Influence of surface chemistry of fluorite-type cathode materials on oxygen reduction reaction

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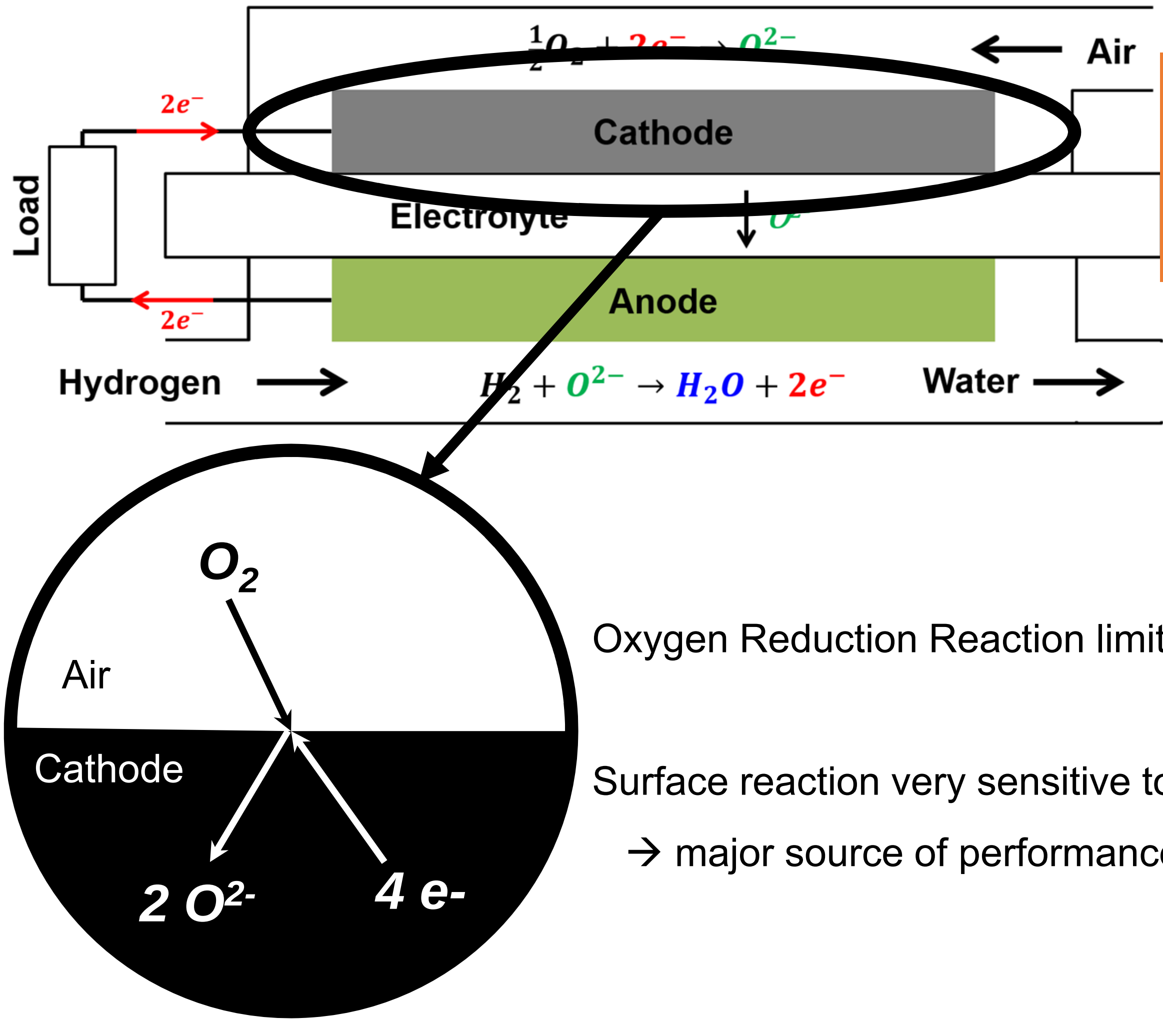
Solid Oxide Fuel Cells



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

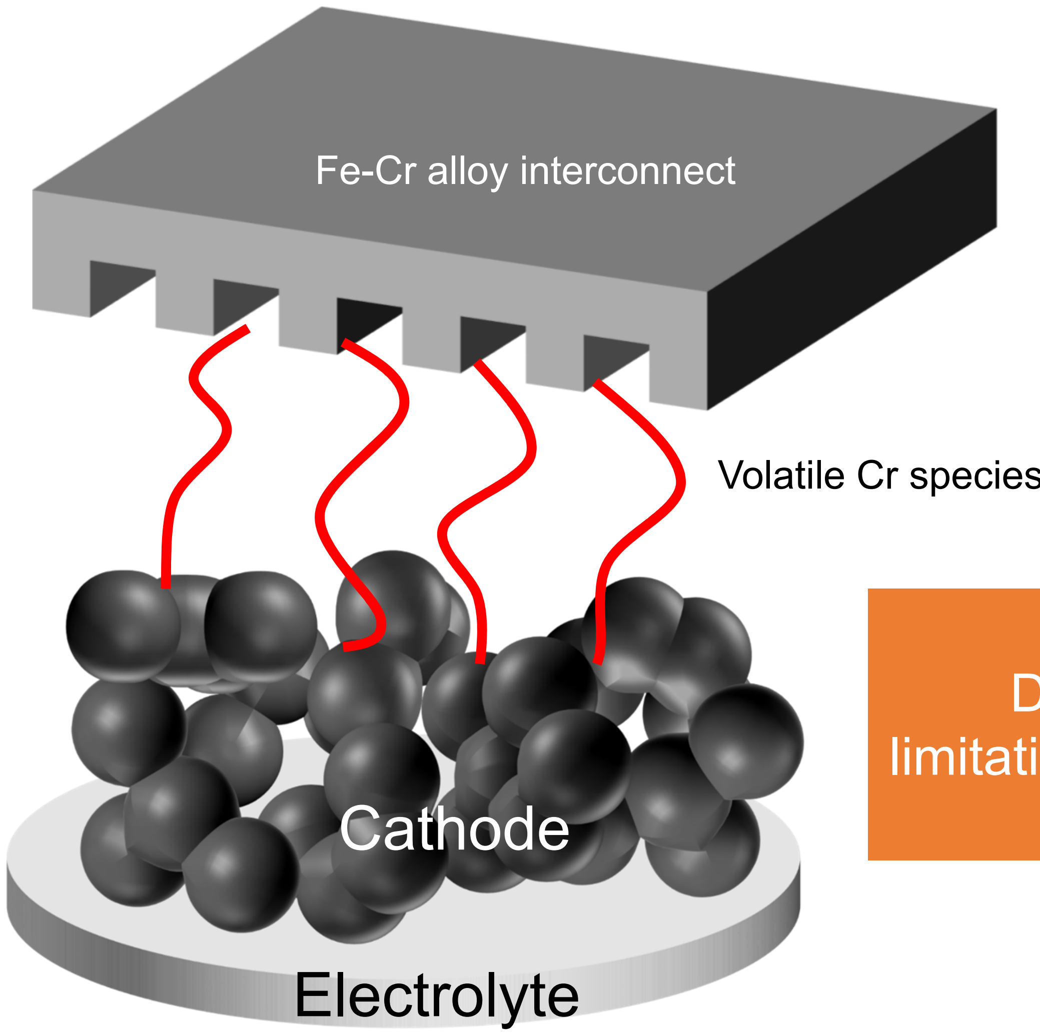
Main drawback to address: performance degradation

