# Self-Regulating Surface Chemistry for More Robust Highly Durable SOFCs

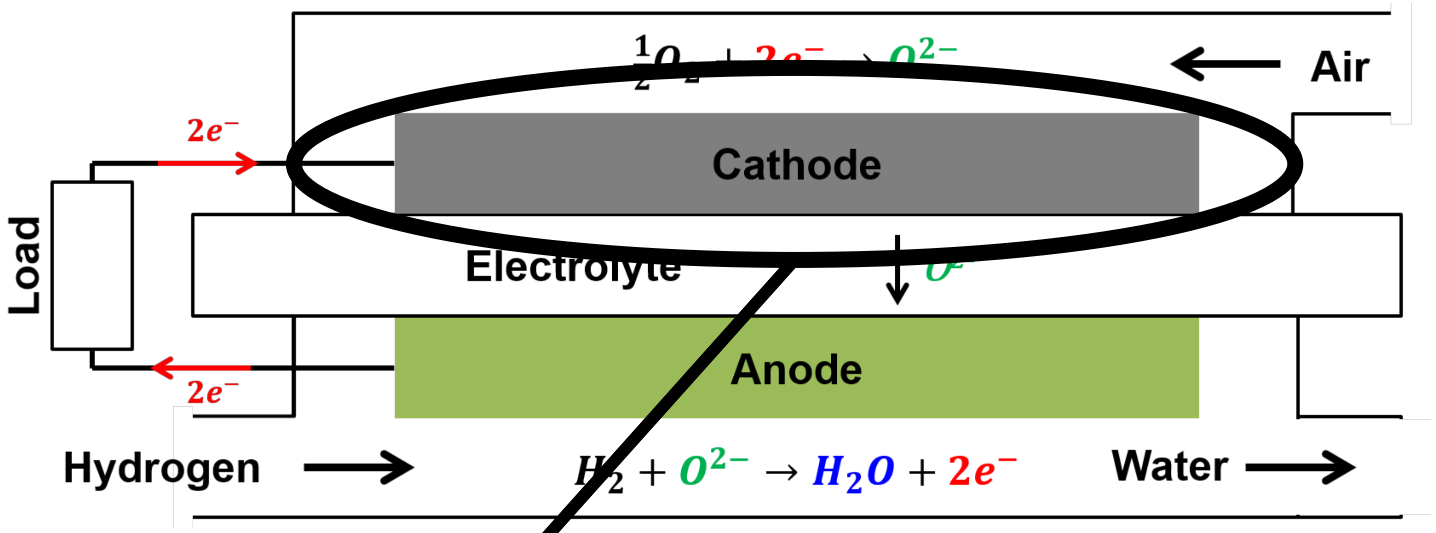
Clement Nicollet, Harry Tuller
Massachusetts Institute of Technology

**18th Annual Solid Oxide Fuel Cell (SOFC) Project Review Meeting**

NATIONAL ENERGY TECHNOLOGY LABORATORY

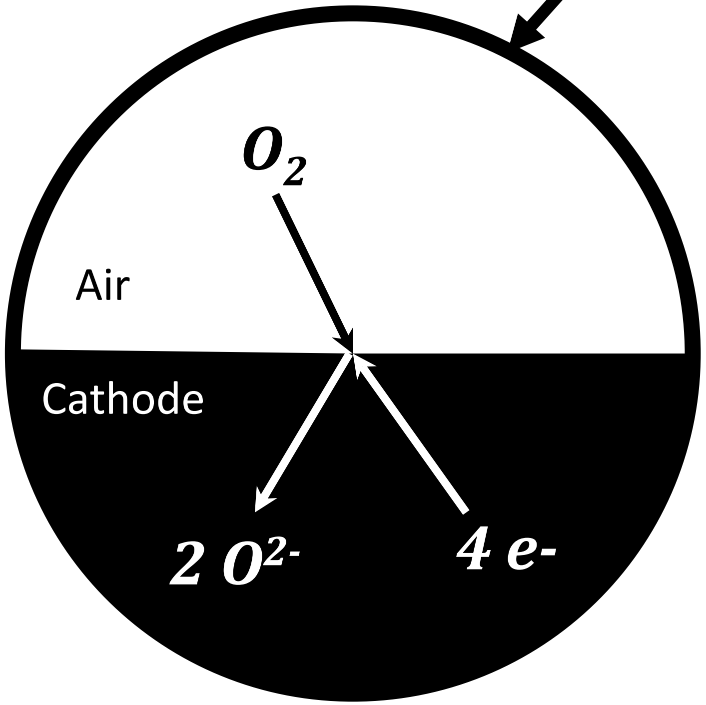
Massachusetts Institute of Technology

# Solid Oxide Fuel Cells




High efficiency
Fuel flexibility
Highly scalable
Produces usable steam (CHP applications)

Main drawback to address: performance degradation



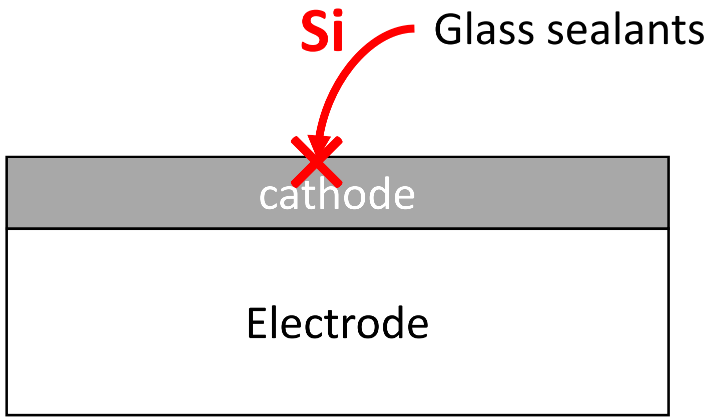

Oxygen Reduction Reaction limited by solid/gas surface exchange reaction rate

Surface reaction very sensitive to contaminants

→ major source of performance degradation

# Main sources of cathode performance degradation

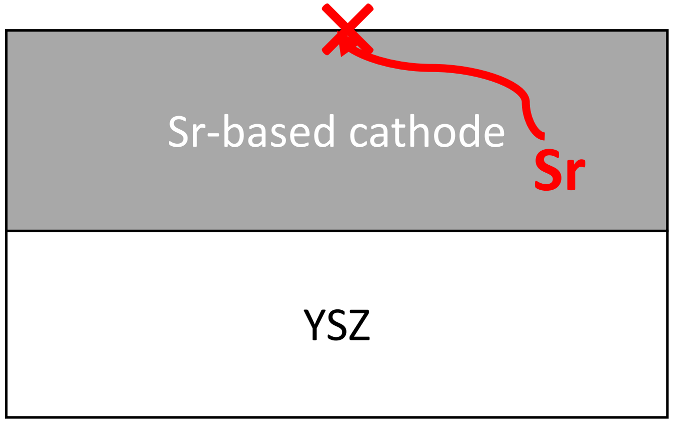
## Si poisoning




Formation of insulating silica blocking active sites

Silicon poisoning observed on YSZ/Pt system (*Hertz, Rothschild, Tuller, J. Electroceram. 22 (2009) 428-435*)

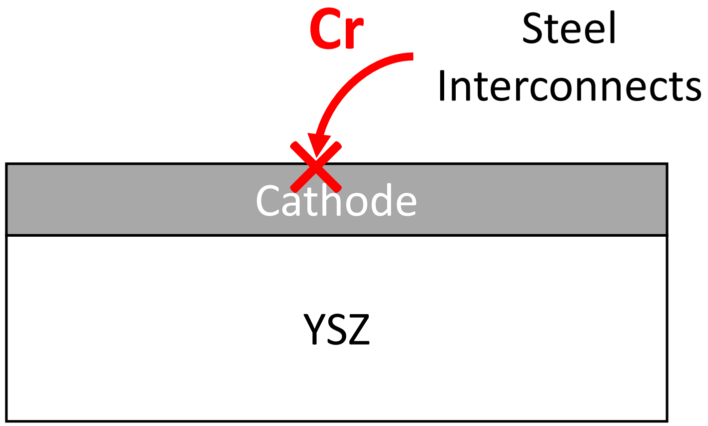
## Sr segregation




Formation of surface SrO blocking active sites

*W. Jung, H.L. Tuller, Energy Environ. Sci., 2012, 5, 5370–5378*

## Cr poisoning

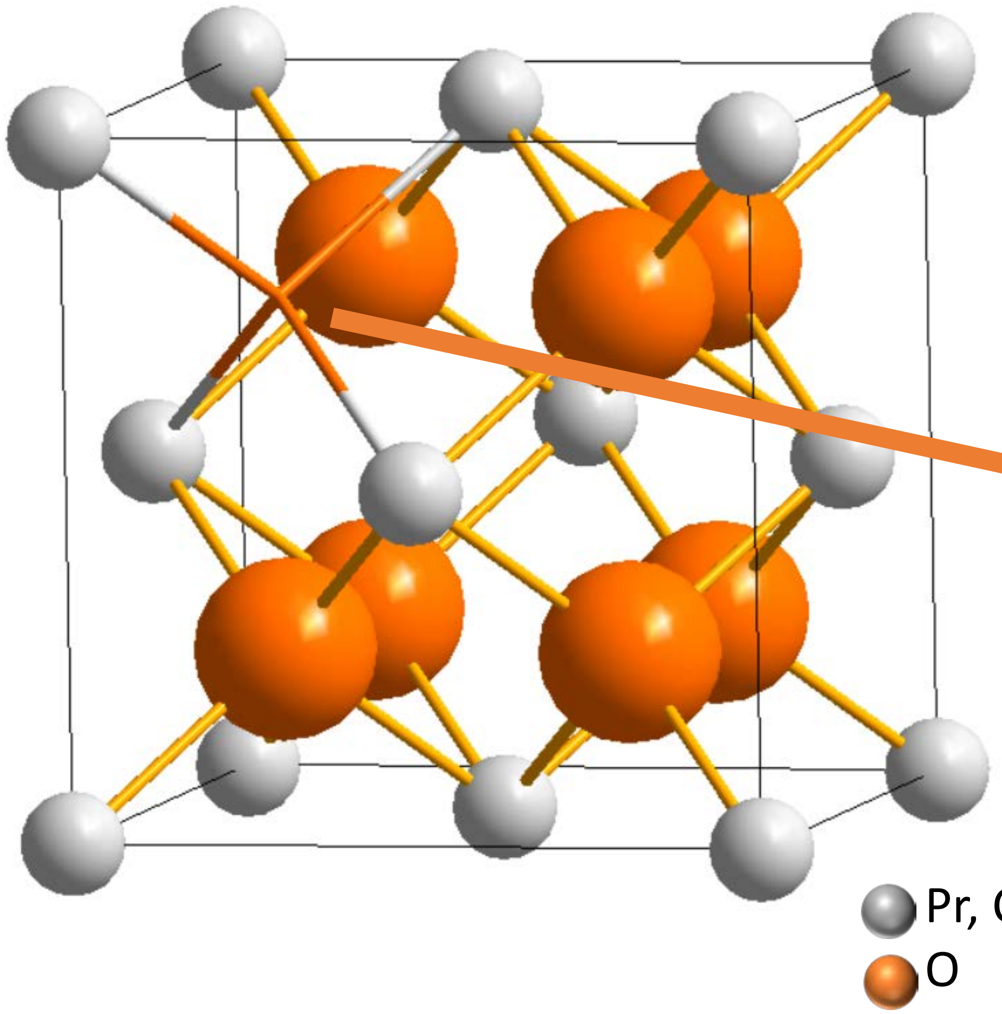



Cr volatile species:
Formation of $Cr_2O_3$ blocking active sites

Review paper: *S. P. Jiang, X. Chen Int. J. Hydrogen Energy* **2014** , *39* , 505

