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Micro-solid oxide fuel cells running on reformed hydrocarbon fuels

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[2] Australian Centre of Microscopy and Microanalysis, The University of Sydney, Sydney, Australia
[3] Laboratory of Thermodynamics in Emerging Technologies, ETH Zurich, Zurich, Switzerland
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[6] Applied Physics, Harvard School of Engineering and Applied Sciences, Cambridge, US
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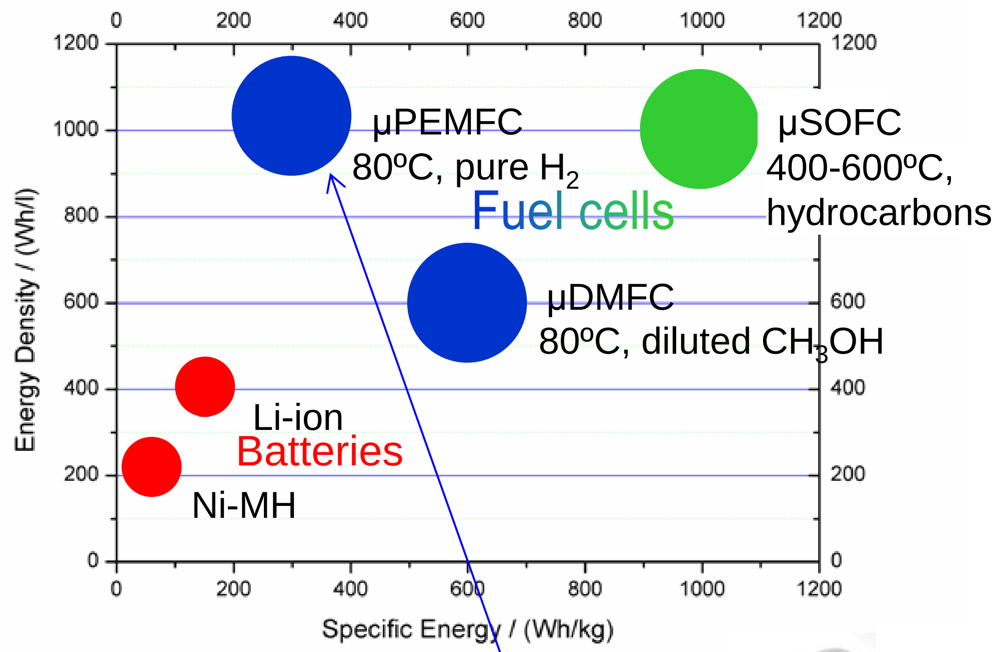
[8] Laboratory of Microengineering for Manufacturing, EPFL, Lausanne, Switzerland
[9] Institute for Micro- und Nanotechnology, NTB, Buchs, Switzerland
[10] International Institute for Carbon Neutral Energy Research (WPI-I2CNER), Kyushu University, Fukuoka, Japan

Sources for mobile energy



Advantages of micro-SOFC:

- high efficiency
- high energy density
- fuel flexibility
- geographically independent

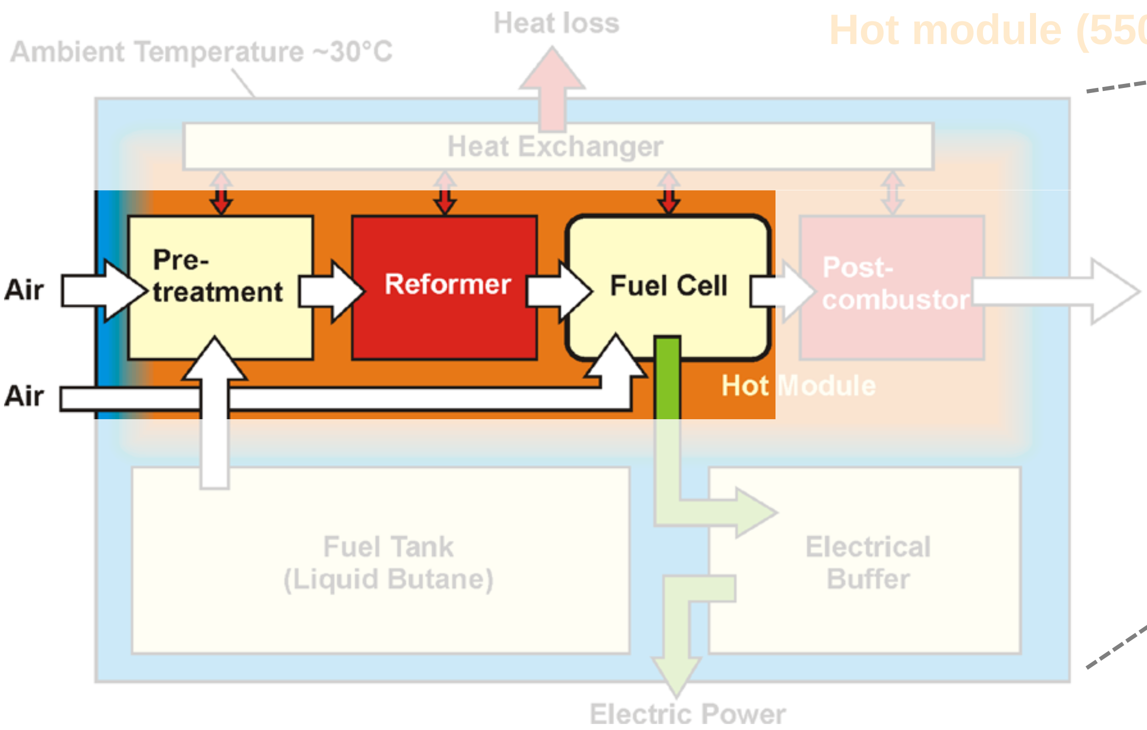
Challenges of micro-SOFC:

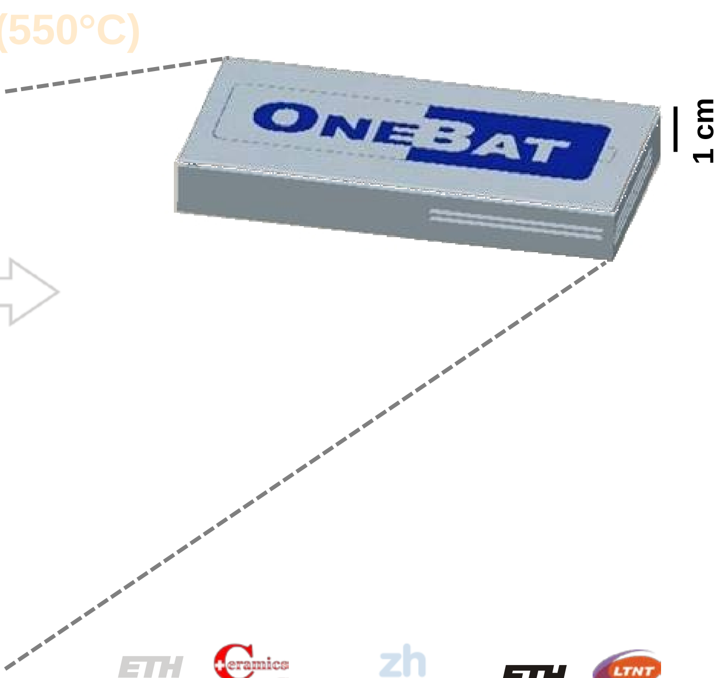
- high temperature

Horizon Minipack is a recharging system based on PEMFC
http://www.horizonfuelcell.com

Adapted from: Manhattan Scientifics & L. Livermore National Laboratories and Sulzer Hexis, 2002.

Micro-fuel cell systems for battery replacement





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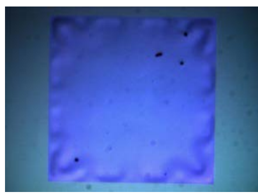
ÉCOLE POLYTECHNIQUE FÉDÉRALE DE LAUSANNE

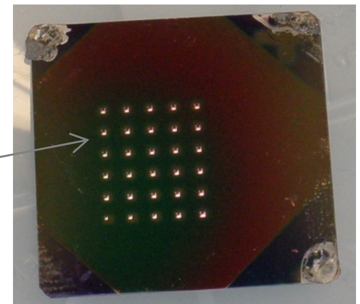
NTB INTERSTAATLICHE HOCHSCHULE FÜR TECHNIK BUCHS

A. Bieberle-Hütter *et al.*, *J. Pow. Sourc.*, 2008.

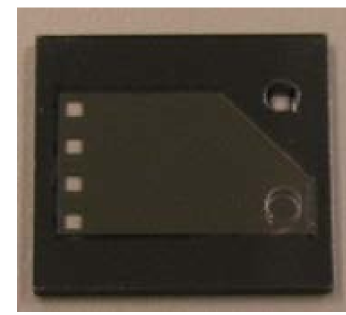
Assembly of glass carrier, reformer and micro-SOFC chip

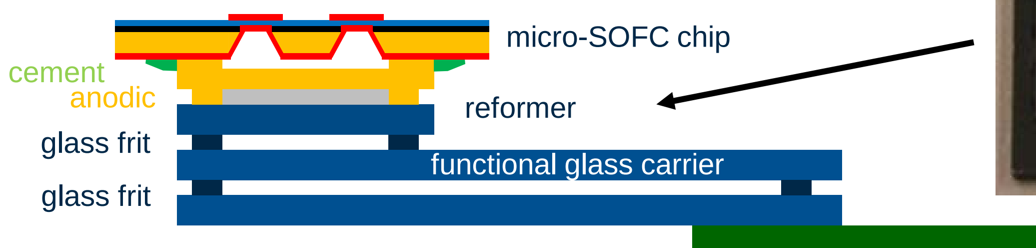
micro-SOFCs on Si chip
(Pt/YSZ/Pt)





micro reformer
(2 wt% Rh/$Ce_{0.5}Zr_{0.5}O_2$)



