National Research Council of Italy

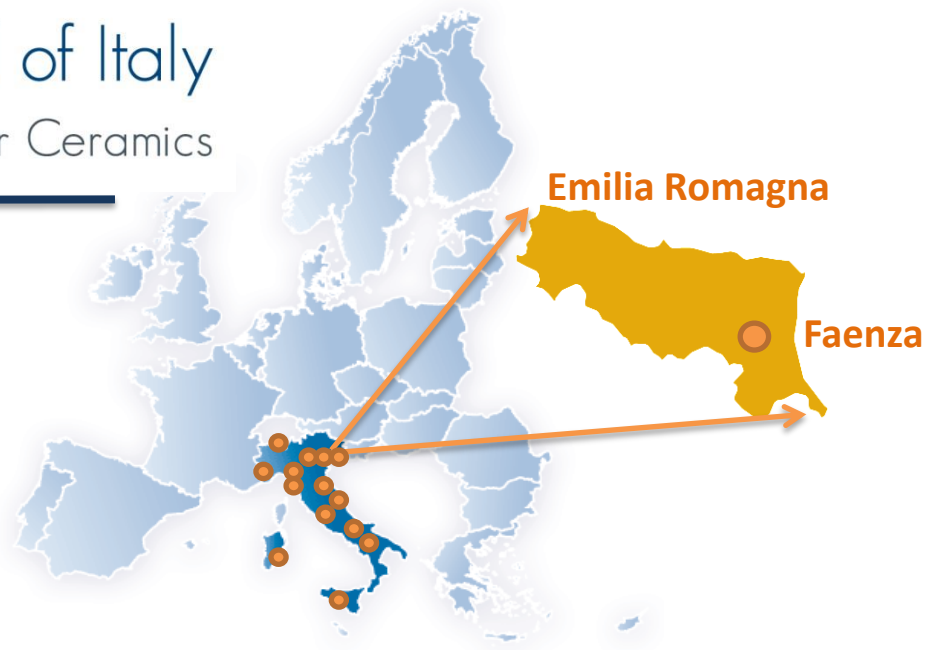
istec Institute of Science and Technology for Ceramics

DSCTM

Dipartimento Scienze Chimiche e Tecnologie dei Materiali

Young Investigator Award 2018

Premio YIA2018 - Chimica per l'Energia Rinnovabile



CONFERENZA DI DIPARTIMENTO 2018

Assisi, 24-26 September 2018

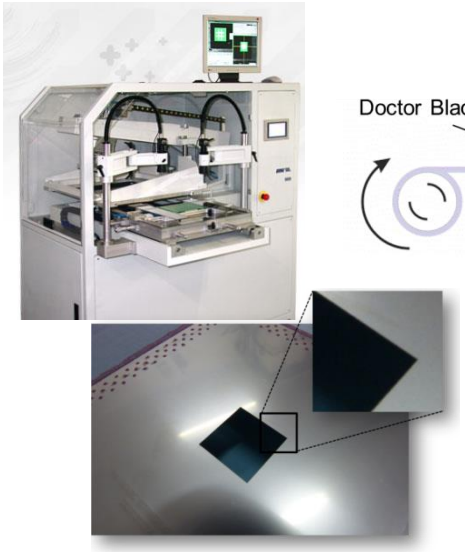
Presented by:

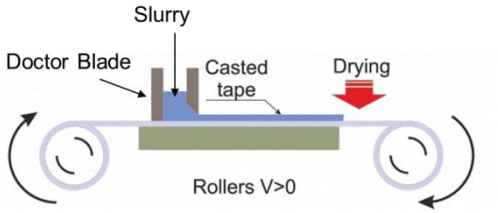
Angela Gondolini

OUTLINE

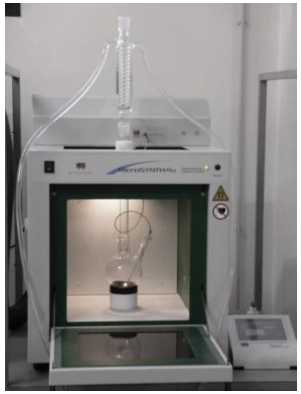
Production of ceramic multilayers for energy applications

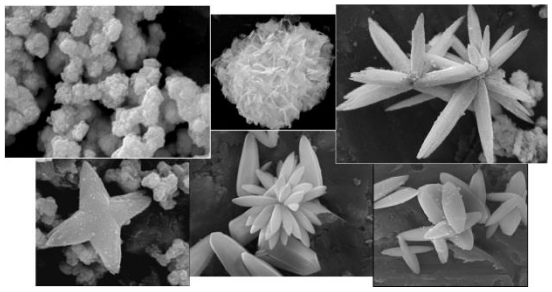
Processes





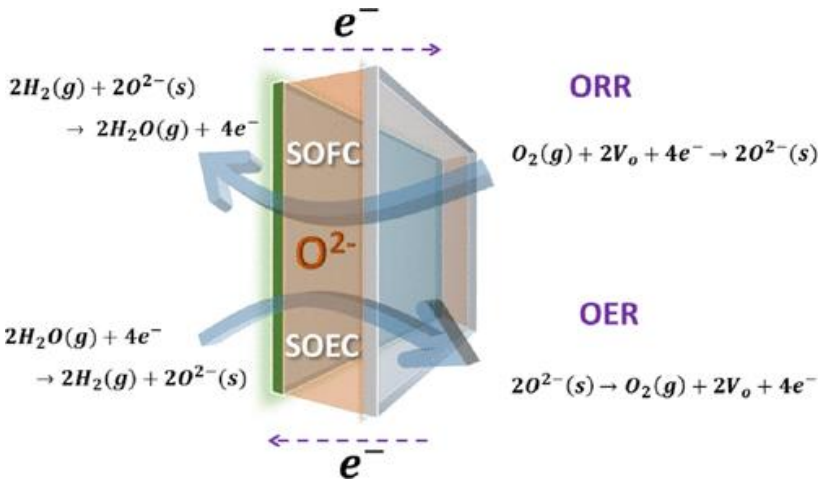
Materials





- Solid Oxide Cells (SOCs)
- Gas Separation Membranes (GSMs)

SOLID OXIDE CELLS



ORR

$O_2(g) + 2V_o + 4e^- \rightarrow 2O^{2-}(s)$

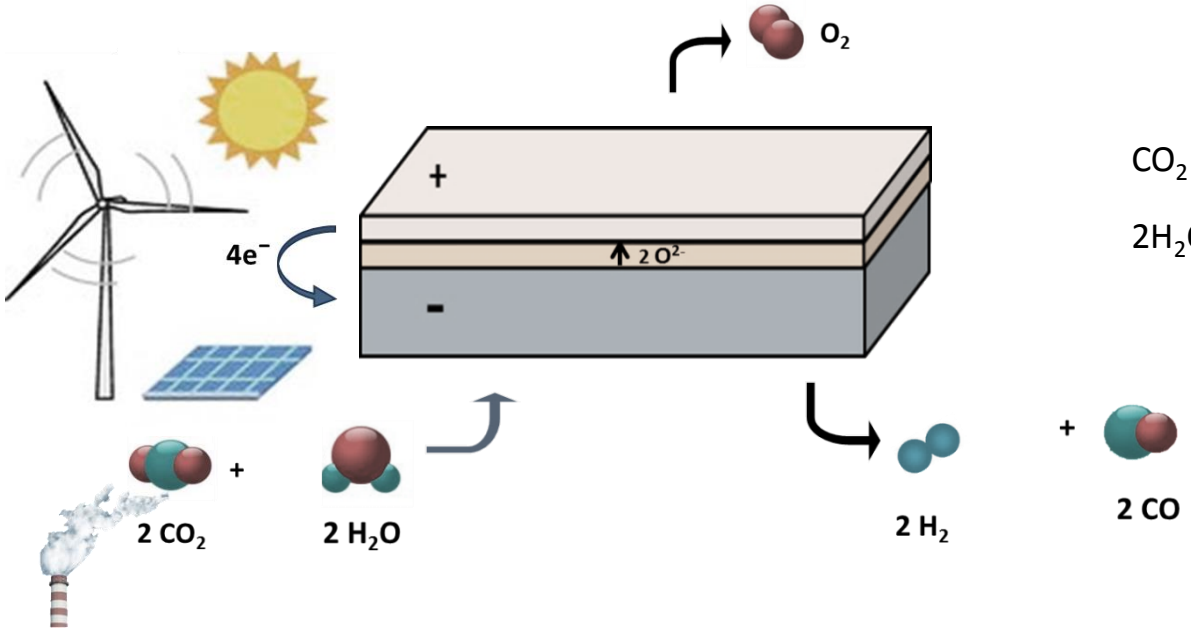
OER

$2O^{2-}(s) \rightarrow O_2(g) + 2V_o + 4e^-$

T = 600-800°C

Efficiency > 80%

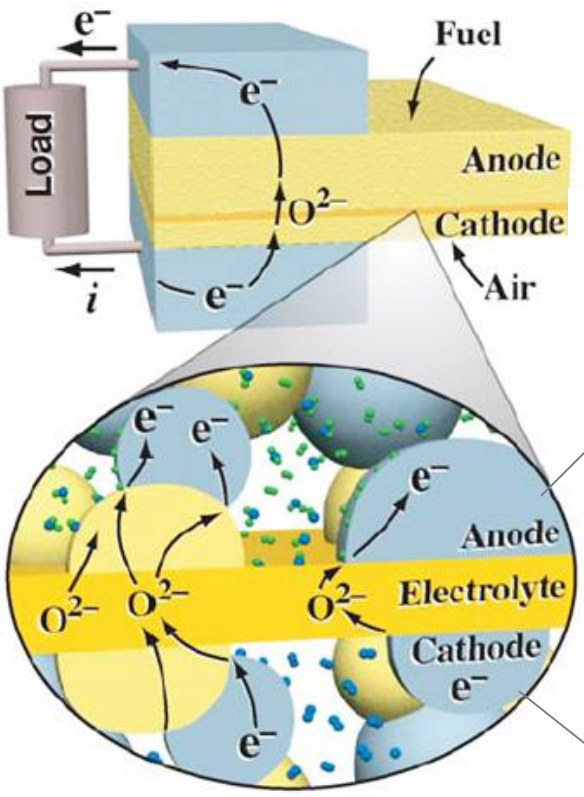
Ceramic-based electrochemical devices for energy conversion



