NETL 21th Annual SOFC Meeting

Robust Highly Durable Solid Oxide Fuel Cell Cathodes – Improved Materials Compatibility & Self-Regulating Surface Chemistry

DE-FE0031668

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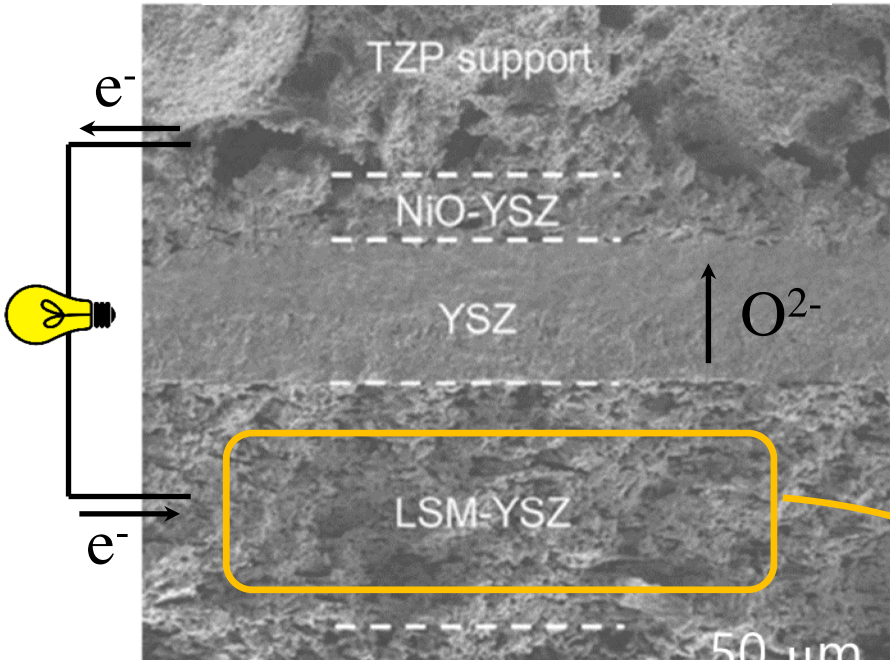
Solid Oxide Fuel Cells

Conventional SOFCs



- All solid state components
- High conversion efficiency
- Fuel flexibility (H_2, C_nH_{2n+2}, ⋯)
- High operating temperature > 800 ^oC
- Fast performance degradation

J. Am. Ceram. Soc., **1993**, *76*, 563. *Science*, **2011**, *334*, 935.

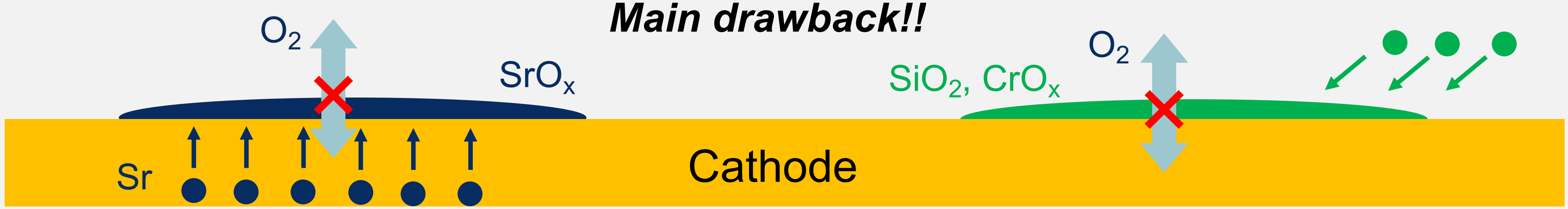
Segregation of non-active ions

Sr-rich phase segregation

Adsorption of impurities

Si- or Cr-related phase

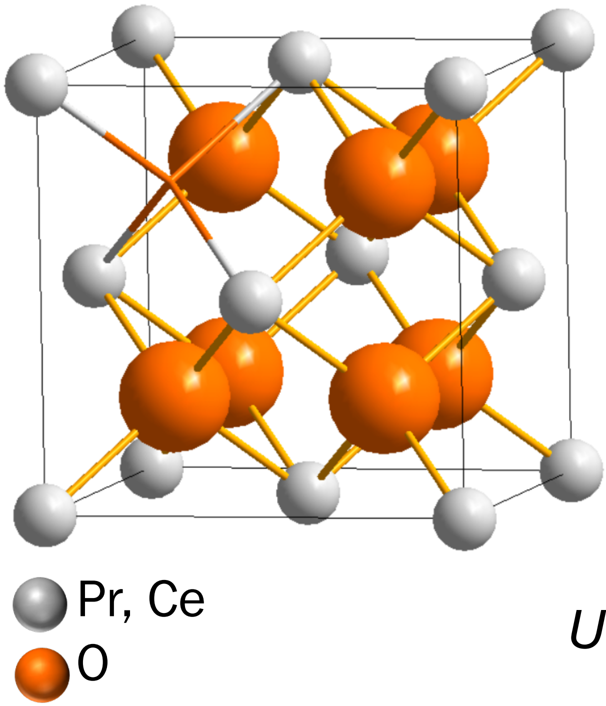
Main drawback!!

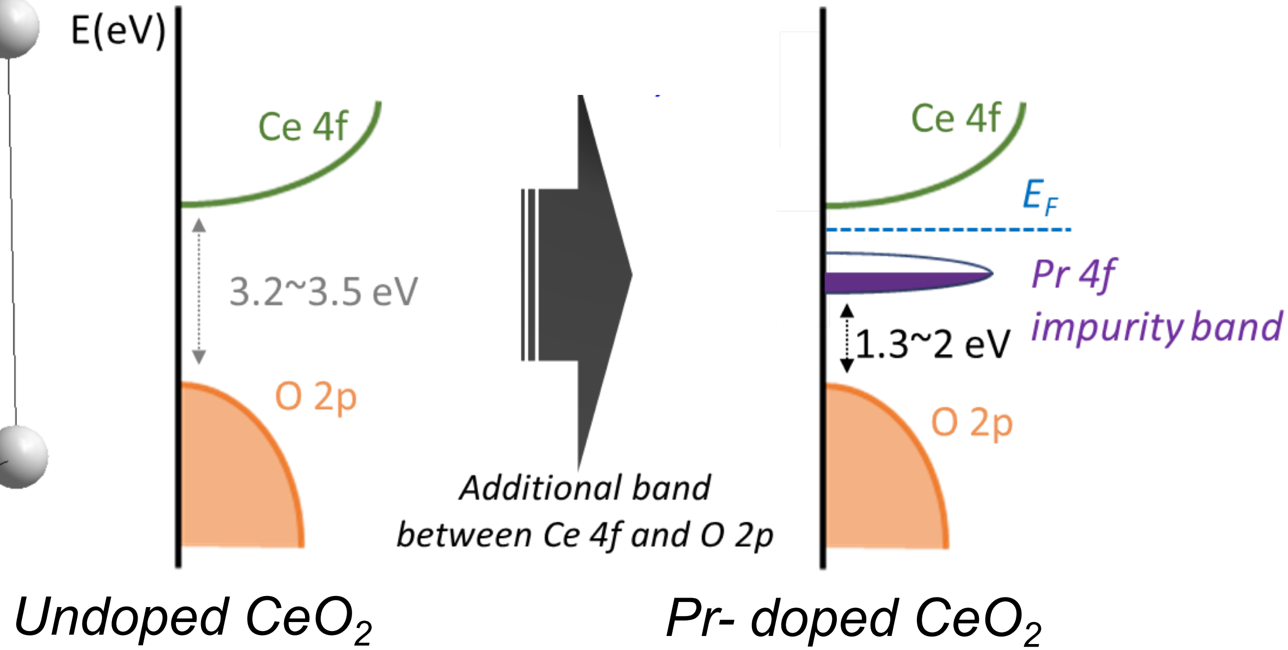


Energy Environ. Sci., **2012**, *5*, 5370–5378., *Chem. Mater.*, **2015**, *27*, 3065-3070

Target: Pr-doped CeO_2 (PCO)

Mixed conducting property in oxidizing atmospheres



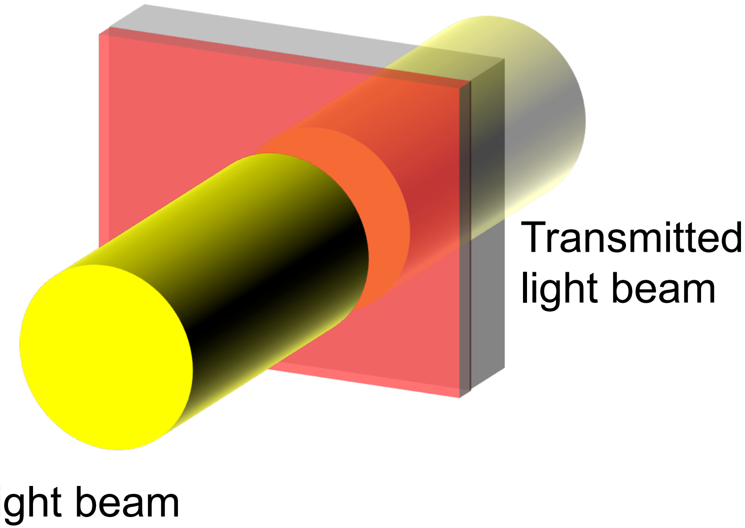


Pr-doped CeO_2 (PCO) is expected to be inherently more resistant to chemical degradation induced by Sr, Cr and Si species due to the absence of Sr source.

