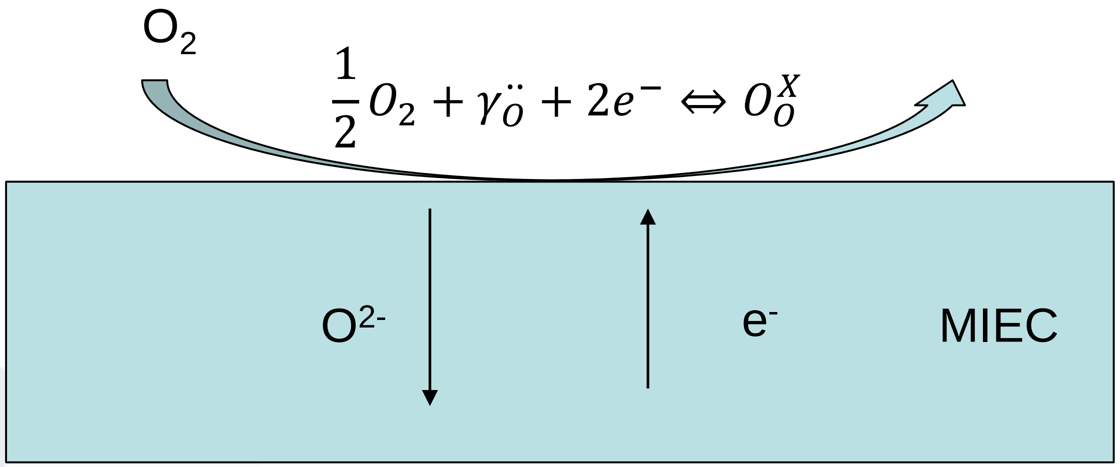
Study of spinel phases for the control of redox properties of air electrodes in Solid Oxide Cells

Simon Guillonneau, Olivier Joubert, Clément Nicollet.

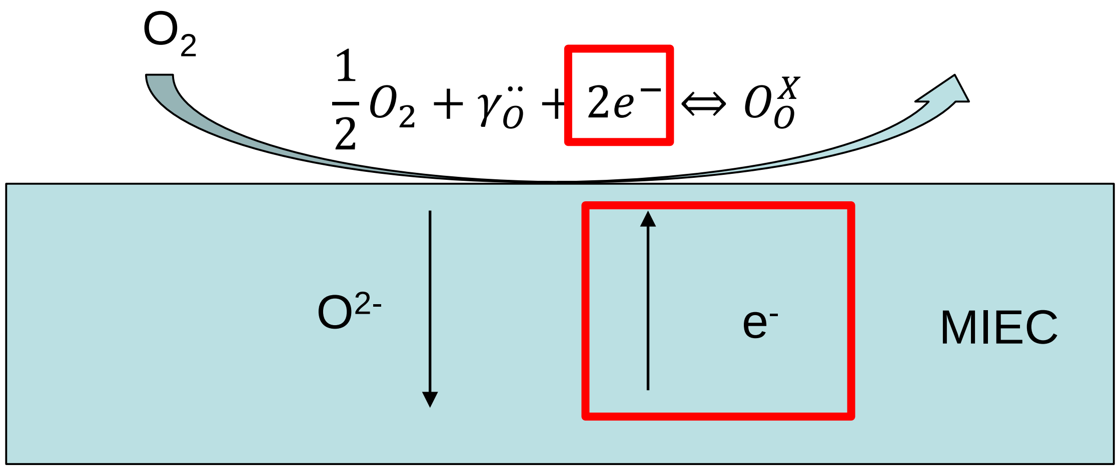
Institut des Matériaux de Nantes Jean Rouxel

