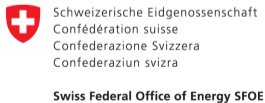


Modeling and simulation of photoelectrochemical hydrogen production

P. Cendula and J. O. Schumacher

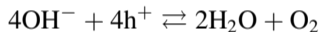
Comsol Conference, Munich, 13th Oct 2016



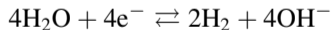
COMSOL
CONFERENCE
2016 MUNICH

Photoelectrochemical (PEC) water-splitting

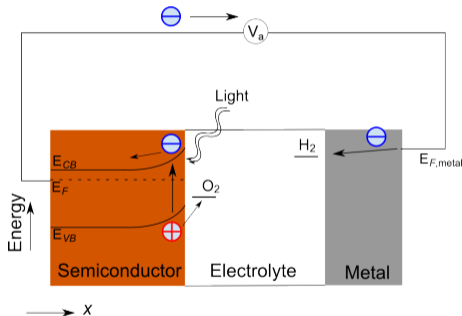
- Light absorption generates electrons and holes which are separated by the electrical field in space-charge region (SCR)
- Holes oxidize water to oxygen at semiconductor



- Electrons (via external wire) reduce water to hydrogen at counterelectrode (CE)



- Hydroxyl ions diffuse from CE to semiconductor

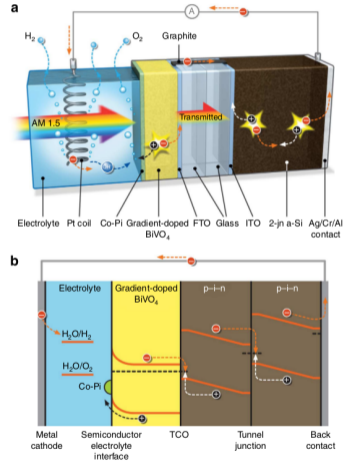


Why tandem PEC devices are needed

- So far, no semiconductor material satisfies all energetic/stability requirements for both oxidation and reduction reactions
- Various options to overcome this limitation and achieve unassisted water splitting^{1,2}
- Tandem - requires well-matched bandgaps of two semiconductors, PEC/PV, PEC/PEC

¹Prevot et al., JPCC 117, 17879 (2013)

²Nielander et al., 10.1039/c4ee02251c



Abdi, Nat.Comm. 4, 2195 (2013)

Photoelectrochemical (PEC) water-splitting

- Benchmark PEC cells reached a hydrogen production efficiency of 12.4% with GaAs¹, recently 12.3% with perovskites²
- The current challenge is to fabricate them economically -> metal oxide semiconductors (Fe_2O_3 , Cu_2O)
- To become economically viable, 10% solar-to-hydrogen (STH) efficiency³ and long-term stability needs to be achieved

¹Khaselev et al., Science 280, 425 (1998)

²Luo et al., Science 345, 1593 (2014)

³Pinaud et al., Energy Environ. Sci. 6, (2013)

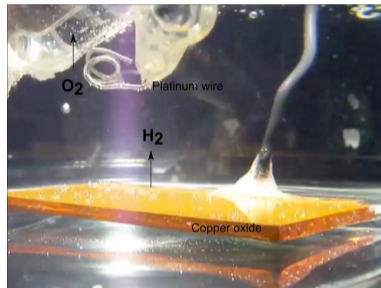


Figure: Courtesy LPI EPFL.

Charge transport model in 1D semiconductor

- Poisson's eq for electrostatic potential ϕ , electron and hole continuity eqs for their concentrations n, p

$$\frac{d^2\phi}{dx^2} = -\frac{q(N_D - n(x) + p(x))}{\epsilon_0\epsilon_r}, \quad (1)$$

$$\frac{\partial n}{\partial t} = +\frac{1}{q} \frac{\partial j_e}{\partial x} + G_e(x) - R_e(x), \quad (2)$$

$$\frac{\partial p}{\partial t} = -\frac{1}{q} \frac{\partial j_h}{\partial x} + G_h(x) - R_h(x), \quad (3)$$

where N_D is donor density in n-type semiconductor, vacuum and relative permittivity is ϵ_0, ϵ_r , electronic charge is q .

