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 (SOECs) 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 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) 2019 Objectives

- Optimize electrolyte formulations and sintering aids capable of densification (>90%) below 1,400°C in oxidizing atmospheres and demonstrate high conductivity (>0.02 Ω.cm^{-1} at 700°C) and bulk structural and chemical uniformity.
- Identify contributions from proton, oxygen ion, and electronic conductivity.
- Fabricate 1-inch SOEC cells using tape cast and other thin-film processing to achieve thin electrolyte (<25 µm) for low ASR.
- Demonstrate the 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 a 200-hour test in real-world electrolyzer operating conditions and establish structural and chemical degradation mechanisms.

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]:

- 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 the presence of high-temperature steam and contaminants such as Cr and Si.

Technical Targets

This project is developing proton-conducting electrolysis cells for large-scale hydrogen production at intermediate temperatures. Insights gained from these studies will be applied toward the design and synthesis of proton-conducting electrolyte materials that meet the following DOE hydrogen production targets in Table 1.

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

FY 2019 Accomplishments

- Synthesized a 50-gram batch of proton-conducting electrolyte (BZY and BZCY-Yb) and electrode materials and successfully demonstrated sol-gel method with quality assurance and repeated experiments.
- Improved total proton conductivity of BZCY-Yb electrolyte using reactive/fugitive sintering aids (nanosized ZnO). The sintering temperature of BZCY-Yb in an oxidizing environment has been lowered to 1,300°C with the densification achieving >97% density. The sintering temperature is 150°C lower than the state of the art (1,450°C).
- Fabricated 1-inch H-SOEC full cells with thin dense electrolyte (15–20 µm) and porous electrodes using Idaho National Laboratory (INL) tape-casting technique.
- Demonstrated 1-inch H-SOEC full cells with a current density of >1.0 A/cm2 @ 1.4 V, low area-specific resistance (0.2 ohm/cm^2, 600°C), and long-term chemical/structural stability (30 hour proven, longer-term in process) in real-world high-temperature steam electrolysis.
- Conducted button-cell testing of steam electrolysis in the temperature range of 600–800°C. Electrochemical performance met the program milestones (1.4 V@1 A/cm^2 and 50-hour performance stability).
- Met program milestones for technical progress and accomplishments (M1-1, 5-1, M6-1).
- Achieved most overall program goals (M4-1 and GNG-BP1) of Budget Period 2 (BP2) and Go/No-Go Decision, with the exception of ongoing long-term stability testing.

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}	≥0.02	0.03
Sintering Temp.	°C	1,450	1,350	1,300
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 a 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 developed and incorporated. During the last year, the project team has made progress in lowering the sintering temperature of the 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 current density of 1.2 A/cm^2 at the 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 National Renewable Energy Laboratory (NREL), Idaho National Laboratory (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 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 area-specific resistance (ASR) and current density to meet the overall project goals (1 A/cm^2 @1.4 V, 700°C).
- Computational analysis: Electrolyte and electrode materials composition is 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.
- Multiscale modeling of H-SOECs will be conducted using NREL node and UConn experimental data, including ionic conductivity as a function of temperature and polarization curves. The modeling results show parametric distributions along the cell area, including current density, species, and temperature for scale-up of the cell/stacks.

The INL-University of Connecticut (UConn) collaboration spanned over the topics for the development of dense electrolyte and performance improvement of the anode. UConn utilized the INL node of "Advanced Materials for Water Electrolysis at Elevated Temperatures." Technical discussions have been held with Dr. Ding (INL) with a focus on materials selection, processing techniques, and electrochemical performance evaluation. UConn also utilized the NREL nodes of "High-Throughput Experimental Thin Film Combinatorial Capabilities," "Multi-Scale Thermochemical and Electrochemical Modeling for Material Scale-Up," "Component and System Design," and "Techno-Economic Analysis of Hydrogen Production." A 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. Further technical discussion with Dr. Zhen Ma led to the development of the H-SOEC electrochemical model based on UConn experimental data.