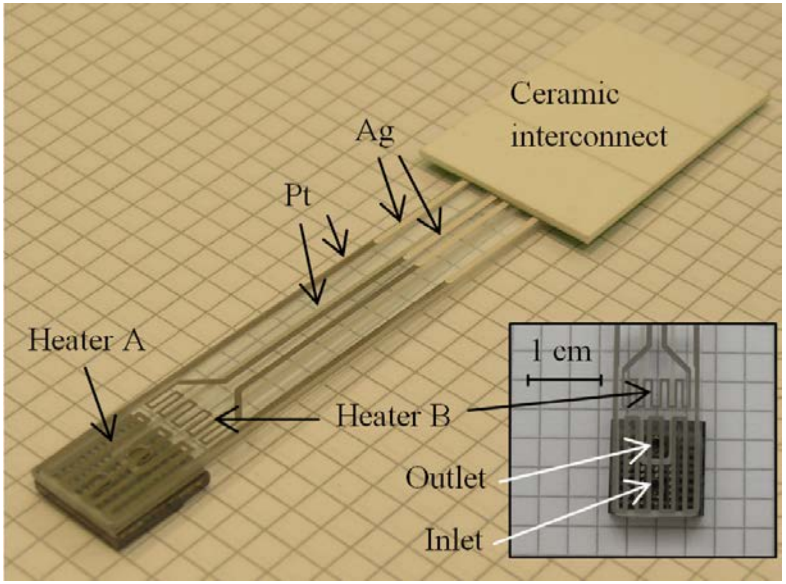


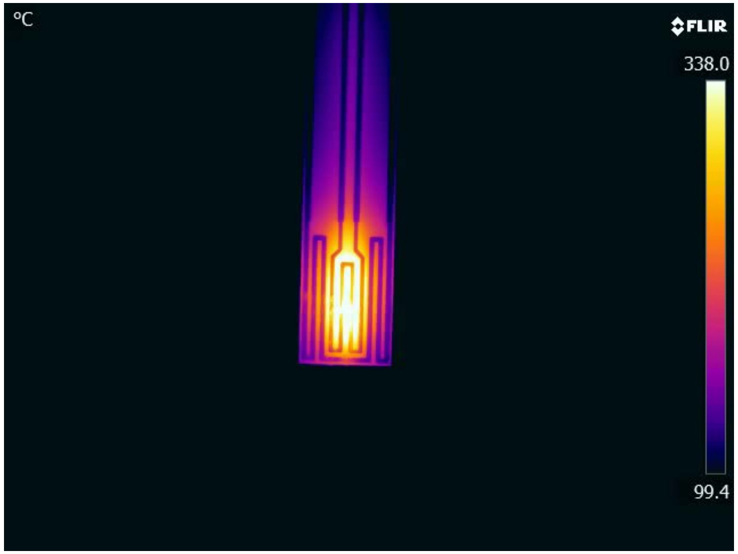
functional glass carrier

(gas supply and heater)

Functional glass carrier

- Fabrication of carrier:
  - Schott AF 32®
    - T_G = 717 ^{0}C
  - Glass frit bonding
    - H = 100 µm

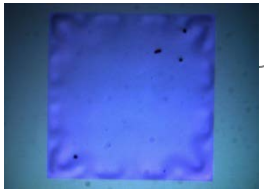


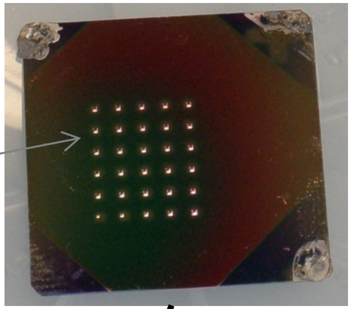


- Fabrication of heaters:
  - Pt and Ag heaters
  - Screen printed heaters
    - Height < 50 µm
  - Heater A: bottom of MR
  - Heater B: before MR inlet

Assembly of glass carrier, reformer and micro-SOFC chip

micro-SOFCs on Si chip
(Pt/YSZ/Pt)





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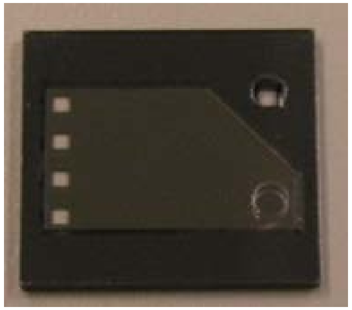
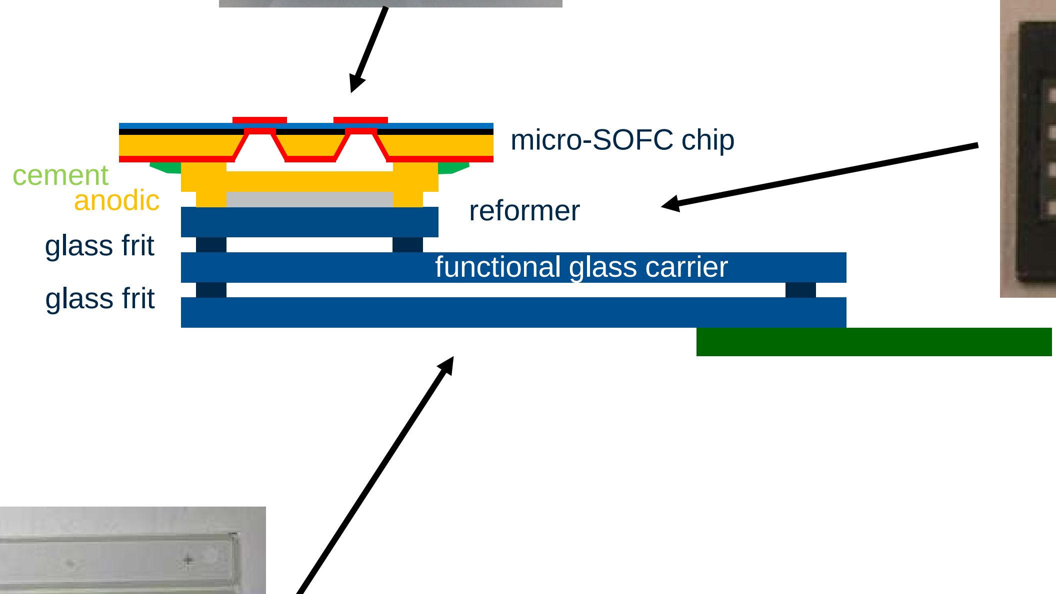
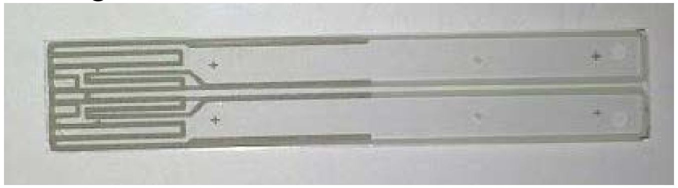




functional glass carrier



(gas supply and heater)

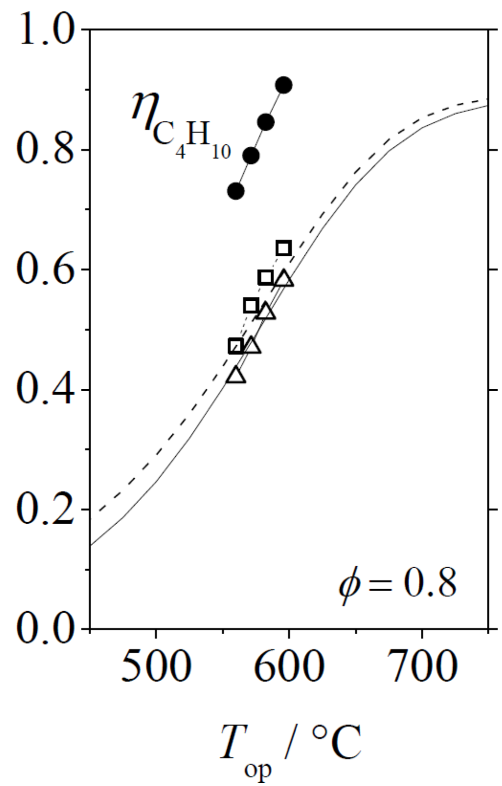
Micro reactor

- Conversion of C_4H_{10} is higher
- H_2 production from C_4H_{10} is higher

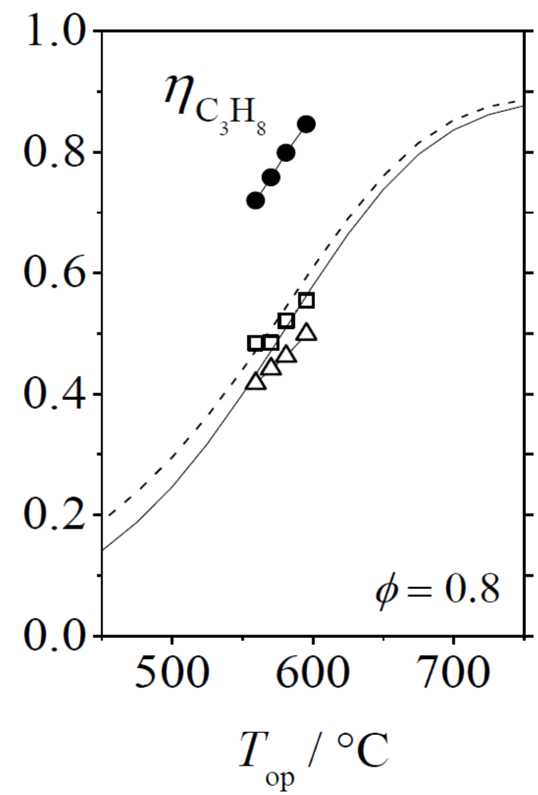
- n-Butane: C/O = 0.7 and C/O = 0.8 are best dilutions

