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TECHNOLOGIES and PROSPECTS FOR PHOTOCHEMICAL CONVERSION AND STORAGE OF SOLAR ENERGY

A survey of the state-of-the-art

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Abstract

Sustainable and renewable generation of energy/electricity by photovoltaic systems or wind energy systems suffer from the mismatch of supply and demand of energy. Storage of energy is often necessary for these systems to become a competing technology for the conventional energy generation. One way to overcome the problem of storage is the development of photochemical systems that use sunlight (photons) directly to drive reversible chemical reactions leading to products that can be used for energy storage.

The present study contains a survey of the state-of-the-art of photochemical conversion and storage of solar energy and the prospects for future application of this technology.

At present, the best systems for photochemical conversion and storage of sunlight are still in the early R&D stage. Most research in this area is directed towards the production of hydrogen as a fuel that could be applied in the future ‘hydrogen energy society’.

Large-scale commercial application of photochemical production of fuel is not to be expected on the short-term and only in niches of the energy market on the long term. The clear advantage of the conversion of sunlight into chemicals is the flexibility it gives to cope with mismatch between supply and demand of solar energy as regard to time and power/capacity.

Much work on the components of photoelectrochemical devices is required to improve the bandgap matching of the applied semiconductors with the desired reactions, to shift the absorption of photons to higher wavelengths in order to use a larger part of the solar energy spectrum, to reduce (photo)corrosion problems of the semiconducting materials and to improve their stability, as well as to improve the performances of the catalysts. Further improvements should be achieved by simple and efficient cell and system design.

The economy of photoelectrochemical conversion processes is expected to be in the range of PV/electrolysis.

Keywords: Photochemical conversion, energy storage, solar energy, survey, prospects.

CONTENTS

SUMMARY

Sustainable and renewable generation of energy/electricity by photovoltaic systems or wind energy systems suffer from the mismatch of supply and demand of energy. Storage of energy is often necessary for these systems to become a competing technology for the conventional energy generation. One way to solve the problem of energy storage is the development of photochemical conversion systems that use sunlight (photons) directly to drive uphill chemical reactions. This leads to a conversion of sunlight into fuels that can be stored for later use.

The present study describes the state-of-the-art of photoelectrochemical conversion and storage of solar energy. Since 1970, work on solar photoelectrochemical processes has led to a good knowledge of the primary processes in the solar to fuel conversion. Nevertheless, the photoelectrochemical conversion systems are still in the early stage of development. Generation of hydrogen from water and sunlight is the target for many developments, and some systems under development aim at the photochemical reduction of carbon dioxide leading to hydrocarbon fuels. Even though the lab-scale systems that are based on semiconducting materials show promising results, the solar to fuel conversion efficiency of the processes is low. The efficiencies of the processes suffer from the very limited utilisation of the total solar spectrum. The best solar to fuel conversion efficiency thus far (12%) is obtained by a tandem cell, which absorbs a larger part of the solar spectrum in two different semiconducting materials.

Future application of photoelectrochemical conversion systems for energy supply, requires the availability of materials that can absorb a large part of the solar spectrum, that are stable in their environment, and having band-gaps that match with the chemical reactions of interest. Also the performance of the catalysts needs to be increased. Since these problems are still very fundamental, much work needs to be done to improve the performance. Large-scale commercial application of these systems is not to be expected within 10 years.

Progress in other fields of photochemical processes can however be beneficial for the solar production of fuel. These fields are the developments of dye-sensitised solar cells, and the development of photochemical detoxification processes. A substantial cost reduction of silicon based PV-cells can also be beneficial for the silicon based photochemical systems as well as the further development of techniques for hydrogen storage.

SAMENVATTING

Opwekking van energie op basis van duurzame bronnen, zoals de opwekking van elektriciteit via windturbines of zonnecellen, heeft als nadeel dat het tijdstip en de hoeveelheid van aanbod en vraag veelal niet overeenstemmen. De mogelijkheid om het aanbod van energie te kunnen opslaan voor gebruik op een later tijdstip is van cruciaal belang voor het vergroten van de toepassingsmogelijkheden van duurzame energie. Een aantrekkelijke manier om opslag van duurzame energie te realiseren is het gebruik van de photonen van het zonlicht om een chemische reactie te laten verlopen die leidt tot de vorming van een brandstof. Op deze wijze wordt zonlicht omgezet in chemische bindingsenergie die kan worden opgeslagen.

In deze studie wordt een beschrijving gegeven van de huidige status van photo-elektrochemische conversie en opslag van zonne-energie. Sinds het begin van de zeventiger jaren is er onderzoek en ontwikkeling gedaan op dit gebied, dat heeft geleid tot een goed begrip van de fundamentele processen die een rol spelen bij de photo-elektrochemische omzetting van (zon)licht in chemische bindingsenergie. Desondanks bevinden de systemen voor omzetting van zonlicht in brandstof zich nog in een vroeg stadium van ontwikkeling. De photochemische productie van waterstof uit zonlicht en water is in veel ontwikkelingen het ultieme doel, maar ook het maken van koolwaterstoffen uit zonlicht, water en kooldioxide wordt onderzocht. De huidige systemen voor deze conversie zijn gebaseerd op halfgeleider materialen en bevinden zich nog op laboratorium schaal. De behaalde rendementen van omzetting van zonlicht in brandstof zijn nog laag. Een belangrijk probleem is dat slechts een beperkt deel van het spectrum van het zonlicht kan worden benut voor de photochemische omzetting. Het hoogste rendement dat is behaald bedraagt 12%. Hiervoor is gebruik gemaakt van een tandem-cel op basis van twee verschillende halfgeleider materialen die elk een deel van het spectrum van het zonlicht benutten.

Om photochemische conversie technieken in de toekomst te kunnen toepassen in de energievoorziening moeten er een aantal problemen van fundamenteel karakter worden opgelost. Het gaat daarbij om het beschikbaar krijgen van een materiaal waarmee een groot deel van het spectrum van zonlicht kan worden geabsorbeerd, een materiaal dat bovendien stabiel is in het toegepaste milieu, en met een bandgap die aansluit bij de gewenste chemische reactie. Daarnaast moet de prestatie van de toegepaste katalysatoren verder verbeterd worden. Nog zeer veel onderzoek is noodzakelijk om de prestaties van de photochemische omzetting op een niveau te krijgen dat commerciële toepassing in zicht komt. Op een termijn van tien jaar is dit niet te verwachten.

De ontwikkeling van de technologie voor de photochemische omzetting van zonlicht in brandstof kan wel profiteren van vooruitgang die wordt geboekt op andere photochemische onderzoeksgebieden. Het gaat daarbij om ontwikkeling op het gebied van kleurstof gesensibiliseerde zonnecellen en om de verdere ontwikkeling van technologie voor het photochemisch reinigen van afvalstromen. Daarnaast kan een reductie in de kosten voor silicium zonnecellen ook gunstig doorwerken in de kosten voor photoelektrochemische systemen op basis van silicium. Ook de verbetering van technologieën voor waterstofopslag draagt positief bij aan de toepasbaarheid van photochemische conversietechnieken.

1. INTRODUCTION

1.1 Use of Solar Energy

Global warming, environmental pollution, and impending shortage of fossil fuel sources are factors that force modern society towards an increase in the utilisation of renewable sources of energy (Steinfeld). Two of the most abundant resources on the surface of the earth are sunlight and water. Sunlight reaches the earth in a quantity that is sufficient to supply the total global energy consumption. (Funken)

The use of solar energy however has several intrinsic drawbacks:
- It is dilute (low power density of an average 1 kW /m2).
- It is intermittent (available during daytime) and can vary largely between summer and winter periods.
- It is unequally distributed over the earth's surface.

To overcome these drawbacks of solar energy, it must be converted into a form of energy that can attain high energy densities and that can be easily stored for long periods of time and can be transported to the place of energy demand.

In general, energy demand is also strongly fluctuating with time leading to a profound mismatch in supply of solar energy and demand for energy. Thus storage of solar energy is a decisive factor in the utilisation of this renewable energy source.

Recently, a study into the opportunities of thermochemical and photochemical solar energy storage was conducted at TNO (Schut). Several systems based on thermochemical and photochemical reactions were analysed on a thermodynamic basis. One of the conclusions concerning photochemical reactions was that the formation of a fuel from sunlight is a very attractive option due to its storage possibilities and the high quality of the energy a fuel can deliver. This fuel can be hydrogen produced directly from water, or hydrocarbons derived from hydrogen and a source of carbon e.g. carbon dioxide.

Ongoing R&D programs in the field of photochemical conversion of solar energy

The production of hydrogen from the decomposition of water using solar energy as the driving force has been a goal of scientist and engineers since the early 1970s. In that period Fujishima and Honda (Fujishima) reported the evolution of hydrogen and oxygen in a photoelectrochemical cell (PEC cell) illuminated with near UV light (Bolton, 1996). In the same period (1974) also the still continuing series of international conferences on *Photochemical Conversion and Storage of Solar Energy* (IPS) started. The subjects of these conferences cover a broad range of topics from biological photosynthesis to semiconductor systems. A comprehensive survey of the R&D topics of the IPS conferences IPS-0 to IPS-10 has been written by Bolton (Bolton, 1995).

The production of hydrogen using renewable sources is an integral part of the 'Hydrogen program' of the Department of Energy, DOE, of the USA (DOE). In this program the whole energy chain for hydrogen, from production, storage, distribution to utilisation is considered. The DOE co-ordinates and sponsors the research done on all these subjects, and publishes proceedings of this program every year. Within this program R&D is performed on several technologies for the production of hydrogen, whether renewable or not.

The International Energy Agency, IEA, is closely involved in this Hydrogen program of the DOE (IEA). The IEA has within the cluster of 'Renewable Energy' two implementing agreements, 'Hydrogen' and 'Solar Power and Chemical Energy Systems', SolarPACES,

[solarpaces] that cover R&D on the conversion of solar energy into fuel. Within the IEA Hydrogen program Annex 10 called 'photoproduction of hydrogen' started in 1995 illustrating the special interest in this subject (Gaudernack). This annex 10 was followed in 1999 by a new task, Annex 14, 'Photoelectrolytic production of hydrogen' which activity is devoted to advance the fundamental and applied science of photoelectrolysis of water (DOE).

1.2 Conversion and storage of sunlight

The conversion processes for solar energy into useful energy forms can generally be divided into:

- thermal processes,
- photonic processes.

