# HydroGEN Seedling: Proton-Conducting Solid Oxide Electrolysis Cells for Large-Scale Hydrogen Production at Intermediate Temperatures

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## Overall Objectives

- Develop proton-conducting solid oxide electrolysis cells (SOEC) and stacks for large-scale hydrogen production at intermediate temperatures.
- Achieve an operating current density (>1 A/cm$^2$) with the performance degradation rate not to exceed the DOE performance metric (<4 mV/1,000 h).
- Demonstrate stable intermediate-temperature (600°–800°C) operation with low area-specific resistance (ASR) through bulk, interface, and surface optimizations
- Meet hydrogen production cost goal (<$2/kg $H_2$) by the use of non-noble and non-strategic cell and stack component materials.

## Fiscal Year (FY) 2018 Objectives

- Select structurally stable electrolyte and electrode materials by density functional theory, first principles, and thermochemical calculations under proton-conducting SOEC operating conditions.
- Develop electrolyte formulations capable of densification (>90%) below 1,400°C in oxidizing atmospheres and demonstrate high conductivity (>0.01 Ω.cm$^{-1}$ at 650°C) and bulk structural and chemical uniformity.
- Fabricate single SOECs using tape cast and other thin-film processing to achieve thin electrolyte (<25 µm) for low ASR.
- Demonstrate electrochemical performance of at least 1 A/cm$^2$ at ≤1.4 V at a temperature of ≤700°C and a relatively stable electrolysis performance (<10 mV/1,000 h) for 50-hour test in real-world electrolyzer operating conditions.

## Technical Barriers

This project addresses the following technical barriers (for high temperature steam electrolysis) from the Hydrogen Production section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan[1]:

- Complex processing and fabrication techniques
- High sintering temperature for proton-conducting electrolyte densification (>1,400 °C)
- Decrease in conductivity during processing and operation
- High-temperature gas sealing and operation with thermal cycling
- Chemical and structural instability in presence of contaminants such as Cr and Si.

## Technical Targets

This project is developing proton-conducting electrolysis cells for the large-scale hydrogen production at intermediate temperature. Insights gained from these studies will be applied toward the design and synthesis of proton-conducting

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[1] https://www.energy.gov/eere/fuelcells/downloads/fuel-cell-technologies-office-multi-year-research-development-and-22

electrolyte materials that meet the DOE hydrogen production targets shown in Table 1.

## FY 2018 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 has 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 of BZCY-Yb at 1,350°C in oxygen shows the densification (>97% density), which is 100°C lower than the state of the art (1,450°C). The conductivity of sintered BZY and BZCY-Yb measured by four-probe technique are ~0.01 and 0.04 S/cm, respectively.
- Proton-conducting SOEC full cells with low ASR have been fabricated using thin dense electrolyte (15–20 µm) and porous electrodes using the Idaho National Laboratory (INL) node.
- Button-cell testing of steam electrolysis in the temperature range of 600°–800°C has been conducted. Electrochemical performance met the program milestones (1.4 V at 1 A/cm$^2$ and 50-hour performance stability).
- Technical progress and accomplishments met the program milestones (Milestone 1-1, 2-1, 3-1, and 4-1, and Budget Period 1 go/no-go).
- The overall program goals for Budget Period 1 and the go/no-go decision have been achieved.

Table 1. Progress Toward Meeting Technical Targets for Intermediate-Temperature Steam Electrolysis

| Characteristic | Units | State of the Art | EERE Proposed Targets | Project Status |
|---|---|---|---|---|
| Electrolyte conductivity | S/cm @ 650°C | ~$10^{-3}$ | ≥0.01 | 0.03 |
| Sintering temperature | °C | 1,450 | 1,350 | 1,350 |
| Electrolyte densification | % | | >90 | ~97 |
| Electrolyte thickness | µm | >25 | <25 | ~15-20 |
| Current density | A/cm$^2$ @ 1.4 V, 700°C | 0.6 | >1.0 | 1.3 |
| Stability | mV/50 hour | | <0.2 | ~0 |

