Performances and limitations of metal supported cells with strontium titanate based fuel electrode: *a step towards the next generation of solid oxide cells*

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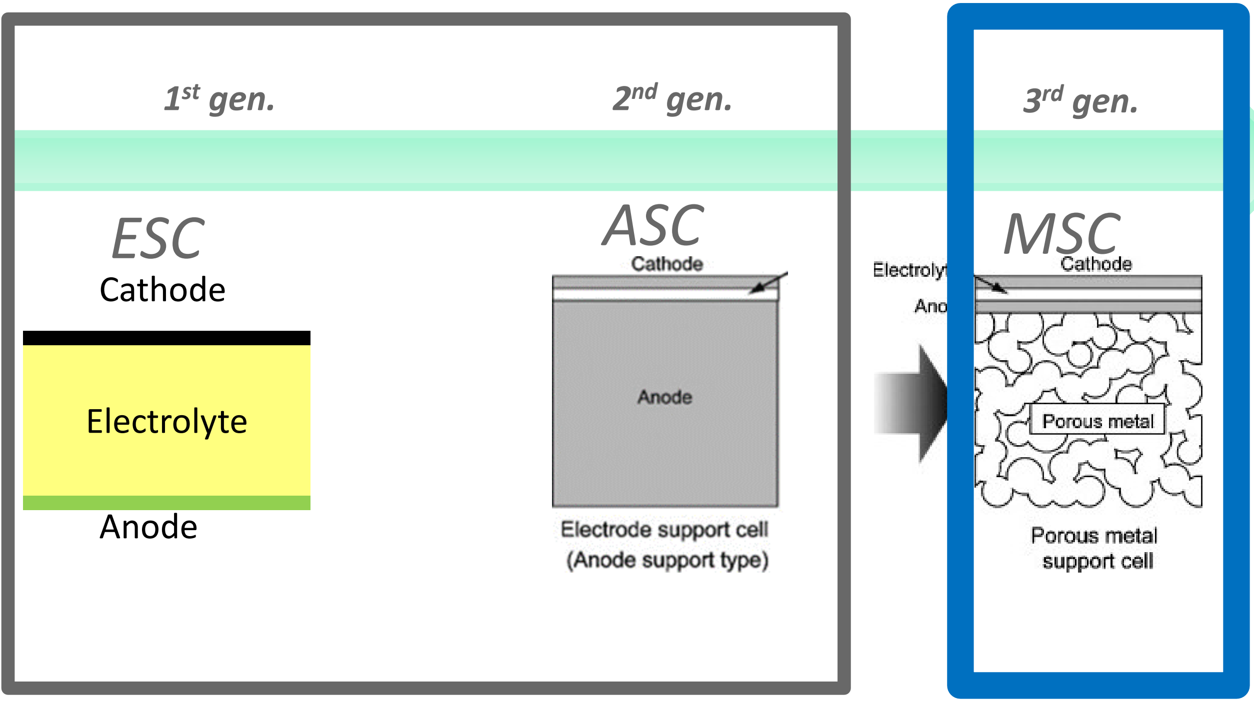
Motivation: towards the next generation SOC

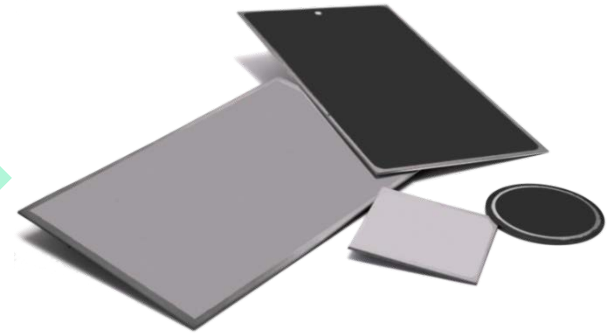
1st gen.	2nd gen.	3rd gen.	4th gen.
ESC	ASC	MSC	
Limited power density Robustness	High power density Sulfur poisoning Fast thermal cycling Redox Cycling	High power density Sulfur poisoning Fast thermal cycling Redox Cycling	High power density Sulfur resistant Thermal cycling Redox Cycling Low cost
Stationary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

Flexible architecture for multiple applications

Which materials for the next generation of SOCs?

Why metal Supported Cells ?





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

Table 1
Summary of candidate support metals.

Metal	CTE (ppm K^{-1})	Cost ($/kg 2009)	Relative oxidation resistance
NiCrAlY	15–16	63	Excellent
Hastelloy-X	15.5–16	22	Excellent
Ni	16.5	18	None[a]
Ni–Fe (1:1)	13.7	9	None[a]
300-Series stainless steel	18–20	2	Poor
400-Series stainless steel	10–12	2	Very good

Note that CTE of electrolytes (YSZ, CGO, LSGM) are 10–12 ppm K^{-1}.

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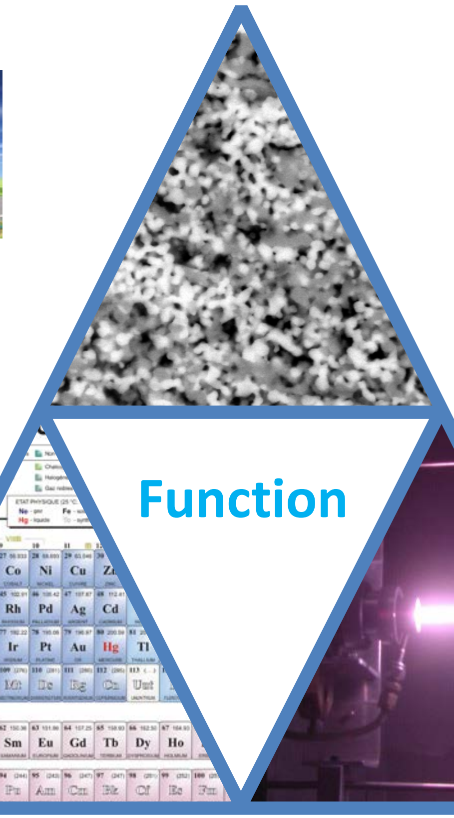
Key performance factors

Catalysis
Sealing
TEC
Reactivity
...

Microstructure / Architecture



Materials

Manufacturing

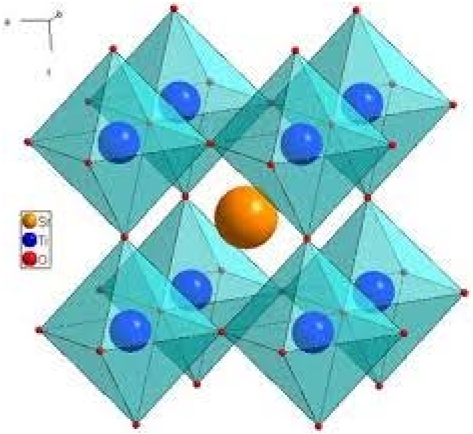
Robustness
Red-ox cycles
Contact
Fuel Utilization
Gas Transport
Balance of Plant
Life Time
Reliability
Start-up time
Poisoning
...

