# Modeling and Simulation of Photoelectrochemical Cells

4th Wädenswil Day of Chemistry
Solar Energy – Chemical Solutions
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Zürcher Hochschule
für Angewandte Wissenschaften
School of Engineering
ICP Institute of Computational Physics

**Dr. Matthias Schmid**
**scmi@zhaw.ch**

# Outline

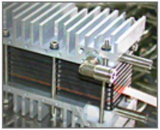
- **Introduction**
  - Institute of Computational Physics (ICP)
  - PEC Research at the ICP
- **Photoelectrochemical Cells**
  - Dye-sensitized Solar Cell
  - Photoelectrochemical Water Splitting
- **Modeling and Simulation of DSCs**
  - Optical Model
  - Electrical Model
  - PECSIM Software
- **Conclusions**

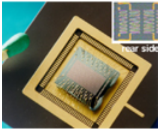


Dr. Matthias Schmid
scmi@zhaw.ch

# The Institute of Computational Physics (ICP)

- Interdisciplinary team of physicists, mathematicians and engineers
- Applied Research at the ICP with focus on numerical modeling and simulation:
  - Electrochemical Cells and Energy Systems
  - Organic Electronics and Photovoltaics
  - Optoelectronic Research Laboratory
  - Multiphysics Software Development
- Spin-off companies:
  - Numerical Modeling GmbH, www.nmtec.ch
  - Fluxim AG, www.fluxim.com
  - Winterthur Instruments AG, www.winterthurinstruments.com







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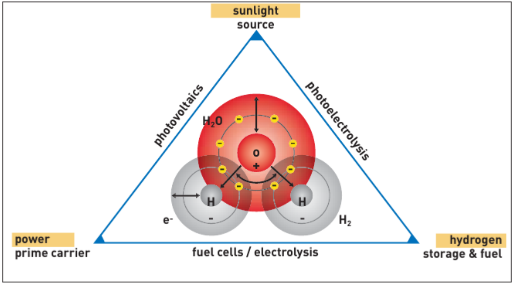
scmi@zhaw.ch

# Possible Future Energy Triangle




Courtesy of Dr. Andreas Luzzi

- Research at the ICP on all three sides of the triangle.


Dr. Matthias Schmid
scmi@zhaw.ch

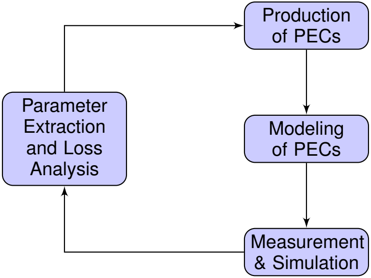
# Photoelectrochemical Cells (PECs)

## Photoelectrochemical Cells

- The dye-sensitized solar cell (DSC)
- The photoelectrochemical cell for water decomposition ($H_2$ production)

- Conversion of sunlight to chemical energy
- Semiconductor photoanode is nanoporous to enhance light harvesting.
- Semiconductor/Electrolyte interface is the key building block.
- Chemical reactions at this interface are crucial (gain and loss).

# Why Modeling and Simulation of PECs?




- Identification and quantification of different loss mechanisms in the energy conversion process
- Interpretation of measurement data and parameter extraction
- Evaluation and assessment of materials and material combinations for the cell production.
- Prediction of optimal cell design

$\Rightarrow$ Acceleration of R & D



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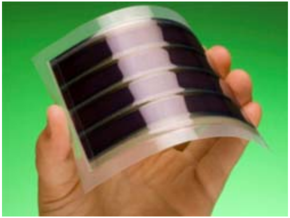
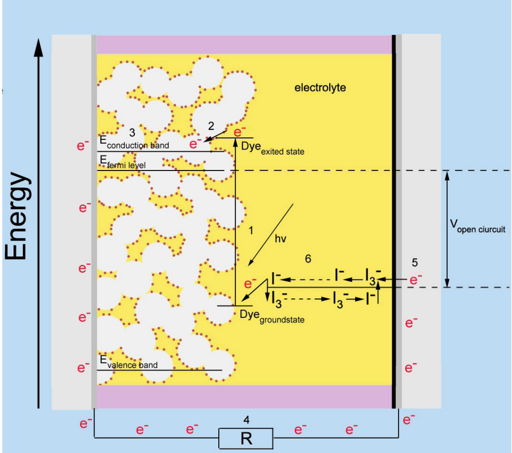
# The Dye-Sensitized Solar Cell (DSC)



