Mitglied der Helmholtz-Gemeinschaft

Joint European Summer School for
Fuel Cell and Hydrogen Technology
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JÜLICH FORSCHUNGSZENTRUM

Solid Oxide Fuel Cells

Current Research & Development Issues

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(IEK-1: Materials Synthesis and Processing)

Overview of Research Fields

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Higher cell performce / lower temperatures
thin-film technology
new materials
(next generation)

Higher stack performce
contacting the cell

Long-term stability
>40.000h
protective coatings
accelerated testing

Cycling
reoxidation, thermal, electrical load

Fuel issues
coking, sulphur

System / Balance of plant
operating the stack
suiteable components
stack sealing

Industrialization
Scalable and cheap manufacturing, materials, components

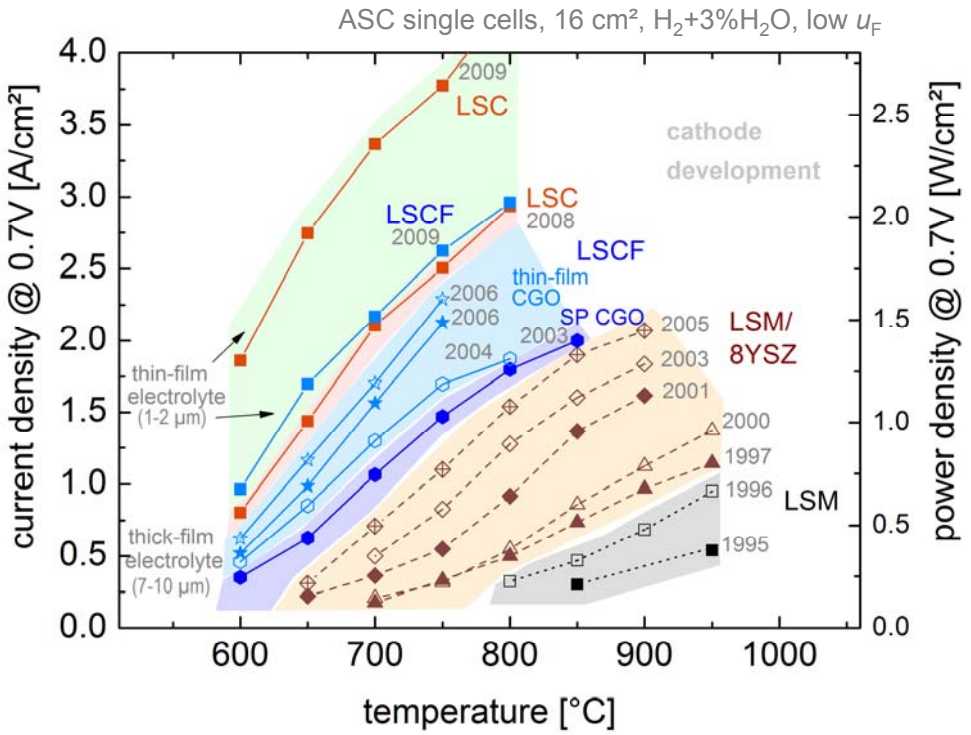
Material solution
Materials / design / processing of cell & stacks

System solution
System / BoP / operating conditions

Contents

1. Increasing the Cell Performance

What has been reached
Very high single cell performance

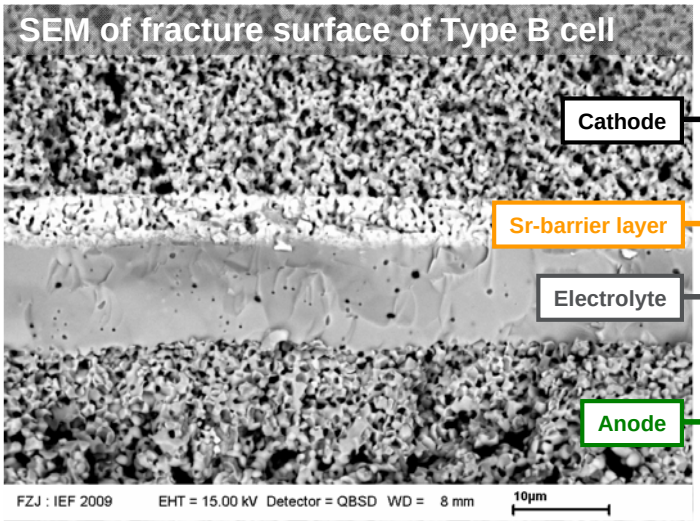


optimization of

- **materials**
- **processing**
- **cell design**

with year of measurement

Screen printed & sintered barrier layer



Cathode → $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF)

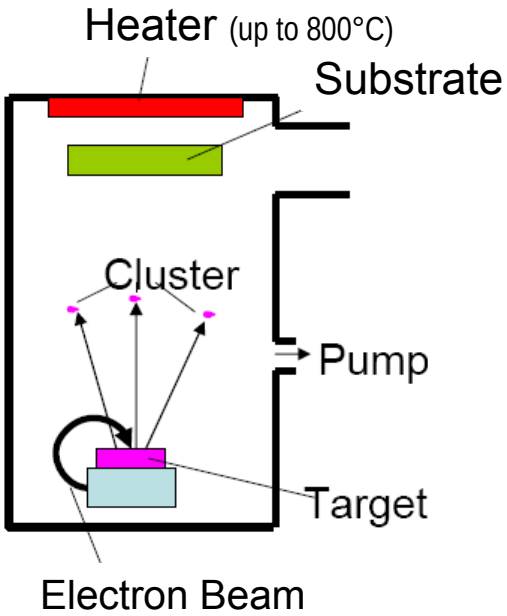
Sr-barrier layer → $Ce_{0.8}Gd_{0.2}O_{2-\delta}$ (CGO)

Electrolyte → 8mol% Y_2O_3-ZrO_2 (8YSZ)

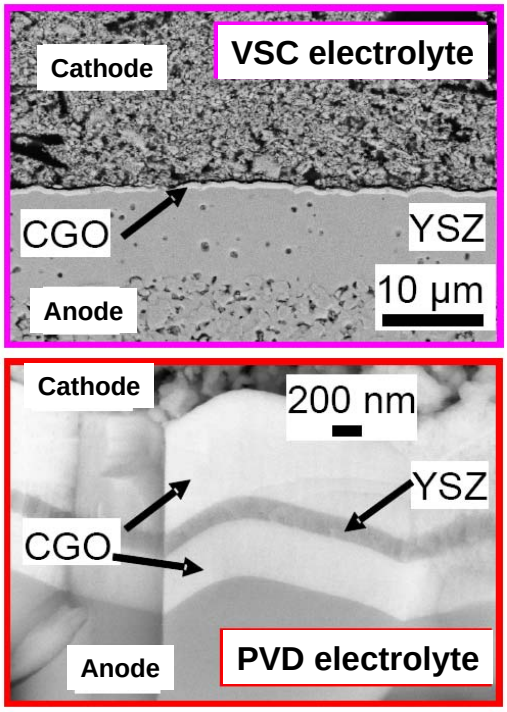
Anode → NiO / 8mol% Y_2O_3-ZrO_2 (8YSZ)

Alternative Manufacturing Routes
Physical Vapor Deposition

Physical **V**apor **D**eposition
(**E**lectron **B**eam PVD, Sputtering)

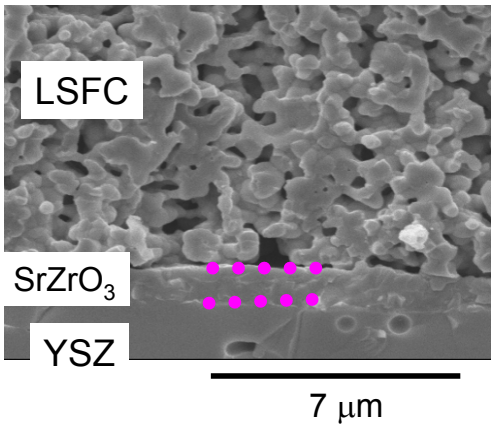


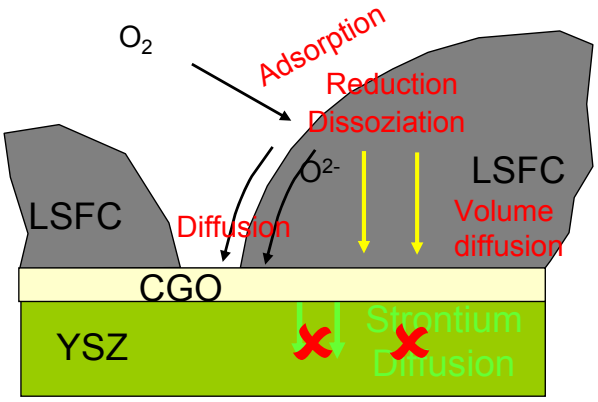
VSC = vacuum slip cast
Jordan-Escalona, PhD thesis



very thin PVD layers => low ASR

Reaction of LSCF with YSZ Electrolyte





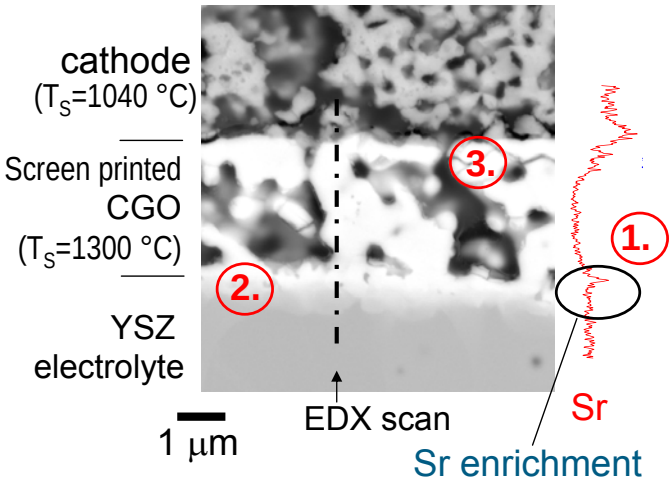
disadvantage

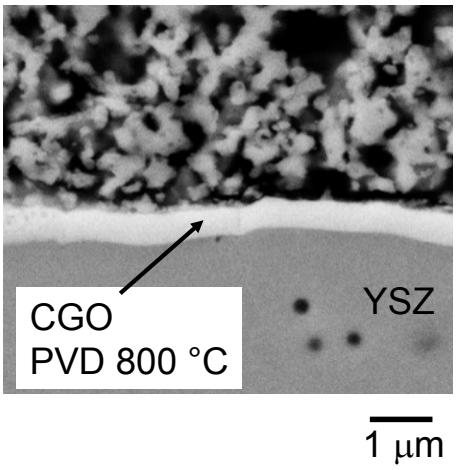
Reaction with YSZ forming $SrZrO_3$

solution

Interlayer $Ce_{0.8}Gd_{0.2}O_{1.9}$

Screen Printed CGO Barrier Layers vs. PVD Layers

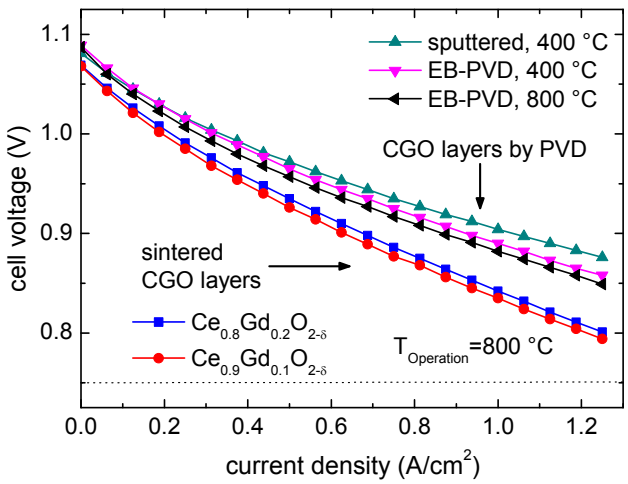


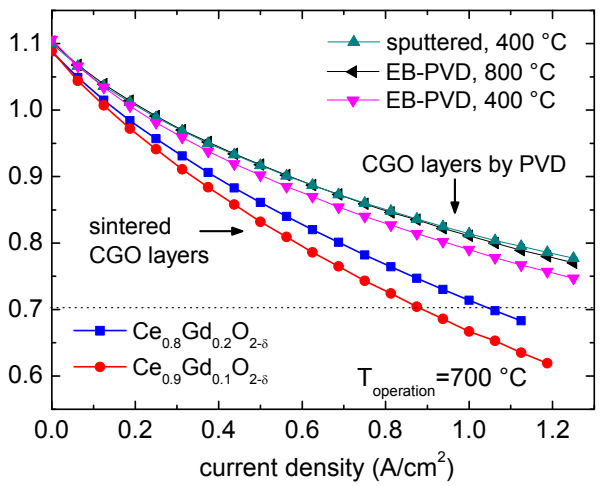


1. Sr diffusion to YSZ, not with PVD barrier
2. Solid state solution of CGO and YSZ, not found with PVD barrier
3. Microstructure: • Screen printed + sintered: sponge-like structure
   ⇒ longer pathways for O^{2-}
   • PVD layers: laminar, tight contact between YSZ and CGO layer (less CGO/LSCF contact)

Different CGO Barrier Layers Electrochemical Performance

Temperature of operation: 800 °C 700 °C

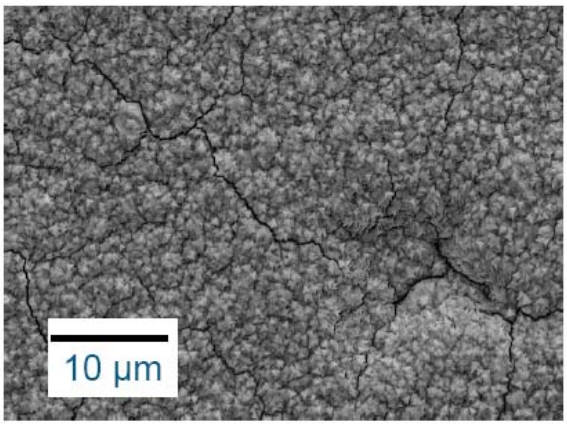




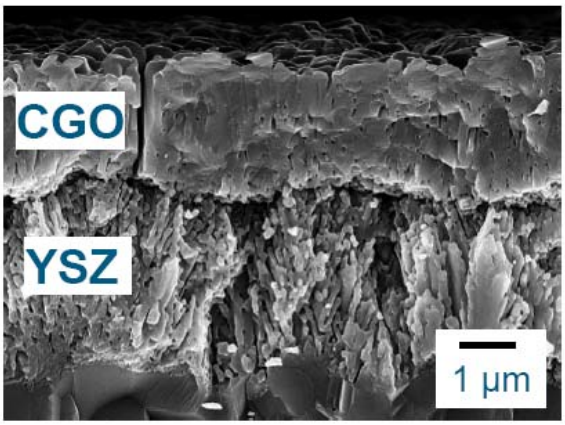
- PVD CGO performs significantly better than sintered CGO barrier, especially at lower operating temperatures
- at 700°C: sintered: 1.0 A/cm²; PVD barrier: 1.7 A/cm² (@0.7V)
- $Ce_{0.8}Gd_{0.2}O_{2-\delta}$ performs better than $Ce_{0.9}Gd_{0.1}O_{2-\delta}$

Nanoscaled Electrolyte Aging

PVD layers produced at 800°C, annealed at 1040°C:
decrease of grain boundaries => volume shrinkage => layers become porous or crack



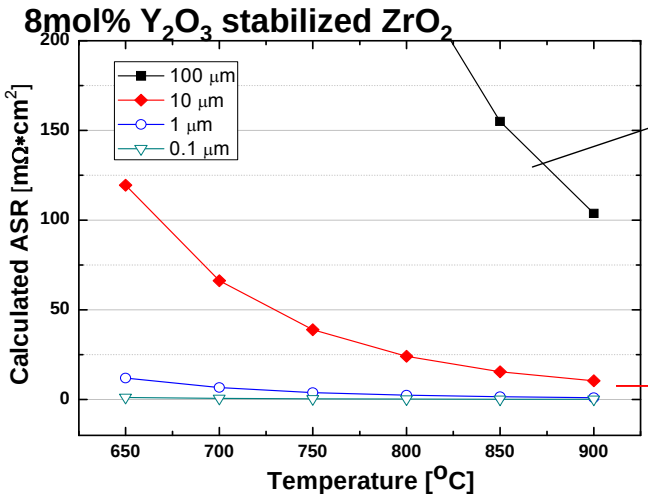
Top surface

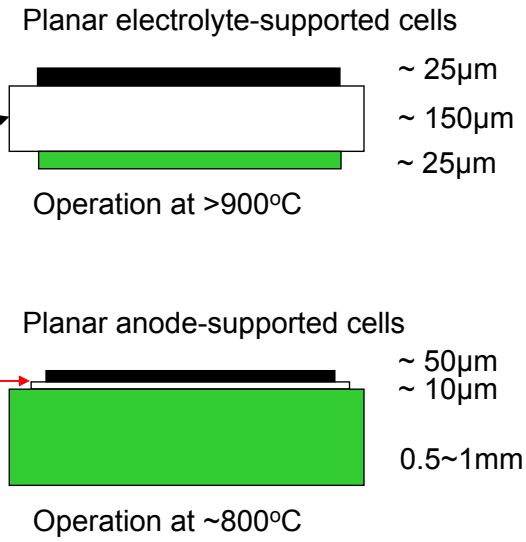


Fracture surface

relevant for operational conditions,
if process temperature is below operating point

Dependence of area specific resistance (ASR) on layer thickness





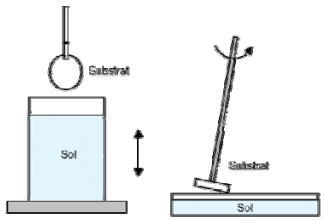
Thinner electrolyte→Lower ASR

Coatings of Nano-Suspensions and Sols

1. Coating
spin- or dip-coating

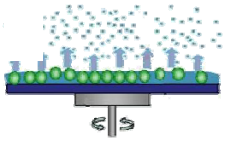
2. Drying
conversion of polymeric sol into gel layer

3. Thermal annealing
conversion of gel layer into ceramic layer (calcination and sintering)



vertical tangential

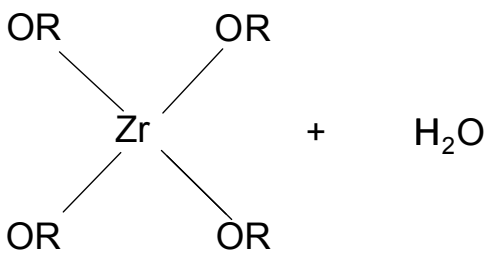
dip coating



spin coating

Sol-Gel Synthesis

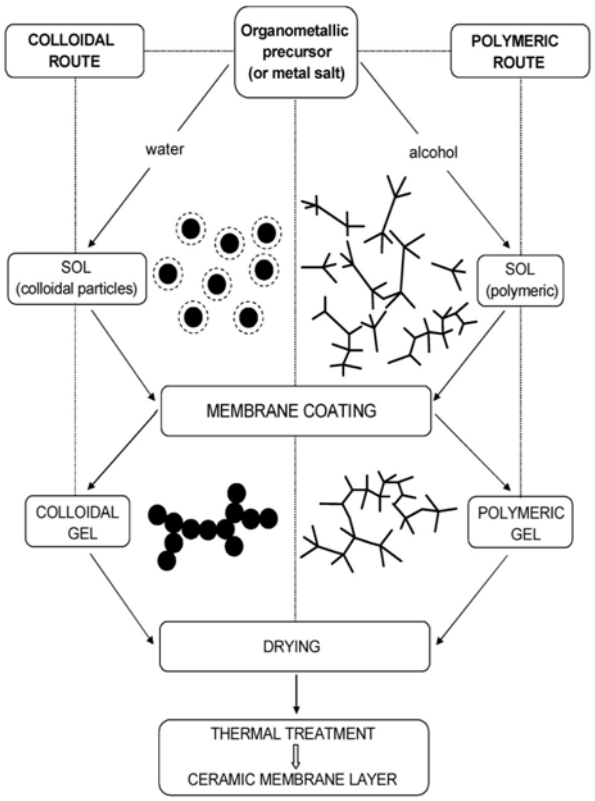
Hydrolysis



OR = alkoxy group

nano-suspension: ~40-100 nm
polymeric sol: 5-15 nm

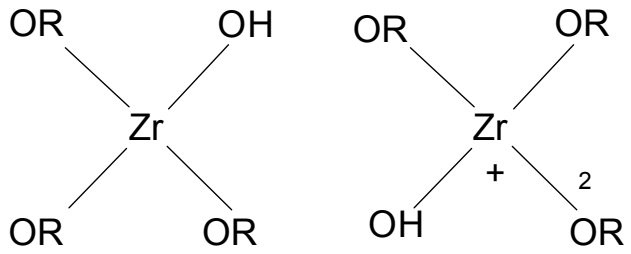
F. Hauler, T. van Gestel, S. Vieweger, IEK-1 (FZ Jülich)

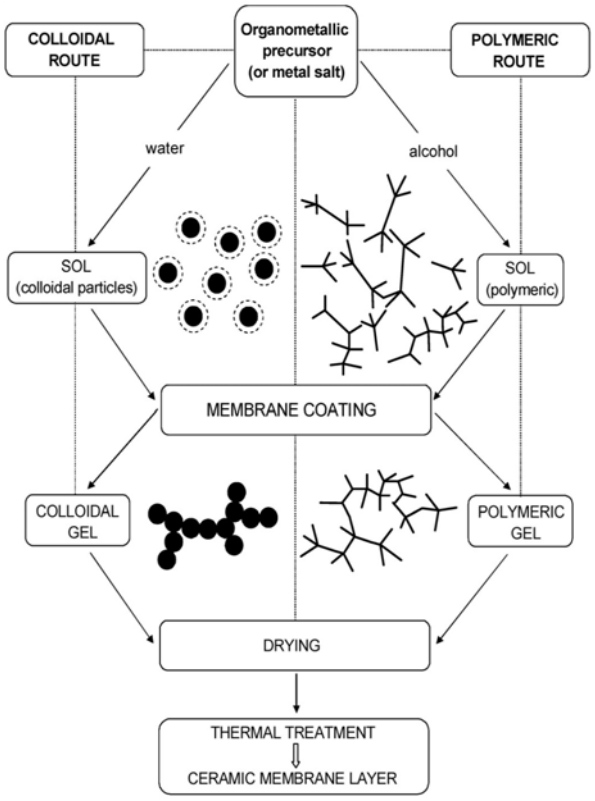


Burggraat & Cot, Inorganic Membrane Science and Technology

Sol-Gel Synthesis

Condensation





nano-suspension: ~40-100 nm
polymeric sol: 5-15 nm

F. Hauler, T. van Gestel, S. Vieweger, IEK-1 (FZ Jülich)

Burggraat & Cot, Inorganic Membrane Science and Technology

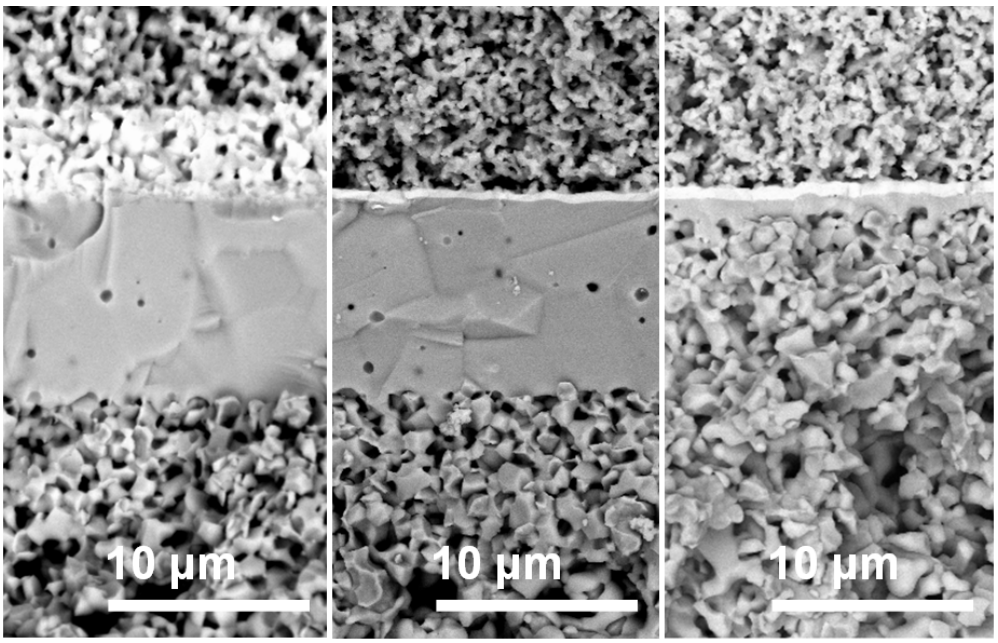
Cells with Thin-Film Coatings

Cathode

Barrier (CGO)

Electrolyte (8YSZ)

