Batterie- und Brennstoffzellensysteme

Stack- und Zellkonzepte für die SOFC

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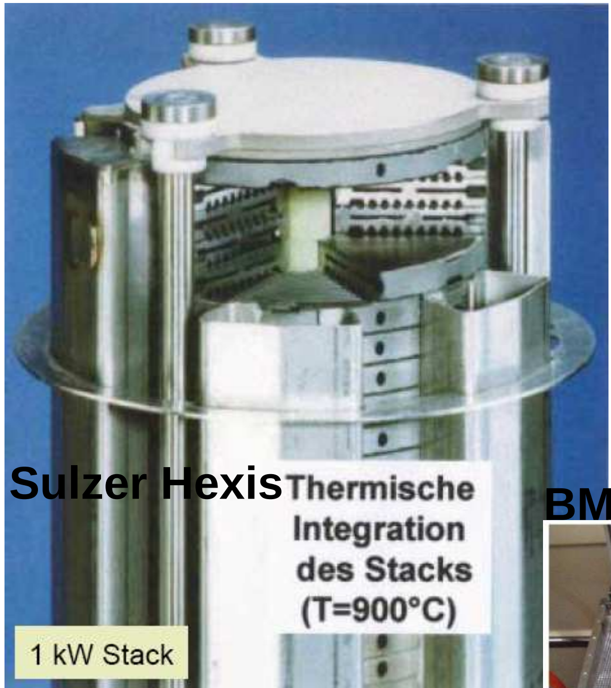
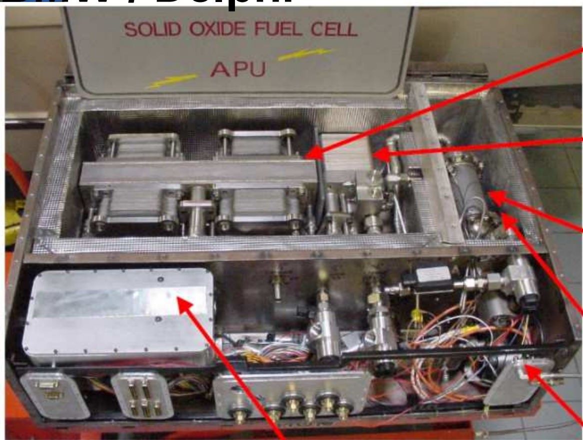
Stack- und Zellkonzepte



Sulzer Hexis

BMW / Delphi



Brennstoffzellen-Stack
Erzeugung elektrischer Energie aus Reformat (H_2 und CO)

Waste **E**nergy **R**ecovery
Restgasverbrennung, Aufheizung Reaktionsluft

Hauptreformer
Aufheizung Stack, Erzeugung von Reformat (20%H_2, 20%CO, 3%CH_4, Rest N_2)

Mikroreformer
Start Hauptreformer

Luft-Gebläse
Reaktionsluft und Kühlluft

Kraftstoff-versorgung

BMW Group

Siemens-Westinghouse

Fuel Cells
Cell Voltage, Internal Resistance and Fuel Cell Efficiencies

Karlsruher Institut für Technologie

thermodynamic efficiency $$\eta_{th} = \frac{\Delta G}{\Delta H} = 1 - \frac{T\Delta S}{\Delta H}$$

electrochemical efficiency $$\eta_{el} = \frac{U_{cell}}{U_{th}} = -\frac{nFU_{cell}}{\Delta G}$$

cell voltage and internal resistance

$$U_{cell} = U_0 - R_{cell} \cdot I_{cell} = U_0 - I_{cell} \cdot \sum_k R_{cell,k}$$

$$\sum_k R_{cell,k} = R_{cathode} + R_{electrolyte} + R_{anode} + R_{contact}$$

fuel utilization $$\beta_f = \frac{\text{used fuel}}{\text{provided fuel}}$$

fuel efficiency $$\eta_f = \frac{I}{I_m}$$

single cell ... stack

---

reforming efficiency $$\eta_{ref} = \frac{\Delta H}{\Delta H_{fuel}}$$

el. system efficency $$\eta_{elS} = \frac{W_{el}}{nFU_{cell}}$$

electrical system efficiency $$\eta_{electrical} = \eta_{th} \cdot \eta_{el} \cdot \eta_f \cdot \beta_f \cdot \eta_{Ref} \cdot \eta_{elS} = \frac{\text{produced electrical energy}}{\text{provided chemical energy}}$$

system (el. p.)

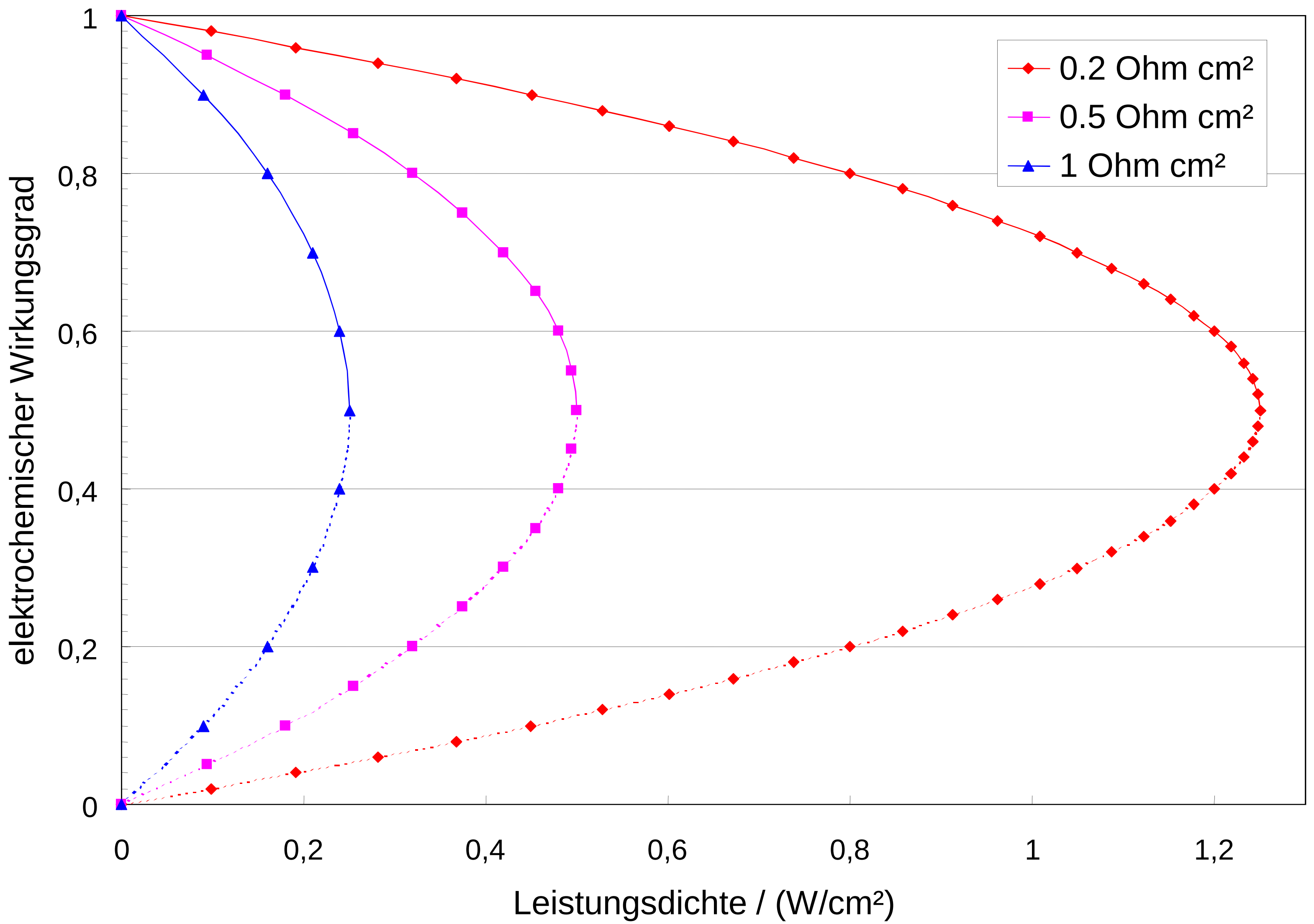
---

thermal system efficiency $$\eta_{thermal} = \frac{\text{usable heat}}{\text{provided chemical energy}}$$

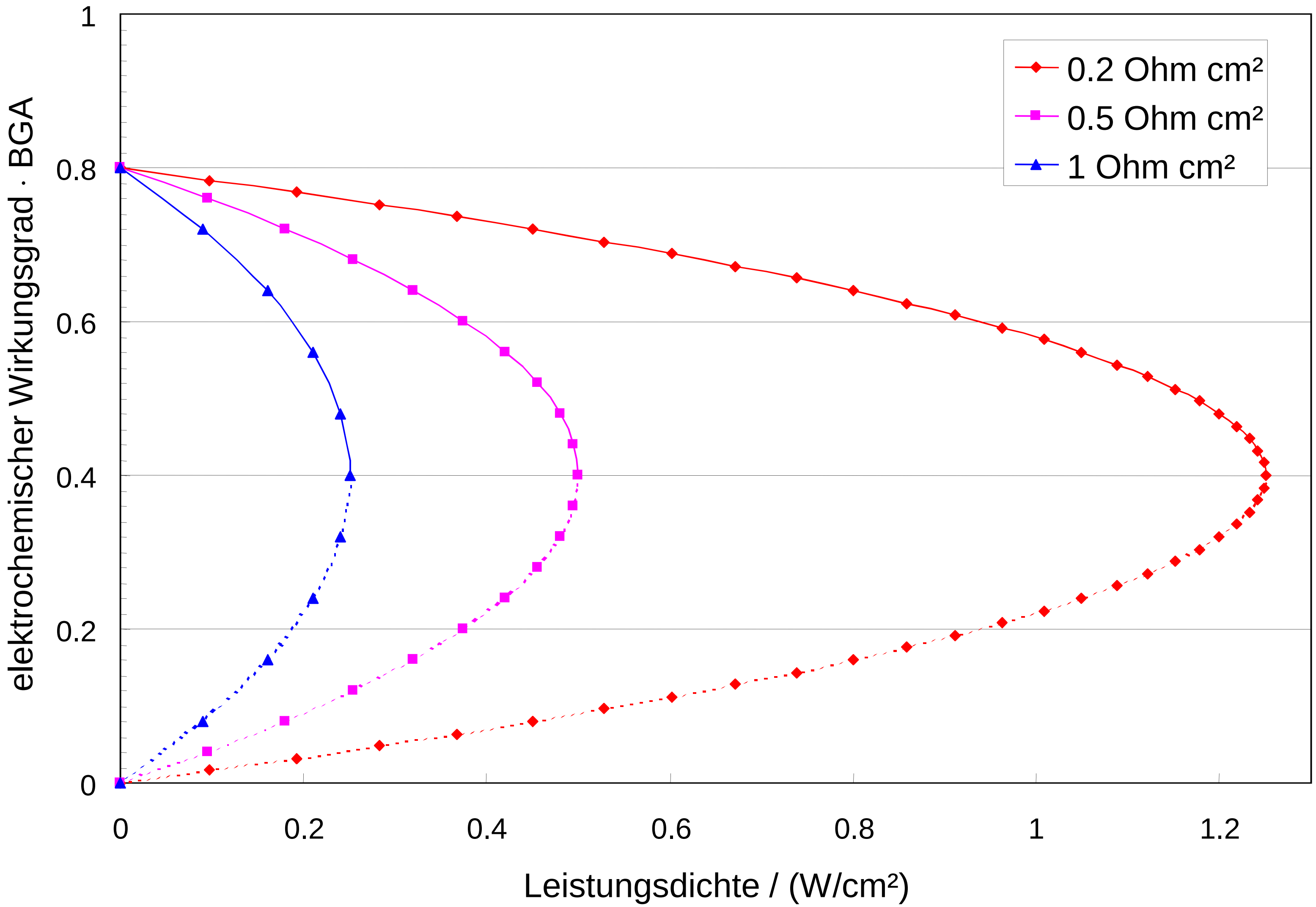
total efficiency $$\eta_{tot} = \eta_{electrical} + \eta_{thermal}$$

CHP-system

Elektrochemischer Wirkungsgrad in Abhängigkeit der Leistungsdichte

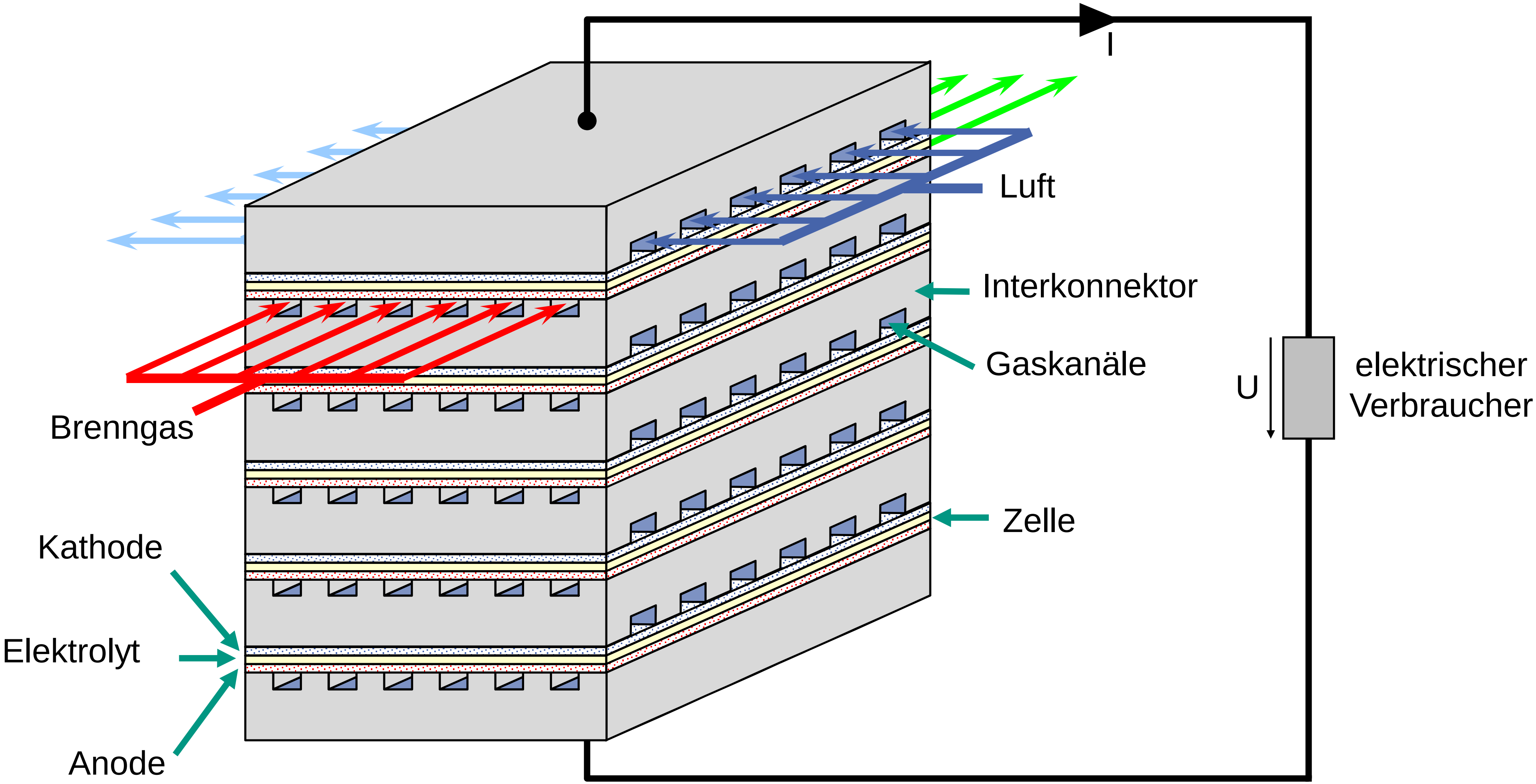


Stack-Wirkungsgrad ($\beta_f \cdot \eta_{el}$) in Abhängigkeit der Leistungsdichte

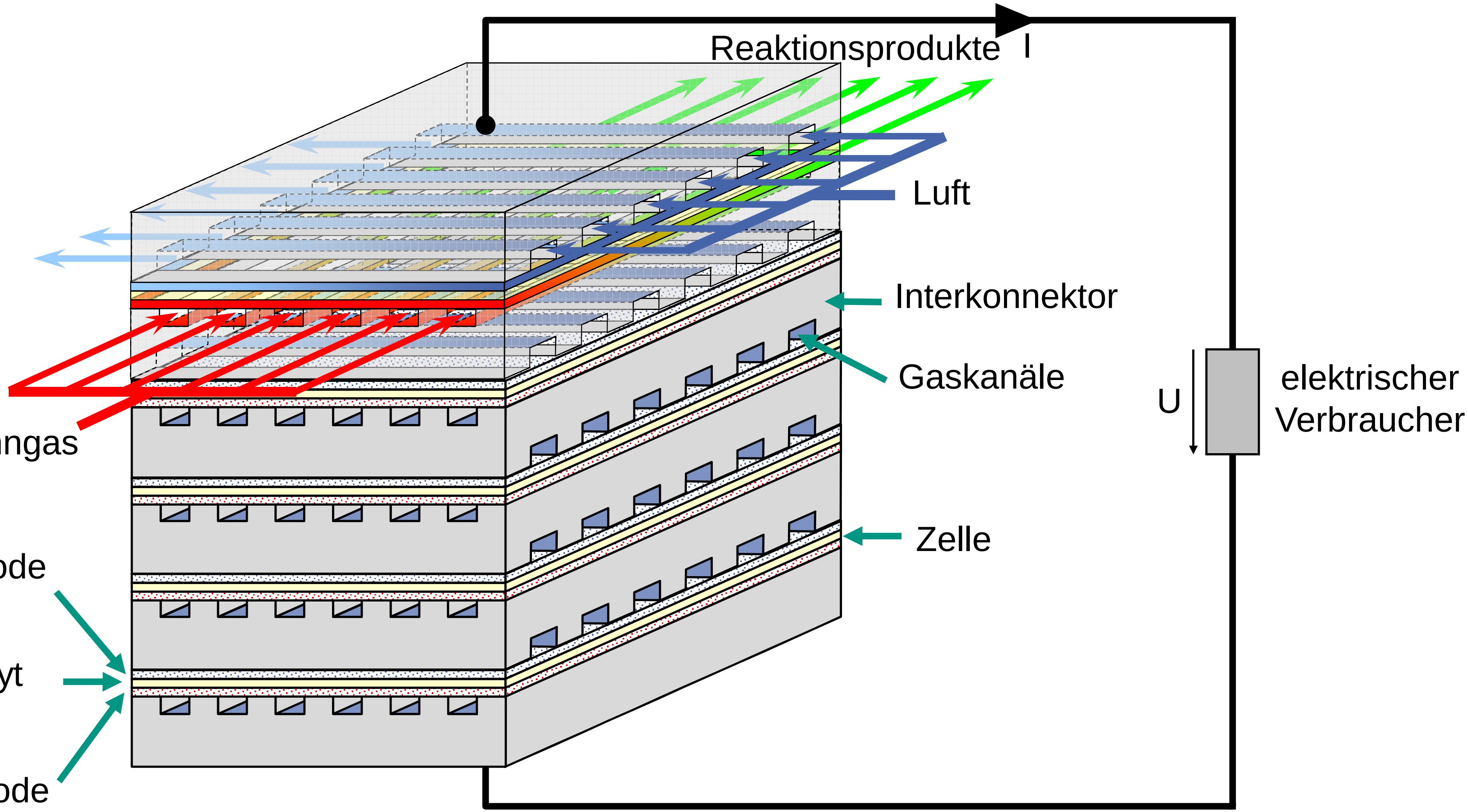


Brenngas-ausnutzung: 80%
(η_f = 1)

