Modeling of SOECs – Physics-based Impedance Analysis of MIEC Electrodes

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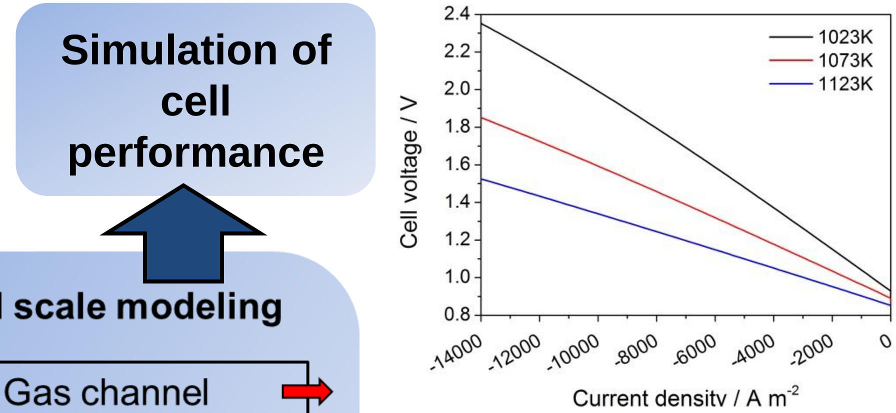
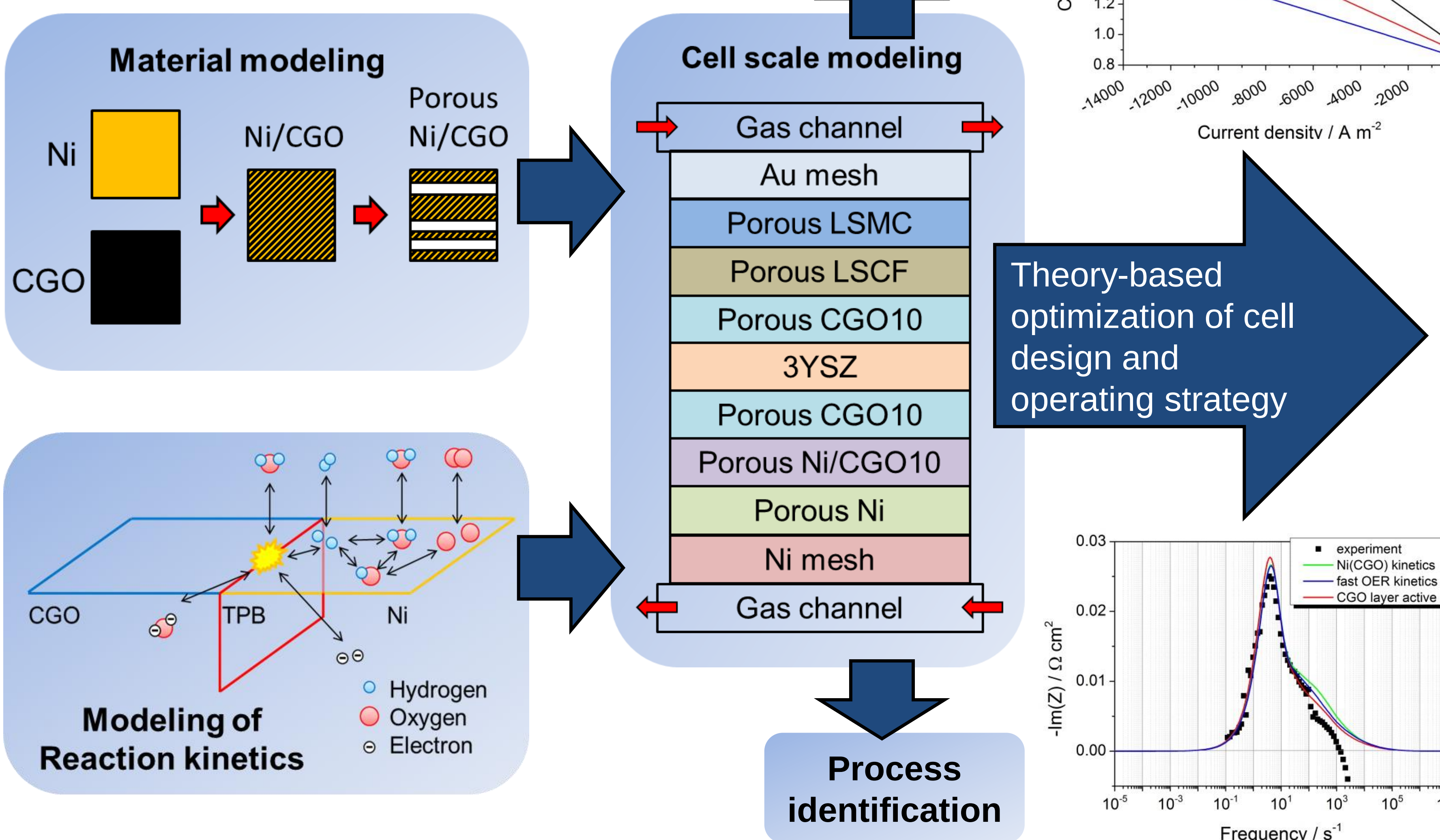
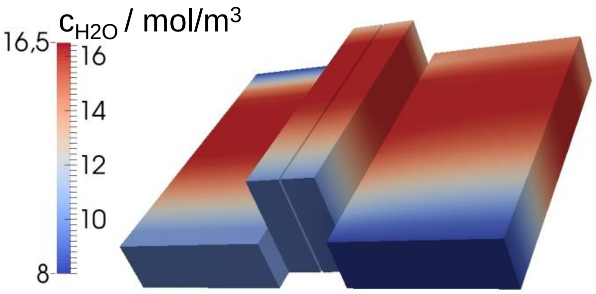
DLR

