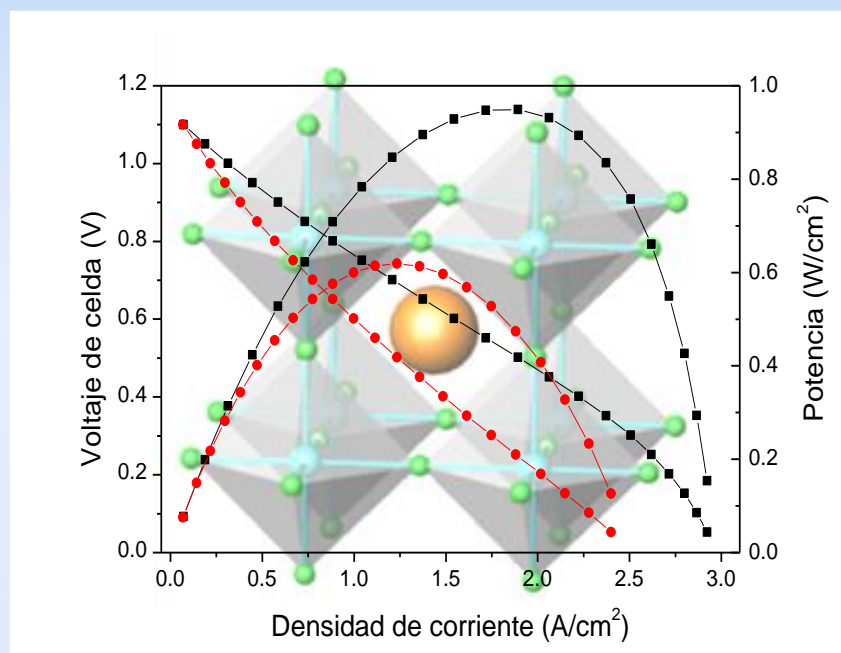


# Desarrollo de nuevos materiales de electrodo para pilas de combustible de óxido sólido



**José Antonio Alonso**

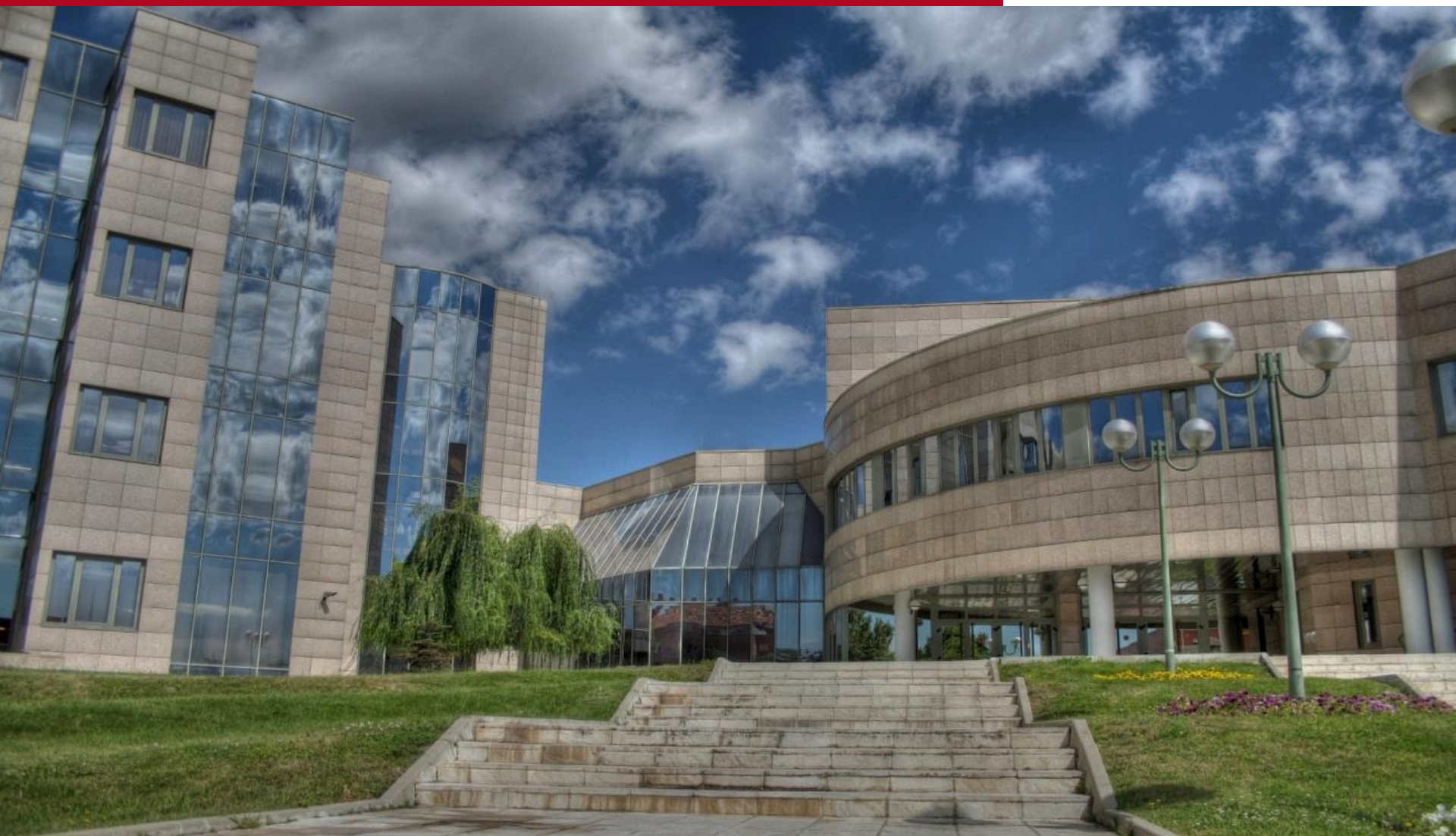
Instituto de Ciencia de Materiales de Madrid  
Consejo Superior de Investigaciones Científicas

Instituto de Ciencia  
de Materiales de Madrid



**CSIC**

CONSEJO SUPERIOR DE INVESTIGACIONES CIENTÍFICAS



## Human resources

136 Research Centres 75 (CSIC) 53 (Joint) 8 (Service)

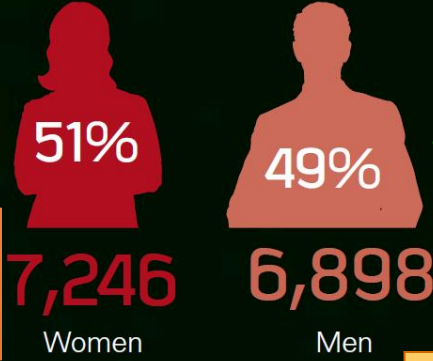
**14,144** People work at the CSIC



## Women and Science

The Gender Equality in Scientific Careers Plan and the CSIC's Women and Science Committee promote equality of opportunity between men and women.

**4,382** Scientist Doctors  
**3,116** Trainee researchers



Calar Alto Almeria



Oceanographic vessel Hespérides

CSIC = 6% of Spanish researchers  
20% of Spain Scientific Output  
45% of patent applications (public sector)

<http://www.csic.es>

# Research Lines at ICMM

Biomaterials and Bioinspired Materials

Energy, Environment and Sustainable Technologies

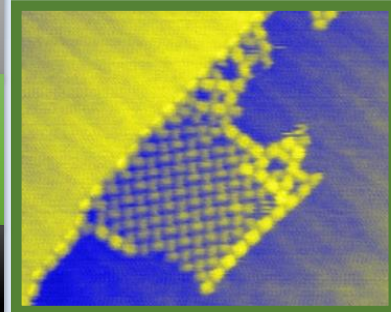
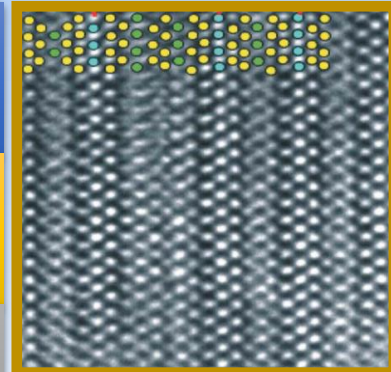
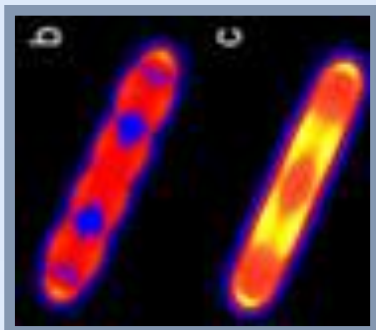
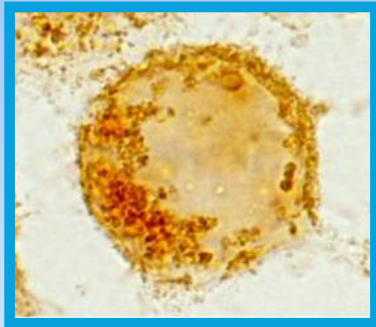
Materials for Information Technologies

