Batterie- und Brennstoffzellensysteme

Stack- und Zellkonzepte für die SOFC

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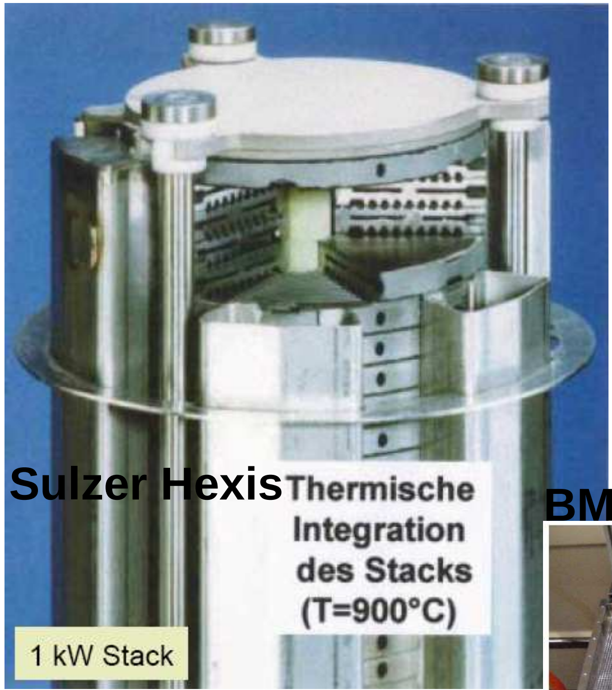
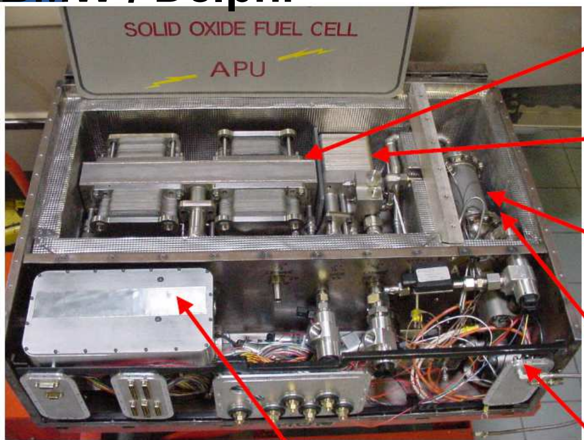
Institut für Werkstoffe der Elektrotechnik

Stack- und Zellkonzepte

Sulzer Hexis



BMW / Delphi



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

Waste Energy Recovery
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

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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

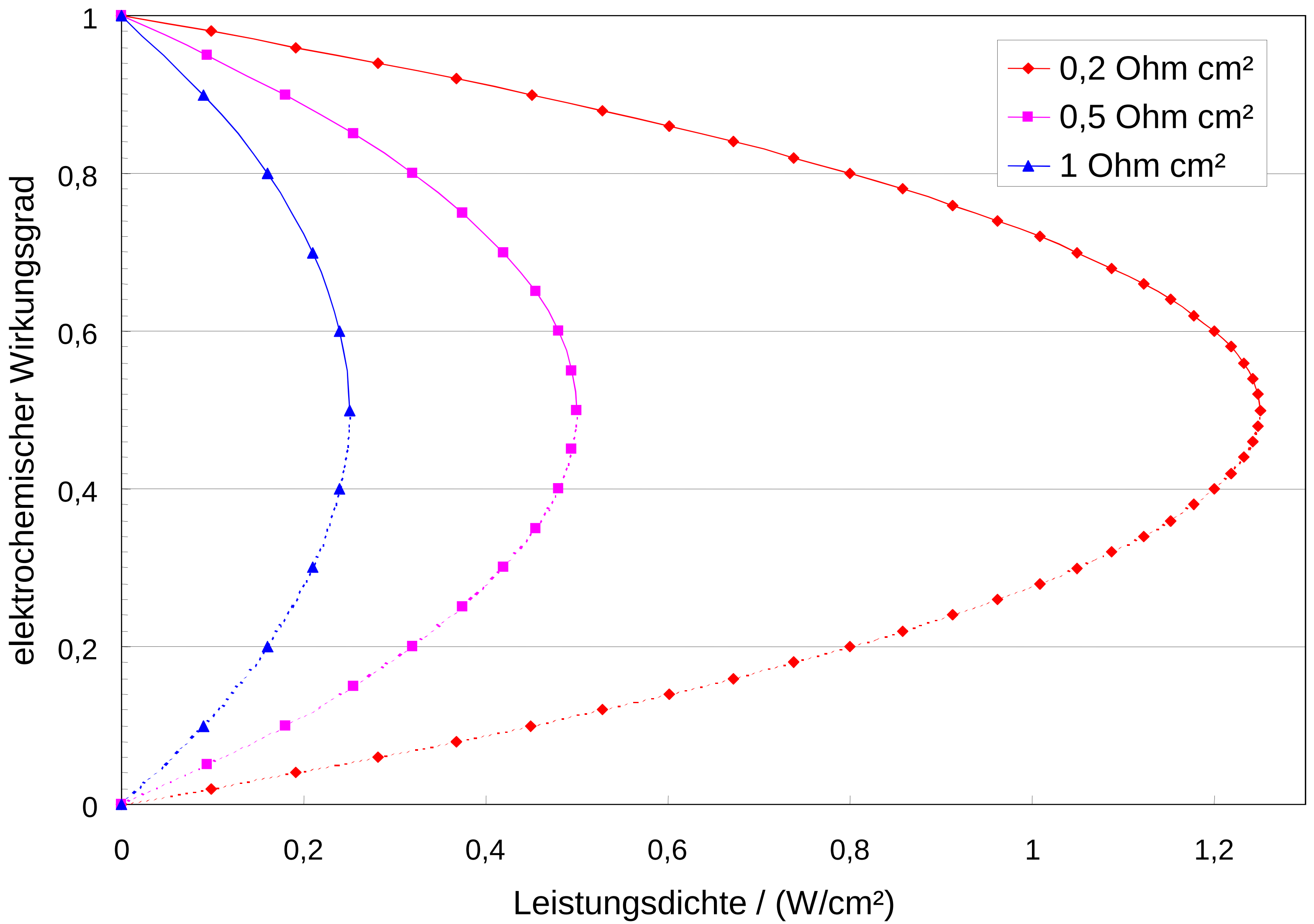
$$\eta_{thermal} = \frac{\text{usable heat}}{\text{provided chemical energy}}$$

total efficiency

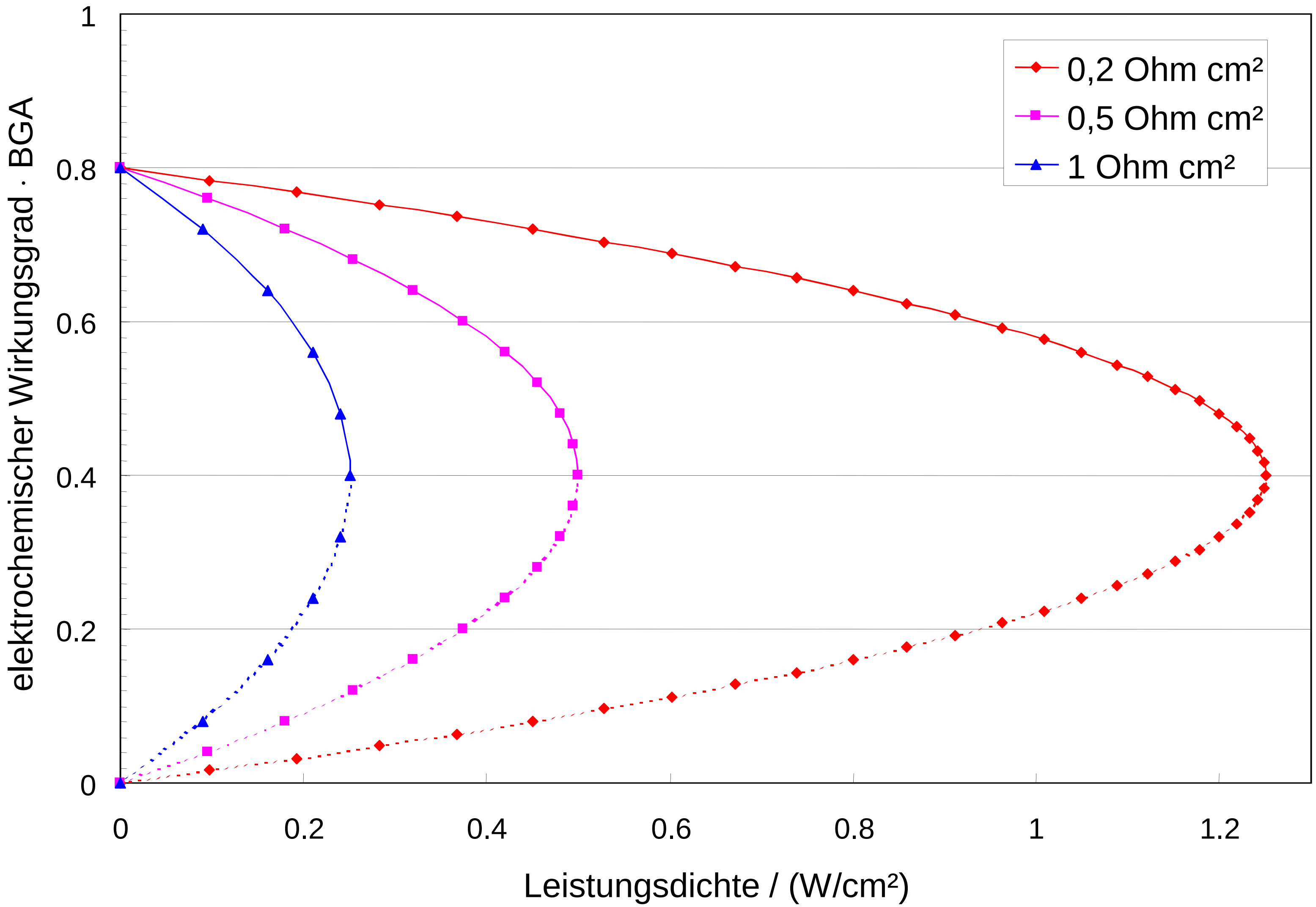
$$\eta_{tot} = \eta_{electrical} + \eta_{thermal}$$

CHP-system

Elektrochemischer Wirkungsgrad in Abhängigkeit der Leistungsdichte

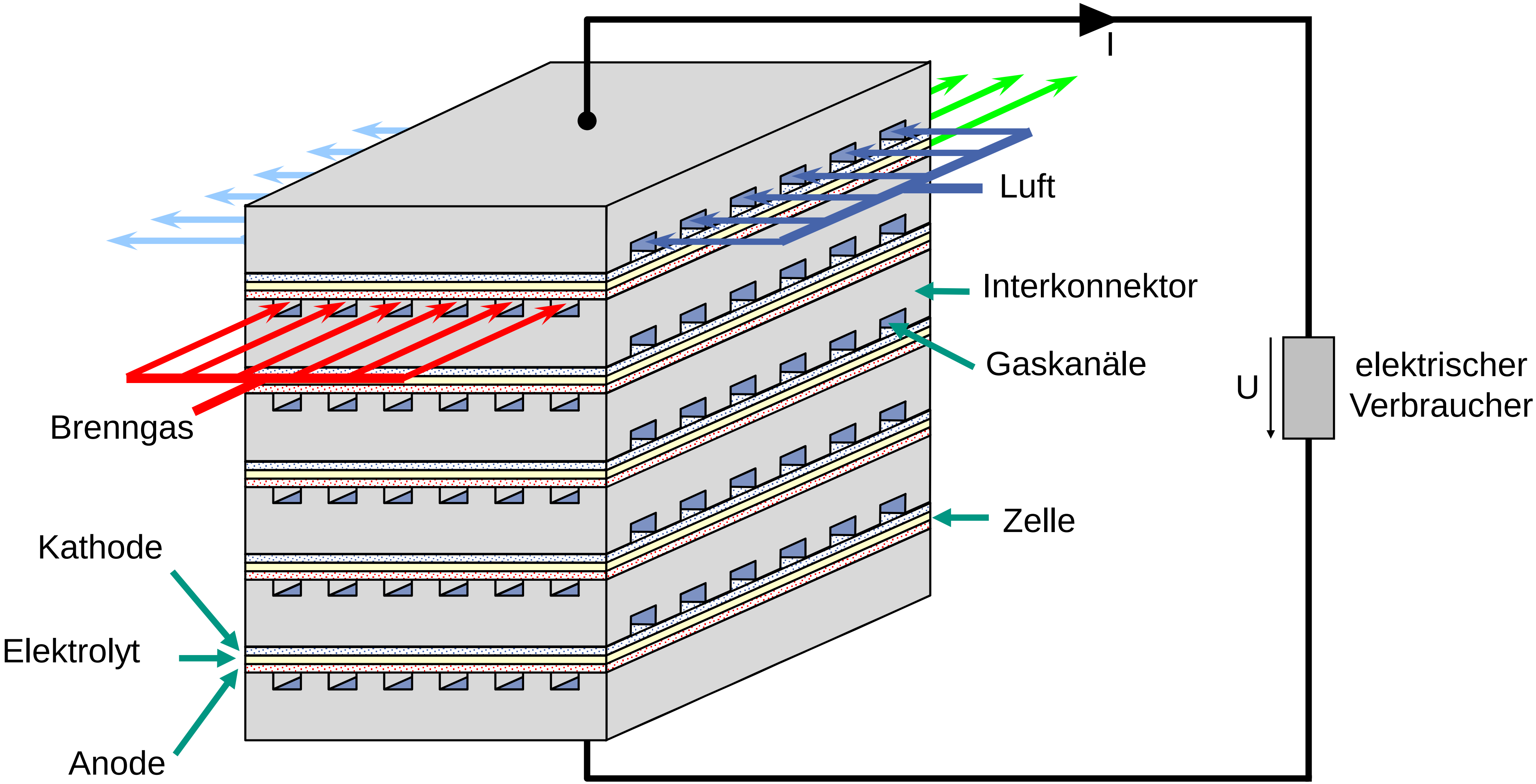


Stack-Wirkungsgrad ($\beta_f \cdot \eta_{el}$) in Abhängigkeit der Leistungsdichte

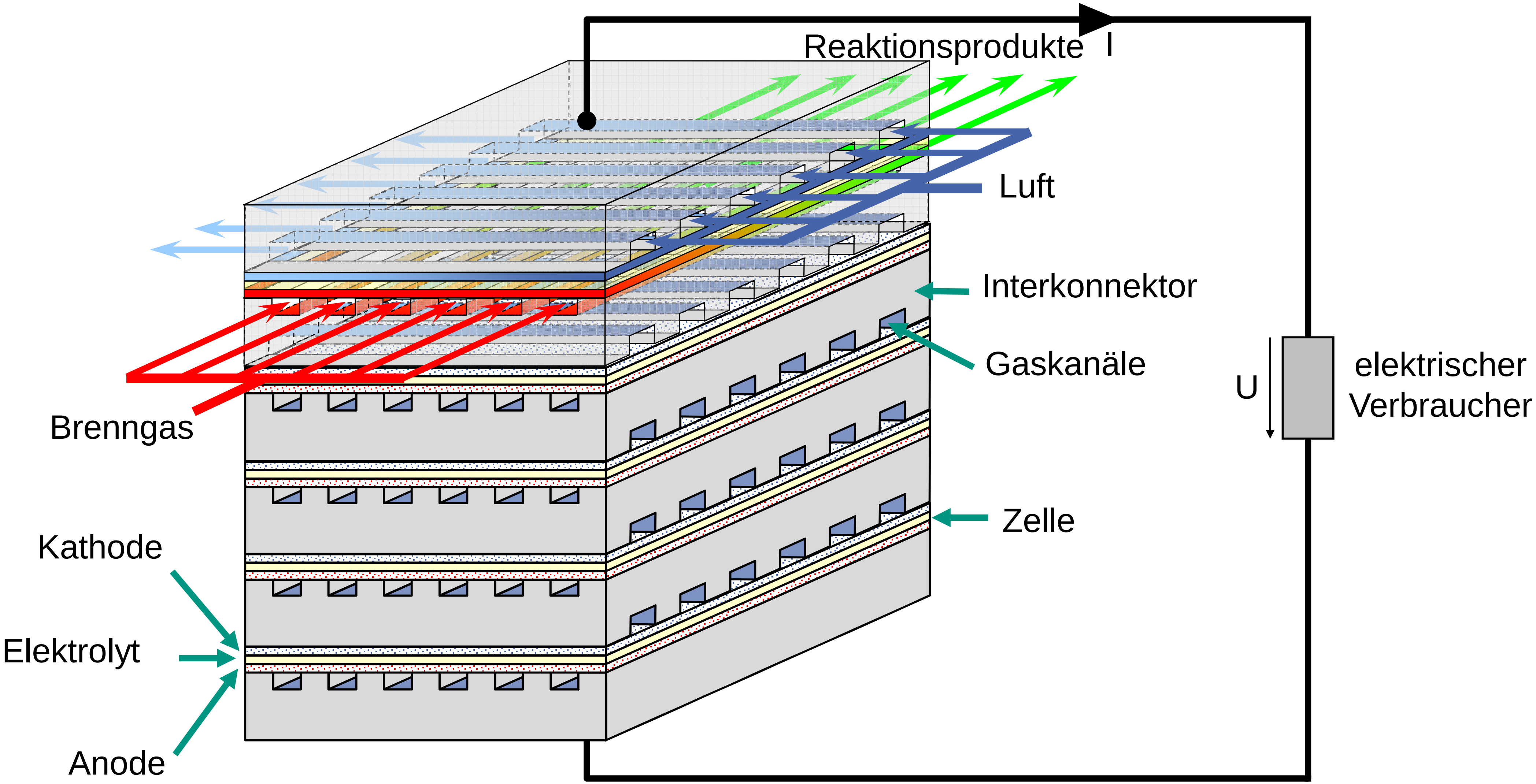


Brenngas-ausnutzung: 80%
(η_f = 1)

