# HydroGEN Seedling: Intermediate Temperature Proton-Conducting Solid Oxide Electrolysis Cells with Improved Performance and Delivery

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Project Start Date: September 1, 2018
Project End Date: August 31, 2021

## Overall Objectives

- Build a continuum electrochemical model to analyze the dependence of steam electrode reaction kinetics on composition, structure, and morphology of the anode.

- Conduct high-throughput screening (HTS) on the composition of catalytic conformal coating.

- Develop a triple conductive anode with area-specific resistance (ASR) of 0.35 $\Omega$cm$^2$ at 600°C under operation conduction.

- Develop a cathode-supported full cell that shows 1A/cm$^2$ electrolyzing current at 1.4 V applied voltage at 600°C.

- Improve the faradaic efficiency of hydrogen production to 70%.

## Fiscal Year (FY) 2019 Objectives

- Construct a continuum electrochemical model including elementary steps with parallel three-phase boundary (3PB) and two-phase boundary (2PB) reaction pathways and identify the possible rate-limiting steps.

- Modify the HTS facility to accommodate the requirement of oxide sample fabrication, perform a test run to show success.

- Develop triple conductive anode with ASR of 0.35 $\Omega$cm$^2$ at 700°C under operation conduction.

- Develop cathode-supported full cell that shows 1A/cm$^2$ electrolyzing current at 1.4V applied voltage at 700°C.

## 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[1]:

- (F) Capital Cost of Hydrogen Generation by Water Electrolysis

- (Q) Operations and Maintenance.

## Technical Targets

This project develops a hydrogen solid oxide electrolysis cell (SOEC) capable of operating at a temperature up to 200°C lower than the current O-SOEC technology. This effort will overcome major barriers in SOEC H$_2$O-splitting anodes at intermediate temperatures that limit the overall performance of the system. Through innovative material discovery, timely characterization using HTS, and model-informed electrode design, an anode with extensively broadened reactive sites will be developed with highly intrinsic electrocatalytic activity.

- Anode materials with ASR target of 0.35 $\Omega$·cm$^2$

- Current densities >1 A/cm$^2$ at 1.4 V/cell at 600°C.

## FY 2019 Accomplishments

- Constructed water-splitting electrochemical reaction model. Presented 3PB and 2PB

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reaction pathways for this triple conductive anode material and identified possible rate-limiting steps.

- Developed HTS facility and showed success in fabrication of the desired oxides.

- Achieved triple conductive anode with ASR of 0.35 $\Omega cm^2$ at 700°C under operation conduction.

- Demonstrated cathode-supported full cell operation at 1 $A/cm^2$ electrolyzing current at 1.2V applied voltage at 700°C.

## INTRODUCTION

DOE funds R&D for low-cost, highly efficient hydrogen production from diverse renewable sources. Water electrolysis based on renewable power is poised to be a viable approach for renewable energy, as the cost of capital equipment is reduced through advanced development, providing the cost of electricity is less than or half of the current average grid price. The capital costs of water electrolysis systems are prohibitive to the widespread adoption of electrolysis technology for low-cost hydrogen production. R&D is focused on developing lower-cost materials with an improved manufacturing capability to lower capital cost requirements while improving the efficiency and durability of the system. To meet these requirements, this project has developed a PGM-free, 600°C operation, cost-effective, and highly active ceramic catalyst. High-temperature electrolysis has the potential to allow for massive hydrogen production through $H_2O$ splitting at electrical efficiencies near 100%. However, current O-SOEC technology is limited by long-term degradation (~1-4%/1000 h) at operating temperatures of ≥800°C. Degradation mechanisms for these O-SOECs include (a) re-crystallization of the LSM-YSZ oxygen electrode, (b) destabilization of YSZ/Ni-YSZ interfaces due to transport of zirconia and Ni to cathode interfaces, (c) oxidation of Ni in high steam conditions, (d) impurity migration to active 3PB regions in the cathode, and (e) formation of voids along grain boundaries. The present project proposes to mitigate these degradation mechanisms by taking advantage of high proton conductivity in $Ba(Zr_{0.1}Ce_{0.7}Y_{0.1}Yb_{0.1})O_{3-\delta}$ (BZCYYb) electrolytes for H-SOECs that separate hydrogen production from $H_2O$ oxidation and operate at milder temperatures to eliminate materials degradation due to cation migration and re-crystallization.