RESULTS

During the first phase of the program (FY 2017), we confirmed that BZCY-Yb prepared using nano-sized fugitive sintering aid and by the sol-gel method, shows uniform bulk structure and higher proton conductivity than that prepared by solid-state sintering method. During the second year (FY 2018), our effort for the synthesis focused on scale-up of the sol-gel process to obtain 50-gram batches of proton-conducting electrolyte and electrode materials and used these materials for the fabrication of solid oxide electrolysis cells. Compositions and formulations have been selected using analytical characterization methods.

Composition and sintering aids have been investigated for the sintering of BZY and BZCY-Yb electrolyte discs in an oxygen environment in the temperature range of 1,250–1,400°C. The SEM and FIB-TEM images (Figure 1) show that a large-sized dense electrolyte (density >95%) was achieved using reactive sintering aids (such as ZnO nanopowder) at 150°C lower than the state of the art (1,450°C). Higher total proton conductivity (>0.06 s/cm, 700°C) of dense electrolyte discs was obtained by the 4-probe measurement method in dry air, humidified air (3% H_2O-air), and 4% H_2/N_2 (Figure 2), meeting with the Milestone M5-1. More testing to identify contributions from proton, oxygen ion, and electronics are in progress.

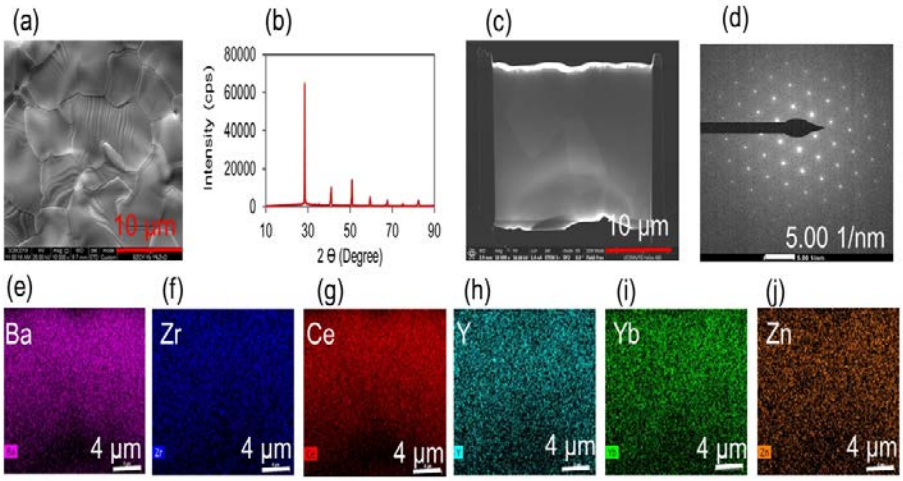

Figure 1. Dense BZCY-Yb electrolyte sintered at 1,300°C in oxygen with clean polycrystalline grains. (a) A SEM image shows large clean grains; (b) the XRD pattern shows single perovskite phase; (c) the FIB-TEM image show dense electrolyte and no secondary phase; (d) select area TEM XRD shows single perovskite structure; and (e-j) select area TEM-EDS maps show uniform elemental distributions of Ba, Zr, Ce, Y, Yb, and Zn in entire select area.

