A Multiscale Model for the Oxygen Reduction and Oxidation Reactions in LSCF Based Solid Oxide Cell

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Outline

• Introduction
• Multiscale Framework
• Simulation Details
• Multiscale Results
• Discussion
• Conclusions
Solid oxide electrolysis cell (SOEC)
Anode: \( 0^2^- \rightarrow 0.5O_2 + 2e^- \)
Cathode: \( H_2O(g) + 2e^- \rightarrow H_2 + O^2^- \)

Solid oxide fuel cell (SOFC)
Anode: \( H_2 + O^2^- \rightarrow H_2O(g) + 2e^- \)
Cathode: \( 0.5O_2 + 2e^- \rightarrow O^2^- \)

Advantage over other normal electrolyzers:
make use of the thermal energy

**Introduction**

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Method to evaluate the cell efficiency:

**I-V Curve**

The whole cell voltage can be split into three parts:

- **Ohmic loss**: $IR = I(R_A + R_E + R_C)$,
- **Anode overpotential (polarization resistance)**: $\eta_A$.
  Nonlinearity comes from the reaction resistance at the interface;
- **Cathode Overpotential (polarization resistance)**: $\eta_C$.
Introduction

Oxygen reduction/oxidation are important steps:

- SOFC cathode part: \(0.5O_2 + 2e^- \rightarrow 0^{2-}\), SOEC anode part: \(0^{2-} \rightarrow 0.5O_2 + 2e^-\)

✓ Oxygen reduction/oxidation resistances are high in solid oxide cells

<table>
<thead>
<tr>
<th>Resistances Comparison for SOFC at 600 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Parameter: (D_{O^{2-}}^{\text{surf}} = 10^{-6} \text{m}^2\text{s}^{-1})</td>
</tr>
<tr>
<td>(\Delta E \approx 0.2\text{~0.3ev})</td>
</tr>
<tr>
<td>Overpotential of hydrogen electrode</td>
</tr>
<tr>
<td>0.1~1 Ωcm²</td>
</tr>
</tbody>
</table>

Contradiction between continuum simulation and DFT calculations

- **Continuum simulation**

  Parameter: \(D_{O^{2-}}^{\text{surf}} = 10^{-6} \text{m}^2\text{s}^{-1}\)

  \(\Delta E \approx 0.2\text{~0.3ev}\)

- **DFT calculations**

  On Co, Fe terminated LSCF (110) surface

  \(\Delta E \approx 1.74\text{~1.9ev}\)


Contradiction!!
DFT+U calculations provide the energy barriers and transition state positions.

Transition state theory calculations provide the reaction rate constants:
\[ k = \frac{k_B T}{h} \exp \left( -\frac{\Delta G}{RT} \right) \]

Calculate the Current density-Overpotential curve using continuum scale simulation.
Simulation Details (Continuum Model)

Electrolyte
(Gd doped CeO₂)

Electrode
(LSCF / La\,_{1-x}\,Sr\,_{x}\,Co\,_{1-y}\,Fe\,_{y}\,O\,_{3-δ})

0.5O\,₂ + 2e⁻ → O²⁻
(SOFC)

0.5O\,₂ + 2e⁻ → O²⁻
(SOFC)
Mechanisms for LSCF based SOFC cathode reactions:

