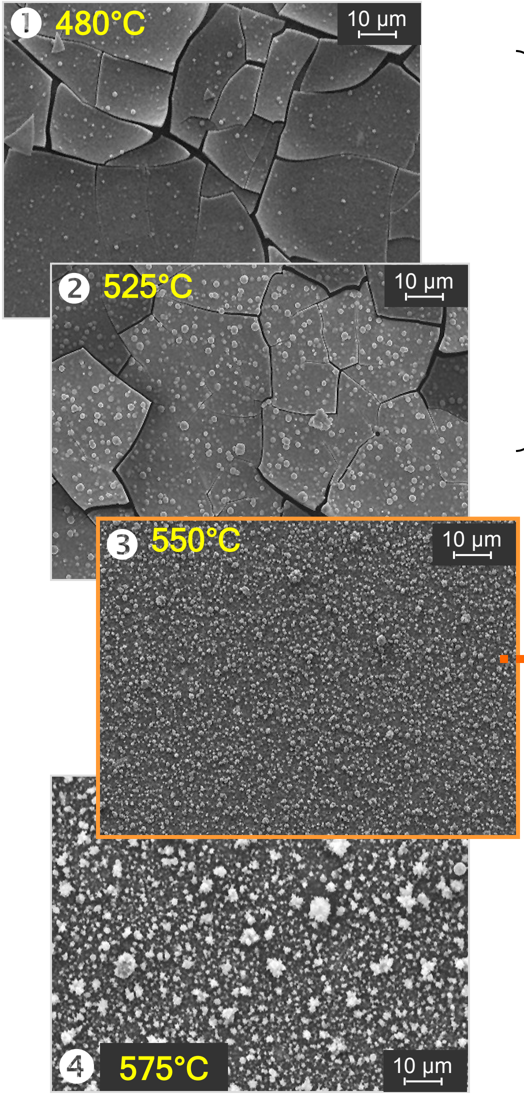
Influence of the substrate temperature



Distance: 27 mm., flow rate: 1.17 ml/h, time: 60 min.

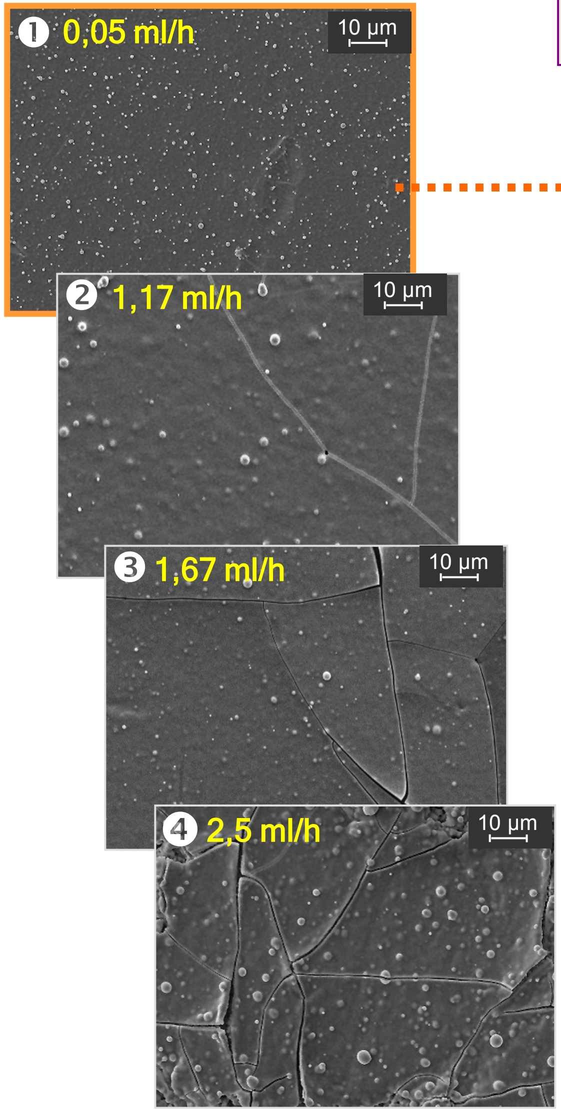
Temperature too low (① et ②): dense film but cracked due to stresses during the drying step (solvent excess)

Appropriated temperature - ③

Equilibrium between quantity of arriving solvent and evaporation

Temperature too high (④): arriving droplets too dried to spread leading to porous film (not enough solvent)

Influence of the solution flow rate



Distance: 47 mm, temperature: 450°C, time: 60 min.

Flow rate appropriated - ①

The lower the flow rate, the denser the film with no cracks

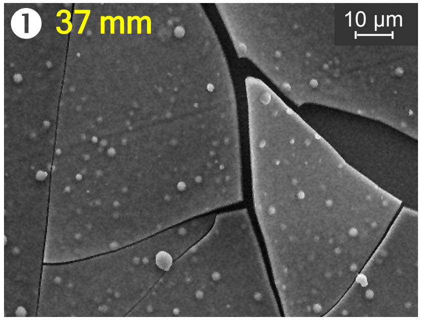
Flow rate too high: wetter film and cracked (②, ③ et ④).

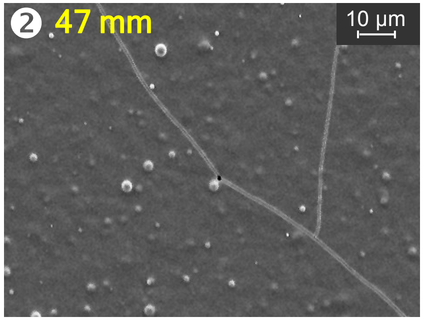
$$* d = 3.78\pi^{\frac{-2}{3}} Q^{\frac{1}{2}} \left(\frac{\rho \varepsilon_0}{\nu \lambda} \right)^{\frac{1}{6}} f_b$$

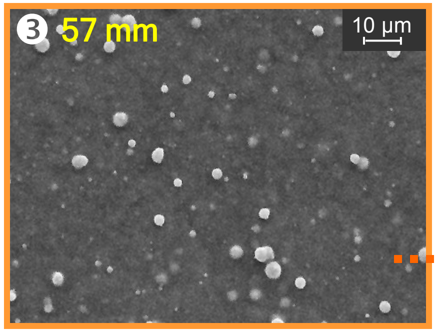
***Ganan-Calvo- Physical Review Letters 79 (2) 1997 pp. 217-220**

Influence of nozzle to substrate distance

Temperature: 450°C, flow rate: 1.17 ml/h, time: 60 min.





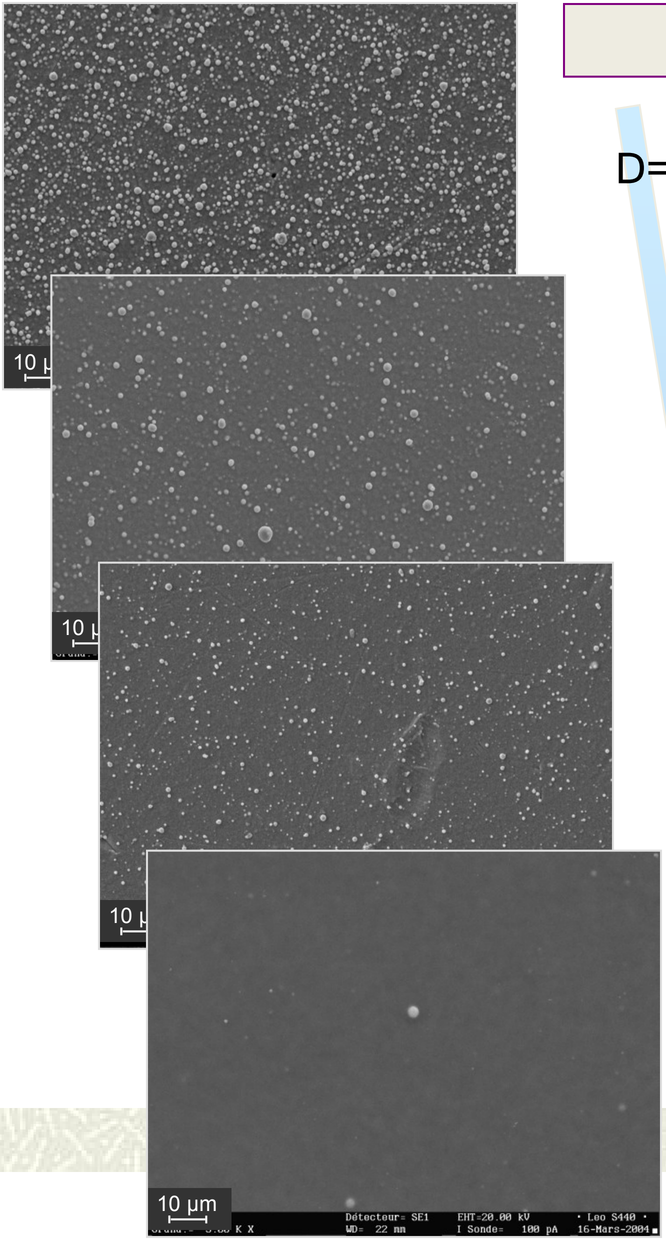


Distance too short : arriving dropets too wet and films cracks (① et ②).

