



Intermediate Temperature Proton-Conducting Solid Oxide Electrolysis Cells with Improved Performance and Durability

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Lawrence Livermore National Laboratory





Project partners

- □ PI West Virginia University (WVU)
- □ Co-PI Colorado School of Mines (CSM)
- □ National Renewable Energy Laboratory (NREL)
- □ Idaho National Laboratory (INL)

Project Vision

Solve long-term degradation of SOECs operating at \geq 800°C by developing an intermediate temperature (IT) H-SOEC that operates at 600°C for > 40,000 hours

Project Impact

- Simultaneous H₂O splitting and H₂ separation eliminating Ni oxidation
- High current densities $> 1.0 \text{ A/cm}^2$ at 1.4 V/cell
- Reduced polarization resistance
- Compatible thermal expansion coefficient of anode and electrolyte for long-term structural integrity
- Manufacturability

* this amount does not cover support for HydroGEN resources leveraged by the project (which is provided separately by DOE)
 HydroGEN: Advanced Water Splitting Materials
 Any proposed future work is subject to change based on funding levels

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Start/End Date	Nov. 2018 – Oct. 2021
Year 1 Funding*	\$292,338





Approach- Summary

Project Motivation

WVU: expertise with all ceramic, nickelate-based electrodes in this study, significant cell fabrication and test facilities

CSM: high-temperature firing and characterization of BZCYYb materials for reliable electrochemical performance (E-XPS)

NREL: high-throughput screening with combinatorial thin-film Ba(ZrYPr)O_{3- δ} deposition on BZCY electrolytes and Pr₂NiO_{4+ δ} thin films

INL: expertise in physics-of-failure and accelerated testing of H-electrolyte development, facilitate cell and stack scale-up

Barriers

- Appropriate electrode with mixed conductivities
- Identification of appropriate electrocatalyst compositions
- Fabrication methodology for a scalable and cost-effective electrocatalyst conformal coatings into the anode functional layers
- Resistance of electrolyte at low temperature and long-term stability



Approach- Summary

Key Impact							
Current target	Units	State of the art	1 st year target	3 st year target			
ASR	Ω ·cm ²	0.57	< 0.35	< 0.35			
Current density	A/cm ²	0.5A @ 1.3V	>1.0 @ 1.4V	>1.0 @ 1.4V			
Degradation	mV/1000 h			4			
Temperature	°C	700	700	600			



H-electrolyte at INL:

- Advanced powder synthesis techniques -sol-gel and nitratecombustion
- Post analysis - SEM/EDX, TEM, **XPS**
- Conductivity improvements

Electrocatalyst at CSM&NREL

- Appropriate electrocatalyst compositions
- High-throughput screening
- Catalysis & local surface activity
- Operando ambientpressure XPS
- **Button cell at WVU** Electrochemical Modeling - H₂O-splitting reaction kinetics - Anode structure and composition **Anodes development** Conformal catalyst layer coating Cell fabrication and performance

characterization



Materials innovation

To lower $R_{p,anode}$, our team engineered the anode microstructure to enhance electrocatalytic activity

- □ PNO-BZCYYb composite anode with triple-conductivity fabricated as the composite backbone
- Electrochemical model development to assess and validate microkinetic reaction mechanisms validated by thin-film electrode experiments
- □ Optimal electrocatalysts will be identified with high-throughput screening (HTS) of thin-film combinatorial coatings and E-XPS for probing local activity and overpotentials for H₂O splitting
- Conformal coating of catalyst will have properties similar to the electrolyte including good H₊-conductivity to enhance the H diffusion and kinetics of bulk H incorporation
- Effective fabrication of SOEC cells with reliable electrocatalyst morphologies will be derived from wet chemical impregnation and/or atomic layer deposition





