

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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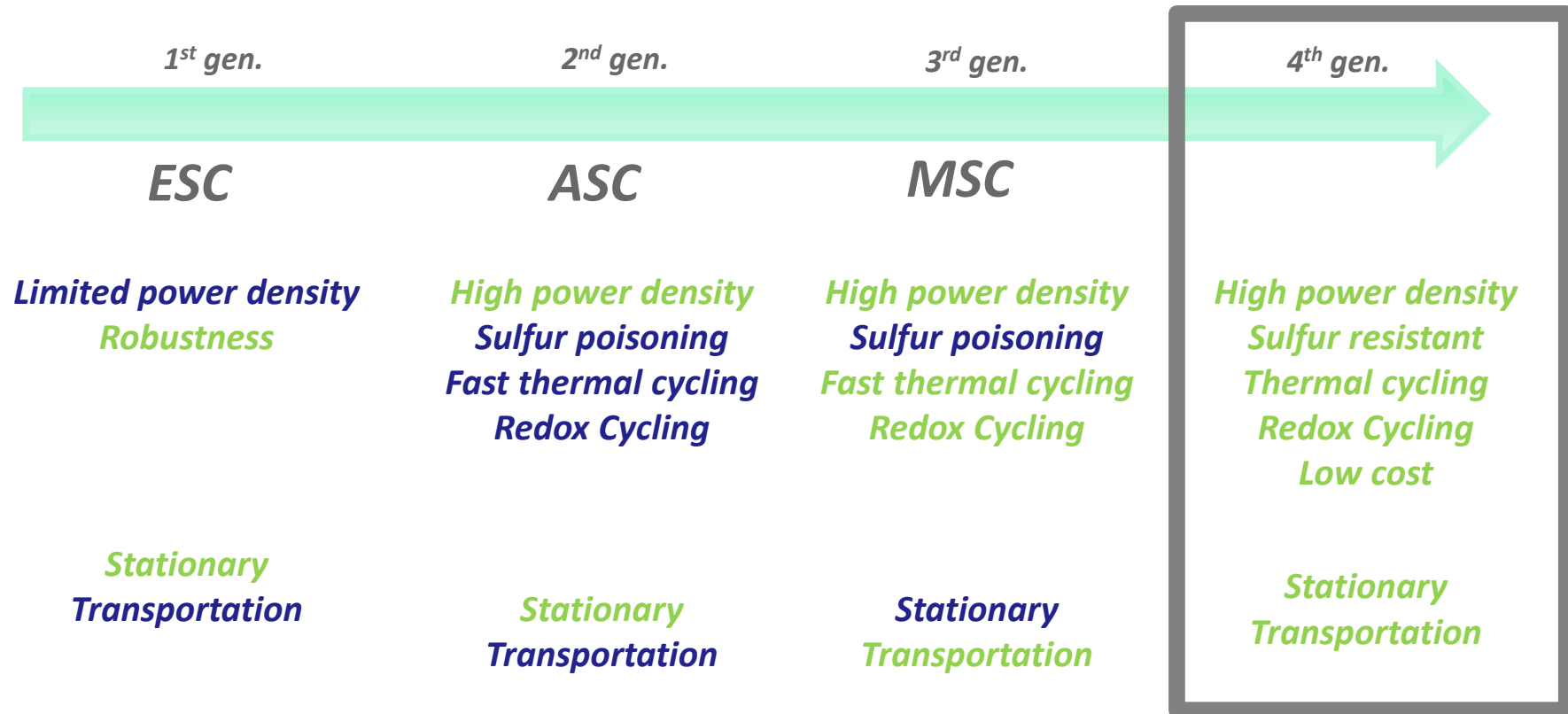
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- 3 Ceraco GmbH, Ismaning, Germany
- 4 CNRS-Universite des Alpes, Grenoble, France



