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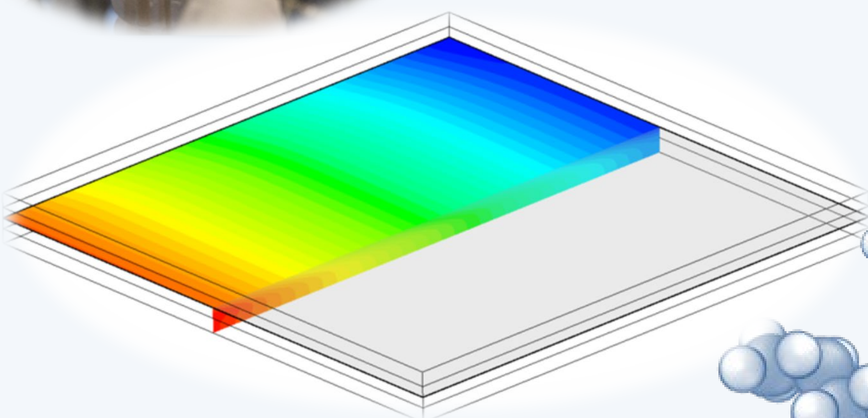
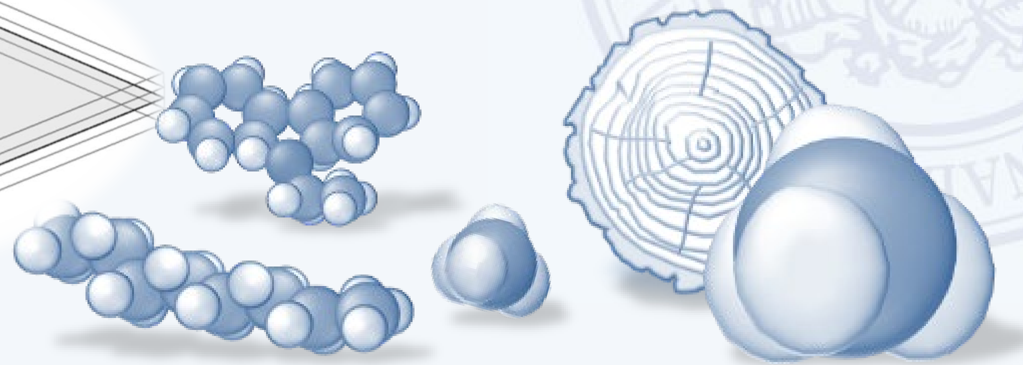
SOFC single cells fed with wood gas: the influence of tar contaminants on cell performance

Yixing Li

Supervisor: Prof. Dr. -Ing. Jürgen Karl





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1. Motivation

- Research background
- Theoretical basics
- Aim of the project

2. Numerical modeling of tar conversion on SOFCs

- Kinetic approaches
- SOFC Fuel Cell With Unresolved Electrolyte Model

3. Experimental setup and results

- Single cell test station and cell housing
- Effect of naphthalene on SOFC at open circuit condition

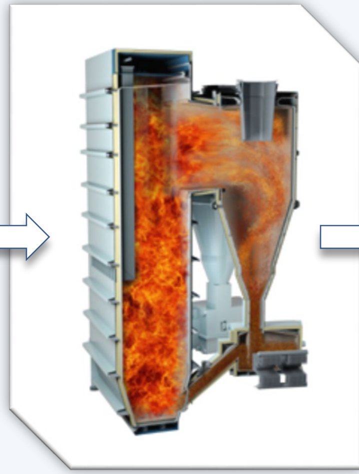
4. Numerical setup and results

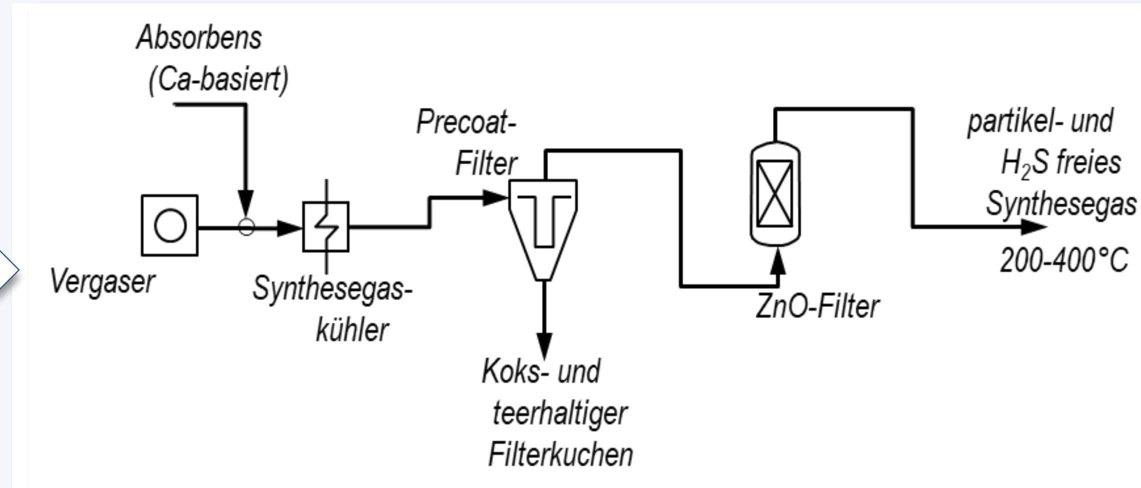
- Comparison between different kinetic approaches
- Comparison between open and closed conditions

5. Conclusion

Research background – biomass integrated gasification-SOFC system

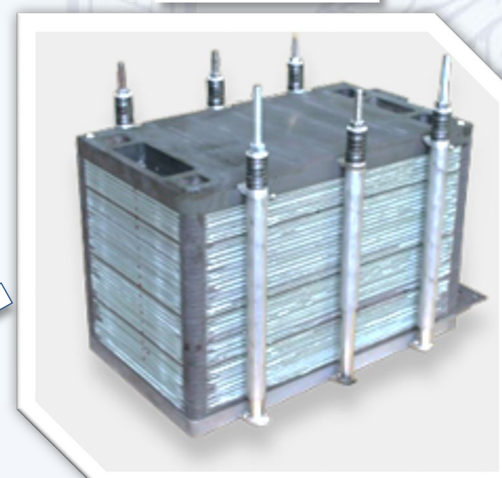

Biomass


Gasification



Gas cleaning

Conversion




Power


Heat

SOFC as an alternative to gas engine in CHP systems:

- High electrical efficiencies
- Higher hydrocarbons could be utilized
  → simpler and cheaper gas cleaning systems

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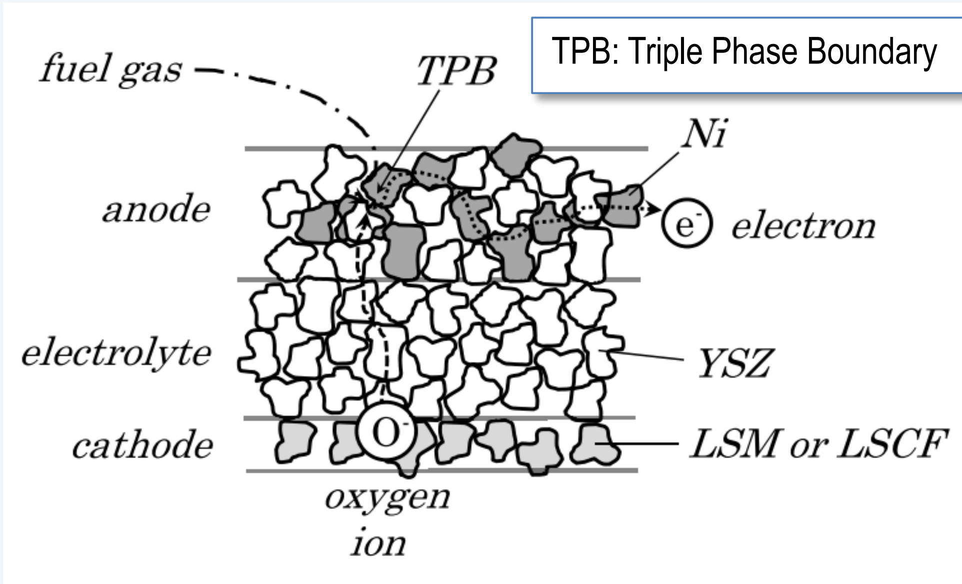
Fundamentals of SOFC – Solid Oxide Fuel Cell



Schematic of SOFC [1]

Anode:

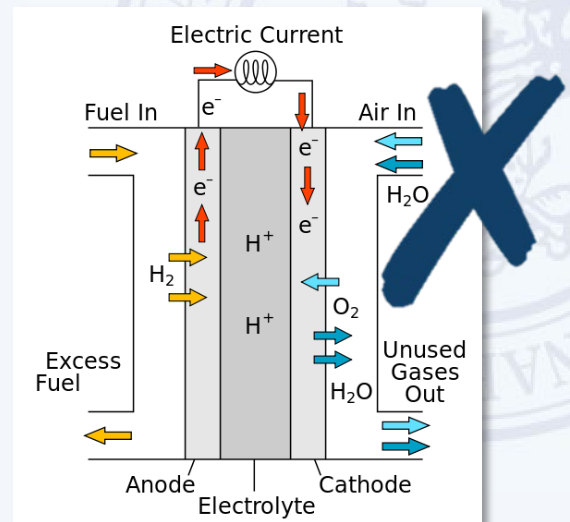
$$H_2 \rightarrow 2H^+ + 2e^-$$
$$CO \rightarrow CO^{2+} + 2e^-$$
$$2H^+ + O^{2-} \rightarrow H_2O$$
$$CO^{2+} + O^{2-} \rightarrow CO_2$$

