Solar Photoproduction of Hydrogen

IEA Technical Report

IEA Agreement on the Production and Utilization of Hydrogen

IEA/H2/TR-96

IEA Agreement on the Production and Utilisation of Hydrogen

SOLAR PHOTOPRODUCTION OF HYDROGEN

by

James R. Bolton
Department of Chemistry
The University of Western Ontario
London, Ontario, Canada N6A 5B7

September 1996

Last edited 21 November 1995

SOLAR PHOTOPRODUCTION OF HYDROGEN

by

James R. Bolton
Department of Chemistry
The University of Western Ontario
London, Ontario, Canada N6A 5B7

This Paper was prepared for the Hydrogen Program of the International Energy Agency and represents the result of Subtask C, Annex 10 - Photoproduction of Hydrogen - of that Program.

Table of Contents

EXECUTIVE SUMMARY 1
1. INTRODUCTION 3
2. EFFICIENCIES AND HOW DEFINED 4
   2.1 Fundamental energy losses and the expression for the limiting conversion efficiency. 4
   2.2 Efficiency expressions for an energy storing system 7
   2.3 Efficiencies in the water splitting reaction. 9
3. THE MEASUREMENT OF SOLAR HYDROGEN PHOTOPRODUCTION EFFICIENCIES 11
4. SURVEY OF THE STATE-OF-THE-ART 15
   4.1 Photochemical Systems 16
   4.2 Semiconductor Systems 18
   4.3 Photobiological Systems 20
   4.4 Hybrid and Other Systems 21
5. TECHNOLOGY ASSESSMENT 22
   5.1 Photochemical Systems 23
   5.2 Semiconductor Systems 24
   5.3 Photobiological Systems 26
   5.4 Hybrid and Other Systems 27
6. GENERAL COMMENTS AND VALUE-ADDED CONSIDERATIONS 27
7. CONCLUSIONS AND RECOMMENDATIONS 29
ACKNOWLEDGMENTS 31
REFERENCES 32

EXECUTIVE SUMMARY

The concept of using solar energy to drive the conversion of water into hydrogen and oxygen has been examined, from the standpoints of: potential and ideal efficiencies, measurement of (and how to calculate) solar hydrogen production efficiencies, a survey of the state-of-the-art, and a technological assessment of various solar hydrogen options.

The analysis demonstrates that the ideal limit of the conversion efficiency for 1 sun irradiance is ~31% for a single photosystem scheme and ~42% for a dual photosystem scheme. However, practical considerations indicate that real efficiencies will not likely exceed ~10% and ~16% for single and dual photosystem schemes, respectively.

Four types of solar photochemical hydrogen systems have been identified: photochemical systems, semiconductor systems, photobiological systems and hybrid and other systems. A survey of the state-of-the-art of these four types has been presented.

The four system types (and their sub-types) have been examined in a technological assessment, where each has been examined as to efficiency, potential for improvement and long-term functionality.

Four solar hydrogen systems have been selected as showing sufficient promise for further research and development:

1. Photovoltaic cells plus an electrolyzer
2. Photoelectrochemical cells with one or more semiconductor electrodes
3. Photobiological systems

4. Photodegradation systems

The following recommendations are presented for the consideration of IEA:

1. *Define and measure solar hydrogen conversion efficiencies as the ratio of the rate of generation of Gibbs energy of dry hydrogen gas (with appropriate corrections for any bias power) to the incident solar power (solar irradiance times the irradiated area).*

2. *Expand support for pilot-plant studies of the PV cells plus electrolyzer option with a view to improving the overall efficiency and long-term stability of the system. Consideration should be given, at an appropriate time, to a full-scale installation as part of a solar hydrogen based model community.*

3. *Accelerate support, at a more fundamental level, for the development of photoelectro-chemical cells, with a view to improving efficiency, long-term performance and multi-cell systems for non-biased solar water splitting.*

4. *Maintain and increase support for fundamental photobiological research with the aim of improving long-term stability, increasing efficiencies and engineering genetic changes to allow operation at normal solar irradiances.*

5. *Initiate a research program to examine the feasibility of coupling hydrogen evolution to the photodegradation of waste or polluting organic substances.*

1. INTRODUCTION

The photoproduction of hydrogen from the decomposition of water using solar energy as the driving force has been a goal of scientists and engineers since the early 1970's when Fujishima & Honda (1972) reported the generation of hydrogen and oxygen in a photoelectrochemical cell using a titanium dioxide electrode illuminated with near ultraviolet light. Since then there has been an explosion of scientific interest and experiments. Now that more than 23 years has elapsed, it is appropriate to take a critical look at the prospects for the solar generation of hydrogen fuel from water.

The conversion of solar energy into useful energy forms can generally be divided into *thermal* and *photonic* processes. In *solar thermal processes*, solar energy is first converted to heat, which can either be used directly, stored in a thermal medium (e.g., water or dry rocks) or converted to mechanical and/or electrical energy by an appropriate machine (e.g., a steam turbine for the generation of electricity). In *solar photonic processes*, the solar photons are absorbed directly into an absorber, without complete conversion to heat. The absorber may convert part of the photon energy to electricity (as in a photovoltaic cell) or store part as chemical energy in an endergonic chemical reaction (as in photosynthesis or the conversion of water to hydrogen and oxygen). This paper focuses on the last process, namely the solar photoproduction of hydrogen.

The discussion of the theme topic is divided into five major parts: an explanation and definition of solar efficiencies (both ideal and practical), the measurement of solar hydrogen photoproduction efficiencies, a review of the state-of-the-art, a technological assessment of the various solar hydrogen options and finally some conclusions and recommendations.

2. EFFICIENCIES AND HOW DEFINED

As with any conversion process, the efficiency of a solar hydrogen photoproduction process is of considerable importance because high efficiency usually translates into lower costs. But all solar processes have theoretical efficiency limits imposed by the nature of the conversion process. Solar thermal processes are limited by the Carnot efficiency; whereas, solar photonic processes are limited by fundamental considerations associated with bandgap excitation. The general requirements and limiting efficiencies for any solar photonic converter have been reviewed by Archer & Bolton (1990).

2.1 *Fundamental energy losses and the expression for the limiting conversion efficiency.*

All solar photonic processes involve excitation of an absorber from a ground to an excited state. The absorber can be an isolated molecule or a semiconductor. A characteristic of the absorber is that it has a definite threshold energy or bandgap energy U_g,. U_g is usually calculated from the wavelength λ_g of the red absorption edge ($U_g = hc/\lambda_g$, where h is Planck's constant and c is the speed of light).

Four unavoidable energy losses associated with solar photonic conversion can be identified:

1. All solar photons with $\lambda \geq \lambda_g$ (λ_g is the bandgap wavelength and $\lambda_g = hc/U_g$) cannot be absorbed and thus are lost to the conversion process.
2. Solar photons with $\lambda \leq \lambda_g$ can be absorbed, but the excess energy (U - U_g) is lost as heat as the absorber "relaxes" to the level of U_g. Unless some process can be devised to "capture" the excited states before they relax, this excess energy is not available to the conversion process.

3. The energy of the excited state is thermodynamically an *internal energy* and not *Gibbs energy*.[a] Thus only a fraction (up to about 75% - see Archer & Bolton, 1990) of the excited state energy can be converted into useful work (e.g., electrical energy) or stored as chemical energy. This is why the voltage of a photovoltaic cell can never be as high as the bandgap potential. For example, a silicon photovoltaic cell, with $U_g = 1.1$ eV, exhibits an open-circuit voltage $V_o \leq 0.8$ V. In a photoelectrochemical cell, these losses show up as part of the overpotential.
4. When a photoconverter is illuminated, the excess chemical potential of the excited states is dependent on their concentration. If all excited states are converted immediately to products (short-circuit condition), the steady-state concentration of the excited states approaches zero and hence the excess chemical potential becomes zero also. Thus no energy can be converted or stored. Conversely, if the rate of product formation approaches zero (open-circuit condition) the steady-state concentration of the excited states (and hence the excess chemical potential) reaches a maximum, but again no energy can be converted or stored because the rate of product formation is zero. The optimum condition (maximum power point) lies somewhere between these two extremes. Since a significant concentration of excited states

---

[a] Note that this is a property of the system (ensemble) and not of an individual excited state. One way of explaining this is to note that excited states are created as a very dilute mixture in a sea of ground states, but the end product (electricity or hydrogen) is concentrated. To reach the concentrated product state an amount of work equal to $T\Delta S_{mix}$ must be done, where ΔS_{mix} is the entropy of mixing. This entropic energy loss is responsible for the difference between the internal energy and the Gibbs energy of the excited states.

exists at the optimum condition, there will always be some loss due to spontaneous emission (fluorescence). Fortunately, this loss factor is small (1-2%).

