tor. Large programmes of experiments are now being planned by NASA and by the National Academy of Sciences, in conjunction with the National Science Foundation, with the object of understanding chemical changes in the lower atmosphere and identifying the various processes that impinge

and depend on it. The behaviour of PAN in the natural atmosphere can be expected to be investigated in detail in the near future. □

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Solar energy

Towards photoelectrolytic power

from Robert W. Cahn

PHOTOELECTROLYSIS, once an electrochemist's plaything, is close to competing with the photovoltaic silicon cell as a means of converting sunlight into power. This development is due to two kinds of advance: an improvement in the requisite semiconducting photoelectrode and subtle treatment of the electrode surface in order to stabilize it against deterioration. A short while ago, an article in *News and Views*¹ described some of the problems associated with electrodes, especially if they are polycrystalline. One way to solve the problems, described in the same issue², is to use a non-aqueous electrolyte; other possibilities compatible with an aqueous electrolyte, and indeed with water electrolysis, are outlined here.

Many of the key inventions in photoelectrolysis have come from the Bell Laboratories, and so repeat the history of the transistor and the photovoltaic cell. Brattain and Garrett of Bell Labs, in 1955, laid down the now classical theory of the illuminated semiconductor-electrolyte junction. The idea of using an illuminated semiconducting electrode as either anode or cathode in an electrolytic cell to produce electric power or chemical products arose naturally from their work, but the very rapid fall in efficiency of electrodes under irradiation was not solved until 1972, when Honda and Fujishima³ reported, in this journal, the stability of (*n*-type) TiO₂ photoanodes. Unfortunately, such electrodes are useless for converting sunlight as the 3-eV energy gap is much too large. Efficient solar conversion requires gaps in the range 1.3 ± 0.3 eV to absorb light in the λ range 1,000 ± 250 nm.

In 1975, Adam Heller joined Bell Labs to initiate a research programme on photoelectrolysis. At that time it was believed that electrodes capable of giving efficient conversion of sunlight could not do so for long, unless astute chemical counter-measures could be applied at the electrode surface. Success has been achieved at Bell by combining several strategies: photocathodes such as *p*-InP (1.3 eV), *p*-GaAs (1.4 eV) or *p*-CdSe (1.5 eV) are intrinsically stabler than (*n*-type) photoanodes⁴; surface recombination of electrons and holes can be reduced by chemical modification of the electrode surface (anodic formation of a thin hydrated indium oxide layer on InP, or absorption of Ru³⁺ ions at

InP or GaAs surfaces); if electrolysis of water is the aim, the incorporation of thin translucent layers of noble metal helps. In these ways^{5,7}, 'solar' efficiencies of up to 16 per cent have been achieved, well up to photovoltaic levels. Such electrodes can be used either as spontaneous cells (without externally supplied electric power) to make electricity, or in photoassisted externally biased cells to electrolyse water; efficiency can be defined either in terms of electrical power saved or of the power available in an ideal fuel cell from the hydrogen evolved, and the resulting efficiencies differ^{8,9}. One can even combine two photoelectrodes, *p* and *n* type, in a single cell, for example, to electrolyse HBr into H₂ and Br₂ (ref. 9).

Honda and Fujishima's cell used single-crystal TiO₂, and the early Bell Labs cells were also based on single-crystal semiconductors. One of the principal advances at Bell was to establish that the same absorption strategy used to improve electrode kinetics — slow down electron-hole recombination — at a monocrystal surface will also lead to stabilization of grain boundaries against recombination: thus, Ru³⁺ ions improve the efficiency of a polycrystalline *n*-GaAs photoanode by a factor of 4, to the point where such electrodes can be used for practical photoelectrolysis¹⁰. This represents a fundamental advantage over photovoltaics, where it has hitherto proved impractical to slow dopant diffusion along grain boundaries in polycrystalline silicon to the point where good *p*-*n* junctions can be made and the lesser cost of polycrystalline material effectively exploited (see refs 4, 8).