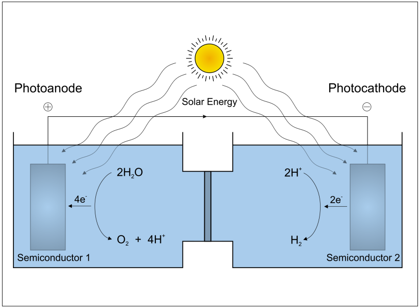
- The dye-sensitized solar cell (DSC) belongs to the class of thin film solar cells.
- DSCs achieve the separation of light harvesting (photosensitive dye) and charge carrier transport (nanoporous $TiO_2$).
- The DSC was developed at EPF Lausanne by M. Grätzel and B. O'Regan in 1991 (Nature 1991; **335**: 7377).
- Conversion efficiencies of $\approx 12\%$ have been reached.

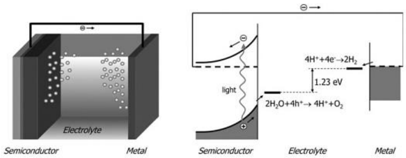
# The Dye-Sensitized Solar Cell

- (1) A photon is absorbed by the dye.
- (2) The excited electron in the dye is injected into the conduction band of the $TiO_2$.
- (3) Electrons diffuse to the anode through the network of $TiO_2$ nanoparticles.
- (4) External circuit.
- (5) At the cathode tri-iodide ions are reduced: $I_3^- + 2e^- \rightarrow 3I^-$.
- (6) The dye is reduced by iodide ions: $2D^+ + 3I^- \rightarrow 2D + I_3^-$



# Photoelectrochemical $H_2$ Production




- Minimum of 1.23 eV is needed for water splitting.
- Efficiencies of this type of PECs is still quite low (order of percents)
- Competition with PV+electrolysis (efficiency of 10-15 percents).



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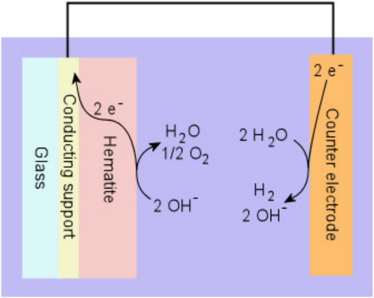
scmi@zhaw.ch

# The Water Splitting Device

- (1) A photon is absorbed by semiconductor photoanode (e.g. hematite).
- (2) The Holes $h^+$ diffuse to the semiconductor/electrolyte interface where oxygen is produced
  $4OH^- + 4h^+ \rightarrow 2H_2O + O_2$
- (3) External circuit
- (4) At the metallic cathode hydrogen is produced
  $4H_2O + 4e^- \rightarrow 2H_2 + 4OH^-$
- (5) $OH^-$ diffuses from the counter electrode to the photoanode.





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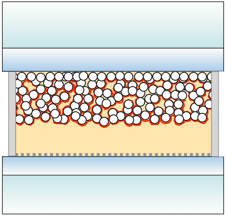
# The DSC Test Device

- Small test DSC device (area 0.28 $cm^2$).
- Different dye types.
- iodide/tri-iodide based electrolyte in ACN/VN mixture.



**1** Glass substrate, 3.88 mm

**2** FTO, 690 nm

**3** Mixed medium, 8 $\mu m$ ($TiO_2$, dye, electrolyte)

**4** Electrolyte, 16 $\mu m$

**5** Platinized FTO, 360 nm

**6** Glass substrate, 2.22 mm



Dr. Matthias Schmid
scmi@zhaw.ch

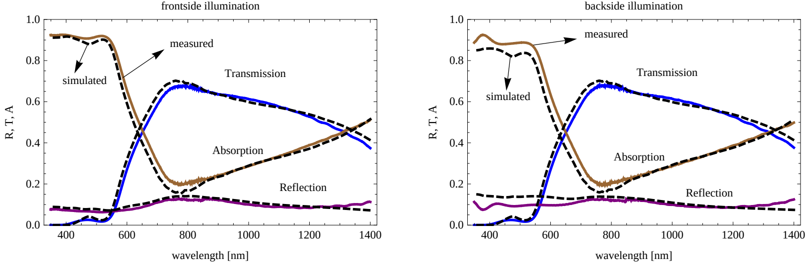
# Optical Model

**Objective:** Simulate the spatially resolved electron generation rate profile $g(x, \lambda)$ and the maximum achievable quantum efficiency $QE_{max}(\lambda)$.