The limiting efficiency η_p of any solar photonic process is given by (Archer and Bolton, 1990)

$$\eta_p = \frac{J_g \Delta\mu_{\mathrm{ex}} \phi_{\mathrm{conv}}}{E_{\mathrm{S}}} \tag{1}$$

where J_g is the absorbed photon flux (photons s^{-1} m^{-2}) with $\lambda \leq \lambda_g$.. J_g may be calculated from the relation

$$J_g = \int_{\lambda_{\min}}^{\lambda_{\mathrm{g}}} \frac{E_{\mathrm{S}}(\lambda)}{(hc/\lambda)} \mathrm{d}\lambda \tag{2}$$

where $E_{\mathrm{S}}(\lambda)$ is the spectral irradiance (W m^{-2} nm^{-1}) and $\lambda_{\min}$ is the minimum wavelength at which the light source has any significant output. The denominator in eq. 2 is the photon energy at wavelength λ. For solar radiation at the Earth's surface, $\lambda_{\min}$ = 300 nm. In practice, the integral in eq. 2 is replaced by a sum over small wavelength bands.

$\Delta\mu_{\mathrm{ex}}$ (J) in eq. 1 is the chemical potential (or Gibbs energy per molecule) of the excited state[b] relative to the ground state and represents the maximum energy available to do work or to be stored as chemical energy.

ϕ_{conv} in eq. 1 is the quantum yield of the conversion process and represents the fraction of the excited states that contribute to the generation of a useful product.

---

[b] The excited state can either be on an isolated molecule or as a pair of delocalized excess electrons and holes in a semiconductor.

Finally, E_S in eq. 1 is the total incident solar irradiance (W m^{-2}).

2.2 *Efficiency expressions for an energy storing system.*

In some solar photonic processes, solar photons drive a chemical reaction that *stores* part of the photon energy as chemical energy of an energy-rich product P (e.g., hydrogen). The efficiency η_C of such a photoprocess is defined as

$$\eta_C = \frac{\Delta G_P{}^o R_P}{E_S A} \tag{3}$$

where $\Delta G_P{}^0$ is the standard Gibbs energy for the energy-storage reaction generating product P, R_P is the rate (mol s^{-1}) of generation of P in its *standard state*,[c] E_S is the incident solar irradiance (W m^{-2}) and A is the irradiated area (m^2).

Bolton et al. (1985) define η_C in a different (but equivalent) way to emphasize the various factors that contribute to η_C.

$$\eta_C = \eta_g \eta_{\text{chem}} \phi_{\text{conv}} \tag{4}$$

[c] Note that if P is not generated in its standard state, then $\Delta G_p{}^0$ must be replaced by ΔG_p, which is the Gibbs energy change appropriate for the state in which P is generated.

η_g is the fraction of the incident solar irradiance that has a photon energy $U \geq U_g$, where U_g is the threshold energy (J) for the photoconversion process (in a semiconductor, U_g is the bandgap energy).[d] η_g is given by

$$\eta_g = \frac{J_g U_g}{E_S} \tag{5}$$

η_{chem} in eq. 4 is the chemical efficiency, that is, the fraction of the excited state energy converted to stored chemical energy. η_{chem} is defined as

$$\eta_{chem} = \frac{U_g - U_{loss}}{U_g} = \frac{\Delta G_P{}^o / n}{U_g} \tag{6}$$

where n is a stoichiometric number equal to the number of photons (assuming $\phi_{conv} = 1$) required to drive the reaction as written. U_{loss} is the actual energy loss *per molecule* in the overall conversion process and thus $U_{loss} = U_g - \Delta G_P{}^0/n$. Note that the U_{loss} in eq. 6 is *not* the same as the energy loss when an excited state is created by a photon with $\lambda < \lambda_g$.

Even for an ideal system, U_{loss} cannot go to zero because, as noted above, the energy of the ensemble of excited states is thermodynamically *internal energy* and not *Gibbs energy*. Entropic considerations dictate that U_{loss} has a minimum value of ~0.3 - 0.4 eV, depending on the value of U_g (Bolton, et al., 1981). In real systems, U_{loss} will be considerably higher.

---

[d] η_g would be the efficiency of the system if all of the energy of the excited state could be utilized, but it cannot.

2.3 *Efficiencies in the water splitting reaction.*

For the water splitting reaction

$$H_2O \longrightarrow H_2 + 1/2\ O_2 \tag{7}$$

Bolton et al. (1985) have suggested five possible schemes, as outlined in Table 1, which involve either single (S) or dual (D) photosystem(s).[e] These schemes are discussed by reference to Fig. 1, which shows the limiting efficiency η_P (eq. 1) as a function of λ_g for standard AM 1.5 solar irradiation and the chemical storage efficiency η_C for various values of U_{loss}. Note that η_C drops off sharply as U_{loss} increases.

Figure 1 and Table 1 go near here

The S1 scheme involves driving reaction 7 with one photon in a single photosystem. This requires high-energy photons and thus, as seen in Fig. 1, the maximum efficiency is low. It is clear that S1 systems can be rejected because the efficiency is too low, even at the ideal limit.

The S2 scheme involves the absorption of a minimum of two photons per hydrogen molecule in a single photosystem. This scheme adapts well to a photoredox sensitization reaction, where one electron is transferred per photon absorbed. The energy required per photon is less than in the S1 scheme, and thus the maximum efficiency is much higher.

---

[e] A *photosystem* is defined as a system with a single absorber coupled into a conversion process. In the case of a dual photosystem, the two photosystems must operate in series with the absorption of a minimum of two photons, one in each photosystem.

The S4 scheme requires a minimum of four photons to drive reaction 7 and is thus not very likely.

Schemes D2 and D4 involve the coupling of two photosystems using two and four photons respectively, where half of the photons are absorbed in one photosystem and half in the other. Because one now has the flexibility of using two different absorbers with two different bandgaps, much higher efficiencies are possible but at the expense of greater complexity.

Table 2 gives calculations for ideal converters and for non-ideal converters with U_{loss} = 0.6, 0.8 and 1.0 eV. A reasonable estimate of U_{loss} for a practical system is ~0.8 eV, which gives possible efficiencies of ~17% (λ_g = 610 nm) for an S2 system and ~27% (λ_1 = 720 nm; λ_2 = 1120 nm) for a D4 system.

It should be noted that this analysis is general and applies to any type of photosystem, be it one based on isolated molecular chromophores or one based on a delocalized solid-state semiconductor system.

The above analysis has not taken account of further losses arising from incomplete absorption, quantum yields less than unity, reflection losses and losses in collecting the gases. Bolton et al. (1985) have made estimates for these losses for reaction 7 and conclude that, in practice, efficiencies for the S2 and D4 systems will not likely exceed ~10% and ~16%, respectively. Weber and Dignam (1984) have made a similar analysis of solar water splitting systems based on photoelectrochemical cells. They conclude that S2 and D4 systems will not exceed ~10% and ~18%, respectively.

There is one other issue, which, although not related to efficiency per se, is of general concern to any solar hydrogen process. It is important that the hydrogen and oxygen be generated in separate compartments so that the evolving gases do not mix. Otherwise a highly explosive 2:1 mixture of hydrogen and oxygen will be evolved, which must then be separated before storage and use. This means that the oxidation and reduction half reactions must be physically separated, perhaps via a membrane, or, in the case of an electrolysis cell, by a wire and perhaps a salt bridge. A membrane separator must be permeable to both electron transfer and proton transfer (in the same direction) to assure overall charge neutrality.

3. THE MEASUREMENT OF SOLAR HYDROGEN PHOTOPRODUCTION EFFICIENCIES

From eqs. 3-5 it might appear that there are many factors to be determined in the measurement of solar hydrogen photoproduction efficiencies; however, in practice, efficiencies are measured using eq. 3, where ΔG_P^0 for reaction 7 is 237,200 J mol^{-1} at 298 K. This requires that no matter what the system, the evolved hydrogen must be collected, separated if necessary from other gases (e.g., oxygen), and measured volumetrically with appropriate corrections for water vapor if present. The factor R_{H_2} in eq. 3 is the moles per second of *pure* hydrogen gas produced by the system, where the hydrogen is generated in its *standard state*. For example, if the hydrogen is generated at a pressure P lower than 1 atm, a term $RT \ln (P^0/P)$ must be subtracted from ΔG_P^0 in eq. 3.

In eq. 3, $E_S A$ is the *total* light power incident on the system. This factor can be determined with a good broadband radiometer that is sensitive from the ultraviolet to the far infrared (Pearcy, 1989). Any losses due to reflection and transmission (incomplete absorption) will lower η_C. On a bright sunny day with the absorber perpendicular to the direction of the sun, the solar irradiance $E_S \approx 1000$ W m^{-2}.

In the case of photoelectrochemical cells, sometimes the cell is biased with an external electrical potential. If this is the case, then the electrical power input (current times bias voltage) must be subtracted from the rate of production of Gibbs energy of the evolved hydrogen. Equation 3 must then be modified to (Parkinson, 1984)

$$\eta_C = \frac{\left(\Delta G_{H_2}{}^{o} R_{H_2} - IV_{bias}\right)}{E_S A} \tag{8}$$

where I is the cell current (A) and V_{bias} is the bias voltage applied to the cell.

The following two examples illustrate how η_C may be measured:

Example 1

A cell with an irradiated area of 30 cm^2 is placed perpendicular to the direction of the sun with an incident irradiance of 1000 W m^{-2} and irradiated for 10 min. During this time the system generates 9.3 mL (0.0093 L) of hydrogen, collected over water at 25°C and 1.0 atm pressure. What is the solar photoproduction efficiency? (The vapor pressure of water at 25°C is 24 torr).