J. Mater. Res., **2012**, 27, 2009. *Solid State Ionics*, **2012**, 225, 194.
Chem. Mater., **2018**, 30, 2600. *Solid State Ionics.*, **2018**, 324, 150.

Previous Work on Surface Activity of PCO

PCO film (PLD) on Y-doped zirconia (YSZ) substrates



Color of PCO depends on Pr valence

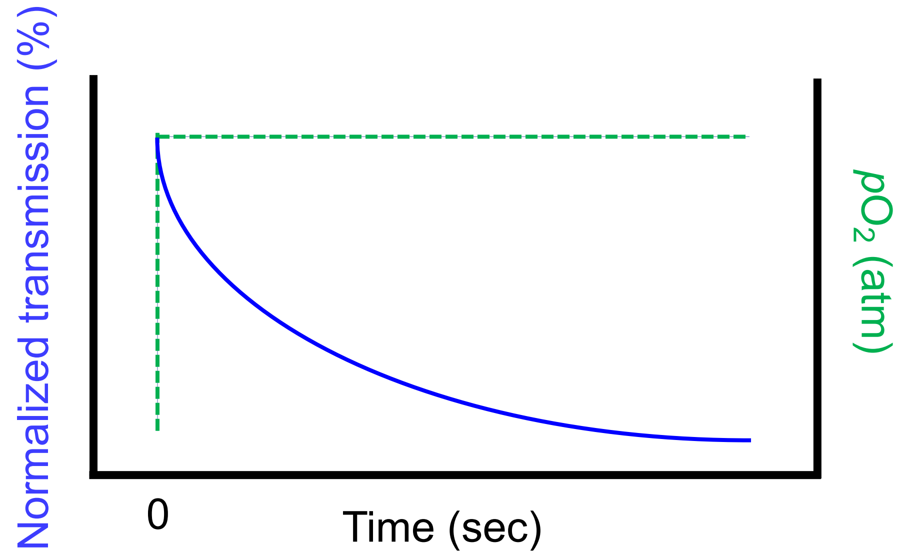
Absorption ↔ oxygen non-stoichiometry

Beer-Lambert law

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

Optical transmission relaxation (OTR)

- No need of current collector electrode
- Current collector contact-free measurement



Step in pO_2 → Transmittance relaxation

Surface exchange coefficient (k_{chem})

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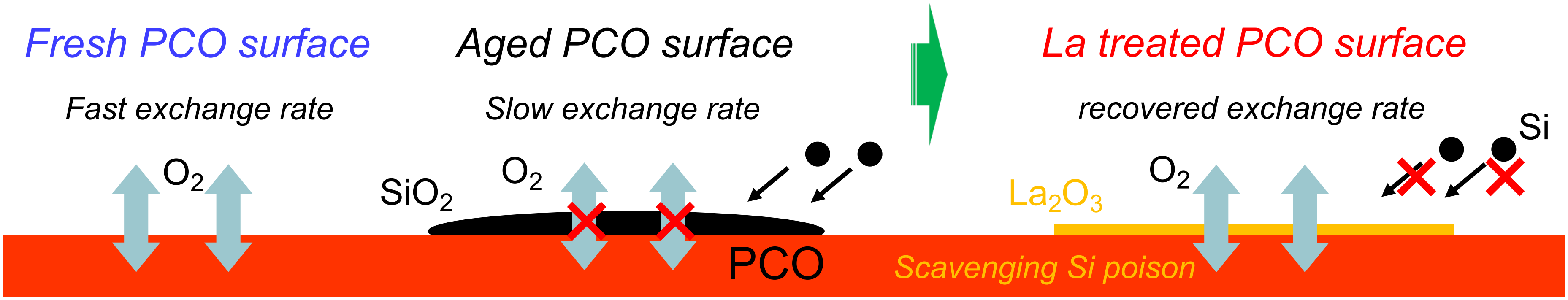
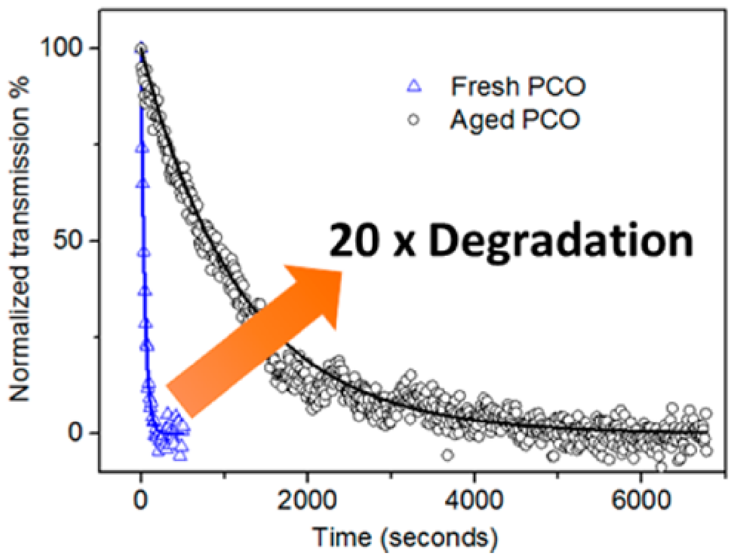
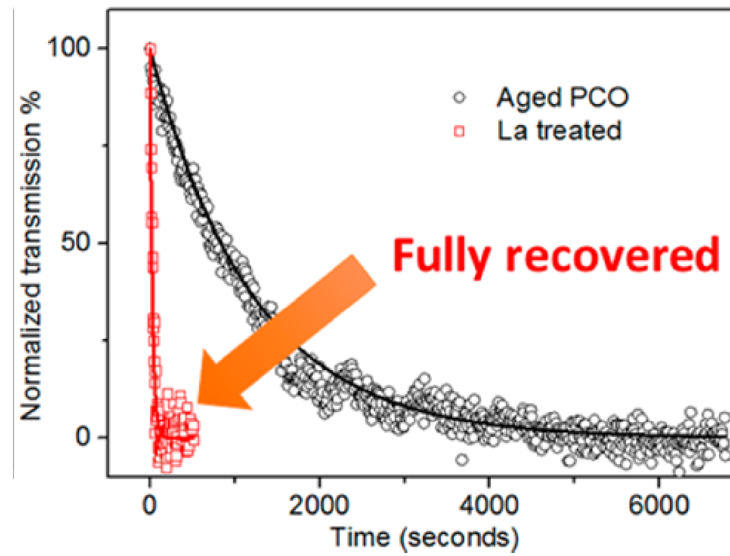
*Chem. Mater., 2014, 26, 1374-1379, Chem. Mater., **2015**, 27, 3065-3070*

Impurity Adsorption (Si) on PCO







Surface impurities can have a significant impact on surface oxygen exchange kinetics and on performance degradation under operation.

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Chem. Mater., **2015**, 27, 3065-3070

Project Action Plan

Objective: Development of highly durable SOFC cathodes achieved through surface chemistry engineering

Tasks	Verification Method
Scavenger exsolution characteristics	• Examine effect of La doping of PCO on Si surface poisoning via thin film study. • Investigate exsolution kinetics of other scavengers such as Ca and Sr as a function of temperature, time and bias.
Reactivity efficacy of scavengers with Si and Cr impurities	• Assess PCO surface oxygen exchange rate with respect to a variety of scavengers by electrical conductivity relaxation. • Investigate key descriptors to predict surface oxygen exchange rate.
Electrochemical characterization of optimized compositions in porous symmetric SOFC cells	• Fabricate optimized highly porous PCO films by PLD and evaluate area-specific resistance (ASR) of symmetric cells. • Analyze surface impurities related ASR and performance degradation over time.

