# Spectroscopic modeling of photoelectrochemical water splitting

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## Introduction

- A photoelectrochemical (PEC) cell uses solar energy to split water to hydrogen and oxygen in single integrated device, Fig. 1
- The integrated nature of PEC cell brings bottlenecks of contradictory physical requirements for the practical device (light absorption, stability, charge transport)
- We work on model-based characterization and matching of the various physical and electrochemical requirements in the PEC cell
- Electrochemical impedance spectroscopy is a suitable tool to characterize recombination and reaction mechanisms

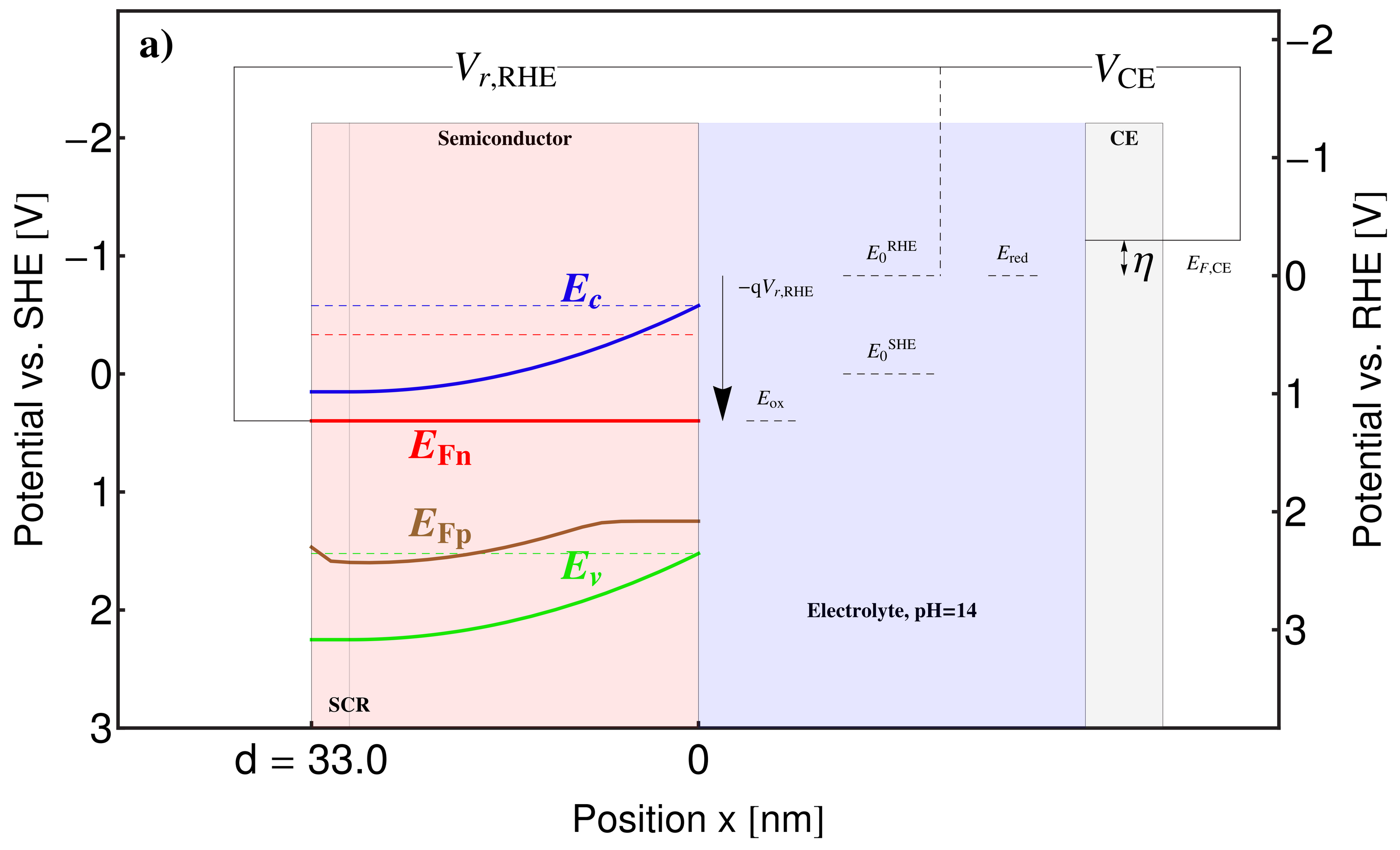


**Figure 1:** *Energy band diagram of a typical PEC cell with n-doped photoanode and metal counterelectrode.[1]*

## Transient Model

1. Poisson eq. + electron and hole continuity equations in the semiconductor
2. Rate constant for water oxidation $k_{trh}$ governs hole current to electrolyte $(x = 0)$

$$j_h(0) = -q\, k_{trh}(p(0) - p_{dark}(0)) \tag{1}$$

3. SRH recombination with trap level at intrinsic level is assumed, hole SRH lifetime is denoted $t_h$
4. Stationary solution (dc) for electron and hole concentrations $n^{dc}, p^{dc}$ and electrostatic potential $\phi^{dc}$ is calculated
5. Harmonic perturbation (ac) in voltage $V_{r,RHE}(t) = V_{r,RHE} + V^{ac}e^{i\omega t}$ causes harmonic perturbation in variables, which can be linearized around the stationary solution

