

Vertieferarbeit

# Model-based performance analysis of a solid oxide co-electrolyzer to produce syngas for industrial applications

Vorgelegt von:

Justus Sebastian Diercks

aus

Köln

Betreuer: M.S. Aayan Banerjee

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# Abstract

In this thesis, a performance analysis and efficiency optimization is carried out for a planar solid-oxide electrolysis cell (SOEC) and applied to a SOEC stack to produce synthesis gas (H<sub>2</sub>/CO) via the co-electrolysis of H<sub>2</sub>O and CO<sub>2</sub>. This process promises to be an efficient chemical energy storage solution while consuming CO<sub>2</sub> and producing an industrially important reactant. As syngas is required in certain specific H<sub>2</sub>/CO-ratios in industrial processes, the production of two such ratios is examined. These are 2:1 for Fischer-Tropsch synthesis and 1.05:1 for hydroformylation.

The analysis and optimization is carried out using a quasi-two-dimensional coflow planar model of solid-oxide cells. The model utilizes mass transport, heterogenous chemistry, electro-chemistry and transport through porous media to describe the cell processes. The used cell and operational parameters are acquired from an extensively used SOEC stack. A base case of the varied parameters is established, upon which the influence of single parameters and efficiency optimization is examined.

The influence of cell length, voltage, temperature, velocity and H<sub>2</sub>-Content of the fuel on conversion, efficiency and the CO<sub>2</sub>-content in the fuel required to obtain a certain syngas ratio is discussed. After, the parameters voltage and H<sub>2</sub>-content in the fuel are fixed to certain values, and an efficiency optimization of the parameters velocity, cell length and temperature is carried out. The resulting efficiencies and syngas yields of the optimization are plotted and possible points of operation are discussed.

A point of operation is chosen and a stack simulation is executed considering heat loss as well as using adiabatic conditions. The temperature distributions of both resulting stacks are discussed and the approach of optimizing the efficiency of a stack to produce a certain syngas ratio using isothermal simulations of single pcells is validated.

Additionally, the influence of the MEA composition as well as the flow rate on heat transport in a single planar cell are examined using adiabatic simulations.

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# Statutory declaration

I declare that I have authored this thesis on the topic

Model-based performance analysis of a solid oxide co-electrolyzer to produce syngas for industrial applications

independently, that I have not used other than the declared sources / resources and that I have explicitly marked all materials which have been quoted either literally or by content from the used sources.

Place and Date

Justus Diercks

# Nomenclature

$A_i$	pre-exponential factor
$A_c$	cross-sectional area of flow channel (m <sup>2</sup> )
$A_s$	specific area (m <sup>-1</sup> )
$B_{q}$	permeability (m <sup>2</sup> )
$C_p$	specific heat capacity (J kg <sup>-1</sup> K <sup>-1</sup> )
$d_p$	particle diameter (m)
$d_{pore}$	pore diameter (m)
D	diffusion coefficient (m <sup>2</sup> s <sup>-1</sup> )
$D_h$	hydraulic diameter (m)
$D_{kl}^{e}$	effective binary diffusion (m <sup>2</sup> s <sup>-1</sup> )
$D_{k Kn}^{e}$	effective Knudsen diffusion (m <sup>2</sup> s <sup>-1</sup> )
$D_{kl}^{DGM}$	DGM diffusion coefficient (m <sup>2</sup> s <sup>-1</sup> )
$\tilde{E}^{0}$	electromotive force at standard pressure (V)
Ecell	cell voltage (V)
$E_{ai}$	activation energy (J mol <sup>-1</sup> )
Eren	reversible cell potential (V)
$E_{th}$	thermoneutral voltage (V)
F	Faraday constant (A s mol <sup>-1</sup> )
$\Delta G$	Gibbs free energy change (J)
Gz	Graetz number
h	specific enthalpy (J mol <sup>-1</sup> ), heat conductivity (J m <sup>-1</sup> s <sup>-1</sup> K <sup>-1</sup> )
$\Delta H$	enthalpy change (J)
Η̈́.	mixture enthalpy
i	current density (A m <sup>-2</sup> )
$J_k$	species flux (mol m <sup>-2</sup> s <sup>-1</sup> )
$k_{f,i}$	forward reaction rate constant
$K_g$	number of gas phase species
$l_e$	thickness of electrolyte (m)
n	number electrons transferred
'n	molar flow (mol h <sup>-1</sup> )
Nu	Nusselt number
p	pressure (Pa)
$p_k$	partial pressure of species k (Pa)
P <sub>e</sub>	MEA perimeter (m)
Pr	Prandti number
Q D	$\frac{1}{2} \frac{1}{2} \frac{1}$
К D	$(J \Pi O \Lambda^2)$
κ <sub>i</sub> Po	Povodde number
Ке ċ	molar production rate (mol $m^2 s^{-1}$ ; mol $m^{-3} s^{-1}$ )
5 A C	entrony change ( LK <sup>-1</sup> )
Δ3 t	time (s)
τ Τ	temperature (K)
17	velocity (m s <sup>-1</sup> )
W.	molecular weight (kg mol <sup>-1</sup> )
X	mole fraction

[X]	concentration (mol m <sup>-3</sup> )
x, y, z	direction co-ordinate (m)
	man and fire attack

Y mass fraction

#### **Greek** letters

β	charge transfer coefficient
γ	normalization factor for current density
$\gamma_m$	percolation probability
δ	Kronecker delta
η	overpotential (V)
θ	surface coverage fraction
λ	thermal conductivity (J s <sup>-1</sup> m <sup>-1</sup> K <sup>-1</sup> )
μ	dynamic viscosity (kg m <sup>-1</sup> s <sup>-1</sup> )
ρ	density (kg m <sup>-3</sup> )
σ	electrical conductivity (S m <sup>-1</sup> )
$\sigma^e$	effective electrical conductivity (S m <sup>-1</sup> )
τ	tortuosity
$v_i$	volume fraction
φ	Channel density (cm <sup>-2</sup> )
φ	porosity

### Subscripts

а	anode
С	channel, cathode
сопс	concentration
е	electrolyte
eff	effective
f	fluid
i, j, k, l	species
m	phase
tot	total

### Abbreviations

B-V	Butler-Volmer
DGM	Dusty-gas model
LSM	Lanthanum strontium manganite
MEA	membrane electrode assembly
PEM	polymer electrolyte membrane
RWGS	reverse water-gas shift
SOEC	solid oxide electrolysis cell
SOFC	solid oxide fuel cell
TPB	three-phase boundary
WGS	water-gas shift
YSZ	Yttria-stabilized zirconia

# 1 Introduction

It is well known, that low temperature fuel cells with polymer electrolyte membranes (PEM) can be used to split water instead of producing energy through a controlled hydrogen-oxygen reaction. Therein, the electrical energy used to split the water molecules is converted to chemical energy and stored in  $H_2$  and  $O_2$ . In the same way, solid oxide electrolysis cells (SOECs) can be used for electrochemical water splitting as well as the co-electrolysis of steam and carbon dioxide. This is due to the effects of the higher operating temperature allowing for the use of cheaper, more stable and less active catalysts, thereby preventing CO-poisoning [1].

The key advantages of co-electrolysis are its energy storage potential, the consumption of carbon dioxide and the production of synthesis gas. Syngas is very commonly used in the chemical industry to produce synthetic fuels or other liquid hydrocarbons via Fischer-Tropsch synthesis or for methanol synthesis and hydroformylation [2]. The prospect of chemically converting carbon dioxide into polymers, hydrocarbons and base chemicals without relying on fossil fuels is highly promising, especially when renewable energy is used to operate the cell.

SOECs are solid state devices consisting of a dense oxygen ion conducting ceramic electrolyte sandwiched typically between a cermet electrode (e.g. Ni/YSZ) and a ceramic composite electrode (e.g. LSM/YSZ). The state-of-the-art cells are usually cermet electrode supported to minimize ohmic drop across the electrolyte thickness and maximize catalytic surface area. Both electrodes use a contact layer or interconnect to attach to the electrical circuit and use gas channels to transport reactants and products. A schematic representation of the cross-section of a planar SOEC used for co-electrolysis is given in Figure 1.

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The production of syngas occurs via the Equations 1.1 and 1.2 at the triple-phase boundary (TPB) of the cathode, while oxygen is produced via Eq. 1.3 at the anode TPB. Since nickel is a very good catalyst for the water-gas shift reaction (WGS) [3], Eq. 1.4 will also occur in the porous cathode. Due to high temperatures, the reaction will be kinetically fast and equilibrium will be reached quickly [4].



Figure 1: Structural sketch of a planar co-flow SOEC for co-electrolysis. Adapted from [5].

