

Development of a membrane for photo-induced hydrogen generation

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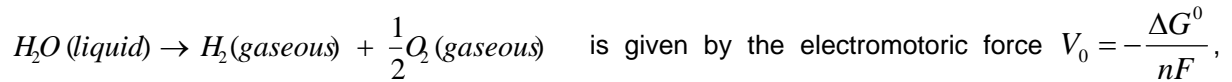
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It is well known that solar cells are able to convert sunlight into electrical energy. Due to the discontinuous availability of sunlight a part of this energy has to be stored, what can be realised by using, for example, rechargeable lithium batteries. Another option is the storage of chemical energy in form of hydrogen, produced by water splitting via solar energy. Compared with battery systems and hydrocarbons such as benzene or diesel, hydrogen has an extraordinary high energy density and can be stored in pressurized bottles or as metal hydrides. The low weight of hydrogen and its high energy content make it also attractive as fuel for mobile applications. For reasons of comparison, 6kg H₂ correspond to 200kWh chemical energy while the weight of a 540kg lithium ion battery is needed to deliver 100kWh electrical energy. Subsequent conversion of this chemical energy into electricity by a fuel cell system (typical efficiency: 50%), the overall energy conversion efficiencies are comparable. Since cheap metal hydrides are presently not yet available for technical application, compressed hydrogen has to be stored in specific containers. Based on present technology, the system weight of 125kg (H₂) still compares favorably with a battery system of 830kg weight.

Therefore to efficiently store chemical energy in form of hydrogen, novel storage systems (e.g. metal hydrides, methanol), but also efficient energy converting systems have to be developed using sunlight as an virtually inexhaustible renewable energy source. For an envisaged future hydrogen economy, efficient catalysts and efficient energy converting devices have to be developed.

In contrast to the process of photosynthesis where non-noble metal catalysts (Mn- and Fe-Ni- clusters) convert CO₂ and water into O₂ and hydrocarbons, presently existing artificial systems - combining solar cells with an electrolyser - employ platinum and ruthenium oxide in the process of water splitting. One of the intriguing research goals is therefore the mimicking of the thylakoid membrane in plants. Therefore, the development of an artificial "water splitting membrane" is of particularly high importance allowing the direct conversion of sunlight into hydrogen and oxygen. Approaches that include organic and inorganic systems to achieve this goal have been proposed. The basic problems relate to the stability of organic artificial systems and therefore, we have introduced a design that uses hitherto inorganic components: a thin film photovoltaic monolithic so called back-to-back tandem structure with integrated catalysts at the photocathode (hydrogen generation) and the photoanode side (oxygen generation) enables water splitting with sunlight (Figure 1). A first prototype has been realized by Neumann et al [1-2] using a chalcopyrite thin film solar cell absorber with a niobium-doped TiO₂ emitter layer and adsorbed platinum particles at the cathode. At the photoanode, a porous TiO₂ layer was used. The achieved photovoltage from the illuminated chalcopyrite solar cell was too small to split water directly because of the small solar photon flux in the spectral region where TiO₂ absorbs. For proof of concept, more intense UV radiation was applied at the anode side to drive the process which resulted in water splitting. The general concept of monolithically integrated systems is favored here because it is considered as more promising with regard to technological applicability and costs when compared to separate photovoltaic-electrolyzer approaches [3-4].

The thermodynamic potential of water dissociation reaction according to the chemical equation



where the free Gibb's enthalpy ΔG^0 is defined by $\Delta G^0 = \Delta H^0 - T\Delta S^0$. At pH = 0 and T = 25°C a value of $V_0 = 1.23V$ is obtained. The main challenges beside the surface stability of the light absorbing material and the stability of the nano-scaled catalysts are so-called overvoltages. In particular the overvoltage at the anode side where four electrons have to be transferred via the electrode – electrolyte interface to oxidize two water molecules to obtain one O_2 molecule, is typically rather large, reaching values between 0.4 and 0.6V. The size of this value strongly depends on the properties of the used catalyst. Because these overvoltages are an inherent limiting parameter of the process, they affect the efficiency

$$\eta_{\text{photoelectrolysis}} = \eta_{\text{PV}} \times \eta_{\text{electrolysis}} \quad \text{with } \eta = \frac{1.23V}{V_{\text{cell}}},$$

of the process substantially.

