

# Screen-printed $\text{La}_{0.1}\text{Sr}_{0.9}\text{TiO}_{3-\delta}$ - $\text{Ce}_{1-x}\text{Gd}_x\text{O}_{2-\delta}$ anodes for SOFC application

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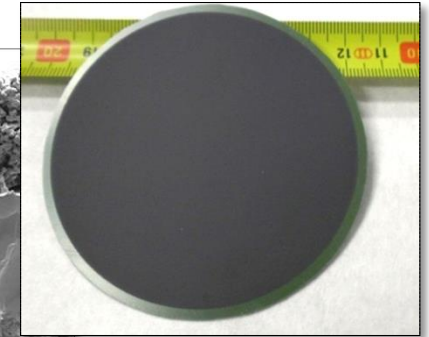
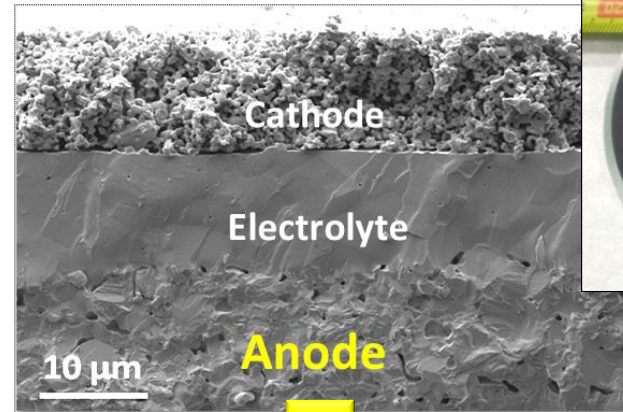
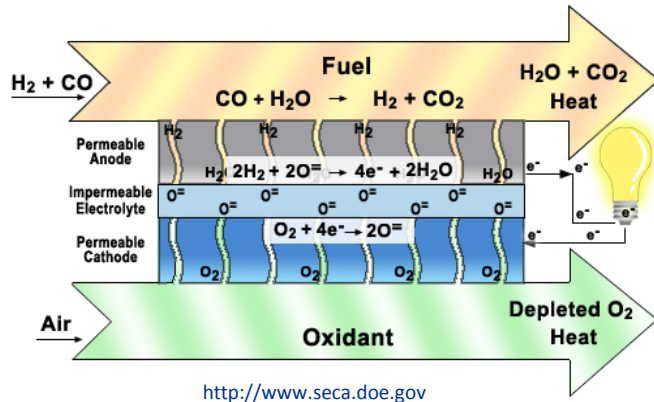
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# Motivation

## Solid Oxide Fuel Cell



## La-doped SrTiO<sub>3</sub> (LST):

- ❖ doping flexibility,
- ❖ good dimensional and chemical stability,
- ❖ TEC comparable with that of ZrO<sub>2</sub>-based electrolyte,
- ❖ high electronic conductivity,
- ❖ tolerance for sulfur poisoning and carbon deposition.

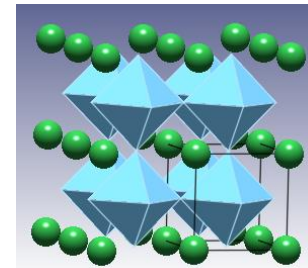
Composite anode with Gd or Sm-doped CeO<sub>2</sub> (GDC or SDC) to increase electrochemical performance

Most common anode material:

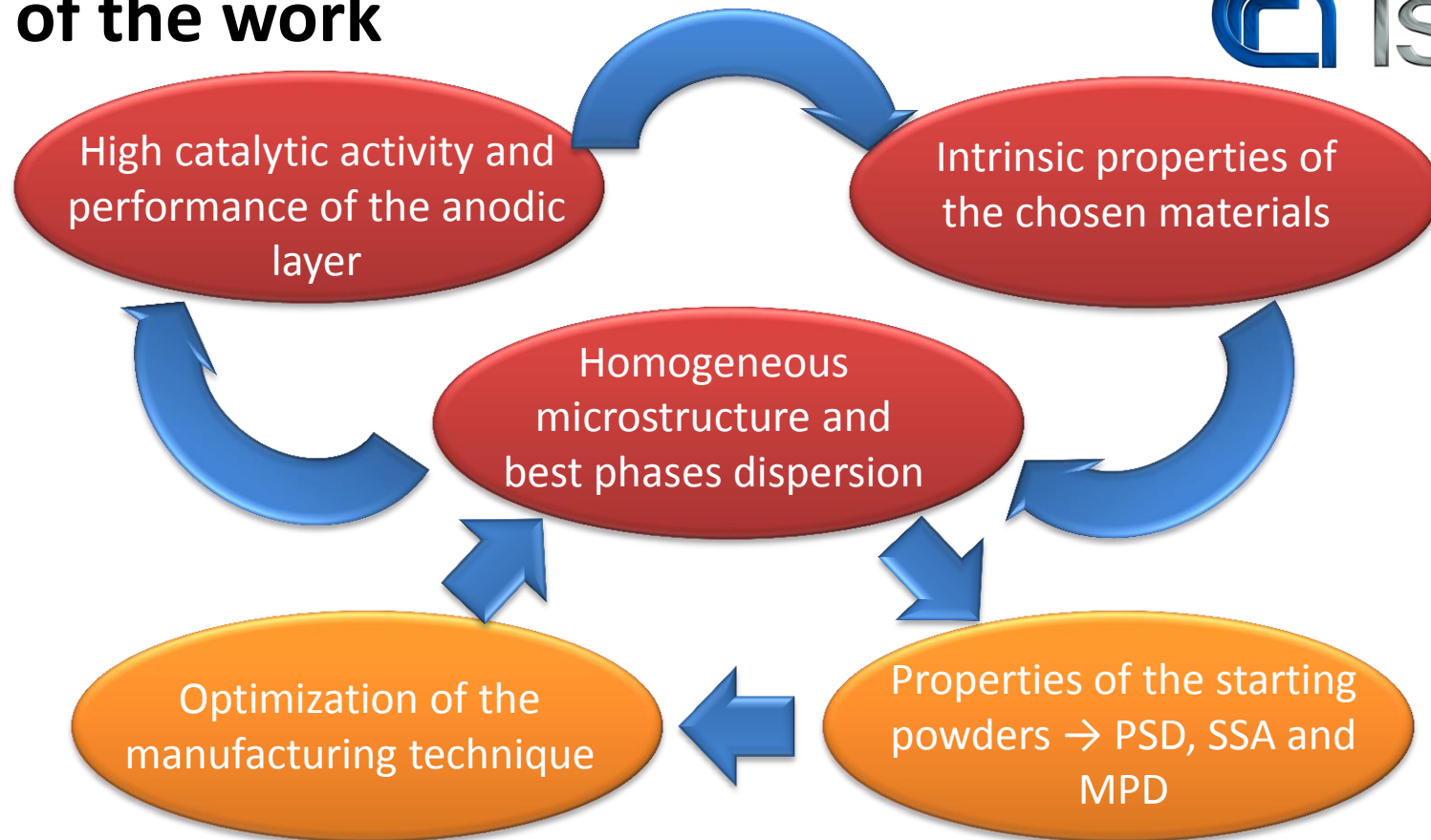
## Ni-based Cermet

it still faces high level of sintering, poor redox stability and high sensitivity towards carbon deposition and sulphur poisoning

## Perovskite materials



# Aim of the work



**Establish an optimized reliable procedure for the production of screen printed LST-GDC anodes in order to fabricate well performing anode.**

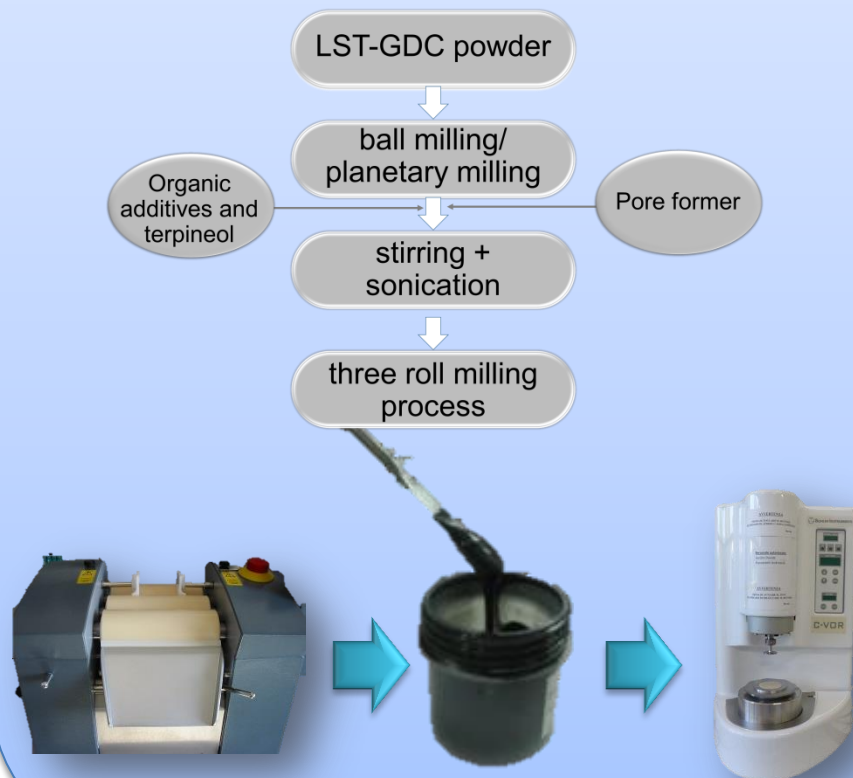


**Evaluate effects of different milling techniques to prepare the inks onto the microstructure and electrochemical performance of the composite anode**

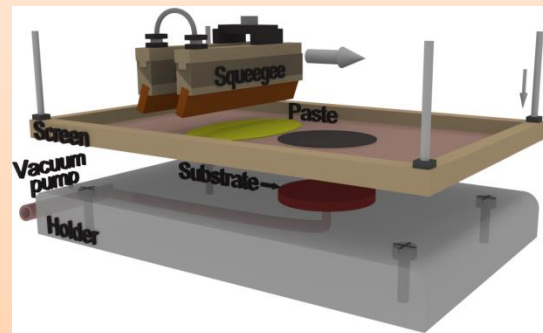
# Experimental

## Inks production & characterization

- Choice of the amount and nature of deflocculant
- Evaluation of conventional ball milling and planetary milling processes eventually coupled with a sonication
- Thermal & rheological characterization



## Screen printing



LST-GDC electrodes ( $\phi=16$  mm) were screen printed onto YSZ pellets to obtain symmetrical cells: processing parameters adjusted to obtain 15  $\mu\text{m}$  thick electrodes. Sintering at 1100°C x 5h.