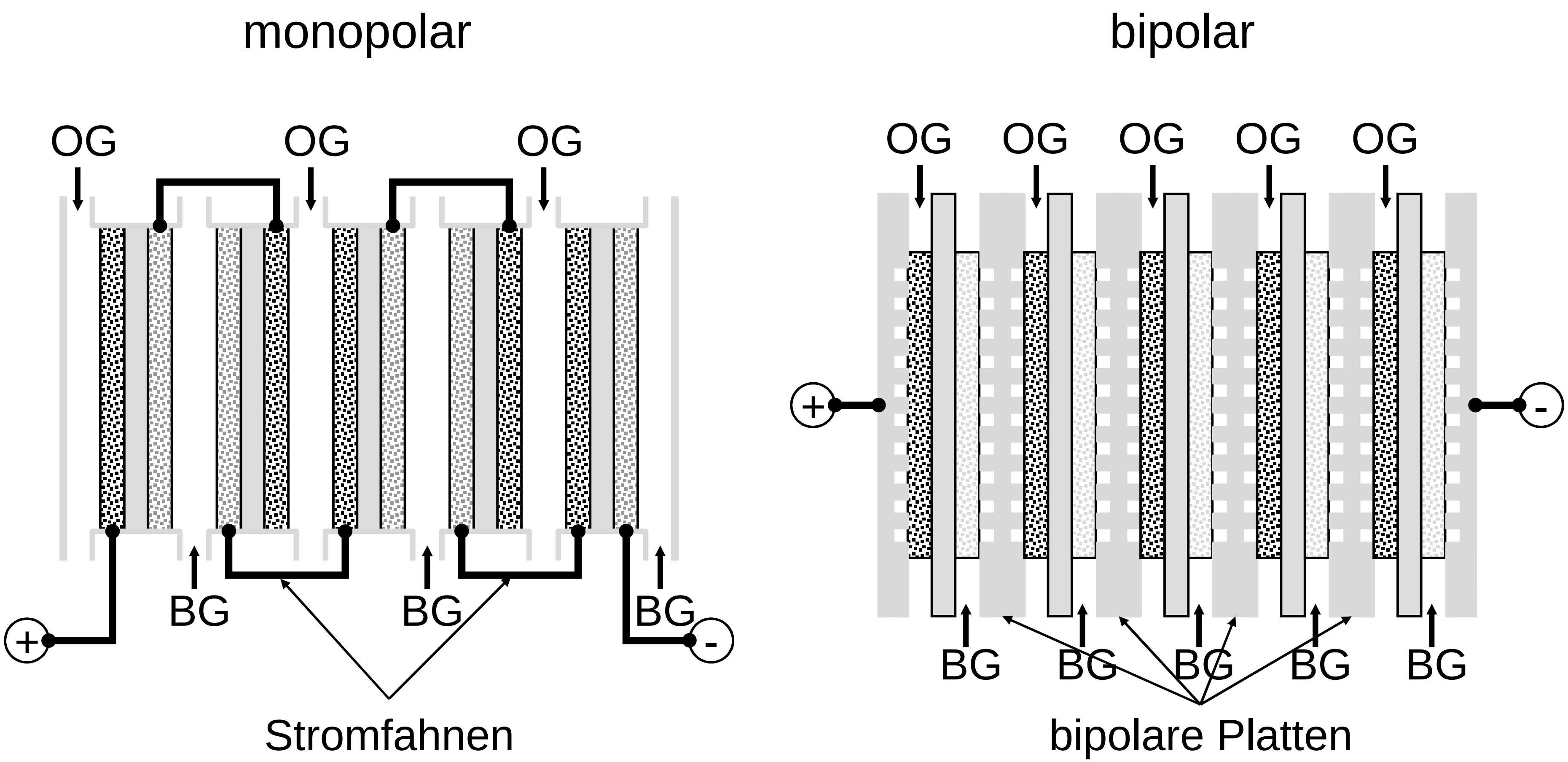
Planarer Brennstoffzellen-Stack



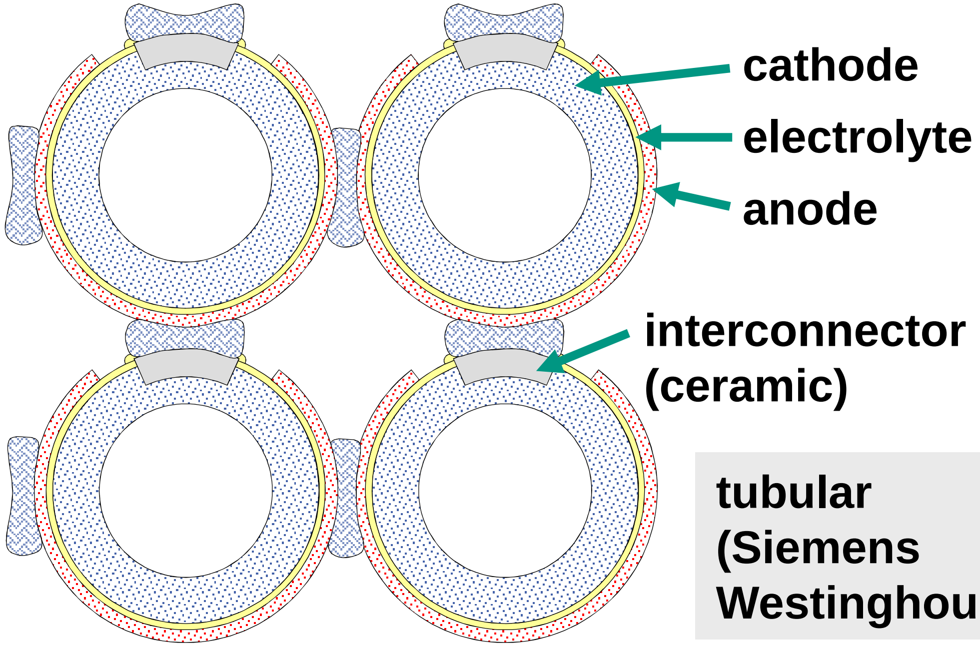
Betriebsbedingungen im Stack



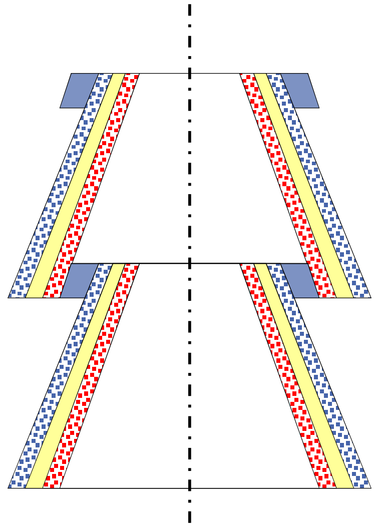
Baukonzepte für Brennstoffzellenstacks



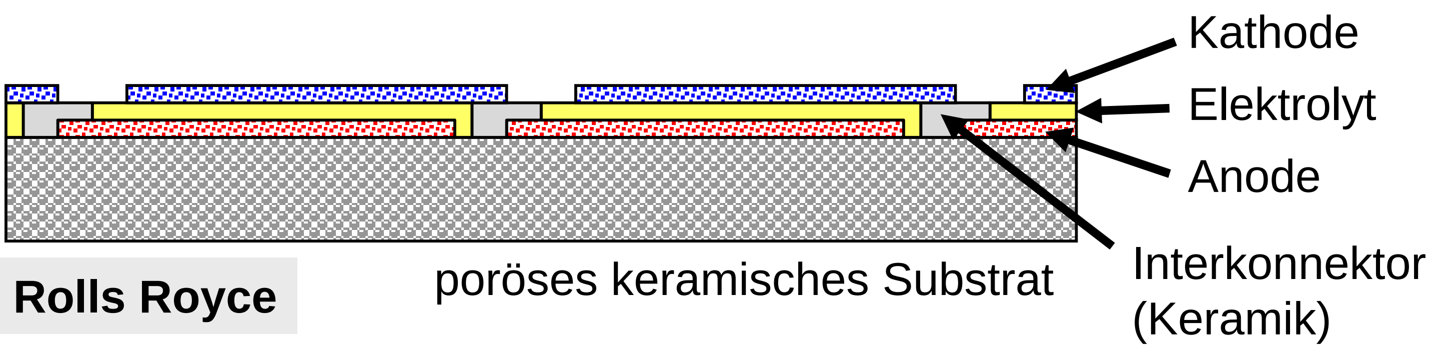
SOFC Stack-Designs („monopolar“)



tubular (Siemens Westinghouse)



tubular (Mitsubishi Heavy Industries)



Rolls Royce

SOFC Stack-Designs („bipolar“)

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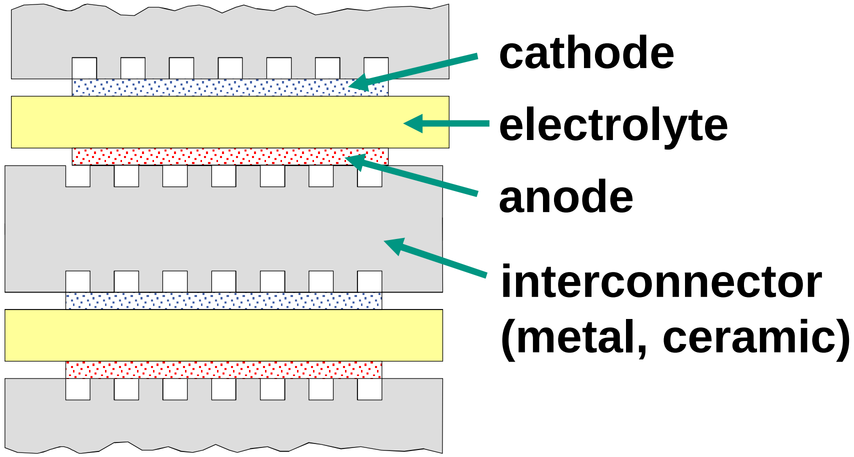
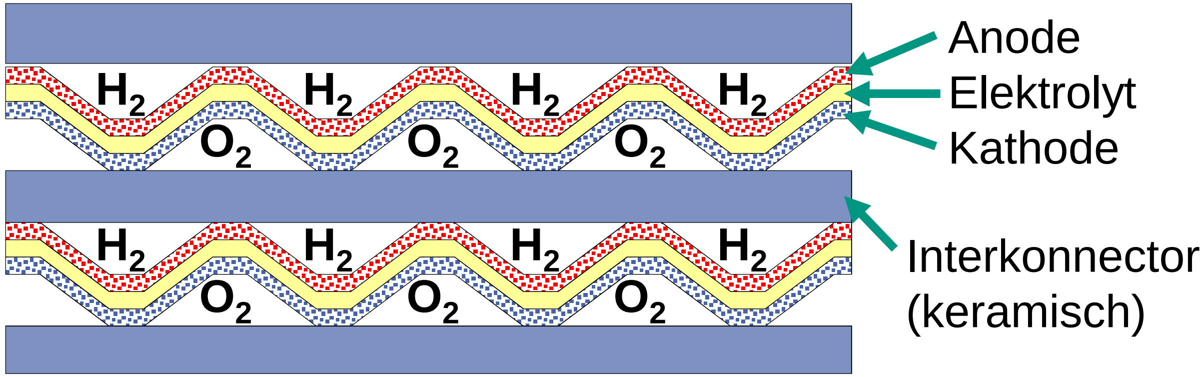
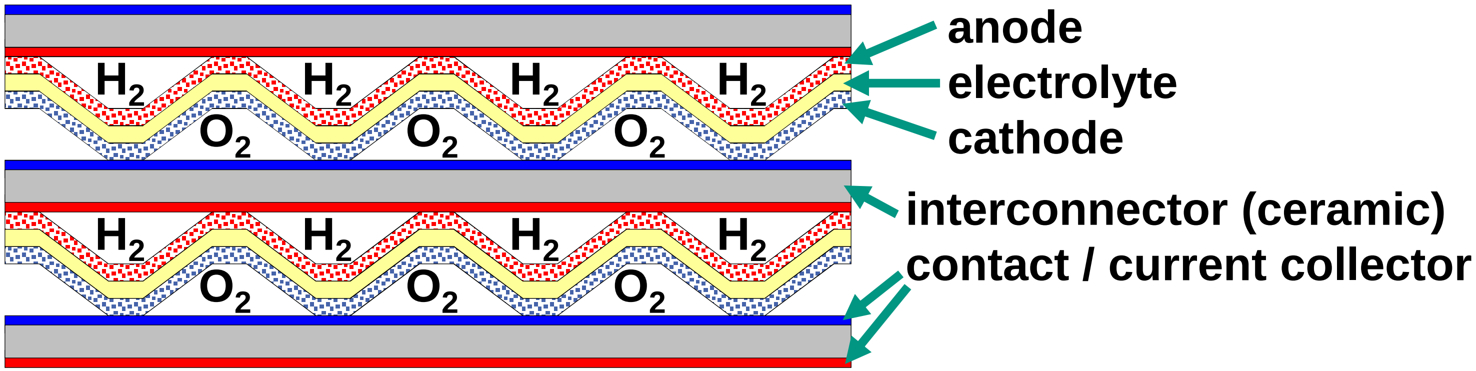


planar (Sulzer)



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)
- **Sulzer**
- 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)
- **H.C. Starck** (ECN / InDEC)
- **Topsoe Fuel Cells** (Risoe)
- **Kyocera**
- **Ceramic Fuel Cells Ltd.**

GTL* supported

- Westinghouse
- **MHI**
- **Rolls Royce**
- **DLR**
- **Topsoe Fuel Cells** (Risoe)
- **Plansee** (FZ-Jülich)

* GTL: Gas Transport Layer

SOFC: Decentralized Power Units, Combined Cycle

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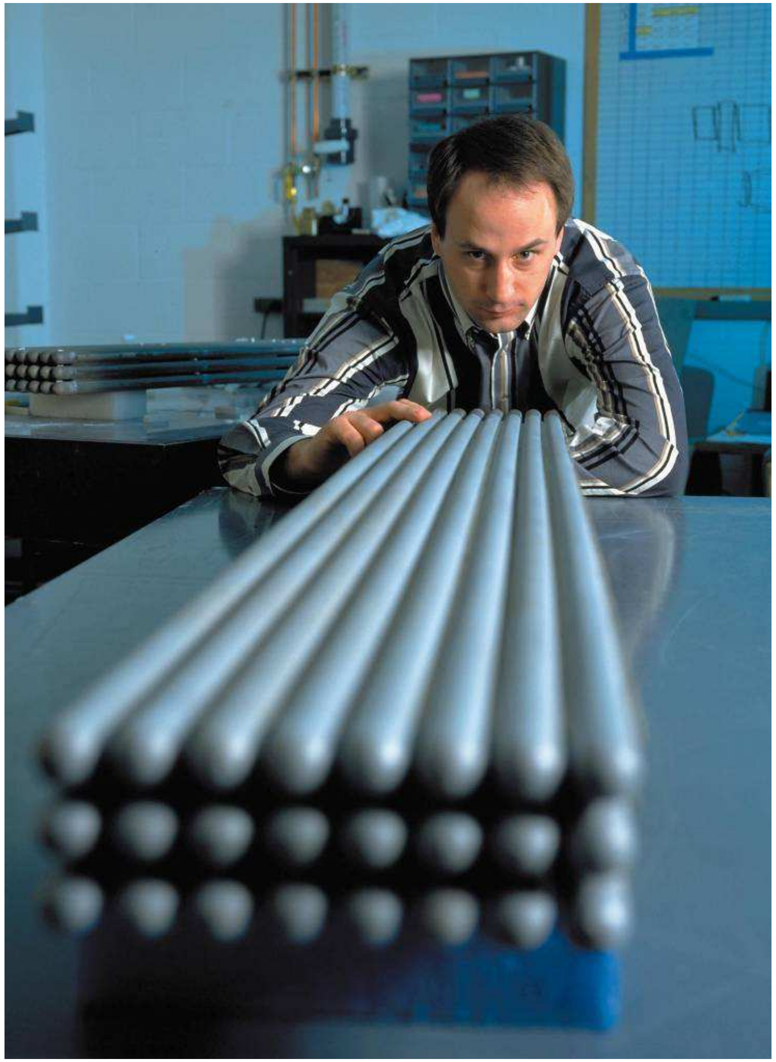
Siemens Westinghouse (SWPC)

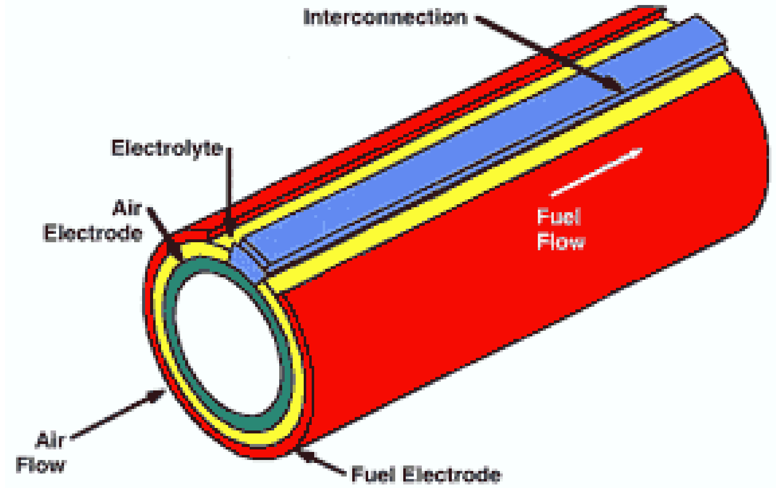
electrical power SOFC	173 kW_{el}
electrical power microturbine	47 kW_{el}
fuel	natural gas
electrical net efficieny	55%

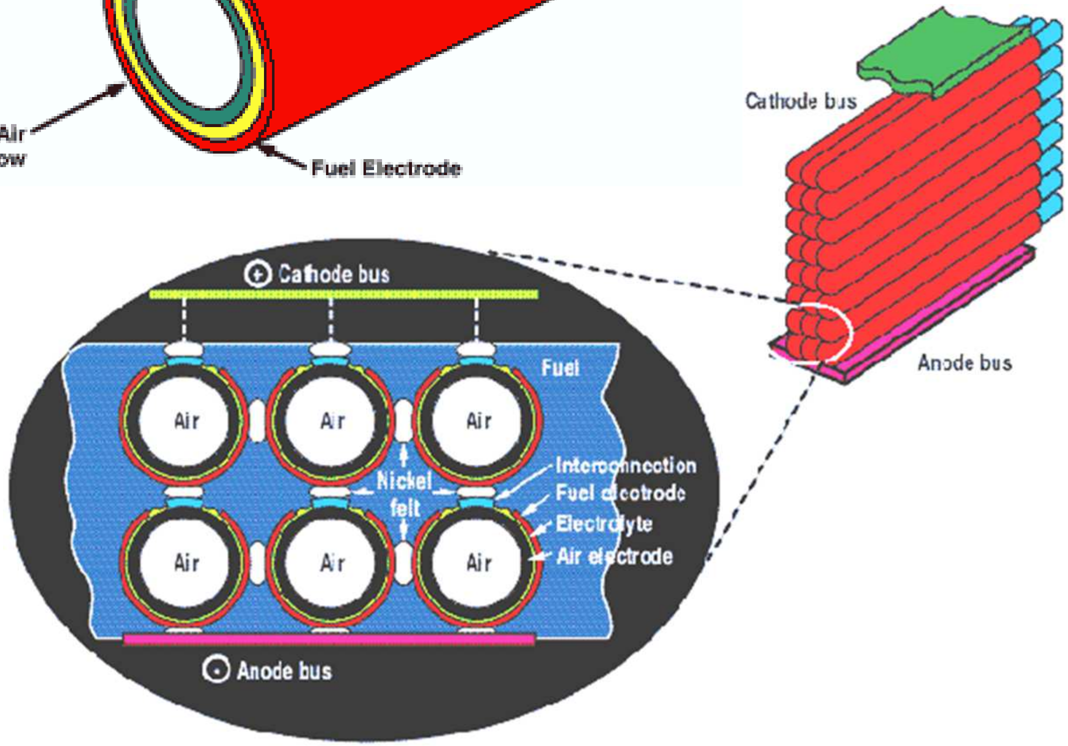
Installation 2000 at Southern California Edison;

since 2001 at NFCR, U.C.Irvine

Siemens Westinghouse Tubular SOFC
Tube Bundle



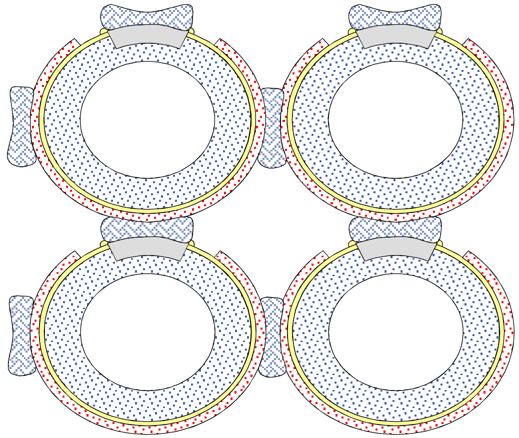




SOFC: Decentralized Power Units (> 100 kW)
Fabrication Technologies

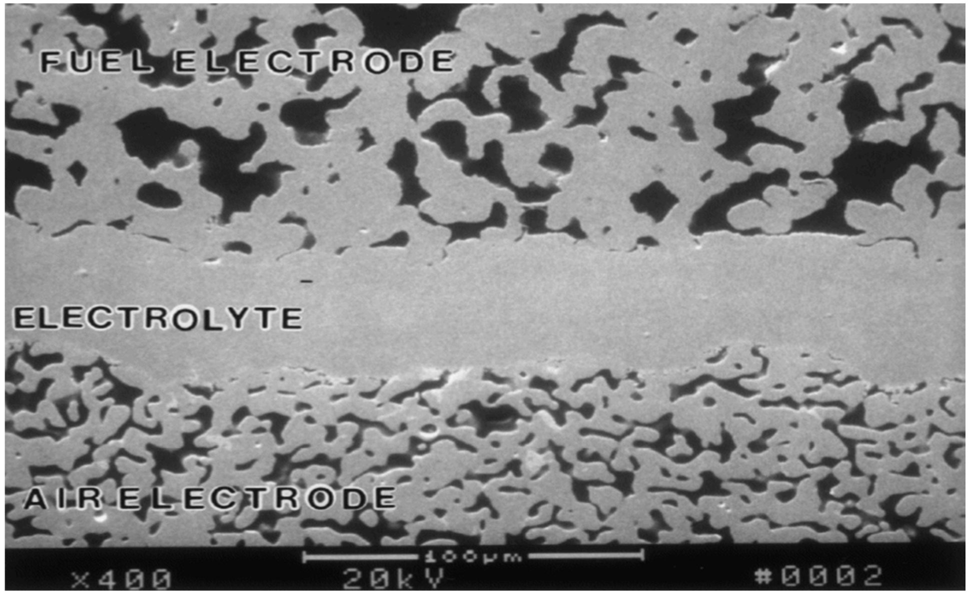
Fabrication Technologies:

- 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)

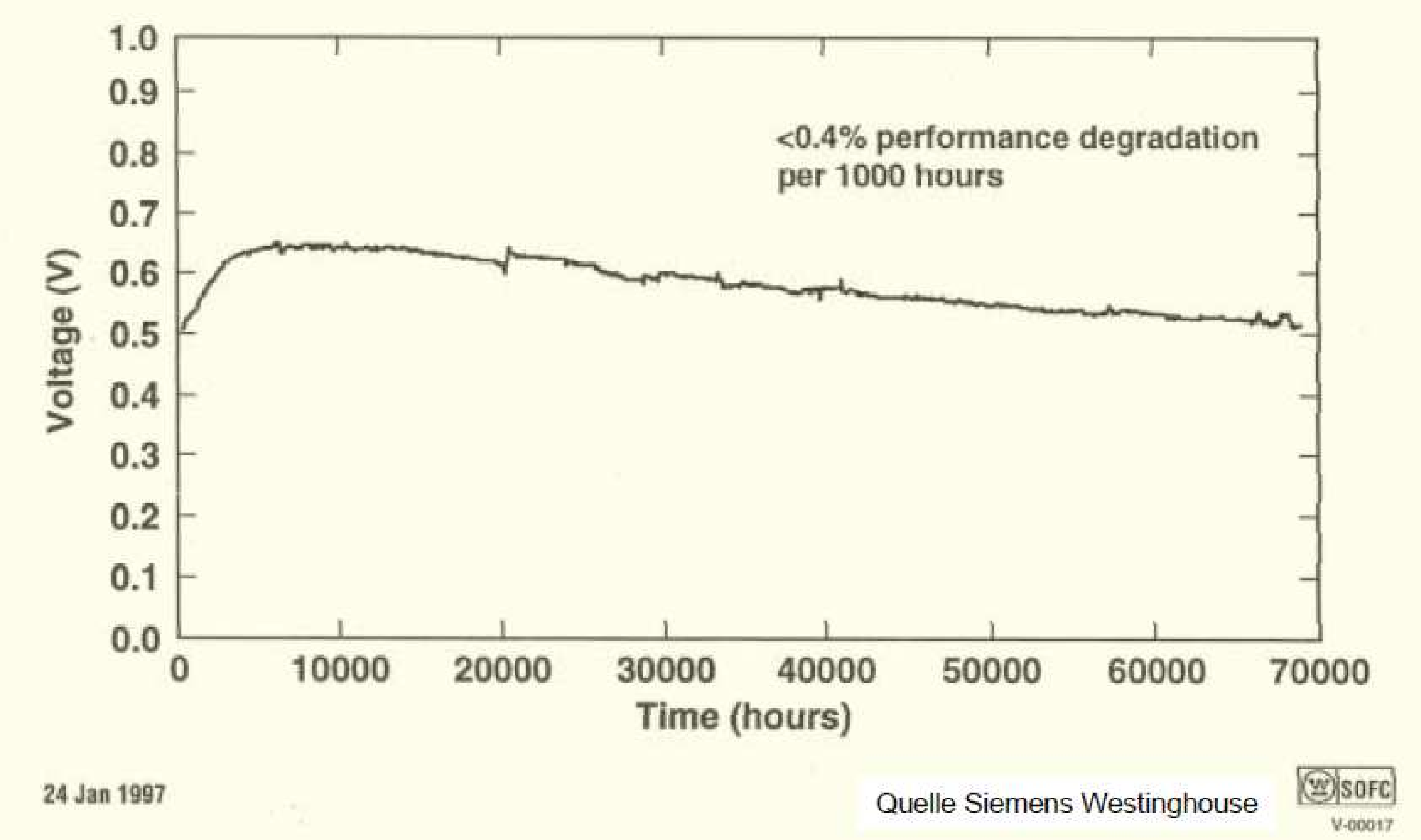
Ausbau der Röhren aus dem Reaktor zur Beschichtung der Kathode mit Elektrolyt mittels EVD (Electrochemical Vapour Deposition)

Quelle Siemens Westinghouse

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

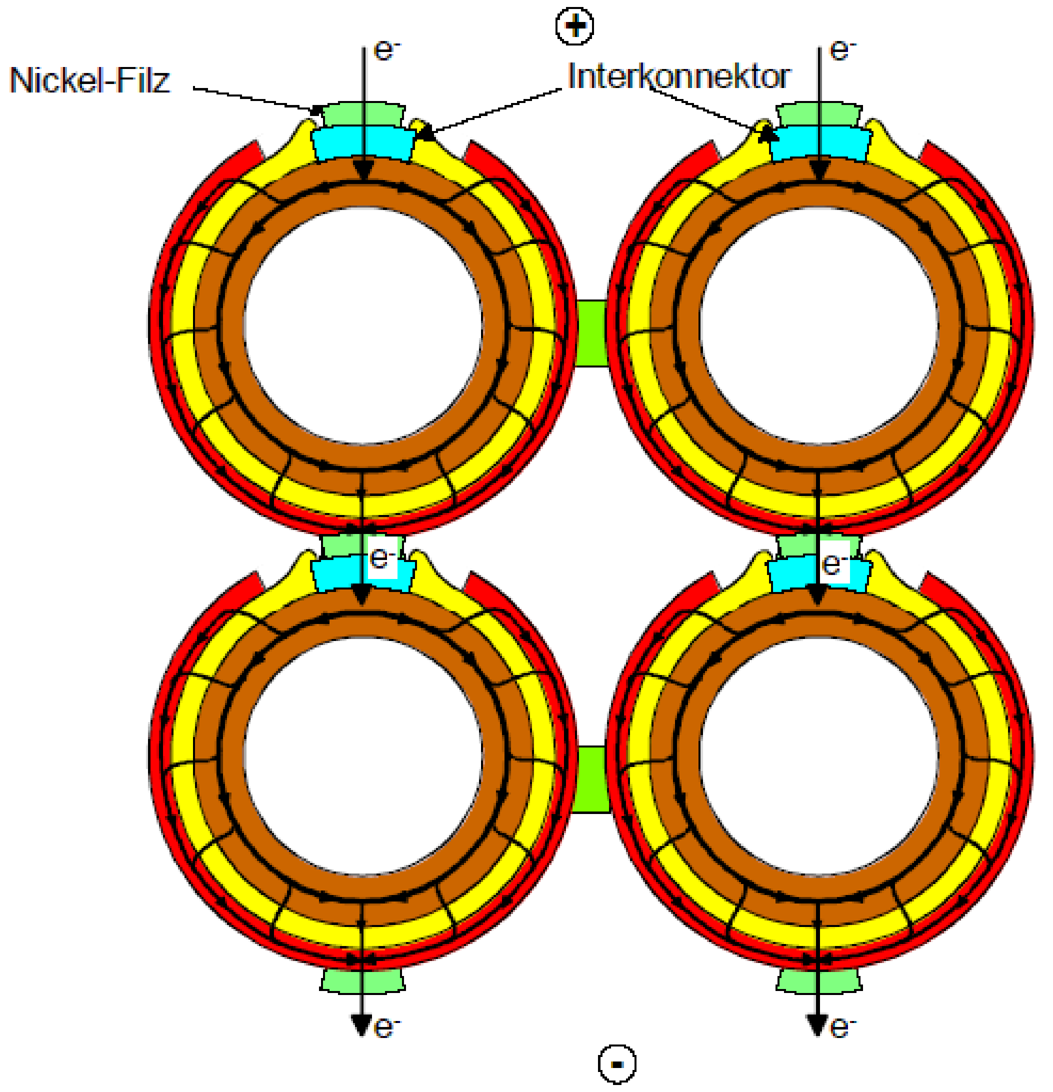
Quelle: FZJ / SWPC

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

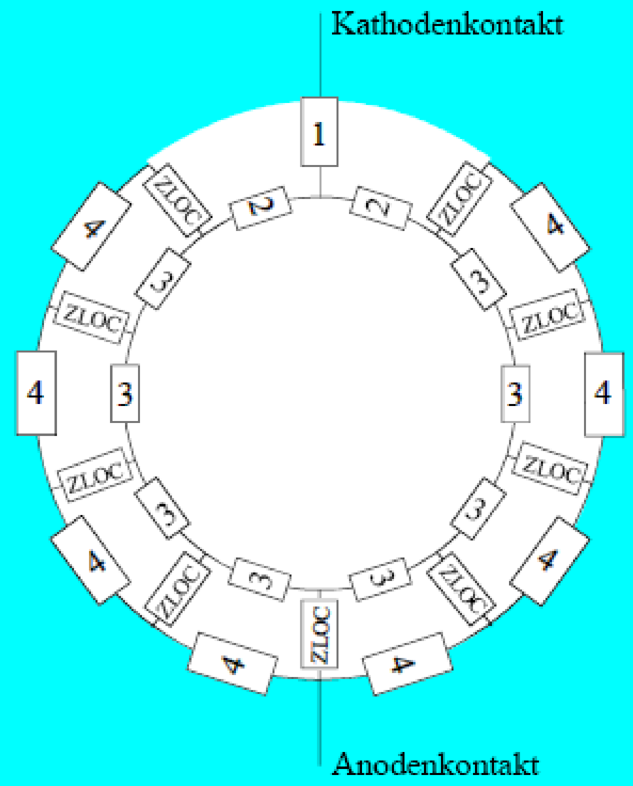


Quelle Siemens Westinghouse

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



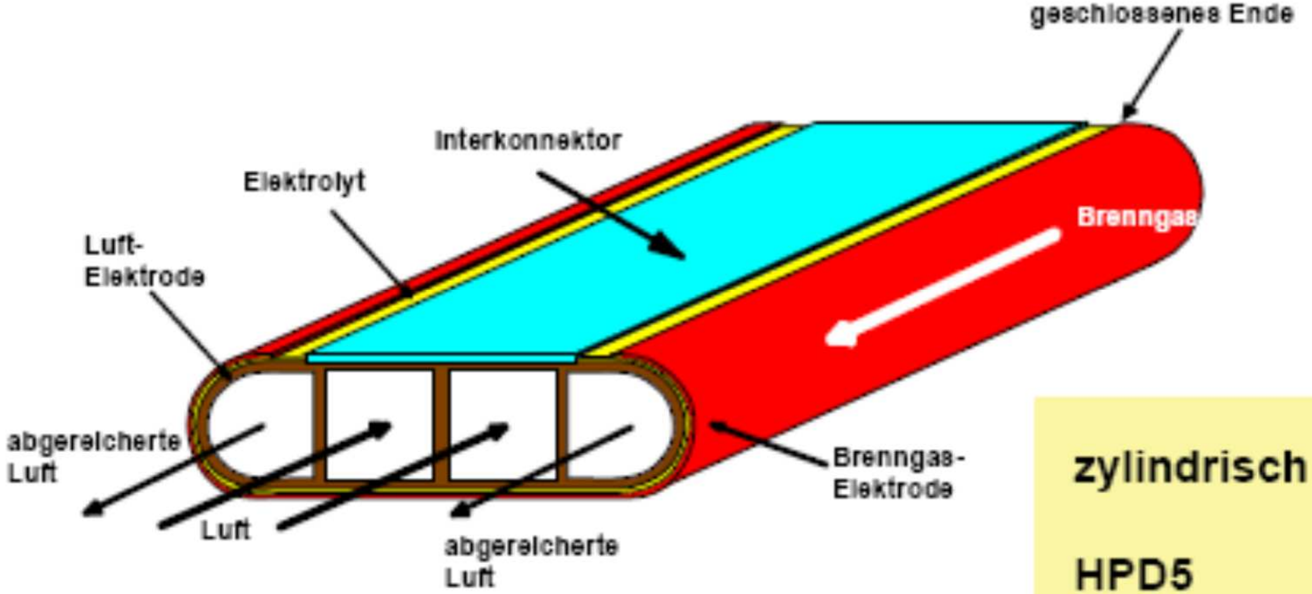
Strompfad von Zelle zu Zelle

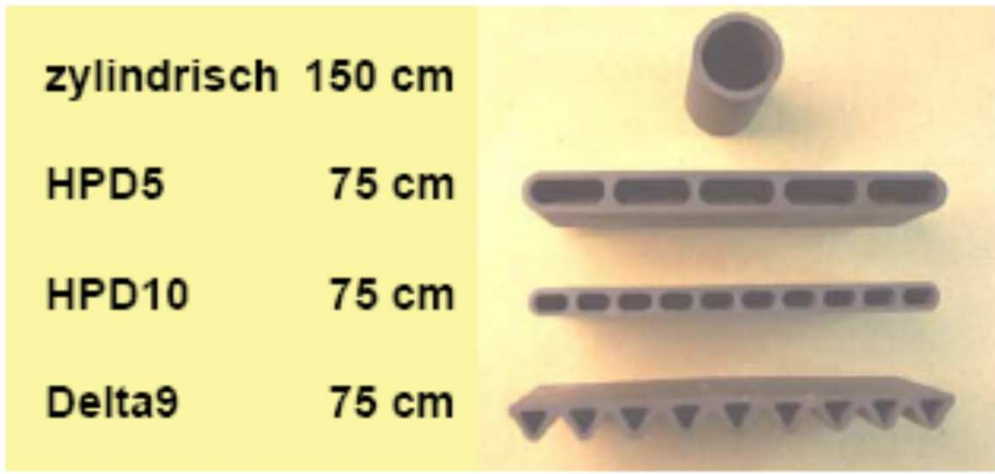


1: Flächenwiderstand IC
2: Bahnwiderstand "Spalt"
3: Bahnwiderstand Kathode
4: Bahnwiderstand Anode
ZLOC: lokaler Widerstand der aktiven Zelle (="Planar")

Quelle Siemens Westinghouse

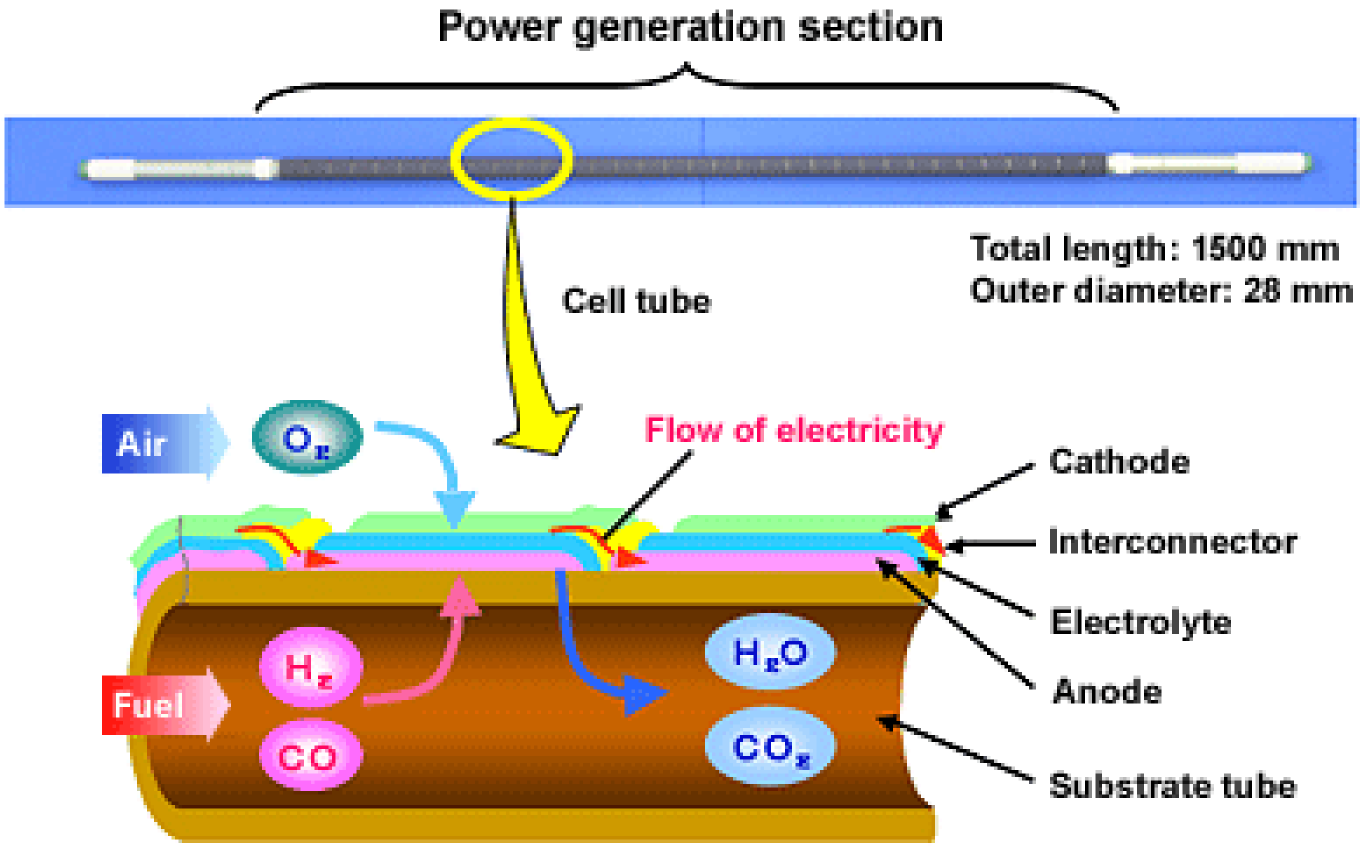
Solid Oxide Fuel Cell
Tubular SOFC-Design (Siemens-Westinghouse)

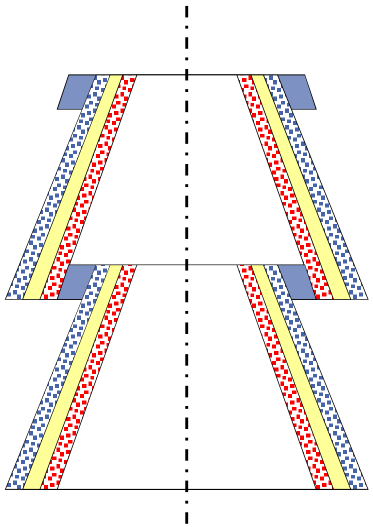




Quelle Siemens

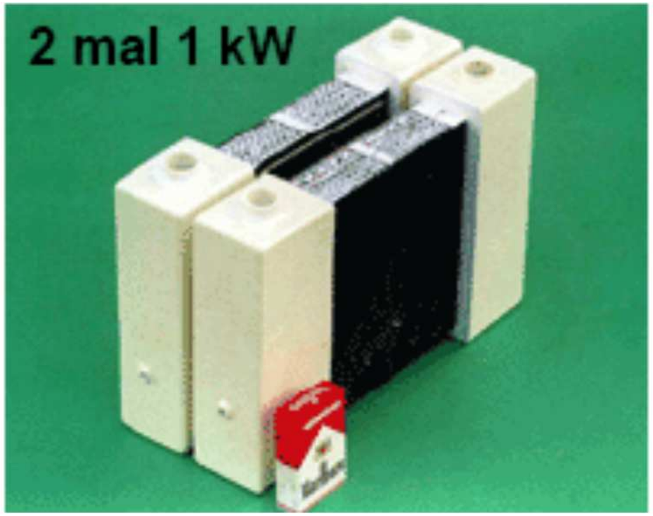
Solid Oxide Fuel Cell
Tubular SOFC-Design (Mitsubishi Heavy Industries)

