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Review

Photovoltaic hydrogen generation

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ABSTRACT

Fuel production via light generated electricity and water splitting is a fundamental quantum solar energy conversion process, which is also applied in nature and, thus, via fossil fuel and biomass, responsible for most of our present energy supply. Significant advantages of this technology are elegant energy conversion mechanisms, applicability at environmental temperatures and potentially high-energy conversion efficiencies. In biological systems hydrogen from water splitting is attached to carbon compounds, which is also a technological option. Since photovoltaic hydrogen generation today is critically limited by ten times too high costs for photovoltaic electricity this review will concentrate on required innovative technology for the conversion of light into electricity. In addition, the challenge of oxygen evolution from water receives major attention. Also strategies aimed at either decentralizing photovoltaic hydrogen generation or centralizing it in specialized power plants are compared and their respective potential evaluated. Photovoltaic hydrogen generation is expected to have a bright future but development from its present negligible contribution to a large-scale technology will require addressing a series of scientific and technological challenges aimed at making it more cost efficient as soon as possible.

1. Introduction

The generation of chemical energy from light at environmental temperature has been a challenge, which is as old as the origin of life on earth. Only by developing such a technology life was able to colonize practically all eco-systems of this planet. For thermodynamic reasons, only a quantum system could accomplish an efficient solar energy conversion at environmental temperature. It is now known that a single quantum absorber would be able to convert approximately 31% of the incident solar energy into useful work. In contrast, a thermal absorber would have to heat up in order to generate power via a limiting Carnot efficiency. Such a system would have to heat up by several hundred degrees in order to reach a comparable energy output. For life this was not a feasible alternative. The photovoltaic system developed by nature is based on green chlorophyll molecules, which absorb solar light and transfer the electrons into electron transfer protein chains, which mediate the conversion of photon energy into photovoltaic energy. The principle of dye-sensitized photovoltaic energy conversion has been demonstrated as a bioanalogue energy system 35 years ago and has, during the past 16 years, seen major progress leading to laboratory cells with up to 11% solar energy efficiency. During the primary processes of photosynthesis the photovoltaic energy is used to split water and to generate chemical fuels. In this process the

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hydrogen from water is essentially attached to carbon compounds, which provide the basis for a wide range of chemical energy carriers and of course the basis for the chemistry of life.

The concept of using photovoltaic energy for the production of chemicals and especially hydrogen has attracted scientific attention since the discovery of silicon photovoltaics. Starting with the first modern energy crisis in 1973 it has seen many studies in relevant books, journals and at international conferences dedicated to solar fuel generation and hydrogen technology (e.g. [1,2]). Generation of solar electricity with silicon solar cells gave access to the wealth of electrochemical techniques for fuel conversion and especially, of course, to the electrolysis of water.

Generally seen, the history of energy systems also saw a gradual change from wood to coal, oil, and natural gas, which increasingly favored highly automatic systems. Hydrogen was soon recognized as a very ideal energy carrier [1] the turnover of which can quite easily be handled and which also generates an environmentally entirely compatible combustion product, water vapor. A sustainable hydrogen economy thus became an idealized vision of an energy future for mankind. In order to follow this path many technological and scientific efforts have already been undertaken. Major problems, which remain, are the quite expensive change to an adapted infrastructure and the difficulty to obtain cheap photovoltaic electricity for its sustainable production from solar energy. Secondary solar energy such as derivable from waterpower, wave power or wind energy is less expensive but in its availability more limited. Today most hydrogen is generated from natural gas and is thus not sustainable. Only under special conditions where electricity is very cheap, hydrogen is generated from waterpower stations.

In order to make solar hydrogen widely available cheap solar electricity would be needed. It is presently not available but due to public subsidies in some countries the photovoltaic industry is rapidly growing and improving its production techniques. It may be expected that the learning curve for this industry will speed up. Part of our review will, therefore, deal with an analysis of development of photovoltaic industry.

Today, more than 90% of photovoltaic activities are concentrated on classical crystallized silicon solar cells. Only 7.8% are related to thin layer solar cells, which include the not yet satisfactorily stable amorphous silicon solar cells and also cells made from other materials, which, however, include rare and toxic elements like cadmium, tellurium, indium, and gallium. A major effort within this review will be concentrated on how to reduce the cost of photovoltaic solar cells. It will be shown that present solar cells have adapted a photovoltaic concept, which inherently requires very stable and consequently also expensive materials. With its dye solar cell concept nature has followed a different photovoltaic strategy, which in the longer term promises more cost-effective photovoltaic technology. This potential will also be analyzed. Another important aspect for the photovoltaic hydrogen future will also be the question, whether the technology should be developed as a centralized or decentralized option. Nature has followed a decentralized strategy, which gave it a high degree of flexibility and creativity. We will, therefore, also compare the advantages of centralized and decentralized photovoltaic hydrogen technology and especially investigate how a decentralized photovoltaic hydrogen technology could look like. The review article aims at a perception of photovoltaic hydrogen research and technology, so as to be able to identify pathways, which can accelerate the development of this important technology.

2. Photovoltaic hydrogen generation – limitations by thermodynamics

The conversion of light into chemical hydrogen energy can either be accomplished by a quantum process or by a solar thermal process. The thermodynamic limitations for such processes have been well studied since the first modern energy crisis (e.g. [3]). While solar thermal processes involve the Carnot efficiency factor and need high temperature differences to the environment in order to be efficient, quantum processes can already be quite efficient at environmental temperatures. This is relevant for the elegant photovoltaic technology. Fig. 1 compares the solar energy conversion efficiency of a simple quantum system absorbing light and of a series of quantum absorbers, which are together utilizing the entire solar spectrum. A quantum system such as a dye molecule or a semiconductor absorbing solar light across an energy gap of 1.3–1.4 eV can generate a maximum energy conversion efficiency of approximately 31%. Towards lower temperatures the efficiency is still rising. It is decreasing towards higher temperatures as Fig. 1 shows. If more than one solar absorber are collaborating such as, for example, two photovoltaic cells in series, the efficiency for quantum energy conversion correspondingly increases. When many solar

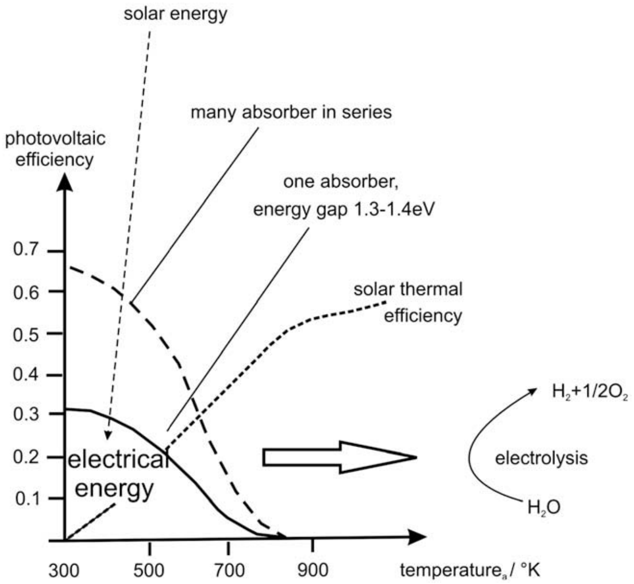

Fig. 1 – The diagram shows the temperature-dependent maximum quantum solar energy conversion efficiency to be expected, in dependence of the absorber temperature, from one and many photovoltaic energy converters in series respectively. Also the expected maximum efficiency from a thermal solar converter is indicated as a comparison.

absorbers are added in series a total efficiency of 68% can be approached. If solar light is concentrated the obtainable solar energy conversion efficiency may further increase because the free energy of the incident photons will correspondingly increase.

Today laboratory solar cells such as mono-crystalline silicon solar cells have reached energy conversion efficiencies of 25%, which for a semiconductor with an energy gap of 1.1 eV is close to the thermodynamic optimum (e.g. [4]). If two or three solar cells are arranged in series to form a stack, energy conversion efficiencies for the production of photovoltaic energy between 30 and 40% have been reached or are feasible (e.g. [5]).

The simplest and most elegant photovoltaic hydrogen generator consists of a solar cell and an electrochemical device, an electrolyser, which is liberating hydrogen from liquid water as indicated in Fig. 2. This process, during which photovoltaic electricity is simply passed through water works at environmental temperature without moving parts, is well established since the early years of electrochemical experience. Numerous laboratory and prototype initiatives have been developed over the years to demonstrate and to test photovoltaic hydrogen generation. One of the most ambitious, early projects was HYSOLAR, a joint German–Saudi Arabian initiative, including a 350 kW demonstration plant, test and research facilities of 10 and 2 kW respectively for research, system studies, education and training [6]. The project showed that the technology works but also pointed attention to practical technological problems which need further consideration [7]. The interest and dedication towards improving the photovoltaic hydrogen technology and preparing it for commercialization unfortunately decreased again as the first modern energy crisis passed and had to wait for the next energy crisis which seems to have arrived now.

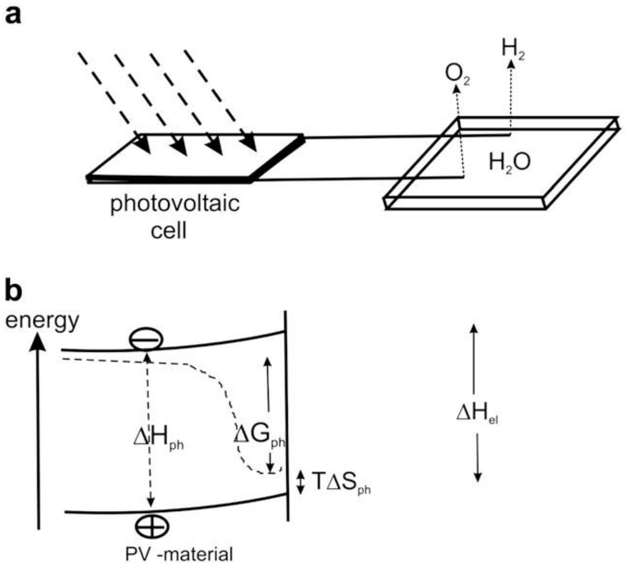

Fig. 2 – This figure illustrates (a) the principle of photovoltaic water hydrolysis and (b) explains that the thermodynamic quantities of the photovoltaic system and of water electrolysis which have to be matched for optimal energy conversion efficiency are enthalpy changes of the photo-system ΔH_{ph} and the water oxidation reaction ΔH_{el}.

The entire process of photovoltaic generation of hydrogen is schematically shown in Fig. 2. A photovoltaic system is coupled to an electrolysis system. What efficiency for hydrogen generation can all together be expected? This will definitely depend on how well the photovoltaic system is matched to the electrochemical system, which is absorbing the energy for hydrogen liberation from water.

Basically the total efficiency for photoelectrochemical generation of hydrogen η_{phel} will be composed of two efficiencies, one is η_{ph} for the transfer of solar energy to photovoltaic energy and the second efficiency η_{el}, the efficiency for electrochemically splitting water for hydrogen production.

$$\eta_{\mathrm{phel}} = \eta_{\mathrm{ph}}\eta_{\mathrm{el}} \tag{1}$$

where η_{ph} accounts for the fraction of energy, which is effectively available for the electrolysis of water. This energy has then to deal with the turnover of the free energy change during water splitting $\Delta G_{\mathrm{H_2O}}$.

