACS Symp. Ser. 146* (1981) 267.
- 34 H. Masuda, A. Fujishima and K. Honda, *Bull. Chem. Soc. Jpn.*, 55 (1982) 672.
- 35 S. B. Deutscher, J. H. Richardson, S. P. Perone, J. Rosenthal and J. Ziemer, *Faraday Discuss. Chem. Soc.*, 70 (1980) 33.
- 36 A. B. Ellis, B. R. Karas and H. H. Strickert, *Faraday Discuss. Chem. Soc.*, 70 (1980) 165.
- 37 J. Rosenthal and B. Westerby, *J. Electrochem. Soc.*, 129 (1982) 2147.