Energy Materials Network
U.S. Department of Energy

HydroGEN
Advanced Water Splitting Materials

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

Raytheon Technologies Research Center
Tianli Zhu
May, 2020

Project ID P154

NREL | Berkeley Lab | Sandia National Laboratories | INL Idaho National Laboratory | Lawrence Livermore National Laboratory | SRNL

Project Overview

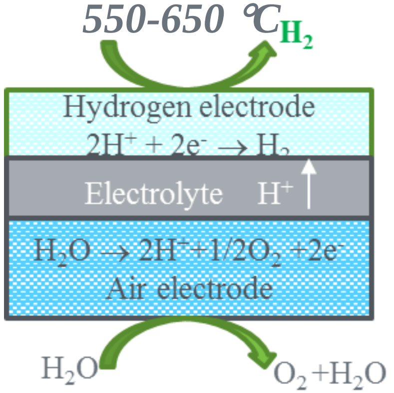
Thin-Film, Metal-Supported High-Performance and Durable Proton-Solid Oxide Electrolyzer Cell

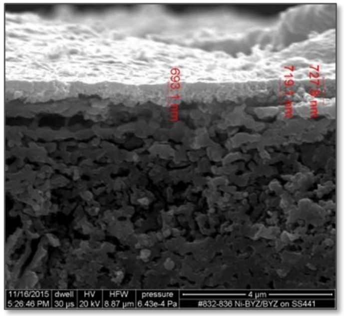
Tianli Zhu, Raytheon Technologies Research Center

Partner organizations: UConn, ElectroChem Ventures

Award #	EE0008080
Start/End Date	10/1/2017 – 3/31/2021
Total project value Cost share	$1.25 M 20%

Proton conducting electrolyzer 550-650 ℃





Thin film deposition for electrolyte

Project Vision

Develop a highly efficient and cost competitive high temperature electrolysis for H_2 generation, by a thin-film, high efficiency and durable metal-supported solid oxide electrolysis cell (SOEC) based on proton-conducting electrolyte at targeted operating temperatures of 550-650ºC.

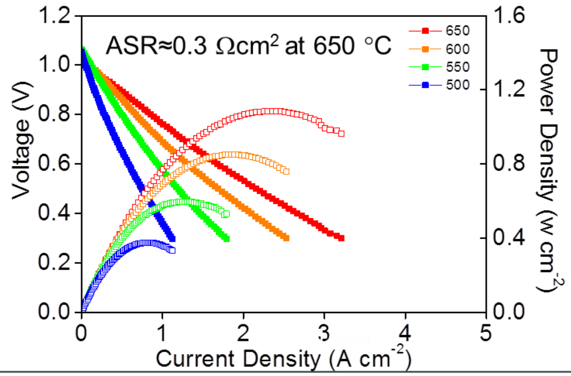
Project Impact

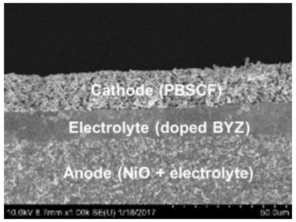
Accelerate the commercialization of high-temperature electrolysis, and advance reversible-SOFC technology for renewable-energy applications.

Approach- Summary

Project Motivation

Anode supported p-SOFC button cell (ARPA-E REBELs)





Key Impact

Metric	State of the Art	Proposed
SOEC Performance	1 A/cm^2 at 1.4 V at 800 ºC	≥1 A/cm^2 at 1.4 V at 650 ºC
SOEC Durability	(1-4)% per 1000 h	<0.4% per 1000 h (~4 mV per 1000 h)
H_2 production Cost	>$4/kg H_2	$2/kg H_2

Barriers

-. Low cost deposition of ceramic layers:

Deposition process without high T sintering: RSDT, SPS, LBNL co-sintering/metal infiltration

-. Metal alloy durability

Proper selection of metal alloys and protective coatings through durability tests

-. Steam electrode and electrolyte stability

INL's high-throughput methodology; molecular dynamics modeling

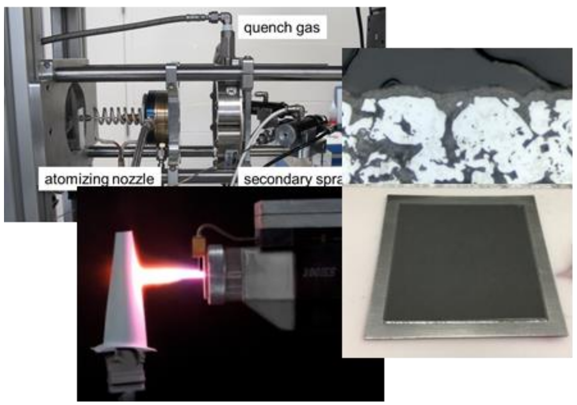
Partnerships

- University of Connecticut (Prof. Radenka Maric): Cell Fabrication (RSDT)
- UTRC SPS Vendor/PW: Suspension Plasma Spray (SPS)
- ElectroChem Ventures (consultant): Metal-supported cell design
- EMS nodes: LBNL, INL & NREL