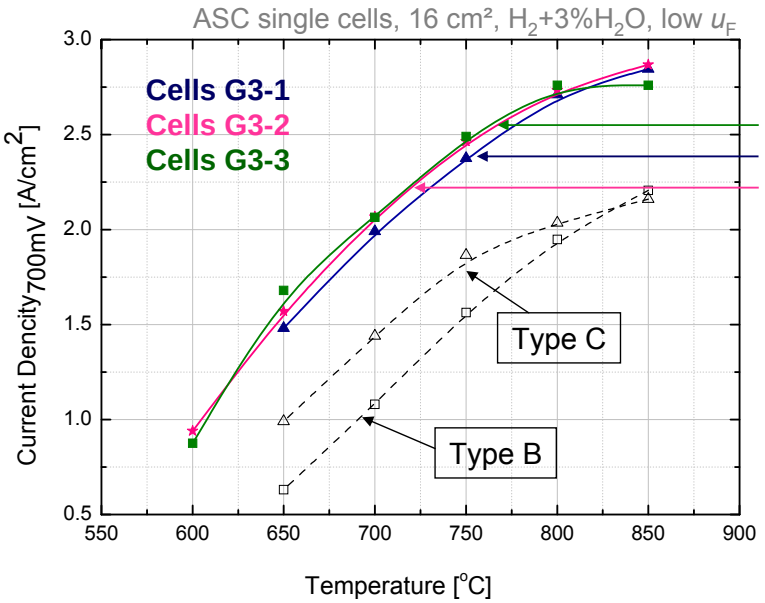
Anode



Type A	Type B	Type C
10 µm 8YSZ + 5 µm CGO	10 µm 8YSZ + 0.5 µm CGO	1 µm 8YSZ + 0.5 µm CGO

F. Han et al., J Power Sources, 2012

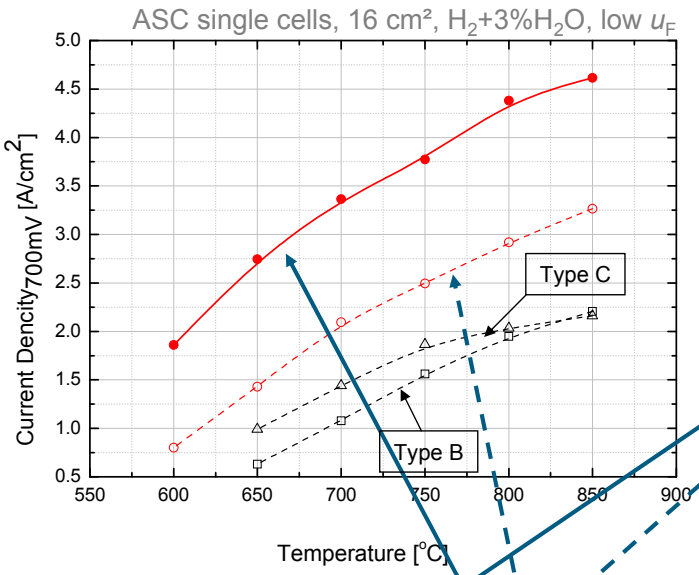
Thin-Film Electrolyte with LSCF Cathode



Cells with ~1 µm electrolyte layer, sputtered CGO layer & LSCF cathode

Currently stacks running (ASC stacks with lowest ASR in Jülich)

Thin-Film Electrolyte with LSC Cathode



Advantage of LSC vs. LSCF:
Highest total conductivity

Drawback:
Large CTE

α_{LSCF} ~ 15-17 ppm/K

α_{LSC} ~ 20-21 ppm/K

$\alpha_{substrate}$ ~ 12-13 ppm/K

Screen-printed **LSC** cathode
Sputtered CGO layer
8YSZ polymeric sol-gel layer
8YSZ nano-suspension layer
8YSZ nano-suspension layer
NiO/8YSZ anode
NiO/8YSZ anode substrate

Cells with ~1 µm electrolyte layer, sputtered CGO layer & LSC cathode

Cells with 5-10 µm thick electrolyte layer, sputtered CGO layer & LSC cathode

*SOFC600 developed by EU project SOFC600

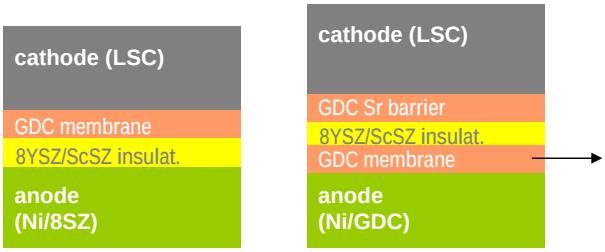
further target: 400°C SOFC

400°C SOFC

Carbon coking, metallic corrosion renders 450-600°C temperature window difficult

400°C would allow to use methanol (decomposes above)

from ASR considerations: 100 nm 8YSZ or 1 µm CGO electrolyte would be sufficient



not necessary, if $T_{manufacturing}$ <1000°C (solid state reaction above)

⇒ extremely smooth/defect free substrates are needed

⇒ new electrodes are needed

High Conducting Electrolyte Materials for Electrolyte Supported Fuel Cells

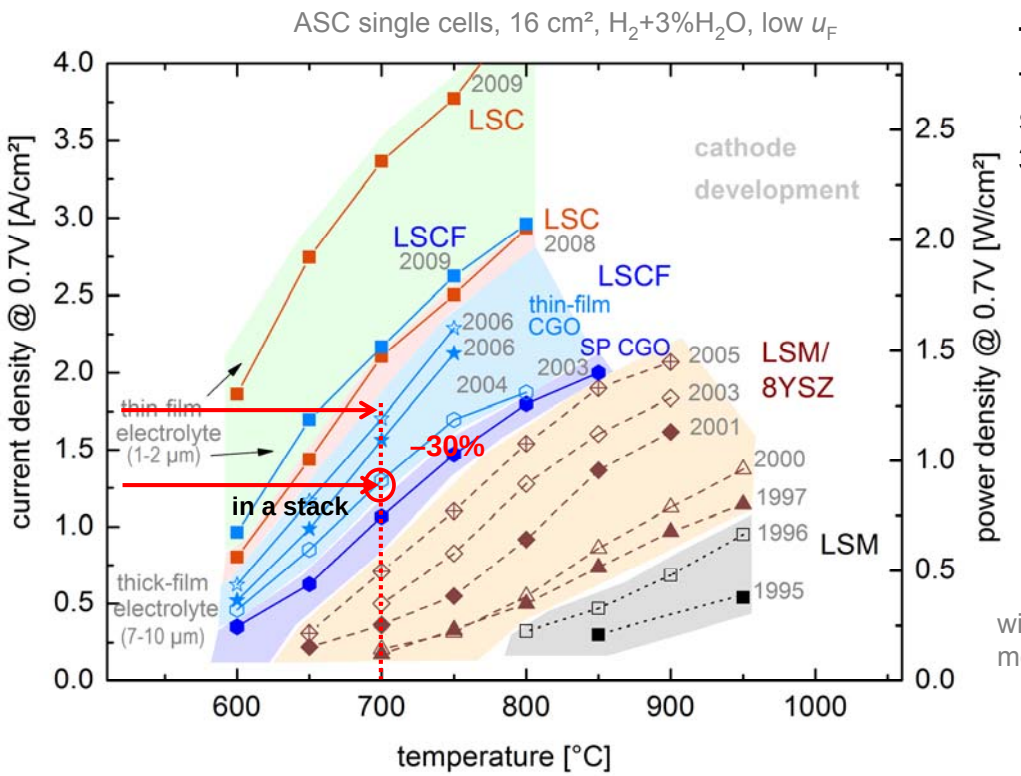
Material	3YSZ	10Sc1CeSZ	YScSZ
ZrO_2 stabilized with	3mol% Y_2O_3	10mol% Sc_2O_3 1mol% CeO_2	Y_2O_3, Sc_2O_3, CeO_2
Bending strength	1000 MPa	250 MPa	665 MPa
$\alpha_{RT..850°C}$	11.2 ppm/K	10.1 ppm/K	10.3 ppm/K
$\sigma_{850°C}$ ($\Omega_{Subst}/\Omega_{ges}$)	2 S/m (52%)	26 S/m (16%)	6.5 S/m (44%)
Typical cell performance, 0.7V, 850°C, H:H_2O=1:1	~ 0.3 A/cm²	0.7 A/cm²	0.5 A/cm²

Source: Kerafol, Eschenbach, Germany

First tests of using LSCF instead of LSM cathodes.

2. Cell vs. Stack Performance

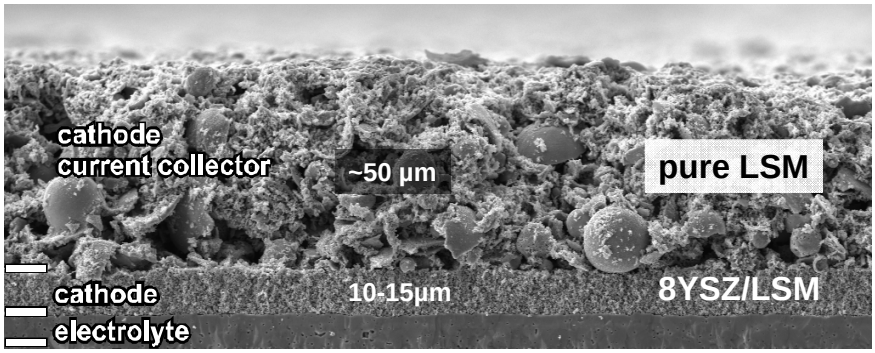
2. Cell vs. Stack Performance



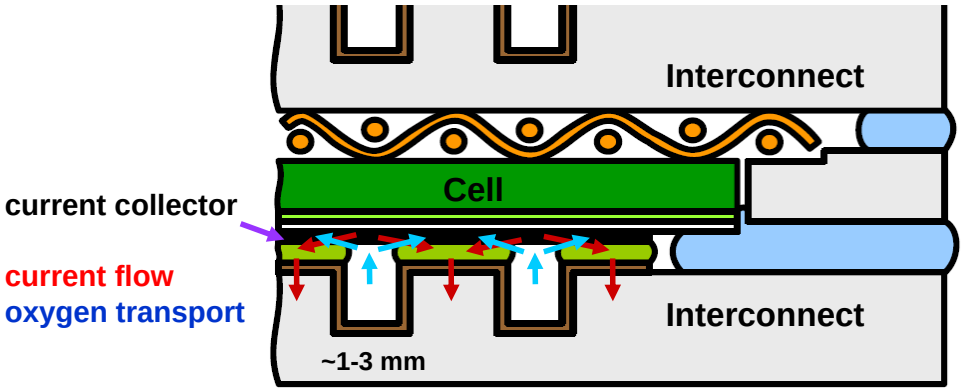
Typical loss from cell to stack test: 30-70%

with year of measurement

Cathode Current Collector

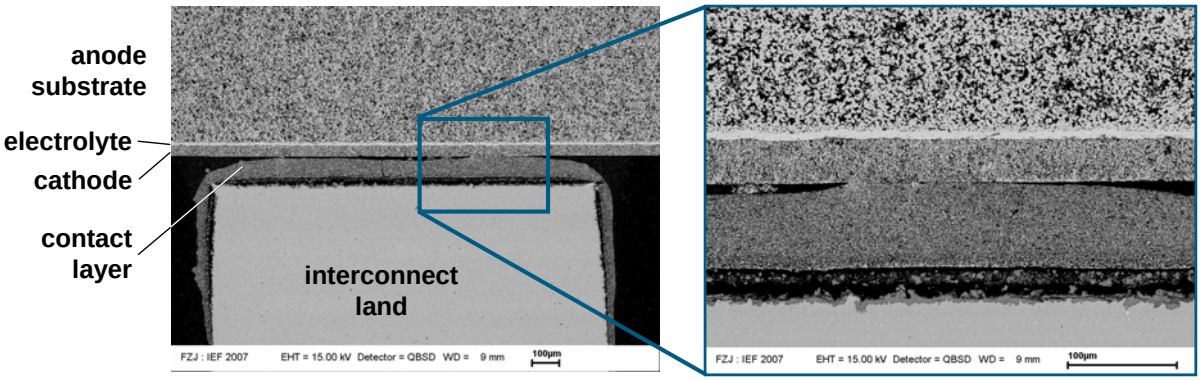


	electric conductivity	porosity
pure LSM	50 S/cm	45%
8YSZ/LSM	25 S/cm	20%



A lot of cell performance is lost in cell contacting inside the stack (30-70%), due to contacting area + contact resistances

Contacting with milled interconnects

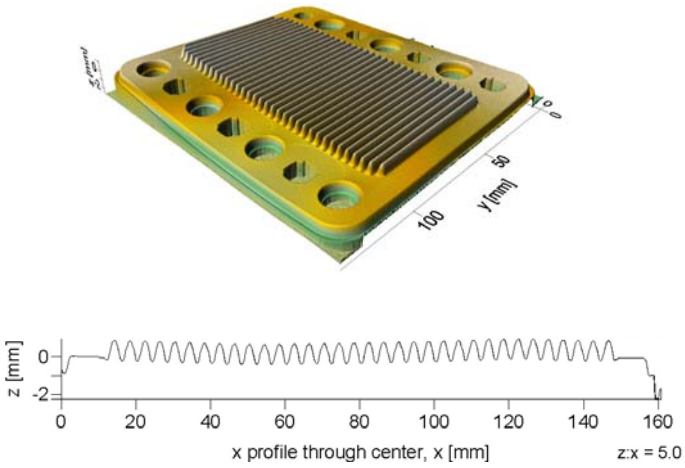


gap between contact layer/interconnect: preparation artefact

porous contact layer by perovskites (e.g. lanthanum manganese cobalt copper oxide)

- **optimize channel/land structure by modeling**
- **use wet coatings (e.g. by screen printing)**
- **apply large compressive loads**

Contacting with stamped interconnects



even more difficult
approx. 30% more losses than for milled interconnects

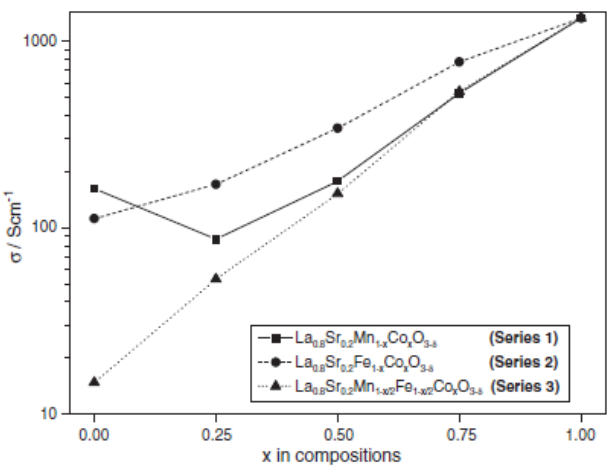
New contact materials?

<u>requirements</u>:
- **porous**
- **compensate thickness inhomogeneities**
- **chemically stable (ox. atm.)**
- **low contact resistance**
- **no sintering during operation**

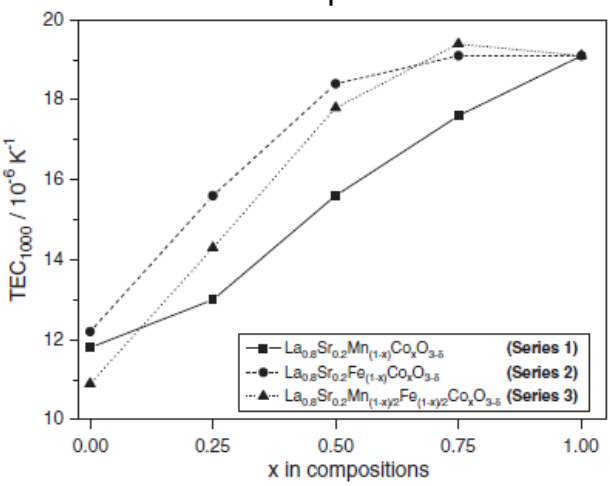
Contact layers - Perovskites

Examples: $(La,Sr)(Mn,Fe,Co)O_{3-\delta}$
$(La,Ca)(Cr,Co,Cu)O_{3-\delta}$

electrical conductivity



thermal expansion

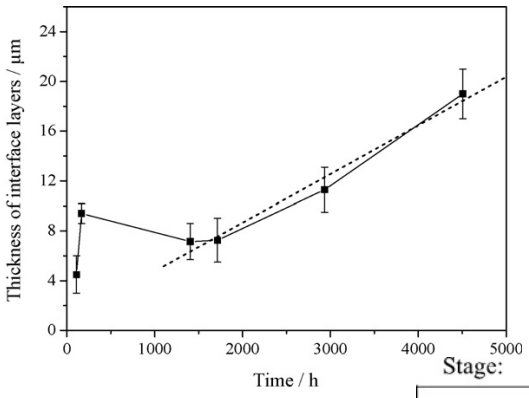


properties governed by Co amount, not so much by 2nd B site cations (Mn, Fe)
High conductivity → large CTE → risk of mechanical delamination

*Tietz et al., SSI 2006

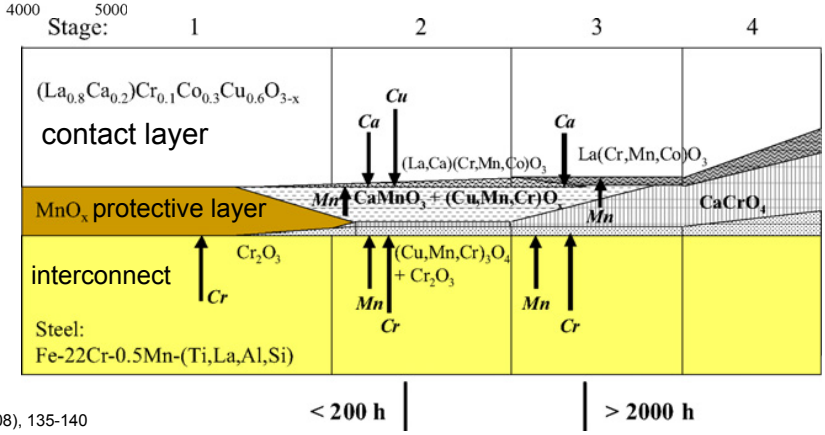
Contact layers - Perovskites

Formation of interface reaction zone



1: formation of Cr_2O_3 layer
2: Cr_2O_3 $(Cr,Mn)_3O_4$ double layer
released Cr → $CaCrO_4$
dense layer of decomposed perovskites on top of protective layer
3: Mn depletion in protective layer
grow of $CaCrO_4$, Ca free perovskite
4: further grow of scales

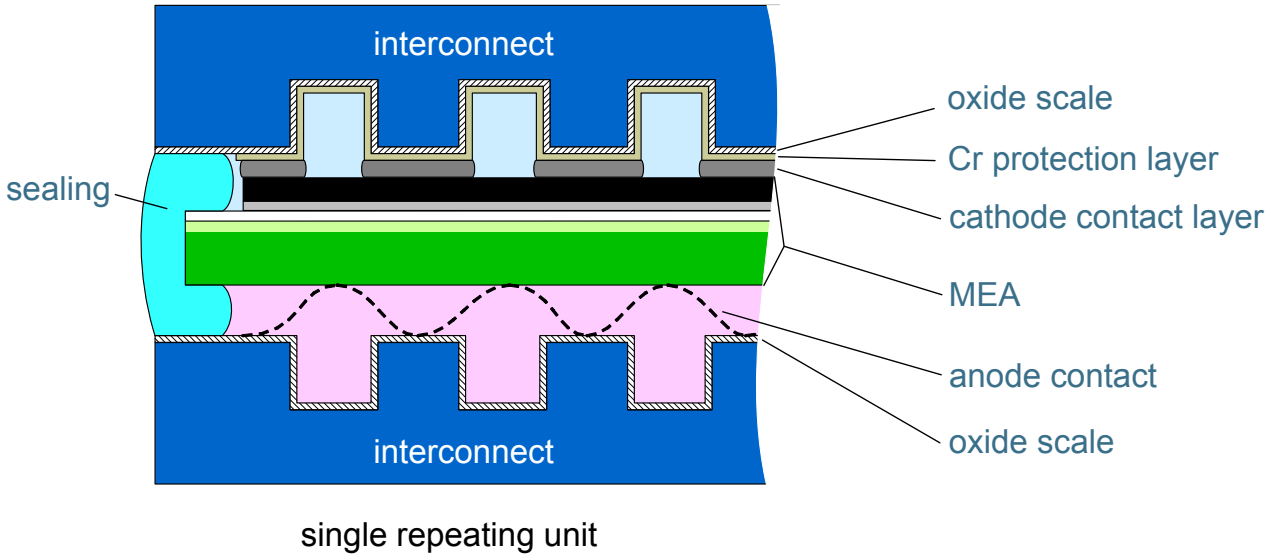
LaMnCoCu based layers:
Cu depletion other time
no further problems with dense MCF protective layers (Cr barrier)



Tietz et al., Mater. Sci. Eng. B 150 (2008), 135-140

3. Long Term Stability

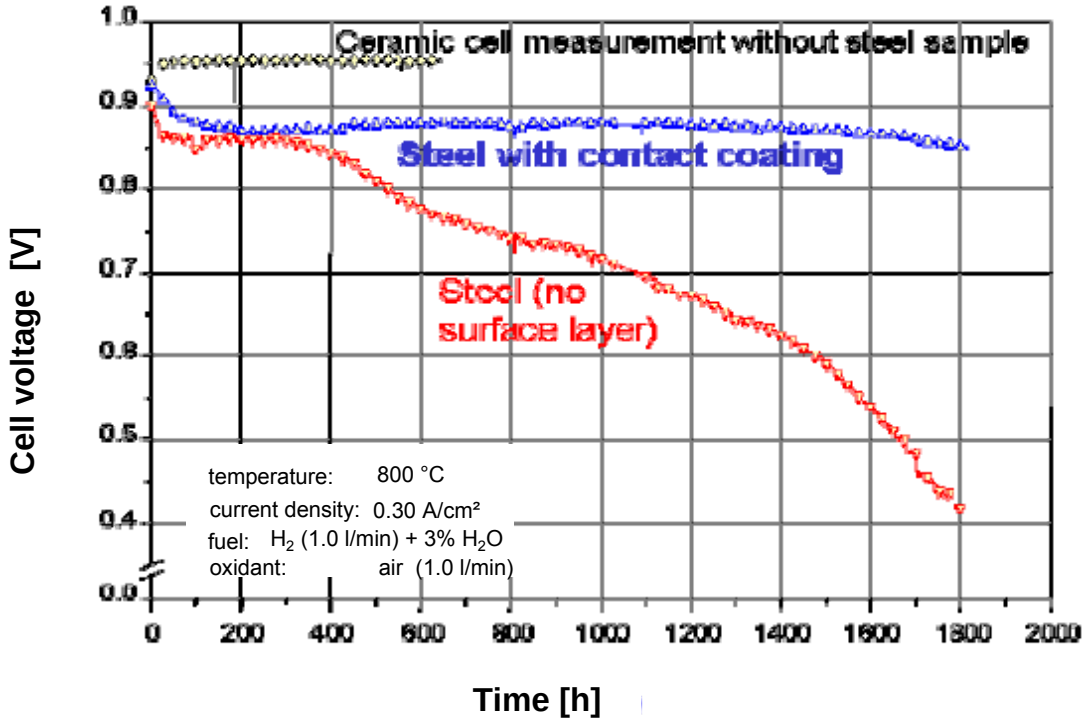
Sources of Degration



*N.H.Menzler et al. Ceram.Eng.Sci.Proc. 2008

→ "internal causes" = interactions / changes within the stack components

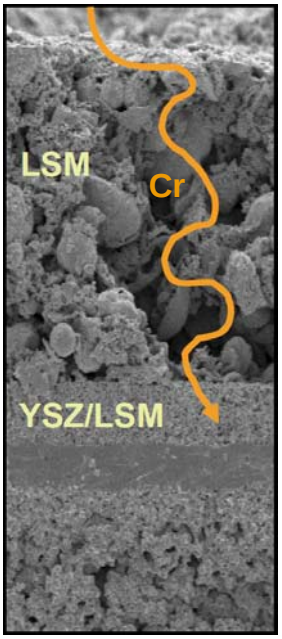
Cell Degradation due to Presence of Interconnect Steel (Cr poisoning)



Meachnisms of Cr-Poisoning

$$(La,Sr)(Co,Fe)O_3 + x\ H_2O \rightarrow (La,Sr_{-x},\square_x)(Co,Fe)O_3 + x\ Sr(OH)_2$$

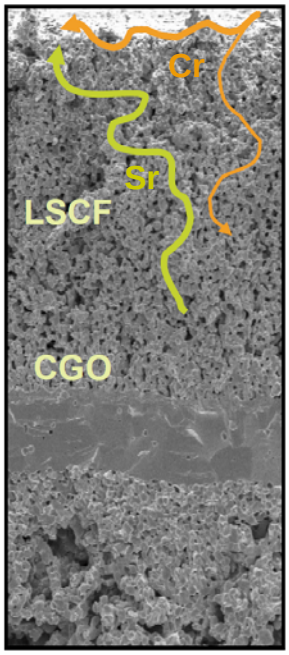
$$CrO_2(OH)_2 + Sr(OH)_2 \rightarrow SrCrO_4 + 2\ H_2O$$



LSCF cathodes
vapor phase transport and reaction at cathode surface

Cathode degradation currently dominant in cells

LSM cathodes
reaction at electrolyte interface
(1) blockage of tri phase boundaries (see below) or
(2) formation o Cr_2O_3+ $(Cr,Mn)_3O_4$ insulating layer between cathode and electrolyte