Context – Transport properties



- Improve OER and ORR kinetics
- σ_{ionic}
- $\sigma_{electronic}$
- MIEC

Context – Redox properties



- Redox properties of the transition metal affect charge transfer

Context – Measurement problem

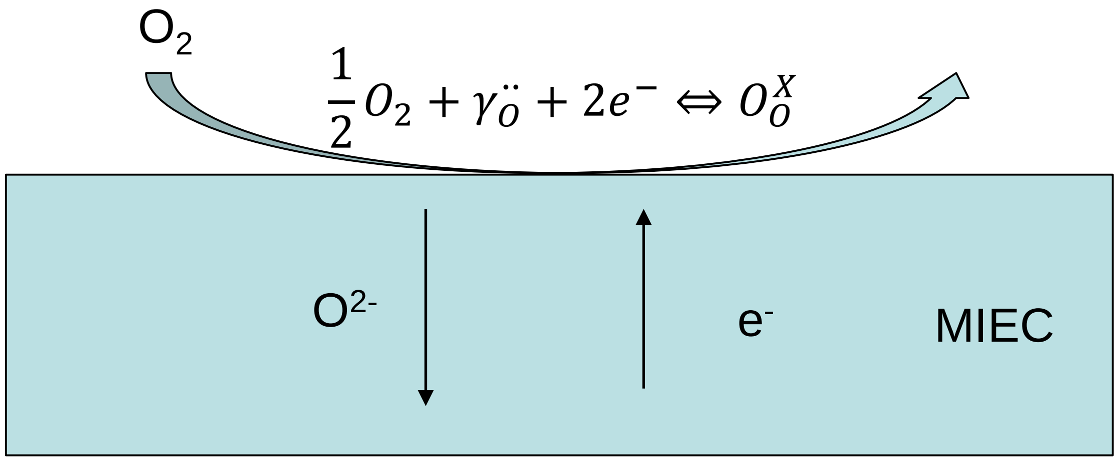
Doping

↓

- Structure
- Redox potential
- Transport properties

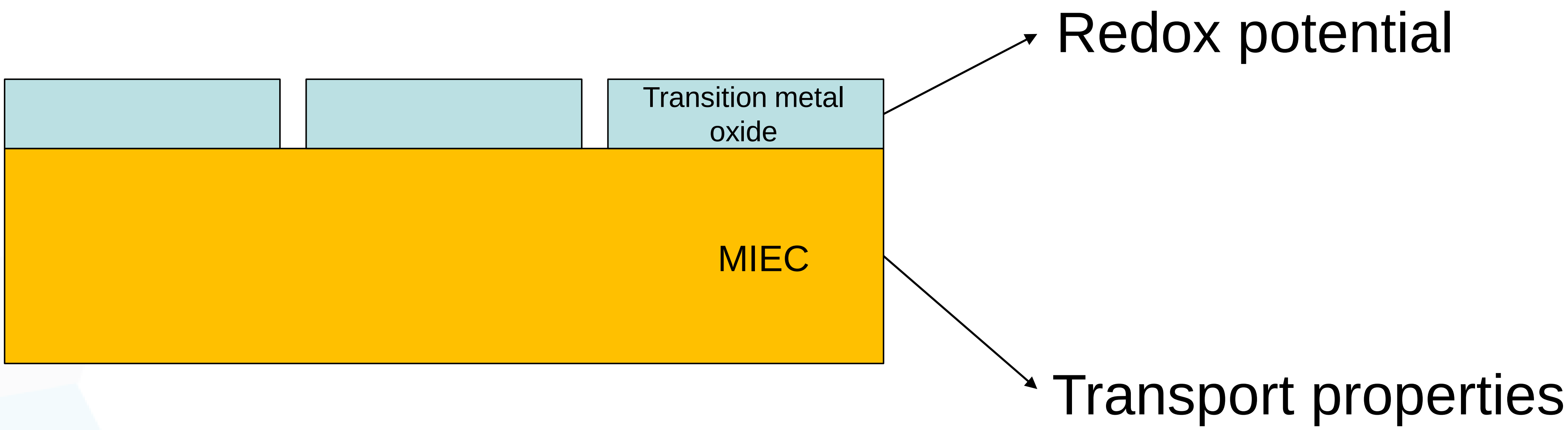
MIEC

Context – k_{chem}



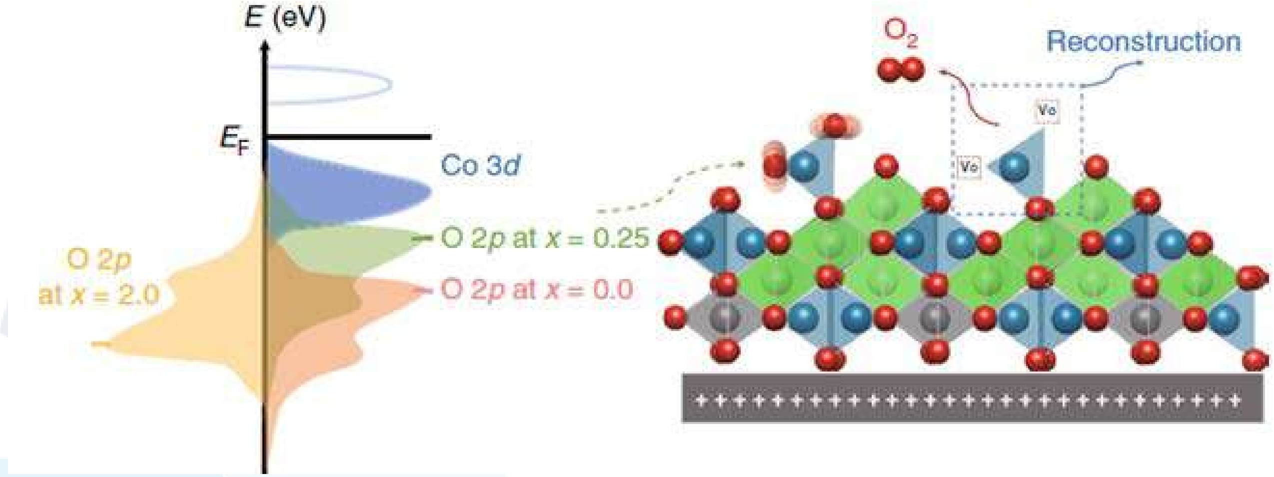
$$k_{chem} = f(\sigma_i, \sigma_e, E^0)$$

Context – Discrimination of transport and redox properties

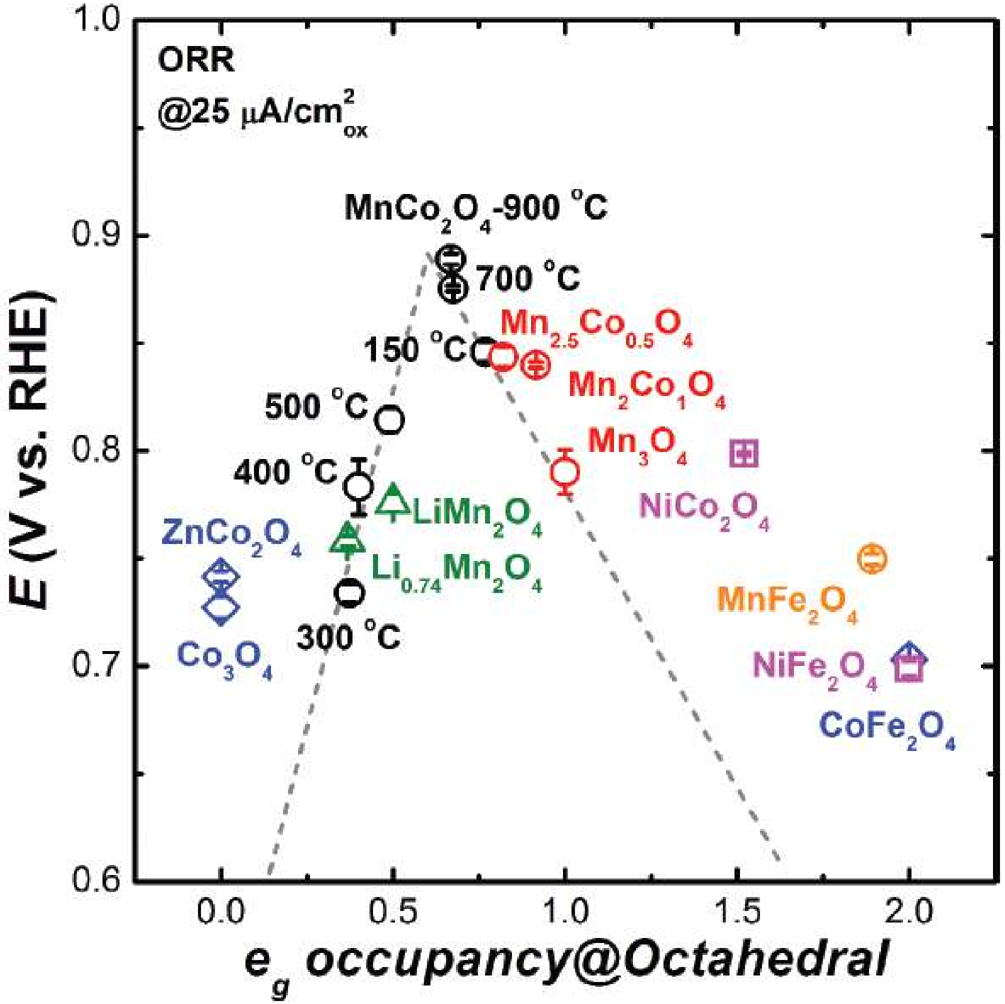


Context – Spinels for oxygen exchange

Literature review



Wu, T., Sun, S., Song, J. *et al.* Iron-facilitated dynamic active-site generation on spinel $CoAl_2O_4$ with self-termination of surface reconstruction for water oxidation. *Nat Catal* **2**, 763–772 (2019).



Wei, C., Feng, Z., Scherer, G. G., Barber, J., Shao-Horn, Y., Xu, Z. J., *Adv. Mater.* 2017, 29, 1606800. https://doi.org/10.1002/adma.201606800

