Mixed La/Pr n=3 Ruddlesden-Popper nickelates as stable and efficient oxygen electrodes for high temperature water electrolysis

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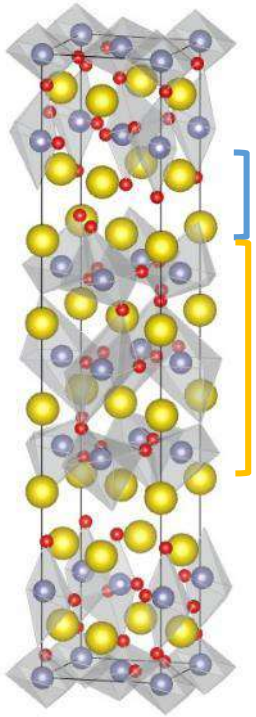
Co-contributors: Vaibhav Vibhu, Sebastien Fourcade, Jean-Marc Bassat and Jacinthe Gamon

3e réunion plénière de la fédération hydrogène FRH2 – 23 - 26 mai 2023
Saint-Gilles-Les-Bains – La Réunion

Layered materials: Alternation of n Perovskite layers + 1 rock-salt layer



Ln (Ln=La, Pr, Nd)

Ni O

Different n-values:

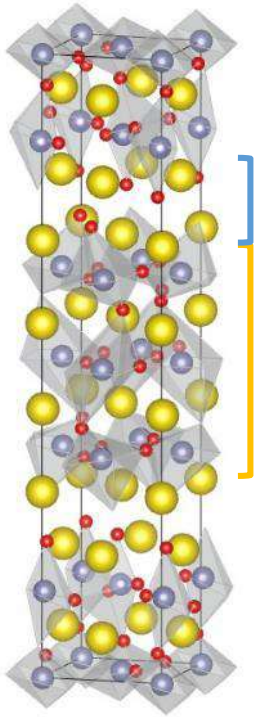
➔ n=1 1 perovskite / 1 rock-salt : $Ln_2NiO_{4+\delta}$

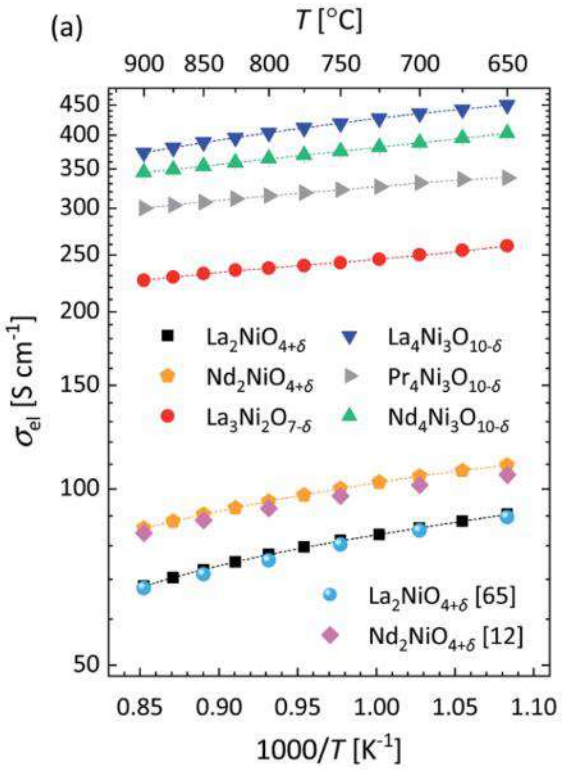
➔ n=3 3 perovskite / 1 rock-salt : $Ln_4Ni_3O_{10\pm\delta}$

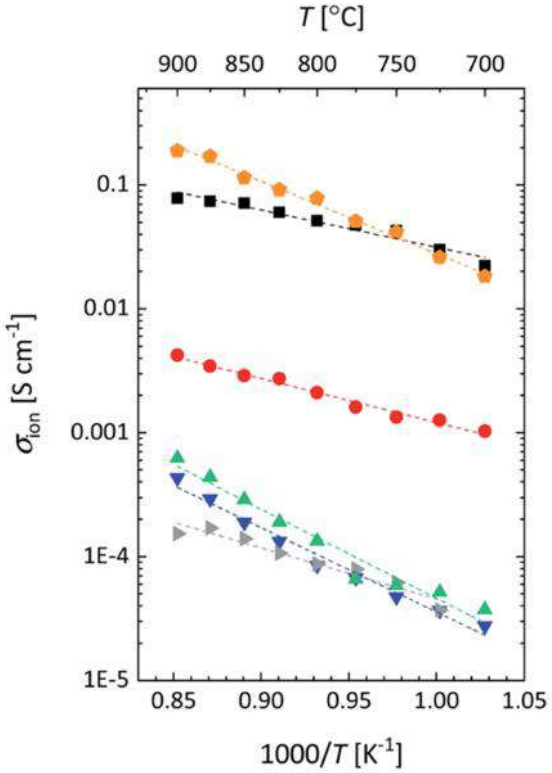
Orthorhombic – Monoclinic systems

Perovskite layers: Electrons conduction pathways

Rock-salt layers: O^{2-} ions conduction pathways



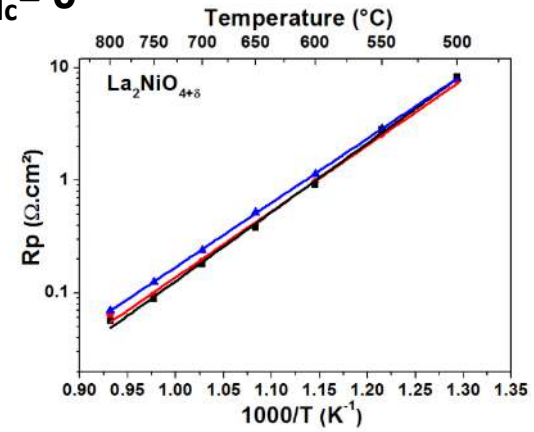




Song, J.; Ning, D.; Boukamp, B.; Bassat, J.-M.; Bouwmeester, H. J. M. S. *J. Mater. Chem. A* **2020**, *8* (42), 22206–22221. https://doi.org/10.1039/D0TA06731Hc

Introduction | Stability & performances of n=1 compounds

I_{dc}= 0



Electrochemical stability

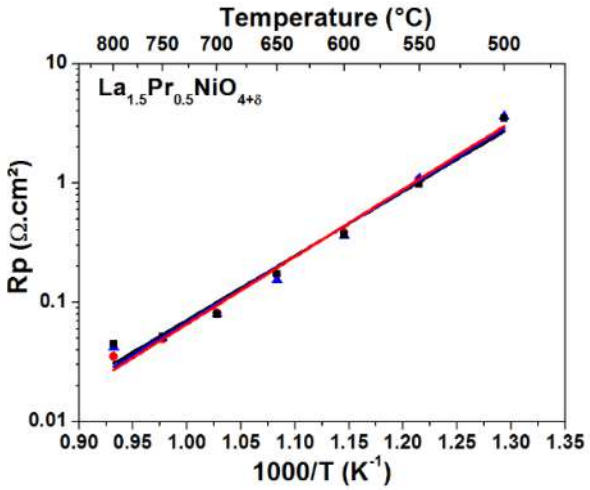
At 700°C

Rp (as prepared)= 0.21 Ω.cm²

Introduction | Alternative n=1 compounds

Mixed La/ Pr compound: To combine La-compound thermal stability and Pr-compound high performances.

I_{dc}= 0



Electrochemical stability

At 700°C

Rp (as prepared)= 0.08 Ω.cm²

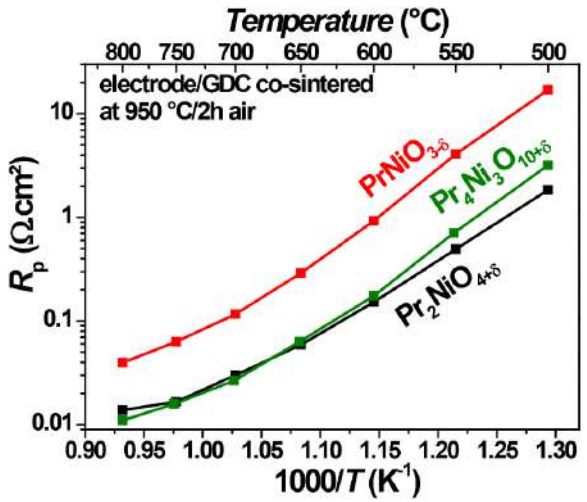
Rp (1 month/ 700°C)= 0.08 Ω.cm²

OK R_p, stable

Vibhu, V.; Rougier, A.; Nicollet, C.; Flura, A.; Fourcade, S.; Penin, N.; Grenier, J.-C.; Bassat, J.-M. *Journal of Power Sources* **2016**, *317*, 184–193. https://doi.org/10.1016/j.jpowsour.2016.03.012

This study | Promising n=3 compounds

$Pr_4Ni_3O_{10+\delta}$



Very good performances

Promising stability

Bassat, J.-M.; Vibhu, V.; Nicollet, C.; Flura, A.; Fourcade, S.; Grenier, J.-C.; Rougier, A. *ECS Trans.* **2017**, *78* (1), 655–665. https://doi.org/10.1149/07801.0655ecst

N. N. Greenwood, A. Earnshaw, "Chemistry of the elements", School of chemistry, University of Leeds, U.K., 1984

[Anderson, Don L.; 'Chemical Composition of the Mantle' in *Theory of the Earth*, pp. 147–175 ISBN 0865421234]

"Lanthanum". price.metal.com. Shanghai Metals Market. 3 February 2020. Archived from the original on 2020-02-03.

Federal Institute for Geosciences and Natural Resources. 22 January 2020. Archived (PDF) from the original on 2020-01-25.

