On the Efficiency and Stability of Photoelectrochemical Devices

BRUCE PARKINSON

Photoconversion Research Branch, Solar Energy Research Institute, Golden, Colorado 80401

Photoelectrochemistry is rapidly becoming a mature field. Initiated in the 1950s and 1960s with studies of the physical chemistry and physics of the semiconductor/electrolyte junction, it has developed extensively as in interdisciplinary science. Major effort has also been directed toward the technology of energy conversion and semiconductor processing. Ideas and techniques from photochemistry, solid-state chemistry, surface science, semiconductor physics, and electrochemistry have been brought to bear on photoelectrochemical problems. The impressive growth in photoelectrochemistry is evident by the increase in the number of scientific publications in the area over the last few years—eight publications in 1975 but more than 500 in 1982.[1] Texas Instruments invested over 20 million dollars jointly with the U.S. Department of Energy to develop an ambitious commercial–residential solar-electrochemical energy conversion system, using relatively cheap-to-manufacture, metal-coated silicon p–n junction microspheres for the electrolysis of HBr to storable H_2 and Br_2. The latter can provide electrical energy on demand via a fuel cell.[2] Remarkable technical progress was made on the system before the project was discontinued at the end of 1983.

Within the last several years, a number of optimistic headlines in the press such as "New Way Reported to Take Hydrogen from Water"[3] and "Research Teams Claim Hydrogen Breakthrough"[4] and "Cracking Water for Fuel?"[5] have been accompanied by the disparagement of "The Hydrogen from Water Hype",[6] "Water Splitting Claims Generate Controversy",[7] and "Water-Splitting Method Questioned".[8] If some of the controversy can be attributed to journalistic misapprehensions, still the greater part reflects a lack of consensus within the field, concerning the measurement, indeed the very meaning, of efficiencies and the significance of stabilities achieved for specific photoelectrochemical cells (PECs). We thus feel it most pertinent to review critically in the Account the state-of-the-art in laboratory prototype cells, the measurement and reporting of efficiencies, and the stability of such devices. Theoretical treatments of the efficiency limits of solar quantum converters have been published[9–13] and need no further elaboration here. Excellent reviews of the fundamental aspects of photoelectrochemistry are also available.[14–17]

Bruce Parkinson was born in Rochester, MN, in 1951. He progressed from basement pyrotechnics and high school science fairs to Iowa State University, where he was exposed to research in the laboratory of D. Johnson. After graduate study in electrochemistry at Caltech under the guidance of F. Anson, he spent a postdoctoral year (1978) at Bell Laboratories with A. Heller and B. Miller. He has worked at the University of Campinas, Brazil, and on the staff of the Ames Laboratory. In 1981 he moved to the Solar Energy Research Institute, where he is now senior scientist.

Light Sources Used in Photoelectrochemical Measurements

The intensity and spectral distribution of the light source is paramount to any efficiency measurement in a device for converting photon energy. The accurate measurement of the intensity of a light source can be nontrivial[18] and the literature has examples of quantum yields[19] of >1.0 caused by errors in light measurement.

The sun is, of course, the ultimate light source for energy conversion. The spectral output of the sun received terrestially is that of a 5900 K black body minus the molecular absorptions of atmospheric or stratospheric ozone, carbon dioxide, and water. The scattering of atmospheric particulates is an additional variable factor. The spectral distribution and total intensity are then related to the atmospheric path length (air mass or AM). The total radiant flux at the surface varies from 75 mW/cm^2 at AM2 (path length equivalent to two atmospheric traverses) to about 100 mW/cm^2 at AM1 (sun at the zenith). The AM0 (outside the atmosphere) value is 135 mW/cm^2. Although universally available, the "sun" is thus not a totally repeatable source but the best one for comparative purposes.

The solar intensity is easily measured with acceptable accuracy by using an NBS traceable spectral pyranometer and a high-impedance voltmeter. Since a 180 steradian pyranometer measures whole sky (direct and diffuse) radiation, care must be taken to avoid errors

(1) Arthur Nozik, private communication, 1984.
(2) J. S. Kilby, J. W. Lanthrop, and W. A. Porter, U.S. Patent 4 021 323 (1977); U.S. Patent 4 100 051 (1978); U.S. Patent 4 136 436 (1979).
(3) Walter Sullivan, *New York Times*, October 8, 1982.
(4) John Hall, *New Scientist* October 14, 1982, p 94.
(5) S. McGuire and P. McAlevey, *Newsweek*, October 18, 1982, p 12.
(6) R. C. Cowen, *Technology Review*, February/March, 1983, p 7.
(7) R. Baum, *Chem. News, Eng.* **60** (October 25), 27 (1982).
(8) L. Garmon, *Sci. News*, **122**(13), 198 (1982).
(9) W. Shockley and H. J. Queisser, *J. Appl. Phys.*, **32**, 510 (1961).
(10) R. T. Ross and M. Calvin, *Biophys. J.*, **7**, 595 (1967).
(11) J. R. Bolton, A. F. Haught, and R. T. Ross in "Photochemical Conversion and Storage of Solar Energy," J. S. Connolly, Ed., Academic Press, New York, 1981, p 297.
(12) G. Porter, *J. Chem. Soc., Faraday Trans. 2*, **79**, 473 (1983).
(13) J. R. Bolton, S. J. Strickler, and J. S. Connolly, *Science*, submitted.
(14) H. Gerischer, "Topics in Applied Physics", B. O. Seraphin, Ed., Springer-Verlag, New York, 1979, Vol. 31, p 115.
(15) A. J. Nozik, *Ann. Rev. Phys. Chem.*, **29**, 189 (1978).
(16) M. D. Archer, *J. Appl. Electrochem.*, **5**, 17 (1975).
(17) M. A. Butler and D. S. Ginley, *J. Mater. Sci.*, **15**, 1 (1980).
(18) More detail and references relating to light sources can be found in R. Matson, R. Bird, and K. Emery, Terrestrial Solar Spectra, Solar Simulation and Solar Cell Efficiency Measurement, SERI/TR-612-964.
(19) The quantum yield is defined as the number of collected electrons per incident photon. It can be a device quantum yield which includes reflection and absorption losses or it can be an internal quantum yield (per photon absorbed). The later value can be very close to unity. Quantum efficiency should not be confused with power conversion efficiency.

