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

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May 2020

Project ID EE0008378

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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)
- Sandia National Laboratory (SNL)

Project Vision
We are solving the long-term degradation problem of SOECs at operating temperatures ≥ 800°C by developing IT H-SOEC at lower operating temperatures 600°C

Project Impact
Enabling significant performance enhancements in SOECs by developing IT H-SOEC
- High current densities > 1.0 A/cm² at 1.4 V/cell
- Long-term operating durability at ~600 °C for (<10 mV/1000 hr)

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

Project Motivation

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

CSM: combinatorial deposition and characterization of materials for reliable electrochemical performance

NREL: high-throughput screening with combinatorial thin-film deposition on electrolytes and electrode.

SNL: Operando measurements to screen the electrocatalyst formula via a lab-based EXPS.

INL: expertise in H-electrolyte development and electrode backbone 3D engineering

<table>
<thead>
<tr>
<th>Current target</th>
<th>Units</th>
<th>State of 2018</th>
<th>1st year target</th>
<th>2nd year target</th>
<th>3rd year target</th>
</tr>
</thead>
<tbody>
<tr>
<td>ASR in run</td>
<td>Ω·cm²</td>
<td>0.57</td>
<td>&lt; 0.35</td>
<td>&lt; 0.35</td>
<td>&lt; 0.35</td>
</tr>
<tr>
<td>Current density</td>
<td>A/cm²</td>
<td>0.5A @ 1.3V</td>
<td>&gt;1.0 @ 1.4V</td>
<td>&gt;1.0 @ 1.4V</td>
<td>&gt;1.0 @ 1.4V</td>
</tr>
<tr>
<td>Degradation</td>
<td>mV/1000 h</td>
<td>--</td>
<td>--</td>
<td>30</td>
<td>10</td>
</tr>
<tr>
<td>Temperature</td>
<td>°C</td>
<td>700</td>
<td>700</td>
<td>600</td>
<td>600</td>
</tr>
</tbody>
</table>

Barriers

- Inadequate activity of electrocatalyst at lower temperature
- Low long-term stability in humified environments
- Lack of scalable and cost-effective electrocatalyst conformal coatings fabrication
- Popped-off electrode layer
An electrochemical model is developed to assess and validate microkinetic reaction mechanisms with thin-film electrode providing guidelines on electrode development.

Optimal electrocatalysts identified with high-throughput screening (HTS) of thin-film combinatorial coatings and E-XPS for probing local activity and overpotentials for H$_2$O splitting.

Conformal coating of catalyst on uniform BZCYYb scaffold providing good H$_+^-$ conductivity and kinetics of bulk H incorporation. Promising in solving electrode layer Popped-off problem during long-term operation.

HydroGEN Consortium resources:

SNL INL NREL
## Approach: Innovation

### Budget period 1&2 scope of work

<table>
<thead>
<tr>
<th>Task or Subtask Title</th>
<th>Milestone Type</th>
<th>Milestone Number*</th>
<th>Milestone Description (Go/No-Go Decision Criteria)</th>
<th>Complete</th>
</tr>
</thead>
<tbody>
<tr>
<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 H₂O splitting.</td>
<td>70%</td>
</tr>
<tr>
<td>3.4</td>
<td>Milestone-Go/No-Go #1</td>
<td>Q4</td>
<td>Cathode-supported H-SOEC button-cell with novel anode developed in this project achieves ASR &lt; 0.35 Ω·cm² and current density &gt; 1.0 A/cm² at 1.4 V at 700 °C.</td>
<td>100%</td>
</tr>
<tr>
<td>1.2</td>
<td>Milestone</td>
<td>Q5</td>
<td>Development of PNO-based anode of model-guided composition with a 0.3 Ω·cm² ASR at 600°C under operation condition</td>
<td>100%</td>
</tr>
<tr>
<td>3.1</td>
<td>Milestone</td>
<td>Q6</td>
<td>Prediction of the requirement of particle size, porosity, thickness and along with improved σ, k and D needed to reach a 0.35 Ω·cm² ASR under operation at 600°C.</td>
<td>100%</td>
</tr>
</tbody>
</table>

### Materials innovation

- PNO-BZCYYb composite anode with triple-conductivity was fabricated as the composite backbone.
- Electrochemical model development for assessing and validating microkinetic reaction mechanisms and performance enhancement guidance.
- Optimal electrocatalysts identified by HTS thin-film combinatorial coatings and E-XPS.
- Conformal coating of catalyst to enhance the H diffusion and kinetics of bulk H incorporation.
Relevance and Impact

By providing a stable and highly-active electrocatalyst at lower temperature, there will be a significant leap in H-SOEC, providing fast and efficient strategy for hydrogen production.