Summary | $La_4Ni_3O_{10+\delta}$, $Pr_4Ni_3O_{10+\delta}$ &, $La_3PrNi_3O_{10+\delta}$ investigation

Powder synthesis

- Le Bail & Rietveld refinement
- Crystalline structure with temperature

Oxygen content

- δ-value
- Oxygen content with temperature

Conductivities

- Pellet densification
- Pulse isotopic exchange

Grain size tuning

- Attrition optimization

Cell preparation

- Tape test
- Preparation of a 3-electrodes setup

Introduction | Nickelates synthesis

Powder synthesis

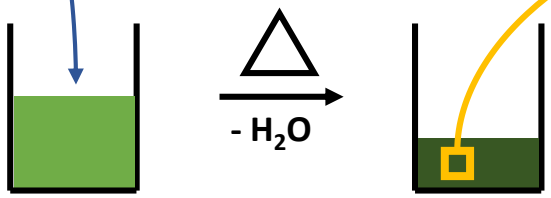
- Tune grain size: Attrition
- Prepare ink
- Screen-printing deposition
- « Sintering » to The GDC substrate
- Adhesion check Tape test

Modified Pechini method: Citrate route

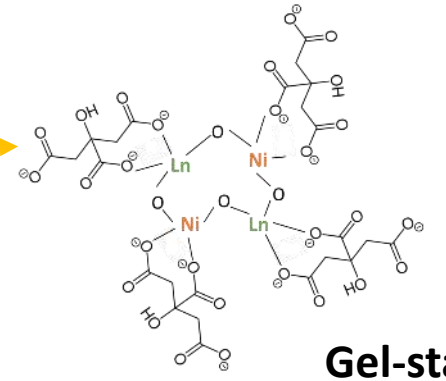
Citric acid

$Ln(NO_3)_3.xH_2O$

$Ni(NO_3)_2.xH_2O$



$- H_2O$



Gel-state

Heating

On flame

Short

Pyrolysis

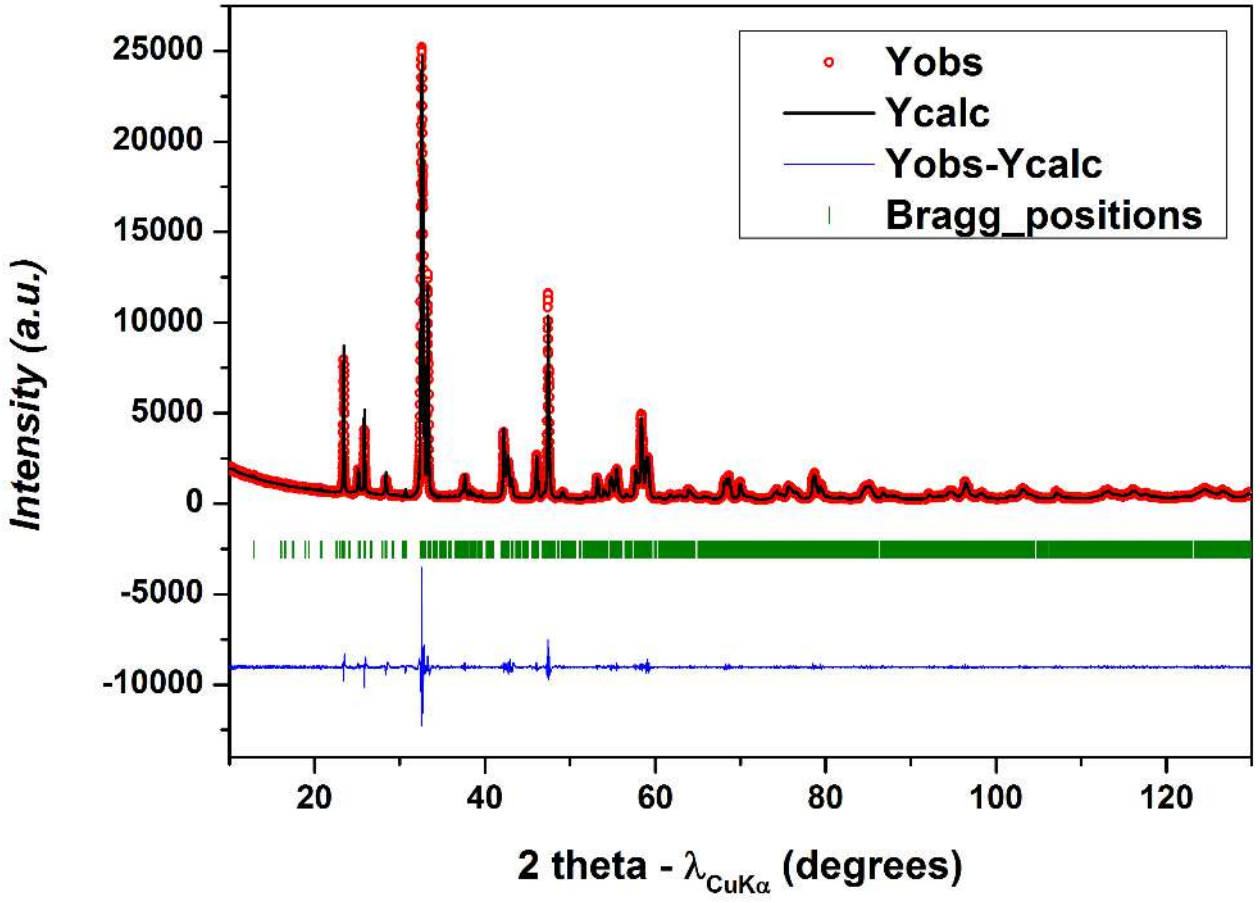
1050°C

$La_4Ni_3O_{10+\delta}$: air

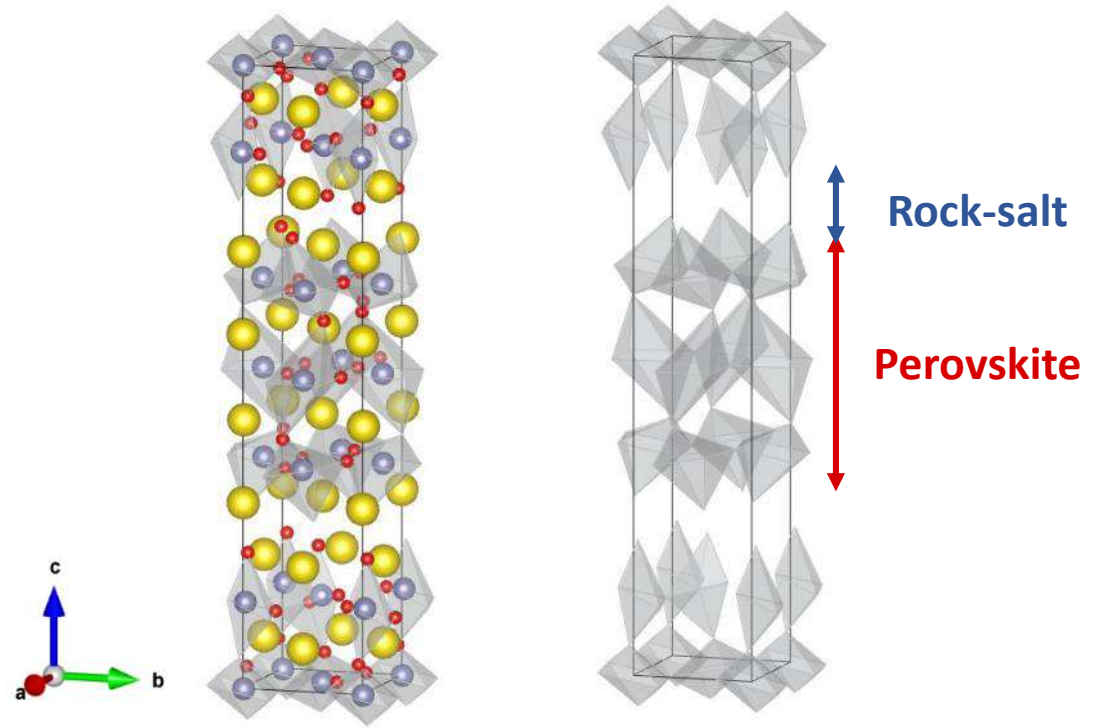
$Pr_4Ni_3O_{10+\delta}$: O_2

$Ln_4Ni_3O_{10+\delta}$

Structure refinement | $Pr_4Ni_3O_{10+\delta}$



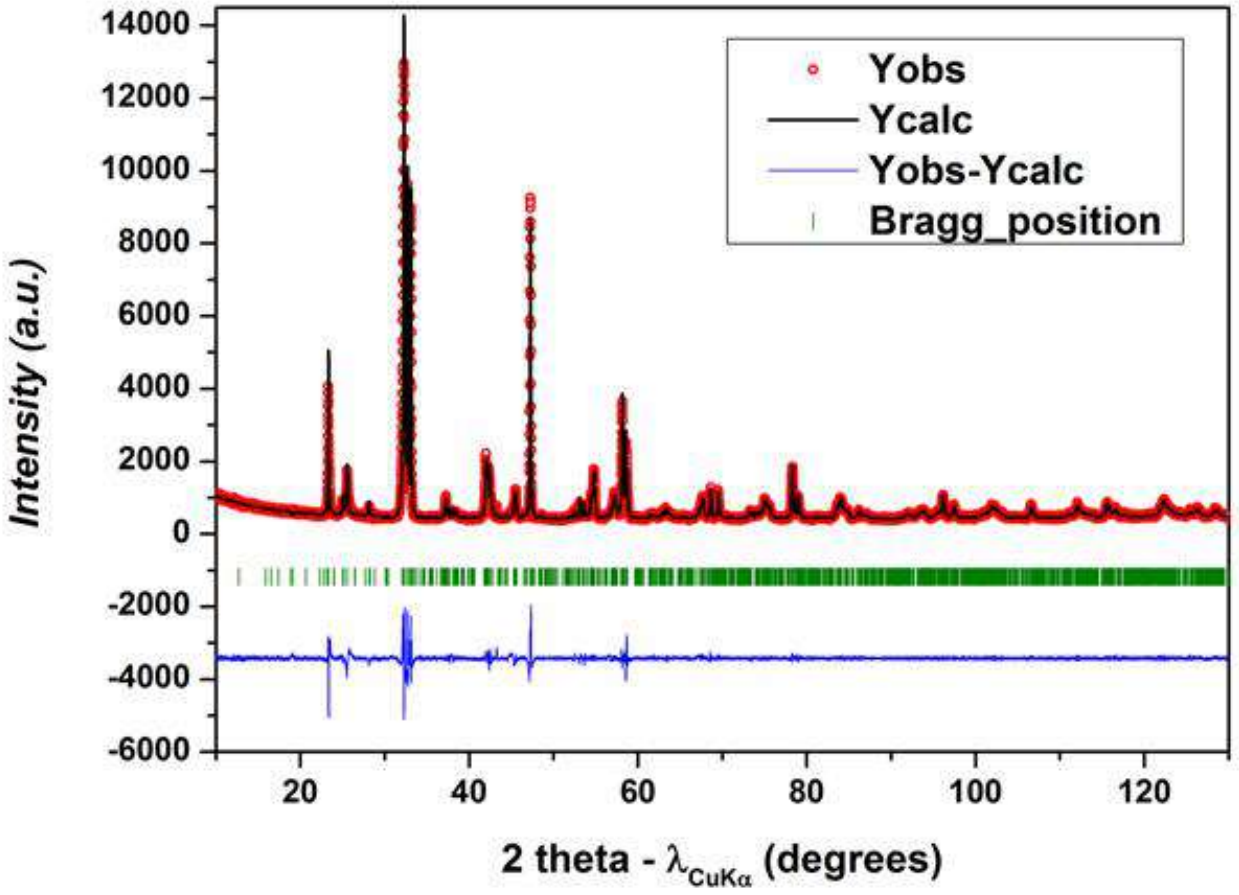
Cell parameter	Fitted	Literature
a (Å)	5.376469 (7)	5.37556 (5)
b (Å)	5.462346 (7)	5.46462 (6)
c (Å)	27.54941 (4)	27.4100 (3)
β (°)	90.29 (16)	90.283 (1)