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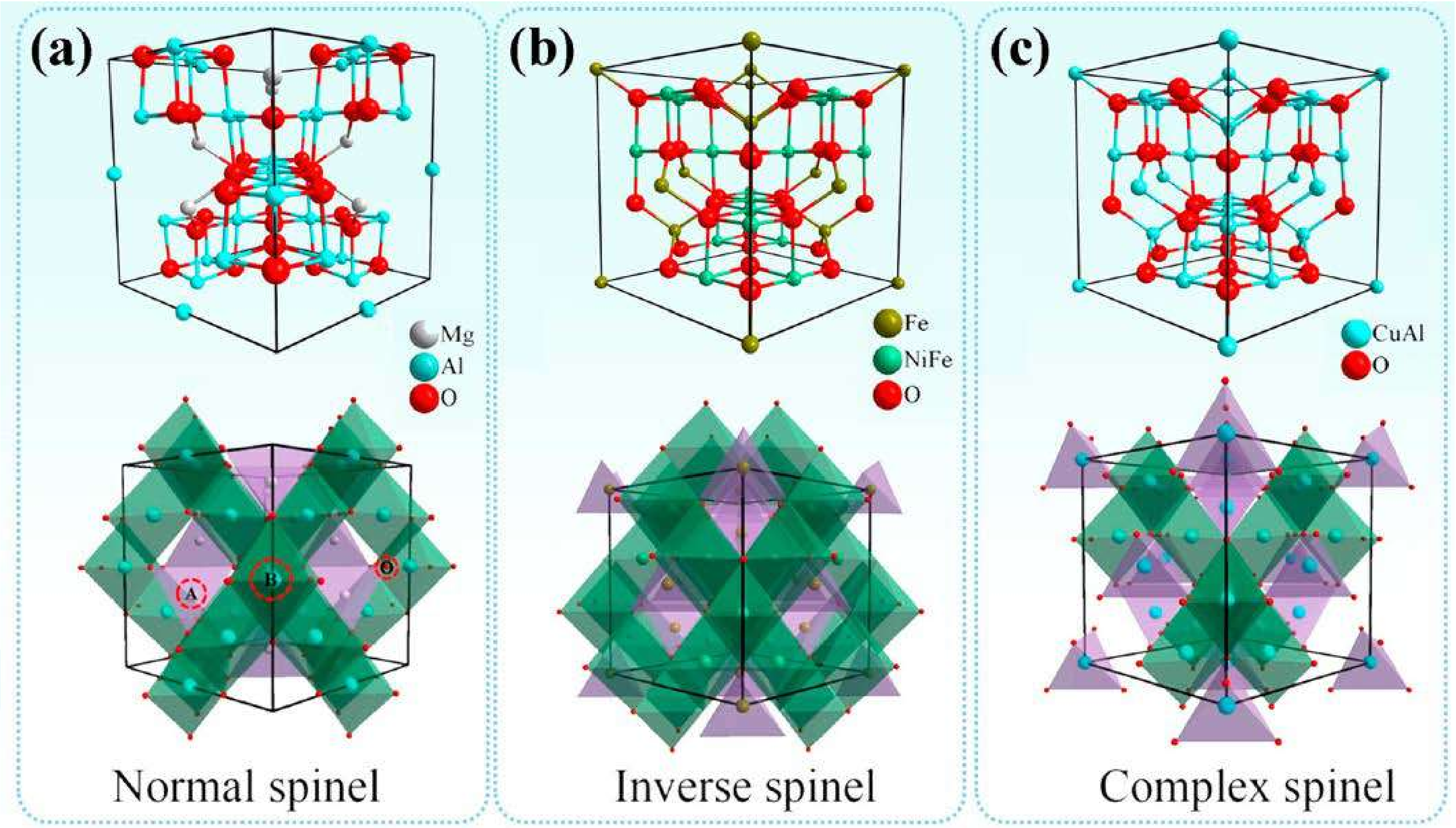
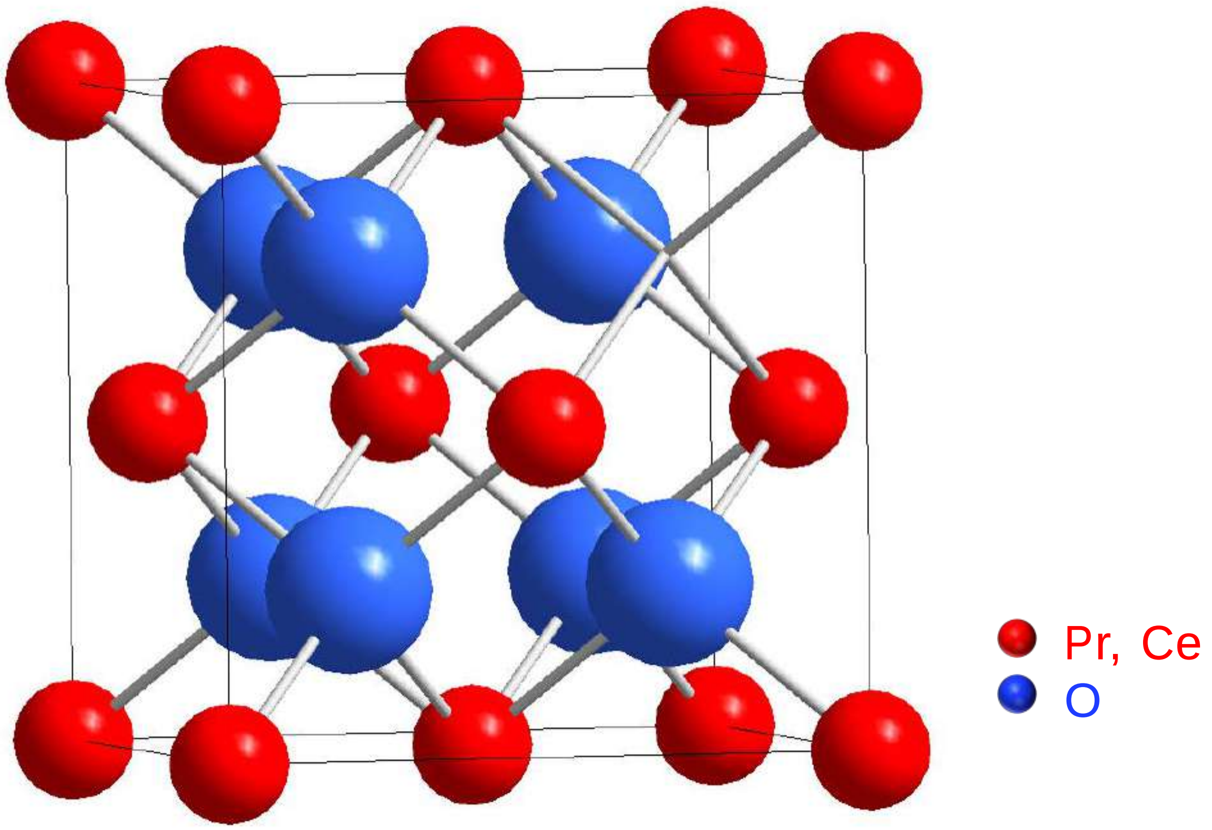
Spinel structure – AB_2O_4



- Only transition metals
- Same structure for different compositions
- Wide range of valence states and site distribution
- Spinel $CoAl_2O_4$:
- E^0 Co^{3+}/Co^{2+} = 1,82 V
- E^0 Al^{3+}/Al = -1,66 V

Chem. Rev. 2017, 117, 15, 10121–10211

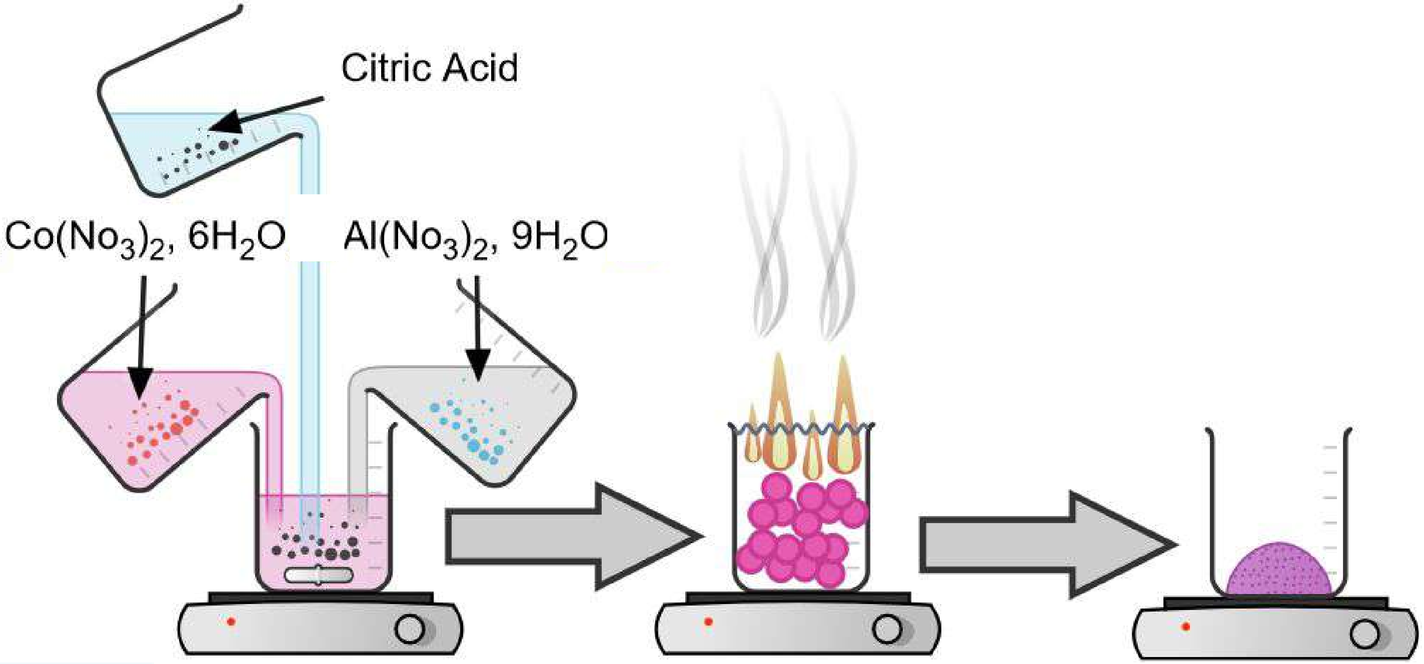
MIEC structure - $Pr_{0.1}Ce_{0.9}O_{2-\delta}$



