Molecular Aspects of Solid State and Interfacial Electrochemistry
Dubna, 26th – 31st August 2012

Materials development for Solid Oxide Fuel Cells - Status and development perspectives

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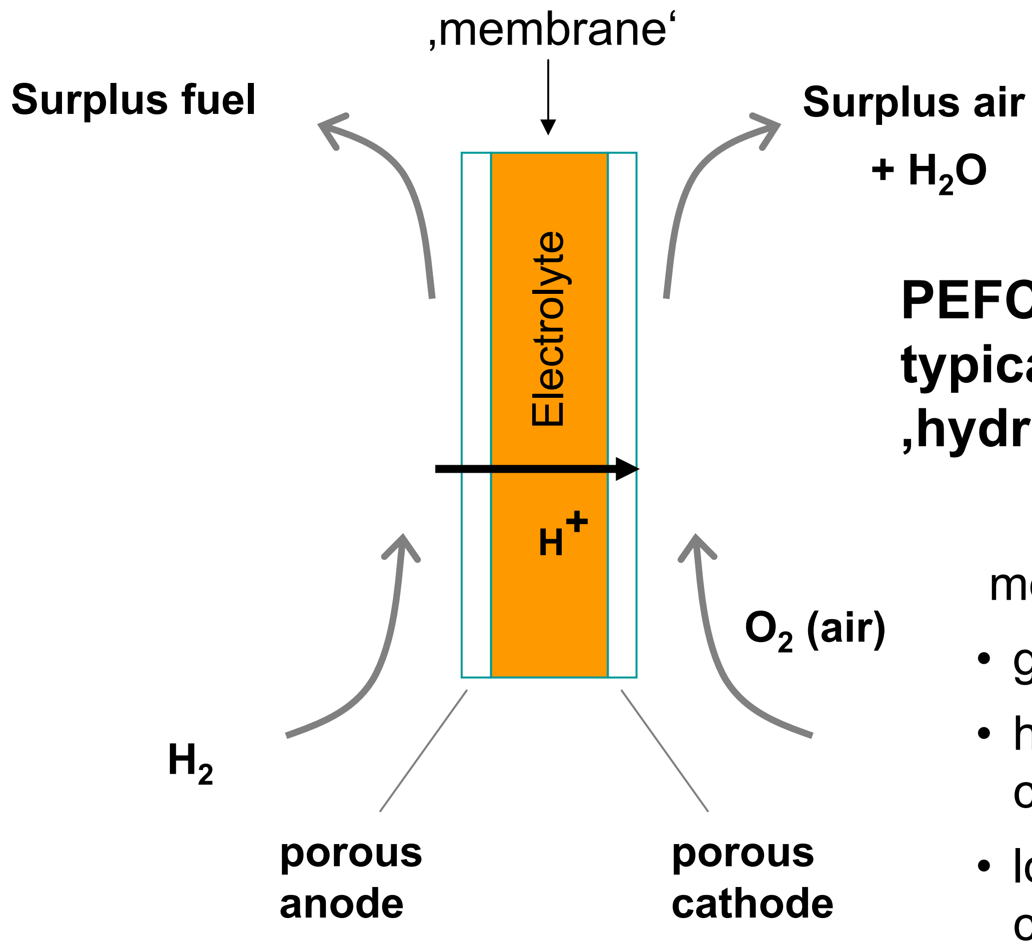
Overview

- introduction to SOFC
- fuel cell applications and their requirements
- fuel cell problems and development goals
- materials development for SOFC
- understanding fuel cell degradation

What is a ‘fuel cell’ and what does it do?

Fuel Cell Principle



PEFC:
typical
‚hydrogen fuel cell‘

membrane properties:

- gas tight
- high ionic conductivity
- low electronic conductivity

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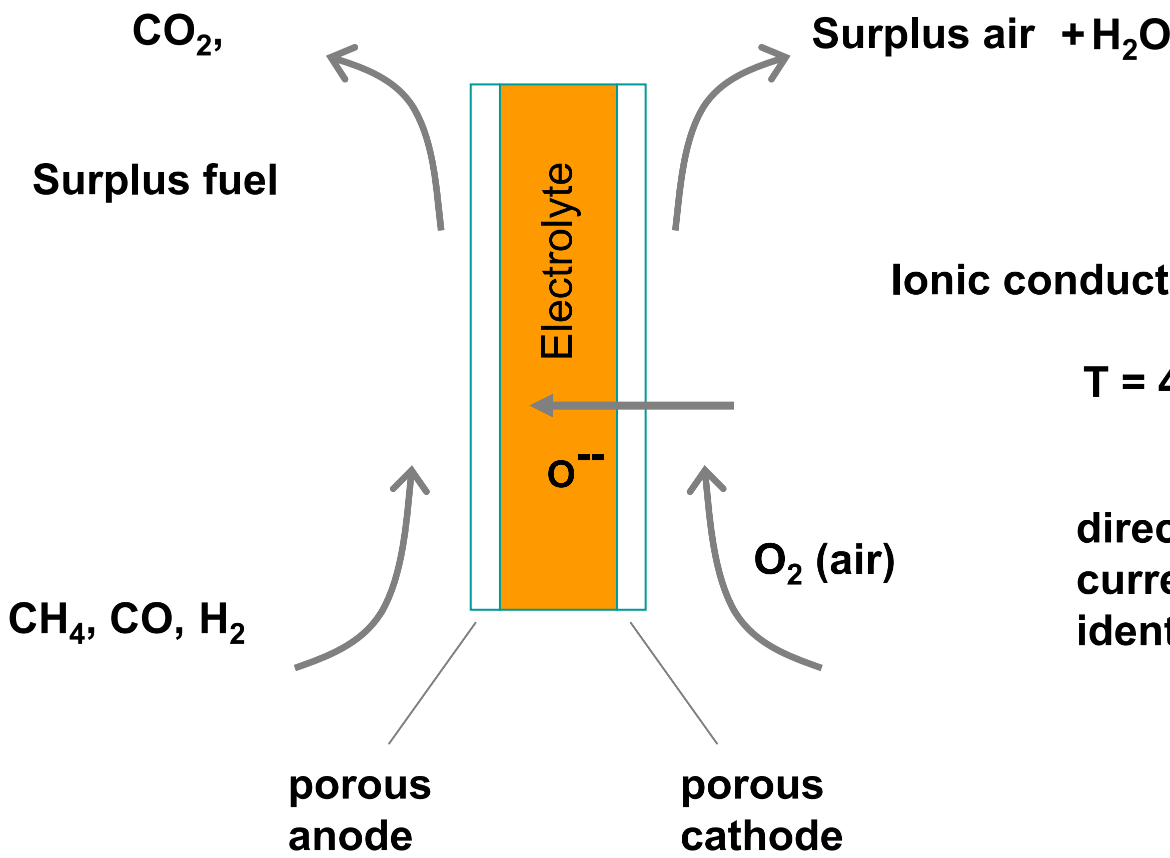
Solid Oxide Fuel Cell



Ionic conductivity = f(T)

T = 400 ... 1000°C

direction of current flow is identical to PEFC!

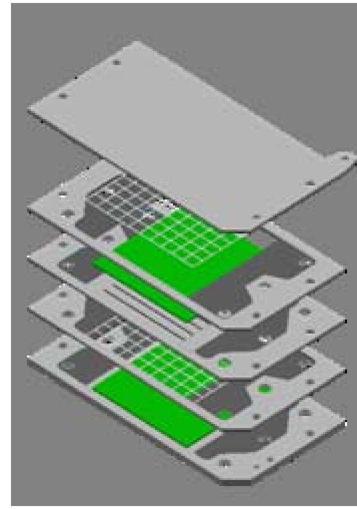
Potential of SOFC in the Future Energy System

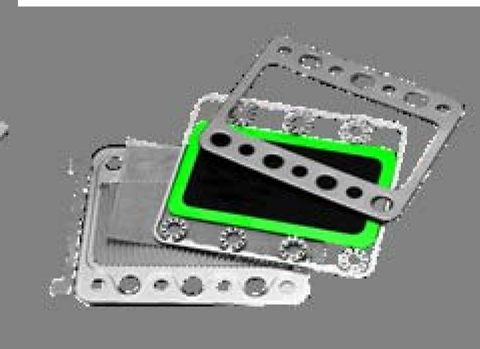
- **fuel flexibility** (H_2, CH_4, C_nH_m, CO, diesel, petrol ...)
- **minimal** need for **fuel processing** for small residential CHP, portable units, APU etc.
- **high electrical efficiency** up to 60% (system, net)
- role in **transition strategies** from fossil feedstock to renewables and to hydrogen (including bio-fuels of various origin, liquid or gaseous, and hydrogen)
- fuel impurity tolerance
- applications range from small scale residential CHP, APU and portable (SOFC) to **large units** in industrial CHP and bulk power production (SOFC and MCFC)

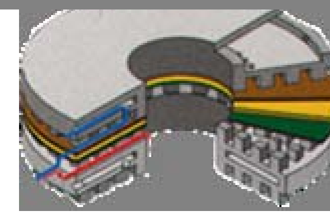
European SOFC Stack Technologies

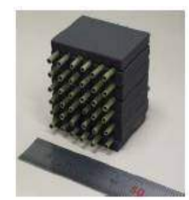
Variety of manufacturers and design types

- planar stacks
  - higher performance
  - compact design
  - mechanically robust
  - simple manifolding
  - lower cost
- tubular stacks
  - resistant to high temperature gradients (*)
  - mechanically robust (*)
  - low power density









(*) thermo-mechanical stability greatly depends on SIZE, not so much on concept

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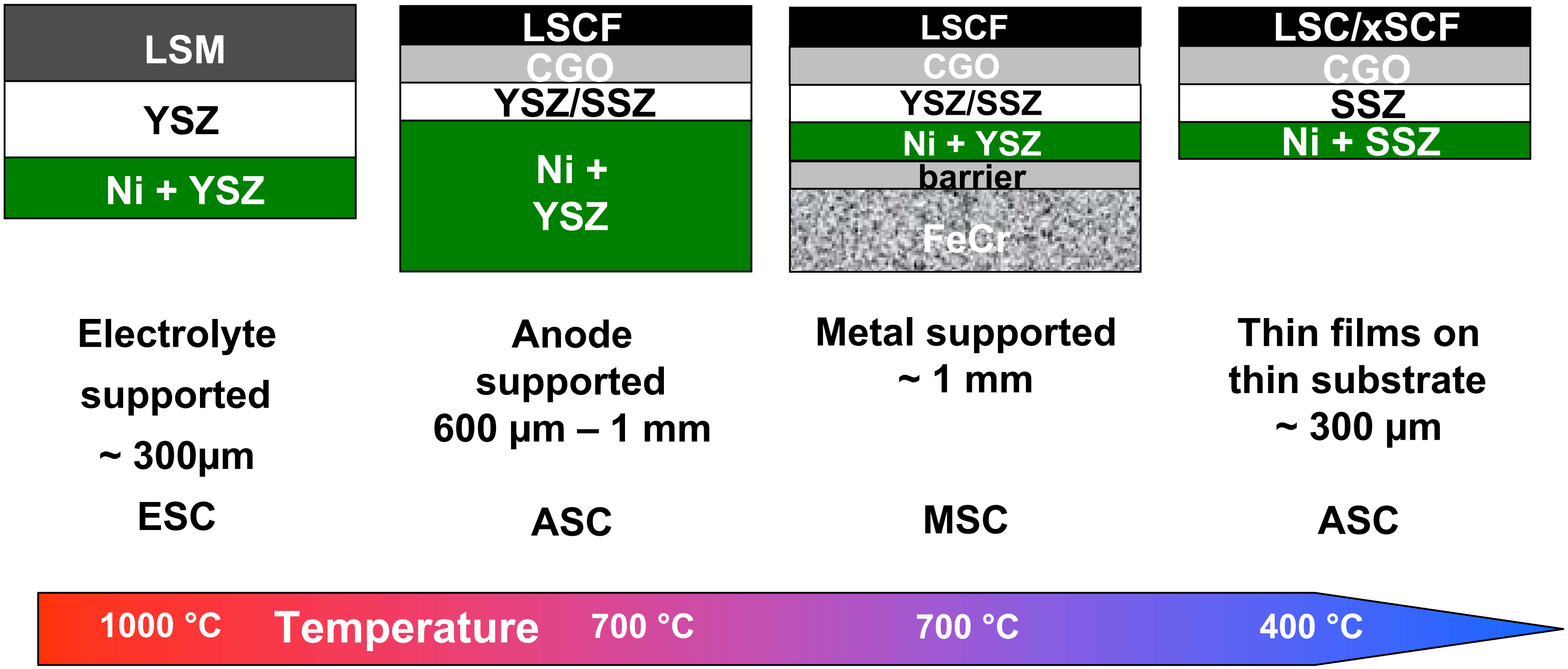
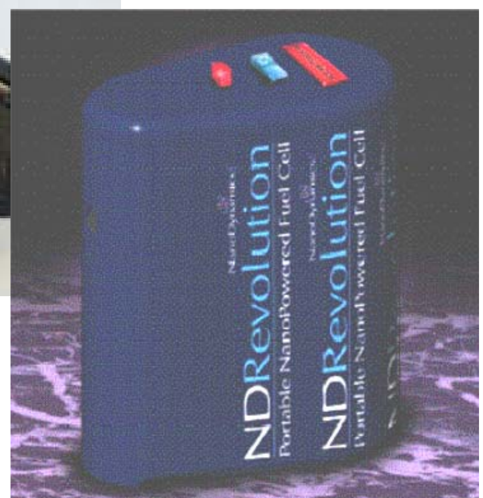
Variety of SOFC Cell Concepts



