Physical Modeling of Solid Oxide Electrolysis Cells in CO-electrolysis mode

G. Futter[1], D. Amaya Dueñas[1], R. Costa [1],
K.A. Friedrich [1], A. Latz [1,2], T. Jahnke [1]

(1) German Aerospace Center (DLR), Stuttgart/Germany

(2) Helmholtz Institute Ulm for Electrochemical Energy Storage (HIU), Ulm/Germany

Outline

I. Motivation

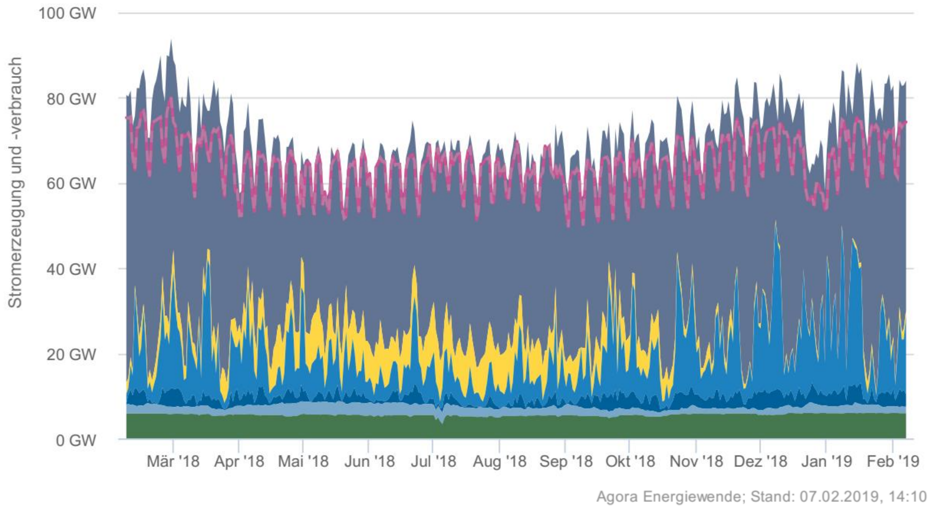
II. Numerical Framework NEOPARD-X

III. SOEC Model
- Features
- Elementary kinetic model
- Validation
- Impedance analysis
- Predictions

IV. Summary

Motivation

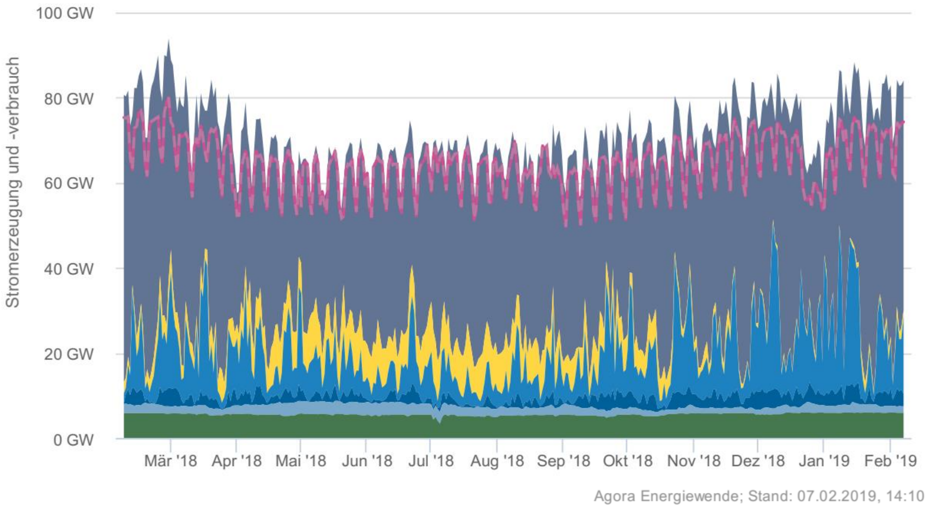
- Electricity from wind turbines and solar panels fluctuates.



- How can we store and use this surplus electricity?

Motivation

- Electricity from wind turbines and solar panels fluctuates.



- How can we store and use this surplus electricity?

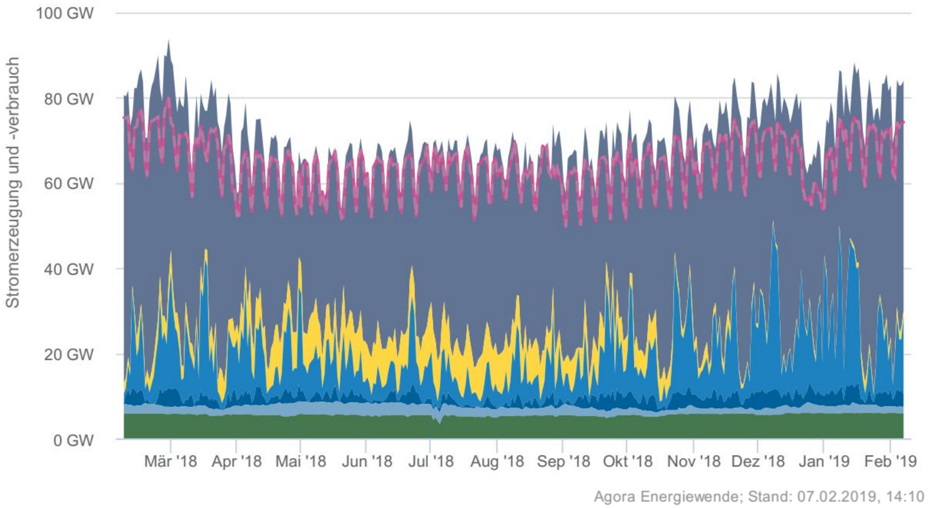
<u>Power-to-Gas with SOECs in co-electrolysis operation:</u>

- Simultaneous reduction of H_2O and CO_2
- Production of syngas (H_2 + CO)

→ Subsequent production of synthetic fuels, …

Motivation

- Electricity from wind turbines and solar panels fluctuates.