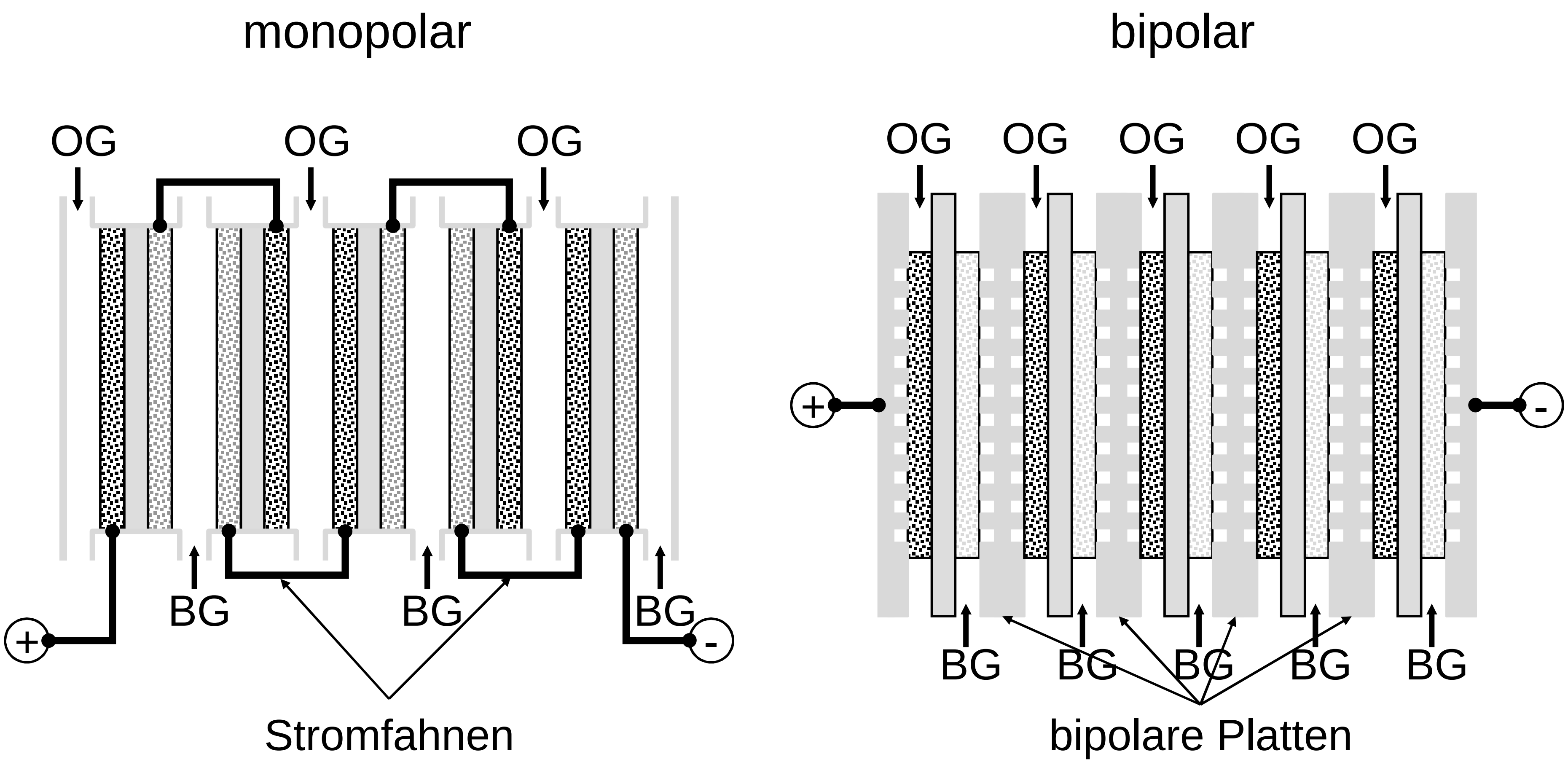
Planarer Brennstoffzellen-Stack



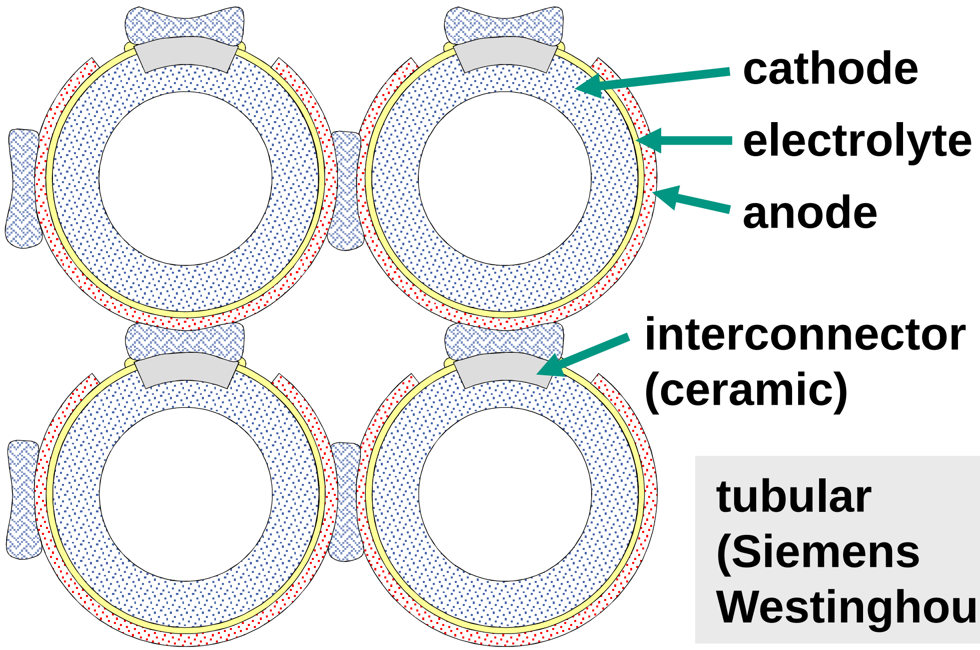
Betriebsbedingungen im Stack



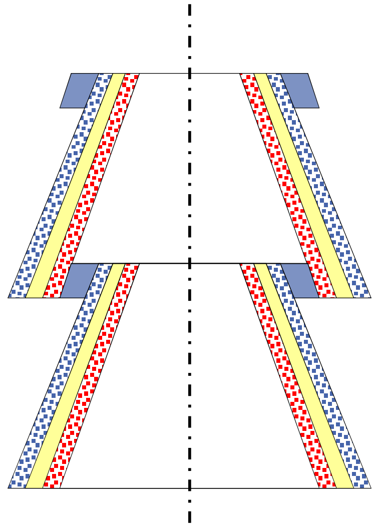
Baukonzepte für Brennstoffzellenstacks



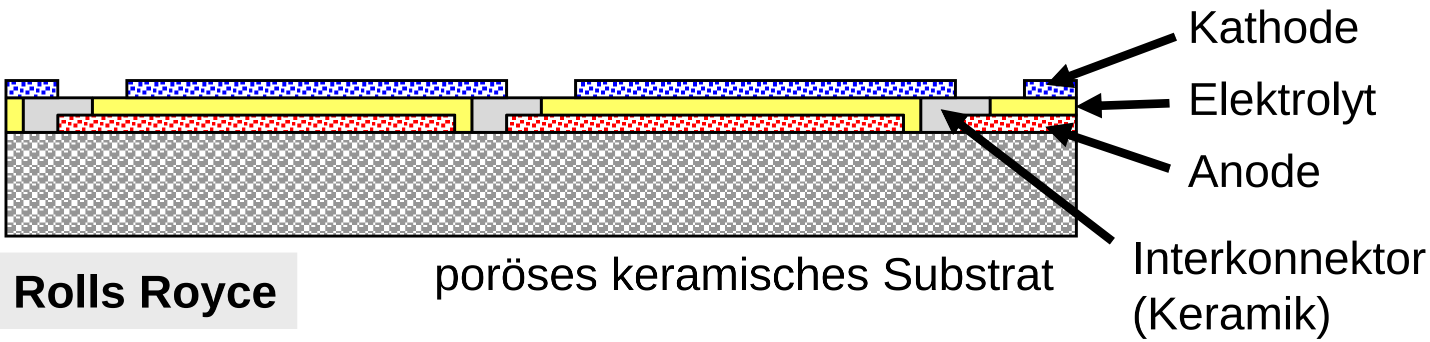
SOFC Stack-Designs („monopolar“)



tubular (Siemens Westinghouse)

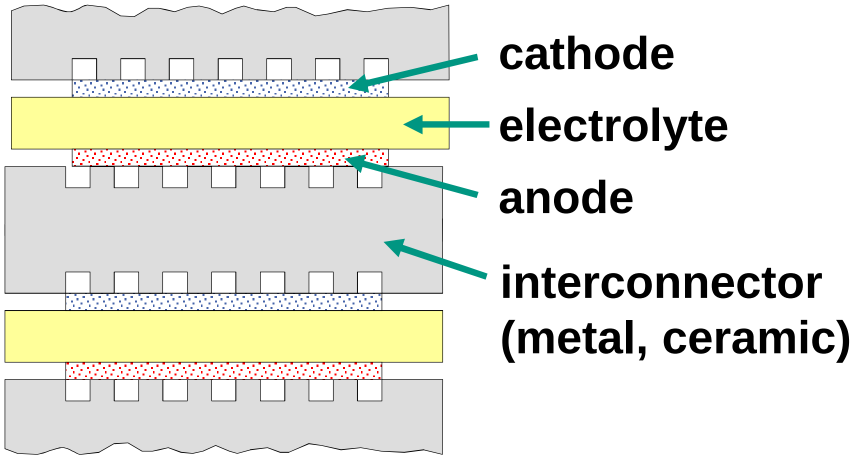


tubular (Mitsubishi Heavy Industries)

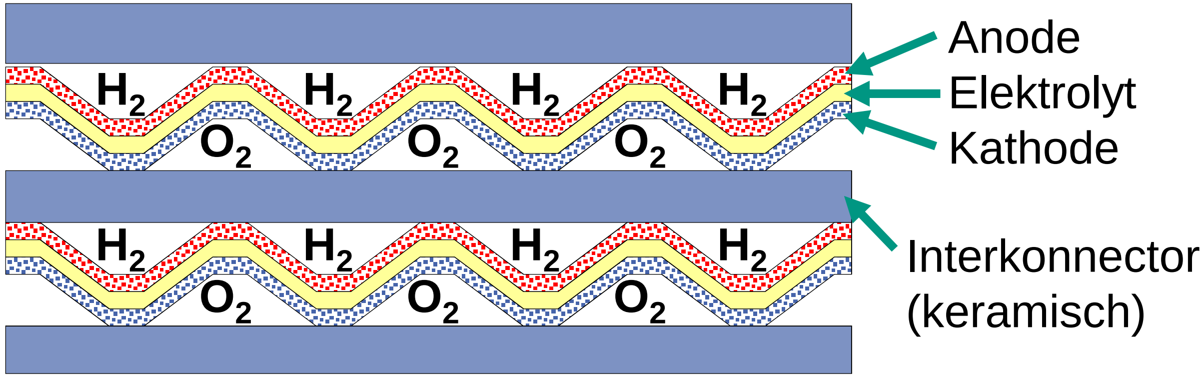


Rolls Royce

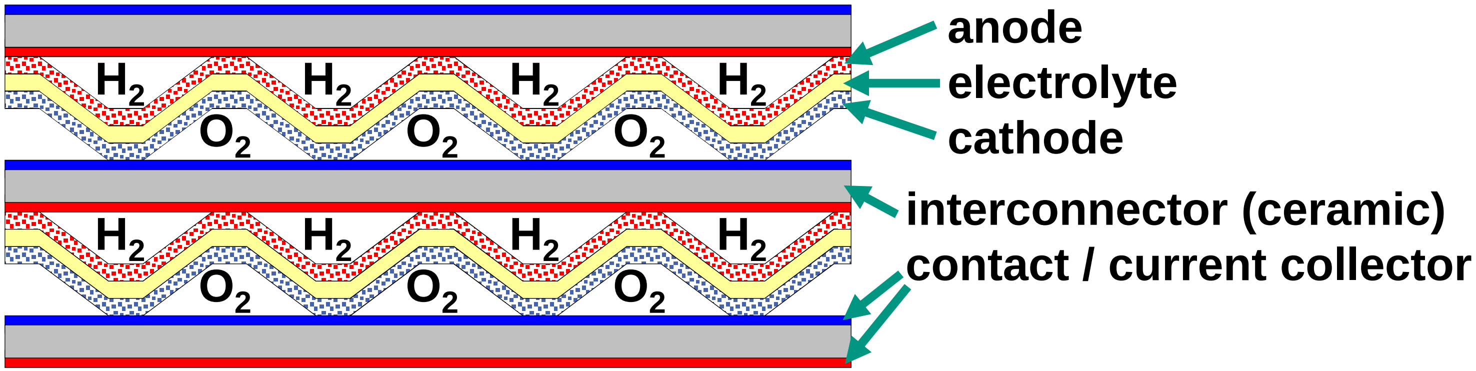
SOFC Stack-Designs („bipolar“)



planar (Sulzer)



Mitsubishi Heavy Industries



monolithic (Argonne National Laboratory)

Solid Oxide Fuel Cell
SOFC-Concepts

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electrolyte supported

- **Murata**
- **Tonen**
- **MHI**
- **Ceramatec**
- **Siemens**
- **Dornier**
- **H.C. Starck** (ECN / InDEC)
- **Hexis**
- **Ceramic Fuel Cells Ltd.**
- **Mitsubishi Materials**
- **Toho Gas**
- **Bloom Energy**

electrode supported

- **Siemens-Westinghouse**
- **Fuji Electric**
- **Allied Signal/Honeywell**
- **Global Thermoelectric** (FZ-Jülich)
- **Delphi** (PNNL)
- **Ceramtec** (FZ-Jülich)
- **Saint-Gobain** (FZ-Jülich)
- **Versa Power**
- **H.C. Starck** (ECN / InDEC)
- **Haldor Topsoe** (DTU/Risoe)
- **Kyocera**
- **Ceramic Fuel Cells Ltd.**

GTL* supported

- **Westinghouse**
- **CERES Power**
- **MHI**
- **Rolls Royce**
- **DLR**
- **DTU/Risoe**
- **Plansee** (FZ-Jülich)

* GTL: Gas Transport Layer

SOFC: Decentralized Power Units, Combined Cycle

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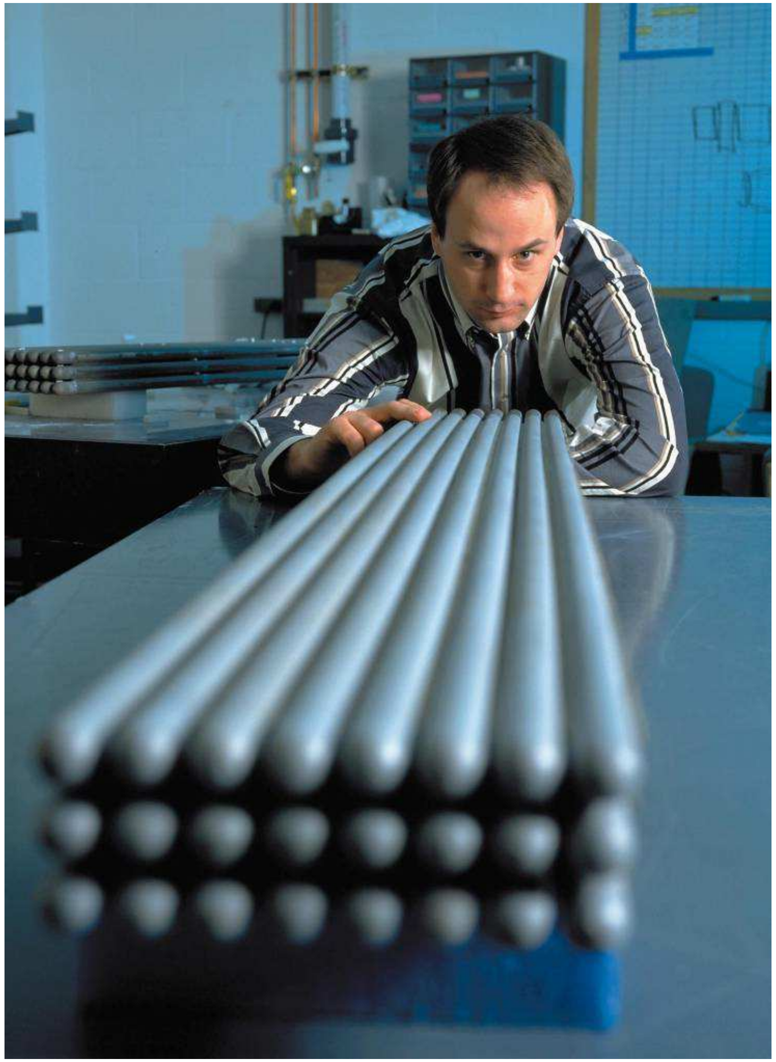
Siemens Westinghouse (SWPC)

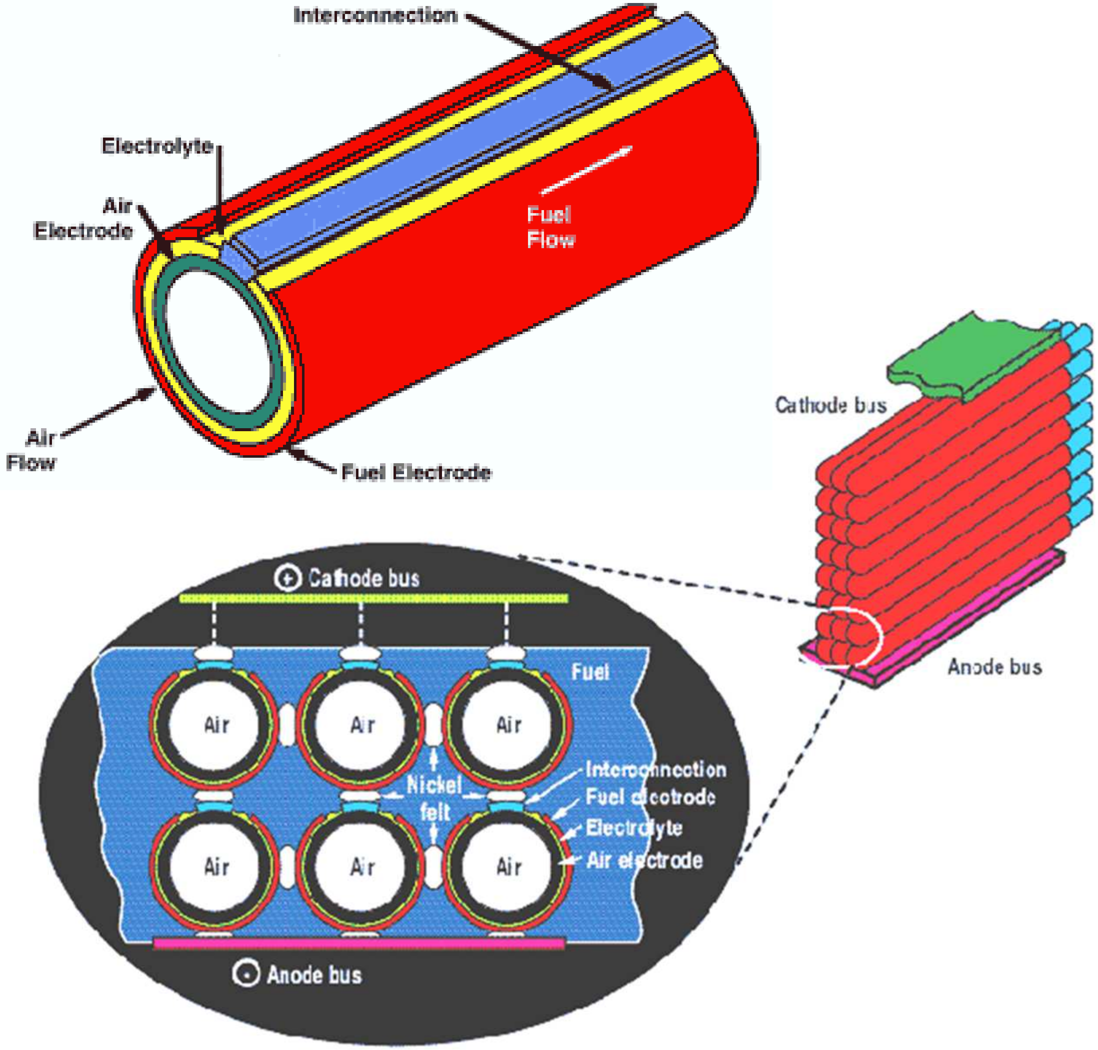
electrical power SOFC	173 kW_{el}
electrical power microturbine	47 kW_{el}
fuel	natural gas
electrical net efficieny	55%

Installation 2000 at Southern California Edison;

since 2001 at NFCR, U.C.Irvine

Siemens Westinghouse Tubular SOFC Tube Bundle

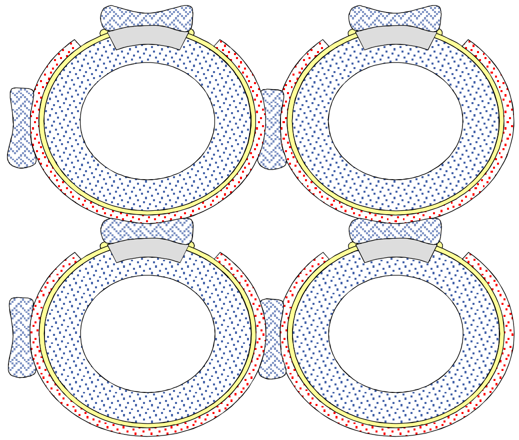


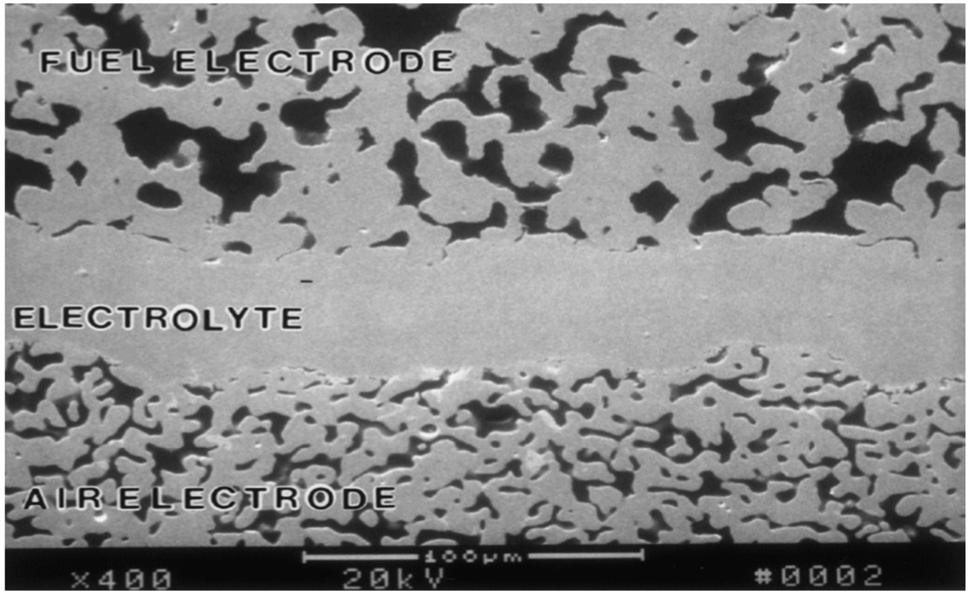


SOFC: Decentralized Power Units (> 100 kW)
Fabrication Technologies

Fabrication Technologies:

- Extrusion moulding and sintering (cathode)
- CVD, EVD, APS (electrolyte)
- Slurry coating and sintering (interconnector)
- Slurry coating and sintering (anode)





Future Demands:

- increased power density
- reengineered fabrication process
- ...
- costs

Solid Oxide Fuel Cell
Tubular SOFC-Design (Siemens-Westinghouse)

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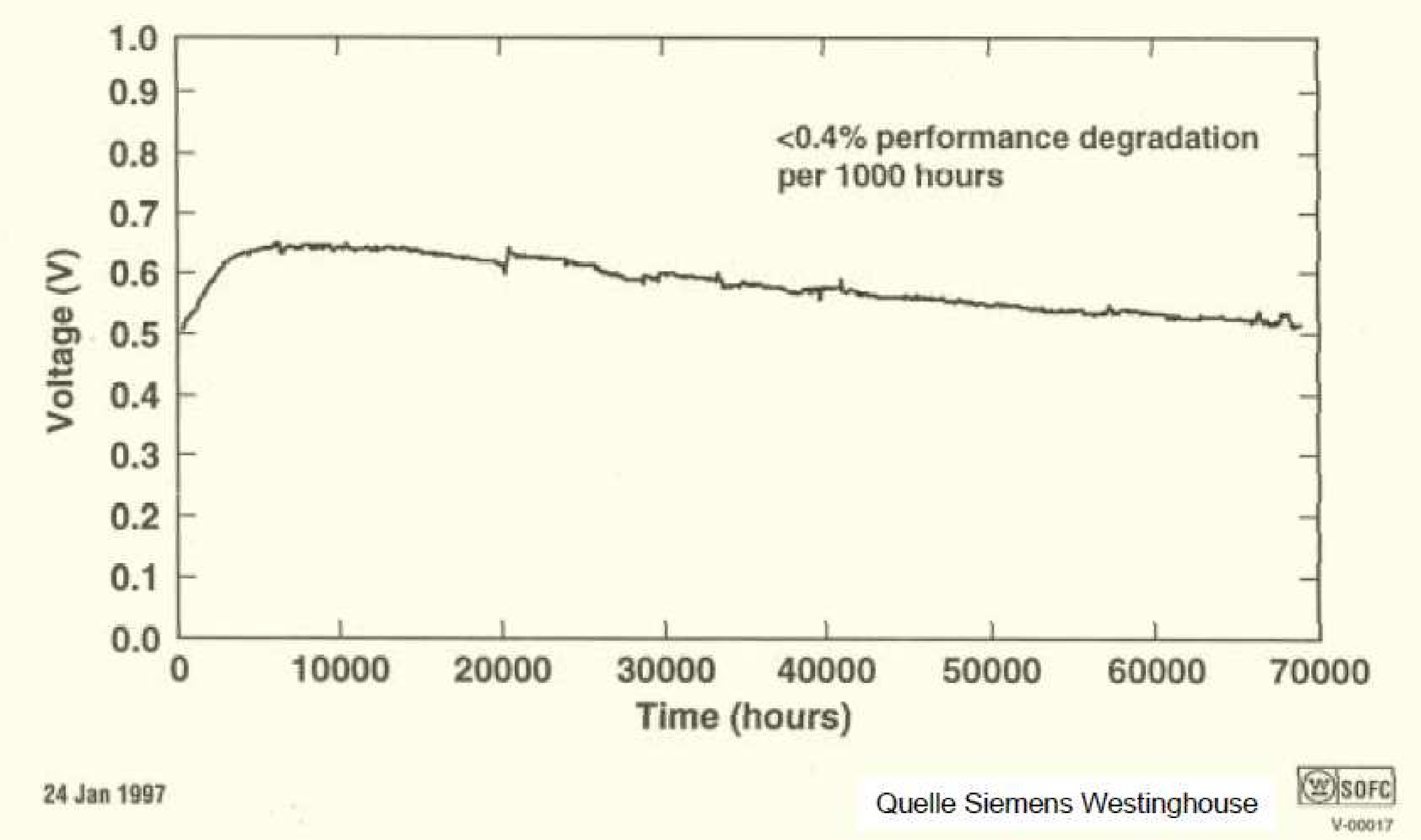
Ausbau der Röhren aus dem Reaktor zur Beschichtung der Kathode mit Elektrolyt mittels EVD (Electrochemical Vapour Deposition)

