DIFFER

A new approach to identify the limiting processes at electrochemical interfaces

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M. Van Berkel


X. Zhang

DIFFER – Science for Future Energy

2 Departments: Solar Fuel and Fusion

Solar fuel program lines:

1. **Non-thermal chemical processes**
2. Functional materials and interfaces
3. Light-matter interaction

Novel non-thermal routes to **improve kinetics** and **selectivity** of **key catalytic processes**

Presentation by Waldo Bongers, this afternoon

DIFFER – Science for Future Energy

2 Departments: Solar Fuel and Fusion

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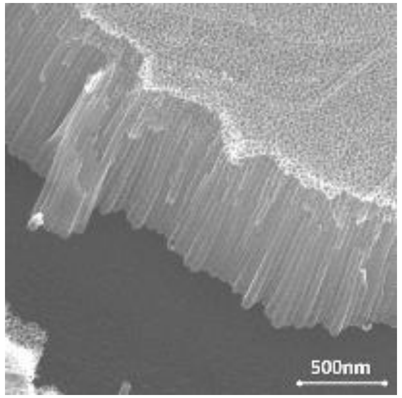
I. Non-thermal chemical processes

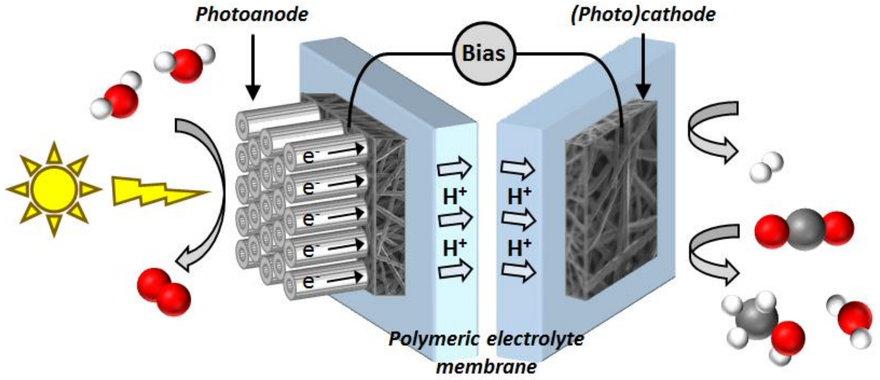
II. Functional materials and interfaces

III. Light-matter interaction

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

Photo-electrochemical cell with new electrodes





T. Stoll et al., Int. J. Hydrogen Energy (2016).

DIFFER – Science for Future Energy

2 Departments: Solar Fuel and Fusion

Solar fuel program lines:

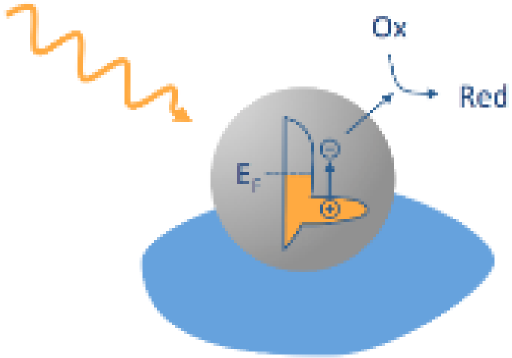
I. Non-thermal chemical processes

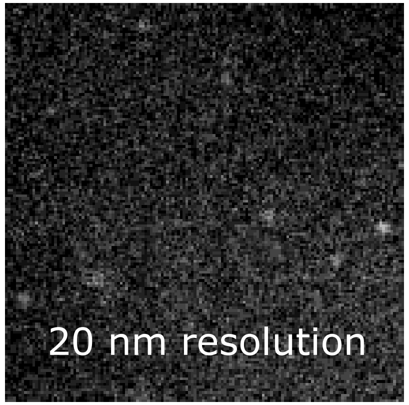
II. Functional materials and interfaces

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

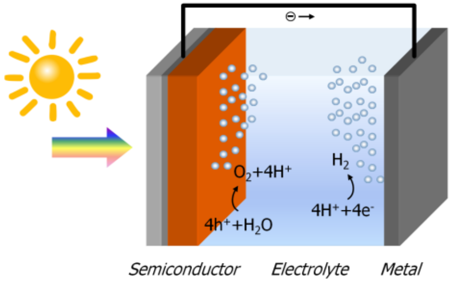




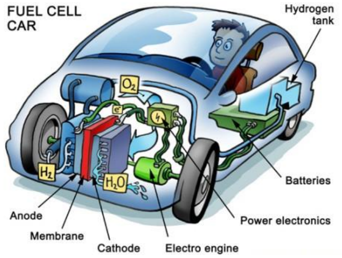
Electrochemical Interfaces

Water splitting

Water splitting

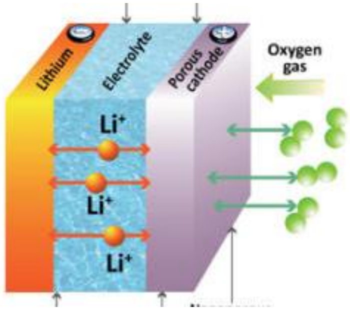


Fuel Cells



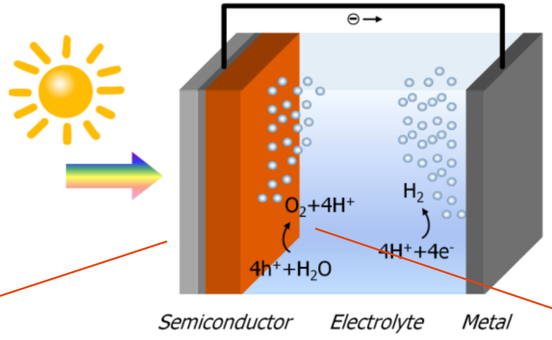
Electrolyser

Batteries

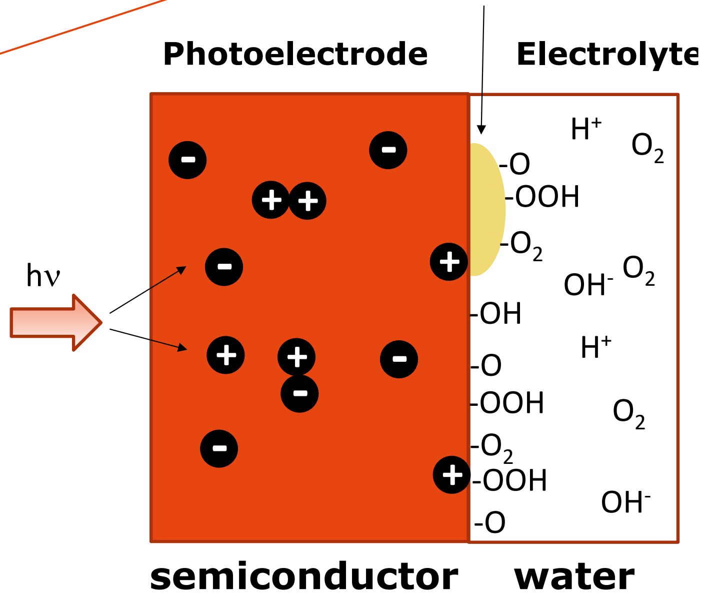


Increase in performance is required!

Photoelectrodes for Water Splitting



Krol and Graetzel (2012).



$$ad + OH^- + h^+ \overset{k1}{\underset{k\_1}{\leftrightarrow}} OH_{ad}$$

$$OH_{ad} + OH^- + h^+ \overset{k2}{\underset{k\_2}{\leftrightarrow}} O_{ad} + H_2O$$

$$O_{ad} + OH^- + h^+ \overset{k3}{\underset{k\_3}{\leftrightarrow}} OOH_{ad}$$

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$$O_{2ad} \overset{k5}{\underset{k\_5}{\leftrightarrow}} O_{2dl} + ad$$

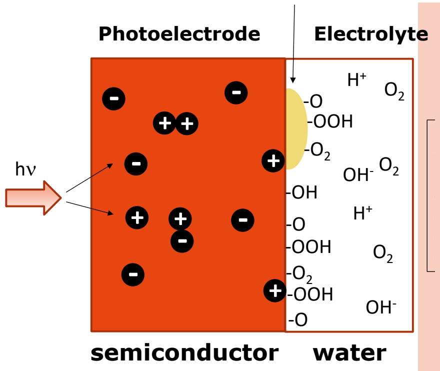
$$O_{2dl} \overset{k6}{\underset{k\_6}{\leftrightarrow}} O_{2aq}$$

Many processes:

- Absorption
- e-hole-separation
- Recombination
- Trapping
- Charge transport
- Electrochemical reactions

Dynamic and complex electrochemical interface.

