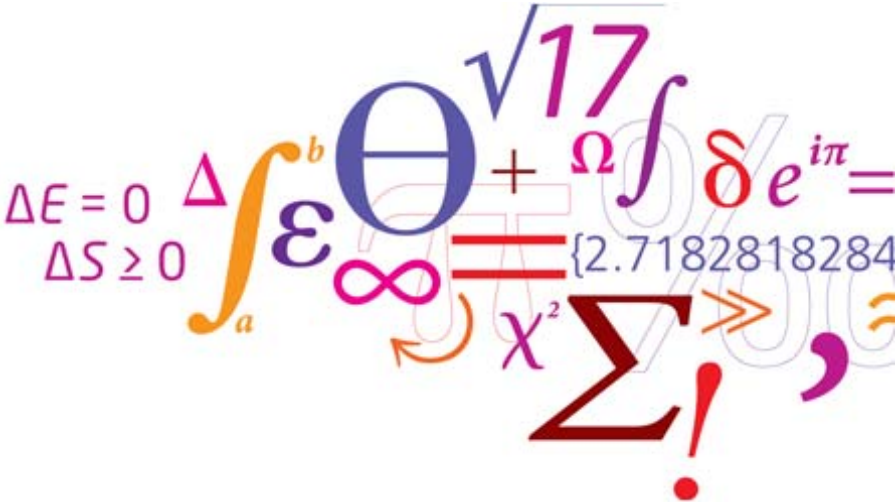
Performance of $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-d}$ and $LaCoO_3$ cathodes deposited by infiltration and spray pyrolysis on $BaCe_{0.2}Zr_{0.7}Y_{0.1}O_{3-d}$

Sandrine Ricote, Nikolaos Bonanos, Per Martin Rørvik, Camilla Haavik, Filip Lenrick, Reine Wallenberg

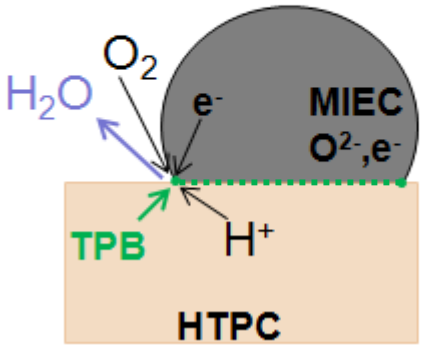


SSPC16, Grenoble
September 14th, 2012

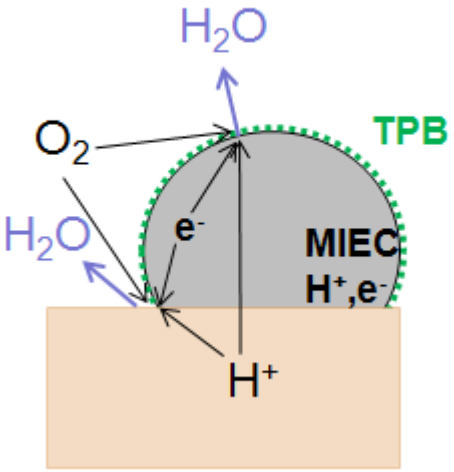
DTU Energy Conversion
Department of Energy Conversion and Storage