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

Surface reaction very sensitive to contaminants

→ major source of performance degradation

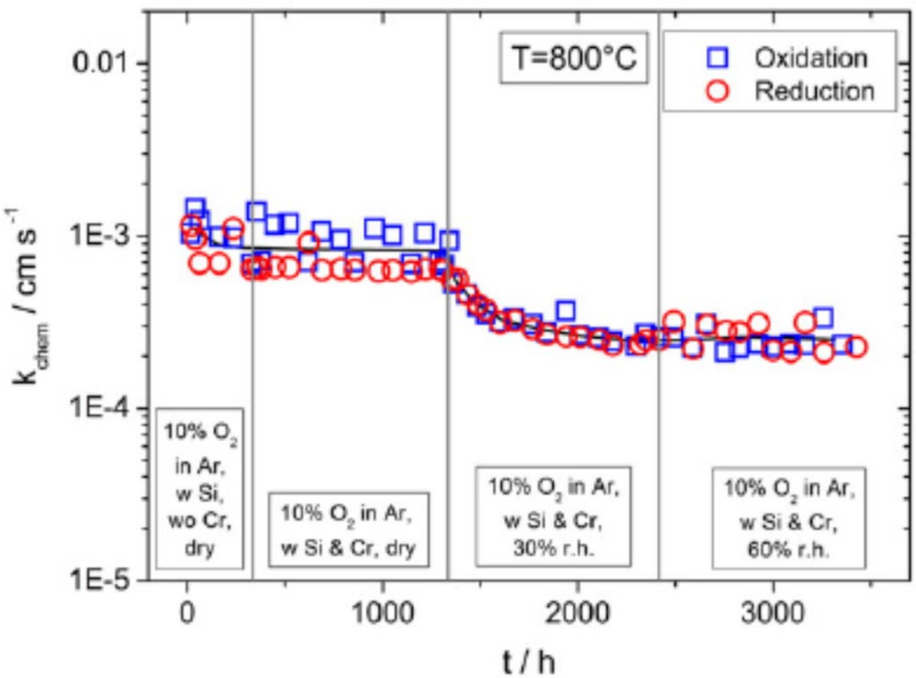
Chromium poisoning of SOFC cathodes

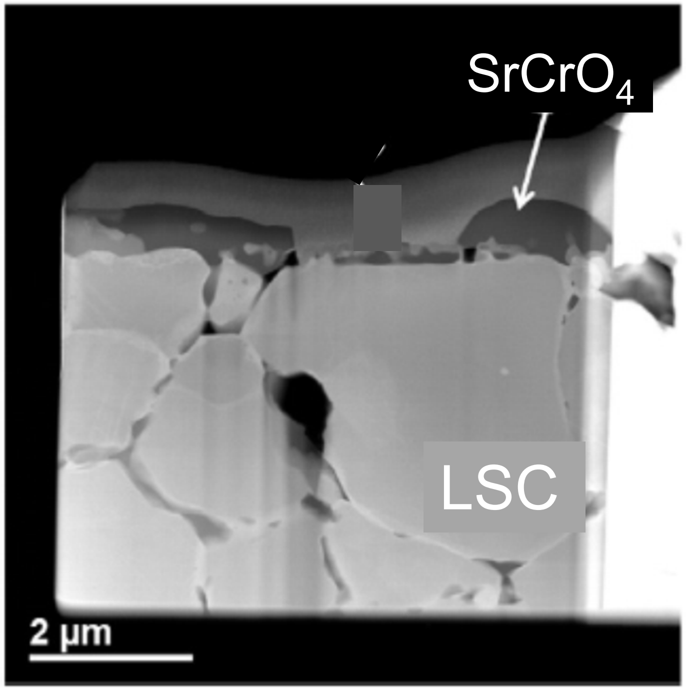


Chromium from interconnect:
Deposition onto cathode active sites
limitation of oxygen surface exchange reaction
Degradation of performance

Cr-poisoning In Sr-containing cathodes

Surface Exchange coefficient k_{chem} of $La_{0.6}Sr_{0.4}CoO_3$ under Cr source

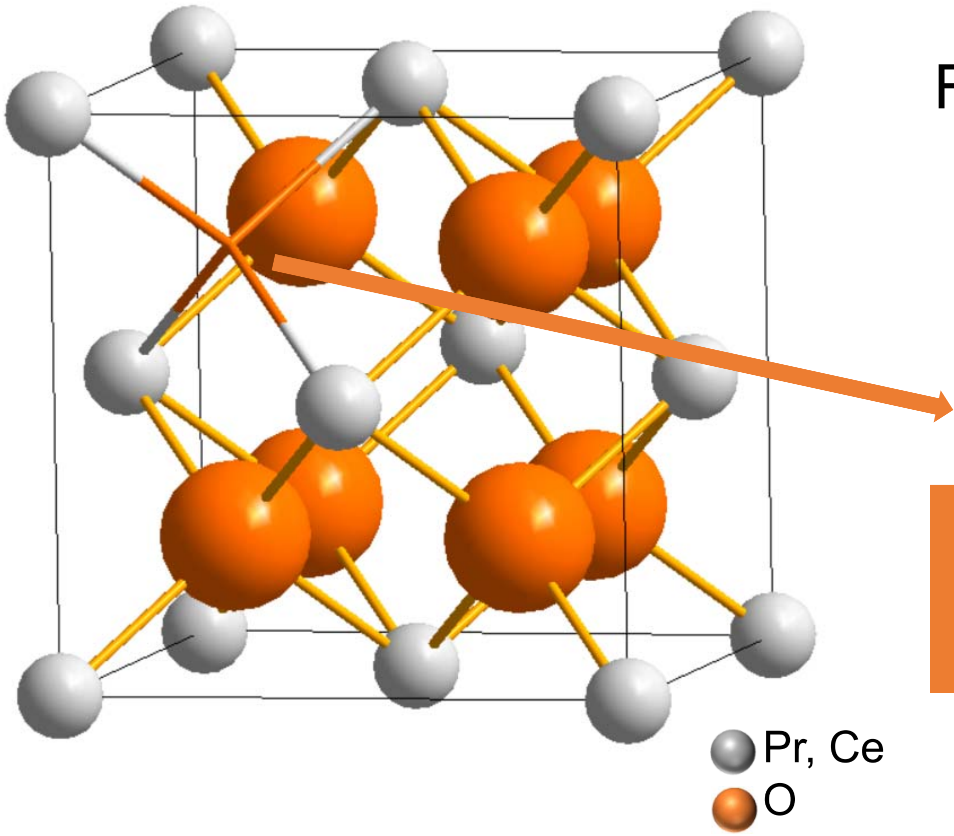




Bucher et al., Solid State Ionics 299 (2017) 26–31

Main degradation in humidified air and due formation of to $SrCrO_4$

Sr-free cathode material – Pr-Ce oxides



Fluorite CaF_2 type structure

Pr mixed valence 3+/4+

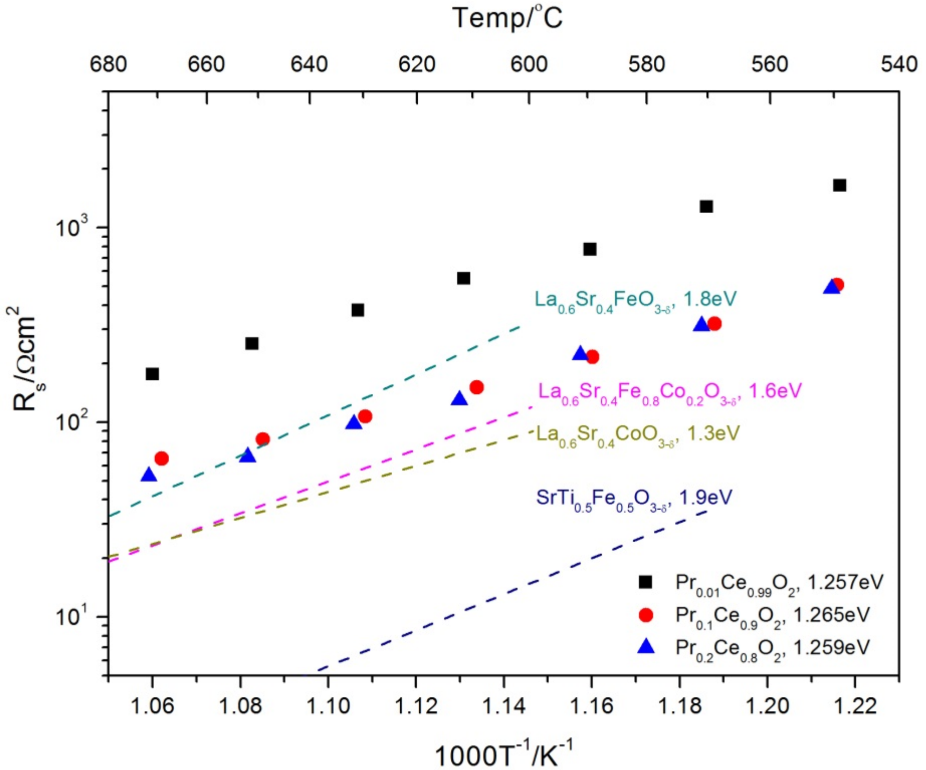
O^{2-} vacancies

High O^{2-} Diffusion & Electrochemical activity
Sr-free
Simple AO material (one cation site)