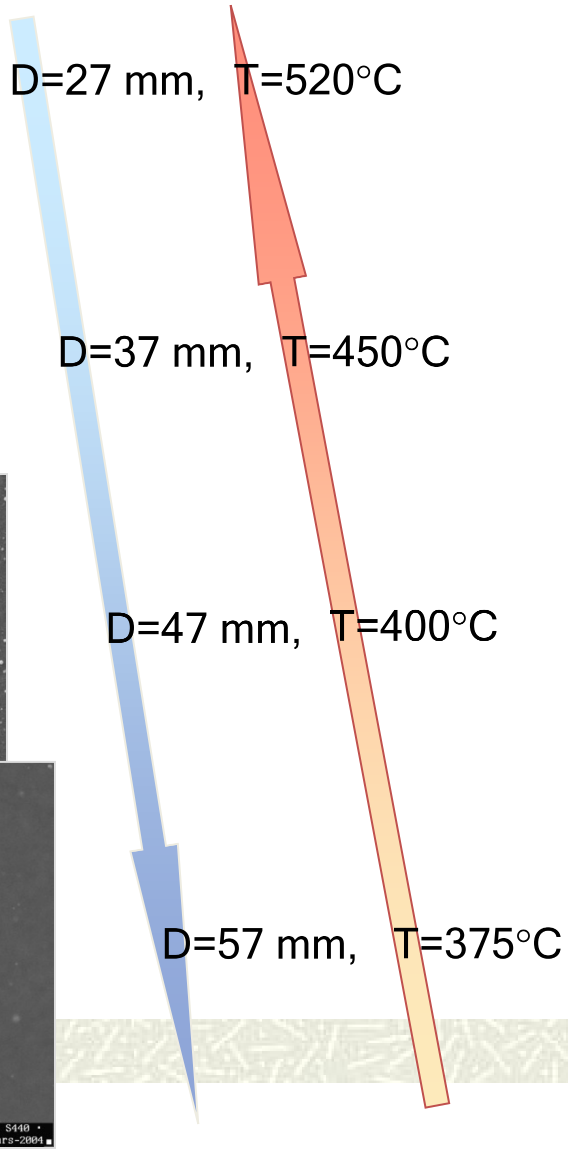
Appropriated distance - ③

A larger distance favors the evaporation of solvent in excess
no cracks

Correlation temperature – working distance



Flow rate: 0.05 ml/h, time: 60 min.



D=27 mm, T=520°C

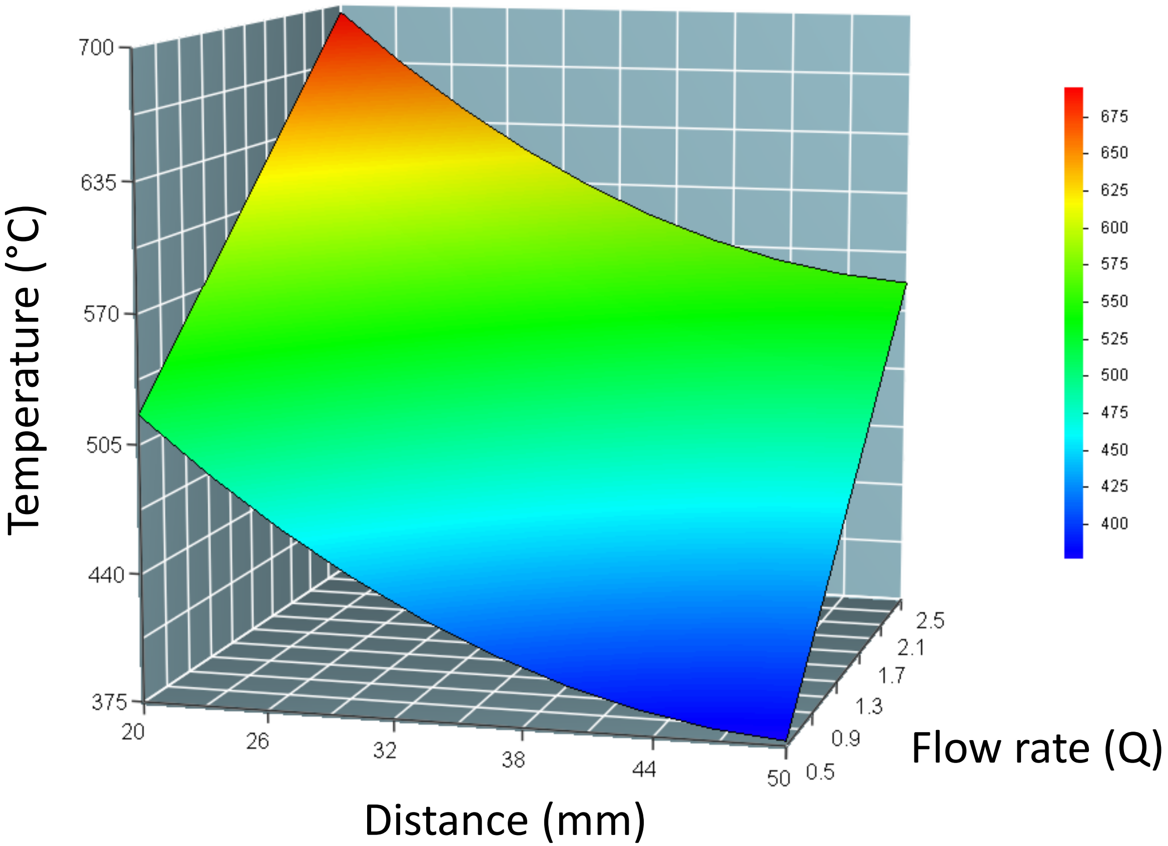
D=37 mm, T=450°C

D=47 mm, T=400°C

D=57 mm, T=375°C

Correlation of process parameters

Flow rate (Q) - Distance (D) - Temperature (T)



Q ⇧ **et** ***D*** ⇩ ⟶ T_s ⇧

R. NEAGU et al., Surface and Coatings Technology, 200 [24] (2006) 6815-6820.

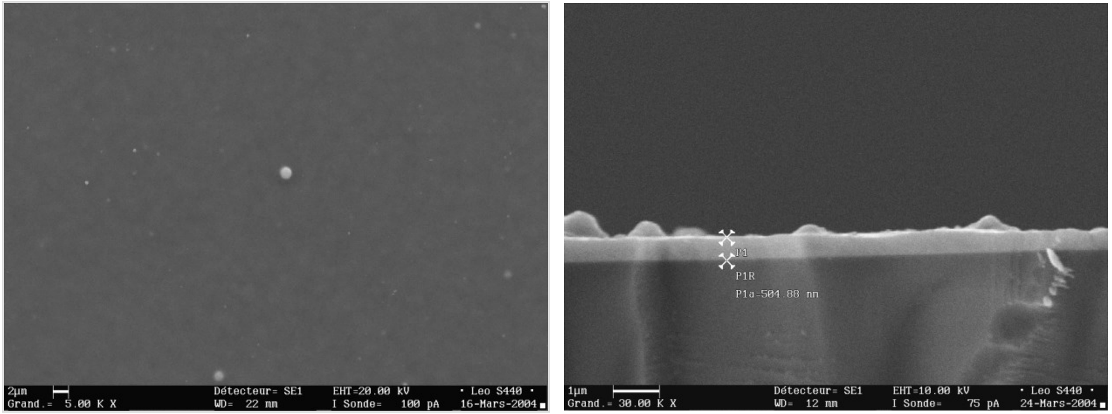
Microstructural characterization - SEM

Dense thin films of cubic and tetragonal zirconia

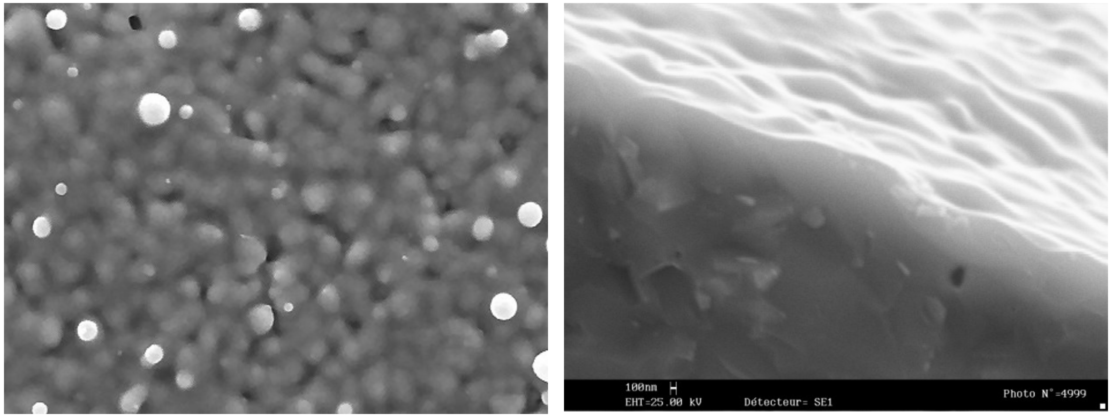
Solution
$(Zr(acac)_4 \cdot 10H_2O + 10\%m\ YCl_3 \cdot 6H_2O)$
in BC - ethanol 1:1

375°C, 57 mm, 0.5 ml/h
60 min.