Main Research Questions



$$ad + OH^- + h^+ \overset{k1}{\underset{k\_1}{\leftrightarrow}} OH_{ad} \quad (1)$$

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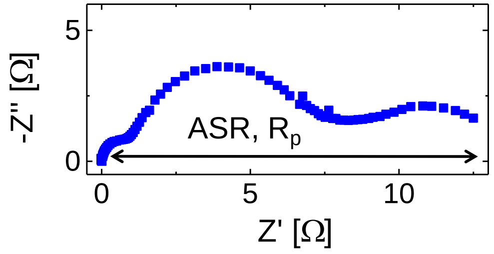
Is this the good reaction mechanism?

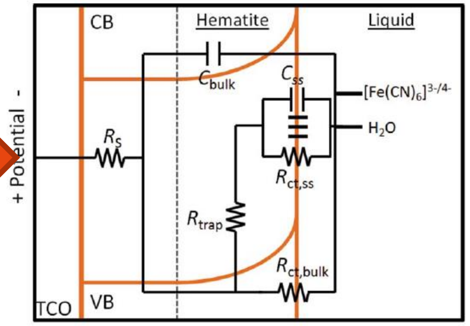
Which process is limiting at the electrochemical interface?

Electrochemical Impedance Spectroscopy



How to relate the experimental data with an electrochemical model?

Equivalent Circuit Fitting

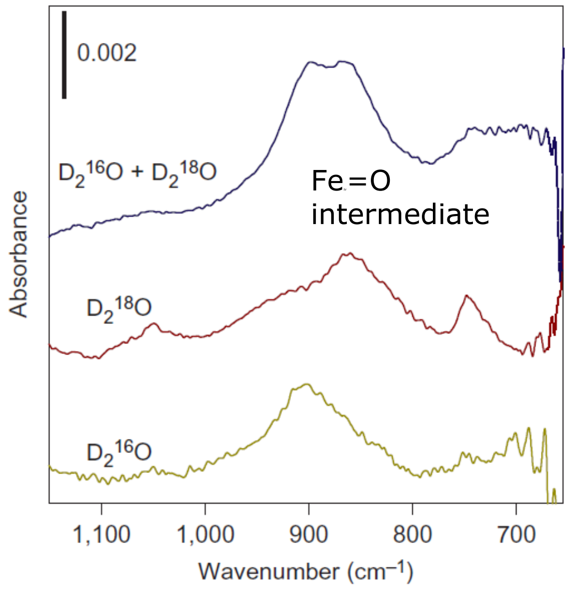


Klahr et al., Energ. Env. Sc. (2012).

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

Which species are present at the interface?

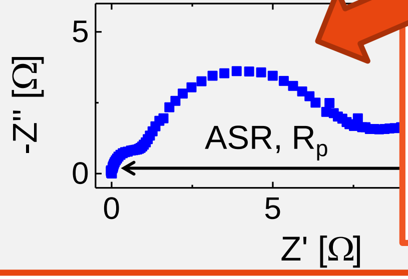
Operando FTIR



Zandi and Hamann, Nat. Chem. (2016).

Our Approach

Experiments



Relate electrochemical data and electrochemical model

Modeling & Simulations

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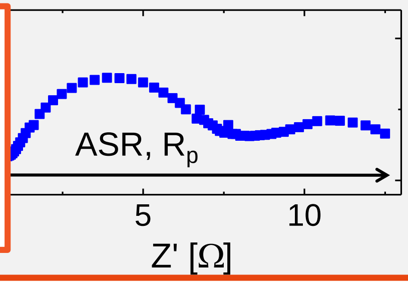


Measure AND simulate the same electrochemical data

Identify the limitations at the electrochemical interface

Fabricate tailored photoelectrodes with advanced chemistry and architecture

Case Study: Photoanode Material Hematite (Fe_2O_3)

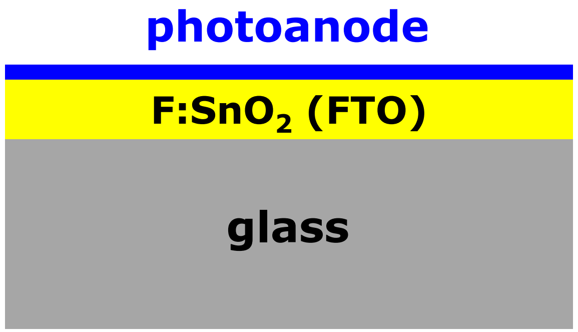
Hematite

=

Fe_2O_3

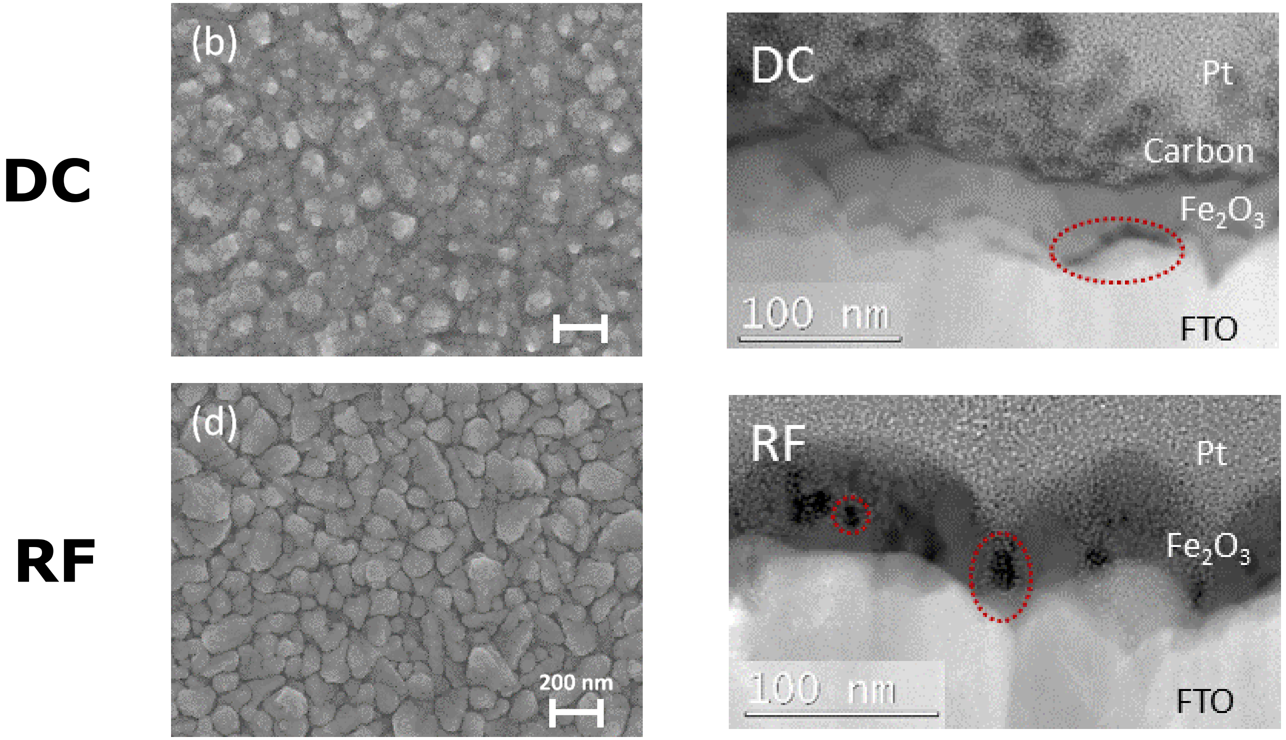
- Suitable bandgap of 2.1 eV
- Abundance
- Non toxic
- Stable
- Low cost

