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

PI: Xingbo Liu
Co-PI: Greg Jackson
EMN Partners: Andriy Zakutayev, Dong Ding

1, West Virginia University; 2, Colorado School of Mines; 3, National Renewable Energy Laboratory; 4, Idaho National Laboratory

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Project Overview

Project partners

- PI - West Virginia University (WVU)
- Co-PI - Colorado School of Mines (CSM)
- National Renewable Energy Laboratory (NREL)
- Idaho National Laboratory (INL)

Project Vision

Solve long-term degradation of SOECs operating at ≥ 800°C by developing an intermediate temperature (IT) H-SOEC that operates at 600°C for > 40,000 hours

Project Impact

- Simultaneous H₂O splitting and H₂ separation eliminating Ni oxidation
- High current densities > 1.0 A/cm² at 1.4 V/cell
- Reduced polarization resistance
- Compatible thermal expansion coefficient of anode and electrolyte for long-term structural integrity
- Manufacturability

* this amount does not cover support for HydroGEN resources leveraged by the project (which is provided separately by DOE)

Any proposed future work is subject to change based on funding levels
Project Motivation

WVU: expertise with all ceramic, nickelate-based electrodes in this study, significant cell fabrication and test facilities

CSM: high-temperature firing and characterization of BZCYYb materials for reliable electrochemical performance (E-XPS)

NREL: high-throughput screening with combinatorial thin-film Ba(ZrYPr)O$_{3-\delta}$ deposition on BZCY electrolytes and Pr$_2$NiO$_{4+\delta}$ thin films

INL: expertise in physics-of-failure and accelerated testing of H-electrolyte development, facilitate cell and stack scale-up

Barriers

• Appropriate electrode with mixed conductivities
• Identification of appropriate electrocatalyst compositions
• Fabrication methodology for a scalable and cost-effective electrocatalyst conformal coatings into the anode functional layers
• Resistance of electrolyte at low temperature and long-term stability
## Key Impact

<table>
<thead>
<tr>
<th>Current target</th>
<th>Units</th>
<th>State of the art</th>
<th>1st year target</th>
<th>3rd year target</th>
</tr>
</thead>
<tbody>
<tr>
<td>ASR</td>
<td>Ω cm(^2)</td>
<td>0.57</td>
<td>&lt; 0.35</td>
<td>&lt; 0.35</td>
</tr>
<tr>
<td>Current density</td>
<td>A/cm(^2)</td>
<td>0.5A @ 1.3V</td>
<td>&gt;1.0 @ 1.4V</td>
<td>&gt;1.0 @ 1.4V</td>
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<tr>
<td>Degradation</td>
<td>mV/1000 h</td>
<td>---</td>
<td>---</td>
<td>4</td>
</tr>
<tr>
<td>Temperature</td>
<td>°C</td>
<td>700</td>
<td>700</td>
<td>600</td>
</tr>
</tbody>
</table>

**H-electrolyte at INL:**
- Advanced powder synthesis techniques
- sol-gel and nitrate-combustion
- Post analysis
- SEM/EDX, TEM, XPS
- Conductivity improvements

**Electrocatalyst at CSM&NREL:**
- Appropriate electrocatalyst compositions
- High-throughput screening
- Catalysis & local surface activity
- Operando ambient-pressure XPS

**Button cell at WVU:**
- Electrochemical Modeling
- H\(_2\)O-splitting reaction kinetics
- Anode structure and composition
- Anodes development
- Conformal catalyst layer coating
- Cell fabrication and performance characterization

### Approach - Summary
Approach - Innovation

Materials innovation

To lower $R_{p,\text{anode}}$, our team engineered the anode microstructure to enhance electrocatalytic activity

