Advanced biomass CCHP based on gasification, SOFC and cooling machines
Solide oxide fuel cell performance with gases from biomass gasification

Gernot Pongratz
Vanja Subotić, Hartmuth Schroettner, Bernhard Stoeckl, Christoph Hochenauer, Andrès Anca-Couce, Robert Scharler

Highlights of Bioenergy Research 2020

6. Central European Biomass Conference
Graz, Austria; January 24th, 2020

TU Graz

Institute of Thermal Engineering, Inffeldgasse 25b, 8010 Graz, Austria, www.iwt.tugraz.at

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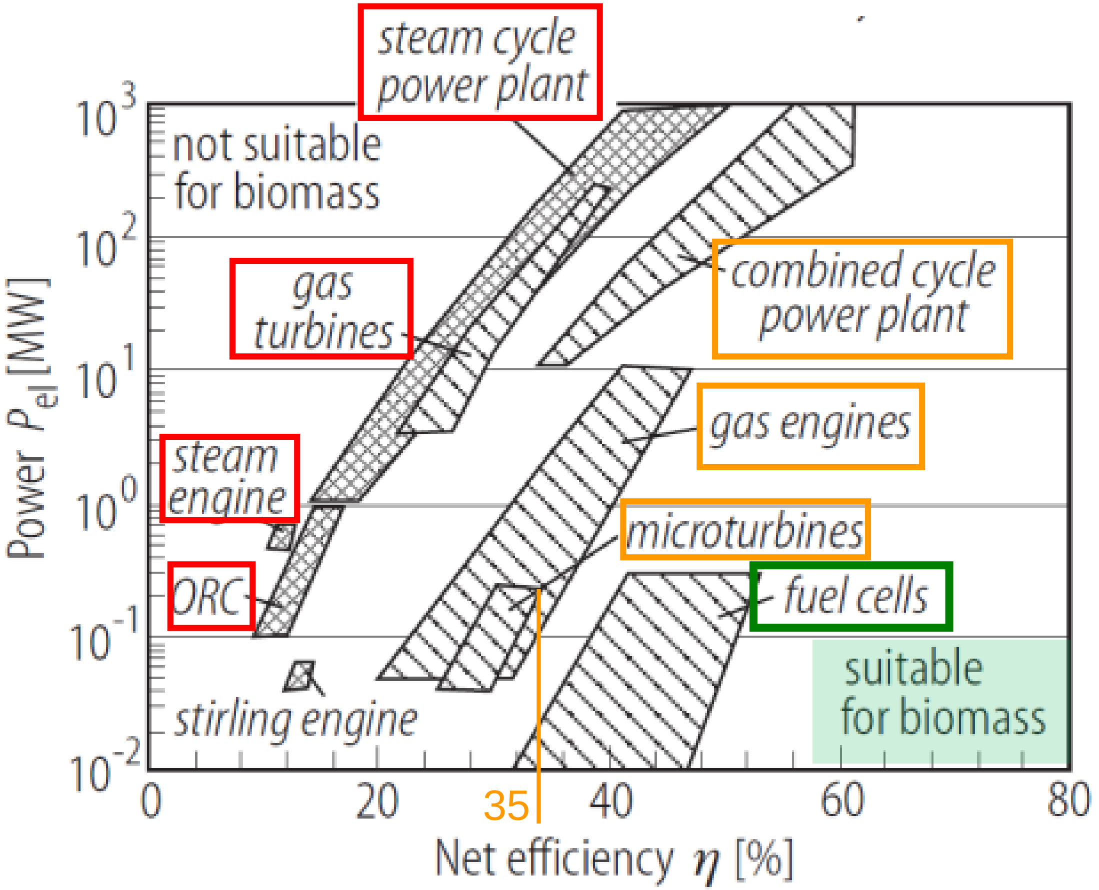
Biomass to power



Hein D., Karl J. (2006): Conversion of biomass to heat and electricity. Energy Technologies: Renewable Energy, Landolt-Boerstein New Series VIII/3C, 374-413

► Combustion based

\+ consolidated technology:

\- η_{el} ~15-25% (only for tens of MW_{th})

► Gasification based

→ *State of the art power generator*: **Gas Engine**

\+ robust & flexible & mature→ cost-effective

\- Carnot limitation + gas cooling → **η_{el} < 35%**

→ *Alternative power generator:* **SOFC**

\+ Hot gas usage + no carnot → **η_{el} > 40%**

\- sensitive to impurities

Contact: gernot.pongratz@tugraz.at

Agenda

- Project overview

- Methodology and results

- Summary & Outlook

Contact: gernot.pongratz@tugraz.at

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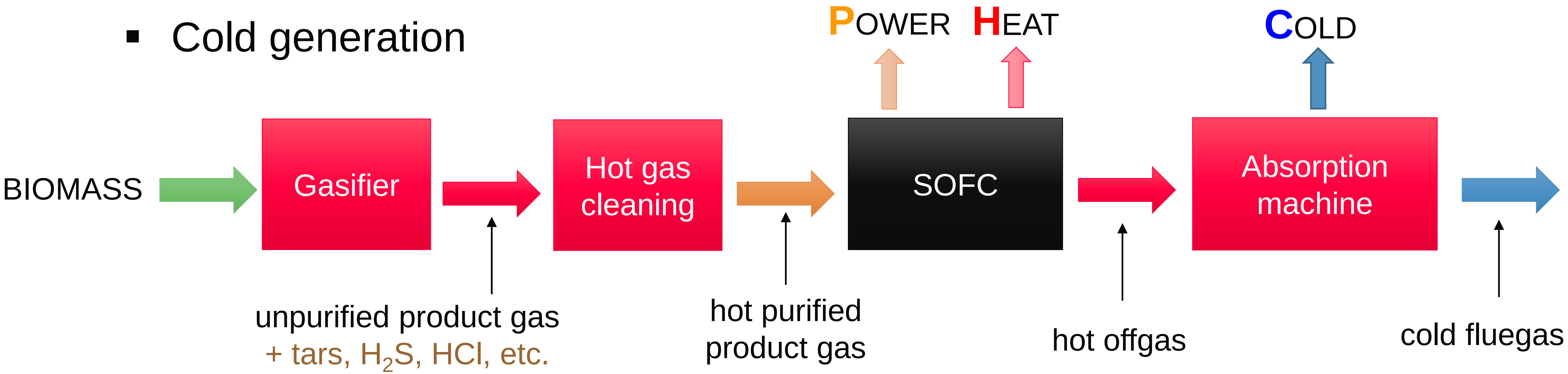
SOFC Combined Cold Heat Power plant

- Net efficiency increase with SOFCs
- Overall efficiency increase with
  - Heat usage
  - Cold generation



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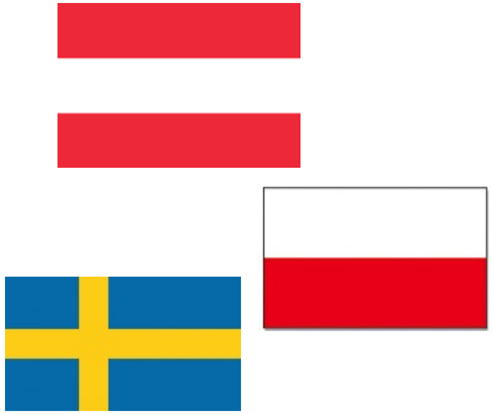
BIO-CCHP: Advanced biomass CCHP based on gasification, solid oxide fuel cells and cooling machines

- ERA-NET Bioenergy project (11th Call)
- Coordinator of project: ITE TU Graz
- Scientific and industrial partners from 3 countries
- April 2018 → March 2021