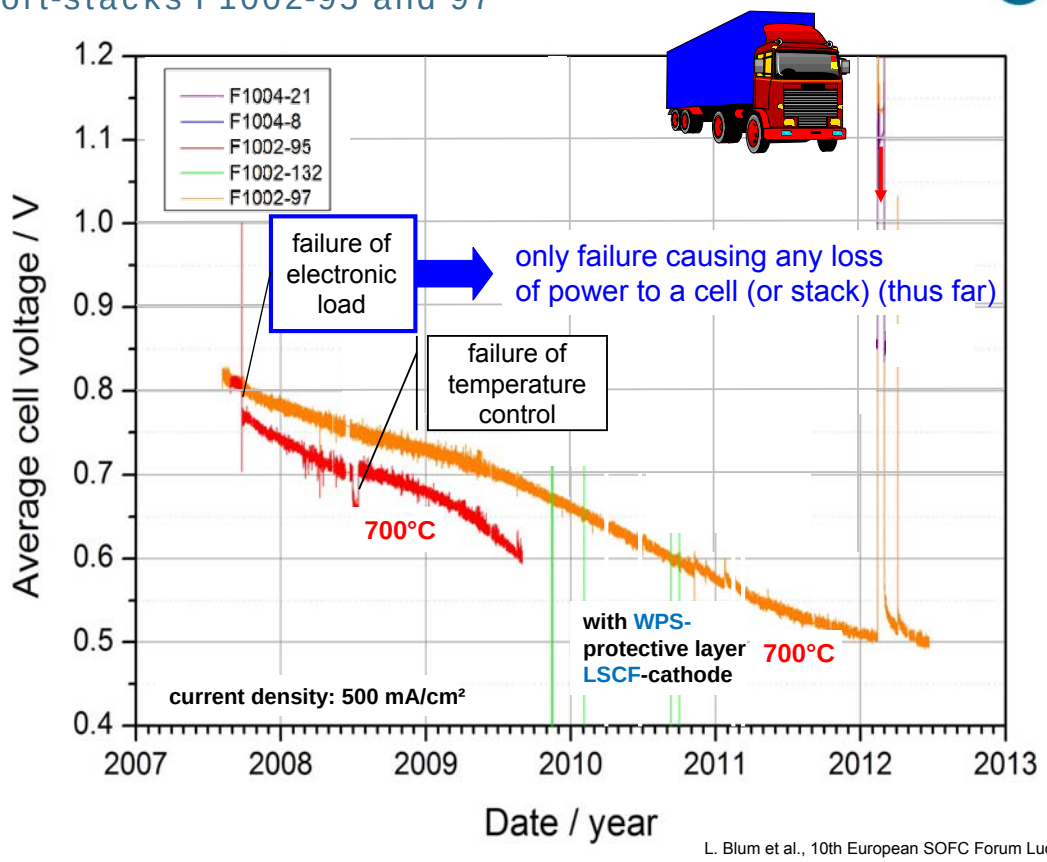


$$2\ CrO_2(OH)_2 + 6\ e^- \rightarrow Cr_2O_3 + 2\ H_2O + ½\ O_2$$

$$Cr_2O_3 + 2\ (La,Sr)MnO_3 \rightarrow MnCr_2O_4 + (La,Sr)_2MnO_4 + 2\ O_2$$

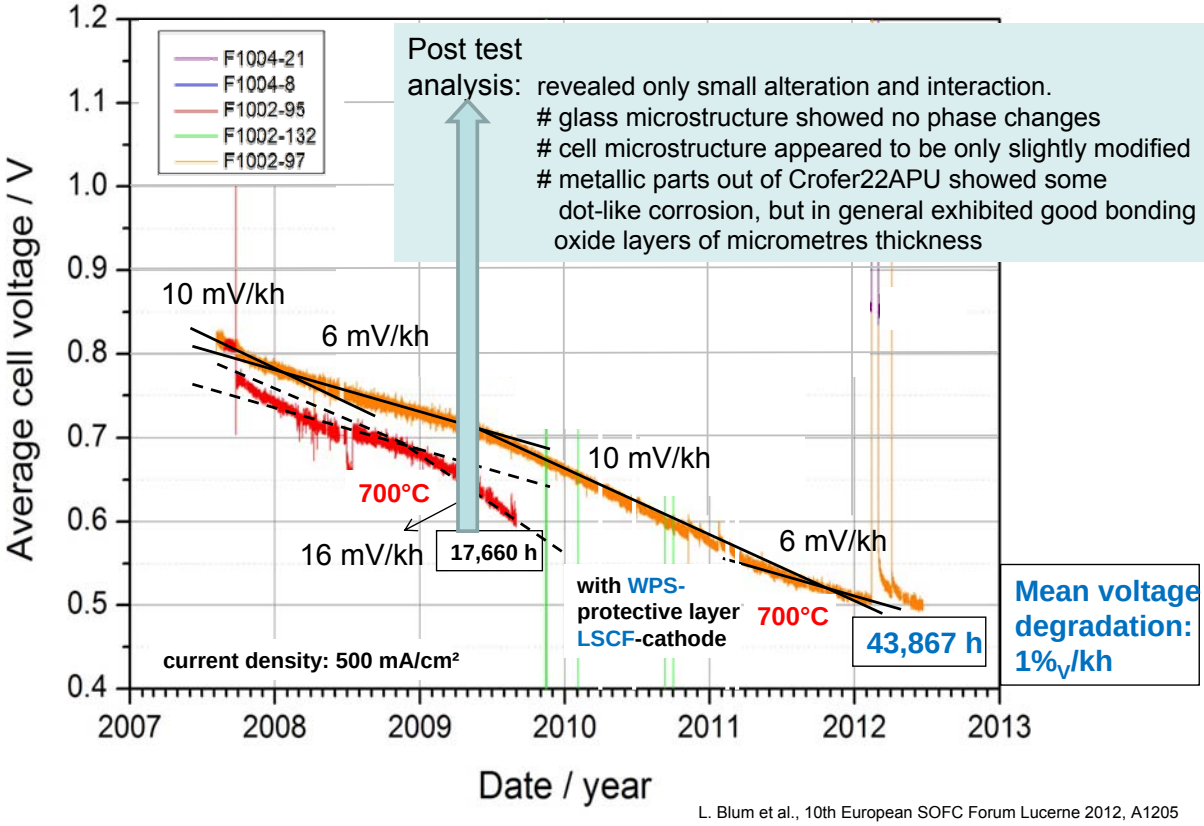
F. Tietz, FZJ

Longest running planar SOFC stack so far short-stacks F1002-95 and 97



L. Blum et al., 10th European SOFC Forum Lucerne 2012, A1205

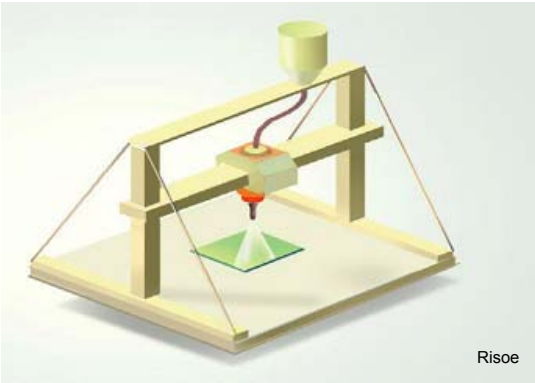
Average cell voltages as function of date for short-stacks F1002-95 and 97

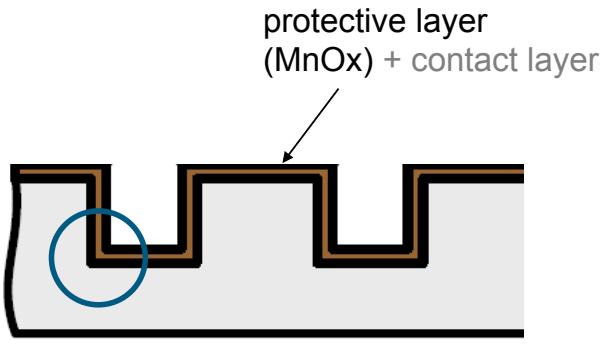


Post test analysis: revealed only small alteration and interaction.
glass microstructure showed no phase changes
cell microstructure appeared to be only slightly modified
metallic parts out of Crofer22APU showed some dot-like corrosion, but in general exhibited good bonding oxide layers of micrometres thickness

L. Blum et al., 10th European SOFC Forum Lucerne 2012, A1205

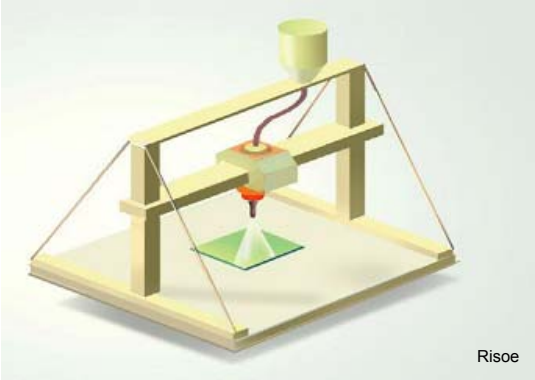
Wet powder sprayed (WPS) protective layers (Cr barrier)

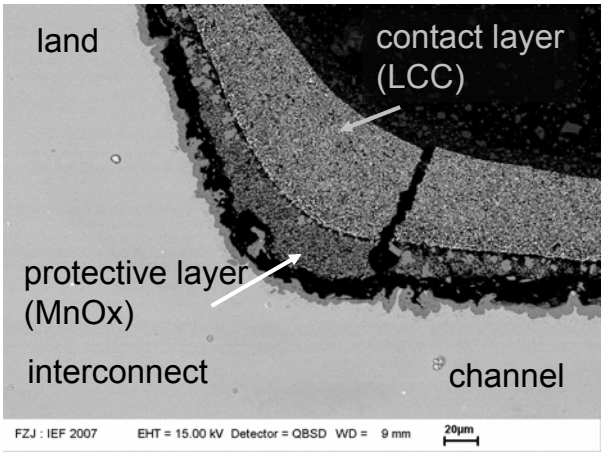




Layer homogeneity

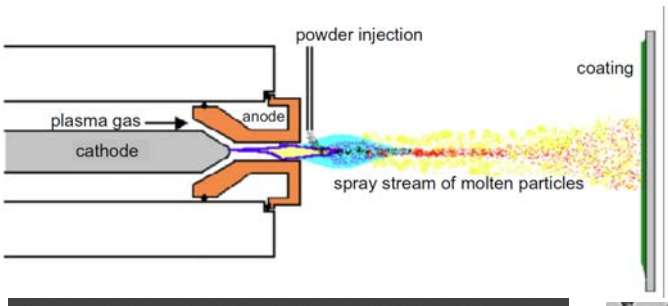
Wet powder sprayed (WPS) protective layers (Cr barrier)



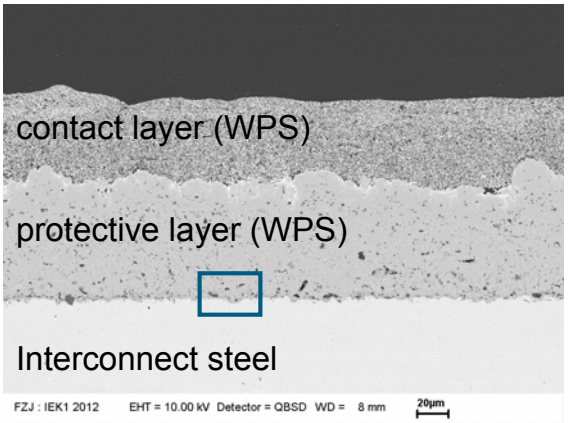


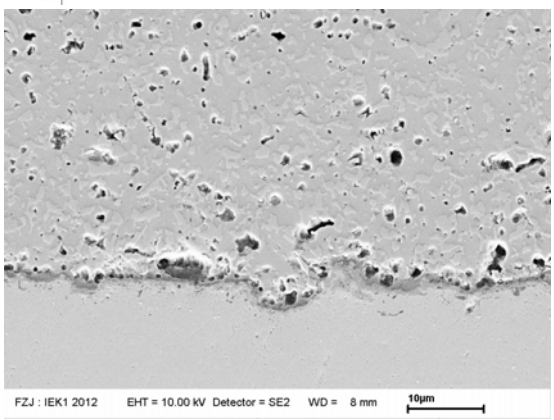
Layer homogeneity
Wet powder sprayed layers are porous (significant Cr permeation)
Chemical reactions and sintering take place

Atmospheric plasma sprayed (APS) protection layers



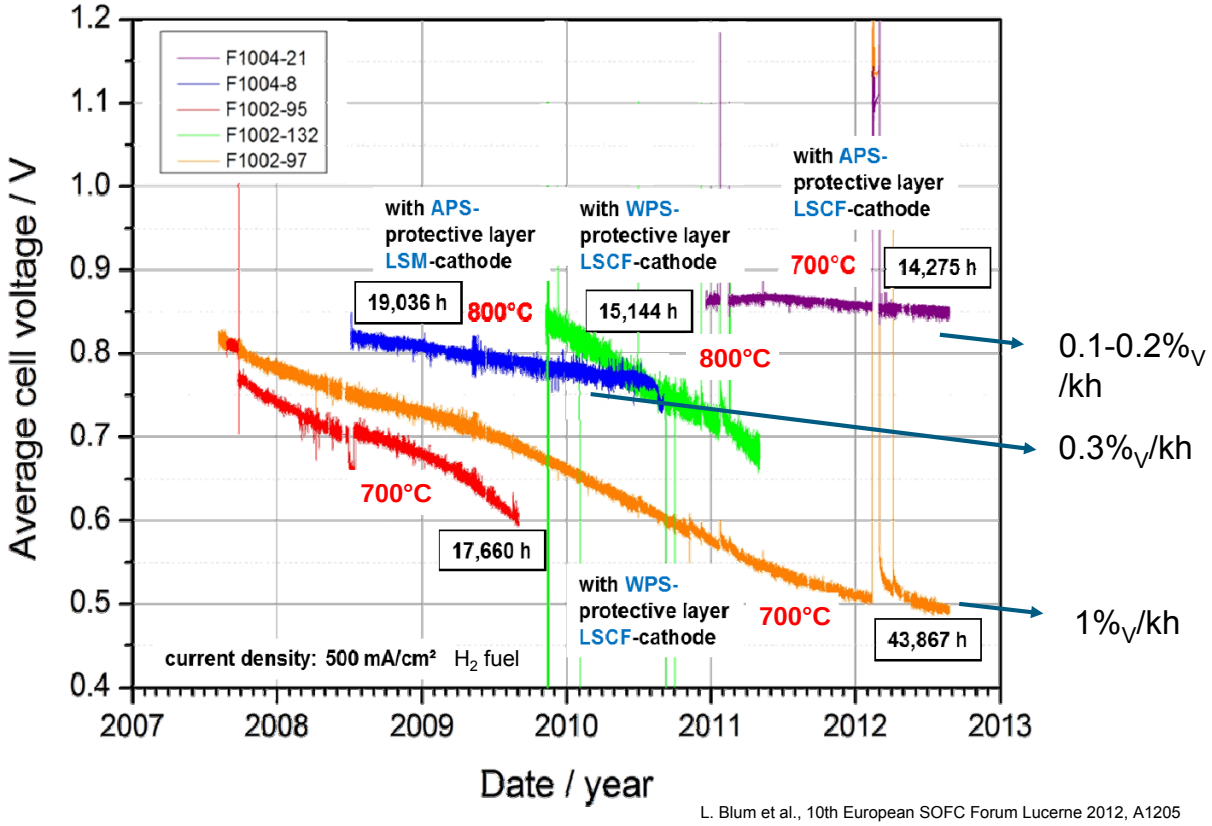
$MnCo_{1.9}Fe_{0.1}O_4$ (MCF spinel)
very dense microstructure
expected to suppres Cr diffusion more efficiently





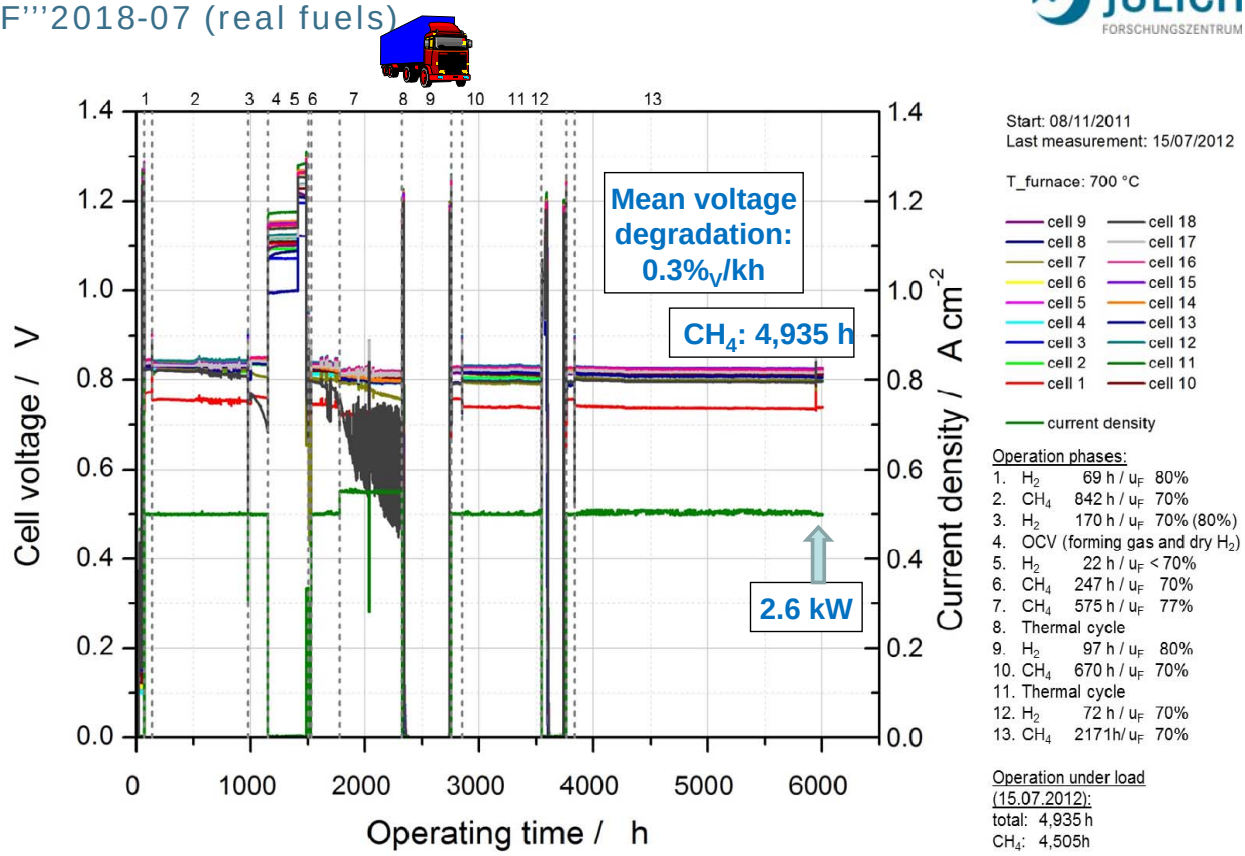
microstructure after stack sealing

Average cell voltages as function of date for short-stacks F10



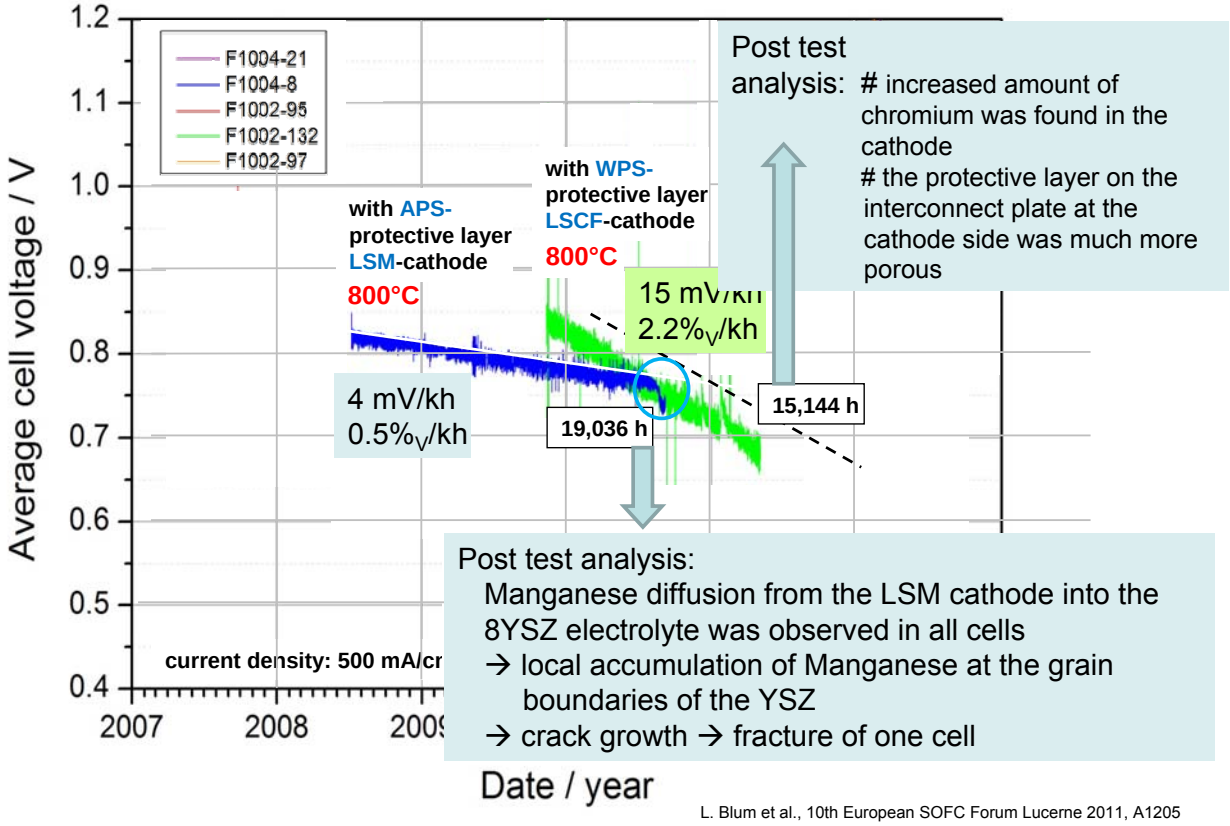
L. Blum et al., 10th European SOFC Forum Lucerne 2012, A1205

Operation behavior as function of time for stack F'''2018-07 (real fuels)



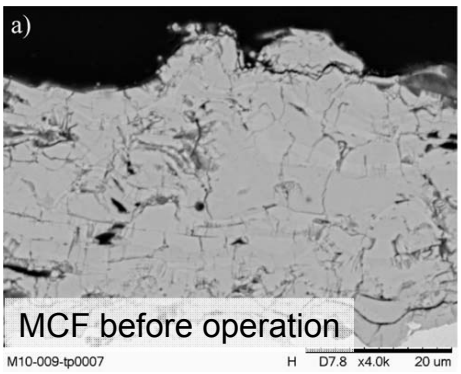
L. Blum et al., 10th European SOFC Forum Lucerne 2012, A1205

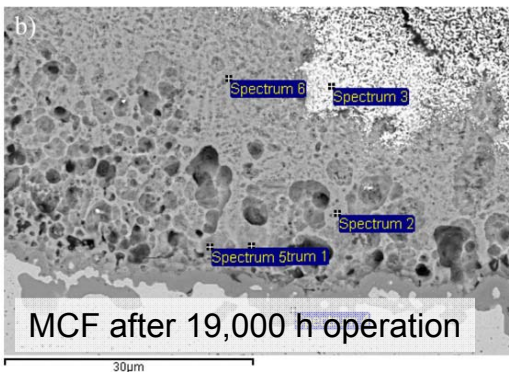
Average cell voltages as function of date for short-stacks F1002-132 and F1004-08



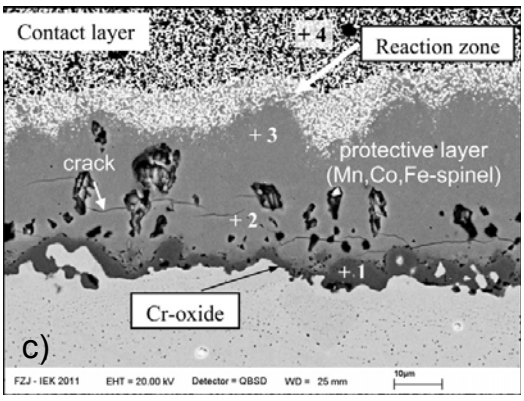
L. Blum et al., 10th European SOFC Forum Lucerne 2011, A1205

Post test analysis of stack with APS protective coating + LSM cathode





t=19,000h
j=0.5A/cm²
u_F=40%
H_2 / 3% H_2O

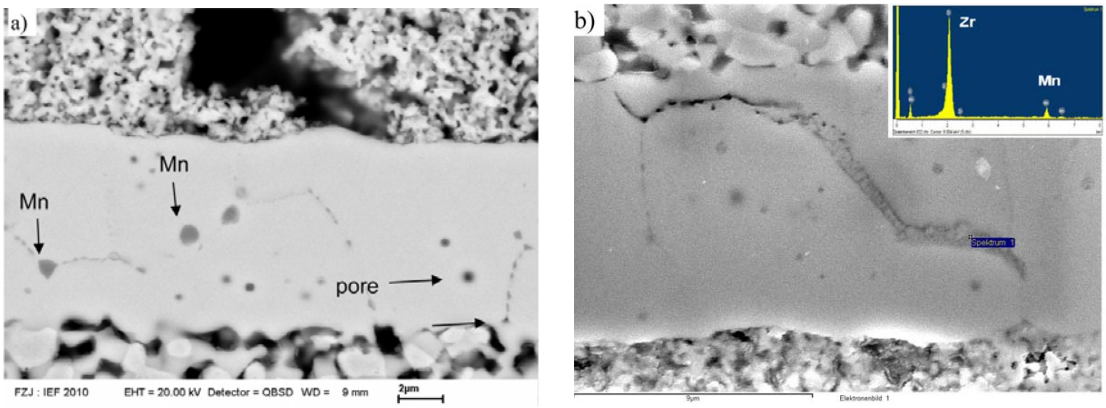


+ healing of as sprayed splat boundaries
+ Cr_2O_3 ~3µm (no spallation/delamination)
+ with almost no Fe
+ no Cr in contact layer
+ almost no Cr in MCF

– MCF becomes partly porous, cracked
– MCF slightly depleted of Co, increase of Mn, Cr
=> origin of residual degradation?