## INTRODUCTION

Proton-conducting solid oxide electrolysis cells (H-SOECs) offer economic and operational advantages for hydrogen production over the state-of-the-art oxygen-ion-conducting SOECs (O-SOECs). The objective of this project is to develop, fabricate, and test SOECs consisting of proton-conducting electrolyte, high-performance electrode, and tailored gas-solid and solid-solid interfaces. Strategies for the mitigation of cell/stack/system degradation resulting from interface separation, densification, and coarsening, and Cr-assisted poisoning are being develop and incorporated. During the last year, the project team has made progress in lowering the sintering temperature of BZCY-Yb electrolyte to 1,350°C and reducing the operating temperature of H-SOECs to 650°C without compromising the hydrogen production rate. Pure hydrogen can be directly produced by H-SOECs at a current density of 1.2 A/cm$^2$ at a temperature of 650°C with an applied voltage of 1.4 V. More work is still needed to improve durability and reliability, develop degradation mechanisms by in operando experiments and materials characterization, and optimize SOEC cell component materials and design using computational tools to meet performance, life, and cost targets.

## APPROACH

Our approach for H-SOEC development leading to large-scale manufacturing and commercialization will rely on utilizing the Energy Materials Network (EMN) and core experimental and computational capabilities at the National Renewable Energy Laboratory (NREL), INL, and Pacific Northwest National Laboratory (PNNL).

- Materials and processes: Innovation in materials and processing techniques are employed to develop electrolyte formulations capable of densification (96%–98% density) below 1,400 °C in oxidizing atmospheres, meet the 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) have been sintered and electrically tested. The process is being optimized to achieve target ASR and current density to meet the overall project goals (1 A/cm$^2$ at 1.4 V, 700°C).

- Computational analysis: Electrolyte and electrode materials composition are optimized for densification, proton conductivity, and structural stability. Select electrode and electrolyte materials have been 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.

The INL-UConn collaboration spanned over the topics for the development of dense electrolyte and performance improvement of the anode. UConn utilized the INL node “Advanced Materials for Water Electrolysis at Elevated Temperatures.” Technical discussions have been held with Dr. Ding (INL) with focus on materials selection, processing techniques, and electrochemical performance evaluation. UConn also utilized the NERL node “High-Throughput Experimental Thin Film Combinatorial Capabilities.” Technical discussion held with Dr. Andriy Zakutayev (NREL) has identified the scope of work for the development of electrolyte chemistry and validation through high-temperature experiments.

## RESULTS

During the first year (FY 2018), proton-conducting electrolyte and electrode materials were selected, synthesized, and utilized for the fabrication of SOECs. We have validated a sol-gel process at 20-gram batch scale for BZY and BZCY-Yb proton-conducting powders.

Sintering of BZY and BZCY-Yb electrolyte discs was conducted in oxygen environment at the temperature range of 1,250°–1,450°C. The scanning electron microscopy and focused ion beam transmission electron microscopy images show that the dense electrolyte (densification >95%) was achieved using reactive sintering aids (such as ZnO nanopowder) at 100°C lower than the state of the art (1,450°C). The conductivity of dense electrolyte discs was measured in dry air and humidified air (3% $H_2O$-air) using the four-probe method (Figure 1). BZCY-Yb prepared by the sol-gel method has shown higher proton conductivity than that prepared by the solid-state method.