The dry pressure of the hydrogen is 736/760 = 0.966 atm. The number of moles of hydrogen generated is

$$n_{H_2} = \frac{PV}{RT} = \frac{0.966 \times 0.0093}{0.082058 \times 298} = 3.67 \times 10^{-4} \text{ moles}$$

where P is the dry pressure (atm) of hydrogen, V is the volume (L) of hydrogen gas generated, R is the gas constant (0.082058 L atm K^{-1} mol^{-1}) and T is the absolute temperature (K). Thus the average rate of hydrogen generation R_{H_2} over the 10 min is $3.67 \times 10^{-4}/600 = 6.12 \times 10^{-7}$ mol s^{-1}.

The incident solar power ($E_S A$) is $1000 \times 0.0030 = 3.0$ W. Thus from eq. 3

$$\eta_C = \frac{237{,}200 \times 6.12 \times 10^{-7}}{3.0} = 0.0483$$

or 4.83%.

Example 2

A suspension of algae is irradiated with sunlight (irradiance 30 W m^{-2}) where the area exposed to the sunlight is 10 cm^2. Highly purified helium gas (saturated with water vapor) is passed through the suspension at a rate of 100 mL min^{-1} and analyzed for hydrogen and oxygen, which are found to be evolved in a 2:1 ratio with the hydrogen concentration at 100 ppmv. What is the solar photoproduction efficiency?

100 mL min^{-1} corresponds to 6.81×10^{-5} mol s^{-1} of carrier gas; hence the rate of production of hydrogen is

$$R_{H_2} = (1.0 \times 10^{-4})(6.81 \times 10^{-5}) = 6.81 \times 10^{-9} \text{ mol s}^{-1}$$

The hydrogen gas is produced at 10^{-4} atm; therefore, the ΔG^0 must be replaced by

$$\Delta G = \Delta G^0 - RT \ln (P^0/P) = 237{,}200 - 8.3145 \times 298.15 \ln (1/10^{-4})$$

$$= 237{,}200 - 22{,}832 = 214{,}368 \text{ kJ}$$

The incident solar power ($E_S A$) is $30 \times 0.0010 = 0.030$ W. Thus from eq. 3

$$\eta_C = \frac{214{,}367 \times 6.81 \times 10^{-9}}{0.030} = 0.0487$$

or 4.87%.

In the literature, there has been some confusion and inconsistencies in the reporting of solar hydrogen efficiencies. In some cases, E_S has included only that part of the solar spectrum absorbed by the system rather than the E_S for the total solar spectrum. This is particularly true in the case of photosynthetic systems, where often efficiencies are reported on the basis of "photosynthetically active radiation" (defined as solar radiation in the 400-700 nm region - see McCree, 1981). In other cases, efficiencies have been calculated only on the basis of the solar light absorbed by the system, rather than the incident broadband total irradiance.

4. SURVEY OF THE STATE-OF-THE-ART

The use of sunlight to drive reaction 7 has been a very popular field of research leading to the publication of several books (Bockris, 1976, 1980; Ohta, 1979; Harriman and West, 1982; Skelton, 1984; Justi, 1987; Bockris et al., 1991), reviews (Balzani et al., 1975; Bolton, 1978; Bolton and Hall, 1979; Grätzel, 1981a; Nozik, 1984; Getoff, 1984; Willner and Steinberger, 1988; Dostrovsky, 1981; Serpone et al., 1992; Bard and Fox, 1995) and close to 1000 research papers. Most systems can be classified under one of five categories: *Photochemical Systems* (sunlight is absorbed by isolated molecules in solution), *Semiconductor Systems* (sunlight is absorbed by a semiconductor, either as a suspended particle in a liquid or as a macroscopic unit in a photovoltaic cell or an electrochemical cell), *Photobiological Systems* (sunlight is absorbed by a leaf chloroplast or alga in a configuration coupled to a hydrogen-generating enzyme), *Hybrid Systems* (involving combinations of the first three) and *Thermochemical Systems*. Since this paper is concerned only with the solar photoproduction of hydrogen, thermochemical systems will not be considered, except in passing.

In this survey of the state-of-the-art, I have not attempted to be comprehensive in the references I have cited, but rather have been selective of those papers that I felt were significant in indicating the state-of-the-art. Where possible, I have given references to reviews, which will provide the reader with more detail and references to other work.

4.1 *Photochemical Systems*

Pure water does not absorb solar radiation, except in the infrared, where photon energies are too low to simulate photochemical action. Thus any photochemical process to drive reaction 7 must involve a *sensitizer*, that is, a molecule or semiconductor that can absorb sunlight and stimulate photochemical reactions which ultimately lead to the generation of hydrogen in reaction 7.

The absorption of a single photon (in the solar wavelength ranges) can, at most, cause the transfer of one electron in a photoredox process. Since reaction 7 is a two-electron process (4 electrons for O_2), catalysts for the storage of electrochemical equivalents are necessary in practical schemes. Figure 2 shows the minimal scheme for a process to split water involving a photochemical sensitizer S with redox storage catalysts *cat-ox* and *cat-red*.

By utilizing sacrificial donors or acceptors to replace the oxidation or reduction half-reactions, respectively, it is possible to study each half reaction separately. Indeed almost all studies to date have been of this type, with very few studies of the complete reaction.

4.1.1 *Reduction Half Reactions*: A popular photochemical system, focused on the reduction half reaction to generate hydrogen in the presence of a sacrificial donor, involves $Ru(bpy)_3^{2+}$ (bpy stands for 2,2′-bipyridyl) (Kalyanasundaram, 1982) as the absorber (see Figure 3 for the scheme); EDTA (ethylenediamine tetraacetic acid) is the sacrificial donor; MV^{2+} (methyl viologen) is the electron relay and colloidal Pt is the hydrogen-evolving redox catalyst (cat-red).

Although this system has been studied extensively, the best overall quantum yield (ϕ_{H_2}) is ~0.3, and there have been significant problems with side reactions, particularly with the degradation of the MV^{2+}. Many other similar systems have been studied using a variety of different dyes (e.g., proflavin), relays (e.g., many other viologens, Co(II) and Rh(II) bipyridyl complexes) and sacrificial donors (e.g., triethanolamine).

4.1.2 *Oxidation Half Reactions*: This half reaction has been less well studied. One such scheme is that of Lehn (1981), as shown in Figure 4. RuO_x particles serve as the redox catalyst (*cat-ox*), and Co^{3+} as the sacrificial acceptor. Only modest quantum yields (~6%) have been reported.

Calzaferri (1993) summarizes his group's work on a system in which silver clusters in a zeolite structure are able to photochemically generate oxygen from water.

4.1.3 *Complete Photochemical Water Splitting Systems*: The only photochemical system, in which a complete water-splitting reaction is reported, is the work of Katakis et al. (1992, 1994). They used tris-[1-(4-methoxyphenyl)-2-phenyl-1,2-ethyleno-dithiolenic-S,S′]tungsten as the sensitizer and MV^{2+} as an electron relay. Remarkably with no other components, they report sustained yields of hydrogen and oxygen in a 2:1 molar ratio. The solution (acetone:water) had to be continuously purged with nitrogen, as the complex undergoes degradative photooxidation in the presence of oxygen. This is an S1 system, and so the reported energy storage efficiency of ~7% is highly suspect. No other groups have as yet attempted to repeat these experiments.

4.2 *Semiconductor Systems*

Here sunlight is absorbed by a semiconductor creating excess electrons in the conduction band of the semiconductor and excess holes in the valence band. If the semiconductor contains a junction (e.g., a *p-n* junction), the chemical potential of the excess carriers can be converted into electricity, as it is in a photovoltaic cell. The electrical energy can then be used to electrolyze water to H_2 and O_2.

Alternatively, the excess electrons and/or holes can undergo chemical reactions at the surface of the semiconductor to produce H_2 and/or O_2, either in a photoelectrochemical cell or in a suspension of semiconductor particles.

4.2.1 *Photovoltaic (PV) Cells Plus Electrolyzer*: This is certainly the most developed option at present because silicon photovoltaic cells routinely achieve efficiencies of >15% and the efficiency of electrolyzers is often >75%.[f] There is extensive fundamental work underway to improve the performance of PV cells. However, research is needed to explore the special requirements of a coupled PV cell/electrolyzer system. Several pilot-plant scale studies are now underway (Winter and Fuchs, 1991; Zahed et al., 1991; Brinner et al., 1992; Szyszka, 1992; Lehman and Parra, 1994). Computer simulations of a PV-electrolyzer system have now been developed (Vanhanen et al., 1994). At the scale of ~10 kW_e, the best overall efficiency for H_2 generation from water is ~6%.

---

[f] The efficiency of an electrolyzer is defined as $\eta_Z = E°/V$, where $E°$ is the thermodynamic cell potential (1.23 V for reaction 7) and V is the voltage appled to the cell under operating condition.

4.2.2 *Photoelectrochemical Cells (PECs)*: Here a light-absorbing semiconductor is either the anode or cathode (or both) in an electrochemical cell. In the famous cell of Fujishima and Honda (1972), a single-crystal of TiO_2 acted as the photoanode, at which oxygen was evolved; electrons released from the anode traveled by a wire to a Pt electrode, at which hydrogen evolved. Although that cell evolved H_2 and O_2 without a bias, the cell was chemically biased because the pH was quite different in the anode and cathode compartments.

