Durability study of the nanostructured $LaPrNiO_{4+\delta}$ electrode for solid oxide cells

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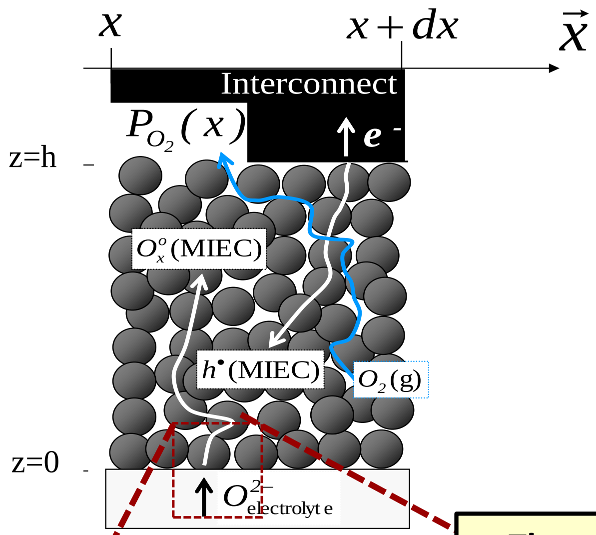
3ème REUNION PLENIERES de la Fédération HYDROGENE (FRH2) du CNRS

22 -26 mai 2023
Saint-Gilles (La Réunion)

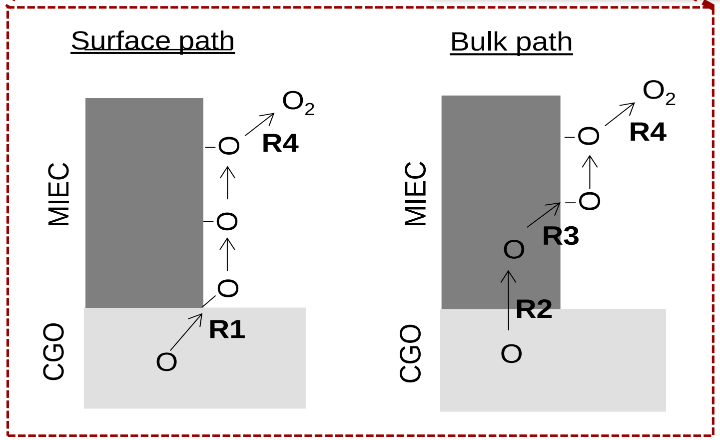
Intermediate Temperature SOCs (IT-SOCs)



Elementary reactions presented for the La$_2$NiO$_{4+\delta}$ (LNO), under SOEC mode

Coll. Jérôme Laurencin, CEA-LITEN
Giuseppe Sdanghi et al., Journal of the Electrochemical Society (2022)
P.h.D Thesis Lydia Yefsah, June 2023, ANR ECOREVE

The reaction mechanism is divided into a series of elementary reactions with two parallel pathways :



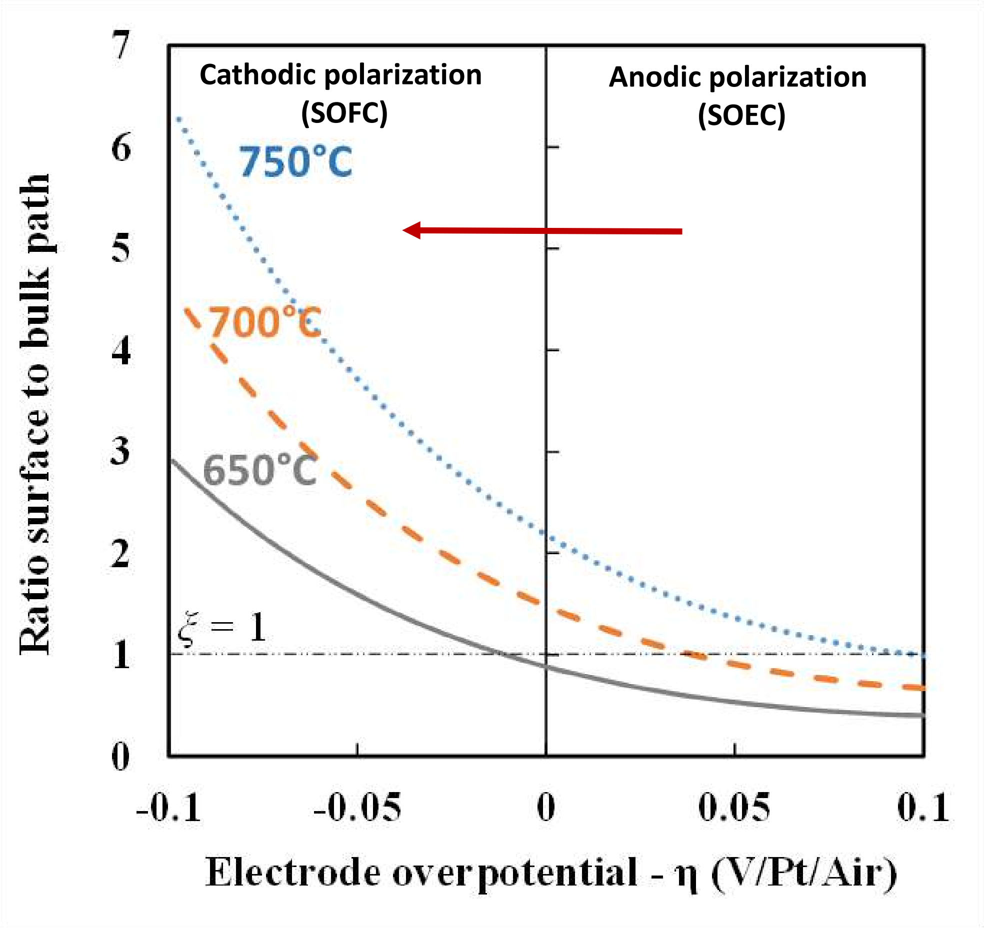
① **Surface path:**
R1: Oxidation at TPBs

③ **Common steps:**
Surface diffusion → **R4**: Oxygen desorption → **Gas diffusion**

② **Bulk path:**
R2: Ionic transfer → **Bulk diffusion** in the oxygen electrode → **R3**: Oxygen excorporation

Understanding of the reaction mechanisms

❑ For LNO electrode

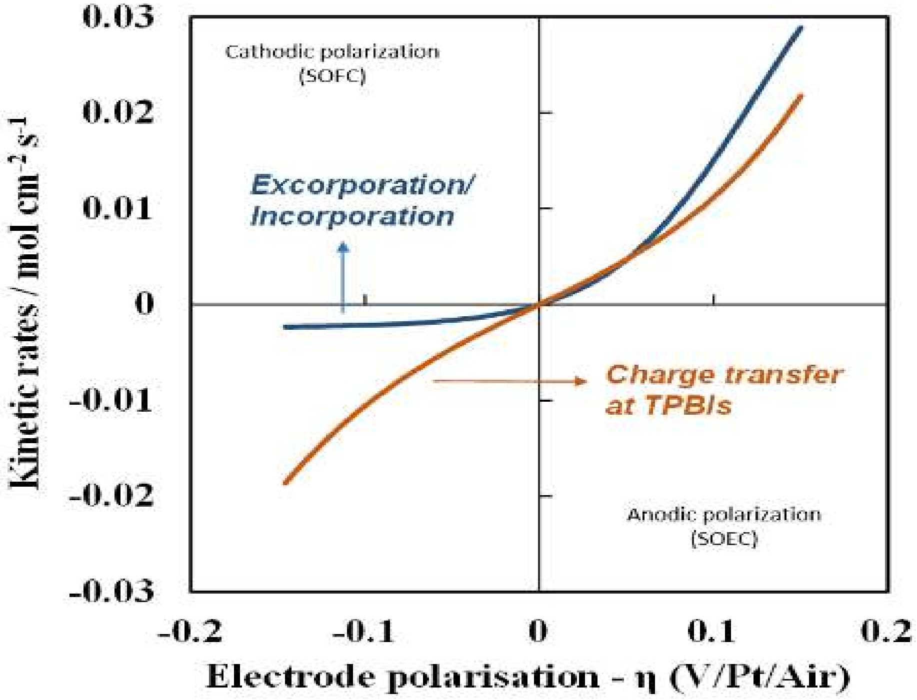


$$\boxed{\xi = \frac{surface\ path}{bulk\ path}}$$

The ratio ξ was found to increase when increasing the **cathodic overpotential (SOFC)**, whatever the investigated temperature

Laurencin, J et al., Electrochimica Acta 2015, 174, 1299–1316

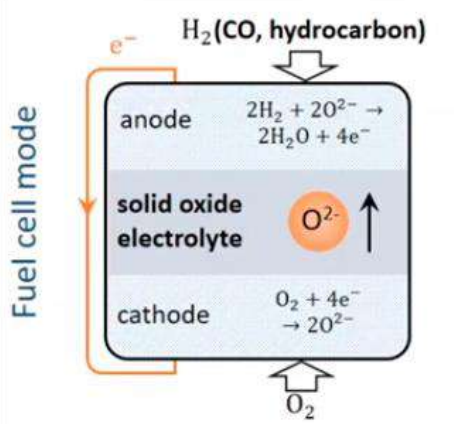
Understanding of the reaction mechanisms



Coll. Jérôme Laurencin, CEA-LITEN
Giuseppe Sdanghi et al., Journal of the Electrochemical Society (2022)
P.h.D. Thesis Lydia Yefsah, June 2023

Under cathodic polarization (SOFC):
the excorporation reaction (bulk path) becomes more and more limited, whereas the direct oxidation at TPBls (surface path) is still active

LNO is progressively depleted in interstitial oxygen under these conditions

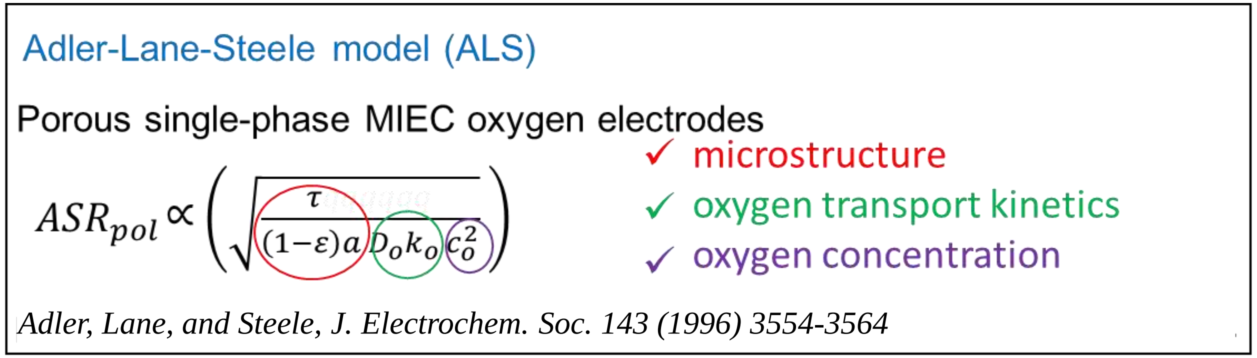


This result explain the dissymmetry of the electrode polarization curves with the better performances observed under anodic polarization (SOEC mode)