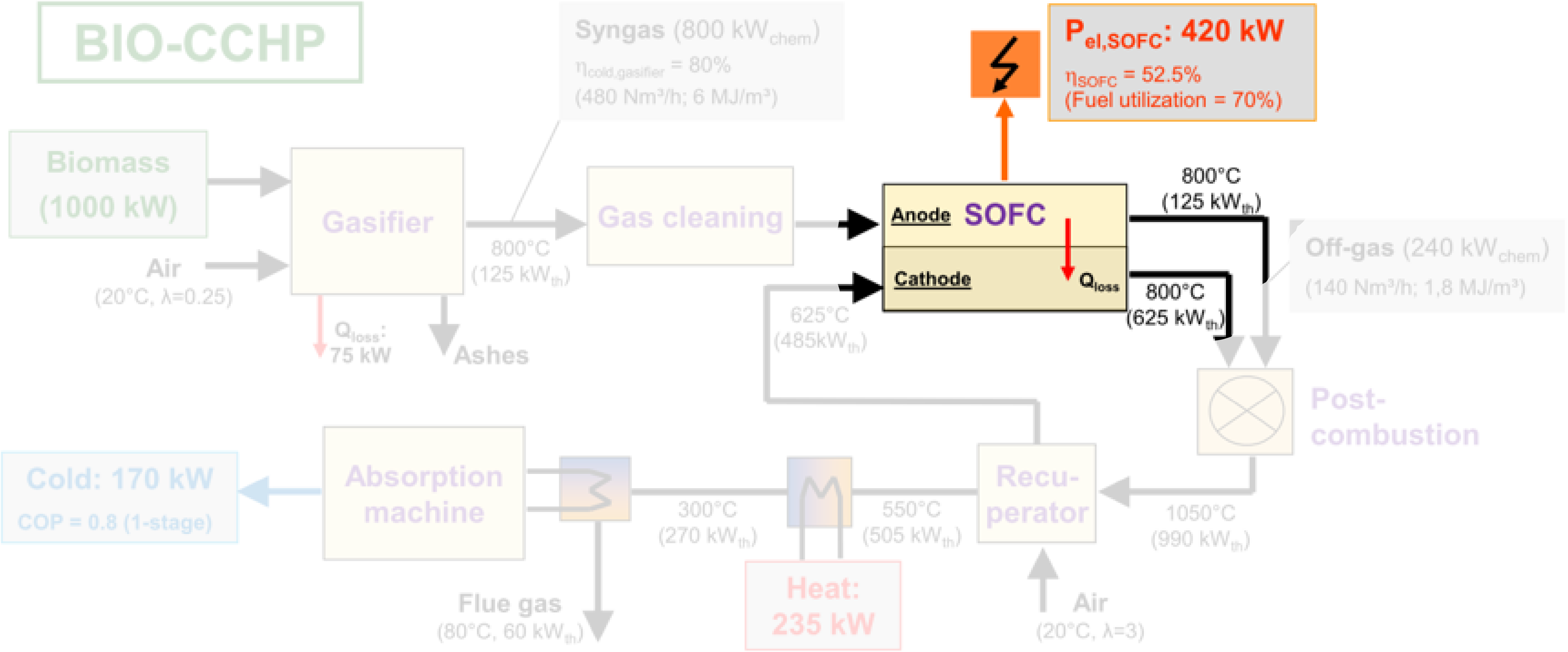


Goals:

- Novel trigeneration system
- Electric efficiency **> 40%**
- Enhanced fuel flexibility

Contact: gernot.pongratz@tugraz.at

Project goal



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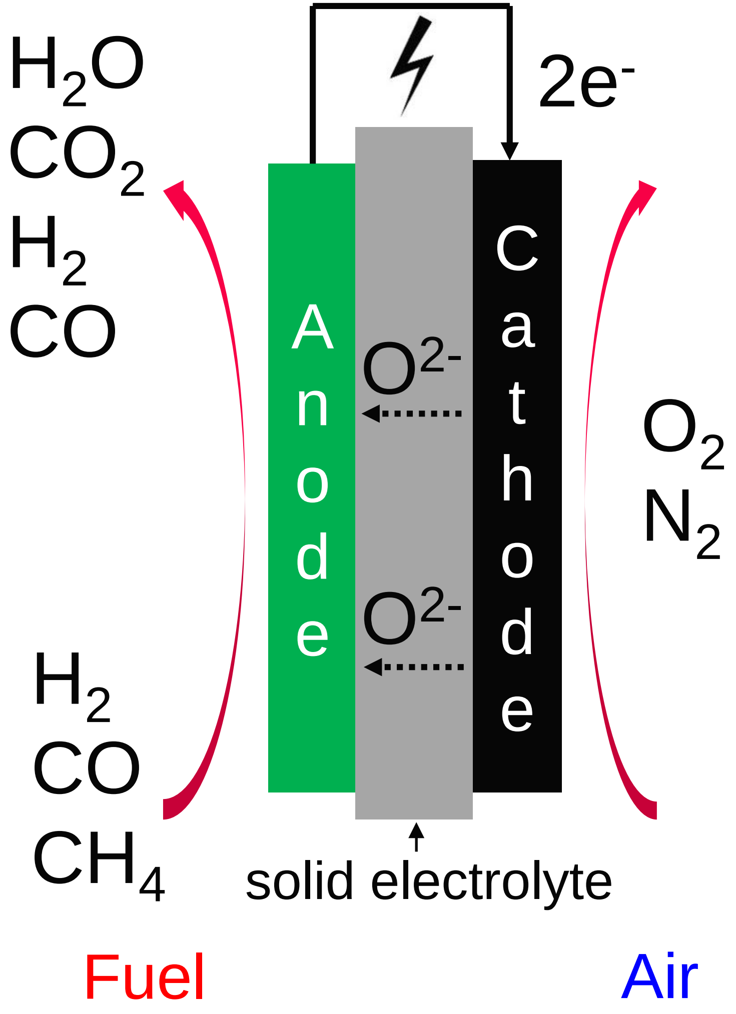
Solid Oxide Fuel Cell

- **S**olid **O**xide **F**uel **C**ell
- 600 – 1000 °C
- H_2 & CO to elecricity
- Internal reforming of CH_4

Degradation

- Sulfur and chlorine
  → poisoning of catalyst
- Low Steam to carbon Ratio (SCR)
  → carbon depositions
- Dependent on celltype



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Development challenges SOFC

Cell performance

Cell degradation
- carbon deposition
- catalyst poisoning

=f

?

Operating point
- product gas feed
- temperature
- electric load

Syngas cleaning level
- tar compounds
- sulfur compounds
- chlorine compounds
- dust

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SOFC goal

define

optimal SOFC operating conditions
and **impurity tolerances**

to ensure

stable, **economic** operation

with

maximum **efficiency**
high **lifetime**

- **Experimental** studies
- **CFD** simulations

(Computational Fluid Dynamics)

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Strategy

In progress

Literature

Evaluation of relevant

- o Product gases
- o Impurity amounts
- o Cell types
  - Substrate
  - Structure

↓

promising test configuration

Short-term experiments

H_2, H_2O, CO, CO_2, CH_4 mixtures

↓

performance influence

addition of H_2S, HCl, Tars

↓

degradation understanding

Long-term experiments

synthetic product gas

↓

operation stability

impure synthetic product gas

↓

operation stability

Short&Long-term experiments

Real coupling

ITE gasifier „real“ conditions

↓

stability & efficiency

CFD modelling

Contact: gernot.pongratz@tugraz.at

Short term testing: Parameter study

Which **ratios** of **carbonaceous species** are advantageous for **FDA/FBS** gas mixtures?

- Cell type with high potential coupling with gasifier
- 50 operating points → CO, CO_2 and CH_4 varied
- Electrochemical characterization

vol% w.b.		Influence CO			Influence CH4			Influence CO2			
H_2	50	50	50	50	50	50	50	50	50	50	50
H_2O	25	25	25	25	25	25	25	25	25	25	25
CO	Reference	5	10	25					5		5
CH_4					5	10	25			5	5
CO_2								15	15	15	15
N_2	25	20	15		20	15		10	5	5	

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Short term testing: Parameter study

→ H_2 >> CO = beneficial

→ H_2O / CH_4 > 1 = recommended

→ CH_4 ↑ instead of CO ↑ = recommended

→ CO_2 ↓ = beneficial

vol% w.b.		Influence CO			Influence CH4			Influence CO2			
H_2	50	50	50	50	50	50	50	50	50	50	50
H_2O	25	25	25	25	25	25	25	25	25	25	25
CO	Reference	5	10	25					5		5
CH_4					5	10	25			5	5
CO_2								15	15	15	15
N_2	25	20	15		20	15		10	5	5	