[1]

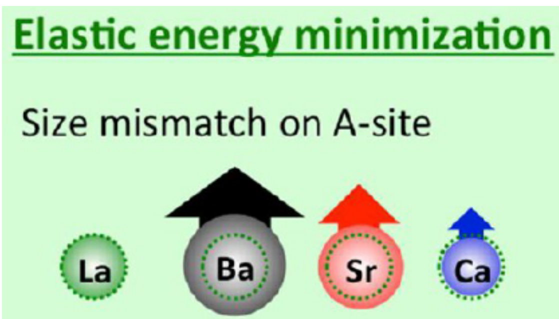
Scavenger exsolution characteristics

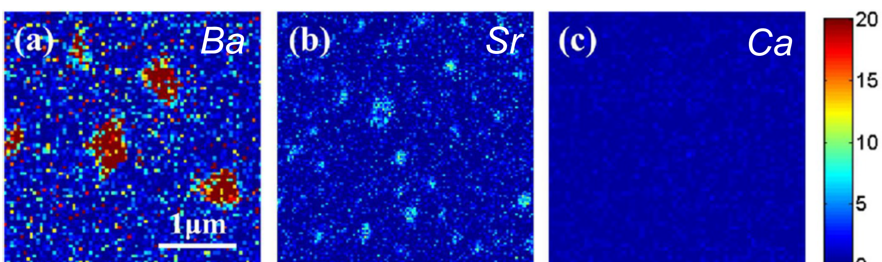
- La doping of PCO versus surface loading -

Self-cleaning Strategy of Poisoned PCO

Cation segregation in perovskite oxides

$La_{0.8}D_{0.2}MnO_3$ (D = Ca, Sr, Ba) thin films

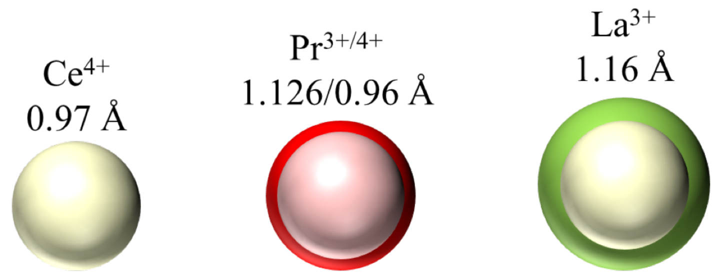




Bilge Yildiz et al. JACS, 135, 2013

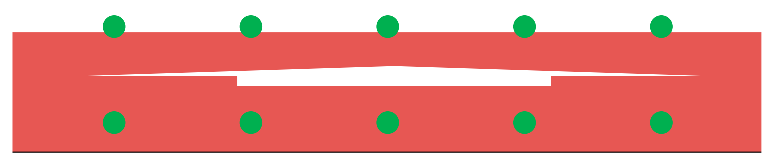
Elastic interactions

Si getter: exsolved La scavenger on PCO surface



$(R_{dopant} - R_{host}) / R_{host}$ (%)

Host cation	Pr^{4+}	Pr^{3+}	La^{3+}
Ce^{4+}	-1.03	16.08	19.58

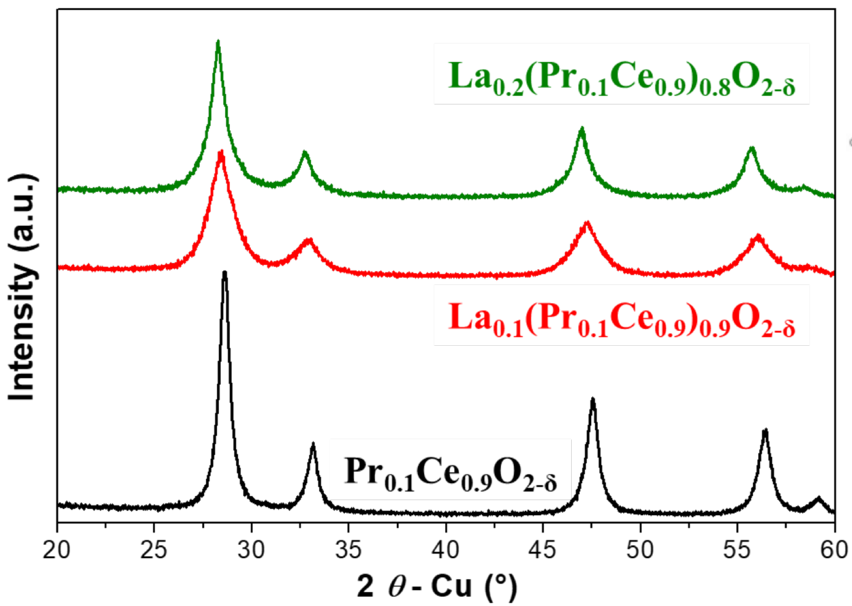


$La_xCe_{0.9-x}Pr_{0.1}O_{2-\delta}$

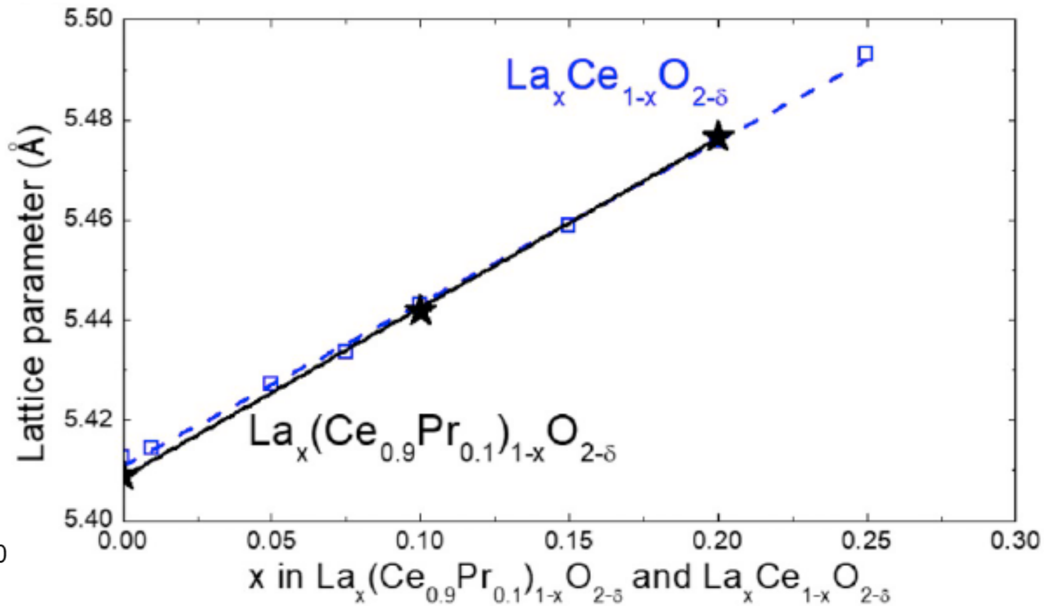
Scavenger exsolution

La-doped PCO10

Crystal structure

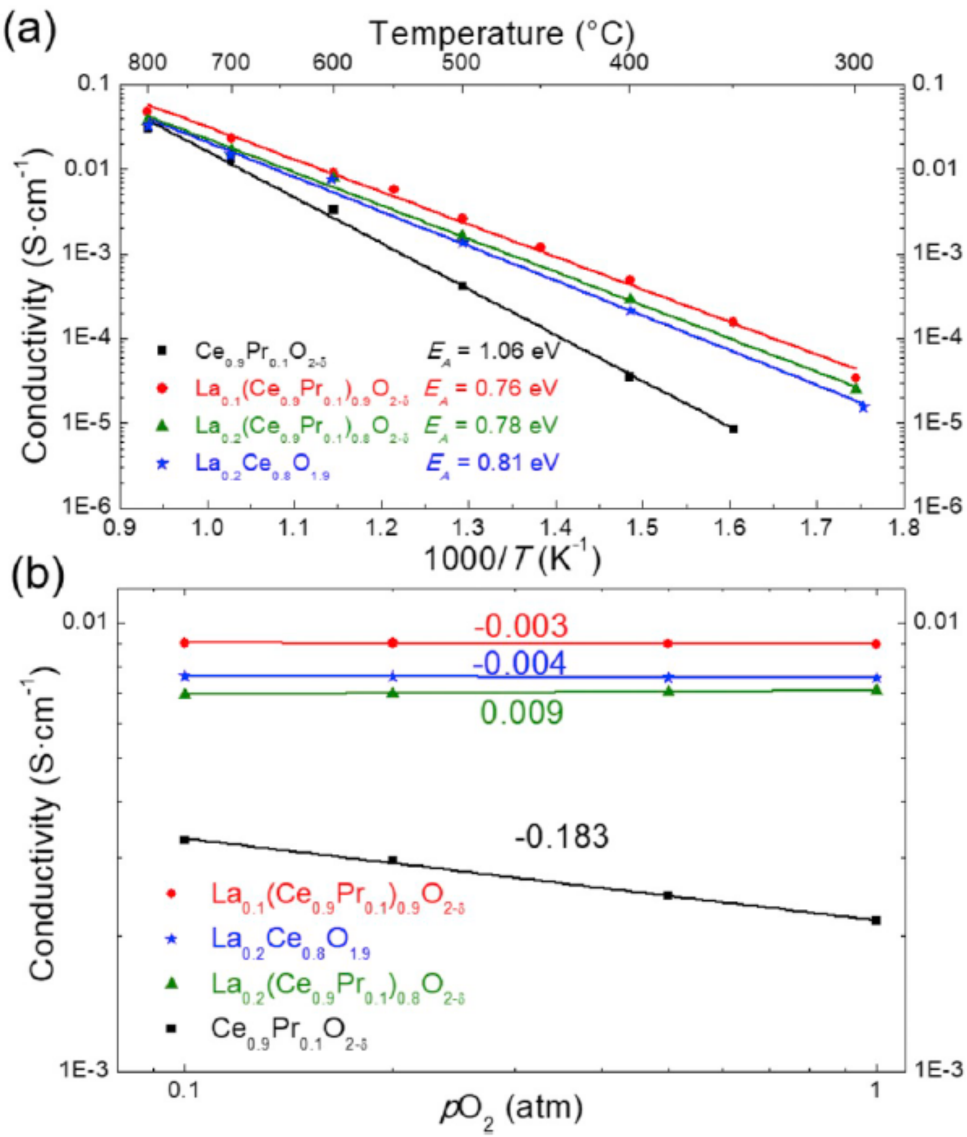


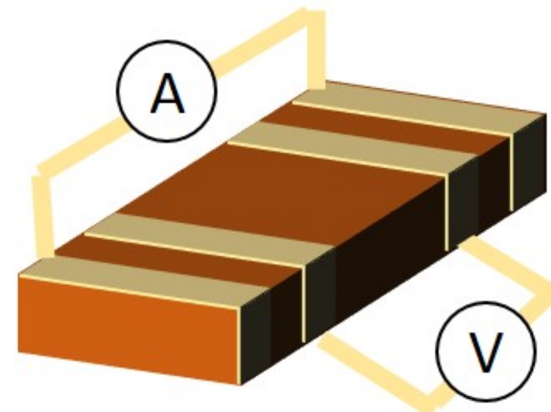
Lattice parameter



- La can be fully inserted and dissolved into ceria lattice.
- La increases lattice parameter of ceria as expected.

