Proton-Conducting Solid Oxide Electrolysis Cells for Large-scale Hydrogen Production at Intermediate Temperatures

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- Olga Marina: Chief Scientist

### INL
- Dong Ding: Materials Engineer

### NREL
- Andriy Zakutayev: Staff Scientist

### Program Manager
- Dr. David Peterson, Department of Energy
Project Overview

Project Partners
UConn: Prabhakar Singh (PI), Boxun Hu, Ugur Pasaogullari (Co-PI)
PNNL: Jeff Stevenson and Olga Marina (Co-PI)

Project Vision
Identify novel materials and processing techniques to develop cost effective and efficient proton-conducting solid oxide electrolysis cells (H-SOECs) for large-scale hydrogen production at intermediate temperatures (600-800˚C) to meet DOE cost and performance targets.

Project Impact
(a) Innovation in materials chemistry – electrolyte and electrode formulations
(b) Use of non-noble and non-strategic cell and stack component materials
(c) Bulk, interface, and surface optimizations to achieve low ASR
(d) High proton-conductivity with a low sintering temperature (<1450˚C)
(e) Operating current density (>1 A/cm²) with the performance degradation rate not to exceed the DOE performance metric (< 4 mV/1000 h)

Key visuals
- Densification at <1400˚C achieved
- Higher conductivity (>0.01 s/cm) obtained
- Uniform bulk phase composition obtained
Innovation and Objectives

Project History
- Extensive background in HT/IT electrochemical systems
- Experience with functional ceramics, electrodics, electrochemical testing, performance degradation and data analysis
- Well established laboratory capabilities in materials processing and characterization
- On going research in SOFC, SOEC and H-SOEC

Key Impact

<table>
<thead>
<tr>
<th>Metric</th>
<th>State of the Art</th>
<th>Proposed</th>
<th>Actual</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conductivity (S/cm)</td>
<td>~10^{-3}</td>
<td>10^{-2}</td>
<td>4x10^{-2}</td>
</tr>
<tr>
<td>Sintering temp. (°C)</td>
<td>&gt;1450</td>
<td>≤1350</td>
<td>1350</td>
</tr>
<tr>
<td>Thickness (µm)</td>
<td>&gt;25</td>
<td>~15-20</td>
<td>20</td>
</tr>
</tbody>
</table>

Barriers
- High sintering temperature for electrolyte densification (>1400°C)
- Decrease in conductivity during processing and operation
- High temperature gas sealing and operation with thermal cycling
- Complex processing and fabrication techniques
- Chemical and structural instability in presence of Cr, and Si contaminants

Partnerships
The research team collaborates with PNNL in developing and testing H-SOEC. Team will heavily leverage EMN network. We will work with NREL, INL and LBNL for the optimization of electrolyte chemistry.
Our approach for H-SOEC development leading to large scale manufacturing and commercialization will rely on utilizing EMN Network and core experimental and computational capabilities at NREL, INL and PNNL.

- Materials and Processes: Innovation in materials and processing techniques are anticipated to develop electrolyte formulations capable of densification (96-98% density) below 1400°C in oxidizing atmospheres, meet electrical conductivity target (>0.01 S/cm) and demonstrate bulk structural and chemical uniformity.
- Synthesis and fabrication processes: Cells utilizing tape cast multi-layer laminated electrolyte (10-20 μM) and electrode (integrated backbone, infiltration, thin film processing) will be sintered and electrically tested. Process will be optimized to achieve target ASR and current density to meet the overall project goals (1 A/cm² @ 1.4 V, 700°C).
- Computational analysis: Electrolyte and electrode materials composition will be optimized for densification, proton conductivity and structural stability. Select electrode and electrolyte materials will be synthesized and electrochemically tested.
- Electrode poisoning and performance degradation mitigation: Electrode delamination and Cr assisted poisoning mechanisms will be developed. Mitigation approaches will be identified.
Relevance & Impact

The proposed research program supports DOE Hydrogen and Fuel Cells Program goals through the development of cost effective and stable cell component materials, processing techniques and architectures to meet hydrogen production cost target of < $2/gge hydrogen.

