Karlsruher Institut für Technologie

European Institute for Energy Research by EDF and KIT

University of Twente The Netherlands

Optimizing the performance of solid oxide electrolysis cells (SOECs) and stacks for Power-to-Gas applications

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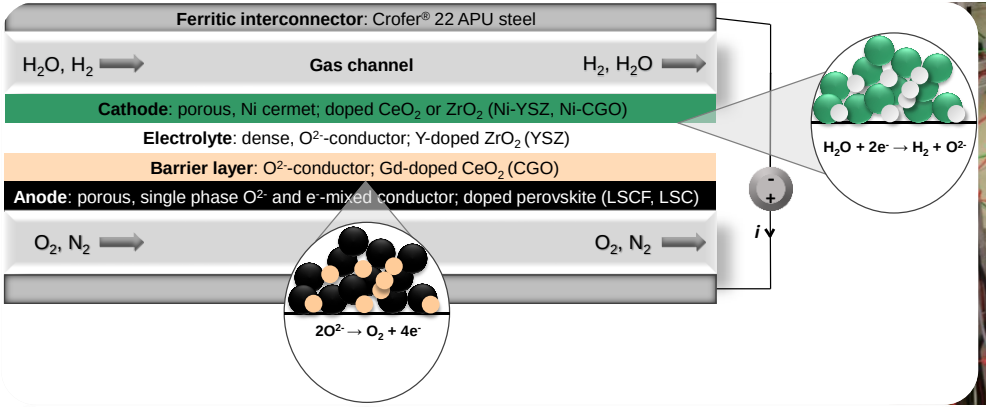
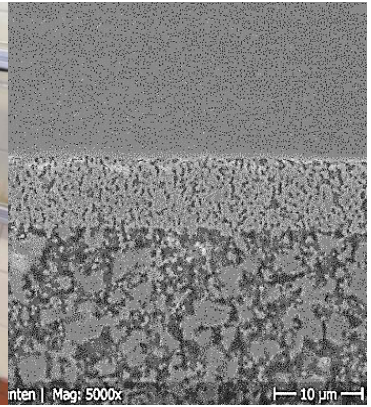




Motivation and Background:
Thermal integration of HT-electrolysis with catalytic methanation

Low-temperature electrolysis (PEM, alkaline):
$H_2O(l) \rightarrow H_2 + 0.5\ O_2$, $\Delta H° = 286$ kJ mol^{-1} (1.48 V)

High-temperature electrolysis (SOEC):
$H_2O(g) \rightarrow H_2 + 0.5\ O_2$, $\Delta H° = 242$ kJ mol^{-1} (1.29 V)

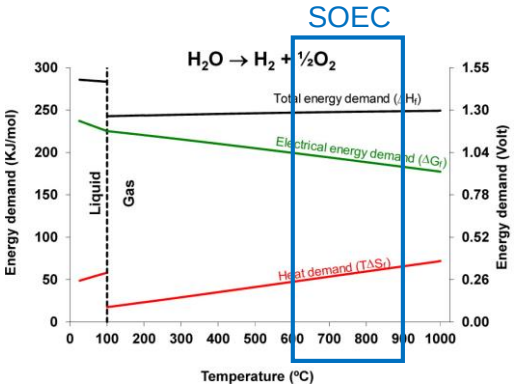


Figure: *Adapted from [1].*

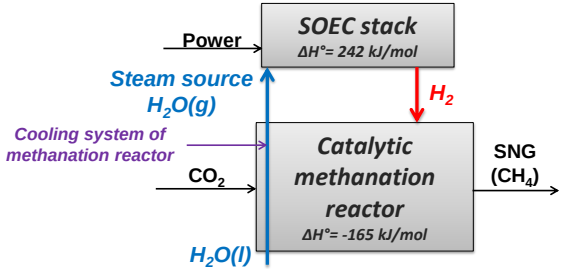


Table: *Advantages and R&D demands of high-temperature (HT) solid oxide electrolysis cells (SOECs) for Power-to-Methane (PtM) applications.*