Initial Project focus

# Model mixed conductor as cathode material – Pr doped ceria (PCO)




Fluorite $CaF_2$ type structure

Pr mixed valence 3+/4+

$O^{2-}$ vacancies

High $O^{2-}$ Diffusion &
Electrochemical activity
Sr-free

# Outline

- Characterization techniques of surface chemistry

- Si poisoning on Pr doped ceria –previous work

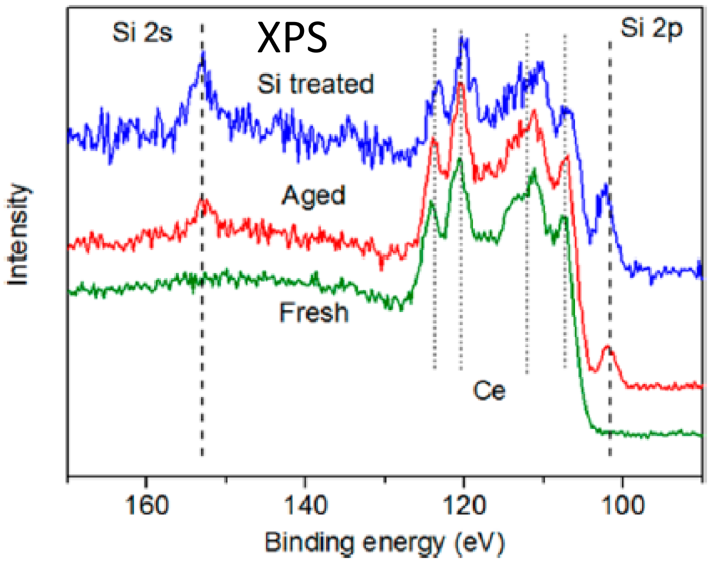
- Presentation of the project

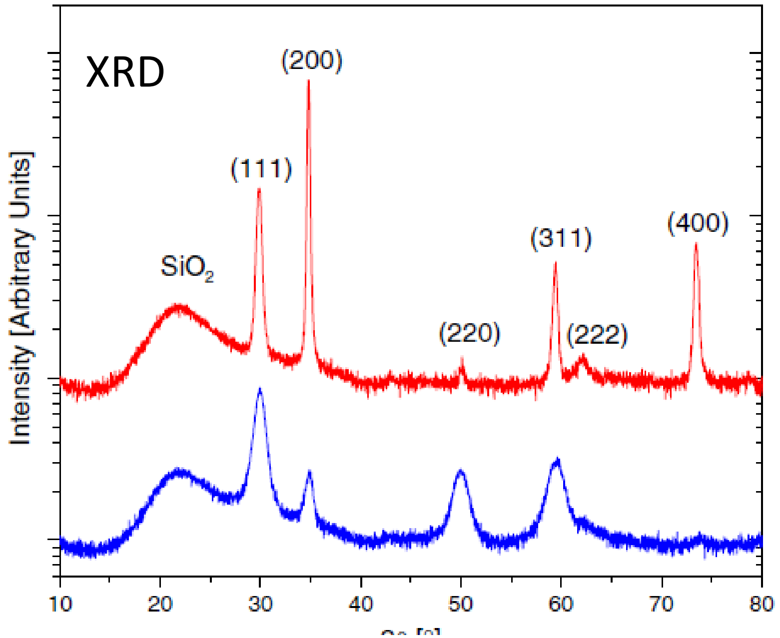
- First results

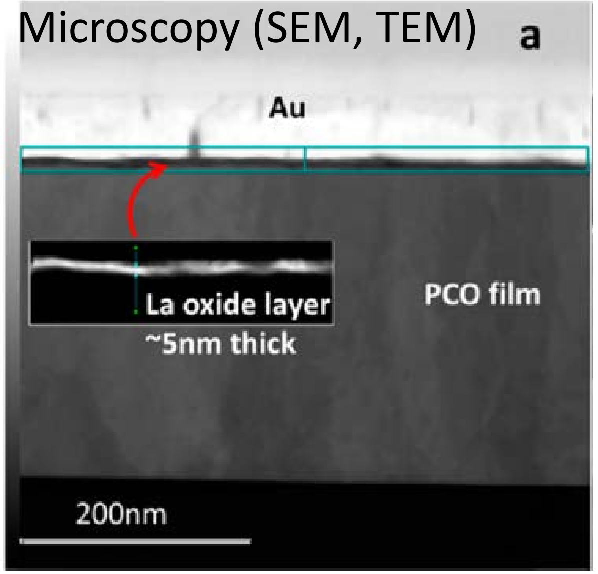
# How to characterize surface poisoning?

# How to characterize surface poisoning

Structure & morphology



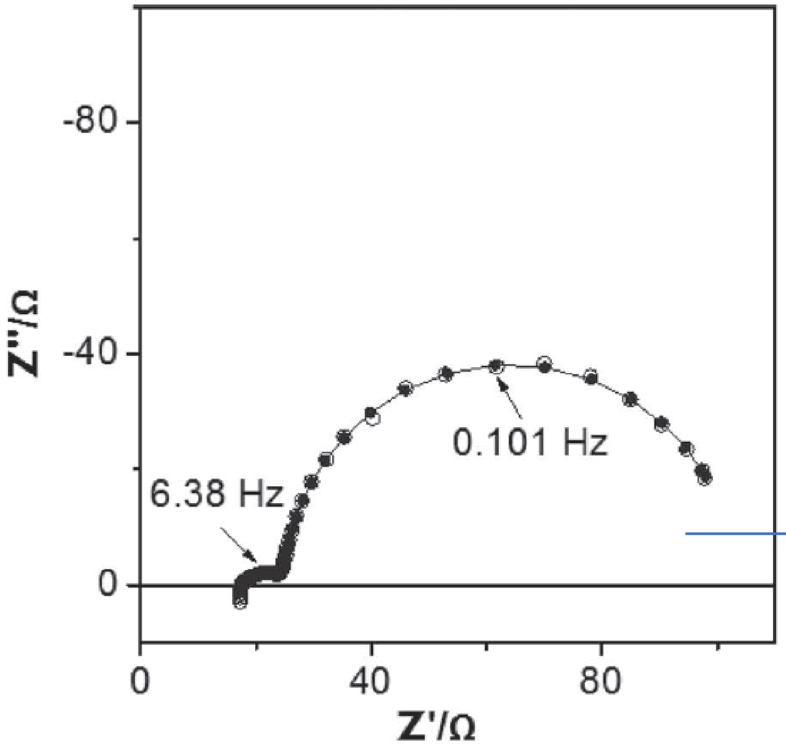



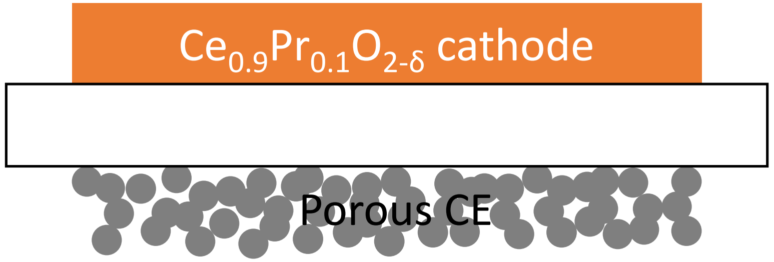

No information on catalytic activity

# Characterization techniques – Oxygen surface reaction rate

Electrochemical Measurements

Impedance Spectroscopy




Thin film electrode

Oxygen reduction limited by surface exchange

$$R_{surface} = \frac{RT}{4F^2}\frac{1}{2r_0}$$

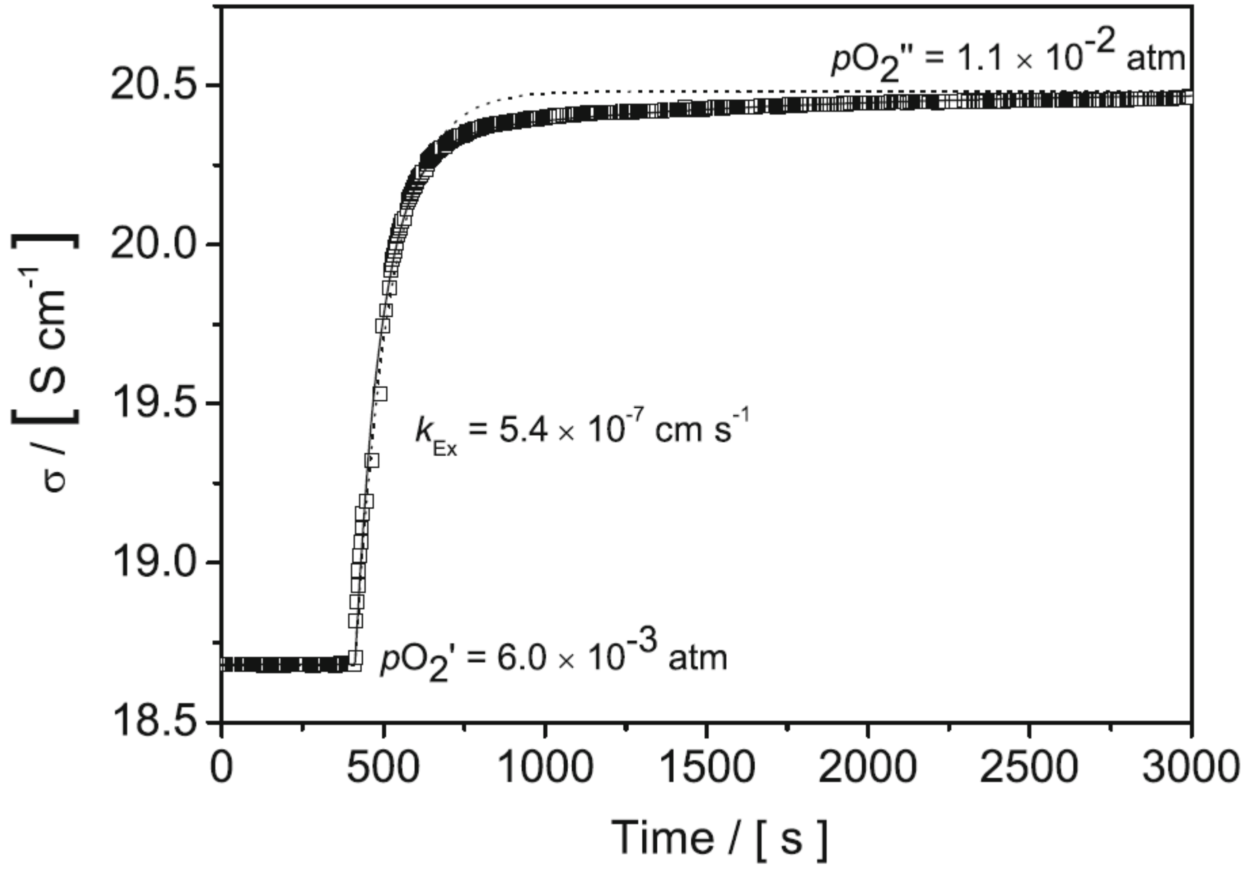
Surface Exchange Reaction Rate

*S.B. Adler, Chem. Rev.* ***2004,*** *104, 4791-4843*

Drawback : Potential influence of metal contacts on surface exchange

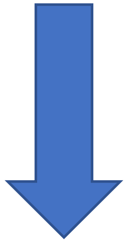
# Characterization techniques – Oxygen surface reaction rate

Conductivity relaxation: Change in conductivity after a step in $pO_2$




*Søgaard, Tuller et al., J. Electroceram. (2011) 27:134–142*

Fit of transient regime



Determination of diffusion coefficient and Surface exchange coefficient

Drawback: need for highly dense bulk ceramics or films and potential impact of metal electrodes on exchange rate.

