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11th Energy Colloquium of the Munich School of Engineering

Utilization of wood gas in a SOFC-stack

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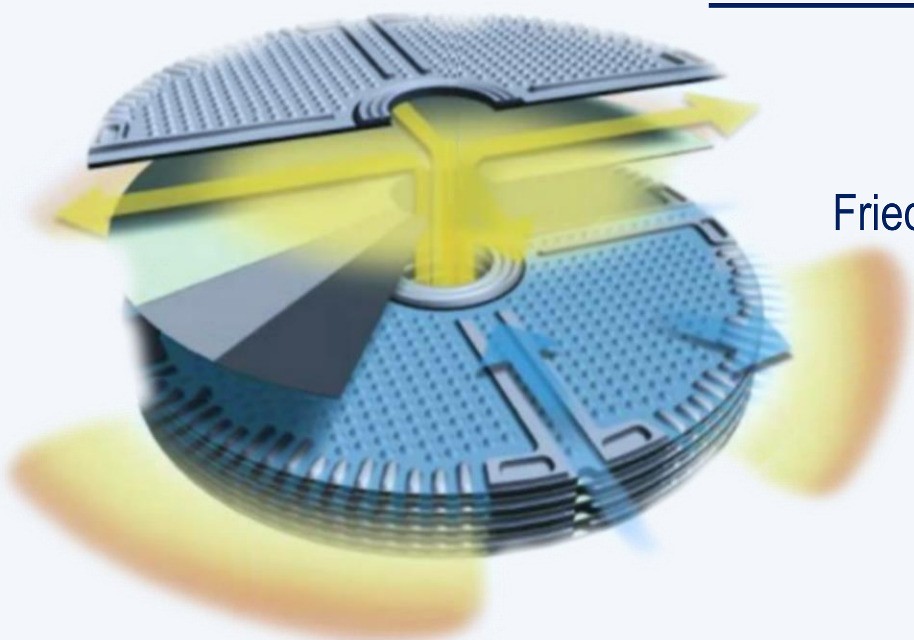

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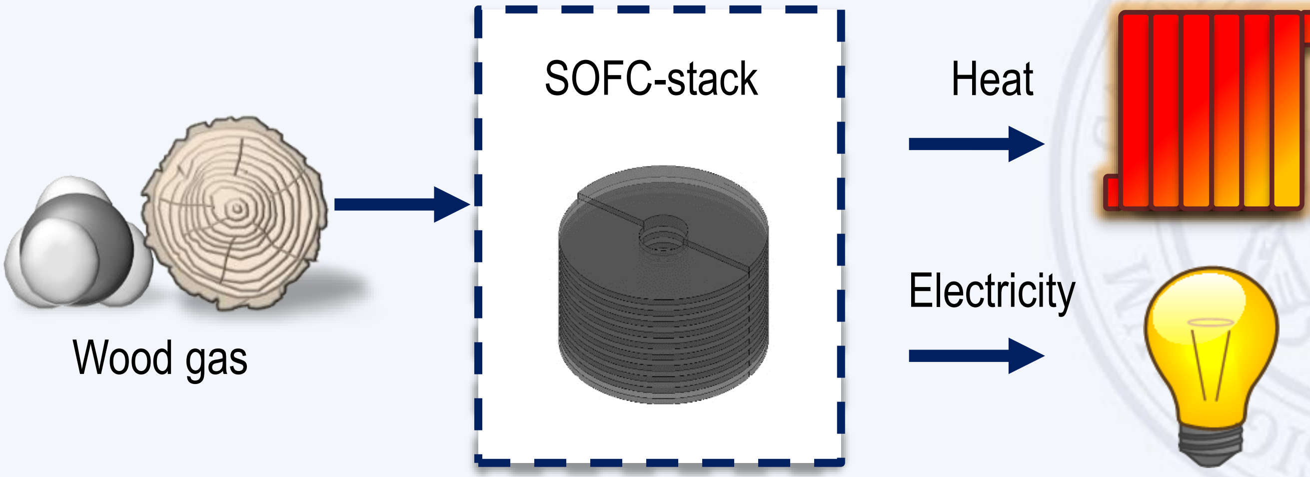
Content

Motivation & Goal

- ***S**olid **O**xide **F**uel **C**ell* offer a large potential for co-generation applications (heat and electricity).
- In a SOFC waste gases can be converted to electricity and heat with minimal environmental damage, challenges are the material degradation and the high costs for developing suitable materials.
- **Goal** of this work is to use electrochemical impedance spectroscopy (EIS) to study the influence of different parameters (e.g fuel, gas flow, temperature, wood gas operation) on the SOFC stack and identify critical operating states during a real wood gas operation.



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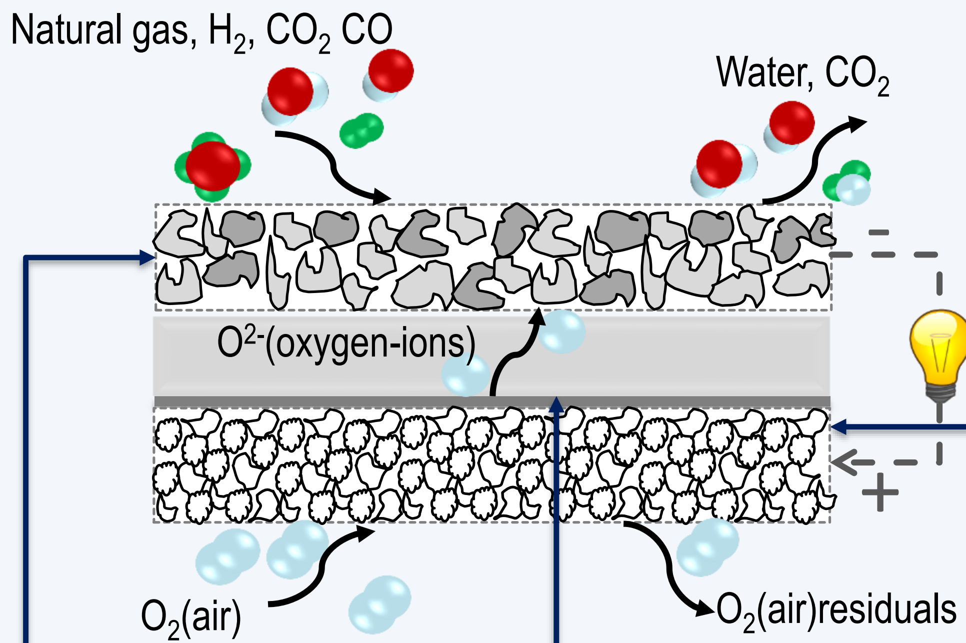
SOFC(Solid Oxide Fuel Cell)