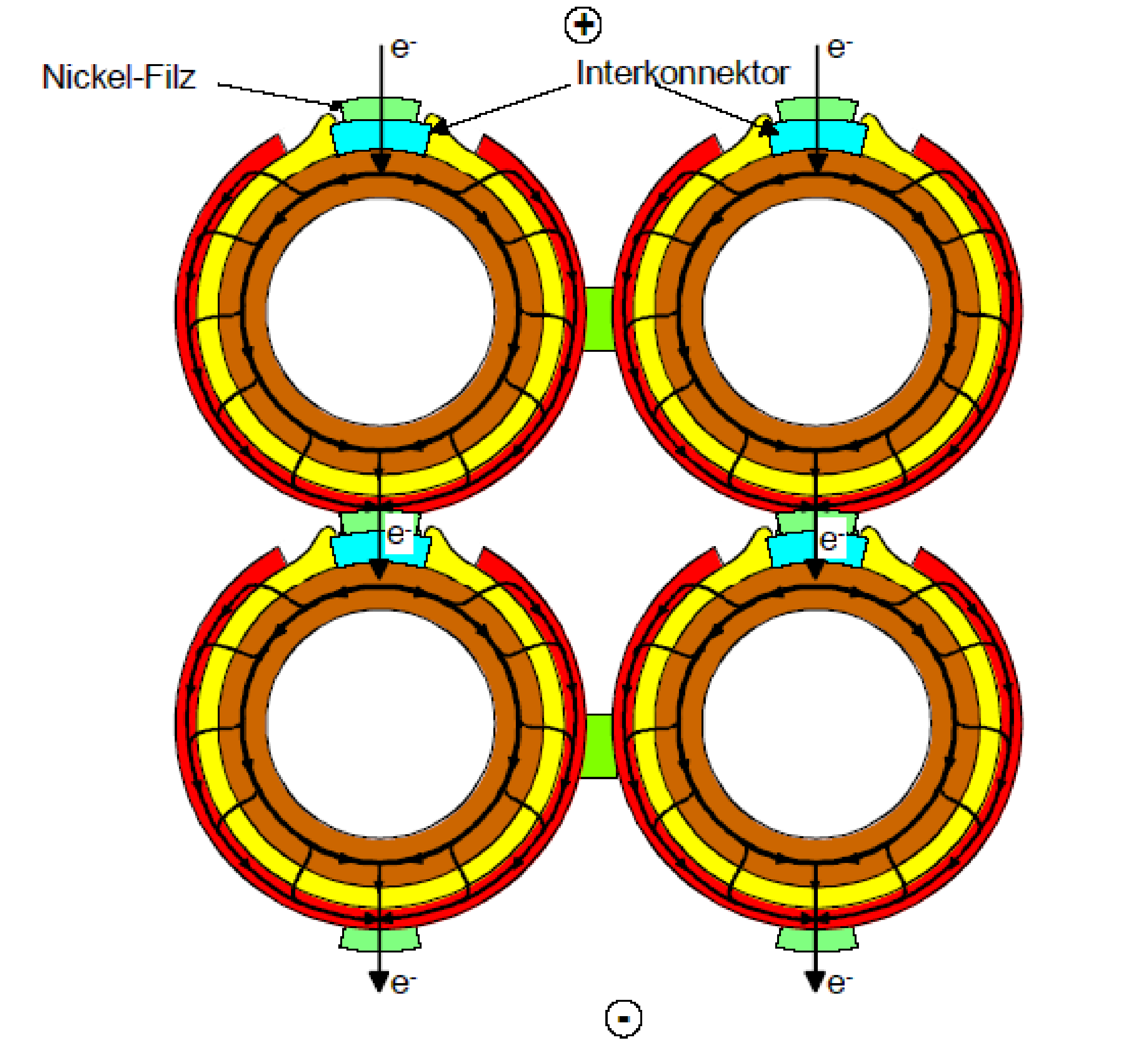
Quelle Siemens Westinghouse

Solid Oxide Fuel Cell
Tubular SOFC-Design (Siemens-Westinghouse)

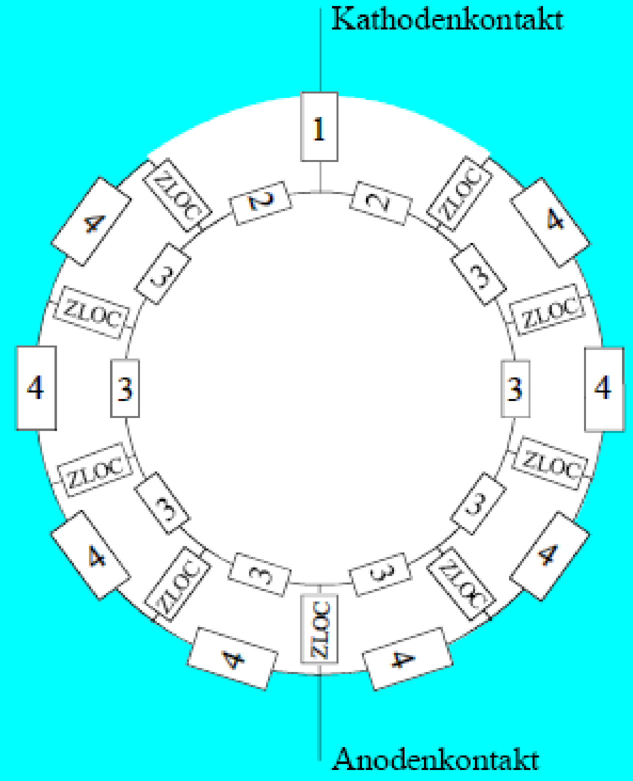
Solid Oxide Fuel Cell
Tubular SOFC-Design (Siemens-Westinghouse)



Solid Oxide Fuel Cell
Tubular SOFC-Design (Siemens-Westinghouse)



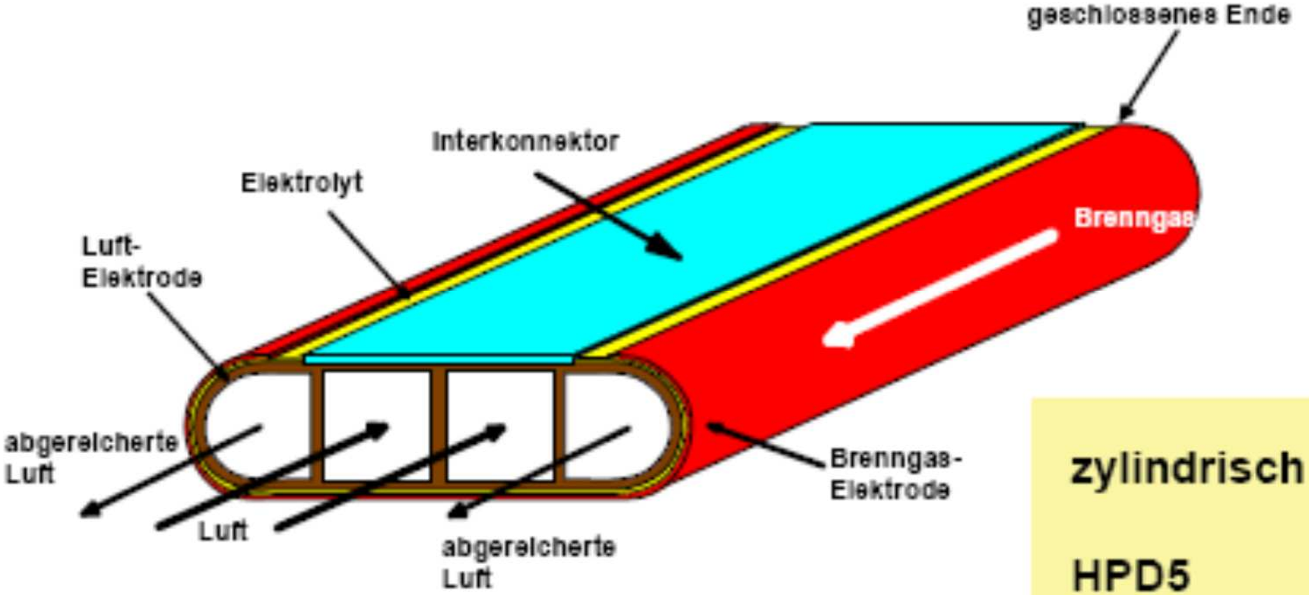
Strompfad von Zelle zu Zelle

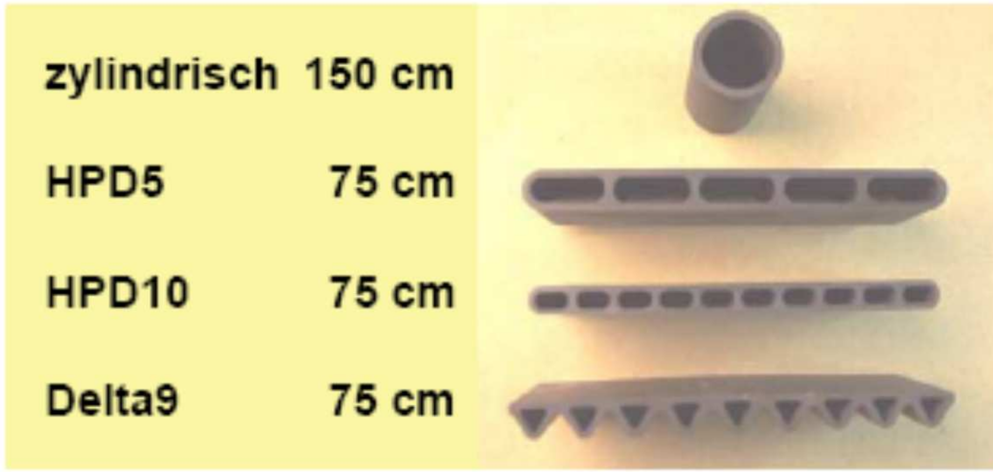


1: Flächenwiderstand IC
2: Bahnwiderstand "Spalt"
3: Bahnwiderstand Kathode
4: Bahnwiderstand Anode
ZLOC: lokaler Widerstand der aktiven Zelle (="Planar")

Quelle Siemens Westinghouse

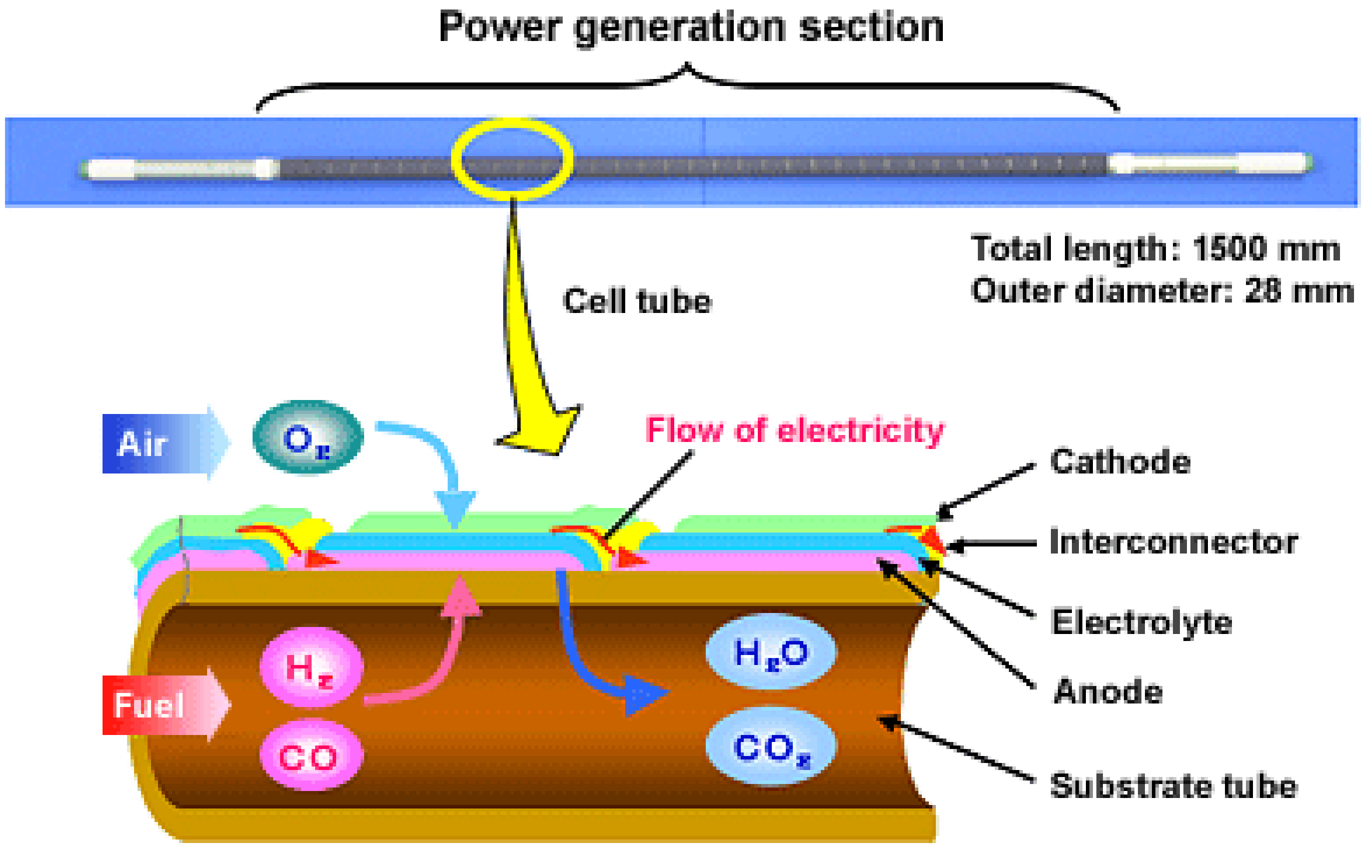
Solid Oxide Fuel Cell
Tubular SOFC-Design (Siemens-Westinghouse)

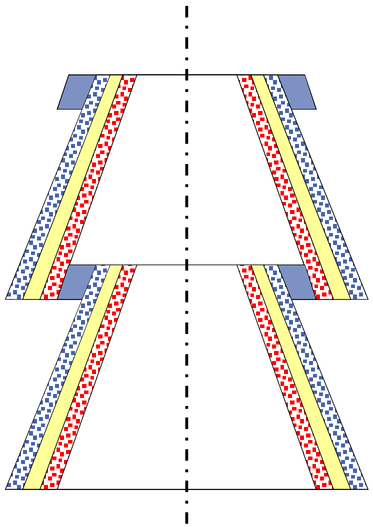




Quelle Siemens

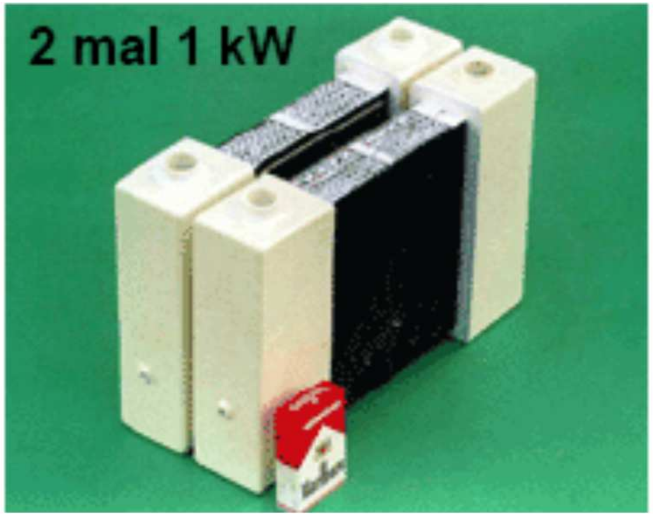
Solid Oxide Fuel Cell
Tubular SOFC-Design (Mitsubishi Heavy Industries)

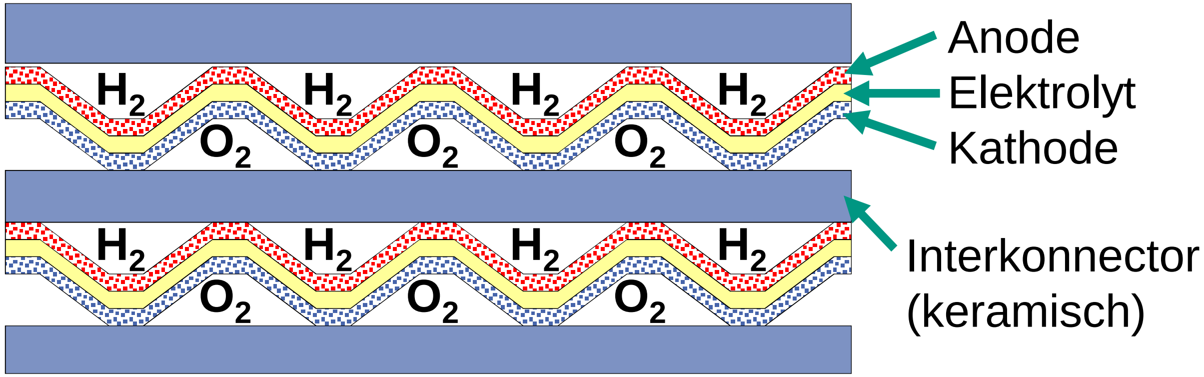




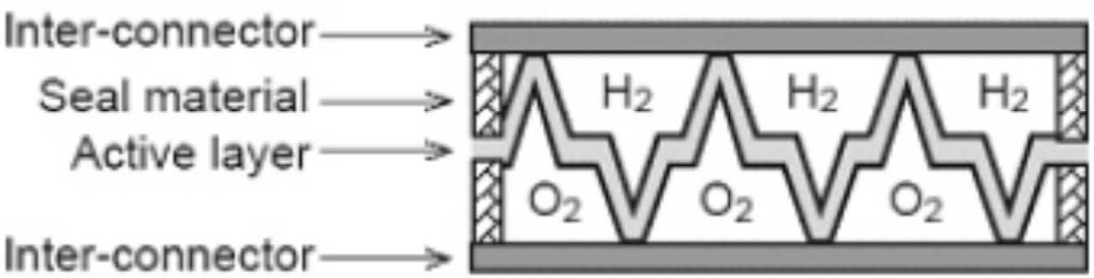
tubular (Mitsubishi Heavy Industries)

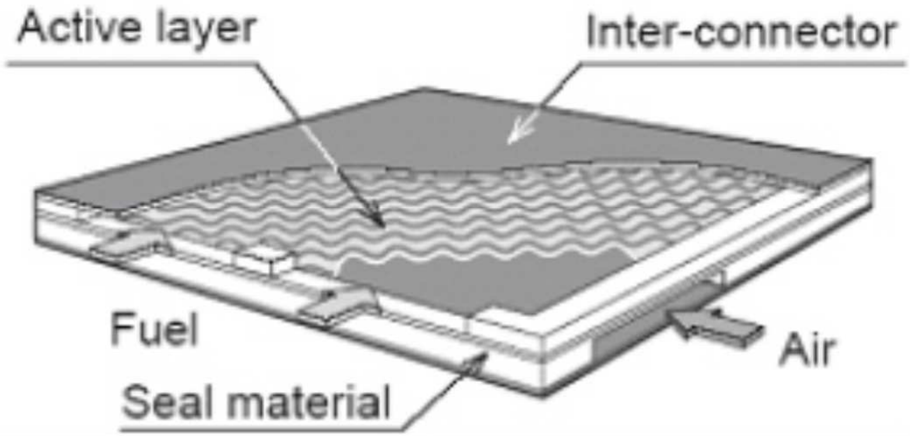
Solid Oxide Fuel Cell
Planar SOFC-Design (Mitsubishi Heavy Industries)





Mitsubishi Heavy Industries





Solid Oxide Fuel Cell
Planar SOFC-Design (Rolls Royce)

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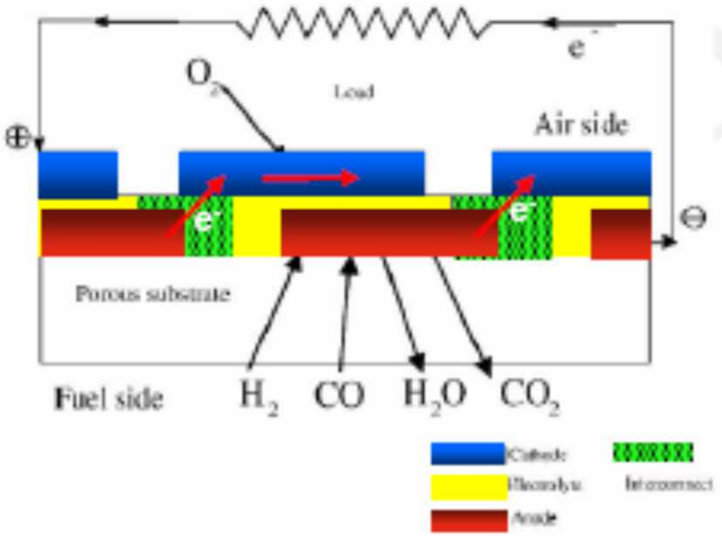
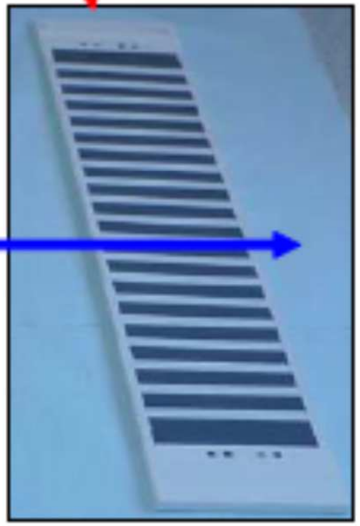
Keramik



Erdgas

Luft



50 W Modul

"planares Design von MHI"

1 kW bei 950°C mit H_2/Luft

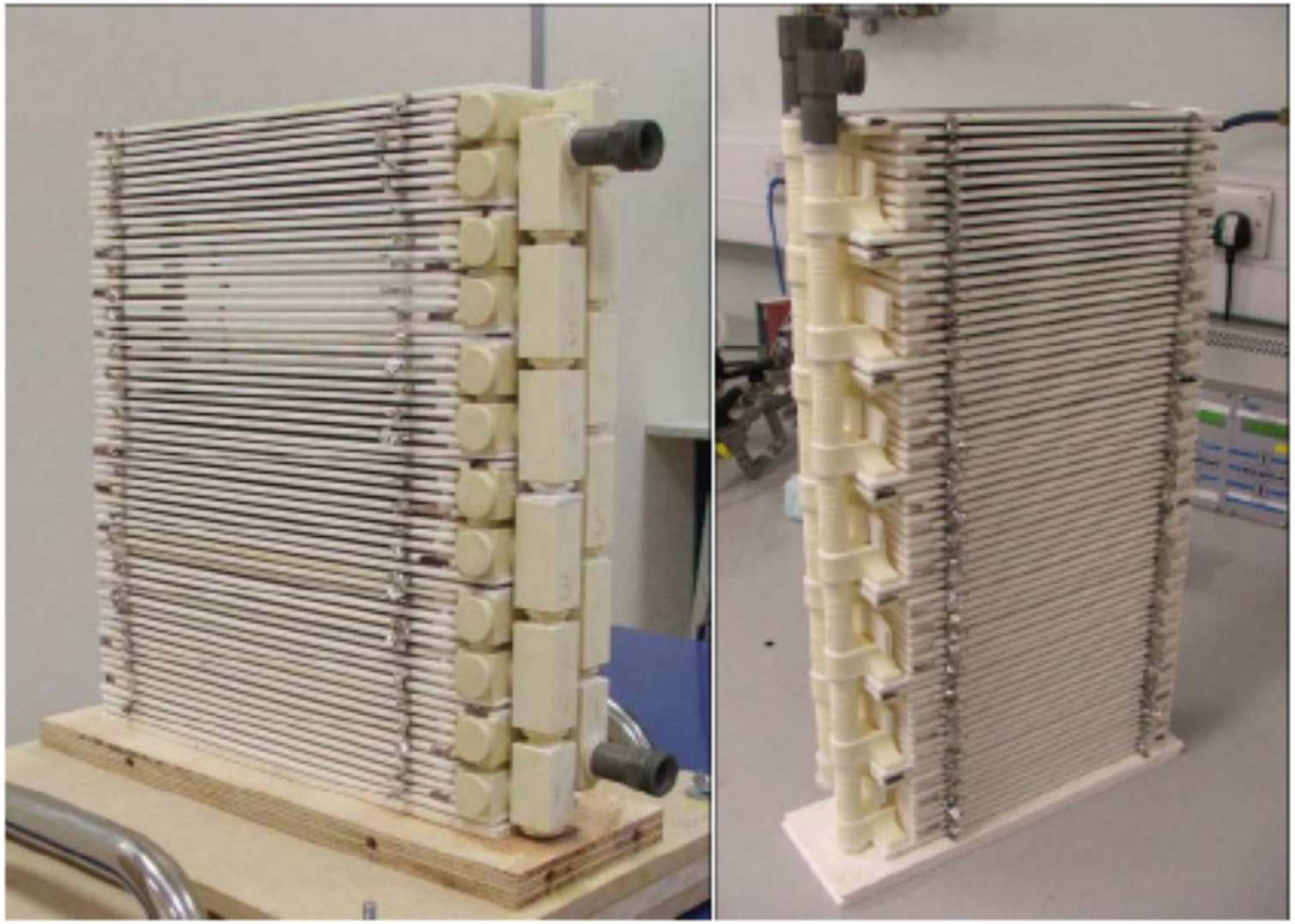
Elektrizität

Dampf

500 W "Bündel"

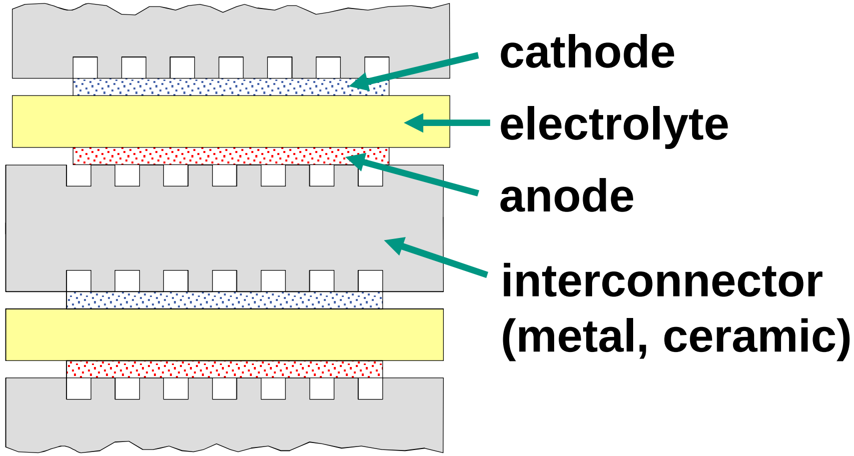
Quelle Rolls Royce

Solid Oxide Fuel Cell
Planar SOFC-Design (Rolls Royce)



