
HydroGEN Seedling: Thin-Film, Metal-Supported High-Performance and Durable Proton-Solid Oxide Electrolyzer Cell

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Overall Objectives

- Demonstrate a thin-film, high-efficiency, and durable metal-supported solid oxide electrolysis cell (SOEC) based on proton-conducting electrolyte at targeted operating temperatures of 550–650°C.
- Develop a high-temperature SOEC cell to meet the DOE performance target of 1.0 A/cm² at 1.4 V and a decay rate <0.4%/1,000 h.
- Phase 2 focuses on demonstrating the feasibility of the proposed concept via electrolysis performance demonstration of a metal-supported single cell up to a 25 cm² scale.

Fiscal Year (FY) 2019 Objectives

- Develop a low-cost electrolyte deposition process for a robust hydrogen electrode.

- Evaluate short term durability (50–200 h) of p-SOEC button cells.
- Study the feasibility of co-sintering as an alternative to suspension plasma spray (SPS) for p-SOEC cells.

This project addresses the following technical barriers from the Hydrogen Production section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan¹:

- Capital cost of hydrogen production by water electrolysis system
- Manufacturing
- Operation and maintenance cost for electrolysis.

Technical Targets

- Demonstrate the feasibility of a low-cost deposition process to enable a \$2/kW hydrogen production cost.
- Evaluate SPS and co-sintering technologies for SOEC cell fabrication. These two technologies are capable of attaining desirable chemical composition & phase through feedstock adjustment and/or process optimization, making them ideal for perovskite-based electrode and electrolyte materials of complex composition. By developing the deposition techniques, combined with a metal cell design, the team aims to demonstrate a low-cost process for cell fabrication.
- Demonstrate a durable electrolysis cell for a targeted performance of >0.8 A/cm² at 1.4 V at T ≤650°C, and <1%/1000 h degradation.
- Leverage the capabilities of the Energy Materials Network (EMN) node at INL for material optimization and durability evaluation, to help identify appropriate electrode and electrolyte materials for SOEC metal-cells and to achieve high performance and a low decay rate. In addition to

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

manufacturing cost, another major cost of a SOEC system is the cost of electricity used for the electrolysis. Therefore, to meet the cost target of \$2/kg H₂, it is critical to reducing electricity usage by having excellent cell performance and a low decay rate.

FY 2019 Accomplishments

- Progressed in SPS process development for a porous hydrogen electrode deposition.
- Identified MnO as a promising sintering aid for the co-sintering approach to reduce the co-sintering temperature of the p-SOEC cell in

order to minimize Si contamination and Ba evaporation.

- Demonstrated durability of p-SOEC button cells for steam electrolysis with no measurable phase change of the PrNiCoO₃ (PNC) and BaZrCeYYb (BZCYYb) material, after long term steam exposure and no measurable degradation of performance at 20% steam up to 100h.
- Demonstrated that BZCYYb-based SOEC cells exhibited adequate performance under electrolysis conditions at 20% and 30% steam.

INTRODUCTION

High-temperature water electrolysis can be a highly efficient and cost-competitive process for hydrogen generation when coupled with nuclear power or renewable sources such as wind or solar. The major challenge is the high degradation rate (1–4%/1000 h) of conventional oxygen-ion-conducting solid oxide electrolyzers due to material and interface degradation at high temperatures (typically 800–1100°C). A stable proton-conducting electrolyte, based on doped-BaZrO₃, enables high ionic conductivity [1, 2], and the electrolysis cell can be operated at 550–650°C. The proposed metal-supported cell design is based on mass-producible metal parts; combined with low-cost thin-film cell deposition techniques, i.e., suspension plasma spray. This design should enable the electrolyzer to meet the hydrogen production cost goal of \$2/kg hydrogen.

APPROACH

This project takes an integrated approach of process development, modeling, and material discovery in the development of a low cost and high-performance SOEC cell based on a proton-conducting electrolyte. United Technologies Research Center (UTRC) focuses on addressing a major challenge in fabricating metal-supported cells, developing a cell deposition process to produce fully sintered or porous ceramic coatings rapidly without high-temperature production steps, such as sintering. The work focuses on the development of an SPS process for cell layer deposition. The SPS is a form of plasma spraying where the ceramic feedstock is dispersed in a liquid suspension before being injected into a plasma jet. It is suitable for producing finely structured or nanostructured coatings with thicknesses between 5–100 μm using suspensions of submicron or nanoscale particles. The fabrication process provides a pathway to overcoming the severe limitations of a conventional, sintered ceramic SOEC with respect to (1) production cost; and (2) the lack of cell mechanical robustness arising from the low mechanical strength and low fracture toughness of perovskite materials.