For the produced syngas to be used in industrial processes, the H<sub>2</sub>/CO-ratio is critical. The most important applications for syngas are methanol synthesis (Eq. 1.5) hydroformylation (Eq. 1.6) and Fischer-Tropsch synthesis (Eqs. 1.7 and 1.8) [2]. For methanol synthesis the required H<sub>2</sub>/CO-ratio is close to 2:1, but due to the influence of the Water-Gas-Shift reaction (Eq. 1.4) both CO and CO<sub>2</sub> are reactants. Therefore, the ideal syngas-ratio is given by  $(H_2 - CO_2)/(CO + CO_2) = 2$  [6,7].

$$CO_2 + 2e^- \rightarrow CO + O^{2-}$$
 (1.1)

$$H_20 + 2e^- \rightarrow H_2 + 0^{2-}$$
 (1.2)

 $2 0^{2-} \to 0_2 + 4 e^- \tag{1.3}$ 

$$CO + H_2 O \rightleftharpoons CO_2 + H_2 \tag{1.4}$$

The syngas ratio required for hydroformylation is stochiometric, i.e. 1:1. However, industrial processes use a slight excess of hydrogen (1.01-1.16) [8], as it assists in the formation of active catalyst species and therefore increases the rate of the reaction [9]. For Fischer-Tropsch synthesis no distinct syngas ratio exists, though it is mostly about 2:1. A decrease in the H<sub>2</sub>/CO-ratio leads to longer, less branched chains (Eq. 1.7 and 1.8) [10] while a hydrogen-excess of 3:1 or higher mainly leads to methanation (1.9) 1.9) [11].

$$2 H_2 + CO \rightarrow CH_3OH \tag{1.5}$$

$$2 R = CH - CH_2 + 2 CO + 2 H_2$$
  

$$\rightarrow R(CH_2)_2 CHO + RCH(CH_3) CHO$$
(1.6)

$$x CO + (2x + 1)H_2 \rightarrow C_x H_{2x+2} + x H_2 O$$
 (1.7)

$$x CO + 2x H_2 \rightarrow C_x H_2 + x H_2 O$$
 (1.8)

$$CO + 3 H_2 \rightarrow CH_4 + H_2O$$
 (1.9)

Modeling a ceramic cell is based on the accurate integration of electro chemistry, surface chemistry, heterogenous catalysis and elementary kinetics as well as charge, gas and heat transport. As each of these processes can inhibit the effective operation of a cell, it is very important to understand each process thoroughly. Consequently, material properties (e.g. thermal conductivity, active area, catalyst, porosity) and operational parameters (e.g. voltage, temperature, fuel composition) can be optimized to improve the cell performance. Therein, modeling a cell is a convenient way to attain new findings.

To achieve commercial yields of the product gases, a scale-up is realized by combining ceramic cells in stacks. Given the size of an industrially used SOEC stack, the behavior of each cell is different depending on its position in the stack. This is due to temperature gradients developing over the stack, as an increase in temperature improves kinetics of the catalytic steps as well as the oxygen ion transport through the solid electrolyte. Therefore, it is not sufficient to model a unit cell and a stack simulation must be carried out to capture the thermal effects.

The experimental performance analysis of SOECs as single cells and stacks for co-electrolysis has been presented many times by several groups [12–16]. Additionally, the modeling of SOECs for co-electrolysis has become of increasing interest over the last years [5,17–20]. Two-dimensional thermal modeling of co-electrolysis in SOECs was performed to investigate the heat/mass transfer dependencies for planar cells [21] as well as to analyze and improve the efficiency and conversion of tubular cells [22,23].

Additionally, a modeling approach to combine co-electrolysis and subsequent conversion by a Fischer-Tropsch in a process environment is used to calculate system efficiency and analyze production costs [24]. There, no efficiency optimization is presented and the focus of the publication is plant operation. In earlier publications of this group, a model based performance analysis of a SOFC under direct internal reforming conditions has been carried out [25], SOFC stacks were modeled two and three dimensionally [26] and a model of a solid-oxide co-electrolyzer for syngas production was developed and validated [5], collectively providing the basis for this approach.

In this work, the performance of a Ni/YSZ-YSZ-YSZ/LSM co-electrolysis cell is analyzed using a 2-D continuum scale multi physics model under isothermal and adiabatic conditions. The influence of various operating parameters such as voltage, temperature, flow rate, hydrogen content and cell length on the production of syngas is studied and the inlet fuel composition varied to produce a syngas ratio suitable for the above described applications. Furthermore, an efficiency optimization of a combination of the afore-mentioned parameters is carried out for the single cell to compare and contrast the optimization results against a 3-D stack simulation.

# 2 Model description

The model used in this work utilizes mass transport, heterogenous chemistry, electro-chemistry and transport through porous media to describe the cell processes. Therein, the reduction of H<sub>2</sub>O and CO<sub>2</sub> is described by modified B-V equations considering multi-step single electron transfer reactions. A parametric quasi-2-D model is used to analyze electrochemical parameters as well as a 42-step elementary heterogenous reaction mechanism for Ni catalysts, consisting of 12 surface species and 6 gas-phase species. The model was validated in an earlier publication of this group [5] by comparing it's results to two sets of experimental data. Any information on the model given in this work was adopted from previous publications of this group [5,25–29] and the DETCHEM<sup>TM</sup> User Manual [30].

### 2.1 Channel flow

The quasi-2-D model assumes one dimensional plug flow in the channels. Therein, the axial diffusion is assumed to be negligible compared to convective transport and radial gradients in flow composition are assumed to irrelevant due to predominant diffusive mixing due to the small channel dimensions. The equation for species continuity in the channel is given by Equation 2.1 and the velocity of the flow can be calculated from the momentum balance equation 2.2.

$$\frac{\partial(\rho_{f}Y_{k})}{\partial t} = -\frac{\partial(\rho_{f}vY_{k})}{\partial z} + \frac{P_{e}}{A_{c}}J_{k}W_{k}, \qquad k = 1, ..., K_{g}$$
(2.1)

$$\frac{\partial(\rho_{f}v)}{\partial t} = -\frac{\partial(\rho_{f}vv)}{\partial z} + v \sum_{k=1}^{K_{g}} \frac{P_{e}}{A_{c}} J_{k}W_{k} \qquad (2.2)$$

Therein  $P_e$  is the perimeter associated with the MEA (width of the channelelectrode interface),  $A_c$  is the cross-sectional area of the channel,  $\rho_f$  is the fluid density, v is the velocity, z is the axial position, t is the time,  $K_g$  is the number of species in the gas,  $W_k$  is the molecular weight and  $Y_k$  is the mass fraction of the species k. The flux at the electrode channel interface  $J_k$  is evaluated using the dusty-gas model (DGM) in chapter 2.2. The density can be described by the ideal gas equation (Eq. 2.3) as constant pressure in the channels is assumed. The average molar weight  $\overline{W}$  is calculated via Equation 2.4. Here, *R* is the universal gas constant, *p* is the pressure and  $X_k$  is the molar fraction of species *k*.

$$\rho_f RT = p\overline{W} \tag{2.3}$$

$$\overline{W} = \sum_{k=1}^{3} X_k W_k \tag{2.4}$$

### 2.2 Porous media transport

Species transport through the porous media is solved one dimensionally along the thickness of the porous structure. This is a reasonable approach due to the electrode thickness being thin compared to its length. The transient form of the reaction-diffusion equation for species transport in the electrodes is given by

$$\frac{\partial(\phi\rho_f Y_k)}{\partial t} = -\sum_{k=1}^{K_g} \frac{\partial(J_k W_k)}{\partial y} + \sum_{k=1}^{K_g} \dot{s}_k W_k A_s$$
(2.5)

Here,  $\phi$  is the porosity and the total density of the gas-phase within the porous structure can be obtained from

$$\frac{\partial(\phi\rho_f)}{\partial t} = -\frac{\partial(J_kW_k)}{\partial y} + \dot{s}_kW_kA_s, \qquad (2.6)$$

where  $\dot{s}_k$  is the heterogeneous molar production rate of k,  $A_s$  is the specific catalyst area available for surface reactions and y is the spatial variable along the thickness of the porous media. The flux at the electrode channel interface  $J_k$  depends on the heterogeneous chemistry within the porous electrode and the local current density i(z). It is calculated via the dusty-gas model (DGM) given by

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$$J_{k} = -\left[\sum_{l=1}^{K_{g}} D_{kl}^{DGM} \nabla[X_{l}] + \left(\sum_{l=1}^{K_{g}} \frac{D_{kl}^{DGM}[X_{l}]}{D_{l,Kn}^{e}}\right) \frac{B_{g}}{\mu} \nabla p\right]$$
(2.7)

The first term of the DGM gives the diffusive flux and is a result of molecular and Knudsen diffusion acting in series. Additionally, the second term represents viscous porous media flow (Darcy flow) acting in parallel with diffusive flux. The model therefore accounts for three different transport mechanisms neglecting the effects of external forces. Here,  $\mu$  is the mixture viscosity and  $X_l$  is the mole fraction. Equation 2.9 gives the effective Knudsen diffusion coefficient while the Kozeny-Carman relationship is used to calculate the permeability  $B_q$ :

$$B_g = \frac{\phi^3 d_p^2}{72\tau (1-\phi)^2}$$
(2.8)

$$D_{k,Kn}^{e} = \frac{\phi}{\tau} \frac{d_{pore}}{3} \sqrt{\frac{8RT}{\pi W_{k}}}$$
(2.9)

The DGM diffusion coefficient  $D_{kl}^{DGM}$  is defined as

$$D_{kl}^{DGM} = H^{-1} \tag{2.10}$$

with H being a matrix of the elements

$$h_{kl} = \left[\frac{1}{D_{k,Kn}^e} + \sum_{j \neq k} \frac{X_j}{D_{kj}^e}\right] \delta_{kl} + (\delta_{kl} - 1) \frac{X_k}{D_{kl}^e}$$
(2.11)

Solving the reaction diffusion equation requires knowledge of the heterogeneous molar production rate  $\dot{s}_k$  as well as the boundary conditions at electrode-gas and electrode-electrolyte interfaces. The species fractions are set to the inlet mass fractions at the electrode-gas interface while at the electrode-electrolyte interface, the species fluxes are set equal to the electrochemical reaction source terms.