- How can we store and use this surplus electricity?

<u>Power-to-Gas with SOECs in co-electrolysis operation:</u>

- Simultaneous reduction of H_2O and CO_2
- Production of syngas (H_2 + CO)

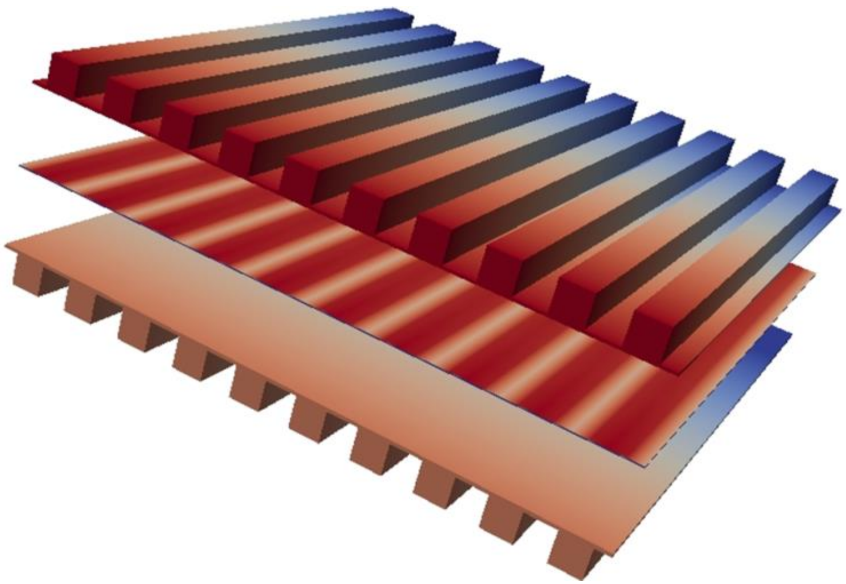
→ Subsequent production of synthetic fuels, …

- Control of the exhaust gas composition of SOECs
- Understanding of degradation phenomena

Numerical Framework NEOPARD-X[1,2]

Numerical **E**nvironment for the **O**ptimization of **P**erformance **A**nd **R**eduction of **D**egradation of **X** (= energy conversion device)

Developed at DLR since 2013 based on the open source software DuMu^X [3] and DUNE [4]



NEOPARD-X[1,2] features

- 2D and 3D discretization of the cells
- Transport models for the cell layers
- Detailed electrochemical models
- Suitable for different technologies
- Transient simulations

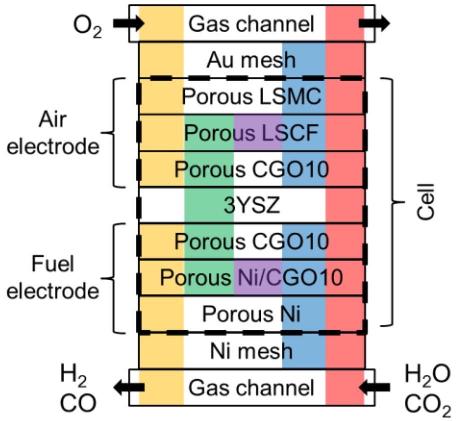
Fields of Application:

- DMFC
- PEMFC
- **SOEC**
- …

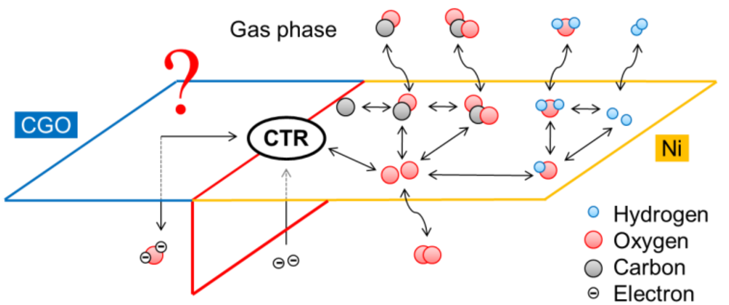
[1]: Futter et al., JPS, 391(2018) 148.
[2]: Futter et al., JPS, 410-411 (2019) 78-90.
[3]: Flemisch et al., 2011, *Adv. Water Resour.*, *34*(9).
[4]: https://dune-project.org/