- Propane: C/O = 0.8 is best dilution

n-Butane



Propane

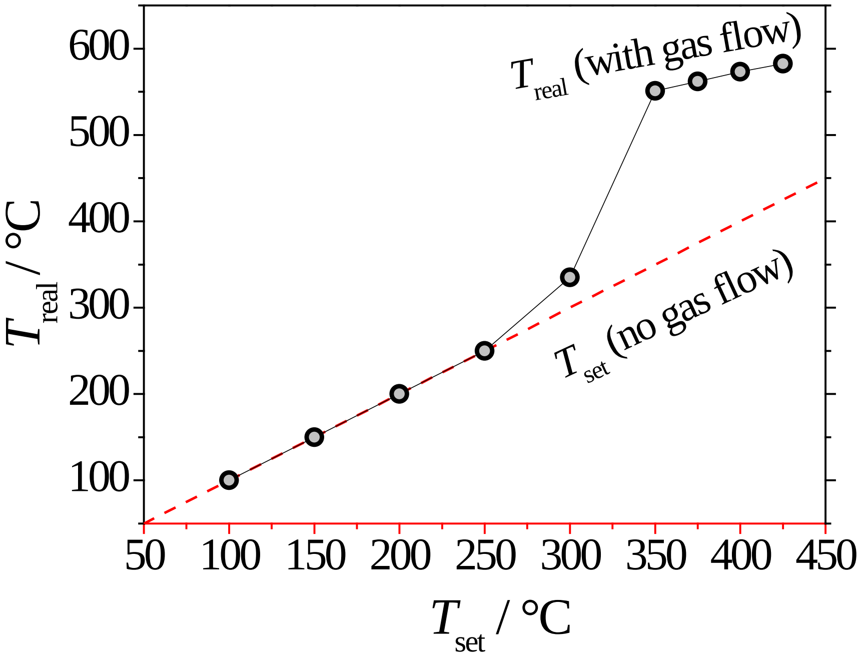


			C_xH_y -species		Syngas-species		
	ϕ		η	x_{CH_4}	ψ_{H_2}	ψ_{CO}	ψ_{syngas}
n-Butane	0.7	Average ± σ [%]	95.2 ±0.1	0.18 ±0.0	66.7 ±0.4	51.7 ±0.5	60.1 ±0.5
		Outlet flow rate [μmol/s]	0.06 ±0.01	0.24 ±0.01	4.43 ±0.14	2.74 ±0.11	7.17 ±0.13
Propane	0.8	Average ± σ [%]	84.3 ±0.4	0.16 ±0.0	55.4 ±0.1	42.5 ±0.1	49.8 ±0.1
		Outlet flow rate [μmol/s]	0.31 ±0.01	0.32 ±0.01	4.33 ±0.01	2.50 ±0.01	6.83 ±0.01

Micro reactor

- Temperature increase behavior during testing
  - Reaction starts > 300 ^{0}C

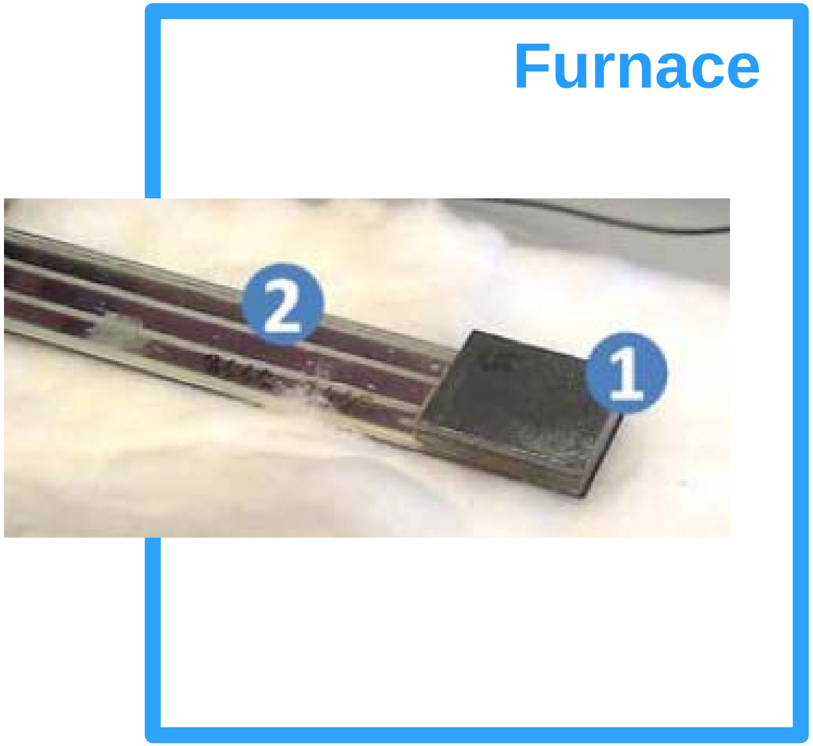
- Higher flow rate results in higher temperature.



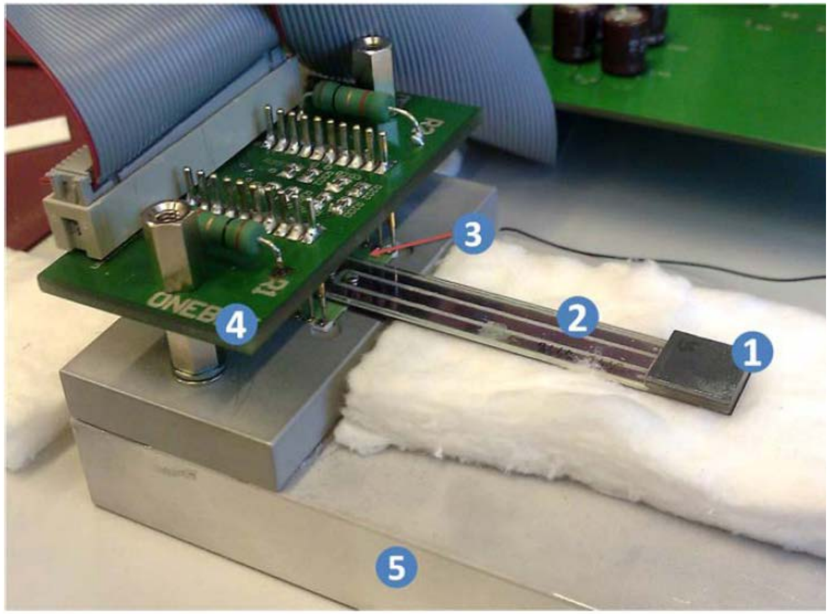
A. Santis *et al.*, *Chem. Eng. Sc*., 2012.

Characterization of micro reformer

... in the furnace



... on the carrier with integrated heaters



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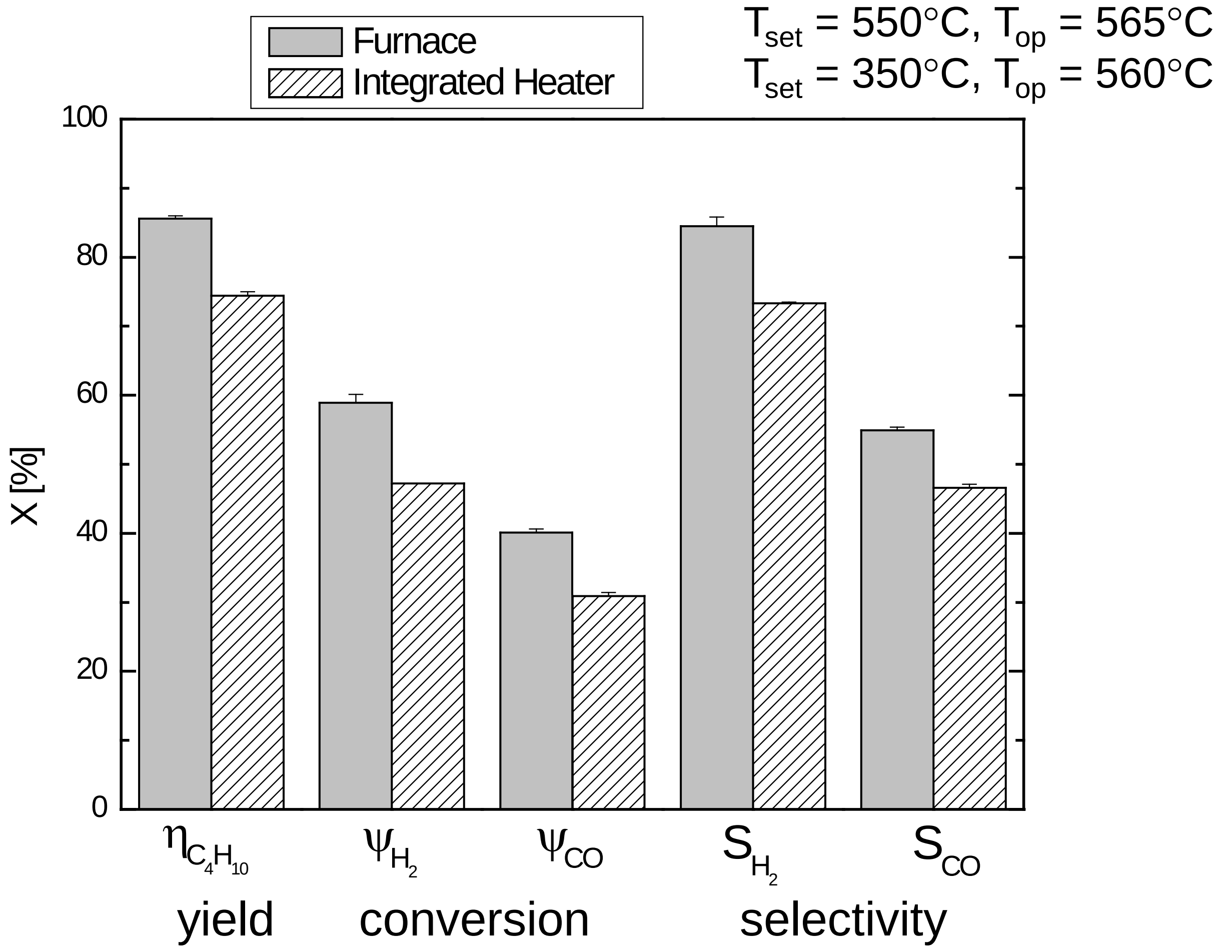
Results of gas analysis

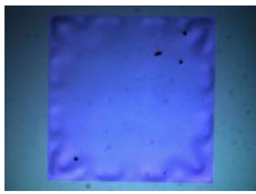
- Less even temperature distribution results in lower yield, conversion and selectivity for the integrated heater setup.
- Better insulation will improve it again.