- Stable
- Good ionic and electronic conductivity
- Defect model available

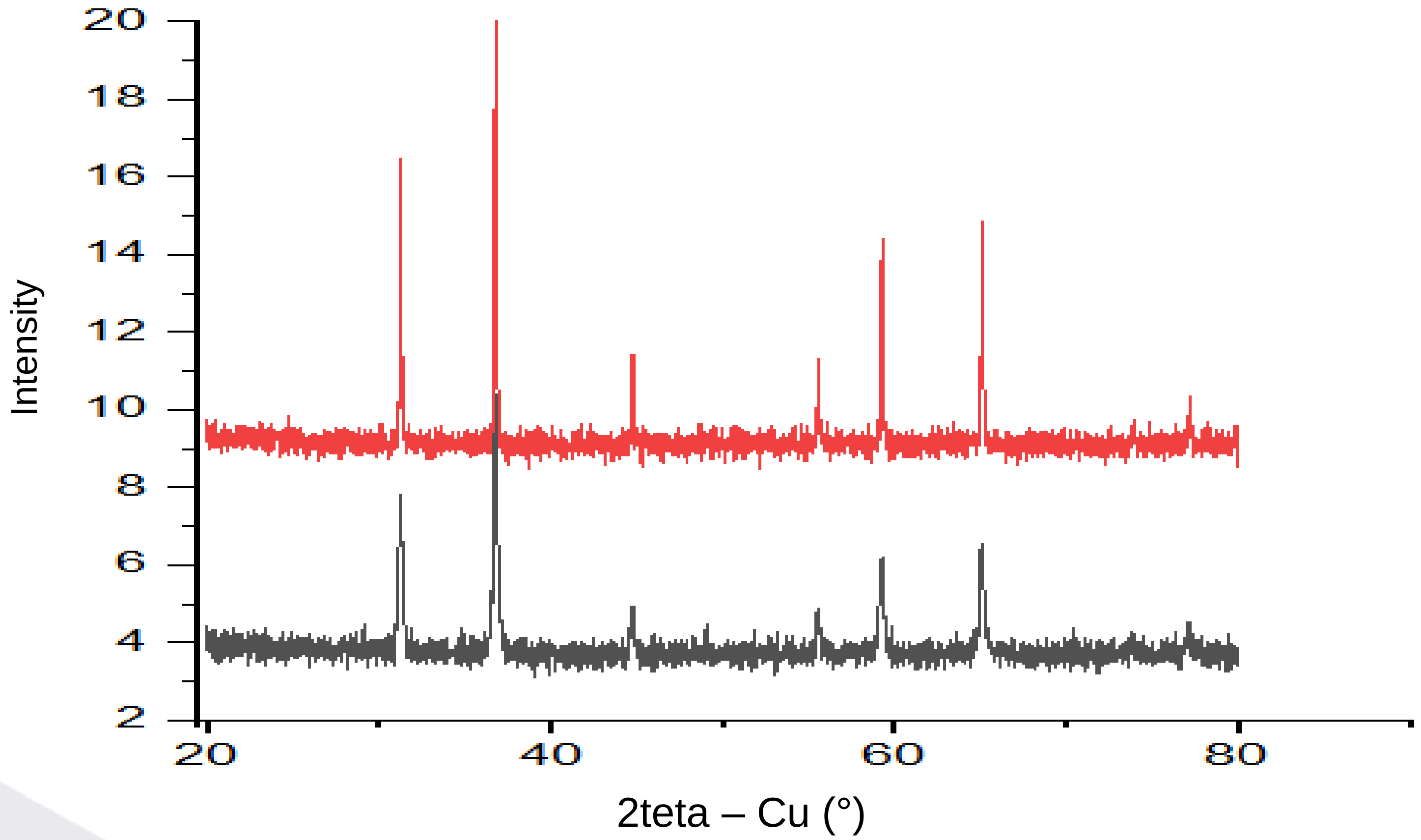
Experimental methods – Spinel synthesis

Spinel synthesis with a thermal treatement et 900°C

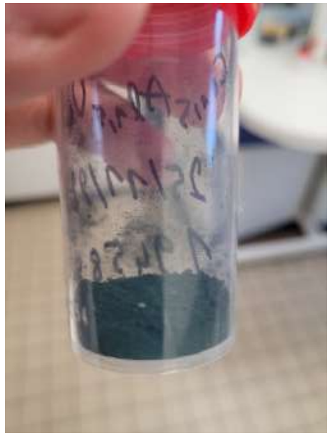


Experimental methods – Spinel caracterisation

Spinel caraterisation by XRD



SG4 $Co_{1,5}Al_{1,5}O_4$



