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Sustainable Solar Hydrogen Production: From Photoelectrochemical Cells to PV-Electrolysis and Back Again

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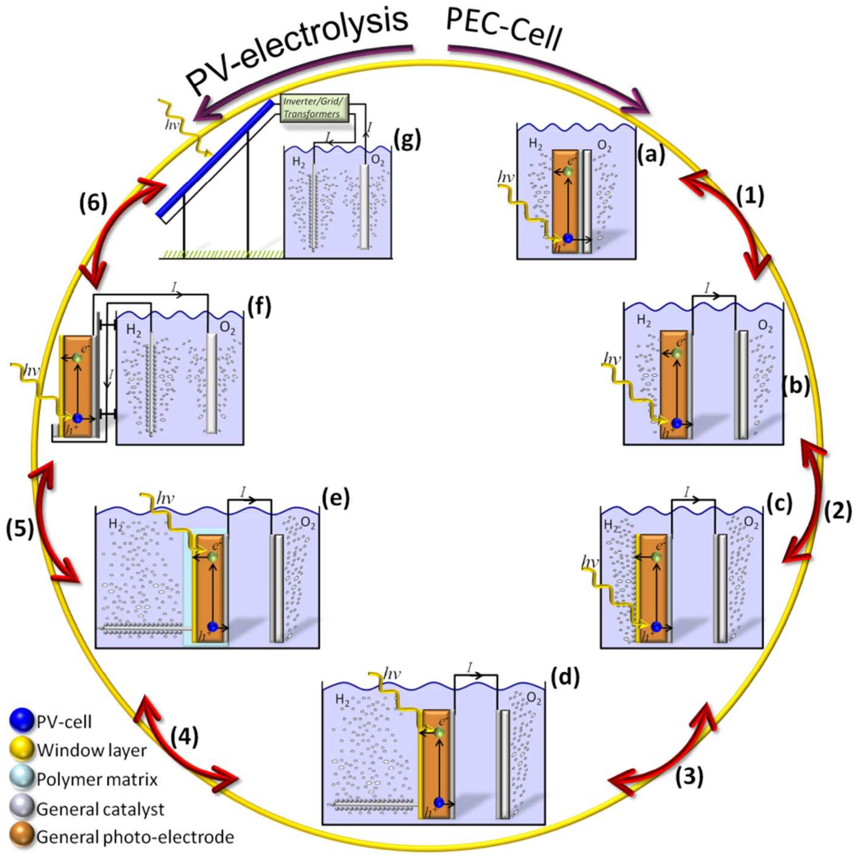

Abstract

Sustainable hydrogen production could, in principle, be accomplished along several different routes, where some of the most promising approaches involve utilization of solar energy. Photoelectrochemical cells (PEC-cells) and PV-electrolyzers for solar hydrogen production are here analyzed and compared. The analysis is performed by theoretically designing a number of intermediate devices, successively going from PEC-cells to PV-electrolyzers. The main physical processes: absorption, charge carrier separation, charge carrier transport, and catalysis are analyzed in the different devices. This demonstrates how the two concepts are related, and how one easily could be transformed and converted into the other. The awareness of the close relationship between PEC-cells and PV-electrolyzers is not as widely recognized as it should be. Traditionally, these two approaches have often been considered as fundamentally different, and are far too seldom analyzed in the same context. We argue that the different device designs for solar hydrogen production best are seen as essentially equivalent approaches, and as topological variations of the same basic theme, and can in many cases be unified under the acronym photo driven catalytic (ODC) devices. We further argue that much is to gain by acknowledge the similarities between PEC water splitting and PV-electrolysis, and that one concept not should be considered without also consider the other. The analysis and discussion presented could potentially lead to an increased fruitful crossbreeding of the accumulated knowledge in the respective sub-discipline, and aid in realizing solar hydrogen production as a sustainable and economical compatible energy alternative.

Broader context

To realize the vision of a sustainable hydrogen economy, inexpensive and efficient ways of producing the hydrogen have to be developed. There are several different approaches for doing this, and here we analyze solar hydrogen production using photoelectrochemical (PEC) cells and PV-cells connected to electrolyzers. Traditionally, these have often been seen as two different approaches. Here we present a framework for the fundamental process involved in solar hydrogen production within which we illuminate the close resemblance between PEC-cells and PV-electrolyzers. These can be seen as essentially identical concepts, and much is to gain by recognizing and acknowledge this dualism. The discussion is supported by a description of a number of intermediate devices that effortlessly bridge the two concepts.

Keywords

Solar water splitting, hydrogen production, water reduction, water oxidation, photochemistry, PEC, PV-electrolysis, electrolysis, PDC

1. Introduction

The hydrogen economy is a vision of a post carbon future, driven by a sustainable energy system[1-3] based on flowing and renewable energy sources, with hydrogen and electricity as primary energy carriers. Hydrogen can be produced as a fuel for power sources in homes, as feedstock for the industry, as fuel for transport, and as a way to deal with the intermittent nature of renewable energy sources; like wind and photovoltaics. A prerequisite for realizing this future is economically compatible means for sustainable hydrogen production. This is not the case today when approximately 96% of the global hydrogen production is based on steam reforming of fossil fuels[4]. Several possible routes for sustainable hydrogen production are under investigation[5-7], including fermentation of biomass[8-10], thermochemical processes[11-13] and photobiological water splitting[14-16]. The focus of this article is on solar assisted hydrogen production using inorganic material, and especially on the relation between different device concepts, ranging from photoelectrochemical cells (PEC-cells) to PV-electrolyzers.

The traditional view of a PEC-cell is that of a monolithic device, that while illuminated in water facilitates both absorption of light and catalysis, whereby hydrogen gas is produced. This approach has so far not resulted in commercially available devices; even though interesting results have been reported in the literature, like for example, the “artificial leaf” from the group of Nocera[17, 18] reaching 2.5 % solar-to-hydrogen- (STH) efficiency. Conventional PV-electrolysis on the other hand represents a distributed solution with standalone PV-cells for efficient absorption and charge carrier separation, and free standing catalysts for the electrochemical redox reactions. This approach is compatible with existing technologies but due to cost and efficiency concerns, only a very limited commercial impact has been reached.

The core question of this paper is whatever or not PEC-cells and PV-electrolyzers are two completely different approaches towards renewable solar hydrogen production and if so, where the transition occurs, or if they best are seen as two essentially equivalent concepts. The classification of a device as a PEC-device or as an immersed PV-electrolysis cell widely differs between authors in published papers. From far apart, they perform the same work. They convert and store solar energy as chemical energy in hydrogen, using water as a hydrogen source. Up close, they appear to be rather different with the PEC-cell as a monolithic, integrated device within the electrolyte, whereas the PV-electrolyzer is a spatially disconnected system composed of well-known parts. From a fundamental perspective, with respect to the physical processes involved, they yet again appear to be essentially identical.

By the analysis of the physics involved presented in this article, we think it is rather clear that the two concepts best are seen as one single unified concept. We have, however, observed that it is fairly common to perceive PEC-cells and PV-electrolyzes as two completely separated concepts. There exist an awareness of the close connection between classical PEC-cells and traditional PV-electrolyzes, and they are from time to time analyzed in the same context[19-23]. The opposite situation where PEC water splitting and PV-electrolysis are thought of, and treated, as two essentially different concepts and not analyzed together is, however, far more common.

The overall goal of this paper is to consolidate the understanding of the conceptual and practical relation between PEC-cells and PV-electrolyzes for solar hydrogen production. A more well spread awareness of the close similarities between the two concepts could lead to an increased and fruitful crossbreeding of the accumulated knowledge in the respective sub discipline.

The paper starts by shortly reviewing the basic physical framework for the hydrogen generating process in terms of: charge carrier generation, separation, transport, and transfer. This is followed by an overview of device concepts ranging from monolithic PEC-cells to

PV-electrolysis, as well as the transition from investigation of half-reactions to manufacturing devices for the full reaction. We also in some depth discuss the problem of device stability and the importance and consequences of the spatial relation between absorption and catalysis. Within this framework, a series of devices, gradually and stepwise ranging from classical PEC-cells to conventional PV-electrolyzers are constructed, which is summarized in figure 8. The transformations taking one device into another are discussed in some detail. The consequences these transformations imply in terms of, for example: the underlying physics, efficiency, stability, choice of material, and possible cost are also discussed. From this analysis, we argue that the close resemblance between PEC-cells and PV-electrolyzers is evident. Finally, the implications of a more well spread understanding of this equivalence between the concepts for further work related to solar hydrogen production is discussed.

2. The fundamentals

The splitting of water into molecular hydrogen and molecular oxygen using solar radiation can conceptually be divided into the four fundamental processes of: charge carrier generation, charge carrier separation, charge carrier transport, and charge carrier transfer at the electrolyte interface[24]. An external quantum efficiency for the reaction, *EQE*, can then be defined as in eqn. (1) where $\square_{gen}$ is the quantum yield of charge carrier generation or light harvesting efficiency, λ the wavelength, $\square_{sep}$ the charge separation efficiency, $\square_{trans}$ the charge transport efficiency, and $\square_{cat}$ the quantum efficiency of the catalytic charge transfer to the desired redox species in the electrolyte. These steps are illustrated in figure 1.a.

$$EQE(\lambda) = \phi_{gen}(\lambda)\phi_{sep}(\lambda)\phi_{trans}\phi_{cat} \qquad (1)$$

This constitutes the fundamental framework on which the subsequent theoretical discussion will be based. Any working device is bound to perform all these four steps well. In this paper, the separate steps will be analyzed in some detail with special focus of how they are expressed in different device concepts spanning from classical PEC-cells to traditional PV-electrolyzers.