thickness : ≈ 300 nm



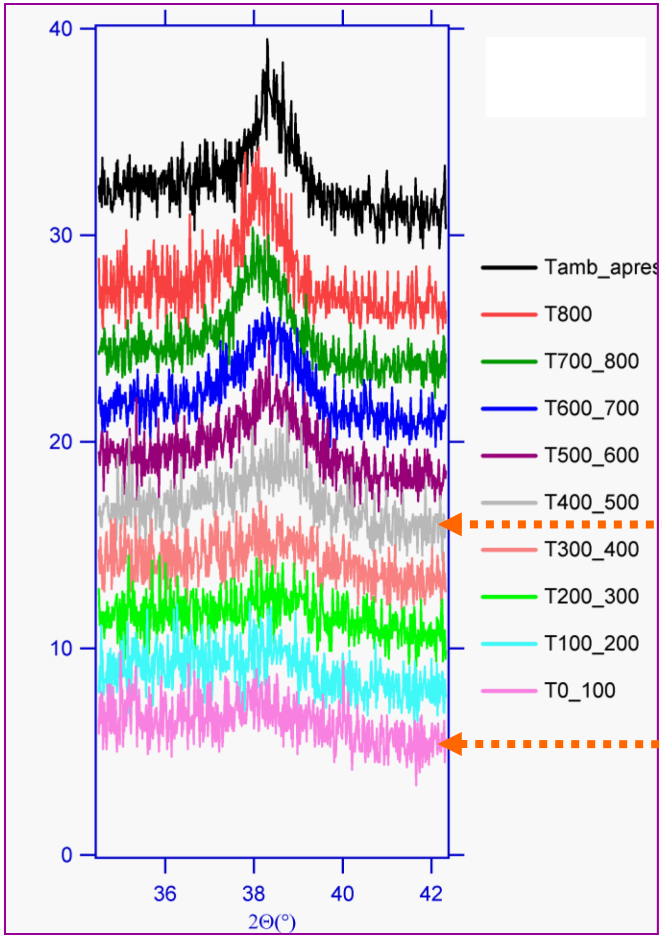
on glass

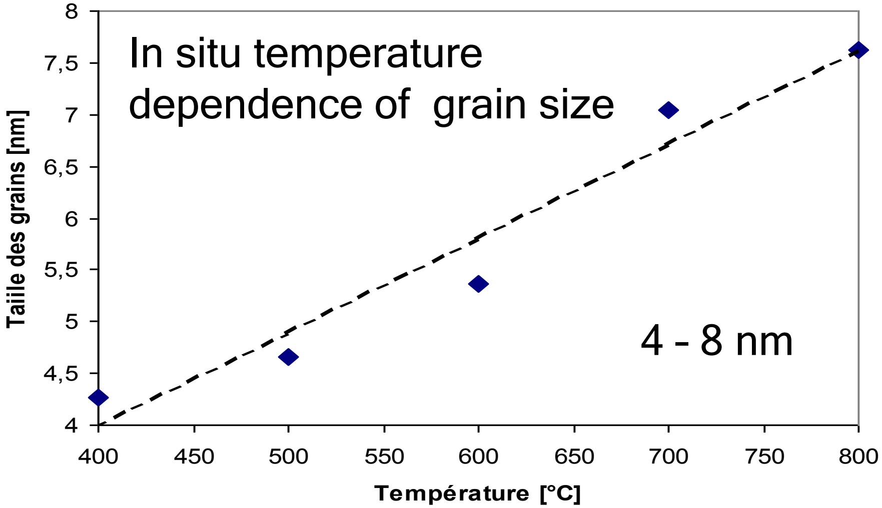


on composite NiO-8YSZ

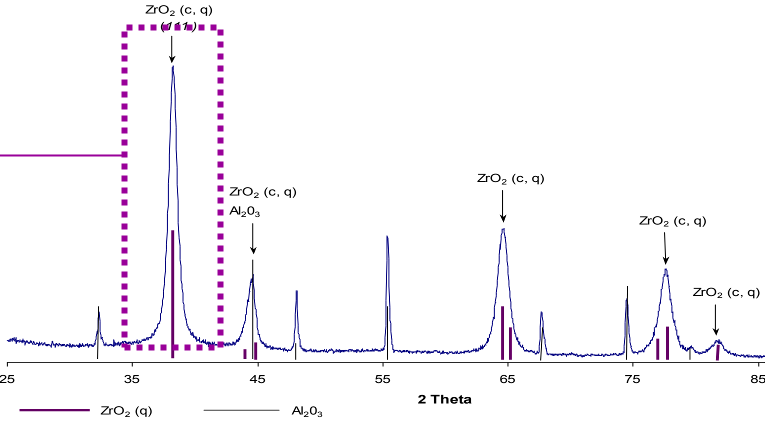
Crystallization of films and grain growth

Tetragonal zirconia annealed up to 800°C, 1h30’, in situ XRD



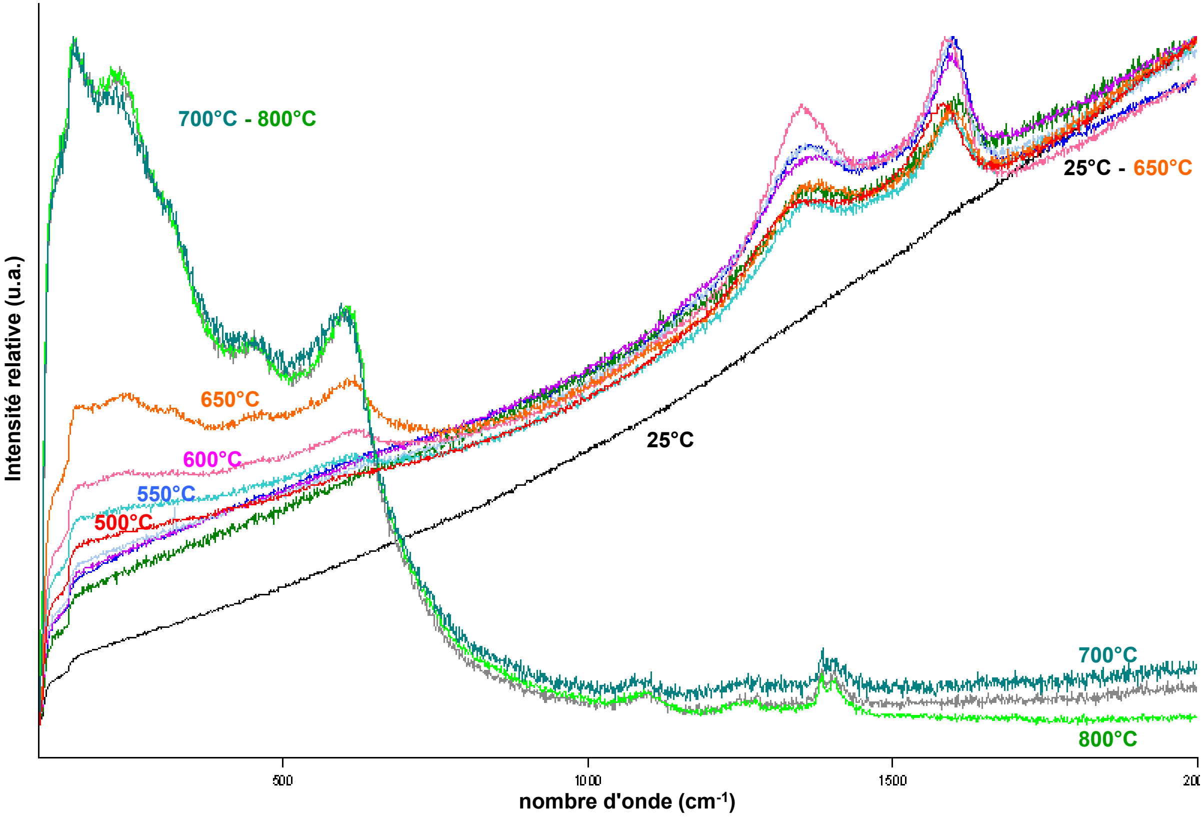


Crystallization at 500°C



Amorphous raw films

Temperature dependence of 8YSZ thin film
In situ Raman spectroscopy



T ≤ 650°C

Organic residues present in the film

T ≥ 700°C

Full decomposition of organic residues

- Cubic 8YSZ spectrum visible from 550°C.

Neagu R., Perednis D., Princivalle A., Djurado E., Surface and Coatings Technology 200 [24] (2006) 6815-6820
Neagu R., Perednis D., Princivalle A., Djurado E., Solid State Ionics 177 [19-25] (2006) 1981-1984
Neagu R., Djurado E., Ortega L., Pagnier T., Solid State Ionics 177 [17-18] (2006) 1443-1449

Conclusions …

- Investigation of ESD process parameters on the microstructure of doped zirconia films (substrate temperature, nozzle to substrate distance, flow rate) → Optimal ESD conditions for the synthesis of dense and nanostructured thin films of YSZ and TZP (300 nm in thickness).
- Determination of single phased tetragonal and cubic films and crystallization temperature (500-650°C) by *in situ* temperature dependence XRD and Raman spectroscopy

Outline

1 - Sonochemistry for the synthesis of controlled nanostructured oxide powders: zirconia and ceria-based oxides

» Ultrasonic Spray Pyrolysis (USP) process – DOE
» ZrO_2 - based powders: morphology and phase transitions
» Physico-chemical properties of CGO powders and sintering behavior
» USP advantages and disadvantages

2 – Electrostatic Spray Deposition for the design of dense and porous films

» Electrostatic Spray Deposition (ESD) process
» Optimization study of the ESD process to coat thin dense zirconia-based films
» Fundamental study of the formation of the ESD layer
» Advanced oxygen electrodes for SOC:
LSCF, CCO, LSM, LSM/YSZ, LPNO
» ESD advantages and disadvantages