Sr-free cathode material – Pr-Ce oxides

Praseodymium doped ceria

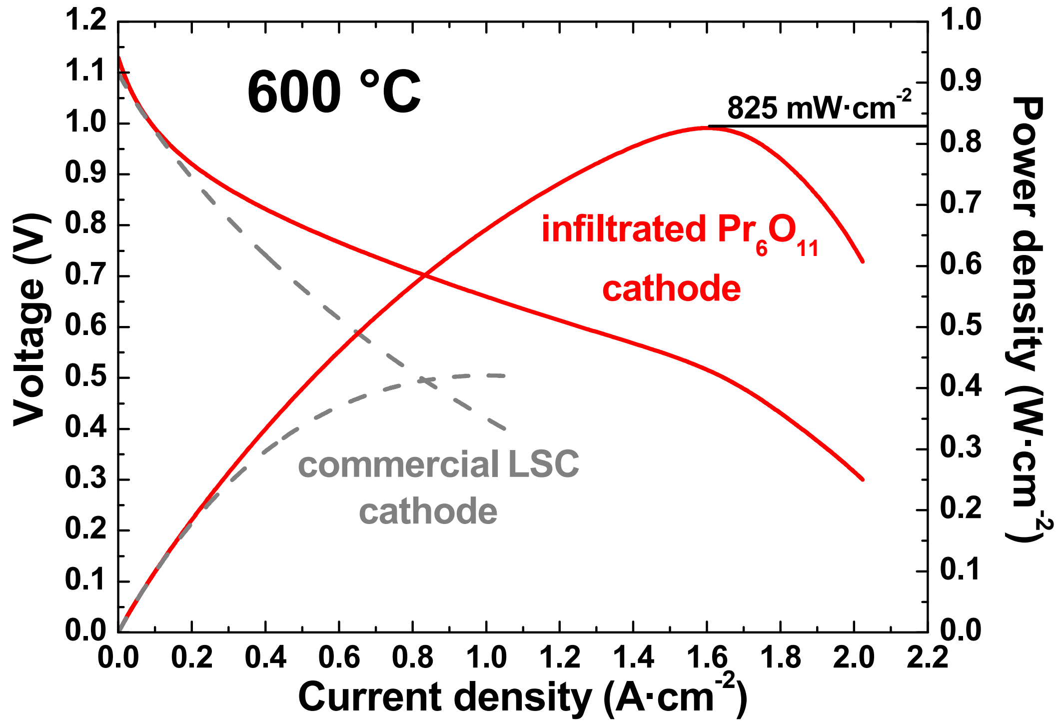
Surface resistance similar to perovskites



*D. Chen, H.L. Tuller, et al., J. Electroceramics, **28**, 62–69 (2012).*

Praseodymium oxide Pr_6O_{11}

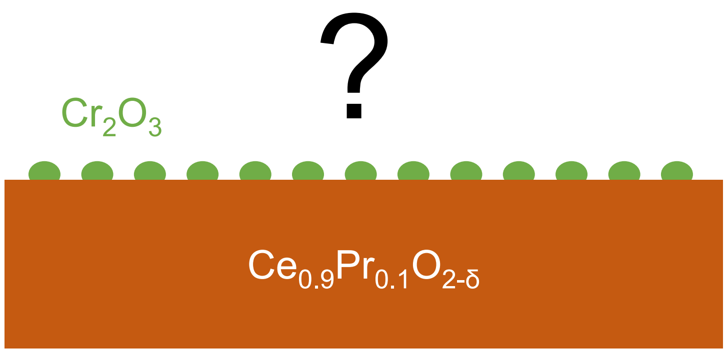
Pr_6O_{11} infiltrated into GDC cathode (on commercial half-cell)
Commercial single cell w/ LSC cathode (same anode/electrolyte)



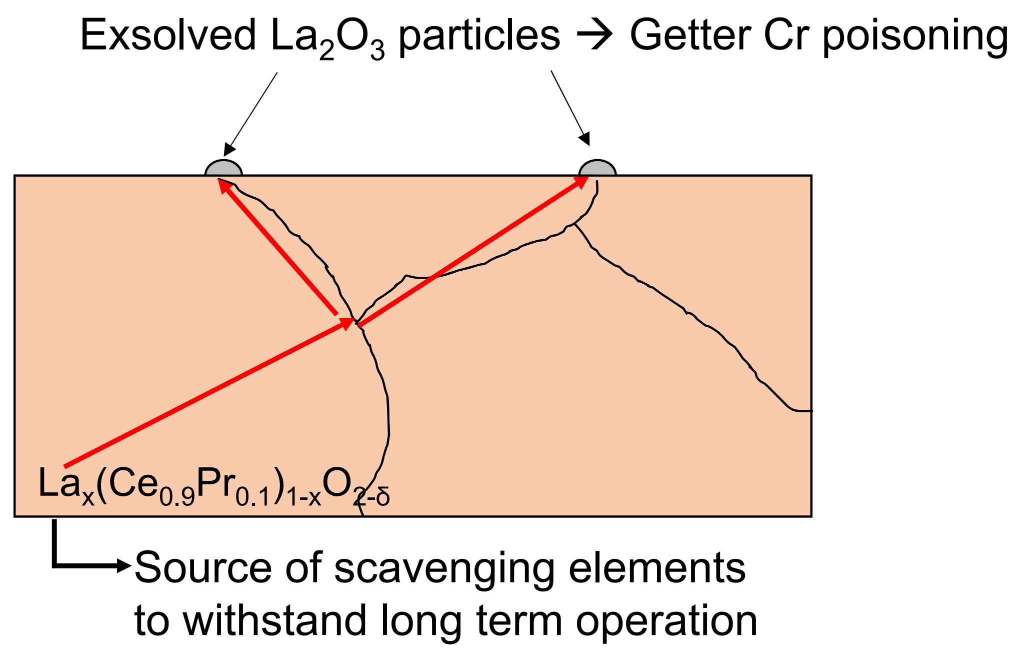
Nicollet et al., Int. J. Hydrogen Energy 41 (34), 15538-15544 (2016)

