Performance of intermediate temperature solid oxide fuel cells with $Bi_{1.5}Er_{0.5}O_3$ based bilayer electrolyte

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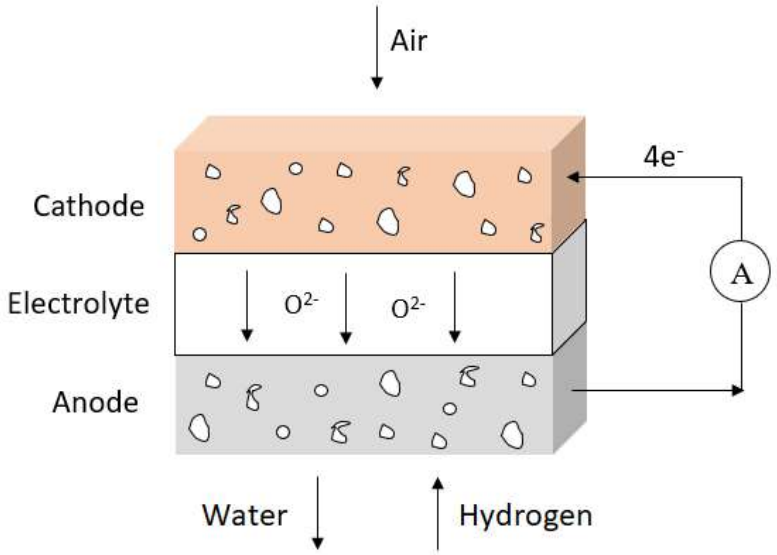
Plenaries FrH_2 2023 – 23 th of May

UCCS Laboratory – Team: MISSP (Lille)

Operating principle of SOFC

Reduction

$O_2\,(g) + 4e^- \longrightarrow 2O^{2-}$



Oxidation

$2H_2\,(g) + 2O^{2-} \longrightarrow 2H_2O(g)$

Overall reaction :

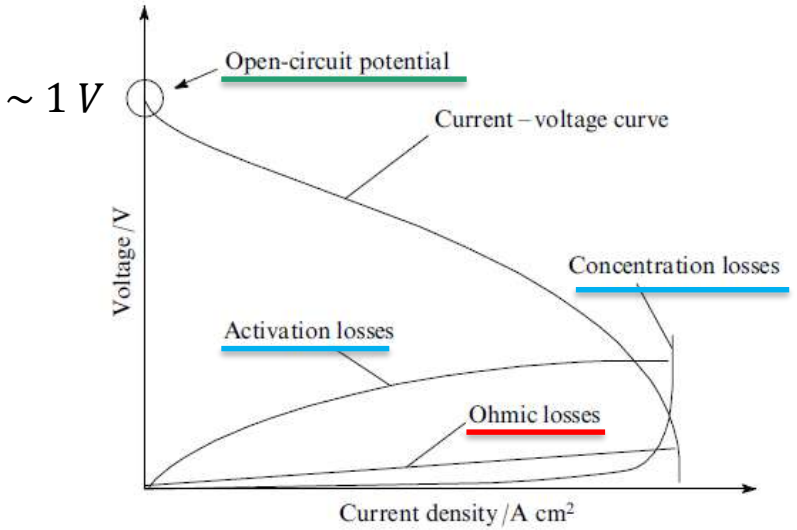
$2H_2(g) + O_2(g) \longrightarrow 2H_2O$ + heat + electricity

Converts the chemical energy into electrical energy

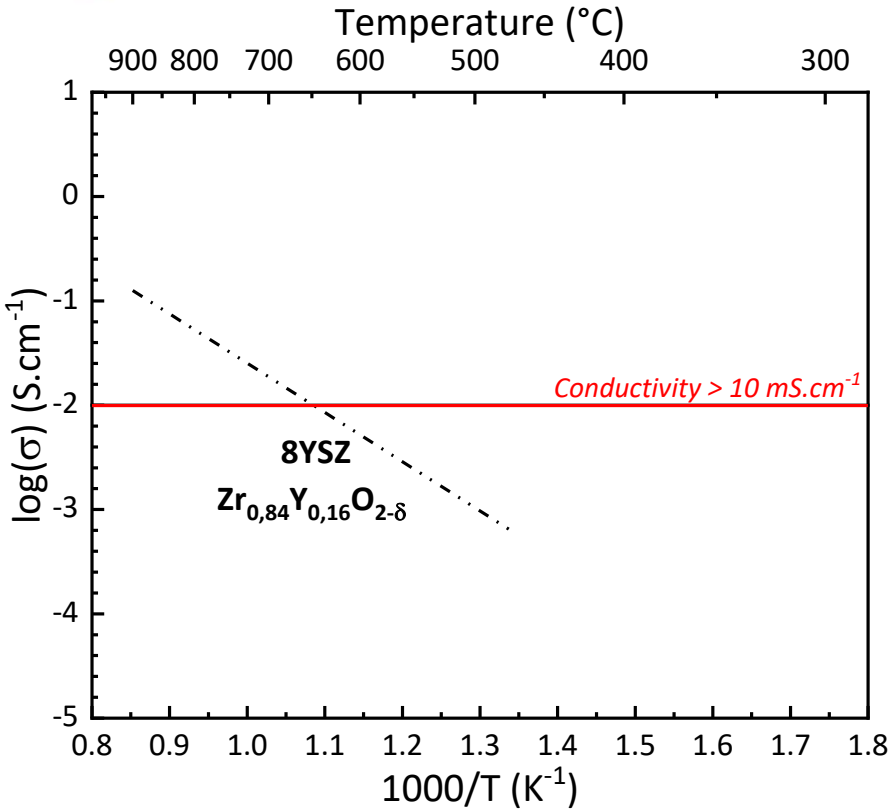
$$\Delta E_{theoretical}(T) = \Delta E°_{theoretical}(T) + \frac{R.T}{4F}.ln\left(\frac{P_{H_2O}^2}{P_{O_2}.P_{H_2}^2}\right)$$

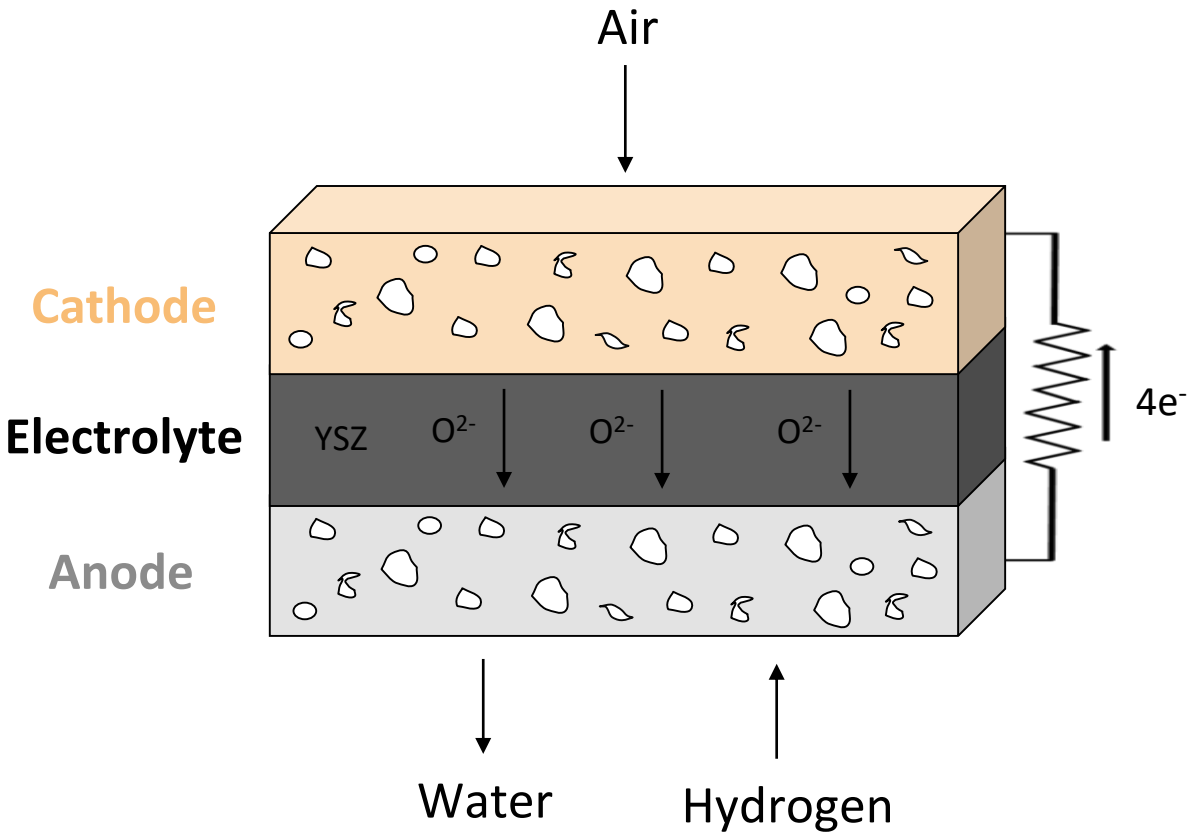
$$\Delta E_{theoretical}(1000°C) \sim 1\ V$$

$$\Delta E_{experimental} = \Delta E_{theoretical} - RI - |\eta_{anode}| - |\eta_{cathode}|$$



Decreasing the operating temperature





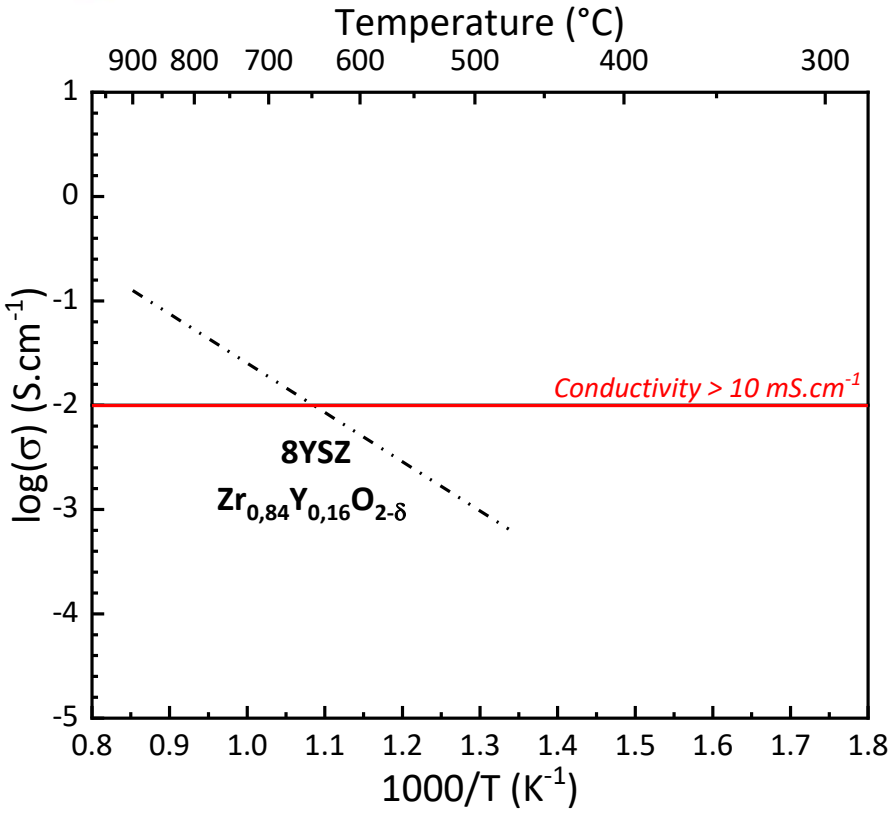
YSZ

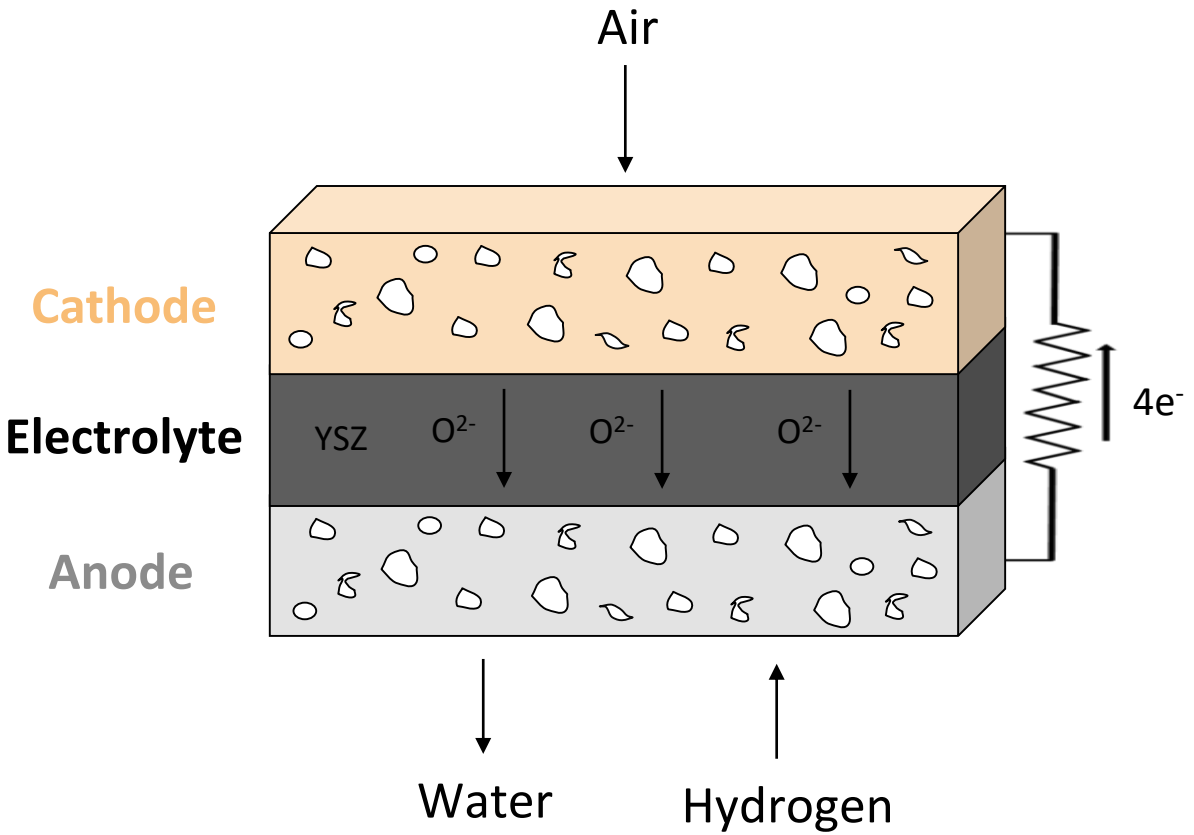
Good mechanical et chemical stability

→ Mediocre conductivity under 700°C

→ Mechanical instability, chemical reactivity, electrode microstructure

Decreasing the operating temperature



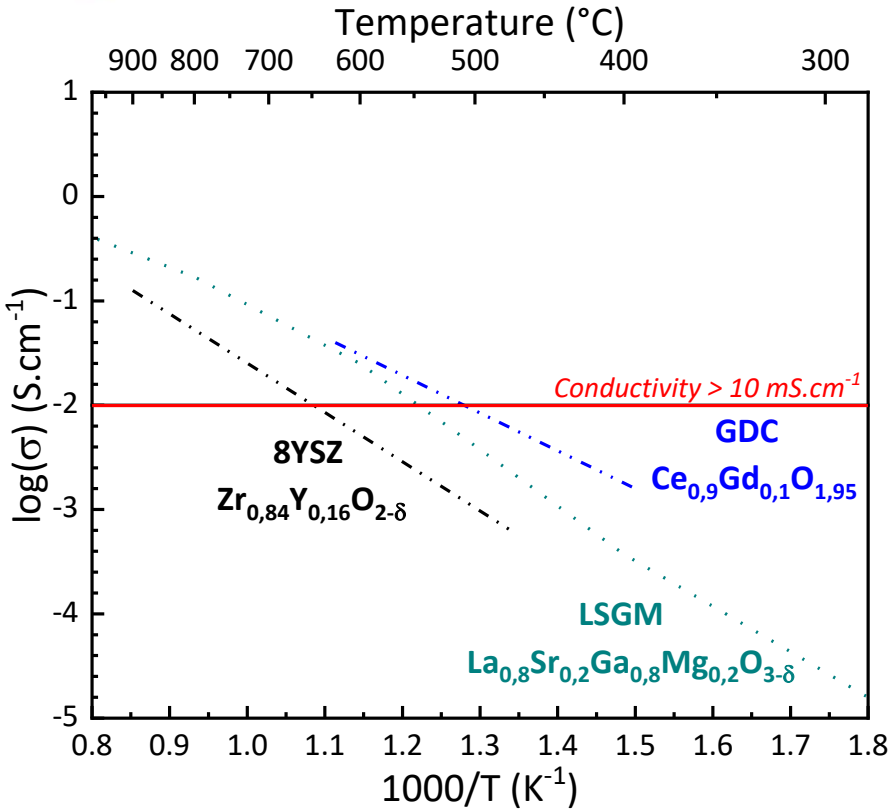


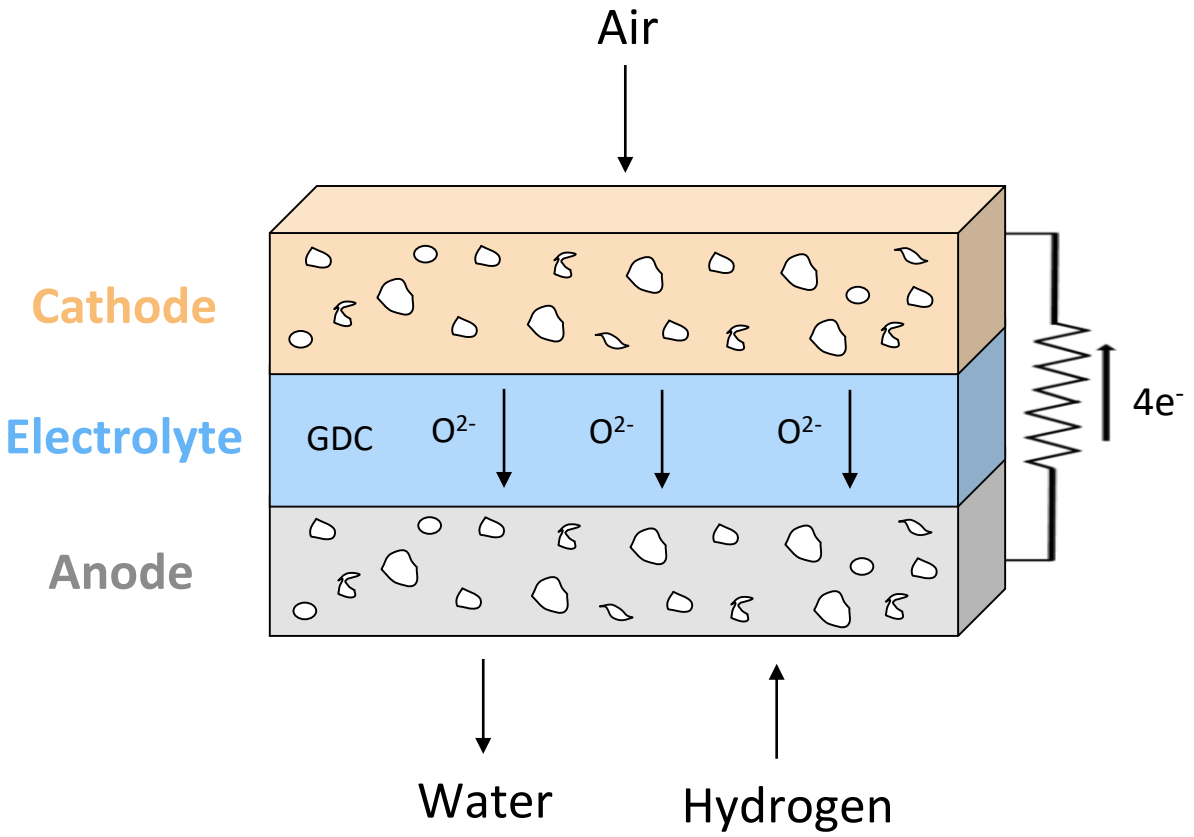
In order to decrease the operating temperature, two approaches are possible :

Decrease the electrolyte thickness ⇨ Limited

Electrolyte with a better ionic conductivity

Electrolytes for Low Temperature SOFC (LT-SOFC)



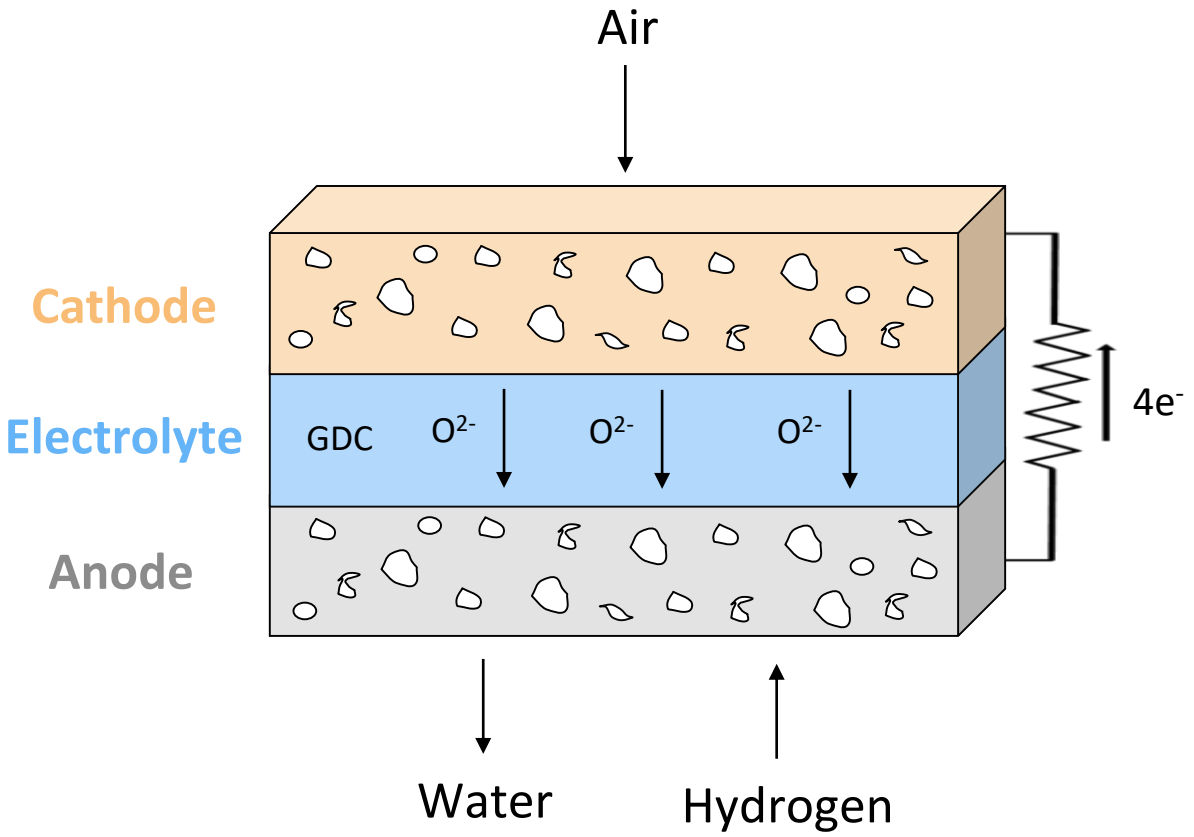


Reduction $Ce^{4+} \rightarrow Ce^{3+}$

Electronic contribution

Bilayered electrolyte

Electrolyte	Thickness	Maximum power density mW.cm^{-2} at			OCV (V) 750°C
		650°C	700°C	750°C	
GDC	**6 µm**	**198**	**263**	**315**	**0,5**



$$\Delta E_{theoretical}\,(1000°C) \sim 1\ V$$

$$\Delta E_{experimental} = \Delta E_{theoretical} - RI - |\eta_{anode}| - |\eta_{cathode}|$$