In the photovoltaic system excitation energy will always be lost due to electronic or molecular relaxation and vibration processes. The heat difference will account for the entropy turnover $Q/T = \Delta S$. The photovoltaic energy can be optimized by minimizing ΔH_{ph}. If light is exciting electrons just across the forbidden energy region of the semiconductor (Fig. 2b) ΔH_{ph} would correspond to the energy gap E_{G} of the material. If the absorbed photon energy is much higher, then ΔH_{ph} is correspondingly higher. The efficiency of the photovoltaic process is correspondingly

$$\eta_{\mathrm{ph}} = \Delta G_{\mathrm{H_2O}}/\Delta H_{\mathrm{ph}} \tag{2}$$

In order to determine the efficiency for water splitting for the purpose of hydrogen generation entropy considerations will also have to be included. The efficiency will, therefore, depend on the temperature-dependent enthalpy change $\Delta H_{\mathrm{H_2O}}(T)$. It follows for the ideal case:

$$\eta_{\text{el-ideal}} = \Delta H_{\mathrm{H_2O}}/\Delta G_{\mathrm{H_2O}} \tag{3}$$

Practical electrolysis includes losses so that the efficiency becomes

$$\eta_{\mathrm{el}} = \Delta H_{\mathrm{H_2O}}/\left(\Delta G_{\mathrm{H_2O}} + \text{losses}\right) \tag{4}$$

A thermoneutral potential E_{tn} is known where no heat turnover is observed during electrolysis. It is found at:

$$E_{\mathrm{tn}} = \Delta H_{\mathrm{H_2O}}/zF = 1.48\ \mathrm{V} \tag{5}$$

If we substitute Eqs. (2) and (4) into Eq. (1) we obtain the efficiency of hydrogen generation via photovoltaic water electrolysis

$$\eta_{\mathrm{phel}} = \Delta H_{\mathrm{H_2O}}/\Delta H_{\mathrm{ph}}\left(1 + \text{losses}/\Delta G_{\mathrm{H_2O}}\right) \tag{6}$$

From this formula (6) it can be deduced that the efficiency for hydrogen generation via photoelectrolysis can be maximized by making the technical–electrochemical losses small as compared to the Gibbs free energy change for water electrolysis $\Delta G_{\mathrm{H_2O}}$. If this can be done it is simply the ratio of the enthalpy for water electrolysis and the enthalpy for the photogenerated charge carriers, which is determining the efficiency η_{phel} for hydrogen generation. It is recognized that by well matching the corresponding enthalpies (Fig. 2) and reducing trivial technical–electrochemical losses the efficiencies for the photovoltaic hydrogen generation can approach 100%. In other words nearly all photovoltaic energy generated by the solar cell can be converted into hydrogen energy provided the catalytic conditions for water splitting are so favorable that the optimization needed can indeed be approached.

This formula (6) derived for photovoltaic hydrogen generation is significantly more optimistic than previous efficiency estimations for photovoltaic water splitting, which consider different cumulative secondary losses [8]. The relevance of relation (6) has been tested experimentally by using a combined silicon–aluminum–gallium–arsenide tandem solar cell, which generated photovoltaic energy with 20% efficiency (Fig. 3). It was directly fitted with catalytic metallic contacts consisting of platinum black and ruthenium dioxide for hydrogen evolution and oxygen evolution respectively. Placed in contact with water hydrogen and oxygen evolved resulting in an effective efficiency for hydrogen generation of 18.3%. This means that more than 90% of photovoltaic energy could indeed be converted into chemical energy of hydrogen [9].

Fig. 3 explains the set-up of this system and the energy conversion elements involved. This experiment projects a quite optimistic picture for long-term photovoltaic hydrogen production. Already this laboratory experiment demonstrates that artificial systems for photo-induced generation of chemical energy can be 36 times more efficient than biomass production in the agro industry where 0.5% efficiency is achieved for chemical fuel generation with a sugar cane crop of three harvests during one year. It does not have to be mentioned that an additional very essential advantage is that no fertile land needs to be consumed for photovoltaic generation of chemical energy.

As already indicated photovoltaic tandem and triple cells have reached efficiencies between 30 and 40% and future solar cells may become even more efficient. Approximately 90% of this efficiency is expected to be available for hydrogen energy generation provided the photovoltaic generator and the electrolysis system are well matched (as explained in Fig. 2). This will guarantee that abundant sustainable chemical energy can be generated that way using a comparatively low surface area of the earth.

There is, however, a key problem, which requires more in-depth considerations. It is the cost factor of photovoltaics. Present photovoltaic solar cells still generate energy, which is 10 times more costly than energy generated from fossil fuels. What are the prospects that this energy may become reasonably economical within the next decades?

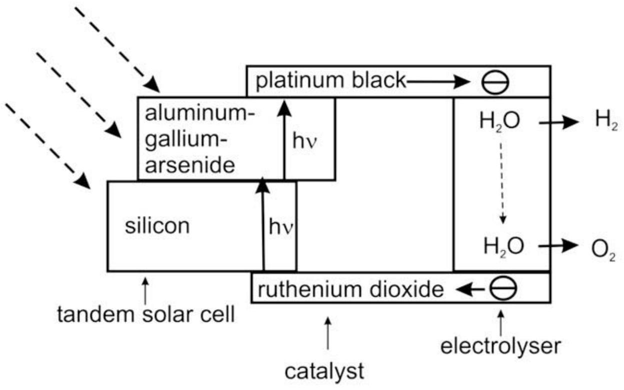

Fig. 3 – Simplified illustration of set-up, which yielded a photovoltaic hydrogen production efficiency of 18.3% or over 90% of the photovoltaic energy output (20%) [9].

3. The problem of cost reduction of photovoltaic technology

During its development over more than 50 years silicon photovoltaic technology has seen a significant cost reduction. A characteristic learning curve was thereby observed. Every doubling of cumulated production decreased production cost by approximately 20% (Fig. 4). Since photovoltaic energy is still 10 times more expensive than energy from fossil fuel the observed learning curve appears to be too shallow. It is, however, known that learning curves can be influenced by different factors. One is of course research. Significant scientific progress could accelerate the learning curve. However, the expectations in the case of crystallized silicon solar cells are not too high since the cells are already reasonably efficient and cutting silicon wafers thinner and thinner has obvious limits.

Additional possibilities for improving the learning curve are experiences gained during production and during operation of photovoltaic systems. If sufficient subsidies are given to support industrial interests the chance for learning will increase and it may be expected that the learning curve for photovoltaics will become steeper.

Today, due to significant subsidizes in individual countries, photovoltaics is experiencing a real boom in the development. Countries like Germany, Spain, and Italy have passed laws, which oblige electricity companies to purchase photovoltaic power between 40 and 50 € cents per kWh (the industrial cost of electricity is approximately 3 € cents per kWh and for private consumers it may reach 20 € cents per kWh). During recent years the solar cell production grew very fast. The newly installed PV power amounted to 1650 MW_p for 2006, which corresponded to a 17% increase compared to the year 2005. However, peak watt means the power measured at noon in full sunshine. To calculate the average power at disposition the total value has to be divided by a factor of 5–7. This means

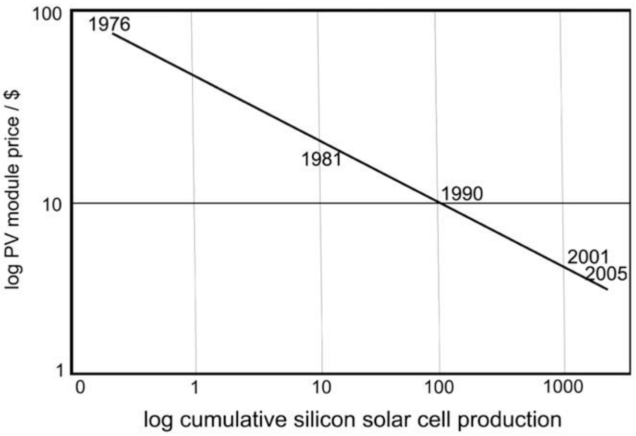

Fig. 4 – Reconstructed double logarithmic plot for cost reduction of PV panels since 1976 (2001 $ value) in dependence of cumulative production.

less than 400 MW of PV power have been added worldwide during the year 2006. The installations would probably have to be replaced every 25 years. The total electricity need of our present world is, however, in the range of 2000 GW and is expected to increase to 6000 GW by the end of this century. Electricity generation for hydrogen fuel for transport and industry is not considered in this estimate. Three to four times as much electricity will accordingly be needed for a sustainable energy economy. These considerations show the challenge, which photovoltaic hydrogen generation is actually facing. The order of magnitude of PV production has to be increased dramatically. This is only to be expected when the costs for photovoltaic systems are falling drastically. At the moment the scarcity of solar-grade silicon has temporarily even increased the price of silicon solar cells, so that the cost decrease shown in Fig. 4 is slowing down. It is for this reason that increasing interest is projected onto thinner (200 μm) silicon wafers and on thin layer photovoltaic technology in general. Industrial priorities are the development of low temperature processing, the increase of the open circuit voltage for a-Si:H/c-Si hetero-structures, and the displacement of the front grid contact to the rear side of the cell to increase the short circuit current. At present the market share for amorphous silicon, cadmium telluride and copper–indium–diselenide–disulfide thin film solar cells is 7.8%. It is hoped that the efficiency of stable amorphous Si can be increased to 10%. Numerous factories are presently being built up to produce thin layer photovoltaic panels. Up to 2012 thin layer photovoltaic cells are expected to reach a share of more than 20%. By that time it is hoped that the production costs for newly developed thin layer photovoltaic equipment would have significantly decreased. Thin layer photovoltaic cells have the advantage that they consume less material and need less time and energy for material production. They also open new application possibilities especially where flexible and transparent photovoltaic cells are requested.

Seen altogether, however, it may be concluded that photovoltaics shows a very dynamic development on a high cost level supported by significant subsidies. The learning curve for silicon solar cells (20% cost reduction with every doubling of accumulated production) appears to be much too slow to have a significant large-scale impact on photovoltaic hydrogen production during the next one to two decades. Thin layer photovoltaic solar cells promise faster progress, however, the photovoltaic materials developed include rare and toxic elements, which are not suitable for the scale of mass production, which would be needed for a sustainable energy economy.

We have realized that due to expected high efficiencies photovoltaic hydrogen production could become a very significant clean energy technology for the future. But the field is now faced with the situation that development of economic photovoltaic cells is a real bottleneck. In detailed studies of the economical prospects of photovoltaic hydrogen have even come to the conclusion that it would be significantly more economic to use photovoltaic electricity directly until approximately 50% of the electricity is derived from sustainable sources (these studies include even the electricity from much cheaper wind energy). Such a scenario is not to be expected before 2030 [10].

This situation justifies the question whether there is a parallel strategy imaginable leading to cheaper alternative photovoltaic systems. The photovoltaic principle applied in silicon solar cells, which requires very stable materials produced at high temperature, is not the only photovoltaic principle applicable. In fact, electricity generation in the photosynthetic membrane and in laboratory nano-solar cells is possible due to a different mechanism. It appears, therefore, to be reasonable to investigate whether a redirection and intensification of photovoltaic research efforts towards new principles could possibly lead to a faster broad commercialization of photovoltaic cells for hydrogen production.

4. Alternative routes to cost-efficient photovoltaics

After half a century of silicon solar cell research and with over 90% of research efforts directed at silicon, solar cells are still fabricated by cutting silicon slices, doping and chemically treating them. The strategy, which is followed with this kind and with related photovoltaic cells, is simply to in-build a thermodynamic potential gradient into the photovoltaic structure. This gradient of chemical potential, which is typically generated as a p–n doping gradient, separates electronic charges generated by light and produces the photocurrent (Fig. 5b). Such a strategy, of course, requires a material, which is able to sustain the thermodynamic potential gradient over many years and up to three decades. In other words, the doping elements should not diffuse away and annihilate the thermodynamic potential gradient. The generated electric

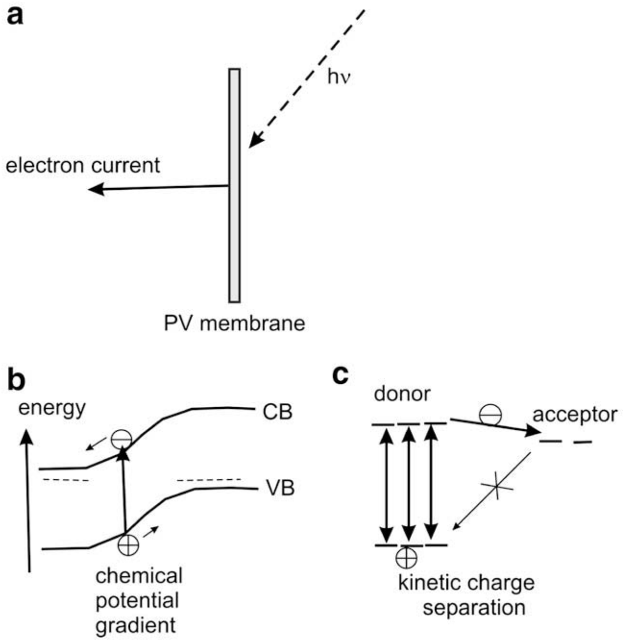

Fig. 5 – (a) A solar cell is just a membrane which allows electrons only to pass in one direction. The mechanism for rectification can be based on an inbuilt thermodynamic potential gradient (as in classical solar cells via p–n doping) (b) or it can be based on kinetic rectification (as in dye or polymer solar cells) (c).

field should not be able to destroy itself by activating undesired ionic currents. Only the most stable materials can sustain such a thermodynamic drive. And this is apparently the reason why quite few materials are suitable for this type of photovoltaic energy conversion principle. Most materials, which can easily be deposited on substrates and which may be composed of nano-particles, cannot sustain such thermodynamic gradients. They would just neutralize themselves within a comparatively short time.