$CO_2 + 4H^+ + 4e^- \rightarrow CO + H_2 + H_2O$

$2H_2O \rightarrow 4H^+ + O_2 + 4e^-$

SOLID OXIDE CELLS

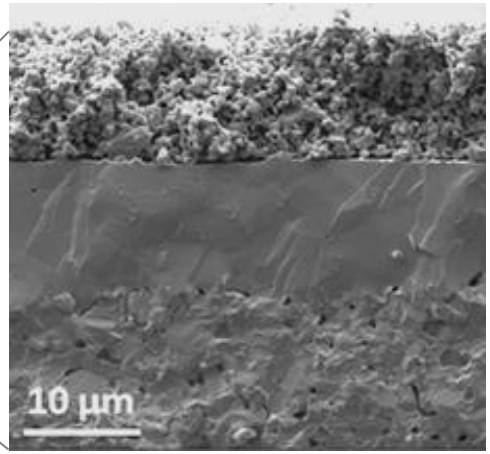


$H_2 \leftrightarrow 2H^+ + 2e^-$

T = 600-800°C

$\frac{1}{2} O_2 + 2e^- \leftrightarrow O^{2-}$

Ceramic-based multilayers with porous-dense porous microstructure

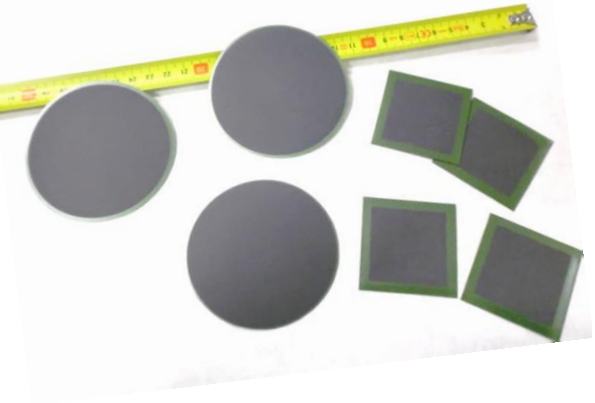


$La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_{3-\delta}$ - $Ce_{1-x}Gd_xO_{3-d}$

8% Y_2O_3 , ZrO_2, $Ce_{1-x}Gd_xO_{3-d}$

Ni – 8% Y_2O_3 , ZrO_2

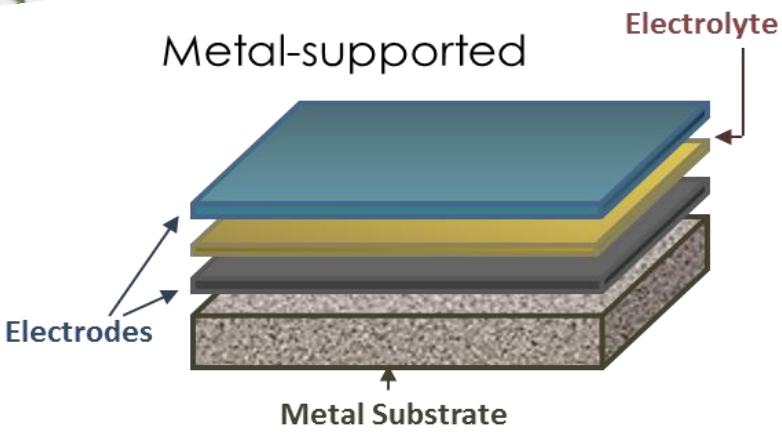
SOLID OXIDE CELLS

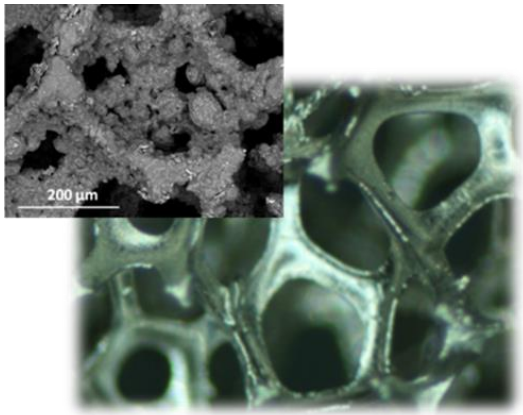


COMMERCIALIZATION

↓ costs

↑ durability

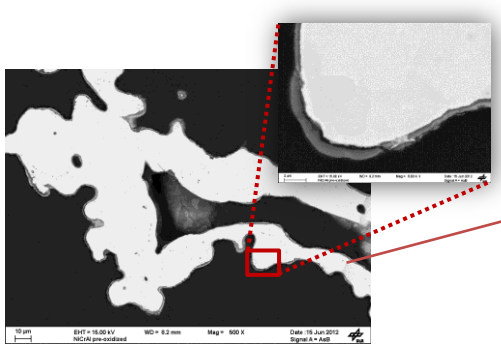


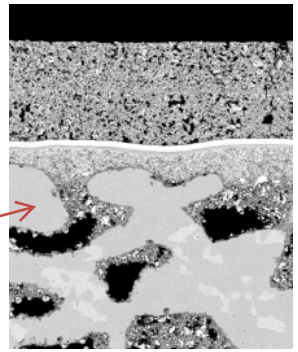


Source: Alantum Europe GmbH

NiCrAl Foam

- High porosity(>80vol%);
- Lower cost
- Al_2O_3 protective scale - ↑ durability



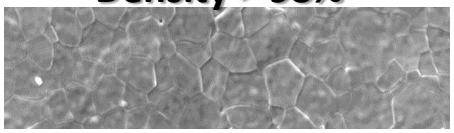


SOLID OXIDE CELLS

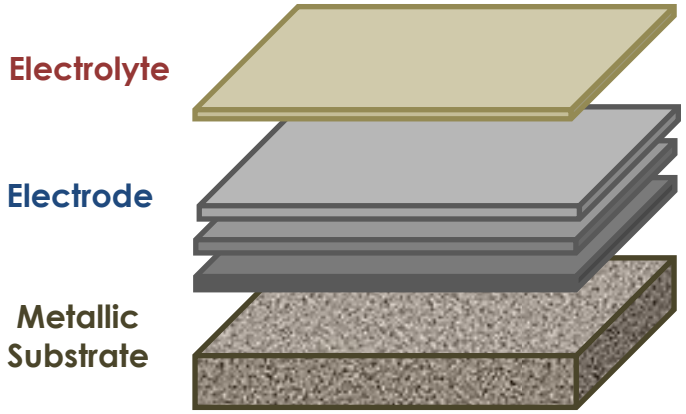
Density/Porosity

CTE (x10^{-6}) [K^{-1}]

Density > 98%

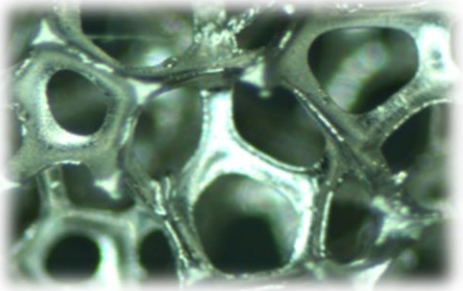


12.5



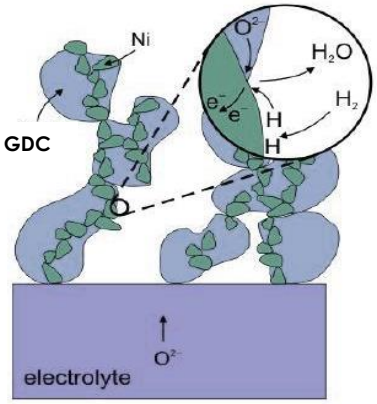
Porosity > 80%

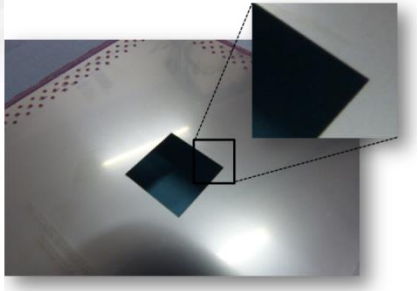
$5\mu m < \phi_{pores} < 800\mu m$

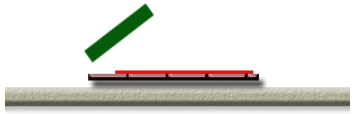


16.0

Ni – $Ce_{0.9}Gd_{0.1}O_{3-d}$ (GDC)

