Self-Regulation of Surface Chemistry in Oxygen Electrodes for Solid Oxide Fuel Cells

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NETL Award DE-FE0026109 Phase 1
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NATIONAL ENERGY TECHNOLOGY LABORATORY

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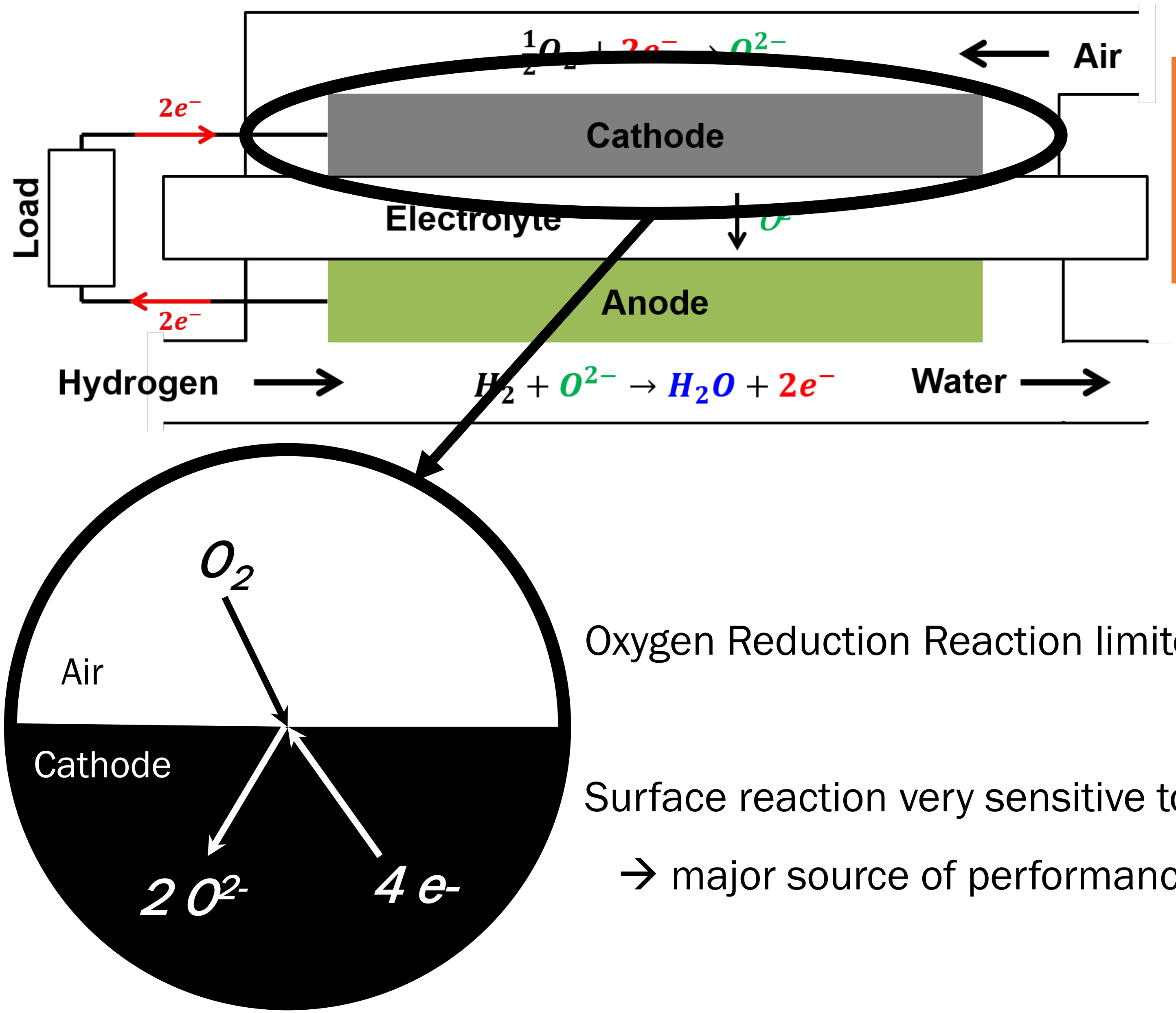
Solid Oxide Fuel Cells



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

Main drawback to address: performance degradation

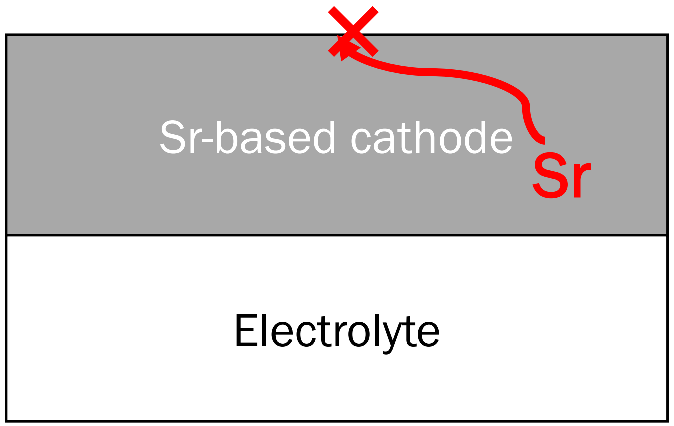
Oxygen Reduction Reaction limited by solid/gas surface exchange reaction rate

Surface reaction very sensitive to contaminants

→ major source of performance degradation

Main sources of cathode performance degradation

Sr segregation

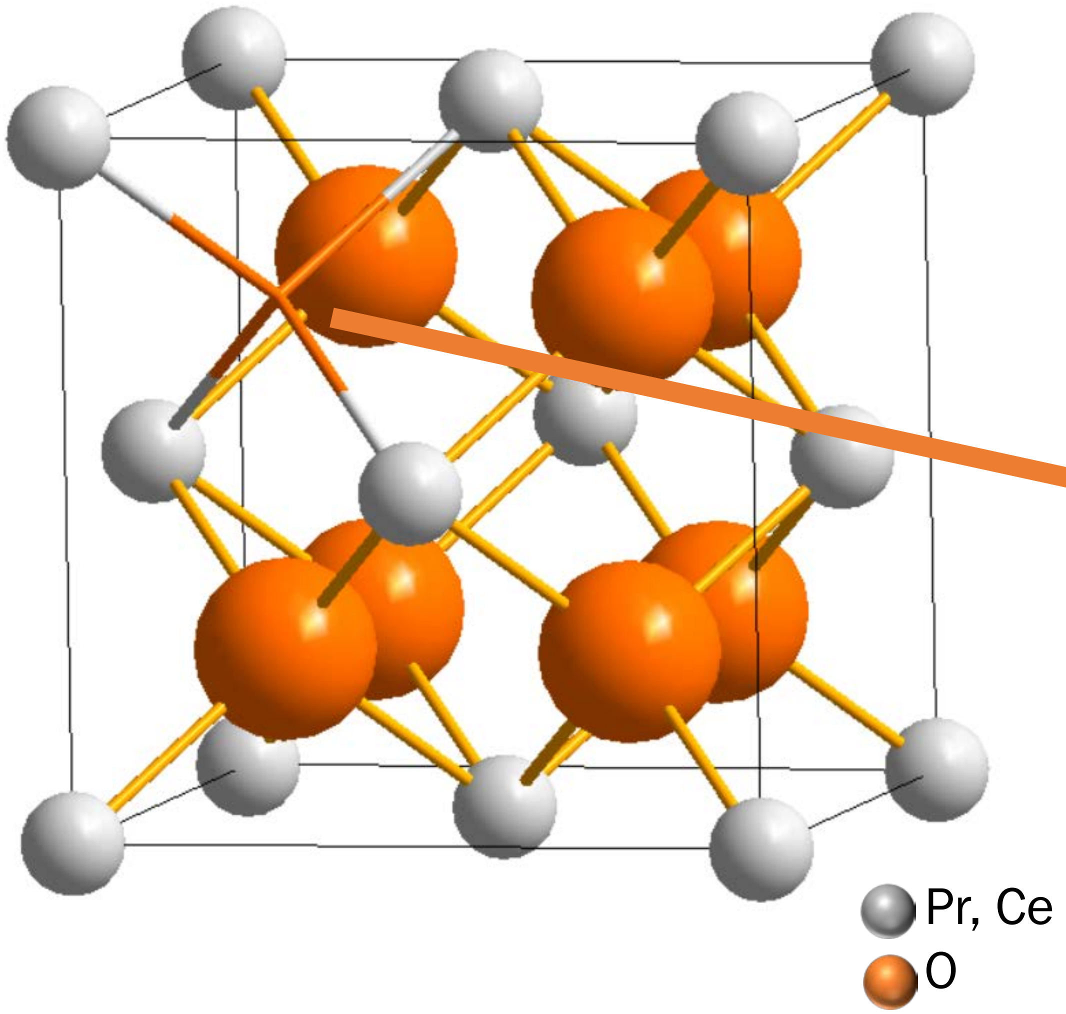


Formation of surface SrO
blocking active sites

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

How to avoid Sr segregation?

Sr-free cathode material – Pr doped ceria (PCO)



