Infiltrated cathode materials for microtubular solid oxide fuel cells

M.A. Laguna-Bercero, H. Monzón, V.M. Orera*
Instituto de Ciencia de Materiales de Aragón (ICMA), Zaragoza, Spain
A.R. Hanifi, J. Cunningham, T. H. Etsell
Department of Chemical & Materials Engineering, University of Alberta, Edmonton, Alberta T6G 2V4, Canada
P. Sarkar
Environment & Carbon Management, Alberta Innovates - Technology Futures, Edmonton, Alberta, T6N 1E4, Canada
orera@unizar.es

Why SOFC?

Siemens-Westinghouse Hybrid Generator

Power: 220kW
SOFC: 200kW, 55%electrical efficiency
Tubular cells
950ºC operation temperature
Stationary applications

ADVANTAGES:

- **Cheap catalysers*** Ni: 0.008 $/g
  Pt: 42.8 $/g
- **Remarkable energetic efficiency**:
  > 60% electrical efficiency. Heat can be used, SOFC+Gas turbine cogeneration system
  > 80% energy efficiency
- **Fuel flexibility**: internal reforming allows the direct use of hydrocarbons: methane or syngas
- **Low pollutant emissions**: High T operation means low NO_x

DISADVANTAGES:

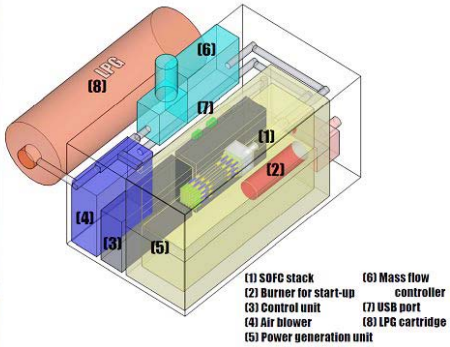
-**High volume and weight**
-High thermal inertia: **long start-up times**
-High temperature operation means ceramics and high temperature metals
-**Aging problems and high cost**

* Market price: July 2013

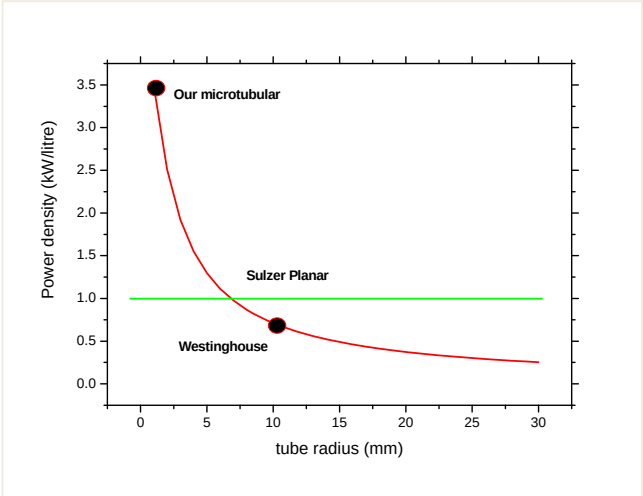
Why microtubular?

Microtubular (< 5 mm diameter)
Portable applications

- ✓ Low T Seals: possibility of using HT silicon
- ✓ High volumetric Power Density 2.5W/cm^3
- ✓ Excellent thermal shock resistance
- ✓ Fast start-up: less than 1 minute
- ✓ Light weight and small volume
- ✓ Life: at least 2000 hours



AIST (Japan)



mT state-of-the-art

Portable applications:
UAVs, batteries

Small devices:
Power range 25 W-2 kW

Acumetrics (USA)

Ultra Electronics AMI (USA)

eZelleron (Germany)

Adelan (UK)

Field test and demonstration

NiO/YSZ support: CIP

Precursor CIP (cold isostatic pressing) fabrication

NiO

YSZ

Conditioning

Powder mixing

Pore former

Acetone

Homogeneization: ultrasonic mixing & mechanical agitation

Anode powder

Binder (PVA)

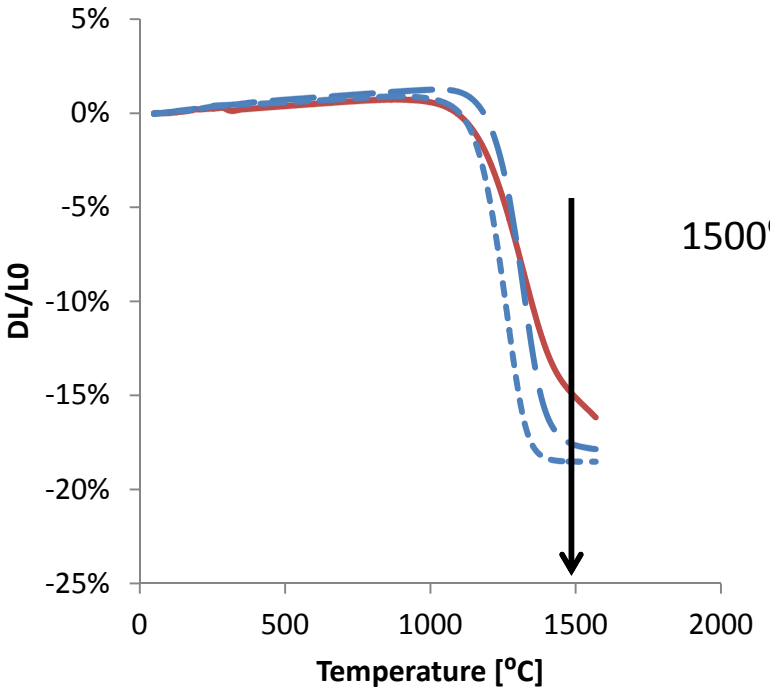
Cold Isostatic Pressing

Pre-sintering

We also fabricate tubes by extrusion, as presented by H. Monzón et al. (keynote presentation)