Budget period 1 scope of work

Task Numbe r	Task or Subtask Title	Milestone Type	Milestone Number*	Milestone Description (Go/No-Go Decision Criteria)	Complete
1	1.1	Milestone	Q1	Construction of the 1-D intrinsic water splitting reaction kinetics model, consistent with the known experimental results	50%
3		Milestone	Q2	Development of H-electrolyte with $\sigma_{H} \geq 0.1~S$ cm^-1 @700°C	20%
2	2.1	Milestone	Q3	Identification of spectroscopic signals from E- XPS on PNO thin-film anodes and BZCYYb electrolyte to correlate with electrochemical activity for anode H_2O splitting	20%
3			Q4	Cathode-supported H-SOEC button-cell with novel anode achieves ASR $< 0.35 \ \Omega \cdot cm^2$ and current density $> 1.0 \ A/cm^2$ at 1.4 V at 700 °C	50%

HydroGEN Consortium resources

- NREL: accelerate materials discovery
- INL: facilitate cell and stack scale-up

Relevance & Impact

Key advantages in low cost hydrogen production

- Direct separation of H₂ production from H₂O oxidation
- Mitigate degradation associated with high temperature
- Reduce the cost of materials at milder temperature
- Improve performance of SOECs with H-conducting electrolyte

R&D fits and EMN nodes utilization

By discovering new materials and designing an appropriate anode microstructure, our project can enable low-cost hydrogen generation production for robust, high-efficiency, electrolysis systems which can accelerate R&D of clean energy technologies, one of the three cores of $H_2@Scale$

NREL's high-throughput screening with combinatorial thin-film electrocatalyst deposition can accelerate the exploration of the compositional space

INL's high throughput materials testing facility will provide prompt response for materials screening to speed up the optimization of BZCYYb electrolyte

Broaden HydroGEN Consortium

Our development of an H-SOEC and related expertise in tools & techniques will broaden the HydroGEN Consortium approaches and expertise in H-SOEC research and related fields.

The materials and designs will enable significant performance enhancements over state-of-the-art SOECs and serve as a basis for a future functional design.

Accomplishments – electrochemical modeling



 $H_2O + 2S \leftrightarrow S - OH_{ad} + S - H_{ad}$ $2S - OH_{ad} \leftrightarrow S - O_{ad} + S - H_{ad}$ $2S - O_{ad} \leftrightarrow 2S + O_2$

$$\begin{split} S - H_{ad} \leftrightarrow S - H_{3PB} \\ S - H_{3PB} + O^X_{O \; BZCYYb} + h^\bullet \leftrightarrow HO^\bullet_{O \; BZCYYb} + S \end{split}$$

$$S - H_{ad} + O_{iPNO}^{``} + h^{\bullet} \leftrightarrow HO_{iPNO}^{`} + S$$
$$HO_{iPNO}^{`} + O_{OBZCYYb}^{X} \leftrightarrow O_{iPNO}^{``} + HO_{OBZCYYb}^{\bullet}$$



Accomplishments – kinetics modeling

$$S1 + 2 as new S2: H_2O + 2h^{\bullet} \leftrightarrow 2H_{ad}^{+} + O_{ad} \qquad Adversely \chi_S$$

$$r_{s2} = r_{s2,0} \left\{ \exp(\alpha_s f \Delta \chi_S) - \frac{C_{H_{ad}^+} C_{O_{ad,eq}}}{C_{H_{ad,eq}^+} C_{O_{ad,eq}}} \exp(-(1 - \alpha_s) f \Delta \chi_S) \right\}$$

$$S3: H_{ad}^+ + O_0^* BZCYYb \leftrightarrow HO_0^* BZCYYb + S \qquad \chi_{3PB}$$

$$r_{s3} = r_{s3,0} \left\{ \frac{C_{H_{ad}^+}}{C_{H_{ad,eq}^+}} \exp(-\alpha_{3PB} f \Delta \chi_{3PB}) - \exp((1 - \alpha_{3PB}) f \Delta \chi_{3PB}) \right\}$$

$$B4: H_{ad}^+ + O_{iPNO}^* \leftrightarrow HO_{iPNO}^* + S \qquad \chi_S$$

$$r_{b4} = r_{s4,0} \left\{ \frac{C_{H_{ad}^+}}{C_{H_{ad,eq}^-}} \frac{C_{i,uptake}}{C_{i,uptake,eq}} \exp(-\alpha_s f \Delta \chi_S) - \exp((1 - \alpha_s) f \Delta \chi_S) \right\}$$