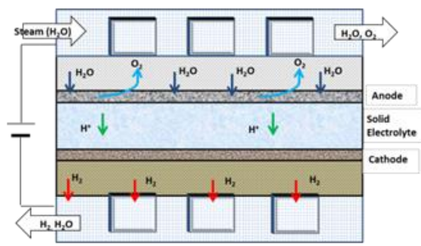
Approach- Integrating Manufacturing, Material & Modeling

Phase 2: 1) develop SOEC metal cell through plasma spray and co-sintering; 2) demonstrate metal cell performance (target: 0.9 V OCV & >0.8A/cm^2 at 1.4 V and T≤650 °C); 3) performance optimization of BYZ-based cell through material optimization; 4) continuing development of p-SOEC model

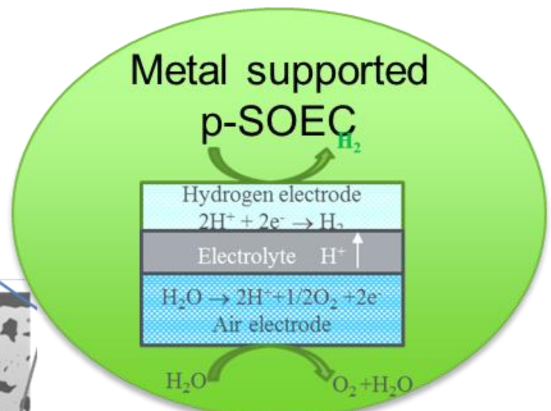
Low cost cell fabrication
Focus: electrolyte
Without high T sintering:
UTRC/PW (SPS), UConn (RSDT)



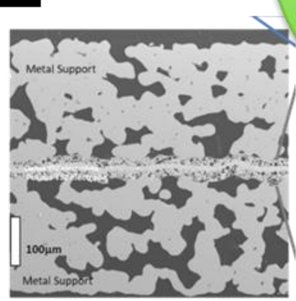
Metal alloy & coating selection
LBNL: oxidation study



Electrochemical modeling
NREL



Co-sintered metal cell
LBNL



Material optimization & button cell testing
INL: high throughput testing stands

Raytheon Technologies

Relevance & Impact

Project Objectives

Develop highly efficient and cost competitive high temperature electrolysis for H_2 generation, by a high efficiency and durable metal-supported solid oxide electrolysis cell (SOEC) based on proton-conducting electrolyte at targeted operating temperatures of 550-650ºC. Focus on developing a low cost, scalable fabrication of metal-supported cells and further material optimization for an efficient & durable p-SOEC.

Project Impact

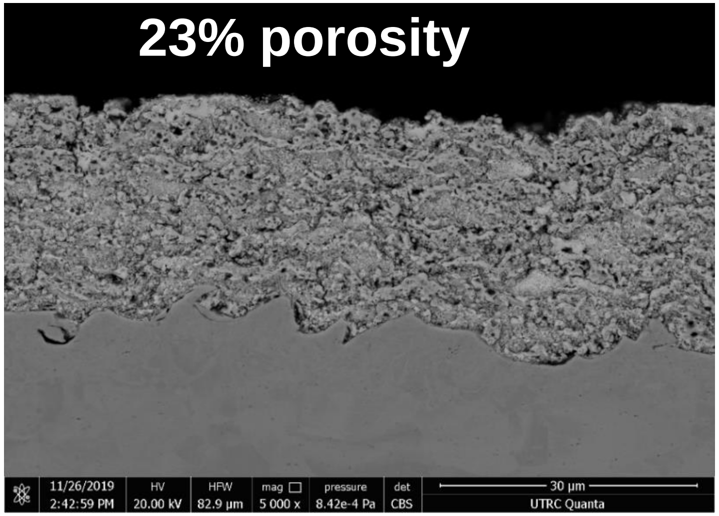
Metric	State of the Art	Project Target
SOEC Performance	**1 A/cm² at 1.4 V** at **800 ºC**	**≥1.0 A/cm² at 1.4 V** on button cells at T ≤ 650 ºC (demonstrated in Phase 1); **≥0.8 A/cm² at 1.4 V** on metal-supported cells at T ≤ 650 ºC
SOEC Durability	(1-4)% per 1000 h	<1% per 1000 h (<10 mV per 1000 h)
H_2 production Cost	>$4/kg H_2	$2/kg H_2 based on cost analysis in Phase 1