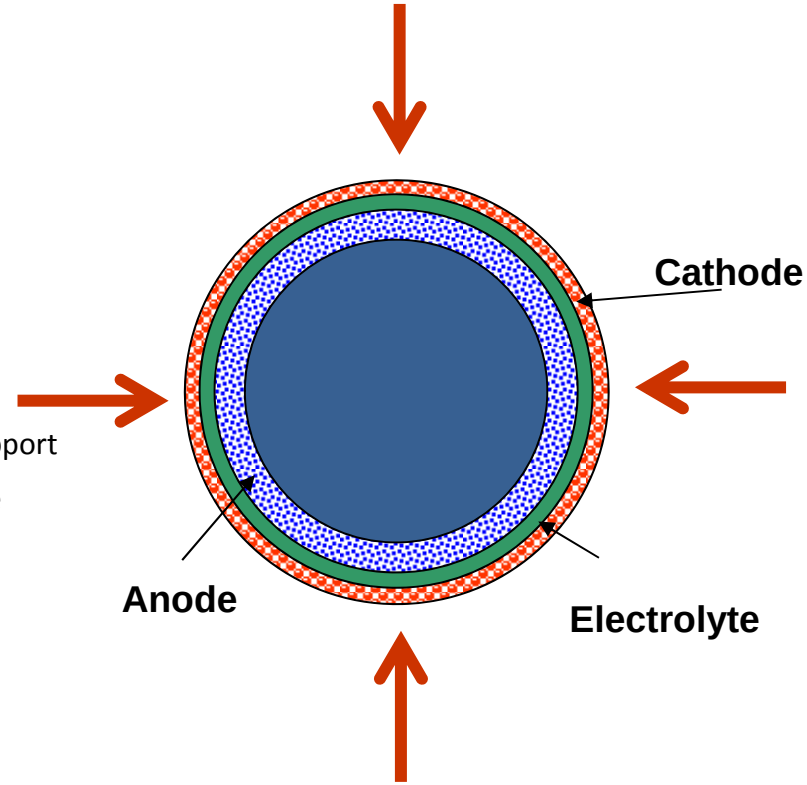
R. Campana et al., J. Power Sources 2009