Fluorite CaF_2 type structure

Pr mixed valence 3+/4+

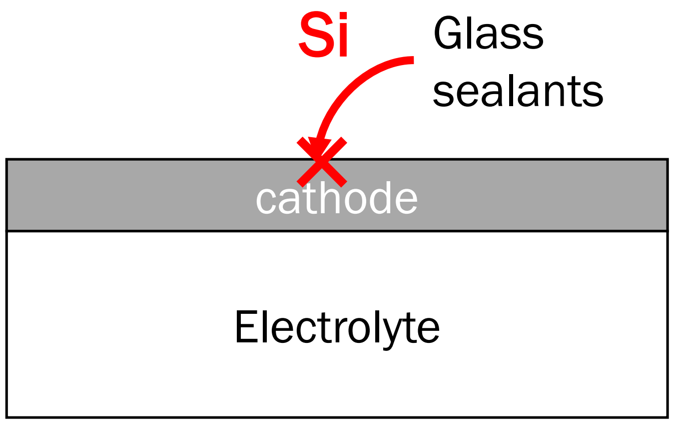
↓

O^{2-} vacancies

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

Main sources of cathode performance degradation

Si poisoning



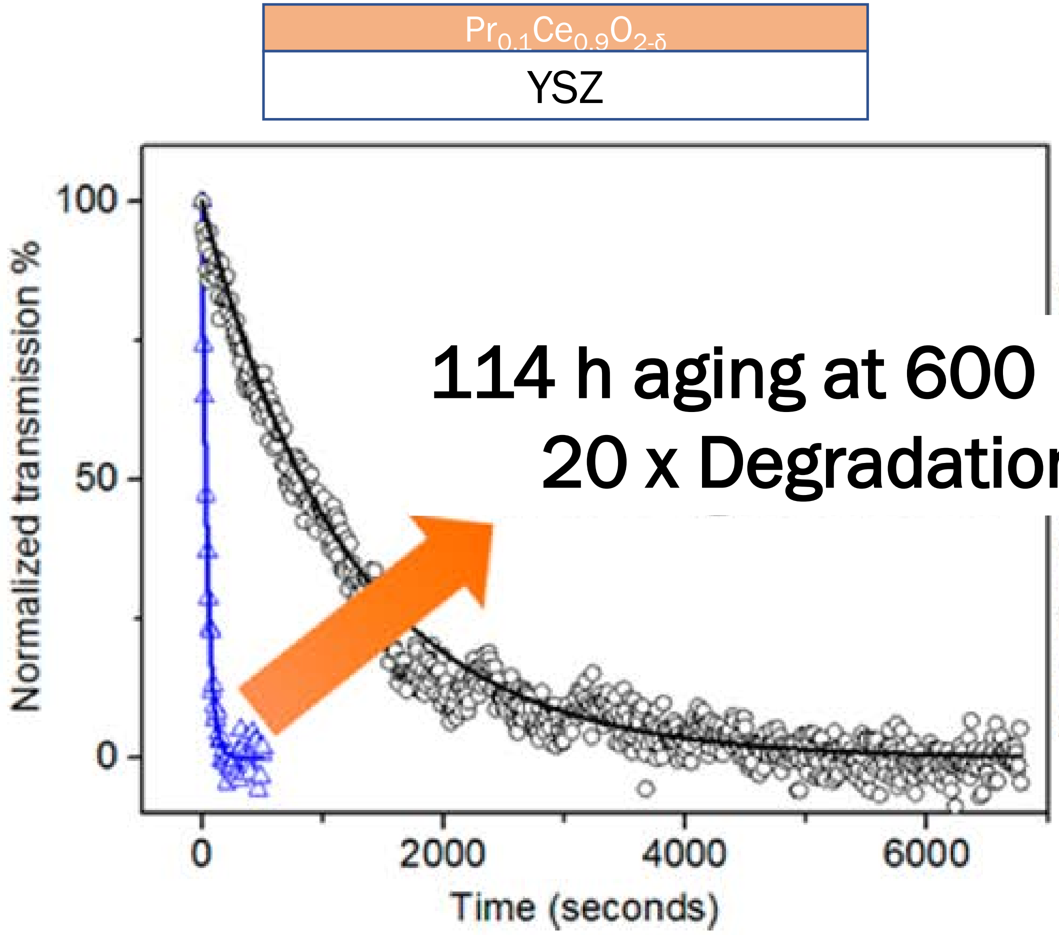
Formation of insulating silica blocking active sites

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

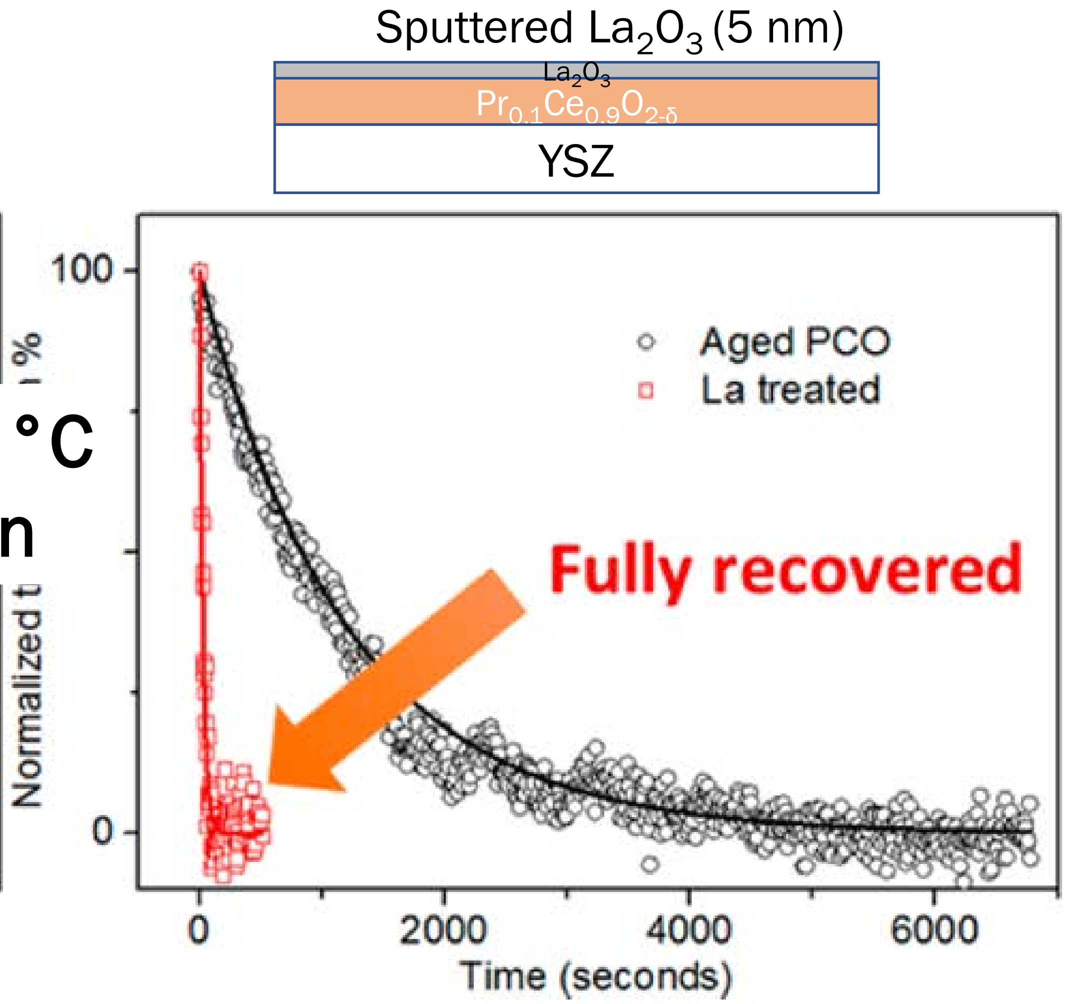
How to limit Si poisoning of Pr-doped ceria electrodes?

Scavenging Si poison with La_2O_3 in Pr-doped ceria films

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



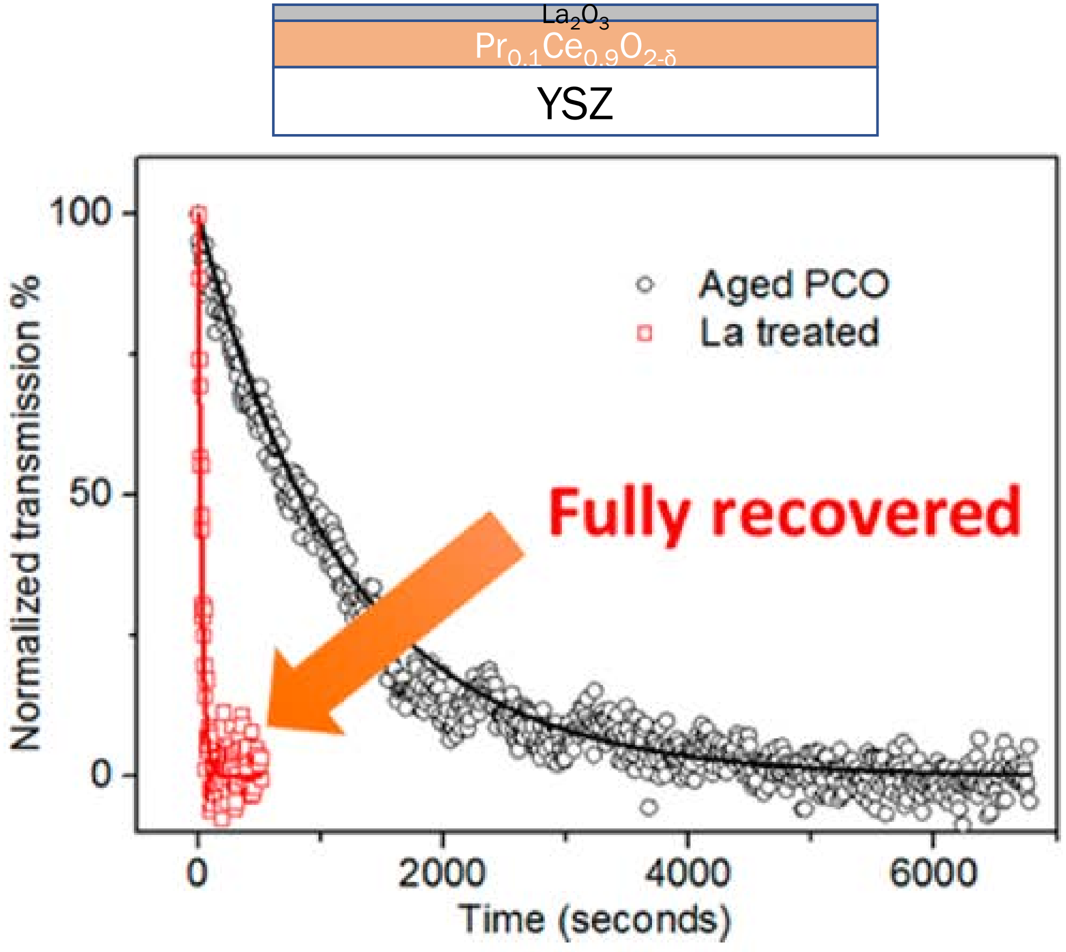
114 h aging at 600 °C
20 x Degradation



La layer traps Si → surface exchange rate recovered

Scavenging Si poison with La_2O_3 in Pr-doped ceria films

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



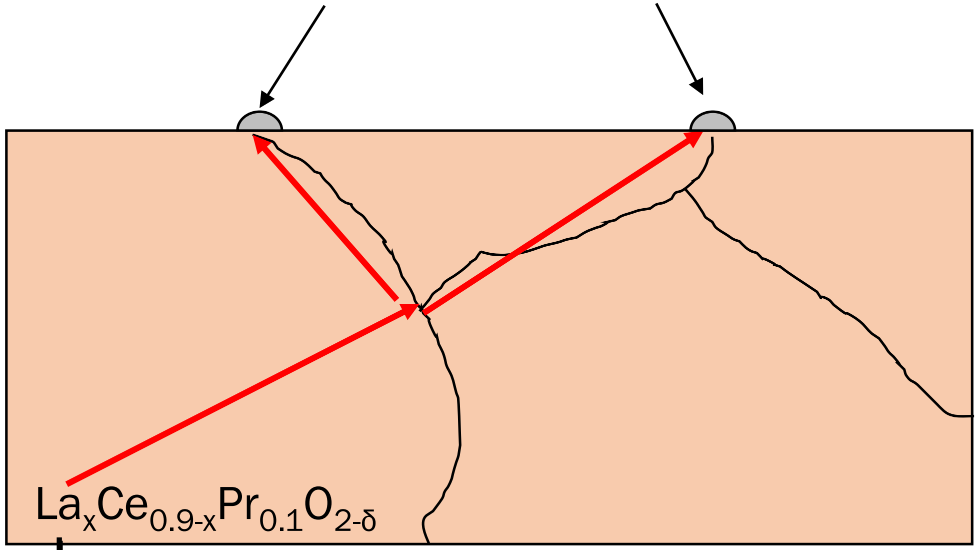
La_2O_3 sputtering → not practical under operation
How to continuously getter Si poisoning?