Nanostructures and Surfaces and Coatings

New Architectures in Materials Chemistry

Photonic Materials

Theory and Simulation of Materials



# Energy Conversion, Harvesting and Storage Group



**Alonso Alonso, José Antonio** - Research Professor  
**Asensio Ariño, M<sup>a</sup> Carmen** - Research Professor  
**Sobrados de la Plaza, Isabel** - Research Scientist  
**Aguadero Garín, Ainara** - Tenured Scientist  
**Amarilla Alvarez, José Manuel** - Tenured Scientist  
**Serrano Sánchez, Federico** – R&C  
**Andersen, Henrik Lyder**, Marie Curie postdoc.  
**Cascos Jiménez, Vanessa** - Postdoc researcher  
**Gainza Martín, Javier** - Postdoctoral researcher  
**Chivite Lacaba, Mónica**- Predoctoral Researcher  
**Sánchez de Bustamante, Lucía**- Predoctoral Researcher

In collaboration with

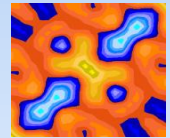
**Martínez Peña, José Luis**- Research Professor ICMM  
**Jiménez, Ricardo**, Research Scientist, ICMM  
**Nemes, Norbert**, Professor, UCM

## Synthesis and Characterization of Materials for...

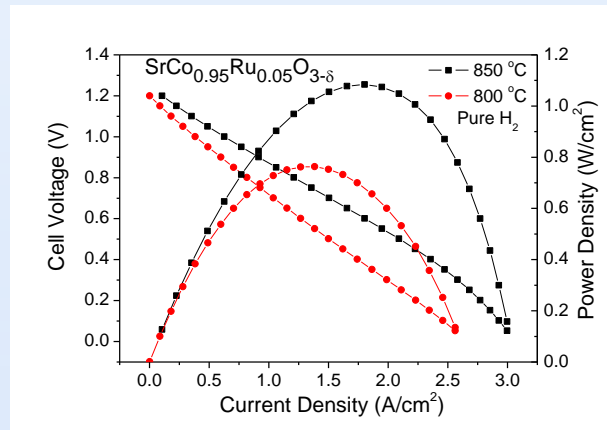
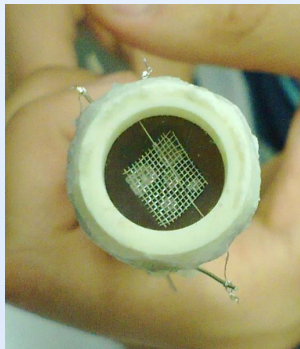
- Fuel cells (SOFC)
- Li and Na batteries (all-solid state)
- Hybrid perovskites (solar harvesting)
- Thermoelectric Materials
- Spintronics: CMR

# Working line on Hydrogen technology

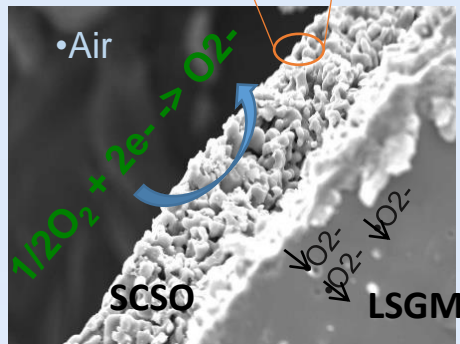
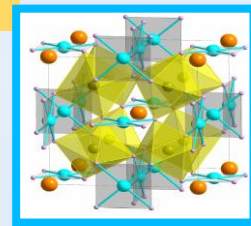
- Solid Oxide Fuel cells (SOFC) and electrolyzers (SOEC): Design and synthesis of novel electrodes and electrolytes; implementation in test cells.
- Developments of novel **metal hydrides**: ex. Perovskites with H prepared under high pressure conditions ( $\text{NaMgH}_3$ ) or Mg-rich hydrides:  $\text{Mg}_2\text{FeH}_6$
- Structural characterization by neutron diffraction, XAS...: structure-properties correlations



Structure-properties

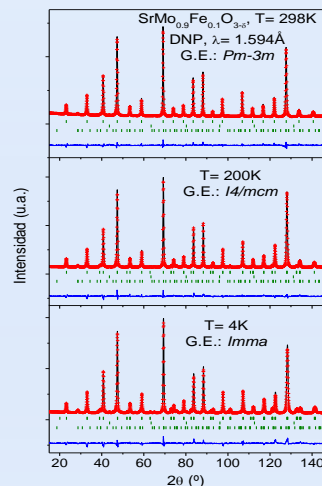


High Pressure synthesis



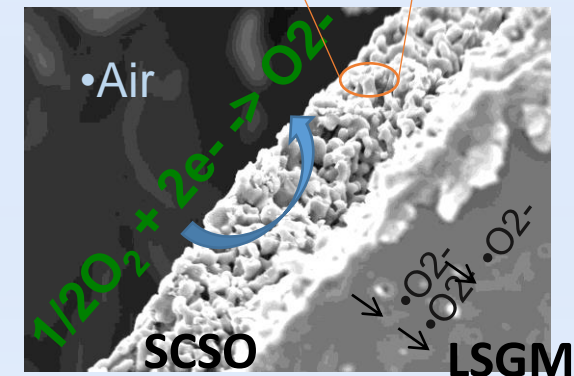
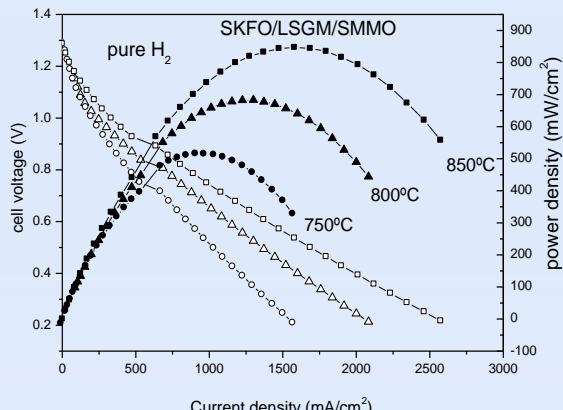
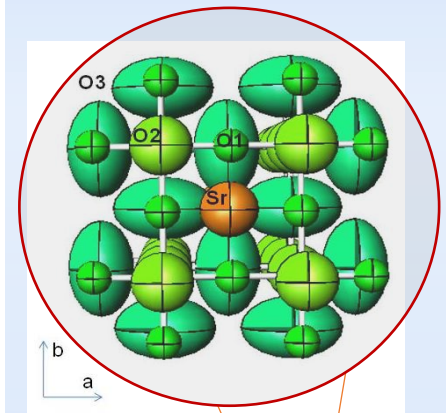
Energy conversion devices

Advanced synthesis



# Materials for energy conversion: electrodes for fuel cells

- Many oxides that have been traditionally studied for their magnetic or transport properties find applications, with subtle modifications, in energy conversion devices: SOFC.
- We have developed new electrodes based upon  $\text{SrFeO}_{3-\delta}$ ,  $\text{LaNiO}_3$ ,  $\text{Sr}(\text{Ba})\text{CoO}_{3-\delta}$ , or  $\text{SrMoO}_3$ , with **huge electronic conductivity** and oxygen diffusion.
- $\text{SrCo}_{0.95}\text{Ru}_{0.05}\text{O}_3$ ,  $\text{LaNi}_{0.8}\text{Mo}_{0.2}\text{O}_3$ ,  $\text{K}_{0.1}\text{Sr}_{0.9}\text{FeO}_{3-\delta}$ ,  $\text{SrMo}_{0.8}\text{Fe}_{0.1}\text{O}_3$  ... **are stable at the working conditions of a SOFC** and deliver power densities up to  $1100 \text{ mW/cm}^2$  as cathodes or anodes in single fuel cells with  $\text{H}_2$  as fuel.

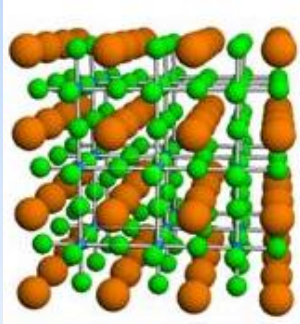




**Cathodes for  
SOFC**

# Cathodes: $\text{SrCoO}_{3-\delta}$ Polymorphs

## Cubic phase (C)



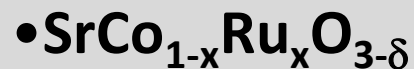
- High electrical conductivity
- High oxygen permability
- Low thermal stability
- Not stable at high T (>600°C)
- Cracking problems on heating and cooling



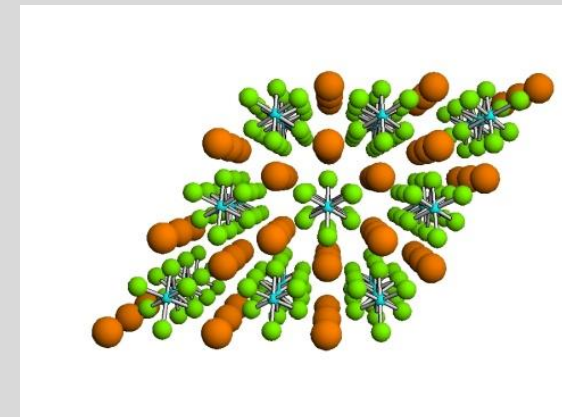
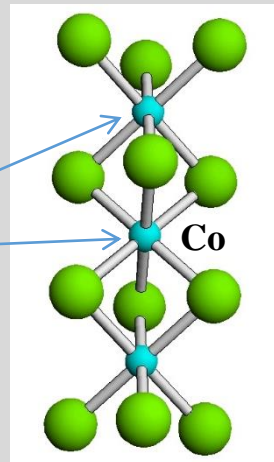
• Not suitable for SOFC

• Stabilization of a cubic perovskite stable at the working T of a cathode in IT-SOFC (650-850 °C).