Until recently⁸, it has not been possible to electrolyse water by either spontaneous or photoassisted photoelectrolysis when a photoelectrode with energy gap ~1.3 eV has been used. The inefficient *n*-TiO₂ photoanode can, however, be so used¹¹ and is, moreover, highly stable chemically (in spite of being an anode and thus more liable to photocorrosion than a cathode). There is therefore much interest in any procedure which holds promise of increasing the photoelectrochemical efficiency of *n*-TiO₂.

This, it appears, can be done in one of two ways: either by departing increasingly from stoichiometry in the direction of oxygen deficiency — TiO_{2-x} (ref. 12); or by 'alloying' TiO₂ with VO₂ (refs 13, 14). Experiments have been done on both single

crystals and sintered polycrystals, and in these stable materials, grain boundaries cause little deterioration relative to monocrystals (though it is not clear why electron-hole recombination at grain boundaries is insignificant, even in the alloyed materials with lower energy gap). The TiO_{2-x} photoanodes, tested with a K₂SO₄ electrolyte and 335-nm wavelength, increased in efficiency up to 21 per cent for $x = 7 \times 10^{-4}$, then decreased. The decrease was attributed to enhanced surface recombination. It should be pointed out that the recorded 21 per cent efficiency is for monochromatic light, not for a solar spectrum.

The Ti_{1-x}V_xO₂ alloys allow the energy gap to be reduced, down to 1.95–2.04 eV (measurements differ), without, it appears, any loss of chemical stability^{13,14} and without deterioration of efficiency when a polycrystal replaces a single crystal. (Ti_{1-x}Nb_xO₂ electrodes were, however, no better than pure TiO₂.) A gap of 2 eV is close to the range for optimum solar efficiency and could be used for a reasonably efficient solar cell. The study of alloyed semiconducting oxide electrodes is only in its infancy, and it may well prove possible to lower the energy gap further without serious loss of chemical stability.

The technological aspects of large-scale photoassisted electrolysis of water have not been examined but it can be most efficiently performed at high temperature, and thus under enhanced pressure, with appropriate electrocatalysts to reduce the hydrogen overvoltage, in devices where multiple layers of anodes and cathodes are interleaved. It is not obvious how such an apparatus could be adapted to permit access of sunlight to the anodes, and if electrolysis is done at ambient temperature and pressure, the loss of efficiency may conceivably outweigh the benefit derived from photoassistance. A study of the combined efficiency of water electrolysis with photoassistance under different conditions would seem to be the next stage in the approach to the capture of sunlight with the aid of semiconductors. □

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1. Hammett, A. & Dennison, S. *Nature* **300**, 687 (1982).
2. Gronet, C.M. & Lewis, N.S. *Nature* **300**, 733 (1982).
3. Honda, K. & Fujishima, A. *Nature* **238**, 37 (1972).
4. Heller, A. *Acc. chem. Res.* **14**, 154 (1981).
5. Heller, A., Miller, B. & Thiel, F.A. *Appl. Phys. Lett.* **38**, 282 (1981).
6. Lewerenz, H.J., Aspnes, D.E., Miller, B., Malm, D.L. & Heller, A. *J. Am. chem. Soc.* **104**, 3325 (1982).
7. Aharon-Shalom, E. & Heller, A. *J. electrochem. Soc.* **130** (in the press).
8. Heller, A. *Solar Energy* **29**, 153 (1982).
9. Levy-Clement, C., Heller, A., Bonner, W.A. & Parkinson, B.A. *J. electrochem. Soc.* **129**, 1701 (1982).
10. Johnston, W.D. Jr., Leamy, H.J., Parkinson, B.A., Heller, A. & Miller, B. *J. electrochem. Soc.* **127**, 90 (1980).
11. Gerstner, M.E. *J. electrochem. Soc.* **126**, 944 (1979).
12. Gantron, J., Lemasson, P. & Marucco, J.F. *Faraday Disc.* **70**, 81 (1980).
13. Lemasson, P., Etman, M., Gantron, J. & Marucco, J.F. *Proc. 4th Int. Conf. on Photochemical Conversion and Storage of Solar Energy*, Jerusalem, August 1982 (in the press).
14. Phillips, T.E., Moorjani, K., Murphy, J.C. & Poehler, T.O. *J. electrochem. Soc.* **129**, 1210 (1982).