A 2D Phenomenological Model for Photoelectrochemical Water Splitting

L. Rodrigues*, N. M. Delgado, T. Lopes, A. Mendes

LEPABE - Faculdade de Engenharia, Universidade do Porto, rua Dr. Roberto Frias, 4200-465 Porto, Portugal

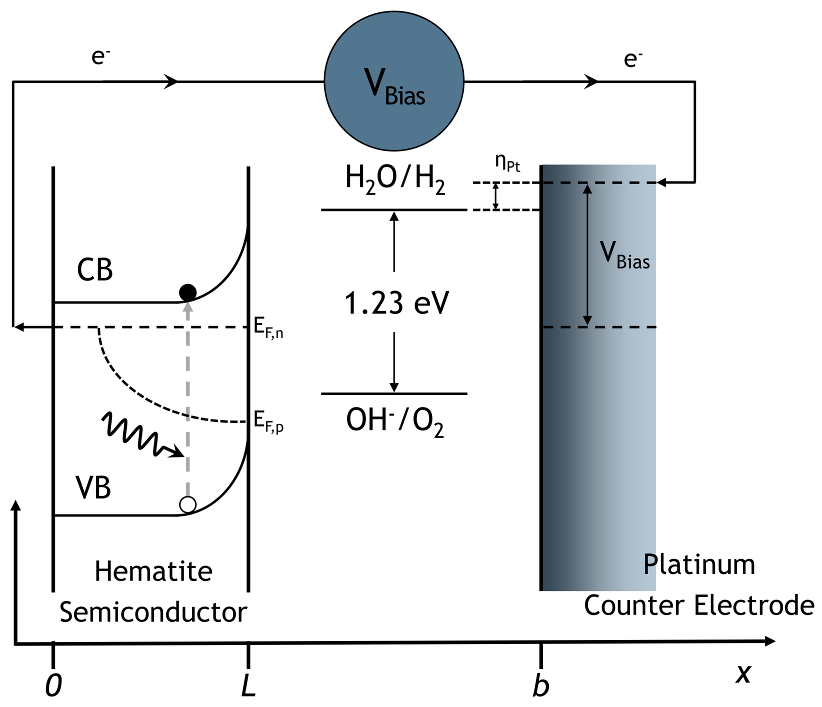
*lrodrigues@fe.up.pt

Motivation

- Photoelectrochemical (PEC) water splitting has been a major research topic in the past decades as it can become a viable alternative to clean hydrogen production [1,2].
- Tools like a simulator can play a critical role in PEC technology, namely predicting the phenomena occurring with the photoelectrochemical system and the development of optimized devices [3,4].
- A 2D phenomenological model was constructed regarding the working principles of a PEC system, a critical step for better understanding the photoelectrode role in a complete PEC system.

Model

PEC cell diagram



The photogenerated electron and hole will partake in the electrochemical reactions at the anode and the cathode, respectively:

Cathode: $2\,\mathrm{H_2O} + 2\,\mathrm{e^-} \rightarrow \mathrm{H_2} + 2\,\mathrm{OH^-}$

Anode: $2\,\mathrm{OH^-} + 2\,\mathrm{h^+} \rightarrow 2\,\mathrm{H_2O} + \frac{1}{2}\,\mathrm{O_2}$

Transport and continuity equation for the charge carriers (n_i):

$$\underbrace{\frac{\partial n_i}{\partial t}}_{\text{Carrier Concentration History}} = \underbrace{\frac{\partial j_i}{\partial x}}_{\text{Charge Flux}} + \underbrace{G(x)}_{\text{Generation Term}} - \underbrace{R(x)}_{\text{Recombination Term}} \quad \text{where } i = \mathrm{e^-, h^+, OH^-}$$