# Optical Absorption in $Ce_{0.9}Pr_{0.1}O_{2-\delta}$

The color of PCO depends on Pr valence

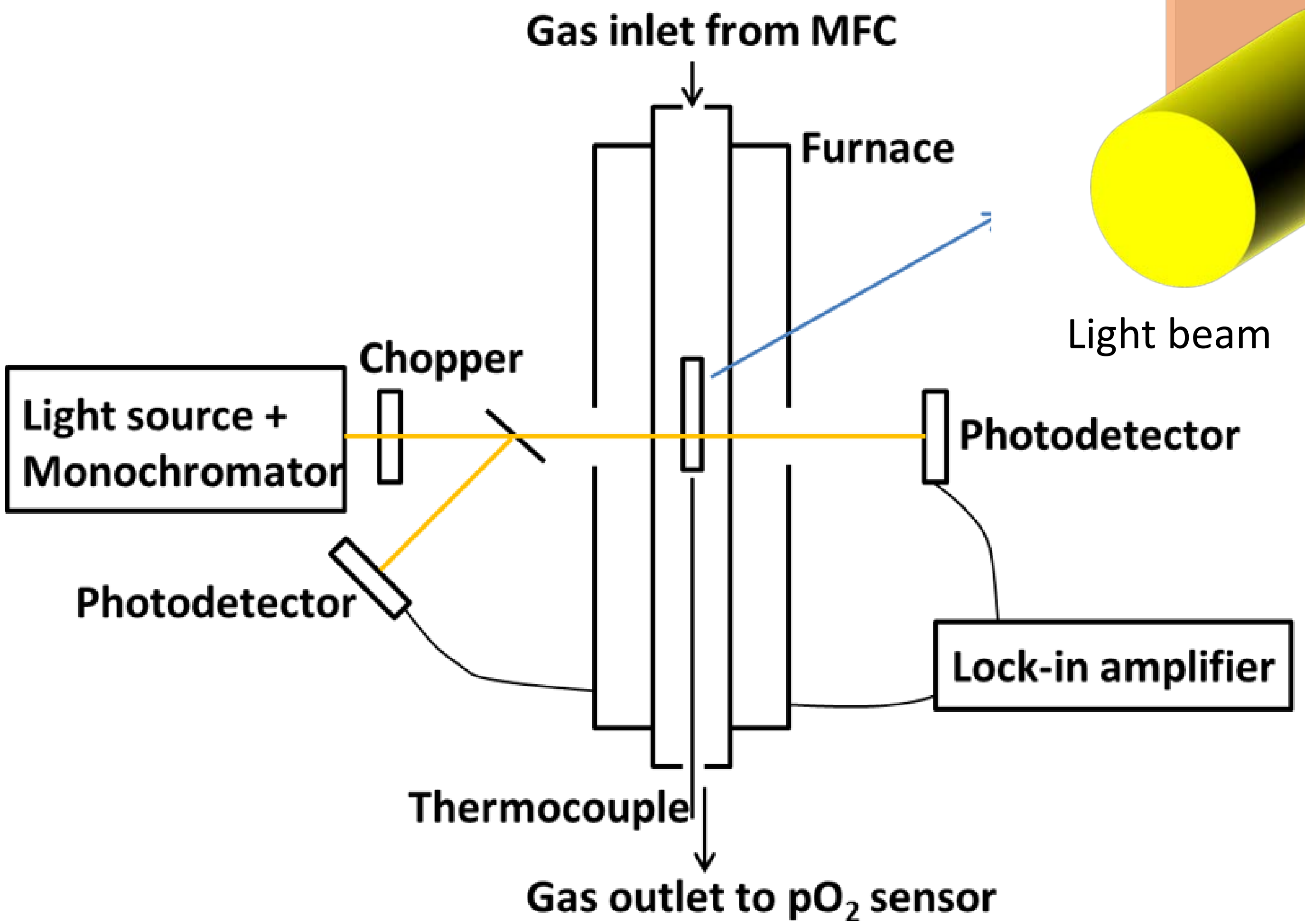
Films prepared by PLD


Optical Absorption ↔ oxygen non-stoichiometry

**Possibility to characterize oxygen exchange reaction by optical measurements**

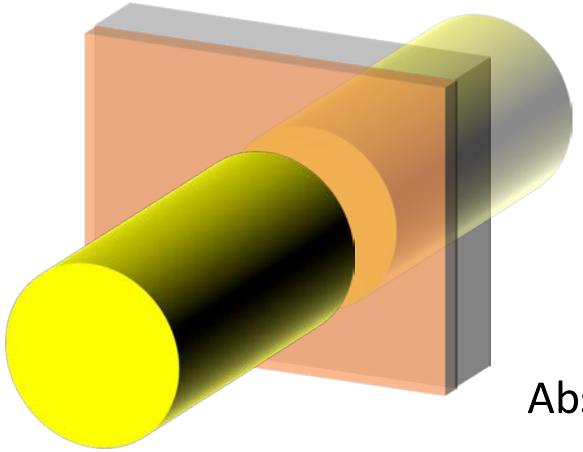
*J.J. Kim. S.R. Bishop, N.J. Thompson, D. Chen and H.L. Tuller, Chem. Mater. 2014, 26, 1374−1379*

# Optical Absorption in $Ce_{0.9}Pr_{0.1}O_{2-\delta}$




PCO film//YSZ

Transmitted Light beam



Light beam

Color of PCO depends on Pr valence

Absorption ↔ oxygen non-stoichiometry

Beer-Lambert law

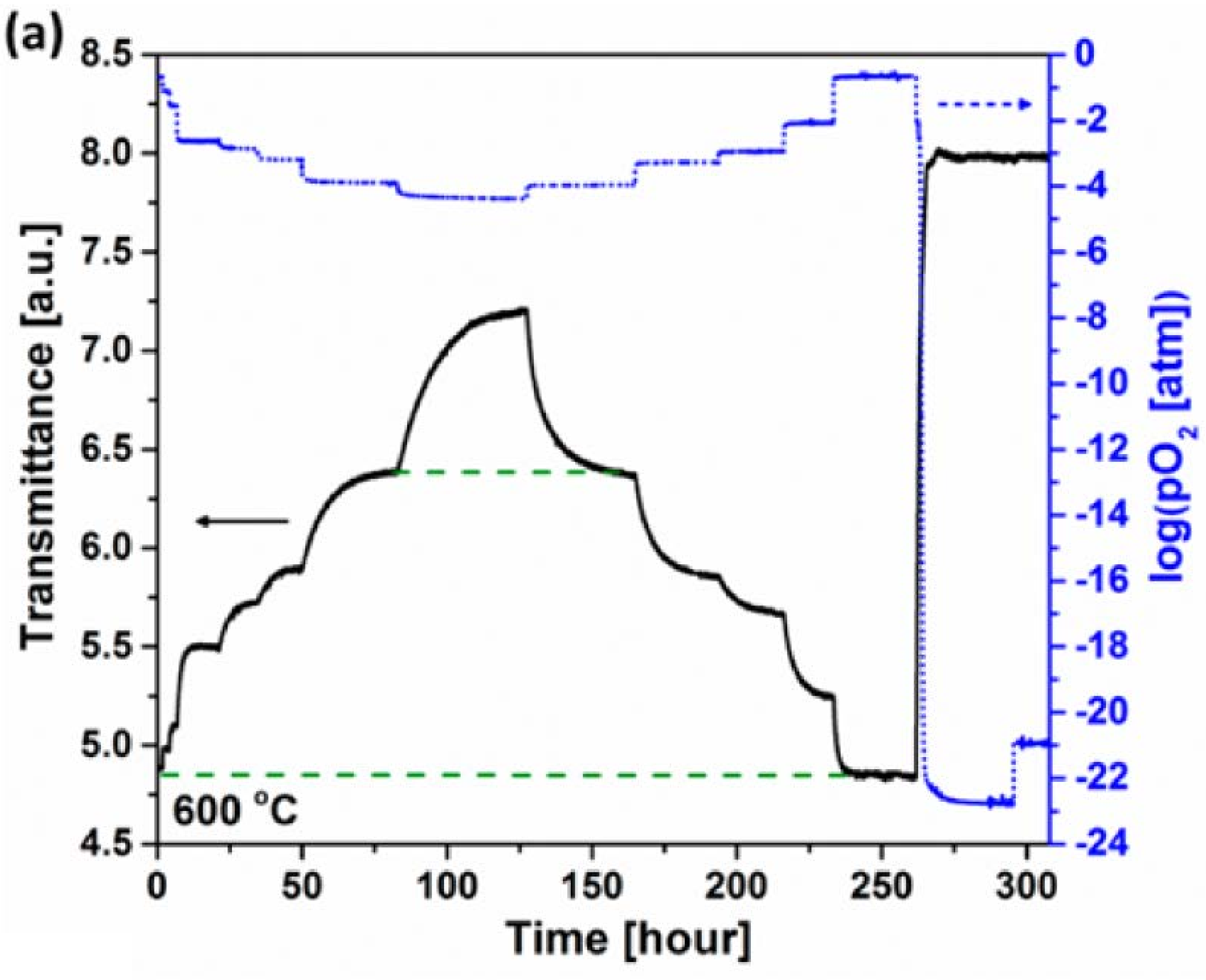
$$\alpha_{Pr^{4+}} = \varepsilon_{Pr^{4+}}[Pr^{4+}]$$

