Introduction

Photoelectrochemical water splitting can convert solar energy directly into hydrogen which can be transformed into liquid fuels. Cheaper and less material can be used for photoelectrochemical water splitting cells and can theoretically reach higher efficiency than PV panels wired to conventional water electrolysis (1).

This Master project investigates 2-scheme photoelectrochemical water splitting devices which can capture a larger part of the solar irradiation spectrum than standard photoelectrochemical water splitting devices. Two models are developed: A device with two porous electrodes connected through a wire for the electron transfer and a device made of particulate semiconductors with electron shuttles to “connect” them. Both systems have their strengths and weaknesses which are highlighted in this project through a variety of simulations made with the commercial FEM software COMSOL Multiphysics® and Matlab.

Photoelectrochemical water splitting

Photoelectrochemical water splitting refers to the dissociation of water into its constituent parts, hydrogen \( \text{H}_2 \) and oxygen \( \text{O}_2 \) using artificial or natural light.

\[
\text{H}_2\text{O} \xrightarrow{1.23 \text{eV}} \text{H}_2 + \frac{3}{2}\text{O}_2
\]

Z-scheme or tandem artificial photosynthesis

The cell potential can be achieved by two absorbers with a 2-scheme model. Hence, the minimum potential of 1.23 V is split into two potentials that can be smaller than 1.23 V. The two 2-scheme models investigated in this project are given here.

Z-scheme with porous electrodes and ohmic contact

Electrochemistry

The equilibrium potential given by the Nerst equation is modified when a current is applied to the system because electron’s energy is added to the redox reaction. The Nerst equation for the equilibrium potential is:

\[
E_{eq} = E^0 + \frac{RT}{nF} \ln \left( \frac{\prod [c_{\text{red}}]}{\prod [c_{\text{ox}}]} \right)
\]

The (modified) Butler-Volmer equation describes how the electrical current on an electrode depends on the electrode potential, considering that both a cathodic and an anodic reaction occur on the same electrode:

\[
i_l = i_0 \left[ \prod \left( \frac{c_{\text{red}}}{c_{\text{red},0}} \right)^{\frac{V_{\text{red},l}}{V_{\text{red},0}}} \cdot \frac{e^{\frac{E_l - \eta}{RT}}}{e^{\frac{E_l - \eta}{RT}}} \right] = i_0 \left[ \prod \left( \frac{c_{\text{ox}}}{c_{\text{ox},0}} \right)^{\frac{V_{\text{ox},l}}{V_{\text{ox},0}}} \cdot \frac{e^{\frac{E_l + \eta}{RT}}}{e^{\frac{E_l + \eta}{RT}}} \right]
\]

 Conservation of mass

The Nernst-Planck equation is a conservation of mass equation used to describe the motion of chemical species in a fluid medium. It describes the flux of ions under the influence of an ion concentration gradient, an electric field and the bulk fluid motion. The steady state Nernst-Planck equation is given by:

\[
N_j = -D_j \nabla c_j - z_j u_i F c_i \nabla \phi_i + w c_j
\]

The current density in the electrolyte is the net flux of all charged species. Taking into account the electroneutrality it leads to the formula:

\[
i_l = F \sum z_j (D_j \nabla c_j - z_j u_i F c_i \nabla \phi_i)
\]

Results

Z-scheme with porous electrodes and ohmic contact

The I-V curve for a photoelectrochemical device with electrodes of 1 cm high and wide and with a separator width of 0.1 mm is presented in the graph below. The concentration overvoltage starts to occur around 800 A/m². The electrolyte conductivity inside the separator in the horizontal direction goes from 14 S/m down to 1 S/m which is realistic.

Particulate semiconductors with electron shuttles

The two particulate semiconductors are very sensitive to the photocurrent density. Already at a photocurrent density of 31 A/m², the concentration overpotential start to appear increasing quickly the cell voltage (Figure below). The two particulate semiconductors have a way smaller limited photocurrent (31 A/m²) compared to the porous electrodes model with similar dimensions (Figure above).

Conclusion

Based on the simulations made on COMSOL Multiphysics®, the system with porous electrodes and ohmic contact appears to have better performance than the particulate semiconductors system. The particulate semiconductors predict mass transport limitations already at photocurrent densities of around 30 A/m² and for similar dimensions the porous electrodes’ system around 800 A/m².
