Electrochemical and degradation behaviour study of different SOFC compounds

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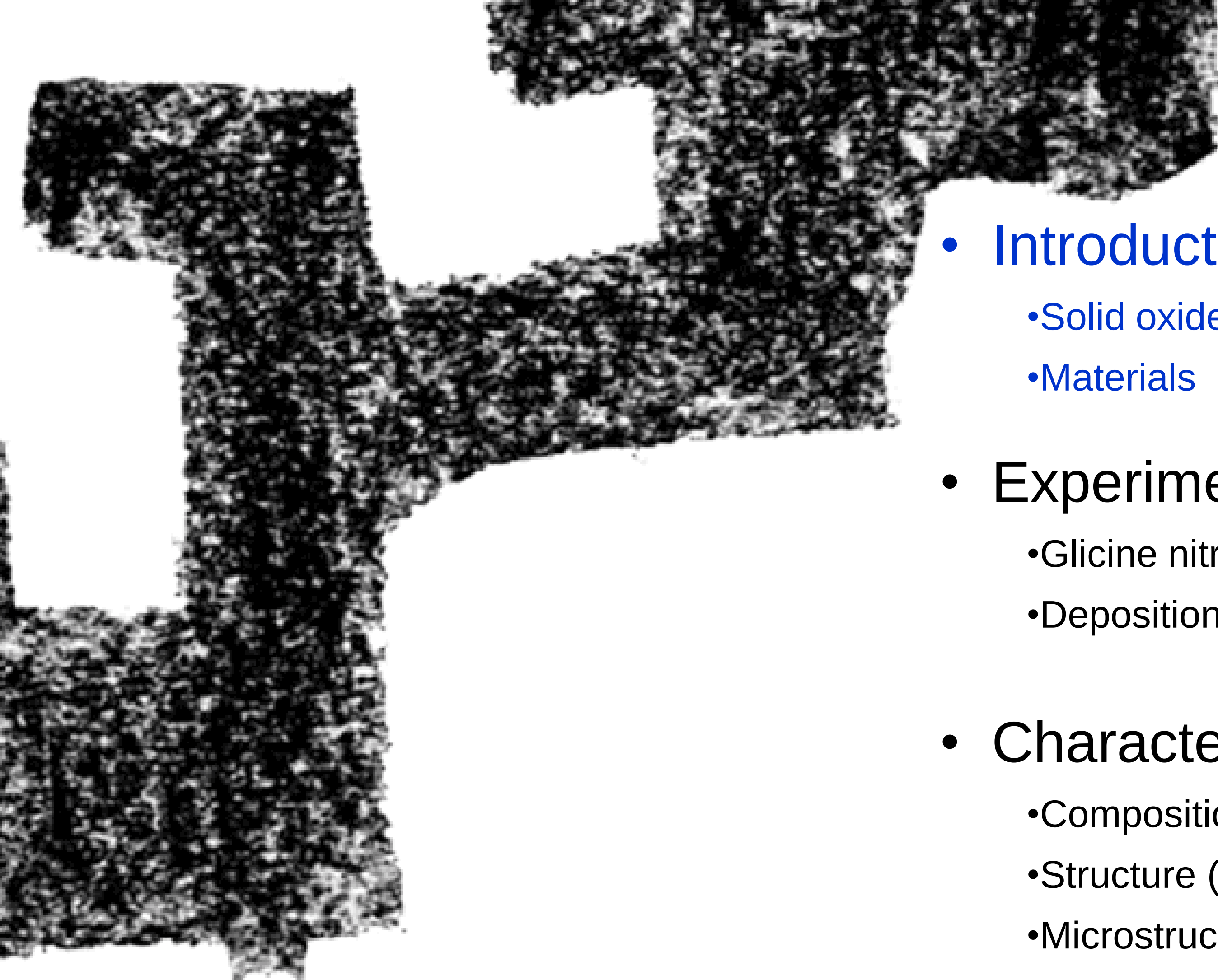
[4] Basque Center for Materials, Applications & Nanostructures (BCMaterials), 48160 Derio, Spain.



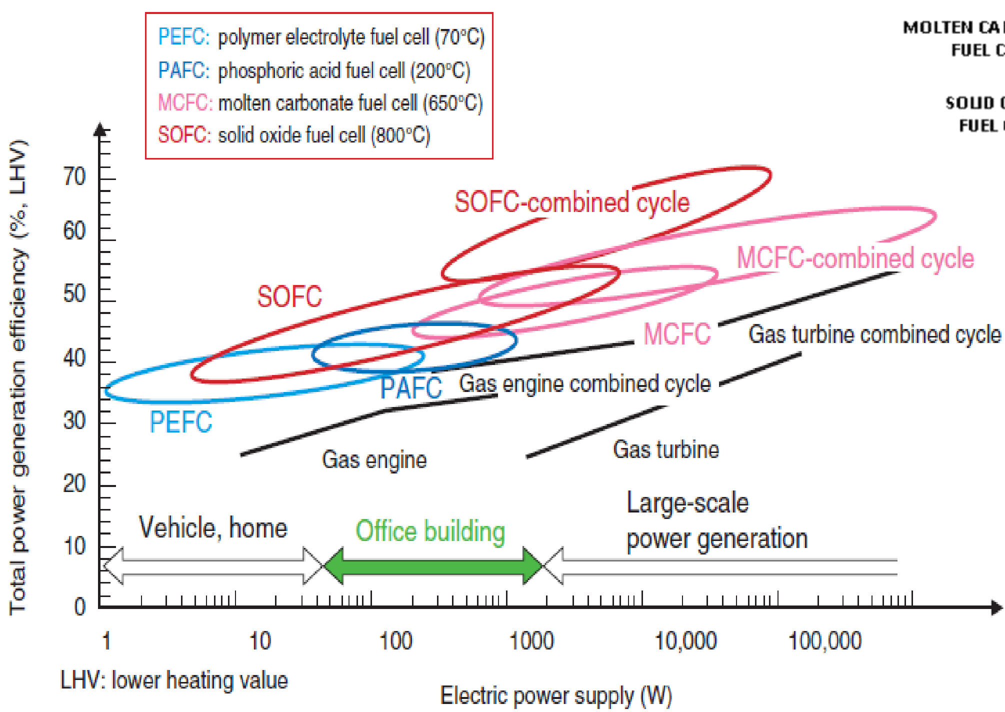
Contents:

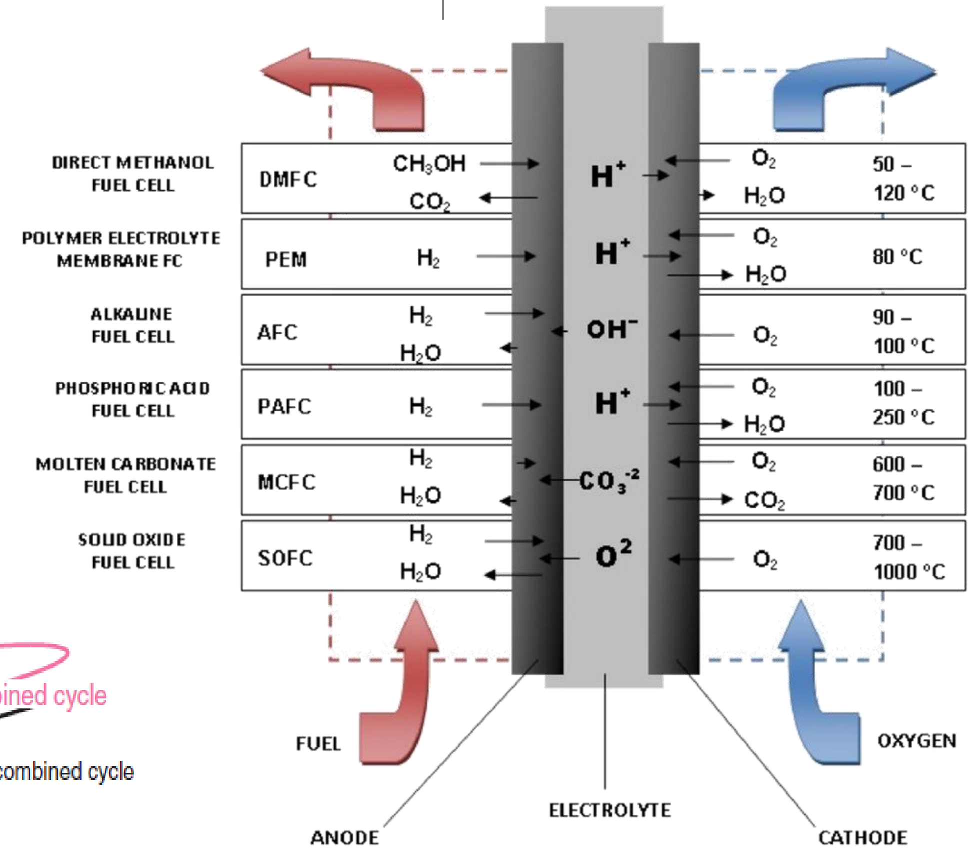
- Introduction
  - Solid oxide fuel cells
  - Materials
- Experimental preparation
  - Glicine nitrate combustion process
  - Deposition process
- Characterization
  - Composition (ICP and XRF)
  - Structure (X-ray)
  - Microstructure (SEM)
  - Degradation test
  - Conductivity
- Conclusions
- Acknowledgments

Fuel Cells

Introduction

• A Fuel Cell is an energy conversion device based on electrochemical cells that directly convert the chemical energy in electrical energy and heat.





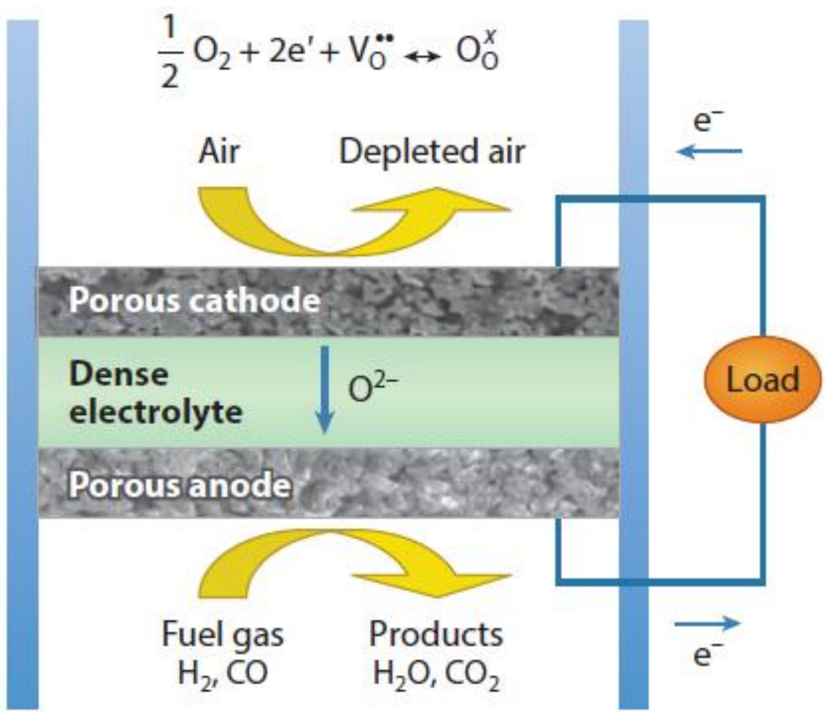
• High electrical efficiency.
• Low environmental impact.
• High fuel flexibility.
• Silent.
• Modulable.

Steele B.C.H., Heinzel A., Nature, 414 (2001) 345-3529.
http://www.fuelcells.org/base.cgim?template=types_of_fuel_cells.