Cathode:

$$\frac{1}{2}O_2 + 2e^- \rightarrow O^{2-}$$

High-temperature operation (700-1000°C)

- Required to maximise the O^{2-} conductivity of the electrolyte
- ✓ Using various fuels (CO, CO_2, hydrocarbon fuels)
- ✓ Direct internal reforming of hydrocarbons



Schematic of PEM[2]

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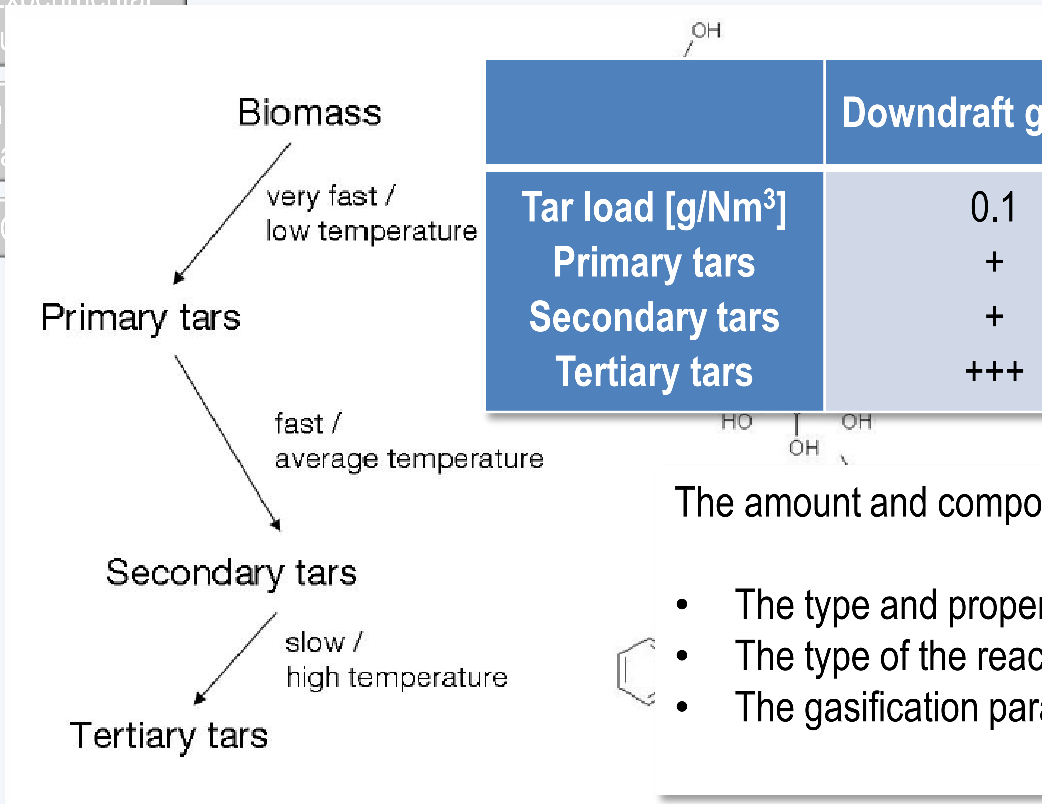
Conversion of tars on SOFC anodes

- **Tar –** from the pyrolysis step of the gasification process of biomass

"Higher-chain hydrocarbons that condense on cooling a biogenic gas"
"All organic components present in the biogenic product gas except gaseous hydrocarbons C1 to C6"
"All organic contaminants with a molecular weight larger than benzene"



Formation of biomass tars [3]

	Downdraft gasifier	Updraft gasifier	Fluidized bed gasifier
Tar load [g/Nm³]	0.1	100	1
Primary tars	+	+++	+
Secondary tars	+	++	++
Tertiary tars	+++	+	++

The amount and composition of tar are strongly dependent on:

- The type and properties of each fuel (biomass)
- The type of the reactor (gasifier)
- The gasification parameters

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Conversion of tars on SOFC anodes

Interaction between tar and SOFC anodes:

\+ Direct electrochemical oxidation

$$C_xH_y + \left(2x + \frac{y}{2}\right)O^{2-} \rightarrow xCO_2 + \frac{y}{2}H_2O + (y + 4x)e^-$$

\+ Steam reforming (SR) with water gas shift reaction (WGS)

$$C_xH_y + xH_2O \leftrightarrow xCO + \left(x + \frac{y}{2}\right)H_2$$

$$CO + \mathrm{H_2O} \leftrightarrow H_2 + \mathrm{CO_2}$$

\+ Dry reforming

$$C_xH_y + xCO_2 \leftrightarrow 2xCO + \frac{y}{2}H_2$$

\- Carbon formation → Degradation

$$C_xH_y \leftrightarrow 2C + \frac{y}{2}H_2$$

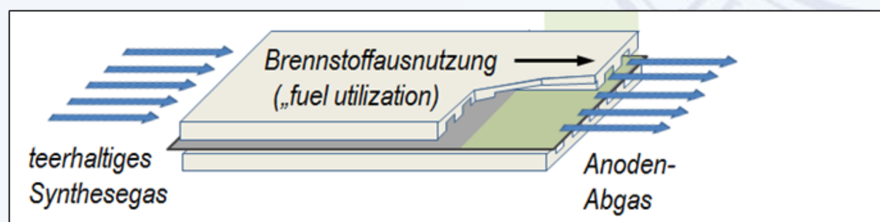
Tolerance level of tar in the producer gas for SOFC: tens to few hundred ppmv

Impacts of tar on SOFC vary with:
- Anode materials
- Operating conditions
- Steam to carbon (S/C) ratio
- Temperature
- Current density
- Interaction with other tars

Further research required:
- ✓ Better understanding of fates of tars on SOFC anodes
- ✓ Suitable operating conditions for long term operation

Purpose of the project

- Investigate the impact of tar model on the performance of SOFC and conversion of tar at different temperatures
- Investigate the interaction between hydrocarbons (e.g. Naphthalene, methane)
- Determinate the temperature-dependent permissible fuel utilization of representative hydrocarbons under load
- Establish the kinetic approaches of steam reforming of tars in CFD model
- Integrate the kinetic approaches into SOFC model



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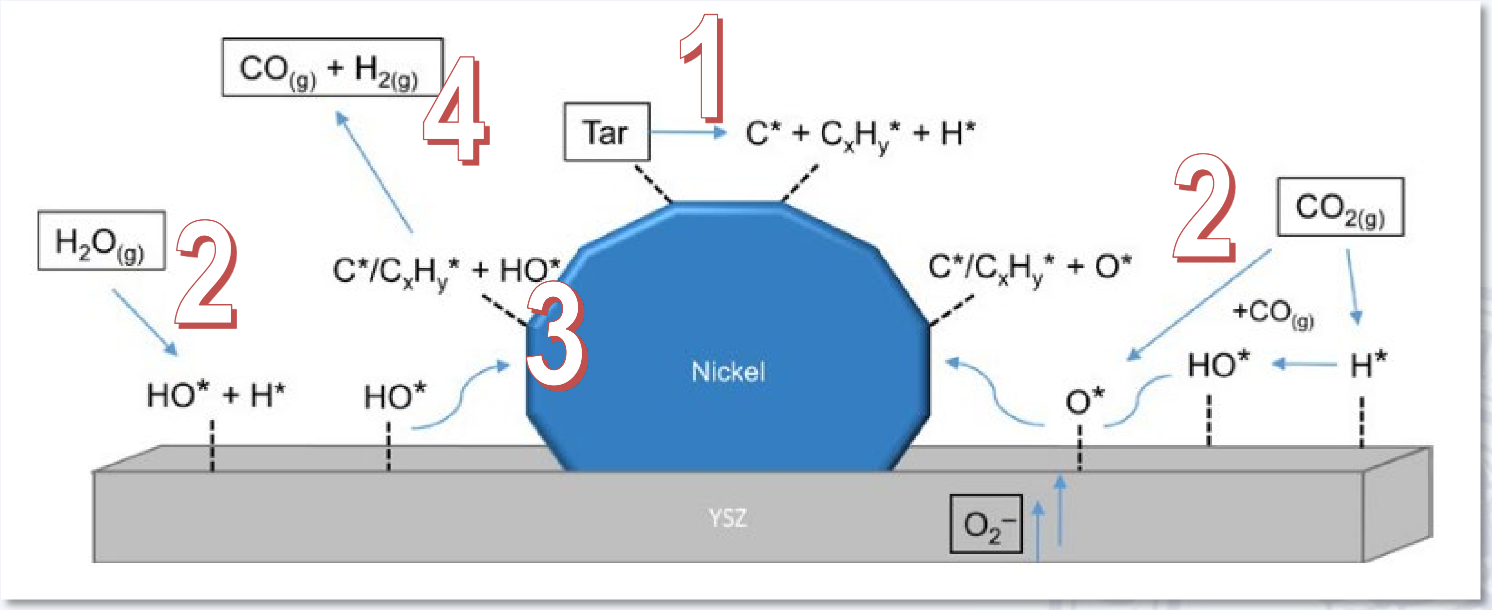
Kinetic approaches of catalyzed tar reforming – reaction mechanism