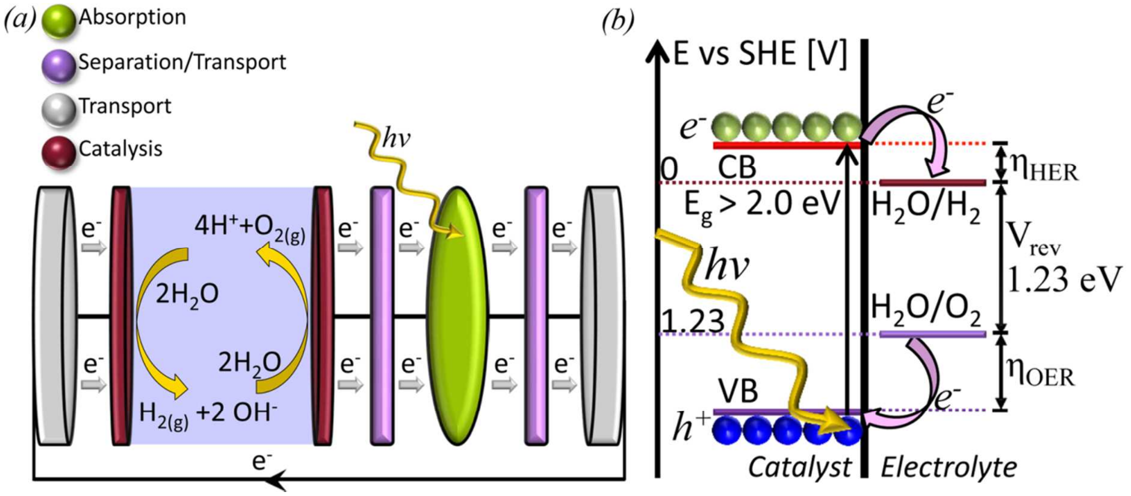

Figure 1. (a) A sketch of the conceptual separation of the function in eqn. (1): Charge carrier generation (absorption), charge carrier separation, charge carrier transport, and charge carrier transfer (catalysis). (b) Illustration of relevant energy levels with respect to catalysis for a single-cell, one band gap device.

Efficient absorption of the incoming light in order to generate excited charge carriers is the first necessary requirement for a water splitting device. The Gibbs free energy for the reaction in eqn. (2) is 237.18 kJ per mol produced H_2, corresponding to a thermodynamic reversible potential of 1.229 V.

$$2H_2O \rightarrow 2H_2(g) + O_2(g) \qquad (2)$$

In order to drive this reaction in practice, additional potentials are needed due to losses associated with charge carrier separation, η_{sep}, transport, η_{trans} , and catalysis, η_{cat}. The useful energy difference between the photogenerated electron and the hole in a semiconductor is the difference between the quasi Fermi levels for the electrons and holes under illumination, rather than the difference in energy between the band edges. This could be seen as the energy penalty for withholding the electric field separating the electrons from the holes. This loss, η_{sep}, is in the order of 0.4 V or more for most PV-materials[25, 26] and accounts for the difference between the band gap energy and the acquired potential under operation. For both the hydrogen and oxygen evolution reaction (HER and OER) some overpotential is needed, representing a further source of potential loss in addition to the losses encountered in a solar cell device. The magnitude of the required overpotential is highly dependent on the choice of catalysts, and η_{cat} below 0.4 V appears to be hard to achieve, at least at high current densities. There will also be resistive losses, η_{trans}, due to charge transport through the absorber, contacts, wires, interfaces and in the electrolyte. The minimum band gap required for a one band gap, single cell device, $E_{g\,min}$, can thus be expressed as in eqn. (3).

$$E_{g\,\min} = 1.23 + \eta_{sep} + \eta_{trans} + \eta_{cat} \qquad (3)$$

The next step in order to perform useful work is to separate the photogenerated electrons in the conduction band from the photogenerated holes in the valence band before they recombine. This separation of charges is intimately linked with charge carrier transport, for which there are two main mechanisms; drift and diffusion. The electron drift current, J_{drift}, is a consequence of mobile electrons in an electric field, ξ, whereas the diffusion current, J_{diff}, is a consequence of concentration gradients. The total electron current, J_e, is the sum of these two contributions as given by eqn. (4), were q is the elementary charge, μ_e the electron mobility, n the concentration of electrons in the conduction band, D_e the diffusion coefficient of the electrons, and ∇ is the nabla operator. The transport of holes is analogous.

$$J_e = J_{drift} + J_{diff} = q\mu_e n\xi + qD_e\nabla n \qquad (4)$$

An absorber morphology investigated for solar hydrogen production is the nanoporous system. These electrodes have a large internal surface area and in many cases dimensions small enough to prevent an electric field to build up within the individual building blocks of the electrode. For the smallest dimensions and for materials with low dielectric constant there is thus no, or very little, band bending[27]. This has the consequence that diffusion, as illustrated in figure 2.a, is the dominating mechanism for charge carrier separation

Once a semiconductor is immersed in an electrolyte, an electric field will form at the interface, which could be used for charge carrier separation as illustrated in figure 2.b. This field is a consequence of the equilibration of the Fermi levels in the two media and is described in terms of a double layer. The electrolyte side of the double layer was first described by Helmholtz[28] and the modern description is based on an inner- and an outer layer[29]. The inner layer, called the Stern layer, has ions physically attached to the surface, forming a stagnant situation where the surface potential, referred to as the Stern potential, can be measured. The diffuse outer layer, or Gouy-Chapman layer, is located outside of the Stern layer with an exponentially declining potential[30]. On the semiconductor side, the effect can be described in terms of a band bending[31]. For a p-type semiconductor, the Fermi level is normally located below the dominating redox potential in the electrolyte. The Fermi level equilibration then results in a downward band bending accompanied by the build-up of an electric field in the semiconductor. The shape of the electric field is given by solving Poisson's equation (5) where ρ is the charge density and ε the permittivity. This can be solved together with the current density equation (4) and the continuity equations (6) were U is the rate of recombination and G is the rate of generation of charge carriers.

$$\nabla \cdot \xi = \frac{\rho}{\varepsilon} \tag{5}$$

$$\nabla \cdot J_e = q(U - G) \tag{6}$$

For semiconductor devices, additional contributions to the charge density is given from doping due to acceptors, $\Delta\rho = q \cdot N_A$ or donors $\Delta\rho = q \cdot N_D$ where N_A and N_B are the doping densities of the acceptors and donors, respectively. The exact solution can be found numerically but the depletion approximation is the commonly used approach. The semiconductor is then conceptually divided into one quasi-neutral region with a space charge density of zero located in the interior of the semiconductor, and one depletion region in contact with the electrolyte with a small carrier concentration equal to the concentration of ionized dopants. Within this approximation, which will give a numerically reasonable description of reality, the electric field in the semiconductor is simply a linear function going from a maximum value, $\xi_{SEI,}$ at the semiconductor electrolyte interface (SEI), to zero at the end of the depletion region, W_d. In the one dimensional case, this is described by eqn. (7) where x is the distance from the SEI, directed into the semiconductor.

$$\xi(x) = \frac{(W_d - x)}{W_d} \xi_{SEI}, \quad 0 \le x \le W_d \tag{7}$$

Both the value of ξ_{SEI} and the width of the depletion layer will be a function of: the permittivity of the semiconductor, the doping density, the energy difference between the Fermi level in the semiconductor, the redox potential in the electrolyte, and to some extent also on the electrolyte concentration and specific absorption of charged species in the SEI. The width of W_d for planar electrodes can easily be measured electrochemically by the Mott-Shottky method[32, 33]. The fundamentals of the electrostatic behavior in the SEI can be found in for example Bard et al.[34] and quantum mechanical considerations have been discussed in Bockris and Kahn[35].

The electric field will facilitate the separation of photogenerated charge carriers generated in the depletion layer. For a p-type semiconductor, the electrons will be transported out to the SEI as illustrated in figure 2.b, while the reversed situation is obtained for n-type semiconductors. For PEC-cells, this is usually the dominant mechanism for charge carrier separation, and henceforward we will refer to this mechanism as the Helmholtz mechanism of charge separation. For nanostructured electrodes, this mechanism will lose in importance as the dimensions of the individual building blocks decrease, and diffusion will gradually become the more dominant mechanism.