Accomplishments: SPS Anode on Metal Supports

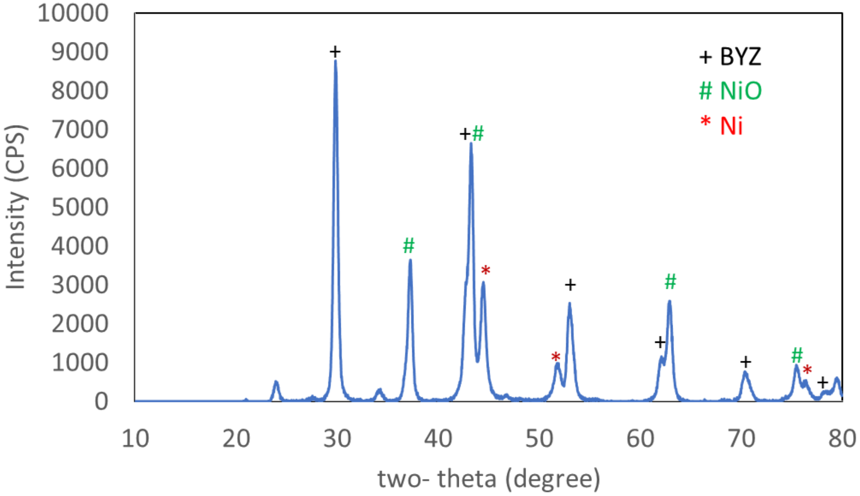
Produced a fully reduced anode with desired composition and porosity.

Target composition: 60/40 NiO/BYZ

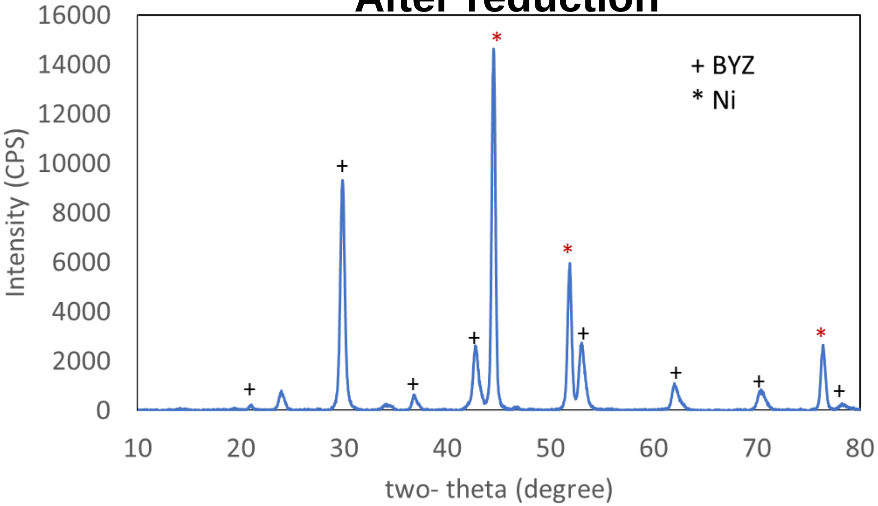
	Theoretical (%)	SEM
Ni	34.6	38.1
Ba	6.3	6.1
Zr	5.0	5.3
Y	1.3	1.4
O	52.8	49.0