Solid Oxide Fuel Cells

SOFC operation principle scheme

Is one of the most promising system for direct chemical energy into electrical energy conversion, maintaining a high overall efficiency.



Reactions that occur depending on the fuel used:

Anode

$$H_2 + O^{2-} \rightarrow H_2O + 2e^-$$

$$CO + O^{2-} \rightarrow CO_2 + 2e^-$$

$$CH_4 + 4O^{2-} \rightarrow 2H_2O + CO_2 + 2e^-$$

Cathode

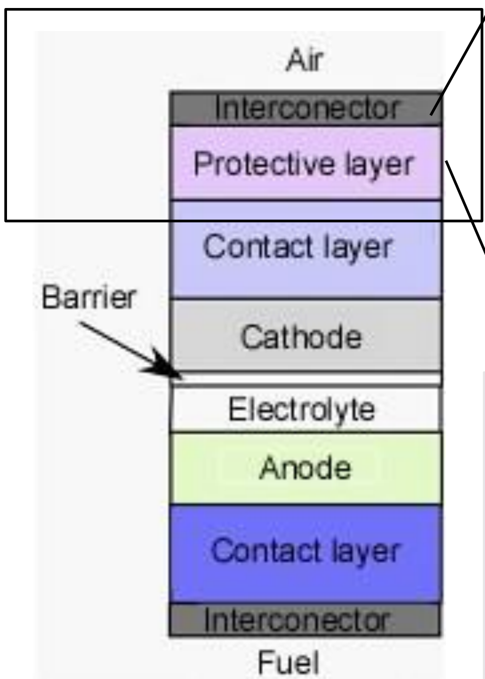
$$O_2 + 4e^- \rightarrow 2O^{2-}$$

Mirzababaei J., Chuang S.S.C., Catalyst, 4 (2014) 146-161.

Studies of SOFC materials

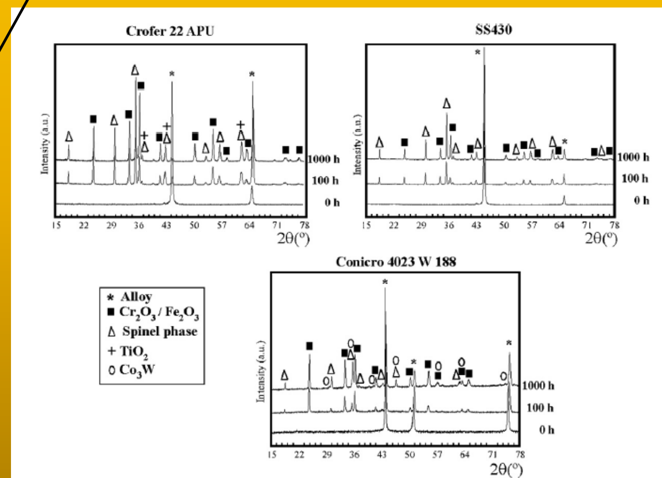
Solid Oxide Fuel Cell

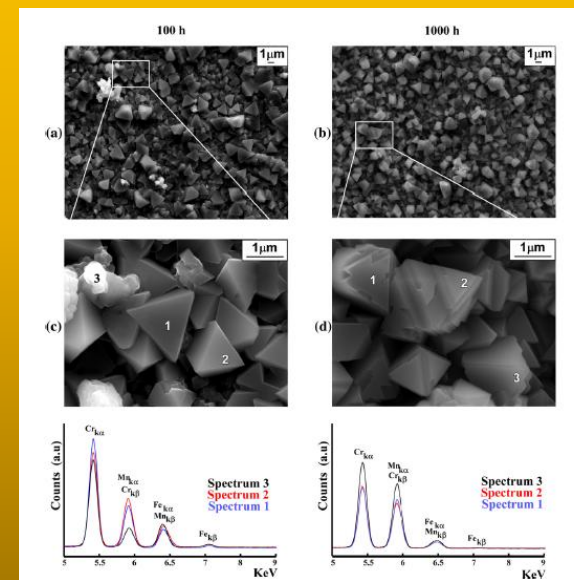
Materials near to the metallic interconector



Interconector

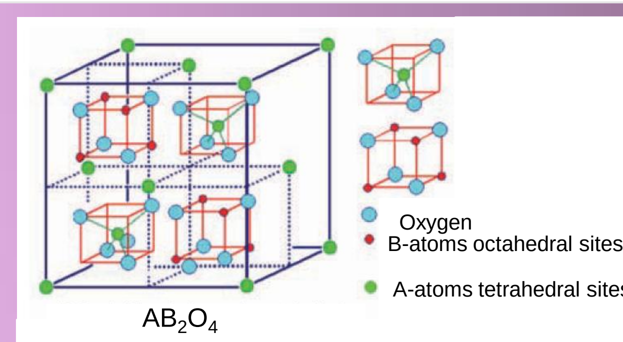
Study of the durability and oxidation produced in different interconectors (Conicro 4023 W 188, Crofer 22 APU, SS430) .





Protecting layer (avoids the cathode pollution with the Cr coming from the interconector).

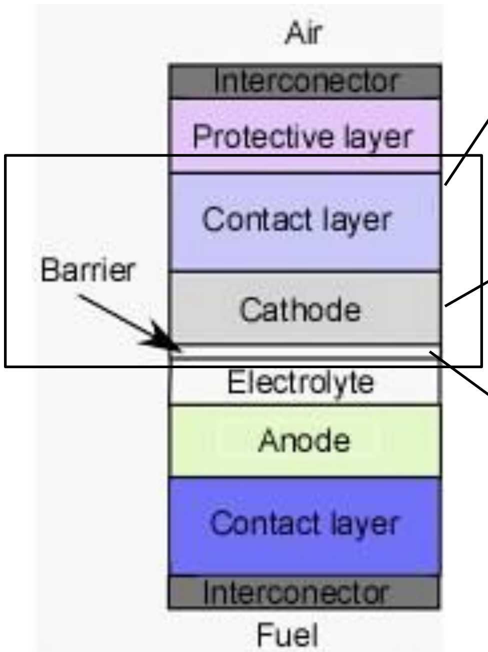
Analysis of the chromium migration and reactivity as a function of composition in the spinel (Mn, Co)$_3$O$_4$.



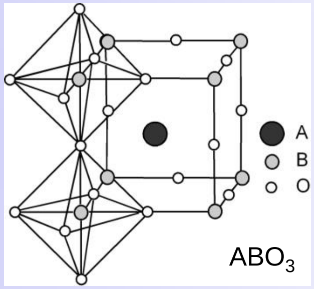
Studies of SOFC materials

Solid Oxide Fuel Cell

Materials near to the ceramic electrolyte (cathode side)

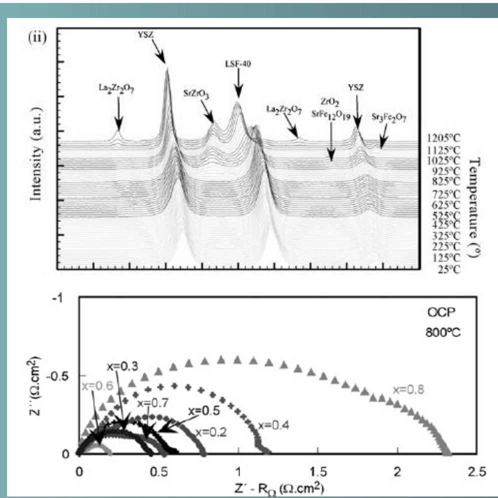


Contact layer (avoids conductivity loses, improves the contact between the cathode and the interconector).
Analysis of the reactivity of different perovskites ABO_3 ($LaNi_{0.6}Fe_{0.4}O_{3-\delta}$ (LNF), $LaNi_{0.6}Co_{0.4}O_{3-\delta}$ (LNC) and $(La_{0.8}Sr_{0.2})_{0.95}Mn_{0.3}Co_{0.1}Fe_{0.6}O_3$ (LSMCF)).

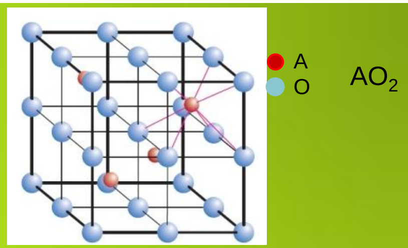


Cathode
Study of $La_{0.60}Sr_{0.40}FeO_3$ reactivity with the contact layer and the SDC barrier.

Synthesis and characterization of $Ln_{1-x}M_xFeO_3$ compounds (Ln = La, Pr, Sm, Nd, Gd; M = Ba, Ca, Sr). Systematic study of the parameters x, $\langle r_A \rangle$ and $\sigma^2(r_A)$.



Barrier (avoids the reactivity between the cathode and the electrolyte).
Chemical reactivity analysis between the cathode and the electrolyte.

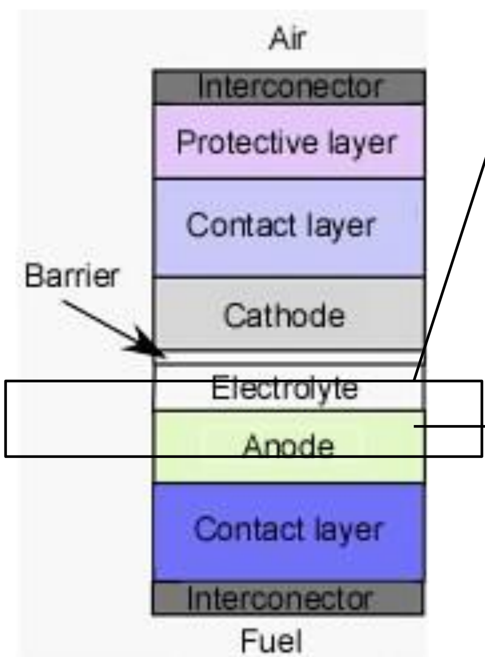


K. Vidal, PdD Thesis: , UPV/EHU, May 2008.
A. Ecija, PdD Thesis, UPV/EHU, September 2012.
A. Morán, PdD Thesis, UPV/EHU, June 2015.
A. Martínez, PdD Thesis , UPV/EHU, June 2009.
V. Miguel, PdD Thesis, UPV/EHU, July 2013.

Studies of SOFC materials

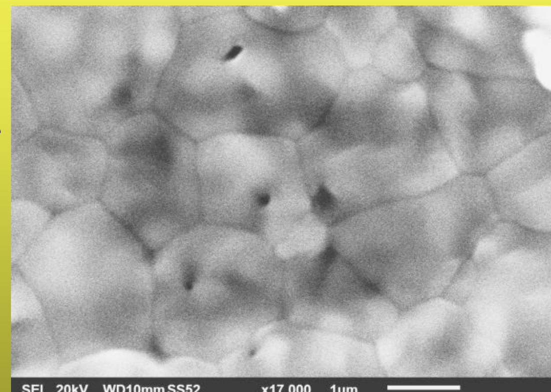
Solid Oxide Fuel Cell

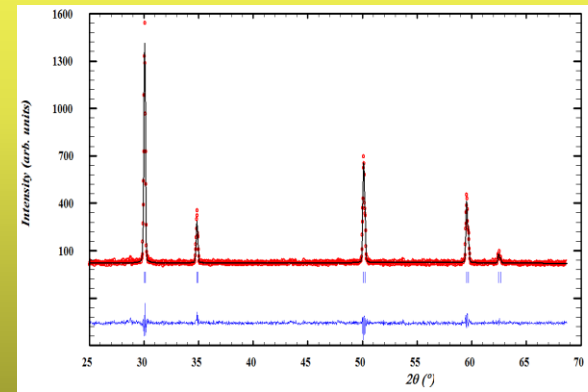
Materials near to the ceramic electrolyte (Anode side)



Electrolyte

Fabrication of YSZ tapes for SOFC applications and study of the density and conductivity of the cells.

