Intermediate Temperature Proton-Conducting Solid Oxide Electrolysis Cells with Improved Performance and Durability

Xingbo Liu, West Virginia University
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High Temperature Electrolysis Review Meeting
Intermediate Temperature Proton-Conducting Solid Oxide Electrolysis Cells with Improved Performance and Durability

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Andriy Zakutayev, National Renewable Energy Laboratory

Project Vision

We are solving the low performance/high degradation of SOECs by developing intermediate-temperature H⁺-conducting SOEC with robust electrode structure and intrinsically advantageous electrode kinetics.

Project Impact

- Expanding the frontier of SOEC development
- Strong support to low cost Hydrogen economy
- Networking complementary expertise of universities and EMN partners

Award # EE0008378
Year 1 Funding $250K

Triple-conducting anode with conformal coating

High-Throughput fast materials screening
Innovation and Objectives

Project history

- Greg Jackson (CSM): surface catalytic activity, in operando environmental XPS.
- Dong Ding (INL): advanced synthesis of proton conducting electrolyte, cell scale-up.
- Andriy Zakutayev (NERL): novel materials for energy applications using HTS combinatorial research methods.

Barriers

- Long-term chemical stability of electrolyte materials in concentrated vapor \(\leftarrow\) Zr-riched phase or buffer layer.
- Morphology of conformal coating \(\leftarrow\) replace infiltration with ALD.
- Long-term real-time measurement \(\leftarrow\) INL physics-of-failure and accelerated testing.

Proposed targets

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<tr>
<th>Metric</th>
<th>State of the Art</th>
<th>Proposed</th>
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<tbody>
<tr>
<td>Parameter 1</td>
<td>0.9A/cm(^2) @850(^\circ)C</td>
<td>&gt;1A/cm(^2) @600(^\circ)C</td>
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<td>Parameter 2</td>
<td>0.3~0.4 (\Omega) cm(^2) ASR@800(^\circ)C</td>
<td>0.35 (\Omega) cm(^2) ASR@600(^\circ)C</td>
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<tr>
<td>Parameter 3</td>
<td>3%/1000h</td>
<td>4 mV/1000 h or 0.3%/1000h</td>
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</table>

Partnerships

- Greg Jackson (CSM): surface catalytic activity, in operando environmental XPS.
- Dong Ding (INL): advanced synthesis of proton conducting electrolyte, cell scale-up.
- Andriy Zakutayev (NERL): novel materials for energy applications using HTS combinatorial research methods.


C. Zhang, G. Jackson etc. “Measuring fundamental properties in operating SOEC by using in situ XPS, Nature Mat. 9, 944"
600°C BZCYYb vs. 800 YSZ

High $\sigma$, low $E_a$ $\rightarrow$ low operation $T$

- Less challenge in stack components
- Easier maintenance
- Slower materials deterioration
- Longer service life

O-SOEC: $O_2$ exsolution leads to popped-off anode layer,
chemical reactions: $La_2Zr_2O_7$, $MnO_2$ etc. Mixture of $H_2$ and $H_2O$ product

H-SOEC: $H_2$ exsolution at cathode with robust Ni/BZCY bond after 1400°C co-sintering, no chemical reactions, dry $H_2$. 
Technology Innovation – Triple Conducting Air Electrode

Air Electrode:

\[ 2H_2O \rightarrow O_2 + 4H^+ + 4e \]

Electrolyte:

\[ H^+ \downarrow \]

Hydrogen Electrode:

\[ 4H^+ + 4e \rightarrow 2H_2 \]

- Real 3-D reactive anode lies in H-conductivity of electrode material
- Inherently good performance compared to O-MIEC
- Develop “conformal” coatings to further extend reaction areas to 2PB.

Traditional: O, e-conducting electrode, active sites at boundaries only

Proposed: H, e-conducting electrode, active at both boundaries and massive inner surface
Ruddlesden-Popper Phase as SOC Electrode

- \( \text{Ln}_2\text{MO}_4 \) - Ruddlesden-Popper structure
- \( \text{ABO}_3 \) perovskite layers stacking alternatively with rock-salt \( \text{Ln}_2\text{O}_2 \) layers

As Air Electrode in SOFC
- High chemical diffusion and surface exchange coefficients.
- Compatible TEC with GDC or LSGM.
- \( \text{O} \)-conduction via Oxygen interstitials
- Relative lower electrical conductivity than Co-based perovskite cathode

As Air Electrode in H-SOEC
- Wide channel for ion (specially H) conduction
- Readily alterable composition


W. Li, B. Guan, X. Zhang, J. Yan, Y. Zhou, X. Liu*, *PCCP 18 (2016) 8502-8511
4.4 at.% H into PNO for every 0.1% weight gain of H₂O.

