Development and Understanding of High-Performance Solid Oxide Electrolysis Cells

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Jason Montgomery (2021)

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Technical Questions Addressed

1. **What is the origin for the electrochemically driven phase change in an SOC electrode?**
   - What would be the theoretical model based on measurable variables to predict this phenomenon?
   - How to validate the theoretical understanding?

   https://www.pnas.org/doi/10.1073/pnas.2203256119

2. **Why is the performance stable while the nickelates go through a severe phase transition?**
   - What is the thermodynamic base for conjugated phenomenon between activity and stability?
   - How does the interface influence the activity/durability relationship?

3. **How to use the understanding of electrochemically driven phase change to develop reliable and reproducible accelerated measurements?**
   - What is the physical process being accelerated?
   - What are accelerated test protocols for other constituents and electrochemical systems?
Technical Questions to Be Addressed

Cost (1$/kg-H₂):
How to achieve high-performance SOECs?

Durability (A/1000-h or W/1000-h):
What are the factors limiting the performance stability of an SOEC?

Technical questions to be addressed by this project

- How to establish theoretical understanding of the durability of SOECs based on measurable variables?
- What are the effects of operating modes (e.g., constant $I$ and constant $V$) and materials properties on the SOEC performance durability?
- How to calculate crack growth rate with respect to measurable properties?
- What are the factors limiting cell current density and durability?
- Is delamination inevitable? Is there a critical condition for the delamination?
- How does the interlayer chemistry at the oxygen electrode side influence current density and performance durability? How about the fuel electrode?
- What’s the proper accelerated test method to study SOECs?
Team Members

Program Managers:
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Personnel at University of Louisiana at Lafayette

Xiao-Dong Zhou  Principal Investigator
Henry Chu  Co-PI and Informatics Center Director
Tom Pesacreta  Co-PI and Microscope Center Director
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Atif Niaz  Postdoc Researcher
Keying Xu  Postdoc Researcher
Christabel Adjah-Tetteh  Graduate student
Scott Blazer  Graduate student
Austin Schilling  Undergraduate student
Solid Oxide Cells: Coupled O$_2^-$/e$^-$ Transport
SOFC to generate electricity; SOEC to produce H$_2$

**Solid Oxide Fuel Cell (SOFC)**

Oxygen electrode: $\frac{1}{2}O_2 + 2e^- \rightarrow O^{2-}$
Electrolyte: High $O^{2-}$ conductivity. Low $e^-$ conductivity.
Fuel electrode: $H_2 + O^{2-} \rightarrow H_2O + 2e^-$

**Solid Oxide Electrolysis Cell (SOEC)**

Oxygen electrode: $O^{2-} \rightarrow \frac{1}{2}O_2 + 2e^-$
Electrolyte: High $O^{2-}$ conductivity. Low $e^-$ conductivity.
Fuel electrode: $H_2O + 2e^- \rightarrow H_2 + O^{2-}$
Analysis of $\mu_{O_2}$ Distribution in Solid Oxide Cells

- Local chemical equilibrium occurs at $\vec{r}$ in the solid electrolyte.
  \[ O_2(\vec{r}) + 4e^-(\vec{r}) \rightleftharpoons 2O^{2-}(\vec{r}) \]
  \[ \mu_{O_2}(\vec{r}) = 2\mu_{O^{2-}}(\vec{r}) + 4F\phi(\vec{r}) \]

- Two independent fluxes are ionic current and electronic current

\[ I_i = \frac{\sigma_i}{2F} \frac{d}{dz} \mu_{O^{2-}} \]
\[ I_e = -\sigma_e \frac{d}{dz} \phi \]

- Governing equations (steady state):
  Oxygen conservation:
  \[ \frac{d}{dz} I_i = 0 \]
  Charge conservation:
  \[ \frac{d}{dz} (I_i + I_e) = 0 \]

<table>
<thead>
<tr>
<th>Boundary</th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrolyte/Fuel electrode ($z = 1$)</td>
<td>$I_e = -\frac{1}{r_{FE}} (\phi^{FE} - \phi^{el})$</td>
</tr>
<tr>
<td>Electrolyte / Oxygen electrode ($z = 0$)</td>
<td>$I_i = \frac{1}{4Fr_{FE}} (\mu^{FE}<em>{O_2} - 4F\phi^{FE} - \mu^{el}</em>{O_2} + 4F\phi^{el})$</td>
</tr>
<tr>
<td></td>
<td>$I_i = -\frac{1}{4Fr_{OE}} (\mu^{OE}<em>{O_2} - 4F\phi^{OE} - \mu^{el}</em>{O_2} + 4F\phi^{el})$</td>
</tr>
</tbody>
</table>
Effect of Operating Voltage on $\mu_{O_2}$ Distribution in the Electrolyte of Solid Oxide Cells