Transport Properties: La-doped PCO10

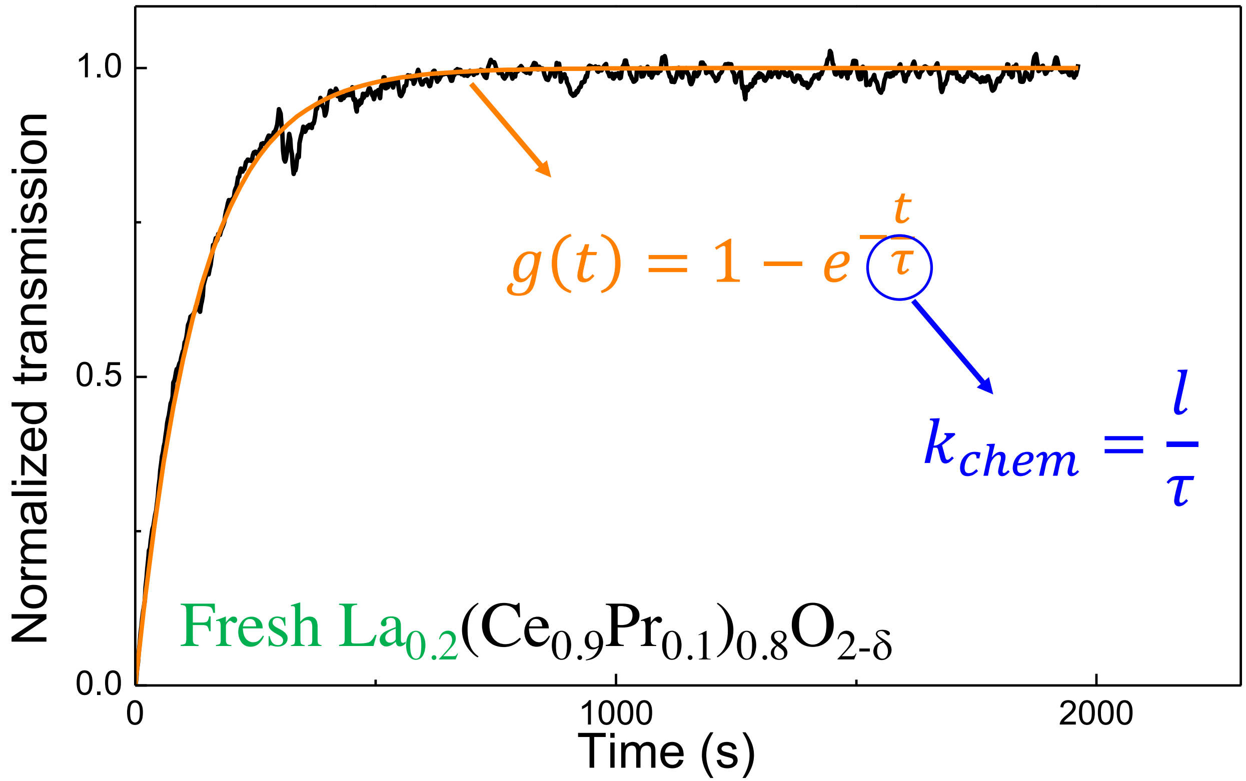




4-point probe conductivity measurement

- La dopant reduces conductivity activation energy (La drives Pr to 4+).
- Ionic conductivity is enhanced by La while retaining a significant electronic component.

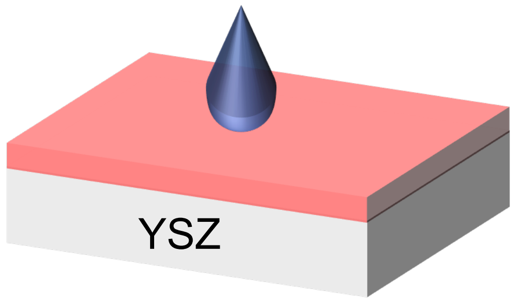
Optical Transmission Relaxation



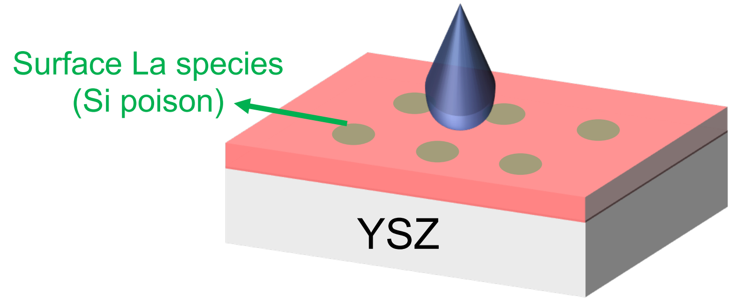
- By fitting transmission relaxation profiles, oxygen exchange coefficient (k_{chem}) values are obtained.

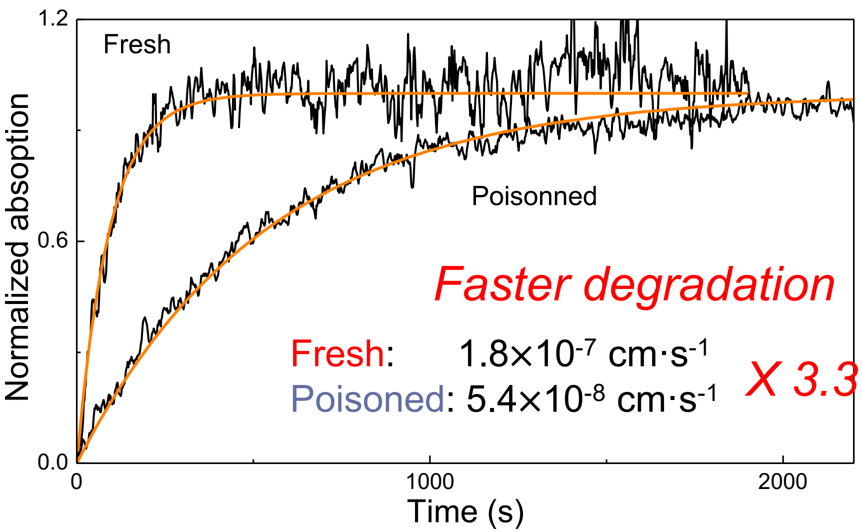
La doping Effect on Si Poisoning

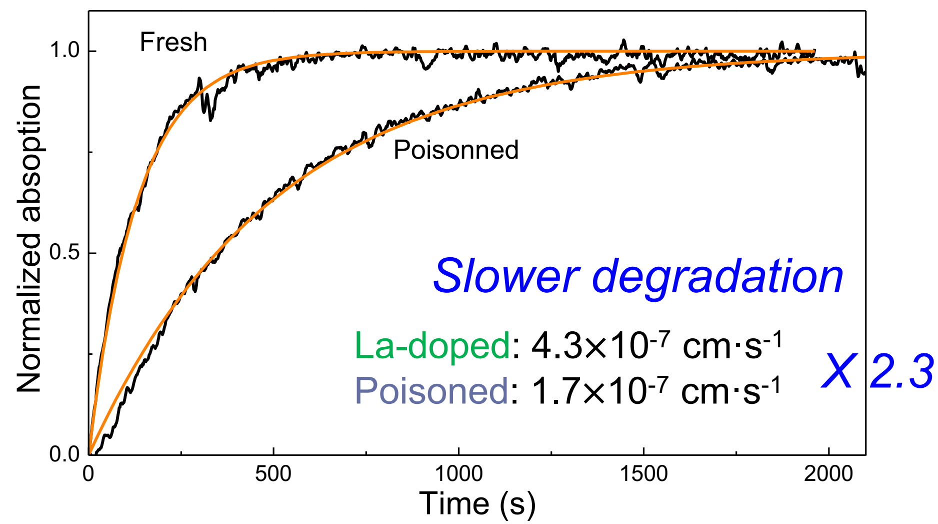
Fresh PCO films



Poisoning with TEOS (Si source)







- La scavenger renders PCO more resistive to Si poisoning.