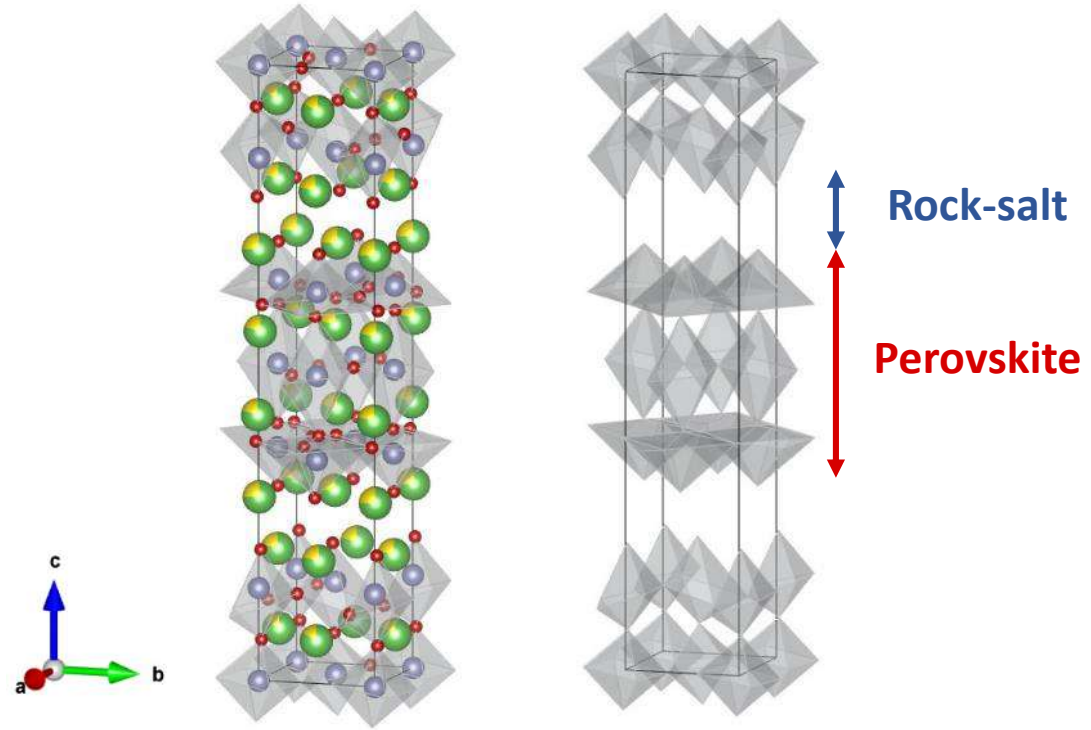
Monoclinic – $P2_1/a$

Song, J.; Ning, D.; Boukamp, B.; Bassat, J.-M.; Bouwmeester, H. J. M. S. *J. Mater. Chem. A* **2020**, *8* (42), 22206–22221. https://doi.org/10.1039/D0TA06731Hc

Structure refinement | $La_3PrNi_3O_{10+\delta}$



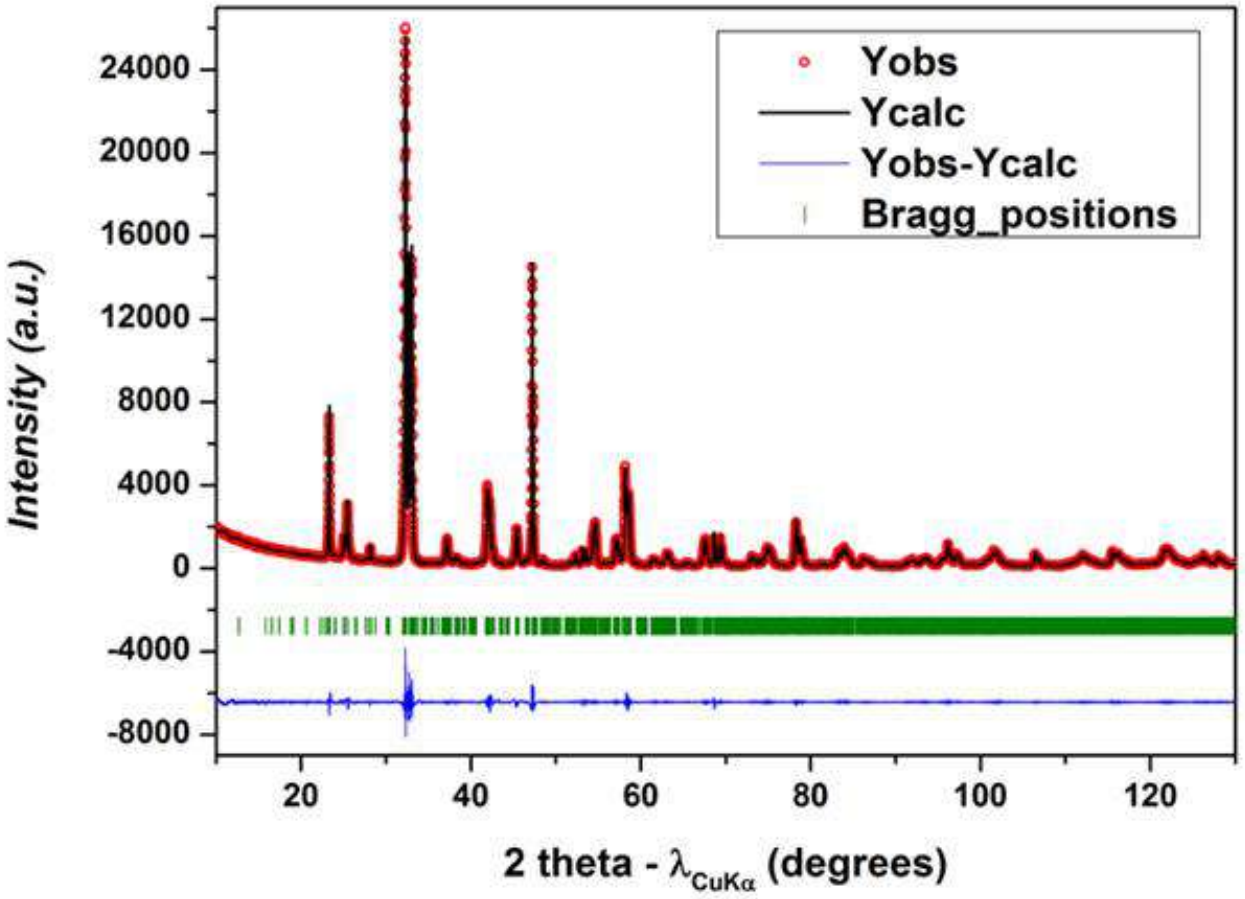
Cell parameter	Fitted	Literature (Fmmm)
a (Å)	5.40531 (8)	5.406 (1)
b (Å)	5.46614 (8)	5.466 (1)
c (Å)	27.889 (10)	27.873 (9)
β (°)	90.2562 (28)	90



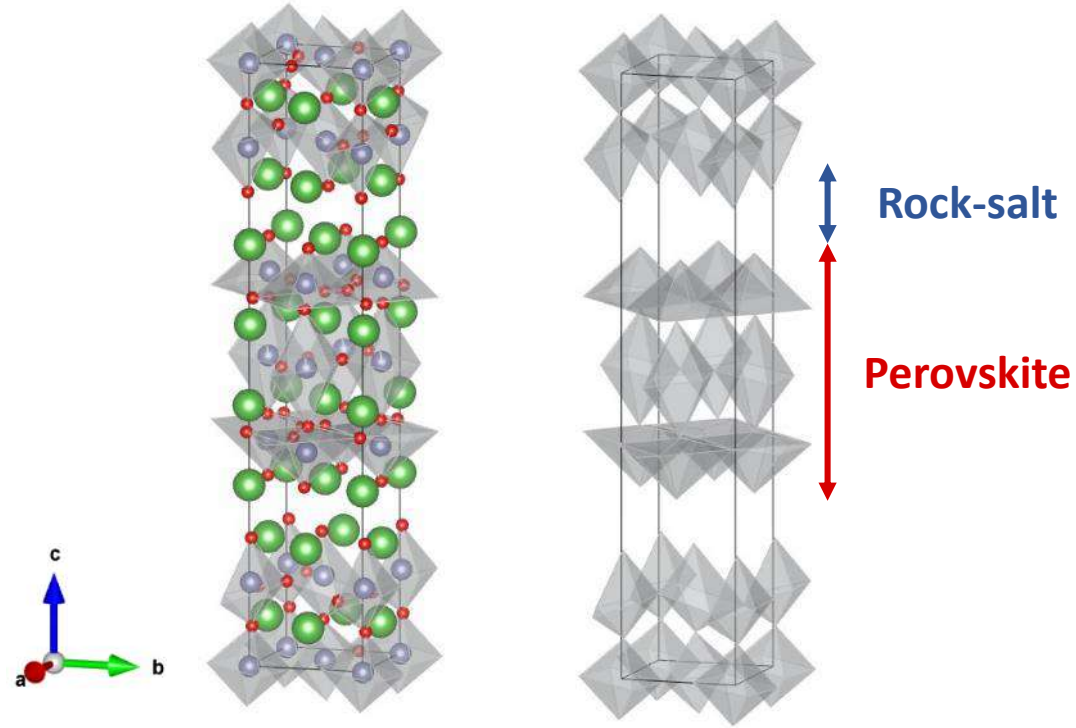
Monoclinic – $P2_1/a$

Yatoo, M. A.; Du, Z.; Yang, Z.; Zhao, H.; Skinner, S. J. *Crystals* **2020**, *10* (6), 428. https://doi.org/10.3390/cryst10060428.