- PNO-BZCYYb composite anode with triple-conductivity fabricated as the composite backbone
- Electrochemical model development to assess and validate microkinetic reaction mechanisms validated by thin-film electrode experiments
- Optimal electrocatalysts will be identified with high-throughput screening (HTS) of thin-film combinatorial coatings and E-XPS for probing local activity and overpotentials for $H_2O$ splitting
- Conformal coating of catalyst will have properties similar to the electrolyte including good $H^+$-conductivity to enhance the $H$ diffusion and kinetics of bulk $H$ incorporation
- Effective fabrication of SOEC cells with reliable electrocatalyst morphologies will be derived from wet chemical impregnation and/or atomic layer deposition

**HydroGEN: Advanced Water Splitting Materials**
**Approach: Innovation**

**Budget period 1 scope of work**

<table>
<thead>
<tr>
<th>Task Number</th>
<th>Task or Subtask Title</th>
<th>Milestone Type</th>
<th>Milestone Number*</th>
<th>Milestone Description (Go/No-Go Decision Criteria)</th>
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<tbody>
<tr>
<td>1</td>
<td>1.1</td>
<td>Milestone</td>
<td>Q1</td>
<td>Construction of the 1-D intrinsic water splitting reaction kinetics model, consistent with the known experimental results</td>
<td>50%</td>
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<tr>
<td>3</td>
<td></td>
<td>Milestone</td>
<td>Q2</td>
<td>Development of H-electrolyte with $\sigma_H \geq 0.1$ S cm$^{-1}$ at 700$^\circ$C</td>
<td>20%</td>
</tr>
<tr>
<td>2</td>
<td>2.1</td>
<td>Milestone</td>
<td>Q3</td>
<td>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</td>
<td>20%</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td></td>
<td>Q4</td>
<td>Cathode-supported H-SOEC button-cell with novel anode achieves ASR $&lt;$ 0.35 $\Omega$·cm$^2$ and current density $&gt;$ 1.0 A/cm$^2$ at 1.4 V at 700 $^\circ$C</td>
<td>50%</td>
</tr>
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</table>

**HydroGEN Consortium resources**

- NREL: accelerate materials discovery
- INL: facilitate cell and stack scale-up
Relevance & Impact

Key advantages in low cost hydrogen production

- Direct separation of H₂ production from H₂O oxidation
- Mitigate degradation associated with high temperature
- Reduce the cost of materials at milder temperature
- Improve performance of SOECs with H-conducting electrolyte

R&D fits and EMN nodes utilization

By discovering new materials and designing an appropriate anode microstructure, our project can enable low-cost hydrogen generation production for robust, high-efficiency, electrolysis systems which can accelerate R&D of clean energy technologies, one of the three cores of H₂@Scale.

NREL’s high-throughput screening with combinatorial thin-film electrocatalyst deposition can accelerate the exploration of the compositional space.

INL’s high throughput materials testing facility will provide prompt response for materials screening to speed up the optimization of BZCYYb electrolyte.

Broaden HydroGEN Consortium

Our development of an H-SOEC and related expertise in tools & techniques will broaden the HydroGEN Consortium approaches and expertise in H-SOEC research and related fields.

The materials and designs will enable significant performance enhancements over state-of-the-art SOECs and serve as a basis for a future functional design.
Accomplishments – electrochemical modeling

\[ H_2O + 2S \leftrightarrow S - OH_{ad} + S - H_{ad} \]
\[ 2S - O_{ad} \leftrightarrow S - O_{ad} + S - H_{ad} \]
\[ 2S - O_{ad} \leftrightarrow 2S + O_2 \]

\[ S - H_{ad} \leftrightarrow S - H_{3PB} \]
\[ S - H_{3PB} + O_0^{\dagger} BZCYYb + h^* \leftrightarrow HO_0^{\dagger} BZCYYb + S \]

\[ S - H_{ad} + O_{i}^{\dagger} PNO + h^* \leftrightarrow HO_{i}^{\dagger} PNO + S \]
\[ HO_{i}^{\dagger} PNO + O_0^{\dagger} BZCYYb \leftrightarrow O_{i}^{\dagger} PNO + HO_0^{\dagger} BZCYYb \]
Accomplishments – kinetics modeling