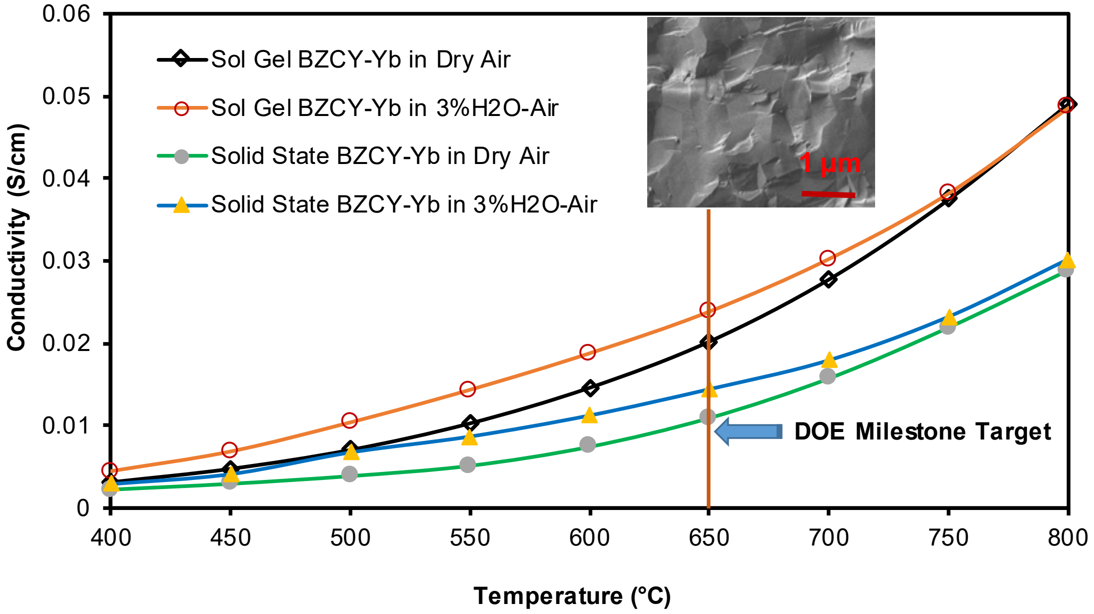

Figure 1. Conductivity of BZCY-Yb discs measured by the four-probe method at temperature range of 400°–800°C in dry and humidified air. All BZCY-Yb discs were sintered at 1,350°C in oxygen. Two types of BZCY-Yb powders were synthesized by sol-gel and solid-state methods, respectively.

H-SOEC full cells with low ASR have been fabricated using thin dense electrolyte (15–40 µm) and porous PBSCF electrodes using the INL node. Button-cell testing of steam electrolysis in the temperature range of 600°–700°C has been conducted using homemade reactors (Figure 2).

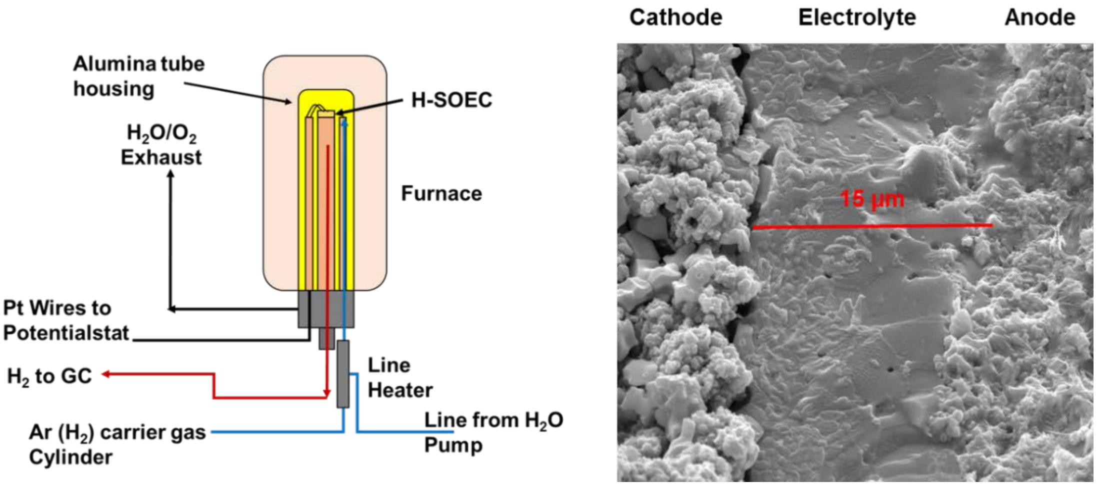

Figure 2. Steam electrolysis setup for the testing of as-fabricated H-SOEC cells with thin BZCY-Yb electrolyte. The anode and cathode were partially shown in the scanning electron microscopy image.

Selected H-SOEC electrolyte and electrode materials' electrolysis performance has been measured and been demonstrated to be relatively stable (<10 mV/1,000 h) for 50-hour tests in real-world electrolyzer operating conditions, meeting Milestone 4-1 (Figure 3). Our recent effort is to improve the current density by lowering ASR and increasing steam concentration and flow rates. Selected H-SOECs have demonstrated 1.20 and 1.32 A/cm$^2$ at ≤1.4 V at a temperature of 650°C and 700°C in steam electrolysis, meeting the Budget Period 1 go/no-go decision point (Figure 4).