- Short diffusion length
- High e-hole recombination rate
- Sluggish kinetics



Sputtering (DC, RF)

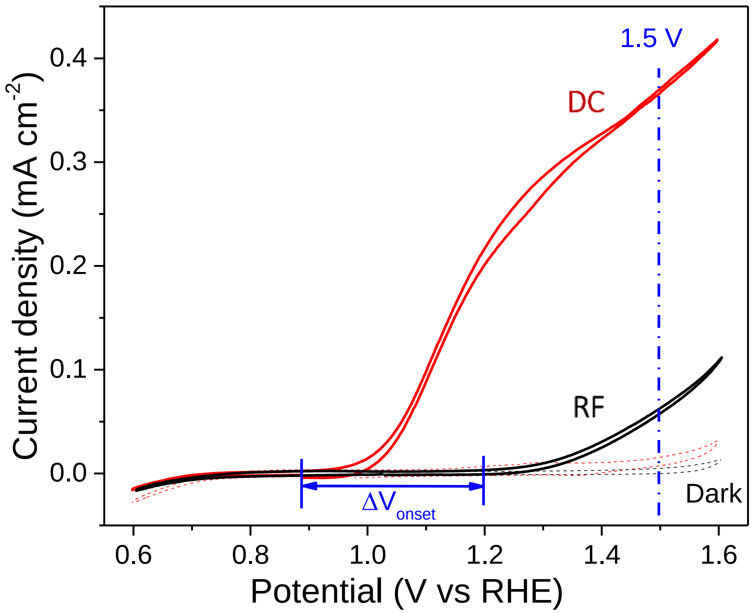
Annealing @ 645°C for 10 min



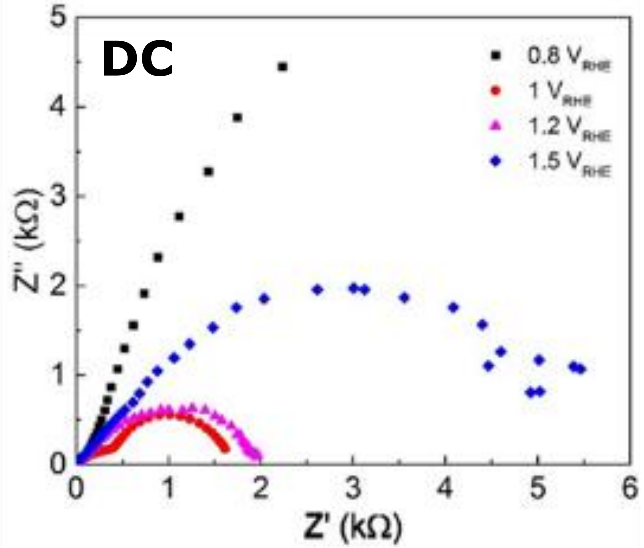
M. Verheijen, TU/e

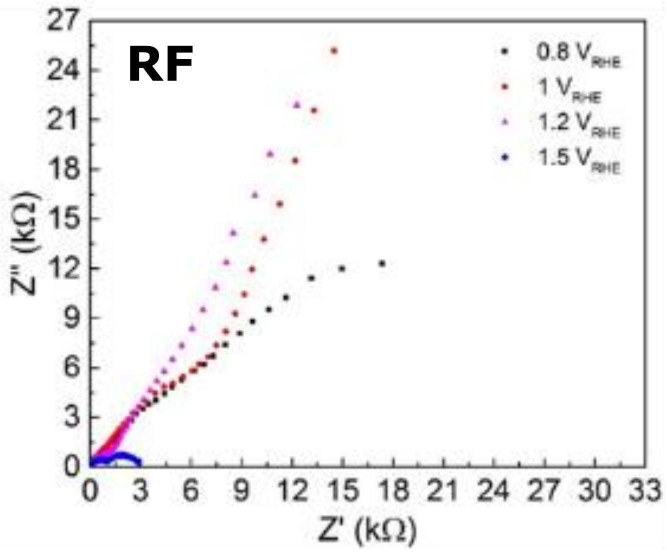
Electrochemical Properties of Fe_2O_3

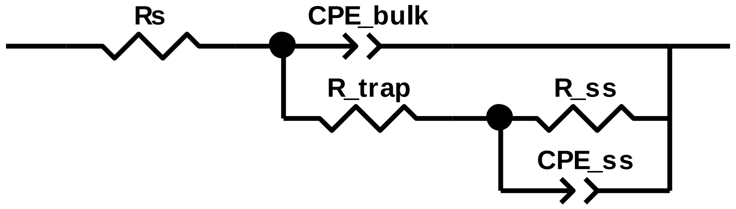
Current-Voltage Curve



Electrochemical Impedance Spectroscopy

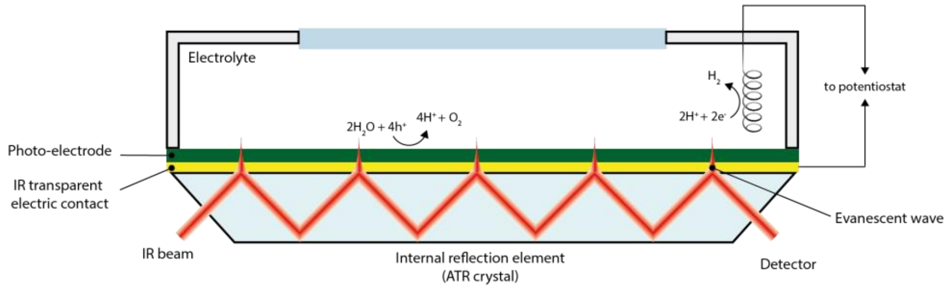






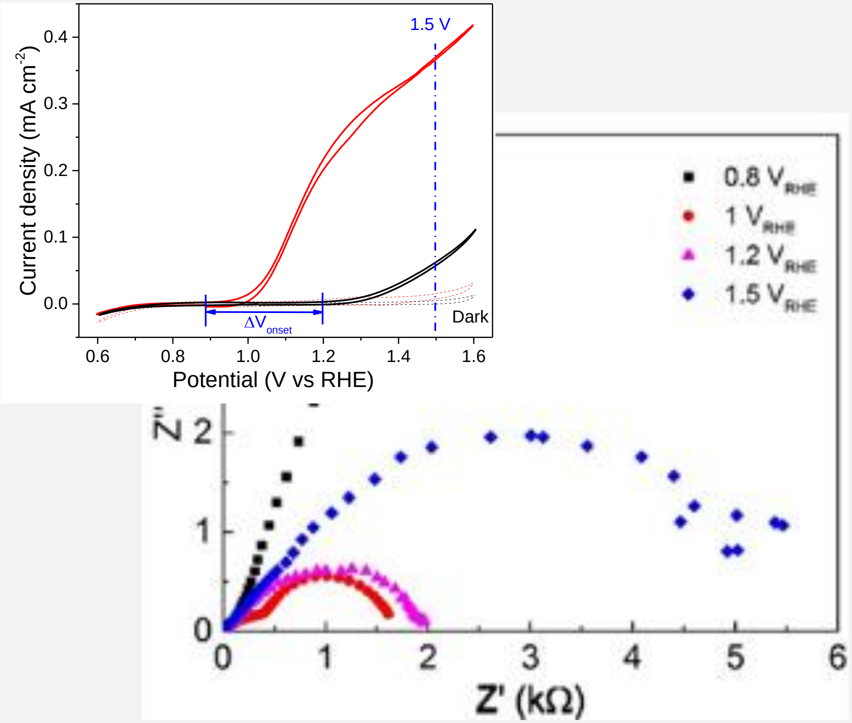
R_{trap}: the resistance associated with the charge recombination at the surface states