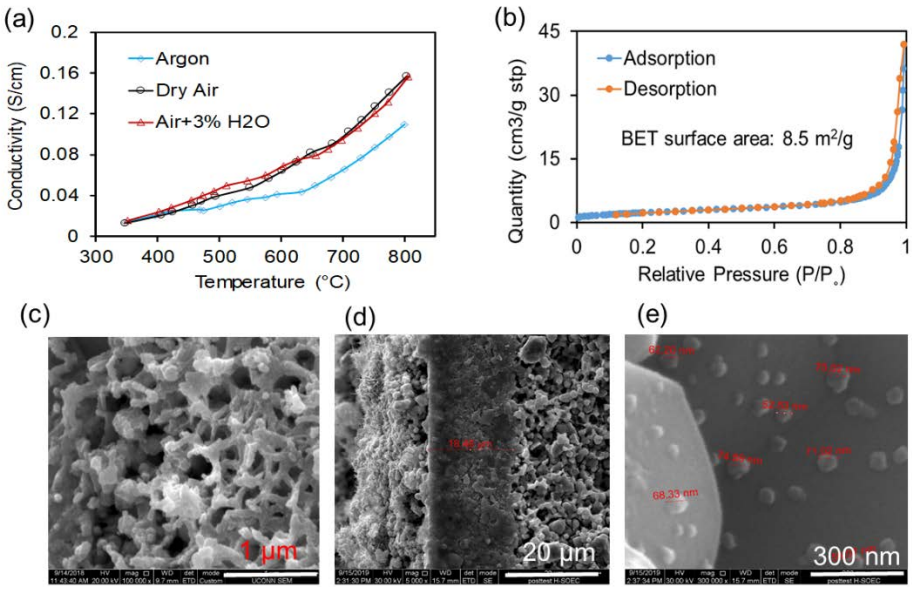

Figure 2. Conductivity, BET surface area, and SEM images of BZCYY-Yb and 1-inch H-SOEC cells. (a) Conductivity of BZCY-Yb disc (sintered at 1,350°C) measured by the four-probe method at temperature range of 400°–800°C in different gas environment; (b) BET surface area of BZCY-Yb powder calcined at 1,350°C without ZnO; (c) a SEM image of porous oxygen electrode; (d) an H-SOEC cell with 19 µm thick BZCY-Yb electrolyte; and (e) Ni nanoparticles in Ni-BZCY-Yb cathode.

The physical properties of the electrolyte and electrode materials (BET surface area, thermal expansion, and mechanical strength) have been measured. BZCY-Yb electrolyte has shown chemical stability in in-situ high-temperature (25–900°C) X-ray diffraction (XRD) experiments in a reduced environment (H_2/Ar). Exposure to five thermal cycles shows that OCV sealing is relatively stable under high-temperature steam electrolysis exposure conditions (Figure 3). Oxygen electrodes (PBSCF, PBLC, and PNC) have been tested in a steam concentration range of 10–75%. Multiscale modeling of H-SOECs has demonstrated temperature distribution across the H-SOECs under various applied voltages (Figure 4). The degradation mechanisms have been developed using operando analysis with electrochemical impedance spectroscopy and post-characterization (SEM, XRD, and FIB-TEM), meeting the Milestone M6-1.