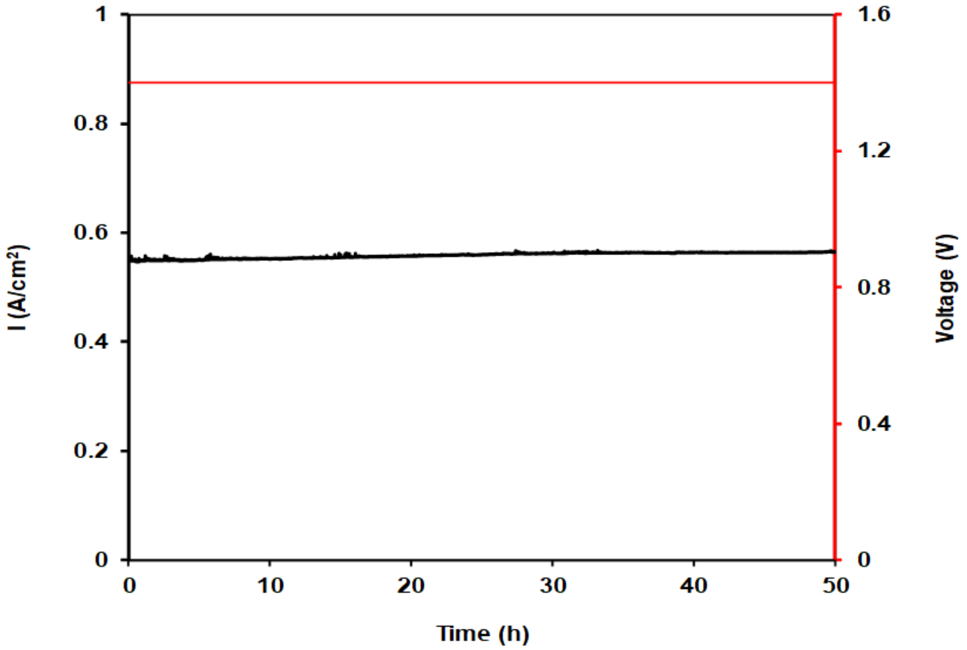

Figure 3. I-t and E-t curve of an H-SOEC cell at 700°C in 50-hour steam electrolysis test

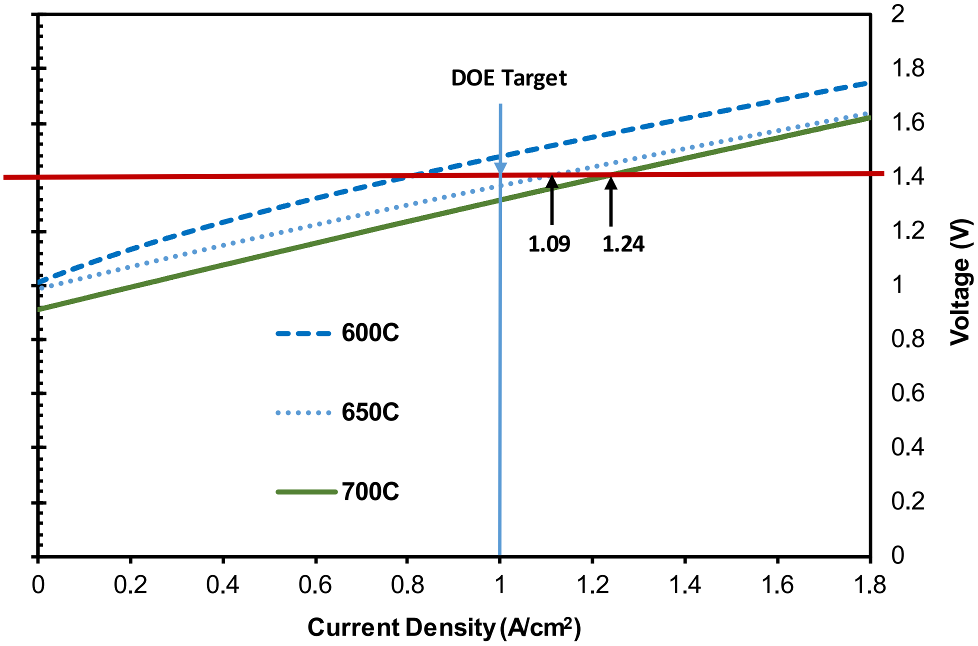

Figure 4. V-I curves of the H-SOEC in steam electrolysis at temperatures of 600°C, 650°C, and 700°C