from nearby interferences such as large white or black objects or shadows. Standard silicon solar cells that provide a short circuit current relatable to the solar flux are also available. However, such standard cells can be recommended only for testing devices with bandgaps close to that of silicon (1.1 eV).

Low-power continuous-wave lasers are convenient light sources for use in photoelectrochemical measurements. Lasers are coherent, monochromatic, and highly collimated light sources, some of which also have a high degree of polarization. To illuminate larger areas uniformly, it is necessary to use elementary mode lasers. Spatial filtering and expansion of the laser to remove inhomogeneities in the beam is advisable but at the expense of power. Because the wavelength of a laser is precisely defined, the total photon flux is easily measured by using either a thermopile or a calibrated photodiode. Efficiency measurements with a laser can be easily duplicated in another laboratory. When a monochromatic source is used for the measurement of the efficiency of the photoconversion, the results can be significantly higher than ones obtained with the sun, especially if the wavelength corresponds to an energy only slightly larger than the energy gap of the semiconductor. It is therefore good and necessary practice to include a spectral response measurement when a laser efficiency is measured and reported.

Broad-band illumination sources available for photoelectrochemical measurements include filament sources and arc lamps. The spectra of filament sources differ from that of the sun in that their black body temperatures are lower and they have outputs where there are absorption bands of ozone, water vapor, and carbon dioxide. Uniform illumination is difficult to achieve with filament lamps because of the inhomogeneity in intensity due to the filaments.

Arc lamps are characterized by the emission lines of the gaseous components. Arc lamps can approximate a point source and provide a spatially more uniform illumination field but can suffer from extensive point to point variations in spectral distribution caused by the temperature differences in the center and the edge of the arc. They also have short-term and long-term fluctuations in intensity. If a water filter is used to remove excess infrared radiation, the measured efficiencies may be severely distorted to the high side since much of this radiation will be present in the solar spectrum.

Several solar simulators are available which compensate for some of these problems. They provide relatively uniform illumination over a sizable area and a spectral distribution which is a reasonable approximation of sunlight.

Photogalvanic Cells

The first type of photoelectrochemical cell for power conversion we shall discuss is the photogalvanic cell.[20a,b] The cells use metal electrodes and produce electricity as a result of light interacting with light-absorbing molecules in solution. The photochemical reaction results in the storage of solar energy by producing both reduced and oxidized species. Preventing back reactions of the photochemically generated oxidizing and

reducing species is a major difficulty for these cells. A complex interaction of kinetic conditions for the various photochemical, chemical, and electrochemical reactions must be simultaneously optimized to achieve high conversion efficiencies. Albery[20a] has dealt theoretically with this complex problem and made progress toward the realization of the kinetically selective electrodes which are required for efficient devices. Additional problems of sensitizing dyes such as self-quenching, solubility, thermal stability, and photostability make the outlook for any practical photogalvanic device bleak. Albery[20a] has set a practical upper limit of about 4% solar conversion efficiency for photogalvanic cells.[20b] The best photogalvanic cell so far constructed has an efficiency of 0.03%.[21] Sacrificial agents are sometimes used in photogalvanic cells for the useful purpose of isolating one-half reaction for more detailed study. Occasionally, however, an efficiency is quoted for such a device. Obviously, these measurements are not energy conversion efficiencies.

The Efficiency of the Semiconductor/Liquid Junctions

Another type of electricity-producing photoelectrochemical device has a semiconductor in contact with a redox electrolyte and is often referred to as electrochemical photovoltaic cell, or semiconductor liquid junction cell. The difficult problem of preventing the back reaction, referred to in photogalvanic cells, is naturally solved by the rectifying junction. The physics behind the operation of these cells is analogous to solid-state Schottky barrier cells (metal/semiconductor junctions). The efficiency of the junction is a function of the semiconductor material parameters, its surface condition, and the properties of the electrolyte, as will be discussed in this section.

One semiconductor parameter which directly influences the solar conversion efficiency is the bandgap or the energy above which excited states can be created in the material. Theoretical calculations show that the optimal bandgap for a single photoelectrode photovoltaic device is 1.3 ± 0.3 eV. However, the optimal bandgap(s) vary with the configuration and function of the device.[13,14]

The driving force, or voltage, generated in a semiconductor photoelectrode is some fraction of the bandgap. In a photovoltaic device it is simply the photovoltage. In a photoelectrosynthetic cell it is related to either the magnitude of a positive free energy change obtainable in the device or to the magnitude of the activation energy barrier which can be overcome to promote a downhill reaction.