Tar conversion mechanism on SOFC anodes [4]

1. Hydrocarbons adsorbed on the nickel sites → C_xH_y*, C* and H*
2. Steam and carbon dioxide adsorbs on the ceramic support → H*, HO* and O*
3. The active species react to CO and H_2
4. The gaseous molecules desorb from the active sites

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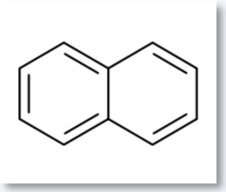
Kinetic approaches of catalyzed tar reforming – reaction kinetics

Motivation
Numerical Modeling
Experimental setup and results
Numerical setup and results
Conclusion

Naphthalene ($C_{10}H_8$) as example



- One lump model: tar disappears by several simultanous reactions

→ Apparent tar conversion rate by single first-order kinetic

Rate equation	Rate constant k [mol s^{-1} m^{-2} bar]		Note
	800°C	900°C	
$r = k \cdot p_{C_{10}H_8}$	0.11	0.33±0.08	Apparent kinetic parameters

- Power law type:

Rate equation	A	E_A [J/kmol]	Note
$r = A \cdot exp(-\frac{E_A}{R \cdot T}) \cdot c_{m,\, C_{10}H_8}$	977.78	5.8·10^{7}	$C_{10}H_8 + 4H_2O \rightarrow C_6H_6 + 4CO + 5H_2$ Nickel catalyzed steam reforming
$r = A \cdot exp(-\frac{E_A}{R \cdot T}) \cdot c_{C_{10}H_8}^{0.2} \cdot c_{H_2}^{0.3}$	4.3·10^{13}	3.32·10^{8}	Nickel catalyzed decomposition

Kinetic approaches of catalyzed tar reforming – reaction kinetics

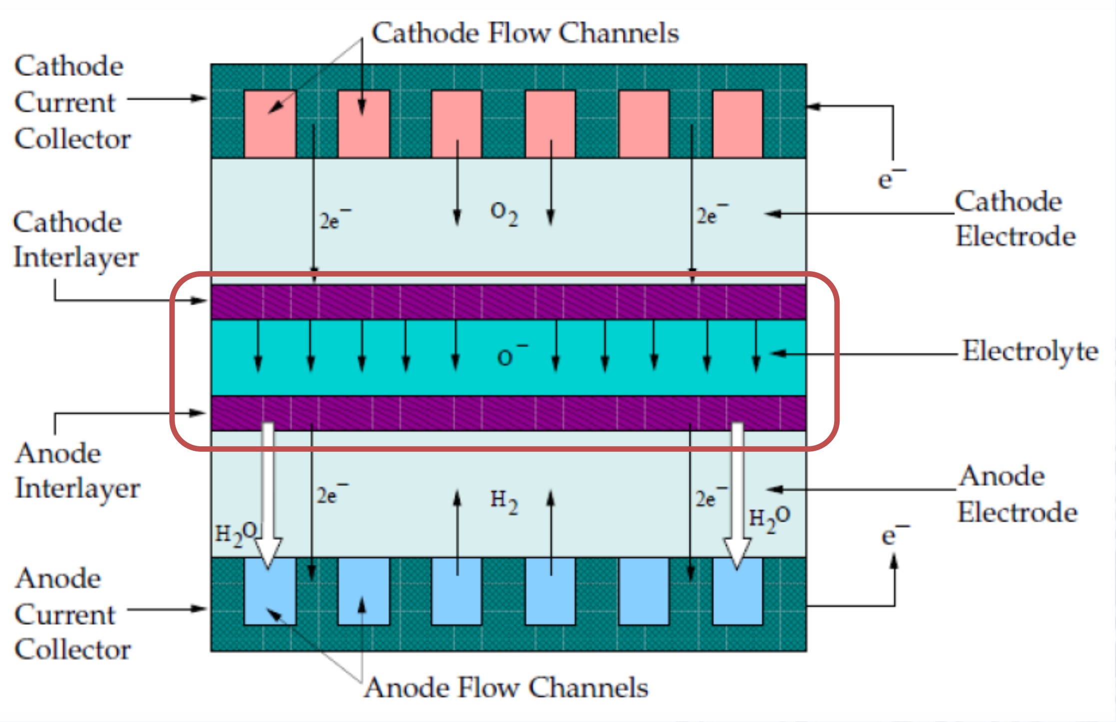
- $C_{10}H_8$ is more strongly absorbed on the nickel catalyst
→ r proportional to occupancy of the adsorption sites

- LHHW (Langmuir-Hinschelwood-Hougen-Watson) type for heterogeneous reactions

Rate equation	Parameters				Note
$r = \frac{A \cdot \exp(-\frac{E_A}{R \cdot T}) \cdot c_{C_{10}H_8}}{1 + K_0 \cdot \exp(\frac{C}{T}) \cdot c_{C_{10}H_8}}$	A	E_A [J/kmol]	K_0 [m³/mol]	C [K]	Nickel catalyzed conversion
	$1.4 \cdot 10^{6}$	$1.49 \cdot 10^{8}$	$1.5 \cdot 10^{-3}$	$1.18 \cdot 10^{4}$	
$r = \frac{k' \cdot p_{C_{10}H_8}}{1 + K' \cdot p_{C_{10}H_8}}$	k'		K' [1/Pa]		Nickel catalyzed steam reforming at lower temperature and elevated pressure
	$9.42 \cdot 10^{-6}$ (649°C) $1.20 \cdot 10^{-5}$ (700°C)		0.042 (649°C) 0.0165 (700°C)		

SOFC Fuel Cell With Unresolved Electrolyte Model

- Unresolved electrolyte: anode and cathode interlayers (TPB) and electrolyte are modeled as a pair of wall and wall-shadow faces – electrolyte interfaces



Schematic of a SOFC [5]

The model simulates:

- ✓ The fluid flow, heat transfer, and the mass transfer in the flow channels and in the porous electrodes
- ✓ The transport of the current and and the potential field in the porous electrodes and in the solid conducting regions
- ✓ The electrochemical reactions at the electrolyte interfaces

Details of SOFC Fuel Cell With Unresolved Electrolyte Model

Conservation of mass, momentum

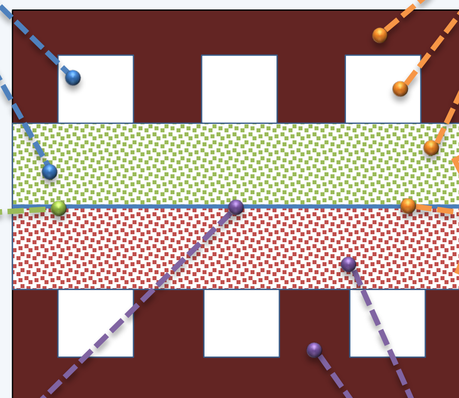
Conservation of energy including ohmic heat generation

Electrochemistry:

$$S_{H_2} = -\frac{i}{2F}$$

$$S_{H_2O} = \frac{i}{2F}$$

$$S_{O_2} = -\frac{i}{4F}$$



Heat of electrochemical reaction:

$$S_h = \frac{\dot{H}_{H_2} + \dot{H}_{O_2} - \dot{H}_{H_2O}}{V_c}$$

Interaction between electrochemistry and electric field:

$$\phi_{jump} = \phi_{Nernst} - \eta_{ele} - \eta_{act,a} - \eta_{act,c}$$

$$\phi_{cell} = \phi_{jump} - \eta_s$$

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Experimental Setup – Gas supply station

Motivation
Numeric Modelin
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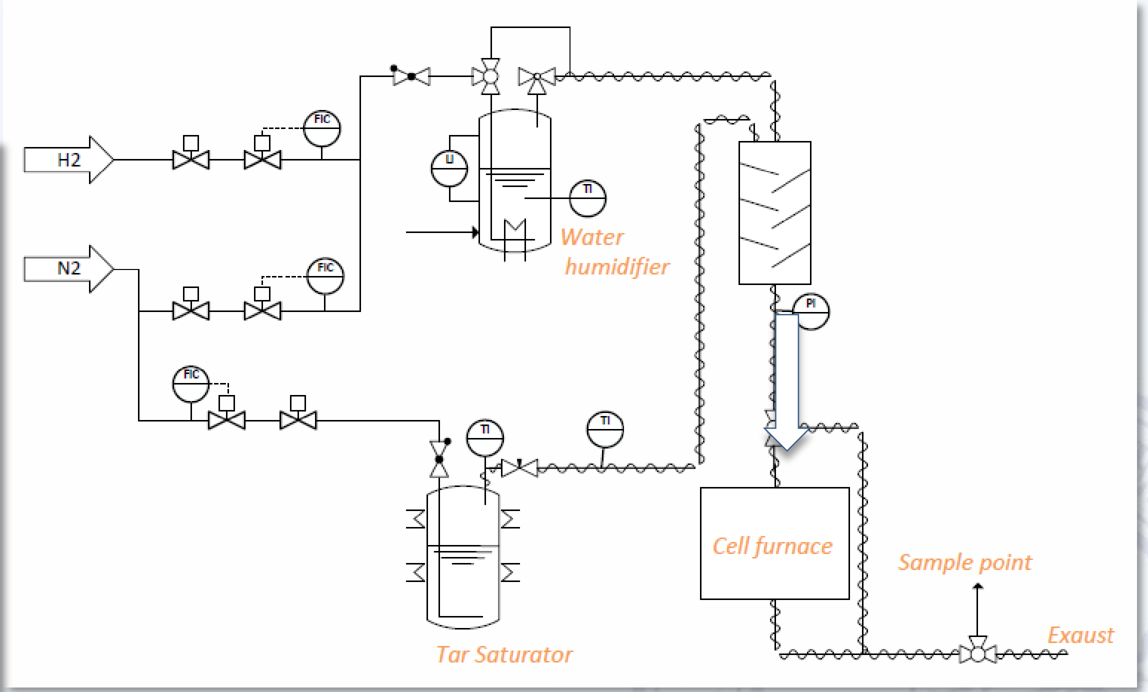