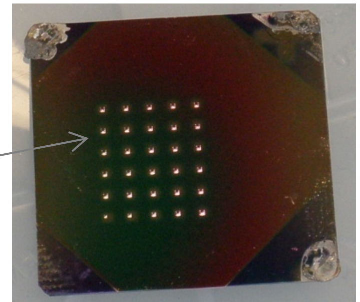


Literature

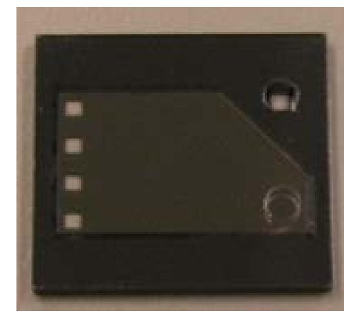
Assembly of glass carrier, reformer and micro-SOFC chip

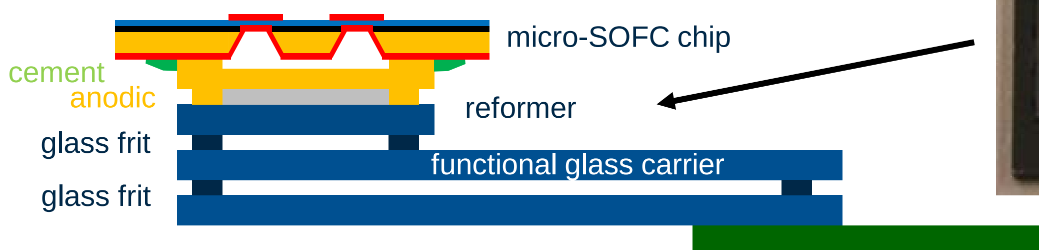
micro-SOFCs on Si chip
(Pt/YSZ/Pt)



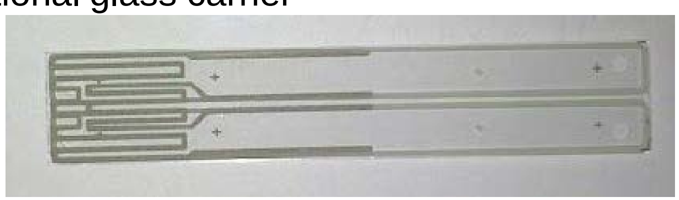


micro reformer
(2 wt% Rh/$Ce_{0.5}Zr_{0.5}O_2$)





functional glass carrier



(gas supply and heater)

Micro-SOFC fabrication

Si Wafer (380 µm), LPCVD-Si_3N_4 (200 nm) on both sides

Window opening (900 µm): photolitho + RIE of Si_3N_4

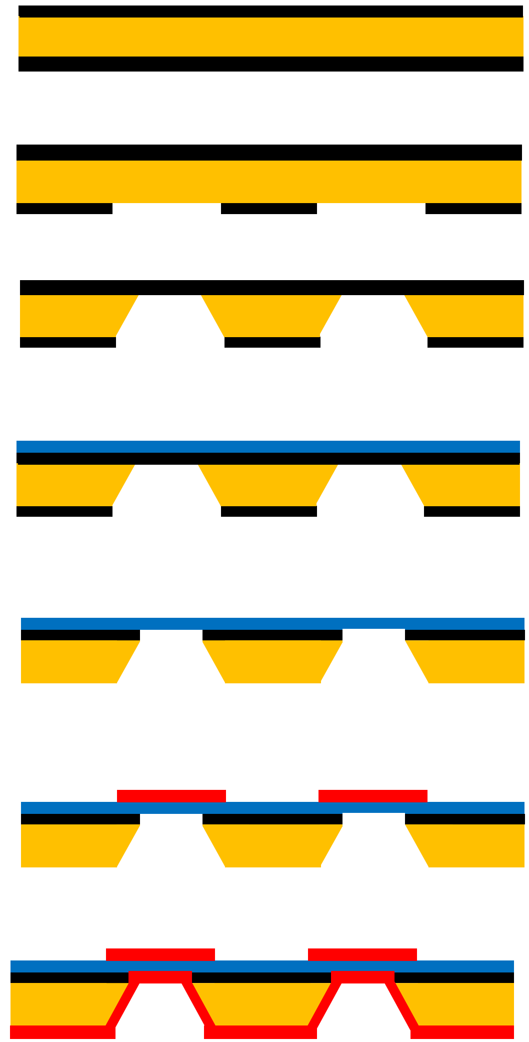
Si wet etching: KOH 20%, 90 °C

YSZ deposition: AA-CVD, PLD, spray pyrolysis

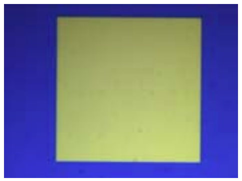
Release of the YSZ membrane by reactive ion etching

Top-side electrode deposition

Back-side electrode deposition



Top-view light micrographs

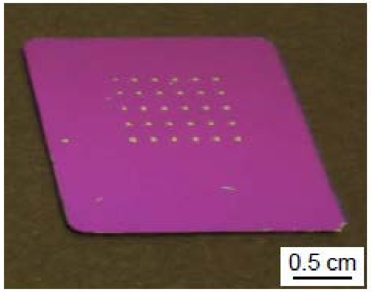


390 µm

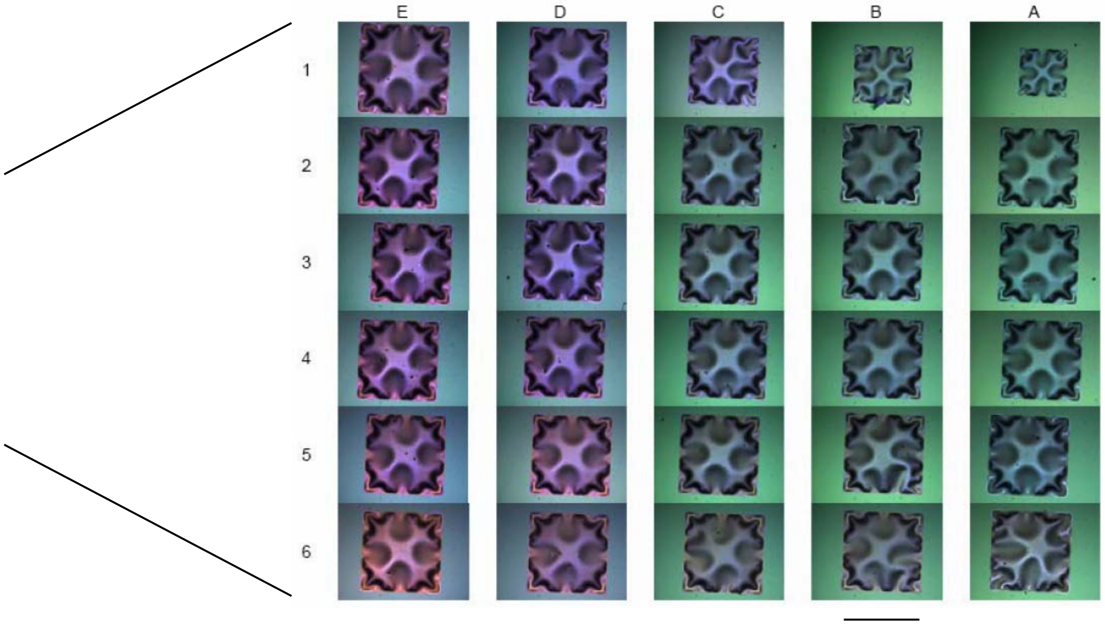
comp. stress

tens. stress

Micro-SOFC fabrication



Test chip

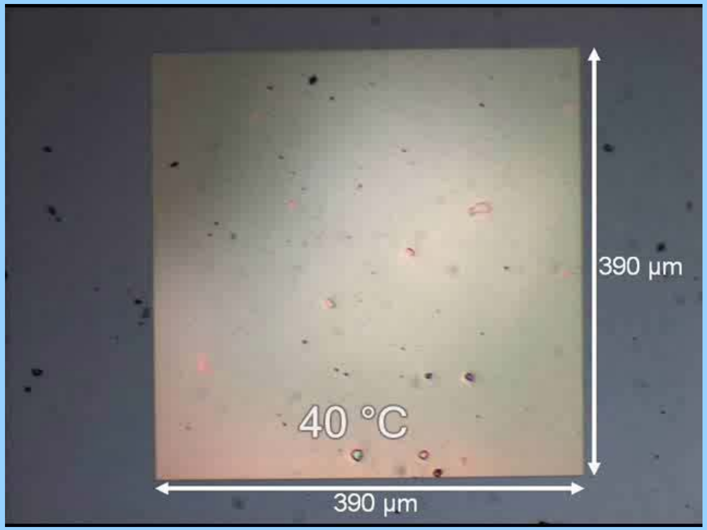


membrane side length: 390 µm

- Test chip: 30 free-standing micro-SOFC membranes
- Membrane yield (%): number of surviving membranes / 30 * 100
- Membrane yield target: ~100 %

Thermomechanical stress

T_{dep} = 25 °C

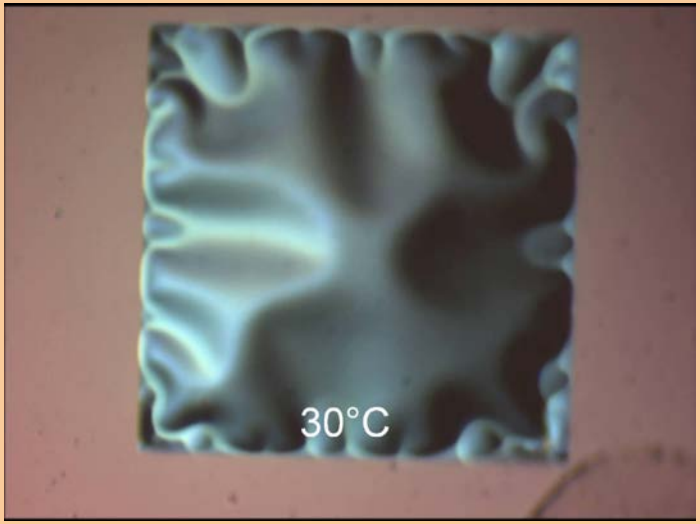


Partially crystalline as-deposited film (PLD)