Scientific Approach

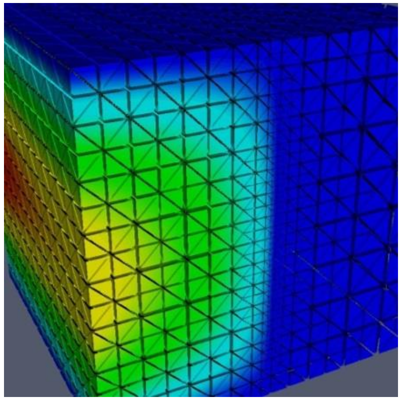




Framework



Generic framework for the simulation of multi-phase flow and transport in porous media

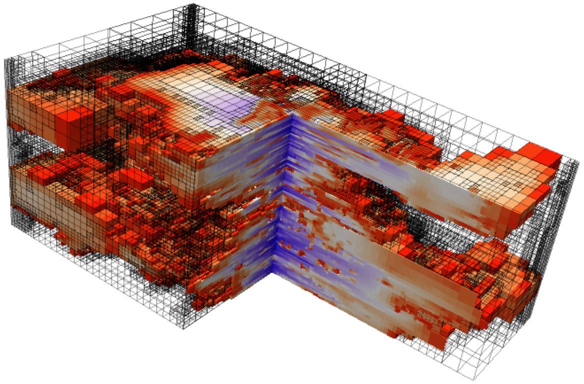


NEOPARD-X

Dumux

DUNE

Framework to investigate performance and degradation of energy conversion devices via transient 2D and 3D simulations



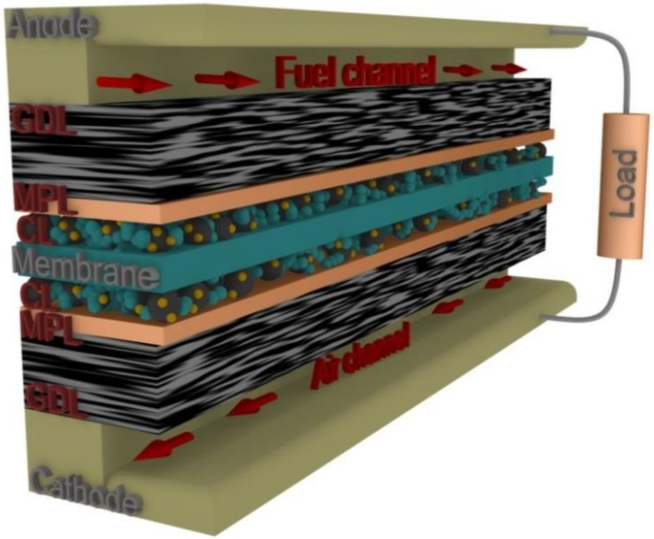
Modular toolbox for solving partial differential equations with grid-based methods

NEOPARD-X: Numerical **E**nvironment for the **O**ptimization of **P**erformance **A**nd **R**eduction of **D**egradation of **X**[1]

- Developed at DLR since 2013

NEOPARD-X features:

- 2D and 3D discretizations of the cells
- Transport models for the cell components
- Electrochemistry models
- Specific fluid systems for the different technologies
- Transient simulations (e.g. impedances)



Field of Application:

- PEMFC
- DMFC
- **SOC**

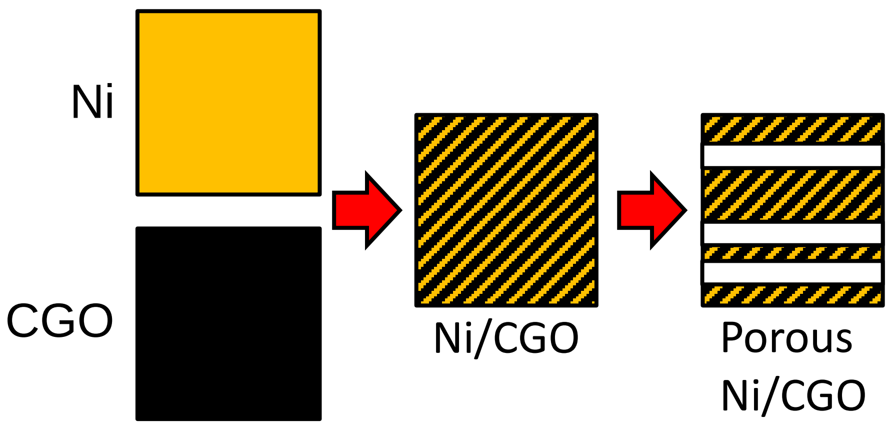
[1]: G.A. Futter, P. Gazdzick, K. A. Friedrich, A. Latz, T. Jahnke, Physical modeling of Polymer-Electrolyte Membrane Fuel Cells: Understanding water management and impedance spectra, submitted.