SG3 $CoAl_2O_4$

Monophase materials obtained by combustion method and sintering at 900°C.

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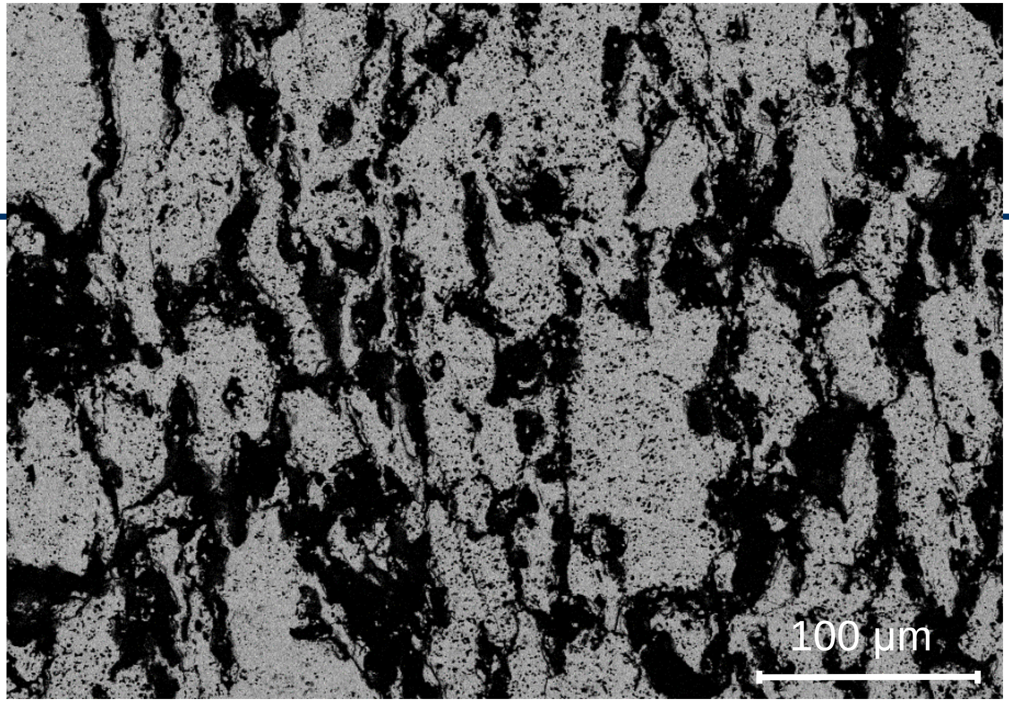
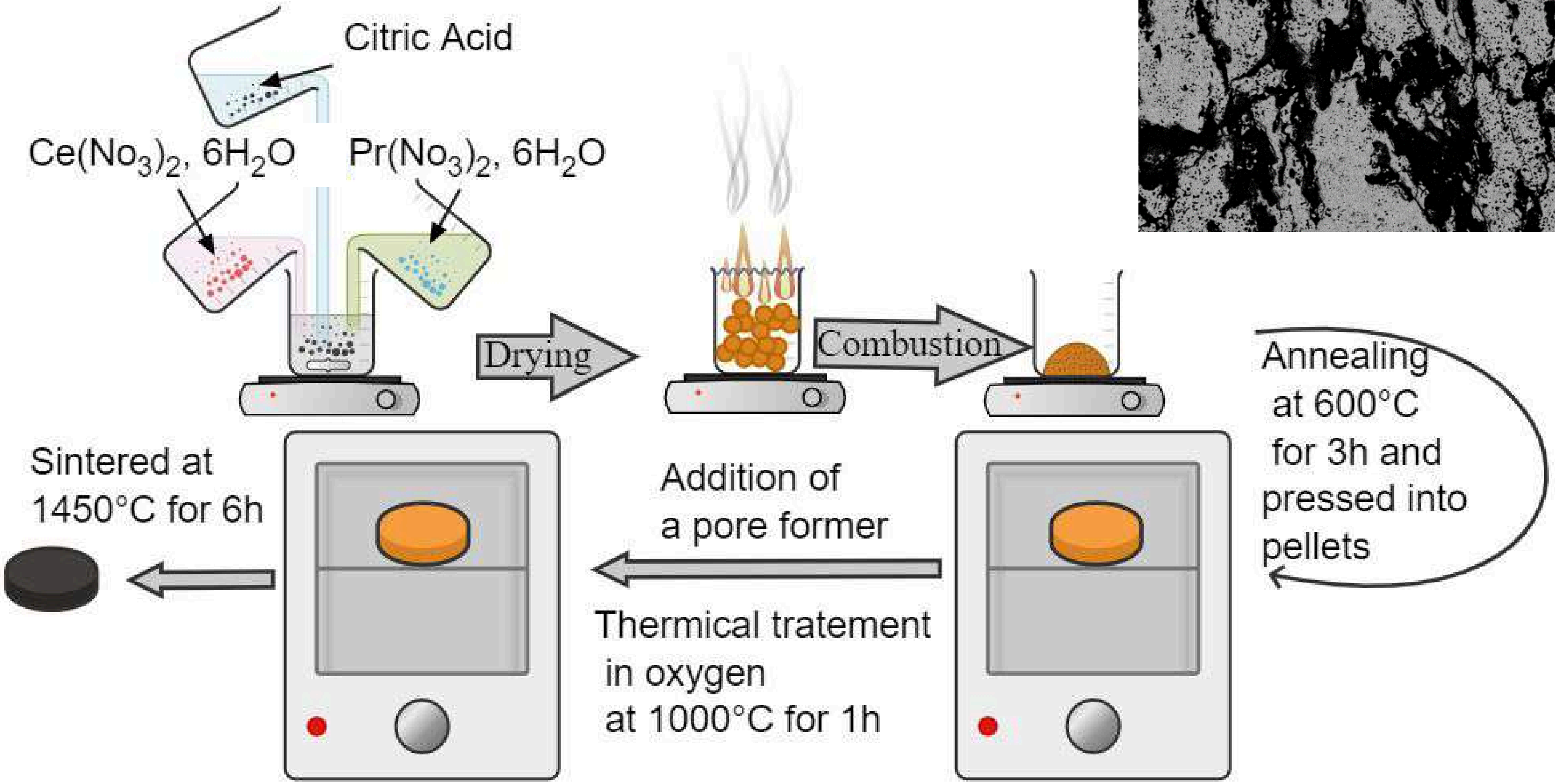
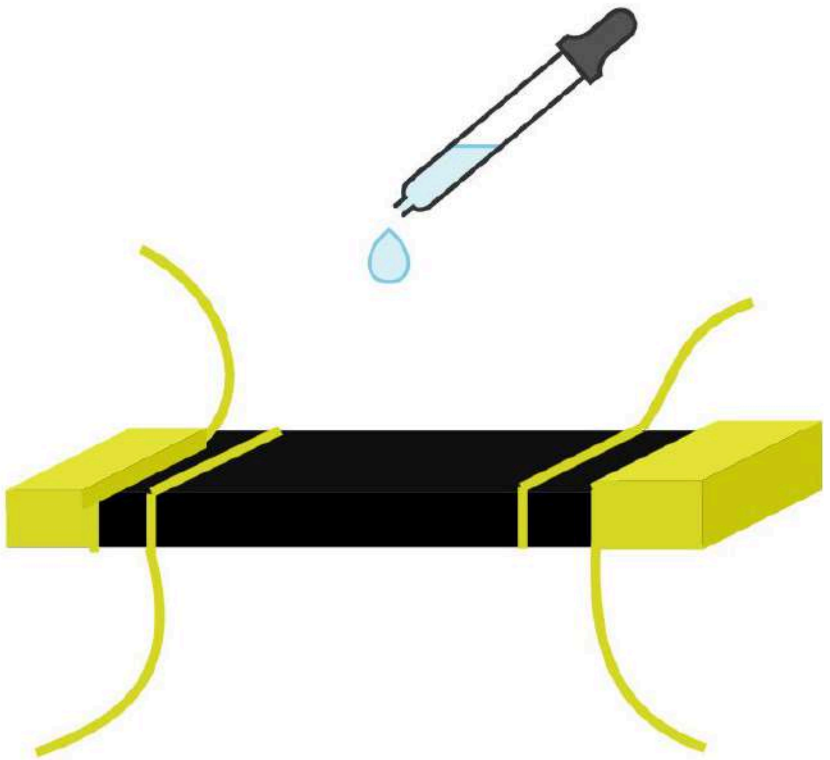
Experimental methods - Synthesis of $Pr_{0,1}Ce_{0,9}O_{2-\delta}$