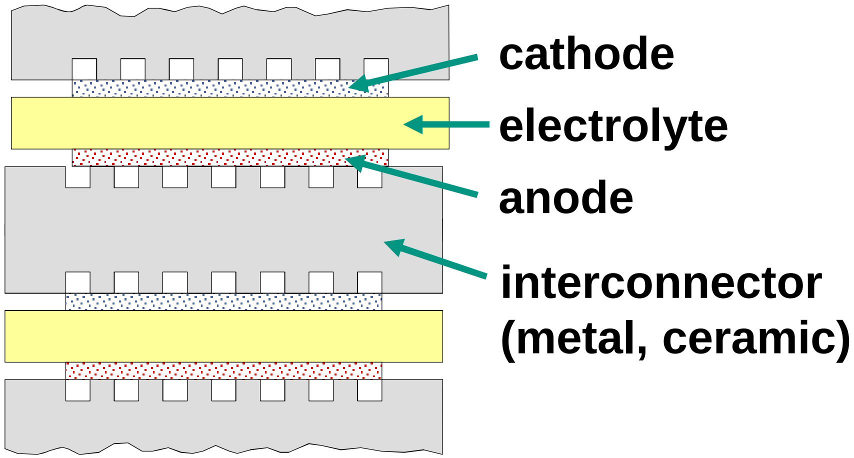
Ein “strip” von RRFCS “fuel cell bundles“ von 2004 and 2005 Designs
(otpimierte Fertigungstechnik und reduzierte Anzahl an Anschlussteilen)
(Luzern 2006)

Solid Oxide Fuel Cell
Siemens Planar 10 kW SOFC Stack



Cathode	LSM
Electrolyte	8YSZ
Anode	Ni/8YSZ-Cermet
Interconnector	$CrFe5Y_2O_31$
layers	80
cells/layer	16, each 50 x 50 mm²
electrode area	2 m²
volume	0.02 m²
el. power	10.7 kW @950 °C
	8.4 kW @850 °C
current density	0.6 A/cm²
fuel utilization	40 ... 50 % (H_2)

Solid Oxide Fuel Cell
Planar SOFC-Design



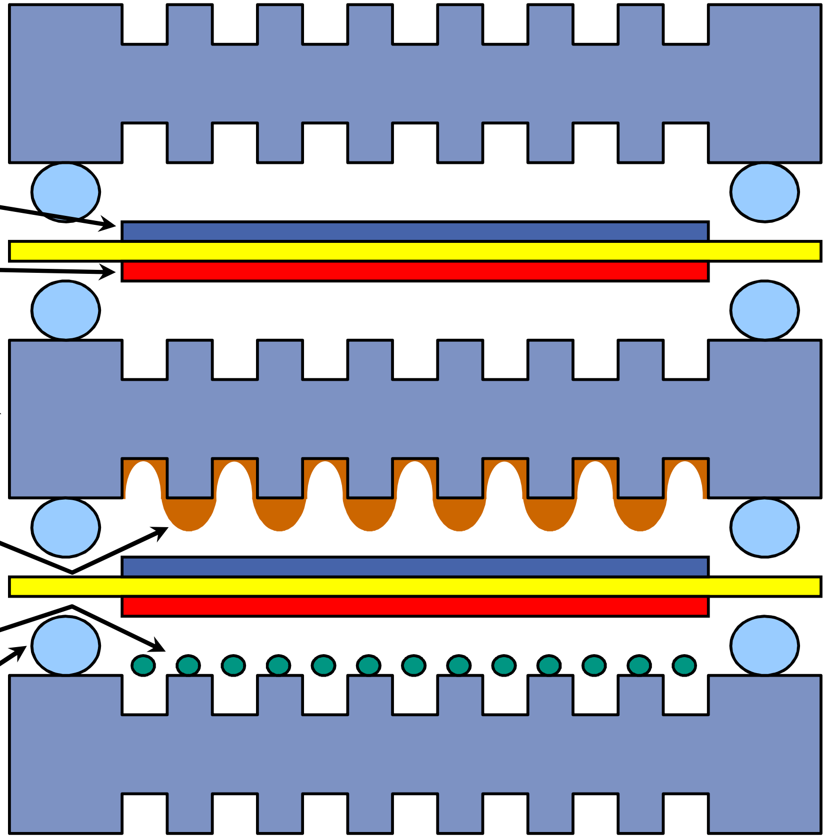
planar
- (Siemens, Dornier)
- Sulzer
- FZ Jülich
- BMW
- Mitsubishi Materials
- PNNL
- Global Thermoelectrics
- ...

Stack Components (Siemens)

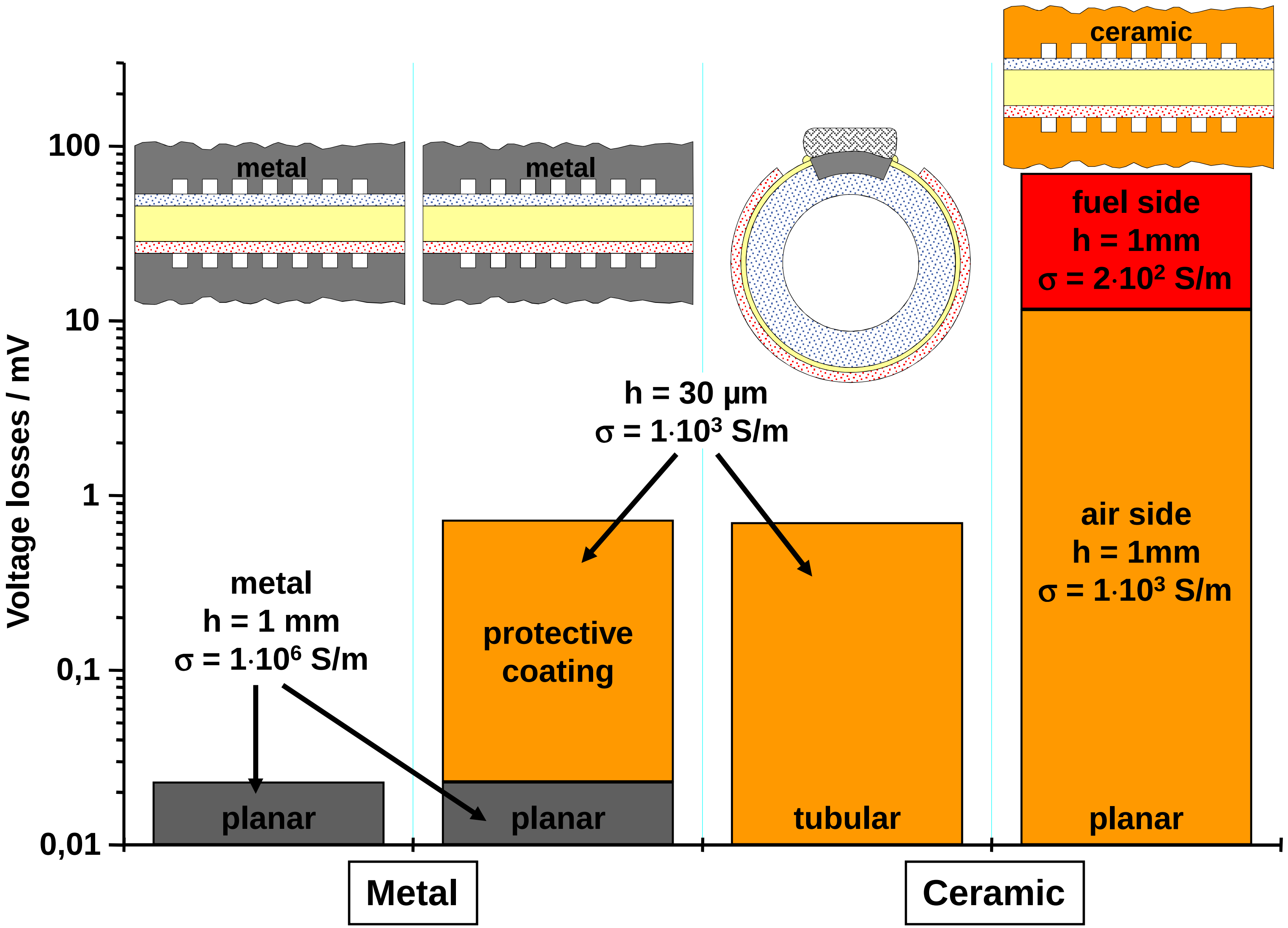
„unsolved“ problems
corrosion of MIC (esp. at high temp. > 850°C)
processing and costs of CIC
gastight sealing
...

Solid Oxide Fuel Cell
Planar SOFC-Design: Ceramic and metallic materials

Materials	Components
$(La,Sr)MnO_3$	cathode
Y_2O_3-doped ZrO_2 (YSZ)	electrolyte
Nickel / YSZ	anode
Cr 5Fe 1 Y_2O_3	bipolar plate
$(La,Sr)CrO_3$ $(La,Sr)CoO_3$	protective coating + functional layer (c)
Nickel-grid	functional layer (a)
glas sealing	joining material



Planar and Tubular SOFC Concepts
Ohmic Losses in Metallic and Ceramic Interconnector

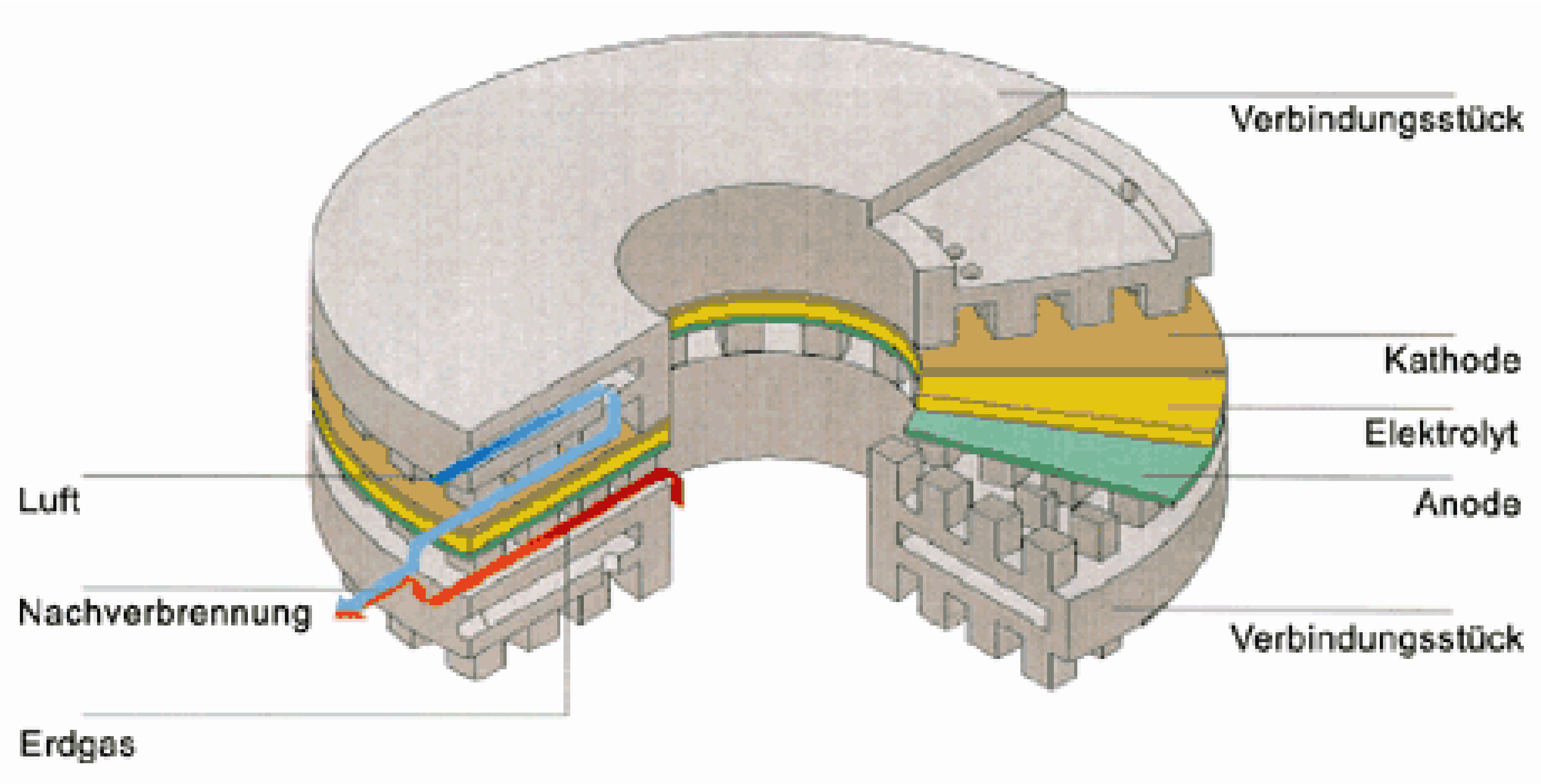


Sulzer Hexis / Hoval
SOFC : 1 kW_{el} / 3 kW_{th} inkl. Zusatzbrenner

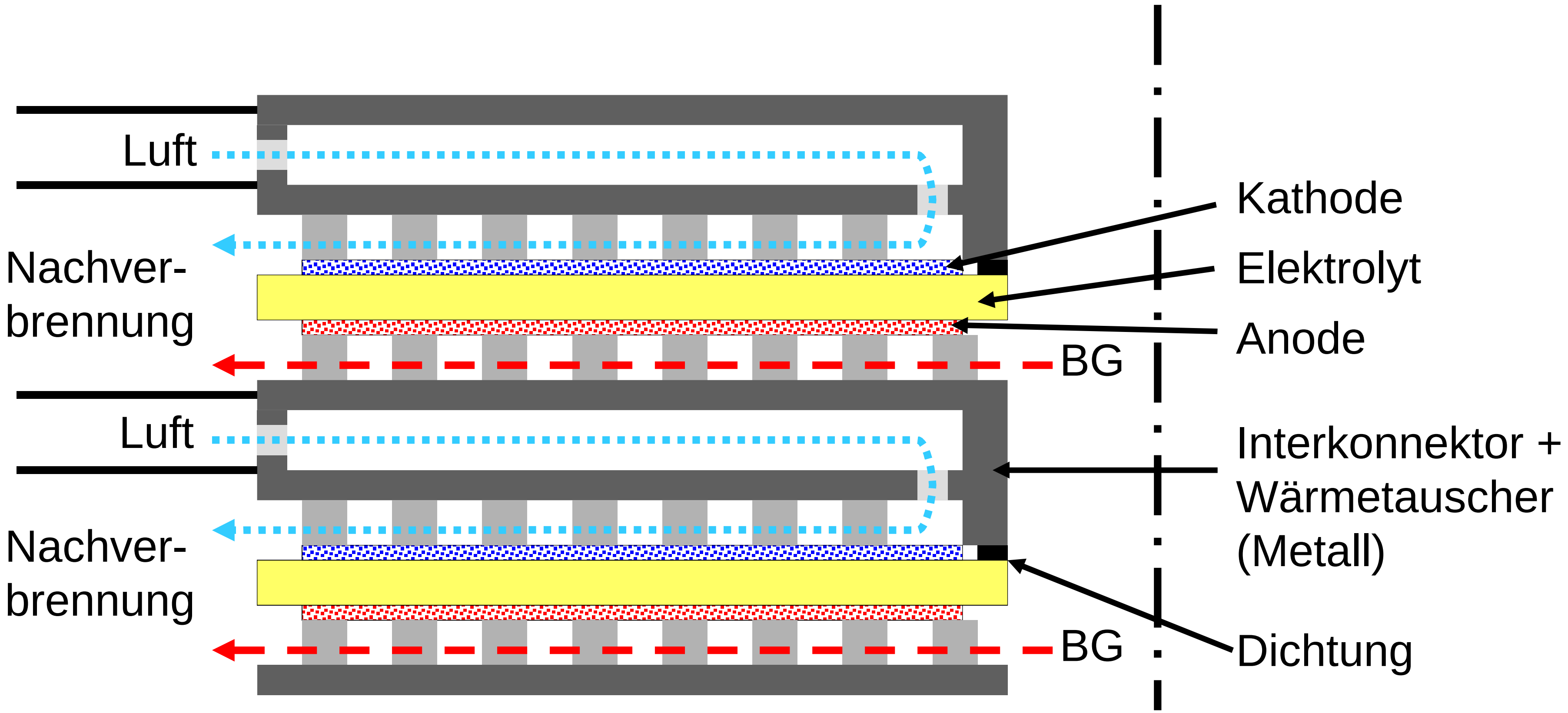
Sulzer Hexis HXS 1000 Premiere

Brennstoffzellen-Typ:	SOFC
Betriebstemperatur:	950°C
elektrische Leistung:	1 kW
thermische Leistung:	2,5 kW
Zusatzbrenner:	12 – 22 kW
el. Nettowirkungsgrad:	25 – 30%
Systemwirkungsgrad:	> 80%
Brennstoff:	Erdgas

Sulzer HEXIS Stackkonzept

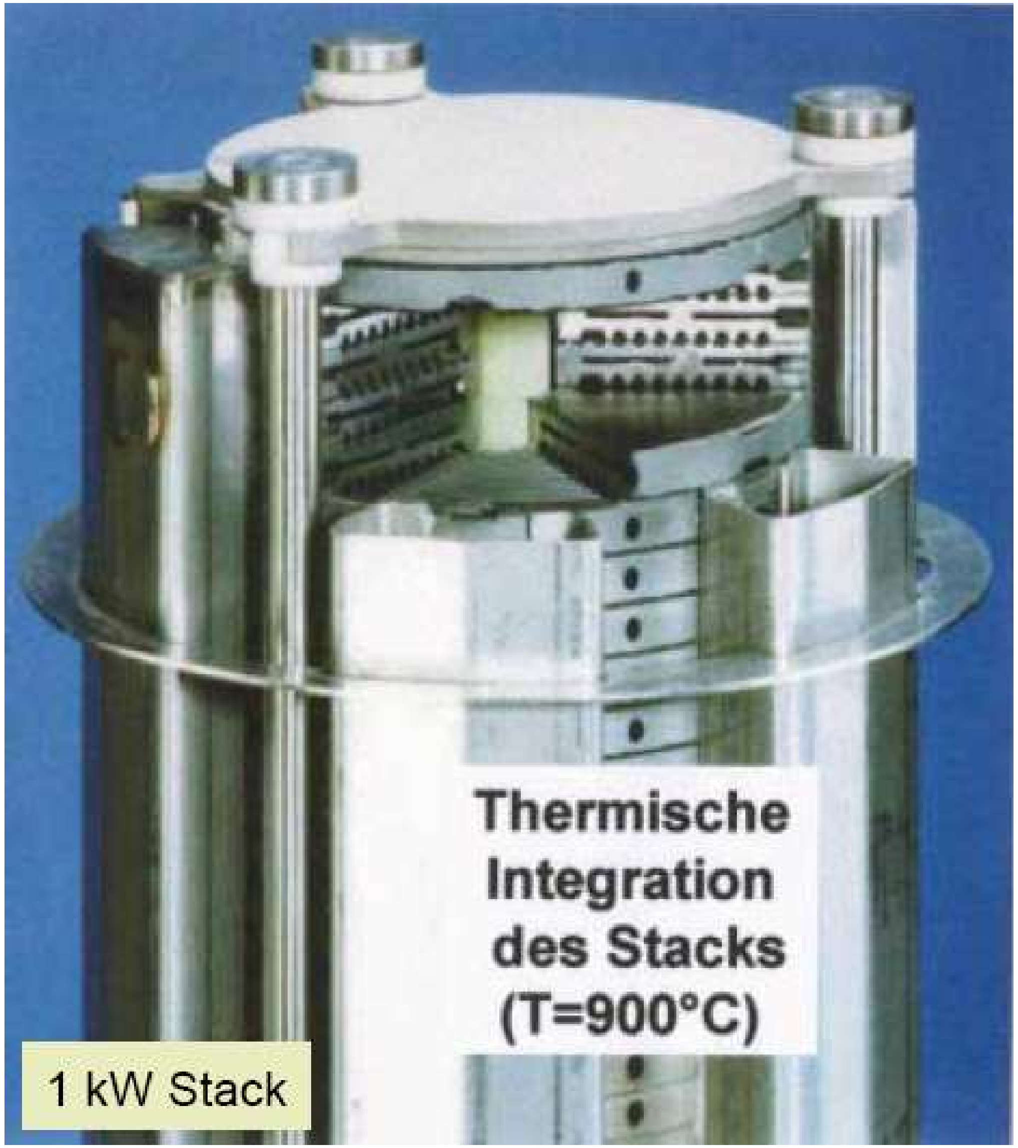


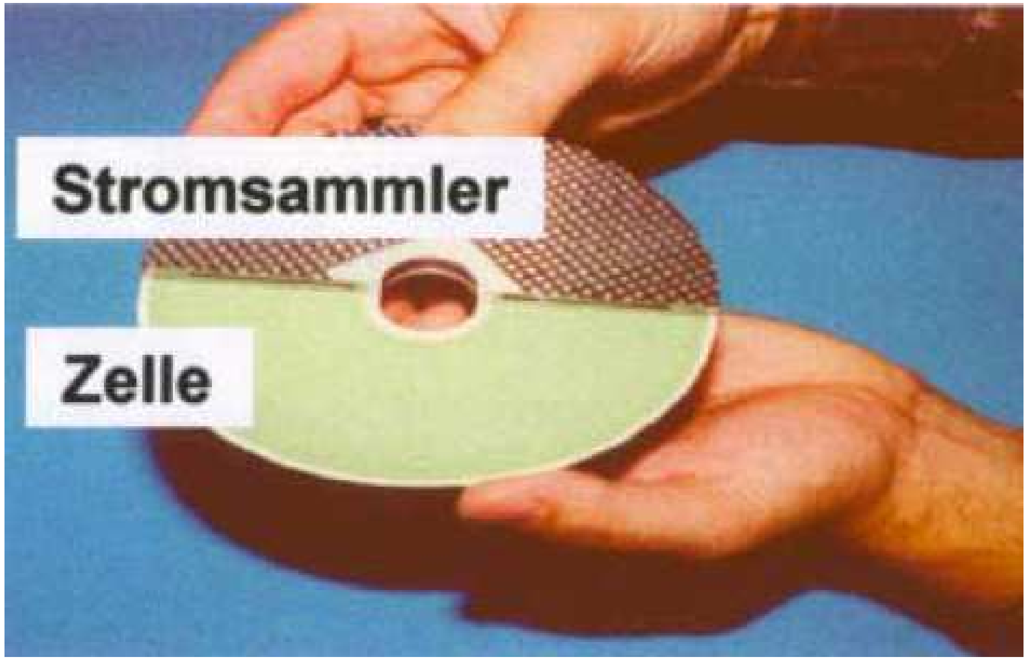
Sulzer HEXIS Stackkonzept



Sulzer Hexis

Solid Oxide Fuel Cell
Planar SOFC-Design (Sulzer Hexis)