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

**Advantage: no electrical contacts**

*J.J. Kim et al., Chem. Mater. 2014, 26, 1374−1379*

# Optical Absorption in PCO




Step in $pO_2$

Change in Oxygen non stoichiometry

Transmittance Relaxation

**Surface exchange coefficient**

*J.J. Kim et al., Chem. Mater. 2014, 26, 1374−1379*

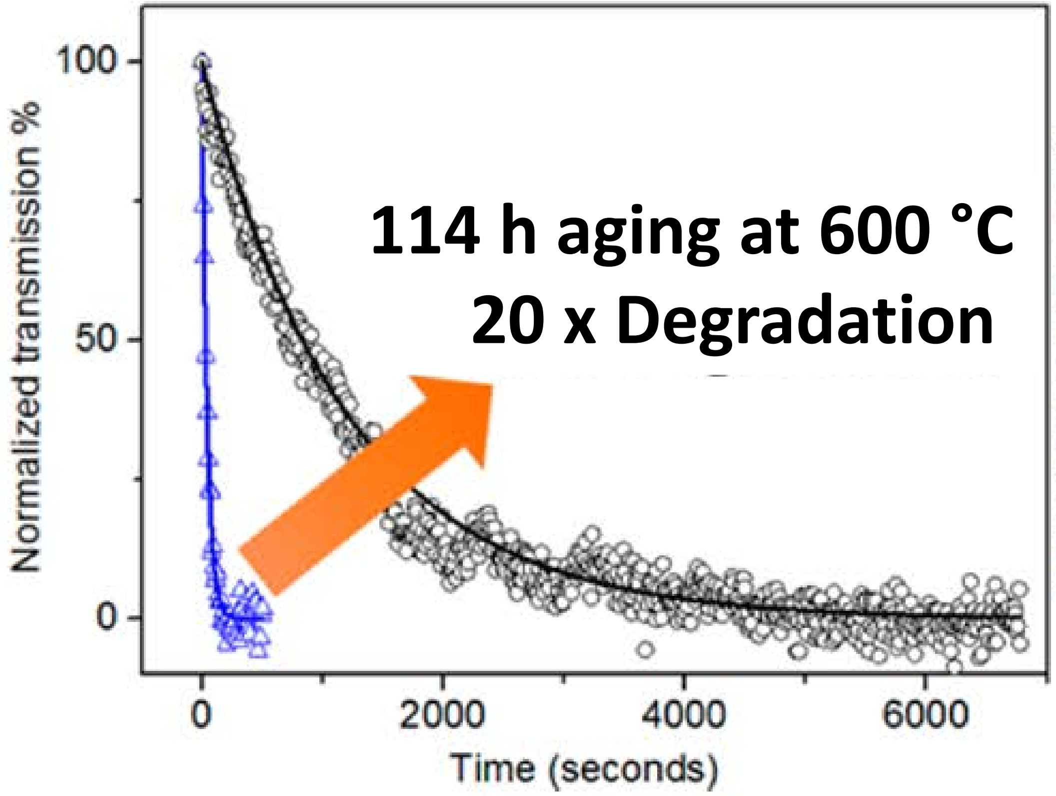
# Si poisoning on PCO oxygen electrodes

# Scavenging Si poison with La in PCO films

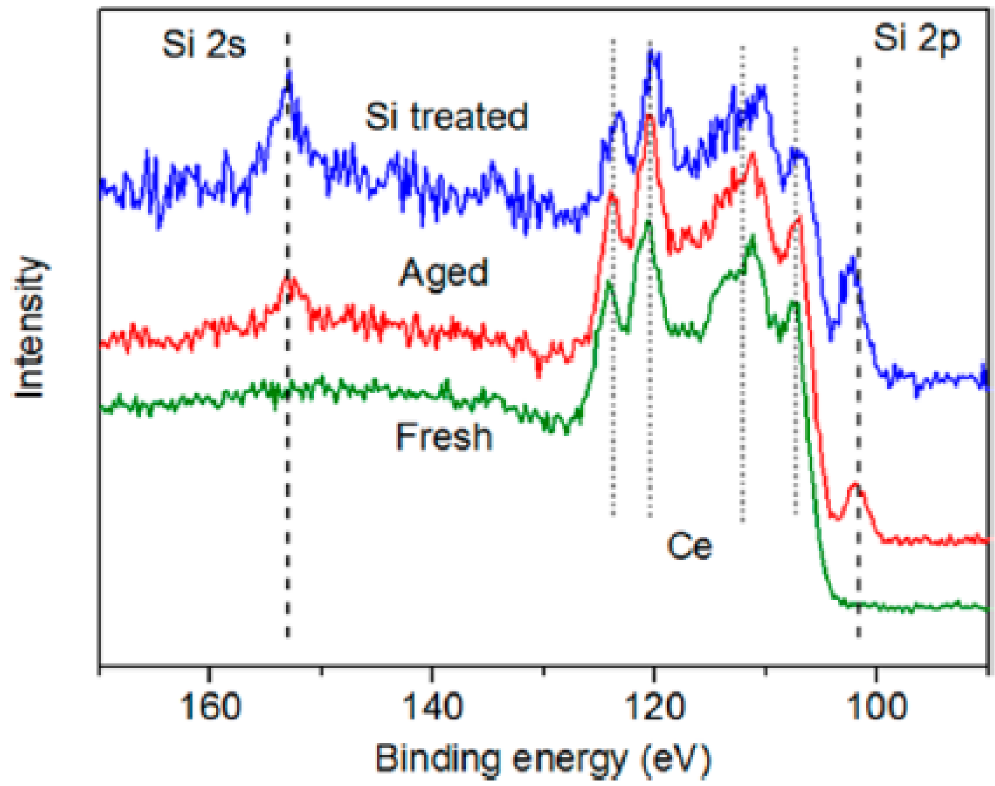
*L. Zhao, S.R. Bishop et al. Chem. Mat. 27 (2015) 3065-3070*