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### 2.3 Energy transport

To acquire the temperature distribution in the fuel channels, the energy equation

$$\frac{\partial(\rho_f C_{pf} T_f)}{\partial t} = -\frac{\partial(\nu \rho_f C_{pf} T_f)}{\partial t} - \frac{h}{H_c} (T_f - T_e) + \frac{h}{H_c} (T_I - T_f) \qquad (2.12)$$

is used. The transport of heat due to the bulk fluid flow is represented by the first term in equation 2.12, while the following terms represent the heat transfer from the channels to the MEA and the heat transfer from the interconnect to the flow channels. The heat transfer coefficient *h* is obtained using the Nusselt number Nu (Eq. 2.13) using an empirical expression (Eq. 2.14) [31] based on the Graetz number Gz (Eq. 2.15).

$$Nu = \frac{hD_h}{k}$$
(2.13)

$$Nu = 3.095 + 8.933 \left(\frac{1000}{Gz}\right)^{-0.5386} exp\left(-\frac{6.7275}{Gz}\right)$$
(2.14)

$$Gz = \frac{D_h}{z} RePr$$
(2.15)

There,  $D_h$  is the hydraulic diameter, k is the thermal conductivity, z is the axial position, Re is the Reynolds number and Pr is the Prandtl number. To solve for the heat released on the surface of the solids, the heat balance equation is used in the form

$$\frac{\partial(\rho C_p T)}{\partial T} = \nabla (k_{eff} \nabla T) + \frac{h}{\delta y} (T_f - T) - \sum_{k=1}^{K_g} \dot{s} W_k A_s h_k + Q_e + Q_{ovp}$$
(2.16)

Here, the first term represents the heat transfer due to conduction and the second term describes the heat transfer at the channel-electrode interface. Therein,  $k_{eff}$  is the effective thermal conductivity and  $\delta y$  is a finite value obtained from the finite volume integration over the discretized cells. The last two terms represent the heat released in the electrolyte  $Q_e$  and the heat generation due to overpotential losses  $Q_{ovp}$ . They are defined as

$$Q_e = -T\Delta S \frac{i}{2F} \tag{2.17}$$

$$\boldsymbol{Q}_{ovp} = \boldsymbol{i}(\boldsymbol{\eta}_a + \boldsymbol{\eta}_{ohm}) \tag{2.18}$$

Here, *i* is the current density and  $\eta_a$  and  $\eta_{ohm}$  represent the activation and ohmic overpotential. The heat balance in the interconnect is obtained using

$$\frac{\partial(\rho C_p T_I)}{\partial T} = \frac{\partial}{\partial z} \left( k \frac{\partial T_I}{\partial z} \right) + \frac{h}{H_I} \left( T_f - T_I \right)$$
(2.19)

with the following boundary conditions:

$$\left. \frac{\partial T}{\partial z} \right|_{z=0} = \mathbf{0}, \qquad \left. \frac{\partial T}{\partial z} \right|_{z=L} = \mathbf{0}$$
 (2.20)

Therein,  $H_I$  is the thickness of the interconnect and L is the length. The conduction within the interconnect is represented by the first term of Equation 2.19, while the second term describes the heat transfer from the channel to the interconnect.

### 2.4 Electrochemistry

Charge transfer chemistry takes place at the three-phase boundary of ionic, electronic and gas phases. In this model, only interfacial charge transfer occurring at electrolyte-electrode interface is considered while distributed charge transfer across the utilization region of the electrodes is omitted. The net current densities of the electrochemically active species are computed to be the normalized sum of currents ( $i_{H_2}$  and  $i_{CO}$ ) through two parallel pathways (H<sub>2</sub>O/H<sub>2</sub> and CO<sub>2</sub>/CO) of charge transfer. A single value of current density is obtained by normalizing the two reaction pathways via charge and mass conservation equations. The two pathways are denoted with the subscripts  $H_2$  and CO. To calculate the cell potential, all irreversibilities occurring during operation are considered. The relation between the current density and the potential for each pathway is given by

$$E_{cell} = E_{rev,H_2} + |\eta_a(i_{H_2})| + \eta_c(i_{H_2}) + \eta_{ohm}(i_{H_2}) + \eta_{conc}(i_{H_2}) \quad (2.21)$$

$$E_{cell} = E_{rev,CO} + |\eta_a(i_{CO})| + \eta_c(i_{CO}) + \eta_{ohm}(i_{CO}) + \eta_{conc}(i_{CO})$$
(2.22)

Here, several overpotential losses  $\eta$  are added to the reversible potential  $E_{rev}$ . These are the activation overpotentials at the anode  $\eta_a$  and cathode  $\eta_c$ , as well as the ohmic  $\eta_{ohm}$  and concentration overpotential  $\eta_{conc}$ . Due to porous media transport being modeled in detail, the concentration overpotential is not treated explicitly while the ohmic overpotential is given by

$$\eta_{ohm} = R_{tot} i \tag{2.23}$$

with  $R_{tot}$  being the total resistance consisting of

$$\boldsymbol{R}_{tot} = \boldsymbol{R}_e + \boldsymbol{R}_c + \boldsymbol{R}_{LSM} + \boldsymbol{R}_{Ni-YSZ} \tag{2.24}$$

where,  $R_{LSM}$  and  $R_{Ni-YSZ}$  are the electronic resistances of both electrode materials and  $R_c$  is the contact resistance of the solid-solid interfaces. Since the magnitudes of the resistances depend on the material and its micro-structure, these resistances are negligible for modern cells when compared to the ionic resistance of the electrolyte  $R_e$ ,

$$R_e = \frac{l_e}{\sigma_{el}^e} \tag{2.25}$$

with  $l_e$  being the thickness of the electrolyte and  $\sigma_{el}^e$  being the effective electrolyte conductivity. The effective conductivities  $\sigma_m^e$  of the phases *m* are calculated via the Nam and Jeon correlation [32],

$$\sigma_m^e = \sigma_m[(1-\phi)\upsilon_m\gamma_m] \tag{2.26}$$

There,  $\sigma_m$  is the conductivity,  $v_m$  is the volume fraction and  $\phi$  is the porosity. The percolation probability  $\gamma_m$  is calculated by an empirical correlation derived by Bertei and Nicoletta [33],

$$\gamma_m = 1 - \left(\frac{4.236 - Z_{m,m}}{2,472}\right)^{3.7} \tag{2.27}$$

including the number of contacts between particles of the phases  $Z_{m,m}$ . The reversible potential  $E_{rev}$  is calculated using the Nernst equation:

$$E_{rev,H_2} = E_{H_2}^0 + \frac{RT}{2F} ln\left(\frac{p_{H_2,c}p_{O_2,a}^{0.5}}{p_{H_2O,c}}\right)$$
(2.28)

$$E_{rev,CO} = E_{CO}^{0} + \frac{RT}{2F} ln \left( \frac{p_{CO,c} p_{O_{2},a}^{0.5}}{p_{CO_{2},c}} \right)$$
(2.29)

Therein,  $E_{rev}$  is the maximum possible potential derived from a cell operating reversibly,  $E^0$  is the electromotive force at standard pressure, which is calculated from thermodynamic data and  $p_i$  is the partial pressure of a gas phase species *i* at the cathode TPB (H<sub>2</sub>, H<sub>2</sub>O, CO, CO<sub>2</sub>) or the anode TPB (O<sub>2</sub>). The dependence of current density on the activation overpotentials is described by a modified Butler-Volmer equation. Kinetic limitations are considered as the rate-limiting step among elementary charge transfer pathways is integrated. The modified B-V equations for the reduction of the reactants as well as for O<sub>2</sub>-formation are

$$i_{H_2} = i_{0,H_2} \left[ exp\left( \frac{(1+\beta_a)F\eta_c}{RT} \right) - exp\left( -\frac{\beta_c F\eta_c}{RT} \right) \right]$$
(2.30)

$$i_{co} = i_{0,co} \left[ exp\left(\frac{\beta_a F \eta_c}{RT}\right) - exp\left(-\frac{(1+\beta_c)F \eta_c}{RT}\right) \right]$$
(2.31)

$$i_{i} = i_{0,0_{2}} \left[ exp\left(\frac{\beta_{a}F\eta_{a}}{RT}\right) - exp\left(-\frac{(1+\beta_{c})F\eta_{a}}{RT}\right) \right]$$
(2.32)

