
Proton-Conducting Ceramic Electrolyzers for High-Temperature Water Splitting

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- Colorado School of Mines, Golden, CO
- Versa Power Systems, Calgary, Alberta, Canada

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Project End Date: March 31, 2021

Overall Objectives

- Develop efficient and durable high-temperature water splitting systems based on proton-conducting ceramic electrolytic cell (PCEC) technology at a temperature $\geq 500^{\circ}\text{C}$ for production of hydrogen at a cost less than \$2/kg H₂.
- Increase PCEC performance to achieve electrical efficiency $>95\%$, with stack area specific resistance (ASR) $<0.15\ \Omega\text{-cm}^2$ at 1 A/cm².
- Develop proton-conducting electrolytic cells with Faradaic efficiency $>95\%$.
- Reduce PCEC degradation level to achieve stack useful operational life ≥ 7 years.
- Develop manufacturing processes to scale up cell area (up to 100 cm²) to reduce fabrication costs.
- Validate the viability of PCEC technology for high-temperature water splitting by design, build, and operation of a stack capable of ≥ 1 kg/day H₂ production at ≥ 1 A/cm².

Fiscal Year (FY) 2019 Objectives

- Conduct optimization of the air electrode under electrolysis operation from both performance and degradation standpoints.
- Perform optimization of the electrolyte composition and morphology to establish long-term stability and to mitigate current leakage.
- Develop database of physical and mechanical properties to be used in PCEC technology scale-up and stack design.
- Develop high-yield PCEC manufacturing processes using common ceramic processing technologies including tape casting and screen printing.
- Establish baseline performance of industrially manufactured protonic ceramic electrolytic cells with $\geq 16\ \text{cm}^2$ active area.

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 Plan¹:

- (F) Capital Cost
- (G) System Efficiency and Electricity Cost
- (J) Renewable Electricity Generation Integration.

Technical Targets

This project will contribute to achievement of the following DOE milestones from the Hydrogen Production section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan:

- Milestone 2.9: Verify the BOP's (balance of plant) ability to meet the 2020 system efficiency targets. (Q1, 2018)

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

- Milestone 2.10: Create modularized designs for optimized central electrolysis systems projected to meet 2020 capital and hydrogen production cost targets. (Q3, 2018)
- Milestone 2.11: Verify the stack and system efficiencies against the 2020 targets. (Q1, 2020)
- Completed >1,000-hour tests of PCEC fuel and steam electrodes to establish baseline performance degradation rates.
- Down-selected preferred electrolyte materials showing potential for higher performance and lower degradation rate than the baseline electrolyte.
- Demonstrated Faradaic efficiency >85% and electric efficiency >75% at 1 A / cm².
- Developed cell manufacturing processes accommodating solid state reaction sintering (SSRS) and enabling fabrication of PCECs larger than 100 cm² size.

FY 2019 Accomplishments

INTRODUCTION

This project is centered on development of an emerging class of proton-conducting ceramic materials utilized in advanced high-temperature water splitting systems with potential of achieving hydrogen production cost of less than \$2/kg H₂. Specifically, the project is focused on using yttrium-doped barium zirconate (BZY) and yttrium-doped barium zirconate-cerate (BCZY) protonic materials as the basis for electrolyte in construction of the PCECs. This class of protonic ceramics has been used recently to achieve world-record power density from a fuel cell operating at 500°C (0.45 W/cm²) [1]. Proton conduction in these ceramics, in the 500°C to 600°C range, is higher than the oxygen ion conduction in conventional solid oxide electrolysis cell materials.

The project will utilize a proton-conducting ceramic electrolyte with a targeted stoichiometry designed to reduce electrical leakage while maintaining high proton conductivity. The high proton conductivities directly enable cells at temperatures 200°C to 300°C lower than conventional solid oxide electrolyzers while maintaining the benefit of utilizing thermal energy (in addition to electrical energy) at below thermal neutral conditions, resulting in the production of hydrogen at very high electrical efficiencies (>90%). The fundamental reduction in temperature that comes from PCEC technology reduces materials cost within the stack and system components, thus reducing capital and operating costs of systems for hydrogen production.

This project's goal is to transition proton-conducting solid oxide electrolyzers from laboratory-scale cell sizes to a functional stack capable of producing over 1 kg/day of hydrogen while maintaining higher than 95% electrical efficiency (lower heating value) at >1 A/cm² current density with a projected stack lifetime greater than seven years.