SOEC Model

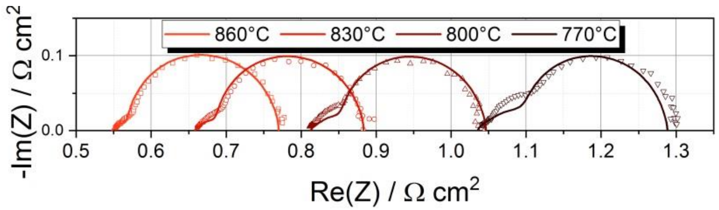
- Modeling domain & features



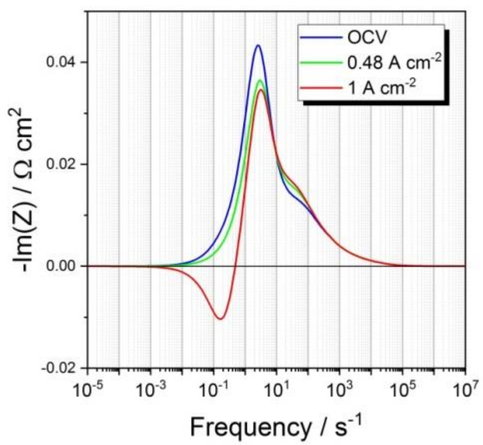
- Elementary kinetic modeling of co-electrolysis and RWGS



- Model validation under various operating conditions



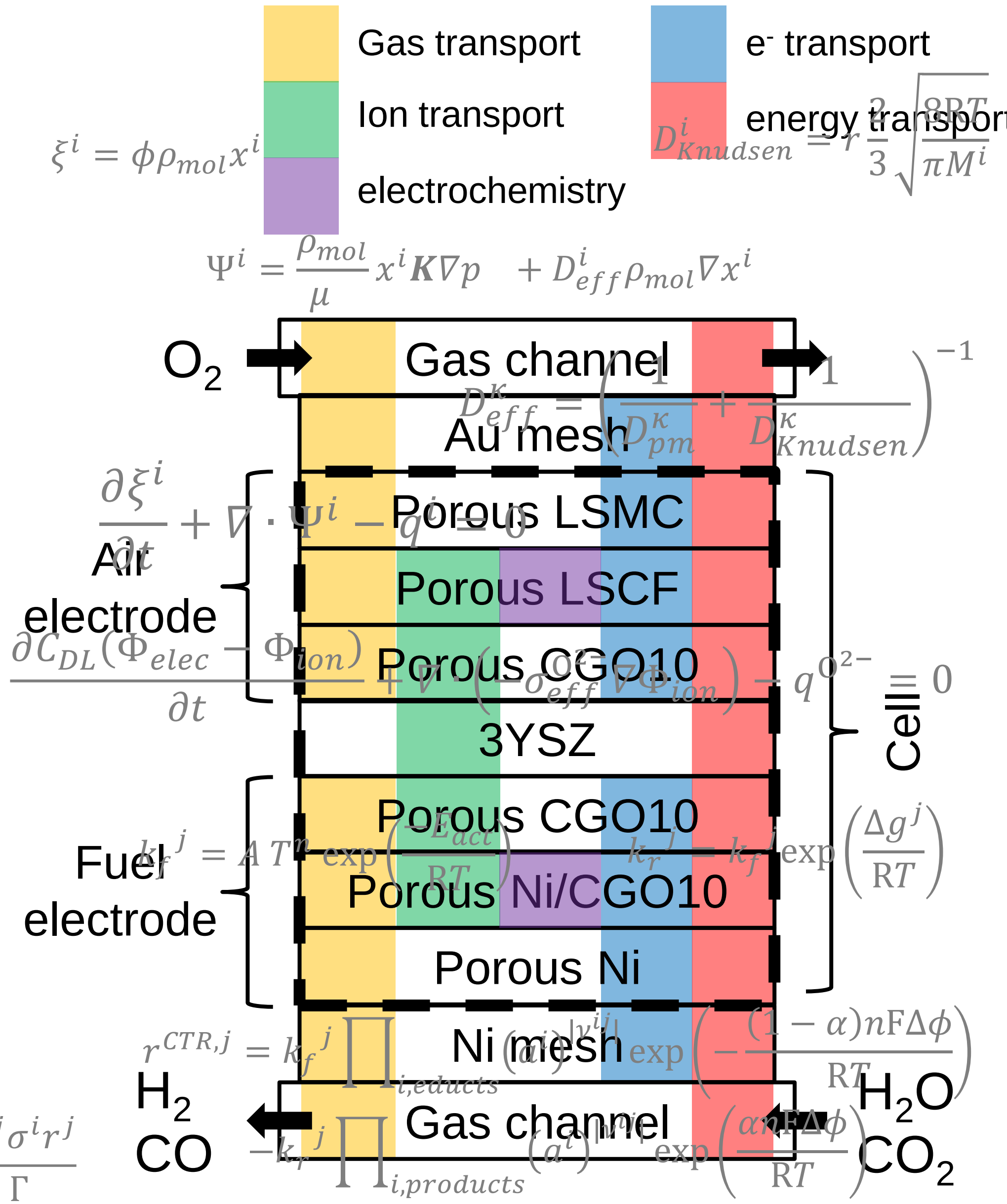
- Impedance analysis & predictions



DLR

SOEC Model

- 11 spatially resolved layers
- Detailed material properties
- Detailed gas transport
- Charge transport
- Energy transport
- Electrochemistry: thermodynamically consistent elementary kinetics
- Model for a commercial electrolyte-supported cell from Sunfire



$$\xi^i = \phi \rho_{mol} x^i$$

$$D^i_{Knudsen} = r\frac{2}{3}\sqrt{\frac{8RT}{\pi M^i}}$$

$$\Psi^i = \frac{\rho_{mol}}{\mu} x^i \boldsymbol{K}\nabla p + D^i_{eff}\rho_{mol}\nabla x^i$$

$$D^\kappa_{eff} = \left(\frac{1}{D^\kappa_{pm}} + \frac{1}{D^\kappa_{Knudsen}}\right)^{-1}$$