Structure refinement | $La_4Ni_3O_{10+\delta}$



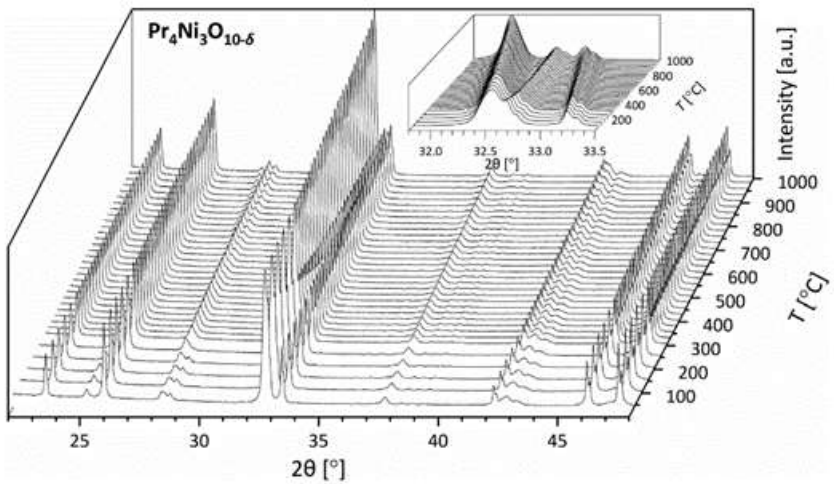
Cell parameter	Fitted	Literature
a (Å)	5.4166 (3)	5.37556Å
b (Å)	5.46544 (3)	5.46462Å
c (Å)	27.96155 (32)	27.4100Å
β (°)	90.198 (1)	90.283°

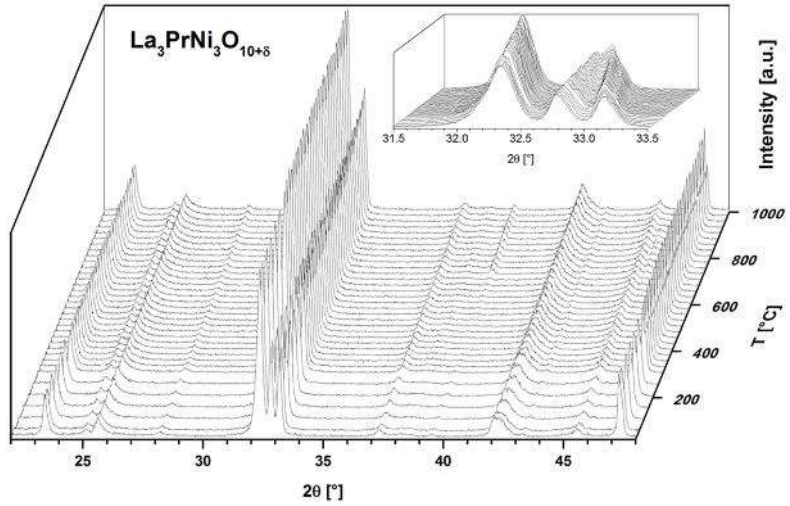


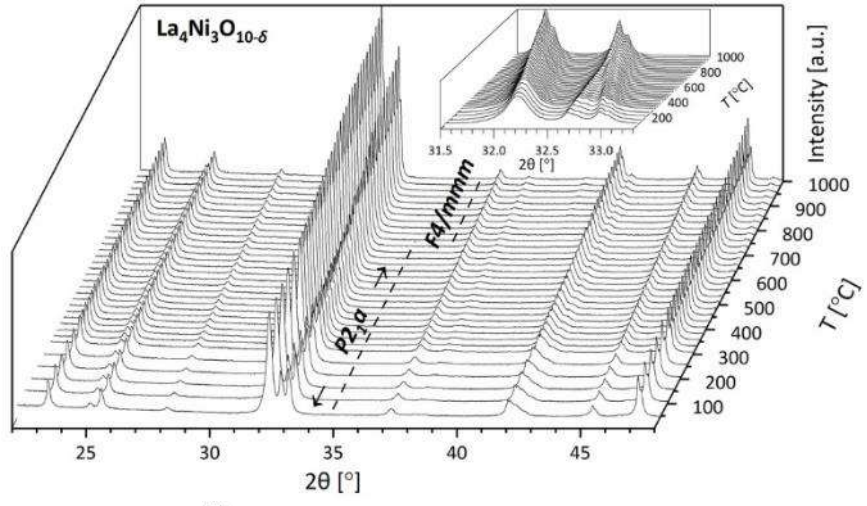
Monoclinic – $P2_1/a$

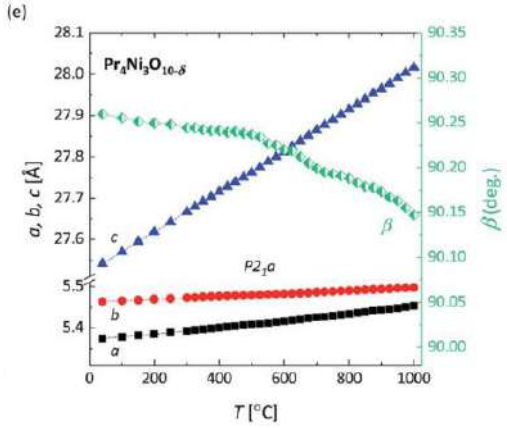
Song, J.; Ning, D.; Boukamp, B.; Bassat, J.-M.; Bouwmeester, H. J. M. S. *J. Mater. Chem. A* **2020**, *8* (42), 22206–22221. https://doi.org/10.1039/D0TA06731H

Structure & Temperature | Phase transitions

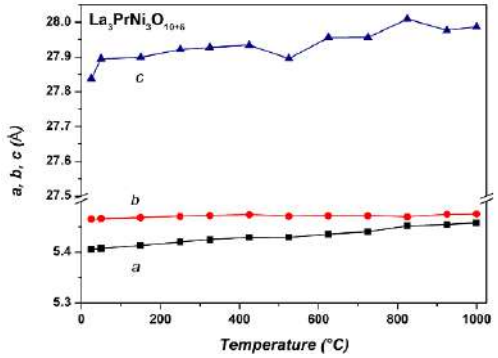




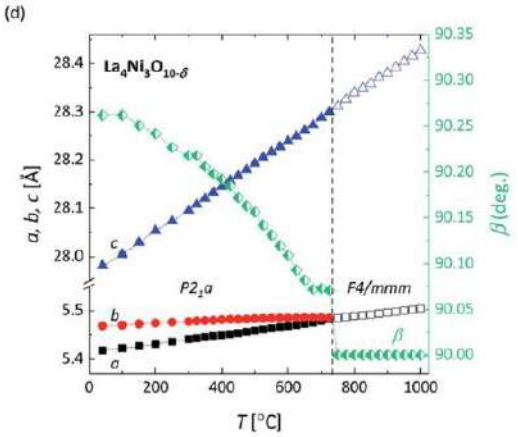




[Song *et al.*]



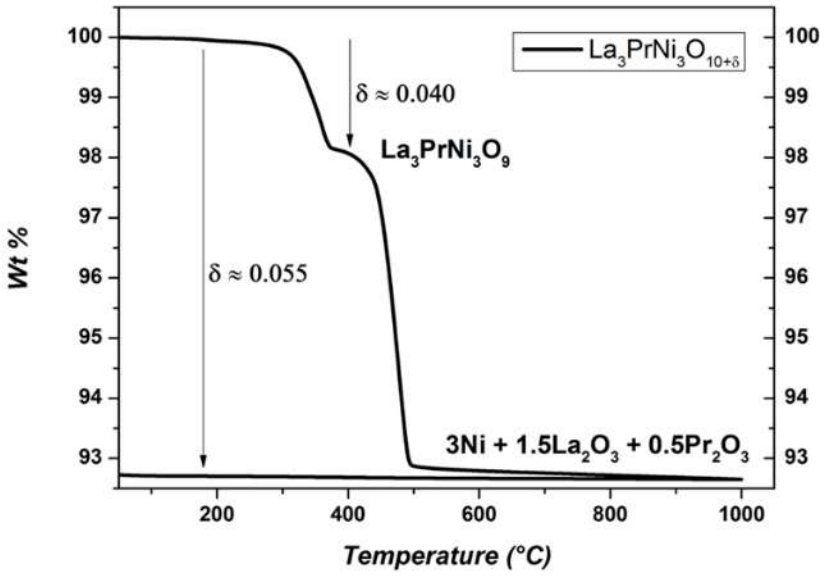
[*This work*]

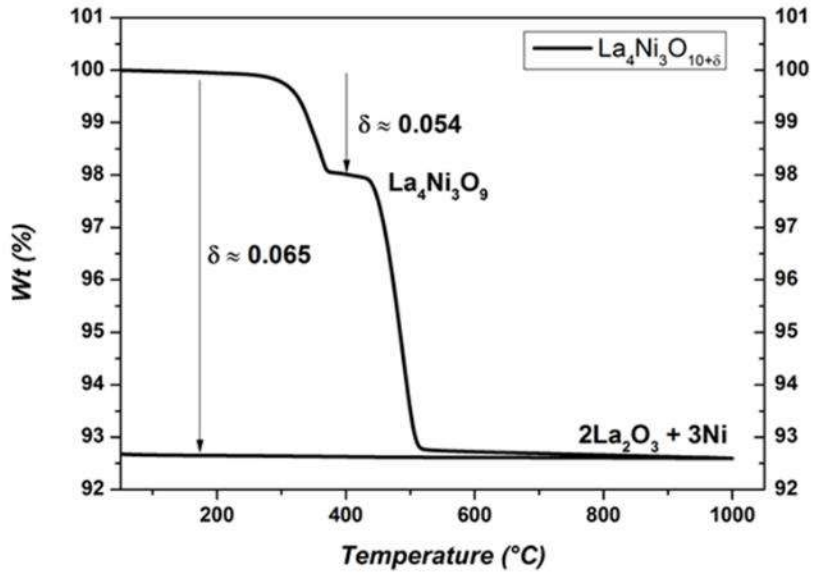


[Song *et al.*]

Song, J.; Ning, D.; Boukamp, B.; Bassat, J.-M.; Bouwmeester, H. J. M. S. *J. Mater. Chem. A* **2020**, *8* (42), 22206–22221.
https://doi.org/10.1039/D0TA06731H