- To produce kWh
- *To store Energy*

DLR

Selection for the next generation with metallic substrates

- *Improving durability of the metallic substrate*
  - ***Implementing alumina forming alloys***
- *Enhancing Sulfur tolerance and redox stability at the anode*
  - ***Perovskite based anode materials***
- *Improving gas tightness while reducing thickness of electrolyte*
  - ***Thin film multi layer electrolyte***
- *Avoiding High T sintering in reducing atmosphere*
  - ***low T processing in air***

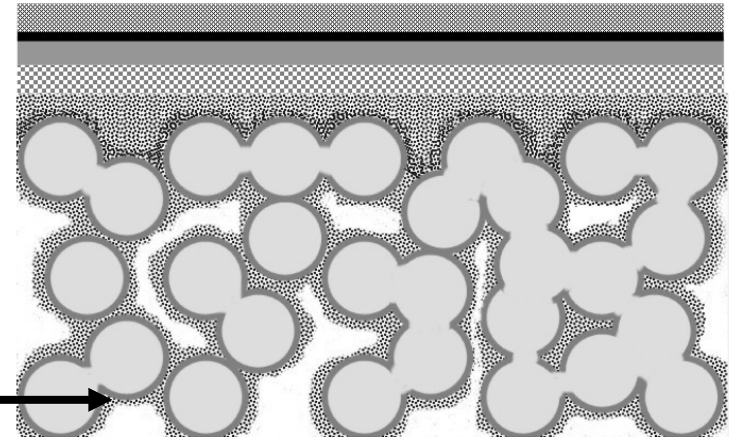


$La_{0,1}Sr_{0,9}TiO_{3-\alpha}$

screen printing

Materials

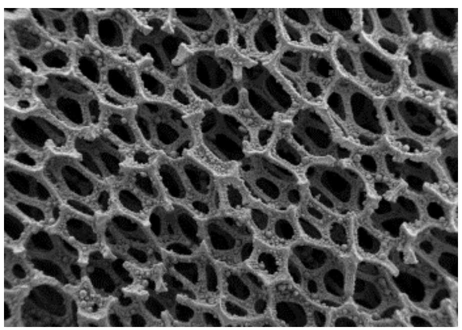
Cathode : $La_{0,4}Sr_{0,6}Co_{0,2}Fe_{0,8}O_{3-\alpha}$
Electrolyte: 8-YSZ / 10-CGO
Composition of the anode: CGO-LST (w/o 5-10%Ni)



Metallic substrate at the fuel side

ALANTUM Innovations in Alloy Foam

CerPoTech Ceramic Powder Technology



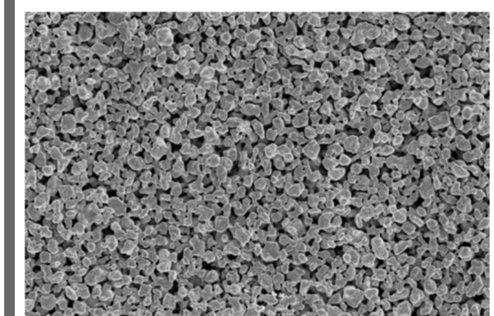
+

Foam NiCrAl #01
450µm pore size

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

1

PLANSEE



ITM
With 5-10wt% catalytic nickel

2

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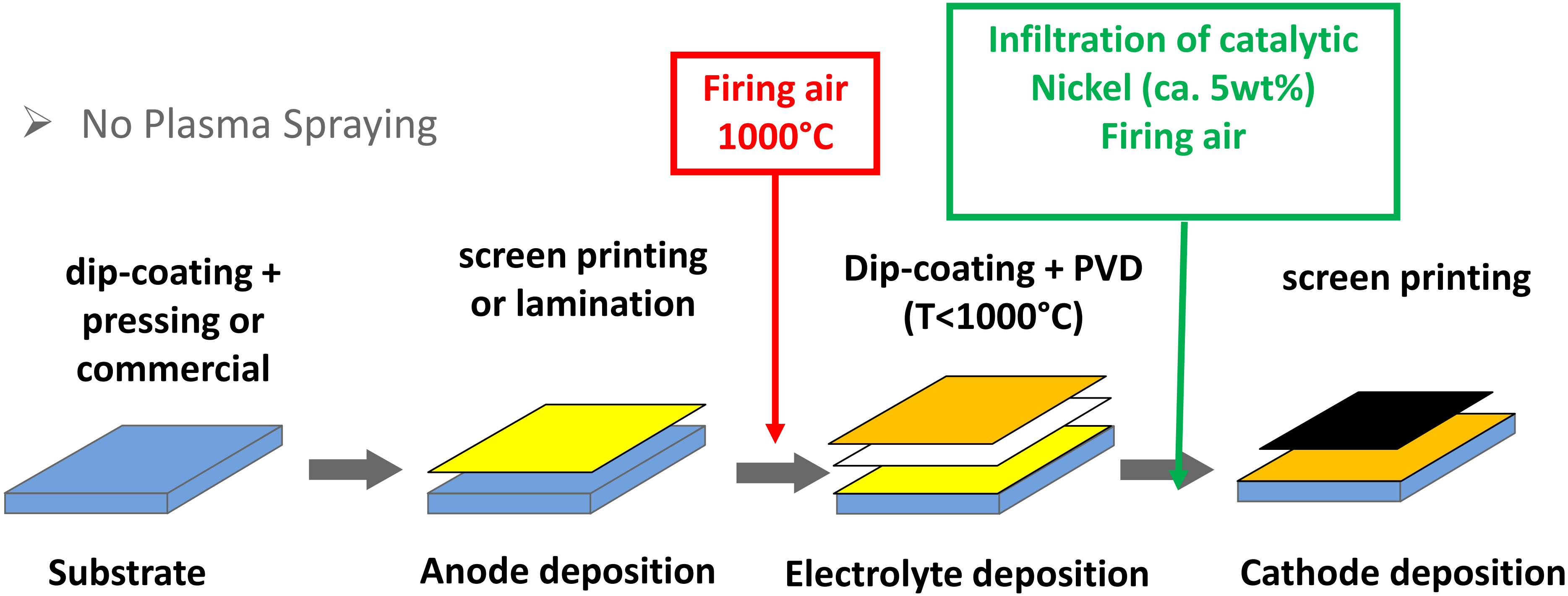
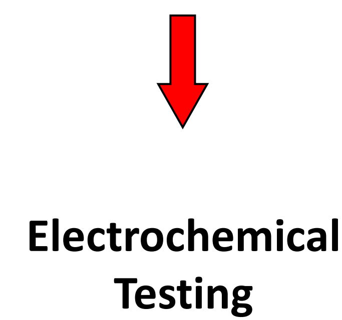
Manufacturing