Electrolyte deposition



1500°

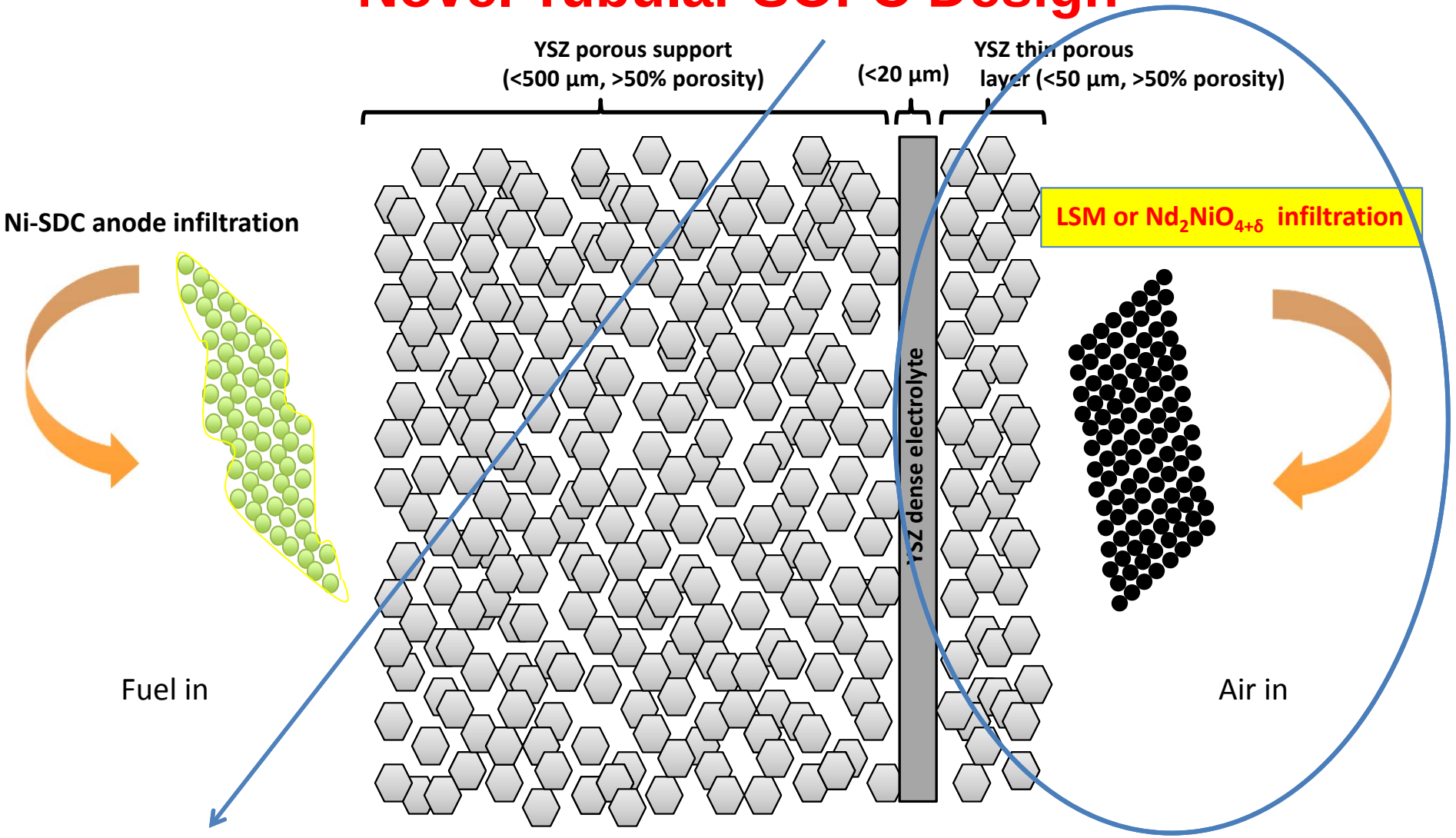
Anode support
YSZ coarse
YSZ fine



Thermal stability of the components not only under operation conditions BUT at sintering temperatures

Infiltration

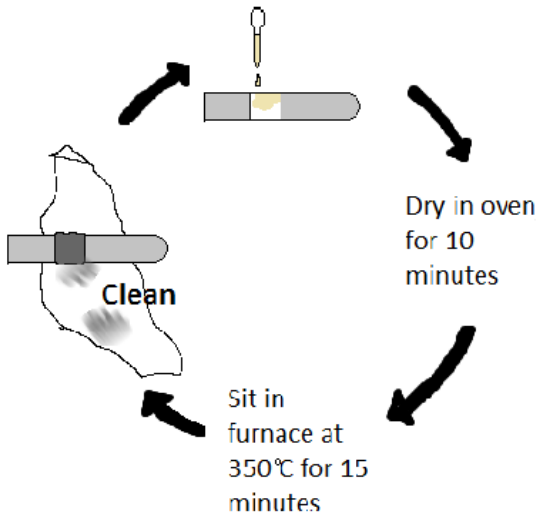
Novel Tubular SOFC Design



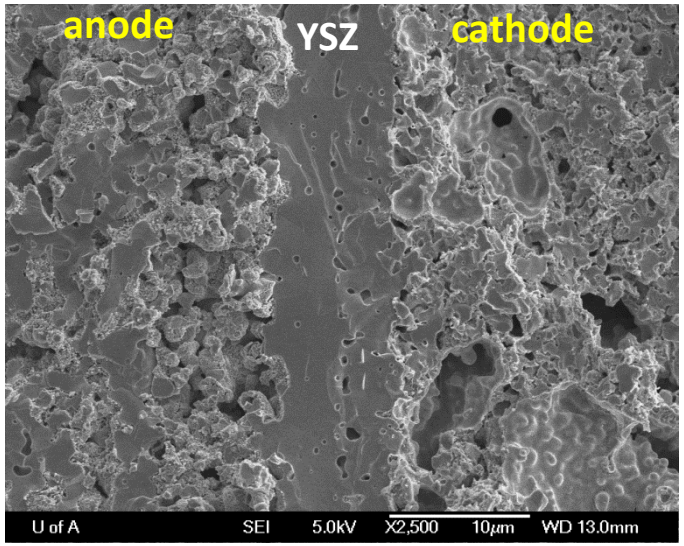
AR Hanifi et al., J Electrochem Soc 2014

Infiltration of LSM

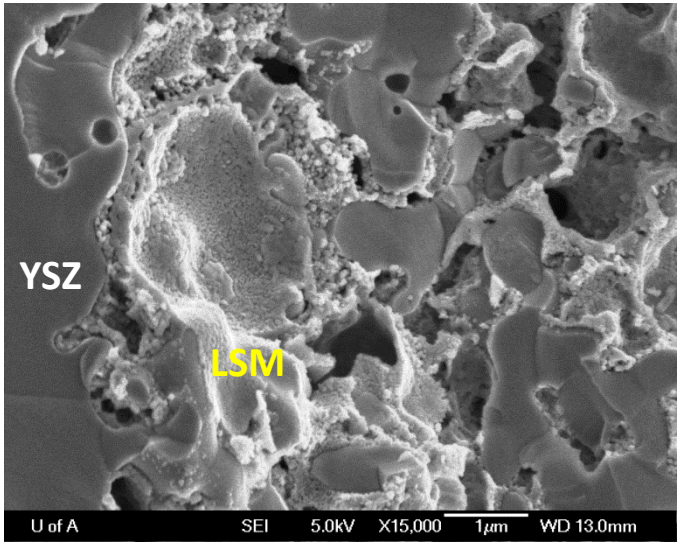
LSM cathode infiltration



LSM ($LaSr_{0.2}Mn_{0.8}O_3$)
• 2.949g lanthanum nitrate
• 0.359 strontium nitrate
• 2.230g manganese nitrate
• 0.3g Triton X-45
• 1.0g deionized water



