

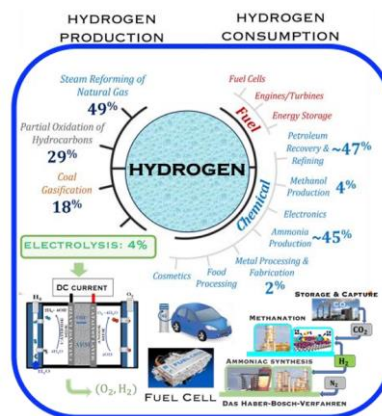
## Advanced Electrochemical Solar Energy Conversion to green Hydrogen and Carbone Dioxide reduction: Learning from the nature

**Prof. Ahmed Ennaoui**

President of the scientif council of IRESEN, Former head of research group and project leader at Helmholtz-Zentrum Berlin für Materialien und Energie

### Summary:

A close look to the figure 1 shows that Hydrogen technology is intensively used for refining and chemicals. However, 95% of the its production is coming from steam reforming of natural gas, which are emitting 830 million tons/year of CO<sub>2</sub>. The environmental impact is challenging for large-scale development. Obviously the use of renewable energy resources can offer zerro emission of greenhouse gases and become the sustainable solution of the future

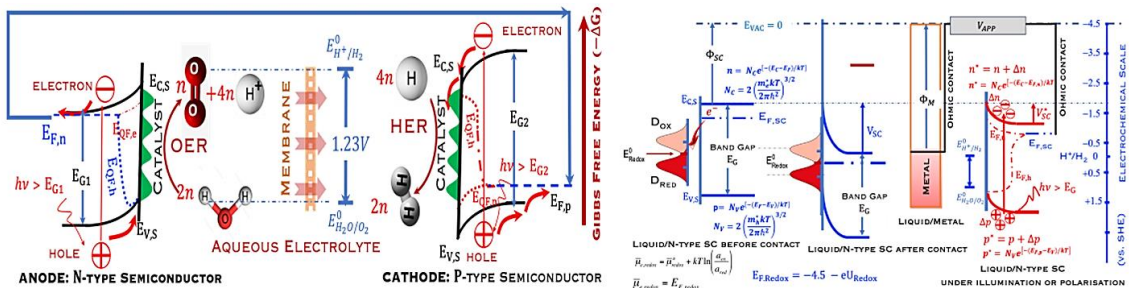


**Figure 1:** Powe to X, showing hydrogen production and consumption adapted from: S. Shiva Kumar and Hankwon Lim, *Energy Reports* 8 (2022), pp. 13793-13813 entitled *An overview of water electrolysis technologies for green hydrogen production*. Only ca. 4% of hydrogen production represents green hydrogen from water splitting using DC electrical energy. The illustration shows a complete scenario of carbon capture utilisation and storage solutions for different industries (e.g. Haber–Bosch process). The highlight includes hydrogen car and fuel cells

Inspired from the nature, “thanks to the photosynthesis process by which plants convert sunlight and water into energy” we will deeply discuss the process of "Photoelectrochemical solar energy conversion" and the conditions to achive efficient solar-to-hydrogen devices. Firstly, we describe a photoelectrochemical Solar cell (PEC) in the dark and under illumination. PEC consists of two photoactive semiconductors working electrodes (n and p-type) immersed in the electrolyte containing suitable aqueous redox electrolyte. The illumination (see Figure 2) of the semiconductor/electrolyte junction with a light having energy greater than the band gap ( $EG$ ) of the semiconductor, we can observe a process similar to the photosynthesis, namely:

- (1) Light absorption
- (2) Charge separation

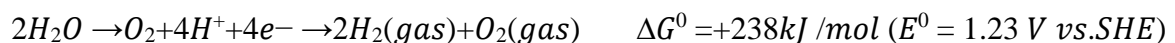
- (3) Charge transport
- (4) Electricity and/or fuel generation



**Figure 2:** Left: Analogy with the “Artificial Photosynthesis Process”, namely: water splitting reactions:  $O_2$  evolution reaction (OER) on the anode surfaces and  $H_2$  evolution reaction (HER) on the cathode surface described in the illustration. The kinetics of (Photo)-Electrochemical electron and ion transfers depend strongly of the catalytic performance of the photo-electrodes. Right: illustration and comparison of a metal, semiconductors (n- and p-type) and redox electrolyte versus two scales (absolute scale vs. vacuum and electrochemical scale vs. Hydrogen SHE)

Upon light excitation, charge carriers (electrons and holes), are generated within the semiconductors. The minority carriers are separated in the space region by the electrical field and move to the Solid/Liquid interfaces. Holes migrate to the n-type semiconductor photoanode surface to complete oxidation of water, the resulting protons ( $H^+$ ) move to the cathode through a membrane and reduced by the photogenerated electrons at the surface of the p-type photocathode liberating green hydrogen ( $H_2$ ).

This is a direct way to convert solar energy into fuels and requires an amount of Gibbs free energy  $\Delta G^0 = 238 \text{ kJ/mol}$  reaction:



We have to keep in mind, that the photoelectrodes must possess an energy gap ( $E_g$ ) exceeding the thermodynamic limit of 1.23 eV. Also, the electron transfer occurs via a single electron process (one photon excites one electron per time). However, the (photo)electrochemical water splitting (4 electrons process) goes through a multistep requires favourable electrocatalyst activities of the photoelectrodes with favorable kinetics to allow such complex OER and HER reactions.

As a matter of semiconductores with photocatalytic performance necessary to achieve the goal, namely: high solar-to-hydrogen energy conversion efficiency. The attendees should be:

- 1) Able to understand the fundamental concepts of semiconductor/Electrolyte junction
- 2) Able to recognize the differences between metal and semiconductor electrode materials;
- 3) Able to identify and explain all processes that occur at Solid/Electrolyte interface namely: majority/minority carriers, charge generation/recombination, band bending, flat band potential, surface states, band shifts, and Fermi Level pinning
- 4) Able to perform Current-Voltage and capacitance measurements and design catalysts in material sciences