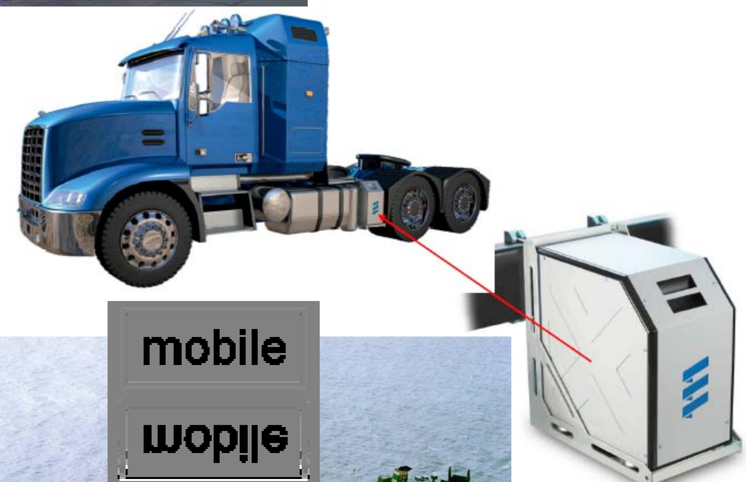
Specific properties with different application opportunities

SOFC Applications

stationary



portable



mobile

Performance of ‚Conventional‘ Products

Service life

- vehicles >10 years (5.000 to 10.000 operating hrs)
- heating boilers (residential power) >10 years (20.000 to 40.000 hrs, frequent cycles possible)
- power generating equipment 10 – 30 years (40.000 to 200.000 operating hours)

Other

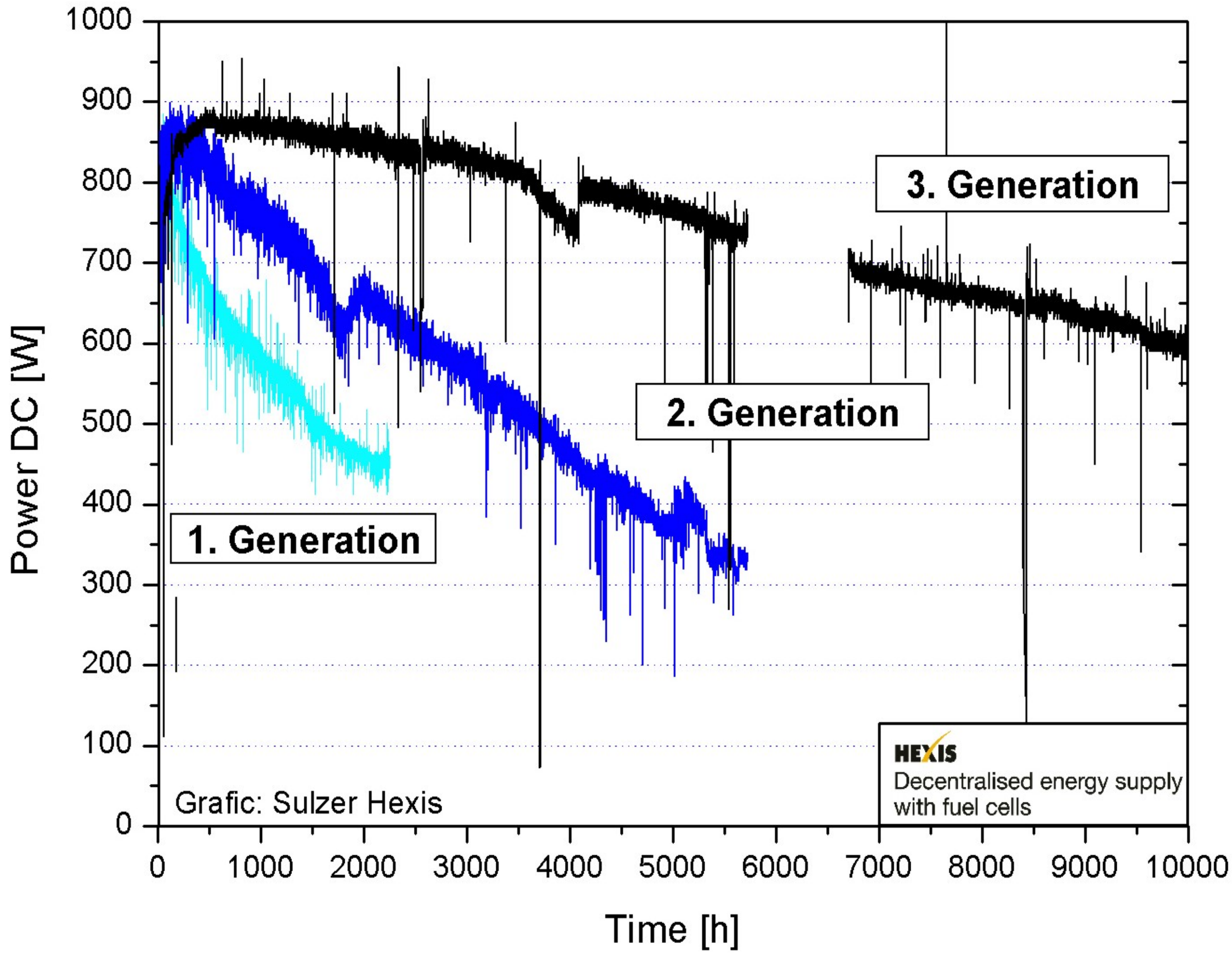
- vibration and shock (road vehicles)
- acceleration (aircraft)
- simple coupling to natural gas supply (boilers/engines)

SOFC Development Challenges

- improved durability under static, transient and cycling conditions
  - redox stability
  - thermal cycling capability
- stack lifetime in excess of 40.000 hrs. (stationary & la
  loss of power at end of life <20%)
- high performance, high efficiency
- arbitrary switch-off and start-up cycles (several 100 t
- tolerance against fuel impurities
- operation without external water supply
- robustness to vibration and mechanical shock
- design of large units and hybrid power plants
- lower cost, increased system compactness, simplification of technology

topics in joint materials, design and systems development

HEXIS: Comparison of ZIP Stack Generations (2000/2002)



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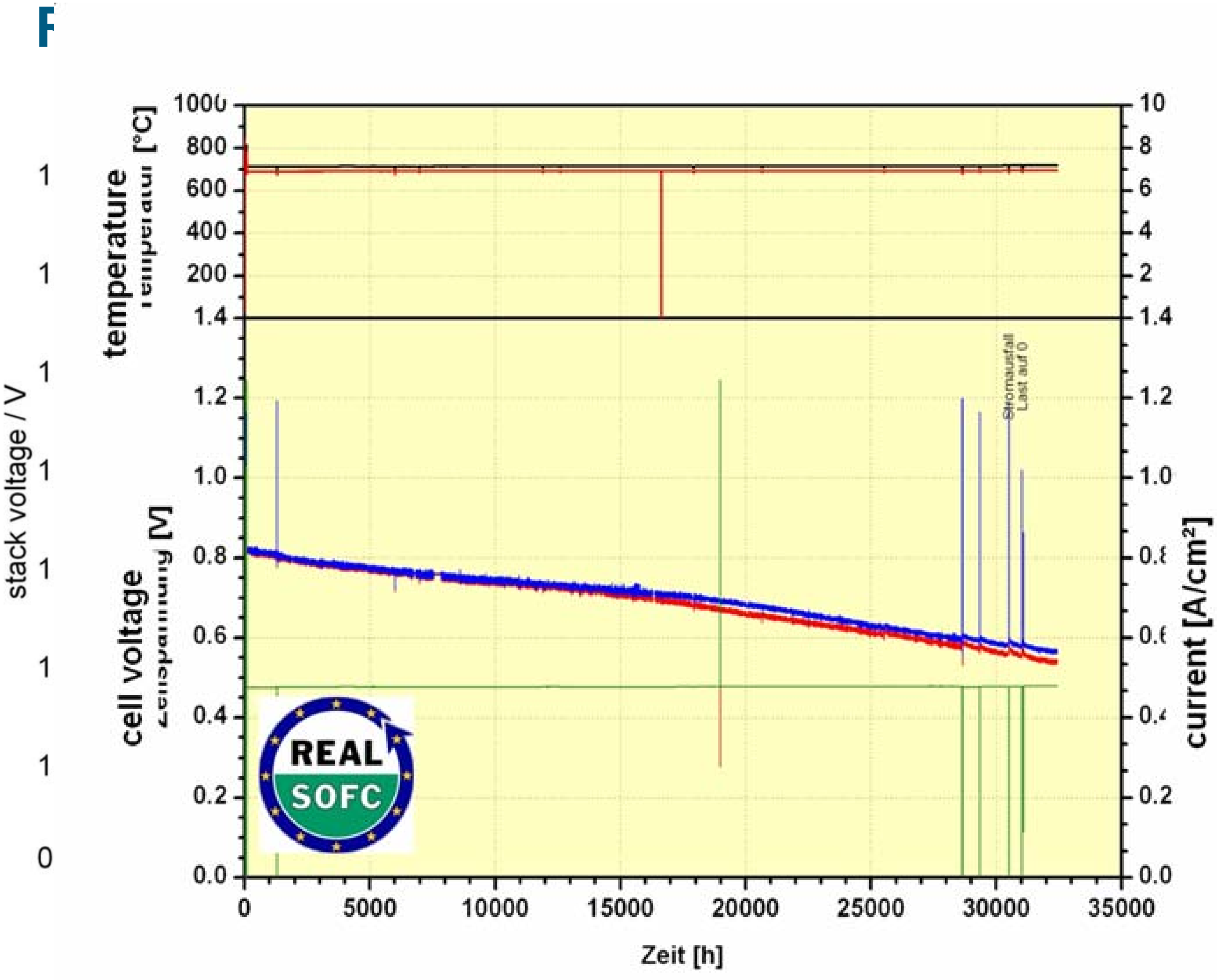
stack voltage / V
temperature
[°C]
cell voltage
[V]
current [A/cm²]
Zeit [h]
Stromausfall
Last auf 0
REAL
SOFC
1000
800
600
400
200
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
5000
10000
15000
20000
25000
30000
35000
10
8
6
4
2

G3

Materials development for SOFC

Increased Performance through Improved Materials

- **low ASR** through
  * low cathode overpotential -> high oxygen ion transfer rates
  * high conductivity of electrodes
  * thin layers
- electrolytes with **higher conductivity**
- hermetic separation of layers
  -> **thinner layers** of highly active but reacting materials
  -> interdiffusion barriers
- mechanically stable **contact layers** with high electric conductivity
- higher performance at **lower temperatures** -> less degradatoin