Here, *i* is the current density,  $i_0$  is the exchange current density and  $\beta$  is the asymmetric charge transfer coefficient. Equation 2.30 and 2.31 refer to the reduction of H<sub>2</sub>O and CO<sub>2</sub>, respectably. But equation 2.32 includes two anode activation overpotentials for each charge pathway. Therefore, based on the type of electrolysis, the index *i* represents either H<sub>2</sub> or CO. The exchange current densities  $i_{0,i}$  (for  $\beta = 0.5$ ) are given by

$$i_{0,H_2} = i_{H_20}^* \frac{\left(p_{H_2}/p_{H_2}^*\right)^{0.25} \left(p_{H_20}\right)^{0.75}}{1 + \left(p_{H_2}/p_{H_2}^*\right)^{0.5}}$$
(2.33)

$$i_{0,CO} = i_{CO_2}^* \frac{\left(p_{CO_2}/p_{CO}\right)^{0.25}}{1 + \left(p_{CO}/p_{CO}^*\right)^{0.5} + \left(p_{CO}/p_{CO_2}^*\right)}$$
(2.34)

$$i_{0,0_2} = i_{0_2}^* \frac{\left(p_{0_2}/p_{0_2}^*\right)^{0.25}}{1 + \left(p_{0_2}/p_{0_2}^*\right)^{0.5}}$$
(2.35)

with  $p^*$  being the equilibrium pressure and  $i^*$  being a fit parameter that is adjusted to represent experimentally observed performance [29]. The derivations of Equations 2.33 to 2.35 and the used values can be found in Refs. [29,34]. To describe the temperature dependence of the exchange current density, an Arrhenius equation is used:

$$i_i^* = k_i exp\left(-\frac{E_i}{RT}\right)$$
(2.36)

Due to both H<sub>2</sub>O and CO<sub>2</sub> being present at the TPB, the relative percentages of the reactants need to be accounted for in order to normalize the net current density. This is realized by the implementation of the factor  $\gamma$ 

$$\gamma = \frac{Y_{H_2O}^{TPB}}{Y_{H_2O}^{TPB} + Y_{CO_2}^{TPB}}$$
(2.37)

into an expression for the overall current density:

$$i = \gamma i_{H_2} + (1 - \gamma) i_{CO} \tag{2.38}$$

Even though this approach has been validated [35,36], it is still an approximation since it is independent of certain factors affecting the current densities at the TPB. These are the ratio of ionic particles, the coordination number of ionic and electronic particles, the fraction overlaps between these particles, the volume fractions of the components, foreign impurities in the TPB and the degradation of the Ni catalyst.

### 2.5 Thermo-catalytic chemistry

To calculate the forward reaction rate constant for the *i*th thermo-catalytic reaction in the cathode a modified Arrhenius expression based on the mean-field approximation is used, given by

$$k_{fi} = A_i \left(\frac{T}{T^0}\right)^{\beta_i} exp\left(-\frac{E_{ai}}{RT}\right) \prod_{k=K_g+1}^{K_g+K_s} \theta_k^{\mu_{ki}} exp\left(-\frac{\varepsilon_{ki}\theta_k}{RT}\right)$$
(2.39)

where *K* is the number of species on the surface ( $K_s$ ) and in the gas phase ( $K_g$ ) with  $\mu_{ki}$  as well as  $\varepsilon_{ki}$  being parameters modeling the order and activation energy dependency on surface coverage  $\theta_k$  of the species *k*.

Additionally,  $E_{ai}$  is the activation energy,  $A_i$  the preexponential factor and  $\beta_i$  the temperature exponent. These values are given as part of the detailed multi-step heterogenous mechanism used in this study, which is presented in [5]. The mechanism accounts for the adsorption/desorption of H<sub>2</sub>, H<sub>2</sub>O, CO, CO<sub>2</sub>, O<sub>2</sub> and CH<sub>4</sub> from the Ni-surface being thermodynamically consistent between 220 °C and 1700 °C. The water-gas shift reaction, methanation, steam reforming, dry reforming, partial and total oxidation of C1-species and the formation of carbon monolayer are all included in the mechanism.

The changes in surface coverage over time are described by

$$\frac{d\theta_k}{dt} = \frac{\dot{s}_k \sigma_k}{\Gamma}, k = K_g + 1, \dots, K_g + K_s$$
(2.40)

with the surface site density  $\Gamma$  (estimated to be 2.66 x 10<sup>-9</sup> mol cm<sup>-2</sup>) and the number of sites required for adsorption of a species  $\sigma_k$ . Additionally, the surface production rate  $\dot{s}_k$  of the species k is used and given by

$$\dot{s}_{k} = \sum_{i=1}^{K_{r}} v_{ki} k_{fi} \prod_{k=1}^{K_{g}+K_{s}} [X_{k}]^{v'_{ki}}$$
(2.41)

Therein,  $K_r$  is the number of surface reactions,  $[X_k]$  is the concentration of species k,  $v'_{ki}$  is the stochiometric coefficient of the reactant and  $v_{ki}$  is the difference in stochiometric coefficients of products and reactants. Furthermore, due to the inlet fuel composition used in this study, gas-phase reactions are neglected.

#### 2.6 Stack model

The stack is modeled as a porous media with straight channels in which all processes except heat transfer are assumed to be in steady state. This assumption is based upon the significantly higher time constant of the heat transfer processes compared to other processes such as mass transport and surface reactions in the channels. Here a transient stack model is used, in which the temperature of the solid phase is decoupled from the gas phase, resulting in the transient three-dimensional heat conduction equation (Eq. 2.42) being solved.

$$\rho C_p \frac{\partial T}{\partial t} = \frac{\partial}{\partial x_i} \left( \lambda_{ij} \frac{\partial T}{\partial x_j} \right) + q \qquad (2.42)$$

Herein,  $\lambda_{ij}$  is the tensor of conductivity, q is the heat source term from the interaction with the channels, T is the temperature, t is the time,  $\rho$  is the density and  $C_p$  is the heat capacity. The heat source term

$$q = -\varphi \frac{\partial \dot{H}_{channel}}{\partial x} + Q_{ohm}$$
(2.43)

is derived from the simulation of single cells and implements the channel density  $\varphi$  (number of channels per cross-sectional area, here 9.87 cm<sup>-2</sup>), the enthalpy flux in the channel  $\dot{H}_{channel}$  and the heat release due to Ohmic losses within the electrolyte  $Q_{ohm}$ . As the pressure in the stack is assumed to be constant, the energy conservation can be expressed as an enthalpy term. Due to the constant pressure, the enthalpy flux is only dependent on the axial heat exchange with the solid phase.

Furthermore, the solid phase (MEA and interconnect) is assumed to be a continuous porous media with global properties calculated via the parallel (e.g. density  $\rho$ , Eq. 2.44) and geometric mean model (e.g. thermal conductivity  $\lambda$ , Eq. 2.45) [37].

$$\lambda_{eff} = \prod_{\substack{i=1\\i}}^{i} \lambda_i^{\nu_i} \tag{2.44}$$

$$\boldsymbol{\rho}_{eff} = \sum_{i=1}^{l} \boldsymbol{\rho}_i \boldsymbol{v}_i \tag{2.45}$$

Therein,  $\lambda_{eff}$  is the effective thermal conductivity,  $\rho_{eff}$  is the effective density and  $v_i$  is the volume fraction of the species *i*. The solid phase heat balance is acquired via integration over time. The obtained solid phase temperature at every axial position is used to solve for gas phase temperature and reaction rates.

#### 2.7 Efficiency model

The definition of efficiency for fuel cells is a widely discussed topic in literature with a number of different approaches due to the variation in fuel cell design and the desired application (e.g. single cell, stack or industrial context) [25,38–40]. As noted by Zhu and Kee [38], the thermal efficiency of any energy conversion device can be described as the work gained from a potential energy input. For co-electrolysis, the potential energy input is the electrical work  $W_e$  and the energy output can be represented by the heat-release associated with full oxidation of the produced syngas  $Q_{out}$ . Therefore, the net thermal efficiency can be defined as

$$\varepsilon = \frac{Q_{out}}{W_e} = \frac{\sum_i \dot{n}_{i,out} \Delta h_{i,out}}{\int i E_{cell} dA}$$
(2.46)

Here, the electrical work  $W_e$  is the product of the voltage  $E_{cell}$  and the current density *i* over the area *A*, whereas the energy output  $Q_{out}$  is calculated via the product of molar flow rates at the fuel channel outlet  $\dot{n}_{i,out}$  of the product *i* (H<sub>2</sub> and CO) and the full combustion enthalpy  $\Delta h_{i,out}$  of the products.

