Les dérivés de $Ca_2Fe_2O_5$ envisagés comme nouveaux matriaux d'anode pour cellule d'électrolyse à oxyde solide.

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3ème Réunion Plénières de la Fédération Hydrogène (FRH2) du CNRS
23 Mai 2023

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Introduction of NOUVEAU

- NOUVEAU is a three-year project starting from **01/09/2022**
- It focuses on making a more **substainable** Solid Oxide Electrolysis Cell (SOEC) technology by developping **NOVEL ELECTRODE COATINGS AND INTERCONNECT**
- An **interdisciplinary** consortium that covers the whole value chain **from** sustainable materials **production to the testing of the final product and product end-of-life options**

NOUVEAU Project participants

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Motivation and objectives

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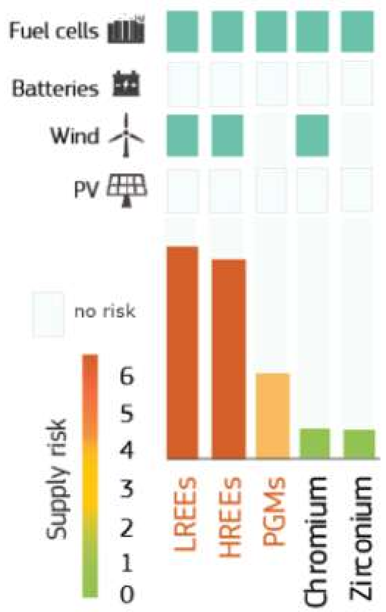


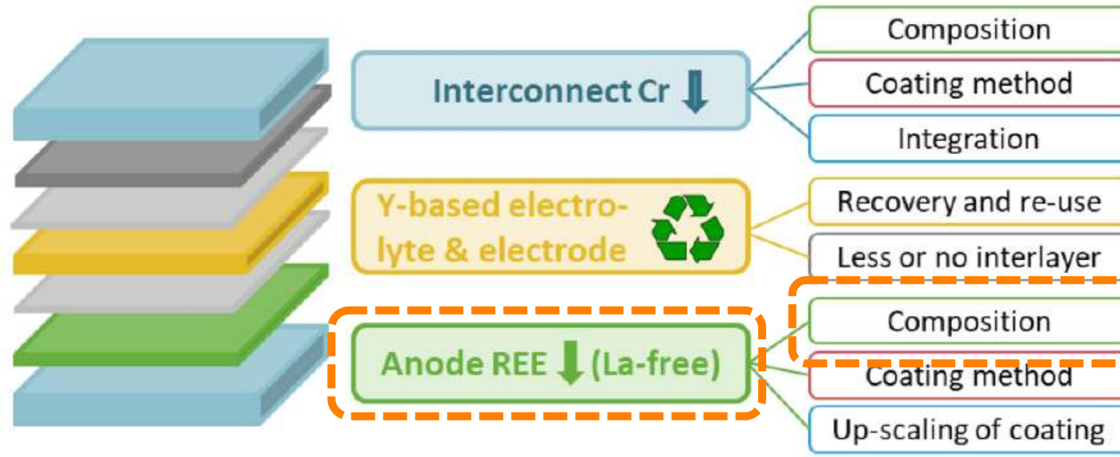
- SOEC contain REE (Rare Earth Elements)
- European commission classifies REE as **raw critical materials**, demand on these materials is expected to rise and EU heavily dependent on its import
- NOUVEAU will work on **alternative materials** to be used in SOEC and the **recycling** of REE for SOEC

- Develop solid oxide cell with **novel electrode materials** with a **reduced amount of REE, PGM (Platinum-Group Metals)**

- **Recycling** target of **50 to 70 %**
- **30 % reduced amount** of **REE (La)**

KEY NUMBERS

Role of UCCS in NOUVEAU project



Task 2.3 Developpment of **La free or reduced** oxygen electrode **[M1-M24]**

Screen printer @ UCCS

- **Calcium based oxides** will be explored in a first step ($Ca_3Co_4O_{9\pm\delta}$, $Ca_2Fe_2O_{5\pm\delta}$ …)
- Depending on the modeling results (WP2), the study will be extended to the most promising La-free oxides
- **Screen printing** will be used for the electrode deposition on YSZ or GDC electrolytes

D3.2 ASR on optimised compositions deriving from $Ca_2Fe_2O_{5\pm\delta}$, $Ca_3Co_4O_{9\pm\delta}$ and promising composition evidenced by modeling in WP2 **[M24]**

Development of La-Free oxygen electrode

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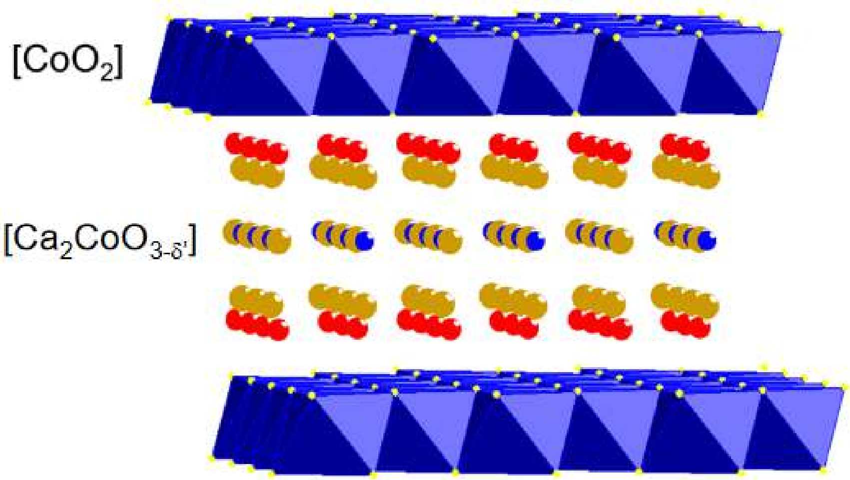
Synthesis and characterisation of new materials and electrochemichal studies

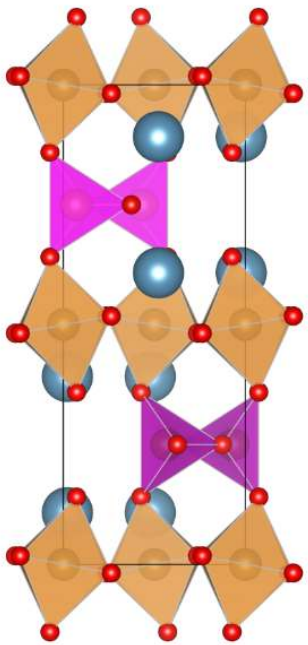


$Ca_3Co_4O_{9\pm\delta}$

Objectives :