## Characterization of symmetrical cells

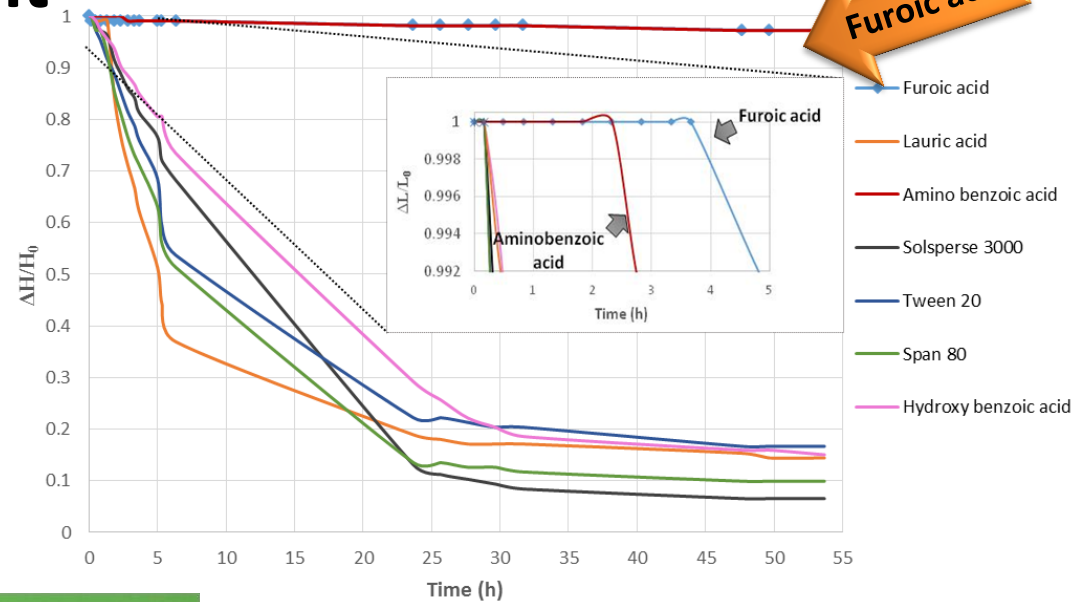
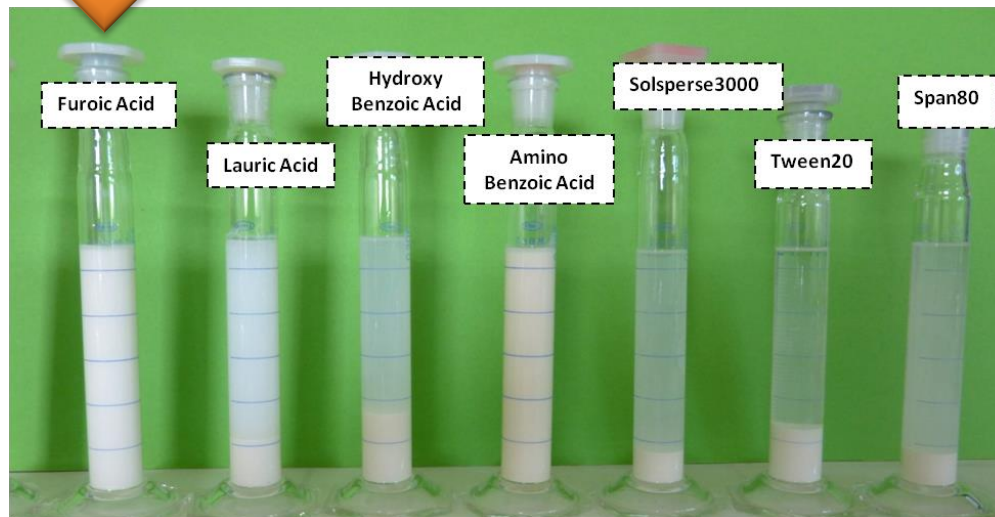
Microstructural and electrochemical characterization



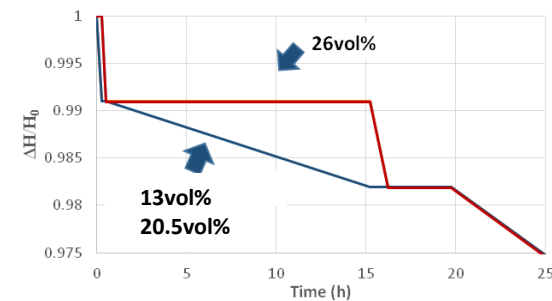
# Results:

## choice of the deflocculant

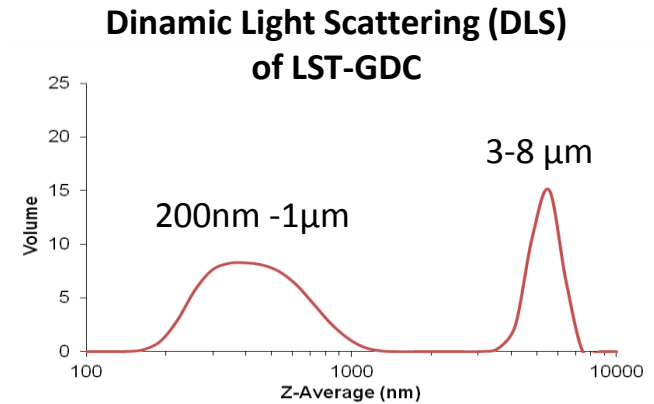
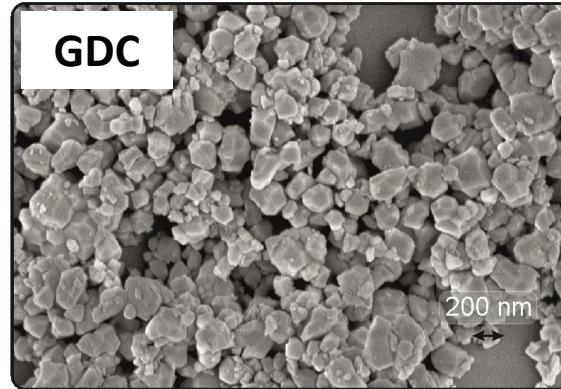
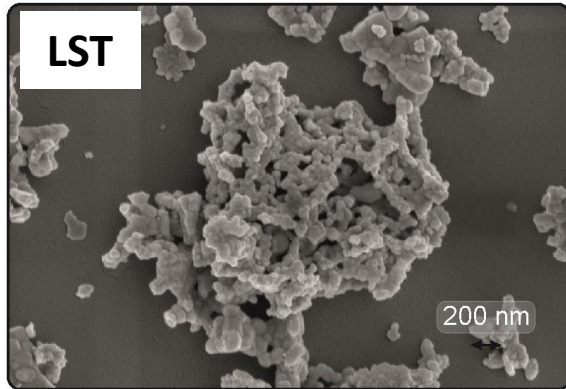
Best dispersing effectiveness achieved using the **heterocyclic compounds** of medium size and with a marked **Brosted-Lewis basic behavior**



Optimization of the **deflocculant concentration** (=26 vol% in respect to the powder)



# Results: influence of the milling treatment



To break down the aggregates....