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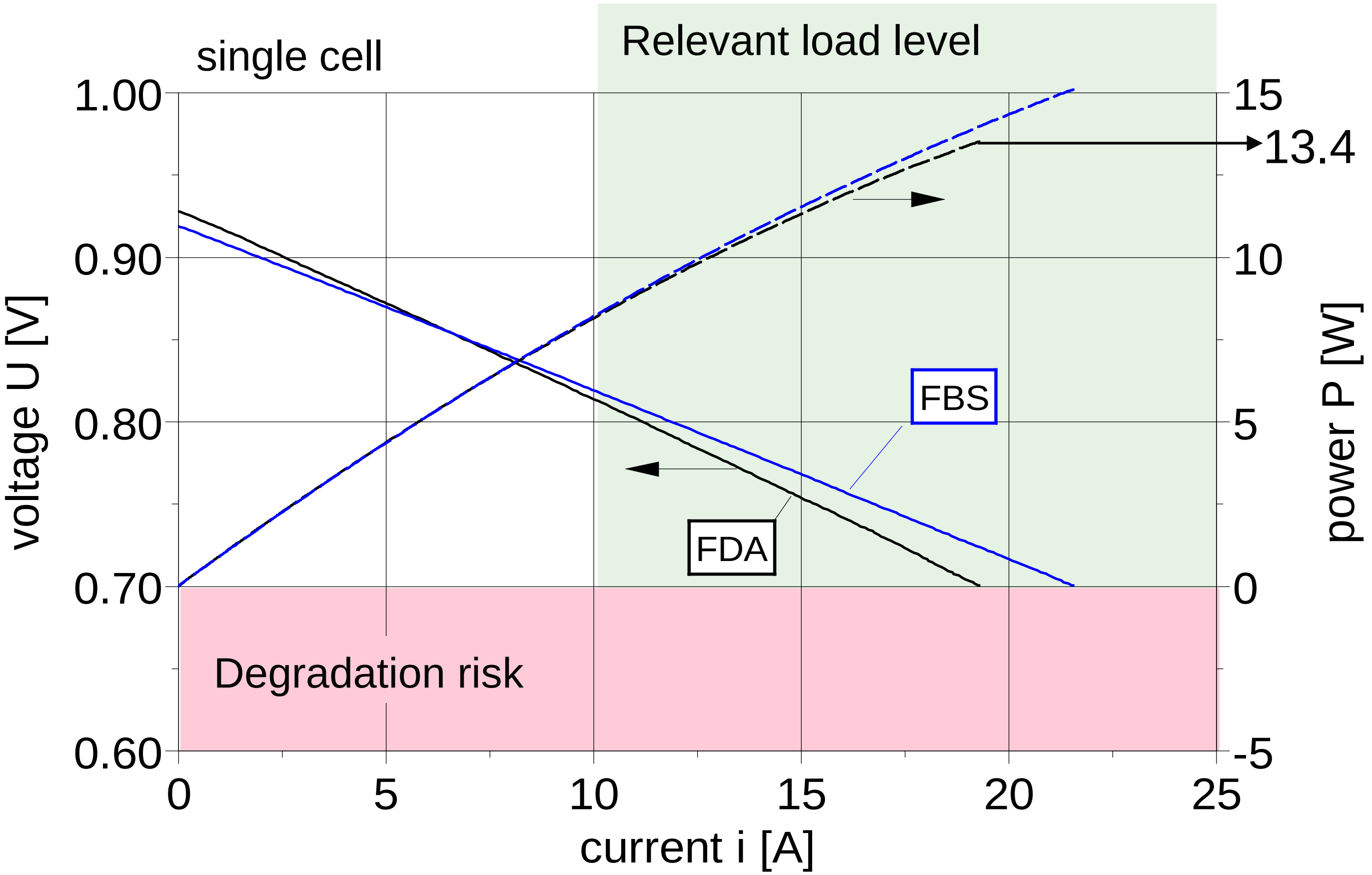
Fixed bed Downdraft Air (FDA) vs. Fluidized bed Steam (FBS)

- P_{max_FBS} > P_{max_FDA}
- FBS stable for 500 h @ 36% H_2O
- FDA also suitable for SOFC
  - **Higher SCR** necessary
  - Agent: Air + steam
  - Product gas steam injection

FBS: performance potential
FDA: suitable with higher SCR



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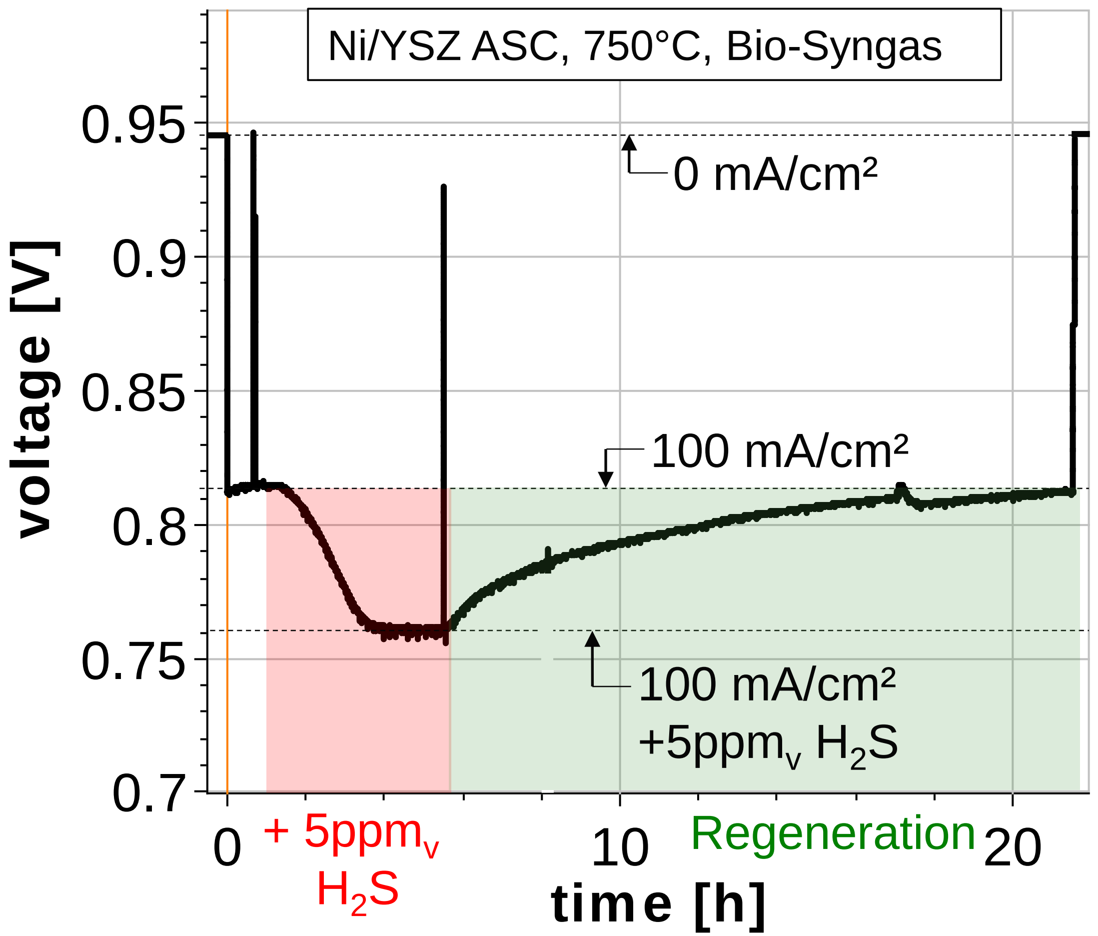
Performance degradation H_2S

Simulation of gas cleaning malfunction at stable operation → H_2S in fuel gas

- Initial voltage drop ↑
  - T ↓
  - H_2S concentration ↑
  - Less tolerant substrate



- Full regeneration up to 10ppm$_v$

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Summary

- Beneficial cell type for coupling identified
- High potential of FBS gasifier for coupling with SOFC claimed
- No degradation using steam-rich FBS gases
- Also high potential for FDA, improved with steam + O_2 enriched air

Contact: gernot.pongratz@tugraz.at

Outlook

Real coupling

- Coupling of cell with in-house FBS gasifier using
    1. sulfur- and tar free gas
    2. sulfur free gas
    3. raw product gas

Synthetic gas mixtures

- Addition of cell contaminants:
  H_2S, Thiophene, HCl, Toluene (as tar content)
- Comparison of different cell types

degradation verification

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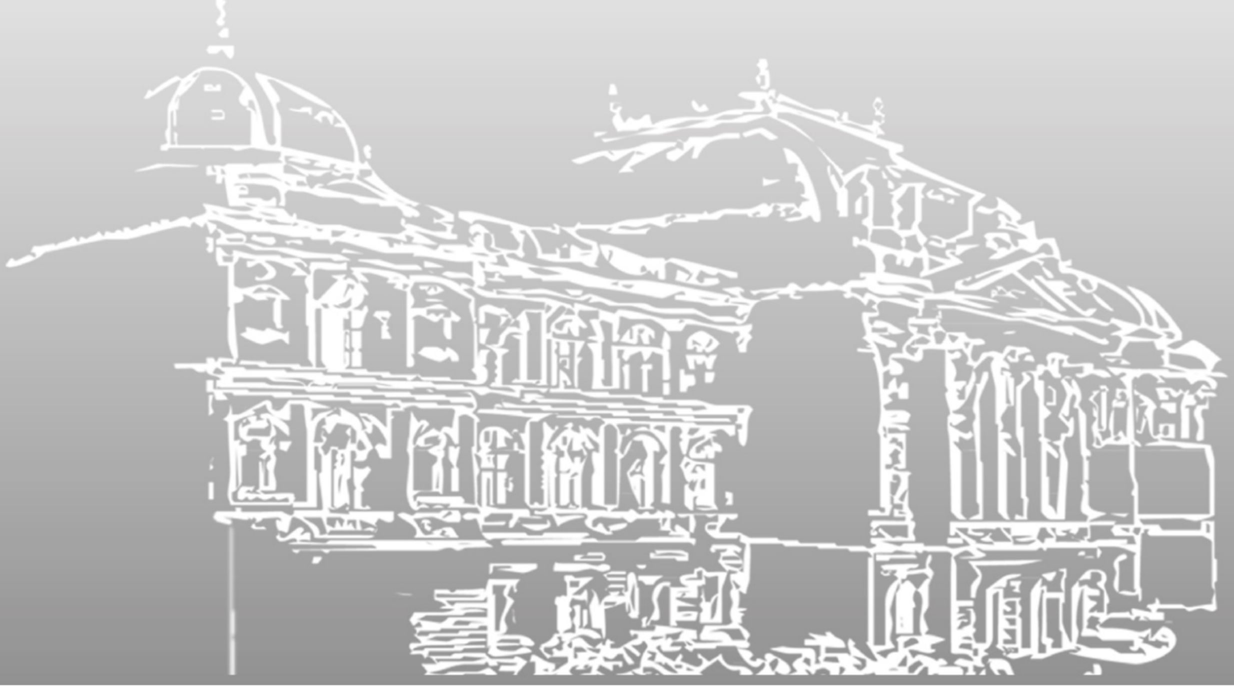