- Good **TEC matching** with the electrolyte

- ASR lower than : **0.2 Ω.cm^2** @ **700 °C**



$Ca_2Fe_2O_{5\pm\delta}$
Brownmillerite

$Ca_2Fe_2O_{5\pm\delta}$: A promising air electrode material

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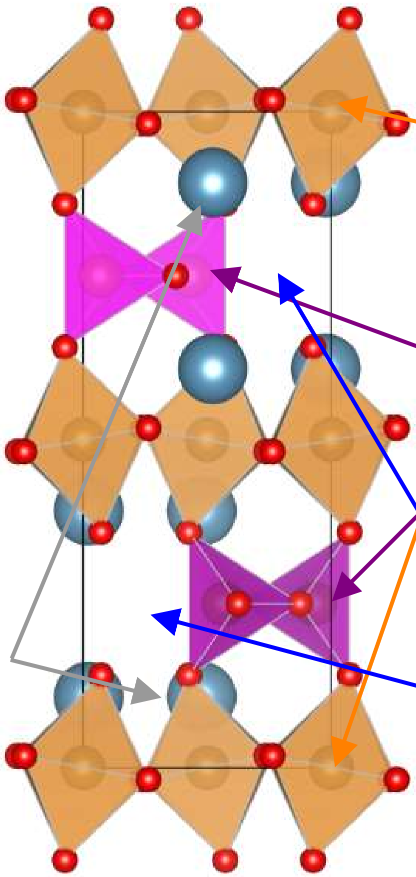


A site cation Ca

1st B site cation BO₆ octahedra Fe

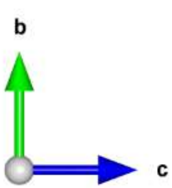
2nd B site Cation BO₄ tetrahedra Fe

Oxygen vacancies forming one dimensional diffusion pathway for oxygen ion migration in tetrahedral layers

Initial value :

➔ **0.86 Ω.cm² @ 700 °C**[1]

➔ **0.29 Ω.cm² @ 700 °C**[1]
Composite 70:30 with GDC



$Ca_2Fe_2O_{5\pm\delta}$ Brownmillerite

[1] *Lee & al, International Journal of Hydrogen Energy 37 (2012) 17217-17224*

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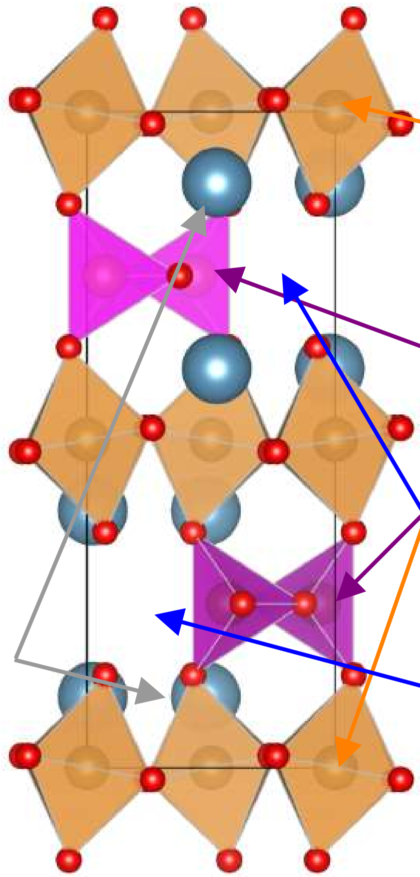
Promising materials derived from dicalcium iron oxide $Ca_2Fe_2O_{5\pm\delta}$ in literature



A site cation
Ca

1st B site cation
BO_6 octahedra
Fe

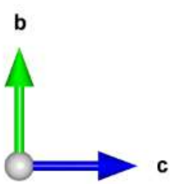
2nd B site Cation
BO_4 tetrahedra
Fe

Oxygen vacancies forming one dimensional diffusion pathway for oxygen ion migration in tetrahedral layers

Partial substitution of Fe by Mn :

➔ **0.22 Ω.cm² @ 750 °C**[2]

$Ca_2Fe_{1.3}Mn_{0.7}O_{5\pm\delta}$



$Ca_2Fe_2O_{5\pm\delta}$
Brownmillerite

[2] Li & al, Journal of Power Sources 238 (2013) 11-16

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Promising materials derived from dicalcium iron oxide $Ca_2Fe_2O_{5\pm\delta}$ in literature

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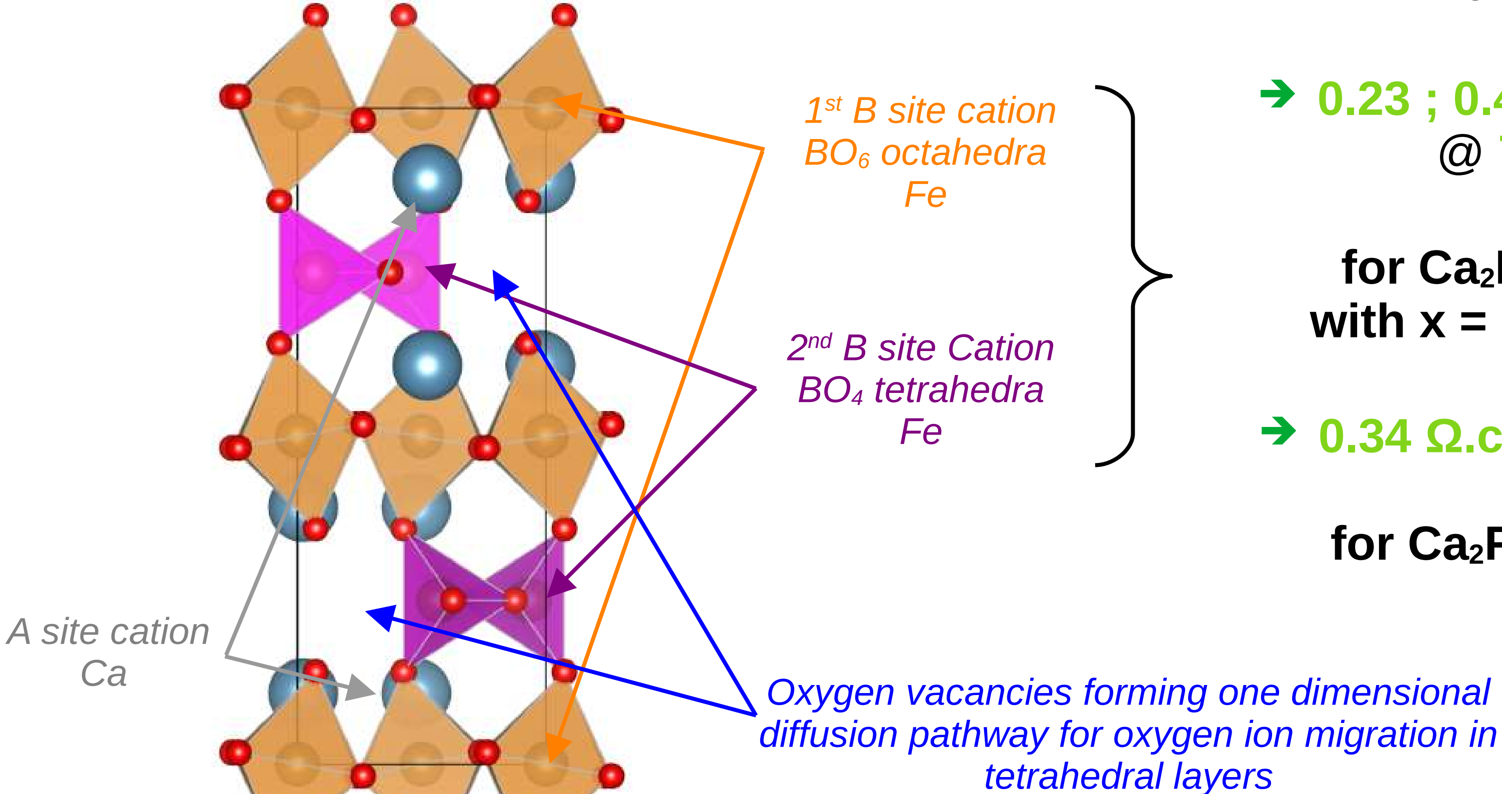
Partial substitution of Fe by Co :