Intermediate Temperature SOCs (IT-SOCs)

Large oxygen electrode overpotential → Enhance the ORR/OER

- Factors affecting ORR/OER



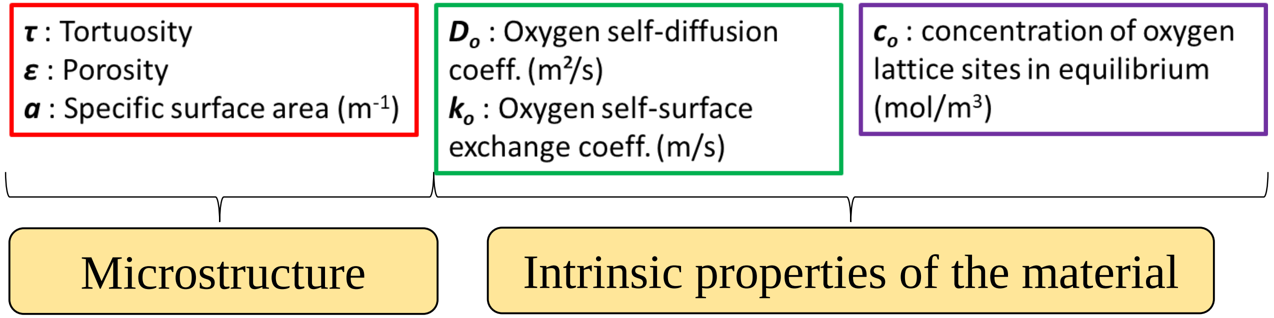
Adler-Lane-Steele model (ALS)

Porous single-phase MIEC oxygen electrodes

$$ASR_{pol} \propto \left(\sqrt{\frac{\tau}{(1-\varepsilon)a D_o k_o c_o^2}}\right)$$

✓ microstructure
✓ oxygen transport kinetics
✓ oxygen concentration

Adler, Lane, and Steele, J. Electrochem. Soc. 143 (1996) 3554-3564



τ : Tortuosity
ε : Porosity
a : Specific surface area (m^{-1})

D_o : Oxygen self-diffusion coeff. (m^2/s)
k_o : Oxygen self-surface exchange coeff. (m/s)

c_o : concentration of oxygen lattice sites in equilibrium (mol/m^3)

Microstructure

Intrinsic properties of the material

Material selection: rare-earth nickelates

x = 0 — x = 2

$La_2NiO_{4+\delta}$
- ✓ Chemically stable
- x High R_{pol}

$Pr_2NiO_{4+\delta}$
- x Poor chemical stability
- ✓ Low R_{pol}

$La_{2-x}Pr_xNiO_{4+\delta}$ [$0 \leq x \leq 2$]

Selected composition: x = 1; **$LaPrNiO_{4+\delta}$ (LPNO)**
Electrolyte: **$Ce_{0.9}Gd_{0.1}O_{2-\delta}$ (GDC)**

Sharma et al. J. Mater. Chem. A 5 (2017) 1120
Takahashi et al., J. Am. Ceram. Soc. 93 (2010) 2329-2333; Amow and Skinner, J. Solid State Electrochem. 10 (2006) 538-546; Vibhu et al., Solid State Ionics 278 (2015) 32-37

INTRINSIC PROPERTIES

- ➢ **mixed ionic-electronic conductor** (MIEC)
- ➢ sufficient **oxygen diffusion** ($3\text{-}5 \cdot 10^{-8}$ cm^2 s^{-1} at 700 °C) and **surface exchange coefficients** ($0.5\text{-}1 \cdot 10^{-6}$ cm s^{-1} at 700 °C)
- ➢ sufficient **conductivity** (70 - 100 S cm^{-1} at 700 °C)
- ➢ similar TEC to GDC electrolyte ($\alpha_{GDC} = 13.8 \cdot 10^{-6}$ K^{-1})
- ➢ phase stability with GDC

+ COMPOSITION

+ MICROSTRUCTURE, ARCHITECTURE

→ increase the specific surface area
→ unique surface and interface properties

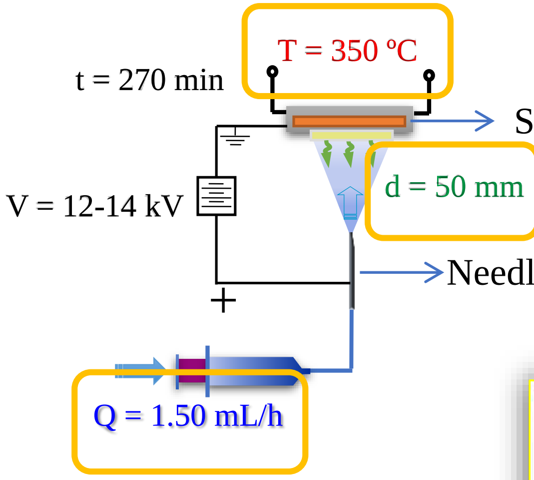
Fan et al, Nano Energy 45 (2018) 148-176

...Performance

...Durability? Limited available literature
Vibhu et al. J. Energy Chem. 46 (2020) 62-70

Electrostatic Spray Deposition (ESD) – Microstructure of AFL

The impacting droplet size plays an important role on the microstructure



Solution of precursors:
La-, Pr-, and Ni-nitrates in
EtOH:H_2O 1:2

Taylor cone

Gañan-Calvo equation on droplet size:

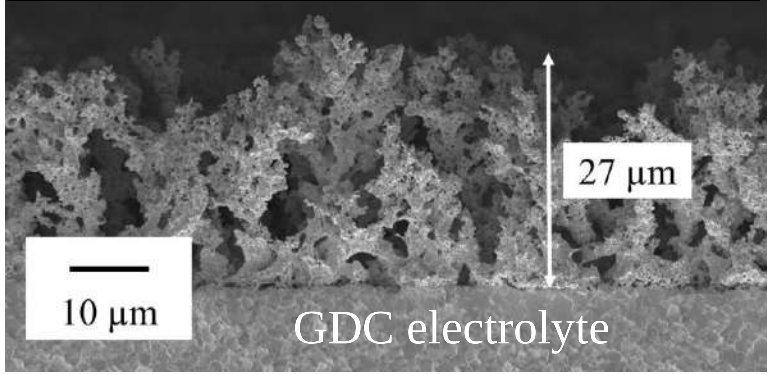
$$d_{size} \propto \left(\frac{\rho \varepsilon_0 Q^3}{\gamma \sigma} \right)^{1/6}$$

- Surface tension, γ (N/m)
- Electrical conductivity, σ (S/m)
- Solution density, ρ (g/cm^3)
- Solution flow rate, Q (ml/h)

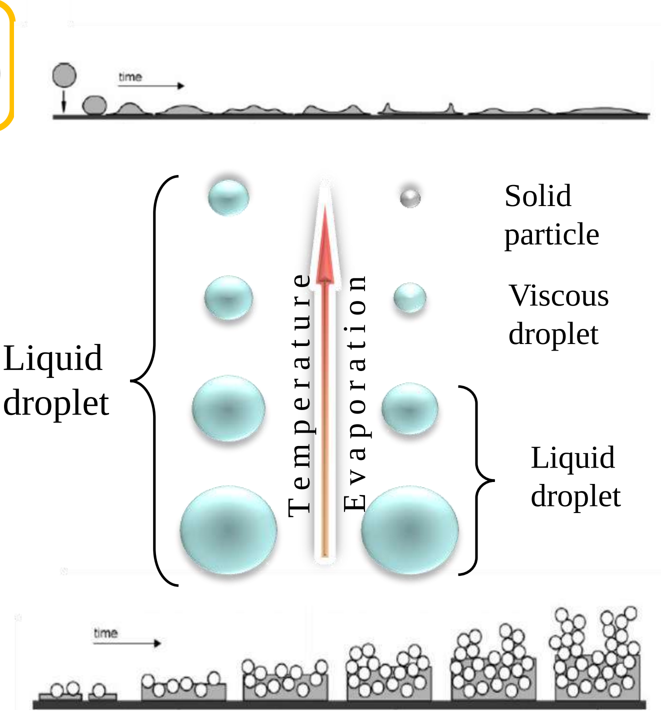
Gañan-Calvo et al. J. Aerosol Sci., 28 (1997) 249-275

SEM, (after sintering at 960 °C, 6 h, air)