Knowledge for Tomorrow



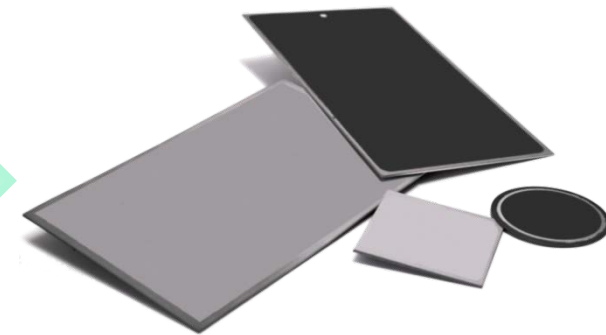
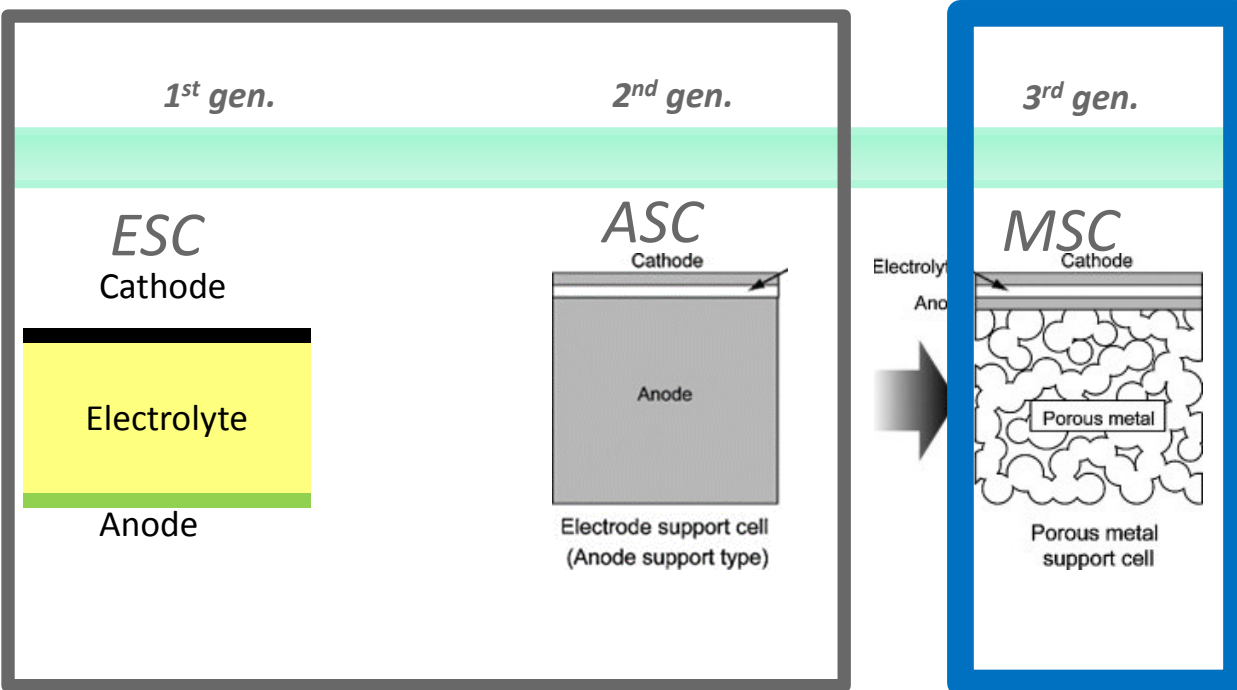
Motivation: towards the next generation SOC



Flexible architecture for multiple applications
Which materials for the next generation of SOC's?



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.

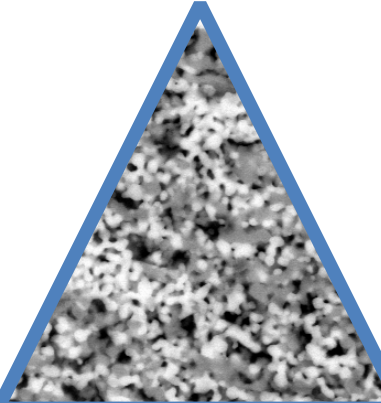
M.C. Tucker / Journal of Power Sources 195 (2010) 4570–4582



Key performance factors

Catalysis
Sealing
TEC
Reactivity
...

Microstructure / Architecture



Robustness

Red-ox cycles

Contact

Fuel Utilization

Gas Transport

Balance of Plant

Life Time

Reliability

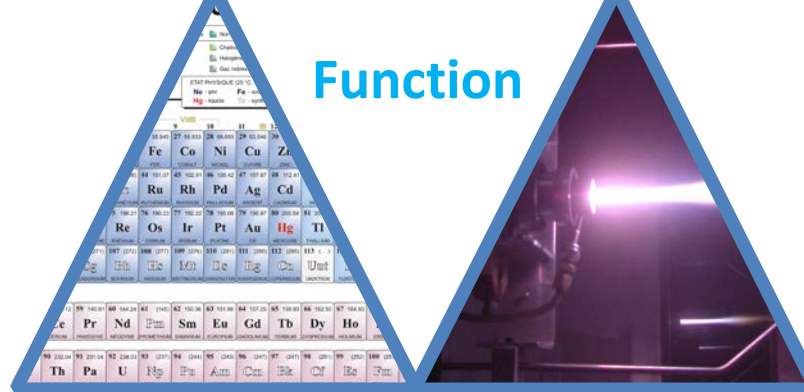
Start-up time

Poisoning

...