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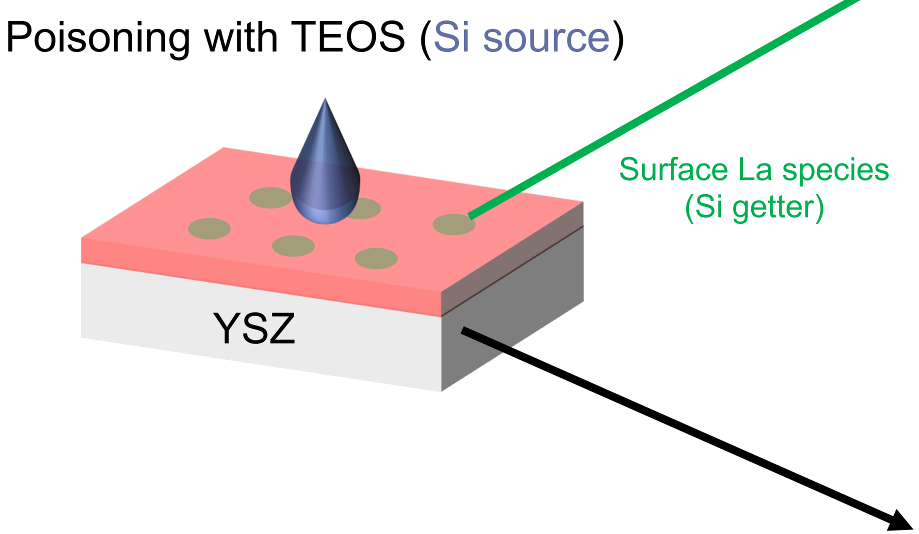
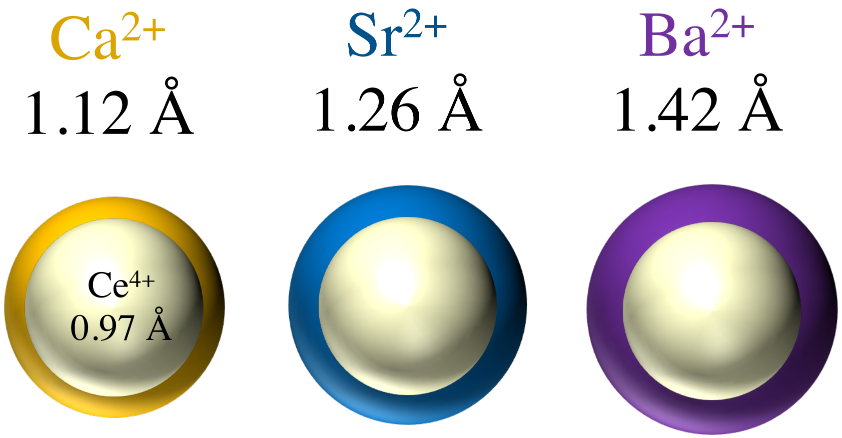
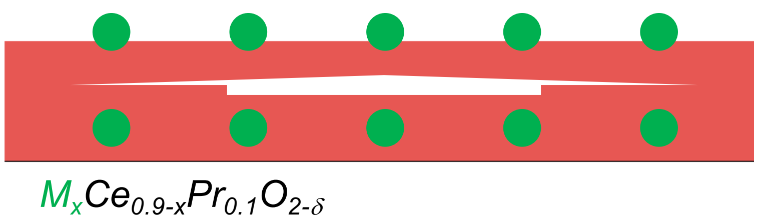
Future Study: Other Scavengers



Type of scavengers
(larger than La^{3+})



Exsolution kinetics



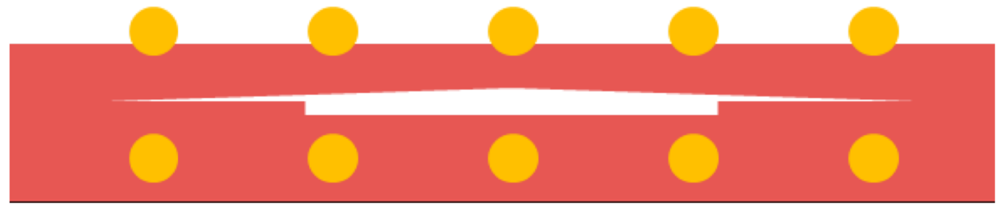
- Concentration
- Temperature
- Oxygen partial pressure
- Time

For Example, Ca Scavenger

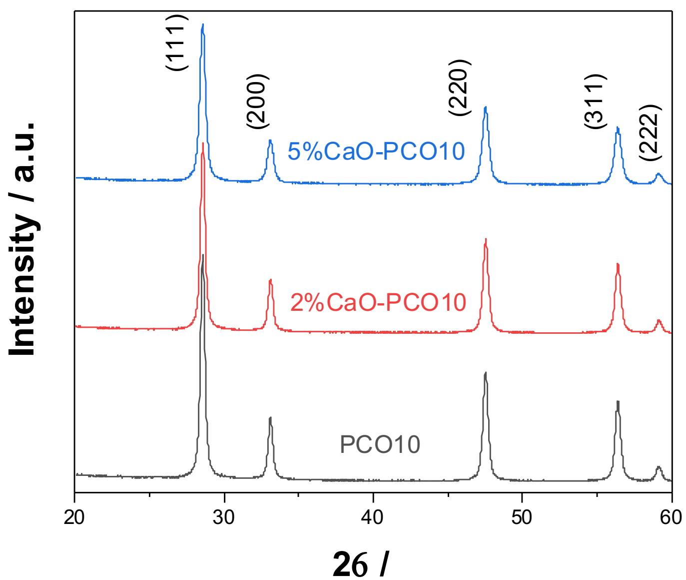
Ca^{2+}

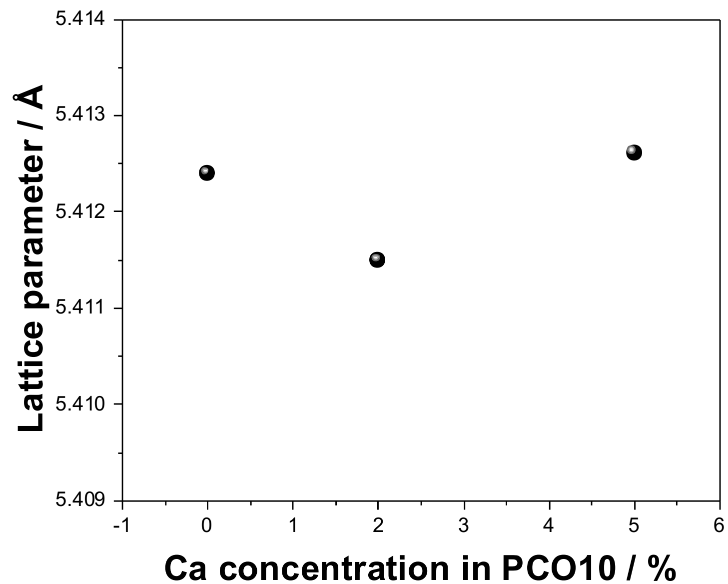
1.12 Å

$Ca_xCe_{0.9-x}Pr_{0.1}O_{2-\delta}$



- Concentration
- Temperature
- Oxygen partial pressure
- Time





- Ca dopant as potential scavenger can be substituted into ceria lattice.

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[2]

Reactivity efficacy of scavengers with Si and Cr impurities

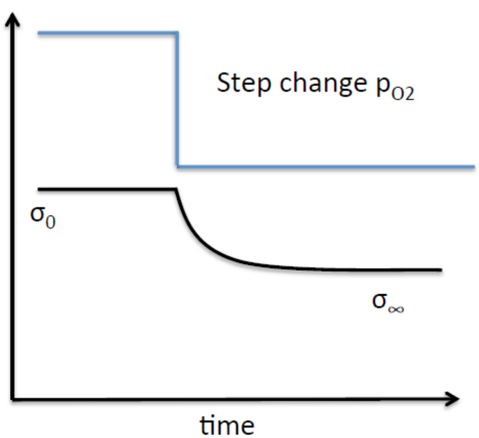
- Surface impurities on PCO cathode -

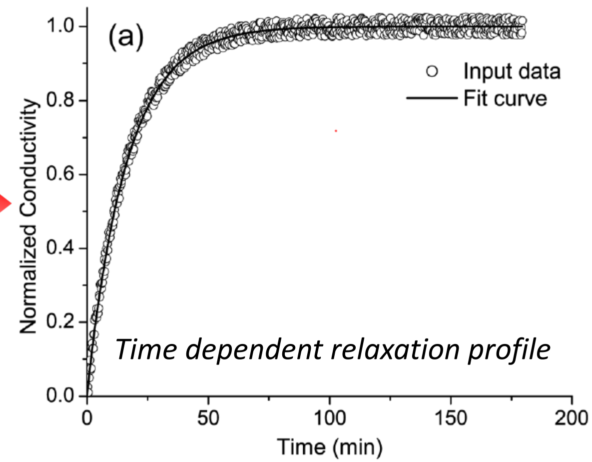
Research Approach

Electrical conductivity relaxation (ECR)