‘Coral-like’ microstructure
Average particle size 130 nm



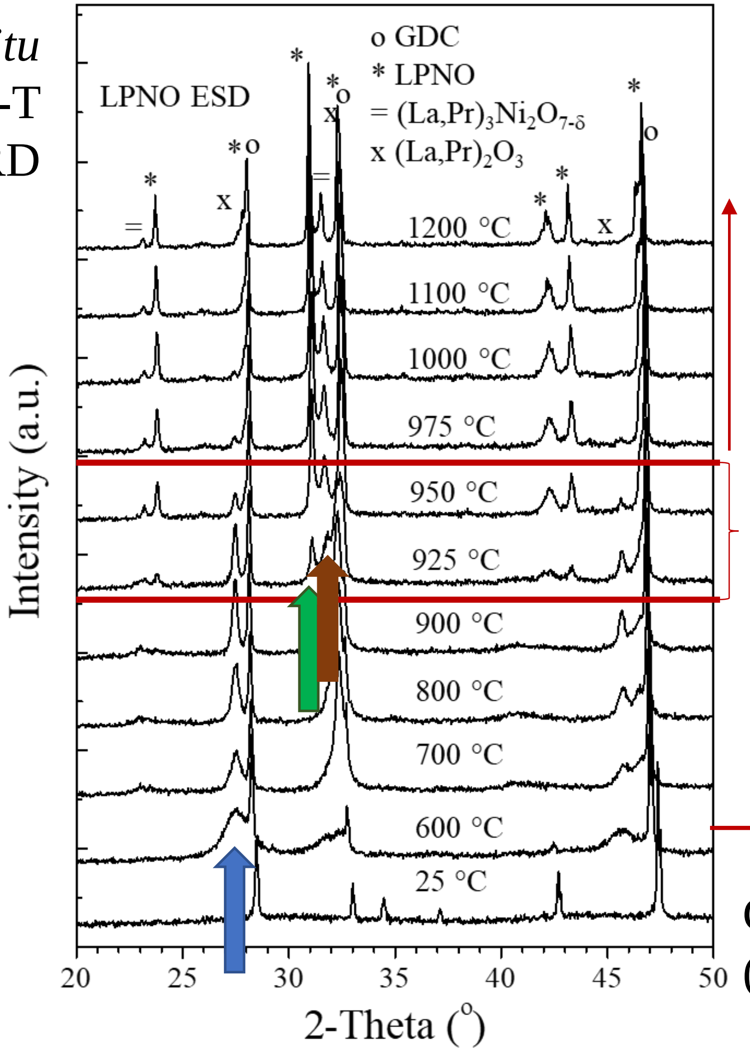
Good adhesion →



Neagu et al. Chem. Mater., 17 (2005) 902-910

Structural properties of ESD-LPNO

In-situ
high-T
XRD



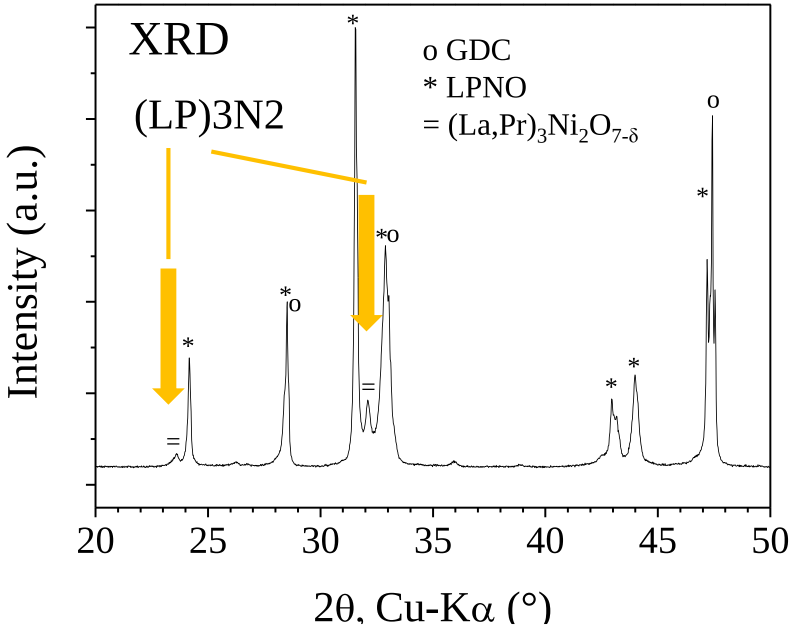
LPNO + $(La,Pr)_3Ni_{2}O_{7+\delta}$ [(LP)3N2]

LPNO + $(La,Pr)_3Ni_{2}O_{7+\delta}$ [(LP)3N2]↑
$(La,Pr)_2O_3$↓

$(La,Pr)_2O_3$

GDC
(electrolyte)

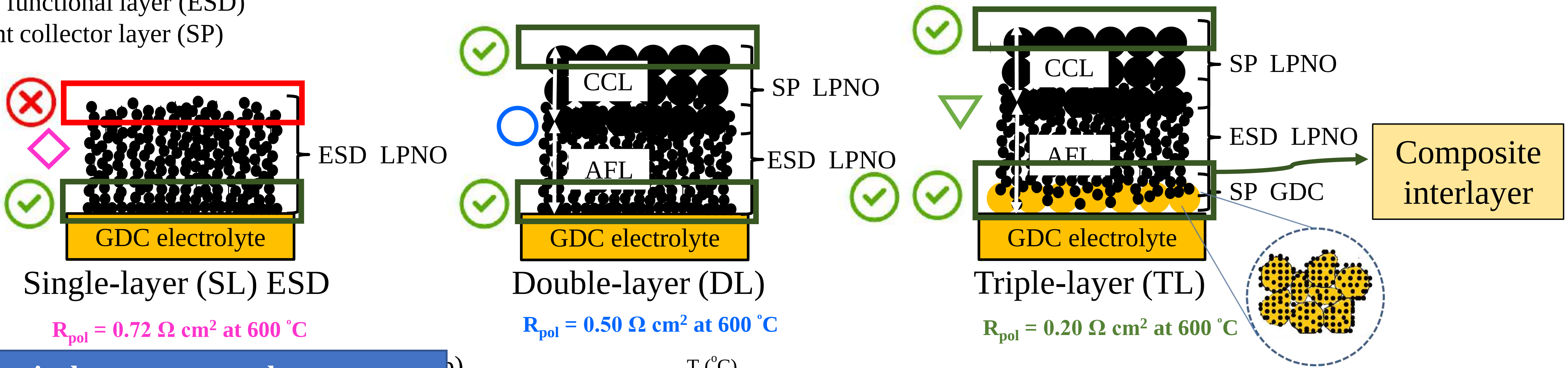
Post-sintering at **960ºC for 6 h** in air



- → Small presence **(LP)3N2**
- → Smaller particle size and open microstructure → more chemically reactive than the SP layer
- → Might improve the performance, but might also add complication on the durability study

Influence of the electrode design on LPNO electrochemical performances

AFL = Active functional layer (ESD)
CCL = Current collector layer (SP)

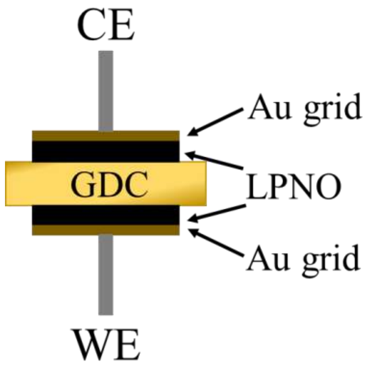


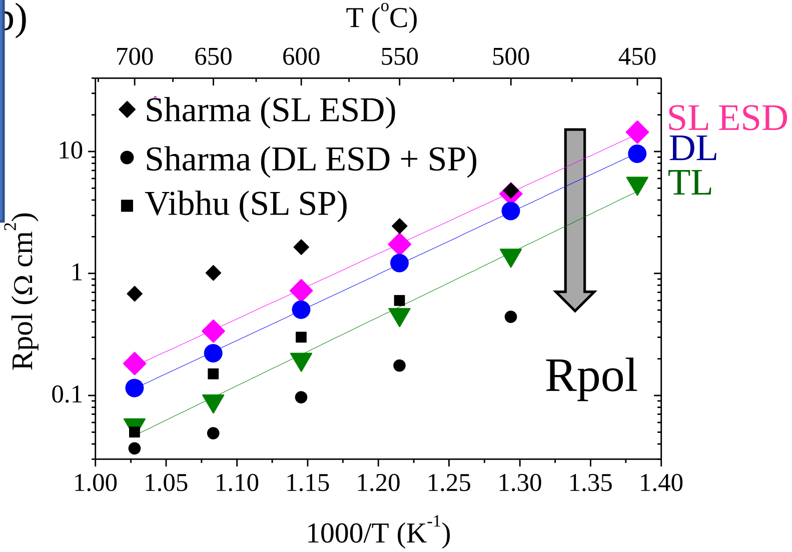
$R_{pol} = 0.72\ \Omega\ cm^2$ at 600 °C

$R_{pol} = 0.50\ \Omega\ cm^2$ at 600 °C

$R_{pol} = 0.20\ \Omega\ cm^2$ at 600 °C

2-point/Symmetrical measurement by EIS (EC-Lab software Bio Logic Instrument)
Frequency analyzer: Autolab 10^{-2} - 10^6 Hz
Signal amplitude: 20 mV, air, OCV, 450-700 °C



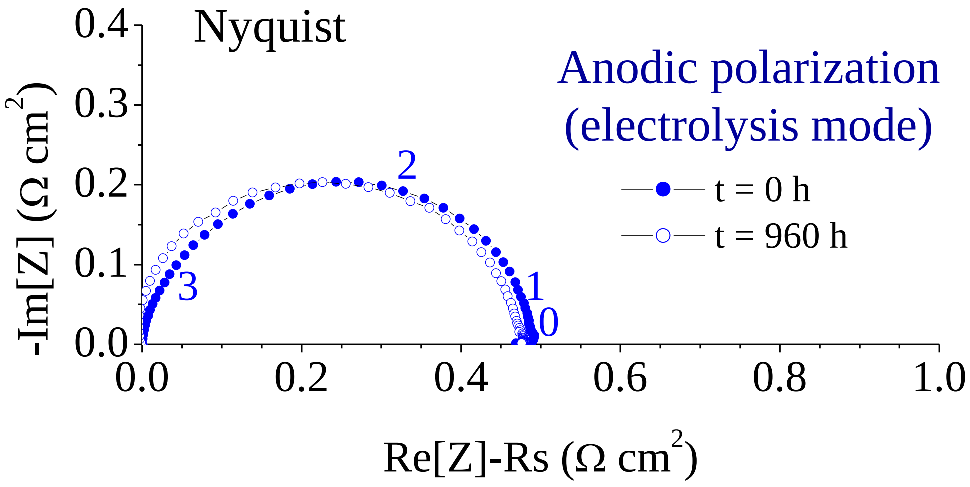


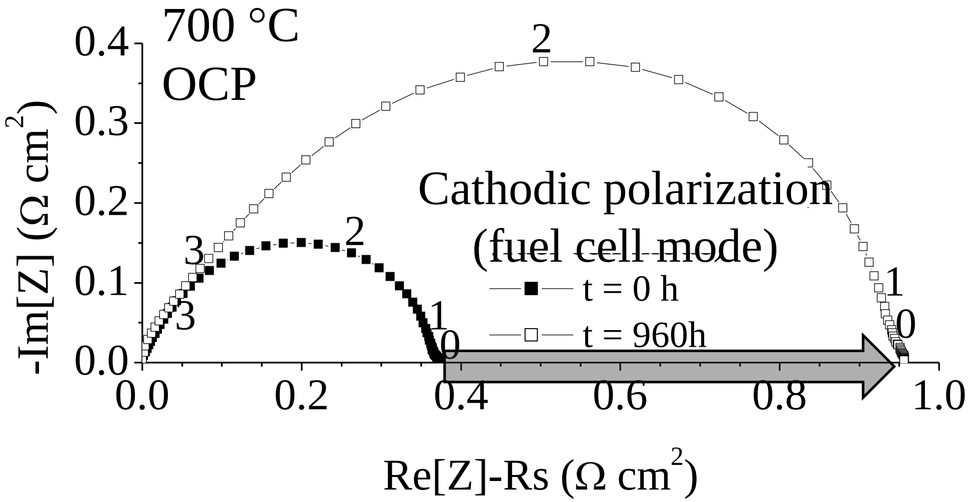
- ➢ Improvement in the design and interfaces leads to better electrode activity
- ➢ (LP)3N2 in the ESD layer is found to be electrochemically active