Function



Materials

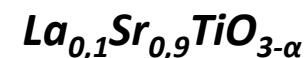
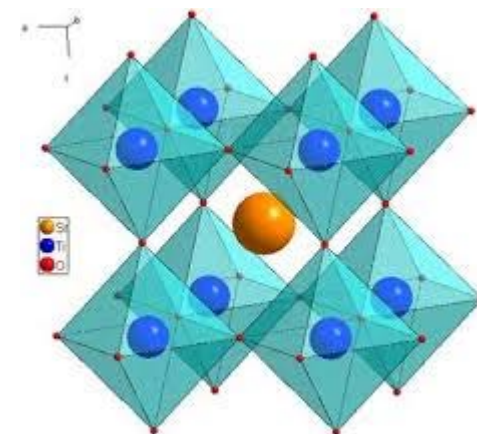
Manufacturing

- To produce kWh
- To store Energy



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***



screen printing



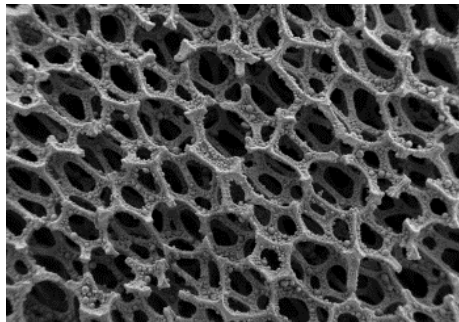
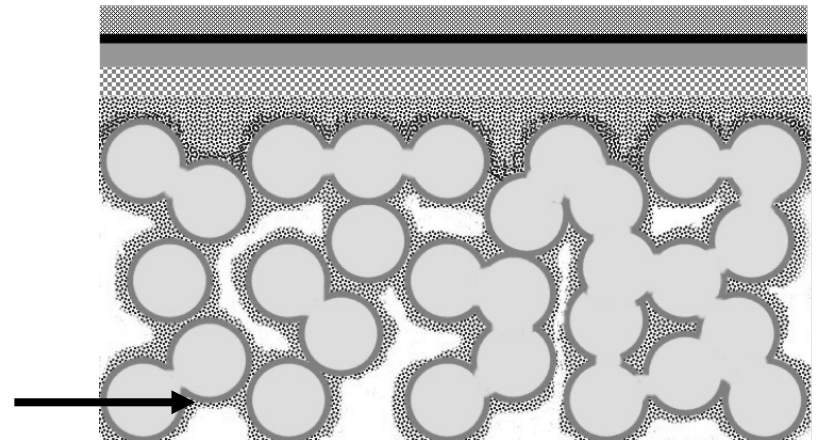
Materials

Cathode : $\text{La}_{0,4}\text{Sr}_{0,6}\text{Co}_{0,2}\text{Fe}_{0,8}\text{O}_{3-\alpha}$

Electrolyte: 8-YSZ / 10-CGO

Composition of the anode: CGO-LST (w/o 5-10%Ni)

Metallic substrate at the fuel side



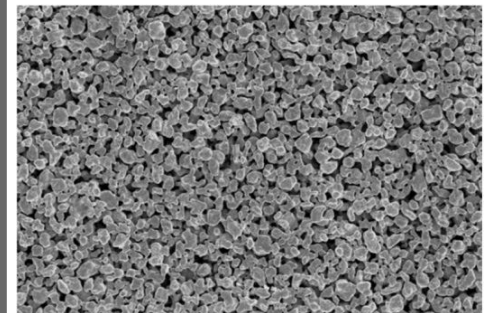
*Foam NiCrAl #01
450μm pore size*

+



$\text{NiO} + \text{La}_{0,1}\text{Sr}_{0,9}\text{TiO}_{3-\alpha}$ (50:50)