Yield after free-etching: ca. 100%

Tensile stress (flat membrane)

T_{dep} = 700 °C



Fully crystalline as-deposited film (PLD)

Yield after free-etching: ca. 100%

Compressive stress (buckled membrane)

A. Evans *et al*., *Fuel Cells*, 2012.

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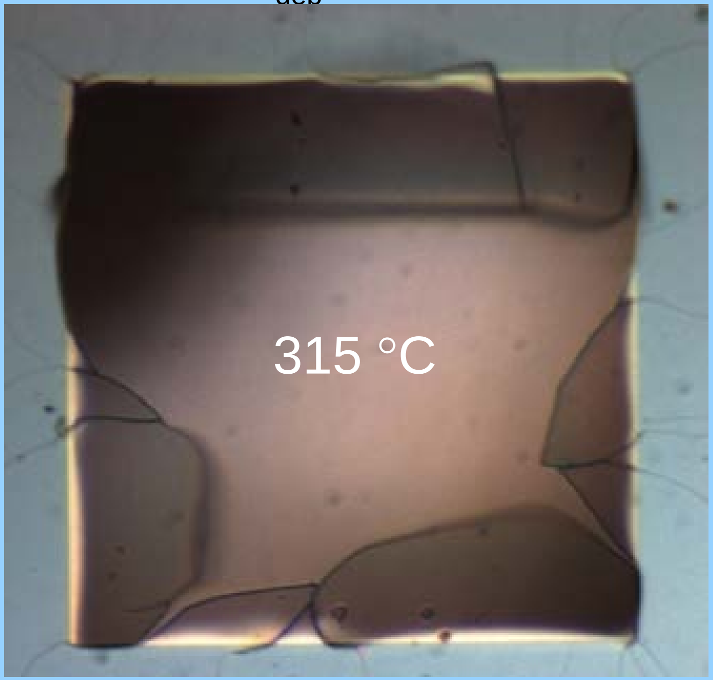
Thermomechanical stress

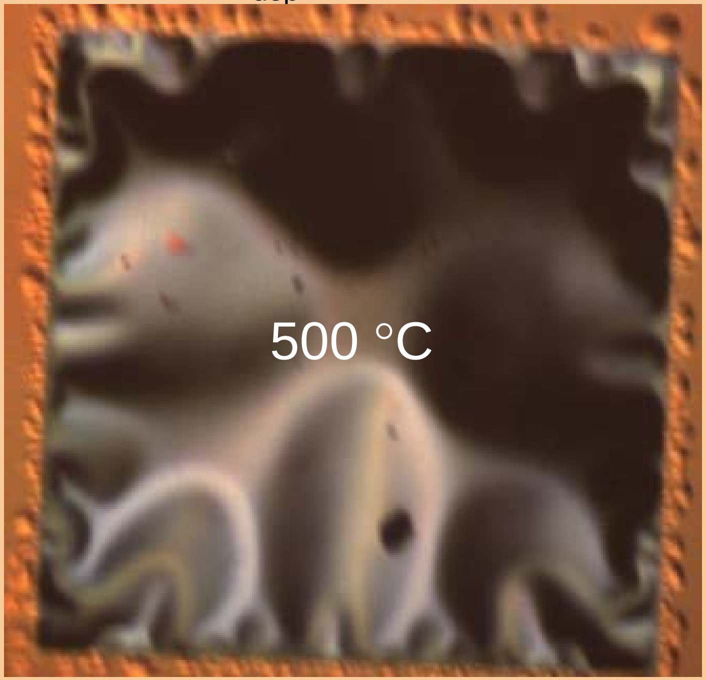
T_{dep} = 25 °C



Crystallization during heating >> tensile stress

Membrane rupture (low yield: < 10 %)

T_{dep} = 700 °C

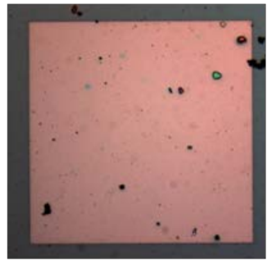
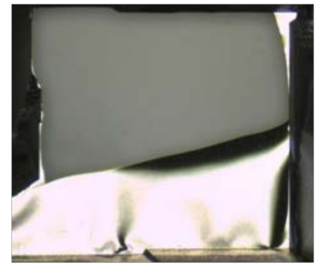
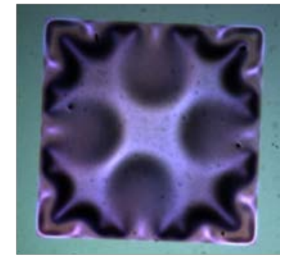


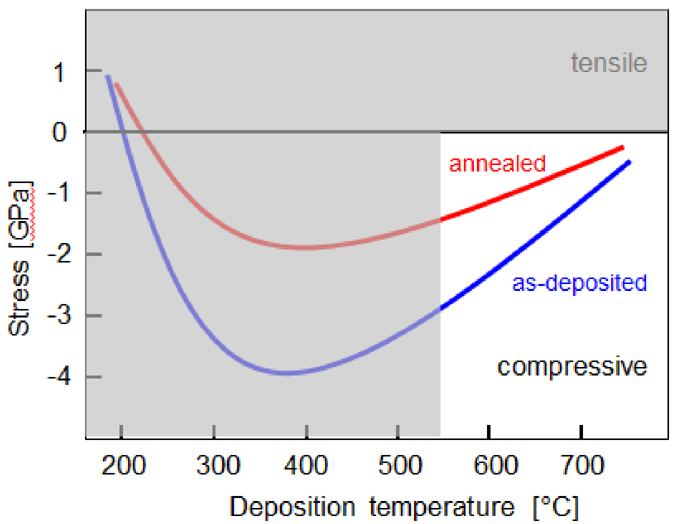
Buckling «apparently» unchanged during heating

Robust membrane (high yield: 100%)

A. Evans *et al*., *Fuel Cells*, 2012.

Residual stress in free-standing YSZ membranes

PLD T_{depo}	25°C	400°C	700°C
free-standing membrane (390x390 µm² 300nm 8YSZ)			
Yield:			
after deposition	98%	0%	>99%
after annealing at 500 ºC	0%	0%	>99%
SAMLAB	--	-2.1 GPa	-1.4 GPa



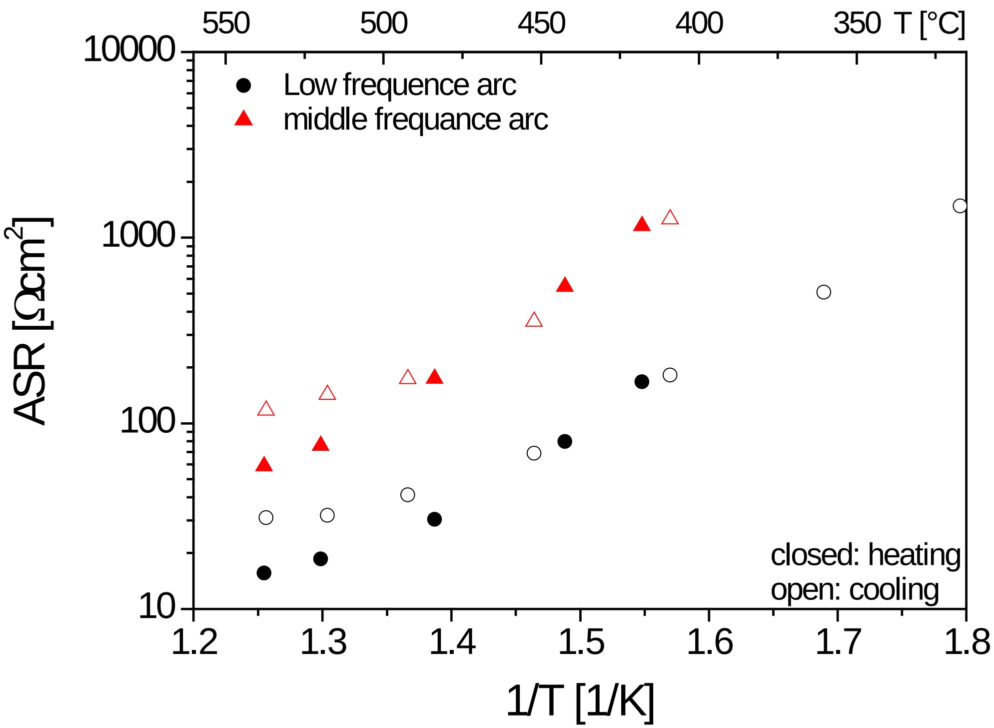
Different stresses $f(T_{depo})$:

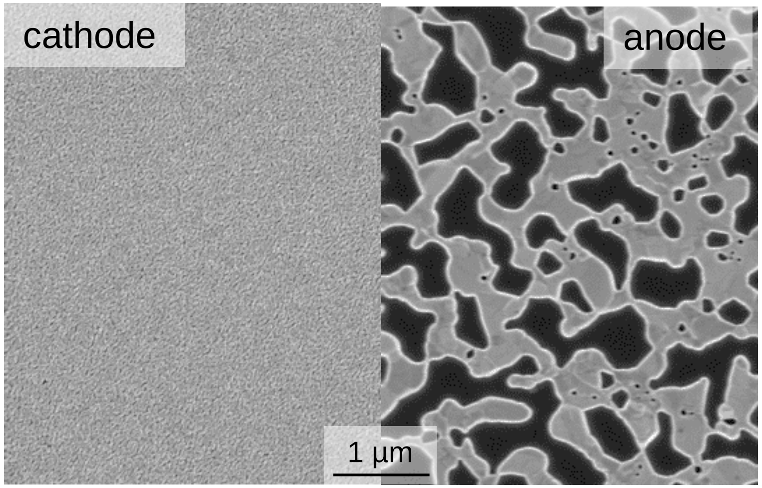
- Tensile and too much compressive stress result in membrane rupture.