Different cathode geometries

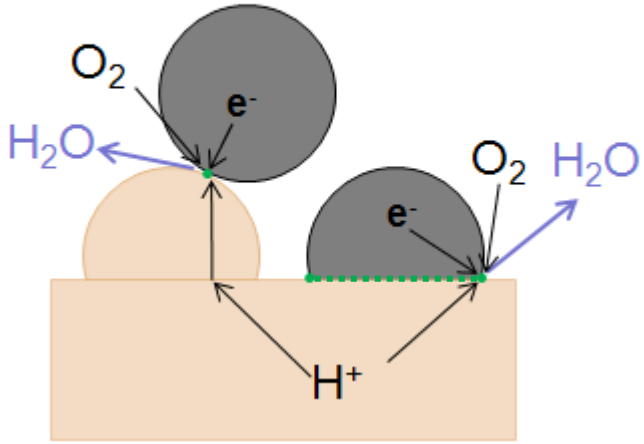
Oxide ion/electron conductor



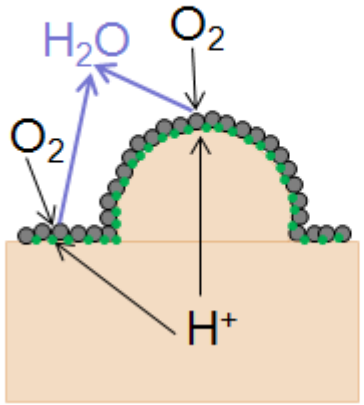
Proton/electron conductor



Composite: Proton conductor/ oxide ion/electron conductor



Infiltrated oxide ion/electron conductor into a proton conductor porous backbone



Part I: LSCF cathode

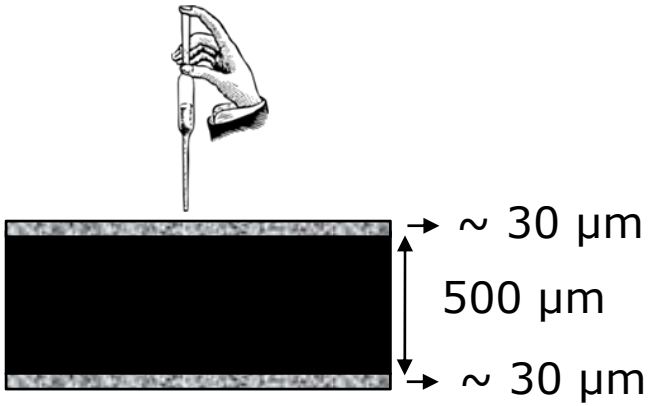
Study of the LSCF cathode on symmetric cells

LSCF cathode: preparation

Study of the LSCF cathode on symmetric cells

Infiltration:

- Preparation of dense BCZY27 ($BaCe_{0.2}Zr_{0.7}Y_{0.1}O_{3-d}$) by solid state reactive sintering
- deposition on porous BCZY27 backbone on both sides by screen printing
- infiltration of LSCF (nitrate solution C=0.04 $mol \cdot L^{-1}$) 12 times
- Calcination 2h at 700ºC in air

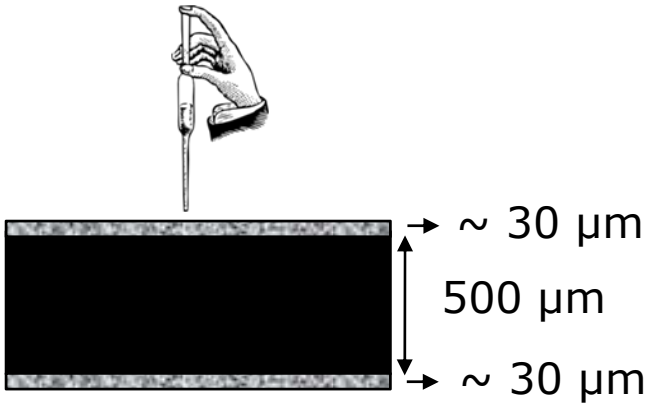


LSCF cathode: preparation

Study of the LSCF cathode on symmetric cells

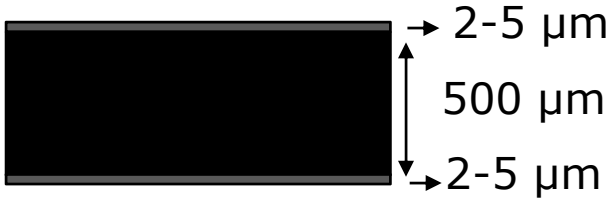
Infiltration:

- Preparation of dense BCZY27 ($BaCe_{0.2}Zr_{0.7}Y_{0.1}O_{3-d}$) by solid state reactive sintering
- deposition on porous BCZY27 backbone on both sides by screen printing
- infiltration of LSCF (nitrate solution C=0.04 mol·L^{-1}) 12 times
- Calcination 2h at 700ºC in air



Spray pyrolysis:

- Preparation of dense BCZY27 by solid state reactive sintering
- LSCF (nitrate solution C=0.04 mol·L^{-1}) spray pyrolyzed on heated BCZY27 (240ºC) substrate for 120 min. Distance airbrush nozzle – substrate: 20 cm.
- Calcination 2h at 700ºC in air



LSCF cathode: preparation

Study of the LSCF cathode on symmetric cells

Infiltration:

- Preparation of dense BCZY27 ($BaCe_{0.2}Zr_{0.7}Y_{0.1}O_{3-d}$) by solid state reactive sintering
- deposition on porous BCZY27 backbone on both sides by screen printing
- infiltration of LSCF (nitrate solution C=0.04 mol·L^{-1}) 12 times
- Calcination 2h at 700ºC in air

Spray pyrolysis:

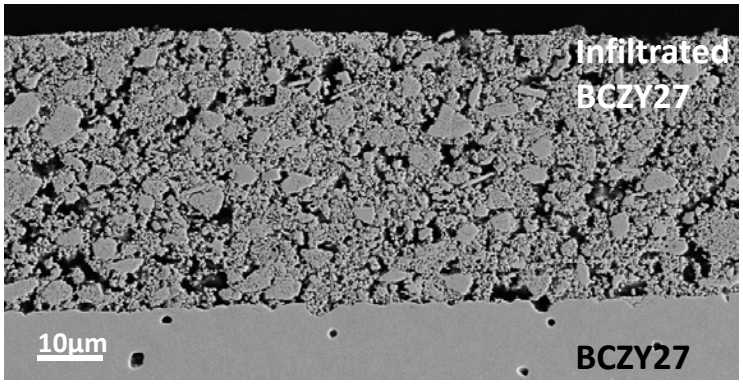
- Preparation of dense BCZY27 by solid state reactive sintering
- LSCF (nitrate solution C=0.04 mol·L^{-1}) spray pyrolyzed on heated BCZY27 (240ºC) substrate for 120 min. Distance airbrush nozzle – substrate: 20 cm.
- Calcination 2h at 700ºC in air