Institute of Thermal Engineering
Graz University of Technology
Inffeldgasse 25b/4, 8010 Graz, Austria

Gernot Pongratz

gernot.pongratz@tugraz.at

Acknowledgment:

FFG Promoting Innovation. ERA-NET Bioenergy

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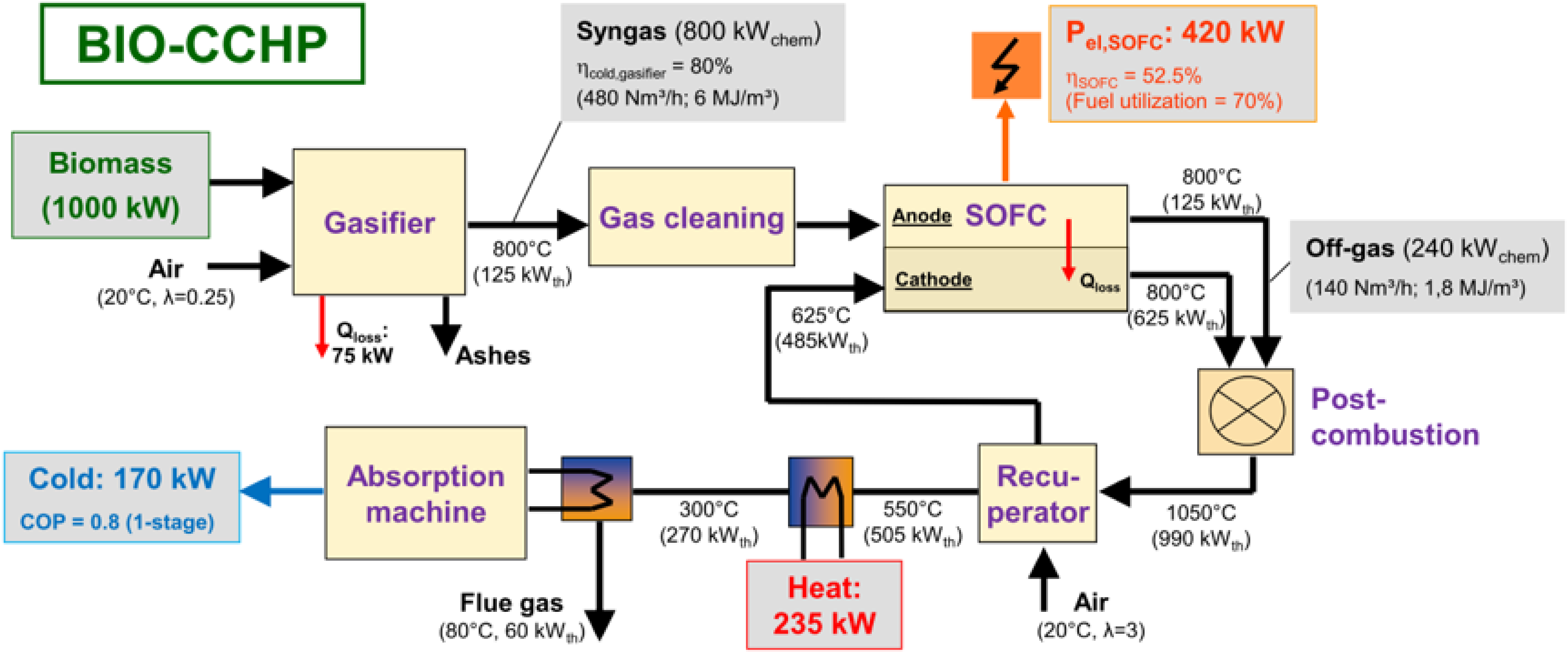
Backup

Project goal



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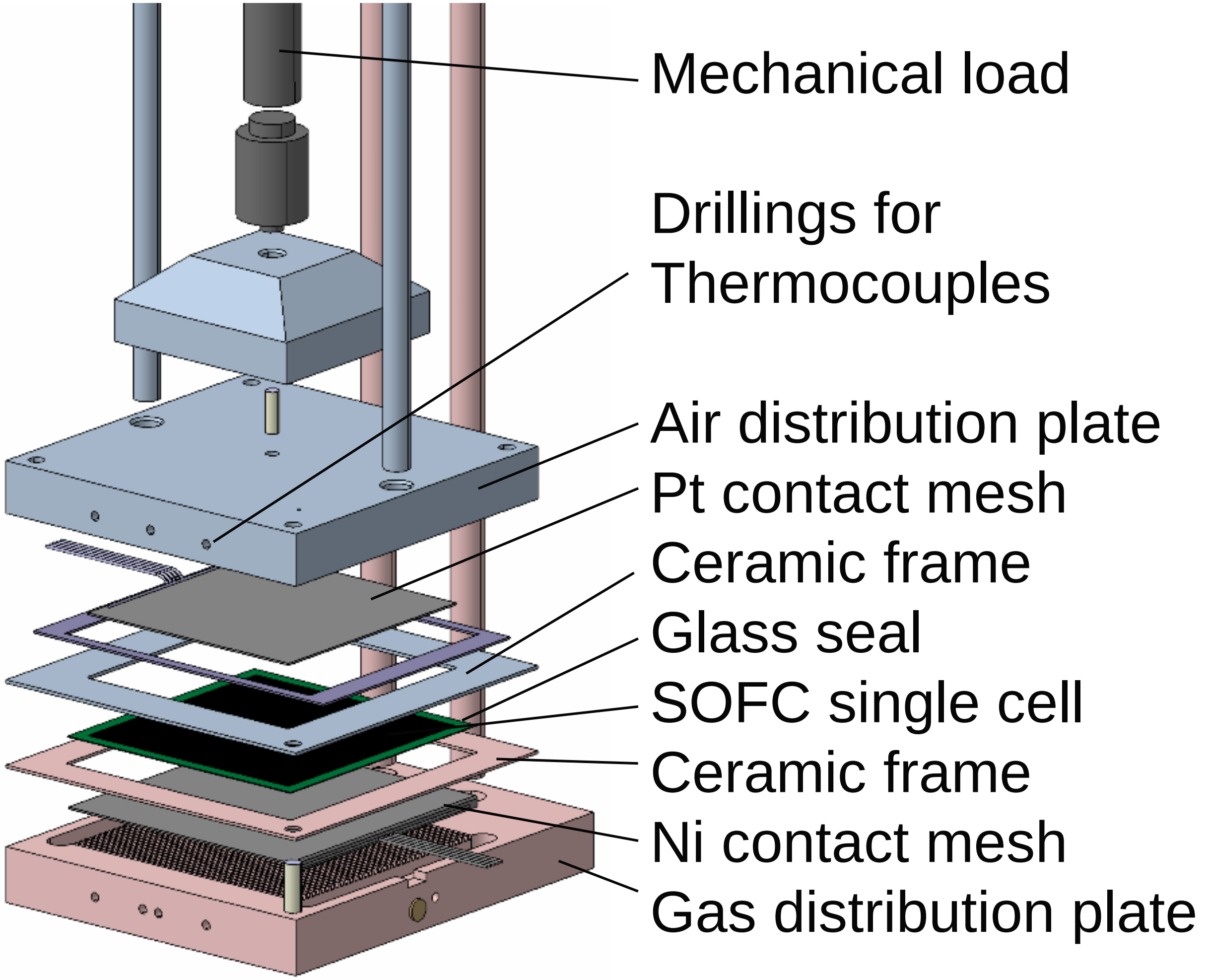
Single cell testing