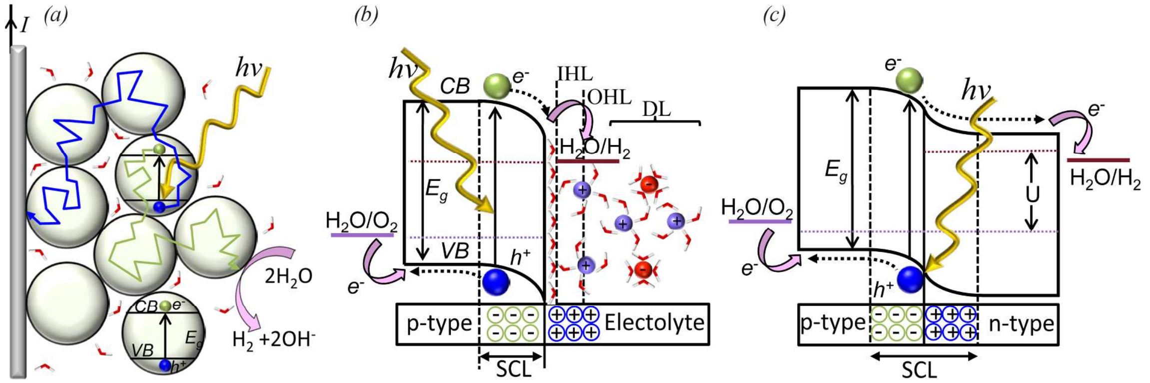

Figure 2. Charge separation by: (a) Diffusion, (b) The Helmholtz mechanism and (c) A solid state pn-junction

An electric field and a depletion layer for charge carrier separation can also be created by the engineering of a solid state pn-junction, as illustrated in figure 2.c. This is the preferred mechanism for charge carrier separation in conventional solar cells, and both homogeneous and heterogeneous pn-junctions can be used. The electric field in the semiconductor will in the depletion approximation be described by the same equation (7) as for the Helmholtz mechanism. There are practical differences between these two mechanisms, but fundamentally they are rather similar and any improved electron drift current in eqn. (4) comes in both cases from the local fields induced from changes in the charge density in the vicinity of the junction. The Helmholtz-approach could thus be viewed as a solid-liquid analogue to the solid-solid pn-junction. In both cases, photogenerated charge carriers are separated by an electric field, developed as a result of a charge imbalance at an interface and described by the same equations. The difference is the aggregation states of the phases meeting at the interfaces and if the charge imbalance is created by absorbed ions or ionized dopant atoms. These two approaches for charge separation do, however, give rise to a set of rather different practical implications, as will be discussed below.

The Helmholtz-approach depends on fewer layers in the solid state material, and would thus presumably allow for simpler synthesis. It is also more compatible with nanostructured electrodes, as a smaller set of manufacturing techniques are available for synthesizing nanostructured solid state pn-junctions. On the other hand, the Helmholtz-approach is more dependent on the nature of the electrolyte and does not provide the same flexibility in terms of separation of the different functionalities as the pn-junction provides.

Regardless of the mechanism for charge carrier separation, there are two distinct types of losses associated with this process. The first is a loss in photocurrent due to recombination, manifested by a lower quantum efficiency, $\square_{sep}$ in eqn. (1). The second is a loss of photopotential, corresponding to η_{sep} in eqn. (3), which has a direct effect on the optical limit and the amount of driving force remaining for the catalysis η_{cat}.

Once the photogenerated charge carriers are separated, they need to be transported to the electrolyte interface where the redox chemistry occurs. This could either be done by drift in an electric field or by diffusion in a concentration gradient. To close the circuit, ion transport in the electrolyte is also required.

Analogous to the charge carrier separation discussed above, there are both photocurrent and photovoltage losses associated with the charge carrier transport. The loss of photocurrent is due to recombination, scattering, and non-radiative transitions which all decrease the transport quantum efficiency, $\square_{trans,}$ in eqn. (1). This can occur in the bulk of the semiconductor but defects, grain boundaries, and interfaces commonly act as main recombination centers. In many cases, this is the dominant loss mechanism in research devices[36]. The photovoltage is subjected to losses due to recombination and parasitic resistances in the absorber material, at interfaces, contacts, and in the electrolyte.

The distance of charge transport could vary several orders of magnitude between different device configurations. In nanoparticle monoliths (figure 3.b), the distance of charge transport can be as short as a few nanometers. In monolithic devices (figure 3.c) it is usually in the order of 1 to 50 µm. For concepts with separated electrodes (figure 4), the distance is usually in the order of centimeters to decimeters and for PV-electrolyzers (figure 5) it could span from a few centimeters to hundreds of kilometers. As known from grid scale power transmission, losses can be reasonable small also over large distances. The current transport will ultimately be limited by the most resistive component, or where the recombination is highest. This is often due to either defects or grain boundaries in the absorber material, or in some of the internal interfaces, of at the semiconductor electrolyte interface, SEI.

When the charge carriers have reached the semiconductor interface, there needs to be a catalytic pathway for the desired redox reactions. The overall water splitting reaction in eqn. (2) is the result of two half-reactions: the oxidation of oxygen in water in an oxygen evolution reaction (OER) and the reduction of hydrogen in water in a hydrogen evolution reaction (HER).

The quantum efficiency of the catalysis, $\Box_{cat}$ in eqn. (1) can be divided into one quantum efficiency for the hydrogen evolution reaction, $\Box_{HER,}$ and one for the oxygen evolution reaction, $\Box_{OER}$, as in eqn. (8).

$$\phi_{cat} = \phi_{HER} \cdot \phi_{OER} \tag{8}$$

At the SEI, the oxidation and reduction of water are only two of several possible competing processes where alternative pathways involve: recombination, non-radiative relaxation via surface states, corrosion of the photoelectrode, and side reactions in the electrolyte. All of these alternative paths are reducing $\Box_{cat}$ in eqn. (1). Side reactions in the electrolyte could be minimized with the use of a suitable electrolyte. Electrode corrosion and non-radiative recombination are, however, serious problems for many investigated materials.

Associated to the catalysis is also a substantial overpotential loss, η_{cat}, which could be divided into separate components for the OER and the HER reaction as in eqn. (9) and illustrated in figure 1.b.

$$\eta_{cat} = \eta_{HER} + \eta_{OER} \tag{9}$$

In the ideal case, the photoabsorber is a good catalyst in itself. The severe constraints set upon the photoabsorber makes this an unlikely possibility. A more versatile approach is instead to co-deposit catalytic particles or employ separate catalysts. The catalysts that historically have been demonstrated to have the lowest overpotentials and highest exchange currents unfortunately include rare and expensive noble metals, like for example: platinum, iridium, and ruthenium. A common research procedure is to use platinum as catalyst while demonstrating proof of concepts, or while specifically investigating absorption, charge carrier separation, or the transport properties[24, 37, 38]. In future commercial devices, more earth abundant and low cost alternatives are, however, needed.

Catalysts can either be deposited on top of the absorber material or on separate electrodes. The importance and consequences of the spatial relation between the photoabsorber and the catalyst yield a rather different set of constraints and possibilities, as will be discussed in some detail in later sections.

3. Design concepts for photo conversion and electrolysis

3.1 Monolithic PEC cells

Born in the aftermath of the 1972 Nature article of Fujishima and Honda[39], demonstrating photodriven water oxidation on TiO_2 by using a small bias, is the dream of a single material PEC-cell capable of driving both photooxidation and photoreduction of water without an external bias. The concept is illustrated in figure 3.a and is appealing in its apparent simplicity. It is a single material that, while illuminated in water, generates hydrogen and oxygen.

The multiple constraints set upon such a material are rather demanding. The band gap needs to be high enough to provide sufficient overpotential, but still small enough to allow absorption of a large part of the solar spectrum. In addition, the absolute positions of the band edges need to straddle the redox levels for the water oxidation and water reduction in order to provide a driving force for the reaction, as illustrated in figure 1.b. This disqualifies many otherwise interesting materials.

The material further needs to be engineered with a mechanism for separation of the photogenerated charge carriers, as well as for transport out to the electrolyte interface without recombining. The semiconductor interface also needs to be catalytic with respect to both oxidation and reduction of water, as well as being stable in water under illumination. It is also highly preferable if the material is non-toxic and based on inexpensive and abundant elements.

Much research has been directed towards the search for such a material, and hundreds of compounds have been investigated with this in mind[40-42]. Combinatorial methods have also been utilized in this search[43-45]. So far, no material performing well in all the fundamental steps has been presented. Given the set of constraints mentioned above it is in our view unlikely that such a material ever will be discovered.

If the device instead is constructed using several different materials, the demands on each individual compound weakens as the combination, and not all the materials by themselves, needs to perform well in the four fundamental processes. This represents a conceptual separation of the active functionality into different materials, and has proven a far more efficient approach for developing working devices.

Several design concepts for monolithic devices involving the combination of different materials are explored and discussed in the literature. One possible approach is the synthesis of an ensemble of monoliths in the form of suspended nanoparticles[41, 46, 47], as illustrated in figure 3.b. This is a solution appealing in its apparent simplicity with no need for electrodes, wiring, or compartmentalization. It is also compatible with scalable and potentially low cost sol-gel synthesis techniques.

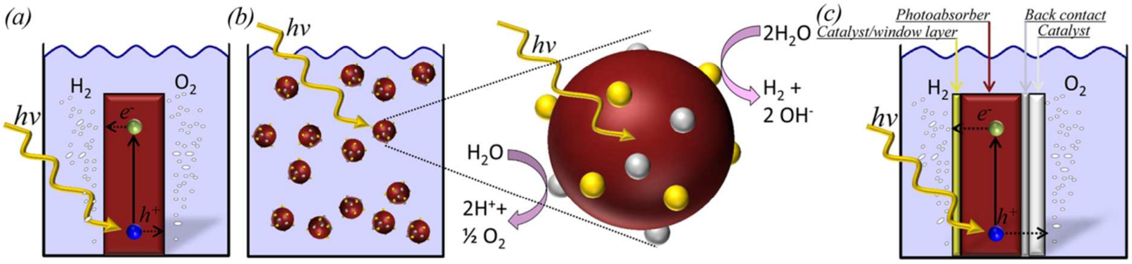

Figure 3. (a) A single-material one cell PEC-device. (b) Basic principle of solar water splitting with suspended nanoparticles with two different co-catalysts. (c) Single-cell monolith for unassisted water splitting based on one photoabsorber and two different catalysts.