Recent progress in photovoltaic solar cell research has, however, shown that nano-materials can nevertheless be used to operate photovoltaic cells. Dye solar cells and polymer–fullerene solar cells are interesting examples. Another example is, of course, the photovoltaic energy system of photosynthetic membranes in which loosely assembled molecular nano-particles are able to convert light into electricity. Dye solar cells have been developed 35 years ago as bioanalogue model systems for primary photosynthetic energy conversion [11,12] using chlorophyll extracted from spinach and related dyes. But these dyes and other dyes proved not to be stable. On the basis of a ruthenium-based dye improved cells have more recently seen a quite dynamic research and development activity [13]. But there are problems which so far have prevented commercial application [14,15]. Polymer solar cells have also a longer history and were originally modeled according to the understanding of classical photovoltaic cells. But they have essentially improved after the addition of fullerene molecules, which are critically important for the now active mechanism [16,17]. Unfortunately their high instability could not yet be overcome.

In contrast to classical silicon photovoltaic cells, it is not an inbuilt thermodynamic potential gradient, which is generating photovoltaic electricity in nano-solar cells. It is rather the fact that molecular or interfacial mechanisms are involved, which allow electrons to migrate only into one of two directions. In the case of the polymer–fullerene solar cell this means that the fullerene is easily accepting electrons but returning them in a very sluggish way. This allows the separation of electrons from holes and to conduct them to the electric contacts of the cell. In the case of the dye solar cell the current rectification is accomplished at the interface between an electrolyte and semiconducting or metallic material faces. The electrolyte used, iodide/iodine, transmits electrons favorably in one direction (iodide donates electrons) but delays electron transfer into the other direction (iodine only sluggishly accepts electrons). The significance of the rectification of electrical currents is visualized in Fig. 5c where the concept of the classical silicon solar cell is compared with the current rectification concept applied in these nano-solar cells.

It should be emphasized that the nano-solar cell photovoltaic principle has only been developed by trial and error and still now the mechanism responsible for electricity generation is discussed in a quite controversial way. In many discussions of the mechanism the critical role of a hindered reverse reaction is not recognized.

It is to some extent surprising that during half a century of photovoltaic research the opportunity of constructing entirely innovative solar cells on the basis of nano-materials has largely escaped attention. The reason for this may be seen in the fact that the photovoltaic mechanism has been approached by an equilibrium physical theory within reversible thermodynamics [18]. It is possible to derive a diode equation, which deduces the photovoltaic cell from the well-known Planck radiation formula. In this way conversion of light into electricity could be understood as the inversion of an electricity-driven light emitting diode. No space for other photovoltaic mechanisms was left.

However, photovoltaic systems are open systems with properties which are only partially reversible. Recently photovoltaic energy conversion was therefore treated as a phenomenon of irreversible thermodynamics [18]. In fact photovoltaic cells are open systems accepting light energy and releasing electricity and heat. Also entropy in form of heat is generated in an irreversible way. These are typical properties for systems subject to irreversible thermodynamics (linear range). They are known to approach a situation where minimum entropy production is observed. This condition is nothing else than the fundamental principle of least action applied to chemistry and thermodynamics. Entropy production is known to be the product of thermodynamic forces F_i and fluxes I_i. When this condition of minimum entropy production is calculated for a photovoltaic cell, it becomes apparent that entropy production, which either leads to entropy generation as heat σ_{irr} or to exported photovoltaic power W, divided by the ambient temperature T_a, is made up of two terms. They are an entropy production derived from transport phenomena, σ_d, and an entropy production derived from chemical phenomena, σ_{ch}.

$$\begin{aligned}\sigma &= \sum_i I_i F_i = \sigma_d + \sigma_{ch} = \eta_{sol}\frac{W}{T_a} + (1-\eta_{sol})\sigma_{irr}\\ &= -\sum_i j_i \nabla\frac{\mu_i}{T} + \sum_i w_i\frac{A_i}{T}\end{aligned} \tag{7}$$

where η_{sol} describes the fraction of energy available as electrical power, as compared to the fraction $(1-\eta_{sol})$ lost irreversibly as heat.

The first term in Eq. (7) (right side) involves the product of a thermodynamic potential gradient $\nabla\mu_i$ and of a thermodynamic flux j_i. The second involves the so-called chemical affinity A_i, which describes the distance of an illuminated chemical system from equilibrium, and a chemical reaction rate w_i. The chemical affinity corresponds to the Gibbs free energy turnover of the system with respect to the extent of the reaction. An inefficient photovoltaic system will see a lot of entropy production leading to heat. An efficient photovoltaic system will apply optimized morphological structures in order to generate photo-electricity, which can be extracted from the photovoltaic cell. The resulting electrical power W can be obtained from relation (7) by resolving it with respect to W. It shows that the factors which have to be controlled and optimized to allow maximum generation of photo-electricity are determined by the two entropy production terms in Eq. (7). In the first case an inbuilt thermodynamic potential gradient (doping gradient) will generate a directed photocurrent as observed in a classical silicon solar cell. In the second case no thermodynamic potential gradient is present but the direction of electron transfer is expressed by the chemical reaction rate w. The driving force in this case will essentially be the chemical affinity A of the photochemical process, which describes the distance from chemical equilibrium, created by photo-excitation.

This irreversible thermodynamic analysis [19] clearly shows that it is not necessary for photovoltaic cells to sustain a thermodynamic potential gradient over a long time period as required by our present day solar cells. It is equally possible to arrange nano- or molecular materials in such a way that electrons only proceed into one direction while exploiting the driving force generated by the photochemically activated system. In fact, in the case of the polymer–fullerene solar cell it could be determined that the photopotential generated corresponds to energy level differences between the absorber (polymer) ground level and the electron first acceptor level (fullerene). The cell ceases to function when the fullerene is replaced by polymers with similar electronic levels but without the property of drastically inhibiting the back reaction of the electron. The last term in Eq. (7) which is responsible for this ''kinetic'' solar energy conversion would simply disappear, because both affinity A and reaction rate w would tend towards very small values.

Fig. 6 offers a simplified view of the principles involved in kinetically determined photovoltaic solar cells. Basically, the affinity, the distance from chemical equilibrium, generated by light produces an electromotive force. This is the well-known mechanism applicable for the conversion of chemical energy into electrical energy in electrochemical batteries. If the electrolyte in front of an electrode would contain photoactive components, photo-induced power would be observed. This type of solar cell system has been described as a photogalvanic cell [20]. The efficiency gained from this type of solar system is low, typically below 1%. The main reason is the high probability for a reverse reaction of electrons from the electrode. Current rectification is needed so that the electrons know where to go. This is accomplished in the kinetically determined solar cell by the chemical reaction rate w in combination with vectorial processes, which together generate the photocurrent I_{ph}. In practice, and taking the polymer–fullerene solar cell as an example, this means that the excited electrons, when transferred to the fullerene, cannot easily react back and percolate towards the solar cell contact.

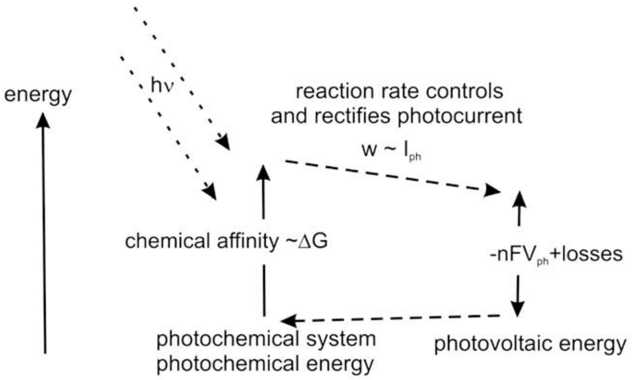

Fig. 6 – Scheme showing how light generated chemical affinity (~ΔG) is producing the electromotive force (the photovoltage V_{ph}) like in an electrochemical cell, while an (oriented) reaction rate w is responsible for the photocurrent I_{ph} (n = charges turned over, F = Faraday constant).

Kinetically determined nano-solar cells seem to offer real opportunities for the long term because solar cells composed of nano-materials and cheap organic compounds become feasible. When thermodynamic potential gradient don't have to be built into solar cell devices but when the driving force only arises during illumination this would be a significant advantage for material development.

A change of technological principles in photovoltaic technology, even if it takes many years, would be highly desirable in order to make the learning curve for photovoltaic hydrogen technology steeper. The cost of photovoltaics is such an important factor that every possible effort should be encouraged towards potentially cheaper photovoltaic technology. One should, therefore, encourage the deviation of significant research money from classical solar cells to innovative kinetically determined solar cells.

In this context also fundamental research is required because the presently mostly used electron transfer theory by Markus mainly focuses on largely reversible electron transfer processes and weak interaction mechanisms. What has to be understood towards kinetically determined solar cells is electron transfer involving polarization of the molecular environment. This is excluded in the Markus theory for electron transfer. It is, however, needed to affect the environment in such a way that the electron cannot find the way back, which makes the charge separation process irreversible and vectorial (Fig. 5a and c). The theoretical challenge involved is outlined in Fig. 7. Science up to now was mostly concentrated on electron transfer with weak or negligible interaction with the molecular surrounding (Fig. 7a). In the future, we need to study mechanisms where electron transfer exerts a feedback activity on the molecular environment so as to interrupt the reverse pathway.

If such mechanisms can be developed and controlled it would no longer be necessary to build permanent thermodynamic potential gradients into solar cell structures. The electrons would kinetically find the unidirectional pathway away from the photo-excited system and simpler and potentially cheaper nano-solar cells would become feasible.

In order to extend our vision of the challenges it is interesting to investigate how nature has accomplished kinetic charge separation within the photosynthetic membrane. Amazingly it has adapted a quite sophisticated mechanism which is explained in Fig. 8, because it can serve as an example of how to construct innovative kinetically determined solar cells.

When electrons are excited within the photosynthetic reaction center a so-called radical pair is formed. Within this the singlet state is converted into the triplet state while simultaneously inducing a change of the polarization of a nuclear spin. During this process some energy is dissipated as heat so that the entire process of spin-reversal is not a quantum but a combined quantum-classical process. The consequence is that the electron from the radical pair triplet cannot react back because it would have to overcome a small activation barrier (0.2 eV) before having to invert the electron spin, which is a highly improbable process (Fig. 8b). Photosynthesis started to function with cyanobacteria approximately 2.3–3.4 billion years ago. Different organisms ranging from algae to plants have adopted this process and all use the

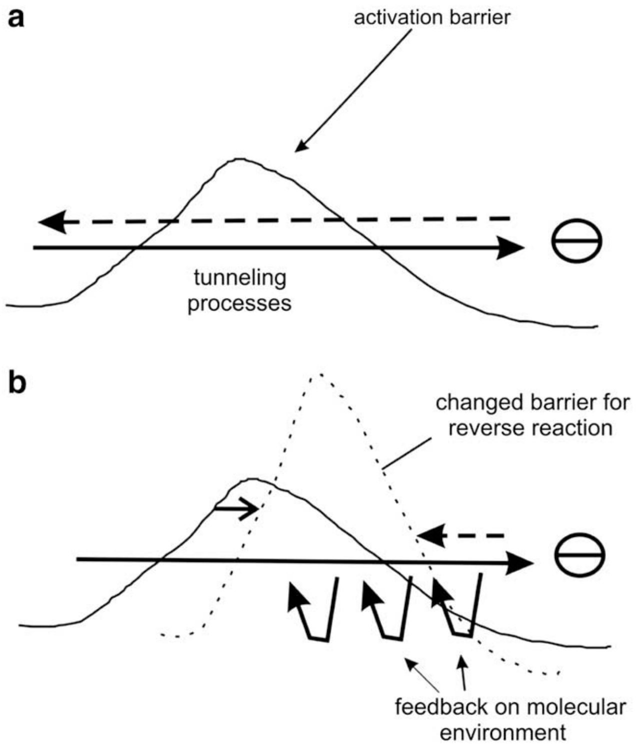

Fig. 7 – This figure outlines the main theoretical and experimental challenge towards kinetically determined nano-solar cells. While in classical electron transfer theory (Marcus theory) the electron cannot get involved in a feedback reaction with the molecular environment (a), such a feedback is required for kinetically determined solar cells (b).