Lanthanum bulk doping for Si trapping

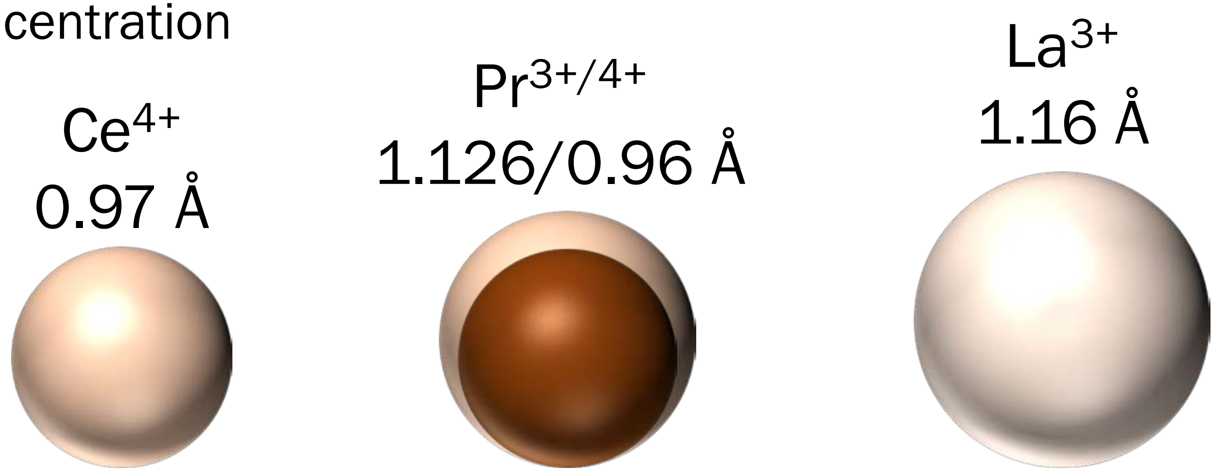
Self-regulation of surface poisoning with La doping

Internal renewable source of La getter

Exsolved La particles → Getter Si poisoning



Scavenging element introduced into ceria in high concentration

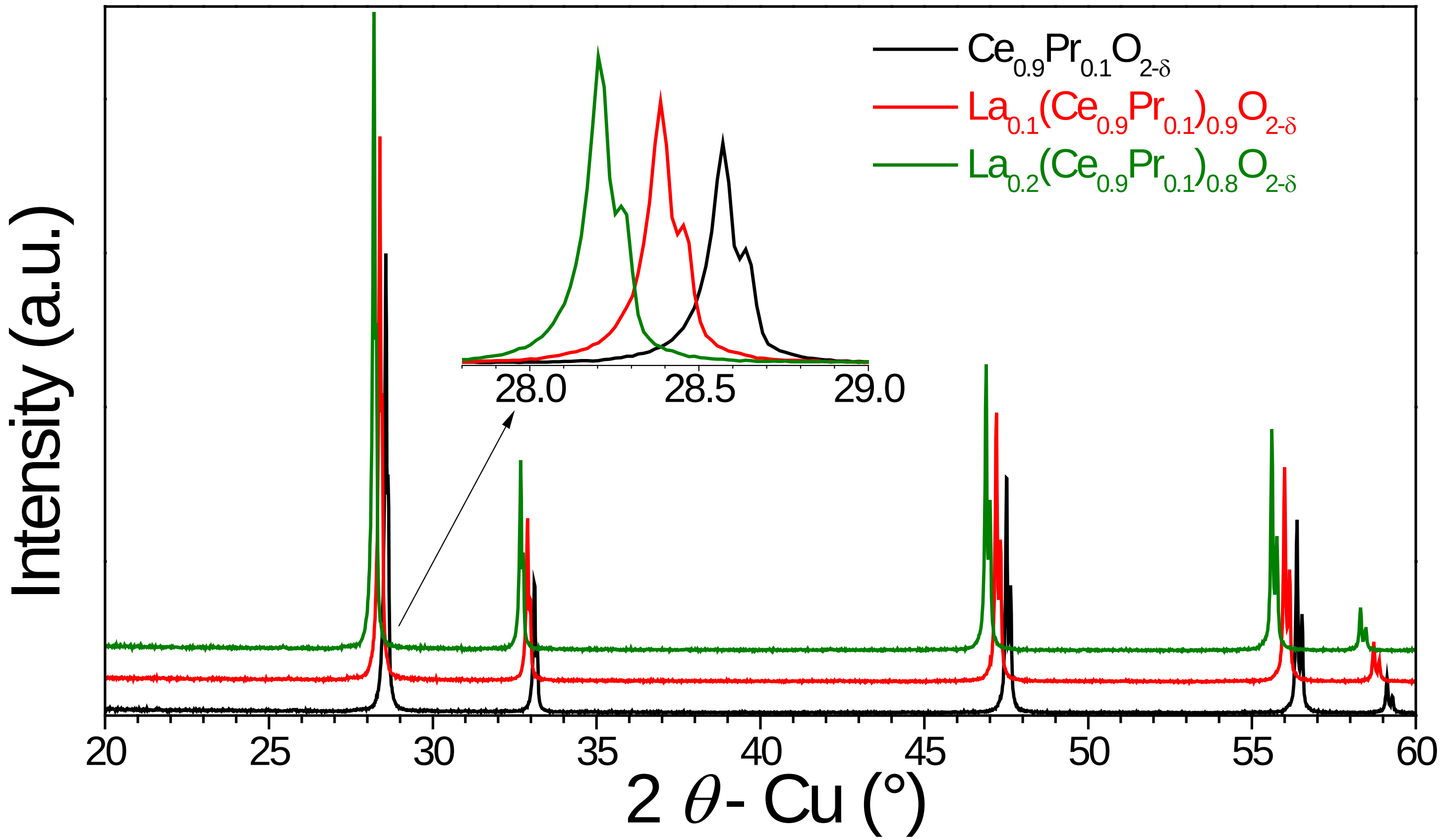


→ Source of scavenging elements to enable long term operation

Self-Cleaning Material

Powder Synthesis – co-precipitation route

X-ray diffraction on synthesized powders



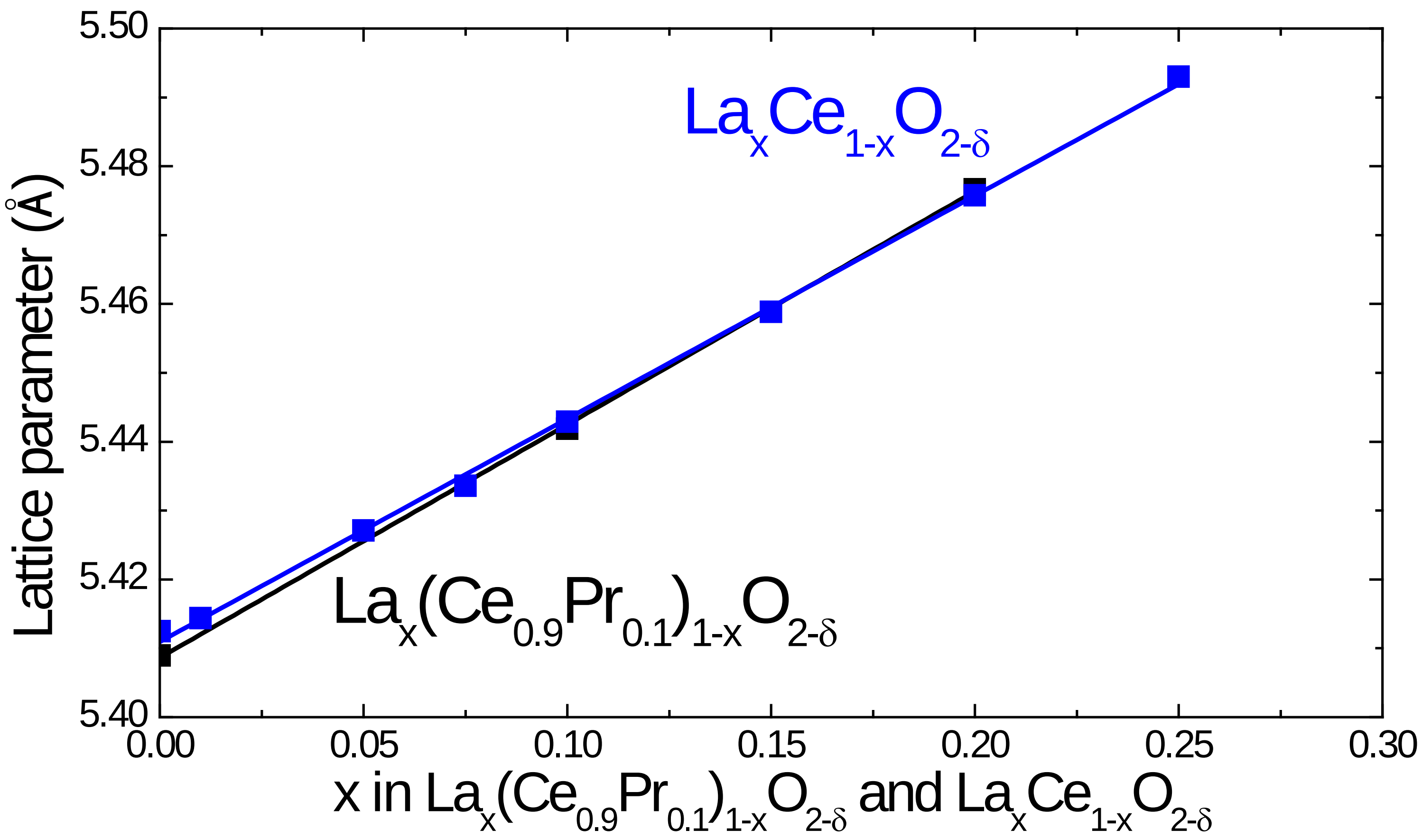
Fluorite structure (SG: Fm-3m)

La insertion in ceria
Significant increase in lattice parameter

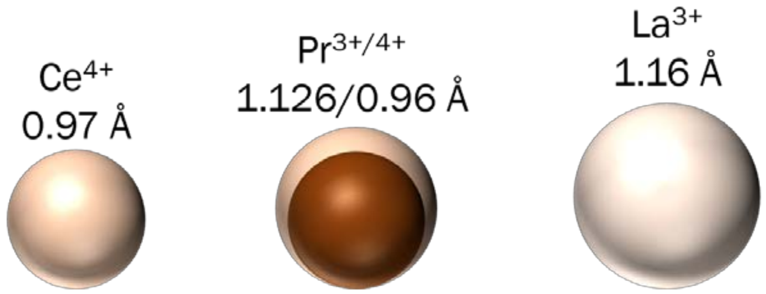
No impurities → La fully soluble in PCO

X-ray Diffraction - Lattice parameters

Comparison of lattice parameters with $La_xCe_{1-x}O_{2-\delta}$ solid solution



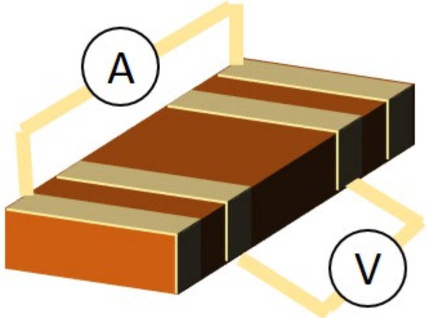
No difference in lattice parameter



La insertion forces Pr in 4+ state?
Influence on transport properties?