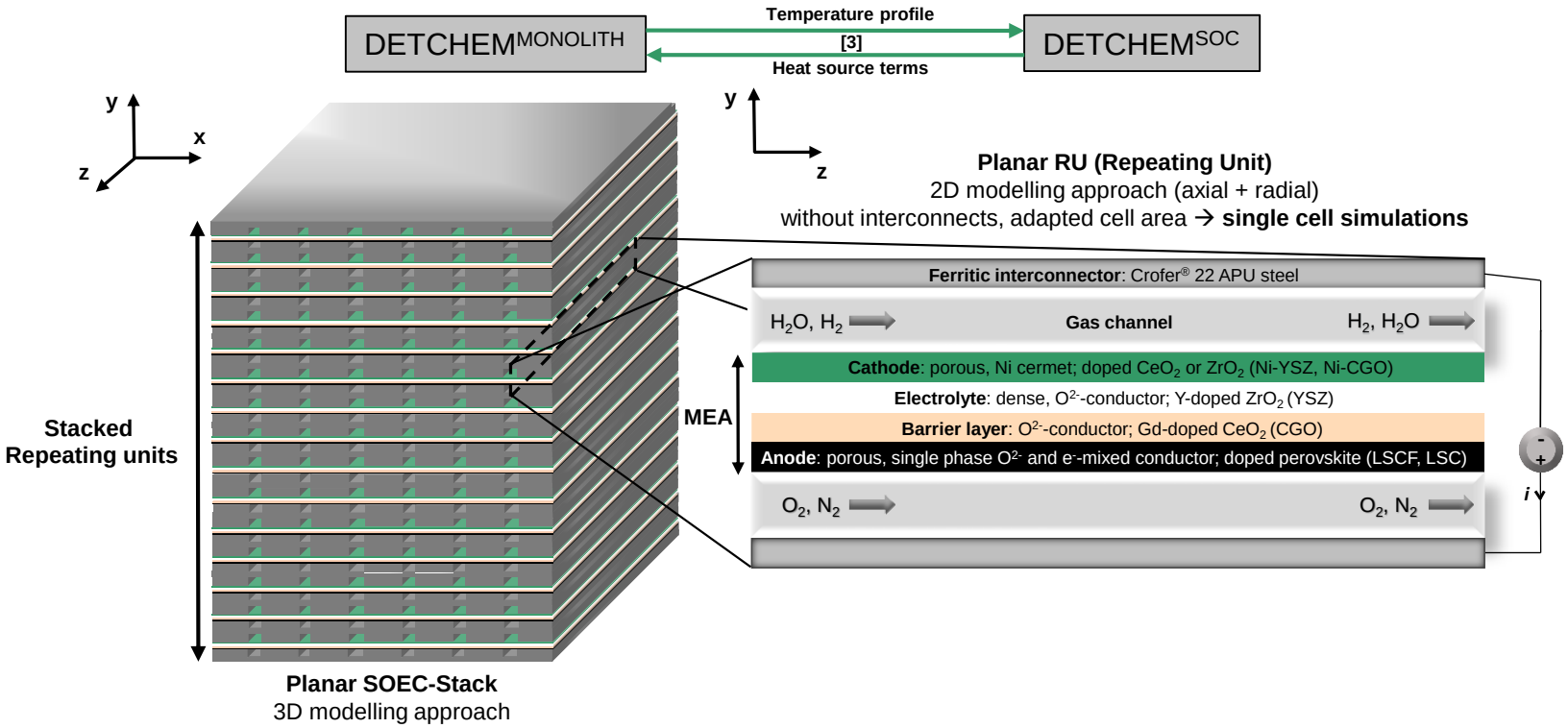
Net system efficiencies **in the range of ~80%** (HHV) experimentally demonstrated [2]

Advantages	R&D requirements
Thermodynamic: High efficiency	Scale-Up
Kinetic: Thermal barriers	Optimization of process parameters
Thermal integration possible	Selection of optimal cell design
Promising perspectives regarding investment costs	Degradation
	Dynamics

concerned in this work

[1] S. Ebbesen, S. H. Jensen, A. Hauch, M. B. Mogensen, *Chem. Rev.* **2014**, *114*, 10697-10734.

Methodology:
Multi-scale modeling framework



[3] A. Banerjee, Y. Wang, J. Diercks, O. Deutschmann, *Appl. Energy* **2018**, *230*, 996-1013.

Methodology:
From single cell to system level

Testing of commerical SOEC cells

- electrode + electrolyte supported configurations

SOEC cell model adaption

- calibration & validation procedure
- Performance analysis
- Optimize operation conditions

Scale-up to stack level

- Optimize operation conditions
- Correlate performance with single cell level

Scale-up to integrated PtM system model

- integrate developed SOEC stack model
- use Matlab® Simulink
- assess and compare different process chains for CNG/LNG production

this presentation

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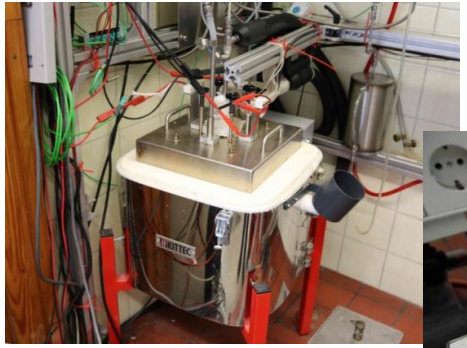
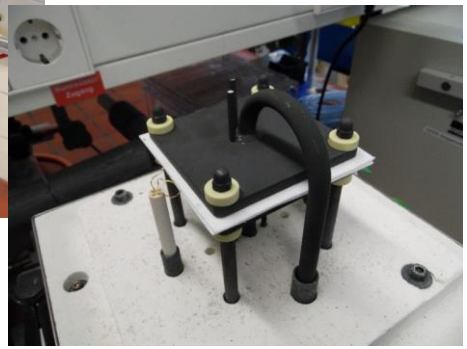
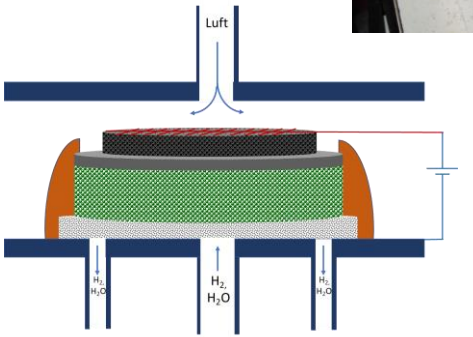
Electrochemical characterization of single cells:
Test facility at the ENERMAT laboratory







