A new approach
to identify the limiting processes
at electrochemical interfaces

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Solar fuel program lines:

I. Non-thermal chemical processes
II. Functional materials and interfaces
III. Light-matter interaction

Presentation by Waldo Bongers, this afternoon
Solar fuel program lines:

I. Non-thermal chemical processes

II. Functional materials and interfaces

III. Light-matter interaction

Understanding the structure-property relations of functional materials and the processes occurring at the electrode-electrolyte interface

Photo-electrochemical cell with new electrodes

Solar fuel program lines:

I. Non-thermal chemical processes
II. Functional materials and interfaces

III. Light-matter interaction

Improve chemical processes by exploring **nanostructured functional materials** to enhance **light capture and absorption** and **charge transport**

Plasmon enhanced catalysis on metal nanoparticles

20 nm resolution
Increase in performance is required!
Photoelectrodes for Water Splitting

Many processes:
- Absorption
- e-hole-separation
- Recombination
- Trapping
- Charge transport
- Electrochemical reactions

Dynamic and complex electrochemical interface.
Which process is limiting at the electrochemical interface?

How to relate the experimental data with an electrochemical model?

What is the physical/chemical meaning of the equivalent circuit elements?

Which species are present at the interface?

Operando FTIR


Our Approach

Experiments

Measure AND simulate the same electrochemical data

Modeling & Simulations

Relate electrochemical data and electrochemical model

Identify the limitations at the electrochemical interface

Fabricate tailored photoelectrodes with advanced chemistry and architecture

ASR, $R_p$

Chemical reactions:

$\text{ad} + \text{OH}^- + h^+ \rightleftharpoons \text{OH}_\text{ad}$

$\text{OH}_\text{ad} + \text{OH}^- + h^+ \rightleftharpoons \text{O}_\text{ad} + \text{H}_2\text{O}$

$\text{O}_\text{ad} + \text{OH}^- + h^+ \rightleftharpoons \text{OOH}_\text{ad}$

$\text{OOH}_\text{ad} + \text{OH}^- + h^+ \rightleftharpoons \text{O}_\text{ad} + \text{H}_2\text{O}$

$\text{O}_\text{ad} \rightleftharpoons \text{O}_\text{ad} + \text{ad}$

$\text{O}_\text{ad} + \text{O}_\text{ad} \rightleftharpoons \text{O}_\text{ad} + \text{O}_\text{ad}$
Case Study: Photoanode Material Hematite (Fe$_2$O$_3$)

Hematite = Fe$_2$O$_3$

- Suitable bandgap of 2.1 eV
- Abundance
- Non toxic
- Stable
- Low cost
- Short diffusion length
- High e-hole recombination rate
- Sluggish kinetics

Photoanode

F:SnO$_2$ (FTO)

glass

Sputtering (DC, RF)

Annealing @ 645°C for 10 min

M. Verheijen, TU/e
Electrochemical Properties of Fe$_2$O$_3$

### Current-Voltage Curve

- **DC**
  - Potential: 0.6 V to 1.6 V vs RHE
  - Current density: 0.0 mA cm$^{-2}$ to 0.4 mA cm$^{-2}$

- **RF**
  - Potential: 0.6 V to 1.6 V vs RHE
  - Current density: 0.0 mA cm$^{-2}$ to 0.4 mA cm$^{-2}$

**Dark**
- Potential: 0.6 V to 1.6 V vs RHE
- Current density: 0.0 mA cm$^{-2}$

\[ \Delta V_{onset} \]

### Electrochemical Impedance Spectroscopy

- **Rs**
- **CPE$_{bulk}$**
- **R$_{trap}$**
- **R$_{ss}$**
- **CPE$_{ss}$**

#### Circuit Model
- **Circuit Model File**: C:\Program Files\SAI\ZModels\160211_Equivalent Circuit_hematite.mdl
- **Mode**: Run Fitting / Selected Points (0 - 0)
- **Maximum Iterations**: 100
- **Optimization Iterations**: 0
- **Type of Fitting**: Complex
- **Type of Weighting**: Calc-Modulus