The bandgap also determines how completely the device can absorb solar photons and create photogenerated carriers, which are excited electrons or holes in the semiconductor. The actual photocurrent depends upon how efficiently the photogenerated carriers in the semiconductor are harvested. Photocurrent results from two main collection mechanisms, separation of carriers in the space charge field (a region of electric field extending into the semiconductor from the semiconductor/electrolyte interface), and diffusion of carriers toward the interface. The net diffusion is the

(20) (a) W. J. Albery, *Acc. Chem. Res.*, 15, 142 (1982), and references therein. (b) N. N. Lichtin in "Solar Power and Fuels", J. R. Bolton, Ed., Academic Press, New York, 1977, p 119.

(21) D. E. Hall, W. D. K. Clark, J. A. Eckert, N. N. Lichtin, and P. D. Wildes, *Ceram. Bull.*, 56, 408 (1978).

Table I

semiconductor	aqueous redox electrolyte	sunlight efficiency, %	stability, coulombs/cm^2	ref
n-GaAs	1 M K_2Se, 0.01 M K_2Se_2, 1 M KOH	12.0	35 000	48, 49
p-InP	0.3 M V^{3+}, 0.05 M V^{2+}, 5 M HCl	11.5	27 000	50
n-GaAs$_{0.72}$P$_{0.28}$	1 M K_2Se	11.0	3 000	51
n-WSe$_2$	1 M KI, 0.01 M KI_3	10.2	400 000	26, 27
n-CuInSe$_2$	6 M I$^-$, 0.1 M Cu^{2+}, 0.1 M In^{3+}	10.1	15 000	52
n-CuInSe$_2$	I_3^-, I$^-$, Cu$^+$	9.5	70 000	53
n-MoSe$_2$	1 M KI, 0.01 M KI_3	9.4	50 000	26
n-CdSe	1 M Na_2S_2, 1 M NaOH	7.2	20 000	53
n-WS$_2$	1 M NaBr, 0.01 M Br_2	6.0		27
n-CdSe	$Fe(CN)_6^{4-}$	12.4	unstable system	55

response to a gradient of carrier concentration created by the removal of carriers at the surface. In any practical, efficient device, both of these mechanisms will contribute to the total current.

The contribution of space charge separated carriers will be larger in semiconductors with direct bandgap transitions. Direct gap materials are characterized by a high absorption coefficient just above the bandgap energy (e.g., GaAs, InP, TiO$_2$). Indirect bandgap materials have a much lower absorption above the bandgap (e.g., Si, GaP). Indirect bandgap materials thus absorb more of the carrier creating photons deeper inside the material and depend more on diffusion for their collection. Long diffusion lengths, the average distance a carrier can move in its lifetime, are difficult to obtain in most materials, especially oxide semiconductors. For these reasons, an oxide with a relatively large (2.3 eV) and indirect bandgap, such as Fe$_2$O$_3$, offers little hope for efficient solar energy conversion.

The presence of the liquid provides the photoelectrochemical device with more flexibility than that obtainable in a Schottky barrier device. The presence of the liquid allows the variation of the acceptor and donor levels of the electrolyte simply by changing the redox potential. Also, the ease with which the junction is formed, simply by immersion in the redox electrolyte, allows the probing of the junction's interfacial chemistry with relative ease. The effect on the device's junction properties of etchants, mechanical treatments, and chemical treatments can be investigated nondestructively and noninvasively, without the need for time-consuming evaporation or dopant diffusion steps. Indeed, photoelectrochemistry may well find its greatest application in the nondestructive, noninvasive evaluation of semiconducting materials at intermediate stages of processing. Although it provides flexibility, the liquid is usually the principal species involved in photocorrosion reactions, a major barrier to the development of photoelectrochemical cells. On the other hand, photocorrosion can be cleverly exploited for the etching of precise shapes for electronic device applications.[22]

In a PEC, single photoelectrode performance can be examined by means of a third electrode or reference electrode to the cell against which its potential can be measured. An efficiency measured with a three-electrode system is a single-electrode efficiency not including the counterelectrode overpotential losses which degrade total cell efficiency. A real system cannot neglect these losses, but at this point of the field's development the isolation of photoelectrode behavior serves a useful experimental purpose. The use of high

area or highly catalytic counterelectrodes in the normal two-electrode cell configuration approaches the same end.

Proper cell design is required for the optimization of the efficiency of any PEC. Not only must the semiconductor parameters be optimum (doping level, carrier diffusion length, resistivity) but also the constitution of the redox electrolyte must be carefully considered. The redox components must be concentrated enough to scavenge all of the photogenerated carriers at the semiconductor/electrolyte interface and to prevent losses due to concentration polarization (depletion of the redox species near the electrode surfaces). The electrolyte must also be very conductive and not highly absorbing in the regions of the solar flux. Resistive losses in the electrolyte should be minimized. Designs for PECs with thin layers of solution and cells employing the liquid as a concentrating element have been discussed elsewhere.[23]

Photovoltaic Energy Conversion Efficiency

The measurement of the efficiency of a photoelectrochemical power-generating cell or of a photogalvanic cell is rather straightforward. Photovoltaic efficiency is calculated with eq 1. V_{max} is the voltage and I_{max} the

$$\eta_1(\%) = (i_{max}V_{max})100/P_{hv}A \qquad (1)$$

current obtained at the maximum power point of the photocurrent–voltage curve for the cell. P_{hv} is the power density of the incident radiation (usually measured in mW/cm^2) and A is the light-collecting area (in cm^2). Table I contains a compilation of some of the most efficient and stable photoelectrochemical photovoltaic cells which have been constructed from single-crystal semiconductor photoelectrodes. An indication of stability, measured as the number of coulombs of charge per square centimeter of photoelectrode area passed through the device, is also shown.

