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# 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/cm<sup>2</sup> at 1.4 V and a decay rate <0.4%/1,000 h.
- Phase 1 focuses on demonstrating the feasibility of the proposed concept via electrolysis performance demonstration of a metal-supported single cell up to 25-cm<sup>2</sup> scale.

## Fiscal Year (FY) 2018 Objectives

- Develop an electrolyte deposition process based on either suspension plasma spray (SPS) or reactive spray deposition technology (RSdT).

- Fabricate metal-supported cells and demonstrate the cell performance for water electrolysis.

## Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan<sup>1</sup>:

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

## Technical Targets

The objective of Phase 1 of this project is to demonstrate the feasibility of a low-cost proton-conducting metal-supported SOEC cell:

- Develop a manufacturing process for barium yttrium zirconate (BYZ)-based proton-conducting electrolyte.
- Demonstrate a proton-conducting metal-supported SOEC cell for water electrolysis for a targeted performance of >0.8 A/cm<sup>2</sup> at 1.4 V at T ≤650°C and <1%/1,000 h degradation projected from short-term durability results.

## FY 2018 Accomplishments

- Demonstrated the SPS process for electrolyte deposition. A hydrogen-electrode-supported button cell with an SPS electrolyte layer exceeded the performance target of 0.8 A/cm<sup>2</sup> at 1.4 V.
- Made significant progress on half-cell fabrication (hydrogen electrode/electrolyte) on metal-supported cells.

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

## 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%/1,000 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-BaZrO<sub>3</sub>, 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., SPS or RSDT) [3]. This design should enable the electrolyzer to meet the hydrogen production cost goal of \$2/kg hydrogen.

## APPROACH

This project leverages electrolyte and electrode materials developed under the Advanced Research Projects Agency–Energy’s REBELS (Reliable Electricity Based on Electrochemical Systems) project, with further advancements through process development, modeling, material discovery, and testing capabilities at United Technologies Research Center (UTRC), University of Connecticut (UConn), and national laboratories through the HydroGEN Energy Materials Network (EMN) consortium. The EMN collaborations include (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 RSDT and SPS; (2) selecting appropriate alloy materials and protective coatings through LBNL’s long-term corrosion testing; (3) optimizing electrolyte and electrode materials at Idaho National Laboratory (INL); and (4) developing an electrolyzer cell model at the National Renewable Energy Laboratory (NREL) for cell-performance optimization.

The main focus of the UTRC and UConn teams is to address a major challenge in fabricating metal-supported cells. The challenge is to develop a cell deposition process to rapidly produce fully sintered or porous ceramic coatings without high-temperature production steps such as sintering. RSDT and SPS are two promising techniques with rapid deposition rates and no high-temperature firing operations, thus enabling high throughput, simple process flow, and automation for lower fabrication cost. 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 µm and 100 µm using suspensions of submicron or nanoscale particles. The RSDT is a flame-based deposition process, depositing films or producing nanopowders through combustion of metal-organic or metal-inorganic compounds dissolved in a solvent. These low-cost fabrication processes provide a pathway to overcome 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.

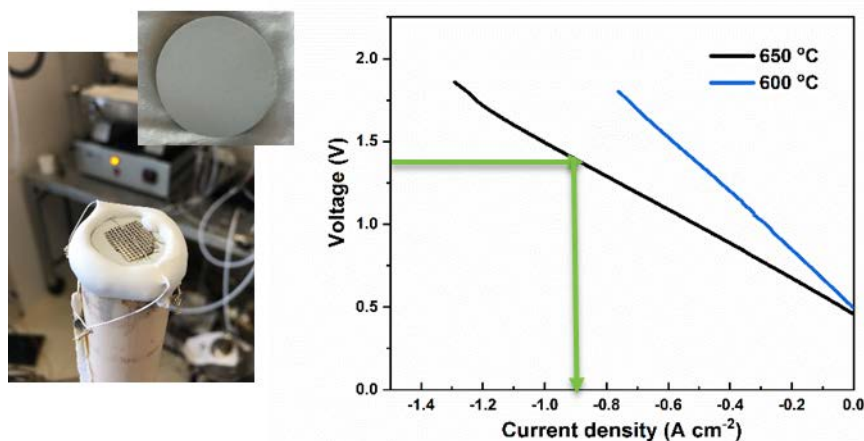
## RESULTS

During FY 2018, UTRC and the team focused on cell fabrication, including the development of SPS for BYZ-based electrolyte deposition, as well as RSDT for electrolyte and steam electrode deposition. The performance of button cells with SPS electrolyte or RSDT layers was evaluated by INL through the HydroGEN EMN consortium.