Performance comparable to state of the art cathode materials

Project description and objectives



Cr poisoning of Pr-doped ceria electrodes

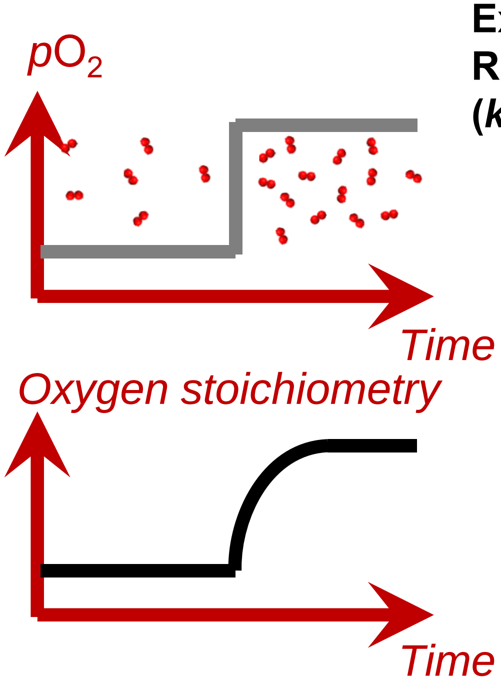


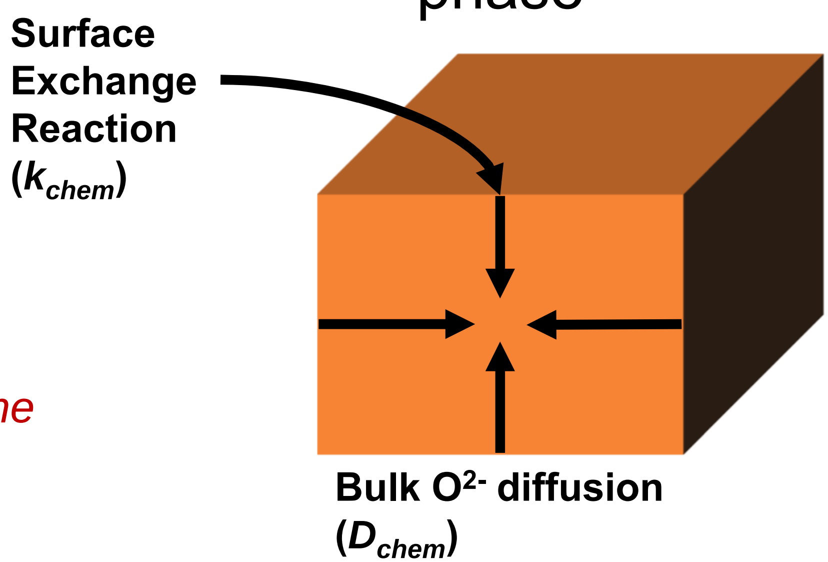
Self-Cleaning Material

Study of the influence of Chromium on PCO surface exchange rate

Measurement of surface exchange coefficient – Conductivity relaxation

Kinetics of oxygen stoichiometry equilibration with the gas phase



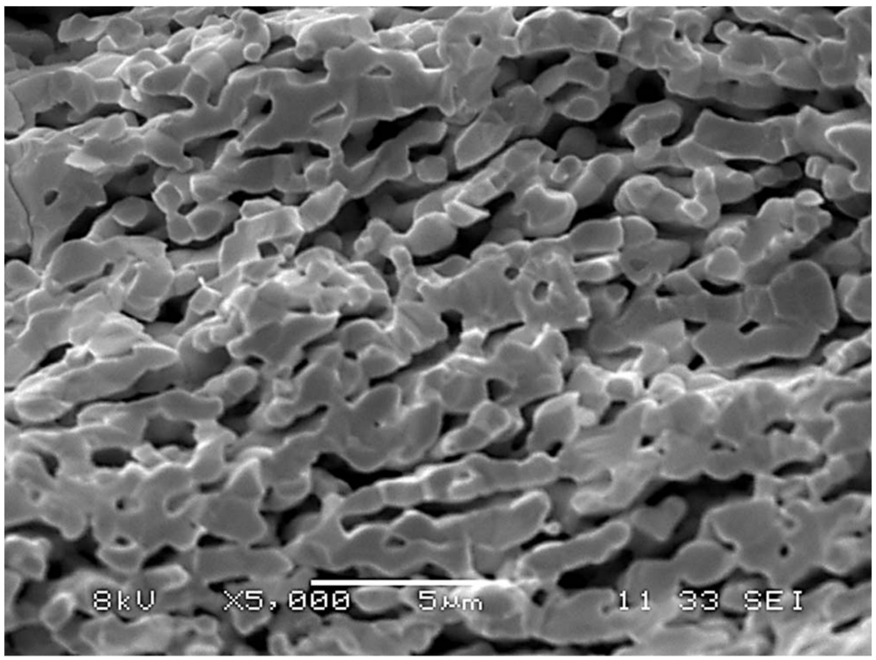


Conductivity transient depends on k_{chem} and D_{chem}

Measurement of surface exchange coefficient – Conductivity relaxation

When l<<K_{Chem}/D, the transport is limited by the surface exchange

Porous sample → Short diffusion length → surface exchange limited



$$g(t) = \frac{\sigma(t) - \sigma(0)}{\sigma_\infty - \sigma(0)} = 1 - \exp\left[-\frac{t}{\tau_r}\right]$$

porosity

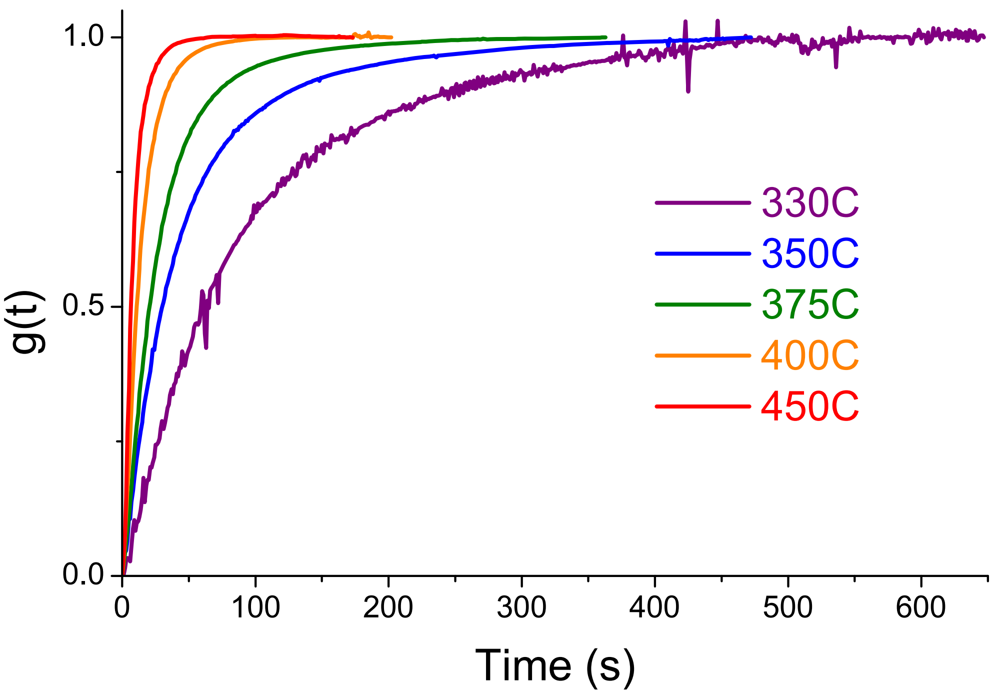
$$\tau_r = \frac{(1 - V_v)}{S_V k_{chem}}$$

Surface area

Ganeshananthan et al. Journal of The Electrochemical Society, ***153*** *12 A2181-A2187 2006*