Many of the cells in Table I have been constructed with commercially available conventional semiconductors, widely used in solid-state electronic devices (Si, GaAs, InP). The group 6 transition-metal dichalcogenide semiconductors are the exception (MoSe$_2$, MoS$_2$, WS$_2$, WSe$_2$, MoTe$_2$). These materials, first suggested and implemented in a photoelectrochemical device by Helmut Tributsch,[24] have demonstrated respectable solar conversion efficiencies and the highest stability yet reached in a photoelectrochemical device.[25-27] The exceptional stability has been ascribed

(22) F. W. Ostermayer, Jr., P. A. Kohl, and R. H. Burton, *Appl. Phys. Lett.*, **43**(7), 642 (1983).

(23) B. A. Parkinson, *Sol. Cells*, **6**, 177 (1982).
(24) H. Tributsch, *Struct. Bonding* (*Berlin*) **49**, 127 (1982), and references therein.
(25) B. A. Parkinson, T. E. Furtak, D. C. Canfield, K. Kam, and G. Kline, *Discuss. Faraday Soc.*, **70**, 233 (1980).

Table II

semiconductor	electrolyte	redox couple	sunlight efficiency, %	stability, coulombs/cm^2	ref
n-GaAs$_{0.72}$P$_{0.28}$	CH$_3$CN–1 M TEABF$_4$	0.1 M Fe(Cp)$_2$/0.5 mM Fe(Cp)$_2^+$	13^a	1000	35
p-Si	CH$_3$CN–1 M TEABF$_4$	0.2 M Co(Cp)$_2^+$/0.5 mM Co(Cp)$_2$	10.5^a	2000	33
n-Si	CH$_3$OH$^-$	(1-hydroxyethyl)ferrocene	10.1^a	3000	36
n-Si	CH$_3$CH$_2$OH	Fe(Cp)$_2$	<1		30
n-GaAs	CH$_3$CN–1 M TEABF$_4$	0.1 M Fe(Cp)$_2$/0.5 mM Fe(CP)$_2^+$	10.0^a	>1000	34
n-GaAs	CH$_3$CN	Fe(Cp)$_2$	2.4		31
n-GaAs	propylene carbonate	Fe(Cp)$_2$	2.3		32

^{a} These efficiencies represent photoelectrode, not cell, efficiencies; a three-electrode potentiostat was used.

Table III

semiconductor	redox electrolyte	sunlight efficiency, %	preparation technique	ref
n-CdSe$_{0.65}$Te$_{0.35}$	1 M Na$_2$S$_2$, 1 M KOH	7.9	painted slurry	56
n-GaAs	1 M K$_2$Se, 0.1 M K$_2$Se$_2$, 1 M KOH	7.8	CVD^a	57
p-InP	0.3 M V^{3+}, 0.05 M V^{2+}, 5 M HCl	7.0	CVD^a	61
n-Si	CH$_3$OH, 1.5 M LiClO$_4$, 0.15 M DMFc,^{c} 0.5 mM DMFc$^+$	7.2	wackercast	62
p-Si	CH$_3$CN	6.5	wackercast	63
α-Si:H (anode)	CH$_3$OH	3.2	rf sputtering	64
n-CdSe	1 M Na$_2$S$_2$, 1 M NaOH	6.5	vacuum coevaporation	65
n-CdSe	1 M Na$_2$S$_2$, 1 M NaOH	6.3	CBD^a	66
n-CdSe	1 M Na$_2$S$_2$, 1 M NaOH	5.3	hot pressed	68
n-CdSe	1 M Na$_2$S$_2$, 1 M NaOH	5.5	electrodeposition	67

^{a} CVD = chemical vaor deposition. ^{b} CBD = chemical bath deposition. ^{c} Decamethylferrocene.

to the d–d nature of the lowest lying, indirect electronic transition in these materials,[24] as well as the inertness of the van der Waals surface to chemical attack. The adsorption of the optimum redox couple, triiodide ion, and the inner sphere electron transfer pathway thus provided is certainly another factor in the success of these materials in photoelectrochemical devices.[28]

The problem with the layered materials is not that the raw materials are expensive (as in the case of indium- and gallium-containing semiconductors) but rather the lack of a technological base akin to that underlying silicon and the III–V materials. It took many years of perfecting the purification and crystal-growth techniques for silicon (another indirect gap material) to attain the necessary materials properties (such as long diffusion lengths) for the mass production of efficient solar cells. We obtained our high solar efficiencies on a few crystals selected from the many that were grown in our laboratory. One of these materials (MoS$_2$ or molybdenite) exists in large natural crystals. We have measured photovoltaic solar conversion efficiencies of as high as 5% on small areas of these relatively impure natural crystals.[29] This efficiency exceeds that of photosynthesis, making cells constructed from molybdenite the most efficient naturally occurring photoconverters known to us.