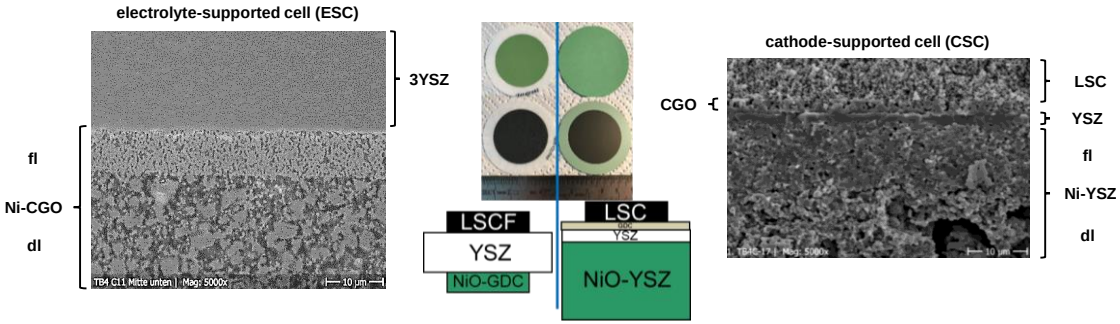
- Test bench from Fiaxell
- Sealed cell housing
  - Avoid thermal reaction between H_2 and air
  - Removal of product gas
- Coupling of test bench to analysis systems
  - product gas flow via MFCs
  - Polarization curves (iV) and Electrochemical Impedance Spectroscopy (EIS)

Model parametrization:
Microstructural analysis

Table: *Model input parameters for isothermal single cell simulations. Units of partial pressures are given in atm. fl: functional layer, dl: diffusion layer.*

Parameter	Value		Reference
Cell parameters	ESC	CSC	
Active cell area	10.18 cm^2		Measurement
Cell length	1.8 cm		Measurement
Channel height	1.0 mm		Measurement
Channel width	5.65 mm		Calculated
Cathode thickness (fl/dl)	7.2 / 25.0 µm	12.6 / 373.0 µm	SEM
Anode thickness	47.5 µm	14.5 µm	SEM
Electrolyte/Barrier layer thickness	81.0 / 7.0 µm	4.0 / 2.6 µm	SEM
Microstructural parameters			
Cathode porosity (fl/dl)	0.2 / 0.3	0.22 / 0.36	SEM
Anode porosity	0.2	0.29	SEM
Cathode particle diameter (fl/dl)	0.44 µm	0.91 / 0.88 µm	SEM
Anode particle diameter	0.4 µm	0.65 µm	SEM
Ni volume fraction in cathode	0.5	0.35	EDX
Material properties			
Ni			
Ni electronic conductivity	$3.27\times10^{4}-10653\times T$ S cm^{-1}		[4]
YSZ			
8YSZ ionic conductivity	$334\times e^{-10300/T}$ S cm^{-1}		[5]
3YSZ ionic conductivity	$37.8\times e^{-8442/T}$ S cm^{-1}		[6]
CGO			
Ionic conductivity	$(1.09\times10^{5}/T)\times e^{-7426.9/T}\times(1+\delta/0.05)$ S cm^{-1}		[7, 8]
Electronic conductivity	$(3.46\times10^{9}/T)\times e^{-28779/T}\times p_{O_2}^{-0.25}$ S cm^{-1}		[7]
Extra oxygen vacancies	$1.3\times10^{4}\times e^{-25530/T}\times p_{O_2}^{-0.25}$		[7]
LSC			
Electronic conductivity	$4860.1-2.986\times T$ S cm^{-1}		[9]
Ionic conductivity	$1.31\times10^{4}\times e^{-93728.8/RT}$ S cm^{-1}		[10]
LSCF			
Electronic conductivity	$983.25-0.627\times T$ S cm^{-1}, T > 923.15 K		[11]
Ionic conductivity	$7.35\times10^{4}\times e^{-14962/T}$ S cm^{-1}		[12]

extracted from SEM, EDX



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Model calibration and validation:
Extract electrokinetics of half-cell reactions

