A Highly Efficient and Affordable Hybrid System for Hydrogen and Electricity Production

Junsung Hong: Phillips 66
Meilin Liu: Georgia Tech

DE-FE0031975

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Acknowledgments

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• Project Overview
• Project Objective
• Technical Approach
• Project Progress
  • Electrolyte Development
  • Air Electrode and Catalyst Development
  • Button Cell Performance
  • Powder Synthesis Scale up and Large Cell Fabrication
• Summary and Future Work
• Acknowledgement
Overview

- **Project Title:** A Highly Efficient and Affordable Hybrid System for Hydrogen and Electricity Production
- **Award No.:** DE-FE0031975
- **Project Timeline:** 09/27/2020 – 02/26/2024
- **DOE/NELT Program Manager:** Andrew O'Connell

| Heli Wang (PI) | Junsung Hong | • Powder synthesis |
| David Ingram | Sarah Bushyhead | • Large cell manufacturing |
| Byunghyun Min | Keri Collins | • Stack fabrication and testing |
| Amin Baghalian | | • System design and operation |
| Meilin Liu (Co-PI) | Nick Kane | • Cell materials development |
| Zhijun Liu | Humphrey Lin | • Catalyst development |
| Yucun Zhou | Xueyuel Hu | • Button cell evaluation |
| Jerry Luo | Gyutae Nam | |
| Conor Evans | | |
Phillips 66 SOFC R&D

Company Overview
• Diversified energy manufacturing and logistics company
• Portfolio includes Midstream, Chemicals, Refining, and Marketing & Specialties businesses
• Process, transport, store, and market fuels and products globally
• #29 on the Fortune 500 list

SOFHC Program
• Launched in 2010
• Proprietary high-performing materials
• Cost-effective fabrication methods
• Unique stack designs
• Fully automated control systems
• Full spectrum of cell/stack manufacturing and testing facilities
Fabrication and Testing Facilities

- >10,000 sq. ft. floor space
- 20+ fuel cell and stack test stations
- Fuel (H₂, CH₄, pipeline NG) processing and treatment
- Steam generation and control
- Large load banks and power supplies
- System instrumentation, control and communication
Project Objectives

• To design, fabricate, and demonstrate a robust, highly efficient, and affordable reversible solid oxide cell (rSOC) system based on a proton conducting electrolyte membrane for hydrogen and power generation.

• The 1-kW prototype system will meet the following technical specifications:
  • Operate the system in a real-world environment.
  • $\geq50\%$ electrical efficiency (LHV of H$_2$) at 0.5 A cm$^{-2}$ in fuel cell mode on H$_2$ at 650 °C.
  • $>85\%$ electrical efficiency (LHV of H$_2$) in electrolysis mode at $\leq$ 650 °C.
  • Demonstrate the potential to $<2$/kg hydrogen.
## Technical Approach

<table>
<thead>
<tr>
<th>Major Tasks</th>
<th>Action Plan</th>
</tr>
</thead>
</table>
| **Materials Development** | • Modify composition of state-of-the-art $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.1}\text{Yb}_{0.1}\text{O}_{3-\delta}$ electrolyte  
  • Develop air electrodes with high ORR/OER activities and excellent tolerance to $\text{H}_2\text{O}$ and Cr-poisoning |
| **Cell Fabrication**      | • Scale up powder synthesis to $>1$ kg /day  
  • Fabricate button cells showing higher performance and good durability  
  • Fabricate $10 \text{ cm} \times 10 \text{ cm}$ cells by low cost and scalable methods |
| **Stack Development**     | • CFD assisted stack design  
  • QC for stack components and assembly  
  • Demonstrate high stack performance in both SOFC and SOEC modes |
| **System Demonstration**  | • Design a 1.0 kW autonomous system with cloud-based control and data communication  
  • Evaluate system performance and achieve efficiency, lifetime and cost targets  
  • Techno-economic analysis to demonstrate $2/\text{kg H}_2$ |
## Project Progress

<table>
<thead>
<tr>
<th>Timeline</th>
<th>Milestone (BP1)</th>
<th>% Complete</th>
</tr>
</thead>
<tbody>
<tr>
<td>12/31/2020</td>
<td>Electrolyte conductivity &gt;0.01 S cm(^{-1}) and ionic transference numbers &gt;0.95 at 600 °C.</td>
<td>100%</td>
</tr>
<tr>
<td>12/31/2020</td>
<td>Electrolyte degradation rate &lt;2%/1000 h at 600 °C.</td>
<td>100%</td>
</tr>
<tr>
<td>03/31/2021</td>
<td>Air electrode with catalysts polarization resistance &lt;0.2 Ω cm(^{2}) at 600 °C.</td>
<td>100%</td>
</tr>
<tr>
<td>06/30/2021</td>
<td>Air electrode with catalysts degradation &lt;2%/1000 h at 600 °C under H(_2)O and Cr.</td>
<td>100%</td>
</tr>
<tr>
<td>07/30/2021</td>
<td>Scale up ceramic powder synthesis to &gt; 1.0 kg per day</td>
<td>100%</td>
</tr>
<tr>
<td>09/30/2021</td>
<td>Button cells 1 W cm(^{-2}) at 0.7 V and 600 °C in fuel cell mode, 1.5 A cm(^{-2}) at 1.3 V and 600 °C in electrolysis mode, and a Faradaic efficiency of 95%.</td>
<td>100%</td>
</tr>
<tr>
<td>03/31/2022</td>
<td>Button cells degradation &lt;2%/1000 h at ≤ 650 °C</td>
<td>100%</td>
</tr>
</tbody>
</table>
| 06/30/2022   | Go/No-Go Decision Point  
10x10 cm\(^{2}\) cells with ≥70% roundtrip efficiency at 0.5 A cm\(^{-2}\), <2% per 500 h at ≤ 650 °C. | 100%       |
Accomplishments to Date