- Nernst voltage: $E_N = \frac{\mu_{O_2}^{OE} - \mu_{O_2}^{FE}}{4F}$
- $V_{cell} < E_N$ Discharging, fuel cell mode
- $V_{cell} > E_N$ Charging, electrolyzer mode

$$\mu_{O_2}^{OE|El} = \mu_{O_2}^{OE} + 4F(V_{cell} - E_N)\frac{r_i^{OE}}{R_{li}} - 4FV_{cell}\frac{r_e^{OE}}{R_{et}}$$

$$p_{O_2} = p_0 \exp\left(\frac{\mu_{O_2} - \mu_{O_2}^0}{RT}\right)$$
The \( p_{O_2} \) Distribution in the Electrolyte of Solid Oxide Cells

- Nernst potential: \( E_N = \frac{\mu_{O_2} - \mu_{O_2}^0}{4F} \)
- \( V_{cell} < E_N \) Discharging, fuel cell mode
- \( V_{cell} > E_N \) Charging, electrolyzer mode
  \[
  \mu_{O_2}^{OE|El} = \mu_{O_2}^E + 4F(V_{cell} - E_N)\frac{r_i^{OE}}{R_{i,t}} - 4FV_{cell}\frac{r_e^{OE}}{R_{e,t}}
  \]

- Under fuel cell mode, \( p_{O_2} < 0.21 \text{ atm}, \) OE|EL is under reducing condition
- Under electrolyzer mode, \( p_{O_2} \) can induce high pressure (42,477 atm @1.4V)

\[ \text{Fuel Cell: } T: 800^\circ \text{C} \]
\[ E_N = 0.94 \text{V} \]
\[ r_i^{OE} = 5 \times 10^{-5} \text{ } \Omega \cdot \text{m}^2 \]
\[ r_e^{OE} = 10^{-4} \text{ } \Omega \cdot \text{m}^2 \]

\[ \text{Electrolyzer: } T: 800^\circ \text{C} \]
\[ 1.2 \text{V} \]
\[ 1.3 \text{V} \]
\[ 1.4 \text{V} \]
\[ 1.5 \text{V} \]
\[ 1.6 \text{V} \]

\[ \text{under reducing condition} \]

\[ \text{under electrolyzer mode} \]

\[ \text{42,477 atm @1.4V} \]
Analysis on Electrochemically Driven Phenomenon

Hence, during cell operation, $\mu_{O_2}$ within the electrolyte is mathematically bounded by corresponding values at the two electrodes (gas phases), meaning $\mu_{O_2}^{\text{cathode}} \geq \mu_{O_2}^c > \mu_{O_2}^a \geq \mu_{O_2}^{\text{anode}}$ which can be derived as follows:

$$
\mu_{O_2}^c = \mu_{O_2}^{\text{cathode}} + 4e(r_i^c|I_i| - r_e^c|I_e|) = \mu_{O_2}^{\text{cathode}} - 4e(r_i^c|I_i| + r_e^c|I_e|) < \mu_{O_2}^{\text{cathode}}
$$

**Reducing condition in the interfaces.** Assuming the ideal gas law for oxygen, we obtain $\mu_{O_2}^{\text{cathode}} = \mu_{O_2}^0 + k_B T \ln(P_{O_2}^{\text{cathode}})$, where $\mu_{O_2}^0$ is standard state gas phase oxygen chemical potential and $P_{O_2}^{\text{cathode}}$ is the oxygen partial pressure at the cathode (gas phase). Eq. [5] gives:

$$
P_{O_2}^c \approx P_{O_2}^{\text{cathode}} \exp\left[-\frac{4e(r_i^c|I_i| + r_e^c|I_e|)}{k_B T}\right]
$$

- $P_{O_2}^c < P_{O_2}^{\text{cathode}}$.
- $P_{O_2}^c / P_{O_2}^{\text{cathode}} \sim (r_i^c|I_i| + r_e^c|I_e|)$.
- $T = 800^\circ C (1073 \text{ K}), (r_i^c|I_i| + r_e^c|I_e|) = 0.2 \text{ V}$; $P_{O_2}^{\text{cathode}} = 0.21 \text{ atm}$; then $P_{O_2}^c \approx 3.7 \times 10^{-5} \text{ atm}$.
- The local oxygen partial pressure (the level of reducing condition) depends on both $r_i^c|I_i|$ and $r_e^c|I_e|$. The most reducing location is at the immediate cathode/electrolyte interface.