**Rs**
- Freedom: Free(+)
- Value: 16.94
- Error: N/A
- Error %: N/A

**CPE$_{bulk}$-T**
- Freedom: Free(+)
- Value: 8.87E-05
- Error: N/A
- Error %: N/A

**CPE$_{bulk}$-P**
- Freedom: Free(+)
- Value: 0.8
- Error: N/A
- Error %: N/A

**R$_{trap}$**
- Freedom: Free(+)
- Value: 380.2
- Error: N/A
- Error %: N/A

**R$_{ss}$**
- Freedom: Free(+)
- Value: 4759
- Error: N/A
- Error %: N/A

**CPE$_{ss}$-T**
- Freedom: Free(+)
- Value: 8.57E-05
- Error: N/A
- Error %: N/A

**CPE$_{ss}$-P**
- Freedom: Free(+)
- Value: 0.8
- Error: N/A
- Error %: N/A

**R$_{trap}$**: the resistance associated with the charge recombination at the surface states

### ATR-FTIR set-up to measure surface species

- **Photo-electrode**
- **IR transparent: electric contact**
- **Internal reflection element (ATR crystal)**
- **Detector**
- **Gas mixture**

\[ 2H_2 + O_2 \rightarrow 2H_2O \]
Case Study: Fe$_2$O$_3$

Experiments

- Identify the limitations at the electrochemical interface

Modeling & Simulations

- Fabricate tailored photoelectrodes with advanced chemistry and architecture

Chemical reactions:

- $ad + OH^- + h^+ \leftrightarrow OH_{ad}$
- $OH_{ad} + OH^- + h^+ \leftrightarrow O_{ad} + H_2O$
- $O_{ad} + OH^- + h^+ \leftrightarrow OO_{ad}$
- $OOH_{ad} + OH^- + h^+ \leftrightarrow O_{2ad} + H_2O$
- $O_{2ad} + O_{ad} \leftrightarrow ad$
- $O_{2ad} + O_{2ad} \leftrightarrow ad$

Graphs:

- Current density vs Potential
- Nyquist plot
- Impedance vs Frequency
Electrochemical Model
Electrochemical Model

Reactions steps

1. \( ad + OH^- + h^+ \overset{k_1}{\leftrightarrow} OH_{ad} \)  
2. \( OH_{ad} + OH^- + h^+ \overset{k_2}{\leftrightarrow} O_{ad} + H_2O \)  
3. \( O_{ad} + OH^- + h^+ \overset{k_3}{\leftrightarrow} OOH_{ad} \)  
4. \( OOH_{ad} + OH^- + h^+ \overset{k_4}{\leftrightarrow} O_{2ad} + H_2O \)  
5. \( O_{2ad} \overset{k_5}{\leftrightarrow} O_{2dl} + ad \)  
6. \( O_{2ad} \overset{k_6}{\leftrightarrow} O_{2aq} \)

Calculation of free energy steps by Density Functional Theory (DFT)

\[
\Delta G_i = nF \left[ - \left( E_v - E_{F,\text{redox},i} \right) \right],
\]

where \( E_{F,\text{redox},i} \) is the redox potential, \( \lambda \) is the solvent reorganization energy, and \( n \) is the number of electrons.

Reaction rate

\[
\bar{k}_{f1} = k_{v,max} \exp \left[ - \frac{(E_v - E_{F,\text{redox},i} - \lambda)^2}{4k_BT\lambda} \right],
\]

\[
\bar{k}_{b1} = k_{v,max} \exp \left[ - \frac{(E_v - E_{F,\text{redox},i} + \lambda)^2}{4k_BT\lambda} \right],
\]

Oxygen Vacancies reduce Overpotential of Fe$_2$O$_3$

Oxygen vacancies are very effective in reducing overpotential. 