Another approach to the stabilization of semiconductor photoelectrodes is the use of nonaqueous solvents to dissolve the electrolyte and redox species. The rationale for this approach is that water is involved in most semiconductor photodecomposition pathways. Early work in nonaqueous solvents, such as acetonitrile and methanol, yielded cells which had low efficiencies due to the higher resistivity of the solvent–electrolyte,

limited solubility of redox species, and poor bulk and surface properties of the semiconductor materials.[30-32] These studies did, however, produce valuable information about the physical and chemical properties of liquid junctions. Recent work has shown that careful control of the materials and surface properties of the semiconductor photoelectrode and proper electrolyte/redox couple design can result in very efficient and stable cells with nonaqueous electrolytes (Table II).[33-36] This work and our work have led to the realization that much of the commerically available single-crystal semiconductor material is not ideal for the efficient conversion of solar energy.

Table III is a compilation of efficiency data for photoelectrochemical cells employing polycrystalline and thin-film photoelectrodes. Polycrystalline materials are important because of their potentially lower fabrication and materials costs. Their usage in photoelectrochemical cells has several advantages over a polycrystalline solid-state device, including the ease of junction formation to uneven surfaces and the fact that dopants used to create a p–n junction do not shunt the device by migrating along grain boundaries. Some polycrystalline photoelectrochemical cells have attained efficiencies up to 75% of that of the comparable single-crystal device.[37]

Fuel and Chemical Producing Cells

The third type of photoelectrochemical cell, a photoelectrosynthetic cell, uses photon energy input to

(26) G. Kline, K. Kam, D. Canfield, and B. A. Parkinson, *Sol. Energy Mater.*, **4**, 301 (1981).

(27) G. Kline, K. Kam, R. Ziegler, and B. A. Parkinson, *Sol. Energy Mater.*, **6**, 337 (1982).

(28) J. A. Turner and B. A. Parkinson, *J. Electroanal. Chem.*, **150**, 611 (1983).

(29) B. A. Parkinson, unpublished results; we thank the Climax Molybdenum Co. for samples of natural molybdenite crystals.

(30) K. D. Legg, A. B. Ellis, J. M. Bolts, and M. S. Wrighton, *Proc. Natl. Acad. Sci. U.S.A.* **74**, 4116 (1977).

(31) P. A. Kohl and A. J. Bard, *J. Electrochem. Soc.*, **126**, 603 (1979).

(32) M. E. Langmuir, P. Hoenig, and R. D. Rauh, *J. Electrochem. Soc.*, **129**, 1705 (1982).

(33) C. M. Lieber, C. M. Gronet, and N. S. Lewis, *Nature (London)*, in press.

(34) C. M. Gronet and N. S. Lewis, *Appl. Phys. Lett.*, **43**(1), 115 (1983).

(35) C. M. Gronet and N. S. Lewis, *Nature (London)* **300**, 733 (1982).

(36) C. M. Gronet, N. S. Lewis, G. Cogan, and J. Gibbons, *Proc. Natl. Acad. Sci. U.S.A.*, **80**, 1152 (1983).

(37) A. Heller, *Acc. Chem. Res.*, **14**, 154 (1981).

produce a net chemical change. If the chemical change results in a net gain of free energy, the cell is called a photoelectrolysis cell. If the cell uses the light energy input to overcome the activation barrier of a thermodynamically downhill reaction, the term photocatalytic cell has been applied. The photovoltaic cells described in the previous section have a zero net change in free energy within the cell, since the object is not net chemical change.

The junction efficiency for photoelectrosynthetic devices is governed by the same principles affecting the photovoltaic devices, but the output/input equivalent is not so transparent. A number of methods for calculating the solar conversion efficiency of a photoelectrolysis device have appeared in the literature. The next section will attempt to review the various methods and discuss the advantages and disadvantages of each. As will be seen, considerable variation in the estimation of the efficiency of a device can result from the method used for the calculation.

The first efficiency calculation is a thermodynamically related measure of the efficiency of the instantaneous conversion of free energy by the device. The inherent assumption involved in this method is that the energy stored in the photoelectrolysis products can be recovered in a hypothetical ideal fuel cell. The equation is given below:

$$\eta_2(\%) = 100(E_{dec} - V_{bias})i_t/P_{hv}A \quad (2)$$

E_{dec} is the Nernstian value for the electrolysis of the solution redox species on which the cell is operating[38] and can change with time depending on the accumulation or removal of products in the solution. The term i_t is the total current flowing in the device, also equal to the sum of the photocurrent and the dark current. V_{bias} is the voltage across the cell. V_{bias} in this equation is defined to be negative if the cell can simultaneously produce electrical power and stored chemical energy. It is positive if an additional power input is needed for the cell to perform the desired electrolysis reaction and V_{bias} is equal to zero at short circuit. Preferably the cell would be run at a V_{bias} and i_t corresponding to the maximum power point of the cell. If multiple products are obtained, the numerator in eq 2 becomes the sum of the free energies stored in all the products. Zafir et al. have dealt with the efficiency of a system with a distribution of products.[39]

Another method has been advocated for the calculation of the efficiency of such cells when they require an additional bias to sustain the photoelectrolysis.[40] The equation used for this method is given below:

$$\eta_3(\%) = 100(i_t)E_{dec}/(P_{hv}A + i_tV_{bias}) \quad (3)$$

Although this appears to be simply the output divided by the input of the device, it does not yield a solar conversion efficiency. Instead the calculation yields an energy throughput efficiency for the device. An example of how misleading this equation can be is when the voltage bias (V_{bias}) exceeds the thermodynamic decomposition potential (E_{dec}). The resulting efficiency may still be large and positive but is insensitive to the solar insolation and only approaches zero well past the point where one is putting in more electrical energy than can be regained even in an ideal fuel cell. This was the case in one of the water-splitting schemes reported in the popular press. Under the same conditions eq 2 would reasonably yield negative efficiencies. This approach also assumes that the electrical power needed for the bias will be available independent of the output of the cell. In reality the bias needed to run the cell most likely will have to come from a feedback of energy from the subsequent energy transducer. This transducer could be a fuel cell, battery, or Carnot engine. In other words, the combined system of photoconverter and energy transducer must have a positive energy output to be converting or storing solar energy. If the energy transducer is an ideal fuel cell, and the system is considered as a whole, then eq 2 applies.