<table>
<thead>
<tr>
<th>Overpotential</th>
<th>0.05 V</th>
<th>0.1 V</th>
<th>0.2 V</th>
<th>0.3 V</th>
<th>0.4 V</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P_{O_2}^c$ (atm)</td>
<td>0.024</td>
<td>0.0029</td>
<td>$3.7 \times 10^{-5}$</td>
<td>$4.9 \times 10^{-7}$</td>
<td>$6.5 \times 10^{-9}$</td>
</tr>
</tbody>
</table>

Points to take

- **Reproducible** results with multiple cells per each condition.
- Phase evolution is **accelerated** with electrochem. operation in full cells.
- Relatively stable cathode materials (in thermal equilibrium) may not be stable in SOFCs.

Dogdibegovic, Wang, and Zhou, PNAS, 2022
Performance Stability vs. Interlayer Chemistry

Points to take:
- Multiple cells for each condition for both PNO and PNNO electrodes
- 3x reduced performance degradation in PNO/PrO\textsubscript{x} cells.
- Stable operation was measured on multiple sets of cells and cathode compositions with the PGCO interlayer.
- Reduced $R_{pol}$ (↑MIEC → ↑$\sigma_e$) due to extended rxn. zone.
- Reduced Rohm (↓Rgb with [Pr]↑)\textsuperscript{1}

Summarized ASR vs. GDC cells.

<table>
<thead>
<tr>
<th></th>
<th>ASR</th>
<th>Ohmic</th>
<th>Electrode</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>PrOx-GDC 500\textsuperscript{th} hour</td>
<td>7%↓</td>
<td>22%↓</td>
<td>15%↓</td>
<td></td>
</tr>
<tr>
<td>PGCO 500\textsuperscript{th} hour</td>
<td>16%↓</td>
<td>28%↓</td>
<td>22%↓</td>
<td></td>
</tr>
</tbody>
</table>

\textsuperscript{1}S. Lübke et al. \textit{SSi}, \textbf{117}, p.229 (1999).

Dogdibegovic, Wang, and Zhou, PNAS
Distribution of $\mu_{O_2}$ in an Electrolysis Cell

Absence of crack formation

Analytical result:

$$\mu_{O_2}(z) = \mu_{O_2}^{OE} \pm 4FI_i \left( r_{iOE}^{OE} + \frac{z}{\sigma_i} \right) - 4FI_e \left( r_{eOE}^{OE} + \frac{z}{\sigma_e} \right)$$

Ionic flux contribution

Electronic flux contribution

- High operation voltage/current raises $\mu_{O_2}$ at OE|EL ($z=0$) in most cases.
- Raising $\sigma_e$ decreases $\mu_{O_2}$ at OE|EL ($z=0$) and reduces Faradaic efficiency

Wang, Y. et al. *Journal of The Electrochemical Society*, 2022 169 044529
Analysis of $\mu_{O_2}$ Distribution in Solid Oxide Cells

Effect of transport properties, constant $V$ and constant $I$

Analytical result at OE:

$$
\mu_{O_2}^{OE|EI} = \mu_{O_2}^{OE} + \left(4F(V_{\text{cell}} - E_N) + 4FV_{\text{cell}}\frac{r_E^{OE}}{R_{e,t}}\right) - \frac{4F(I_t r_i^{OE})}{R_{e,t}} + 4F(E_N - R_{i,t} I_t) \frac{r_i^{OE}}{R_{i,t}}
$$