- The simulations are performed using a ray tracing algorithm and accounts for multiple internal reflections and absoprtion losses in the cell.
- The optical simulation incorporates coherent (matrix transfer method) and incoherent optics.
- The nanoporous $TiO_2$ layer is treated as an effective medium.
- The indices of refraction and extinction coefficients of the materials are needed as input.
- The model is validated by R and T measurements on the complete device.
- $g(x, \lambda)$ is input for the electrical model.


Dr. Matthias Schmid
scmi@zhaw.ch

# Simulation of Reflection and Transmission




- Accurate description of scattering is needed in future.
- Problem: to get accurate optical constants for the materials.



Dr. Matthias Schmid
scmi@zhaw.ch

# Electrical Model

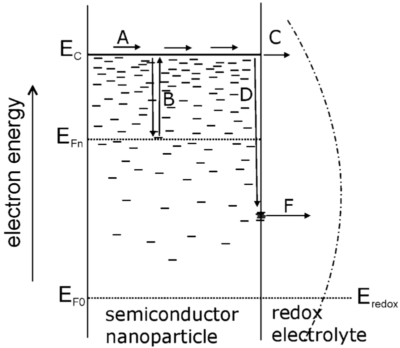
**Objective:** Simulate IV characteristic $j(V)$ and the quantum efficiency $QE(\lambda)$.

- The electrochemical potentials (Fermi energy for electrons and redox energies for ions) are solutions of a system of coupled non-linear PDEs.
- The electric model accounts for recombination at the $TiO_2$/electrolyte interface and transport limitations in the $TiO_2$ and the electrolyte.
- Trapping to an exponential distribution of localized band gap states is taken into account using the quasi-static approximation.


Dr. Matthias Schmid
scmi@zhaw.ch

# Basic processes in the electrical model

- Multiple-Trapping (MT) model for diffusion, trapping and recombination.
- only electrons in the conduction band contribute to the diffusion current.
- A: electron transport through extended states.
- B: trapping/detrapping at an exponential distribution of localized band gap states.
- C: direct electron transfer from the conduction band ($\rightarrow U_{cb}$).
- D/F: trapping by and electron transfer from surface band gap states ($\rightarrow U_t$).




Source: Bisquert, J. Phys. Chem B., 108, 7, 2004



Dr. Matthias Schmid
scmi@zhaw.ch

# Equations of the electrical model

The electrical model is based on continuity equations for electrochemical potentials (e.g. quasi-Fermi energy for electrons in the $TiO_2$):

$$\underbrace{\frac{C_e(E_{Fn})}{e}\frac{\partial E_{Fn}}{\partial t}(t,x)}_{\text{charge } \dot{Q}} = \frac{\partial}{\partial x}\underbrace{\left[\frac{\sigma_e(E_{Fn})}{e}\frac{\partial E_{Fn}}{\partial x}\right]}_{\text{current } j} - \underbrace{eU(E_{Fn})}_{\text{recombination}} + \underbrace{e\eta G(t,x)}_{\text{generation}}$$

Including the PDEs for the electrolyte we obtain:

$$\frac{C_e}{e}\frac{\partial E_{Fn}}{\partial t}(t,x) = \frac{\partial}{\partial x}\left[\frac{\sigma_e}{e}\frac{\partial E_{Fn}}{\partial x}\right] - eU(E_{Fn}, E_{I_3}, E_{I^-}) + e\eta G(t,x)$$

$$\frac{C_{I_3}}{e}\frac{\partial E_{I_3}}{\partial t}(t,x) = \frac{\partial}{\partial x}\left[\frac{\sigma_{I_3}}{e}\frac{\partial E_{I_3}}{\partial x}\right] + \frac{1}{2}eU(E_{Fn}, E_{I_3}, E_{I^-}) - \frac{1}{2}e\eta G(t,x)$$