Adapted from: I. Garbayo *et al.*, *Solid State Ionics*, 2012.

A. Evans *et al.*, *Fuel Cells*, 2012.

ASR of Pt in fuel cell conditions





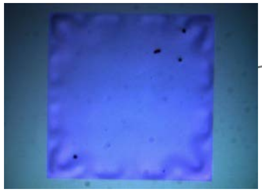
cathode: 300 sccm air
anode: 60 sccm H_2 in 240 sccm N_2

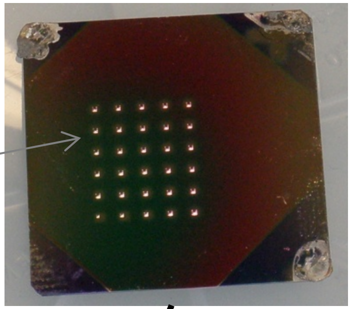
Pt thin films tested on YSZ single crystal

- ASR of the electrodes are stable over heating and cooling
- Microstructure is different depending on the seen environment

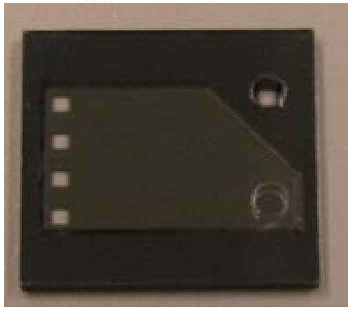
Assembly of glass carrier, reformer and micro-SOFC chip

micro-SOFCs on Si chip
(Pt/YSZ/Pt)

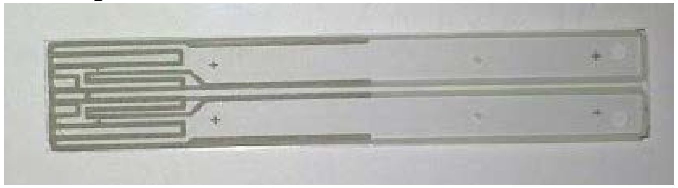




micro reformer
(2 wt% Rh/$Ce_{0.5}Zr_{0.5}O_2$)



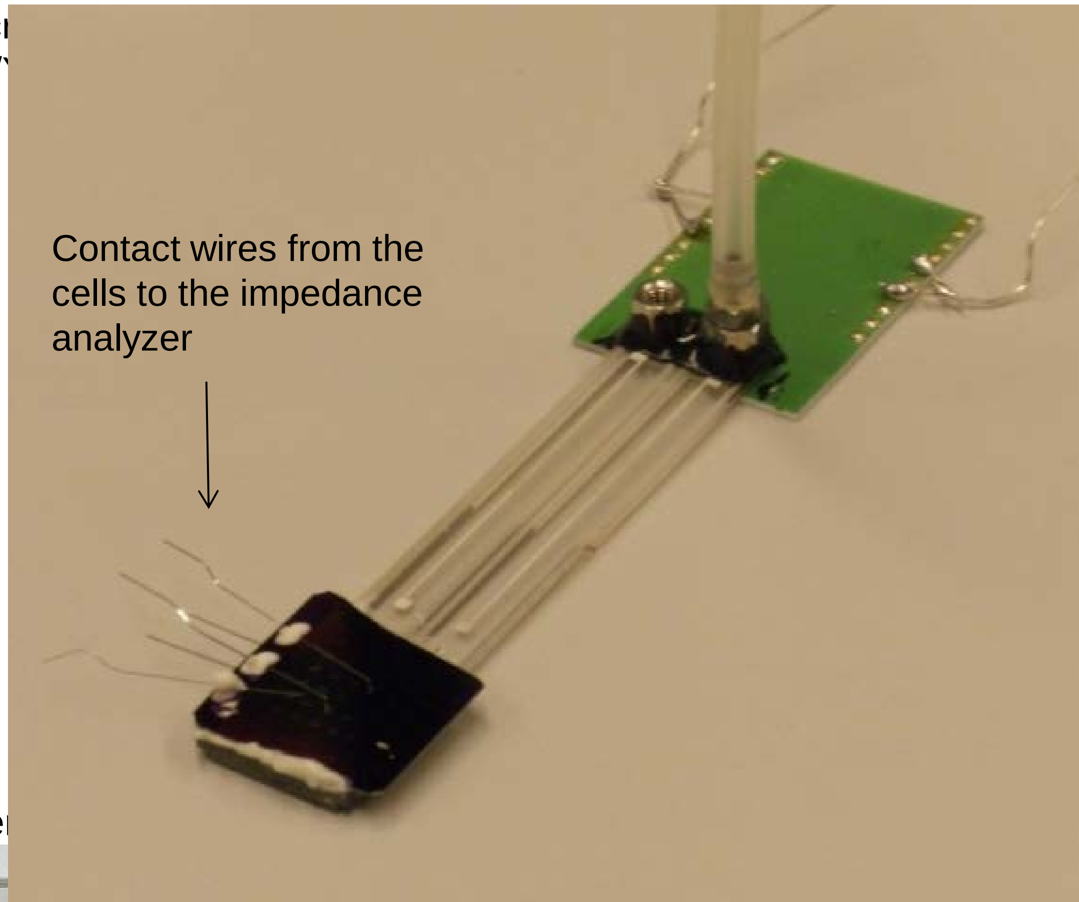
functional glass carrier



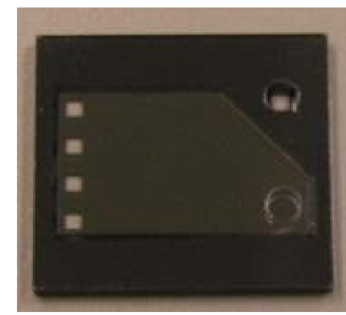
(gas supply and heater)

Assembly of glass carrier, reformer and micro-SOFC chip

micr
(Pt/Y



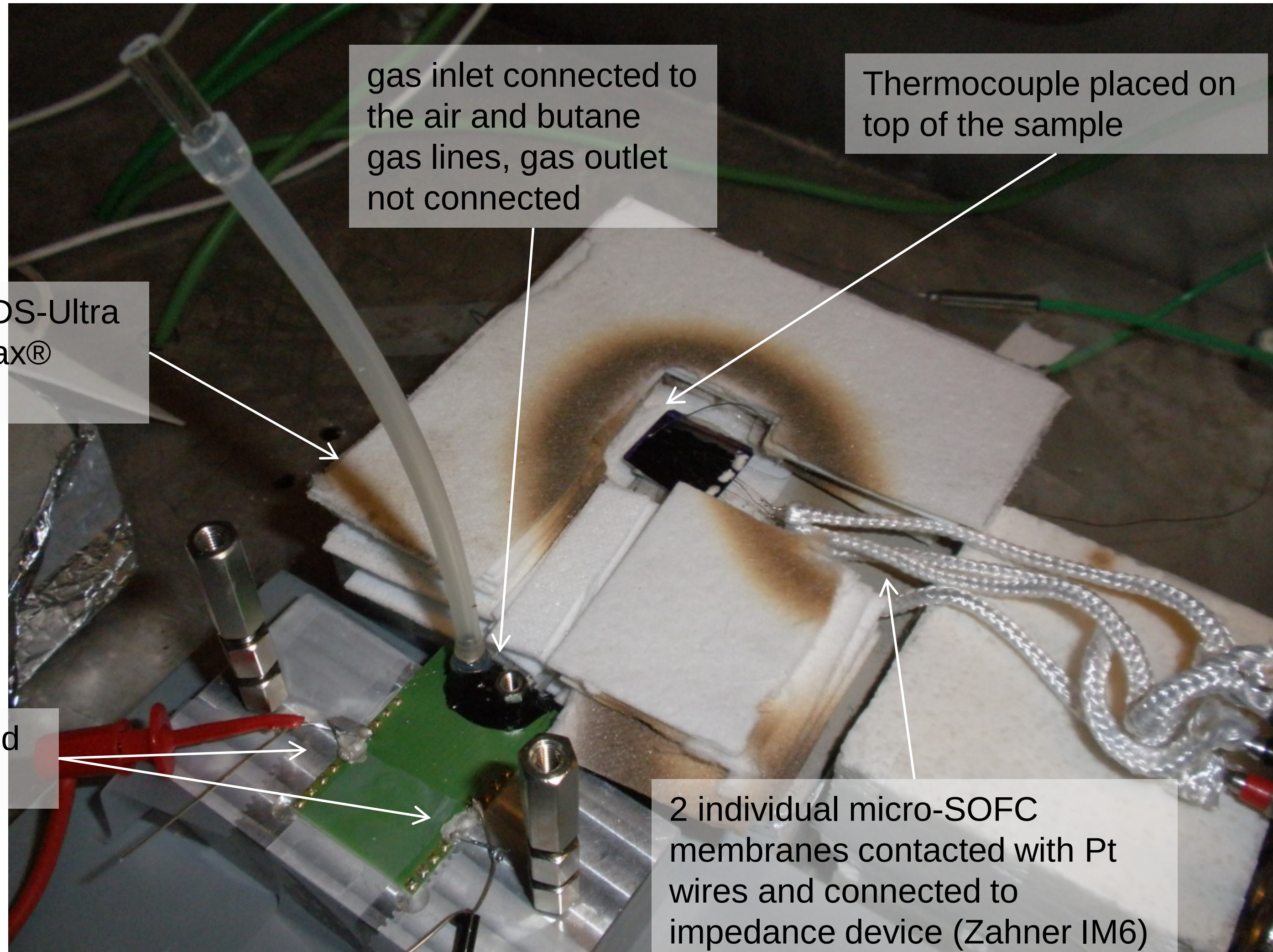
nicro reformer
2 wt% Rh/$Ce_{0.5}Zr_{0.5}O_2$)