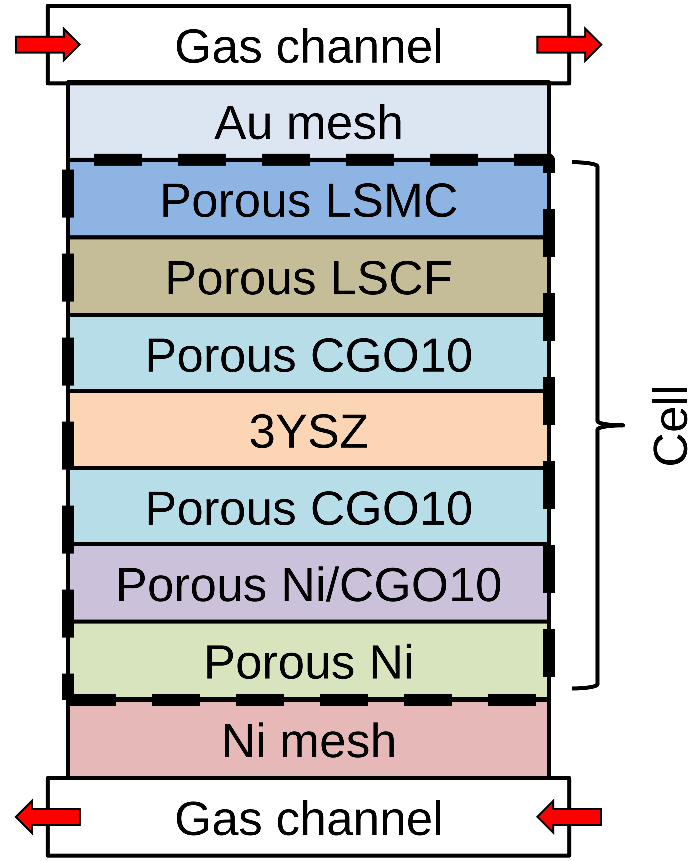
Material Modeling

- Calculation of bulk phase properties
  → σ_{ion}, σ_{elec}, λ, c_p, ρ in the relevant T-range

- Calculation of average properties of mixed phases (e.g. Ni/CGO)

- Calculation of effective properties in in porous structures or meshes

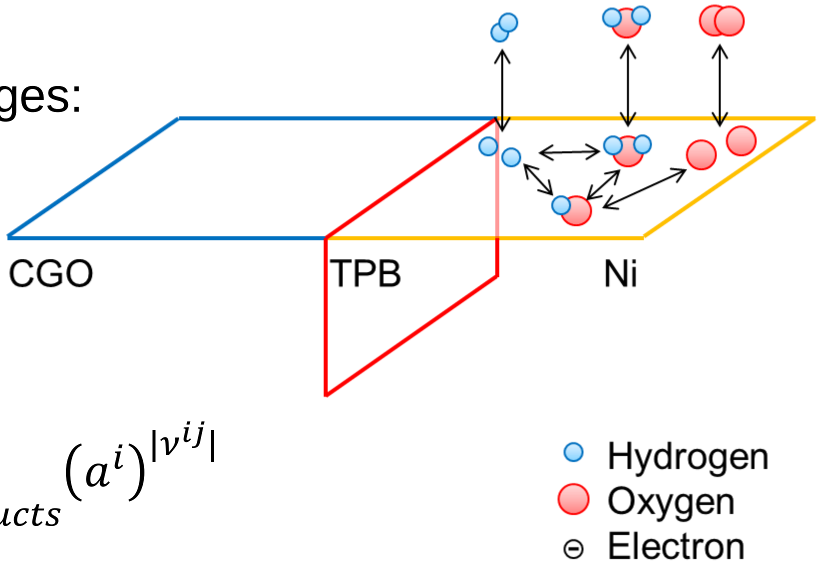




Elementary Kinetic Framework

- Balance equations for e.g. surface coverages:

$$\frac{\partial \theta^i}{\partial t} = q^i \qquad q^i = \sum_j \frac{\nu^{ij} \sigma^i r^j}{\Gamma}$$



- Reaction rate:

$$r^j = k_f{}^j \prod_{i,educts} \left(a^i\right)^{|\nu^{ij}|} - k_r{}^j \prod_{i,products} \left(a^i\right)^{|\nu^{ij}|}$$

- Thermodynamic consistency:

$$\Delta h^j = \sum_i \nu^{ij} h^i{}_0$$

$$\Delta s^j = \sum_i \nu^{ij} s^i{}_0$$

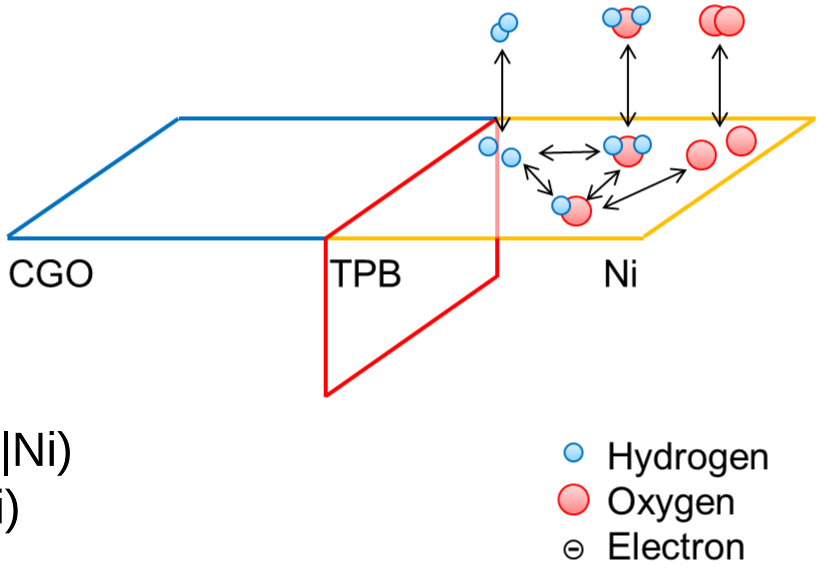
$$\Delta g^j = \Delta h^j - T \Delta s^j$$