Tar saturator – N_2 as carrier gas saturated with naphthalene

Experimental Setup – Furnace and ceramic housing for fuel cell

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Numerical setup and results
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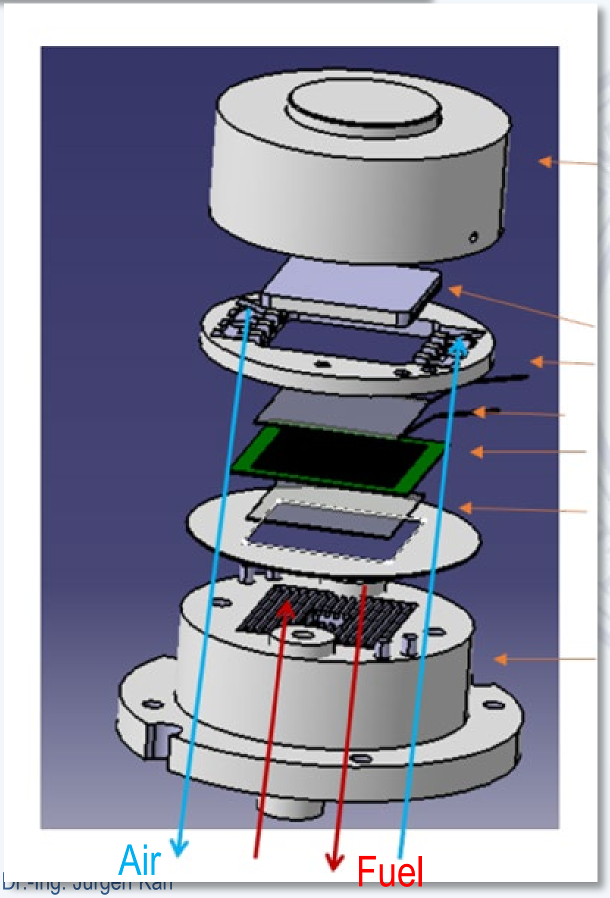
Up to 1000°C



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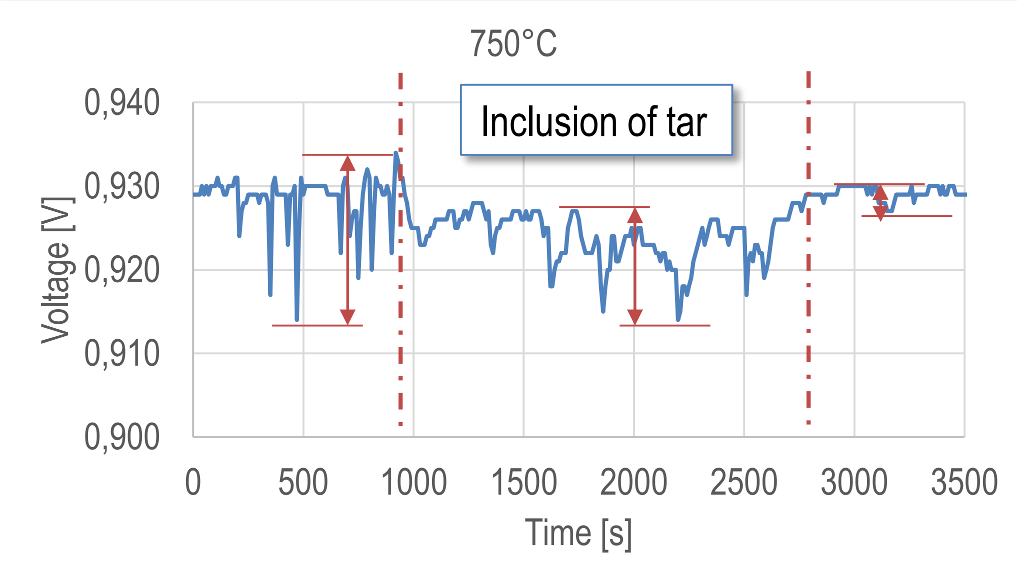
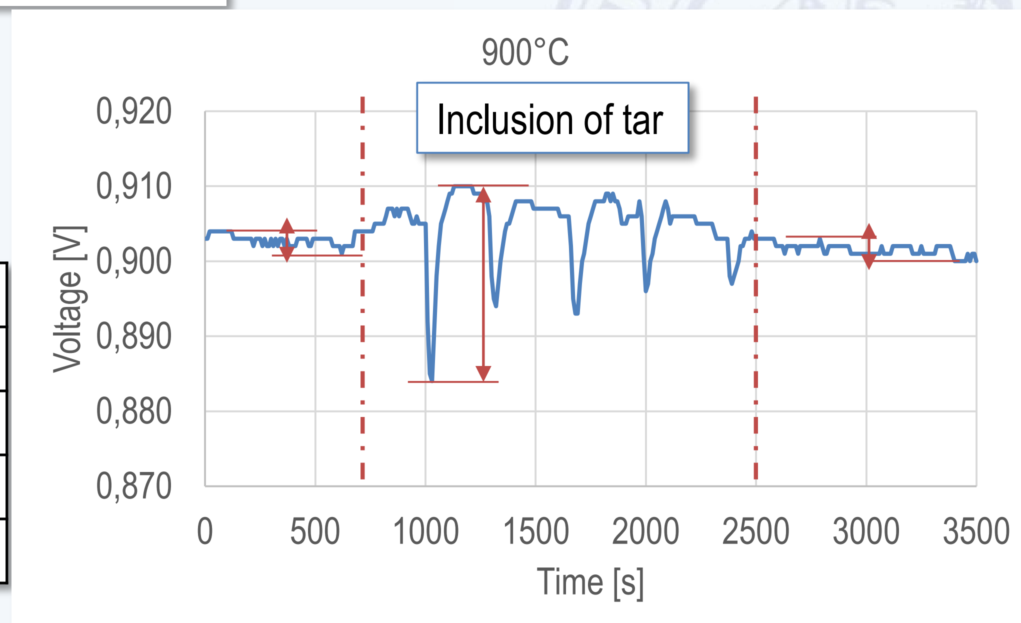
Open circuit voltage in different temperatures



- Naphthalene has a negative effect on voltage of SOFC at lower temperature
- Negetive effects could be recovered once naphthalene is removed
- Probable reasons for oscilation of voltage:

- Unstability of water humidifier and tar humidifier
- Possible condense of naphthalene in the pipeline



Flow rate [ml/min]	600			
Gas composition	H_2	N_2	H_2O	$C_{10}H_8$
	35%	35%	30%	5g/Nm^3
Temperature [°C]	750, 800, 850, 900			
Last	Open circuit			

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Comparison with theoretical Nernst voltage