1



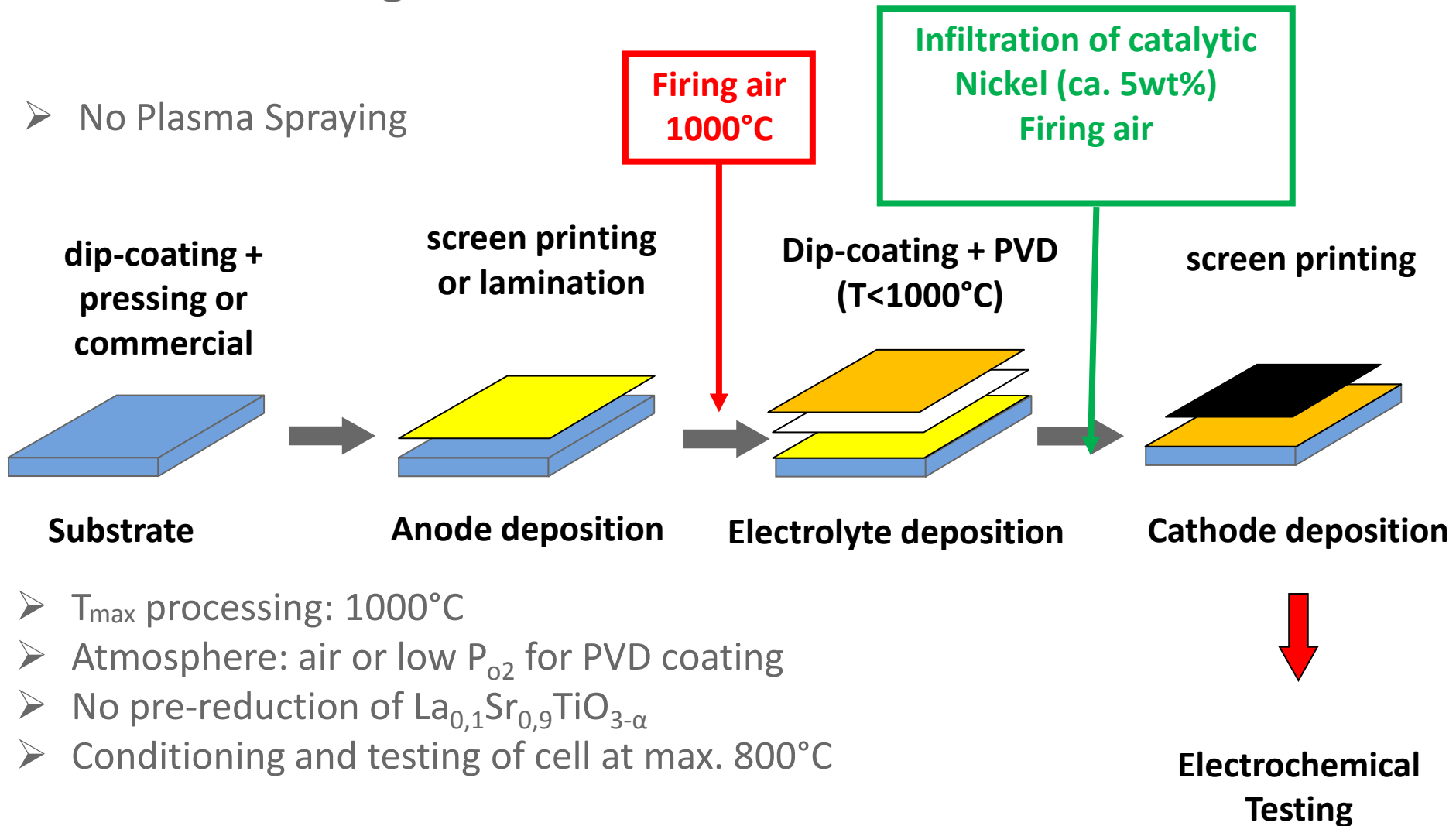
Ferritic stainless steel

2



Manufacturing

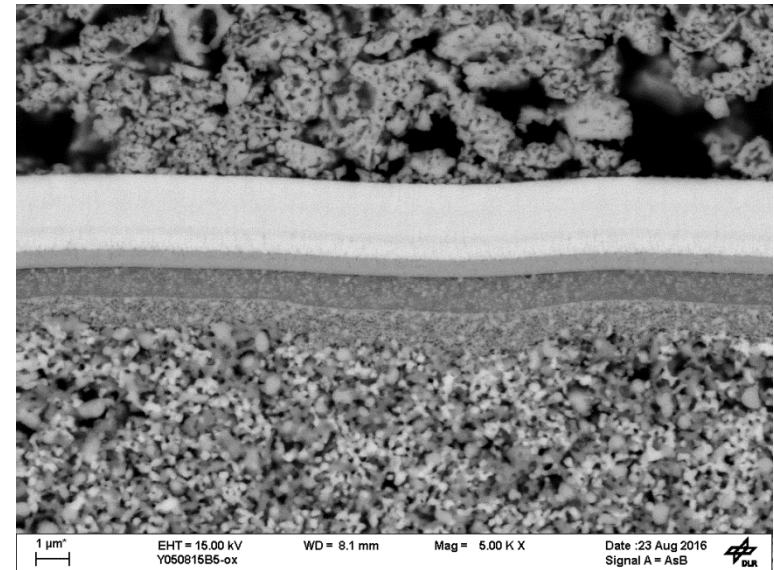
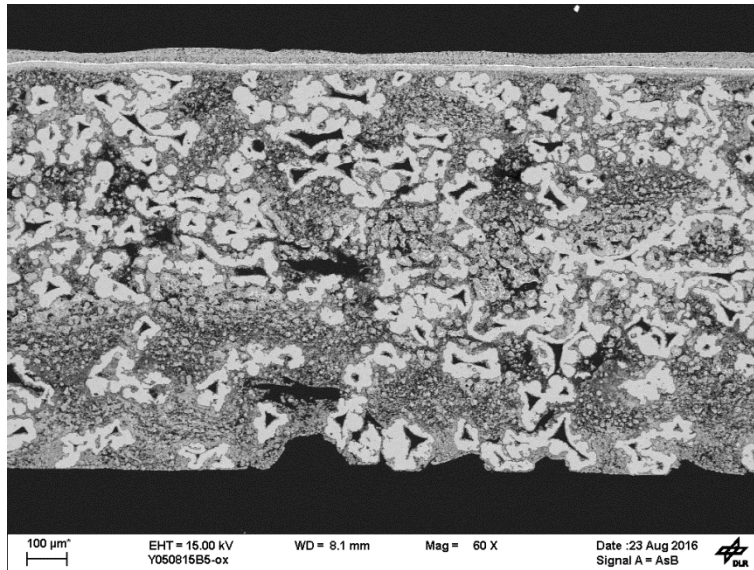
- No Plasma Spraying



- T_{\max} processing: 1000°C