• Doping the Co positions with a **highly charged** ion ( $\text{Sb}^{5+}$ ,  $\text{Nb}^{5+}$ ,  $\text{Mo}^{6+}$ ...), prevents the formation of competitive hexagonal 2H phase



Chains of  $\text{CoO}_6$  octahedra sharing faces de-stabilized by repulsion among highly charged ions

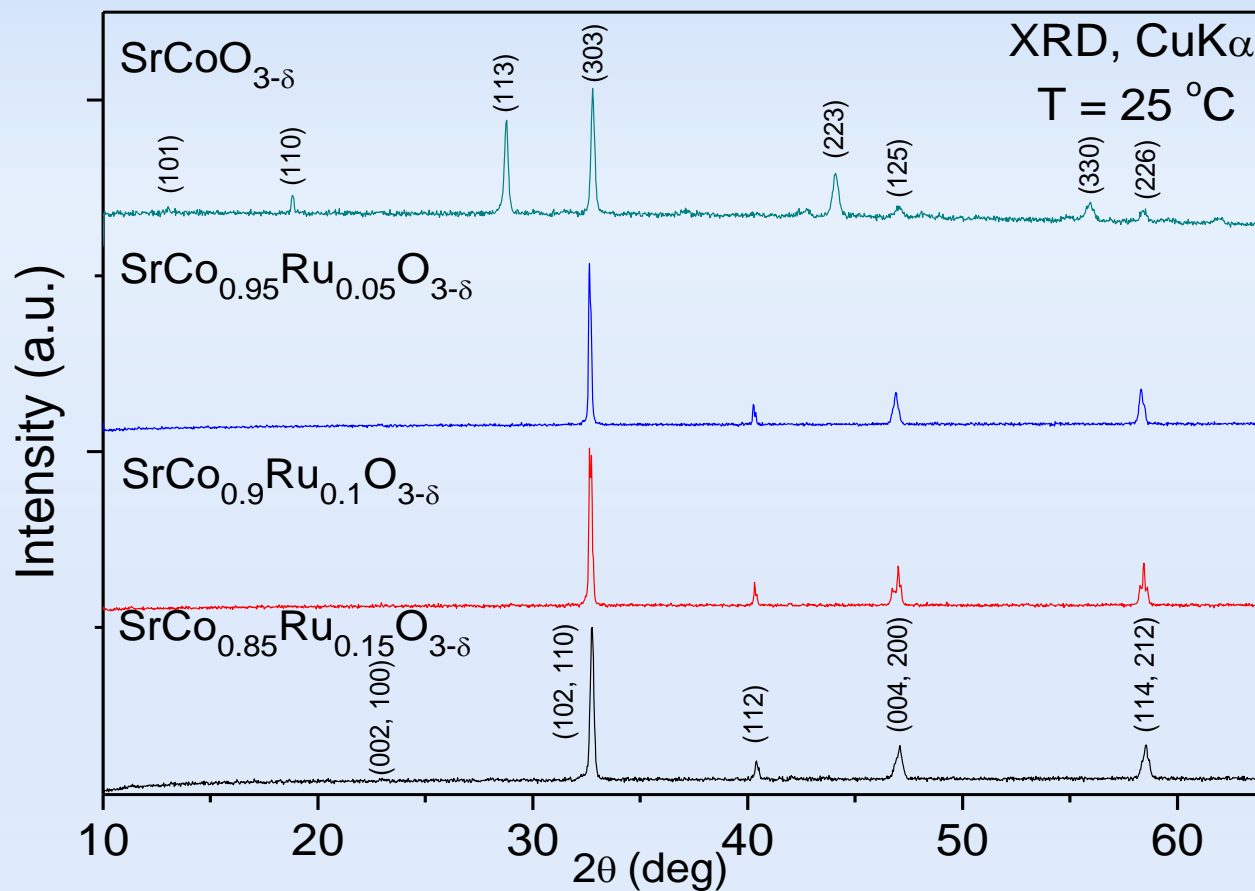


Unwanted Hexagonal 2H  $\text{SrCoO}_3$

# Crystal structure of $\text{SrCo}_{1-x}\text{Ru}_x\text{O}_{3-d}$ ( $x=0.05, 0.1, 0.15$ )

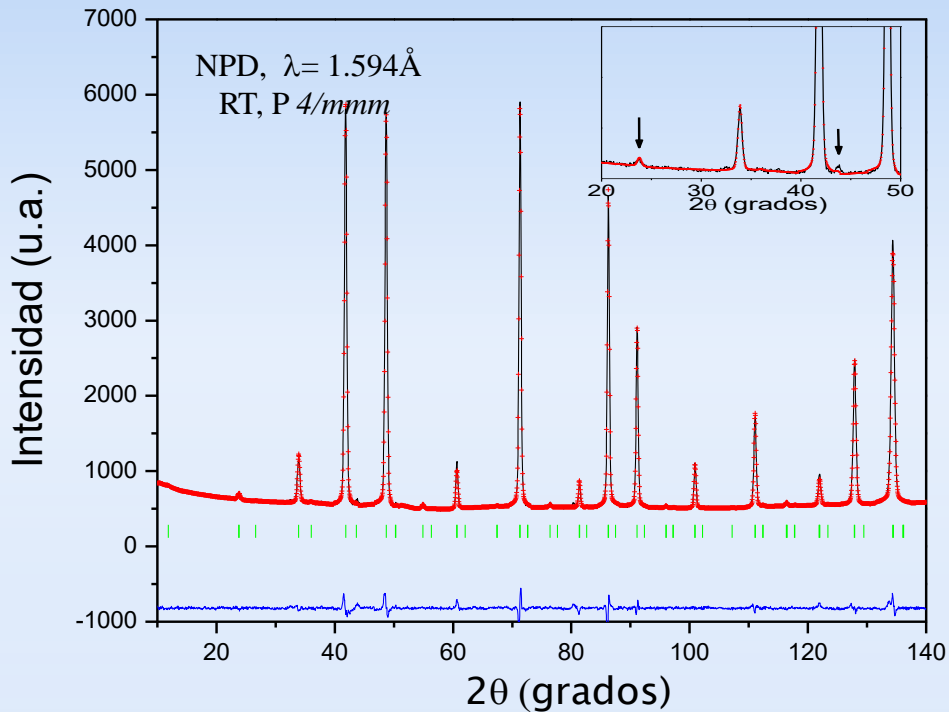


Synthesis by citrates techniques (Soft Chemistry) followed by mild temp. treatments



