EVOLVE FUEL CELL

Preparation and characterization of metal supported solid oxide fuel cells with screen-printed electrodes and thin-film electrolyte

Feng HAN[1]*, Robert SEMERAD[2], Patric SZABO[1], Rémi COSTA[1]

feng.han@dlr.de

[1]Institute of Engineering Thermodynamics, German Aerospace Center (DLR), Stuttgart, 70569, Germany

[2]Ceraco Ceramic Coating GmbH, Ismaning, 85737, Germany

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FCH FUEL CELLS AND HYDROGEN JOINT UNDERTAKING

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Content

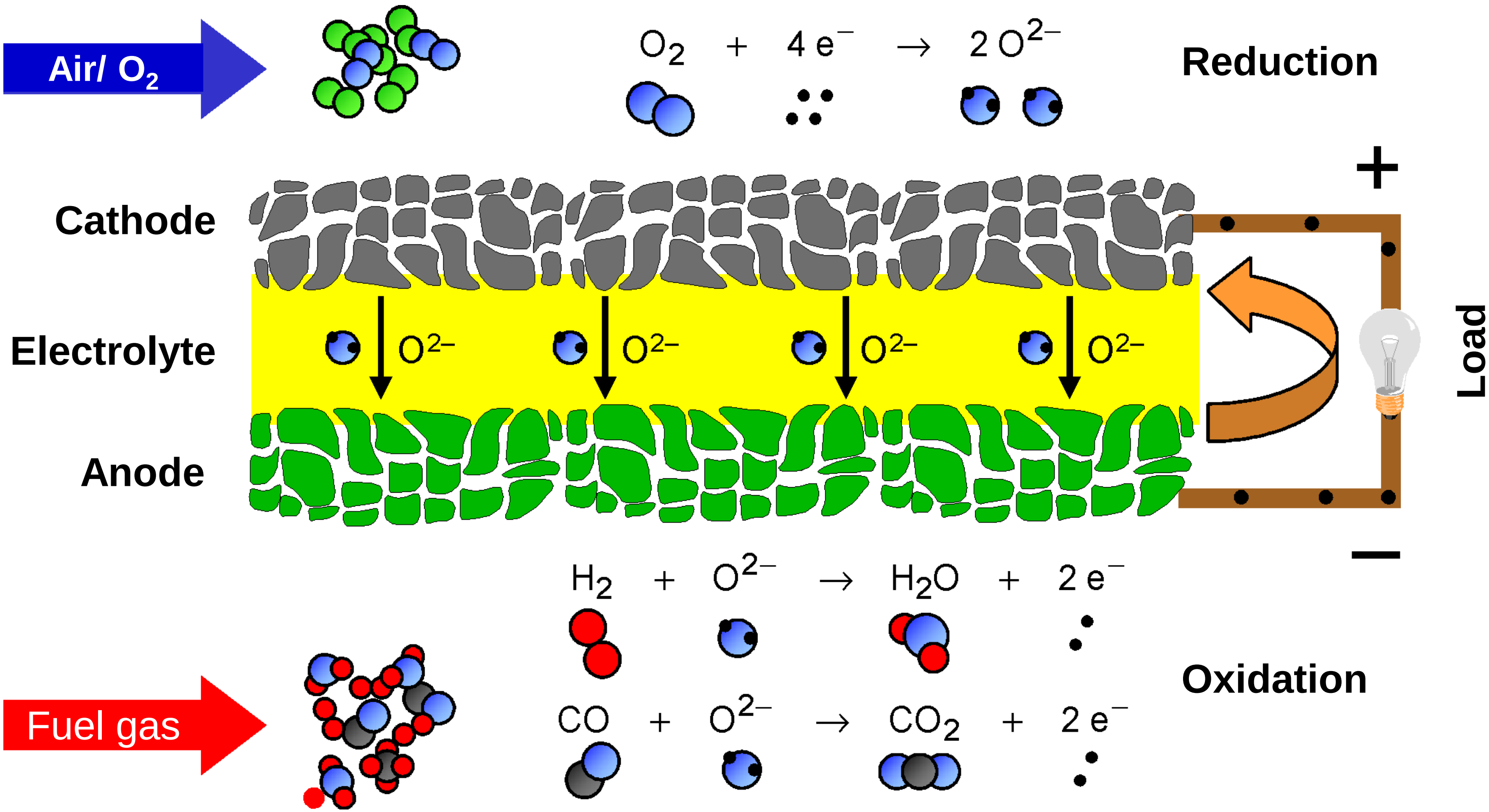
Introduction of SOFCs

Processsing of planar SOFCs

MSC with screen-printed electrodes and thin-film electrolyte

Summary & Perspectives

Repetition of Basic Principle



Source : L.G.J. de Haart, IEF-3, FZJ

Motivation: towards the next generation SOC

1st gen.	2nd gen.	3rd gen.	4th gen.
ESC	*ASC*	*MSC*	
Limited power density	*High power density*	*High power density*	*High power density*
Robustness	*Sulfur poisoning*	*Sulfur poisoning*	*Sulfur resistant*
	Fast thermal cycling	*Fast thermal cycling*	*Thermal cycling*
	Redox Cycling	*Redox Cycling*	*Redox Cycling*
			Low cost
Stationary	*Stationary*	*Stationary*	*Stationary*
Transportation	*Transportation*	*Transportation*	*Transportation*

Flexible architecture for multiple applications

Which materials for the next generation of SOCs?

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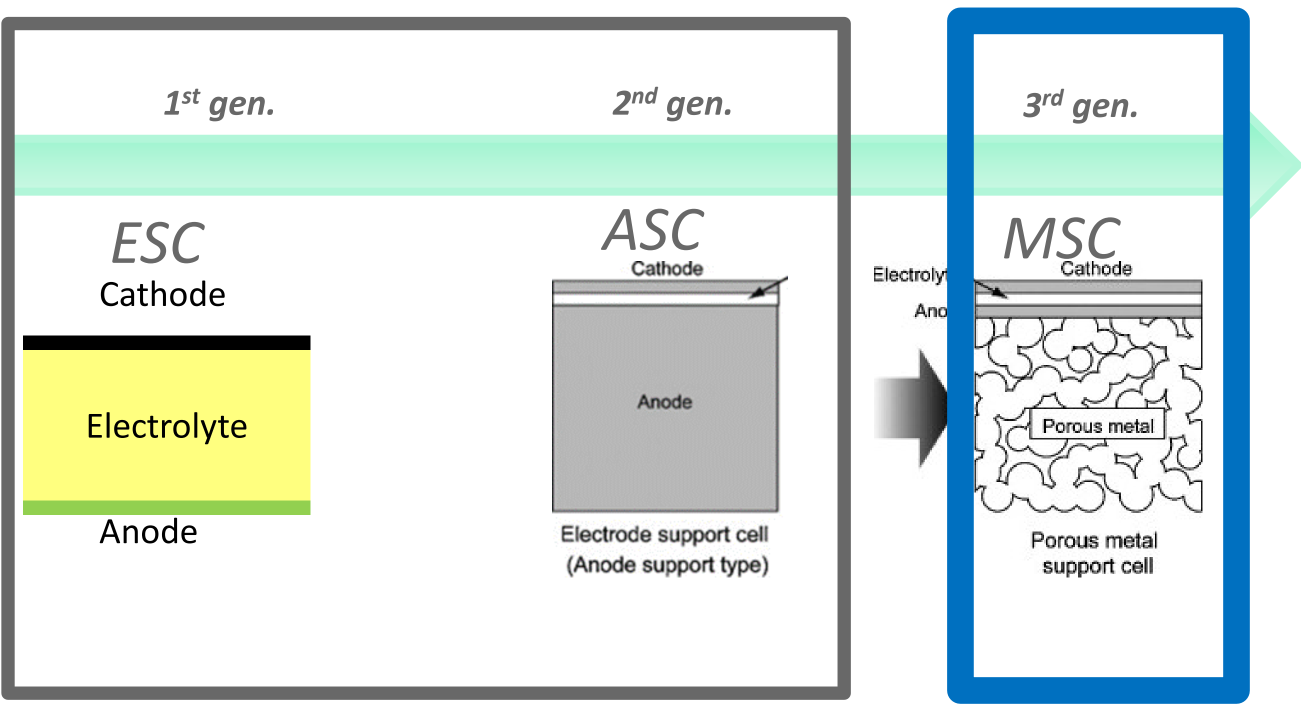
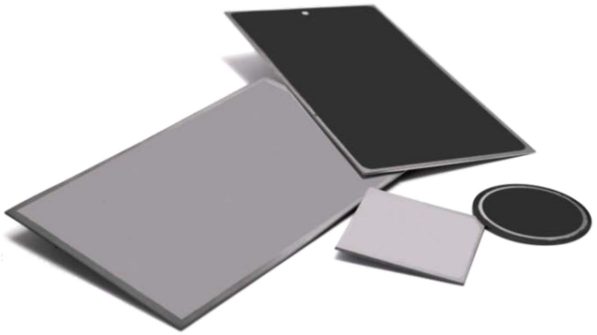
Potential Advantages of Metal Suppoerted Cells