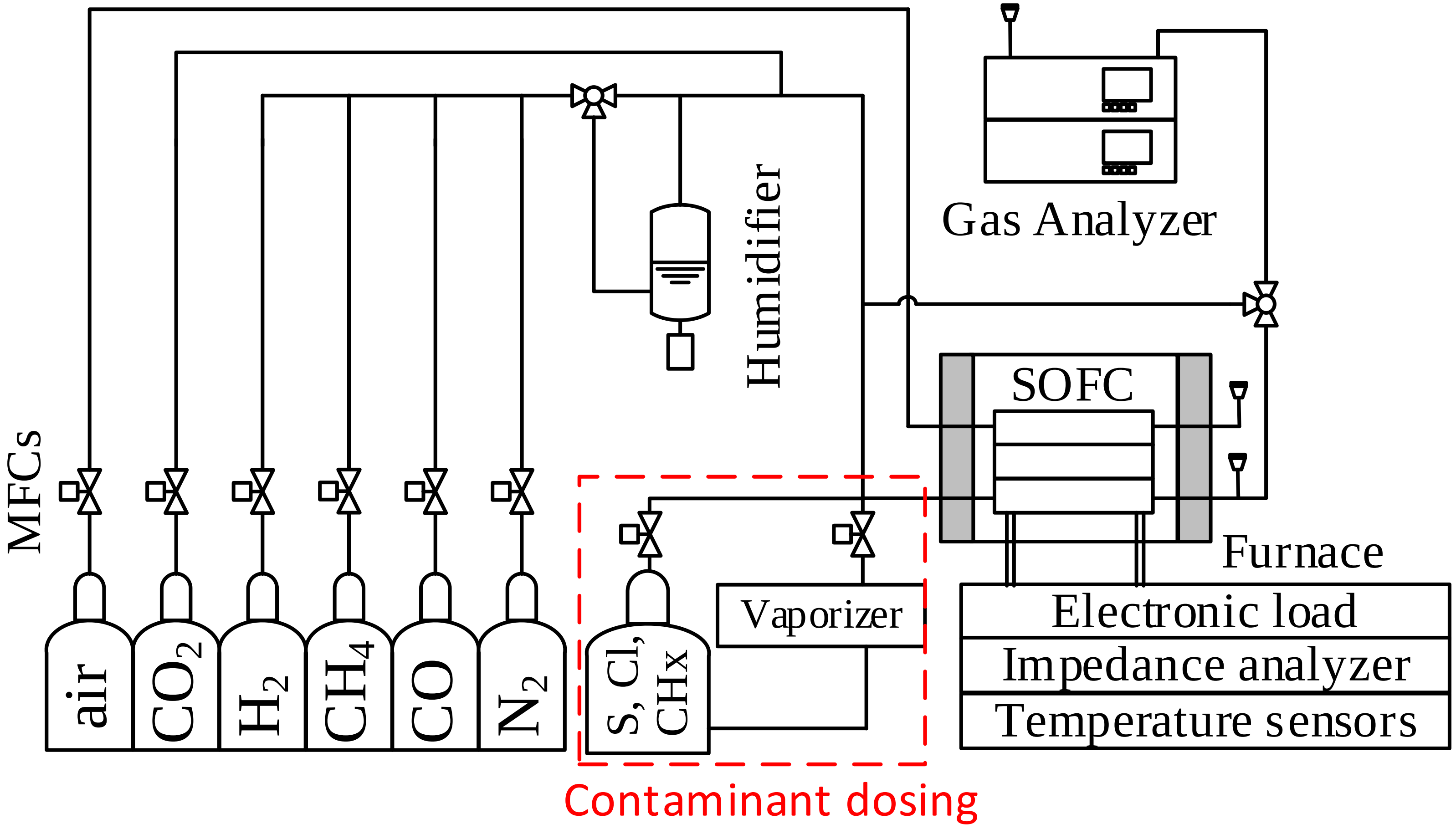
- Ceramic cell housing
- Commercially available cells with 80cm^2 active area
- In-situ measurements:
  - IVC, EIS
  - Temperature distribution
- Post-mortem analyses:
  - SEM, EDX



IVC...current-voltage-curve
EIS...electrochemical impedance spectroscopy
SEM...scanning electron microscopy
EDX... energy-dispersive X-ray spectroscope

Testrig

- Main gas componentes
- Dry/wet operation
- Gas analysis
- Contaminant dosing
  - gaseous
  - liquid + vaporizer



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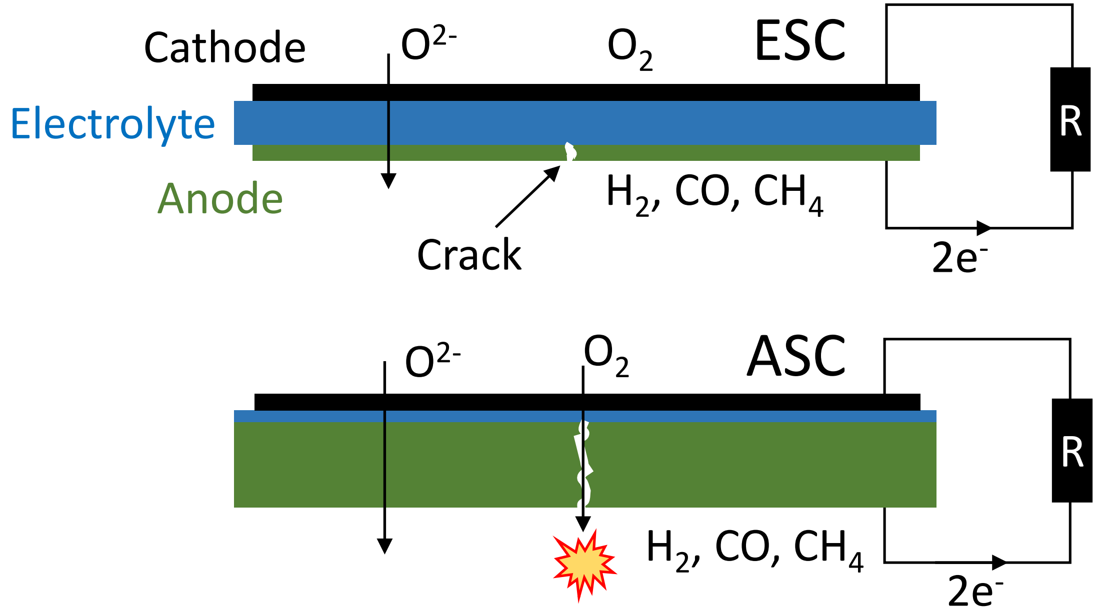
Cell type comparison

- ***Substrate***: Ni/GDC most degradation tolerant commercially available substrate
- ***Cell structure***: Failure due to substrate degradation less severe in ESC than in ASC

ESC-SOFC with **Ni/GDC** anode fuelled with **FBS** gasifier-like **product gas** most promising configuration



Ni/GDC...nickel/gadolinium-doped ceria
ESC...electrolyte supported cell
ASC...anode supported cell

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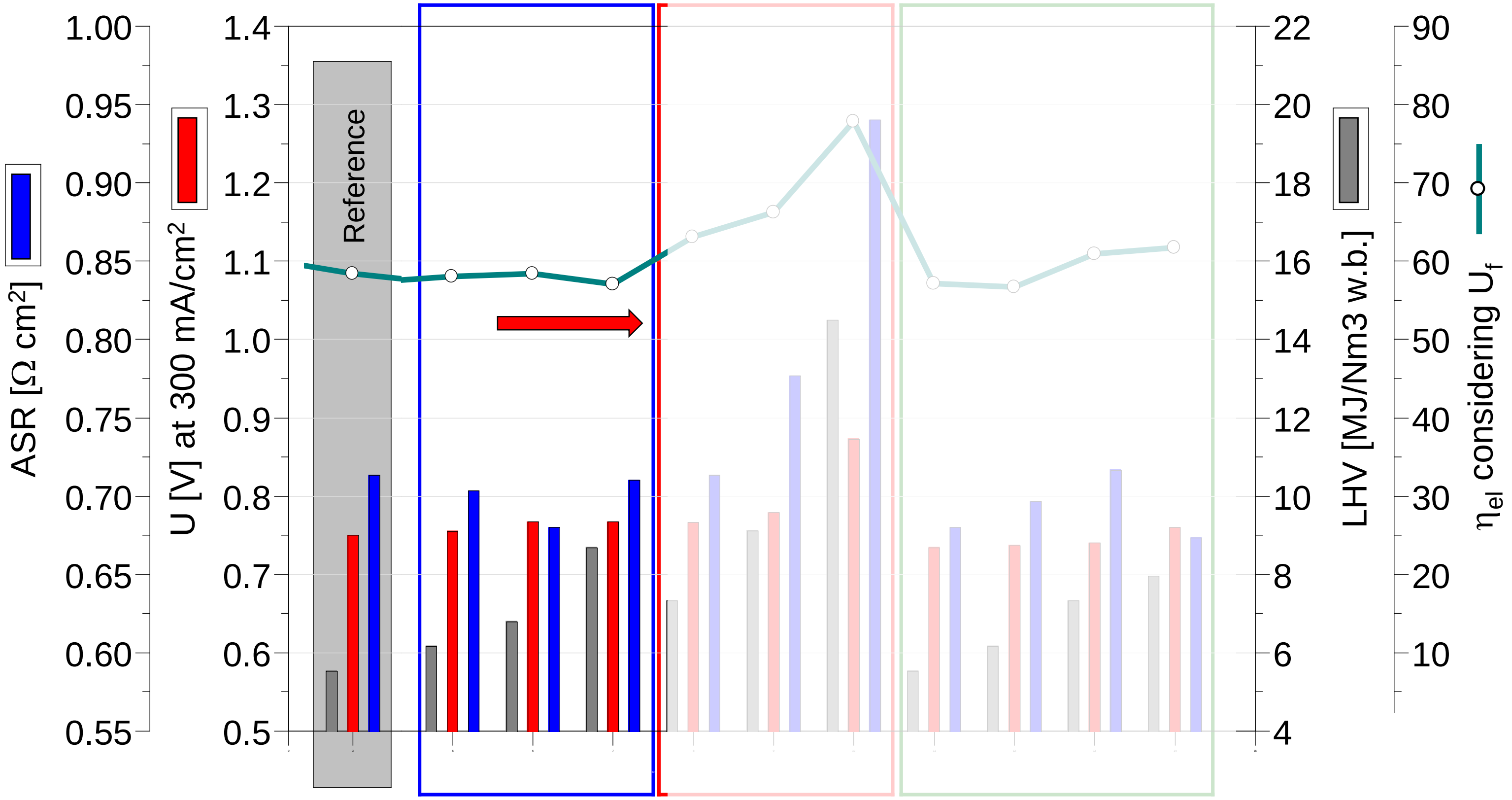