As coated



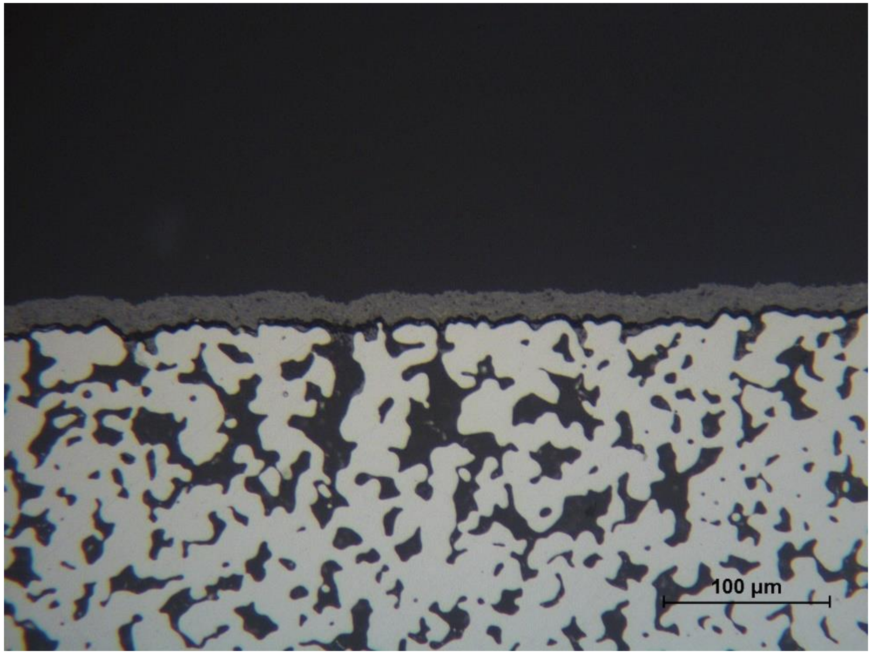
After reduction

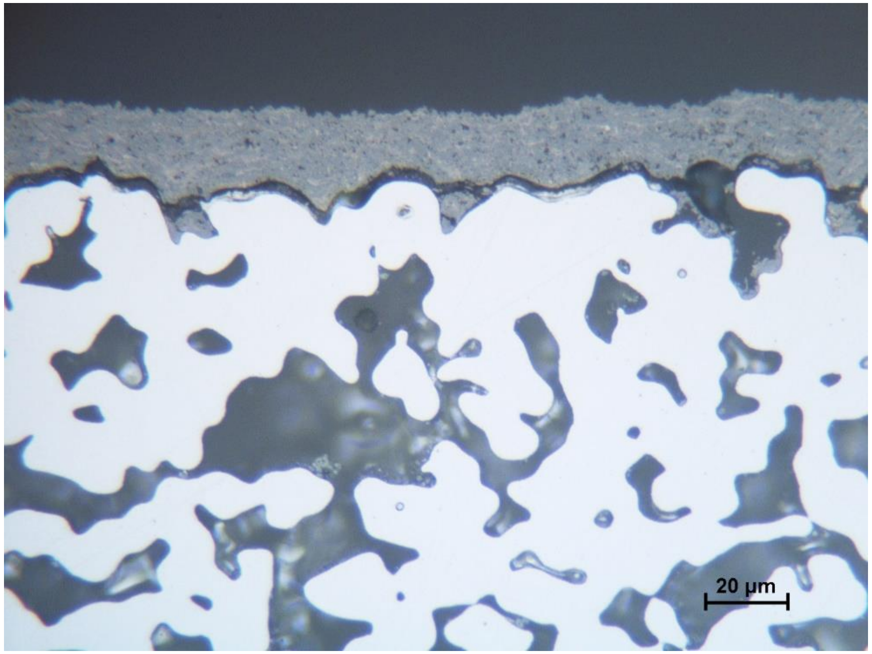


Accomplishments: SPS Anode on Porous Metal Supports

Demonstrated ~20 µm SPS NiO coating on porous metal sheet

Next step: coat porous metal sheet with NiO+BYZ electrode.

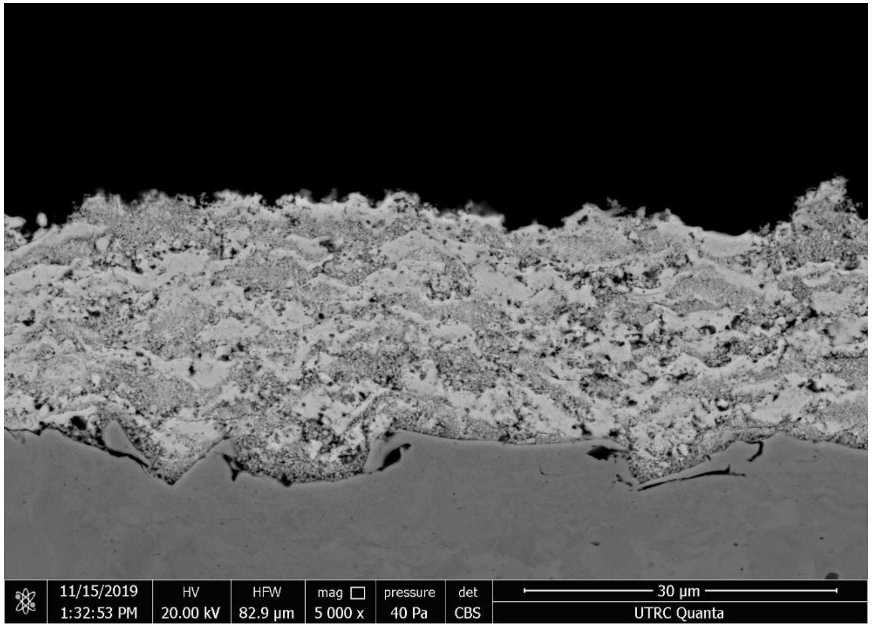




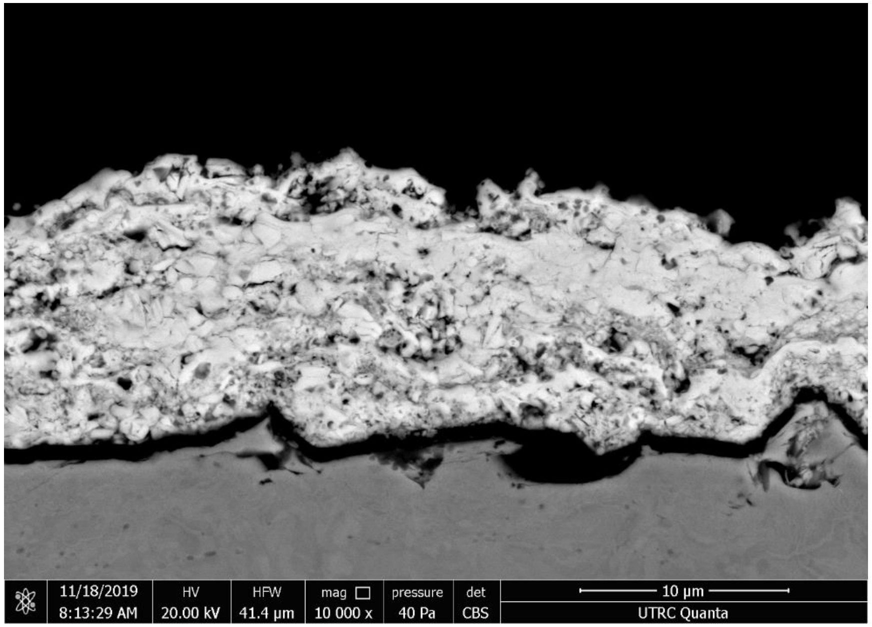
Accomplishements: SPS Electrolyte Optimization in Progress