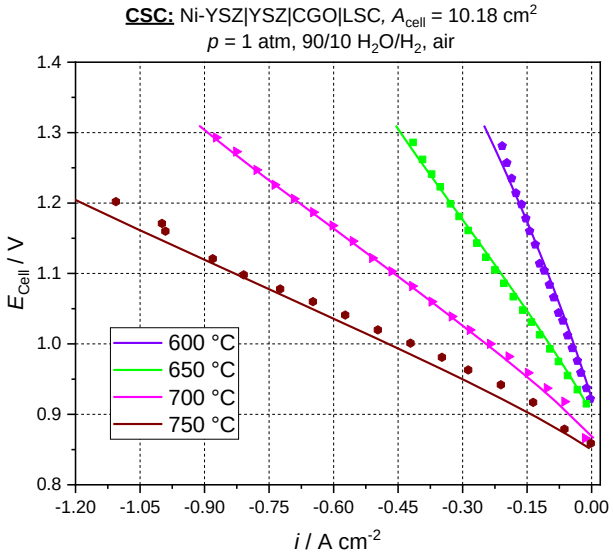
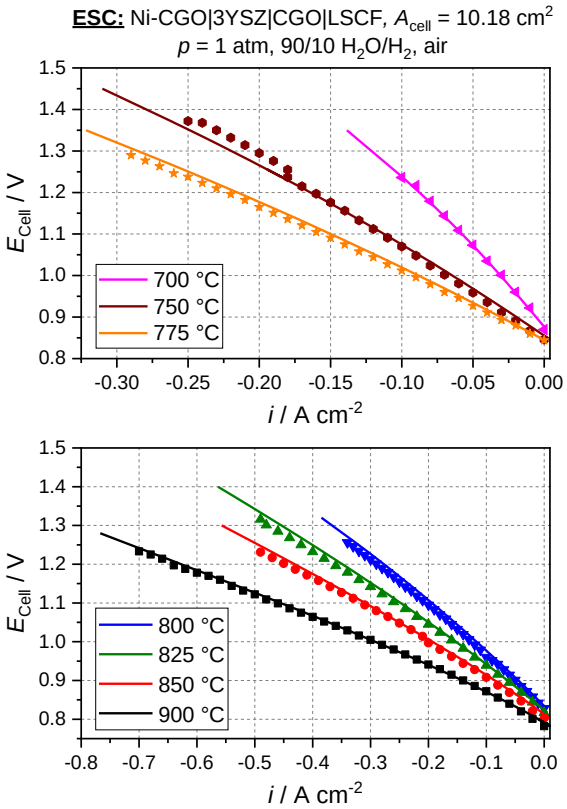


Figure: *Comparison of simulated (continuous) and measured (dotted) polarization curves of a cathode-supported cell (CSC) at p = 1 atm, T = 600-750 °C, 90/10 H_2O/H_2, air.*



- Model able to reach a near-quantitative accordance with experimental iV-data for both cell types
- Activation energies and pressure exponents (preferably from high-pressure data) for all materials used from literature

Model calibration and validation:
Extract electrokinetics of half-cell reactions

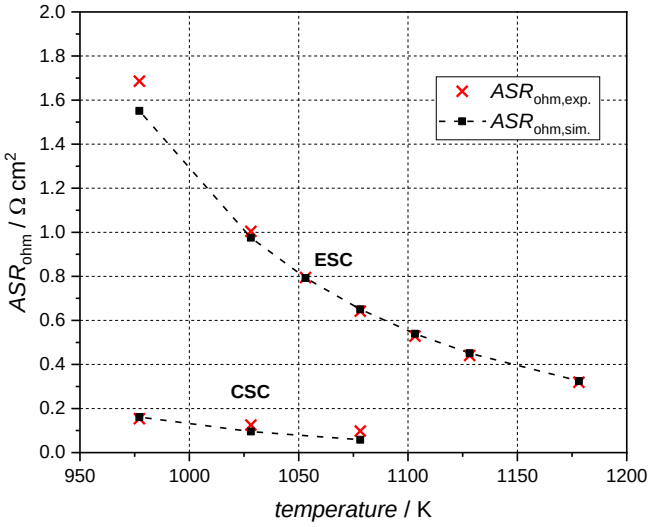


Figure: *Comparison of simulated and measured ohmic resistances of the ESC and CSC single cells. Experimental ASR values were extracted from EIS measurements (HF intercepts) at OCV at different temperatures. Aside from the ohmic resistance of the electrolyte itself, simulated ASR values also contain the ohmic resistance contributions due to charge transport across the electrodes.*

Table: *Butler-Volmer fit parameters acquired from the single cell calibration procedure. Units of partial pressures are given in atm.*

Parameter	Value	
Cell type	***ESC***	***CSC***
Cathode material	Ni-CGO	Ni-YSZ
Exchange current density / (A cm^{-1} or A cm^{-2})	$5.9\times10^{3}\times e^{-111900/RT}\times p_{H2}^{0.01}\times p_{H2O}^{0.08}$	$0.048\times e^{-105000/RT}\times p_{H2}^{-0.1}\times p_{H2O}^{0.33}$
Anodic CT-coefficient	1.5	1.18
Cathodic CT-coefficient	0.5	0.82
Anode material	LSCF	LSC
Exchange current density / A cm^{-2}	$1.8\times10^{3}\times e^{-138000/RT}\times p_{O2}^{0.11}$	$6.0\times10^{4}\times e^{-150000/RT}\times p_{O2}^{0.22}$
Anodic CT-coefficient	0.5	1.3
Cathodic CT-coefficient	0.5	0.7

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Model calibration and validation:
Pressurized operation

Use literature data:

Pressure influence on physico-chemical processes:

- **Reversible voltage:**

$$E_{\mathrm{rev}} = \frac{\Delta G_{\mathrm{r}}^{0}}{2F} + \frac{RT}{2F}\ln\left(\frac{p_{\mathrm{H_2,fe}} p_{\mathrm{O_2,ae}}{}^{0.5}}{p_{\mathrm{H_2O,fe}}}\right)$$

- **Porous medium gas transport:**

$$J_k = -\left[\sum_{l=1}^{K_{\mathrm{g}}} D_{kl}^{\mathrm{DGM}} \frac{\partial [X_l]}{\partial y} + \left(\sum_{l=1}^{K_{\mathrm{g}}} \frac{D_{kl}^{\mathrm{DGM}}[X_l]}{D_{l,\mathrm{Kn}}^{\mathrm{eff}}}\right) \frac{B_{\mathrm{g}}}{\mu_{\mathrm{g}}} \frac{\partial p}{\partial y}\right]$$

- **Electrochemical kinetics:**

$$i_{0,\mathrm{H_2/H_2O}} = A_{\mathrm{H_2/H_2O}} exp\left(-\frac{E_{\mathrm{H_2/H_2O}}}{RT}\right) f\left(p_{\mathrm{H_2}}, p_{\mathrm{H_2O}}\right)$$

$$i_{0,\mathrm{O_2}} = A_{\mathrm{O_2}} exp\left(-\frac{E_{\mathrm{O_2}}}{RT}\right) f\left(p_{\mathrm{O_2}}\right)$$

- **Electrical conductivities:**

$\sigma_{\mathrm{el/io}}$ due to stoichiometry changes, oxidation states...

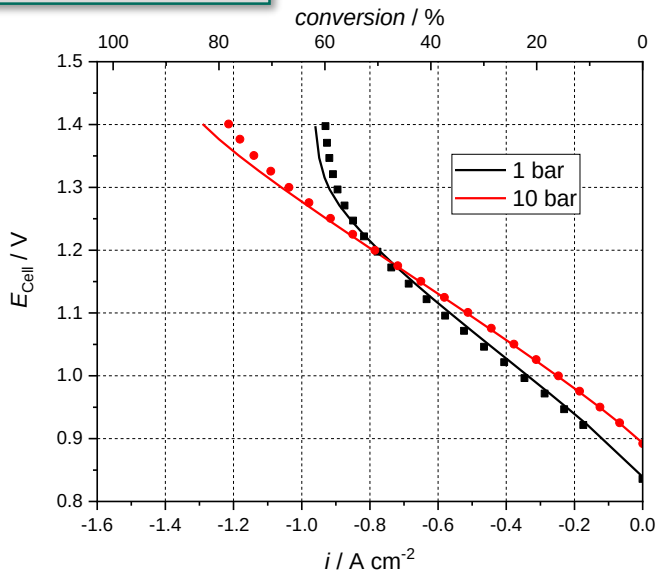


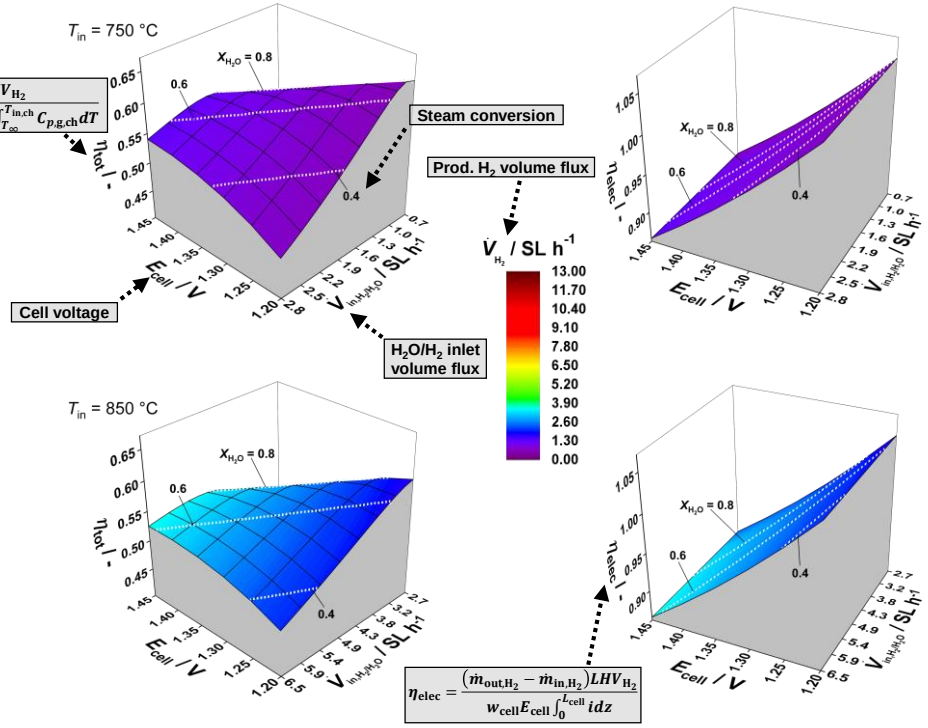
Figure: *Comparison of simulated (continuous) polarization curves with experimental data (dotted) of an cathode-supported Ni-YSZ|YSZ|CGO|LSCF|LSC single cell from Bernadet et al. [13]. A_{cell} = 3.14 cm^2, T = 800 °C, 35/58.5/6.5 $N_2/H_2O/H_2$, air.*

[13] L. Bernadet, G. Gousseau, A. Chatroux, J. Laurencin, F. Mauvy, M. Reytier, *Int. J. Hydrogen Energy* **2015**, 40, 12918-12928.