ATR-FTIR set-up to measure surface species



Case Study: Fe_2O_3

Experiments



Modeling & Simulations

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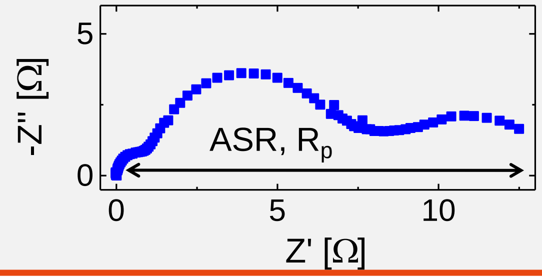
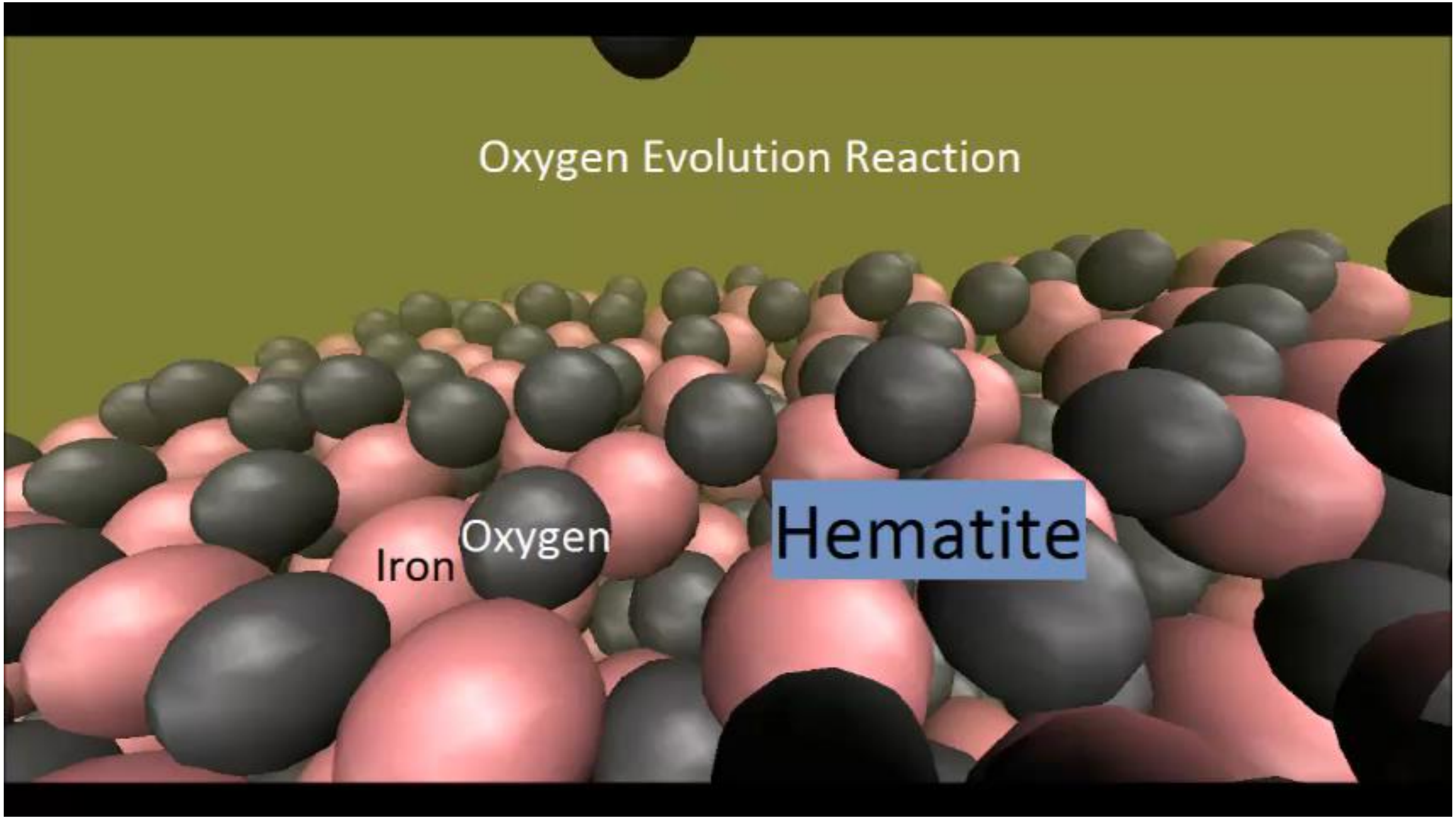


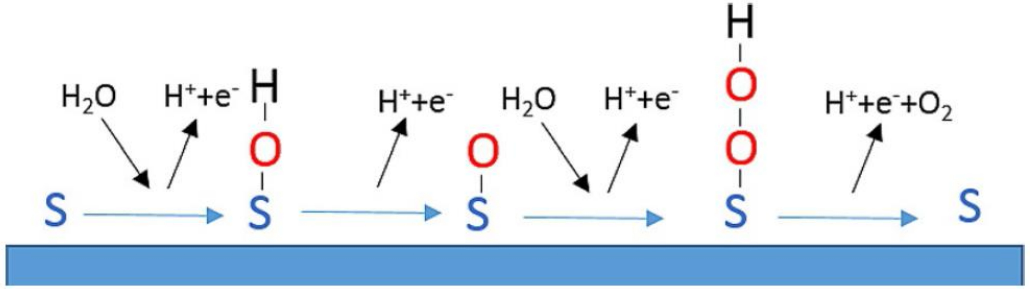
Identify the limitations at the electrochemical interface

Fabricate tailored photoelectrodes with advanced chemistry and architecture

Electrochemical Model



Electrochemical Model



Rossmeisl and Nørskov, J. Electroanal. Chem. (2007).

Zhang and ABH, ChemSusChem (2016).

Reactions steps

$$ad + OH^- + h^+ \underset{k\_1}{\overset{k1}{\leftrightarrow}} OH_{ad} \quad (1)$$

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George, ABH et al. (2018) submitted.

Reaction rate

$$\overline{k_{fi}} = k_{v,max} \exp\left[-\frac{(E_v - E^0_{F,redox,i} - \lambda)^2}{4k_BT\lambda}\right],$$

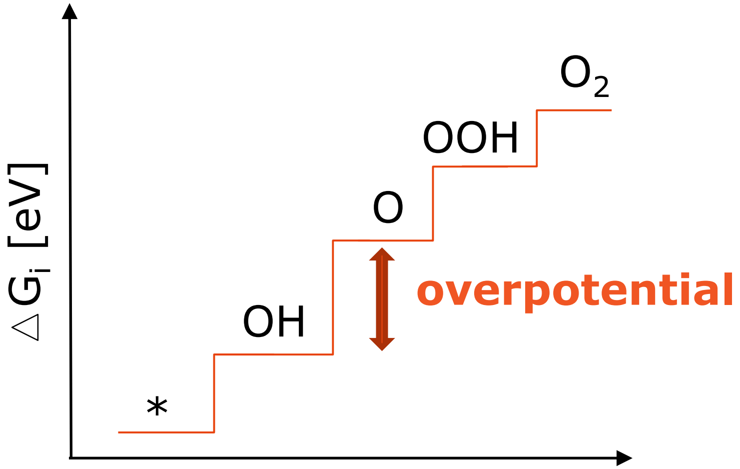
$$\overline{k_{bi}} = k_{v,max} \exp\left[-\frac{(E_v - E^0_{F,redox,i} + \lambda)^2}{4k_BT\lambda}\right],$$