Solar Thermal processes

In solar thermal processes the solar energy is first converted to heat, which can either be used directly, or stored in a thermal medium or converted to mechanical or electrical energy using an appropriate machine. Solar thermal processes can be divided in *low temperature* applications, generally based on flat plate collector systems, and *high temperature* applications, where the sunlight is used in a concentrated form by using parabolic mirrors. Temperatures up to 2000°C can be reached in this manner.

An example of a solar thermal application in the *low* temperature range is domestic water heating systems, where solar heat is converted to sensible heat of the water. In this application the storage density is limited as well as storage time.

An example of a *high* temperature application is the solar production of steam in parabolic through power plant, operated in California (Solarpaces). Other possible applications are thermochemical cycles that use high temperatures to drive a chemical reaction in one direction to store solar thermal energy. The stored energy can be released at times of energy demand by letting the reaction proceed in the reverse direction. In this context several thermochemical reactions are being investigated at research institutions. Examples are the Zn/ZnO-H_2O cycle where solar thermal energy is used for producing hydrogen (Steinfeld) and the synthesis and decomposition of NH_3 using solar thermal energy (Lovegrove).

Solar Photonic processes

In solar photonic processes the photons of sunlight are used as the driving force in the conversion process (Bolton, 1996). The use of photons of the sunlight is possible in several ways:

- photochemical processes,
- semiconductor systems,
- photobiological processes.

In *photochemical* processes sunlight is absorbed in isolated molecules, being reactants or catalysts, in solution. The molecule absorbs a photon and reaches its excited state. The energy of excitation is than transferred to electrons that are necessary to drive a chemical reaction.

In *semiconductor* systems the sunlight is absorbed in a semiconductor material. The absorption of a photon results in the transfer of an electron from its valence band to its conduction band. This electron can be used to drive a chemical reaction. The semiconductor can be in the form of a small particle suspended in a liquid or in the form of a film deposited on a support, built into a macroscopic unit like a photovoltaic cell or an electrochemical cell.

Photobiological processes are based on absorption of photons by a leaf chloroplast or algae. Photosynthetic organisms use photons of the sunlight for an energy storing reaction. Energy storage is based on the reduction of carbon dioxide to form carbohydrates. It is possible to modify conditions in these systems such that the photosynthetic process is coupled to a hydrogen-generating enzyme.

1.3 Scope of this study

As pointed out in the previous section, several options are available for the utilisation of solar energy. For effective use of solar energy, the storage of it is necessary to overcome the mismatch in supply and demand of this renewable source of energy. In a previous study at TNO (Schut) it was found that the photochemical conversion of solar energy into high-grade chemical energy is very attractive. In this way solar energy is converted into a fuel that can store energy in a very condensed manner and can be used at any time to produce high-grade energy.

The present study is focused on the solar photonic processes. It deals with the photochemical conversion and storage of solar energy. Within this study two different conversion technologies are considered:

- photochemical processes,
- photoelectrochemical systems based on semiconductor materials.

These systems have the possibility to transform solar energy directly into chemical energy. These systems sometimes are referred to as ‘Artificial trees’ or ‘Artificial leafs’ (Grätzel), since the net effect of these systems is the production of a fuel (hydrogen, hydrocarbons or carbohydrates) using sunlight, water and carbon dioxide as input.

Excluded from the present study are photobiological processes and photovoltaic devices. The production of hydrogen by photovoltaic systems combined with water electrolysis is used in the present study to serve as a reference case for the economic evaluation of the photochemical and semiconductor systems that are developed.

Since photochemical conversion of solar energy appears to be in the early stage of development questions that should be answered in this study are:

- What is the state-of-the-art of the technology?
- What are the conversion efficiencies?
- What are the prospects?

In a separate study, conducted by TNO, the aspects of incorporation of the systems for solar photochemical fuel production, storage and utilisation in the built environment are explored.

1.3.1 The approach

To obtain an overview of the present status of the photochemical conversion of solar energy a limited literature search has been conducted. Especially recent review articles on the present subject have been gathered.

The Internet has served as a quick source of information when looking for more details on some interesting systems. It was, however, striking to find many hits in the field of photochemical conversion of solar energy, that lead to publications of research into very fundamental aspects of photochemical systems. Little information was found dealing with complete systems for conversion of solar to chemical energy. This illustrates the early stage of development these systems are still in, despite many years of research. Obviously many fundamental aspects still need to be investigated in this area. A list of institutions working in the field of photochemical conversion of solar energy and their Internet addresses are given in the appendix.

Also experts involved in the photochemical conversion and storage of solar energy are consulted for their view on this subject. These are experts at the Netherlands Energy Research Foundation, ECN, (Z.S. Rak, S. Spoelstra,) at the Deutsches Zentrum fur Luft und Raumfahrt, DLR (K.H. Funken), the California Institute of Technology, CalTech (N.S. Lewis), the National Renewable Energy Laboratory, NREL, (J.A. Turner), and Brookhaven National Laboratory, BNL (E. Fujita).

2. PHOTOCHEMICAL CONVERSION OF SOLAR ENERGY

In this chapter the theoretical background of photochemical conversion processes is described shortly, starting with the primary photophysical processes. These form the basis of the photochemical conversion techniques that are described in section 2.2 and in section 2.3. In the last section the theoretical efficiencies of photochemical conversion processes are described.

2.1 Primary photophysical processes

The energy E (in joules) of a single photon is given by the Planck equation (Pförtner)

$$E = h\nu = \frac{hc}{\lambda}$$

where h is Planck's constant (6.6265×10^{-34} J·s), ν the frequency of radiation (s^{-1}), c the velocity of light (2.9979×10^{8} m/s), and λ the wavelength (m). One mole of photons is also defined as one Einstein. Usually the energies transferred in photochemical reactions exceed the typical activation energies of thermal reactions and also the dissociation energies of chemical bonds (Table 2.1).

Table 2.1 *Photon energies at different wavelengths compared with dissociation energies of elected single bonds*

Wavelength, nm	*Energy, kJ/einstein*	*Single bond*	*Dissociation energy, kJ/mol*
200	598.2	HO – H	498
250	478.6	H – Cl	432
300	398.8	H – Br	366
350	341.8	Ph – Br	332
400	299.1	H – I	299
450	265.9	Cl – Cl	240
500	239.3	Me – I	235
550	217.5	HO – OH	213
600	199.4	Br – Br	193
650	184.1	$Me_2N – NMe_2$	180
700	170.9	I – I	151

When a system is irradiated, the light may be transmitted, scattered, refracted, or absorbed. The first law of photochemistry, states that only light, which is absorbed by a molecule, is effective in producing a reaction, which changes the molecule. This implies that there must be some overlap between the range of wavelengths of the light entering the system and those absorbed by the starting material.

A universal integral quantum yield φ defines the number of events, which occur per photon absorbed by the system

$$\varphi = \frac{\text{number of events}}{\text{number of photons absorbed}}$$

In this generalized form, φ can be used to describe photo-excitation and physical deactivation processes of a typical organic molecule, as shown in the Figure 2.1.

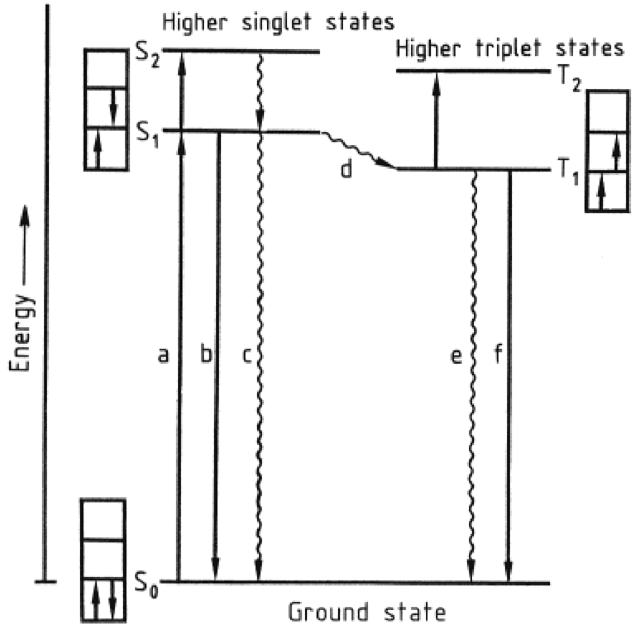

Figure 2.1 *Modified Jablonski diagram of the energy levels for a typical organic molecule. Vibrational levels are omitted for clearness. (Pförtner). The transitions a to f are defined as follows (the lifetime in s is given in parentheses) :*
a) Excitation of ground state to first level excited state $S_o + h\nu \rightarrow S_1$ *(*10^{-15}*) ; b) Internal conversion (IC)* $S_1 \rightarrow S_o + \Delta$ *(*$10^{-9} - 10^{-7}$*) ; c) Fluorescent emission (F)* $S_1 \rightarrow S_o + h\nu_F$ *(*$10^{-11} - 10^{-6}$*) ; d) Intersystem crossing [ISC(S)]* $S_1 \rightarrow T_1 + \Delta$ *(*$10^{-11} - 10^{-8}$*) ; e) Phosphorescent emission (P)* $T_1 \rightarrow S_o + h\nu_P$ *(*$10^{-3} - 10^{+2}$*) ; f) Intersystem crossing [ISC(T)]* $T_1 \rightarrow S_o + \Delta$ *(*$10^{-3} - 10^{+2}$*) (Pförtner)*

Any photochemical conversion process requires as an initial step the absorption of photon energy and conversion into internal energy of the first excited state of the molecule or material.

2.2 Photochemical systems

For a photochemical system to be able to absorb sunlight and convert it into a high-grade energy carrier that can be easily stored for later use, the energy of excitation needs to be transferred to electrons. These electrons are necessary to drive the chemical reactions. The following three consecutive steps are necessary, illustrated for the photochemical water splitting reaction:

- Visible light absorption.
- Conversion of excitation energy to redox energy.
- Concerted transfer of electrons to water molecules leading to the formation of H_2 energy storage compound and/or the formation of O_2.