Another method which has been suggested for calculating the efficiency of a photoelectrolysis device is the energy-saved efficiency. The equations used are given below for an isolated electrode (eq 4) or a full cell (eq 5):

$$\eta_4(\%) = \frac{100(V_{save}^{half})i_t}{P_{hv}A} = \frac{100(V_{max} + V_p - E°)i_t}{P_{hv}A} \quad (4)$$

$$\eta_5(\%) = \frac{100(V_{save}^{full})i_t}{P_{hv}A} = \frac{100(E°_c - E°_a + V_{max} + V_{pc} + V_{pa})i_t}{P_{hv}A} \quad (5)$$

where V_p is the polarization loss at the electrode in the half-cell case, and V_{pa} and V_{pc} are the polarization losses at the anode and the cathode in the case of the full cell. $E°$, $E°_c$, and $E°_a$ are the respective standard potentials. The efficiencies (η_4 and η_5) represent the amount of energy saved by a solar input in comparison with the same process occurring on a dark metal electrode or electrodes. In other words, the overpotential losses normally associated with the metal electrodes are supplied by the photoconverter and as such are considered in the conversion efficiency.

For photoreactions such as hydrogen generation this approach works very well because reproducible comparison electrodes such as high-surface-area noble-metal electrodes are available. However, a low overpotential reproducible electrode for the evolution of oxygen would be a controversial subject among most electrochemists. The main difficulty with this approach is that the more noncatalytic the comparison electrode, the higher the photoconversion efficiency resulting from the use of eq 4 and 5.[40] For solar-induced hydrogen evolution at a p-type InP electrode plated with catalytic noble-metal islands, this method has given solar single-electrode efficiencies from 20% to 40% larger than the values obtained from eq 2.[41,42]

The same p-type electrode can be coupled to a n-WSe$_2$ or n-MoSe$_2$ photoanode and the spontaneous photoelectrolysis of HI or HBr can be achieved.[43] The

(38) The Nernstian decomposition potential is given by $E_{dec} = E°_{cell} - RT/nF \ln([products]/[reactants])$, where $E°_{cell}$ is the standard cell potential and [products] and [reactants] are the respective activities.

(39) M. Zafrir, M. Ulman, Y. Zuckerman, and M. Halmann, *J. Electroanal. Chem.*, 159, 373 (1983).

(40) J. O. M. Bockris and O. J. Murphy, *Appl. Phys. Commun.*, 2(3), 203 (1982-1983).

(41) A. Heller and R. G. Vadimsky, *Phys. Rev. Lett.*, 46, 1153 (1981).

(42) E. Ahran-Shalom and A. Hller, *J. Electrochem. Soc.*, 129, 2865 (1982).

(43) C. Levy-Clement, A. Heller, W. A. Bonner, and B. A. Parkinson, *J. Electrochem. Soc.*, 129, 1701 (1982).

Table IV

photoelectrode(s)	type cell	products	reactants	energy cutoff, eV	ref
n-MoSe₂, p-InP(Pt)	p–n	H_2, Br_2	HBr	1.35	43
n-MoSe₂, p-InP(Pt)	p–n	H_2, I_2	HI	1.35	43
n-MoSe₂	PE[a]	H_2, SO_4^{2-}	H^+, SO_2	1.09	66
n-WSe₂, p-WSe₂	p–n	H_2, I_2	HI	1.20	67
p-InP(Pt)	PAE[b]	H_2, O_2	H_2O	1.35	41, 42
p-GaP	PC	NH_3	N_2, H^+	2.3	68
p-GaP	PE	CH_3OH, CH_2O	CO_2, H^+	2.3	69, 70
n-TiO₂, p-GaP	PE	H_2, O_2	H_2O	3.0	71, 72
n-SrTiO₃	PE	H_2, O_2	H_2O	3.2	73
p-LuRhO₃, n-TiO₂	p–n	H_2, O_2	H_2O	3.0	74
p-InP, n-WSe₂	p–n	S^{2-}, I_2	S_x^{2-}, I^-	1.35	75
p-InP	PAE	H_2, O_2	H_2O	1.35	76
p-InP	PAE	HCO_2H	H^+, CO_2	1.35	45
n-TiO₂	PC[c]	$Ph_2C{=}O$	$Ph_2C{=}CH_2$, O_2	3.0	77
p-CdTe	PC	CO	CO_2, H^+	1.5	78
n-Fe₂O₃, p-Fe₂O₃	PE	H_2, O_2	H_2O	1.2	79
n-Ru$_x$Fe$_{1-x}$S₂	PAE	H_2, O_2	H_2O	1.2	83, 84
n-TiO₂ [Tl(I)/Tl(III)]	PC	propylene oxide	$CH_2{=}CH_2CH_3$	3.0	80
n-CdS (polymer RuO₂)	PAE	O_2	H_2O	2.5	81, 82

[a] PE = photoelectrolysis. [b] PAE = photoassisted electrolysis. [c] PC = photocatalytic.

monochromatic (632.8 nm) conversion efficiency for the photoelectrolysis of HBr in a two-photoelectrode cell was 7.8% with use of eq 2 (in this case eq 3 yields the same value because V_{bias} = 0) and 11.2% from eq 5. If the same cell is used to photoelectrolyze HI and simultaneously produce electrical power [with monochromatic (514.5 nm) light], the efficiency goes from 5.2% from eq 2 to 6.9% from eq 5. If eq 3 is used and V_{bias} is allowed to go negative, the resulting efficiency is 5.6%.

