Developing Stable Critical Materials and Microstructure for High-Flux and Efficient H$_2$ Production through Reversible Solid Oxide Cells

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University of South Carolina
Pacific Northwest National Lab

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Outline

• Background
• Project Objectives
• Technical Approaches
• Project Schedule
• Milestones
• Success Criteria
• Risk Management
SOFC vs. ICE

SOFCs have lower emissions ($CO_2$, $SO_x$ and $NO_x$), noise and maintenance than ICEs

$$\eta_c = \frac{T_H - T_C}{T_H} < 30\%$$
Thermodynamic Advantage of SOECs for H$_2$O Splitting

\[ H_2 + \frac{1}{2}O_2 \xrightarrow{\text{SOFC}} \xrightarrow{\text{SOEC}} H_2O \]

\[ \Delta H: \text{total chemical energy} \]
\[ \Delta G: \text{electricity demand} \]
\[ Q = T \Delta S \]

Higher efficiencies

Cell voltage (V)

Energy (kJ/mol)

Temperature (°C)

Current density (A·cm$^{-2}$)

Lower capital cost

Alkaline

PEM

Solid oxide

Renewable Sustainable Energy Rev., 2011, 15, 1–23

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Thermodynamic Advantage of SOECs for H₂O Splitting

\[ H_2 + \frac{1}{2} O_2 \xrightarrow{SOFC} H_2O \]

SOFC cell

SOEC cell

\[ P = V_{cell} \times I \]

\[ Q = (E_{tn} - V_{cell}) \times I > 0 \]

\[ Q = (E_{tn} - V_{cell}) \times I < 0 \]

\[ E_{tn} = -\frac{\Delta H_f(H_2O)}{2F} = 1.286V \text{ @ } 800^\circ C \]

\[ E_n = -\frac{\Delta G_f(H_2O)}{2F} = 0.977V \text{ @ } 800^\circ C \]

\[ \eta_{SOFC} \text{ (max)} = \frac{\Delta G_f(H_2O)}{\Delta H_f(H_2O)} = \frac{E_n}{E_{tn}} = 75.9\% \text{ @ } V_{cell} = E_n \]

\[ \eta_{SOEC} \text{ (max)} = \frac{\Delta H_f(H_2O)}{\Delta H_f(H_2O)} = 100\% \text{ @ } V_{cell} = E_{tn} \]
HT-SOECs vs. Alkaline vs. PEM Electrolyzers

Efficiency (%)
- SMR
- SOEC
- PEM
- Alkaline

Cost ($/kg H₂)
- SMR
- SOEC
- PEM
- Alkaline

CO₂ emission per kg H₂ produced
- SMR
- Alkaline
- PEM
- SOEC

Benchmark
Barriers to SOCs Commercialization

• **Cost**: high costs in materials and manufacturing of cells, modules and systems
• **Reliability**: performance degradation in electrodes, electrolyte, interconnects and current collectors
High Priority Research in SOCs

• Reducing the operating temperature of SOCs from current 700-800°C to 600-700°C
  • Discovery of new high conductivity electrolytes (The Holy Grill)
  • Discovery of new highly active electrode materials
  • Nanostructuring existing electrodes
  • Shutting down impurity-related degradation mechanisms
Early Work on Bilayer Oxygen Electrode (BLOE)

$\text{SrCo}_{0.9}\text{Ta}_{0.1}\text{O}_{3-\delta}(\text{SCT})@\text{LSCF-GDC}$

Yang, and Huang, *J. Mater. Chem. A*, 2020, 8, 82-86.
BLOE’s Cr-, H₂O- and CO₂-Tolerance

Yang, and Huang, J. Mater. Chem. A, 2020, 8, 82-86.
Early Work on Barrier Layer Free (BLF) OEs

Early Work on Barrier Layer Free (BLF) OEs

Recent Work on BLF Cell vs. Standard Cell

HE substrate: 300 μm ScSZ-Ni; HE functional layer: 10 μm ScSZ-Ni; SSZ electrolyte: 10 μm; LSM-BYC OE: 25 μm
Long-Term Stability of BLF-OE at 550°C and Low Current Density

![Graph showing the stability of BLF-OE over time at 550°C with low current density.](image)
Distribution of Overpotentials: BLF Cells