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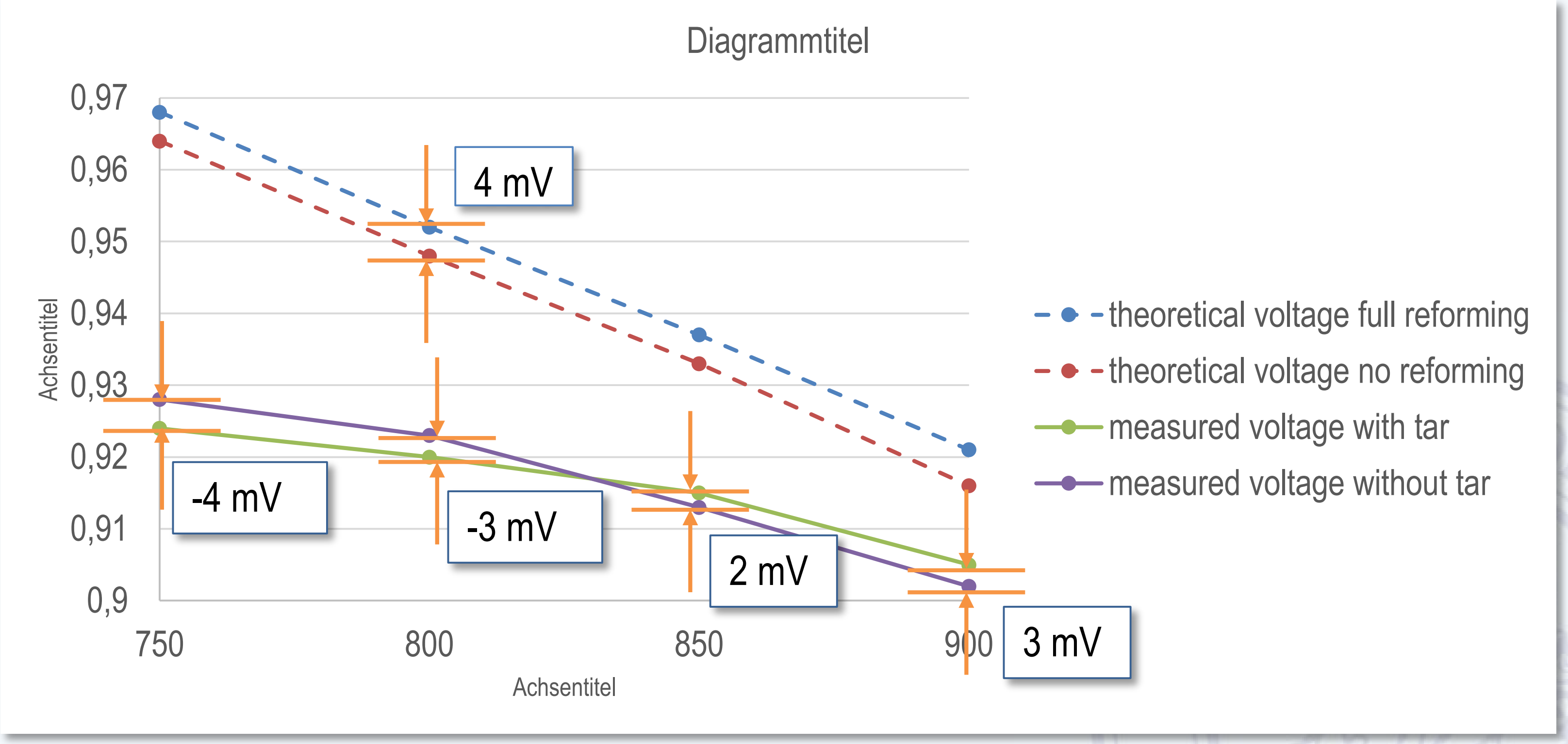
Numerical setup and results
Conclusion



- A full reforming of Naphthalene could lead to a voltage increase of 4 mV theoretically
- Naphthalene conbribute more to voltage at higher temperature
- Naphthalene was not reformed completely
- 30-40 mV difference to theoretical Nernst voltage due to gas leaking

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Numerical model description and setups

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Numerical Modeling
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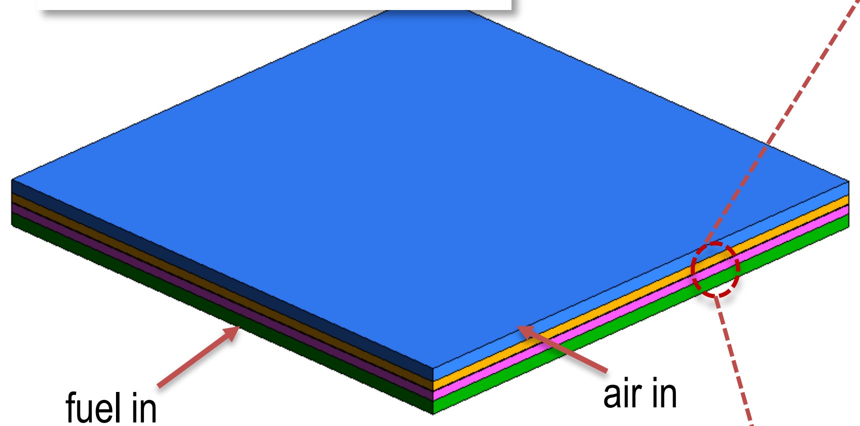
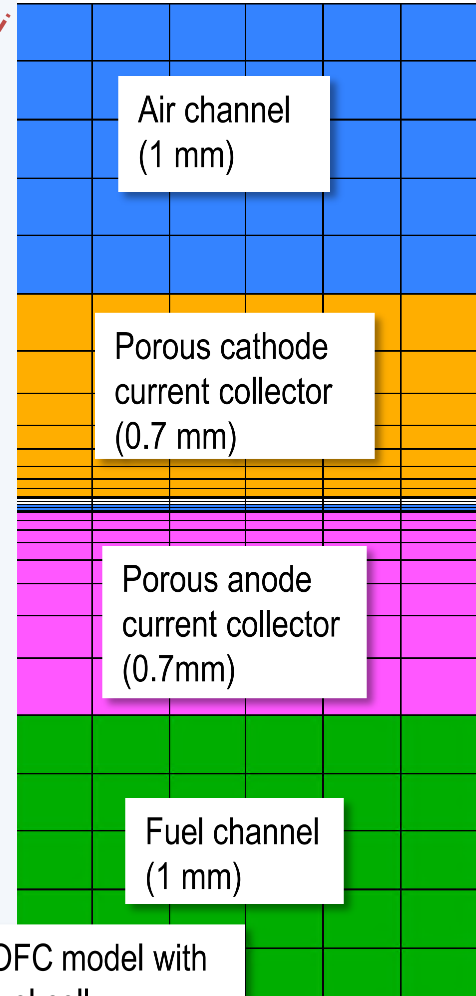
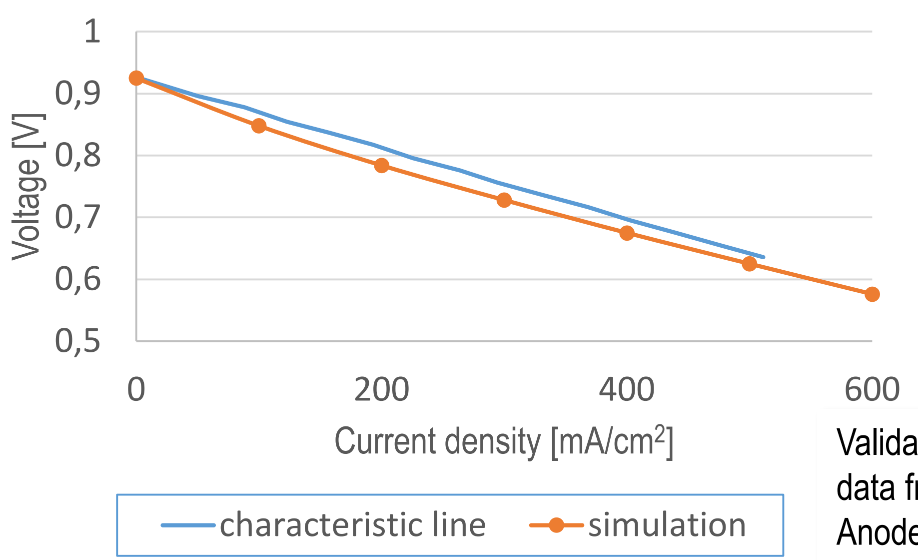
3-dimensional planar SOFC
Dimensions: 40*40 mm^2



- Simplification:
One channel for fuel gas / air flow
Current collectors modeled as porous area





Validation of the SOFC model with data from Kerafol fuel cell
Anode: 1 l/min 50% H_2+ 50% H_2O
Cathode: 1 l/min air
Temperature: 850°C

Numerical model description and setups

- Assumption:
- Only electrochemical reaction of H_2 considered
- 2 species reaction considered:

only in area where Ni exists (anode, Nickel meshes)