For the production of hydrogen and oxygen from water the reactions below are involved

$2H_2O + 2e- \rightarrow H_2 + 2OH^-$, E°= - 0.41 V versus NHE (normal hydrogen electrode)
$2H_2O + 4e- \rightarrow O_2 + 4H^+ 4e-$, E°= + 0.82 V versus NHE

The energy of 1.23 eV per electron transferred corresponds to a wavelength of λ=1008 nm. However water does only absorb solar radiation in the infrared where photon energies are too low to drive the photochemical splitting of water. Thus any photochemical process to drive this reaction must involve a sensitizer, that is a molecule or semiconductor that can absorb sunlight and which ultimately leads to the generation of hydrogen.

The absorption of a single photon by a photosensitizer usually causes the transfer of one electron. Since the above reactions are multi-electron processes, catalysts for the storage of electrochemical equivalents are required.

In first approach photochemical systems for water splitting reaction, involving several compounds were proposed. In these systems each function is fulfilled by one molecule. This gives systems consisting of:

- A photosensitizer (PS) able to absorb visible light to generate excited species with useful redox properties.
- A compound R which can be reduced or oxidized by quenching of the excited species, and
- A third component (catalyst) able to collect several electrons and transfer them to the reacting species (water).

In practice difficulties arise from recombination of charge pairs in so-called back electron transfer (e.g. between PS^+ and R^-) leading to charge separation for only short lifetimes. In the case of multimolecular systems this back reaction is prevented by the use of a fourth compound, an electron donor, D. This donor reacts with the quenched photosensitizer to return it in its original state.

A schematic representation of such a photochemical system is given below in Figure 2.2

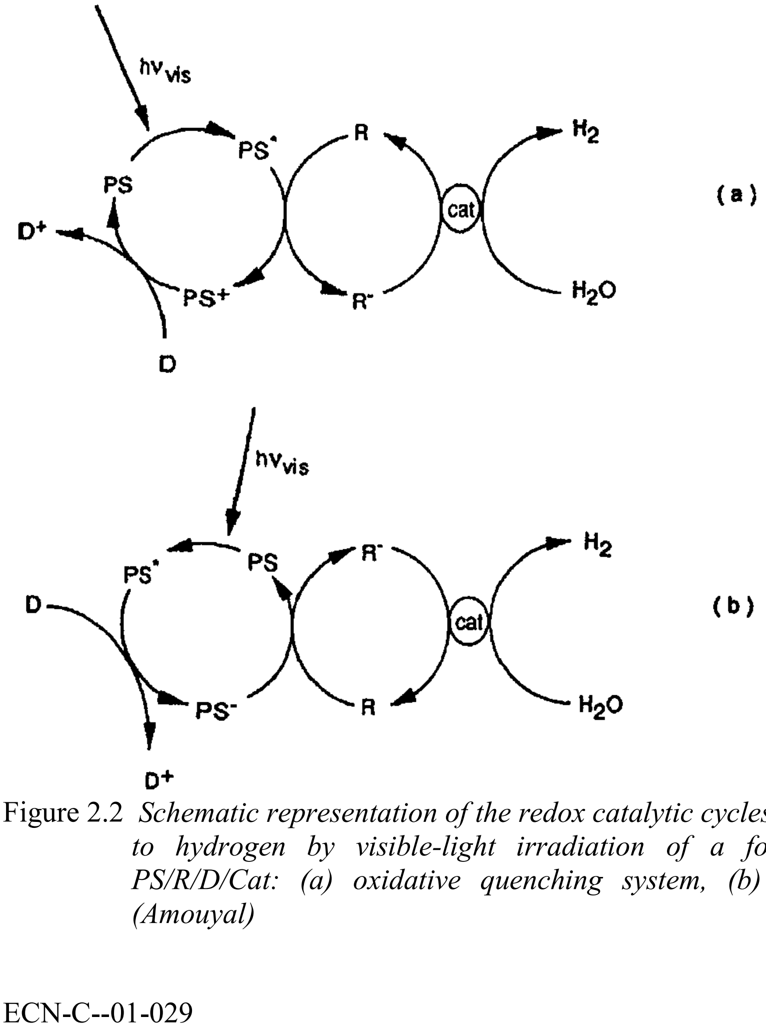

Figure 2.2 *Schematic representation of the redox catalytic cycles in the photoreduction of water to hydrogen by visible-light irradiation of a four component model system PS/R/D/Cat: (a) oxidative quenching system, (b) reductive quenching system. (Amouyal)*

2.3 Semiconductor systems

Semiconductor systems differ from photochemical systems in the sense that sunlight is absorbed by a semiconductor material, and creates excess electrons in the conduction band and excess holes in the valence band. If this semiconductor contains a junction (e.g. a p-n) junction the chemical potential of the excess carriers can be converted into electricity, as is done in photovoltaic cells.

Alternatively the excess electrons and/or holes can undergo chemical reactions at the surface of the semiconductor to produce chemicals that can store the photon energy, like hydrogen gas produced from water. These reactions can be done either in a photoelectrochemical cell or in a suspension of semiconductor particles.

The only difference between a photoelectrochemical and a photovoltaic device is that in photoelectrochemistry (PEC), a semiconductor – electrolyte junction is used as the active layer instead of the solid-state junctions in photovoltaics. In both cases, a space charge region is formed where contact formation compensates the electrochemical potential differences of electrons on both sides of the contact, Figure 2.3. The position of the band edges of the semiconductor at the interface can be assumed in a first approximation to be dependent only on the pH of the solution and independent of the potential (Fermi level) of the electrode or the electrolyte. Hence, upon illumination, *electrons in the conduction band* of the semiconductor reach the electrode surface and can reduce redox couples whose redox potentials are located *below* the conduction band (i.e., their electrochemical potential *U* is more positive). *Holes in the valence band* can oxidize species with a redox potential more negative than (i.e., *above*) the band edge of the valence band at the interface.

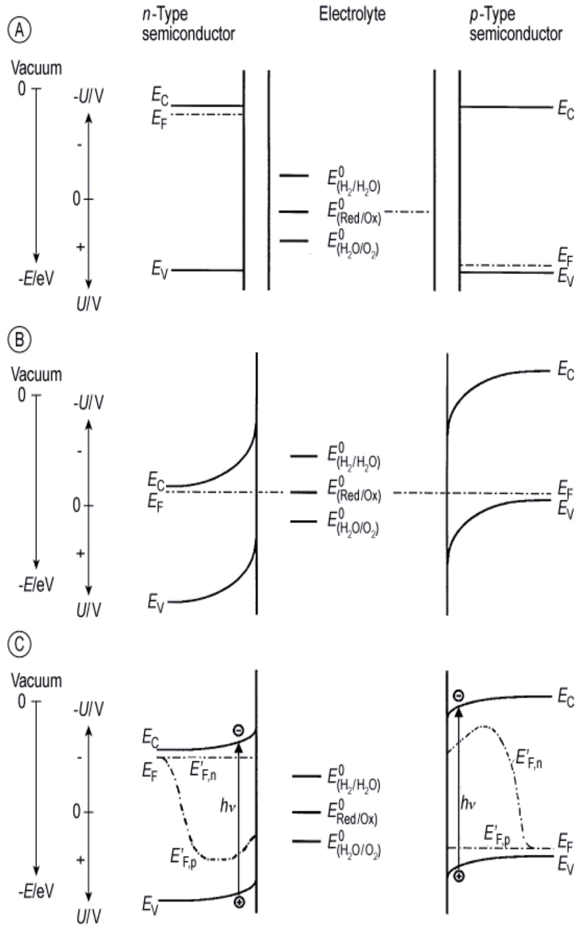

Figure 2.3 *Formation and use of a depletion layer and its electric field when a semiconductor connects to an electrolyte (Meissner).*

E = electron potential; – E = electron energy with respect to the vacuum level; E_C *= lower conduction band edge;* E_V *= upper valence band edge;* E_F *= Fermi level;* $E'_{F,n}$ *and* $E'_{F,p}$ *= quasi Fermi levels of electrons and holes, respectively, under illumination (hν);* E^0 *= standard redox potentials of the redox couples indicated.*

A) n- and p-type semiconductor of the same kind before contacting the electrolyte; B) Equilibrium situation in the dark with both semiconductors forming a space charge layer at the surface compensating the chemical potential difference of electrons in the three materials; C) Photovoltage formation (splitting of the quasi Fermi levels $E'_{F,n}$ *and* $E'_{F,p}$*) under illumination enabling direct water splitting.*

Using these principles two types of photoelectrochemical cells (PEC cells) can be built. If the redox system oxidised at one electrode is reduced (regenerated) at the counter electrode, the *regenerative PEC cell* can convert light energy into *electrical energy*. This is shown in Figure 2.4.

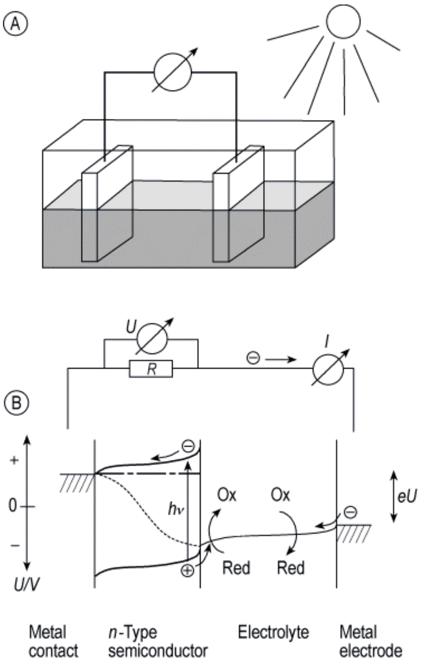

Figure 2.4 *Regenerative photoelectrochemical (PEC) solar cell (Meissner).*
A) Principal setup; B) Electron energy diagram for an n-semiconductor – electrolyte – metal configuration.

If, however, the two half cells are separated, e.g., by an ion exchange membrane, two different reactions can be used to store *chemical energy* directly, see Figure 2.5.

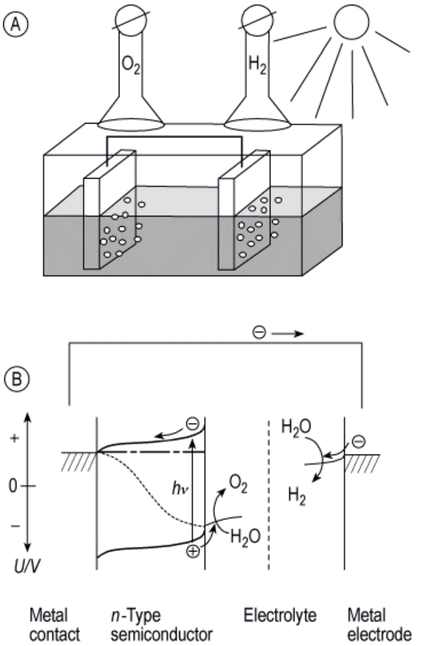

Figure 2.5 *Direct solar water splitting using semiconductor electrodes (Meissner).*
A) Principal setup; B) Electron energy diagram for an n-semiconductor – electrolyte – metal configuration.