The maximum energy output available in an electrolysis cell is equal to the Gibbs free energy of the reaction  $\Delta G$ , while the thermal energy available is the enthalpy of the reaction  $\Delta H$ . Therefore, the amount of heat being produced by a reversibly running fuel cell  $Q_{rev}$  is the difference of these two values [41].

$$\mathbf{Q}_{rev} = \Delta G_i - \Delta H_i = -T\Delta S_i \tag{2.47}$$

To consider energy losses due to heat generation in the cell, the term is integrated into Equation 2.48, wherein  $\Delta S_i$  is the change in molar entropy associated with the reduction reactions of both reactants *i* given in Equations 1.1 and 1.2. To accommodate for hydrogen (or CO) in the inlet fuel stream, the term  $\Delta \dot{n}_i = \dot{n}_{i,out} - \dot{n}_{i,in}$  is introduced, with  $\Delta \dot{n}_i$  representing the amount of hydrogen (and CO) produced in the cell, leading to the following definition of efficiency:

$$\varepsilon = \frac{\sum_{i} \Delta n_{i} \Delta h_{i,out}}{\int i E_{cell} dA + \sum_{i} \Delta n_{i} T \Delta S_{i}}$$
(2.48)

The thermoneutral voltage  $E_{th}$  is a parameter used to evaluate the requirements of thermal management of high temperature cells. It is given by

$$E_{th} = \frac{\Delta H}{nF} \tag{2.49}$$

where n is the number of electrons transferred in a reaction and F is the Faraday constant. Therefore, the thermoneutral voltage can be understood as the heat of the reaction per transferred unit of charge. As it is the case in this study, electrolyzers must be operated at voltages above the thermoneutral voltage to generate heat [42], due to the electric energy applied to the cell exceeding the energy consumed by the processes.

## 2.8 Computational procedure

To solve the governing equations, the single planar cell is discretized into finite volumes with identical width. While the fuel and air channel as well as the electrolyte are treated as one dimensional, the thicknesses of the cathode is discretized into 30 and the anode into 5 volumes. These values (including the electrolyte) were adjusted with changes in thickness mentioned in chapters 3.2.2 and 3.2.3.

The solution is acquired using a space marching algorithm in axial direction. The axial length of the cell is discretized into 40 cells and for each axial position a solution is obtained when steady state is achieved. For each axial position, the converged solution from the previous position is used to provide the initial values. Convergence of the entire solution is achieved after few iterations.

Due to the close coupling and non-linearity of the differential-algebraic set of equations used to describe a single cell and the size of a stack of cells, a high amount of computational time is required for a stack simulation. The same is true for adiabatic conditions compared to isothermal modeling of a single cell. The amount of computational time required to carry out simulations becomes especially important when a large amount of simulations is needed. As three parameters are varied in four steps each for two syngas ratios, 128 points of operation are optimized to produce the desired syngas ratio, resulting in several hundred simulations.

Therefore, the computational time required to achieve a certain result is minimized using isothermal simulations of a representative single cell to optimize the efficiency of co-electrolysis to produce syngas at a certain H<sub>2</sub>/CO-ratio. After the isothermal optimization, a chosen point of operation is used to model a stack. Thereafter, the isothermal results at the efficiency maxima are compared to the adiabatic stack simulations. To validate this approach, simulations of the same cases in adiabatic and isothermal conditions were carried out as a preface to this study. It was found, that the differences were negligible for the efficiency optimization.

# 3 Results and discussion

To study the effect of various parameters on syngas production and efficiency of the cell, an intensively used and tested SOEC-stack is used to acquire cell parameters. The chosen planar cell is the F-design used by Forschungszentrum Jülich since 2003 [43]. It has been their "standard for testing progress in materials" [43] and has been used to build stacks of different cell sizes (50x50 mm, 100x100 mm, 200x200 mm) [43] and cell-numbers (2 [12], 4 [44], 5 [44], 36 [45], 60 [43]). The modeled cell used for co-electrolysis is a Ni/8YSZ-8YSZ-LSM/LSM electrolysis cell. The acquired parameters of the cell size, materials used and operational parameters are listed in Table 1; the material properties are given in Table 2.

Component	Material	Thickness / µm				
Cathode contact layer	Ni-mesh	-				
Cathode substrate	Ni/8YSZ	1000				
Cathode functional layer	Ni/8YSZ	10				
Electrolyte	8YSZ	10				
Anode functional layer	LSM/8YSZ	15				
Anode contact layer	Perovskit-type oxide (LCC10)	-				
Anode current collector	LSM	70				
Interconnect	Crofer22APU [12]	2500 [12]				

 Table 1: Materials and Thicknesses of the SOEC-components. All data is adapted from [46] if not indicated otherwise.

To investigate single parameters a base case needs to be established. In our study, the base case is based on a cell in the F10-design from which the cell parameters are obtained. The operational parameters used were found to be typical values. All parameters are given in Table 3. Unless mentioned otherwise, an inlet fuel gas composition of 40 mol-%  $CO_2$  and 60 mol-%  $H_2O$  is used.

As the focus of this study is to optimize the design and operation of an SOEC cell and stack to produce a certain molar syngas ratio, the flows are listed as molar instead of mass.

Parameter	Value	Unit	Reference		
	Ni-8YSZ				
Average pore radius	0.5	μm	Estimate		
Average particle diameter	2.5	μm	Estimate		
Porosity	0.35	-	Estimate		
Tortuosity	3.8	-	Estimate		
Specific heat capacity	620	J·kg⁻¹·K⁻¹	[47]		
Density	4820	kg∙m⁻³	Calculated from [48,49]		
Thermal conductivity	4.7	J⋅m <sup>-1</sup> ⋅s <sup>-1</sup> ⋅K <sup>-1</sup>	[47]		
	8	SYSZ			
Specific heat capacity	620	J·kg⁻¹·K⁻¹	[47]		
Density	5940	kg∙m⁻³	[48]		
Thermal conductivity	2.1	J⋅m <sup>-1</sup> ⋅s <sup>-1</sup> ⋅K <sup>-1</sup>	[47]		
	LSN	M/8YSZ			
Average pore radius	0.5	μm	Estimate		
Average particle diameter	2.5	μm	Estimate		
Porosity	0.35	-	Estimate		
Tortuosity	3.8	-	Estimate		
Specific heat capacity	130	J·kg⁻¹·K⁻¹	[50]		
Density	3710	kg∙m⁻³	[51]		
Thermal conductivity	3.6	J⋅m <sup>-1</sup> ⋅s <sup>-1</sup> ⋅K <sup>-1</sup>	[52]		
Crofer22APU					
Specific Heat capacity	660	J·kg⁻¹·K⁻¹	[53]		
Density	7700	kg∙m⁻³	[53]		
Thermal conductivity	24	J·m⁻¹·s⁻¹·K⁻¹	[53]		

Table 2: Properties of the materials used. All values were taken at operating conditions, thedensity of the materials is an absolute with the porosity already considered.

Table 3: Acquired cell and operational parameters used in the base case.

Parameter	Value	Unit	Reference
Size	100x100	mm	[46]
Active area	80	cm <sup>2</sup>	[46]
MEA Length	88.4	mm	Calculated from active area
MEA Width	88.4	mm	Calculated from active area
Channel height	1	mm	Estimated from [46]
Channel width	4.47	mm	Estimated from [46]
Temperature	1023	К	-
Velocity	0.6	m⋅s⁻¹	-
Voltage	1.5	V	-

### 3.1 Influence of the water-gas shift reaction

It is well established that the water-gas shift reaction plays an important role in solid oxide co-electrolyzers [4,17]. This is due to nickel, a very good catalyst for the WGS reaction, being present in the porous cathode [3]. To evaluate the influence of the water-gas-shift reaction (Eq. 3.1) on the production of syngas a series of simulations at two temperatures (923 K and 1023 K) is carried out with and without surface chemistry enabled. As stated in chapter 1, due to high temperature, the reaction is kinetically fast and equilibrium will be reached quickly [4].

$$CO + H_2 O \rightleftharpoons CO_2 + H_2 \tag{3.1}$$

The WGS reaction has a molar enthalpy of -41.2 kJ mol<sup>-1</sup> and the Gibbs free energy is negative at the examined temperatures, but increases with increasing temperature making the reaction endergonic over approximately 1100 K [54].



Figure 2: Syngas ratios in dependency of the inlet fuel composition for the two temperatures with and without surface chemistry enabled.

Figure 2 shows the syngas ratio produced in dependency of the amount of carbon dioxide in the fuel. With WGS allowed the resulting syngas ratios are higher for both temperatures.

Since the WGS reaction is less exergonic at higher temperatures it has a bigger influence on the Syngas ratios and conversion at 923 K than at 1023 K. Therefore, even though the syngas ratio without surface chemistry is lower at 923 K compared to the simulation at 1023 K, the syngas ratio is higher at 923 K than at 1023 K when surface chemistry is activated.



Figure 3: CO<sub>2</sub>- (left) and H<sub>2</sub>O-Conversion (right) in dependency of the inlet fuel composition for the two temperatures with and without surface chemistry enabled.

Figure 3 shows that all conversions increase with increasing temperature. Additionally, WGS leads to a generally higher H<sub>2</sub>O-Conversion and generally lower CO<sub>2</sub>-Conversion. This proves the direction of the WGS/RWGS reaction is WGS. This is true for both temperatures. Moreover, the CO<sub>2</sub>- and H<sub>2</sub>Oconversion decrease with the amount CO<sub>2</sub> in the feed if no surface chemistry is allowed. The opposite is the case when surface chemistry is not included.