Figure 2 shows a schematic energy diagram where the dependency of the working potentials V_W at the electrodes of half cells from the current density is shown. Although no numbers are given in the diagram a current density of e.g. 10mAcm^{-2} can necessitate a potential V_{cell} which is 30% to 50% higher than the thermodynamic value of 1.23V.

Application of these considerations to the semiconductor-electrolyte phase boundary demands that the absolute positions of the semiconductor conduction and valence band are located such that the reduction reaction of protons to H_2 can proceed from the conduction band and that the valence band is energetically located below the potential for anodic water decomposition. In addition, with semiconductors, one needs a driving force for charge separation as reflected in the energy band bending. Also, resistive losses in the electrolyte and series resistance have to be taken into account. This adds up to a value of about 2.2eV - 2.3eV for the energy gap of a suited semiconductor. The respective energy diagram is shown in Fig.3 together with the basic fuel generation reaction schemes. With a limiting energy gap of $\sim 2.3\text{eV}$, the theoretical solar energy conversion efficiency for a single junction is in the range of 14% under AM 1.5 conditions. Therefore, the use of tandem structures that evolve hydrogen and O_2 appears more promising with respect to higher system efficiencies [5].

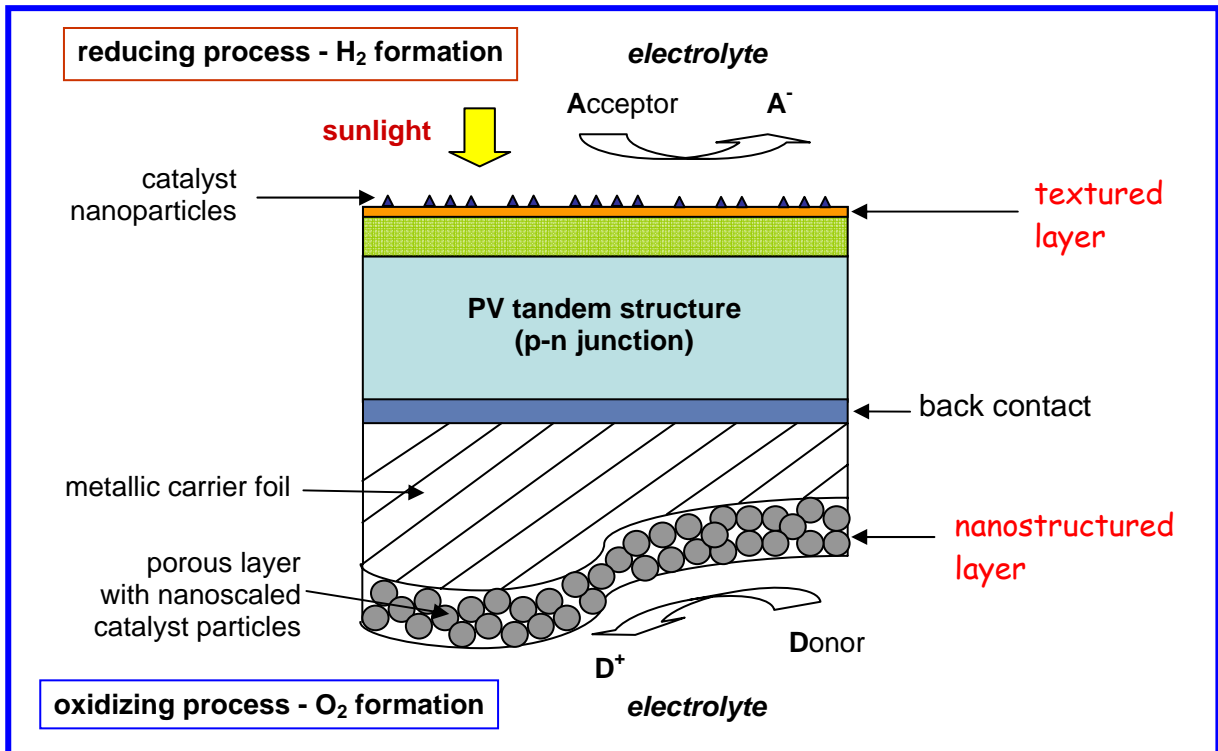


Fig.1: Schematic cross section of a water splitting membrane combining a thin film tandem solar cell structure with nano-scaled catalysts to generate hydrogen at the cathode and oxygen at the anode side under irradiation of the device with sunlight after immersion in water (adapted from [2]).