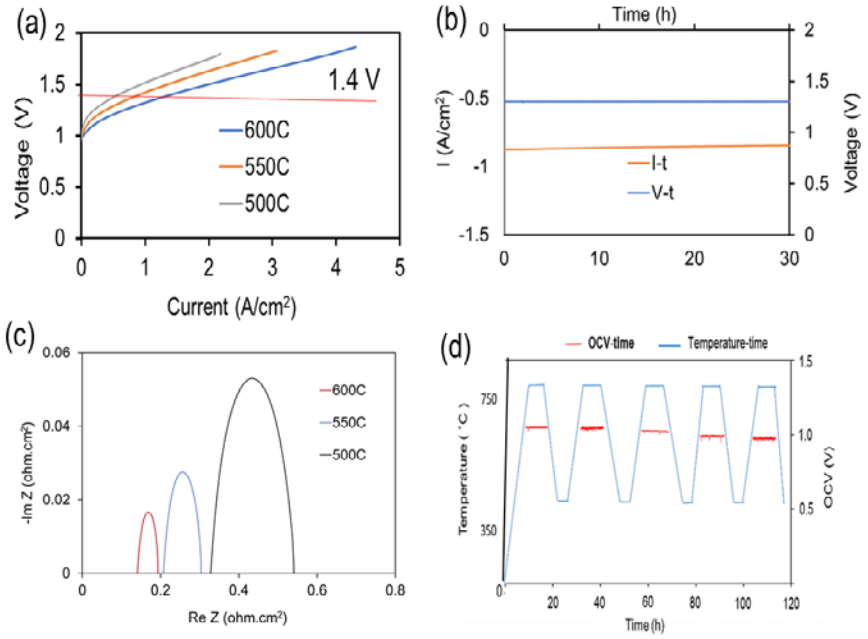

Figure 3. Electrochemical performance and stability of as-fabricated 1-inch H-SOEC cells with thin BZCY-Yb electrolyte. (a) I-V curves of typical 1-inch H-SOECs at the temperature range of 500°–600°C; (b) 30 hour I-t data when applied a constant voltage of 1.4 V (long-term test is in process); (c) EIS spectra of H-SOECs; and (d) five thermal cycles at operating temperature range of 300°–750°C.

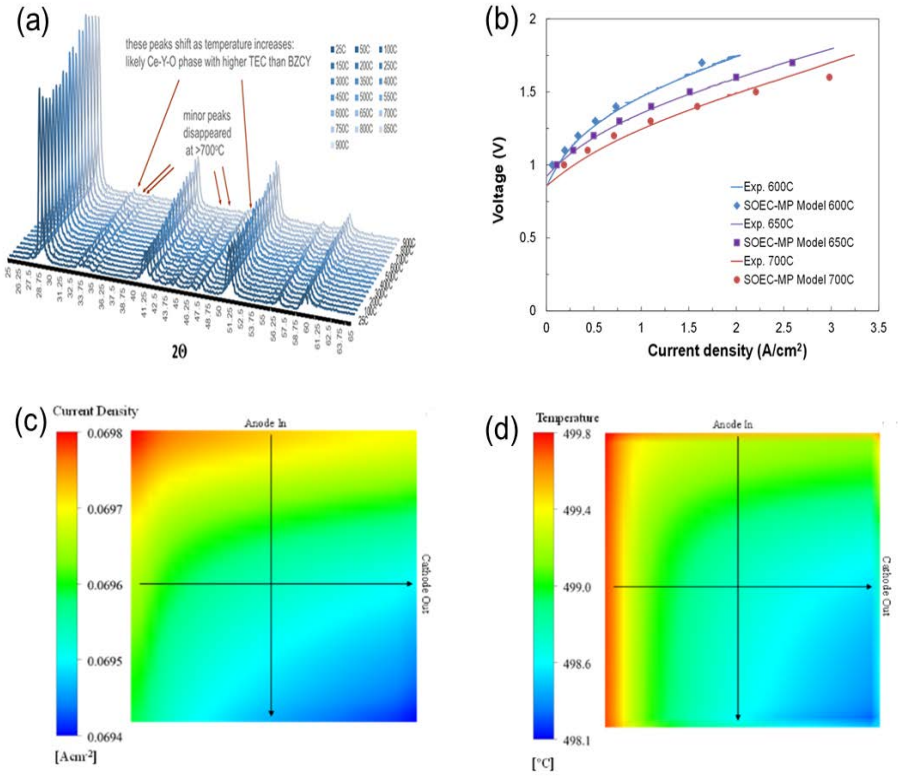

Figure 4. In situ high-temperature XRD patterns of BZCY-Yb and modelling data of H-SEOCs. (a) In situ XRD patterns of BZCY-Yb electrolyte in reduced H_2/Ar atmosphere at temperature range of 25°–900°C; (b) H-SOEC-Multiphysics (MP) Model of UConn testing data (from PNNL); and (c and d) modeling of current and temperature profile using computation fluid dynamics (from NREL).

