Nickel-free Hybrid Metal-Ceramic Supported SOFC

R. Costa

remi.costa@dlr.de

Alantum Europe GmbH: R. Poss,
ARMINES: A. Chesnaud, F Willot
CerPoTech: G. Syvertsen,
CNR: M. Viviani, A. Sanson
Grenoble INP: L. Dessemond
Ceraco GmbH: R. Semerad
Saan Energi: A. Ansar

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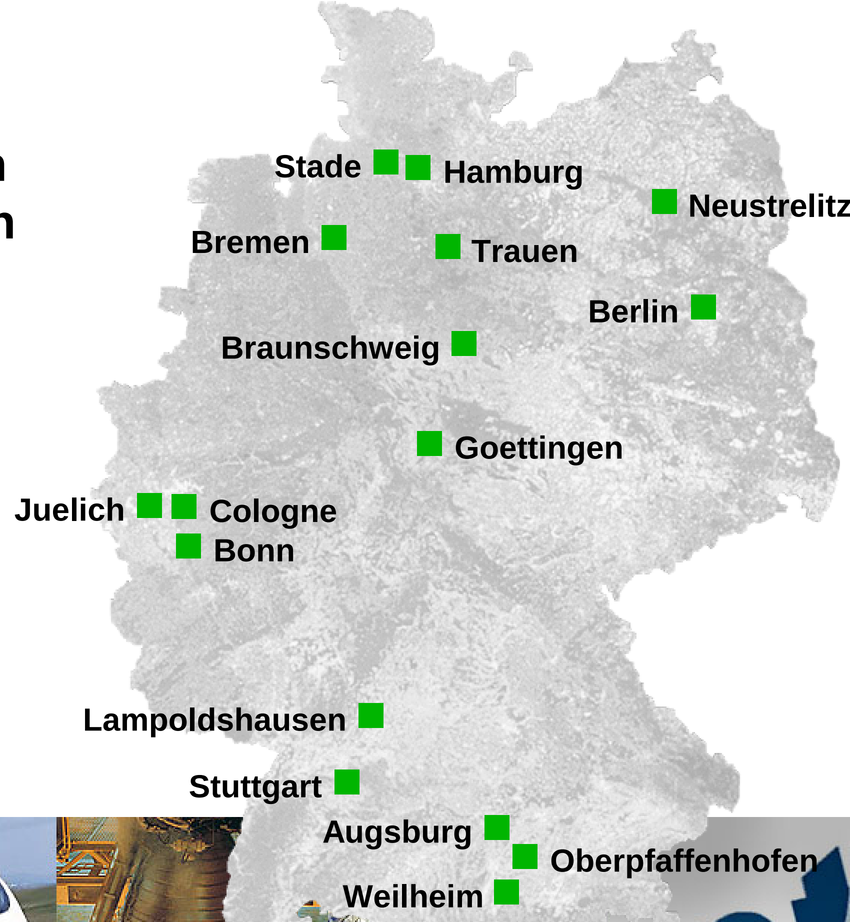
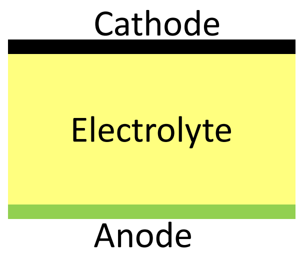


Generations of planar SOFCs

1st gen.

ESC

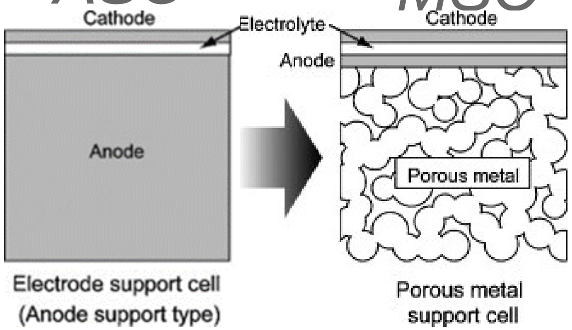


Limited power density
Fuel flexibility
Robustness

Stationary
Transportation

2nd gen. / *3rd gen.*

ASC / MSC



2nd gen. (ASC):

High power density
Fuel flexibility
Sulfur poisoning
Thermal cycling
Redox Cycling

Stationary
Transportation

3rd gen. (MSC):

High power density
Fuel flexibility
Sulfur poisoning
Thermal cycling
Redox Cycling

Stationary
Transportation

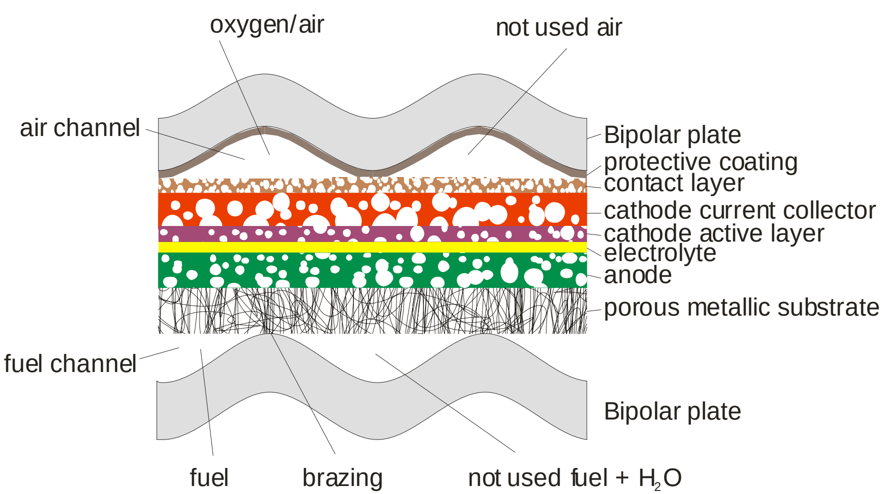
3rd Gen. SOFC: MSCs at DLR

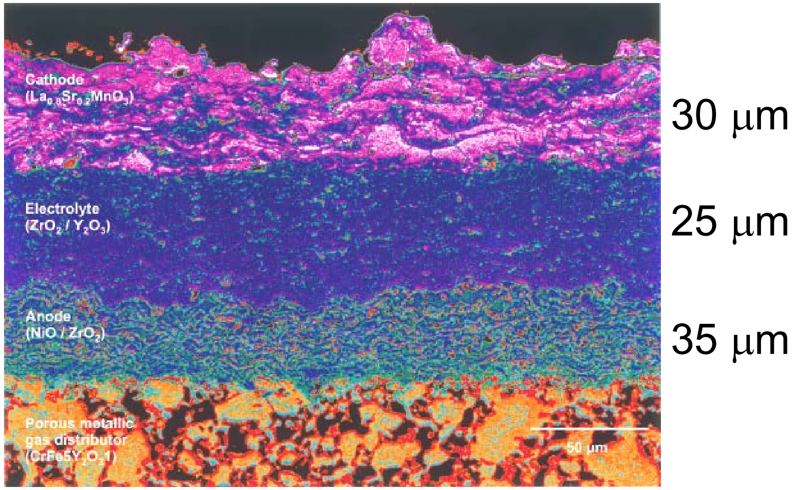
Plasma Deposition Technology

Ferritic Substrates and Interconnects

Compact Design with Thin Metal Sheet Substrates

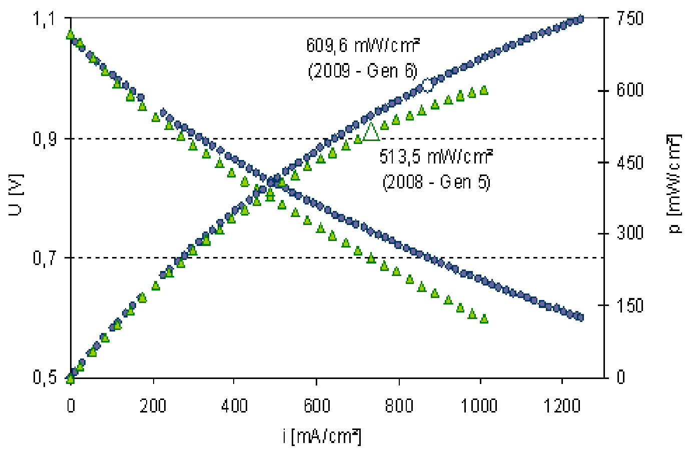
Brazing, Welding and Glass Seal as Joining and Sealing Technology