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

YSZ

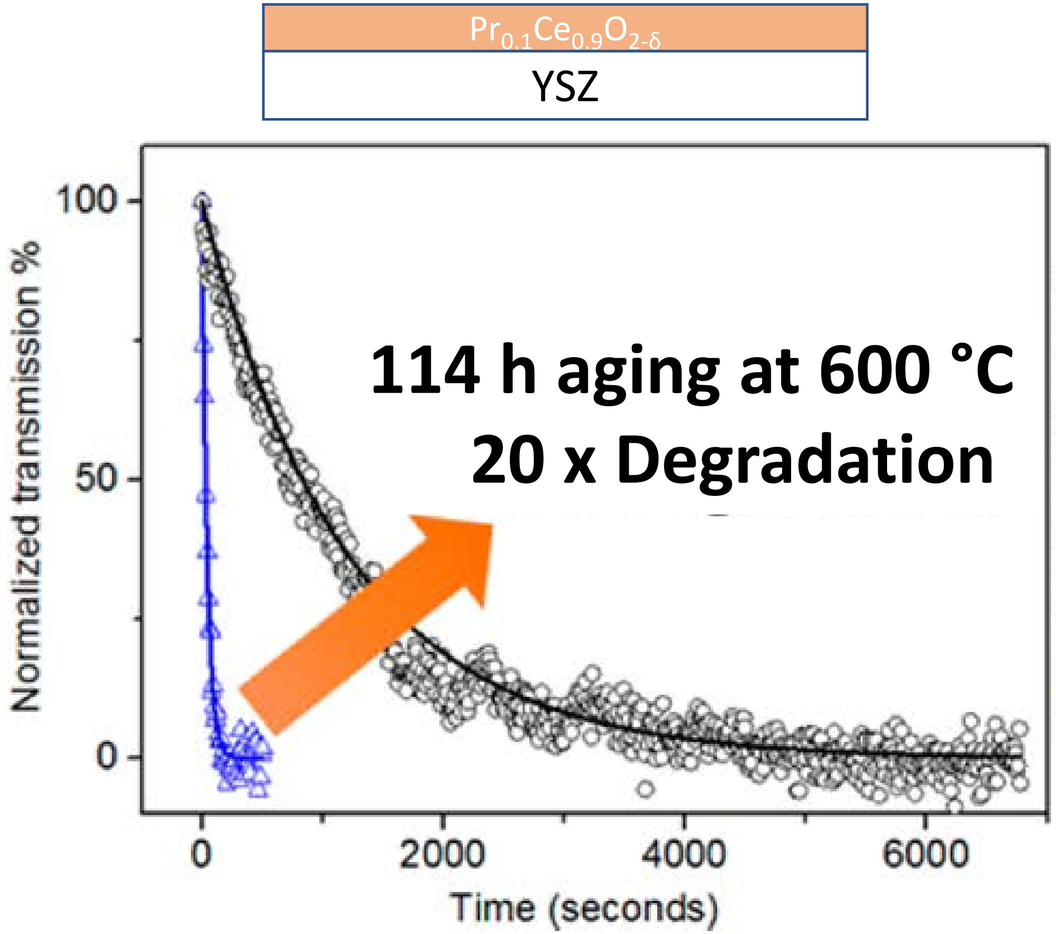


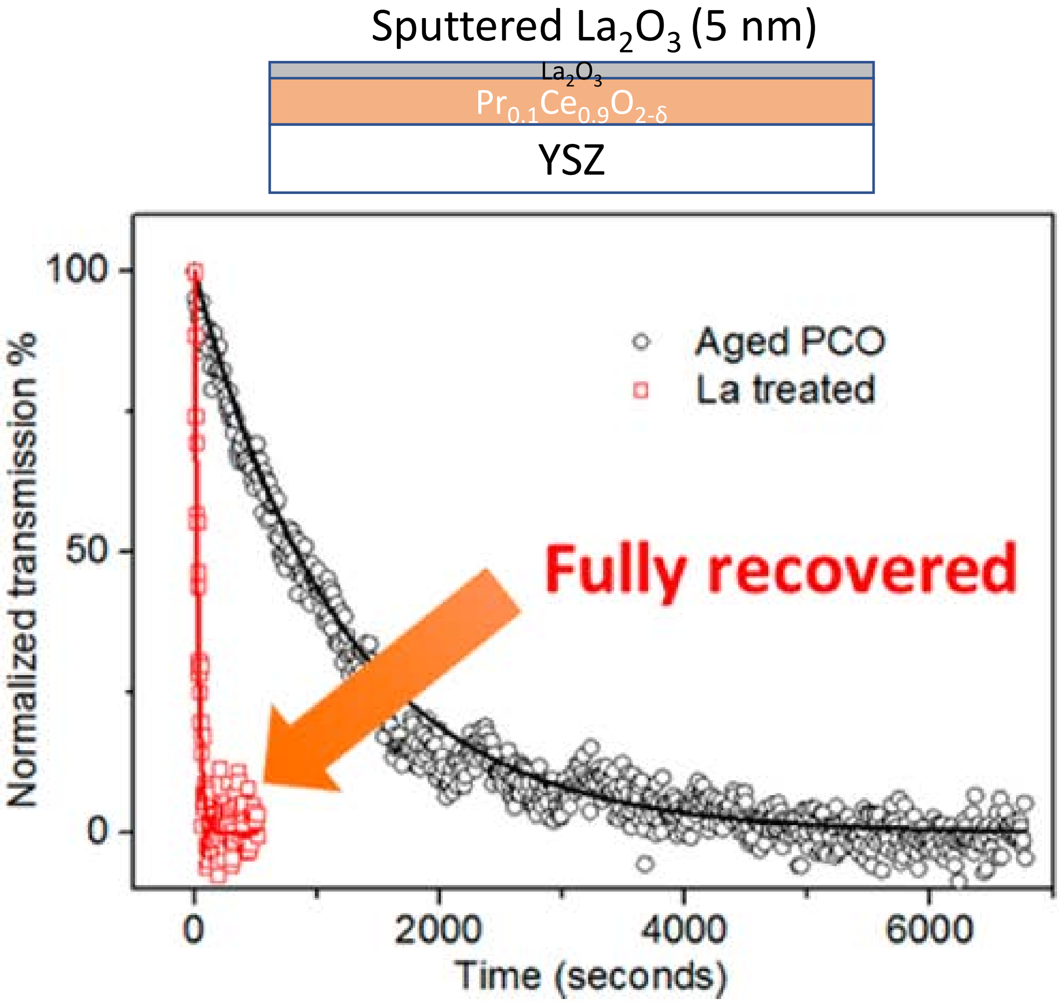

X-ray photoelectron spectroscopy



# Scavenging Si poison with La in PCO films

*L. Zhao, S.R. Bishop et al. Chem. Mat. 27 (2015) 3065-3070*

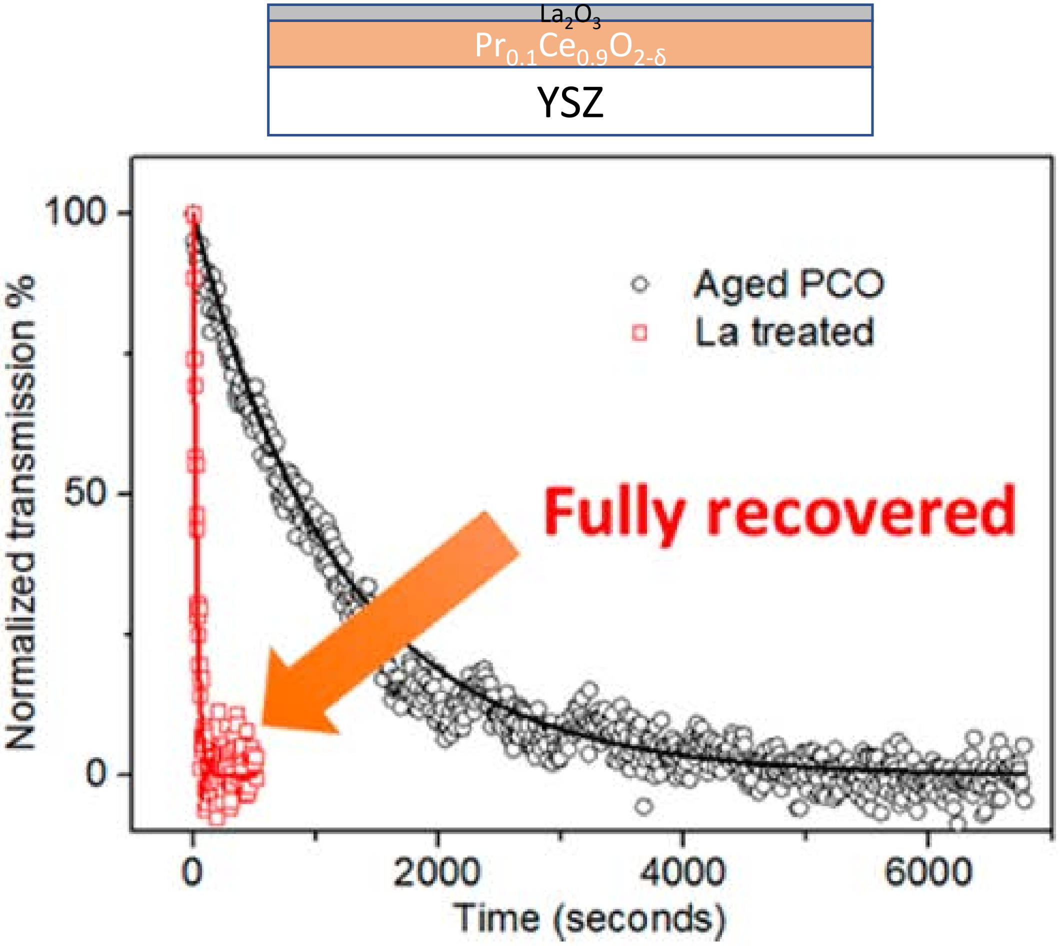



La layer traps Si → surface exchange rate recovered

# Example of scavenging Si segregant with La in PCO films

*L. Zhao, S.R. Bishop et al. Chem. Mat. 27 (2015) 3065-3070*




## Project objectives

How does it work?

$La_2O_3$ react w/ Si ?

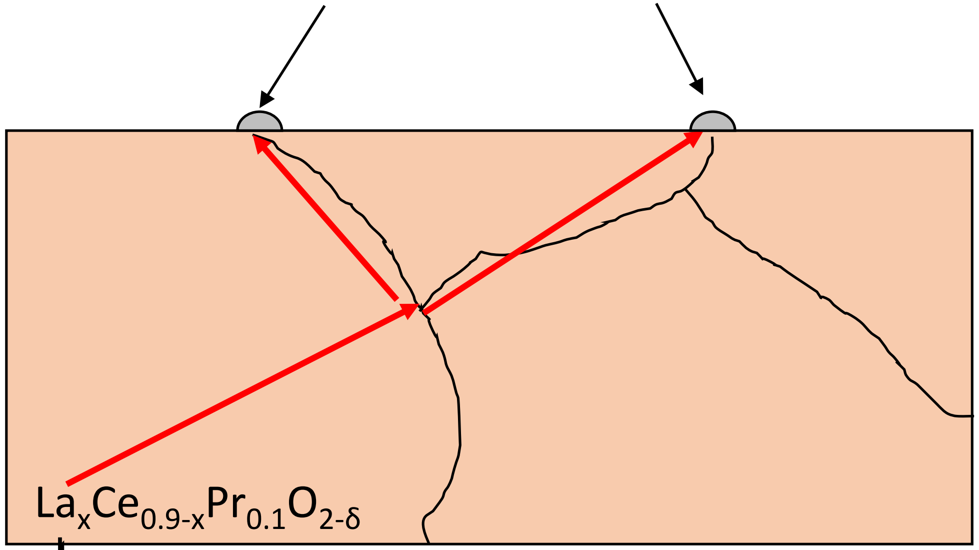
$La_2O_3$ breaks Si layer?

$La_2O_3$ sputtering → not practical under operation

# Exsolution Proposal

## Internal renewable source of La getter

Exsoluted La particles → Getter Si poisoning




Scavenging element introduced into ceria in high concentration

| $Ce^{4+}$ | $Pr^{3+/4+}$ | $La^{3+}$ |
| --- | --- | --- |
| 0.97 Å | 1.126/0.96 Å | 1.16 Å |

Source of scavenging elements to enable long term operation

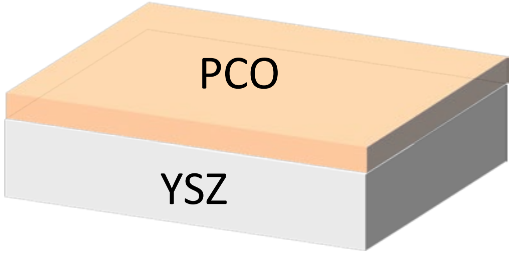
**Self-Cleaning Material**

# Three approaches – Three tasks

## Study on powders

**Objectives:**
Determination of La solubility in PCO
Determination of exsolution thermal treatment

## Study on films




**Objectives:**
Study of $La_2O_3$ effect on surface exchange
Study of their efficacy on Si and Cr poisoning

## Study on real SOFC cathodes

Electrochemical performance and stability
At realistic operating conditions

# Study of exsolution mechanisms on powders samples

**Selection of La amounts in and $Ce_{0.9}Pr_{0.1}O_{2-\delta}$ (PCO)**

Citrate-nitrate Synthesis of La-PCO

Determination of Solubility limit

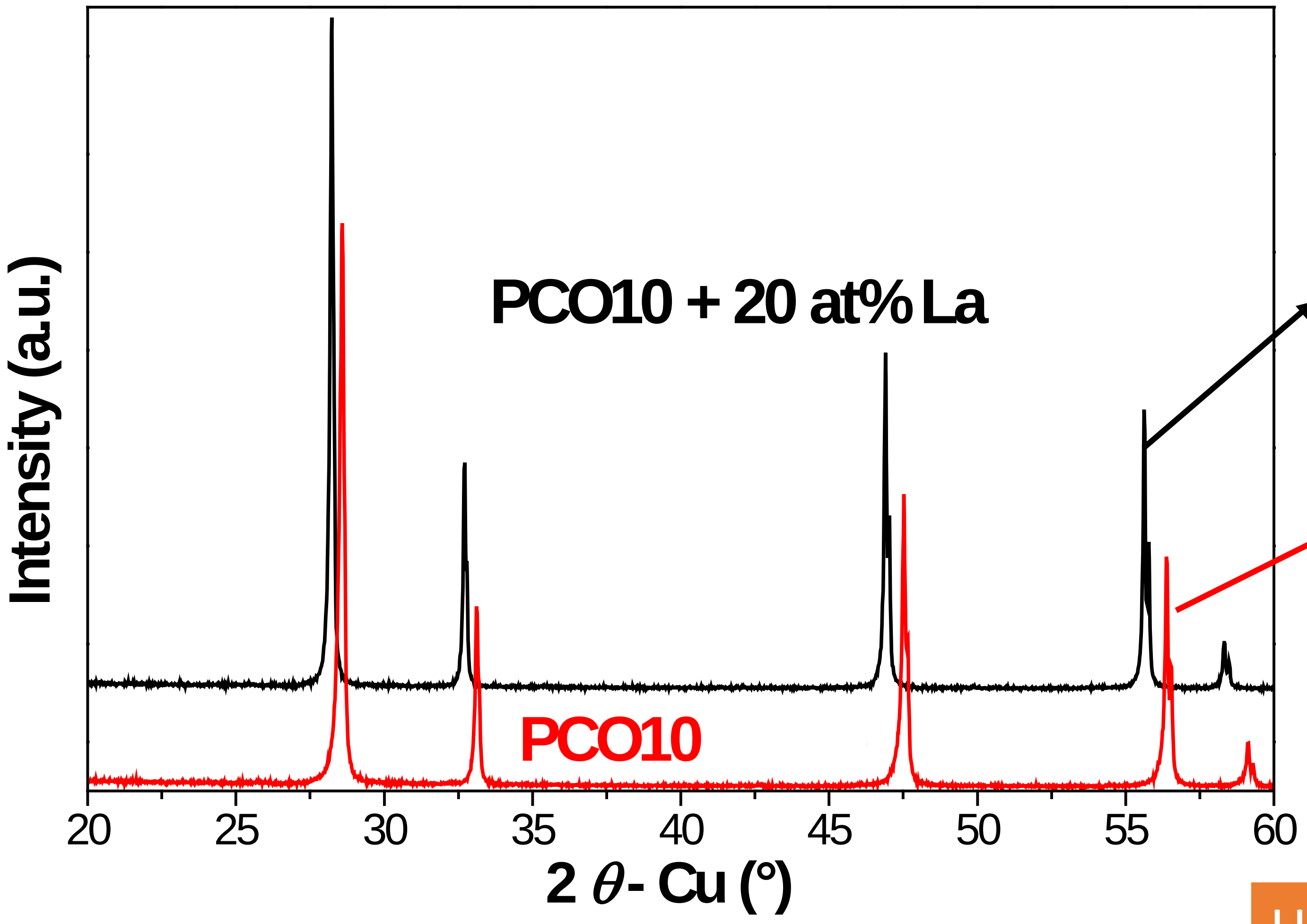
PCO - 10 at% La
PCO - 20 at% La

Determination of Exsolution thermal treatment

Preparation of Pulsed Laser Deposition Targets for film deposition

# Powder Synthesis – Combustion method

X-ray diffraction on synthesized powders




a = 5.4775 Å

a = 5.4084 Å

Fluorite structure (SG: Fm-3m)

La insertion in ceria
Significant increase in lattice parameter

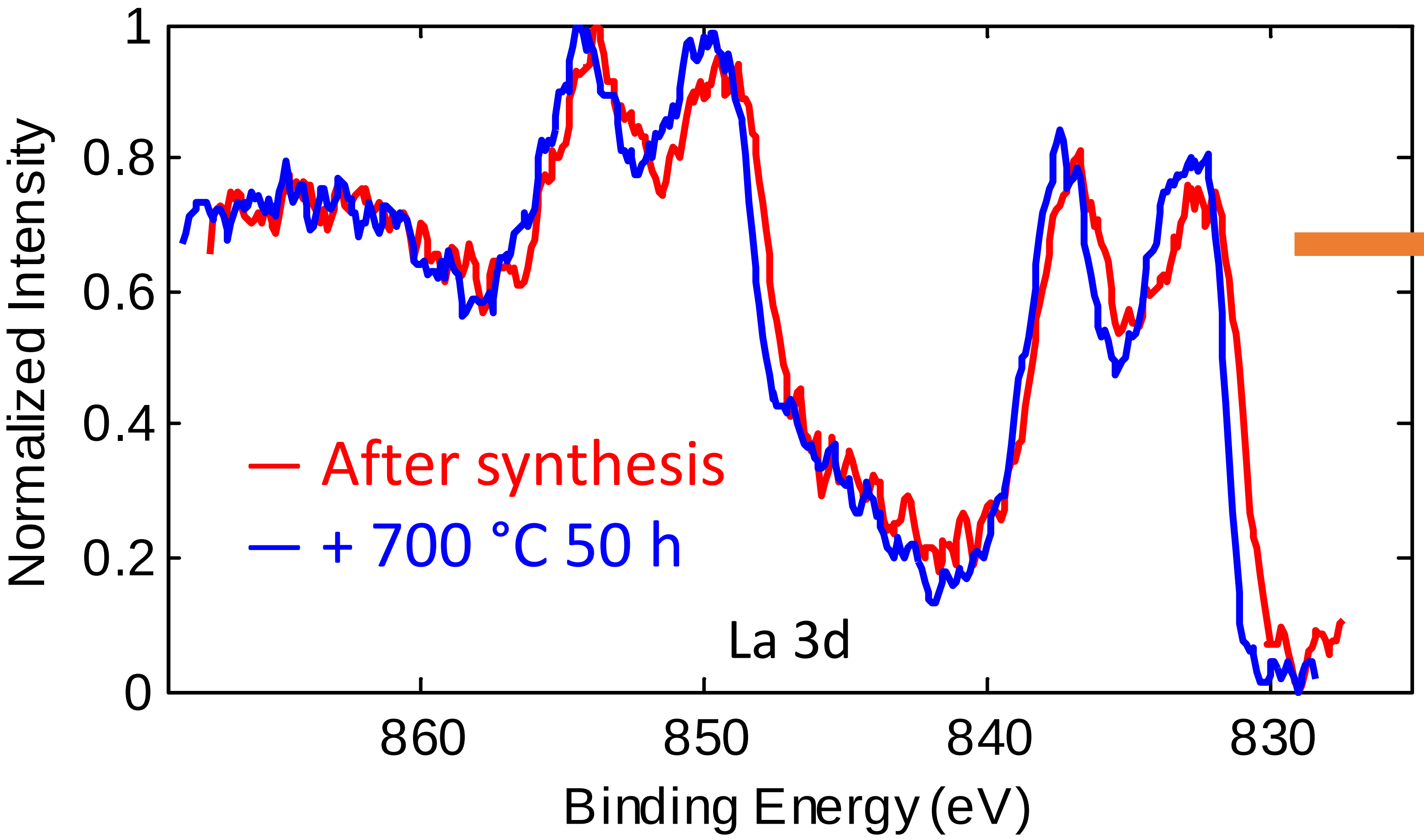
No impurities → 20 % La fully soluble in PCO

How to make La segregate on surface?