$E^0_{F,redox,i}$: redox potential

λ: solvent reorganization energy

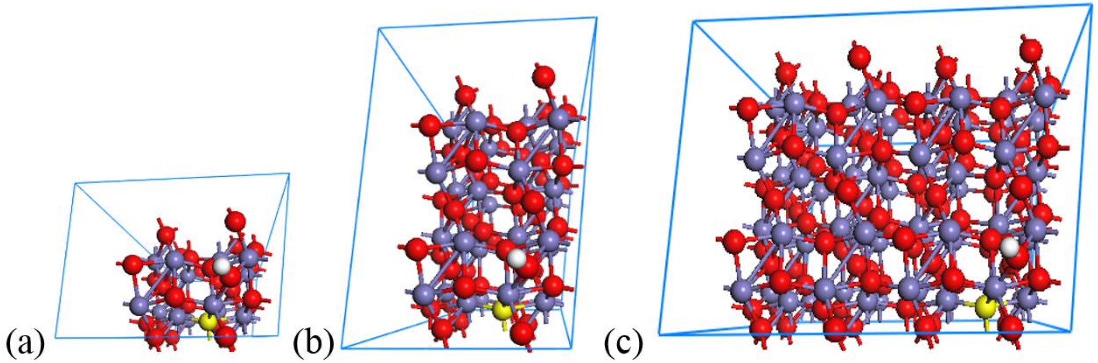
$$\Delta G_i = nFE^0_{F,redox,i}$$

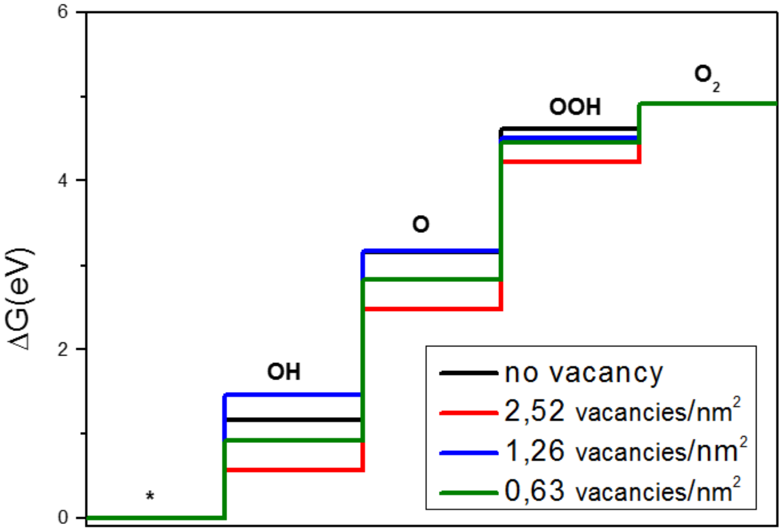
Calculation of free energy steps by Density Functional Theory (DFT)

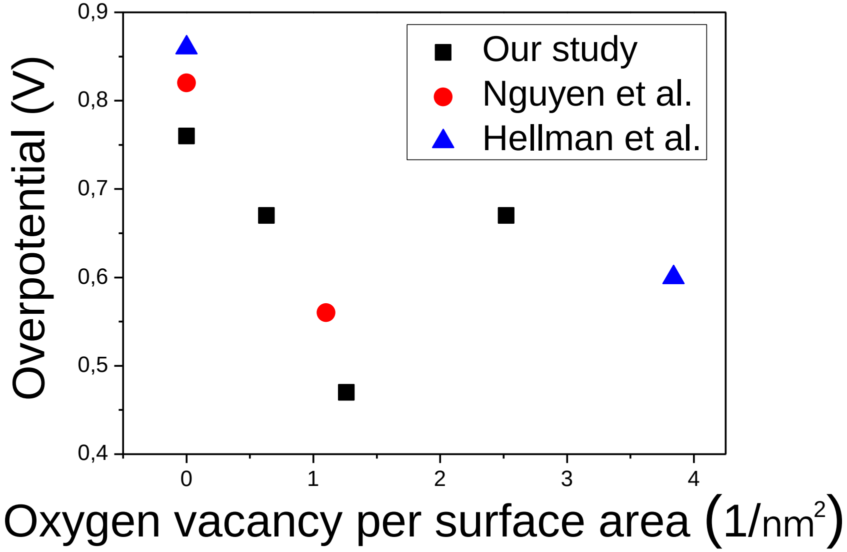


Rossmeisl and Nørskov, J. Electroanal. Chem. (2007).

Oxygen Vacancies reduce Overpotential of Fe_2O_3







Oxygen vacancies are very effective in reducing overpotential.

Zhang, ABH et al., J. Phys. Chem. C (2016).

Electrochemical Model


Reactions steps

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$$\overline{k_{b\iota}} = k_{v,max} \exp\left[-\frac{(E_v - E^0_{F,redox,i} + \lambda)^2}{4k_BT\lambda}\right],$$

Formulation of adsorption equation

$$\frac{d\theta_{OH}}{dt} = K_1[x_{OH^-}]\theta - K_{\_1}\theta_{OH} - K_2\theta_{OH}[x_{OH^-}] + K_{\_2}\theta_O[x_{H_2O}] \quad (9)$$

$$\frac{d\theta_O}{dt} = K_2\theta_{OH}[x_{OH^-}] - K_{\_2}\theta_O[x_{H_2O}] - K_3\theta_O[x_{OH^-}] + K_{\_3}\theta_{OOH} \quad (10)$$

$$\frac{d\theta_{OOH}}{dt} = K_3\theta_O[x_{OH^-}] - K_{\_3}\theta_{OOH} - K_4\theta_{OOH}[x_{OH^-}] + K_{\_4}\theta_{O_2}[x_{H_2O}] \quad (11)$$

$$\frac{d\theta_{O_2}}{dt} = K_4\theta_{OOH} - K_{\_4}\theta_{O_2} - K_5\theta_{O2} + K_{\_5}.\theta.x_{O_2dl} \quad (12)$$

$$\frac{dx_{O_2dl}}{dt} = K_5\theta_{O2} - K_{\_5}.\theta.x_{O_2dl} - K_6x_{O_2dl} + K_{\_6}.x_{O_2aql} \quad (13)$$

$$\theta = 1 - \theta_{OH} - \theta_O - \theta_{OOH} - \theta_{O2} \quad (14)$$

Formulation of charge balance

$$j_f = (K_1[x_{OH^-}]\theta + K_2\theta_{OH}[x_{OH^-}] + K_3\theta_O[x_{OH^-}] + K_4\theta_{OOH}[x_{OH^-}]).qe.N_0 \quad (15)$$

$$j_b = (K_{\_1}\theta_{OH} + K_{\_2}\theta_O[x_{H_2O}] + K_{\_3}\theta_{OOH} + K_{\_4}\theta_{O_2}[x_{H_2O}]).qe.N_0 \quad (16)$$

$$j_{Total} = j_f - j_b \quad (17)$$

George, van Berkel, Zhang, ABH, submitted (2018).

Non-Linear State Space Mo


→ Control Theory approach

→ Collaboration with fusion department DIFFER

Single input

(Applied voltage)

→

- Electrochemical model
  (Reaction mechanism)

$$A+B \underset{K_{bi}}{\overset{K_{fi}}{\leftrightarrows}} C+D$$

- Reaction rates
- Mass and charge balance equations

→

Single output

(Current density)

↓

4 state variables

concentration of intermediate species

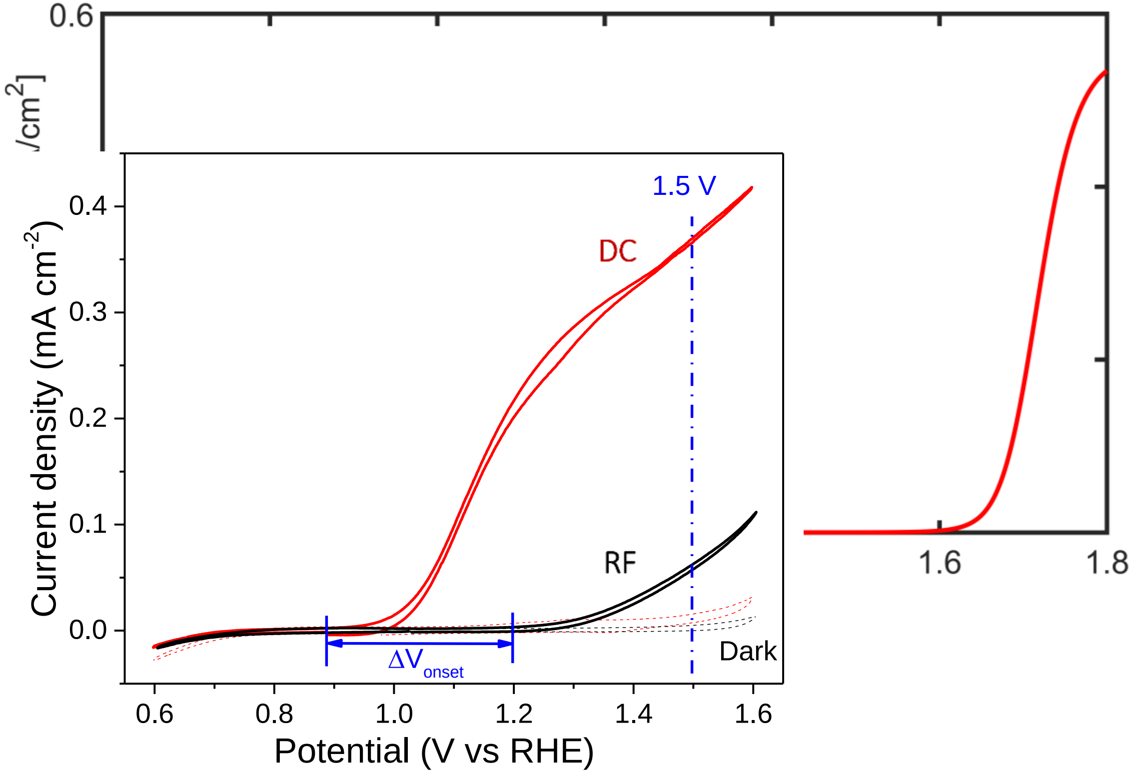
→ Linearization → Laplace transform → Impedance calculation

George, van Berkel, Zhang, ABH, submitted (2018).