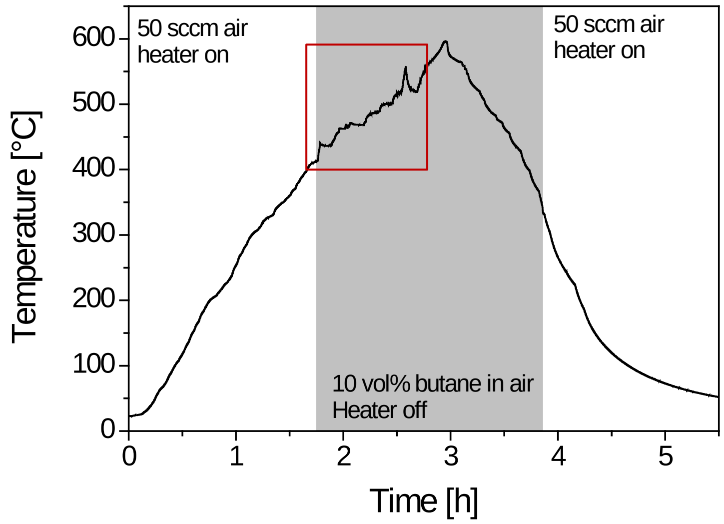
functional glass carrie

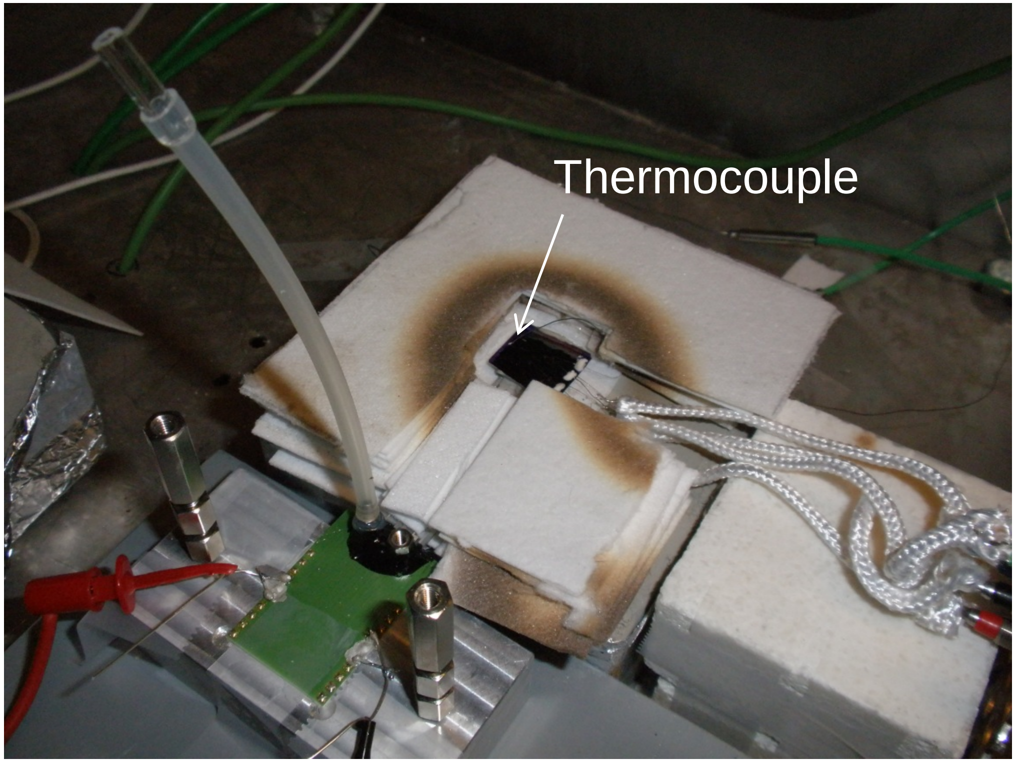
(gas supply and heater)

Assembly of glass carrier, reformer and micro-SOFC chip



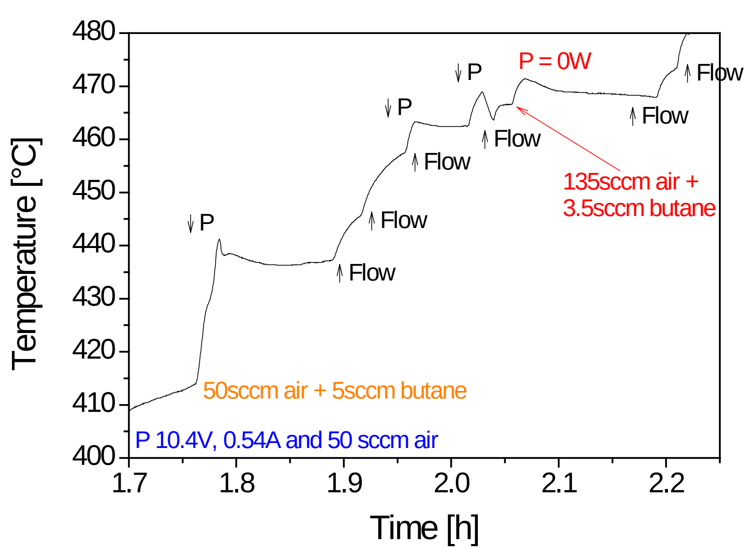
Temperature program

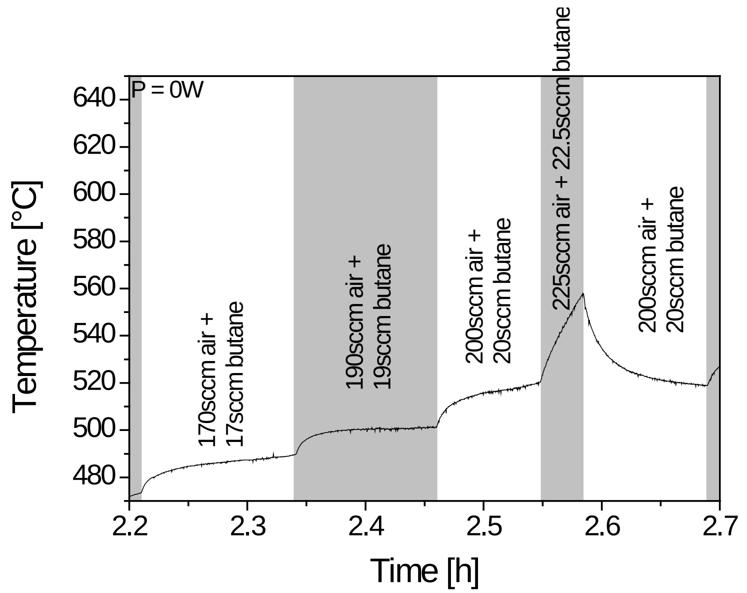




- Heating ramp done by increasing voltage
- Temperature measurement on the sample is accurate

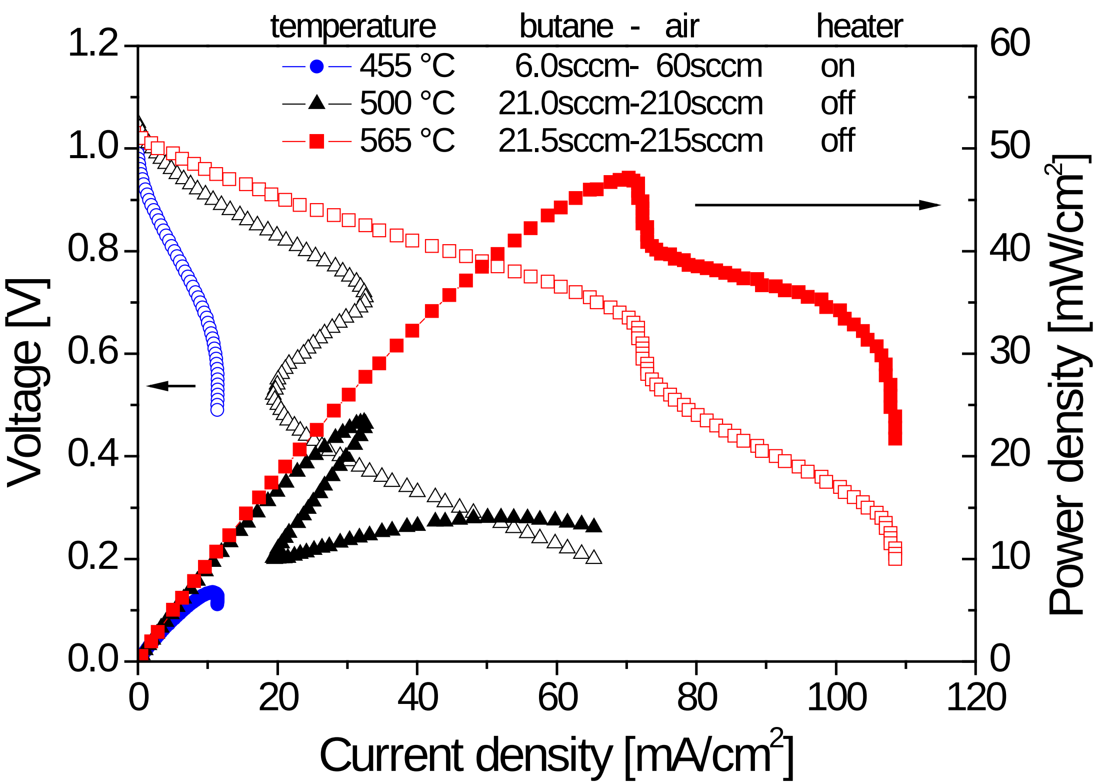
Temperature program



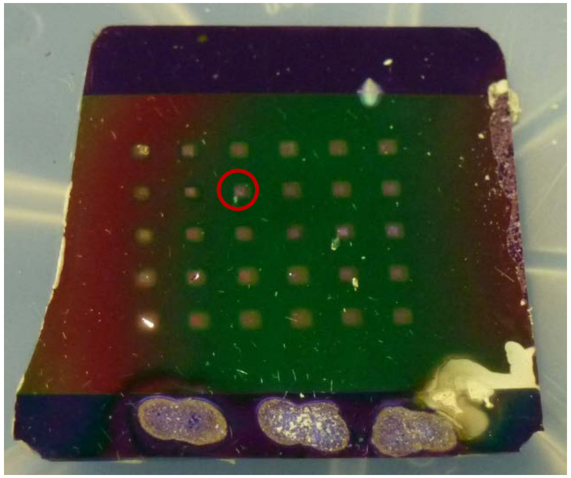


- Self sustained reaction of the reformer heats the assembly further
  - Increasing flow results in increasing temperature
- Almost stable temperature reached after 2 min