Materials for Increases in Performance

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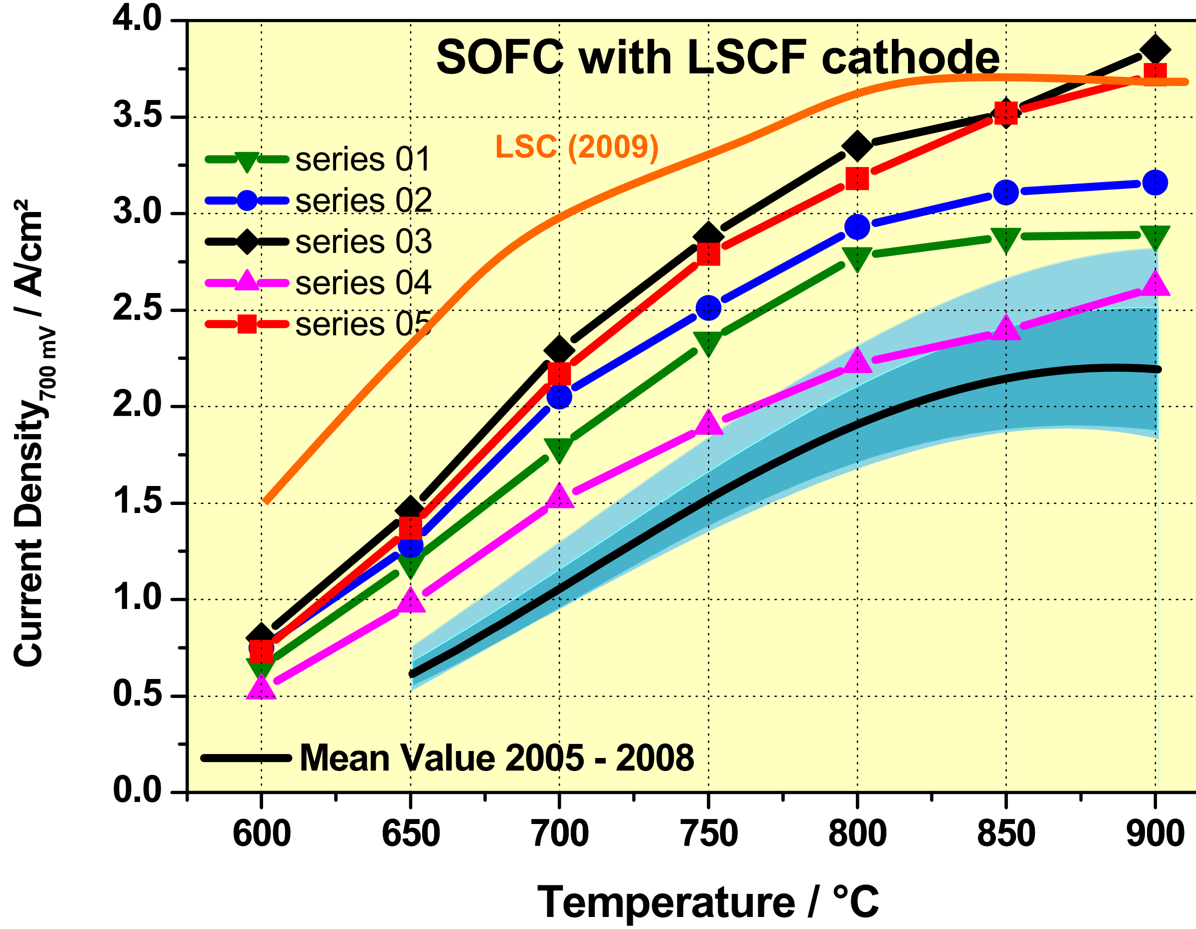
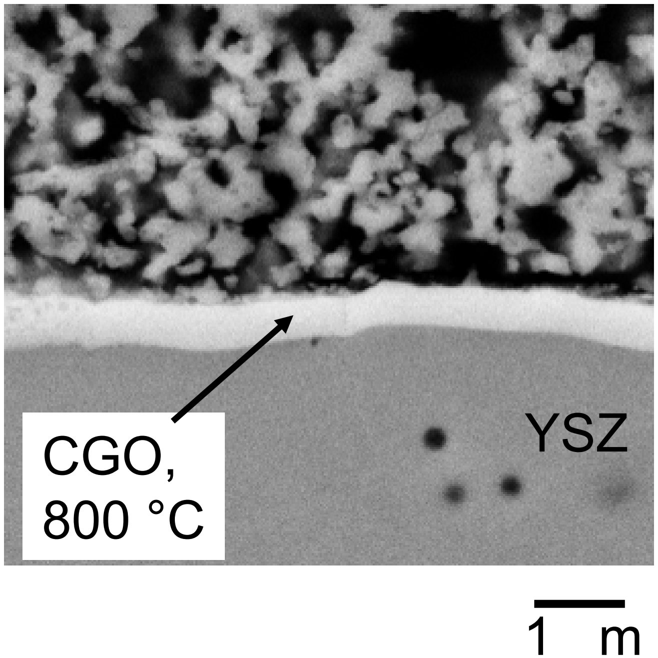
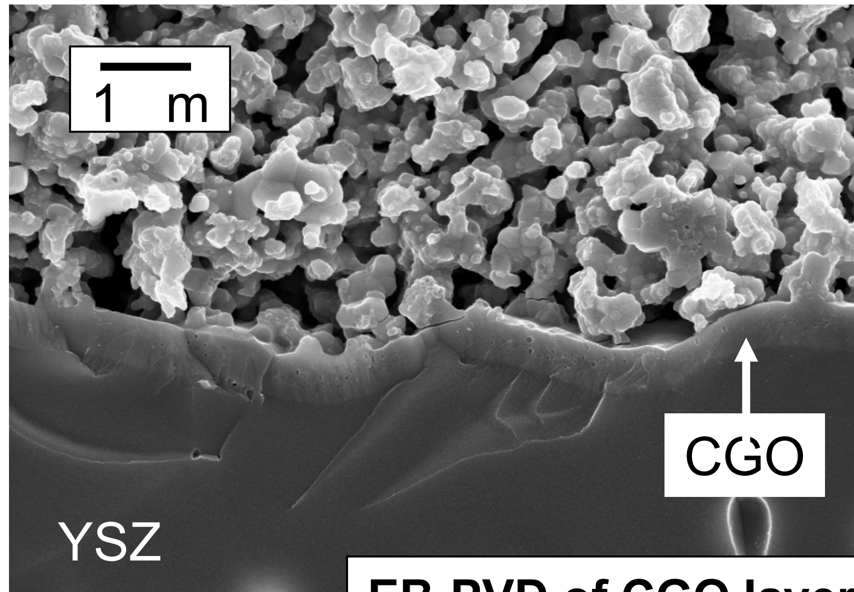


from LSM to LSC:

Lanthanum-Strontium-Manganite .... Lanthanum-Strontium-Cobaltite

Materials Processing: Diffusion Barrier for LSFC Cathodes





EB-PVD of CGO layer at target temperature 800°C

EB - PVD layers: thin, dense, gas tight structure,

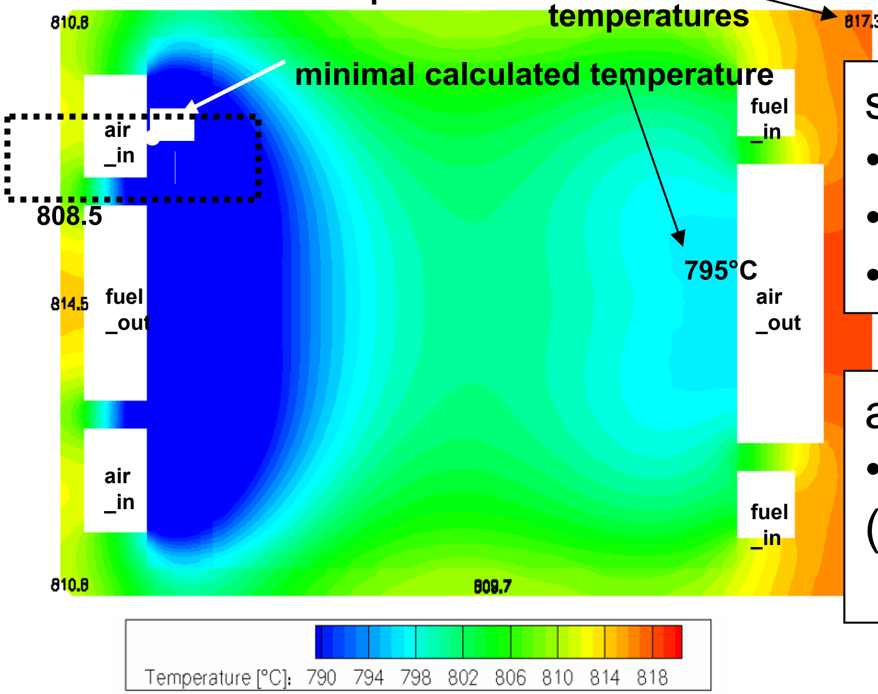
strong bonding of YSZ & CGO layer

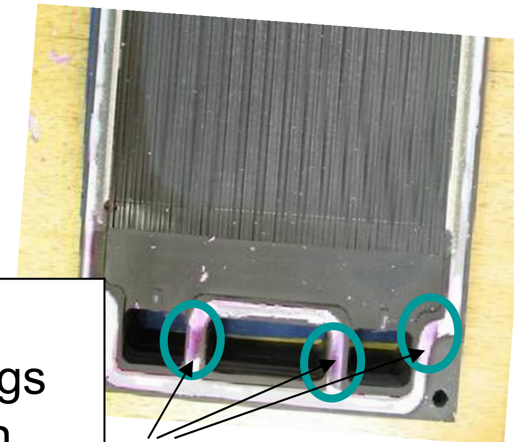
Thermal Cycling Requirements

- thermal cycles:
  - 'cold start' 20°C … 200°C, 'warm start' >400°C up to 600 … 750°C
- goals:
  - no gas leakages from stack (safe operation)
  - rapid start-up (30 minutes for road APU)

FEM-simulation of this part

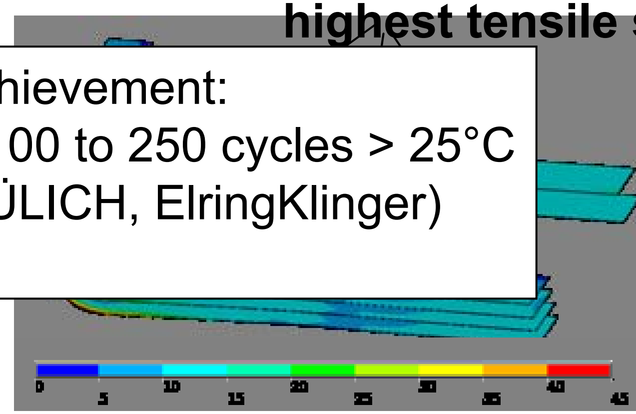
measured temperatures





solutions:
- strong sealings
- robust design
- compliant design

highest tensile stress



achievement:
- 100 to 250 cycles > 25°C (JÜLICH, ElringKlinger)

Strengthened Glasses

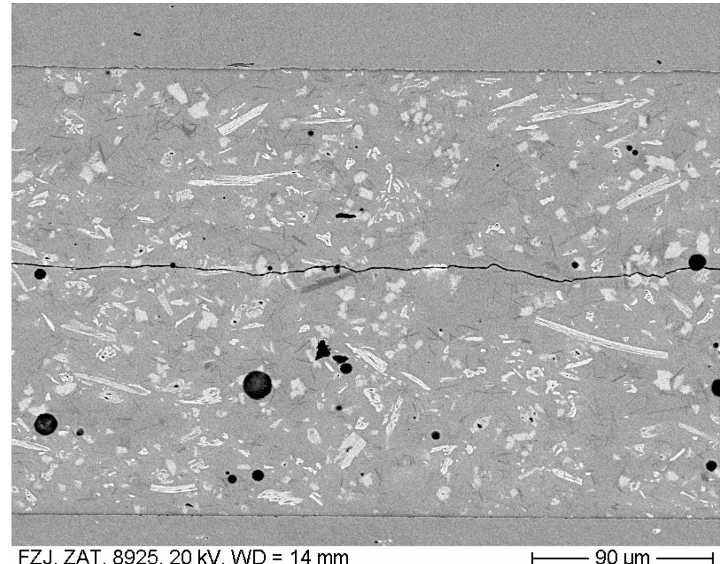
1. Fiber reinforcement of Ba-Ca-Silicate glass matrix by YSZ fibers

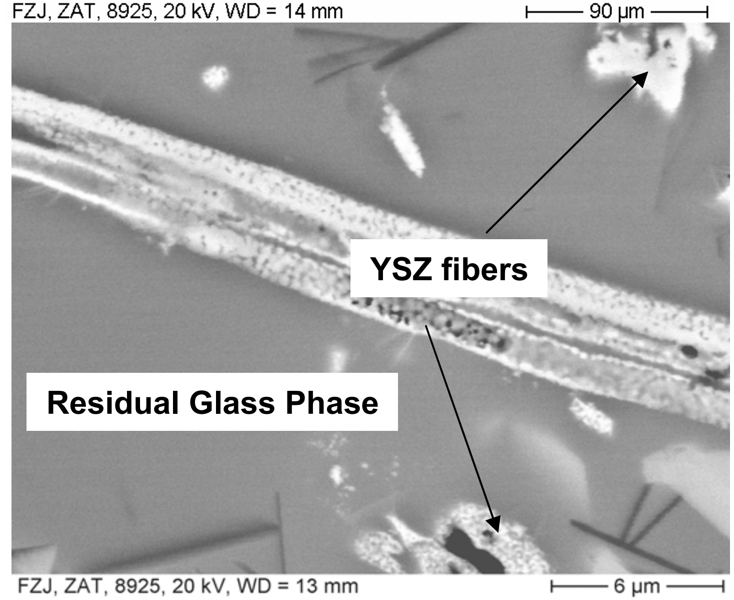
- Reduced crystallization kinetics of matrix
- Low porosity of the joint
- Minimal interactions of fibers

Linear correlation between thermal expansion and amount of filler

2. Doping of glass with ductile material (e.g. silver)

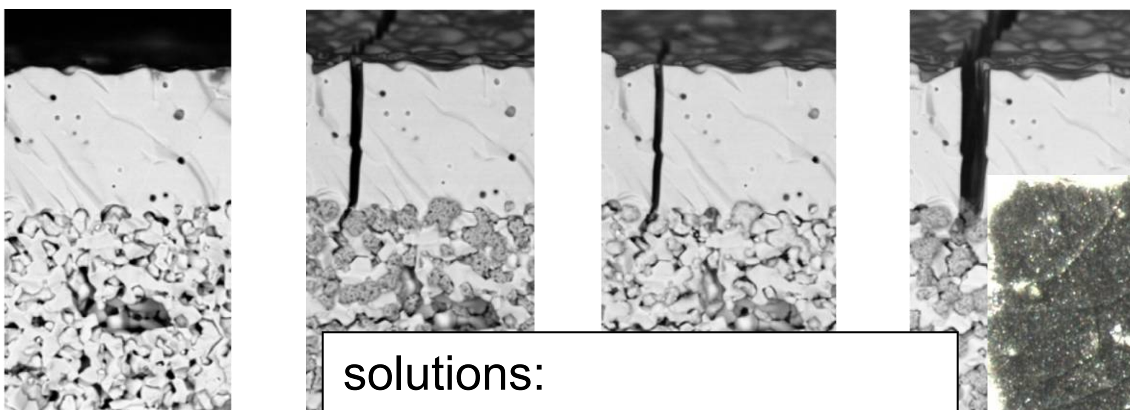
- increased strength
- but also increased conductivity