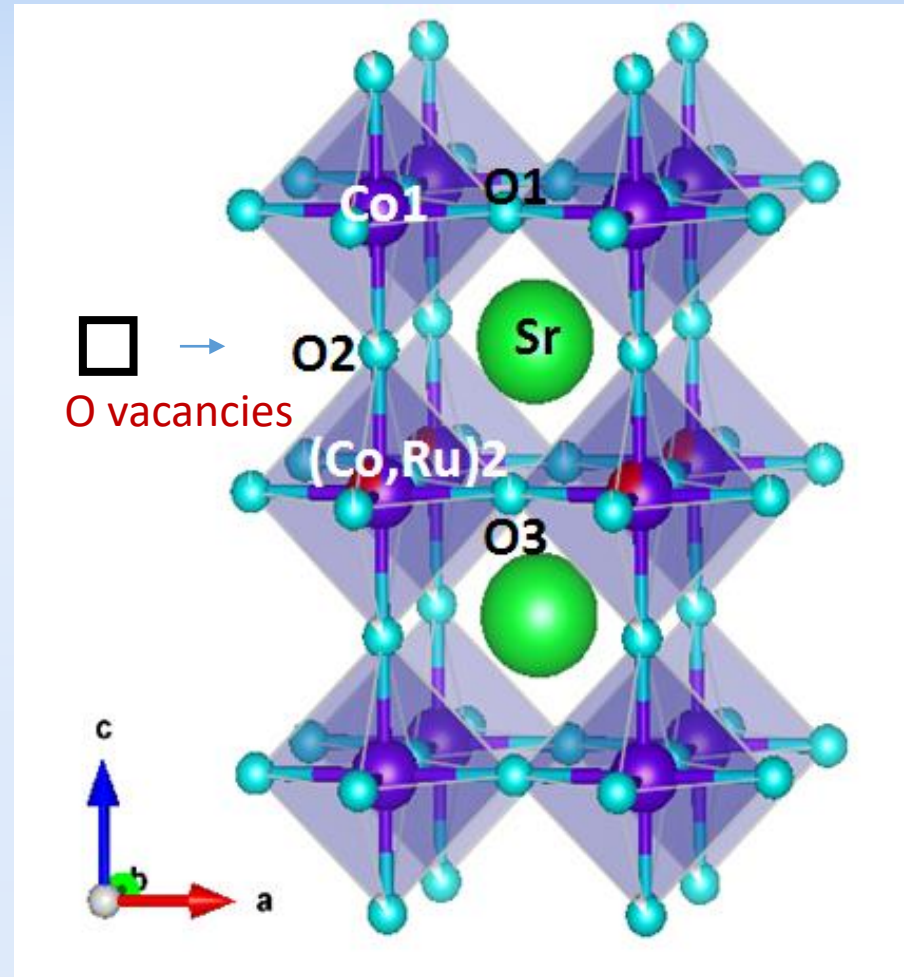
No hexagonal phase  
Cubic to XRD

# True tetragonal symmetry by neutron powder diffraction

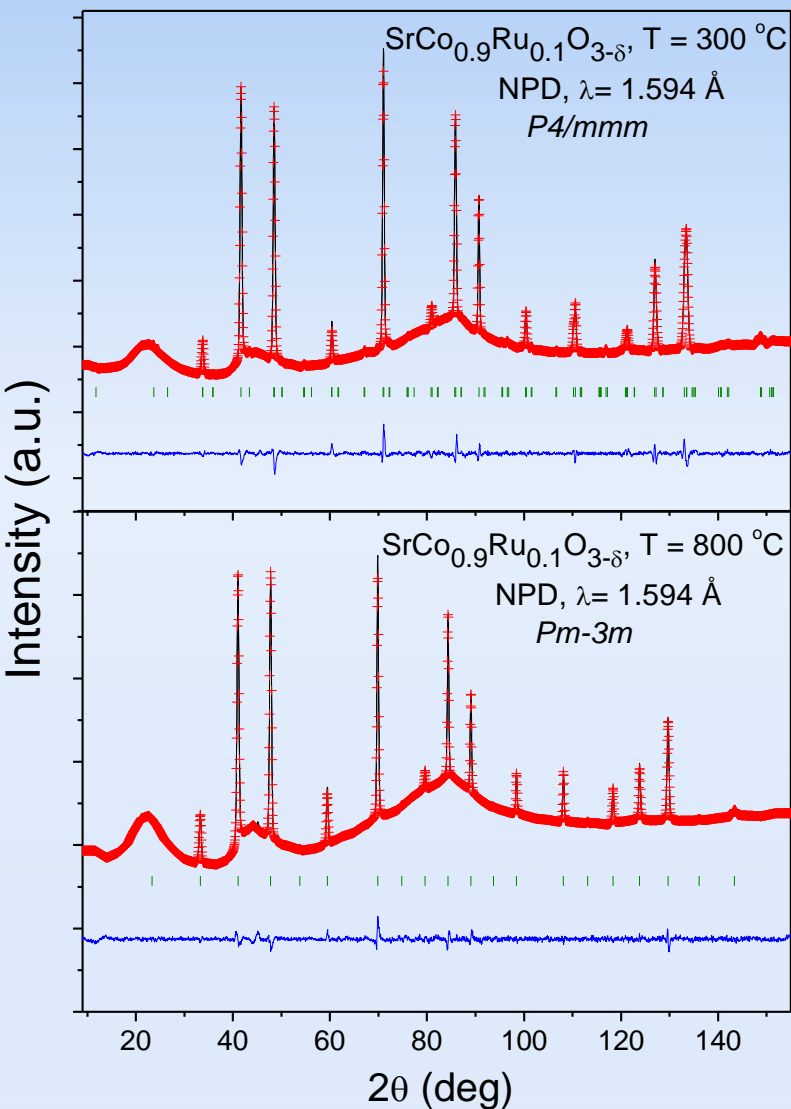


Layers of  $\text{Co}_1\text{O}_6$  octahedra alternating with  $\text{Co}_2\text{O}_6$  deficient in O.

Oxygen vacancies and large thermal factors  $\rightarrow$  high mobility of  $\text{O}^{2-}$



# Crystal structure evolution of $\text{SrCo}_{0.9}\text{Ru}_{0.1}\text{O}_{3-d}$ by “in situ” NPD



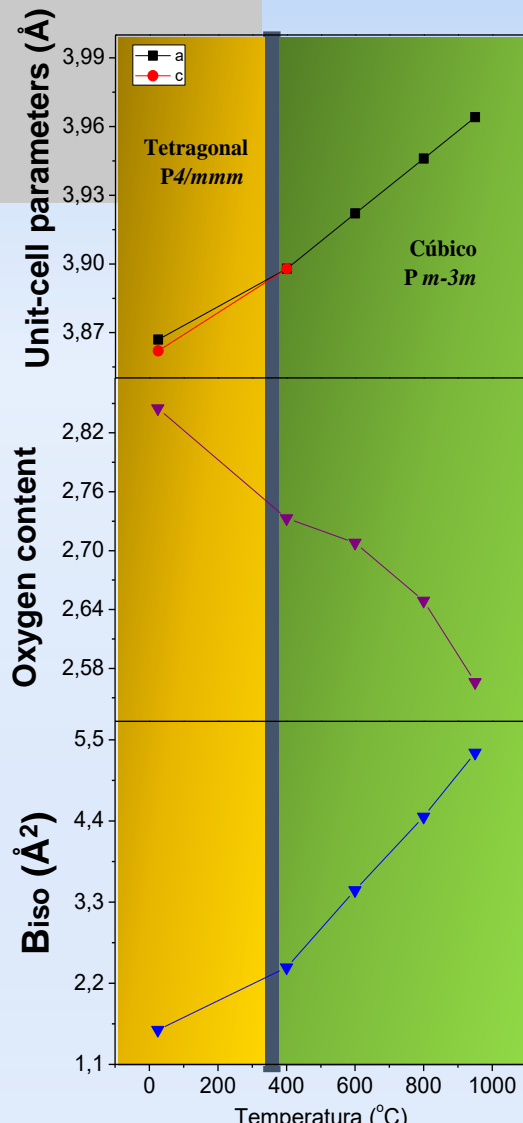
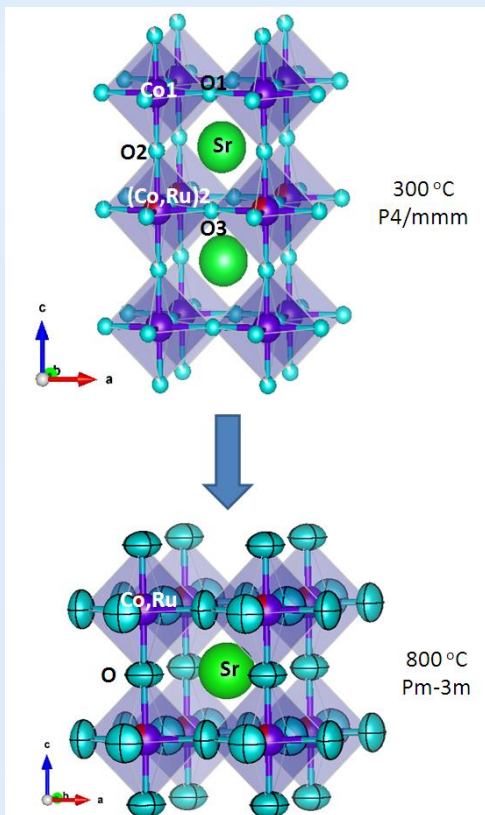
Phase transition between 300 and 600 °C