S1 + 2 as new S2: $H_2O + 2h^* \leftrightarrow 2H_{ad}^+ + O_{ad}$  \textit{Adversely} $\chi_S$

$$r_{s2} = r_{s2,0} \left\{ \exp(\alpha_s f \Delta \chi_S) - \frac{C_{H_{ad}^+} C_{O_{ad}}}{C_{H_{ad,eq}^+} C_{O_{ad,eq}}} \exp(-(1 - \alpha_s) f \Delta \chi_S) \right\}$$

S3: $H_{ad}^+ + O_{O_{BZCYYB}}^X \leftrightarrow H O_{O_{BZCYYB}}^* + S$  \textit{\(\chi_{3PB}\)}

$$r_{s3} = r_{s3,0} \left\{ \frac{C_{H_{ad}^+}}{C_{H_{ad,eq}^+}} \exp(-\alpha_{3PB} f \Delta \chi_{3PB}) - \exp((1 - \alpha_{3PB}) f \Delta \chi_{3PB}) \right\}$$

B4: $H_{ad}^+ + O_{i_{PNO}}^\cdot \leftrightarrow H O_{i_{PNO}}^\cdot + S$  \textit{\(\chi_S\)}

$$r_{b4} = r_{s4,0} \left\{ \frac{C_{H_{ad}^+}}{C_{H_{ad,eq}^+}} \frac{C_{i,uptake}}{C_{i,uptake,eq}} \exp(-\alpha_s f \Delta \chi_S) - \exp((1 - \alpha_s) f \Delta \chi_S) \right\}$$

B5: $HO_{i_{PNO}}^\cdot + O_{O_{BZCYYB}}^X \leftrightarrow O_{i_{PNO}}^\cdot + H O_{O_{BZCYYB}}^*$  \textit{\(\chi_{2PB}\)}

$$r_{b5} = r_{s5,0} \left\{ \exp((\alpha_{2PB}) f \Delta \chi_{2PB}) - \frac{C_{i,uptake}}{C_{i,uptake,eq}} \exp((1 - \alpha_{2PB}) f \Delta \chi_{2PB}) \right\}$$

\[ \chi_S = \varphi(M)_B - \varphi(M)_S \]
\[ \chi_{2PB} = \varphi(El) - \varphi(M)_B \]
\[ \chi_{3PB} = \varphi(El) - \varphi(M)_S \]
\[ \chi_{3PB} = \chi_{2PB} + \chi_S \]
\[ \chi_S = \frac{F \left( C_{H_{ad}^+} - C_{H_{ad,eq}^+} \right)}{C_S} \]
\[ \Delta \chi_{2PB} = E_{app} \]
\[ \Delta \chi_{3PB} = E_{app} + \Delta \chi_S \]
Accomplishments – formulation of the model

\[ N_i = \frac{1}{RT} (-D_i^{\text{eff}} \frac{\partial y_{i\text{p}}}{\partial z}) \]

\[ \frac{\partial (\rho \varphi)}{\partial t} = \text{div}(\Gamma \cdot \text{grad} \varphi) + S_\varphi \]

Boundary condition

\[ \begin{align*}
D_{b,z} \left( \frac{\partial^2 C_{i,\text{uptake},x=0}}{\partial x^2} \right) &= r_b5 \\
\frac{C_{H_{\text{ad}},x=0}}{C_{H_{\text{ad},eq}}} \exp(f \Delta x_s) &= \exp(f \Delta x_{2PB}) \\
C_{i,\text{uptake},x=l} &= C_{i,eq}
\end{align*} \]

Finite control-volume method

Time-discretization

\[ \int_{t}^{t+\Delta t} \varphi_p \, dt = [\theta \varphi_p + (1 - \theta) \varphi_p^0] \Delta t \]