1. Transport of $O_2$ in gas phase
2. Reaction R1: [adsorption of $O_2$ on LSCF surface]
   \[ O_2 \rightarrow O_{2,ads} \]
3. Transport of $O_{2,ads}$ on LSCF surface
4. Reaction R2: [$O_{2,ads}$ fill in a vacancy on surface]
   \[ O_{2,ads} + V_{O}^{suf} + 2e^- \rightarrow O_{2,suf}^{2-} \]
5. Transport of $O_{2,suf}^{2-}$ on LSCF surface
6. Reaction R3: [split of $O_{2,suf}^{2-}$]
   \[ O_{2,suf}^{2-} + V_{O}^{suf,n} \rightarrow 2O_{suf}^{-} \]
7. Transport of $O_{suf}^{-}$ on LSCF surface
8. Reaction R4: [$O_{suf}^{-}$ transports to the bulk]
   \[ O_{suf}^{-} + V_{O} + e^- \rightarrow V_{O}^{suf} + O^{2-} \]
9. Transport of $O^{2-}$ in bulk LSCF
10. Reaction R5: [$O^{2-}$ transports across the interface]
    \[ O^{2-} + V_{O}^{ele} \rightarrow O_{ele}^{2-} + V_{O} \]
Transport equations \( (i= O_2, O_{2,ads}, O^{2-}, O^{2-}_{2,suf} \text{ and } O^{2-}_{suf}) \)

\[
\frac{d}{dz} \left[ -\frac{\phi}{\tau} D_i \left( \frac{dC_i}{dz} - \frac{n_i FC_i}{RT} \frac{d\phi}{dz} \right) \right] = r_i
\]

Expression for \( \frac{d\phi}{dz} \)

\[
I(e^-) + I(O^{2-}) = I = I(O^{2-})(\text{bottom})
\]

\[
-\sigma \frac{d\phi}{dz} + 2FD_{O^{2-}} \left( \frac{dC_{O^{2-}}}{dz} - \frac{2FC_{O^{2-}}}{RT} \frac{d\phi}{dz} \right) = 2FD_{O^{2-}} \frac{dC_{O^{2-}}}{dz} (\text{bottom})
\]

Expressions for the reaction rates:

\[
O_2 \rightarrow O_{2,ads} \text{ [example]}
\]

\[
r^\text{suf}_{R1} = A_{suf} \{ k^+_1 \text{suf} C_{O_2} - k^-_{1,\text{suf}} O_{2,ads} \}
\]

Boundary conditions:

Top: \( C_{O_2} = \frac{p}{RT} , \frac{dC_i}{dz} = 0 \) \( (i= O_{2,ads}, O^{2-}, O^{2-}_{2,suf} \text{ and } O^{2-}_{suf}) \)

Bottom: \( -D_{O^{2-}} \frac{dC_{O^{2-}}}{dz} = -r^\text{int}_{R5} , \frac{dC_i}{dz} = 0 \) \( (i= O_2, O_{2,ads}, O^{2-}_{2,suf} \text{ and } O^{2-}_{suf}) \)

Physical parameters in the model:

- Reaction Rate Constants \( k \)
- Diffusivities \( D \)
- Surface Area Parameters \( \phi, \tau, A_{suf} \ldots \)
Simulation Details (Transition State Theory)

\[ k = \frac{k_B T}{h} \exp\left(-\frac{\Delta G(T,C)}{k_B T}\right) \]

\[ D = \frac{\lambda^2 k_B T}{z h} \exp\left(-\frac{\Delta G(T,C)}{k_B T}\right) \]

\[ \Delta G(T) \]
- Gibbs free energy \( G(T) \) of \( O_2, O_{2,ads}, O^{2-}, O^{2-}_{2,suf} \) and \( O^-_{suf} \) need to be calculated.

\[ \Delta G(C) \]
- \( \Delta G(C) \) term for specific reaction steps are from experimental observations

Example: \( \Delta G_{D_{O^{2-}}(C_{V_O})} = 2\gamma_{bulk}\frac{\Delta C_{V_O}}{C_{O^{2-}}^{max}} \)

<table>
<thead>
<tr>
<th>Species</th>
<th>Place</th>
<th>( G(T) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( O_2, O_{2,ads} )</td>
<td>Gas phase</td>
<td>( F_{\text{electronic}} + F_{\text{translation}} + F_{\text{vibration}} + F_{\text{rotation}} + PV )</td>
</tr>
<tr>
<td>( O^{2-}, O^{2-}<em>{2,suf} ) and ( O^-</em>{suf} )</td>
<td>LSCF</td>
<td>( \approx F = F_{\text{electronic}} + F_{\text{vibration}} )</td>
</tr>
</tbody>
</table>

\[ F_{\text{electronic}} = E_0 \]

\[ F_{\text{vibration}} = 0.5 \sum_{m=1}^{3N} h v_m + k_B T \sum_{m=1}^{3N} \ln(1 - \exp(-\frac{h v_m}{k_B T})) \]