The small dimension of the particles enables diffusion to be a sufficient mechanism for both charge separation and transport. To increase the catalytic activity of the surface, which not likely is catalytic towards both the oxidation- and reduction reaction, a co-catalyst can be deposited on the surface. It is even possible to imagine two different co-catalysts as in figure 3.b, even if that represents a greater practical challenge. A possible drawback with this design is that oxygen and hydrogen are evolved at essentially the same place, leading to non-negligible problems with the back reaction as well as an unavoidable need for a subsequent separation step of the evolved gases. The spatial limitation in the small particles implies challenges regarding the separations of the basic functionalities, leading to severe restrictions on the materials involved even though less so than for the single material monoliths.

Another possible monolithic design is to construct multilayered electrodes, as illustrated in figure 3.c. This approach is compatible with pure PEC-cells, buried PV-junctions as well as PV-electrolysis. It is also compatible with a rather large set of synthesis techniques involving sol-gel, electrodeposition, spray pyrolysis, and vapor deposition techniques, like for example: ALD, CVD, and PVD. The larger dimensions involved compared to the suspended nanoparticle approach increases the flexibility in terms of which materials that can be used and how they could be combined. Several different working devices along this line are reported in the literature, like for example: the 2.5 % efficient "artificial leaf" from the group of Nocera et al.[18], and the 10 % efficient CIGS based device we recently reported in EES[48].

3.2 PEC cells with separate electrodes

A small conceptual step away from the multilayered monolithic structure, in figure 3.c is to spatially separate the cathode from the anode. Instead of letting the majority carriers generated in the absorber material go through a back contact to a second electrode, as in figure 3.c, they can be transported by use of a wire from the back contact to the counter electrode, as in figure 4.a. In terms of the fundamental processes, it is only the distance of charge transport that separates the two concepts. This introduces the disadvantage of macroscopic wiring for connecting the individual electrodes and an extra resistive element which directly can affect η_{trans} and $\square_{trans}$. More importantly is, however, the increase in flexibility in terms of: geometrical configurations, synthesis procedure, and the number of materials that can be used, that is introduced by this topological transformation. The different electrodes can, for example: be developed, manufactured, and investigated separately. All this have potential beneficial impacts on the device performance.

It turns out that the most efficient devices described in the literature belong to this class of devices, like for example: the 7.8 % efficient cell based on triple junction amorphous silicon from Rocheleau et al.[49], the 12.4 % cell based on $GaInP_2/GaAs$ from Khaselev and Turner et al.[50] and a 10.5 % cell based on CIGS we recently reported[48]. An illustration of the benefit of this approach is given by the "artificial leaf" of Nocera et al.[17, 18], which increased its efficiency from 2.5 % to 4.5 % while taken from a monolithic design into one with separate electrodes [18]. This was probably mainly a result of transport limitation in the electrolyte. These devices are usually described as PEC or PV/PEC devices.

There are several different versions of this concept. The most straightforward design is one photoactive electrode and a counter electrode with solely a catalytic function, as in figure 4.a. It could be either an n-type semiconductor photoanode, as in figure 4.a, or a p-type photocathode. It is also possible to construct the single photoactive electrode as a tandem cell, which is the case in the devices from Khaselev et al.[50, 51] and Recee et al.[18].

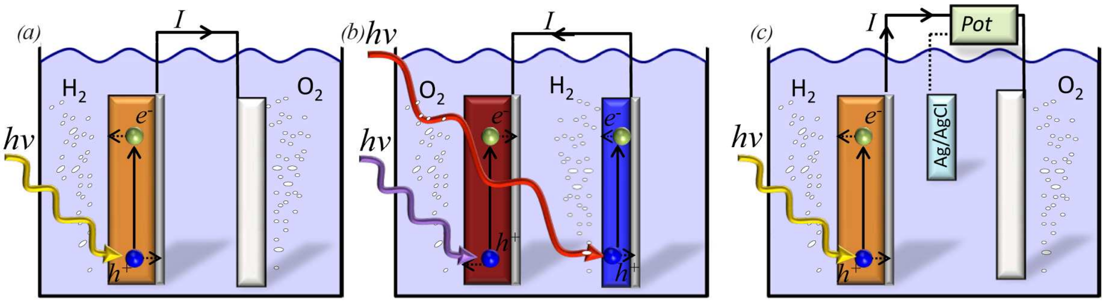

Figure 4. (a) A one-cell PEC-device with separated electrodes. (b) A two-cell tandem PEC-device with separate electrodes. (c) Standard three-electrode setup for a one cell PEC-device for the H_2 half-reaction.

A somewhat more elaborate approach is to use two photoactive electrodes, as in figure 4.b, which essentially represent a spatially separated tandem concept. There are several examples of such devices described in the literature, like for example: a 4.9 % device based on $BiVO_4$ and a tandem junction a-Si developed by Abdi et al.[38] and a 3.1 % device based on WO_3 and a dye sensitized solar cell presented by Brillet et al.[52].

From the research perspective, geometries with spatially separated electrodes have the additional advantages of enabling investigation and optimization of the two half-reactions independently, using conventional three-electrode measurements as in figure 4.c. This is reflected in the fact that the vast majority of articles on solar water splitting concern themself with investigation of half-reactions. Half-reactions are simpler to investigate than the full reaction, and are therefore more compatible with the isolation and study of more fundamental aspects of the process. The macroscopic charge transport, for example, enables the efficiency to be extracted from the photocurrents, which is simpler to measure than the flow of the generated molecular hydrogen. It is also believed that once efficient materials for the two half-reactions are found, it should in principle be possible to combine them into a device for the overall reaction. Examples of materials that have generated a lot of interest in the literature for the half-reactions are Fe_2O_3[53, 54], TiO_2[55, 56], WO_3[57, 58], $BiVO_4$[59, 60], ZnO[61, 62], and Cu_2O[37, 63] to mention a few, but hundreds of other compounds have also been investigated for this purpose[40-42].

3.3 PV-electrolysis

One step from the monolithic design in figure 3.c is to spatially separate one of the catalysts into a separate electrode, as shown in figure 4.a. A simple conceptual extension is to separate also the second catalyst from the photoabsorber, resulting in a configuration with three electrodes as in figure 5.a. The photoelectrode could be placed either within the electrolyte or outside it, where the later configuration in most cases would be the more convenient choice. This would be described as PV-electrolysis.

Water electrolysis has been known since 1801[64] and in its simplest form, it only involves a power source connected to two metal electrodes in a conducting electrolyte. Any power source could be used, but for sustainable hydrogen production in the TW scale, only solar and wind are realistic options[65]. Of the various investigated approaches to solar hydrogen production, PV-electrolysis is the technologically most mature solution and the one closest to the market. This is due to the fact that the PV-part and the catalysts can be developed, optimized, and tested independently of each other. Both solar cells and water electrolyzers are commercially available and could be connected either directly, as in figure 5.a, or through the grid, as in figure 5.b.

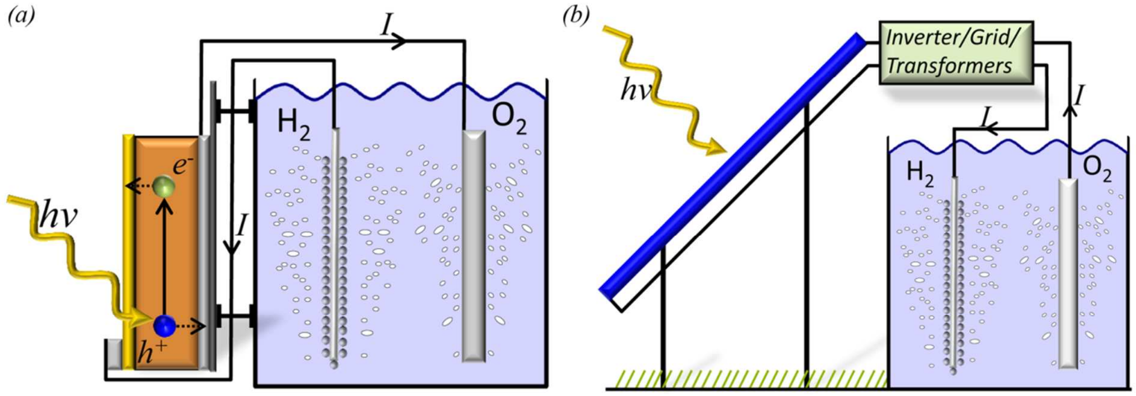

Figure 5. (a) PV-electrolysis configuration. (b) Grid connected PV-electrolysis

If connected to the grid, the losses in the power lines towards the end user is typically in the order of 7%[66], resulting in a transmission efficiency of 93%. Conventional electrolyzers often use expensive noble metals for the catalysis, and to balance the associated capital cost they are operated at high current densities. This inevitably leads to rather high overpotentials, even for good catalysts and the electrolyzers commonly operate above 1.8V, corresponding to an efficiency of 68% using the lower heating value of hydrogen. The figures for alkaline electrolyzers are roughly within the span 50-70%[20, 67] whereas solid polymer and solid oxide electrolyzers have the capacity to be somewhat more efficient[20, 68]. A 15 % efficient solar cell will thus correspond to a STH-efficiency of 9.5% (15·0.93·1.23/1.8). This is an estimate of what is readily achievable, and could certainly be improved with further optimization. These systems are thus capable of STH-efficiencies high enough to be of technological relevance, and it turns out that cost rather than efficiency has been hampering them from commercial success. Within the contemporary energy system, steam reforming of natural gas is still a cheaper alternative to hydrogen production. This may, however, change as the cost of solar cells has dropped substantially over the last years, and thin film as well as silicon solar cells begin to reach grid parity in parts of the world[69, 70]. The bottleneck then more shifts towards cost and efficiency of the catalysts.