Temperature: 650 °C- 1000 °C
Electrolyte: ceramic (3% mol Yttria-stabilized-zirconia,3YSZ)

At anode the oxidation of the fuel takes place , a large variety of fuels can be used (methane, hydrogen, biogas..)

Electrolyte is permeable to O^{2-} ions at high temperatures (>800°C)

At cathode the reduction of the oxygen takes place , but normally air is used in practical operation

SOFC(Solid Oxide Fuel Cell)

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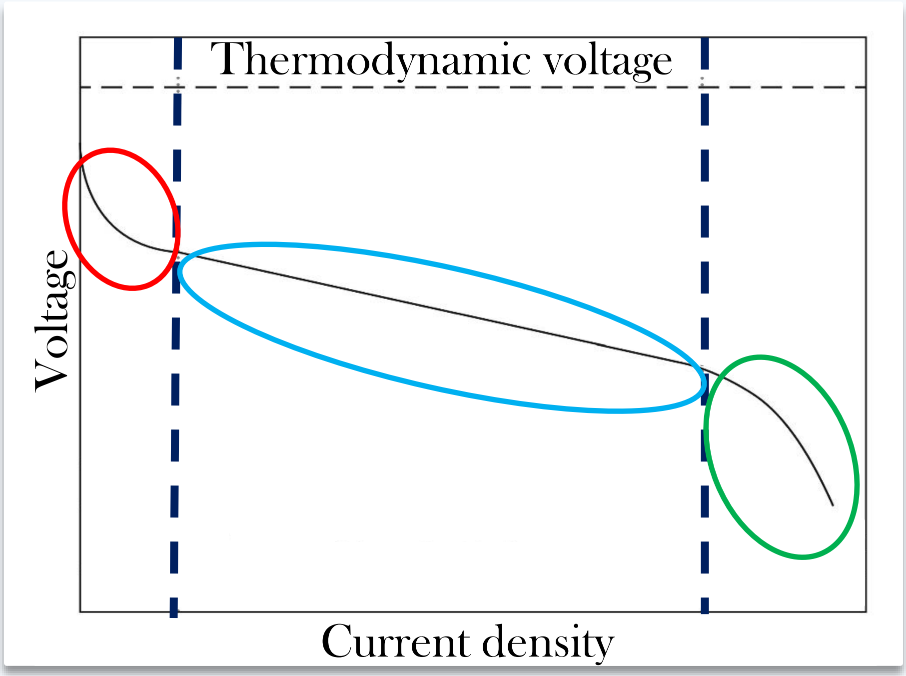
- Characterization of a fuel cell using the voltage-current curve
- Thermodynamically predicted voltage (Nernst potential) of a fuel cell is lower due to unavoidable losses.



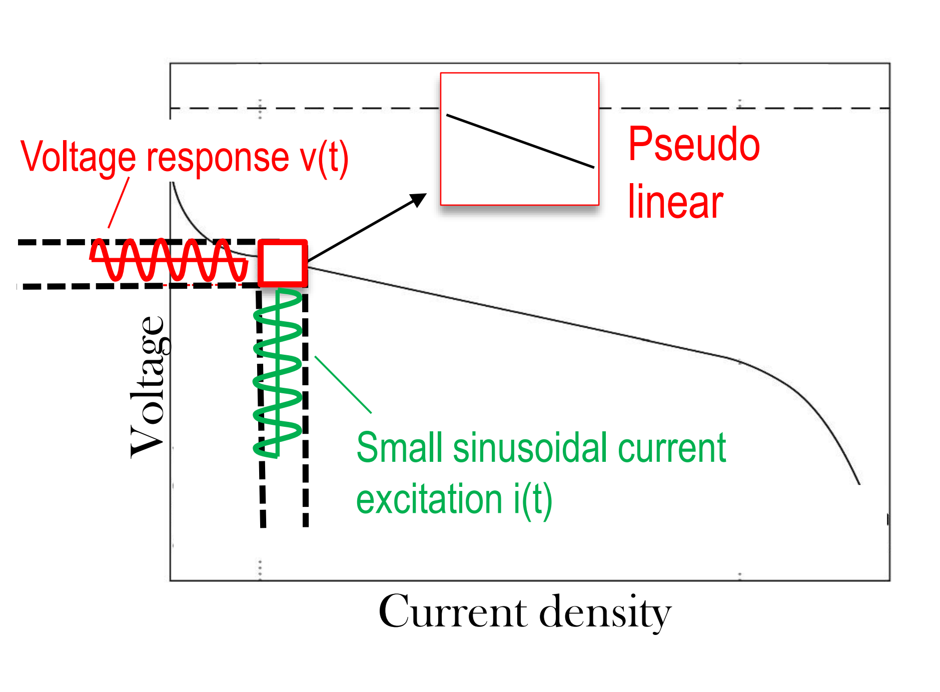
Activation region
Activation losses due to inertia of the cathode reduction at the beginning of the reaction