Electronic contribution

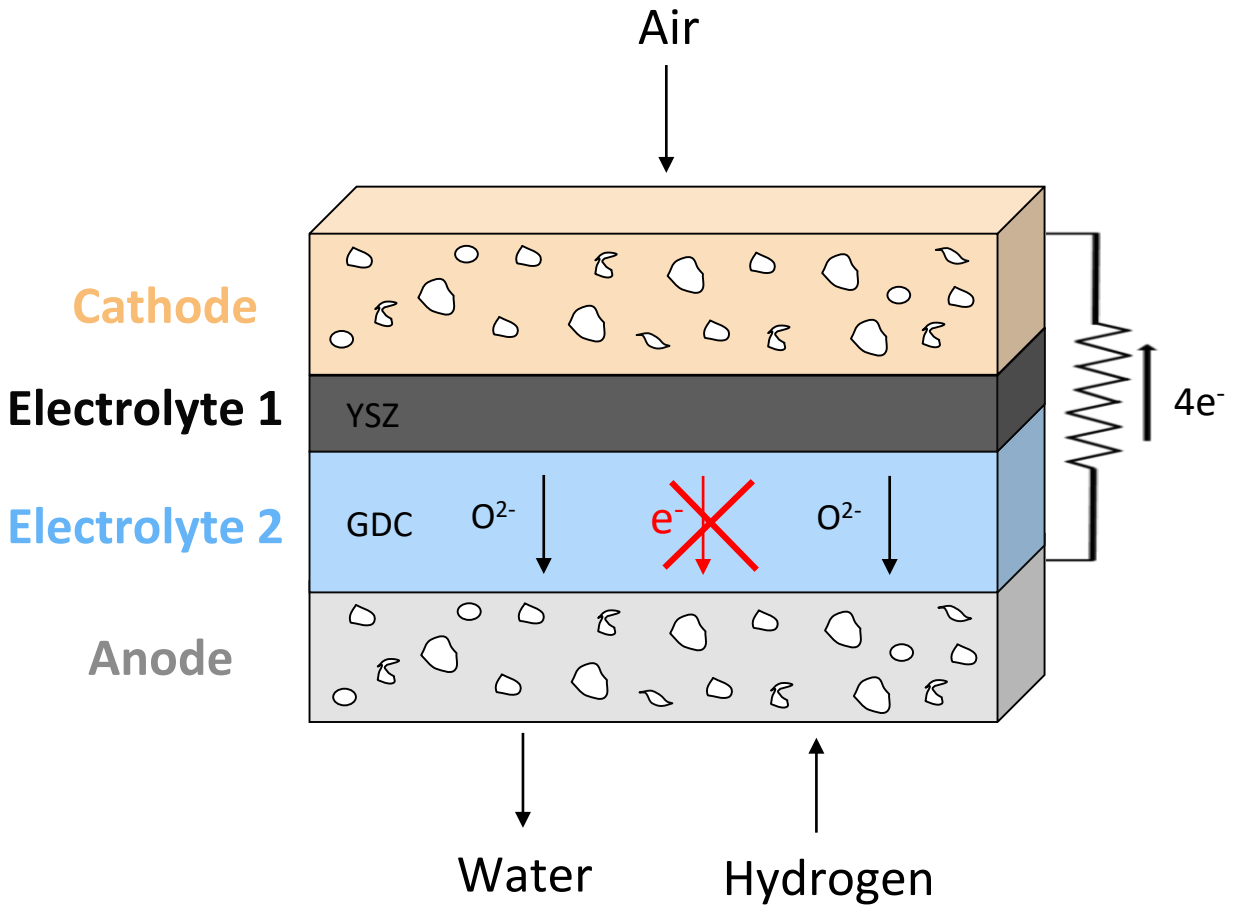
Bilayered electrolyte

Electrolyte	Thickness	Maximum power density mW.cm^{-2} at			OCV (V) 750°C
		650°C	700°C	750°C	
GDC	6 µm	198	263	315	0,5
YSZ / GDC	330 nm / 6 µm	188	430	587	0,67
YSZ / GDC	1 µm / 6 µm	-	301	438	1,05

YSZ blocks the electronic contribution

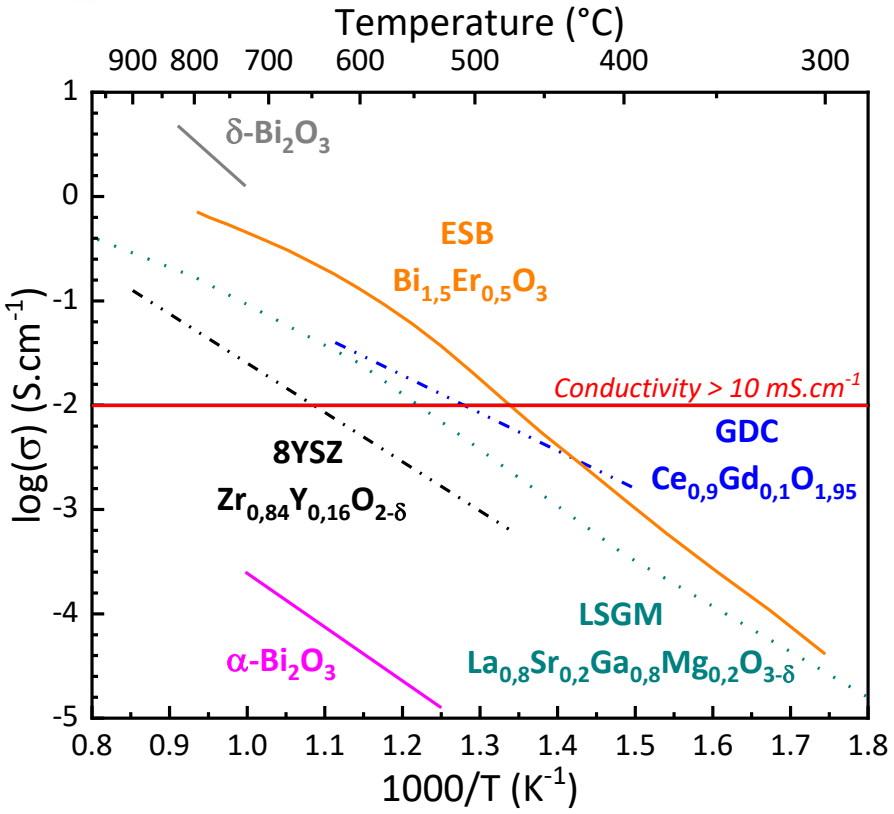
$$\Delta E_{theoretical}(1000°C) \sim 1\ V$$

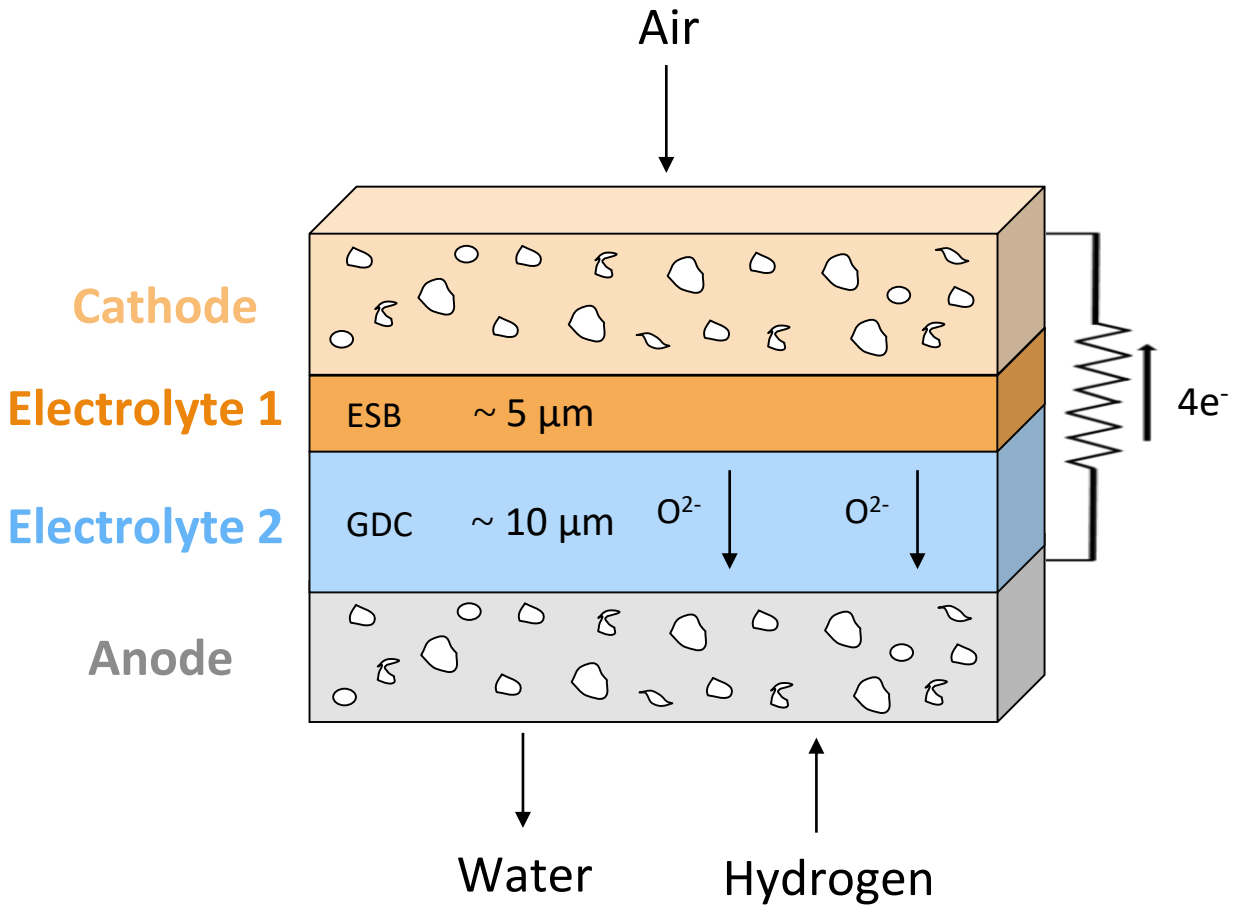
$$\Delta E_{experimental} = \Delta E_{theoretical} - RI - |\eta_{anode}| - |\eta_{cathode}|$$



Cho et al., Electrochim. Acta, 56 (2011) 5472

Bilayered electrolyte

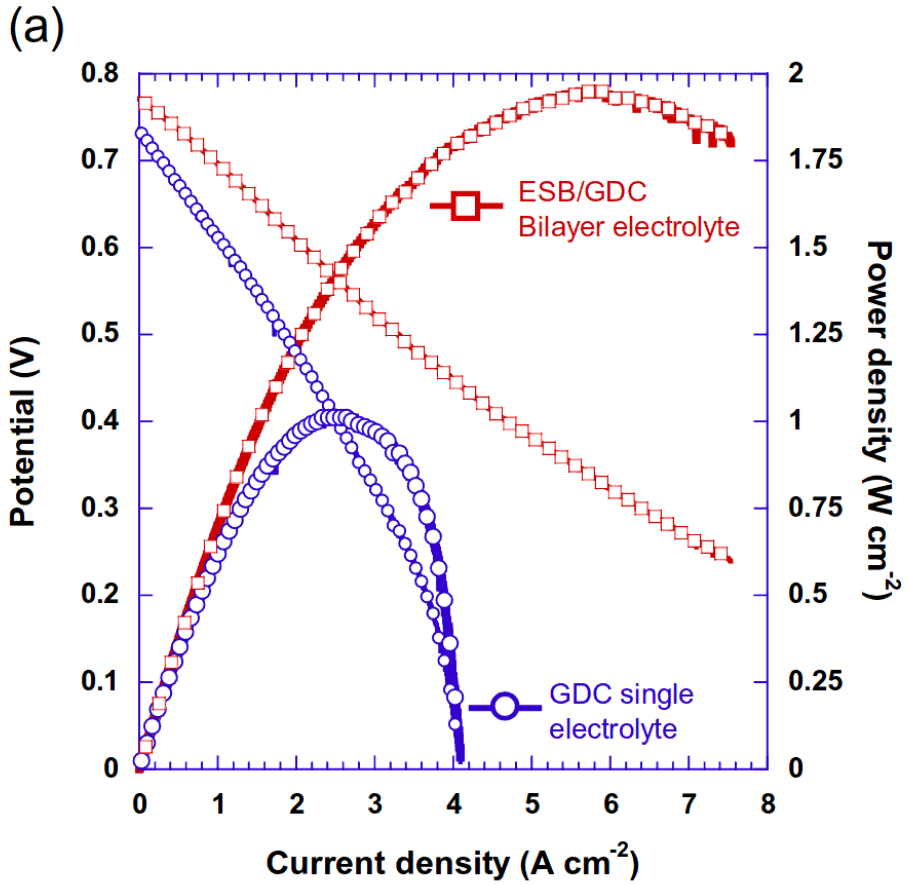


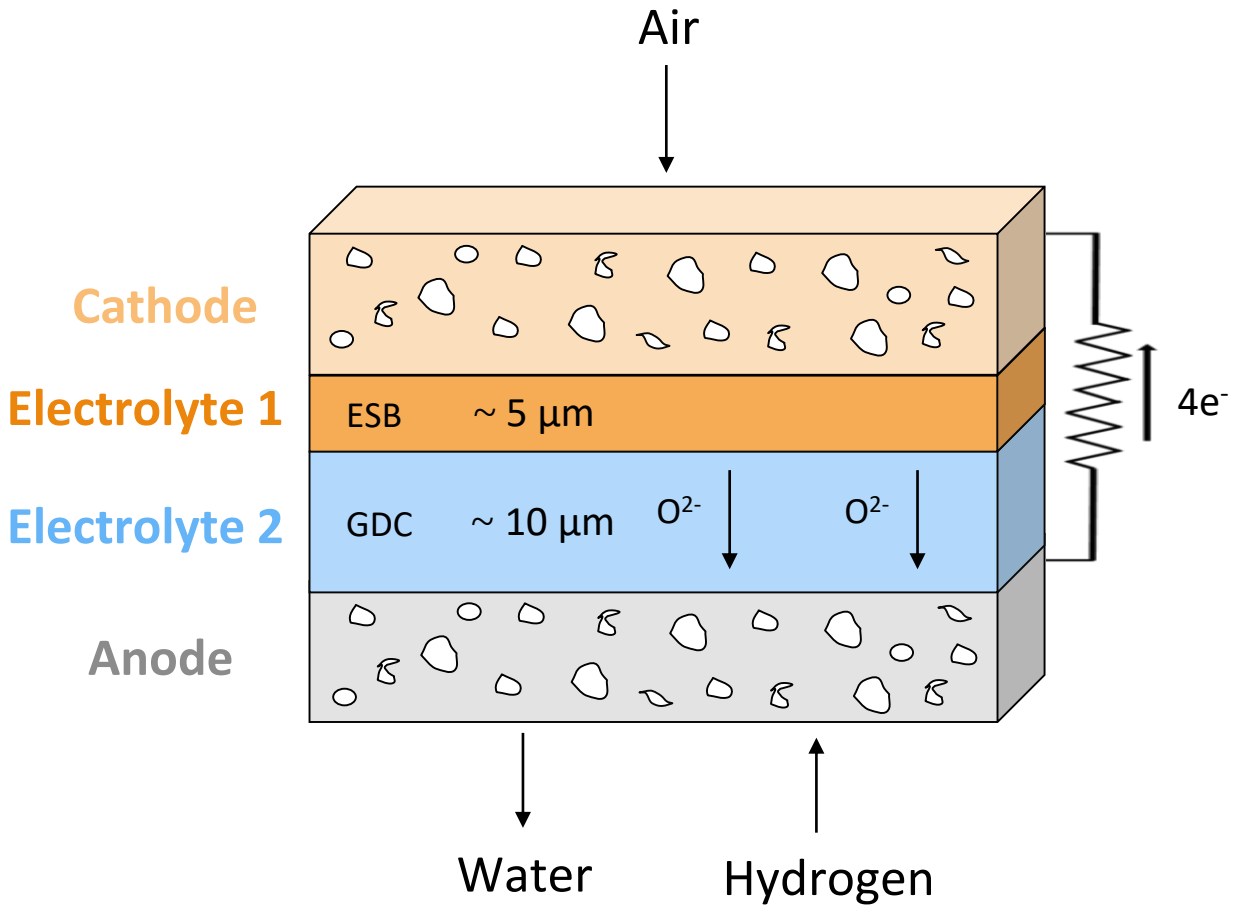


Maximum power density ~ **1.5 W.cm^{-2}** at 650°C with $La_{0,80}Sr_{0,20}MnO_{3-\delta}$/ $Bi_{1.5}Er_{0.5}O_3$ (LSM/ESB) cathode or **1.95 W.cm^{-2}** with $Bi_2Ru_2O_7$-ESB cathode

Ahn et al. Electrochem. Comm., 11 (2009) 1504
Wachsman, American Ceramic Society Bulletin, 39 (2014) 773

Bilayered electrolyte





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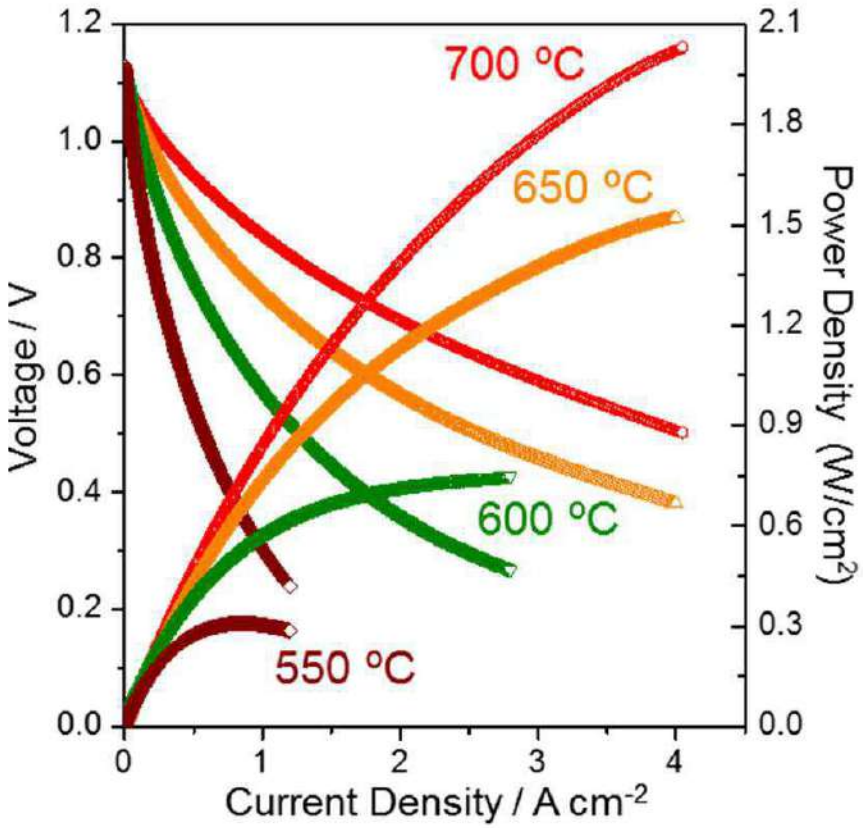
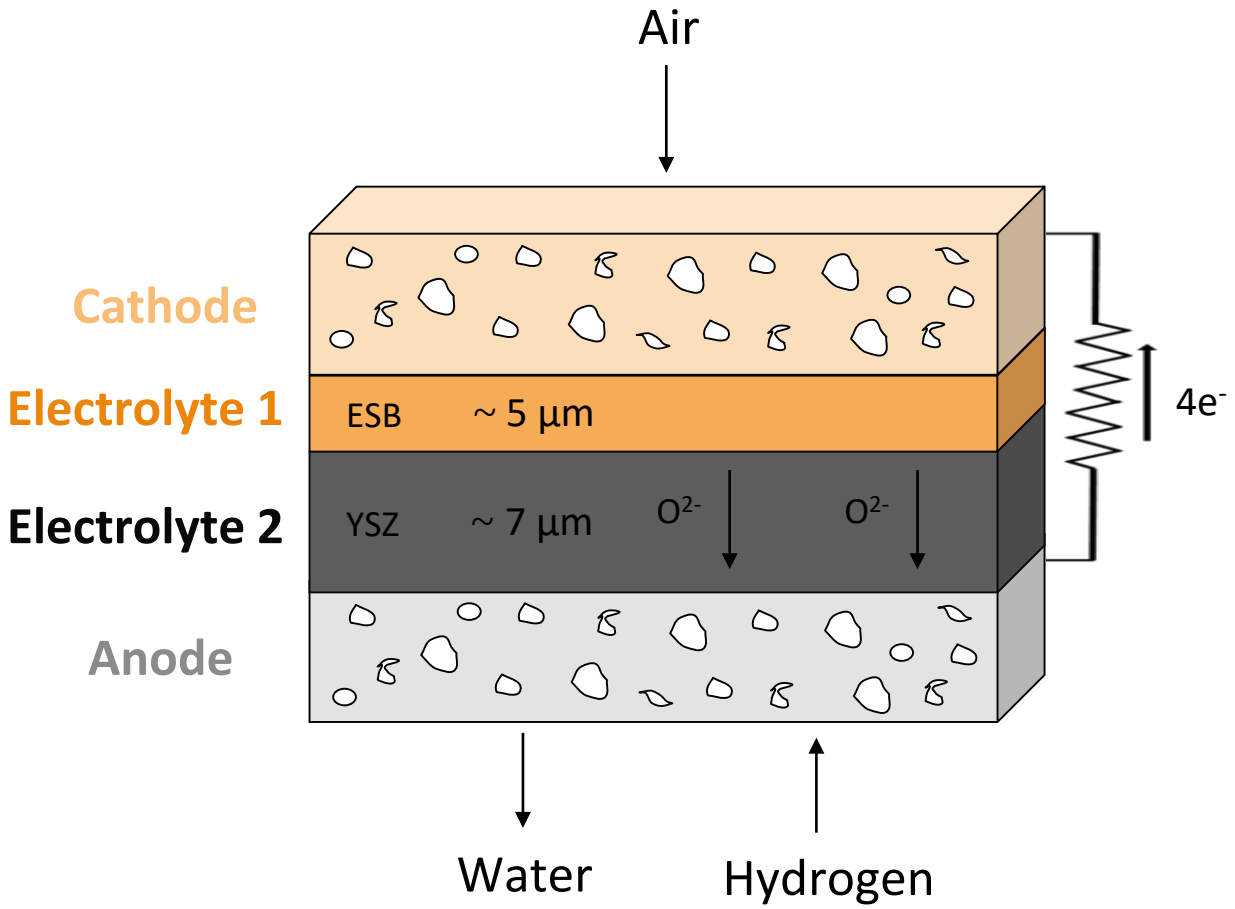
Bilayered electrolyte





Maximum power density ~ **1.62 W.cm^{-2}** at 650°C with
$La_{0,80}Sr_{0,20}MnO_{3-\delta}$/ $Bi_{1.5}Er_{0.5}O_3$ (LSM/ESB) cathode