# Exsolution on powder

Thermal treatment on PCO10 - 20% La at 700 °C for 50 h

X-ray photo electron spectroscopy




No significant change before & after treatment

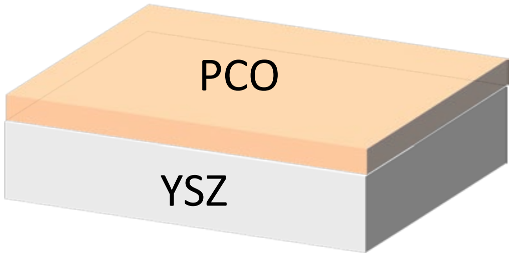
Longer treatment (500 h) in progress

# Three approaches – Three tasks

## Study on powders

**Objectives:**
Determination of La solubility in PCO
Determination of exsolution thermal treatment

## Study on films



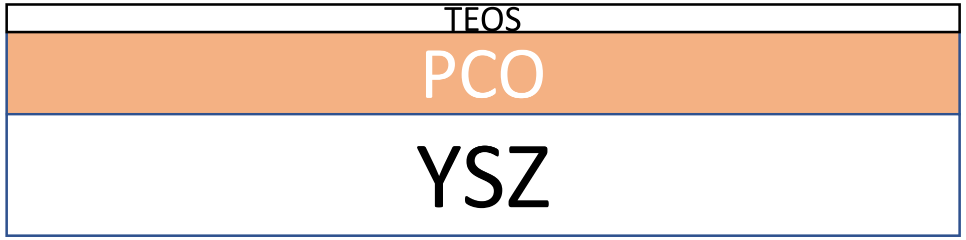

**Objectives:**
Study of $La_2O_3$ effect on surface exchange
Study of their efficacy on Si and Cr poisoning

## Study on real SOFC cathodes

Electrochemical performance and stability
At realistic operating conditions

# Understanding the role of La on Si poisoning

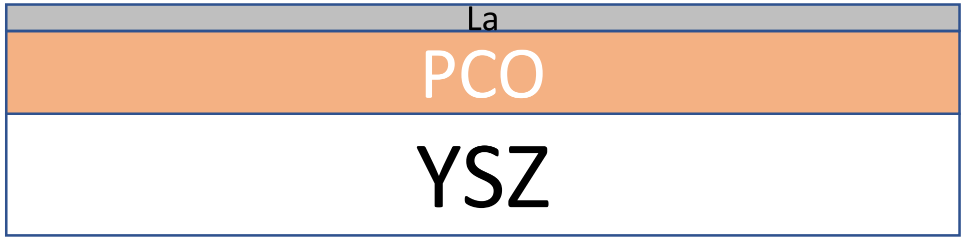
Bringing Si in a controlled way → Tetra Ethyl Ortho Silicate (TEOS) solutions with various concentrations




Surface exchange rate = f (Si poisoning)

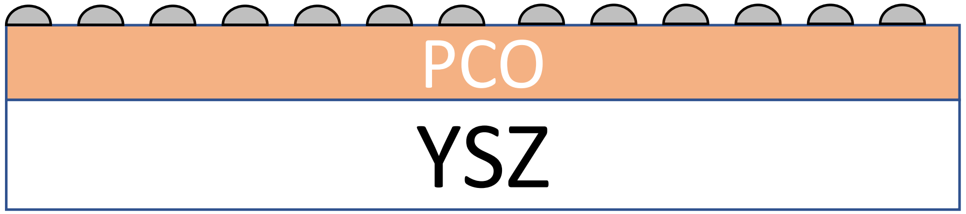
Effect of morphology of La layer ***(surface treatment instead of exsolution)***

La thin film




Characterization of La impact on surface exchange rate w/ and w/o Si

La nanoparticles

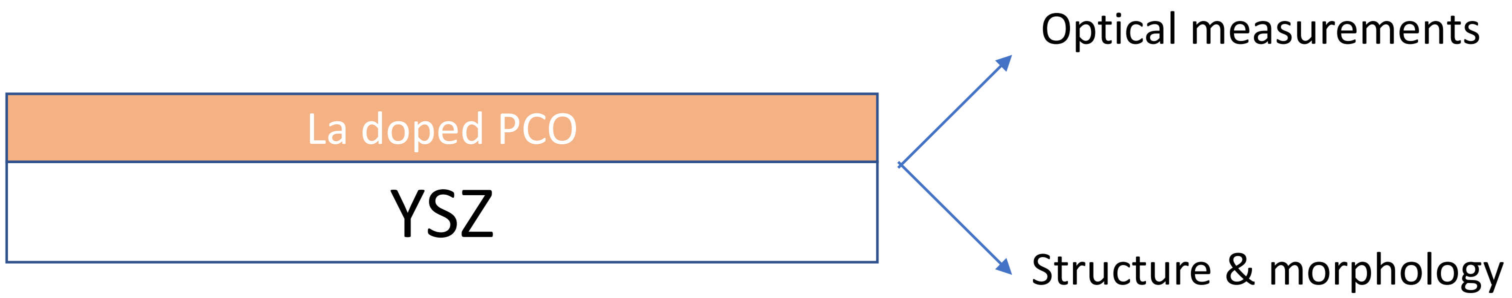



What the La/Si reaction forms? (La silicates)

# Study of exsolution on thin films

Exsolution of $La_2O_3$ with thermal treatment determined on powder samples

Analysis of exsolved particles on PCO films:




Morphology of films (epitaxial, polycristalline etc)

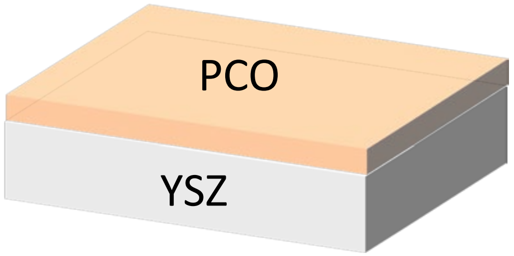
- Morphogy and composition of exsolved particles
- Effect of exsolved particles on surface exchange rate (w/ and w/o Si/Cr poisoning)

# Three approaches – Three tasks

## Study on powders

**Objectives:**
Determination of La solubility in PCO
Determination of exsolution thermal treatment

## Study on films




**Objectives:**
Study of $La_2O_3$ effect on surface exchange
Study of their efficacy on Si and Cr poisoning

## Study on real SOFC cathodes

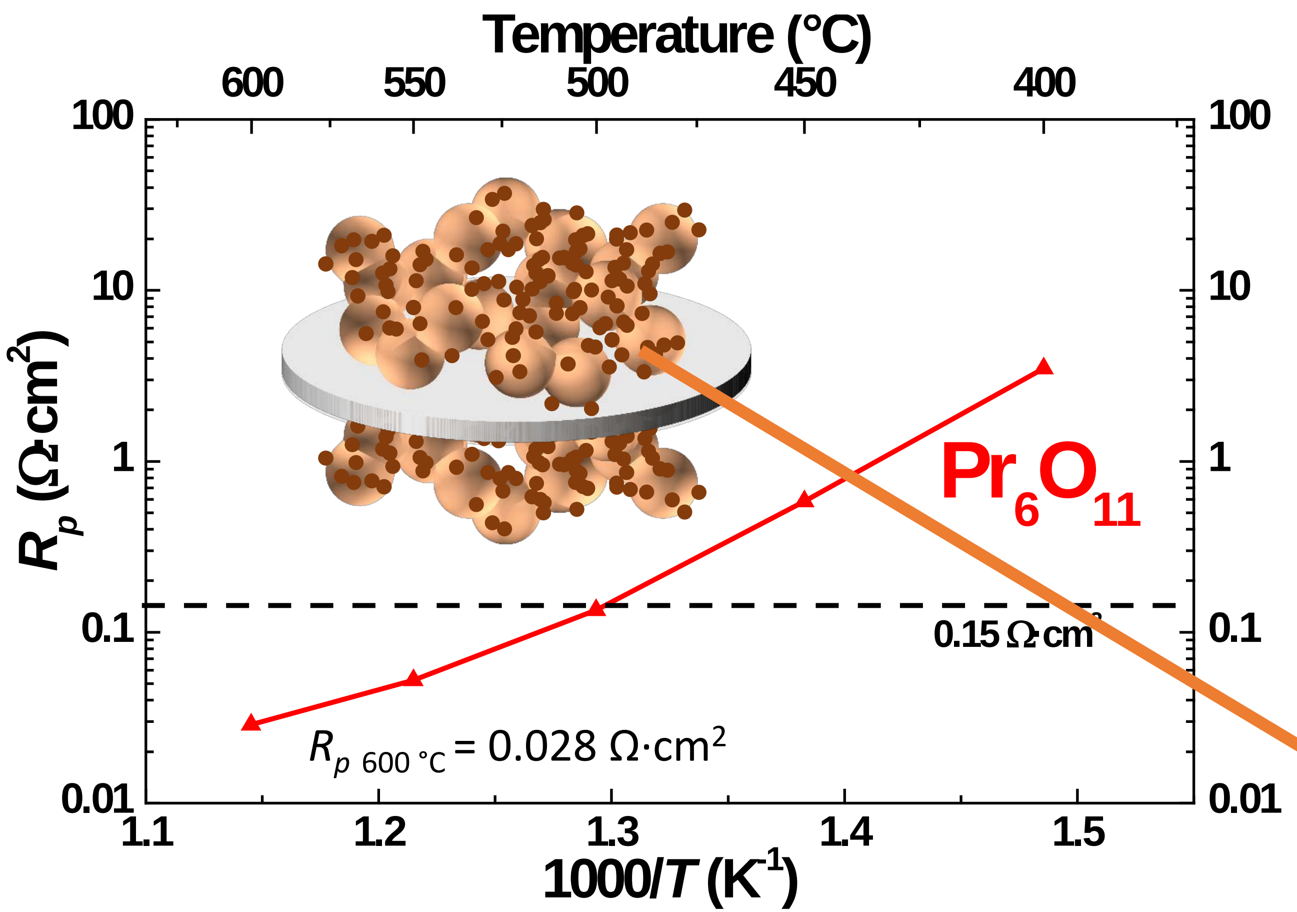
Electrochemical performance and stability
At realistic operating conditions