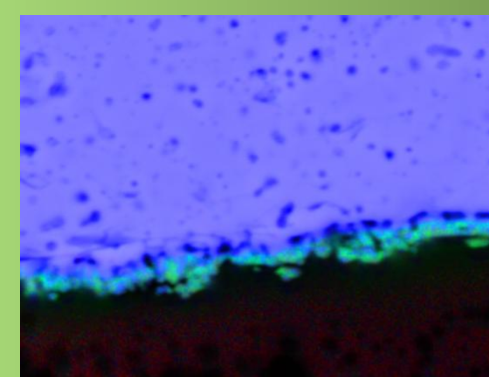




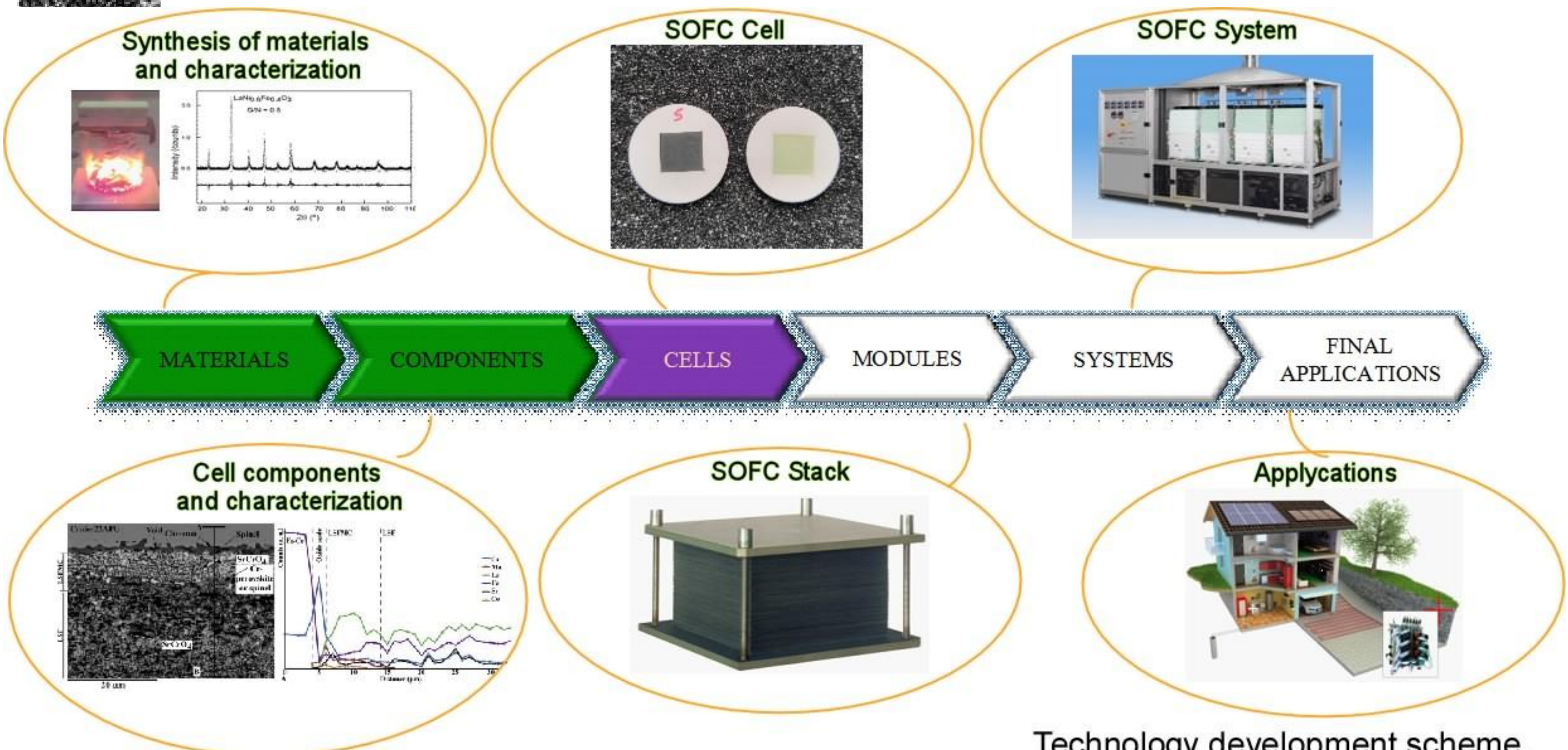
Anode

Synthesis and characterization of NiO-YSZ anode. Systematic study of the composition, the morphology and conductivity of the powders.

Analysis of the deposition in YSZ tapes by spraying.



A. Wain, "Scalable synthetic method for IT-SOFCs compounds", 12th European SOFC & SOE Forum. Lucerne. 5-8 July of 2016.



Technology development scheme.

Large-scale synthesis of SOFC materials | Materials

Large-scale synthesis of:

NiO-$(ZrO_2)_{0.92}(Y_2O_3)_{0.08}$ (Ni-YSZ anode)

$(ZrO_2)_{0.92}(Y_2O_3)_{0.08}$ (YSZ electrolyte)

$Ce_{0.8}Sm_{0.2}O_{1.9}$ (SDC barrier)

$La_{0.6}Sr_{0.4}FeO_3$ (LSF40 cathode)

$LaNi_{0.6}Fe_{0.4}$ (LNF60 contact layer)

$MnCo_{1.9}Fe_{0.1}O_4$ (MCF10 protective layer)

Scale

High scale synthesis of the components of the cell has been done through glycine-nitrate combustion method. In this way, syntheses of 20g batches have been carried out for each compound.

I. Perez-Fernandez, 21st World Hydrogen Energy Conference 2016. Zaragoza. June 2016.
A. Wain, 12th European SOFC & SOE Forum. Lucerna. July 2016.

Focus of research

In this research, six pure compounds used as SOFC components have been synthesized by the fast and reproducible combustion method, obtaining good properties for their manual spray deposition on top of YSZ tapes.

The different layers have been characterized by Scanning Electron Microscopy and electroquemical impedance spectroscopy to study their influence on the properties of these cells as IT-SOFC material.

K. Vidal, A. Morán-Ruiz, A. Larrañaga, J. M. Porras- Vazquez, P. R. Slater, M. I. Arriortua, Solid State Ionics, 269 (2015) 24-29.
Z. Wang, X. Huang, Z. Lv, Y. Zhang, B. Wei, X. Zhu, Z. Wang, Z. Liu , Ceramics International, 41 (2015) 4410-4415.
L. Jia, X. Wang, W. Li, K. Li, B. Chi, J. Pu, L. Jian, S. Yuan, J. Power Sources, 253 (2014) 138-142.

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Synthetic methods

Experimental preparation

Comparison of synthetic methods for the preparation of electrode materials.

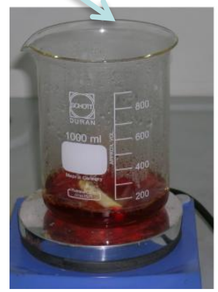
Synthetic methods	Description	Advantages	Disadvantages
Solid state reaction	Grinding Mixture Thermal treatment of the mixing precursor	Easy reproducibility Low cost There are no aqueous or gaseous waste Easy of transferring it to other compositions	Low purity Low homogeneity Imprecise stoichiometry
Sol-gel	Formation of the gel from solutions of cationic and organic* precursors Calcination/sintering	Fine and homogeneous powder	High amounts of organic compounds Nitrous gases High cost
Spray pyrolysis	Thermal decomposition of aqueous solution of nitrates in drops within a hot reaction chamber Sometimes, application of organic complex for the reduction of nitrates	Fine and homogeneous powder	Expensive equipment Difficult to scale up for mass production
Co-precipitation	Co-precipitation of corresponding cations (hydroxides, carbonates, oxalates,…) Calcination/sintering	Fine and homogeneous powder Low cost	Different solubility of the cations Aqueous waste problems Difficult of transferring it to other compositions

* Systems commonly used are citric acid, ethylene glycol (Pechini method), glycine/nitrate and polyacrylic acid).

Glycine nitrate combustion process

Metal nitrates were dissolved in distilled water

Glycine/nitrate molar ratio of 1:1



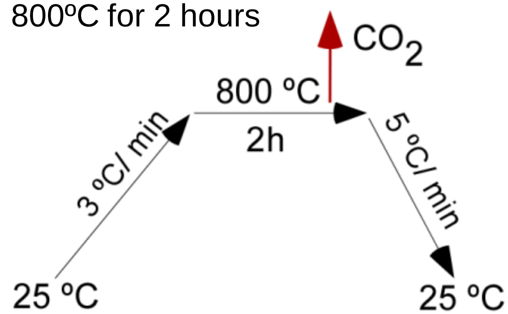
Precursor solution

Resulting viscous liquid autoignited at about 450ºC

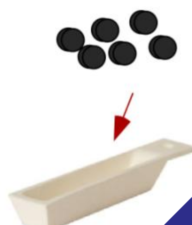
Viscous gel

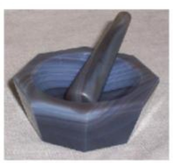
Combustion ~ 450ºC

Calcined in air at 800ºC for 2 hours

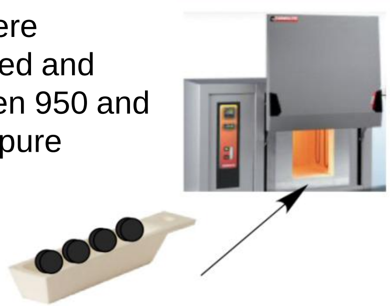


Precursor powders





Obtained powders were subsequently pelletized and calcined in air between 950 and 1150ºC to obtain the pure sample

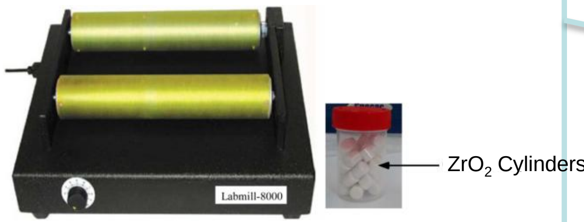


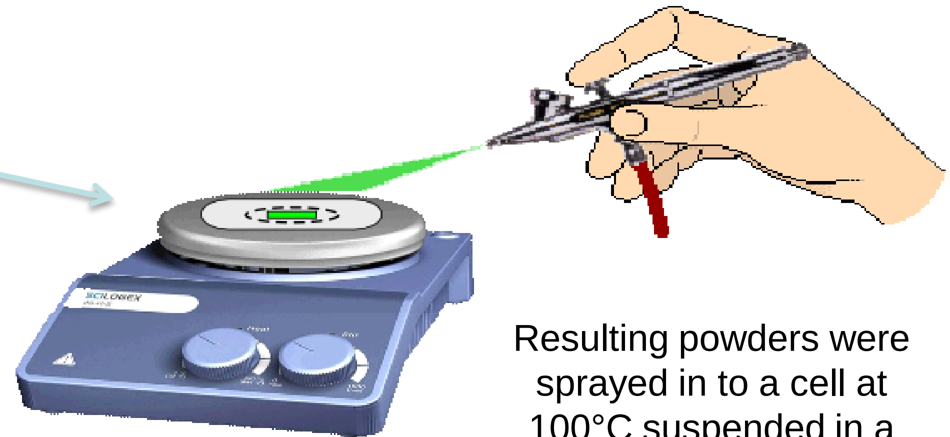
Final products

Deposition process

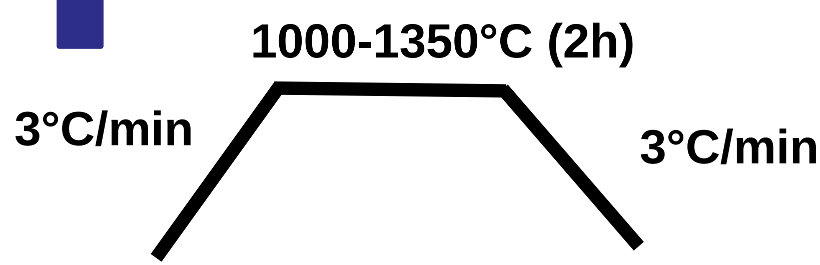
Experimental preparation

Compounds were ball milled for 24h

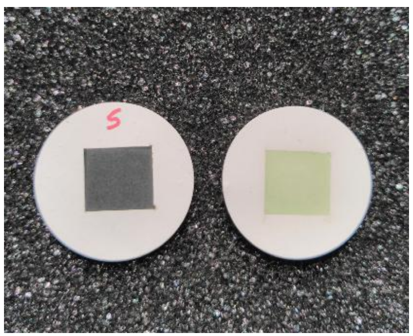




Resulting powders were sprayed in to a cell at 100°C suspended in a isopropanol solution.