- Lambert-Beer generation for 1 sun illumination AM15G

$$G_e = G_h = \int_{\lambda_{min}}^{\lambda_g} \alpha(\lambda) \Phi_{AM15G}(\lambda) e^{-\alpha(\lambda)x} d\lambda.$$

- SRH recombination $R_e = R_h$ with trap level at intrinsic level, hole SRH lifetime is t_h

Charge transport model in 1D semiconductor

- Drift-diffusion equations for current densities

$$j_e = +q\mu_e V_{th} \frac{\partial n}{\partial x} - e\mu_e n \frac{\partial \phi}{\partial x},$$
$$j_h = -q\mu_h V_{th} \frac{\partial p}{\partial x} - e\mu_h p \frac{\partial \phi}{\partial x},$$

where charge mobilities are denoted μ_e, μ_h and $V_{th} = 0.026$ V is thermal voltage.

- Variables solved for n, p, ϕ in Semiconductor Module

Boundary conditions

- Potential at semiconductor/liquid junction is implemented with Schottky barrier (height changes with applied voltage) model and band edge pinning (tricky)

$$\phi(0) = \text{const} \quad (4)$$

- Ohmic back-contact is assumed

$$\phi(d) = V_a. \quad (5)$$

- Hole current

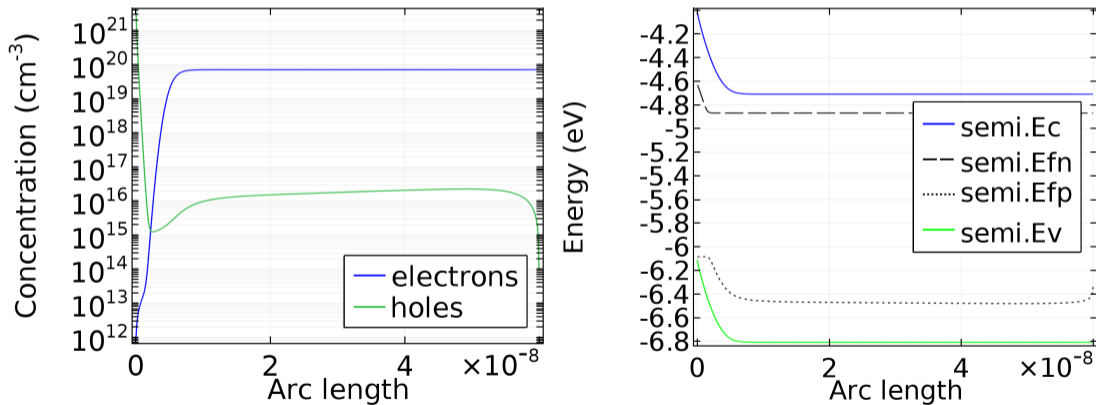
$$\begin{aligned} j_h(0) &= -q k_{trh}(p(0) - p_{dark}), \\ j_h(d) &= -q r_s(p(d) - p_{dark}). \end{aligned}$$

- Electron current

$$\begin{aligned} j_e(0) &= 0, \\ j_e(d) &= +q r_s(n(d) - n_{dark}). \end{aligned}$$

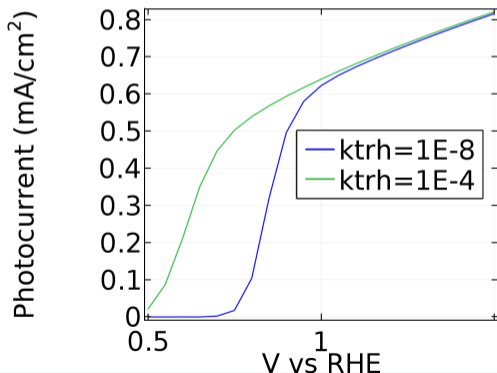
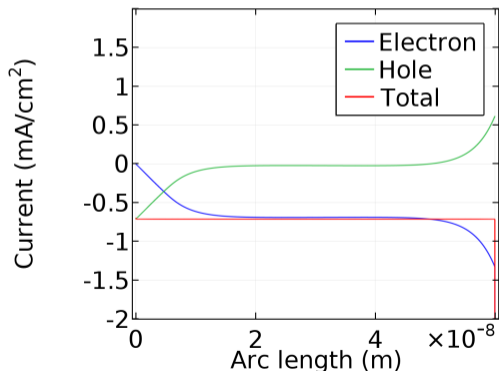
Stationary results @ 1.2 V