If the solar cell is connected directly to the electrolyzer instead of providing power over the grid, the need for inverters and the losses in the grid are removed. This also reduces some of the balancing of system costs on both the solar cell and the electrolyzer side, making it possible to get closer to economical competiveness. A drawback would be that the electrolyzer will be driven by a more variable power source, leading to less optimal use of the electrolyzer, possible counter benefiting the advantage of excluding the grid and the inverters[71].

4. From half-cells to cells for the full reaction

Several well investigated semiconductors, like for example: Fe_2O_3[53, 54], TiO_2[55, 56], WO_3[57, 58], $BiVO_4$[59, 60], ZnO[61, 62], and Cu_2O[37, 63] are by them self all incapable of unbiased overall water splitting in single-cell configurations. Either the band gap is too low, or the band edge positions are only suitable for one of the half-reactions. In a working device, these semiconductors need to be combined with an additional photoabsorber providing the additional driving force for the full reaction. The standard approach to solve this problem is to construct tandem devices based on two semiconductors with different band gaps. It is common with the implicit argument that if the investigated material shows promise for one of the half-reactions, it should in principle be possible, to in a later stage, combine it with another material, and thereby construct a device for overall water splitting. Specific tandem combinations are sometimes also suggested, like the possibility to combine a Fe_2O_3 photocathodes with a DSSC[52, 72] in a tandem configuration. Tandem devices increase the complexity compared to one bad gap single-cell devices, but have the potential of providing higher efficiencies and enables the use of absorber materials that can drive only one of the half-reactions.

The devices described in the literature reaching the highest efficiencies have so far been realized with tandem concepts. Some of the more notable are the 12.3% efficient GaAs/$GaInP_2$ cell from Khaselev and Turner[50], frequently referred as the record cell, a variation of Khaselev's cell reaching 16.5 %[51], and a 15 % efficient device based on GaInP/GaInAs connected to a PEM-cell and a solar concentrator from Peharz et al.[73]. Multijunctions based on amorphous silicon have also been used for making promising devices, like the 7.8% efficient cell by Rocheleau et al.[49] and Nocera's artificial leaf[18,19] mentioned in Section 3.2.

An alternative approach to utilize low band gap materials is to connect several absorber units in series. Once having a module capable of absorbing light and efficiently separating and transporting the photogenerated charge carriers, several of these can be interconnected in series. This decreases the photocurrent density by a factor equal to the number of connected cells, but the voltage difference between the cathode and the anode increases by the same factor, and if several cells are used, this will provide enough driving force for the full reaction. The total area of the absorption decreases by the dead area in the interconnecting scribes made when the cells are interconnected in series, but this loss of area is below 8 % of the total area in state-of-the-art thin film solar cell modules.

Over the decades, the idea of devices based on series interconnected cells are mentioned from time to time[21, 74-77], but have never been an idea as widely spread as the use of tandem devices. An example of a water splitting device based on series interconnected cells is the 10 % efficient CIGS based device recently constructed by our group[48].

5. The problem of stability

Stability in water under illumination is a major problem for several otherwise promising photoabsorbers. The record cell of Khaselev and Turner[50] does for example degrade in the time frame of a day[78]. So does also Cu_2O[37], CIGS[24], and CdS[79] to mention just a few examples. Successfully addressing this problem is crucial, as a working device probably has to be stable during decades of operation to be economically competitive.

One approach is to simply discard the use of all unstable photoabsorbers and instead go for inherently stable semiconductors, like for example TiO_2 and Fe_2O_3. These semiconductors tend to have their own set of limitations that need to be solved in order to construct efficient devices, like for example: the high band gap of TiO_2 or the poor hole transport properties of Fe_2O_3[72]. To only focus on inherently stable semiconductors may, however, be an unnecessary restricted strategy. An alternative is instead to develop strategies for stabilizing efficient but fragile photoabsorbers.

In a classical PEC-configuration, the stability problem is inherent to the semiconductor/electrolyte interface, rather than to the bulk of the photoabsorber. At the interface, where the redox chemistry occurs, the local environment tends to be rather hostile. The local pH can be either high or low; the environment is strongly oxidizing or reducing; and there could be plenty of free radicals around. One possible strategy for protecting the surface is by ensuring the presence of an available reaction path with more favorable kinetics than the degradation reaction.

Another approach is to remove the surface prone to degradation from the electrolyte interface, and replace it with a more stable surface. This could mean depositing a window layer on top of the fragile photoabsorber, as illustrated in figure 6. In addition to stability, several additional requirements are set upon such a window layer. It needs to be transparent, unless the back contact is transparent. The band edges need to match the photoabsorber so that minority carriers easily are injected into the material and not blocked at this additional interface. It also needs to facilitate minority carrier injections into the catalyst on top of the window layer. The charge transport through the window material needs to be efficient. It is also important that this layer does not compromise with the charge carrier separation efficiency.

The conceptually simplest version of a window layer is a stable, transparent semiconductor with low resistance, as illustrated in figure 6.c. TiO_2 has with some success been used as such a protective layer on Cu_2O[37] and thin layers of Ni have been used to protect silicon[80]. In such a configuration, the window layer has only a small effect on the charge carrier generation, $\square_{gen}$. If the window layer not is entirely transparent in the visible, $\square_{gen}$ may decrease somewhat, but it could also increase if the layer is antireflective. The window layer represents an additional resistive element and an additional interface which potentially could decrease $\square_{trans}$ and increase η_{trans} as well as prolonging the distance of charge transport. If carefully engineered, these effects could be minimized. If a catalyst is deposited directly at the photoabsorber, as in figure 6.b, or on top of the window layer, as in figure 6.d, it should not considerably affect neither $\square_{cat}$ or η_{cat}, given that the same catalyst is used. If a solid state pn-junction is used for charge carrier separation, neither $\square_{sep}$ or η_{sep} will be affected as the separation is occurring spatially separated from the window layer. If the mechanism for charge carrier separation instead is by the Helmholtz mechanism, $\square_{sep}$ may be affected. The window layer may, depending on its thickness, doping density, and specific absorption to species in the electrolyte, affect the distance the electric field, generated by the charge imbalance at the window layer/electrolyte interface, penetrates into the photoabsorber. The width of the depletion layer may thus decrease and negatively affect $\square_{sep}$.

A protective window layer introduces an additional material to be matched with the other materials, and thus to some extent makes the device more complicated. The possibility to transform an unstable, but otherwise promising, absorber material into a stable and working device does, however, make this approach well worth investigating.

A more elaborate approach is to make the window layer multifunctional. This inevitably increases the demand set upon the window layer but may lead to overall simpler devices with less internal components. The surface protective property could be combined with the function of catalysis, as in figure 6.c, or with charge carrier separation. Finding a semiconductor combining the properties of a stable window layer with efficient catalysis is a simpler problem than finding a stable photoabsorber that also is a good catalyst and has good charge transport properties, as were the demands for the simplest monolithic design in Section 3.1. It may, nevertheless, be to hope for more than what is reasonable to find.

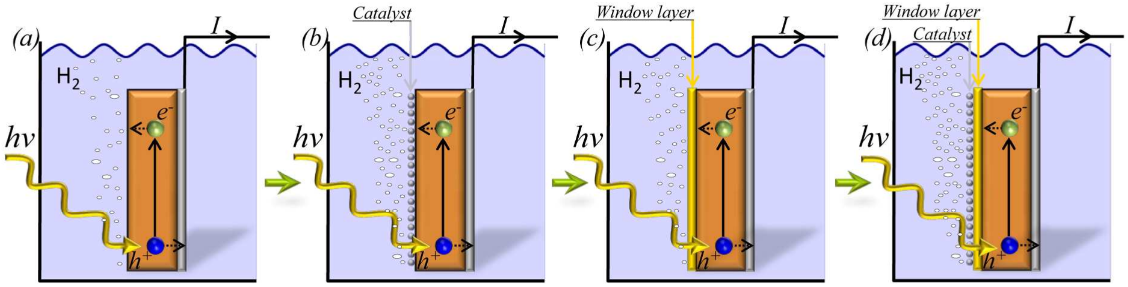

Figure 6. (a) Photocathode in a PEC-configuration. (b) Photocathode with an additional catalyst on the surface. (c) Photocathode with a transparent window layer. (d) Photocathode with both a transparent window layer and an additional catalyst.