Optimization of operating conditions of SOEC single cells:
Parametric analysis

ESC: Ni-CGO | 3YSZ | CGO | LSCF, A_{cell} = 10.18 cm^2
p = 1 atm, 90/10 H_2O/H_2, air

$$\eta_{tot} = \frac{(\dot{m}_{out,H_2} - \dot{m}_{in,H_2})LHV_{H_2}}{w_{cell}E_{cell}\int_0^{L_{cell}} i dz + \sum_{ch}\dot{m}_{in,ch}\int_{T_\infty}^{T_{in,ch}} C_{p,g,ch}dT}$$



$$\eta_{elec} = \frac{(\dot{m}_{out,H_2} - \dot{m}_{in,H_2})LHV_{H_2}}{w_{cell}E_{cell}\int_0^{L_{cell}} i dz}$$

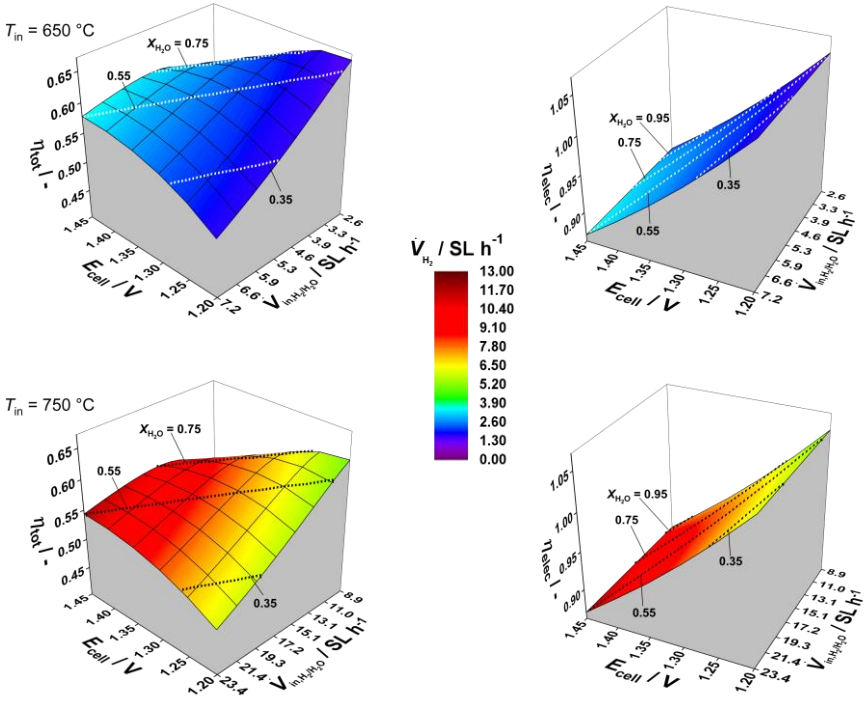
Table: *Confrontation of single cell efficiency definitions.*

η_{tot} (LHV, DC)	η_{elec} (LHV, DC)
With respect to total heat+electrical energy input	With respect to electrical input
System scale (coupling with catalytic methanation, BoP):	
Theoretical minimum; zero thermal integration or recuperation	Theoretical maximum; zero steam generation or electrical heating required

- **Oppositional trends** between η_{elec} and $\dot{V}_{H_2}$
- Surpassing conv. of ~80% leads to performance losses due to **reactant starvation zones**

Optimization of operating conditions of SOEC single cells:
Parametric analysis

CSC: Ni-YSZ│3YSZ│CGO│LSC, A_{cell} = 10.18 cm^2
p = 1 atm, 90/10 H_2O/H_2, air



- Efficiency losses at conv. >75% (compared to >80%, KeraCell III)
- Electrode-supported cell design achieves significantly higher performance, e.g.:

Table: *Comparison of single cell performances.*

Operation conditions	Electrode-supported cell		Electrolyte-supported cell	
	$\dot{V}_{H_2}$	η_{tot}	$\dot{V}_{H_2}$	η_{tot}
@750 °C, 1 atm, 1.3 V, 80% conv.,*	**6.5 SL h^{-1}**	60.4%	**0.8 SL h^{-1}**	60.4%

*inlet: 90/10 H_2O/H_2, air

→Pre-Identification of suitable operation windows for stack simulations.