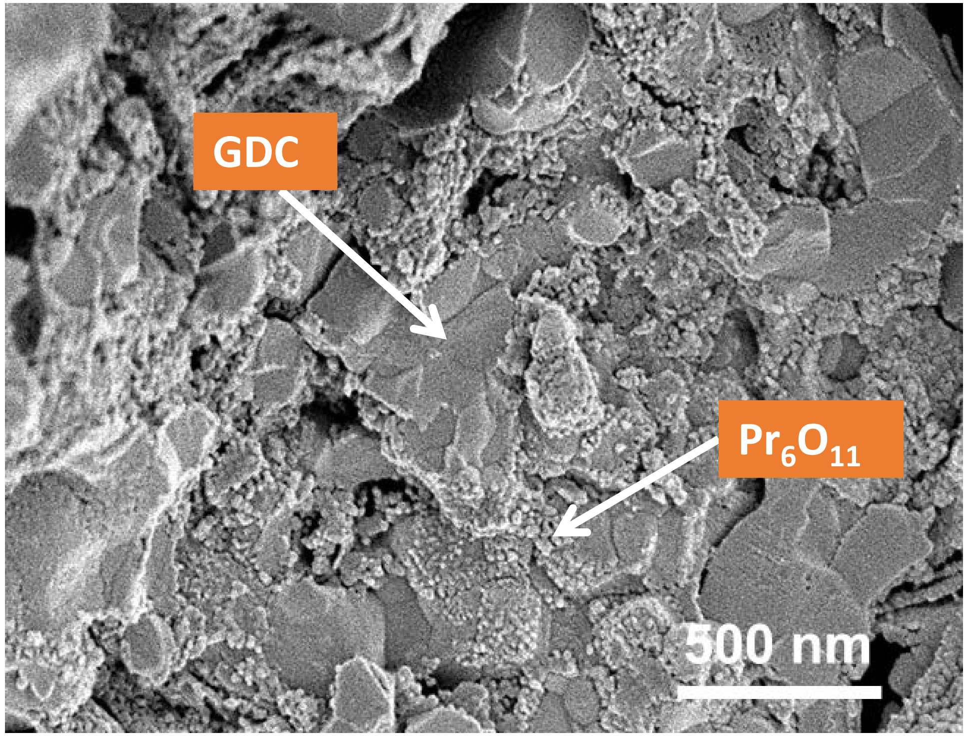
} Use of infiltration to produce highly efficient composites (1)

*(1) C. Nicollet, PhD Thesis, 2016*

# Application on porous composite Electrodes

Infiltrated Composite GDC/$Pr_6O_{11}$




Replacing GDC backbone with La-PCO

*C. Nicollet et al. Int. J Hydrogen Energy, 2016, 41 (34) 15538-15544*

# Future work

Work on Si poisoning and La getter:

- Controled study of Si poisoning
- Analysis of $La_2O_3$ effect on suface exchange reaction

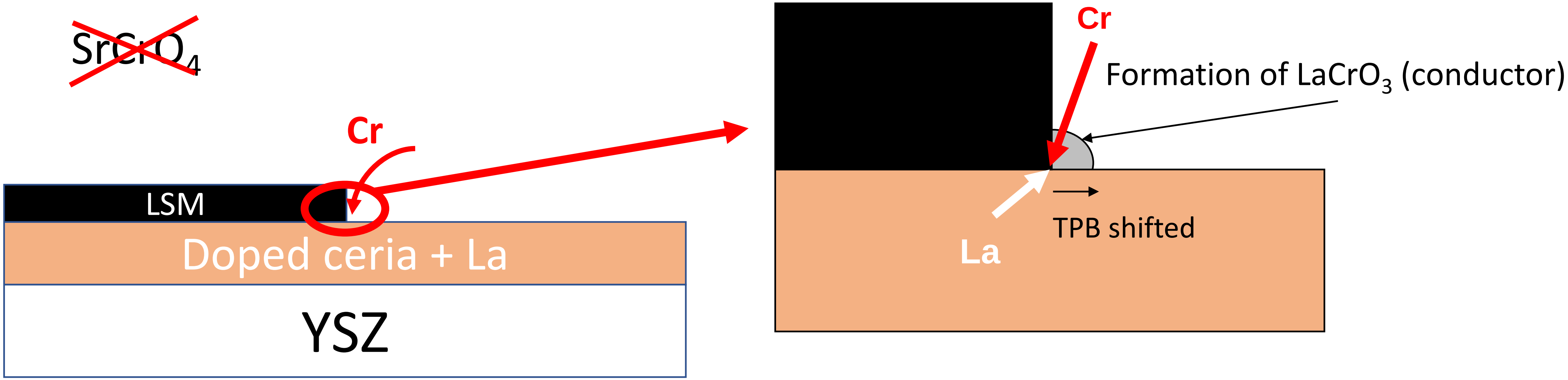
Proof of concept of exsolution as internal source of gettering element?

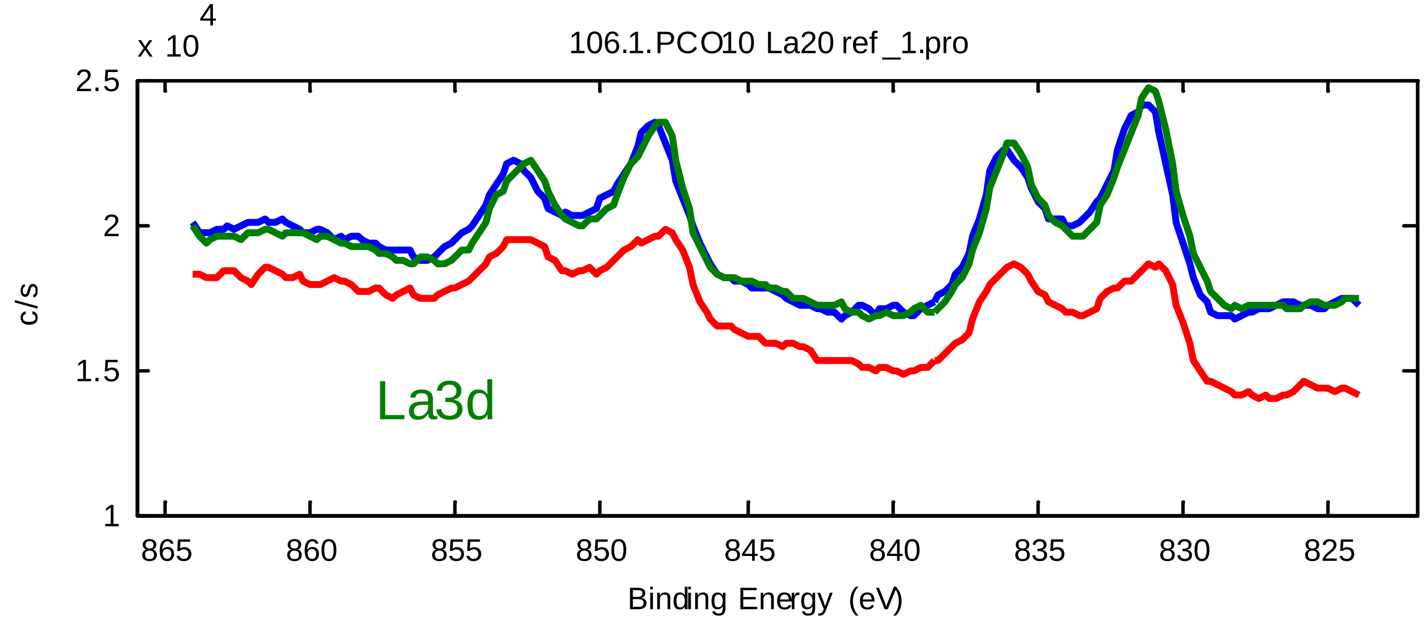
Application to other - cathodes materials?
- poisoning elements?

# Thank you for your attention

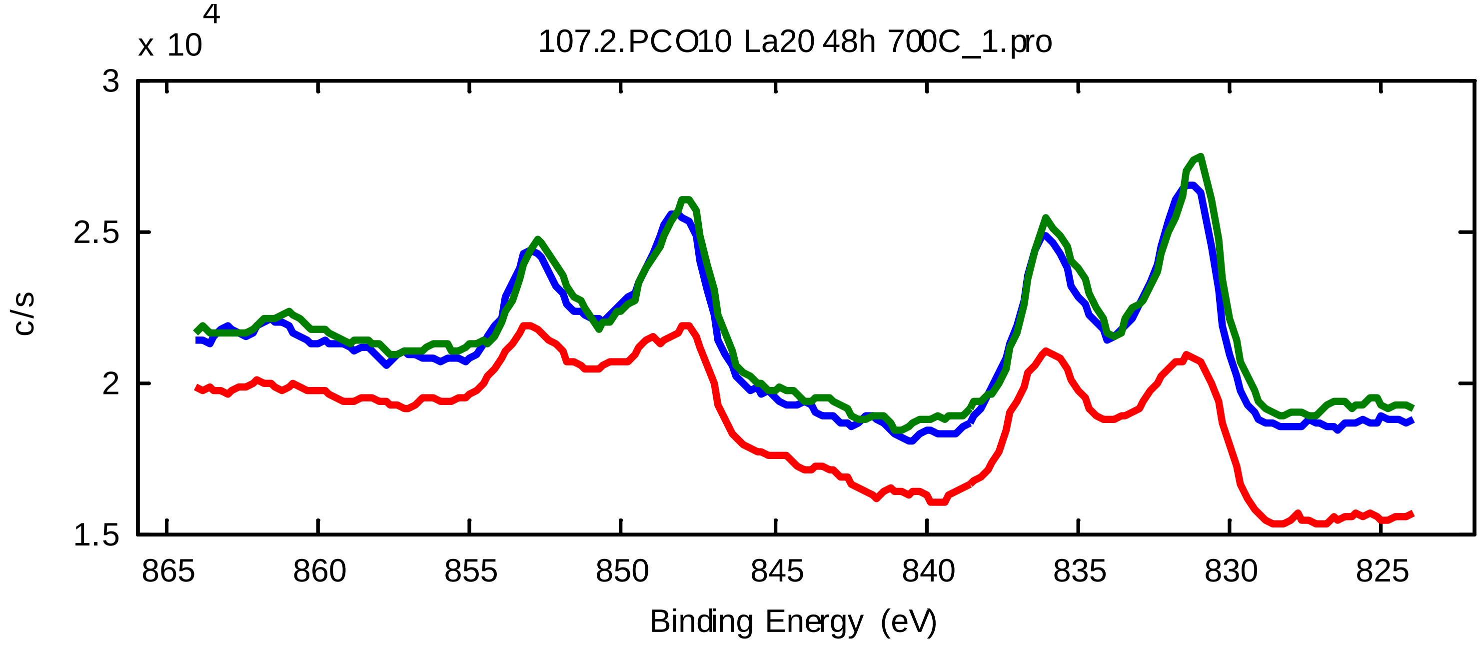
Acknowledgement : NETL Award DE-FE0026109 Phase 1