vol% w.b.		Influence CO			Influence CH4			Influence CO2			
H_2	50	50	50	50	50	50	50	50	50	50	50
H_2O	25	25	25	25	25	25	25	25	25	25	25
CO	Reference	5	10	25					5		5
CH_4					5	10	25			5	5
CO_2								15	15	15	15
N_2	25	20	15		20	15		10	5	5	

Increasing CO fraction

At **H_2 / CO < 5** stagnating power output as CO oxidizes before reacting via WGS to high reactive H_2

$$CO + H_2O \Leftrightarrow CO_2 + H_2$$

H_2 >> CO beneficial

$$ASR = \frac{\Delta U_{loss}}{i} \; [\Omega cm^2]$$

...Area specific resistance at i = 300 mA/cm²

OCV...open circuit voltage

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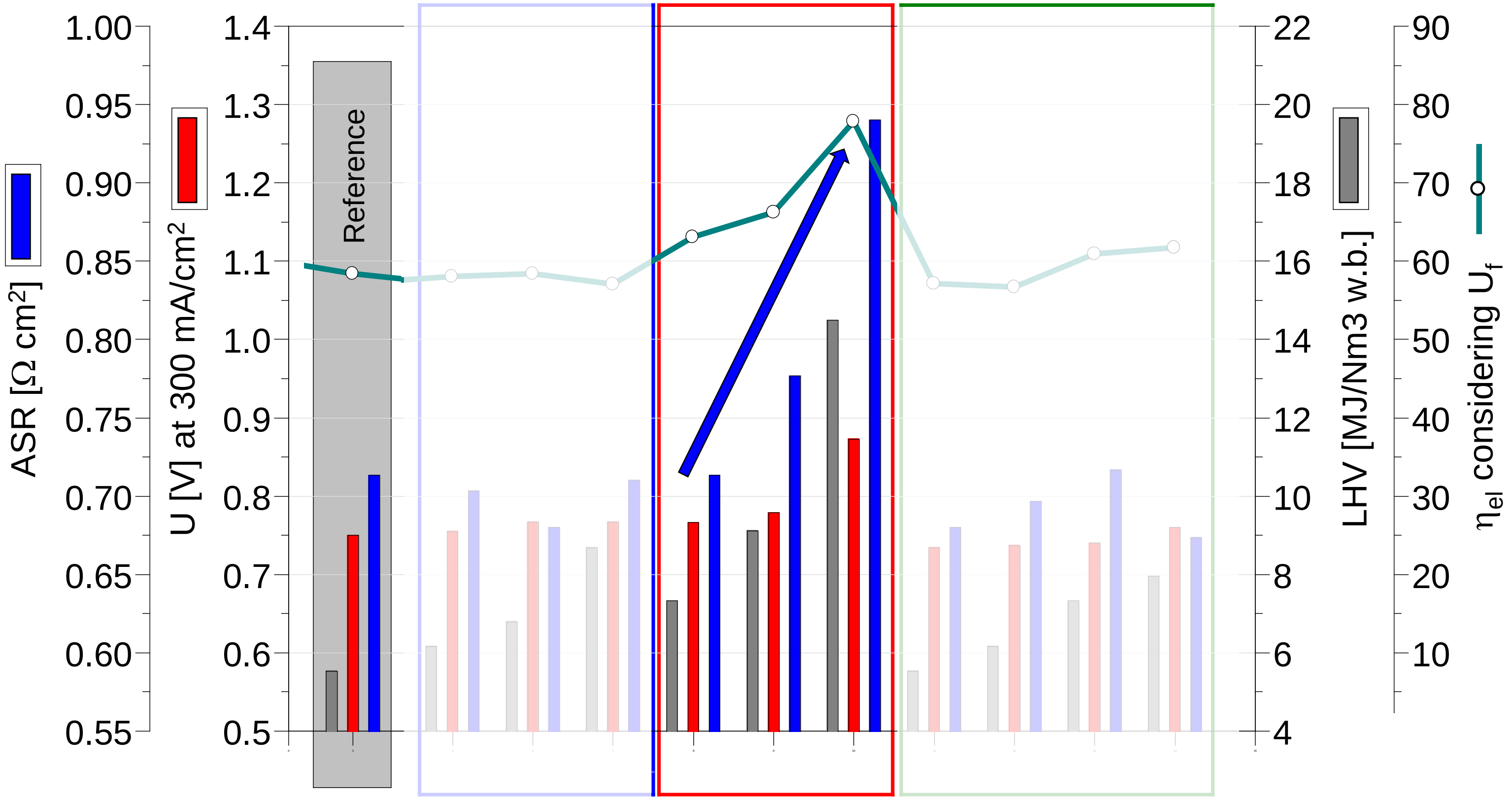

vol% w.b.		Influence CO			Influence CH4			Influence CO2			
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H_2O	25	25	25	25	25	25	25	25	25	25	25
CO	Reference	5	10	25					5		5
CH_4					5	10	25			5	5
CO_2								15	15	15	15
N_2	25	20	15		20	15		10	5	5	

Increasing CH_4 fraction

At **H_2O / CH_4 < 1** disproportionately high ASR increase as H_2O gets "used up" in methane reforming leading to high voltage losses