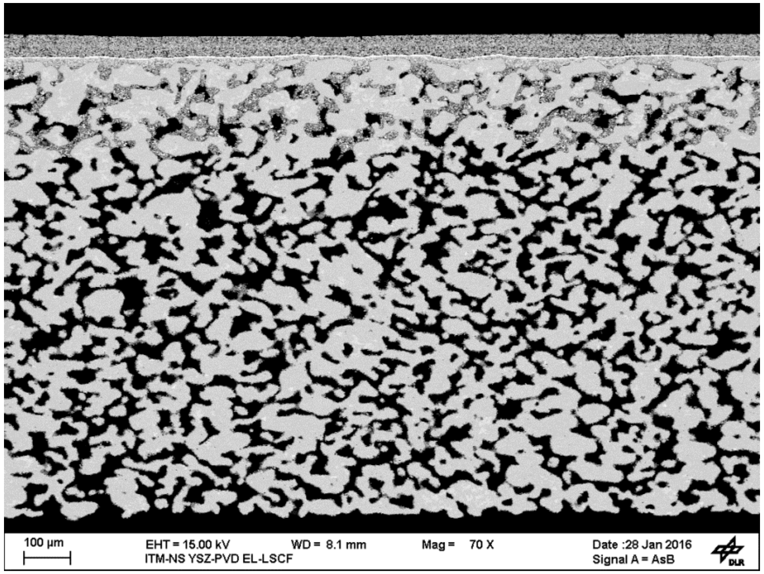
- No Plasma Spraying

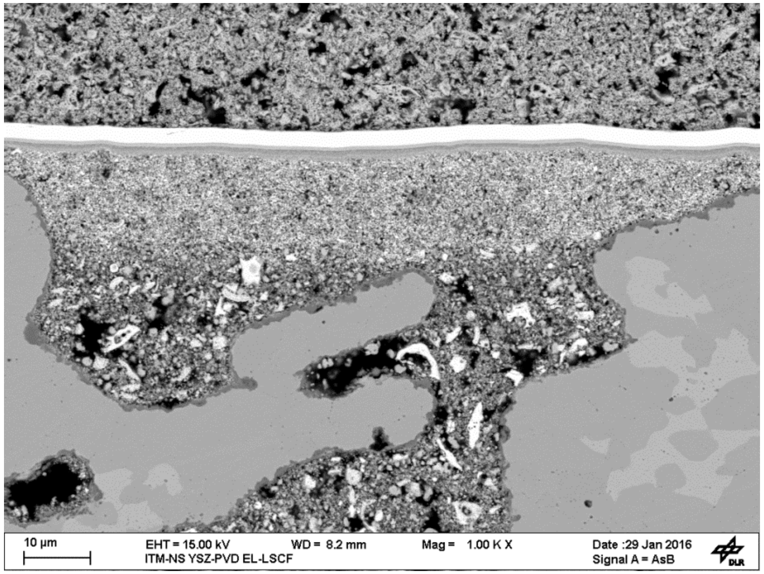


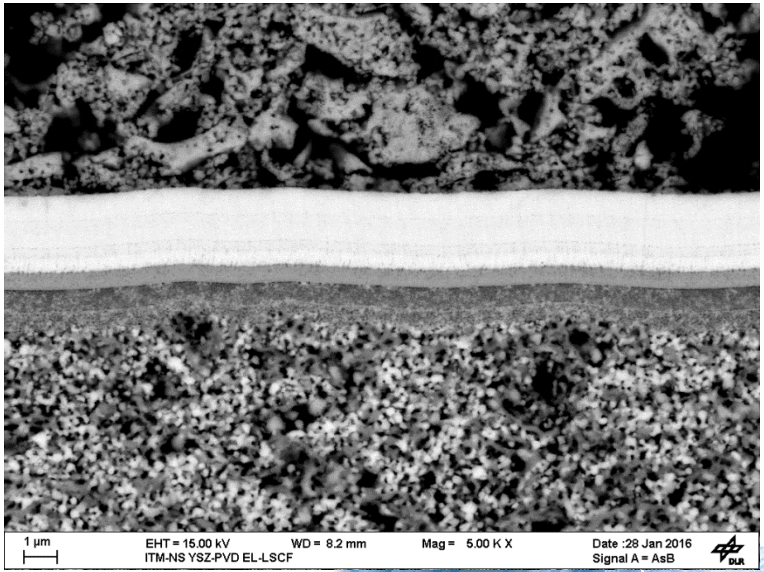
- T_{max} processing: 1000°C
- Atmosphere: air or low P_{o2} for PVD coating
- No pre-reduction of $La_{0,1}Sr_{0,9}TiO_{3-\alpha}$
- Conditioning and testing of cell at max. 800°C