**ALL REACTIONS from (1) to (2),**

\[ 2h + O_{i}^{2-} \leftrightarrow 0.5O_{2} + V_{i} \]
\[ 2h + O_{0}^{x} \leftrightarrow 0.5O_{2} + V_{0}^{**} \]

loss of charge carriers, decrease \( \sigma_{e} \)

**From (2) to (3)**

\[ H_{2}O + 0.5O_{2} + 2V_{i} \leftrightarrow 2OH_{i}^{'} + 2h \]
introduce H⁺-conducting and increase \( \sigma_{e} \)
Preliminary performance of PNO-based anodes, as compared with LSM & LSCF.

<table>
<thead>
<tr>
<th>Anode composition</th>
<th>T (°C)</th>
<th>$R_p$ (Ω cm$^2$)</th>
<th>source</th>
</tr>
</thead>
<tbody>
<tr>
<td>LSM-YSZ</td>
<td>840</td>
<td>0.65</td>
<td>Ref [36]</td>
</tr>
<tr>
<td>LSCF-BZCYZ</td>
<td>800</td>
<td>0.3</td>
<td>Ref [37]</td>
</tr>
<tr>
<td>PNO-BZCYYb</td>
<td>700</td>
<td>0.25</td>
<td>Present result</td>
</tr>
<tr>
<td>(PNO-BZCYYb)+BZYP</td>
<td>700</td>
<td>0.12</td>
<td>Present result</td>
</tr>
</tbody>
</table>

700°C, at OCV 0.4bar $P_{H_2O}$
- BZCYYb-PNO
- (BZCYYb-PNO)+BZYP infiltration

Performance of primary cathode supported Ni/BZCY//BZCY//PNO-BZCY full cell

<table>
<thead>
<tr>
<th>Cell configuration</th>
<th>Steam in anode (atm)</th>
<th>T (°C)</th>
<th>Polarization resistance (Ωcm²)</th>
<th>Current density (mA/cm²)</th>
<th>Applied potential/overpotential (V)</th>
<th>Year and Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pr₂NiO₄+δ-BZCY//BaZr₀.₂Ce₀.₆Y₀.₂O₃-₅ (20 μm)//Ni-BZCY</td>
<td>0.4</td>
<td>700</td>
<td>0.31</td>
<td>977</td>
<td>1.3/0.37</td>
<td>This study</td>
</tr>
<tr>
<td>Pr₂NiO₄+δ-BZCY//BaZr₀.₂Ce₀.₆Y₀.₂O₃-₅ (20 μm)//Ni-BZCY</td>
<td>0.4</td>
<td>600</td>
<td>0.4</td>
<td>600</td>
<td>1.3/0.33</td>
<td>This study</td>
</tr>
<tr>
<td>Sm₀.₅Sr₀.₅CoO₃-δ-BCZY//BaCe₀.₅Zr₀.₃Y₀.₂O₃-₅ (20 μm)//Ni-BCZY</td>
<td>0.5</td>
<td>700</td>
<td>0.57</td>
<td>500</td>
<td>1.3/0.35</td>
<td>2010[23]</td>
</tr>
<tr>
<td>(LaSr)CoO₃-δ-BZCYbCo//BaCe₀.₄₈Zr₀.₄₄Yb₀.₁Co₀.₀₂O₃-δ (45 μm)//Ni-BCZYbCo</td>
<td>0.3</td>
<td>700</td>
<td>-</td>
<td>60</td>
<td>1.3/0.30</td>
<td>2011[22]</td>
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<tr>
<td>(La₀.₇₅Sr₀.₂₅)₀.₃₅Mn₀.₃₀₅Cr₀.₃₅₀₅O₃-δ-BCZY//BaCe₀.₅Zr₀.₃Y₀.₁₆Zn₀.₀₄O₃-δ (75 μm)/Ni-BCZY</td>
<td>0.03</td>
<td>700</td>
<td>~21.4</td>
<td>1000</td>
<td>1.3/1.17</td>
<td>2012[28]</td>
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<td>La₀.₆Sr₀.₄Co₀.₂Fe₀.₈O₃-δ-BZCY//BaCe₀.₅Zr₀.₃Y₀.₁₆Zn₀.₀₄O₃-δ (2mm)//Ni-BCZY</td>
<td>0.03</td>
<td>800</td>
<td>7</td>
<td>25</td>
<td>1.3/0.67</td>
<td>2013[29]</td>
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<tr>
<td>Ba₀.₅Sr₀.₅Co₀.₂Fe₀.₈O₃-δ-BZCY//BaCe₀.₅Zr₀.₃Y₀.₁₆Zn₀.₀₄O₃-δ (2mm)//Ni-BCZY</td>
<td>0.03</td>
<td>800</td>
<td>14.4</td>
<td>23</td>
<td>1.3/0.6</td>
<td>2013[29]</td>
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<td>La₀.₆Sr₀.₄Co₀.₂Fe₀.₈O₃-δ-BZY20//BaZr₀.₈₅Y₀.₂O₃-δ (15 μm)//Ni-BZY20</td>
<td>0.03</td>
<td>700</td>
<td>-</td>
<td>208</td>
<td>1.3/0.57</td>
<td>2015[24]</td>
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<td>LaNi₀.₆Fe₀.₄O₃-δ//La₂NiO₄+δ-BCZD//BaCe₀.₅Zr₀.₃Dy₀.₂O₃-δ (30 μm)//Ni–BCZD</td>
<td>0.9</td>
<td>700</td>
<td>-</td>
<td>300</td>
<td>1.3/0.37</td>
<td>2016[52]</td>
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<td>Sr₂Fe₁₉Mo₀.₅O₆-δ-BaZr₀.₈₅Y₀.₂O₃-δ//BZY(16 μm)//Ni–BZY</td>
<td>0.03</td>
<td>650</td>
<td>-</td>
<td>310</td>
<td>1.3/0.45</td>
<td>2017[53]</td>
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### Project Timeline