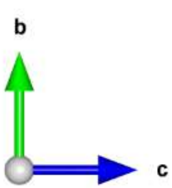
➔ **0.23 ; 0.4 ; 0.6 Ω.cm^2 @ 750 °C**[3]

for $Ca_2Fe_{2-x}Co_xO_{5\pm\delta}$ with x = 0.2 ; 0.4 ; 0.6

➔ **0.34 Ω.cm^2 @ 750°C**[4]

for $Ca_2Fe_{1.8}Co_{0.2}O_{5\pm\delta}$





$Ca_2Fe_2O_{5\pm\delta}$
Brownmillerite

[3] *Li & al, International Journal of Hydrogen Energy 35 (2010) 9151-9157*

[4] *Baijnath & al, International Journal of Hydrogen Energy 44 (2019) 10059-10070*

$Ca_2(Fe, Co, Mn)_2O_{5\pm\delta}$ as potential candidate for oxygen electrode

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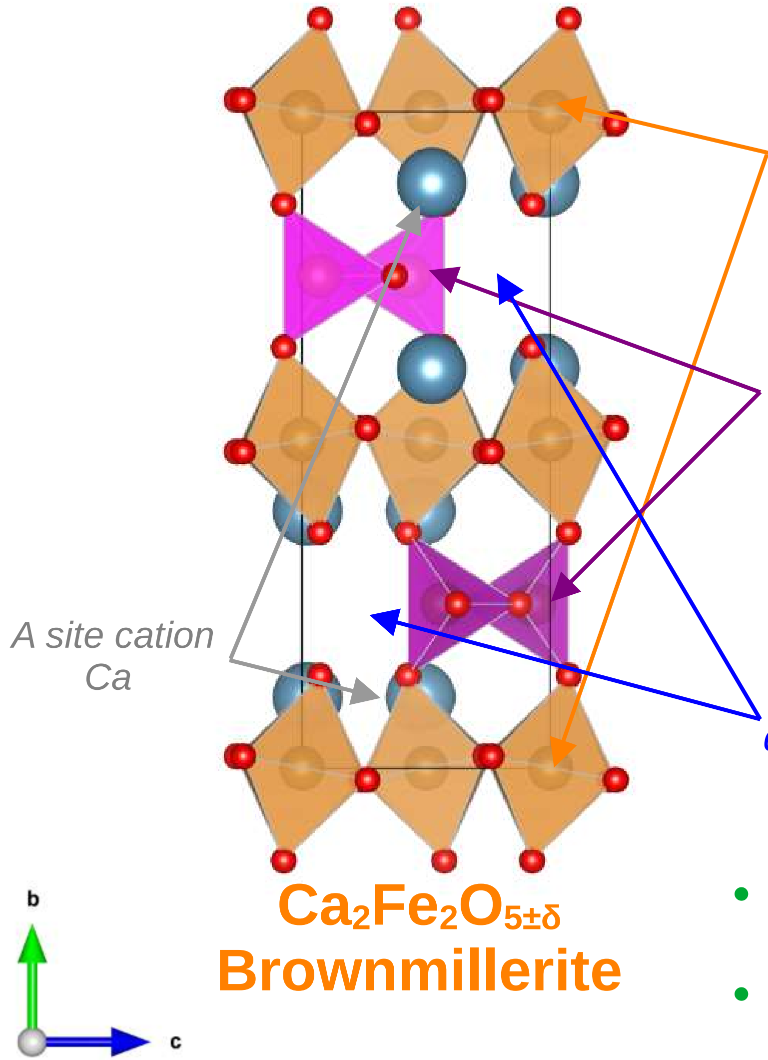

1st B site cation
BO_6 octahedra
Fe

2nd B site Cation
BO_4 tetrahedra
Fe

Oxygen vacancies forming one dimensional diffusion pathway for oxygen ion migration in tetrahedral layers

$Ca_2Fe_2O_{5\pm\delta}$
Brownmillerite

Partial substitution of Fe by 3d metal transition :
Mn, **Co** …

- Mainly low cost precursors ($CaCO_3$, **<u>$MnCO_3$</u>**, *$CoCO_3$* and Fe)

- Mainly single phase conductor

- « Low temperature » (<800°C)

- Confirm the **good performances** already reported for these materials and **go ahead in their optimization**
- Reassess the **impact of partial substitution** of iron in $Ca_2Fe_2O_5$ by manganese or cobalt