- Constant $V_{\text{cell}}$: $\downarrow r_i^{OE}$, $\downarrow \mu_{O_2}^{OE|EI}$
  - Operation reaches a maximum $\mu_{O_2}^{OE|EI}$
- Constant $I_t$ operation has linear $\mu_{O_2}^{OE|EI}$ - $\tau_i^{OE}$ relation.
- Constant $I_t$ operation is only suitable for stable oxygen electrodes.
- $\uparrow r_E^{OE}$ significantly $\downarrow \mu_{O_2}^{OE|EI}$

$$
\begin{align*}
\left(\frac{\partial \mu_{O_2}^{OE|EI}}{\partial r_i^{OE}}\right)_{V_{\text{cell}}} &= 4F \frac{V_{\text{cell}} - E_N}{R_{i,t}} \left(\frac{R_{i,t} - r_i^{OE}}{R_{i,t}}\right) \\
\left(\frac{\partial \mu_{O_2}^{OE|EI}}{\partial r_E^{OE}}\right)_{V_{\text{cell}}} &= 4FV_{\text{cell}} \left(\frac{R_{e,t} - r_E^{OE}}{R_{e,t}}\right) \\
\left(\frac{\partial \mu_{O_2}^{OE|EI}}{\partial I_t}\right)_{I_t} &= 4FI_t \left(\frac{R_{e,t} - r_E^{OE}}{R_{e,t}}\right) \\
\left(\frac{\partial \mu_{O_2}^{OE|EI}}{\partial r_i^{OE}}\right)_{I_t} &= 4F(E_N - R_{i,t} I_t) \left(\frac{R_{e,t} - r_E^{OE}}{R_{e,t}}\right)
\end{align*}
$$

Analysis of $\mu_{O_2}$ Distribution in Solid Oxide Cells

Effect of electrolyte thickness and fuel composition

\[
\left( \frac{\partial \mu_{O_2}^{\text{EL}}}{\partial l} \right)_{V_{\text{cell}}} = -4F \left( V_{\text{cell}} - E_N \right) \frac{r_i^{\text{OE}}}{\sigma_l R_{i,t}} + 4F \frac{V_{\text{cell}}}{\sigma_e R_{e,t}^2} \frac{r_e^{\text{OE}}}{r_e^{\text{OE}}}
\]

\[
\left( \frac{\partial \mu_{O_2}^{\text{EL}}}{\partial l} \right)_{I_i} = -4FI_i \frac{r_i^{\text{OE}}}{\sigma_l R_{e,t}} + 4F \frac{r_i^{\text{OE}}}{\sigma_e R_{e,t}^2} + 4F \frac{r_i^{\text{OE}}}{\sigma_e R_{e,t}^2}
\]

- ↓ electrolyte thickness ($l$), ↓ $\mu_{O_2}^{\text{EL}}$


- ↑ $H_2$ vol% can significantly ↓ $\mu_{O_2}^{\text{EL}}$ (constant $V$)
- $\mu_{O_2}^{\text{EL}}$ is stable with change $H_2$ vol% (constant $I$)
**$p_{O_2}^{TPB}$ : Transport Property Effect**

- $p_{cr} = 5,878$ atm with crack radius of 1 μm
- A low $r_i^{OE}$ is preferred to suppress $p_{O_2}^{TPB}$. At a constant $V_{cell}$ of 1.4 V, the critical $r_i^{OE}$ is $\sim 5.4 \times 10^{-5}$ Ω m². For a constant $I_i$ of 7,300 A/m², the critical $r_i^{OE}$ is $7.5 \times 10^{-5}$ Ω m².
- A constant current electrolysis is not suitable for studying an unstable electrode material, which potentially leads to the formation of cracks and even electrode delamination.
- A high $r_e^{OE}$ is in favor of reducing $p_{O_2}^{TPB}$.

\( p_{O_2}^{TPB} \): Operation Condition Effect

- \( V_{cell} \) is higher than 1.44 V leads to \( p_{O_2}^{TPB} > p_{cr} \) under the simulated conditions.
- A low H\(_2\) vol% in the fuel electrode results in a high \( p_{O_2}^{TPB} \) at constant voltage operation and a concentration less than 32% can lead to crack growth.
- The effect of H\(_2\) vol% on \( p_{O_2}^{TPB} \) is marginal under a constant current electrolysis.

SOEC with a Penny-shaped Crack Criterion for Griffith Crack to Propagate

- The crack can not conduct $I_l$ or $I_e$. On the surface of crack
  \[ I_l \cdot n_{crack} = 0 \quad I_e \cdot n_{crack} = 0 \]
- At the edge of the crack (r=c) is TPB
  \[ \frac{1}{2} O_2(\text{crack}) + 2e^- (OE) \rightleftharpoons O^2-(SE) \]
- $\Delta G_m < 0 \iff \mu^\text{crack}_O < \mu^\text{TPB}_O$:
  Oxygen moves out from the crack
- $\Delta G_m > 0 \iff \mu^\text{crack}_O > \mu^\text{TPB}_O$:
  Oxygen pumped into the crack
- The existing crack can propagate when the pressure inside the electrolyte exceeds the critical value $p_{cr}$.
- $p^\text{TPB}_{O_2}$ is the highest pressure can be reached.
- $p^\text{TPB}_{O_2} > p_{cr}$: crack can propagate