Joh *et al.* ACS Appl. Mater. Interfaces 9 (2017) 8443–8449

Objectives

ANR-BiBeLots

BIsmuth BasEd LOw Temperature Sofc

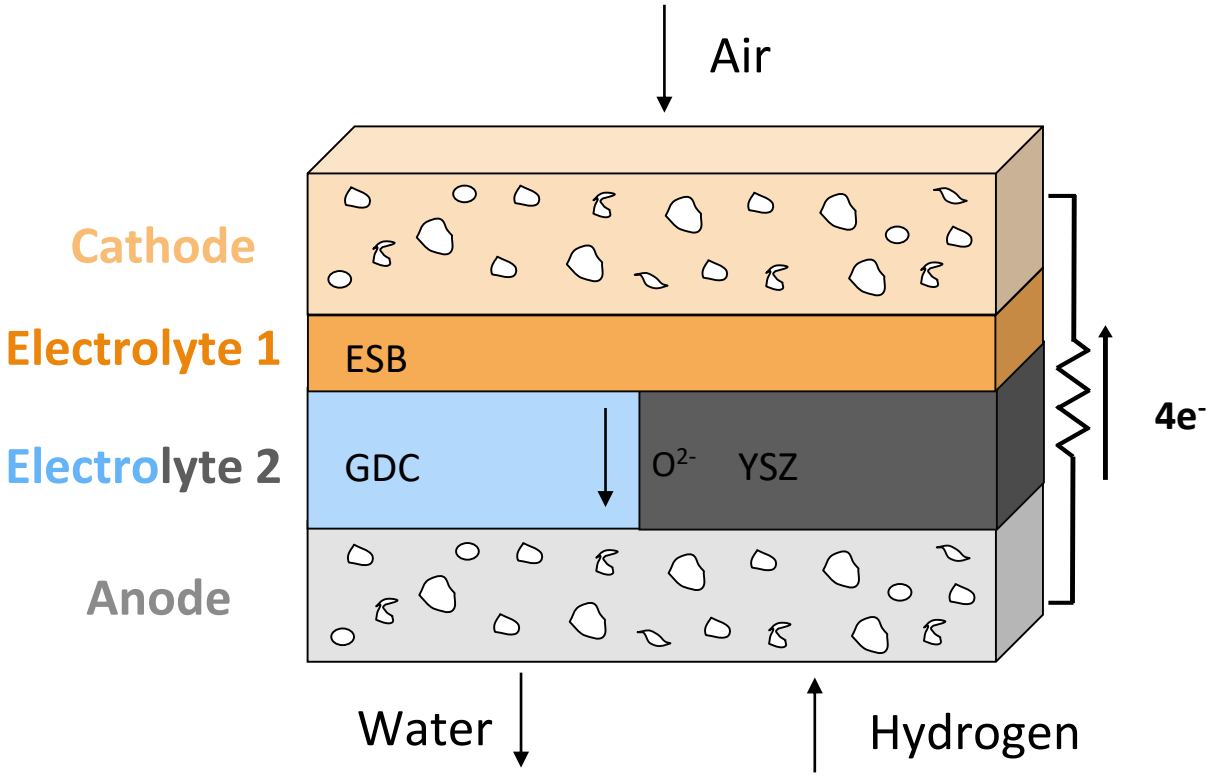
ESB densification

Ni-YSZ commercial half-cells with YSZ

Ni-3YSZ | 8YSZ

Ni-GDC half-cells with GDC

Ni-GDC | GDC



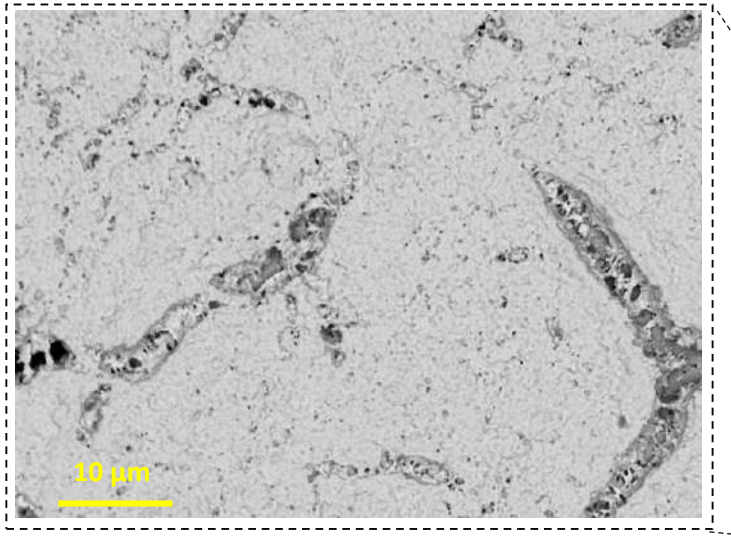
Deposition of a thin dense ESB layer

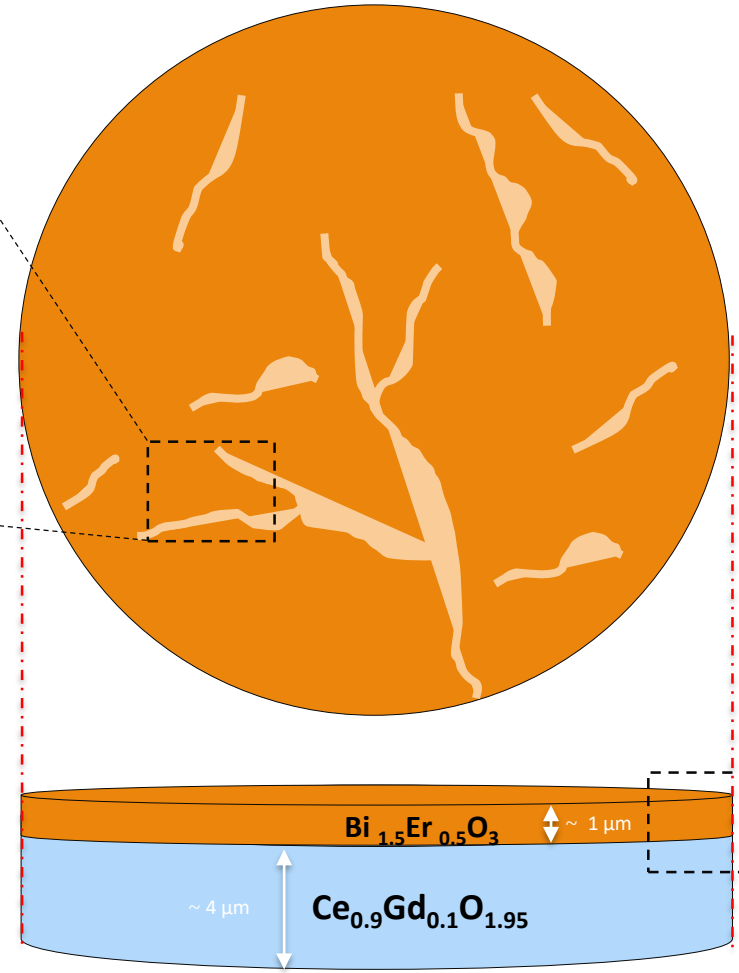
Optimization of Erbium Stabilised Bismuth Layer

The French Research network on Hydrogen energy

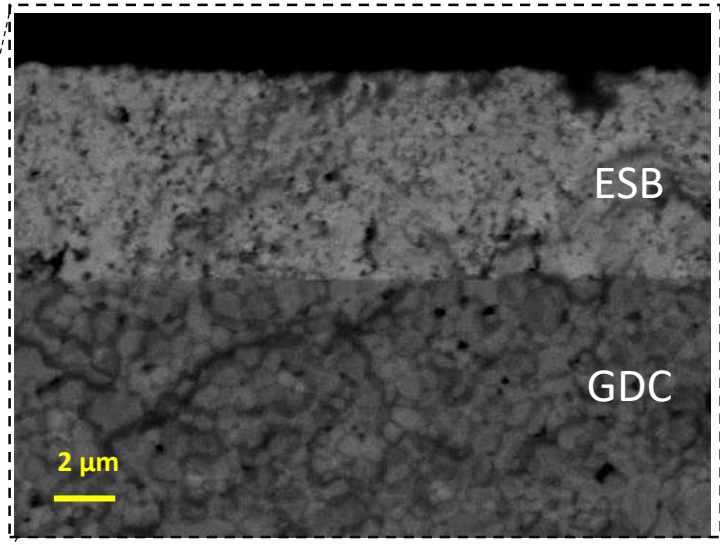
Material /binder/ dispersant / plasticizer / solvant

Large cracks





Closed porosity



ESB/PVB ratio
⇒ Ink viscosity
⇒ Mineral charge

Quantity of the plasticizer
⇒ Mechanical properties of the green film

Temperature profile
⇒ Drying process
⇒ Burn off step
⇒ Sintering temperature

Starting material
⇒ Grain size
⇒ Dispersant
⇒ Milling conditions

Optimization of Erbium Stabilised Bismuth Layer

18 % ESB / 10% PVB / 1% TEA / 5% PEG400 / 66 % Ethanol

Starting material

⇒ ESB (citrate route)