Synthesis $Ca_2(Fe, Co, Mn)_2O_{5\pm\delta}$: Ternary diagram

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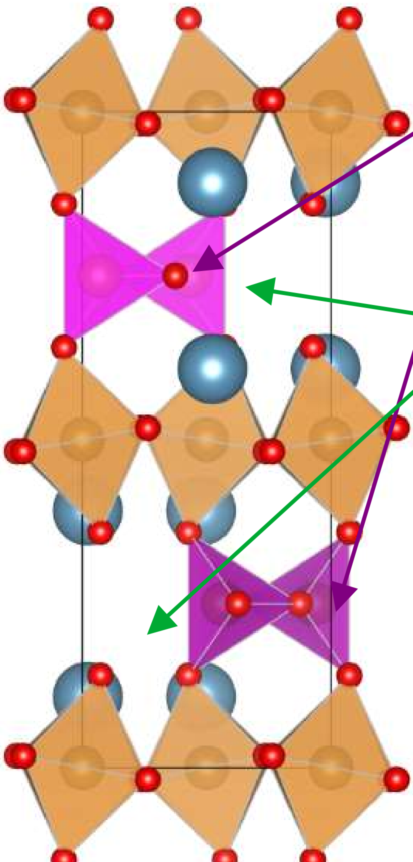
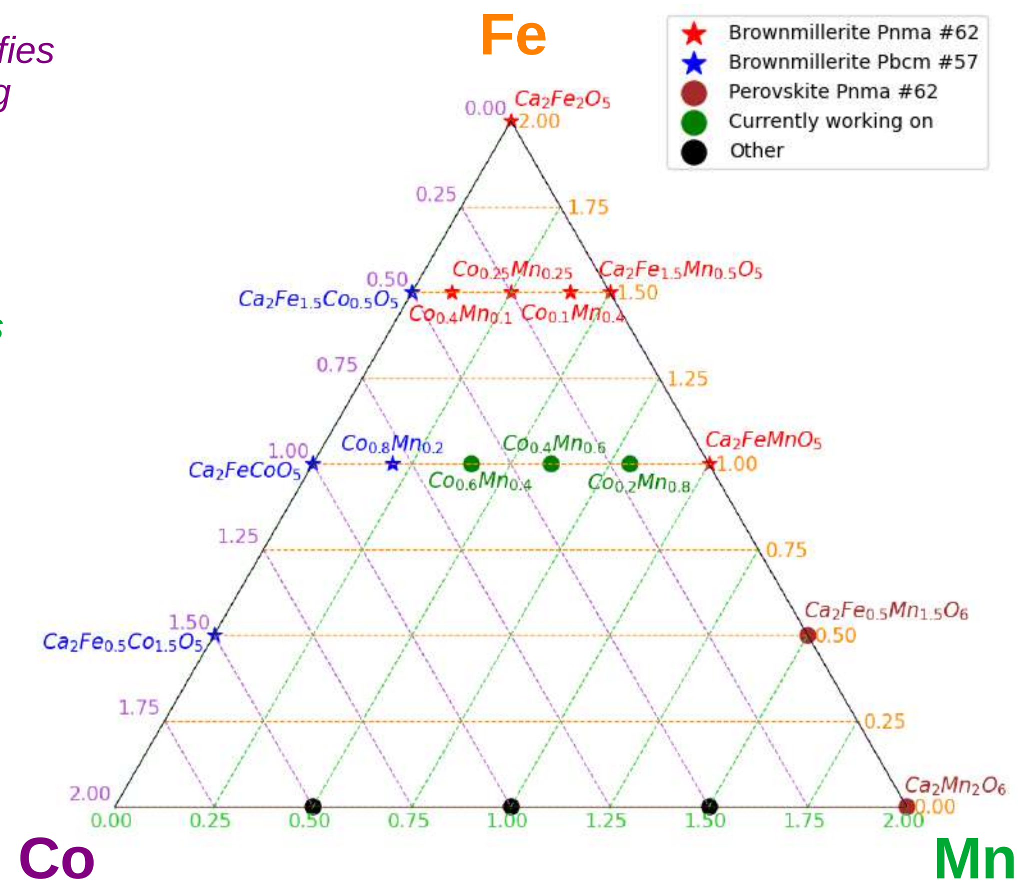


Co-substitution modifies Td-chains ordering

Mn-substitution changes δ and offers flexible coordination

Tunning of the stability and the transport properties

$Ca_2Fe_2O_{5\pm\delta}$ Brownmillerite



*Powders prepared via a **nitrate citrate route**: single phase obtained after annealing at different temperatures from 800°C to 1100°C instead of 1200°C by solid state route in the literature*

First EIS results on symmetrical cell

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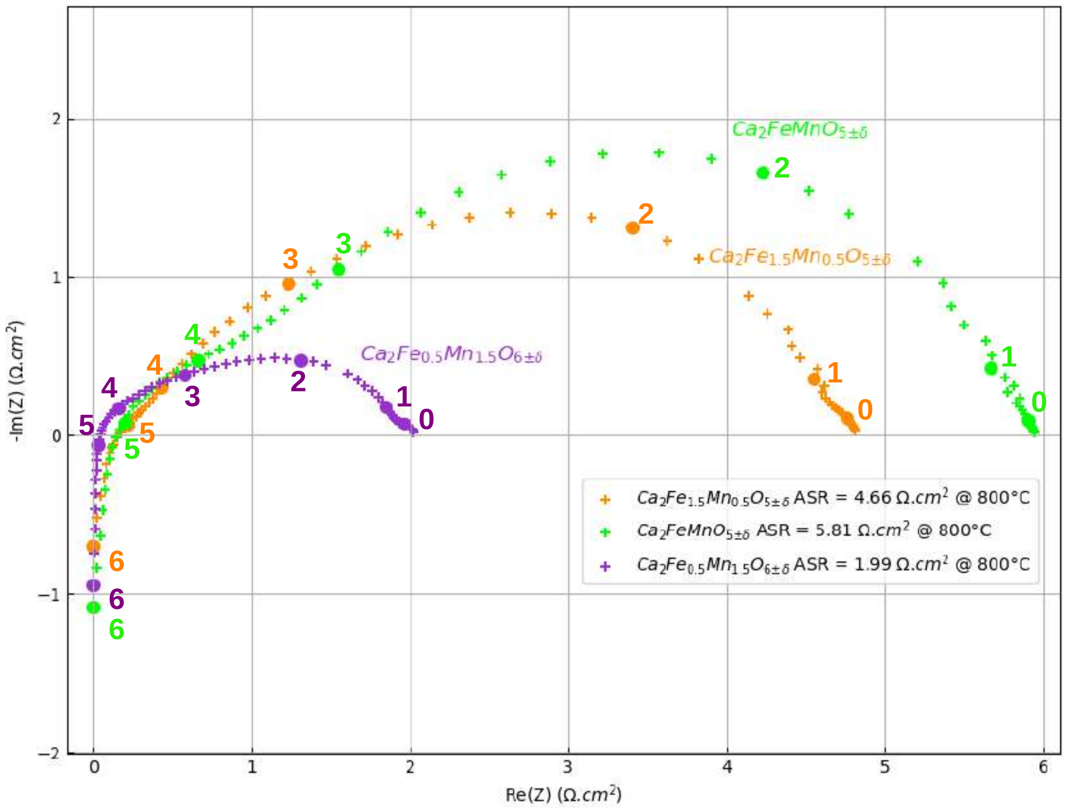
Nyquist plot for symmetrical cells
Anode material : $Ca_2Fe_{2-x}Mn_xO_{5\pm\delta}$ with x = 0.5, 1, 1.5



Mismatch with ASR values reported in the litterature

Potential Explanations

- **Incompatible microstructure**
- **Current collection problem**
- **Gas diffusion problem**

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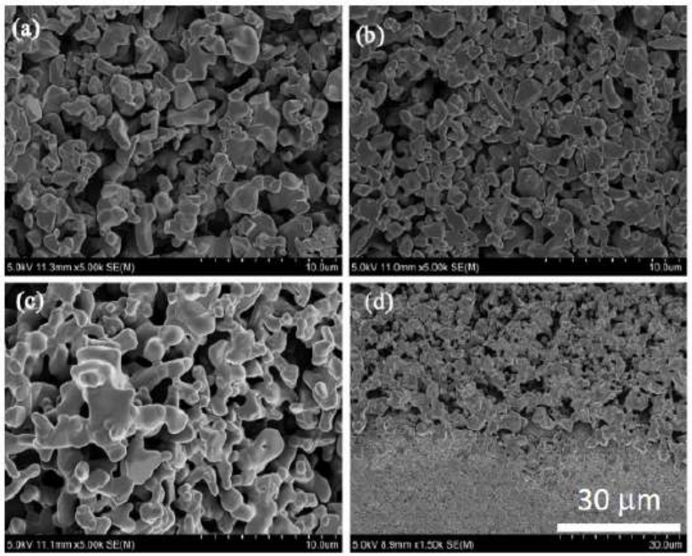
Checking the materials microstructure