Oxygen deficiency decrease from

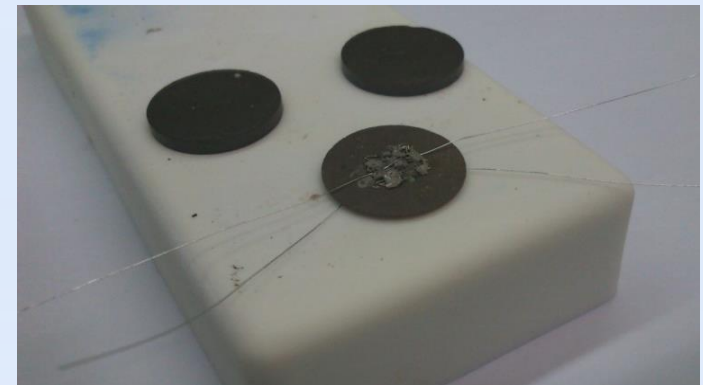
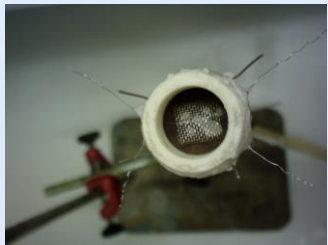
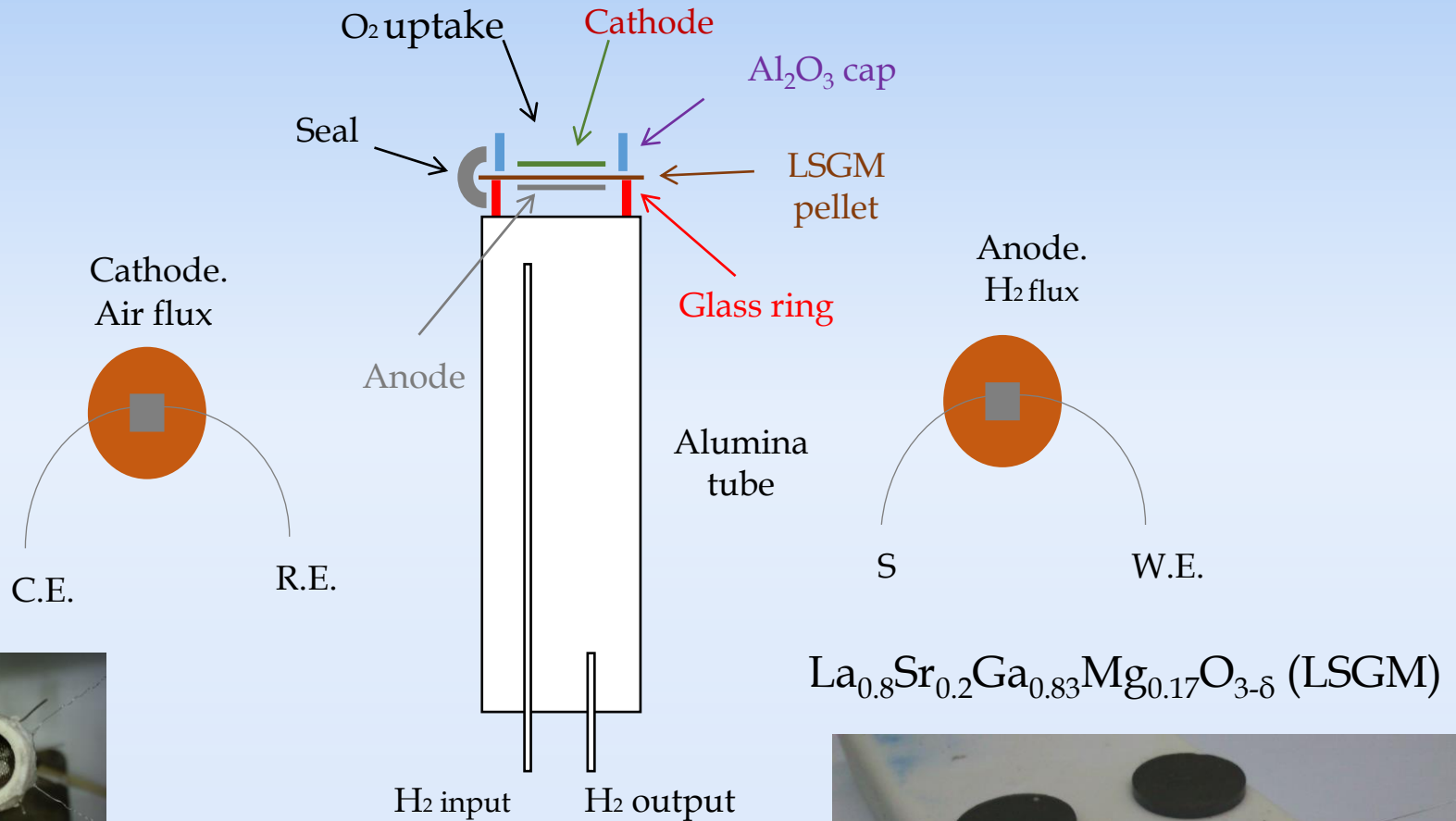
$\text{SrCo}_{0.9}\text{Ru}_{0.1}\text{O}_{2.83}$  at 25 °C to

$\text{SrCo}_{0.9}\text{Ru}_{0.1}\text{O}_{2.54}$  at 800 °C

Huge amount of O vacancies

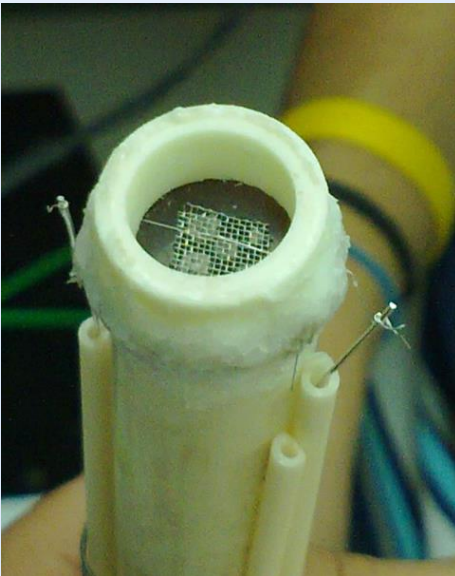
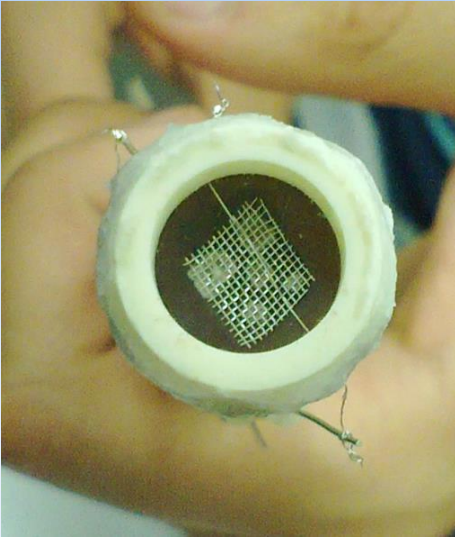


# Setup of a SOFC single-cell



Anode y Cathode deposited on LSGM pellets (300 μm)

# • Setup of a SOFC single-cell

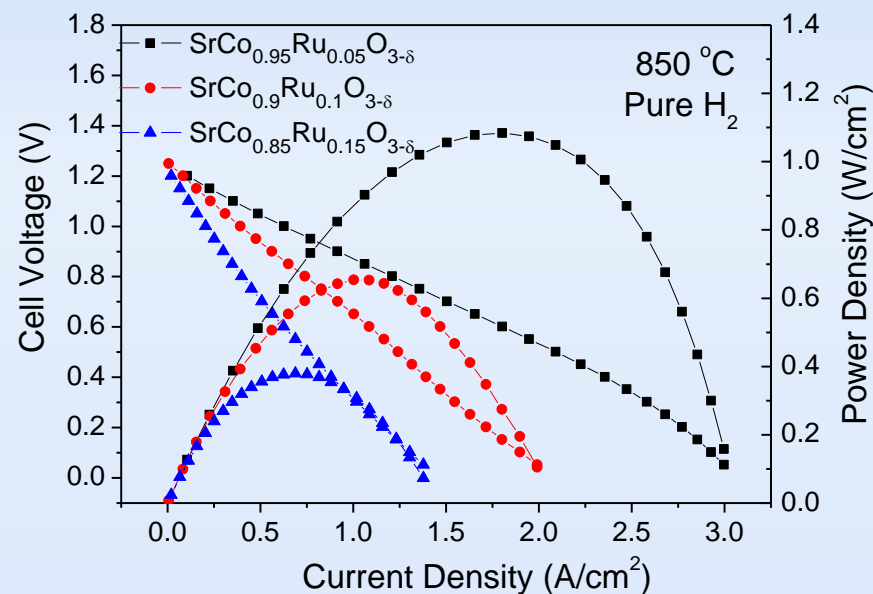
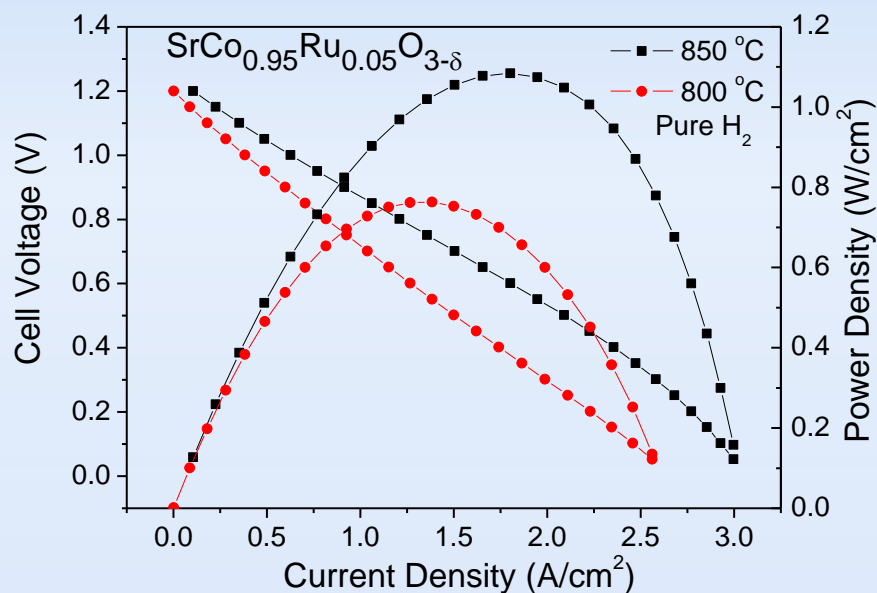


• Working T between 700 - 850 °C.