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

$$-\frac{\partial C_{DL}(\Phi_{elec}-\Phi_{ion})}{\partial t} + \nabla\cdot\left(-\sigma^{O^{2-}}_{eff}\nabla\Phi_{ion}\right) - q^{O^{2-}} = 0$$

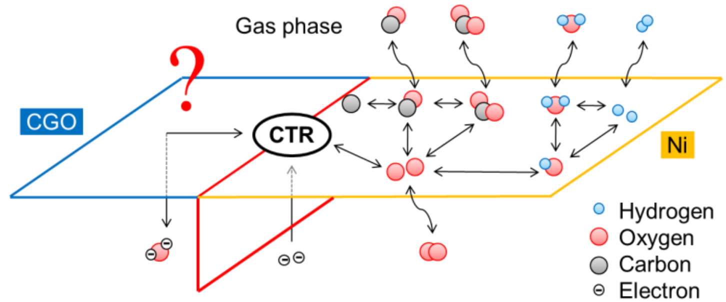
$$k_f^j = A\,T^n \exp\left(\frac{-E_{act}}{RT}\right)$$

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

$$r^{CTR,j} = k_f^j \prod_{i,educts} (a^i)^{|\nu^{ij}|} \exp\left(-\frac{(1-\alpha)nF\Delta\phi}{RT}\right) - k_r^j \prod_{i,products} (a^i)^{|\nu^{ij}|} \exp\left(\frac{\alpha nF\Delta\phi}{RT}\right)$$

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

Elementary Kinetic Modeling



- Elementary kinetic modeling of co-electrolysis and RWGS on nickel:

$H_2(g) + 2(Ni) \rightleftarrows 2H(Ni)$
$O_2(g) + 2(Ni) \rightleftarrows 2O(Ni)$
$H_2O(g) + (Ni) \rightleftarrows H_2O(Ni)$
$CO_2(g) + (Ni) \rightleftarrows CO_2\,(Ni)$
$CO(g) + (Ni) \rightleftarrows CO(Ni)$

$CO_2\,(Ni) + (Ni) \rightleftarrows CO(Ni) + O(Ni)$
$OH(Ni) + (Ni) \rightleftarrows H(Ni) + O(Ni)$
$2OH(Ni) + (Ni) \rightleftarrows H_2O(Ni) + O(Ni)$
$H(Ni) + OH(Ni) \rightleftarrows H_2O(Ni) + (Ni)$

[1]

$O(Ni) + 2e^{-} \rightleftarrows (Ni) + O^{2-}(CGO)$

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

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

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

$$r^{CTR,j} = k_f{}^j \prod_{i,educts} (\theta^i)^{|\nu^{ij}|} \exp\left(-\frac{(1-\alpha)n\mathrm{F}\Delta\phi}{\mathrm{R}T}\right) - k_r{}^j \prod_{i,products} (\theta^i)^{|\nu^{ij}|} \exp\left(\frac{\alpha n\mathrm{F}\Delta\phi}{\mathrm{R}T}\right)$$

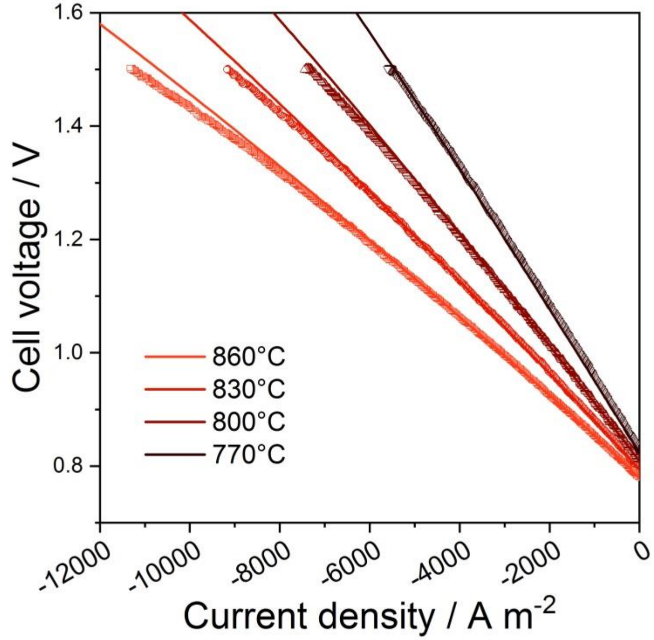
→ From elementary kinetic considerations the charge transfer step is the same, disregarding the fuel (H_2O or CO_2)

DLR

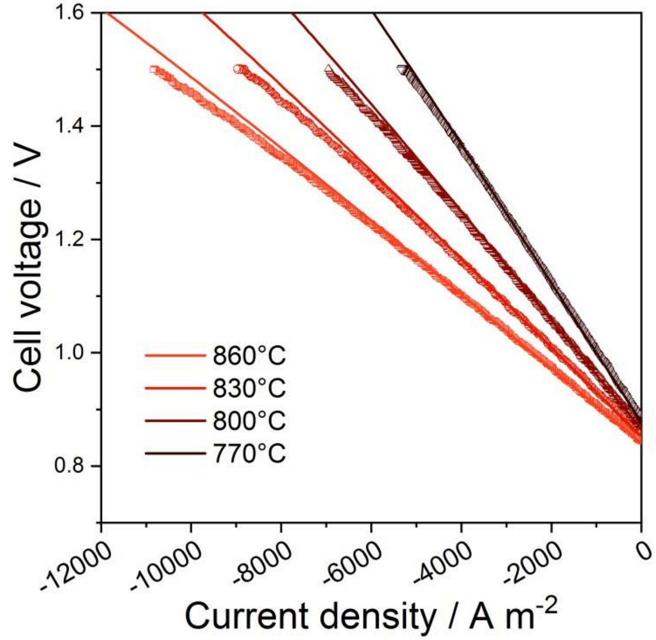
[1]: Janardhanan & Deutschmann, JPS 62 (2006) 1192-1202.