It can therefore be concluded that due to the impact of the WGS reaction more  $CO_2$  is required in the fuel to obtain a certain syngas ratio. As will be shown later in this work, the amount of  $CO_2$  in the feed can exceed 60 %.

## 3.2 2D-temperature analysis

### 3.2.1 Temperature distribution

To investigate the heat generation in a single cell a cathode supported cell was modeled adiabatically with the parameters of the base case. The resulting twodimensional temperature distribution over the MEA is given in Figure 4. Additionally, the one-dimensional temperature distributions along the length of the cell for the fuel and air channel are depicted.



Figure 4: 2D-temperature distribution of the cathode-supported cell at a velocity of 0.6 m s<sup>-1</sup> and a voltage of 1.5 V.

Figure 4 does not support the approximation of the cell as being isothermal, since the maximum temperature gradient over the MEA is approximately 24 K. Also, all temperatures in the MEA and in the gas channels exceed the inlet gas temperature of 1023.15 K, as significantly more heat is generated than consumed. For both operating voltages, the hottest spot in the MEA is the TPB (MEA depth = 35  $\mu$ m) after about 10 mm of the cell.



Figure 5: 2D-temperature distribution of the cathode-supported cell at a velocity of 0.6 m s<sup>-1</sup> and a voltage of 1.4 V.

Since the operating voltage exceeds the thermoneutral voltage of co-electrolysis (approximately 1.36 V), the heat generated by overpotential losses exceeds the heat consumed by the endothermic electrolysis reactions. To investigate the impact of the overpotential losses, a second cell was modeled using a voltage of 1.4 V. The resulting temperature distribution is presented in Figure 5 and shows a decrease in maximum temperature of 19 K compared to the case with 1.5 V, while the temperature distribution pattern is unharmed. As less heat is generated by a voltage closer to the thermoneutral voltage, this proves that the temperature increase in the MEA is substantially due to overpotential losses.

To further investigate the heat generation and consumption, the heat fluxes acquired for an operational voltage of 1.5 V are plotted in Figure 6. As the heat generated by the water-gas shift reaction can be neglected, the remaining exothermic contributions are the overpotential losses and entropy dissipation. The heat released by the combination of the two factors exceeds the heat consumed by the endothermic reaction, leading to the increase in temperature. As all heat fluxes decrease with increasing length, the temperature minimum is found at the end of the cell.



Figure 6: Absolute heat fluxes at a voltage of 1.5 V of the cathode-supported cell.

Figure 7 depicts the current density and conversion of both reactants in dependency of the cell length for both voltages. Over the length of the cell, the production rate of syngas decreases, leading to a decreasing slope of the conversion graphs. Due to less energy being consumed by the electrolysis reaction, the current density decreases towards the end of the cell. The opposite is the case at the beginning of the cell, where the maximum in current density is found and the production rate of syngas is high. Thereby, the decrease in heat consumption and heat generation over the length of the cell and the decrease in temperature towards the end of the cell can be explained.



Figure 7: Current density and conversion of the reactants over the length of the cell for both voltages.

#### 3.2.2 MEA configuration

To investigate the heat transport between the air and fuel channel and the resulting temperature distribution over the MEA assembly, further adiabatic simulations are executed. The difference between fuel and air inlet temperatures was set to be 100 K, while keeping the fuel inlet temperature at 1023.15 K and lowering the air inlet temperature to 923.15 K. The MEA was cycled through cathode-, electrolyte- and anode-supported configurations, with the exact thicknesses being indicated in the description of each figure.



Figure 8: 2D-temperature distribution of the cathode-supported cell. The thicknesses are:  $l_{cathode} = 1010 \ \mu m; \ l_{electrolyte} = 10 \ \mu m; \ l_{anode} = 15 \ \mu m.$ 



Figure 9: 2D-temperature distribution of the anode-supported cell. The thicknesses are:  $l_{cathode} = 15 \ \mu m; l_{electrolyte} = 10 \ \mu m; l_{anode} = 1010 \ \mu m.$ 



Figure 10: 2D-temperature distribution of the electrolyte-supported cell. The thicknesses are:  $l_{cathode} = 15 \ \mu m; \ l_{electrolyte} = 1010 \ \mu m; \ l_{anode} = 15 \ \mu m.$ 

All three cells (Figure 8 - Figure 10) show a rapidly increasing temperature in the air channel, which matches the fuel channel temperature at the end of the channel. Additionally, all three cells show a increase in temperature at the beginning (cell length of 5 mm) of the fuel channel which is slowly decreasing over the length of the channel. This is due to the development of the MEA temperature in axial direction. In all three cells, the coolest spot in the MEA is found at the very beginning of the channel. For the anode and electrolyte supported cells this spot is colder than the inlet temperature of the inlet gas stream. The cathode supported cell shows generally lower temperatures than with an inlet air temperature of 1023.15 K (Figure 6). For none of the three cells a significant temperature gradient over the thickness of the MEA is observed. This is due to the thinness of the MEA (1.035 mm) compared to its length (89.4 mm).

Comparing the temperature distribution of the electrolyte supported cell (Figure 10) to the temperature distributions of the electrode supported cells (Figure 8 and Figure 9), it is apparent that in the electrolyte supported cell the temperature of the MEA and the fuel channel temperature is generally lower than in the electrode supported cells. The electrolyte supported cell shows an approximately five times lower conversion and an approximately six times lower current density at the same applied voltage, the lower temperature can first and foremost be attributed to less heat generation by overpotential losses and entropy dissipation in the cell.

Compared to the high temperature differences of electrolyte and electrode supported cells, the temperature distributions of both electrode supported cells are quite similar. Nevertheless, the temperature distribution pattern of the anodesupported cell is different than the temperature distribution of the anode supported cell. This is due to the changed position of the TPB and is especially apparent at the beginning of the cell, whereas at the end of the cells the temperature distribution patterns in both MEAs are nearly identical.

### 3.2.3 Velocity influence on temperature

In the literature, it is argued that the use of higher flow rates in both channels can be essential to maintain a certain cell temperature within the limits of durable electrode performance, being especially relevant for the long-term operation of SOFCs [25]. This may not be relevant for SOECs, since it was found in this work, that the dominating electrolysis reactions lead to a generally endothermic operation. Nevertheless, temperature control is still important for SOECs since degradation of cell performance for electrolysis mode is higher than for fuel cell mode and "the main bottleneck at present for industrial applications" [12]. To examine whether this experimental requirement applies to electrolysis cells, an additional adiabatic simulation is carried out using a velocity of 0.15 m s<sup>-1</sup>. The resulting two-dimensional temperature-plot is given in Figure 11 and is compared to the cell using a velocity of 0.6 m s<sup>-1</sup> given in Figure 8.



Figure 11: 2D-temperature distribution of the cathode-supported cell at a velocity of 0.15 m s<sup>-1</sup>.

Figure 11 shows that a lower velocity leads to a lower overall MEA temperature, faster rise in temperature in the air channel and a lower temperature in the fuel channel. The hot spot in the MEA also shifts towards the beginning of the cell. These effects are all consequences of the increased residence time allowing for an increase in heat exchange between both channels and the interconnect. Therefore, higher flow rates are found not to be a requirement for temperature control in single cell SOECs.

## 3.3 Effects of single parameters

In chapter 3.2 it was shown that the adiabatic cases develop higher temperatures than the isothermal cases due to the heat generation of overpotential losses and entropy dissipation. As will be shown in the following chapters, a higher temperature leads to an increase in cell performance. Since the approach of this work focuses on optimizing a stack, the characteristics of the parameter optimization need to be as close to the stack simulation as possible.

The stack model described in chapter 2.6 and used in chapter 3.5 includes heat loss, whereas the isothermal and adiabatic models do not use such a term. This leads to a decrease in overall temperature and smaller temperature gradients in the stack simulations. Thus, the use of adiabatic simulations of a single cell at the same inlet temperature as the stack lead to increased performance values being obtained during the optimization. Therefore, isothermal simulations can be used as a conservative estimate of the stack regarding the performance while requiring a minimum of computational time. Hence, isothermal simulations of a single cell are the better option for optimizing a stack than adiabatic simulations of a single cell are used to investigate the influence of the cell parameters and to optimize the stack.

In the following subchapters, the effect of variations of the parameters temperature, cell length, velocity, voltage and H<sub>2</sub>-content on conversion, efficiency and the amount of CO<sub>2</sub> required in the fuel to achieve a certain syngas ratio are examined.

### 3.3.1 Temperature

The operating temperature of an electrolysis cell is vital to its efficient operation. As an increase in operating temperature benefits kinetics of the catalytic steps as well as the oxygen ion transport through the solid electrolyte, it results in a higher power density at the same voltage [5]. Therefore, the operating cell temperature is a key parameter to optimizing the performance of a SOEC. In this chapter, the operating temperature is varied to investigate its influence on conversion, syngas ratio and efficiency.



Figure 12: Dependency of reactant conversion (left) and the amount of CO<sub>2</sub> required in the fuel to achieve a certain syngas ratio (right) on inlet fuel temperature.