$$\frac{C_{I^-}}{e}\frac{\partial E_{I^-}}{\partial t}(t,x) = \frac{\partial}{\partial x}\left[\frac{\sigma_{I^-}}{e}\frac{\partial E_{I^-}}{\partial x}\right] - \frac{3}{2}eU(E_{Fn}, E_{I_3}, E_{I^-}) + \frac{3}{2}e\eta G(t,x)$$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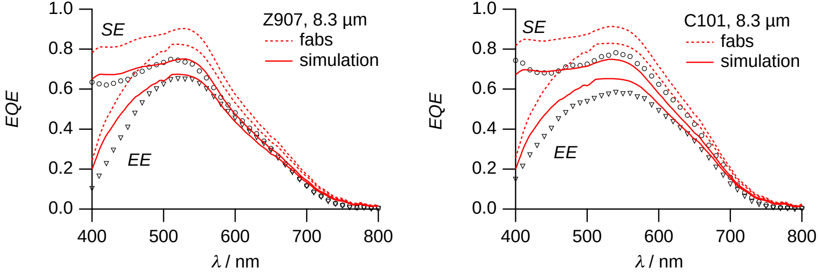
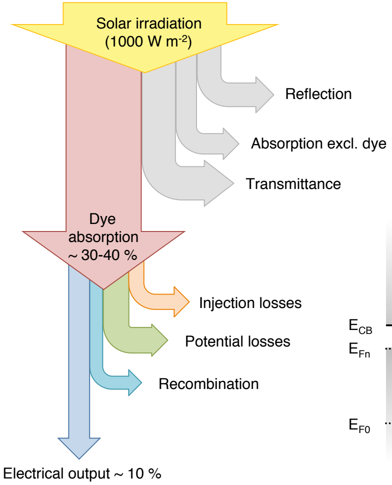
# Simulation of Quantum Efficiency

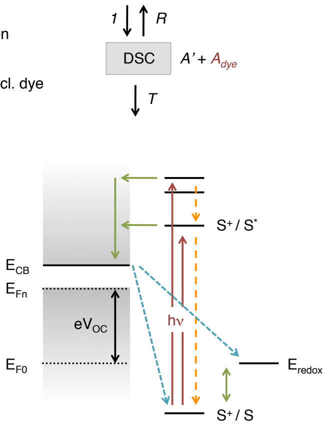



- The coupled optical and electrical model is validated by QE measurements.
- Comparison of measurement and simulation allows to extract steady state parameters.[1]

[1] Wenger et al., J. Phys. Chem. C, **2011**, 115 (20), pp 10218–10229

# Quantitative Loss Analysis

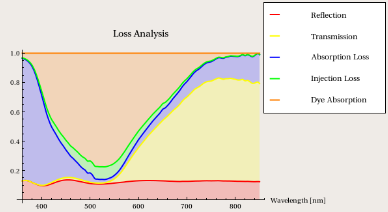


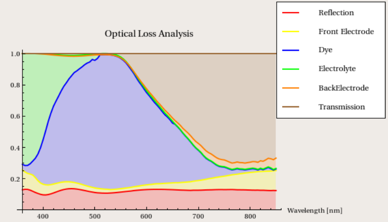



Dr. Matthias Schmid
scmi@zhaw.ch

# Quantitative Loss Analysis




| | Power [W·m$^{-2}$] | Current [mA·cm$^{-2}$] |
|---|---|---|
| **Incident Light** | **618.8** | **29.99** |
| Reflection | 76.52 | 3.73 |
| Transmission | 176.09 | 10.25 |
| Absorption Loss | 90. | 3.94 |
| **Total Optical Loss** | **342.6** | **17.93** |
| Injection Loss | 27.62 | 1.21 |
| Recombination | 47.82 | 2.07 |
| Potential Loss | 135.5 | 0. |
| Series Resistance Loss | 5.4 | 0. |
| Shunt Resistance Loss | 0. | 0. |
| **Total Electrical Loss** | **216.34** | **3.27** |
| **Output** | **59.85** | **8.79** |




| | Power [W·m$^{-2}$] | Current [mA·cm$^{2}$] |
|---|---|---|
| Absorption Front Glass | 14.07 | 0.8 |
| Absorption Front FTO | 20.08 | 0.97 |
| Absorption Pore Electrolyte | 6.03 | 0.23 |
| Absorption Bulk Electrolyte | 40.35 | 1.35 |
| Absorption Rear FTO | 4.47 | 0.28 |
| Absorption Rear Glass | 4.99 | 0.3 |
| **Absorption Loss** | **90.** | **3.94** |
| **Dye Absorption** | **276.19** | **12.06** |