Pristine

1% GDC

550°C

2% GDC

4% GDC
Long-Term Stability of BLF-OE at 650°C and High Current Density

- LSM/BYC ± 1.0A/cm² at 650°C

Graphs showing the change in ORR and OER with time for LSM/BYC ± 1.0A/cm² at 650°C.
Distribution of Overpotentials: Baseline Cell

LSCF+GDC/GDC/ScSZ/ScSZ+Ni

Half-cell performance tested in air with three-electrode method
Full cell performance tested in 50%H₂O-H₂

SOFC 700°C

SOEC 700°C

Over potential (V) vs. I (A/cm²)
Project Objectives

• The **overarching goal** is to advance reduced temperature ZrO$_2$-based SOCs technology for high-efficiency and low-cost power and H$_2$ production
  • Developing BLF OEs to address performance issue at reduced temperatures
  • Developing BLOEs to address delamination and Cr-poisoning issues
  • Developing porosity-graded HE microstructure to minimize concentration polarization
  • Validating the developed new materials/microstructure in small- and large-area cells
  • Developing physics-based electro-chemo-mechano model to comprehend fundamental understanding on OE delamination
Technical Approach I: (1) Developing Stable BLF OE at 600-650°C and High Current Density

- Understand degradation mechanisms
- Use LSM skeleton to host BYC NPs
Technical Approach I: (2) ALD Supercycle to Fabricate SCT Overcoat for BLOE

<table>
<thead>
<tr>
<th>Precursor</th>
<th>Precursor column T</th>
<th>ALD reactor T</th>
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</thead>
<tbody>
<tr>
<td>Sr</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1) Sr(thd)$_2$, $(\text{thd}=2,2,6,6$-tetramethyl-3,5-heptanediione)</td>
<td>110-200°C, 90-120°C</td>
<td>190-270°C, 150-270°C</td>
</tr>
<tr>
<td>2) Sr($^3\text{Pr}_3\text{Cp}$)$_2$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1) Bis(cyclopentadienyl)cobalt</td>
<td>110°C, 140°C</td>
<td>200°C, 270°C</td>
</tr>
<tr>
<td>2) Cobalt(III) acetylacetonate (Co(acac)$_3$)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ta</td>
<td>Pentaethoxytantalum (PET, Ta(OCH$_3$)$_5$)</td>
<td>160°C</td>
</tr>
</tbody>
</table>
Technical Approach II: Symmetrical Three Electrode Half Cell (STEHC)

Xinfang Jin and Kevin Huang, J. Electrochem. Soc. 2020, 167 124501
The STEHC Procedure to Extract Overpotential

**DC-biased EIS method**

\[ \eta = \int_0^j R_p(j) \, dj \]

At a given T

At a given T and time

EIS spectrum at T, I and time

1. \( R'_O \) cm²
2. Overpotential

\( R_o \)
\( R_o + R_p \)

\( j, \text{A/cm}^2 \)

At a given T

Time, h

\( \text{WE} \)
\( \text{RE1} \)
\( \text{CE} \)

\( \text{OER} \)
\( \text{ORR} \)

\( \text{WE} \)
\( \text{RE2} \)

\( \text{EIS workstation} \)

\( \text{O}_2^\cdot \)
This set of data is used for validating our electrochemical model.
Technical Approach III: TPD Method for Determining the Rate of Oxygen Evolution in OE

\[
\ln \left( \frac{\varphi}{T_m^2} \right) = -\frac{E}{RT_m} - \ln \left( \frac{E}{AR} \right) + C
\]

\[
k(T) = Ae^{-E/RT}
\]

\[
A = -\frac{E}{RT_m^2} \times \frac{\varphi e^{E/RT_m}}{d\left(\frac{df(\alpha)}{d\alpha}\right)_{T=T_m}}
\]

\[
f(\alpha) = k(T)t = (1 - \alpha)^n
\]
Technical Approach IV: Phase Inversion Method to Fabricate Open Structured HE Substrate

$$O^{2-} = \frac{1}{2}O_2 + 2e^-$$

$$H_2O + 2e^- = O^{2-} + H_2$$
Technical Approach V: Button and Large-Area Cells Testing at PNNL

High throughput test stand

Pressurized test stand
Technical Approach VI: Developing Electro-Chemo-Mechano-Model at OE/Electrolyte Interface

- Model construction
- Failure mode and mechanisms identification
- Mitigation strategy development