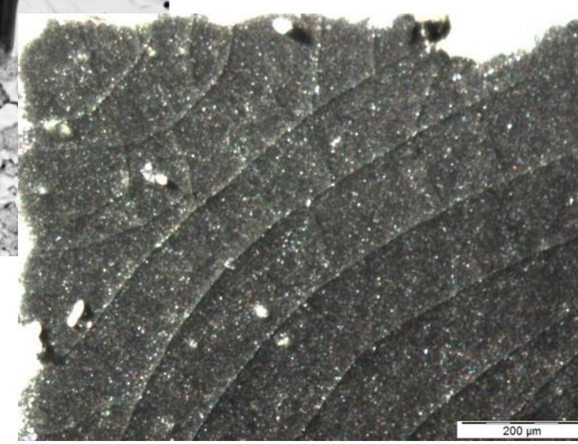


Redox Cycling Requirements

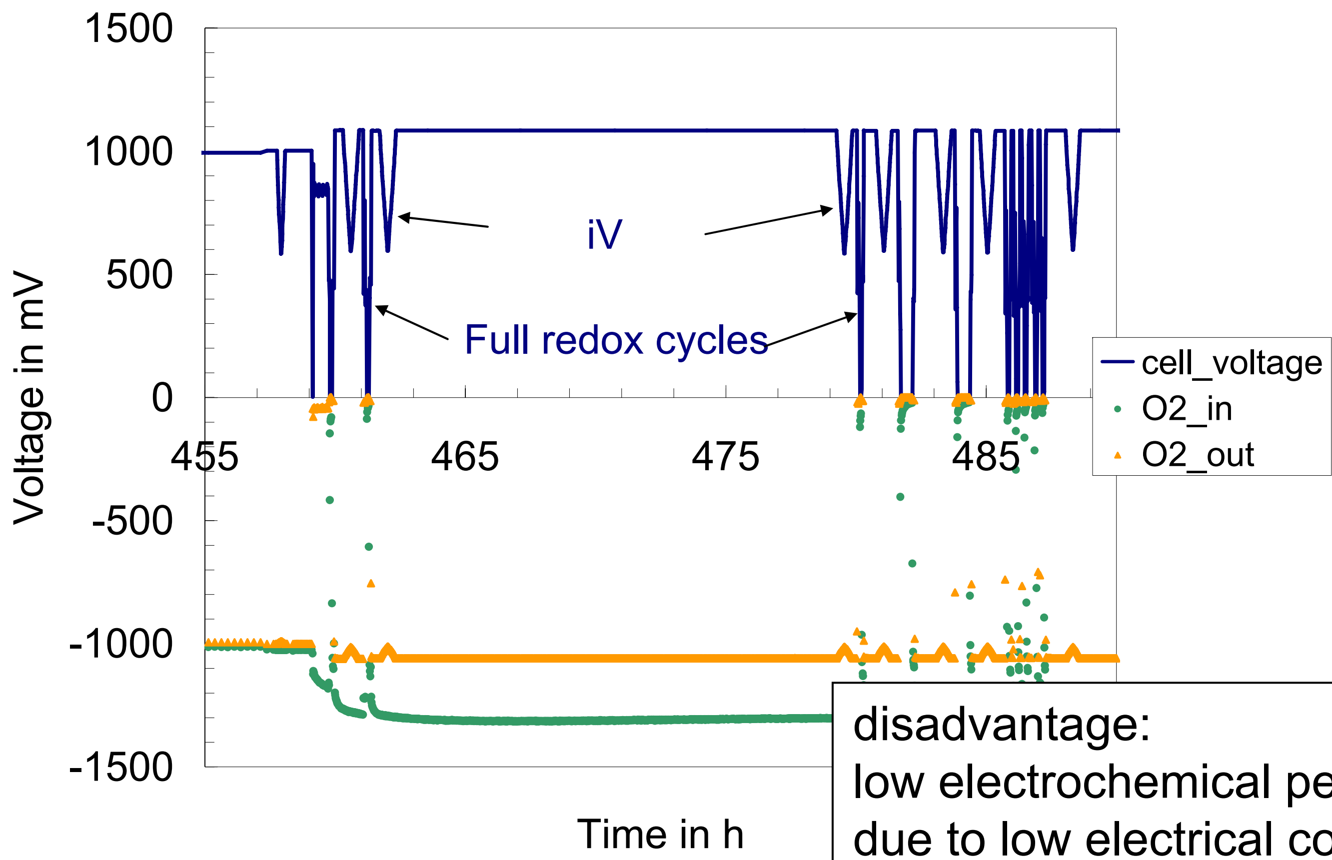
- redox cycles:
  - after stack shut-down air will flow to the fuel electrode
  - Ni in Ni-YSZ anode will re-oxidise to NiO_2
  - NiO_2 has higher volume and will cause mechanical damage to cell
- goals:
  - no gas leakages from stack (safe operation)
  - rapid start-up (30 minutes for road APU)



solutions:
- system control of temperature and fuel flow
- robust cells



Anode Redox Stability – SrTi Anode

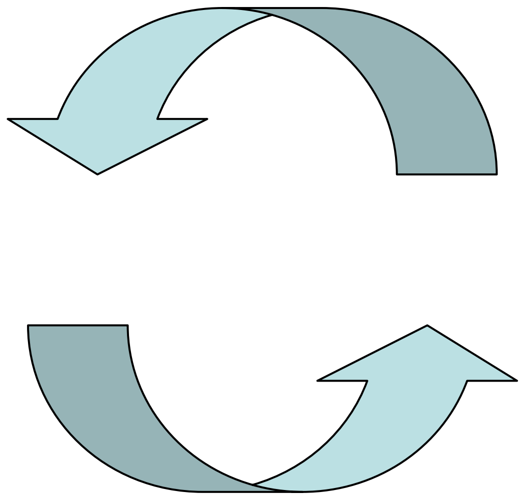


disadvantage:
low electrochemical performance
due to low electrical conductivity

Consolation of Conflicting Properties

low degradation

high performance



good handling and processing properties

improved robustness

(cost)

for instance:
redox stable materials (SrTi, LSMC),
with low conductivity and brittle structure

Interaction of Materials Developers and Manufacturers

‚improved‘ or ‚promising‘ material

→ processing properties

→ modified ‚compromise‘ material

→ processing ‚tricks‘

→ composite materials

→ functional ‚improved‘ component

building a bridge from materials research to component manufacturing

Outlook

Materials

- currently **best performing** materials have already been known for many years (no surprises)
- optimisation is necessary with respect to processing and **<u>cost</u>**
- **Lifetime** is still insufficient (but: trade-off with cost)
- **breakthroughs** are nevertheless necessary (new materials integrated with processing and manufacturing)

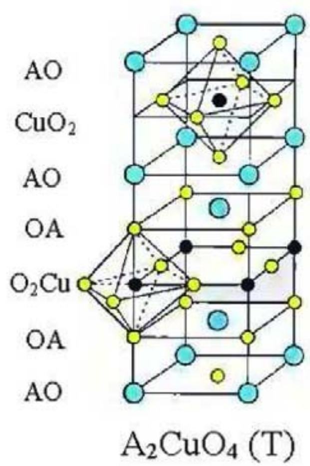
RTD challenges

- **purpose-designed** materials incl. *ab-initio* understanding
- **low-cost**, standardised, mass-production oriented manufacturing
- extended **lifetime** of components, **robustness**
- sufficient testing capacity for reliably & rapidly predicting materials performance (**optimisation loops**!)

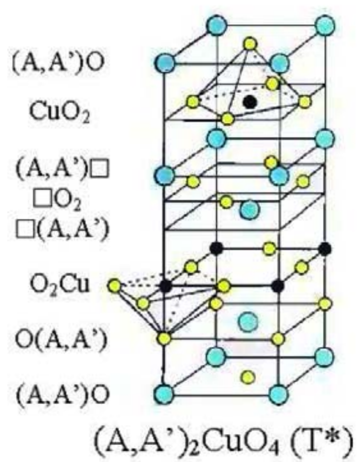
Project N-KATH

- cooperation between FZ-Juelich, MSU and BIC, and company HC Starck
- 'design' of cathode perovskite material according to theoretical considerations and models
- synthesis of materials
- verification in SOFC cell experiments

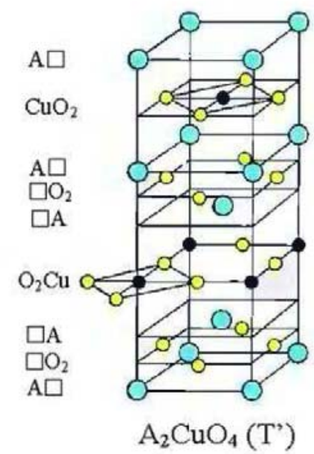
Layered perovskites: which structure blocks are necessary for good O-conductivity?



La_2CuO_4



$Pr_{1.6}Sr_{0.4}CuO_4$



Pr_2CuO_4

Understanding fuel cell degradation

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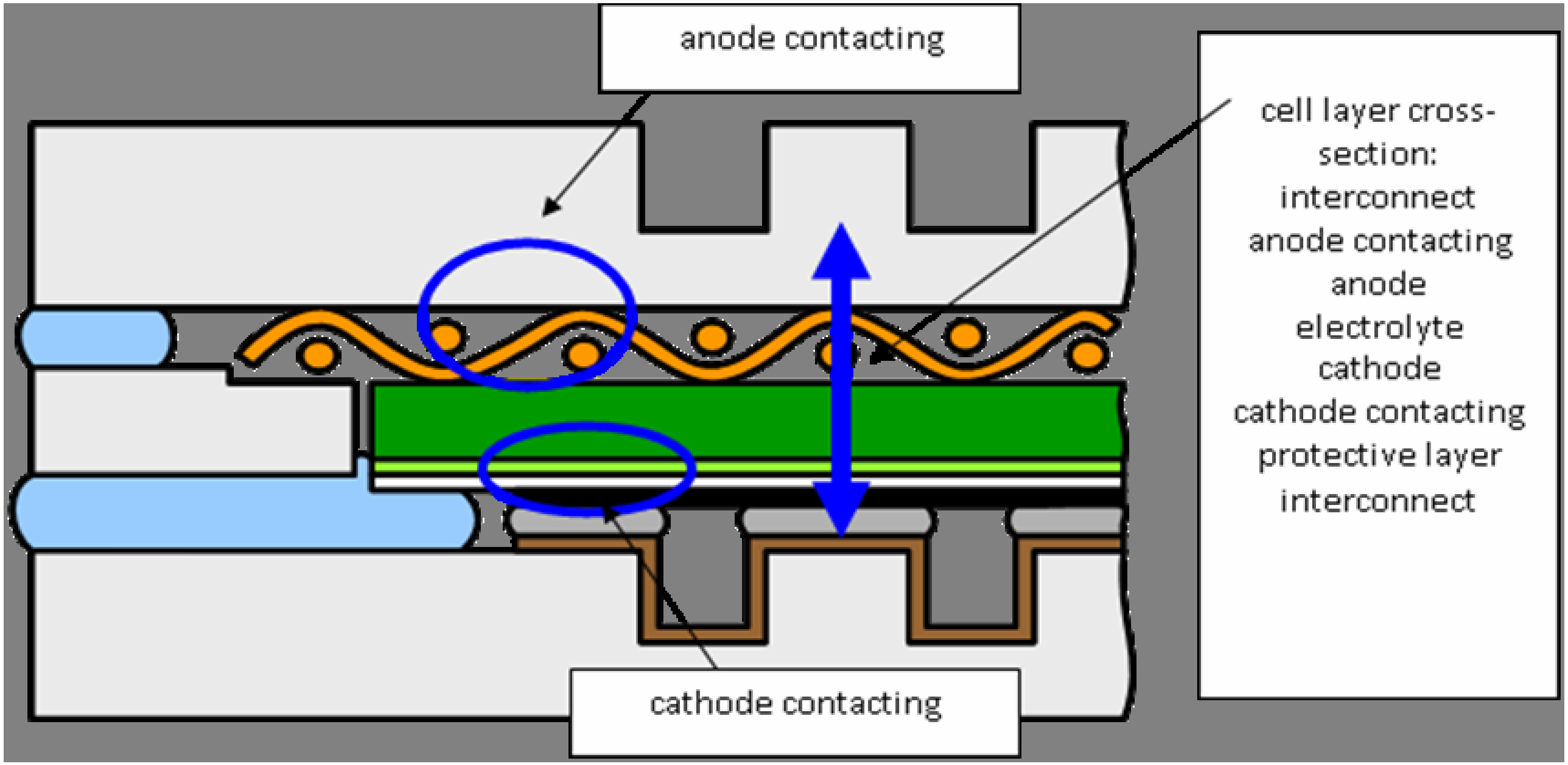
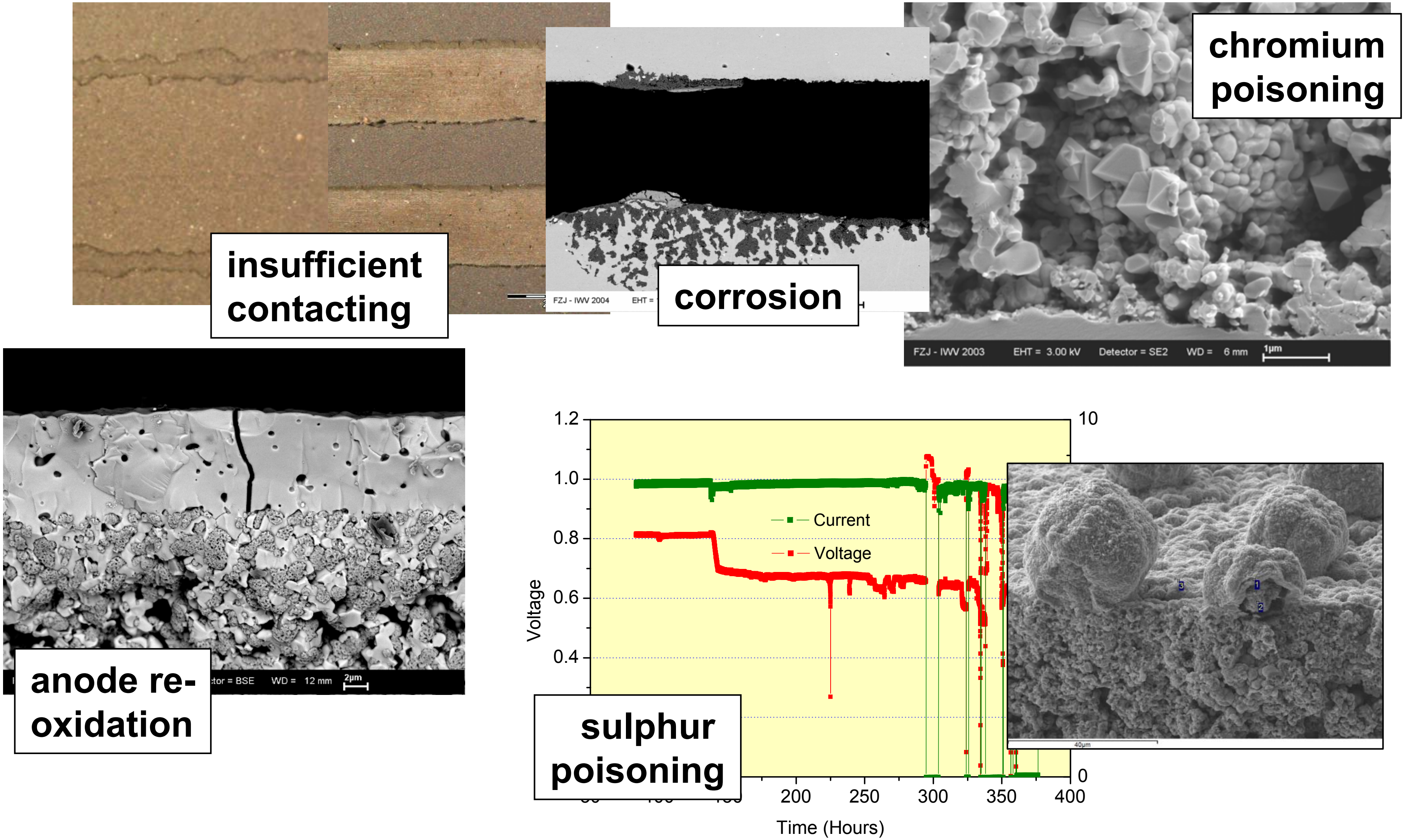
Stack repeating unit