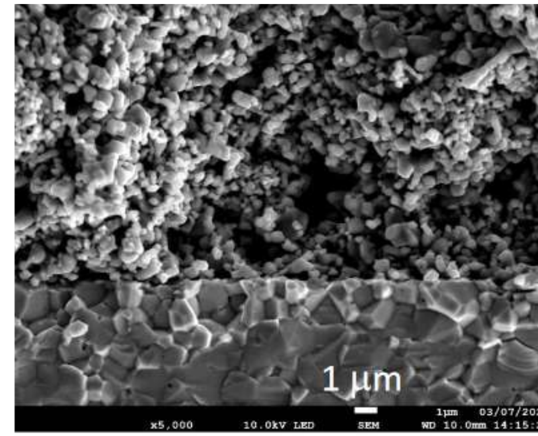
SEM images of $Ca_2Fe_{1.3}Mn_{0.7}O_{5\pm\delta}$ electrode sintered at 900 °C (a) ; 1000 °C (b) ; 1100 °C (c); and (d) cross-section of symmetrical cell

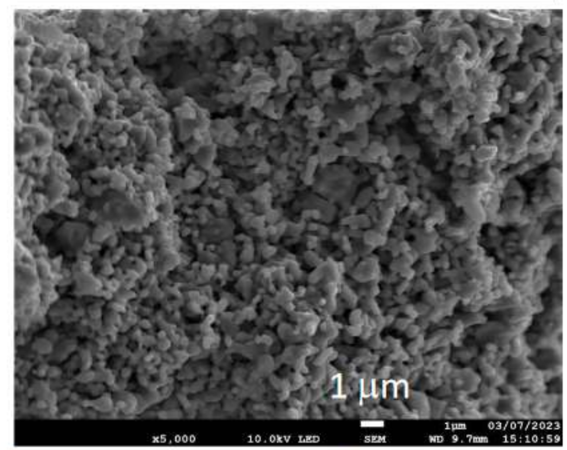


Li & al, Journal of Power Sources 238 (2013) 11-16

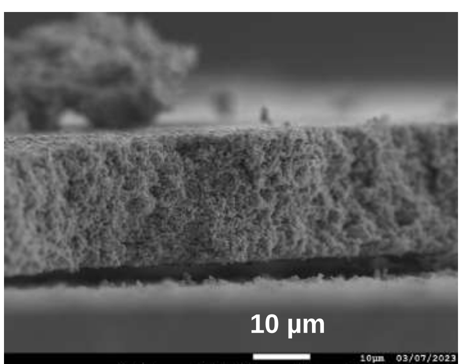
Denser electrode due to smaller grains

Cross-section image of symmetrical cell for $Ca_2FeMnO_{5\pm\delta}$





Cross-section image of symmetrical cell for $Ca_2Fe_{0.5}Mn_{1.5}O_{6\pm\delta}$



Electrode delamination for $Ca_2Fe_{0.5}Mn_{1.5}O_{6\pm\delta}$

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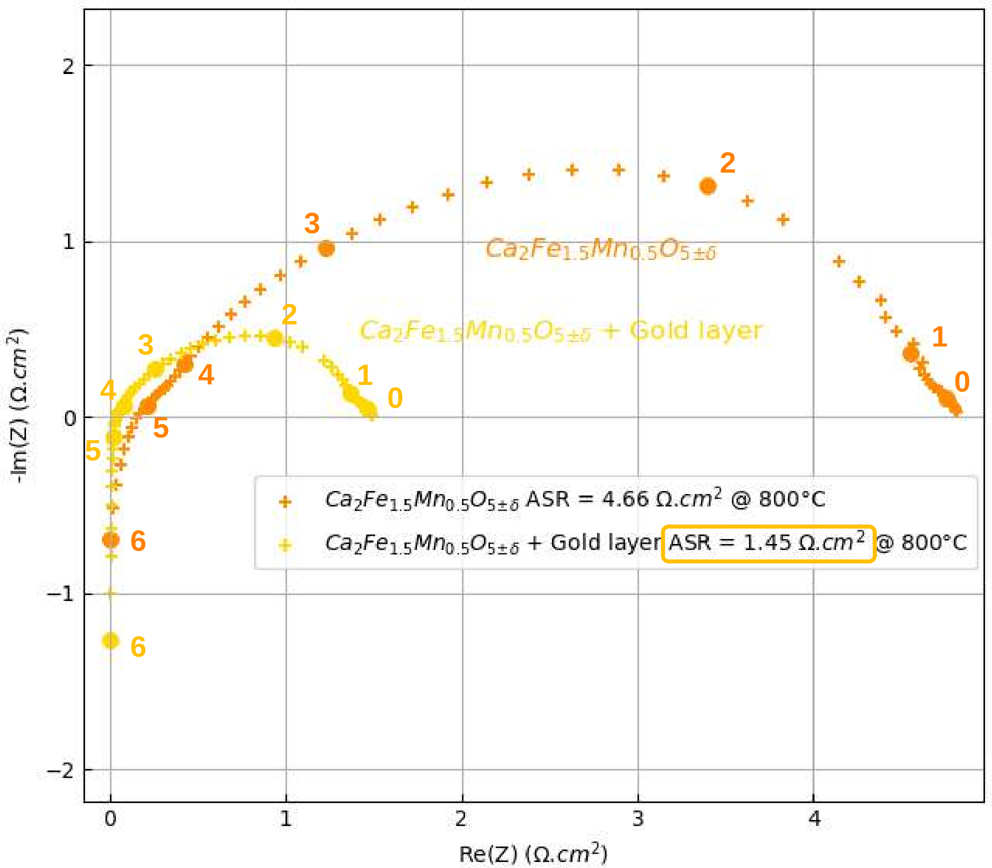
Testing current collection

Nyquist plot for symmetrical cells

Anode material : $Ca_2Fe_{1,5}Mn_{0,5}O_{5\pm\delta}$ with and without Gold layer