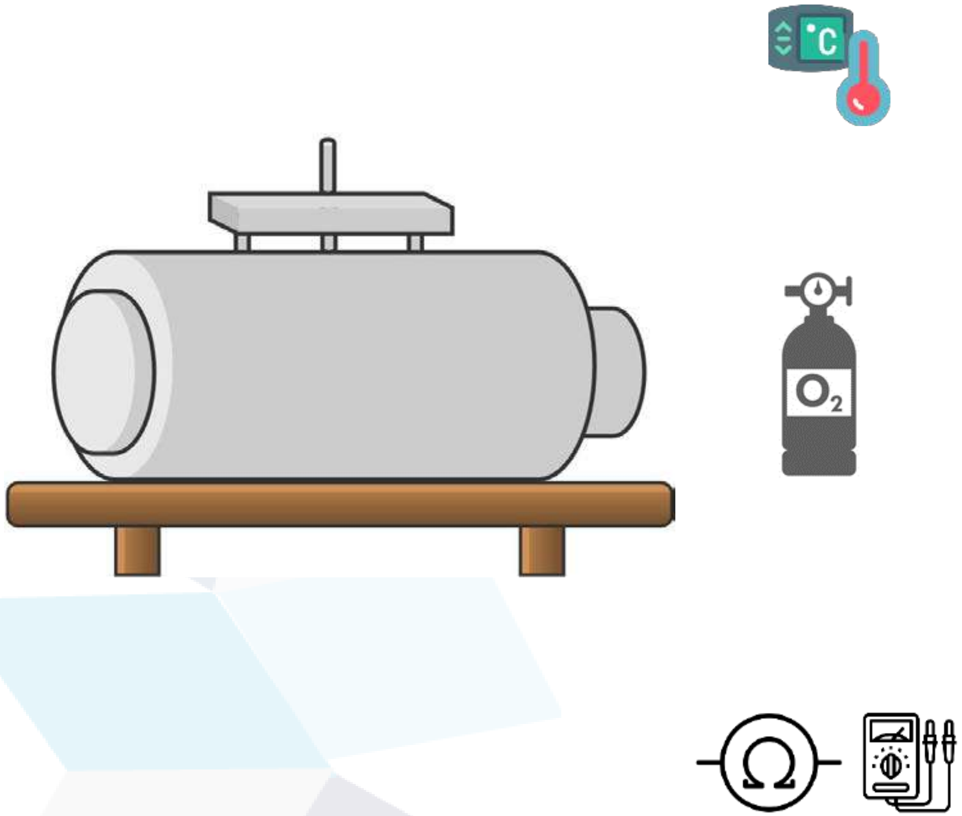
Experimental methods – Infiltration

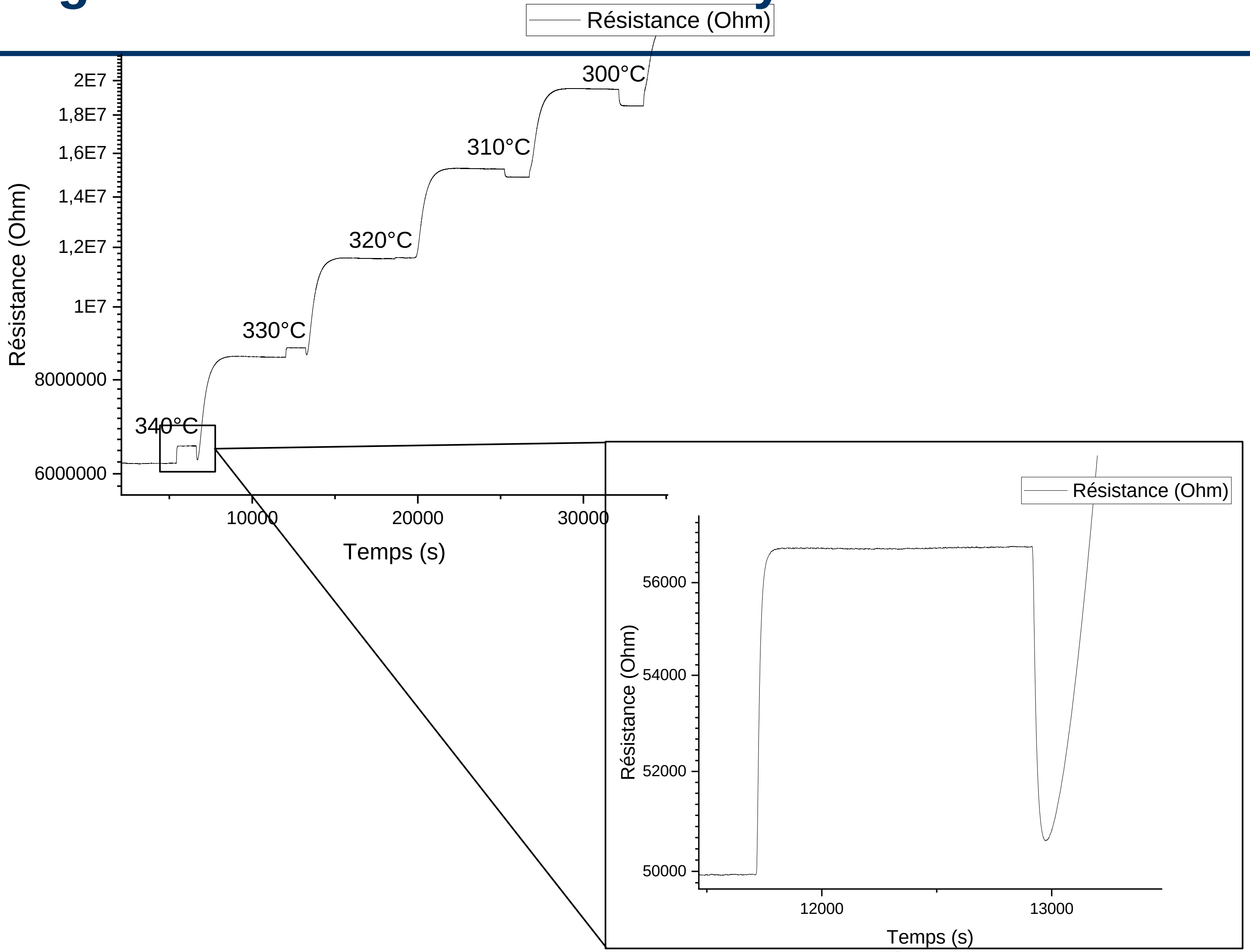
Method and composition



- $0,1\ \%$; $0,3\ mol.L^{-1}$ in 10 mL of ethanol
- $Al(NO_3)_3,9H_2O$
- $Co(NO_3)_2,6H_2O$

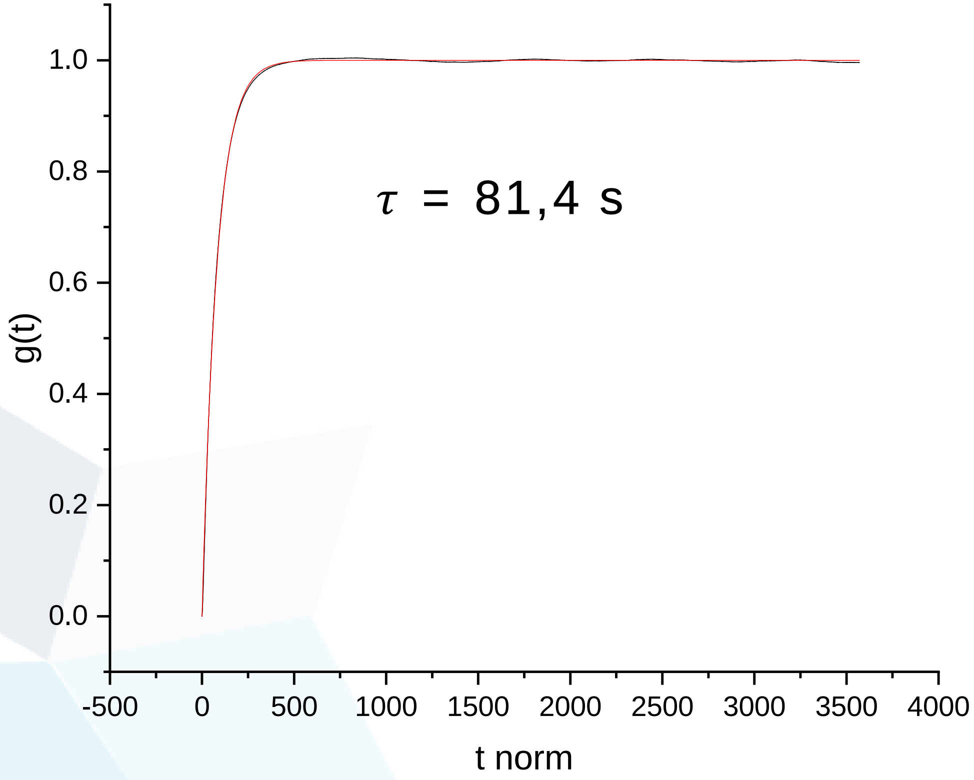
Mesurement of surface exchange coefficient -Conductivity relaxation