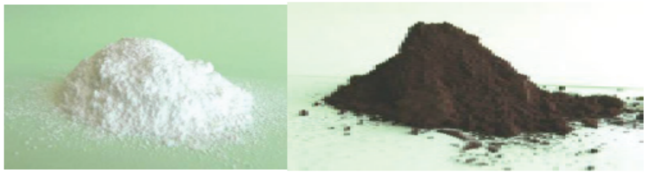


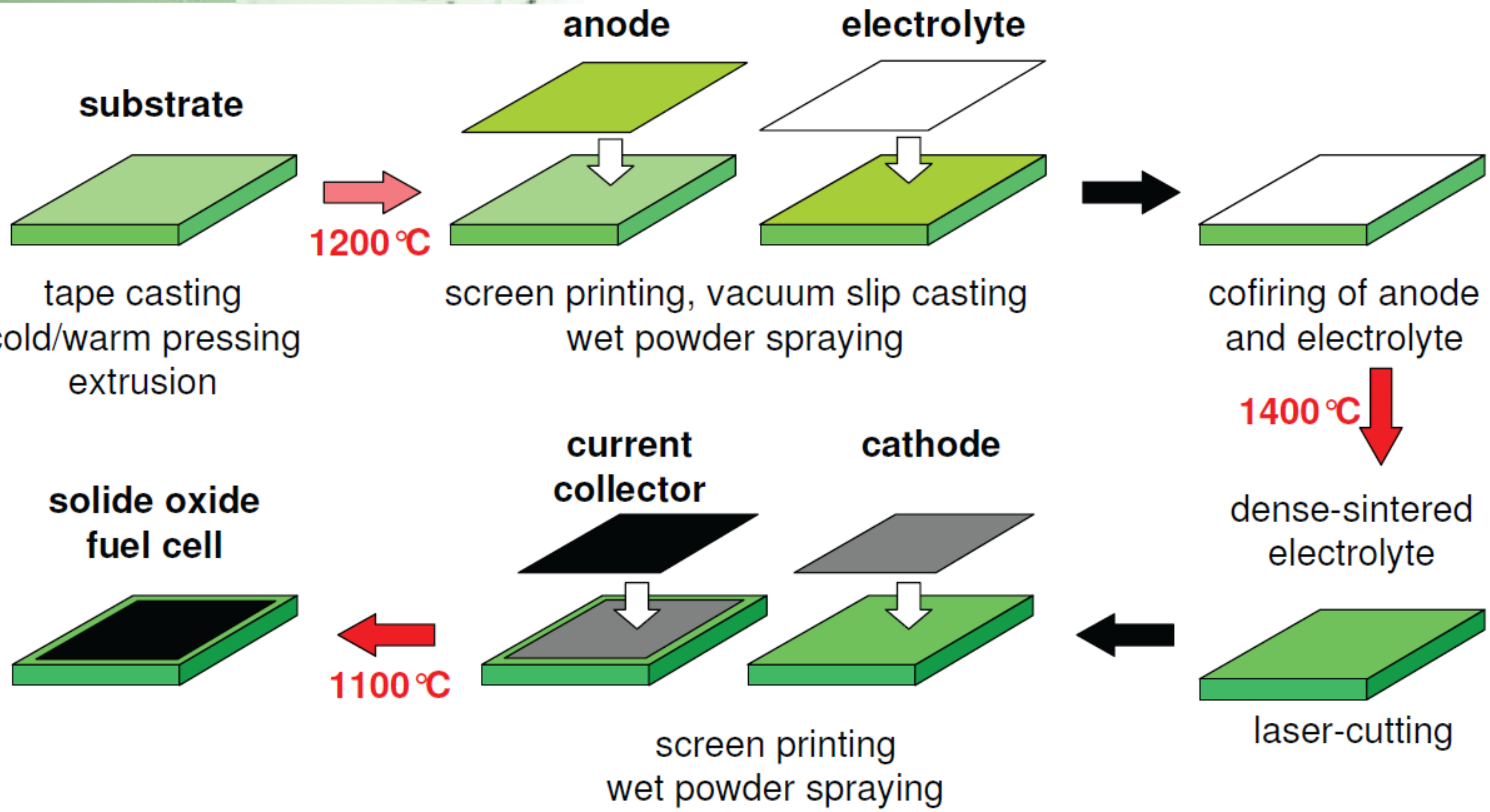
- To Replace ceramic components by metals
- Operating temperature > 600 °C
- Atmosphere: Hydrogen / or Synthetic Gas, Air
- Reversible operation

Metal supported Cell (MSC):

- High robustness
- High resistance against thermal and redox cycling
- Good integration into interconnects (bipolar plates) via brazing or welding
- Low cost of metal support and cell materials (thin layers)
- High electronic and thermal conductivity

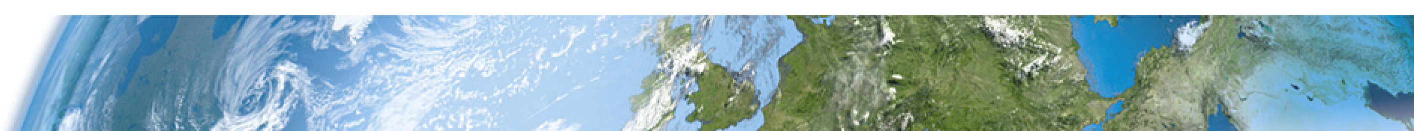
Manufacturing Route (conventional ASC)





M. Bram, IEF-1, FZJ

Alternatives without sintering: plasma spraying, PVD



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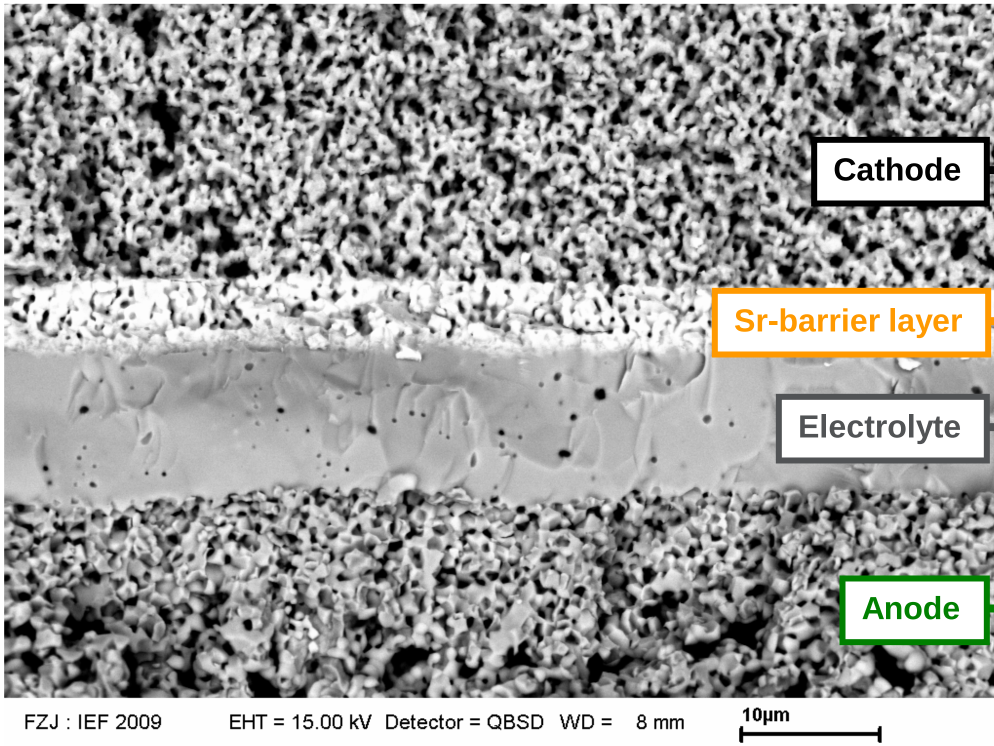
SEM fracture surface of anode-supported SOFC

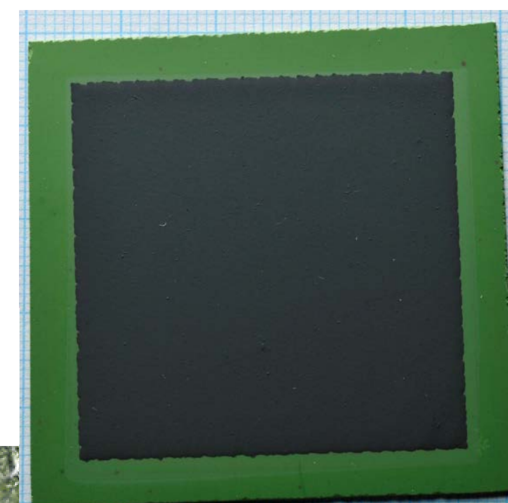


$La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF)

$Ce_{0.8}Gd_{0.2}O_{2-\delta}$ (CGO)

8mol% Y_2O_3-ZrO_2 (8YSZ)

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



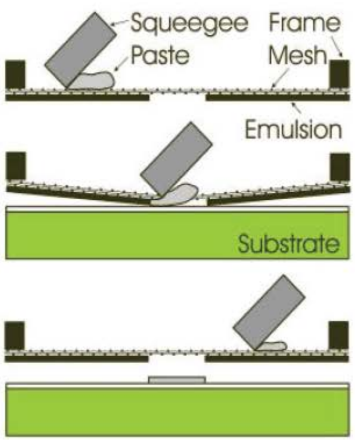
Sintered single cell
50mmx50mm

Screen Printing

origin: printing industry (non-paper prints, e.g. CD etc.) to print letters and graphics

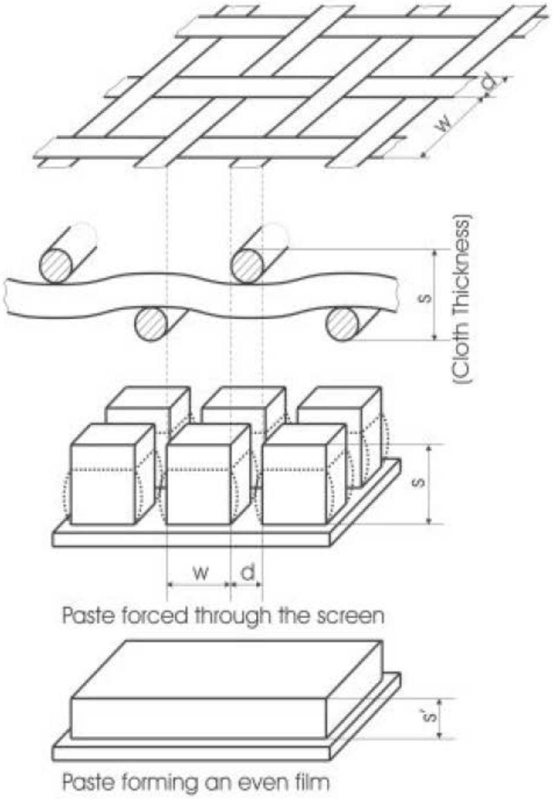
ceramic applications: large screen opening (50-70% open area)
easy to create contured coatings

thickness of dried layer ~1/4..1/2 of wet layer (spreading and drying)
=> 5 .. 100 µm feasable



printing scheme

threads by polymer, steel, or liquid crystal polyarylates



screen mesh and wet film

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Screen Printing Paste Preparation

powder (d_{50}~0.1..50µm)
solvent (e.g. terpineol)
dispersant

↓

mill / homogenize

binder (e.g. etyhl cellulose)
solvent (e.g. terpineol)