Quelle: Sulzer Hexis

Oxide Ion Conductivity of Electrolyte Materials
Temperature Limits for Electrolyte and Electrode Supported Cell

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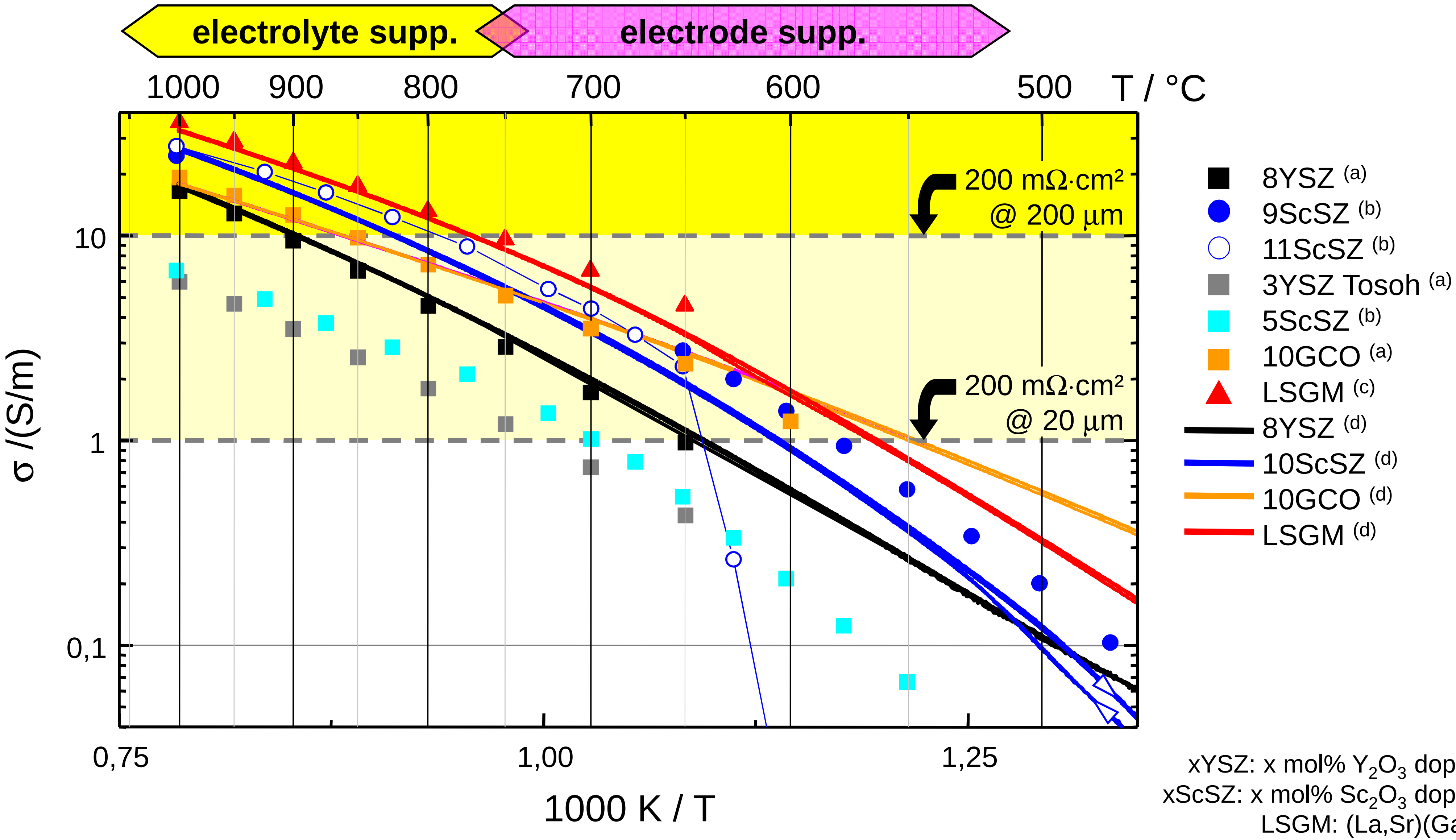
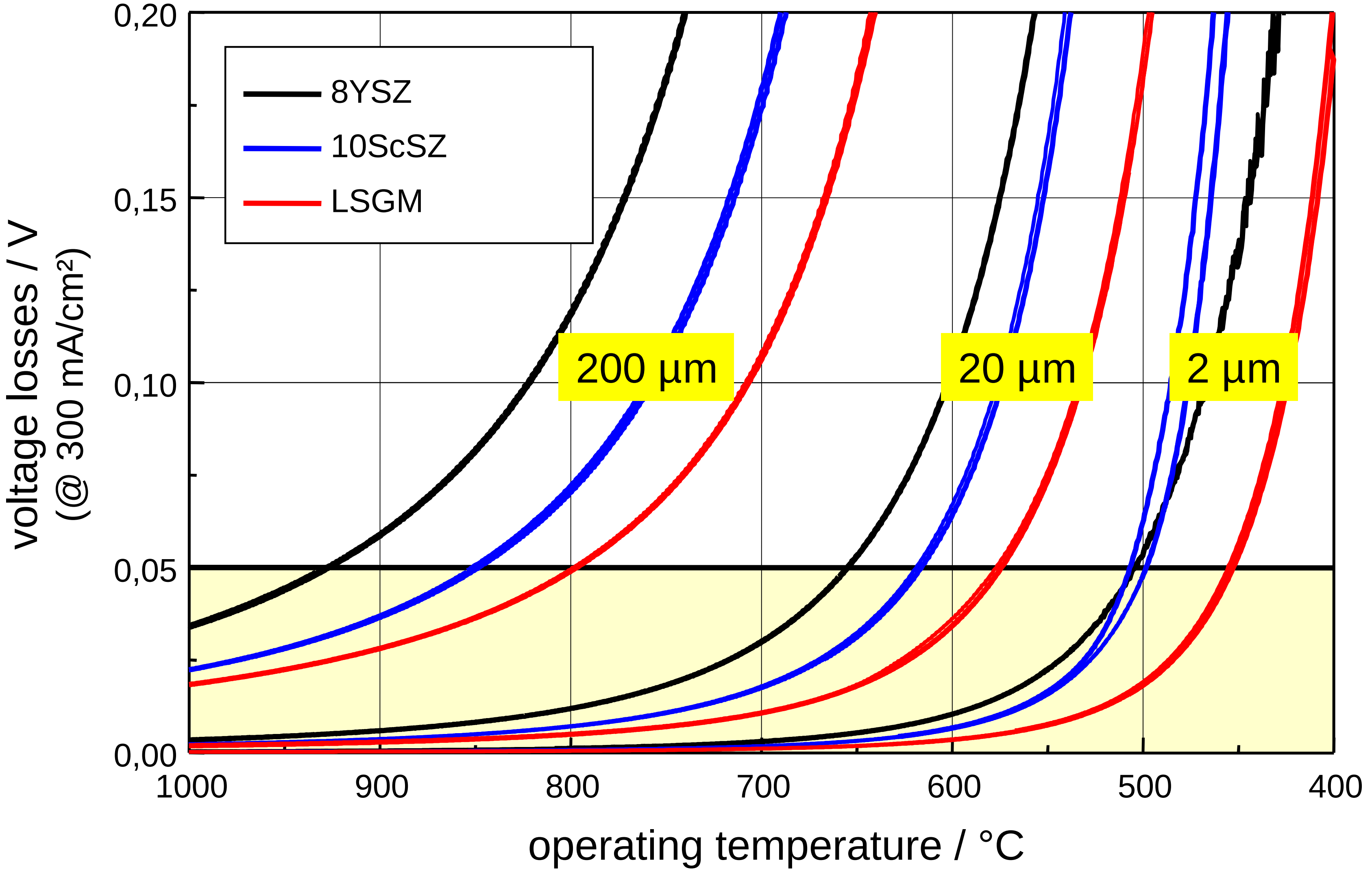


xYSZ: x mol% Y_2O_3 doped ZrO_2
xScSZ: x mol% Sc_2O_3 doped ZrO_2
LSGM: (La,Sr)(Ga,Mg)O_3

Oxide Ion Conductivity of Electrolyte Materials

Electrolyte Losses as a Function of Operation Temperature and Electrolyte Thickness



Solid Oxide Fuel Cell
Planar Cells

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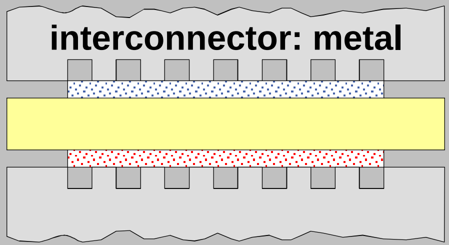
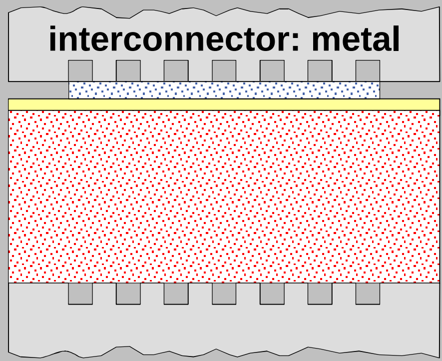
800 - 1000 °C



electrolyte supported

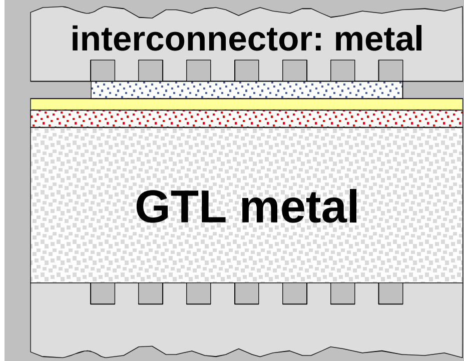
electrolyte: 150 μm
electrodes: 50 μm
GTL: -

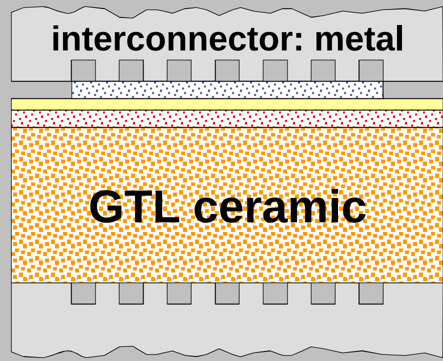
< 800 °C



electrode supported*
(anode or cathode)

< 20 μm
50 / > 500 μm
-



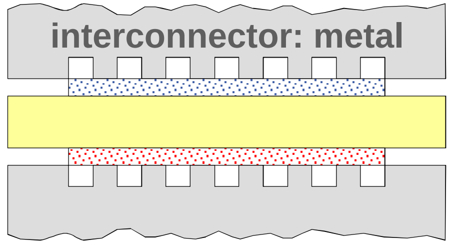


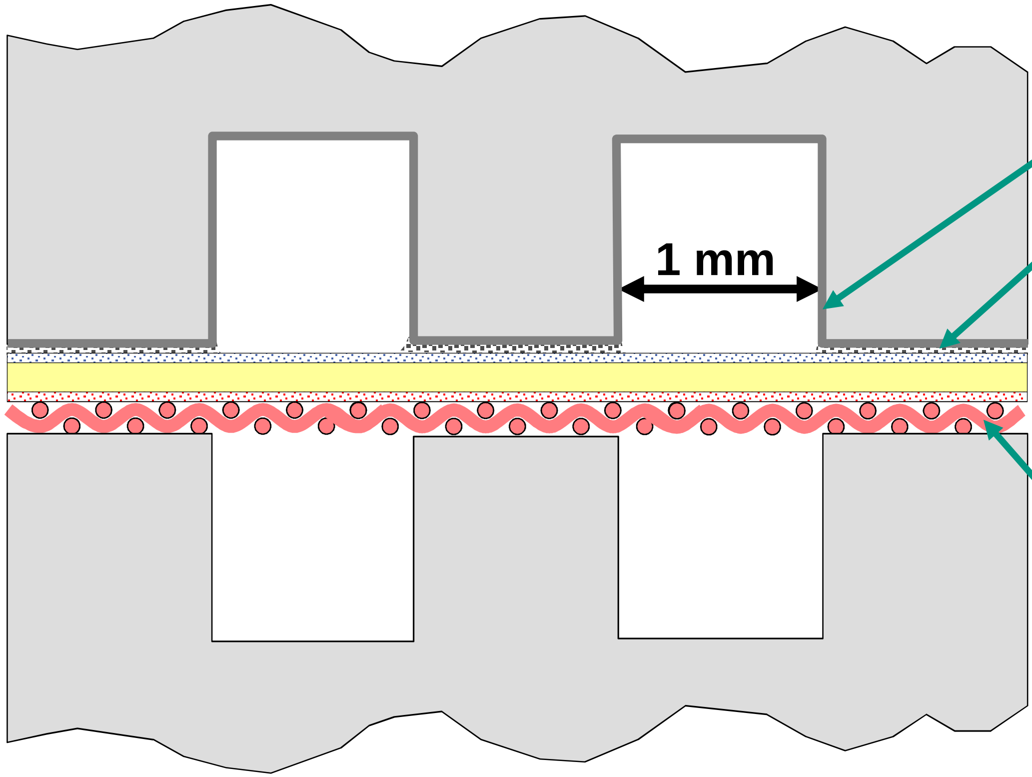
GTL supported
(GTL: Gas Transport Layer)

< 20 μm
50 μm
> 500 μm

*Thickness of Electrodes and Electrolyte similar for tubular SWPC concept

SOFC - Stack Design
Planar Design with Electrolyte Supported Single Cell



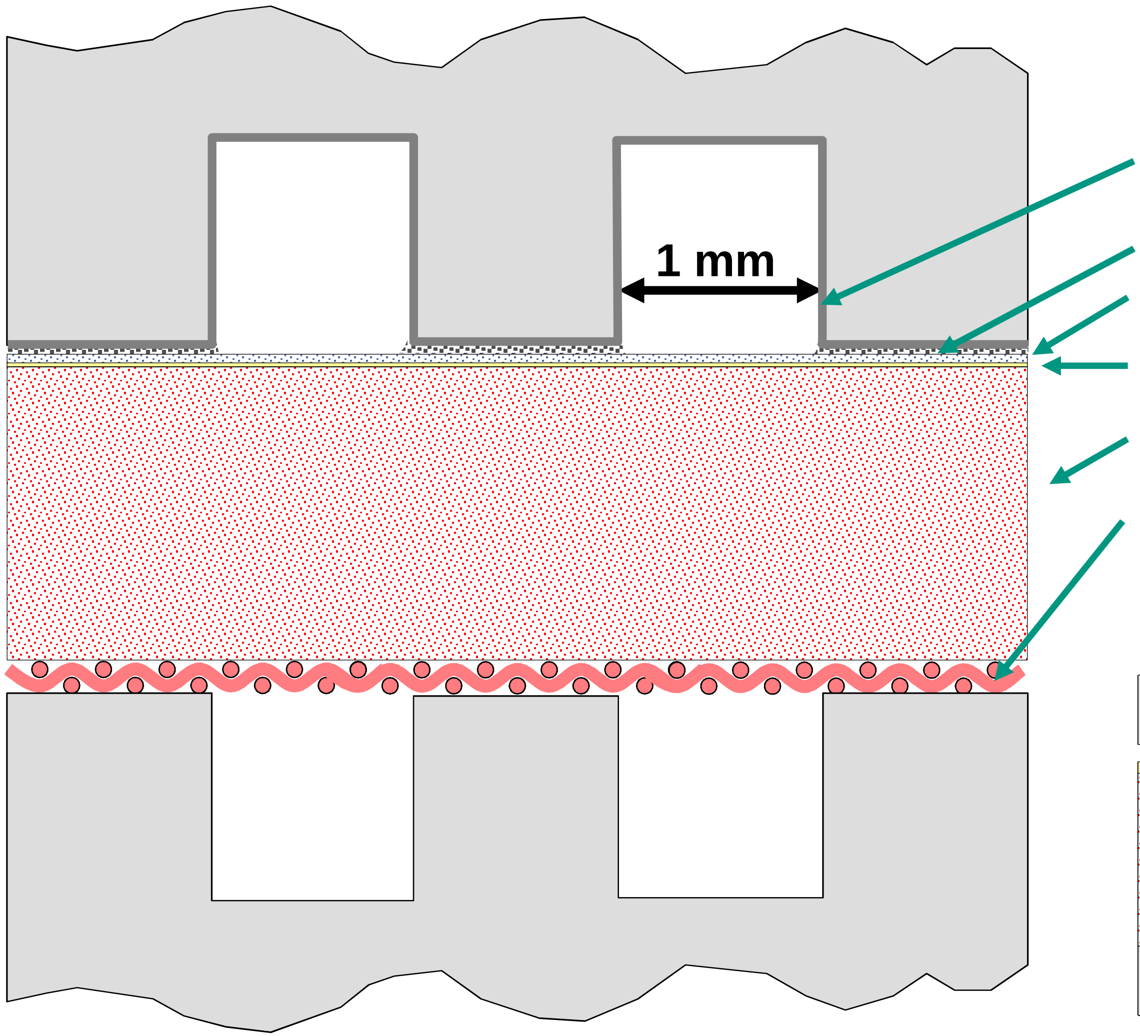


coating	50 µm	LSCr, LSM
contact layer	50 µm	LSC, LSM
cathode	50 µm	LSM, LSM/YSZ (LSCF, ...)
electrolyte	150 µm	8YSZ, 3YSZ, (10ScSZ, GCO)
anode	50 µm	Ni/YSZ
contact layer	~200 µm	Ni-grid

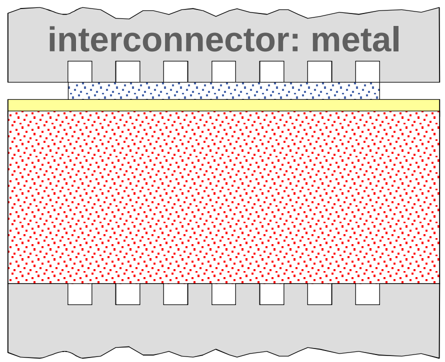
Siemens, Sulzer

LSCr: Sr doped $LaCrO_3$
LSC: Sr doped $LaCoO_3$
LSM: Sr doped $LaMnO_3$
LSCF: $(La,Sr)(Co,Fe)O_3$
nYSZ: n mol% Y_2O_3 doped ZrO_2
nScSZ: n mol% Sc_2O_3 doped ZrO_2
GCO: Gd doped CeO_2
Ni/YSZ: Ni/YSZ-Cermet

SOFC - Stack Design
Planar Design with Anode Supported Single Cell



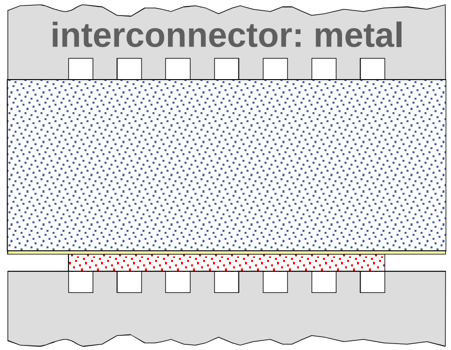
coating	**50 μm**	**LSCr, LSM**
contact layer	**50 μm**	**LSC, LSM**
cathode	**50 μm**	**LSM, LSM/YSZ**
electrolyte	**~10 μm**	**8YSZ, 10ScSZ**
anode	**1500 μm**	**Ni/YSZ**
contact layer	**~200 μm**	**Ni-grid**

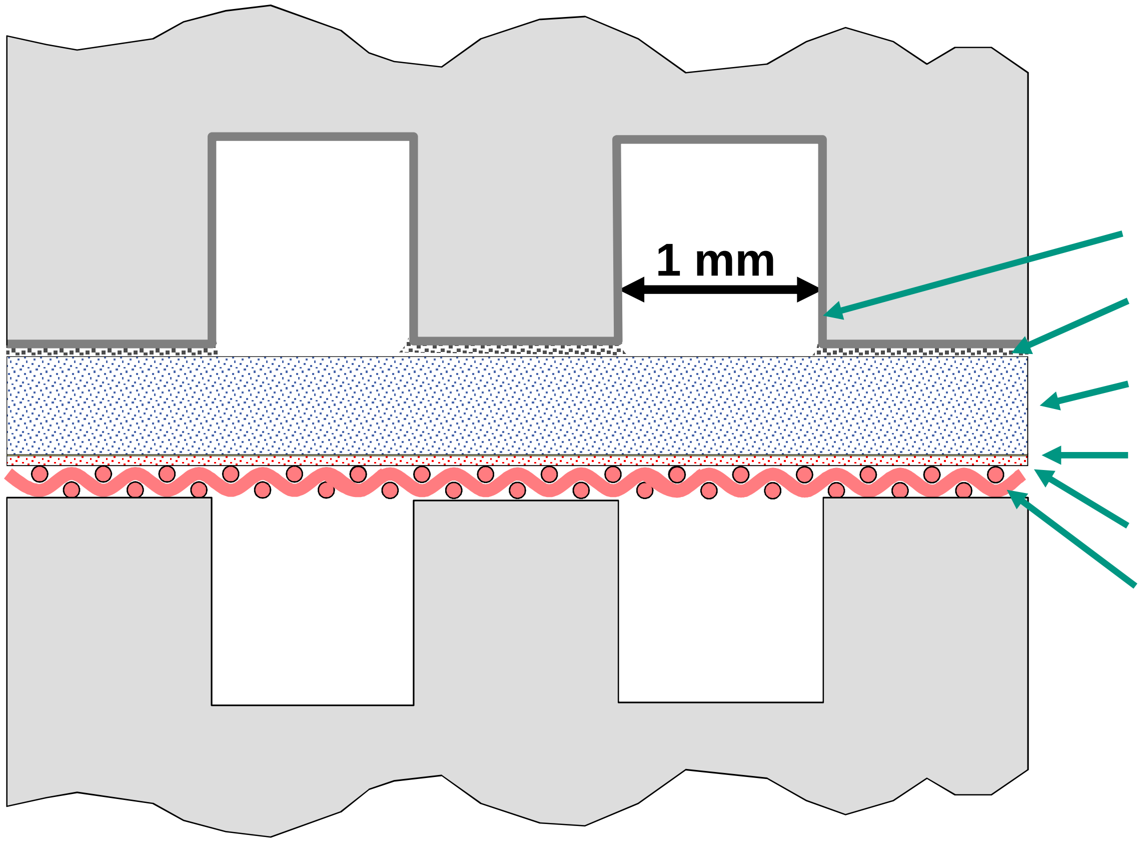


LSCr: Sr doped $LaCrO_3$
LSC: Sr doped $LaCoO_3$
LSM: Sr doped $LaMnO_3$
LSCF: $(La,Sr)(Co,Fe)O_3$
nYSZ: n mol% Y_2O_3 doped ZrO_2
nScSZ: n mol% Sc_2O_3 doped ZrO_2
GCO: Gd doped CeO_2
Ni/YSZ: Ni/YSZ-Cermet

Allied Signal, FZ Jülich, ECN

SOFC - Stack Design
Planar Design with Cathode Supported Single Cell





coating	**50 µm**	**LSCr, LSM**
contact layer	**50 µm**	**LSC, LSM**
cathode	**500 µm**	**LSM, ...**
electrolyte	**~10 µm**	**8YSZ, 10ScSZ, ...**
anode	**50 µm**	**Ni/YSZ, ...**
contact layer	**~200 µm**	**Ni-grid**