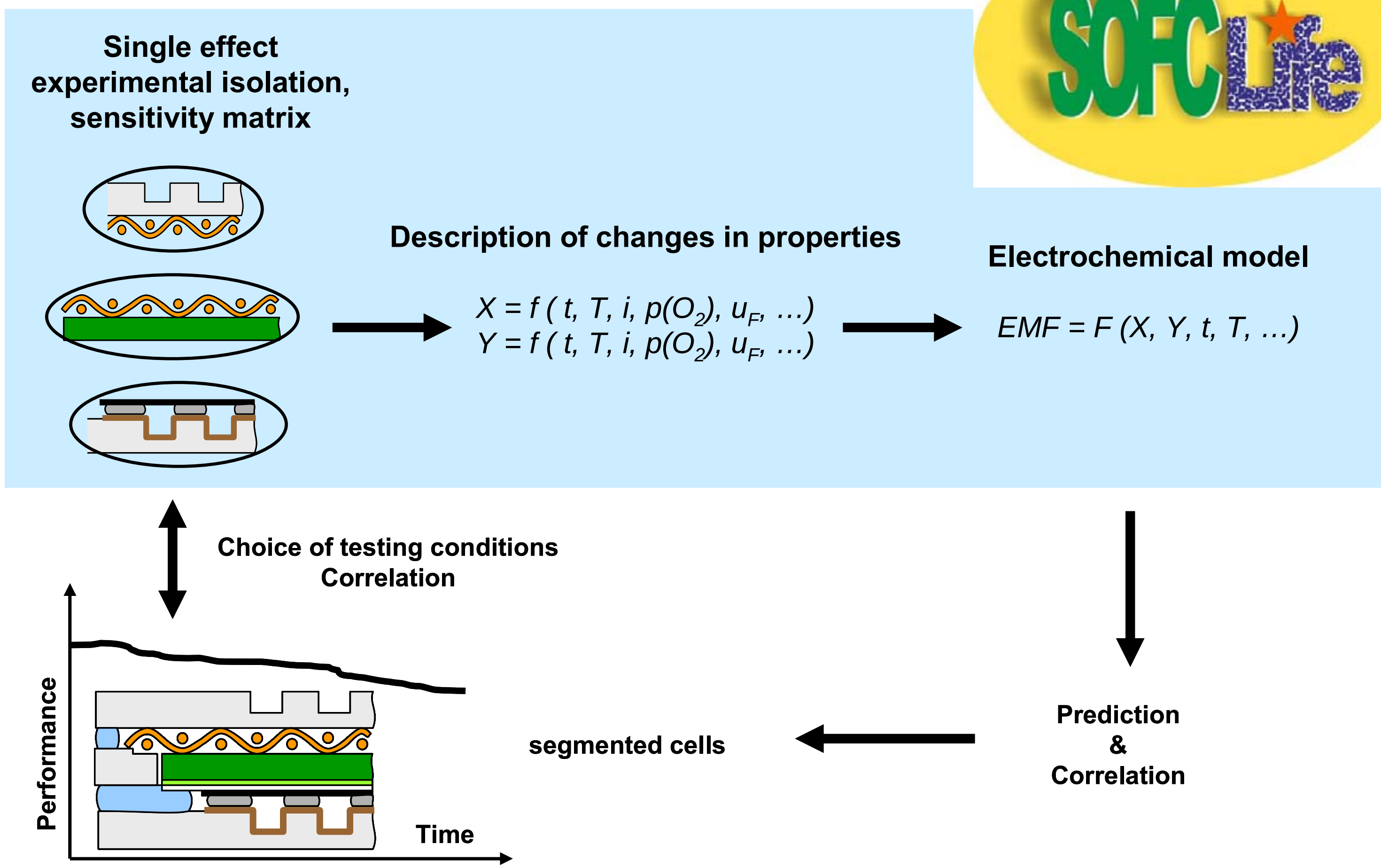


SOFC repeating unit components to be addressed and details of the specific layers that interface with each other

Variety of Degradation Phenomena



Understanding degradation



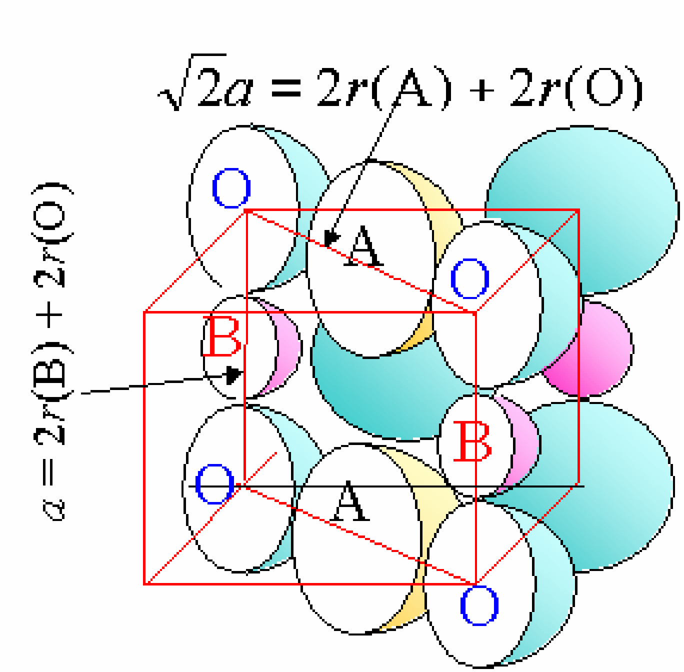
The quantification and prediction of single contributions with respect to their behaviour over time is the key expected outcome of this project

Degradation types

1. continuous, steady degradation
   - initialisation phase (sintering, saturation)
   - constant slope phase
   - progressive degradation phase (EoL)
2. degradation after ‚events‘
   - thermal cycle
   - redox cycle
3. degradation after ‚incidents‘
   - malfunction of BoP components
   - malfunction of control
   - external influence (shock, grid outage etc.)