↓

homogenize / filter

three roll mill

↓

ready to print paste

clean room preferable

↓

printing

↓

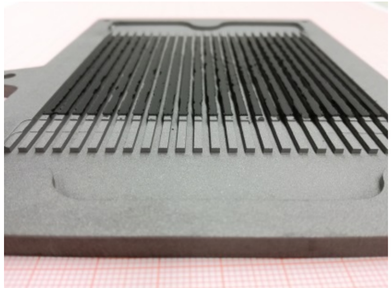
drying

Paste for Energy Devices at DLR

1. SOFC/SOEC
2. PEMFC/PEMEC
3. Battery
4. Thermoelelectric Generator
5. Gas Separation Membrane

Paste for SOFC functional layers

1. Anode: NiO-YSZ, NiO-GDC, NiO-BCZY, LST-NiO
2. Cathode: LSM-YSZ, LSCF, LSC
3. Electrolyte: YSZ, GDC, BCZY
4. Contact layer: LSCF
5. Sealing: glass sealant



Contact coating for Bi-polar plate

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Objectives in this work

Demonstration of the feasibility of the cell concept and design

Development of metal supported SOFCs without nickel as structural components, improving redox cycling stability and sulfur tolerance.

Deposition of gas-tight thin-film electrolyte (~3 μm thick) layers

Apply perovskite based materials for anode functional layer in MSC

Material Selection

- *Improving durability of the metallic substrate*

➢ ***Implementing alumina forming alloys (NiCrAl)***

- *Enhancing sulfur tolerance and redox stability at the anode*

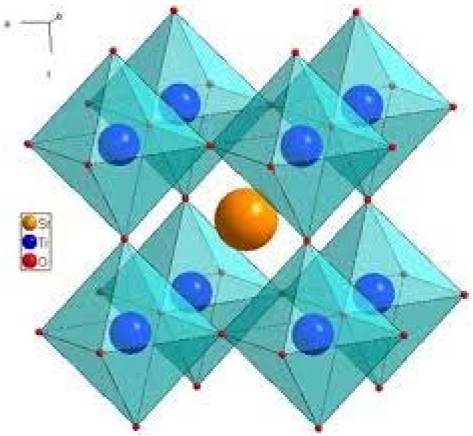
➢ ***Perovskite based anode materials***

- *Ensuring the electrolyte with good gas tightness and electrical property*

➢ ***Multi-layered thin film***

- *Avoiding High T sintering and reducing atmosphere*

➢ ***low T (max. 1000 °C) processing in air***



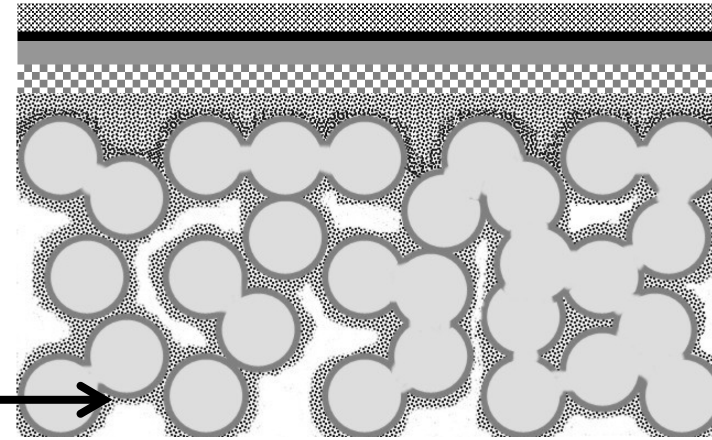
$La_{0,1}Sr_{0,9}TiO_{3-\alpha}$

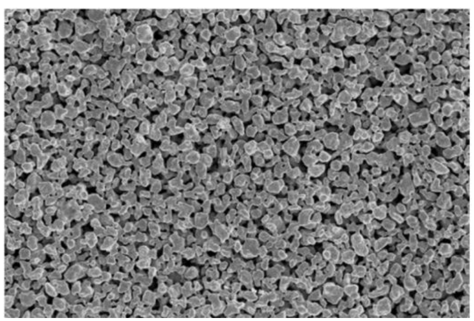
screen printing

Materials and Architecture

Cathode : $La_{0,4}Sr_{0,6}Co_{0,2}Fe_{0,8}O_{3-\alpha}$ (LSCF)
Electrolyte: 8YSZ / GDC10
Composition of the anode: GDC10-LST (w/o 5-10%Ni)

Metallic substrate at the fuel side



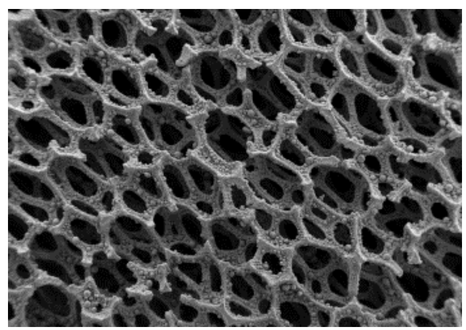


Porous steel
pore size <50µm

Type 1

ALANTUM
Innovations in Alloy Foam

CerPoTech
Ceramic Powder Technology



Metal foam (NiCrAl)
pore size 450µm

+

$La_{0,1}Sr_{0,9}TiO_{3-\alpha}$
$NiO + La_{0,1}Sr_{0,9}TiO_{3-\alpha}$ (50:50)

Type 2

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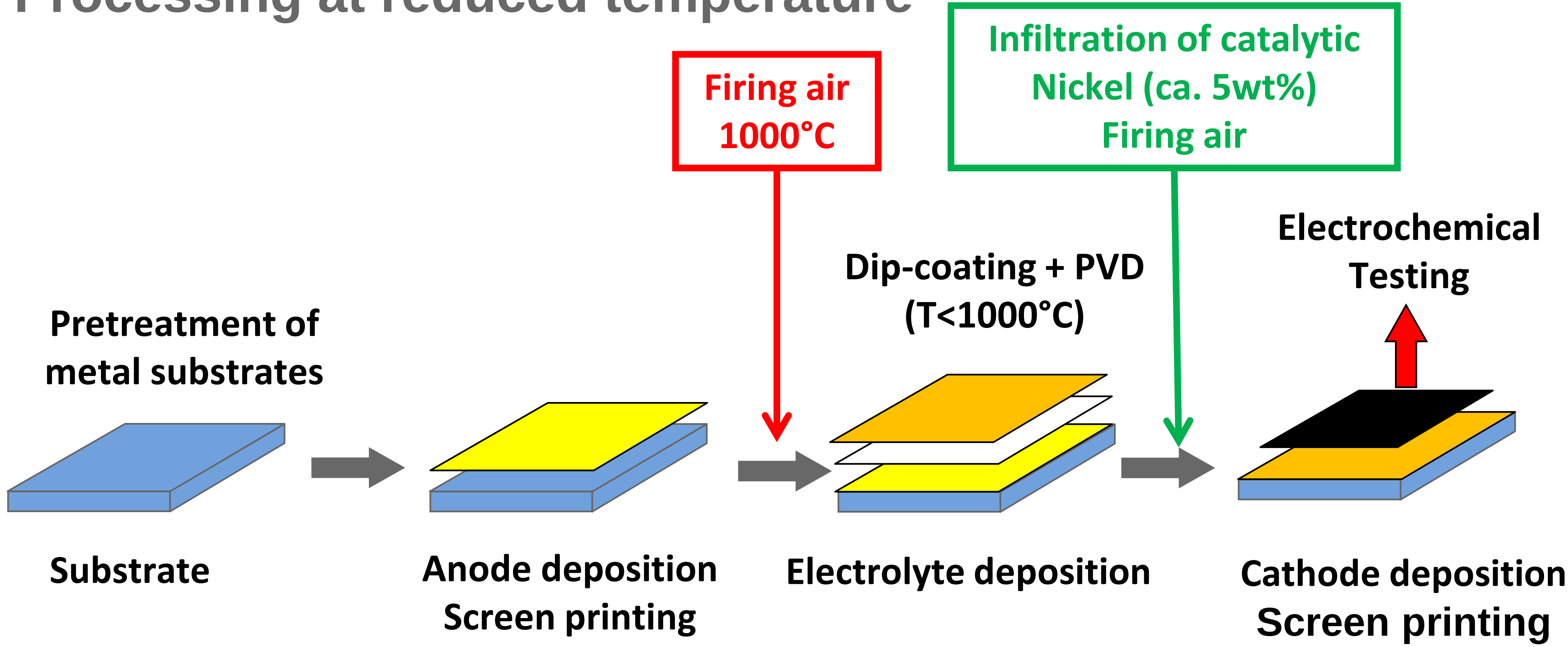
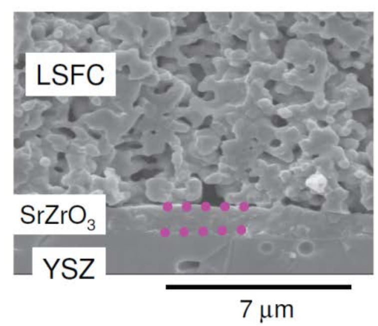
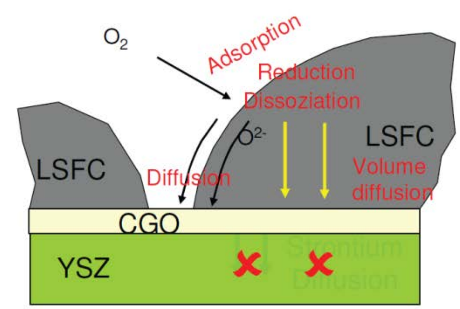
Processing at reduced temperature