✓ **Electrolyte**: Complete electrolyte development with conductivity $>0.01 \text{ S cm}^{-1}$ in Ar (3%H$_2$O), ionic transference numbers $>0.95$ and degradation rate $<2\%$ per 1000 h in cell operating conditions at 600 ºC

✓ **Air Electrode with catalyst**: Complete air electrode with catalyst development with a polarization resistance of $<0.2 \Omega \text{ cm}^2$ at 600 ºC in Air (3% H$_2$O) and a degradation rate of $<2\%$ per 1000 h at 600 ºC under the presence of H$_2$O and Cr contaminants for over 500 h

✓ **Button cell Performance**:
  • Fabricated high-performance button cells with the power density of $1.2 \text{ W cm}^{-2}$ at 0.7 V and 600 ºC in fuel cell mode, current density of $2.0 \text{ A cm}^{-2}$ at 1.3 V and 600 ºC in electrolysis mode, and a Faradaic efficiency of over 95%
  • Completed durability evaluation of the button cell for at least 1000 h with a degradation rate of $<2\%$ per 1000 h at $\leq$ 650 ºC

✓ **Powder synthesis**: Established in-house powder synthesis capability $>1500 \text{ g/day}$

✓ **Large cell fabrication**: Fabricated flat, robust 10 cm×10 cm cells, which demonstrated 77% roundtrip electrical efficiency and a degradation rate of 1.3%/1000 h
Electrolyte Development

- $\text{BaHf}_{0.1}\text{Ce}_{0.7}\text{R}_{0.2}\text{O}_{3.5}$ (BHCR172, R = Yb, Er, Y, Gd, Sm)

- The ordered dopant structures could be beneficial to proton conductivity
  
  - The SAED pattern of BHCYb172 is characteristic of a typical cubic perovskite lattice
  
  - As the ionic radius of R increases, the peak positions shift to lower angles
Conductivity and Ionic Transference Number

- Trivalent dopants with an intermediate ionic radius can offer balanced lattice distortion and free volume, giving the highest conductivity.

- Y- and Yb-doped electrolytes show desirable conductivity of ~0.02 S cm⁻¹ and ionic transference number of >0.97 at 600 °C, making them good candidates for ReSOCs.
Chemical Stability Against CO₂ and H₂O

- **BHCYb172** showed high chemical stability against CO₂ and H₂O
  - Ba(Hf,Ce)O₃-based proton conductors are more stable in high concentration of H₂O than CO₂
  - Yb-doping positively affects the stability of the electrolyte materials

Understanding of the Enhanced Chemical Stability

• **Gibbs free energy (ΔG)** of the reaction between BHCYb172 and H₂O is higher than that of the Er- and Y-doped electrolytes.

• The superiority of Yb-doping in **suppressing surface CO₂ and H₂O adsorption**.

Chemical Compatibility with NiO

- Larger dopants tend to react with NiO at 1400 °C, forming BaR₂NiO₅ secondary phase.

- BHCYb172 demonstrates excellent chemical compatibility with NiO.
At 600 °C, SOFC: $PPD=1.21 \ W \ cm^{-2}$; SOEC: 1.3 V, current density $= 2.0 \ A \ cm^{-2}$

Roundtrip electric efficiencies of 84% and 79% at 650 and 600 °C, respectively

A low degradation rate of 0.8% /1000 h
Catalyst Development

- Catalyst was developed for PrBa_{0.8}Ca_{0.2}Co_{2}O_{5+\delta} (PBCC) air electrode by the solution infiltration process.
Enhanced Activity and Stability

- Catalyst-coated PBCC air electrode shows enhanced activity and stability against $\text{H}_2\text{O}$ and Cr

![Graph showing temperature vs. resistance for coated and PBCC electrodes.](image)

![Graph showing resistance vs. time for bare and coated PBCC electrodes exposed to S430L.](image)
• The peak power density of catalyst-coated PBCC single cell is \(2.02 \text{ W cm}^{-2}\) at 650 °C, an over 35.5% improvement.
Enhanced Cell Performance and Stability

- Catalyst-coated PBCC single cell demonstrates a current density of -3.22 A cm\(^{-2}\) at 650 °C (22.4% improvement) and -1.99 A cm\(^{-2}\) at 600 °C (22.3% improvement).
- In SOEC mode, the single cell demonstrates good stability.
Flexural Strength of Proton Conducting Cells

![Image: A photograph of a sample with lines indicating stress and strain.]