**1. Conventional  
ball milling**



**2. Planetary  
Milling**



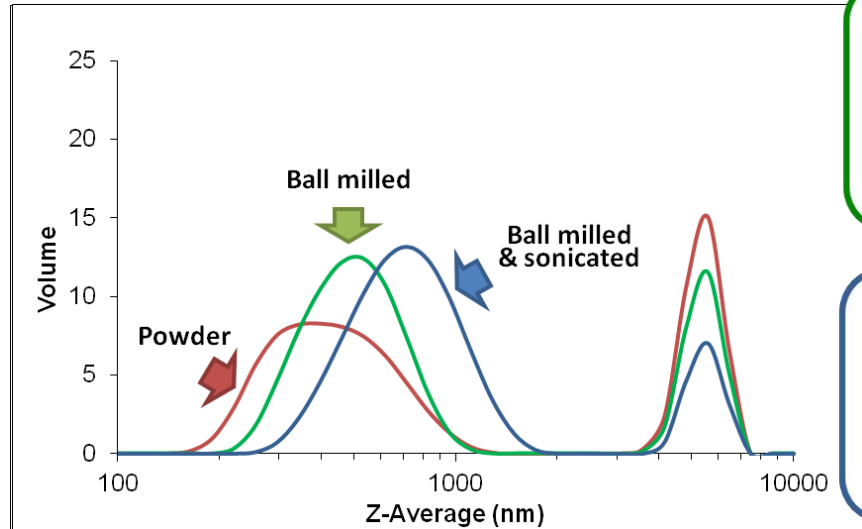
**Sonicating  
probe**



**How does the particle  
distribution change using the  
different treatments?**

# Results:

## influence of the milling treatment



Conventional  
ball milling



➤ 1<sup>st</sup> peak narrower

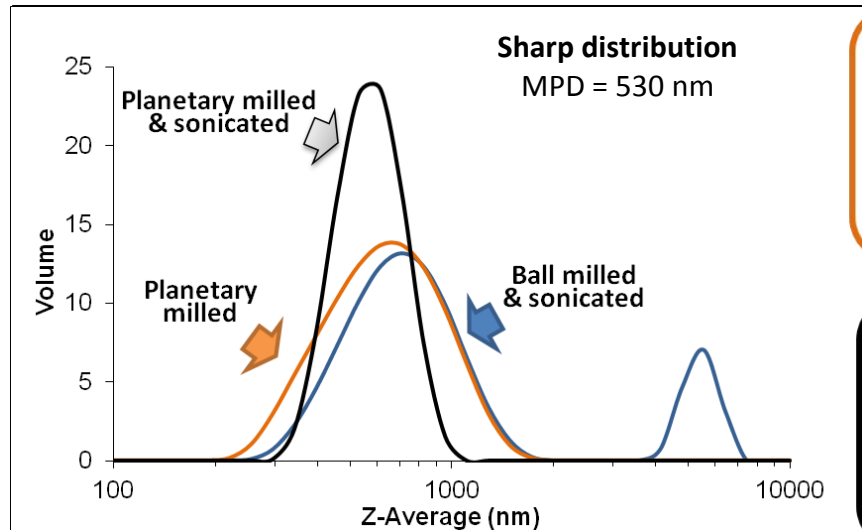
➤ ↓ volume large aggregates



Sonicating  
probe



Trend more  
pronounced



Planetary  
Milling



Elimination of the  
large aggregates

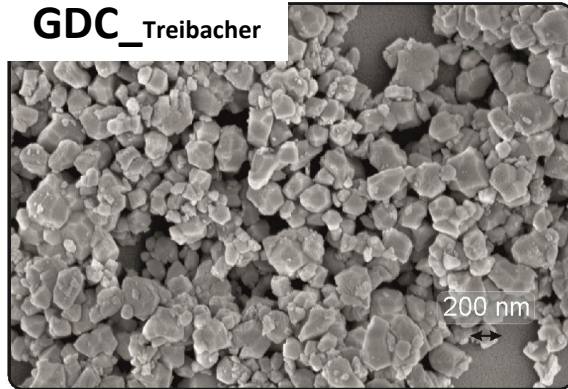


Sonicating  
probe

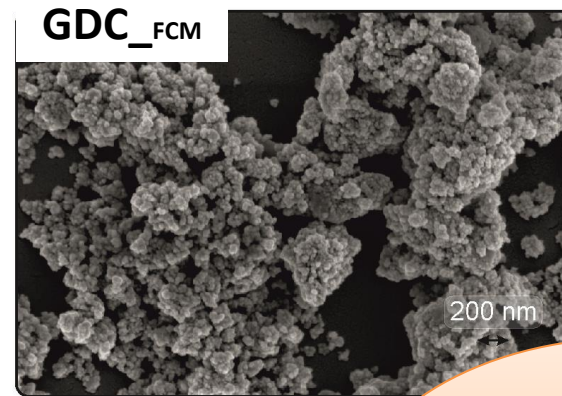
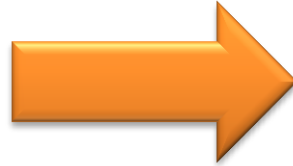


# Results:

## influence of the specific surface area

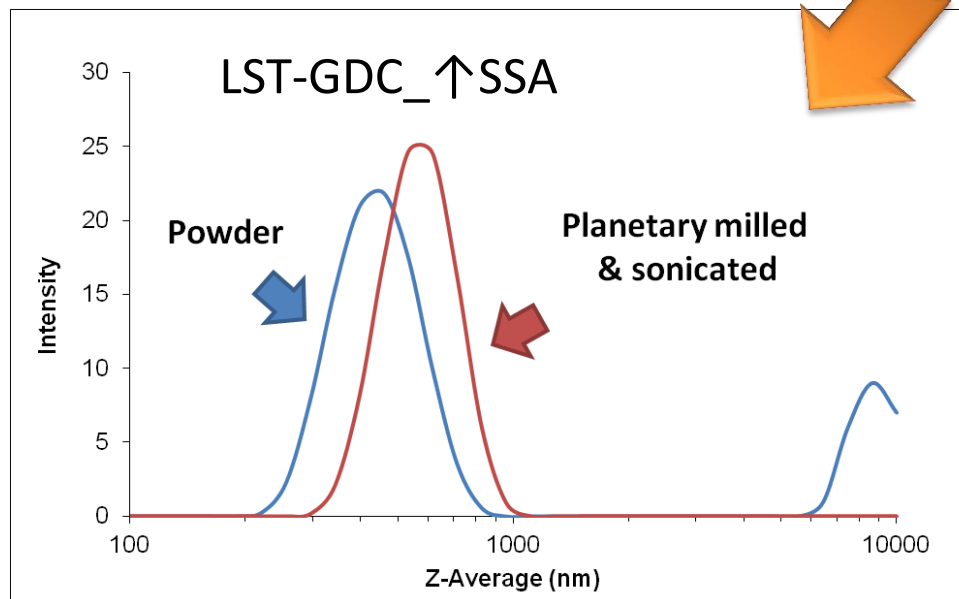


SSA = 9.10 m<sup>2</sup>/g



SSA = 36.5 m<sup>2</sup>/g

Higher SSA to increase  
the active surface



**Monomodal  
distribution**  
MPD = 570 nm



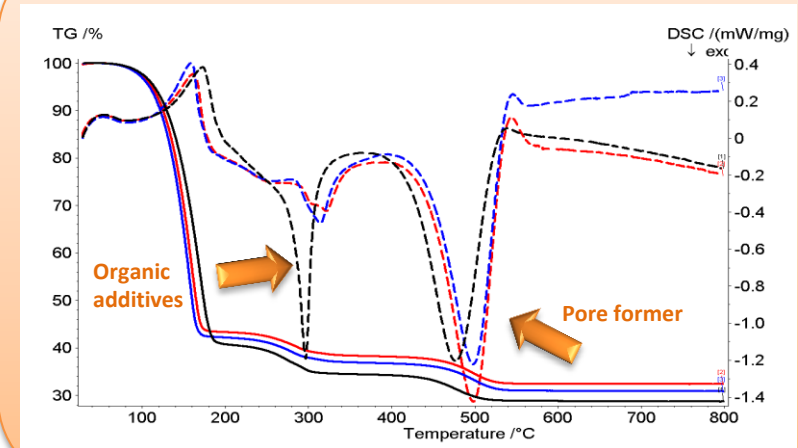
# Results:

## Inks formulations & characterizations

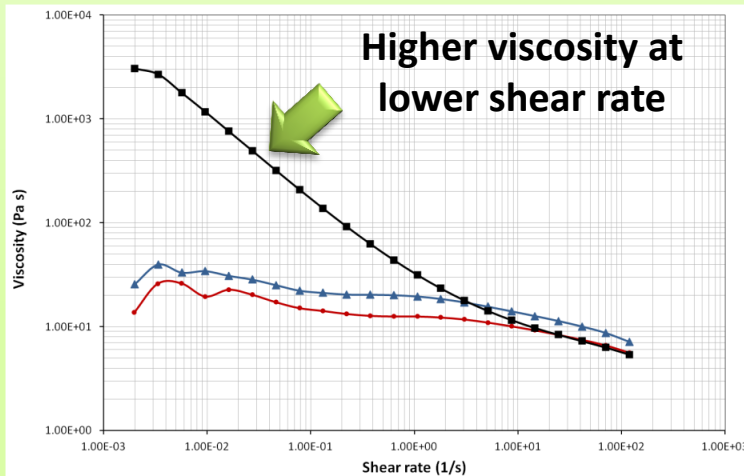
Vol %	LST-GDC	LST-GDC mill	LST-GDC ↑SSA
SLT	3.39	3.36	3.16
GDC	3.39	3.36	3.16
Solvent	82.61	81.79	77.03
Dispersant	2.14	3.11	8.74
Binder	5.57	5.51	5.19
Pore former	2.90	2.87	2.71

Re-optimization of the deflocculant amounts through analyses of the particle size distribution of suspensions

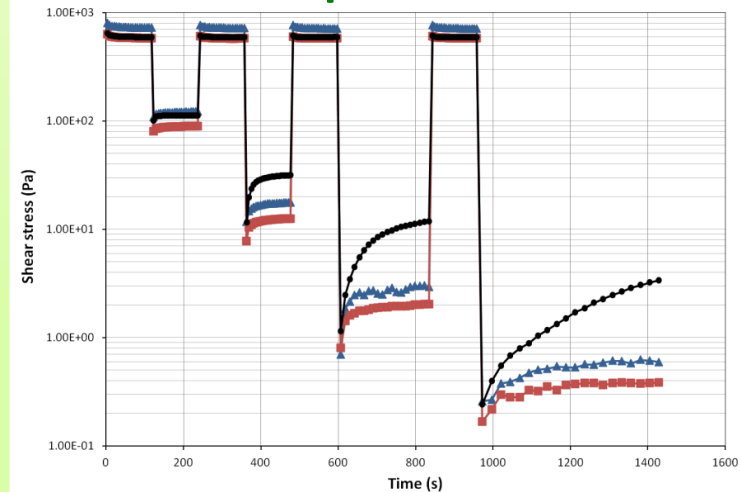
### Thermal behaviour



### Flow curves

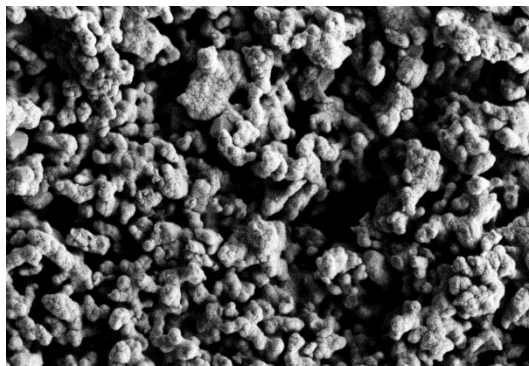
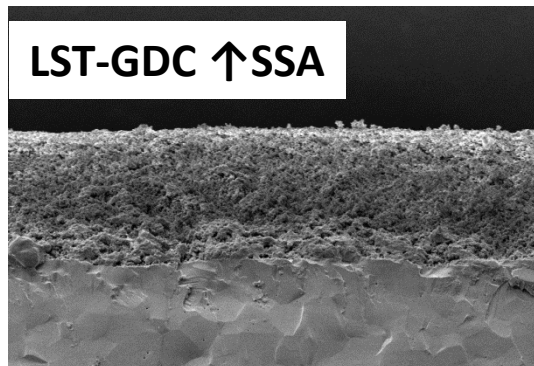
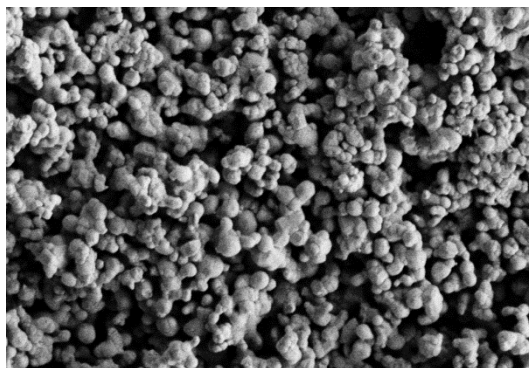
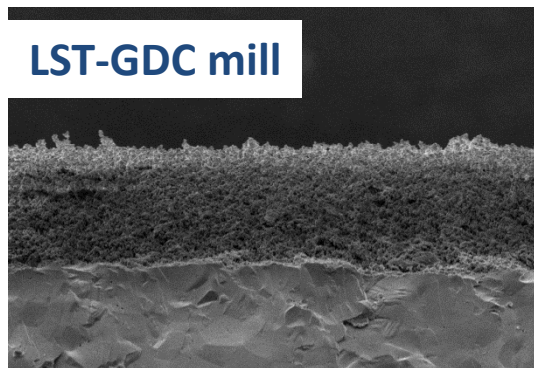
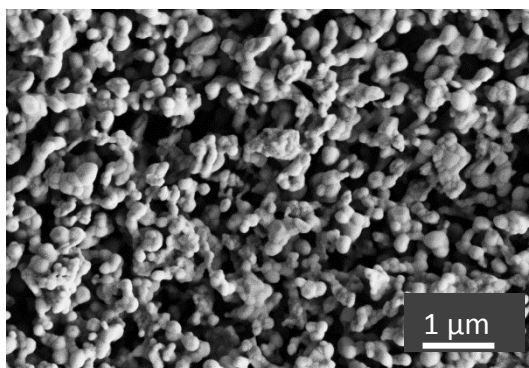
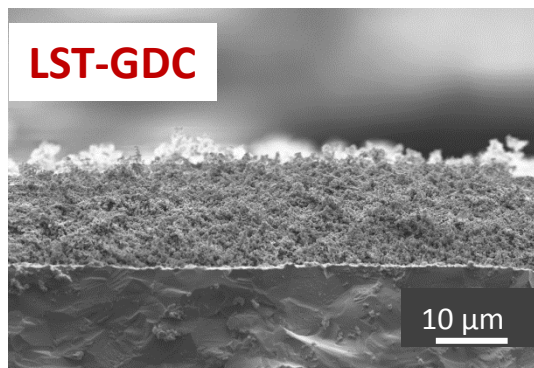