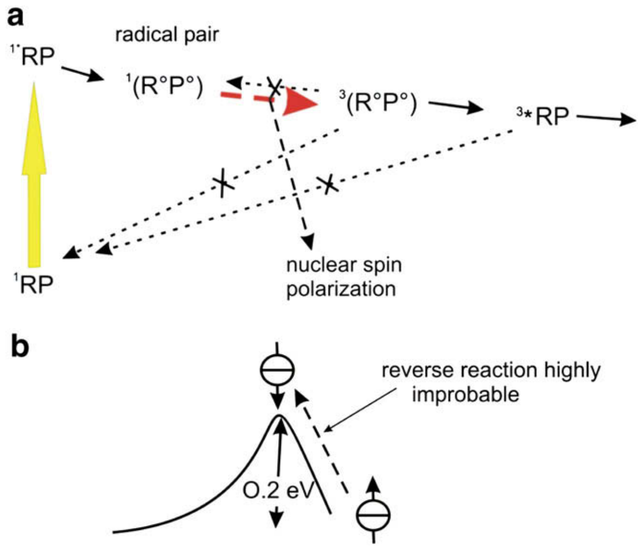

Fig. 8 – (a) Scheme explaining how a photo-induced nuclear spin polarization process inverts the electron spin so as to make its reverse reaction highly improbable, as explained in (b).

same photochemically induced dynamic nuclear spin polarization to avoid reverse reaction of the electron. This indicates that the strategy for rectifying electronic currents in the absence of a significant thermodynamic potential gradient was an important evolutionary step, which could not easily be replaced by other mechanisms. This fact should encourage modern science to really concentrate on ways of tailoring solar cells by kinetically controlling electron transfer processes in order to develop kinetically functioning semipermeable photovoltaic membranes (Fig. 5a and c).

It is of significant interest for photovoltaic hydrogen technology that a major research effort is oriented towards kinetically determined solar cells. They promise cheaper and easier production techniques and thus a faster track towards a photovoltaic hydrogen economy.

5. Photovoltaics and accompanying technology

There have been several proposals that Europe should produce photovoltaic energy in the Sahara desert of northern Africa in order to generate hydrogen for shipment or piping to Europe. The main argument was, of course, the 50–80% higher radiation input. It is, however, a remarkable fact that today's silicon solar cells, when placed into hot sunshine, which may increase their surface temperature from 10 to 80 °C, will loose one-third of their solar efficiency. This means a 15% efficient solar cell will then only work with 10% efficiency. The advantage of higher solar input is consequently lost to a large extent and this is due to the still quite simple and insufficient secondary technology involved in photovoltaic panels. The energetic end use value of imported hydrogen would roughly be the same as that of locally produced photovoltaic electricity [21].

Our present solar cells basically absorb all solar energy, even those parts, especially in the infrared, which are not at all useful. In addition, a glass cover works towards a greenhouse effect, which keeps the heat inside. How solar systems should be constructed to largely avoid heating can be seen in the example of green leafs of plants. The use of evaporating water for cooling wherever water is common – but in desert regions green leaves have to stay cool even without evaporation. Leafs are optically optimized in such a way that only the required and actually used radiation is absorbed. All the rest is either reflected or passing the green leafs. In addition, very light structures providing low heat capacities and optimal aerodynamic movements for getting rid of heat keep the temperature under solar conditions typically below 40–50 °C. There is an urgent need to optimize photovoltaic cells with respect to the temperature reached and biological systems, which had similar problems, could act as interesting examples for bionic studies. First steps in this direction have been made [22]. Much improved secondary photovoltaic technology will contribute towards a decrease of effective costs of photovoltaic energy.

An important cost factor of photovoltaics is also encapsulation. The glass/EVA (ethylene-vinyl-acetate)/aluminum structures of PV panels make up to one-third of the total costs. Organic encapsulation materials will especially be needed for flexible thin layer solar cells and they promise much lower costs. However, suitable materials have still to be identified and very little research is proceeding in this direction. Studies of protective transparent layers which plants use on green needles, leaves and stems suggest that besides waxes, they contain reducing components like alcohols and esters, which act as antioxidants against photochemical damage. In addition they contain terpenes, especially triterpenes, which have antibacterial, fungicide and antiviral properties. The protective coating of the Bushman candle, Sarcocaulon patersonii, which reaches a thickness of 1 mm because it has also to resist frequent sand blowing and abrasion, has been tested as protection for thin layer solar cells [23]. It consists to 80% of triterpenes, which are technically not known as materials for encapsulation. It is obvious that future organic photovoltaic encapsulation materials will have to combine at least four different properties. They will have to provide favorable optical and mechanical properties. They have in addition to provide antioxidants to fight photochemical degradation and they will have to contain ingredients, which keep destructive microorganisms off. All together the encapsulation material must become much cheaper than present materials for the price for photovoltaic energy to decrease significantly.

6. Electricity and hydrogen: competitors and partners

There is no doubt that electricity has become a very fundamental and diversified energy system for our industrial civilization. Many machines and devices can be elegantly operated using electricity. The same is also the case for biological systems where electrical or better electrochemical energy plays a fundamental role as an intermediate energy form in practically all biological activities. In photosynthesis light is first converted into electricity and subsequently into chemical energy. When animals are eating chemical energy is converted into electrical energy before being reconverted into chemical energy of specialized fuels. Also biology knows, of course, electrical energy systems, such as electrically membranes and electric signal transmission in nerves. It knows sensors and also computer activity as performing in our brain. While industrial technology uses mostly electronic circuits for its electrical systems biology intensively applies protonic electrical circuits. It uses them to synthesize chemical energy carriers as well as to drive rotating motors for propagation (the flagella of bacteria).

During the photosynthetic process biology uses light generated electricity in order to split water. Hydrogen is not handled as a gas but finally attached to carbon compounds, which allows generation and handling of a large variety of useful energy carriers and chemicals.

But nature has also learned to efficiently reconvert the organic compounds into electricity via the fuel cell principle. This became possible because nature was able to evolve very efficient catalysts, which facilitate multi-electron transfer at ambient temperature. In technology we are presently aiming at an energy system, which is organized in a similar way but which is based on the simplest possible energy carrier, hydrogen. As Fig. 9 (right side) explains, light is captured to produce electricity, which generates hydrogen via electrolysis. Hydrogen can drive a fuel cell, which in turn can produce electricity for the most diverse applications. Both systems, the biological (Fig. 9, left side) and the technological one, are based on an efficient inter-conversion of light into electrical and chemical energy. Nature was able to develop efficient energy catalysts for multi-electron transfer. It can consequently use complicated molecules for intermediate energy storage.

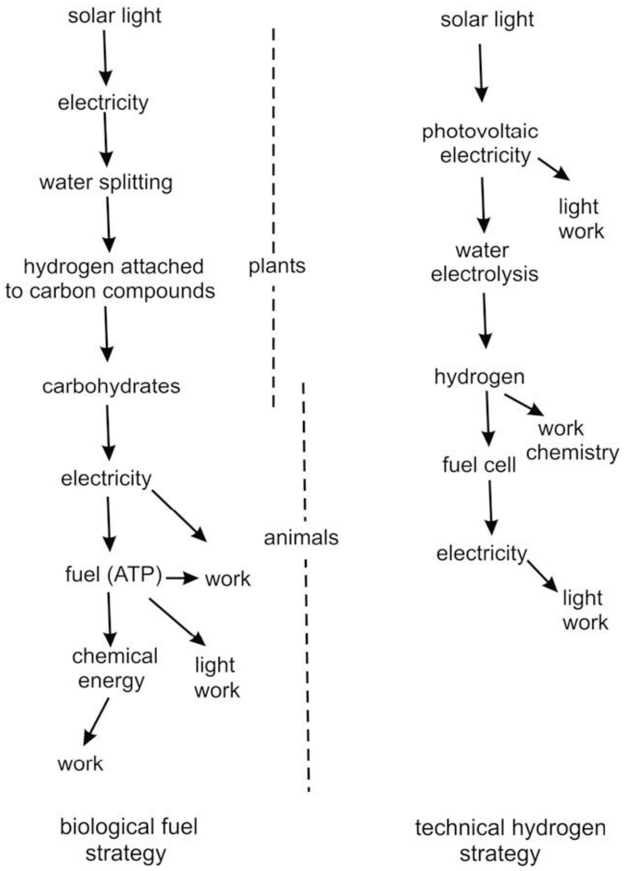

Fig. 9 – Schemes comparing the flow sheets of the biological fuel strategy with that for hydrogen technology.

Technology at the moment still struggles with efficient (and economic) catalysis of hydrogen turnover in electrochemical devices. It appears that nature apparently did not choose hydrogen for intermediate energy storage because hydrogen would have to be handled in gas form, which would have dramatically affected the whole infrastructure. Carbon compounds are of course also needed for structural materials and the chemical infrastructure. Technology, on the other hand, takes advantage of the easy exchange of electrons between electrodes, protons and hydrogen for inter-conversion of chemical and electrical energy. On the other hand, of course, it has to live with the disadvantage of a more complicated energy storage technology via hydrogen. It may be that at the long term, when more sophisticated and efficient catalysts become available, hydrogen will partially and gradually be replaced by energy-storing, hydrogen-containing carbon compounds, which can be handled in the liquid state.

From these considerations, it can be deduced that electricity and hydrogen may develop to become very interdependent partners in an elegant and well-balanced energy system. The main domains of electricity will be light production, communication and industrial production. The main domains of hydrogen may become energy storage for making solar energy available at all times and it may also be transport via fuel cells. Of course, also for chemical industry hydrogen will become important where relevant industrial sectors may become clean by replacing carbon by hydrogen for steel production and comparable chemical technologies. Evidently hydrogen will also play an increasing role in air transport and space technology.

7. Concentrated or decentralized photovoltaic hydrogen technology

After demonstrating that more than 90% of photovoltaic energy could be converted into hydrogen energy and after discussing ways to decrease the still forbiddingly high price of photovoltaic energy, we should concentrate on the question of how photovoltaic hydrogen should later be handled. Should it mostly be produced in centralized electrolysis stations based on highly optimized and efficient large installations? Or should there simultaneously be a major effort to develop photovoltaic hydrogen technology on a small scale so that it becomes accessible for very different technological energy products.