$$k_f{}^j = A\, T^n \exp\left(\frac{-E_{act}}{\mathrm{R}T}\right)$$

$$k_r{}^j = k_f{}^j \exp\left(\frac{\Delta g^j}{\mathrm{R}T}\right)$$

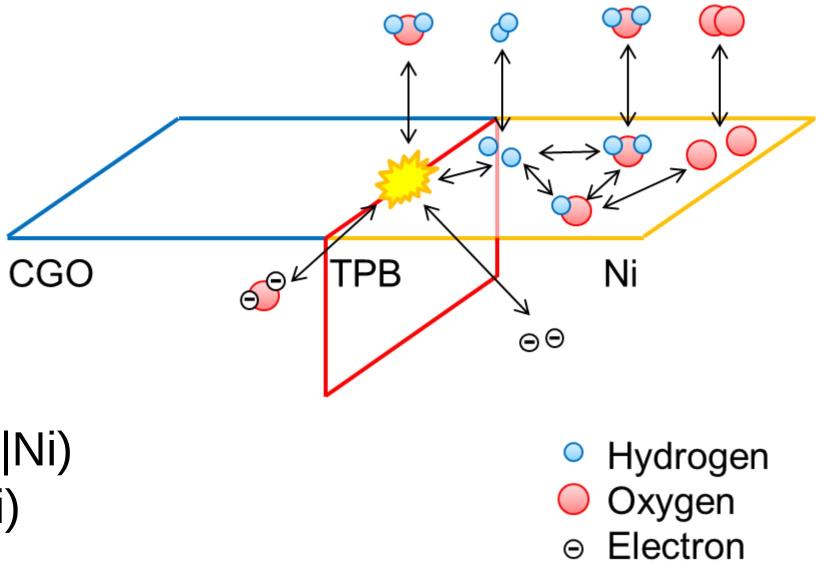
Elementary Reactions in the Fuel Electrode

- Reactions at the gas/nickel interface:



1. $H_2[g] + 2(g|Ni) \rightleftharpoons 2H(g|Ni)$
2. $H_2O[g] + (g|Ni) \rightleftharpoons H_2O(g|Ni)$
3. $O_2[g] + 2(g|Ni) \rightleftharpoons 2O(g|Ni)$
4. $2OH(g|Ni) \rightleftharpoons H_2O(g|Ni) + O(g|Ni)$
5. $H(g|Ni) + OH(g|Ni) \rightleftharpoons H_2O(g|Ni) + (g|Ni)$
6. $H(g|Ni) + O(g|Ni) \rightleftharpoons OH(g|Ni) + (g|Ni)$

Elementary Reactions in the Fuel Electrode



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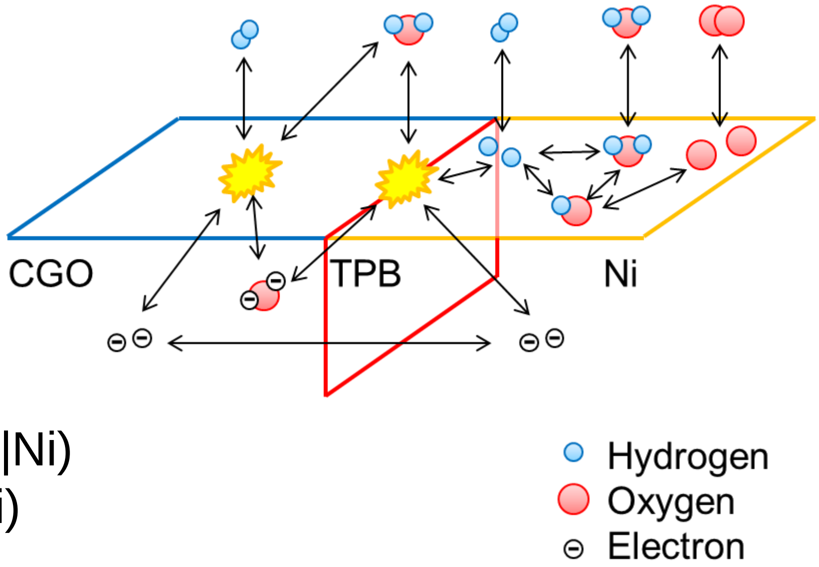
- Charge transfer reactions:

    1. $2e^-[Ni] + H_2O[g] + 2(g|Ni) \rightleftharpoons 2H(g|Ni) + O^{2-}[CGO]$

Elementary Reactions in the Fuel Electrode



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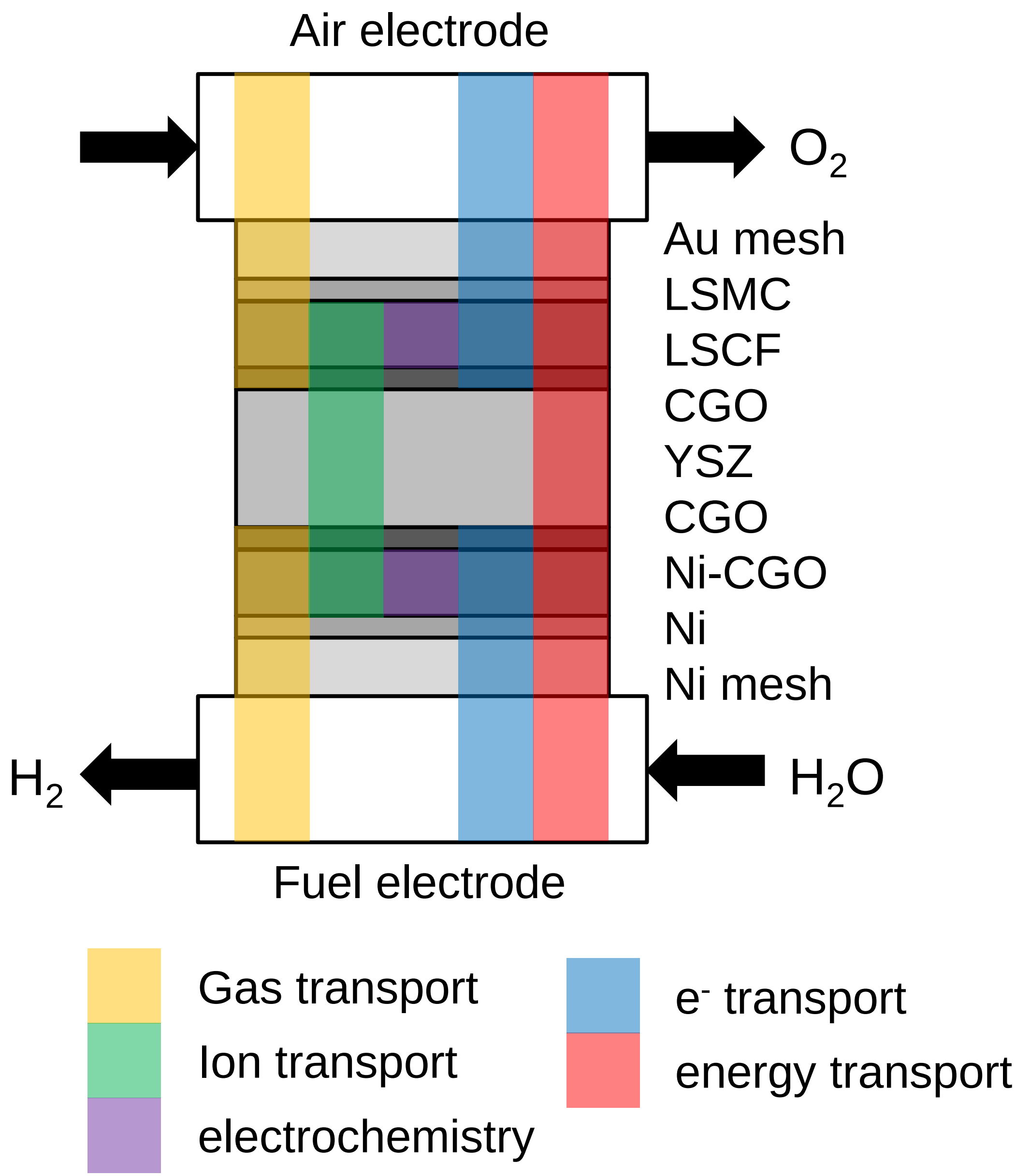
  2. $2e^-[CGO] + H_2O[g] \rightleftharpoons H_2[g] + O^{2-}[CGO]$

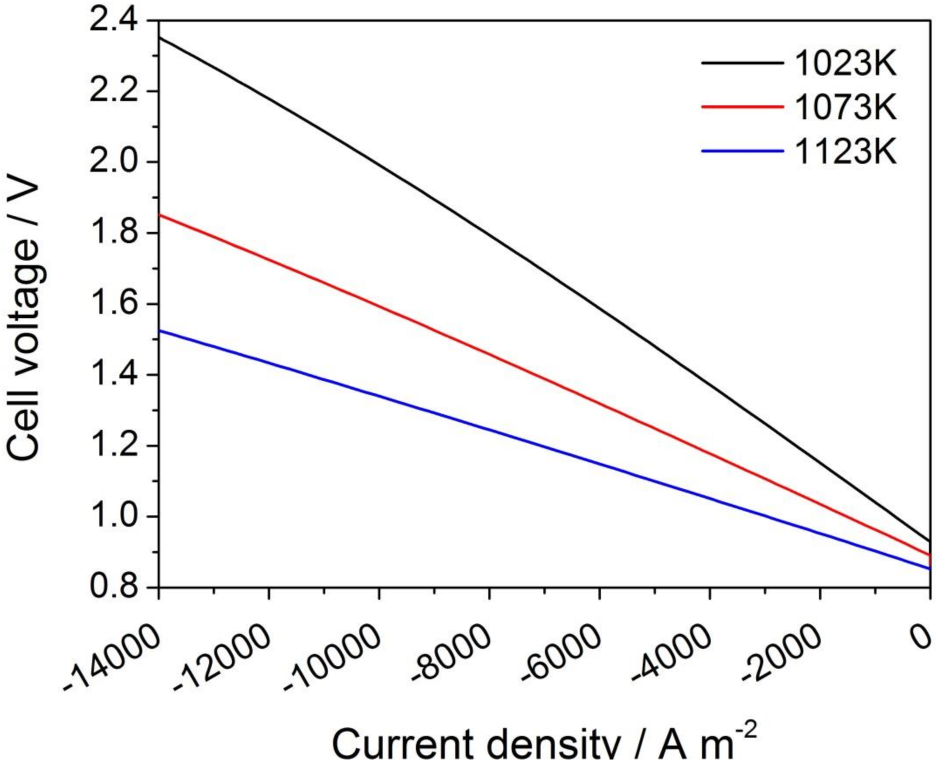
SOEC Model

- 11 spatially resolved layers
- Detailed material properties
- Thermodynamic properties of chemical species
- Detailed gas transport
- Charge transport
- Energy transport
- Electrochemistry:
  global or elementary kinetics