Phase 2 electrolyte layer optimization focuses on developing a fully dense layer. Desired electrolyte composition by SPS was demonstrated in Phase 1

Phase 1
16% porosity



Phase 2 first trial
~10% porosity

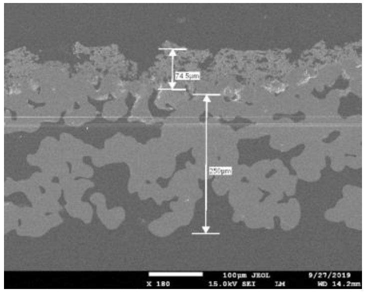


Accomplishment: Metal-Supported Cell Fabrication by Co-sintering

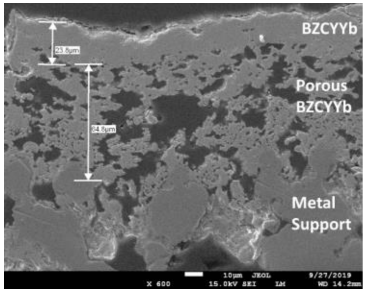
Sintering aid lowers sintering temp 100°C to 1350°C, to mitigate Si and Cr migration from metal support

BZCYYb + 2wt% MnO
on P434L (PII metal cast) 1350°C

Painted bilayer

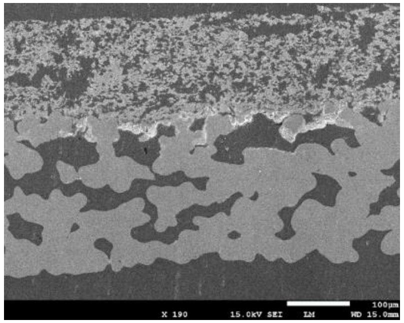


Painted trilayer



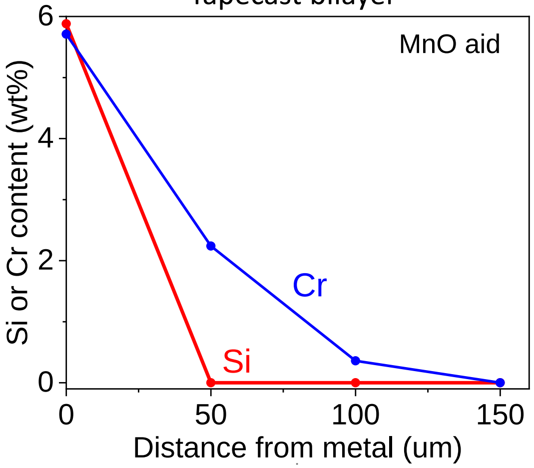
Good elyte densification
Need to eliminate cracks → tapecasting