7.1. *Electrolysers for large-scale hydrogen production*

Today, approximately 600 billion Nm^3 hydrogen are produced worldwide, mostly via reforming from natural gas in refineries. This amount of hydrogen from fossil energy corresponds to approximately 1.5% of the world energy consumption. Much less than 1% of hydrogen is generated via electrolysis. Because of high costs such production activities are typically linked to huge waterpower installations like the Aswan dam where surplus of electric power is put to practical use. Today basically three technologies are available, which convert electricity into hydrogen via electrolysis. They comprise alkaline electrolysis, electrolysis in acid medium (PEM-electrolysis) and water vapor electrolysis at high temperatures. From the Gibbs equation

$$\Delta G = \Delta H - T\Delta S \tag{8}$$

a reversible decomposition voltage of 1.23 V can be deduced as

$$U_{\mathrm{rev}} = E_0 = \frac{\Delta G^0}{zF} = \frac{237\ \mathrm{kJ\,mol^{-1}}}{2{\cdot}96486\ \mathrm{C\,mol^{-1}}} = 1.23\ \mathrm{V} \tag{9}$$

as well as a thermoneutral decomposition voltage of 1.48 V

$$U_{\mathrm{th}} = E_0 = \frac{\Delta G^0}{zF} = \frac{286\ \mathrm{kJ\,mol^{-1}}}{2{\cdot}96486\ \mathrm{C\,mol^{-1}}} = 1.48\ \mathrm{V} \tag{10}$$

In Fig. 10 the principle of an alkaline electrolyser is compared with that of a polymer electrolyte membrane (PEM) electrolyser. The alkaline electrolyser (Fig. 10a) typically uses potassium hydroxide as a basic electrolyte and an OH^- permeable diaphragm. The membrane is based on nickel oxide on a nickel mesh in combination with zirconium oxide on polymer. For the anode reaction alloys of nickel/cobalt/iron are used as well as Raney nickel (Ni–Al). For the cathode nickel and platinum/carbon are used. The overall reaction of water electrolysis into hydrogen and oxygen can be split into the following two partial reactions:

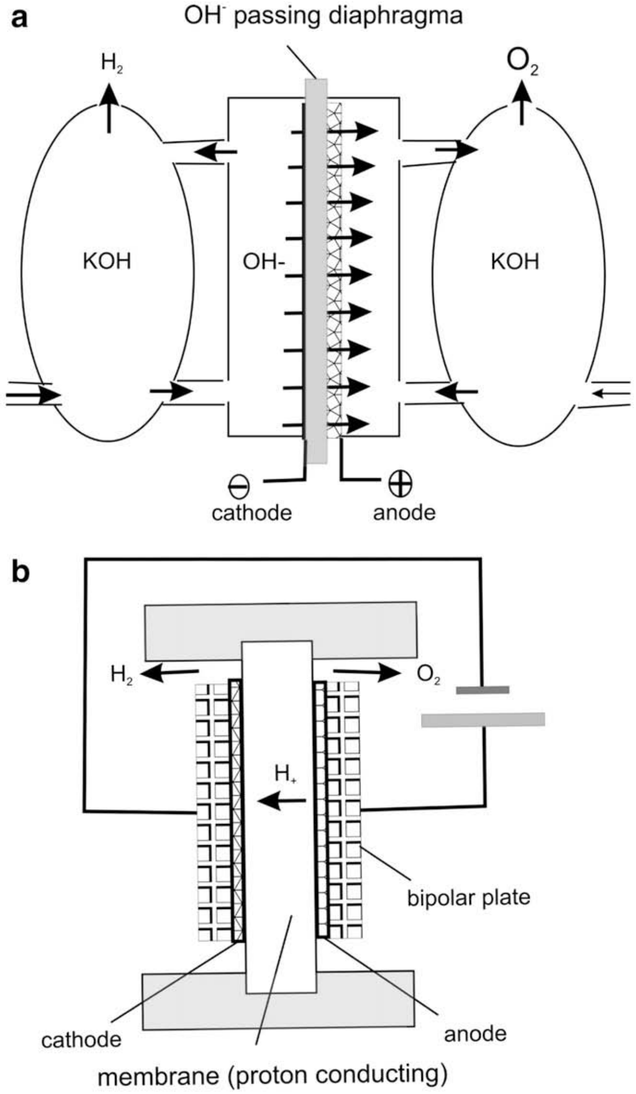

Fig. 10 – The structure and function of an alkaline electrolyser (a) is compared with that of a polymer electrolyte electrolyser (b).

$$\text{Cathode}: \quad 2H_2O + 2e^- \rightarrow H_2 + 2OH^- \tag{11}$$

$$\text{Anode}: \quad 2OH^- \rightarrow O_2 + H_2O + 2e^- \tag{12}$$

A stack design is typically used and current densities of 200–400 mA/cm^2 are normally operated with applied pressures between 7 and 30 bar and up to 200 bar. Commercial pressure electrolysers are available for hydrogen generation between 1 and 760 Nm^3/h corresponding to a power range between 5 and 3.6 MW. At the Aswan dam and near Cusco, Peru, installations of 156 and 22 MW respectively are operating.

Pure water instead of KOH can be used in polymer electrolyte membrane (PEM) water electrolysers in combination with a catalyst covered semi-permeable membrane of a perfluorated polymer with sulfonic acid groups as solid electrolyte. PEM electrolysers are based on a simpler system structure without pumped potassium hydroxide circuit and can be operated at higher current densities and efficiencies. However, more expensive materials are needed to cope with increased corrosion problems. The following partial reactions are proceeding:

$$\text{Cathode}: \quad 2H^+ + 2e^- \rightarrow H_2 \tag{13}$$

$$\text{Anode}: \quad H_2O \rightarrow 1/2O_2 + 2H^+ + 2e^- \tag{14}$$

This PEM technique has, therefore, mostly found access to the lower power range of H_2 production (smaller than 10 Nm^3/h). The function of a PEM electrolyser is schematically shown in Fig. 10b. Typically platinum is used on the cathode and iridium on the anode. Variations are possible especially when the system operation is inversed to function as a fuel cell. Current densities of 600–1000 mA/cm^2 can be handled in PEM electrolysers. Several companies are offering PEM electrolysers in the power range between 100 W and 50 kW. PEM electrolysers can have efficiencies exceeding 80%. However, because of their small dimension the good cell efficiency could not be transferred to the system level. A very promising device with challenging research opportunities in catalysis towards a reversible oxygen electrode is a system which can work as an electrolyser in the forward direction and as a fuel cell in the reverse reaction. A prototype with such properties has, for example, been developed by ISE Freiburg, Germany. It is expected that systems of this kind will see a systematic development to high reliability and efficiency. Because of the high cost of photovoltaic energy and the still high cost for the combined electrolyser fuel cell system, this technology is presently performing on the laboratory-scale only and in pilot installations. Because of the high relevance of this technology, it will be treated in a parallel review by Milan M. Jaksic in this journal.

According to relations (8) and (9) the voltage needed for water electrolysis will decrease with rising temperature. The reason is that increasingly more energy will be provided in the form of heat. In addition, the high temperature improves the reaction kinetics, which lowers electrical losses. This technique is known as ‘‘high temperature vapor electrolysis’’, ‘‘Hot Elly’’ from its German name and a project supported by public funds two decades ago [24].

In fact, at temperatures between 900 and 1000 °C hydrogen can be produced with 30–50% less electrical energy. The process occurs with a solid-state electrolyte fabricated as a tube, with water vapor passing through for electrolysis. On the inner cathode surface water vapor is reduced to hydrogen and the oxygen passes through the heated solid electrolyte to the anode, where oxygen is liberated. The Hot Elly process yielded 92% electrical efficiency, which is significantly higher than that obtained with lower temperature electrolysers [24]. There is today renewed interest for high temperature electrolysis, which could also be readily integrated into solar tower power stations [25]. Its cost is still too high due to the electricity cost (already the industrial, and not the 10 times higher PV electricity costs) which cannot further be reduced due to thermodynamic limitations.

On the basis of presently available technology the conversion of concentrated photovoltaic power into hydrogen via alkaline, PEM or high temperature vapor electrolysers will see a straightforward development aimed at a large market. Since this will not support the idea of a highly decentralized solar energy economy we should, however, also investigate whether photovoltaic hydrogen generation on a very small scale and with alternative techniques will find its place in future energy technology.

7.2. *Photovoltaic hydrogen production in small systems*

From biology we know that the conversion of light into chemical energy on nano- and microscopic scale can support a highly diversified and interconnected energy system. We should therefore ask ourselves whether small systems for photovoltaic hydrogen generation could not at the long term become valuable elements of a sustainable energy economy. An effort should, therefore, be made here to think about possible examples of such solar hydrogen systems.

It has previously been mentioned that a series stack of photovoltaic cells generating photovoltaic electricity with 20% efficiency could be made to produce hydrogen with an overall efficiency of 18.3%, which is more than 90% [9]. The problem with such laboratory models is that the photovoltaic systems selected cannot easily be placed into water and are not available as reasonably stable membranes, which could be used for direct photoelectrolysis of water. For this aim one could again look at the example of the photosynthetic membrane, which absorbs light in order to split water and generate a chemical energy carrier. How could such a system be technically reproduced and could it be handled in such a way as to save materials and production costs? More specifically we should ask the question, how a membrane-based photovoltaic generator for hydrogen could look like and what efforts would be needed to develop such a system? From the beginning it should be very clear that photovoltaic hydrogen should involve a separate generation of hydrogen and oxygen in different spaces in order to avoid production of an explosive gas mixture. Our studies led us to the conclusion that the simplest geometry of a photovoltaic hydrogen generator would be a tube or a cable, which is inside separated into two halves by the photovoltaic membrane (Fig. 11a). Light should enter this cable from one side via a transparent plastic linear lens, a strip of transparent plastic along the tube. Light should be reflected from the internal cable surface and absorbed by the photovoltaic membrane. This membrane should have the property of being corrosion stable and generating oxygen on one side and hydrogen on the other side. Periodically along the membrane there should be sections able to exchange protons in order to avoid the build-up of pH gradients. A tube or a cable, which is separated into two halves via a hydrogen generating membrane, could be used as a versatile solar energy converter in highly decentralized applications. The water running through this membrane-separated tube could carry hydrogen on one side and oxygen on the other side. Rolled up into a coil it could serve as a solar energy collector on the roof providing both hydrogen to a fuel cell via a gas exchange unit and solar heat to a heat-storing unit (Fig. 11b).

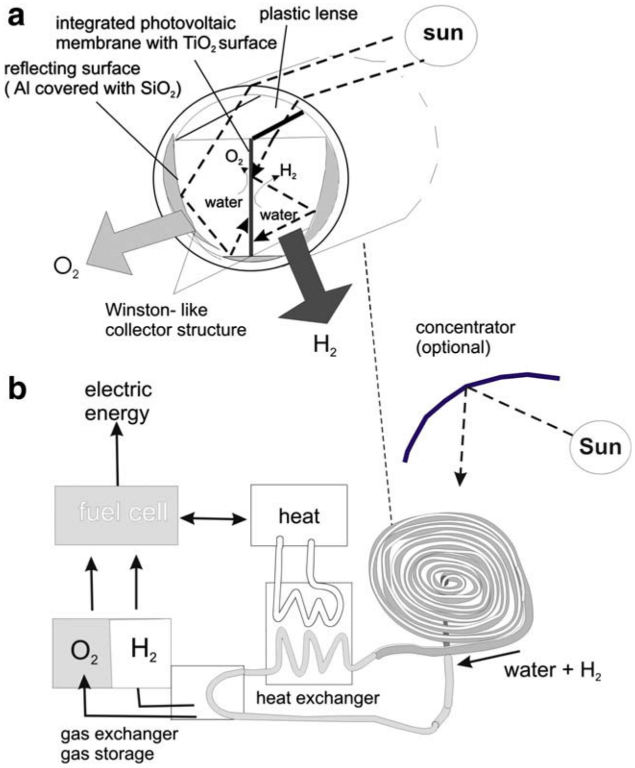

Fig. 11 – The simplest geometry for photovoltaic hydrogen collection in small dimensions is a water carrying tube, separated by the hydrogen/oxygen generating membrane. (a) Structure of the tube, (b) tube acting as solar collector and supplying hydrogen and heat.

A major challenge is, of course, the development of a hydrogen generating membrane, which is sufficiently solar energy efficient and stable at the long term. The structure of this membrane should be modeled on the basis of the example of the photosynthetic membrane in which electrons are excited via two subsequent quantum steps. This is necessary in order to well utilize the available spectrum of solar energy and also in order to generate a potential difference exceeding 1.23 V needed for water splitting. If only one excitation step would be selected only solar light with a wavelength smaller than 600 nm could be applied. In contrast to the photosynthetic membrane where hydrogen from water splitting is finally attached to organic molecules the artificial fuel generating membrane would, during illumination, produce oxygen on one side and hydrogen on the other. A first effort to develop such a membrane was undertaken in our laboratory [26]. The idea was to use a titanium foil linking a photocatalytic TiO_2-layer on one side and a modified CIS (copper–indium–gallium–selenide) solar cell on the other side. A photoreaction would induce TiO_2 to oxidize water to molecular oxygen on one side. The excited electron would then pass from the TiO_2-conduction band via the titanium into the valence band of the CIS thin layer solar cell. From there the second photo-process would excite the electron into the conduction band of the CIS-cell from where it would pass via an optical oxide window to the water interface where hydrogen could be developed. The standard optical window of the CIS-cell is zinc oxide. Zinc oxide is known to be unstable in the presence of water and UV illumination. For this reason the CIS-cell was modified replacing the zinc oxide window with a niobium-doped TiO_2-window. This worked satisfactorily, though with a smaller energy efficiency compared with a standard CIS-cell due to still needed interfacial adaptation and optimization.