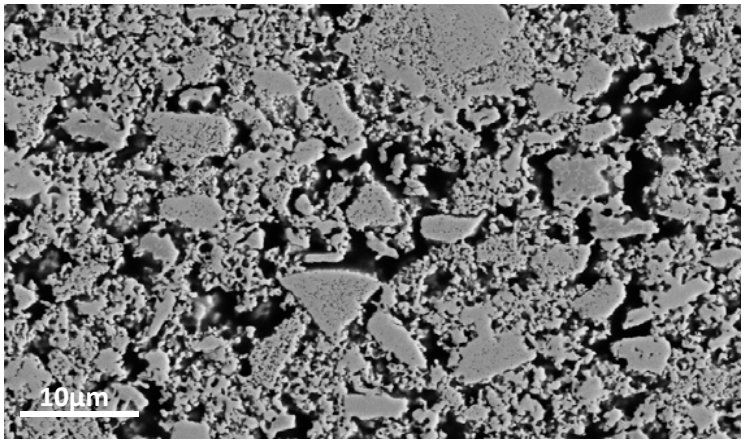
In both cases, single phased LSCF

LSCF cathode: microstructure

Infiltration:

-Thickness cathode: 30-40 microns

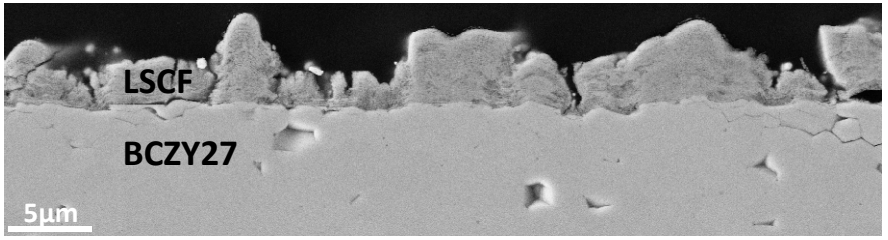


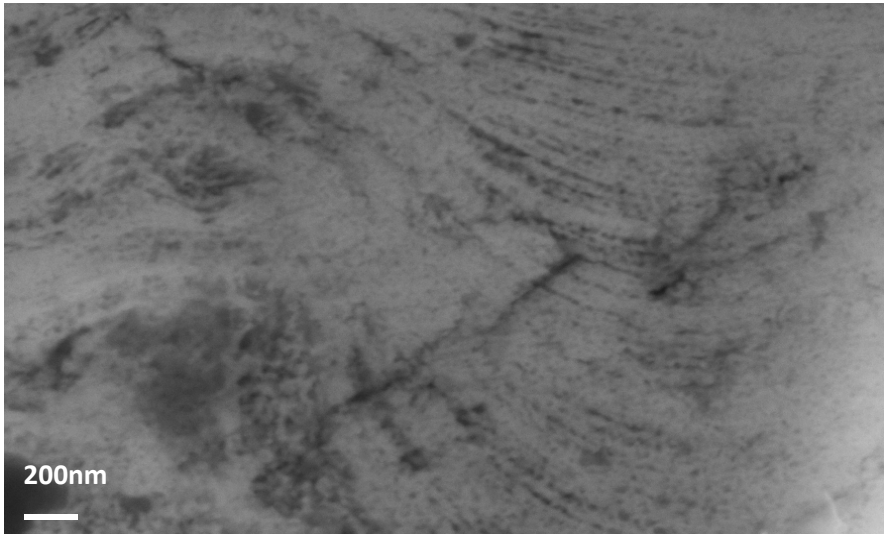


- Porosity: 35 ± 2%
- **Micro-scale pores**

Spray pyrolysis:

- Thickness cathode: 2-5 microns





- Porosity: 37 ± 5%
- **Nano-scale pores**

LSCF cathode: AC spectroscopy

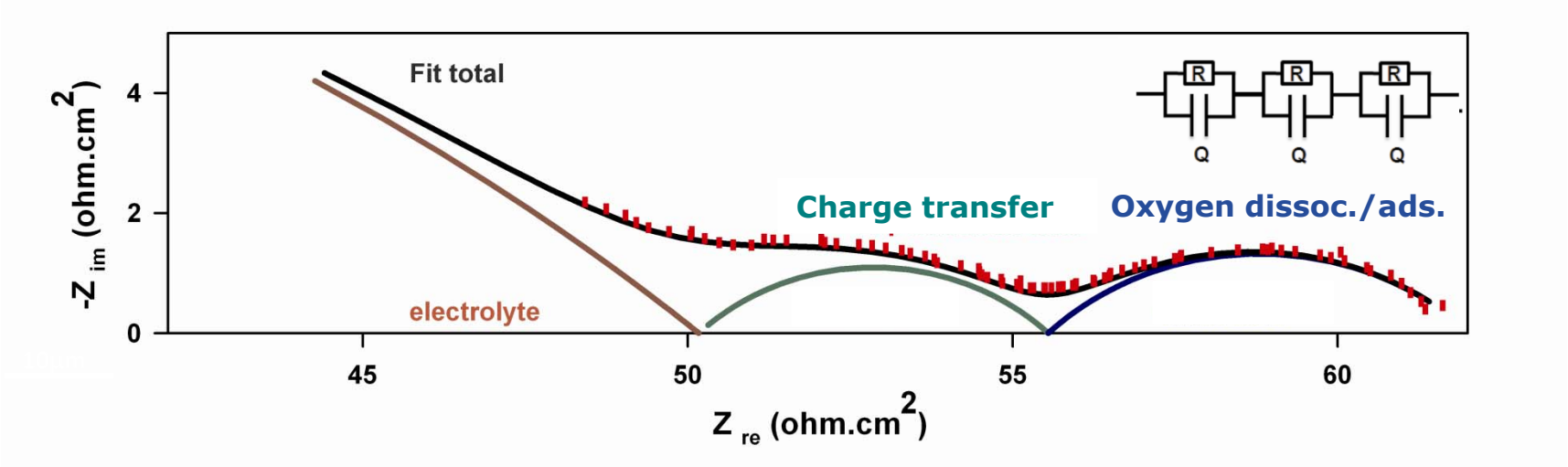
Symmetric cells painted with Au current collectors

Measurement in air, pH_2O=0.001 atm from 450 to 600ºC.

Spectra fitted with (RQ)(RQ)(RQ)

2 cathode components:

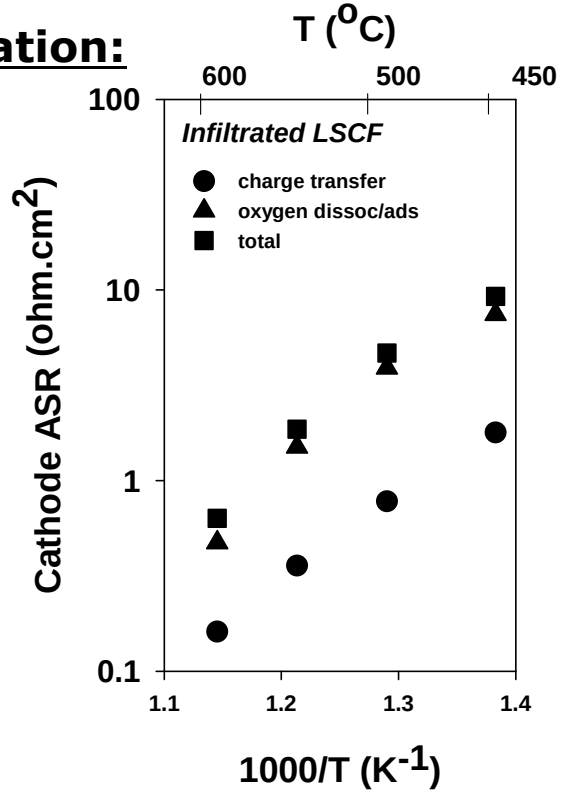
- Middle range frequency: charge transfer
- Low frequency: oxygen dissociation/adsorption



Spectrum on infiltrated cell, air, pH_2O=0.001 atm at 500ºC

LSCF cathode: AC spectroscopy

Infiltration:

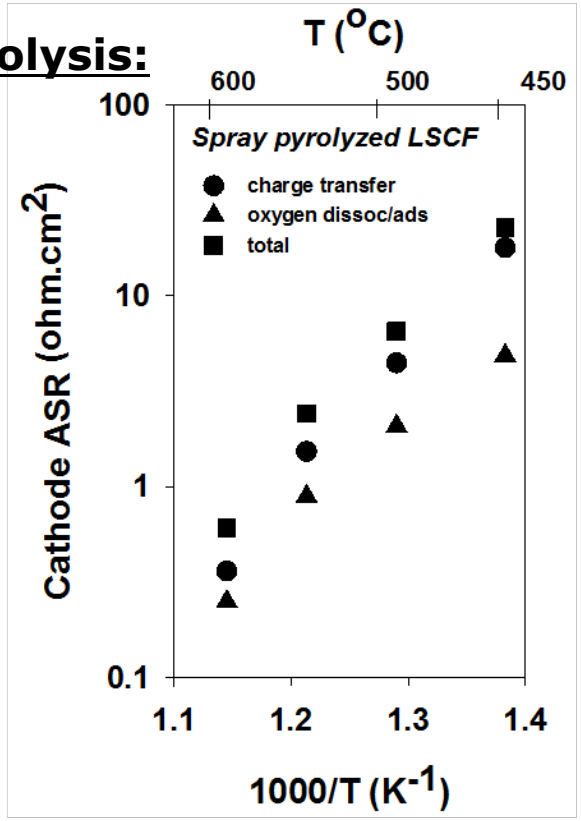


- Limited by oxygen ads./dissoc.