Assistance of E-XPS and high-throughput from CSM together with HydroGEN nodes (SNL NREL) will provide fast screen of electrocatalyst formula and support the microkinetic modeling development.

- The spectroscopic signals from E-XPS will identify features in the O1s peak related to surface hydroxides and the cation oxidation states that correlate with high H2O-splitting activity. Spatial resolution based on distance from the Au current collector will provide a measure of electrochemical activity for spreading the active electrocatalyst surface area.

- The E-XPS testing of the electrocatalysts will provide critical spectroscopic signals that will enable the team including WVU to develop improved microkinetic models that can assess what impact the enhanced electrocatalyst activity may have on full cells designation.

Fabricate 3D-structured mesh-like electrode structure from INL provides backbone structure with high porosity, the mechanical strength, particle size and porosity are balanced upon firing conditions.
**Modelling-Perspective**

**Electron Transfer**

- **Bi-pathway kinetics**
  - S1 → S2 → S3 → J_{diff} → S6 → S7

- **Convection diffusion**
  \[
  \frac{\partial C_i}{\partial \tau} = D_i \nabla^2 C_i + \bar{V} \nabla C_i
  \]

- **Surface active site**
  \[
  \Gamma_M \quad \Gamma_O \quad \theta_i^0
  \]

- **Specific gas diffusivities**
  \[
  D_i = \frac{D_{i,Kn}^{\text{eff}} D_{ij}^{\text{eff}}}{D_{i,Kn}^{\text{eff}} + D_{ij}^{\text{eff}}}
  \]

- **Specific gas kinetics**
  \[
  J = \frac{P_i}{\sqrt{2\pi MR_g T}}
  \]

- **Size-specific surface**
  \[
  \left(\frac{\Delta S}{\Delta V}\right)_{ads} = \frac{6}{d_g} (1 - \varepsilon)
  \]

- **SpClP specific length**
  \[
  S_{tpbl} = S_{tpbl,0} \left(1 - \frac{\varepsilon - \varepsilon_{f,cc}}{1 - \varepsilon_{f,cc}}\right) \frac{d_{g,0}^3}{d_g^3}
  \]

**Accomplishments – Electrochemical modeling**
Accomplishments– Electrochemical modeling

**Model Capability**

- WVU models are being adopted by Mines into Cantera thermochemical open framework for use by others in design.

**Surface Site**

- Surface coverage of case 1
- Electrode thickness (micron)
- θ_H
- θ_H2O
- θ_↓
- θ_↓−
- 0.4V
- 0.05V

**Mass Diffusion**

- H_↑, HO_−, O_↑ diffusion flux @ 0.4V
- Flux (mol/s)

**Local contributions**

- Current Contribution (A/cm²) @ 0.3V Overpotential
- Electrode depth (microns)

**Gas Transportation**

- Electrolysis current (A/cm²) @ 0.3V Overpotential
- Electrode depth (microns)

**HydroGEN: Advanced Water Splitting Materials**
Accomplishments – Electrochemical modeling

**Model prediction on performance**

**H₂O kinetics ∝ Electrolysis**

**O₂ kinetics are less related**

**Structure factors**

HydroGEN: Advanced Water Splitting Materials
Accomplishments—E-XPS

**PNO preliminary experiment**

- **PO$_2$ = 1mTorr**
- **PO$_2$ = 50mTorr**
- **PO$_2$ = 100mTorr**

- PNO film synthesized at 50mTorr PO$_2$ has the most stable structure and morphology

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HydroGEN: Advanced Water Splitting Materials
Accomplishments– E-XPS

**PNO deposition on BCZYYb pellet**

- PNO film deposited on BCZYYb pellet showed stable structure and morphology after annealing 1250°C.

SEM was conducted at CSM.
Stability of BZYP+PNO structure

As-deposited (PNO+BZYP)

900° C

1000° C

1100° C

1200° C

Both PNO and BZYP films are stable above 1100° C

BZYP+PNO deposition on BCZYYb

- E-XPS is currently in-progress in CSM.

