Physical Modeling of Co-Electrolysis in Solid Oxide Electrolysis Cells

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Motivation

With increasing penetration of renewable energy into the energy system, the number of periods where the power generation exceeds the demand rises.

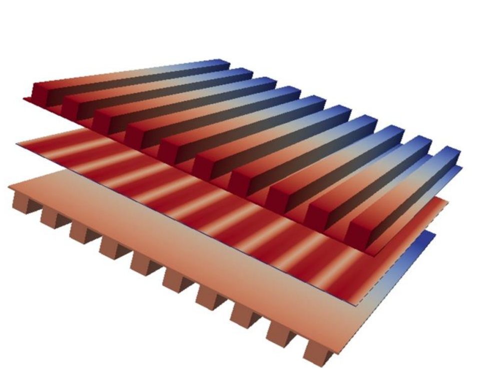
In the KOPERNIKUS Project Power-to-X different technologies to convert and store this surplus electricity are investigated. Solid oxide electrolysis cells (SOECs) are capable to efficiently produce syngas (H_2 + CO) via co-electrolysis of water and carbon dioxide. The obtained syngas can be converted into e.g. liquid fuels via the Fischer-Tropsch-synthesis in subsequent processes.

To understand how operating conditions like temperature, pressure and fuel composition influence the performance, the product composition (H_2/CO-ratio) and degradation of SOECs, a physics-based cell-level model has been developed. The model has been validated with polarization curves and impedances under various operating conditions. An optimization of the operating conditions based on the syngas composition has been performed.

Modeling approach – NEOPARD-X[1]

Transient and macro-homogeneous formulations of mass-, charge- and energy balances:

$$\frac{\partial \xi^i}{\partial t} + \nabla \cdot \Psi^i - q^i = 0$$



Mass:

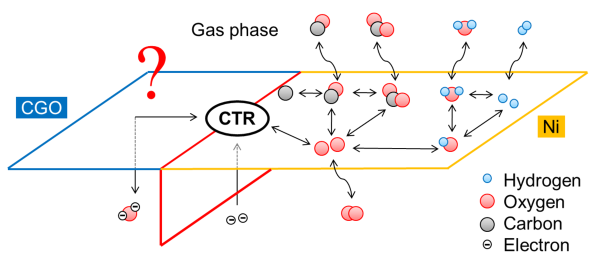
- Darcy's law in combination with Stefan-Maxwell- and Knudsen diffusion in the porous electrodes

Charge:

- Ohm's law for electrical- and ionic currents

Chemical and electrochemical reactions:

- Co-electrolysis and RWGS are modeled using thermodynamically consistent elementary kinetics



Energy:

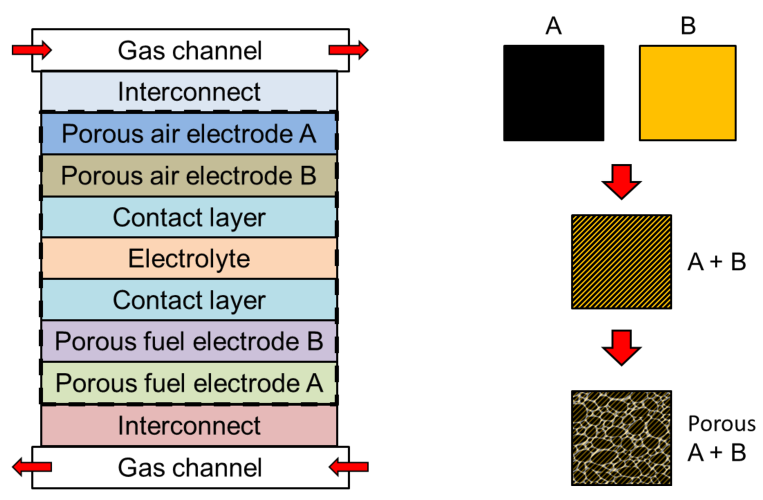
- Energy transport due to mass- and charge transport
- Heat formation due to ohmic heating
- Heat formation due to elementary reactions

Material modeling:

- Derivation of effective properties from bulk properties and structural parameters

Model geometry:

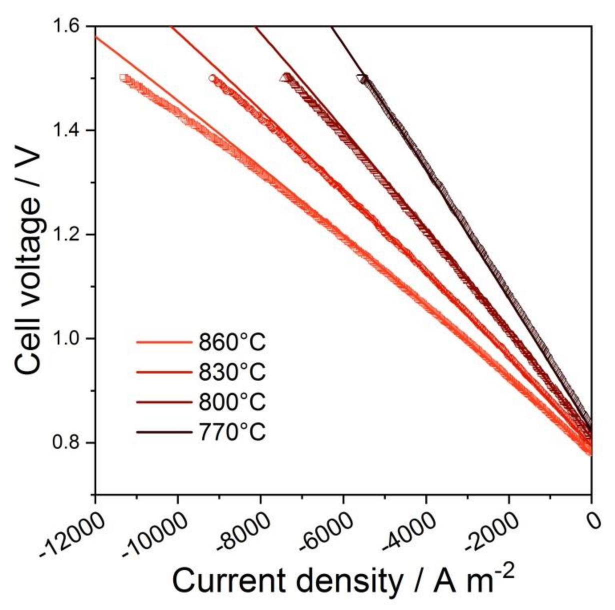
- The 11 layers of the single cell including gas channels are spatially resolved in 2D or 3D



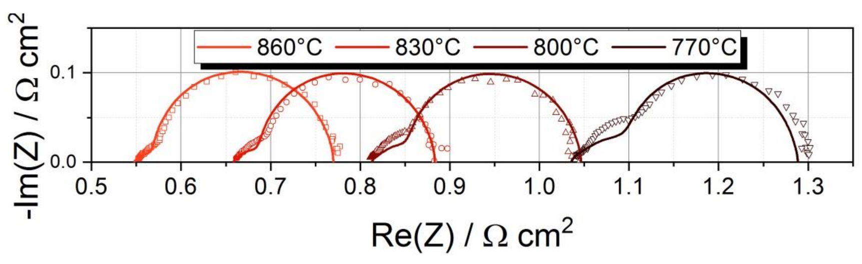
Results

Model validation:

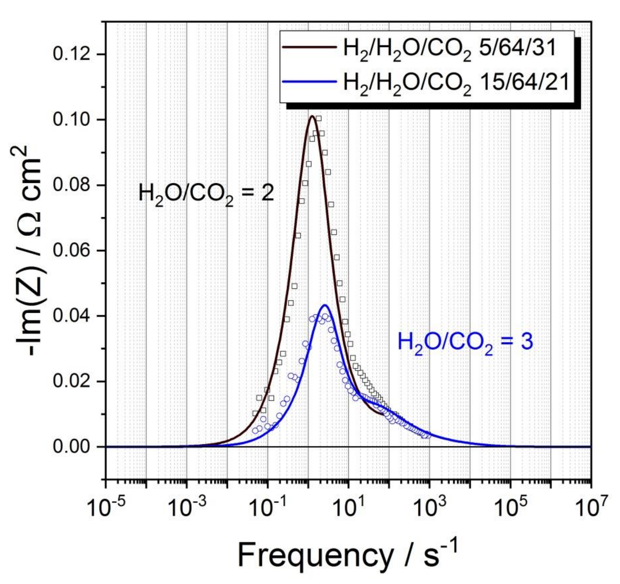
- Simulated and experimental polarization curves at various temperatures and gas compositions:



Effect of temperature on polarization curves at 5% H_2, 63.7% H_2O, 31.3% CO_2



Impedance spectra at OCV for 5% H_2, 63.7% H_2O, 31.3% CO_2 and various temperatures