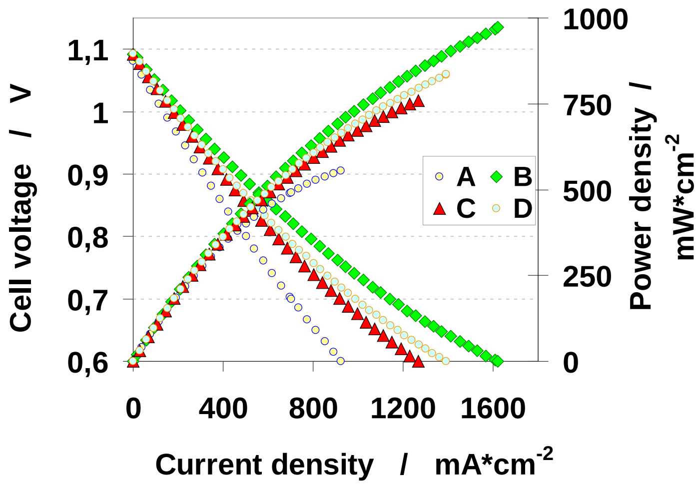


(not in scale)

3rd Gen. SOFC: MSCs at DLR



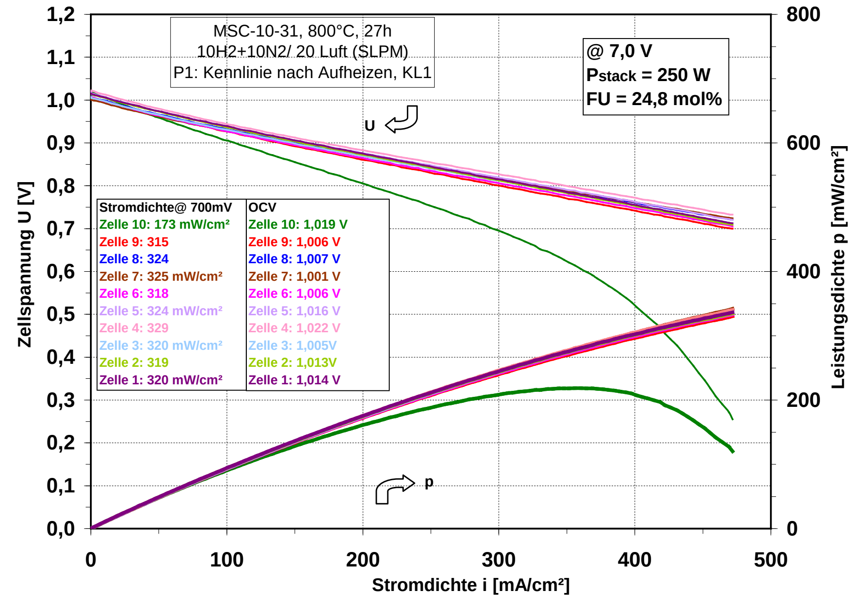
APS



SPPS

MSC Cell

12.5 cm² cell at 800°C; H_2/N_2 and air



10 Cells Stack

100 cm² single cells at 800°C; H_2/N_2; air

- *P. Szabo, J. Arnold, T. Franco, M. Gindrat, A. Refke, A. Zagst, A. Ansar, ECS Transactions, 2009 (25) 2 p.175-185*
- *D. Soysal, A. Ansar, Z. Ilhan, R. Costa, ECS transactions, 2011 (35) 1 p.2233-2241*

Beyond the 3rd Gen. SOFC: Issues to be adressed for improving MSCs

- **Cr-poisoning at the cathode side > Protective coating required**

- **Improve tolerance toward sulfur poisoning**
- **Life time of metal substrate if stationary applications are considered**
- **Hermitic electrolyte**

→ Which materials and architecture for the next generation of SO(F)C?

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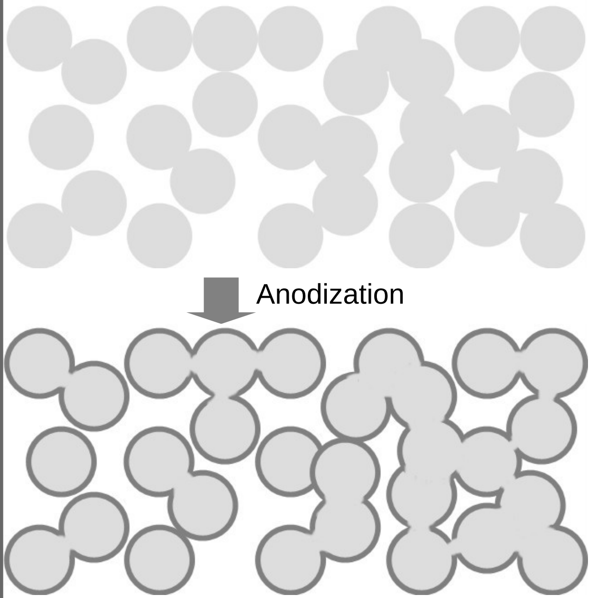
Metal substrate resistant toward oxidation



Metallic alloy foam (such as FeCrAlY), capable of forming alumina protective scale
Excellent mechanical properties, but high sensitivity to chemical reactions (high degradation)

Oxidized metal alloy foam, with stable aluminum oxide scale
Excellent mechanical properties and stable oxide scale to protect against chemical reactions (low degradation), but poor or no electronic conductivity

Formation of an Al_2O_3 **layer as a durable protective coating**

Al rich alloys, on the basis of MCrAl(Y) with M being Fe, Ni, Co or a mixture

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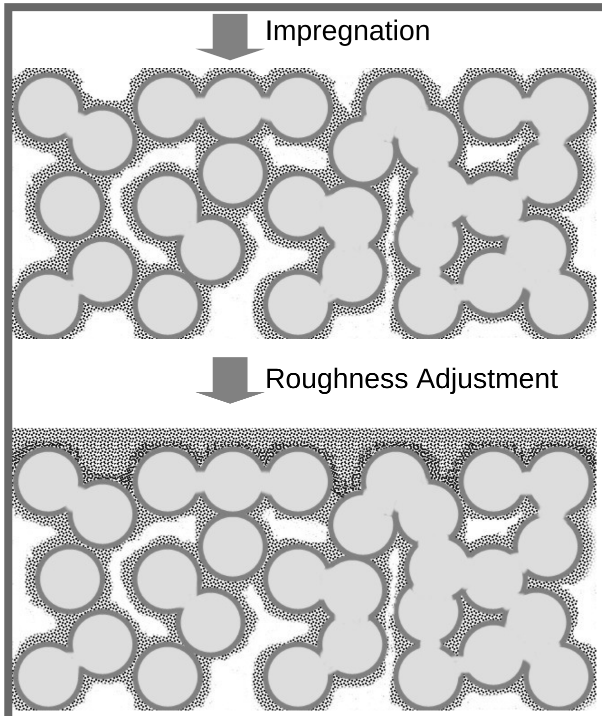

Anode current collector - Oxidized alloy foam with impregnated conductive ceramic (LSCM or LST).
Excellent mechanical properties and stable oxide scale to protect against chemical reactions (low degradation), high electronic (and ionic) conductivity

Smooth current collector
Low roughness surface ready for coating of functional layers of cell

Infiltration with an electronic conductor (ideally a ceramic)

Target : 100 S/cm

Dense La0.1Sr0.9TiO3 (800°C):
- sintering in H_2: σtot ≈ 150 S/cm

O. Marina et al. Solid State Ionics, 149 (2002) 21-28.
S. Hashimoto et al. Journal of Alloys and Compounds, 397 (2005) 245-249.
Y. Tsvetkova et al. Materials and Design, 30 (2009) 206-209.