- Atmosphere: air or low P_{O_2} 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 Metal Foam Substrate



Microstructure:

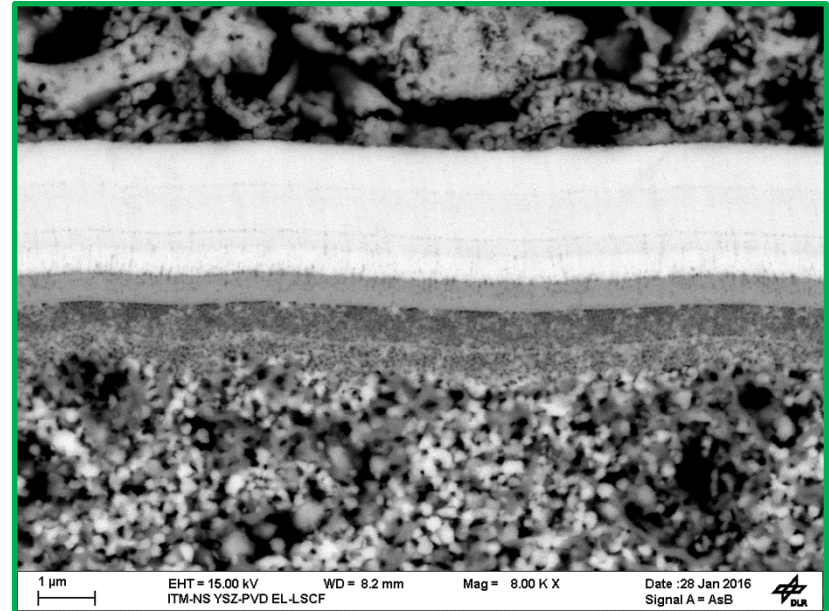
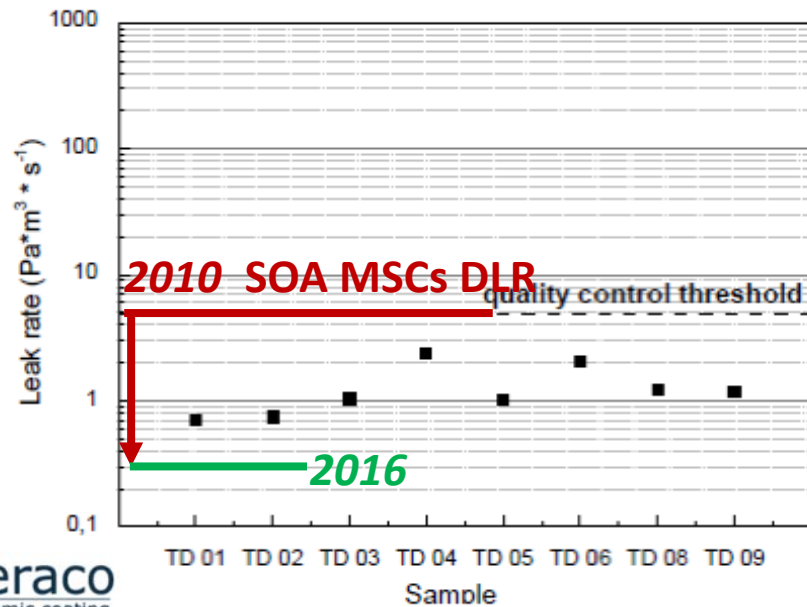
Hermiticity of the electrolyte

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!!!