Malzbender et al., Journal of Power Sources 201 (2012) 196– 203

Mn Enrichment in 8YSZ Electrolyte after 19,000h

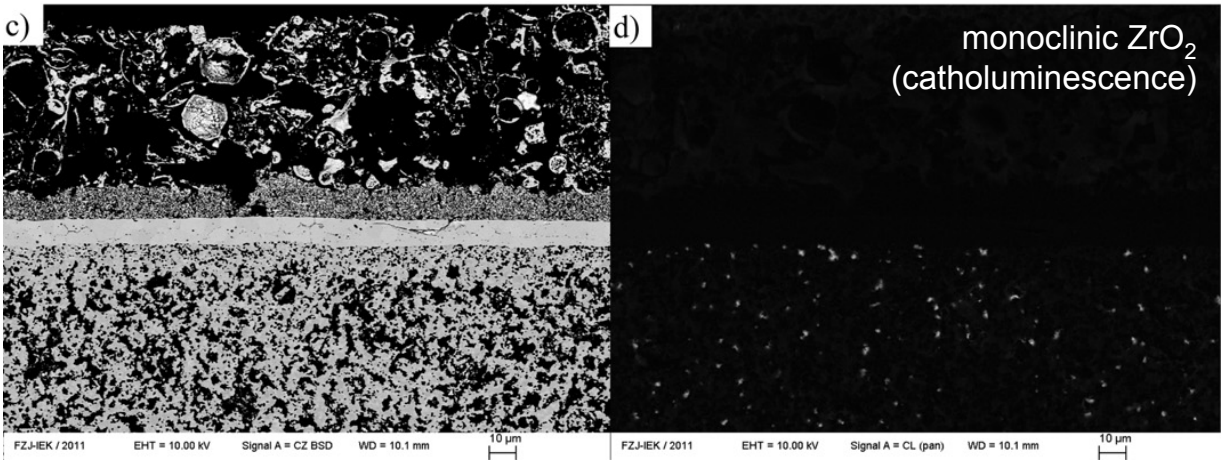


Mn accumulation in 8YSZ electrolyte on grain boundaries => separation of electrolyte,

LSM cathodes ($La_{0.65}Sr_{0.3}O_{3-\delta}$) also need cathode side barriers (e.g. CGO) for long time operation (like LSCF)

Malzbender et al., Journal of Power Sources 201 (2012) 196– 203

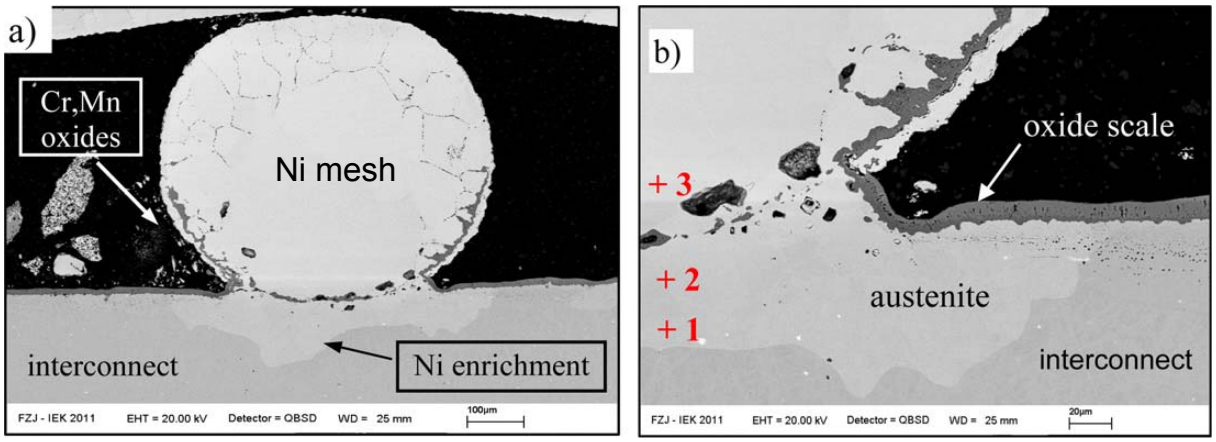
8YSZ Stability after 19,000h



Formation of monoclinic ZrO_2 only in small grains in anode (no problem for electrolyte)

Malzbender et al., Journal of Power Sources 201 (2012) 196– 203

Ni/interconnect reaction



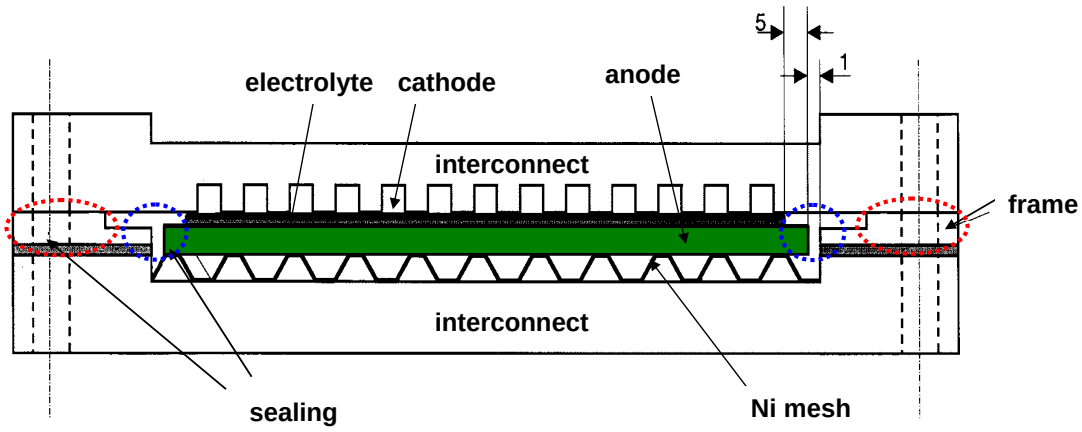
Welded interfaces of Ni mesh and interconnect (Crofer 22APU)

austenitisation of steel (large CTE, faster corrosion)
up-to now no limitation,
could change, if long-term operation and therm+redox cycles are combined

Malzbender et al., Journal of Power Sources 201 (2012) 196– 203

4. Stack Sealings

Sealing of SOFC stacks



sealing location 1: dense; isolating (short-circuit, otherwise)

sealing location 2: dense, not necessarily isolating (electrolyte is already isolating)

=> sealing in location 1 and 2 CAN be different

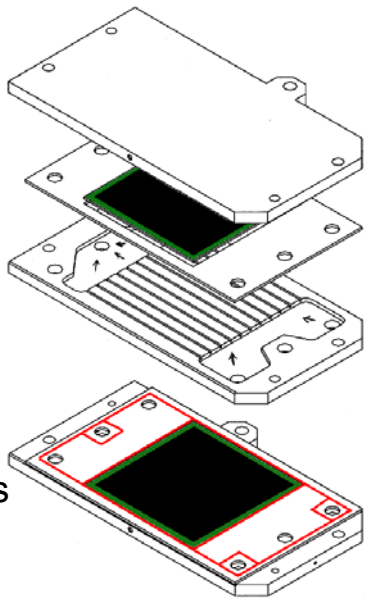
Sealing concepts and designs

planar, internal manifold

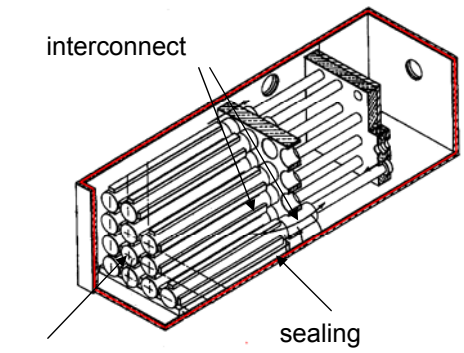
sealing at hot locations

problems today:

mechanical stability, gas-tightness after cycling

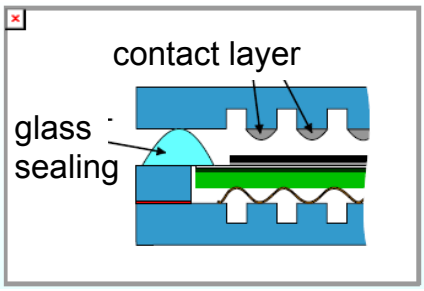


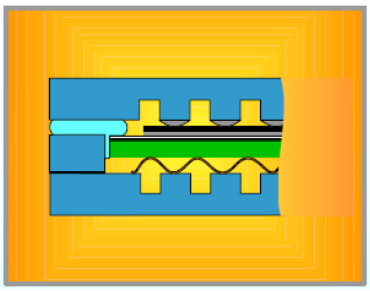
tubular

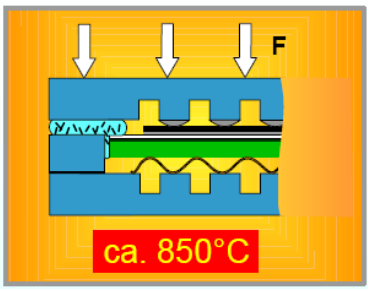


Sealing only for the outer container, not at hot locations (design depending)

Sealing procedure



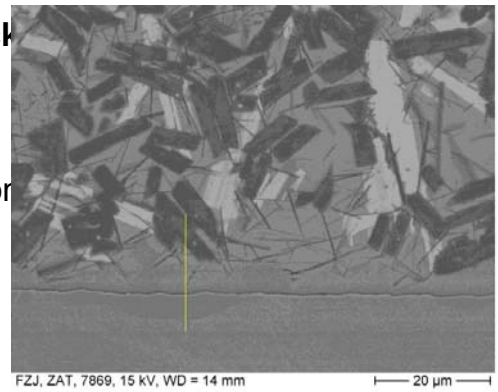




- **assemblied stack**

no contact between

cathode and intercon



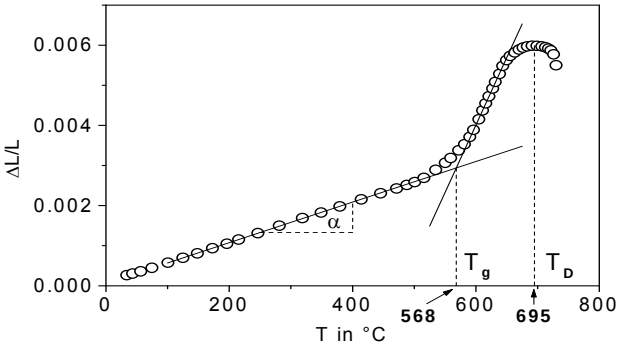
- **dwelling / sealing temperature**

contact (external load)
glass crystallization
(not before settling)
adapted shrinkage of glass
and contact layer
dwelling long enough

Glass Sealing

requirements for planar sealings:
- high electric resistance (>2 kΩ/cm²) (not fulfilled for SiO_2, sodium silicate glasses)
- adapted CTE ($\Delta\alpha$<1.5 10^{-6} K^{-1})
- mechanical loads (typical strength only 15 MPa, E = 70 GPa, ΔT=750K)
- intert against: ceel, steel, atmosphere (reducing + oxizing)

glass type	α_L in 10^{-6} K^{-1}
ULE (SiO_2-TiO_2 glass)	0.0
silica glass, 50 ppm OH	0.3
silica glass, 1200 ppm OH	1.0
DURAN®, Pyrex®	3.3
DGG-1 (float glass)	9.4
special solder glasses	35.0

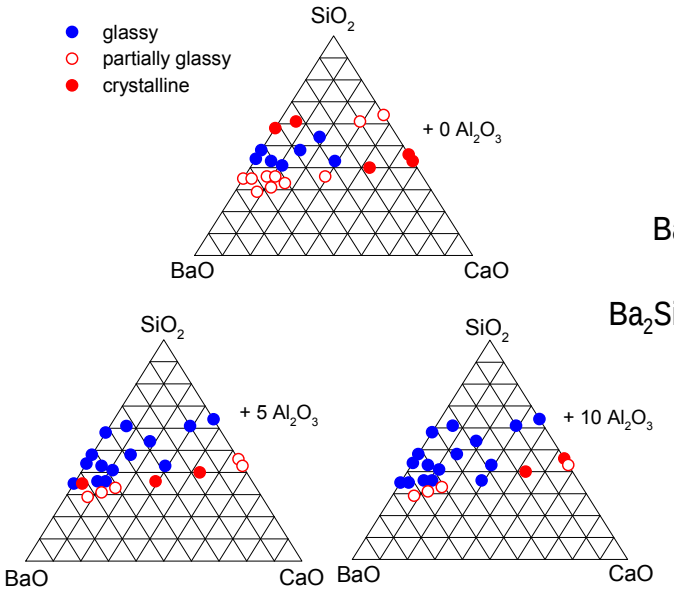


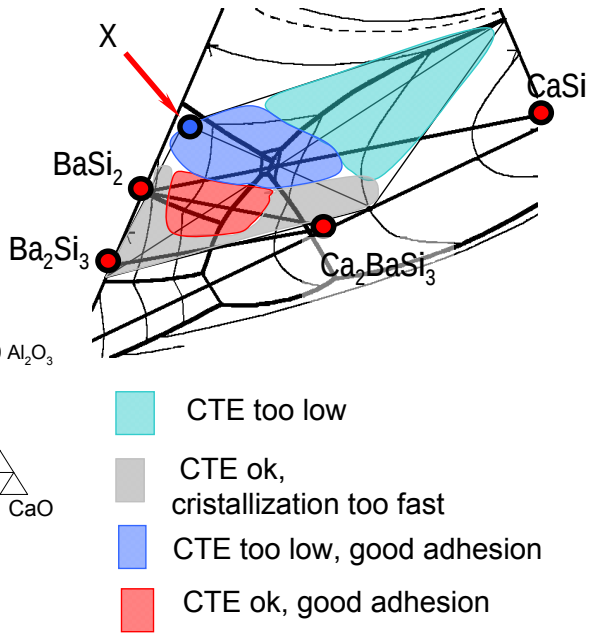
sealing process / glass transition
crystallization by change in CTE

CTE (electrolyte): 10-12 ppm/K

traditional/commercial glasses
not suitable
=> new developments started
~10 years ago
materials, interactions, manufacturing

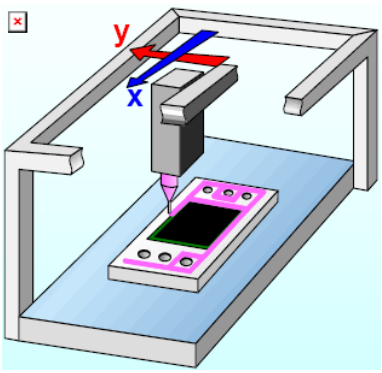
Glass, glass ceramics
System BaO - CaO - Al_2O_3 - SiO_2





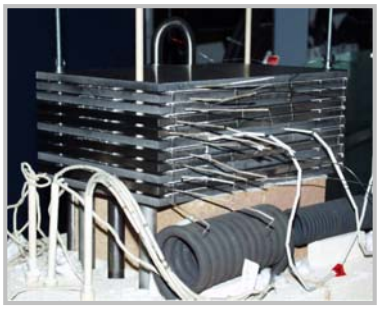
toughening with ceramic fibers/fillers (YSZ)

Glass sealed stack



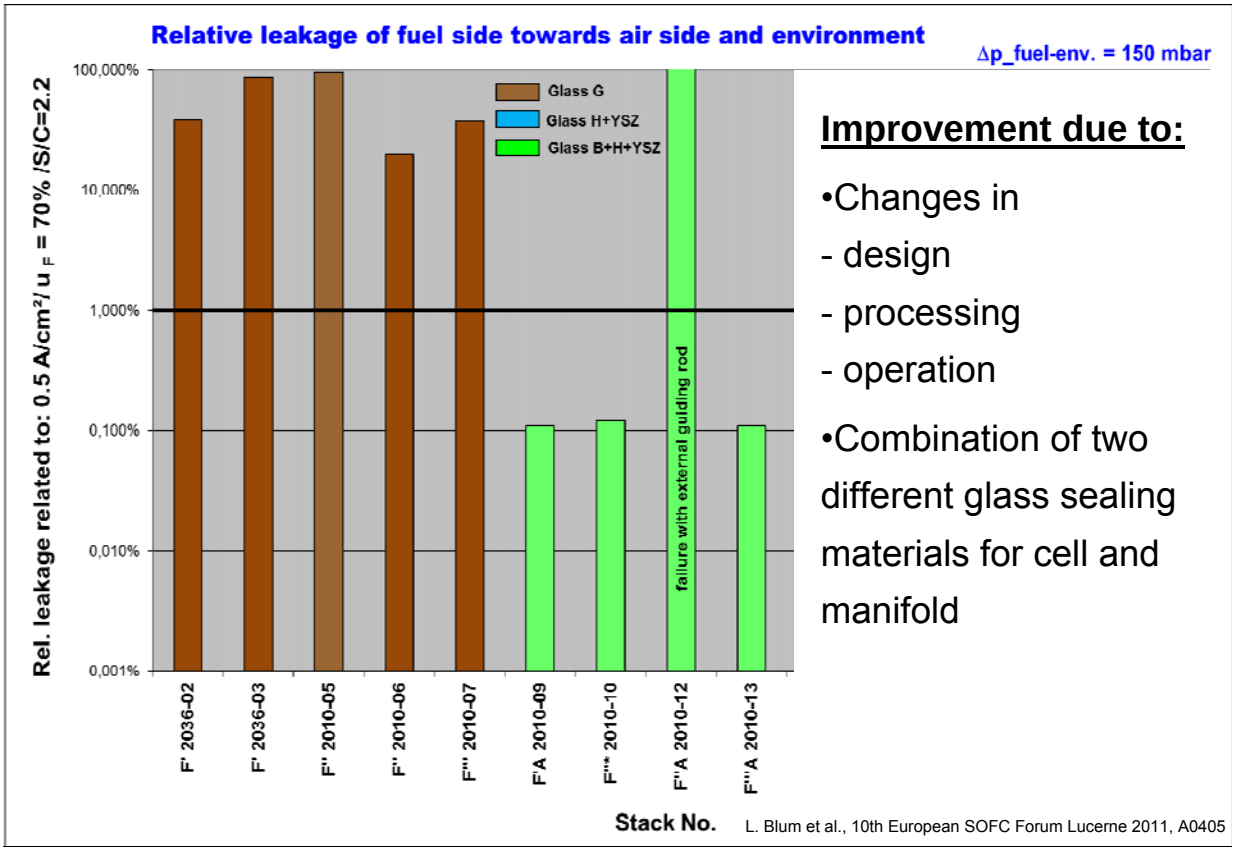
x-y dispenser

interconnects
with glass paste



stack assembly

Stack Development based on improvements of design and processing

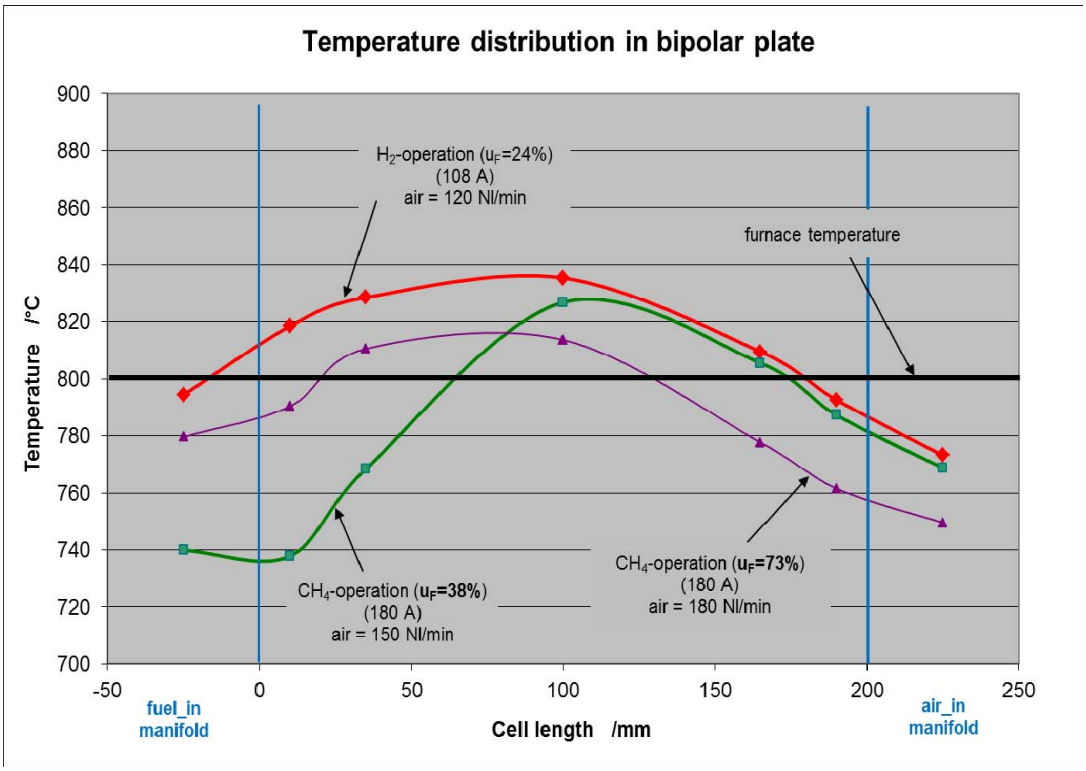


Improvement due to:

- Changes in
  - design
  - processing
  - operation
- Combination of two different glass sealing materials for cell and manifold

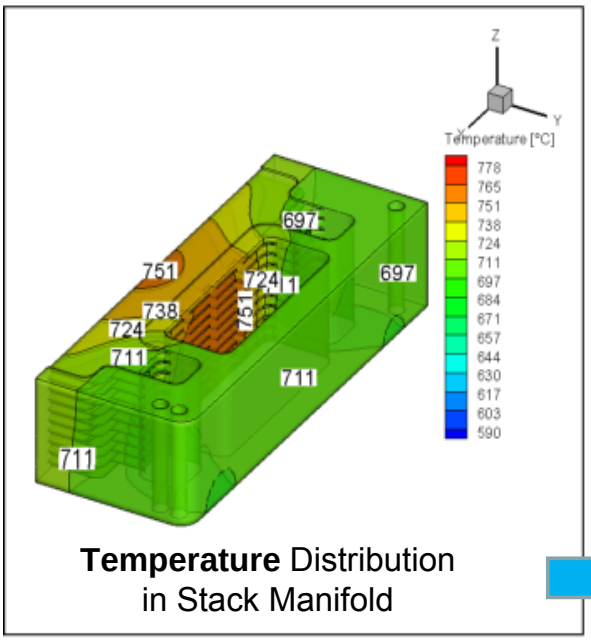
L. Blum et al., 10th European SOFC Forum Lucerne 2011, A0405

Measured temperature distribution in a 1 kW stack (10 layers 20x20 cm²) from $fuel_{in}$ to $fuel_{out}$ (= air_{in}) in case of different fuel gases and fuel utilization u_F

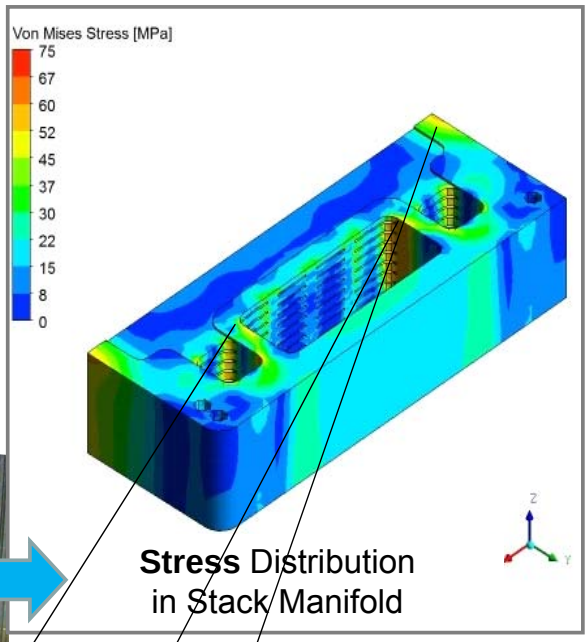


L. Blum et al., 10th European SOFC Forum Lucerne 2011, A0405

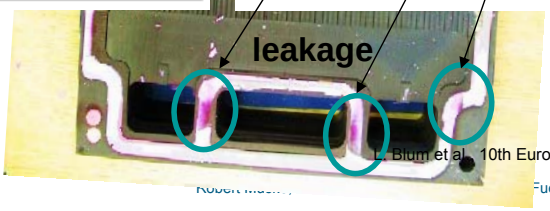
CFD and FEM Analysis of Stack for further design improvement