H-SOECs have several intrinsic advantages over O-SOECs. Recent progress in BZCYYb has provided higher conductivity electrolytes for reduced $R_{bulk}$ at intermediate temperatures (600°C), and further efforts are beginning to address the rate-limiting $H_2O$-splitting reaction in the anode to lower $R_{p,anode}$. Lower temperature and improved chemical compatibility of BZCYYb electrolytes address many of the durability concerns for SOECs yet increases $R_{p,anode}$. To reduce $R_{p,anode}$ at these intermediate operating temperatures, a mixed proton, and electron-conducting anode is more needed than the traditional mixed oxygen and electron conductor in the O-SOECs. The former can expand the region of both $H_2O$ dissociation and $H^+$ incorporation into the composite electrode instead of limited only to the electrode/electrolyte interface.

## APPROACH

The team aims to identify highly active, ($e^-$, $O^{2-}$, $H^+$) triple-conducting electrocatalysts and develop conformal coating methods for depositing these catalysts into composite anode functional layers to lower the dominant anode polarization resistance ($R_{p,anode}$) associated with $H_2O$-splitting in H-SOECs. Our proposed H-SOECs cell architecture uses a BZCYYb-based proton conducting electrolyte, a Ni-BZCYYb composite cathode, and a doped-BZY, such as $Ba(ZrYPr)O_{3-\delta}$ (BZYP), conformally coated onto a $Pr_2NiO_{4+\delta}$-BZCYYb (PNO-BZCYYb) composite anode functional layer. The conformal coating of a triple-conducting BZYP catalyst will increase $H_2O$-splitting activity and, thus, lower $R_{p,anode}$ and required operating temperatures. We have collaborated with National Renewable Energy Laboratory's Materials Discovery Lab (Dr. Andriy Zakutayev) with combinatorial studies in thin-film electrocatalysts characterized in operando with electronic x-ray photoelectron spectroscopy to rapidly evaluate $H_2O$-splitting activity. These studies will support the development of microkinetic models for improved design of the microstructure of the coated composite anode functional layers to enable unprecedented performance at lower temperatures and thus superior durability. Our proposed development approach possesses critical advantages that will enable significant performance enhancements over state-of-the-art O-SOECs.

With hydrogen-conducting electrolytes, only pure $H_2$ is produced in the supporting Ni composite cathode, which eliminates the stability concern due to the oxidation of Ni in the concentrated vapor atmosphere experienced in the O-SOECs. Triple-conducting ($e^-$, $O^{2-}$, $H^+$) anode materials (based on PNO) provide reactive sites for $O_2$ formation reaction and $H^+$ incorporation and will extend the electrochemically active area beyond 3PB interfaces to sustain low $R_{p,anode}$ even at 600°C. A conformal catalyst coating (based on $Ba(ZrPr)O_3$) optimized for $H_2O$ splitting in the anode functional layer will further lower $R_{p,anode}$ and maintain long-term structural integrity due to matching of thermal expansion with the composite anode. Optimal electrocatalysts will be identified with HTS of thin-film combinatorial coatings and E-XPS for probing local activity and overpotentials for $H_2O$ splitting. An electrochemical model will be developed to assess and validate microkinetic reaction mechanisms with thin-film electrode experiments. The validated model will be adopted for porous electrode architectures to inform electrode design based on rate-limiting steps (for $H_2O$ splitting, H incorporation, and $O_2$ formation) under high-current operating conditions. Effective fabrication of SOEC cells with reliable electrocatalyst morphologies will be derived from wet chemical impregnation and/or atomic layer deposition (ALD). This approach overcomes deficiencies in traditional catalyst infiltration to ensure a robust electronic/ionic pathway through the functional layer over the SOEC lifetime.