Dispersant

⇒ Triethanolamine

Binder/Plasticizer

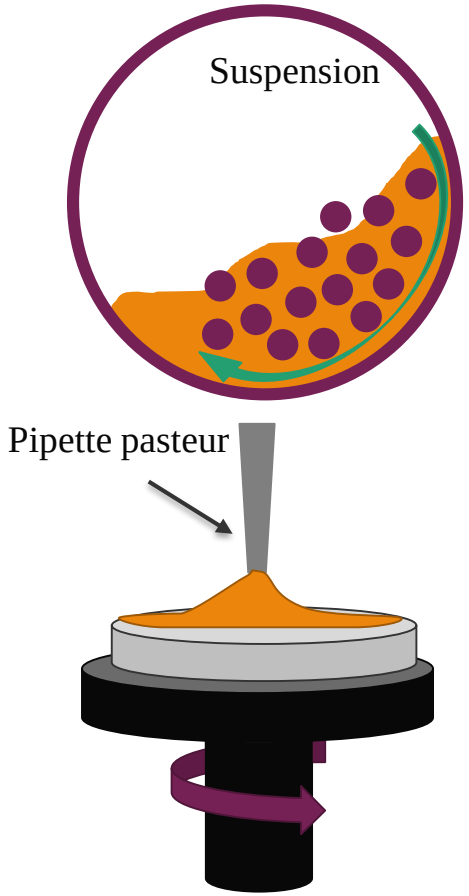
⇒ Polyvinyl Butyral/PEG 400

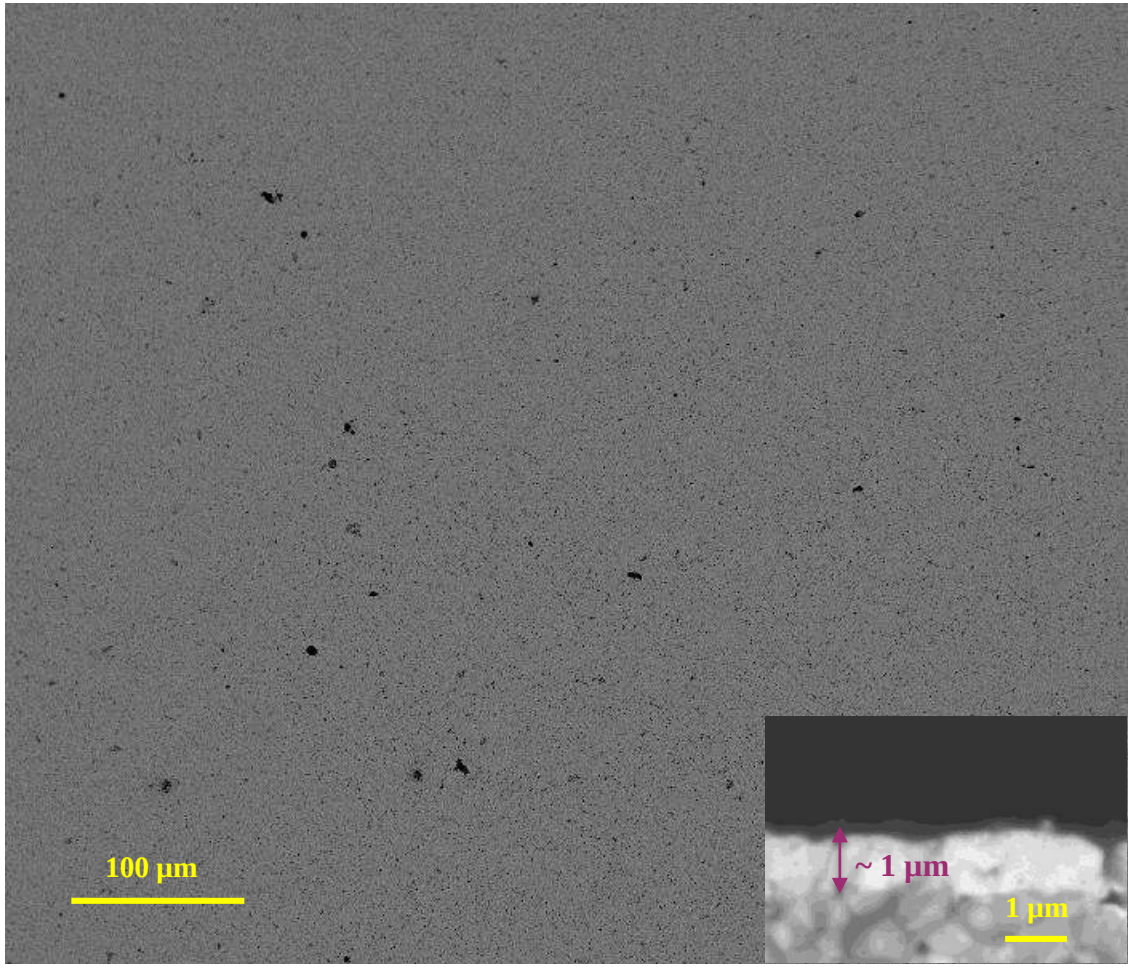
Solvant

⇒ Ethanol

Dispersion

Ball milling for 24 h
700 rpm

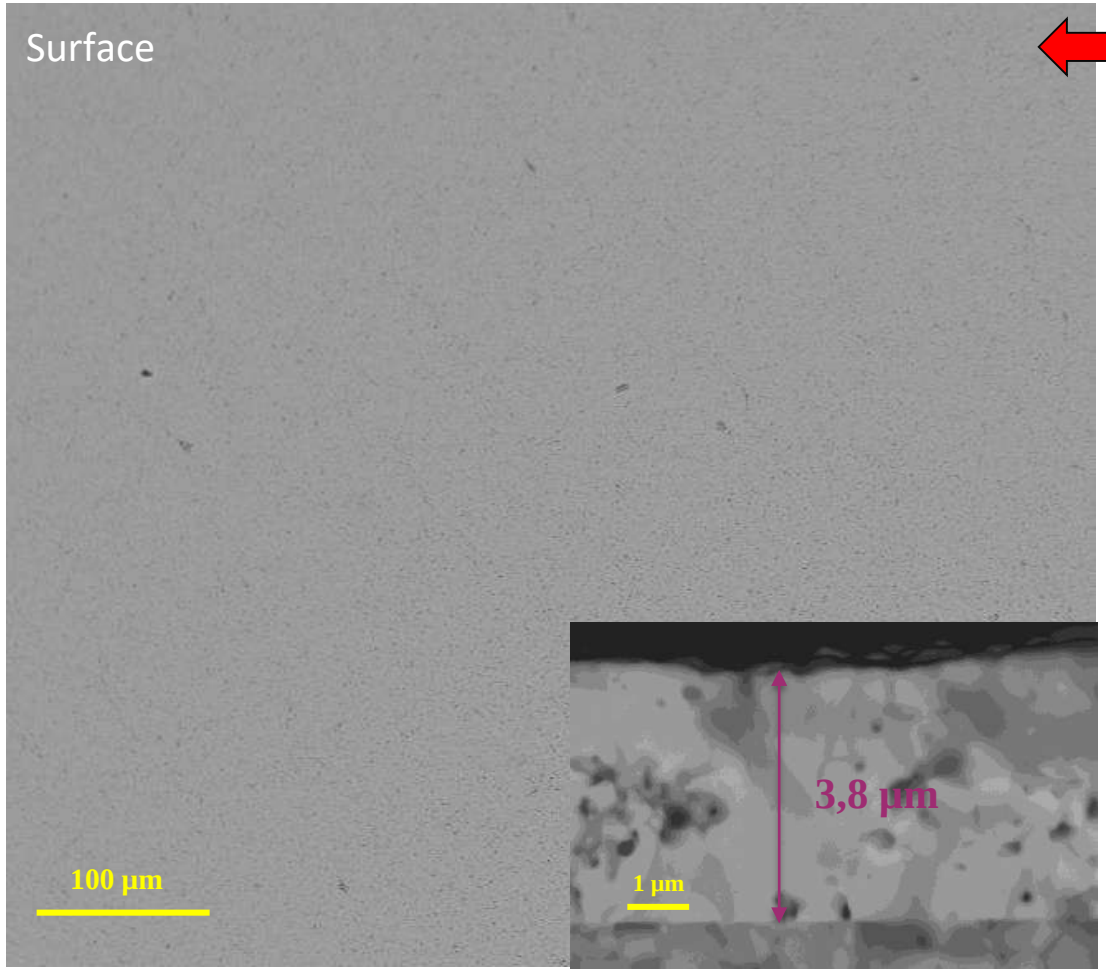


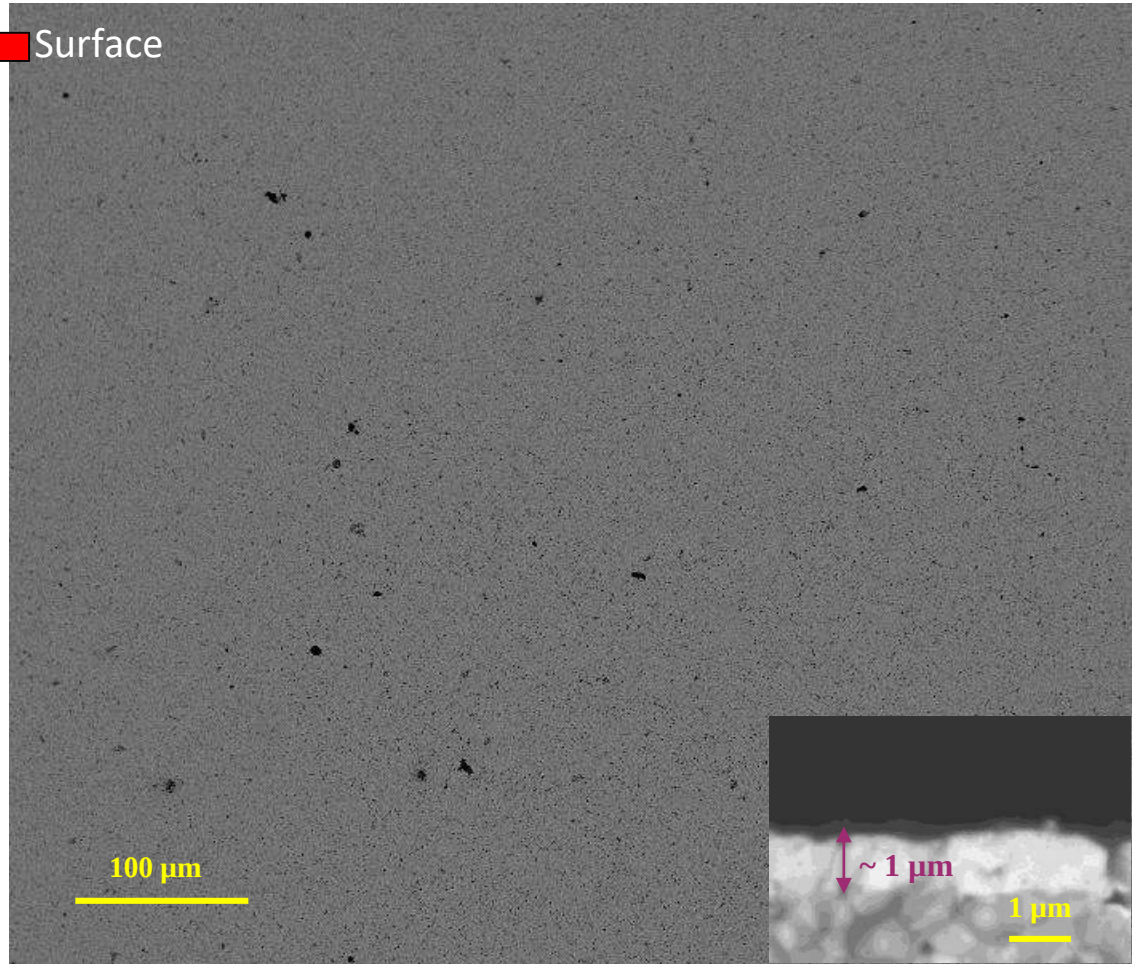


Optimization of Erbium Stabilised Bismuth Layer

18 % ESB / 10% PVB / 1% TEA / 5% PEG400 / 66 % Ethanol

Increasing thickness

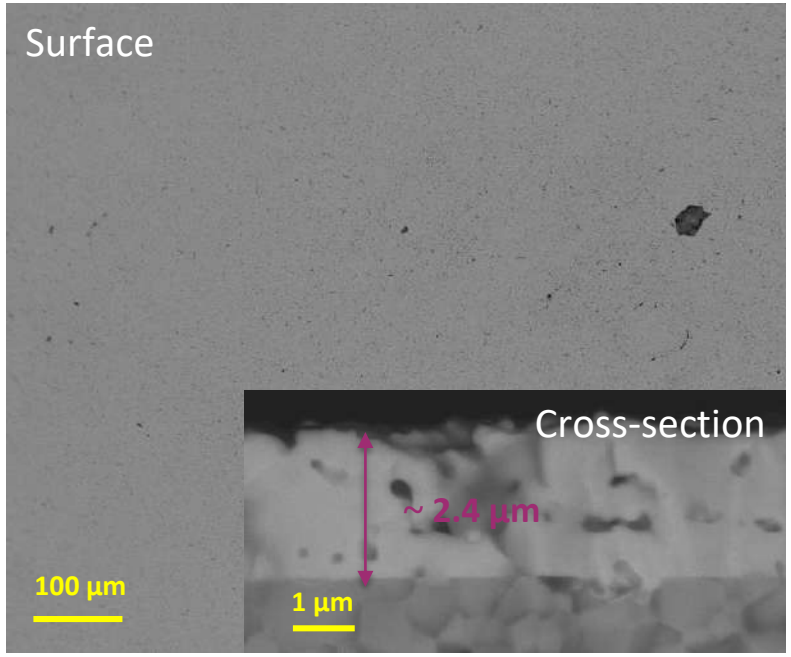




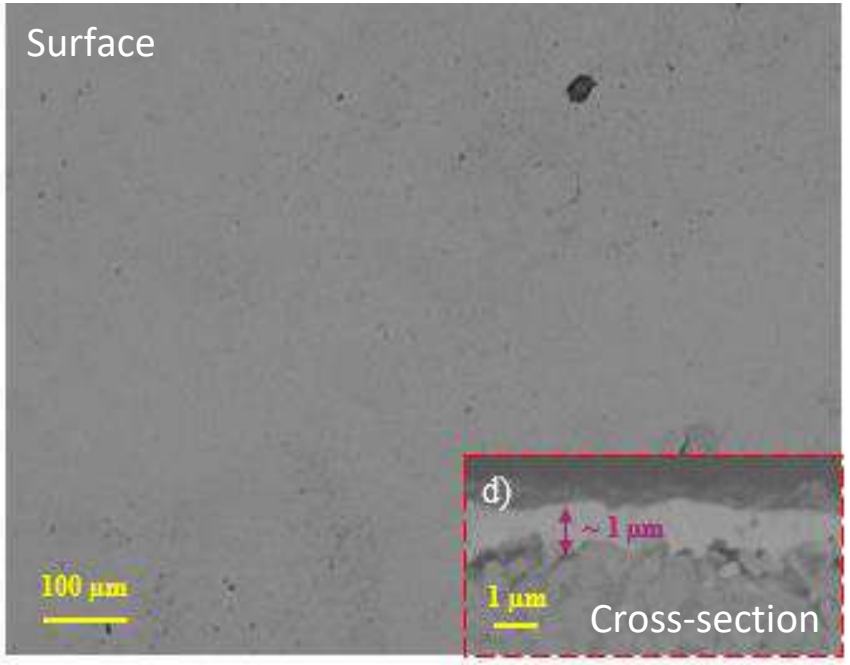
Ink versatility

$Bi_{1.5}Er_{0.5}O_3$

Spin Coater

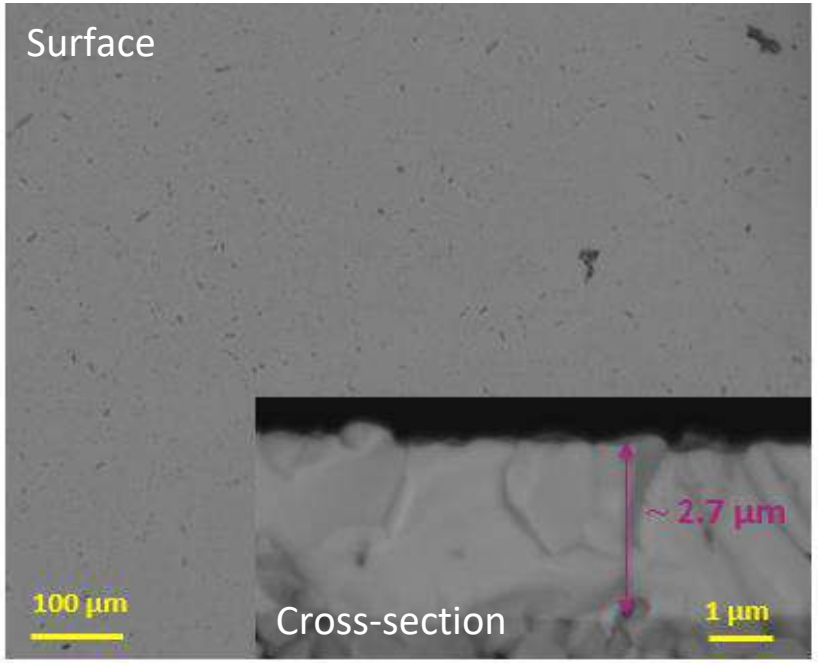


Screen printing



$Bi_{1.5}Y_{0.5}O_3$

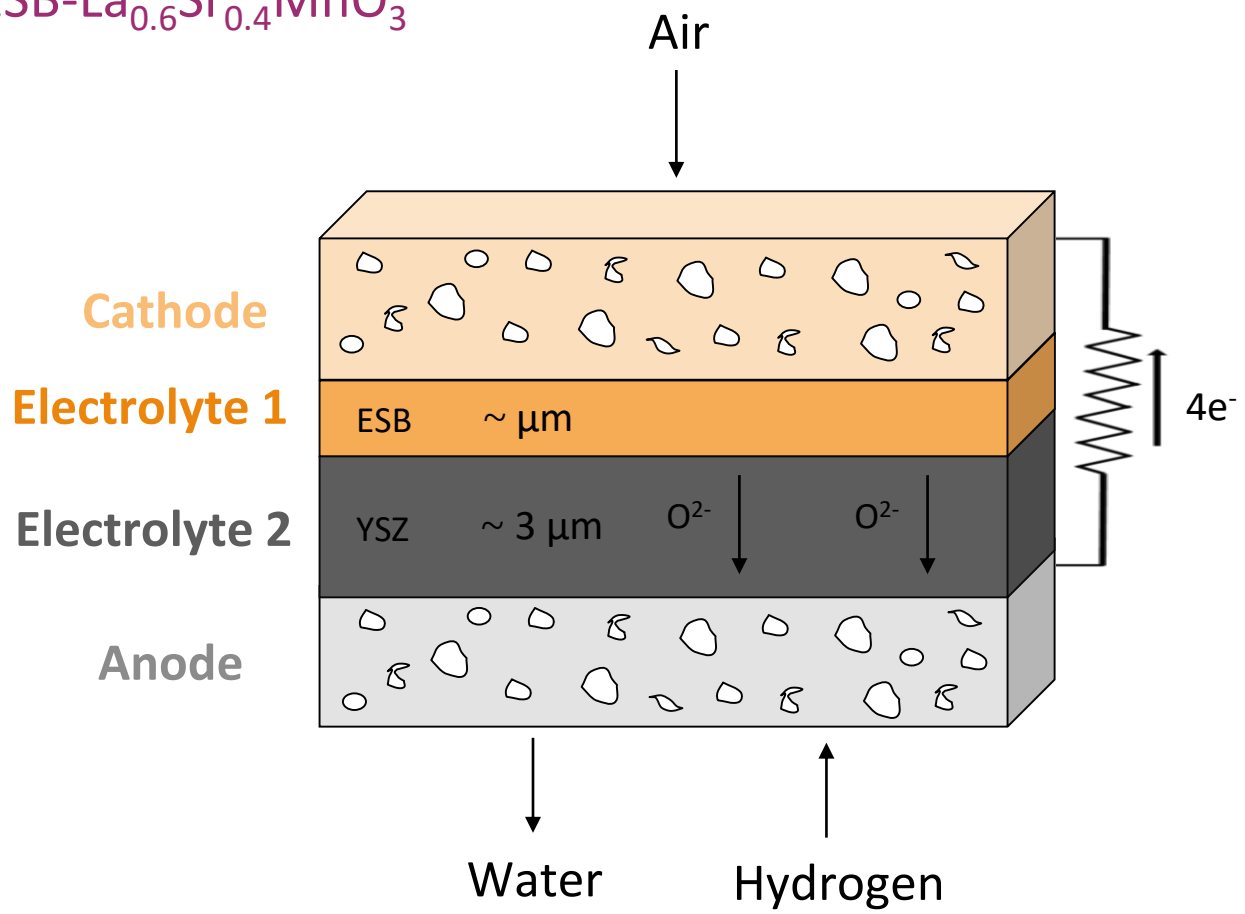
Spin Coater



Elcogen cell with ESB I ESB-$La_{0,6}$ – Cell composition

Ni-3YSZ | 8YSZ | ESB | ESB-$La_{0.6}Sr_{0.4}MnO_3$

Composition		Épaisseur (en µm)
Electrolyte	8YSZ	3
Anode fonctionnelle	NiO-3YSZ	30
Anode support	NiO-3YSZ	370

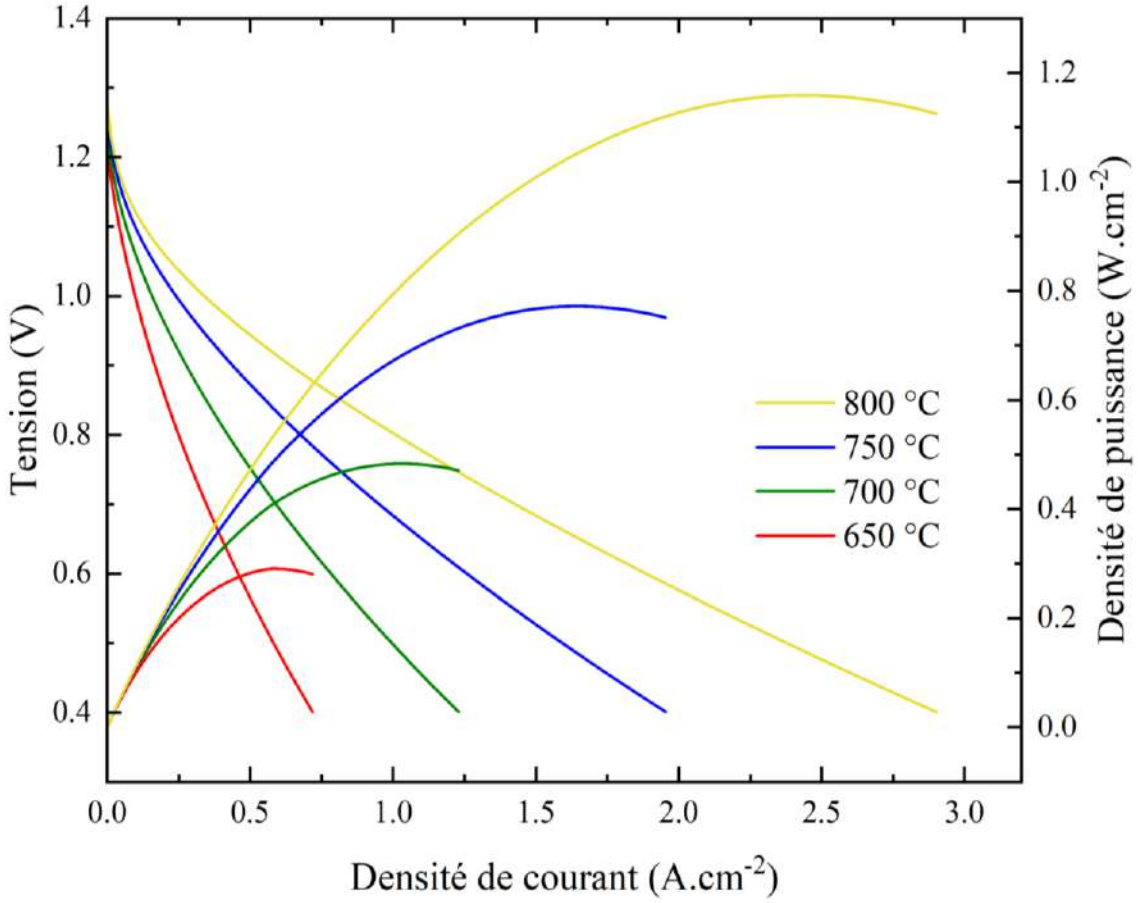


Cell performance – Elcogen cell with ESB I ESB-$La_{0,6}$

Ni-3YSZ | 8YSZ | ESB | ESB-$La_{0.6}Sr_{0.4}MnO_3$

Air : 600 ml/min
Hydrogen : 150 ml/min

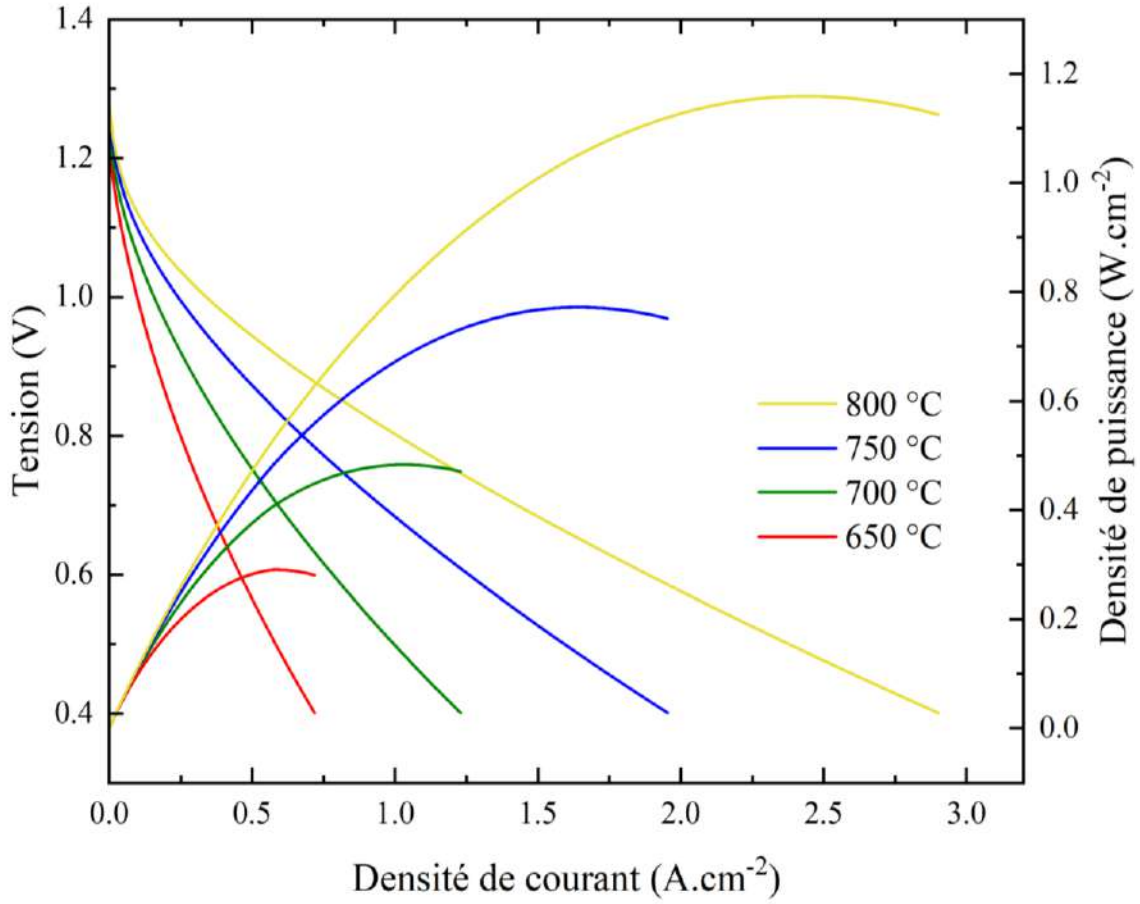
Temperature (°C)	OCV (V)	Maximal power density ($W.cm^{-2}$)
650	1,2	0,29
700	1,2	0,48
750	1,2	0,77
800	1,2	1,16



Cell performance compared to literature

Compared to literature

Anode	Electrolyte	Cathode	Maximal power density ($W.cm^{-2}$)	
			700 °C	650 °C
Ni-YSZ	YSZ (7 µm) / ESB (5 µm)	$La_{0,8}Sr_{0,2}MnO_3$-ESB	2,08	1,62
Ni-YSZ	YSZ (3 µm) / ESB (0,4 µm)	$La_{0,6}Sr_{0,4}MnO_3$-ESB	0,48	0,29



10.1149/1.3570175

Cell composition - Post-Mortem

Ni-3YSZ | 8YSZ | ESB | ESB-$La_{0.6}Sr_{0.4}MnO_3$

Felt

Cathode :

$\varphi_{ESB - La0,6}$ = 13 µm

Électrolyte :

φ_{ESB} = 0,38 µm

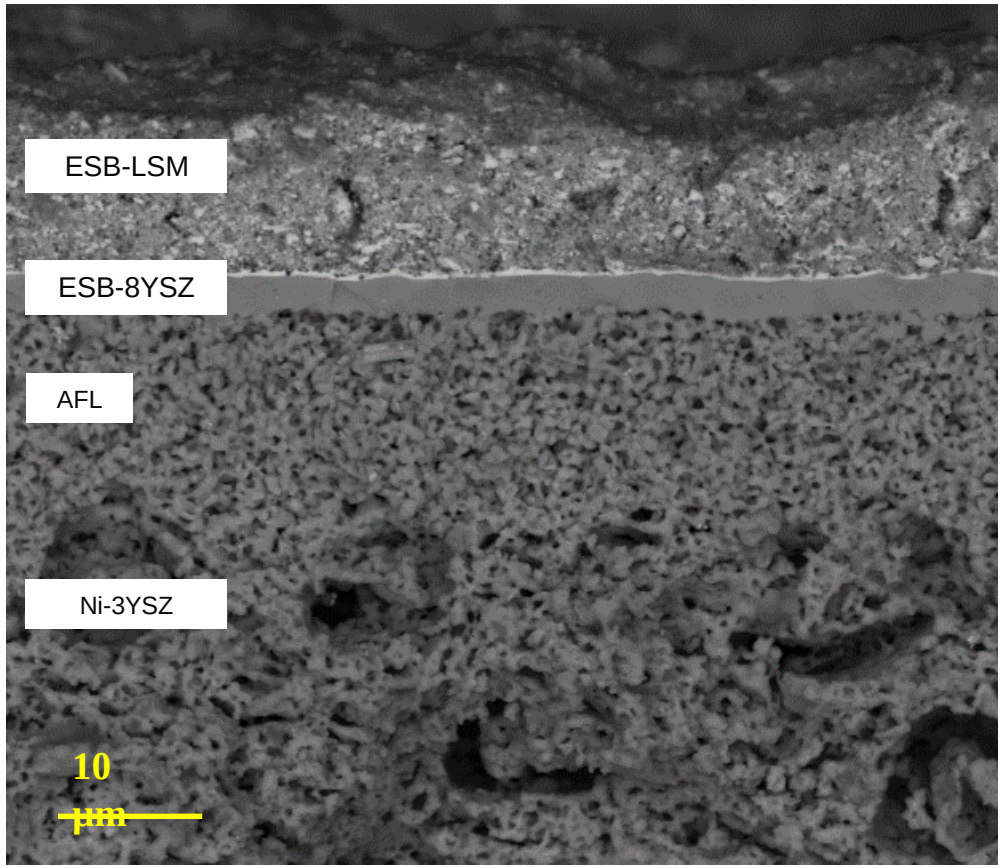
φ_{8YSZ} = 2,9 µm

AFL :

φ = 14 µm

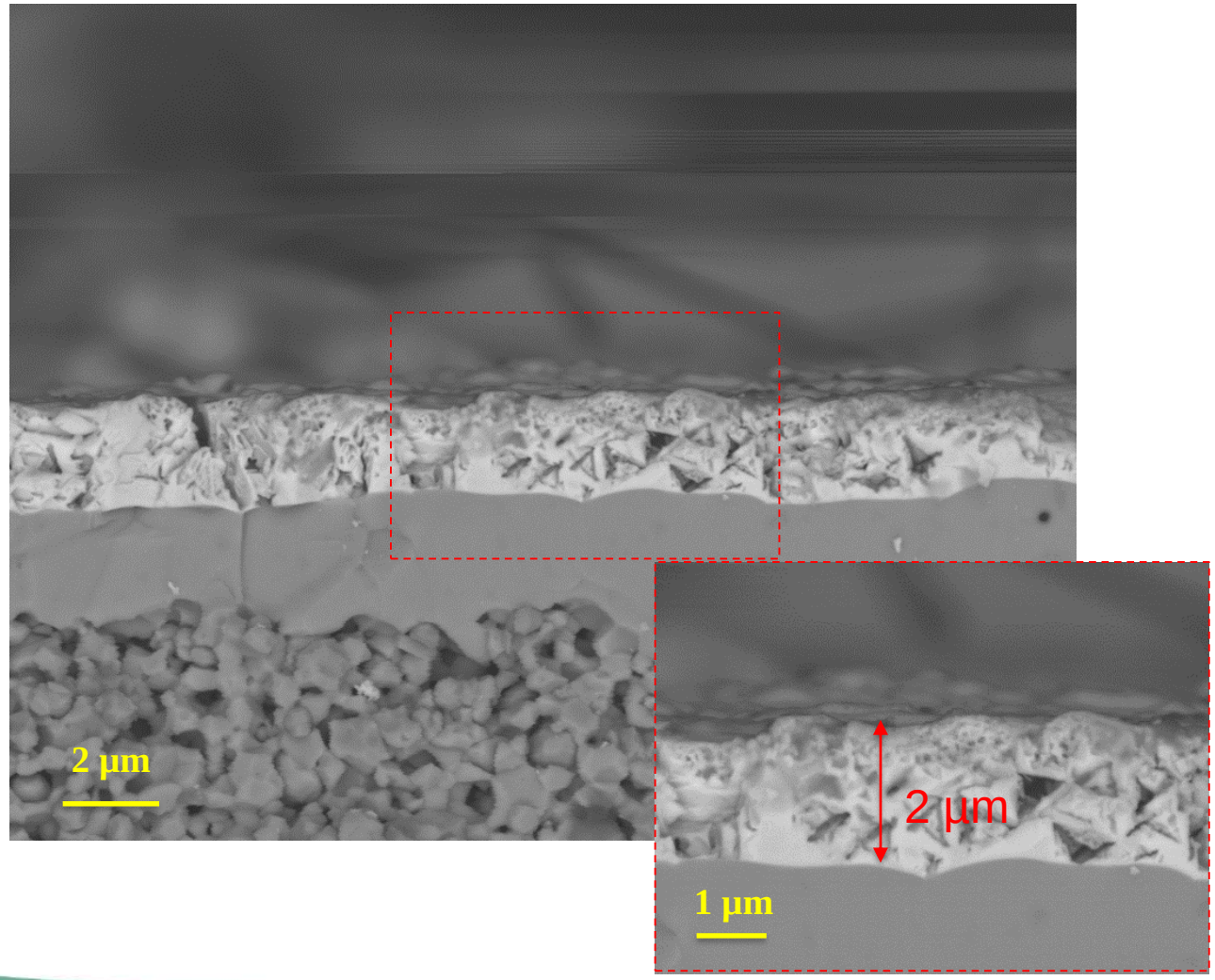
Anode :