Temperature Distribution in Stack Manifold

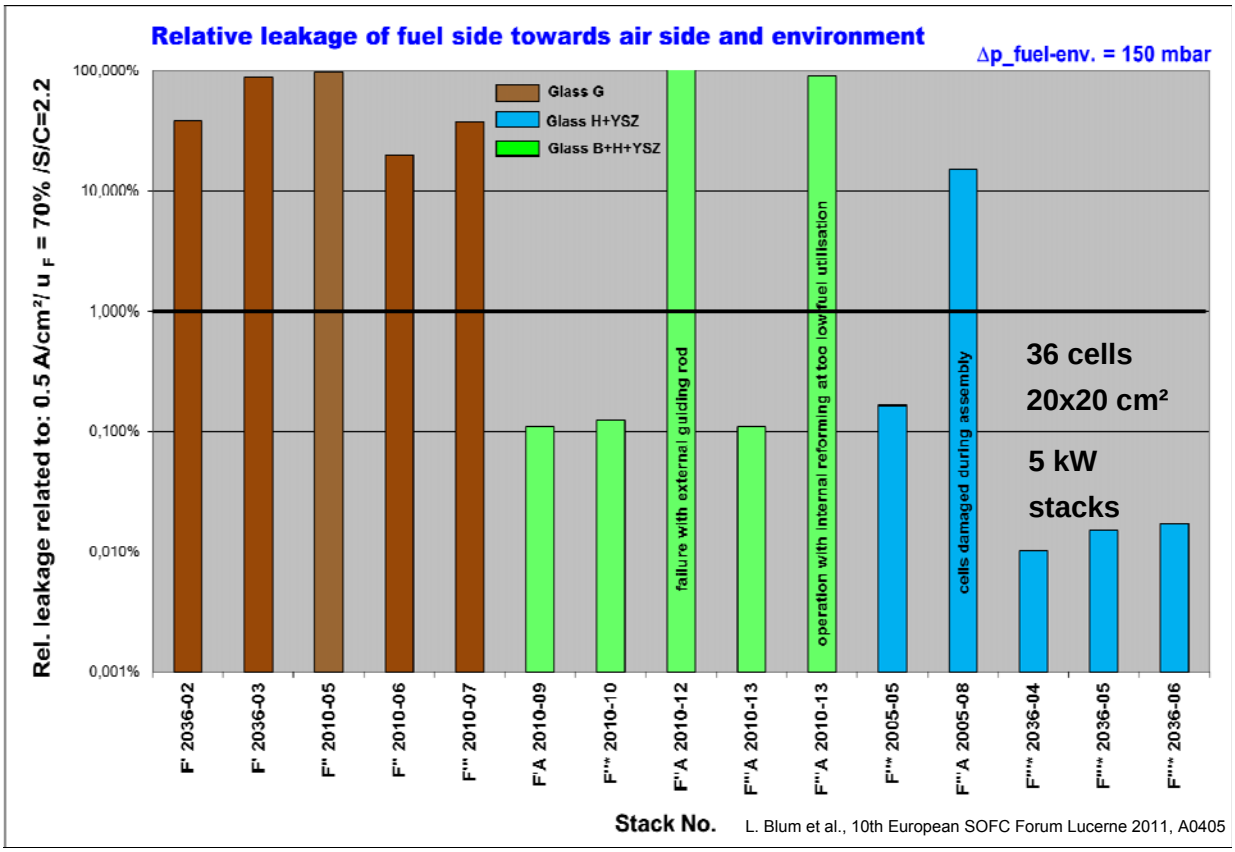


Stress Distribution in Stack Manifold



L. Blum et al., 10th European SOFC Forum Lucerne 2011, A0405

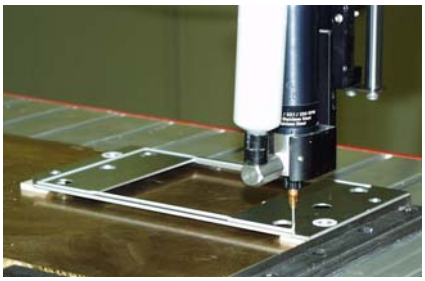
Stack Development based on improvements of design and processing



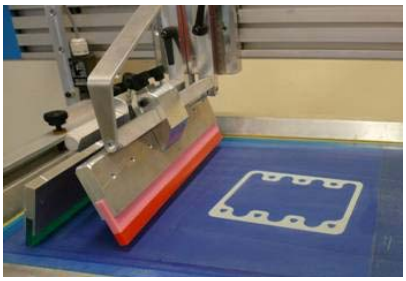
L. Blum et al., 10th European SOFC Forum Lucerne 2011, A0405

Application of Sealing of ASCs

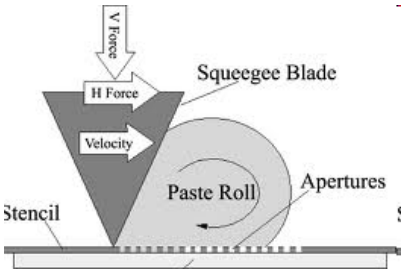
dispenser



screen printing

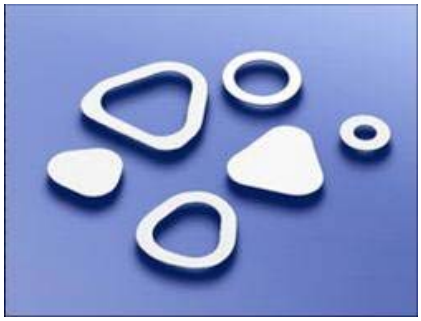


stencil printing



(metallic mask and blade)

stamped, tape-cast foils



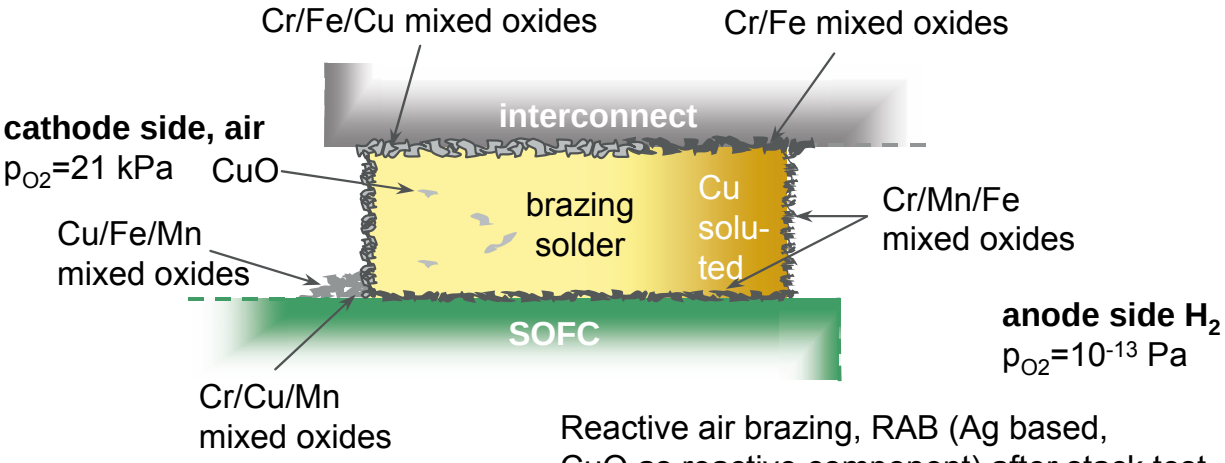
Kerafol, HC Starck

characteristics:

dispenser: very flexible, slow, not scalable
screen printing: fast, flexible, special screens for large thicknesses (0.3 .. 0.5 mm)
stencil printing: large thicknesses, requires very flat support
stamped foils: basic shapes very accurate, shrinkage due to large amount of organics, limited material efficiency (recycling)

D. Federmann, S. Groß, ZAT, FZ Jülich

Metallic Brazing



Reactive air brazing, RAB (Ag based, CuO as reactive component) after stack test

- reaction zone of classical RAB solders lead to mechanical failure
→ pure Ag (without CuO) more difficult to wet, but better stability
- especially reducing condition lead to aging
- pre-oxidation of interconnect steel necessary
- interconnect brazing => insulation layer necessary (e.g. by thermal spraying, difficult to make completely "brazing solder" dense)

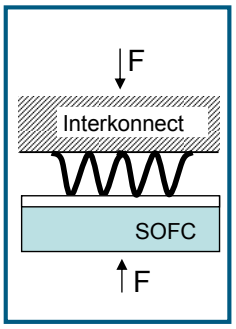
B. Kuhn, PhD Thesis, FZ Jülich, 2009

Alternative Compressible Sealings

Metals

- massive sealing
  Ag wire,
- structures sealings
  E ring
  C ring
  O ring
- stamped sealings

  interconnect steal
  laser cut / stamped

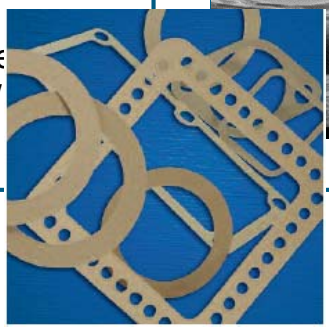


Alternative Compressible Sealings

Metals

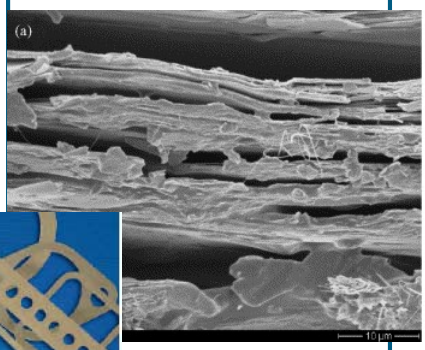
- massive sealing
  Ag wire,
- structures sealings
  E ring
  C ring
  O ring
- stamped sealings

  interconne
  laser cut /



Mica

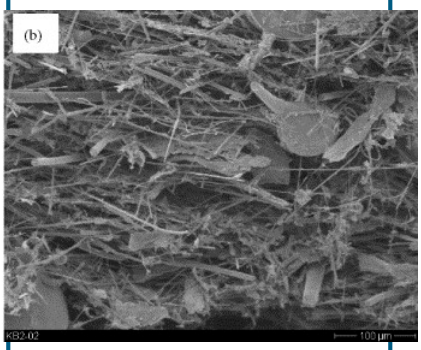
- mica powder
  in pastes / mica paper



thermiculite

Ceramics

- ceramic powder with
  binder/paper



Bram et al., J. Power Sources 2004

Alternative Compressible Sealings

JÜLICH FORSCHUNGSZENTRUM

Metals

- massive sealing
  Ag wire,
- structures sealings
  E ring
  C ring
  O ring
- stamped sealings

  interconnect steal
  laser cut / stamped

Mica

- mica powder
  in pastes
- mica paper + binder
- mica paper + binder
  and metallic inlay

$AB_2(X,Si)_4O_{10}(O,F,OH)_2$
A=K; X=Al
B=Zn,Cr,V,Ti,Mn,Mg

cut / laser cut / stamped

Ceramics

- ceramic powder with binder
- cermic paper with ceramic filler

(e.g. fiber felts)

Global Thermoelectric 2002

Al_2O_3, SiO_2, Al_2O_3-SiO_2
cut / laser cut

combinations possible

Bram et al., J. Power Sources 2004

Alternative Compressible Sealings

JÜLICH FORSCHUNGSZENTRUM

Metals

- works with realistic loads (< 5 N/mm)
  leak-rates < $2{,}4 \cdot 10^{-4}$ hPa·dm³/s·mm
- elastic recovery neglectible
- significant creep
  ⇒ thickness ↑
  ⇒ fillings (Glimmer)
- insulation layer necessary

Mica

- high leakages even with high loads (> 28,6 N/mm)
- highest elastic recovery (800°C) approx. 50 - 60 µm for thickness 1 mm
- no creep (pure mica), stability problems
  ⇒ incapsulation

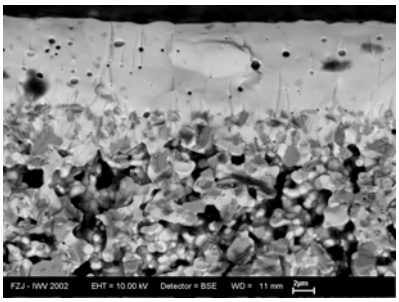
Ceramics

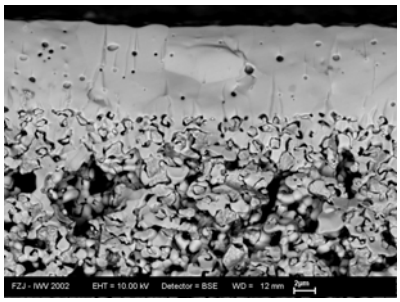
- high leakages even with high loads (> 28,6 N/mm)
- low elastic recovery (800°C)
  approx. 10 - 20 µm for thickness 1 mm
- further deformation (creep, fiber rearrangement)
- little overal potential

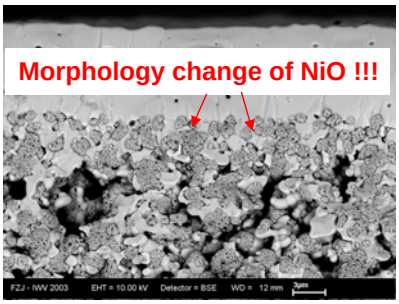
→ combination of metallic sealing (structured) and mica filling

5. Reoxidation
System or Material Solution?

Ni-Cermets
Reoxidation







Manufacturing:

Oxidized state
8 YSZ + **NiO**

Addition of Ni as NiO => ceramic procesing
- small particle sizes
- sintering on air

Operation:

Reduced state
8 YSZ + **Ni**

NiO => Ni under anodic conditions;
formation of current paths

Re-oxidation during operation:

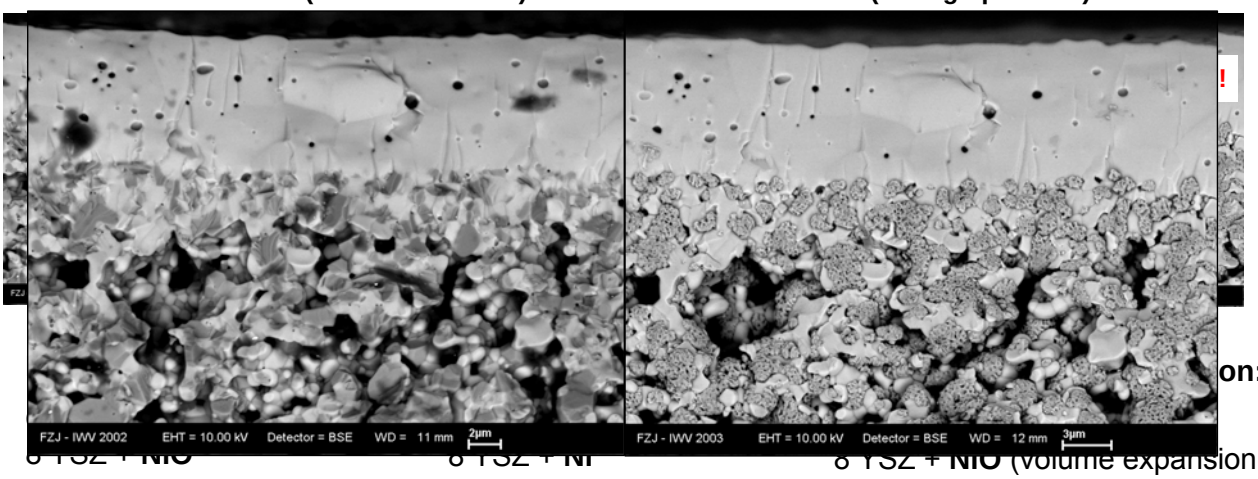
Oxidized state
8 YSZ + **NiO** (volume expansion)

Ni may re-oxidize to NiO under bad operation conditions like ingress of air on anode side (leakage, cleaning reformer by burning C deposits)

J. Malzbender *et al.*, *Solid State Ionics* **176** (2005), 2201-2203.

Ni-Cermets
Reoxidation

oxidized (as manufactured) | reoxidized (during operation)



on:

8 YSZ + NiO (volume expansion)

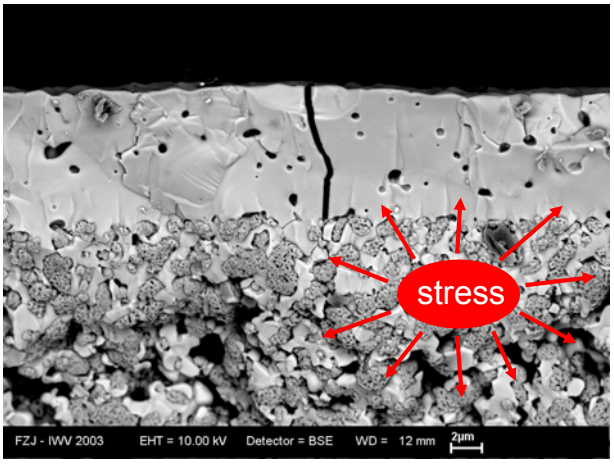
Addition of Ni as NiO => ceramic procesing
- small particle sizes
- sintering on air

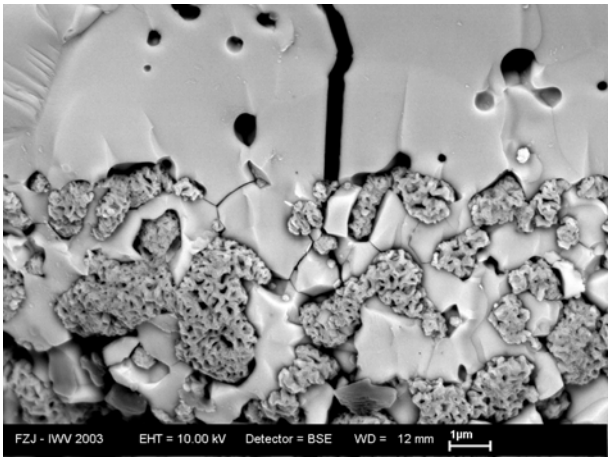
NiO => Ni under anodic conditions;
formation of current paths

Ni may re-oxidize to NiO under bad operation conditions like ingress of air on anode side (leakage, cleaning reformer by burning C deposits)

J. Malzbender *et al.*, *Solid State Ionics* **176** (2005), 2201-2203.

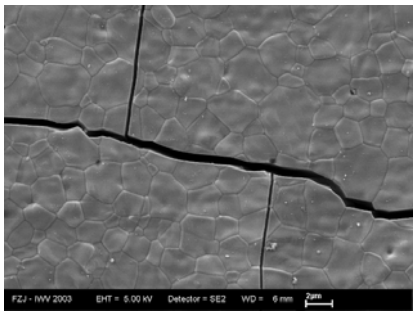
Ni-Cermets
Reoxidation





electrolyte cracks after re-oxidation

top view
intragranular cracks



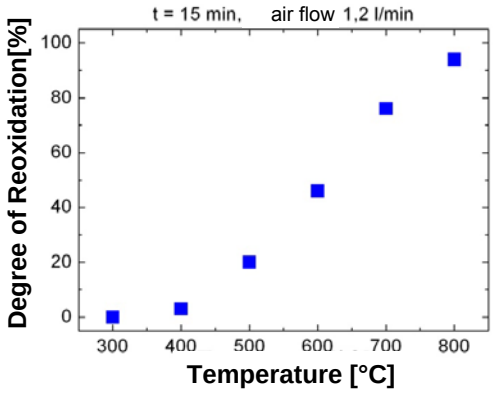
$\delta_{\text{tensile sress}} >$
$\text{Strength}_{\text{YSZ}} + \delta_{\text{residual compressive stress}}$
(~ 1000 MPa)

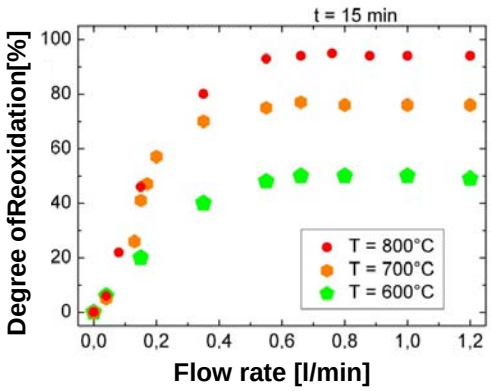
Damages due to Reoxidation Anode Supported Cells

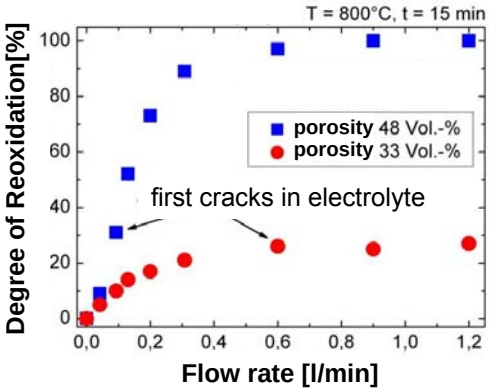
Different types of ASCs after 100 redox cycles
800°C (50x 1min air flow, 50x 10min air flow)

A. Weber, in J. Garche (Ed.), Encyclopedia of Electrochemical Power Sources, Oxford: Elsevier, (2009).

Ni-Cermets Reoxidation Studies on ASCs (Half-Cells)







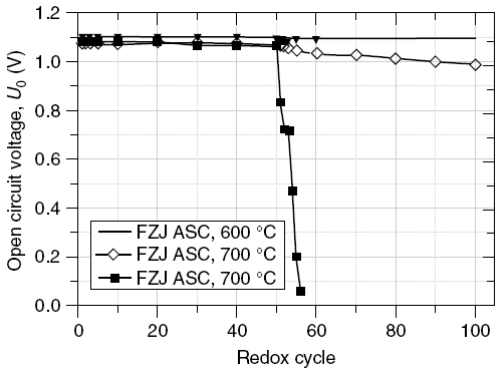
If a **fixed** amount of air has to pass the anode, the damage is less
- the lower the temperature
- the faster the flow
- the denser the substrate

the system (BOP) has to provide a solution

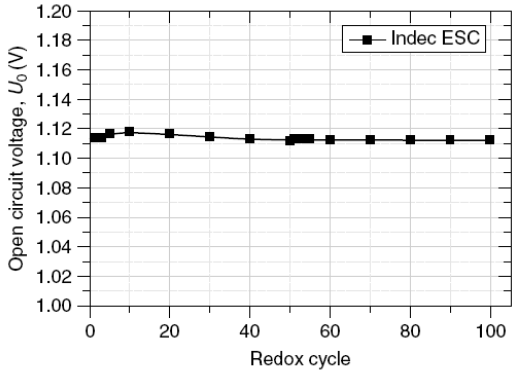
M. Ettler, PhD Thesis, 2009
E. Ivers-Tiffée *et al.* inHandbook of Fuel Cell, Vol. 6, Chap. 64

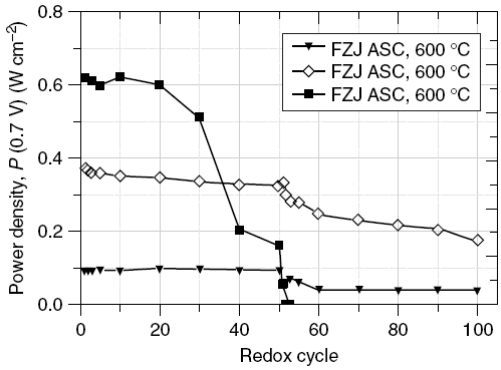
Reoxidation
Comparison between ASCs and ESCs

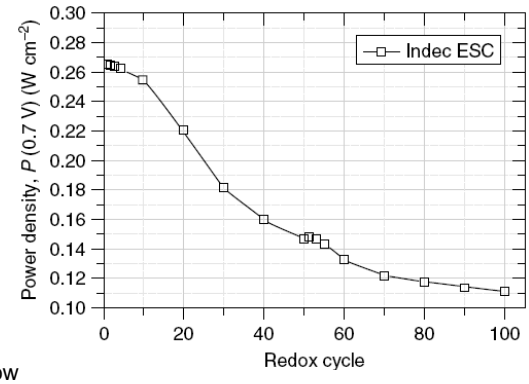
partly catastrophic damage in ASCs



progressing damage in ESCs (~50%)







redox cycle 1-50: 1min air flow, cycle 51-100: 10 min air flow

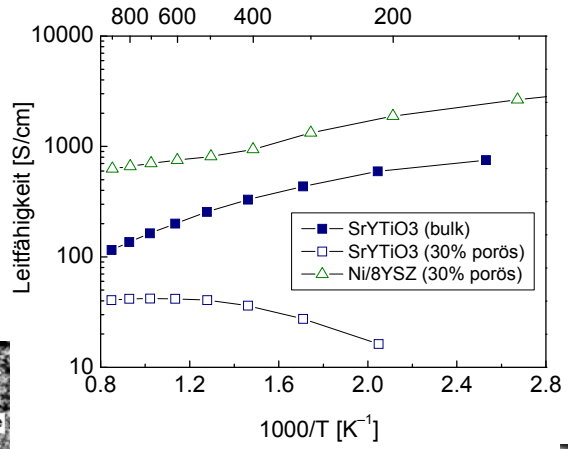
E. Ivers-Tiffée *et al.* in Handbook of Fuel Cell, Vol. 6, Chap. 64

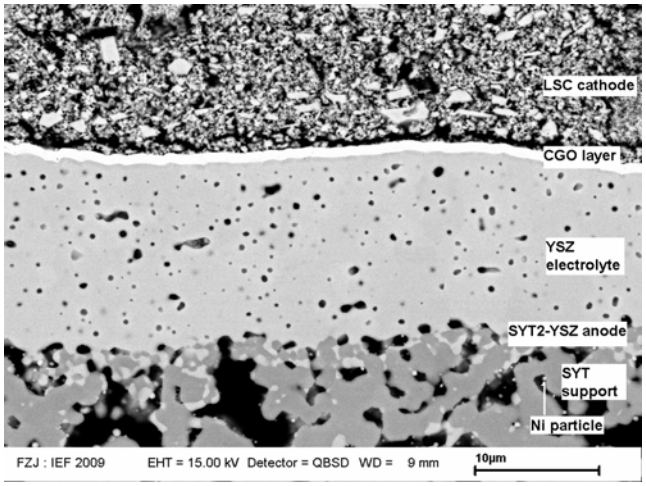
Perovskite Anode Materials

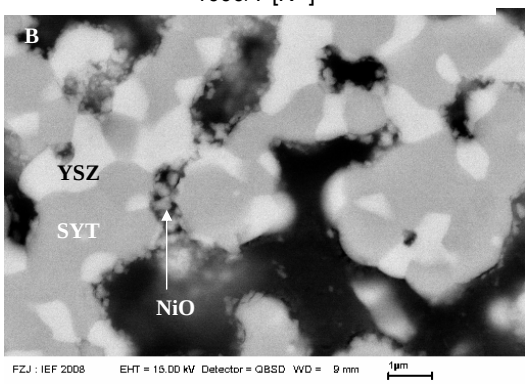
no Ni-Cermet is fully redoxstable
⇒ new materials

e.g. $Sr_{0.89}Y_{0.07}Ti_{1.1}O_{3-\delta}$ (SYT)

- acceptable conductivity
- no reoxidation
  (but Ti valence change $Ti^{3+} \Leftrightarrow Ti^{4+}$)
- 3% NiO infiltrated for catalytic activity

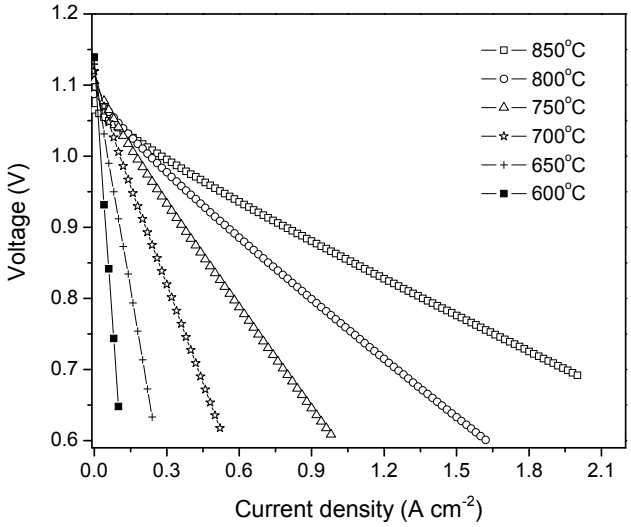






Q. Ma, IEK-1, FZJ

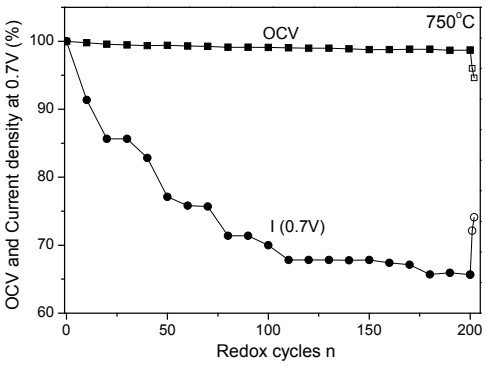
Typical iV-characteristics of the SYT based cells (5.0 x 5.0 cm²) (tested in KIT)

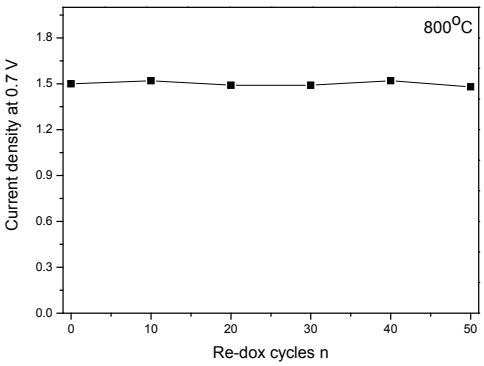


The actual data for all the tested cells so far varied from 1.0 to 1.5 A cm^{-2} at 0.7 V and 800 ° C.