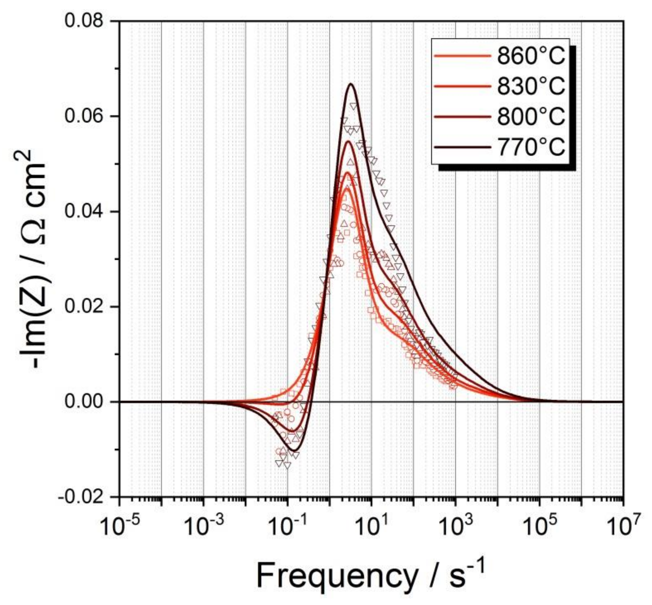


Effect of gas composition on impedance at OCV

- ➢ Good agreement between simulation and experiment
- ➢ Model predicts increasing resistance with decreasing temperature, mainly due to the ohmic resistance of the electrolyte
- ➢ Low frequency resistance is temperature independent and caused by mass transport losses along the channel
- ➢ High frequency resistance is due to kinetic losses and decreases with increasing temperature

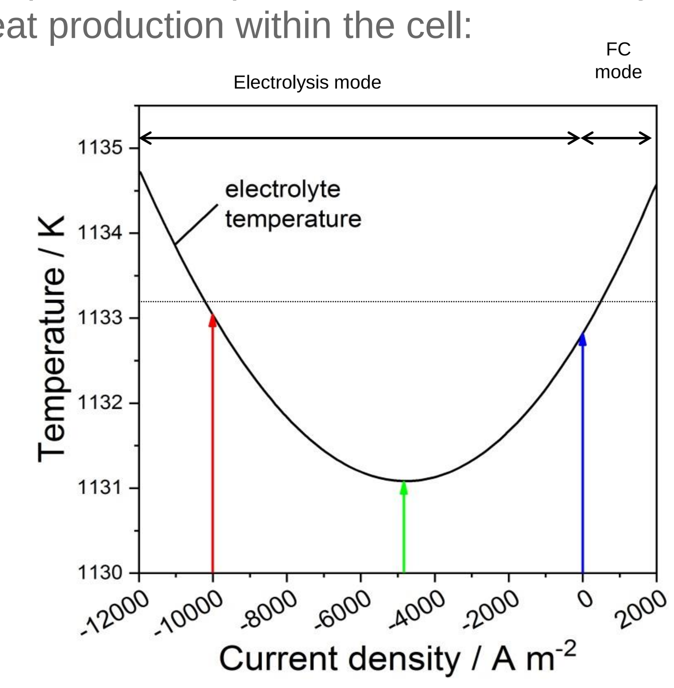
Model-based impedance analysis:

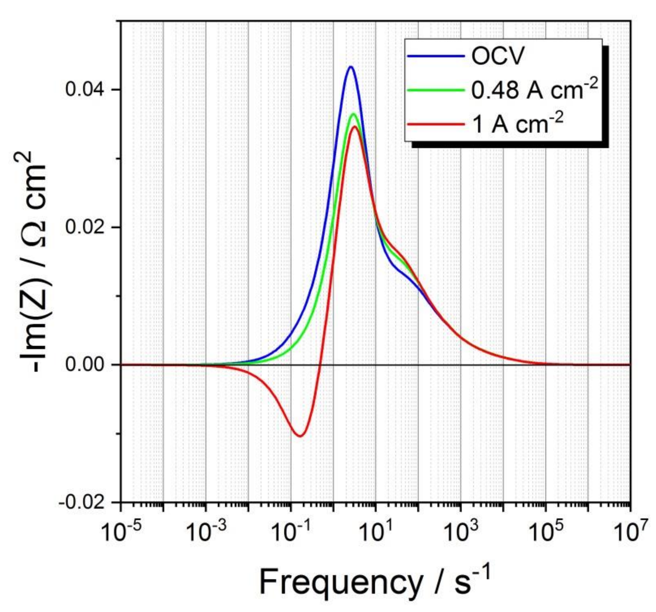
- An inductive loop is observed at low frequency under certain operating conditions:



Impedances at 0.6A/cm² with H_2O/CO_2=2.04

- The inductive behavior originates from the temperature dependent ion conductivity and the heat production within the cell:





Current density dependent cell temperature and impedances. The dashed line marks the operating temperature