Cathode Materials: Stability

thermodynamical stability and kinetics:
perovskites ABO_3



$(La,Sr)MnO_3$

$(La,Sr)FeO_3$

$(La,Sr)CoO_3$

$(La,Sr)(Co,Fe)O_3$

$(La_{0.9},Sr_{0.1})MnO_3$

$(La_{0.7},Sr_{0.3})MnO_3$

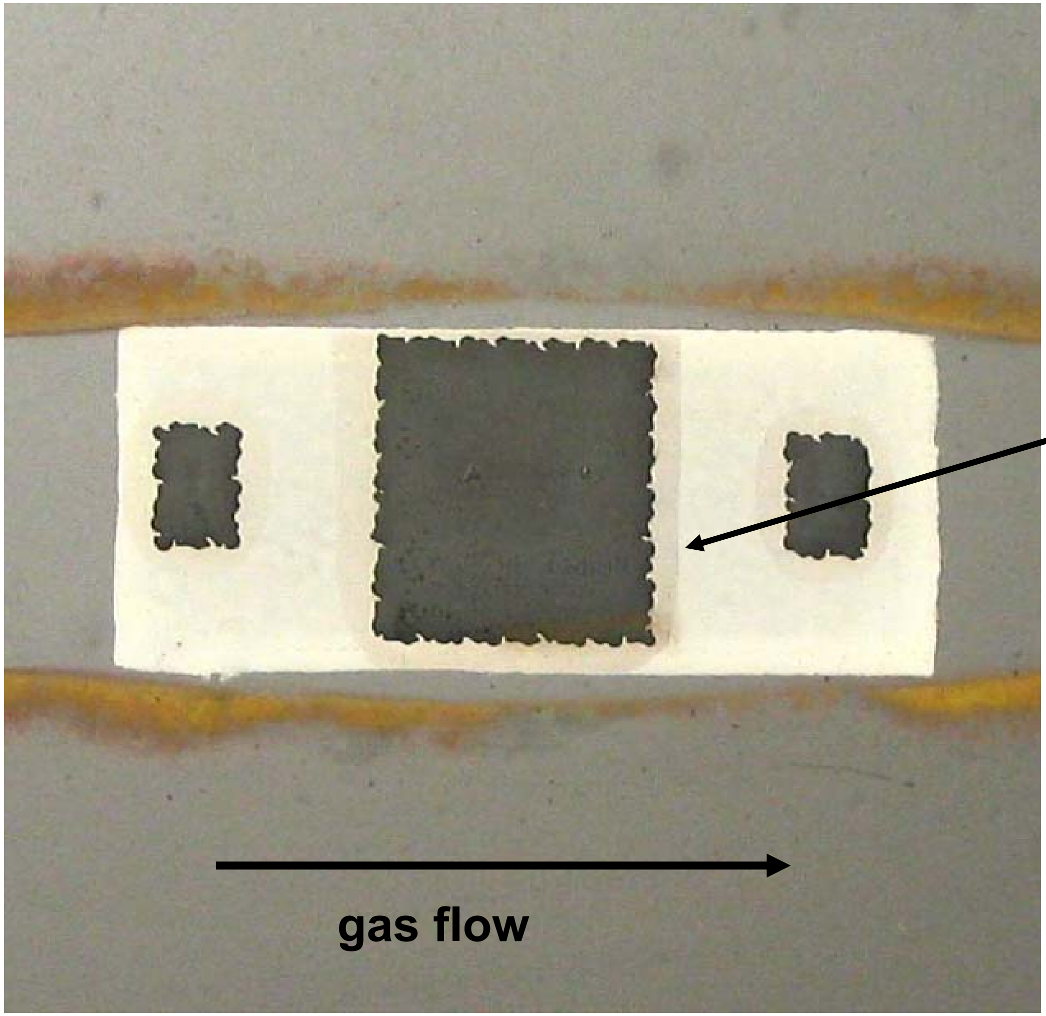
$(La_{0.7},Sr_{0.3})_{0.99}MnO_3$

$(La_{0.7},Sr_{0.3})MnO_{3\pm\delta}$

$(La_{1-x}Sr_x)_yFe_{1-z}(Ni,Cu)_zO_{3-\delta}$

source: Yokokawa, EMPA

Cathode Materials: Volatility



Sr deposition

source: Tietz/Mai

Anode Substrate: Particle Agglomeration

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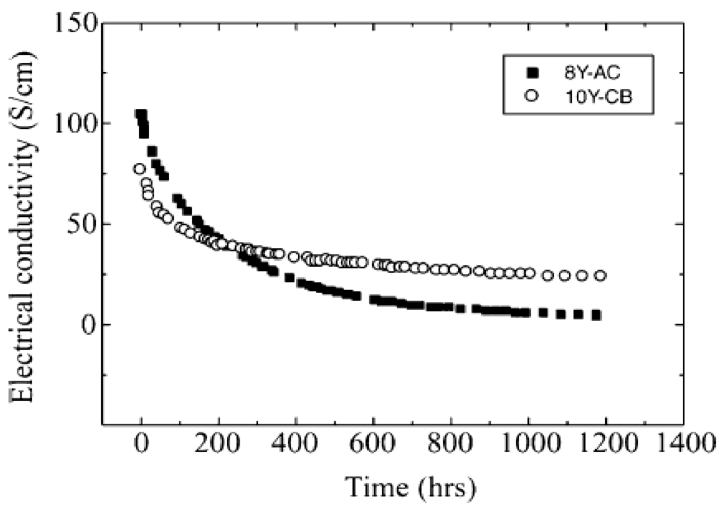
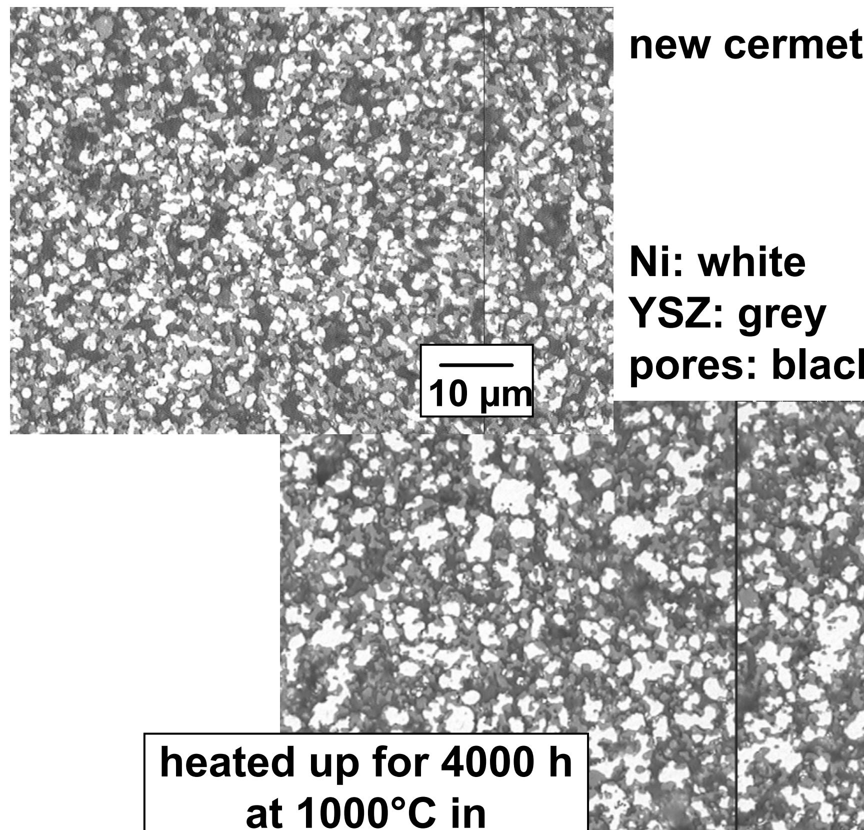
- temperature-induced tendency of metals to decrease free energy, i.e. to minimize the surface area and agglomerate
- examples: anode substrate Ni-YSZ cermet



K.S. Lee et al. / J. Solid State Electrochem. 11 (2007)1295



new cermet

Ni: white
YSZ: grey
pores: black

heated up for 4000 h at 1000°C in $Ar/4\%H_2/4\%H_2O$

Three-Dimensional Characterisation

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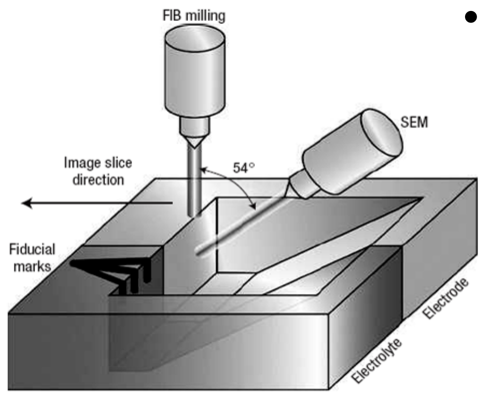
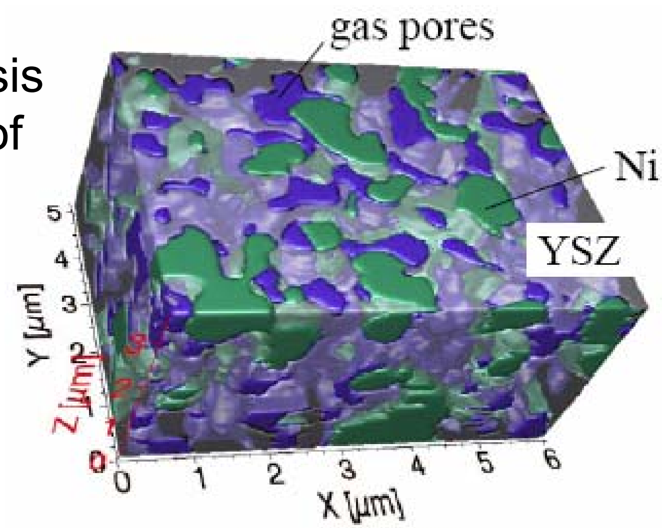
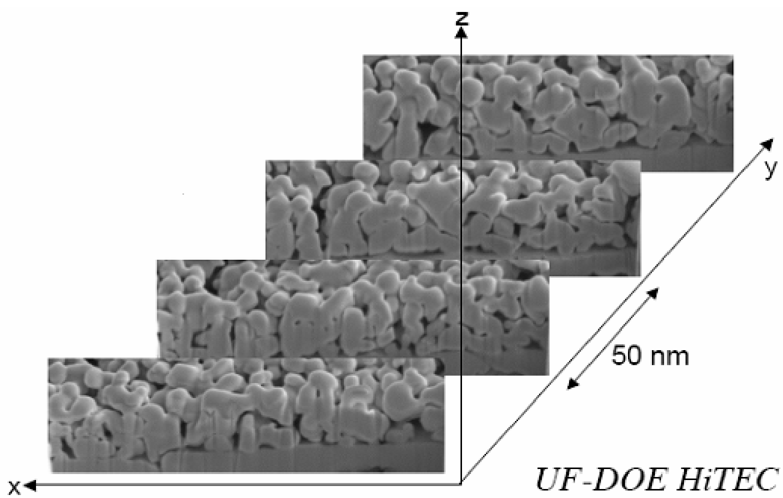
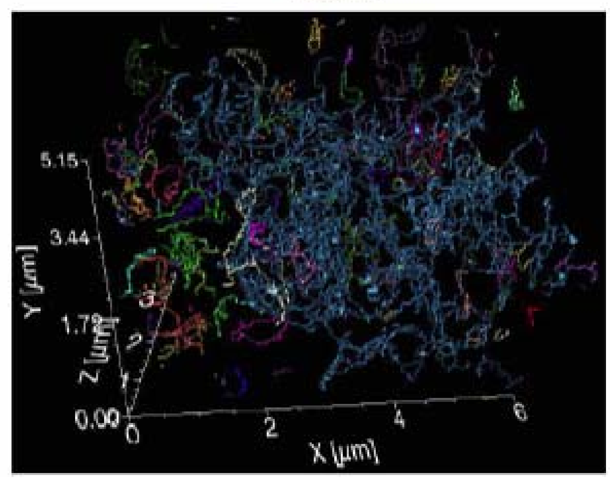
- FIB/TEM analysis
- reconstruction of 3-D structure from ‚slices‘