## CONCLUSIONS AND UPCOMING ACTIVITIES

Our project team has validated a sol-gel process for the synthesis of proton-conducting electrolyte materials at 20-gram scale. Dense BZCY-Yb disc (density ~97%) was obtained at a low sintering temperature (~1,350°C) for 6 hours using ZnO nanopowder as sintering aids and the BZCY-Yb's conductivity measured in 3% $H_2O$-air by the four-probe method reaches 0.024 S/cm at 650°C. Fabricated Ni-BZCY-Yb ‖BZCY-Yb (1% ZnO)‖ PBSCF cells with a thin electrolyte (<25 µm) have demonstrated stable electrolysis performance and polarization for 50 hours and the cell current density reaches 1.20 A/cm$^2$ and 1.32 A/cm$^2$ at ≤1.4 V at a temperature of and 650°C and 700°C, respectively. Our technical progress and accomplishments meet the program milestones, and the overall program goals of Budget Period 1 and the go/no-go decision have been achieved.

Large-scale manufacturing and commercialization will rely on utilizing the EMN and core experimental and computational capabilities at NREL, INL, and PNNL. This project uses INL tape-casting facilities to fabricate full cells with porous electrodes and thin electrolyte and uses NREL high-throughput experimental thin film combinatorial capabilities to optimize thin electrolyte compositions. Long-term tests at cell and SOEC stack levels will be conducted to validate the overall project target of degradation rate <4 mV/1,000 h at 1A/cm$^2$, electrical efficiency >95%, and cost of hydrogen production <$2/gasoline gallon equivalent hydrogen.

## FY 2018 PUBLICATIONS/PRESENTATIONS

1. Boxun Hu, Ashish N. Aphale, Michael Reisert, Seraphim Belko, Olga A. Marina, Jeffry Stevenson, and Prabhakar Singh, "Solid Oxide Electrolysis for Hydrogen Production: From Oxygen Ion to Proton Conducting Cells," 233rd ECS Meeting, Seattle, WA, May 13–17, 2018.
2. Boxun Hu, Michael Reisert, Ashish Aphale, Seraphim Belko, Olga Marina, Jeff Stevenson, Dong Ding, and Prabhakar Singh, "Barium Zirconate Based Electrolyte Densification Using Reactive Sintering Aids," 43rd International Conference and Exposition on Advanced Ceramics and Composites (ICACC 2019), Daytona FL, 2019, accepted.
3. Boxun Hu, Olga A. Marina, Ashish N. Aphale, Dong Ding, Hanping Ding, Andriy Zakutayev, Jeffry Stevenson, and Prabhakar Singh, "Stable Proton-Conducting Solid Oxide Electrolysis Cells for Pure Hydrogen Production at Intermediate Temperatures," 2019 Materials Research Society Spring Symposia on Advanced Water Splitting, April 22–26, 2019, Phoenix, Arizona, submitted.
4. Boxun Hu, Michael Reisert, Ashish Aphale, Seraphim Belko, Olga Marina, Jeff Stevenson, Dong Ding, and Prabhakar Singh, "Hydrogen Production by Intermediate Temperature Steam Electrolysis Using Proton-Conducting Solid Oxide Electrolysis Cells," in preparation.

## REFERENCES

1. "Sintering and Stability Issues of $BaZr_{0.1}Ce_{0.7}Y_{0.1}Yb_{0.1}O_3$ Electrolyte for SOFCs," in *Advances in Solid Oxide Fuel Cells and Electronic Ceramics*, Ed. N.P. Bansal (John Wiley & Sons, 2015): P22–26.