- Fe_2O_3 photoanode material parameters used, however many parameter uncertainties exist!



Stationary results @ 1.2 V

- Numerical IV curve does not perfectly reproduce the experimental IV => our set of model assumptions and material parameters needs to be altered
- IV response couples all kinetic effects inside one response curve => reducing the parameter uncertainty is not unambiguous



Frequency-domain perturbation study

- 1 Stationary solution $n^{dc}, p^{dc}, \phi^{dc}$ is calculated
- 2 Harmonic perturbation in voltage $V_a(t) = V_a + V^{ac} e^{i\omega t}$ causes harmonic perturbation in variables => linearization

$$p(t, x) = p^{dc}(x) + p^{ac}(x) e^{i\omega t}, \dots$$

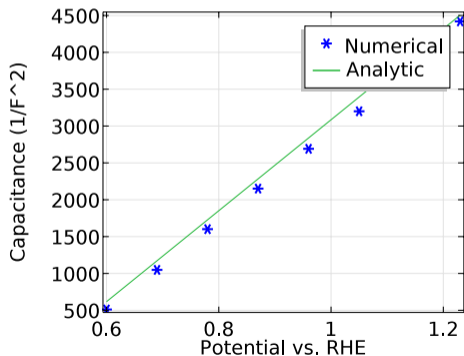
- 3 Differential equations for perturbed variables

$$i\omega p^{ac} = -\frac{1}{q} \frac{\partial j_h^{ac}}{\partial x} - R_h^{ac}, \dots$$

- 4 Numerical solution and calculation of impedance $Z = \frac{V^{ac}}{j^{ac}}$
- 5 Framework is general and can be used for many spectroscopic/transient techniques

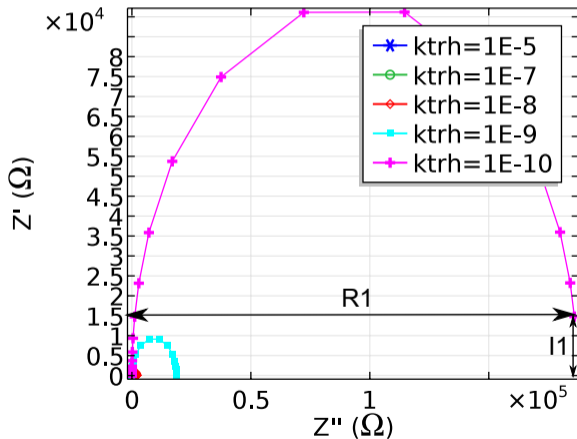
Impedance in the dark (Mott-Schottky)

- Frequency is fixed and applied voltage V_a is increased
- The Mott-Schottky theory approximates the impedance by series connection of resistor and space-charge capacitance C_{SC} , thus implying $\frac{A^2}{C_{SC}^2} = \frac{2V_{SC}}{e\epsilon_r\epsilon_0 N_D}$.
- From Comsol solution, we obtain capacitance as $C_{SC}^{-2} = \omega^2 \text{imag}(Z)^2$.