## RESULTS

### Electrochemical model development for $H_2O$-splitting anode design

During Budget Period 1 (BP1), a one-dimensional numerical model is developed to simulate the physical bi-pathway of the intrinsic water splitting reaction on a SOEC anode from multi-step charge-transfer kinetics. We treat the overall water splitting reduction as a multiple-step charge-transfer process, in which the 2PB and 3PB interfacial reaction rates, as well as the gas/anode surface reaction rates, are phenomenologically applied with Butler-Volmer type expressions using electrochemical driving forces.

The reaction step for water splitting consists of seven elementary steps, which can be separated into three categories. The surface (3PB) pathway and the bulk (2PB) pathway share the first three reaction steps (surface dissociative adsorption) and were followed by surface diffusion and reaction (3PB) and incorporation and bulk reaction (2PB) respectively.

More specifically, the convection flow ($P_{O2}$ and $P_{H2O}$) of gas-phase water and oxygen are modeled by extending Fick's law and the kinetic theory of gas, taking into consideration the surface coverage of different species and partial pressure of steam vapor and oxygen. The oxygen desorption reaction is formulated into two equations, which are $S6$ and $S7$. Here the oxygen desorption in $S6$ is treated as the second charge transfer reaction whose kinetics can be expressed by Butler-Volmer type expressions. While the $S7$ reaction (and the $S1$ reaction) is treated as only thermal desorption (adsorption). To model the gas phase diffusion, convection, and adsorption kinetics, the physical parameters of the cathode structure and gas phase are valued. Given the close-packing theory, the particle stack is regarded as a face-centered cubic lattice, assuming maximum compactness and the porous cathode structure can be treated as a random packing of spheres whose porosity is obtained by removing particles. The practical anode microstructure can be treated as the continuous connected 0.5 μm particles (based on SEM of samples) with the gas pores treated as removed particles. For reaction S1 and S7, the chemisorption of molecular water is the first step of water-splitting, which takes one of the surface-active site. The oxygen desorption is the end of a whole set of water-splitting reaction, which releases the surface-active site and allows the new set of water-splitting reaction. The kinetic theory of gases can calculate the kinetics of the adsorption and desorption process.

$$H_2O_{(g)} + S_M \leftrightarrow S \leftrightarrow H_2O_{ad} \qquad\qquad S1$$

$$H_2O_{(g)} + 2S_O + h^\bullet \leftrightarrow 2H_{ad}^+ + O_{ad}^- \qquad\qquad S2$$

$$H_{ad}^+ + O_{O\ BZCYYb}^X \leftrightarrow HO_{O\ BZCYYb}^\bullet + S_O \qquad\qquad S3$$

$$H_{ad}^+ + O_{o\ PNO}^X \leftrightarrow HO_{o\ PNO}^\bullet + S_O \qquad\qquad B4$$

$$HO_{o\ PNO}^\bullet + O_{O\ BZCYYb}^X \leftrightarrow O_{o\ PNO}^X + HO_{O\ BZCYYb}^\bullet \qquad\qquad B5$$