- ➢ Inductive behavior occurs if temperature increases with current density, i.e., if an increasing current leads to an increasing ion conductivity

Model-based optimization of operating strategy:

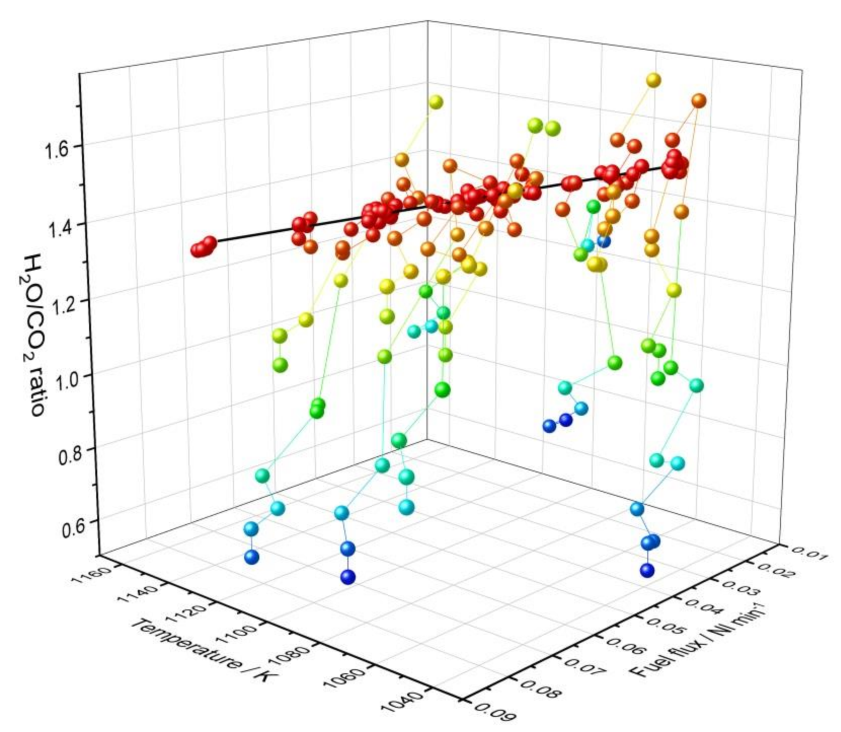
- Goal: find optimal operating temperature, inlet gas composition and fuel flow rate to obtain requested syngas composition and fuel utilization at the thermoneutral voltage
- For the optimization the physical model is coupled with a constrained Nelder-Mead method [2]
- Minimization of error function

$$f\left(x_{H_2O}, x_{CO_2}, T, \dot{m}\right) = w_1 \left|\frac{x_{H_2,out}}{x_{CO,out}} - 2\right| + w_2 |FU - 70|$$

- – H_2/CO ratio in outlet syngas: $\frac{x_{H_2,out}}{x_{CO,out}}$
- – Fuel utilization:

$$FU = FU^{H_2O}\frac{x^{H_2O}}{x^{H_2O}+x^{CO_2}} + FU^{CO_2}\frac{x^{CO_2}}{x^{H_2O}+x^{CO_2}}$$

- – Weights: $w_1 = 100$; $w_2 = 1$



Visualization of 17 optimization runs with random initial parameters. Lowest errors are marked in red.

- ➢ Optima lie on a straight line in parameter space
- ➢ Obtained relations between optimal temperature, fuel flux and inlet gas composition:

$$\dot{m} = 4.1125 \times 10^{-4}\, T \; - \; 0.40204$$

$$\frac{x_{H_2O}}{x_{CO_2}} = -0.00222\, T + 3.87953$$

- ➢ Operating conditions can be varied according to these relations without changing the fuel utilization and product gas composition
- ➢ This approach might be used to ensure constant syngas composition at varying load

References

[1]: Futter et al., JPS 391 (2018), 148-161. doi: 10.1016/j.jpowsour.2018.04.070

[2]: Le Floc'h, SSRN (2012). doi: 10.2139/ssrn.2097904

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KOPERNIKUS PROJEKTE P2X Die Zukunft unserer Energie

The authors gratefully acknowledge funding by the German Federal Ministry of Education and Research (BMBF) within the Kopernikus Project P2X: Flexible use of renewable resources – exploration, validation and implementation of 'Power-to-X' concepts.