• Anode fed by pure H<sub>2</sub>; cathodic side open to air atmosphere

# Cathode performance in test SOF-cell

- Electrolyte supported configuration, with LSGM (300  $\mu\text{m}$ )



- Power  $\text{Ru}_{0.05}$  at 800 °C: 770  $\text{mW}/\text{cm}^2$
- Power at 850 °C: **1100  $\text{mW}/\text{cm}^2$**

- Power  $\text{Ru}_{0.1}$ : 660  $\text{mW}/\text{cm}^2$
- Power  $\text{Ru}_{0.15}$ : 384  $\text{mW}/\text{cm}^2$

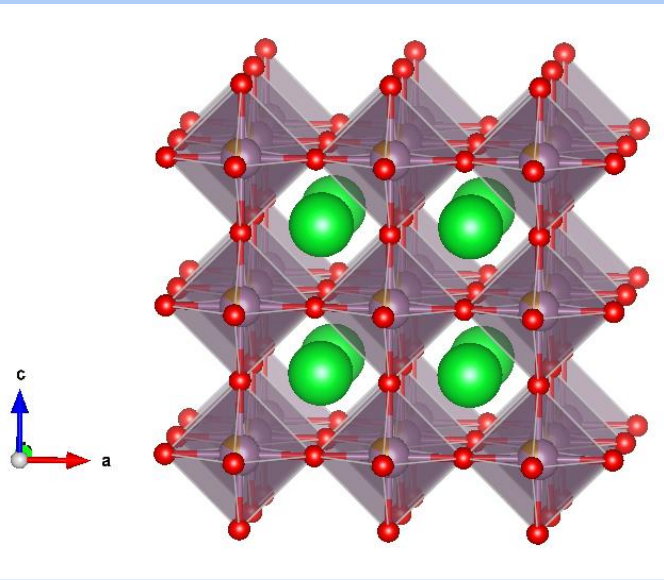
V Cascos et al, ACS Applied Energy Materials 3, 6709-6716 (2020)

M Chivite et al, ACS Applied Energy Materials, 6, 1046 (2023)



**Anodes for  
SOFC**

# • Novel **anodes**: derivatives of $\text{SrMoO}_3$



- Metallic behavior
- High electronic conductivity at RT ( $\sigma = 10^4 \text{ Scm}^{-1}$ )
- Stable in reducing atmosphere ( $\text{Mo(IV)} \longrightarrow$  easiness to incorporate oxygen vacancies)
  - Mo suitable to catalyze fuel oxydation
- Stoichiometric oxide
- No diffusion of oxygen ions  $\longrightarrow$  Low ionic conductivity

• Cubic phase (arystotype)

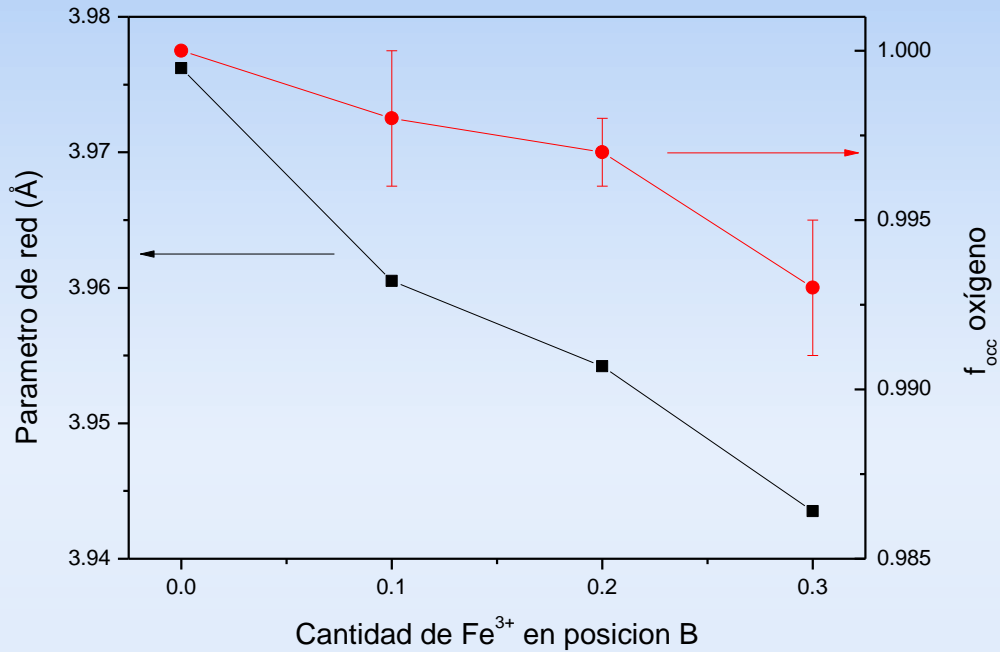
↓  
• Not suitable for IT-SOFC

• WE AIM

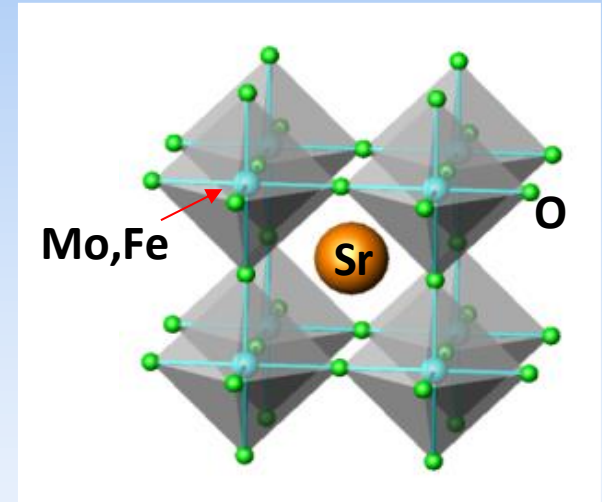
• Chemical Substitution in  $\text{SrMoO}_3$  with aliovalent B elements ( $\text{SrMo}_{1-x}\text{B}_x\text{O}_{3-\delta}$ )  $\rightarrow$  introduce oxygen vacancies  $\rightarrow$  mixed ionic-electronic conductor, useful as anode in SOFC

• B = Fe, Cr, Ga, Mg...

# • $\text{SrMo}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ : crystallographic characterization



• Space group:  $Pm-3m$

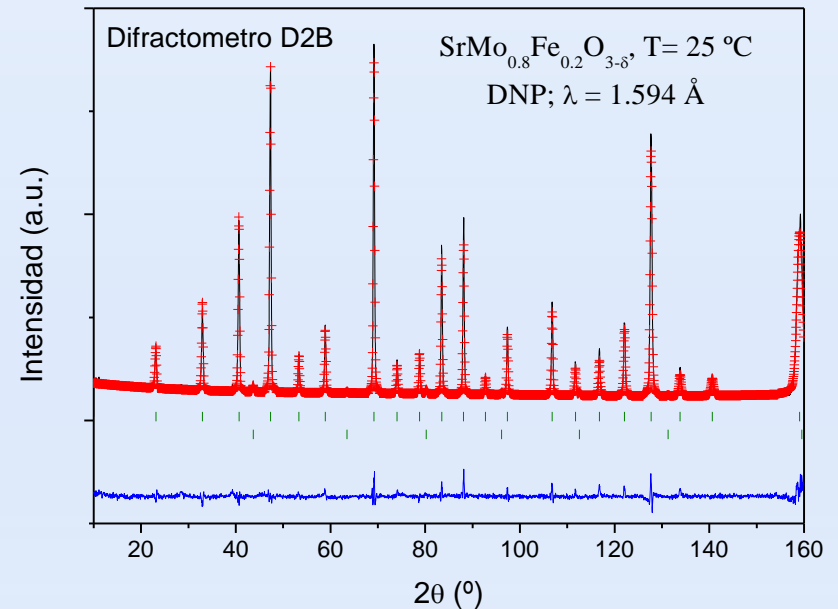


• Unit-cell parameters decrease with Fe contents

•  $\text{SrMo}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$  ( $\delta \sim 0$ )

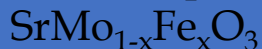
↓

•  $\text{Sr}(\text{Mo}^{\text{IV}}\text{Mo}^{\text{V}})_{0.8}\text{Fe}_{0.2}\text{O}_3$  (Mixed Mo valence)