Fabrication options for electrolyte:

1. PVD
2. Plasma-spray (VPS)
3. Sintering
4. Sol-gel





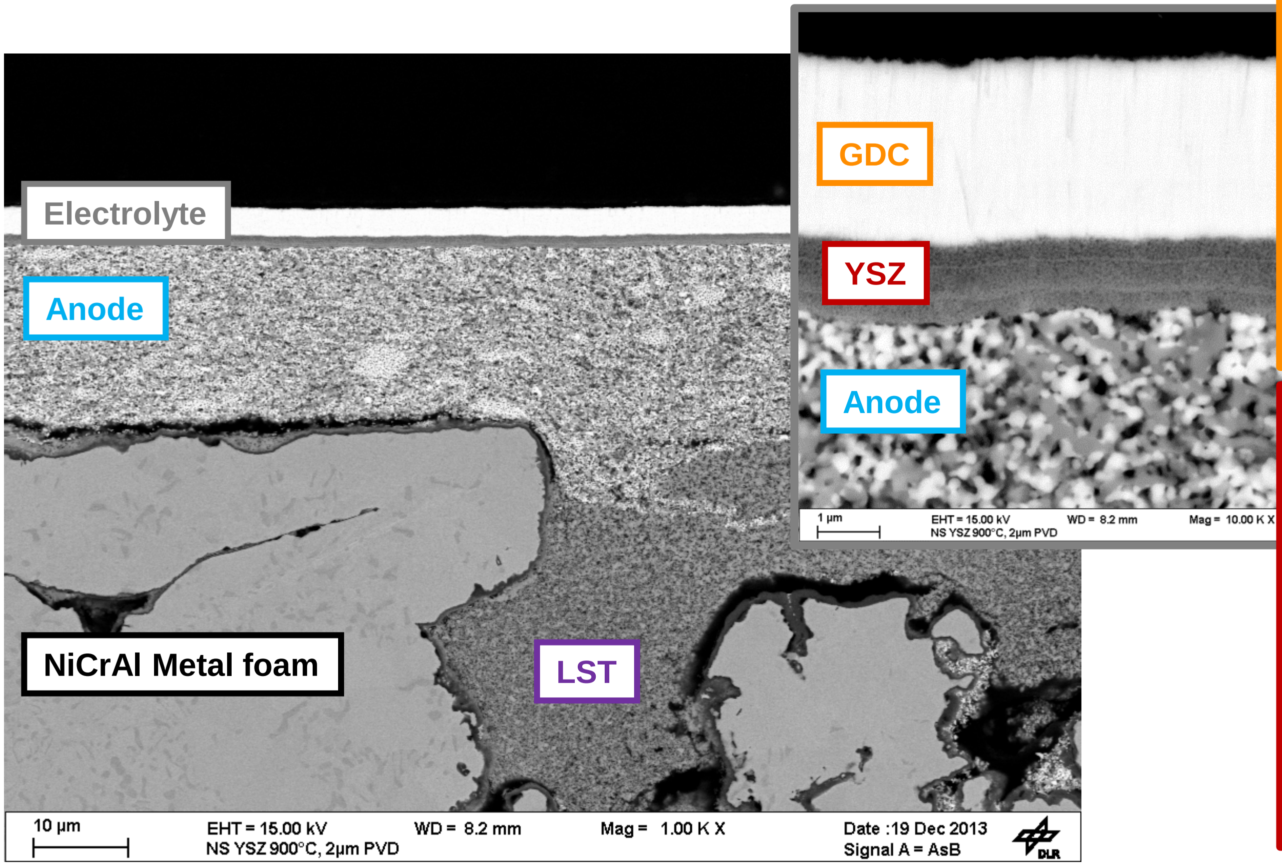
disadvantage

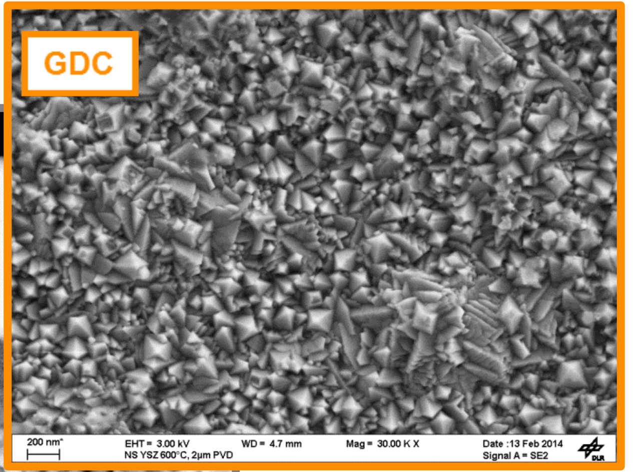
Reaction with YSZ forming $SrZrO_3$

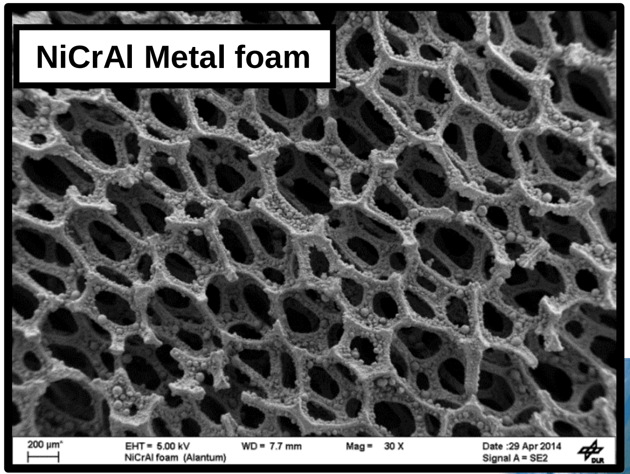
solution

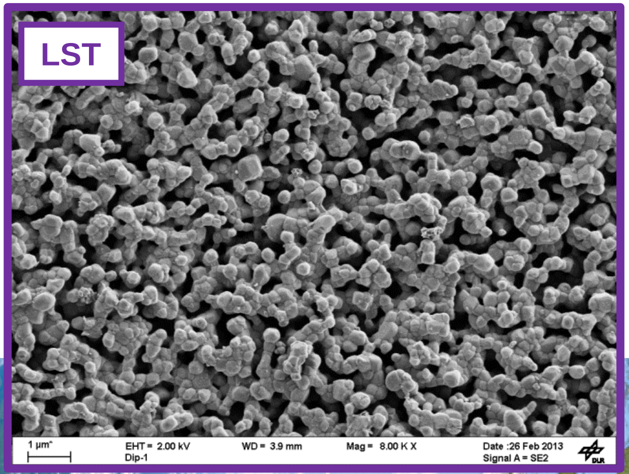
Interlayer $Ce_{0.8}Gd_{0.2}O_{1.9}$

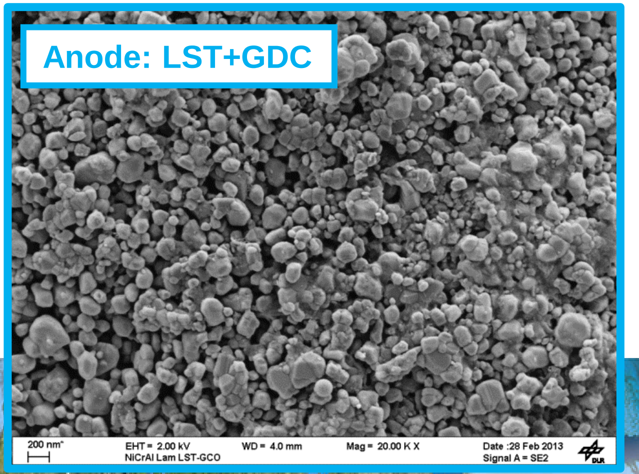
A Way to Thin Electrolyte