FUNDAMENTAL STUDY OF THE FORMATION OF THE ESD LAYER

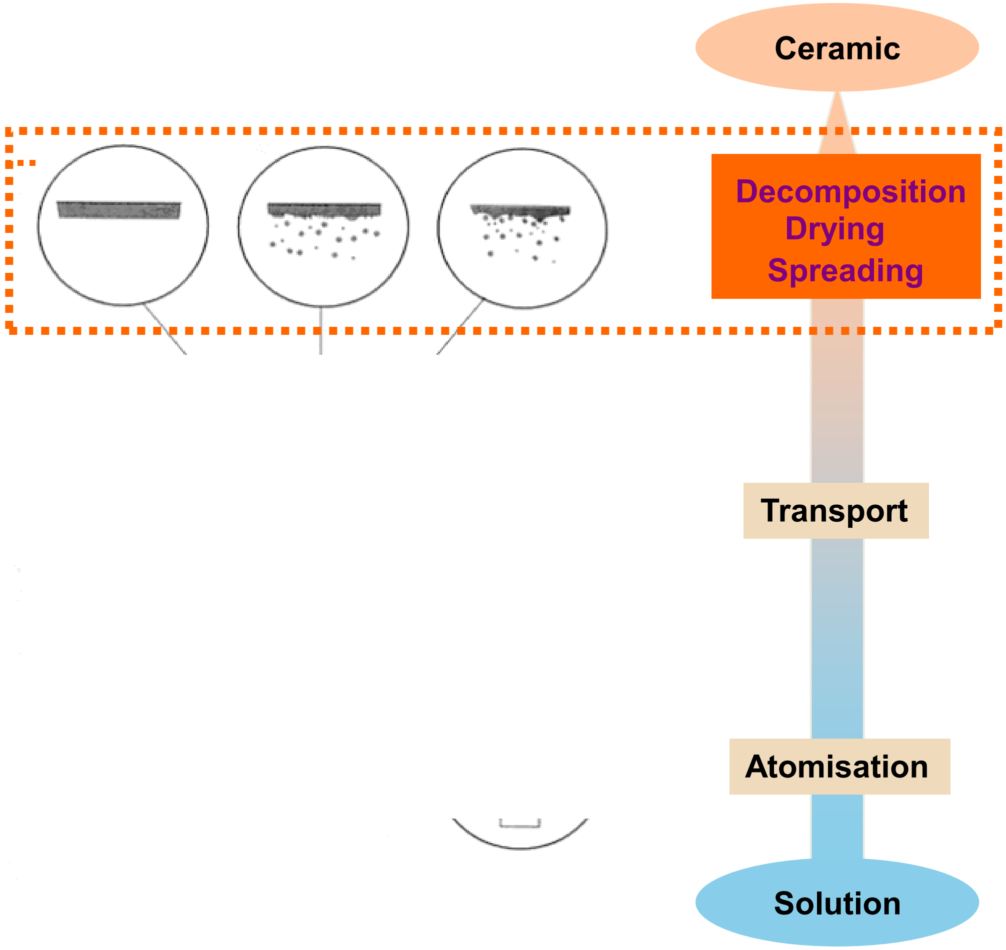
Two phenomena:

- Spreading and drying of droplets

Combined mechanism → dense (under)layer
spreading/evaporation/precipitation

- Film growth

Preferential landing → porous film



Ceramic

Decomposition
Drying
Spreading

Transport

Atomisation

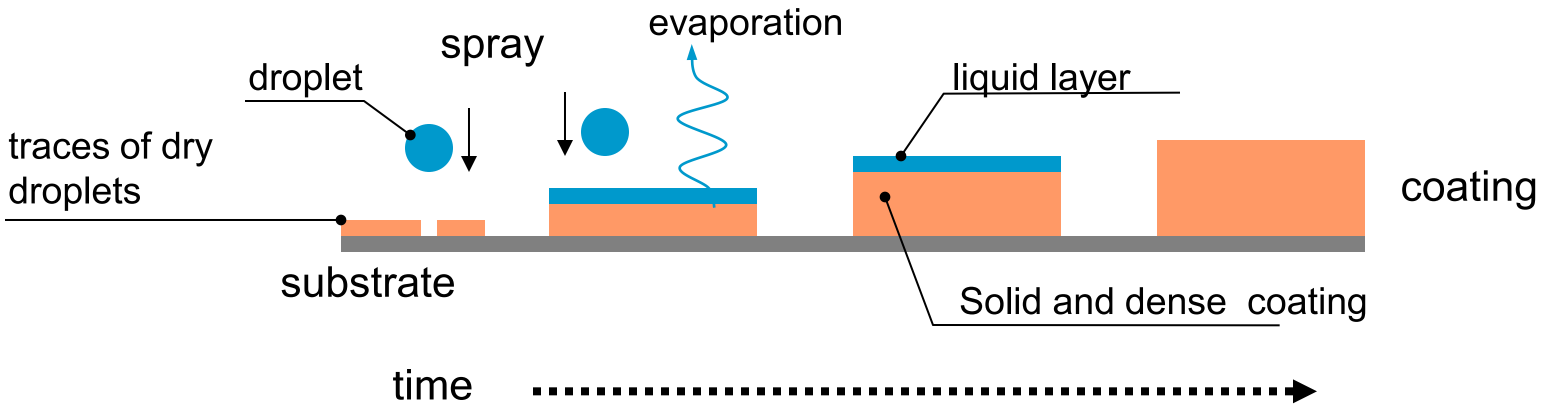
Solution

R. NEAGU et al., Chemistry of Materials, 17 [5] (2005) pp. 902-910

Growth of a dense layer

- In the ideal case (droplets of the same size, no particles)
- Coating only by spreading - evaporation - precipitation.

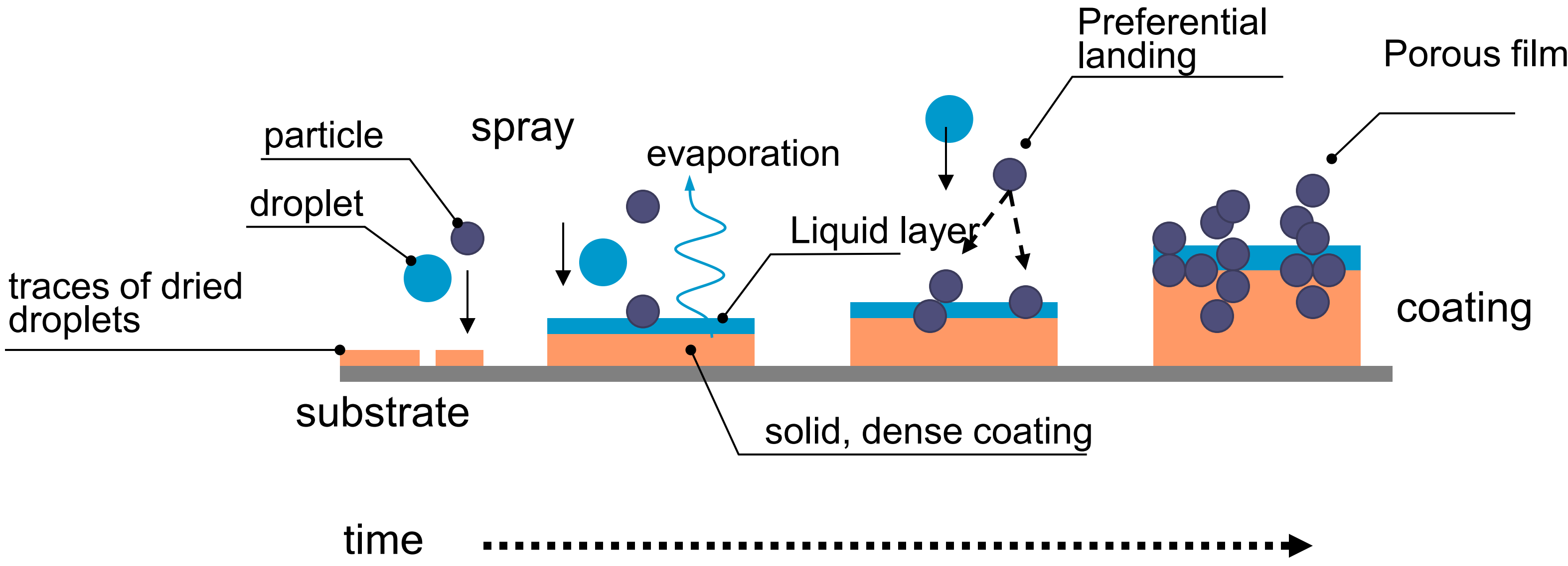
A perfect coating is expected



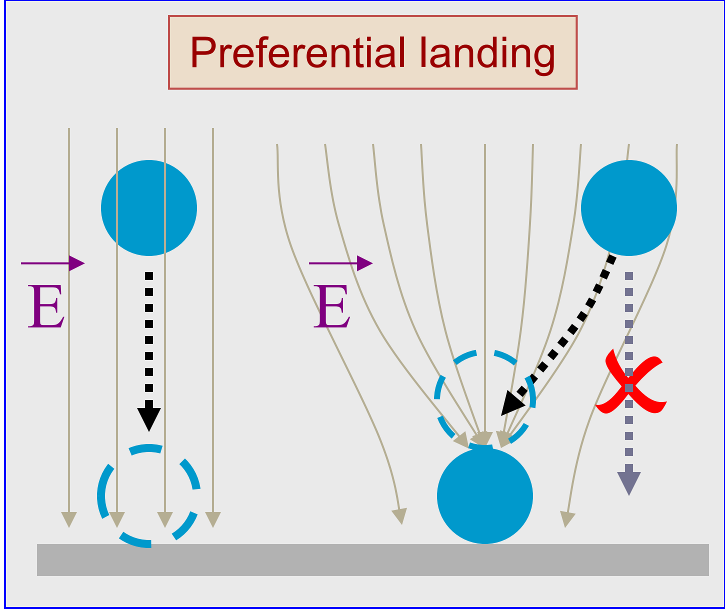
equilibrium impacting solvent/evaporating solvent

Growth of a porous layer

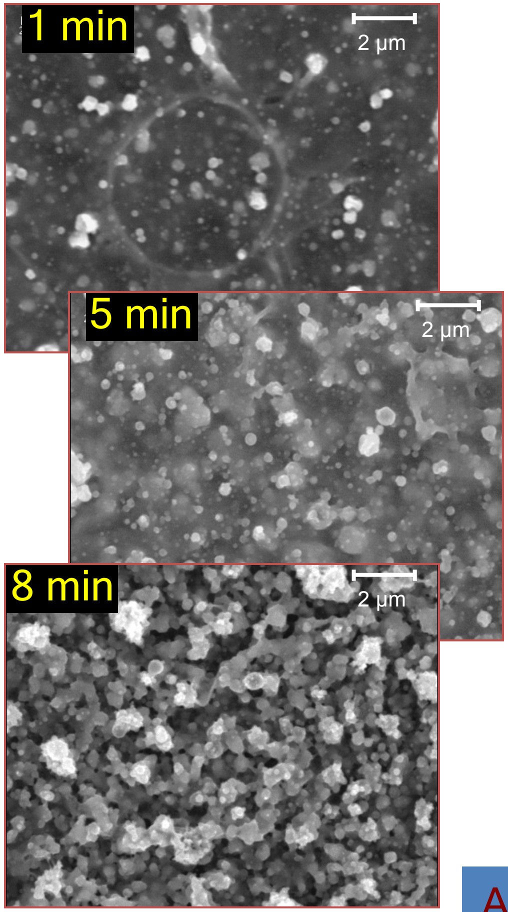
- For a multi-jet atomisation cone, (mixture of droplets and particles) the coating is consisted of 2 layers:
  - A dense sub-layer, formed by spreading- evaporation - precipitation of large droplets,
  - A porous layer above, due to preferential landing of particles and droplets.