Monitoring bulk conductivity with abrupt change in surrounding environment → Measure D and k

k: oxygen exchange coefficient (cms^{-1}), k↑ surface activity ↑

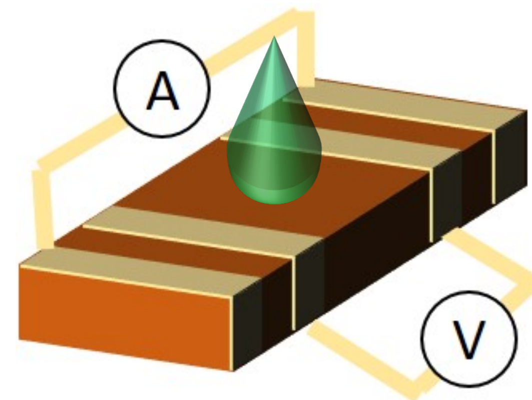




Time dependent relaxation profile

*J. Mater. Chem. A, **2014**, 2, 2405. J. Mater. Chem. A, **2018**, 6, 13082.*

Porous bar pellets



- Solid state method
- Alumina tube reactor
- 4 point probe measurements
- **Infiltrates: 20 μL of Cr nitrates**
- 250 °C – 600 °C
- 0.1 – 0.2 atm pO_2

$k_{chem} \propto f$(Cr concentration, annealing time)

For surface reaction limit

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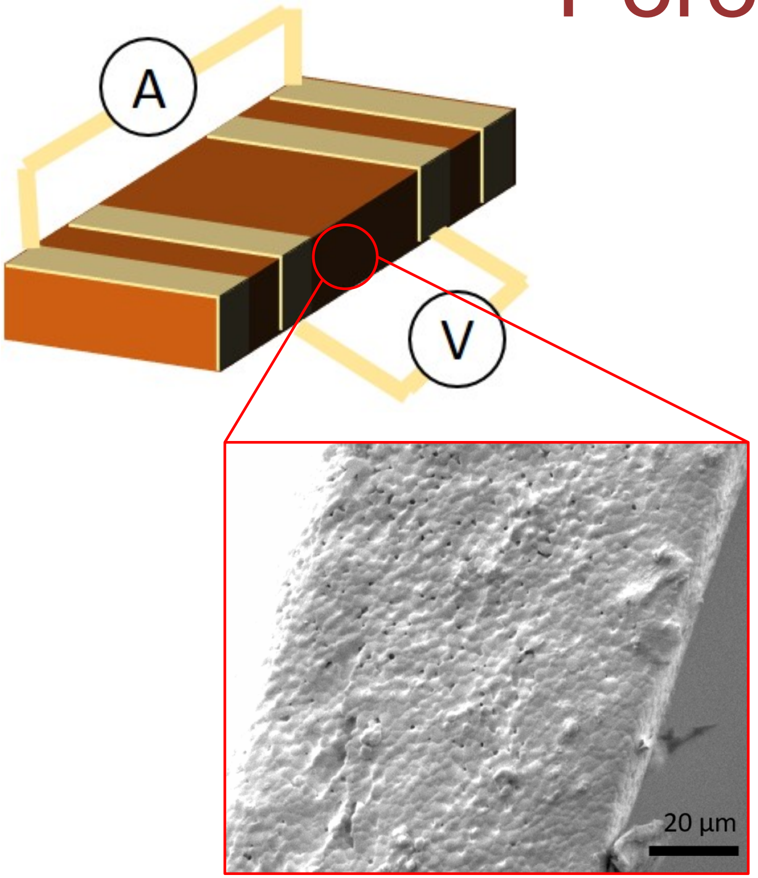
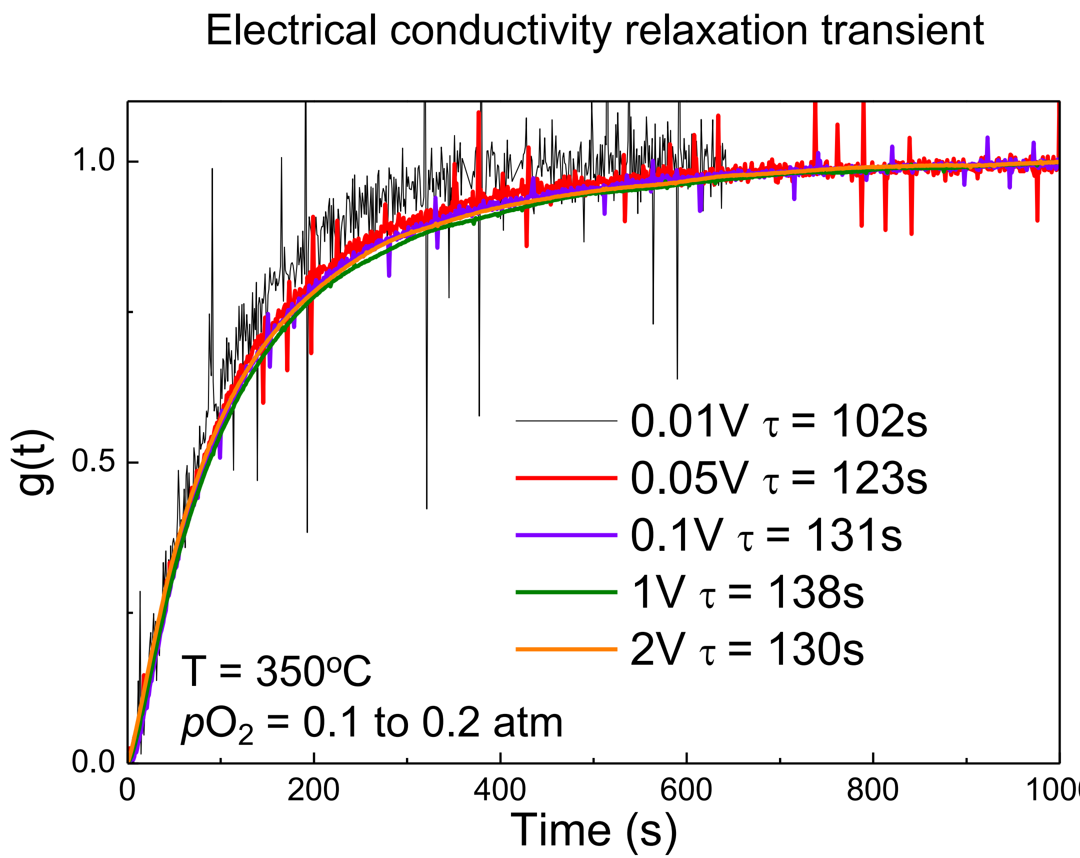
Oxygen Exchange Coefficient of PCO10 Porous Bar Pellet





- Magnitude of applied voltage determined not to be key parameter in influencing determination of oxygen exchange coefficient.

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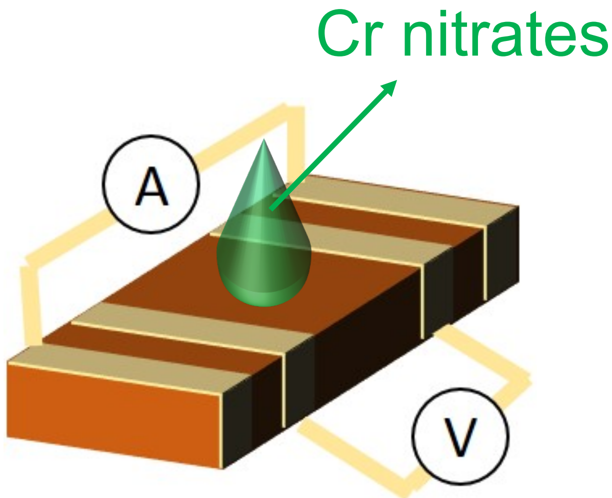
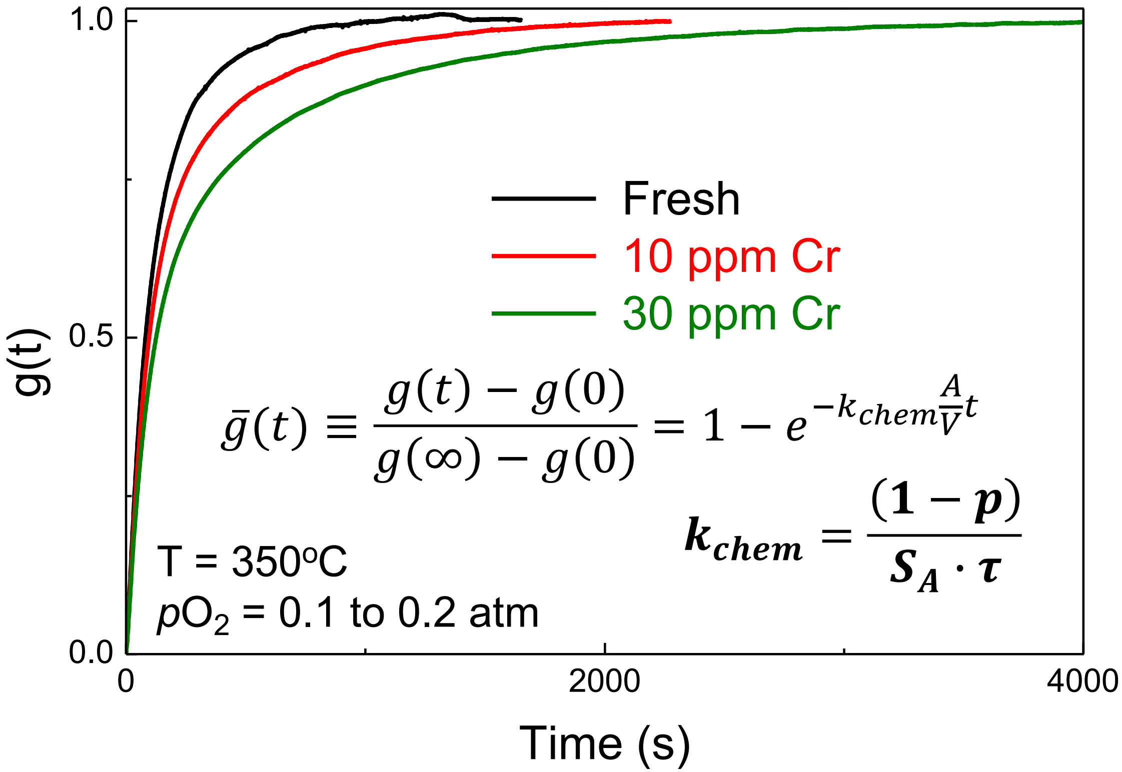
Adsorption of Cr Impurity on PCO10