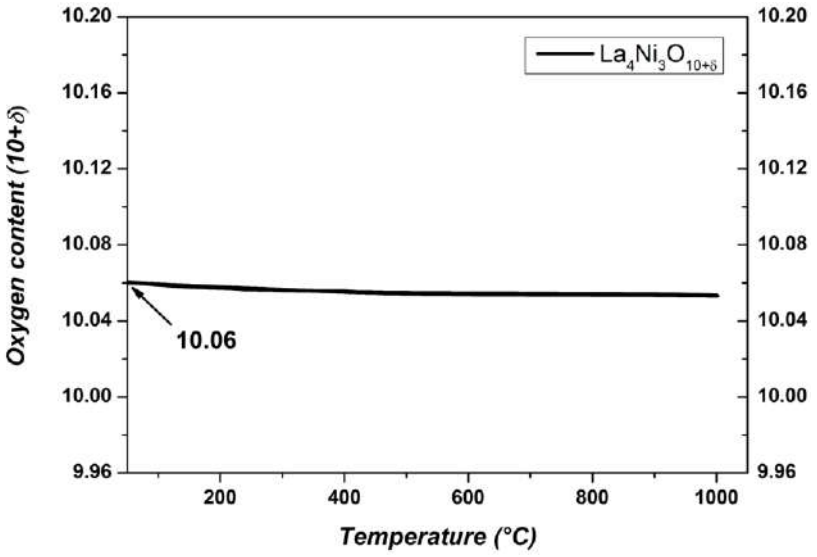
Oxygen content | δ-value



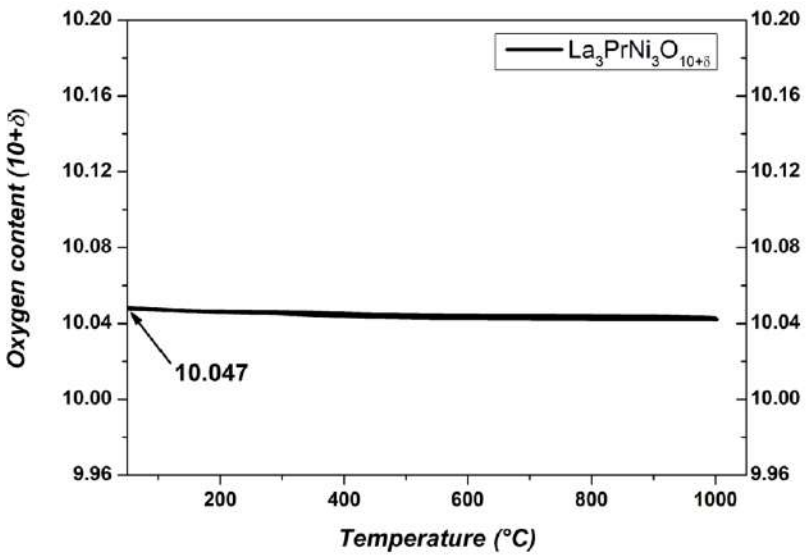


Material	δ-value	Source	Synthesis	Gas
$Pr_4Ni_3O_{10+\delta}$	- 0.21 ± 0.03	Song. J *et al.*	1000°C/ 125h	O_2
	0.1 ± 0.01	Vibhu *et al.*	1000°C/ 48h	
$La_4Ni_3O_{10+\delta}$	0.06 ± 0.005	*This work*	1050°C/ 60h	Air
	- 0.15 ± 0.04	Song. J *et al.*	1050°C/ 132h	
	0.06	Sharma *et al.*	1050°C/ 4h	
$La_3PrNi_3O_{10+\delta}$	0.047 ± 0.008	*This work*	1050°C/ 60h	Air

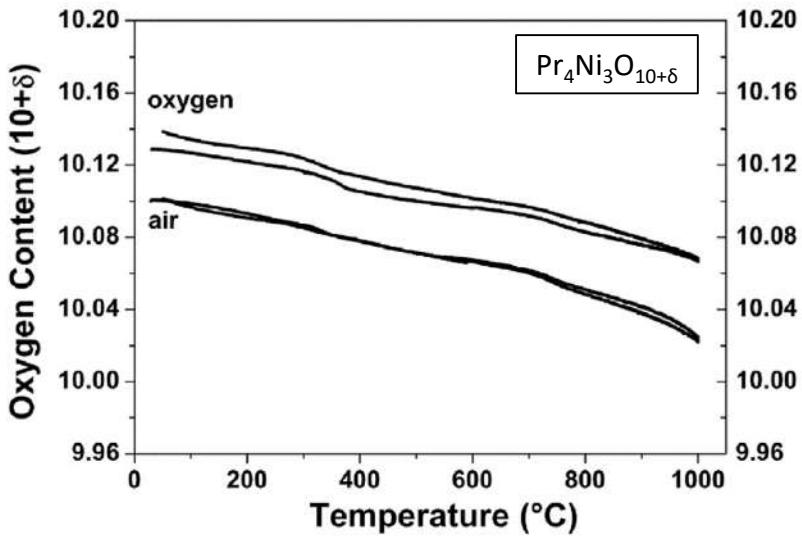
Oxygen content | Evolution in air



[*This work*]



[*This work*]



[*Vibhu et al.*]

Stable in air till 1000°C

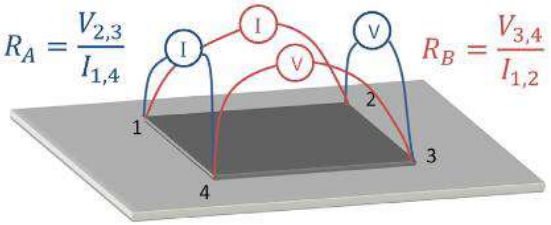
Material « breathing » is observed in air

Conductivities | Possible characterizations

Electronic conductivity

4-probes characterization

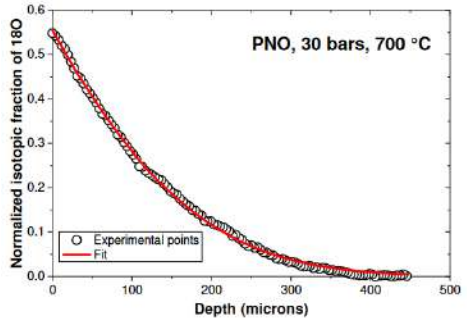
➔ **Need >96% dense pellet**



Ionic conductivity

IEDP & ECR

➔ **Need >96% dense pellet**



Anions diffusion pathways

Neutron diffraction

➔ **Possible on powder**

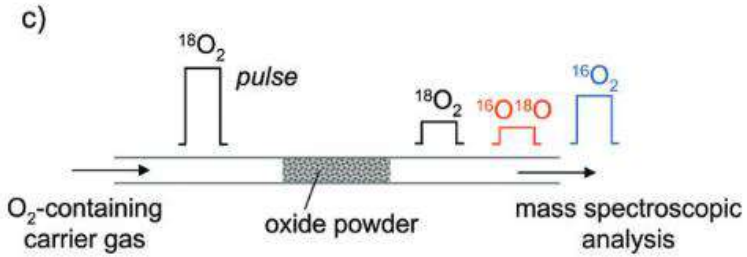
➔ **Neutron diffraction beam time Granted june 2023**

NEUTRONS FOR SOCIETY

Oxygen exchange rates

Pulse isotopic exchange

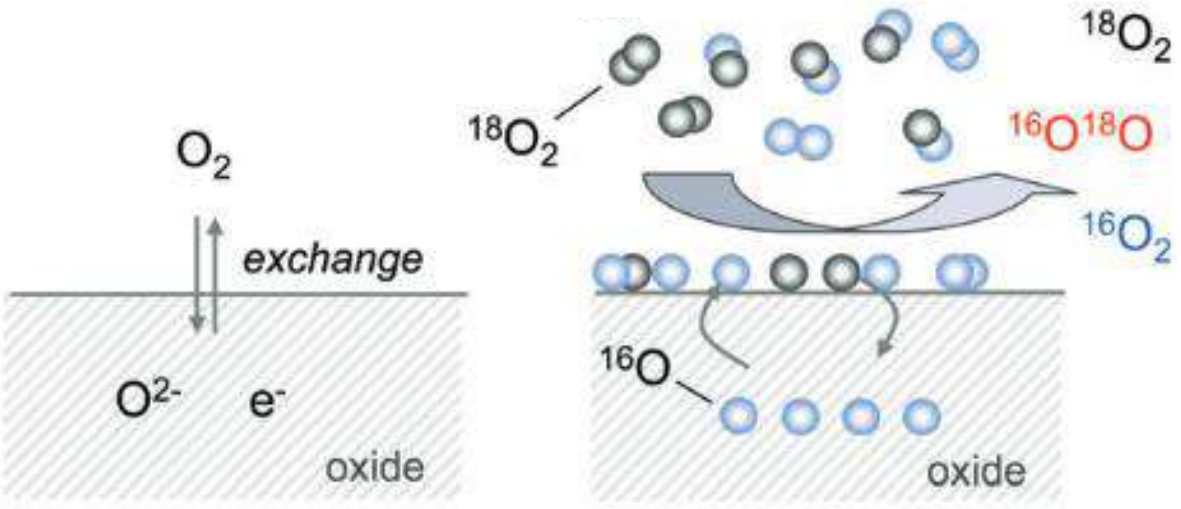
➔ **Possible on powder**

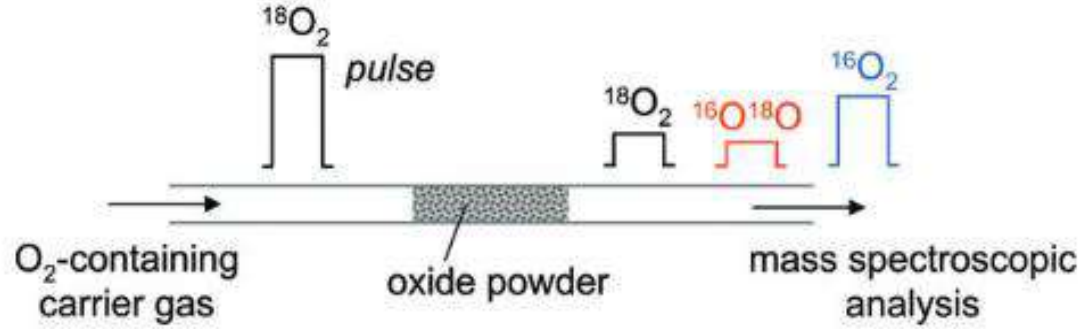


Densification | Different strategies

Material	Uniaxial press	Isostatic press	Annealing conditions	Relative density	Pellet
$La_4Ni_3O_{10+\delta}$	4MPa/ 5min	Ø	1050°C/ 350h/ air	**72%**	
$La_3PrNi_3O_{10+\delta}$	4MPa/ 5min	Ø	1050°C/ 350h/ air	**82%**	
$La_4Ni_3O_{10+\delta}$	4MPa/ 5min	300MPa/ 2min	**1050°C/ 686h/ air - annealing in progress**		
$La_3PrNi_3O_{10+\delta}$	4MPa/ 5min	300MPa/ 2min	**1050°C/ 686h/ air - annealing in progress**		
$Pr_4Ni_3O_{10+\delta}$	4MPa/ 5min	300MPa/ 2min	**1050°C/ 512h/ O_2 - annealing in progress**		