$$B5: HO_{iPNO}^* + O_{0}^* BZCYYb \leftrightarrow O_{iPNO}^* + HO_{0}^* BZCYYb} \qquad \chi_{2PB}$$

$$r_{b5} = r_{s5,0} \left\{ \exp((\alpha_{2PB}) f \Delta \chi_{2PB}) - \frac{C_{i,uptake}}{C_{i,uptake,eq}}} \exp((1 - \alpha_{2PB}) f \Delta \chi_{2PB}) \right\}$$

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Accomplishments – formulation of the model

$$N_{i} = \frac{1}{RT} \left(-D_{i}^{eff} \frac{\partial y_{i}p}{\partial z} \right)$$

$$\frac{\partial (\rho\varphi)}{\partial t} = div(\Gamma \cdot grad\varphi) + S_{\varphi}$$

Boundary condition
$$\int D_{b,z} \left(\frac{\partial^{2}C_{i,uptake,x=0}^{-}}{\partial x^{2}} \right) = rb5$$

$$\int D_{b,z} \left(\frac{\partial^{2}C_{i,uptake,x=0}^{-}}{\partial x^{2}} \right) = rb5$$

$$\int D_{s,z} \left(\frac{\partial C_{H_{x=l}^{+}}}{\partial x} \right) = 0$$

$$C_{i,uptake,x=l} = C_{i,eq}^{-}$$



$$\int_{t}^{t+\Delta t} \varphi_{p} dt = \left[\theta \varphi_{p} + (1-\theta)\varphi_{p}^{0}\right] \Delta t$$

Unsteady diffusion to reach the steady state

 $i_{3PB} = nF\left(D_{s,z}\left(\frac{\partial C_{H_x^+}}{\partial x}\right)\right)$

Accomplishments – HTS of anode and catalyst

 $NiO + Pr_6O_{11}$: ball milled in acetone for 22 h and fired for 10 h at 1350 °C



 $BaCO_3 + ZrO_2 + Pr_6O_{11}$: ball milled in acetone for 22 h, fired for 20 h at 1400°C



Accomplishments - environmental XPS studies

- Initial testing of PNO reference samples on Scienta-Omicron HIPP Lab System at Mines begun February 2019 with assistance from Dr. K. Xerxes Steirer
- Reference samples (PNO and BCZYYb) are being characterized with environmental XPS without electrochemical bias
 - Gas composition H_2O , H_2O/O_2 and H_2O/H_2 to ~ 10 mbar
 - Temperatures up to 600°C
 - Exploring the following peaks in
 - PNO O 1s and Ni 2p with initial studies
 - BCZYYb O 1s, Y 3d, Ce 3d, and Yb 4d
 - Current design of thin-film electrochemical for E-XPS testing at Mines
 - Multiple PNO films will provide a basis for combinatorial catalyst coatings in collaboration with NREL to explore overpotentials through binding energy shifts as a function of catalyst composition



Accomplishments - H⁺ conducting electrolyte

- Initiated study on improving conductivity, stability, and sinterability of BCZYYb system by adjusting Zr/Ce ratio
- Synthesized BCZYYb7111 powder sent to WVU for evaluation

Solid-state reaction synthesis flow chart





Pressing













BCZYYb powder

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Accomplishments - button cell development