- Concentration: 0.002 M, 20 μL for 10 ppm Cr
- Annealing: 600°C 1 h in air



- Cr_2O_3, as solution of Cr nitrate, infiltrated onto PCO surface, lowers surface oxygen exchange rate (k_{chem}).
- Exchange rate decreases with higher Cr poisoning concentrations.

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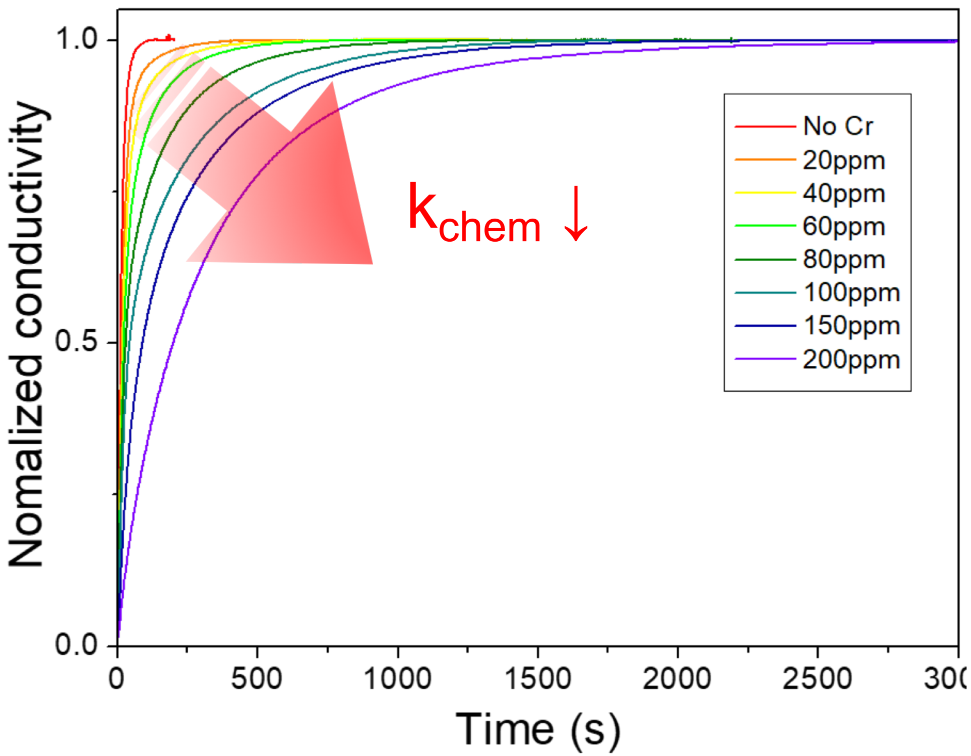
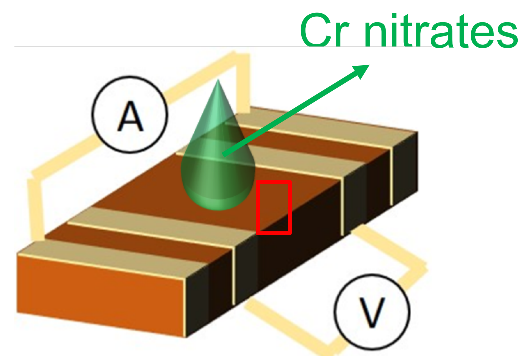
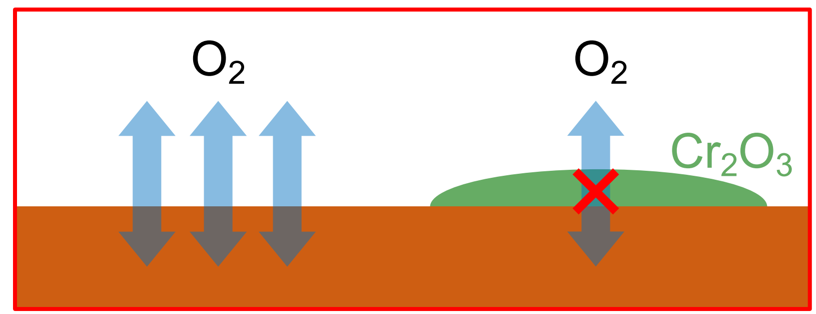
$g(t)$: *conductivity of oxide at time* t,
A: *exchange area*, V: *volume*, p: *porosity*, SA: *surface area*, τ: *time constant*

Evolution of k_{chem} vs. Cr Concentration







Unpoisoned

Cr-poisoned

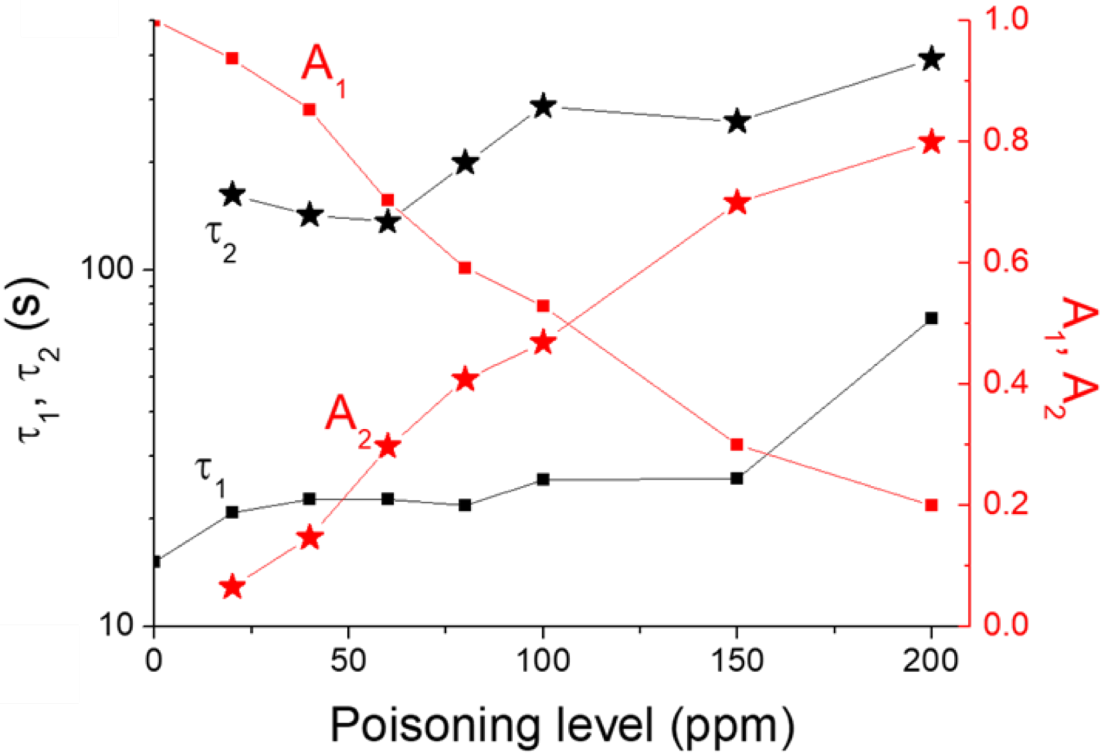
$$g(t) = A_1\left(1 - e^{-t/\tau 1}\right) + A_2\left(1 - e^{-t/\tau 2}\right)$$

- Response is characterized by two time constants associated with two types of surface regions.