ASR 600ºC air, pH_2O=0.001atm:

Rp = 0.63 Ω·cm²

Spray pyrolysis:



- Limited by charge transfer

ASR 600ºC air, pH_2O=0.001atm:

Rp = 0.61 Ω·cm²

Performance of the cathode: highly dependent on the microstructure

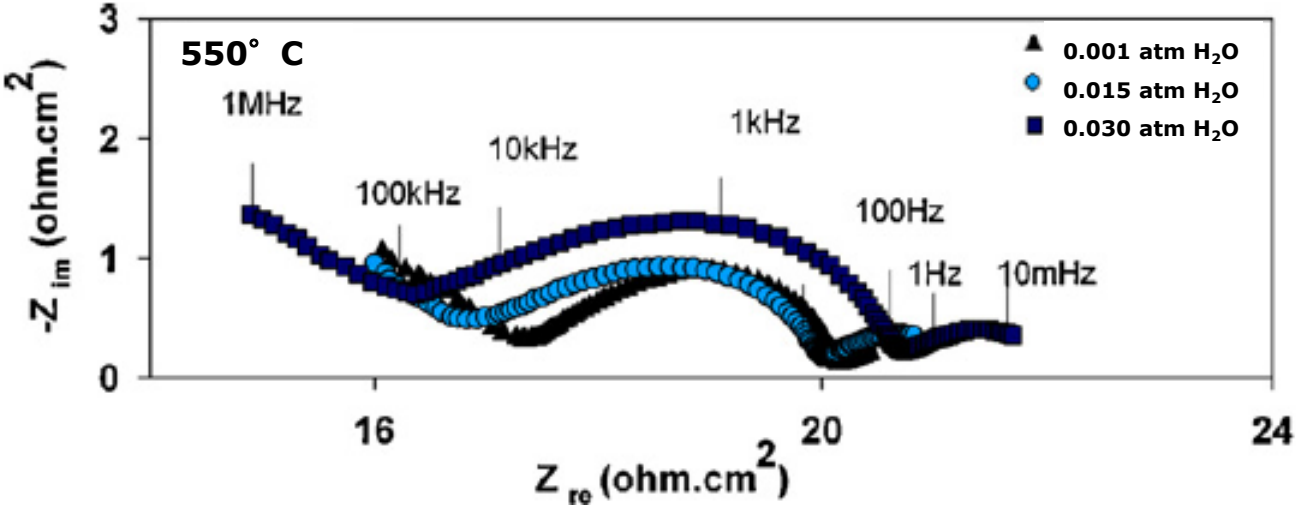
Lowest values reported for LSCF

LSCF cathode: AC spectroscopy

Increase of the ASR when increasing the water vapor pressure.

➔

A



	n
	0
	0
	0
	0
	1/2
	1/2
	1
	1

Grimaud [3] studied LSCF, BSCF, $Pr_2NiO_{4+\delta}$ and $PrBaCo_2O_{5+\delta}$ (PrBCo)

BSCF, $Pr_2NiO_{4+\delta}$,PrBCo: proton incorporation and decrease of ASR with increasing pH_2O

LSCF: no proton incorporation and increase of ASR with increasing pH_2O

Active sites limited to the TPBs at the interface cathode/electrolyte.

➔ Increase of ASR with increasing pH_2O for LSCF has its origin at the TPBs.

1 F. He, T. Wu, R. Peng, C. Xia, J. Power Sources, 2009, 194, 263–268.
2 R. Peng, T. Wu, W. Liu, G. Meng, J. Mater. Chem., 2010, 20,6218-6225
3 A. Grimaud, PhD thesis, Université de Bordeaux, ICMCB-CNRS, 2011.

Part II: $LaCoO_3$ cathode

Study of the LC cathode on symmetric cells

$LaCoO_3$ cathode preparation:

- $LaCoO_3$: preparation of a 1 mol·L^{-1} solution ➔ High loading
- No carbonate formation (which can happen with Sr)
- Pure electronic conductor ~660 S·cm^{-1} at 600ºC

Is oxide ion conduction necessary in the cathode of PCFC?

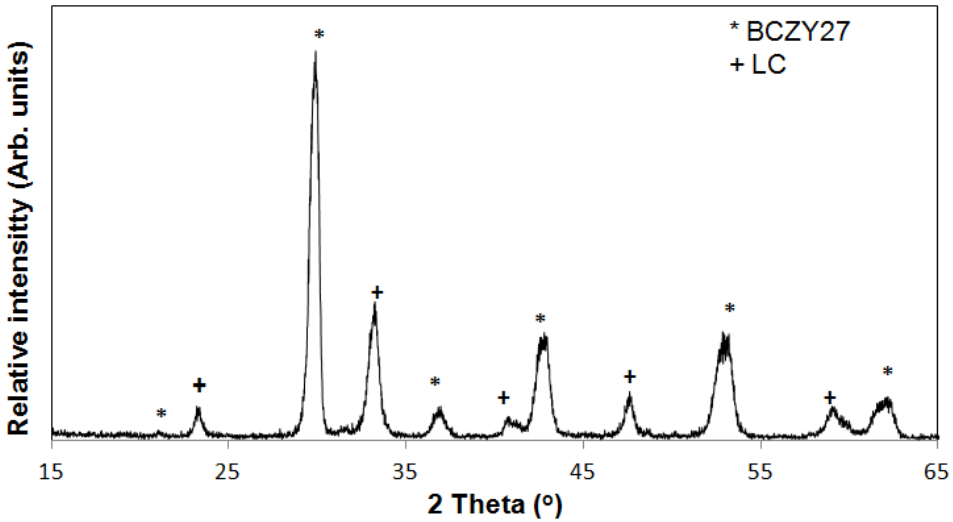
$LaCoO_3$ used as an infiltrate in CGO backbone in SOCF:0.079 Ω·cm^2 at 600ºC [4]