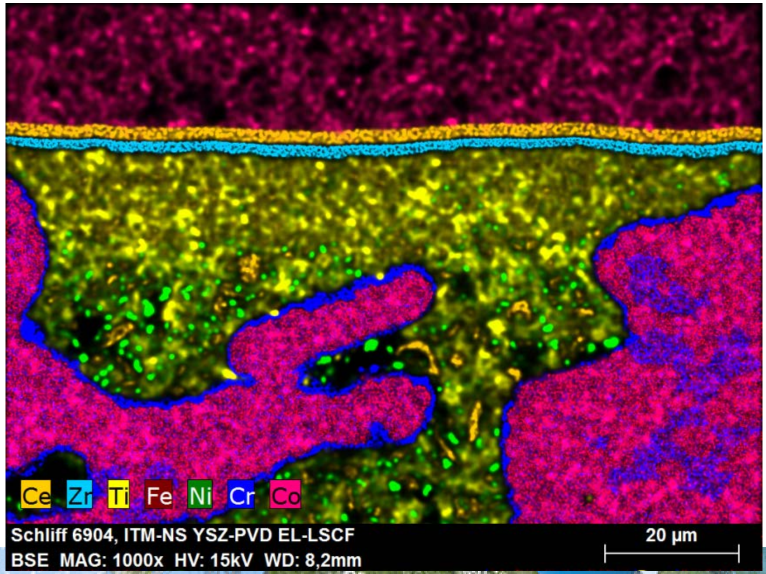


MSC with ferritic steel substrate

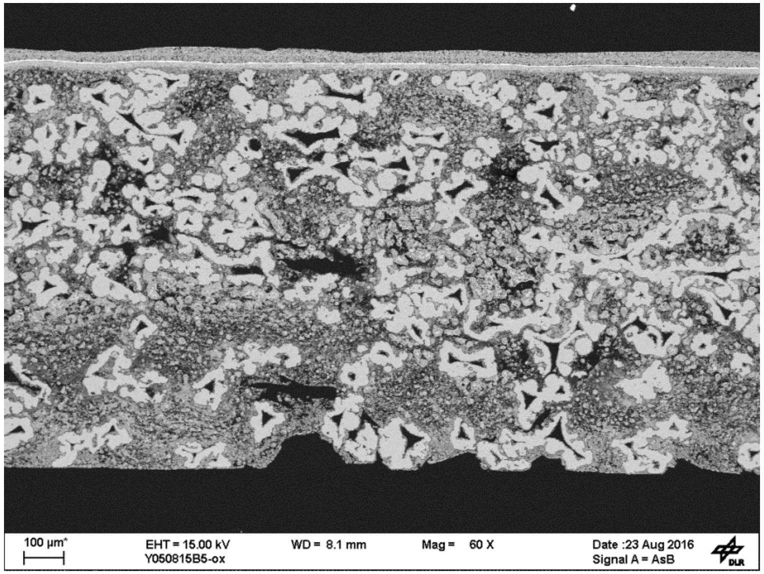


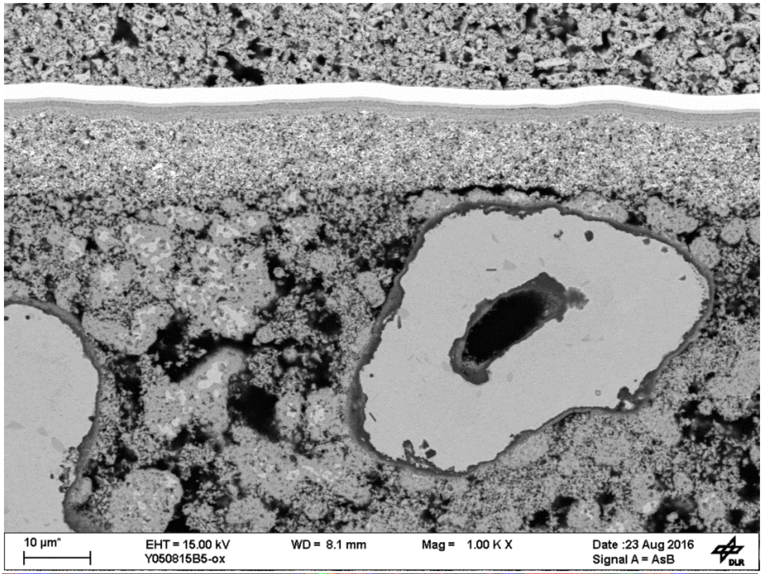


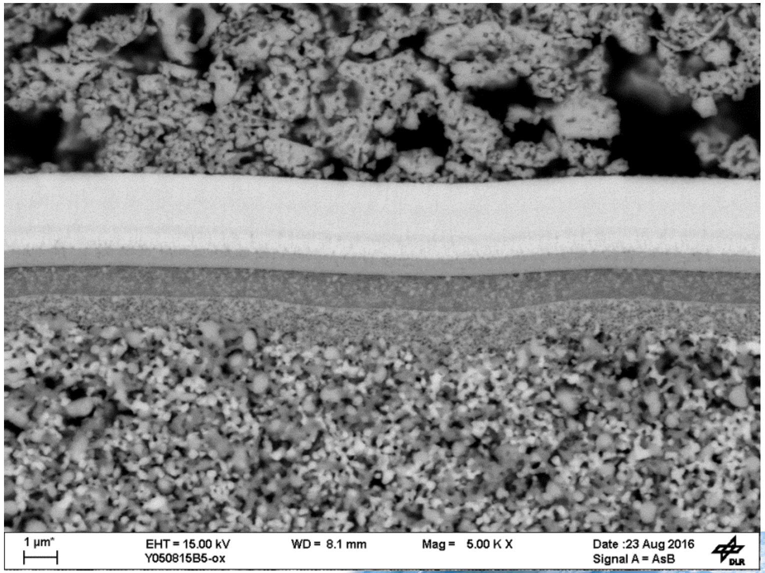


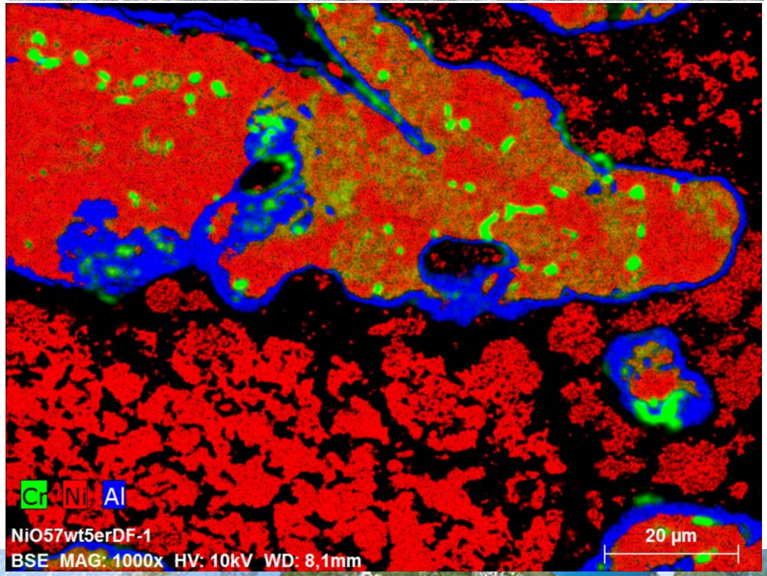


MSC with Metal Foam Substrate









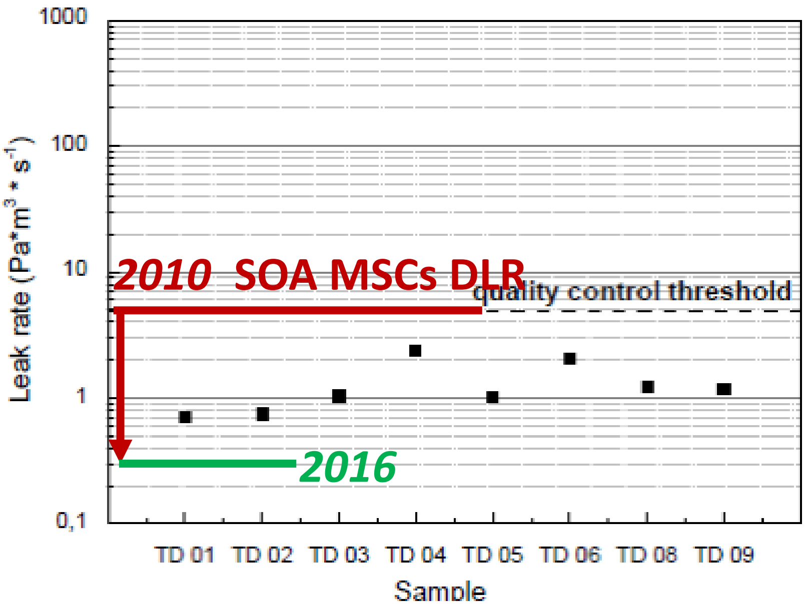
Microstructure:
Hermiticity of the electrolyte