Model Validation

- Gas composition:
  5% H_2, 63.7% H_2O, 31.3% CO_2
- H_2O/CO_2 ratio: 2.04



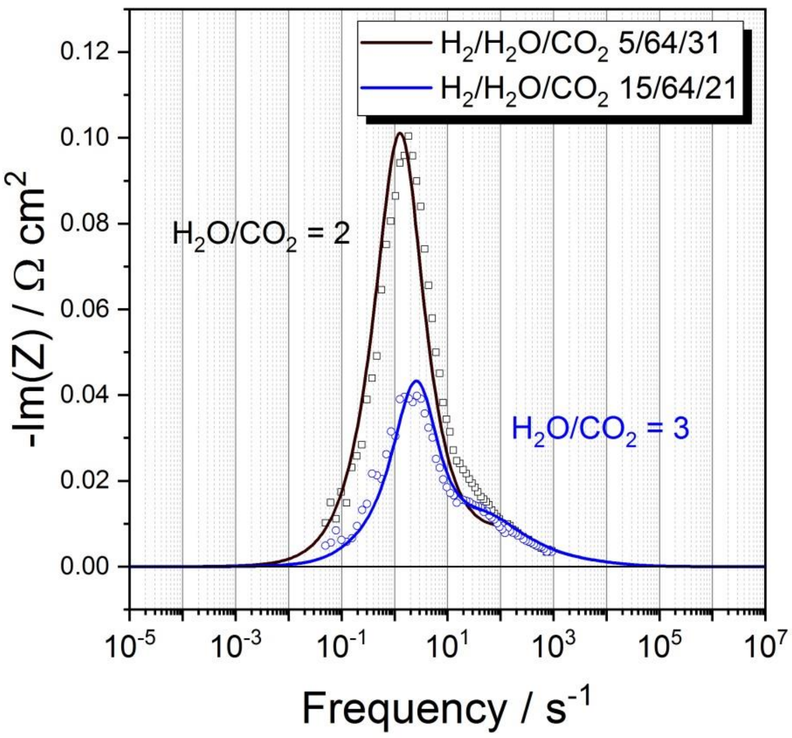
- Gas composition:
  15.1% H_2, 63.7% H_2O, 21.2% CO_2
- H_2O/CO_2 ratio: 3.00



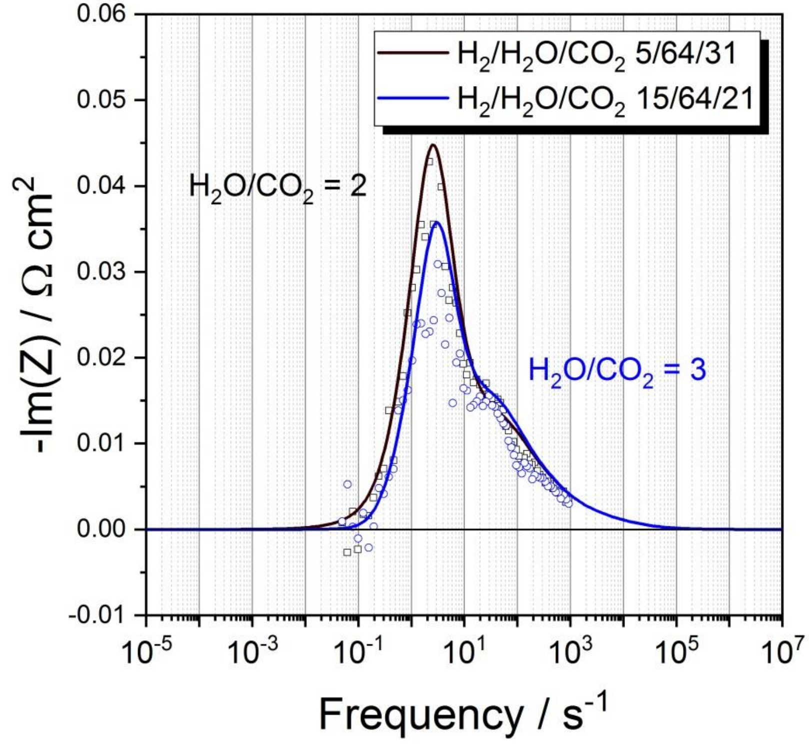
→ OCV decreases with higher CO_2 content of the gas
→ Efficiency decreases with decreasing temperature