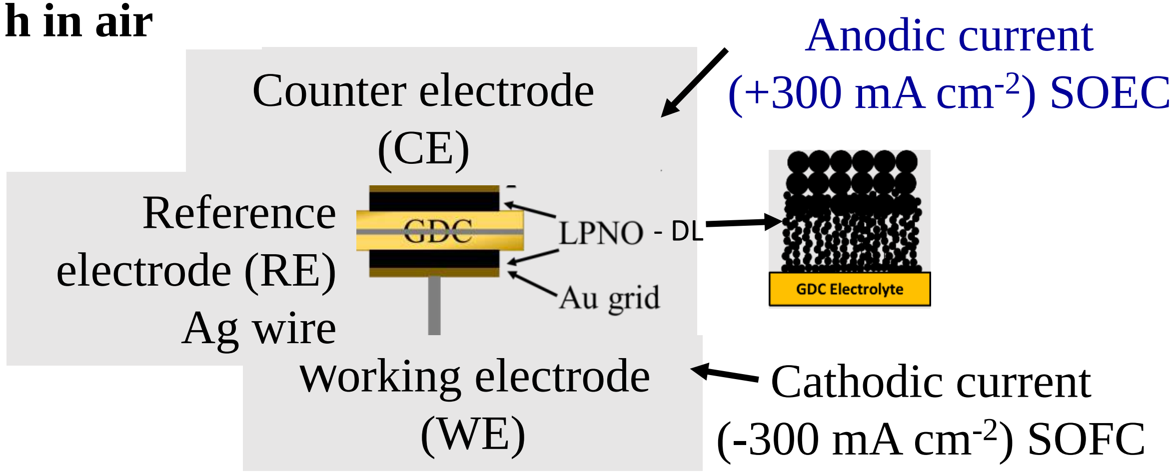
***NI Khamidy** et al., Journal of Electroanalytical Chemistry 2019*

1. Durability in symmetrical cell (SOEC and SOFC modes)

EIS before and after ageing under polarization at 700 °C for 960 h in air







Counter electrode (CE)

Reference electrode (RE)

Ag wire

Working electrode (WE)

Anodic current ($+300$ mA cm^{-2}) SOEC

Cathodic current (-300 mA cm^{-2}) SOFC

- 3-electrode measurements
- Symmetrical cell of double-layer electrode (38 µm thick)

➢ **Almost no change on the R_{pol} of the anodic side (SOEC)**

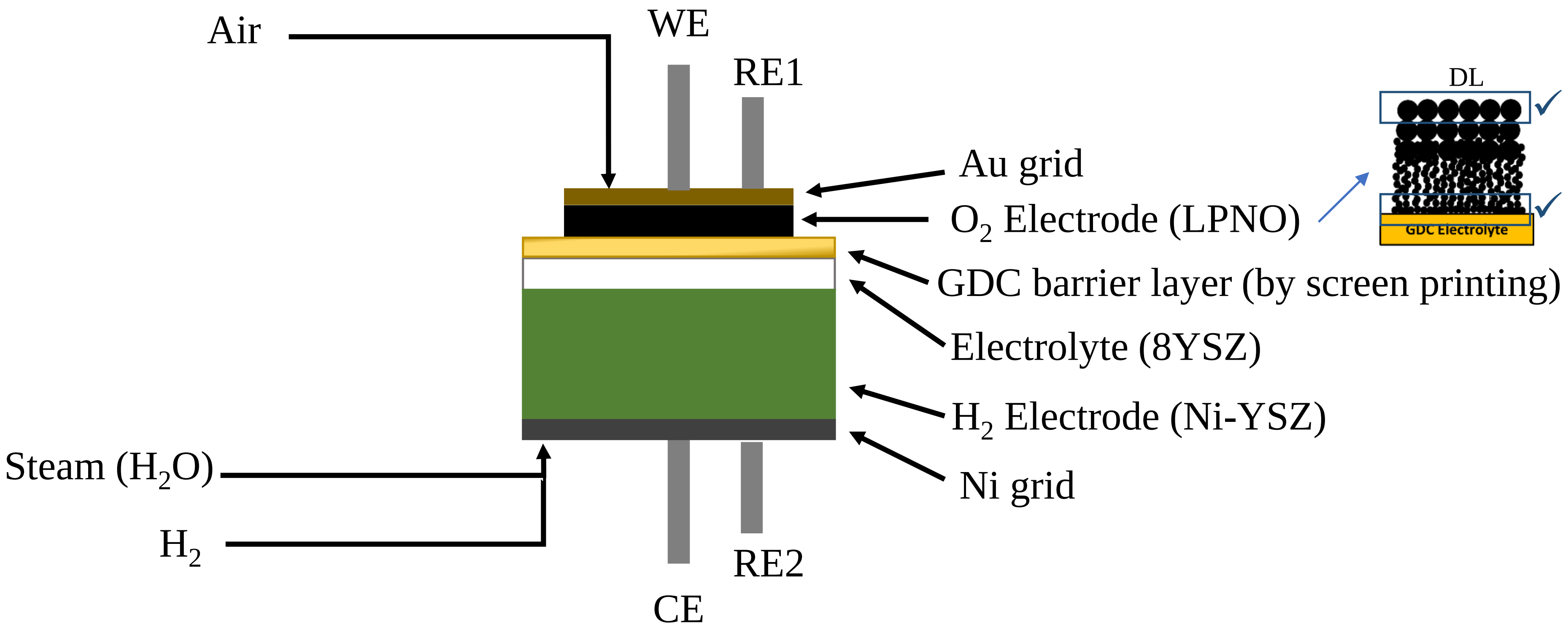
➢ **Strong increase of the R_{pol} on the cathodic side (SOFC)**

LPNO: **degradation in SOFC**, **stable in SOEC** → in line with a study from ICMCB, Bordeaux for $La_{2-x}Pr_xNiO_{4+\delta}$ (x = 0, 0.5, 2)

Vibhu et al, J. Energy Chem. 46 (2020) 62-70

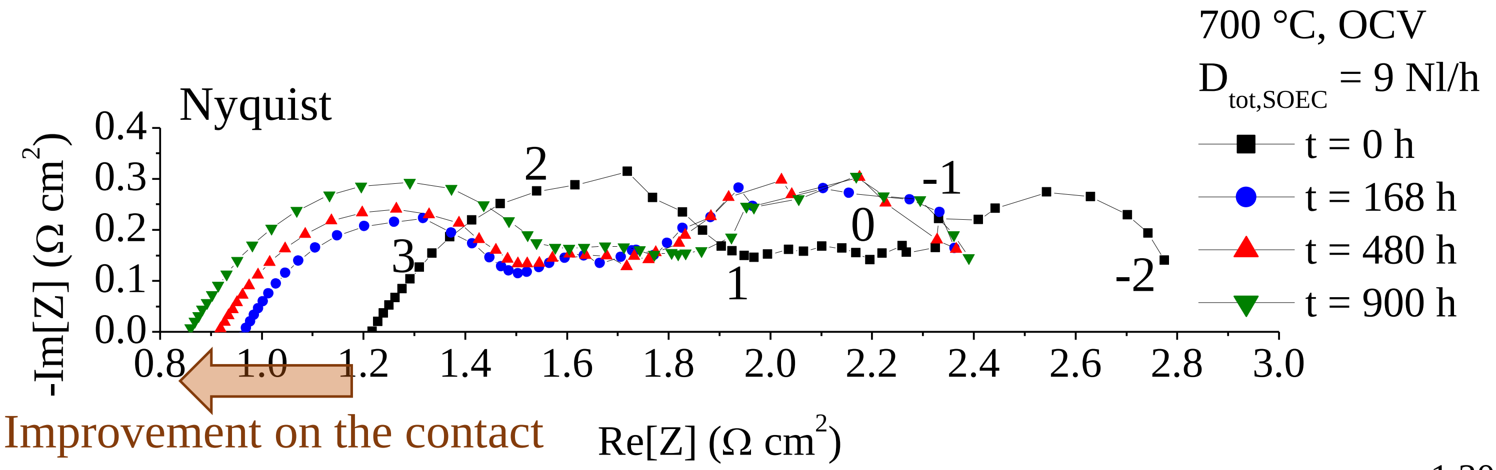
2. Preliminar durability on a real SOEC (complete cell)

- Commercial hydrogen electrode-supported half-cell at 700 °C for ~ 900 h
- H_2O/H_2 = 90/10, steam conversion rate = 20%
- Anodic polarization of 200 mA cm^{-2} on the oxygen electrode (electrolysis mode)
- Glass sealing was carried out at 860 °C for 1.5 h.

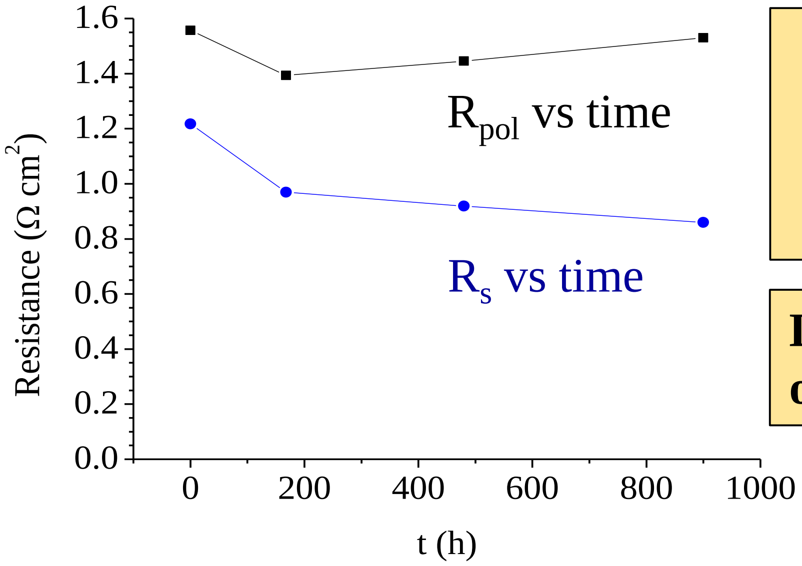


2. Preliminar durability on a real SOEC (complete cell)

EIS before and after ageing under anodic polarization and time (SOEC mode)

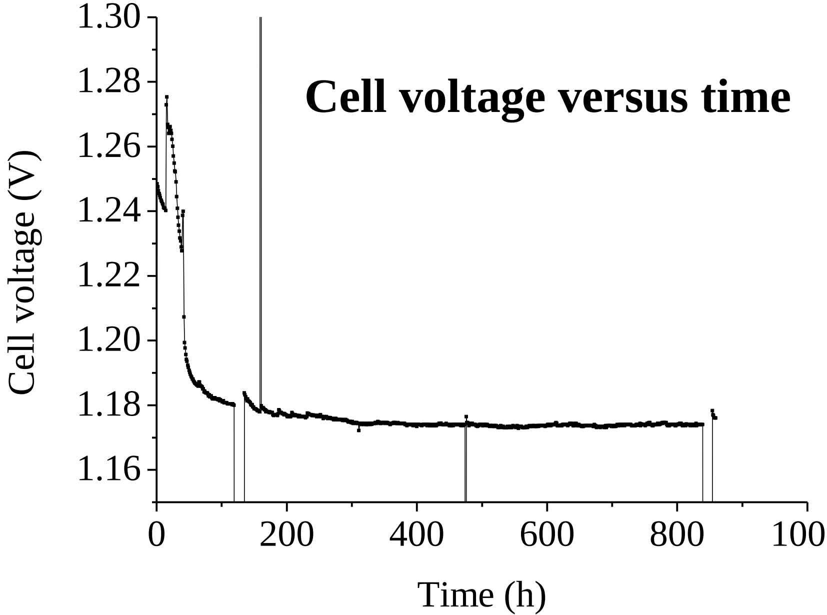


Improvement on the contact



Improvement on the electrode performance in the beginning, followed by a stable performance