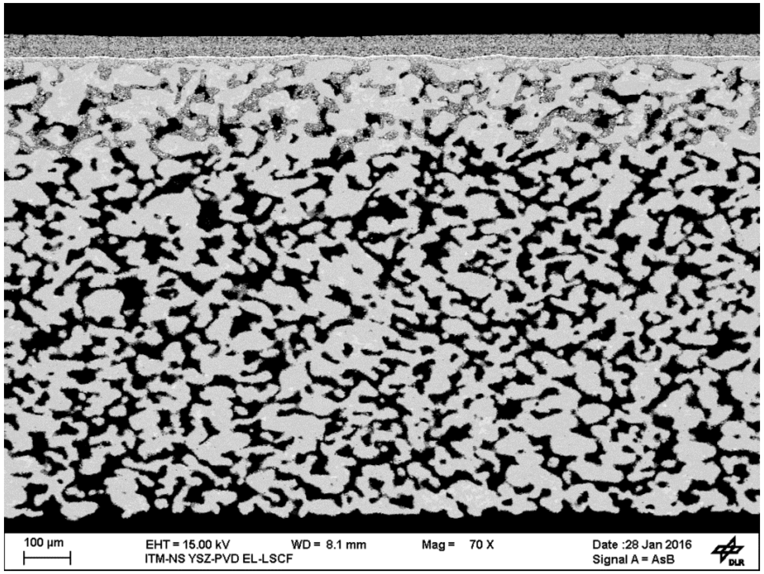


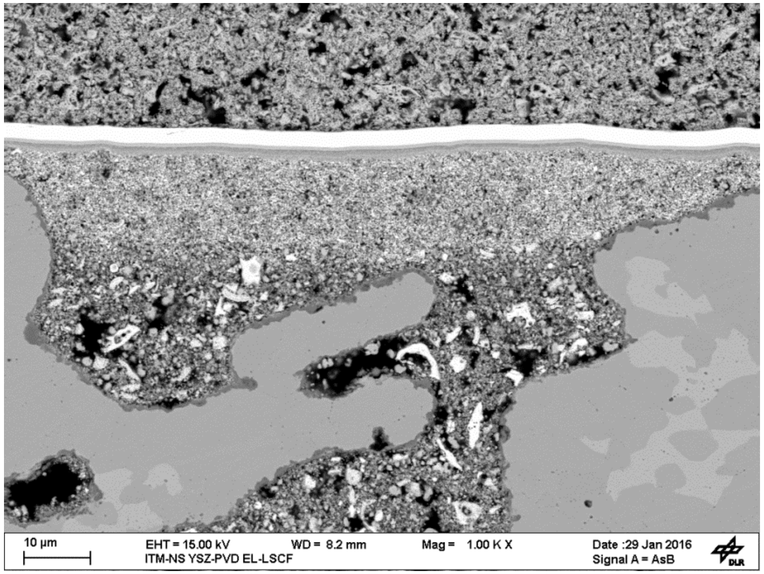




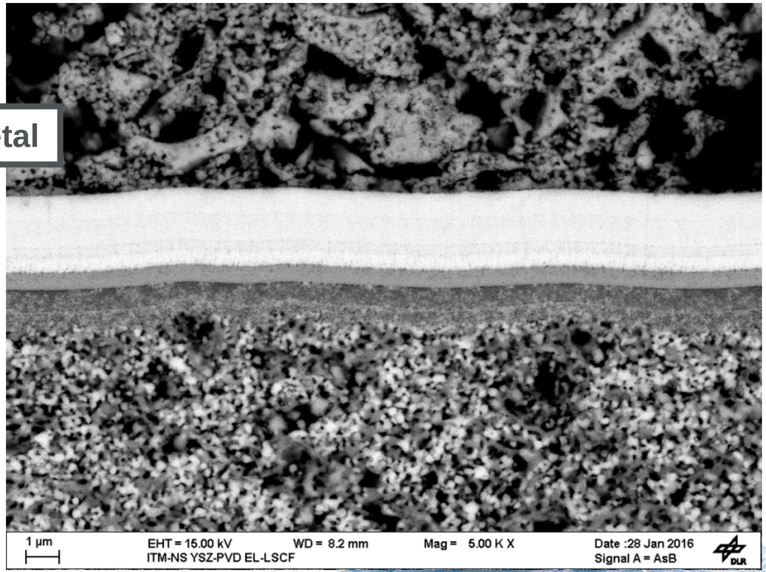


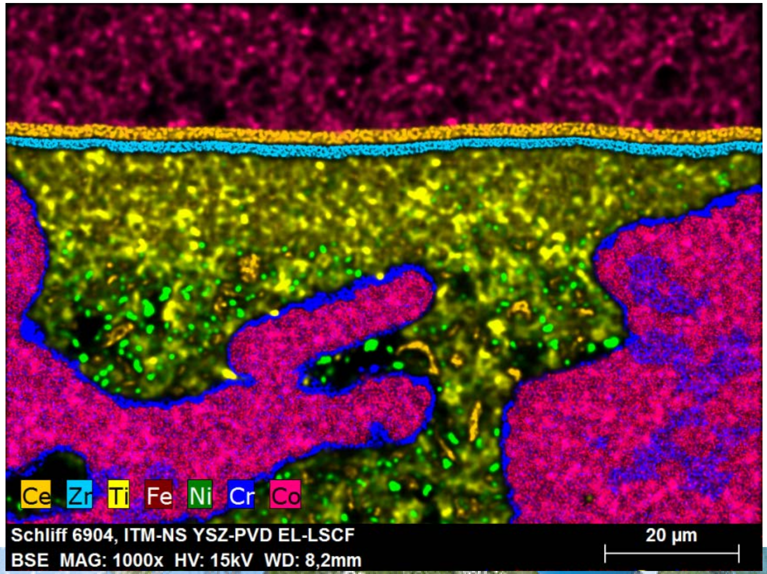
MSC with ITM Substrate (Type 1)



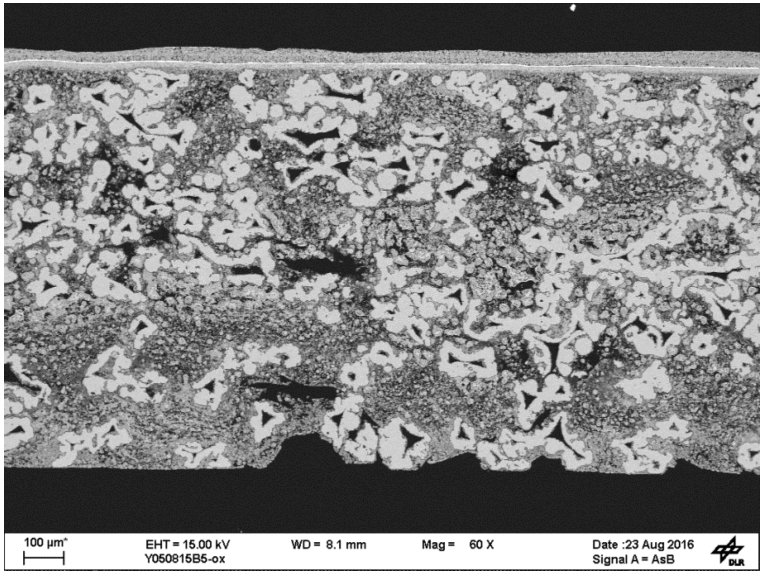


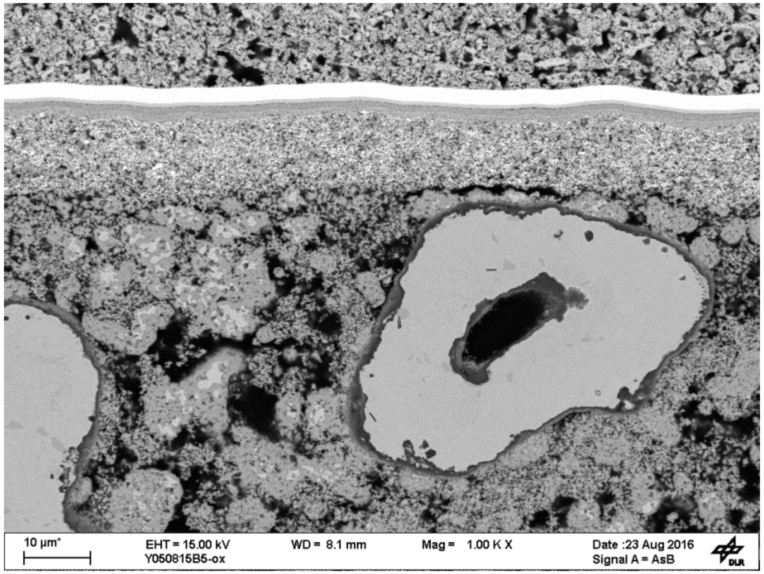
Porous metal

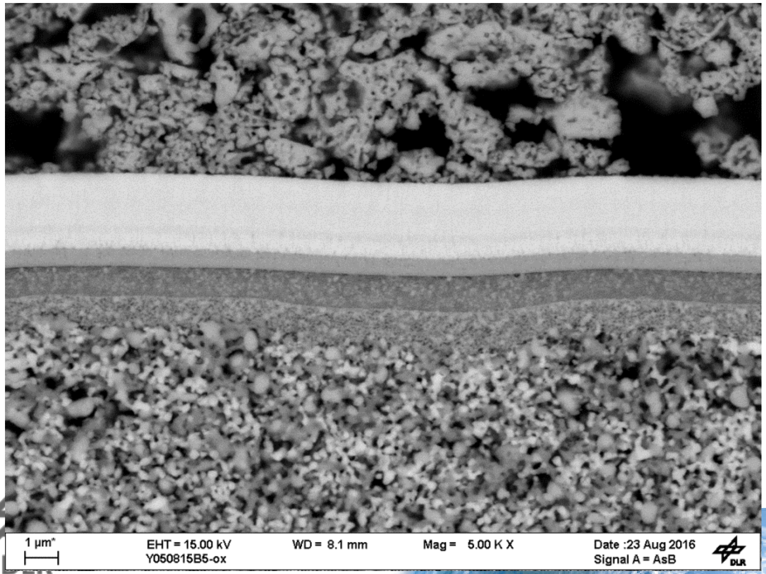


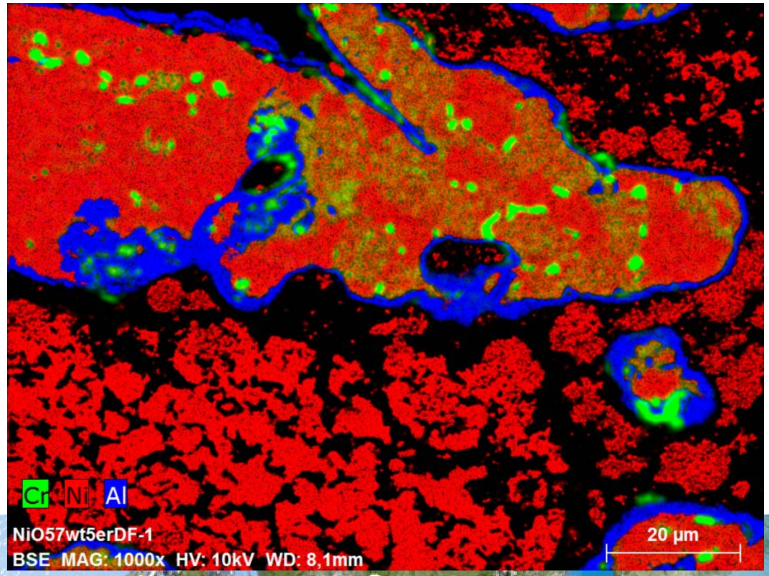


MSC with Metal Foam Substrate (Type 2)