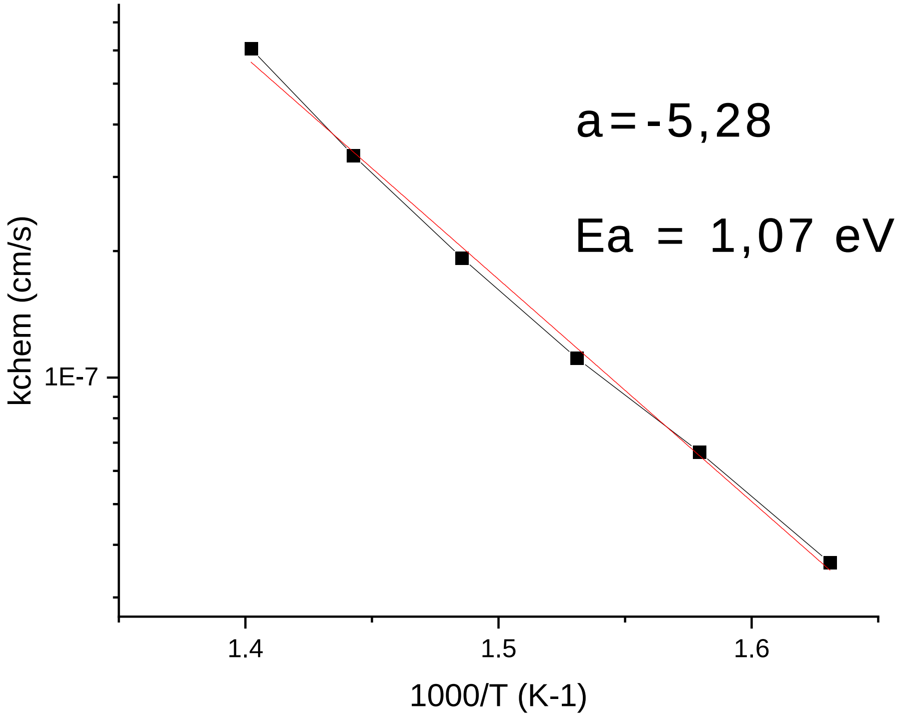


Measurement of surface exchange coefficient - Conductivity relaxation

Determination of k_{chem} from relaxation profiles

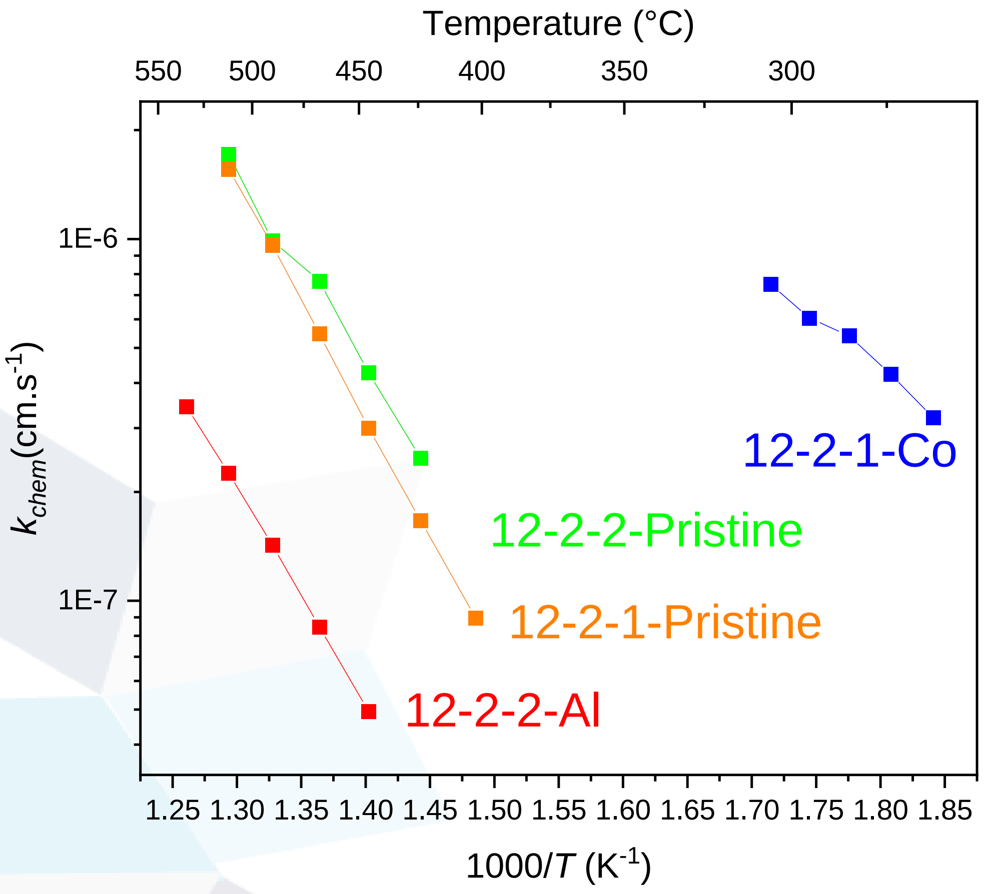


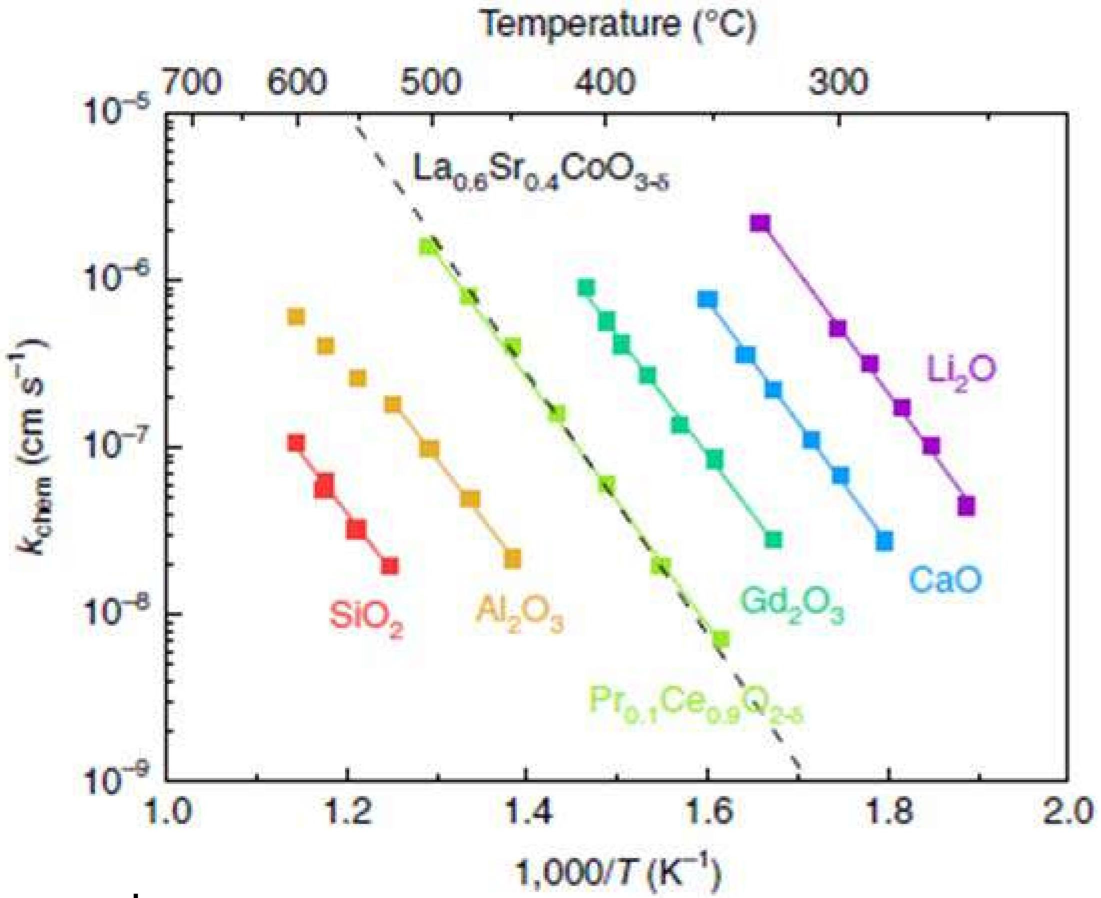
$$g(t) = \frac{C(t) - C_0}{C_\infty - C_0} \equiv \frac{\sigma(t) - \sigma_0}{\sigma_\infty - \sigma_0} = 1 - e^{-\left(\frac{t}{\tau}\right)}$$



$$k_{chem} = \frac{1 - \nu_V}{S_V \times \tau}$$

Infiltration with Al_2O_3 and Co_3O_4





- k_{chem} Al consistent with previous work
- k_{chem} Co consistent with Insaf

Nicollet, C., Toparli, C., Harrington, G.F. *et al.* Acidity of surface-infiltrated binary oxides as a sensitive descriptor of oxygen exchange kinetics in mixed conducting oxides. *Nat Catal* **3**, 913–920 (2020). https://doi.org/10.1038/s41929-020-00520-x