Model Validation

<u>OCV:</u>



<u>0.6 A/cm²:</u>

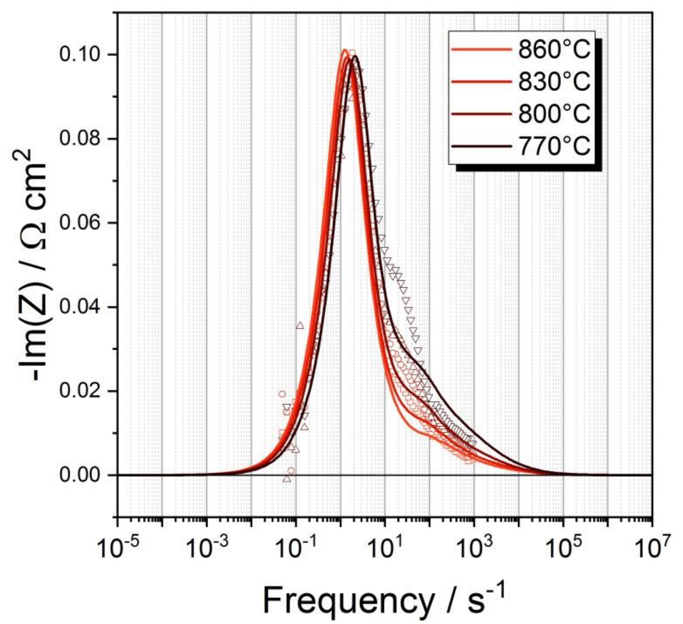


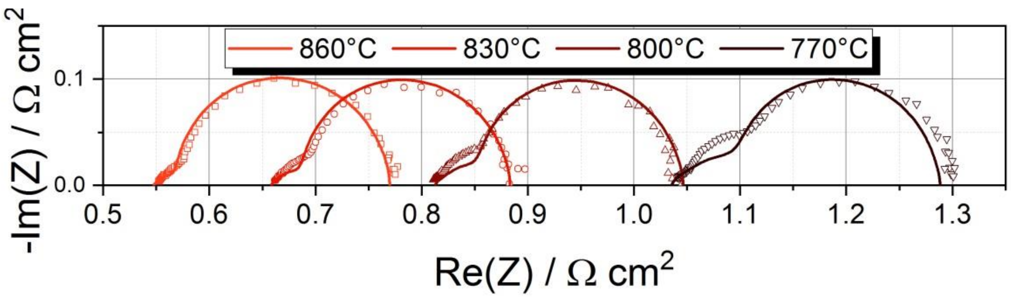
→ H_2O (and H_2) improves the efficiency at OCV and under load

Model Validation

- Gas composition: 5% H_2, 63.7% H_2O, 31.3% CO_2 → H_2O/CO_2 = 2.04

<u>OCV:</u>





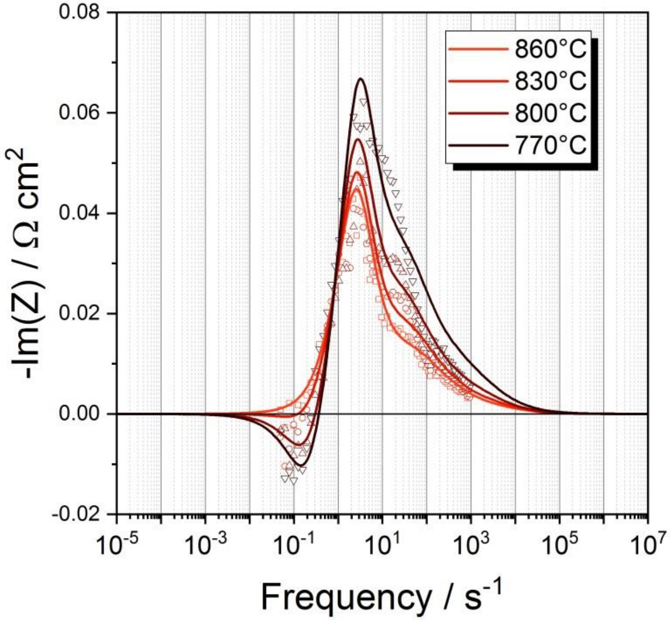
- Peak at ~ 1Hz is temperature independent
- Peak at 10-100 Hz increases with decreasing temperature

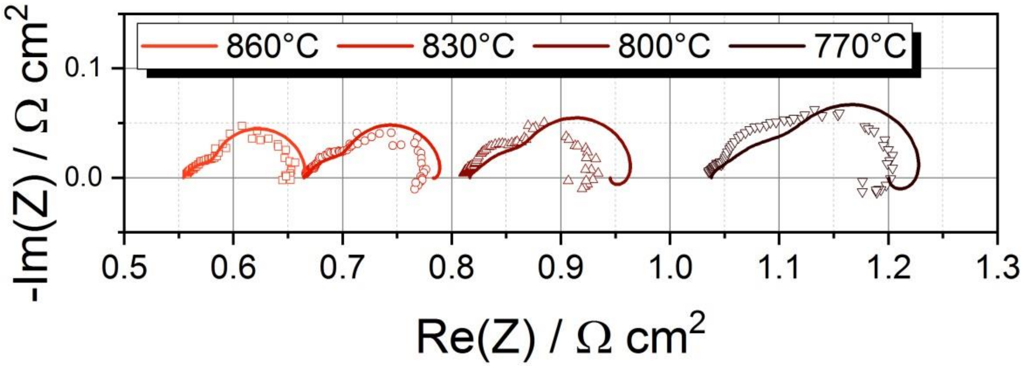
→ At ~ 1Hz: Mass transport losses
→ 10-100 Hz: Kinetic losses due to charge transfer reaction