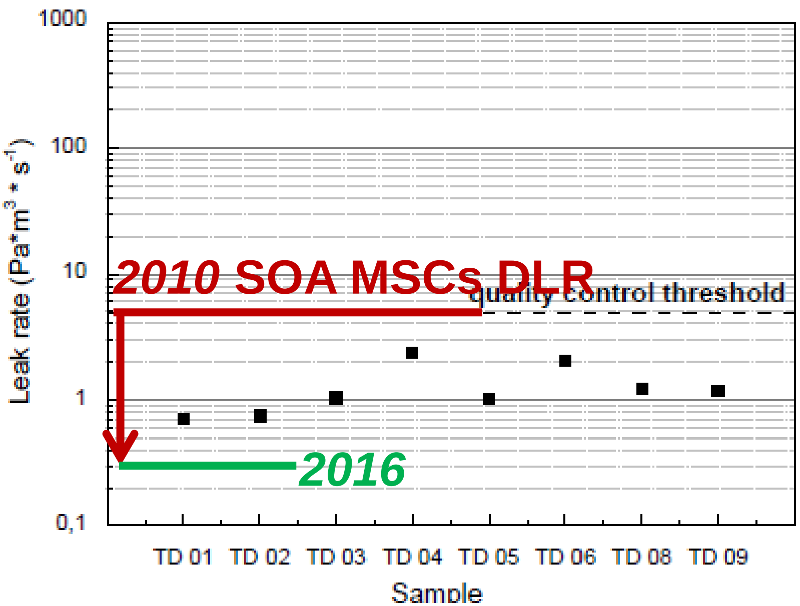
Hermiticity of the electrolyte

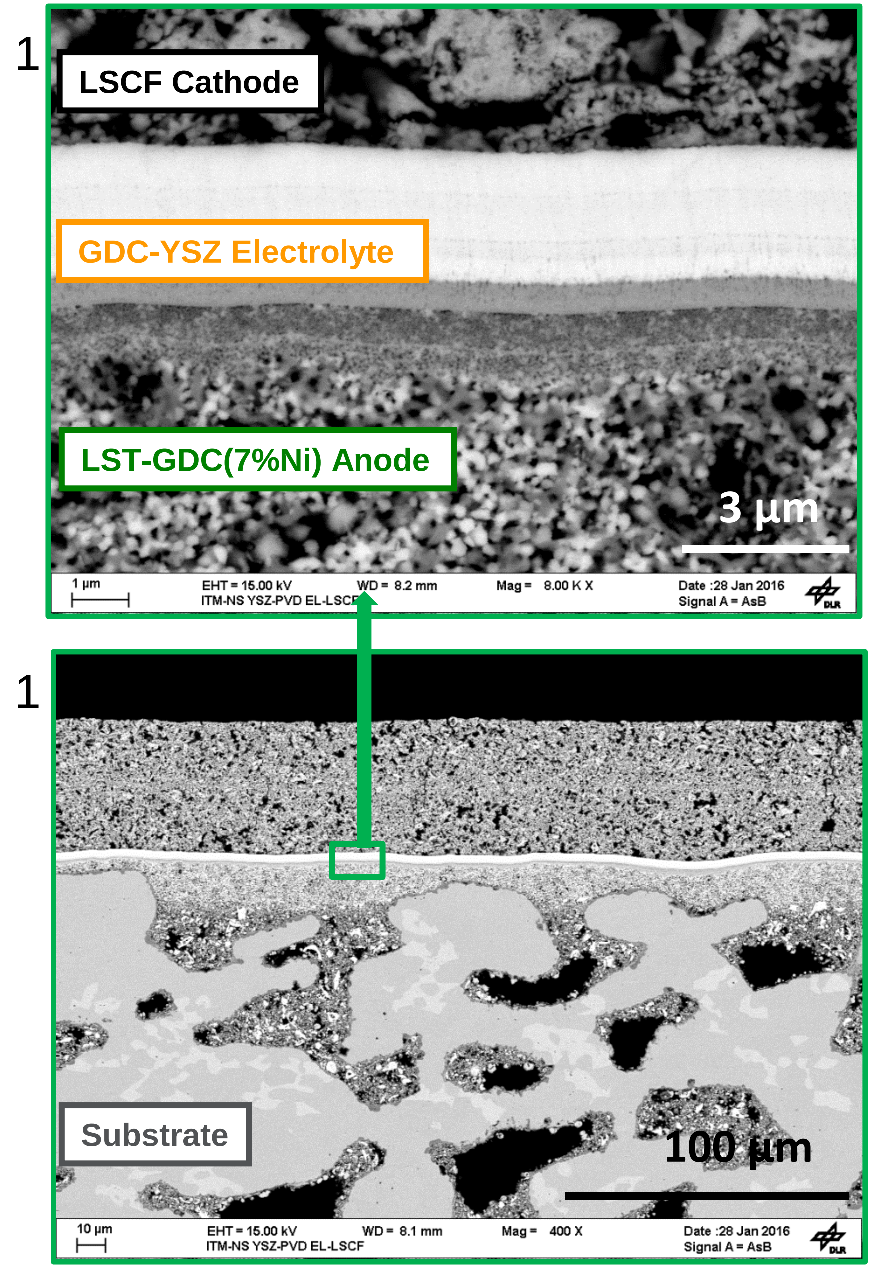
Compared to DLR Plama Sprayed MSCs:

Gas tightness improved by 1 order of magnitude

Material consumption reduced

- PVD: 1,2mg/cm² of YSZ + 1,5mg/cm² of CGO
- PS MSCs: 20-30 mg/cm² of YSZ





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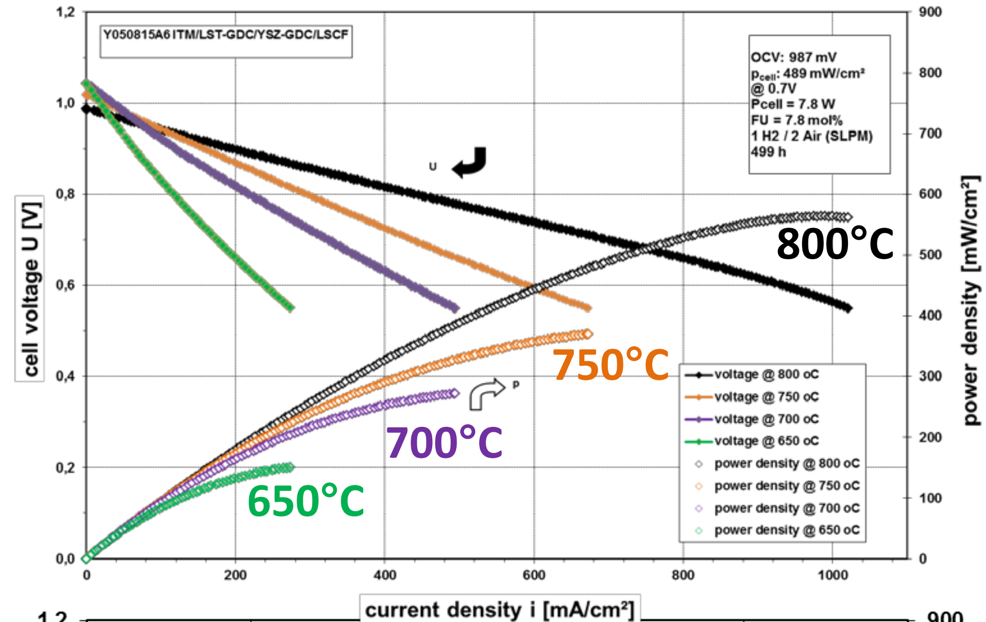
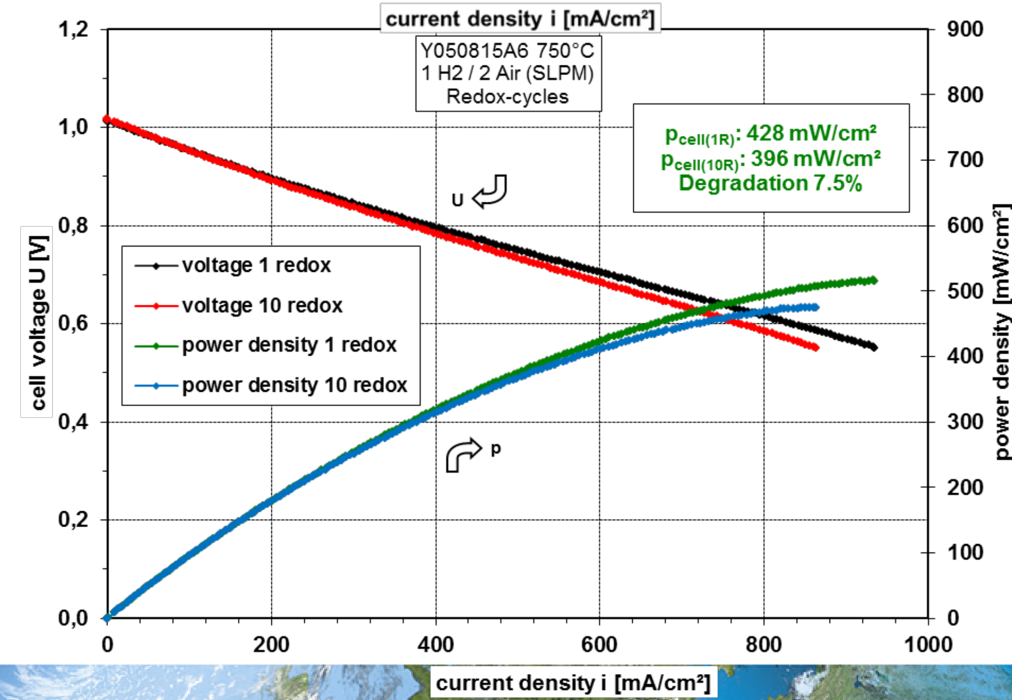
Performance *Cell type 1*
ITM (w 5-10wt%Ni) – 16cm²