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Scale-up from cell to planar stack level:
Simulation parameters

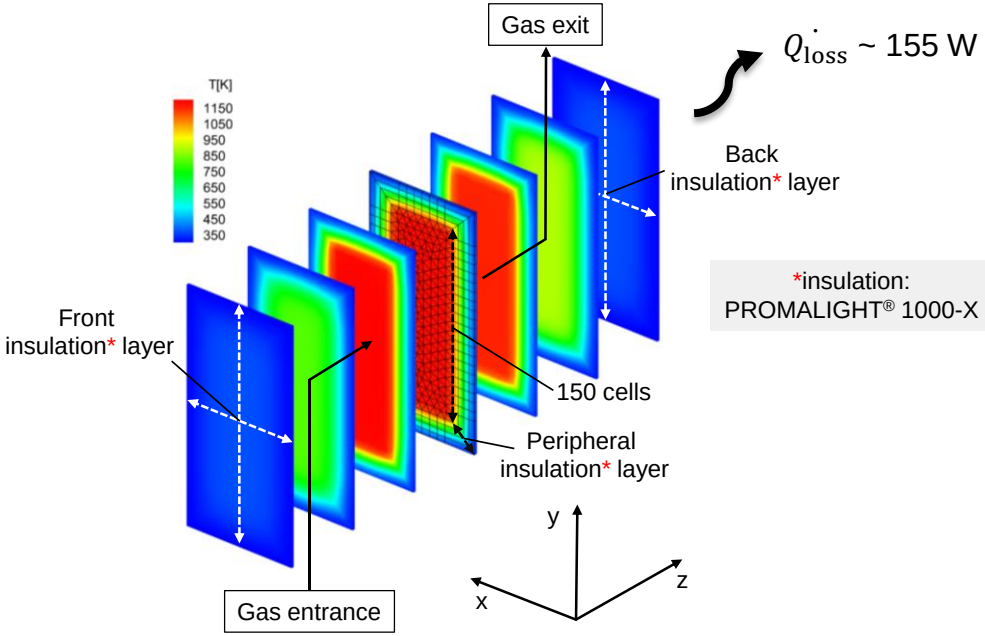
Table: Model input parameters for stack simulations.

Parameter	Value	Reference
Stack parameters		
Active cell area	127.8 cm^2	[14]
Active cell length	9 cm	[14]
Active cell width	14.2 cm	[14]
Channels per layer	24	[14]
Channel height	1.0 mm	[14]
Channel width	4.4 mm	Calculated [14]
Interconnect thickness	0.5 mm	[14]
Cells per Stack	150	Simulation
Insulation layer thickness	5 cm	Simulation
Cell / Microstructural / Kinetic parameters	...	
Operating conditions		
Temperature	1073.15-1173.15 K	Simulation
Pressure	1-20 bar	Simulation
Inlet gas composition	90-95% H_2O, air	Simulation
Conversion	75-85%	Simulation

single cell simulations

from procedure before

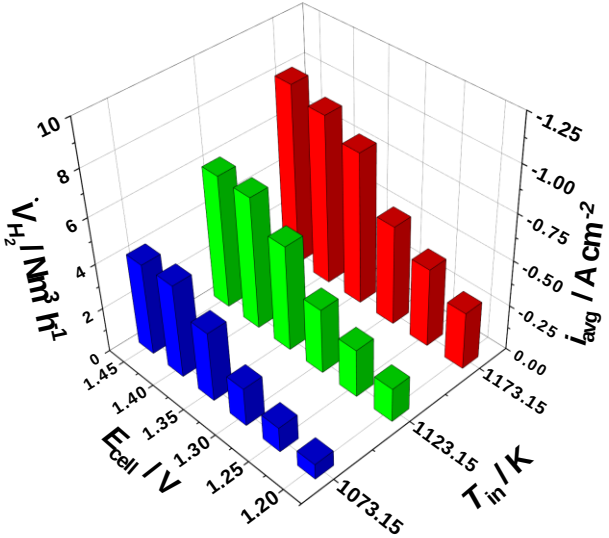
ESC: Ni-CGO | 3YSZ | CGO | LSCF, 150-cell stack
T_{in} = 850 °C, E_{cell} = 1.4 V, p = 1 atm, 90/10 H_2O/H_2, air

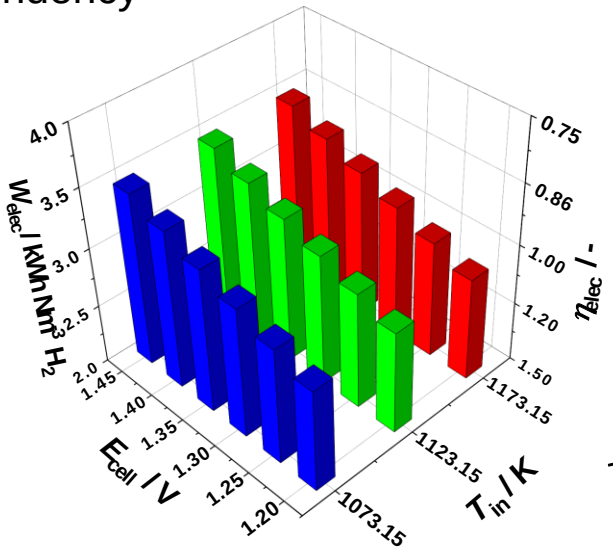


[14] L. van Biert, M. Godjevac, K. Visser, P. V. Aravind, *Appl. Energy* **2019**, 250, 976-990.