Current-voltage curves of the cell for six different temperatures ranging from 600 to 850° C. The OCV of the cell is 1.09V at 800°C. The power output is 1.22 A cm^{-2} at 0.7 V and 800°C

Redox stability of SYT based single cells (5.0 x 5.0 cm²)

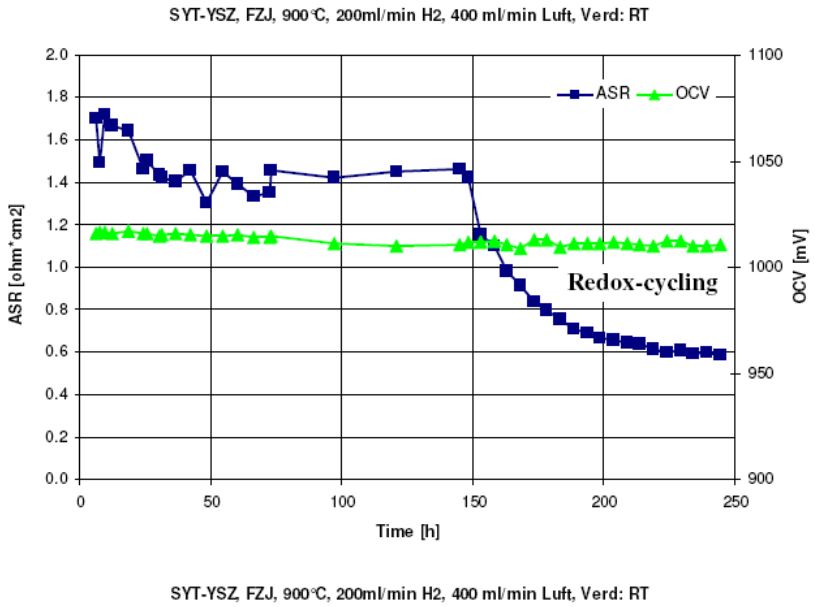




OCV and current density at 0.7 V of a cell in dependence of the number of redox cycles at 750 °C. after 200 redox cycles, the OCV only decreased by 1.3 %, the performance of the cell decreased by 35 %. ***Test protocol for one redox cycle: Solid dot: 10 min in air and 10 min in H_2. Hollow dot: 5 h in air and 5 h in H_2.***

Current density at 0.7 V of a cell in dependence of the number of redox cycles at 800°C. ***Test protocol for one redox cycle: 10 min in air and 2 h in H_2.***

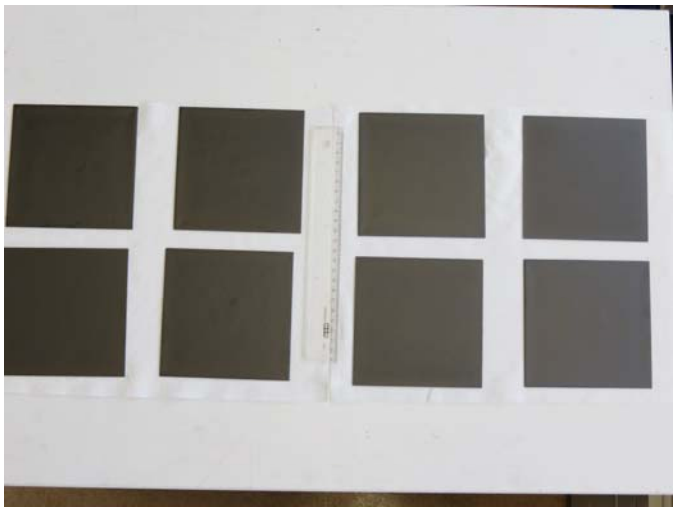
Performance of ESCs (Hexis, ∅ 2 cm) based on SYT-YSZ anodes



SYT-YSZ, FZJ, 900°C, 200ml/min H2, 400 ml/min Luft, Verd: RT

Time dependence of ASR for the ESC of SYT-YSZ (3 wt% Ni) / ScSZ / LSCF. The performance of standard Hexis-ESCs based on Ni-YSZ anode at similar conditions is about 0.3 ohm cm^2

Stack building (10 x 10 ~ 13 x 13 cm^2 single cells)



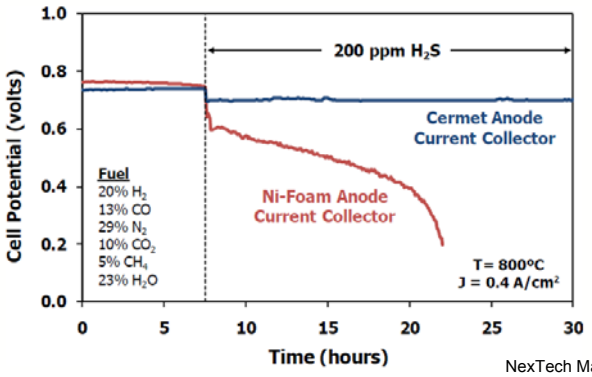
Original plates after warm-pressing: 30 × 30 ×0.16 cm^3 can be cut into suitable size for single cell fabrication.

Qualified 10 x 10 ~ 13 x 13 cm^2 single cells were already fabricated. Stack buiding and testing are continuing.

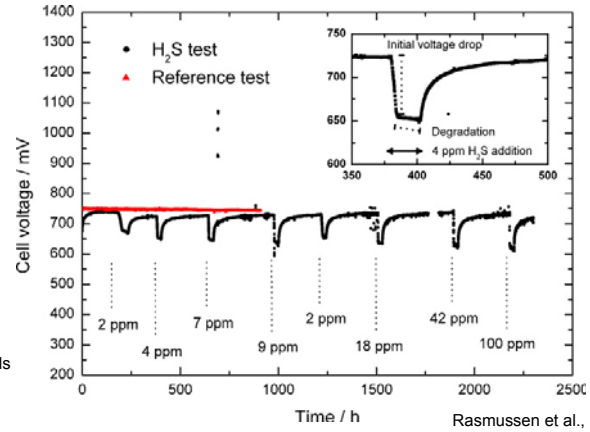
Main problem/challenge of perovskites: mechanical propertiers (strength)

6. Fuel and Fuel Impurities

Sulfur Poisoning



NexTech Marials



Rasmussen et al., J. Power Sources 191 (2009) , 534

Irreversible destruction of Ni anode for large S amount

degradation & partly recovery for small S amounts

S present in all fuels
(upto 5000 ppm in American diesel,
2000 ppm in doemstic fuel oil,
10 ppm in [cleaned] natural gas)

Sulfur Poisoning
Reactions

S adsorption on catalyst (Ni) surface (dominant <50 ppm)

$$H_2S(g) \leftrightarrow HS_{ads} + H_{g/ads} \leftrightarrow S_{ads} + H_{2,g/ads}$$

Reaction with Ni

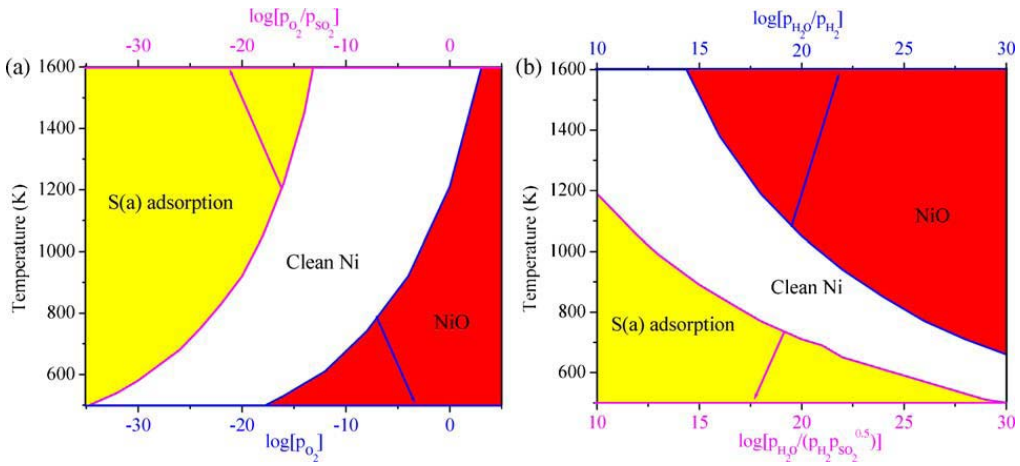
$$Ni + H_2S \leftrightarrow NiS + H_2$$
$$3Ni + xH_2S \leftrightarrow Ni_3S_x + xH_2$$

adsorbed S (1) hinders H_2/H_2O diffusion, and (2) stops CO shift reaction (carbon part of fuel does not contribute to performance anymore)

Rasmussen et al., J. Power Sources 191 (2009) , 534

Sulfur Poisoning
Surface Generation / Operating Conditions

S regeneration:
(1) increase fuel untilization, (2) increase O^{2-} concentration at TPB
(3) introduce O_2, (4) H_2O to the anode, (5) increase temperature



Favorable: $O_2+S \rightarrow SO_2$ $\quad$ $H_2O+S \rightarrow H_2+SO_2$

Drawback: $\frac{1}{2}O_2+Ni \rightarrow NiO$ $\quad$ $H_2O+Ni \rightarrow H_2+NiO$

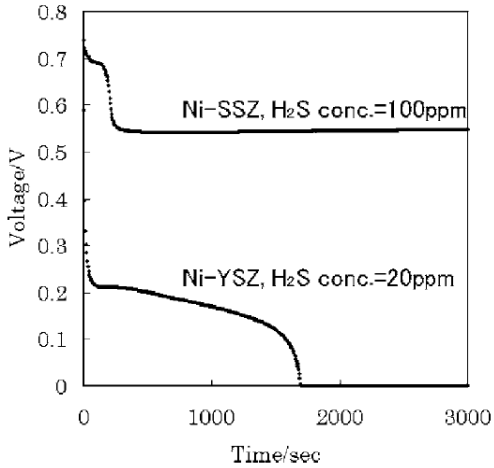
$S+2O^{2-} \rightarrow SO_2+4e^-$

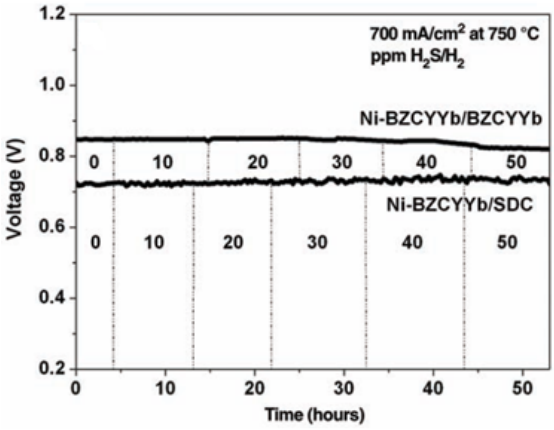
J.H.Wang, et.al., Journal of Power Sources, 176 (2008), 23
cf. J.H.Wang, et.al., Electrochem. Comm., 9 (2007), 2212

Sulfur Poisoning
S Tolerant SOFC

Ceramic anodes infiltrated with Ni still affected => approaches:

(1) ceramic anodes without Ni
(2) MeS anodes (low performance, CO poisoning)
(3) Electrolytes that allow ectrochemical oxidation of S





ScSZ instead of YSZ (provide O^{2-} for S oxidation)

K.Sasaki, et.al., J. of The Electrochem. Soc., 153(11),2006, A2023-A2029.

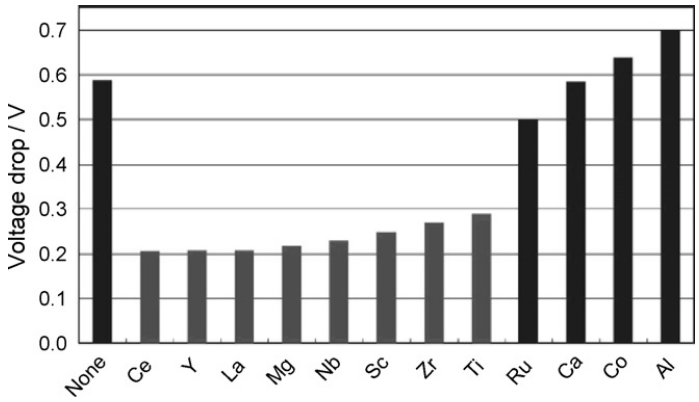
new electrolyte materials
$BaZr_{0.1}Ce_{0.7}Y_{0.1}Yb_{0.1}O_{3-\delta}$

L.Yang, et.al., Science, 326, 2009, 126-129.

Sulfur Poisoning
S Tolerant SOFC

approaches:

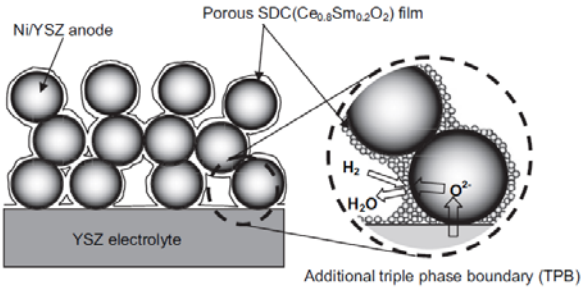
(4) Coat Ni surface (Nb_2O_5, BaO)
(5) Infiltrate traditional Ni/8YSZ cermets

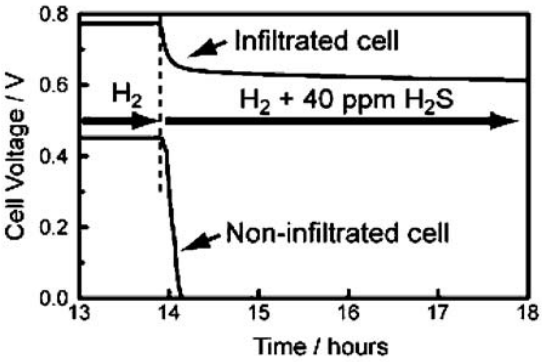


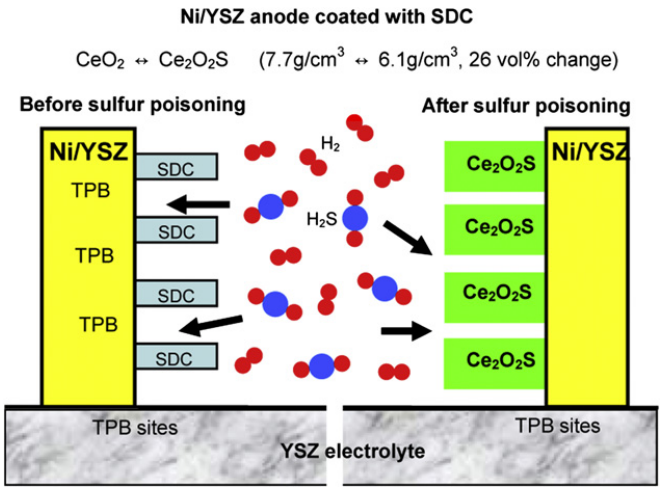
Cell voltage drop with various additives impregnated in porous anode at 200mAcm^{-2} (800°C, H_2S concentration = 20 ppm, H_2/CO 100:0, electrolyte/SSZ, anode/Ni–YSZ + impregnated additives)

K. Sasaki, et al., J. Electrochem. Soci. 153 (11) (2006) A2023–A2029

Sulfur Poisoning
S Tolerant SOFC







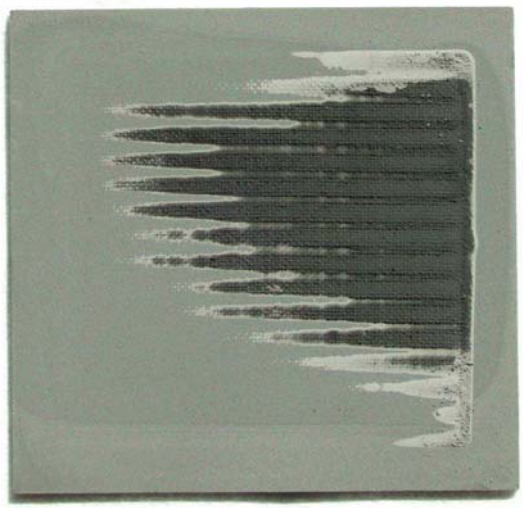
$$2CeO_{2-x}(s) + H_2S(g) + (1-2x)H_2(g) \leftrightarrow Ce_2O_2S(s) + 2(1-x)H_2O(g)$$

$$Ce_2O_2S(surf.) + 4O^{2-} \rightarrow 2CeO_{(2-\delta)}(s) + (1-\delta)SO_2(g) + 8e$$

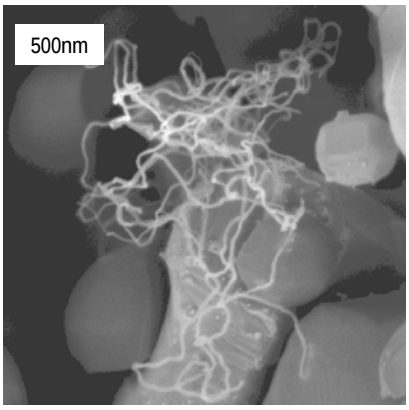
Processing issue: GDC+8YSZ react >1000°C
(ok for sol-gel, electrolyte supported cells)

H.Kurokawa, et.al., Electrochemical and Solid-State letters, 10(9),2007, B135-B138.
dense GDC layers: cf. Xu et al., J. Power S. 158 (2011), B1405

Carbon Deposition on Ni Cermets
Metal Dusting



50x50mm



Ni carbide
not stable
under operating
conditions

C filaments grow
inside Ni grains
⇒ grains burst
⇒ cell disintegrates

after operation for 10 h in mixture of 0.1% C_2H_2 and base reformate 300 mA/cm² and 650ºC

⇒ carbon fuel with Ni cermet anodes (and/or substrates) needs operating temperatures >650°C!
⇒ or material solution (similar to S problem)

A. Weber, presented in Nara, SOFC-X, 2007
c.f. A. Weber, in J. Garche (Ed.), Encyclopedia of Electrochemical Power Sources, Oxford: Elsevier, (2009).
cf. Yang et al, Nature Communications 2 (2011), 357

7. Metal Supported Cells (MSC)

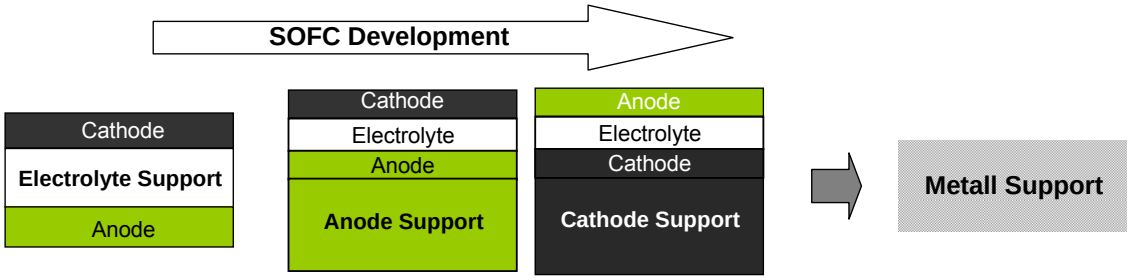
APUs on the road

KOHLER Diesel APU
Kohler Power Systems
1 or 2 cylinder diesel (0.35-0.7L)
(air or water cooled)
3.5-12.5 kW
68-71 dB
120-300L, 110-250kg

Delphi SOFC APU (ASC)
5kW announced for 2012
15% less fuel than diesel APU
requires *low-sulfur diesel*
η_{el} ~ 30% (diesel, 40% with nat. gas)
T_{op}=700°C
incl. independent vehicle heater

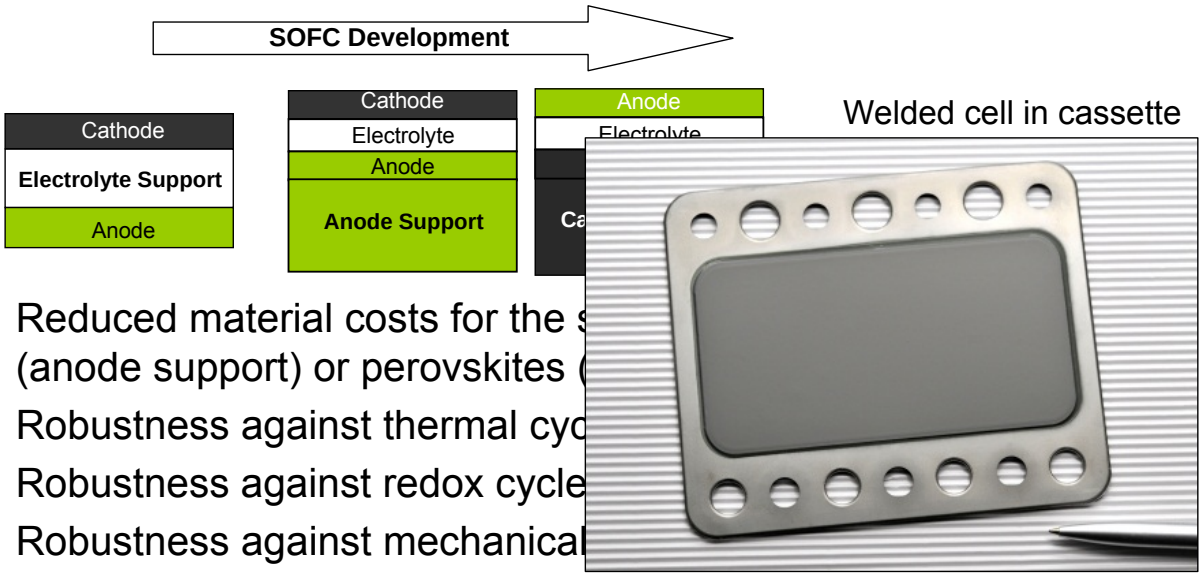
http://www.kohlerpower.com ⇒ one target application for MSCs http://www.sae.org/mags/aei/INTER/8222

Potential of Metal Supported Cells



- Reduced material costs for the support compared to Ni/YSZ (anode support) or perovskites (cathode support)
- Robustness against thermal cycling
- Robustness against redox cycles
- Robustness against mechanical stresses
- Stack integration of cells via brazing or welding
- High electronic conductivity
- High thermal conductivity

Potential of Metal Supported Cells



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- Robustness against mechanical
- Stack integration of cells via brazing or welding
- High electronic conductivity
- High thermal conductivity

Materials for metal SOFC supports Requirements and available products

conductive oxide scale	→	Cr_2O_3-formers (Ti add. for better adherence) no Al_2O_3-formers
appropriate CTE (electrolyte, anode: 10-13 ppm/K)	→	ferritic steels (with approx. 20-26% Cr) no austenites
mechanical properties (not brittle, feasible for stamping / welding)	→	ferritic steels, Ni-base no Cr-based alloys
creep stability / HT strength (no creep at high temp.)	→	oxide dispersed strengthened (ODS, P/M), laves phases (I/M), addition of Mo, Nb

ITM (Plansee), P/M
Fe-26Cr-(Mo, Ti, Y_2O_3)

Crofer 22APU (ThyssenKrupp)
Fe-22Cr-(Mn, Ti, La)
Crofer 22 H (ThyssenKrupp)
Fe-22Cr-(W, Nb, Si)