@ 750°C 1slpm H_2 / 2slpm air

OCV: 1,03V
Power density at 0,7 V ca. 430 mW/cm²
(520 mW/cm² @ 800°C)

No OCV drop after 10 redox cycles





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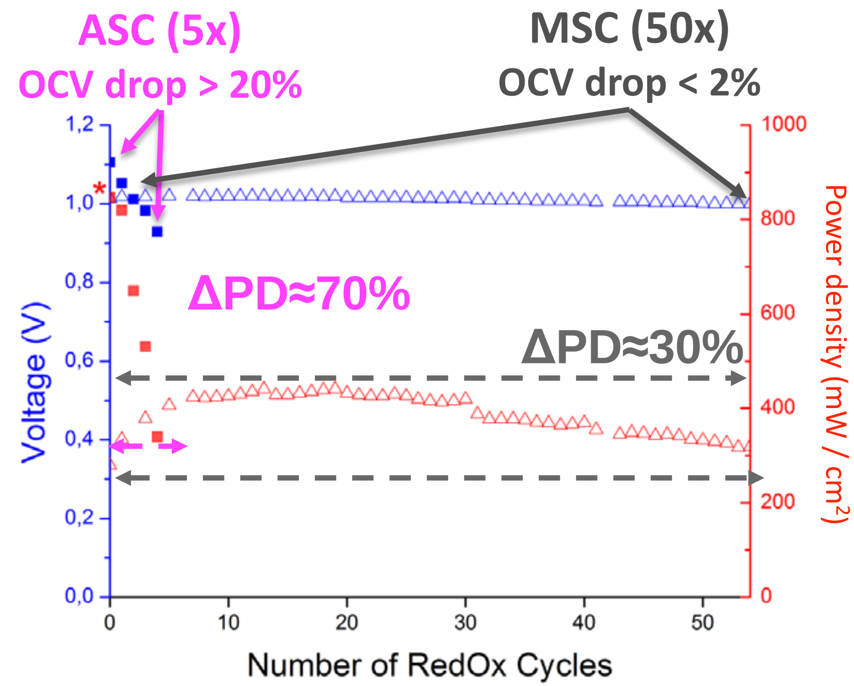
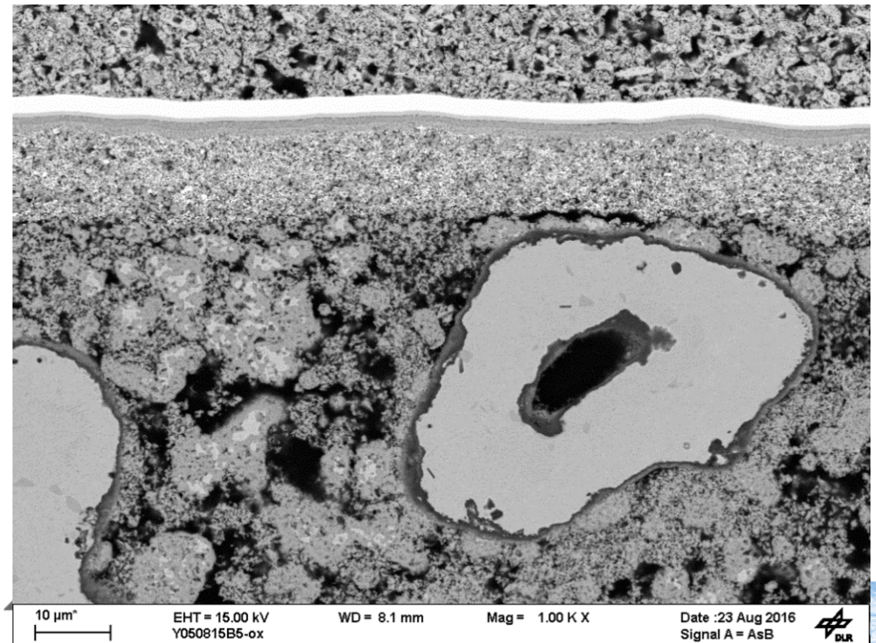
Performance *Cell (Type 2)*

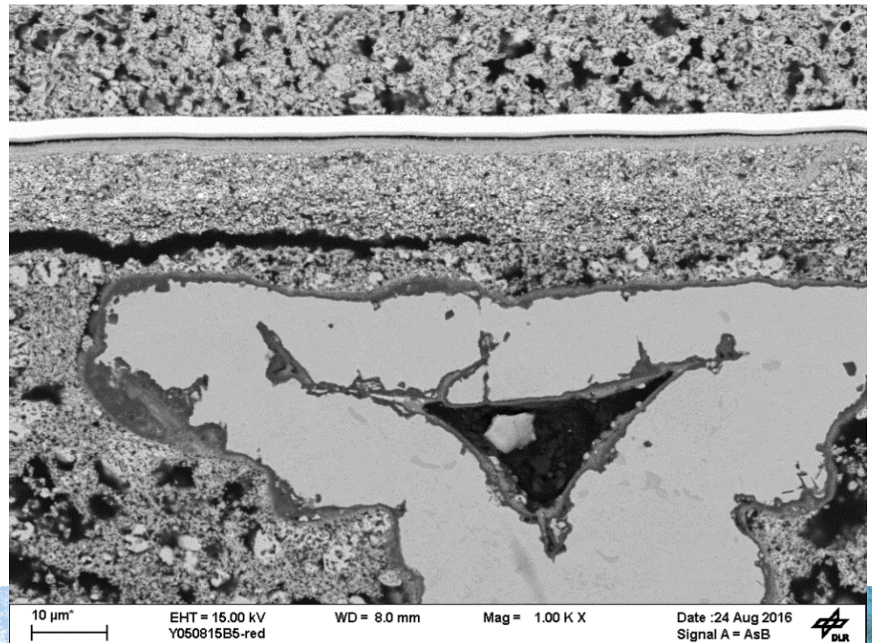
NiCrAl + LST + NiO – (w 5-10wt%Ni)



@ 750°C 1slpm H_2 + 3% water / 1 slpm air
OCV: 1,03V
Power density at 0,7 V ca. 430 mW/cm²
OCV drop of less than 2% (50cycles)

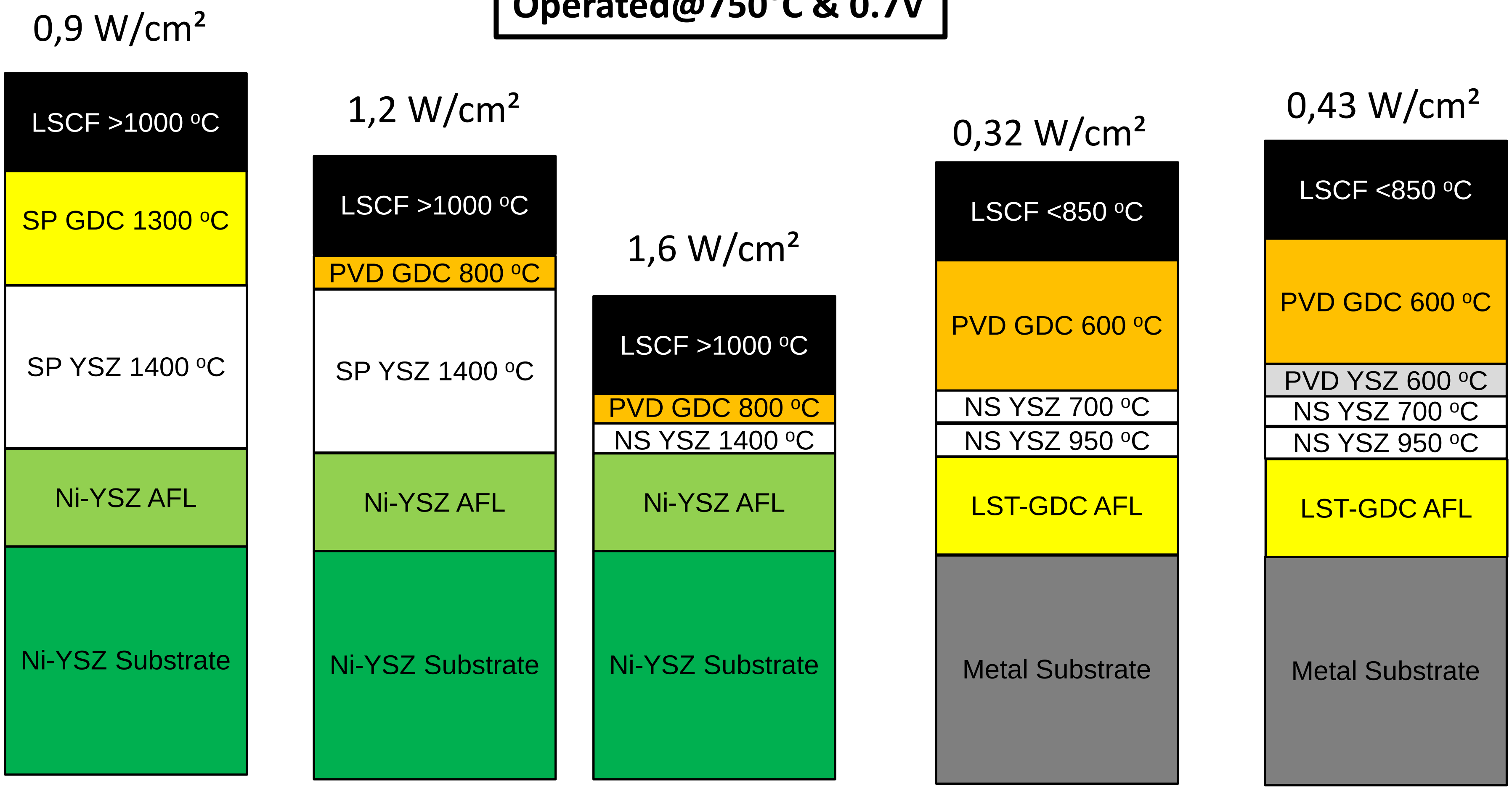
- **good tolerance toward redox cycles**
- **Performance enhancement with addition of catalytic nickel**