Cell configuration	Steam in anode (atm)	т (°С)	Polarization resistance (Ωcm²)	Current density (mA/cm²)	Applied potential /overpotential (V)	Year and Ref
Pr ₂ NiO ₄₊₀ -BZCY	0.4	700	0.31	977	1.3/0.37	This study
Pr ₂ NiO _{4+ō} -BZCY	0.4	600	0.4	600	1.3/0.33	This study
Sm _{0.5} Sr _{0.5} CoO _{3-δ} -BCZY	0.5	700	0.57	500	1.3/0.35	2010 <u>23</u>
(LaSr)CoO _{3.5} -BZCYbCo	0.3	700	-	60	1.3/0.30	201122
$(\text{La}_{0.75}\text{Sr}_{0.25})_{0.95}\text{Mn}_{0.5}\text{Cr}_{0.5}\text{O}_{3.5}\text{-BZCYZ}$	0.03	700	~21.4	1000	1.3/1.17	2012 ²⁸
La _{0.6} Sr _{0.4} Co _{0.2} Fe _{0.8} O ₃₋₅ -BZCYZ	0.03	800	7	25	1.3/0.67	2013 ²⁹
Ba _{0.5} Sr _{0.5} Co _{0.8} Fe _{0.2} O _{3-δ} -BZCYZ	0.03	800	14.4	23	1.3/0.6	2013 ²⁹
$\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}\text{-BZY20}$	0.03	700	-	208	1.3/0.57	2015 ²⁴
$LaNi_{0.6}Fe_{0.4}O_{3.5}/La_2NiO_{4+\delta}\text{-}BCZD$	0.9	700	-	300	1.3/0.37	2016 ⁵²
$Sr_{2}Fe_{1.5}Mo_{0.5}O_{6-\delta}$ -Ba $Zr_{0.8}Y_{0.2}O_{3-\delta}$ /	0.03	650	-	310	1.3/0.45	2017 <u>53</u>

- 550°C

-**▲**— 650°C

—**—**700°C

1.2

1.6

W. Li, B. Guan, L. Ma, S. Hu, N. Zhang, X Liu*: Highly Performing Triple-Conductive Pr2NiO4+8 Anode for Protot HydroGEN: Advanced Water Splitting Materials Conducting Steam Solid Oxide Electrolysis Cell, J. Mat. Chem. A 6 (2018) 18057-18066

Accomplishments - electrolyte stoichiometry issue due to Ba diffusion and water attack



As-prepared

Pure BZCYYb

BZCYYb electrolyte film densified on Ni-BZCYYb substrate



600°C 60 vol.% vapor 72 h

Orthorhombic double-peak to tetragonal single-peak upon Ba diffusion



10.0um

As-prepared



600°C 60 vol. % vapor after ~3 day cell measurement

Purposely synthesized Ba doped sample

Accomplishments-La₂Ce₂O₇ (LCO) improved stability in 60vol.% vapor





Z' (Ωcm^2)



Cell configuration	Steam (atm)	T (°C)	l (mA/cm²)	Applied potential	Year and Ref
Pr.NiO…,// LCO/BZCYYb(20 um)//Ni-BZCYYb	0.6	700	975	1.3/0.40	This study
	0.6	600	330	1.3/0.35	This study
Sm _{0.5} Sr _{0.5} CoO _{3-δ} -BCZY//BaCe _{0.5} Zr _{0.3} Y _{0.2} O _{3-δ} (20 μm)//Ni-BCZY	0.5	700	500	1.3/0.35	2010 <u>36</u>
(LaSr)CoO _{3-δ} -BZCYbCo//BaCe _{0.48} Zr _{0.4} Yb _{0.1} Co _{0.02} O _{3-δ} (45 μm)//Ni-BCZYbCo	0.3	700	60	1.3/0.30	2011 <u>37</u>
La _{0.6} Sr _{0.4} Co _{0.2} Fe _{0.8} O _{3-δ} -BZY20//BaZr _{0.9} Y _{0.1} O _{3-δ} (15 μm)//Ni-BZY20	0.03	700	208	1.3/0.57	2015 <u>³⁸</u>
		600	50	1.3/0.44	2015 <u>³⁸</u>
Sr ₂ Fe _{1.5} Mo _{0.5} O _{6-δ} -BZY//BaZr _{0.8} Y _{0.2} O _{3-δ} (16 μm)//Ni–BZY	0.03	600	214	1.3/0.40	2017 <u>39</u>
La ₂ NiO ₄₊₅ -BaCe _{0.2} Zr _{0.7} Y _{0.1} O ₃₋₅ //BCZY27(25µm)//Ni-BCZY27	0.07	700	82	1.3/0.46	2015 <u>40</u>
La₂NiO₄₊₅-BaCe₀₅Zr₀₃Dy₀₂O₃₋₅//BCZD(30µm)//Ni-BCZD	0.9	700	300	1.3/0.37	2016 <u>41</u>
		600	176	1.3/0.37	