Symmetrical cells prepared in a similar way as LSCF infiltrated ones:

6 infiltrations of 1 mol·L^{-1} solution

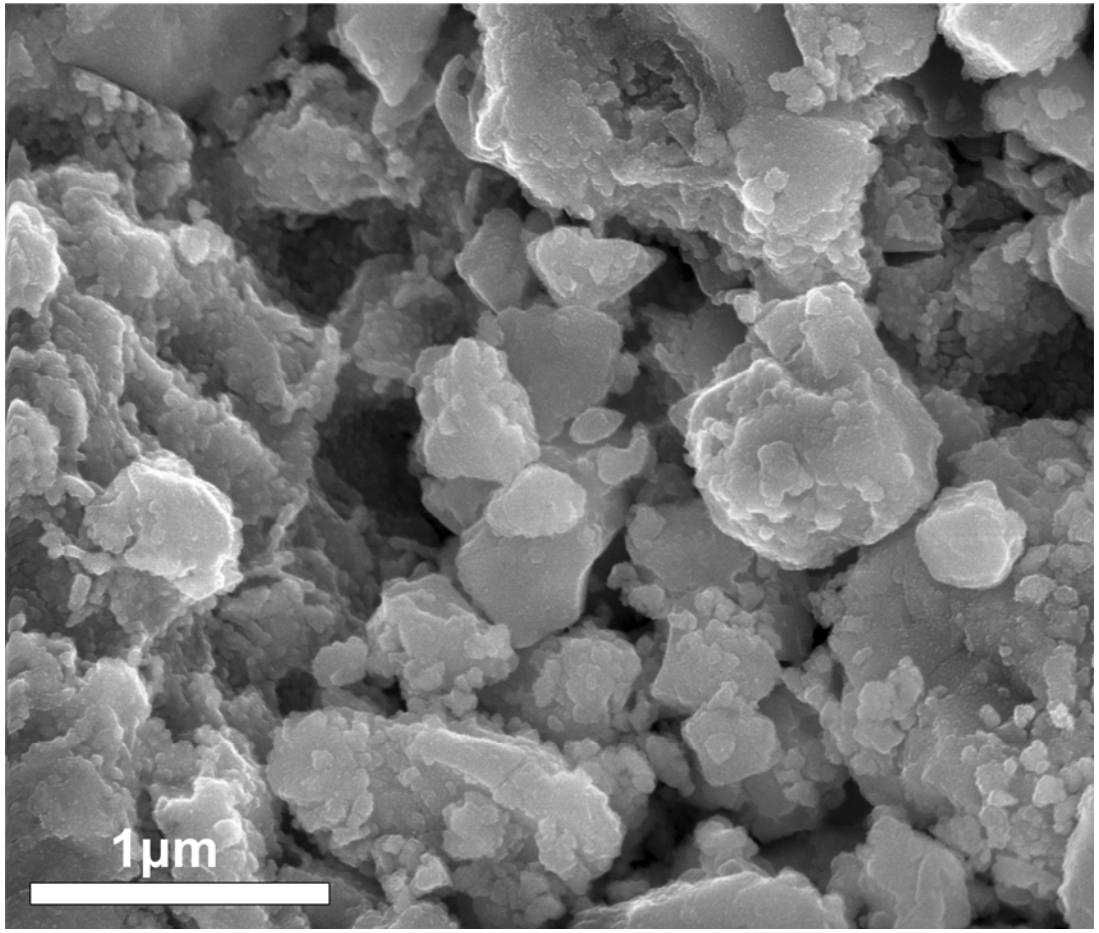
Calcination 2 h at 600ºC

Single phased $LaCoO_3$



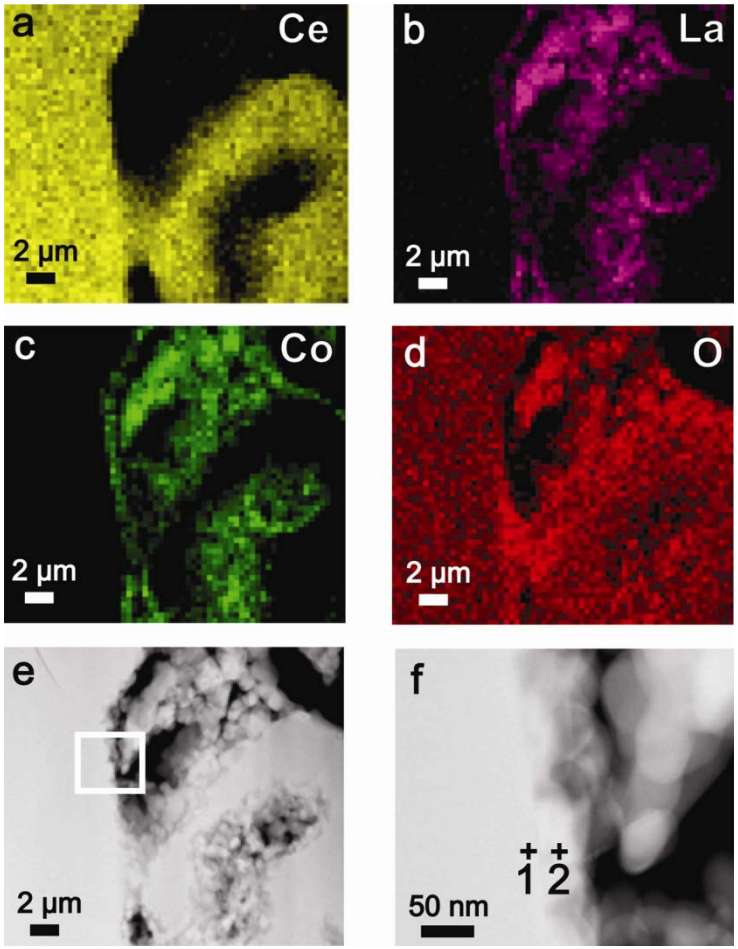
