Surface Chemistry, Electronic Structure, and Activity of SOFC Cathode Films

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Solid Oxide Fuel Cells Cathode Materials

- SOFC cathode materials
  : Main barrier to achieve higher power

- Oxygen Reduction (OR) at SOFC cathode
  Structure
  Composition ↔ OR kinetic
  Electronic structure


Surface Structure and Chemistry: A-Site Rich?

- Sr rich in A-site \cite{1}

\[ \text{Sr} \downarrow \text{La} \uparrow \text{Sr} \]


- Formation of (La,Sr)O \cite{2}

(\text{La,Sr})\text{CoO}_3 \text{ annealed at 650 C in air}


- Formation of (La,Sr)_2\text{MnO}_4 \cite{3}

To control cation segregation for enhanced activity & stability, driving forces must be quantitatively understood.

Objective

- Quantitatively assess the **key driving forces** of cation segregation on perovskite oxide surfaces

- Determine the **chemical composition** and **structure** of secondary phases on the surface upon cation enrichment

- Assess the effects on **electrochemical activity**
Hypothesis for Cation Segregation in Perovskites

Elastic energy minimization + Electrostatic repulsion minimization → Cation Segregation
**Approach**

**Surface Chemical State**
- X-ray Photoelectron Spectroscopy (XPS)
- Nanoscale Auger Electron Spectroscopy (n-AES)

**Surface Electronic Structure**
- Scanning Tunneling Microscopy / Spectroscopy (STM/STS), *in situ*

**Mechanisms, Energetics and Kinetics of Cation Segregation**
- Electronic structure (DFT+U)
To systematically induce *elastic energy differences*, radius of the selected dopant cations is varied.

<table>
<thead>
<tr>
<th>Host</th>
<th>Dopant</th>
<th>Ca$^{2+}$</th>
<th>Sr$^{2+}$</th>
<th>Ba$^{2+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>La$^{3+}$</td>
<td>$\Delta r$ (Å)</td>
<td>-0.02</td>
<td>0.08</td>
<td>0.25</td>
</tr>
<tr>
<td></td>
<td>$\Delta r/r_0$ (%)</td>
<td>-1.5</td>
<td>5.9</td>
<td>18.4</td>
</tr>
<tr>
<td>Sm$^{3+}$</td>
<td>$\Delta r$ (Å)</td>
<td>0.10</td>
<td>0.20</td>
<td>0.37</td>
</tr>
<tr>
<td></td>
<td>$\Delta r/r_0$ (%)</td>
<td>8.1</td>
<td>16.1</td>
<td>29.8</td>
</tr>
</tbody>
</table>

Increasing *dopant size* relative to the host cation.
Control of Electrostatic Interactions

Seven models to represent the variation of *electrostatic interactions* are constructed by controlling the distribution of charged oxygen- and cation-vacancies.

LaMnO$_3$ or SmMnO$_3$

Increasing *attractive interaction* to the dopant cation to the surface
Both Elastic and Electrostatic Drivers are Important

LaMnO$_3$

\[ E_{\text{Segr}} \text{ (eV)} \]

Model

\begin{tabular}{cccccccc}
1 & 2 & 3 & 4 & 5 & 6 & 7 \\
\hline
\( V_{\text{La}} \) & \( V_{\text{La}} \) & \( + V_{\text{O}} \) & \( + V_{\text{O}} \) & & & \\
\end{tabular}

SmMnO$_3$

\[ E_{\text{Segr}} \text{ (eV)} \]

Model

\begin{tabular}{cccccccc}
1 & 2 & 3 & 4 & 5 & 6 & 7 \\
\hline
\( V_{\text{La}} \) & \( V_{\text{O}} \) & \( V_{\text{O}} \) & \( V_{\text{La}} \) & & & \\
\end{tabular}

Han and Yildiz, in preparation.
To systematically induce elastic energy differences, radius of the selected dopant cations is varied.