F.Han, R. Semerad, R. Costa, *patent pending*

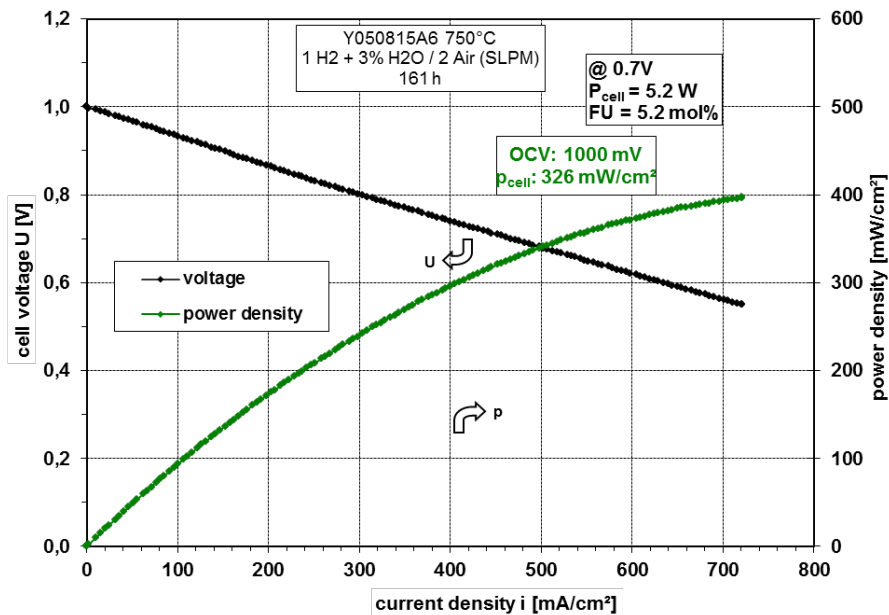
ceraco
ceramic coating



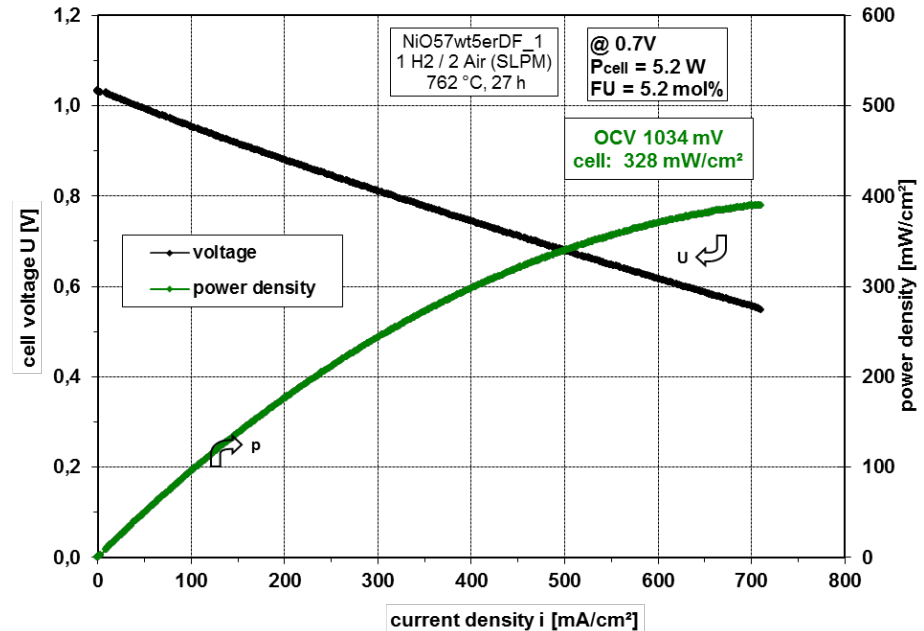
Performance

ferritic stainless steel vs NiCrAl (w. LST:NiO)

(Anode Functional Layer: LST:CGO w 5-10wt%Ni) – 16cm²



ferritic stainless steel



NiCrAl (w. LST:NiO)

