Modeling and Simulation of Photoelectrochemical Cells

4th Wädenswil Day of Chemistry
Solar Energy – Chemical Solutions
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**
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:
  - Fluxim AG, www.fluxim.com
  - Winterthur Instruments AG, www.winterthurinstruments.com
Possible Future Energy Triangle

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

Courtesy of Dr. Andreas Luzzi
# 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

⇒ Acceleration of R & D
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**
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 Cells

Photoelectrochemical Water Splitting

**Photoelectrochemical H₂ 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).

Dr. Matthias Schmid
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.
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**
The DSC Test Device

- Small test DSC device (area 0.28 cm²).
- 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 µm (TiO₂, dye, electrolyte)
4. Electrolyte, 16 µm
5. Platinized FTO, 360 nm
6. Glass substrate, 2.22 mm
Optical Model

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

- The simulations are performed using a ray tracing algorithm and accounts for multiple internal reflections and absorption 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.
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
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.
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/detrappping 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 ($\rightarrow U_t$).

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$_2$):

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

Including the PDEs for the electrolyte we obtain:

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

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

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

Quantitative Loss Analysis

Solar irradiation (1000 W m^-2)

Reflection
Absorption excl. dye
Transmittance

Dye absorption ~ 30-40 %
Injection losses
Potential losses
Recombination

Electrical output ~ 10 %

Dr. Matthias Schmid
scmi@zhaw.ch
Quantitative Loss Analysis

<table>
<thead>
<tr>
<th>Incident Light</th>
<th>Power [W/m²]</th>
<th>Current [mA·cm²]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>618.8</td>
<td>29.99</td>
</tr>
</tbody>
</table>

| Reflection     | 76.52        |
| Transmission   | 176.09       |
| Absorption Loss| 90.0         |

| Total Optical Loss | 342.6 | 17.93 |

| Injection Loss   | 27.62 | 1.21  |
| Recombination    | 47.82 | 2.07  |
| Potential Loss   | 135.5 | 0.0   |
| Series Resistance Loss | 5.4 | 0.0 |
| Shunt Resistance Loss | 0.0 | 0.0 |

| Total Electrical Loss | 216.34 | 3.27 |
| Output               | 59.85  | 8.79 |

---

<table>
<thead>
<tr>
<th>Absorption Front Glass</th>
<th>Power [W/m²]</th>
<th>Current [mA·cm²]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>14.07</td>
<td>0.8</td>
</tr>
</tbody>
</table>

| 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  | 0.26 |
| Absorption Rear Glass  | 4.99  | 0.3  |

| Absorption Loss        | 90.0  | 3.94 |
| Dye Absorption         | 276.19 | 12.06 |
Modeling and Simulation of DSCs

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 validated 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.

Dr. Matthias Schmid
scmi@zhaw.ch
Procedure for DSC Simulation

1. Optical modeling (based on ray-tracing and thin-film optics)\(^2\):
   ⇒ normalized generation rate \( g(\lambda, x) \)
   ⇒ \( EQE_{\text{max}}(\lambda) \)

2. Solve the coupled (in general non-linear) system of PDEs for the stationary state.\(^1\)
   ⇒ Electrochemical Potentials \( \{ E_{Fn}^0(x), E_{I_3}^0(x), E_{I^-}^0(x) \} \)
   ⇒ IV-Curve, \( EQE(\lambda) \), loss analysis

3. Linearize the PDEs around \( \{ E_{Fn}^0(x), E_{I_3}^0(x), E_{I^-}^0(x) \} \) and solve the linear system in Fourier space
   ⇒ Transfer functions \( \{ \hat{E}_{Fn}(\omega, x), \hat{E}_{I_3}(\omega, x), \hat{E}_{I^-}(\omega, x) \} \)

4. From the transfer functions \( \{ \hat{E}_{Fn}(\omega, x), \hat{E}_{I_3}(\omega, x), \hat{E}_{I^-}(\omega, x) \} \) small amplitude transient experiments can be simulated:
   ⇒ EIS, IMVS, IMPS, Photovoltage/Photocurrent decay

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**
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.