If the window layer is properly doped, it will together with the absorber material constitute a solid state heterogeneous pn-junction and thereby be vital for the charge separation. Window layers of ZnO have been demonstrated to work in this way while deposited on CIGS[24], and ultrathin films of Ni while deposited on silicon[80], which demonstrate the concept in practice.

Besides dealing with the problem of stability, the idea of a protective window layer in PEC-devices turns out to have several interesting and important conceptual and practical implications, which will be detailed in the next section.

6. Importance of catalyst geometry

For the electrodes in figure 6.d and 7.a, the catalyst is deposited on top of the protective window layer. If the mechanism for charge carrier separation is by a solid state pn-junction, additional possibilities opens up for the topological design of the catalyst. Instead of letting the minority carriers be transported perpendicularly through the window layer out to the catalyst, the path of charge transport can be prolonged. The charge carriers can be transported in the plane of the window layer and be collected at a conductor, loaded with a catalyst, placed perpendicularly to the electrode, as in figure 7.b. The window layer must have a fairly low resistance for this to work, otherwise η_{trans} will increase. Possible alternatives for such a window layer are for example ZnO:Al, Sn_2O:In, TiO_2, and MgO. The drawback with this configuration is a possible increase in η_{trans} and a decrease in $\square_{trans}$ due to longer distance of charge transport and due to parasitic charge transfer at the part of the window layer/electrolyte interface not covered by the catalyst. The real advantage with this approach is the practical possibilities allowed by this topological transformation.

With the geometrical configuration of figure 7.b, using a low resistive window layer and a vertical catalyst, no desired charge transfer reactions occur at the interface between the window layer and the electrolyte. The interface is thus not essential for the water splitting reaction and could be removed by covering the surface with a transparent, inert and protective polymer coating[48], as in figure 7.c. This coating is only penetrated by the perpendicular, catalyst loaded, current collector. If perfectly transparent, this additional layer does not directly change the physics in terms of charge carrier absorption, separation, transport, and transfer. It does, however, solve the problem of stability by completely separating the fragile photoabsorber and the window layer from the aggressive electrolyte. If the window layer not is conductive enough, the polymer coating allows for the deposition of a metal current collector on the top of the window layer, as is standard for PV-cells. This decreases the resistive losses, η_{trans}, but also decreases $\square_{gen}$ by a few percent due to the shadowing effect.

Besides from solving the problem of stability, the introduction of a stable polymer coating and a perpendicularly catalyst has an additional set of advantages. By letting the catalyst be deposited perpendicularly with respect to the absorber material, the absorption losses in the catalyst, which can be substantial[24], will to a large degree be avoided. It also allows for using a completely different area of the catalytic material compared to the area of the photoabsorber. This enables the use of less efficient and more low cost catalysts demanding a higher surface area. The polymer coating and the metal grid may, however, lead to some absorption losses. The flexibility in terms of electrolyte composition increases greatly and more aggressively, but also more potent, electrolytes can be used, as they no longer need to be compatible with the absorber material and the window layer. This can have large positive effects on the required overpotential[24]. The demands on the window layer also weaken as it no longer needs to be stable in contact with the electrolyte but only has to be transparent and conductive.

This may seem like a small change to the configuration of the PEC-cell. The consequences it bears with it may, however, shift the perspective on how the problem of solar water splitting is perceived and addressed. It is interesting that so small a change can have so large an impact on device engineering and performance. By introducing an inert polymer coating, a short metal wire, and by letting the charge transport be prolonged from the nm to the cm range: the stability problem is solved, there is a potential gain in absorption, a broader set of electrolytes can be used, and more geometrical freedom in the design of the device can be allowed. Sealing procedures with resins or glass are used in the commercial PV-industry today and it is possible that future application of solar hydrogen production also will follow this route.

The length of the conductor penetrating the polymer cover is rather insignificant. A very small conceptual step to take is to increase the length of the conductor, and therby increasing the physical separation between the functionality of absorption and catalysis. Once the conductor is long enough, the photoelectrode can be placed outside the electrolyte, and connected to the catalyst loaded electrode in the electrolyte by a wire, as in figure 7.d. This transformation has no effect, whatsoever, on the physics of the charge carrier generation, the separation, or the catalysis. Of the fundamental processes only the charge transport is influenced, which is affected by a longer distance of transport in a low resistive wire.

The removal of the photoelectrode from the electrolyte does, however, provide access to a complete range of further advantages. The protective polymer cover is no longer needed and can be removed, even if some surface protection will be needed when operating under outdoor conditions. The stability problem caused by the interface to the electrolyte is not only solved, it is removed all together. There are no longer any losses due to absorption or reflection in the air/container and container/water interfaces. A large set of electrolytes can be used and optimized with respect to the catalyst. The constraints on the catalysts are less severe, and they can be positioned behind the photoabsorber and no longer need to be transparent. They could also be synthesized independently from the absorber material. All this makes it easier to draw upon the wealth of research performed on water electrolysis, as most of the constraints due to interference with the absorber material are removed. It also opens up for a more modular approach where the photoabsorber and the catalysts can be developed, tested, optimized, and exchanged independently.

This last configuration in figure 7.d corresponds to classical PV-electrolysis, which often is considered as something completely different from photoelectrochemical water splitting using PEC-cells. The described set of transformations do illustrate how closely related the two concepts are, and how a monolithic PEC-cell almost seamlessly can be transferred into a PV-electrolysis setup and back again.

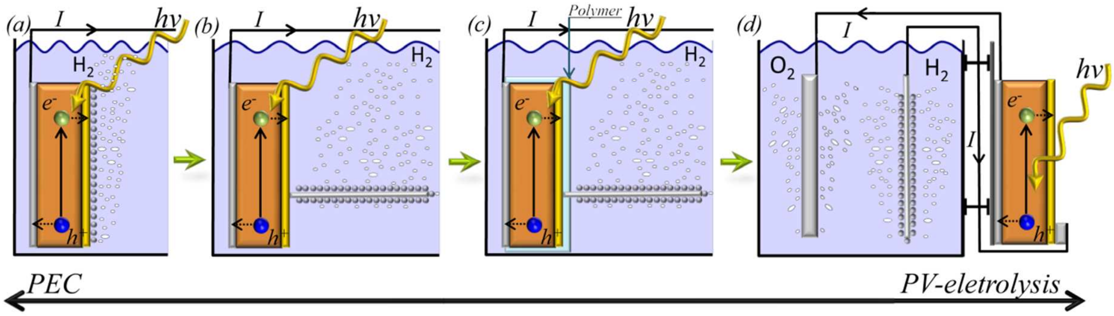

Figure 7. (a) A PEC-cell with a protective window layer on top of which a catalyst is deposited. (b) The catalyst is instead deposited on a conductor placed perpendicular to the window layer. (c) A stable and transparent polymer is coated around the photoelectrode and the window layer, and penetrated by the catalyst loaded perpendicular conductor. (d) By increasing the distance of the perpendicular conductor, the photoelectrode can be removed from the electrolyte and the polymer coating can be removed. This transforms the system into a traditional PV-electrolysis setup.

By simply changing the distance of charge transport trough a number of small transformations, each having a limited impact on the underlying physics, the different worlds are bridged without much of a problem.

An argument sometimes seen in the literature[5, 21] to why PEC-cells and PV-electrolyzers are fundamentally different, and why PEC-cells have an inherent higher potential, concerns the area of the catalyst. The core of the argument is that that catalysts in a PEC-configuration do not need to be as efficient as for PV connected electrolyzers, as their surface areas should be much larger. For a PEC-device, the simplest geometry gives that the projected area of the catalyst will equal the area of the photoabsorber, leading to current densities around 10 mA/cm^2 for a good device. Commercial electrolysers, which could be connected to PV-cells, tend to be operated at considerably higher current densities. This unavoidably leads to high overpotentials, unless expensive noble metal catalysts are used, and even then, the overpotential is a serious efficiency problem. Because of the lower current density, a PEC-catalyst can be less efficient than the PV-catalyst and may still be operated at a lower overpotential. At a first glance this may seem to make the PEC-configuration a more efficient approach.

Unfortunately, this argument does not hold under a more careful scrutiny. If the geometrical configuration of the catalyst used in a PEC device would be beneficial, it would be straightforward to incorporate it in a free-standing electrolyzer. Any catalyst that can be deposited on a photoabsorber could in principle be deposited on another conducting substrate of the same area, with the benefit of no absorption losses by blocking the path of the incoming light. The reverse is, however, not true as not all catalyst can be deposited on fragile photoabsorbers. The cost of the increased amount of substrate is sometimes used as a counterargument to this. The flexibility and the possible set of substrates are likely far greater for catalyst deposition than for integrated photoabsorber/catalyst deposition, why this probably is a minor problem.

An important but maybe not obvious consequence of depositing a metal catalyst on a separate electrode, instead of directly on the absorber material, is that the constraint of band edge positions overlapping the water redox levels is removed. By spatially separating the absorber from the catalyst, and utilizing metal substrates for the catalyst, the Fermi levels in the resulting electrodes will tune themselves towards the water redox levels, allowing the device to utilize the full driving force in terms of the potential difference between the two poles of the absorber module.