Preferential landing



SEM observations:



400°C

Roughness of the coating increases versus time. The porous film is formed due to the impacting particles (drying droplets during the transport)

After a sufficient deposition time, the microstructure is no more the result of the evaporation - precipitation but the effect of the preferential landing.

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Advanced oxygen electrodes for SOC

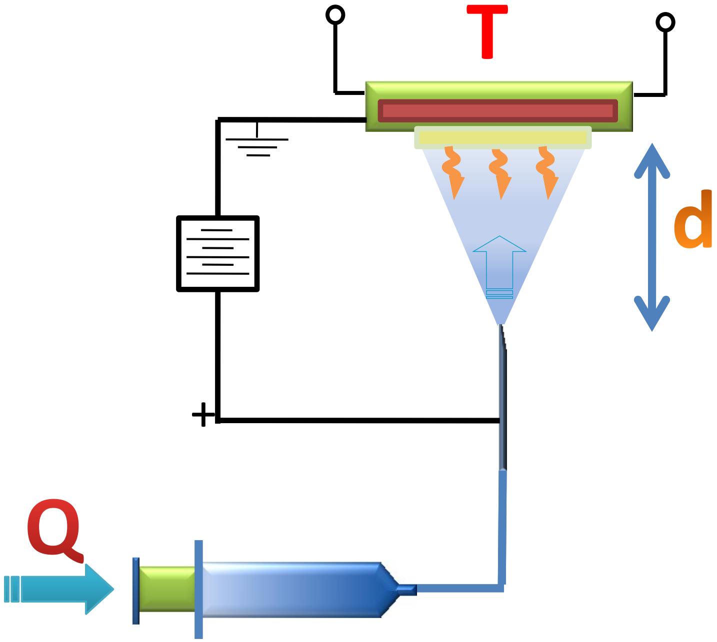
Porous LSCF6428 films

$Ce_{0.9}Gd_{0.1}O_{2-\delta}$ substrates

- Isostatic pressing (Praxair powders)
- Sintering @ 1450 °C / 4h in air
- ∅ = 18 mm /~1 mm thick
- $\rho_r \geq$ 95 %

$La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ solution

- $La(NO_3)_2$, $SrCl_2$, $Co(NO_3)_2$ and $Fe(NO_3)_2$ mixed in
  - EtOH:BC (1:2 vol.%)
  - EtOH:H_2O (1:5 vol.%)
- Concentration = 0.02 mol/L



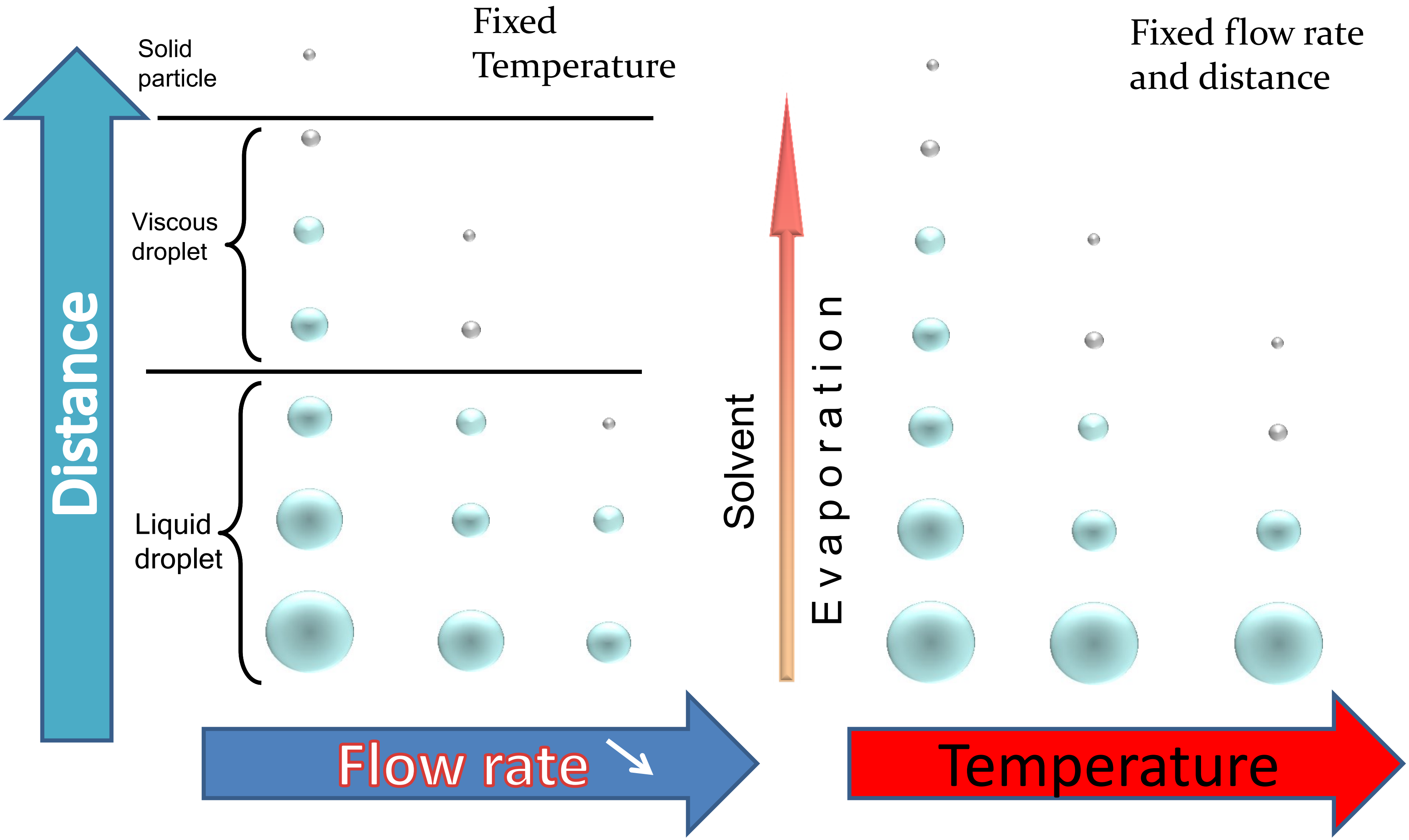
ESD variable parameters:

275 °C ≤ T ≤ 450 °C

15 mm ≤ d ≤ 58 mm

0.34 mL/h ≤ Q ≤ 1.59 mL/h

Droplet size



Fixed Temperature

Solid particle

Viscous droplet

Liquid droplet

Distance

Flow rate ↘

Solvent Evaporation

Fixed flow rate and distance

Temperature

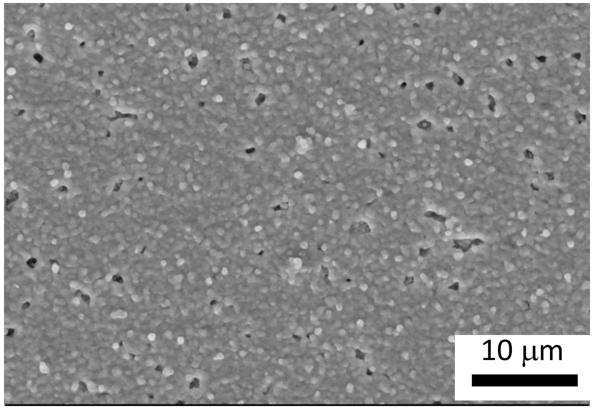
Influence of deposition parameters, ***Q***

T = 300 ºC
d = 30 mm

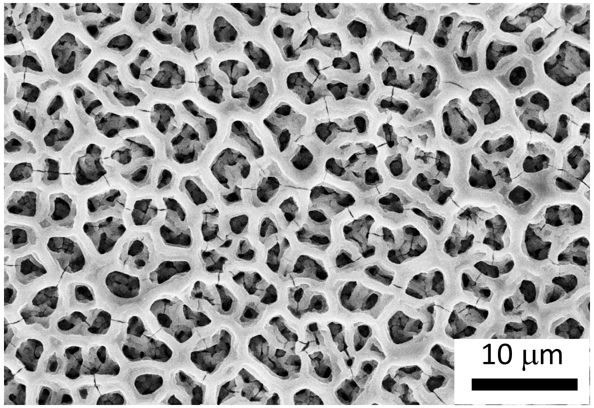
Flow rate ↗
droplet size ↗

$$droplet \propto \left(\frac{\rho \varepsilon_0 \boxed{Q^3}}{\gamma \sigma} \right)^{1/6}$$