$$O_{ad}^- + h^\bullet \leftrightarrow O_{ad} \qquad\qquad S6$$

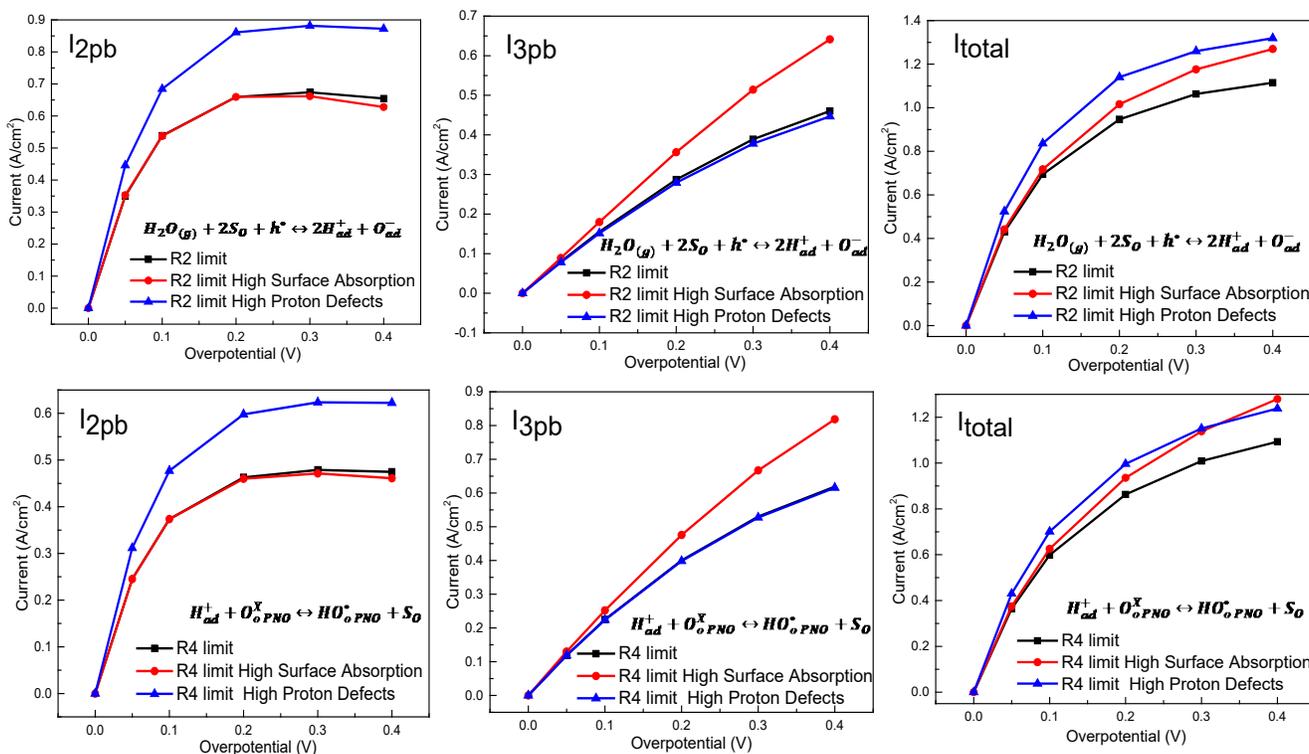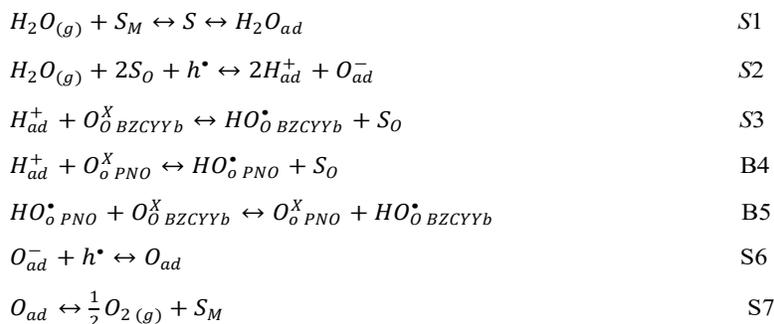$$O_{ad} \leftrightarrow \tfrac{1}{2}O_{2\ (g)} + S_M \qquad\qquad S7$$



Figure 1. Polarization behavior of 2PB and 3PB currents and the total current under different limiting scenarios