Hybrid current collector mechanically and chemically stable in both oxidant and reducing atmosphere

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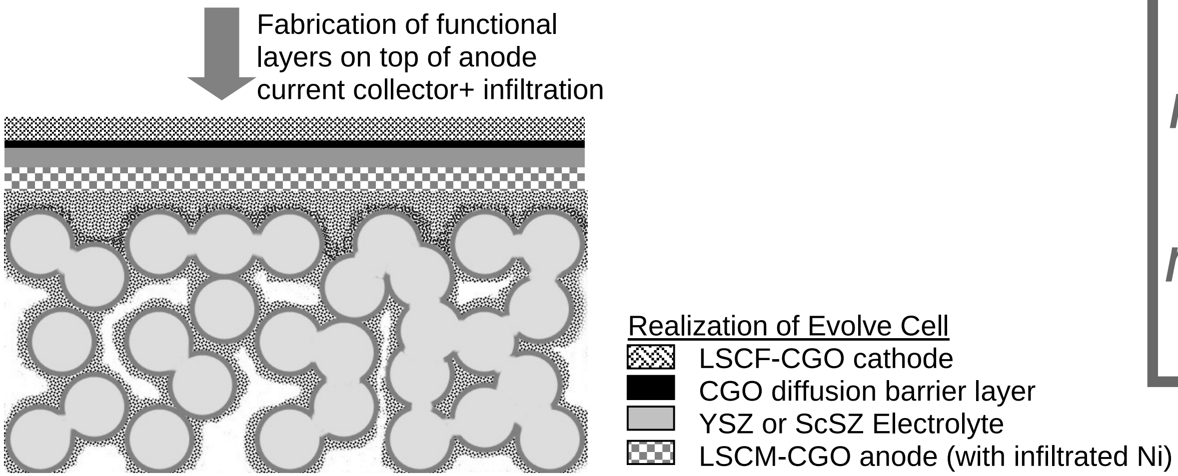

Use of perovskite materials at the anode and cathode, being modified by addition of suitable catalysts

High power density, Sulfur resistant, Fuel flexibility, Thermal cycling, Redox Cycling

Stationary applications …

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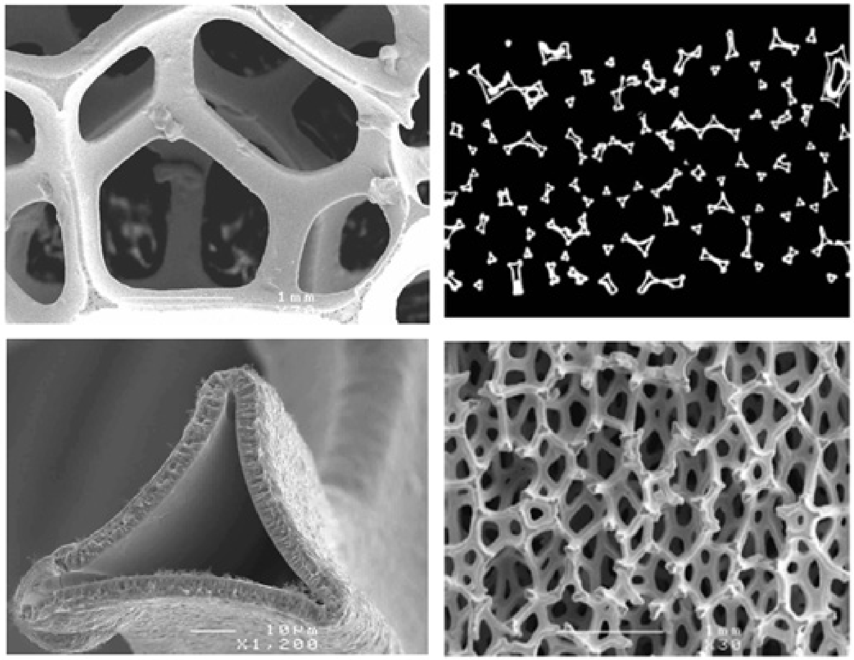

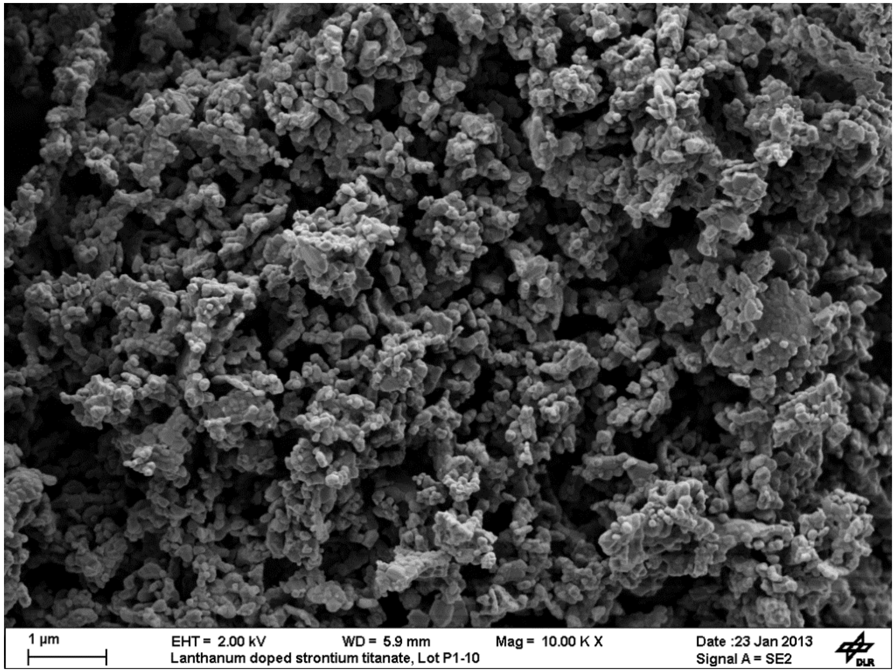

Composition of the anode: $Ce_{1-x}Gd_xO_{2-\alpha}$ / $La_{0,1}Sr_{0,9}TiO_{3-\alpha}$
Electrolyte: 8-YSZ
Cathode : $Ce_{1-x}Gd_xO_{2-\alpha}$ / $La_{0,4}Sr_{0,6}Co_{0,2}Fe_{0,8}O_{3-\alpha}$

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Development strategy

1cm² | 15-20 cm² | 100 cm²

- Reactivity tests
- Conductivity measurement
- Understanding the behaviour

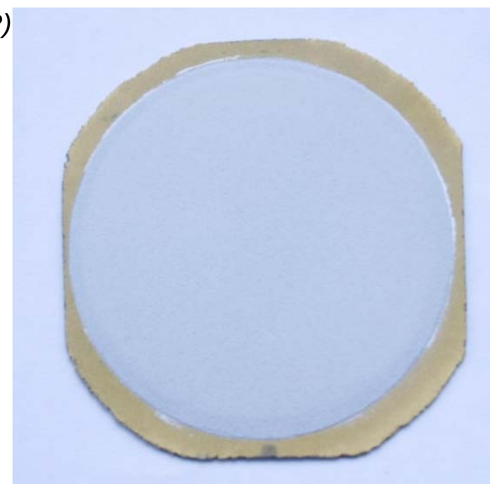
- Shaping strategy
- Prototype
- Testing and optimization