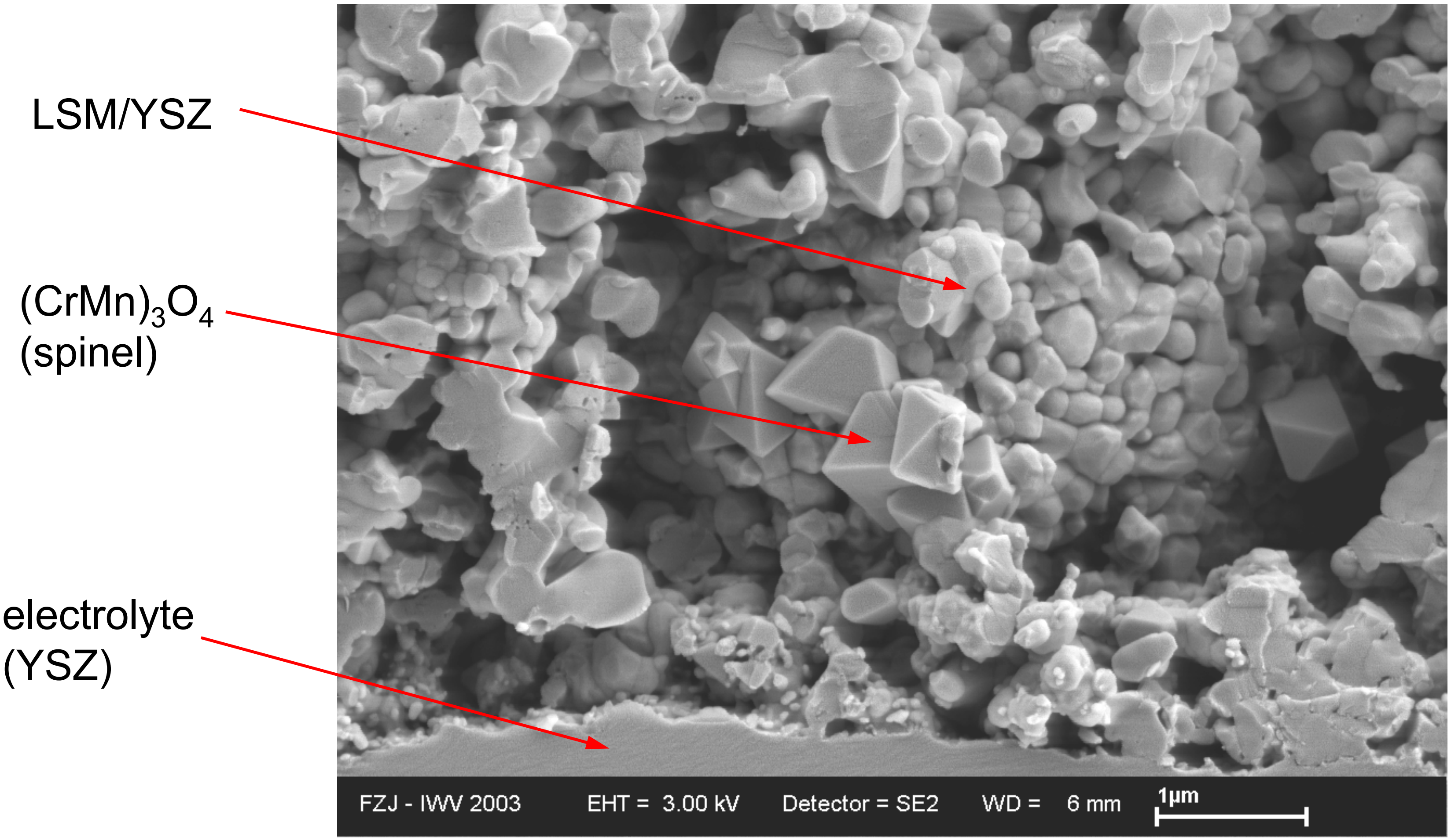




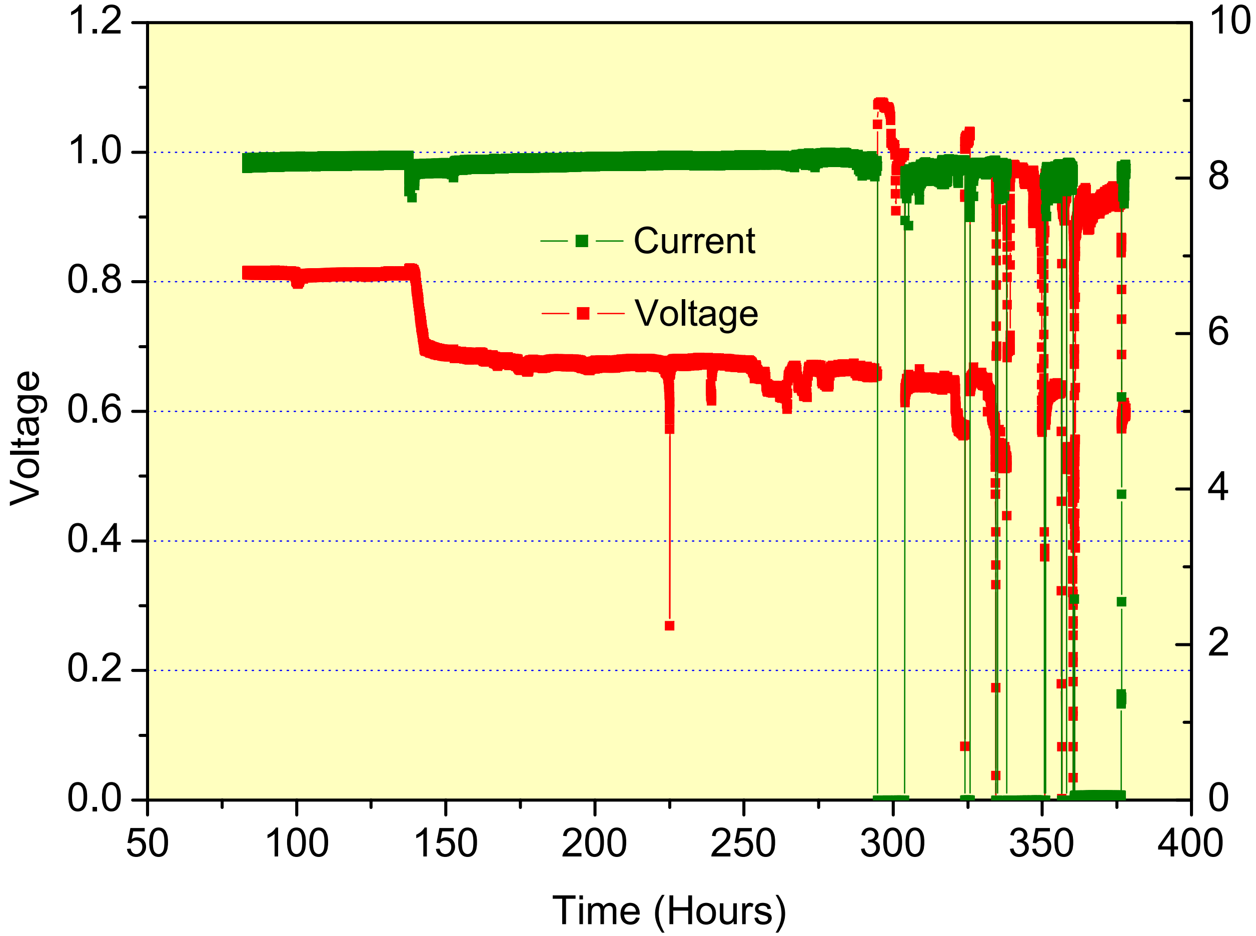


J.R. Wilson et al. / Nature Materials 5(2006)541

Chromium Poisoning: Microscopic Findings



Sulphur Poisoning – The Phenomenon



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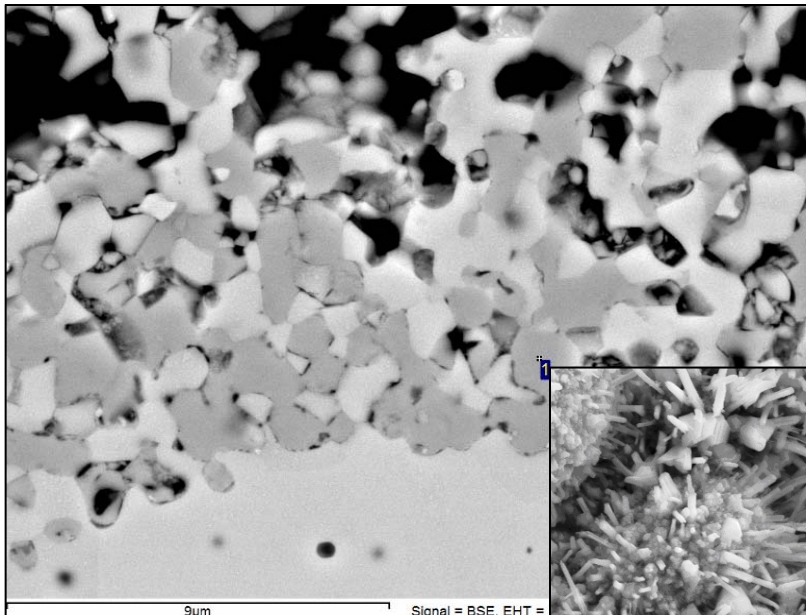
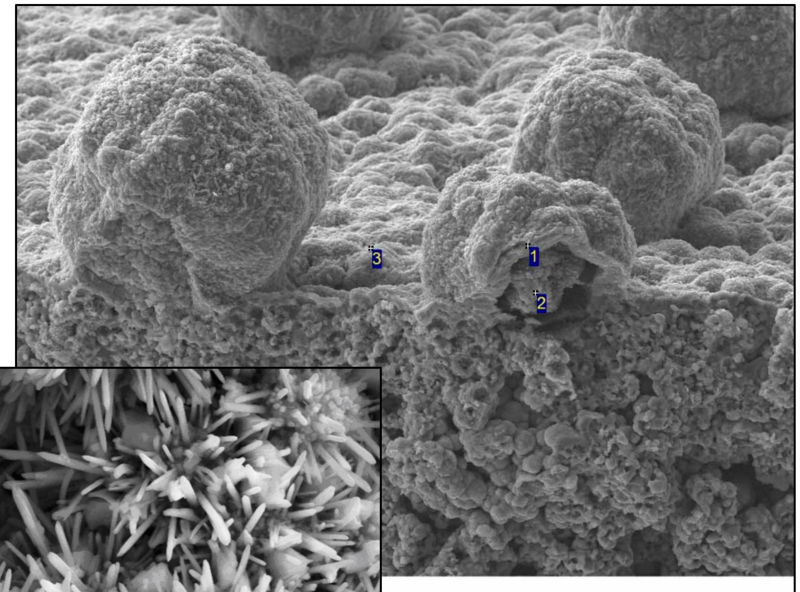
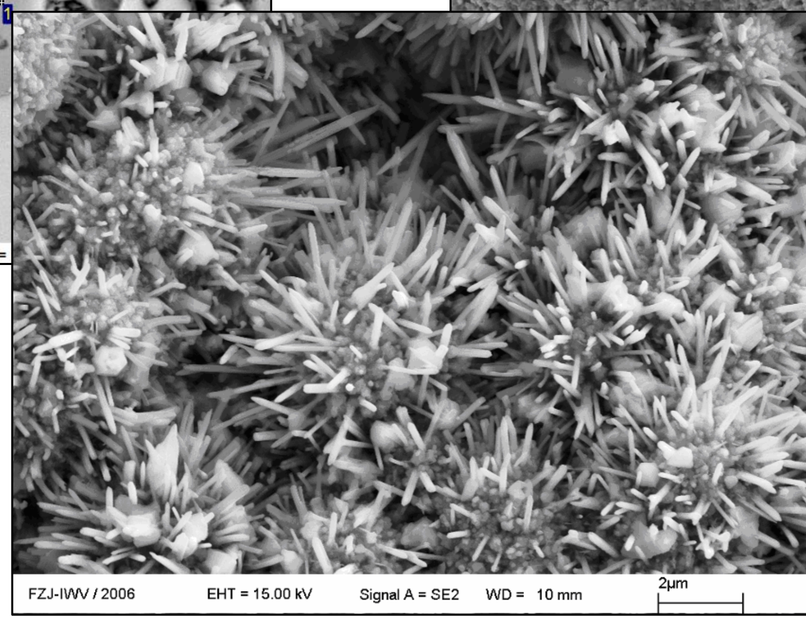
Sulphur Poisoning: Microscopic Findings







bulk material deposition

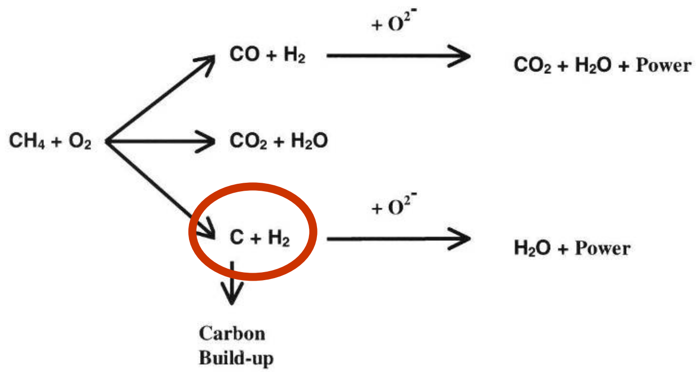
- ► **Reduction of porosity**
- ► **Elimination of catalytically active Ni**

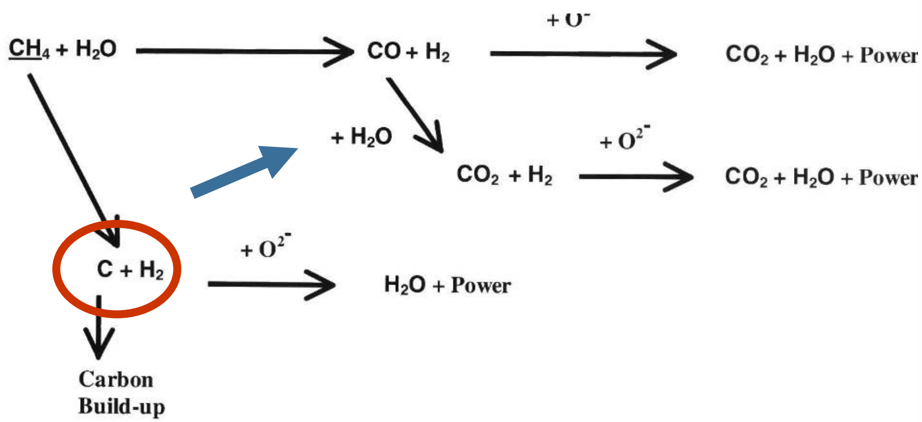
surface deposition

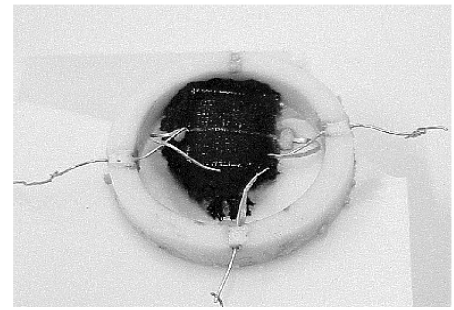
- ► **Elimination of catalytically active Ni**

Coking – Carbon Buildup in Internal Reforming

carbon build-up due to hydrogen and oxygen stochiometry mismatch (Boudouard Reaction)







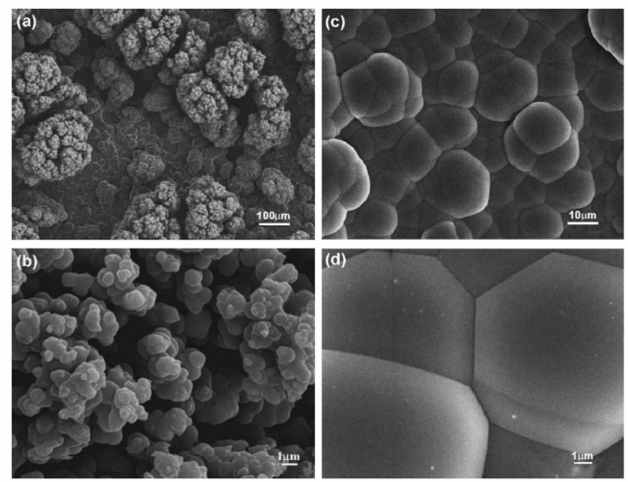


Fig. 4. The morphology of carbonaceous deposits on the surface of an anode containing 10 wt.% CeO_2 and 20 wt.% Cu after long-term testing in *n*-butane at 1173 K.