Interface between infiltrated electrodes and electrolyte



1. A. R. Hanifi, A. Torabi, M. Zazulak, T. H. Etsell, L. Yamarte, P. Sarkar, M. C. Tucker, "Improved Thermal and Redox Cycling Resistant Ceramic Fuel Cells", ECS Transaction, 35 [1], 409-418, 2011.

Experimental setup

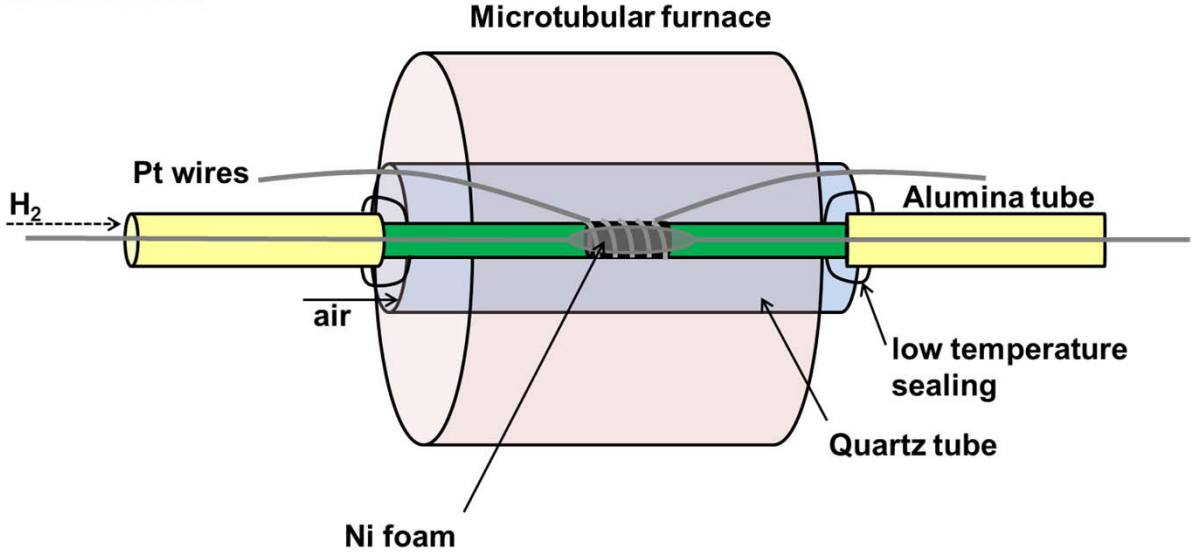
Gas lines: H2, N2, air

Fuel Cell bench:
- Mass flow control
- Humidifiers
- TC control

Heated lines

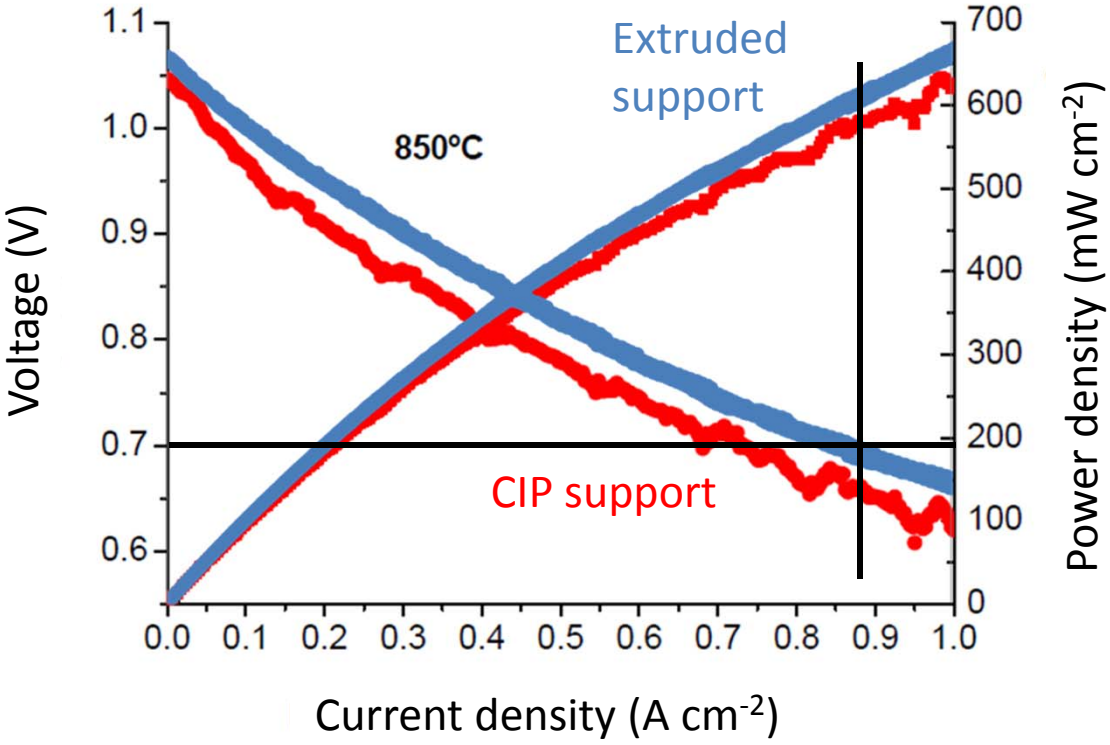
Computer

Potentiostat/Galvanostat/FRA



Electrochemical characterization

Standard cells fabricated at ICMA (LSM/YSZ by dip coating)



Geometry	I (mA/cm² at 0.7V)	Labs
m-tube	800	ours
m-tube	150	Sammes
m-tube	900	Ding & Liu
m-tube	800	Kim et al.
Planar	1160	Basu et al.
Planar	1000	Souza

Competitive power output

T = 850 °C

850-900 mA/cm² at 0.7 V
600-700 mW/cm² at 0.7V