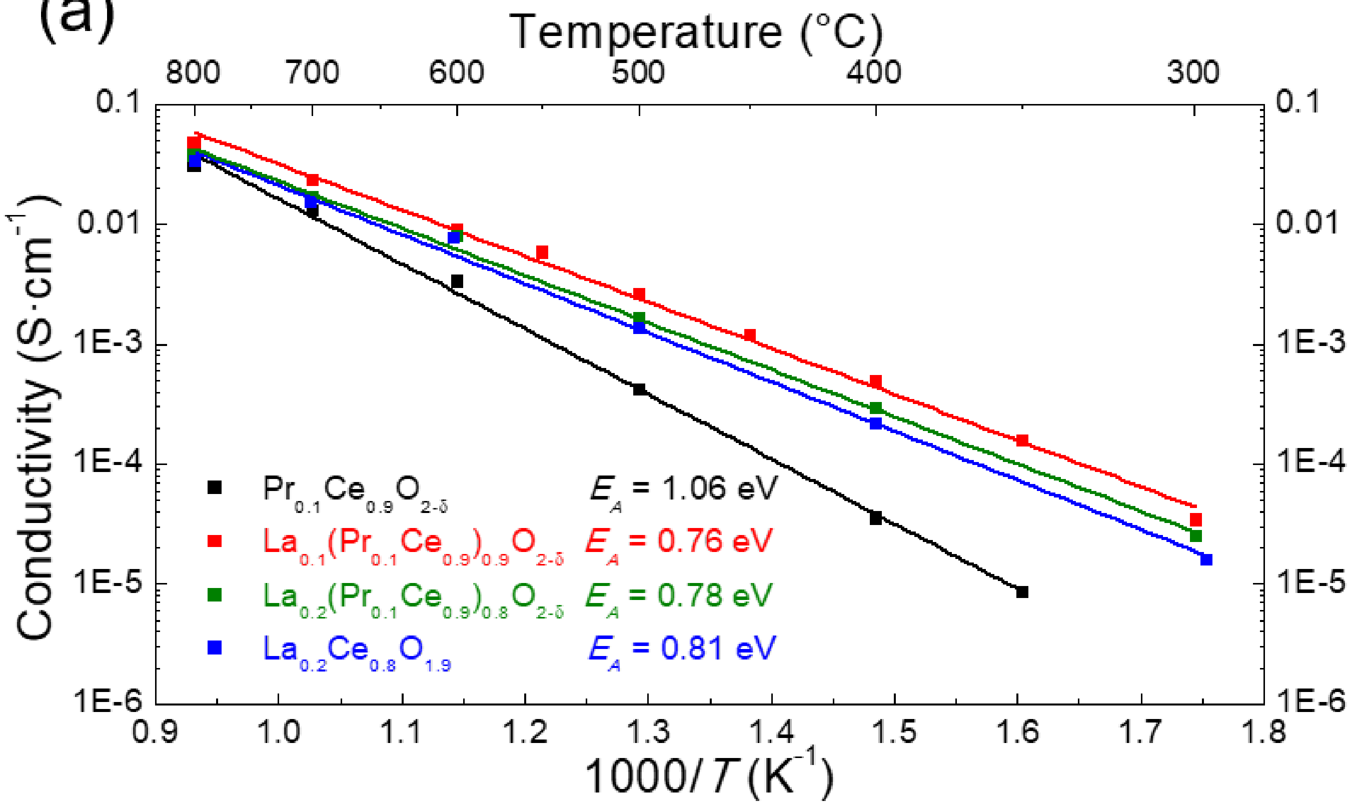
Hamm et al., Z. Anorg. Allg. Chem. **2014**, *640, (6),* 1050–1053

Transport properties: Electrical Conductivity



Four points conductivity measurements

(a)

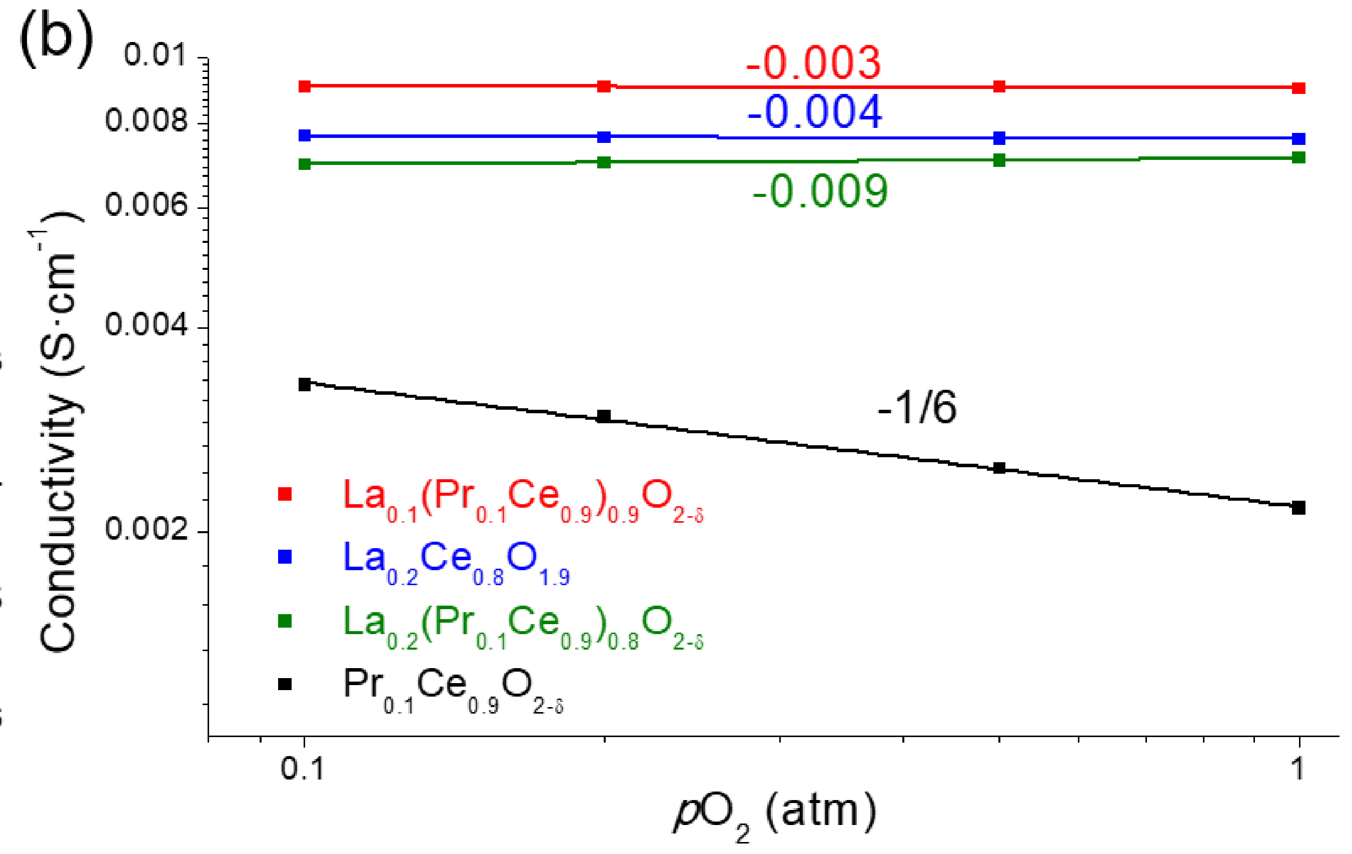


La doping increases vacancy concentration

Lower E_a: vacancy concentration less dependant on Pr oxidation state

Transport properties: Electrical Conductivity

pO$_2$ dependance of conductivity



$$O_O \rightarrow V_O^{\cdot\cdot} + 2e' + 1/2O_2$$

$$[V_O^{\cdot\cdot}] \cdot n^2 p_{O_2}^{1/2} = K_r$$

La-doping: ionic conductivity ↗

e- conductivity ↘

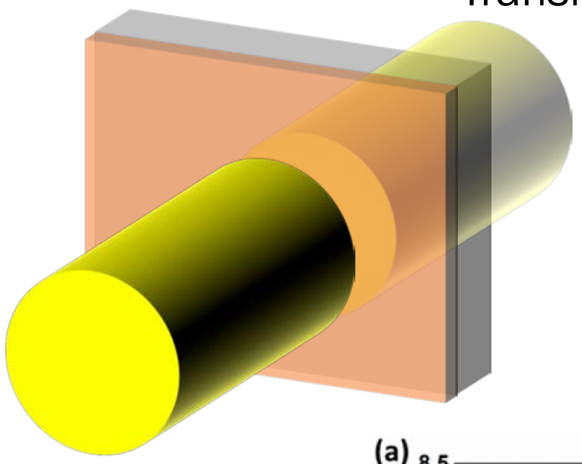
Influence on Surface Exchange Rate?

Influence of La doping on surface exchange rates

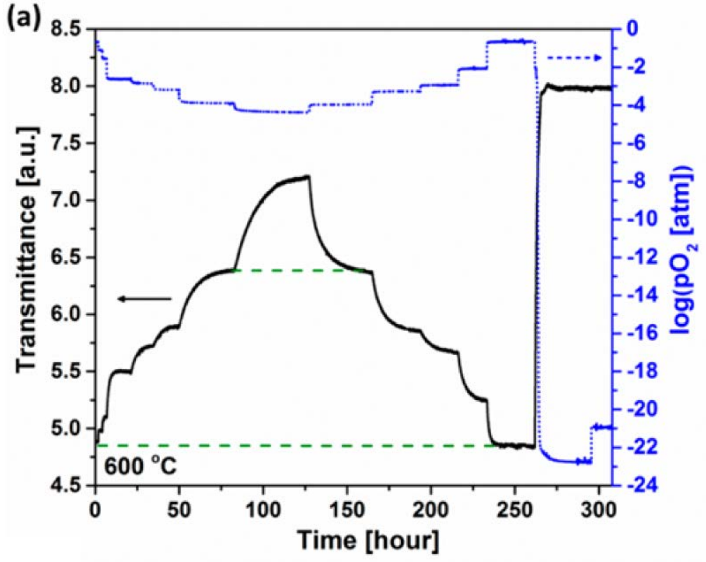
Optical Absorption in $Ce_{0.9}Pr_{0.1}O_{2-\delta}$