# La and Mn doping for Cr poisoning at TPBs

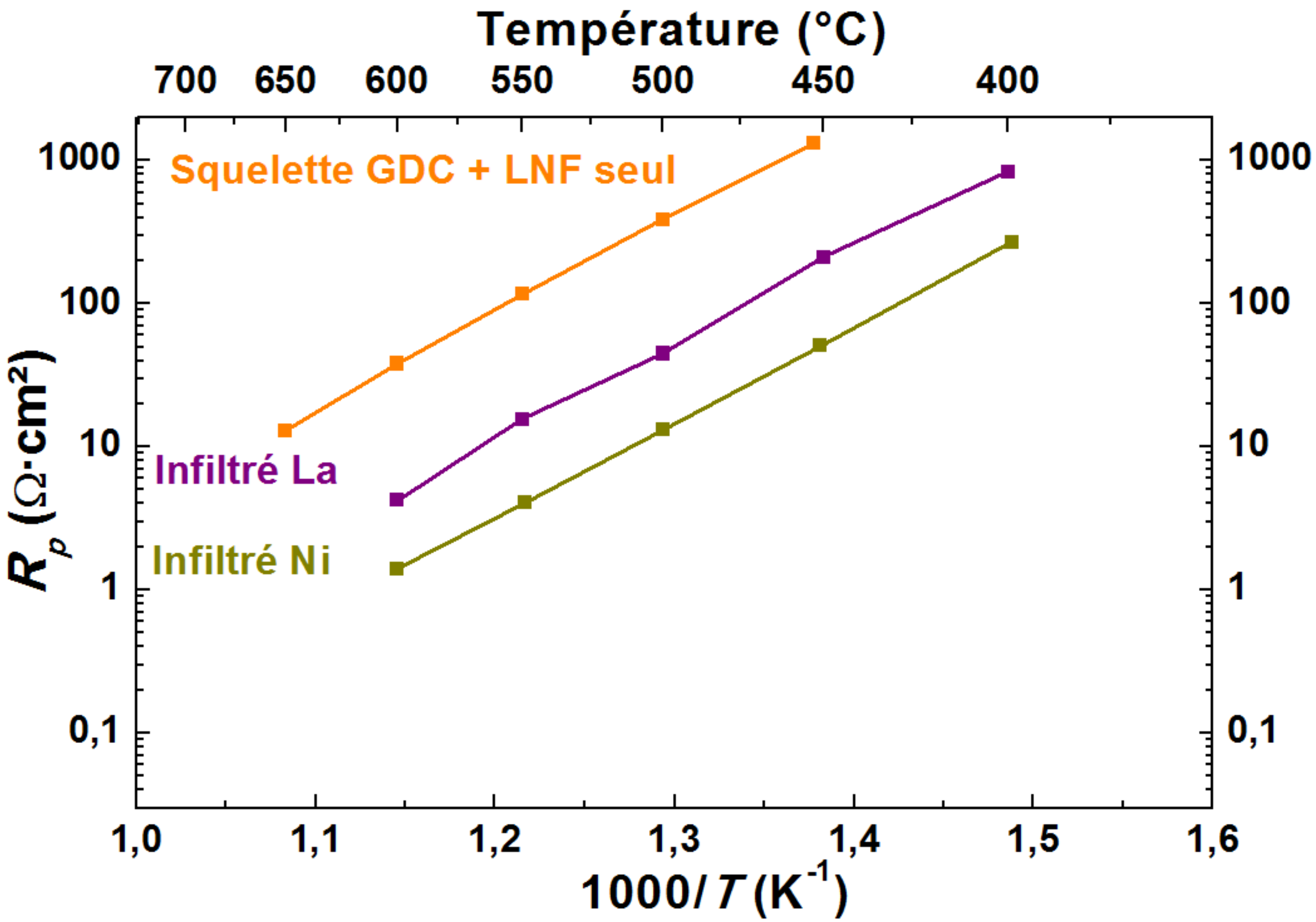





initial




700 °C 50 h


Température (°C)
700
650
600
550
500
450
400
Squelette GDC + LNF seul
Infiltré La
Infiltré Ni
$R_p$ (Ω·cm²)
1000
100
10
1
0,1
1,0
1,1
1,2
1,3
1,4
1,5
1,6
1000/$T$ (K$^{-1}$)

# Ionic radii

| Element | charge | coordinence | Ionic radius (Å) |
|---|---|---|---|
| Ce | +4 | 8 | 0.97 |
| Gd | +3 | 8 | 1.053 |
| Pr | +3 | 8 | 1.126 |
| Pr | +4 | 8 | 0.96 |
| La | +3 | 8 | 1.16 |
| Mn | +2 | 8 | 0.96 |
| Hf | +4 | 8 | 0.83 |

# Exsolution - Systems considered

Composite electrode: Ceria based material + (La,Sr)$MnO_3$ (LSM)

Ionic conductor
Gd doped ceria (GDC)

Mixed conductor
Pr doped ceria(PCO)

Scavenging elements
La → efficient toward Si poisoning
Mn → expected efficiency toward Cr poisoning

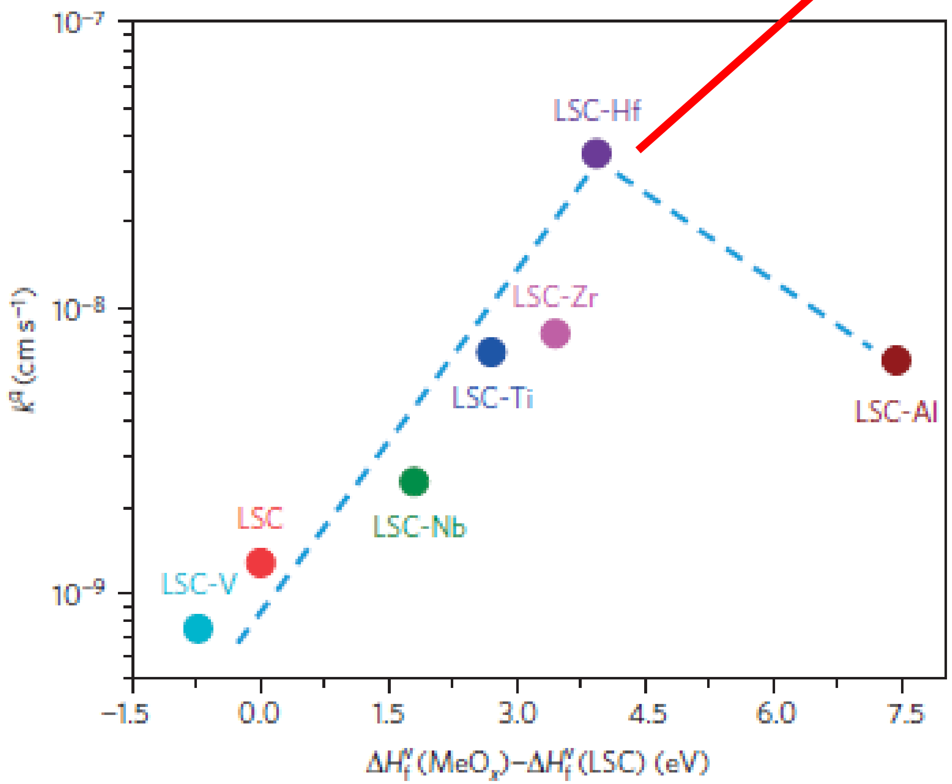
Four systems to be studied: GDC-La, PCO-La, GDC-Mn, PCO-Mn

# Limiting Sr segregation

ARTICLES
PUBLISHED ONLINE: 13 JUNE 2016 | DOI: 10.1038/NMAT4659
nature materials

## Improved chemical and electrochemical stability of perovskite oxides with less reducible cations at the surface

Nikolai Tsvetkov[1,2†], Qiyang Lu[1,3†], Lixin Sun[1,2], Ethan J. Crumlin[4] and Bilge Yildiz[1,2,3*]




**Exsolution of Hf from GDC/PCO?**

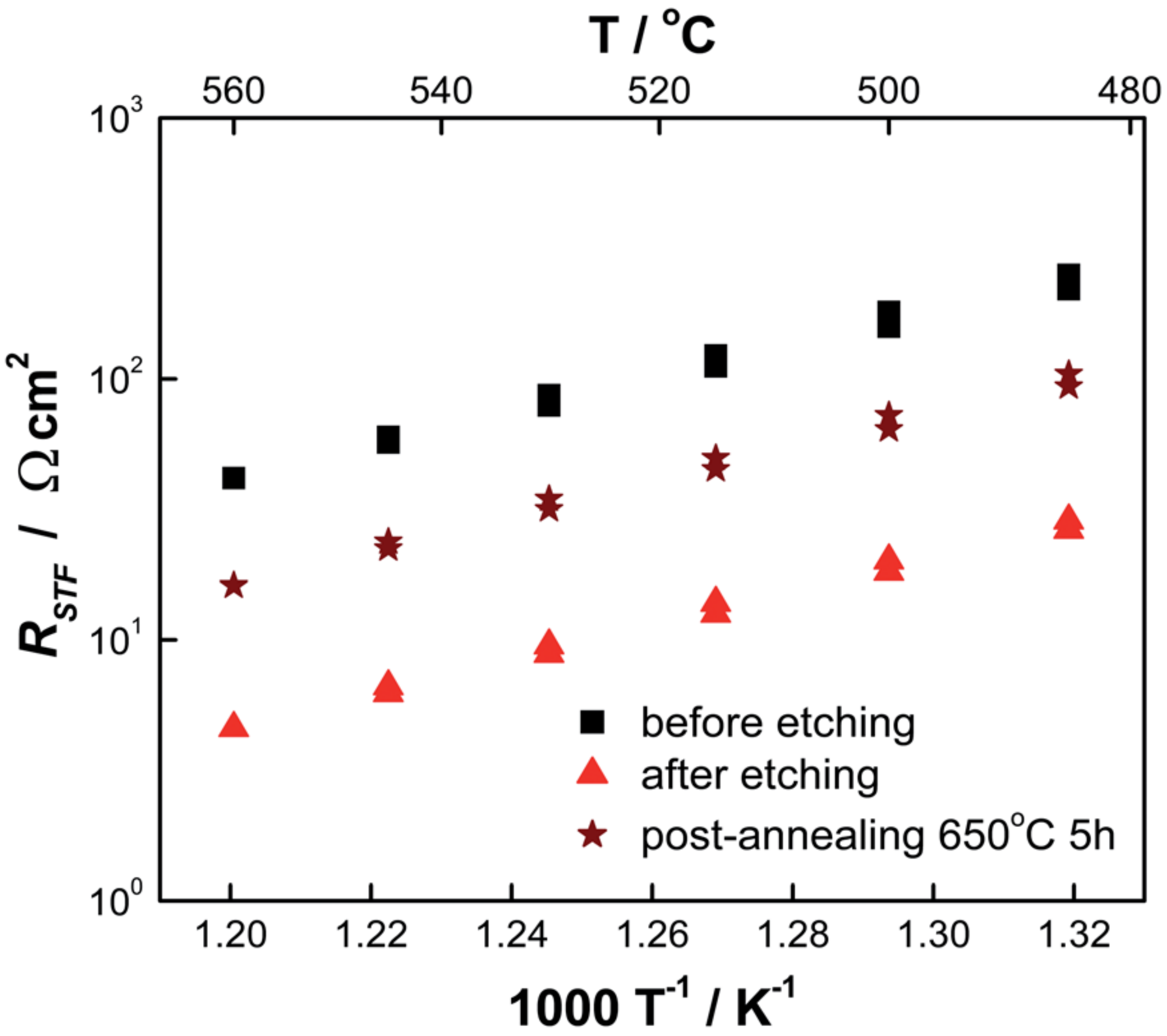
Risk: Hf can react with La to form $La_2Hf_2O_7$ (Insulating like $La_2Zr_2O_7$?)
*Smirnova et al., Journal of Crystal Growth 377 (2013) 212-216.*

Alternative: using Sr-free materials!
$Pr_6O_{11}$

*Nicollet et al., Int. J. Hydrogen Energy 41 (34) (2016) 15538-15544*

# Surface etching?

## $SrFeO_{3-\delta}$ Polarization resistance




Continuous Sr segregation

*W. Jung et al., Energy Environ. Sci., 2012, 5, 5370–5378*