LSM infiltration

Sample code LSM1

TPL: **T**hin **p**orous **l**ayer of YSZ coated on electrolyte for cathode infiltration

Infiltration of LSM × 2 into a thin porous layer

Cell details	Before infiltration	After infiltration
TPL weight gain upon infiltration with LSM (%)	-	23.66
Vol.% YSZ	100	78.05
Vol.% LSM	0	21.95
Open porosity of the TPL	50	39.3

Sample code LSM2

Infiltration of LSM × 4 into a thin porous layer

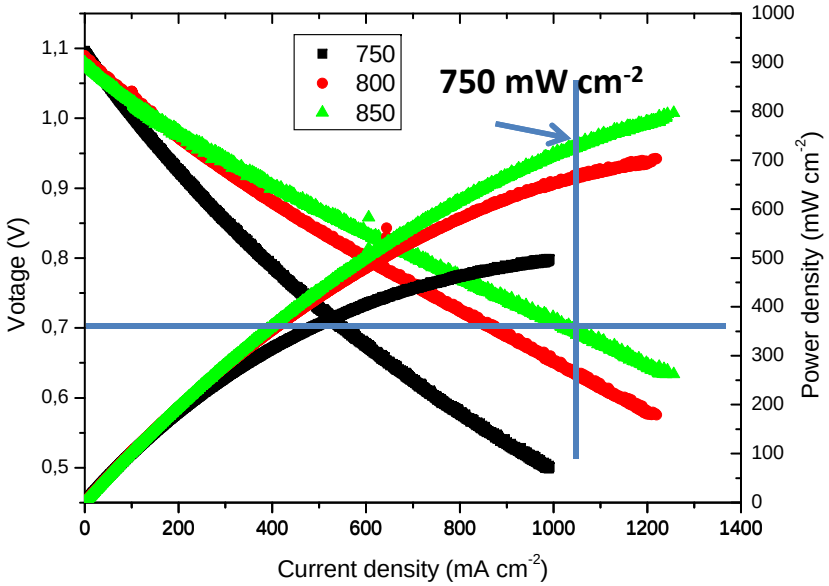
Cell details	Before infiltration	After infiltration
TPL weight gain upon infiltration with LSM (%)	-	37.5
Vol.% YSZ	100	64.74
Vol.% LSM	0	35.26
Open porosity of the TPL	50	33

Note that standard LSM/YSZ cathodes are 50/50 (in vol.%)

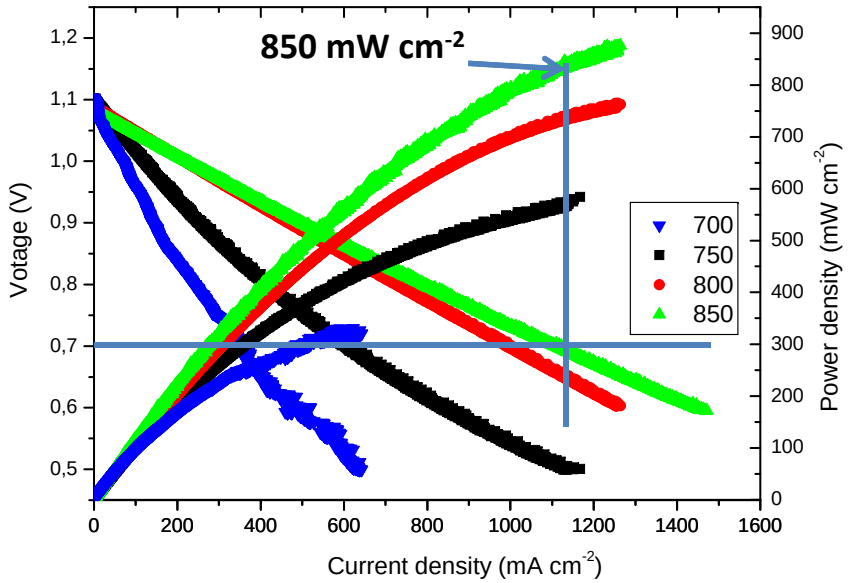
Electrochemical characterization

Novel cells fabricated at ICMA & U. Alberta (LSM infiltration x2 onto porous YSZ)