At the time when this project started published reports suggested that carbon-doped TiO_2 can use blue light for photo-induced oxygen evolution [27]. Unfortunately this turned out not to be true [28]. The photocurrent generated can oxidize organic and inorganic species but not water. This presently limits solar energy efficiency of the entire membrane to the efficiency of TiO_2 for oxygen evolution with near ultraviolet light. It could, however, be shown that the entire membrane is photoactive and evolves oxygen on one side and hydrogen on the other [29]. The energetic scheme of such an artificial bio-analogue membrane for water splitting and fuel generation is shown in Fig. 12. It thus essentially combines two photo-excitation steps with two catalytic reactions, one is the liberation of oxygen from water on the anodic side and the second the transfer of electrons for hydrogen evolution on the opposite, cathodic side. Efficient and economic catalysts for hydrogen evolution from water have well been described in the literature [30].

Catalysis for efficient water oxidation and especially for photo-oxidation of water remains a major research challenge, which we will have to discuss in some detail in the following.

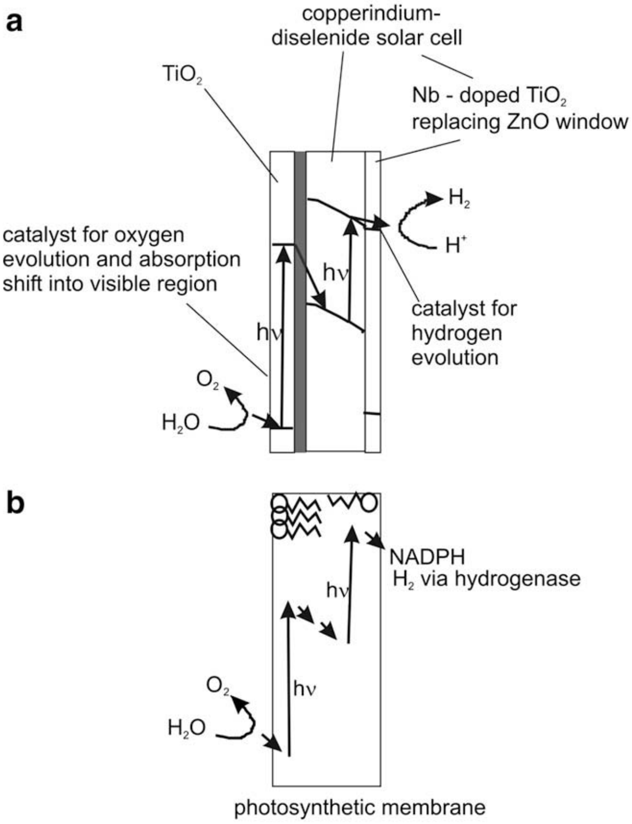

Fig. 12 – (a) Artificial TiO_2 lined water splitting membrane using two photo-excitations. (b) The photosynthetic membrane for comparison.

The hydrogen fuel technology proposed in Fig. 11 via a hydrogen generating solar collector may be an example of how photovoltaic hydrogen technology could be decentralized and scaled down to be used in small applications and even integrated in individual innovative solar energy powered devices. It needs much less material and infrastructure compared to a centralized photovoltaic hydrogen production. It could also become the basis for much creativity with respect to decentralized solar energy applications. For example, solar energy could be converted into hydrogen, which is stored and reutilized via a small fuel cell for powering laptops and other equipment of everyday life. In order to accomplish this, we have to learn much more about miniaturized systems for water splitting and hydrogen generation. If we learn to handle such miniaturized water splitting and fuel generating technology we could approach a similar flexibility as nature via its diverse photosynthetic systems both microscopically and macroscopically. Today photosynthesis works not only in the tropical and temperate regions but also in the Antarctica down to −18 °C where lichens, which combine algae and fungi, have adapted to generate fuel under such extreme conditions. Knowledge in this field will, at the long term, also benefit human technologies aimed at extreme conditions such as space exploration.

8. The key role of photocatalytic water splitting for hydrogen generation

It has been mentioned that the problem of catalysis for hydrogen evolution from water has been essentially solved with abundant and cheap materials [30]. However, hydrogen energy is only sustainable when the electron for proton reaction is ultimately extracted from the water during oxygen evolution. During combustion, hydrogen combines again with oxygen for water generation. Since the first modern energy crisis, 35 years ago, solar-induced water splitting has been in the focus of interest [2], though with very fluctuating and far too low financial support. It is again in the focus of interest today with its soaring fossil fuel prices [31]. The key problem with oxygen liberation from water is that the most efficient thermodynamic potential at $E_0 = 1{,}23\,\text{V}$ is described as a 4-electron extraction process. This means that the transfer of all 4 electrons is subject to a similar low energy turnover. If the extraction of one of these electrons from water requires significantly more energy, this will make the entire process correspondingly less favorable. Extraction of four electrons with comparably low energy turnover is, however, not accomplished in practice if not a highly sophisticated catalyst is handling the electron transfer process. If the conditions only allow extraction of one electron from water an oxidation potential of $E_0 = 2.8\,\text{V}$ will, for example, adjust. This is approximately observed at the titanium dioxide electrode when a photo-generated hole is reacting via the energetically low valence band of this photocatalytic material. The energy conversion pathway in this case is consequently very unfavorable leading to radical intermediates. A multi-electron transfer process, which is energetically needed, has to be catalyzed by a molecular environment, which safeguards the transfer of 4 electrons with approximately equivalent energy turnover. This is a significant challenge, which nature in the photosynthetic membrane has solved via a manganese complex. Two pairs of manganese ion centers in an oxide–calcium environment absorb 4 positive charges, which, in a highly catalytic process, are then neutralized by extraction of 4 electrons from water. During the last three decades all imaginable organic manganese cluster compounds have been synthesized and tested for water splitting. None of these has shown a behavior, which is nearly comparable with the properties of the biological manganese complex. A puzzling property of this complex is, by the way, that it is molecularly quite weakly bonded and that the manganese centers can easily be extracted and replaced. Because in photosynthesis water oxidation is occurring at a much lower over potential than in comparable processes in electrochemistry, we have suggested that the manganese compound extracts electrons via a kinetically self-organized mechanism [32]. The first electron transferred induces a change, which favors the second, which in turn favors the third, and the fourth. If the set of equations is solved and the feedback action is varied and optimized, it is found that the kinetic formalism can be reduced to one equation describing how the first electron is ‘‘slaving’’ the others to enable a self-organized mechanism of multi-electron transfer [33,34]. In such a process, of course, dynamic molecular changes are expected, since the manganese atoms thereby change their oxidation states and their coordination. Such necessary molecular rearrangement can, in principle, easily be handled via manganese complexes since manganese can readily change its coordination structure. If this concept proves to be correct, water splitting catalysts will have to be identified in the form of three-dimensional, disordered, and loosely arranged structures which are able to change their morphology and which can easily be penetrated by protons. And a very characteristic property of such a catalyst will be that it is able to handle electronic charges in a highly non-linear way. Such properties are, by the way, interestingly already recognized in calcium–manganese oxides ($CaMnO_3$, $Ca_{1-x}Pr_xMnO_3$) which contain the same elements as the manganese catalyst for oxygen evolution, as well as similar bond lengths within their structure. They show indeed a strong non-linear correlation between the behavior of electrons and the crystal lattice, which is dramatically affected by external forces such as magnetic and electric fields, pressure or even illumination, which changes the population of electronic states. Polarons, electrons combined with lattice distortions, are able to undergo collective movements, which give rise to such phenomena like the ‘‘colossal magnetoresistance effect’’, where small magnetic, electric, photon, or strain fields are inducing large changes in electron concentrations and thus resistivity [35–37]. Exactly this kind of collective properties is expected to give the $Ca–O_x–Mn_4$ reaction center its excellent properties as multi-electron transfer catalyst. But we have a longer way to go to understand them.

Few illuminated materials have, by the way, the properties to react with water. Nature handles all major electrocatalytic processes of energy conversion via transition metal centers involving manganese, molybdenum, iron, cobalt or copper. This, of course, suggests that coordination chemical mechanisms are involved. Indeed, semiconducting materials, which supply electrons or holes via energy bands derived from transition metals, show very specific interfacial properties by allowing a simultaneous exchange of coordinated ligands. If the semiconductor ruthenium disulfide is illuminated and polarized as an anode oxygen evolution occurs with a quantum efficiency exceeding 60% [38]. The energy gap of this material is too low to allow water splitting without applied electrical supporting potential. However, this material shows that, when electrons are turned over in such a way that water species adsorb to the interface forming hydroxide–oxide complexes, a stepwise oxidation of water may occur. In this case the dynamically changing ruthenium–hydroxide–oxide–peroxide complex provides the catalytic environment for reasonably favorable multi-electron transfer processes. This is apparently also the reason why ruthenium oxide as a metallic catalyst shows very favorable properties for water oxidation too. Photo-induced coordination chemistry is, therefore, a key to water oxidation. However, if abundant transition metals should be put to work, which cannot reach very high oxidation states, transition metal clusters will be required to accommodate four positive charges for water oxidation. This is obviously the way nature proceeded by developing the manganese complex, which contains four manganese atoms. A key precondition for oxygen evolution is, as we have seen, electron extraction via transition metal d-states, which are chemically able to react with water in a specialized catalytic environment. Similar properties are expected from the already mentioned calcium-containing manganate perovskites, which are presently under investigation. They provide holes on d-states and simultaneously are also characterized by a manganese oxide–calcium molecular environment. Such a model system may help us to learn more about parameters, which nature has optimized towards the highly efficient manganese complex. It is expected that the ability of calcium manganates to get involved in cooperative charge carrier dynamics [35–37] will turn out to be crucial for water oxidation.

During the seventies of the last century, a lot of effort was developed towards oxygen evolving electrode materials. During this time the photocatalytic properties of titanium dioxide during UV illumination were discovered [39], which conduced towards self-cleaning TiO_2 interfaces on diverse technical surfaces [40]. This special type of photocatalytic process is, as already mentioned, energetically inefficient and has, therefore, not helped to solve the problem of efficient photocatalytic oxygen evolution for energy purposes. However, TiO_2 is a very cheap and thermodynamically stable material. Efforts to catalytically modify its interfaces for energetically more favorable processes of oxygen evolution are, therefore, interesting. It might be necessary to introduce specific catalysts into the TiO_2 interface, which are able to accumulate holes for inducing a multi-electron transfer oxidation of water for oxygen liberation at more favorable thermodynamic potential. Numerous other materials, especially oxides of transition metals, have been and are still being tested as catalysts for oxygen evolution from water. Reasonably good photoactivity for water oxidation was found with tantalates of the composition $KTaO_3$, $NaTaO_3$ and $LiTaO_3$, especially in the presence of co-sputtered NiO [41]. Again, however, the photosensitivity is limited to the ultraviolet region by energy gaps between 3.6 and 4.7 eV. The compound oxide semiconductor $In_{0.9}Ni_{0.1}TaO_2$, optimized with a Ni/NiO catalyst, absorbs at the transition to the blue region (402 nm) where it oxidizes water with 0.66% efficiency [42]. An interesting parallel approach to water oxidation concentrates on a phenomenon which became known from photography. Here water is oxidized while Ag^+ is in a parallel reaction reduced to Ag [43]. There are also studies in which two photocatalysts, one for oxygen evolution and one for hydrogen evolution, are combined for water splitting [44,45].

Both theoretical and experimental knowledge in this field of photocatalytic water splitting is presently not sufficient to lead it into a dynamic and creative area of scientific and technological development. New ideas and materials are needed. Nano-scale materials are presently in the focus of interest. Since electronic charge transfer, interfacial dynamics, and chemical reactions take place on the nano-scale, efforts to manipulate and assemble nano-scale materials nurture the hope that scalable methods for splitting water with sunlight for hydrogen production can be identified. Not only water splitting but also hydrogen storage and catalytic electrodes for fuel cells may be developed that way.