A light-absorbing semiconductor is either the anode or cathode (or both) in an electrochemical cell. A famous example in this respect is the cell of Fujishima and Honda (Fujishima), where a single TiO_2 crystal acted as the photoanode at which oxygen was evolved. The electrons released from the anode travelled through a wire to a Pt electrode at which hydrogen was evolved.

In addition a small bias voltage can be applied over the electrodes to increase the potential difference between them and enhance the chemical reaction.

In another approach the semiconductor particles are suspended as tiny particles in a solvent, usually an aqueous solution. Here the semiconductor system operates much like the reduction half reaction of the photochemical system where the semiconductor particle replaces the molecular absorber. Excess conduction band electrons reduce the electron relay and excess holes oxidize the (sometimes sacrifacial) donor.

Figure 2.6 illustrates the processes in a microheterogeneous system of colloidal semiconductor particles. Locally separated catalysts of e.g. platinum and ruthenium dioxide are deposited on the surface of the semiconductor to promote the formation of hydrogen and oxygen. For particles of large band-gap semiconductors a sensitisation mechanism is required. The sensitizer can by light excitiation inject an electron into the conduction band of the semiconductor, followed by the redox reactions leading to water decomposition.
In such a microheterogeneous systems hydrogen and oxygen are produced in the same compartment. Therefore measures need to be taken to separate both reaction products and to avoid explosion hazards.

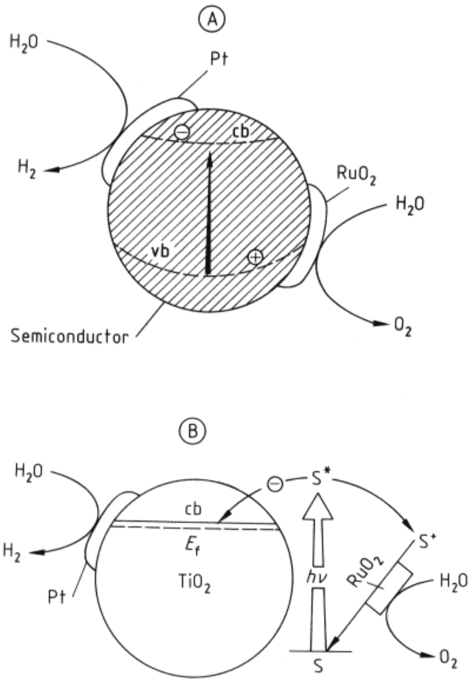

Figure 2.6 *Schematic representation of a colloidal semiconductor particle in a microheterogeneous system. (Häussinger).*
A: catalytic water cleavage through bandgap excitation of colloidal semiconductors B: Complete water photolysis scheme through sensitisation of a semiconductor particle (vb = valence band ; cb = conduction band, E_F *= Fermi energy).*

2.4 Efficiencies of photochemical conversions

As with any energy conversion process, the efficiency of a solar photochemical conversion process is of much importance, since it is directly connected with the costs of the process. Solar photonic processes are limited by fundamental considerations associated with band-gap excitation (Bolton, 1996). All solar photonic processes involve excitation of an absorber from the ground state to an excited state. This absorber can be an isolated molecule or a semiconductor. A characteristic of the absorber is the threshold energy or bandgap energy, U_g, which is usually calculated from the wavelength λ_g by $U_g = hc/\lambda_g$, with h is Planck's constant and c the speed of light.

There exist *four* unavoidable energy losses in any solar photonic conversion:

1. Photons with $\lambda > \lambda_g$ are unable to transfer the semiconductor or photosensitizer from its ground state to the excited state. These photons are lost to the conversion process.
2. Photons with $\lambda \leq \lambda_g$ can be absorbed but the excess energy of the photons with wavelengths shorter than the threshold wavelength is lost as heat when the absorber 'relaxes' to the level U_g.
3. The energy of the excited state is thermodynamically 'internal energy' and not Gibbs energy. Therefore only a fraction of this internal energy can actually be converted into useful work (e.g. electrical energy) or stored as chemical energy. This fraction is about 75%. This loss factor shows up as a (part of) the necessary over-potential.
4. The last loss factor is the loss of excited state energy due to spontaneous emission, fluorescence of the absorber. This loss factor is only 1-2%.

The efficiency expression for any solar photonic system thus becomes:

$$\eta_p = \frac{J_g \Delta\mu_{ex} \phi_{conv}}{E_s}$$

where J_g is the absorbed photon flux (photons s^{-1} m^{-2}) with $\lambda \leq \lambda_g$, $\Delta\mu_{ex}$ is the Gibbs energy of the excited state (J) and Φ_{conv} is the quantum yield. E_s is the total incoming solar irradiance (J s^{-1} m^{-2}).

The efficiency for conversion of solar photon energy to chemical energy is defined as:

$$\eta_c = \frac{\Delta G_p^o R_p}{E_s A}$$

ΔG_p^o (J mol^{-1}) is the standard Gibbs energy for the chemical reaction forming the product(s) P, R_p (mol s^{-1}) the rate at which the products are formed, and A the irradiated area.

The above considerations are based on a single photosystem with one band-gap. One way to increase the theoretical efficiency is the coupling of two photosystems (a photoanode and a photocathode) that gives the flexibility of using two bandgaps, but at the expense of more complicated photosystems.

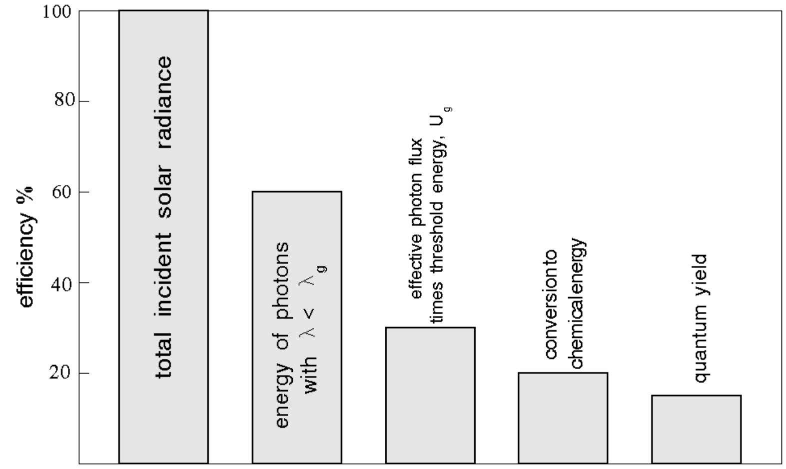

Figure 2.7 *Schematic illustration of the remaining energy content due to energy losses in a photochemical conversion process (the relative heights are arbitrary)*

Theoretical efficiencies for solar photolysis of water are 23.5% for a single photosystem and 32.3% for a dual photosystem, assuming 0.6 eV overpotential in both cases. (Bolton, 1996).

The losses that add up to the theoretical unavoidable ones, arise from incomplete absorption of the sunlight, quantum yields that are less than unity, losses due to reflection of sunlight and losses in collecting the produced chemicals.

Estimated attainable efficiencies for practical systems that are able to split water are 10% for single photosystems and 18% for dual systems (Bolton, 1996).

3. SURVEY OF STATE-OF-THE-ART OF SOLAR PHOTOCHEMICAL CONVERSION

In searching for information on photochemical conversion and storage of solar energy, much literature is found in which this subject is mentioned as an ultimate goal of photochemistry. However, the content of many articles often consists of quite fundamental studies of parts of the conceptual system. These fundamental studies comprise bandgap tuning of semiconducting materials by means of changing some specific properties. Especially in the area of TiO_2 semiconducting material many recent publications deal with the mixing of other oxides or incorporating metal ions into the titania in order to obtain a shift in the absorption of photons into the visible region. Also catalysis of the envisaged reactions is an area that attracts great attention of research and development.

Approximately 80% of the systems in development deal with the photochemical splitting of water to produce hydrogen and oxygen, and some systems are directed towards the reduction of carbon dioxide, producing hydrocarbons.

Within the IEA hydrogen programme (IEA) a broad spectrum of conversion technologies for the renewable production of hydrogen are studied amongst which the photochemical conversion. Recent results of this work are described in the proceedings of the US Department of Energy Hydrogen program review (DOE). In these systems hydrogen is the energy carrier to be produced.

In other systems the reduction of CO_2 is recognised as an attractive option for making hydrocarbons or methanol. This technology is attractive in that it combats global warming by consuming CO_2 and would link easier to existing energy infrastructure than hydrogen (Serpone). Especially methanol seems an attractive fuel since it can be looked upon as a storage medium for hydrogen, but has the advantage that it is liquid under normal conditions of pressure and temperature, it can be stored and transported as easily as gasoline, and can be used in many existing combustion devices. The energy storage density of methanol is about half that of gasoline and in addition methanol could be used as feedstock for organic chemicals.

3.1 Photochemical systems

In the field of direct photochemical systems a detailed analysis of the state-of-the-art is presented by Amouyal (Amouyal) and a more general review by Bolton (Bolton, 1996). At present only one system is reported to have directly split water into oxygen and hydrogen using sunlight as the only driving force (Katakis, 1992, 1994).

This is a homogeneous system consisting of tris-(1-(4-methoxyphenyl)-2-phenyl-1,2-ethylenedithiolato)tungsten as the photoabsorber and as catalyst and methylviologen as a reversible electron acceptor, in a mixture of acetone:water (60:40). This system produced H_2 and O_2 with a 4% and after further improvement even 7% quantum yield in the visible region (400-500 nm). This has been recognised as an important result, that should be independently confirmed (Bolton, 1996). The proposed reaction scheme for this system is as shown in Figure 3.1.

Up till now this experiment has not been confirmed at other laboratories. Also the reported efficiency of 7% for this so-called s1 (single photon) system is higher than the theoretical possible value. This could be caused by the use of different definitions of the efficiency of solar to chemical energy.