Figure 12 depicts the dependency of reactant conversion and the amount of  $CO_2$  required in the fuel to achieve a certain syngas ratio on the cell temperature. As conversion is increasing exponentially with an increase in temperature, a smaller mole fraction of  $CO_2$  is required in the fuel to achieve a certain syngas ratio.

Figure 13 shows that an increase in temperature leads to a decrease in efficiency within the range studied. The opposite trend is found in chapter 3.4. The difference between these two cases is the presence of hydrogen in the optimization simulations. Adding hydrogen to the fuel leads to significantly lower  $H_2O$ -conversion and for 873 K and 932 K to the consumption of hydrogen via the reverse water-gas shift reaction (Eq. 3.1).

An increase in temperature, therefore has a higher impact on the conversion of cells using hydrogen in the fuel stream leading to an increasing efficiency. Hence, the efficiencies of cells containing hydrogen in the fuel are showing the opposite temperature dependence than cells not containing hydrogen. A detailed analysis of the influence of hydrogen in the fuel is given in chapter 3.3.5.



Figure 13: Dependency of the efficiency on inlet fuel temperature.

### 3.3.2 Length

To investigate the influence of cell length, three sizes (F5, F10 and F20) of the Fdesign were investigated. The F5-design with an active area of approximately 15.5 cm<sup>2</sup> and a MEA-length of 39.4 mm was used as the minimum and the F20design with an active area of approximately 360 cm<sup>2</sup> [44] and a MEA-length of 189.4 mm represented the maximum length analyzed.

Figure 14 shows the increase of both  $CO_2$ - and  $H_2O$ -conversion with increasing cell length. As the relative increase of the  $CO_2$ -conversion is higher than the relative increase in  $H_2O$ -conversion, the required molar fraction of  $CO_2$  in the feed consequently decreases with increasing length.



Figure 14: Dependency of reactant conversion (left) and the amount of CO<sub>2</sub> required in the fuel to achieve a certain syngas ratio (right) on the length of the cell.

As Figure 15 depicts, the influence of the cell length on the efficiency of the cell is very low. However, a clear trend is displayed, as efficiency is decreasing with increasing cell length. This can be explained by a slight decrease in the slope of the conversion graphs with increasing cell length while the electric work is directly proportional to the area the voltage is applied to.



Figure 15: Dependency of the efficiency on the length of the cell.

#### 3.3.3 Velocity

In experimental setups mass or molar flow rates are used to express the amount of fuel and air flowing through the channels. Flow rate is an important operational parameter since it largely impacts the amount of fuel produced and amount of reactant needed. Thus, it also has a major influence on the economic viability of a cell or stack. As the cell size and thereby the channel volumes are constants in the base case of this model, the influence of the flow rate is evaluated by altering the velocity of air and fuel flow simultaneously. The resulting graphs for the molar fraction of  $CO_2$  in the feed to achieve a certain syngas ratio and the reactant conversion are given in Figure 16.



Figure 16: Dependency of reactant conversion (left) and the amount of CO<sub>2</sub> required in the fuel to achieve a certain syngas ratio (right) on the velocity.

A decrease in velocity leads to an exponential increase in conversion for both  $H_2O$  and  $CO_2$ . Due to the relatively higher increase in  $CO_2$ -Conversion, the molar fraction of  $CO_2$  required in the feed to achieve the syngas ratios decreases with decreasing velocity. The impact of lower flow rates on the efficiency of the cell is shown in Figure 17.



Figure 17: Dependency of the efficiency on the velocity.

Since the efficiency drop at low flow rates is not significant compared to other parameters (e.g. temperature) studied, it can be argued that operating the cell at low flow rates is beneficial. The advantages of low flow rates are high conversion and a minimal amount of CO<sub>2</sub> required to obtain the required syngas ratio. On the other hand, this reduces the amount of product gas obtained.

#### 3.3.4 Voltage

Another key parameter in the performance optimization of a SOEC is the applied voltage. It determines the electrical energy supplied to the active area of the cell directly influencing the cell efficiency (see Eq. 2.48). Figure 18 depicts the influence of the applied voltage on the reactant conversion and amount of CO<sub>2</sub> in the feed to obtain a certain syngas ratio.



Figure 18: Dependency of reactant conversion (left) and the amount of CO<sub>2</sub> required in the fuel to achieve a certain syngas ratio (right) on the cell voltage.

It is apparent from Figure 18 that conversion of both reactants gradually increases with increasing voltage, while the molar fraction of  $CO_2$  required in the feed to obtain the syngas ratios decreases slightly with an increasing voltage. This is due to a slight difference in the slope of the graphs of  $CO_2$ - and  $H_2O$ -Conversion. Figure 19 depicts the distinct decrease of efficiency with increasing voltage.

Therefore, even though conversion increases with increasing voltage, it cannot compensate the increase in energy input.



Figure 19: Dependency of the efficiency on the cell voltage.

### 3.3.5 H<sub>2</sub>-Content

In experimental setups an amount of "pure hydrogen is added to the flow to guarantee a reducing atmosphere and avoid oxidation of nickel" [13]. This is due to the potential of nickel being oxidized to NiO at high H<sub>2</sub>O/H<sub>2</sub>-ratios [13], reducing the cells performance due to a decrease in active sites. In many experimental SOEC publications an amount of 10 % hydrogen is used [5,13–15,55,56]. To understand the impact of this experimental requirement, the effect of an increasing molar fraction of hydrogen in the fuel channel is examined. The resulting correlations are shown in Figure 20. Here, the conversion of CO<sub>2</sub> increases and the conversion of H<sub>2</sub>O decreases with increasing H<sub>2</sub>-content. This can be explained with the influence of the WGS-reaction. As H<sub>2</sub> is a product of the WGS-reaction, the equilibrium shifts towards the reactants and reverse watergas-shift reaction (RWGS) becomes more important, leading to the consumption of hydrogen for low temperatures. This also consumes additional CO<sub>2</sub> in the feed and produces additional water, thereby leading to the trends in conversion. Due to the presence of less water in the feed at an obtained syngas ratio of 1.05 (see Figure 20), the influence on the conversion is bigger, leading to a steeper slope.



Figure 20: Dependency of reactant conversion (left) and the amount of CO<sub>2</sub> required in the fuel to achieve a certain syngas ratio (right) on the H<sub>2</sub>-Content in the inlet fuel.

Figure 21 shows a pronounced decrease of efficiency with increasing H<sub>2</sub>-Content in the inlet fuel. The decrease in H<sub>2</sub>O-conversion and the decreasing amount of fuel (H<sub>2</sub>O and CO<sub>2</sub>) in the fuel channel lead to a decrease in the produced fuel, with the energy input ( $W_e$ ) not decreasing proportionally. This decrease in efficiency due to the use of  $H_2$  in the fuel has to be considered when assessing the results of the 3D-optimization (chapter 3.4), since the use of 10 %  $H_2$  reduces the obtained maxima by a few percent in efficiency. This effect becomes obvious here as an efficiency of nearly 75 % is achieved with no  $H_2$  in the feed and Base Case parameters, while the values found in the final 3Doptimization (chapter 3.4) do not exceed 73 %.



Figure 21: Dependency of the efficiency on the  $H_2$ -Content in the inlet fuel.

Another interesting aspect of the use of hydrogen in the fuel is the production of methane in the SOEC. A previous experimental study [57] obtained a significant amount of methane (2.86 %) when running a SOEC at 923 K and 2 V using a reactant composition of 25% H<sub>2</sub>, 25 % CO<sub>2</sub> and 50 % H<sub>2</sub>O diluted in an argon stream. Figure 22 depicts the increase in methane production with increasing hydrogen content in the feed. However, the produced molar fractions are negligible (a maximum of 0.0014 %) The results match the expectations since this simulation uses a lower voltage (1.5 V) higher temperature (1023 K) and lower H<sub>2</sub> in the feed (10 %). All these factors were found to decrease the methane production of a cell by Li [57]. It can therefore be concluded that methane production does not influence the syngas ratios produced in the cell.



Figure 22: Dependency of the amount of methane produced on the  $H_2$ -Content in the inlet fuel.

### 3.4 3D-Optimization

For the efficiency optimization, cell length, velocity and temperature are chosen as the parameters to be optimized. Therefore, the other two parameters of the base case are fixed. For the H<sub>2</sub>-content an amount of 10 % in the inlet fuel is chosen due to the experimental requirement described in chapter 3.3.5, thereby sacrificing a few percent of efficiency. The voltage is fixed at 1.5 V as a tradeoff of low conversion at voltages below 1.5 V and increasing efficiency losses with increasing voltage (chapter 3.3.4).

Based on the results in chapter 3.3, a variation of four steps in a certain analysis window is used for each of the three parameters. Specifically, temperatures of 923 K, 973 K, 1023 K and 1073 K, velocities of 0.3 m s<sup>-1</sup>, 0.45 m s<sup>-1</sup>, 0.6 m s<sup>-1</sup> and 0.75 m s<sup>-1</sup> and cell lengths of 3.94 cm, 8.94 cm, 13.94 cm and 18.94 cm were investigated. This leads to a three-dimensional optimization space with 64 optimization points. For each syngas ratio, a separate optimization is carried out, in which the inlet composition is optimized to obtain the desired syngas ratio. Subsequently, an efficiency calculation is performed and the molar flow rate is calculated. For each temperature, a three-dimensional contour plot is created and the molar flow rate  $\dot{n}$  integrated via color-mapping.