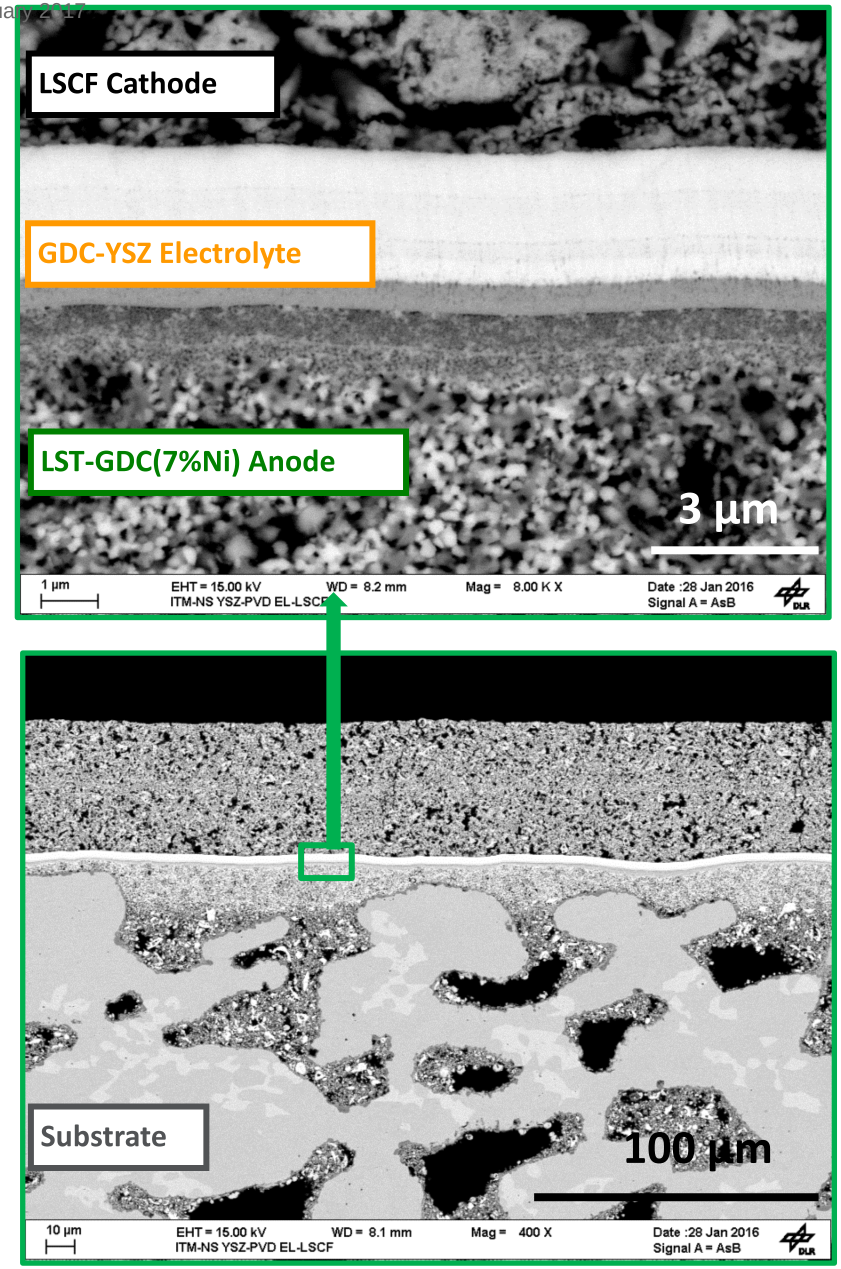
Gas tightness improved by 1 order of magnitude *(compared with PS)*

Material consumption reduced by 1 order of magnitude

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

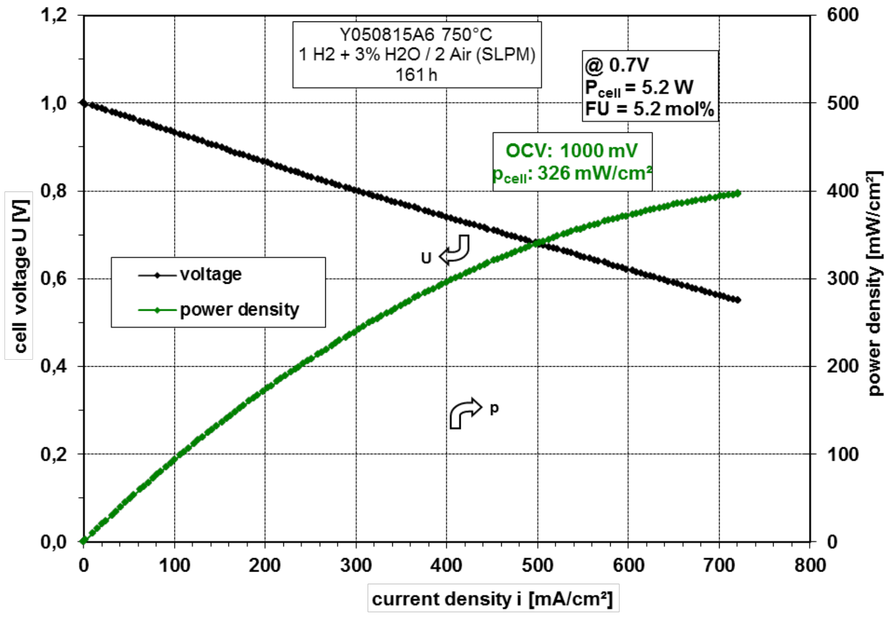
!!! Sensitive to Pinholes!!!



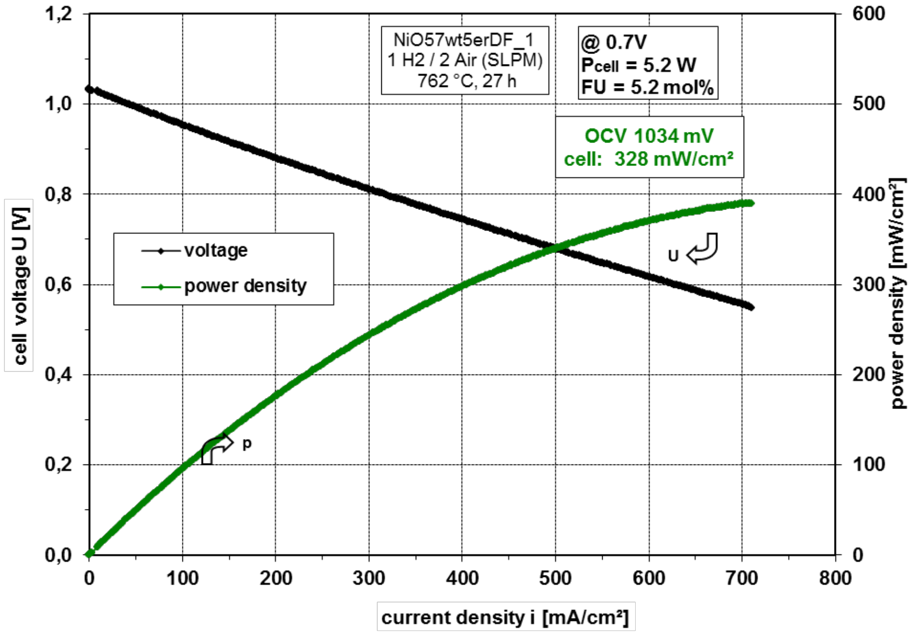


Performance

ITM (ferritic stainless steel) vs NiCrAl (w. LST:NIO)
(Anode Functional Layer: LST:CGO w 5-10wt%Ni) – 16cm²