APPROACH

The project addresses three fundamental issues that have hampered the development of proton-conducting ceramics in fuel cell and electrolysis operation. The first is the manufacturing limitation associated with the multistage high-temperature firing process required to produce large-area cells. The second is the lack of steam electrode materials designed for rugged, efficient electrolysis operation. The third—associated with PCEC operation—is the electrical leakage under reverse bias present in common protonic electrolyte materials.

The baseline electrolyte material is BaCe_{0.7}Zr_{0.1}Y_{0.1}Yb_{0.1}O_{3-δ} (BCZYYb7111) perovskite. While this material has demonstrated good ionic conductivity and faradaic efficiency near 500°C, it is probable that the “7111” stoichiometry is not optimal. Similarly, the baseline steam electrode is also a perovskite, BaCo_{0.4}Fe_{0.4}Zr_{0.1}Y_{0.1}O_{3-δ} (BCFZY). This “triple-conducting oxide” transports oxygen ions, protons, and electrons, and has shown strong performance across a range of fuel cell and electrolysis operations. Performance will be further improved through (1) modifications in materials stoichiometry, thereby improving conductivity and water-vapor dissociation for electrolysis operation, and (2) blending of the BCFZY electrode material with the BCZYYb electrolyte material, resulting in a multi-phase electrode that may extend the length of the triple-phase boundaries and promote efficient water electrolysis.

To meet the project's goals of 95% electrical efficiency at 1.0 A/cm² with ASR <0.2 Ω-cm², the following materials challenges will be addressed:

- Seek alternative electrolyte stoichiometry to achieve high electrical efficiency at high current density levels while maintaining high Faradaic efficiency over 400°–600°C temperature range.
- Quantify the baseline BCFZY steam-electrode performance and develop optimized steam electrodes to reduce over-potentials in electrolysis operation over 400°–600°C temperature range.
- Perform mechanical and thermal characterization of cell materials including thermal expansion, strength, and fracture resistance. These mechanical properties will be compared with those of conventional YSZ.

Concurrent to cell optimization, fabrication processes suitable for high-throughput manufacturing will be developed to transition from button cell fabrication limits to industrially relevant cell sizes suitable for stack and system integration. This work focuses on decreasing manufacturing variation, tightening process controls, and moving to industrial materials preparation, handling, deposition, and firing techniques. The approach will consist of necessary modifications and fine-tuning to the existing anode-supported solid oxide fuel cell manufacturing processes utilizing tape casting, screen printing, and co-firing. This project will transition PCEC production to a tape cast fuel electrode support layer, screen printed electrolyte and electrodes, and an optimized SSRS firing. This approach will enable the larger cell sizes required for stack integration. During manufacturing scale-up, quality assurance methods for integration into stack repeat units will be applied including controls for flatness, shrinkage, and cell thickness. Pilot-scale cell manufacturing will be deployed to produce adequate quantities of cells for stack development and the fabrication of the milestone 1 kg/day stack prototype.

RESULTS

A protonic-ceramic electrolysis cell utilizing the baseline BCZYYb7111 electrolyte supported on a fuel electrode consisting of a two-phase composite of nickel and BCZYYb7111 and all-ceramic composite steam electrode of 20 wt % BCZYYb7111 and 80 wt % BaCo_{0.4}Fe_{0.4}Zr_{0.1}Y_{0.1}O_{3-δ} (BCFZY) was tested for its performance and efficiency. This cell resulted in low over-potential at high current densities (Figure 1a). At the target operating current density of 1,000 mA/cm², the terminal voltage was only 1.24 V, which is below the thermoneutral voltage, $V_{TN}=1.28$ V at 600°C, resulting in a voltaic efficiency of 103% based on the lower heating value of hydrogen. Faradaic efficiency (Figure 1b) decreased near open circuit conditions. This is because the electrolyte works as a hydrogen-separation membrane when the charge current density is very low, and thus a counter-flux of hydrogen occurs across the membrane that counteracts the electrolytically produced hydrogen. The net hydrogen production rate increases as the electrolysis current density increases to overcome the counter flux of proton diffusion. Then, the Faradaic efficiency starts to increase with increasing current density, reaches a maximum, and begins to fall again, which is attributed to the drop in $P(\text{H}_2\text{O})$ and increase in $P(\text{O}_2)$ resulting in the increase in electronic transport number, thereby negatively impacting Faradaic efficiency. Overall electricity-to-hydrogen energy conversion efficiencies are shown in Figure 1c for two scenarios. The first one excludes the thermal energy needed for electrolysis below the electroneutral voltage V_{TN} ; the second scenario includes the additional electric power needed to maintain a heat balance in the system when operating below V_{TN} . The results shown in Figure 1 indicate that a Faradaic efficiency of 98% and energy efficiency >95% is achievable at a current density of 1 A/cm² even at low steam concentrations of 20%.