@ 750°C 1slpm H₂ (w. H₂O)/ 2slpm air

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

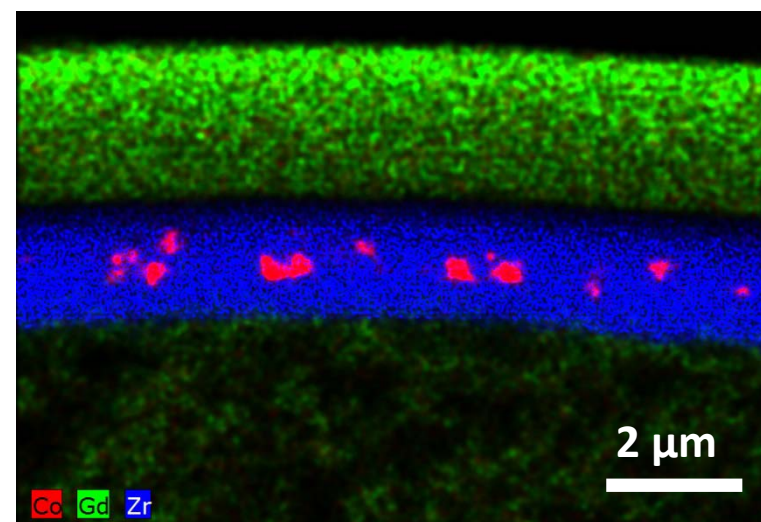
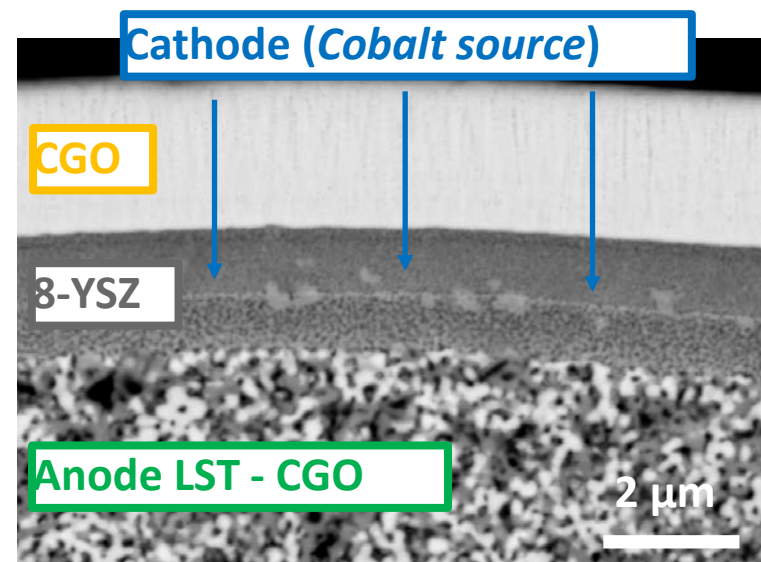
Power density at 0,7 V ca. 320 mW/cm² (improved up to 450 mw/cm²)

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



Degradation of interfaces *multi-layer electrolyte*

Cation diffusion



Increase of electronic transport?



Degradation of interfaces

Redox cycles (30 min in O₂ @750°C)