The PEC-cells of figure 3.c and the PV-electrolysis cell of figure 5.a tend to be treated as two fundamentally different systems and are described in separate narratives that seldom mix. We argue that it is more appropriate to see them as essentially the same concept, which is evident if the different configurations are decomposed in terms of the fundamental processes described in Section 2.

The same photoabsorbers can be used in both setups, and $\square_{gen}$ is thus potentially equal. For the charge carrier separation, there are different alternatives. A solid state pn-junction can be used in both systems, making $\square_{sep}$ and η_{sep} equal. The Helmholtz mechanism is a common choice for charge carrier separation in PEC-cells and seemingly less compatible with PV-electrolysis. If this turns out to be a more efficient mechanism, it is, however, possible to incorporate this also for the PEC-case by using, for example, a dye sensitized solar cell. This has the additional benefit that the redox couple and the SEI can be optimized to a larger degree. The $\square_{sep}$ and η_{sep} can thus be made rather similar also in this case. The largest difference is in the charge carrier transport, and as the PV-electrolysis depends on more wires and interfaces than the PEC-cell, additional resistive elements are introduced that can decrease $\square_{trans}$ and increase η_{trans}. The additional resistive elements included in the case of PV-electrolysis are, however, very small as conduction in metals over short distances is effective. The catalysis is identical in the two systems except for the thermalization of electrons into a metal and use of a substrate different from the photoabsorber material in the PV-configuration. As any catalyst that can be employed in the PEC-case also can be employed in the PV-electrolysis setup, $\square_{cat}$ and η_{cat} are more or less identical, given that the same catalysts are used and that the new substrate not affects the overpotential.

7. Bridging the concepts

The forgoing analysis show the close relation between PEC-cells and PV-electrolyzers and that they in many cases can be regarded as essentially equivalent approaches to the problem of solar hydrogen generation; at least while analyzed within the framework of the fundamental physical processes outlined in Section 2. The foregoing theoretical discussion illustrates how the gap between these two seemingly different concepts can be bridged. The chain of transitions employed will here be summarized and analyzed in some more detail. A graphical summary is given in figure 8, and numbers below are referring to this figure.

The starting point will be the monolithic PEC-cell in figure 8.a. As described in Section 3.1, these come in several different versions, differing in the number of materials used and in the spatial relation between the core functionalities. The photoabsorber can either stand alone or be combined with a back contact or a surface layer. Zero, one, or two different catalysts can be deposited on the photoabsorber, the back contact, or the window layer. All the different mechanisms for charge carrier separation discussed in Section 2 are compatible with the monolithic PEC-design.

The first transition (1), conceptually linking the PEC-cell to the PV-electrolysers, separates the monolith into two free standing electrodes and connects them by a wire. For the multilayered monolith in (a), this is essentially only a topological transformation of the back contact. The possible variations in terms of absorption, mechanism for charge carrier separation, and catalysis are essentially the same for (a) and (b), and the same set of materials could be used in both. If a working device is manufactured using two separate electrodes, it is in principle straightforward to weld them together back to back and thereby getting the monolith in (a). The two-electrode approach is, however, somewhat more flexible in practice and the devices with the highest efficiencies described in the literature are of type (b) rather than type (a).

The second transition into (c), is somewhat more arbitrary and is here pictured as the introduction of a protective surface layer on the photoabsorber with a catalyst deposited on top. The surface layer has, if properly designed, a positive impact on the stability. It also brings with it a potential preference in terms of the mechanism for charge carrier separation. As pointed out in Section 5, a photoabsorber with a protective surface layer is compatible with both the Helmholtz mechanism and a solid state pn-junction, but favors the use of pn-junctions. Linguistically, this is a conceptual divider in the literature, and these configurations tend to be referred to as PV/PEC-devices. The surface layer and the catalyst, separated from the photoabsorber, are compatible with both (a) and (b), explaining the arbitrariness of the dividing line.

With a surface layer, transition (3) is possible, which is the transformation of the catalyst into a perpendicular position with respect to the photoabsorber as illustrated by configuration (d) and discussed in Section 6. The vertical catalyst in (d) demands lower resistance in the window layer than does (c). The most important aspect of this transition is that (d) not is compatible with the use of the Helmholtz mechanism for charge carrier separation, but demands a solid state pn-junction. If a solid state pn-junction is used in (c), transformation (3) only implies a difference in the distance of charge transport.

If a vertical catalyst is used, transition (4), into configuration (e) involving a protective polymer coating is conceptually straightforward. In terms of the physical processes discussed in Section 2, this transition has a very small effect. It does, however, solve the stability problem and the demands on the window layer, in terms of stability and low resistance, decreases. This configuration is also directly compatible with interconnecting several individual cells in series, which is impossible to achieve in design (a)-(d) due to short circuiting of the front contacts of the individual cells by ion transport in the electrolyte. All designs so far, using pn-junctions for charge separation, are compatible with tandem cells.

Transition (5) simply involves increasing the distance of the catalyst covered conductor, which enables the photoabsorber to be placed outside the electrolyte, as in configuration (f). This step implies a set of distinct advantages as described in Section 6. Geometrically, this represents what traditionally is known as PV-electrolysis. This disconnects the spatial dependence between the photoabsorber and the catalyst. Thereby it enables transition (6) into a standalone PV-module connected to a free-standing electrolyzer as in configuration (g). The connection between the PV-module and the electrolyser can either be direct or through the grid.

In transition (3), the Helmholtz mechanism for charge carrier separation must be abandoned in favor of pn-junctions. The PV-electrolysis setups in (f) and (g) are, however, once again compatible with the Helmholtz mechanism, as any PV-cell could be used. It is thus possible to use a classical PEC-cell but with a more optimized redox couple than water as a PV-cell driving the electrolyzer.

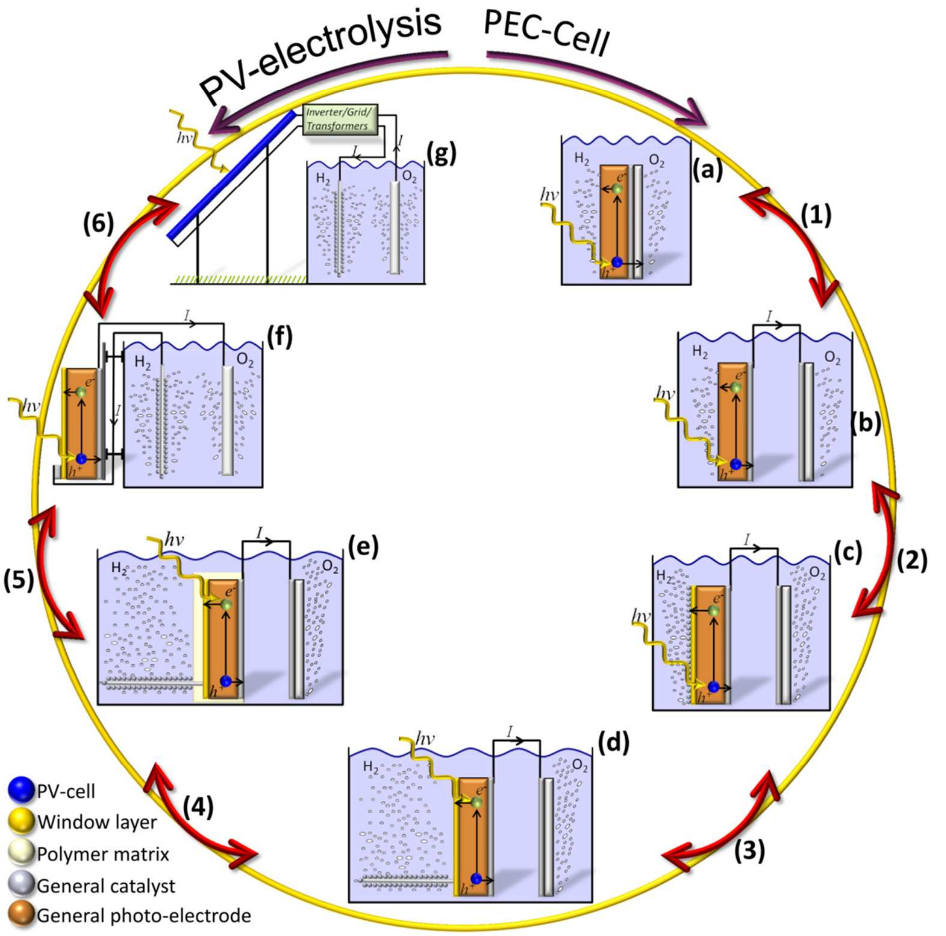

Figure 8. Illustration of a gradual transition in six steps from a monolithic PEC-device, (a), to a free standing electrolyzer connected to a PV-cell through the grid.

This series of transitions demonstrates that photoelectrochemical water splitting and PV-electrolysis essentially are varieties of the same processes. The reason PEC-cells and PV-electrolyzers often have been seen as two entirely different concepts are most likely of historical origin. The PEC-cells started to be investigated in a time when solar cells were expensive to an extent far beyond what could ever make a PV-electrolysis setup reasonably compatible in economic terms. The concept of the PEC-cell then offered a potential route to something cheaper than the solar cell of the past, without even needing the noble catalyst in the electrolyzer. The quest for working PEC-materials then started, forming a field with an inner logic of its own as so often happens in research. The different mechanisms for charge carrier separation, i.e. the Helmholtz mechanism and the solid state pn-junction, have seemingly conceptually separated the two approaches. Together with the visual difference of having the PEC-cell located within the electrolyte and the PV-cell outside of it, this has, far too often, kept researchers from seriously comparing and analyzing them with the same set of methods and using the same way of calculating the efficiencies.