- upscaling

(CNR ISTEC)

10mm

(DLR)



10mm

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Evaluation of the anodic electrocatalyst

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Evaluation of the electrocatalyst

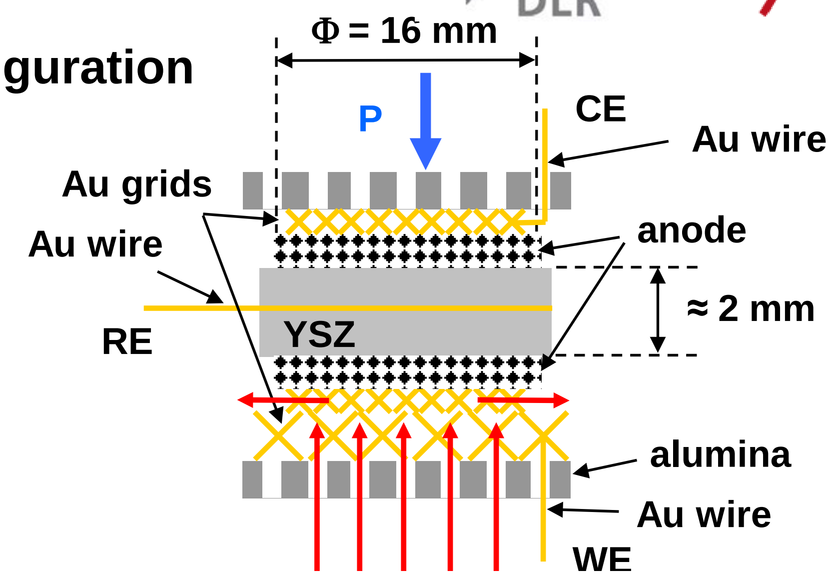
- **Symetrical cells tested in 3-electrodes configuration**

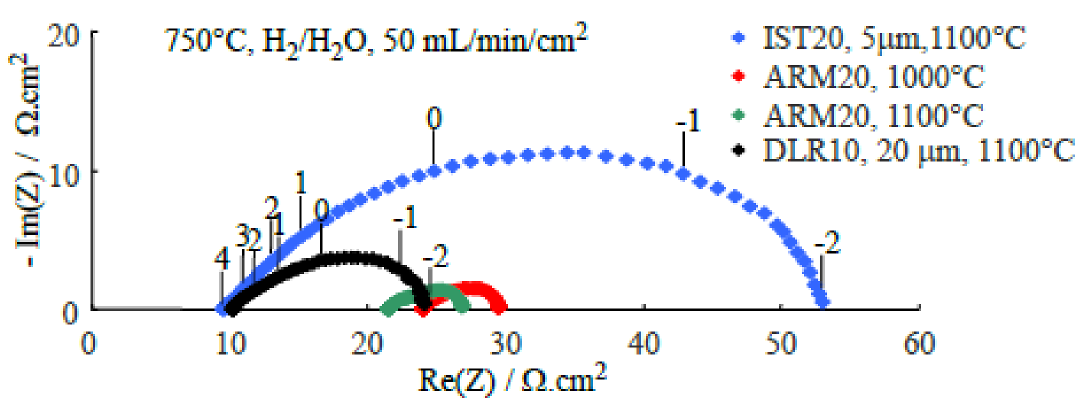
- **Experimental conditions**

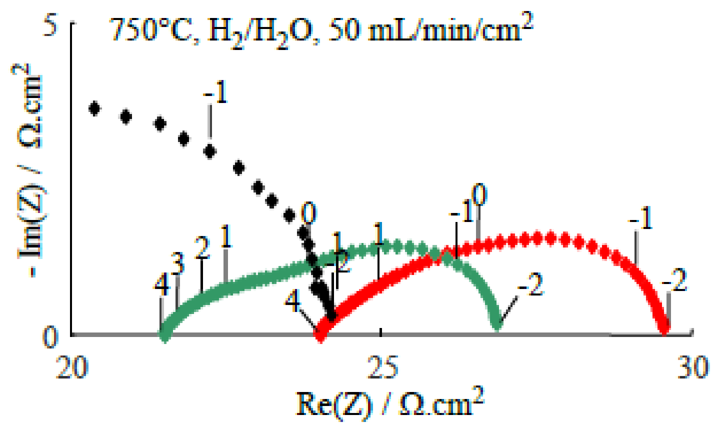
Gas composition, gas flow, Temperature

- **Elaboration parameters**

Composition, Thickness porosity







Rpol decreases: increase in thickness and/or decrease of the pore size

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Evaluation of the electrocatalyst

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Electrokinetic modeling

- **Reaction mechanism and kinetic data**

	Reaction	k^0	E^{act} (kJ·mol^{-1})
	LST/CGO phase		
R1:	$H_2 + 2\,O_{LST} \rightleftharpoons OH_{LST} + OH_{LST}$	$1.5\cdot10^{14}$ cm^2·mol^{-1}·s^{-1}	50.0
R2:	$H_2O + O_{LST} + \square_{LST} \rightleftharpoons 2\,OH_{LST}$	$1.0\cdot10^{18}$ cm^2·mol^{-1}·s^{-1}	122.0
R3:	$O_{LST} + O_{LST} \rightleftharpoons O_2 + \square_{LST}$	$1.0\cdot10^{22}$ cm^2·mol^{-1}·s^{-1}	260.0
	YSZ/CGO phase		
R4:	$O^{\times}_{O\,YSZ} + V^{\cdot\cdot}_{CGO} \rightleftharpoons O^{\times}_{O\,CGO} + \square_{CGO}$	$1.0\cdot10^{22}$ cm^2·mol^{-1}·s^{-1}	50.0
	Charge-transfer reactions		
C1:	$O^{\times}_{O\,CGO} + \square_{LST} \rightleftharpoons V^{\cdot\cdot}_{CGO} + O^{1-}_{LST} + e^-$	$4.9\cdot10^{11}$ cm^2·mol^{-1}·s^{-1}	129.0
C2:	$O^{1-}_{LST} \rightleftharpoons O_{LST} + e^-$	$5.2\cdot10^{3}$ cm^2·mol^{-1}·s^{-1}	39.0

- **Thermodynamic data**

Species, i	h_i (kJ·mol^{-1})	s_i (J·K^{-1}·mol^{-1})
LST-CGO phase		
$\square_{LST}$	0	0
O_{LST}	–85.6	139
OH_{LST}	–199.0	0
O^{1-}_{LST}	–114.0	139
$O^{\times}_{O\,CGO}$	–236.0	0
$V^{\cdot\cdot}_{O\,CGO}$	0	0
YSZ phase		
$O^{\times}_{O\,YSZ}$	–236.0	0
$V^{\cdot\cdot}_{O\,YSZ}$	0	0

⇒ **detailed multistep (electro-)chemical mechanism**

⇒ **thermodynamically consistent kinetic modeling**

⇒ **evaluation of main performance limitation processes**

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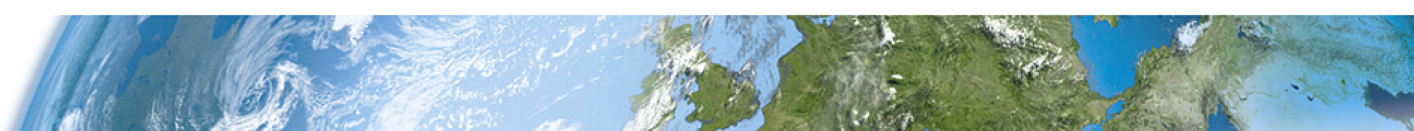