LSM1 (infiltrated x2)

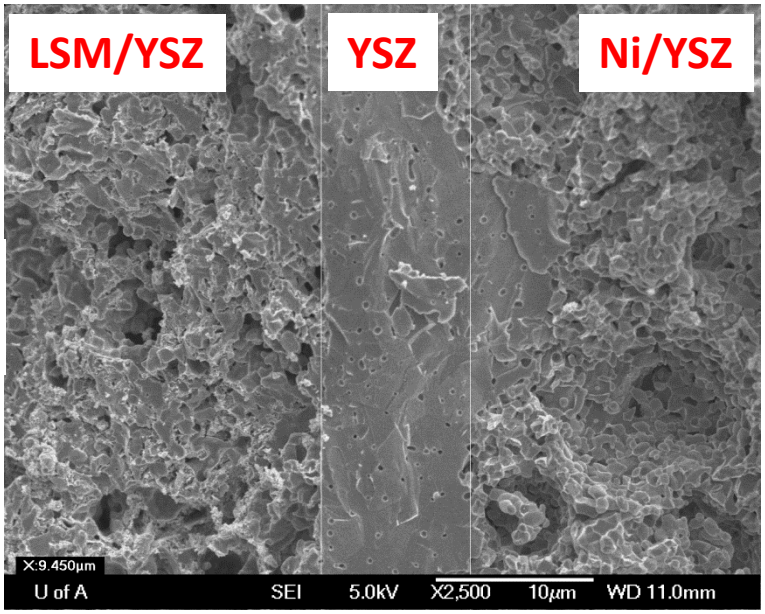


LSM2 (infiltrated x4)

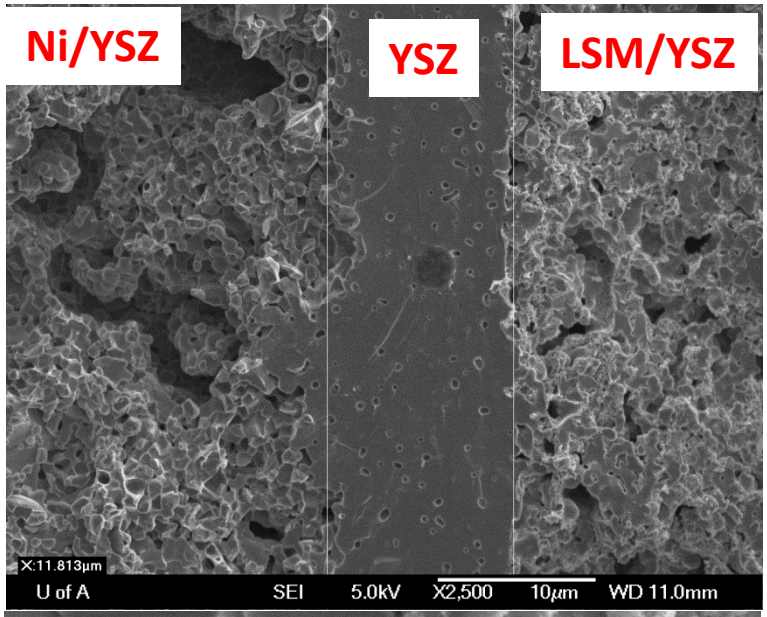


Microstructure

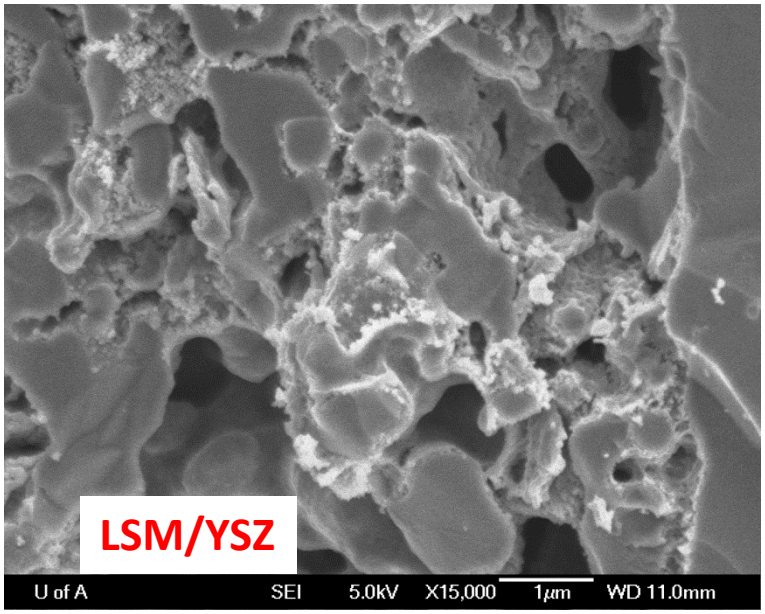
LSM1 (x2)