![Image: A graph showing stress (σ) vs. strain (ε) for different cells.]

- **YZS cell electrolyte up**: Avg - 70 MPa
- **BHCYb cell electrolyte up**: Avg - 75 MPa
- **BHCYb cell electrolyte down**: Avg - 82 MPa

**BHCYb cells meet the targeted 75 MPa value!**
10cm x 10cm Cells

4-inch cell

H₂ (3% H₂O) / Air (20% H₂O)
Effect of Applied Load on the Cell

- With increasing applied load on the cell, the cell performance was enhanced.
- The reduced $R_\Omega$ and LF $R_p$ indicate the improvement of (i) the contact between the interconnect and electrodes and (ii) sealing under the applied load.

650 °C
$\text{H}_2(10\%\text{H}_2\text{O}) / \text{Air (25}\%\text{H}_2\text{O})$

$R_\Omega$ decrease by contact

$\text{LF } R_p$ decrease

Higher Applied Load $\rightarrow$ Higher Performance
Effect of Steam Concentration

- With increasing H_2O concentration (in H_2), the SOEC mode performance was improved.
- The presence of steam further hydrates the electrolyte, improving the ionic conductivity and kinetics.
The 1100-h EC mode operation of BHCYYb cells shows very small degradation (1.4%ΔV/1kh), demonstrating high durability and achieving the targeted specification (<2% per 500 h)!
Long-Term Testing of 10cm x 10cm Cells - Cell #2

The 1100-h EC mode operation of BHCYYb cells shows very small degradation (1.2%ΔV/1kh), demonstrating high durability and achieving the targeted specification (<2% per 500 h)!
Developed BaHf$_{0.1}$Ce$_{0.7}$Yb$_{0.2}$O$_3$ electrolyte with high conductivity and stability

Developed highly active and stable catalyst-coated PBCC air electrode

Developed high-performance and durable reversible cells based on proton conductors

- Peak power density of 1.2 W cm$^{-2}$ and electrolysis current density of 2 A cm$^{-2}$ at 1.3 V and 600 °C
- 1000 h operation at 600 °C with a low degradation rate of ~1% per 1,000 h

Fabricated 10 cm × 10 cm cells

- Roundtrip electrical efficiency of 77% at 0.5A/cm$^2$, 650 °C
- 1000 h operation at 650 °C with a low degradation rate of ~1.3% per 1,000 h
## Proposed Future Work

<table>
<thead>
<tr>
<th>Date</th>
<th>Milestone (BP2)</th>
<th>% Complete</th>
</tr>
</thead>
<tbody>
<tr>
<td>02/2023</td>
<td>Complete the stack design and components development</td>
<td>60%</td>
</tr>
<tr>
<td>05/2023</td>
<td>Complete the fabrication and evaluation of up to 3 short stacks (&lt; 0.25 kW).</td>
<td>30%</td>
</tr>
<tr>
<td>08/2023</td>
<td><strong>Complete 1 kW stack testing</strong> with ≥55% fuel cell at 0.5 A cm⁻², and &gt;90% electrolysis at ≤ 650 °C, &lt;2% per 1000 h degradation.</td>
<td>Not started</td>
</tr>
<tr>
<td>10/2023</td>
<td>Complete the system design and integration, complete a thermodynamic analysis.</td>
<td>Not started</td>
</tr>
<tr>
<td>12/2023</td>
<td>Complete evaluation of the 250 W system with ≥50% fuel cell efficiency at 0.5 A cm⁻², and &gt;85% electrical efficiency at ≤ 650 °C.</td>
<td>Not started</td>
</tr>
<tr>
<td>02/2024</td>
<td><strong>Demonstrate the potential to produce hydrogen at a cost of $2 per kilogram</strong> based on a cost of electricity of $30 per MWhr.</td>
<td>Not started</td>
</tr>
<tr>
<td>02/2024</td>
<td>Complete the establishment of a thermodynamic model to analyze the energy balance and global efficiency of the system.</td>
<td>Not started</td>
</tr>
<tr>
<td>02/2024</td>
<td>Evaluate 1.0 kW rSOC system performance at the relevant operating conditions and model: efficiency, durability, degradation, life of electrolysis cell.</td>
<td>Not started</td>
</tr>
<tr>
<td>02/2024</td>
<td><strong>Complete a techno-economic analysis (TEA)</strong> based on test data on the rSOC system or components for the defined application</td>
<td>Not started</td>
</tr>
</tbody>
</table>
Thank you

DOE/NETL  Andrew O'Connell
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Conor Evans

Q&A