Tapecast bilayer



Need thinner, high quality tape → vendor

Tapecast bilayer



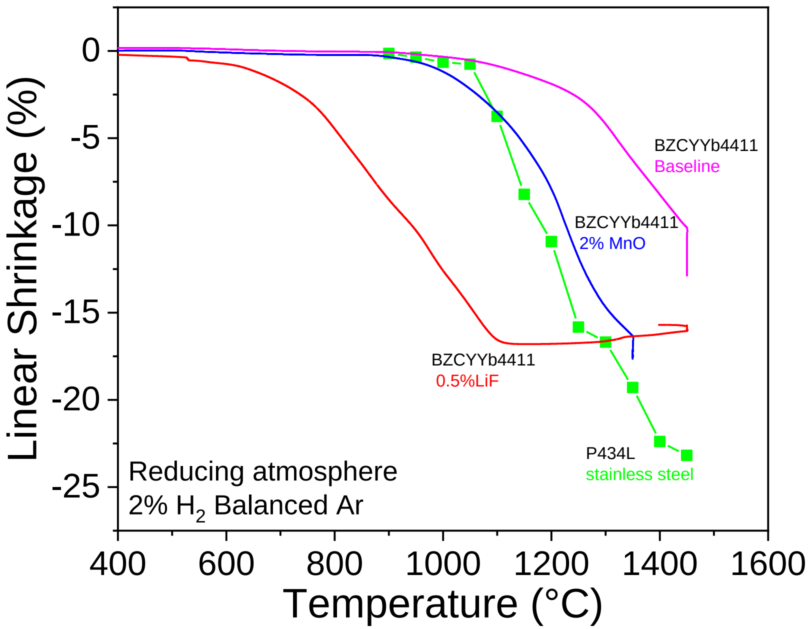
Thickness can be optimized

Correct BZCYYb phase is expected at elode/elyte interface for thick electrode

Accomplishment: Metal-Supported Cell Fabrication by Co-sintering

Matching shrinkage of BCZYYb and LBNL metal support

Good match with 2wt% MnO

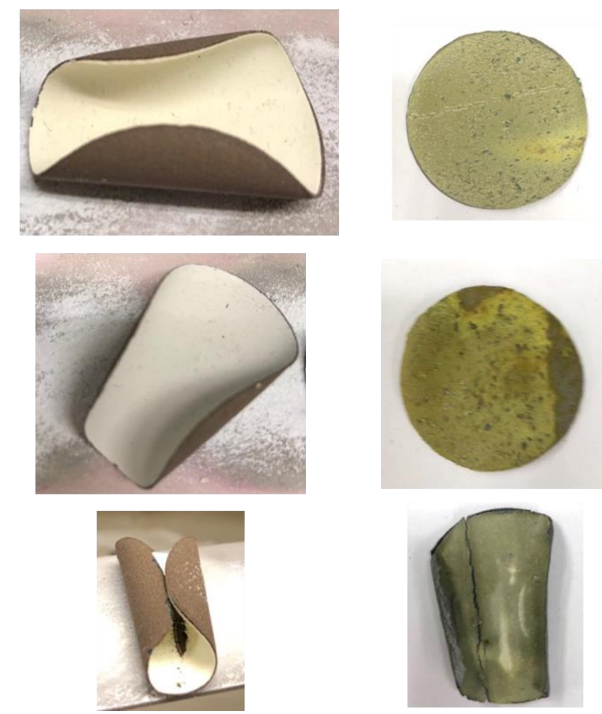


Debinded | Sintered

BZCYYb4411

With MnO

With LiF



Now preparing Metal/BCZYYb (MnO) laminates

If shrinkage matching needs further optimization:

- precoarsen BCZYYb to delay sintering to >1050°C
- smaller metal particles to enhance sintering

Effective matching with Mn-oxide sintering aid

Accomplishment: Faraday Efficiency Study at INL

Identified effect of compositions of doped-BYZ on Faraday Efficiency

FE on BCZYYb7111, BCZYYb4411 and BZY20 electrolyte have been measured at different temperatures, steam concentrations and electrolysis voltages.

Operating conditions

Results show the trend:

P_{H2O}↑ → FE↑

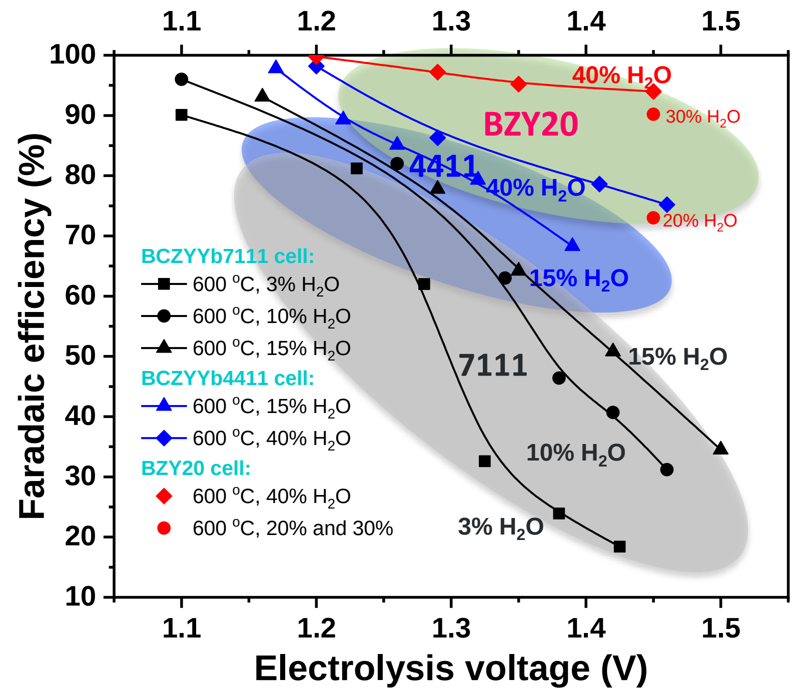
V↑ → FE↓

T↓ → FE↑

Materials

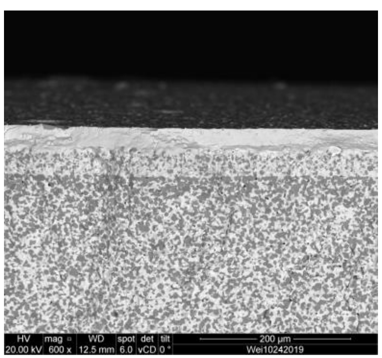
1. *BZY20*
2. *BCZYYb4411*
3. *BCZYYb7111*