### SPS Process Development and Results

The hydrogen electrode, consisting of NiO and doped-BYZ, was mechanically pressed into a disc and fired at high temperature for sintering. The electrolyte layer was coated by Pratt & Whitney using SPS with a targeted thickness of 20–30 µm for an initial demonstration. No post heat treatment was applied to the electrolyte layer. An open circuit voltage (OCV) of 0.9 V at 500°C was obtained on a half cell with SPS electrolyte on a sintered hydrogen electrode. A similar cell, coated with INL’s steam electrode material, was tested for water electrolysis. The steam electrode is exposed to an open chamber while a ceramic tube is used to feed wet oxygen (~3% H<sub>2</sub>O) pointing toward the active electrode area. On the hydrogen electrode side, diluted

hydrogen (~20% H<sub>2</sub>) was used to reduce NiO and then gradually increased to pure hydrogen for fast reduction to obtain the OCV. In the test, 20% H<sub>2</sub>/Ar was used to sweep the electrode. A current density of 0.91 A/cm<sup>2</sup> was obtained at 650°C and 1.4 V, as shown in Figure 1. This performance exceeded the project target for Phase 1 (i.e., 0.8 A/cm<sup>2</sup> at 650°C and 1.4 V). This result demonstrated that the SPS process is a promising path to produce a high-performance electrolyte at a low manufacturing cost as it eliminates the high-temperature sintering (typically >1,400°C) required to achieve a dense BYZ-based proton-conducting electrolyte. Further optimization of the SPS process is focused on improvement of the density of the electrolyte layer.



**Figure 1.** Left: 1-inch button cell and testing rig at INL. Right: The current-voltage curves of an anode-supported button cell with BYZ-based electrolyte (deposited by SPS) and INL's steam electrode, at 600°C and 650°C. The green arrow indicates the performance at 1.4 V and 650°C, which exceeded the performance target of Phase 1.

The same SPS process was used for electrolyte deposition on the metal-supported cells. In this case, the hydrogen electrode (NiO + electrolyte) was 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 H<sub>2</sub>/Ar at high temperatures. The thickness of the hydrogen electrode layer was about 20–30 μm. Typically, 3x3 cm<sup>2</sup> cells were fabricated and cut into 1-inch round cells for testing at INL, as shown in Figure 2. The performance measured was much lower, achieving a current density of 0.25 A/cm<sup>2</sup> at 1.4 V. This was due to erosion of the hydrogen electrode during the SPS deposition for the electrolyte, which also caused defects in the electrolyte layer. Because the hydrogen electrode on the metal-supported cell was not as strong as the sintered pellets, the team is evaluating potential modifications to the SPS process without altering the properties of the SPS electrolyte layer. The long-term goal is to develop a plasma spray process for the electrode deposition thus enabling a low-cost manufacturing process for a complete cell.

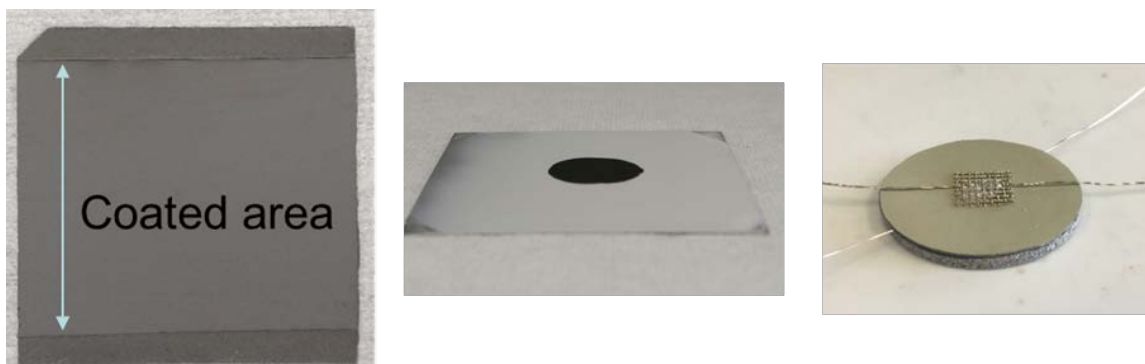


Figure 2. Left: A hydrogen-electrode coated metal cell. Middle: A 3x3 cm<sup>2</sup> cell with hydrogen electrode, SPS electrolyte, and steam electrode (3/8-inch circle). Right: 1-inch round cell assembled for testing at INL.