### Thixotropic behaviour



# Results:

## Microstructural characterization



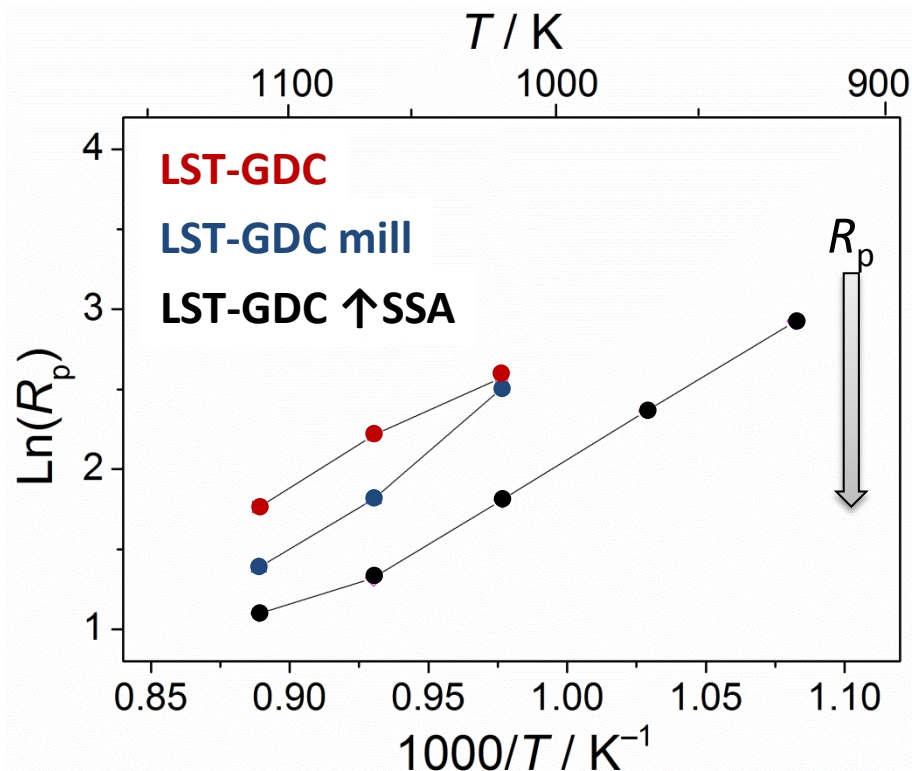
**Similar microstructures** with a well-leveled surface even in the case of the highly viscosity ink

	Porosity (vol %)	Organics in the green layers (vol %)
<b>LST-GDC</b>	56 ± 1	58.4
<b>LST-GDC mill</b>	60 ± 3	63.1
<b>LST-GDC ↑SSA</b>	68 ± 2	72.4