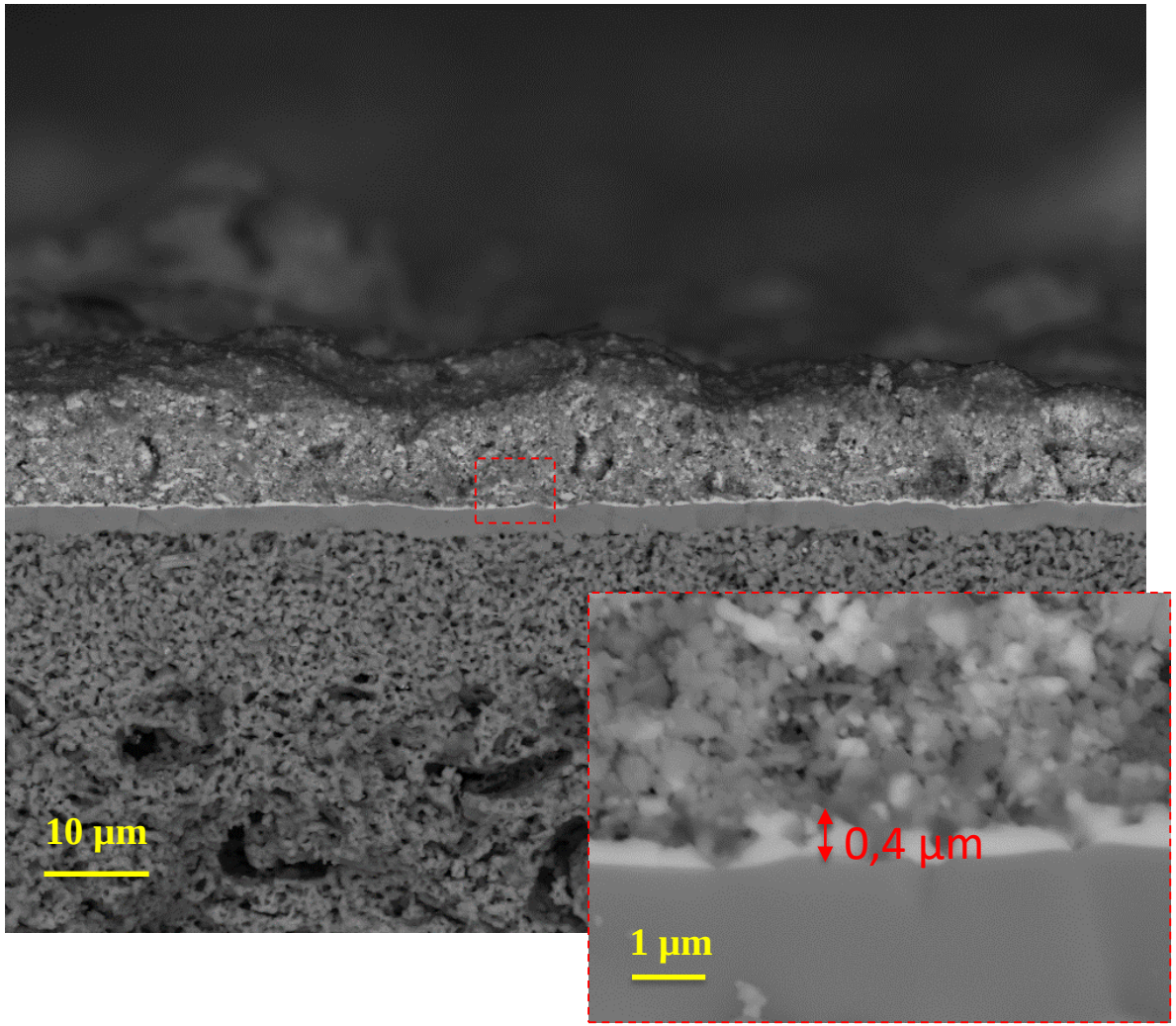
$\varphi_{Ni - 3YSZ}$ = 370 µm



SEM cathode side - Post-Mortem

Ni-3YSZ | 8YSZ | ESB | ESB-$La_{0.6}Sr_{0.4}MnO_3$

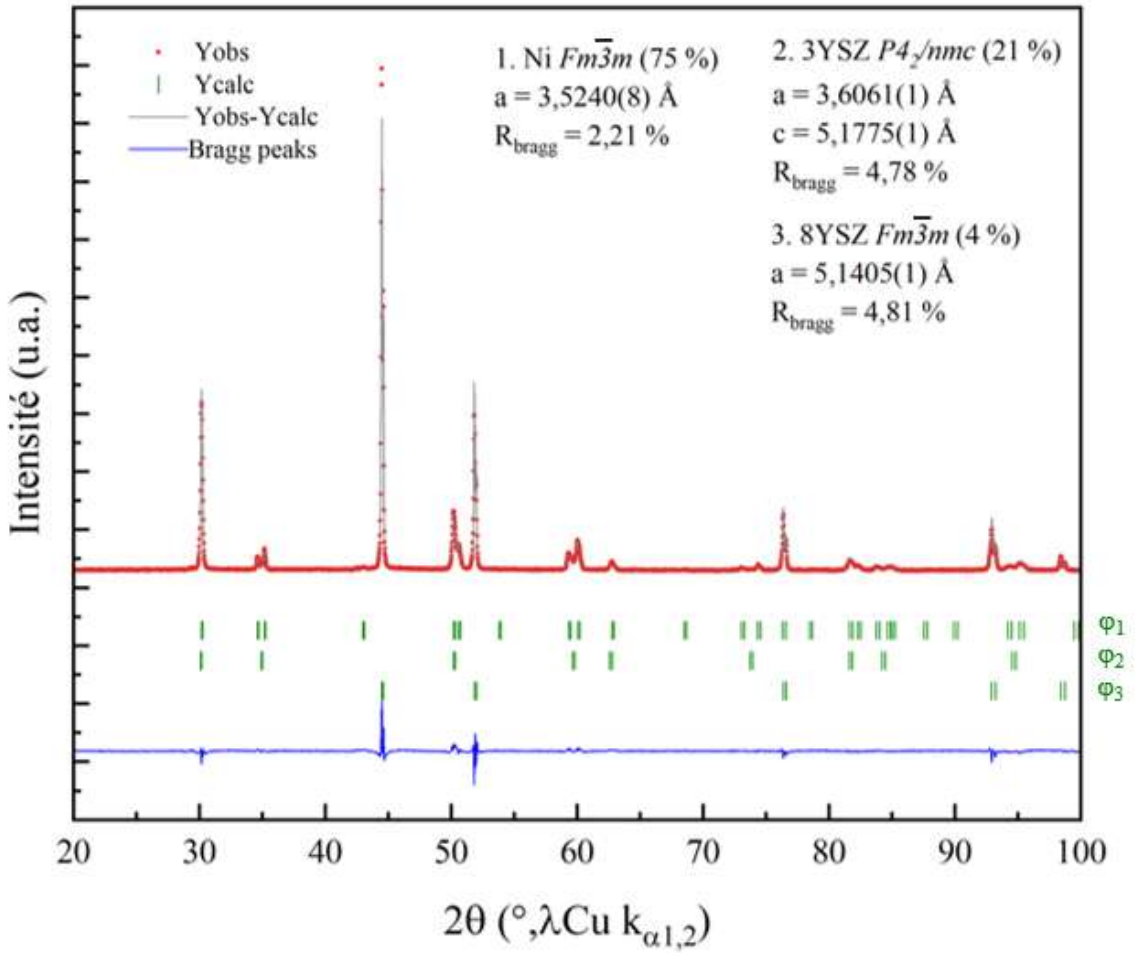




Rietveld refinement - Post-Mortem

Ni-3YSZ | 8YSZ | ESB | ESB-$La_{0.6}Sr_{0.4}MnO_3$

Anode side



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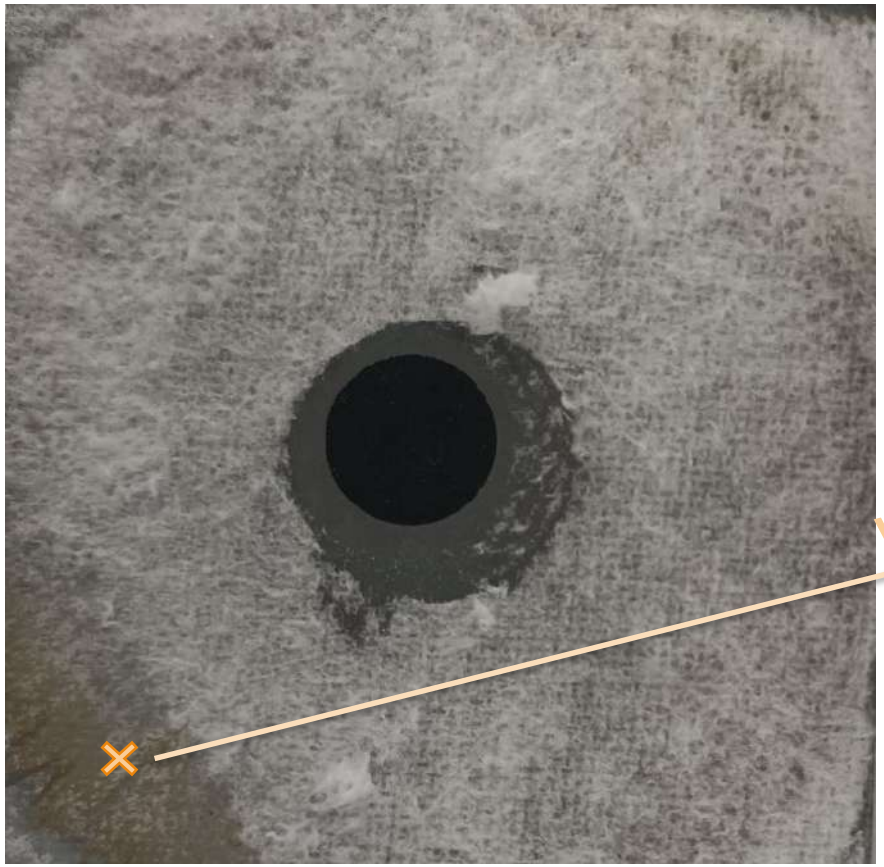
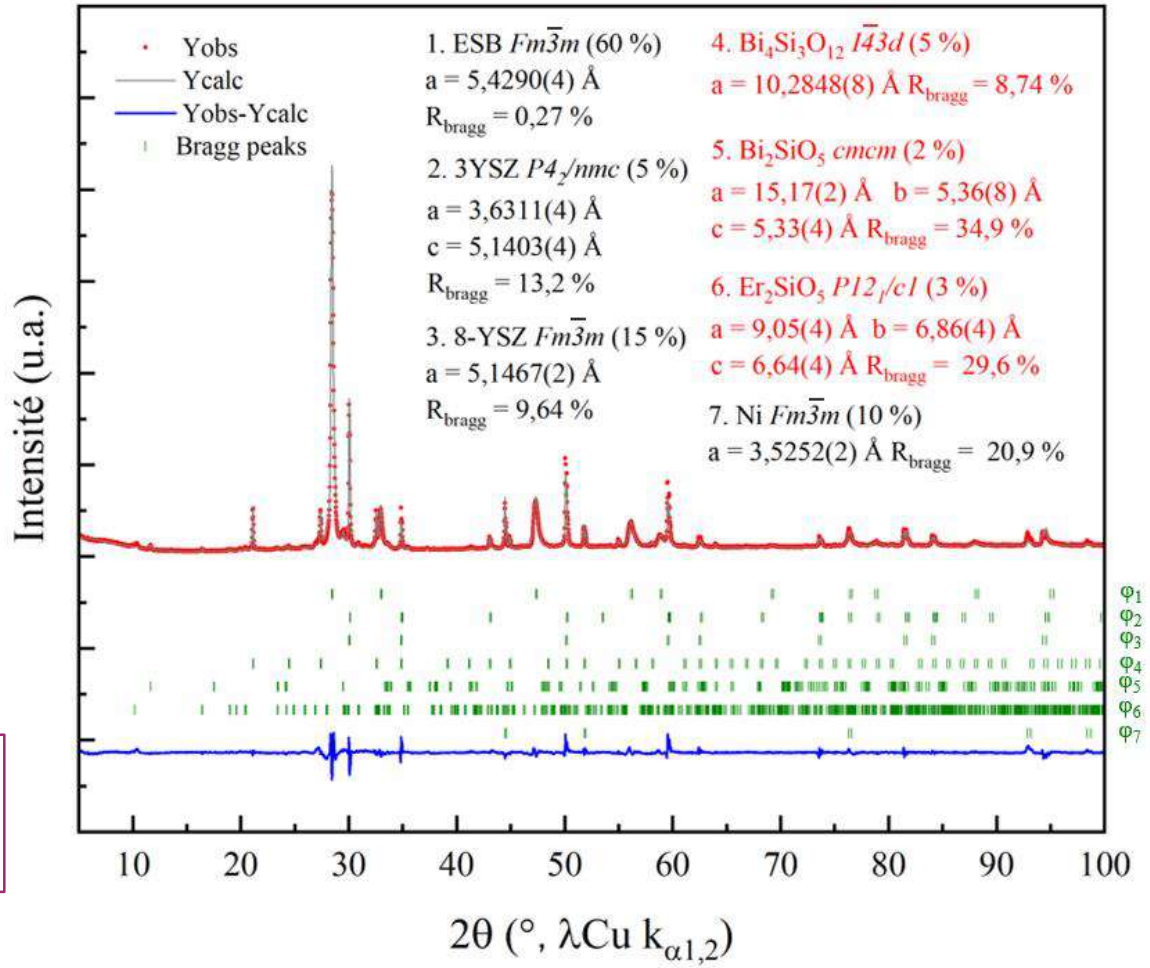


Reactivity between the felt and ESB or LSM ?

Without cathode

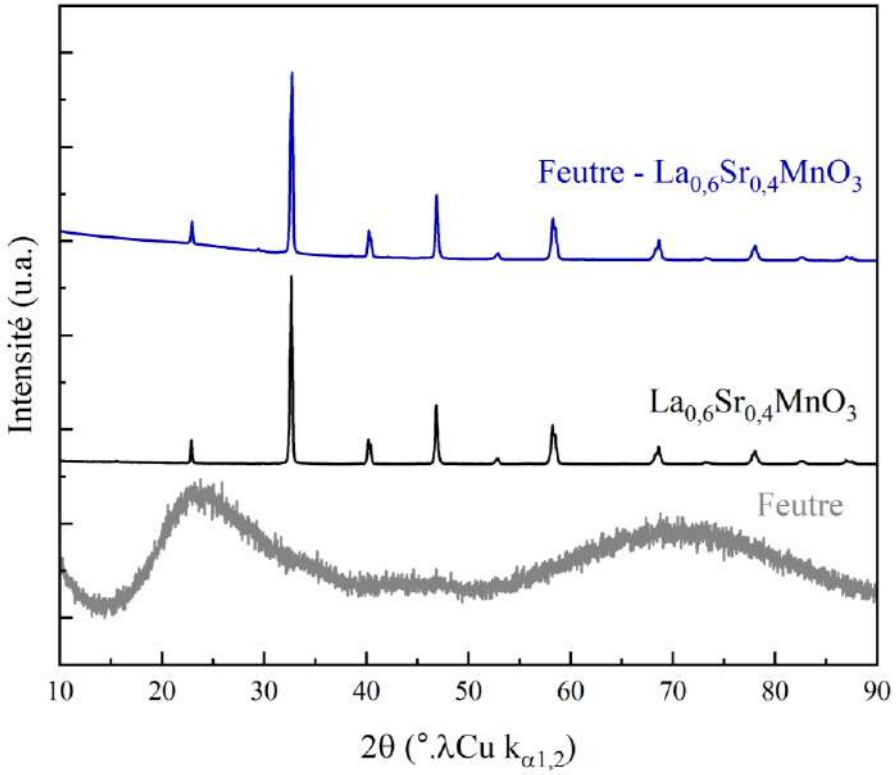
New phases : 10 %



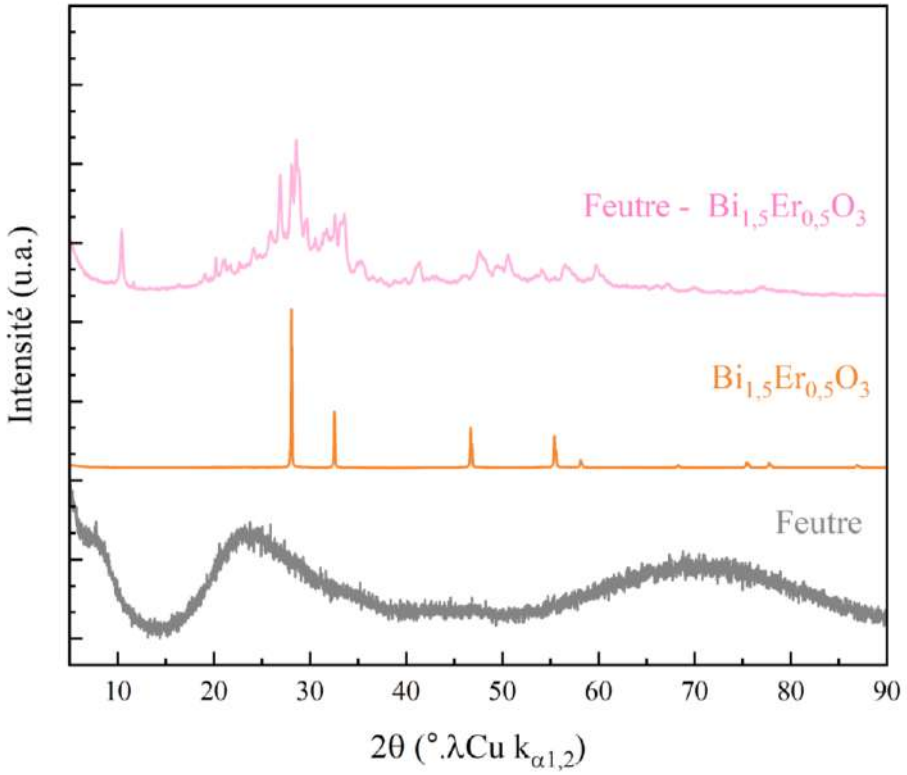
Reactivity between ESB and felt – XRD results