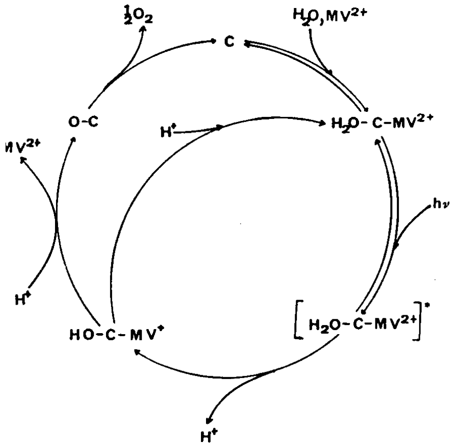

Figure 3.1 *Tentative reaction scheme for the photochemical splitting of water (Katakis, 1992). C represents the photoabsorber tris-(1-(4-methoxyphenyl)-2-phenyl-1,2-ethylenedithiolato) tungsten, MV is the reversible electron acceptor methylviologen.*

Experts in the field of photochemical systems (Andriesse, Amouyal, Meissner, Bolton, 1996) agree in their conclusion that despite progress made in several areas of the conversion steps of photochemical systems, no complete system has yet been *confirmed* to work.

The conclusion of the DOE panel B2 on 'solar hydrogen production' with regard to homogeneous photochemical systems is: ‘a fairly detailed understanding exists regarding the mechanisms obtaining in homogeneous systems that yield hydrogen upon irradiation with visible light. Unfortunately, most of the characterised systems require a sacrificial donor or acceptor, are subject to efficiency lowering side reactions, and make poor use of the entire solar spectrum. *True, efficient water-splitting systems remain elusive*‘(Koval).

3.2 Semiconductor systems

Photochemical conversion of solar energy to chemical energy can be accomplished by the use of semiconducting materials. These materials need to be photosensitive in a certain part of the solar spectrum. Absorption of a photon with a wavelength that is equal or shorter than the threshold wavelength will lead to excitation of an electron from the upper valence band to the lowest conduction band.

The size (eV) and the position of the bandgap are of great importance with regard to the threshold wavelength and to the chemical stability (photo-oxidation) at the photoanode. The size of the bandgap must be sufficient to drive the desired reaction and the position of the bandgap must be such that the redox potentials of the desired reactions are enclosed by the bandgap of the used material. In Figure 3.2 this is illustrated for the case of the water splitting reaction. The reduction and oxidation potentials of water are plotted in the band-gap spectrum of several semiconducting materials.

Chemical reactions with a high uphill Gibbs energy of reaction require high energy of photons, thus short wavelength, corresponding to large bandgap materials. High ΔG reactions can be driven as multi electron processes which lowers the required photon energy. To split water electrons of 1.23 eV are required. To reach high efficiencies in solar-to-chemical energy conversion the bandgap energy of the semiconductor should be slightly higher than the minimal required bandgap energy of the redox couple. Much higher bandgap energies of the semiconductor lead to a smaller part of the solar spectrum to be used.

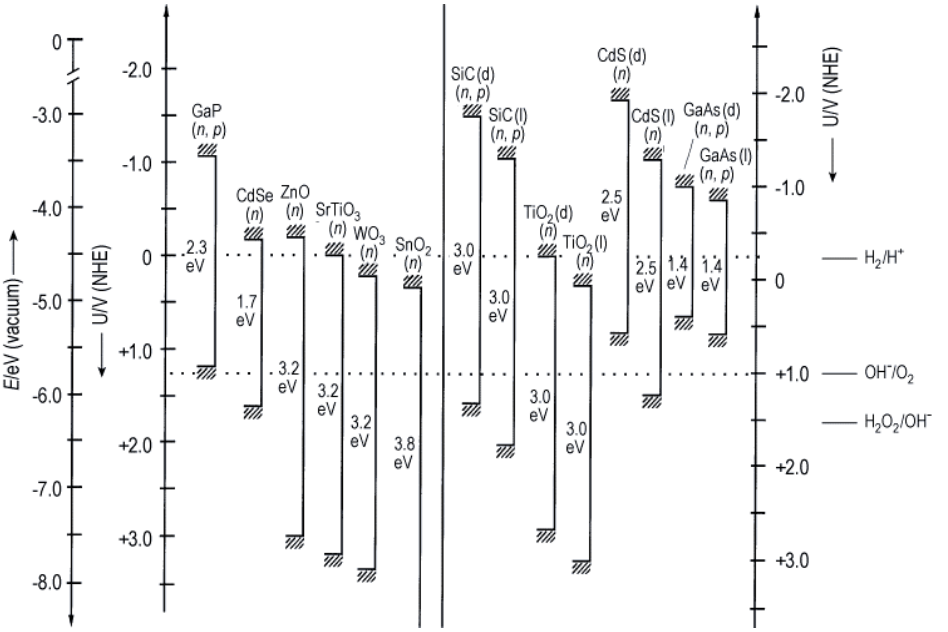

Figure 3.2 *Band edge positions of semiconductors as determined in photoelectrochemical experiments in aqueous solutions. The values on the left are literature data whereas the values obtained in the dark (d) and under illumination (l) in the right half of the diagram were determined in the author's laboratory. For each material the bandgap between the lower conduction and the upper valence band edge is shown as it is fixed at the semiconductor – electrolyte interface. For comparison, the vacuum energy scale as used in solid state physics and the electrochemical energy scales, with respect to a normal hydrogen electrode (NHE) and an saturated calomel electrode (SCE) as reference points, are shown as well as the standard redox potentials of water in acidic solution (Meissner).*

The photochemical systems that utilise the properties of semiconducting materials are described in the following sections, where a distinction is made between photoelectrochemical cells and microheterogeneous systems.

3.2.1 Photoelectrochemical cells

Japanese scientists reported the first photo-electrochemical cell that could split water by itself in 1972 (Fujishima), but it had an efficiency of only about 1% because the electrode material, titanium dioxide, did not absorb much light. In the following years lots of research has been devoted to the development of photoelectrochemical cells (PEC).

At present the systems that have proved to be able to convert photonic energy into useful chemical energy (mainly hydrogen by splitting of water) are still on a laboratory scale. The solar to chemical energy efficiency of some of these systems is nevertheless promising, and high enough to continue R&D to improve the performance and decrease their costs.

National Renewable Energy Laboratory, USA
American scientists at the National Renewable Energy Laboratory, Colorado USA, have thus far developed the system with the highest efficiency. They created a combined cell that splits water into hydrogen and oxygen with efficiency as high as 12.4% using solar light (Khaselev). The device is build from a unique combination of a gallium indium phosphide ($GaInP_2$) photoelectrochemical cell directly connected to a gallium arsenide (GaAs) photovoltaic cell. The scheme of this cell is shown below in Figure 3.3.

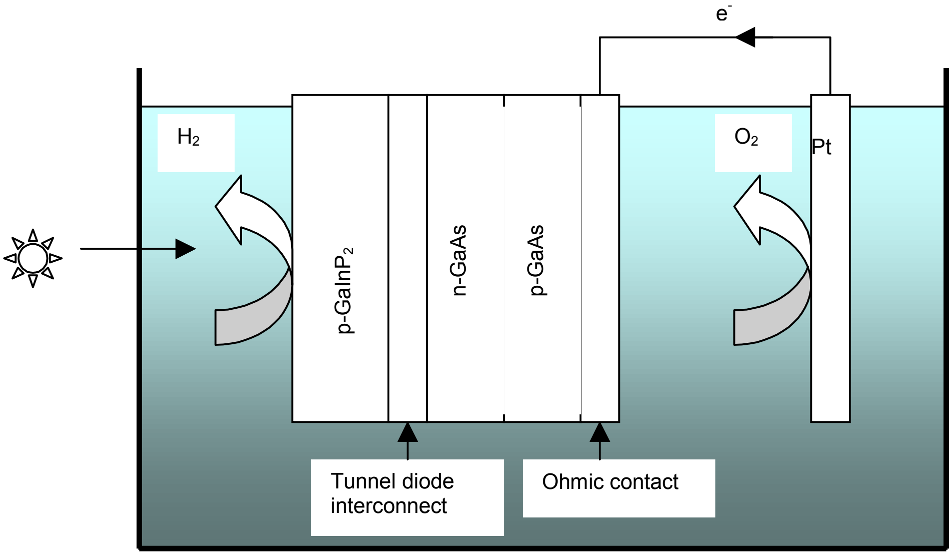

Figure 3.3 *The NREL photovoltaic-photoelectrochemical tandem cell (Khaselev)*

However, the device's long-term stability is currently unknown and the used materials are toxic and very expensive.

The high efficiency of this system is made possible by the use of two separate semiconducting materials with different bandgaps, $GaInP_2$ 1.83 eV and GaAs 1.42 eV, which enables the absorption of a greater part of the solar spectrum.

The drawbacks of this tandem-cell concerning the materials used in this device have certainly been distinguished, and will prevent this system from being commercially applied on a large scale. However, further development of this system is undertaken to support the development of system technology. This system technology can then be applied on a large scale as soon as photochemical conversion techniques based on cheaper, more stable and non-toxic materials are developed.

The application of GaAs for the photovoltaic part of this system is considered of academic interest, since its high cost and toxicity have also prevented the use of GaAs on a commercial basis for high efficiency PV cells.

Hawaii Natural Energy Institute, USA

Such a cheaper and non-toxic system might be the system based on silicon. In this approach, which is also an American development carried out at the Hawaii Natural Energy Institute (Univ. of Hawaii, Honolulu) a multi-junction amorphous silicon solar cell is used as photoelectrode and the solar-to-hydrogen efficiency is 7.8%. This is about 75% of the solar to electricity efficiency of the solar cells used, see Figure 3.4. A Further increase in efficiency is expected through optimisation of cell and reactor design (Miller).

Efficiencies of 15% are mentioned as attainable by using a new class of low-cost copper indium diselenide materials. This system in fact is not a PEC system in the true sense of the word since it lacks a semiconductor/electrolyte interface. It can better be considered as a direct-coupled PV cell with electrolysis.