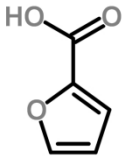




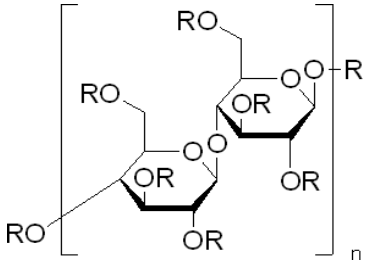


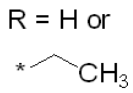
Deposition of more than one layer

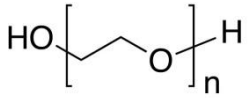
SOLID OXIDE CELLS

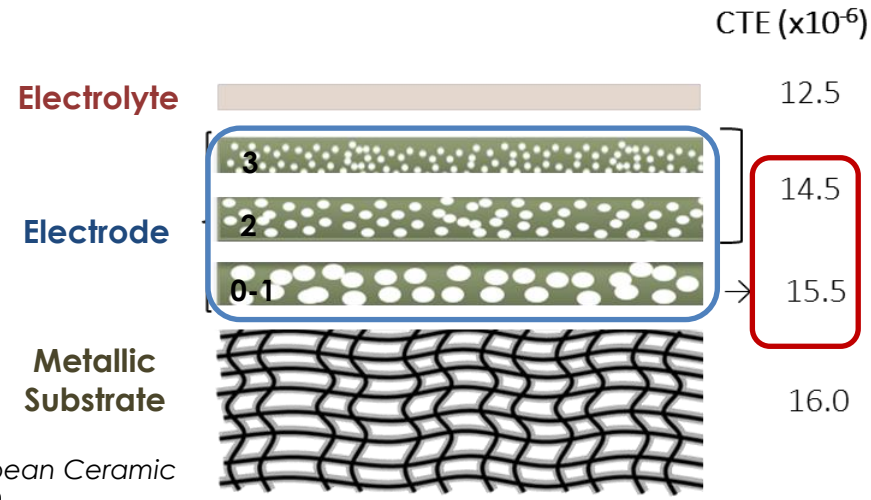


wt%	0	1	2	3
GDC	13.9	27.8	24.4	24.4
Ni	78.7	64.8	56.9	56.9
Dispersant	1.2	1.2	1.1	1.1
Binder	2.3	2.3	8.0	8.0
Plasticizer	3.9	3.9	9.7	9.7









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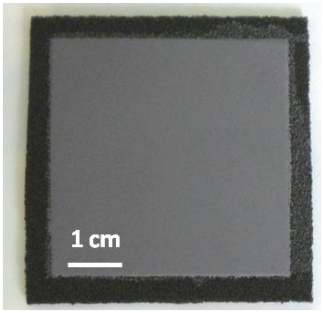
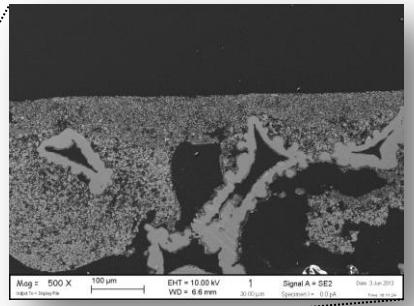
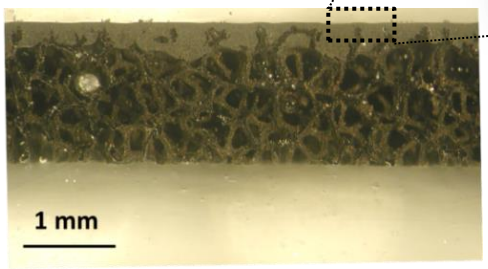
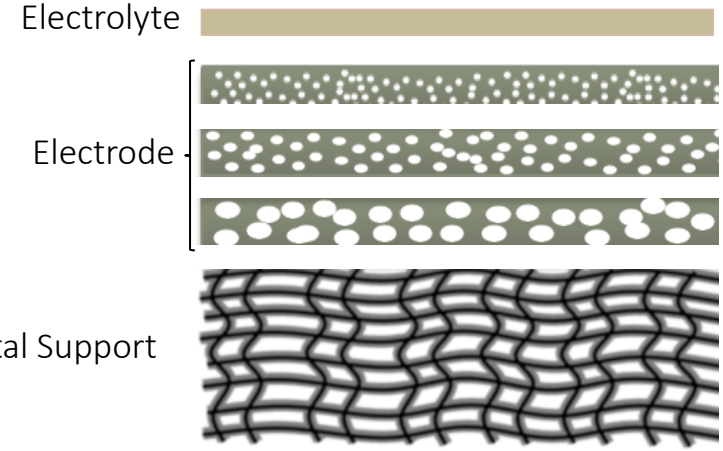
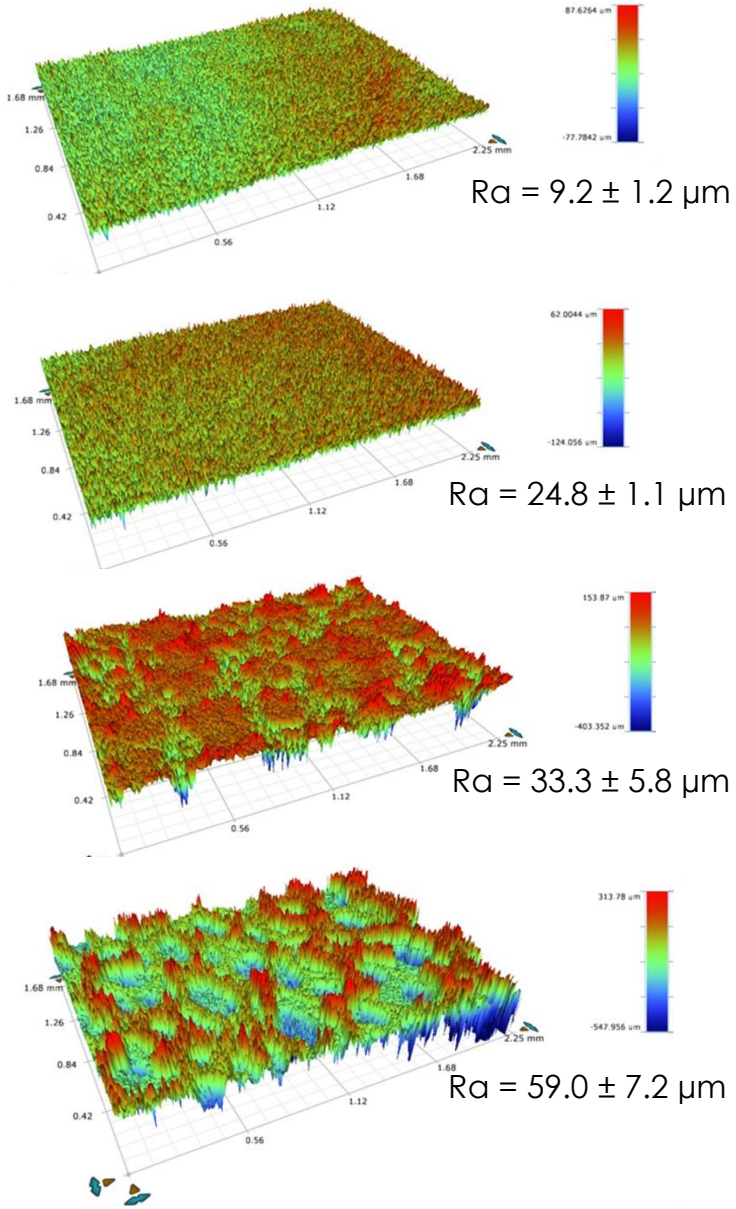
SOLID OXIDE CELLS



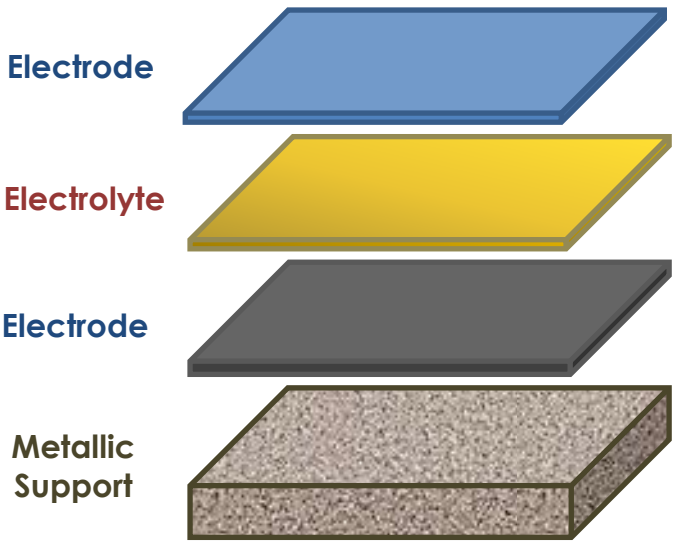




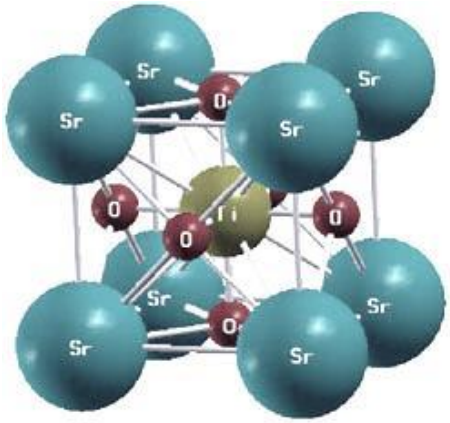




SOLID OXIDE CELLS



Substitution of La in the A site



$La_{0.1}Sr_{0.9}TiO_{3-a}$ - GDC

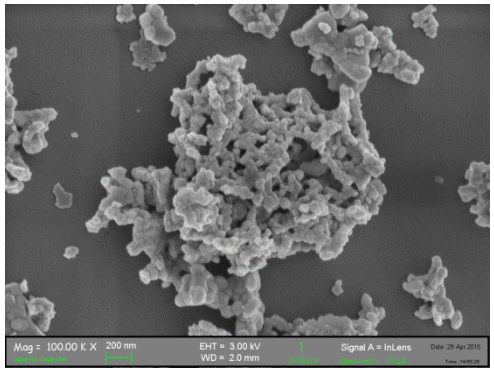
Properties:

- Catalytic
- Conductivity
- Chemical Stability

Tolerance to:

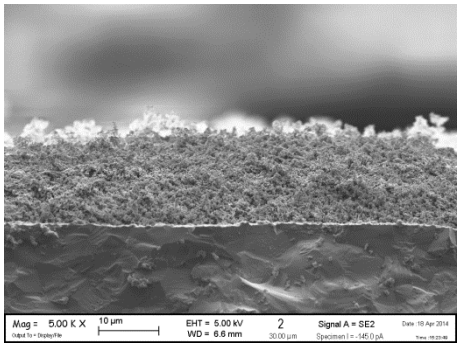
- Sulfur poisoning
- C deposition
- Redox cycles

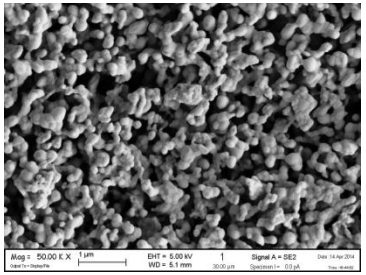
Electrode efficiency



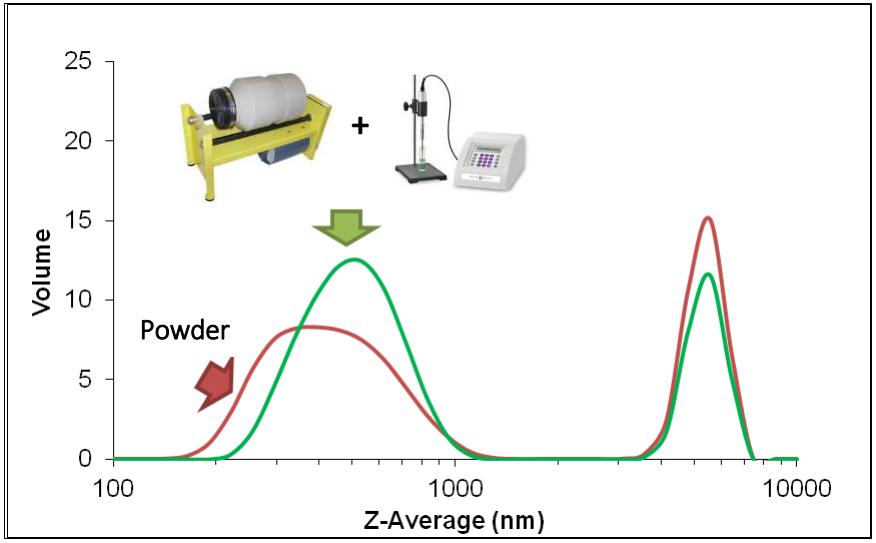
Powder Treatment

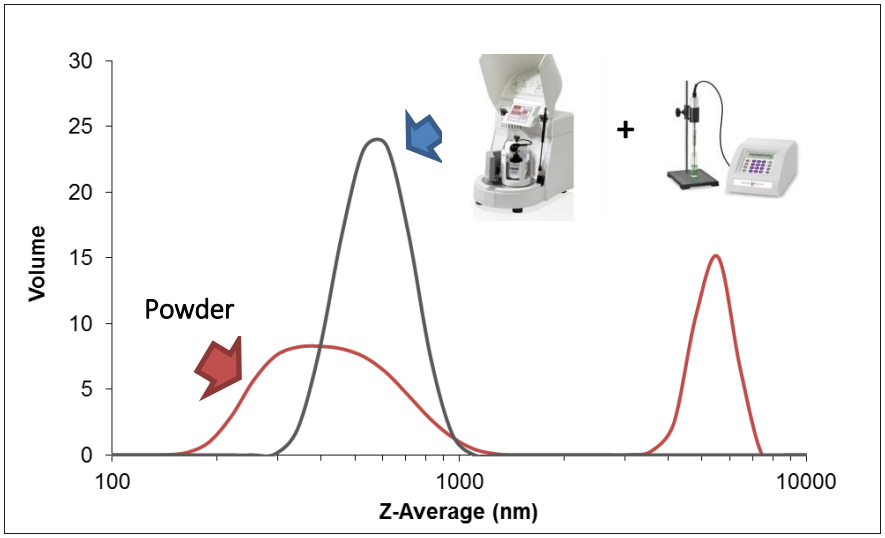
Milling & Sonication
↑ SSA

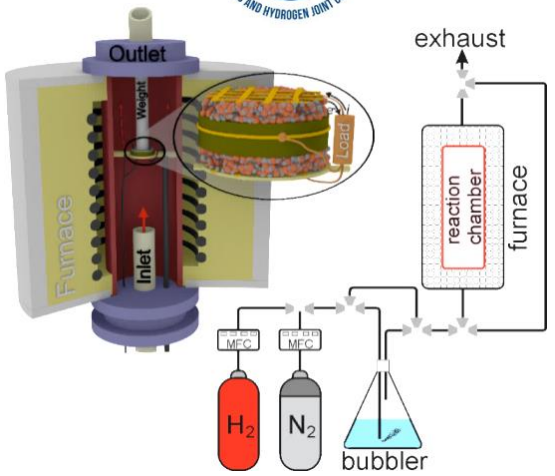




SOLID OXIDE CELLS







↓Polarization↑ Efficiency

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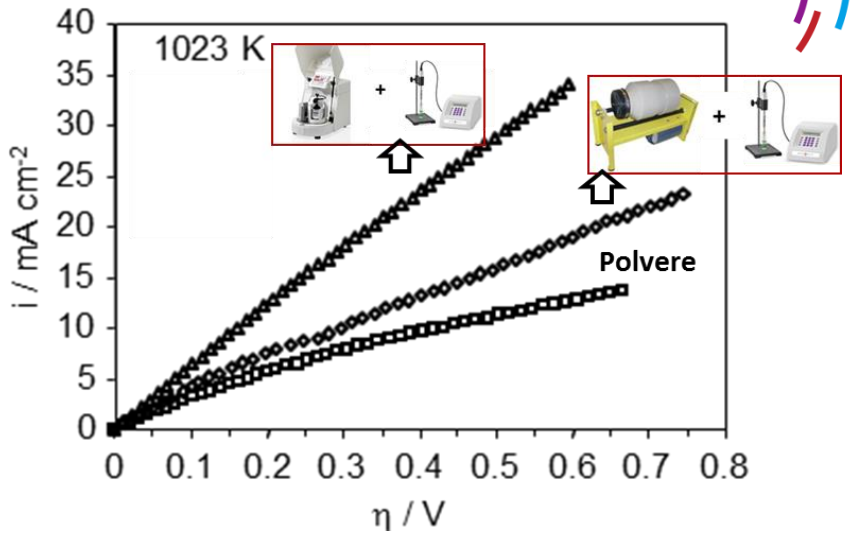
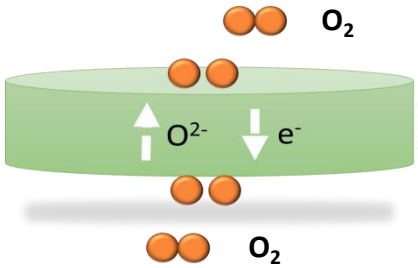