LSCr: Sr doped $LaCrO_3$
LSC: Sr doped $LaCoO_3$
LSM: Sr doped $LaMnO_3$
LSCF: $(La,Sr)(Co,Fe)O_3$
nYSZ: n mol% Y_2O_3 doped ZrO_2
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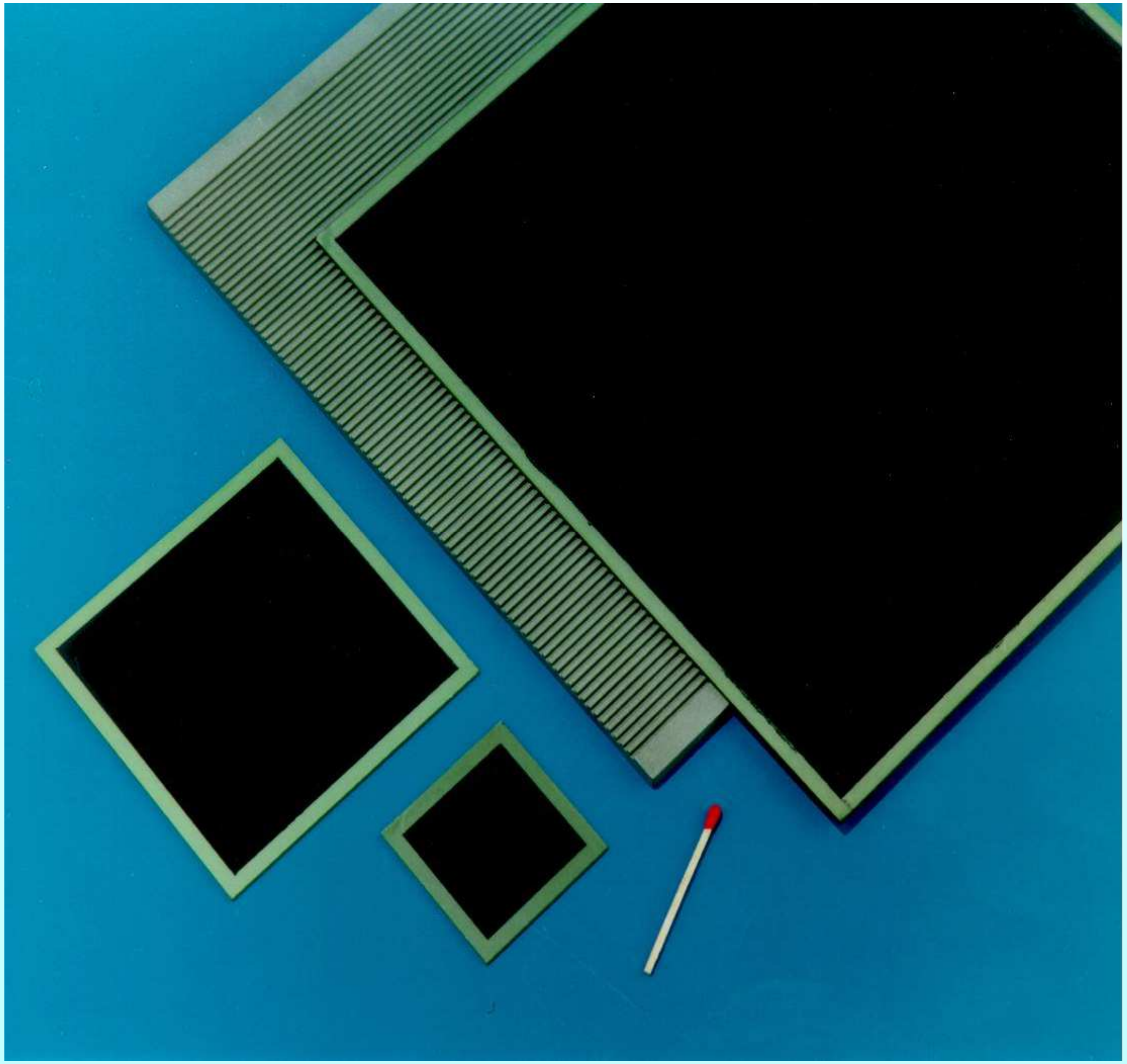
Ni/YSZ: Ni/YSZ-Cermet

IWE

Substrat-Zelle FZJ

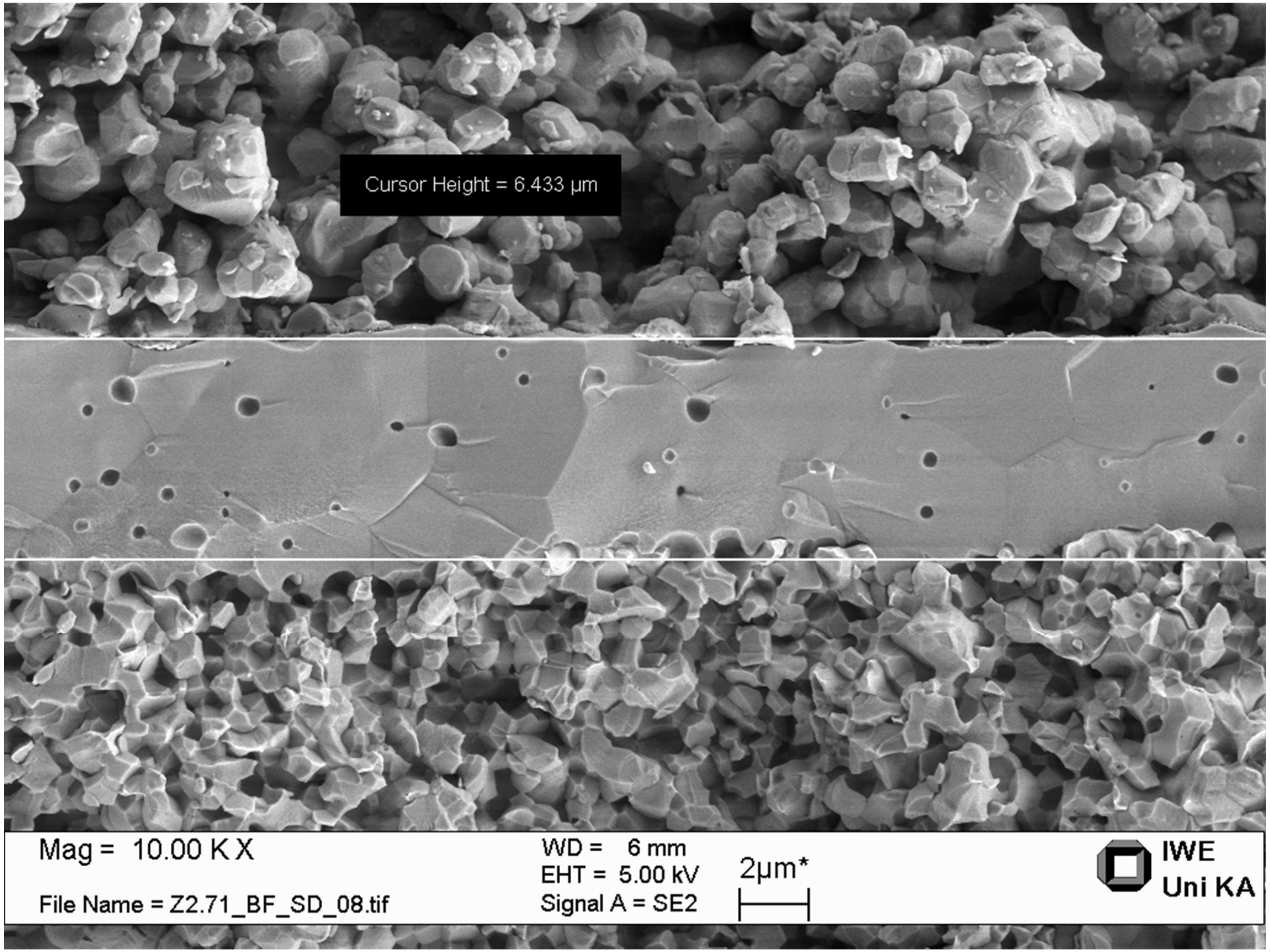


25 x 25 cm²

10 x 10 cm²

5 x 5 cm²

Bruchfläche
Elektrolytschicht der Zelle 1545



Elektrolytdicke:

6,4 µm

Kathode

Elektrolyt

Anode

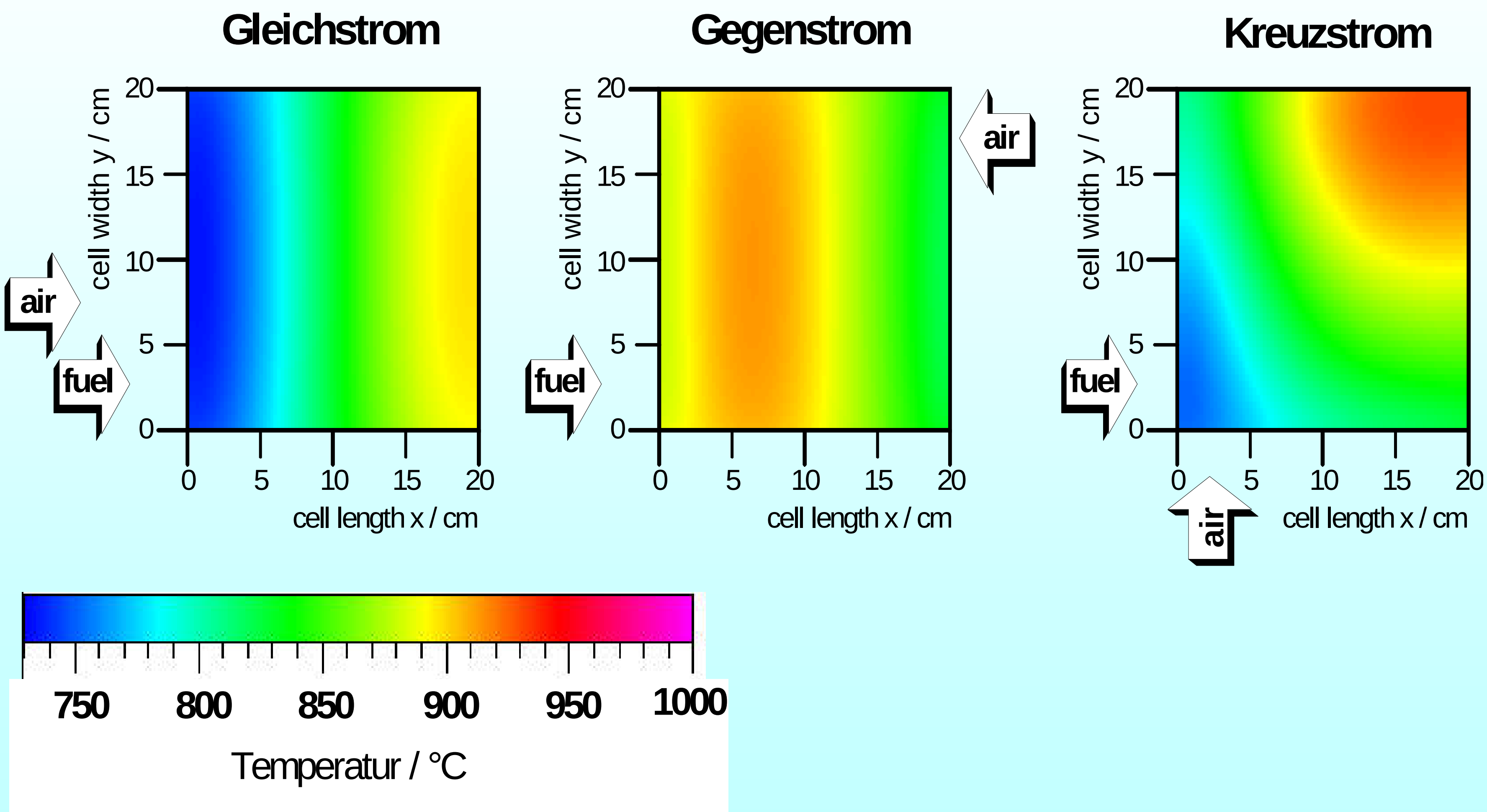
Stack Design

B-Design
with cross-flow
and
external manifold,
1995

Stack Design

D-Design
with cross-flow
and
internal manifold,
1999

Modellierung: Temperaturverteilung bei interner Reformierung



Stack Design

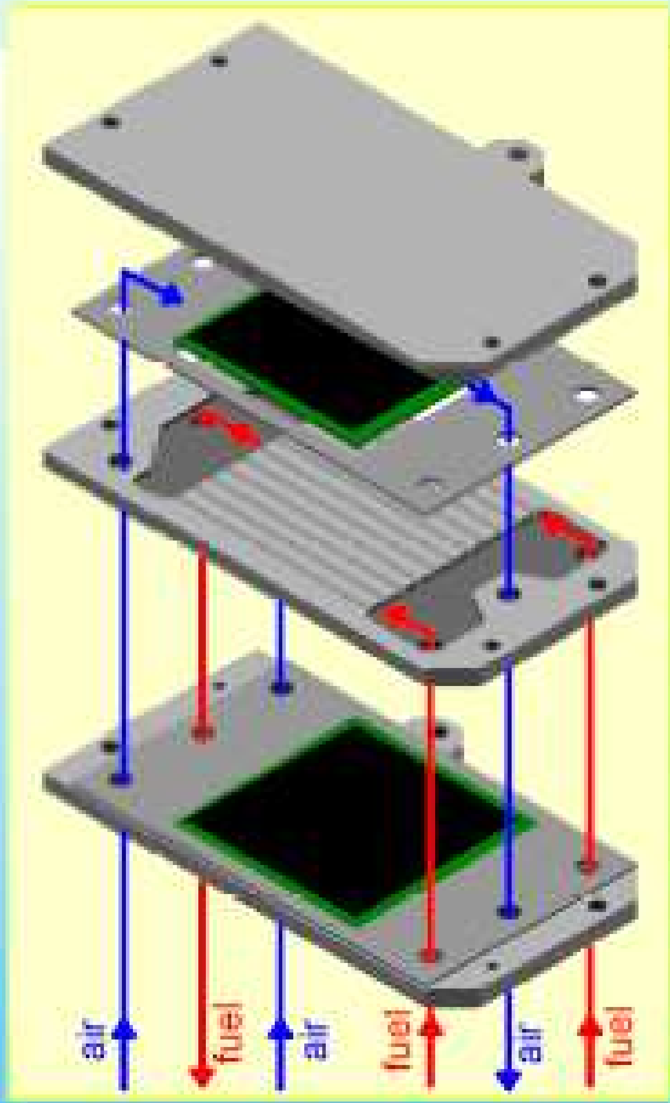
E-Design Stack Technology

Internal manifold:

sealing only in one plane perpendicular to the stacking direction

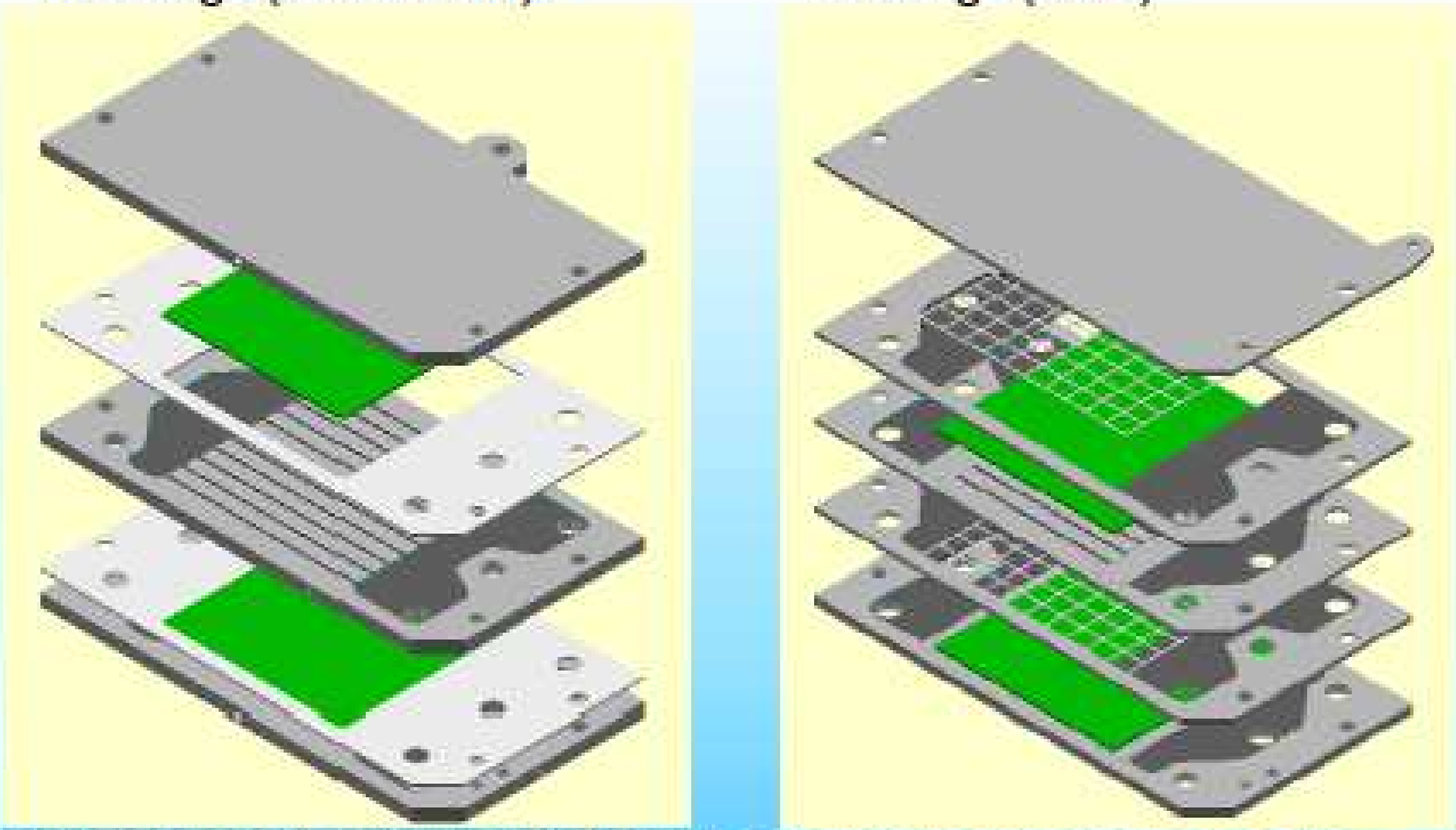
Parallel gas flow:

using counter flow results in a more homogeneous temperature distribution in case of internal reforming (results of stack-modelling)



Stack Design

E*-Design (status 2001) F-Design (2002)

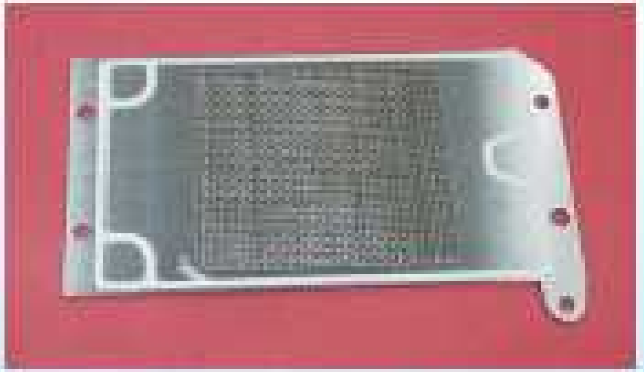


reduced manufacturing effort using a coarse nickel mesh as a gas distribution and contact element on the anode side

Stack Design

F-Design – status today

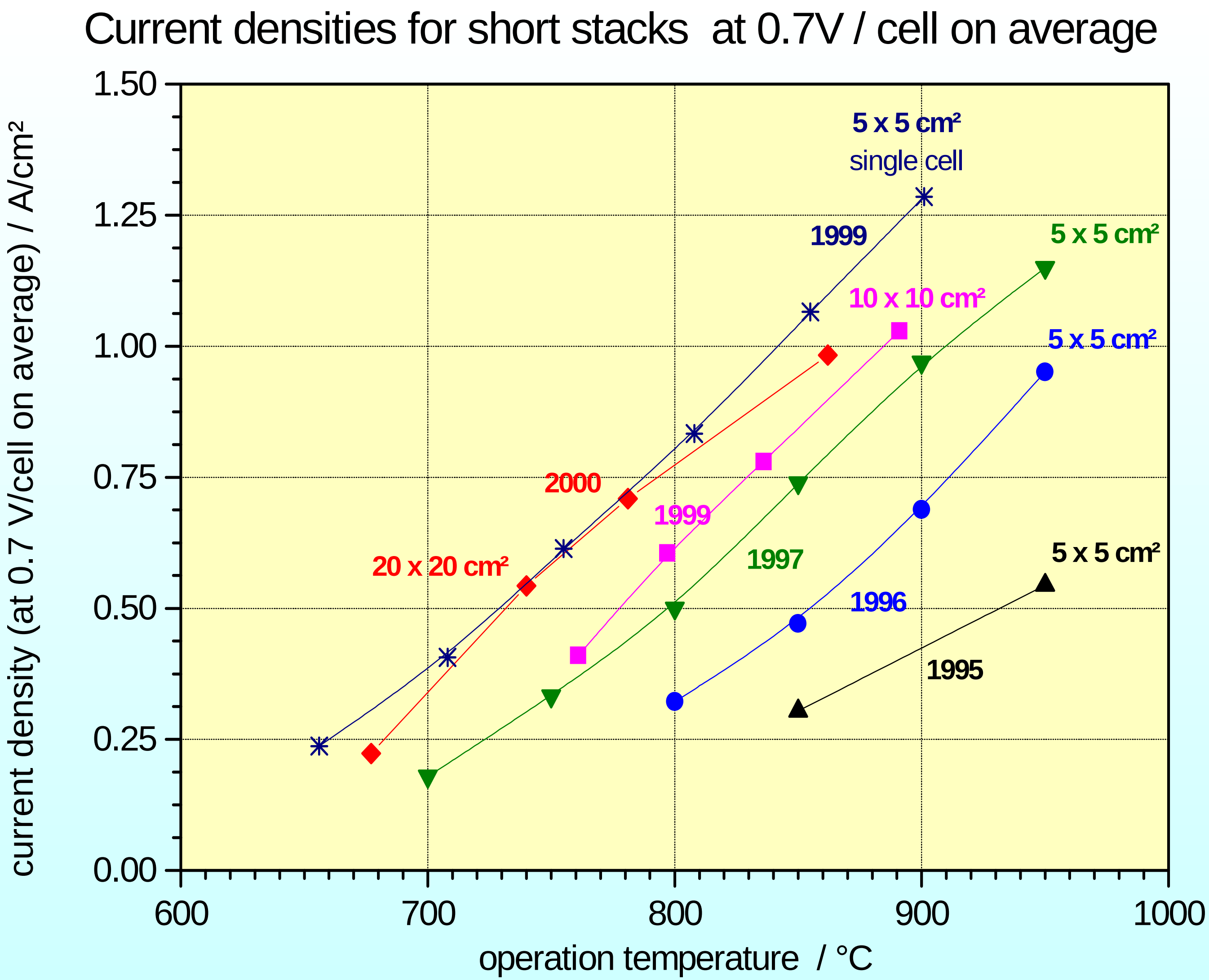
frame thickness 2.5mm



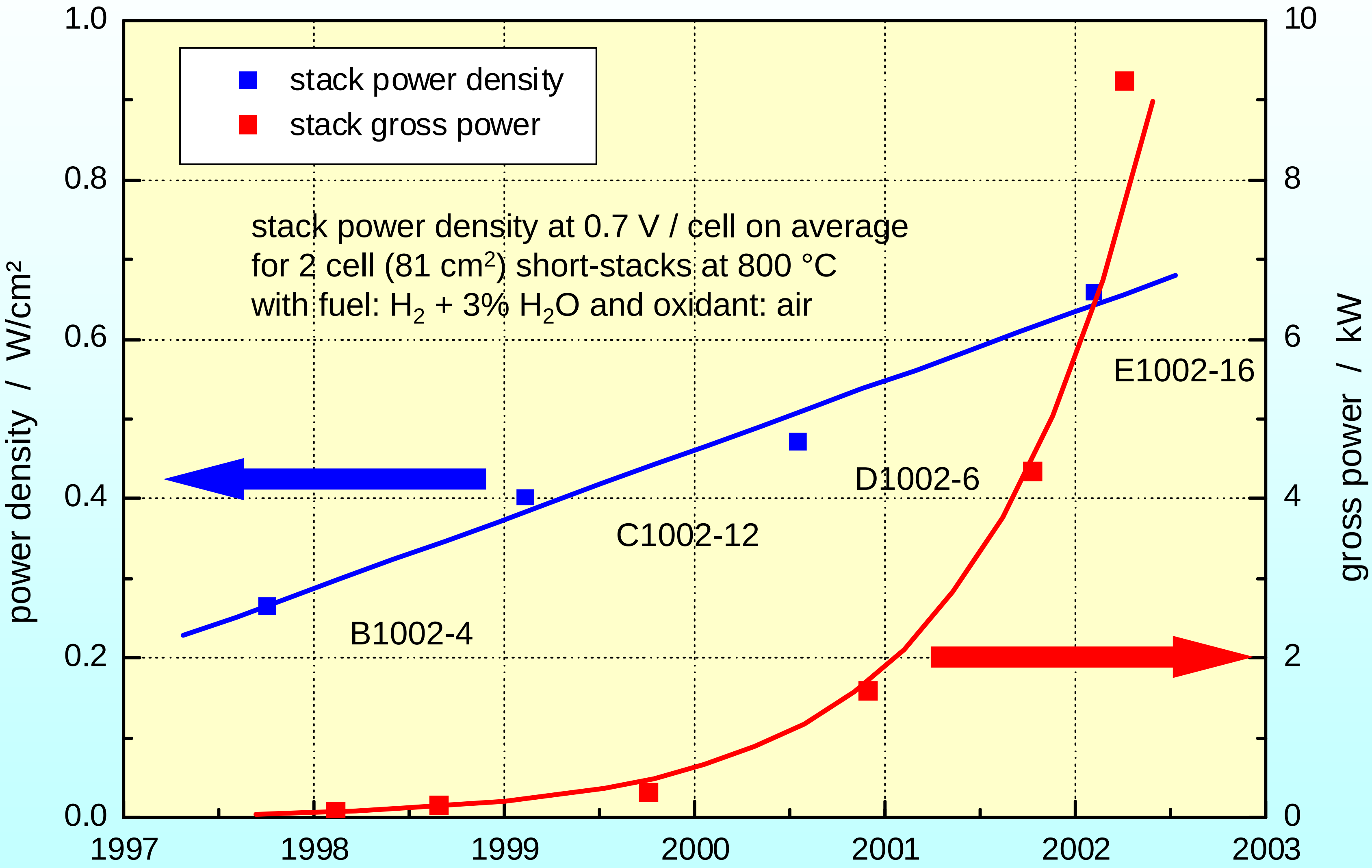
interconnector thickness
1.5 to 4 mm (depending on variant)