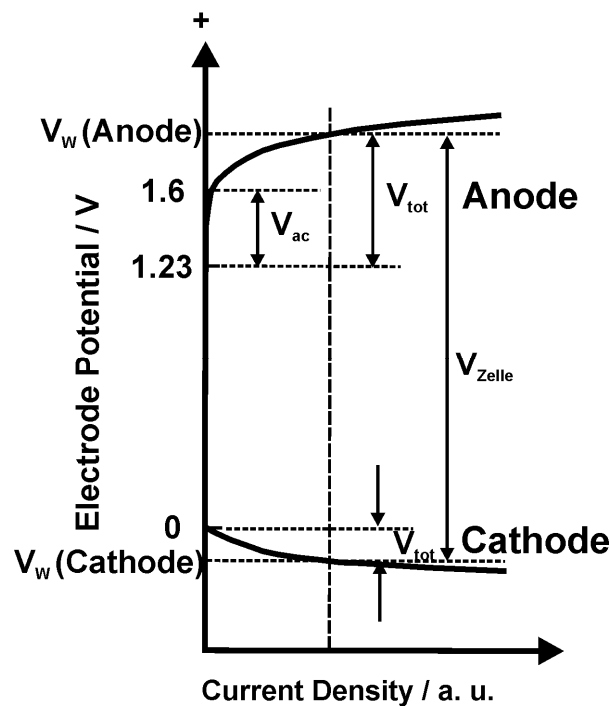


Fig.2: Schematic representation of the dependency of the current density from the applied potentials V_w at the cathode and the anode side. The I-U curves shown increase exponentially with increasing current density. The current density especially ascends at the anode side where oxygen evolution occurs during water splitting.

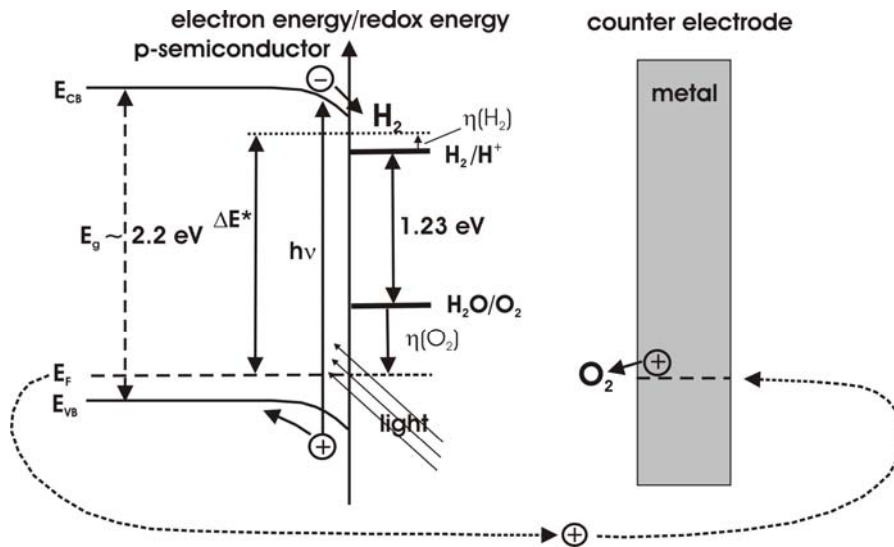


Fig.3: Overall energetic restraints for the evolution of H₂ and O₂ at semiconductor-electrolyte interfaces; η denotes the overpotentials (V_w) in electrochemical notation, ΔE^* is the cell voltage V_{cell} of Fig.2. The system drawn uses a p-type semiconductor at which H₂ evolution takes place by electron injection into the electrolyte from the conduction band. O₂ evolution energies are included to visualize the overall energetic situation.

- [1] H.Tributsch, B. Neumann; International Journal of Hydrogen Energy 32 (2007) 2679.
- [2] B. Neumann, F. Birau, B. Johnson, C. A. Kaufmann, K. Ellmer, H. Tributsch; phys. stat. sol. B 245 (2008) 1849.
- [3] N.S. Lewis, Nature 414 (2001) 589
- [4] A.J. Bard, M.A. Fox, Acc. Chem. Res. 28 (1995) 141
- [5] C.A. Grimes, O.K. Varghese, S. Ranjan; Light, Water, Hydrogen, The Solar Generation of Hydrogen by Water Photoelectrolysis, Springer, Berlin, 2007.