In FY 2019, UTRC continues its collaboration with the National Laboratories through the HydroGEN EMN Consortium in several areas, including: (1) working with Lawrence Berkeley National Laboratory (LBNL) on developing a co-sintering and catalyst infiltration technology for metal-supported cell fabrication as an alternative approach to reactive spray deposition technology and SPS; (2) optimizing electrolyte and electrode materials at Idaho National Laboratory (INL); and (3) developing an electrolyzer cell model at National Renewable Energy Laboratory (NREL) for cell-performance optimization.

RESULTS

p-SOEC Cell Fabrication

During Phase 1, the team successfully demonstrated SPS as a feasible deposition process for the barium yttrium zirconate (BYZ)-based electrolyte without sintering steps. The performance of the hydrogen-electrode supported cell, with an SPS electrolyte layer and INL's steam electrode, demonstrated high electrolysis performance that exceeded the project's Phase 1 target. Building on the successful deposition of the electrolyte by SPS onto a sintered anode cell, the team proceed to apply the SPS electrolyte onto the metal-supported cells. In this case, the hydrogen electrode (NiO + electrolyte) was first deposited onto a porous metal substrate

(Crofer® APU 22 or SS430 porous metals from GKN) using a doctor blade process. The electrode was sintered in H₂/Ar at high temperatures. The thickness of the hydrogen electrode layer was about 20–30 μm. The electrolyte layer was then deposited by SPS. The metal-supported cells showed much lower performance due to erosion of the hydrogen electrode during the SPS deposition for the electrolyte, which also caused defects in the electrolyte layer.

In Phase 2, recognizing the need for a mechanically robust hydrogen-electrode, UTRC aimed to develop an improved process for hydrogen-electrode deposition. The initial electrode deposition process development focused on demonstrating the feasibility of depositing a porous hydrogen-electrode layer by SPS. The process development started with identifying acceptable SPS process parameters by depositing NiO on a non-porous metal substrate. Aqueous slurries of NiO were used as the feedstock. The coating thicknesses were around 20 μm. By adjusting process parameters, different porosities of the coating were achieved. The coating was mostly NiO, with some minor Ni phase indicating some reduction of the NiO during the deposition. Figure 1 shows two cross-section SEM images, one with a dense coating with less than 5% porosity and the other with a porous coating with ≈13% porosity, respectively. The porosity was based on image analysis of two representative high magnitude SEM images per each sample. The results indicated that a thin porous layer could be achieved by SPS deposition. The reduction of the NiO layer to Ni is expected to increase the porosity due to volume changes between the phases. The impact of the addition of BYZ on the porosity of the layer will be examined and if needed, process parameters will be adjusted accordingly.

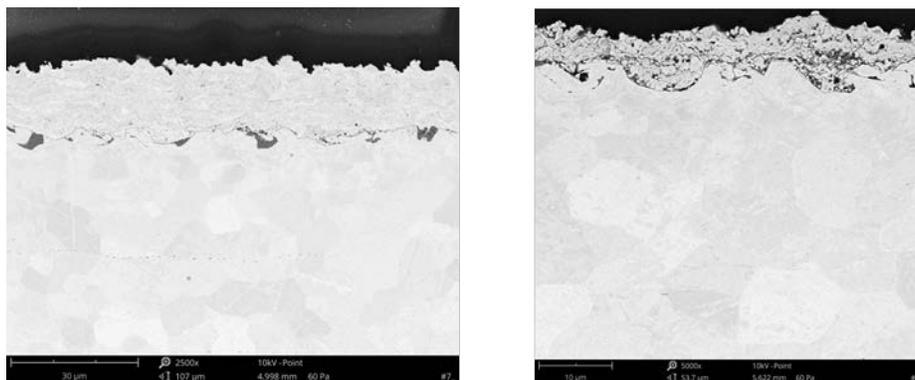


Figure 1: Cross section image of NiO SPS layer on metal substrate, porosity is 4% (left) and ~17% (right).

SPS is a high-throughput process with deposition in minutes and requires no high-temperature production steps, such as sintering. It has a simple process flow and easy automation, which offers the potential to lower the cost of process, equipment, and labor. Preliminary cost analysis indicated that the cell fabrication cost could be as low as \$9/cell for 100 cm² active area/cell, assuming that the electrodes and electrolyte are deposited by an automated SPS process. Figure 2 shows the approximate allocation of the cost. The cost of the stainless steel porous metal support was based on projected production costs from potential suppliers. The cost of the cell layer deposition includes the estimated powder feedstock cost from powder suppliers and the cost of an automated SPS process (both gases and labor cost). It was previously shown that the p-SOEC button cell could achieve >1.0 A/cm² at 1.4 V at 600°C [3]. Assuming a similar performance at the stack level, and \$0.037/kWh electricity [4], the estimated hydrogen production cost is less than \$2/kg H₂.