Mortar pestle grinding ⟶ 800 °C – 12 h

Felt - $La_{0.6}Sr_{0.4}MnO_3$

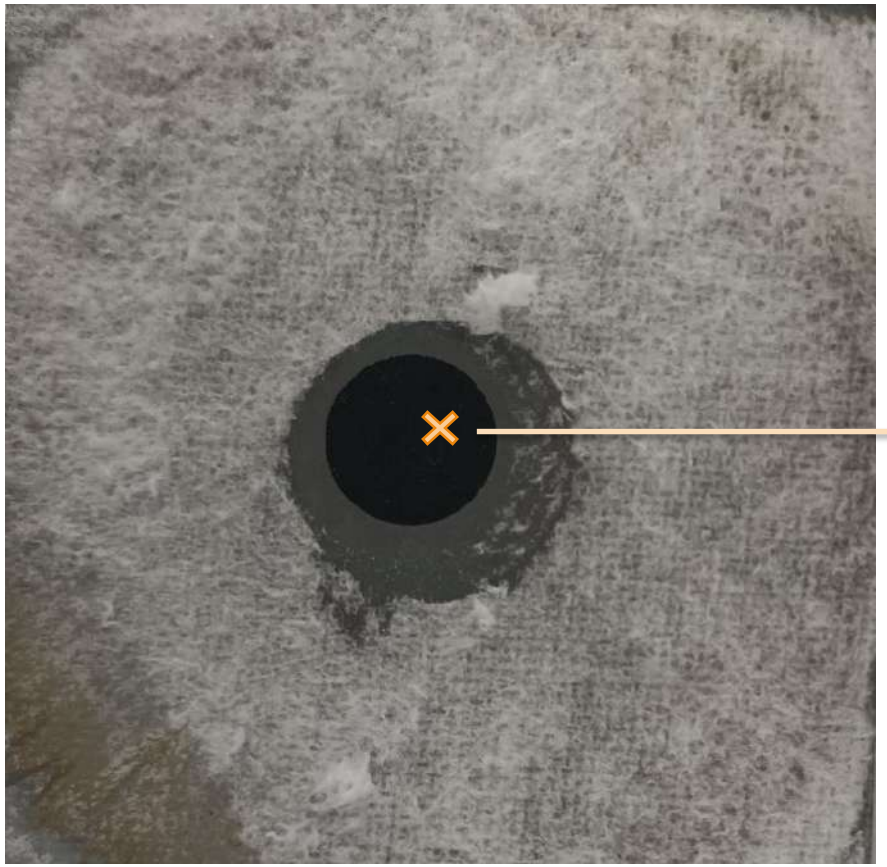


Felt – $Bi_{1.5}Er_{0.5}O_3$

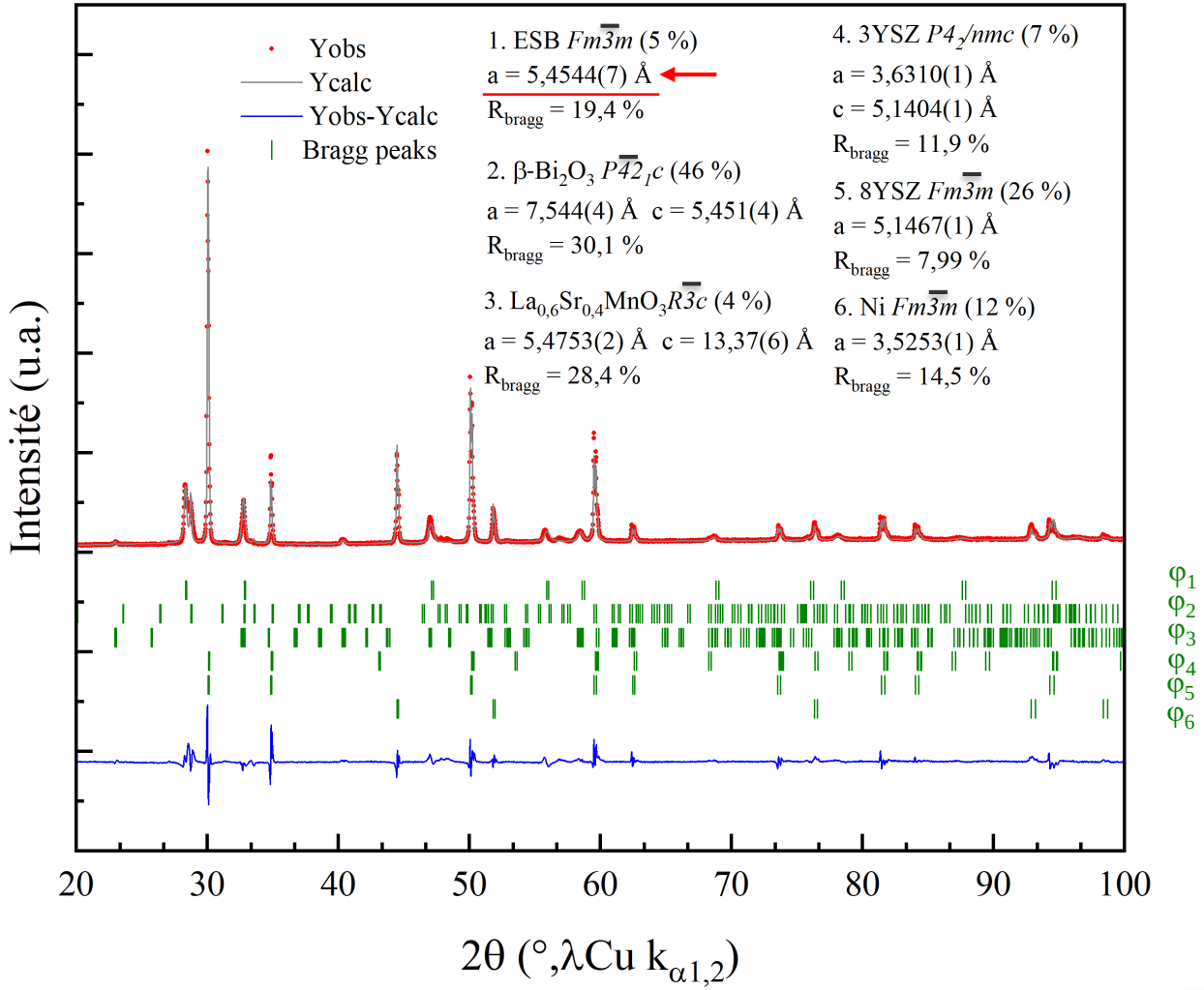


Rietveld refinement - Post-Mortem

Ni-3YSZ | 8YSZ | ESB | ESB-$La_{0.6}Sr_{0.4}MnO_3$



Cathode side



Rietveld refinement - Post-Mortem

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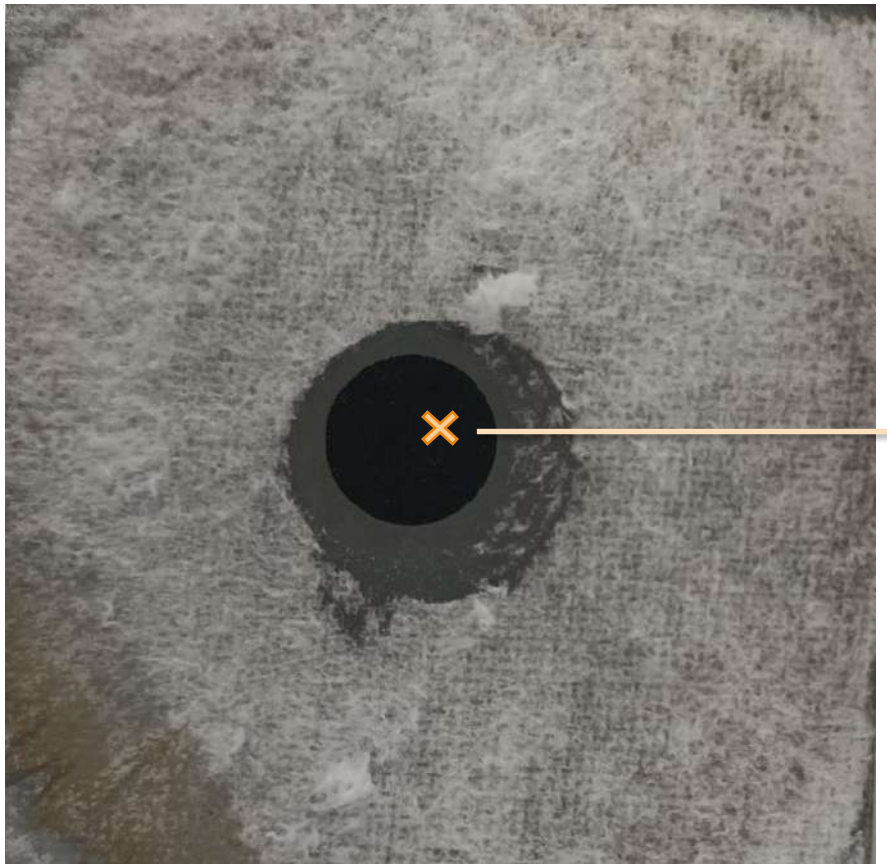
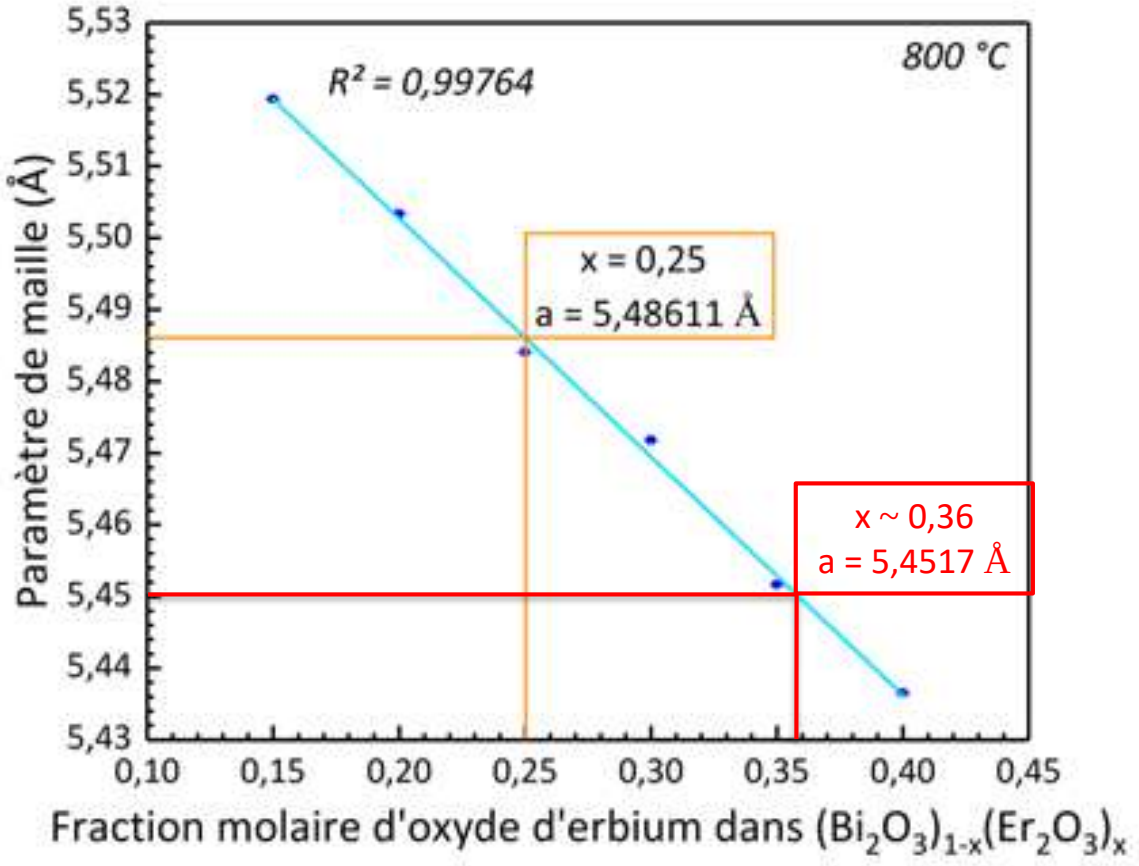
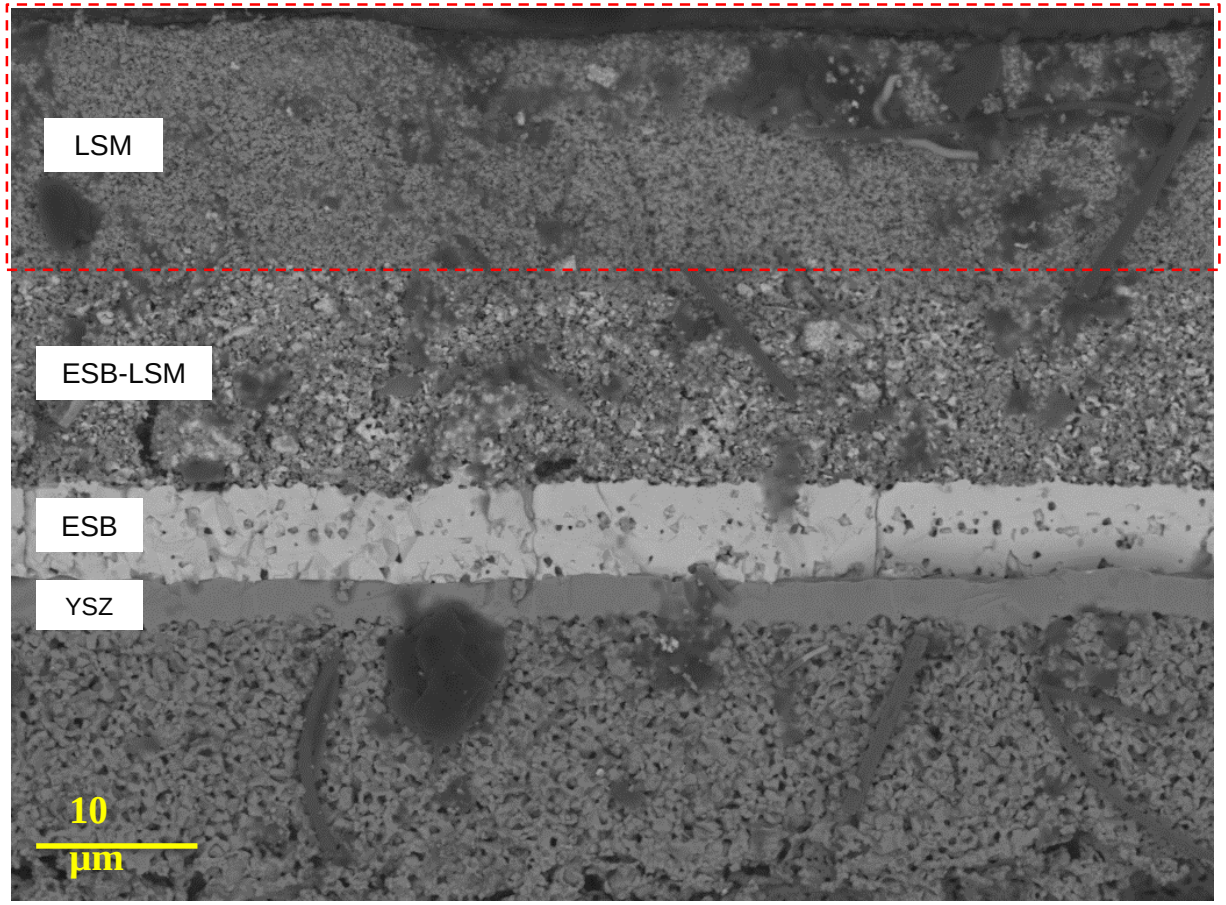




Adding LSM as current collector - SEM of cell PM

Ni-3YSZ | 8YSZ | ESB | ESB-$La_{0.6}Sr_{0.4}MnO_3$ |$La_{0.6}Sr_{0.4}MnO_3$



Current collector :

$\phi_{La0,6}$ = 15 µm

Cathode :

$\phi_{ESB - La0,6}$ = 13 µm

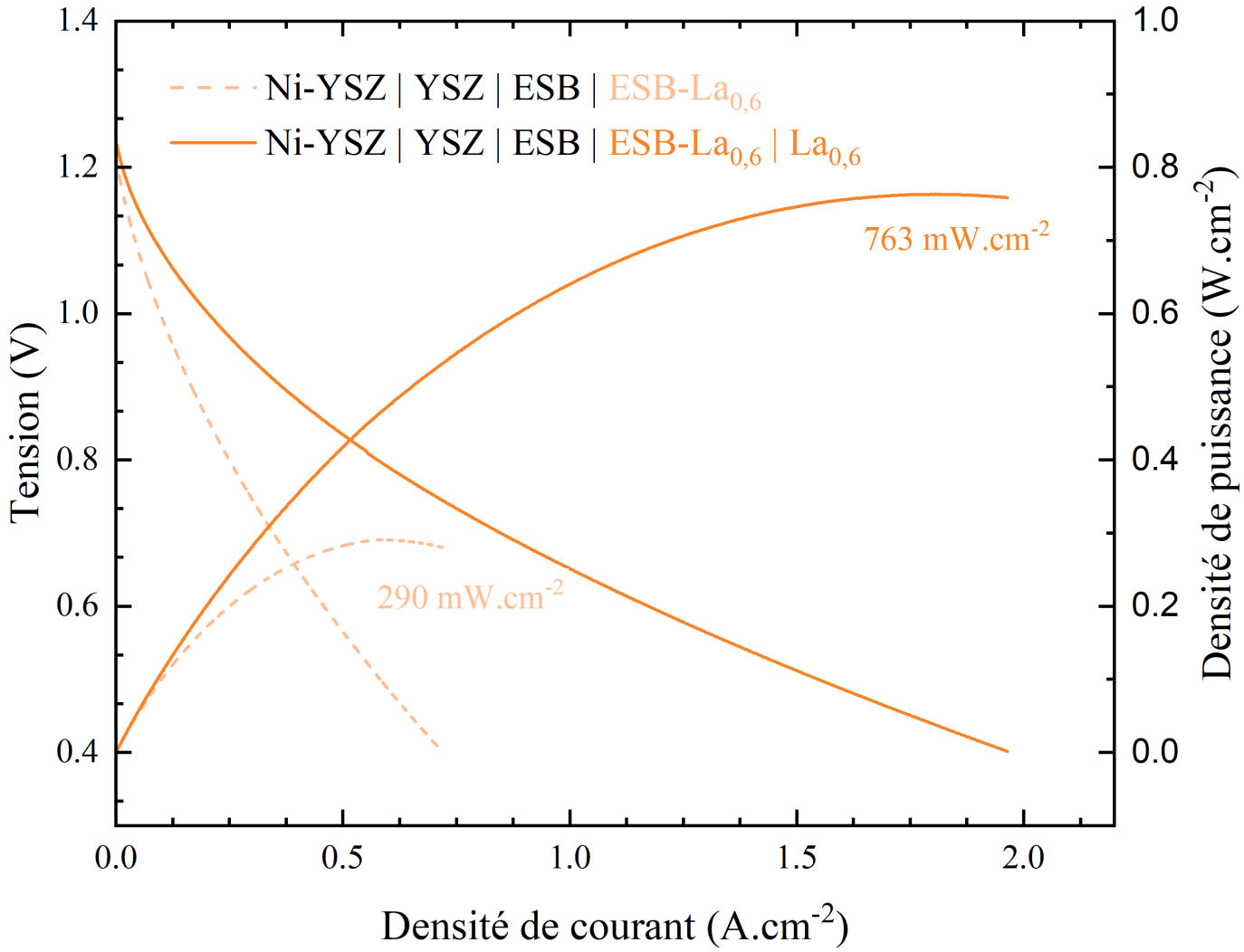
Electrolyte :

ϕ_{ESB} = 5,6 µm

ϕ_{8YSZ} = 2,9 µm

Adding a current collector (LSM) to prevent ESB from reacting with the felt

Cell performance – Current collector effect



With current collector

0,76 W.cm^{-2}

Without current collector

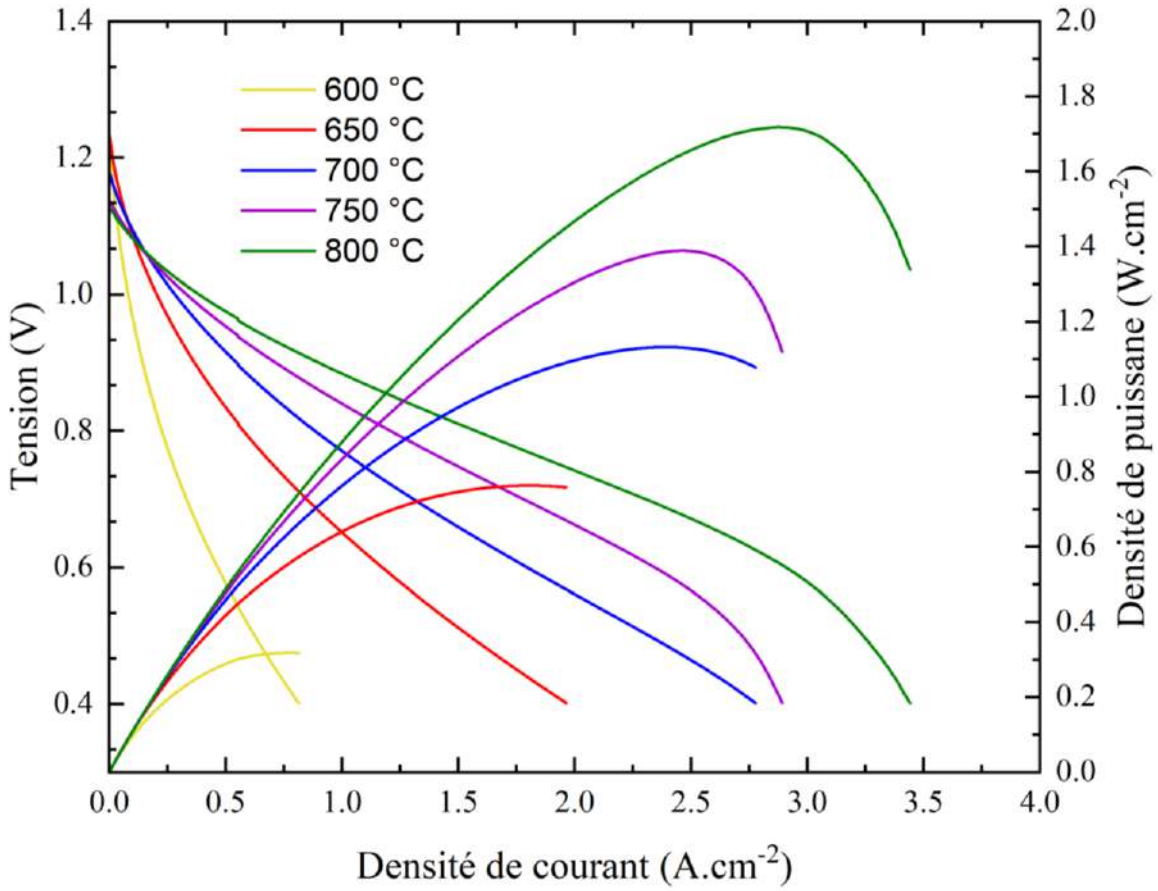
0,29 W.cm^{-2}

Cell performance – Current collector effect

Ni-3YSZ | 8YSZ | ESB | ESB-$La_{0.6}Sr_{0.4}MnO_3$ |$La_{0.6}Sr_{0.4}MnO_3$

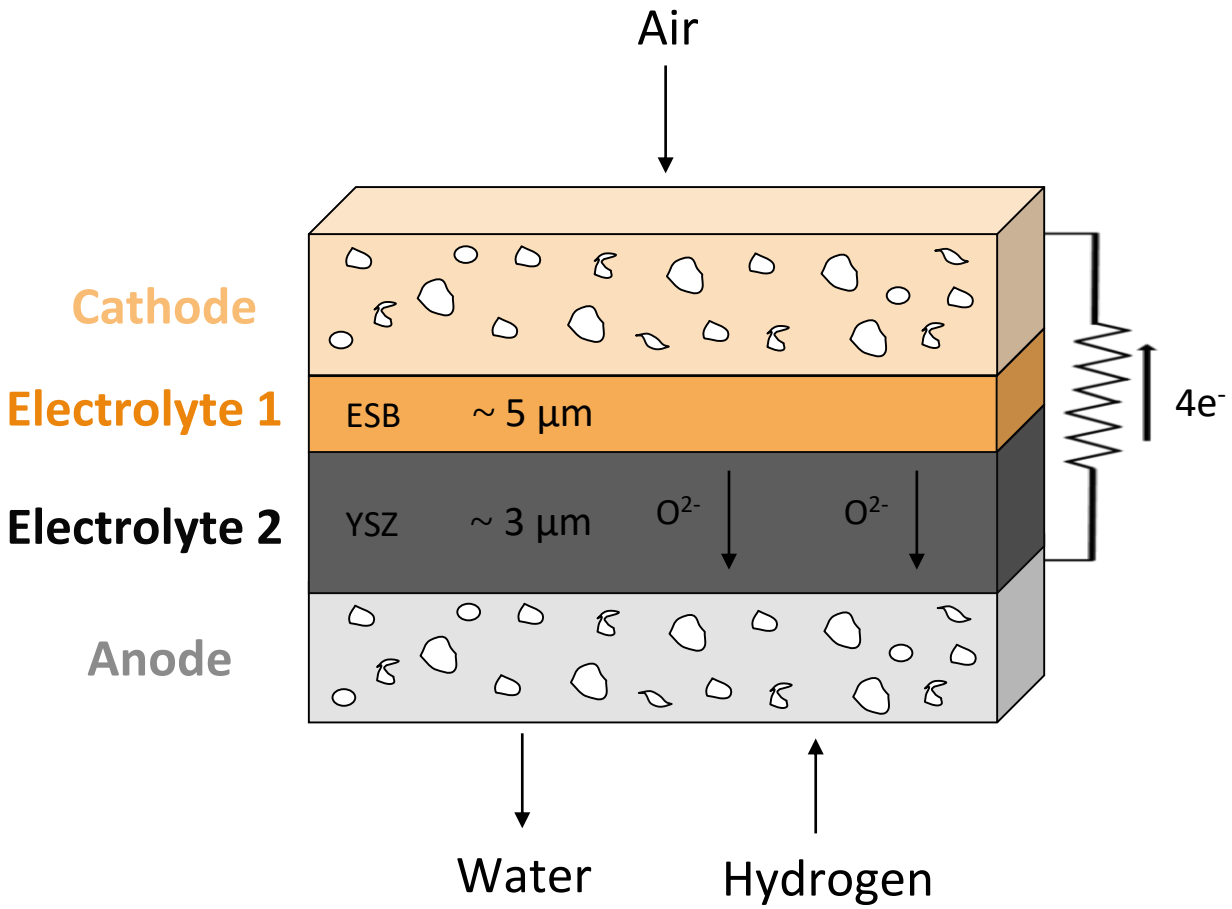
100% H_2 (150 ml/min)
Air : 600 ml/min

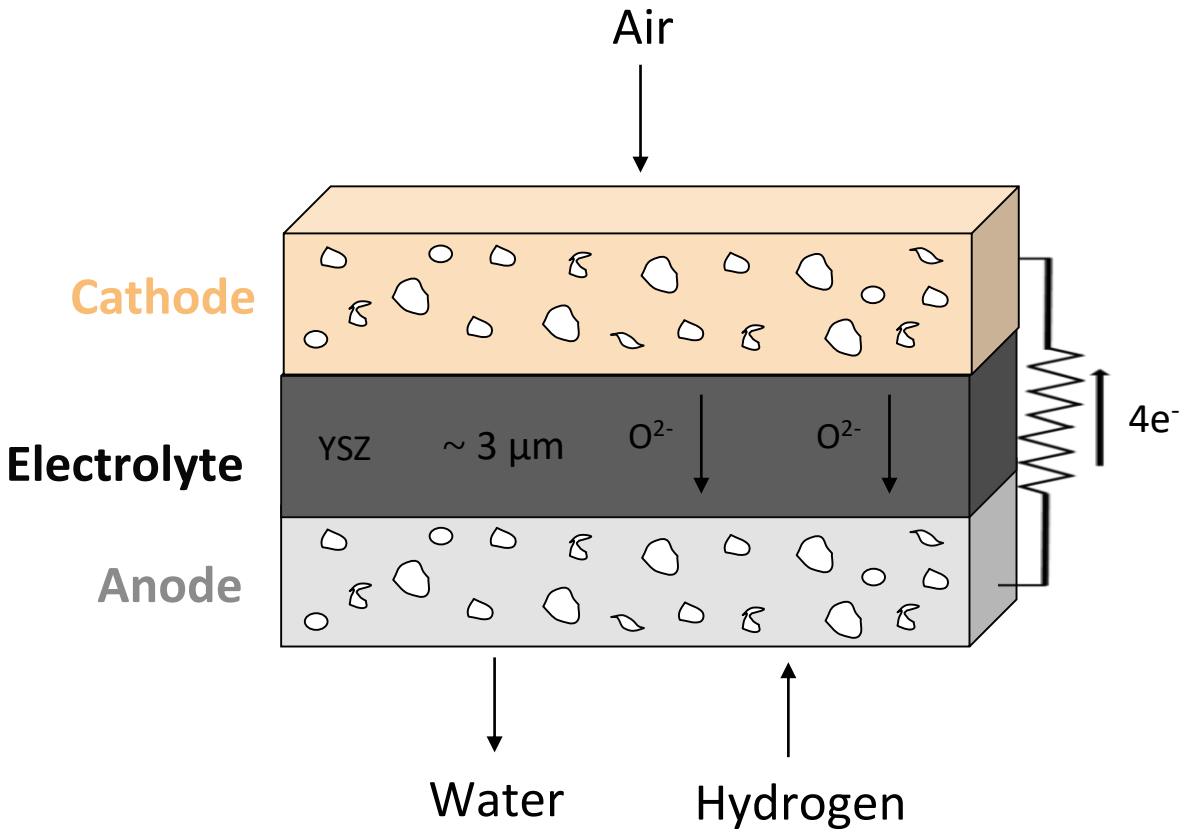
Température (°C)	OCV (V)	Densité de puissance maximale ($W.cm^{-2}$)
600	1,22	0,35
650	1,23	0,76
700	1,18	1,12
750	1,26	1,41
800	1,13	1,74



Cell performance – ESB effect

Ni-3YSZ | 8YSZ | ESB | ESB-$La_{0.6}Sr_{0.4}MnO_3$ |$La_{0.6}Sr_{0.4}MnO_3$





Cell performance – ESB effect

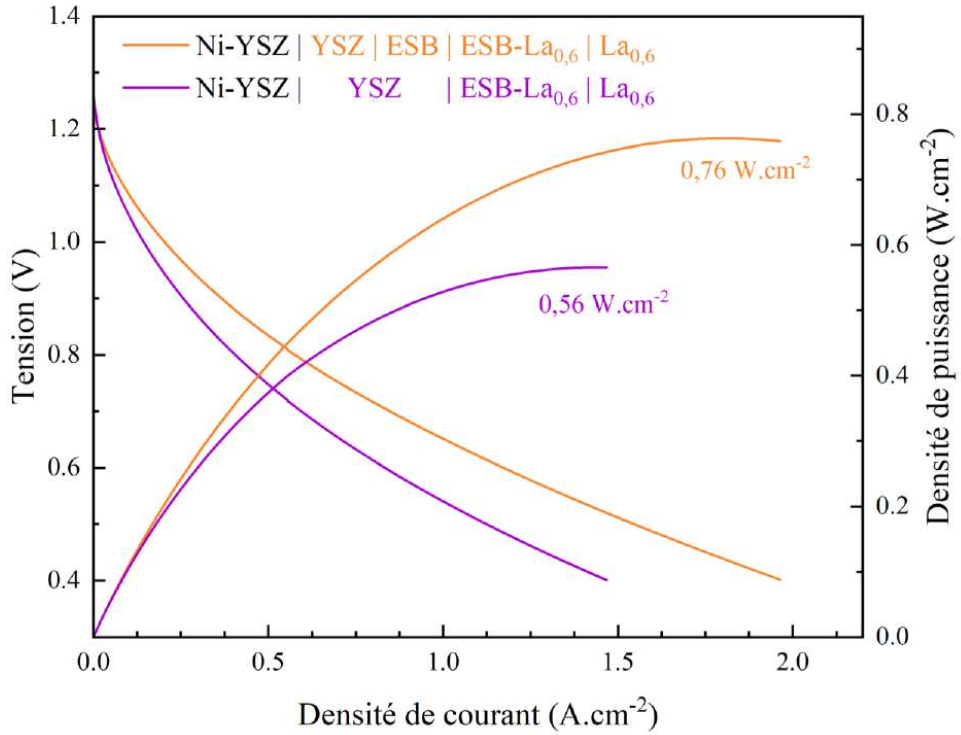
With or without ESB at 650 °C

With current collector

Electrolyte	Cathode	Maximal power density at 650 °C
YSZ (7 µm) / ESB (5 µm)	La0,8-ESB	1,62
YSZ (3 µm)	La0,6-ESB	0,56
YSZ (3 µm) / ESB (5,6 µm)	La0,6-ESB	0,76