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Evaluation of the electrocatalyst

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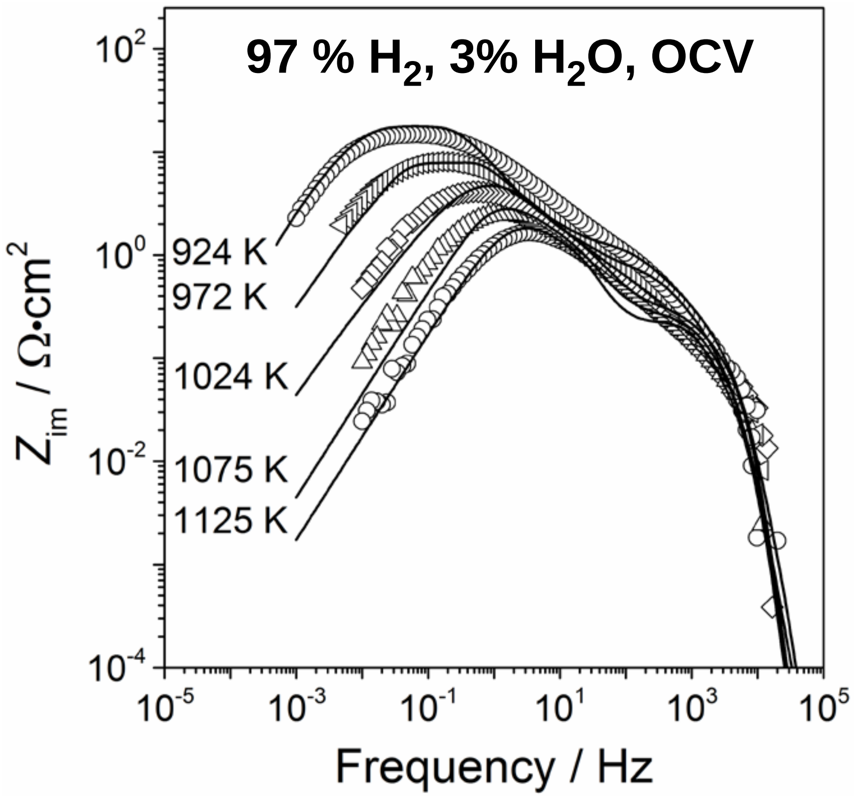
Electrochemical results: IST20



- **LST-CGO20, 50 vol%-50 vol % screen printing**
- **Data**
  - **Anode: 15 µm**
  - **Electrolyte: 925 µm**
  - **Mesh: 700 µm**
  - **Inlet: 50 mL/min/cm^2**
  - **Active surface area: 4.6 10^4 m^2/m^3**

⇒ **- qualitative agreement between modeling and experiments**

- three main impedance features

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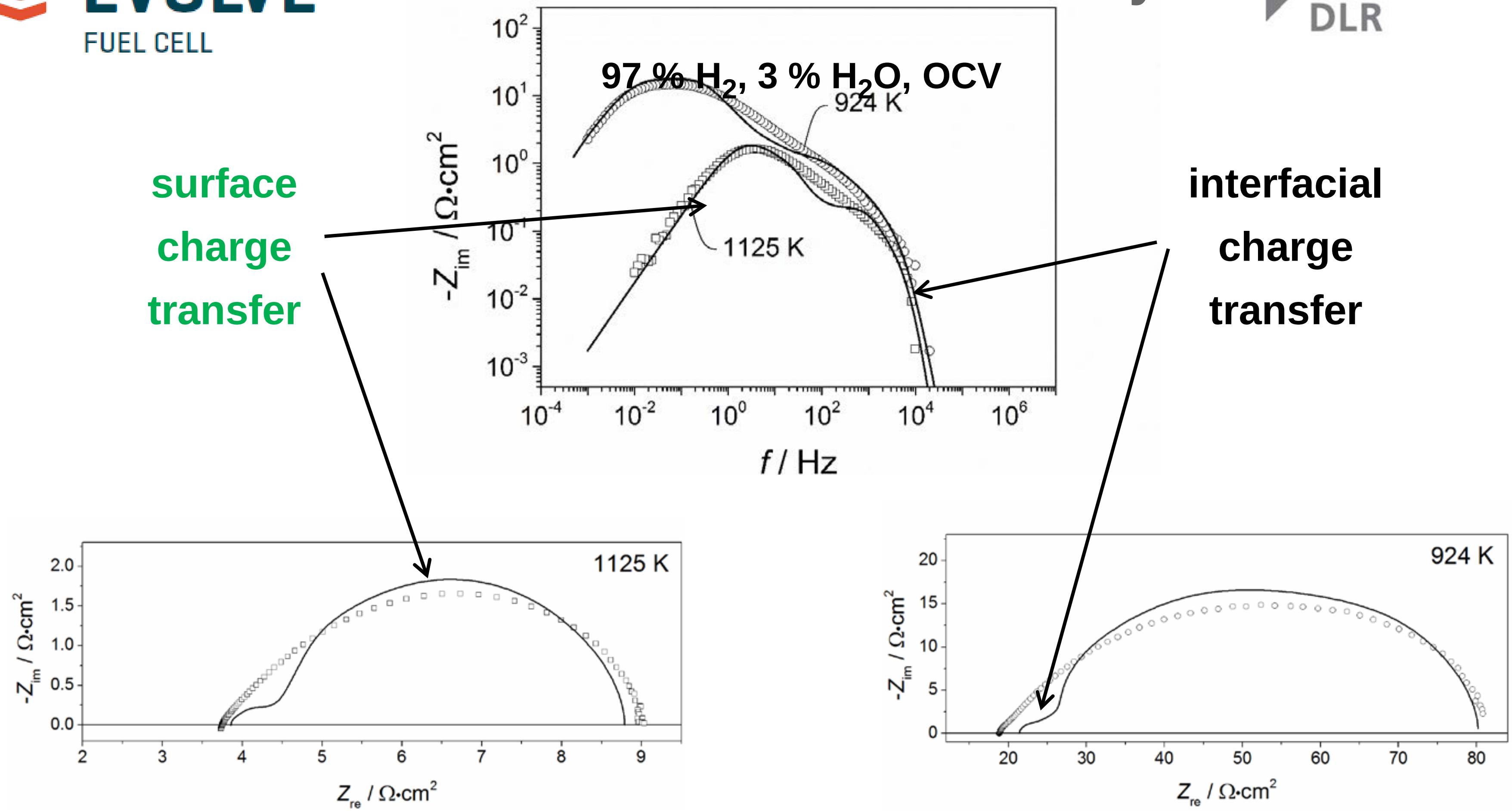
Evaluation of the electrocatalyst



⇒ **- unambiguous assignment of impedance features**

- influence of surface chemistry

Efficient LST based anodes requires high specific surface area

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Evaluation of the electrocatalyst