<table>
<thead>
<tr>
<th>Task Description</th>
<th>Q 1</th>
<th>Q 2</th>
<th>Q 3</th>
<th>Q 4</th>
<th>Q 5</th>
<th>Q 6</th>
<th>Q 7</th>
<th>Q 8</th>
<th>Q 9</th>
<th>Q 10</th>
<th>Q 11</th>
<th>Q 12</th>
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<tbody>
<tr>
<td><strong>Task 1: Electrochemical modeling on reaction kinetics, compositional and structural effects</strong></td>
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<td>1.1: H$_2$O-splitting reaction kinetics modeling</td>
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<td>1.2: Anode structural &amp; composition effects</td>
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<td><strong>Task 2: High throughput screening on anode and catalyst compositions</strong></td>
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<td>2.1: in operando E-XPS of anode</td>
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<td>2.2: HTS of electrocatalyst</td>
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<td><strong>Task 3: Development of button cells</strong></td>
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<td>3.1: H-electrolyte development</td>
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<td>3.2: Anode development</td>
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<td>3.3: Development of the catalyst layer through conformal coating technology</td>
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<td>3.4: Cathode supported button cell development</td>
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<td>3.5: Post-mortem examination</td>
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<td><strong>Task 4: Short stack demonstration to meet the performance and durability target</strong></td>
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<td>4.1: Short stack fabrication &amp; assembly</td>
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<td>4.2: Performance &amp; durability measurements</td>
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<td>4.3: Post-mortem examination</td>
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- ✧: Milestone
- ★: Go/No-Go
Research Tasks – Phase I (Year 1)

- **Task 1.0:** Electrochemical model development for H$_2$O-splitting anode design (M1-M12)
  - **Subtask 1.1:** Modeling of the intrinsic water splitting reaction kinetics (M1-M12)
  - **Milestone Q1:** Construction of the 1-D model, consistent with experimental results.

- **Task 2.0:** HTS to develop anode and catalyst material formulas
  - **Subtask 2.1:** Development of in operando E-XPS for anode characterization
  - **Milestone Q3:** Identification of spectroscopic signals from E-XPS on PNO thin-film anodes and BZCYYb electrolyte to correlate with electrochemical activity for anode H$_2$O splitting.
  - **Subtask 2.2:** HTS for conformal coating of electro-catalyst for H$_2$O splitting
Research Tasks – Phase I (Cont’d)

- **Task 3.0:** Development and characterization of button cells (M1-M12)
  - **Subtask 3.1:** H-electrolyte development and optimization (M1-M12)
  - **Milestone Q2:** Development of H-electrolyte with a conductivity ≥ 0.1 S/cm at 700 °C.
  - **Subtask 3.2:** Development and characterization of anode material (M4-M12)
  - **Subtask 3.3:** Development of catalyst layer through conformal coating technology (M7-M12)
  - **Subtask 3.4:** Fabrication and characterization of cathode supported H-SOEC (M7-M12)
  - **BUDGET PERIOD 1 GO/NO-GO DECISION POINT:** Cathode-supported H-SOEC button-cell ASR < 0.35 Ω·cm², current density >1.0 A/cm² at 1.4 V/cell electrolyzing potential at 700 °C.
  - **Subtask 3.5:** Post-mortem examination of button cells (M10-M12)
Effective Leveraging of the EMN Resource Nodes

INL-Advanced Electrode and Solid Electrolyte Materials for Elevated Temperature Water Electrolysis

- Synthesis and optimization of $\text{BaZr}_{1-x-y-z}\text{Ce}_x\text{Y}_y\text{Yb}_z$ H-electrolyte.
- Planar, 5cm x5cm full cells, short-stack.

✓ More focused studies
✓ Complementary expertise

NERL-High-Throughput Experimental Thin Film Combinatorial Capabilities

- HTS composition for electrocatalytic conformal coating on $\text{Pr}_2\text{NiO}_{4+\delta}$ anode backbone

✓ Fast blanket screening
✓ Optimal materials

NERL CoO-CuO example

Composition of Goal performance

$\text{CeO}_2$, $\text{Y}_2\text{O}_3$