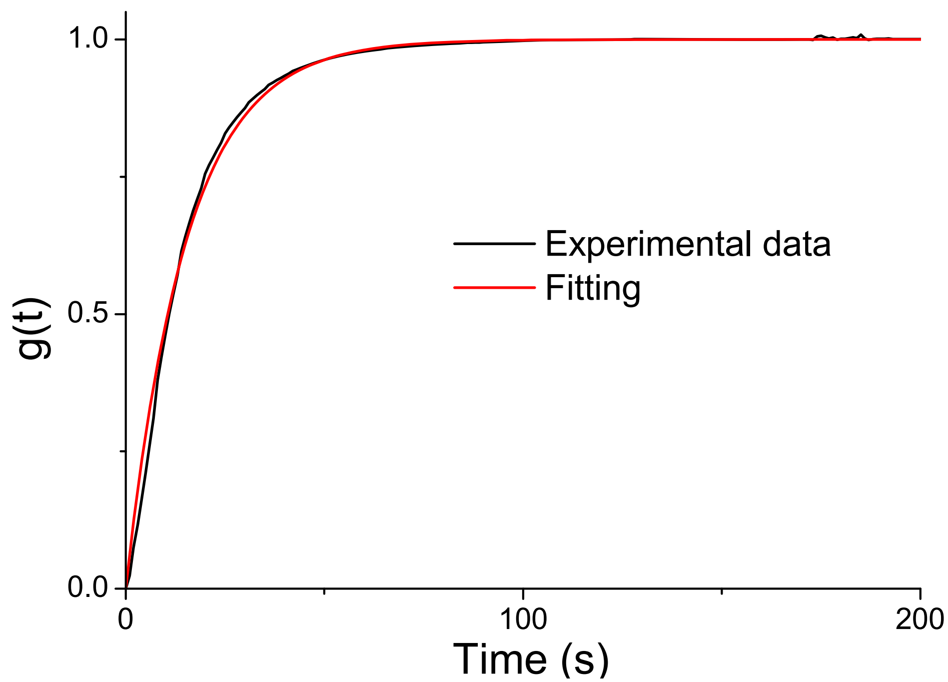
Conductivity relaxation on PCO

Normalized Conductivity vs. time at different Temperatures



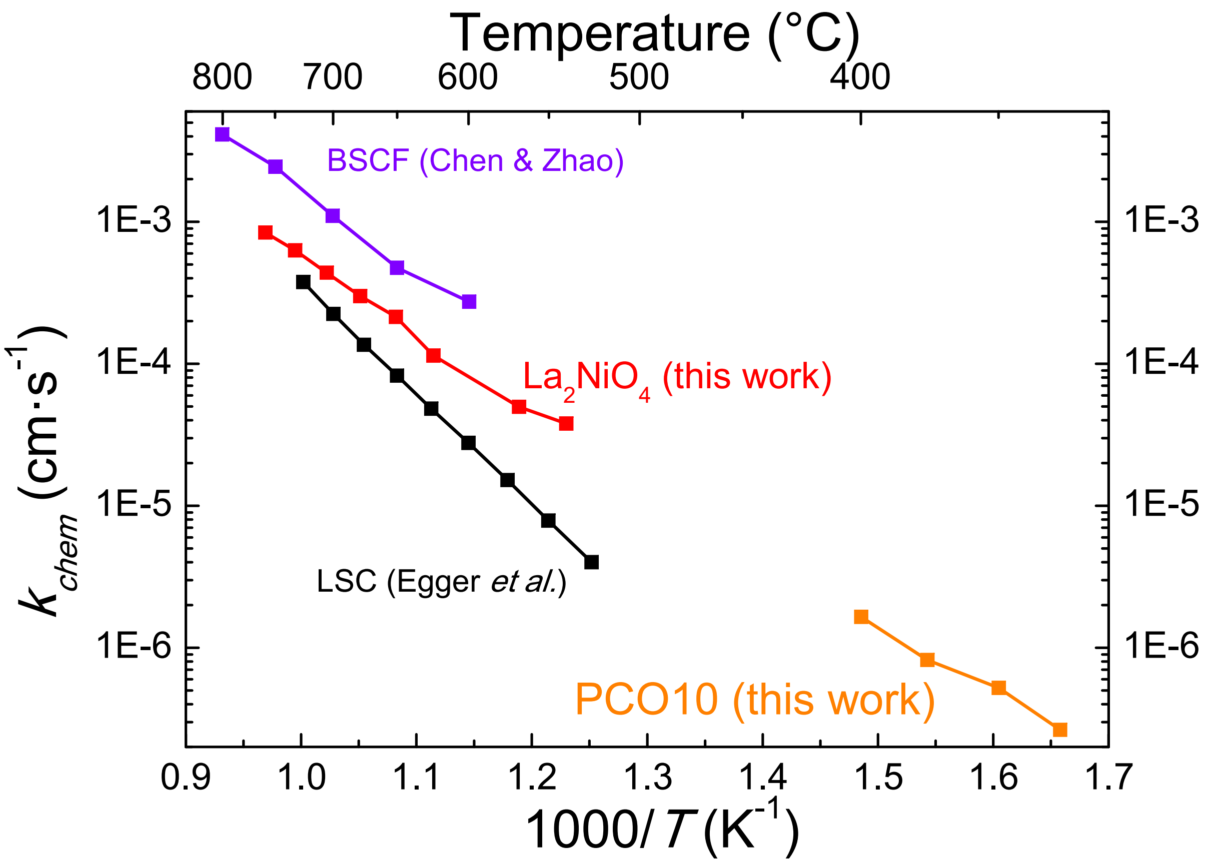
Normalized Conductivity vs. time @ 400C
Data and Fitting Curve

$$g(t) = \frac{\sigma(t) - \sigma(0)}{\sigma_\infty - \sigma(0)} = 1 - \exp\left[-\frac{t}{\tau_r}\right]$$



Surface exchange coefficient of PCO

Before chromium poisoning experiments



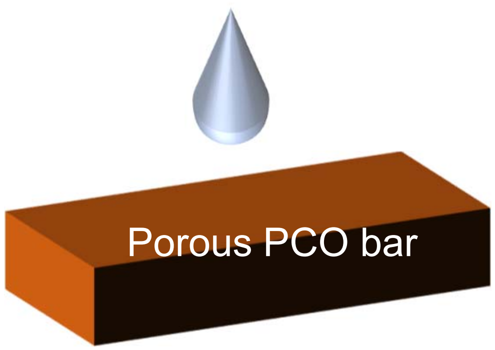
High surface exchange coefficient
Comparable to state-of-the-art materials

Conductivity relaxation on porous samples
→ Easier preparation
→ High surface (more reliable)
→ Enable measurement at low temperatures

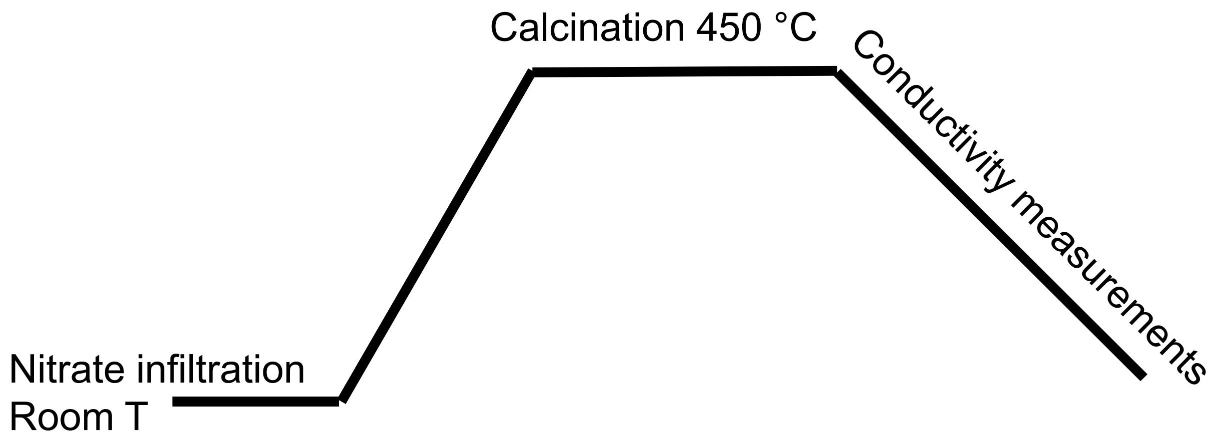
Egger et al., Solid State Ionics 225 (2012) 55–60
Chen & Zhao International Journal of Hydrogen Energy 36 (2011) 6948-6956

Chromium poisoning study - strategy

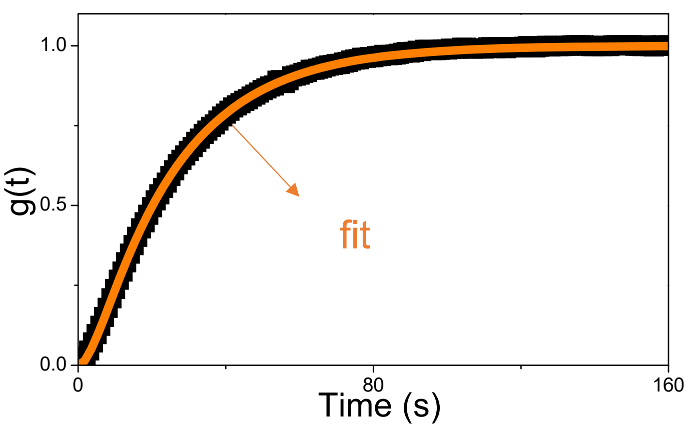
Artificial poisoning with $Cr(NO_3)_3$ solution