Ni-3YSZ | 8YSZ | ESB | ESB-$La_{0.6}$ |$La_{0.6}$

Ni-3YSZ | 8YSZ | | ESB-$La_{0.6}$ |$La_{0.6}$



10.1149/1.3570175

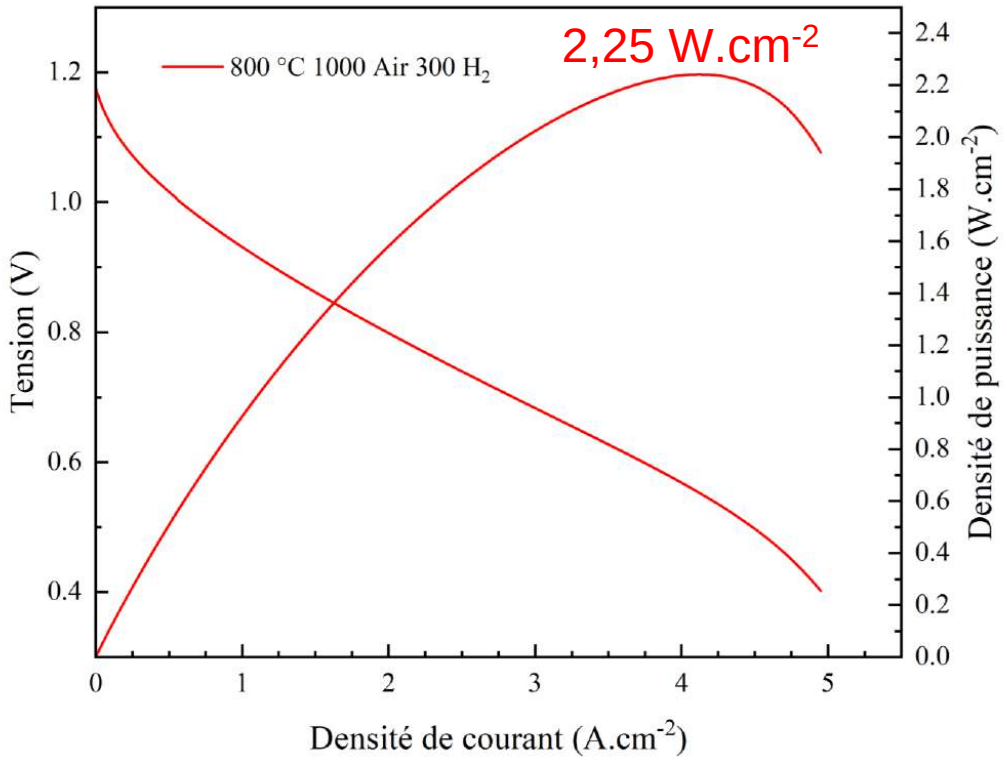
Cell performance - Current collector effect

Ni-3YSZ | 8YSZ | ESB-$La_{0.6}Sr_{0.4}MnO_3$ | $La_{0.6}Sr_{0.4}MnO_3$

With current collector

Electrolyte	Cathode	Maximal power density at 650 °C
YSZ (7 µm) / ESB (5 µm)	La0,8-ESB	1,62
YSZ (3 µm)	La0,6-ESB	0,56
YSZ (3 µm) / ESB (5,6 µm)	La0,6-ESB	0,76

100% H_2 (300 ml/min)
Air : 1000 ml/min

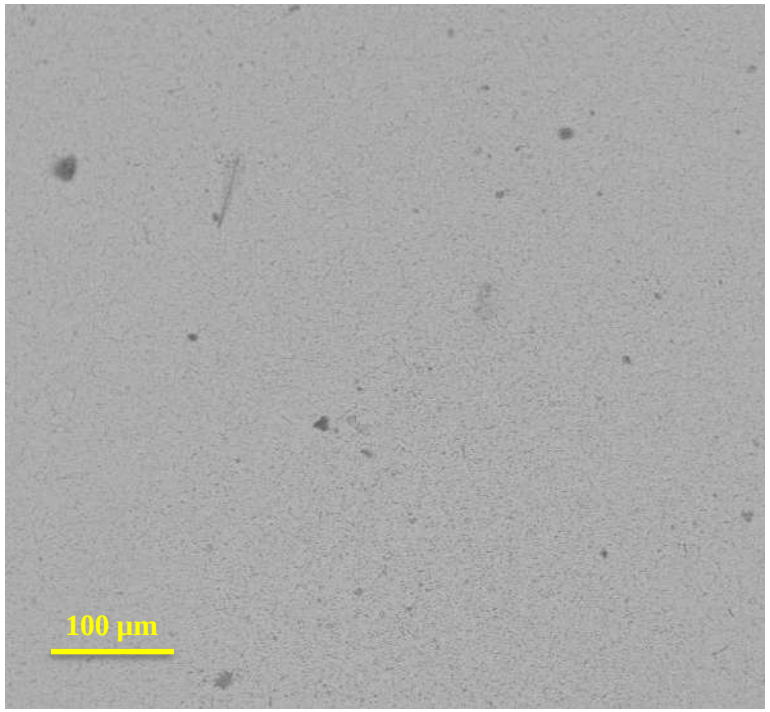


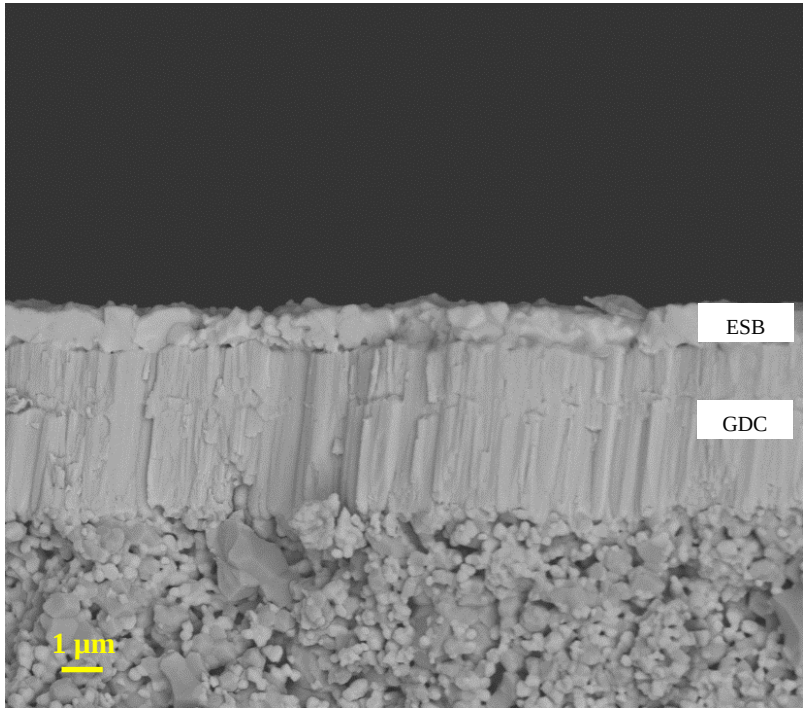
Promising results !

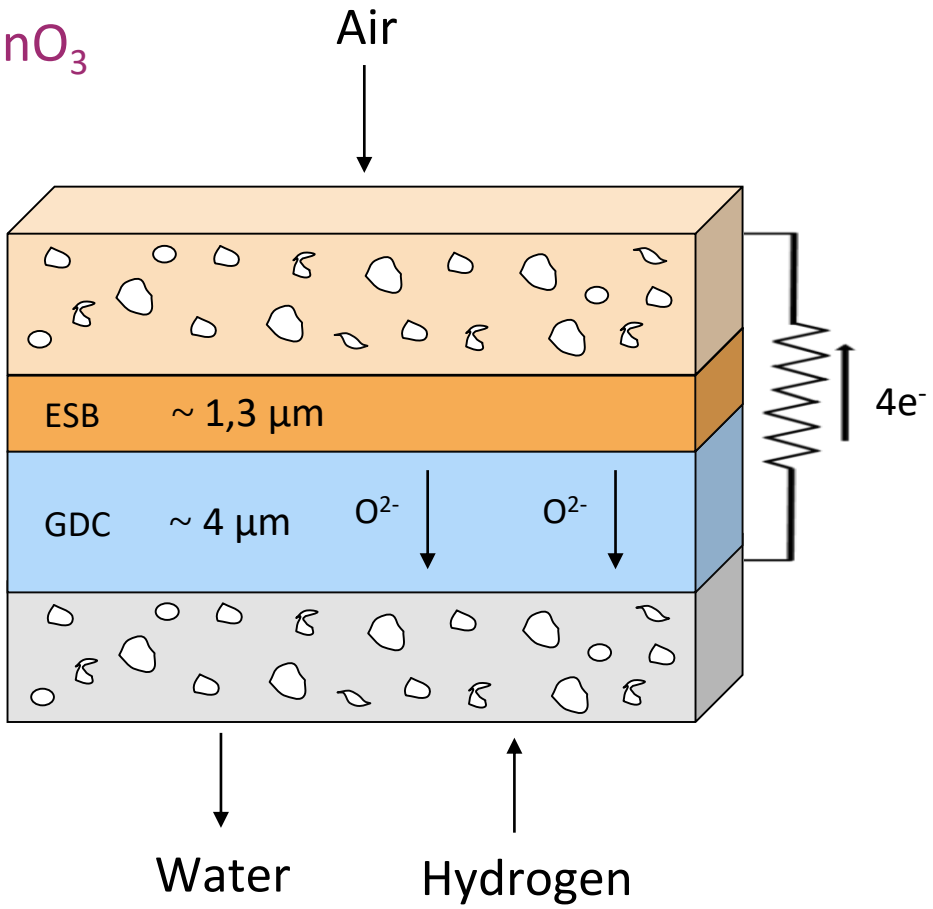
10.1149/1.3570175

GDC half-cell with ESB I ESB-$La_{0,6}$ - Post mortem

Ni-GDC |GDC | ESB | ESB-$La_{0.6}Sr_{0.4}MnO_3$

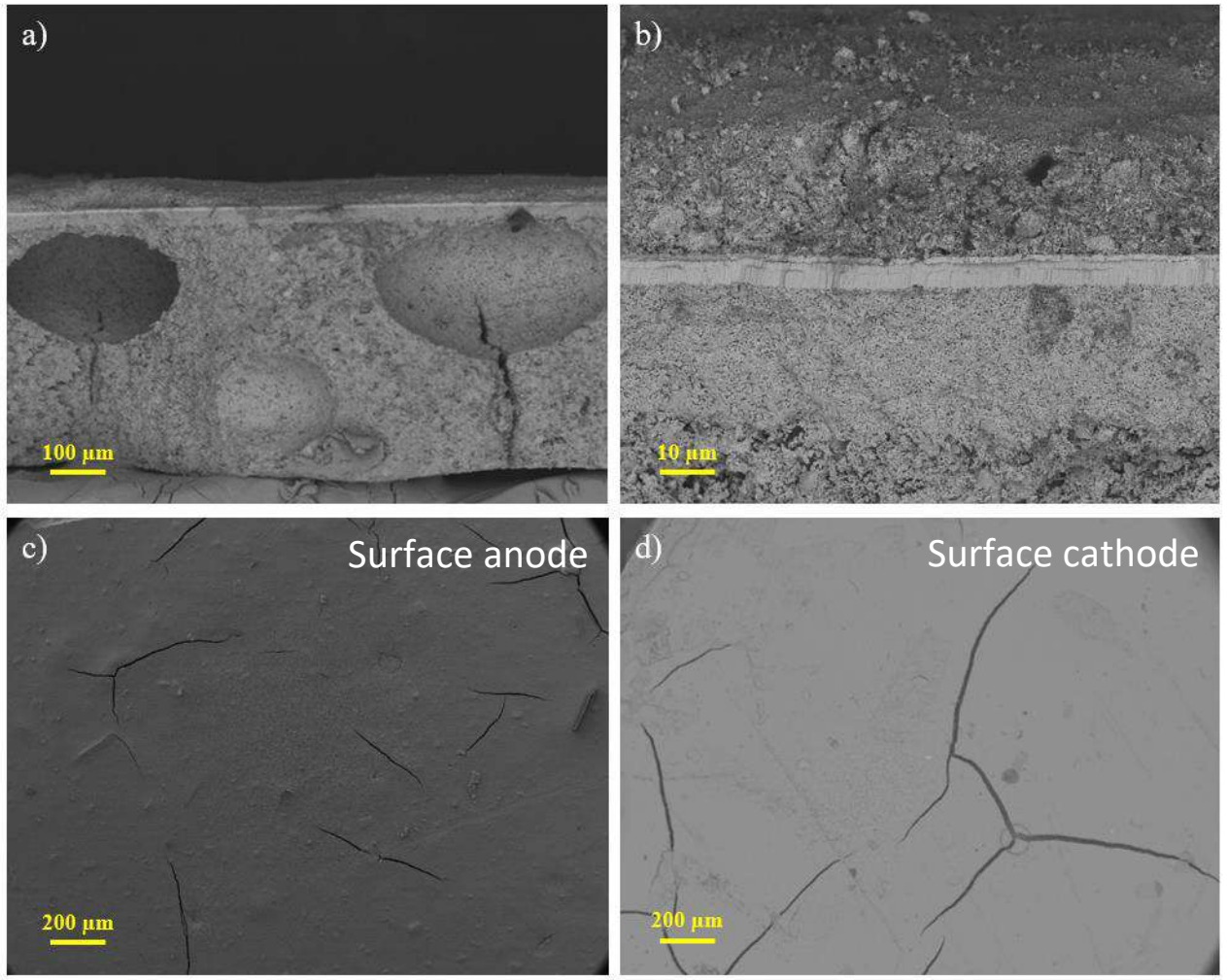


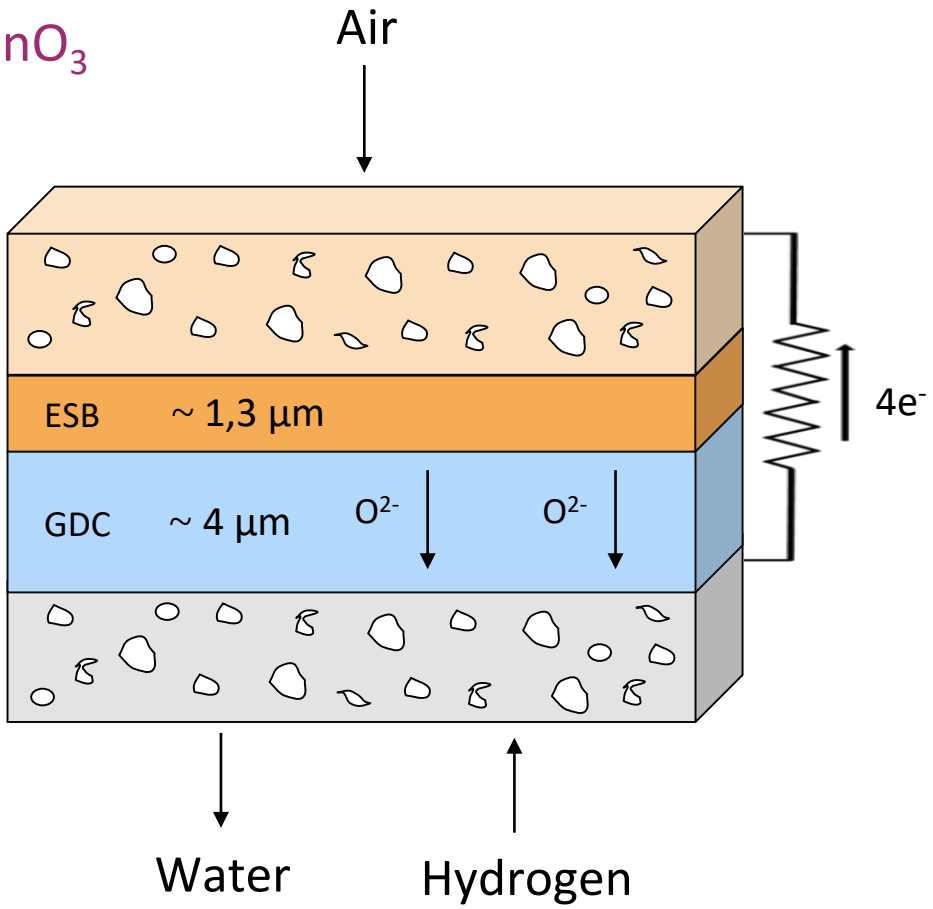




GDC half-cell with ESB I ESB-$La_{0,6}$ - Post mortem

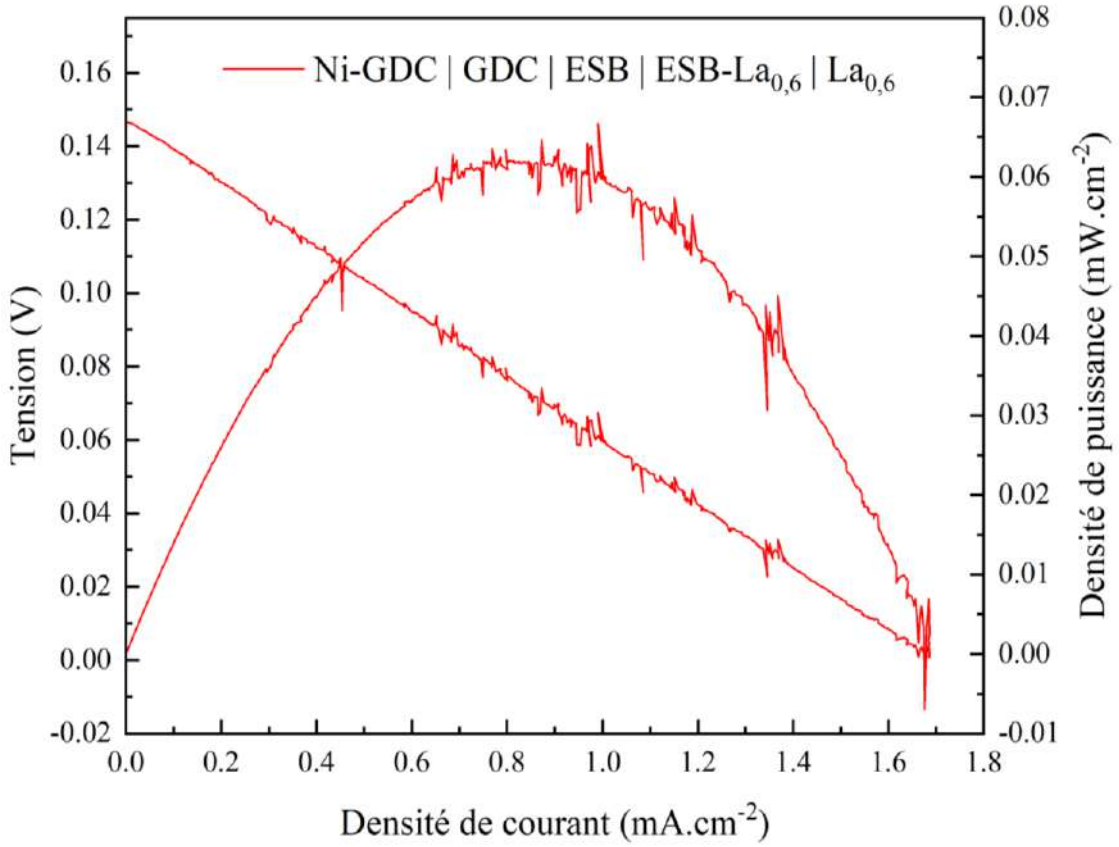
Ni-GDC |GDC | ESB | ESB-$La_{0.6}Sr_{0.4}MnO_3$

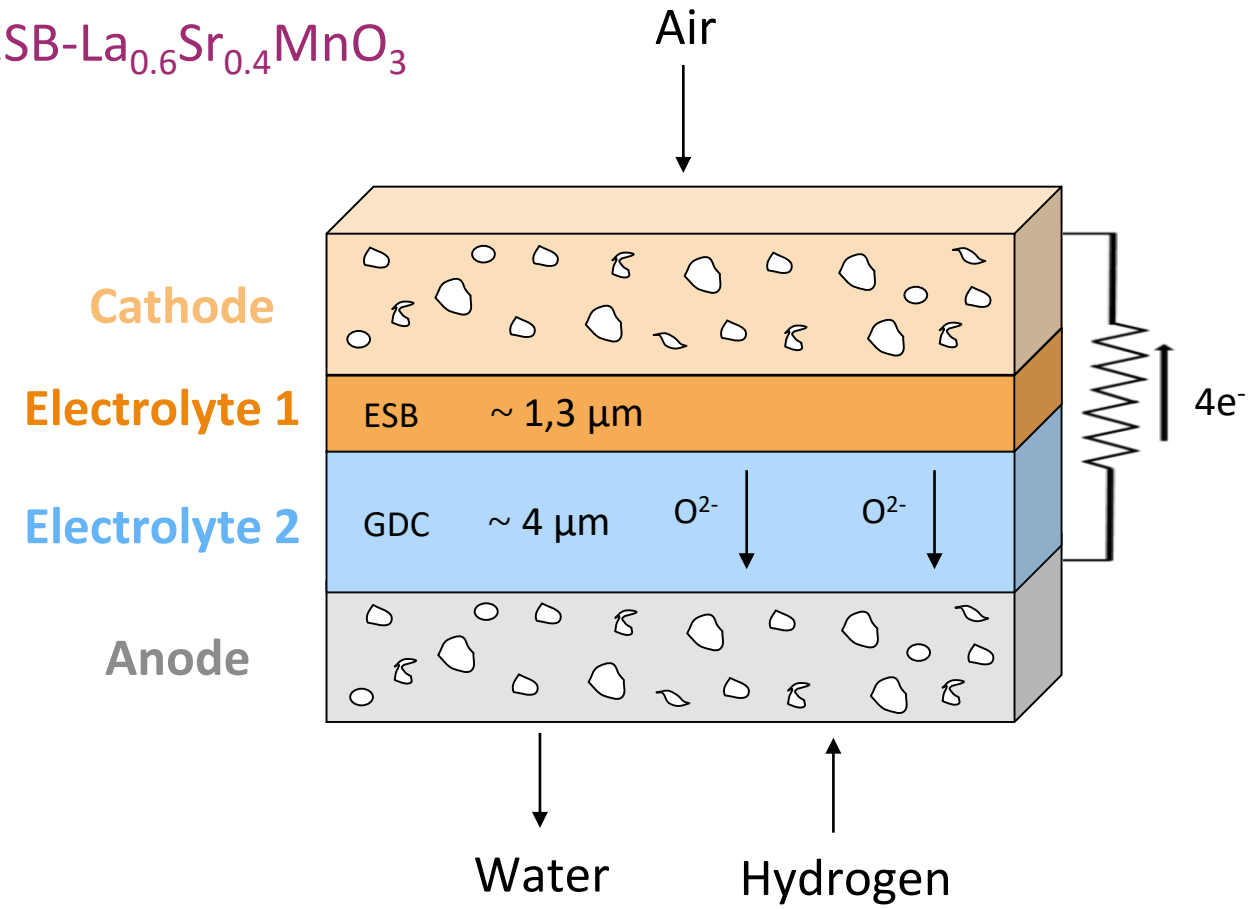




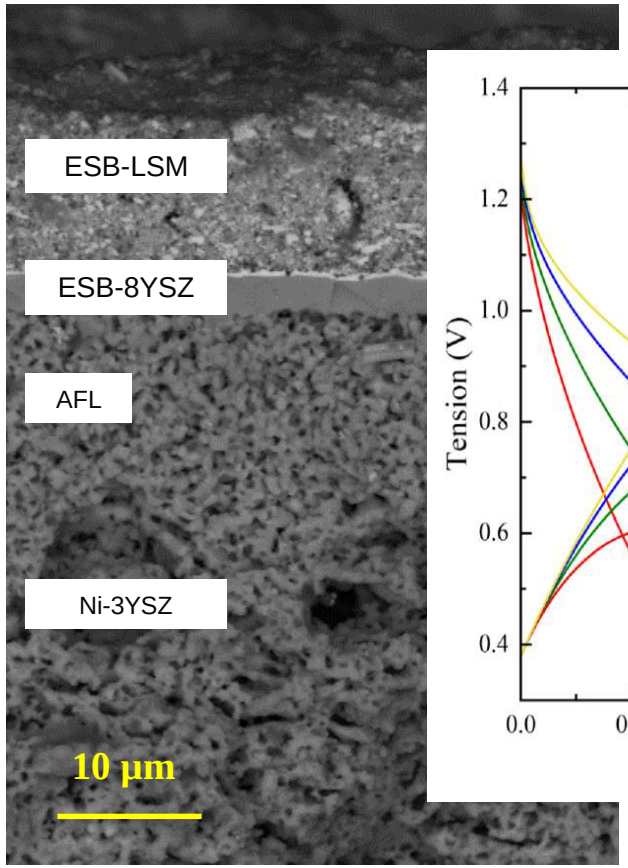
GDC half-cell with ESB I ESB-$La_{0,6}$ – Cell performance