Pulse isotopic exchange | Principle





Allows reaching some parameters

R_0: Balanced exchange rate under equilibrium conditions

R_a: Rate of dissociative adsorption

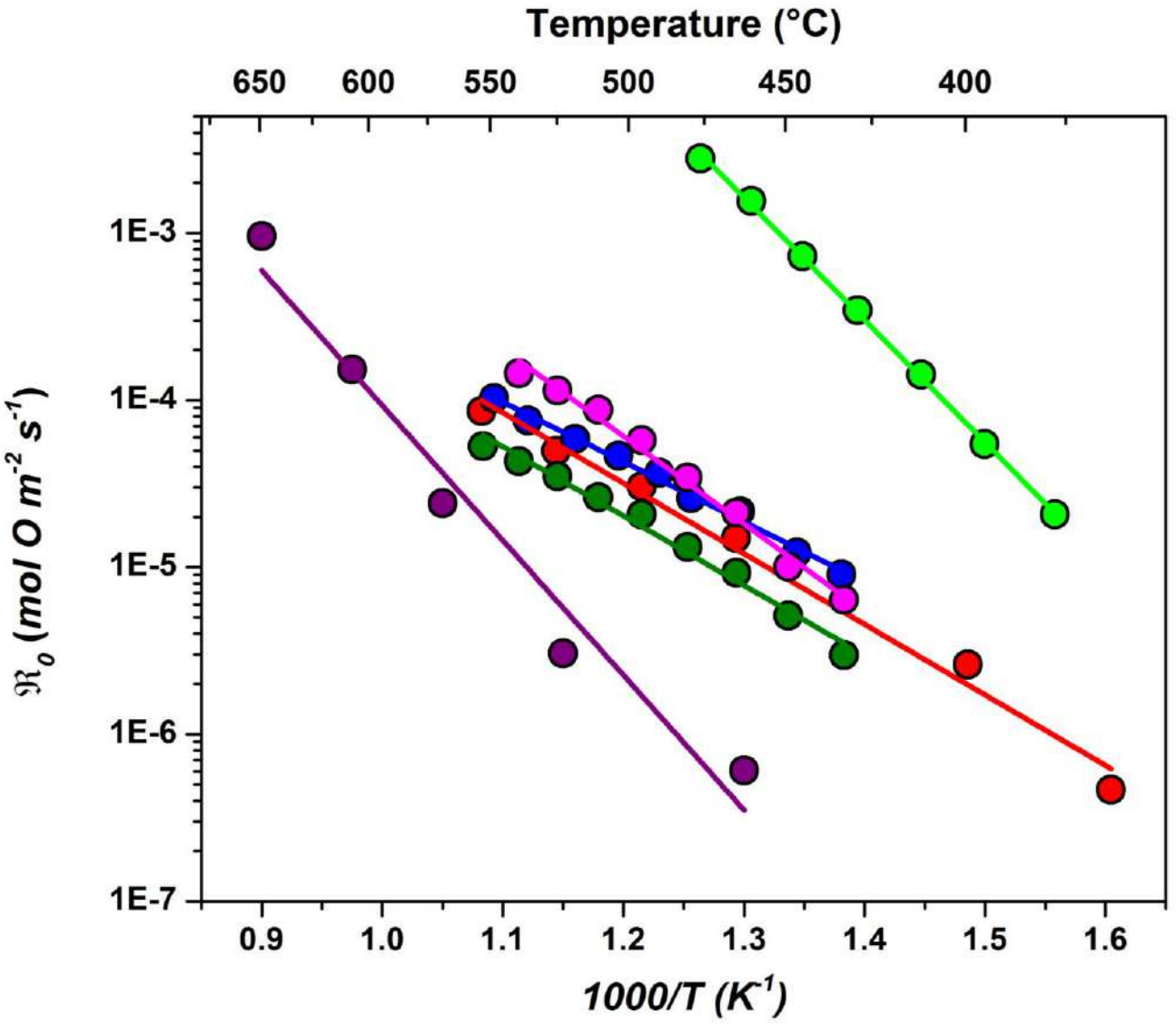
R_i: Rate of oxygen incorporation in the lattice

$$\text{Step 1}: O_2^* \underset{\overline{\Re}_a}{\overset{\Re_a}{\rightleftharpoons}} 2O_{ad}^*$$

$$\text{Step 2}: O_{ad}^* \underset{\overline{\Re}_i}{\overset{\Re_i}{\rightleftharpoons}} O_{lattice}$$

Bouwmeester, H. J. M.; Song, C.; Zhu, J.; Yi, J.; Van Sint Annaland, M.; Boukamp, B. A.. *Phys. Chem. Chem. Phys.* **2009**, *11* (42), 9640. https://doi.org/10.1039/b912712g

Pulse isotopic exchange | Results



- BSCF Bouwmeester *et al.*
- $La_4Ni_3O_{10+\delta}$ Steinberger Wilckens *et al.*
- $La_4Ni_3O_{10+\delta}$ this work
- $Pr_4Ni_3O_{10+\delta}$ this work
- LSCF Gamon *et al.*
- LSCF Benson *et al.*

LSCF: reference SOCs air electrode material

BSCF: reference oxygen exchange material

[Majewski, A. J.; Khodimchuk, A.; Zakharov, D.; Porotnikova, N.; Ananyev, M.; Johnson, I. D.; Darr, J. A.; Slater, P. R.; Steinberger-Wilckens, R. Oxygen Surface Exchange Properties and Electrochemical Activity of Lanthanum Nickelates. *Journal of Solid State Chemistry* **2022**, *312*, 123228. https://doi.org/10.1016/j.jssc.2022.123228]

[Bouwmeester, H. J. M.; Song, C.; Zhu, J.; Yi, J.; Van Sint Annaland, M.; Boukamp, B. A. *Phys. Chem. Chem. Phys.* **2009**, *11* (42), 9640. https://doi.org/10.1039/b912712g]

Introduction | Grain size tuning

Powder synthesis

Tune grain size: Attrition

Prepare ink

Screen-printing deposition

« Sintering » to The GDC substrate

Adhesion check Tape test

Fine powder = High surface area = Higher catalytic activity

As prepared powder

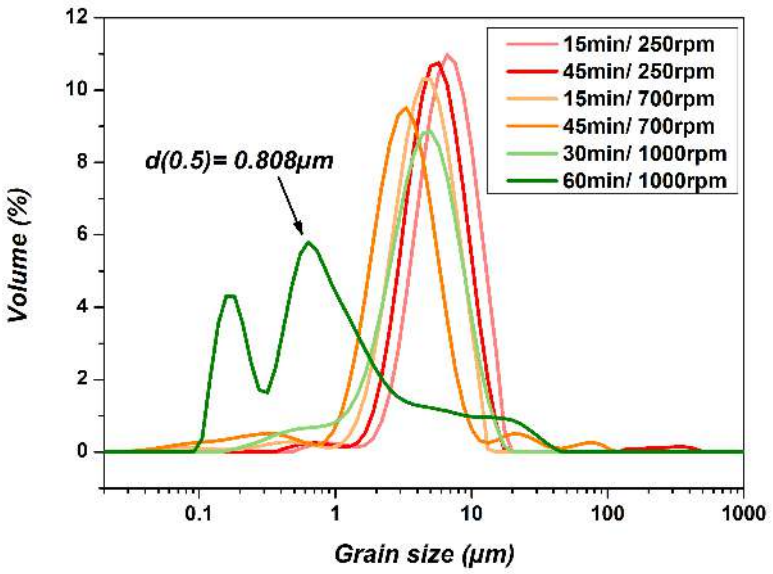
Grain size= 3.5µm

Attrited powder

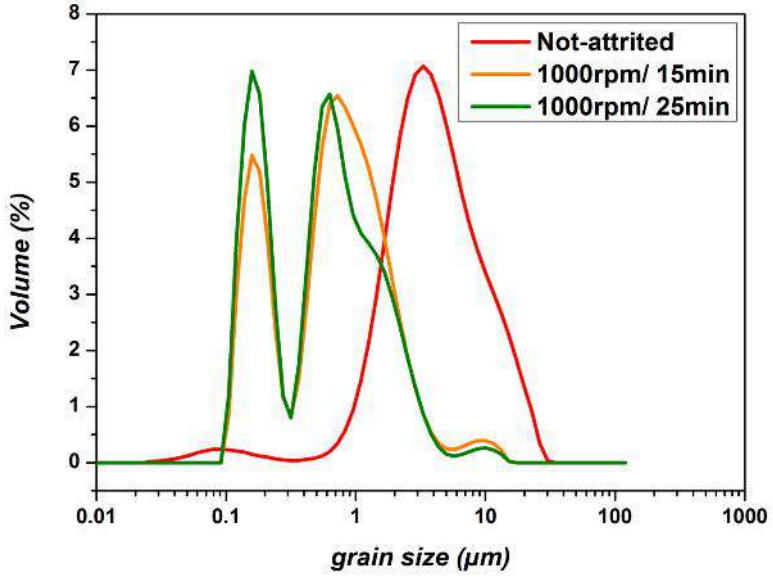
Grain size= 0.6-0.8µm

Symmetrical cells preparation | Attrition optimization

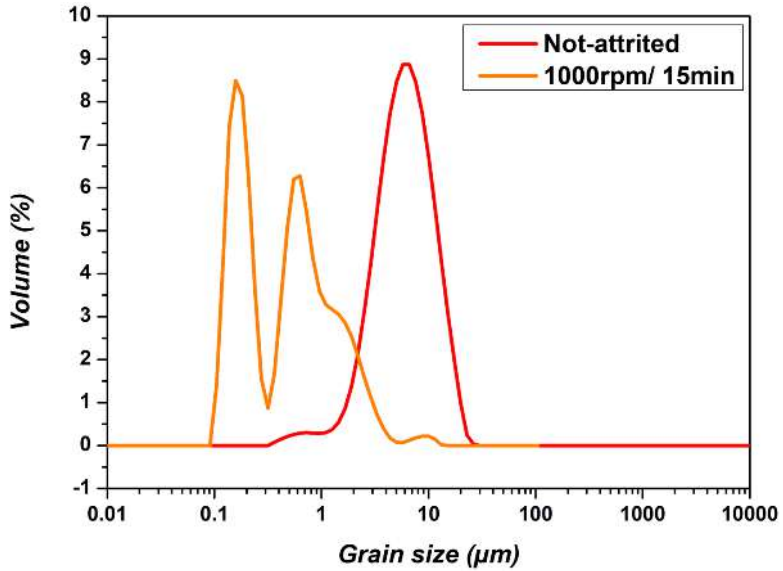
Aimed grain size: 0.6-0.8 µm according to Vibhu *et al*.