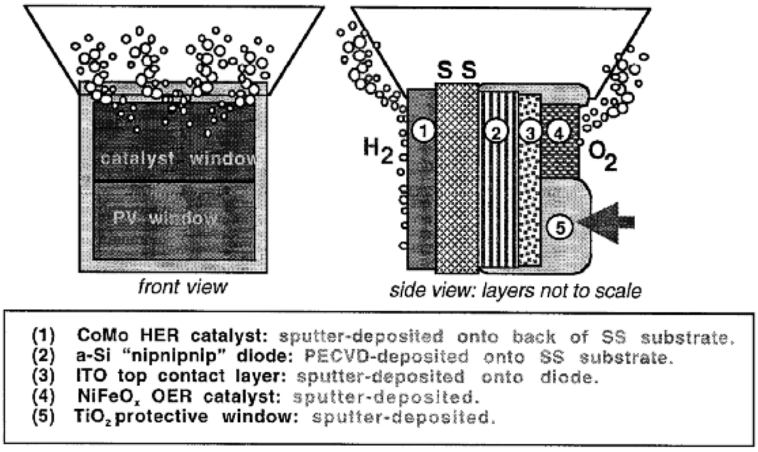

Figure 3.4 *Layout for the fully integrated planar photoelectrode based on multi-junction silicon solar cells (Miller). (HER= hydrogen evolving reaction, OER= oxygen evolving reaction, ITO = Indium Tin oxide, transparent conductive front contact)*

Swiss Federal Institute of Technology, Switzerland

Another tandem device for direct water cleavage into hydrogen and oxygen by visible light was developed by Prof. Grätzel's group from the Swiss Federal Institute of Technology in collaboration with two research groups from the Universities of Geneva and Bern (Augustinski, Grätzel). The efficiency of the tandem device is approximately 4-5%. The layout of this system is depicted below in Figure 3.5.

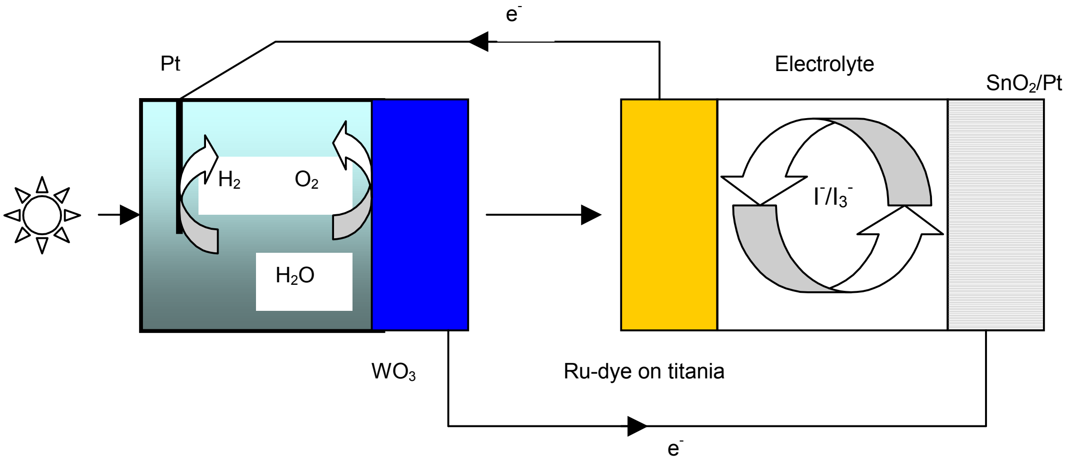

Figure 3.5 *Circuit diagram of the tandem cell for water cleavage by visible light (Grätzel)*

Tungsten trioxide is used as the photoanode and dye-sensitised titania is used in the regenerative PEC cell to provide electrons for the reduction reaction. This tandem device is an extension of the development of the so-called Grätzel cell, named after its inventor. This is a PV cell based on a TiO_2 electrode, which is sensitised with a dye to enlarge the solar absorption. This dye is based on a metal-organic complex of ruthenium and directly linked to the titania. In the PV field the Grätzel cell is considered as the cheap alternative for Si-based solar cells. The solar-to-electricity efficiency of this type of cell still needs improvements, as well as its long-term stability.

In the tandem device the WO_3 is used as a transparent nanocrystalline film that absorbs the bleu part of the solar spectrum and the dye sensitised titania absorbs the green and red part.
In another reaction using a 0.1N methanol solution, hydrogen and CO_2 were evolved at the electrodes with an efficiency of about 10%. This indicates that this system might be particularly interesting for degradation of organic waste solutions, combined with hydrogen production.

Hitachi Research Laboratory, Japan

Another approach in the field of photochemical conversion is aimed at the reduction of CO_2. Japanese scientists from Green Center, the Hitachi Research Laboratory developed a photo-electrochemical cell in which in one cell at the photoanode water is split into protons (H^+) and oxygen. The protons are transported to the second cell where it reacts with carbon dioxide to form methane, ethane or other hydrocarbons, The system layout is shown in Figure 3.6. The system works with an efficiency of about 12% under the UV irradiation, but unfortunately only 0.3% under solar irradiation (Ischikawa). The thin film photocatalyst consists of sol-gel deposited TiO_2 on titanium metal as a substrate. The proton separator is a Nafion® membrane that conducts protons and the electrocatalyst consists of platina or copper modified with zinc oxide. At the photocatalyst side water is oxidized to form oxygen and protons. The electrons are transferred outside the proton separator towards the other cell compartment where the protons, electrons and carbon dioxide catalytically recombine according to the reactions given in Figure 3.6. Further fundamental research on this system should be focused on the atomic level of the reaction mechanism at the photocatalyst. A detailed understanding of this reaction mechanism is needed in order to design better photocatalysts that eventually will operate with solar irradiation.

The work on this system has been transferred from Hitachi's Green Center to the Japanese RITE institute (Research Institute of Innovative Technology for the Earth). Further progress since 1996 has not been reported thus far.

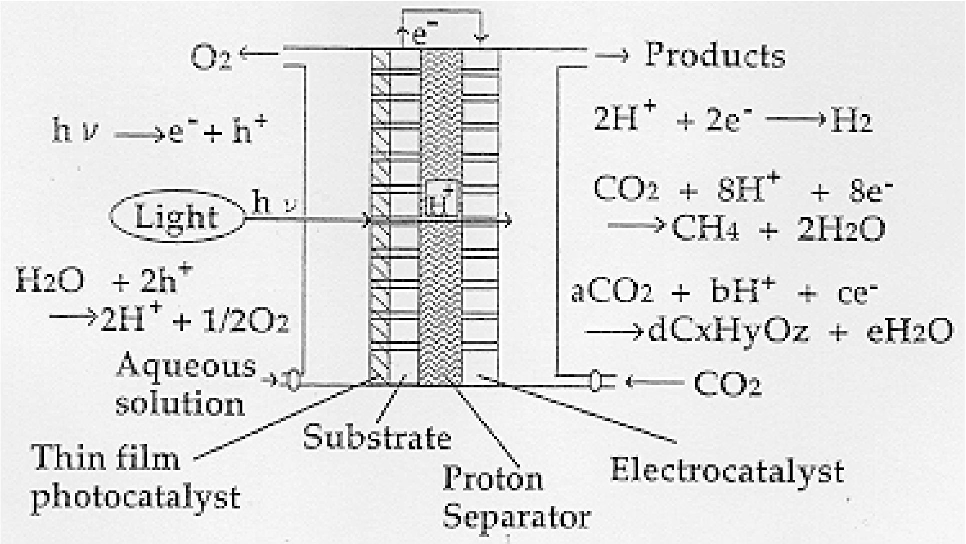

Figure 3.6 *Photo-electrochemical reactor for the reduction of CO_2 to produce hydrocarbons (Ischikawa)*

Very recently, also scientists from Banaras Hindu University in India had built a PEC-cell for solar hydrogen production using indium oxide and vanadium oxide doped nanostructured titania as a photocatalyst (Karn, 1999, 2000). They reported successful shift of the photoabsortion of titania towards wavelengths of 500nm.

In the Netherlands, an EET-Kiem project was conducted where STORK, ECN, Delft University of Technology and Everest Coatings were involved (Spoelstra). This project was focussed on increasing the absorption of visible light in the TiO_2 photocatalyst by incorporating other elements in its structure, and to construct a prototype photoelectrochemical reactor like the one in Figure 3.6 to demonstrate the proof-of-principle. In this project it was proven that photoelectrochemical reduction of carbon dioxide to methanol and methane was possible under UV-light irradiation.

3.2.2 Microheterogeneous systems

Photocatalytic water cleavage systems based on aqueous dispersions of semiconductor particles are cheaper then PEC cells but their efficiency is generally lower. The additional drawback is that hydrogen and oxygen are produced simultaneously in the same compartment. Arakawa et al. in Japan using a RuS_2/SiO_2 photocatalyst (Arakawa) developed such systems, as well as Lee from South Korea using a Ni/perovskite layered photocatalyst (Lee), and Hara from the Tokyo University of Technology using a Cu_2O photocatalyst (Hara) and scientists from the University of Valencia using a molybdenum catalyst (Catalyst).

Japanese scientists have undertaken efforts in photocatalytic reduction of CO_2 using microheterogeneous systems (Anpo). In their system semiconducting titania was included within the framework of mesoporous zeolites. The idea for the use of porous carrier materials is explored also in Switzerland at the Calzaferri research group of the University of Bern (Calzaferri). Zeolites can increase the selectivity of a specified reaction and due to their large surface area can increase efficiency of the reaction system due to high dispersion of the photocatalyst. Promising results were reported with UV irradiation of the system, but no results were given for solar irradiance.

Tryk et al. (Tryk) recently stated for *microheterogenous* semiconductor systems that the complete water splitting reaction to H_2 and O_2 using solar irradiation without the benefit of sacrificial agents has been an elusive goal, even though many systems have proved to work in UV irradiation. The semiconductor materials that are investigated for use in photocatalytic particulate systems are, TiO_2, CdS, ZnS, WO_3, AgCl, $BiVO_4$, layered oxide compounds, layered perovskites and tantalum oxide.

The major problem in designing an efficient photoelectrochemical system for the generation of fuel, is the development of an efficient photocatalyst that responses very well to visible light irradiation.

4. STORAGE OF SOLAR ENERGY

The R&D on photochemical conversion of solar energy to fuel is mainly focused on the production of hydrogen (Khaselev, Miller, Grätzel, DOE). Few systems are developed for the production of hydrocarbons (Ischikawa, Spoelstra) as methane, ethane, or methanol from water and carbon dioxide.