The simulation of this model requires parameters, including surface equilibrium concentration, proton defects equilibrium concentration, surface and bulk diffusivity, exchange rate constants of each reaction, volume-specific surface area, surface adsorption site density, equilibrium surface hydrogen ion coverage, etc. The theoretical surface adsorption site density can be obtained with the lattice parameters of PNO and the reaction mechanism of water splitting. The adsorption of water and splitting requires a half octahedron of B-site elements and surrounding oxygen. The calculated surface-active density is $1.1\times10^{-9}$mol/cm$^2$. The proton defects equilibrium concentration at 600°C can be obtained from the published TG data of PNO materials. Following a similar approach, the theoretical value of proton defects concentration is about $1\sim2\times10^{-4}$mol/cm$^3$. The surface capacity is based on various electrochemical data that can approximate $1\times10^{-4}$F/cm$^2$ order for PNO in water at 600°C. For different conditions, such as different test gas compositions, the PNO will be exposed to different surface adsorption status, which gives different surface hydrogen ion equilibrium coverage. The value could range from 1% to dozens. For different catalysts and dopants, this value also changes. Overall, several parameters will be set with different values for the simulation of different test conditions and different materials conditions. The numerical model has already been explicitly integrated and coded with MATLAB 2018. Instead of direct evaluation of the steady-state solutions, a finite control-volume analysis was adopted with time-discretization to analyze the unsteady diffusion equations for the anode, and utilizes a time-discretization solver to reach steady-state.

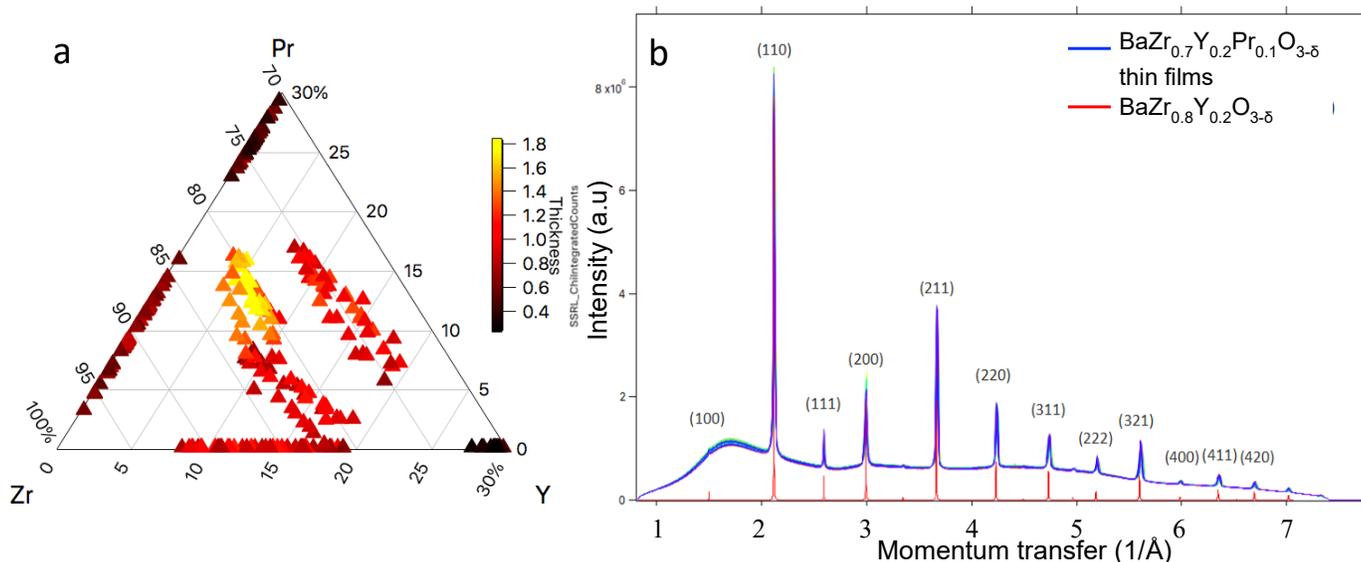## HTS of the formula for anode and catalyst materials