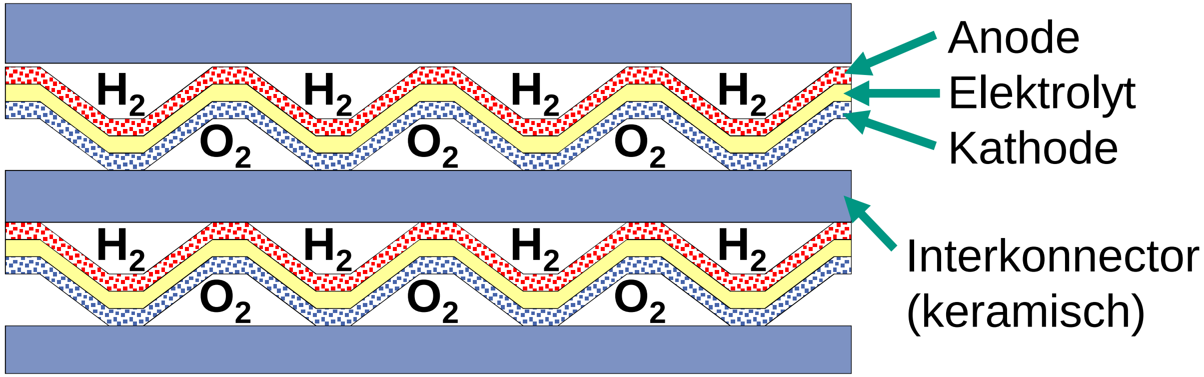




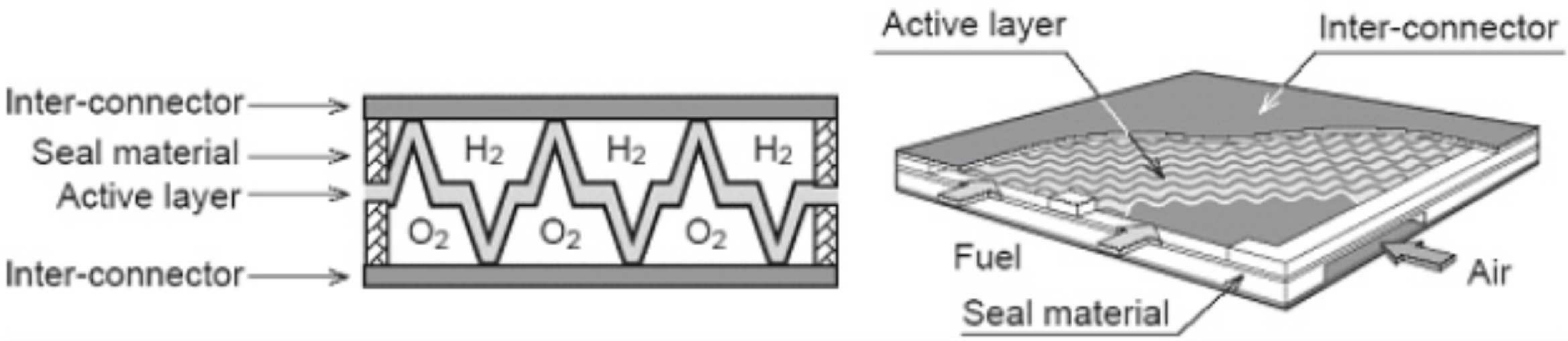
tubular (Mitsubishi Heavy Industries)

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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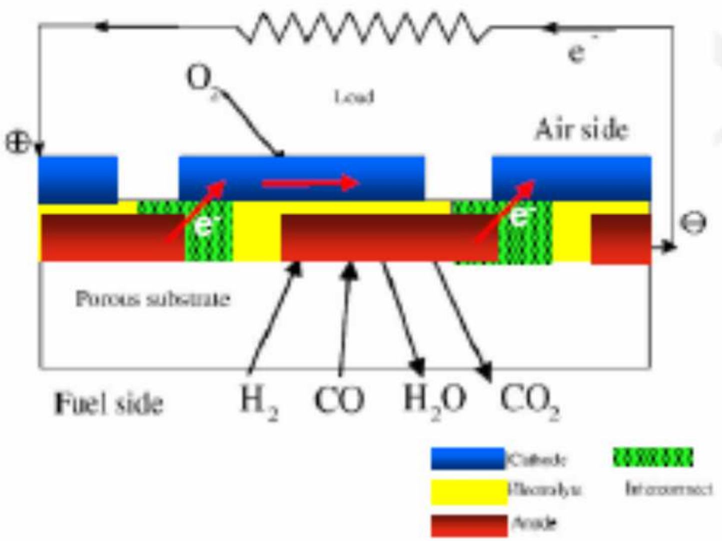
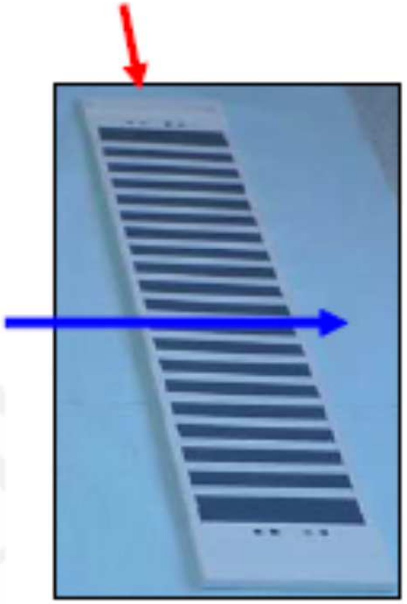
Keramik



Erdgas

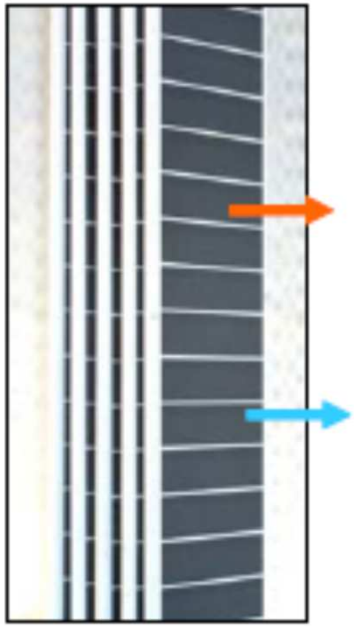
Luft



50 W Modul

"planares Design von MHI"

1 kW bei 950°C mit H_2/Luft



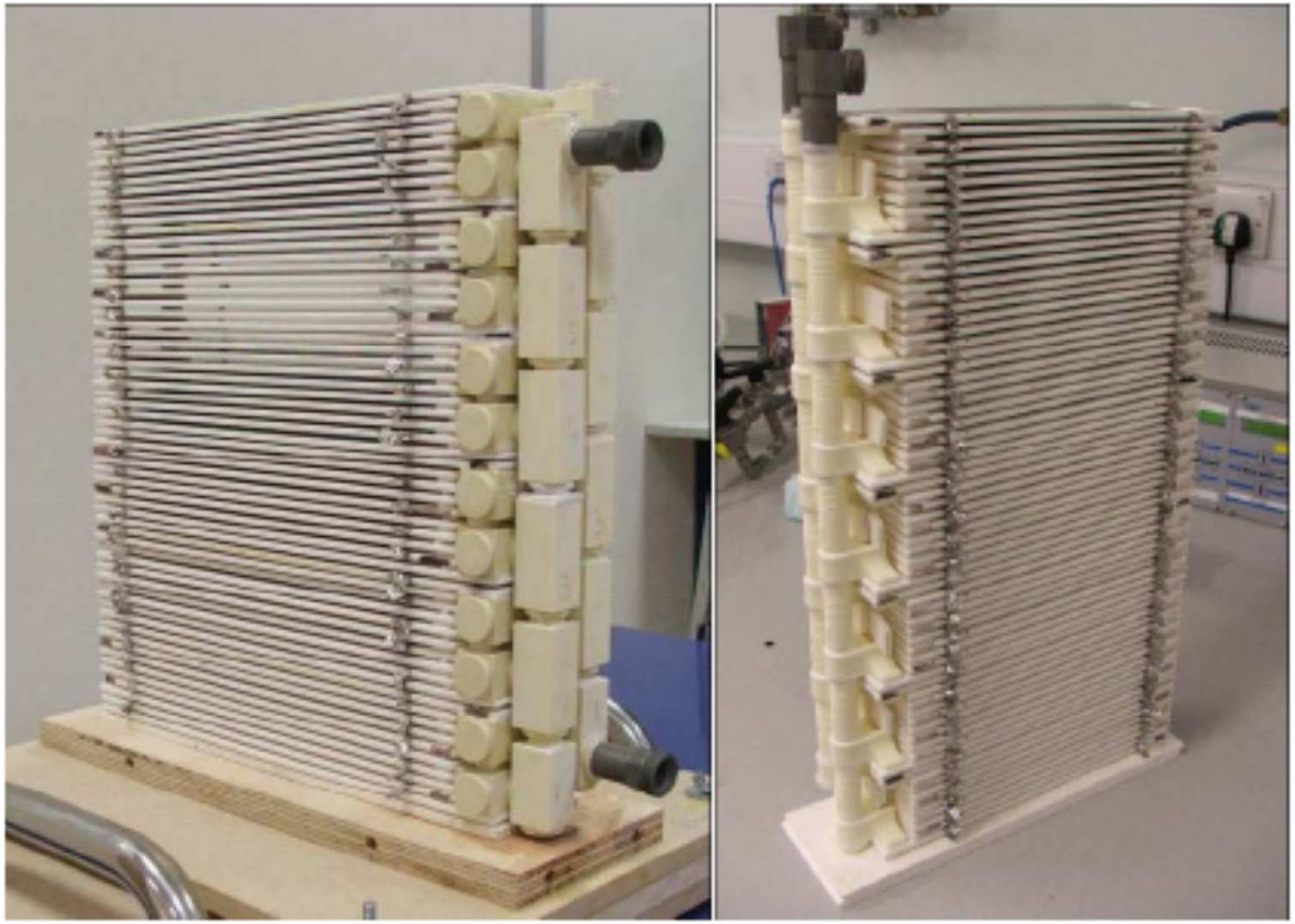
Elektrizität

Dampf

500 W "Bündel"

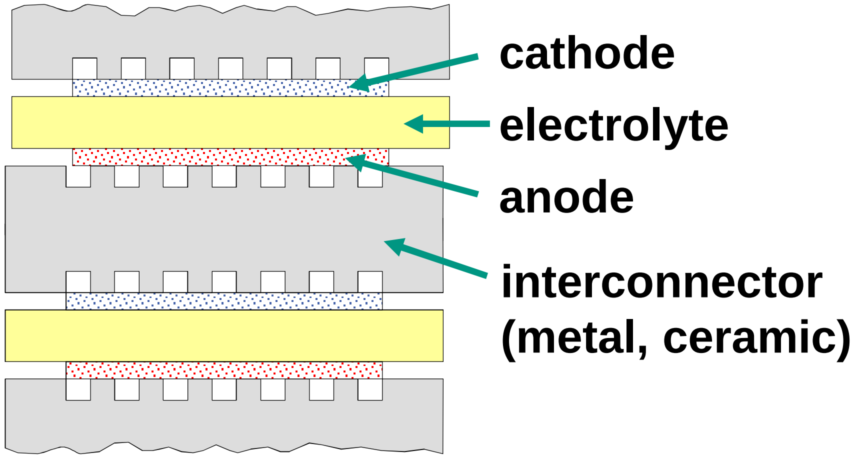
Quelle Rolls Royce

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



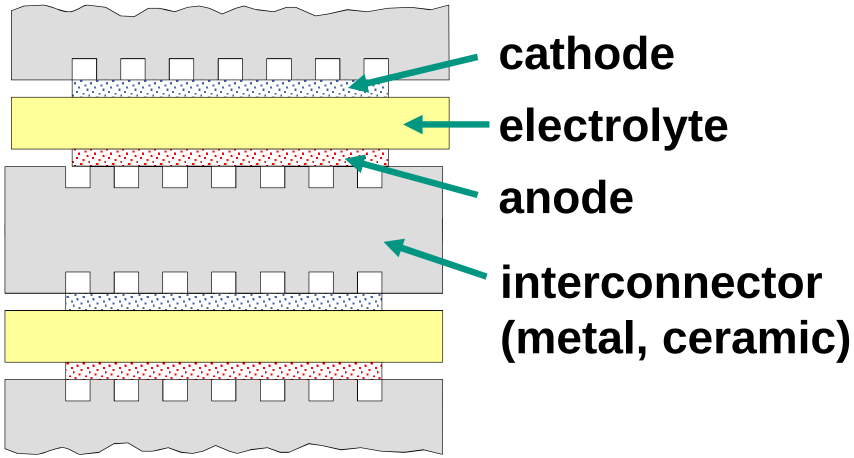
Ein “strip” von RRFCS “fuel cell bundles“ von 2004 and 2005 Designs
(otpimierte Fertigungstechnik und reduzierte Anzahl an Anschlussteilen)
(Luzem 2006)

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

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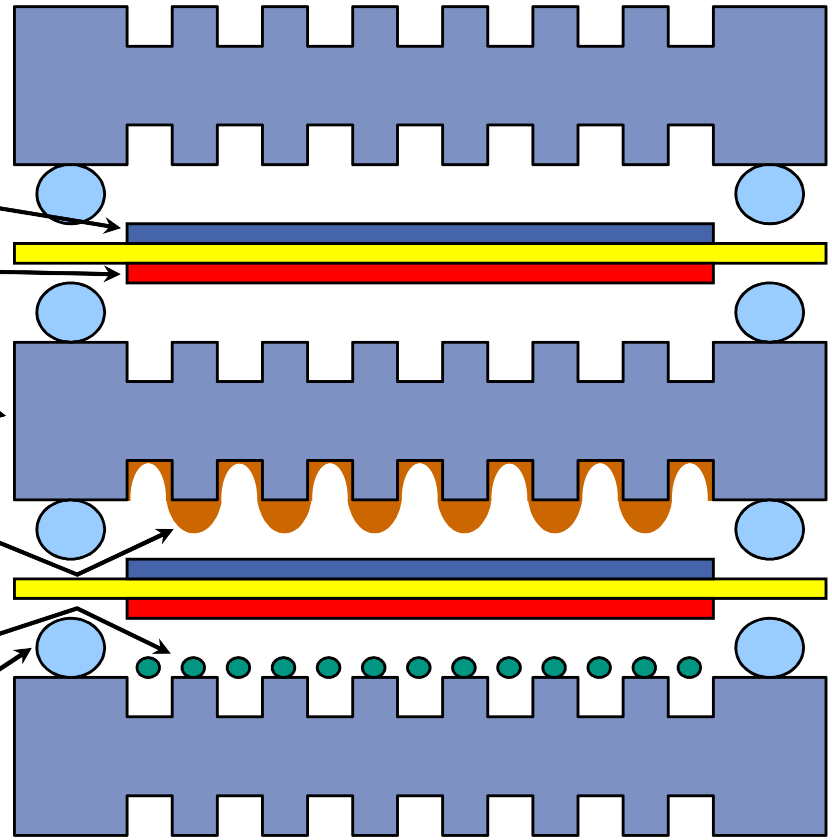
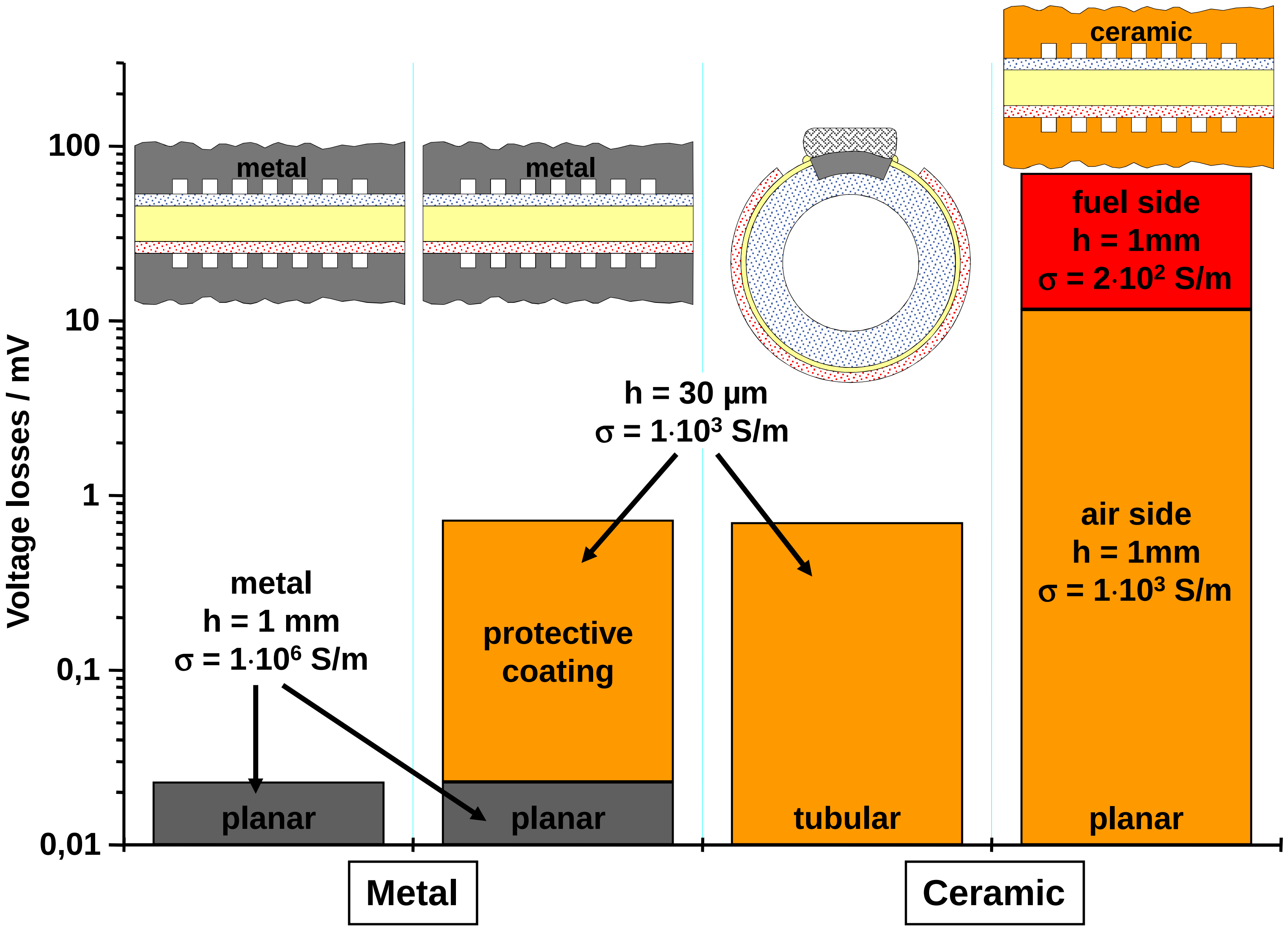
Materials	Components
$(La,Sr)MnO_3$	cathode
Y_2O_3-doped ZrO_2 (YSZ)	electrolyte
Nickel / YSZ	anode
Cr 5Fe 1 Y_2O_3	bipolar plate
$(La,Sr)CrO_3$ $(La,Sr)CoO_3$	protective coating + functional layer (c)
Nickel-grid	functional layer (a)
glas sealing	joining material