Ohmic region
Losses due to ionic and electronic conduction, contanct resistances

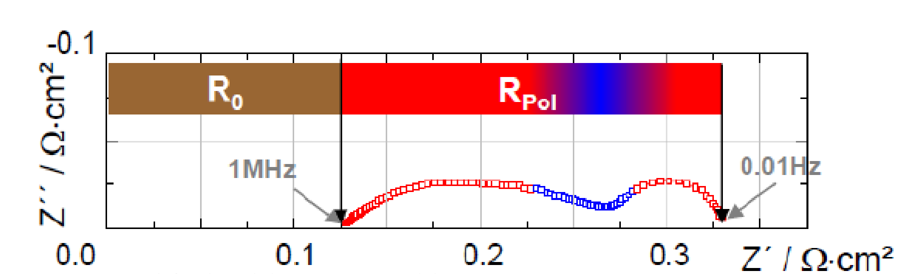
Concentration region
Losses due to the mass transport

Electrochemical impedance spectroscopy

- Electrochemical impedance spectroscopy (EIS) is a established method for characterizing the individual physical processes of a fuel cell
- A periodic current signal is impressed on the system, the voltage response is measured
- Calculation of impedance Z from Ohm's law and phase shift φ



- Nyquist-diagram shows imaginary and real part of the impedance
- Each arc characteristic for a process in the fuel cell



SOFC, ASC anode, 750 °C

Distribution Relaxation Time (DRT)

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Introduction
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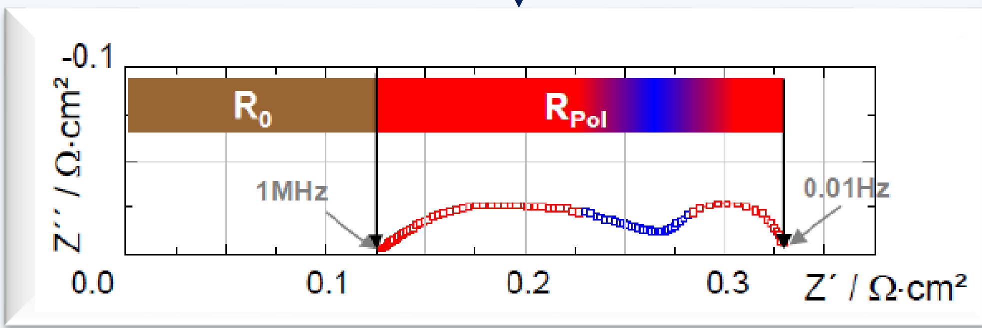
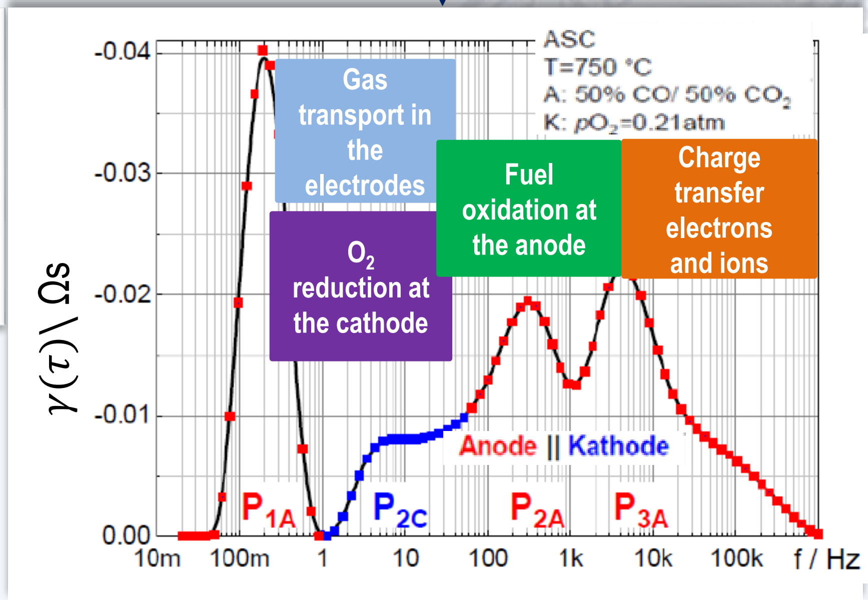
- Each physical process in a SOFC in characterized by a time constant τ known as relaxation time
- The DRT analysis classifies the single processes occurring in a SOFC based on their relaxation times

From **Nyquist-plot** using $\underline{Z}(j\omega) = R_{pol}\int_0^\infty \frac{\gamma(\tau)}{1+j\omega\tau}d\tau$ to **DRT-analysis**



Nyquist Plot, EIS-plot
Anode supported (ASC) SOFC cell



DRT-plot

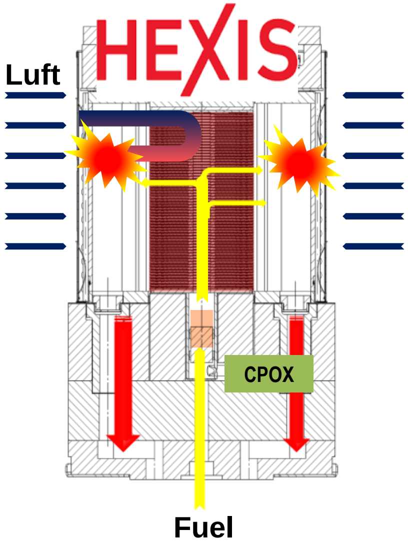
Experimental setup

The experimental setup consists of:

Allothermal gasifier

Fuel : 0,14 kg/h
Temperature: 800°C
Pressure: 0,6 bar
Medium: steam
Gas composition: tars, H_2, CO, CO_2, N_2, CH_4

1 kW_{el} SOFC Stack



N of cells: 62
Temperature: 820°C
Area pro cell: 110 cm^2
Elektrolyte: 3YSZ,
Standard fuel: Natural gas with pre-reformer

Electrochemical unit

Measurement: electrochemical impedance spectroscopy
Device: Frequency response analyser (FRA)
Mode: galvanostatic (current excitation)
AC-Current: 100-200 mA

Department Chemie- und Bioingenieurwesen (CBI) • Lehrstuhl für Energieverfahrenstechnik • Prof. Dr.-Ing. Jürgen Karl

Overview measurements

Overview measurements

Operating parameters

- Fuel: hydrogen and natural gas at 820°C
- Gas flow: natural gas, 2,1 l/min, 2,5 l/min and 2,9 l/min at 820 °C
- Temperature: 2,5 l/min natural gas at 800°C, 820 °C, 850°C

Critical conditions

- H/C ratio variation: syngas mixed with hydrogen to reach H/C 30, H/C 13 and H/C 4 at 820 °C
- Wood gas vs. syngas at 820°C
- Degradation

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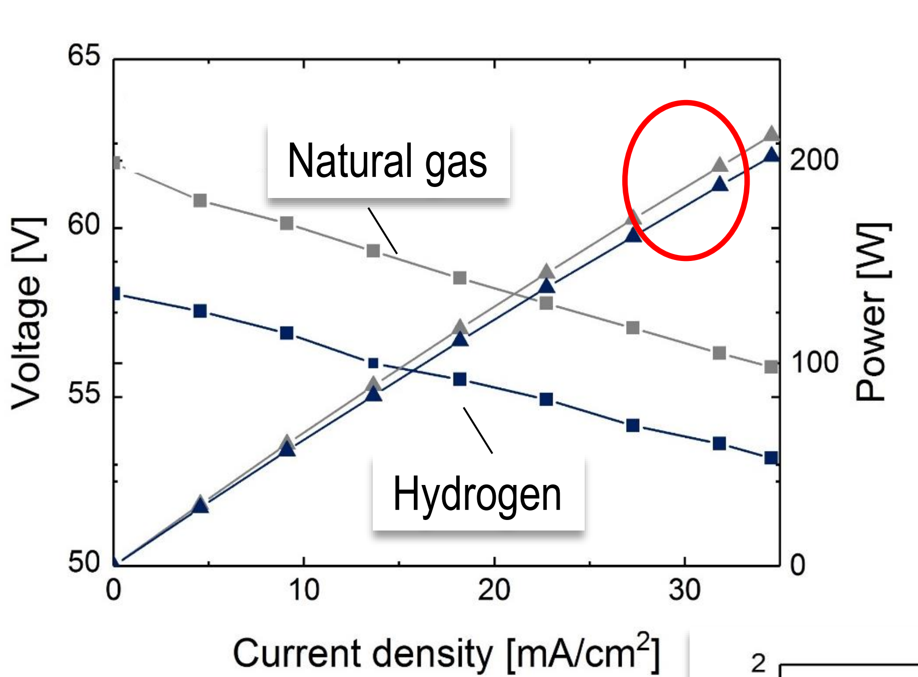
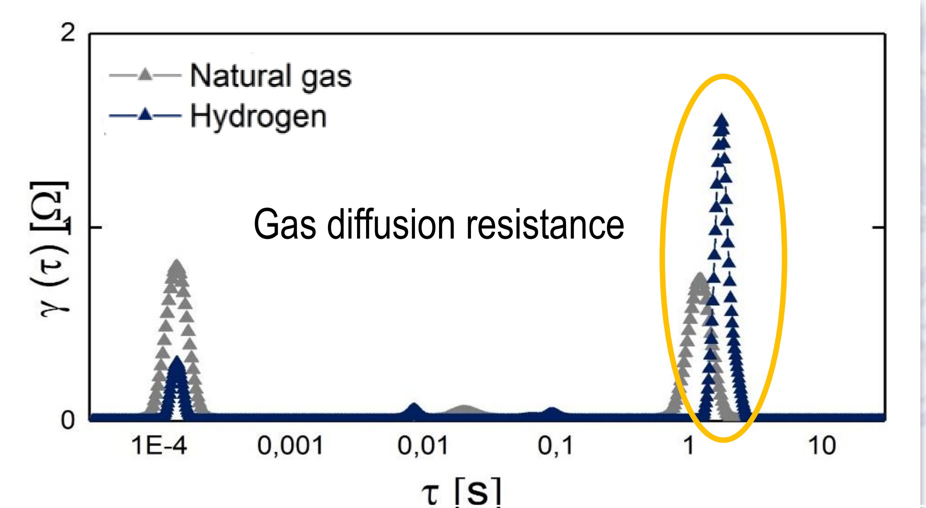
Variation of the fuel



UI/power curve of natural gas and hydrogen at 820 °C

Limitation of the power to 230 W because of the electronic setup

Higher voltage of the stack in natural gas mode than in hydrogen mode due to pre-reforming in CO and H_2 (λ_{air} = 0.27) visible in the UI-curve as well as in the gas diffusion peak