Model Validation

- Gas composition: 5% H_2, 63.7% H_2O, 31.3% CO_2 → H_2O/CO_2 = 2.04

<u>0.6 A/cm² (0.5 A/cm² for 770°C):</u>



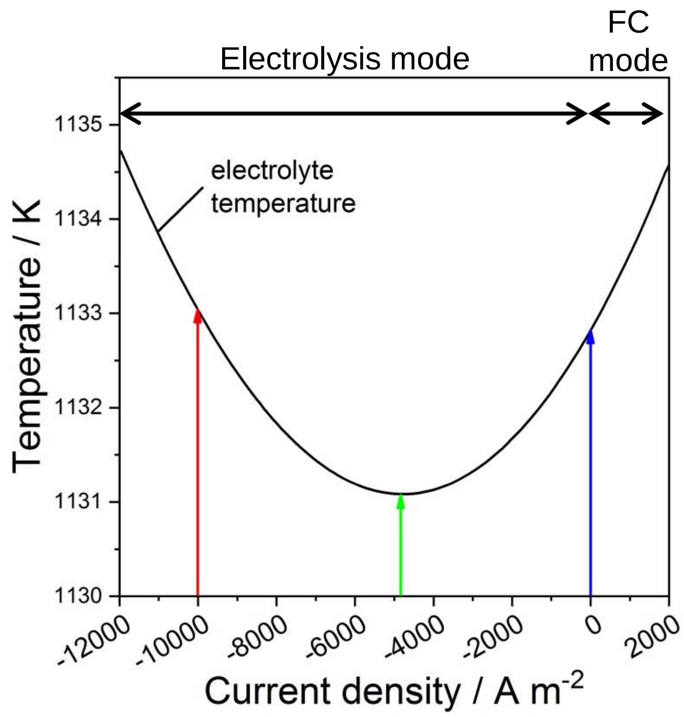


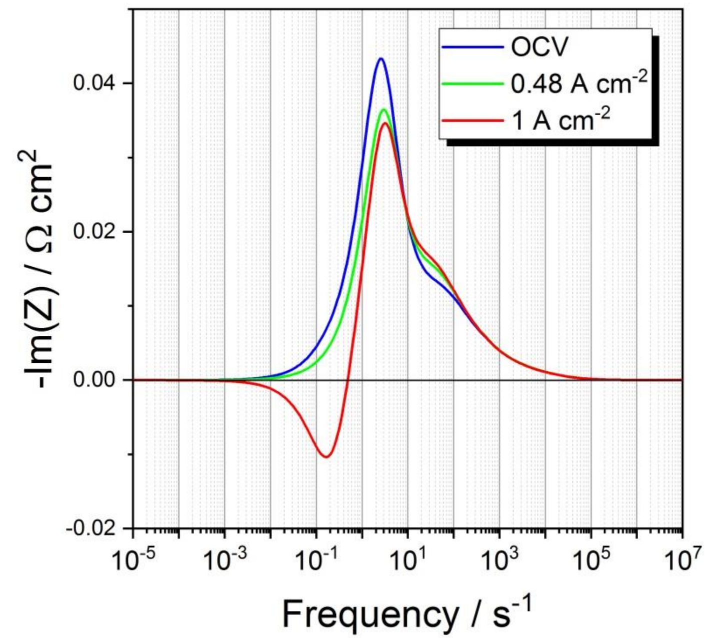
- Inductive peak becomes visible at ~ 0.1 Hz
- Inductive peak increases with decreasing temperature

→ Where does induction come from?

Impedance Analysis

- Simulation of impedance spectra at OCV, 0.48 and 1 A/cm², $H_2O/CO_2 = 3.00$:

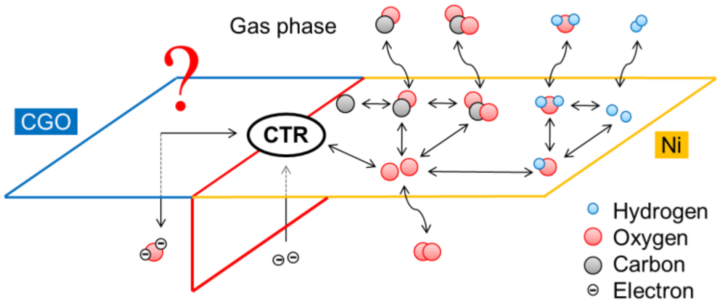




- Electrolyte ion conductivity increases with temperature

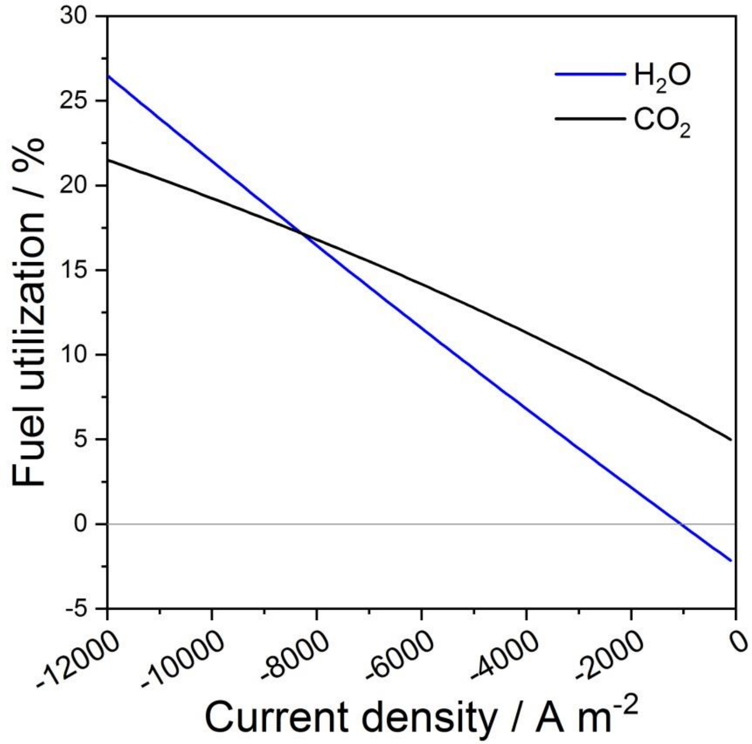
→ Inductance at a given current density depends on $\frac{\partial T}{\partial i}$, i.e. $\frac{\partial \sigma}{\partial i}$