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

6. Inserting the linearization into drift-diffusion equations and using the stationary solution brings us to differential equations for perturbed variables

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

7. Numerical solution and calculation of impedance $Z = \frac{V^{ac}}{j^{ac}}$

## Results

- The transient model described above is implemented in Comsol Multiphysics software
- We've used material parameters of hematite photoanode[1] for following calculations
- Without light illumination, impedance spectra at low frequency are used to extract doping level and flatband potential of the photoanode from the comparison with the Mott-Schottky analytic formula, Fig.2
- Under light illumination, transient simulations for range of frequencies $10^{-3}$-$10^{7}$ Hz is undertaken and presented in the form of Nyquist plot, Fig.2
- Nyquist plot consists of single semicircle, pointing to capacitive behavior of the electrode.

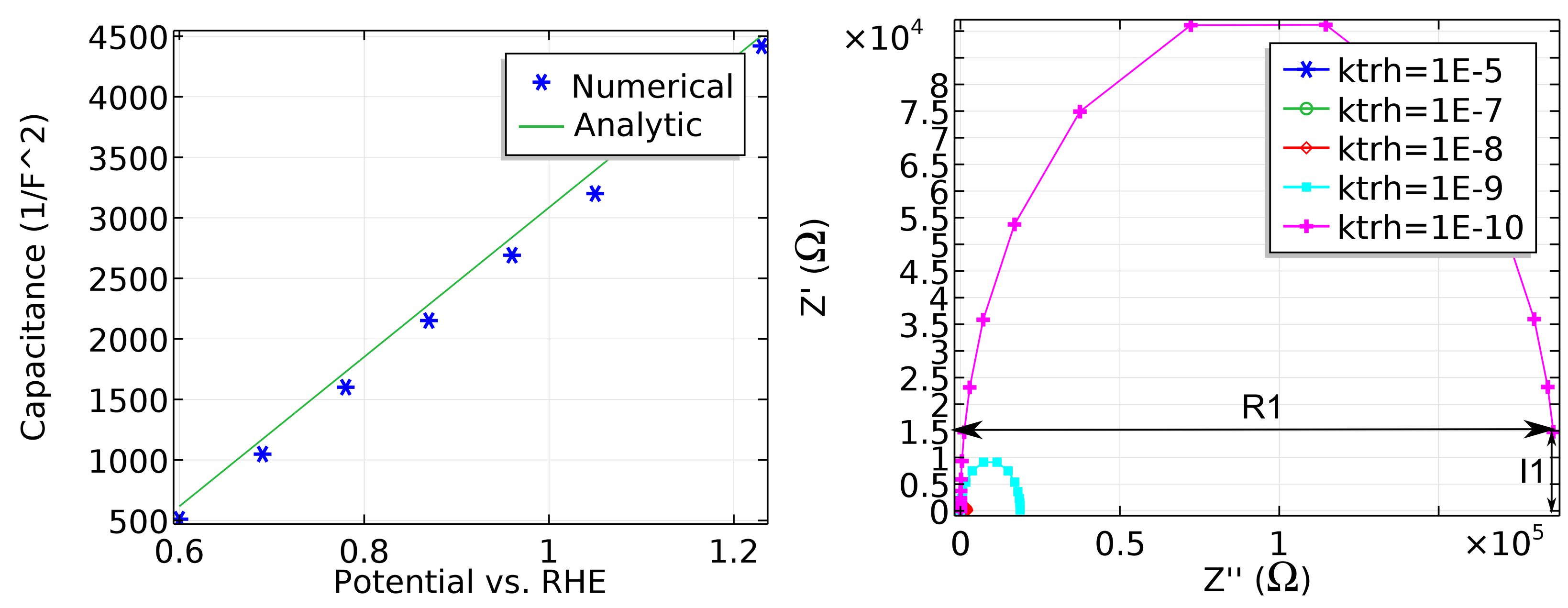


**Figure 2:** *(Left) Mott-Schottky plot of impedance in the dark. (Right) Nyquist plot of impedance under illumination for various values of $k_{trh}$ and fixed potential 0.7 V vs. RHE.*