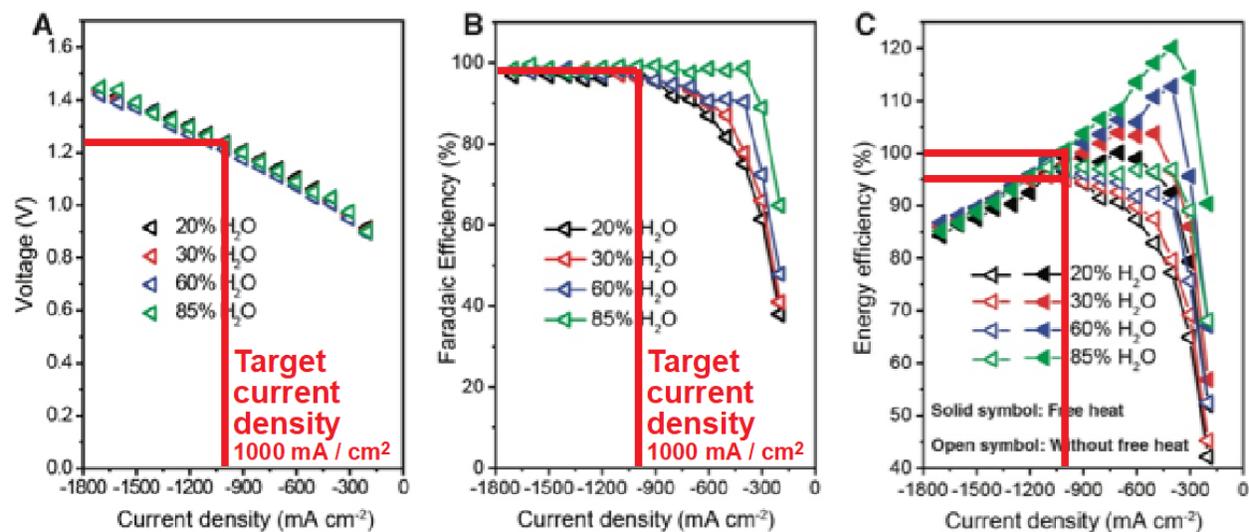


Figure 1. Electrochemical performance of a PCEC at a number of steam-feed concentrations. (A) Polarization curve, including target operating current density of 1 A/cm²; (B) Faradaic efficiency; and (C) energy efficiency. All data shown at 600 °C.

The characterization of the steam and fuel electrodes performance degradation rates was performed in symmetrical button cells. An external impedance analyzer was used to measure the performance over time. Preliminary results are shown in Figure 2. Fuel-electrode degradation over ~1,800 hours is shown at left, while steam-electrode degradation over ~1,000 hours is shown at right. The gaps in data between the two figures reflect sharing of a single impedance analyzer across two experiments. The high DC resistance in the tests is due to using very thick BCZYYb7111 electrolyte layer (1 mm) in the symmetric cells. Degradation is not observed in the fuel electrode at 550 °C and 50% H₂O/50% Ar. The steam electrode showed a significant increase in both the DC and electrode-polarization resistances during a stabilization period <200 hours followed by a minor increase in the remainder of the 1,000-hour testing period.