8.1. *Photoelectrochemical experience towards nano-scale photocatalysis*

The hope today is that nano-science will bring a major progress by optimizing and linking structure and function at the nano-scale. One expectation, of course, is that interfaces can be used to manipulate energy carriers. Many aspects of nano-materials are dominated by interfacial properties. Another expectation is that nano-scale structures can be assembled via self-organization to create highly functional macroscopic systems with new properties [46,47]. An entirely new paradigm for developing new energy technologies is expected. Very small nano-particles also offer, via the quantum size effect and via its effect on thermodynamic properties, interesting opportunities for tailoring optical properties. However, the experience already gained in semiconductor electrochemistry using electrodes of mono-crystalline and poly-crystalline materials may indicate limits. If a mono-crystalline photoelectrode already degrades, can this be expected to stop when the same material is provided in nano-shape? The experience unfortunately is that this is not the case. Nano-particles, when exposed to ambient humidity, are typically even more reactive, because they are dominated by large surfaces, which control reactivity and the access of reactants. They often also tend to coagulate and have to be surface treated to be chemically reasonably stable. However many properties are still unknown or are little investigated. By learning about nano-particles, we will learn to understand and control interfacial properties. This is important for advancing catalytical science. There will be definitely new opportunities.

8.2. *Semiconductor electrochemical systems for hydrogen generation*

While photosynthetic systems for solar fuel generation are based on membrane processes with anodic oxygen evolution and cathodic fuel generation proceeding on opposite membrane sides scientific research in the seventies and eighties of the past century concentrated on energy converting electrochemical systems using electrodes made of photoactive semiconductor materials for anodes or cathodes [48,49]. This is shown in Fig. 13(a), where such a photoelectrochemical cell composed of a photoactive n-type semiconductor anode and a metal cathode is schematically shown as well as via a corresponding energy scheme.

The semiconductor, which has a valence band and a conduction band separated by a forbidden energy region, thermodynamically equilibrates with the electrolyte and may therefore build up an electrical field within the space charge layer close to the interface. This is reflected in a bending of the energy band towards the semiconductor–electrolyte interface. When electrons are excited in an n-type semiconductor by light from the valence band into the conduction band the hole is expected to migrate towards the electrolyte interface where it can engage in interfacial reactions.

A most desired process is a favorable reaction with water during which 4 electrons per liberated oxygen molecule are transferred into the valence band of the semiconductor. The electrons excited in the semiconductor are conducted towards the metallic counter electrode where they are expected to reduce protons for hydrogen liberation. Besides this classical electrochemical set-up photochemical diodes were studied for the same purpose of hydrogen generation [50] (Fig. 13b). Such systems can be understood as miniaturized forms of photoelectrochemical cells. The photoactive semiconductor material and the metal counter electrode are made smaller and smaller so that they just consist of a semiconductor grain with an attached metal dot. Such a system may, nevertheless, drive a photoelectrochemical reaction including the separation of charge and the evolution of hydrogen and oxygen. When making the photochemical diode increasingly smaller one finally gets to colloids, which are known to become involved in quantum size phenomena (Fig. 13c). This means that they, when becoming smaller than approximately 2–3 nm in size, their energy gap becomes larger and the diverse optical–electronic properties change. A lot of research has been and is presently performed with such nano-sized light-absorbing materials.

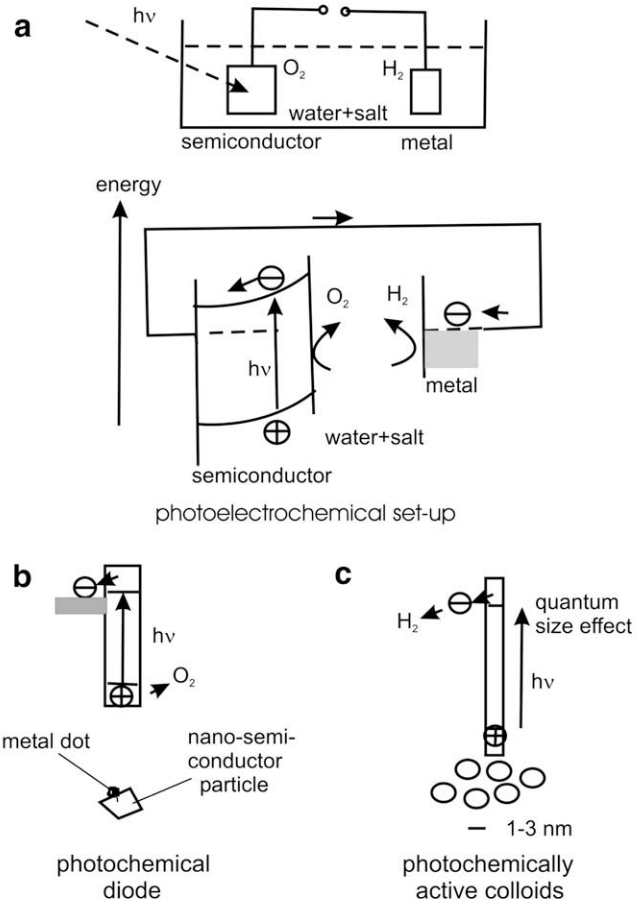

Fig. 13 – Schemes explaining electrochemical set-up (a) as well as photochemical diode (b) and colloid structures (c) of photovoltaic fuel generating systems.

During the last three decades, many semiconducting materials have been tested with respect to their ability for photovoltaic energy conversion and fuel generation. Also photoactive p-type and n-type electrodes were combined in the same electrochemical cell to take advantage of both photo-potentials [51]. Solar cell efficiencies between 8.2 and 12.4% were observed using InP/GaAs and $GaInP_2$/GaAs combinations respectively [52,53]. Most systems turned out not to be stable in the long term. One important reason is explained in Fig. 14, comparing silicon electrodes with electrodes made of layer-type semiconducting materials like MoS_2, WS_2, or PtS_2. Energy schemes of the corresponding materials are shown, which visualize that in silicon a hole generated after excitation of an electron corresponds to a missing chemical bond in the valence energy band. When more of these missing chemical bonds are conducted towards the electrolyte interface a stepwise degradation and dissolution of the silicon material will be the consequence.

When, in contrast, a layer-type transition metal dichalcogenide is photo-excited, the missing electron in the valence band does not correspond to a missing chemical bond because the valence band is derived from the metal d-state. This implies that a metal d–d-transition has been generated, which in this material is quite efficient due to some mixing with other electronic states. The missing electrons, however, increase the oxidation state of the transition metal with the consequence that surface positioned transition metals will interact with the electrolyte and change their ligand composition [54]. To compensate stepwise arriving holes they attach OH^--groups from water forming hydroxide, oxide and peroxide complexes. If they are favorable so that they permit peroxo-complexes with oxygen as intermediate states, molecular oxygen may be liberated.

This is, for example, the case with platinum disulfide [55]. Molybdenum and tungsten disulfide as well show this property as long as the van der Waals surface of this layer-type material is quite perfect. However, when edge sites are present the oxidation complexes tend not to liberate oxygen but to involve also the sulfur species, which is energetically positioned below the d-valence band (Fig. 14b), and to generate sulfate. This process obviously leads to the photo-degradation of the metal sulfide. A similar process occurs with iron disulfide (FeS_2) [56]. But when iron is replaced with ruthenium to form ruthenium disulfide (RuS_2), which has the same crystal

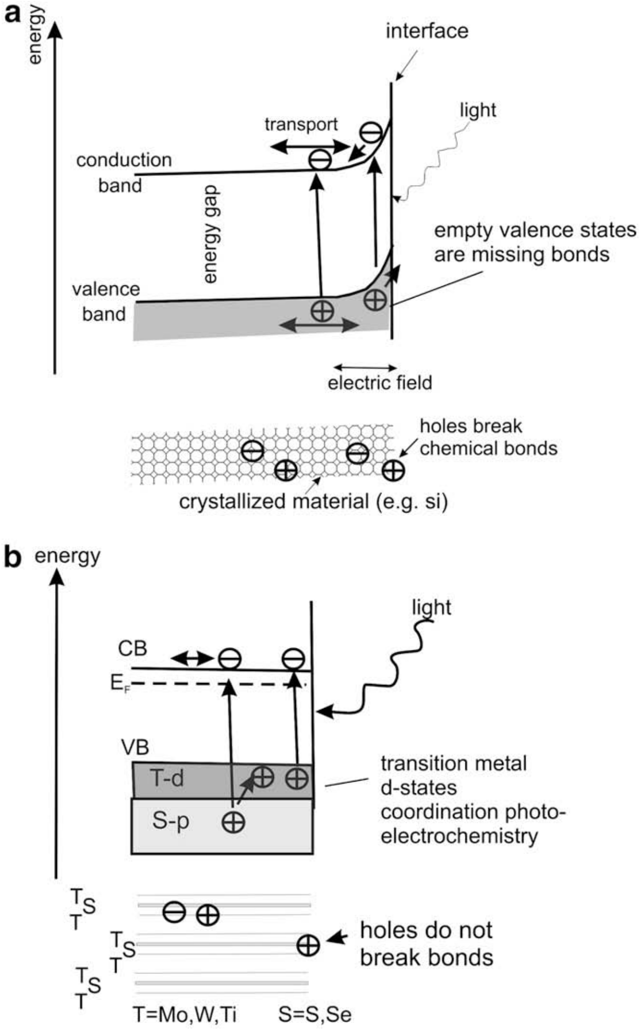

Fig. 14 – Energy and structure schemes comparing silicon (a) and Mo, W disulfides (b) with respect to photo-induced interfacial reactivity and stability.

and electronic structure, no sulfide is formed but oxygen is evolved from water [38]. The property of semiconductors to liberate oxygen from water clearly depends on their electronic structure. Most materials have no tendency to photo-react with water. Photo-induced interfacial coordination chemical reactions are needed, which may induce water species to form metal complexes, which are gradually oxidized and may, thereby, liberate oxygen. Only if such an oxidative process is generated, which liberates oxygen from water, it makes sense to use the separated electron for hydrogen evolution at the counter electrode. If electrons would be donated from other molecular species than water, the process would be ''sacrificial'' and typically not sustainable.

Hydrogen evolution is catalytically a well-investigated and well-functioning process [30,57]. Hydrogen evolution catalysis was also studied at photoelectrodes, for example on p-type Si [58]. Electrode stability and the attachment of hydrogen evolution catalysts are still open questions. But the function of hydrogen evolution catalysis is electronically quite well understood. On the basis of the Brewer intermetallic bonding model, it was found that whenever metals of the left half of the transition series with empty or half-filled d-orbitals are alloyed with metals of the right half of the transition series with internally paired d-electrons, a synergism is observed for hydrogen evolution catalysis. It can exceed the catalytic effects of precious metals and of the well-known Raney-Ni. Examples are $MoCo_3$, WNi_3, VNi_3, and WFe_3 [30]. It can therefore be concluded that the scientific problem of hydrogen evolution has been solved in a satisfactory way. This does however not mean that all technical problems are optimally handled. A significant effort should continue towards the improvement of technical hydrogen evolution electrodes, which are stable and highly efficient at the long term.

Because of photo-degradation of the semiconductor material and photocorrosion during oxygen evolution (e.g. with ZnO), which is for structural–electronic reasons unavoidable with most light-adsorbing semiconductor materials, there are presently only a few electrochemical systems known, which can be used for oxygen (and thus sustainable hydrogen) evolution from water in the laboratory. Selected examples are shown in Fig. 15. When strontium titanate, $SrTiO_3$, an oxide only absorbing in the ultraviolet, is used as an anode in combination with a metal cathode, then oxygen and hydrogen evolve during ultraviolet illumination (Fig. 15a). Such a system also works as a photochemical diode (Fig. 13b), however, hydrogen and oxygen are mixed which is technically not desirable. RuS_2 is a low energy gap photoelectrode for water oxidation with up to 60% quantum efficiency, when a supporting electrode potential is provided (Fig. 15b) [38]. Because of the d-band structure of the valence band it is kinetically stable and does not react to ruthenium sulfate. However, at elevated electrode potential, some RuO_4 is liberated. Semiconductor electrodes with p- and n-type character can be added to provide together the voltage for water splitting. This is, for example, possible by combining n-GaAs and p-InP (Fig. 15c). In this case, instead of using an external assisting potential the metal counter electrode for hydrogen evolution is replaced by a p-type semiconductor. It can generate a photo-induced hydrogen evolution process, which adds a potential difference to the system in such a way that TiO_2 in combination with a p-type photocathode (for example indium phosphide) can maintain the photo-induced water splitting process. However electrode stability problems arise, which in some studies have been counteracted by using protective layers which mediate the transfer of charge carriers, but prevent direct access of water.