One-inch diameter H-SOEC full cells with thin dense electrolyte (15–40 μm), porous oxygen electrodes have been fabricated using a tape-casting method (using INL node). Steam electrolysis testing of these H-SOECs in the temperature range of 550–700°C has been conducted in our laboratory using reactors designed at UConn. Selected H-SOEC cell performance has been measured and demonstrated to be relatively stable (<10 mV/1,000 h) for a 30-hour test in real-world electrolyzer operating conditions. Area-specific resistance (0.2 $\Omega.cm^2$) and current density (1.2 A/cm^2) of the 1-inch diameter cells have met with Go/No-Go decision point.

Our recent effort consists of improving the stability of H-SOECs in high concentrations of steam by optimizing oxygen electrode and proton-conducting electrolyte and developing long term degradation mechanisms of electrode and electrolyte materials. The current measurement of the transference numbers to identify proton, oxygen ion, and electronic contributions from BZCY-Yb and BZY will help in understanding the proton, oxygen ion, and electron transfer in these electrolysis cells and explain observed experimental phenomena. Through the selection of high proton transfer electrolyte at optimal operating temperatures, high energy efficiency, and high Faradic efficiency will be achieved to meet with the BP2 Go/No-Go decision point and hydrogen production cost goal (<\$2/kg H_2).

CONCLUSIONS AND UPCOMING ACTIVITIES

Our project team has scaled up the sol-gel process for the synthesis of proton-conducting electrolyte materials at 50-gram scale. With the addition of only 1wt % of nanosized sintering aid, dense BZCY-Yb discs (single perovskite phase, large clean grains, density ~97%) have been obtained at a lower sintering temperature (~1300°C, 5 hours). The BZCY-Yb's conductivity, measured in 3% H_2O-air by the four-probe method, reached 0.08 $S.cm^{-1}$ at 650°C. Fabricated 1-inch diameter H-SOEC cells with a thin electrolyte (<25 μm) have demonstrated stable electrolysis performance and polarization losses for 30 hours and the cell current density reached 0.8 A/cm^2 and 1.2 A/cm^2 at ≤1.4 V at a temperature of and 550°C and 650°C, respectively. Our technical progress and accomplishments meet the program milestones, and the overall program goals of the Budget Period-2 (except long-term 200-hour test, which is ongoing) and Go/No-Go Decision will be achieved.

Large-scale manufacturing and commercialization will rely on utilizing EMN Network and core experimental and computational capabilities at NREL, INL, and PNNL. This project uses INL tape-casting facilities to fabricate full cells with thin electrolyte and porous electrodes and also uses NREL high-throughput experimental thin-film combinatorial capabilities to optimize electrolyte compositions. During hase 3, a 200-gram batch proton-conducting electrolyte with high conductivity will be synthesized for 2-inch diameter H-SOECs. By utilizing stable electrodes in high steam concentrations, long-term tests (>500 hour) at cell and SOEC stack levels (3-cells) will be conducted to validate the overall project target of degradation rate <4 mV/1000 h at $1A/cm^2$, electrical efficiency >95%, and cost of hydrogen production <\$2/gasoline gallon equivalent (gge) hydrogen.

FY 2019 PUBLICATIONS/PRESENTATIONS

1. B. Hu, Z. Ma, P. Singh, "Experimental Testing and Modeling of Reversible Proton-conducting Solid Oxide Electrolyzers for Large-scale Hydrogen Production and Renewable Energy Storage," accepted, to be submitted to Frontiers in Energy Research.
2. H. Ding, D. Ding, B. Hu, P. Singh, et al. "Self-Sustainable Protonic Ceramic Electrochemical Cells Using A Triple-Phase Conducting Electrode for Hydrogen and Power Production," submitted to Nature Communication.
3. B. Hu, M. Reisert, A. Aphale, S. Belko, O. Marina, J. Stevenson, D. Ding , P.Singh, "Hydrogen Production by intermediate temperature steam electrolysis using Proton-conducting Solid Oxide Electrolysis Cells Sintered at Low Temperatures with nanosized Sintering Aids," in preparation.

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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, P22-26, 2015.