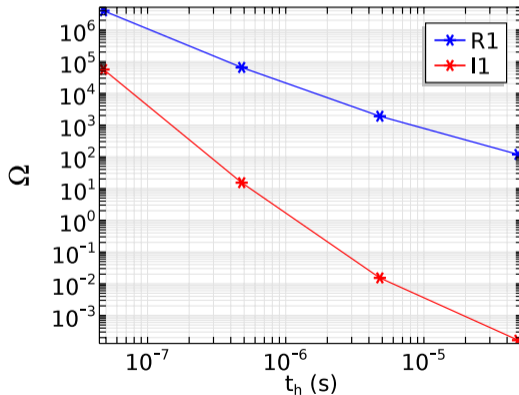
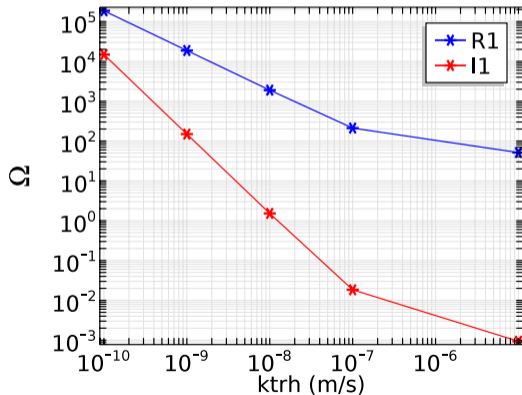
Photoelectrochemical impedance

- We investigated the dependence of real (R_1) and imaginary (I_1) part of lowest frequency impedance on parameters k_{trh} and t_h



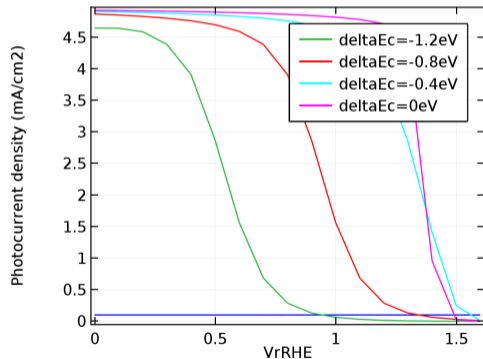
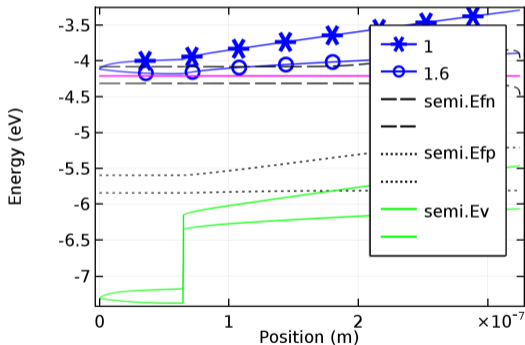
Extraction of rate constant and hole lifetime

- The linear relation between R_1 and k_{trh} , as well as between R_1 and t_h is obtained from simulations
- => parameter extraction from comparison of measured and simulated impedance data



Heterojunction devices

- Additional layers provide chemical stability, photovoltage or charge selectivity
- $\text{TiO}_2/\text{Cu}_2\text{O}$ photocathode : how band offset (ΔE_c) between semiconductor layers changes photocurrent onset potential



Summary and Outlook

- Numerical drift-diffusion calculations of the photoelectrochemical impedance
- Extraction of these two parameters from the comparison of slope of measured and simulated data
- Detail validation of the model with measured data for hematite is challenging due to uncertainties in values of material parameters/processes => further investigations of recombination and charge transfer kinetics needed

Thank you for attention!

Hematite (α -Fe₂O₃) parameters

Symbol	Value	Description
pH	14	pH value
V_{fb}	+0.5 V vs. RHE	Flatband potential
N_D	$2.9 \cdot 10^{18} \text{ cm}^{-3}$	Donor concentration
N_C	$4 \cdot 10^{22} \text{ cm}^{-3}$	Density of states of conduction band
N_V	$1 \cdot 10^{22} \text{ cm}^{-3}$	Density of states of valence band
ϵ_r	32	Relative permittivity
E_g	2.2 eV	Bandgap energy
d	33 nm	Thickness of semiconductor
I_0	1000 Wm^{-2}	Illumination power density
τ_h	48 ps	Hole lifetime
L_h	5 nm	Hole diffusion length
α	$1.5 \cdot 10^7 \text{ m}^{-1}$	Absorption coefficient