$$C_{10}H_8 + 10H_2O \leftrightarrow 10CO + 14H_2$$

$$CO + \mathrm{H_2O} \leftrightarrow H_2 + \mathrm{CO_2}$$

everywhere where CO and H_2O exist

- 2 kinetic approaches of steam reforming used

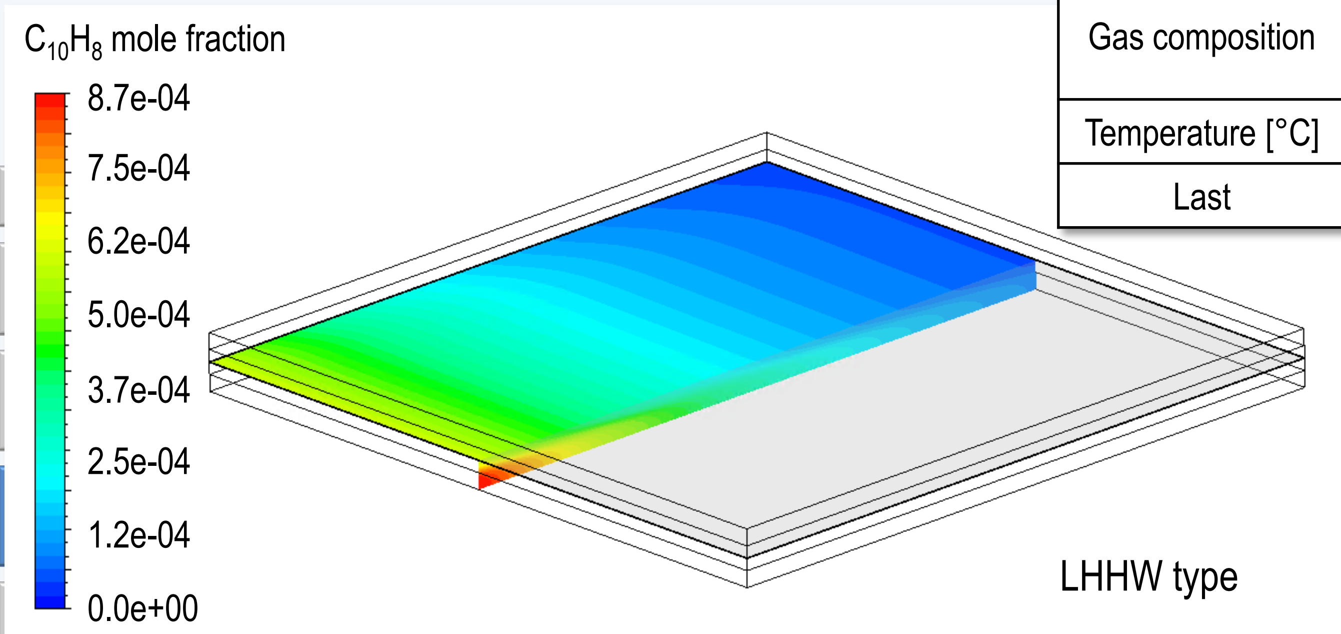
1: LHHW type

$$r = \frac{A \cdot \exp(-\frac{E_A}{R \cdot T}) \cdot c_{C_{10}H_8}}{1 + K_0 \cdot \exp(\frac{C}{T}) \cdot c_{C_{10}H_8}}$$

2: Power law type

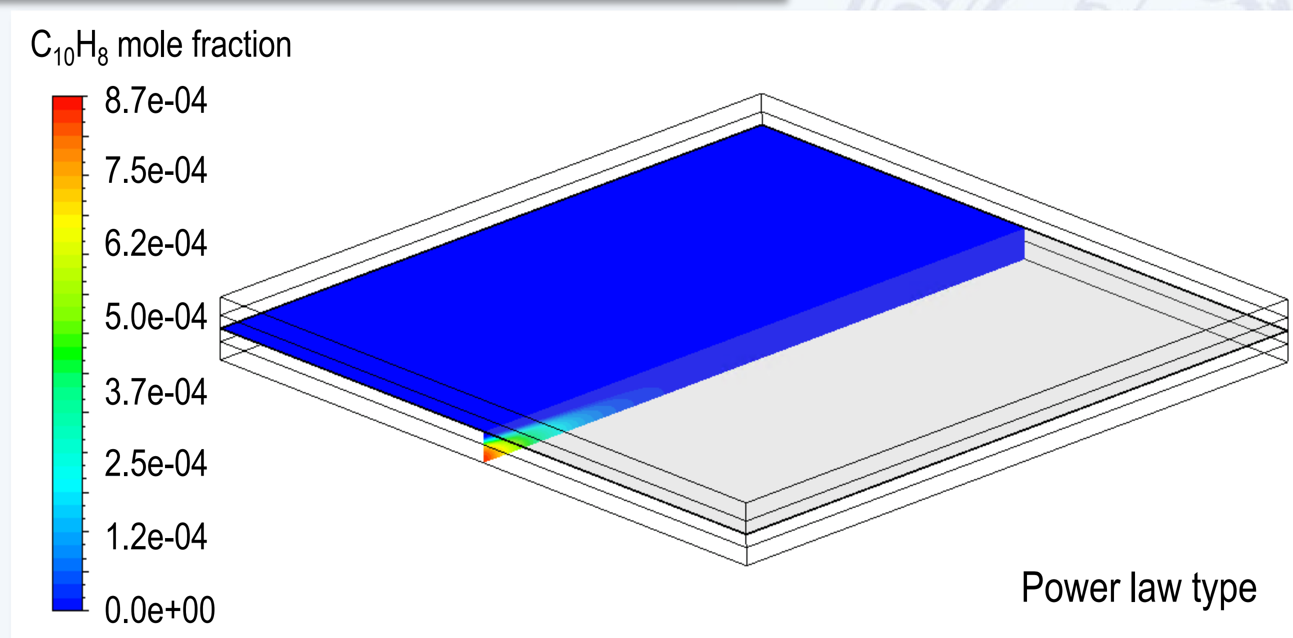
$$r = A \cdot \exp(-\frac{E_{A,j}}{R \cdot T}) \cdot c_{C_{10}H_8}^{0.2} \cdot c_{H_2}^{0.3}$$

Flow rate [ml/min]	600			
Gas composition	H_2	N_2	H_2O	$C_{10}H_8$
	35%	35%	30%	5g/Nm^3
Temperature [°C]	850			
Last	Open circuit			



$C_{10}H_8$ mole fraction on anode/electrolyte interface (half part) and crosssection of anode gas area

- LHHW type: $C_{10}H_8$ is not completely reformed (conversion rate: 89.8%)
- Power law type: $C_{10}H_8$ is quickly and completely reformed



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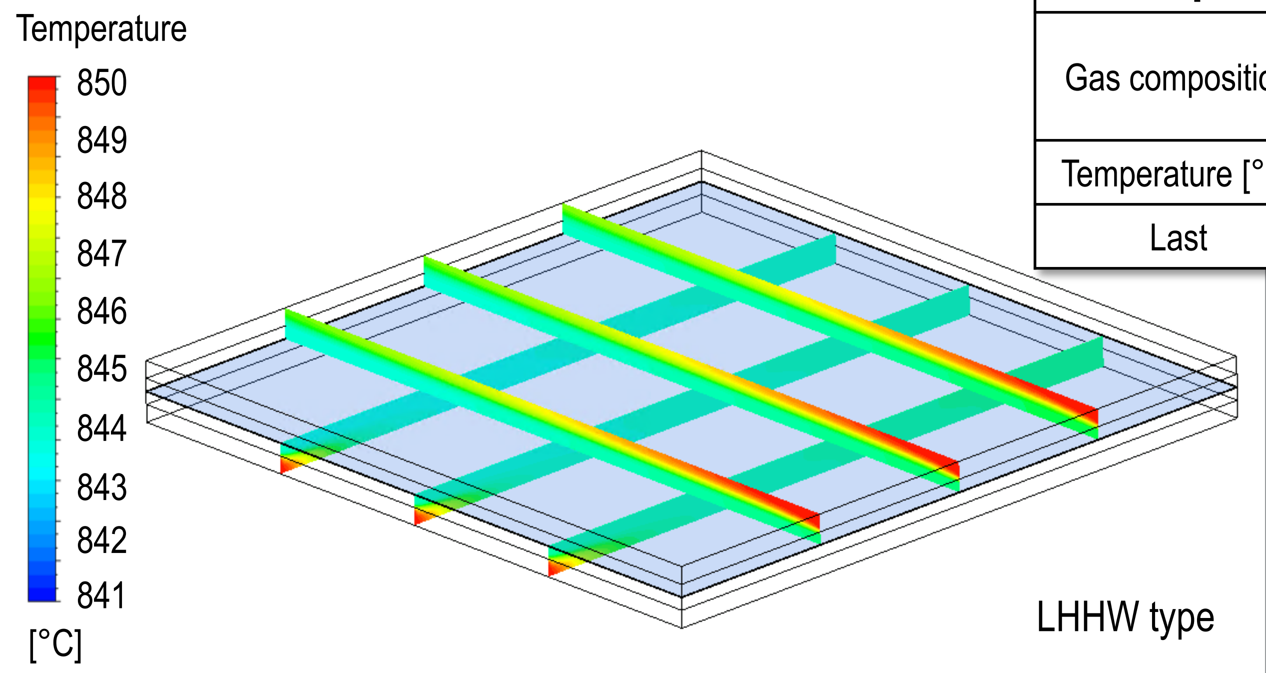
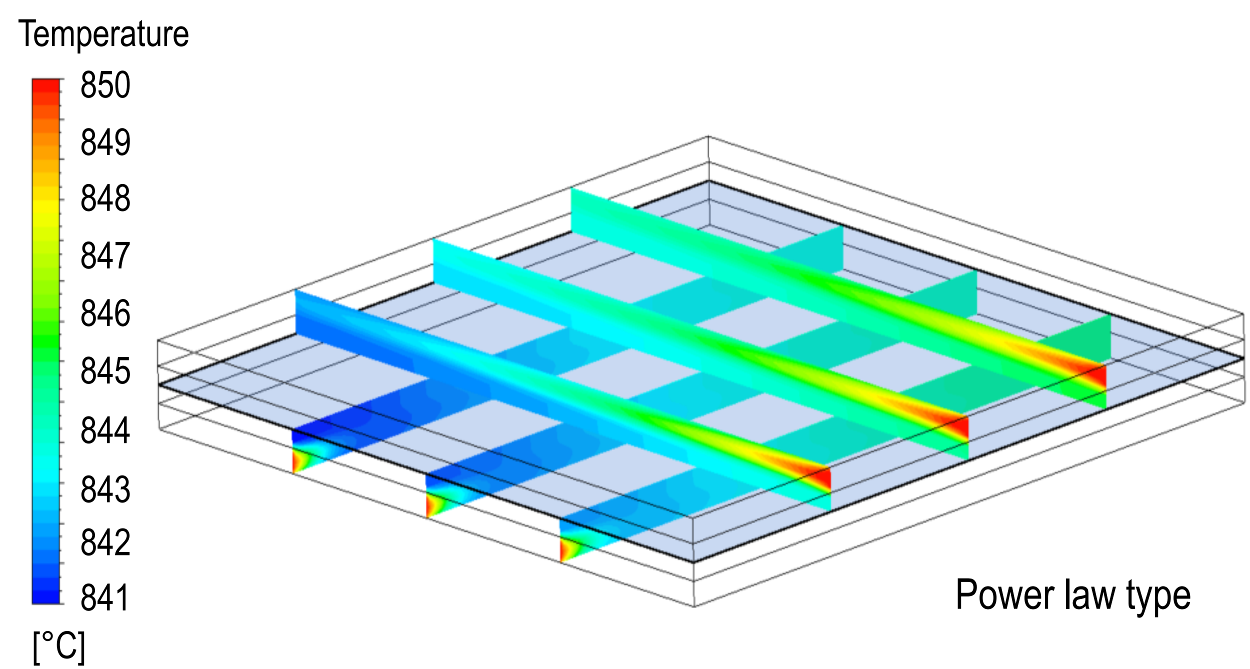
Temperature [°C]	850			
Last	Open circuit			