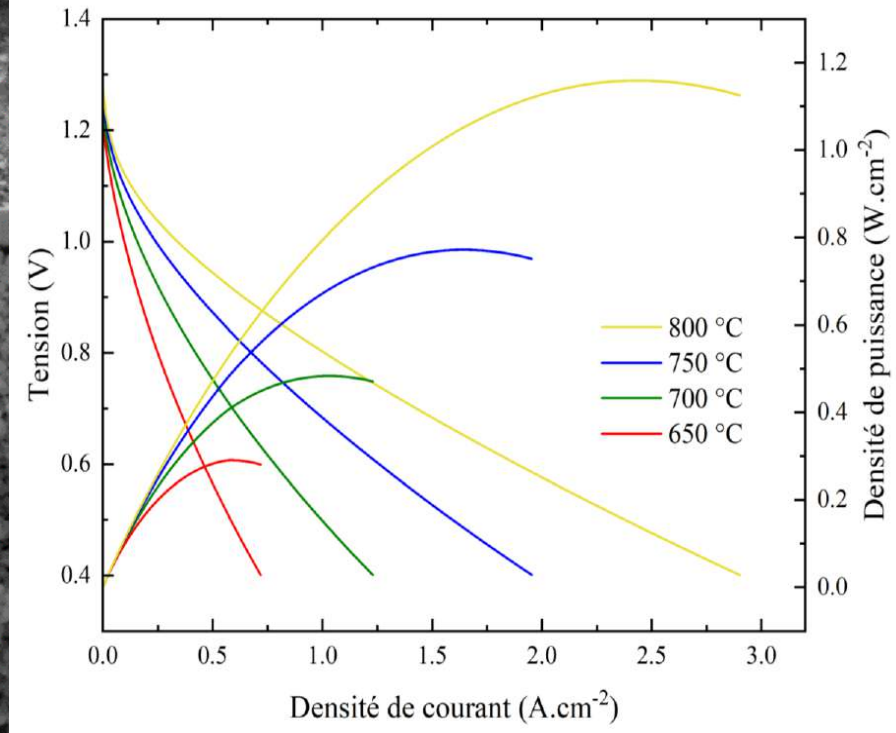
Ni-GDC |GDC | ESB | ESB-$La_{0.6}Sr_{0.4}MnO_3$

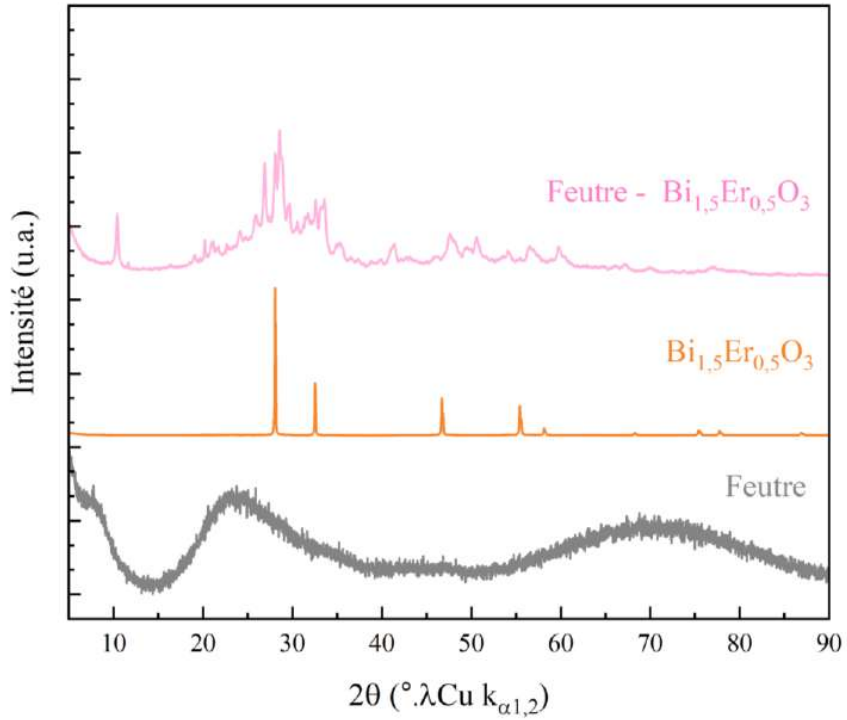




Conclusion & perspectives

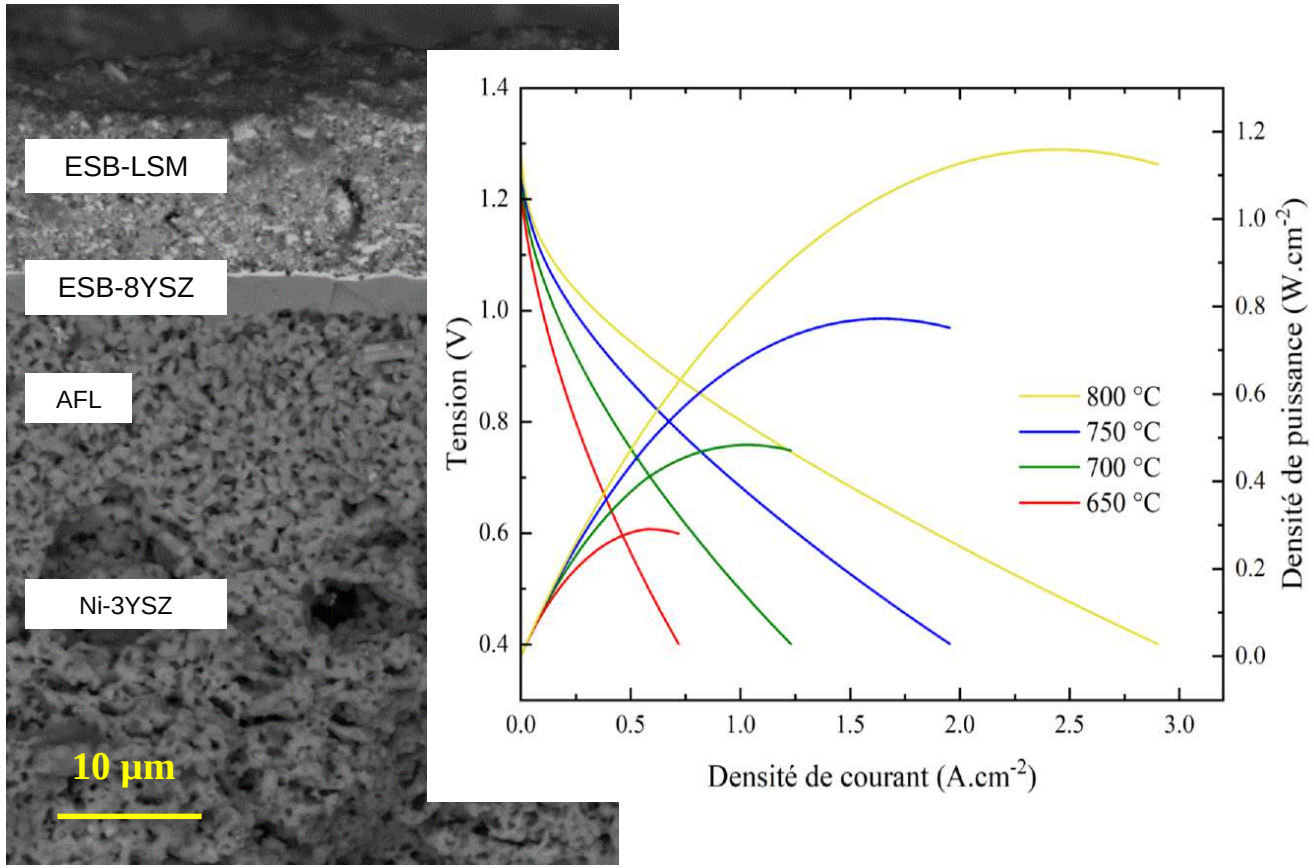


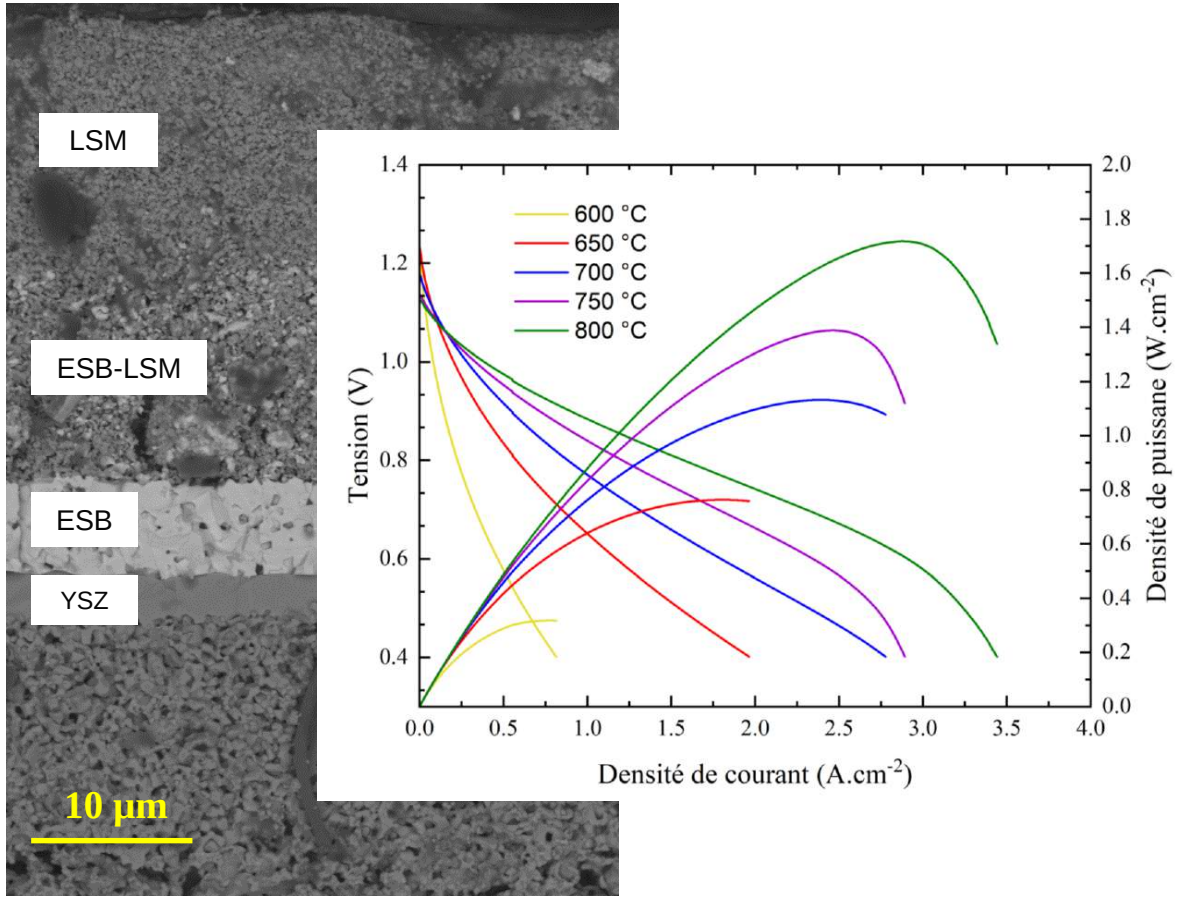




Conclusion & perspectives

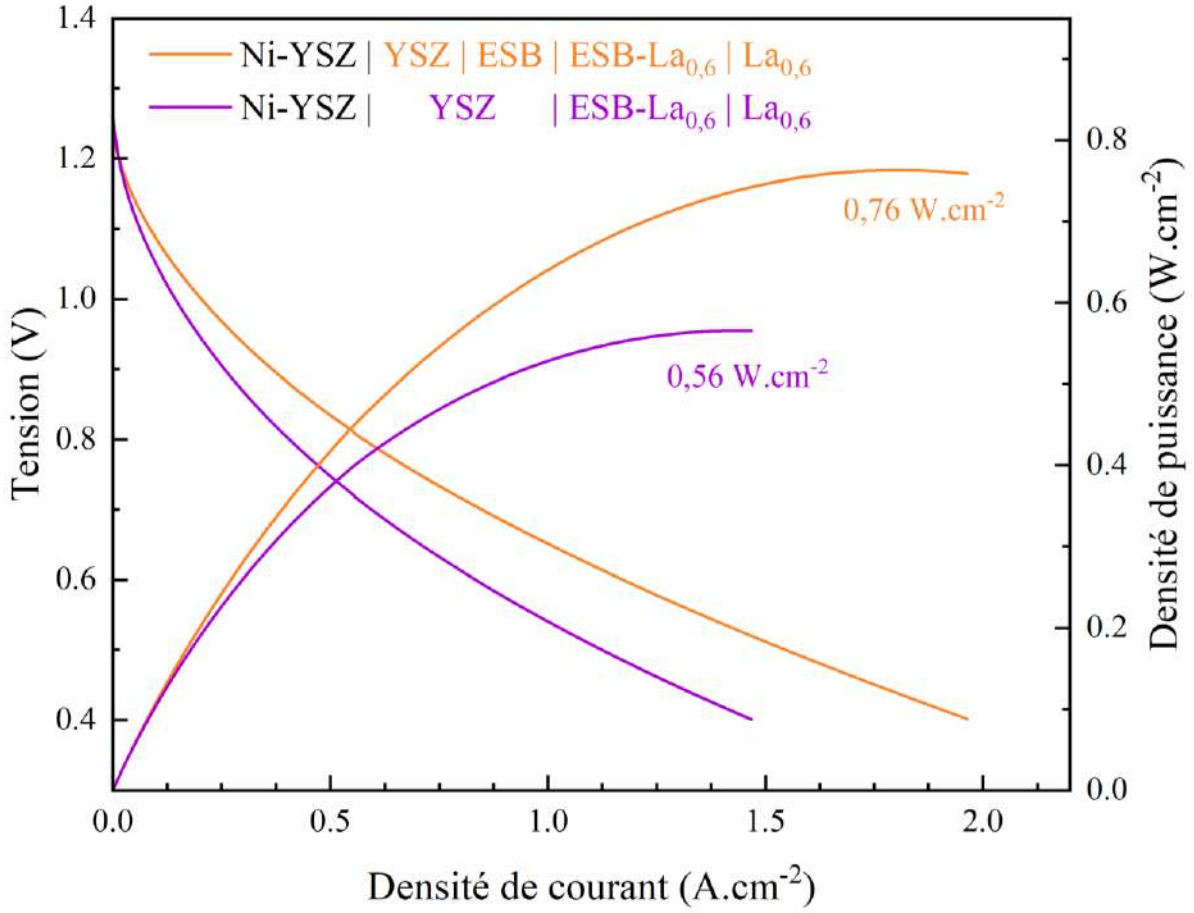
LSM protection





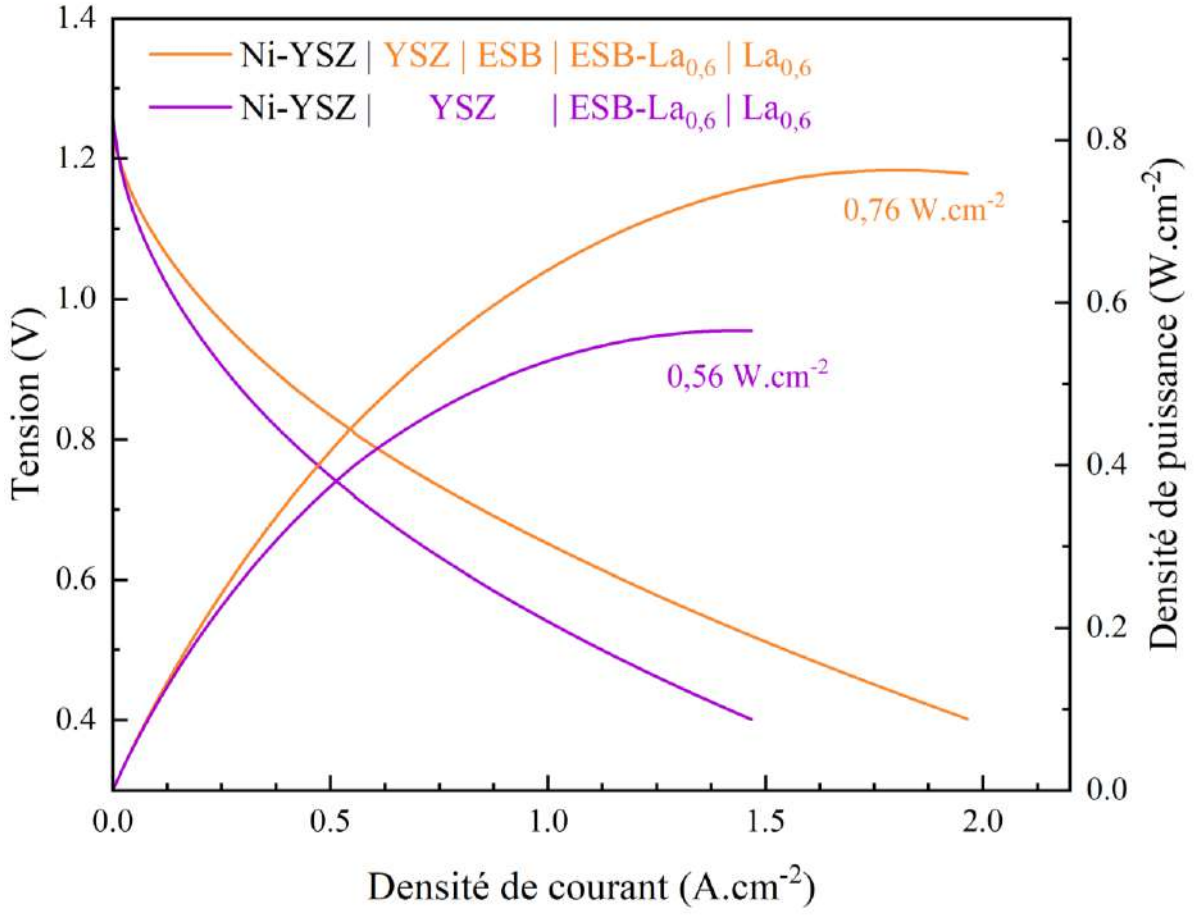
Conclusion & perspectives

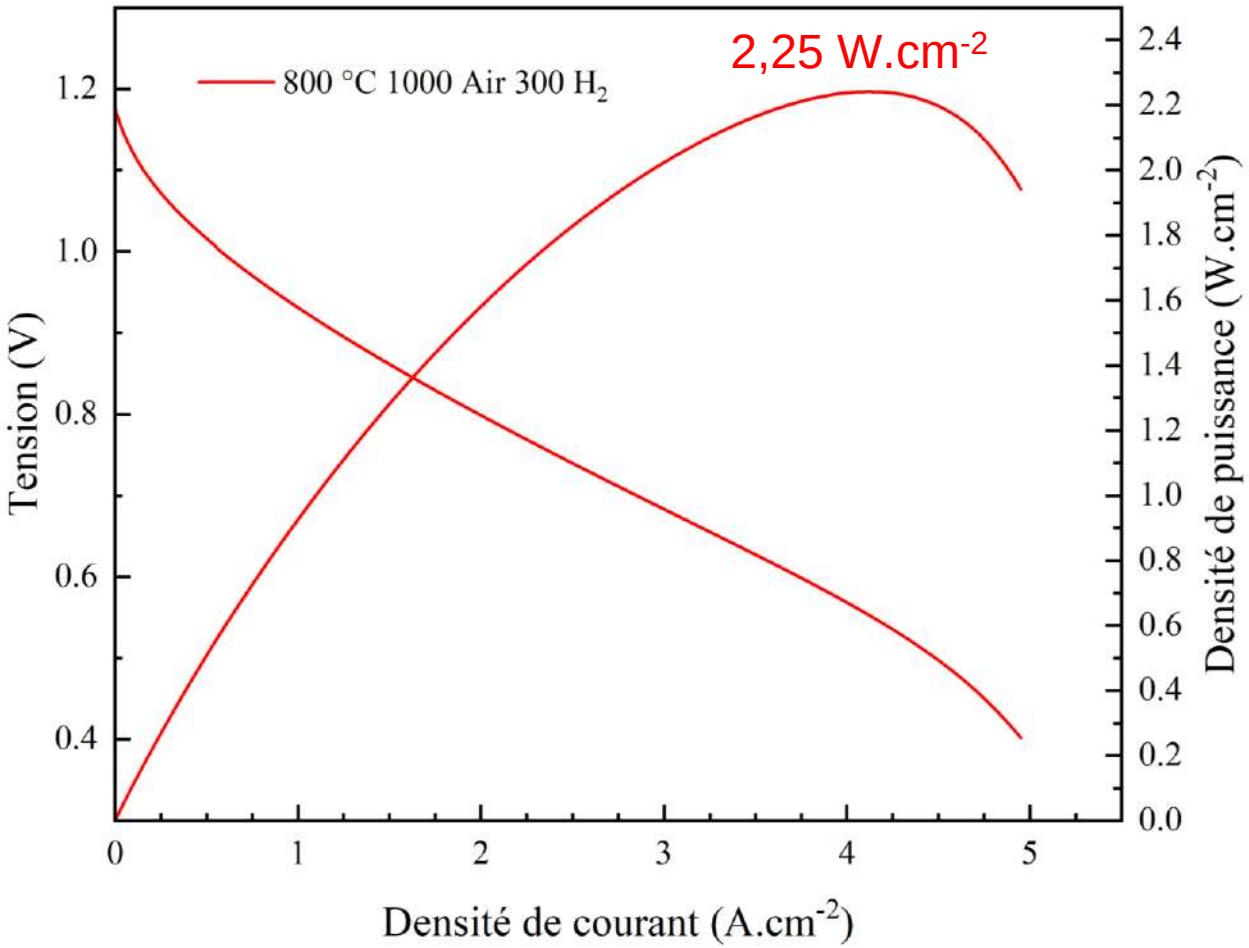
100% H_2 (150 ml/min)
Air : 600 ml/min



Conclusion & perspectives

100% H_2 (300 ml/min)
Air : 1000 ml/min





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UNITÉ DE CATALYSE
ET CHIMIE DU SOLIDE

Soukaina Mountadir

Thanks for your attention

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