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

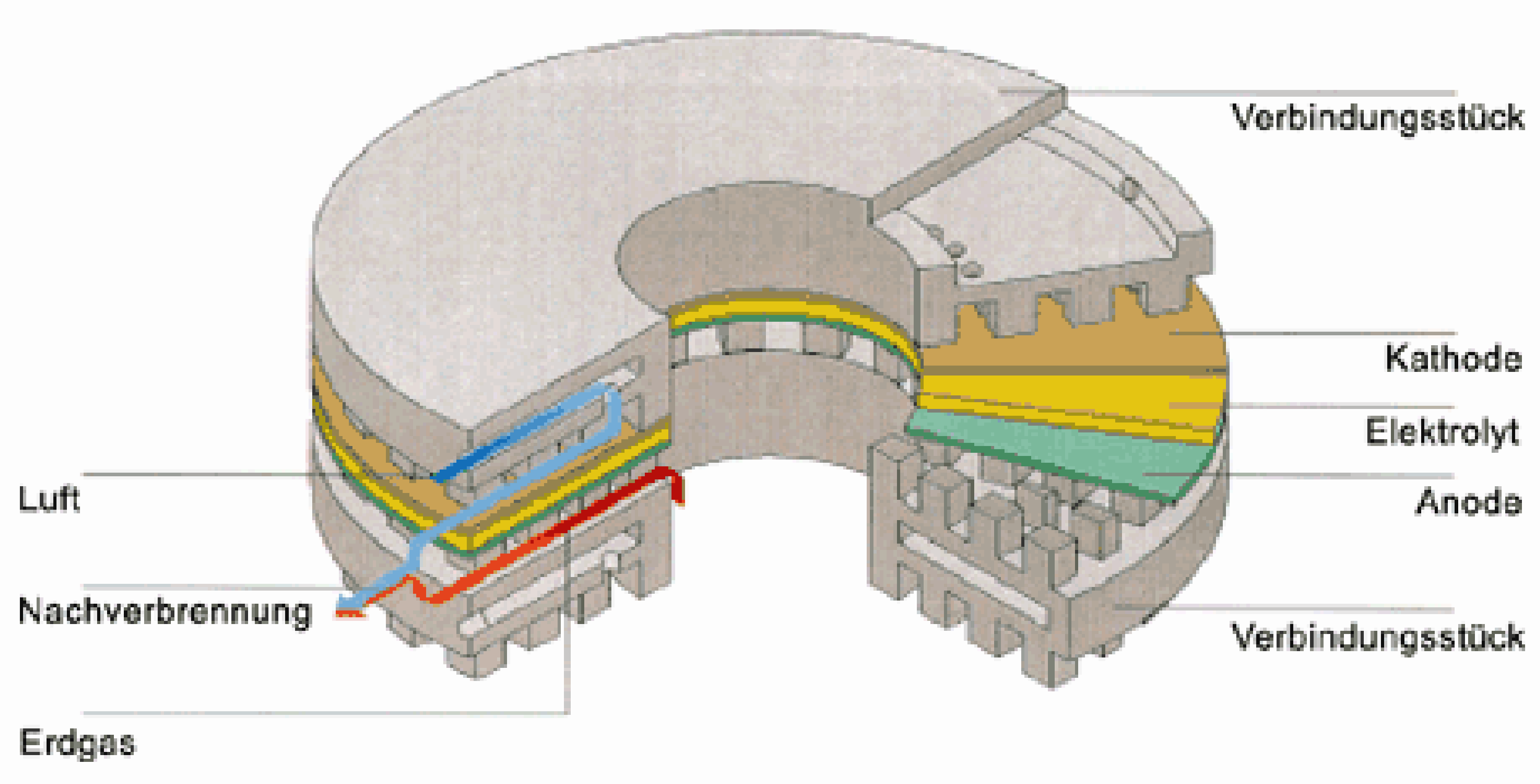


Sulzer Hexis / Hoval
SOFC : 1 kW_{el} / 3 kW_{th} inkl. Zusatzbrenner

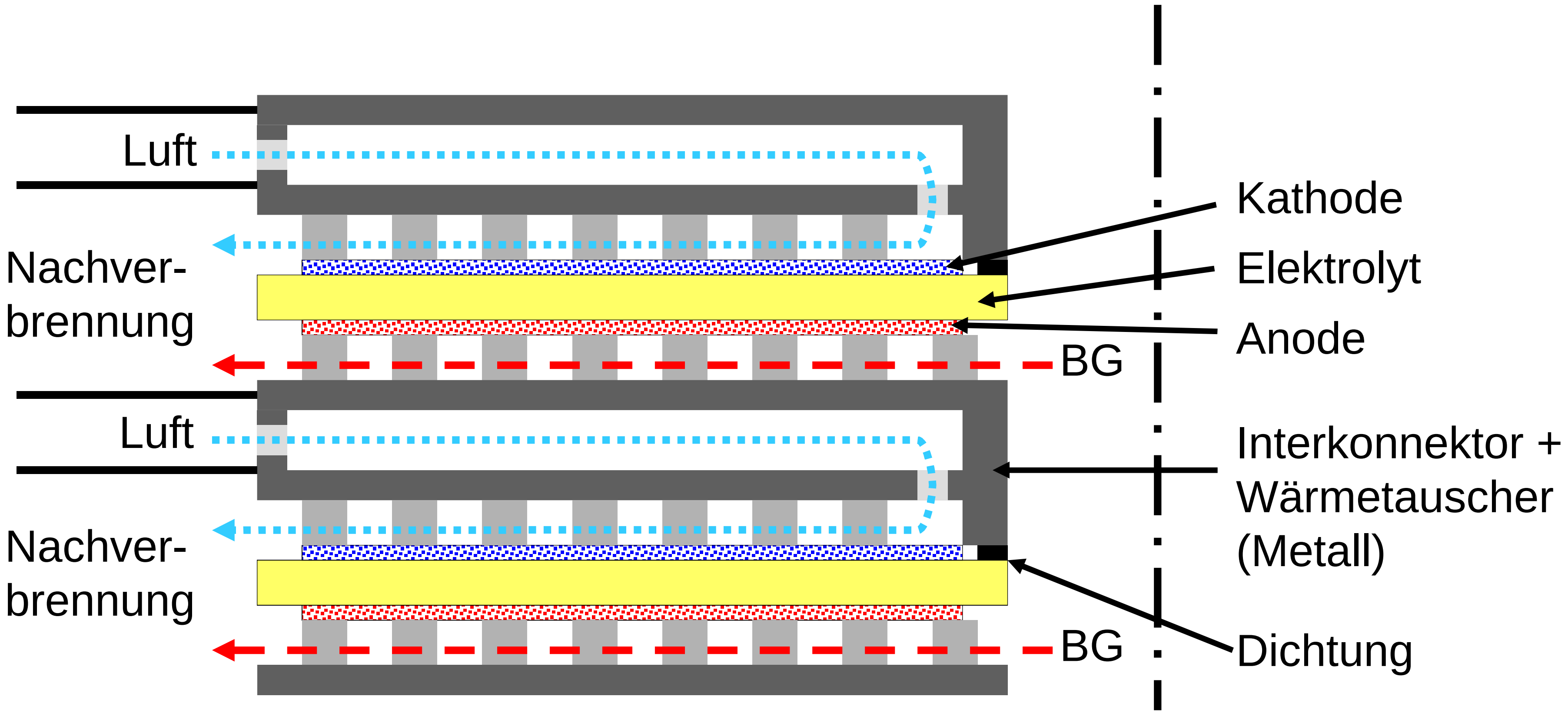
Sulzer Hexis HXS 1000 Premiere

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

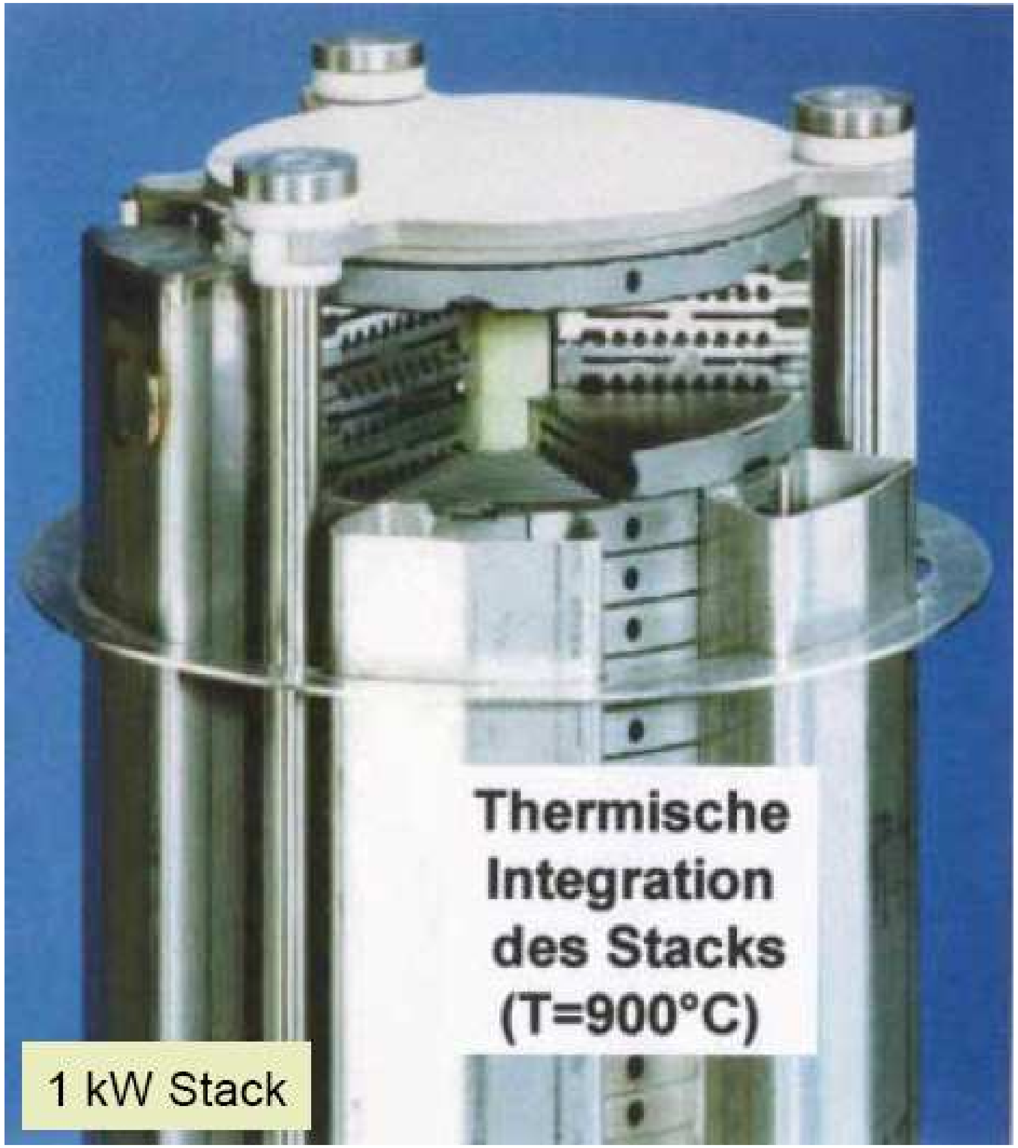


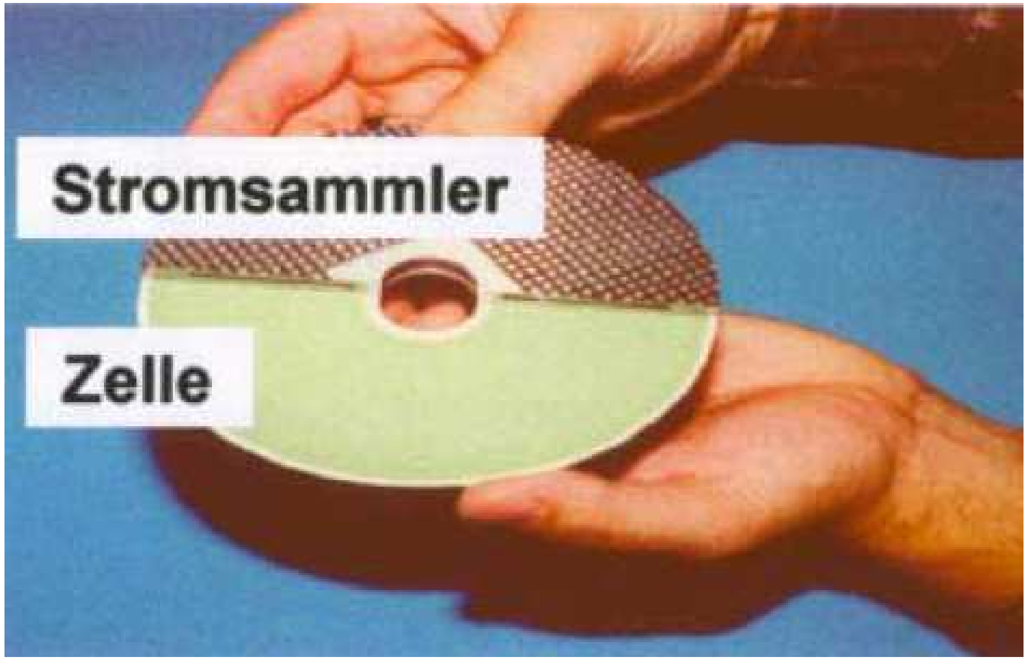
Sulzer HEXIS Stackkonzept



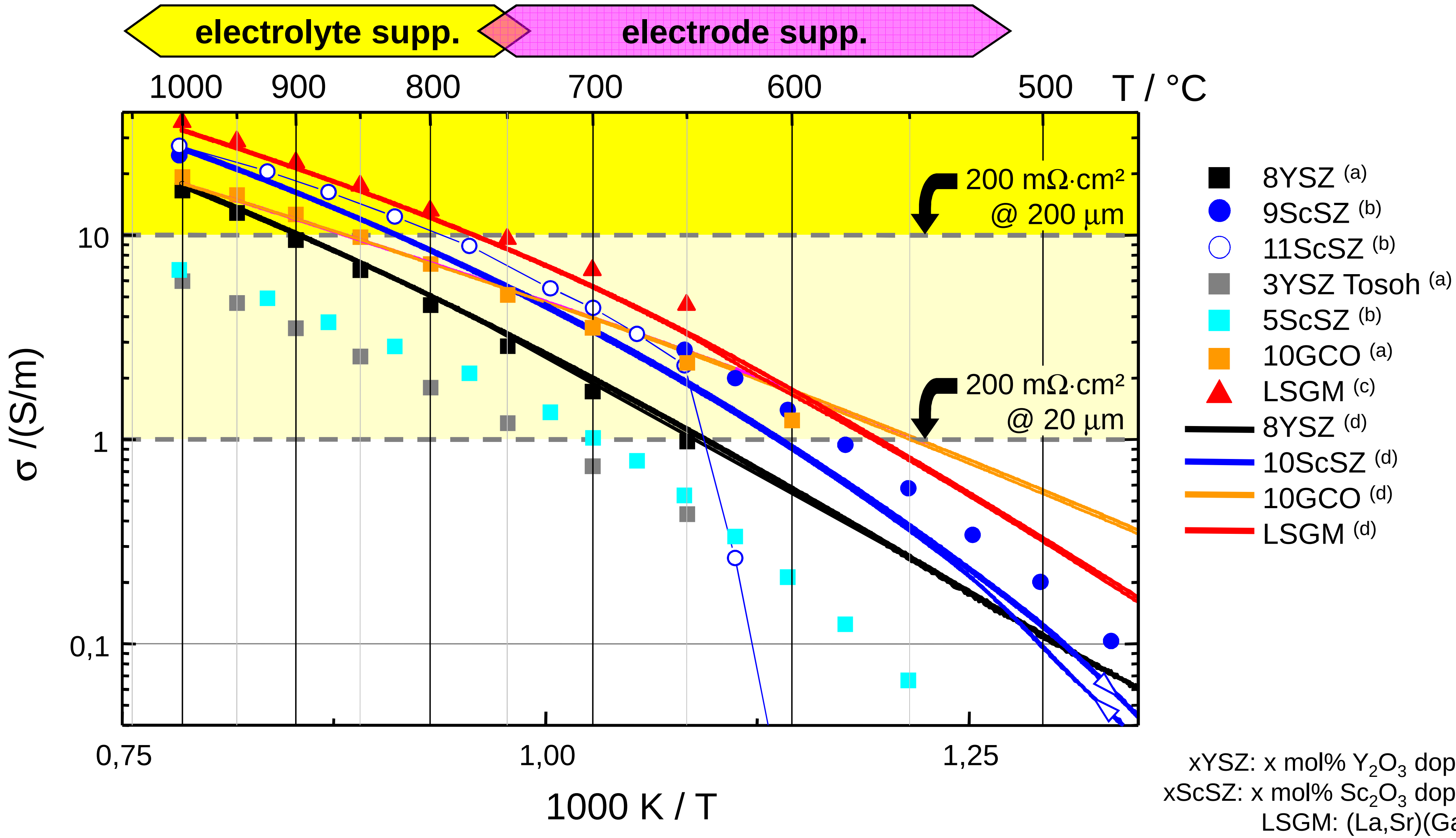
Sulzer Hexis

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





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



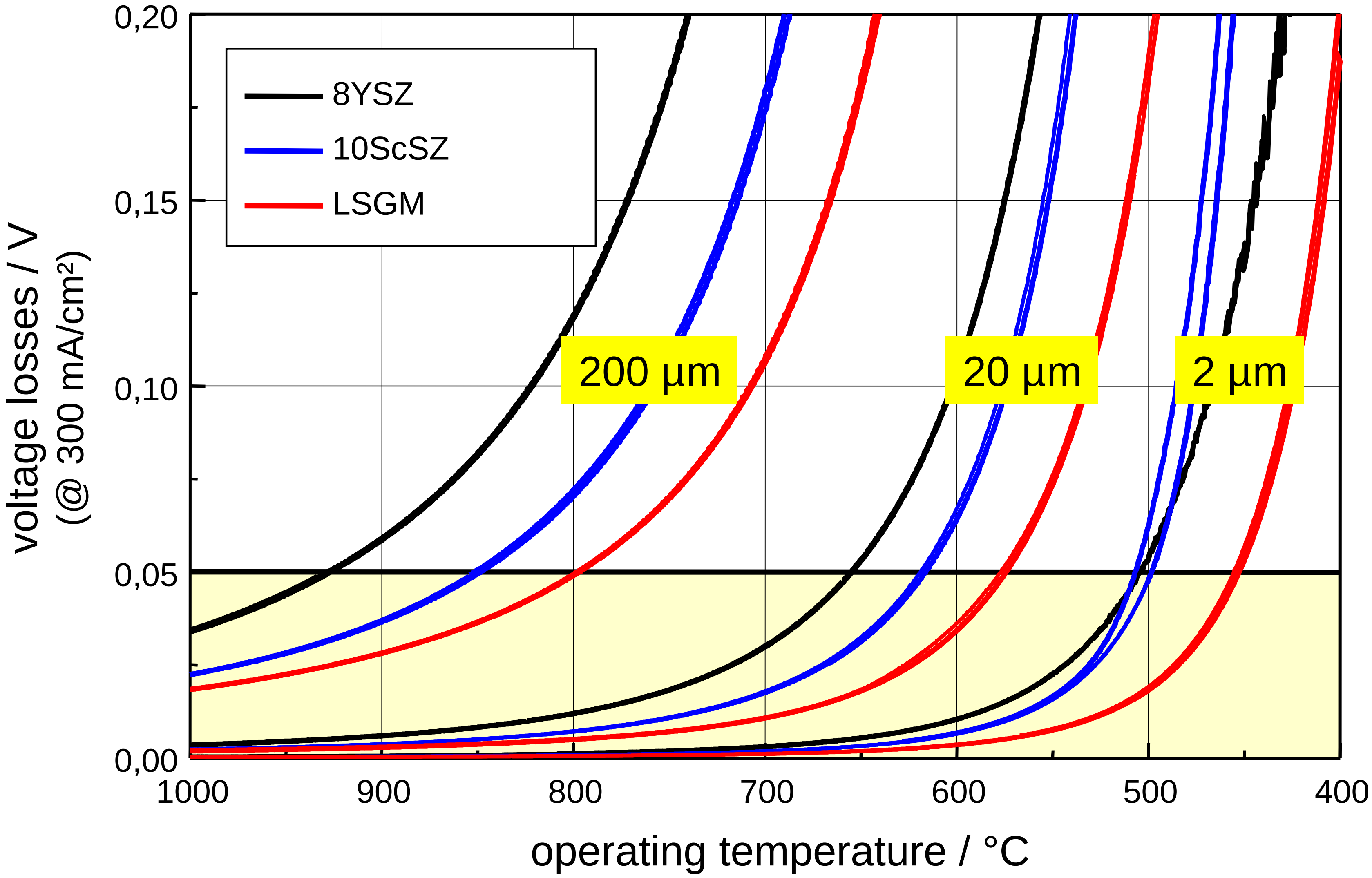
xYSZ: x mol% Y_2O_3 doped ZrO_2

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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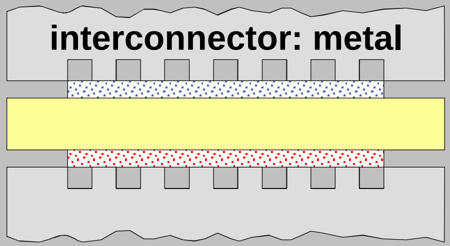
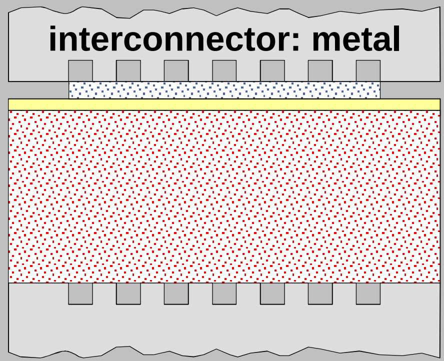
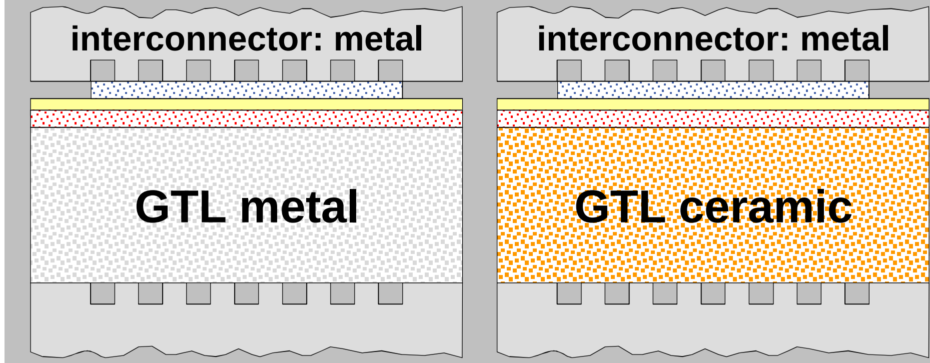
800 - 1000 °C	< 800 °C	
		
electrolyte supported	**electrode supported*** **(anode or cathode)**	**GTL supported** (GTL: Gas Transport Layer)
electrolyte: 150 µm	**< 20 µm**	**< 20 µm**
electrodes: 50 µm	**50 / > 500 µm**	**50 µm**
GTL: -	**-**	**> 500 µm**

*Thickness of Electrodes and Electrolyte similar for tubular SWPC concept

SOFC - Stack Design
Planar Design with Electrolyte Supported Single Cell

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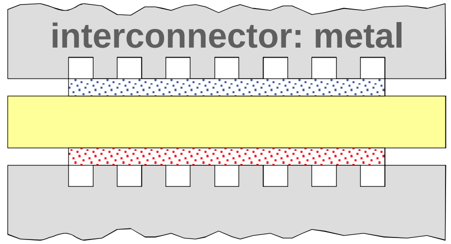