Model Predictions



- Fuel utilization of H_2O and CO_2: $FU^i = \frac{\dot{m}^i_{in} - \dot{m}^i_{out}}{\dot{m}^i_{in}} \times 100\%$

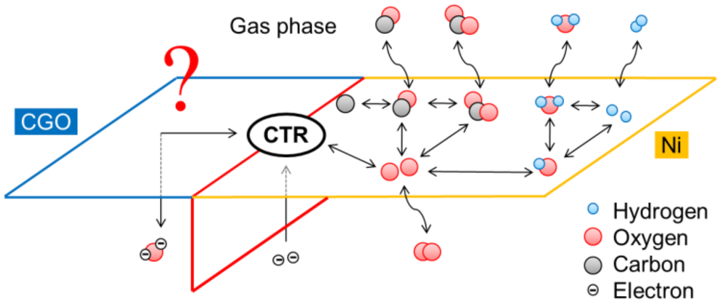
RWGS:
$CO_2 + H_2 \rightarrow CO + H_2O$



→ At low current density the H_2O utilization becomes negative due to RWGS

DLR

Model Predictions



- Ratio between H_2O- and CO_2-electrolysis from balance for O(Ni):

RWGS:
$CO_2 + H_2 \rightarrow CO + H_2O$

H_2O: OH(Ni) + (Ni) ⇄ H(Ni) + O(Ni)
CO_2: CO_2 (Ni) + (Ni) ⇄ CO(Ni) + O(Ni)
CTR: O(Ni) + 2e$^-$ ⇄ (Ni) + O^{2-}(CGO)

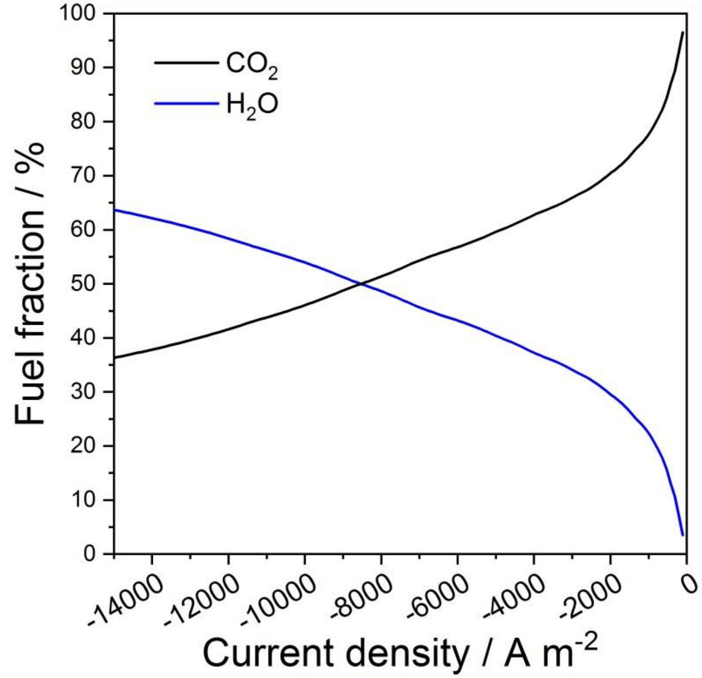
If $r^{\mathrm{H_2O}} < 0 \rightarrow$ RWGS:

$$X^{\mathrm{CO_2}} = \frac{1}{V_{CL}} \int_{\Omega_{CL}} \frac{r^{\mathrm{CO_2}} + r^{\mathrm{H_2O}}}{r^{CTR}} dV$$

If $r^{\mathrm{H_2O}} > 0 \rightarrow$ WGS:

$$X^{\mathrm{CO_2}} = \frac{1}{V_{CL}} \int_{\Omega_{CL}} \frac{r^{\mathrm{CO_2}}}{r^{CTR}} dV$$

$$X^{\mathrm{H_2O}} = 1 - X^{\mathrm{CO_2}}$$



→ CO_2-electrolysis at low current, H_2O-electrolysis at high current

DLR

Summary

I. A detailed 2D non-isothermal transient SOEC model including thermodynamically consistent elementary kinetics has been developed and validated under various operating conditions

II. Experimentally observed inductive phenomena are explained from physical theory: They are caused by an increase of ionic conductivity with current/temperature

III. In co-electrolysis, mainly CO_2 is converted at low current and H_2O is converted at high current

Thank you for your attention

georg.futter@dlr.de

KOPERNIKUS
P2X PROJEKTE
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.

DLR