DRT-plot natural gas and hydrogen in OCV, T=820 °C

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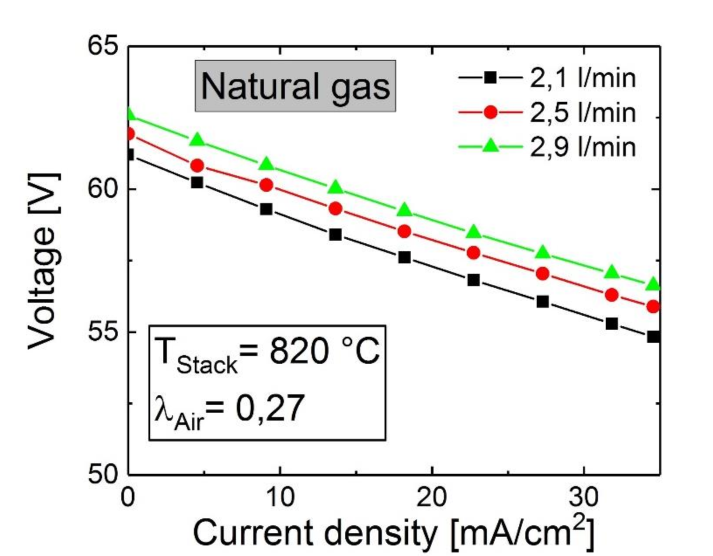
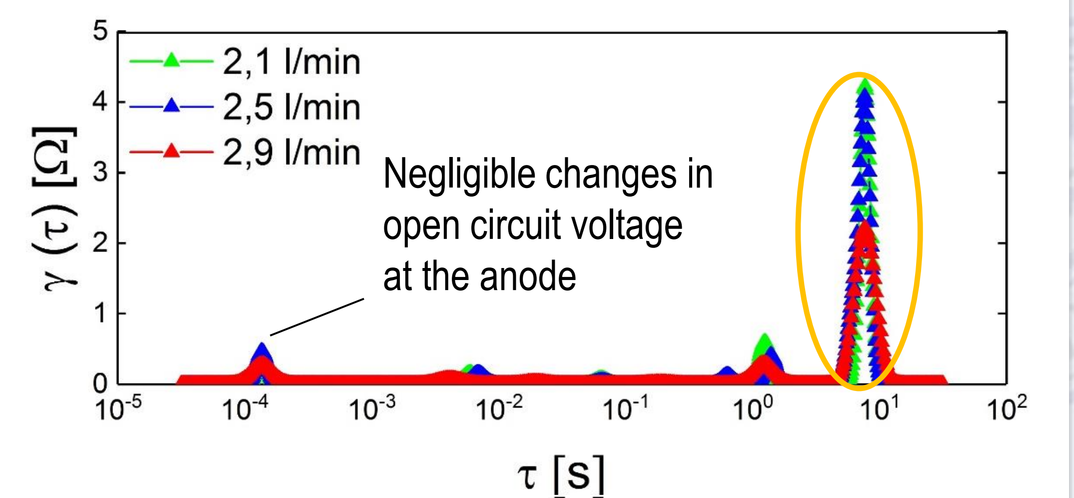
Variation of the gas flow



UI-curve natural gas at different gas flow concentrations, T=820 °C

A growth of gas flow increases the cell performance and the quantity of generated heat

Gas diffusion resistances increase(τ =1-10s) with decreasing gas flow, therefore the performance as well decreases



DRT-plot natural gas at different gas flow concentrations, T=820 °C

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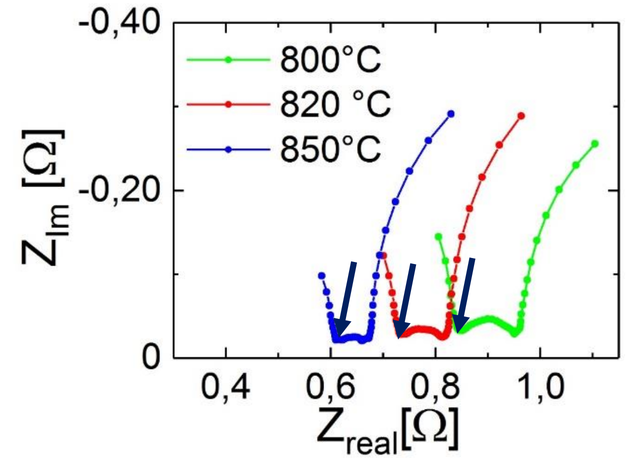
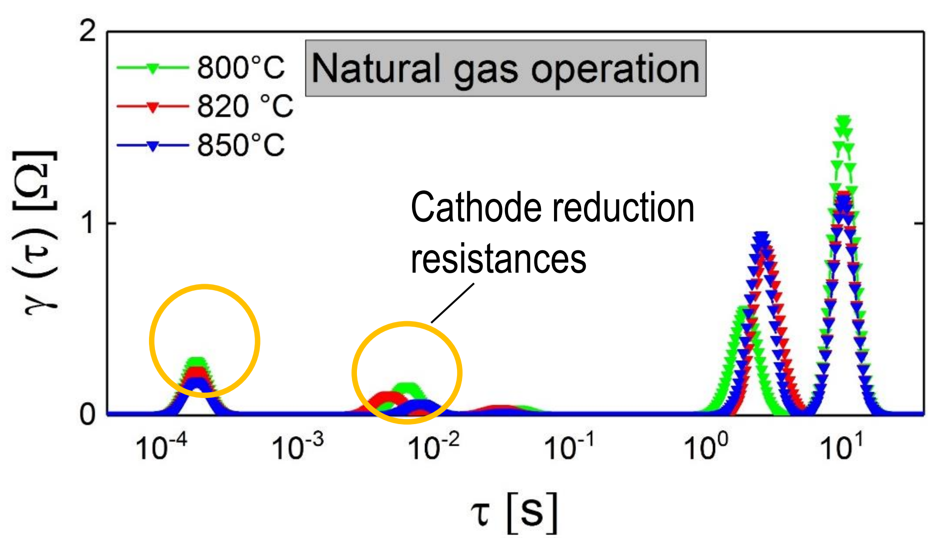
Variation of the temperature

An increase of the temperature results in an increase of the cell performance and the quantity of generated heat. This is caused by a growth of the ionic conduction of the electrolyte with higher temperatures.
In Nyquist plot this corresponds to a decrease the ohmic resistance



Nyquist-plot natural gas at different temperatures, gas flow = 2,5 l/min and OCV.