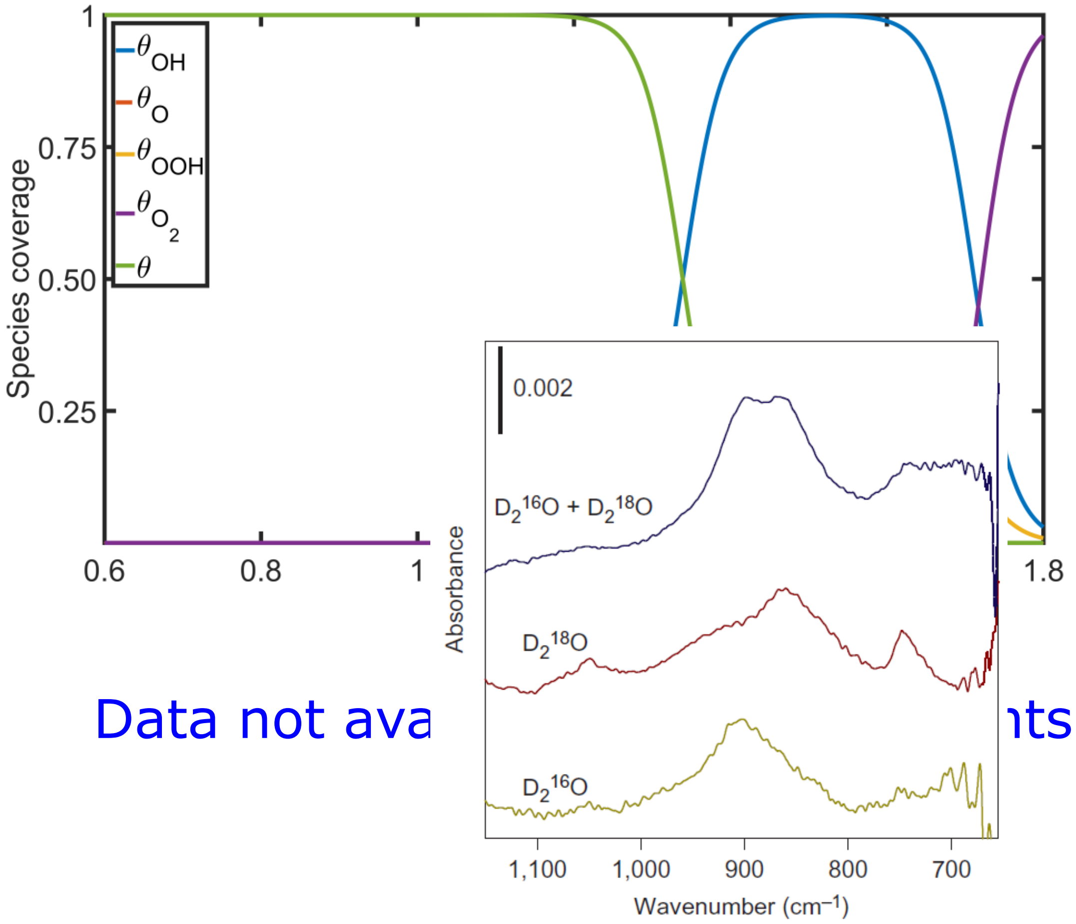
State-space modeling code set-up for water splitting.

Simulated Electrochemical Data

Current-Voltage Plot



Surface Coverage Plot

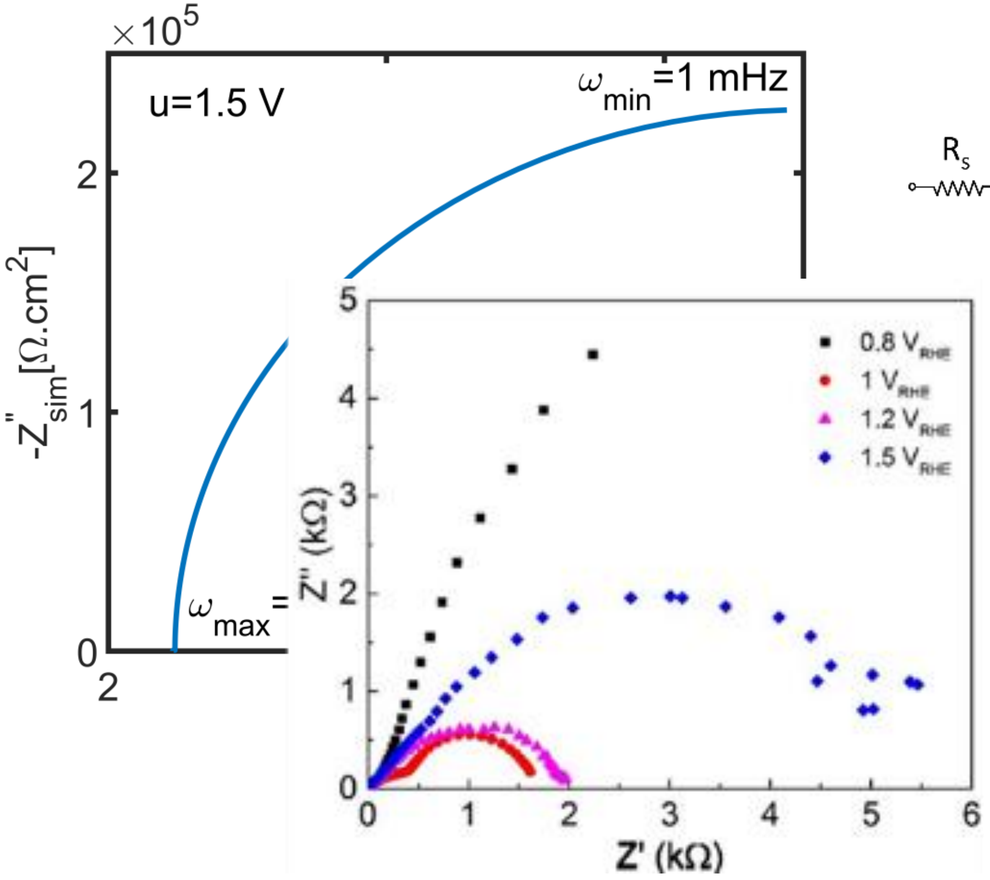


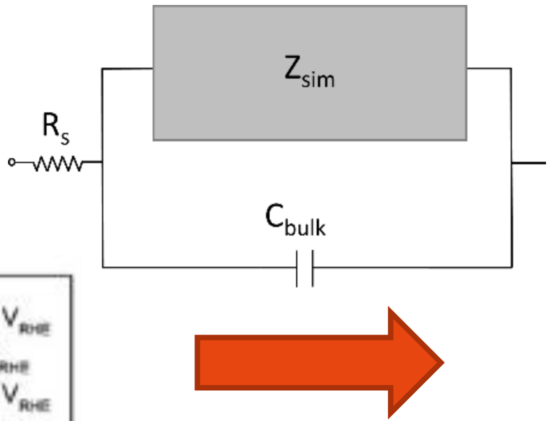
George, van Berkel, Zhang, ABH, submitted (2018).