- Masking sheets of PNO + BZYP film and Au coat patterns have been fabricated for E-XPS.
- NREL has conducted the deposition of PNO+BZYP and gold coating with patterned masks.

Accomplishments– E-XPS
• Mines has re-established operation of the on-campus Scienta-Omicron E-XPS machine as of last month.
• Initial tests measured cation and O 1s peaks in dry environments.
• Wet environments at temperature are next step without electrochemical excitation.
• An E-XPS stage for electrochemical excitation has been purchased for testing in this coming quarter.
Accomplishments – Electrolyte

**Composition effect on $\sigma_i$ of BCZYYb-7111, 4411 and BZY20**

<table>
<thead>
<tr>
<th>Gas conditions</th>
<th>Activation energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry air</td>
<td>0.45 eV</td>
</tr>
<tr>
<td>Wet air</td>
<td>0.51 eV</td>
</tr>
<tr>
<td>Dry 5% H$_2$</td>
<td>0.34 eV</td>
</tr>
<tr>
<td>Wet 5% H$_2$</td>
<td>0.36 eV</td>
</tr>
</tbody>
</table>

Conductivity of BCZYYb7111 as a function of temperature and gas conditions

Conductivity of BCZYYb7111 as a function of temperature and oxygen partial pressure
The conductivity measurement as functional of oxygen partial pressure and steam concentration has shown the electron leakage for BCZYYb7111 under reducing condition and the higher over-potential leads to more leakage in the electrolytes.

INL developed a model with defect chemistry and the experimental conductivities as input to predict the leakage behaviors under practical conditions within both electrolytes.

- BZY20 shows much lower leakage when the over-potential is under 0.175 V;
- Increased steam concentration decreases the leakage for both cases;
- BCZYYb7111 shows the issue with electron conduction, increasing overall leakage.
Accomplishments – Anode materials

Doped Pr$_2$NiO$_4$

(a) Pr$_{2-x}$Ba$_x$NiO$_4$ at 600°C in 60 vol.% steam Air

(b) ASRs in 60 vol.% steam Air 550-700°C

(c) apparent activation energy ($E_a$) derived from the ASR results.

0.08 Ωcm$^2$ achieved @600°C

(d) Four-probe DC electrical conductivity of Pr$_{2-x}$Ba$_x$NiO$_4$
Accomplishments – Anode materials

**H₂O kinetics**

- Oxygen surface exchange coefficient ($k$) and bulk diffusion coefficient ($D$).
- Transition of the electrical conductivity upon gas atmosphere shift from dry N₂ to 60 vol.% water vapor containing N₂.

**O₂ kinetics**

- Bar charts showing the changes in $k$ and $D$ with temperature and $P_{O_2}$ changes from 0.04 to 0.02 atm.
Accomplishments - Anode conformal coating

Uniform anode backbone
INL initiated the work on optimization of the synthesis of 3D ceramic textile electrode backbone for incorporating VWU’s electrode catalyst with infiltration method.

- The synthesis temperature was attempted between 700~900 °C and preliminary result shows high porosity of 64.4% and good mechanical strength can be achieved at 800 °C;
- The synthesis method can be easily for scaling up to make large electrode.
Accomplishments– Button Cell performance

Go-No/Go Criterion 1\textsuperscript{st} year

Hit 1A/cm\textsuperscript{2} at 1.2 V @ 700\degree C vs. the goal 1.4V

0.30 \ensuremath{\Omega}cm\textsuperscript{2} @ 700\degree C vs. the goal 0.35 \ensuremath{\Omega}cm\textsuperscript{2}
Accomplishments— Button Cell performance

Hit 0.82A/cm² at 1.3 V @ 600°C

$\text{H}_2\text{O}$ kinetics $\propto$ Electrolysis

$\text{O}_2$ kinetics are less related

in consistence with the model predication

0.58 $\Omega\text{cm}^2$ @ 600°C
Combinatorial studies are difficult to set up to ensure no false positives or negatives are produced. Unless the testing is being done in a relevant environment, misleading results may occur. **Response:** the team aims to understand and promote the materials from a more comprehensive evaluation setting. It is indeed challenging to keep high fidelity standard across very different experimental sets. We screened routes ever possible to our ability to minimize the discrepancy in this combinatorial studies. Composition, phase and condition are made the same or very similar between E-XPS, electrochemical and modeling studies.