Pr doped ceria film (PLD) on Y-doped zirconia substrate*

Transmitted Light beam



Light beam



*single crystal substrate

Color of PCO depends on Pr valence

Absorption ↔ oxygen non-stoichiometry

Beer-Lambert law

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

Step in pO_2

↓

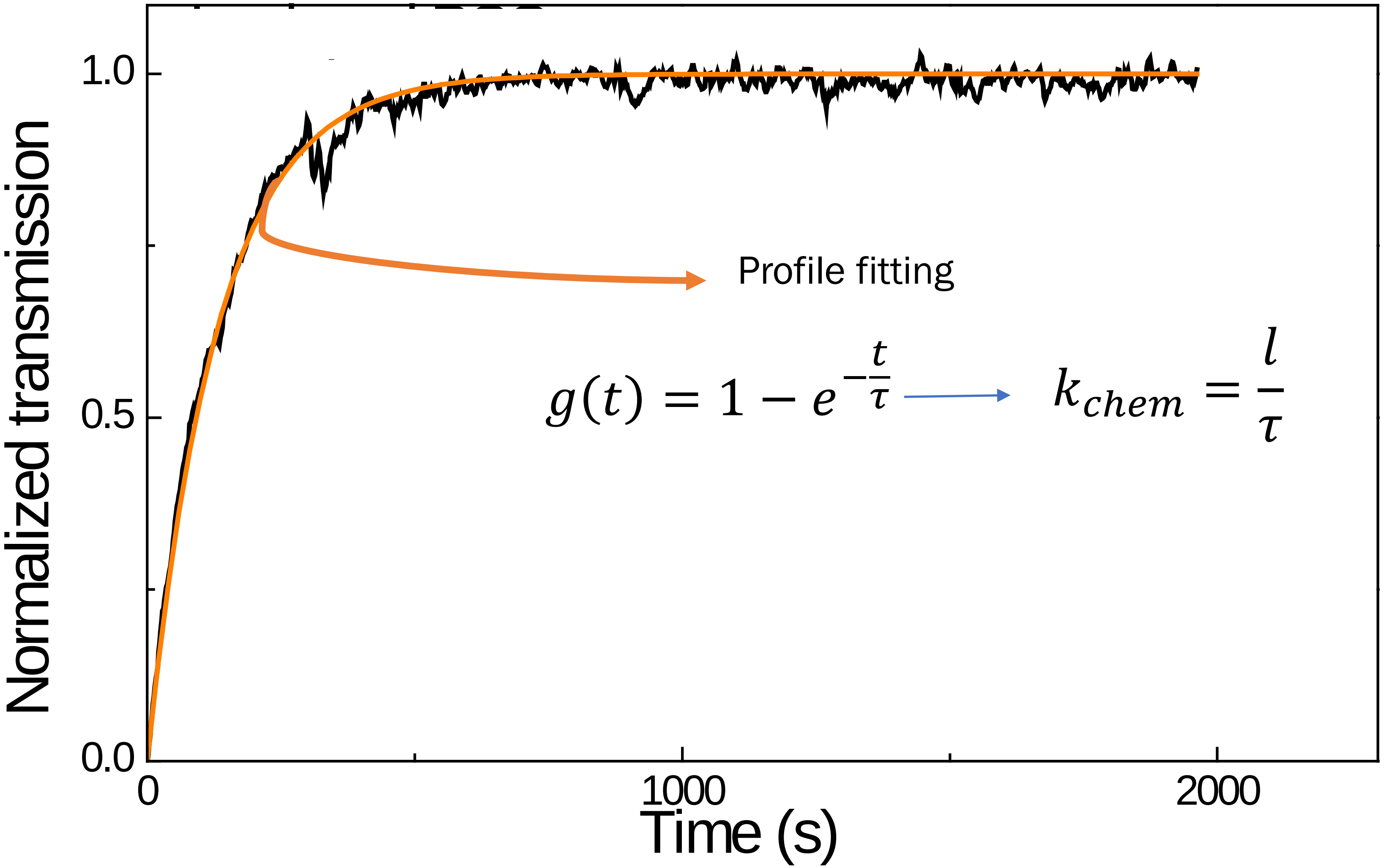
Transmittance Relaxation

↓

Surface exchange coefficient

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

Optical transmission relaxation (pO_2 step 0.1-0.2 atm)

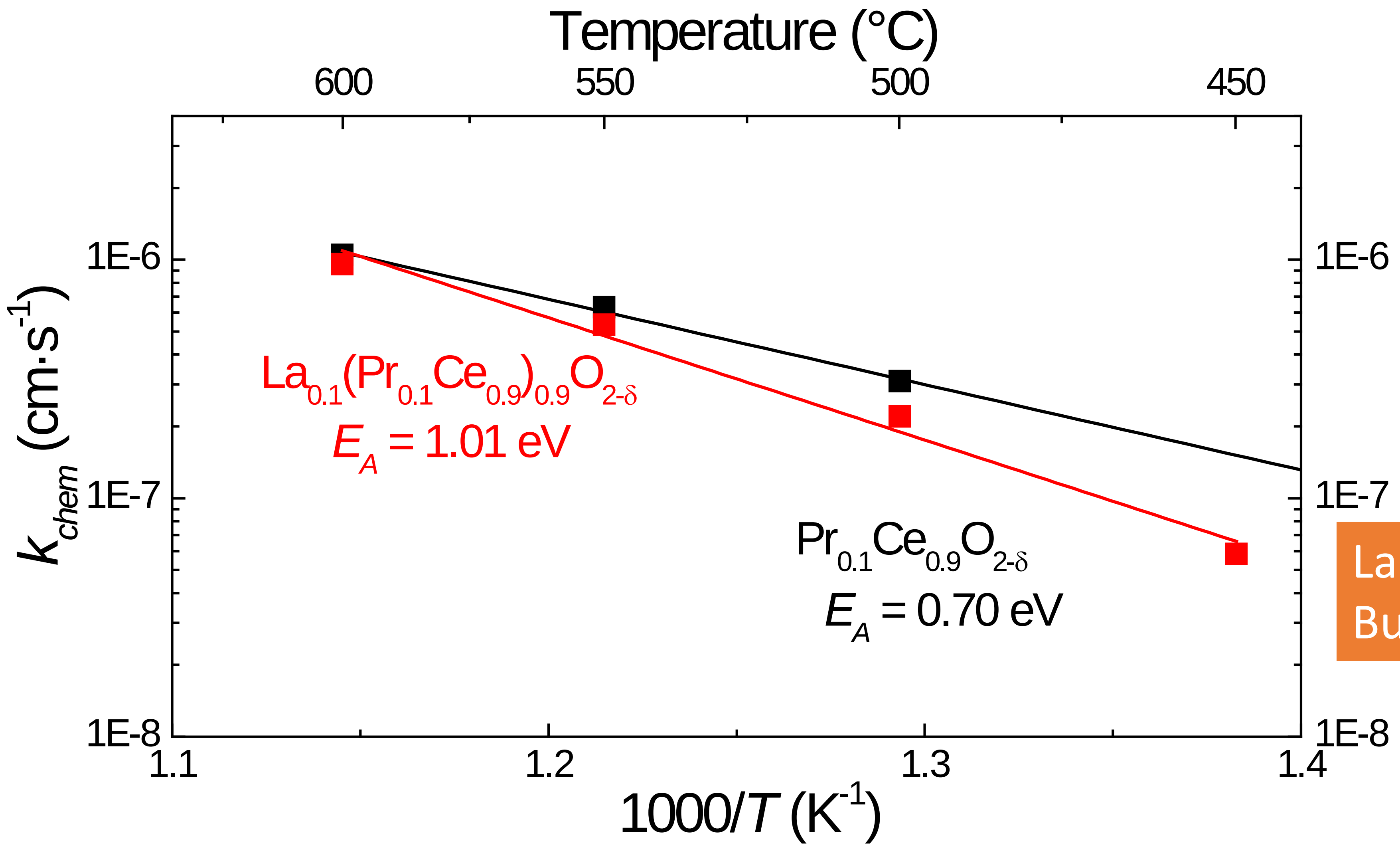


$$g(t) = 1 - e^{-\frac{t}{\tau}} \rightarrow k_{chem} = \frac{l}{\tau}$$

Effect of La doping on surface exchange rate?

Influence of La doping On surface exchange coefficient

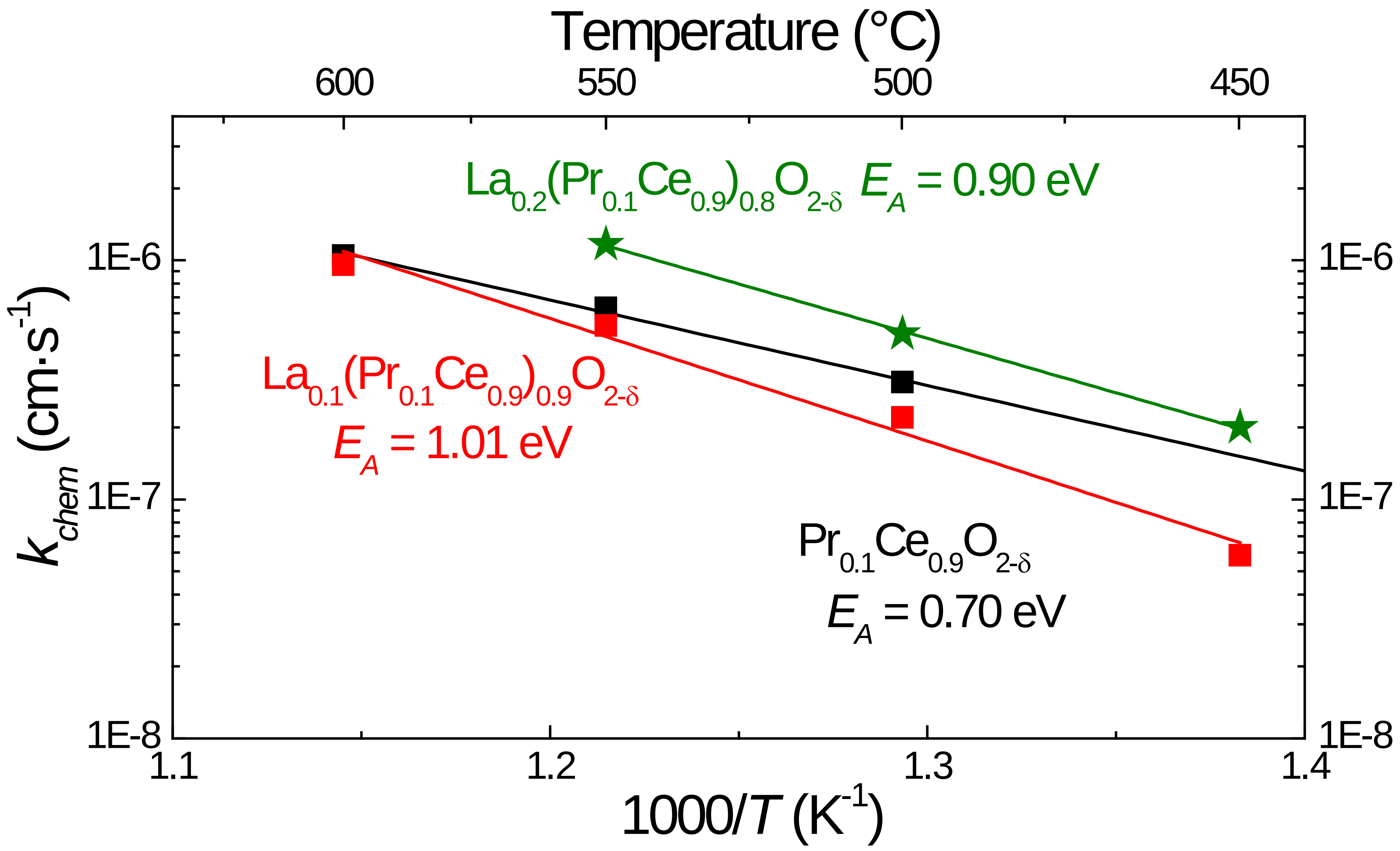
Optical Absorption in $La_x(Ce_{0.9}Pr_{0.1})_{1-x}O_{2-\delta}$