$$CH_4 + H_2O \Leftrightarrow CO + 3H_2$$

H_2O / CH_4 > 1 recommended

$$ASR = \frac{\Delta U_{loss}}{i}\ [\Omega cm^2]$$

...Area specific resistance at i = 300 mA/cm²

OCV...open circuit voltage

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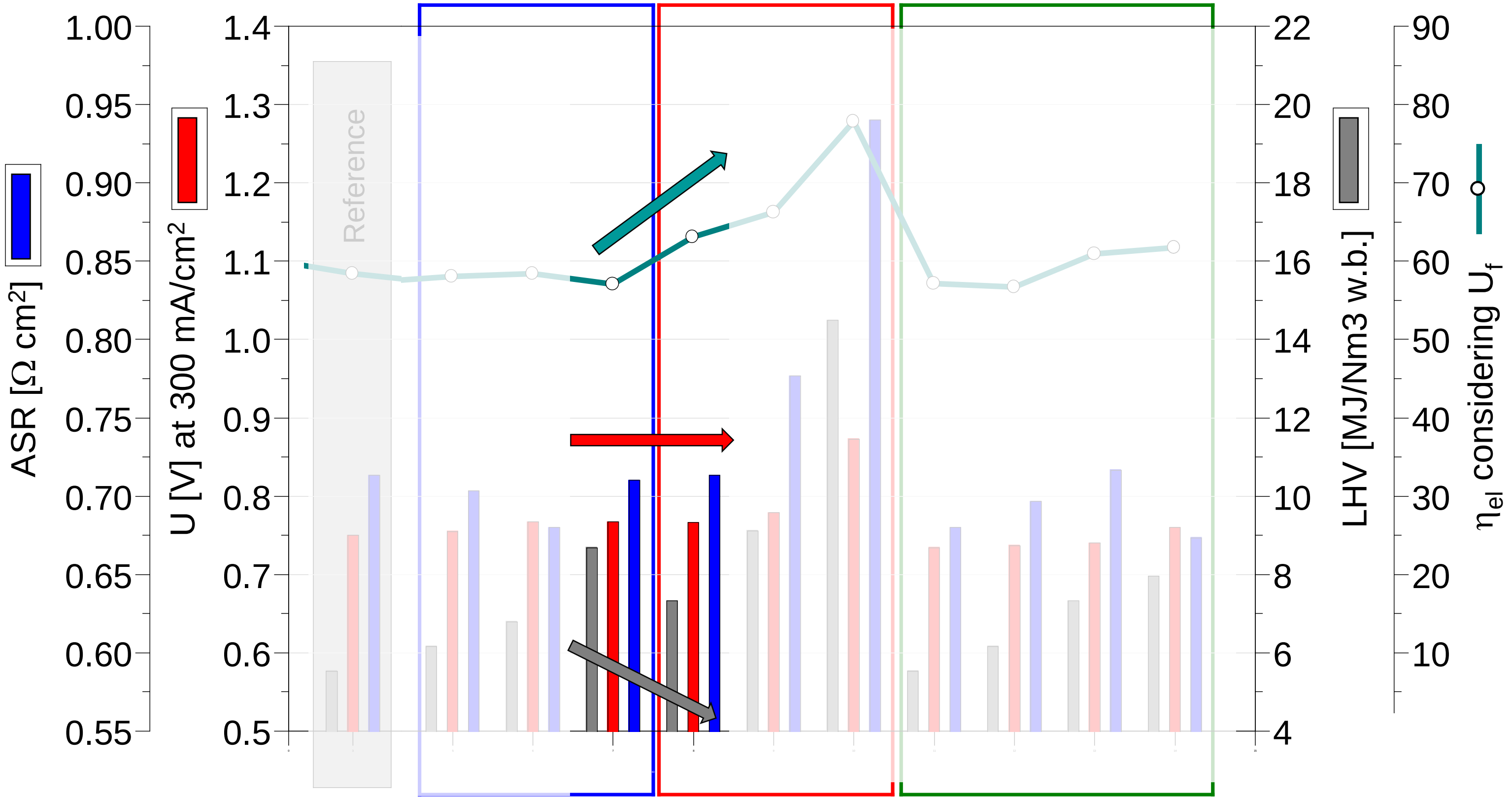

vol% w.b.		Influence CO			Influence CH4			Influence CO2			
H_2	50	50	50	50	50	50	50	50	50	50	50
H_2O	25	25	25	25	25	25	25	25	25	25	25
CO	Reference	5	10	25					5		5
CH_4					5	10	25			5	5
CO_2								15	15	15	15
N_2	25	20	15		20	15		10	5	5	

Comparing CO with CH_4

P(5% CH_4) = P(25% CO)

despite 16% smaller LHV

→ η_{el} increased

small CH_4 amounts preferable to larger CO amounts

$$ASR = \frac{\Delta U_{loss}}{i} \; [\Omega cm^2]$$

...Area specific resistance at i = 300 mA/cm²

OCV...open circuit voltage

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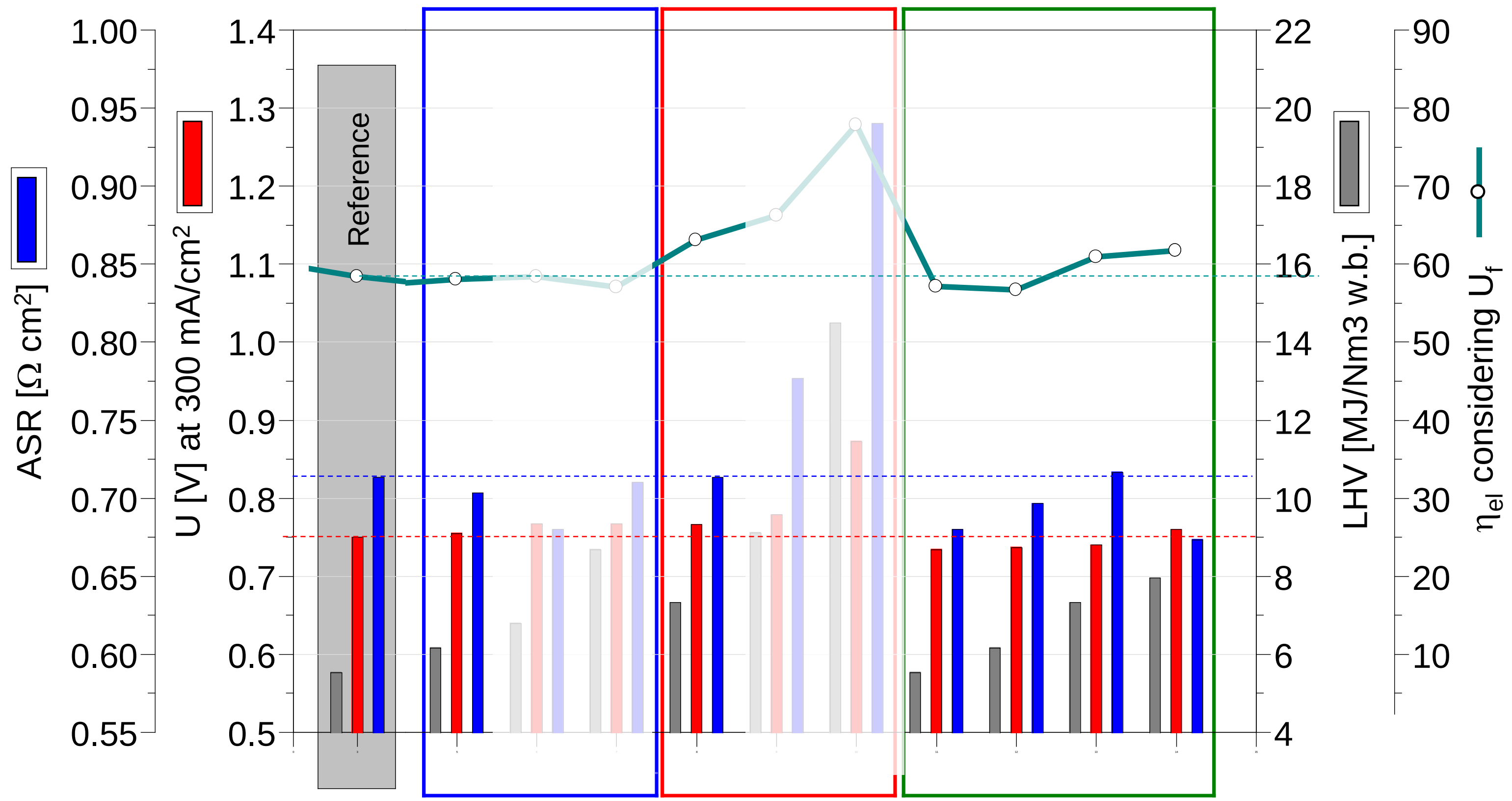

vol% w.b.		Influence CO			Influence CH4			Influence CO2			
H_2	50	50	50	50	50	50	50	50	50	50	50
H_2O	25	25	25	25	25	25	25	25	25	25	25
CO	Reference	5	10	25					5		5
CH_4					5	10	25			5	5
CO_2								15	15	15	15
N_2	25	20	15		20	15		10	5	5	

Addition of CO2

Even small CO_2 amount turns high reactive H_2 into less reactive CO via WGS

→ performance decrease

$$CO + H_2O \Leftrightarrow CO_2 + H_2$$

CO_2 ↓ beneficial

$$ASR = \frac{\Delta U_{loss}}{i}\ [\Omega cm^2]$$ ...Area specific resistance at i = 300 mA/cm²

OCV...open circuit voltage

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FDA vs. FBS product gas

Product gas of steam-blown fluidized bed gasifier (**FBS**) **compared** to air-blown fixed bed downdraft (**FDA**) gasifier:

vol% w.b.	H_2	H_2O	CO	CO_2	CH_4	N_2	SCR	H_2/CO	LHV [MJ/Nm^3 w.b.]
FDA	16	15	17	13	3	36	0.8	0.94	4.6
FBS	24	37	15	13	7	4	1.7	1.6	6.5

Bridgwater 1995 / 2009, Pfeifer 2011, internal data

+ higher lower heating value (LHV)
+ higher H_2 / CO ratio → less voltage losses expected
+ higher steam-to-carbon ratio (SCR) → less carbon deposition risk