<table>
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<tr>
<th>Host cation</th>
<th>Size mismatch</th>
<th>Dopant</th>
</tr>
</thead>
<tbody>
<tr>
<td>La$^{3+}$</td>
<td>$\Delta r = r_{\text{host}} - r_{\text{dopant}}$ (Å)</td>
<td>Ca$^{2+}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-0.02</td>
</tr>
<tr>
<td></td>
<td>$\Delta r/r_0$ (%)</td>
<td>-1.5</td>
</tr>
</tbody>
</table>

La$_{0.8}$D$_{0.2}$MnO$_3$ ~20nm La$_{0.8}$Ba$_{0.2}$MnO$_3$ LBM
SrTiO$_3$ (100) La$_{0.8}$Sr$_{0.2}$MnO$_3$ LSM
La$_{0.8}$Ca$_{0.2}$MnO$_3$ LCM

Pulse laser deposition (T = 815 °C in pO$_2$ = 10 mTorr)
**Annealing Induced Changes**

**Structural changes (AFM)**

- **RT**
- **530 °C**
- **830 °C**

**Chemical changes (Sr 3d)**

- Emission angle = 0
- Emission angle = 80

**Segregation in perovskites**

**Secondary phase formation**

**Normalized cation intensity ratio**

- Sr/Mn
- Sr/La

**Temperature (°C)**

- 0
- 200
- 400
- 600
- 800
- 1000

**Normalized S_{surface}/S_{lattice}**

- Emission angle = 80
- Emission angle = 0

**Binding Energy (eV)**

- 140
- 136
- 132
- 143
- 149

- 140
- 136
- 132
- 143
- 149

**AFM images**

- RT
- 530 °C
- 830 °C

**Graphs**

- Segregation in perovskites
- Secondary phase formation

**Chemical analysis**

- Sr/Mn
- Sr/La
Effects of Size Mismatch on Dopant Segregation

RT  530 °C  830 °C

LBM

LSM

LCM

Annealing in air for 1 hr

Normalized cation intensity ratio vs. Temperature (°C)

Ba/Mn  Sr/Mn  Ca/Mn

Ba/La  Sr/La  Ca/La
Localized Chemical Identification

LBM after annealing at 830 °C

Auger electron spectroscopy: elemental mapping (left) and point spectra (right)
Effects of Oxygen Pressure on Dopant Segregation

Cation intensity ratio away from the surface phases (background data was used if no features exist)
Effects of Oxygen Pressure on Dopant Segregation

Cation intensity ratio away from the surface phases (background if no features exist)
Effects of Oxygen Pressure on Dopant Segregation

Annealing in high $pO_2$

Annealing in low $pO_2$
Annealing-induced surface phases are *insulating*

\[
\begin{align*}
E_{g,\text{LBM}}, \ E_{g,\text{LSM}} &\sim 2 \text{ eV}, \ E_{g,\text{BaO}} \sim 4.5 \text{ eV}, \ E_{g,\text{SrO}} \sim 5.7 \text{ eV}
\end{align*}
\]
Summary

Surface segregation

Segregation = Elastic + Electrostatic

Agglomeration

Summary
Future Work

- Surface *electronic* structures using scanning tunneling microscopy / spectroscopy.
- *Electrochemical* properties using impedance spectroscopy.
Acknowledgements

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✓ Prof. C. Ross and Prof. H. L. Tuller at MIT for the use of their PLD system.
Supplementary
Angle-Resolved X-ray Photoelectron Spectroscopy

Information depth varies with an emission angle

\[ I = I_\infty \exp\left(-\frac{d}{\lambda \cos \theta}\right) \]

Probe the chemical composition with a depth information

(Escape depth of Sr 3d is \(~6\text{nm with } \theta=0\), and \(~1\text{nm with } \theta=80^\circ\))
HR XPS for dopant peaks
To extract more information from HR XPS, especially to identify the chemical composition of surface layer or secondary phase.

→ This can be useful to describe segregation before forming secondary phases on the surface.

→ Still working on this analysis.
Other thoughts on this difference (high $pO_2$ vs. low $pO_2$)

If there is strong interaction between the oxygen vacancy (+) and cation vacancy (-), more oxygen vacancies on the surface in UHV would attract more cation vacancies on the surface. Then, it will be difficult for cations to diffuse towards the surface, and/or the cation vacancies will provide rooms for segregated cations? But, we need to know the diffusivity of cations at 500-800°C to see they are mobile enough
Effects of Oxygen Pressure on Dopant Segregation

Cation intensity ratio using XPS (left) and AES (right)
Effects of Vacancy Distribution on Dopant Segregation

Annealing in high pO$_2$

Annealing in low pO$_2$

Elastic (dopant size mismatch) + Electrostatic (charged defects distribution)