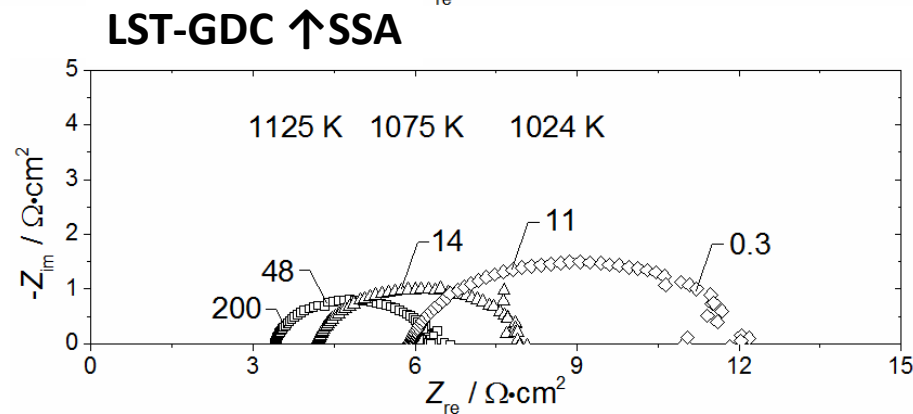
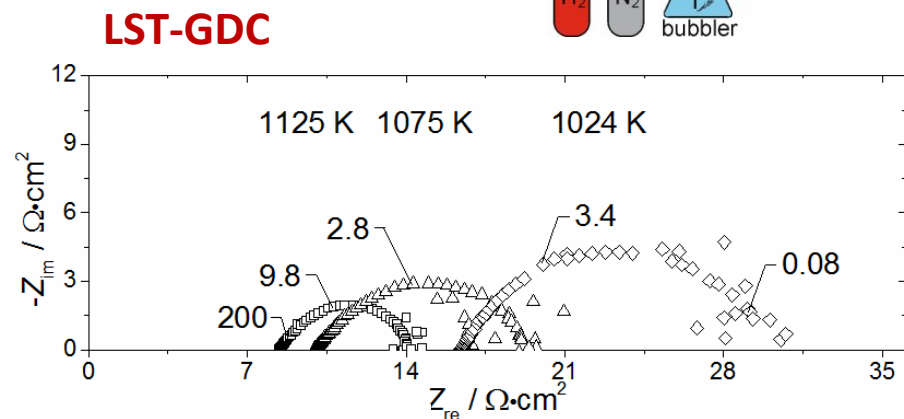
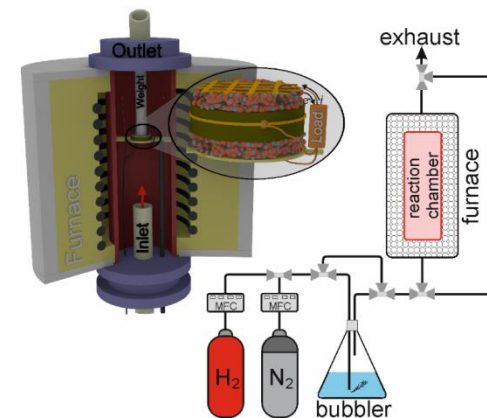
**High values of porosity** → in accordance with the vol % of the organics present in the different anodic layers.

# Results:

## Electrochemical characterization



The symmetrical cell with LST-GDC↑SSA shows significantly improved performance



# Conclusions

The influence of the processing parameters on the microstructures and electrochemical behavior of screen printed LST-GDC anodes was evaluated. In particular :

- The deflocculant amount must be adjusted when a powder milling treatment is implemented into the process to obtain well-disperse and homogenous suspension.
- Planetary milling coupled with sonication treatment results the best procedure to produce monodispersal and homogeneous inks.
- The milling treatment does not affect so much the thermal and reological behaviour of the resulting inks as well as the microstructures of the sintered anodes BUT improves the electrochemical performances.
- The use of GDC with an higher SSA in combination with the optimized milling treatment leads to inks with slightly different thermal and reological properties BUT with a significant improvement of the performance.

**Other than the intrinsic properties of the electrodic materials, the production process plays a critical role to implement the performance of an electrode!!**

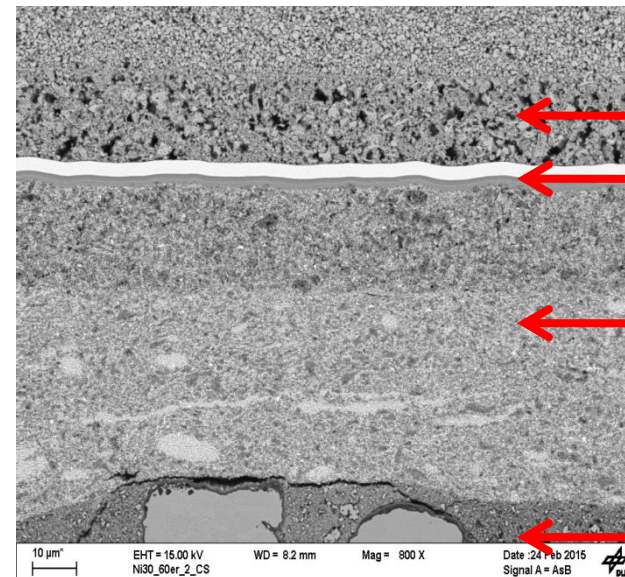


# Acknowledgement



**Project EVOLVE: Evolved materials and innovative design for high-performance, durable and reliable SOFC cell and stack**

FCH JU (303429) DLR coordinator  
Nov. 2012 - Oct.2016



LSCF cathode  
Bi-layer thin  
film electrolyte

Ni-free  
perovskite  
based  
anode

Substrate

- Implementation of  $\text{SrTiO}_3$  based anode materials
- Reduction of Nickel content at the anode side
- Thin film electrolyte



# Thank you for your attention!