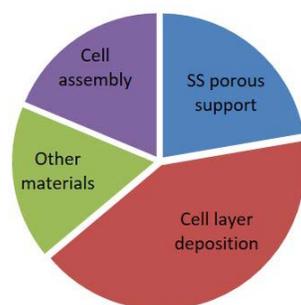


Figure 2. Preliminary cost analysis of a metal cell by SPS deposition process.

Co-sintering was evaluated as an alternative deposition technology to SPS for p-SOEC. The main challenges for the co-sintering fabrication approach include contamination of the electrolyte with Si and Cr from the metal support, incomplete electrolyte sintering, and evaporation of Ba. These issues can be alleviated by reducing the sintering temperature. The addition of sintering aids is a common approach to achieve this goal, but it was determined that conventional sintering aids for BZCYYb such as NiO, ZnO, and Co₃O₄ are ineffective in a reducing atmosphere. However, MnO was determined to be a feasible alternative sintering aid and was incorporated into half cells.

MnO was found to improve sintering in a reducing atmosphere. Figure 3 compares sintering curves for BaZrCeYO_x (BZCY) and BZCYYb with various MnO loadings to that of ferritic stainless steel metal support composition 434L. The addition of MnO drives the BZCY sintering curves to approximately 150°C lower temperature. A tri-layer half cell with MnO-BZCYYb electrode and electrolyte was fabricated by painting the ceramic layers onto a bisque fired metal support, as shown in Figure 3. Good densification of the MnO-BZCYYb electrolyte was achieved after firing at 1350°C. Debinding stress while burning out the painted binder caused substantial cracking in the ceramic layers. This will be addressed in the future by preparing the metal and ceramic layers by tape casting and using a similar binder in all layers so as to burn out the binder from all layers simultaneously.

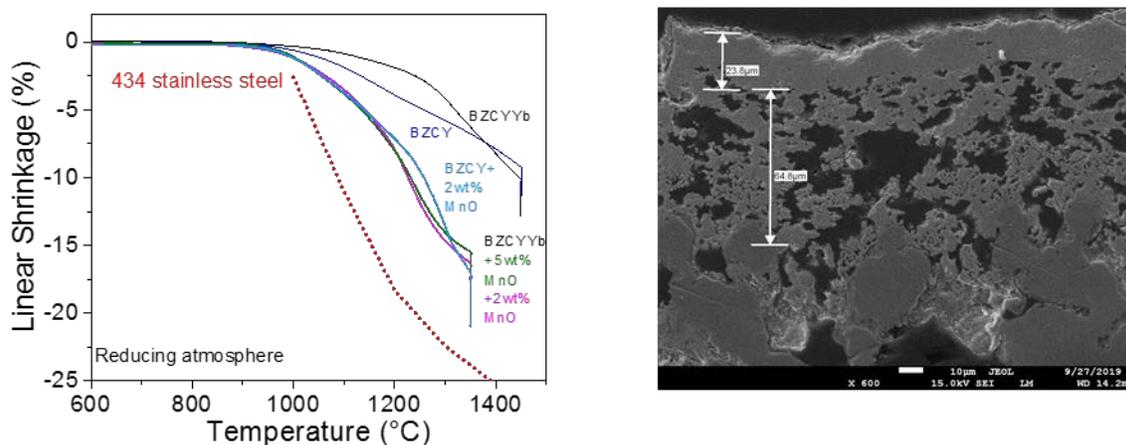


Figure 3. (left) Sintering curves for BZCY and BZCYYb with various MnO loadings (solid lines) and stainless steels (dashed line); (right) Trilayer cell with 434L support and MnO-BZCYYb porous electrode and dense electrolyte fired at 1350°C.

p-SOEC Material Durability

One of the project goals is to evaluate the durability of the p-SOEC. The durability of the electrolyte and electrode materials was tested under relevant steam electrolysis conditions at INL. The PNC and BZCYYb electrolyte powders were placed in a well-sealed quartz tube for the experiment. Air with 50% steam was passed through the tube, and the temperature was maintained at 600°C for 500 hours. The XRD patterns of the powder before and after the 500-hour treatment were obtained. The results showed that there was no measurable phase change of the PNC and BZCYYb material, respectively, after long term steam exposure.