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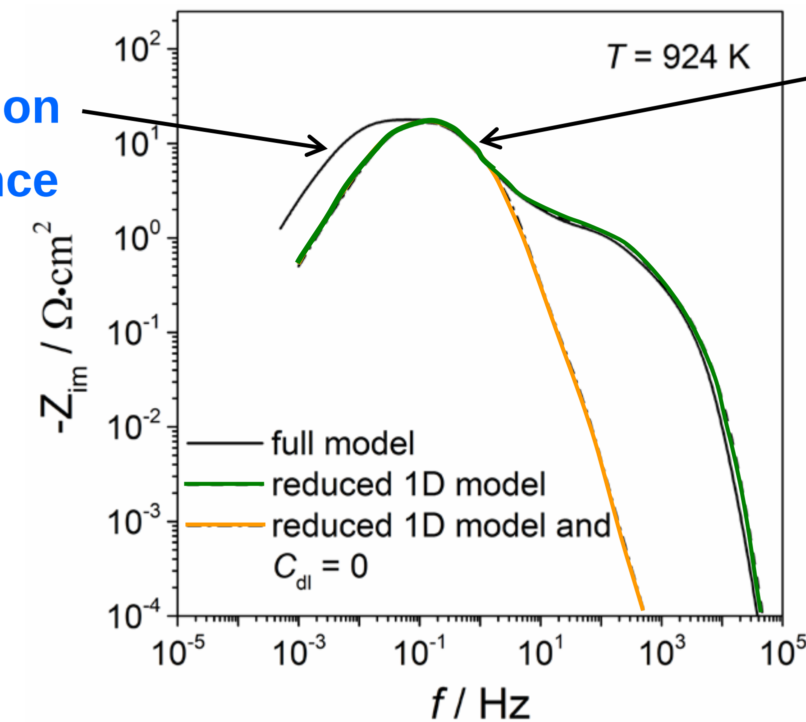
gas conversion impedance

H_2O dissociation



Solid line:

full model

Dashed line:

reduced to 1D

⇒ ideal supply channel transport

Dashed-dotted line:

reduced to 1D with C_{DL} = 0

⇒ - separation of transport and chemistry

- cell design optimization

V. Yurkiv, G. Constantin, A. Hornes, A. Gondolini, E. Mercadelli, A. Sanson, L. Dessemond, R. Costa, submitted to Journal of Power Sources

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Evaluation of the current collector

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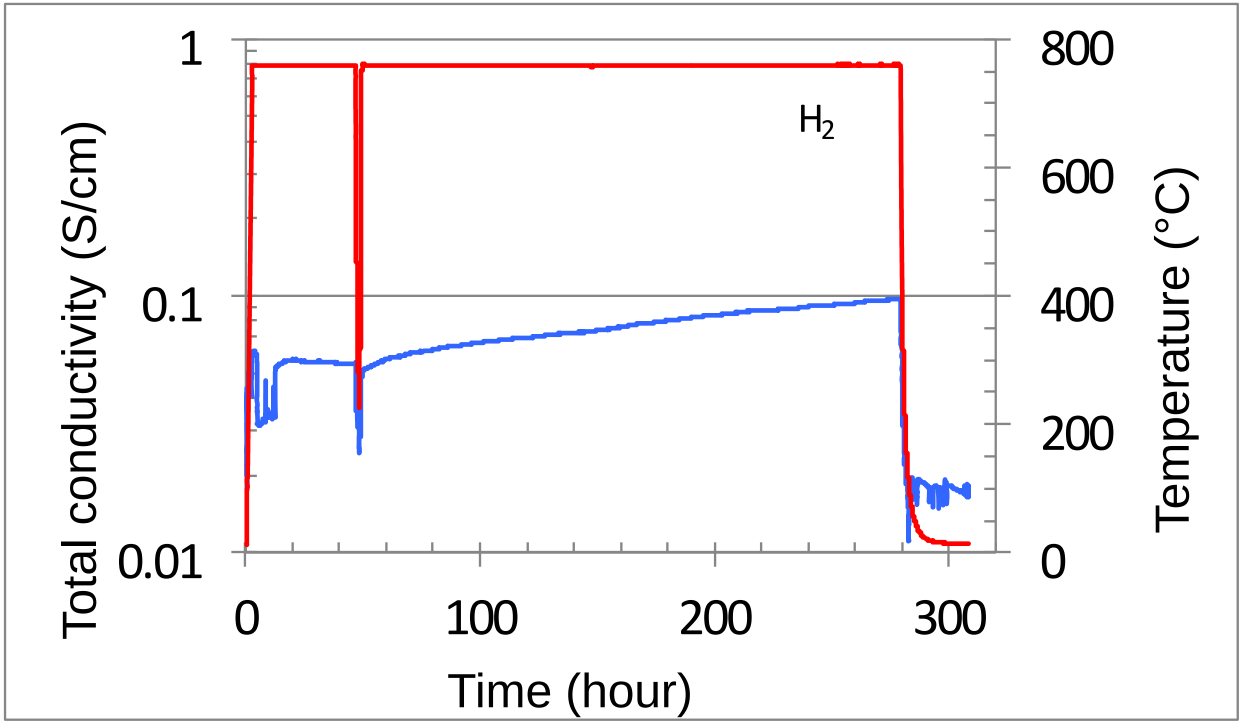
Evaluation of the current collector

Consiglio Nazionale delle Ricerche

LST-NiCrAl current collector > Cathode sintering leads to full reoxidation of LST
Evaluation of in-situ reduction of LST during stack sealing/commissioning



Reduction at 750 °C under H_2

Total conductivity << 100 S/cm

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Evaluation of the current collector

Consiglio Nazionale delle Ricerche

LST-NiCrAl current collector > Cathode sintering leads to full reoxidation of LST
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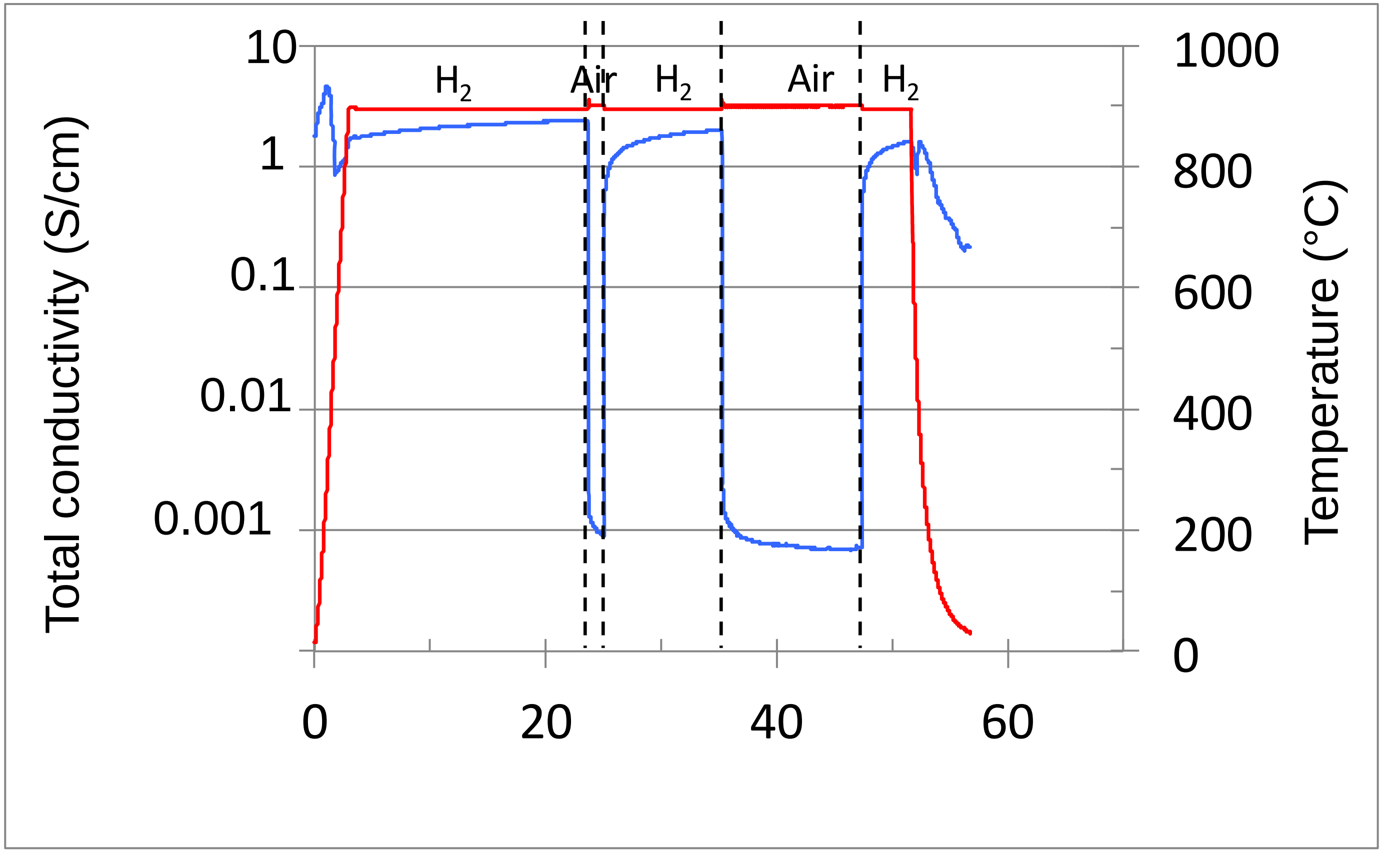