LPNO is also stable in SOEC operation for the complete cell



Summary on durability

	Symmetrical cell	Complete cell
SOFC	Strong degradation (rate 15.5 V% kh^{-1}; 219 mV kh^{-1})	
SOEC	Stable performance	Stable performance

Different behavior in SOFC and SOEC operation

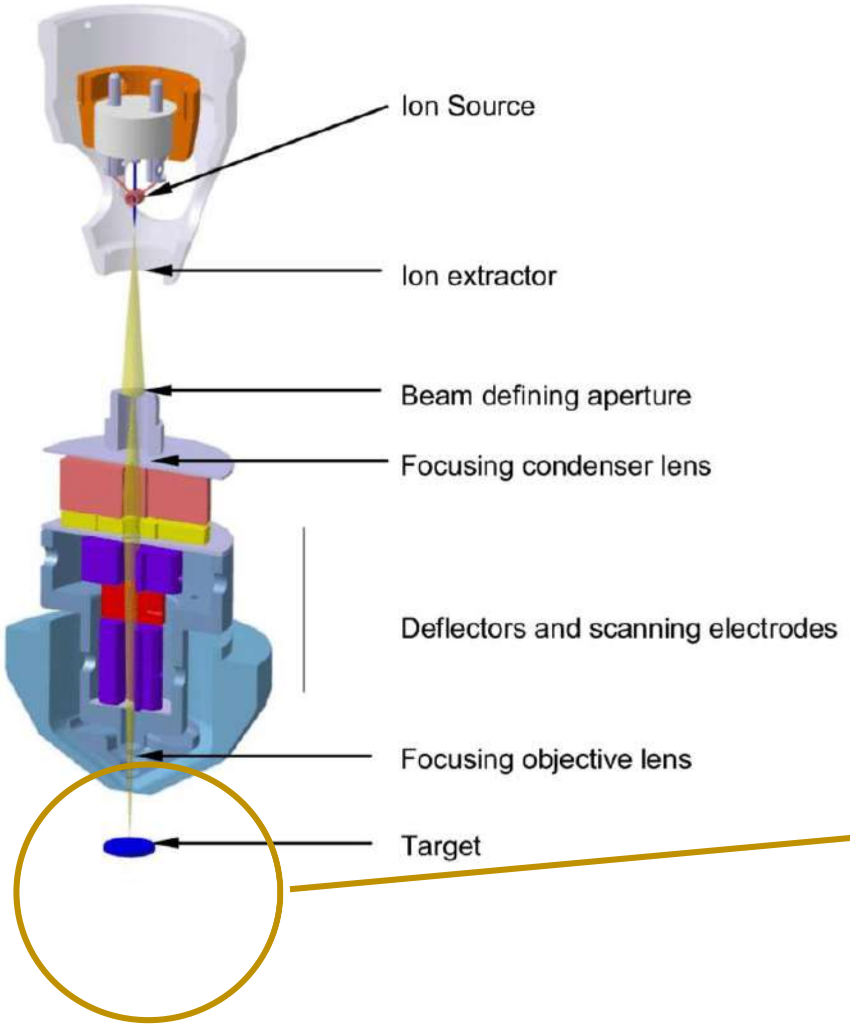
- ➢ Microstructural changes
- ➢ Structural destabilization
- ➢ Interdiffusion, reactivity
- ➢ Delamination on the cathodic sides

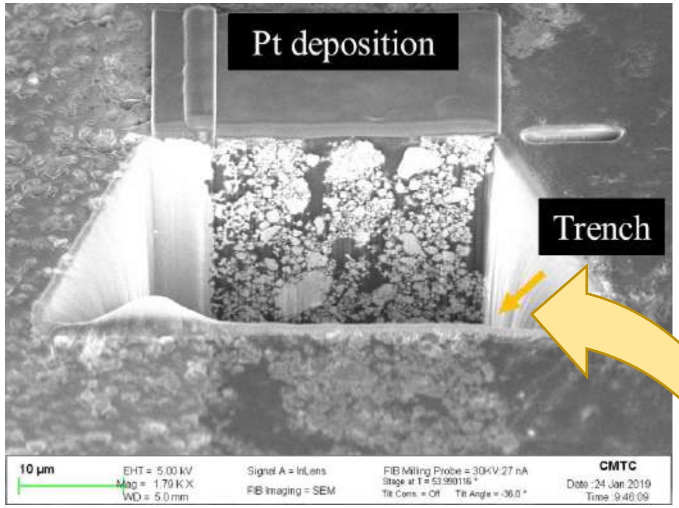
?

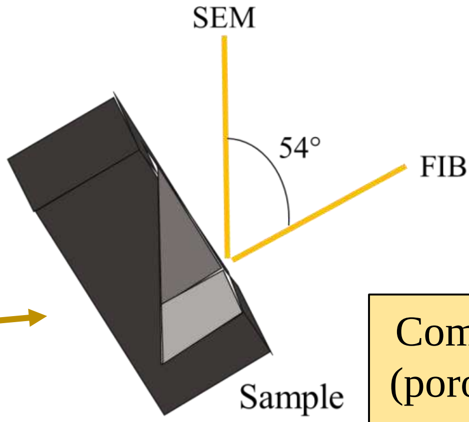
Post-mortem analyses are required to understand the different behavior of LPNO under cathodic and anodic polarizations

***NI Khamidy** et al, Journal of Power Sources 450, 2020, 227724*

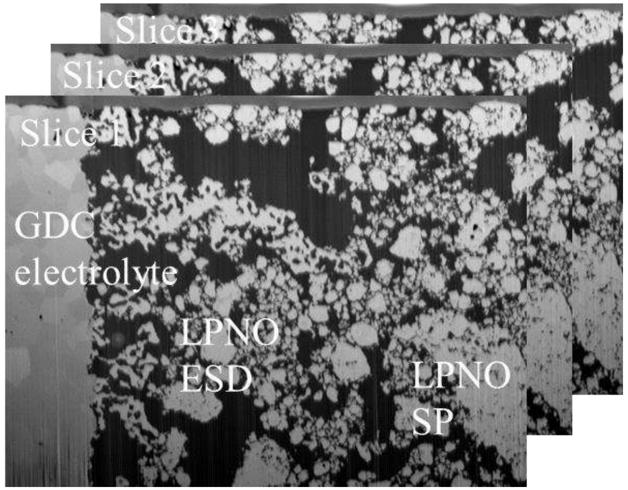
Microstructural characterizations: FIB-SEM and 3D reconstruction



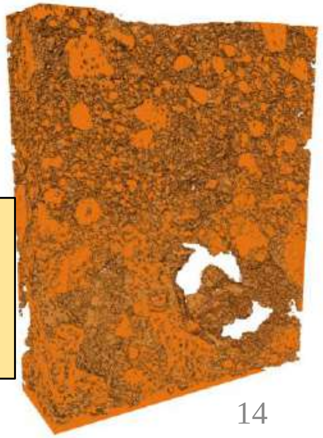




FIB-SEM Images

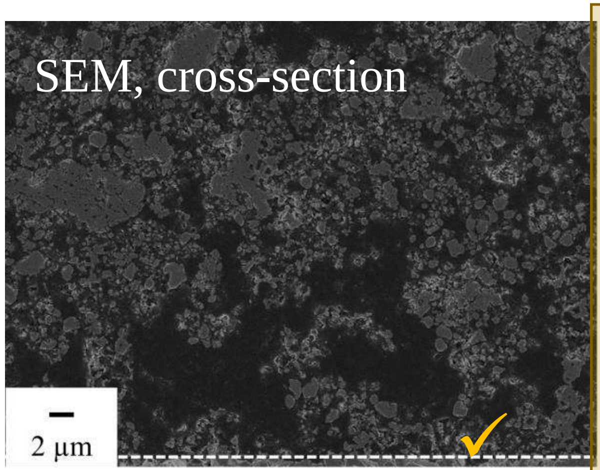


3D reconstruction

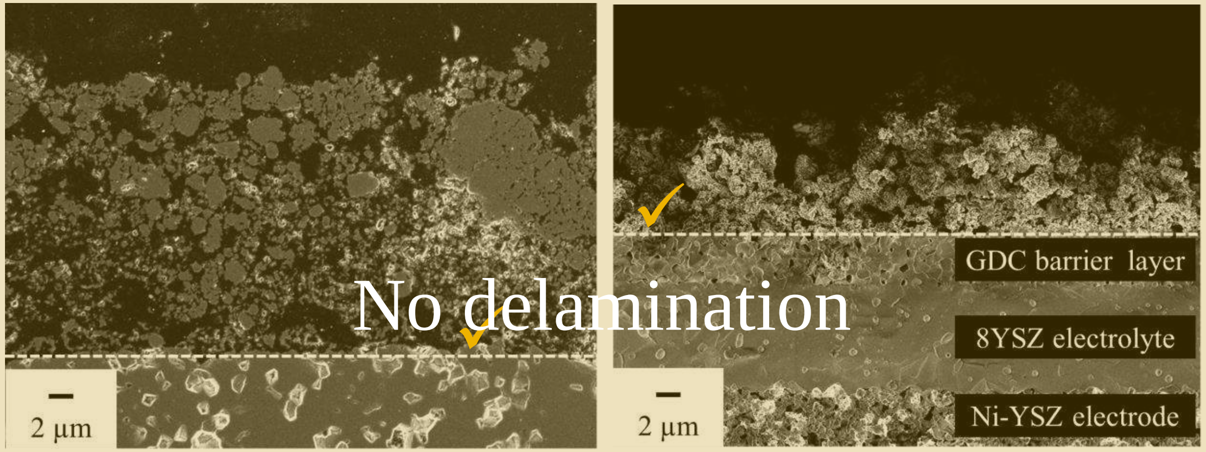


Computation of microstructural properties (porosity, tortuosity factor, specific surface area, etc…) by in-house MATLAB codes