ITM (ferritic stainless steel)



NiCrAl (w. LST:NIO)

@ 750°C 1slpm H_2 (w. H_2O)/ 2slpm air

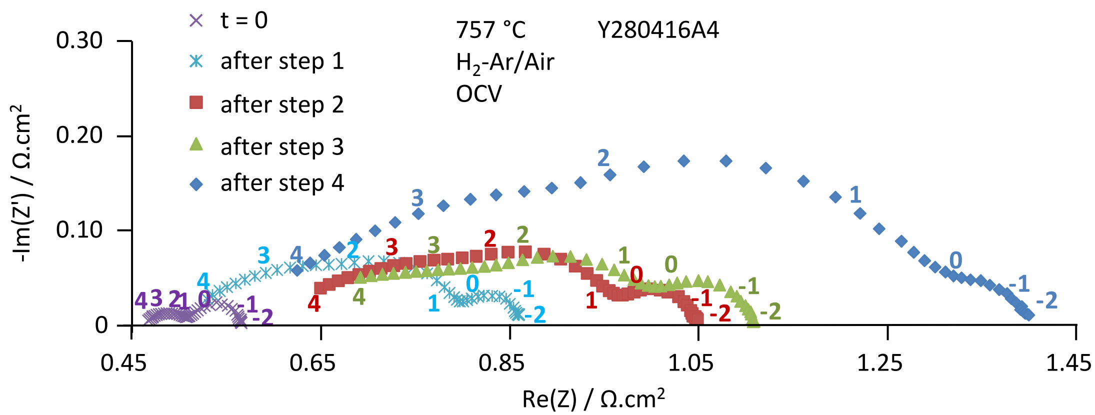
OCV: ca. 1V (!!! Pinhole !!!) (Electronic transport in electrolyte?)

Power density at 0,7 V ca. 320 mW/cm² (improved up to 450 mw/cm²)

Performance nearly independant in tested condition from the substrate (Manufacturability)

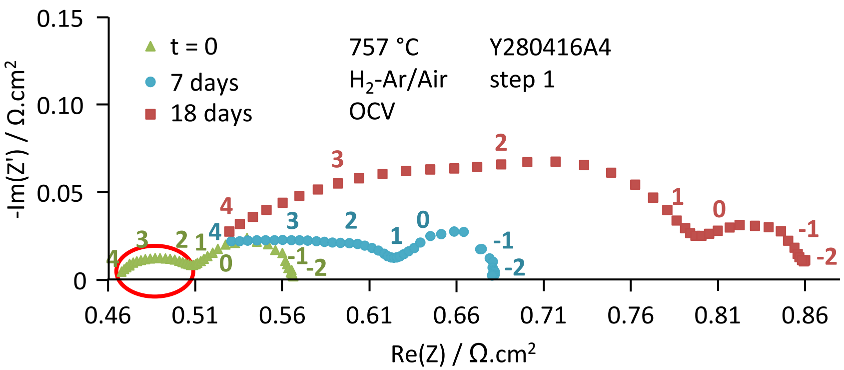
Interfaces and Electrodes aged during operation

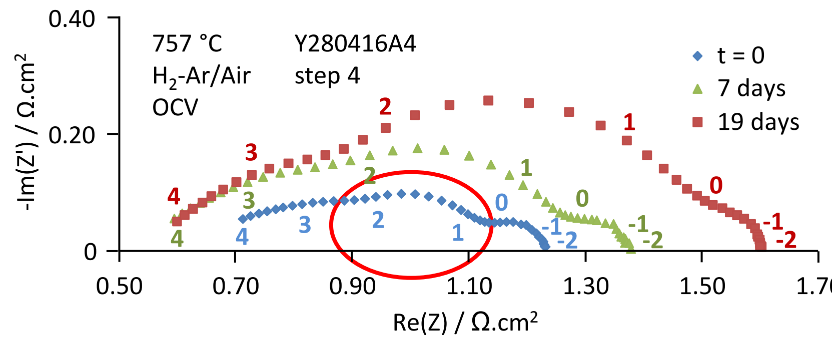
Metal foam substrate - operation 1500 hours