Since 1972, there has been considerable progress [Gerischer (1981) presents a thorough overview of the theory, Nozik (1981) gives a good overview of the various PEC devices, Heller (1984) gives an excellent analysis of efficiencies of various PEC systems and the review by Getoff (1990) and the book by Pleskov (1990) provide more recent analyses]. The most efficient cells (~13%) are those involving a *p*-InP photocathode, onto which tiny islands of Pt have been deposited. Cells involving *n*-CdS, *n*-TiO_2 or *n*-$SrTiO_3$ as photoanodes, have achieved efficiencies of ~10%.

A group in Texas (Cervera-March and Smotkin), 1991; Smotkin et al., 1986, 1987) coupled several photoelectrochemical cells, without wire connections, in a bipolar array and thus achieved water photolysis without any external bias. They have used cells based on *n*-TiO_2 and CdS.

A photoelectrochemical cell containing both an *n*-type semiconductor photoanode and a *p*-type semiconductor photocathode would have the potential for a much higher efficiency because it would be a D4 system (see Section 2). However, very little work has been done on such a combination.

4.2.3 *Microheterogeneous Systems*: Here the semiconductor is in the form of tiny particles suspended in a solvent (usually an aqueous solution). [The book by Kalyanasundaram (1987) provides a good overview of this subject.] The process operates much like the reduction half reaction of the photochemical system, except that the semiconductor particle takes the place of the molecular absorber. Excess conduction-band electrons reduce the electron relay and excess holes oxidize the sacrificial donor. *n*-TiO_2, *n*-$SrTiO_3$ and *n*-CdS have been used in this manner [see reviews by Grätzel (1981b) and Willner and Steinberger-Willner (1988)].

There have been some attempts to load a semiconductor, such as TiO_2, with Pt and RuO_2 islands, which act as reduction and oxidation catalysts, respectively. Some unconfirmed claims of complete water photolysis have been reported (Borgarello et al., 1981a,b) with this system, but the results have been strongly criticized (Willner and Steinberger-Willner, 1988).

4.3 *Photobiological Systems*

Photosynthetic organisms carry out an energy-storing fuel production reaction, which stores solar energy in vast quantities all over the world. Normally, photosynthetic systems do not evolve hydrogen, but rather reduce CO_2 to carbohydrates. However, it is possible to modify conditions such that the reducing end of the photosynthetic process (Photosystem I) is coupled to a hydrogen-evolving enzyme, such as hydrogenase or nitrogenase. Three recent reviews (Greenbaum, 1988b; Benemann, 1994a,b; Markov et al., 1995) cover this field quite well.

The most effective photobiological systems for H_2/O_2 evolution are those based on microalgae, such as green algae and cyanobacteria.

Green algae produce hydrogen after incubation under anaerobic conditions, during which hydrogenase is synthesized and activated. When these dark-adapted algae are returned to the light, they evolve H_2 and O_2 initially at efficiencies approaching 12% (Greenbaum, 1988a), but yields fall off as normal photosynthesis is reestablished.

Nitrogen-fixing cyanobacteria can produce hydrogen, catalyzed by the nitrogenase enzyme, if the bacteria are starved of N_2.

Efficiencies under ideal conditions approach ~10%; however, a major difficulty is that the algal systems saturate at solar irradiances above ~0.03 suns. Thus genetic engineering will be required to reduce the size of the antenna chlorophyll pool to allow higher irradiances to be used. A recent paper by Greenbaum et al. (1995) shows promise that higher efficiencies (perhaps approaching 15-20%) may be possible in certain mutants of *Chlamydomonas reinhardii* algae, which lack Photosystem I.

4.4 *Hybrid and Other Systems*

4.4.1 *Hybrid Systems*: Some hybrid systems have been investigated. For example, it is possible to adsorb molecular dyes onto the surface of a semiconductor and thus sensitize the action of the system to wavelengths longer than those that would be absorbed directly by the semiconductor itself. Also there have been reports of photoelectrochemical cells based on chloroplast preparations in the electrolyte or adsorbed onto an electrode. However, none of these systems have been successful in efficient hydrogen production.

4.4.2 *Photodegradation Systems*: There is another option for *solar* hydrogen production that does not involve the evolution of oxygen. In this case an organic substrate, which may be a

pollutant, is used as the sacrificial donor in a reduction half reaction. There is no net energy storage (indeed most of these reactions are exergonic), but hydrogen is produced at the same time as a surplus or even polluting organic compound is oxidized. For example, the reaction

$$CH_3COOH(aq) + O_2 \longrightarrow 2\ CO_2 + 2\ H_2 \qquad (7)$$

is exergonic by 392.3 kJ but the fuel value of the H_2 produced is 474 kJ. The process involves the conversion of one fuel (CH_3COOH, with a fuel value of 866 kJ) into another fuel (2 H_2, with a fuel value of 474 kJ). The potential added value is in the destruction of a pollutant. For example, UV light (and also sunlight) is now used to oxidize organic pollutants to CO_2 and H_2O. It may be possible to modify these processes so that hydrogen would be produced as a byproduct.

5. TECHNOLOGY ASSESSMENT

In this section a general technology assessment of the various solar hydrogen technologies will be presented. I will not attempt a detailed economic assessment [such an assessment has been given by Biddle et al. (1985)]; however, I will begin by restating an analysis I carried out six years ago for an IEA Workshop (Bolton, 1989) because this emphasizes the constraints placed on any solar conversion process by the characteristics of solar radiation, as received at the Earth's surface.

Solar radiation is quite diffuse, having a normal irradiance of only ~1 kW m^{-2} in bright sunlight. This means that, if the average irradiance (over 24 hours a day and 365 days per year) is ~200 W m^{-2} (typical of the southwestern USA), the total annual solar energy received is 6.31 GJ. If the conversion efficiency is ~10%, then the useful energy (say as electricity) is 631 MJ or 175 kWh.

This is equivalent to 2660 moles of H_2 or ~66 standard m^3 of H_2. At \$0.25/m^3, the annual value of this hydrogen per m^2 of collector area is only \$16.50. At a 10% return on investment, the maximum capital cost that would be reasonable is \$165 per m^2. It is interesting that Biddle et al. (1985) come to a very similar conclusion (\$162 per m^2) and note that only 36% of the capital cost is that of the solar reactor and collector system; the other 64% is comprised of piping and reactor support, field piping, gas compression and balance of plant. This means that any system for the solar generation of hydrogen from water will have to be very simple and fabricated from very cheap materials. Exotic and costly substances, such as Ru, are clearly too expensive for any practical system. The analysis also indicates that efficiency is the key to practical economic systems and that any system with an efficiency <10% doesn't have much of a chance to succeed.

5.1 *Photochemical Systems*

No photochemical system has as yet approached an efficiency of 10%; indeed it is arguable that no complete solar water splitting process has yet been demonstrated and confirmed in several other laboratories. Photochemical systems suffer from several difficulties:

1. The molecular absorber must remain robust through millions of cycles. Under normal sunlight conditions, each molecule would receive ~10^6 photons per year. This means that the quantum yield for photodegradation reactions (which would destroy the photosensitizer) must be $<10^{-6}$. This is a very severe constraint.

2. Unless contained in a highly ordered system, excited-state molecules formed by light absorption must diffuse in solution to encounter quenchers where electron-transfer can take place. Diffusion in a liquid is a relatively slow process and so excited-state lifetimes must be long (or quencher concentrations very high) to allow this primary photochemical process to take place. Long lifetimes open the door to degradative side reactions (e.g., with O_2).

3. Even if the primary electron-transfer process occurs efficiently (high quantum yield), the energy-wasting back-electron transfer is always spontaneous and will occur unless elaborate methods are employed to minimize this ubiquitous reaction. This is probably the reason that the photochemical energy storage reaction of photosynthetic organisms occurs in highly organized reaction center proteins.

4. All systems studied to date produce H_2 and O_2 together, and these bubble out as a 2:1 highly explosive mixture. Some method must be employed to separate the gases. This will add to the costs.

Given the above difficulties, my prognosis for photochemical systems is low.

5.2 *Semiconductor Systems*

Semiconductors are much more robust than molecular chromophores and thus show considerably more promise. Because electrons and holes can rapidly delocalize through the bulk semiconductor, recombination (i.e., the back reaction) is less of a problem, but still prevalent.

5.2.1 *Photovoltaic Cells Plus Electrolyzer*: The photovoltaic (PV) cell is currently the most successful device for the conversion of solar photons into an energy form other than heat. Si PV

cells have now exceeded 20% efficiency (at 1 sun, i.e., an irradiance of 1000 W m^{-2}), and commercial PV modules are now available with cell efficiencies of ~18%. Tandem GaAs/GaAlAs PV cells have achieved efficiencies of over 30%.

With the success of PV cells, it is natural to examine the coupling of a PV array to generate solar electricity, which then can drive an electrolyzer system to convert water into hydrogen and oxygen. As noted in Section 4.2.1, this has been achieved on a pilot-plant scale (~10 kW_e) with an overall efficiency of ~6%. Undoubtedly with improvements in the component efficiencies and coupling of the systems, efficiencies in excess of ~10% can be expected in the near future.