Microstructural characterizations: SEM and 3D reconstruction



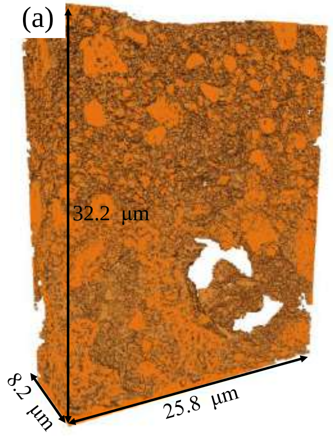
Pristine double-layer electrode

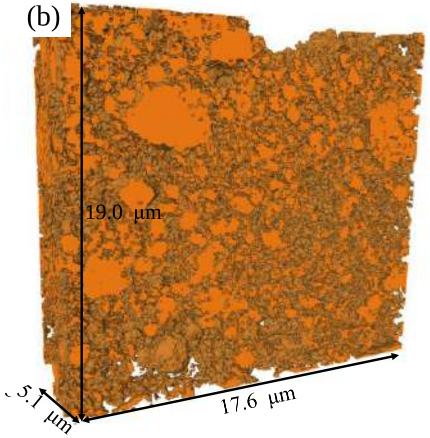


Anodic side (SOEC) symmetrical cell
(700 °C, 960 h, i_{dc} = 300 A cm^{-2})

Complete cell operating in SOEC
(700 °C, 900 h, i_{dc} = 200 A cm^{-2})

Cathodic side (SOFC) symmetrical cell
(700 °C, 960 h, i_{dc} = 300 A cm^{-2})





	Pristine electrode	Anodic side symmetrical cell
Porosity (%)	59.02	63.06
Mean particle diameter (µm)	0.22	0.18
Specific surface area (μm^{-1})	1.86	1.70
Tortuosity factor	1.69	1.49

SOEC
- Stable performance
- No delamination
- No microstructural changes

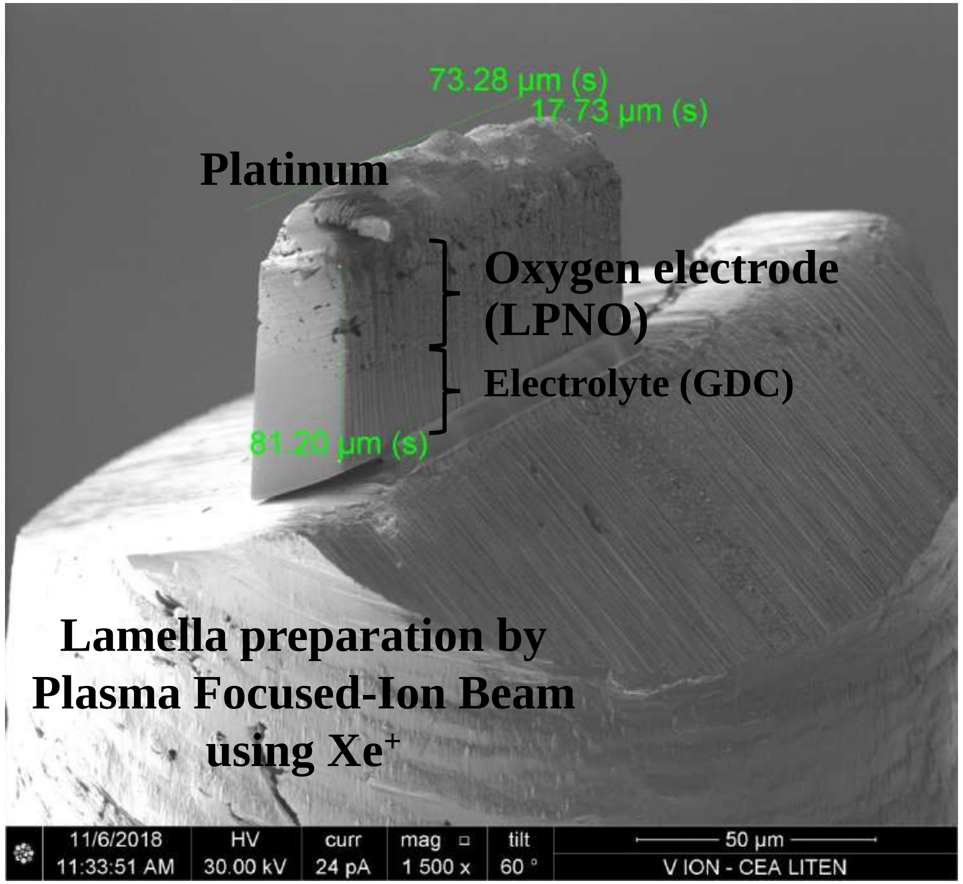
SOFC
- Strong degradation
- Delamination

Structural characterization: Synchrotron µ-XRD and µ-XRF

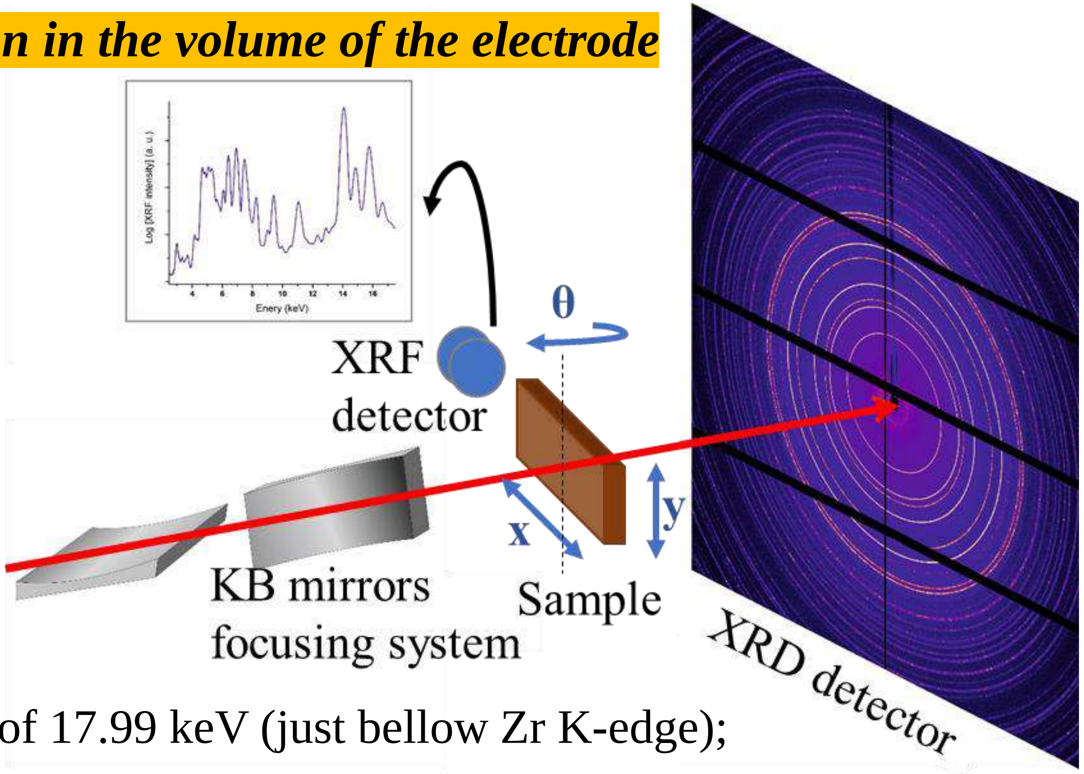
On a beamline at Swiss Light Source (SLS), Paul-Scherrer Institute (PSI), Switzerland

In collaboration with Federico Monaco (CEA-Liten) and Dario Ferreira Sanchez (PSI)

Objectives: detection of phases and elemental distribution in the volume of the electrode



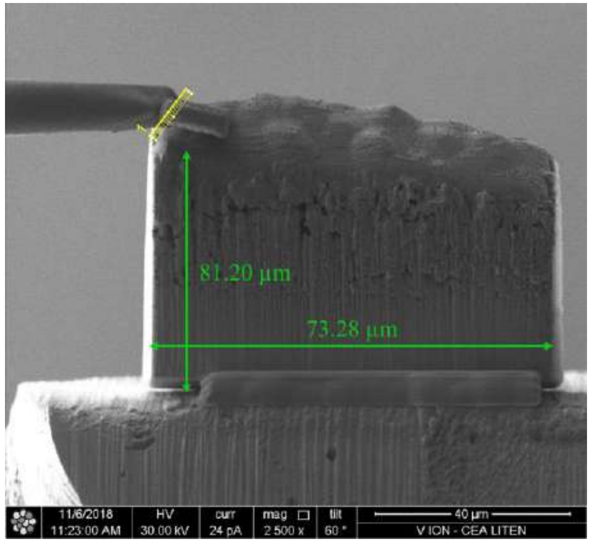
Lamella preparation by Plasma Focused-Ion Beam using Xe^+



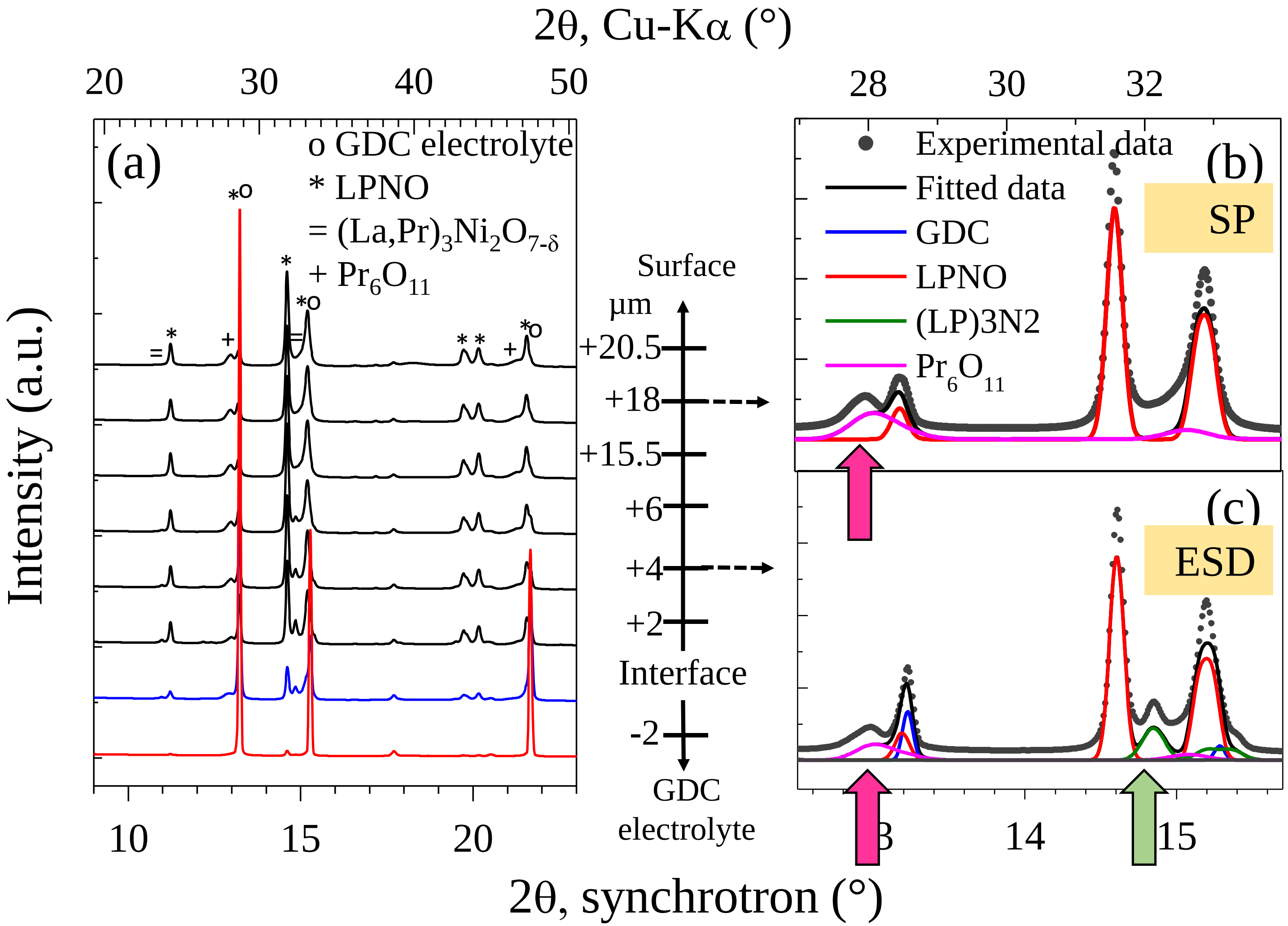
- Energy of 17.99 keV (just bellow Zr K-edge);
- Pencil beam, spot size smaller than 1 µm^2;
- 2D projection, XY scans;
  - XRF + XRD patterns measured simultaneously;
  - Standard step sizes used: 500 nm, and 250 nm for zoom over selected areas