DRT-plot natural gas at different temperatures, gas flow = 2,5 l/min and OCV .

Decrease of the oxidation resistance at the anode and at the cathode with an increase of temperature due to a sink of kinetics losses

Variation of the H/C ratio

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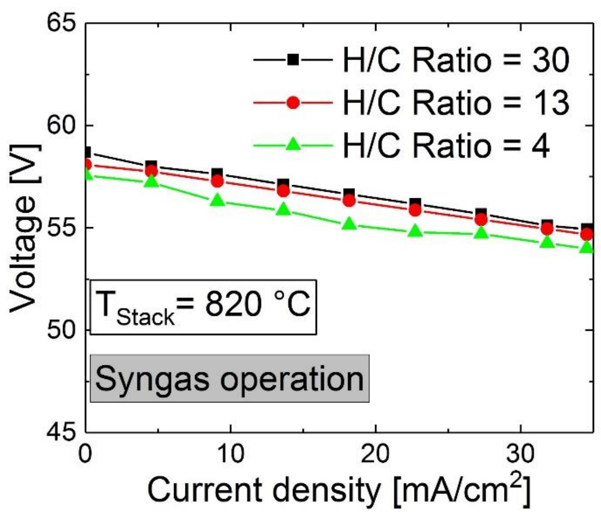
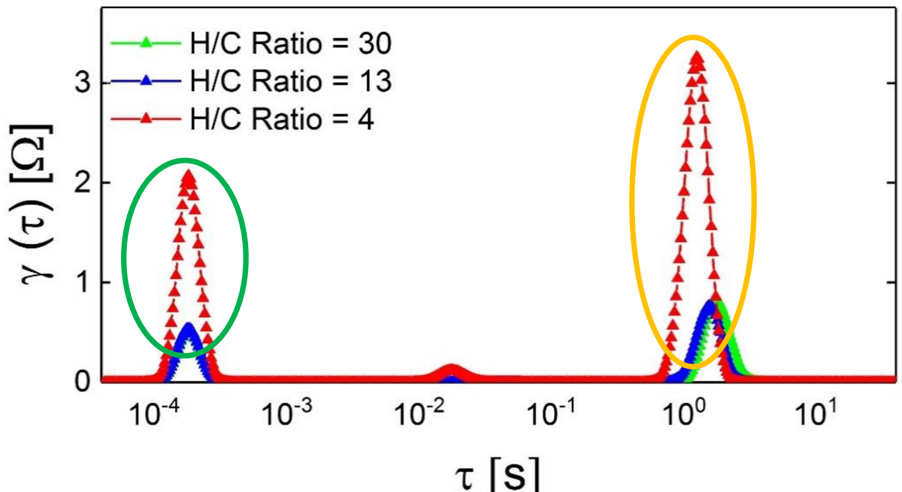


UI-curve from syngas operation, T=820 °C.

Goal of this test this preliminary test is to observe the effect of different H/C ratios on the thermal behavior of the SOFC stack

Small H/C Ratios (higher carbon fraction) mean larger gas molecules increase the CO_2 concentration at the anode and hinder gas diffusion (t= 1-10 s)

Small H/C ratios also mean that more electrons have to be transferred per fuel gas atom, higher resistance for the oxidation process at the anode (peak at t= 10-4 s)



DRT-Plots of syngas operation different H/C ratios, T=820 °C.