[4] *A.J. Samson, M. Søgaard, N. Bonanos, Electroch.and Solid State Letters 15 (4) (2012) B1*

$LaCoO_3$ cathode: microstructure



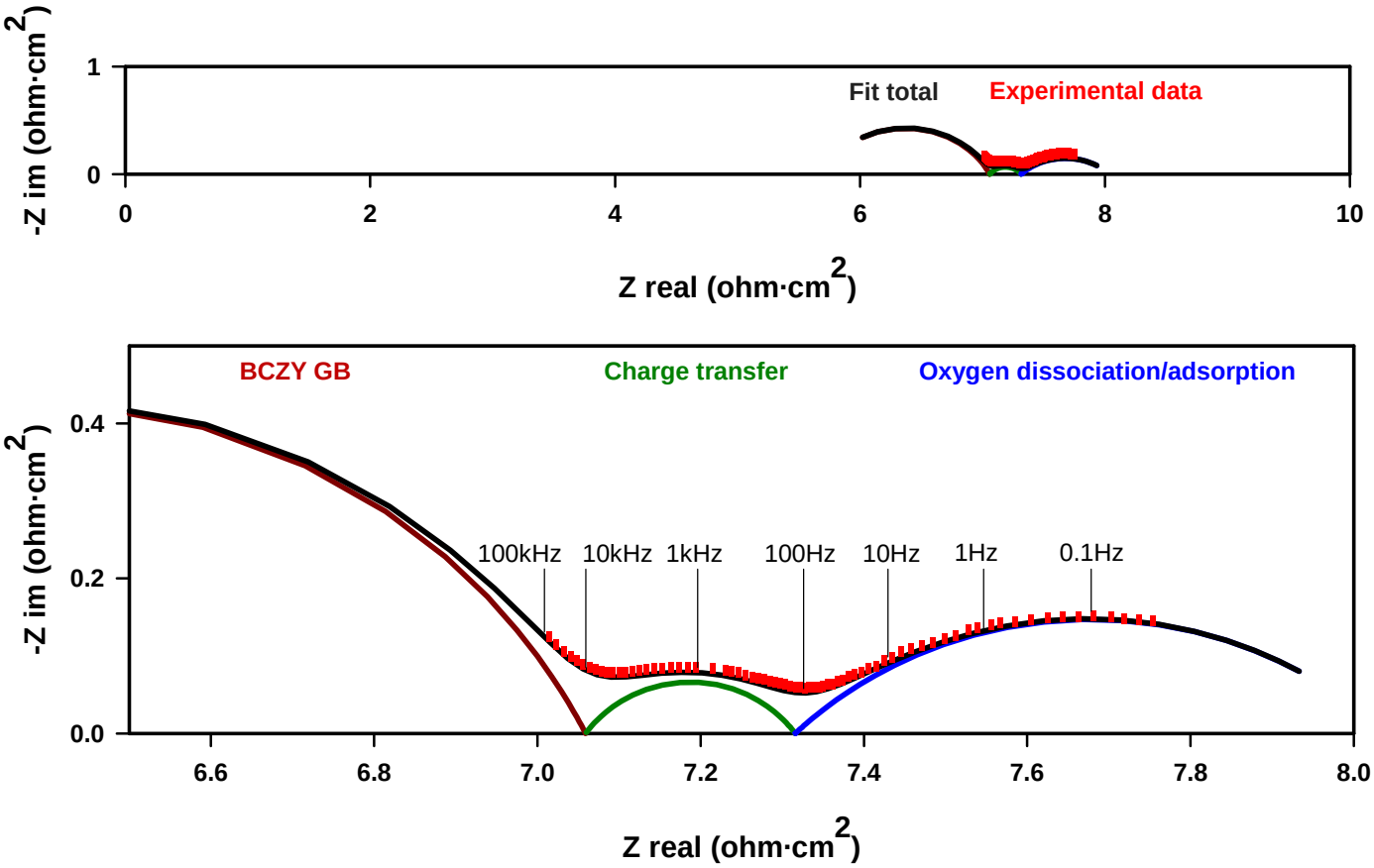
The BCZY27 grains (200-500nm) are covered with much smaller grains (estimated to 60 – 80 nm by TEM)