- The ground state energies \( E_0 \) are to be calculated with DFT+U calculations
- The vibrational frequencies \( v_m \) are to be calculated with finite displacement method
**Density Functional Theory + U (DFT+U):**

**VASP**
- GGA+U - PBE for the exchange and correlation functional is used
- Energy cutoff : 500 eV
- Forces on each ion are less than 0.05 eV/Å
- All the calculations are spin polarized
- Migration energy barriers : the climbing image nudged elastic band (CI-NEB) method
- On-site correlation to the 3d manifolds of Fe$^{3+}$ and Co$^{3+}$: $U_{\text{eff}} = U - J = 4.0 \text{eV}$ for both ions

**DFT+U rather than DFT**
- “DFT results predict a strongly metallic system, while DFT+U results predict a half-metallic system, which agrees with the experiment.”
- DFT results are not accurate for some parameters like vacancy formation energy.

**Vacancy formation energy value for LSCF:**
- $E_{V_O} = E_{\text{defective}} + 0.5E_{O_2} - E_{\text{host}}$
- Calculation results: $E_{V_O} = [0.94, 1.03] \text{eV}$

<table>
<thead>
<tr>
<th>dE</th>
<th>Article</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.036eV</td>
<td>Bucher et al.</td>
</tr>
<tr>
<td>0.777eV</td>
<td>Gryaznov et al.</td>
</tr>
<tr>
<td>1.14eV</td>
<td>Mizusaki et al.</td>
</tr>
<tr>
<td>1.14eV</td>
<td>Wachsman et al.</td>
</tr>
<tr>
<td>1.55eV</td>
<td>Jun et al.</td>
</tr>
</tbody>
</table>

**Experimental vacancy formation energy results**

- **DFT+U results are consistent with experimental results**
Free energy profile for reaction $O_2 + 4e^- + 2V_0 \rightarrow 2O^{2-}$

LSCF (La$_{0.6}$Sr$_{0.4}$Co$_{0.25}$Fe$_{0.75}$O$_{3-\delta}$) 100

Surface structure:
- Sr, O layer
- Co, Fe, O layer
- La, Sr, O layer

Diagram showing the energetics and states involved in the reaction.
Simulation Details (DFT+U Simulation)

Free energy profile for reaction $O^{2-} + V_{O}^{\text{ele}} \rightarrow O_{\text{ele}}^{2-} + V_{O}$
## Simulation Details (DFT+U Simulation)