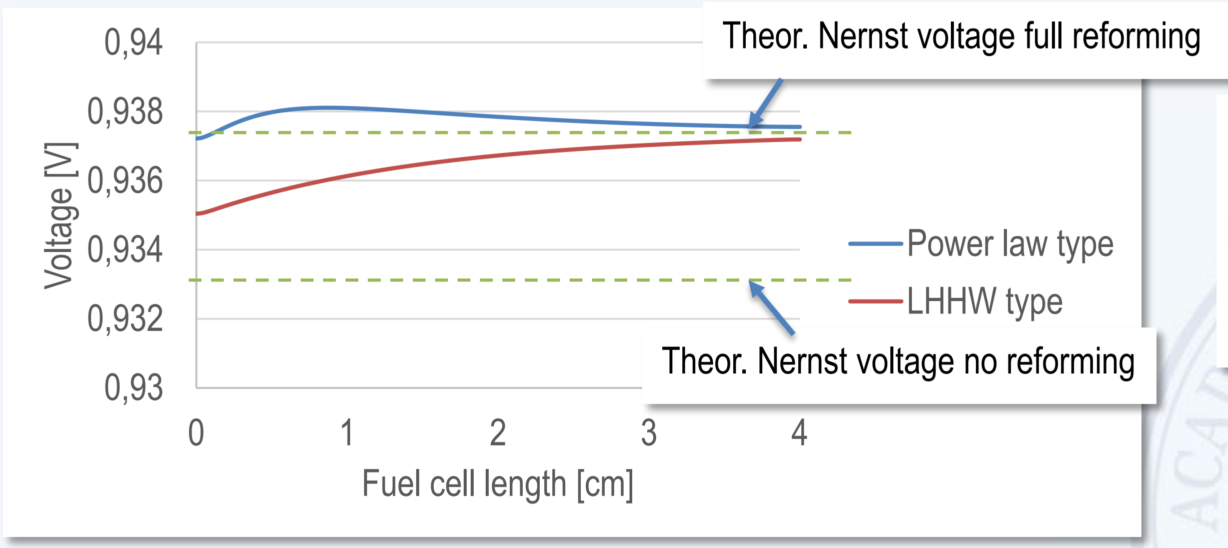
Temperature on several crosssections of cathode and anode gas area

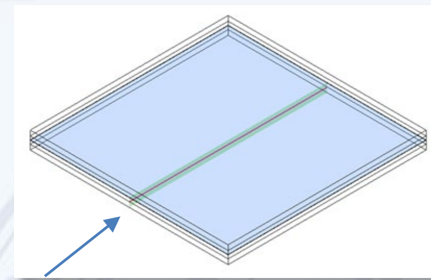
- LHHW type: Distribution of temperature more even
- Power law type: a quick local temperature drop of 9°C



Flow rate [ml/min]	600			
Gas composition	H_2	N_2	H_2O	$C_{10}H_8$
	35%	35%	30%	5g/Nm³
Temperature [°C]	850			
Last	Open circuit			

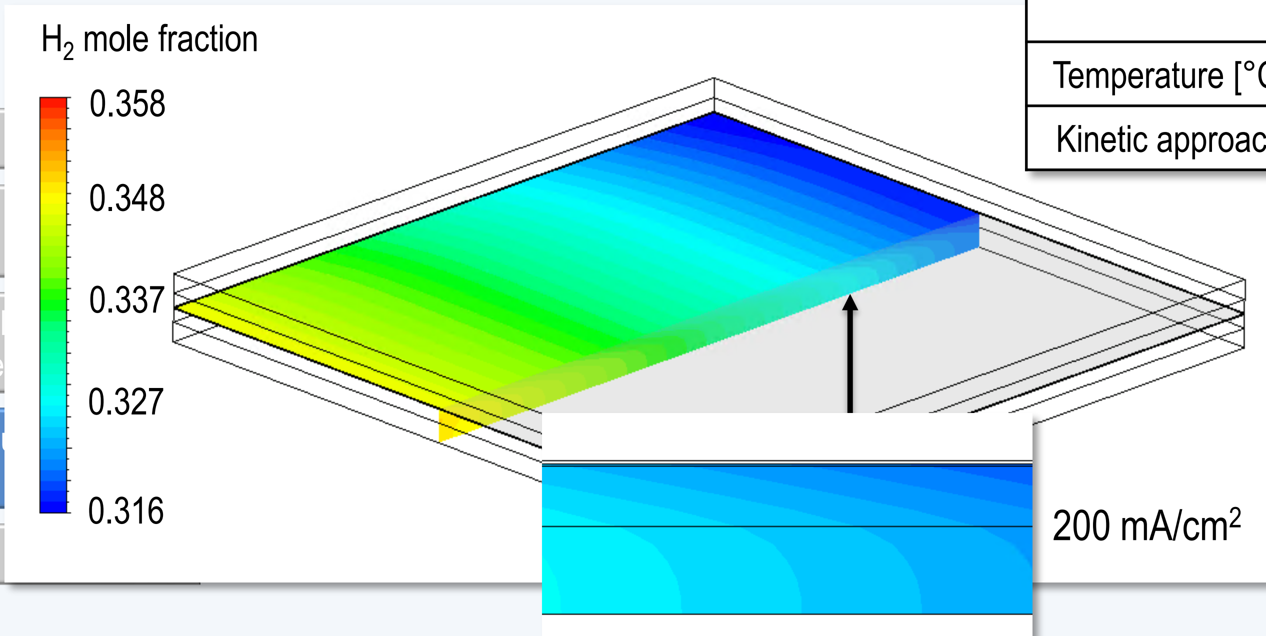
Nernst voltage along the symmetry line on the anode/electrolyte interface





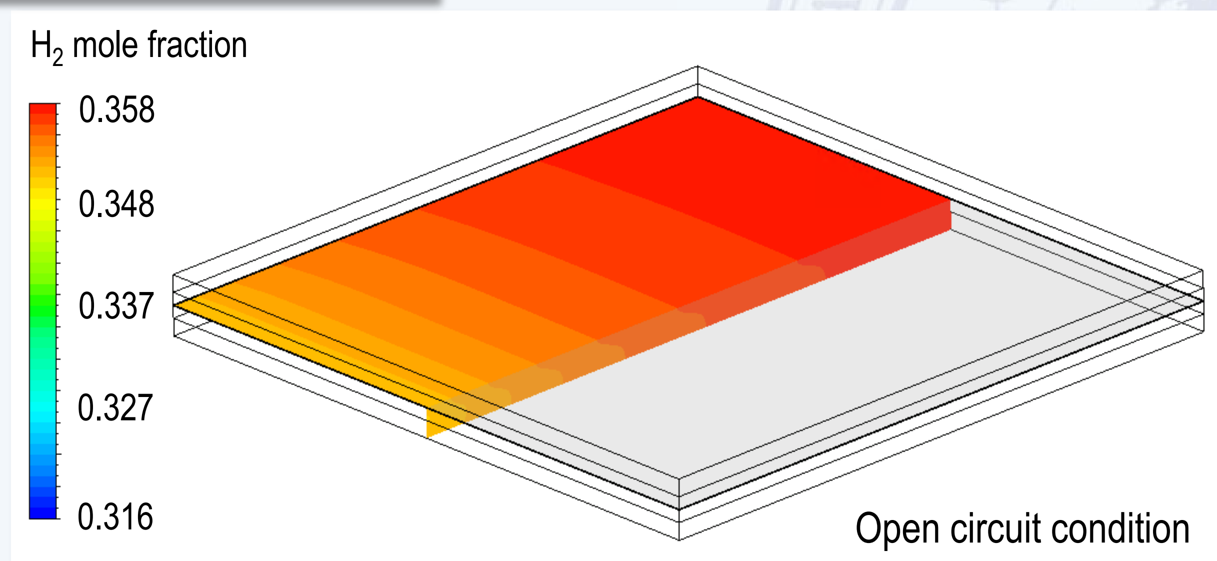
- The resulting ocv of two different kinetic types only varies in couple mVs
- Using LHHW type to simulate the closed circuit condition