$LaCoO_3$ cathode: microstructure



La and Co are only present in the cathode depth

$LaCoO_3$ cathode: AC spectra



Spectrum in air, pH_2O=0.010 atm at 500ºC

Rp=0.11 and 0.39 Ω·cm² at 600 and 500ºC in air, pH_2O=0.01 atm

Lowest values reported so far

Conclusions:

Spray pyrolysis and **infiltration** of the cathode material in a proton conducting oxide backbone: **good low temperature methods for cathode preparation:**

Nano particles: increase of the number of TPBs.

Cathode performance highly dependent on microstructure:

LSCF infiltrated and spray pyrolysed: similar ASR (**0.63 and 0.61 Ω·cm^2,air 600°C**)

But limited respectively by oxygen ads./dissoc. and charge transfer.

ASR $LaCoO_3$ infiltrated cathode in air pH_2O=0.01atm

0.11 and 0.39 Ω·cm^2 at 600 and 500°C

Oxygen conduction is not necessary for the cathode process in a PCFC

when infiltrating the cathode material

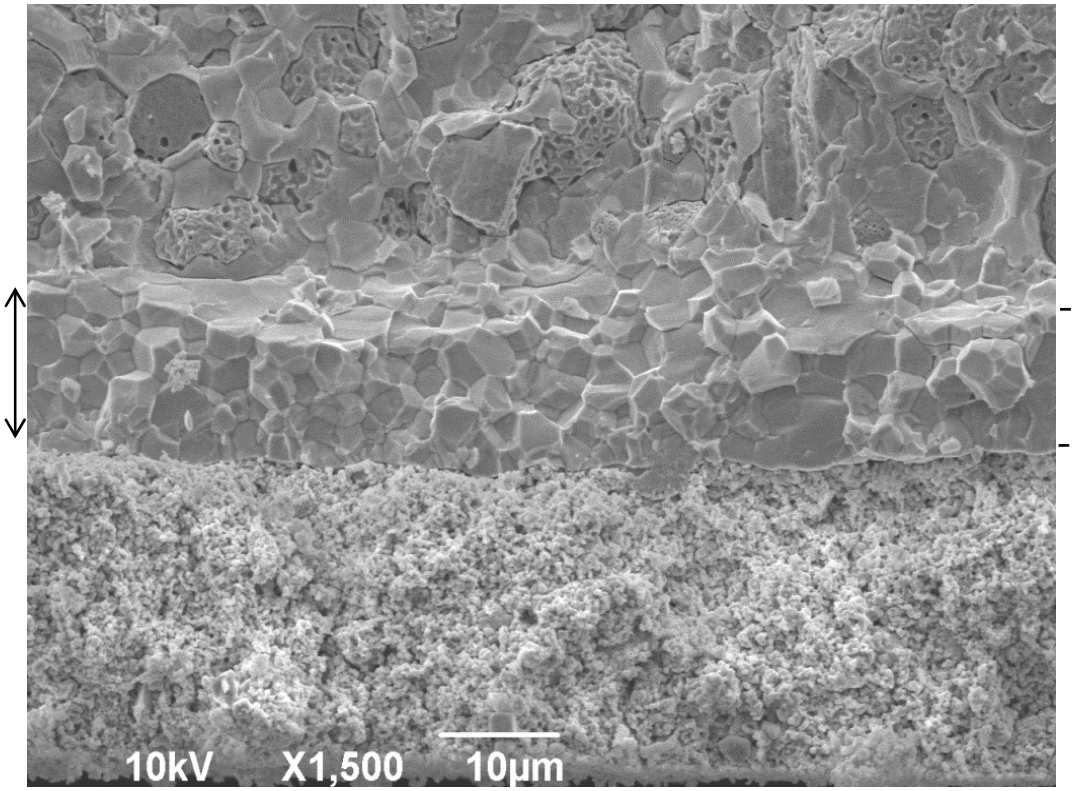
Future work:

LC infiltrated BCZY27 cathode will be tested in a full cell configuration

- 65% NiO/BCZY27 anode (300 microns)
- Thin BCZY27 film (1wt% NiO as sintering aid)

} from CoorsTek

Both on planar and tubular cells



10-12 microns

Anode

Electrolyte

Cathode

Thank you for your attention

Funding: nextgenFCmat project (*Next generation fuel cell materials)*