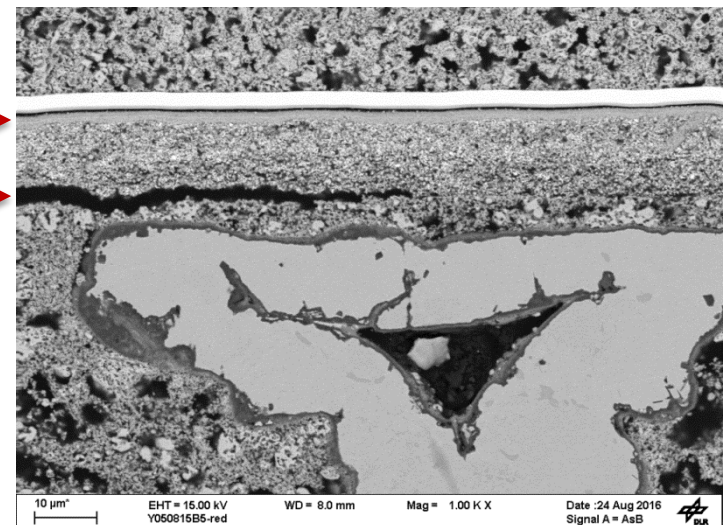
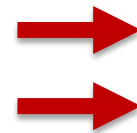
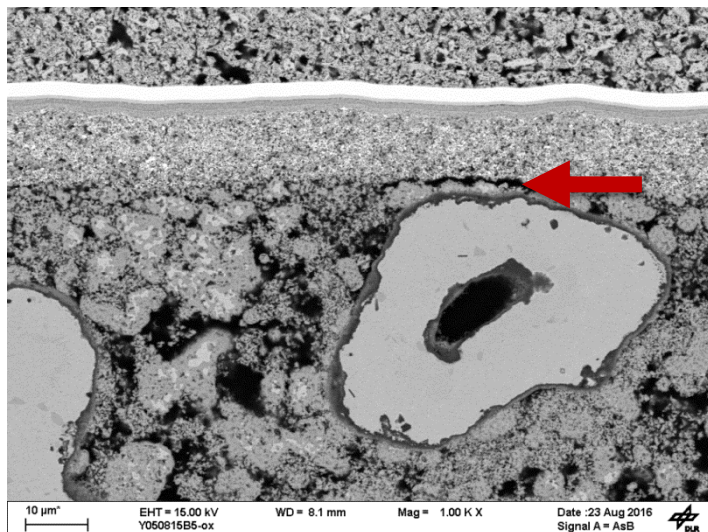
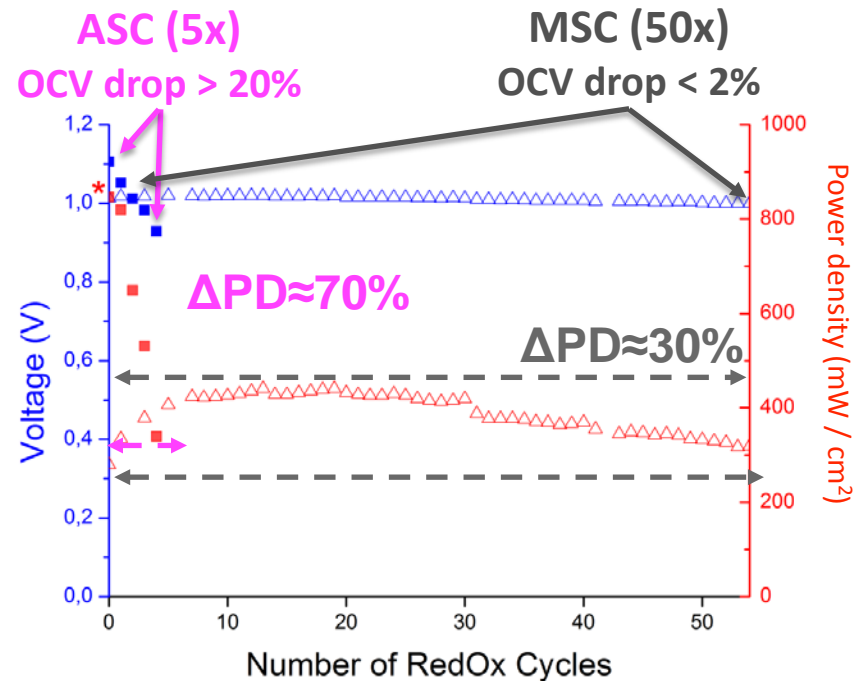
No fatal failure of the electrolyte

○ NiCrAl « armored » substrate?

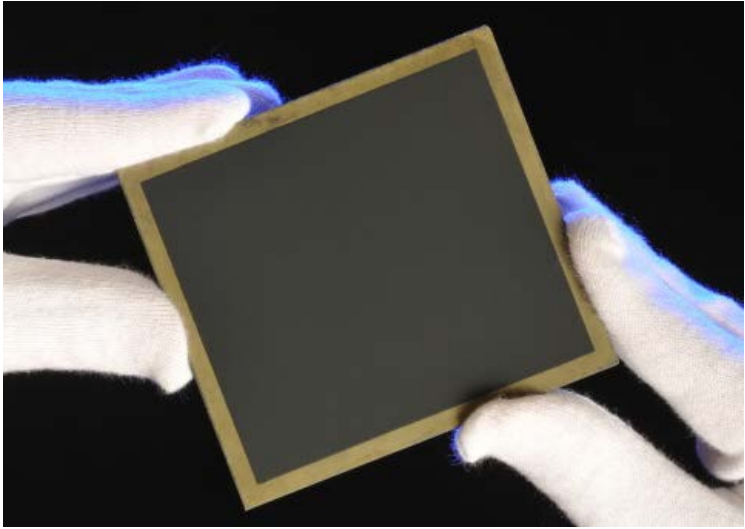
Performance still affected

Cracks due to repeated volume expansion of nickel during oxidation

Ni rearrangement?



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 observed*
 - ***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!