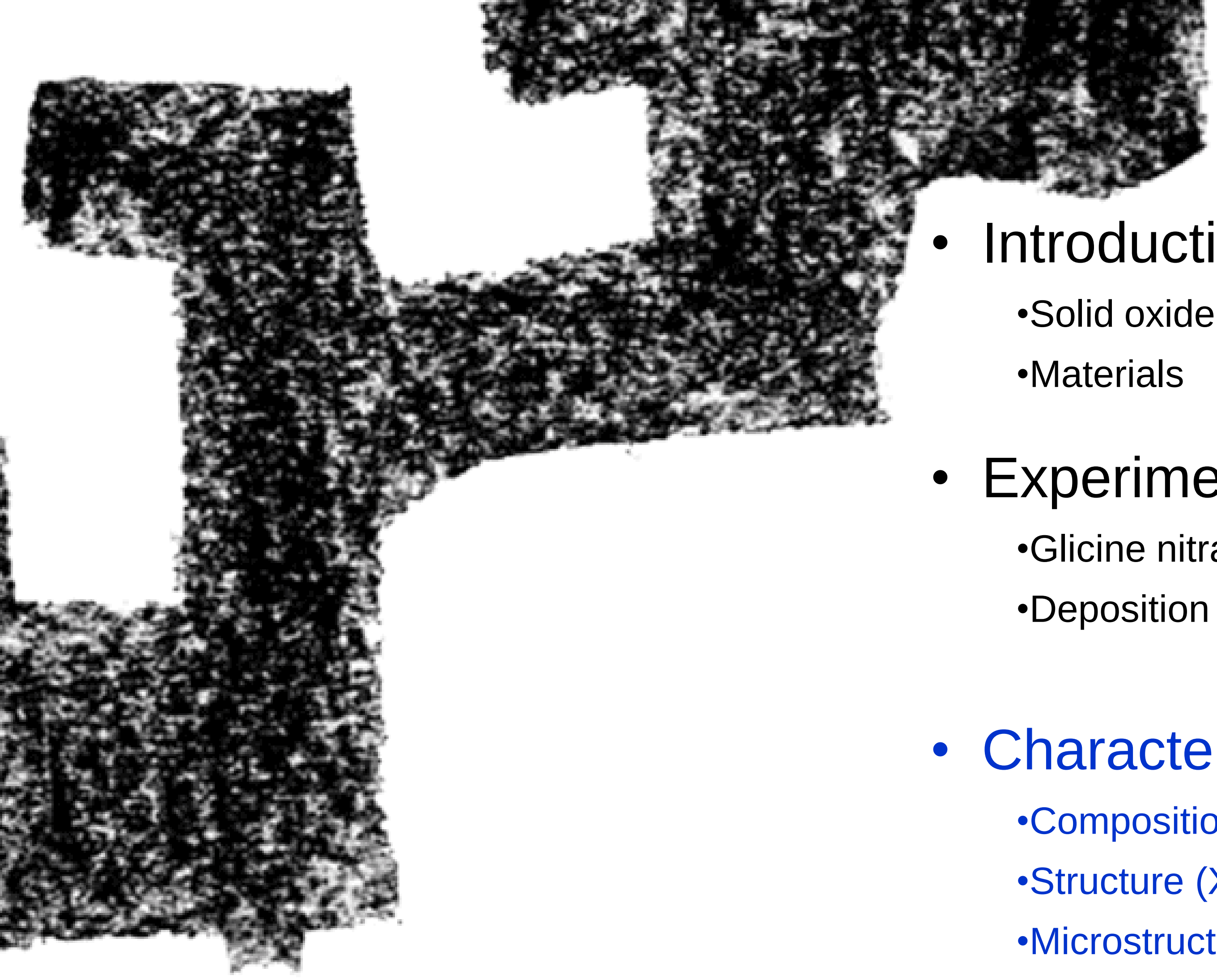
After applying each layer a heat treatment has been performed in order to cosinterify the layers between them.



Electroquemistry
SEM
Degradation test

Samples

Layers deposited on YSZ tapes
NiO-YSZ
LSF40
SDC
SDC+LSF40
SDC+LSF40+LNF60
SDC+LSF40+MCF10
SDC+LSF40+LNF60+MCF10



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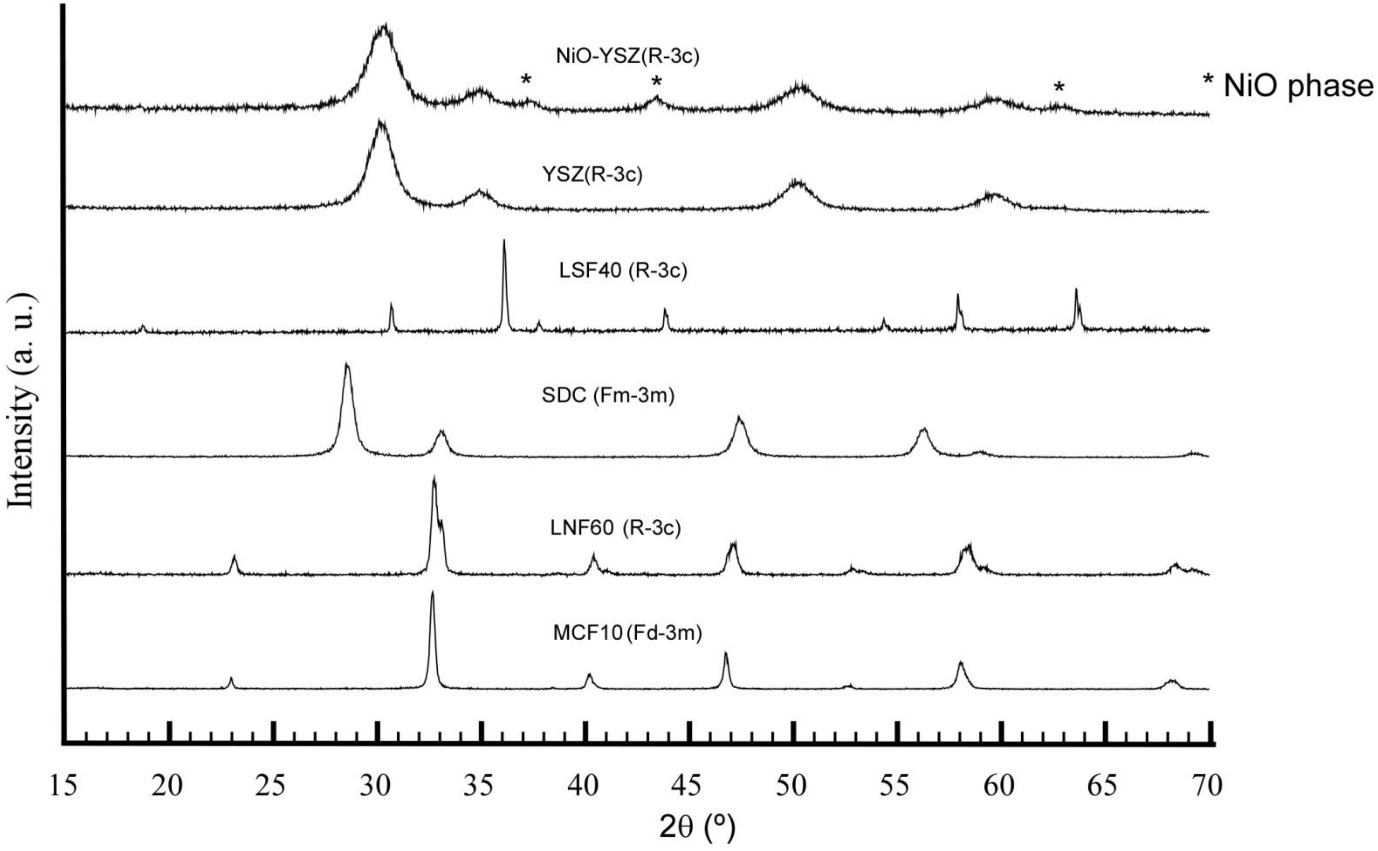
X-ray diffraction (XRD)



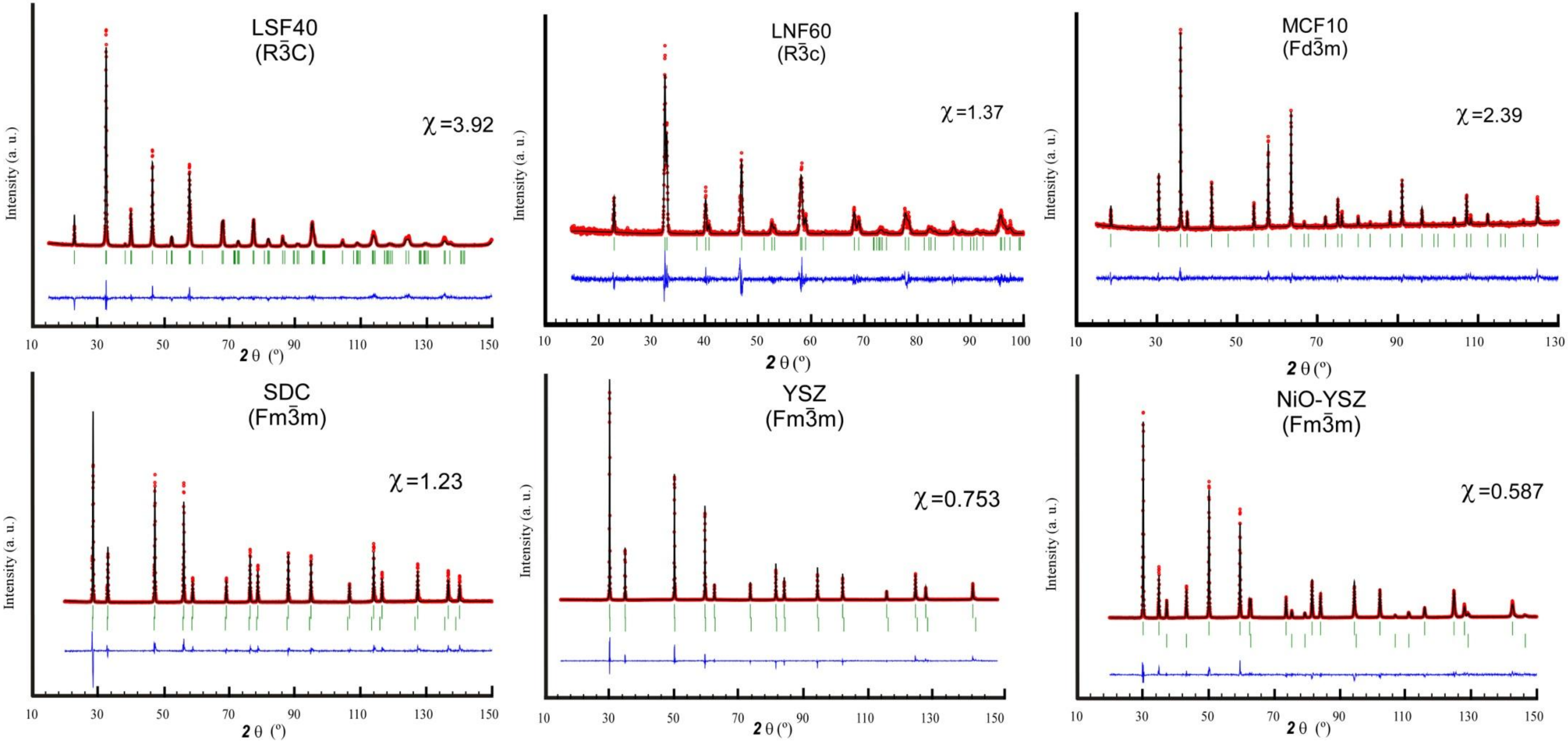
The patterns reveal that all the samples are single-phased and no impurity phase is detected.