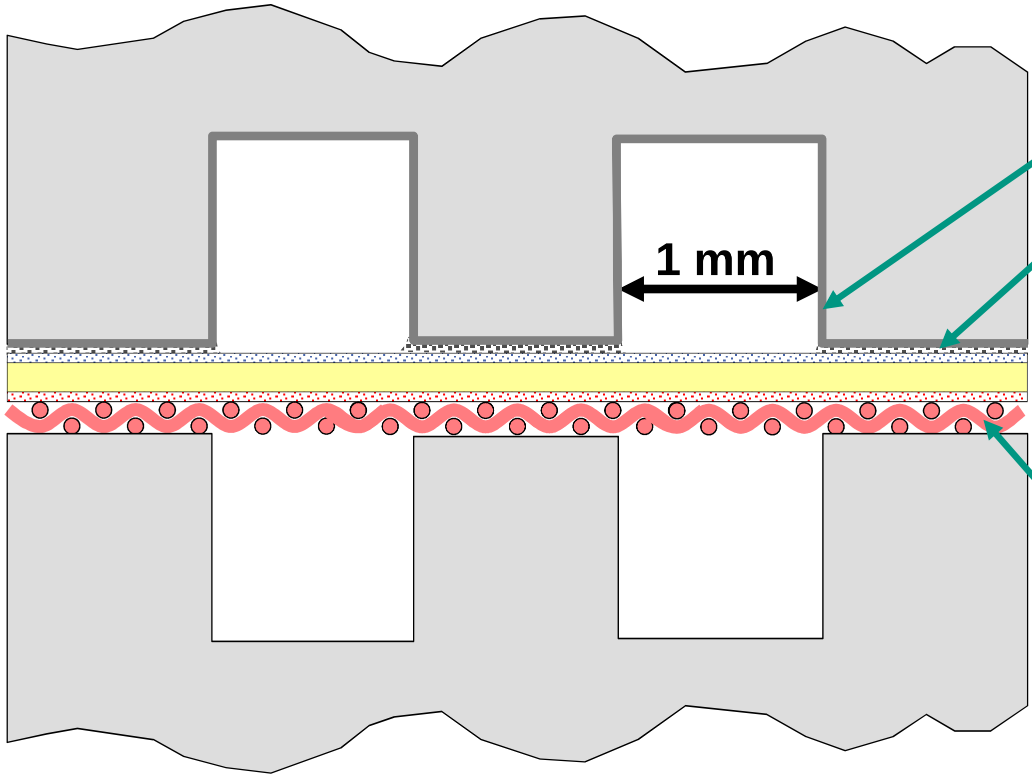




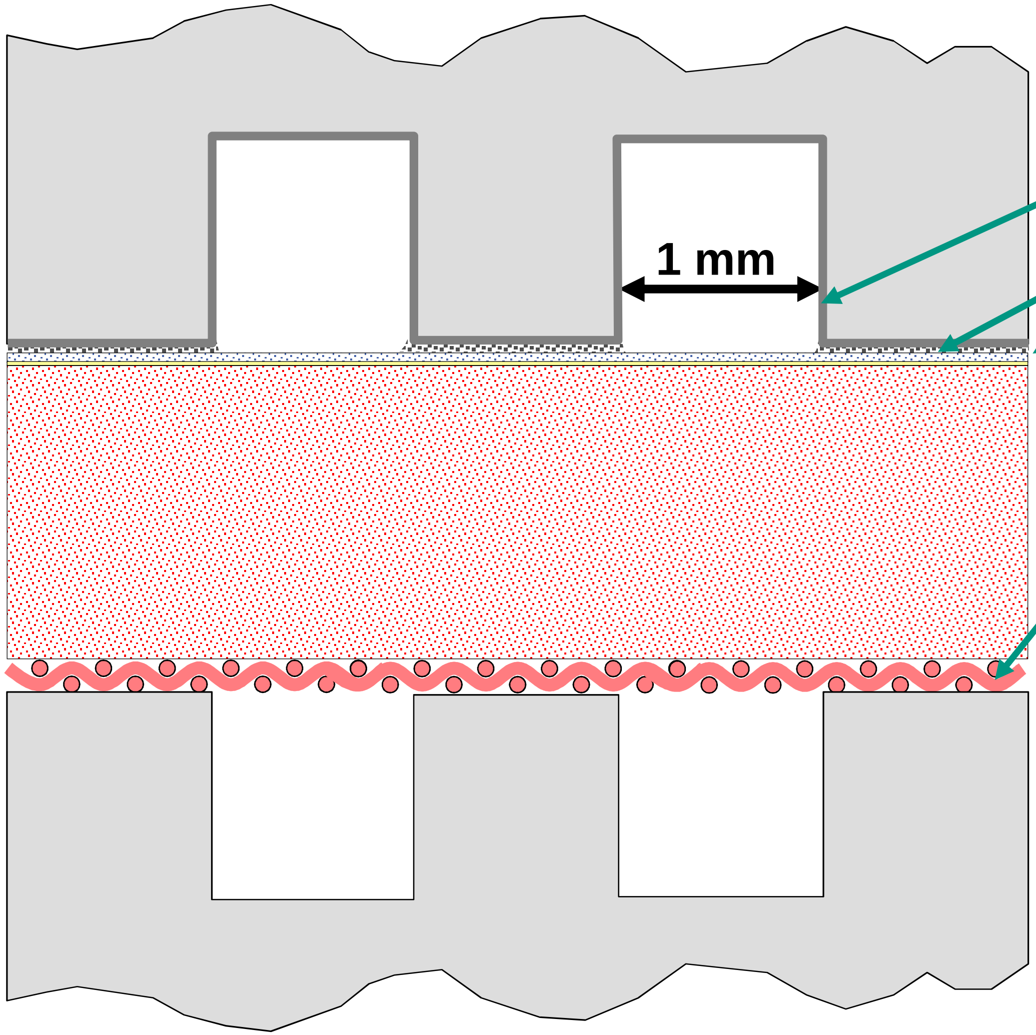
coating	50 µm	LSCr, LSM
contact layer	50 µm	LSC, LSM
cathode	50 µm	LSM, LSM/YSZ (LSCF, ...)
electrolyte	150 µm	8YSZ, 3YSZ, (10ScSZ, GCO)
anode	50 µm	Ni/YSZ
contact layer	~200 µm	Ni-grid

Siemens, Sulzer

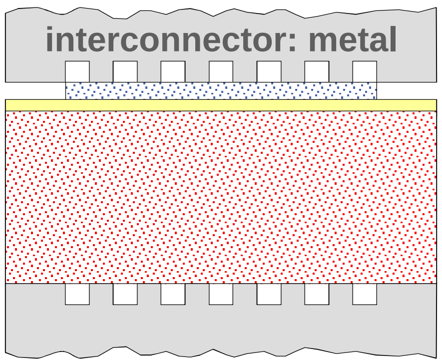
LSCr: Sr doped $LaCrO_3$
LSC: Sr doped $LaCoO_3$
LSM: Sr doped $LaMnO_3$
LSCF: $(La,Sr)(Co,Fe)O_3$
nYSZ: n mol% Y_2O_3 doped ZrO_2
nScSZ: n mol% Sc_2O_3 doped ZrO_2
GCO: Gd doped CeO_2
Ni/YSZ: Ni/YSZ-Cermet

SOFC - Stack Design
Planar Design with Anode Supported Single Cell

Karlsruher Institut für Technologie



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**

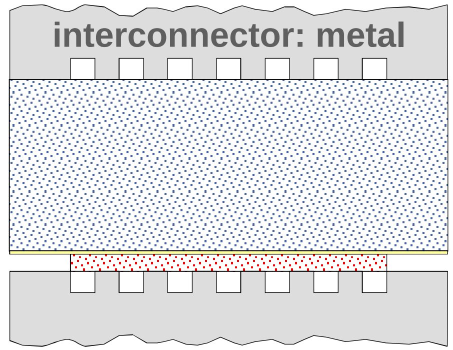


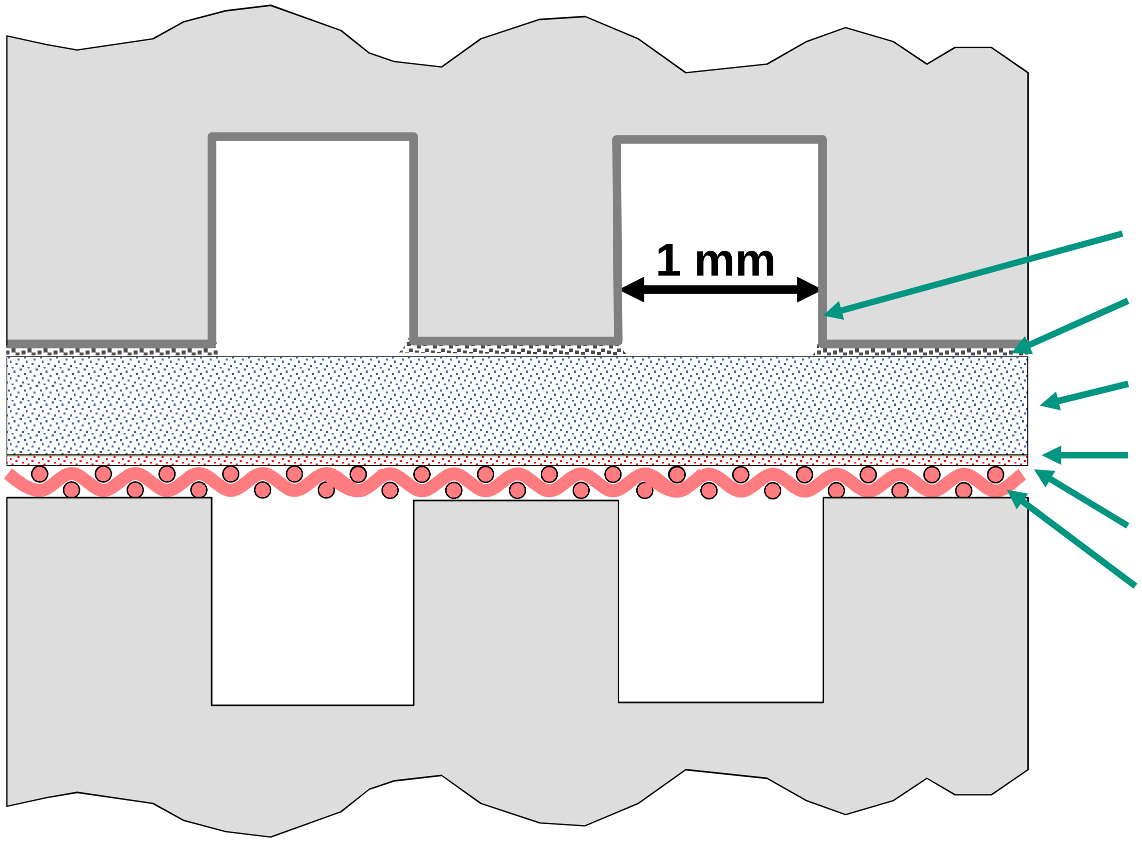
LSCr: Sr doped $LaCrO_3$
LSC: Sr doped $LaCoO_3$
LSM: Sr doped $LaMnO_3$
LSCF: $(La,Sr)(Co,Fe)O_3$
nYSZ: n mol% Y_2O_3 doped ZrO_2
nScSZ: n mol% Sc_2O_3 doped ZrO_2
GCO: Gd doped CeO_2
Ni/YSZ: Ni/YSZ-Cermet

Allied Signal, FZ Jülich, ECN

SOFC - Stack Design
Planar Design with Cathode Supported Single Cell

Karlsruher Institut für Technologie



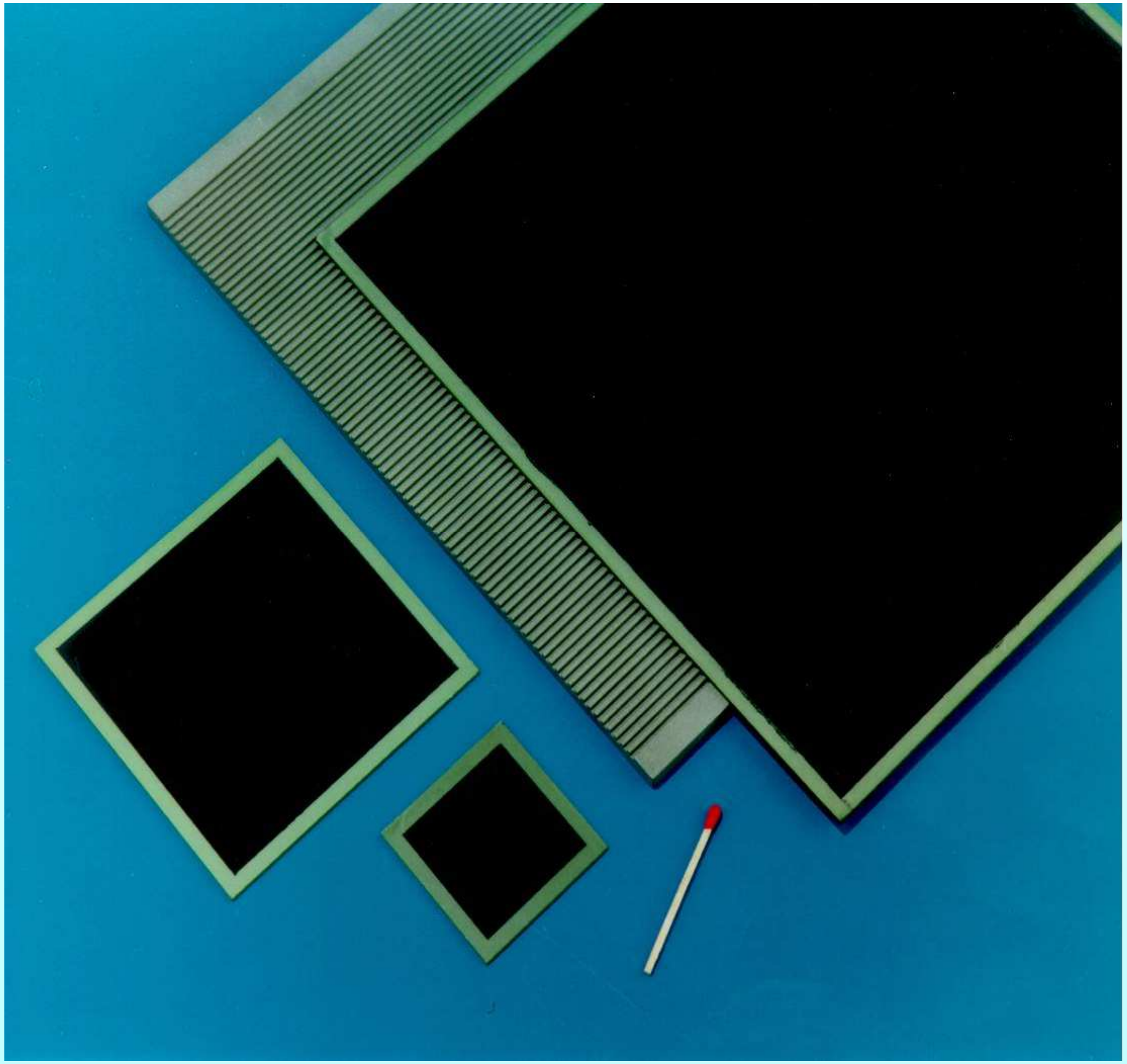


coating	50 µm	LSCr, LSM
contact layer	50 µm	LSC, LSM
cathode	500 µm	LSM, ...
electrolyte	~10 µm	8YSZ, 10ScSZ, ...
anode	50 µm	Ni/YSZ, ...
contact layer	~200 µm	Ni-grid