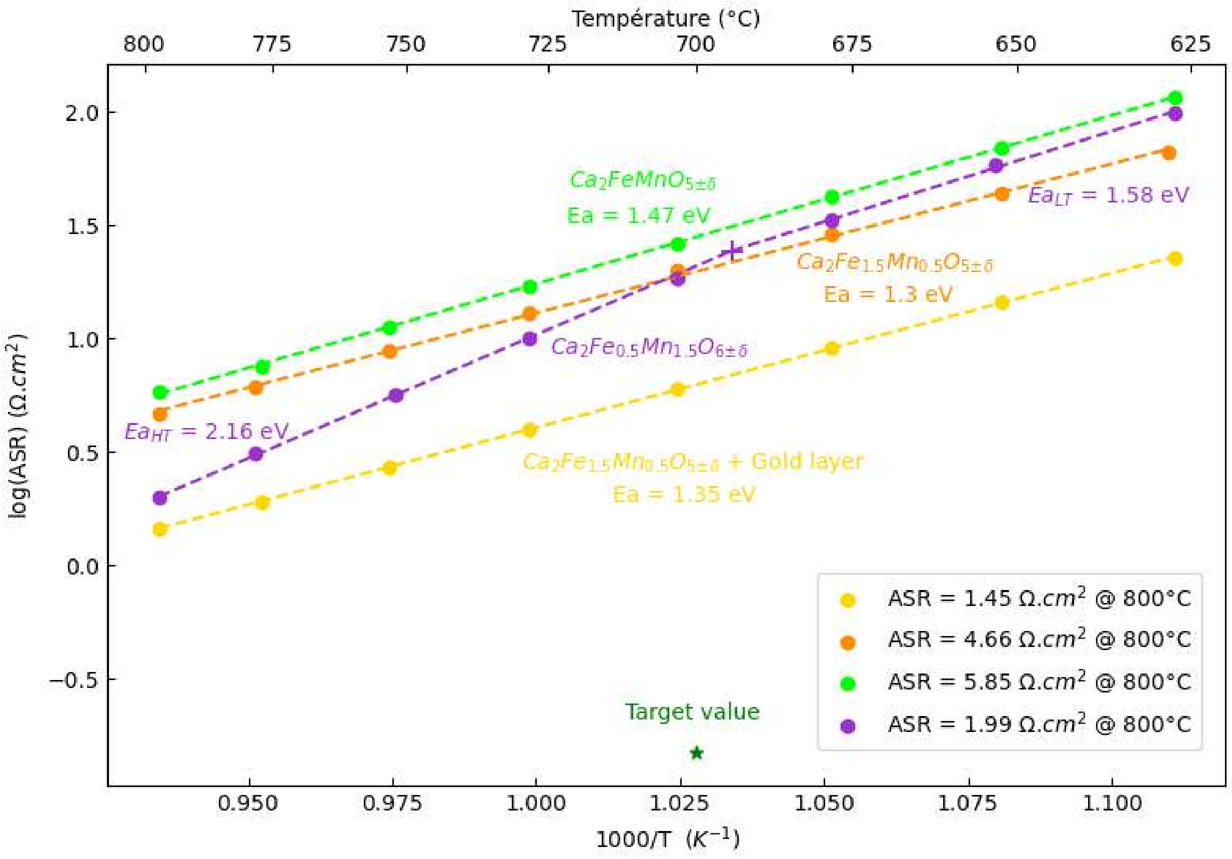


ASR impoved by adding a gold layer on top of the anode material

Problem of current collection

Testing current collection

Arrhenius plot for symmetrical cells
Anode material : $Ca_2Fe_{2-x}Mn_xO_{5\pm\delta}$ with x = 0.5, 1, 1.5



Problem of current collection

Potential Explanation

Low electrical conductivity ??

Probing Electrical conductivity of materials

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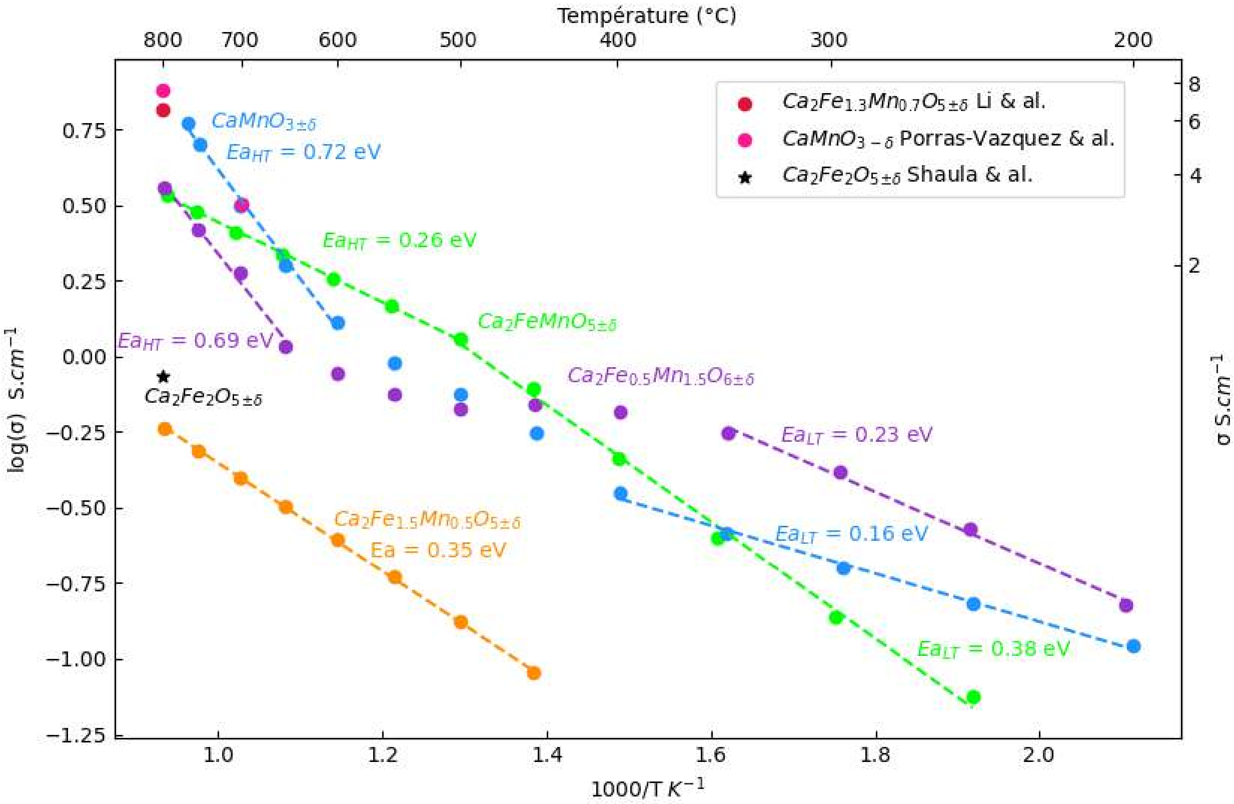
Arrhenius plot of electrical conductivity
$Ca_2Fe_{2-x}Mn_xO_{5\pm\delta}$ with x = 0.5, 1, 1.5



Low electrical conductivity

Admitted values for air electrode material :

σ_{el} > **100 S.cm^{-1}**

σ_i > **0.01 S.cm^{-1}**

Electrical conductivity need to be improved

Li & al, Journal of Power Sources 238 (2013) 11-16
Porras-Vazquez, Dalton Trans, (2013), 42, 5421
A.L. Shaula & al, Solid State Ionics 177 (2006) 2923–2930

Meantime, investigation on the other side of the ternary diagram shows interesting results...