Results

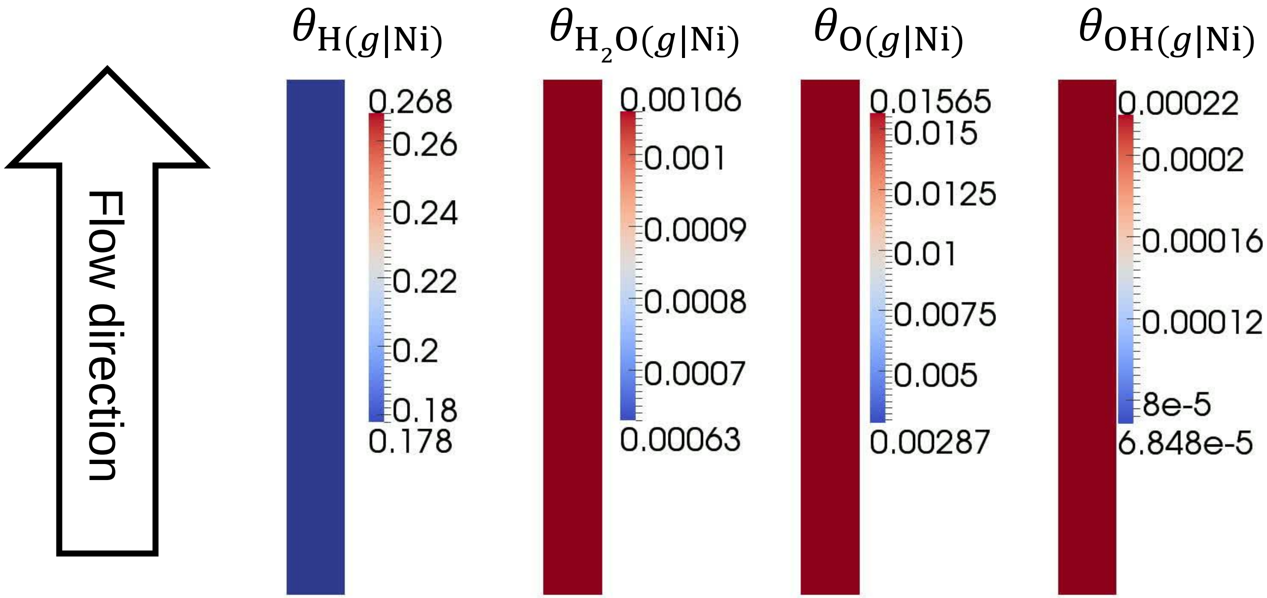
Influence of the cell temperature on the modeled material properties and the cell performance: 20% H_2 80% H_2O, $p=10^5$ Pa



- Lower OCV for elevated temperature
- Decreased electrolyte resistance for elevated temperature
- Electrolyte = main source of voltage losses in an electrolyte supported cell

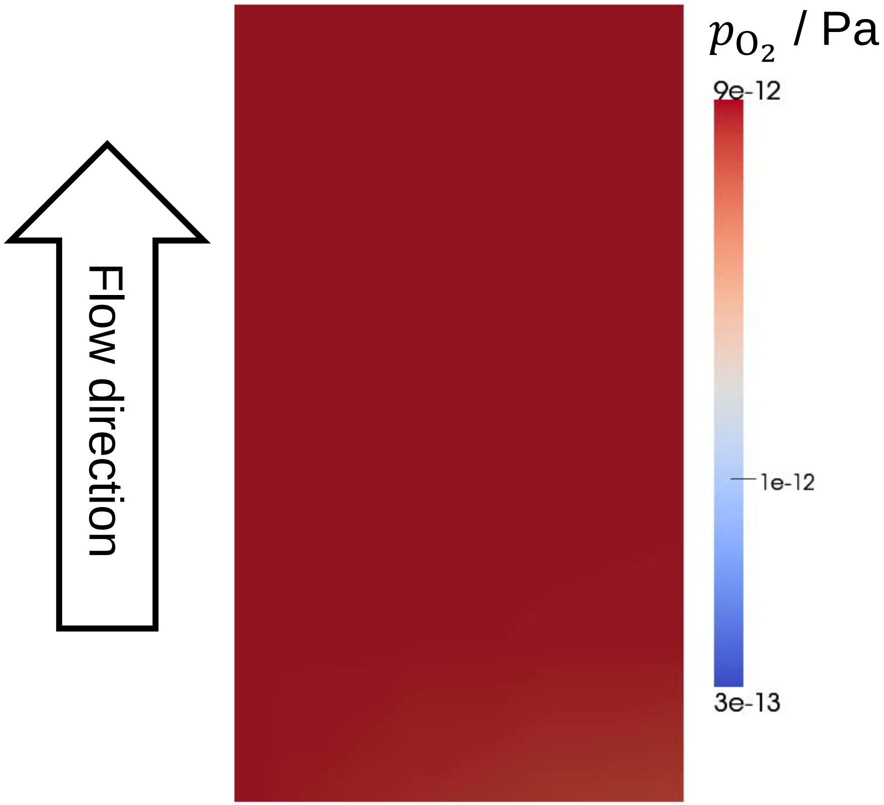
Results

Distribution of the surface species in the fuel electrode along the channel during polarization curve simulation: 20% H_2 80% H_2O, T= 1123K, p=10^5 Pa



Ergebnisse

Distribution of oxygen in the fuel electrode: 20% H_2 80% H_2O,
T= 1123K, p=10^5 Pa



- Electrical Conductivity of CGO critically depends on the oxygen partial pressure[1]:

  $$\sigma_{elec} \sim \left(p_{O_2}\right)^{-\frac{1}{4}}$$

- Modeling of elementary reactions allows determination of the O_2-concentration

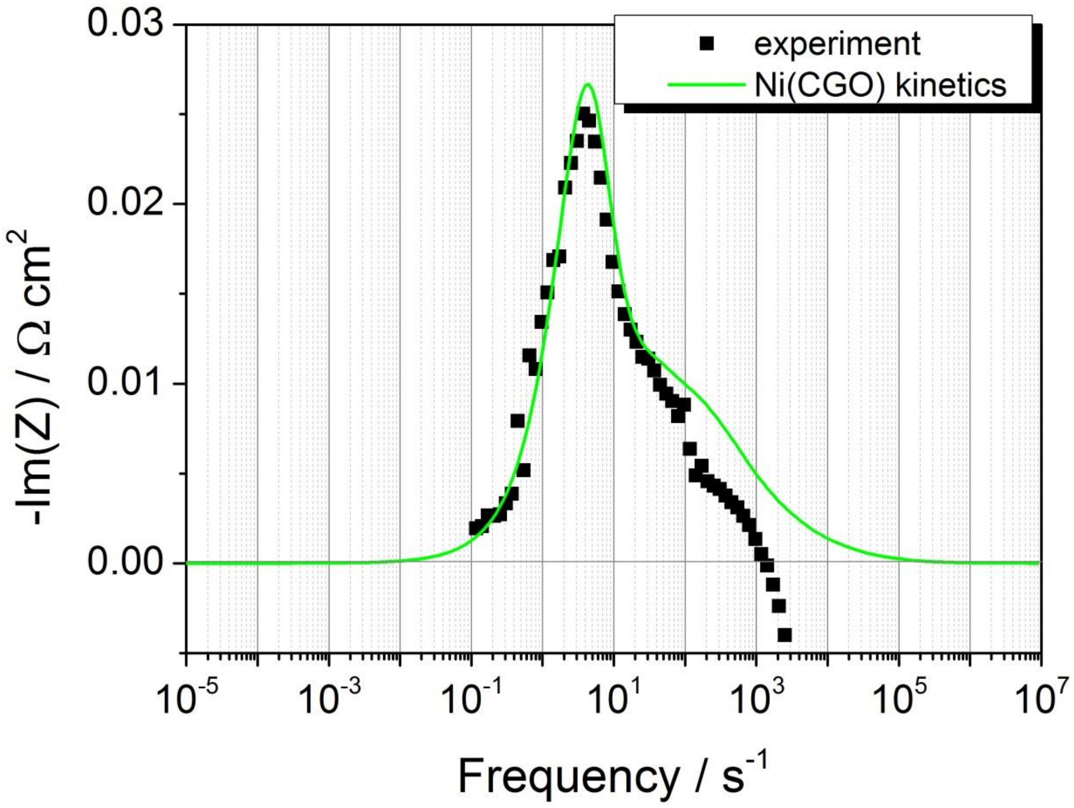
→ Materials behave differently on the fuel- and air electrode

[1]: Steele, Solid State Ionics, 29(2000),95-110.

DLR

Results

Impedance simulation: 50% H_2 50% H_2O, T= 1123K, p=10^5 Pa, OCV



- Characteristic frequencies and order of magnitude of effects are quantitatively reproduced by the model
- However, deviations above > 300 Hz

Results

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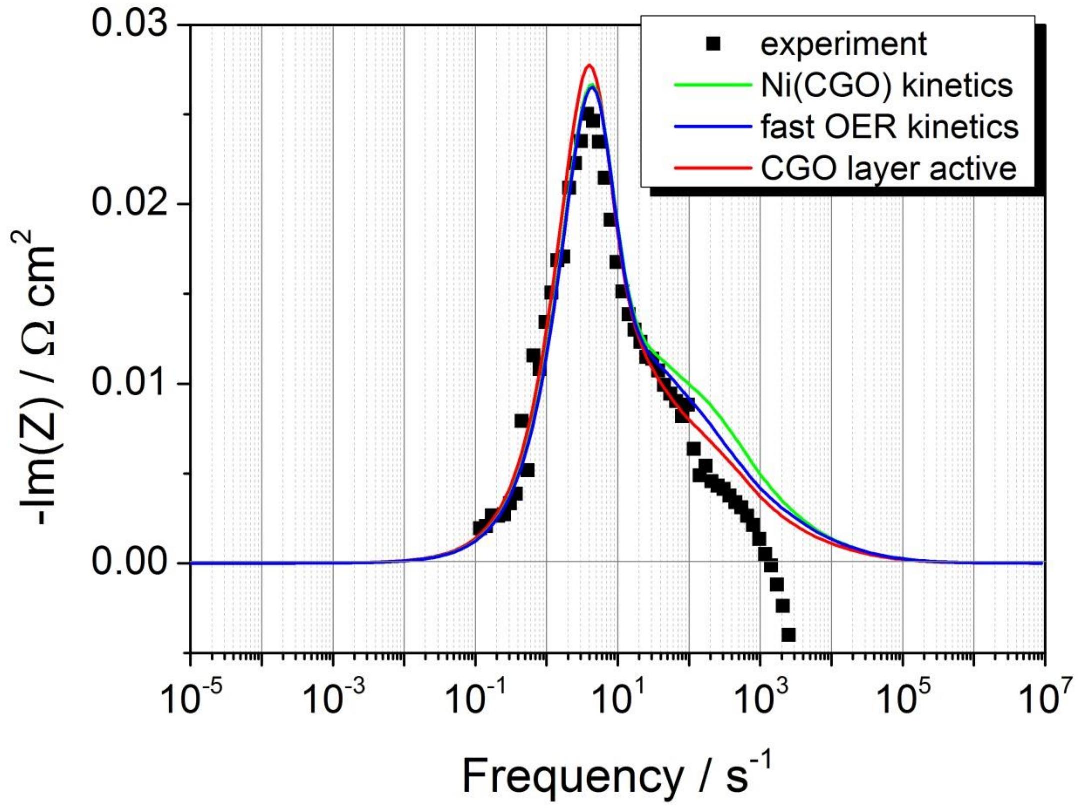
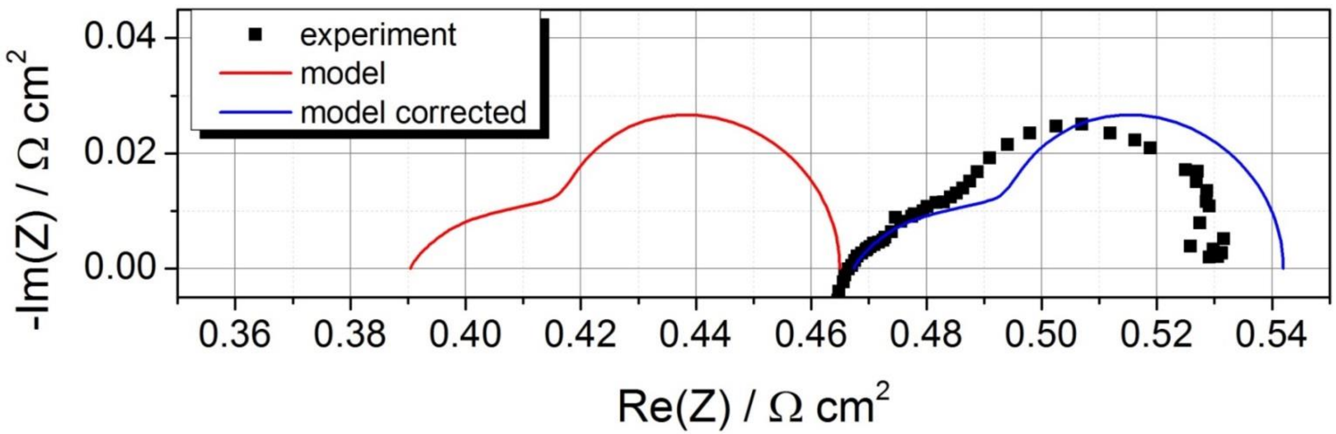