IWE

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

Substrat-Zelle FZJ

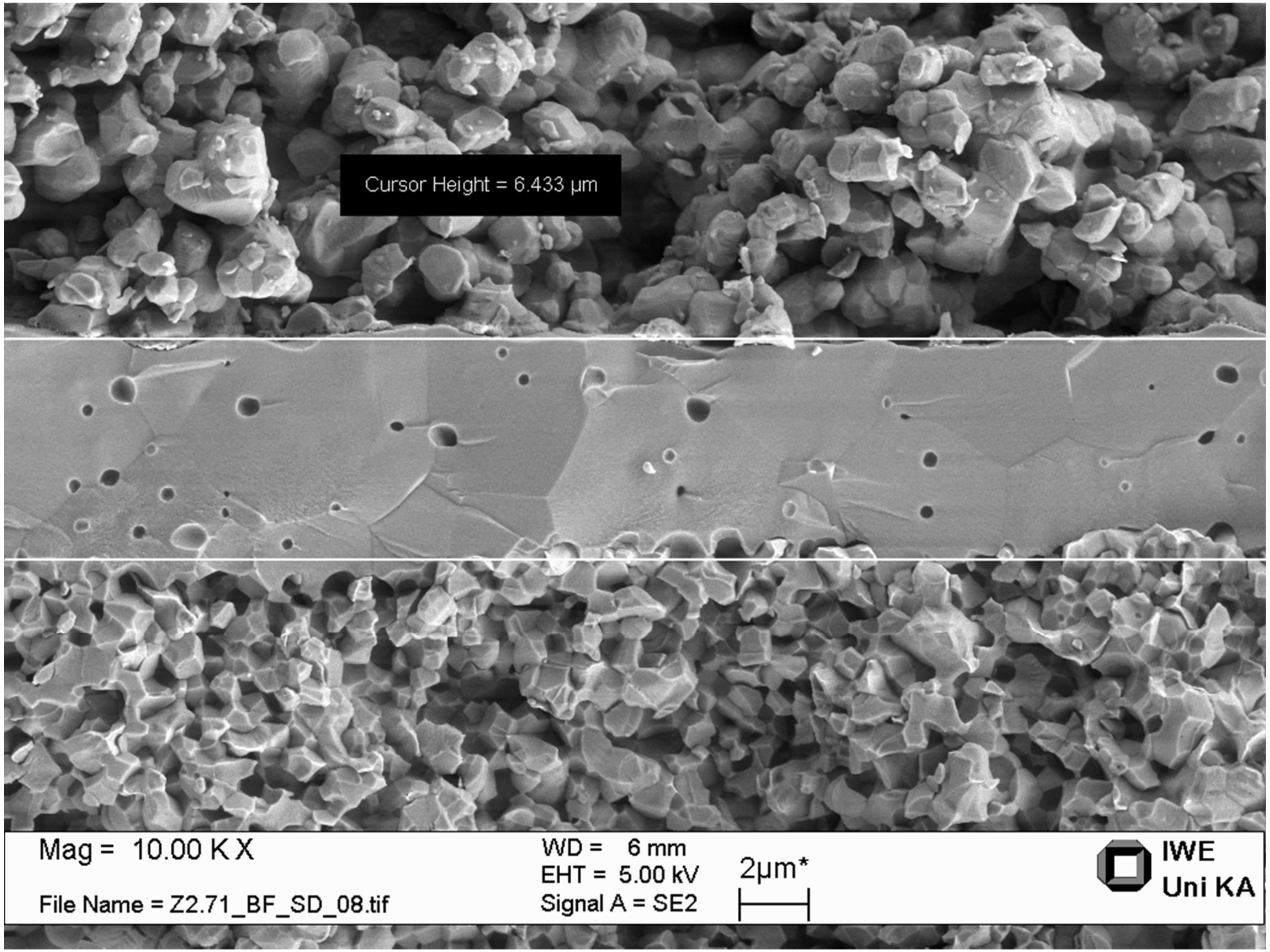


25 x 25 cm²

10 x 10 cm²

5 x 5 cm²

Bruchfläche
Elektrolytschicht der Zelle 1545



Elektrolytdicke:

6,4 µm

Kathode

Elektrolyt

Anode

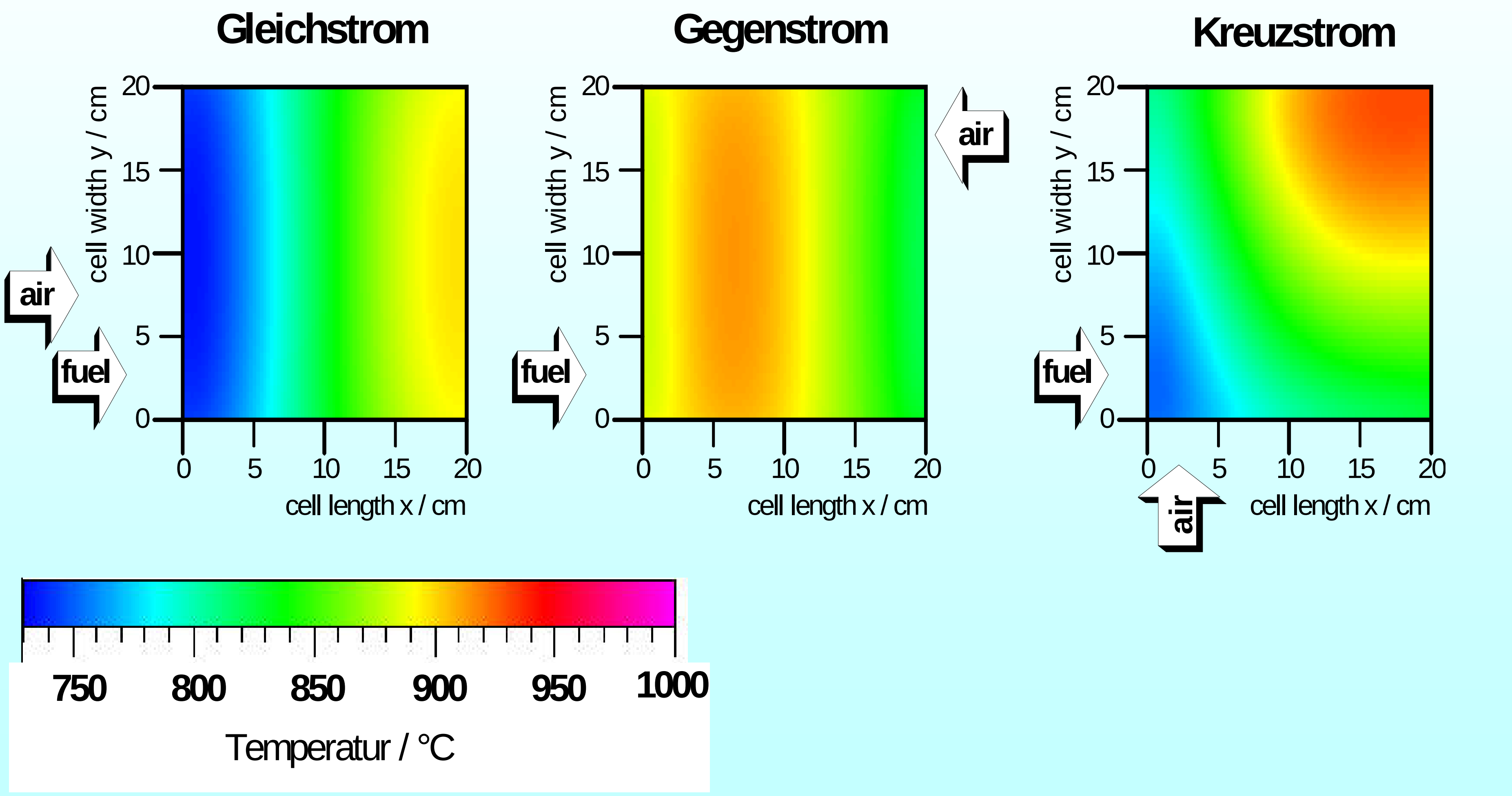
Stack Design

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

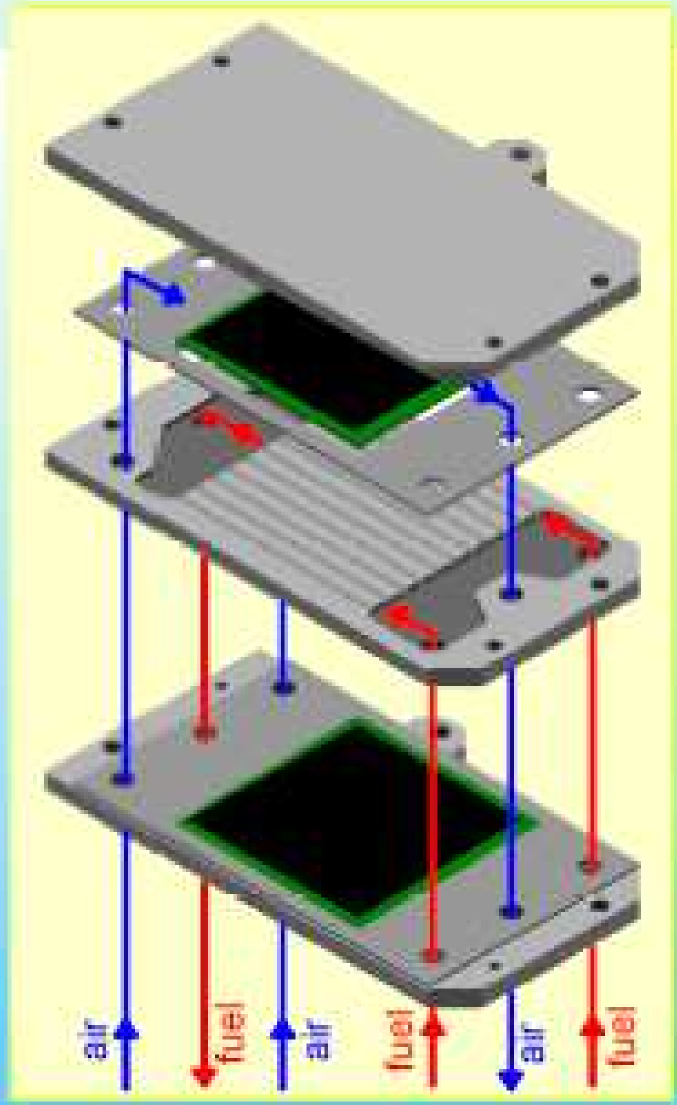
E-Design Stack Technology

Internal manifold:

sealing only in one plane perpendicular to the stacking direction

Parallel gas flow:

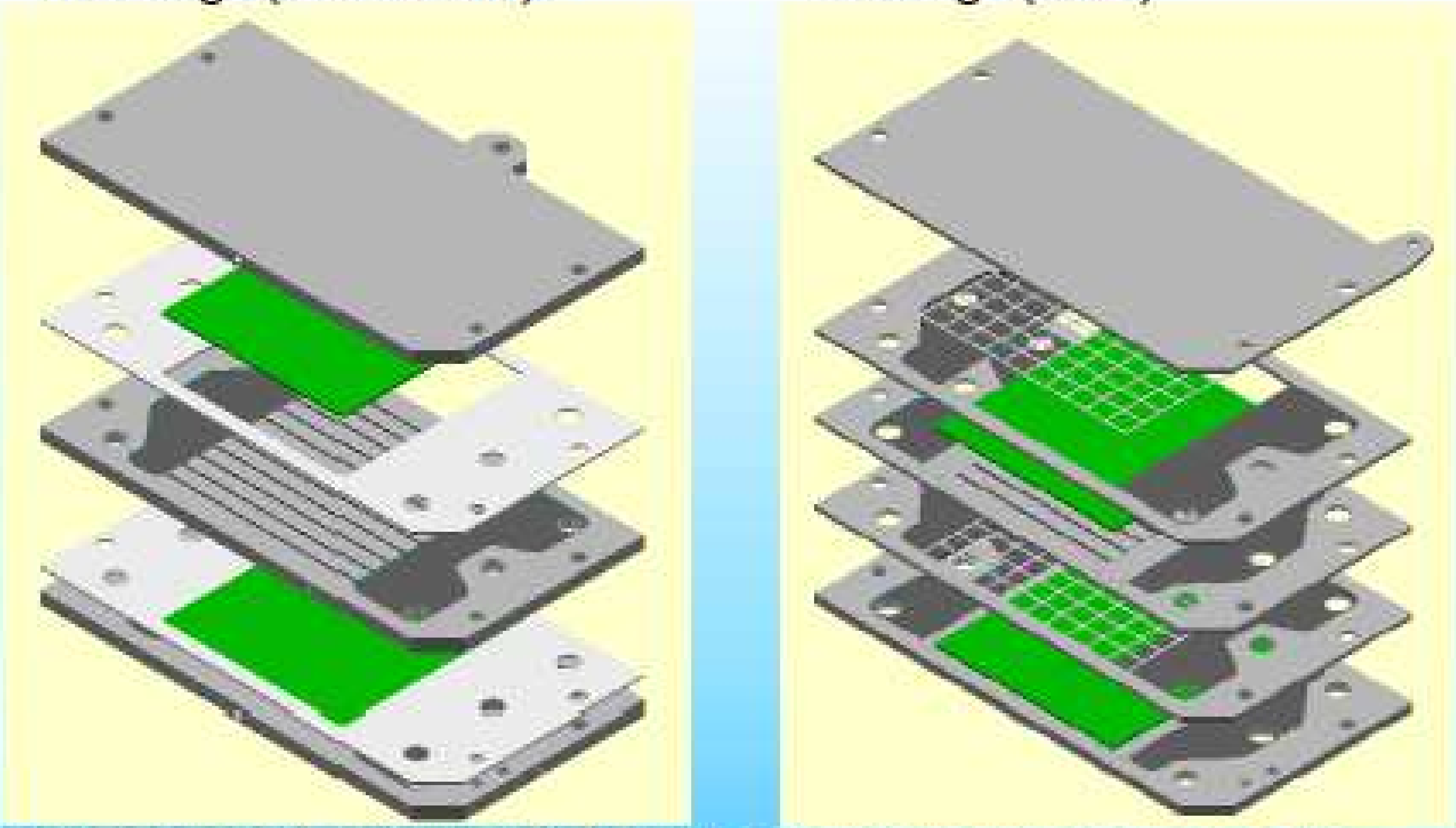
using counter flow results in a more homogeneous temperature distribution in case of internal reforming (results of stack-modelling)



Stack Design

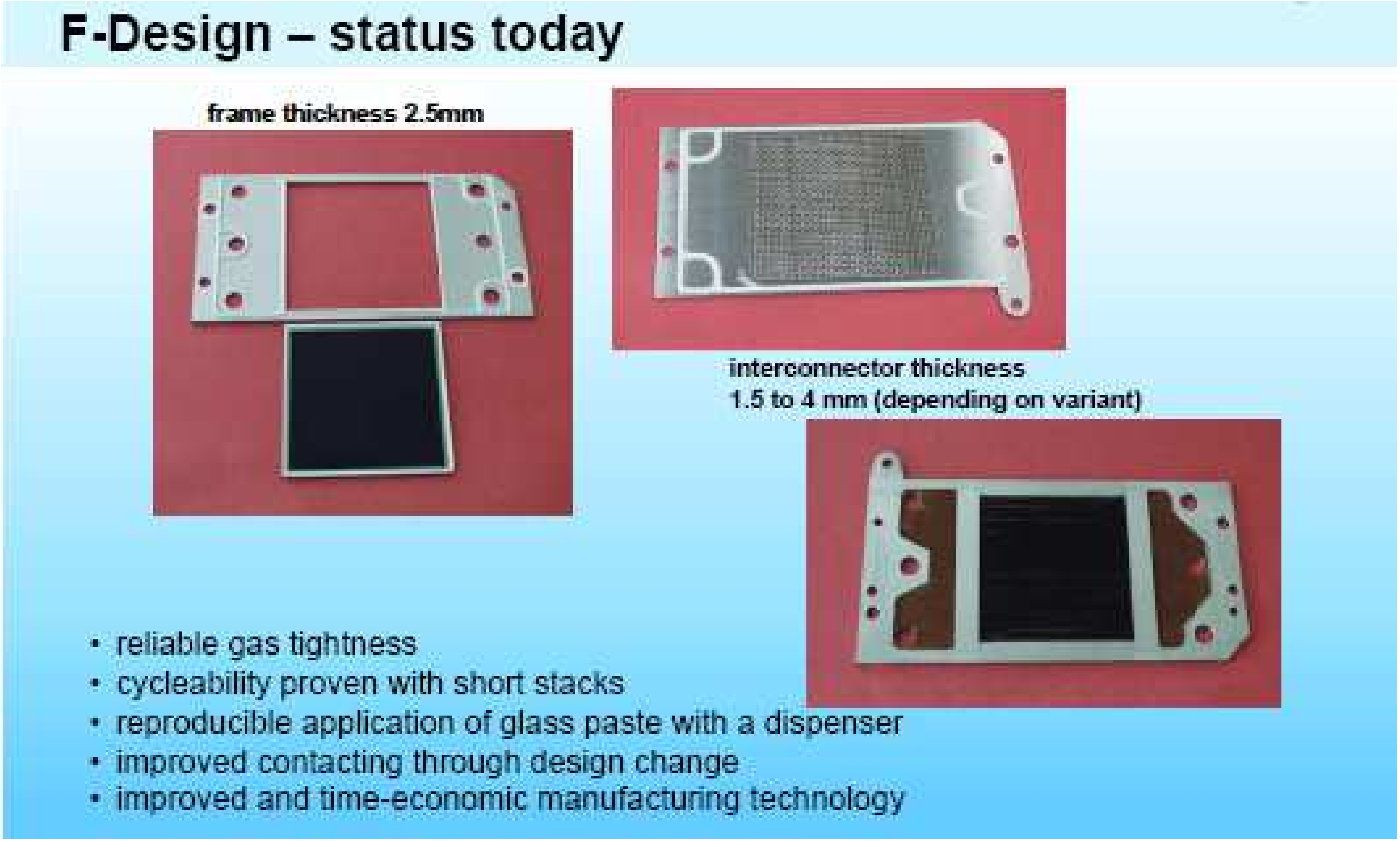
E*-Design (status 2001)

F-Design (2002)

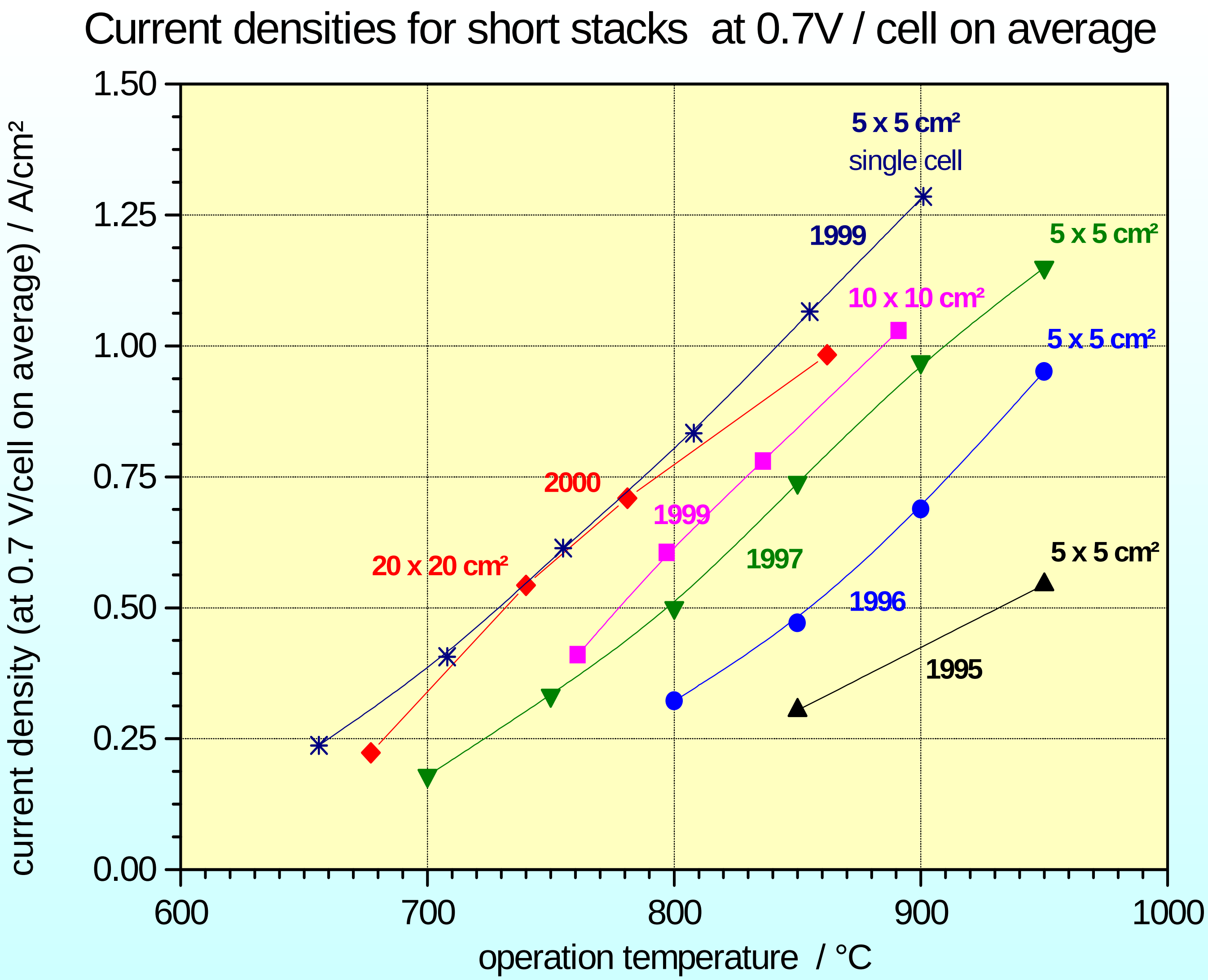


reduced manufacturing effort using a coarse nickel mesh as a gas distribution and contact element on the anode side