La doping → ionic conductor
But weak influence on k_{chem}

Influence of La doping On surface exchange coefficient

Optical Absorption in $La_x(Ce_{0.9}Pr_{0.1})_{1-x}O_{2-\delta}$

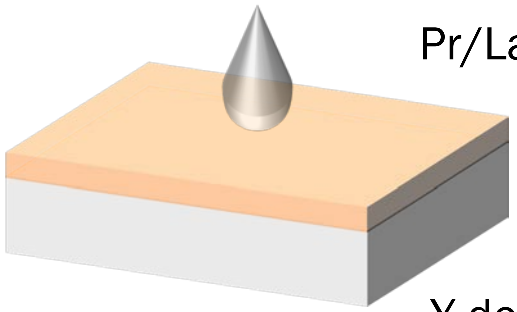


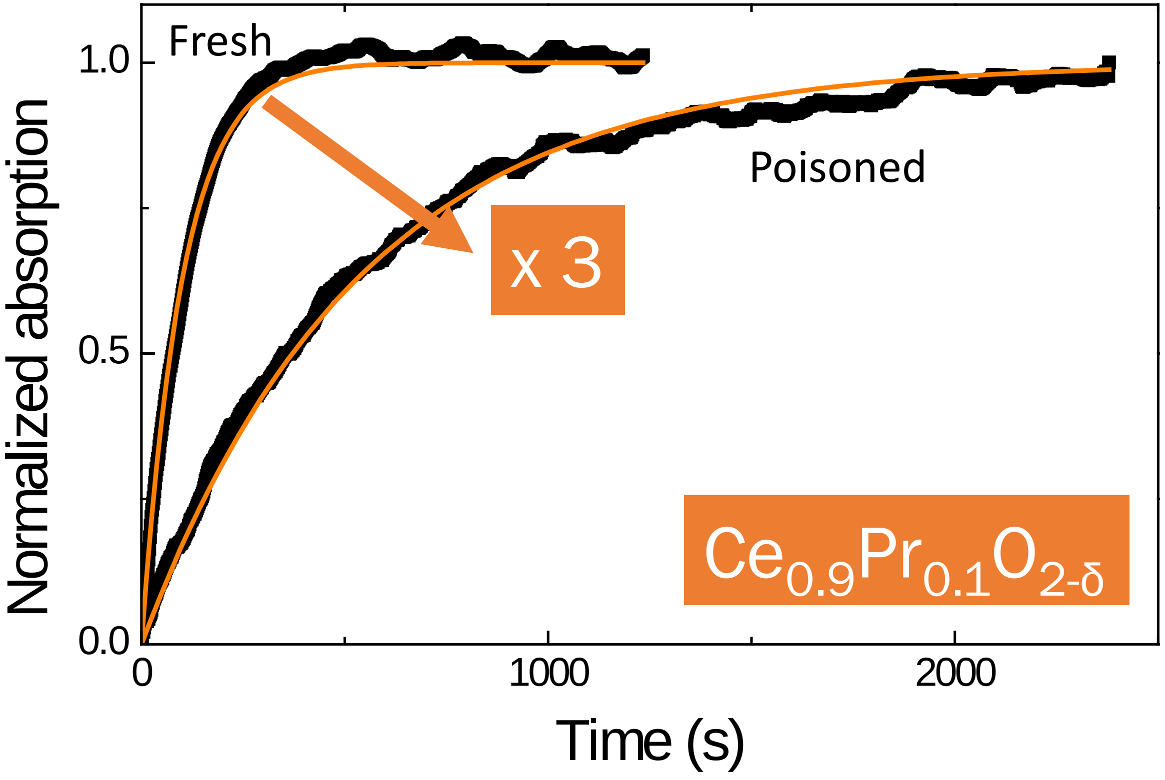
La segregation?

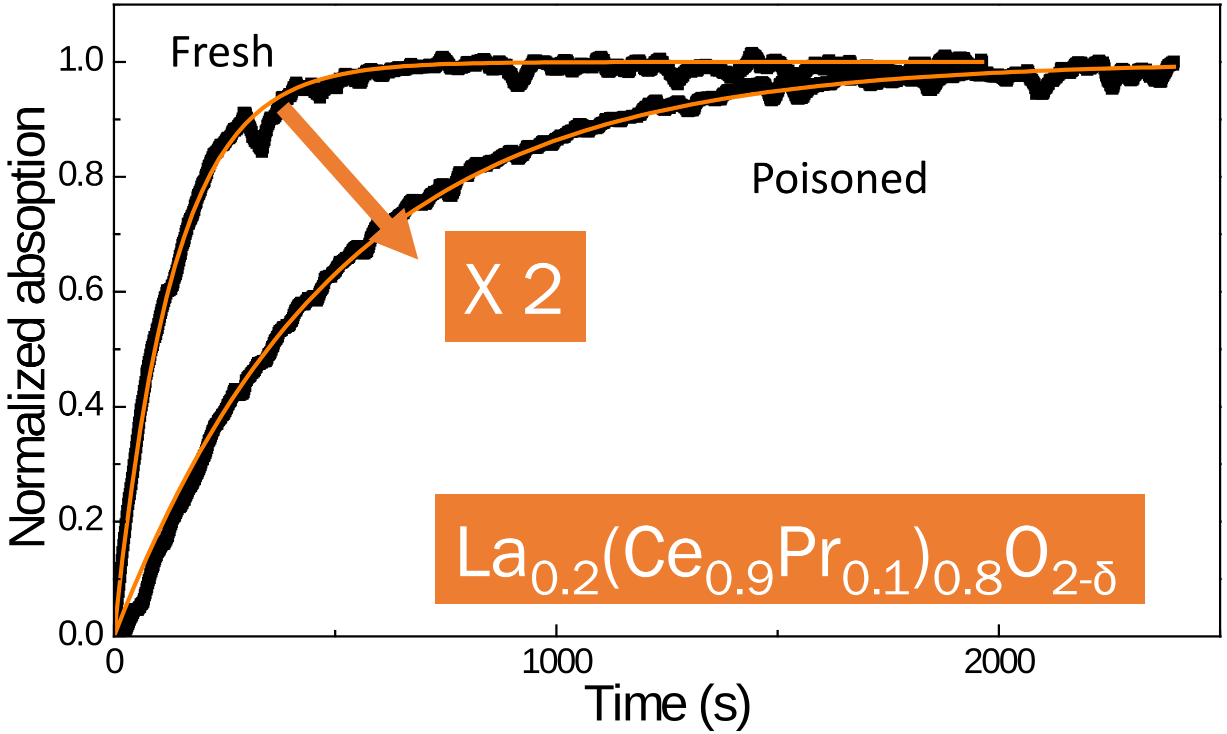
Resistance to Silicon poisoning

Resistance to Si poisoning

Poisoning with TEOS (10 ppm)

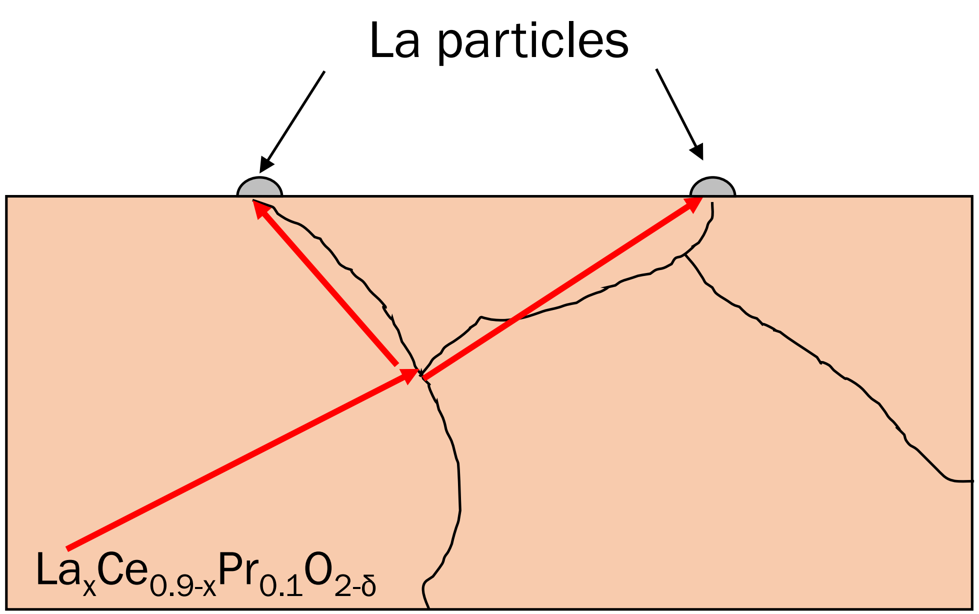




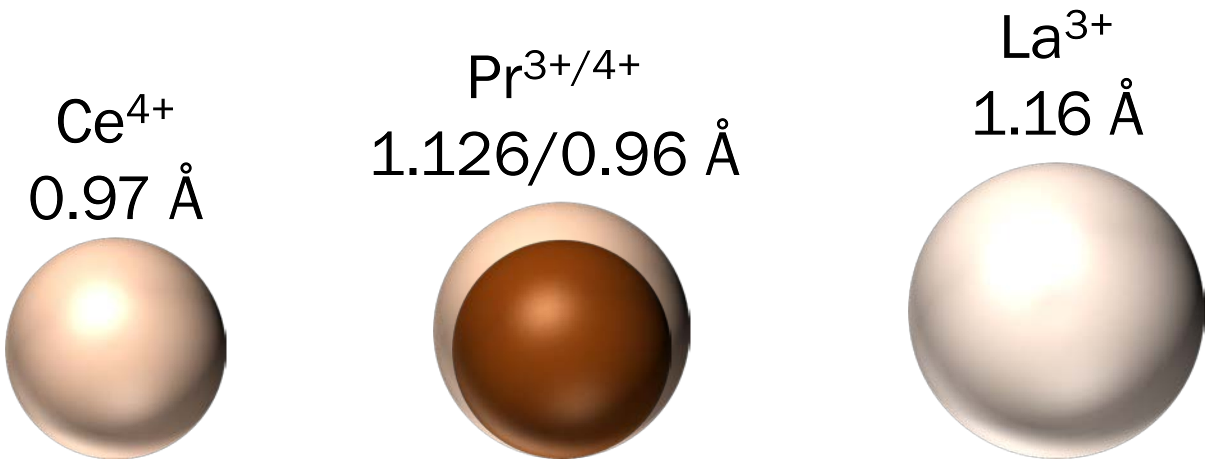


La doping → Slightly lower degradation
More La on surface?