Structural characterization: Synchrotron µ-XRD and µ-XRF

µ-XRD across the electrode thickness



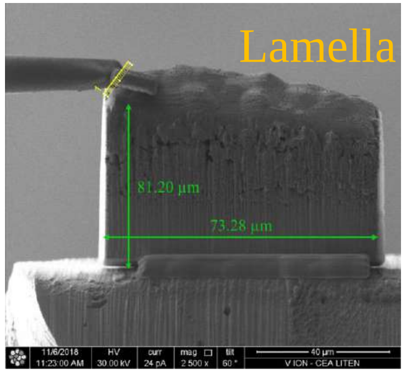
Pristine double-layer electrode



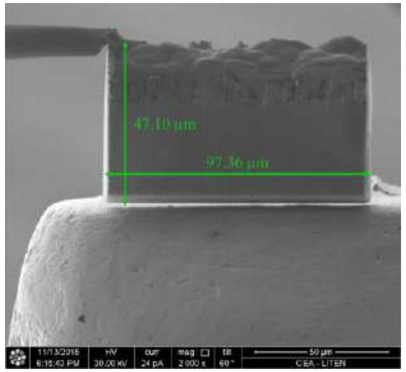
Pr_6O_{11} in both ESD and SP layer
(not detected with lab XRD)

(LP)3N2 only in ESD layer
(in line with lab XRD)

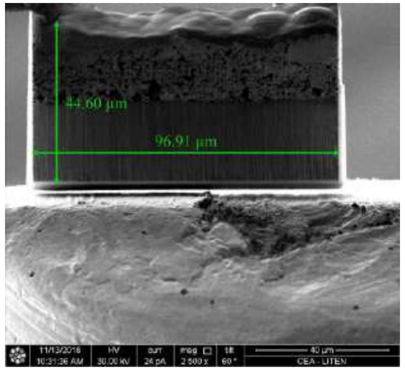
Structural characterization: Synchrotron µ-XRD and µ-XRF



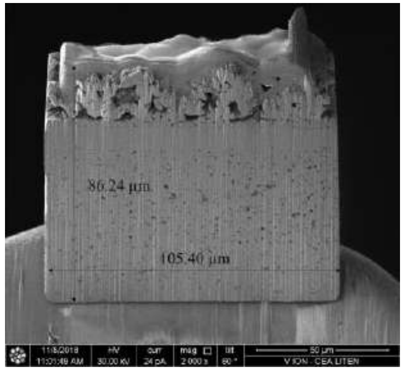
Pristine double-layer electrode



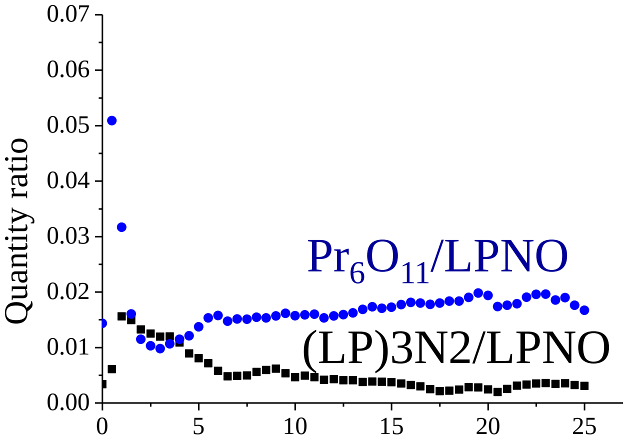
Thermally-aged ESD layer
(700 °C for 1000 h in air)

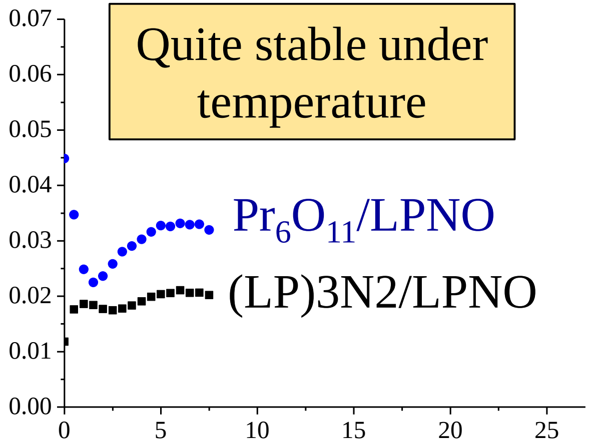


Anodic side (SOEC) symmetrical cell
(700 °C, 960 h, i_{dc} = 300 A cm^{-2})

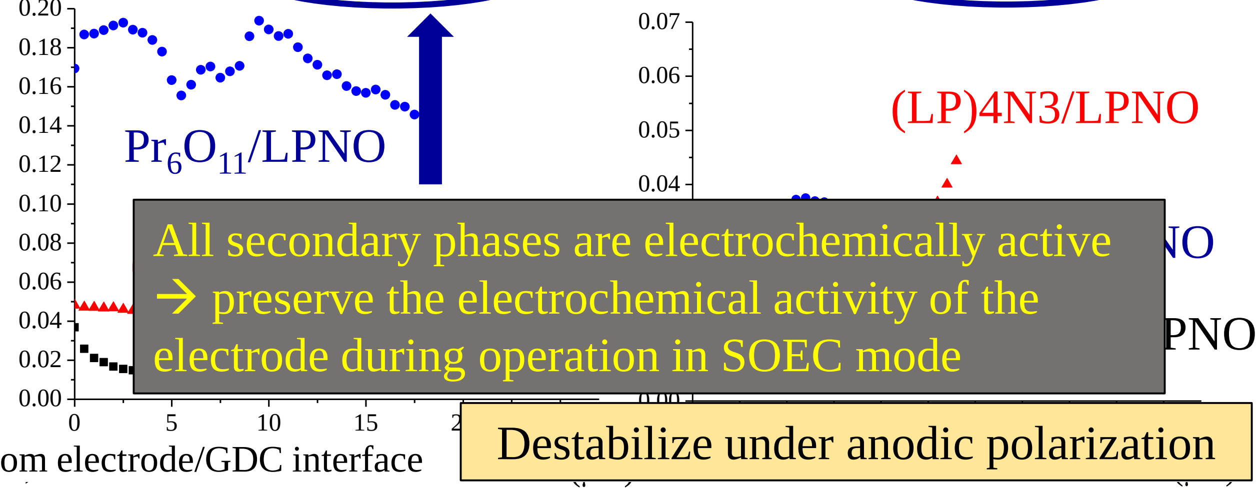


Complete cell operating in SOEC
(700 °C, 900 h, i_{dc} = 200 A cm^{-2})





Quite stable under temperature



All secondary phases are electrochemically active → preserve the electrochemical activity of the electrode during operation in SOEC mode

Destabilize under anodic polarization

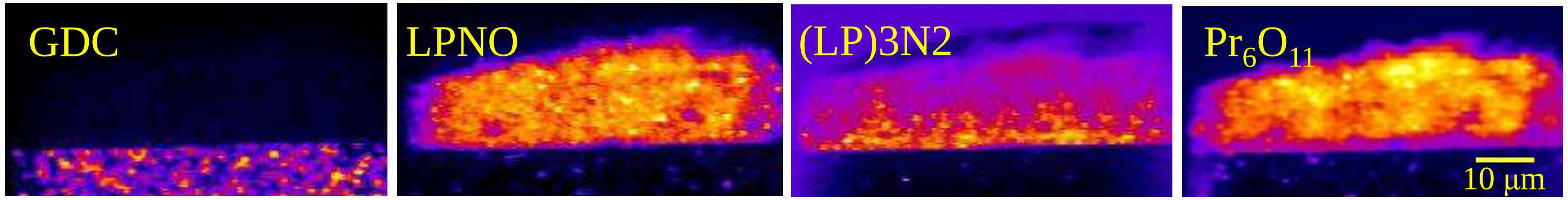
(LP)3N2 = $(La,Pr)_3Ni_2O_{7+\delta}$

(LP)4N3 = $(La,Pr)_4Ni_3O_{10-\delta}$

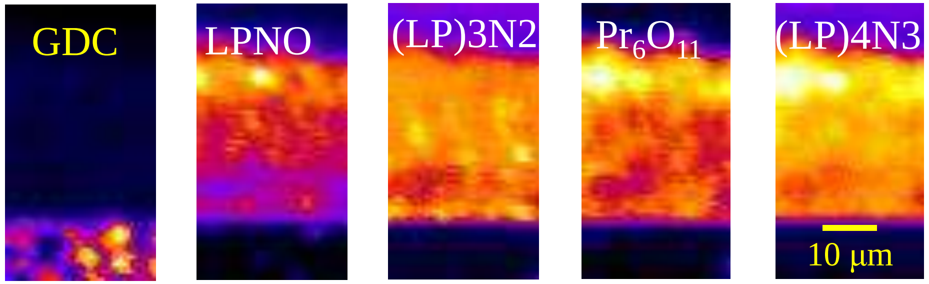
Structural characterization: Synchrotron µ-XRD and µ-XRF