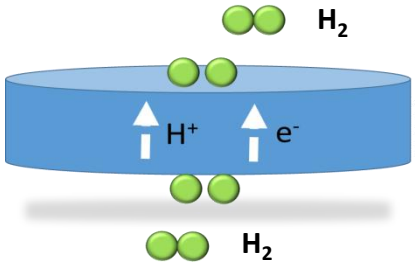
GAS SEPARATION MEMBRANES

Selective Separation of gases (O_2, H_2) using dense ceramic membranes

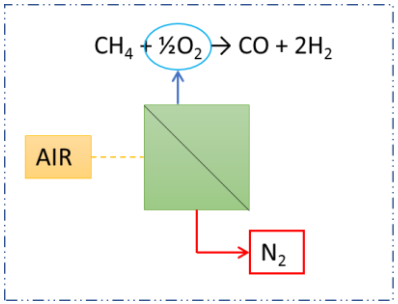
→ Electrochemical Mechanism

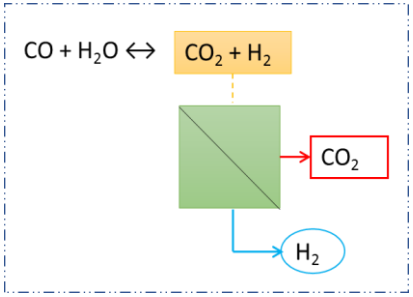


T_{oper} = 500-800°C

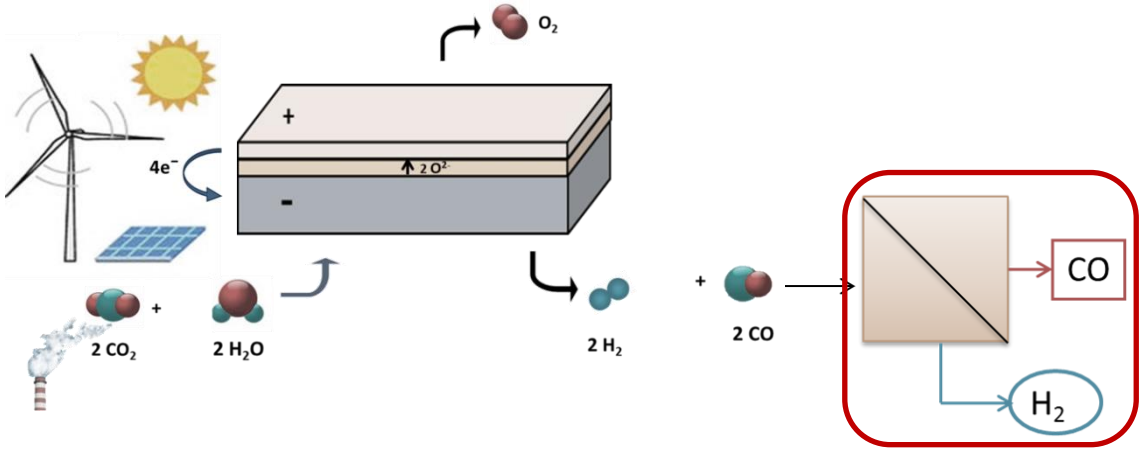


Applications



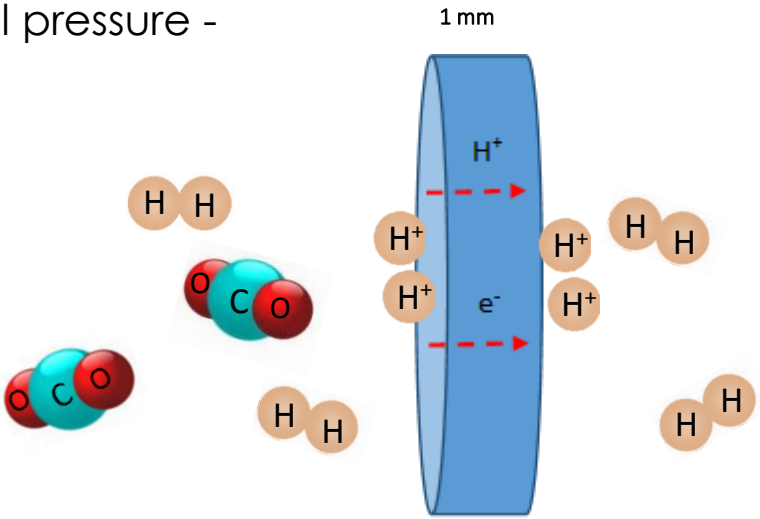


Applicability in different industrial processes (600-800°C)



H_2 SEPARATION MEMBRANES

Higher H_2 partial pressure - Dissociation:
$H_2 \rightarrow 2H^+ 2e^-$



Lower H_2 partial pressure - Recombination:
$2H^+ 2e^- \rightarrow H_2$

«pressure-driven» separation

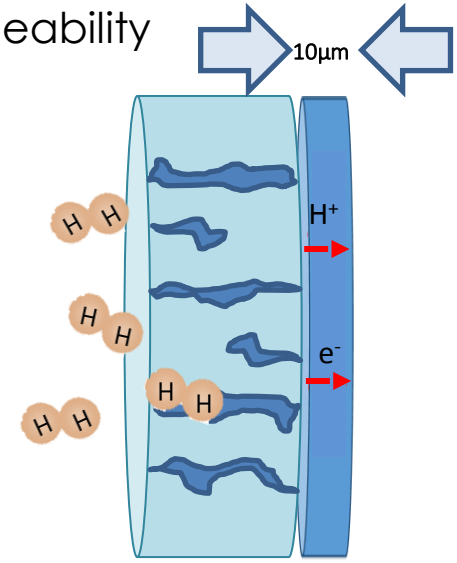
$$j_{H_2} = \frac{RT}{4F^2L}\frac{\sigma_{H^+}\sigma_{el}}{\sigma_{H^+}+\sigma_{el}}\ln\left(\frac{P'_{H_2}}{P''_{H_2}}\right)$$

Process parameters

Geometry

Material Properties

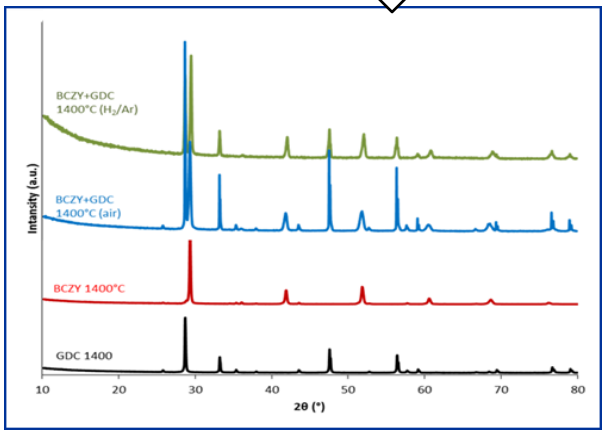
↑ permeability



$BaCe_{0.55}Zr_{0.3}Y_{0.15}O_3/Ce_{0.8}Gd_{0.2}O_{2-\sigma}$ (BCZY/GDC)

- High proton conductivity
- Good CO_2 stability

$$BaCeO_3 + xCO_2 \leftrightarrow xBaCO_3 + Ba_{(1-x)}CeO_{(3-x)}$$

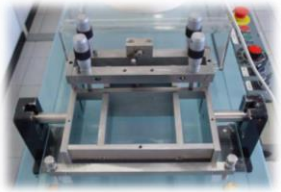


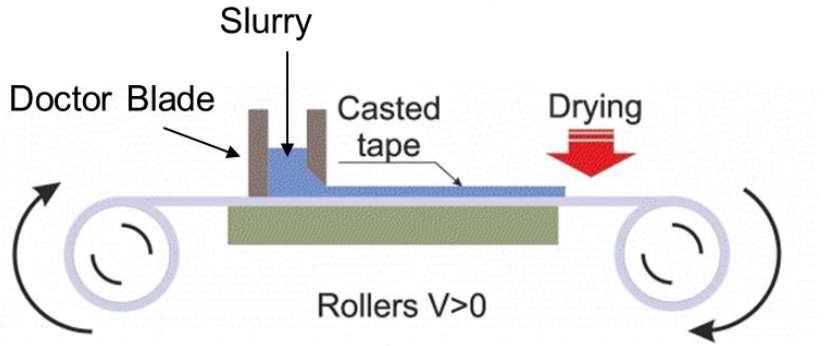
H_2 SEPARATION MEMBRANES

Slurry preparation

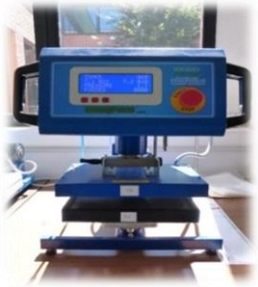
- Support
- Membrane

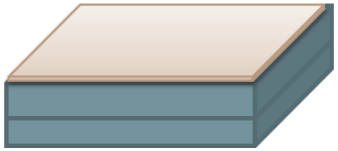
Casting





High Temperature consolidation



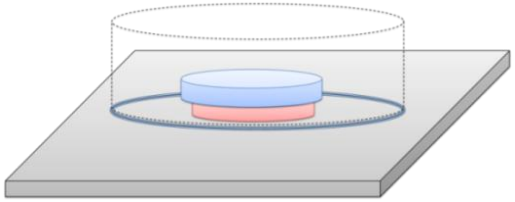


H_2 SEPARATION MEMBRANES

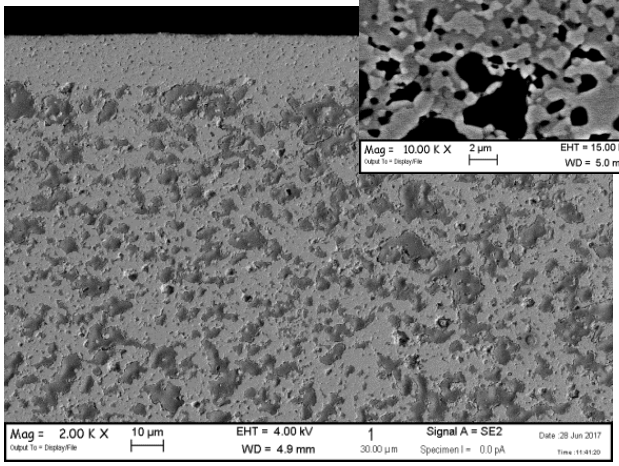
BaO evaporation

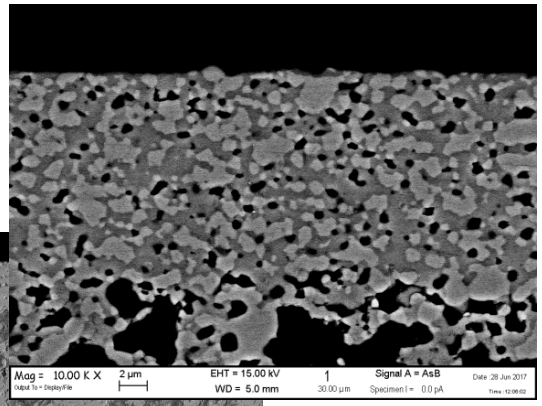
$$BaCeO_3 \rightarrow xBaO \uparrow + Ba_{(1-x)}CeO_{(3-\partial)}$$