H. M. Rietveld, J. Appl. Crystallogr., 2 (1969) 65-71.

Larson A.C., Von Dreele R.B., "GSAS: General Structure Analysis System", LAUR, 86, 1994.

X-ray diffraction (XRD)

Rietveld method, program Fullprof



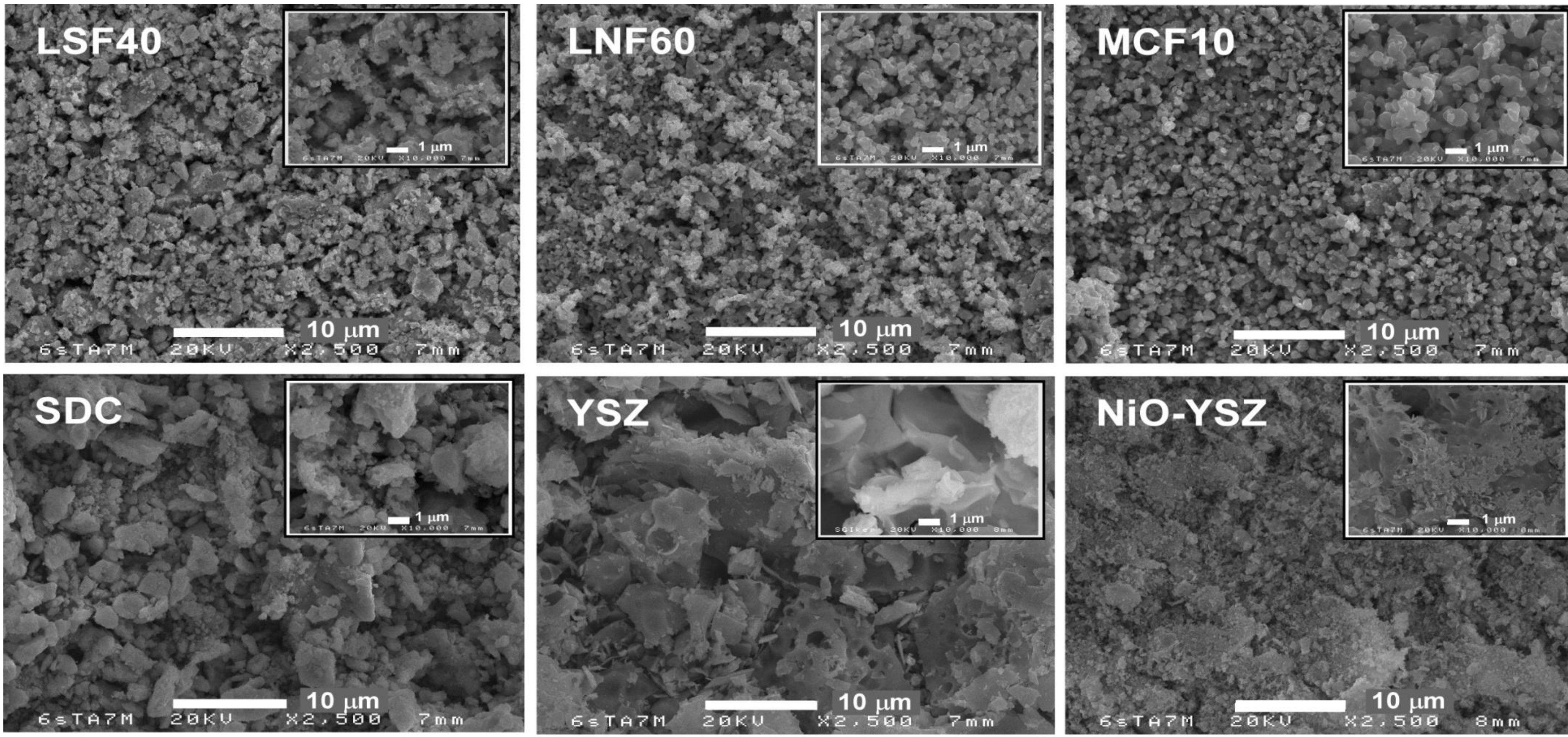
Results on the Rietveld analysis of these powder diffraction patterns, show the different crystal structures of the samples.

H. M. Rietveld, J. Appl. Crystallogr., 2 (1969) 65-71.

Larson A.C., Von Dreele R.B., “GSAS: General Structure Analysis System”, LAUR, 86, 1994.

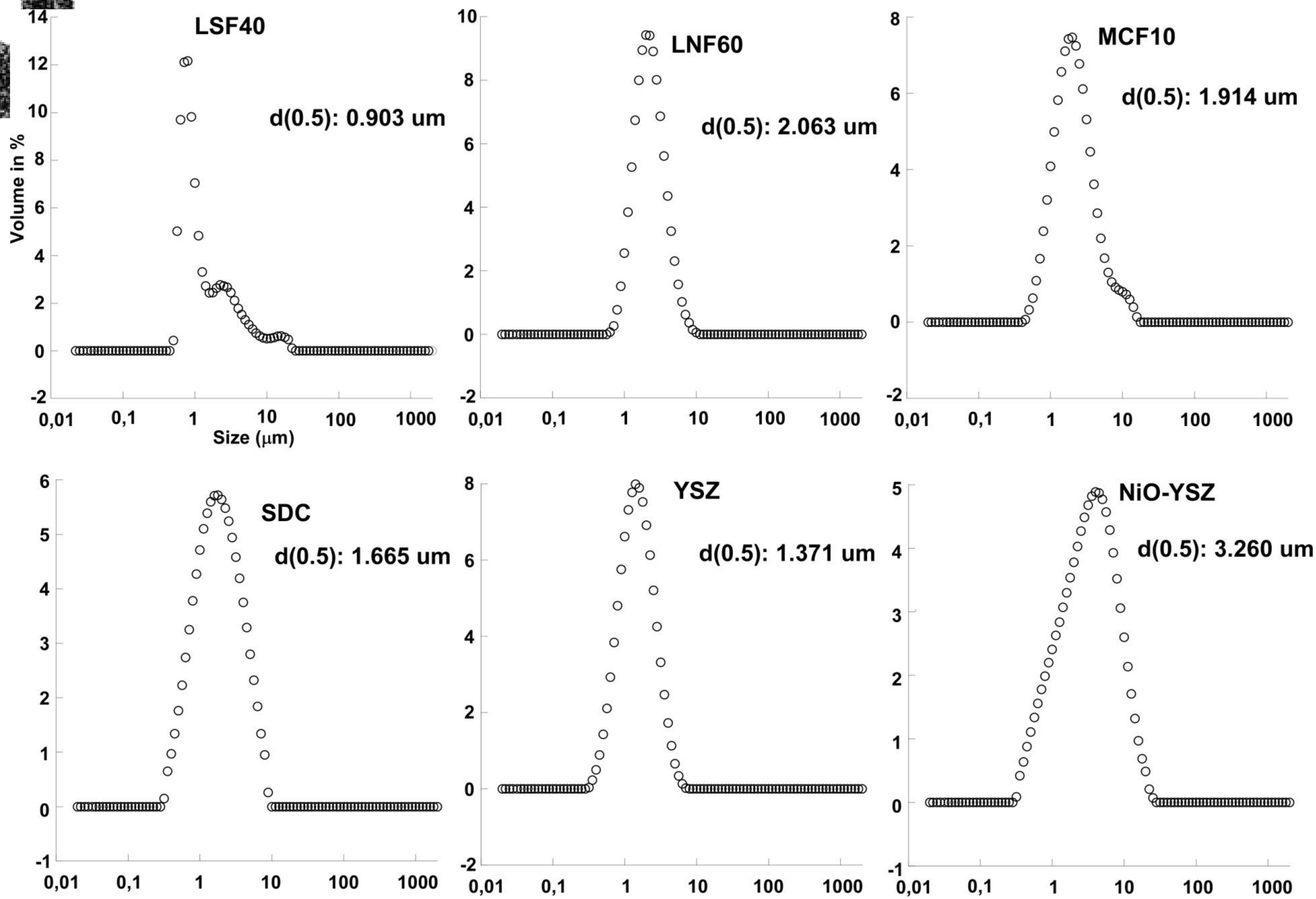
Scanning Electron Microscope (SEM)

In all the cases, the agglomerates formed during the combustion reaction are usually soft and easy to break due to the higher escaping gases for these samples.



K. Vidal, A. Morán-Ruiz, A. Larrañaga, J.M. Porras-Vazquéz, P.R. Slater, M:I: Arriortua, Solid State Ionics, 269 (2015) 24-29.

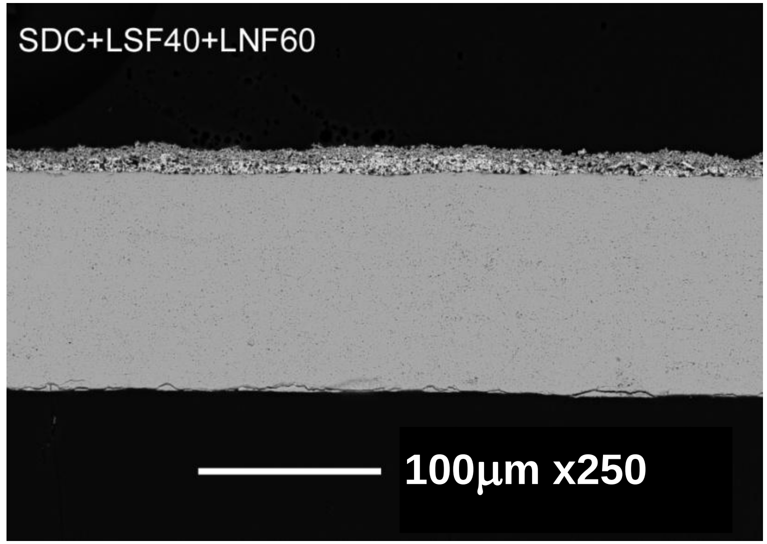
Laser Dispersion Analyzer



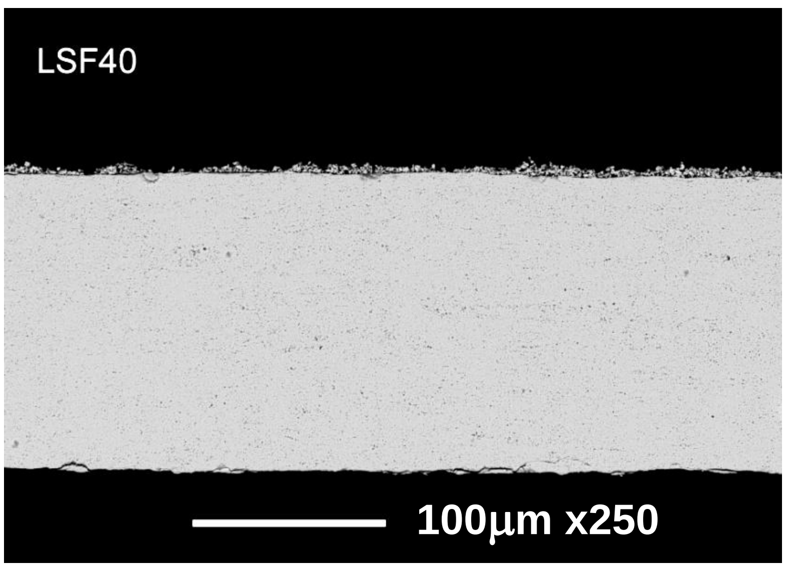
Results on the Master Sizer 2000 laser dispersion analyzer, show grain sizes from 0.5 to 10μm.