Currently the cost of a PV array is ~$6/Wp.[g] At 10% efficiency, this would impose a capital cost of ~$2400 per m^2 at an average solar irradiance of 250 W m^{-2}. The electrolyzer might add another ~$100 per m^2. Thus the PV cell/electrolyzer option is ~16 times that estimated for an economic system. As the costs of PV cells drop and overall efficiencies improve, it is reasonable to expect that this gap will narrow considerably in the near future.

5.2.2 *Photoelectrochemical Cells (PECs)*: PECs have the advantage of combining the PV cell and the electrolyzer into one system without wires. PECs potentially have the same favorable characteristics as do PV cells. One advantage over PV cells is that no semiconductor/ semiconductor junction is required; the junction is formed spontaneously at the semiconductor/ electrolyte interface. However, a potential disadvantage is that PECs can exhibit photocorrosion leading to the dissolution and degradation of the active photoelectrode.

---

[g] A peak watt (Wp) is defined as the generation of 1 W of electrical power, when the PV cell is illuminated by sunlight with an irradiance of 1 kW m^{-2}.

Efficiencies of PECs designed to split water are so far quite encouraging; however, except for the work of Smotkin and coworkers (Cervera-March and Smotkin, 1991; Smotkin et al., 1986, 1987), there have been very few larger-scale studies aiming toward a practical system. There have not been any studies at the pilot-plant scale.

5.2.3 *Microheterogeneous Systems*: These systems suffer from most of the same disadvantages as the photochemical systems (Section 5.1). It is not likely that viable systems will be developed based on this option.

5.3 *Photobiological Systems*

Photobiological systems have the distinct advantage that the collector system self assembles. Thus as long as the cells can be kept alive and viable for extended periods of time, the capital costs of such a systems are potentially quite low. However, there may be considerable costs involved in the fabrication of reactor systems necessary to maintain the organisms under optimum conditions. As noted in Section 4.3, these systems saturate at unacceptably low irradiances. Nevertheless, there is a reasonable possibility that this deficiency can be removed by genetic engineering. Another major disadvantage is that hydrogen and oxygen are generated together and must be separated rapidly to avoid an severe explosion hazard. Benemann (1994) has proposed a two-stage process in which green algae would be cultivated in large open ponds to produce a high carbohydrate algal biomass, which then becomes the substrate for the production of hydrogen in closed tubular photobioreactors.

5.4 *Hybrid and Other Systems*

5.4.1 *Hybrid Systems*: Since no hybrid systems have yet been developed that give significant amounts of water splitting, this option is not viable at present.

5.4.2 *Photodegradation Systems*: By using solar energy to couple hydrogen evolution to the photodegradation of organic pollutants, value is added to the photodegradation process. The use of UV or solar light to destroy organic pollutants in contaminated waters is quite expensive, with treatment costs varying between $1 and $50 per kg of pollutant removed. If hydrogen could be evolved at the same time as organic pollutants are photodegraded, considerable value could be added to the process. This option has not been pursued very much in the literature, but, in my opinion, it deserves to be examined in considerable detail.

6. GENERAL COMMENTS AND VALUE-ADDED CONSIDERATIONS

Much has been made of the added value of hydrogen as a fuel [see books by Bockris (1976, 1980), Justi (1987), Ohta (1979) and Skelton (1984)] in terms of its favorable environmental aspects (no CO_2 emissions, no organic air pollutants, very little CO). There is little argument that a cheap method for generating hydrogen from water using solar energy would be highly desirable. The question to be answered here is: "Can solar photoproduction of hydrogen compete with other solar methods of generating hydrogen?". The competition is primarily in two technologies:

1. Solar thermochemical hydrogen generation reactions

2. Wind electricity plus electrolyzer

Many solar thermochemical hydrogen generation systems [see Sato (1979)] have been proposed; however, all are quite complex and none has shown potential for a practical economic system.

On the other hand, wind-generated electricity is already a significant component in the electrical capacity of some utilities (e.g., in California). To the extent that wind-generated electricity competes with photovoltaic generation, this option will be more or less economic than the photoproduction of hydrogen. At present wind-generated electricity is cheaper than photovoltaic-generated electricity; however, that picture may change in the future.

In my opinion, excessive stress on economics should be avoided when considering new technologies for hydrogen production, such as the photoproduction option. My approach would be to pick a few promising systems, set realistic development targets and then evaluate again in perhaps five years.

Finally, there is one other very important value-added factor in research on the solar photoproduction of hydrogen. This research area is exciting and environmentally meaningful. As a result, many bright scientists have been attracted to this field. The result has been not only steady progress in the direct goal of the solar photoproduction of hydrogen, but also considerable "spin-offs" in other applied areas. For example, advances in the development of photosensors, biosensors, microelectronics, molecular electronics, and the photodegradation of pollutants has been aided considerably by research initially conducted with a focus on solar photoconversion

processes. It is highly probable that many more spin-offs will accrue in the future through continued support of this research objective.

7. CONCLUSIONS AND RECOMMENDATIONS

It now remains for me to summarize with some conclusions and formulate some recommendations. The possibility of using cheap solar energy to generate hydrogen, a virtually non-polluting and extremely clean fuel, from water has been an exciting prospect for scientists and engineers for several decades. Although progress has been slower than many of us hoped, there are some systems that show sufficient promise to justify further investments in research and development. The four processes that in my opinion deserve further attention are:

1. PV Cells plus Electrolyzer
2. Photoelectrochemical Cells
3. Photobiological Systems
4. Photodegradation Systems

I believe that the other systems do not show enough promise to justify support from targeted programs. Many will continue to be developed through basic research programs, so they will not be totally neglected if my recommendations are followed.

My recommendations are as follows:

1. *Define and measure solar hydrogen conversion efficiencies as the ratio of the rate of generation of Gibbs energy of dry hydrogen gas (with appropriate corrections for any bias power) to the incident solar power (solar irradiance times the irradiated area).*

2. *Expand support for pilot-plant studies of the PV Cells plus Electrolyzer option with a view to improving the overall efficiency and long-term stability of the system. Consideration should be given, at an appropriate time, to a full-scale installation as part of a solar hydrogen based model community.*

3. *Accelerate support, at a more fundamental level, for the development of photo-electrochemical cells, with a view to improving efficiency, long-term performance and multi-cell systems for non-biased solar water splitting.*

4. *Maintain and increase support for fundamental photobiological research with the aim of improving long-term stability, increasing efficiencies and engineering genetic changes to allow operation at normal solar irradiances.*

5. *Initiate a research program to examine the feasibility of coupling hydrogen evolution to the photodegradation of waste or polluting organic substances.*

If implemented, I am convinced that these policies will see significant development in some practical solar hydrogen systems within the next decade. It will also provide the base for the advance of other options that should become viable in the 15-25 year time period.

ACKNOWLEDGMENTS

I am grateful for the assistance of Prof. David O. Hall, Prof. Sten-Eric Lindquist, Dr. Mihaela Stefan and Dr. John Turner for their critical analysis of the paper and to Prof. David O. Hall and Dr. Eli Greenbaum for their assistance in assembling material on photobiological processes.

REFERENCES

Archer MD, Bolton JR (1990) Requirements for ideal performance of photochemical and photovoltaic solar energy converters. J. Phys. Chem. 94: 8028-8036.

Balzani V, Moggi L, Manfrin MF, Bolletta F, Gleria M (1975) Solar energy conversion by water photodissociation. Science 189: 852-856.

Bard AJ, Fox MA (1995) Artificial photosynthesis: solar splitting of water to hydrogen and oxygen. Acc. Chem. Res. 28: 141-145.

Benemann JR (1994a) Feasibility analysis of photobiological hydrogen production. In: Proceedings of the 10th World Hydrogen Energy Conference, 20-24 June, Cocoa Beach, FL.

Benemann JR (1994b) Photobiological hydrogen production. In: Proceedings of the 29th Intersociety Energy Conversion Engineering Conference, 7-12 August, Monterey, CA.

Biddle JR, Peterson DB, Fujita T (1985) Solar photochemical process engineering for production of fuels and chemicals. Int. J. Hydrogen Energy 10: 633-643.

Bockris JO'M (1976) Energy: The solar hydrogen alternative, The Architectural Press, London, UK.

Bockris JO'M (1980) Energy options - real economics and the solar hydrogen system, Wiley, New York.

Bockris JO'M, Veziroglu TN, Smith D (1991) Solar hydrogen energy, Macdonald, London, UK.

Bolton JR (1978) Solar fuels. Science 202: 705-711.

Bolton JR (1989) Economics of solar energy conversion using a product value analysis. Chimia 43: 226-227.

Bolton JR, Hall DO (1979) Photochemical conversion and storage of solar energy. Ann. Rev. Energy 4: 353-401.

Bolton JR, Haught AF, Ross RT (1981) Photochemical energy storage: An analysis of limits. In: Connolly JS (Ed) Photochemical conversion and storage of solar energy, Academic, New York, pp 297-330.

Bolton JR, Strickler SJ, Connolly JS (1985) Limiting and realizable efficiencies of solar photolysis of water. Nature (London) 316: 495-500.

Borgarello E, Kiwi J, Pelizzetti E, Visca M, Grätzel M (1981a) Photochemical cleavage of water by photocatalysis. Nature (London) 289: 158-160.