Electrochemical Model

Reactions steps

\[ \text{Reactions steps} \]

\[ \begin{align*}
\text{ad} + \text{OH}^- + h^+ & \leftrightarrow \text{OH} \text{ad} \\
\text{OH} \text{ad} + \text{OH}^- + h^+ & \leftrightarrow \text{O} \text{ad} + \text{H}_2\text{O} \\
\text{O} \text{ad} + \text{OH}^- + h^+ & \leftrightarrow \text{OOH} \text{ad} \\
\text{OOH} \text{ad} + \text{OH}^- + h^+ & \leftrightarrow \text{O}_2\text{ad} + \text{H}_2\text{O} \\
\text{O}_2\text{ad} & \leftrightarrow \text{O}_{2\text{dl}} + \text{ad} \\
\text{O}_{2\text{dl}} & \leftrightarrow \text{O}_{2\text{aq}}
\end{align*} \]

Rate equation

\[ \begin{align*}
\text{Rate equation} \\
\bar{k}_f & = k_{v,\text{max}} \exp \left[ -\left( \frac{E_v - E_{F,\text{redox},i} - \lambda}{4k_BT\lambda} \right)^2 \right] \\
\bar{k}_b & = k_{v,\text{max}} \exp \left[ -\left( \frac{E_v - E_{F,\text{redox},i} + \lambda}{4k_BT\lambda} \right)^2 \right]
\end{align*} \]

Formulation of adsorption equation

\[ \begin{align*}
\frac{d\theta_{\text{OH}}}{dt} & = K_1[x_{\text{OH}^-}]\theta - K_{-1}\theta_{\text{OH}} - K_2\theta_{\text{OH}}[x_{\text{OH}^-}] + K_{-2}\theta_O[x_{\text{H}_2\text{O}}] \\
\frac{d\theta_O}{dt} & = K_2\theta_{\text{OH}}[x_{\text{OH}^-}] - K_{-2}\theta_O[x_{\text{H}_2\text{O}}] - K_3\theta_O[x_{\text{OH}^-}] + K_{-3}\theta_{\text{OOH}} \\
\frac{d\theta_{\text{OOH}}}{dt} & = K_3\theta_O[x_{\text{OH}^-}] - K_{-3}\theta_{\text{OOH}} - K_4\theta_{\text{OOH}}[x_{\text{OH}^-}] + K_{-4}\theta_{O_2}[x_{\text{H}_2\text{O}}] \\
\frac{d\theta_{O_2}}{dt} & = K_4\theta_{\text{OOH}} - K_{-4}\theta_{O_2} - K_5\theta_{O_2} + K_{-5}\theta.x_{O_{2\text{dl}}}
\end{align*} \]

Formulation of charge balance

\[ \begin{align*}
j_f & = (K_1[x_{\text{OH}^-}]\theta + K_2\theta_{\text{OH}}[x_{\text{OH}^-}] + K_3\theta_O[x_{\text{OH}^-}] + K_4\theta_{\text{OOH}}[x_{\text{OH}^-}]).\text{qe}.N_0 \\
j_b & = (K_{-1}\theta_{\text{OH}} + K_{-2}\theta_O[x_{\text{H}_2\text{O}}] + K_{-3}\theta_{\text{OOH}} + K_{-4}\theta_{O_2}[x_{\text{H}_2\text{O}}]).\text{qe}.N_0 \\
j_{\text{Total}} & = j_f - j_b
\end{align*} \]

Non-Linear State Space Model

Control Theory approach

Collaboration with fusion department DIFFER

Single input
(Applied voltage)

→ Linearization → Laplace transform → Impedance calculation

Electrochemical model
(Reaction mechanism)

\[ \begin{align*}
  k_{fi} & : A + B \rightleftharpoons C + D \\
  k_{bi} & : \text{Reaction rates} \\
  & : \text{Mass and charge balance equations}
\end{align*} \]

4 state variables
concentration of intermediate species

Single output
(Current density)

State-space modeling code set-up for water splitting.

Simulated Electrochemical Data

Current-Voltage Plot

Surface Coverage Plot

Data not available from experiments


Simulated Impedance Data

Electrochemical Impedance Spectra

Case Study: Fe$_2$O$_3$

Next: do parameter variations and include more processes in the modeling

Collaboration with fusion department DIFFER

Case Study: WO$_3$

**Experiments**


**Modeling & Simulations**

Kishore et al., Catalysis Today (2018).

Si nanowires + 50 nm WO$_3$ by ALD

3.5 µm
**Conclusion and Outlook**

- **Electrochemical interfaces** are the key to improve performance of electro-chemical energy applications.

- **(Multi-scale) modeling** is required to tackle this challenge.

- We can simulate electrochemical data that can be **directly compared to electrochemical measurements**.

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Thank you

• E. Zouthout
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