Interactions with NREL

To develop the high-throughput screening with combinatorial studies of $Ba(Zr_{1-x-y}Y_xPr_y)O_3$ -based phases, NREL is now working together with CMS on the synthesis and sintering of Ba, Zr, Pr pellet precursors. Samples will be characterized at the CSM E-XPS facility. The outcome data will give useful guidance on the **subtask 1.1** modeling, **subtask 3.2** anode development, and **subtask 3.3** catalyst layer development.

Interactions with INL

Recently improved BZCYYb electrolyte powder using advanced powder synthesis techniques has been synthesized and sent by INL to WVU. With this powder, WVU is now working on the button cell application. I-V, EIS, and polarization curves will be examined, and the button cell will be used in **subtask 3.3**.

Expected benefits

The characterization of BZCYYb-PNO materials and button cell with BZCYYb-LCO bi-layer will benefit HydroGEN Consortium by enriching the materials system database and providing guidance for future functional designs. Modeling the water-splitting kinetics will serve as basis for understanding the electrolysis mechanism and improving performance.

Remaining Challenges and Barriers

- Optimizing numerical programming to establish the relationship between physical parameter and mathematic model
- Exploring new methods to solve cracking problems of the electrocatalyst pellet for PLD of anode and catalyst
- Using pulsed laser deposition to fabricate the combinatorial thin films
- HTS composition for electrocatalytic conformal coating on $Pr_2NiO_{4+\delta}$ anode backbone
- Optimizing electrolyte composition and manufacturing
- Improving the cell fabrication to meet the first year performance target



Remainder of FY 2019

- Complete the electrochemical 1-D model of the anode reaction in H-SOEC
- Continue working on high temperature screen of anode and catalyst
- Characterize PNO & BCZYYb with E-XPS without electrochemical bias
- **Explore the effect of Zr/Ce ratio on electrolyte properties**
- Combinatorial catalyst layer coating on button cell with enhanced activity

FY 2020

- Optimize electrolyte properties of BaCe_{0.8-x}Zr_xY_{0.1}Yb_{0.1}O₃ (x=0.1, 0.2, 0.4) system
- Further develop cell stability
 - Start modeling structural effects in a pratical porous electrode



- Framework of electrochemical model on anode reaction in H-SOEC has been established
- High Throughput Screening of anode and catalyst has started
- Button cell performance of PNO-base H-SOEC is close to Year 1 target
- Effort on improving cell stability shows promising results



Reaction Design The thin films will be characterized by: Crystallinity (XRD) Structure (XRD) Combinatorial Film Deposition (PLD) Composition (XRF) Surface chemistry (XPS) Single target Binary target Ionic/electronic conductivity (Impedance Spectroscopy) (BZO-BZY, BZO-BZP, BZY-BZP) (BZO, BZY, BZP, PNO) Activation Energy (Impedance Spectroscopy) Annealing (if required) Materials Characterization Depth profile XRD XRF Impedance 0.30 1 25-20 0.28 15 Ternary deposition optimization 10 (BZYP) **BZYP** deposition on PNO substrate Points HRTEM/EDS XPS Fuel Cell Integration 20 25 30 35 40 45 50

20(degrees)

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Technology Back-Up

NREL will develop Ba(ZrYPr)O_{3- δ} thin film sample libraries with Zr/Y/Pr composition gradients as well as gradient-free baseline samples to establish the BZYP combinatorial synthesis process.