The results of the optimizations show very little differences between the two syngas ratios, as illustrated in Figures 23 and 24. The maxima and minima, in efficiency and yield, are identical for both H<sub>2</sub>/CO-ratios and the differences are less than 1 % in efficiency for the maximum values and approximately 5 % for the minimal efficiencies. This means, that a single planar cell can be optimized to efficiently produce both syngas ratios without changing structural and operational parameters except for the inlet fuel composition. Therefore, in the following only the optimization at a syngas ratio of 2:1 is used to discuss the points of operation.



Figure 23: Results of the three-dimensional efficiency optimization at a syngas ratio of 2:1. The efficiency is plotted against velocity and cell length for different temperatures, while the yield of syngas is included using color-mapping.

The decision for a certain point of operation is largely dependent on the application, the availability of waste heat, electricity costs (if voltage is a parameter), available space, CO<sub>2</sub> availability and individual preferences. This is made clear with displaying the advantages and disadvantages of three points of operation.

If the maximum efficiency of the cell is the priority, then the operation of an 18.94 cm long cell at a temperature of 1023 K and a velocity of 0.3 m s<sup>-1</sup> is the optimum. Even though a velocity of 0.3 m s<sup>-1</sup> leads to the maximum efficiency, increasing the velocity to 0.75 m s<sup>-1</sup> whilst decreasing the efficiency from 72.1 % to 70.6 %, significantly increases the yield from 32.5 mmol h<sup>-1</sup> to 46.2 mmol h<sup>-1</sup>. If the available space is limited, a cell length of 8.94 cm and a velocity at 0.75 m s<sup>-1</sup>, yields an efficiency of 67.7 % and a yield of 30.8 mmol h<sup>-1</sup>, numbers lower but comparable to the most efficient case. In any case, these are tradeoffs that cannot be decided generally and the decision on a certain point of operation depends on the individual requirements.



Figure 24: Results of the three-dimensional efficiency optimization at a syngas ratio of 1.05:1. The efficiency is plotted against velocity and cell length for different temperatures, while the yield of syngas is included using color-mapping.

Another interesting premise is the availability of waste heat, since both the air and fuel streams need to be heated to the inlet temperature before entering the channels. Even though a heat exchanger can be used to transfer heat from the product gas stream to the inlet gas stream, gas heating can still significantly decrease the overall efficiency of the cell. If waste heat is available, the operation at 1073 K can be the preferred choice and a velocity of 0.75 m s<sup>-1</sup> can be used to produce the maximum amount of syngas, since the efficiency losses due to increasing the velocity are negligible. When no waste heat is available, the chosen operational temperature might be 923 K, with the efficiency maximum at a cell length of 18.94 cm and a velocity of 0.3 m s<sup>-1</sup>.

## 3.5 Stack simulation

As described in chapter 2.6, the stack simulation requires the calculation of additional parameters applicable to the whole solid structure and the insulation. To accommodate for the properties of each part of the MEA as well as the interconnect material (Table 2), the parallel and geometric mean model is used (Eqs. 2.44 and 2.45). These include the volume fraction (calculated from Table 1) of each material as a normalization parameter. For the insulation, an Al<sub>2</sub>O<sub>3</sub>-foam with a porosity of 0.9 is used to acquire the parameters. The resulting properties are given in Table 4.

Parameter	Value	Unit	Reference			
Solid						
Thermal conductivity	12.3	J⋅m <sup>-1</sup> ⋅s <sup>-1</sup> ⋅K <sup>-1</sup>	-			
Specific heat capacity	641	J·kg⁻¹·K⁻¹	-			
Density	6522	kg∙m⁻³	-			
Insulation						
Thermal conductivity	0.2	J⋅m <sup>-1</sup> ⋅s <sup>-1</sup> ⋅K <sup>-1</sup>	Estimate from [58]			
Specific heat capacity	1127	J·kg⁻¹·K⁻¹	[49]			
Density	395	kg∙m <sup>-3</sup>	Calculated from [49]			

Table 4: Calculated properties of the stack for the solid phase and the insulation.

A stack simulation of an 18.94 cm long cell at an inlet temperature of 1023 K and a velocity of 0.75 m s<sup>-1</sup> is performed. The dimensions of the stack modeled are 20 channels in parallel and 20 cells stacked on top of each other. Therefore, the width of the stack is 8.94 cm and the stack height is 9.07 cm. The channel density is calculated to be 9.866 cm<sup>-2</sup>. The insulation is chosen to be 2 cm thick and the surrounding temperature is set as 298.15 K. The inlet fuel composition is adopted from the optimized point in chapter 3.4, being 10 % H<sub>2</sub>, 38.07 % CO<sub>2</sub> and 51.93 % H<sub>2</sub>O. A scheme of the resulting stack using adiabatic conditions and allowing for heat loss is given in Figure 25 and 26, respectively. Therein, each channel represents two channels horizontally and vertically. The insulation is not shown. Both stacks were not solved until steady state was reached and the temperature distribution after 1490 s (adiabatic) and 136 s (heat loss) is presented.



Figure 25: Results of the stack simulation under adiabatic conditions.

Figure 25 shows a steady temperature increase in axial direction resulting in a maximum temperature of over 1200 K. The temperature difference of the adiabatically modeled stack amounts to over 120 K compared to the adiabatic simulation of a single cell (Figure 4). However, the temperature differences of single channels at the same axial position are negligible. This means that in an adiabatic simulation of a stack, the position of a cell in the stack does not influence the performance of a cell.



Figure 26: Results of the stack simulation with heat loss.

A significantly lower maximum temperature of 1032 K and a smaller gradient over the cell length (27 K) is obtained when allowing for heat loss in the stack. The beginning and end of the stack show decreases in temperature as no insulation is attached here. For this stack, the deviations of the stack temperature from the inlet temperature are small and the middle of the stack can be approximated as isothermal. The temperature differences between single channels at axial positions are less 1 K at axial positions not close to the inlet or outlet and less than 5 K at the channel inlet and outlet. Therefore, in the stack allowing for heat loss, the position of a channel in the stack is no parameter resulting in significant performance variations. Due to the above described temperature profiles, it can be concluded that the observed heat generation in the adiabatic simulations is balanced by the heat loss of the stack. As a result, lower axial temperature gradients as well as more uniform temperature distributions along the height and width of the stack with little variation from the inlet temperature are obtained. This results goes to show that our approach of using isothermal simulations of single cells to optimize a stack is valid.

# 4 Conclusions and Outlook

A three-dimensional efficiency optimization has been successfully performed for two syngas-ratios and one of the efficiency maxima has been successfully used in a stack simulation. The approach made in this thesis is to isothermally model a unit cell of a SOEC stack during co-electrolysis and optimize cell and operational parameters to efficiently produce syngas for industrial applications. An adiabatic simulation of a single channel is used to depict the two-dimensional temperature profile over the MEA and the temperature distribution over the length of the fuel and air channel. Here, the temperature was found to vary in a very small range, thereby again proving the isothermal approach to be reasonable.

The influence of cell and operational parameters on conversion, efficiency and the required CO<sub>2</sub> in the feed to obtain a certain syngas ratio is described explicitly. The used parameters are temperature, voltage, cell length, velocity and H<sub>2</sub>-content in the fuel. Subsequently, the efficiency optimization of three parameters (cell length, velocity and temperature) for two desired syngas ratios was carried out.

Therein, very little differences between the two syngas ratios are found. Additionally, it is found that high temperatures and long cells lead to the highest efficiencies, while the influence of the velocity is negligible at high temperatures. However, the yield is increasing with increases in all three parameters. The operation of an 18.94 cm long cell at a temperature of 1023 K and a velocity of 0.75 m s<sup>-1</sup> is chosen for the stack simulation to efficiently operate the stack at a reasonable temperature while generating an adequate yield.

The stack simulation is carried out adiabatically as well as considering heat loss. Under adiabatic conditions, temperature increases steadily along the cell length reaching a maximum temperature of over 1200 K, while the temperature gradients over the width and height of the cell are negligible. When heat loss is considered, the maximum temperature obtained is 1032 K while the maximum axial temperature gradients are decreased significantly. Hence, the stack can be approximated as isothermal for axial positions not close to the inlet or outlet. Hence, the isothermal approach of the three-dimensional efficiency optimization using isothermal simulations of single cells is validated. Furthermore, two-dimensional temperature distributions over the MEA are obtained using adiabatic simulations and the influences of MEA configuration and inlet gas velocity on the temperature distributions are examined.

In further studies, SOEC-stack simulations of additional points of operation will be performed and compared to the isothermal optimization. The stack results will then be implemented in a context of an industrial application including a heat recovery system to obtain an overall efficiency including the cost of heat generation. With the integration of the stack into an industrial context, we hope to show that isothermal modeling of a single channel can be used to gain optimization results applicable to an industrial scale, whilst minimizing the computational time required.

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