Assignment of degradation based electrokinetic modeling

increase of R_s and R_{pol}





degradation of interfaces

contact between ionic conductors

degradation of electrodes

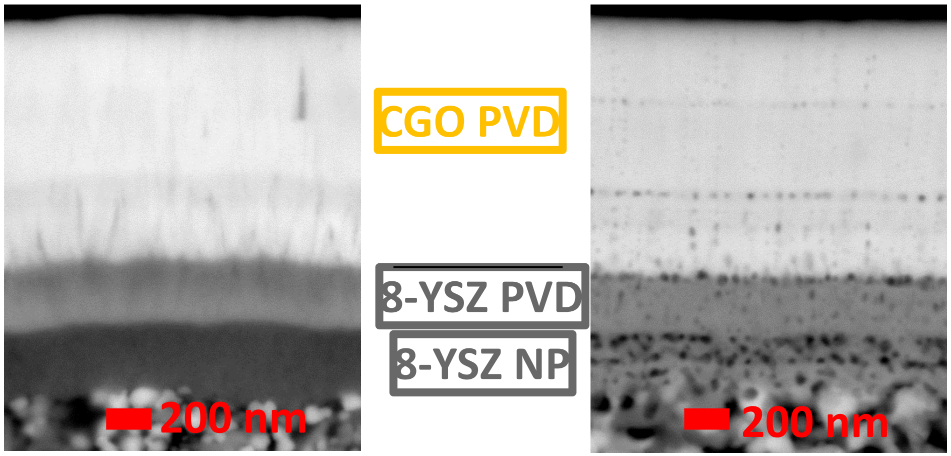
anode & cathode

V. Yurkiv et al., Journal of Power Sources, 287 (2015) 58 - 67

Degradation of interfaces

multi-layer electrolyte

interfaces in Electrolyte



Before

After

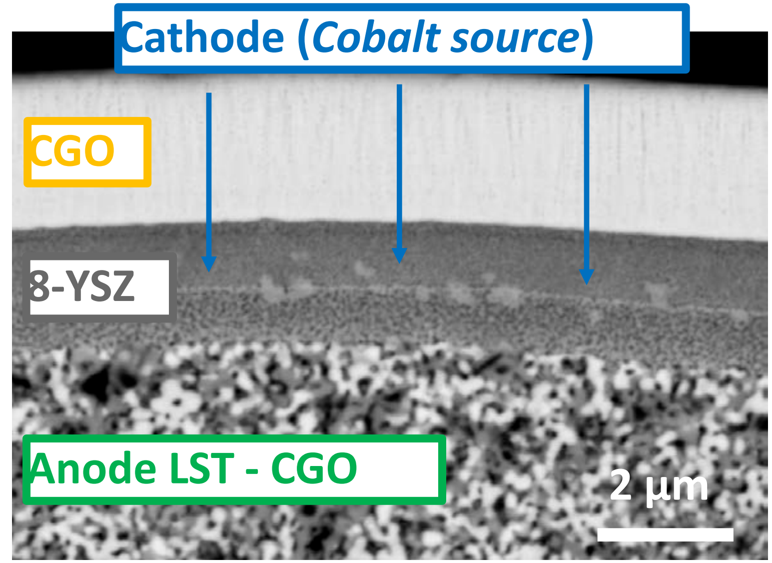
Fine pores in the PVD layer

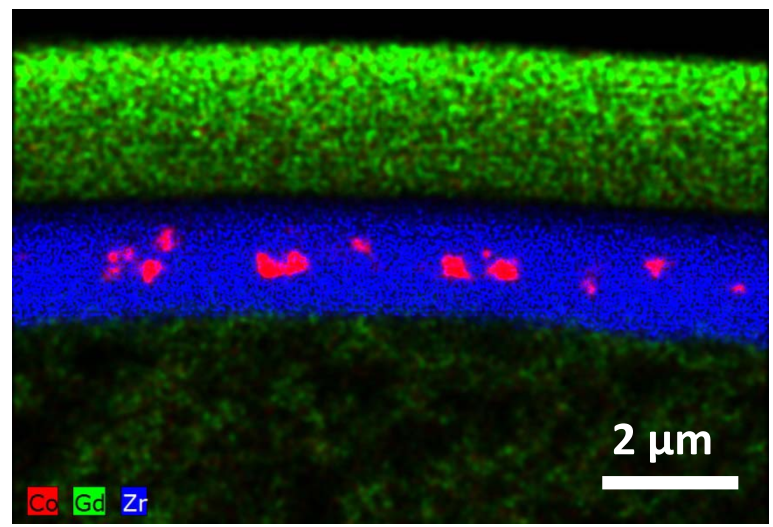
Sintering of the nano-porous Layer

No measured influence on leak rate

Impact on apparent resistivity of the layer an ionic transfer (?)

Cation diffusion





Increase of electronic transport?

DLR

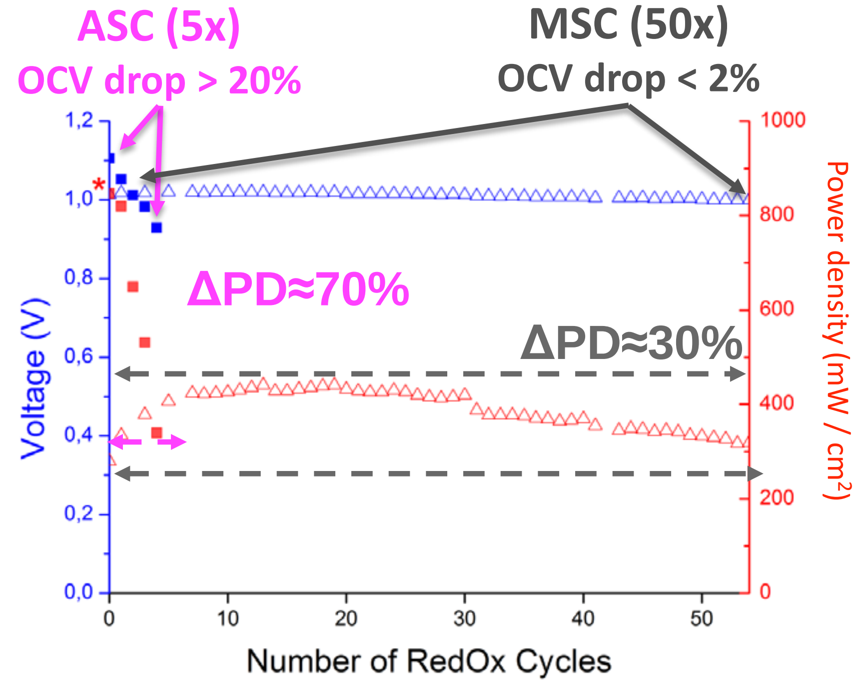
Degradation of interfaces

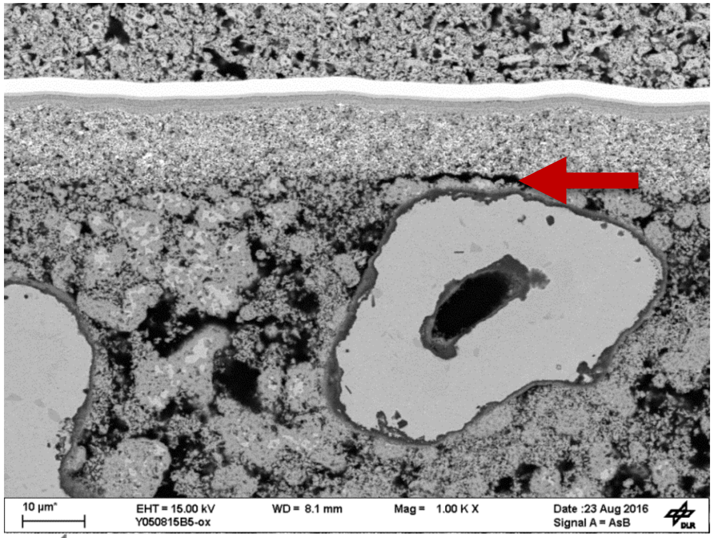
Redox cycles (30 min in O_2 @750°C)

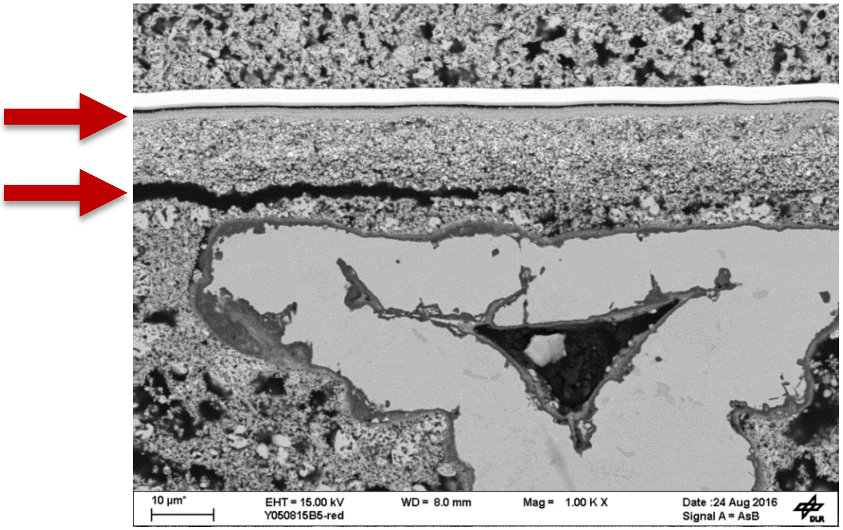
No fatal failure of the electrolyte
- NiCrAl « armored » substrate?