Reduction at 900 °C under H_2

Total conductivity << 100 S/cm

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Full Cell Processing

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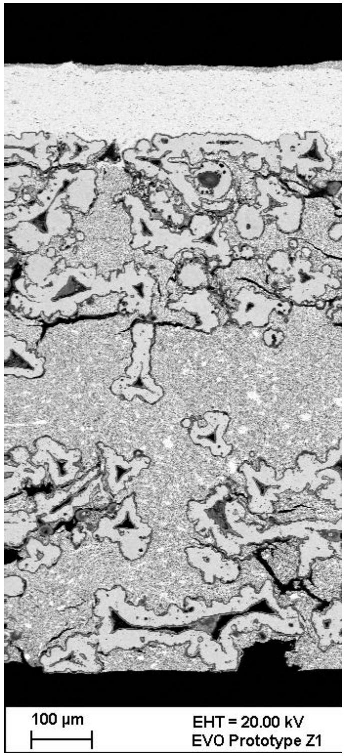
First demo Prototype through Plasma Spraying Route

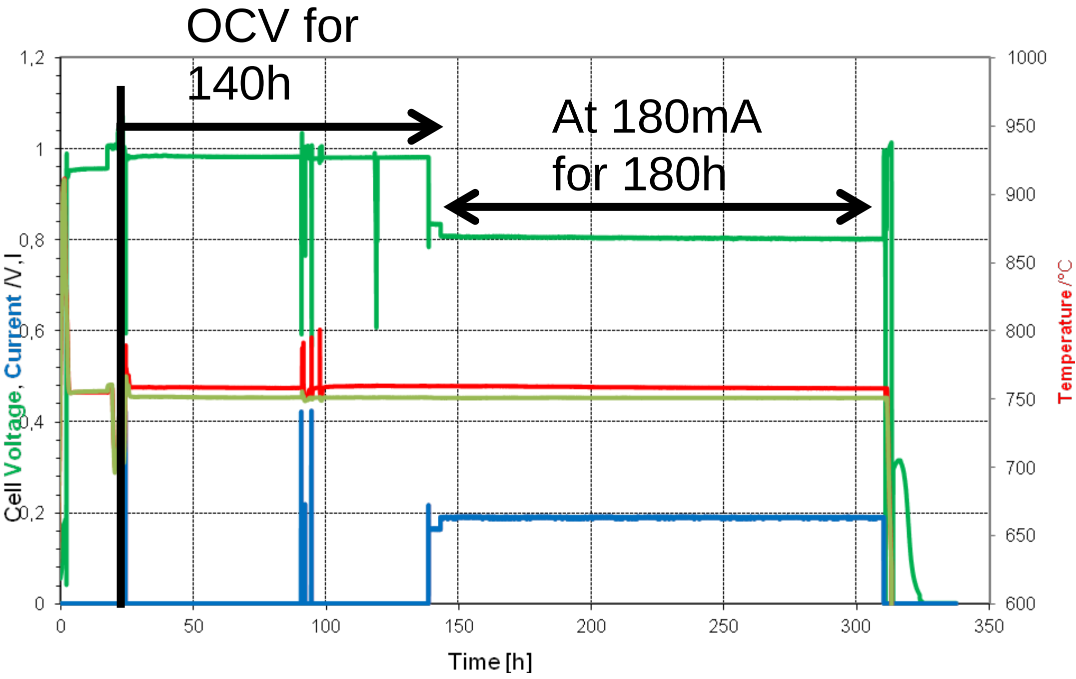
Low risk approach using the know how from DLR for spraying YSZ layers. No need of sintering step.



Cathode

100µm thick electrolyte

Co-pressed LST-CGO infiltrated NiCrAl foam



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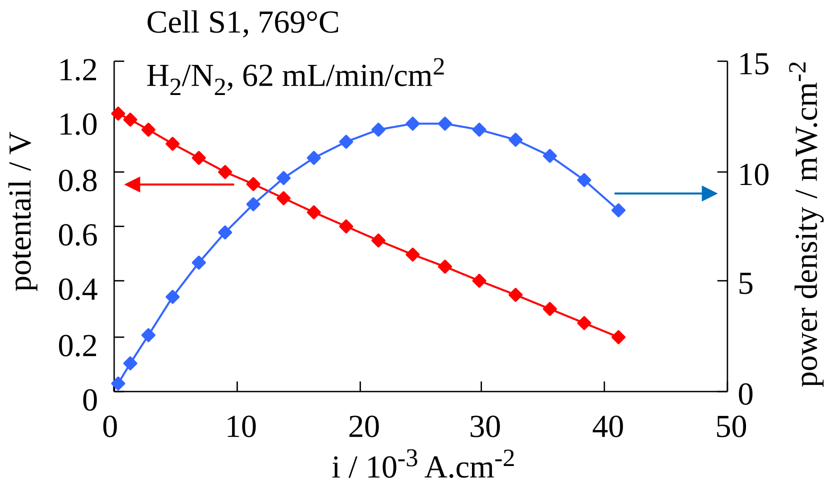
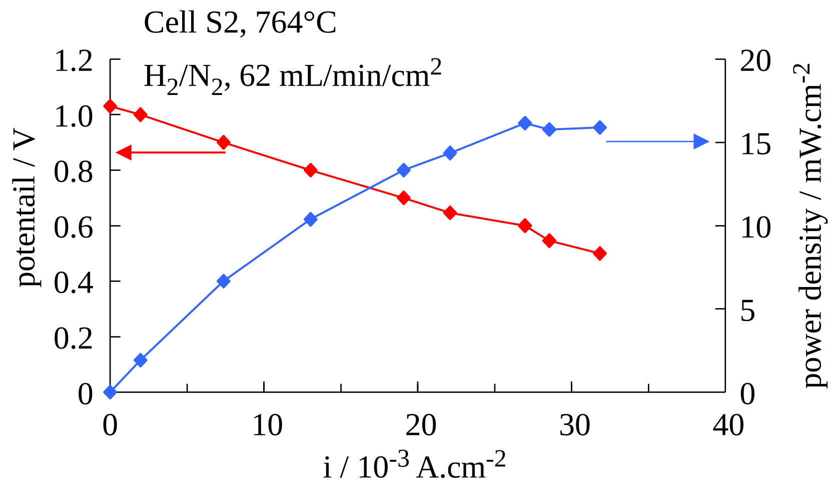
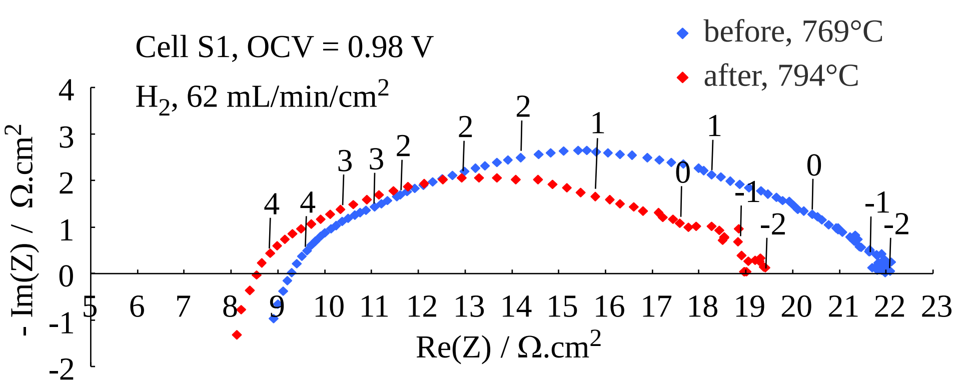
Prototype