Storage of the fuel produced is necessary to overcome the mismatch in time of supply of solar energy and demand for energy. The storage of hydrocarbons that are liquid, like methanol or ethanol can be accomplished very easily in a storage tank provided with appropriate safety measures to avoid explosion hazards. For storage of a gaseous fuel, hydrogen or methane several options exist, like compressed gas storage, gas liquefaction, or gas absorption.

A key parameter of any energy storage device is the energy storage density expressed by weight or by volume. For *liquid fuels* this energy storage density is generally high both by volume and by weight. This has made liquid fuels attractive for use in stationary and mobile applications.

For *gaseous fuels* the energy storage density by volume depends largely on the pressure at which it is stored. The higher the pressure of the gas the higher the volumetric storage density, but the more energy is consumed for the compression. Liquefaction of gaseous fuels even further increases the storage density, but at the expense of even more energy consumption. The absorption of hydrogen in metals is also a way to increase the volumetric energy storage density, but in this case the weight of the energy storage increases significantly.

In Table 4.1 the energy densities of several fuels in their standard states are given. The figures illustrate that the volumetric storage density of the gasses is very low compared to the liquid fuels.

Table 4.1 *Energy storage densities of different fuels.(Haüssinger, Leijendekkers, Schut)*

Fuel	Density at 25°C and 1 bar [$kg \cdot m^{-3}$]	Energy storage density by volume [$MJ \cdot m^{-3}$]	Energy storage density by weight [$MJ \cdot kg^{-1}$]
Methane (gas)	$650 \cdot 10^{-3}$	32.5	50
Hydrogen (gas)	$84 \cdot 10^{-3}$	10.1	120
Methanol (liquid)	790	16600	21
Gasoline (liquid)	725	31200	43
Oil (liquid)	920	37700	41

The required capacity of an energy storage device must be calculated from the annual pattern of supply and demand of energy. From these patterns the needs for short term and long term storage capacity can be calculated. These patterns can vary much with the application. For example the demand for energy of a family house is completely different than for an office building, with regard to time, capacity and the ratio between demand for electricity and heat.

Parameters for the selection of the storage capacity are based on the cost of the storage, the size and the weight. For mobile applications weight and size are the most important factors, whereas for stationary applications the cost factor often is decisive.

4.1 Hydrogen storage

Most of the photoelectrochemical conversion systems, which are presently in development, aim at the production of hydrogen. Several technological options for hydrogen storage are available. (Haüssinger, Hyweb) The technologies presently in service, can be divided into stationary, large-size storage systems, stationary small-size storage systems, and mobile storage systems. *Compressed hydrogen gas* storage of various pressures ranges and sizes are considered state-of-the-art. Stationary small-size storage systems consist of steel cylinders or pressure vessels with volumes ranging from 50 to 400 litres at pressures of 200 bar. For mobile applications pressure tanks made of composite materials have been developed recently to reduce the weight of the storage system (Hyweb). The storage technology for *liquid hydrogen* is available at present thanks to the extensive application in space travel. Liquid hydrogen storage tanks are insulated with double walls (Dewar vessels), the space between which is evacuated and filled with insulating material. Loss of hydrogen due to evaporation ranges from 3% to less than 0.03% on a daily basis, where the lower loss rate is obtained with the larger vessels. The sizes of liquid hydrogen storage tanks range from 0,1 to 5000 m^3.

Storage of hydrogen in pressure vessels is the most economic aboveground storage method for storage times less than 30 hours. For storage times exceeding 30 hours liquid hydrogen storage becomes the better alternative from an economic point of view (Haüssinger). However, the energy consumption to liquefy the hydrogen amounts 1/3 of the energy that is stored.

New developments in the storage of hydrogen lie in the field of cryo-adsorption. Hydrogen is adsorbed on suitable adsorbents at moderate pressure (40 bar) and low temperature (-200 to –150°C). The storage density is however lower than with liquid hydrogen due to the volume taken up by the adsorbent. Adsorbent materials, which are light, porous and with a high specific surface are suitable as adsorbing agents. The most recent development is the adsorption of hydrogen in carbon nanotubes or micro-fibers.

Another storage technology for hydrogen that is being developed is the storage as metal hydride. Several metals or metal alloys reversibly absorb hydrogen. In this process hydrogen is incorporated in the lattice of the host material. A disadvantage of metal hydride storage is its high weight, due to the use of large amounts of metal.

Hydrogen could also be stored as ‘liquid organic hydrogen’. With the help of hydrogenation-dehydrogenation processes the combinations of benzene-cyclohexane or toluene-methylcyclohexane are suitable storage reactions for hydrogen. The endothermic dehydrogenation reaction requires heat, whereas in the exothermic hydrogenation reaction heat must be supplied. Systems based on this technology are still in the experimental stage and will only be economically viable for very large long-term storage systems, due to the investment cost of hydrogenation and dehydrogenation plants (Padro).

In Table 4.2 the conditions and energy densities of three options for hydrogen storage are compared.

Table 4.2 *Comparison of storage systems for hydrogen (Haüssinger)*

Storage method	Hydrogen content	Storage mass [kg]	Hydride material [kg]	Operating pressure [Bar]	Operating temperature [°C]	Energy density [$MJ \cdot kg^{-1}$]	[$MJ \cdot m^{-3}$]
Liquid H_2	57 litre	20	-	4	-253	23	3400
Gaseous H_2	45 m^3	120	-	300	-20 +50	4	1980
Metal Hydride	4 kg	320	220	50	-20 -100	1.5	3000

5. TECHNOLOGY ASSESMENT

The direct photoelectrochemical conversion of sunlight into a fuel has the benefit of producing an energy carrier that can easily be stored, which is not the case in the conversion of sunlight into electricity as is done by photovoltaic systems. In the previous chapter the state-of-the-art of photochemical conversion technologies is described. Despite over 20 years of research, at present the photochemical conversion technologies are still in the academic R&D and pre-commercial stage.

As far as direct photochemical conversion is concerned, this appears to be no viable option for the production of energy carriers that can be stored. Of the semiconductor based systems the photo-electrochemical cell has the best options for future application. Microheterogeneous systems based on semiconductors in the form of fine particles have not yet proved to work appropriate.

Considering the fairly academic R&D stage of the photochemical conversion systems it would be not very meaningful to make a comparison between several options for sustainable fuel/hydrogen production and rank the different photochemical conversion options accordingly. Many aspects of the photochemical conversion technology are not yet defined and there are still multiple options for PEC cells. The increase in efficiency of solar-to-fuel conversion during the last thirty years from less than 1% (Fujishima) to 12,5% (Khaselev) at present for the most advanced tandem PEC/PV system is nevertheless quite promising.

Photoproduction of fuel as a technology has definite advantages over other options of energy conversion, being sustainable, consists of a non-polluting closed loop, leads to a storable energy carrier and sunlight and reactants (water in the case of hydrogen fuel) are present in large amounts. In order to compare it to other sustainable solar technologies leading to the production of a fuel the most appropriate technology is the coupling of a PV system to an electrolyser system. This system can convert water into hydrogen and oxygen. The overall solar-to-hydrogen efficiency of such a system is almost 10%, assuming 12% efficiency for solar to electricity and 80% electricity to hydrogen efficiency.

In the following paragraphs only the PEC-cells due to their most advanced R&D stage are considered. According to Bolton (Bolton 1996) these semiconductor systems are much more robust than molecular systems and thus show more promise.

5.1 Technology

As far as the technology is concerned several general criteria apply to the photoelectrochemical conversion of solar energy to fuel. A first criteria of solar to fuel systems should be the efficiency of the system. An optimum is to be found in the cost of the system, determined by its complexity and the price of materials used, and the conversion efficiency.

Concerning the materials to be used in a PEC cell several criteria apply. They must be stable over the period of their service life (>20 years) under solar irradiation and thermal and chemical conditions applied. The materials to be used in the PEC systems should also be present in sufficient amounts (e.g. noble metal catalytic materials) and be affordable. Furthermore the materials should be non-toxic, and non-polluting, which also holds for the additional materials, used in the large-scale manufacture of the PEC devices. The storage and transport of the fuel produced by the PEC system should be cheap and safe. For systems producing hydrogen as a fuel several technologies for storage and transport options are available being high-pressure systems, cryogenic systems and storage as a metal hydride, see Chapter 4. For methane or methanol producing systems the storage and transportation can be much less complex than for hydrogen, because of the better link with existing infrastructure.

To become a successful energy generation option the PEC cells need to be incorporated into the existing energy infrastructure with a minimum of modification. A PEC system should produce a fuel that is stable, storable and transportable and environmentally compatible

5.2 Economy

Block and Melody performed an economic analysis for PEC systems with PV/electrolysis as the reference situation, being a presently available technology that converts photons into hydrogen (Block). Based on the (at that time) predicted efficiencies and costs for PV cells for the year 2010 the required efficiency of a PEC system should be in the range of 15 to 20% at a system cost of 150 [\$/m^2 of reactor area], in order to be economically viable.

In the review paper of Bolton (Bolton 1996) a short analysis of the economic aspects of hydrogen production is made. Because all PEC devices with reasonable solar conversion efficiencies are still on a lab scale, it is not possible to make an economic comparison of several PEC systems based on the projected capital cost and efficiencies.

In this approach the maximum capital cost for a PEC system is calculated, assuming reasonable conversion efficiency and market prices for the products the system delivers. The other way around is to assume capital costs for the PEC device and calculate the minimal efficiency for a system to be economically viable.

Based on a 10% solar-to-hydrogen efficiency and a market price of \$0,25 per normal m^3 of hydrogen the maximum capital cost for 1 m^2 of collector area is \$165. This implies that any system for solar to hydrogen conversion will have to be very simple of design and be fabricated from cheap materials. The use of noble metals as catalysts should be very limited and also the semiconducting material must be cheap. Any photochemical system with an efficiency of less than 10% has not much chance of success.

Mann et al. (Mann, 1998) made an extensive techno-economic analysis of different options for the production of hydrogen from sunlight, wind and biomass. In their first analysis (Mann, 1996) viability of the silicon based PEC system was established, forming the basis for further R&D on this system. The expensive tandem cell based on $GaInP_2/GaAs$, despite its higher conversion efficiency cannot produce hydrogen economically.