**Figure 2.** (a) Ternary diagram of Zr/Y/Pr composition gradient in the pulsed laser deposition, (b) synchrotron x-ray diffraction result of the prepared $BaZr_{0.7}Y_{0.2}Pr_{0.1}O_{3-\delta}$ thin film

HTS of the conformal coating catalyst was set up. A successful run was realized at the end of BP1. Figure 2(a) shows the combinatorial $Ba(Zr,Y,Pr)O_{3-\delta}$ thin films prepared by a pulsed laser deposition technique. Each sample library is measured at 44 locations for structural and compositional analysis. The verification of phase purity was carried out by synchrotron x-ray diffraction. The BZYP thin films were successfully synthesized, showing the cubic perovskite structure as illustrated in Figure 2(b).

## Development and characterization of button cells

The cathode-supported cell was made using a die-pressing spin coating method. The BZCYYb electrolyte was densified at 1,300°C with a ZnO sintering aid (~1 wt %). A pure PNO anode was sintered 1,150°C. The electrochemical measurements of the I-V curve and electrochemical impedance spectroscopy were carried out to judge the fulfillment of the BP1 goal quantitatively. The cell was measured with dry $H_2$ fed to the cathode and 60 vol % steam containing air fed to the anode. The microstructure of samples was examined by scanning electron microscopy. The electrochemical performance is shown in Figure 3. The Go/No-Go requirements have been met in both the current density level and the full cell ASR level. The 1 A/cm$^2$ current density target was realized by applying 1.2 V electrolyzing potential as referenced to the set goal of 1.4 V. The ASR was measured as 0.3 $\Omega$cm$^2$ vs the 0.35 $\Omega$cm$^2$ target. Judging by these metrics, the objectives have been accomplished for BP1.
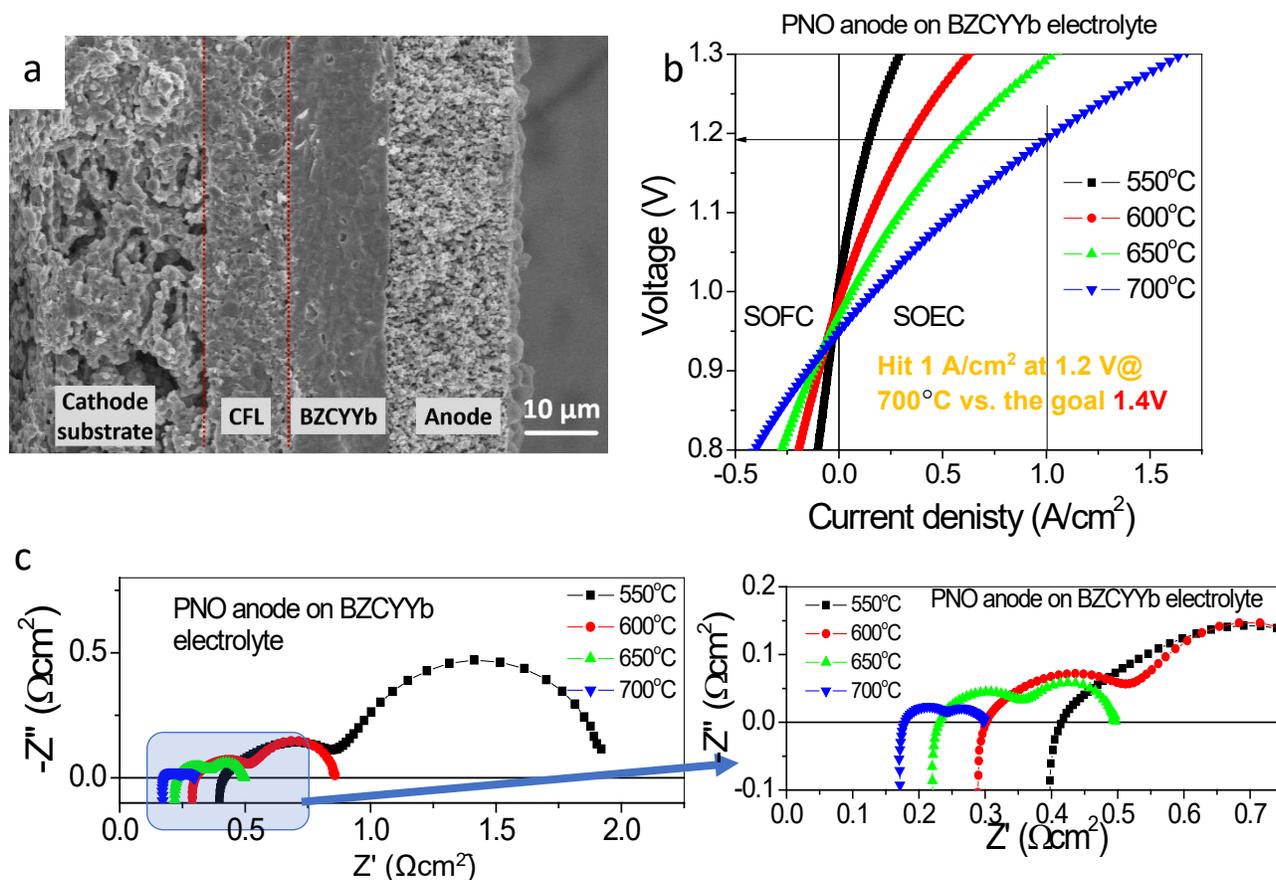
Figure. 3 (a) SEM cross-sectional of cathode supported H-SOEC with PNO anode, (b) electrochemical performance of cathode supported H-SOEC with PNO single-phase anode, (c) EIS measured at different temperature of the corresponding full cell