0.34 mL/h



1.5 mL/h

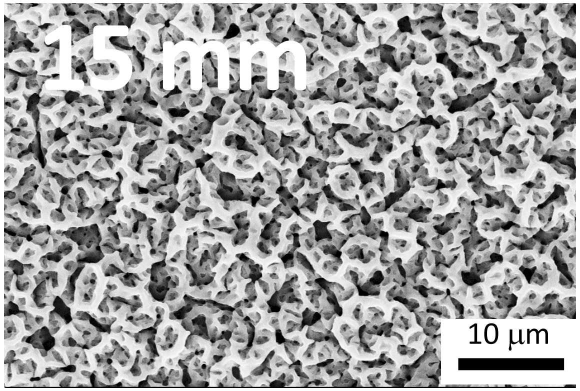


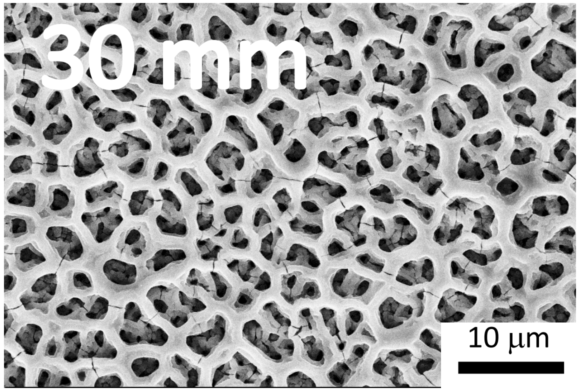
Flow rate, *Q*

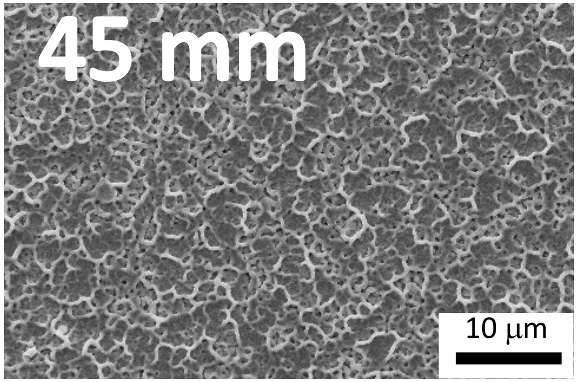
A. M. Gañan-Calvo, J. Davila and A. Barrero, *J. Aerosol Sci*, **28**, 249 (1997)