# SrMo<sub>1-x</sub>Fe<sub>x</sub>O<sub>3-δ</sub>: reversibility, thermal expansion and performance in SOFC

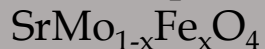
Perovskite phase



*Pm3m*

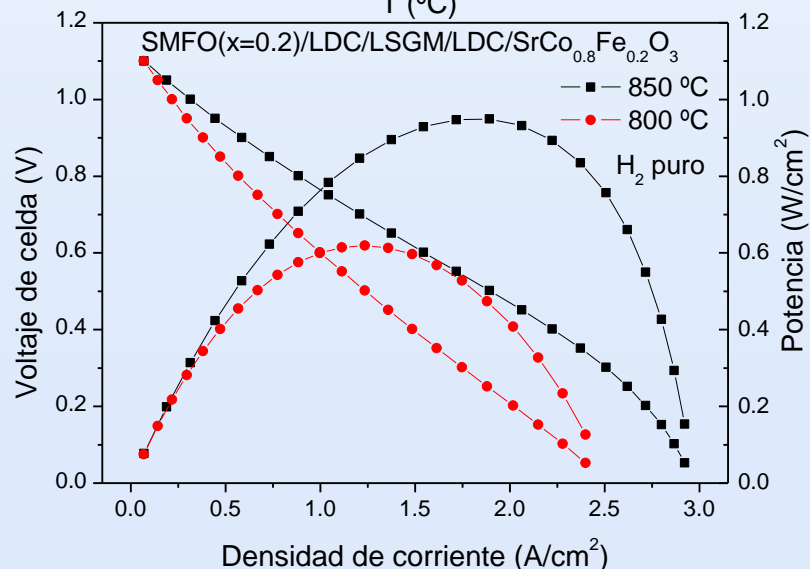
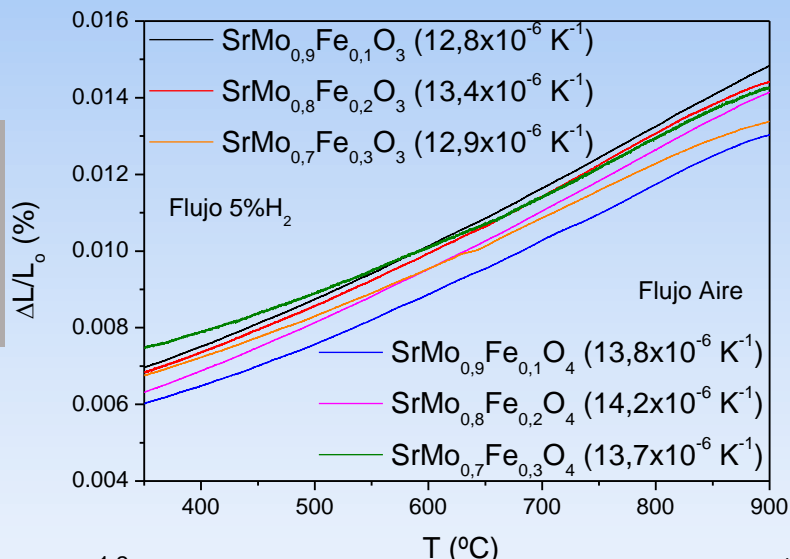
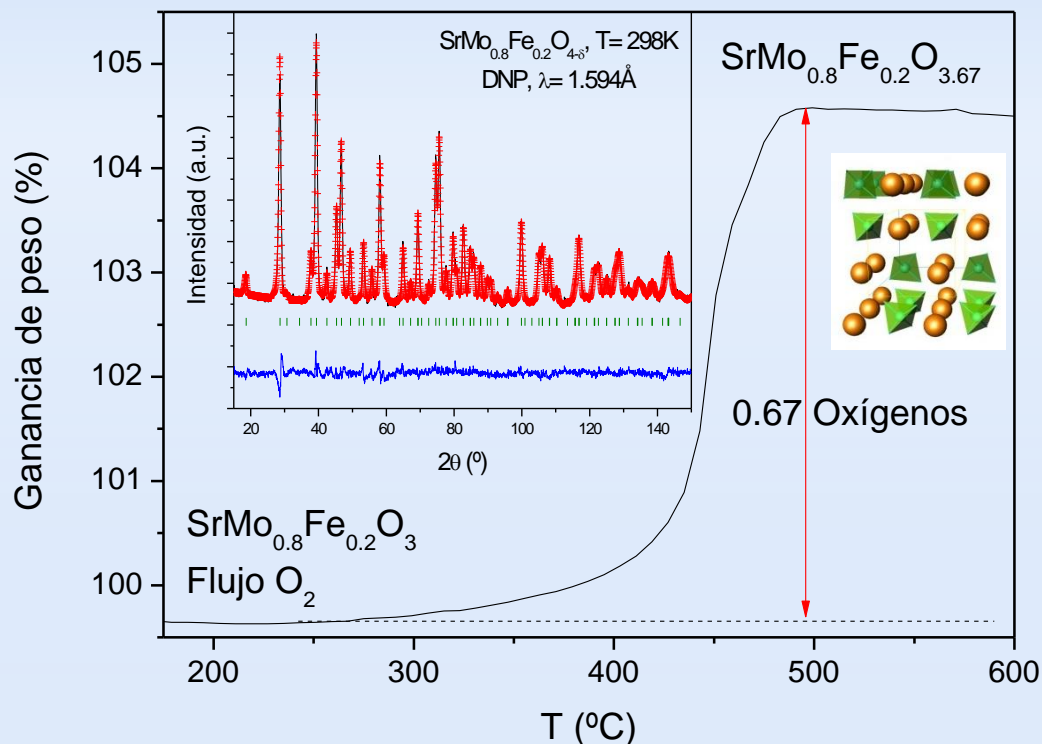
Reducing atmosphere

Scheelite phase



*I4<sub>1</sub>/a*

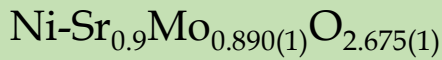
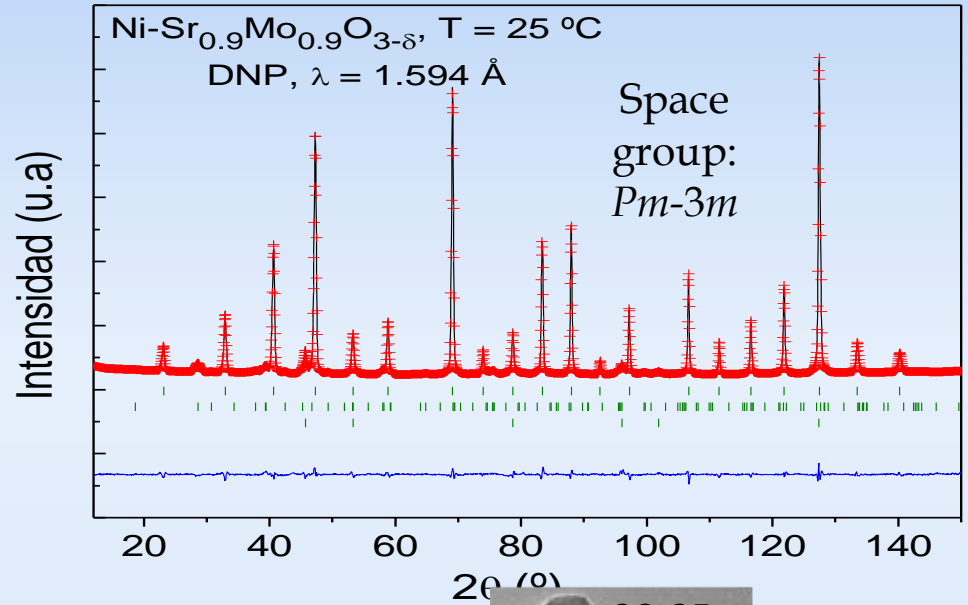
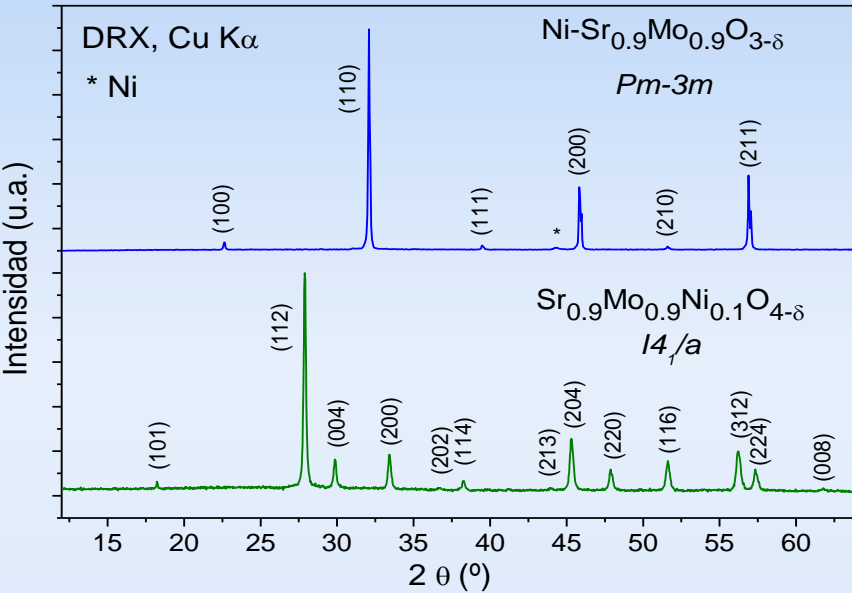
Oxydizing atmosphere



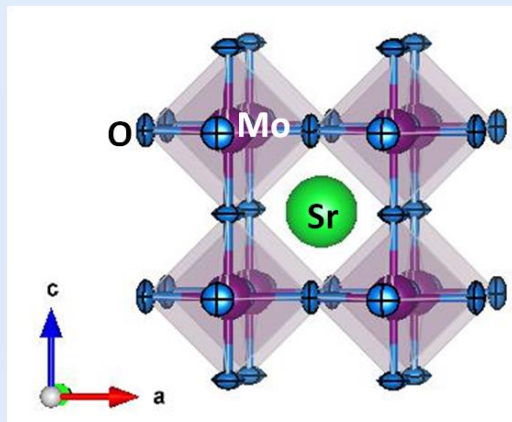
Defect Scheelite with O vacancies by NPD

R. Martínez-Coronado, et al, *J. Power Sources*, 258, 76 (2014)  
V. Cascos, et al, *Renew. Energy*, 111, 476 (2017).  
V. Cascos, et al. *Materials* 13, 4441 (2020)

# Ni-Sr<sub>0.9</sub>Mo<sub>0.9</sub>O<sub>3-δ</sub>: Segregation of Ni nanoparticles upon reduction

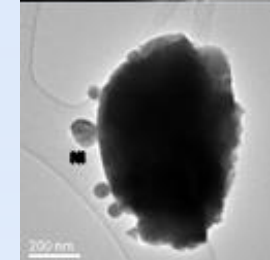
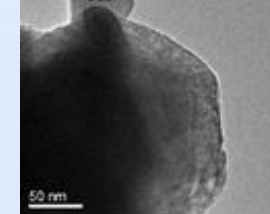