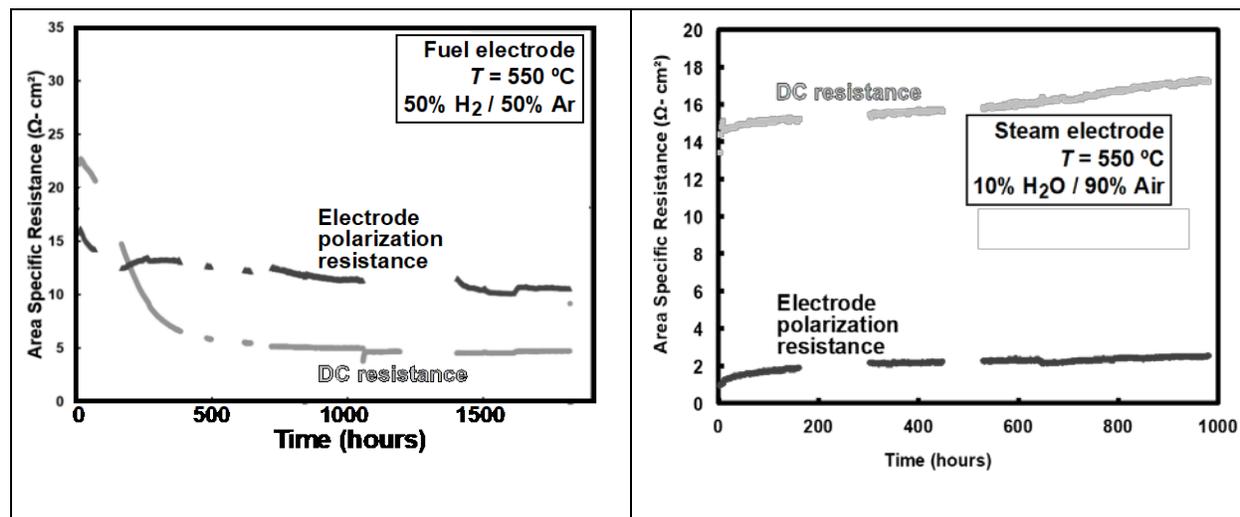


Figure 2. Degradation in fuel (left) and steam (right) electrodes over time

Recent studies have shown improved stability in an electrolyte with a stoichiometry containing more zirconia and less ceria, specifically BaCe_{0.4}Zr_{0.4}Y_{0.1}Yb_{0.1}O_{3-d} (BCZYYb4411), over the baseline BCZYYb7111 electrolyte. The higher zirconia content has been found to improve stability in protonic ceramic electrochemical devices. A symmetric cell featuring a ~1-mm-thick BCZYYb4411 electrolyte sandwiched between two 20- μ m-thick steam electrodes comprising a nickel-BCZYYb4411 composite in 97% H₂ + 3%

H₂O gas environment exhibited negligible performance degradation (Figure 3a). Similarly, a symmetric cell of steam electrodes has resulted in very stable ASR in a 10% steam environment as compared to the high degradation rate of the baseline BCZYYb7111.

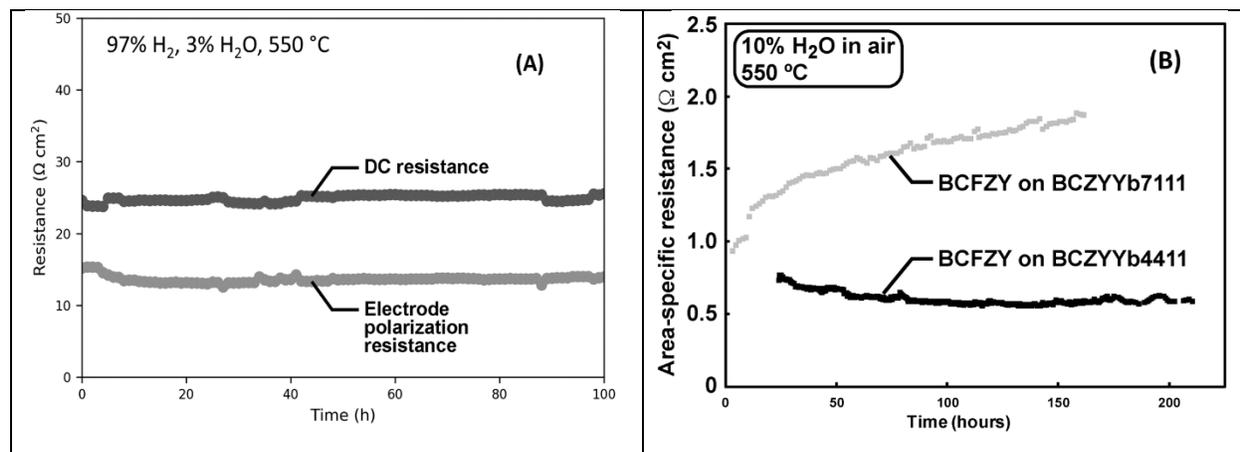


Figure 3. Results of the long-term testing of BCZYYb4411 electrolyte in symmetric button cells. (A) DC and polarization resistances of fuel electrode exposed to 97% H₂ + 3% H₂O at 550 °C showed ~1%/1,000-h degradation. (B) Steam electrode composed of BCZYYb4411 electrolyte showed a stable performance as compared to the steam electrode made of BCZYY7111.