figures courtesy of Jörger & He

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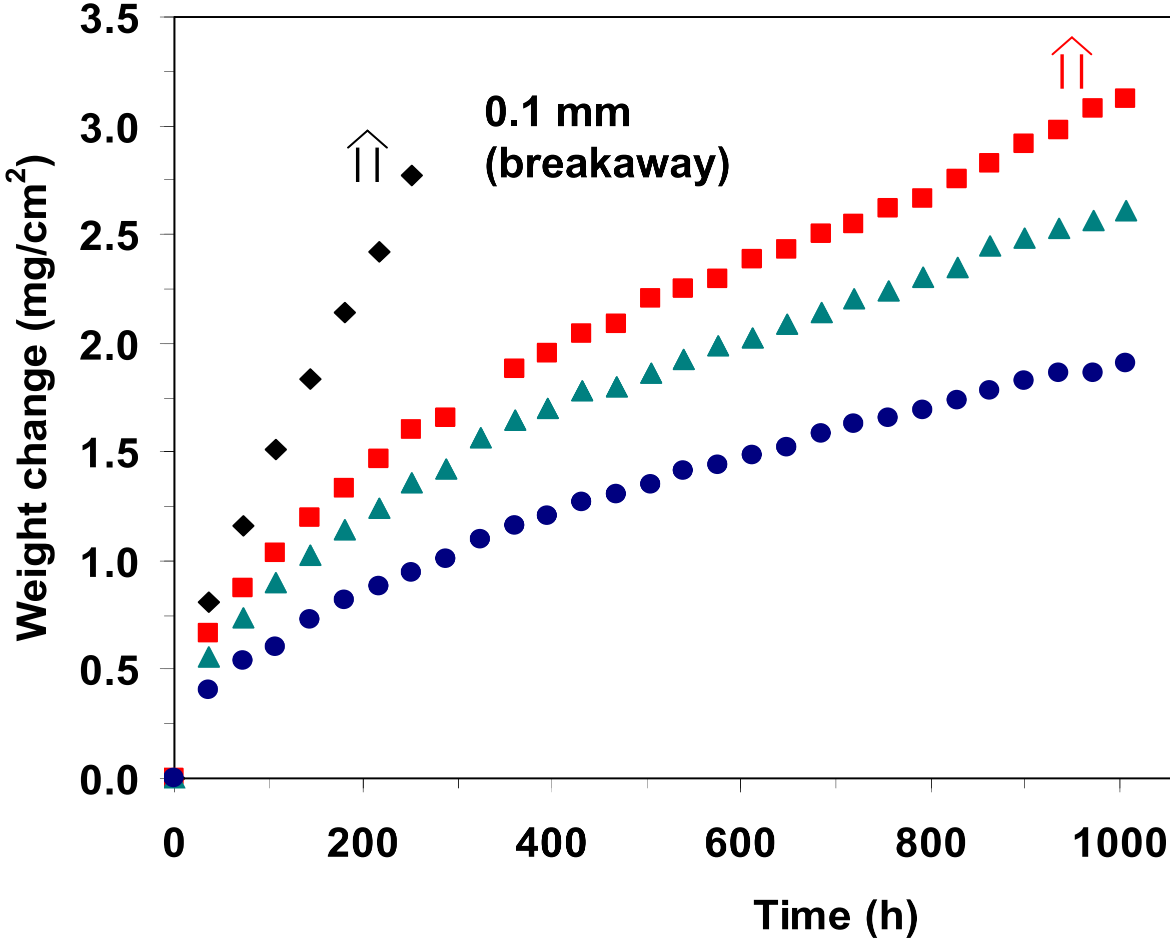
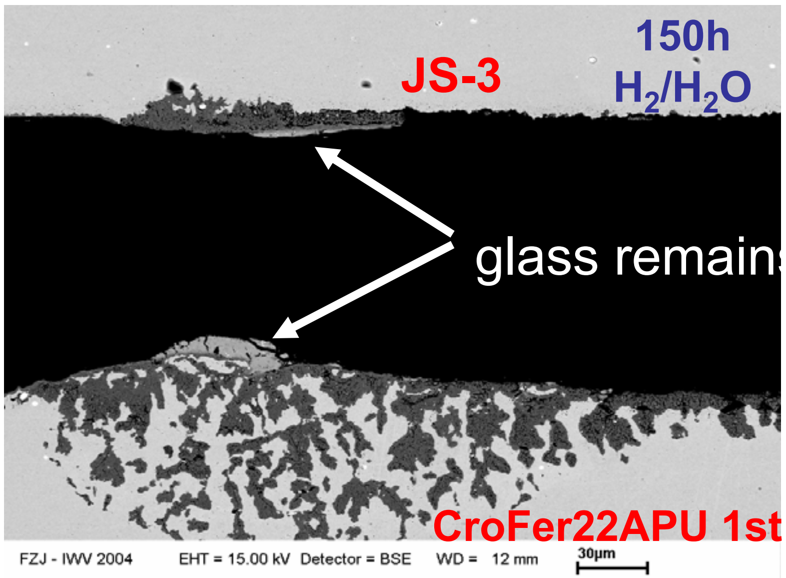
Break-Away Corrosion

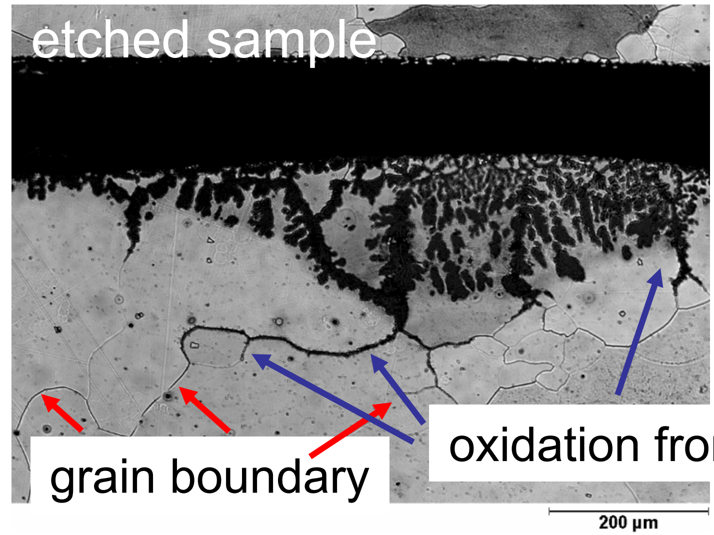
Cyclic Oxidation of Ferritic Steel Crofer 22 APU in Air at 900°C



k_p–dependence on specimen thickness

Interaction of Glass Sealant and Ferritic Interconnect





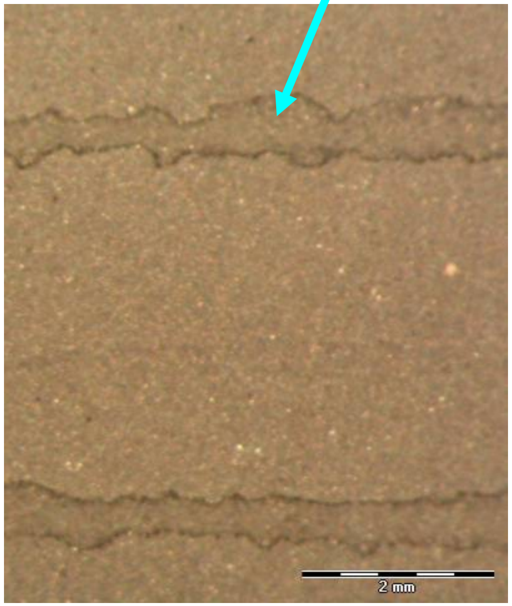
optimal matching of steel and sealing materials is vital:

- good adhesion = chemical interaction
- but: no excessive corrosion

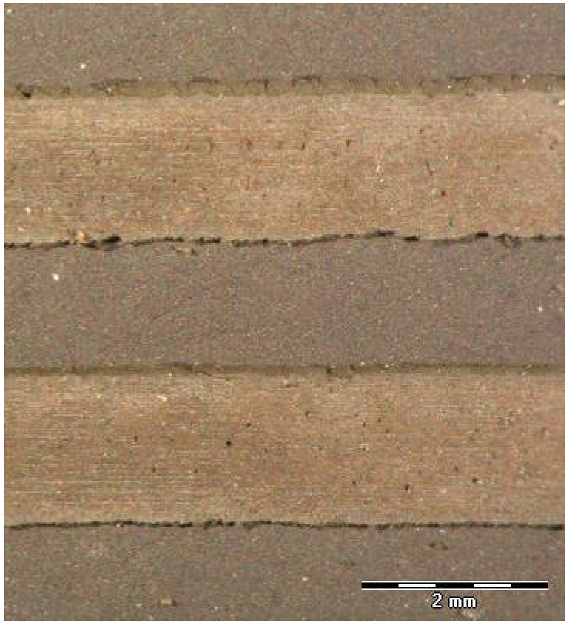
High Degradation due to Contacting problems

Contact trace on cathode

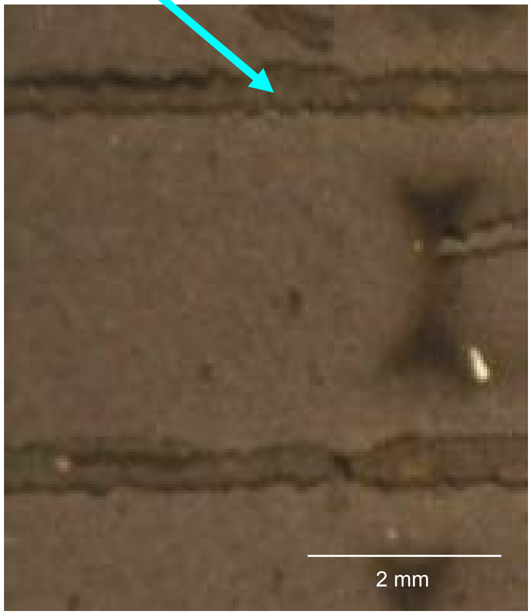
high local current due to narrow contacting ‚ridge‘



820 mV - 336 mA/cm²



770 mV - 336 mA/cm²



880 mV - 298 mA/cm²

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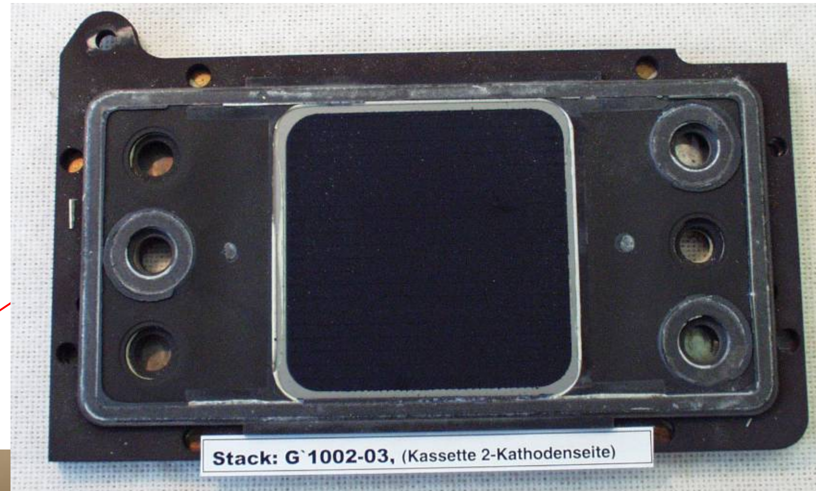
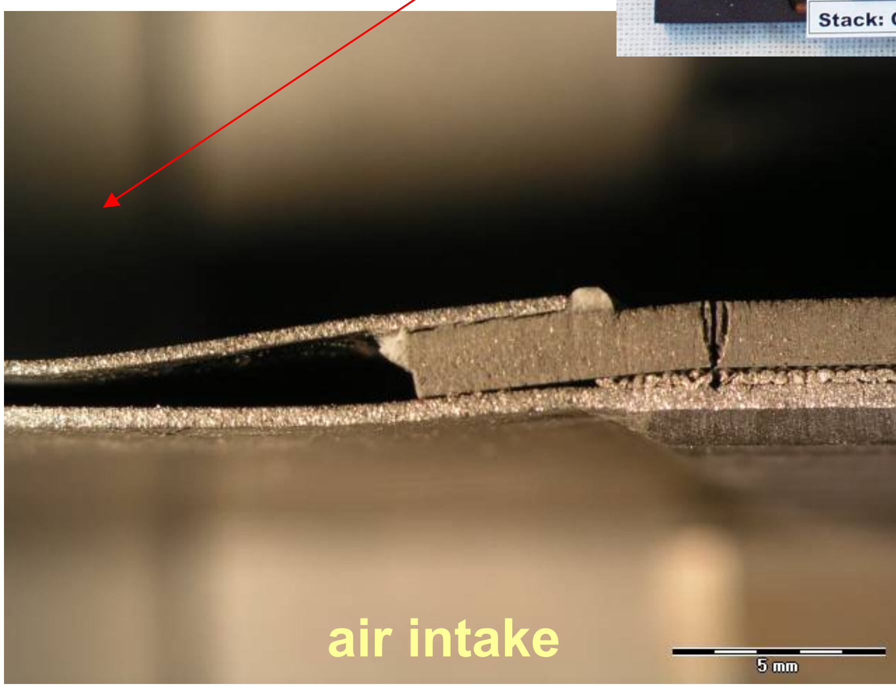
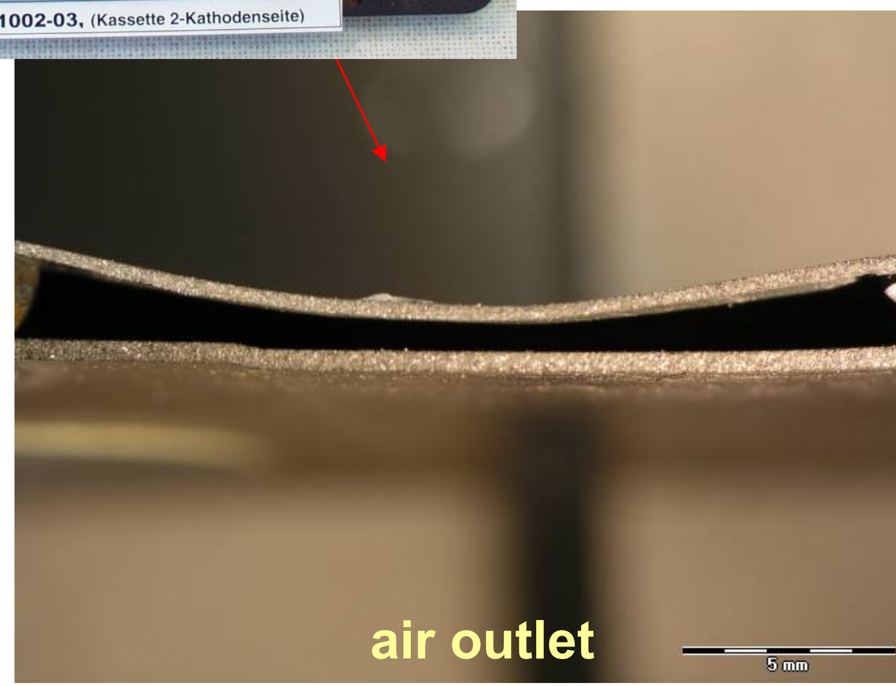
Thermo-Mechanics

low strength of steels at high temperatures







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Conclusions

- materials development is crucial in improving the performance of electrochemical devices (like fuel cells)
- developments have to be coordinated with practical aspects of technology
- the understanding of materials behaviour is just as important as the development of ‘new’ materials
- microscopy and tomography are essential tools in doing so
- lifetime modelling can help in developing accelerated testing and prediction methods for materials and components

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MMLCR=SOFC, N-KATH

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