Unsteady diffusion to reach the steady state

\[ \begin{align*}
\frac{\partial C_{H_x^+}}{\partial t} &= D_{s,z} \left( \frac{\partial^2 C_{H_x^+}}{\partial x^2} \right) + r_{s2} - r_{s3} - r_{b4} \\
\frac{\partial C_{i,\text{uptake}}}{\partial t} &= D_{b,z} \left( \frac{\partial^2 C_{i,\text{uptake}}}{\partial x^2} \right) - \frac{\Delta S}{\Delta V} r_{b4}
\end{align*} \]

\[ i_{2PB} = n_F \frac{\Delta S}{\Delta V} D_{b,z} \left( \frac{\partial C_{i,\text{uptake}}}{\partial x} \right)_{x=0} \]

\[ i_{3PB} = n_F \left( D_{s,z} \left( \frac{\partial C_{H_x^+}}{\partial x} \right) \right)_{x=0} \]
Accomplishments – HTS of anode and catalyst

NiO + Pr₆O₁₁: ball milled in acetone for 22 h and fired for 10 h at 1350 °C

Post-synthesis, single-phase. Green peaks from holder.

BaCO₃ + ZrO₂ + Pr₆O₁₁: ball milled in acetone for 22 h, fired for 20 h at 1400°C

Post-synthesis, single phase. Green peaks from holder.
Accomplishments - environmental XPS studies

• Initial testing of PNO reference samples on Scienta-Omicron HIPP Lab System at Mines begun February 2019 with assistance from Dr. K. Xerxes Steirer

• Reference samples (PNO and BCZYYb) are being characterized with environmental XPS without electrochemical bias
  – Gas composition H₂O, H₂O/O₂ and H₂O/H₂ to ~ 10 mbar
  – Temperatures up to 600°C
  – Exploring the following peaks in
    • PNO – O 1s and Ni 2p with initial studies
    • BCZYYb – O 1s, Y 3d, Ce 3d, and Yb 4d

• Current design of thin-film electrochemical for E-XPS testing at Mines

• Multiple PNO films will provide a basis for combinatorial catalyst coatings in collaboration with NREL to explore overpotentials through binding energy shifts as a function of catalyst composition
Accomplishments - H⁺ conducting electrolyte

• Initiated study on improving conductivity, stability, and sinterability of BCZYYb system by adjusting Zr/Ce ratio

• Synthesized BCZYYb7111 powder sent to WVU for evaluation

Solid-state reaction synthesis flow chart

- Raw precursors
- Mixing for 48 h
- Pressing
- 3 cycles
- Grinding
- Calcination

Ball milling

Pressing
Calcination

BCZYYb powder
Accomplishments - button cell development

ALL POSSIBLE REACTIONS 700°C from (1) to (2),

\[ 2h + O_2^{2-} \leftrightarrow 0.5O_2 + V_i \]
\[ 2h + O_0^{0x} \leftrightarrow 0.5O_2 + V_0^{**} \]
loss of charge carriers, decrease \( \sigma_e \)

From (2) to (3)

\[ H_2O + 0.5O_2 + 2V_i \leftrightarrow 2OH_i^+ + 2h \]
introduce proton conducting and increase \( \sigma_e \)

\[ H_2O + O_i^{i'} + V_i \leftrightarrow 2OH_i^+ \]
\[ H_2O + O_0^{0x} + V_0^{**} \leftrightarrow 2OH_0^+ \]
introduce proton conducting but no \( \sigma_e \) change

Possible H-conduction channel


HydroGEN: Advanced Water Splitting Materials
Accomplishments - electrolyte stoichiometry issue due to Ba diffusion and water attack

Orthorhombic double-peak to tetragonal single-peak upon Ba diffusion

Purposely synthesized Ba doped sample
Accomplishments—La₂Ce₂O₇ (LCO) improved stability in 60vol.% vapor

Better stability

Note: all single phase electrodes
Collaboration Effectiveness

Interactions with NREL
To develop the high-throughput screening with combinatorial studies of Ba(Zr\(_{1-x-y}\)Y\(_x\)Pr\(_y\))O\(_3\)-based phases, NREL is now working together with CMS on the synthesis and sintering of Ba, Zr, Pr pellet precursors. Samples will be characterized at the CSM E-XPS facility. The outcome data will give useful guidance on the subtask 1.1 modeling, subtask 3.2 anode development, and subtask 3.3 catalyst layer development.