<table>
<thead>
<tr>
<th>Parameters</th>
<th>$\Delta E(0)(\text{eV})$</th>
<th>$\Delta G(T) - \Delta E(0)(\text{eV})$</th>
<th>$\Delta G(T)(\text{eV})$</th>
<th>Values ($s^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k^+_{1,\text{suf}}$</td>
<td>-0.7</td>
<td>1.1337</td>
<td>0.4337</td>
<td>$2.06198 \times 10^{11}$</td>
</tr>
<tr>
<td>$k^-_{1,\text{suf}}$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>$2.2347 \times 10^{13}$</td>
</tr>
<tr>
<td>$k^+_{2,\text{suf}}$</td>
<td>-0.615</td>
<td>0.7364</td>
<td>0.1214</td>
<td>$6.06167 \times 10^{12}$</td>
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<tr>
<td>$k^-_{2,\text{suf}}$</td>
<td>0</td>
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<td>0</td>
<td>$2.2347 \times 10^{13}$</td>
</tr>
<tr>
<td>$k^+_{3,\text{suf}}$</td>
<td>0.653</td>
<td>0.16083</td>
<td>0.8138</td>
<td>$3.3939 \times 10^{9}$</td>
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<tr>
<td>$k^-_{3,\text{suf}}$</td>
<td>2.153</td>
<td>0.19023</td>
<td>2.3432</td>
<td>$2.2664 \times 10^{7}$</td>
</tr>
<tr>
<td>$k^+_{4,\text{suf}}$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>$2.2347 \times 10^{13}$</td>
</tr>
<tr>
<td>$k^-_{4,\text{suf}}$</td>
<td>1.17</td>
<td>-0.09572</td>
<td>1.07428</td>
<td>$2.03546 \times 10^{8}$</td>
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<tr>
<td>$k^+_{4,\text{suf}}$</td>
<td>1.94</td>
<td>-0.03236</td>
<td>1.9076</td>
<td>$2.5033 \times 10^{4}$</td>
</tr>
<tr>
<td>$k^-_{3,\text{suf}}$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>$2.2347 \times 10^{13}$</td>
</tr>
<tr>
<td>$k^+_{5,\text{suf}}$</td>
<td>1.3162</td>
<td>-0.03241</td>
<td>1.2838</td>
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</tr>
<tr>
<td>$k^-_{1,\text{int}}$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>$2.2347 \times 10^{13}$</td>
</tr>
<tr>
<td>$k^+_{1,\text{int}}$</td>
<td>0.6807</td>
<td>0</td>
<td>0.6807</td>
<td>$1.43 \times 10^{10}$</td>
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<tr>
<td>$k^-_{2,\text{int}}$</td>
<td>1.452</td>
<td>0.08218</td>
<td>1.53418</td>
<td>$1.4151 \times 10^{6}$</td>
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<tr>
<td>$k^+_{2,\text{int}}$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>$2.2347 \times 10^{13}$</td>
</tr>
<tr>
<td>$k^-_{3,\text{int}}$</td>
<td>0.7</td>
<td>0.1457</td>
<td>0.8457</td>
<td>$2.406 \times 10^{9}$</td>
</tr>
<tr>
<td>$k^+_{3,\text{int}}$</td>
<td>0.706</td>
<td>0</td>
<td>0.706</td>
<td>$1.088 \times 10^{10}$</td>
</tr>
<tr>
<td>$k^-_{4,\text{int}}$</td>
<td>1.3685</td>
<td>0.1453</td>
<td>1.5138</td>
<td>$1.7635 \times 10^{6}$</td>
</tr>
<tr>
<td>$k^+_{4,\text{int}}$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>$2.2347 \times 10^{13}$</td>
</tr>
<tr>
<td>$k^-_{5,\text{int}}$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>$2.2347 \times 10^{13}$</td>
</tr>
<tr>
<td>$k^+_{5,\text{int}}$</td>
<td>1.7985</td>
<td>0</td>
<td>1.7985</td>
<td>$8.1395 \times 10^{4}$</td>
</tr>
<tr>
<td>$k^-_{6,\text{int}}$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>$2.2347 \times 10^{13}$</td>
</tr>
<tr>
<td>$k^+_{6,\text{int}}$</td>
<td>0.5297</td>
<td>0</td>
<td>0.5297</td>
<td>$7.3046 \times 10^{10}$</td>
</tr>
</tbody>
</table>
Simulation Details (DFT+U Simulation)

**Diffusion of** $O_{\text{suf}}^-$

\[ D = \frac{\lambda^2 k_B T}{4 \hbar} \exp \left( - \frac{\Delta G(T)}{k_B T} \right) \]

\[ \approx 3.08769 \text{ev} \]

**Diffusion of** $O_{2,\text{suf}}^{2-}$

\[ \approx 1.2787 \text{ev} \]