### RSDT Process Development and Results

The team at UConn focused on developing a RSDT process for the deposition of a dense electrolyte based on doped BYZ and a porous Pr(Ba<sub>0.5</sub>Sr<sub>0.5</sub>Co<sub>1.5</sub>Fe<sub>0.5</sub>)O<sub>5</sub> (PBSCF) steam electrode. The electrolyte deposition time was about 105 minutes, resulting in an electrolyte layer with a thickness of 1–3 μm. There was no post heat treatment. Figure 3 shows the surface image of the deposited electrolyte on a hydrogen-electrode-supported cell, confirming the formation of a dense electrolyte layer. The steam electrode layer was porous with a cauliflower structure, as shown in Figure 3. The as-deposited electrode layer showed no X-ray diffraction peaks. After annealing at 650°C for 1 hour, X-ray diffraction peaks showed that crystalline PBSCF was forming. In addition, microscopy analysis showed appropriate mixing of the elemental components of the PBSCF while energy-dispersive X-ray spectroscopy data showed that the chemical composition matched the desired composition within the error range of the equipment. The cells will be tested for steam electrolysis to demonstrate the performance of the electrolyte and steam electrode layers deposited by RSDT.

Metal-supported half cells were also fabricated using RSDT. The hydrogen electrode was deposited on a porous metal substrate by doctor blade and sintered in H<sub>2</sub>/Ar as described earlier. The electrolyte was deposited by RSDT. The cell reached a maximum OCV of 0.55 V at 600°C and 0.82 V at 700°C. However, the OCV was not stable. Modifications of the deposition process and testing are being evaluated to improve the cell performance.

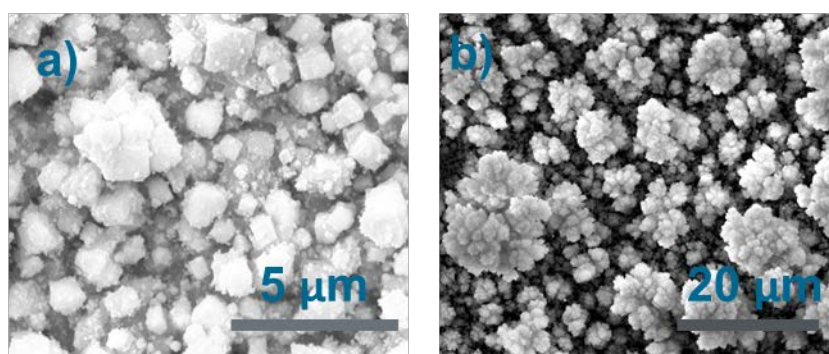


Figure 3. Scanning electron microscopy micrographs of (a) BYZ-based electrolyte deposited by RSDT and (b) PBSCF steam electrode deposited by RSDT

### CONCLUSIONS AND UPCOMING ACTIVITIES

In summary, the team successfully demonstrated SPS as a feasible deposition process for the BYZ-based electrolyte. The performance of the hydrogen-electrode-supported cell, with a SPS electrolyte layer, demonstrated high electrolysis performance (with INL's steam electrode) that exceeded the project's Phase 1

target. The SPS electrolyte was applied to metal-supported cells with a doctor-bladed hydrogen electrode. The metal-supported cells showed lower performance due to a less robust anode layer on a porous metal substrate. The team also made significant progress in RSDT process development for both electrolyte and steam-electrode deposition. A hydrogen-electrode-supported cell, with RSDT electrolyte and electrode, will be tested at INL to demonstrate the performance of the RSDT electrolyte and steam electrode.

In addition, the collaboration with the HydroGEN EMN nodes (LBNL, INL, and NREL) provided critical support to address technical barriers in metal alloy durability; electrode/electrolyte material optimization and stability; and SOEC modeling. Various combinations of metal alloys and protective coatings were identified as acceptable for proton-SOEC conditions. High-performance proton electrolytes and steam electrodes were identified by INL. The button cell performance exceeded the DOE performance target. An electrochemical model and a cell model were developed by NREL for SOEC characterization and simulation and are expected to provide performance modeling of the SOEC cell/stack performance for material scale up. In addition, INL provided critical support in cell performance testing for UTRC and UConn.

The proposed effort for Phase 2 is to develop 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, new material discovery, and SOEC cell/stack modeling.

## FY 2018 PUBLICATIONS/PRESENTATIONS

1. T. Zhu, “Thin-Film, Metal-Supported High-Performance and Durable Proton-Solid Oxide ElectrolyzerCell,” poster at DOE Annual Merit Review, June 2018.
2. T. Zhu, “Thin-Film, Metal-Supported High-Performance and Durable Proton-Solid Oxide Electrolyzer Cell,” presented at High Temperature Electrolysis review meeting at Idaho National Laboratory, September 2018.

## REFERENCES

1. K.D. Kreuer, “Proton-Conducting Oxides,” *Annu. Rev. Mater. Res.* 333 (2003): 333–359.
2. S. Choi, C.J. Kucharczyk, Y. Liang, X. Zhang, I. Takeuchi, H. Ji, and S.M. Haile, “Exceptional power density and stability at intermediate temperatures in protonic ceramic fuel cells,” *Nature Energy* 3, no. 3 (2018): 202–210.
3. R. Maric, J. Roller, and R. Neagu, *Journal of Thermal Spray Technology* 20, no. 4 (2011): 696–718.