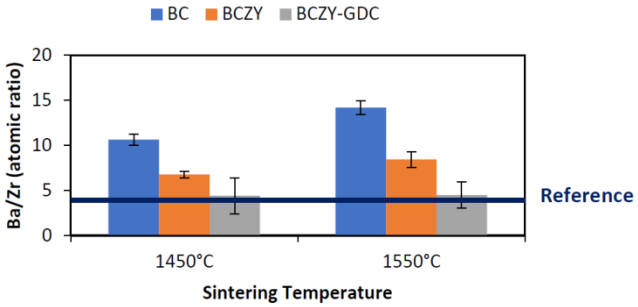
Ba sources in the sintering atmosphere

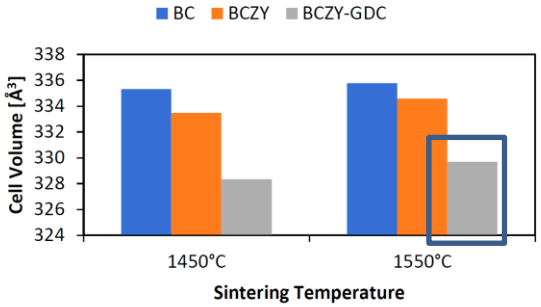


$$BaCeO_3 \rightleftarrows xBaO(g) + Ba_{(1-x)}CeO_{(3-\partial)}$$





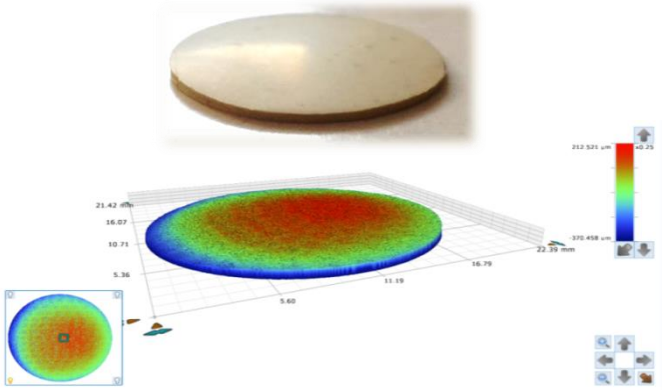


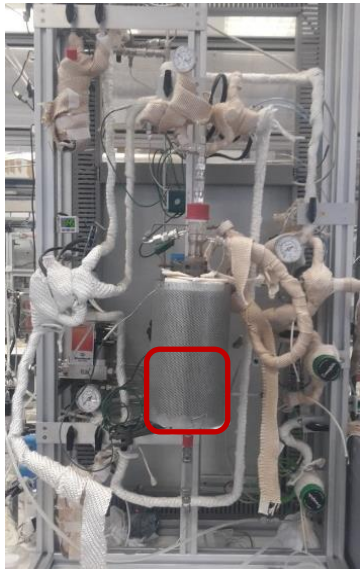


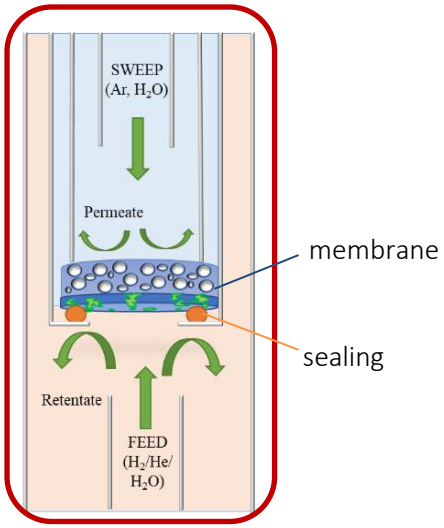
Compatibility with literature data for $BaCe_{0,65}Zr_{0,20}Y_{0,15}O_{3-\delta}$

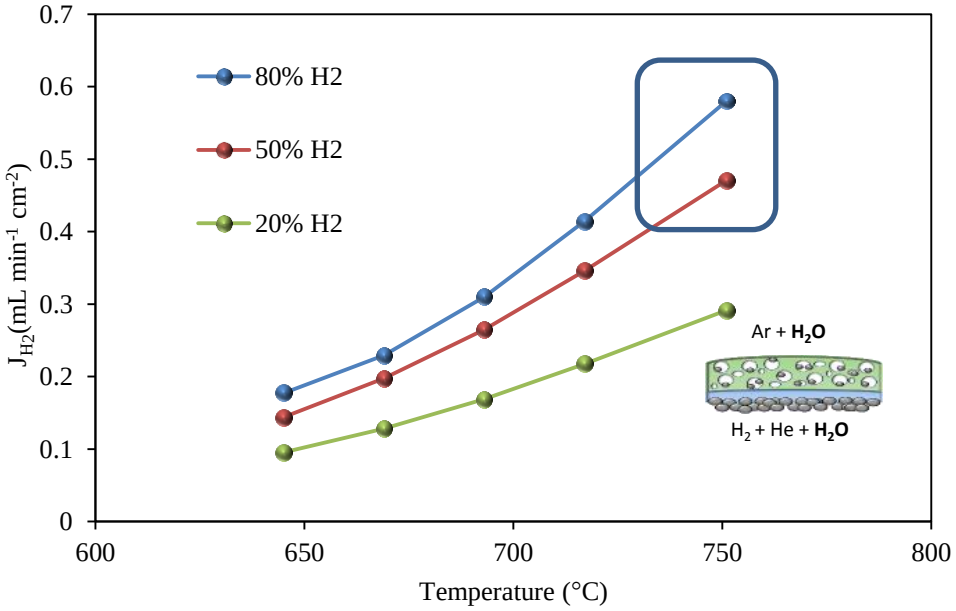
H_2 SEPARATION MEMBRANES

D. Montaleone et al. J. Mater. Chem. A, 2018, 6,15718









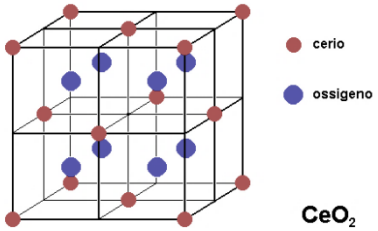
H_2 SEPARATION MEMBRANES

Membrane Material	Thickness dense membrane (μm)	Gas atmosphere Feed - Sweep	T (°C)	J_{H2} (mL min^{-1} cm^{-2})
$SrCeO_3$-based hydrogen separation membranes				
$SrCe_{0,95}Y_{0,05}O_{3-\delta}$	50	dry 80% H_2 in He - Ar	950	0.1
$SrCe_{0,95}Tm_{0,05}O_{3-\delta}$	150	dry 10% H_2 in He - 20% O_2 in N_2	900	0.16
$SrCe_{0,7}Zr_{0,2}Eu_{0,1}O_{3-\delta}$	33	dry 100% H_2 - He	900	0.23
		wet (3% H_2O) H_2 - He	900	0.21
$BaCeO_3$-based hydrogen separation membranes				
$BaCe_{0,85}Tb_{0,05}Zr_{0,1}O_{3-\delta}$	20 / 50	dry 50% H_2 in He - Ar	900	0.22 / 0.08
$BaCe_{0,65}Zr_{0,20}Y_{0,15}O_{3-\delta}$ - $Ce_{0,80}Gd_{0,20}O_{2-\delta}$	20	wet 50% H_2 in He - wet Ar	750	0.47
$BaCe_{0,65}Zr_{0,20}Y_{0,15}O_{3-\delta}$ - $Ce_{0,80}Gd_{0,20}O_{2-\delta}$	20	dry 50% H_2 in He - wet Ar	750	0.68
$BaCe_{0,65}Zr_{0,20}Y_{0,15}O_{3-\delta}$ - $Ce_{0,80}Gd_{0,20}O_{2-\delta}$	650	wet 50% H_2 in He - wet Ar	755	0.27
Ni-$BaCe_{0,7}Zr_{0,1}Y_{0,2}O_{3-\delta}$	30	wet 50% H_2 in N_2 - Ar	750	0.15
Ni-$BaCe_{0.95}Tb_{0.05}O_{3-\delta}$	90	dry 50% H_2 in N_2 - He	750	0.55
Ni-$BaCe_{0,7}Zr_{0,1}Y_{0,1}Yb_{0,1}O_{3-\delta}$	44	wet 50% H_2 in He - N_2	750	0.46
Other ceramic systems				
$La_{26,78}W_{5,22}O_{55,83}$	25	wet 10% H_2 in Ar - Ar	1000	0.14
$Ce_{0,8}Sm_{0,2}O_{2-\delta}$	35	dry 40% H_2 in N_2 - Ar	900	0.007

POWDER SYNTHESIS

CeO_2

$Ce_{1-x}Gd_xO_{2-d}$

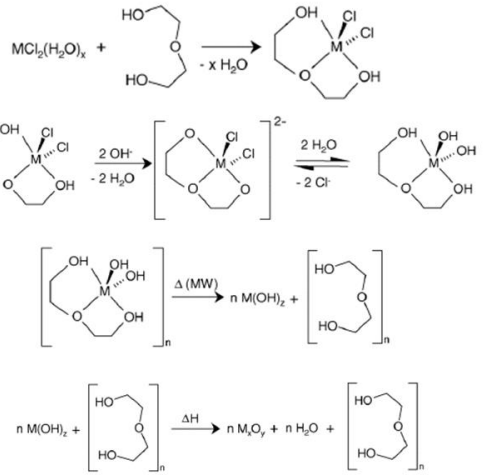


Applications:

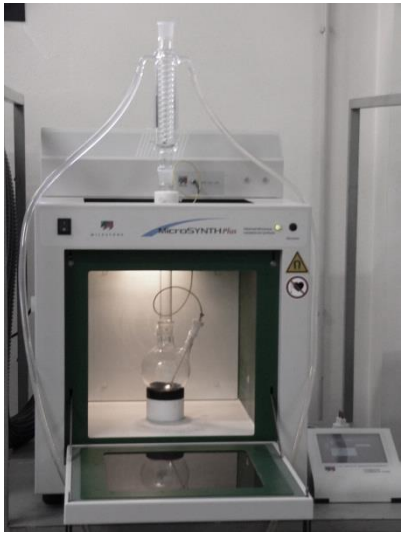
- Catalysis
- Phase wiht good ionic conductivity for SOC e SM applications