- reliable gas tightness
- cycleability proven with short stacks
- reproducible application of glass paste with a dispenser
- improved contacting through design change
- improved and time-economic manufacturing technology

Entwicklung der Stackleistungsdaten



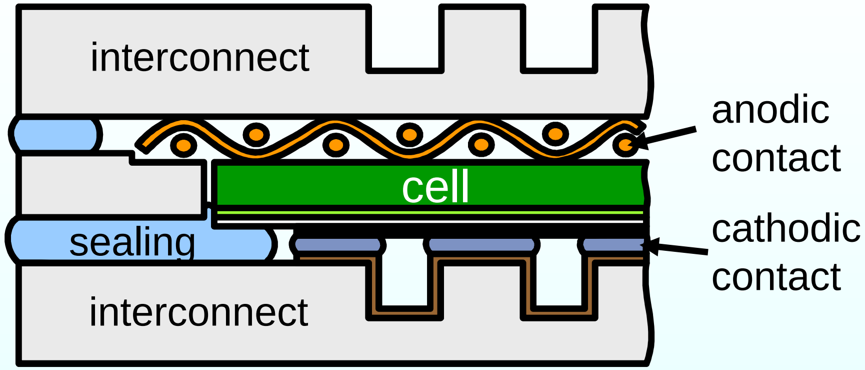
Stack development at FZJ



Materials development

Stack design and modelling

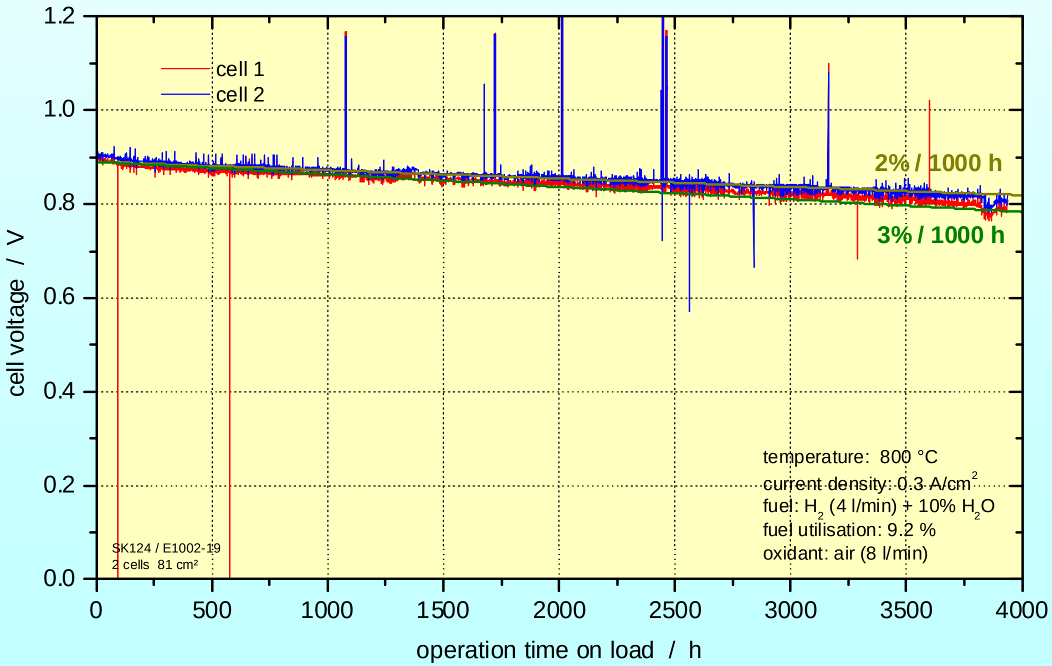
Processing technologies

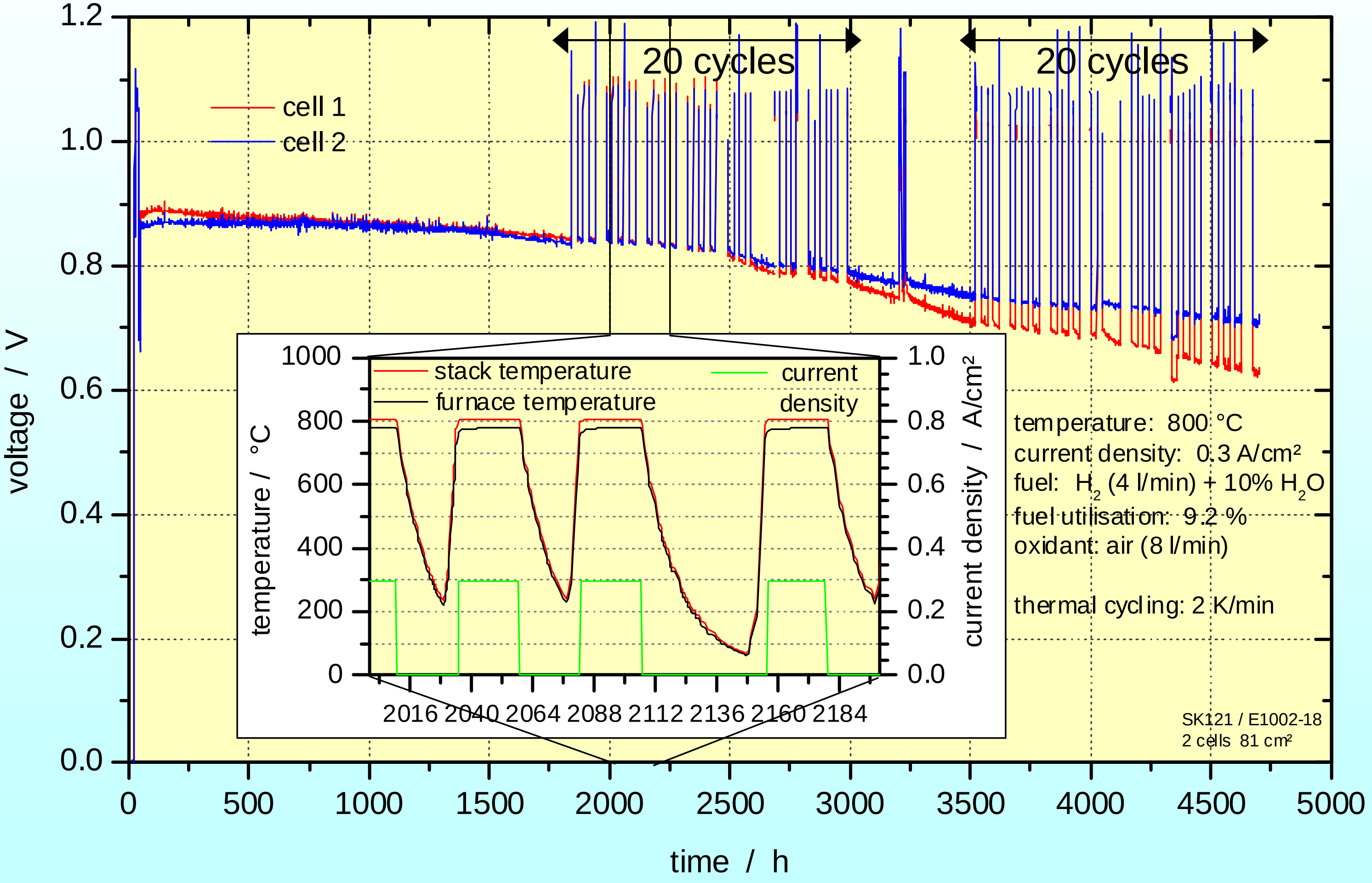


cross-section of a SOFC stack

Aims / Results:

- **High power density**
- **High durability**
- **Thermal cyclability**





20 cycles
20 cycles
cell 1
cell 2
voltage / V
time / h
0
500
1000
1500
2000
2500
3000
3500
4000
4500
5000
0.0
0.2
0.4
0.6
0.8
1.0
1.2
stack temperature
furnace temperature
current density
temperature / °C
current density / A/cm²
2016 2040 2064 2088 2112 2136 2160 2184
temperature: 800 °C
current density: 0.3 A/cm²
fuel: H2 (4 l/min) + 10% H2O
fuel utilisation: 9.2 %
oxidant: air (8 l/min)
thermal cycling: 2 K/min
SK121 / E1002-18
2 cells 81 cm²

Power Stacks at FZJ 2

40 cell stack 20 cm x 20 cm generating 9,2 kW at 800+ °C using hydrogen

With hydrogen: **9,2 kW**

0,63 W/cm²

300 A @ 30,6 V;

0,83 A/cm² @ 0,765 V/cell

With Methane: **5,4 kW**

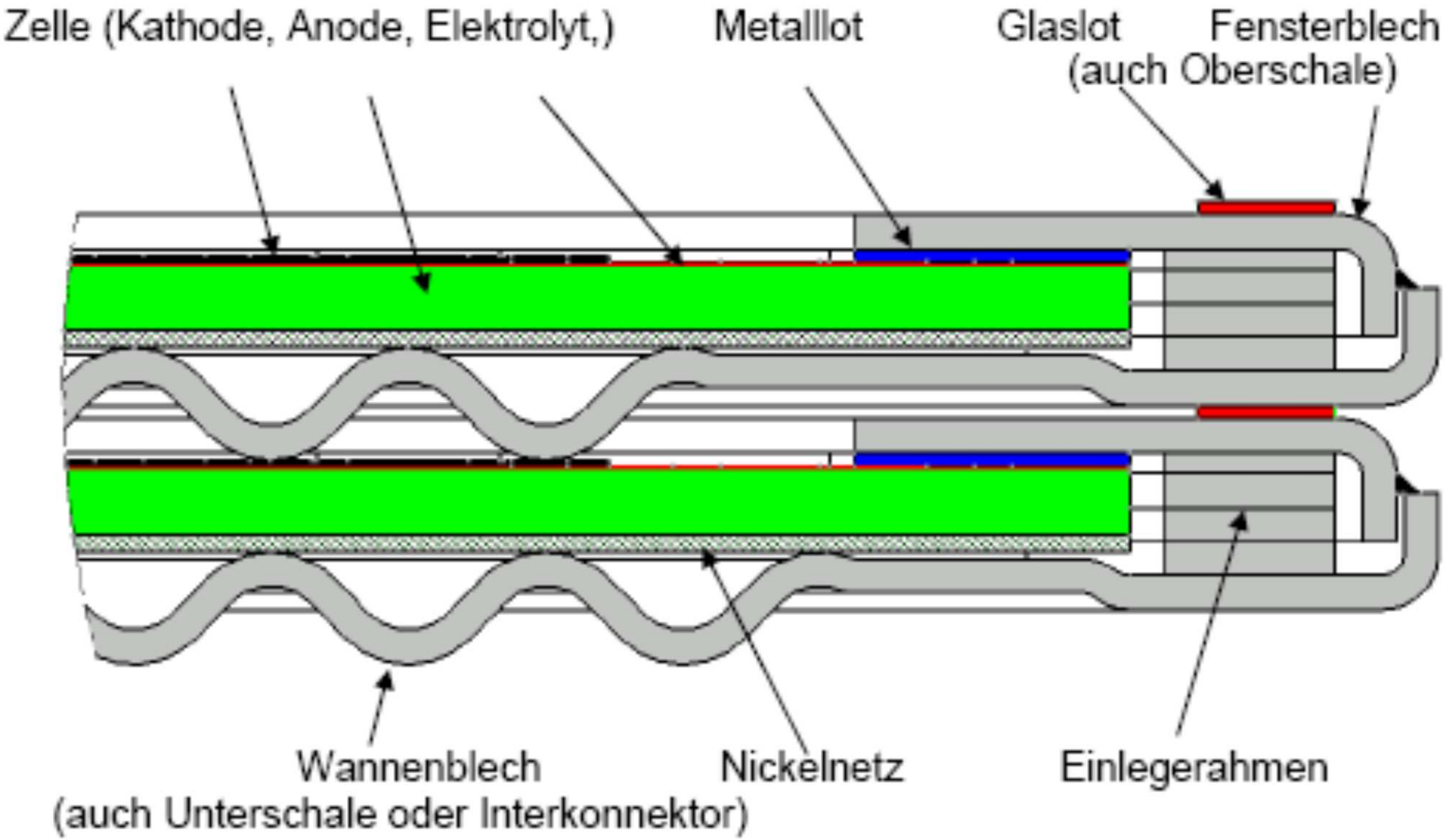
0,38 W/cm²

180 A @ 30,2 V;

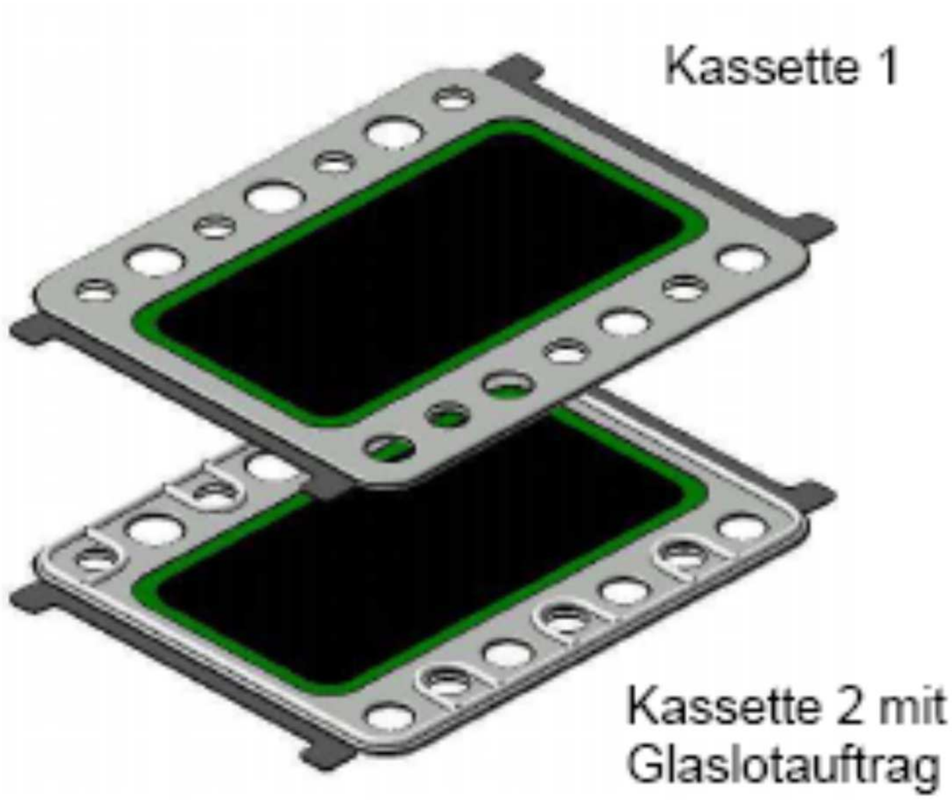
0,50 A/cm² @ 0,755 V/cell

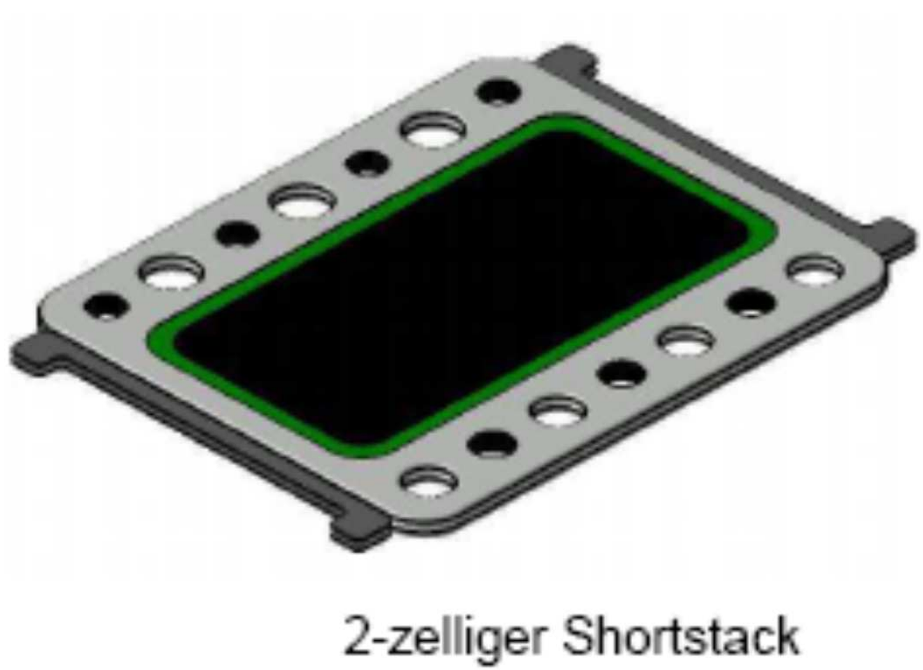
Fuel:	90% H_2 / 10% H_2O	7% H_2 / 31% CH_4 / 62% H_2O
Utilisation:	76 % @ 300 A	59 % @ 180 A
Oxidant:	Air	Air
Stoichiometry:	2 @ 300 A	3.5 @ 180 A

SOFC Stack Design
Leichtbaustack

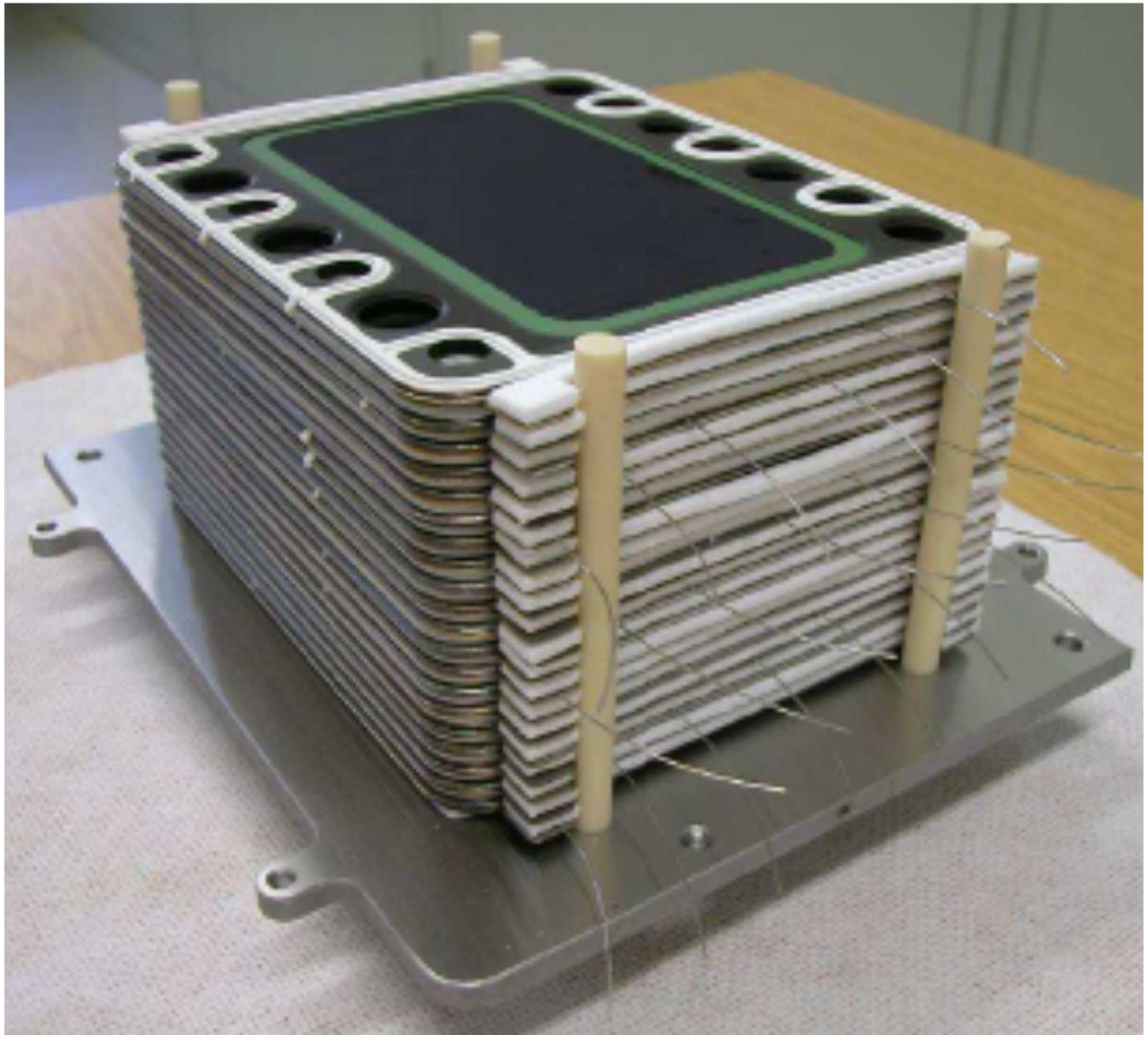


SOFC Stack Design
Aufbau eines Leichtbaustacks





SOFC Stack Design
Leichtbaustack-Kassette



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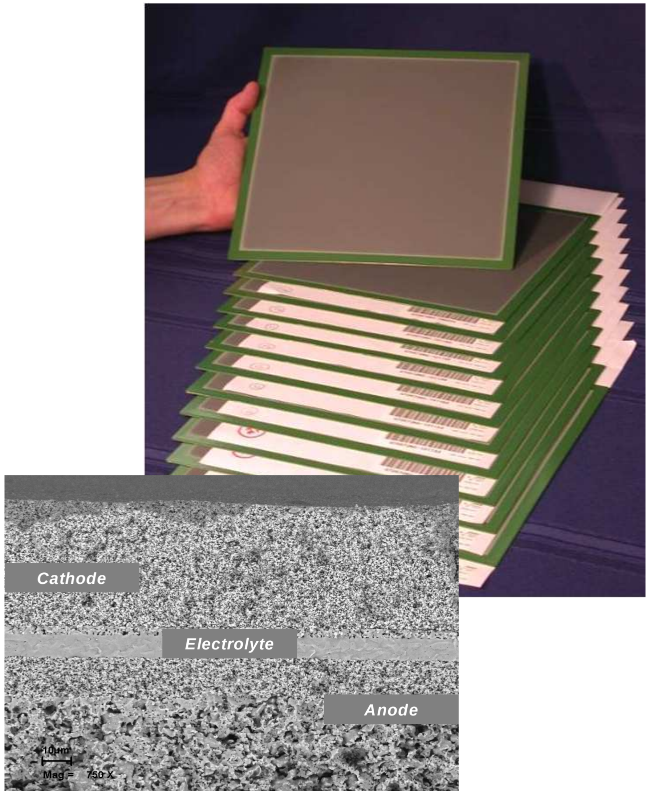
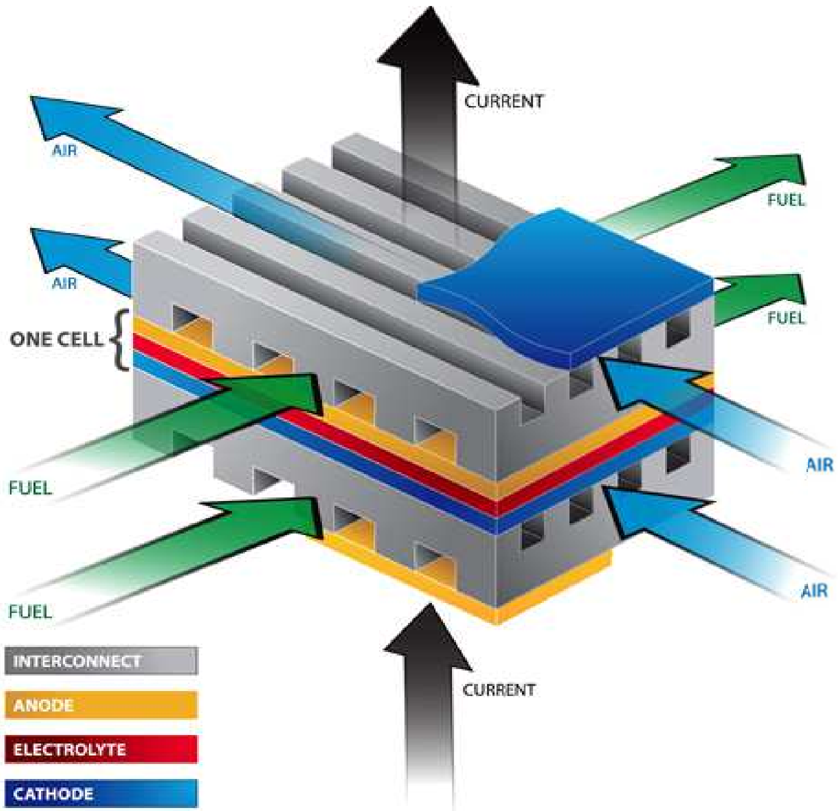
Ultra-Clean, Efficient, Reliable Power