In the comparison with wind/electrolysis and PV/electrolysis the assumption for the PEC system are for the year 2020 an efficiency of 14% and \$120 for photocatalyst and membrane material per m^2 area. In this analysis the PEC system is contained in a housing, which is shaped to concentrate the sunlight by a factor of five in order to reduce the required total reactor area. The result of their comparison of PEC-generated hydrogen with wind- and PV-generated hydrogen using several scenarios indicates a competing price for hydrogen produced by PEC in comparison to PV/electrolysis. The option for wind/electrolysis appears to result in the lowest selling price of hydrogen.

Spoelstra (Spoelstra 2000) recently reported a techno-economic evaluation of photoelectrochemical systems. In this evaluation the PEC systems cannot compete on the basis of price of hydrogen produced with conventional ways of hydrogen production nor with the other renewable ways (Wind- or PV/electrolysis) of hydrogen production. This remains valid even for the year 2020. The assumed conversion efficiency ranged from 4 to 8% and investment costs ranged from 100 to 300 (\$/m^2). Future PEC systems thus should have conversion efficiencies which are much higher than 8% with investment costs lower than 100(\$/m^2) to become really economically competitive with other renewable ways of fuel production.

The above figures for efficiencies and system costs of PEC devices must be seen as goals for the further development. If it becomes clear in future development that these goals are not within reach, further development of PEC devices for large-scale hydrogen production should be critically reviewed against actual economic constraints.

As long as the PEC systems are in their pre-commercial R&D stage, as is the case at present, economic evaluation of this technique serves as a way to set the targets in the development.
Other solar-to-fuel technologies, which are also in the R&D stage, are those based on for example thermochemical reactions. The sunlight is here concentrated to drive an endothermic chemical reaction to obtain products (fuels) that can be converted on a different time to release the stored energy. Developments in this area of energy conversion are in the R&D stage as well, but can become competitive with PEC systems in the long term. Examples of these systems are the Zn/ZnO-H_2O cycle (Steinfeld) and the NH_3 cycle (Lovegrove)

At present non-renewable hydrogen production methods, are based mainly on steam reforming of hydrocarbon feedstocks. For ammonia and methanol production the required hydrogen is produced by steam reforming of methane ($CH_4 + H_2O \rightarrow 3H_2 + CO$). Steam reforming is expected to continue as it requires low capital costs and low production costs. The energy efficiency of methane conversion is 85% (Serpone). When natural resources for steam reforming become low, prices for the production of hydrogen in this way will increase and economic competition between renewable and non-renewable hydrogen production will increase. This situation is not to be expected within the next ten years.

6. PROSPECTS

After going through a series of articles dealing with the subject of photochemical conversion and storage of solar energy, the general impression is that at present the best systems for photochemical conversion and storage of sunlight are still in the early R&D stage. Most research in this area is directed towards the production of hydrogen as a fuel that will be applied in the future ‘hydrogen energy society’.

Large-scale commercial application of solar photochemical production of fuel is not to be expected on the short-term and only in niches of the energy market on the long term. The clear advantage of the conversion of sunlight into chemicals is the flexibility it gives to cope with mismatch between supply and demand of solar energy as regard to time and power/capacity. The advantage over PV-battery systems is the long-term storage ability it offers when appropriate chemicals are produced.

Despite the advantages of photochemical conversion, it still has to compete with technological alternatives, which are also based on renewable sources of energy like sun, wind and biomass.

The problems that are to be solved before photochemical conversion can compete with other renewable/sustainable technologies are still very fundamental in character. These problems are:
- poor matching of semiconductor bandgap with solar spectrum,
- instability of the semiconductor in the aqueous phase,
- energetic mismatch between the semiconductor band-gap and the reactions of interest,
- poor kinetics of the electrode reactions.

Much work on PEC devices is required to improve the bandgap matching of semiconductors with the desired reactions, to shift the absorption of wavelengths to higher values in order to use a larger part of the solar energy spectrum, to reduce (photo)corrosion problems of the semiconducting materials and improve their stability, and to improve the performances of the catalysts. Further improvements should be achieved by simple and efficient cell and system design.

The economy of photoelectrochemical conversion processes is expected to be in the range of PV/electrolysis. Since no actual pilot-plants of PEC systems have been built a more detailed economic comparison of PV/electrolysis and PEC as hydrogen fuel producing technologies cannot be done at the moment.

In certain situations promising economics were found for photoelectrochemical production of hydrogen. This is in those situations where hydrogen production is performed in conjunction with photodegradation of organic waste. Efficiency improvements seen with organic pollutants (from 4% up to 9%), combined with the cost benefit of combining degradation of organic pollutants with hydrogen production show some promise for commercial application (DOE).

Developments and progress in other areas of (solar) energy research can be profitable for the development and economy of photoelectrochemical conversion techniques. These areas are:
- efficiency and stability improvement and further cost reduction of regenerative dye-sensitised solar cells,
- development of hydrogen storage and transportation techniques for future automotive applications,
- cost reduction for the production of silicon based PV systems will also reduce costs of silicon based PEC systems,
- increase in the application of TiO_2 as a photocatalyst in solar detoxification processes.

Other developments in the field of utilisation of renewable energy that are competing with photoelectrochemical conversion are:

- solar thermochemical systems,
- photobiological production of hydrogen (Annex 15 of the IEA Hydrogen programme (DOE, Gaudernack)),
- biomass conversion systems,
- the development of batteries and supercapacitors for direct storage of electricity from photovoltaic systems and wind turbines.

6.1 Expert opinion

From John Turner, Senior Scientist at the National Renewable Energy Laboratory (NREL) in Golden, USA, who is involved in the development of the PEC device described in Paragraph 3.2.1 (Khaselev) the following information was received from personal communication through Rien Rolloos (TNO-Bouw):

> ‘Since current commercial electrolyzers suffer from high capital costs, they are a major contributor to the cost of electrolytically produced hydrogen. Combining the electrolyzer with the PV system eliminates one of the high cost components of a PV-hydrogen generation system. This type of monolithic system also reduces semiconductor processing since surface contacts, interconnects and wiring are no longer necessary. This configuration requires only the piping necessary for the transport of hydrogen to an external storage system or gas pipeline. While the cost of a working photoelectrolysis system may be less than that of a corresponding PV/electrolysis system, it will still be 3-4 times more expensive than hydrogen generated via steam reforming of natural gas.
>
> *Now in conclusion – the hype:*
> The splitting of water using a semiconductor immersed into an aqueous solution has been termed the 'Holy Grail of Photoelectrochemistry'. Many photoelectrochemical systems have shown the ability to use sunlight to split water into hydrogen and oxygen, however, none to this point have done it with an efficiency as high as 12.4% (Khaselev). The promise of their device is that it shows us that it is possible to take two of our most abundant natural resources, sunlight and water, and with high efficiency, directly generate an energy carrier, hydrogen, that is non-polluting and totally recyclable.
>
> *And the reality:*
> At present, the device (Khaselev) is not an economical way to produce hydrogen from water and sunlight. Even with an ideal system, photoelectrochemically produced hydrogen would still be 3-4 times more expensive than current hydrogen from steam reforming of natural gas. To make this system economical, government mandates and incentives for renewables must be implemented. Additionally, basic research on this and similar systems must continue. Long term, consistent funding, supporting basic research is needed to bring these technologies and the promise of a renewable based hydrogen energy economy to commercial viability’.

Karl-Heinz Funken, head of the Solar Chemistry division of the Solar Energy Technology department of the Deutsches Zentrum für Luft- und Raumfahrt (DLR), was also asked for his vision on photoelectrochemical conversion of solar energy to fuel. In his answer he also stresses the need for cheap technologies.

> ‘For energetic purposes the fuel produced (hydrogen, methanol etc.) is a mass product which must compete with a fuel produced by other methods like solar thermochemical methods. These non-photochemical processes have the potential to produce the solar fuels at much lower costs than the photochemical procedures. To my opinion systems could be realised technically but at costs, which would be significantly higher than alternatives.’

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APPENDIX A INSTITUTIONS ACTIVE IN THE FIELD OF PHOTOCHEMICAL CONVERSION AND STORAGE SOLAR ENERGY

- National Renewable Energy Laboratory, Golden Colorado, USA, www.nrel.gov
- Hawaii Natural Energy Institute, school of ocean and earth science and technology, University of Hawaii at Manoa, Honolulu, USA, www.soest.hawaii.edu/HNEI/hnei.html.
- Brookhaven National Laboratory, Upton, NY, USA, www.bnl.gov.
- Research Institute of Innovative Technology for the Earth (RITE), Kyoto, Japan http://www.rite.or.jp/english/.
- University of Tokyo, school of engineering, department of applied chemistry, Tokyo, Japan, http://www.appchem.t.u-tokyo.ac.jp/appchem/ (japanese).
- Paul Scherrer Institute, Villigen, Switzerland, www1.psi.ch.
- Ecole Polytechnique Fédérale de Lausanne, (Swiss federal institute of technology) EPFL, Institute of physical chemistry, Lausanne, Switzerland, www.epfl.ch, and dcwww.epfl.ch/icp/ICP-2/icp-2.html.
- University of Bern, dept. of chemistry, The Calzaferri Research Group, Bern, Switzerland, http://iacrs1.unibe.ch/start.html.
- Deutsches Zentrum für Luft- und Raumfahrt, (DLR), Solare Energietechnik, Köln-Porz, Germany, www.dlr.de/ET.
- Hahn-Meitner Institut, Solar energy Research, Berlin, Germany, www.hmi.de.
- Netherlands Energy Research Institute, ECN, Petten, The Netherlands www.ecn.nl.
- Delft University of Technology, department of applied inorganic chemistry, Delft, The Netherlands www.stm.tudelft.nl/tac/theme_c.htm.
- National Center for Scientific Research 'Demokritos' Institute of Physical Chemistry, Athens, Greece, http://macedonia.nrcps.ariadne-t.gr/Demokritos/personal.html.

Other Internet links in the field of photochemical conversion of solar energy

- Hydrogen Information Network Home Page, www.eren.doe.gov/hydrogen.
- Hydrogen Energy Research information, http://home.osti.gov/hyd/hydhome.html.
- EUROSOLAR European Solar Energy Association http://www.eurosolar.org/.
- International Solar Energy Society, ISES, www.ises.org.
- The American Solar energy Society, www.ases.org.
- The European Photochemistry association, EPA http://www.unibas.ch/epa.
- International Solar Server http://www.solarinfo.de/de/site/news/start.html.
- Hyweb, hydrogen fuel cell energy information, http://www.hydrogen.org/index-e.html.