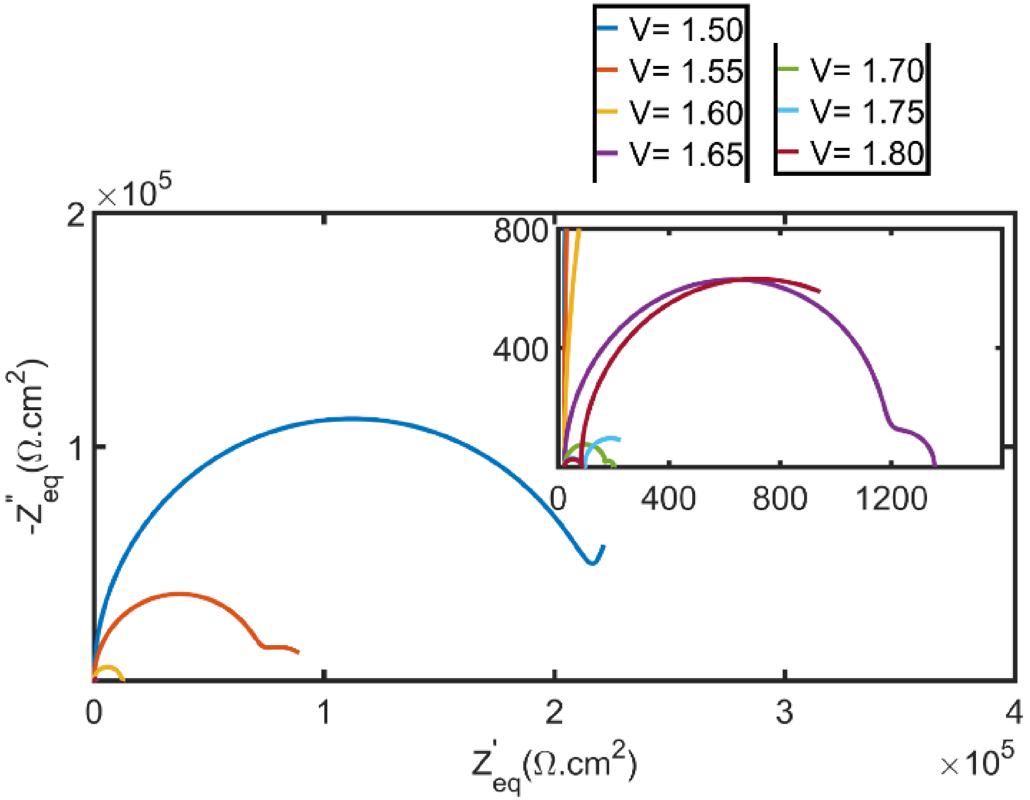
Zandi and Hamann, Nat. Chem. (2016).

Simulated Impedance Data

Electrochemical Impedance Spectra

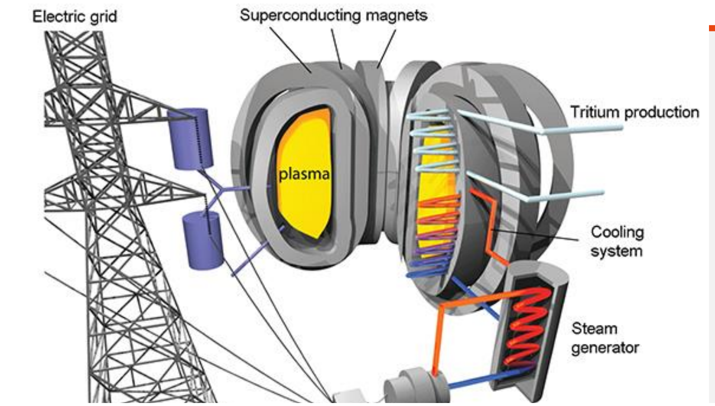




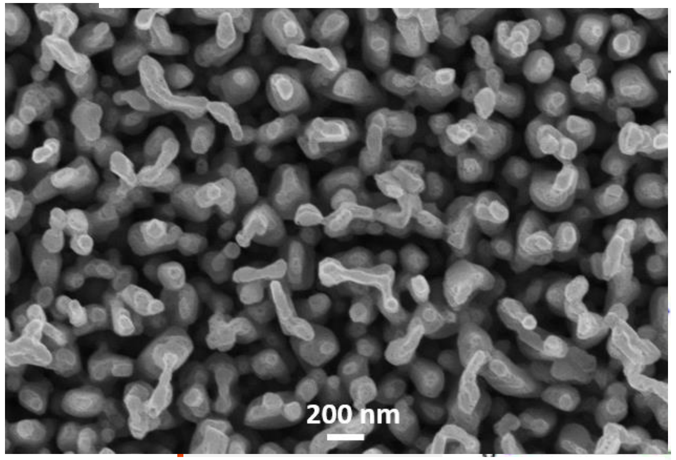


George, van Berkel, Zhang, ABH, submitted (2018).

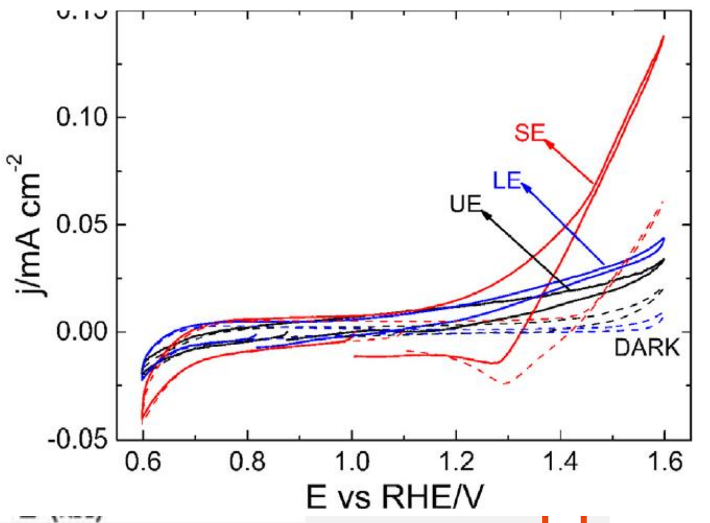
Case Study: Fe_2O_3



Collaboration with fusion department DIFFER



Sinha et al., Electrochimica Acta (2017).



Modeling & Simulations

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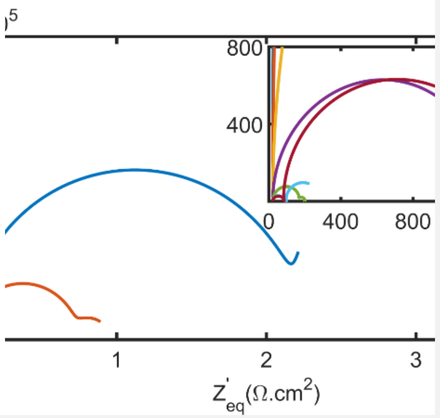
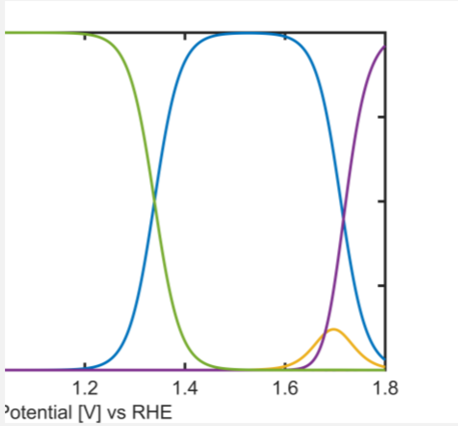
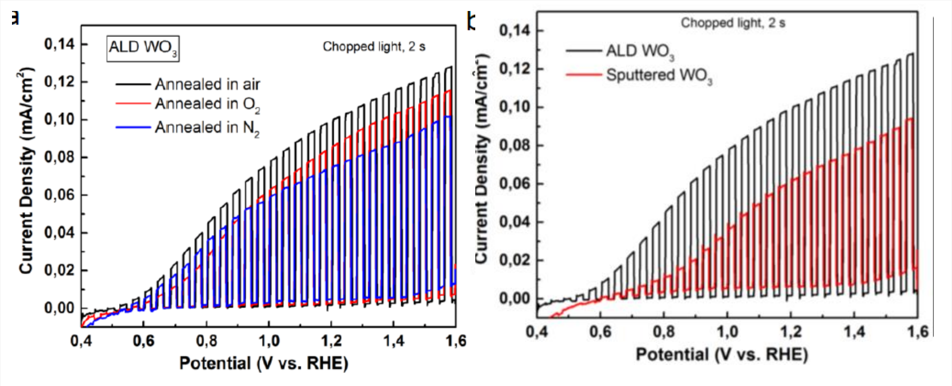