Borgarello E, Kiwi J, Pelizzetti E, Visca M, Grätzel M (1981b) Sustained water cleavage by visible light. J. Am. Chem. Soc. 103: 6324-6329.

Brinner A, Bussmann H, Hug W, Seeger W (1992) Test results of the HYSOLAR 10 kW PV-electrolysis facility. Int. J. Hydrogen Energy 17: 187-197.

Calzaferri G (1993) Towards artificial photosynthesis: experiments with silver zeolites, Part 3. In: Tian ZW, Cao Y (Eds) Photochemical conversion and storage of solar energy, International Academic Publishers, Beijing, China, pp 141-157.

Cervera-March S, Smotkin ES (1991) A photoelectrode array system for hydrogen production from solar water splitting. Int. J. Hydrogen Energy 16: 243-247.

Dostrovsky I (1991) Chemical fuels from the sun. Sci. American Dec.: 102-107.

Fujishima AK, Honda K (1972) Electrochemical photolysis of water at a semiconductor electrode. Nature (London) 238: 37-38.

Gerischer H (1981) The principles of photoelectrochemical energy conversion. In: Cardon F, Gomes WP, Dekeyser W (Eds) Photovoltaic and photoelectrochemical solar energy conversion, Plenum, New York, pp 199-245.

Getoff N (1984) Basic problems of photochemical and photoelectrochemical hydrogen production from water. Int. J. Hydrogen Energy 9: 997-1004.

Getoff N (1990) Photoelectrochemical and photocatalytic methods of hydrogen production: a short review. Int. J. Hydrogen Energy 15: 407-417

Grätzel M (1981a) Artificial photosynthesis: water cleavage into hydrogen and oxygen by visible light. Acc. Chem. Res. 14: 376-384.

Grätzel M (1981b) Light-induced charge separation and water cleavage in microheterogeneous aqueous systems. Faraday Discuss. Chem. Soc. 70: 359-374.

Greenbaum E (1988a) Energetic efficiency of hydrogen photoevolution by algal water splitting. Biophys. J. 54: 365-368.

Greenbaum E (1988b) Hydrogen production by algal water splitting. In: Lembi CA, Waaland JR (Eds) Algae and human affairs, Cambridge University Press, Cambridge, UK, pp 284-304.

Greenbaum E, Lee JW, Tevault CW, Blankinship SL, Mets LJ (1995), CO_2 fixation and photoevolution of H_2 and O_2 in a mutant of *Chlamydomonas* lacking photosystem I. Nature (London) 376: 438-441.

Harriman A, West MA (Eds) (1982) Photogeneration of hydrogen, Academic, London, UK.

Heller A (1984) Hydrogen-evolving solar cells. Science 233: 1141-1148.

Justi EW (1987) A Solar hydrogen energy system, Plenum, New York.

Kalyanasundaram K (1982) Photophysics, photochemistry and solar energy conversion with tris(bipyridyl)ruthenium(II) and its analogues. Coord. Chem. Rev 46: 159-244.

Kalyanasundaram K (1987) Photochemistry in microheterogeneous systems, Academic, Orlando, FL.

Katakis DF, Mitsopoulou C, Konstantatos J, Vrachnou E, Falaras P (1992) Photocatalytic splitting of water. J. Photochem. Photobiol. A: Chem. 68: 375-388.

Katakis D, Mitsopoulou C, Vrachnou E (1994) Photocatalytic splitting of water: increase in conversion and energy storage efficiency. J. Photochem. Photobiol. A: Chem. 81: 103-106.

Lehman P, Parra C (1994) Hydrogen fuel from the sun. Solar Today, Sept./Oct.: 20-22.

Lehn J-M (1981) Photoinduced generation of hydrogen and oxygen from water. In: Connolly JS (Ed) Photochemical conversion and storage of solar energy, Academic, New York, pp 161-197.

Markov SA, Bazin MJ, Hall DO (1995) The potential of using cyanobacteria in photobioreactors for hydrogen production. In: Advances in Biochemical Engineering Biotechnology (in press).

McCree KJ (1981) Photosynthetically active radiation. In: Lange OL, Nobel PS, Osmond CB, Ziegler H (Eds) Physiological plant ecology, Vol. 12A of Encyclopedia of plant physiology, New Series, Springer-Verlag, Berlin, Germany, pp 41-55.

Nozik AJ (1981) Photoelectrochemical devices for solar energy conversion. In: Cardon F, Gomes WP, Dekeyser W (Eds) Photovoltaic and photoelectrochemical solar energy conversion, Plenum, New York, pp 263-312.

Nozik AJ (1984) Survey and prognosis for present and future approaches to hydrogen production. J. Less-Common Metals 103: 1-4.

Ohta T (Ed) (1979) Solar-hydrogen energy systems, Pergamon, Oxford, UK.

Parkinson B (1984) On the efficiency and stability of photoelectrochemical devices. Acc. Chem. Res. 17: 431-437.

Pearcy RW (1989) Radiation and light measurements. In: Pearcy RW, Ehleringer J, Mooney A, Riendel PW (Eds) Plant physiological ecology, Chapman and Hall, London, UK, pp 97-116.

Pleskov YV (1990) Solar energy conversion: a photoelectrochemical approach, Springer-Verlag, Berlin.

Sato S (1979) Thermochemical hydrogen production. In: Ohta T (Ed) Solar hydrogen energy systems, Pergamon, Oxford, UK, pp 81-114.

Serpone N, Lawless D, Terzian R (1992) Solar fuels: status and perspectives. Solar Energy 49: 221-234.

Skelton LW (1984) The solar hydrogen energy economy, Van Nostrand Reinhold, New York.

Smotkin E, Bard AJ, Campion A, Fox MA, Mallouk T, Webber SE, White JM (1986) Bipolar TiO_2/Pt semiconductor photoelectrodes and multielectrode arrays for unassisted photolytic water splitting. J. Phys. Chem. 90: 4604-4607.

Smotkin E, Bard AJ, Campion A, Fox MA, Mallouk T, Webber SE, White JM (1987) Bipolar CdSe/CoS semiconductor photoelectrode arrays for unassisted photolytic water splitting. J. Phys. Chem. 91: 6-8.

Szyszka A (1992) Demonstration plant, Neunburg vorm Wald, Germany, to investigate and test solar-hydrogen technology. Int. J. Hydrogen Energy 17: 485-498.

Vanhanen JP, Kauranen PS, Lund PD, Manninen LM (1994) Simulation of solar hydrogen energy systems. Solar Energy 53: 267-278.

Weber MF, Dignam MJ (1984) Efficiency of splitting water with semiconducting photoelectrodes. J. Electrochem. Soc. 131: 1258-1265.

Willner I, Steinberger-Willner B (1988) Solar hydrogen production through photobiological, photochemical and photoelectrochemical assemblies. Int. J. Hydrogen Energy 13: 593-604.

Winter C-J, Fuchs M. (1991) HYSOLAR and Solar-Wasserstoff-Bayern. Int. J. Hydrogen Energy 16: 723-734.

Zahed AH, Bashir MD, Alp TY, Najjar YSH (1991) A perspective of solar hydrogen and its utilization in Saudi Arabia. Int. J. Hydrogen Energy 16: 277-281.

GLOSSARY

A irradiated area (m^2)

$E°$ thermodynamic standard cell potential (V) for an electrochemical cell

E_{bias} bias voltage (V) applied to a photoelectrochemical cell

E_S total solar irradiance ($W\ m^{-2}$)

$E_S(\lambda)$ spectral irradiance ($W\ m^{-2}\ nm^{-1}$) at wavelength λ

I current (A) in a photoelectrochemical cell

J_g absorbed photon flux (photons $s^{-1}\ m^{-2}$) with $\lambda \leq \lambda_g$ (see eq. 2)

n stoichiometric number equal to the number of photons (assuming $\phi_{conv} = 1$) required to drive a photochemical storage reaction as written

P dry pressure of hydrogen

R gas constant ($L\ atm\ K^{-1}\ mol^{-1}$)

R_{H_2} rate ($mol\ s^{-1}$) of generation of hydrogen gas

R_P rate ($mol\ s^{-1}$) of generation of product P

T absolute temperature (K)

U energy (J)

U_g bandgap or threshold energy (J), that is, the minimum photon energy which will excite the system

U_{loss} energy (J) lost to heat when an excited state is converted to a product.