⇒ - **stable OCV and polarization curves for 50 hours**

- **10-15 $mW.cm^{-2}$ at 0.7 V in H_2-air**
- **leakage (OCV_{exp} < OCV_{Nernst})**

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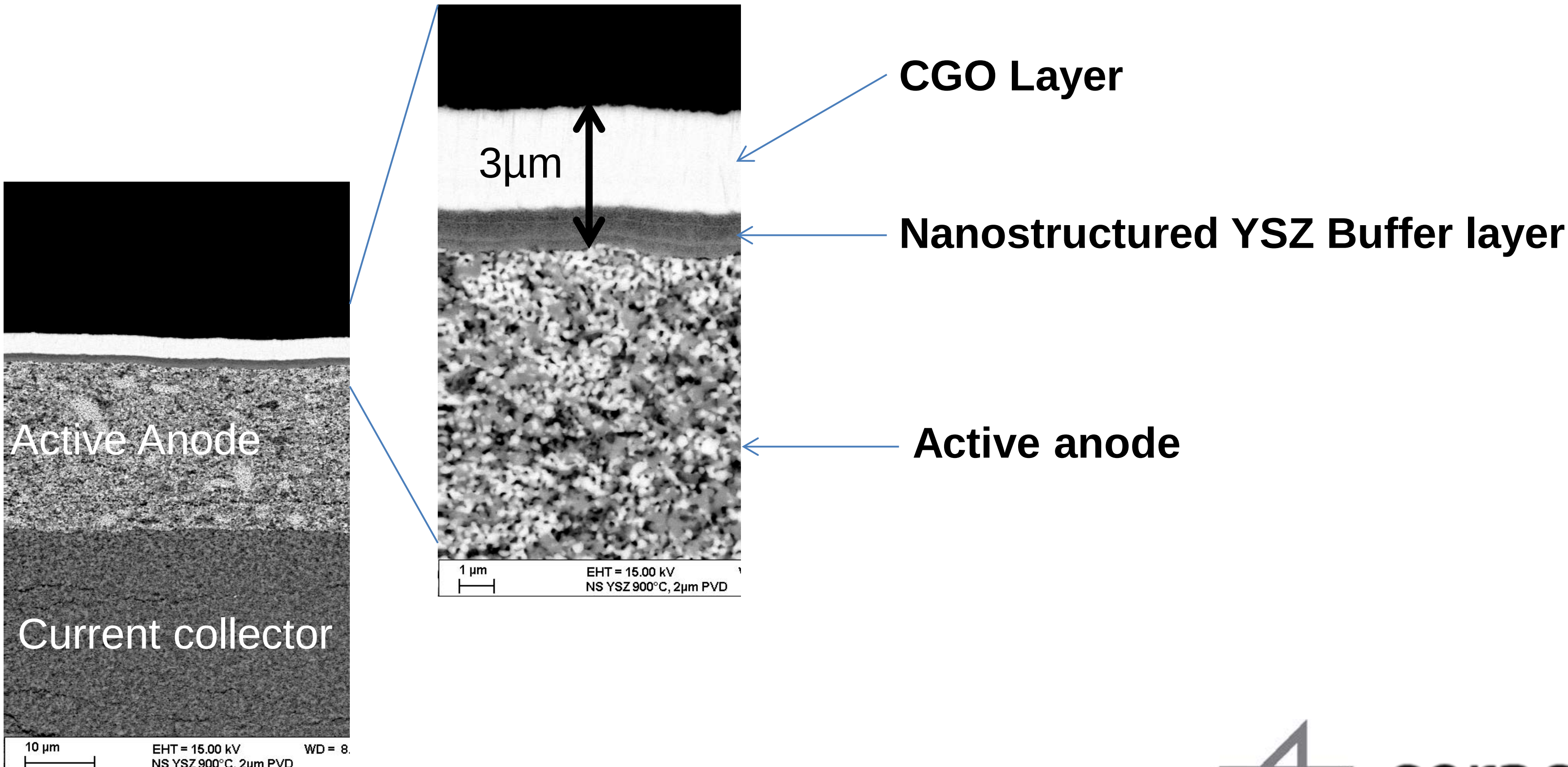
towards thin films electrolyte



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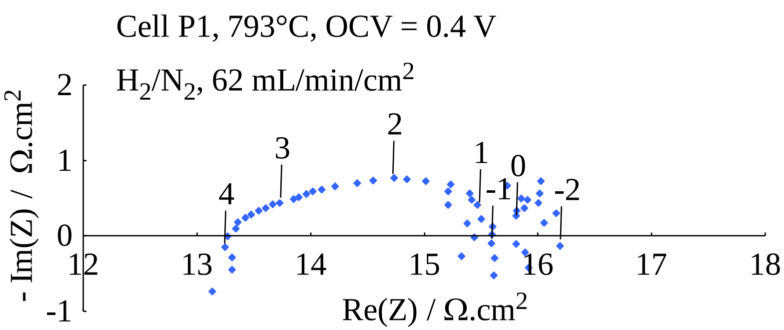
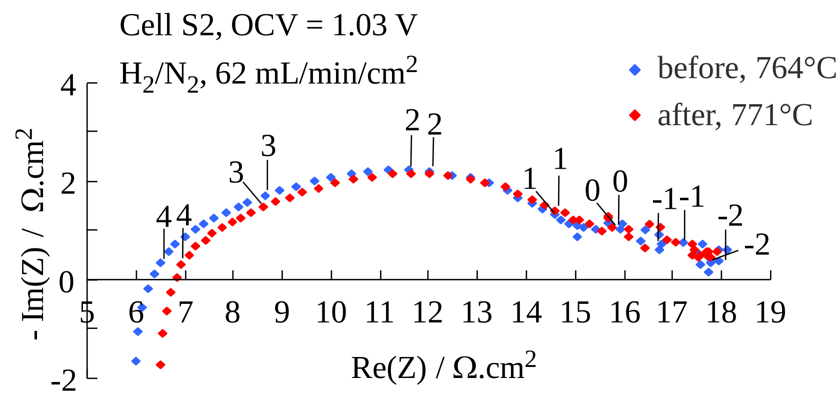
towards thin film electrolytes





Cell P: - **low OCV**

- **no polarization curves**

- **high R_s but low R_{pol}**

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Conclusion & perspectives

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

  Requires high specific surface area
  Requires specific treatment for full activation

- *Reducibility and maximum level of perovskites electrocatalysts needs to be enhanced*

- *Implementation of metals seems necessary to achieve conductivity target in the current collector*

> demonstration up to 100cm² cell of SOC

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Acknowledgement

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New Energy World JU fuel cells & hydrogen for sustainability

F. Han (for coatings), V. Yurkiv (modelling),
G. Schiller,
Prof. K.A. Friedrich,

DLR ALANTUM Innovations in Alloy Foam SAAN ENERGI CerPoTech Ceramic Powder Technology Grenoble INP ARMINES National Research Council of Italy ceraco ceramic coating

Thank you for your attention!