Influence of deposition parameters, *d*

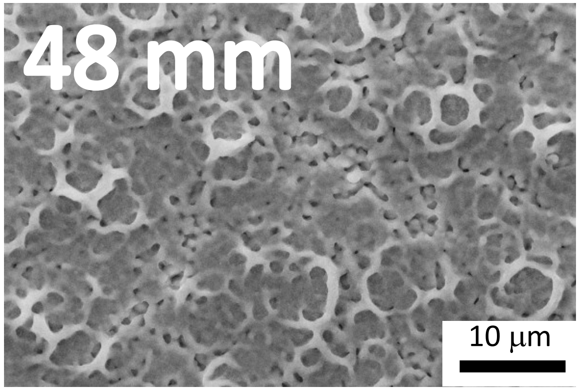
T = 300 °C
Q = 1.5 mL/h

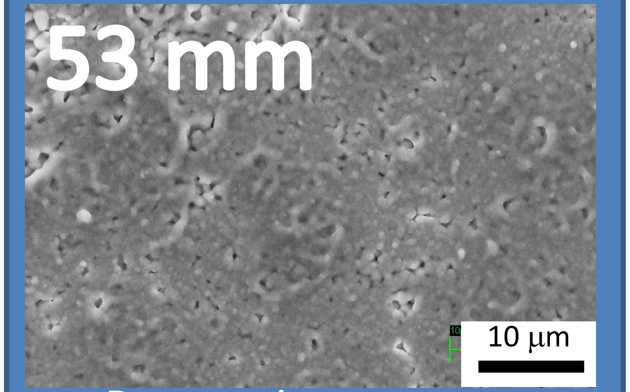




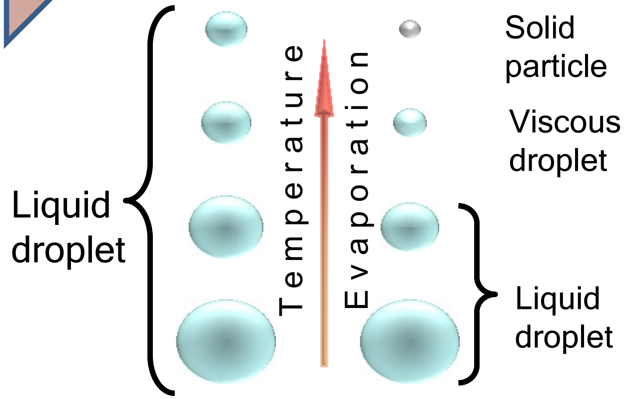


Distance, *d*





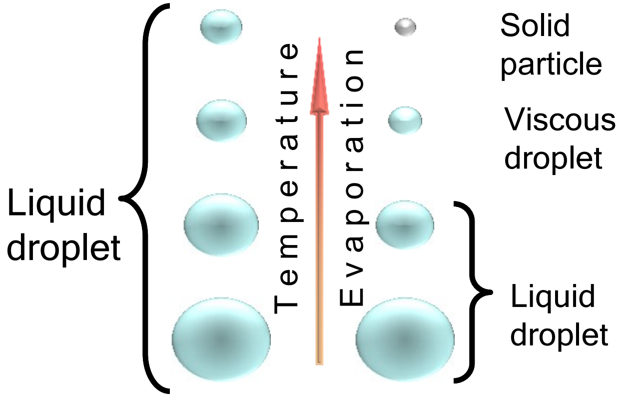
Dense microstructure

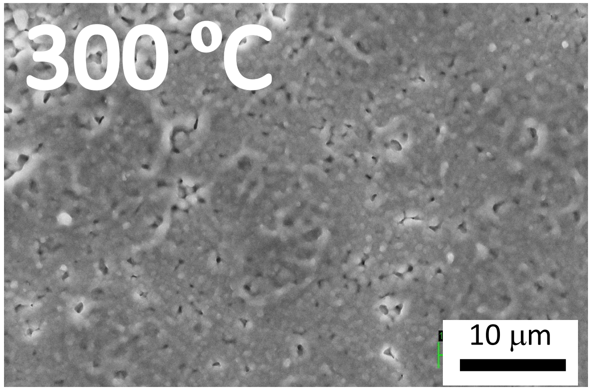


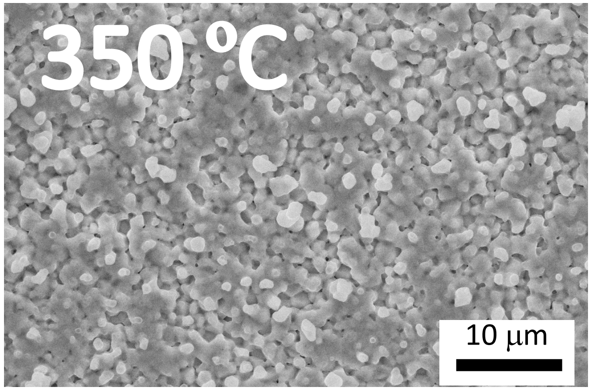
Influence of deposition parameters, *T*

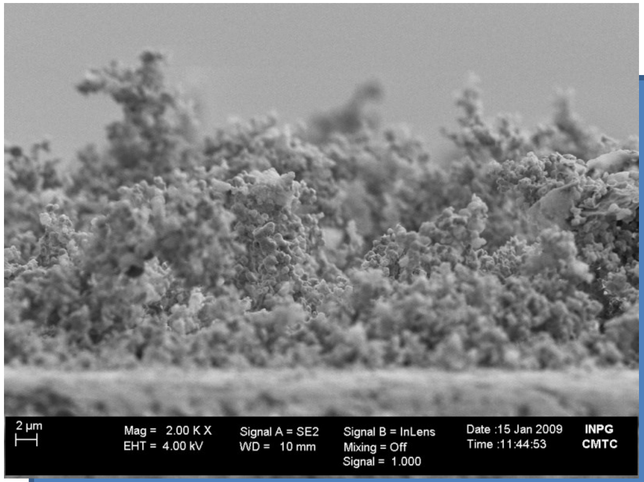
d = 53 mm
Q = 1.5 mL/h

Temperature ↗
droplet size ↘









Coral microstructure

Temperature, *T*

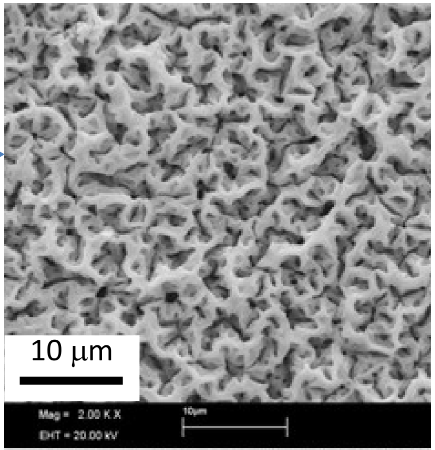
Heat Treatment

Annealing for 2h in air

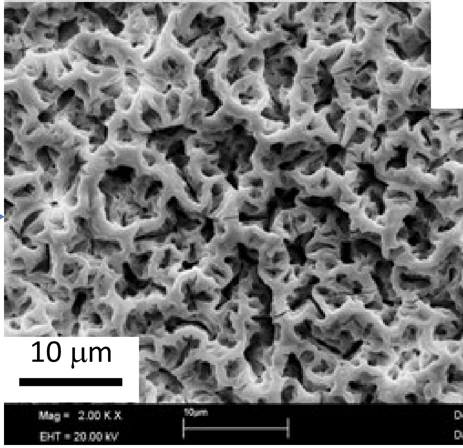
Δ - CGO
* - LSCF

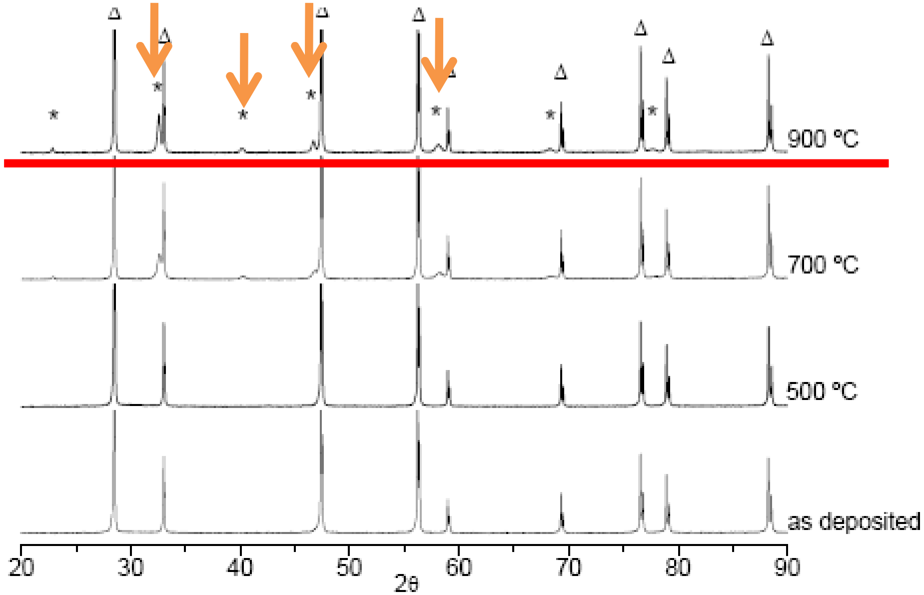
T = 300 °C
d = 15 mm;
Q = 1.5 mL/h

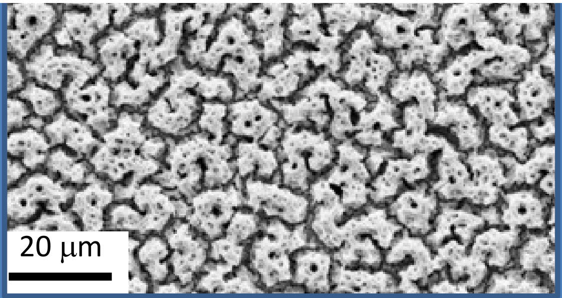
1 h



2 h



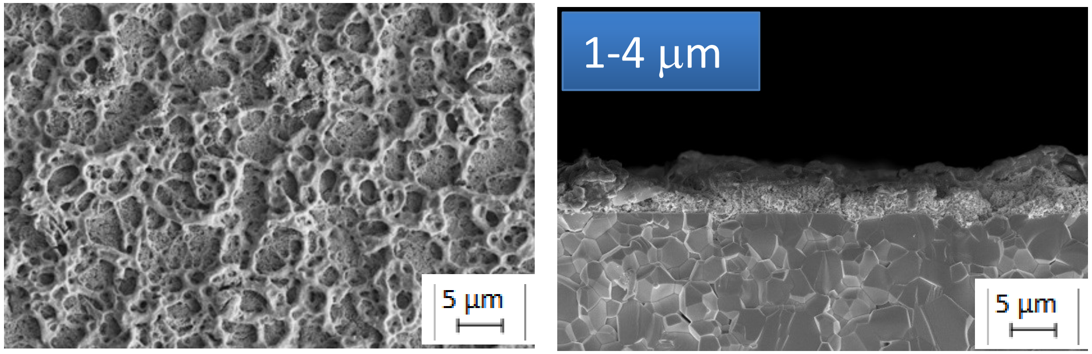




Pillar microstructure

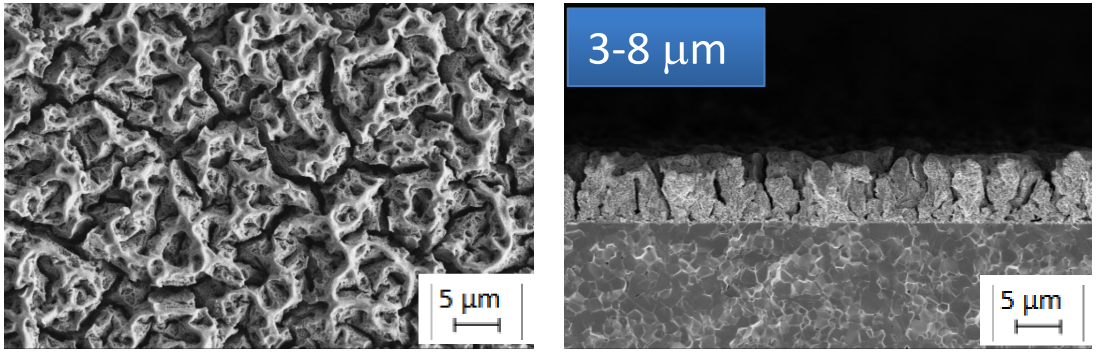
Microstructure vs. Electrochemical Performance

Dense



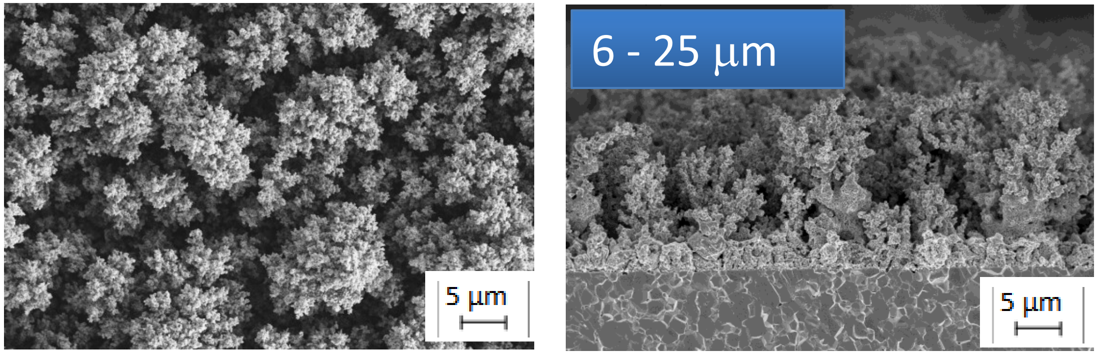
Parameters	
T **/ °C**	300
Q **/ mL/h**	1.59
d **/ mm**	25 - 35
Film thickness (µm)	1 – 4

Columnar



Parameters	
T **/ °C**	300 - 350
Q **/ mL/h**	1.5 – 1.59
d **/ mm**	15 - 20
Film thickness (µm)	3 – 8

Coral

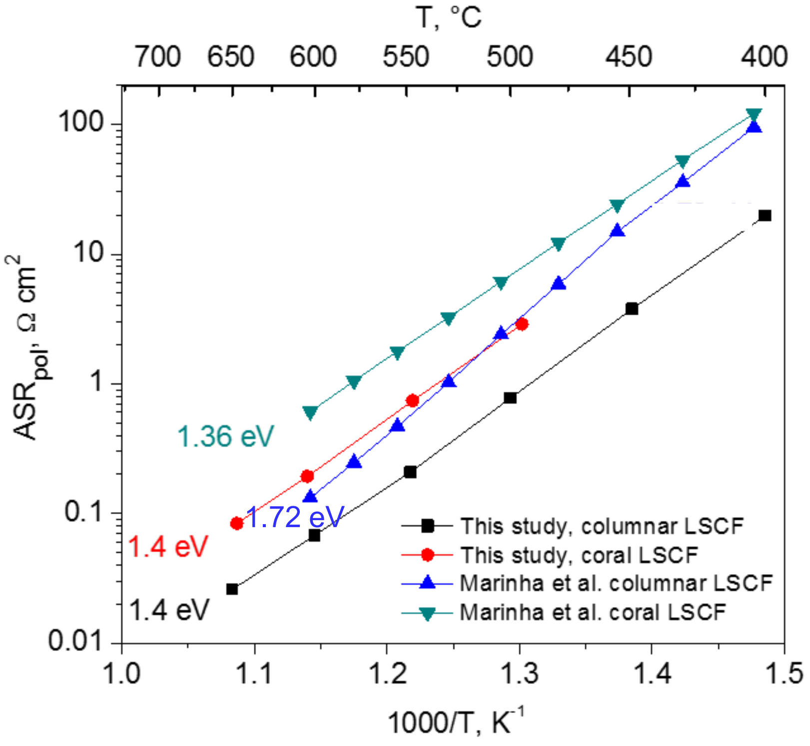


Parameters	
T **/ °C**	375 – 450
Q **/ mL/h**	1.02 – 1.59
d **/ mm**	35 - 58
Film thickness (µm)	6 – 25

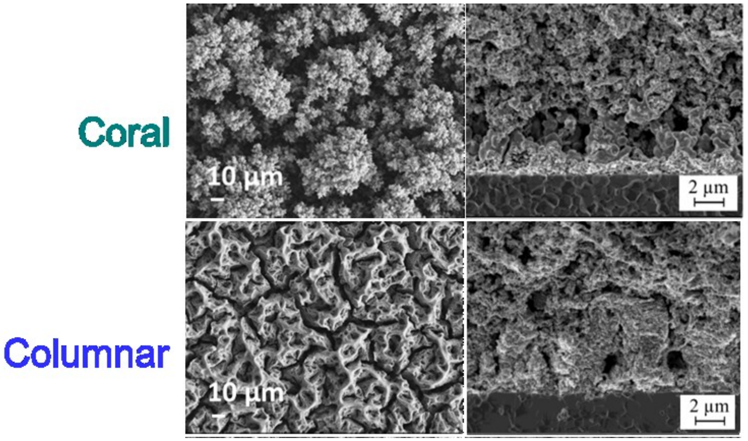
Influence of microstructure on LSCF electrodes

Area Specific Resistance

$$ASR_{pol} = \frac{R_{chem}}{2} \times Area_{cathode}$$



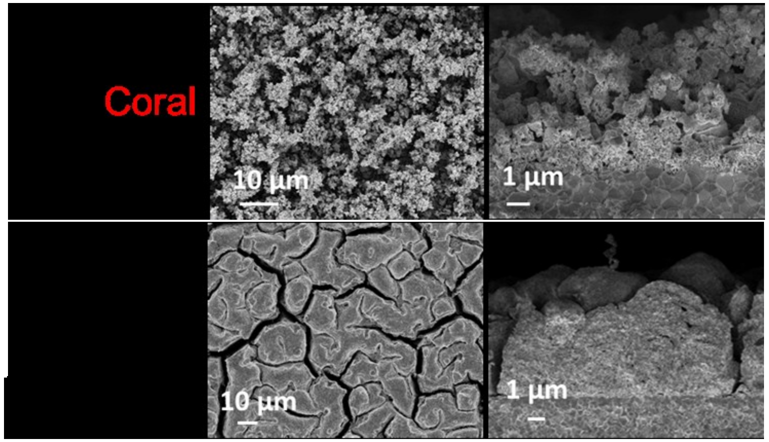
Symmetrical cell, OCV



a = $16\ \mu m^{-1}$

a = $8\ \mu m^{-1}$

Marinha, D., PhD Thesis 2010 Grenoble INP.



a = $19\ \mu m^{-1}$

Celikbilek O., PhD Thesis 2016 Grenoble INP.