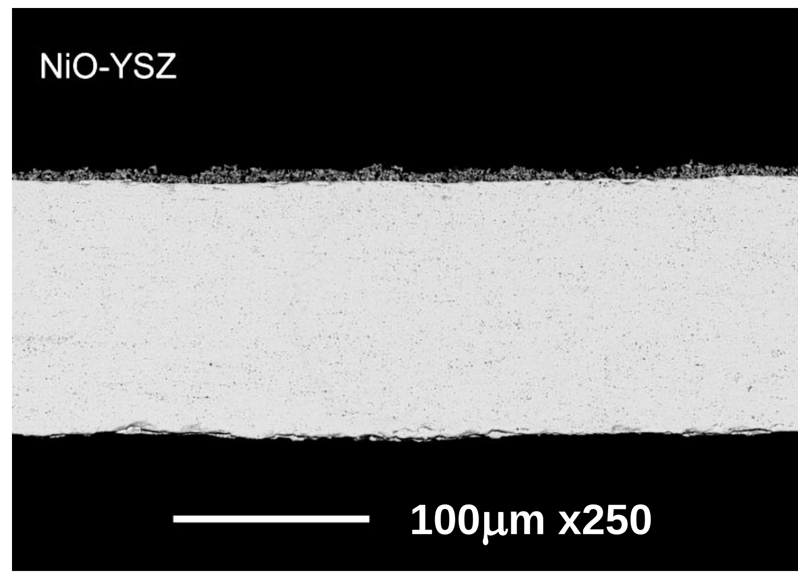
Scanning Electron Microscope (SEM)

SEM micrographs of deposited layers cross-section sintered between 1000 and 1150ºC.



All the cells, except LSF40, exhibit layers with uniform microstructures and similar thicknesses varying in differences of 2-4 µm





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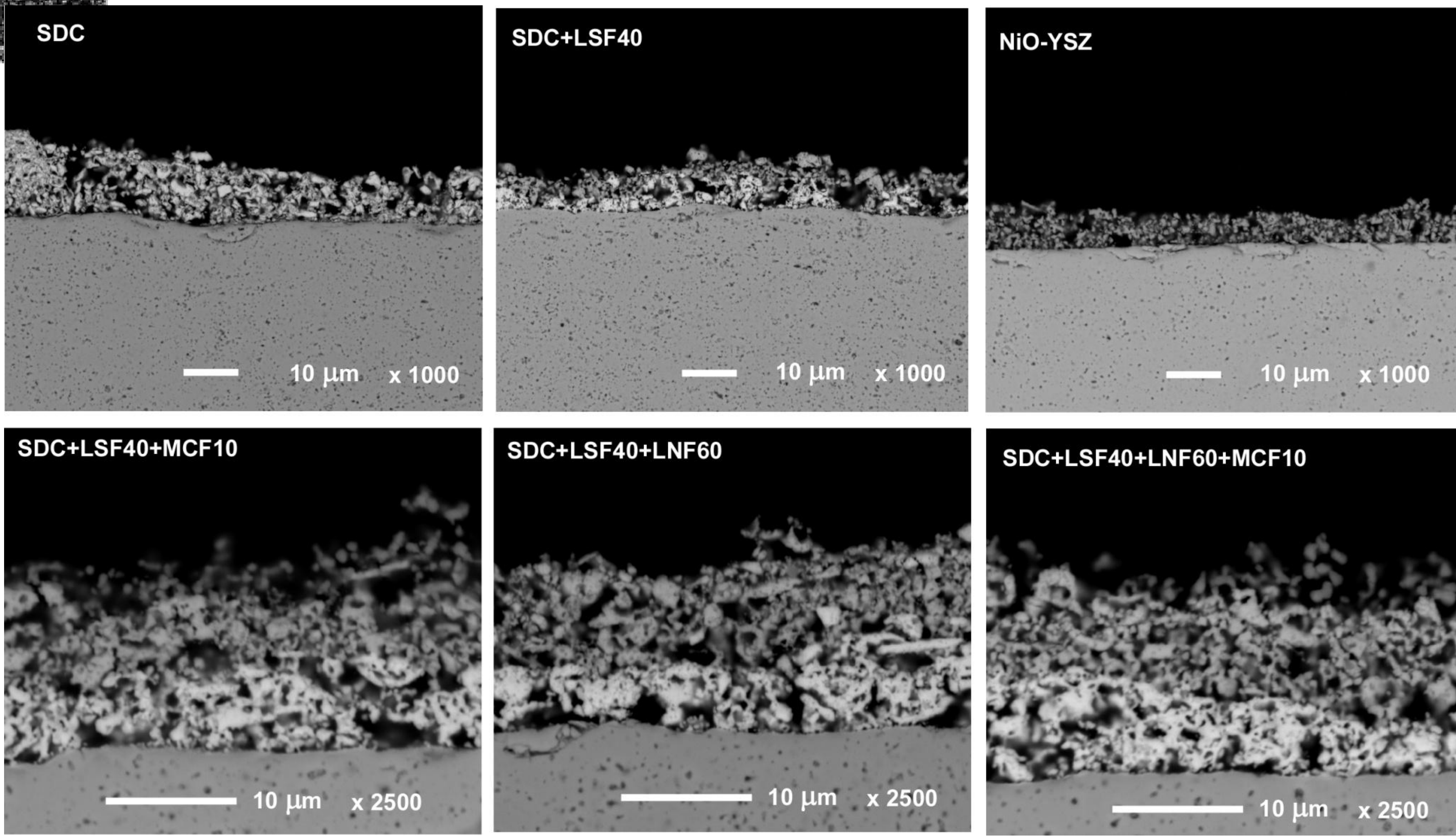
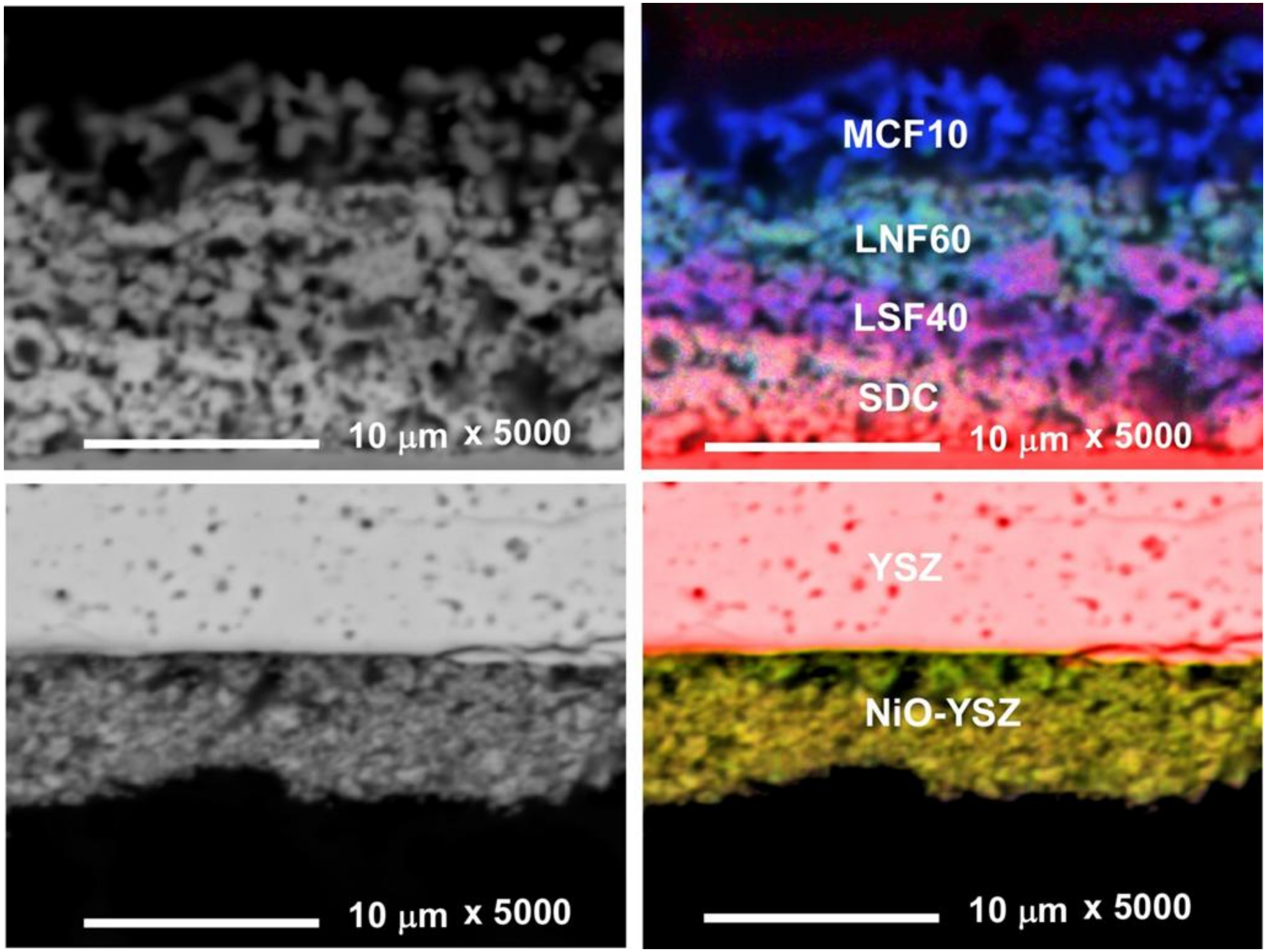
Scanning Electron Microscope (SEM)



The electrodes and other layers present typical porous microstructure while the electrolyte show a density of a 95%. The interface has proven to be quite good between the different layers.