Wang, Y. et al. *Journal of The Electrochemical Society*, 2022 169 044529
Propagation of a Crack

\[ \frac{dc}{dt} = \frac{3k}{16\pi\gamma_{eff}c} (\mu_{O_2}^{TPB} - \mu_{O_2}^{crack}) \]

Crack growth ↑
- A higher electrolysis voltage
- A higher \( r_i^{OE} \)
- A lower \( r_e^{OE} \)
- A higher \( \sigma_e \)

Wang, Y. et al. Journal of The Electrochemical Society, 2022 169 044529
Theoretical OCV 

Measured OCV

T: 750°C
Air: 1000 sccm
H₂: 400 sccm

Role of Microstructures: the porosity (ε) and tortuosity (τ).

A high ε/τ value will result in a high Faradaic current at the electrolyte/electrode interface.
Reversible Cell Performance

The good match between theoretical OCV and measured OCV indicates good seal and the correct steam concentration.

<table>
<thead>
<tr>
<th>Steam %</th>
<th>OCV theoretical</th>
<th>OCV measured</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>1.118 V</td>
<td>1.087 V</td>
</tr>
<tr>
<td>20</td>
<td>1.021 V</td>
<td>1.011 V</td>
</tr>
<tr>
<td>70</td>
<td>0.920 V</td>
<td>0.917 V</td>
</tr>
</tbody>
</table>
Effect of Interlayer on SOFC Performance

Observation
- Polarization resistance is relatively higher in GDC cells as observed before
- Ohmic ASR is observed to change with current density especially in GDC cells

COMPOSITION
- Anode – NiO - YSZ (commercial)
- Cathode – LSCF
Effect of Interlayer SOEC Performance

- ~32% improvement in water splitting current density at 1.4V was achieved with PGCO buffer layer.
- Cathode activity is enhanced by substituting GDC with PGCO
- A significant decrease in ohmic ASR is observed in PGCO cell with time as compared to cell with GDC.
- An increase in initial performance is noticed even after 12hrs of operation for both cells
- Longer cell durability test time will be needed to compare degradation rates of both cells.
We obtained a set of 326 SEM images (Slice id # from 001 to 651 in increments of 2), each of which is 1536 by 1024, 8 bits per pixel. We initiated work to detect and track the pores in this initial set.

Our goal in this phase is to extract the holes, represented by the black image regions (hereinafter referred to as “blobs”), and track them. We can then calculate the tortuosity measure from the sequence of tracked blobs.

The extraction and tracking processes are being developed in parallel. The ultimate goal is to use deep learning for extraction of the blobs. To facilitate the development of the tracking process, we temporarily use a simple thresholding method to extract the blobs.
Image Segmentation

Input: Original FIB-SEM images

Split images into tiles

Tile size: 256x256

128x128x32 → 256x256x32

128x128x64

64x64x64 → 64x64x128

32x32x128

32x32x256

16x16x256

16x16x256

32x32x256

64x64x128 → 128x128x64

256x256x3

convolutional + ReLu

max pooling

Transposed Convolution + ReLu

Transposed Convolution + Convolutional
A sequence of 4 slices (Slice ID #323 to 329) shown left to right. A random set of 26 blobs (bounding boxes in orange) were selected from Slice 323 (left) and tracked in the 4 slices using blob location.

Ongoing work is to incorporate shape and size in the matching criterion and to allow forking or joining of tracked paths.
Tortuosity

- Suppose we have a sequence of $N$ tracked blobs with centroids $x_i$ for $i = 0, \cdots, N - 1$.
- Let $d_s$ be the shortest distance between $x_0$ and $x_{N-1}$ so that $d_s = \|x_0 - x_{N-1}\|$
- Let $d_p$ be the path distance from blob to blob: $d_p = \sum_{i=0}^{N-2} \|x_i - x_{i+1}\|$
- Define Tortuosity $\tau$ as
  \[ \tau(\{x_0, \cdots, x_{N-1}\}) = \frac{d_s}{d_p} \]
- $\tau$ varies between 0 and 1
  - $\tau = 1$ when $d_p = d_s$ the shortest distance
Development and Understanding of High-Performance Solid Oxide Electrolysis Cells

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