MSC with thin-film electrolyte vs. ASC with sintered YSZ

Operated@750°C & 0.7V



Poor redox stability

Good redox stability

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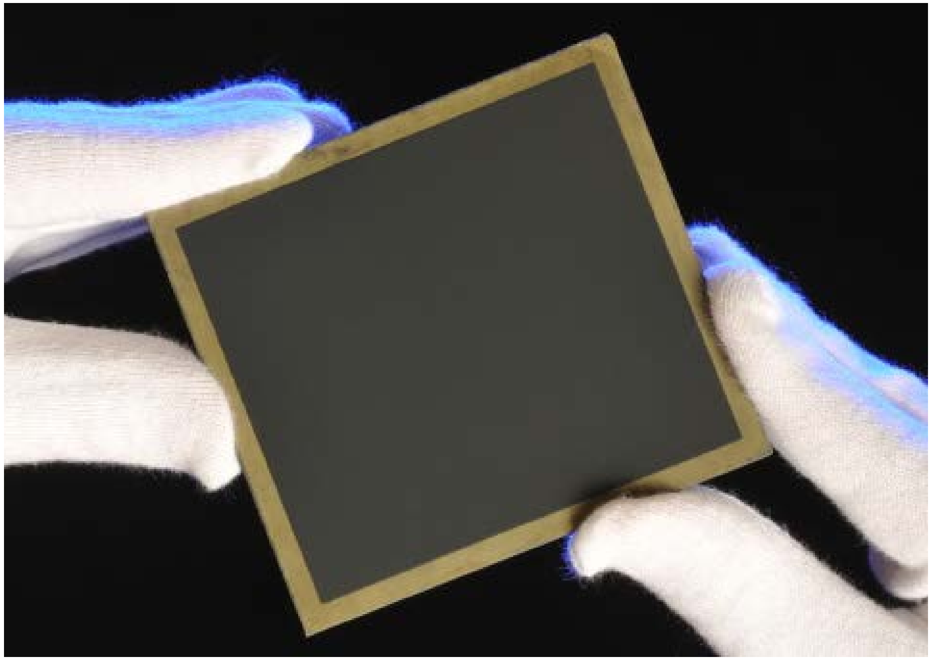
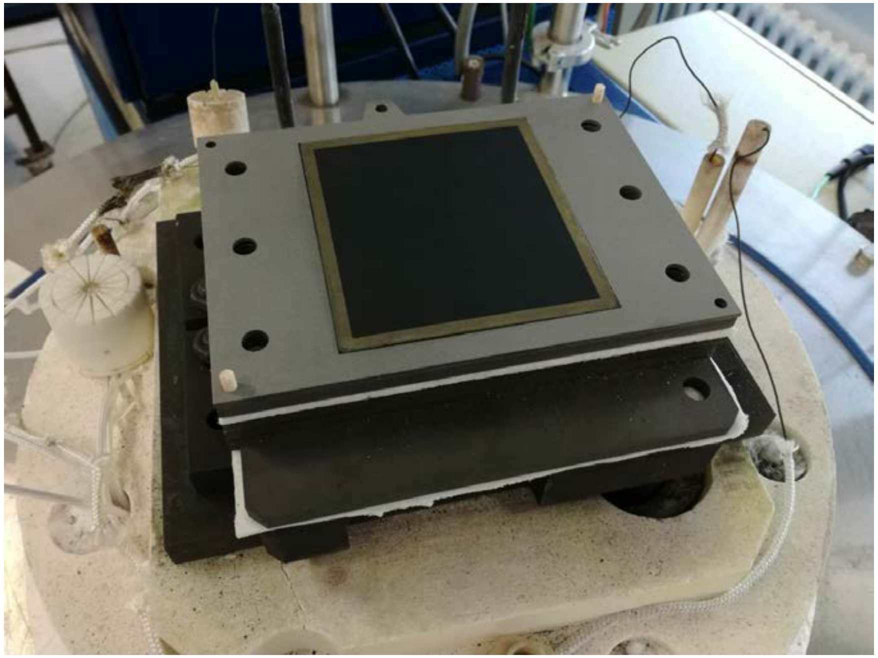
Up-scaled cells for stacks





- Size up to 90 mm x 100 mm
- Laser cut substrate
- Infiltrated Ni catalyst

- Leak rate moderate or poor
- Stackable cells 8 pcs
- Needs for LT sealing solution

Conclusion & Perspectives

- *MSCs cell with various substrates (Stainless Steel & NiCrAl) delivered fair Power density despite low nickel content (< 10wt%)*
- *OCV drop of less than 2% for 50 forced redox cycles (30min in Oxygen) at 750°C*
- *Thin film electrolyte technology developed and demonstrated*
- *Estimated cost reduction: 20 Euro for a 10cm^2x10 cm^2 cell (10 MW per year)*

- **LST based anode materials can operate without pre-reduction at high temperature (>1000°C)**
- *Without addition of catalysts in LST based anode is performance limited*

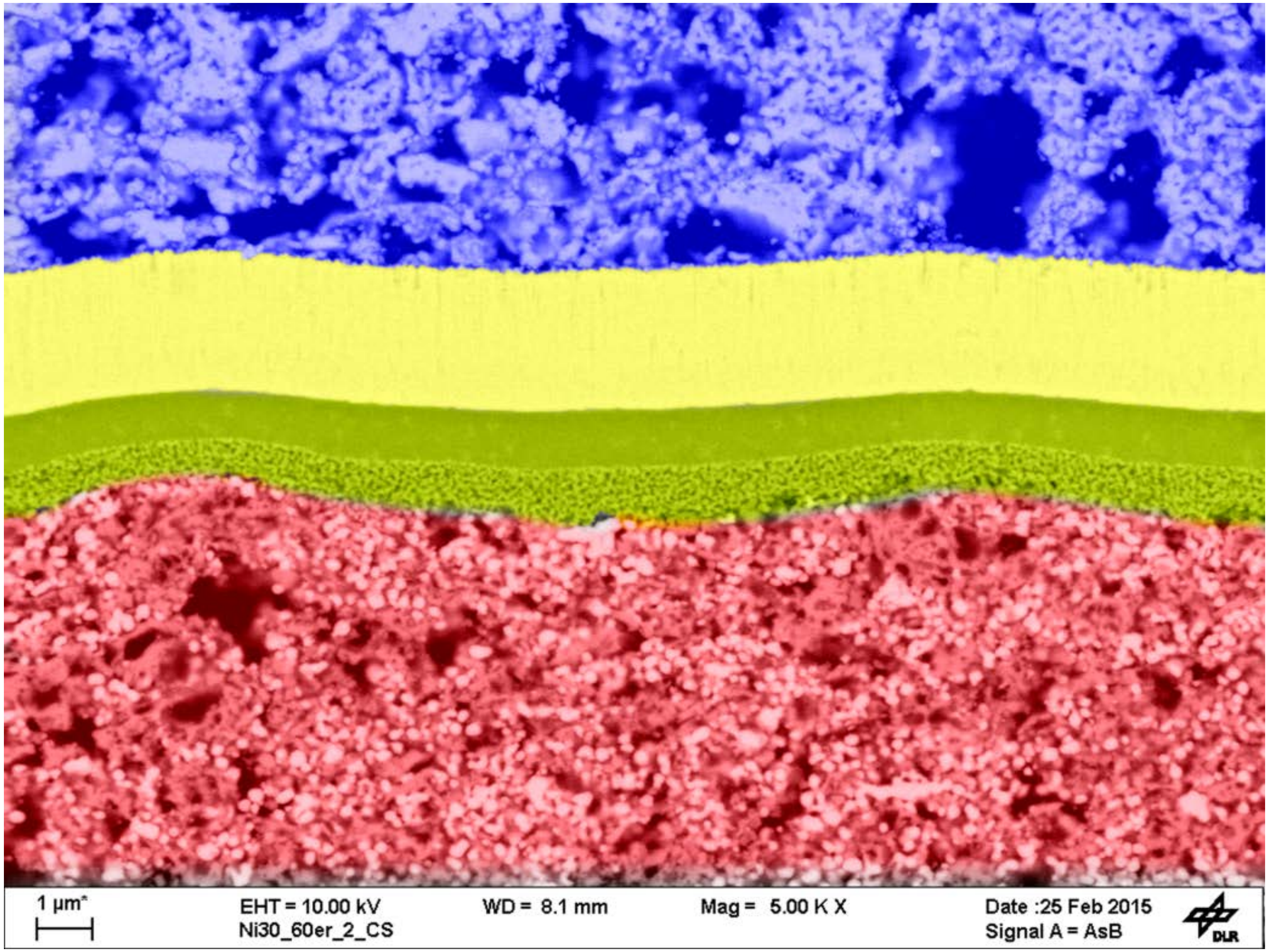
- *Degradation issue at the cathode*
- *Operando migration of cobalt from the cathode size in the electrolyte layer*

- *Improvement of the cathode performance*
- *Development of appropriate low T sealing (750°C) solutions*
- *Implementation in Single Repeat Unit and Test for completing Assessment*
- *Assessment against Sulfur Poisoning*

Acknowledgement

This work was funded by the European Union's Seventh Framework Programme (FP7/2007-2013) for the Fuel Cells and Hydrogen Joint Technology Initiative under grant agreement n°303429.

Thanks for your attention!



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