The durability of the button cell, consisting of NiO+BZCYYb hydrogen electrode, BZCYYb electrolyte, and PNC steam electrodes was tested under 20% and 30% steam. Figure 4 shows the current density of the button cell with time at 500°C and 1.4 V. There was no measurable degradation of the performance at 20% steam up to 100 h, while a slight decrease of the current density was observed under 30% steam. Further durability tests will look at the effect of higher steam concentration on the decay rate of the p-SOEC cell.

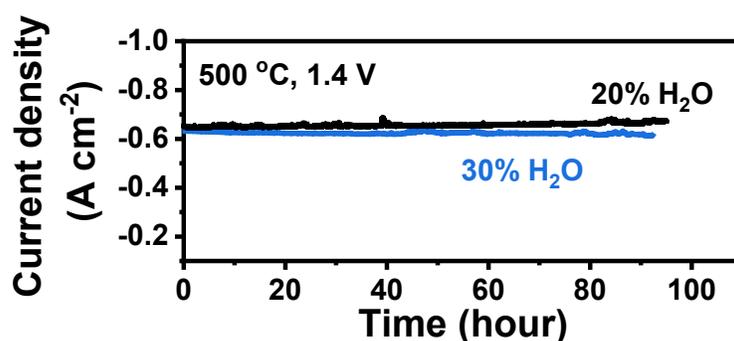


Figure 4. Performance of NiO+BZCYYb|BZCYYb|PNC button cells with time at 500°C and 1.4 V under different steam concentration.

CONCLUSIONS AND UPCOMING ACTIVITIES

In summary, the team demonstrated that SPS is a feasible deposition process for a porous NiO layer. Further development will focus on the deposition of a porous hydrogen electrode based on a NiO + BYZ composition. The preliminary cost analysis indicated that SPS is a low-cost manufacturing process for the SOEC cell, which is critical to enable the p-SOEC technology to meet DOE's hydrogen production cost target of \$2/kg H₂.

In addition, the collaboration with the HydroGEN EMN nodes (LBNL, INL, and NREL) provided critical support to address technical barriers in manufacturing, material evaluation, and modeling. The LBNL team has identified a promising sintering aid to reduce the co-sintering temperature of the p-SOEC cell to minimize Si contamination and Ba evaporation. The INL team demonstrated that BZCYYb-based SOEC cells exhibited adequate performance under electrolysis conditions at 20% and 30% steam. An electrochemical model and a cell model are being developed by NREL for SOEC characterization and simulation, and is expected to provide performance modeling of the SOEC cell/stack performance.

The team will continue the proposed effort for Phase 2, focusing on developing a plasma-based deposition process for the hydrogen electrode, while further improving the SPS process for BYZ-based electrolytes through feedstock and process optimization. The team will also continue the collaboration with the HydroGEN EMN nodes on alternative cell deposition technology development, material optimization and SOEC cell/stack modeling.

FY 2019 PUBLICATIONS/PRESENTATIONS

1. R. Wang, G.Y. Lau, D. Ding, T. Zhu, M.C. Tucker, "Approaches for Co-Sintering Metal-Supported Proton-Conducting Solid Oxide Cells with Ba(Zr,Ce,Y,Yb)O₃ Electrolyte," *International Journal of Hydrogen Energy*, 44 (2019): 13768-13776

2. T. Zhu, “Thin-Film, Metal-Supported High-Performance and Durable Proton-Solid Oxide Electrolyzer Cell,” 2019 Hydrogen and Fuel Cells Program Annual Merit Review, Oral Presentation, Crystal City, VA, April 29–May 1, 2019.

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1. Kreuer, K.D. “Proton-Conducting Oxides.” *Annu. Rev. Mater. Res.* 333 (2003): pp 333-359.
2. Choi, Sihyuk; Kucharczyk, Chris J.; Liang, Yangang; Zhang, Xiaohang, Takeuchi, Ichiro; Ji, Ho-II and Haile, Sossina M. “Exceptional power density and stability at intermediate temperatures in protonic ceramic fuel cells.” *Nature Energy*, 3, no. 3 (2018): pp 202-210.
3. Zhu T., Thin-Film, Metal-Supported High-Performance and Durable Proton-Solid Oxide Electrolyzer Cell, 2019 Hydrogen and Fuel Cells Program Annual Merit Review, Oral Presentation, Crystal City, VA, April 29 – May 1, 2019.
4. Peterson, D., Overview of US.DOE efforts on H₂ Production from Water Electrolysis, ElectroHyPEM workshop, 2014