TiO_2 needs UV illumination for the photoreaction with water, since holes from the O 2p valence band are responsible for the reaction, which in this case leads to radical intermediates. TiO_2 has, however, a smaller energy gap compared with $SrTiO_3$. Since the conduction band of TiO_2 is positioned slightly lower than the hydrogen levels, a supporting potential is needed for using TiO_2 with a metal counter electrode for oxygen and hydrogen production. This is shown in Fig. 15(d).

Also cathodically functioning p-type semiconductors, which photo-liberate hydrogen, may be subject to photocorrosion. The hydrogen may become inserted into the material thus making the material brittle or it may interact with components of the material, like with phosphorous of InP, forming the toxic gas PH_3 (Fig. 15c).

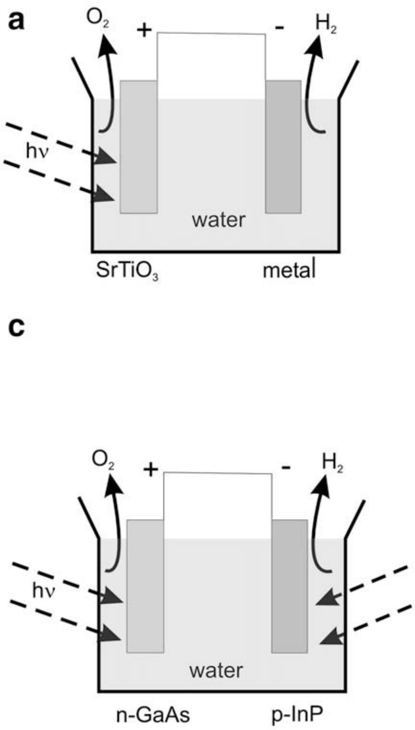

Fig. 15 – Scheme of different demonstrated water splitting electrochemical systems. (a) $SrTiO_3$ anode/metal cathode; (b) RuS_2 anode/supporting voltage/metal cathode; (c) n-GaAs anode/p-InP cathode; (d) TiO_2 anode/supporting voltage or solar cell/ metal.

This short summary of earlier work and experience shows that it is very difficult to identify photoactive materials, which can support photo-induced electrolysis of water without corrosion. There is presently great hope that nano-structured materials may provide scalable and hierarchically organizable structures for photo-induced water splitting and fuel generation. However, on a molecular level these materials may, with respect to stability, behave similarly to mono-crystals of large size, which have frequently been studied in the past. Major efforts should, therefore, be concentrated on long-term stability of such materials. Nature had similar problems with the long-term stability, which have been addressed by self-organization processes, repair mechanisms, kinetic stabilization, or specific processes aimed at limiting unwanted side reactions. In any case, profound studies will be needed to better understand the function of electronic processes with respect to interfacial fuel generating mechanisms. The promise of a technically successful handling of such semiconductor electrochemical hydrogen generating mechanisms would be the possibility of developing a miniaturized hydrogen fuel technology. Small photoactive systems could produce hydrogen supplied to fuel cells. Chemical compounds can store energy up to 20 times more efficient than electrical storage systems in reference to the weight. Miniaturized hydrogen generating and utilizing energy systems are imaginable at the long term provided the mentioned material problems can be controlled and handled. Of course, new materials and material combinations will be the key issue for innovation in this field.

This will also be the case for another technical challenge with respect to photovoltaic water splitting. If the prophecy of Captain Nemo (Jules Verne) should come true that energy will one day come out from seawater, we have better to learn how to liberate oxygen from seawater without simultaneously liberating chlorine, due to its NaCl salt content. At $pH = 0$ the redox potential of the chloride/chlorine is only slightly more positive than that of the water/oxygen system. The potential difference increases by 59 mV with every pH unit, because of the pH dependence of the water redox potential, but remains within half a volt of the redox potential of Cl^-/Cl_2. If water is oxidized with high current density, this can become a problem. How to deal with it is already discussed in a book from 1980 by Bockris [1], but more selective electrode materials are highly desirable. The best performing laboratory electrodes, which may yield 99.8% oxygen from seawater electrolysis, interestingly contain manganese oxide as catalyst [59]. This reminds us of evolution of photosynthesis which started in the sea. If nature would not have succeeded in avoiding chlorine evolution from its manganese center, the building-up of our life supporting atmosphere and of higher life itself would not have been possible. We have in this respect to learn how to avoid chlorine evolution in order to continue nature's sustainable energy strategy on a high industrial level.

9. Discussion

In this review on photovoltaic hydrogen generation we attempted a critical assessment of this multi-disciplinary technology in terms of science, technology and economical prospects. Fact is that photovoltaic hydrogen generation, as it functions today, is still much too expensive to be a realistic alternative for the short or medium term. Hydrogen generated from natural gas is simply much cheaper than hydrogen generated from industrial electricity. And photovoltaic electricity today is approximately 10 times more expensive than the cost of electricity from fossil fuel. It is for this reason that photovoltaic hydrogen production is still a technology limited to laboratory-scale or smaller pilot plant installations. The bottleneck for the implementation of the photovoltaic hydrogen technology is the too slow learning curve for photovoltaic systems. Due to generous subsidizing models in several countries the photovoltaic industry is presently booming and seeing yearly rates of increase between 30 and 40%. However, this growth occurs from a low production volume, which now amounts to approximately 2 GWp. This is the power generated by solar cells at noon in full sunlight. For an average throughout day and night this power has to be divided by 5. The resulting 400 MW has to be compared with expected 6000 GW of electricity consumption worldwide by the end of this century. In addition the photovoltaic equipment will have to be replaced every 20 years. It has also to be considered that photovoltaic hydrogen generation will not compete with electricity demand but should supply the much bigger market section of mobility, energy storage and industrial chemistry. At the end of this century it may amount to a dimension between 10,000 and 20,000 GW. The expected challenge for photovoltaic hydrogen generation technology is, therefore, enormous.

The main challenge is that man must identify photovoltaic technologies with a much higher cost reduction potential than expected from present day silicon photovoltaics, which still relies on cutting crystallized silicon slices for etching and integrating them into photovoltaic panels. Also the presently available thin layer photovoltaic cell technologies do not offer a significant cost reduction opportunity. The reason is mainly the limitation for scaling up initiatives due to the content, in the thin layer photovoltaic materials, of rare and toxic elements such as cadmium, indium, arsenic, and selenium. The indium reserve, for example, was estimated to be equivalent to 70 GWp of solar cell power. This quantity has to be divided approximately by 5 to yield a continuously supplied power of 14 GW (for a solar cell lifetime). While the CIS cells could still become thinner a big problem is the competition for indium for the display screen market. CIS cells can therefore only temporarily supply a comparatively small market. While, of course, the present trend of photovoltaic cost reduction via mass production should be supported, a system change would be desirable, which could generate a much steeper learning curve. A system change does not come along alone and requires substantial efforts.

In the present review it has been attempted to identify the direction of such a possible system change. Our present photovoltaic technology is based on only one of two major possibilities for photovoltaic cell function. In our present silicon and related solar cells a thermodynamic potential is built into the device structure mostly by providing a gradient in p–n doping, which, during illumination, generates photocurrent fluxes. The materials used, however, must sustain this inbuilt gradient for 20 years. Only the most stable and most durable materials can support this. This is exactly what makes these materials expensive since they have to be produced at elevated temperature. The second and nearly unexplored way to operate a photovoltaic cell is to allow passage of excited electrons only in one direction within a semi-organized material pattern, while taking advantage of a photo-generated deviation from chemical equilibrium. Such a property is much less demanding with respect to material behavior, since it characterizes a semi-permeable membrane which has no inbuilt gradient with a permanent tendency to destroy itself. This intelligent mechanism is, for example, applied in photosynthetic membranes, where a spin state change in combination with a small activation barrier effectively prevents the electron from a reverse reaction. Kinetic rectification principles also work in modern nano-structured solar cells like dye solar cells or polymer–fullerene solar cells, which already function in research laboratories. The problem is that the fundamental science for current rectification via molecular kinetic mechanisms is not established and that at present practically very limited research is undergoing with respect to the fundamental principles involved. Part of the money, which is presently invested for support of classical silicon photovoltaic technology, should better be invested into a research program on alternative kinetically determined solar cells. They, at the long term, promise much cheaper materials and more cost-efficient mass production. Technological success in this direction would better support the vision of economic photovoltaic hydrogen generation as a fundamental technology for a sustainable energy future. Other, secondary technologies aimed at more cost efficient and intelligent encapsulation and reducing the heating of solar cells should also be considered.

The greatest promise of photovoltaic hydrogen generation arises from the experimentally demonstrated fact that it allows a much higher efficiency for chemical fuel production than biomass technologies. The solar energy efficiency of a photovoltaic hydrogen generation experiment, outlined in this review [9], was 36 times as high as biomass production efficiency via three harvests of sugar cane (totaling 0.5% efficiency). Provided the photovoltaic technology can really be made much cheaper the technology has indeed the potential for mass production of sustainable energy on a large scale. In addition, it will not compete with food producing agriculture since photovoltaic systems can be installed on houses and roofs or on infertile land.

This review has also analyzed whether the emphasis of technology should be on highly centralized hydrogen generation photovoltaic units or on decentralized photovoltaic hydrogen technology. The conclusion reached is that both directions should be followed. When we learn to use photovoltaic hydrogen producing techniques in very small units we will be able to open up many more and innovative application possibilities. An example has been given on the basis of a hydrogen producing tube or cable through which water flows and which is separated by a photovoltaic hydrogen generating membrane in two halves. It was discussed that, when coiled up to a solar collector, such systems could supply hydrogen and heat to fuel cells and heating systems respectively. Many distinct small technological devices could well use the energy-storing capacity of photovoltaically generated hydrogen for different applications.

In order to support development of such systems photoelectrochemical research on water splitting and hydrogen generation has to be reactivated and conduced to major success. Photovoltaic hydrogen generation will see a major breakthrough when a cheap photocatalyst for water oxidation can be identified. There is little need for improved catalysts for hydrogen evolution, because the existing ones are efficient and reasonably cheap [30]. But catalysts for water oxidation to molecular oxygen are a bottleneck and a big scientific challenge. Such photocatalysts will be needed as particles with inbuilt photovoltaic activity or, better, covering a membrane, which allows photo-induced charge separation between opposite membrane surfaces like in the biological photosynthetic membrane or in a laboratory prototype (Fig. 12). The oxygen evolution catalyst has to be a material with the tendency to react with water once it is positively charged. It has been demonstrated that transition metals with coordination chemical properties have this ability. With the manganese complex nature has also selected the coordination chemical pathway. But the reactivity with water is only a necessary, not yet a sufficient condition for efficient water splitting. The chemistry of the oxygen evolution catalyst is faced with a demanding 4-electron transfer in combination with significant conformation changes resulting from coordination chemical mechanisms and a high rate of proton turnover. It is expected to be a kinetically self-organizing catalyst, the properties of which we still have to learn to understand. It was pointed out that semiconducting materials, calcium manganates, which are characterized by the same elements and similar structures as the manganese water oxidation catalyst, are able to deal with electrical charges in a highly non-linear way. Cooperative charge transfer phenomena may be the key to efficient water oxidation [60]. Major effort should be developed in this direction.

While presently much hope is seen with respect to innovation focused on nano-materials the experience gained two to three decades ago with semiconductor photoelectrochemistry will have to be reactivated and extended to avoid unnecessary drawbacks. We have to go on to systematically broaden our knowledge on the interaction of light with materials for the generation of electricity and fuels. When new nano-scale material compositions are studied with respect to photovoltaic hydrogen generation we should attempt to incorporate the wide knowledge obtained from the study of mostly single crystalline semiconducting and catalytic compounds. This will allow focusing on some real challenges, the interrelation between photo-efficiency and crystalline structure, the interrelation between electronic structure and photocatalytic performance, and the interrelation between structure, chemistry and long-term stability of the reacting interfaces.

Photovoltaic hydrogen generation technology offers a huge promise for a sustainable energy economy but massive research in a few innovative directions will be required to make it become real in a not too distant future. Old ideas [61] as well as new ones [62] will have to be brought together for a new dynamics of photoelectrochemical progress. The community interested in photovoltaic hydrogen should not wait until photovoltaic electricity becomes reasonably cheap. It should encourage massive parallel development of kinetically determined solar cells based on nano-materials, should tackle the big challenge of photocatalytic water splitting with adequate experimental and theoretical tools and reflect about how decentralized photovoltaic hydrogen could later penetrate our industrial world to revitalize it with sustainable energy.

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