Flow rate [ml/min]	600			
Gas composition	H_2	N_2	H_2O	$C_{10}H_8$
	35%	35%	30%	5g/Nm^3
Temperature [°C]	850			
Kinetic approach	LHHW type			



H_2 mole fraction on anode/electrolyte interface (half part) and crosssection of anode gas area

- H_2 is quickly consumed due to electrochemical reaction
- More H_2 depleted in the anode and Ni meshes area as a result of diffusive transport limitations in porous region



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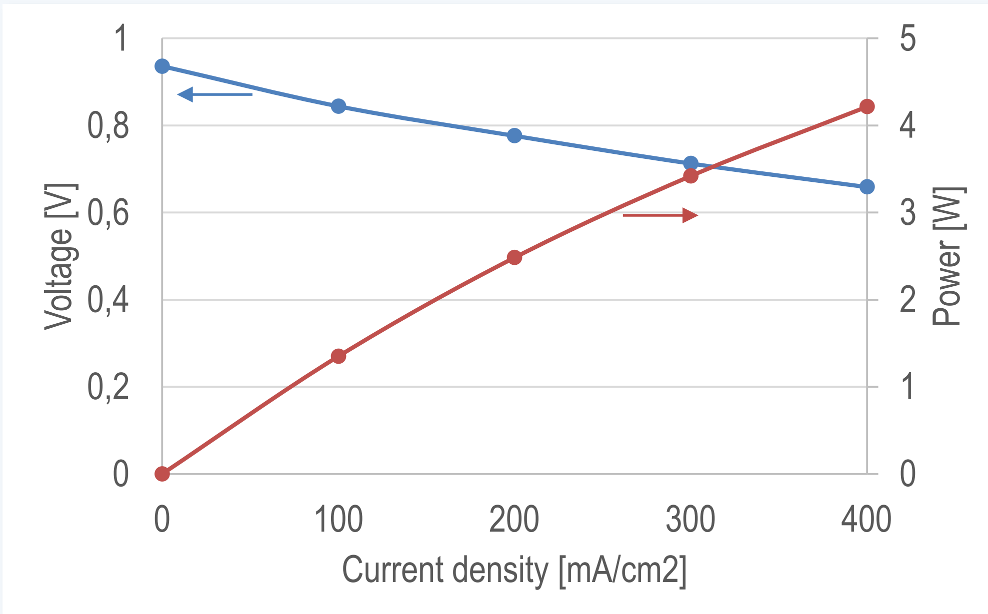
Kinetic approach	LHHW type			

Polarisation curve



- Further validation required

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Conclusion

1. Preliminary work of investigating the effect of naphthalene as model tar on SOFC has been done

- Steam reforming of naphthalene contributes to an increase of ocv at higher temperatures (>800°C)
- The LHHW type of kinetic approach is more plausible to represent the fate of naphthalene on SOFC anodes
- The electrochemical reaction overweights the naphthalene steam reforming at closed circuit condition

2. Further study needed to:

- Investigate the conversion of naphthalene on SOFC
- Validate the model

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Thanks for attention!

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Nernst voltage

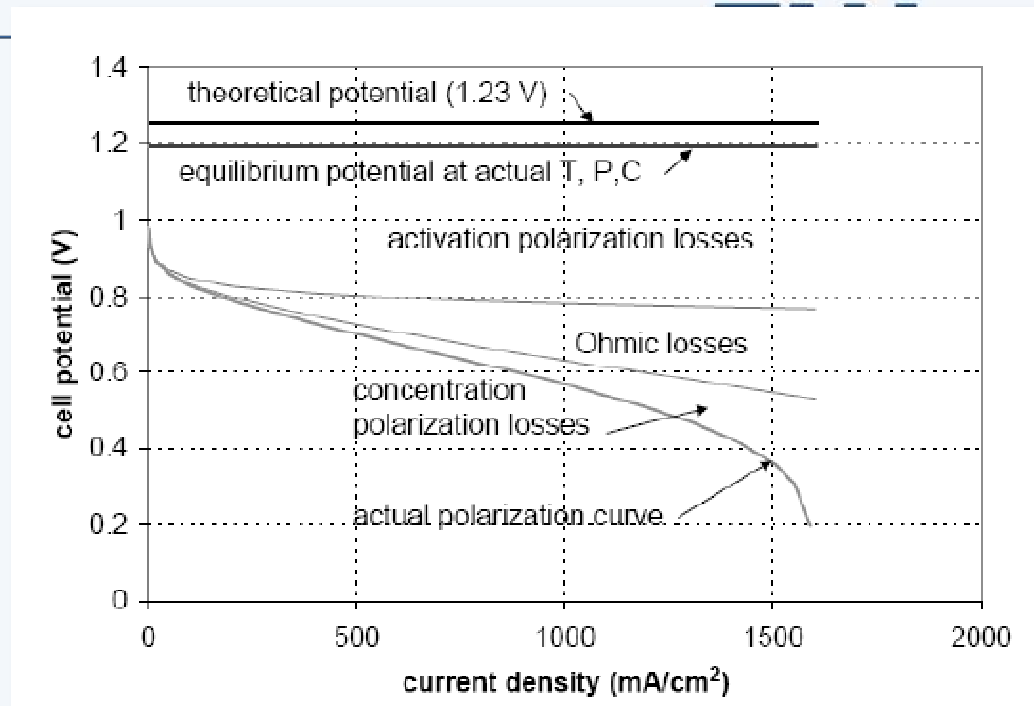
$$U_N = \frac{\dot{n}_{fuel} \cdot \Delta_r G_{(T,p)}}{I} = \frac{\dot{n}_{fuel} \cdot \Delta_r G_{(T,p)}}{\dot{n}_{el} \cdot F} = -\frac{\Delta_r G_{(T,p)}}{z \cdot F}$$

$$= -\frac{\Delta_r G_{(T)}}{z \cdot F} - \frac{R \cdot T \cdot lnQ}{z \cdot F} = -\frac{\Delta_r G_{(T)}}{z \cdot F} - \frac{R \cdot T}{z \cdot F} \cdot \ln\left(\frac{p_{H_2O} \cdot P_0^{1/2}}{p_{H_2} \cdot p_{O_{2,cathode}}^{1/2}}\right)$$

When all gas components are in equilibrium →

$$U_N = \frac{R \cdot T}{z_{O_2} \cdot F} \ln\left(\frac{p_{O_2,cathode}}{p_{O_2,anode}}\right)$$

Polarisation



The potential field has a "jump" condition applied to the two sides of the wall/wall-shadow faces

$$\phi_{jump} = \phi_{Nernst} - \eta_{ele} - \eta_{act,a} - \eta_{act,c}$$

- ϕ_{Nernst}: Nernst voltage
- η_{ele}: ohmic overpotential of the electrolyte
- $\eta_{act,a}$, $\eta_{act,c}$: activation overpotential of electrodes

$$\phi_{cell} = \phi_{jump} - \eta_s$$

- η_s: ohmic loss in the solid conducting regions

Butler-Volmer equation:

$$i = i_{0eff} \cdot \left[e^{\frac{\alpha_a n \eta_{act} F}{RT}} - e^{-\frac{\alpha_c n \eta_{act} F}{RT}} \right]$$

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Material Properties

Electrochemical properties	
anode exchange current density	1500 A m^2
cathode exchange current density	512 A m^2

Electrical properties	
Anode conductivity	$3.33 \cdot 10^5$ (ohm m)$^{-1}$
Cathode conductivity	7937 (ohm m)$^{-1}$
Current collector conductivity	$1.5 \cdot 10^7$ (ohm m)$^{-1}$
Anode contact resistance	$1 \cdot 10^{-7}$ ohm m^2
Cathode contact resistance	$1 \cdot 10^{-8}$ ohm m^2
Electrolyte resistivity	0.1 ohm m

Material properties for gas mixture	
Density	incompressible ideal gas
Specific heat capacity	mixing law
thermal conductivity	ideal gas mixing law
viscosity	ideal gas mixing law
thermal diffusion coefficient	kinetic theory

Material properties	
Anode	
Density	6200 kg m^{-3}
Specific heat capacity	650 J kg^{-1} K^{-1}
Thermal conductivity	10 W m^{-1} K^{-1}
Porosity	0.45
Tortuosity	4.5
Cathode	
Density	6000 kg m^{-3}
Specific heat capacity	900 J kg^{-1} K^{-1}
Thermal conductivity	11 W m^{-1} K^{-1}
Porosity	0.35
Tortuosity	4.5
Anode-cc	
Density	8900 kg m^{-3}
Specific heat capacity	446 kg^{-1} K^{-1}
Thermal conductivity	91 W m^{-1} K^{-1}
Porosity	0.4
Tortuosity	1.5
Cathode-cc	
Density	21200 kg m^{-3}
Specific heat capacity	140 kg^{-1} K^{-1}
Thermal conductivity	72 W m^{-1} K^{-1}
Porosity	0.856
Tortuosity	1.5