V volume (L) of hydrogen generated

V voltage (V) applied to an electrochemical cell under operating conditions

V_o open-circuit voltage (V) of a photovoltaic cell

ΔG_P^0 standard Gibbs energy (J mol^{-1}) for the energy-storage reaction generating product P

ΔS_{mix} entropy of mixing (J K^{-1} mol^{-1})

$\Delta\mu_{ex}$ chemical potential (or Gibbs energy per molecule) (J) of the excited state relative to the ground state, representing the maximum energy available to do work or to be stored as chemical energy

ϕ_{conv} conversion quantum yield, which represents the fraction of the excited states that go on to generate a product, rather than relax to the ground state

η_C energy storage efficiency (eq. 3 or 4), which represents the efficiency of conversion of light energy into the stored chemical energy of a chemical product

η_{chem} fraction of the excited state energy that is converted to stored chemical energy of a product (eq. 6)

η_g hypothetical (unattainable) efficiency (eq. 5), which represents the efficiency that would be obtained if the relaxed energy of the excited states could be converted to chemical or electrical energy

η_P limiting (or ideal) conversion efficiency (eq. 1), representing the maximum possible conversion efficiency for any photoconverter operating with a bandgap wavelength λ_g

η_Z efficiency of a water electrolysis cell

λ wavelength (nm)

λ_g bandgap or threshold wavelength (nm)

λ_{min} minimum wavelength at which a light source has a significant output

Table 1 Classification systems for solar water photolysis schemes[a]

Scheme classifi-cation	No. of photo-systems	n = Minimum no. of absorbed photons per H_2	Reaction
S1	1	1	$H_2O \xrightarrow{1\,h\nu} H_2 + 1/2\,O_2$
S2	1	2	$H_2O \xrightarrow{2\,h\nu} H_2 + 1/2\,O_2$
S4	1	4	$H_2O \xrightarrow{4\,h\nu} H_2 + 1/2\,O_2$
D2	2	2	$H_2O \xrightarrow{h\nu_1 + h\nu_2} H_2 + 1/2\,O_2$
D4	2	4	$H_2O \xrightarrow{2\,h\nu_1 + 2\,h\nu_2} H_2 + 1/2\,O_2$

a. Taken from Bolton et al. (1985).

Table 2 Solar conversion efficiencies and other related data for solar photolysis of water using global AM 1.5 solar radiation[a]

Scheme	Conditions	Ideal effic. η_p(%)	Chem. effic. η_C(%)	U_{loss} per photon (eV)	Threshold wavelengths (nm) λ_{th} or λ_1	λ_2
S1	Ideal limit	5.3	---	0.49	420	---
S2	Ideal limit	30.7	---	0.37	775	---
S2	Chemical conversion	---	23.5	0.60	680	---
S2	Chemical conversion	---	17.4	0.80	610	---
S2	Chemical conversion	---	12.7	1.00	555	---
S4	Ideal limit	30.6	---	0.31	1340	---
D2	Ideal limit	42.4	---	0.38[b]	655	930
D4	Ideal limit	41.0	---	0.31[b]	910	2610
D4	Chemical conversion	---	32.3	0.60	785	1465
D4	Chemical conversion	---	27.1	0.80	720	1120
D4	Chemical conversion	---	21.6	1.00	655	925

a. Taken from Bolton et al. (1985).
b. Average U_{loss} per absorbed photon.

Figure Captions

Figure 1 Efficiencies for conversion of solar radiation to stored Gibbs energy using single-bandgap devices. The full curve shows η_p, the ideal limiting efficiency. The vertical lines at 420, 775 and 1340 nm show the maximum threshold wavelengths for the water photolysis reaction (reaction 7) carried out by S1, S2 and S4 schemes, respectively, under ideal conditions. The descending curves through the dots show the changes in efficiencies and bandgap wavelengths for values of U_{loss} greater than the optimum; the numbers at the dots are the respective values of U_{loss} in eV per photon at those points. [Taken from Bolton et al. (1985)].

Figure 2. Minimal scheme for the photo-chemical splitting of water. *cat-red* is a catalyst capable of storing reducing equivalents, *cat-ox* is a catalyst capable of storing oxidizing equivalents and S is the photochemical sensitizer.

Figure 3. Scheme for the photochemical generation of hydrogen in a reduction half reaction.

Figure 4. Scheme for the photochemical generation of oxygen in an oxidation half reaction.

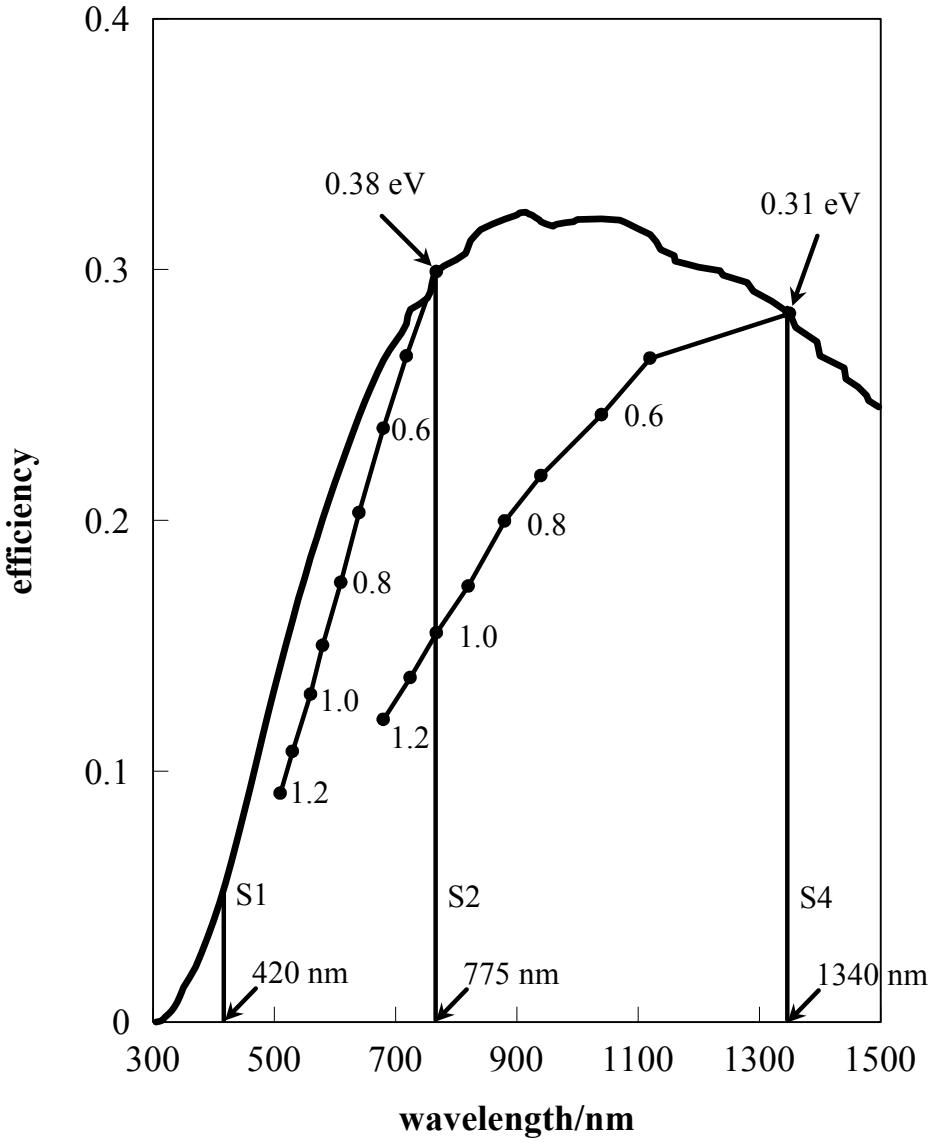
0.4
0.3
0.2
0.1
0
efficiency
0.38 eV
0.31 eV
0.6
0.8
1.0
1.2
0.6
0.8
1.0
1.2
S1
S2
S4
420 nm
775 nm
1340 nm
300
500
700
900
1100
1300
1500
wavelength/nm