Next: do parameter variations and include more processes in the modeling

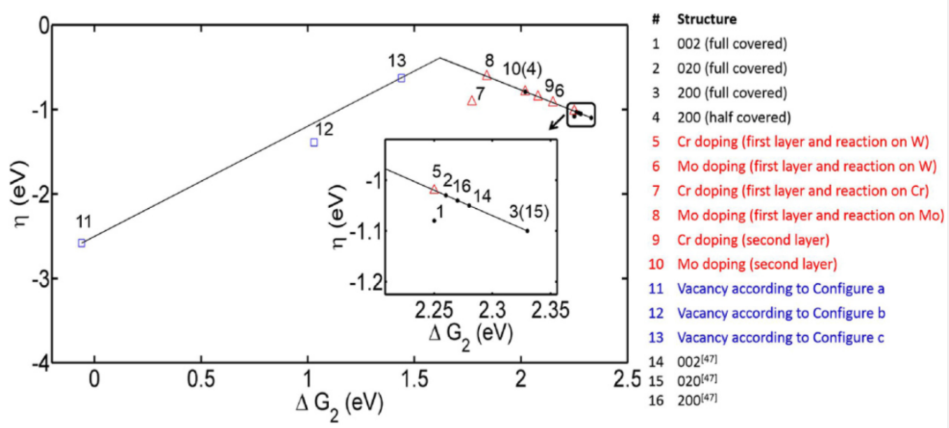
Case Study: WO_3

Experiments



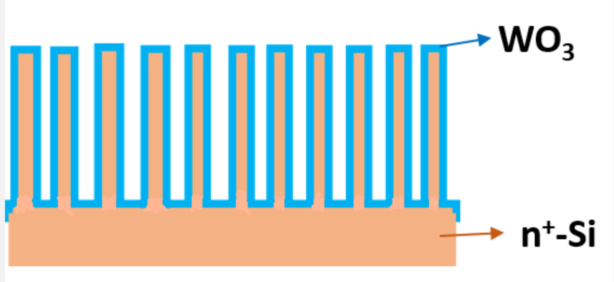
Zhao et al., ACS Energy Materials, submitted.

Modeling & Simulations

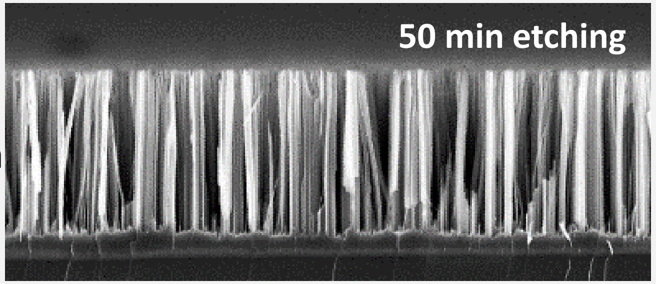


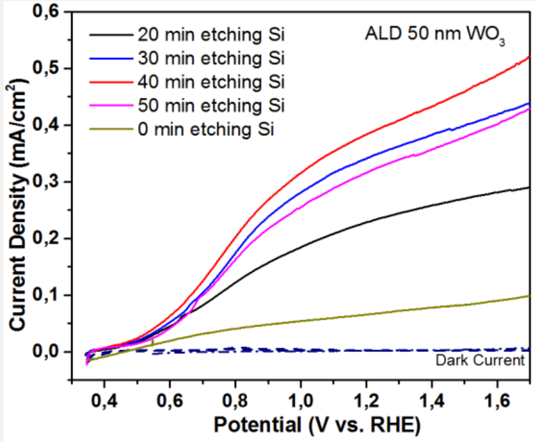
Kishore et al., Catalysis Today (2018).

Si nanowires + 50 nm WO_3 by ALD



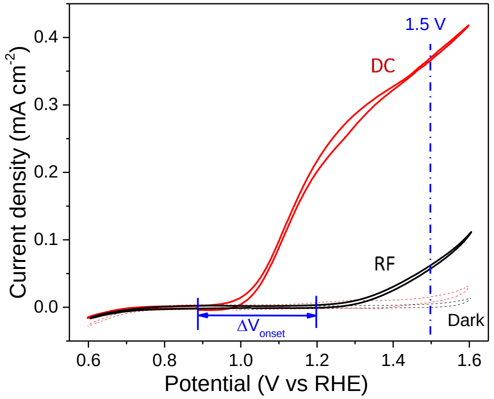
3.5 µm

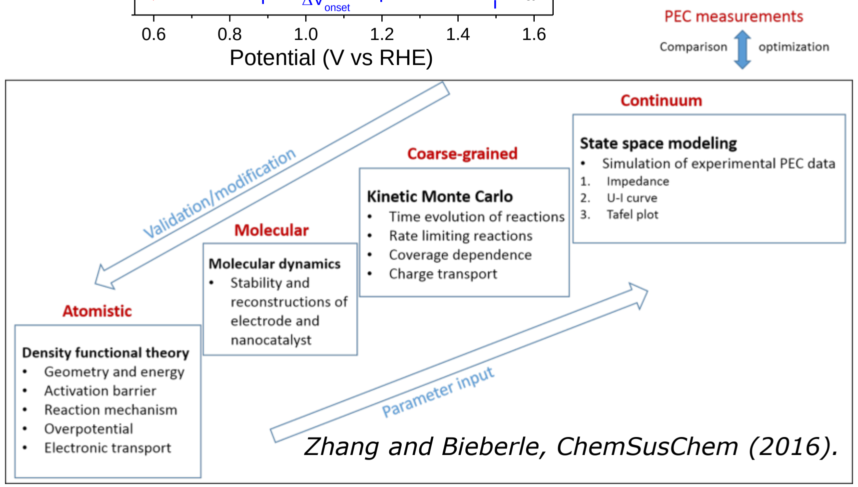




Conclusion and Outlook

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

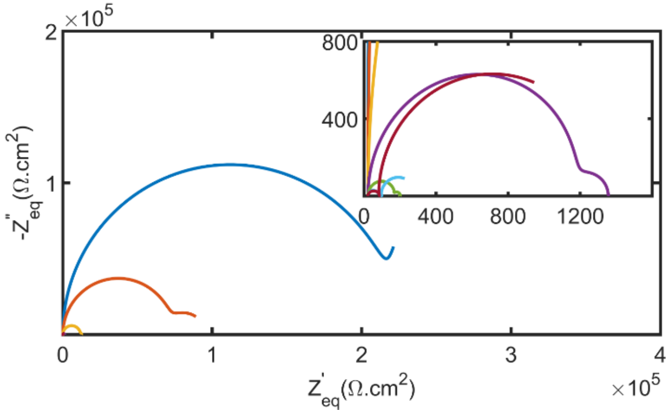


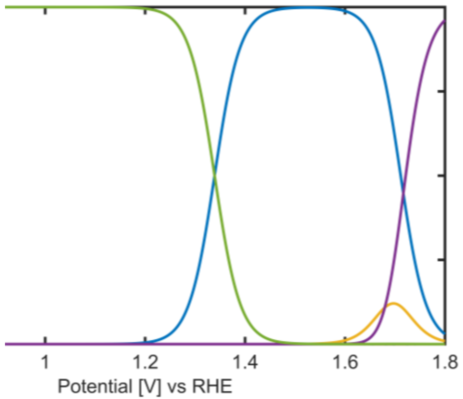


Zhang and Bieberle, ChemSusChem (2016).

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

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





Thank you

- E. Zouthout
- H. Genuit

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