Taking advantage of low temperatures measurements



Conductivity relaxation
Surface exchange rate



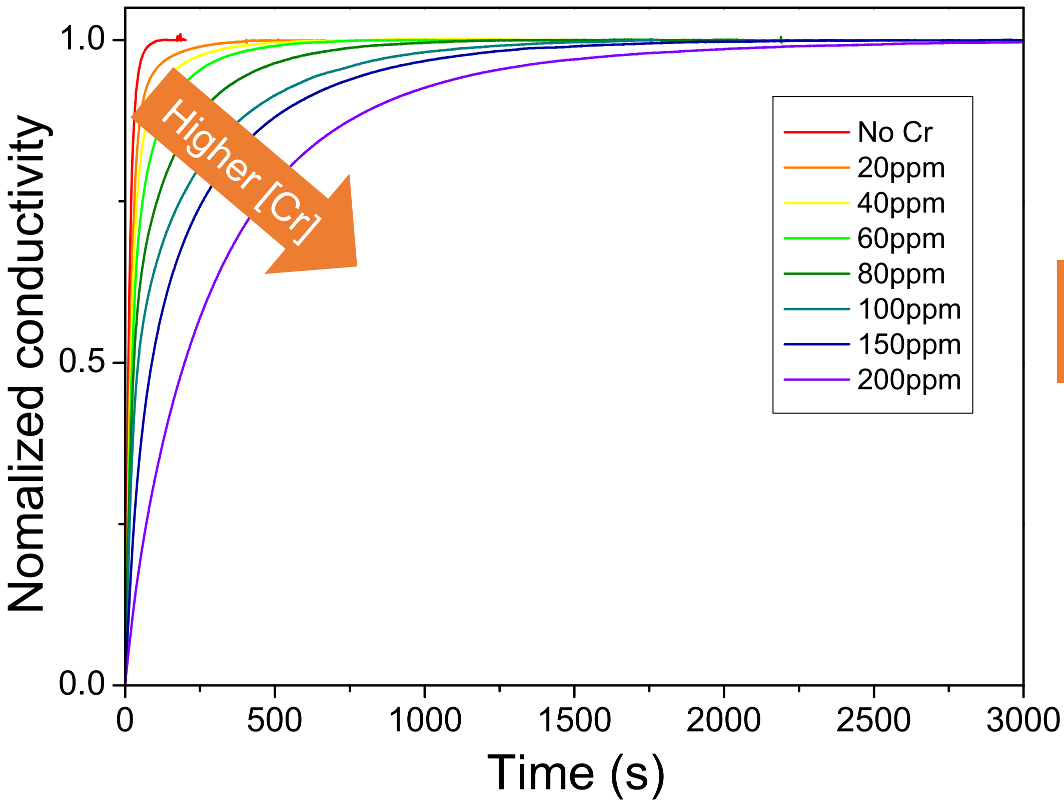
Difference between masking and reactive poisoning

Calcination 450 °C

Annealing 800 °C

Chromium poisoning on PCO

Conductivity transient after Cr poisoning increment (calcination at 450 °C)
Measurement at 400 °C

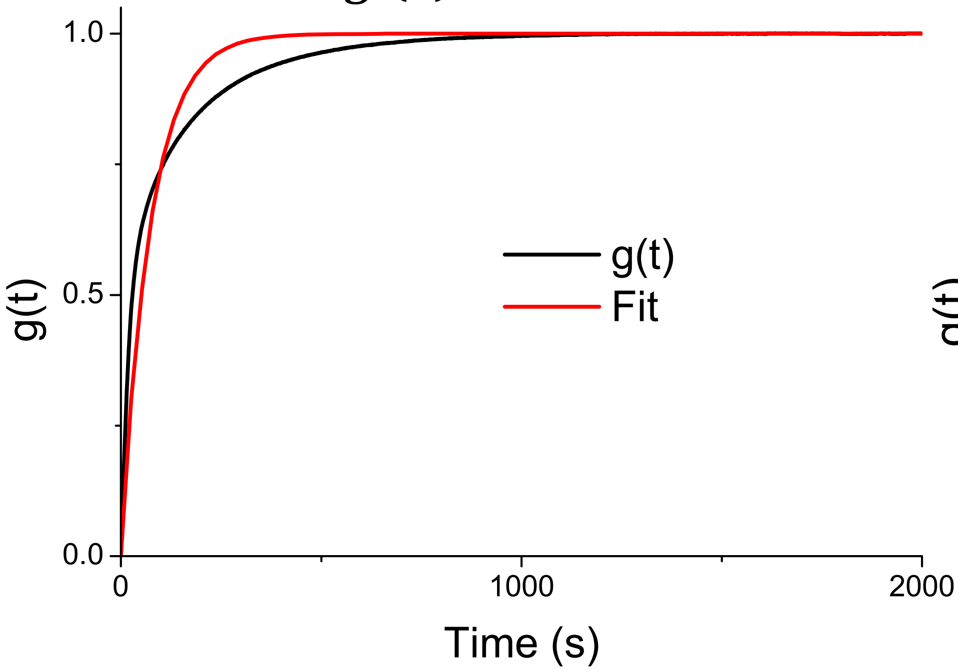


Degradation of the surface exchange rate even with low temperature calcination

Chromium poisoning on PCO

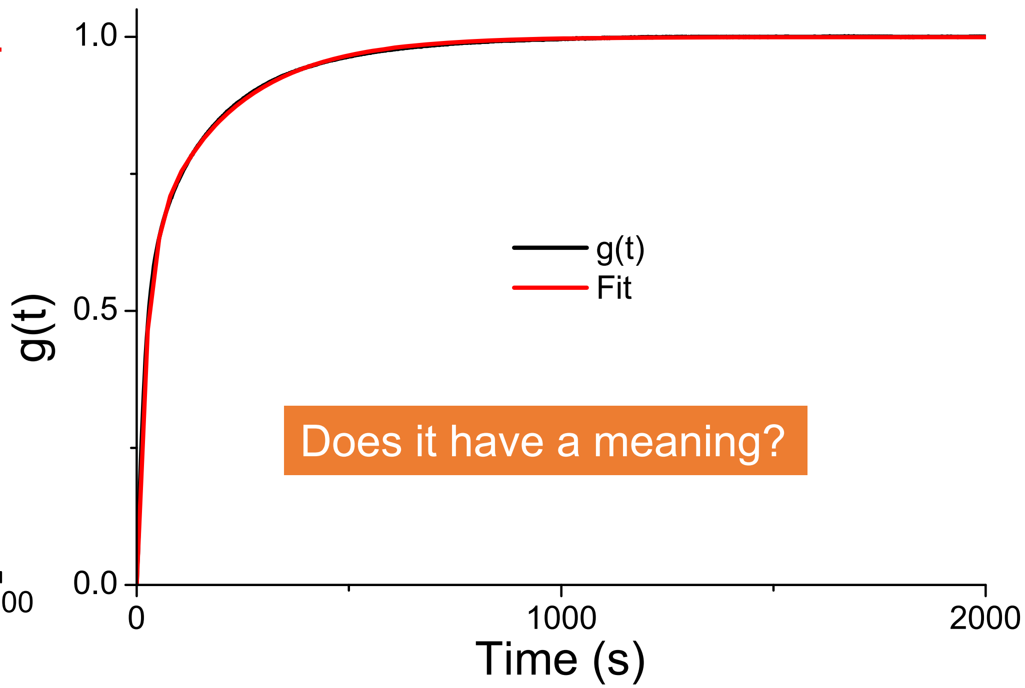
Cr level - 80ppm
Normalized Conductivity vs. time
400C
Data and Fitting Curve

$$g(t) = 1 - e^{-t/\tau}$$



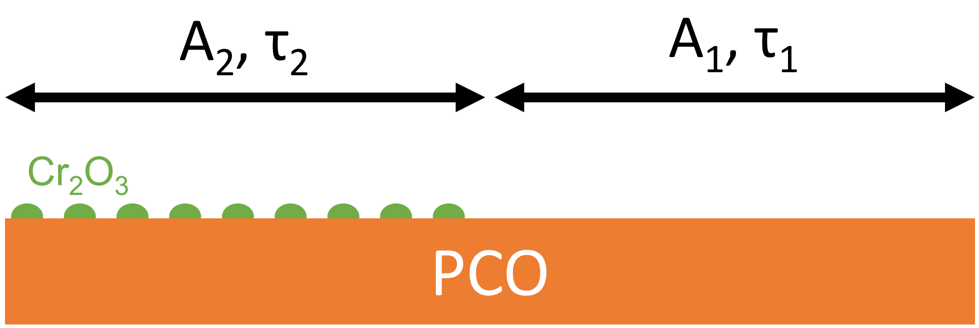
$$g(t) = A_1\left(1 - e^{-t/\tau_1}\right) + A_2\left(1 - e^{-t/\tau_2}\right)$$