- We investigated the dependence of real ($R_1$) and imaginary ($I_1$) part of lowest frequency impedance on parameters $k_{trh}$ and $t_h$, for potential 0.7 V vs. RHE slightly higher than flatband potential (0.5 V vs. RHE), Fig.2
- The linear relation between $R_1$ and $k_{trh}$, as well as between $R_1$ and $t_h$ is obtained from simulations, Fig. 3
- Thus, governing processes for semicircle size are both electron-hole recombination and rate of water oxidation
- The values of water oxidation rate and hole lifetime can be extracted from comparison of measured and simulated impedance data, once the model is validated for certain PEC cell

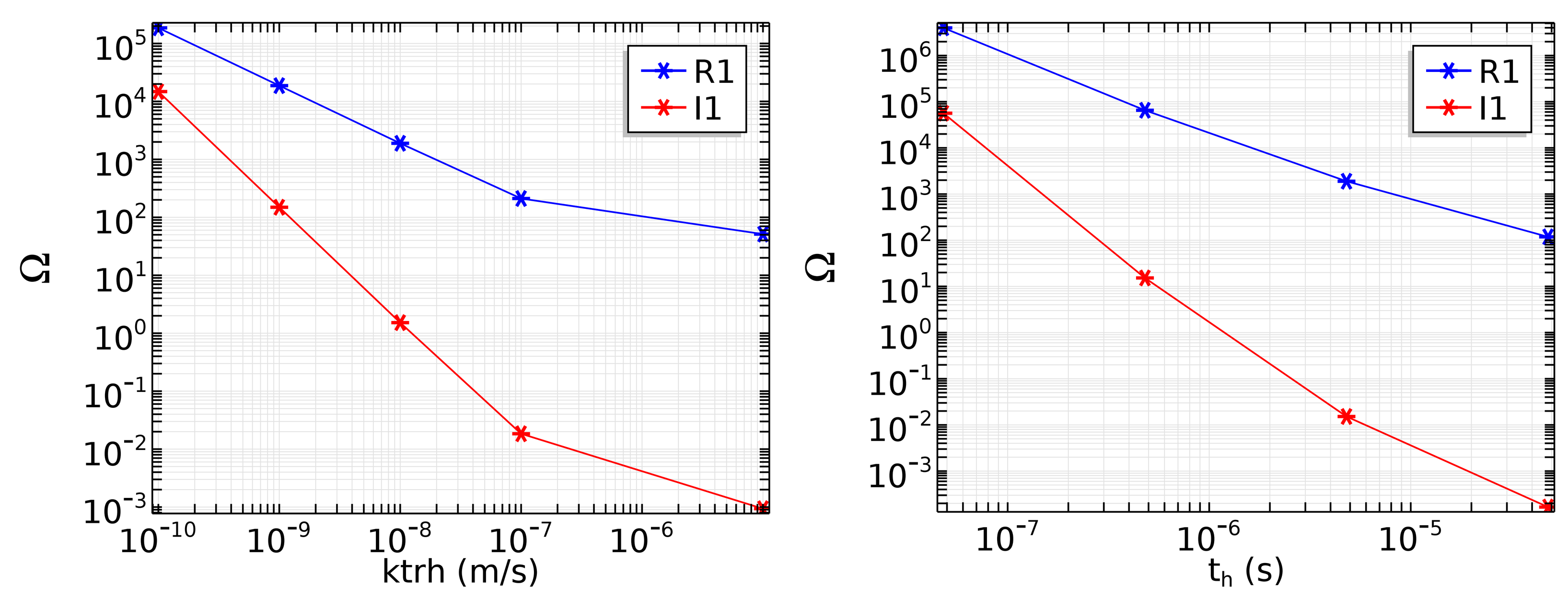


**Figure 3:** *Dependence of lowest frequency ($10^{-3}$ Hz) impedance for 0.7 V vs. RHE on (left) rate of water oxidation $k_{trh}$ for fixed $t_h = 48 \cdot 10^{-7}$ s and (right) hole recombination lifetime $t_h$ for fixed $k_{trh} = 10^{-8}$ m/s.*

## Conclusions

- Full numerical drift-diffusion calculations of the electrochemical impedance were conducted
- The linear dependence of abscissa (real part) in Nyquist plot on hole lifetime and water oxidation rate was observed, enabling 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 some material parameters

## References

[1] Peter Cendula, S. David Tilley, Sixto Gimenez, Matthias Schmid, Juan Bisquert, Michael Graetzel, and Juergen O Schumacher. Calculation of the Energy Band Diagram of a Photoelectrochemical Water Splitting Cell. *Journal of Physical Chemistry C*, 118(51):29599–29607, 2014.