Single	binary	ternary
BaZrO ₃	$BaZrO_3 + BaZr_{0.7}Y_{0.3}O_3$	BaZrO ₃ + BaZr _{0.7} Y _{0.3} O ₃ + BaZr _{0.7} Pr _{0.3} O ₃
$\begin{array}{c} BaZr_{0.7}Y_{0.3}\\O_3\end{array}$	$BaZrO_3 + BaZr_{0.7}Pr_{0.3}O_3$	
$\begin{array}{c} BzZr_{0.7}Pr_{0.3}\\O_3\end{array}$	BaZr _{0.7} Y _{0.3} O ₃ + BaZr _{0.7} Pr _{0.3} O ₃	
Pr ₂ NiO ₄		

- Pulsed laser deposition system will be used for the combinatorial thin films.
- Preliminary tests will be conducted with single and binary targets with different temperature, pressure, pulse, etc.
- Thin films will be deposited on glass and ITO substrates and characterized for composition, structure, morphology, thickness, impedance, etc.





Effective Leveraging of the EMN Resource Nodes

INL-Advanced Electrode and Solid Electrolyte Materials for Elevated Temperature Water Electrolysis

- Synthesis and optimization of BaZr_{1-x-y-z}Ce_xY_yYb_z H-electrolyte
- Planar, 5cm x5cm full cells, short-stack



NREL-High-Throughput Experimental Thin Film Combinatorial Capabilities

• HTS composition for electrocatalytic conformal coating on $Pr_2NiO_{4+\delta}$ anode backbone



NERL CoO-CuO example

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 \checkmark

Any proposed future work is subject to change based on funding levels 2^{23}

Technology Back-Up

O 1s E-XPS spectra of of the BaZr_{0.9}Y_{0.1}O_{2.95} (a) SPS, (b) SSR and (c) HT pellets as a function of the incident X-ray energy (710, 800 eV) at 300°C at a p(H₂O) of 100 mTorr. The 3 different photon energies provide spectra over 6, 8 and 11 Å respectively. The "lattice" component (orange) represents the perovskite structure in the near-surface regions while the "surface" component (green) is for partially hydrated surface secondary phases on the film with "OH-" corresponding to the hydration/adsorbed species (blue). The "steam" component is represented in purple.

Accomplishments-E-XPS on BaZr_{0.9}Y_{0.1}O_{2.95}



Any proposed future work is subject to change based on funding levels



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Optimization of electrolyte properties of $BaCe_{0.8-x}Zr_{x}Y_{0.1}Yb_{0.1}O_{3}$ (x=0.1, 0.2, 0.4) system

Electroryte synthesis and	evaluation				
Measure electrical	Electrolyte Integration				
conductivity in different gas conditions and temperatures	Fabricate dense electrolyte membrane on electrode	Electrolyte Determination			
Examine structure stability in high vapor conditions at 700°C	support sintered under 1450°C and send powder/cells to WVU	Examine electrolyte and electrode polarization resistances in SOEC			
	Support WVU with INL's high temperature R2R manufacturing capability	Measure Faradaic efficiency under different electrolysis current densities to			
		composition			

Any proposed future work is subject to change based on funding levels

Technology Back-Up



Publications and Presentations

- Wenyuan Li, Bo Guan, Liang Ma, Zhongqiu Li, Hanchen Tian, <u>Xingbo Liu*</u>: Synergistic Coupling of Proton-Conductors BaZr_{0.1}Ce_{0.7}Y_{0.1}Yb_{0.1}O_{3-δ} and La₂Ce₂O₇ to Create Chemical Stable, Interface Active Electrolyte for Steam Electrolysis Cells, <u>Submitted to ACS Applied Materials & Interfaces (2019), under revision</u>
- Yi Wang, Wenyuan Li, <u>Xingbo Liu*</u>: Degradation of Solid Oxide Electrolysis Cell: Phenomina, Mechanisms, and Emerging Mitigation Strategies, <u>Submitted to Journal of</u> <u>Materials Science & Technology (2019), under review</u>.
- Wenyuan Li, Bo Guan, Liang Ma, Shanshan Hu, Nan Zhang, <u>Xingbo Liu*</u>: Highly Performing Triple-Conductive Pr₂NiO_{4+δ} Anode for Proton-Conducting Steam Solid Oxide Electrolysis Cell, <u>Journal of Materials Chemistry A 6 (2018) 18057-18066</u>