$La_4Ni_3O_{10+\delta}$



$La_3PrNi_3O_{10+\delta}$

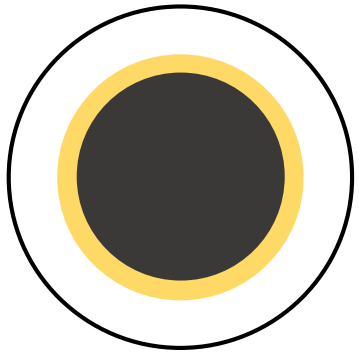


$Pr_4Ni_3O_{10+\delta}$

Post-attrition XRD: slight amorphization, no crystallites breaking

Symmetrical cells preparation | Adhesion test- $La_4Ni_3O_{10+\delta}$

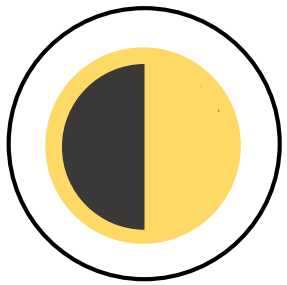
Aimed adhesion: The porous layer mustn't go off when pulling out a tape from it



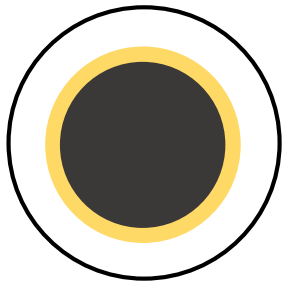
Electrolyte: 3YSZ

Barrier layer: CGO

Electrode: Nickelate



Poor adhesion

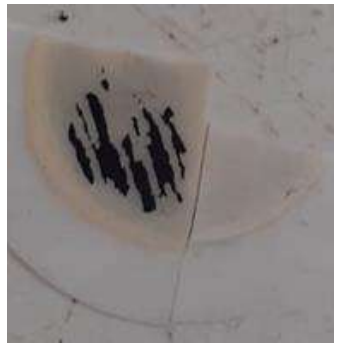


Good adhesion

950°C/ 2h

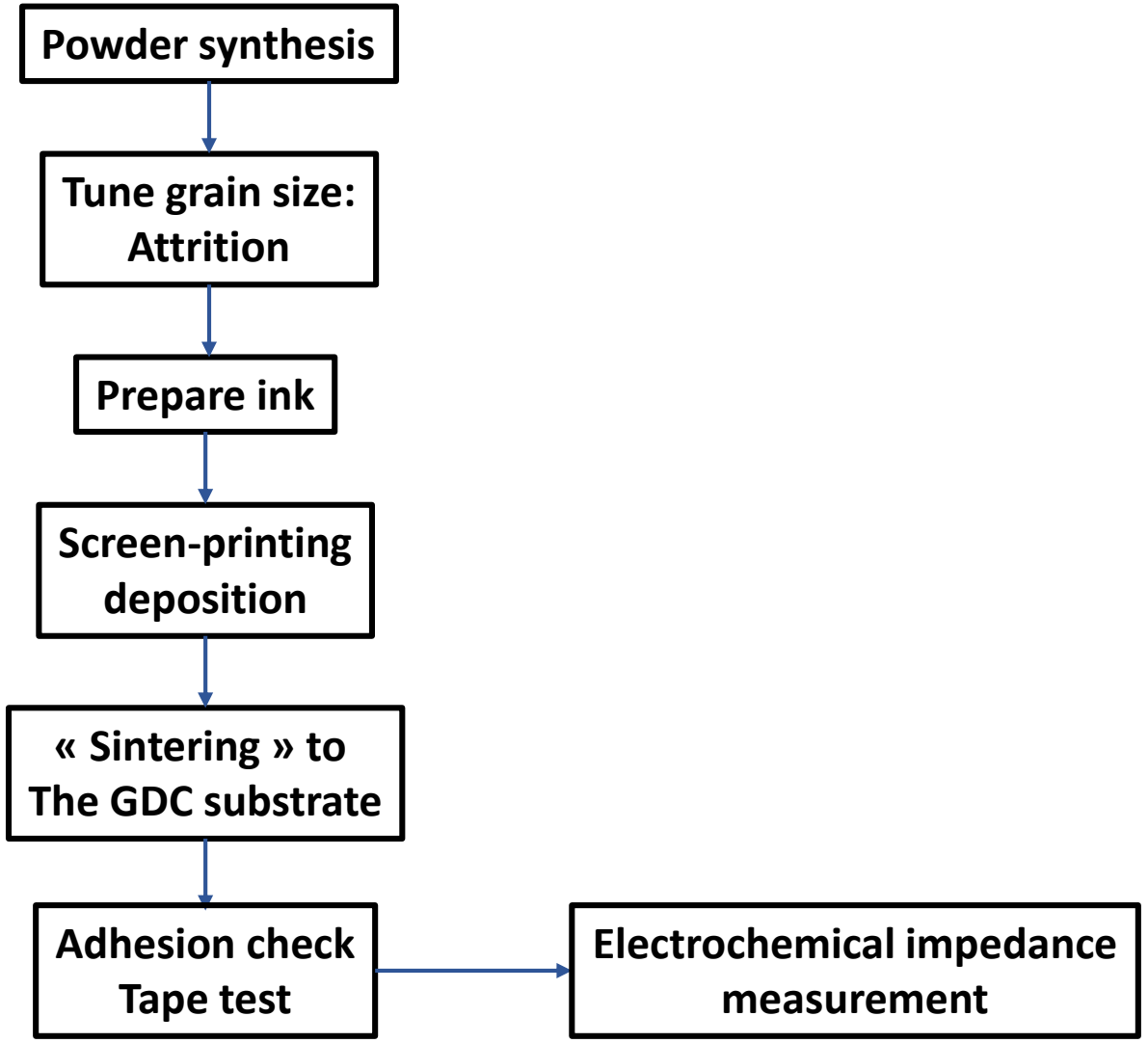
950°C/ 6h

1050°C/ 2h

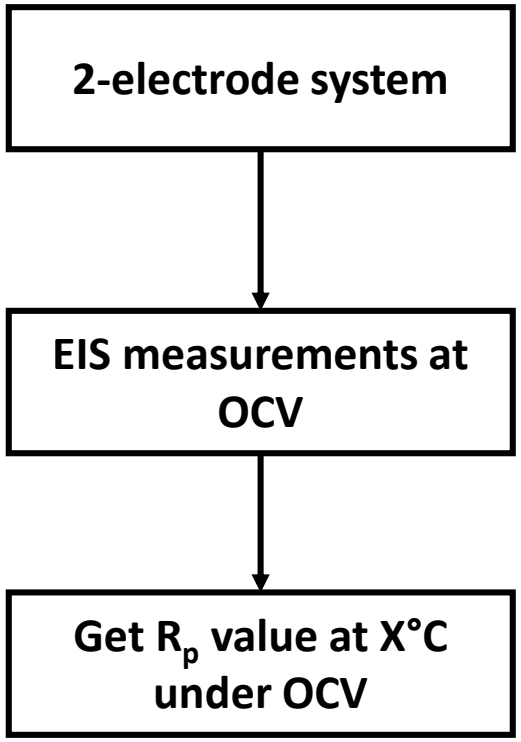


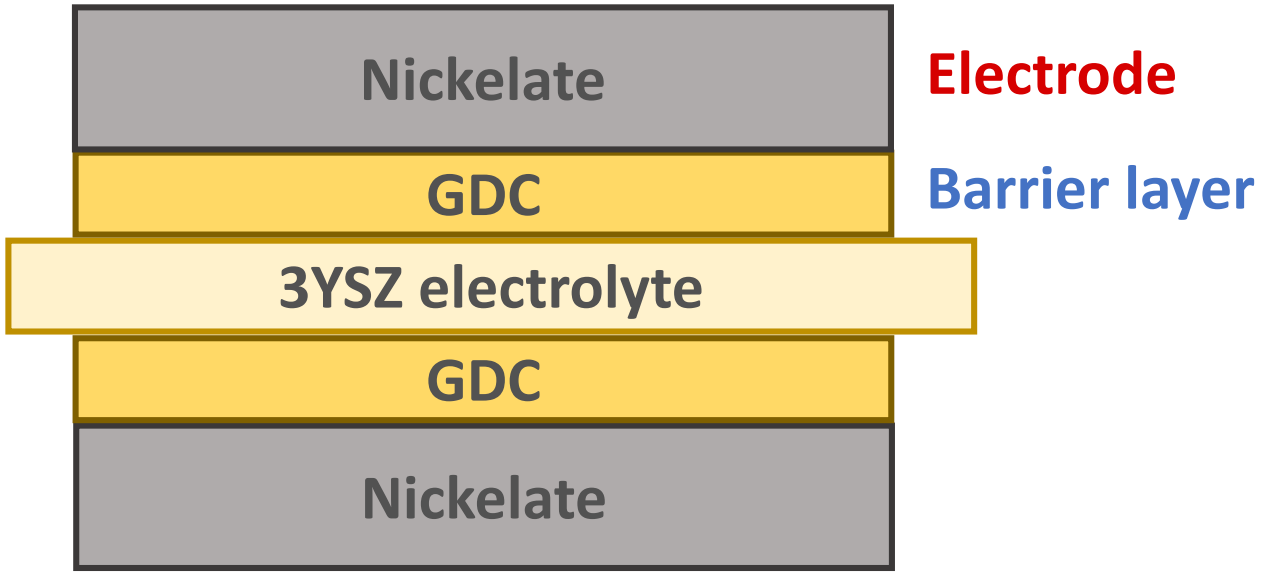
1050°C/ 6h

Symmetrical cells preparation | A long journey



EIS | 2-electrodes system





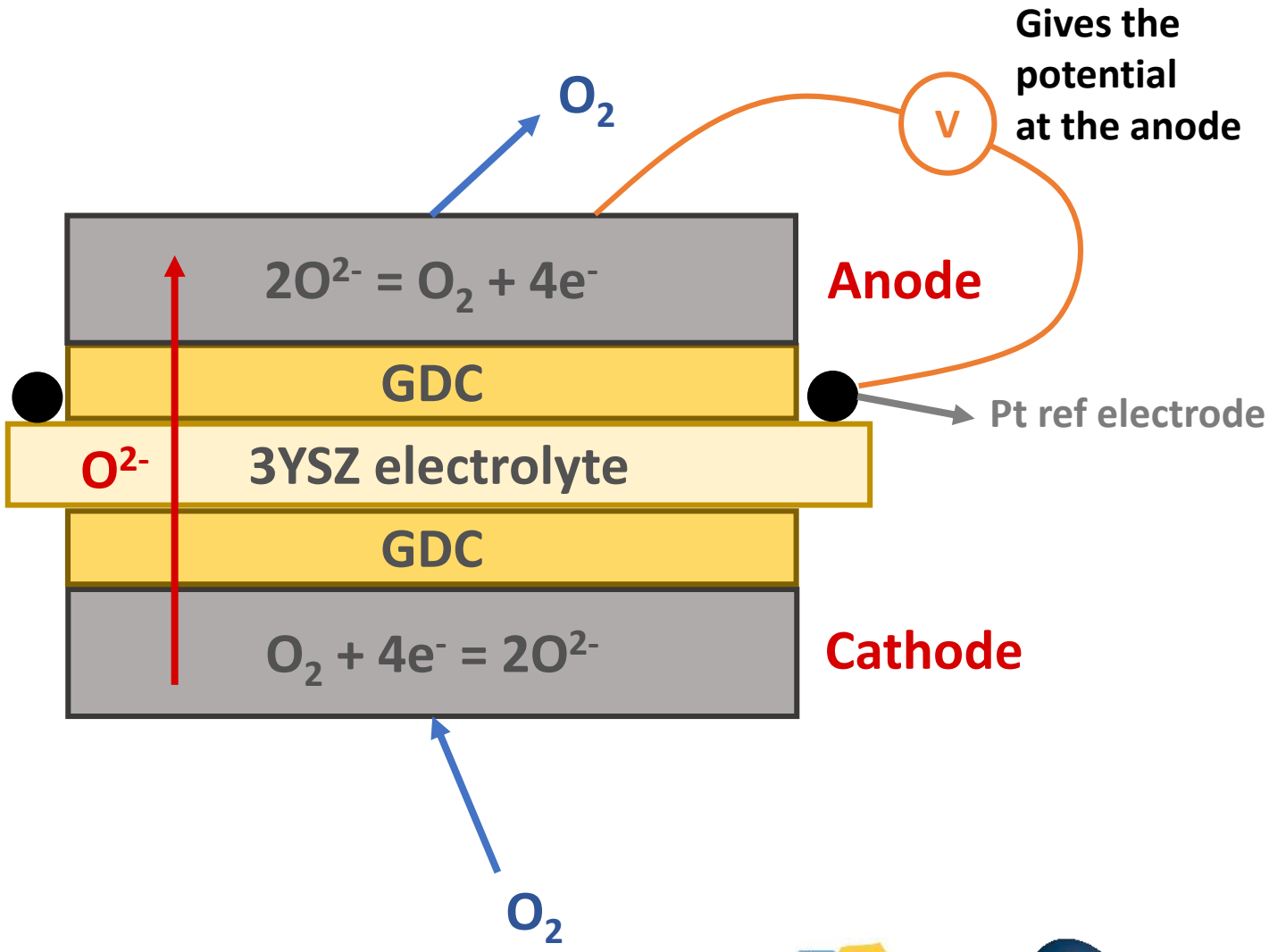
EIS | 3-electrodes system

3-electrode system

Ageing under current $0.3A.cm^{-2}$

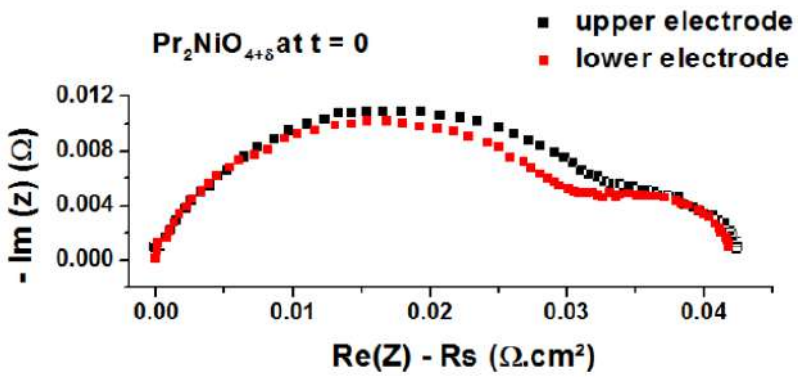
EIS measurements at OCV

Rp after ageing under current at certain temperature



2-electrodes system

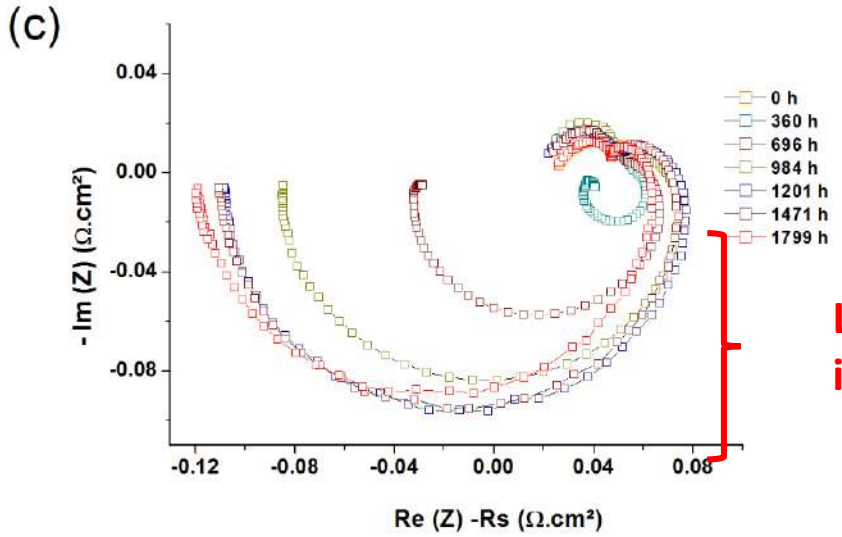
i_{dc}=0



Work on PNO

3-electrodes system

SOEC mode – i_{dc}= -0.3A.cm^{-2}

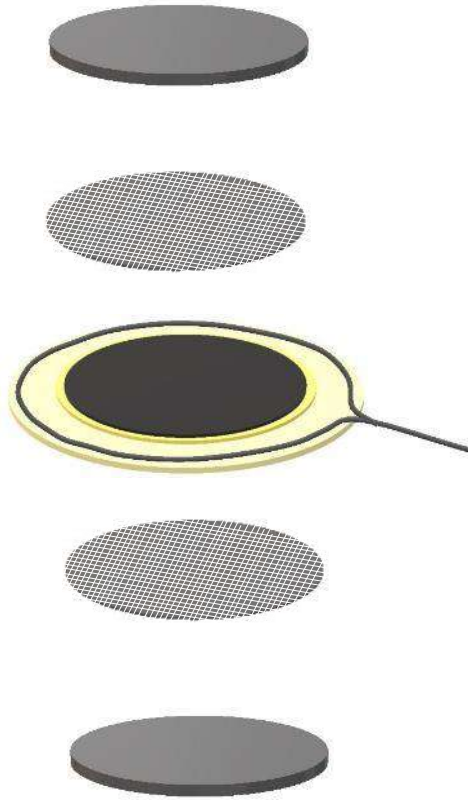