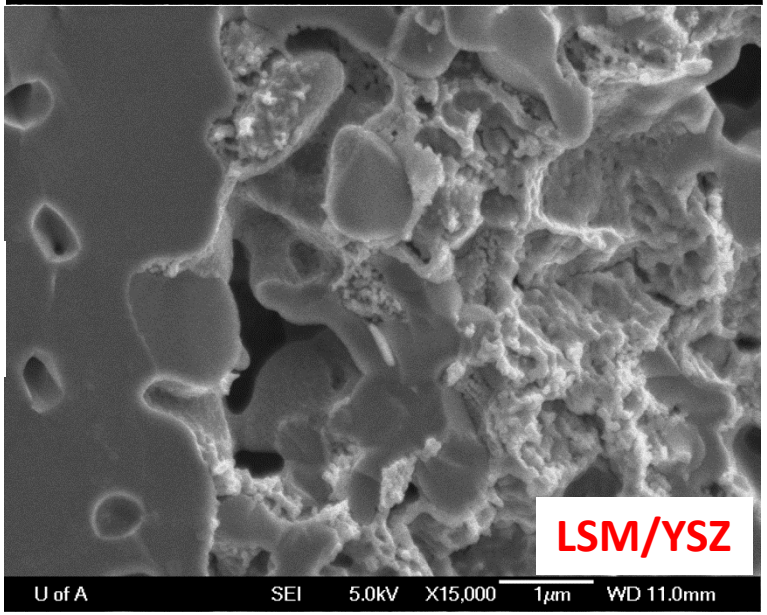
LSM2 (x4)



LSM1 (x2)

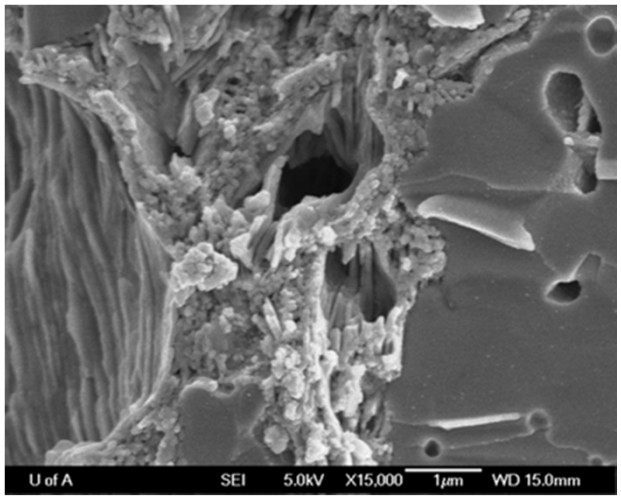


LSM2 (x4)

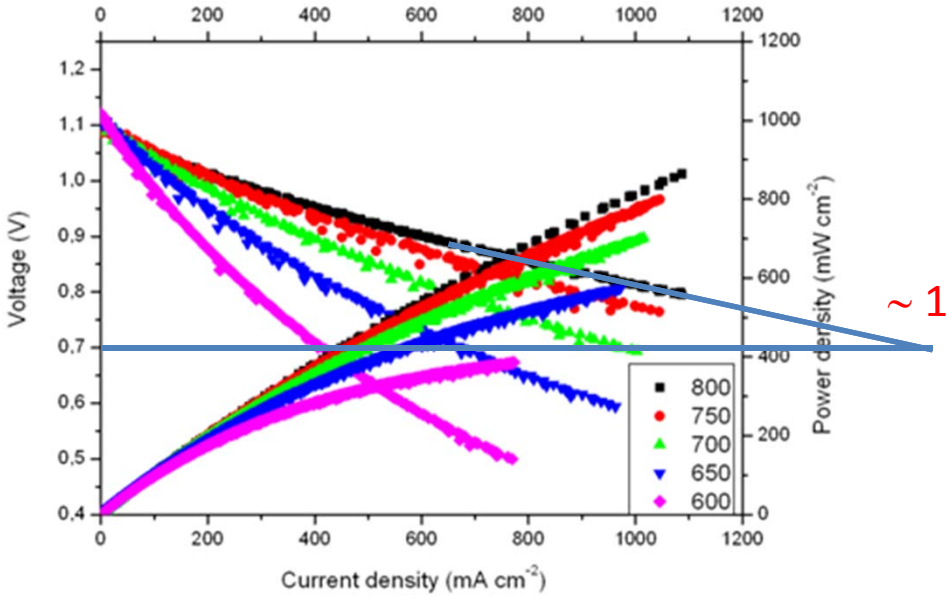


$Nd_2NiO_{4+\delta}$ infiltration

Novel cells fabricated at ICMA & U. Alberta ($Nd_2NiO_{4+\delta}$ onto porous YSZ)