Now as time has passed and the price of solar cells has reach competiveness, there is no reason for withholding this intellectual discrepancy between the two subfields of solar hydrogen production. The two concepts should be recognized for their similarities and put on an equal footing, and much is to gain by comparing and analyzing them together. PEC-cells and PV-electrolyzers could therefore preferably be classified together. As it in both cases is a question of photo driven catalytic hydrogen production we propose the unifying term: Photo Driven Catalytic Devices. The acronyms would then be PDC-devices, where the merits and science of the materials and processes involved would be in focus instead of the particular device topology.

An example from the literature of how different PEC-cells and PV-electrolyzers have been perceived can be given by comparing the response given for the record devices of Khaselev and Turner[50, 51]. In both of these articles, tandem devices based on GaAs/$GaInP_2$ were described. The configuration of the device described in the Science article from 1998[51] corresponds to configuration (b)/(c) in figure 8. It is a tandem cell composed of p-GaAs/n-GaAs/p-$GaInP_2$ with a tunnel juntion between the n-GaAs and the p-$GaInP_2$. A platinum electrode was used as a counter electrode and platinum nanoparticles were deposited on the surface of the $GaInP_2$. This device was described as a monolithic PV/PEC device and it was demonstrated to reach 12.4 % STH-efficiency. It is frequently referred to as the record device for hydrogen production by water splitting. It should also be noticed that in the article, it was described as something different from a PV-electrolyser, and as something which could give cost benefits compared to that. It should also be noted that the stability of this device is a known problem[51, 81,] and it is claimed to be very expensive[81, 82].

In the second article, published in 2001[52], a device which basically is the same tandem cell, but which better is described by configuration (f), was constructed. Instead of deposition platinum particles on the surface of the $GaInP_2$ and imersing the device in the electrolyte, the photoabsorber was kept outside the electrolyte and a front contact was deposited on the $GaInP_2$ atached to a wire leading to a separate platinum electrode. The other electrode was still a platinum electrode, but instead of free standing it was deposited on the back side of the backcontact. In the article, the device was described as an integrated multijunction PV-electrolyser, and as something standing apart from a classical PEC-device. It was, however, framed as similar to a PEC-device in that the area of the catalysts was identical to the solar cell area. The measured efficiency of this device reached over 16 % STH-efficiency and the stability was not a problem as it was for the device in the first article.

These two articels from Khaselev and Turner[50, 51] give an excellent illustration of some of the core points in this article. It is a clear example how easily a device could be transformed from something closer to a classical PEC-device, to something closer to a traditional PV-electrolysis system. It also illustrates how the chain of transitions in figure 8 can increase both the stability and the efficiency of the device. These two articles are also an illustration of how a large part of the water splitting community fails to see the equivalence between PV-electrolyzers and PEC-systems. The analysis in this article illustrates that the two devices in many aspects can be seen as essentially equivalent. The first device, which is closer to a classical PEC-device, is with its 12.4 % STH-efficiency frequently claimed as the record device for solar hydrogen production. The second device, which is closer to a PV-electrolyzer, is more efficient than the first device and reaches over 16 % STH-efficiency, but is far more seldom claimed to be the record device. This is illustrated by the fact that the second article gets less than 13 % of the number of citations the first article obtains, according to the Web of Science. The literature also contains other examples where devices reaching very high efficiencies get relatively little attention in terms of citations if they preferably are described as PV-electrolysis devices rather than PEC-devices[73, 83].

8. Costs considerations

Once a device is working and is stable, overall cost is probably the single most important parameter. A device that cannot produce hydrogen at a price that is at least comparable to the market price (including subsidies) is at its best an opportunity for increasing knowledge and a steppingstone towards a better device. At its worst, with respect to sustainable energy production, it remains forever an academic curiosity.

To estimate and compare final prices for technologies still under development is notoriously hard and unreliable, and we have no ambition to make a thorough analysis here. We will, however, give some general guidelines of thought connected to the transitions in figure 8. An important concept while comparing prices is that the measure of importance is the price of the hydrogen produced over the lifetime of the device divided by the price of the device, and not the price of the device itself. A more expensive device can very well give cheaper hydrogen, given that the increased cost is offset by an increased efficiency, or a longer span of operation. The overall cost of the produced hydrogen can coarsely be divided in cost of: materials, device production, work effort, installations, maintenance, balancing of system costs, and separation of gases. Changing the device configuration often changes more than one of those costs, further complicating a direct comparison.

A fundamental idea within the context of PEC-cell development is that a PV-electrolyzer of type (f) not will be able to compete with a good PEC-cell of configuration (a) in terms of cost for the hydrogen, simply because such a cell would be much more expensive to produce. Today the opposite is true. Cells of configuration (f) and (g) can be bought or assembled, and produce hydrogen that is still more expensive than if produced from non-renewable sources, whereas cell of configuration (a), (b), (c), (d) and (e) at the moment would produce hydrogen that would be even far more expensive than that. It is probably true that a cell of configuration (a) has the potential of reaching the cheapest production cost for the device, but it is not sure that this will be sufficient.

We will not try to predict which configuration that in the long run will give the cheapest hydrogen, but we would like to advocate a sound principle of reflection concerning prices during both fundamental research, as well as in device development. Every time a new material or working device is demonstrated, it is reasonable to perform a thought experiment where the different configurations of figure 8 are considered. Could another device-architecture be more efficient, to such a degree that the higher cost could be offset, or could it be worth compromising with the efficiency if the production cost could be lowered? By asking these simple questions, the focus of attention could be directed towards the device concept that most likely would be of most use, given the specific limitations imposed by the material systems under investigation.

9. Summary and conclusions

In this article, PEC-cells and PV-electrolyzers for solar hydrogen production are analyzed. The analysis is performed by reviewing the physics behind the process of solar hydrogen production, and a number of intermediate devices are theoretically designed which illustrate how a classical PEC-device, stepwise and gradually can be converted into a conventional PV-electrolyzer.

These two different concepts are from time to time analyzed in the same context, indicating an awareness of this in part of the community working with these problems. The way the bulk of the literature treats the connection between PEC-cells and PV-electrolyzers, as well as citation patterns, does, however, indicate that this awareness is far from satisfactory. We hope that the analysis, the argumentation, and the presentation in this article will increase the understanding of the close resemblance between PEC-cells and PV-electrolyzers. We firmly believe that much is to gain by a more well spread recognition and acceptance for this close similarity, and that one concept not should be considered without also consider the other. The unifying acronym *Photo Driven Catalytic* (PDC) Devices is suggested, where the merits and science of the materials and processes involved should be in focus instead of the particular device topology.

This point of view could potentially accelerate a fruitful crossbreeding of the accumulated knowledge in the respective sub-discipline. This bears the promise of more efficient devices for solar hydrogen production that eventually may be a working source for sustainable hydrogen production, economically compatible on the open market.

10. Acknowledgement

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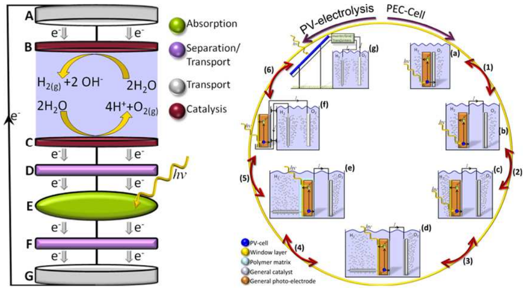
TOC



A theoretical analysis of different device concepts for solar hydrogen production, demonstrating the close similarities between Photoelectrochemical cells and PV-electrolyzers.

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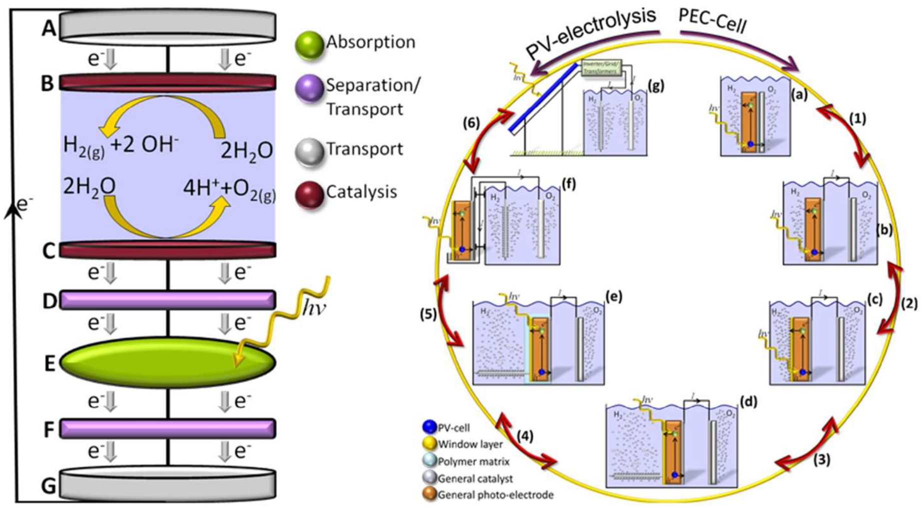

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