◆ **Diffusivity on the LSCF surface is very small**

<table>
<thead>
<tr>
<th>Parameters</th>
<th>$\Delta E(0)$(eV)</th>
<th>$\Delta G(T) - \Delta E(0)$(eV)</th>
<th>$\Delta G(T)$(eV)</th>
<th>$\lambda$(Å)</th>
<th>Values (m$^2$s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_{O^{2-}}$</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>(9.73~15.85)$\times10^{-10}$</td>
</tr>
<tr>
<td>$D_{O_2}$</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>$1.2\times10^{-5}$</td>
</tr>
<tr>
<td>$D_{O_2,\text{ads}}$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>3.843</td>
<td>$8.25\times10^{-7}$</td>
</tr>
<tr>
<td>$D_{O_{2,suf}}^{2-}$</td>
<td>1.1623</td>
<td>0.1164</td>
<td>1.2787</td>
<td>1.9215</td>
<td>$2.0639\times10^{-13}$</td>
</tr>
<tr>
<td>$D_{O_{suf}}^{2-}$</td>
<td>2.99</td>
<td>0.09769</td>
<td>3.08769</td>
<td>3.843</td>
<td>$2.6851\times10^{-21}$</td>
</tr>
</tbody>
</table>
### Multiscale Results

![Graph of Overpotential vs. Current Density](image)

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Experimental Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_{\text{surf}}$ (surface area per volume)</td>
<td>$5 , \mu\text{m}^2/\mu\text{m}^3$</td>
</tr>
<tr>
<td>$A_{\text{int}}$ (interface area)</td>
<td>$0.6 , \mu\text{m}^2/\mu\text{m}^2$</td>
</tr>
<tr>
<td>$\phi_{\text{gas}}$ (porosity of gas phase)</td>
<td>0.4</td>
</tr>
<tr>
<td>$\phi_{\text{LSCF}}$ (porosity of LSCF)</td>
<td>0.6</td>
</tr>
<tr>
<td>$\tau_{\text{gas}}$, $\tau_{\text{LSCF}}$ (tortuosity)</td>
<td>1.46</td>
</tr>
</tbody>
</table>
Discussions

Sensitivity Analysis

\[ S_e = \frac{\partial I/I}{\partial P_a/P_a} \approx \frac{\Delta I/I}{\Delta P_a/P_a} \]

<table>
<thead>
<tr>
<th>Parameters</th>
<th>( \Delta P_a/P_a )</th>
<th>( S_e (\eta = -0.08722) \approx 0 )</th>
<th>( S_e (\eta = 0.062555) \approx 0 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k_{1,suf}, k_{1,suf}^+ )</td>
<td>0.05</td>
<td>[0.466,0.477]</td>
<td>[0.460,0.476]</td>
</tr>
<tr>
<td>( k_{2,suf}, k_{2,suf}^+ )</td>
<td>0.05</td>
<td>[0.0091,0.0136]</td>
<td>[0.00225,0.0344]</td>
</tr>
<tr>
<td>( k_{3,suf}, k_{3,suf}^+ )</td>
<td>0.05</td>
<td>[0.0272,0.0334]</td>
<td>[0.00225,0.00939]</td>
</tr>
<tr>
<td>( k_{4,suf}, k_{4,suf}^+ )</td>
<td>0.05</td>
<td>[0.467,0.482]</td>
<td>[0.477,0.481]</td>
</tr>
<tr>
<td>( k_{int}, k_{int}^+ )</td>
<td>0.05</td>
<td>[0.0272,0.0334]</td>
<td>[0.00225,0.00939]</td>
</tr>
</tbody>
</table>

✓ Surface reaction is more important than interface reaction
✓ Bulk diffusion of oxide ion is also a key step
Conclusions

1. The multiscale approach eliminate free parameters and increases the reliability of the model.

2. Multiscale modeling proves to be successful in simulating the Overpotential-Current density curve for oxygen reduction/oxidation in SOFC/SOEC.

3. Surface reaction is more important than interface reaction, and reduce the surface reaction barriers can greatly enhance the cell efficiency.

4. Bulk diffusion of oxide ions is a key transport step.
Thank you for your attention!

Questions?