In some cases ΔH values are used in place of the free energy or E_{dec} (1.47 rather than 1.23 in the case of H_2O) in eq 2, 3, and 5. This assumes that the products will be burned to recover the stored energy as heat rather than recombined in a fuel cell to produce free energy; the result is higher apparent conversion efficiencies. In the ideal cell, the electrolyte must pick up heat from the surroundings; neglecting this energy input can lead to efficiencies greater than 100% and is not thermodynamically consistent.

Although the accurate measurement and reporting of efficiencies is important in assessing the progress in photoelectrochemical energy conversion, there are other important considerations related to the commercialization of any device. The first is the cost per unit energy produced or the economic value of the chemicals synthesized by the device. Other factors, such as the societal preference for liquid fuels over gaseous fuels, may also be important.

A photocatalytic device may not have a favorable energy balance but may offer savings over conventional energy intensive methods of producing a particular product. Photoexcited semiconductors can produce products different from these obtained through conventional thermal pathways and, in some cases, produce them more selectively.[44] The photodecomposition of toxic wastes and pollutants to harmless small molecules (CO_2, H_2O, N_2) would be examples of desirable photocatalytic processes. Conventional measures of catalyst efficiency, turnover rates and turnover numbers, would be the preferred method of evaluation since the solar conversion efficiency calculated with eq 2 would be negative.

The high efficiencies reported for photoelectrochemical electricity production, hydrogen generation, and photoelectrolysis of halo acids have not been matched for photoreactions proceeding through more kinetically difficult multielectron transfers. The half reactions of special interest for energy conversion include oxygen production from water, N_2 reduction to ammonia, or CO_2 reduction to methanol.

My colleague, Paul Weaver, and I have recently demonstrated the selective two-electron uphill photoreduction of CO_2 to formic acid.[45] The reduction was accomplished with an enzyme catalyst, formate dehydrogenase. A p-type indium phosphide photocathode was used to photoreduce a mediator, methyl viologen, which in turn couples to the enzyme to reduce the CO_2 near the reversible potential for the production of formate. A storable fuel is produced and a potentially environmentally troublesome gas is fixed by the coupling of biotechnology to photoelectrochemical energy harvesting. However, the limited stability of the enzyme is one of many problems this system must overcome in order to be of practical interest.

Table IV shows some of the more interesting and efficient photoelectrosynthetic devices. For reasons obvious from the previous discussion, no efficiency numbers are included in this table.

Stability Considerations

The lifetime of the device is critical to any economic analysis of any photoconversion system. Lifetime considerations must also be a factor in the realistic reporting of a device efficiency. What criteria should be used to determine if a device is stable? How stable must a system be before an efficiency measurement is justified? Most researchers, in academia at least, do not want to spend months testing a device for stability in order to report on its merits as a photoconverter. Accelerated testing (testing the device at high solar fluxes or high current density) can reduce the time needed for stability evaluations, but all the assumptions and pitfalls associated with accelerated testing then must be considered. Recent theoretical modelling has

(44) M. A. Fox, *Acc. Chem. Res.*, **16**, 314 (1983).

(45) B. A. Parkinson and P. F. Weaver, *Nature (London)*, **309(5964)**, 148 (1984).

promise as an aid in the prediction of the lifetimes of semiconductor photoelectrodes.[46]

An exact criterion for stability has not been proposed and I cannot offer any. However, we can take a lesson from the people who study catalysis. No one would describe a system as catalytic unless the total number of moles of product exceeds the number of moles of catalyst in the system. We can apply similar criteria for a photoconversion system. At a minimum the system should not show a significant decline in its output when operated under load at solar illumination intensities or over a period of time such that the total number of moles of product (chemicals or electrons) exceeds the total number of moles required to totally decompose the system through its most demanding decomposition route. In reality, this excess should be greater by a large fraction, perhaps as much as 1000 times, to assure that the system is indeed stable. The WSe_2 cell in Table I is the only cell to my knowledge which comes close to meeting this 1000 times requirement.[27] That cell was illuminated under load for 10 months continuously, a solar equivalent of about 3 years, still far short of the 20-year lifetime so often discussed for a viable solar conversion system.

Conclusion

I have attempted to discuss the types of photoelectrochemical devices and the methods for evaluating their efficiencies and have given several examples of both from work done in my laboratory and elsewhere. It is hoped that this will clear up some of the confusion among chemists who read about advances in photoelectrochemistry in the various scientific, trade, and popular journals. It is also hoped that it will provide a basis for the uniform reporting of efficiencies among photoelectrochemists, or at least provide a starting point for further discussions on this topic. In any case there is no substitute for careful experimental control and accurate reporting of all the experimental conditions when an efficiency measurement is made. The recently proposed ACS guidelines for the publication of research in or outside of the scientific literature should also be considered.[47]

Photoelectrochemical measurements can give valuable information about many materials properties of semiconductors and be an aid in materials processing, and thus research in the area does not necessarily have to lead directly to a large-scale solar energy converting system to be worthwhile. However, should future photoelectrochemical research provide clever new approaches to increasing the stability and efficiency while decreasing the cost of PEC-based systems, future articles in the popular press can report about real hope for decreasing our dependence on nonrenewable and pollution-prone energy sources.