2D XRD maps

Pristine DL electrode



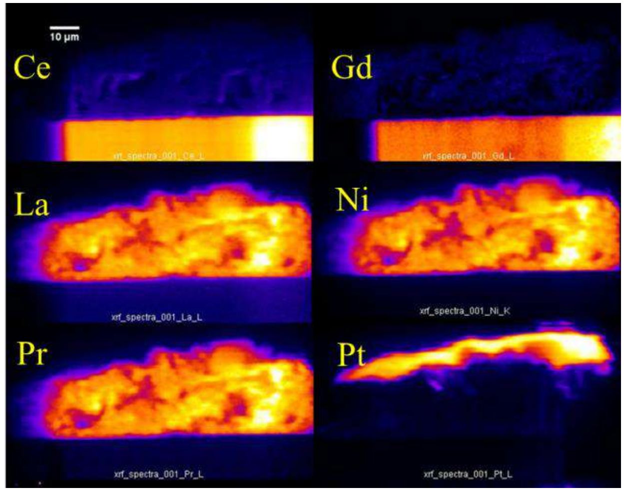
Anodic side (SOEC) symmetrical cell



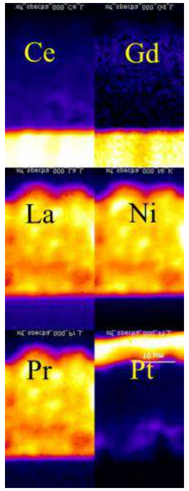
Uniform destabilization under polarization regardless of the microstructure (SP or ESD)

2D XRF maps

Pristine DL electrode

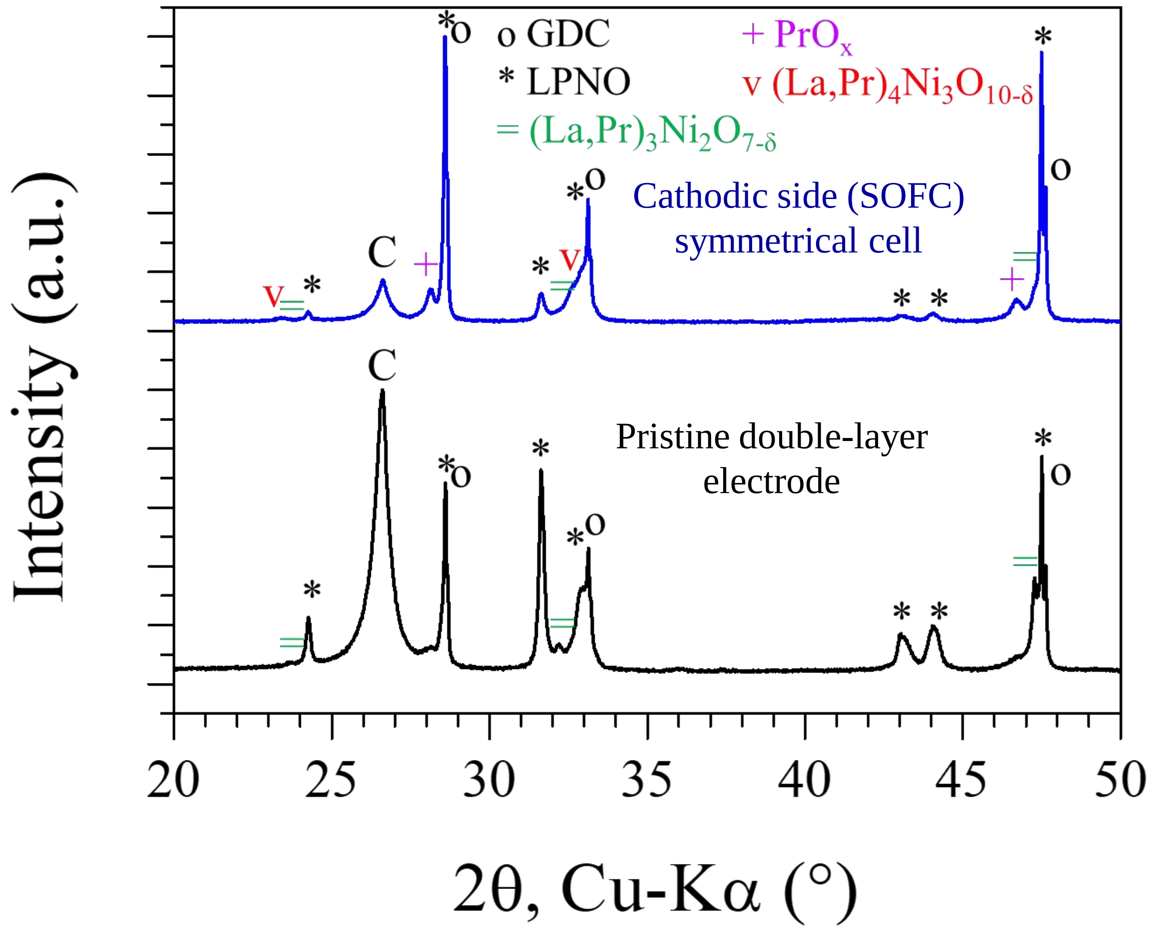


Anodic side (SOEC) symmetrical cell



No sign of element diffusion between the LPNO electrode and the electrolyte

Structural characterization: Laboratory XRD



Cathodic side symmetrical cell:
LPNO + (LP)3N2 + PrO_x + (LP)4N3

Same decomposition products as for the anodic side, but quantitative comparison is not available

Summary

	<u>Thermal aging</u> ESD layer (700 °C for 1000 h)	<u>SOEC operation</u> Symmetrical and complete cells (700 °C for +900 h)	<u>SOFC operation</u> Symmetrical cells (700 °C for +900 h)
Performance		Stable	Strong degradation
Interface		No delamination	Strong delamination
Microstructure		No changes	
Structural stabilization	Relatively stable	Chemical destabilization into the same compounds	

The chemical destabilization of LPNO might be accelerated under SOFC
(low oxygen partial pressure)

Proposed explanations:

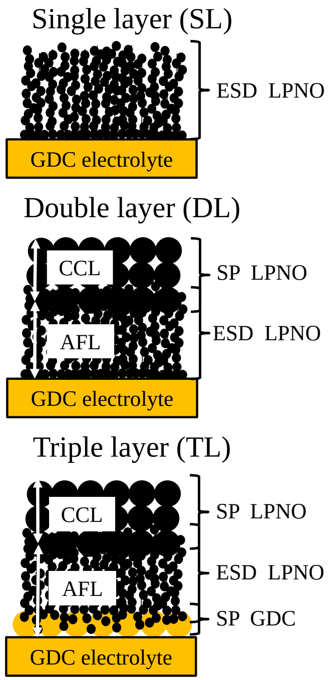
- Depletion of oxygen interstitial under cathodic polarization
  → stronger destabilization especially at the electrode/electrolyte interface
  → inducing delamination
- Phase transition of Pr_6O_{11} under reducing atmosphere

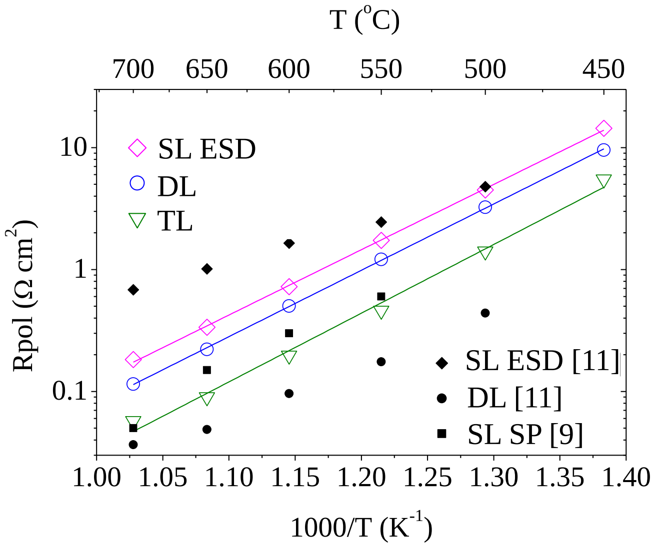
Hyde et al, Phylos. Trans. R. Soc. A 259 (1966) 583-614

The different microstructures between ESD and SP layers do not affect the destabilization

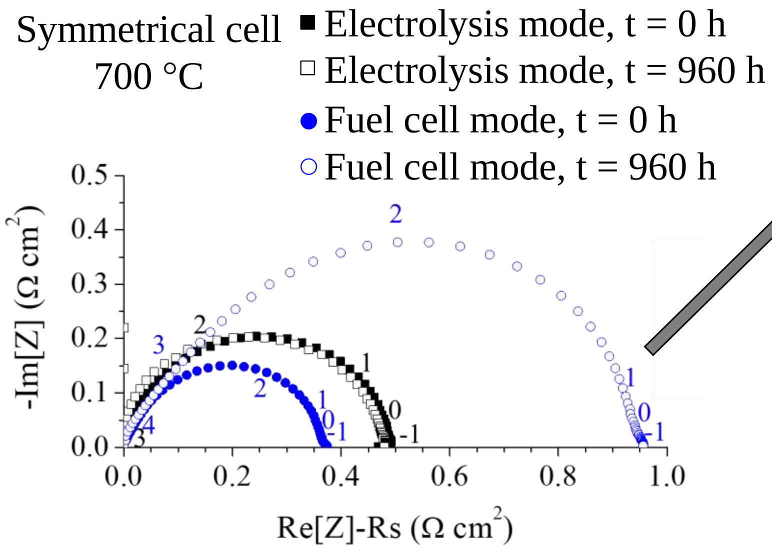
***NI Khamidy** et al, Journal of Power Sources 450, 2020, 227724*

Conclusion

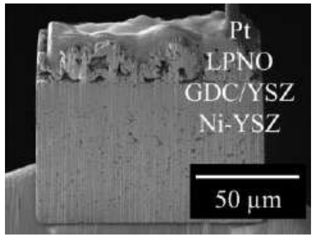




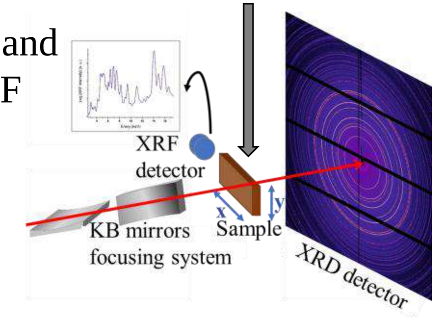
- LPNO = $LaPrNiO_{4+\delta}$
- GDC = $Ce_{0.9}Gd_{0.1}O_{2-\delta}$
- ESD = Electrostatic Spray Deposition
- SP = Screen Printing
- AFL = Active Functional Layer
- CCL = Current Collector Layer



Lamella of the complete cell (p-FIB)



µ-XRD and µ-XRF



- Microstructure, interfaces, and electrode design play an important role on the electrochemical activity of LPNO electrode
- The best electrochemical performance is found for the triple-layer architecture

- Secondary phases ((LP)3N2, Pr_6O_{11}, (LP)4N3) are electrochemically active
- LPNO electrode shows a promising durability as an oxygen electrode for solid oxide electrolysis cell (SOEC)

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