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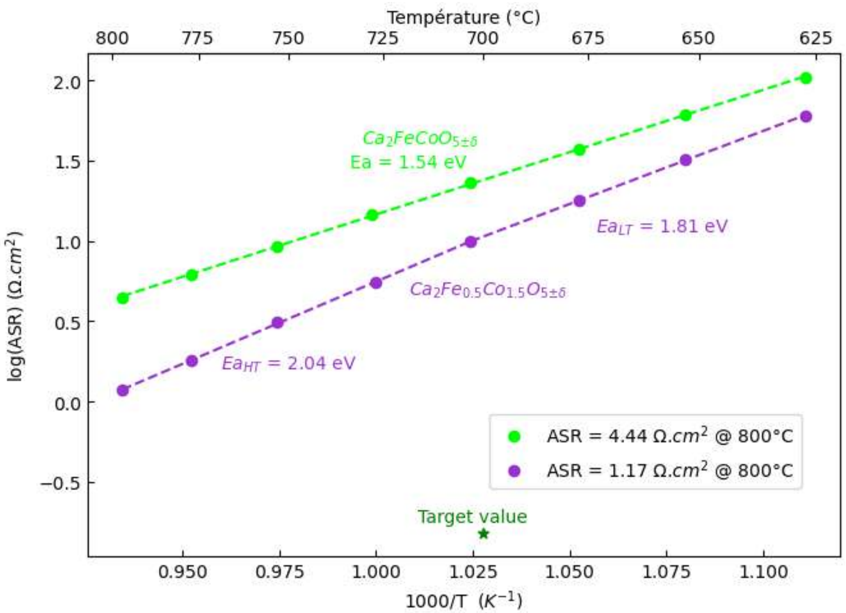
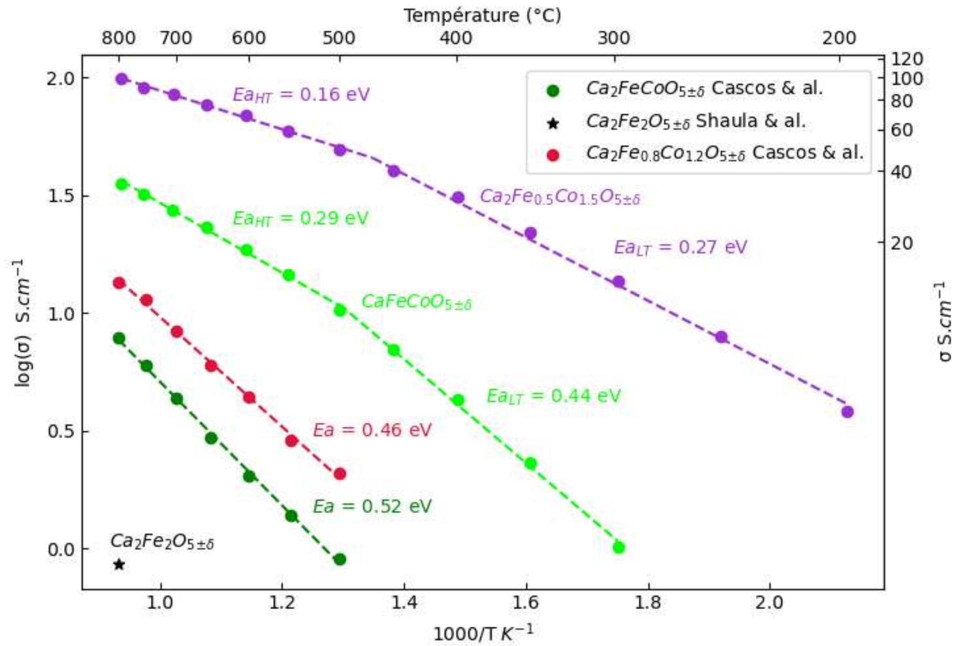
Arrhenius plot for symmetrical cells
Anode material : $Ca_2Fe_{2-x}Co_xO_{5\pm\delta}$ with x = 1, 1.5



Arrhenius plot of electrical conductivity
$Ca_2Fe_{2-x}Co_xO_{5\pm\delta}$ with x = 1, 1.5



Lower ASR value
ASR = 1.17 Ω.cm² @ 800°C

Increased electrical conductivity
σ_{max} = 98 S.cm^{-1} @ 800 °C

Li & al, International Journal of Hydrogen Energy 35 (2010) 9151-9157
Cascos & a, International Journal of Hydrogen Energy 40 (2015) 5456-5468

Currently working on : Increasing Electrical conductivity to lower ASR value

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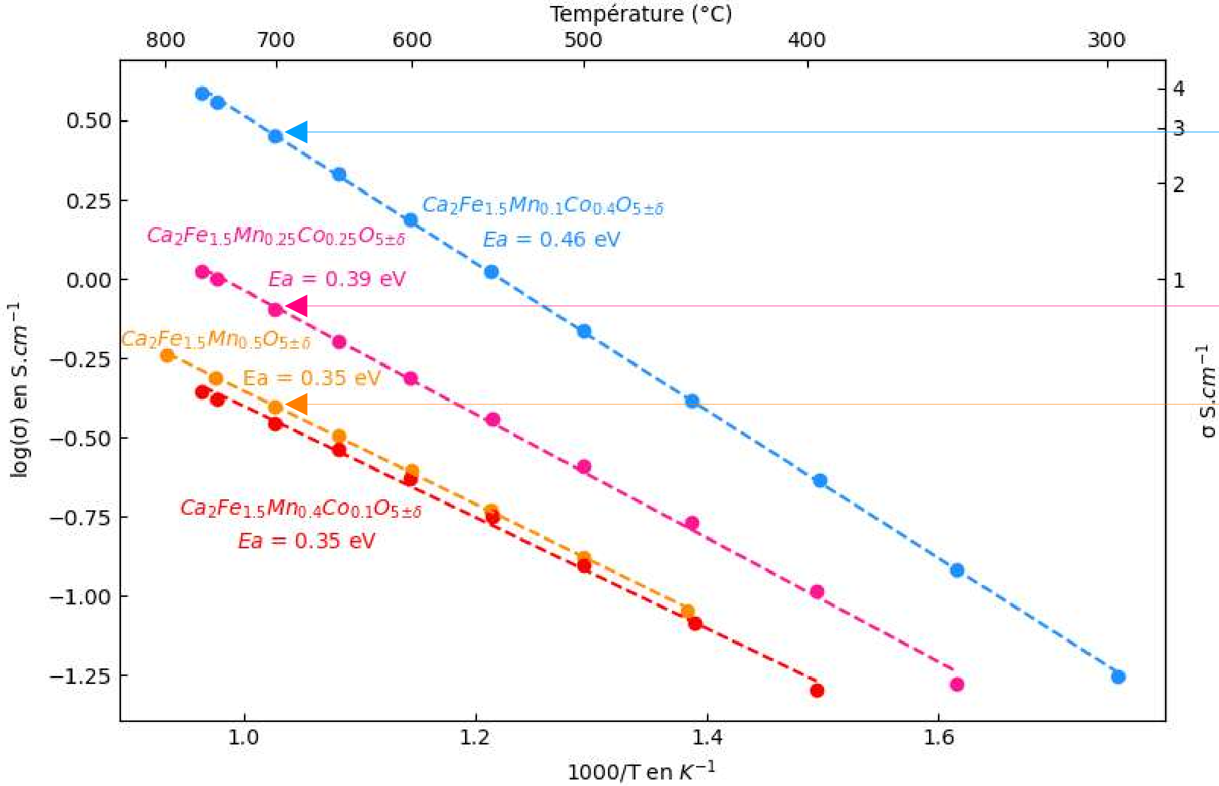
Effect of Co-substitution on electrical conductivity for $Ca_2Fe_{1,5}Mn_{0,5-x}Co_xO_{5\pm\delta}$ with x = 0, 0.1, 0.25, 0.4



Electrical conductivity values @ 700 °C

σ = 3.87 $S.cm^{-1}$

σ = 1.05 $S.cm^{-1}$

σ = 0.57 $S.cm^{-1}$

The **electrical conductivity** is **increased** by **partial substitution** for Mn with Co

Some reflective elements for a collaboration with the modeling team...