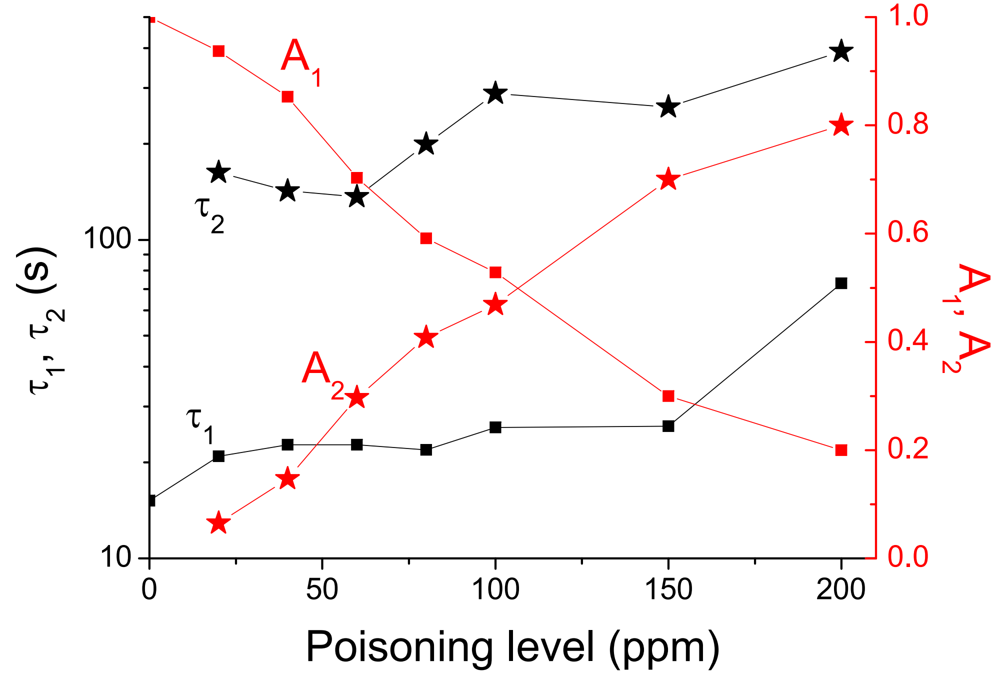
$$A_1 + A_2 = 1$$



Fitting conductivity transients after poisoning

$$g(t) = A_1\left(1 - e^{-t/\tau_1}\right) + A_2\left(1 - e^{-t/\tau_2}\right)$$

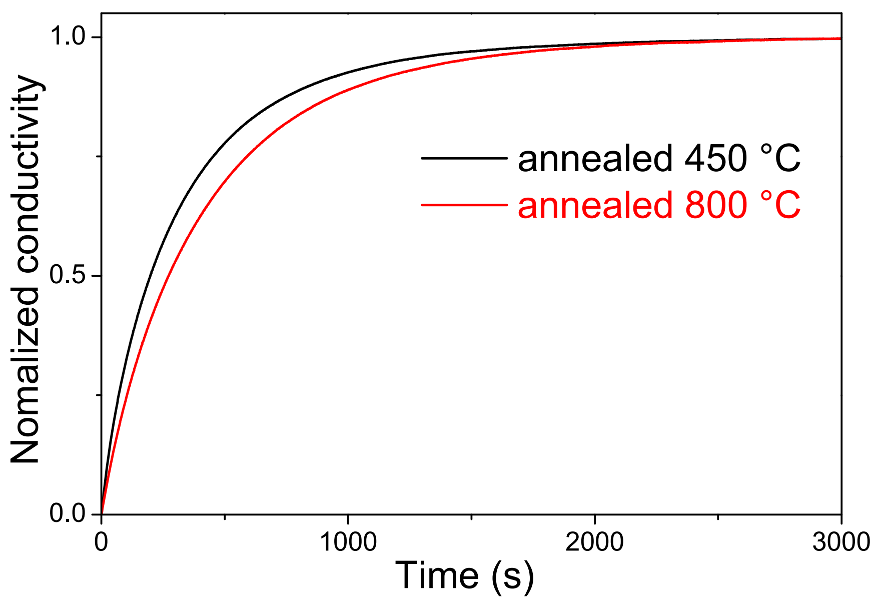


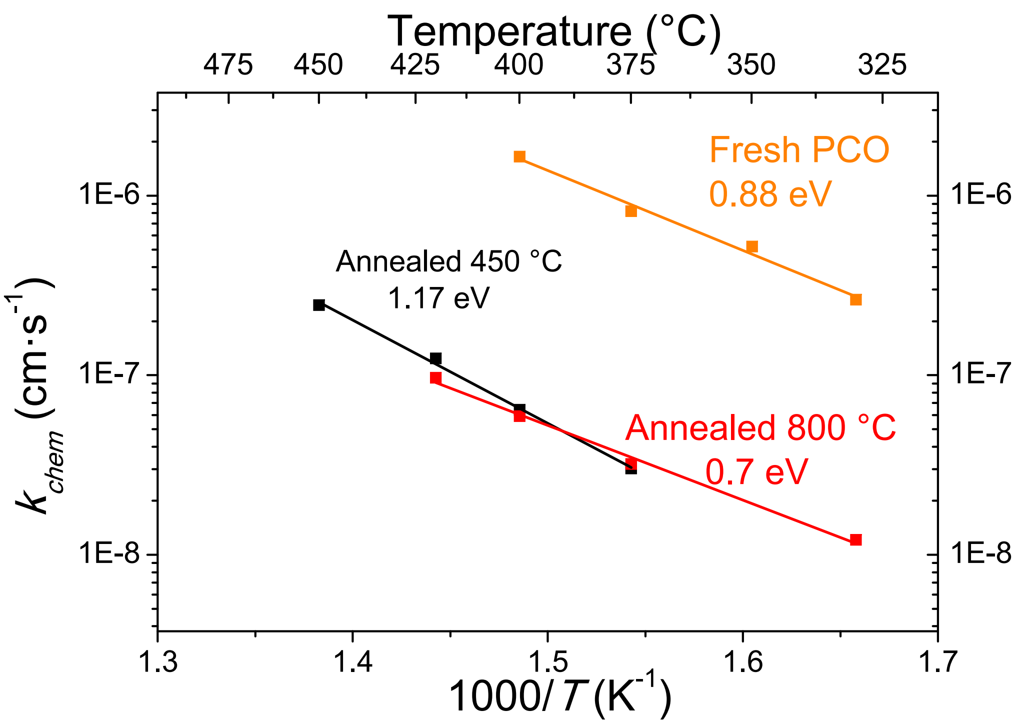


A_1: fraction of the pristine surface
τ_1: related to k_{chem} of the pristine surface
A_2: fraction of the poisoned surface
τ_2: related to k_{chem} of the poisoned surface

Masking or reactivity?

Relaxation profile at 400 °C after 200ppm poisoning



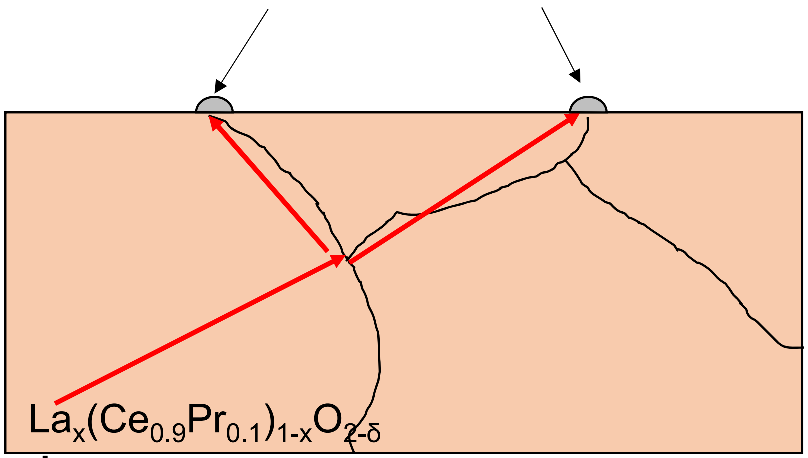


Annealing at 800 °C further degrade surface exchange coefficient
Change of activation → change of material/reaction mechanism?