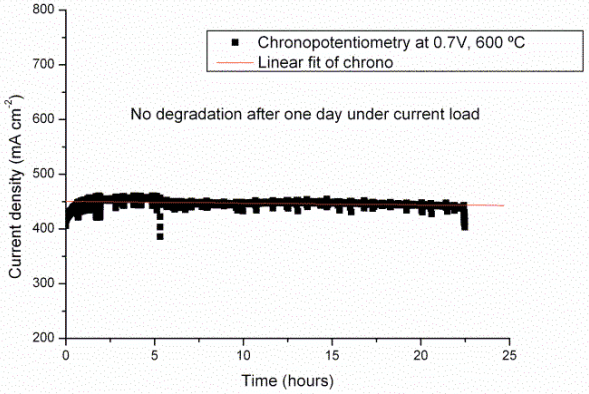
Interface between the YSZ electrolyte and porous YSZ infiltrated with the Nd-nickelate



~ 1 Wcm^{-2}

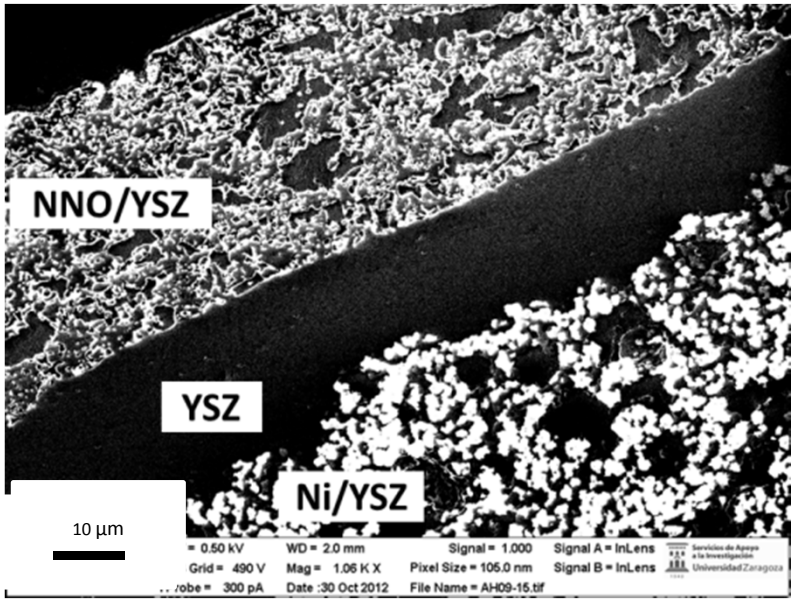
$Nd_2NiO_{4+\delta}$ reacts with YSZ at typical sintering temperatures (above 1000 ºC)

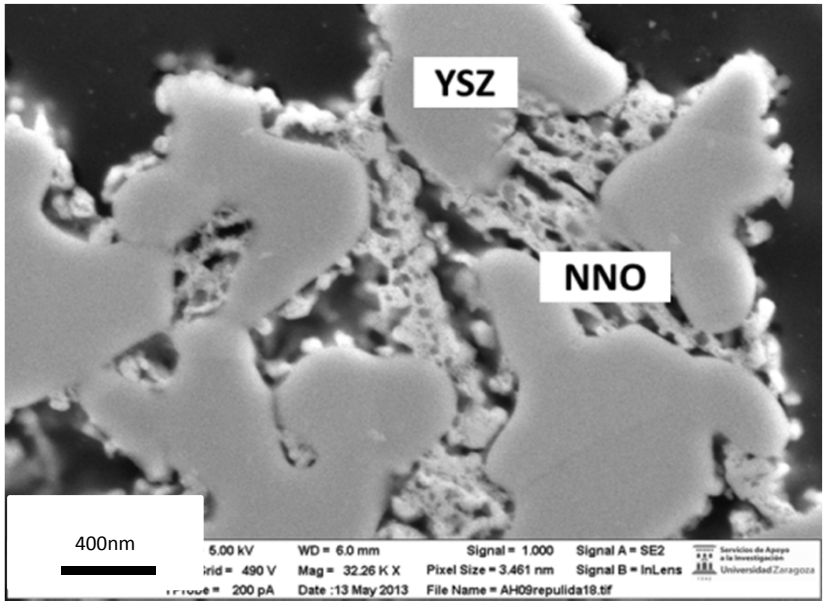
This reactivity is avoided by infiltration (calcination temperatures of 850 ºC)



Laguna-Bercero et al. submitted to J. Mater Chem A

Microstructure





No microstructural evolution after the electrochemical experiments

Laguna-Bercero et al. submitted to J. Mater Chem A

Conclusions

-Anode supported mT-SOFC using LSM/YSZ and $Nd_2NiO_{4+\delta}$ /YSZ cathodes prepared by infiltration were fabricated and characterized.

-Cells with infiltrated cathodes present better performance than analogue cells fabricated by dip-coating, using less amount of the electronic phase.

-At 850 °C and 0.7V:Standard cells (LSM/YSZ/pore 30/30/40): 0.6-0.7 Wcm^{-2}

LSM infiltrated (LSM/YSZ/pore 13.32/52.6/39,3): 0.75 Wcm^{-2}

LSM infiltrated (LSM/YSZ/pore 23.6/43.4/33): 0.85 Wcm^{-2}

(composition in vol%)

$Nd_2NiO_{4+\delta}$ infiltrated: ~ 1 Wcm^{-2}

-Infiltrated LSM and $Nd_2NiO_{4+\delta}$ electrodes seem to be stable after short-term operation conditions