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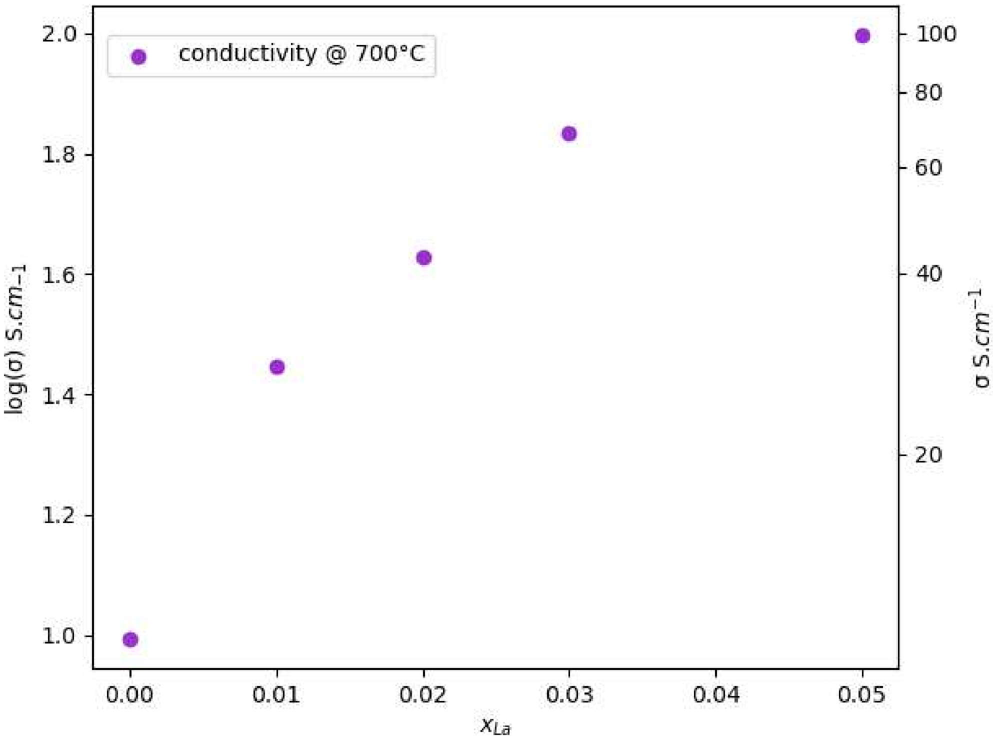
Effect of La-substitution on electrical conductivity for $Ca_{1-x}La_xMnO_{3\pm\delta}$ with x = 0, 0.01, 0.02, 0.03, 0.04, 0.05



	$CaMnO_{3\pm\delta}$	$CaMn_{0.95}Si_{0.05}O_{3\pm\delta}$
Oxidation state of Mn	3.93	3.56
Conductivity ($S.cm^{-1}$) @ 700°C	3.2	38.1

Partial substitution of Mn with Si increases Mn^{3+}/Mn^{4+} covalency and improves electrical conductivity

Could such behavior be exported to $Ca_{2-y}M_yFe_{2-x}Mn_xO_{5\pm\delta}$ series ??

- **Type of M cation for partial substitution on A site : La, Bi, Y ...**
- **Stoechiometry**
- **Possibility of both A and B site doping**

Data adapted from :
Liu & al, Chemical Engineering Journal 408 (2021) 127364

Porras-Vazquez, Dalton Trans, (2013), 42, 5421

CONCLUSION AND PERSPECTIVES

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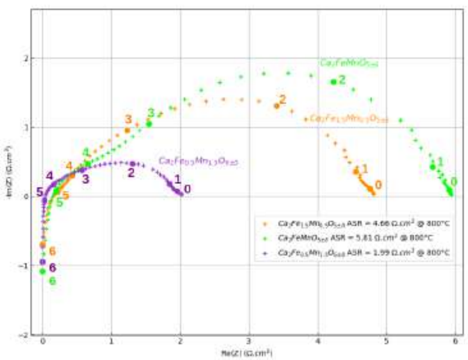
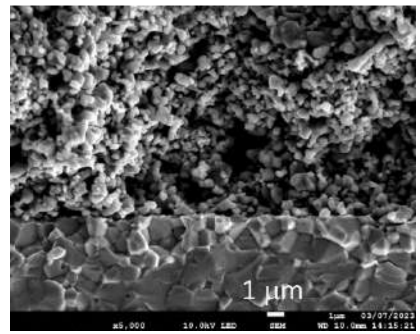
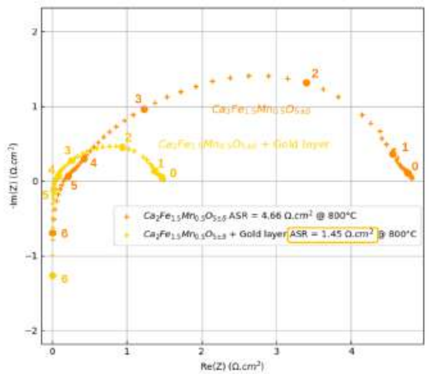
- Thin powders of $Ca_2Fe_{2-x}Mn_xO_{5\pm\delta}$ with x = 0.5, 1, 1.5 were prepared by a nitrate citrate route. Single phase were obtained after annealing at 1100°C instead of 1200°C by solid state route in the literature

- **First measurements of ASR** on symmetrical cells led to rather **high ASR compared to the literature**







These high values can be partly explained by a too dense microstructure but also by a too low electrical conductivity

- Best ASR is obtained for the Mn rich composition: **$Ca_2Fe_{0.5}Mn_{1.5}O_{6\pm\delta}$**
  ASR = 1.99 Ω.cm^2, σ_{el} = 3.61 S.cm^{-1} @ 800°C

Work going on:

→ **Partial substitution on the A site** with La, Bi, Y is in progress to increase the electrical conductivity
→ The **microstructure** will be improved by **coarsening** the ceramic grains
→ The **influence** of **cathode thickness** on ASR will be explored for **$Ca_2Fe_{0.5}Mn_{1.5}O_{6\pm\delta}$**

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NOVEL ELECTRODE COATINGS AND INTERCONNECT
FOR SUSTAINABLE AND REUSABLE SOEC

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Thank you for your attention

https://www.nouveau-project.eu/