Versa Power's SOFC Approach

- Planar anode-supported cells
- Cross-flow gas delivery
- Stainless steel sheet metal interconnects
- Stacks can be integrated into various arrangements, depending on power applications



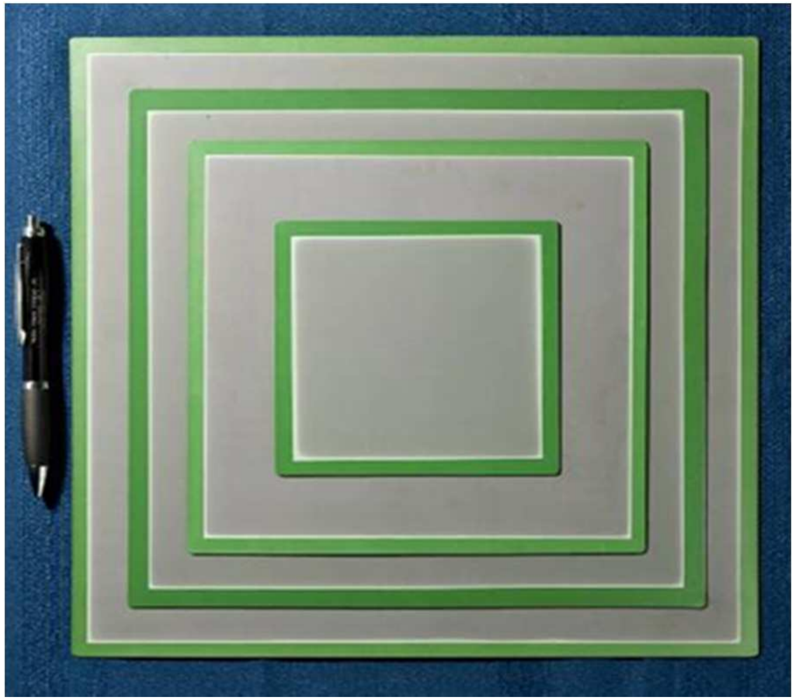



HARROP


HARROP

Cell Overview

- The techniques used to make cells are: **T**ape casting, **S**creen printing and **C**o-firing (the **TSC** Process)
- Capable of operating between 650 to 800ºC with high power density
- Cell has been scaled-up from 10 x 10 cm^2 (81 cm^2 active area) to 25 x 25 cm^2 (550 cm^2 active area) to facilitate stack scale-up



Component	Materials	Thickness	Porosity	Process
Anode	Ni/YSZ	0.5 mm	~ 40%	Tape casting
Electrolyte	YSZ	5 - 10 μm	< 5%	Screen printing
Cathode	Conducting ceramic	10 - 50 μm	~ 30%	Screen printing

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Stack Development

Scale Up

- Scaled up from 28 cells up to 120 cells
- Stack power from 1 kW to 15 kW

Performance Improvement

- Higher power density
- Higher fuel utilization
- Higher direct internal reforming

Cost Reduction

- Reduced stack cost to meet SECA cost targets

Endurance Enhancement

- Improved stack thermal and flow management
- Incorporated TSC3 cells
- Incorporated advanced flow media

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SECA Stacks

Stack Size	Phase I Quantity	Phase II Quantity	Phase III Quantity	Total
Short Stacks 6 - 32 Cells	39	43	16	98
Full Size Stacks > 64 cells	6	9	15	30
Total Quantity	45	52	31	128
Total kW	126	255	262	643


Phase III stack block (96-cell)


6-cell short stack

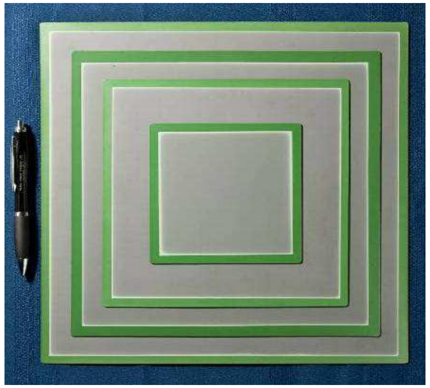

16-cell short stack

Phase I stack block (64-cell)

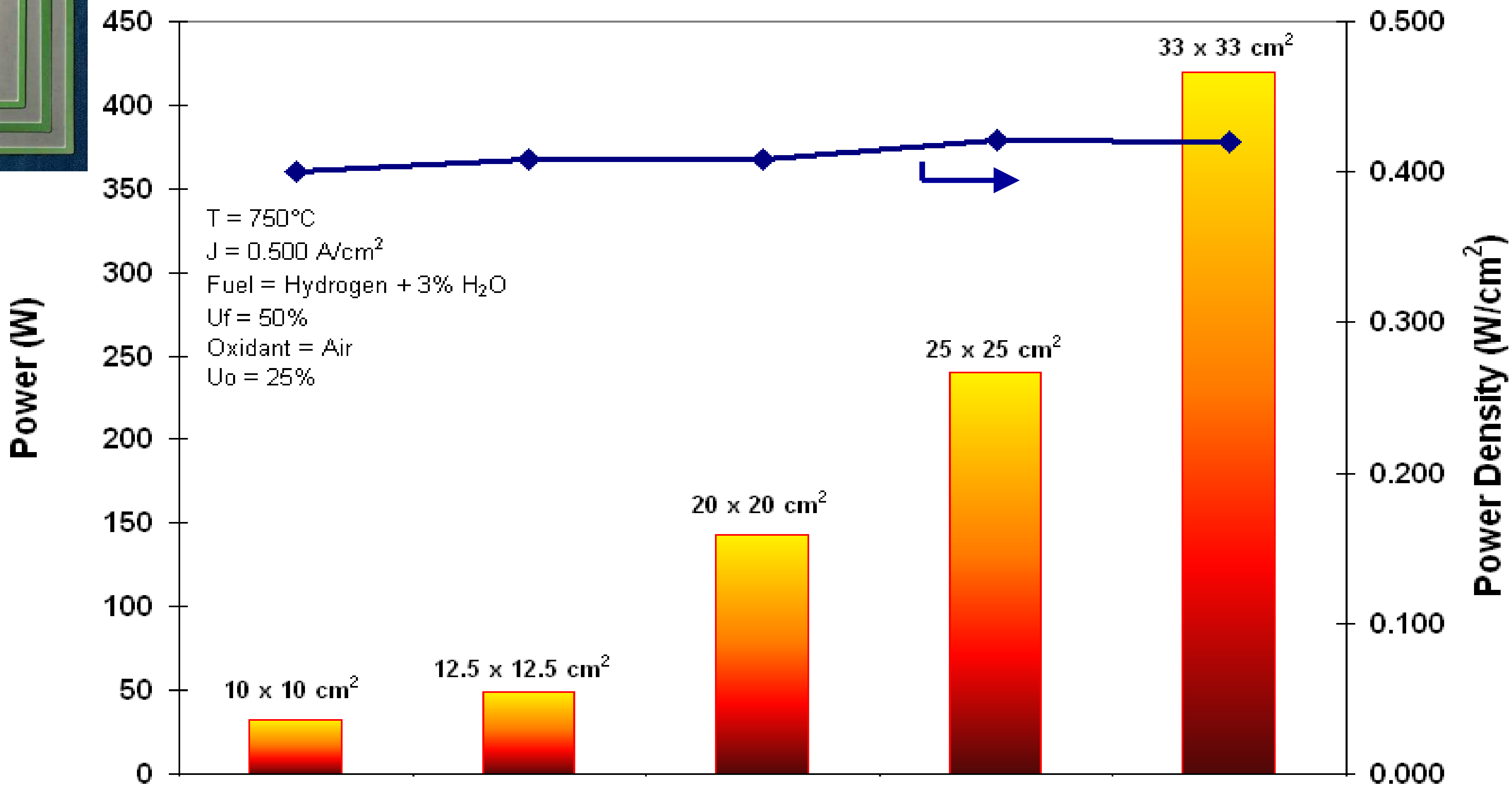

Phase II stack block (92-cell)


Phase II stack (120-cell)

Cell Power at 0.500 A/cm²

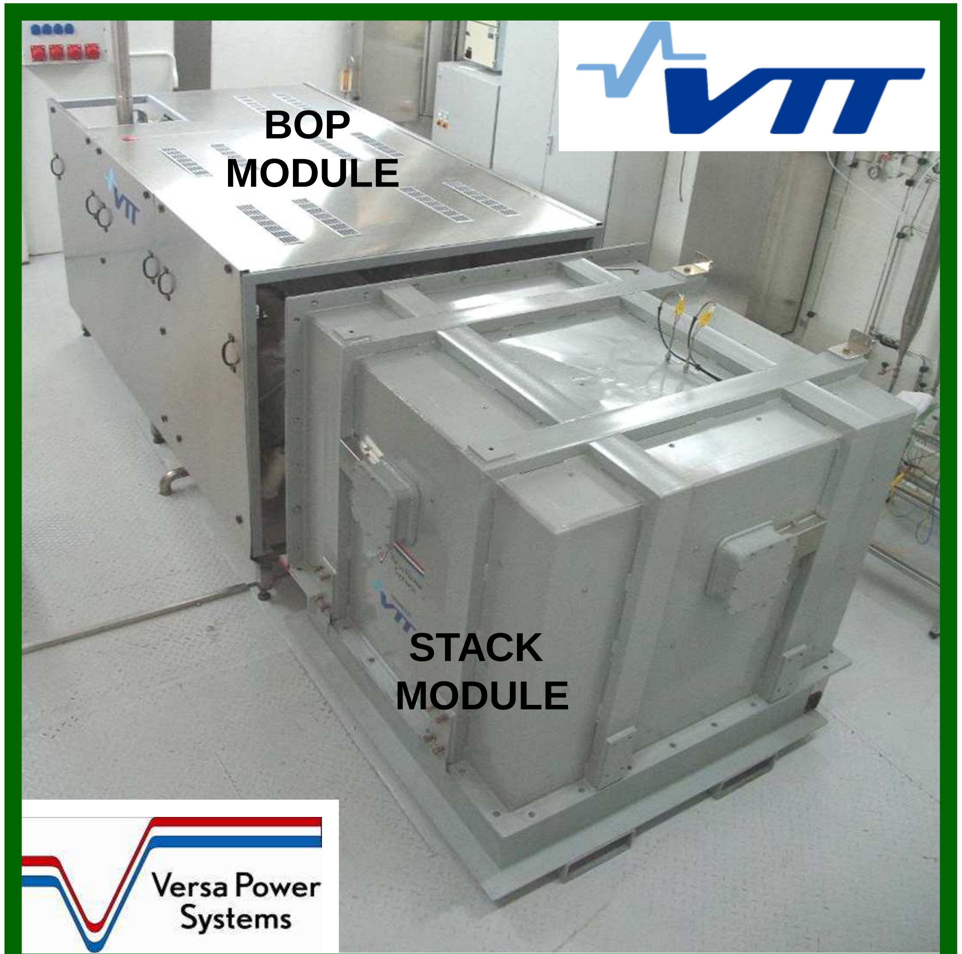


Stainless Steel Current Collectors, Cross-Flow Gas Delivery



Power (W)	32	49	143	241	420
Cell Voltage (V)	0.80	0.82	0.82	0.84	0.84

10 kW SOFC Demo Unit at VTT



VPS 10 kW SOFC stack module integrated with VTT BoP module

- VPS has collaborated with VTT Technical Research Centre of Finland since 2010 to produce and operate a 10 kW fully integrated SOFC system
  - Single stack
  - Modular design
  - Natural gas fueled
  - Warm anode recycle loop
  - Grid connected
  - Thermally self-sustained

Stack Cell Count	80
Stack Current	160.6 A
Cell Voltage	857 mV
Stack Voltage	68.57 V
Module Power	11.013 kW
Fuel Utilization - System	80.4%
Module Efficiency (LHV)	66%

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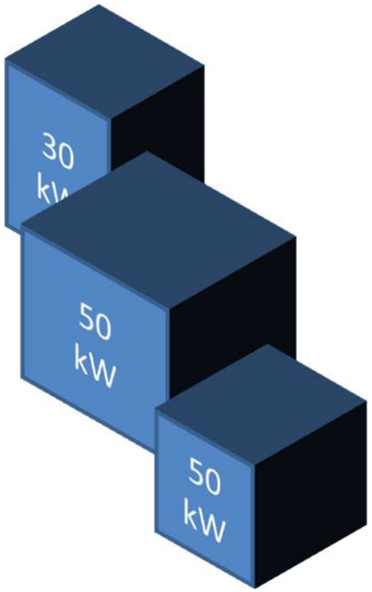
SOFC Module Design & Packaging

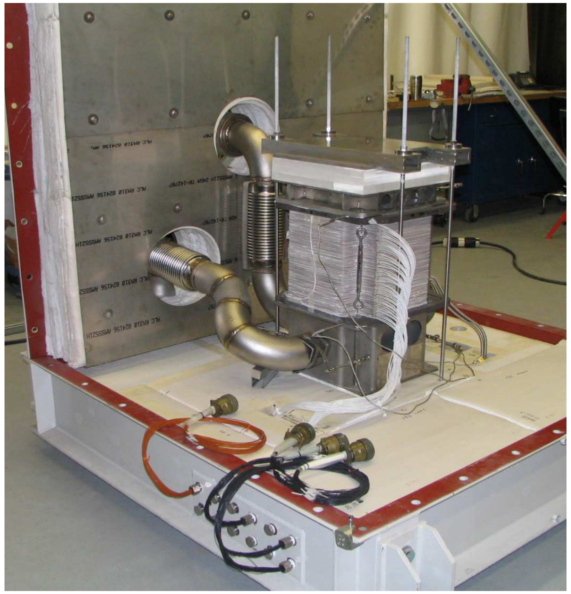
SOFC Module design has evolved to be more integrated & compact

- Custom engineered equipment & components have been developed
  - Permits thermal management of the stacks
  - Simplifies the system by reducing insulation, containment systems, pipe/duct length, and total part count
  - Improves thermal performance, and reduces plant parasitic flow losses
- Reduces footprint of module
  - Piping and ducting more compact, and minimizes hot piping/duct penetrations in vessel
- Reduces footprint of total plant by having less external equipment
- Smaller system with fewer parts & less material = lower cost



MODULE (kW)	STATUS	Level of Integration
30	Built	No Integration. Single Stack or Tower in an insulated vessel
50	Built	Manifold assembly, HX
50	In Process	Manifold assembly, HXs, Reformer

30 kW Module



- Demonstrated use of a vessel design based on FCE's commercial MCFC product line
  - Improved insulation, instrumentation, power, & piping interface with test facility
- Sucessfully operated with towers up to three stacks tall
- Vehicle for eight long-term tests from 10kW to 30kW
- Instrumental in validating thermal and flow CFD models
- Established methods for multi-stack modules

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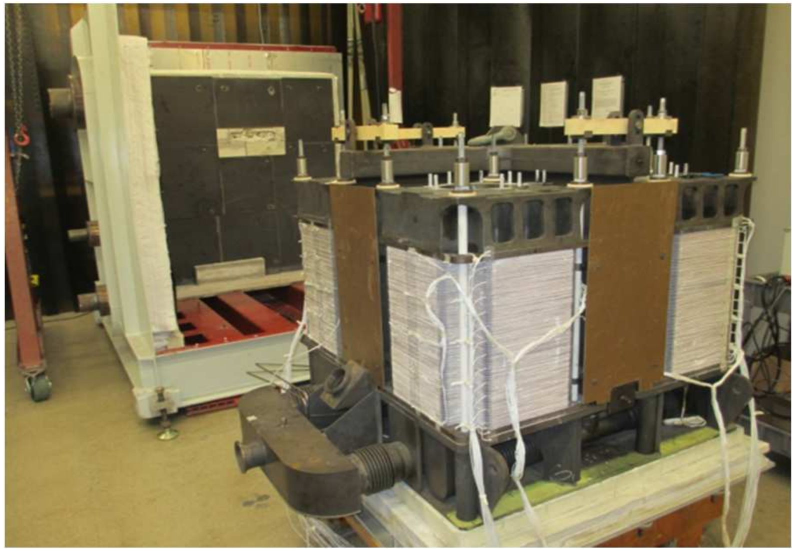
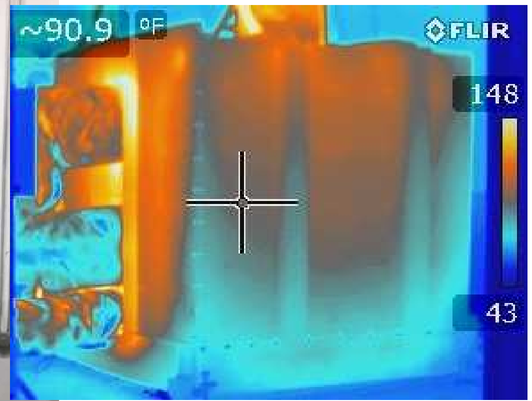
50 kW Module

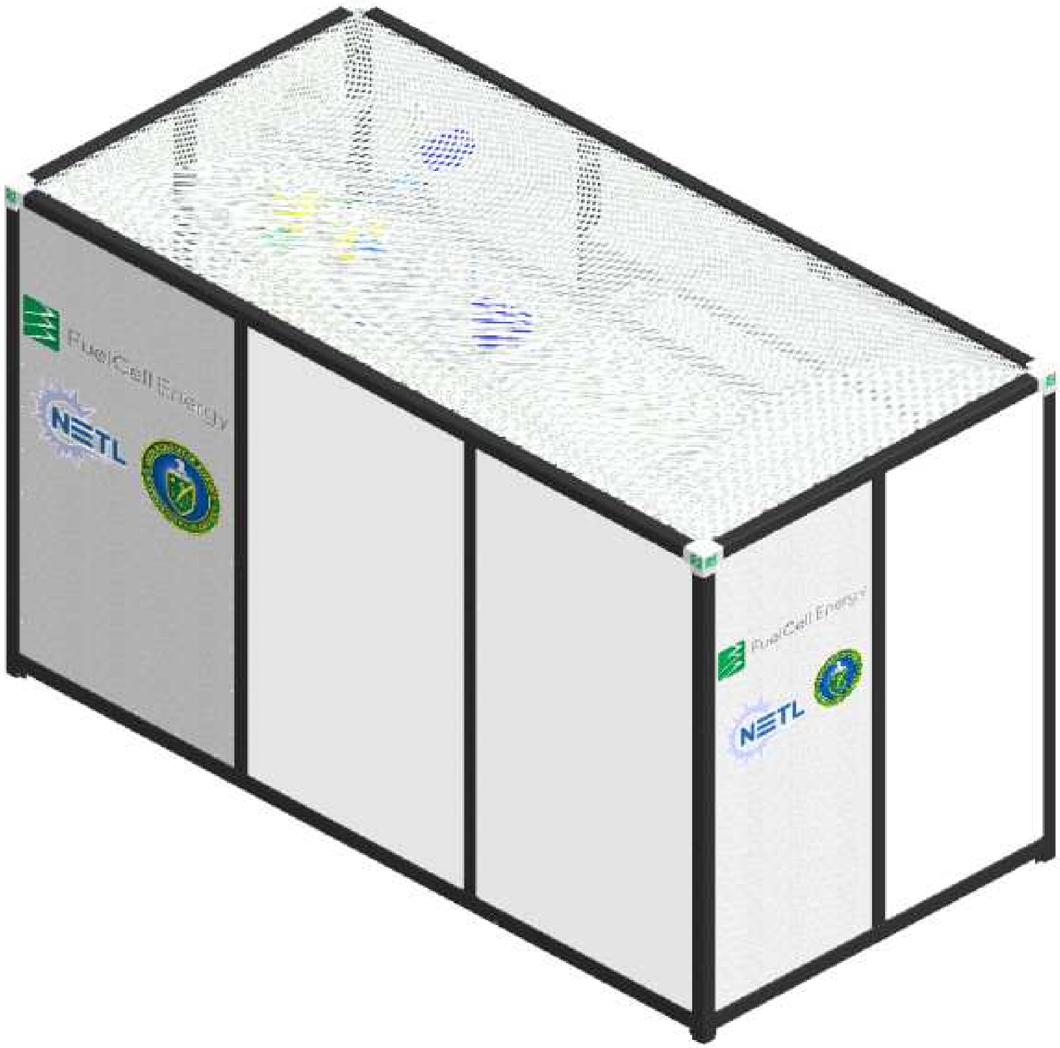




- Demonstrated integrated manifold assembly, nominally four 96-cell stack blocks, but components designed for full (2X) tower flows
- Fully self contained and thermally self sustaining
- Successfully validated many completely new components developed under the SECA contract
- Will be the basis for future (commercial) SOFC module designs

Stack Current	187.4 A
Cell Voltage	819 mV
Stack Voltage	78.64 V
Gross Module Power	58.96 kW
Fuel Utilization - System	81%
Module Efficiency (LHV)	65%

50 kW SOFC Power Plant



A packaged SOFC power plant has been designed which is:

- Compact for easy shipping and siting
- Expandable to higher power module with no increase in foot print or envelope
- Accessibility for service
- Suitable for CHP