There is a reasonable outline of the next steps. It would be good to see some modeling added to guide materials composition selection. **Response:** our electrochemical continuum modeling is capable of guiding/predicting electrode reaction limits vs. materials physiochemical properties, electrode/electrolyte mixture composition and electrode microstructure. D, k values, gas diffusion, charge transfer under detailed structural and potential parameters are all considered and optimized. But this model is not capable of deriving optimal chemical stoichiometric composition of steam electrode from the aimed physiochemical properties.

It is suggested that the team do the durability testing in a lower steam concentration (below 60%). **Response:** experimental results shows steam concentration higher than 30 vol.% won’t introduce a perceptible influence to the performance. We use up to 60 vol% steam to unveil possible chemical stability issue in long-term operation of electrolyte and electrode.
Collaboration: Effectiveness

**Interactions with NREL:**
To develop the High-throughput screening with combinatorial studies of \( \text{Ba(Zr}_{1-x-y}\text{Y}_{x}\text{Pr}_{y})\text{O}_{3} \)-based phases, NREL is now working together with CMS on the synthesis and sintering of Ba, Zr, Pr pellet precursors for HTS. The sample will be characterized by CSM E-XPS facility. The outcome date will give useful guidance on the **Task 1** modeling, **subtask 3.2** anode development and **subtask 3.3** catalyst layer development.

**Interactions with INL:**
Recently studied BZCYYb series electrolyte properties on conductivities and electronic leakage will provide guidance on button cell designation. The 3D Ceramic Textile electrode is expected to significantly improve the button cell performance. 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 enrichment of related materials system database and guidance for the future functional designation. The modeling of the water-splitting kinetic will serve as basis of understanding the mechanism of electrolysis and improvement of the performance
Remaining Challenges and Barriers

❖ Updating modeling programming to connect the physical properties and electrochemical impedance response

❖ Improving electrode faradic efficiency >80% and durability in high steam concentration

❖ Balance between durability and catalytic activity within a full cell

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

**Remainder of FY 2020**

- Model prediction of the requirement needed to reach a $0.35 \, \Omega \cdot cm^2$ ASR @ 600°C.
- Continue working on high temperature screen of anode and catalyst
- Characterization PNO & BCZYYb with E-XPS without electrochemical bias
- Exploring the effect of Zr/Ce ratio on electrolyte’s properties
- Combinatorial catalyst layer coating on button cell with enhanced activity
- Full cell durability characterization with degradation <30 mV/1000 hr.

**FY 2021**

- Optimization of electrolyte properties for higher faradic efficiencies
- Further development on cell stability with degradation <10 mV/1000 hr.
- Cathode-supported H-SOEC button-cell with 3D hierarchical structure anode

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

- Electrochemical model on anode reaction, structural and composition effects of H-SOEC has been established
- PNO + BZYP film and Au coat patterns have been fabricated by NREL
- E-XPS is currently in-progress in CSM
- Composition effects on BZCYYb electrolyte characterized experimentally
- Defect chemistry model developed to predict the leakage behaviors of electrolyte under practical conditions
- 3D Ceramic Textile (3D-CT) Oxygen Electrode initiated
- Conformal catalyst coating technology established
- Year 1 target of Button cell performance of PNO-base H-SOEC achieved
- Model guided anode materials with ASR<0.3 developed

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)

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

NREL will perform deposition of 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>
<td></td>
</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.
- The thin films will be deposited on glass and ITO substrates and characterized for composition, structure, morphology, thickness, Impedance and so on.

Any proposed future work is subject to change based on funding levels.
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 BaZr$_{1-x-y-z}$Ce$_x$Y$_y$Yb$_z$ H-electrolyte.
- Planar, 5cm x 5cm full cells, short-stack.

✓ More focused studies
✓ Complementary expertise

NERL-High-Throughput Experimental Thin Film Combinatorial Capabilities

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

✓ Fast blanket screening
✓ Optimal materials

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.
Publications and presentations


- Wenyuan Li, Bo Guan, Liang Ma, Zhongqiu Li, Hanchen Tian, **Xingbo Liu***: Synergistic Coupling of Proton-Conductors BaZr0.1Ce0.7Y0.1Yb0.1O3-δ and La2Ce2O7 to Create Chemical Stable, Interface Active Electrolyte for Steam Electrolysis Cells, *ACS Applied Materials & Interfaces* 11 (2019) 18323-18330