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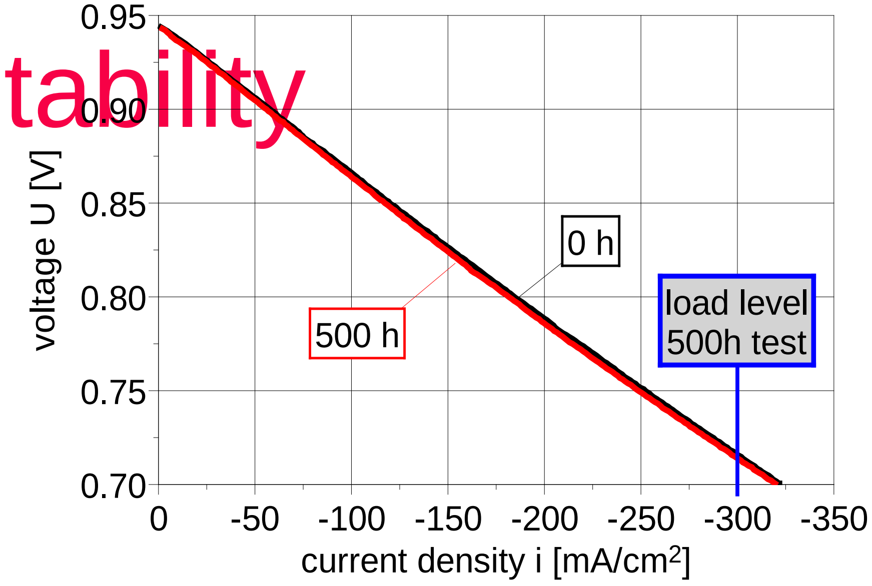
Long-term testing: degradation stability

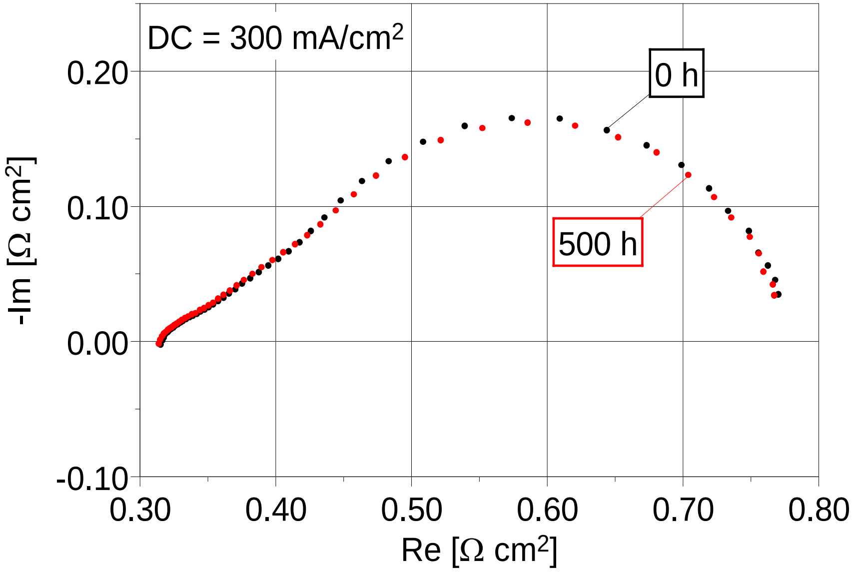
Is it possible to run the **cell stable** on a **steam-rich** product gas **without nickel re-oxidation** for many hours?



Operating point

- Simulated FBS product gas
- 80% of maximum achievable load
- 500 h stability experiment
- Cell measurements every 2 h

No degradation identified



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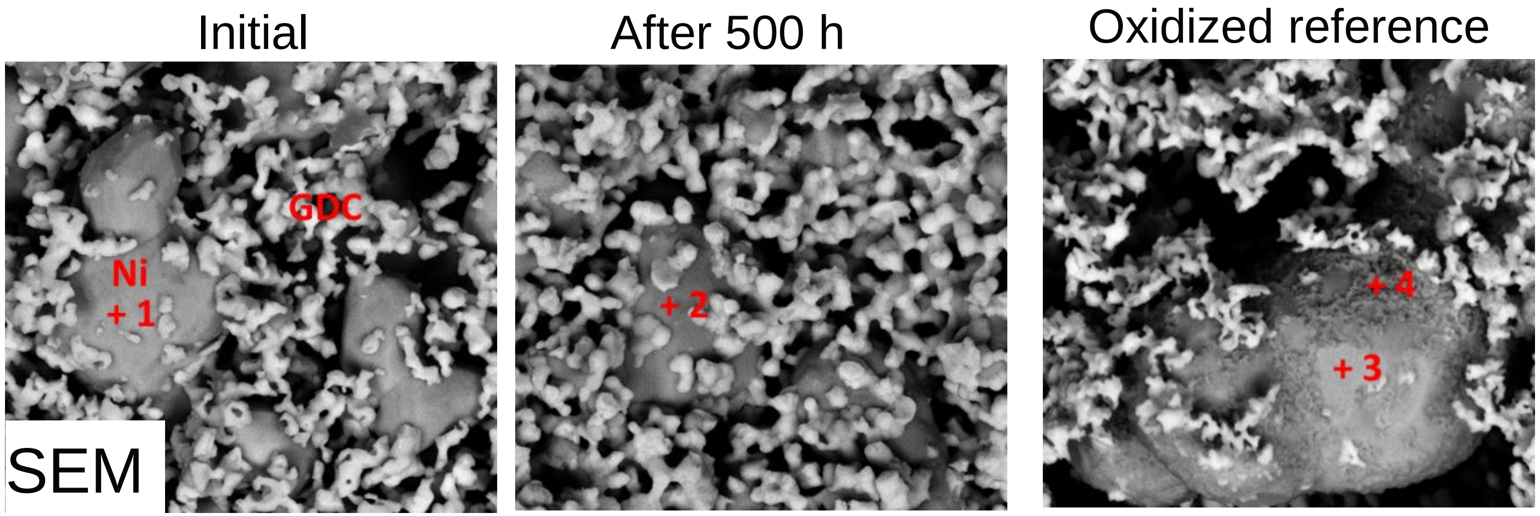
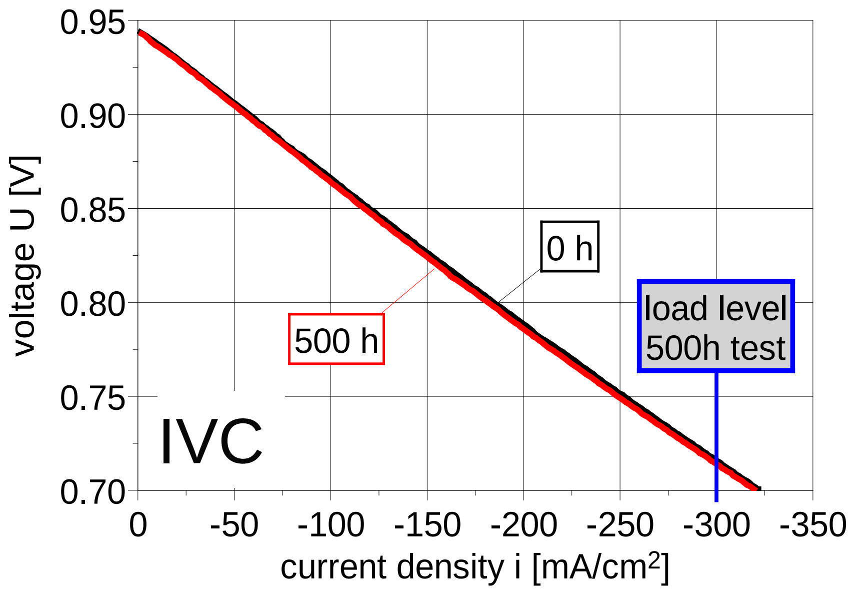
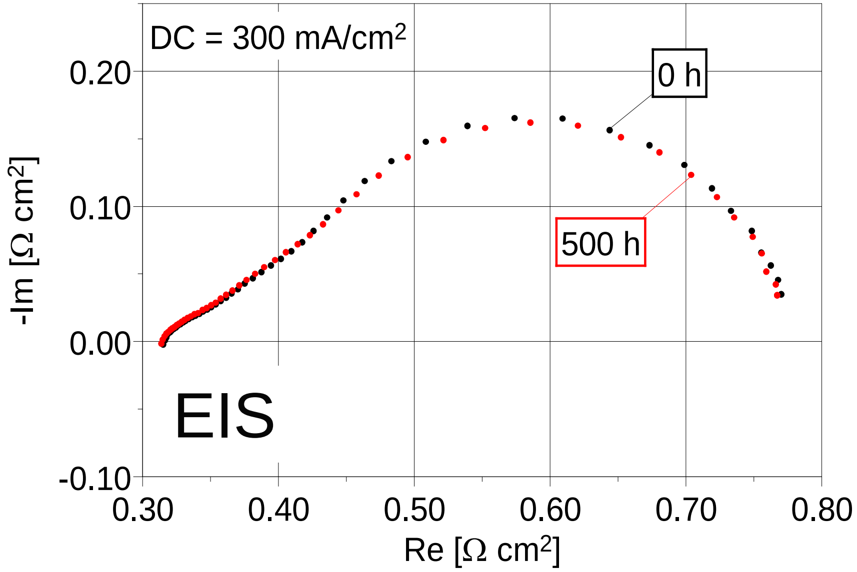
Degradation analysis

No performance and microscopic substrate **degradation** detected

FBS gas **suitable** for Ni/GDC SOFC







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