Hastelloy X (Haynes)
Ni-22Cr-Fe-Mo-Co-W
(but ~16 ppm/K)

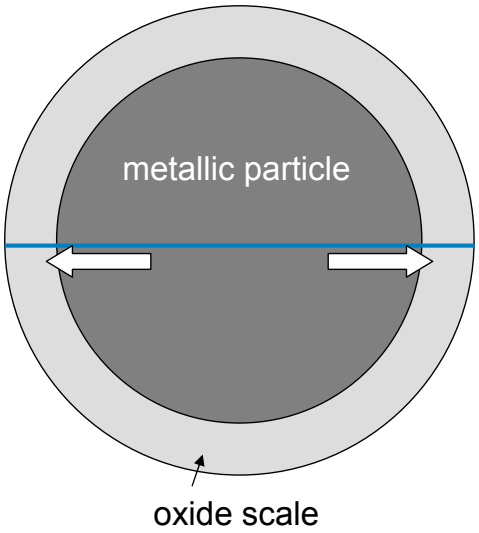
ZMG 232L (Hitachi Metals)
Fe-22Cr-Ni-Mn-Si-Zr-La

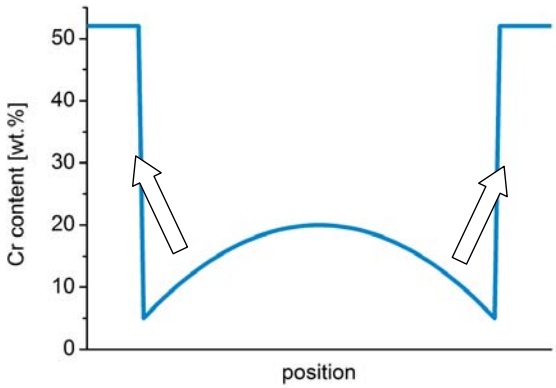
Sanergy HT, 1C44Mo20 (Sandvik)
Fe-22Cr-(Mn-Mo-Nb-Ti)

Lab-steel (JFE Corp.)
Fe-20Cr-Si-Mn-Nb-Mo-La

all materials already used for metallic interconnects

The Cr depletion problem



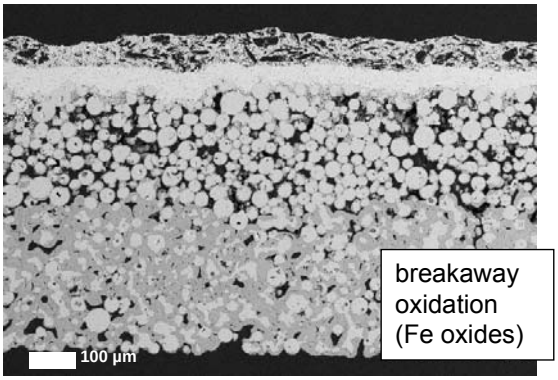


- formation of Cr_2O_3 scales leads to depletion inside particle
- if < ~16% Cr ⇒ brake-away oxidation (Fe oxidizes)

⇒ size of Cr reservoir important (particle size, sheet thickness)

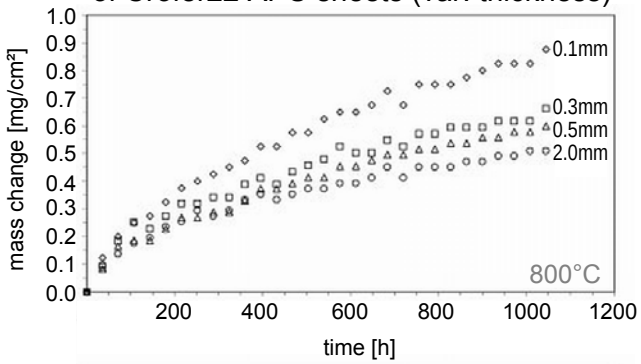
- too much Cr in raw material ⇒ formation of σ-phase (brittle)

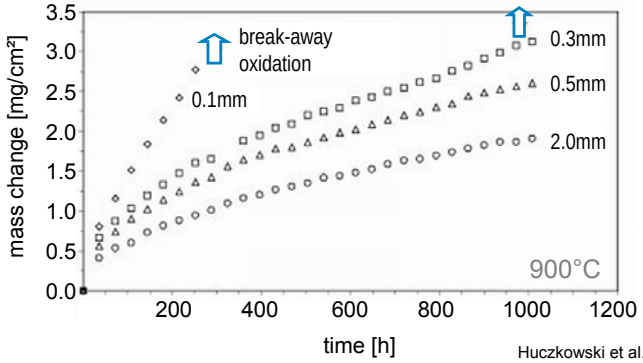
Break-away oxidation
Influence of Cr reservoir



⇒ coarser microstructure in metal support preferable (may be more difficult to coat etc.)

weight change during oxidation
of Crofer22 APU sheets (var. thickness)

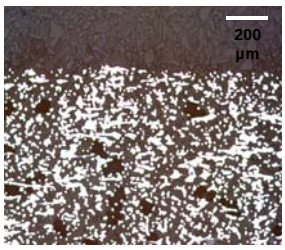


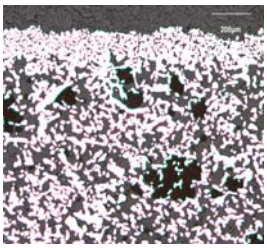


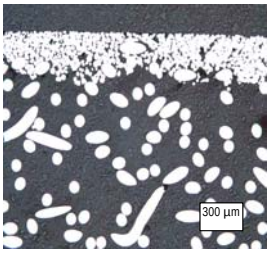
Huczkowski et al.,
Materials and Corrosion 55, 825

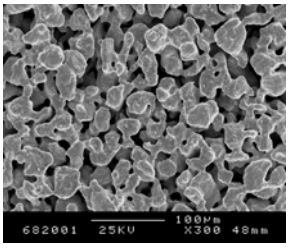
MSC Supports
Manufacturing Routes (I)

Substrate	Felts	Foams	Knit fabric	Sintered plate
Material	Ni	Fe-22Cr-5Al-0,1Y	Fe-22Cr-0,5Mn	Fe-26Cr (Y_2O_3)
Thickness [mm]	~ 1,0	~ 1,8	~ 1,0	~ 1,0
Porosity [%]	~ 85	~ 80	~ 90	~ 50
Supplier	Bekaert, Belgium	Technetics, USA	Rhodius, Germany	Plansee AG, Austria





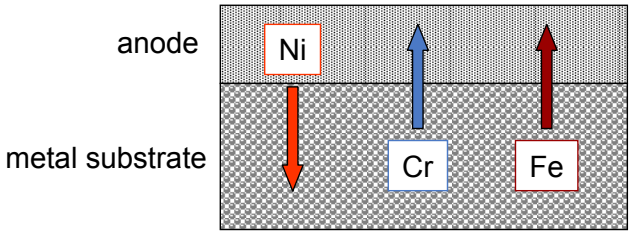




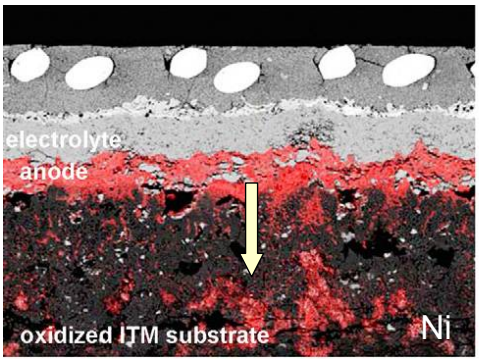
Source: DLR

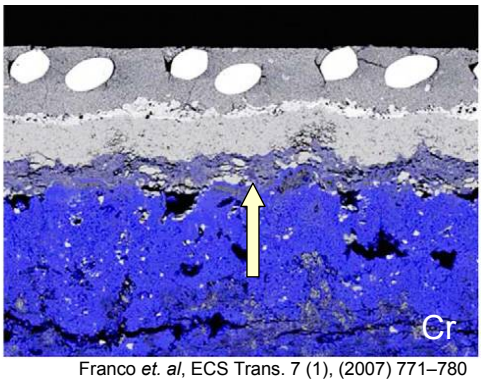
Th. Franco, Plansee

Interdiffusion Issues



plasma sprayed anode + electrolyte



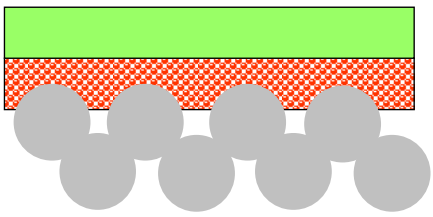


Franco *et. al*, ECS Trans. 7 (1), (2007) 771–780

Fe-Ni austenitic phase formed (large CTE ~17-20 ppm/K)
leads to cumber / delamination / bad performance

Diffusion Barrier Layers

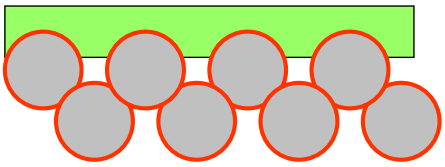
diffusion barrier layer



- Sintering
- Plasma-spraying

- layer must be porous
- high electrical conductivity

diffusion barrier coating



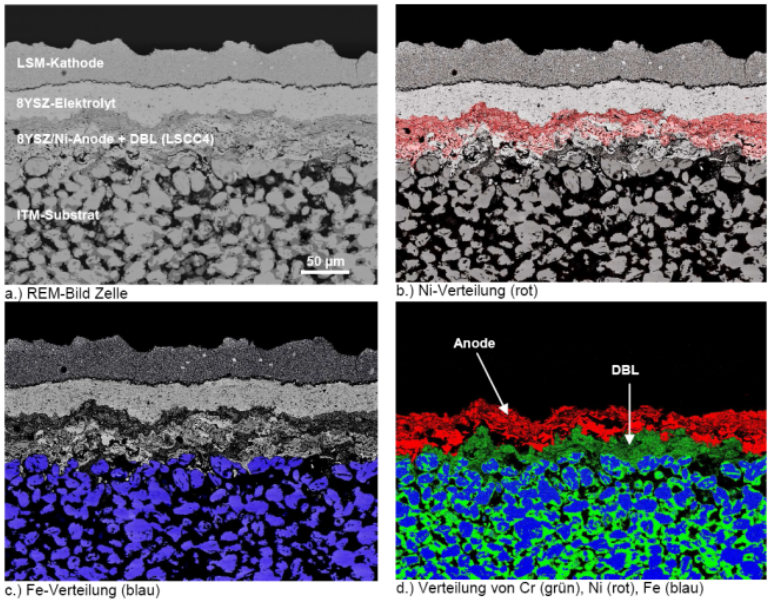
- Inherent growing oxide scales
- PVD/CVD

- coating must be dense
- lower conductivity can be compensated by using thin coatings

Effectiveness of Plasma-Sprayed Diffusion Barrier Layer

JÜLICH FORSCHUNGSZENTRUM

Performance of Integrated DBL Layers



a.) REM-Bild Zelle
b.) Ni-Verteilung (rot)
c.) Fe-Verteilung (blau)
d.) Verteilung von Cr (grün), Ni (rot), Fe (blau)

Th. Franco, PhD-Thesis, Universität Stuttgart, 2009

Facts

- The use of 20 µm DBL layer has improved the long-term stability up to more than 2500 hrs. (Degradation rates < 2.5%/1000 hrs.)
- EDX measurements and mathematical studies have indicated relatively low diffusion of Fe, Ni and Cr into the DBL
- Post investigations of measured cells show no significant diffusion and low degradation of ITM substrate

▶ **A chemical stable DBL is necessary at substrate/anode-interface and could be successfully integrated by plasma sprayed $LaCrO_3$ layers**

PLANSEE

Technology Comparison Dense Electrolytes on MSCs

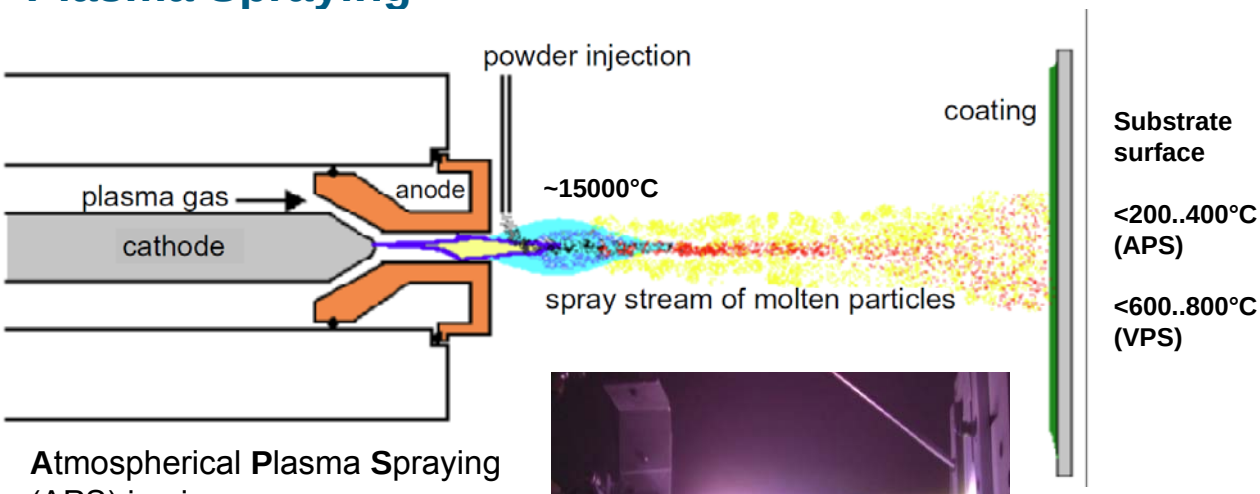
JÜLICH FORSCHUNGSZENTRUM

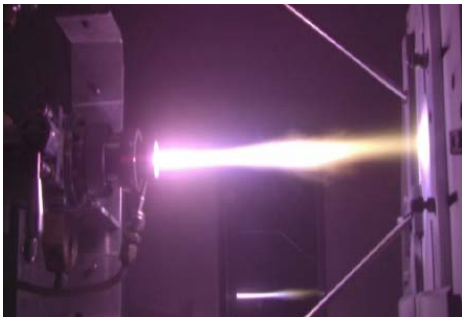
	Conventional Sintering	Plasma Spraying (APS/VPS)*	Thin-Film (no sintering e.g. PVD,CVD)	Sol-Gel (sintering)
Thickness	5-20 µm	30-70 µm	<5 µm	< 2 µm
Substrate temperature	1300-1400°C	~300°C (APS) ~700°C (VPS) (inhomogeneous)	<800°C	~1200-1400°C
Gas-tightness	excellent	problematic (esp.for thin layers)	good (smooth surface required)	good
Ionic conductivity	very good	problematic (splats)	excellent	excellent
Power output 800°C, (LSCF) **	1-1.7 W/cm² (ASC)	~ 0.6 W/cm² (MSC)	1-1.5 W/cm² (ASC & MSC)	~ 2.2 W/cm² (ASC)

** single cells, H_2+3%H_2O

* new LPPS may achieve better results

Anode Coating Techniques
Plasma Spraying

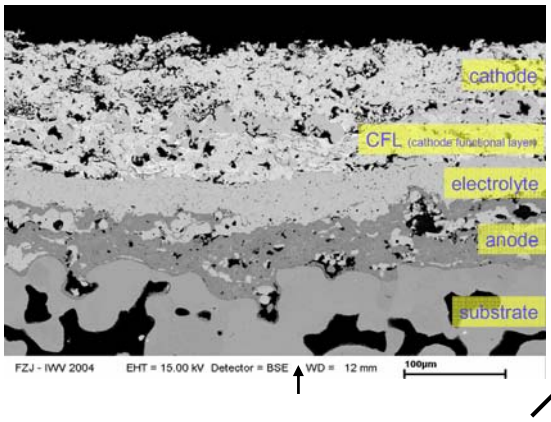




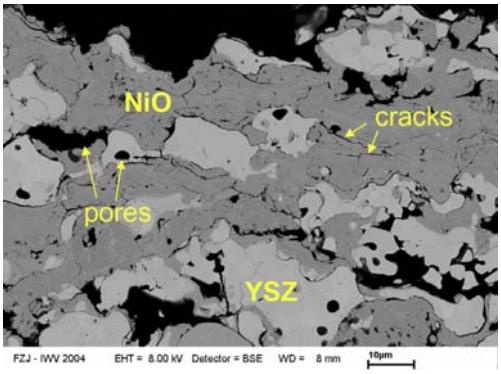
Atmospherical **P**lasma **S**praying (APS) in air
Vacuum **P**lasma **S**praying (VPS) in low pressure

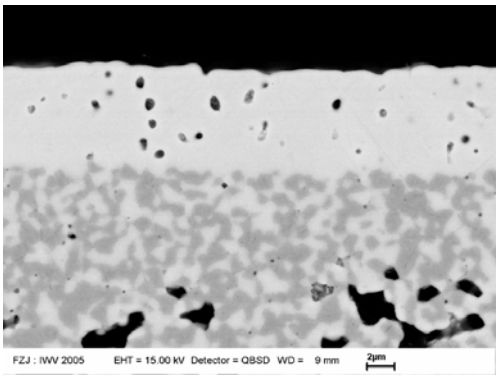
energy transfer to samples is **less than with sintering** (e.g. **interesting for metallic substrates**)

Plasma Sprayed Microstructures



Atmospheric Plasma Spraying (APS)





vacuum slip-cast anode 1400°C/5h

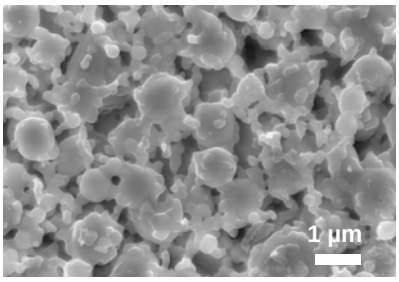
difficulties in plasma spraying

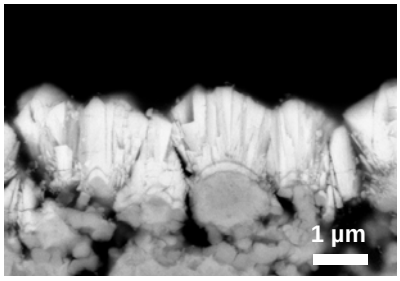
- only larger thicknesses (>=30µm)
- inhomogeneous layers
- coarse microstructure
- bad transversal conductivity due to inter-splat cracks in the layer

Thin-Films Require a Good Support to Become a Film (PVD)

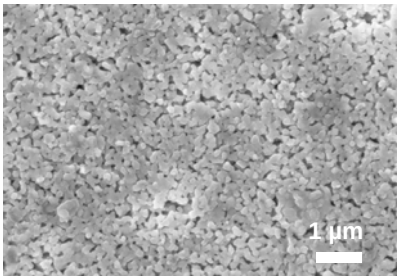
surfaces without PVD coating

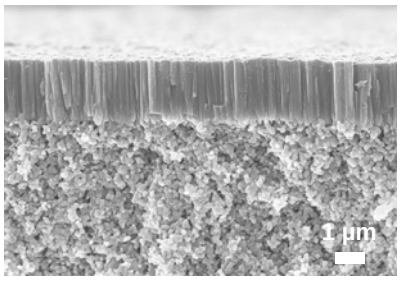
cross section / fracture surface with PVD coating





too coarse





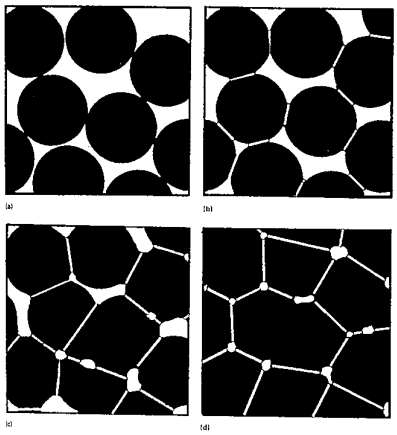
fine enough

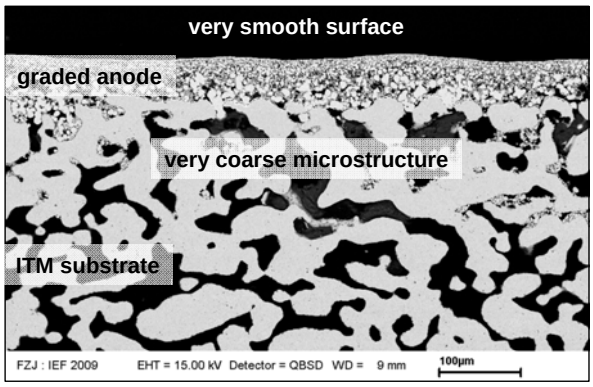
EB-PVD ca. 1.7 µm GDC

Anodes for MSCs
MSC Support on Anode Side

- metallic Ni coarsens much faster than NiO
- if not laminated afterwards, anode can not be sintered in air

⇒ post infiltration of Ni, or
⇒ specially composed and sintered cermet anode





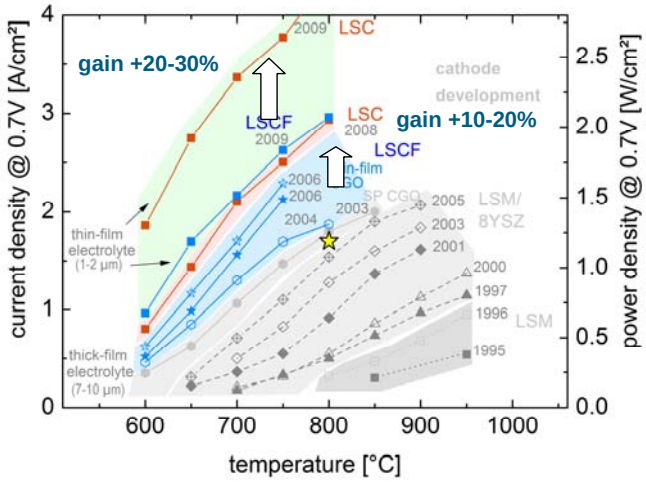
SEM cross section of ITM substrate with fully screen printed graded MSC anode

Cathodes for MSCs
MSC Support on Anode Side

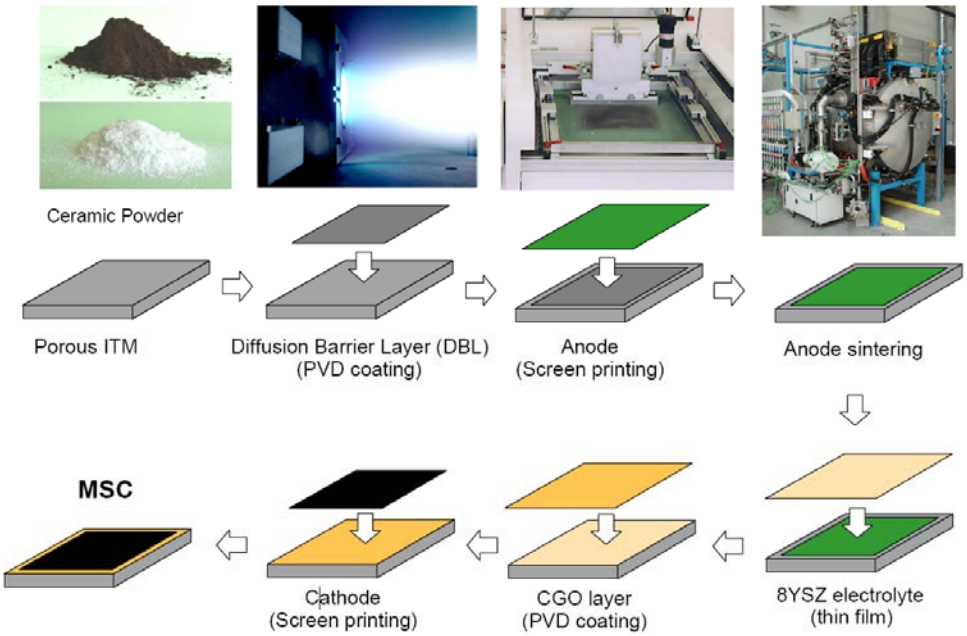
- can not be sintered in air
- LSCF loses approx. 30% performance without sintering

⇒ use unsintered high performance cathode (deal with thermal expansion mismatch)

ASC performance gain from LSCF (sintered) to LSC (unsintered) cathode

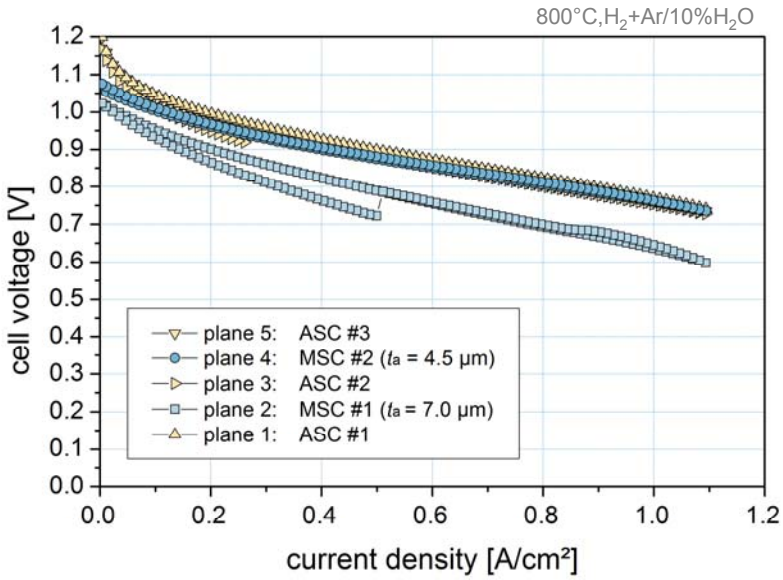


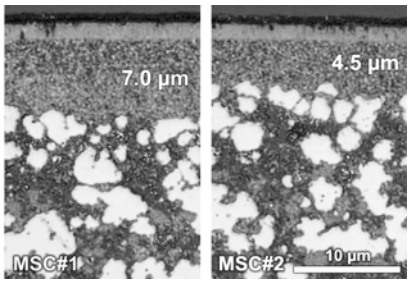
Possible Manufacturing Route of MSCs with Thin-Film Electrolyte