PCEC manufacturing scale-up proceeded with fabrication of 25 cm² cell sizes with active area of 16 cm² using the conventional processes including tape casting, screen printing, and firing of the cell layers. A 5-cm x 5-cm BCZYYb4411 cell was tested for electrolysis operation from 500°C to 650°C up to 1 A/cm² and the polarization curves are presented in Figure 4.

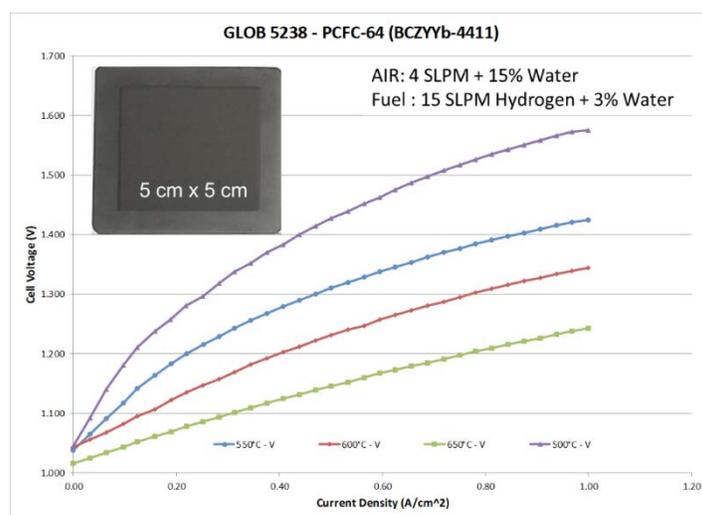


Figure 4. Performance of 5-cm x 5-cm PCEC using BCZYYb4411 electrolyte as a function of temperature

CONCLUSIONS AND UPCOMING ACTIVITIES

Significant progress was accomplished in validating the PCEC performance with high Faradaic efficiency >90% and electrical efficiency higher than 95% using BCZYYb7111 electrolyte composition. The stability of operation and electrode performances were further improved by switching to an electrolyte with a higher zirconium to cerium ratio (i.e., BCZYYb4411). Low-cost and scalable manufacturing methods were developed to sinter protonic ceramic cells at temperatures below 1,500°C in sizes larger than 5-cm x 5-cm, which were

prepared by tape casting, screen printing, and SSRS co-sintering of the cell layers. Cells with active area of 16 cm² were tested using both BCZYYb7711 and BCZYYb4411 in electrolysis modes.

The future activities will include further improvements in cell performance and reduction of the degradation rates. Manufacturing process improvements will be continued with the intention to fabricate 100 cm² size cells. Additionally, the PCEC technology will be extended to design and fabrication of stacks. Testing of manufactured PCEC stacks will be performed to verify various facets of the design including glass seal firing, contact validation, and performance degradation. Ultimately, a milestone stack suitable for hydrogen production ≥ 1 kg H₂/day will be fabricated and tested. The design work will also include thermal and flow modeling of PCEC stacks using relevant compositions and temperatures. A preliminary techno-economic analysis of the PCEC system will be conducted. The activities will include the design of a PCEC-based system followed by the development of cost models for both the PCEC stack modules and the balance-of-plant equipment. The results of the economic cost models will be used in H2A analysis to determine the levelized cost of centralized hydrogen production.

FY 2019 PUBLICATIONS/PRESENTATIONS

1. H. Ghezel-Ayagh, “Proton-Conducting Ceramic Electrolyzers for High-Temperature Water Splitting,” DOE Hydrogen and Fuel Cells Program 2019 Annual Merit Review and Peer Evaluation Meeting, Crystal City, VA, April 29–May 1, 2019.

REFERENCES

1. C. Duan, J. Tong, M. Shang, S. Nikodemski, M. Sanders, S. Ricote, A. Almansoori, and R. O’Hayre, “Readily Processed Protonic Ceramic Fuel Cells with High Performance at Low Temperatures,” *Science* 349 (2015): 1321–1326.