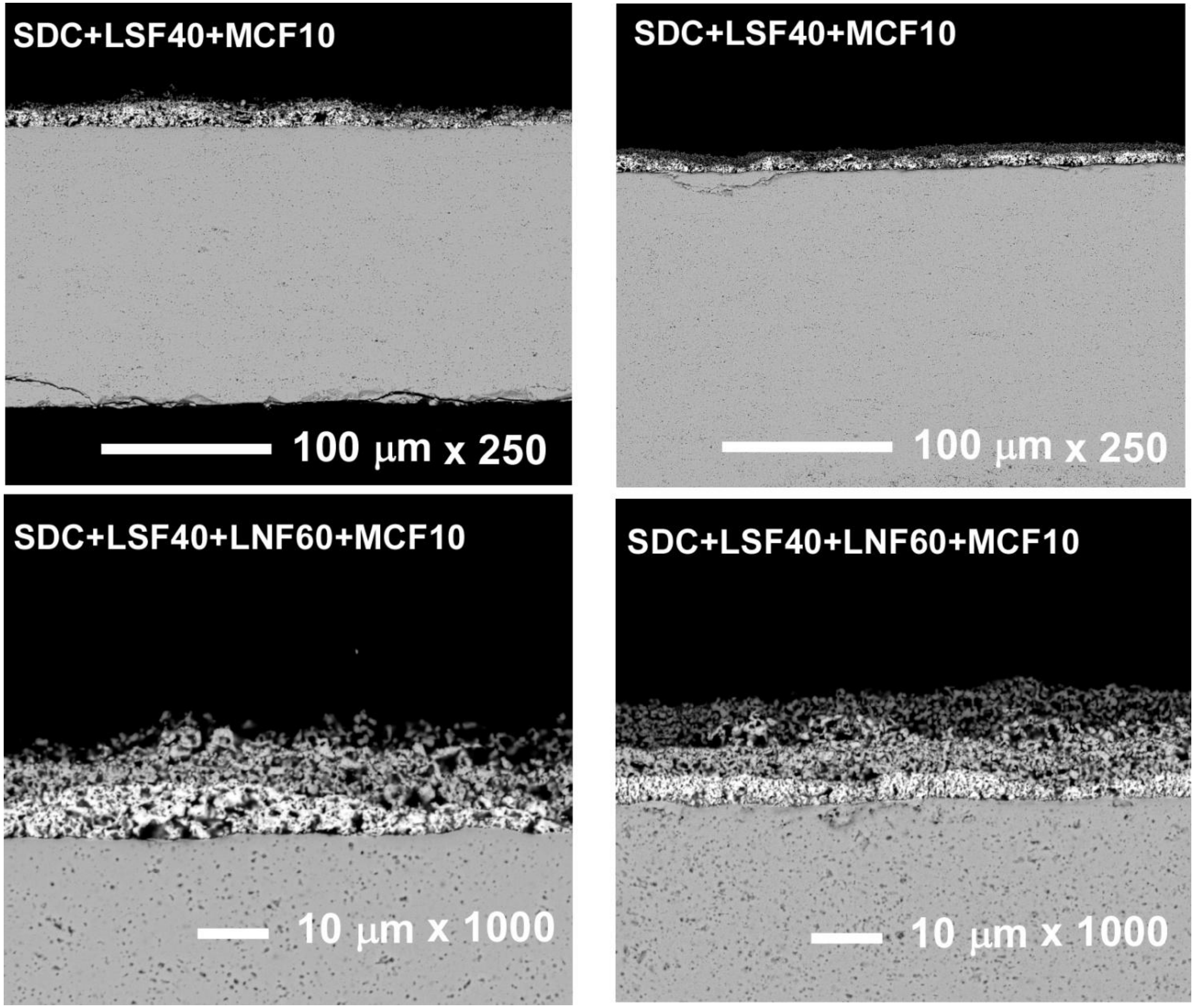
Scanning Electron Microscope (SEM)



Cross-section of the cells and EDX mapping of the selected zone. The thicknesses of the layers can be estimated between 3 and 5μm. A poor penetration between layers is observed.

Degradation Test

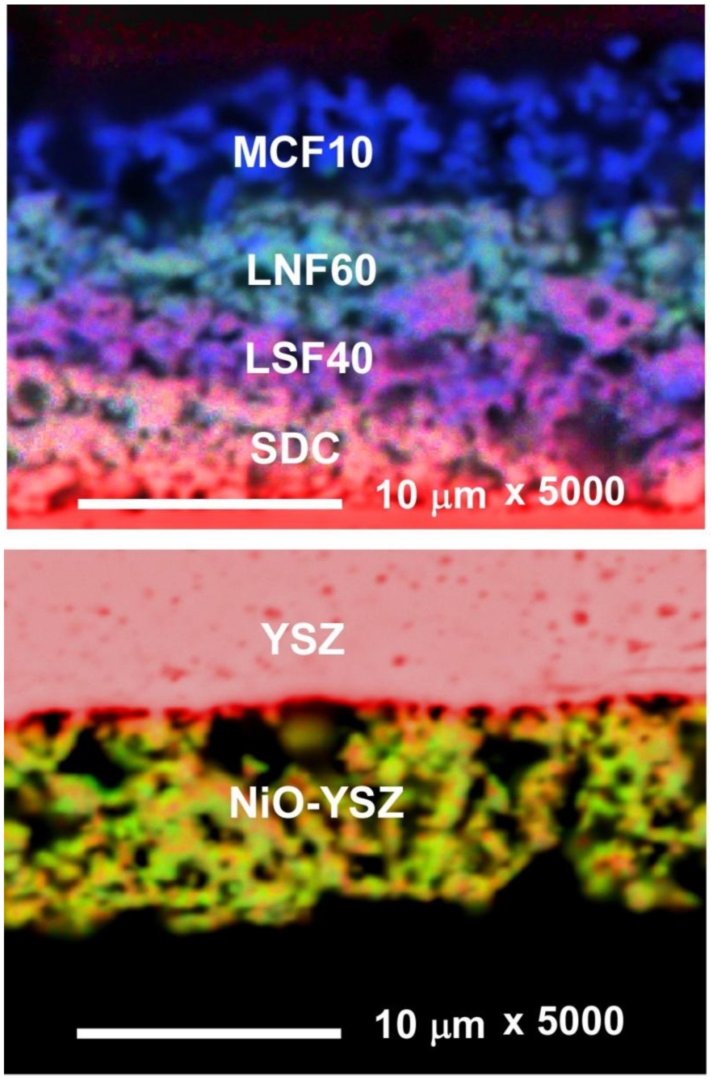
Before thermal treatment **After thermal treatment**



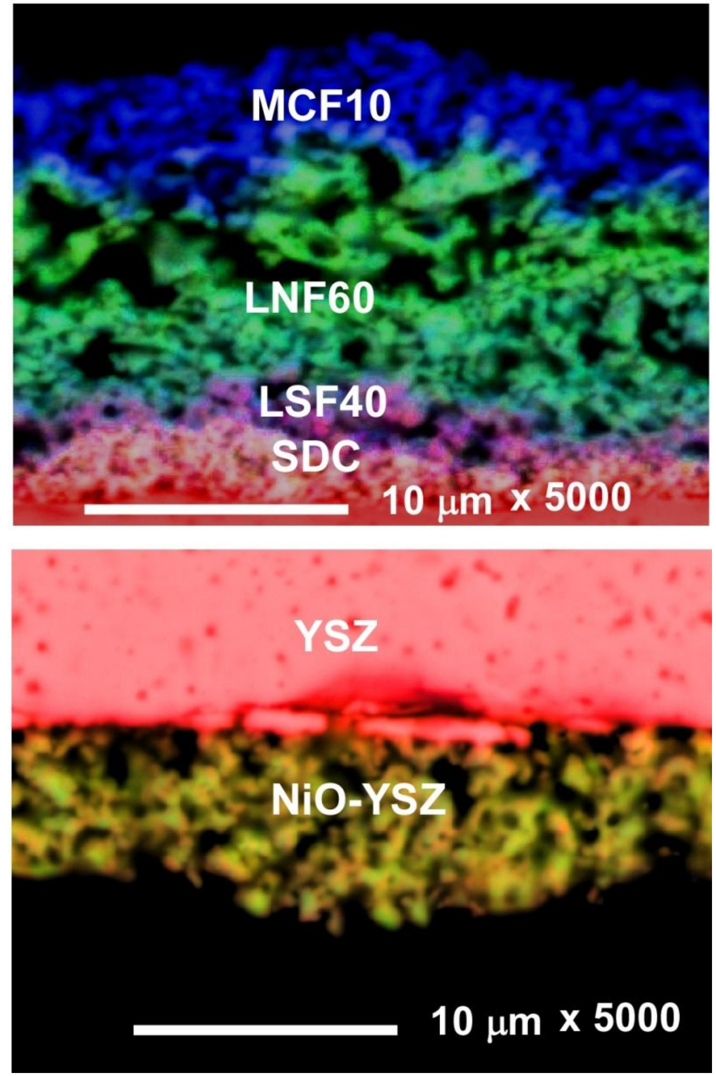
No degradation can be appreciated between layers after 200h at 800ºC.

Degradation Test

Before thermal treatment

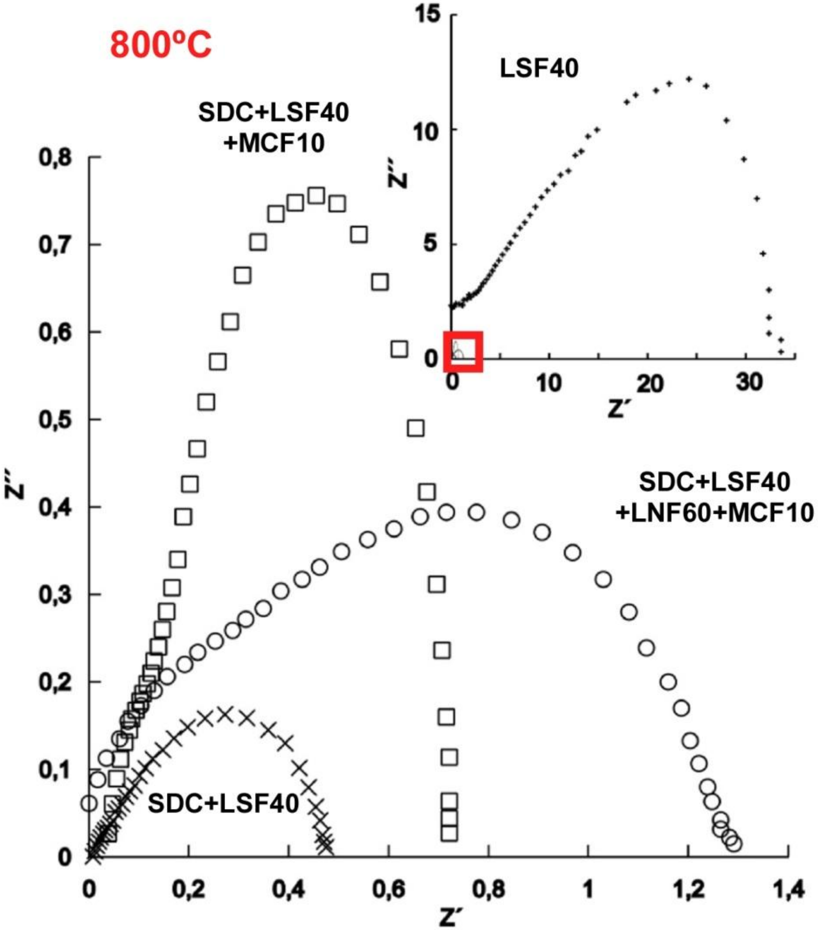


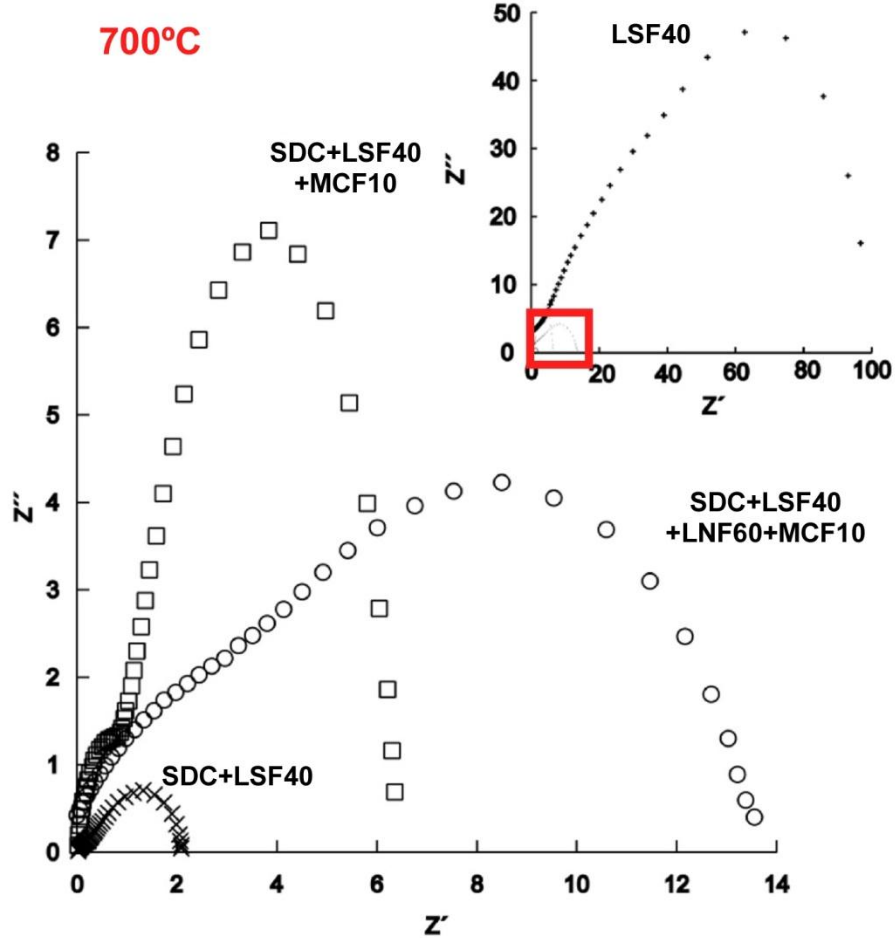
After thermal treatment



No degradation can be observed between layers after 200h at 800ºC.