Large inductive loops impeding the analysis

Vibhu, V.; Rougier, A.; Nicollet, C.; Flura, A.; Fourcade, S.; Penin, N.; Grenier, J.-C.; Bassat, J.-M. *Journal of Power Sources* **2016**, *317*, 184–193. https://doi.org/10.1016/j.jpowsour.2016.03.012

Set-up sketch

Setup under development



Pt pierced plate current collector

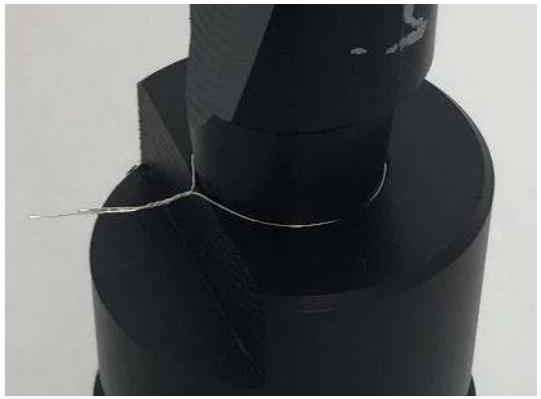
Pt grid

Symmetrical cell

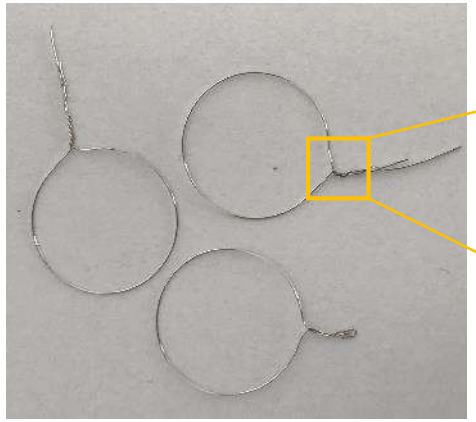
+ Screen-printer upgrades

Help received from Jerôme Laurencin

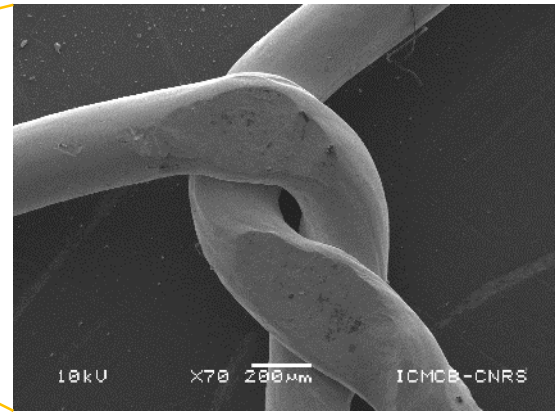
EIS | The Pt reference electrode



Shaping really tricky!



Hard to get a perfect circle!



Welding by one spot welder

After several careful steps the 3 electrodes cell is eventually ready for EIS measurements

Outlooks

Structural & conductivities characterization

Neutrons diffraction

4-probes measurements

IEDP

ECR

Electrochemical measurements

EIS at OCV

Ageing under current

Complete cell characterization

Promising materials

Electrolysis assessment of $La_{1.5}Pr_{0.5}NiO_{4+\delta}$

Synthesis, characterization and, electrochemistry of $La_{2.25}Pr_{0.75}Ni_2O_{7+\delta}$

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Zonghao Shen

Thanks for your attention

Do not hesitate if you have any question!