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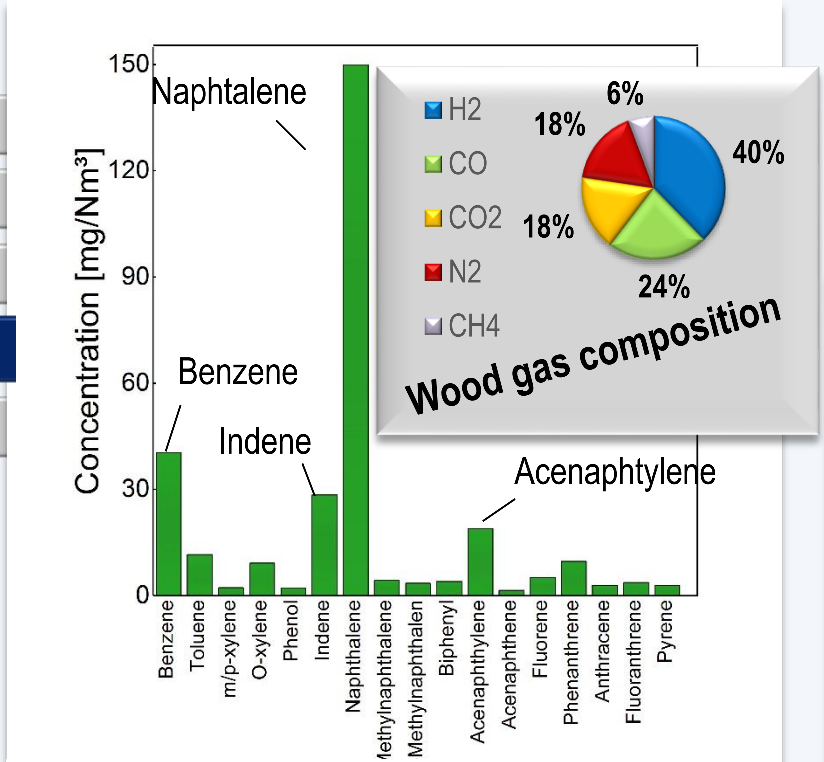
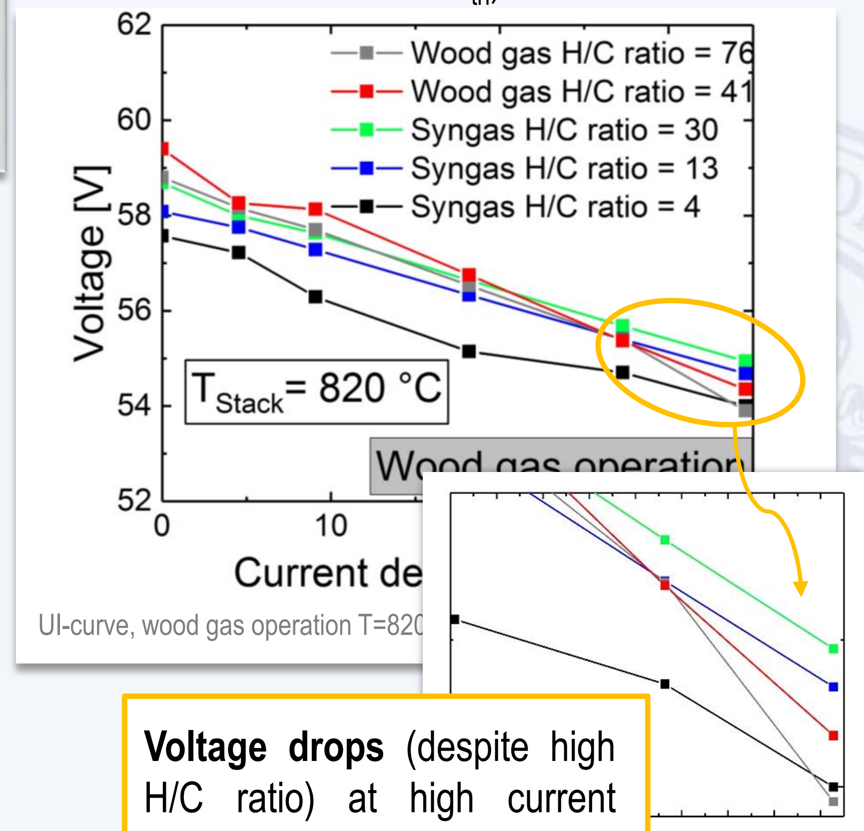
Syngas vs. Wood gas



Tars content of the wood gas flow

Approx. 200 mg/m³ of tars (naphtalene, benzene, acenaphtylene, inden etc.) were measured upstream of the cell, H_2S removed

Wood gas was mixed with **hydrogen** in concentrations of 2 l/min (H/C = 76) and 4 l/min (H/C=41) to maintain a LHV of 2 kW_{th} (minimal LHV for Hexis SOFC-stack: 1.27 kW_{th})



UI-curve, wood gas operation T=820

Voltage drops (despite high H/C ratio) at high current densities

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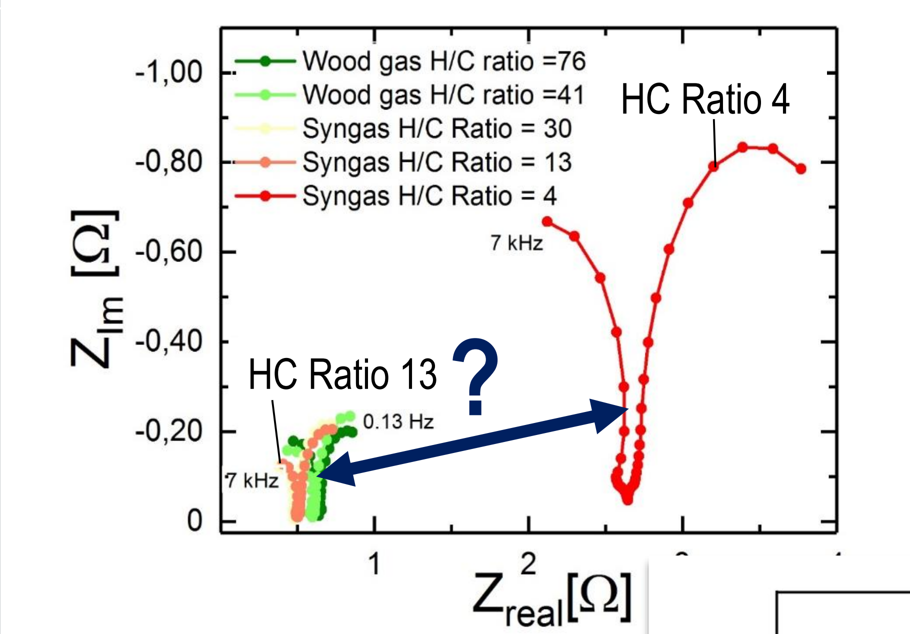
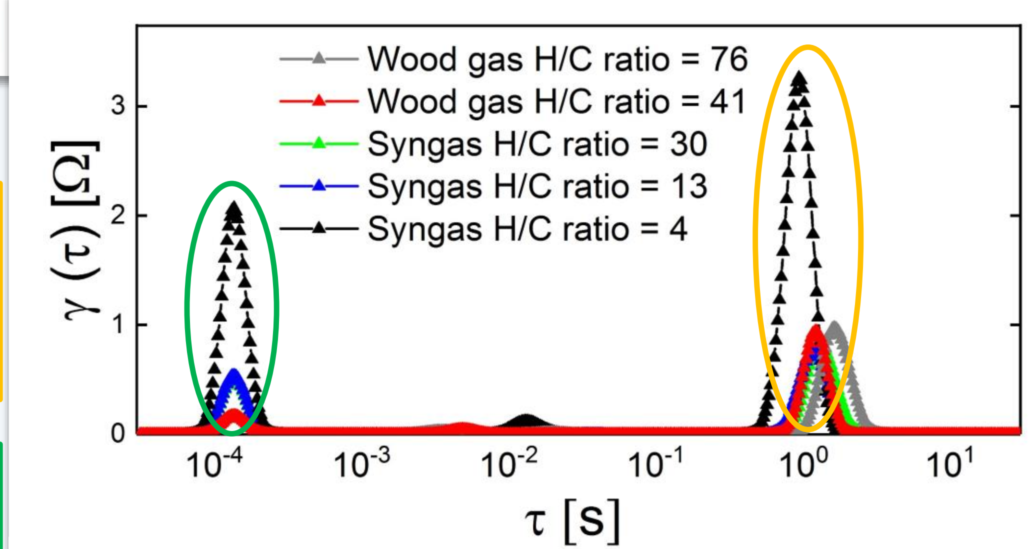
Syngas vs. woodgas