How to induce lanthanum segregation



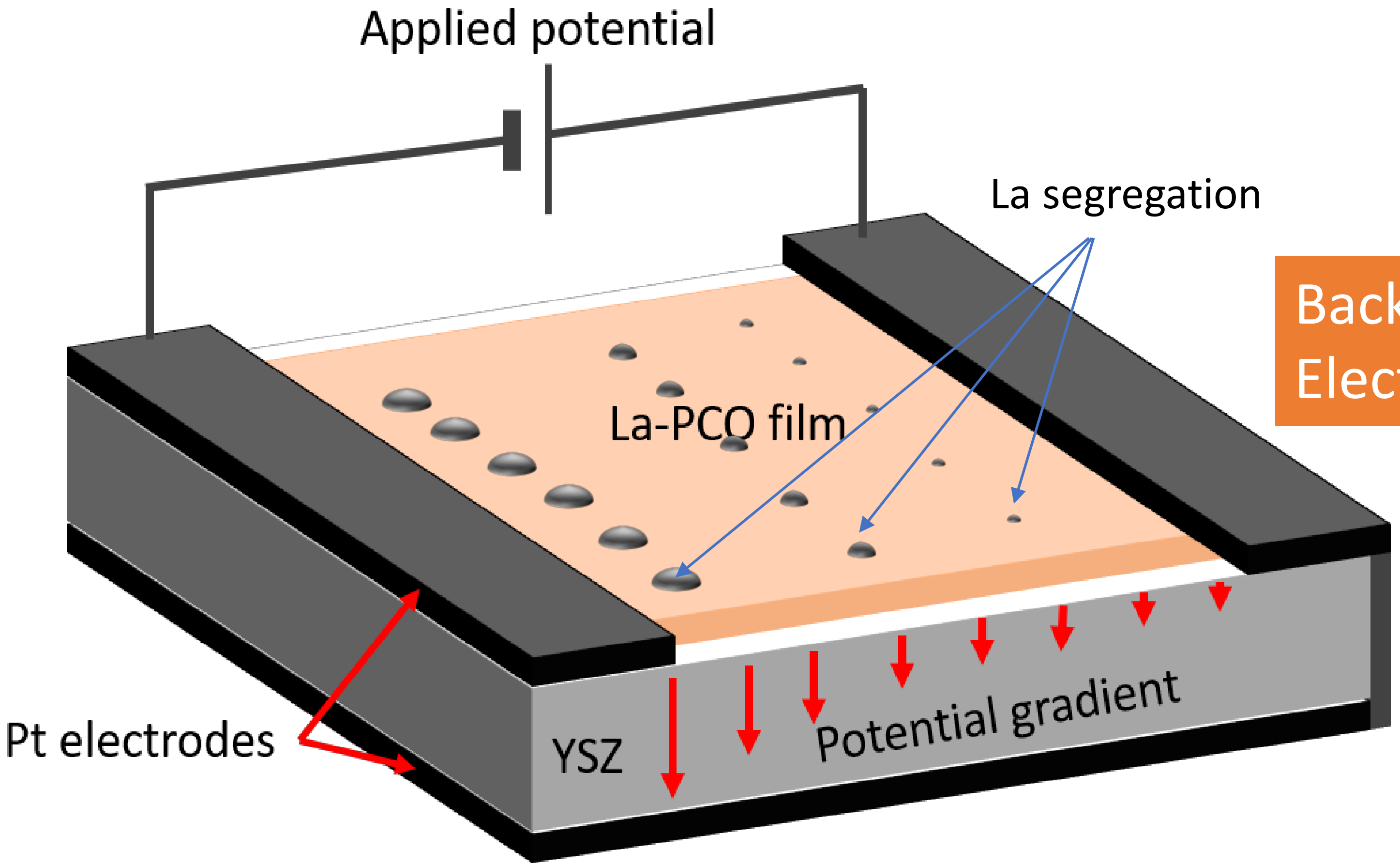
Driving forces for segregation:
- Lattice strain
- Electrostatic potential gradient



Reduction/Oxidation?
Electrical potential effect?

How to induce lanthanum segregation

Electrical potential → reduction of Pr → change in lattice strain
→ migration of charged defects (La'_{Ce})

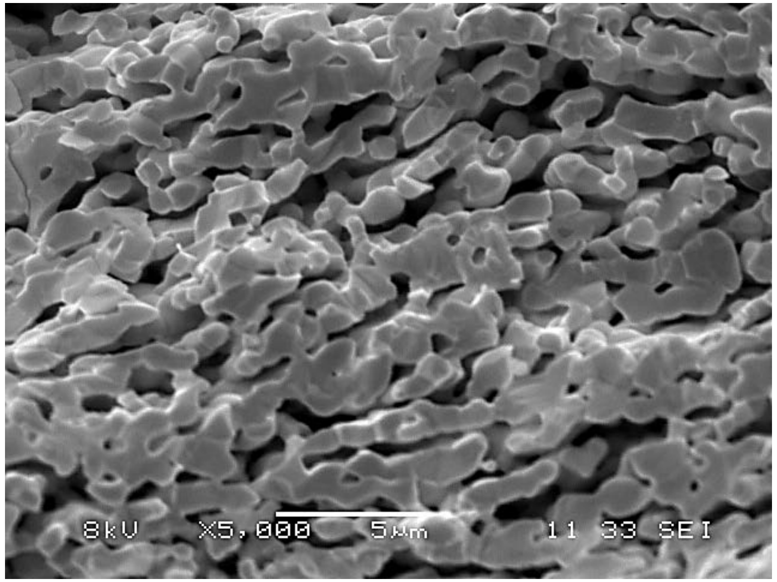


Back-electrode setup: systematic study
Electrical potential / La segregation

Influence of surface La on k_{chem}

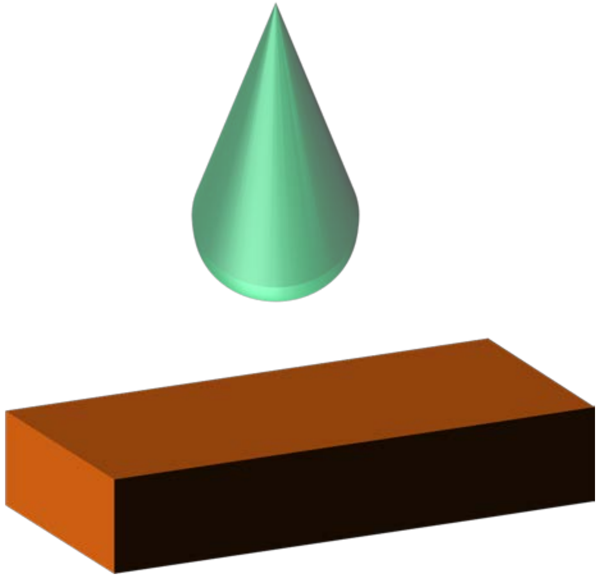
Surface modification: infiltration

Preparation of Porous PCO bars



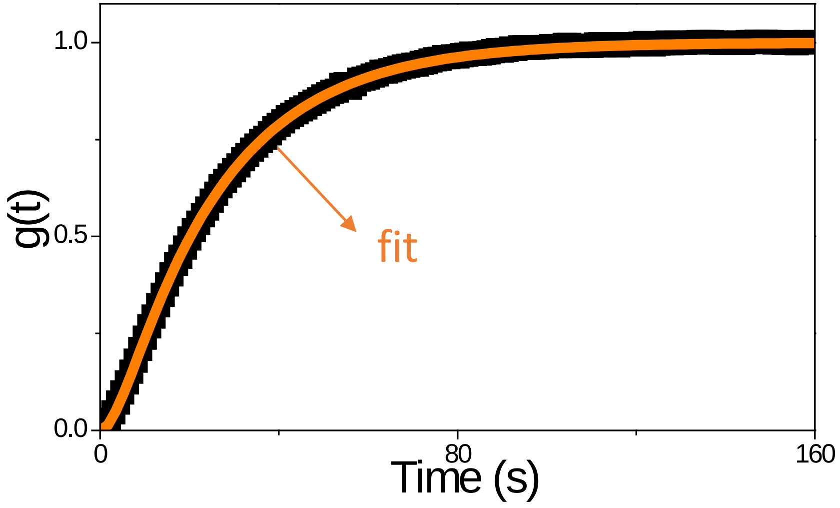
Pressing + sintering

Infiltration with La nitrate



Calcination 600°C

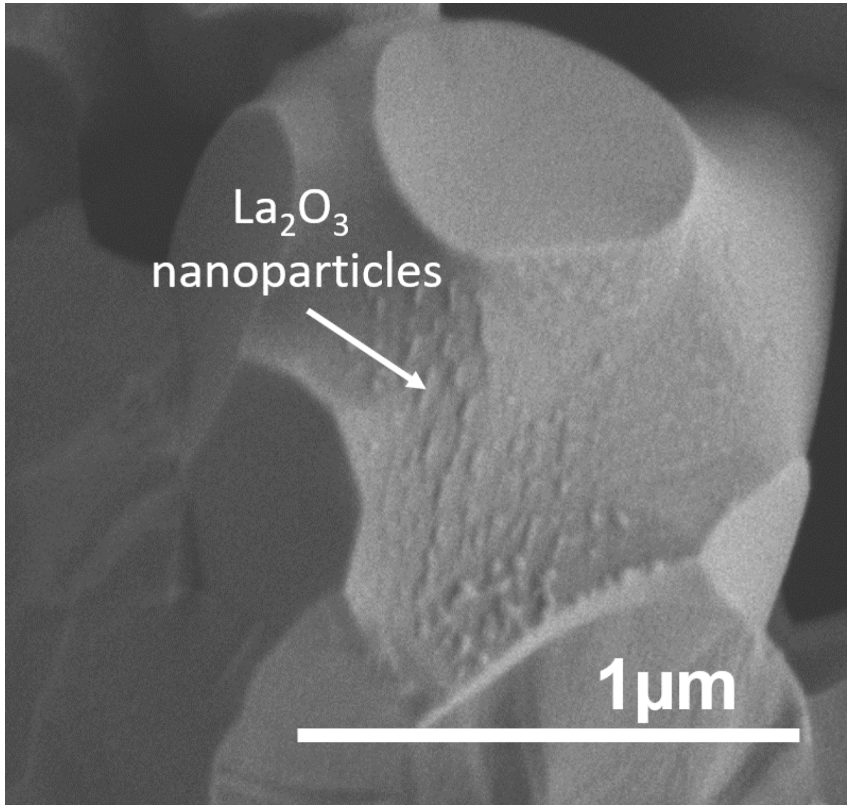
Conductivity relaxation
Surface exchange rate