Interactions with INL
Recently improved BZCYYb electrolyte powder using advanced powder synthesis techniques has been synthesized and sent by INL to WVU. With this powder, WVU is now working on the button cell application. I-V, EIS, and polarization curves will be examined, and the button cell will be used in subtask 3.3.

Expected benefits
The characterization of BZCYYb-PNO materials and button cell with BZCYYb-LCO bi-layer will benefit HydroGEN Consortium by enriching the materials system database and providing guidance for future functional designs. Modeling the water-splitting kinetics will serve as basis for understanding the electrolysis mechanism and improving performance.
Remaining Challenges and Barriers

- Optimizing numerical programming to establish the relationship between physical parameter and mathematic model
- Exploring new methods to solve cracking problems of the electrocatalyst pellet for PLD of anode and catalyst
- Using pulsed laser deposition to fabricate the combinatorial thin films
- HTS composition for electrocatalytic conformal coating on Pr$_2$NiO$_{4+\delta}$ anode backbone
- Optimizing electrolyte composition and manufacturing
- Improving the cell fabrication to meet the first year performance target

Any proposed future work is subject to change based on funding levels.
Proposed Future Work

Remainder of FY 2019
- Complete the electrochemical 1-D model of the anode reaction in H-SOEC
- Continue working on high temperature screen of anode and catalyst
- Characterize PNO & BCZYYb with E-XPS without electrochemical bias
- Explore the effect of Zr/Ce ratio on electrolyte properties
- Combinatorial catalyst layer coating on button cell with enhanced activity

FY 2020
- Optimize electrolyte properties of BaCe$_{0.8-x}$Zr$_x$Y$_{0.1}$Yb$_{0.1}$O$_3$ (x=0.1, 0.2, 0.4) system
- Further develop cell stability
- Start modeling structural effects in a practical porous electrode

Any proposed future work is subject to change based on funding levels.
Project Summary

- Framework of electrochemical model on anode reaction in H-SOEC has been established
- High Throughput Screening of anode and catalyst has started
- Button cell performance of PNO-base H-SOEC is close to Year 1 target
- Effort on improving cell stability shows promising results

Any proposed future work is subject to change based on funding levels
Technology Back-Up

The thin films will be characterized by:
- Crystallinity (XRD)
- Structure (XRD)
- Composition (XRF)
- Surface chemistry (XPS)
- Ionic/electronic conductivity (Impedance Spectroscopy)
- Activation Energy (Impedance Spectroscopy)
NREL will develop Ba(ZrYPr)O$_{3-\delta}$ thin film sample libraries with Zr/Y/Pr composition gradients as well as gradient-free baseline samples to establish the BZYP combinatorial synthesis process.

<table>
<thead>
<tr>
<th>Single</th>
<th>binary</th>
<th>ternary</th>
</tr>
</thead>
<tbody>
<tr>
<td>BaZrO$_3$</td>
<td>BaZrO$<em>3$ + BaZr$</em>{0.7}$Y$_{0.3}$O$_3$</td>
<td>BaZrO$<em>3$ + BaZr$</em>{0.7}$Y$<em>{0.3}$O$<em>3$ + BaZr$</em>{0.7}$Pr$</em>{0.3}$O$_3$</td>
</tr>
<tr>
<td>BaZr$<em>{0.7}$Y$</em>{0.3}$O$_3$</td>
<td>BaZrO$<em>3$ + BaZr$</em>{0.7}$Pr$_{0.3}$O$_3$</td>
<td></td>
</tr>
<tr>
<td>BzZr$<em>{0.7}$Pr$</em>{0.3}$O$_3$</td>
<td>BaZr$<em>{0.7}$Y$</em>{0.3}$O$<em>3$ + BaZr$</em>{0.7}$Pr$_{0.3}$O$_3$</td>
<td></td>
</tr>
<tr>
<td>Pr$_2$NiO$_4$</td>
<td></td>
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</tr>
</tbody>
</table>

