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

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Solid Oxide Fuel Cells

- All solid state components
- High conversion efficiency
- Fuel flexibility ($\text{H}_2$, $\text{C}_n\text{H}_{2n+2}$, …)
- High operating temperature $> 800 \, ^\circ\text{C}$
- Fast performance degradation

**Segregation of non-active ions**

*Sr-rich phase segregation*

**Adsorption of impurities**

*Si- or Cr-related phase*

*Main drawback!!*

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

Target: Pr-doped CeO$_2$ (PCO)

Mixed conducting property in oxidizing atmospheres

$\text{Pr, Ce O}$

Undoped CeO$_2$

Pr-doped CeO$_2$

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.

Previous Work on Surface Activity of PCO

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

Optical transmission relaxation (OTR)

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

Color of PCO depends on Pr valence

Absorption ↔ oxygen non-stoichiometry

Beer-Lambert law

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

Step in $pO_2 \rightarrow$ Transmittance relaxation

Normalized transmission (%) vs. Time (sec)

Surface exchange coefficient ($k_{chem}$)
Impurity Adsorption (Si) on PCO

Fresh PCO surface
Fast exchange rate

Aged PCO surface
Slow exchange rate

La treated PCO surface
recovered exchange rate

O₂  SiO₂  O₂

PCO

Scavenging Si poison

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

Chem. Mater., 2015, 27, 3065-3070
## Objective: Development of highly durable SOFC cathodes achieved through surface chemistry engineering

### Tasks

<table>
<thead>
<tr>
<th>Tasks</th>
<th>Verification Method</th>
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| 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          | • 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.                                                                                |
| with Si and Cr impurities                  |                                                                                                                                                   |
| Electrochemical characterization of        | • Fabricate optimized highly porous PCO films by PLD and evaluate area-specific resistance (ASR) of symmetric cells.  
                                          | optimized compositions in porous symmetric SOFC cells.  
                                          | • Analyze surface impurities related ASR and performance degradation over time.                                                                     |
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

Elastic energy minimization

Size mismatch on A-site

Si getter: exsolved La scavenger on PCO surface

Ce$^{4+}$
0.97 Å

Pr$^{3+/4+}$
1.126/0.96 Å

La$^{3+}$
1.16 Å

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

<table>
<thead>
<tr>
<th>Host cation</th>
<th>Pr$^{4+}$</th>
<th>Pr$^{3+}$</th>
<th>La$^{3+}$</th>
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<tbody>
<tr>
<td>Ce$^{4+}$</td>
<td>-1.03</td>
<td>16.08</td>
<td>19.58</td>
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</table>

La$_x$Ce$_{0.9-x}$Pr$_{0.1}$O$_{2-\delta}$

Elastic interactions

Scavenger exsolution

Bilge Yildiz et al. JACS, 135, 2013
La-doped PCO10

Crystal structure

- 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

- La scavenger renders PCO more resistive to Si poisoning.

\[ \text{Faster degradation} \]
- Fresh: \[ 1.8 \times 10^{-7} \text{ cm s}^{-1} \]
- Poisoned: \[ 5.4 \times 10^{-8} \text{ cm s}^{-1} \] \times 3.3

\[ \text{Slower degradation} \]
- La-doped: \[ 4.3 \times 10^{-7} \text{ cm s}^{-1} \]
- Poisoned: \[ 1.7 \times 10^{-7} \text{ cm s}^{-1} \] \times 2.3
Future Study: Other Scavengers

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

Poisoning with TEOS (Si source)

Surface La species (Si getter)

Exsolution kinetics

Ca$^{2+}$
1.12 Å

Sr$^{2+}$
1.26 Å

Ba$^{2+}$
1.42 Å

Ce$^{4+}$
0.97 Å

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

- Concentration
- Oxygen partial pressure
- Temperature
- Time
For Example, Ca Scavenger

- Ca dopant as potential scavenger can be substituted into ceria lattice.
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 ($\text{cms}^{-1}$), $k \uparrow$ surface activity $\uparrow$

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

**Porous bar pellets**

- Solid state method
- Alumina tube reactor
- 4 point probe measurements
- **Infiltrates: 20 $\mu$L of Cr nitrates**
- 250 °C – 600 °C
- 0.1 – 0.2 atm $p_O_2$

*For surface reaction limit*

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• Magnitude of applied voltage determined not to be key parameter in influencing determination of oxygen exchange coefficient.
Adsorption of Cr Impurity on PCO10

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

- \( \text{Cr}_2\text{O}_3 \), as solution of Cr nitrate, infiltrated onto PCO surface, lowers surface oxygen exchange rate \( (k_{\text{chem}}) \).
- Exchange rate decreases with higher Cr poisoning concentrations.

\[
\bar{g}(t) \equiv \frac{g(t) - g(0)}{g(\infty) - g(0)} = 1 - e^{-k_{\text{chem}}A/Vt} \\
T = 350^\circ\text{C} \\
\rho\text{O}_2 = 0.1 \text{ to } 0.2 \text{ atm} \\
k_{\text{chem}} = \frac{(1 - p)}{S_A \cdot \tau}
\]
Evolution of $k_{\text{chem}}$ vs. Cr Concentration

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

- Response is characterized by two time constants associated with two types of surface regions.
As Cr poisoning level increases, fraction of Cr-poisoned surface increases, while, in turn, fraction of pristine PCO surface decreases.

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

- \( A_1 \): fraction unpoisoned regions
- \( \tau_1 \): time constant unpoisoned regions
- \( A_2 \): fraction Cr-poisoned regions
- \( \tau_2 \): time constant Cr-poisoned regions
• 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

Poisoning source (Si or Cr)

Scavenger source (La)

Scavenger source (La)

Poisoning source (Si or Cr)
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
Thank you for your attention!!