Figure 1

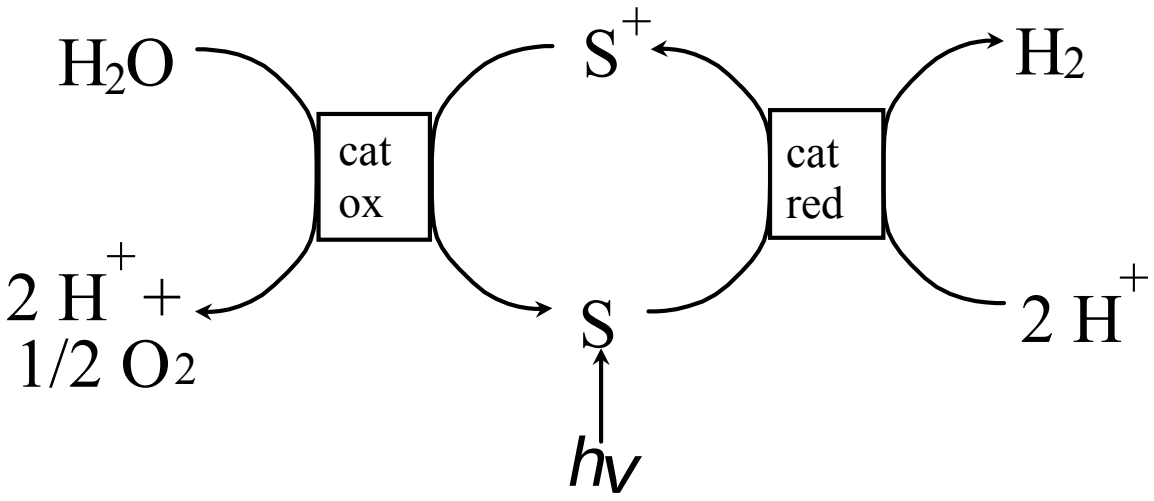

Figure 2

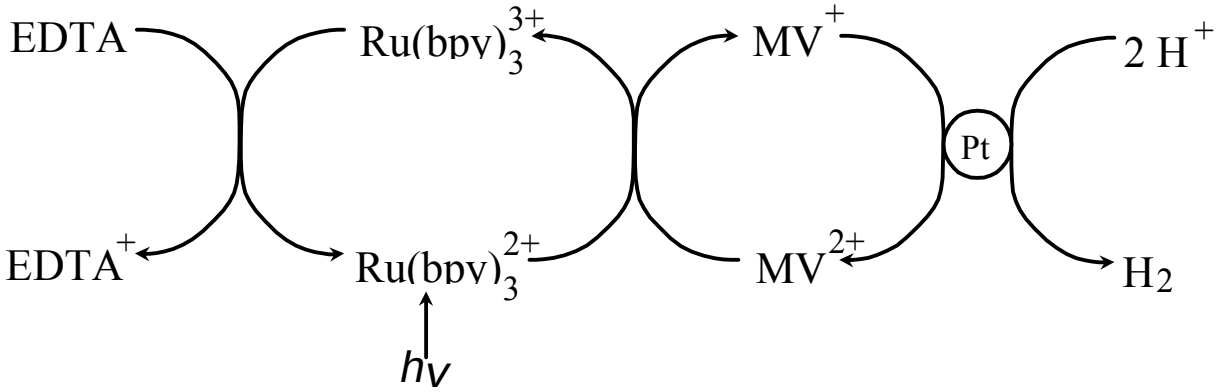

Figure 3

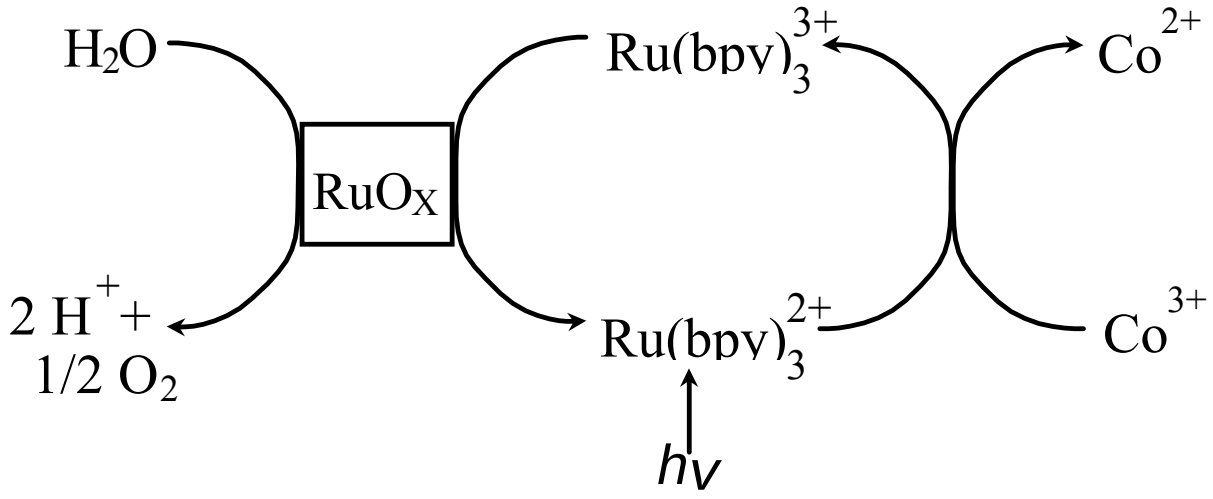

Figure 4

EXECUTIVE COMMITTEE

IEA HYDROGEN EXECUTIVE COMMITTEE ADDRESS LIST

Executive Committee Members

CANADA
Mr. N.R. Beck
Natural Resources Canada
580 Booth Street, 13th Floor
Ottawa, Ontario, KIA 0E4
Tel: 1 613 996 6022
Fax: 1 613 996 9416
email:
nick.beck@cc2smtp.nrcan.gc.ca

Alternate:
Mr. Andrew T.B. Stuart
The Electrolyser Corp. Ltd.
122 The West Mall, Etobicoke
Toronto, Ontario, M9C 1B9
Tel: 1 416 621 9410
Fax: 1 416 621 9830

EUROPEAN UNION
Dr. Abraham Bahbout (Vice-Chairman)
Joint Research Centre
Ispra Establishment
I-21020 Ispra (Va)
Tel: 39 332 78 9985
Fax: 39 332 78 9523

GERMANY
Dr. N. Stump
Forschungszentrum Jülich GmbH
BEO
D-52425 Jülich
Tel: 49 2461 61 47 44
Fax: 49 2461 61 28 40

Alternate:
Dr. Piotr Malinowski
Forschungszentrum Julich GmbH,
BEO
D-52425 Jülich
Tel: 49 2461 61 39 34
Fax: 49 2461 61 28 40

ITALY
Dr. Antonio Ciancia
ENEA - Advanced Energy Technologies
Branch
S.P. 83 - Via Anguillarese 301
00060 Rome
Tel: 39 6 30 48 43 09
Fax: 39 6 30 48 63 57

JAPAN
Mr. Katsuhiko Hayashi
New Sunshine Program Promotion HQ
AIST, MITI
1-3-1 Kasumigaseki
Chiyoda-ku
Tokyo 100
Tel: 81 3 3501 9287
Fax: 81 3 3501 9489

THE NETHERLANDS
Dr. Antoon Kipperman
NOVEM
P.O. Box 8242
NL-3503 RE Utrecht
Tel: 31 30 2 36 34 44
direct: 39 34 28
Fax: 31 30 2 31 64 91
email: nlnovtki@ibmmail.com

NORWAY
Mr. Trygve Riis
The Research Council of Norway
Box 2700 St. Hanshaugen
N 0131 Oslo
Tel: 47 2203 7347
Fax: 47 2203 7307
email: trygve.riis@nfr.no

Alternate:
Mr. Bjørn Gaudernack (see Operating Agents)

SPAIN
Dr. Antonio G. Garcia-Conde
INTA - Det. Sistemas de Energiea
Ctra. de Ajalvir Km 4
28850 Torrejon de Ardoz (Madrid)
Tel: 34 1 520 1478
Fax: 34 1 520 1614
email: glezgca@inta.es

Alternate:
Mr. Rafael Luque Berruezo
INTA - El Arenosillo
Ctra. Matalascañas, km.27.2
21130 Mazagón (Huelva)
Tel: 34 59 536097
Fax: 34 59 376294

SWEDEN
Dr. Wiktor Raldow
NUTEK
S-117 86 Stockholm
Tel: 46 8 681 9370
Fax: 46 8 681 9280

SWITZERLAND
Dr. Gerhard Schriber
Swiss Federal Office of Energy
Belpstrasse 36
CH-3003 Bern
Tel: 41 31 322 56 58
Fax: 41 31 382 44 03
email:
Gerhard.Schriber@Bew.admin.ch

Alternate:
Dr. Thomas H. Schucan
Paul Scherrer Institute
CH-5232 Villigen PSI
Tel: 41 56 310 27 43
Fax: 41 56 310 21 99
email: schucan@psi.ch

TURKEY
Dr. I.E. Türe
TUBITAK - Marmara Research Center
P.O. Box 21, Gebze
41470 Kocaeli
Tel: 90 262 641 2273
Fax: 90 262 641 2309

UNITED STATES
Mr. Neil P. Rossmeissl (Chairman)
U.S. Department of Energy
Forrestall Building (EE-142)
1000 Independence Ave. SW
Washington, DC 20585
Tel: 1 202 586 8668
Fax: 1 202 586 0784
email:
neil_rossmeissl.doe.hq.gov

Alternate:
Dr. Russell Eaton III
Golden Field Office
National Renewable Energy Laboratory
1617 Cole Blvd.
Golden, Colorado 80401
Tel: 1 303 275 4740
Fax: 1 303 275 2905

UNITED KINGDOM
Dr. David Hall
Division of Life Sciences
King's College London
University of London
Campden Hill Road
London W8 7AH, United Kingdom
Tel: 44 171 333 4317
Fax: 44 171 333 4500

Operating Agents

TASK 10
Mr. Bjørn Gaudernack
Institute for Energy Technology
P.O. Box 40
N-2007 Kjeller, Norway
Tel: 47 63 80 6179
Fax: 47 63 81 2905

TASK 11
Ms. Catherine E. Gregoire Padró
Hydrogen Program Manager
National Renewable Energy Laboratory
1617 Cole Blvd.
Golden, Colorado 80401-3393, USA
Tel: 1 303 275 2919
Fax: 1 303 275 2905
email:
gregoire@tcplink.nrel.gov

TASK 12
Mr. William Hoagland
W. Hoagland & Associates, Inc.
7467 Spy Glass Ct.
Boulder, Colorado 80301, USA
Tel: 1 303 530 1140
Fax: 1 303 530 1385
e-mail:
hoaglanb@tcplink.nrel.gov

ExCo Secretariat

Ms. Carolyn C. Elam
National Renewable Energy Laboratory
1617 Cole Blvd.
Golden, Colorado 80401-3393, USA
Tel: 1 303 275 3780
Fax: 1 303 275 2905
e-mail: elamc@tcplink.nrel.gov

IEA Secretariat/Paris

Mr. Takashi Okano
International Energy Agency
Energy Technology Policy Division
2, rue André-Pascal
75775 Paris CEDEX 16, France
Tel: 33 1 45 24 98 93
Fax: 33 1 45 24 94 75