Relevance, impact and innovation:

- Enables the use of proton conducting electrolyte < 700°C
- Produces pure hydrogen without the need of separation
- Electrolyte densification temperature reduced to ~1350-1400°C for >97% density
- Improved conductivity (>0.01S/cm) obtained at lower temperatures 550-750°C
- Fabrication of thin electrolyte (~10 μM) cells using multi-layer low cost tape cast process
- Examines large scale manufacturing using R2R
- Develops mechanistic understanding of electrochemical performance degradation
- Identifies approaches for the mitigation of electrode poisoning
### Comparison of H-SOEC and O-SOEC Cells

**H-SOEC**

```
H_2 → 4e^- + 4H^+ → 2H_2
2H_2O → O_2 + 4H^+ + 4e^- 
```

- Porous cathode
- Electrolyte
- Porous anode

**O-SOEC**

```
H_2O → 4e^- + 4H^+ → 2H_2 + 2O_2
```

- Porous cathode
- Electrolyte
- Porous anode

### Attributes

<table>
<thead>
<tr>
<th>Attributes</th>
<th>H-SOECs</th>
<th>O-SOEC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Operating Temperature</td>
<td>550-750°C</td>
<td>650-850°C</td>
</tr>
<tr>
<td>Electrolyte conductivity</td>
<td>0.01 S.cm(^{-1}) at 650°C</td>
<td>0.015 S.cm(^{-1}) at 850°C</td>
</tr>
<tr>
<td>Products</td>
<td>Pure H(_2)</td>
<td>H(_2)O + H(_2)</td>
</tr>
</tbody>
</table>

**Advantages of lowering operating temperature:**
- Reduce Cr evaporation and mitigate materials degradation
- Use of lower cost metals, alloys and coatings in BOP
- Ease of gas sealing
- Increased cell/stack durability
- Reduced cost of hydrogen production
Accomplishments

- Proton conducting-electrolyte and electrode materials have been selected and synthesized using sol-gel and conventional solid state ceramic processing methods. The powder synthesis process have been validated at 20 gram batch scale for BZY and BZCY-Yb proton-conducting powders.
- BZY and BZCY-Yb electrolyte discs have been prepared using reactive/fugitive sintering aids (nanosized ZnO). Sintering at 1350°C in oxygen show the densification (>97% density). The conductivity of sintered BZY and BZCY-Yb has been measured by 4-probe technique and found to be ~ 0.01 and 0.04 S/cm.
- H-SOEC full cells with low area specific resistance have been fabricated using thin dense electrolyte (15-40 µm) and porous electrodes using INL node.
- Button cell testing of steam electrolysis in the temperature range of 600-800°C has been initiated. For benchmarking, a standard O-SOEC cell has been fabricated and tested for 100 hours.
- Technical progress and accomplishments meet the project milestones (M1-1, 2-1, M3-1).
- The overall program goals of the Budget Period 1 Go/No-Go Decision will be achieved.
INL Advanced Materials for Water Electrolysis at Elevated Temperatures
(Experts: Drs. Dong Ding and Henping Ding)

The INL-UConn collaboration spanned over the topics for the development of dense electrolyte and performance improvement of the anode. Technical discussions have been held with Dr. Ding with focus on materials selection, processing techniques and electrochemical performance evaluation. The tasks include:

**Task 1:** Development of electrolyte densification technique and determination of corresponding ionic conductivities (Q1-Q2)-This task consists of the identification of dopants, powder synthesis and processing techniques that results in the development of dense electrolyte (>95-97%) supported on porous electrode backbone. Transition metal and lanthanide group dopants have been experimentally evaluated. We have received proton-conducting half-cells and full cells (1 cm diameter) for SOEC testing and characterization. The measured conductivity and the thickness (~20 µm) of dense electrolyte meets the project milestones. INL will provide large size full cells (1.3 cm or 2.5 cm diameter) and electrode materials for SOEC testing.

**Task 2:** Anode microstructural modification for performance improvement (Q3-Q4): This task consists of identification of infiltration techniques and microstructural modifications to reduce electrode polarization. Mechanisms will be developed for polarization losses. We have discussed the use of INL capability to fabricate full cells with porous electrodes and thin electrolyte using tape-casting technique (and UConn-made electrode and electrolyte materials). Tape cast multi-layer laminated samples will be sintered and tested to achieve target ASR and current density to meet the overall project goals.
Technical discussion held with Dr. Andriy Zakutayev has identified scope of work for the development of electrolyte chemistry and validation through high temperature experiments.