- Characteristic frequencies and order of magnitude of effects are quantitatively reproduced by the model
- However, deviations above > 300 Hz

→ Possible explanations:
1. OER kinetics in the air electrode
2. CGO layer is electrochemically active

Results

Impedance simulations: 50% H_2 50% H_2O, T= 1123K, p=10^5 Pa, OCV



- In the model, ohmic resistance is underestimated by 0.077 Ohm cm^2

→ Possible reasons:

- Contact resistances
- Formation of mixed crystals at the YSZ/CGO interface with low conductivity
- Inaccurate relation for the electrolyte ionic conductivity

Next Steps

1. Further validation of the H_2O electrolysis kinetics with experiments

2. Extension of the elementary kinetic model to account for
   - Co-electrolysis
   - Reverse-water-gas-shift (RWGS)

3. Validation of the co-electrolysis kinetics

→ Theory-based optimization of cell design and operating strategy

Thank you for your attention

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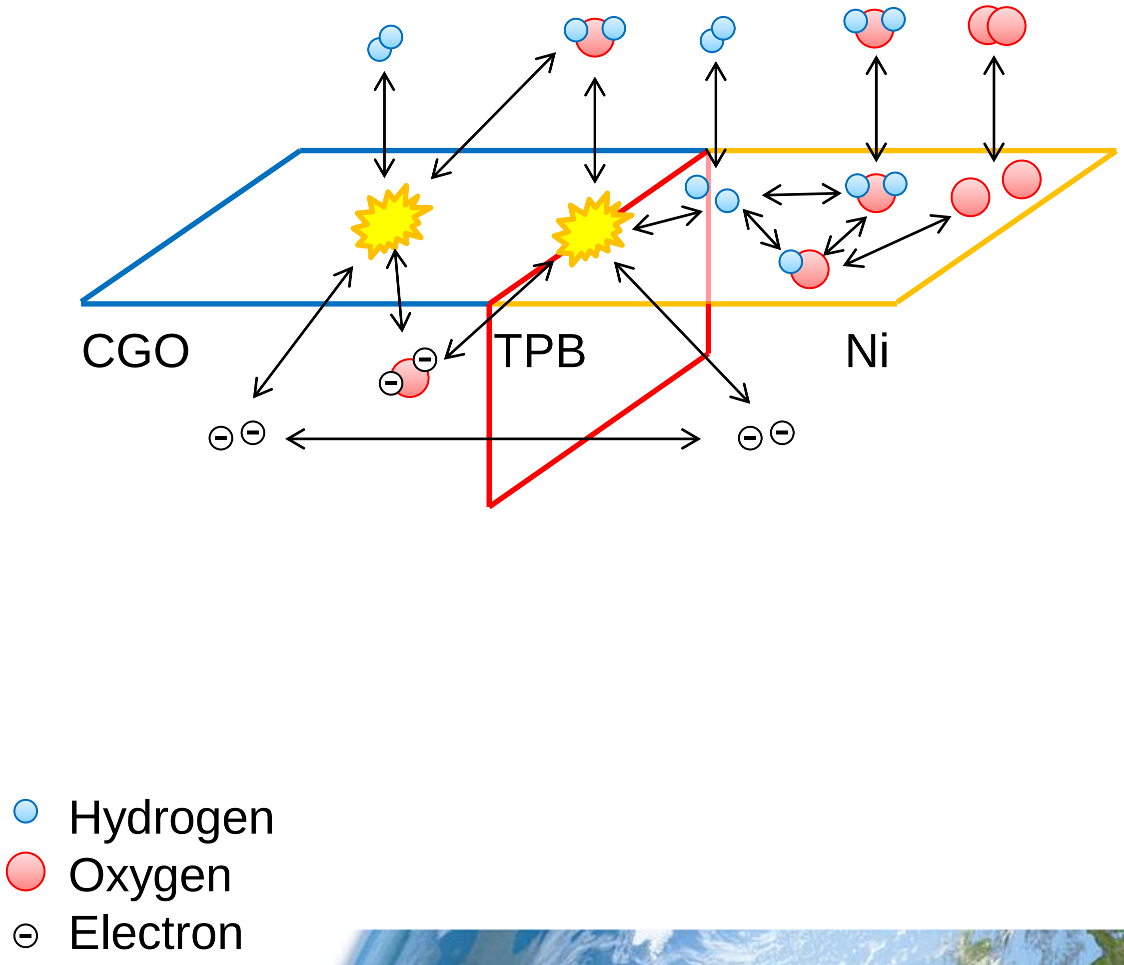
CGO
TPB
Ni
Hydrogen
Oxygen
Electron