- Pulsed laser deposition system will be used for the combinatorial thin films.
- Preliminary tests will be conducted with single and binary targets with different temperature, pressure, pulse, etc.
- Thin films will be deposited on glass and ITO substrates and characterized for composition, structure, morphology, thickness, impedance, etc.
Technology Back-Up

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

NREL-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

Composition of Goal performance

NERL CoO-CuO example

Any proposed future work is subject to change based on funding levels
O 1s E-XPS spectra of the BaZr_{0.9}Y_{0.1}O_{2.95} (a) SPS, (b) SSR and (c) HT pellets as a function of the incident X-ray energy (710, 800 eV) at 300°C at a p(H_{2}O) of 100 mTorr. The 3 different photon energies provide spectra over 6, 8 and 11 Å respectively. The “lattice” component (orange) represents the perovskite structure in the near-surface regions while the “surface” component (green) is for partially hydrated surface secondary phases on the film with “OH” corresponding to the hydration/adsorbed species (blue). The “steam” component is represented in purple.

**Accomplishments-E-XPS on BaZr_{0.9}Y_{0.1}O_{2.95}**

Any proposed future work is subject to change based on funding levels.
Optimization of electrolyte properties of \( \text{BaCe}_{0.8-x}\text{Zr}_x\text{Y}_{0.1}\text{Yb}_{0.1}\text{O}_3 \) \( (x=0.1, 0.2, 0.4) \) system

**Electrolyte synthesis and evaluation**
- Measure electrical conductivity in different gas conditions and temperatures
- Examine structure stability in high vapor conditions at 700°C

**Electrolyte Integration**
- Fabricate dense electrolyte membrane on electrode support sintered under 1450°C and send powder/cells to WVU
- Support WVU with INL’s high temperature R2R manufacturing capability

**Electrolyte Determination**
- Examine electrolyte and electrode polarization resistances in SOEC
- Measure Faradaic efficiency under different electrolysis current densities to determine the optimal composition

Any proposed future work is subject to change based on funding levels
Technology Back-Up

Accomplishments-Performance Update

Our JMC-A Results

PNO-BZCY composite on $\text{BaZr}_{0.2}\text{Ce}_{0.6}\text{Y}_{0.2}\text{O}_3$

Technology Status Now

Pure PNO on $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.1}\text{Yb}_{0.1}\text{O}_3$

HydroGEN: Advanced Water Splitting Materials
• Wenyuan Li, Bo Guan, Liang Ma, Zhongqiu Li, Hanchen Tian, Xingbo Liu*: Synergistic Coupling of Proton-Conductors BaZr$_{0.1}$Ce$_{0.7}$Y$_{0.1}$Yb$_{0.1}$O$_{3-\delta}$ and La$_2$Ce$_2$O$_7$ to Create Chemical Stable, Interface Active Electrolyte for Steam Electrolysis Cells, Submitted to ACS Applied Materials & Interfaces (2019), under revision.


• Wenyuan Li, Bo Guan, Liang Ma, Shanshan Hu, Nan Zhang, Xingbo Liu*: Highly Performing Triple-Conductive Pr$_2$NiO$_{4+\delta}$ Anode for Proton-Conducting Steam Solid Oxide Electrolysis Cell, Journal of Materials Chemistry A 6 (2018) 18057-18066.