The HTE combinatorial node at NREL is responsible for the investigation of combinatorial libraries of Y-substituted BaZrO$_3$ (BZY). Other minor additives (e.g. transition metals, alkali earth, rare-earth) that have a potential to improve BZY’s sinterability without inducing secondary phases or impeding protonic and electronic charger transport. The films are characterized at NREL for composition, structure, morphology, and electrical properties at room temperature. These NREL thin film results will be compared to the UConn bulk synthesis results, in order to determine how thin film morphology and ceramic sinterability correlate with each other. At later phases of the project, optimized thin film compositions may be deposited at NREL on ceramic or metallic supports provided by UConn.
## Project Tasks and Milestones

<table>
<thead>
<tr>
<th>Task or Subtask Title</th>
<th>Milestone Type</th>
<th>Milestone Number*</th>
<th>Milestone Description</th>
<th>Anticipated Quarter</th>
<th>Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>Program management and plan</td>
<td>Milestone</td>
<td>M1-1</td>
<td>Program priorities established in consultation with program manager.</td>
<td>1</td>
<td>Priorities were established at Q1</td>
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<tr>
<td>Development of proton conducting electrolyte and electrode materials</td>
<td>Milestone</td>
<td>M 2-1</td>
<td>Candidate electrolyte and electrode material compositional space for H-SOECs are selected based on guidance from advanced modeling tools and analytical techniques.</td>
<td>1</td>
<td>M2-1 was met and reported at Q1</td>
</tr>
<tr>
<td>Fabrication and electrochemical performance evaluation of single-cell SOEC</td>
<td>Milestone</td>
<td>M3-1</td>
<td>First selected proton conducting electrolyte synthesized with a density of &gt;90% and a proton conductivity of at least 0.01 S/cm at 700 °C</td>
<td>2</td>
<td>Milestone M3-1 was meet and reported at Q2 (Dense%: &gt;95% at 1350°C, conductivity &gt;0.04 at 700°C)</td>
</tr>
<tr>
<td>Characterization of selected electrolyte and electrode materials</td>
<td>Milestone</td>
<td>M4-1</td>
<td>Selected H-SOEC electrolyte and electrode materials electrolysis performance is measured and is relatively stable (&lt;10 mV/1000 h) for 50-hour test in real-world electrolyzer operating conditions.</td>
<td>3</td>
<td>On going</td>
</tr>
<tr>
<td>Go/No-Go Decision point</td>
<td>GNG-BP1</td>
<td></td>
<td>Developed proton-conducting electrolyte has a low sintering temperature (&lt;1450 °C) and a proton conductivity of at least 0.01 S.cm⁻¹ at 650 °C, a thickness of &lt;25 μm, and a density of &gt;90%. Developed electrolyte/electrode materials provides stable electrolysis performance and polarization for at least 50 hours showing initial performance of at least 1 A/cm² at ≤1.4 V at a temperature of ≤700 °C</td>
<td>4</td>
<td>On going</td>
</tr>
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</table>
Synthesis of BZY/BZCY-Yb by Sol-gel method

20-gram batch synthesis of BZY and BZCY-Yb proton-conducting materials has been validated using Sol-gel method.
The conductivity of dense BZCY-Yb (0.04 s/cm) and BZY (0.01 s/cm) electrolyte meets with the target of Milestone 3-1 (0.01 s/cm at 700°C).
Lower Temperature Sintering of BZY Electrolyte

Dense BZY/BZCY-Yb electrolyte has been fabricated using isostatic pressing and reactive sintering methods at low temperature (<1450˚C) with sintering aids (ZnO, CuO, and Pr₂O₃).

BZY, BZCY-Yb pellet by isostatic pressing (1.6 cm diameter)

Dense BZY and BZCY-Yb electrolyte (~1.3 cm diameter)

Sintering BZY/BZCY-Yb at different gases/PO2
Effects of Sintering Aids and Temperature

1250°C, 1% ZnO

1300°C, 1% ZnO

1350°C, 1% ZnO

Sintered for 6 Hrs. in Oxygen

1350°C, 1% Pr$_2$O$_3$

1350°C, 1% Mn$_2$O$_3$

1350°C, no ZnO

Full densification achieved at 1350°C with ZnO sintering additive
BZCY-Yb sintered at 1350°C

Fractured surface after sintering at 1350°C for 6 Hrs. Samples show full densification and absence of 2nd phase in bulk/ GB (with 1% ZnO additive)

No ZnO peaks are observed.