Evolution of k_{chem} vs. Cr Concentration

$$g(t) = A_1\left(1 - e^{-t/\tau 1}\right) + A_2\left(1 - e^{-t/\tau 2}\right)$$

- A_1: fraction unpoisoned regions
- τ_1: time constant unpoisoned regions
- A_2: fraction Cr-poisoned regions
- τ_1: time constant Cr-poisoned regions



- As Cr poisoning level increases, fraction of Cr-poisoned surface increases, while, in turn, fraction of pristine PCO surface decreases.

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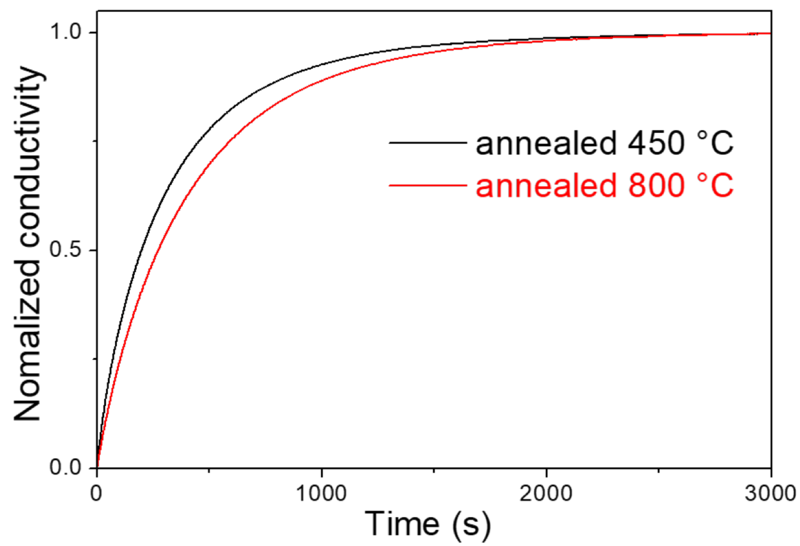
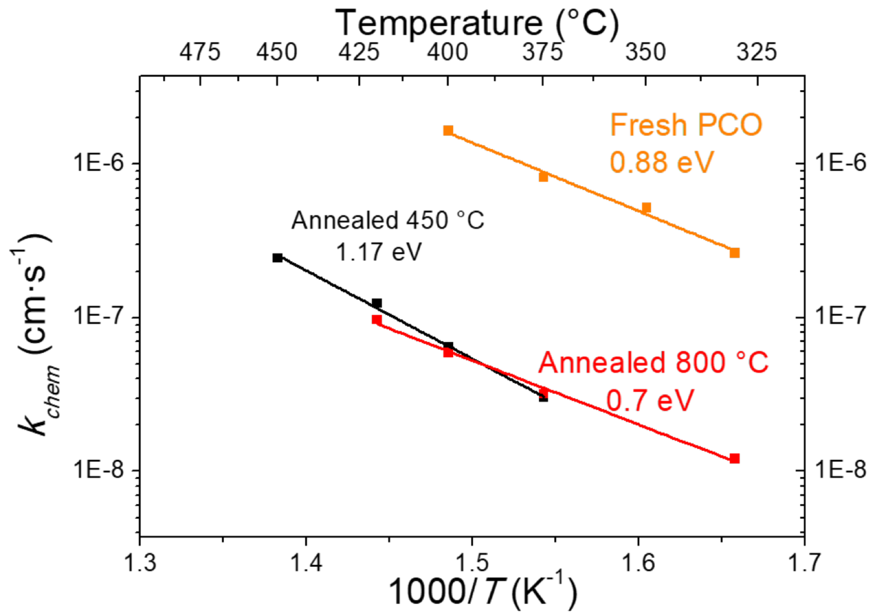
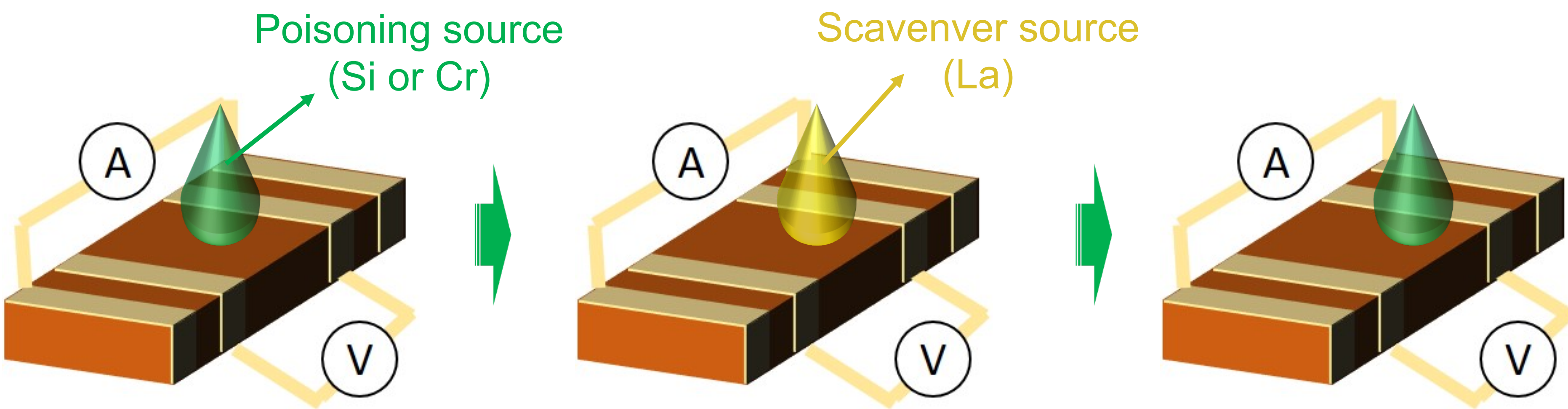
Cr Annealing Temperature Effect

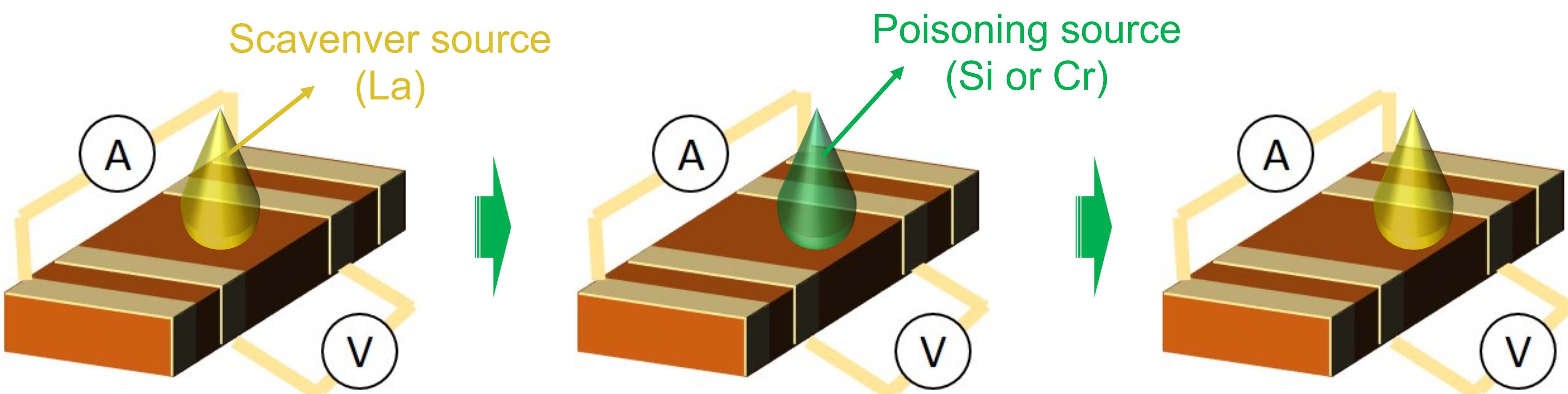




- Slight change in oxygen exchange rate observed with anneal temperature.
- Regardless of annealing temperature, Cr impurities on PCO surface found to be detrimental for oxygen exchange kinetics.

Future Study: Examine Role of Scavenger in Enhancing Initial k_{chem} vs. Recovery after Poisoning





Acknowledgement

- Title: “Robust highly durable solid oxide fuel cell cathodes – Improved materials compatibility & self-regulating surface chemistry”
- Funding Opportunity Number: DE-FOA-0001853
- Specific FOA area of interest: AOI 1 – Solid Oxide Fuel Cells (SOFC) Core Technology Research: Cell and stack degradation
- Program Manager: Steven R. Markovich

NATIONAL ENERGY TECHNOLOGY LABORATORY

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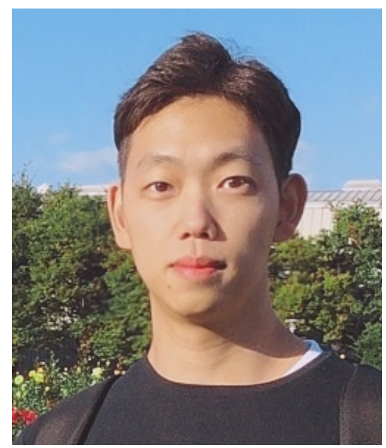

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Prof. Harry L. Tuller

Thank you for your attention!!