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# PECSIM Software

## "PECSIM" = Photo-Electro-Chemical SIMulation software

- PECSIM is a simulation software for the systematic model-based analysis and optimization of dye-sensitized solar cells (DSCs)
- The software supports R&D on dye-sensitized solar cells.
- PECSIM is based on a validaded physical model for DSCs. The model consists of a coupled optical and electrical model.
- The software is equipped with a simple graphical user interface (GUI).
- PECSIM is written in Mathematica language. Either a license of the Mathematica Player Pro or a full license of Mathematica is needed to run the software.


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scmi@zhaw.ch

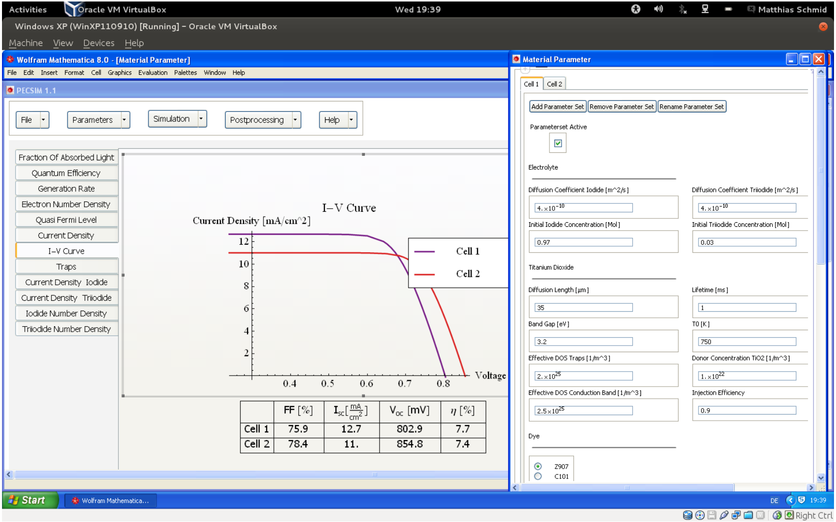
# Procedure for DSC Simulation

1. Optical modeling (based on ray-tracing and thin-film optics)[2]:
   $\Rightarrow$ normalized generation rate $g(\lambda, x)$
   $\Rightarrow$ $EQE_{max}(\lambda)$
2. Solve the coupled (in general non-linear) system of PDEs for the stationary state.[1]
   $\Rightarrow$ Electrochemical Potentials $\{E^0_{Fn}(x), E^0_{I_3}(x), E^0_{I^-}(x)\}$
   $\Rightarrow$ IV-Curve, $EQE(\lambda)$, loss analysis
3. Linearize the PDEs around $\{E^0_{Fn}(x), E^0_{I_3}(x), E^0_{I^-}(x)\}$ and solve the linear system in Fourier space
   $\Rightarrow$ Transfer functions $\{\hat{\varepsilon}_{Fn}(\omega, x), \hat{\varepsilon}_{I_3}(\omega, x), \hat{\varepsilon}_{I^-}(\omega, x)\}$
4. From the transfer functions $\{\hat{\varepsilon}_{Fn}(\omega, x), \hat{\varepsilon}_{I_3}(\omega, x), \hat{\varepsilon}_{I^-}(\omega, x)\}$ small amplitude transient experiments can be simulated:
   $\Rightarrow$ EIS, IMVS, IMPS, Photovoltage/Photocurrent decay

[2] Wenger et al. J. Phys. Chem. C, **2011**, 115 (20), pp 10218–10229


Dr. Matthias Schmid
scmi@zhaw.ch

# PECSIM Screenshot



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# Conclusions

- Dye-sensitized solar cells and cells for water photodecomposition are two kinds of photoelectrochemical cells. They harvest light and convert its energy to chemical energy.
- Chemical reactions at the semiconductor/electrolyte interface are crucial for their energy conversion process.
- Photoelectrochemical cells combine optics, nanophysics and electrochemistry.
- Modeling and Simulation of photoelectrochemical cells is an important tool to accelerate research and development.

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