Influence of microstructure in LSCF columnar electrodes

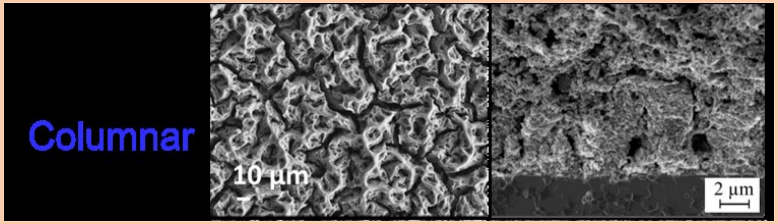
CCL by SP, KIT Karlsruhe

Static ESD

900 °C/2h, air

4-5 µm columnar width

ASR$_{pol}$ = 0.13 Ω cm^2 at 600°C



Marinha, D., PhD Thesis 2010 Grenoble INP.

a = <u>8 µm^{-1}</u>

D. Marinha et al, Chem. Mater. 23 [24] (2011) 5340-5348

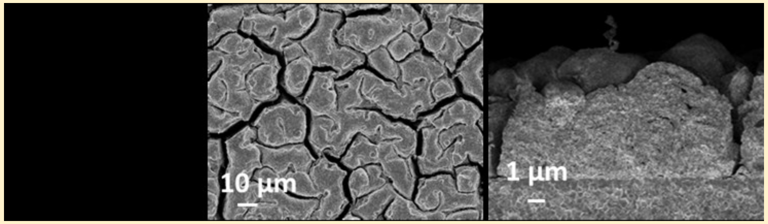
CCL by SP, LEPMI

Moving ESD

800 °C/2h, air

10-15 µm columnar width

ASR$_{pol}$ = 0.06 Ω cm^2 at 600°C, the best in the literature



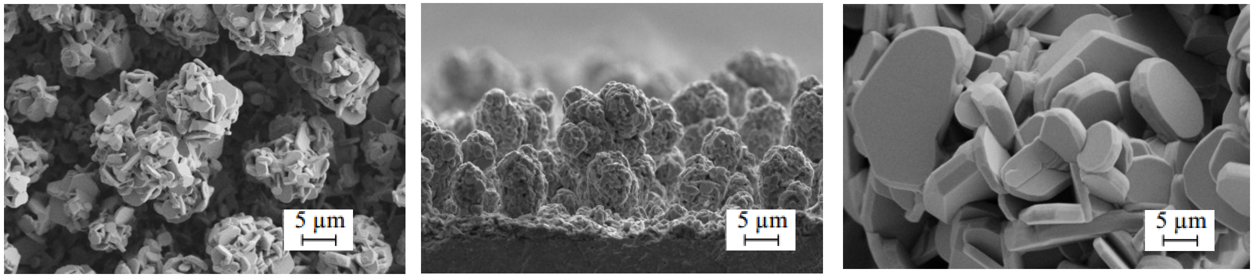
Celikbilek O., PhD Thesis 2016 Grenoble INP.

a = <u>19 µm^{-1}</u>

O. Celikbilek et al, J. Power Sources 333 (2016) 72-82

Fabrication by ESD of advanced oxygen electrodes for SOFC

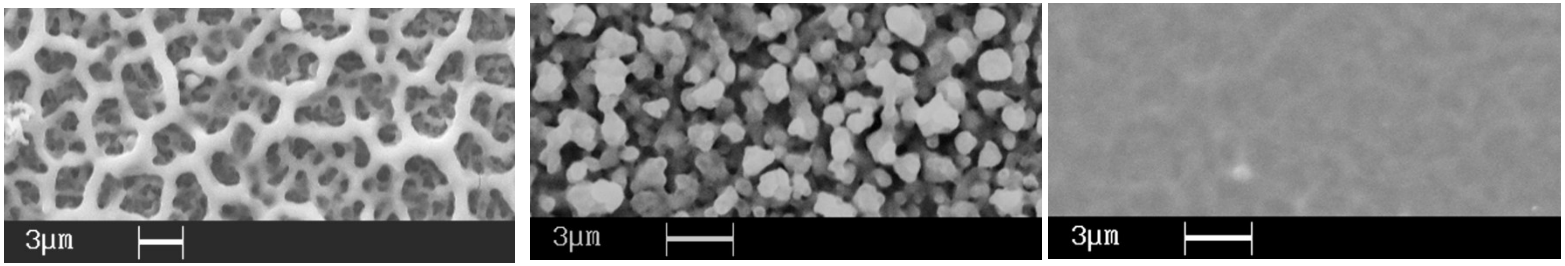
$Ca_3Co_4O_{9+\delta}$



E. Djurado et al., *Solid State Ionics* **2016**, *286*, 102.

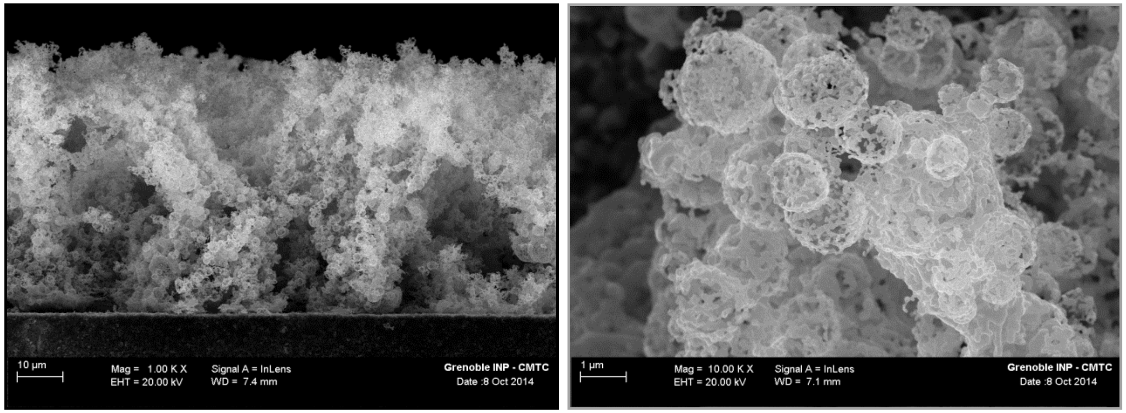
$(La_{0.85}Sr_{0.15})_{0.95}MnO_{3-\delta}$ (LSM)

Composite: LSM + YSZ



A. Princivalle, et al., *Chemistry of Materials*, **2005**, *17*, 1220..

$La_{2-x}Pr_xNiO_{4+\delta}$



R. Sharma, et al., *Mater. Chem. A, **2016**, 4,12451.*

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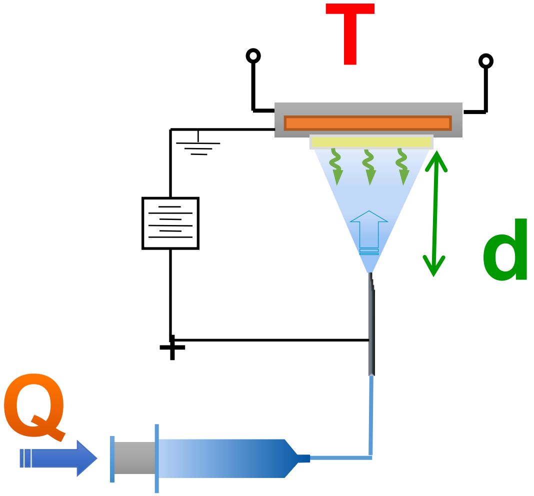
» USP advantages and disadvantages

2 – Electrostatic Spray Deposition for the design of dense and porous films

» Electrostatic Spray Deposition (ESD) process
» Optimization study of the ESD process to coat thin dense zirconia-based films
» Fundamental study of the formation of the ESD layer
» Advanced oxygen electrodes for SOC:
LSCF, CCO, LSM, LSM/YSZ, LPNO
» ESD advantages and disadvantages

ESD advantages and disadvantages

- ✓ Tailored morphology and composition
- ✓ Porosity control independently of grain size
- ✓ Good adhesion
- ✓ Simple and low cost process
- ✓ Deposition in air
- ✓ Large choice of precursors
- ✓ Low deposition temperature
- ✓ Good reproducibility
- ✓ Double injection (composite)



- ✓ Large number of dependent parameters
- ✓ Thermal treatment after deposition to get crystallization
- ✓ Interpenetration of layers

The
END

Thank you for your attention

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