Charge Carriers Source Terms

Photogeneration

$$G_i\,(x) = \eta_{\mathrm{inj}}\alpha(\lambda)I_0\exp^{-\alpha(\lambda)(L-x)}$$

Recombination

$$R(x) = \mathrm{k}\,\Delta n_{e^-} \qquad \mathrm{k} = \frac{1}{\tau_s}$$

Energy Balance

$$\eta_{Pt} = V_{Bias} + E_g - \Delta E_F - \Delta V_{BB} - \frac{\Delta G}{nF} - \eta_{Sc} - \eta_{Ohmic} - \eta_{conc}$$

Semiconductor Energetics

$$E_G = |E_{CB} - E_{VB}| \qquad \Delta E_F = |E_{CB} - E_F| \qquad \Delta V_{BB} = |E_{FB} - E_F|$$

Water Reduction Potential

$$E_{\mathrm{H_2O/H_2}} = E^{\circ}_{\mathrm{H_2O/H_2}} - \frac{k_B T}{2\mathrm{q}}\ln\left(\frac{n_{\mathrm{H_2}}(b)n^2_{\mathrm{OH^-}}(b)}{\mathrm{n^3_{st}}}\right)$$

Water Oxidation Reaction

$$R_{oxi} = -k_{\mathrm{oxi}}\,n_{h^+}\,q$$

Butler-Volmer Equation

$$J_{cell} = J_0\left[\frac{n_{\mathrm{H_2O}}}{n^{ref}_{\mathrm{H_2O}}}exp\left(\frac{\beta nq\eta_{PT}}{k_B T}\right) - \frac{n_{\mathrm{H_2}}n^2_{\mathrm{OH^-}}}{n^{ref}_{\mathrm{H_2}}\left(n^{ref}_{\mathrm{OH^-}}\right)^2}exp\left(\frac{-(1-\beta)nq\eta_{PT}}{k_B T}\right)\right]$$

Results

Parametric Analysis of different variables

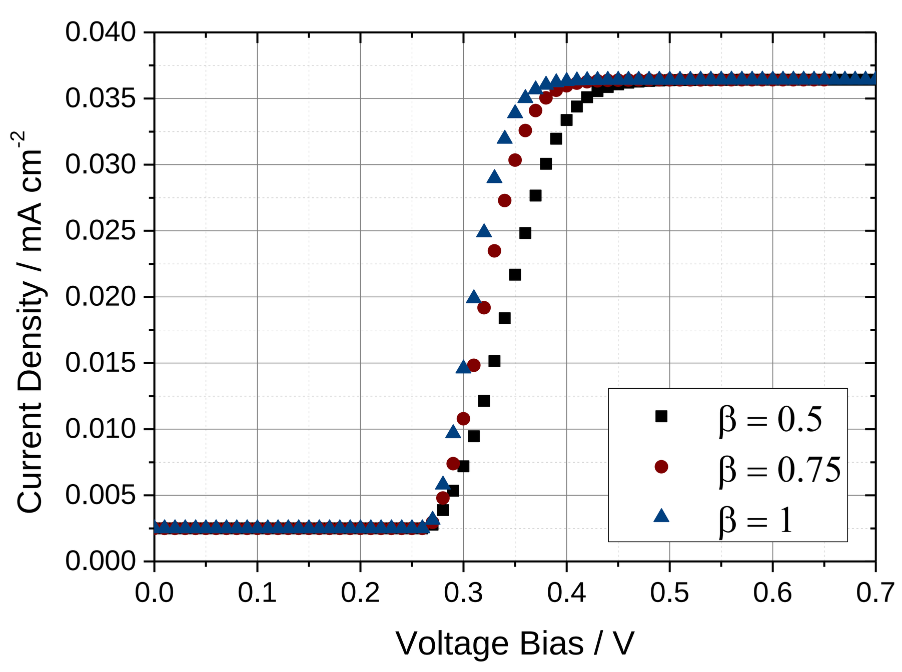


Fig. 1 - Current densities obtained for different charge transfer coeficientes (β).