## CONCLUSIONS AND UPCOMING ACTIVITIES

In BP1, the electrochemical continuum model framework was established and successfully showed the ability to correctly predict the influence of different rate-limiting steps on the 2PB and 3PB reaction pathways and the overall reaction kinetics. HTS fabrication has proven success in $Ba(ZrYPr)O_{3-\delta}$ composition with different ratio between Zr/Pr/Y. Single-phase has been verified on the thin film, which is ready for later electrochemical characterization. PNO anode material was investigated in terms of stability in steam, chemical compatibility with electrolyte and electrochemical activity towards water splitting. High-performing full cells have been achieved. The electrolyzing performance met the target of BP1 regarding the current density and ASR. In the next BP, the continuum will be expanded to contain the structural and compositional effects as seen in a practical anode/electrolyte composite electrode. The model will predict the requirement of particle size, porosity, thickness, along with improved $\sigma$, $k$, and $D$ to reach a $0.35\ \Omega \cdot cm^2$ ASR under operation at 600°C. HTS will continue with in-situ environmental-XPS to correlate the binding energy change of several element to the reaction rate of water splitting process on supported simple films. Conformal coating will be carried out with the guidance of HTS on the composition of the $Ba(ZrPrY)O_3$ electrocatalyst to lower the operation temperature to 600°C while maintaining the performance.

## FY 2019 PUBLICATIONS/PRESENTATIONS

1.   W. Li, B. Guan, L. Ma, Z. Li, H. Tian, X. Liu, "Synergistic Coupling of Proton-Conductors $BaZr_{0.1}Ce_{0.7}Y_{0.1}Yb_{0.1}O_{3-\delta}$ and $La_2Ce_2O_7$ to Create Chemical Stable, Interface Active Electrolyte for Steam Electrolysis Cells," *ACS Applied Materials & Interfaces* 11 (2019): 18323-30.

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