Electrochemical Impedance Spectroscopy (EIS) First attempts





Impedance measurements of the symmetric cells were performed at 700 and 800ºC.

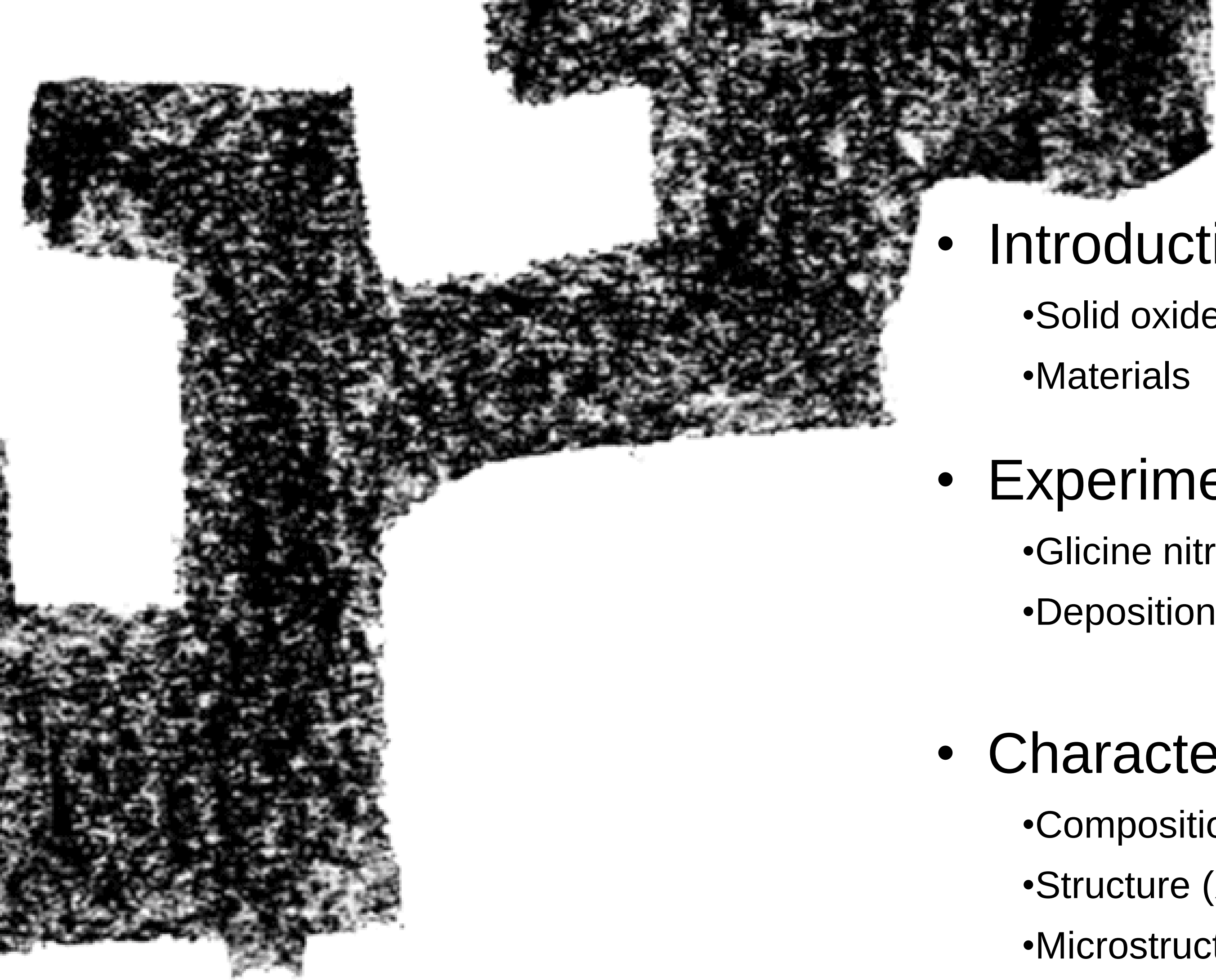
Electrochemical Impedance Spectroscopy (EIS) First attempts

Samples	T^a(ºC)	$R_\Omega(\Omega\cdot cm^2)$	Capacitance($F\cdot cm^2$)		
			C_2	C_3	C_4
SDC+LSF40	700	3.468	$1.82\cdot10^{-2}$	$7.80\cdot10^{-3}$	$6.92\cdot10^{-5}$
SDC+LSF40	800	1.353	$2.65\cdot10^{-2}$	$3.52\cdot10^{-3}$	
SDC+LSF40+ MCF10	700	2.534	$1.74\cdot10^{-2}$	$2.27\cdot10^{-3}$	
SDC+LSF40+ MCF10	800	0.8492	$1.43\cdot10^{-2}$	$2.30\cdot10^{-2}$	
SDC+LSF40+ LNF60+MCF10	700	2.267	$1.19\cdot10^{-2}$	$8.28\cdot10^{-3}$	
SDC+LSF40+ LNF60+MCF10	800	1.041	$1.56\cdot10^{-2}$	$9.71\cdot10^{-4}$	
LSF40	700	46.29	$6.71\cdot10^{-3}$	$5.39\cdot10^{-4}$	$5.20\cdot10^{-6}$
LSF40	800	26.33	$1.05\cdot10^{-3}$	$5.84\cdot10^{-5}$	$4.67\cdot10^{-7}$

The polarization resistance increases with the decreasing temperature due to the lower mobility of ions.

The polarization resistance increase with the number of layers.

The cell without SDC layer present worse response than the cells with barrier.



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Conclusions

•The synthesized powders (NiO-YSZ, SDC, LSF40, LNF60, and MCF10) have revealed good properties for their deposition on to YSZ tapes.

•The glycine-nitrate combustion method has demonstrated to be a fast, scalable and reproducible method for the synthesis of SOFC compounds.

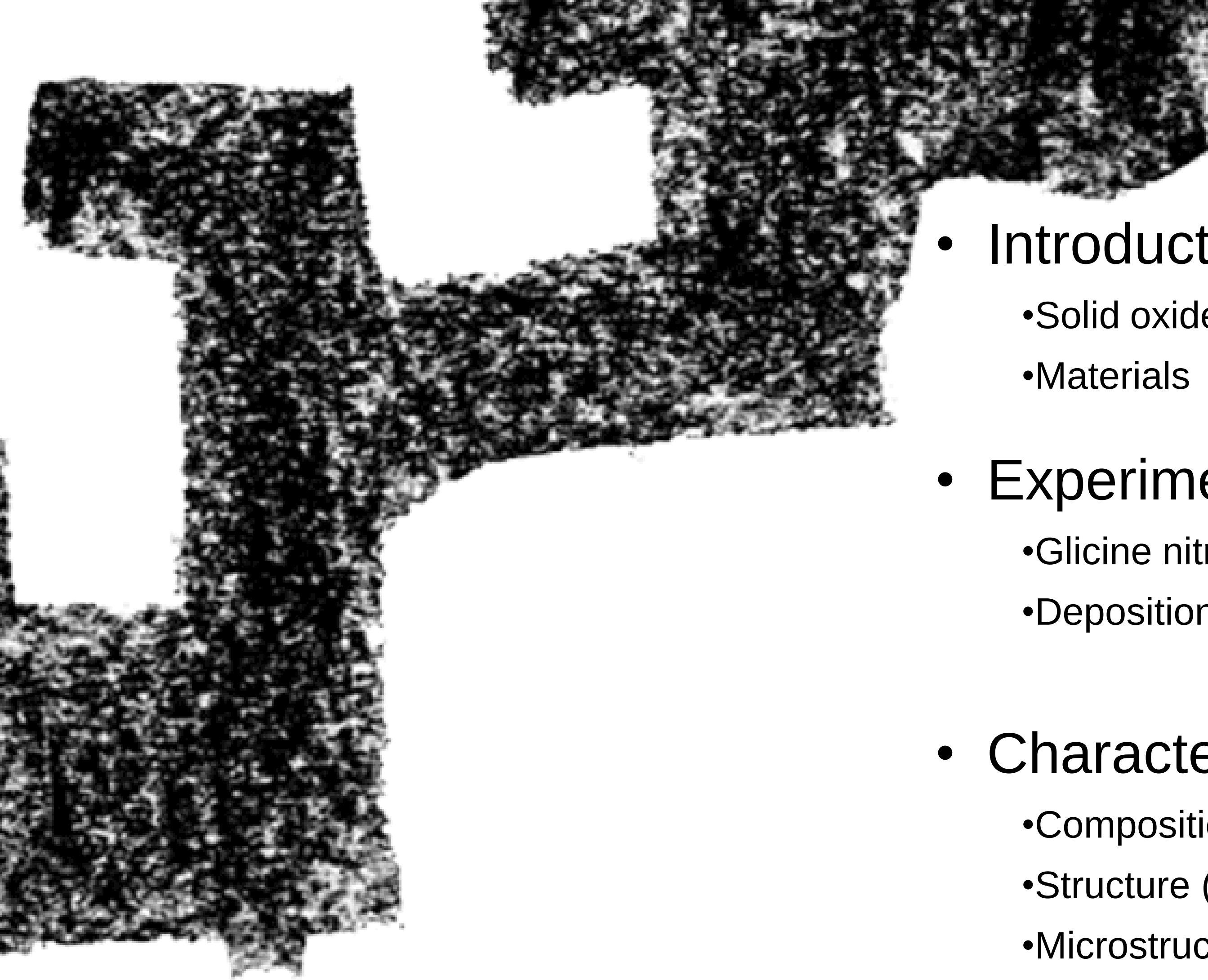
•Layers show an homogeneous deposition and an appropriate microstructure for the electrodes.

•The SDC layer improves the contact with the electrolyte and the conductivity of the cells.

•No degradation in the microestructure is observed in the cells after 200h of thermal treatment.

•The first attempts of EIS measurements, presents a good previous electrochemical behavior of cells.

•Studies varying the thickness and the porosity of the layers are required in order to improve the behavior of the cells.



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Acknowledgments

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Thank you very much for your attention

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