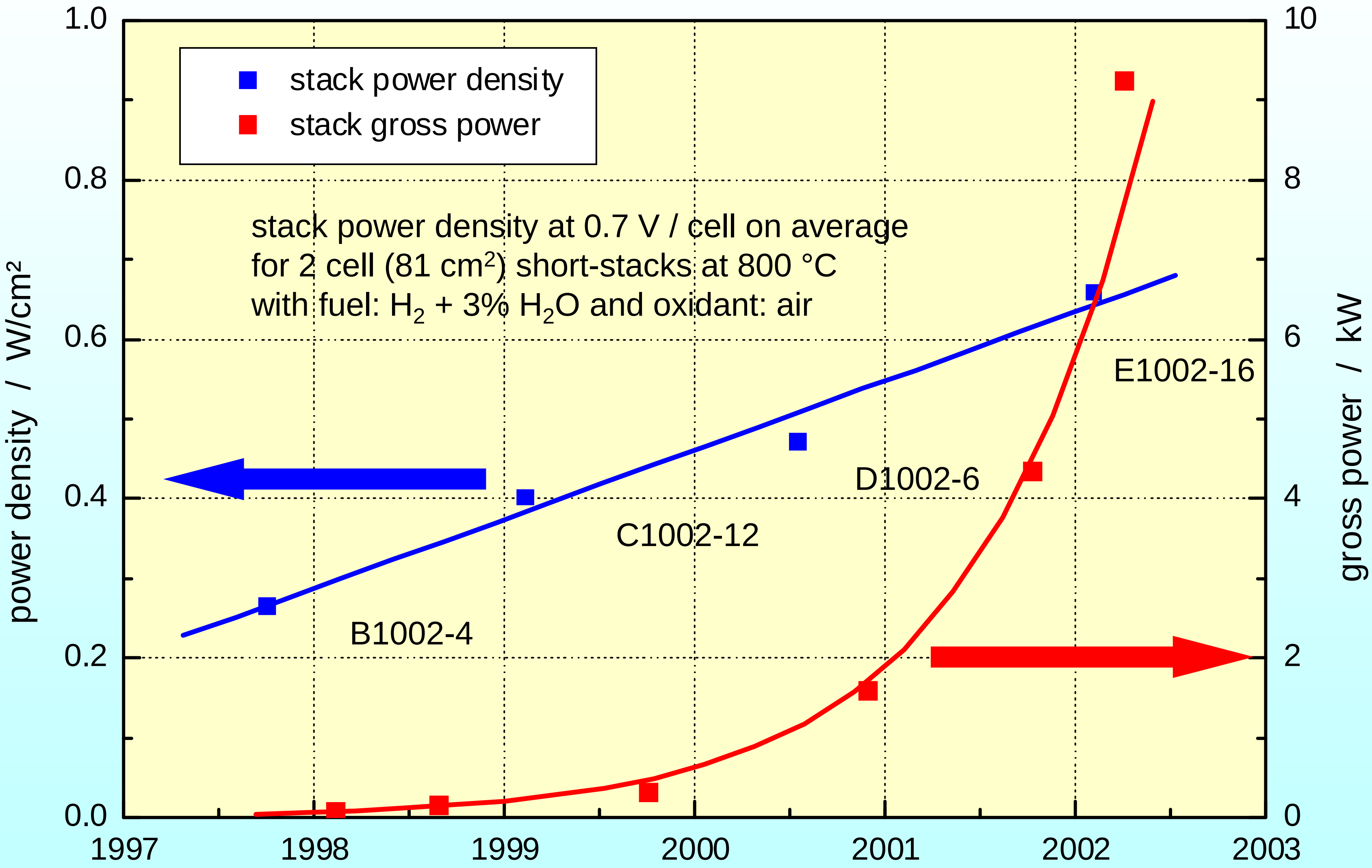
Stack Design



Entwicklung der Stackleistungsdaten



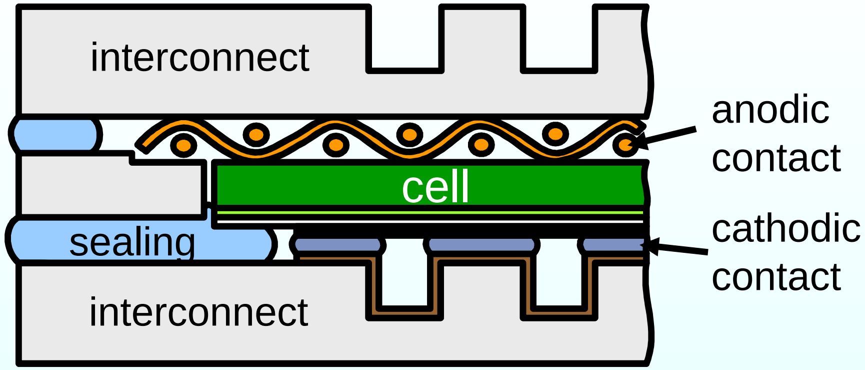
Stack development at FZJ



Materials development

Stack design and modelling

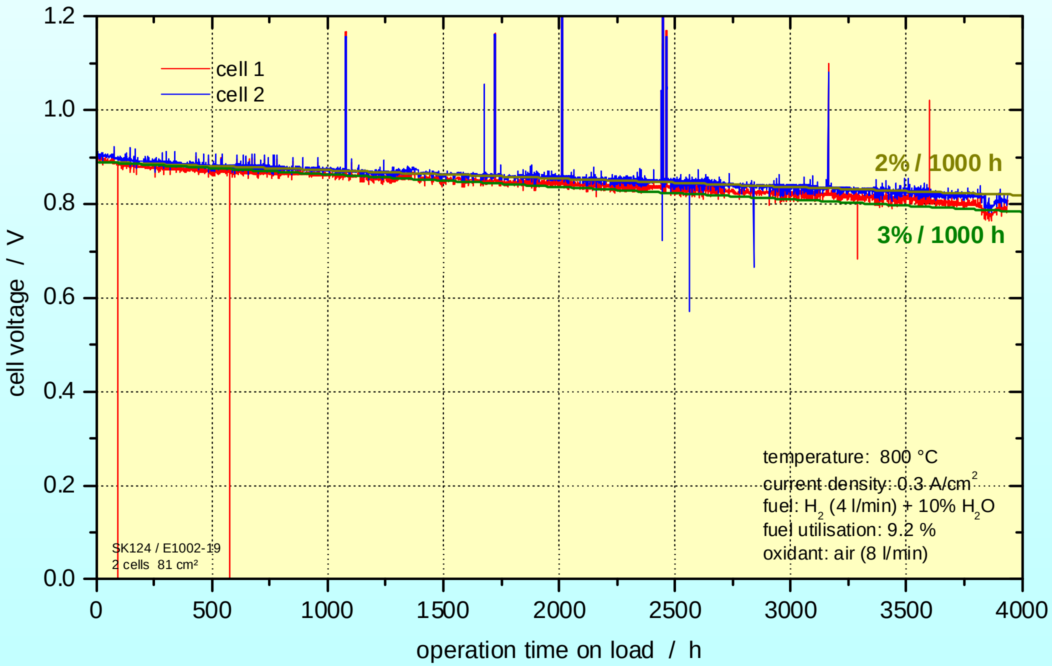
Processing technologies

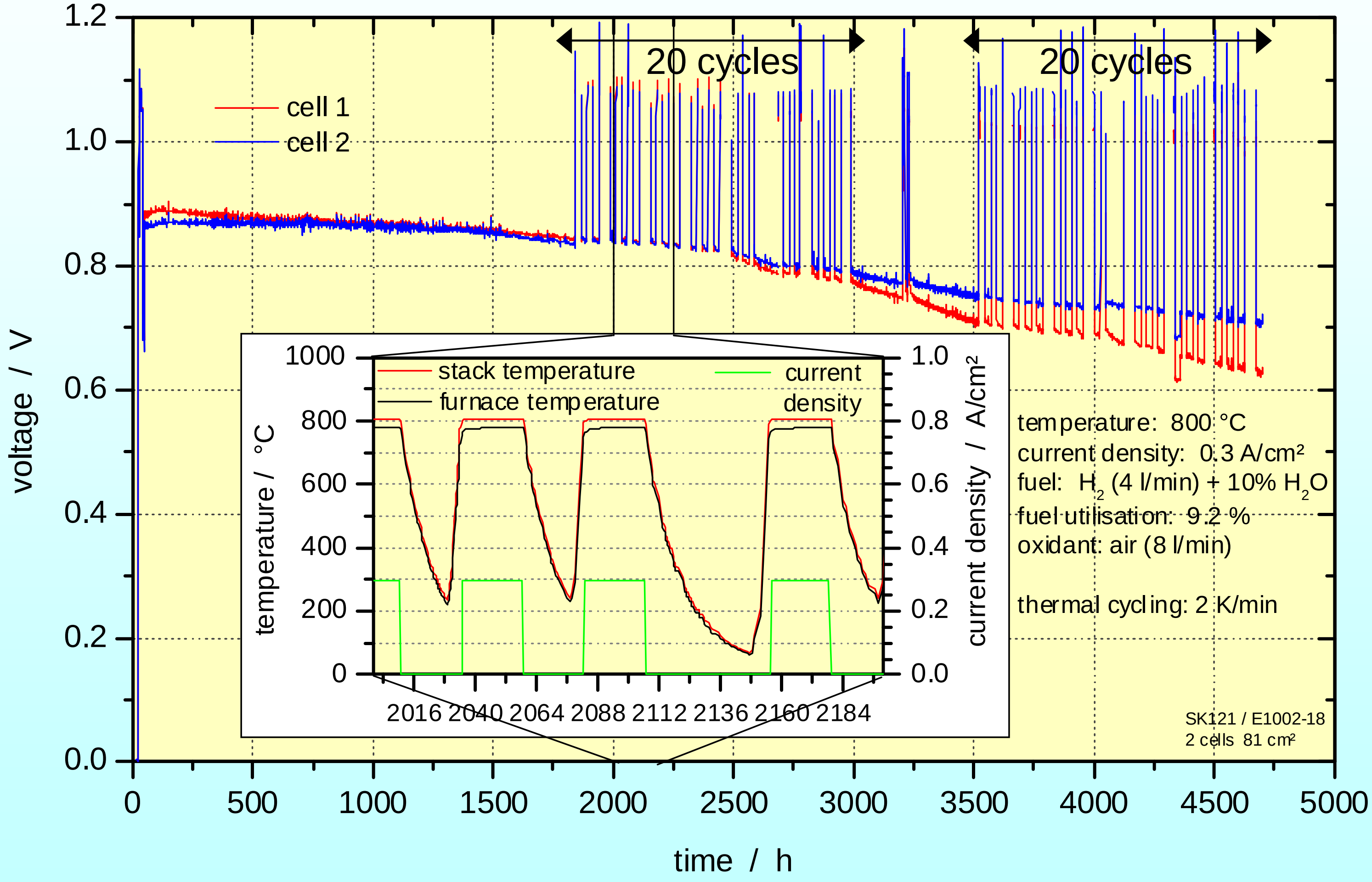


cross-section of a SOFC stack

Aims / Results:

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




voltage / V
time / h
cell 1
cell 2
20 cycles
20 cycles
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**

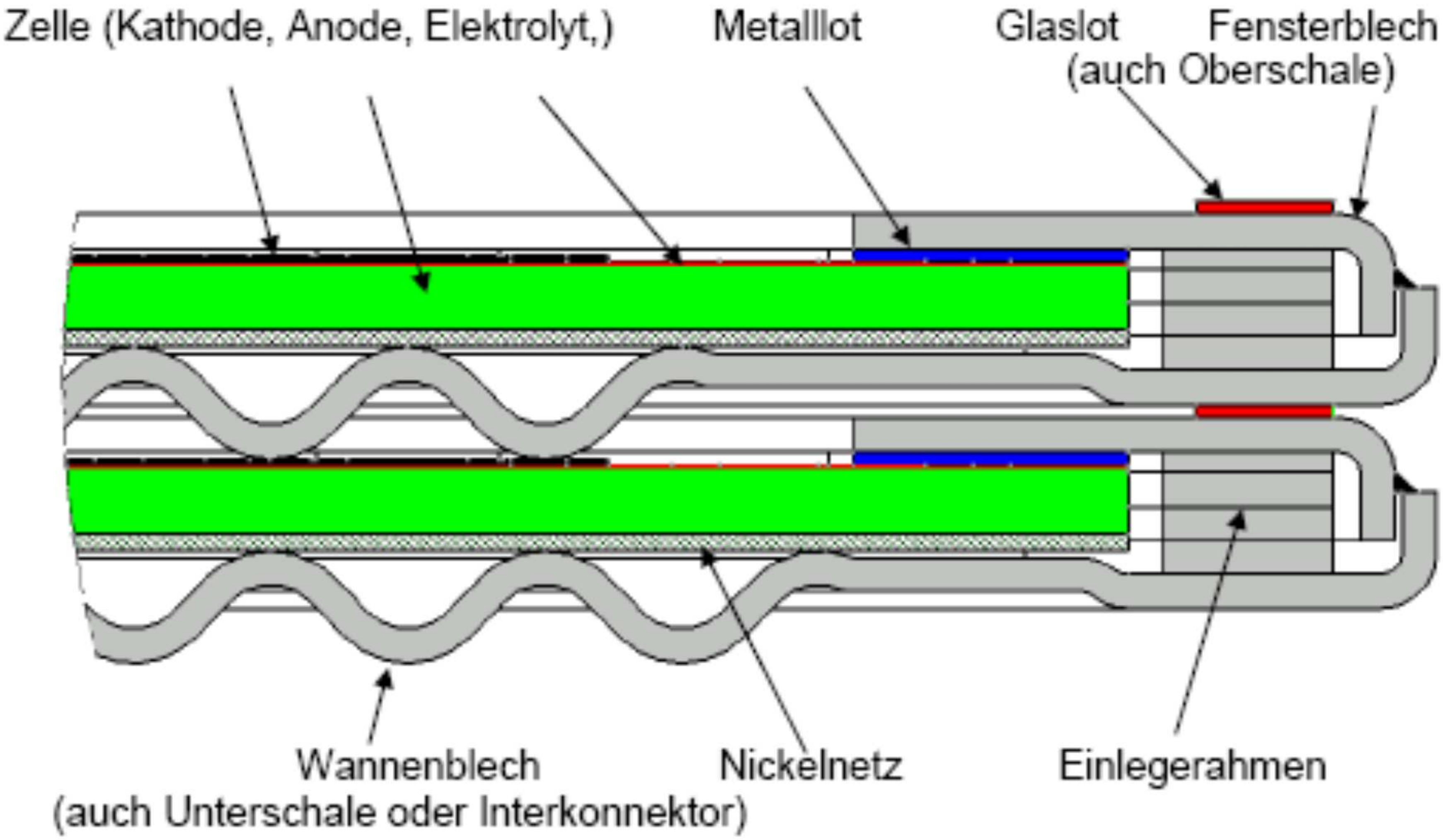
0,38 W/cm²

180 A @ 30,2 V;

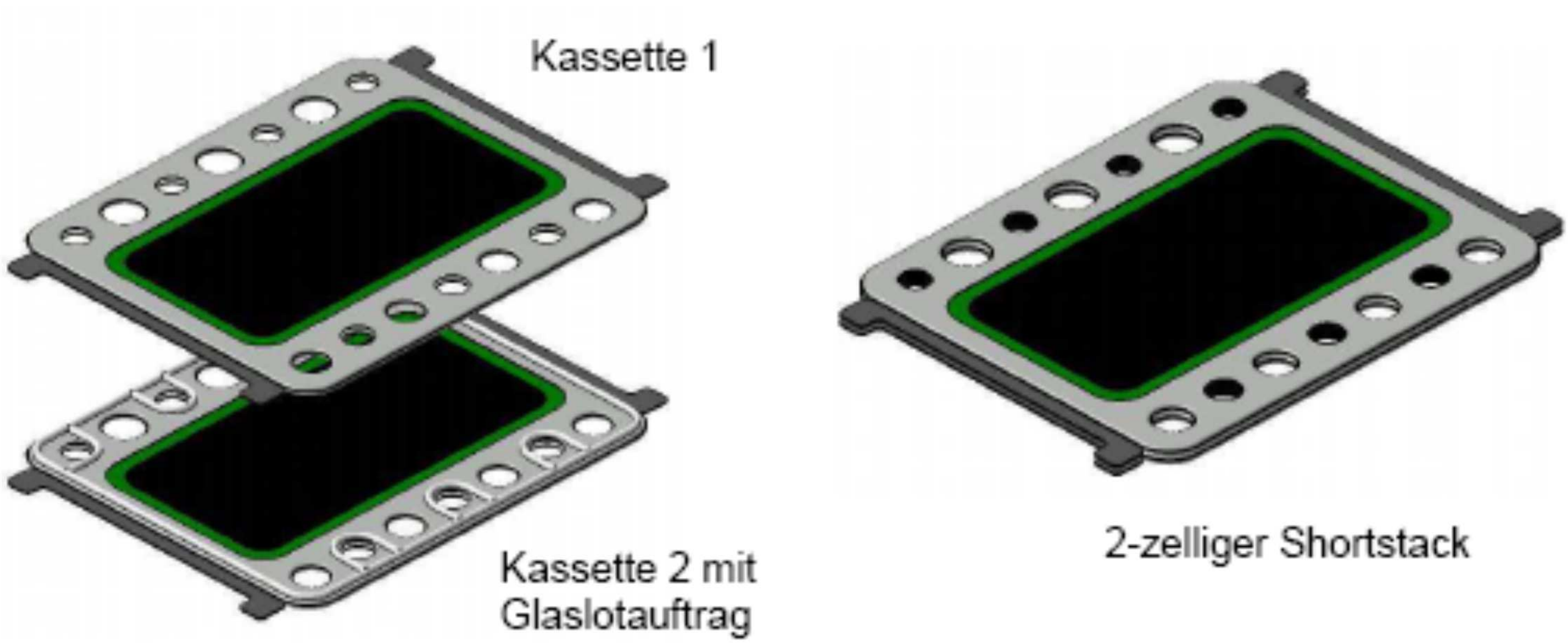
0,50 A/cm² @ 0,755 V/cell

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