Optimization of SOEC stack performance:
Temperature and voltage dependency

ESC: Ni-CGO│3YSZ│CGO│LSCF, 150-cell stack
p = 1 atm, 90/10 H_2O/H_2, air, 80% conv.

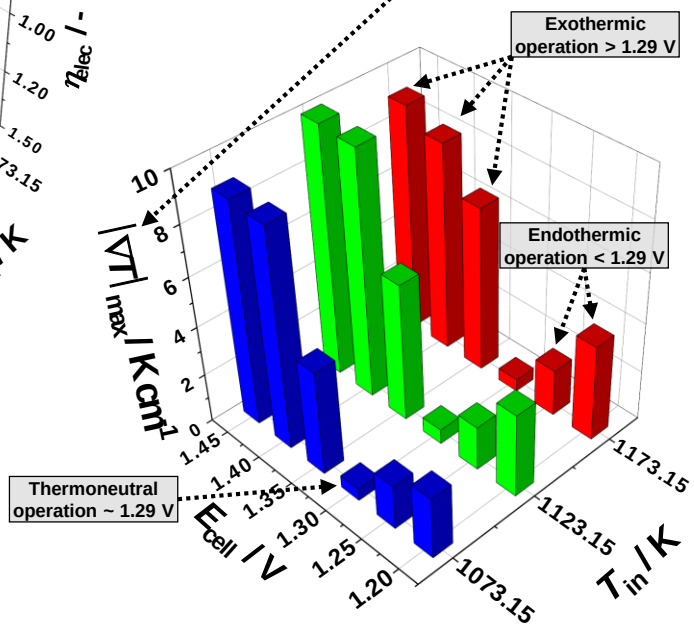




All simulations are performed considering

Lower/upper bounds:

- $0.4 \leq \frac{\dot{V}_{air}}{\dot{V}_{H_2+H_2O}} \leq 8$
- $0 \leq |\nabla T|_{max} \leq 10$ K cm^{-1}



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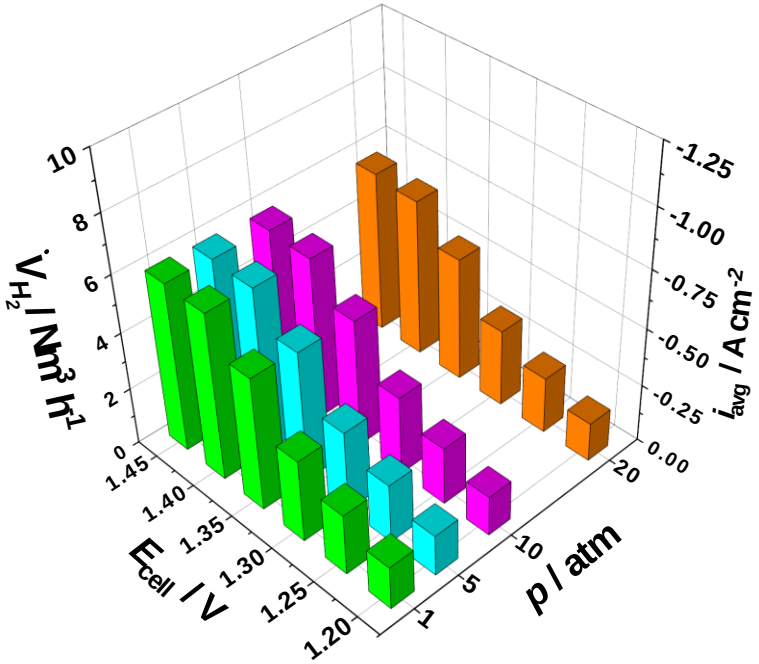
Optimization of SOEC stack performance:
Pressure dependency

ESC: Ni-CGO│3YSZ│CGO│LSCF, 150-cell stack
T = 850 °C, 90/10 H_2O/H_2, air, 80% conv.



- For the electrolyte-supported cell design, pressurized operation leads to a performance decrease
- Still, the **pressure influence** is relatively **low**

Optimal steady-state operation conditions for ESC-based SOEC-stack:

- T_{stack} ~ 850 °C
- E_{cell} = 1.3-1.35 V (reaching η_{elec} > 90%, moderate temperature gradients, system scale: heat generation for recuperation)
- conv. ~ 75-85 %
- p not too high
- X_{in,H_2O}~ 90-95%

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Summary

- Multi-scale modeling framework applied for SOEC cells and stacks performing steam electrolysis for PtM-application
- Electrochemical/microstructural characterization of two different cell designs
- Scale-up to the **150-cell stack-level**, application-oriented simulations
- Performance discrepancy between cell and stack level revealed
- **Optimized operation conditions** on stack-scale identified

Next steps

- Comparison with CSC-based stack-level results
- Scale-up to the integrated system level (Matlab® Simulink)
  - ***How do the optimal operation conditions on integrated system scale differ from the one of the SOEC-stack itself (as identified)?***
  - ***How large is the influence of the electrode design on net system performance?***

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[14] L. van Biert, M. Godjevac, K. Visser, P. V. Aravind, *Appl. Energy* **2019**, *250*, 976-990.

Acknowledgements

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Thank you for your attention!