NiO-BZCY-Yb/ZnO-BZCY-Yb Half Cell
H-SOEC full cells have been fabricated with thin dense electrolyte (15-40 µm). Above SEM images shows a typical Ni-BZCY-Yb‖BZCY-Yb half cell. Ni-BZY‖BZY‖LSCF-BZY cell are being fabricated. Both H-SOEC cells will be tested in Q3 and Q4.
The O-SOEC cell shows stable performance under thermal neutral voltage condition for 100 hours in Cr-free atmosphere. The posttest cell show porous electrode/electrolyte interface (no delamination).
Summary

- 20 gram batch BZY and BZCY-Yb powders have been synthesized using sol-gel method.
- BZY and BZCY-Yb electrolyte discs have been prepared with sintering aids (nano-size ZnO, Mn$_2$O$_3$, and Pr$_2$O$_3$) at sintering temperatures of 1350 and 1450°C in O$_2$.
- The conductivity of sintered BZY and BZCY-Yb, as measured by 4-probe technique, are 0.01 and 0.04 s/cm respectively.
- Ni-BZY‖BZY‖ LSCF-BZY and Ni-BZCY-Yb‖BZCY-Yb‖LSCF-BZCY-Yb full cells have been fabricated with thin dense electrolyte (15-40 µm) and porous electrodes.
- Sintering at 1350°C in O$_2$ with ZnO additive show full densification (>97% density) and absence of 2$^{nd}$ phase in the bulk.
- Technical progress and accomplishments meet the project milestones (M1-1, 2-1, M3-1).
- The overall program goals of the Budget Period 1 Go/No-Go Decision will be achieved.

Proposed Future Work

Phase-I Plan:
• Electrochemical performance evaluation of single-cell H-SOECs
• Stability tests of selected H-SOEC electrolyte and electrode materials for 50-hour in real-world steam electrolyzer operating conditions
• Characterization of electrochemical, electrical, chemical properties of developed proton-conducting electrolyte and electrode materials

Proposed Phase-II Work Plan:
• Initiate computational materials design and optimization for chemically and structurally stable ceramic electrodes and electrolyte.
• Optimize electrolyte and electrode chemistry for densification, conductivity and structural stability.
• Develop and optimize electrode structure for optimum electrocatalytic activity.
• Develop thin film co-processing techniques for the fabrication of electrode-electrolyte composite layers.
• Evaluate and analyze electrochemical performance of H-SOECs under real-world / systems operating conditions to validate the significant improvement in operating current density (>1 A/cm²) using new proton-conducting electrolyte, tailored hydrogen and oxygen electrodes, and optimized cell designs with low ASR (<0.4 Ω/cm²) at 650-750°C.
• Conduct long-term tests at cell and SOEC stack levels to validate the overall project target of: degradation rate <4 mV/1000 h at 1A/cm², electrical efficiency >95%, and cost of Hydrogen production < $2/gge H₂.
• Estimated budget for phase II: $460,250 for year 2 and $477,250 for year 3.
**Project Vision**

Develop innovative, cost effective and efficient proton-conducting solid oxide electrolysis cells (H-SOECs) for large-scale hydrogen production at intermediate temperatures (600-800°C).

**Task 2 (Q1-Q2):** Development of electrolyte densification technique and determination of corresponding ionic conductivities.
- INL provided proton-conducting half-cells and full cells (1.0 cm diameter) for SOEC testing and characterization.
  - The measured conductivity and the thickness (~20 µm) of dense electrolyte meets the project milestones.
- INL will provide large size full cells (1.3 cm or 2.5 cm diameter) and electrode materials for SOEC testing.

**Task 3 (Q3-Q4):** Anode microstructural modification for performance improvement and develop mechanisms for polarization losses.
- UConn-made electrode and electrolyte materials
- Tape cast multi-layer laminated samples will be sintered and tested

**Task 4 (Q3-Q4):** Characterization of selected electrolyte and electrode materials.
- NREL High-Throughput Experimental (HTE) Thin Film Combinatorial Capabilities

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- Full densification achieved <1400°C sintering in air
- Electrical conductivity >.01S/cm obtained below 700°C
- Meets Program Milestones
Sintered Electrolyte at Low Temperatures

BZY sintered at 1450°C for 6 h, 1% ZnO in O₂ atmosphere; Density: 90%

BZCY-Yb sintered at 1350°C for 6 h, 1% ZnO in O₂ atmosphere, Density: 96%
Conductivity Measurement and Densification Studies

- Measurements obtained at UConn and PNNL show that the conductivity of dense BZCY-Yb (0.04 s/cm) and BZY (0.01 s/cm) electrolyte meets with the DOE Target of Milestone 3-1 (0.01 s/cm at 700°C).
- Experiments and characterization performed at UConn and PNNL show full densification at 1350°C after sintering in air. The bulk phase remains free of GB precipitates.
In 100 hour testing of O-SOEC cell in a Cr-free atmosphere, Ewe-time plot shows no observable voltage drop of Ewe. EIS spectra also show no change of Rohm and Rp during the test.