(46) K. W. Frese, *J. Phys. Chem.*, submitted.

(47) *Chem. Eng. News*, **61** (September 26), 39 (1983).

(48) B. A. Parkinson, A. Heller, and B. Miller, *Appl. Phys. Lett.*, **36**, 521 (1978).

(49) B. A. Parkinson, A. Heller, and B. Miller, *J. Electrochem. Soc.*, **126**, 955 (1979).

(50) A. Heller, B. Miller, and F. A. Thiel, *Appl. Phys. Lett.*, **38**, 282 (1981).

(51) C. M. Gronet and N. S. Lewis, *J. Phys. Chem.*, in press.

(52) D. Cahen and Y. W. D. Chen, *Appl. Phys. Lett.*, submitted.

(53) S. Menezes, H. J. Lewerenz, and K. J. Bachmann, *Nature (London)*, **305**, 615 (1983).

(54) A. Heller, K. C. Chang, and B. Miller, *J. Electrochem. Soc.*, **124**, 697 (1977).

(55) K. W. Frese, Jr., *Appl. Phys. Lett.*, **40**(3), 275 (1982).

(56) G. Hodes, *Nature (London)* **285**, 29 (1980).

(57) A. Heller, H. J. Lewerenz, and B. Miller, *Ber. Bunsenges. Phys. Chem.*, **84**, 592 (1980).

(58) A. Heller, personal communication, Sept. 1982.

(59) C. W. Cogan, C. M. Gronet, J. F. Gibbons, and N. S. Lewis, *Appl. Phys. Lett.*, **44**(5), 539 (1984).

(60) N. S. Lewis, personal communication, Feb. 1984.

(61) C. M. Gronet, N. S. Lewis, G. W. Cogan, G. R. Moddel, J. F. Gibbons, and H. Wiseman, *J. Electrochem. Soc.*, in press.

(62) M. A. Russak, J. Reichman, C. Creter, and J. DeGarlo, "Fifth Photoelectrochemical Cell Contractors' Review", Golden, CO, June 15–16, 1982.

(63) R. D. Rauh, "Fifth Photoelectrochemical Cell Contractors' Reviews", Golden, CO, June 15–16, 1982.

(64) B. Miller, A. Heller, M. Robbins, S. Menezes, K. C. Chang, and J. Thomson, Jr., *J. Electrochem. Soc.*, **124**, 1019 (1977).

(65) Tomkiewicz, "Fifth Photoelectrochemical Cell Contractors' Review", Golden, CO, June 15–16, 1982.

(66) G. S. Calabrese and M. S. Wrighton, *J. Am. Chem. Soc.*, **103**, 6273 (1981).

(67) F. R. F. Fan and A. J. Bard, *J. Electrochem. Soc.*, **128**, 945 (1981).

(68) C. R. Dickson and A. J. Nozik, *J. Am. Chem. Soc.*, **100**, 8007 (1978).

(69) M. Halman, *Nature (London)*, **275**, 113 (1975).

(70) T. Inoe, A. Fujishima, S. Konishi, and K. Honda, *Nature (London)*, **277**, 637 (1979).

(71) A. J. Nozik, *Appl. Phys. Lett.*, **29**, 159 (1976).

(72) H. Yoneyama, H. Sakamoto, and H. Tamura, *Electrochimica Acta*, **20**, 341 (1975).

(73) M. S. Wrighton, A. B. Ellis, P. Wolczanski, D. L. Morse, H. B. Abrahamson, and D. S. Ginley, *J. Am. Chem. Soc.*, **98**, 2774 (1976).

(74) H. S. Jarrett, A. W. Sleight, H. H. Kung, and H. L. Gilson, *J. Appl. Phys.*, **51**, 3916 (1980).

(75) P. G. P. Ang, C. J. Liu, A. A. Rossignuolo, A. J. Tiller, and A. F. Sammells, *Proc. Electrochem. Soc.*, **82–3**, 697 (1982).

(76) P. G. P. Ang and A. F. Sammells, *J. Electrochem. Soc.*, submitted.

(77) M. A. Fox and C. C. Chen, *J. Am. Chem. Soc.*, **103**, 6757 (1981).

(78) I. Taniguichi, B. Aurian-Blajeni, and J. O'M. Bockris, *J. Electroanal. Chem.*, **157**, 179 (1983).

(79) C. Leygraf, M. Hendewerk, and F. A. Somorjai, *J. Catal.*, **78**, 341 (1982).

(80) J. A. Switzer and E. L. Moorhead, *J. Electrochem. Soc.*, **129**, 2232 (1982).

(81) A. J. Frank and K. Honda, *J. Phys. Chem.*, **86**, 1933 (1982).

(82) A. J. Frank and K. Honda, *J. Electroanal. Chem.*, **150**, 673 (1983).

(83) H. M. Kühne and H. Tributsch, *J. Electrochem. Soc.*, **130**(6), 1448 (1983).

(84) H. M. Kühne and H. Tributsch, *Ber. Bunsenges. Phys. Chem.*, **88**, 19 (1984).