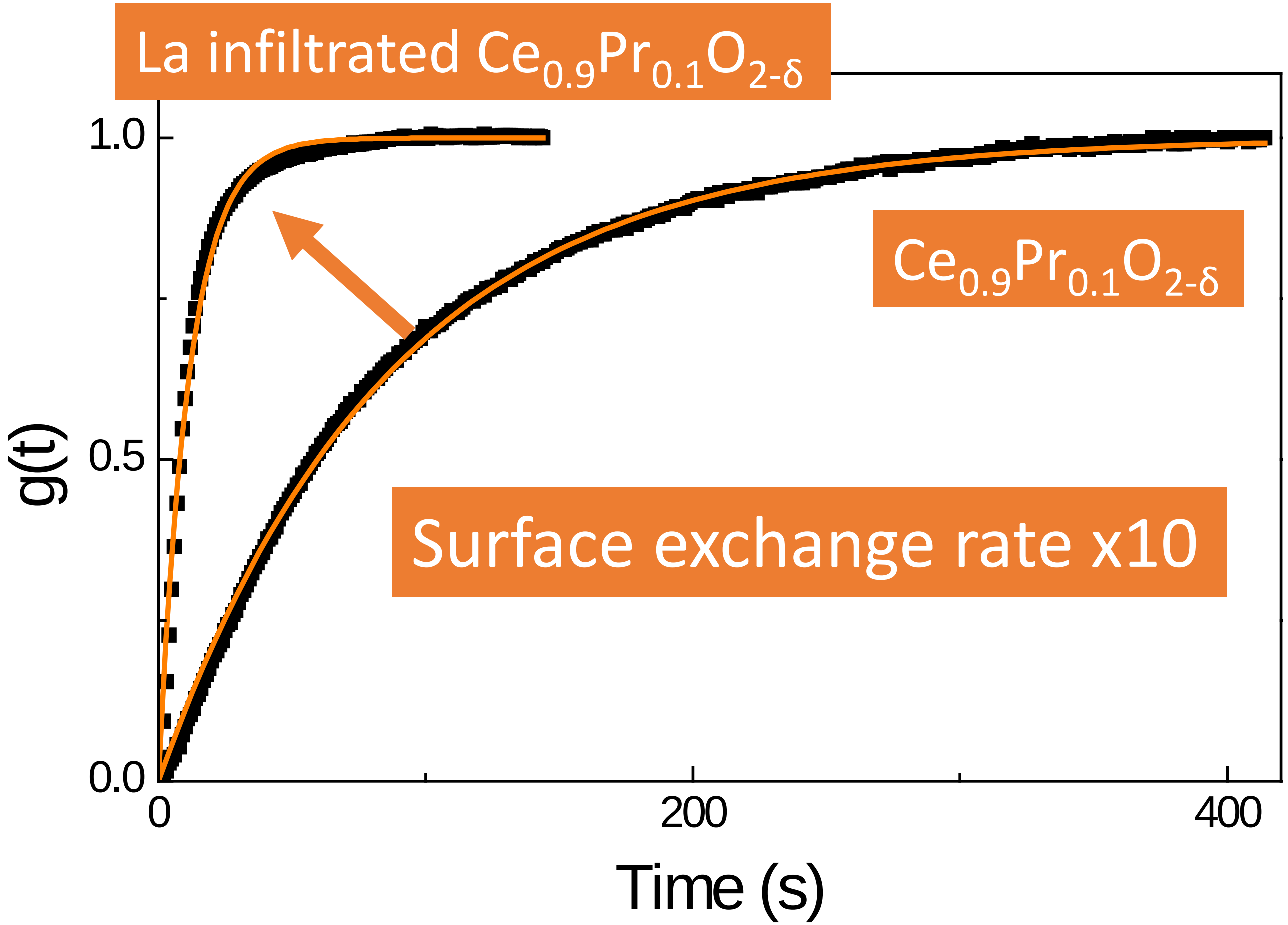


G(t): normalized conductivity

Surface modification: La infiltration

Comparison of surface exchange rates w/ & w/o La infiltration





Oxygen exchange rate increased with single valent oxide?

Conclusions

Best conductivity for intermediate composition $La_{0.1}(Pr_{0.1}Ce_{0.9})_{0.9}O_{2-\delta}$

Increase of surface exchange rates with $La_{0.2}(Pr_{0.1}Ce_{0.9})_{0.8}O_{2-\delta}$

Slight improvement of Si poisoning resistance with La doping

Surface exchange x10 with La infiltration

Perspectives

Long term continuous poisoning experiments

Segregation of La through reducing treatment or electrical potential

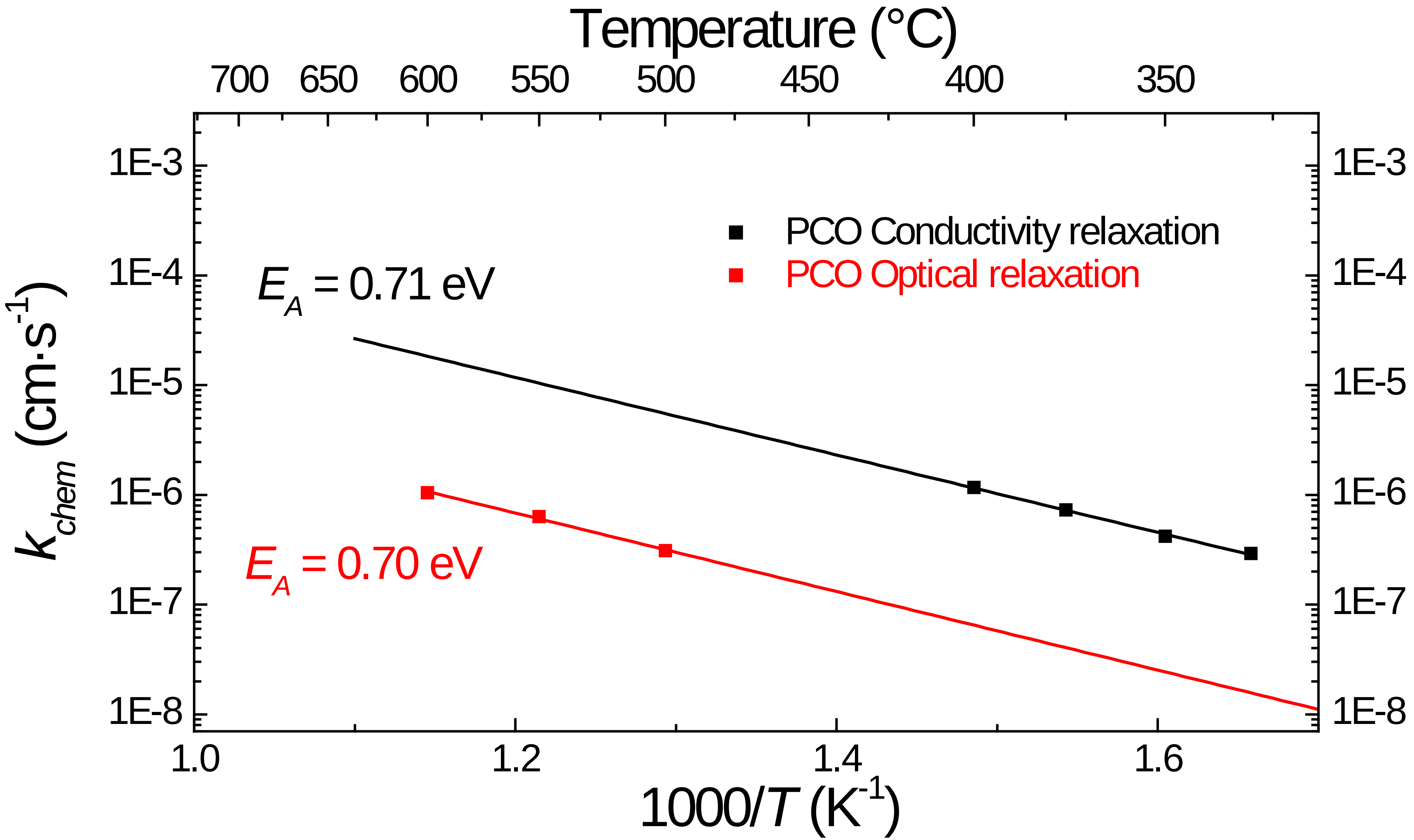
Surface analysis to better understand La influence on surface exchange

Other elements?

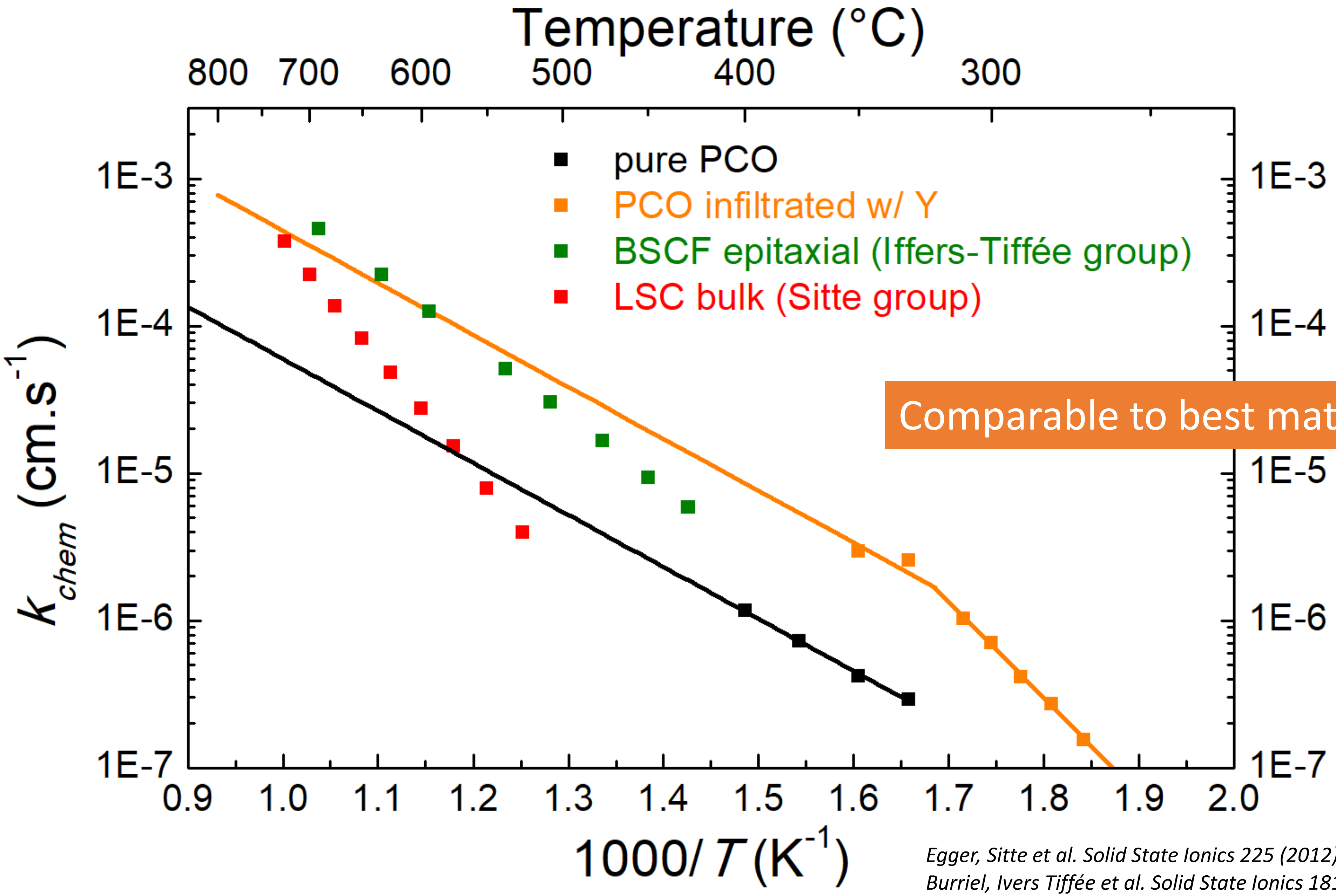
Acknowledgment: NETL Award DE-FE0026109 Phase 1
Program Manager: Dr. Joseph Stoffa

Thank you for your attention

Comparison PCO bulk and film k_{chem}



Surface modification: Oxygen surface exchange rate



Comparable to best materials in literature

Egger, Sitte et al. Solid State Ionics 225 (2012) 55–60
Burriel, Ivers Tiffée et al. Solid State Ionics 181 (2010) 602–608