Nyquist-plot syngas operation and wood gas at different H/C ratio, T= 820 °C.



Due to the limitation of the gasification plant's output and the technical challenges of the SOFC plant, **no critical operating conditions** were observed. However it probably lies between H/C ratio 4 and 13



DRT-plot syngas operation and wood gas at different H/C ratio, T= 820 °C.

Tars obviously increase the gas diffusion resistances (lower resistances would have been expected with H/C = 76).

Negligible influence of tars in the oxidation at the anode

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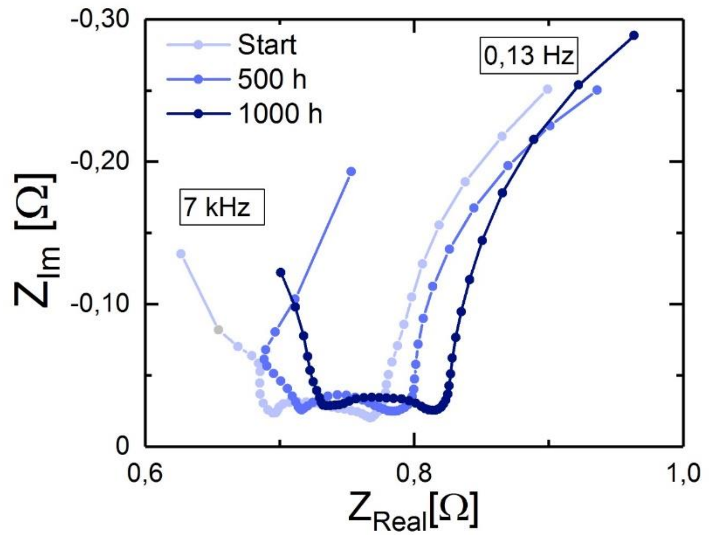
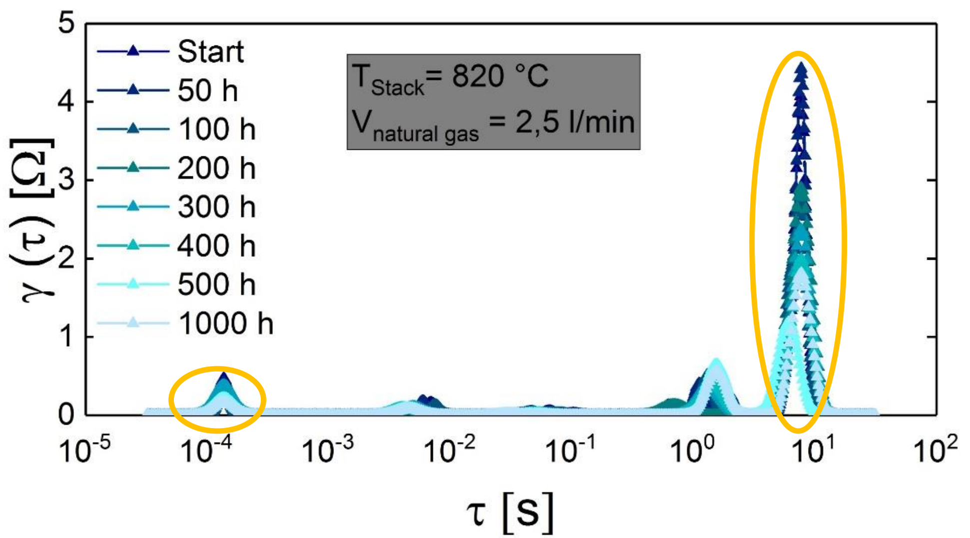
Degradation



Nyquist-plot natural gas operation at the beginning, after 500 and 1000 hours, T= 820 °C.

In an operation time **over 1000 hours**, one sees a displacement of the ohmic resistance (electrolyte resistances) on the real axis of the Nyquist-plot due to the degradation of the stack

Oxidation and gas diffusion resistances at the anode decrease over time most likely because of **carbon agglomeration** that was already present at the beginning of these measurements in the stack. This kind of degradation is regenerative and can be overcome with natural gas, having decomposed into H_2 and CO, which reacts with and removes the agglomerated carbon



DRT-plot natural gas operation at the beginning, after 50,100, 200, 300, 400, 500, and 1000 hours, T= 820 °C.

Summary & Outlook

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- An increase of temperature and gas flow results in a growth of the cell performance
- Because of the pre-reforming the Hexis stack show higher performance in natural gas operation
- Due to the technical limitations of the plant, no critical conditions can be observed during operation with wood gas.
- Wood gas (CO_2, "large" molecules) increases diffusion resistance on the anode side
- For a more detailed quantification of the effect of the tars, further measurements are necessary
- Degradation effects can be noticed in an increase of the ohmic resistance but they are not visible in the anode resistances due to the cleaning of the agglomerated carbon

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