Structural characterization needed

Project description and objectives

Exsolved La_2O_3 particles → Getter Cr poisoning



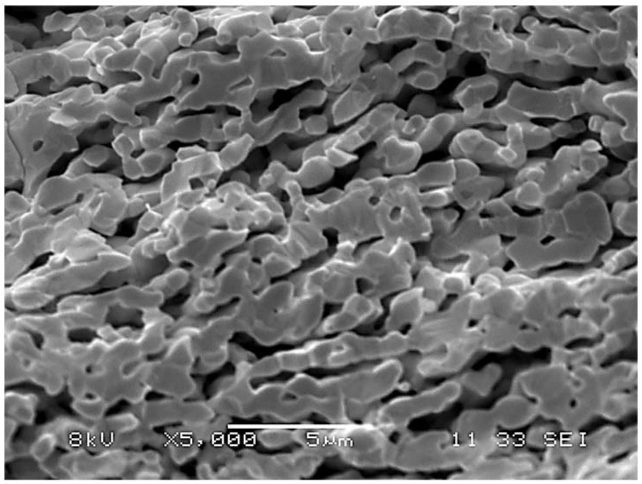
Source of scavenging elements to withstand long term operation

What is the influence of La_2O_3 prior to Cr poisoning?

Surface modification: infiltration

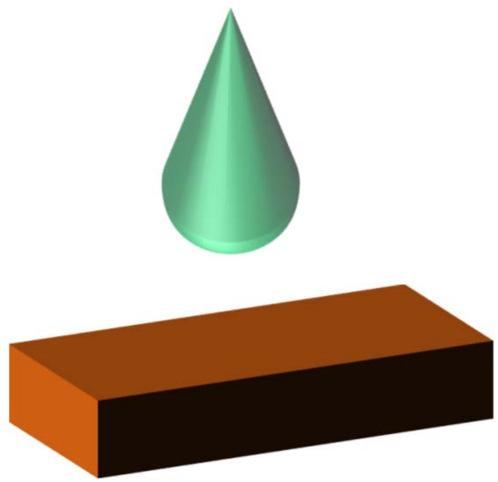
Influence of La_2O_3 (and other RE oxides) in realistic porous microstructures

Preparation of Porous PCO bars



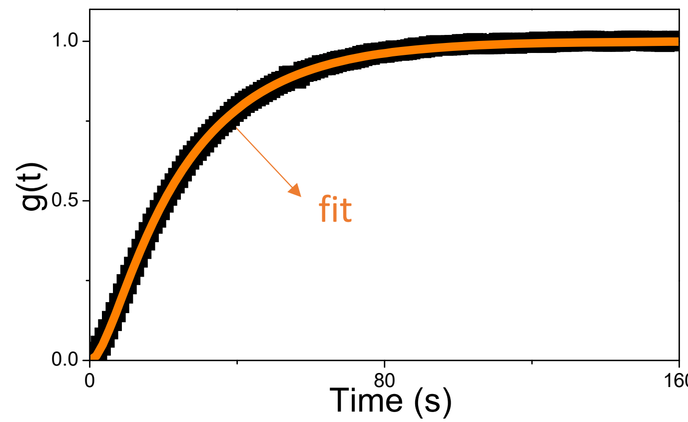
Pressing + sintering

Infiltration with rare earth nitrates



Calcination 600°C

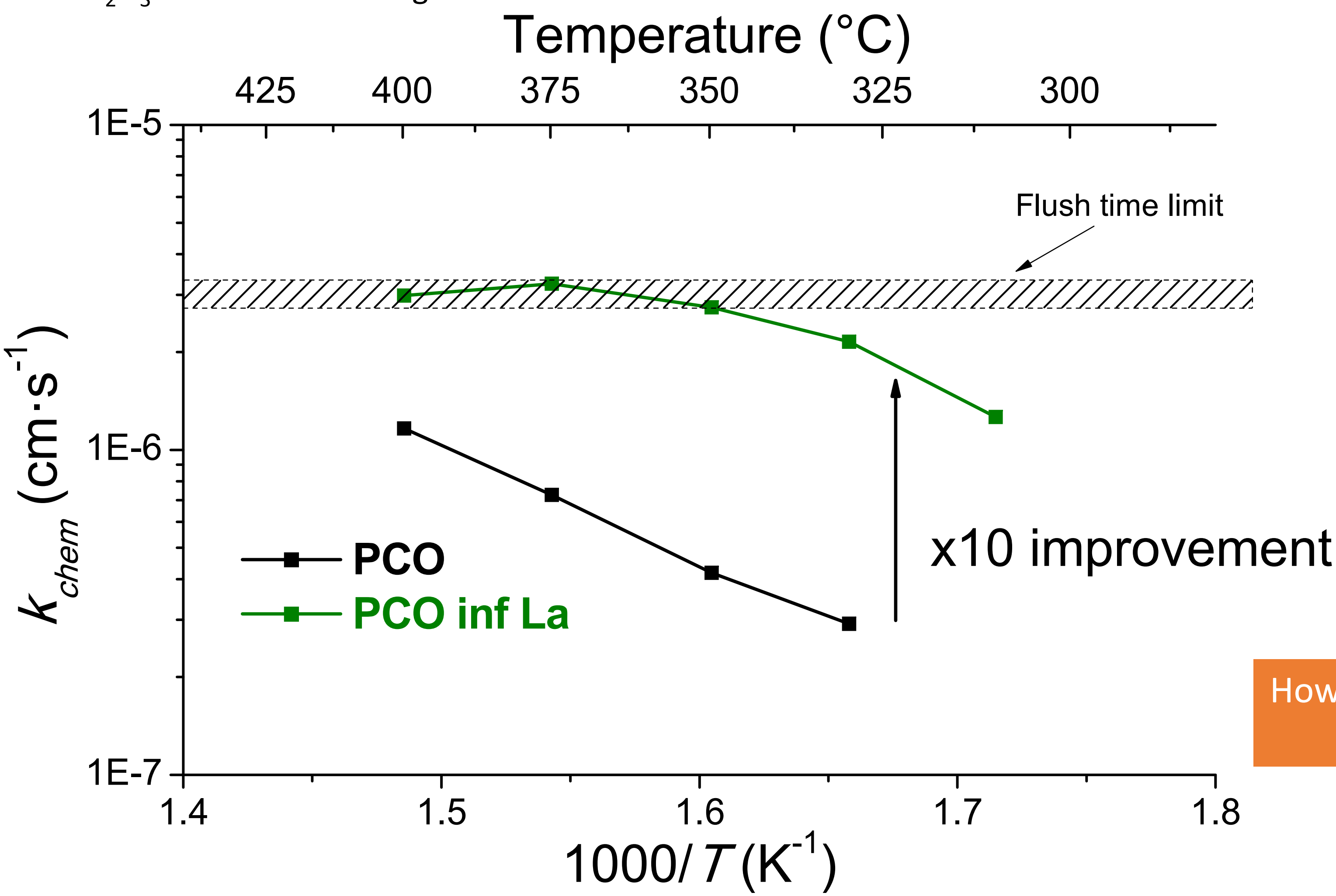
Conductivity relaxation
Surface exchange rate



G(t): normalized conductivity

Surface modification: Oxygen surface exchange rate

Effect of La_2O_3 on surface exchange rate of PCO



How does La_2O_3 (insulator) improve k_{chem}?

Conclusions & perspectives

- First measurements of Cr poisoning on PCO
- Degradation of k_{chem} even after low temperature annealing
- La_2O_3 strongly enhances k_{chem} of PCO

Perspectives

- Study to be repeated with $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (for reference)
- Study of Cr poisoning on Pr_6O_{11}
- Exsolution of scavenging element (La) to heal Cr poisoning

Thank you for your attention

Acknowledments: Tamar Kadosh
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