POLYOL METHOD

Direct nucleation in poly alcohol solvent (eg. EG o DEG), starting from a precursor solution



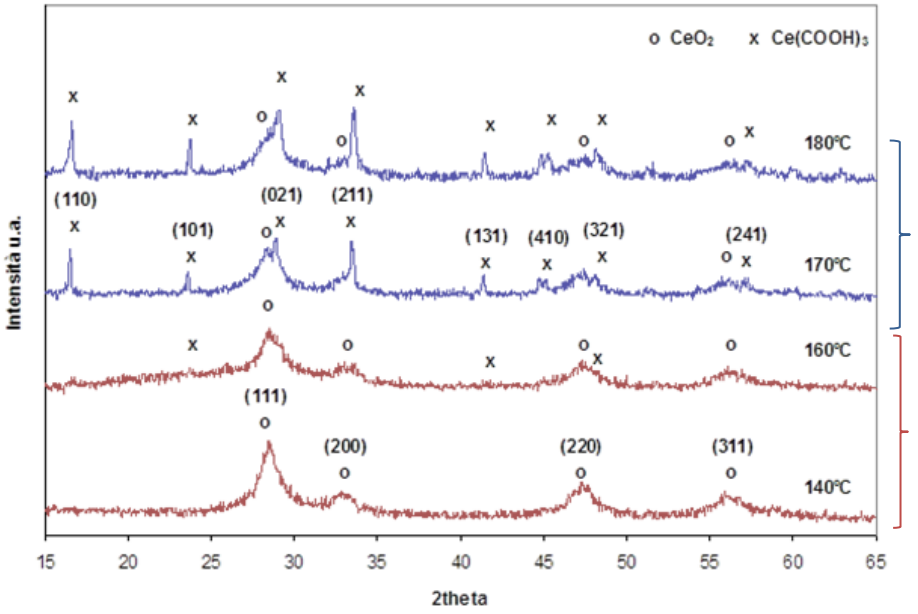
→ **Nanometric powder**



Microwave heating is used:

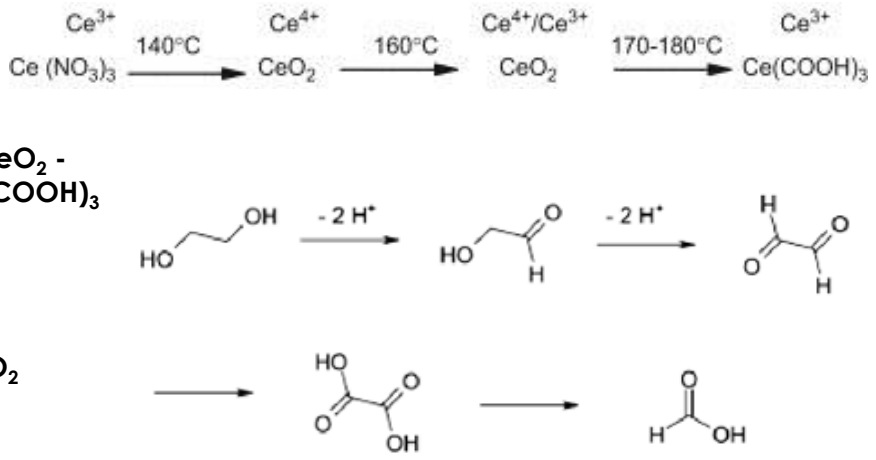
- Fast & homogeneous
- In situ cristallization