Great amount of O vacancies due to Mo and Sr deficiency



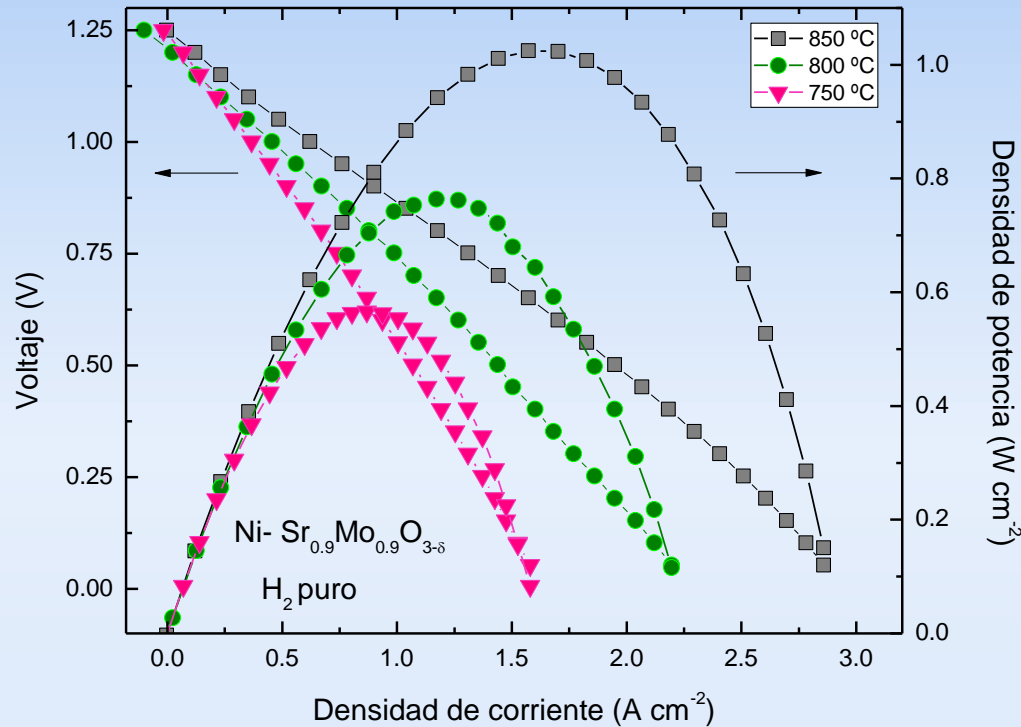
25 °C

30-35 nm



HR-TEM:  
Exsolved Ni nanoparticles at the surface of perovskite matrix

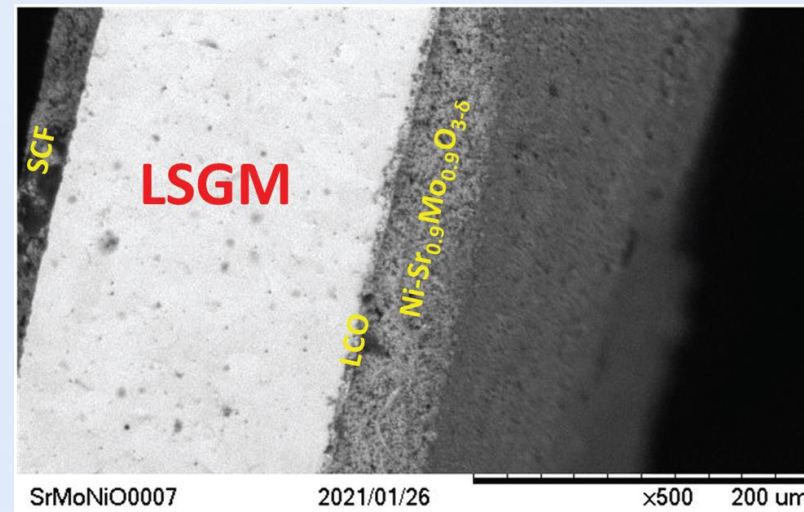
# Ni-Sr<sub>0.9</sub>Mo<sub>0.9</sub>O<sub>3-δ</sub>: single-cell tests and SEM post-mortem



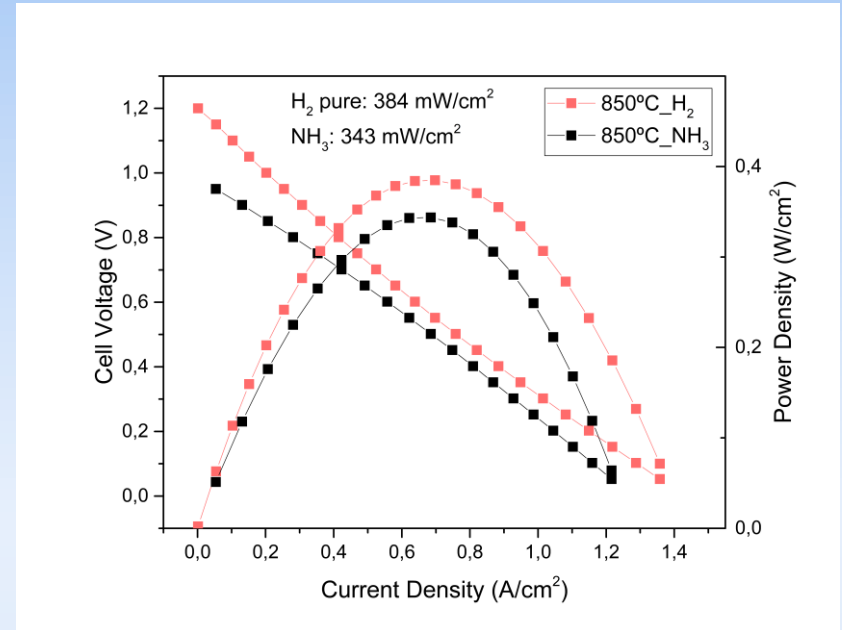
Good porosity favours gas diffusion and fuel oxidation at the anode

Excellent performance as anode materials

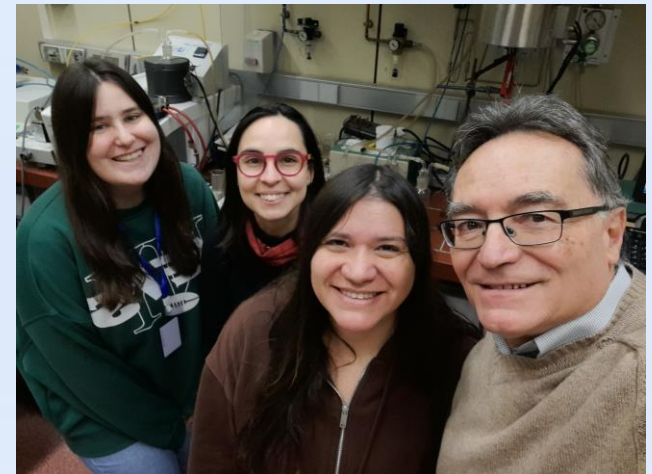
A. Larralde et al; New Journal of Chemistry 45 12041 (2021)



# Using $\text{NH}_3$ as fuel for SOFC



Preliminary results:  
A test cell with  $\text{SrFe}_{0.5}\text{Co}_{0.45}\text{Ru}_{0.05}\text{O}_3$  as cathode and  $\text{SrMo}_{0.9}\text{Fe}_{0.1}\text{O}_3$  as anode directly fed with  $\text{NH}_3$  delivers comparable power density as with  $\text{H}_2$  at 850°C.



# Conclusions

- The cubic phase (3C) of  $\text{SrCoO}_{3-\delta}$  has excellent catalytic properties for  $\text{O}_2$  reduction, as well as  $\text{O}^{2-}$  diffusion, may be stabilized with suitable doping of Co (by highly-charged elements) and outperforms as **cathode** in SOFC.
- Perovskite-type oxides derived from  $\text{SrMoO}_3$  can be suitably modified to make good **anode materials** for SOFC, advantageously replacing conventional cermet.
- Anode Materials with **exsolved Ni nanoparticles** exhibit a significant catalytic activity for  $\text{H}_2$  oxidation, in  $\text{Ni-Sr}_{0.9}\text{Mo}_{0.9}\text{O}_{3-d}$
- Test fuel cells **directly fed with  $\text{NH}_3$**  exhibit comparable power densities as those fed with pure  $\text{H}_2$  at  $850^\circ\text{C}$ , with  $\text{SrMo}_{0.9}\text{Fe}_{0.1}\text{O}_3$  as anode material.
- Neutron diffraction is a powerful tool in the characterization of **energy-related materials**, helping to establish structural features related to the performance as electrodes, in MIEC oxides.

# Thank you for your attention



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Mónica Chivite

Dra. M.T. Fernández-Díaz (ILL)

Dra. Loreto Troncoso (U. Austral, Valdivia)

Dra. Ana Larralde (U. San Martín, Buenos Aires)

Dra. Patricia Rivas (U. San Martín, Buenos Aires)