Franco et al.: SOFC-XII, 2011

MSC with Similar Stack Performance like ASCs

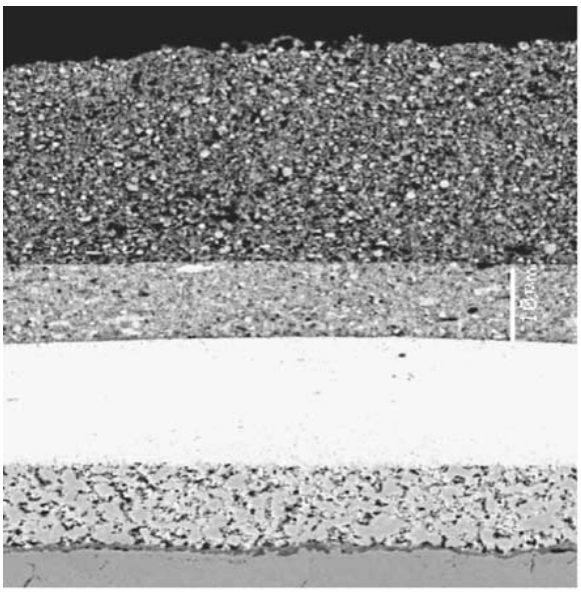




MSC with thin layers: same power output like state-of-the-art ASC in a stack

Rüttinger, Mücke et al.: SOFC-XII, 2011

Electro-phoretic Deposition + Sintering of Electrolyte (Ceres Power)



400 mW cm^{-2}
570°C (H_2)

contact layer ~25µm

cathode ~10µm (LSCF/CGO)

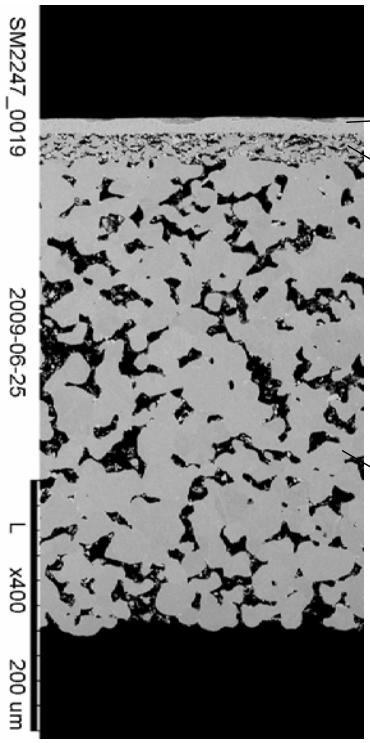
electrolyte ~10-20µm
CGO10 ⇒ $T \leq 600$°C

anode ~10µm

steel substrate ~200µm
1.4509 (17%Cr, Ti-Nb Fe) ⇒ $T \leq 600$°C

P. Bance et al, J. Power Sources 131 (2004) 86-90
N.P. Brandon et al., J. Fuel Cell Sci. Technol. 1 (2004), 61-65

Lamination, Post-Infiltration of Anode (Risoe, Denmark)



electrolyte:
tape cast
ScYSZ

anode:
CGO20 + 10%Ni
post-infiltrated

substrate:
tape cast
22% Cr =
Sanergy class steel

1. electrolyte/substrate laminated
2. co-fired(Ar/H_2)
3. anode post-infiltrated
4. calcin. (350°C/2h air)
5. LSC-cathode screen printing (formerly LSCF/CGO)

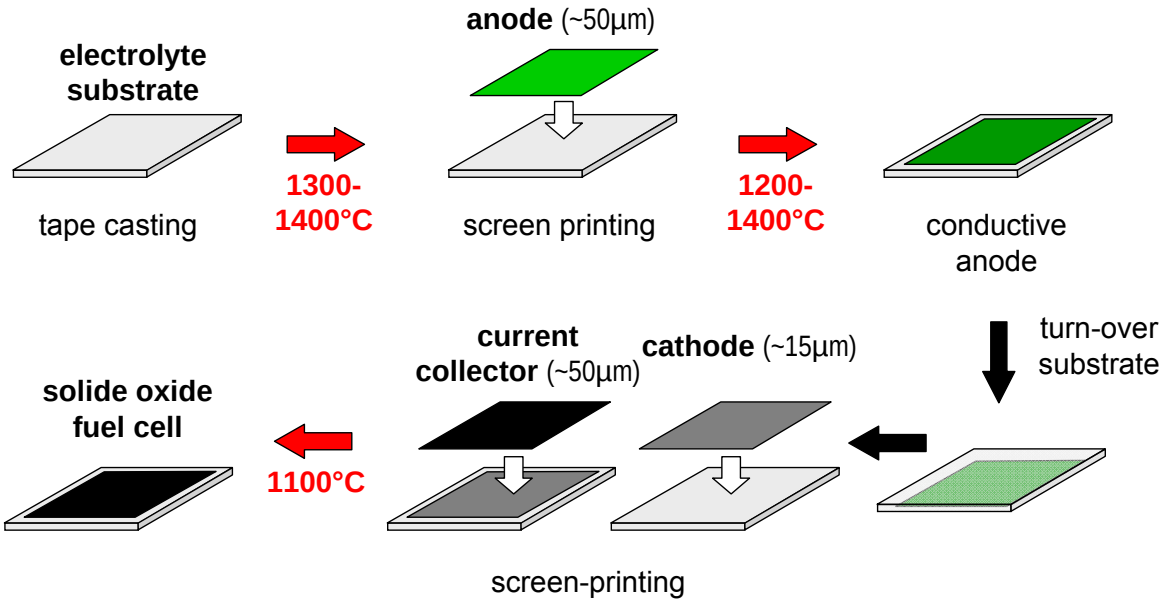
up-to 3.0A/cm² at 800°C H_2
(1cm² act. cell area)
100 redox cycles
ca. 5%/1000h V degr.
@ 655°C 0,25Acm^{-2}

P. Blennow et al. 9th European Solid Oxide Fuel Cell Forum, Lucerne, 2010, 16-1

8. Industrial Manufacturing (Costs and Scalability)

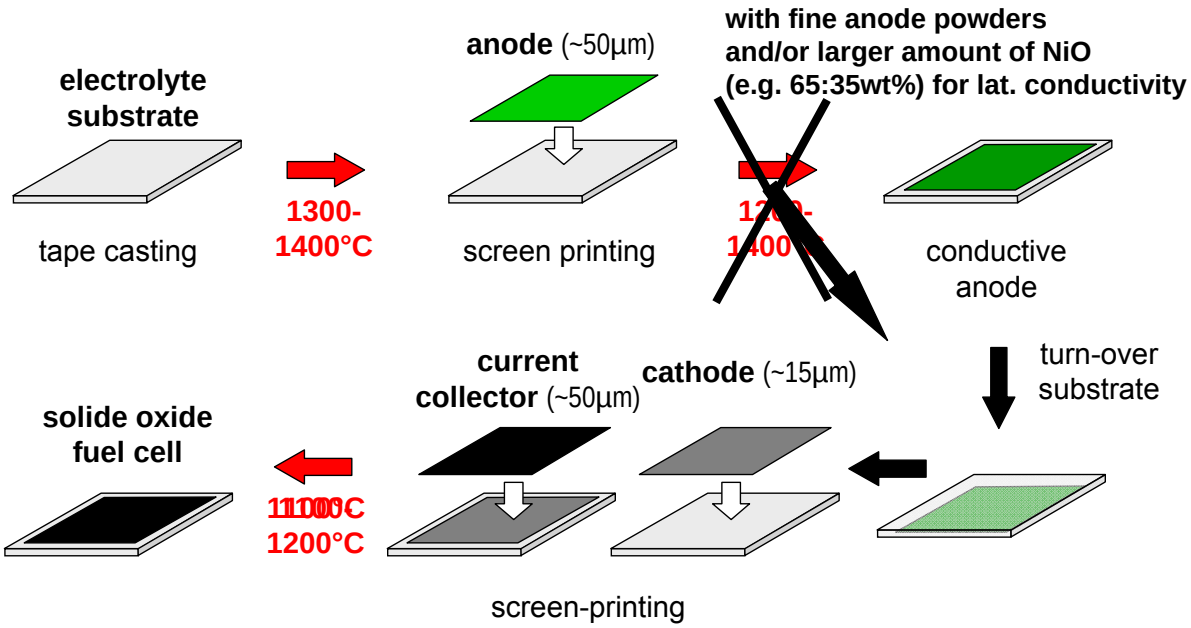
Manufacturing Route ESCs (conventional)

typical SOFC manufacturing is ceramic processing
everything starts with a powder



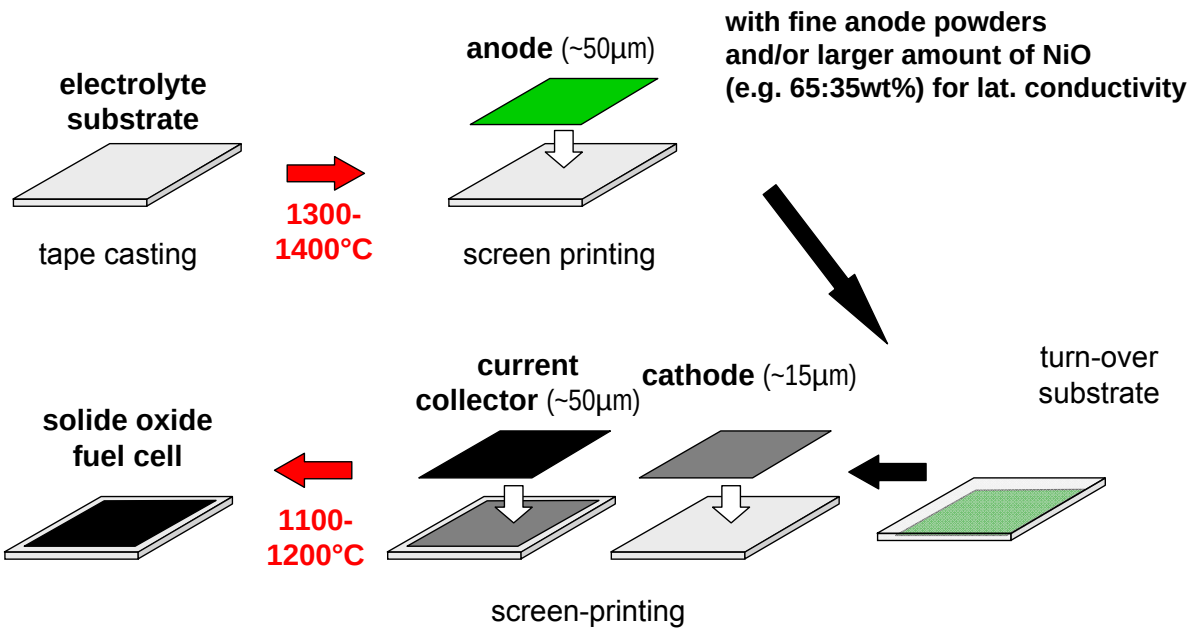
Manufacturing Route ESCs (optimized)

typical SOFC manufacturing is ceramic processing
everything starts with a powder



Manufacturing Route ESCs (optimized)

typical SOFC manufacturing is ceramic processing
everything starts with a powder

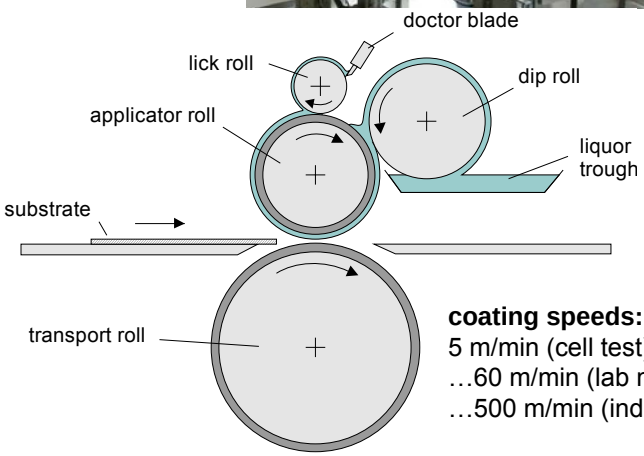


Continuous Coating Technology

Scale-up from dozen (lab-scale) via thousands (small series) to millions (mass manufacturing)
question: is screen printing the technique of choice?

answer: presumably not;
because much equipment necessary
(high invest costs)
single layer deposition is time consuming
(screen kneeling, printing, screen lifting)

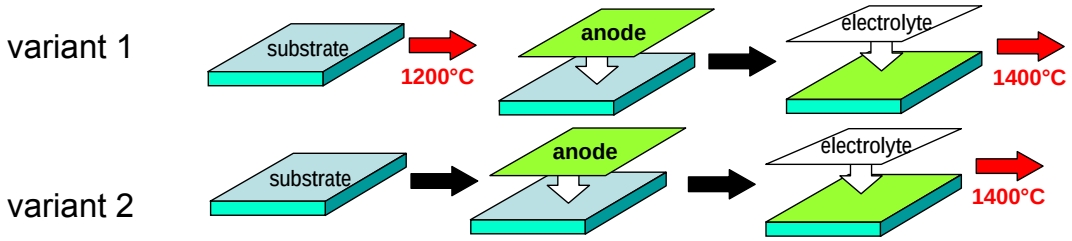
alternatives:
continuous technologies like roll-coating or curtain coating



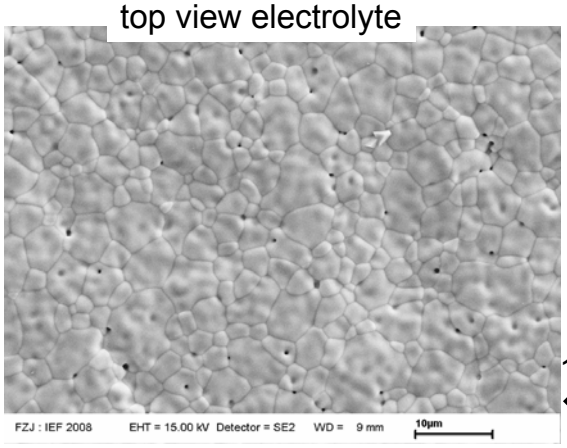
coating speeds:
5 m/min (cell test)
…60 m/min (lab machine)
…500 m/min (industry)

*Büchler et al.: ECS Trans. 2009;
Menzler et al.: 35th Int. Conf. & Exp. Adv. Ceram. Comp. 2011;
Mücke et al., J. Power Sources, 2011

Roll Coating

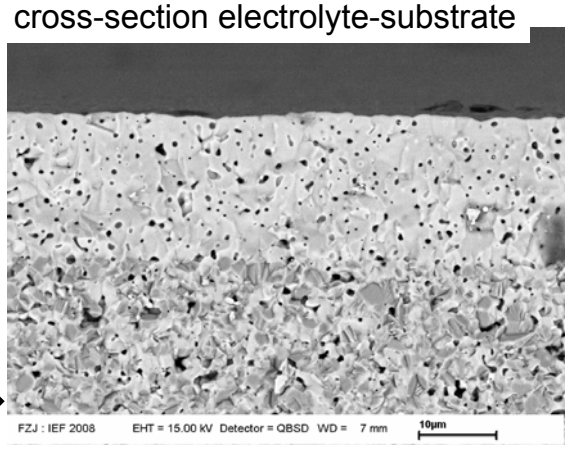


top view electrolyte



10 µm

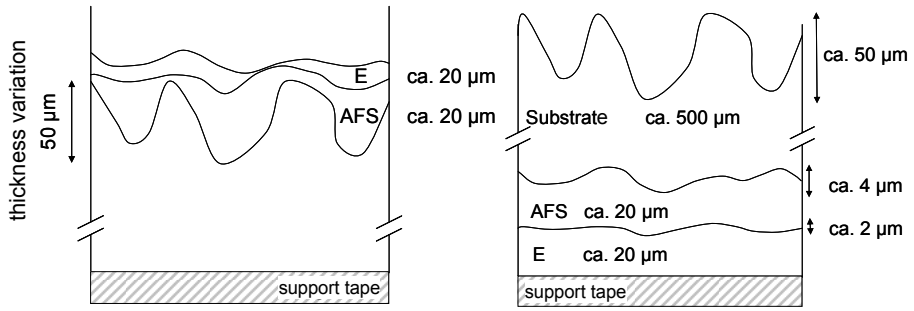
cross-section electrolyte-substrate



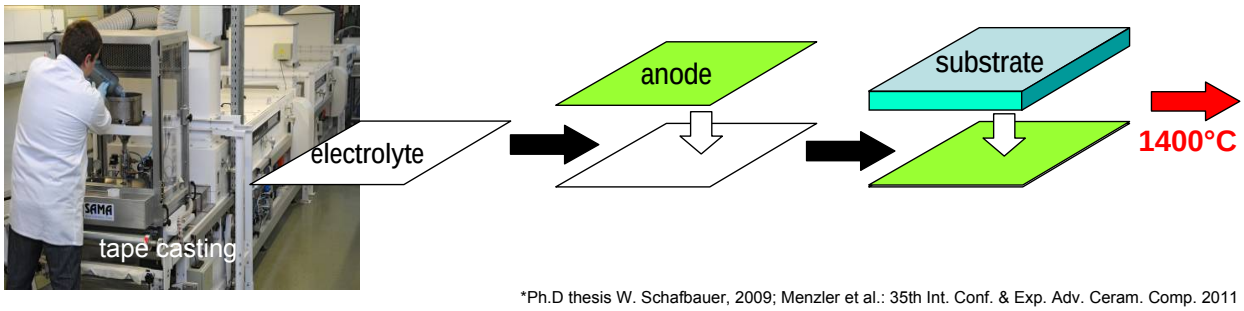
*Büchler et al.: ECS Trans. 2009;
Menzler et al.: 35th Int. Conf. & Exp. Adv. Ceram. Comp. 2011;
Mücke et al., J. Power Source, accept. 2011

All-Tape-Cast Half-Cells

problem: thin functional layers on coarse porous support

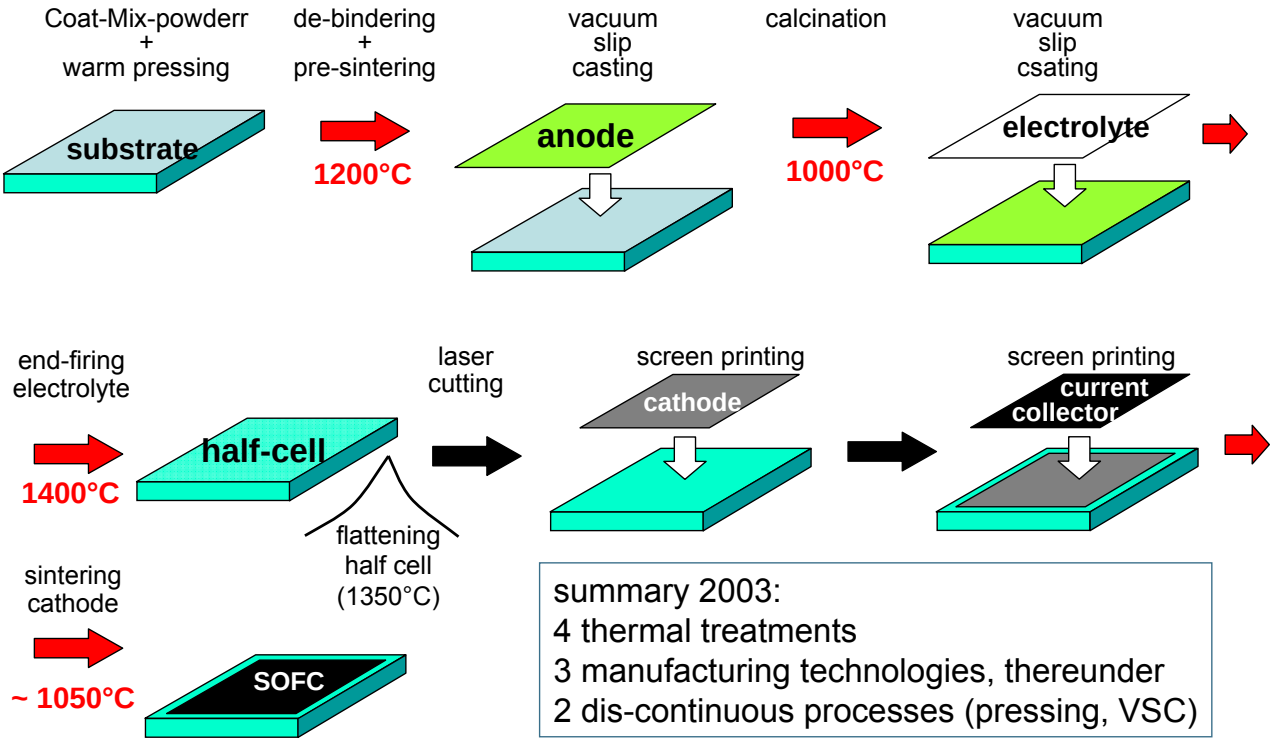


solution: reverse tape casting, from
substrate → anode → electrolyte, to
electrolyte → anode → substrate



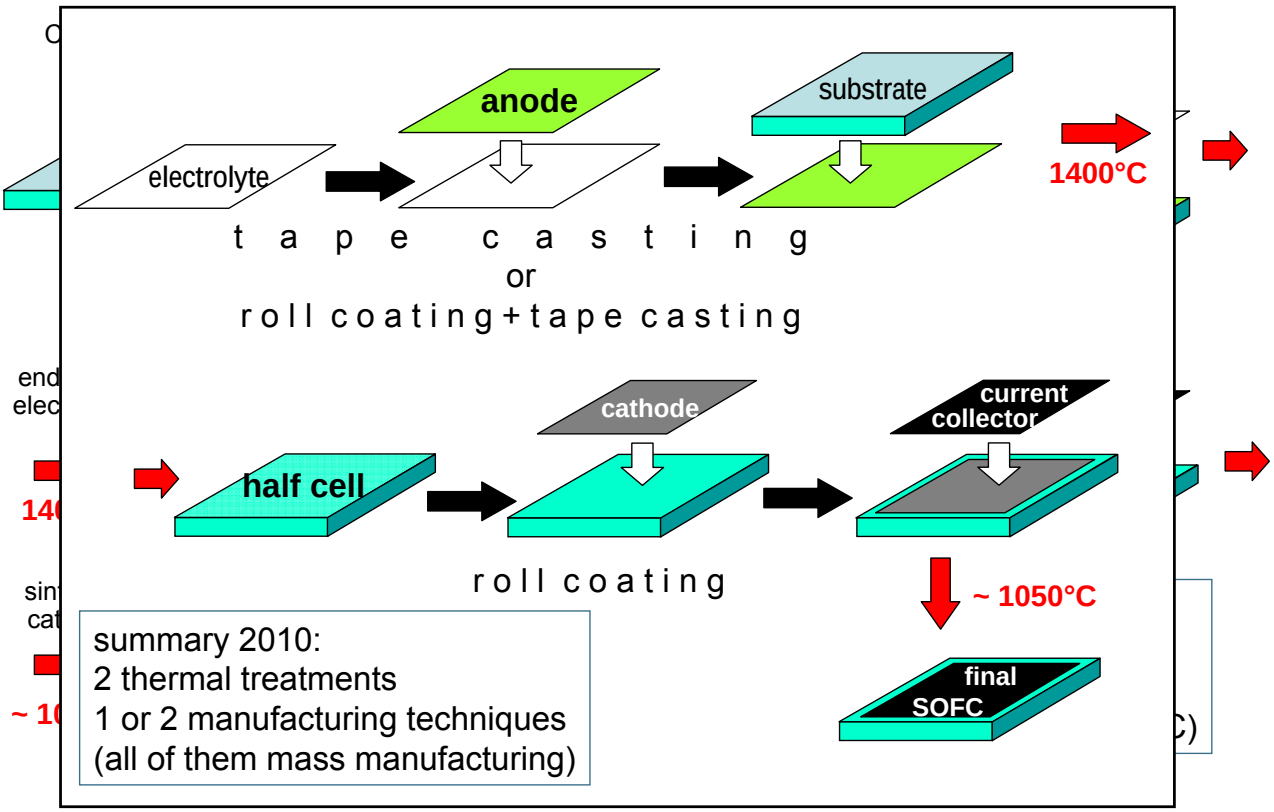
*Ph.D thesis W. Schafbauer, 2009; Menzler et al.: 35th Int. Conf. & Exp. Adv. Ceram. Comp. 2011

Summary: Innovative Cell Manufacturing



summary 2003:
4 thermal treatments
3 manufacturing technologies, thereunder
2 dis-continuous processes (pressing, VSC)

Summary: Innovative Cell Manufacturing



summary 2010:
2 thermal treatments
1 or 2 manufacturing techniques
(all of them mass manufacturing)

Summary

Bring SOFC to the people (real life applications)

long term stability
(40,000-80,000h stationary,
5,000-15,000h mobile appl.)
accelerated testing
(requires understanding)

real field operation
(sulfur, high u_F,
combine loads/cycle),
most test capacity

lower the costs
(industrial manufacturing)
may allow cheap
replaceable modules

← (but keep the running system)

Next generation SOFC

new materials,
e.g. ceramic anode,
metallic substrate

thin film technologies
400°C SOFC
(new electrodes)

prove feasability for
manufacturing and
operation (a button cell
is not enough)

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Dr. Frank Tietz • Dr. Sven Uhlenbruck • Dr. Tim Van Gestel •
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