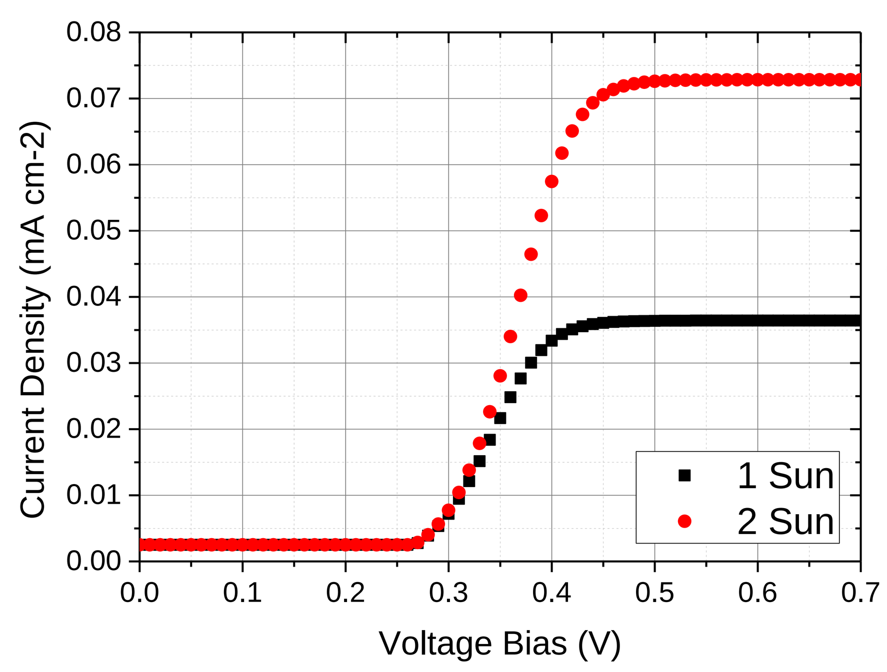


Fig. 2 - Current densities obtained for different light intensities.

Charge Carrier profiles in the semiconductor

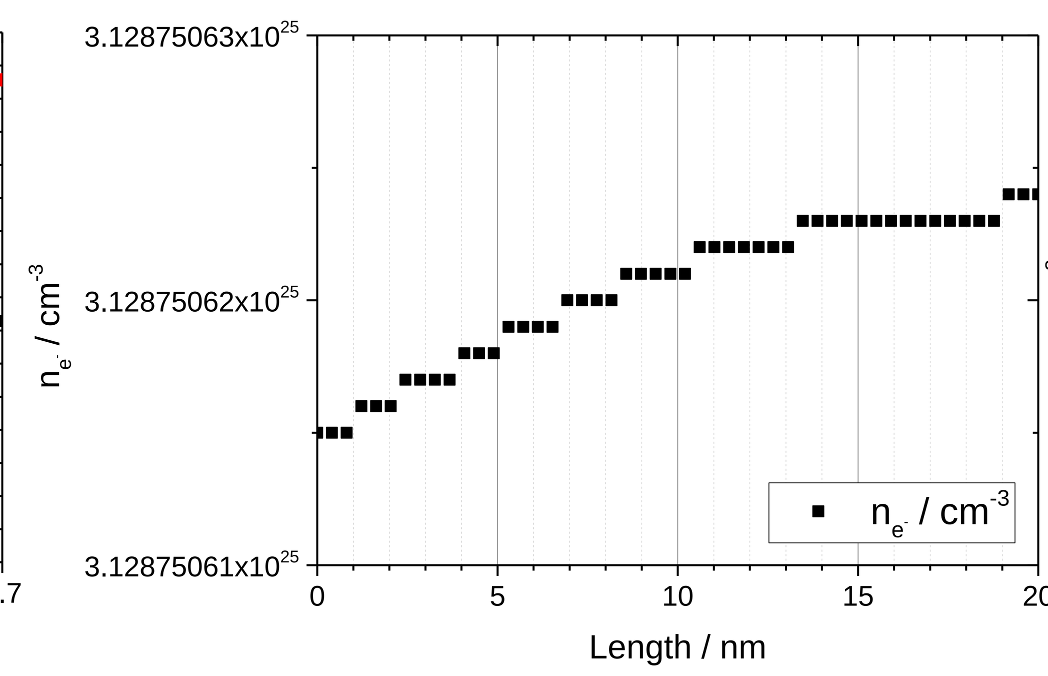


Fig. 3 - Electron density profile inside the semiconductor.