Performance still affected
Cracks due to repeated volume expansion of nickel during oxidation

Ni rearrangement?

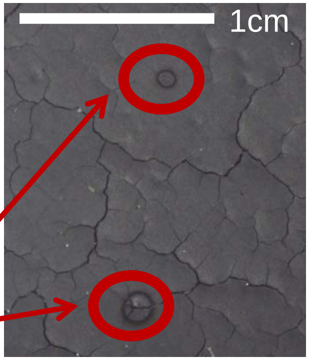




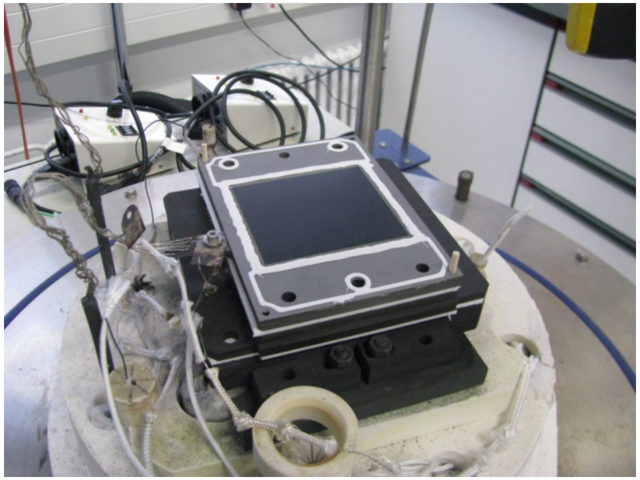


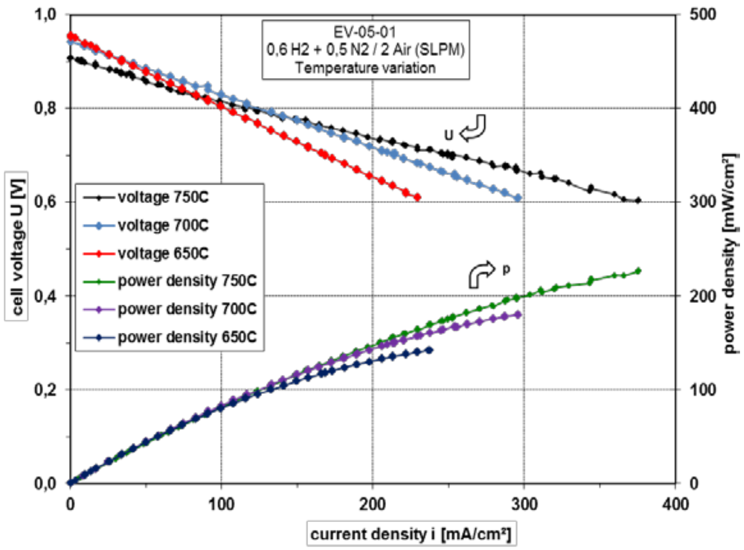
DLR

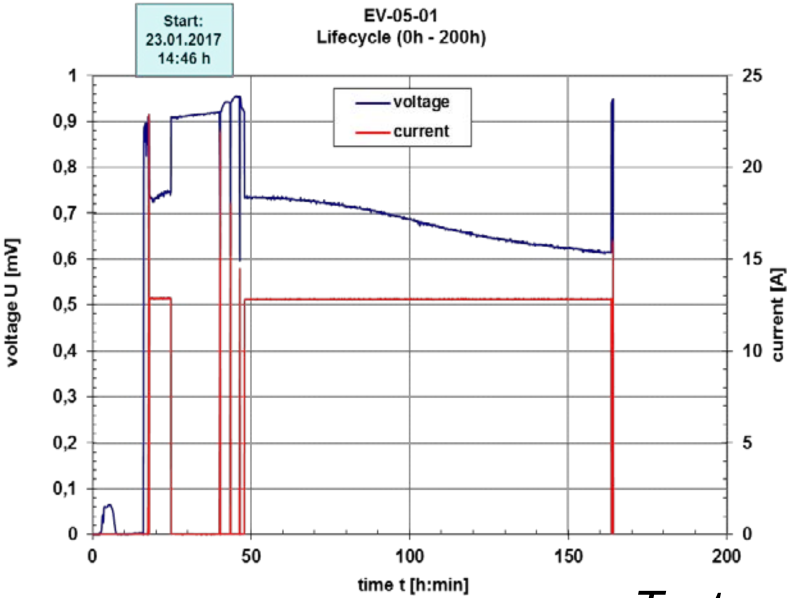
Up-scaling



- size up to 90 mm x 100 mm
- moderate OCV (!!! pinholes !!!)
- Power density for 1 level stack at 166 mW/cm^2 @ 750 °C and at 0,7 V
- adapt sealing solution in order not to age the interfaces and electrolyte (Low T sealing)

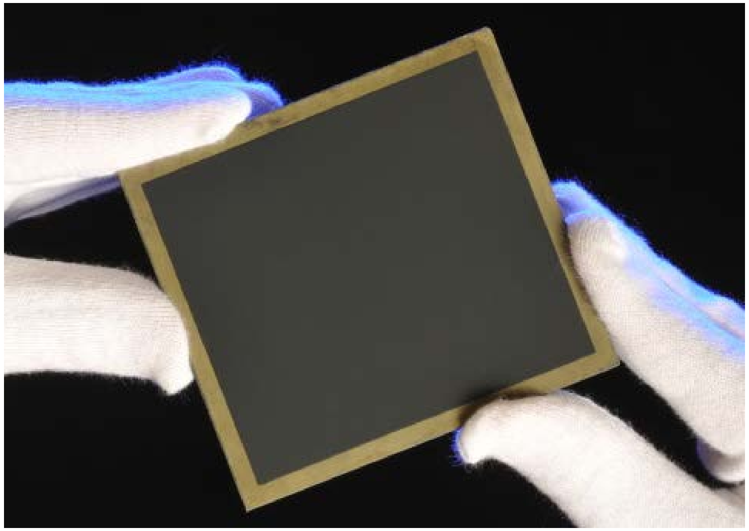






Test running…

Conclusion & Perspectives



- *metal supported cell with LST were produced. Processing route has been designed to tackle requirements for manufacturing.*
- ***Thin film electrolyte technology developed and demonstrated.***
- ***Power Density > 400 mW / cm² at 750°C** and 0,7V is obtained. Addition of nickel was necessary to enhance kinetic at the fuel electrode.*

- *OCV drop of less than 2% for 50 forced redox cycles (30 min in Oxygen) at 750°C*
- *Integrity of the electrolyte is maintained but delamination of Anode functional layer is observe*

- ***Cell-Architecture can be up-scaled at stack size and is economically realistic***

- ***Degradation of the interfaces in the multi-layer electrolyte (Lower operating T)***
- ***Both fuel electrode are subject to degradation (new set of materials)***
- ***Investigation in electrolysis operation***

Acknowledgements

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Thanks for your attention!