CeO_2 POWDER SYNTHESIS

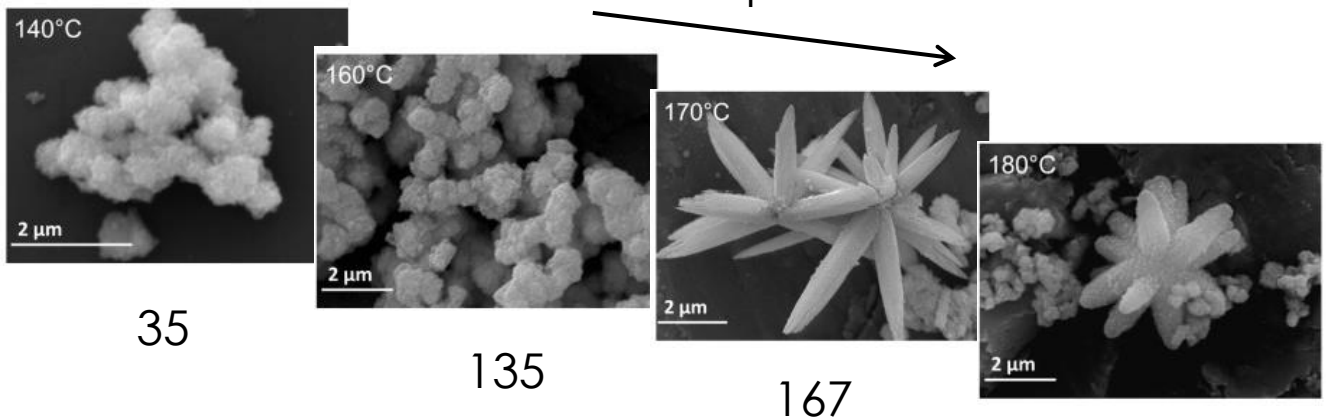


CeO_2 - $Ce(COOH)_3$

CeO_2

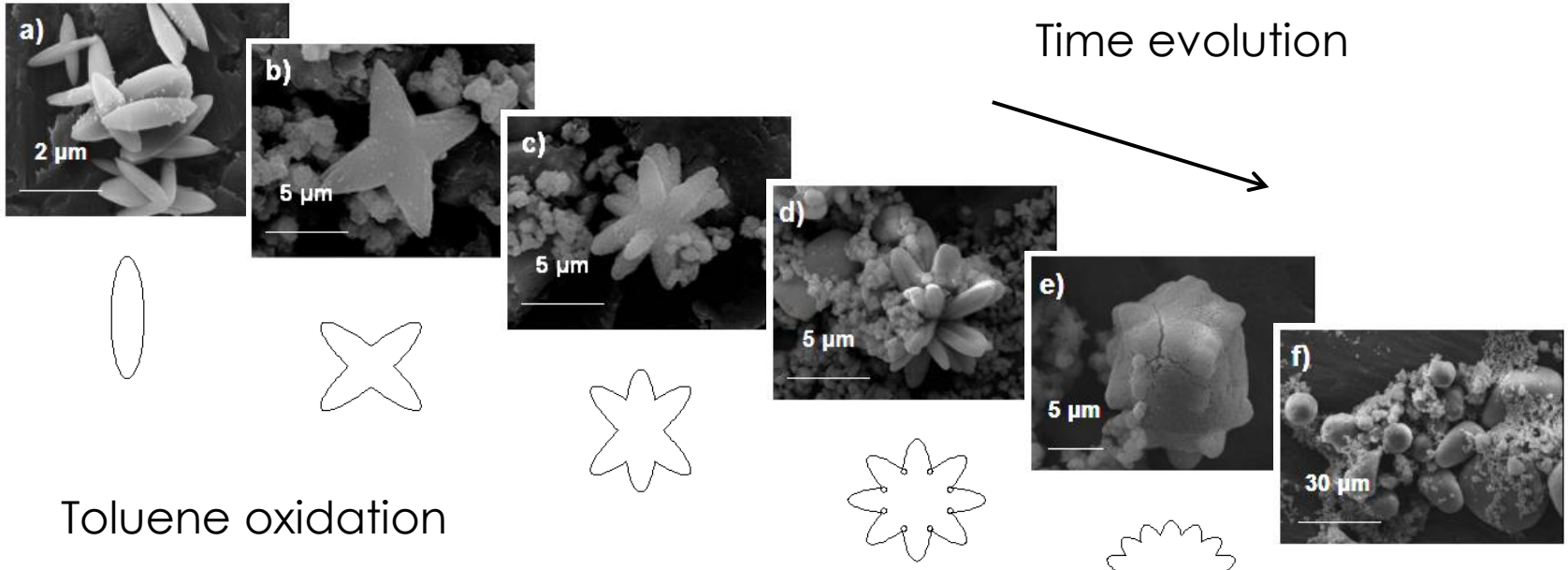


Temperature

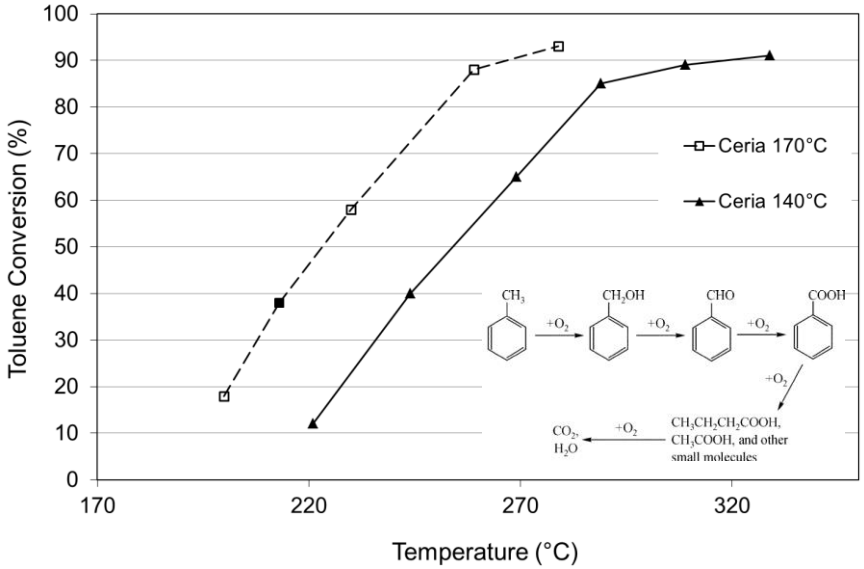


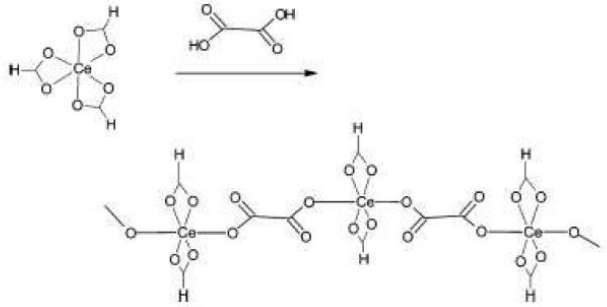
SSA (m^2/g)	35	135	167	146

CeO_2 POWDER SYNTHESIS



Toluene oxidation



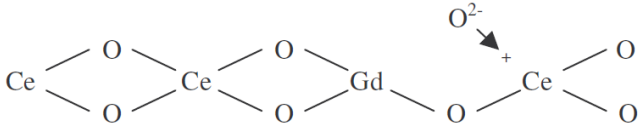


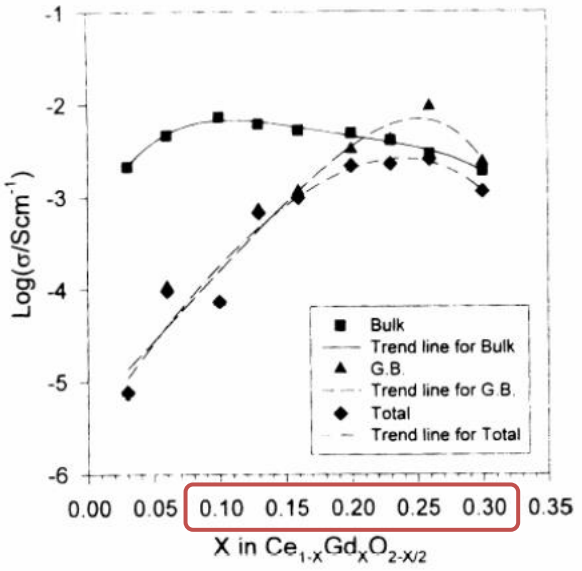
Formation and growing mechanism

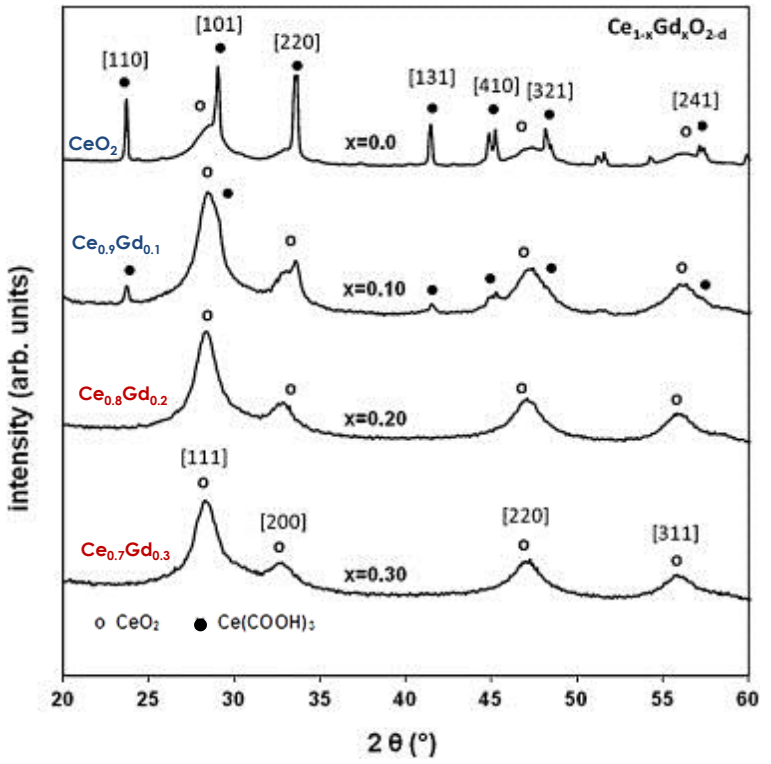
$Ce_{1-x}Gd_xO_{2-d}$ POWDER SYNTHESIS

Doping of CeO_2 with Gd

↑ Ionic conductivity







[Gd]

$Ce_{1-x}Gd_xO_{2-d}$ – $Ce,Gd(COOH)_3$

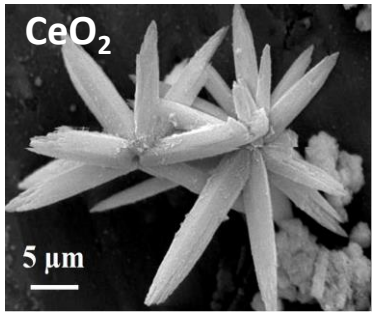
$Ce_{1-x}Gd_xO_{2-d}$

A Gondolini et al. Ceramics International 37 (4), 1423-1426

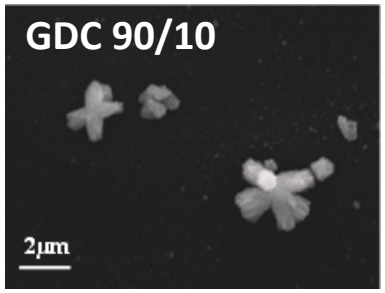
A Gondolini, et al. Journal of nanoscience and nanotechnology 15 (5), 3636-3640

$Ce_{1-x}Gd_xO_{2-d}$ POWDER SYNTHESIS

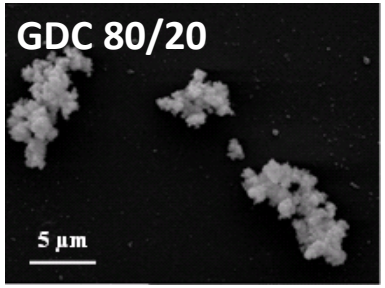
[Gd]



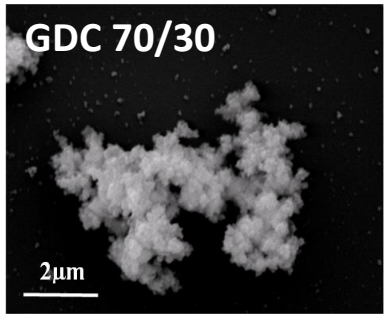
167 m^2/g



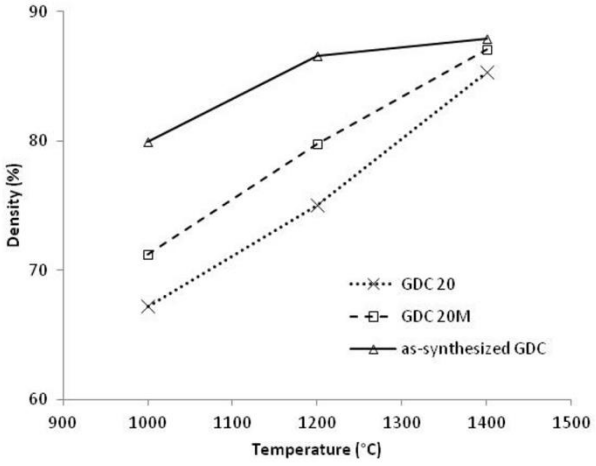
78 m^2/g

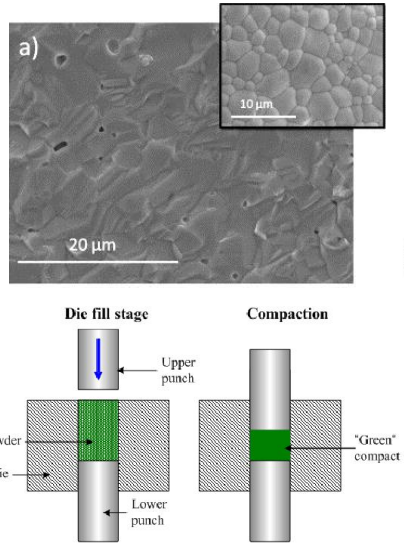


51 m^2/g

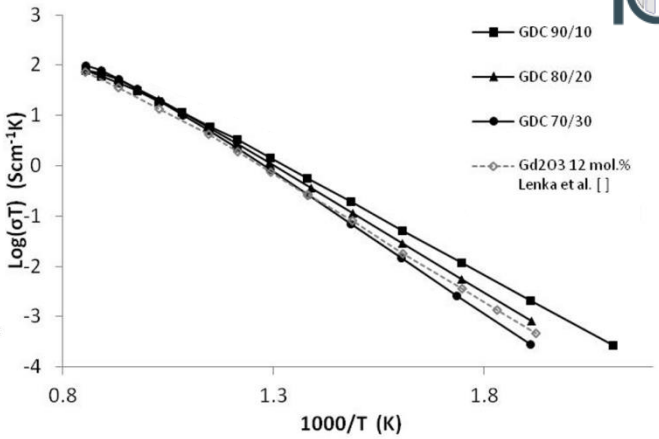


26 m^2/g





Ionic conductivity



A Gondolini et al. Journal of the European Ceramic Society 33 (1), 67-77

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THANKS FOR YOUR KIND ATTENTION