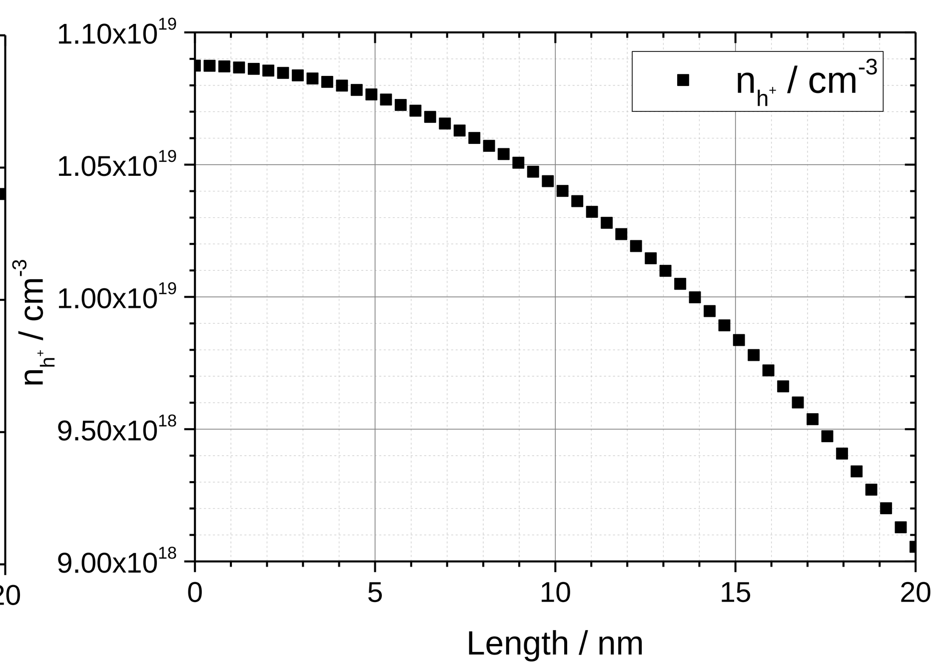


Fig. 4 - Hole density profile inside the semiconductor.

Conclusions and Future Work

- A complete 2D PEC phenomenological model was implemented using ANSYS *Fluent*. The model performs as expected, as shown in the simulated *J-V* curves presented in Fig. 1- Fig.4:
  - ✓ Increasing the charge transfer coefficient increases the slope of the onset curve, as shown in Fig.1;
  - ✓ Increasing the light intensity will expectedly increase the current density obtained;
  - ✓ The electrons and holes profiles have their lowest values at the boundary where they leave the semiconductor.
- A better assessment of the oxidation reaction needs to be done as the current density obtained is lower than the experimental results reported in the literature for similar systems. Accordingly, further improvements needs to be added to the model to better describe experimental curves.

References

[1] Vilanova, A., et al., Solar water splitting under natural concentrated sunlight using a 200 cm² photoelectrochemical-photovoltaic device. Journal of Power Sources, 2020. 454: p. 227890.

[2] Zhou, D. and K. Fan, Recent strategies to enhance the efficiency of hematite photoanodes in photoelectrochemical water splitting. Chinese Journal of Catalysis, 2021. 42(6): p. 904-919.

[3] Andrade, L., et al., Transient phenomenological modeling of photoelectrochemical cells for water splitting – Application to undoped hematite electrodes. International Journal of Hydrogen Energy, 2011. 36(1): p. 175-188.

[4] Dumortier, M., S. Tembhurne, and S. Haussener, Holistic design guidelines for solar hydrogen production by photo-electrochemical routes. Energy & Environmental Science, 2015. 8(12): p. 3614-3628.

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