Cell voltage and power density

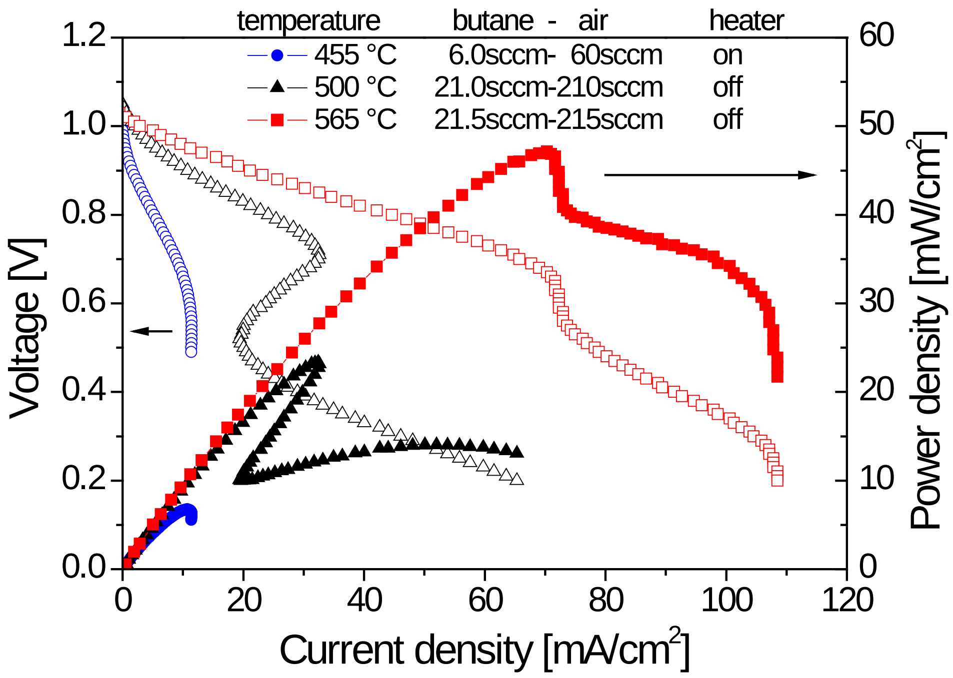


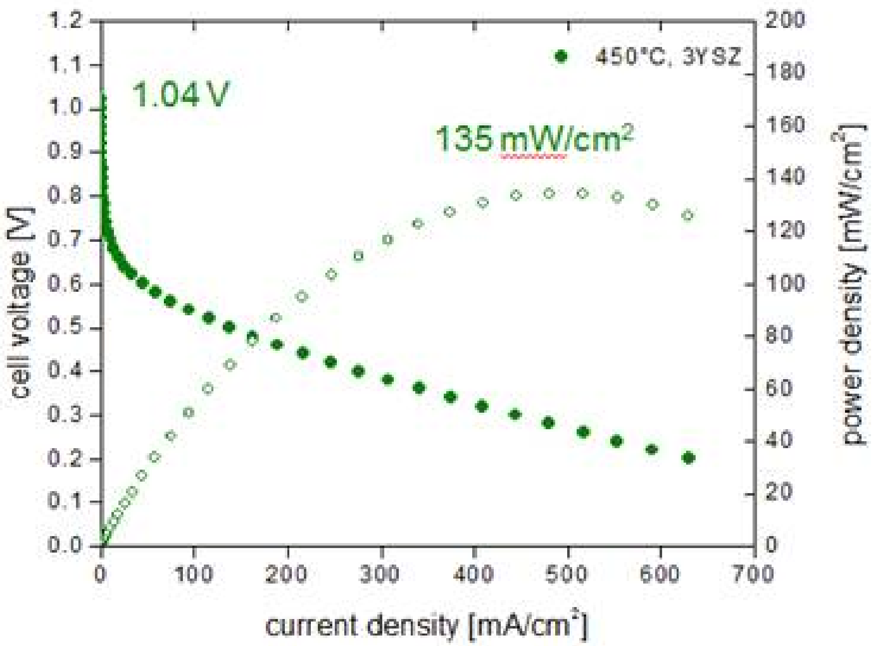
After testing



- Theoretical open circuit voltage was achieved!
  - Gas-tight membranes
- Maximum power density of about 50 mW/cm^2 at 565 ºC!
- All membranes survived the testing program (maximal temperature of 596 ºC)!

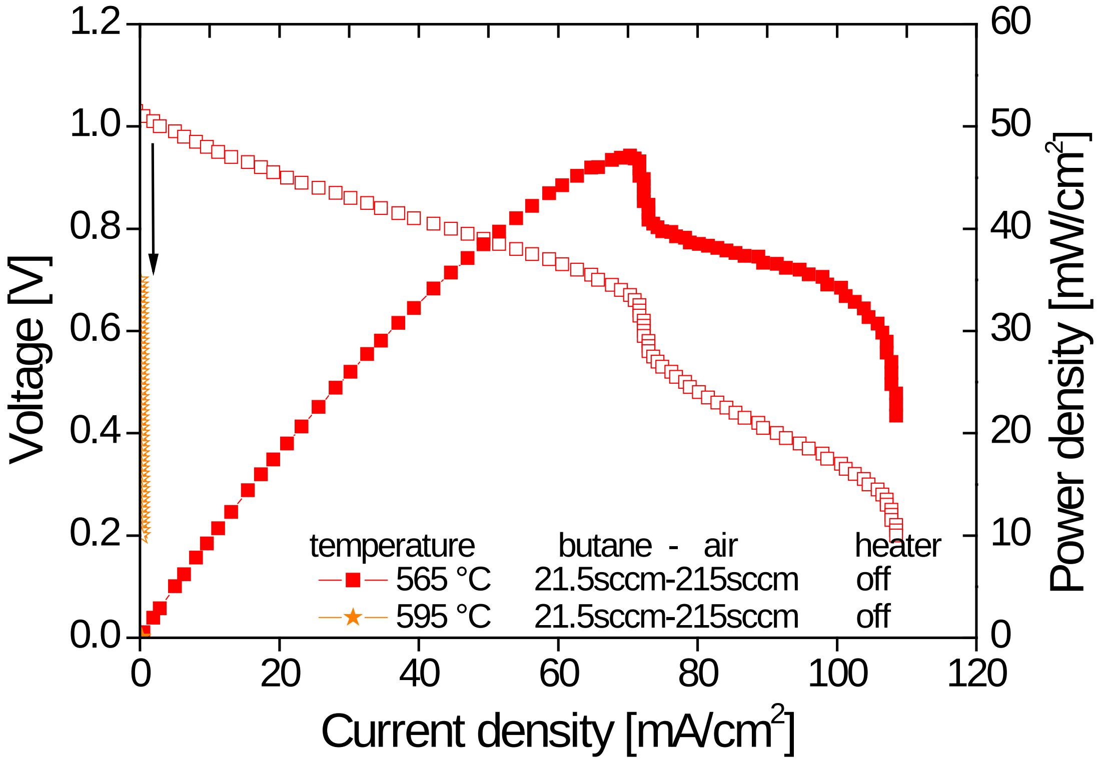
Cell voltage and power density – comparison

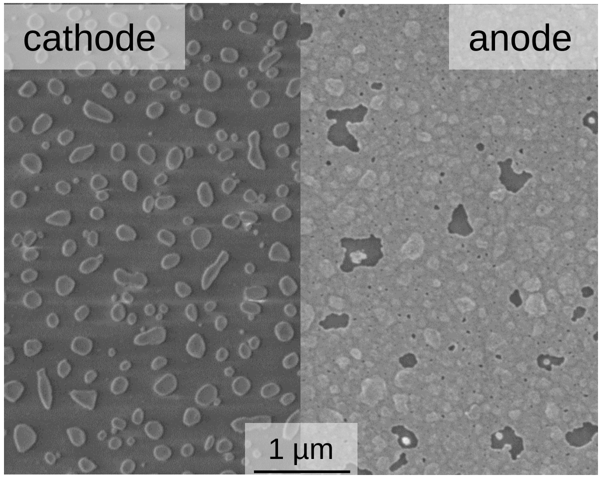




- Strange curve shape at ~0.7 V, most likely due to excess water at the gas outlet.

Cell voltage and power density – decrease in OCV





- Long-term testing not possible due to instable Pt-electodes
  - Cathode agglomerates more severe most likely due to the surface roughness of the electrolyte layer
- Gas leak of ceramic paste results in lower OCV

Summary

- Assembly of the glass carrier, reformer and micro-SOFC chip works.
- The heater was able to heat up the assembly till the self sustained reaction of the reformer sets in.
- Further heating was achieved by increasing the flow of butane and air.
- Theoretical OCV and a maximum power density of about 50 mW/cm^2 at 565 ° C was achieved.

Outlook

- Excess of water results in unstable current-voltage curve.
- Integration of more stable (and active) electrode materials in order to achieve a better stability and higher power density
  - Metal alloys: Pt-Y-Al
  - Ceramics: LSC, LSMC
- Cement paste starts to leak at 550 ° C, which resulted in an unstable temperature due to complete combustion of the fuel.
- Current collection of the membranes should be improved
  - On the chip with connection path
  - To the out side with wire bonding

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