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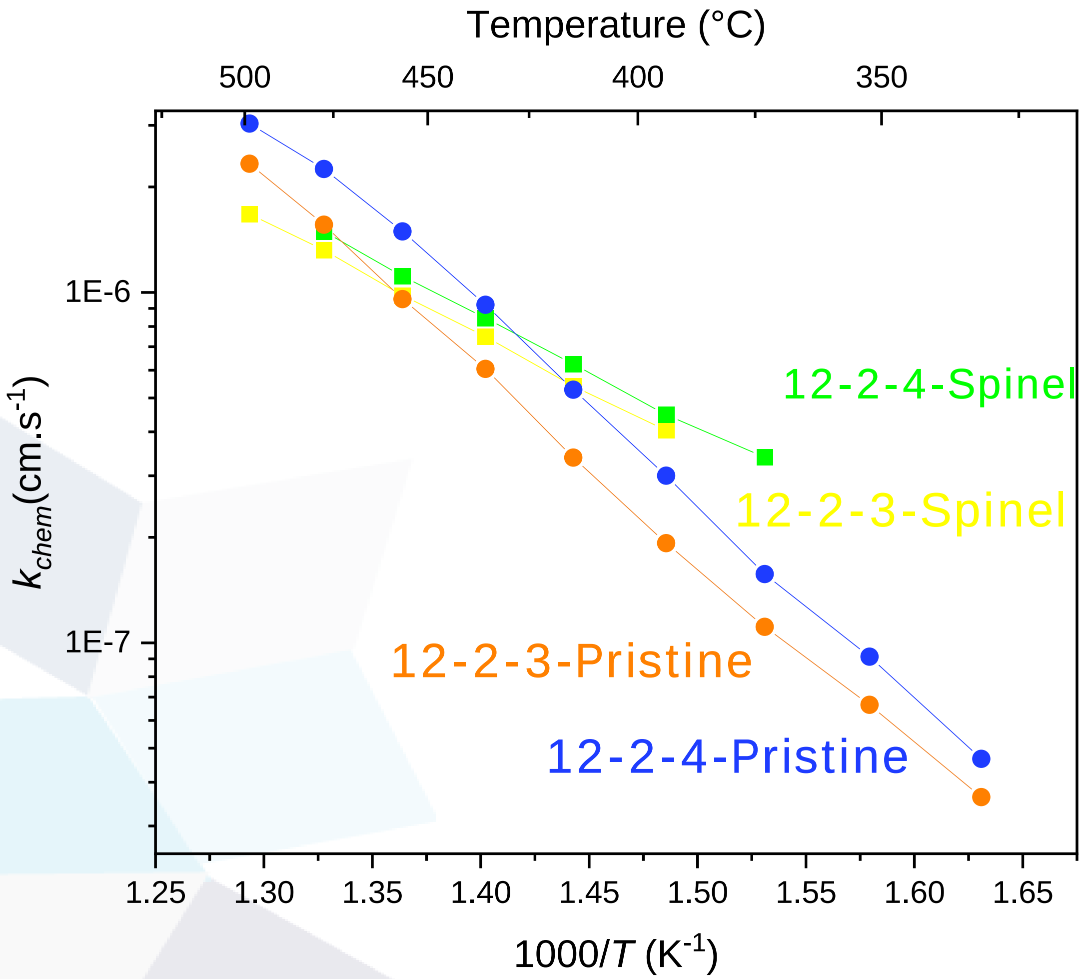
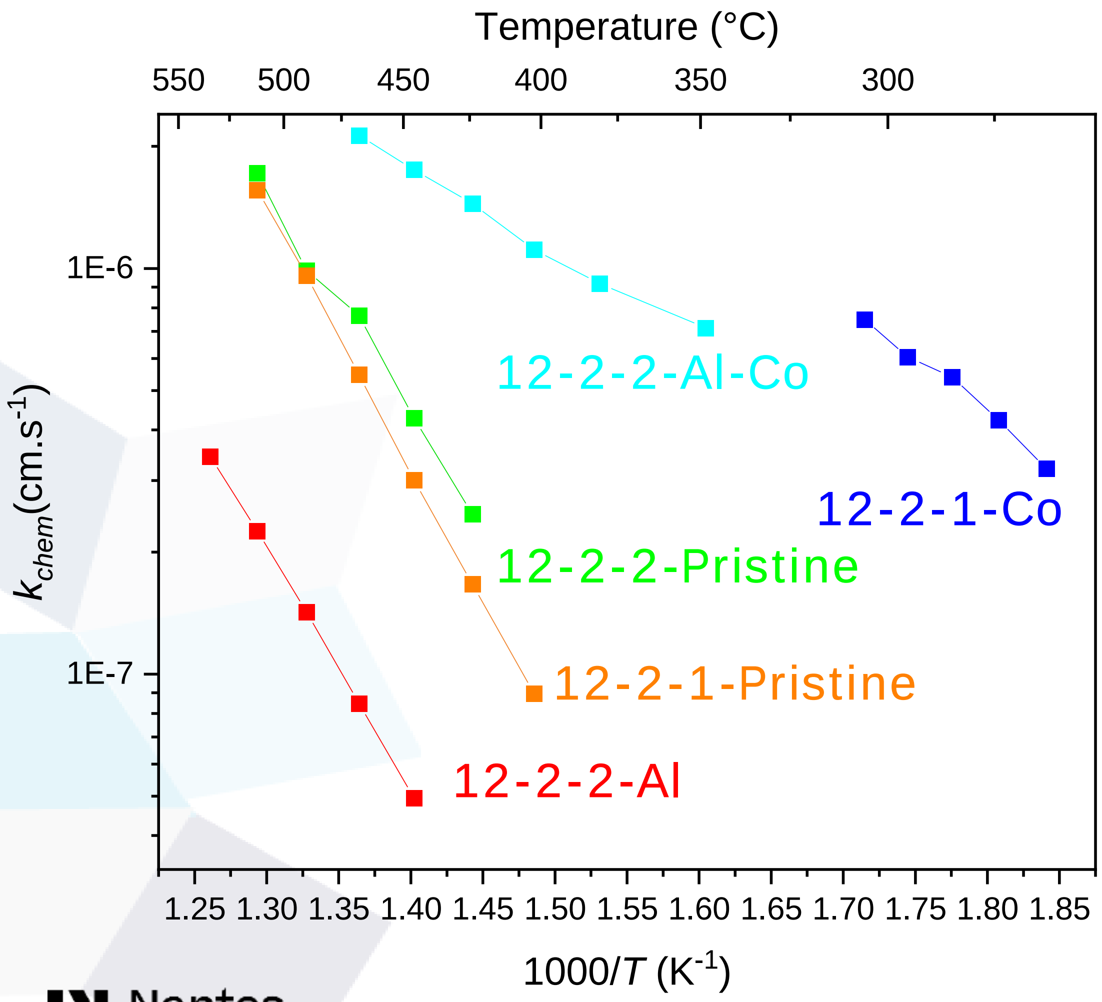
Infiltration with Spinel $CoAl_2O_4$



- Decrease of Activation energy
- Same k_{chem} than pristine : Effect of cobalt, aluminium or both ?

Infiltration with cobalt after aluminium infiltration

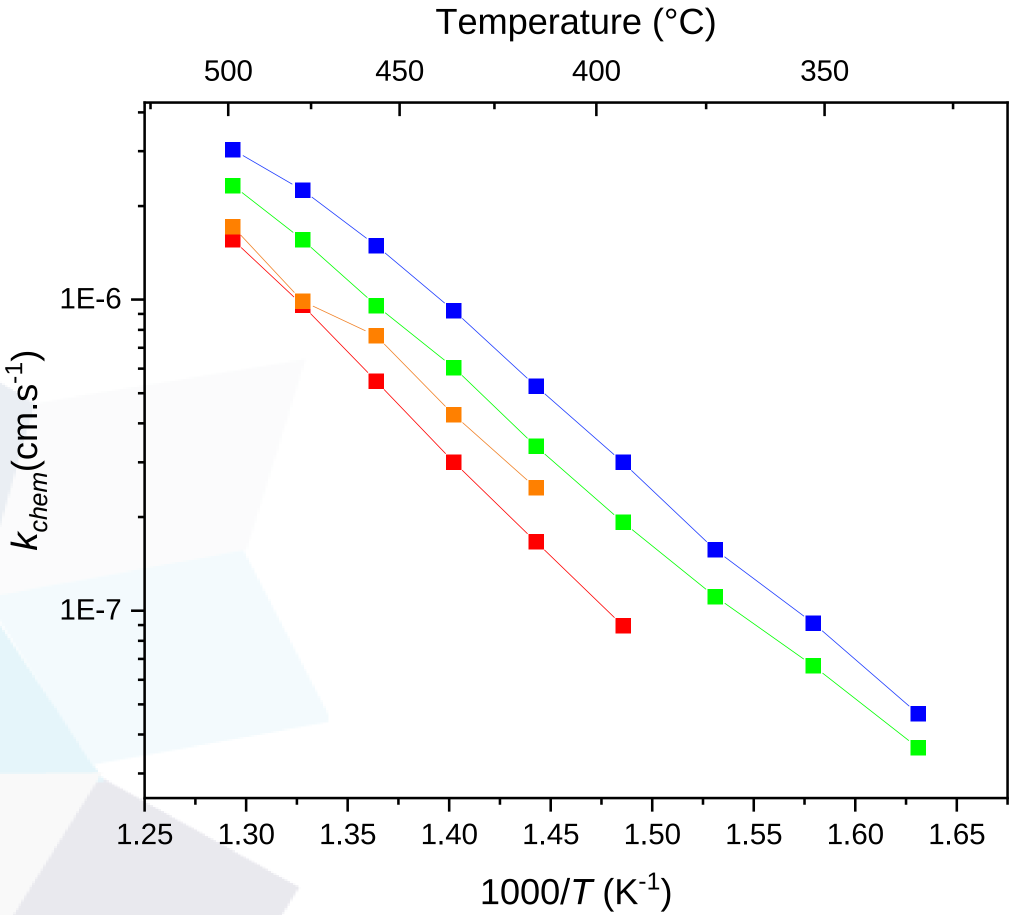
Protocol : measurement – Al infiltration - measurement - cobalt infiltration - measurement



- Same Activation energy than cobalt
- Effect of cobalt stronger and not the aluminium one

Discussions – Repeatability

Comparison of measurements on all PCO sample before infiltration



- Measurement of Initial kchem (pristine) not repeatable
- Improvement of the measurement protocol needed

Conclusion

- Conductivity relaxation on infiltrated MIEC can help studying redox properties of transition metals

- Spinel are formed « in-situ » ? Effect of spinel or transition metal oxide ?

- Improve repeatability of the measurement procedure

Thank you !