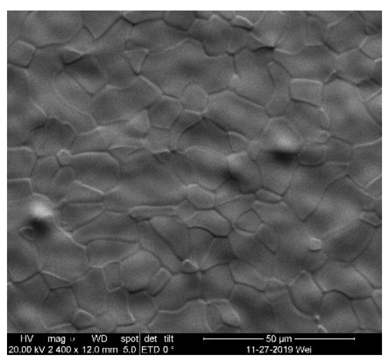
Ce↓ → FE↑



FE results at 600 °C

Extensive efforts in densifying BZY20 at 1500 °C without sintering aids



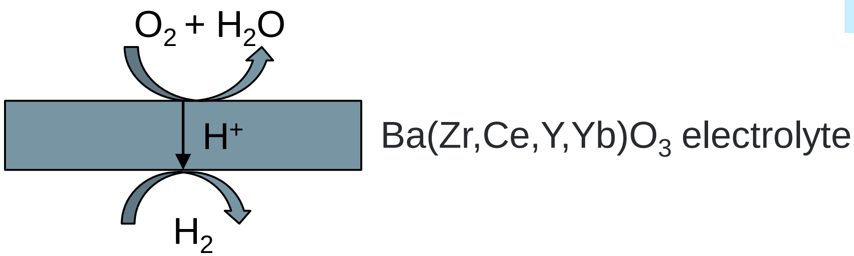


Dense BZY20 film

Accomplishment: Faraday Efficiency Study at INL

Mechanism of electronic leakage:

INL's results show similar trend in recent literature based on $BaZr_{0.7}Ce_{0.2}Y_{0.1}O_3$ electrolyte



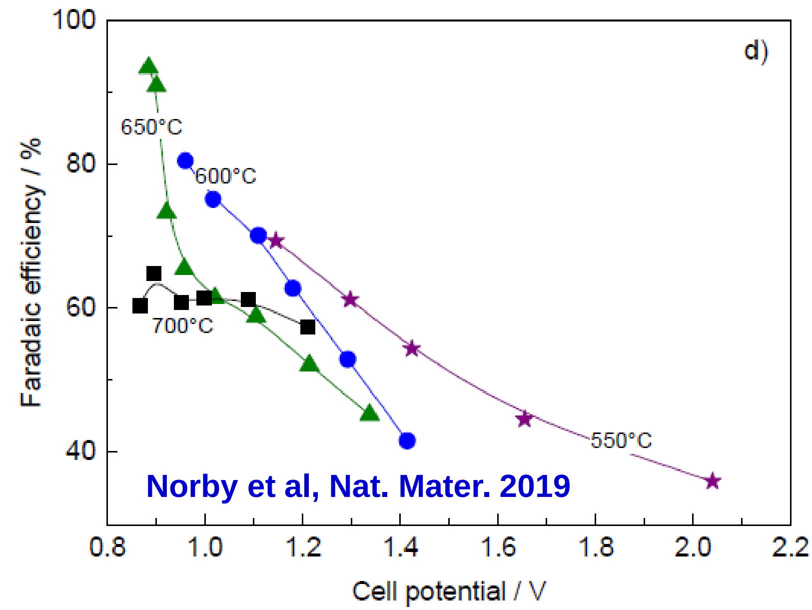
O_2 side: hole formation $\frac{1}{2}O_2 + V_O^{\cdot\cdot} \rightarrow O_O^{\times} + h^{\cdot}$

$$[h^{\cdot}] = K_{ox}\,[OH_O^{\cdot}]\,p_{H_2O}^{-\frac{1}{2}}\,p_{O_2}^{\frac{1}{4}} = K_{ox}\exp\left(\frac{F(E-E^0)}{RT}\right)$$

H_2 side: electron formation

$$2Ce_{Ce}^{\times} + O_O^{\times} \rightarrow V_O^{\cdot\cdot} + 2Ce_{Ce}' + \frac{1}{2}O_2$$

$$\sigma_e = \sigma_e^{\circ} exp\left(\frac{F\left(E^{\circ} - E\right)}{RT}\right) = \sigma_e^{\circ} exp\left(-\frac{FE}{RT}\right)$$



Hydration reaction:

$$H_2O + V_O^{\cdot\cdot} + O_O^{\times} \rightarrow 2OH_O^{\bullet}$$

Proton formation reaction competes with hole formation to effectively decrease hole concentration

High steam concentration results in high FE

One of Mitigation strategies

Options for higher Electrolysis Performance

A new and critical criteria **for evaluating the feasibility of electrolyte in p-SOECs should be established based on the consideration in Faraday efficiency and the cell activity.**

Effective electrolysis current density **is the product of apparent current density and FE, which represents the hydrogen production rate.**

$$i_{eff} = iapp \times FE$$

BCZYYb4411: (e.g., at 1.45 V and 600 ºC)
i_{eff}= 1.40 A cm^{-2} × 75.2% = 1.05 A cm^{-2}

BZY20:
i_{eff}= 0.75 A cm^{-2} × 96.0% = 0.72 A cm^{-2}

Potential Strategies on improving BYZ-based SOEC performance:

#1: Cell manufacturing strategies incorporating different material selection

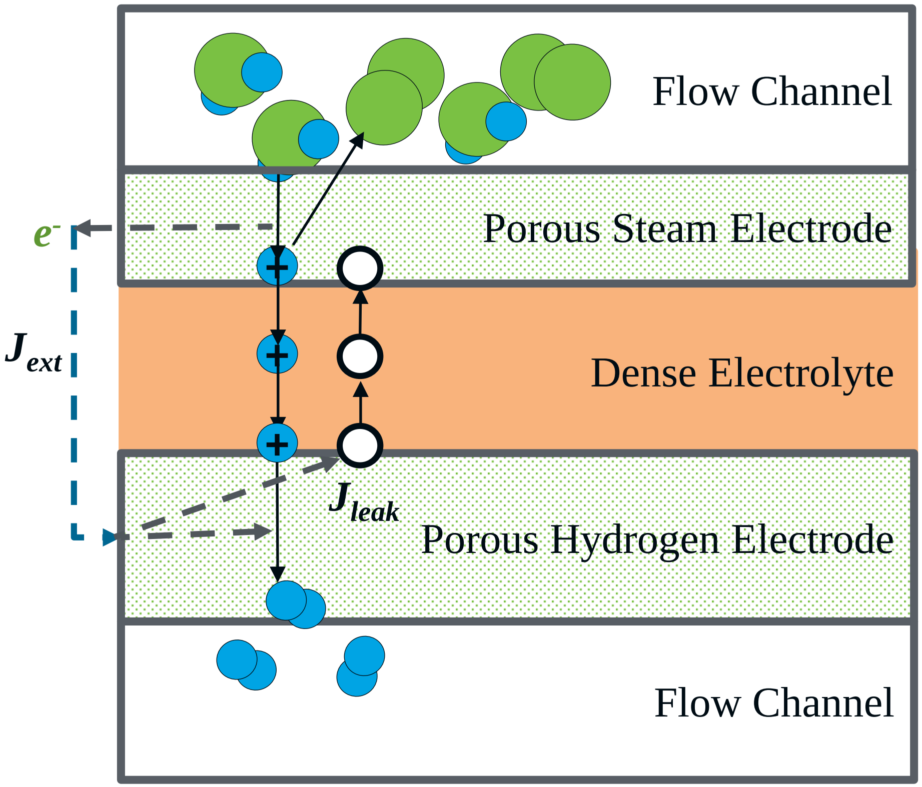
#2: Improving conductivity of BZY20-based electrolyte by element doping (Redox) and sintering process

#3: Optimizing operating conditions for BCZYYb4411 electrolyte

Thermal/Electrochemical Modeling of SOEC (NREL)

Developing electrochemical model for current leakage prediction

Model based on a recent paper on H-SOFC current leakage*



Steam-Electrode:
Species: H_2O, O_2, Equation: Fick's Law
BCs: Species concentrations

Interface + Electrolyte:
Species: H^+, $h^{\cdot}$, $V^{\cdot\cdot}$, O^x
Equation: charge, ion, hole, vacancy
BCs: Equilibrium and defect chemistry.

H_2-Electrode
Species: H_2, Equation: Fick's Law
BCs: RHS: $[H_2] = [H_2]_{bulk} + \frac{\tau}{2FD_{eff}} J$

* Reference:[1] Zhang, J. H., Lei, L. Bin, Liu, D., Zhao, F. Y., Ni, M., and Chen, F., "Mathematical Modeling of a Proton-Conducting Solid Oxide Fuel Cell with Current Leakage," J. Power Sources, 400(2018), pp. 333–340.

Model Results: Leakage Current

- Leakage current occurs in the H_2E as electrons and holes re-encounter each other after leaving the steam electrode:

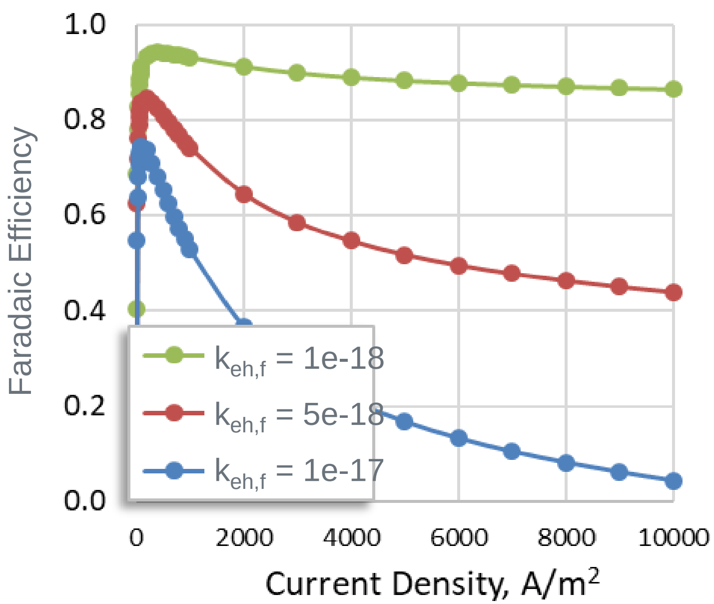
$$O_O^X \rightleftharpoons O_O^{\bullet} + e'$$

- This can be modeled using a mass-action type source term, which allows the leakage current to be expressed as:

$$i_{leak} = \frac{F}{S_C}\left(k_{eh,f} - k_{eh,b}\frac{iS_C}{F}[O_O^{\bullet}]\right)$$

where $k_{eh,f}$ is a tuning parameter to be determined from experimental data

- Leakage becomes worse at higher current densities, and reduces the Faradaic efficiency of the cell



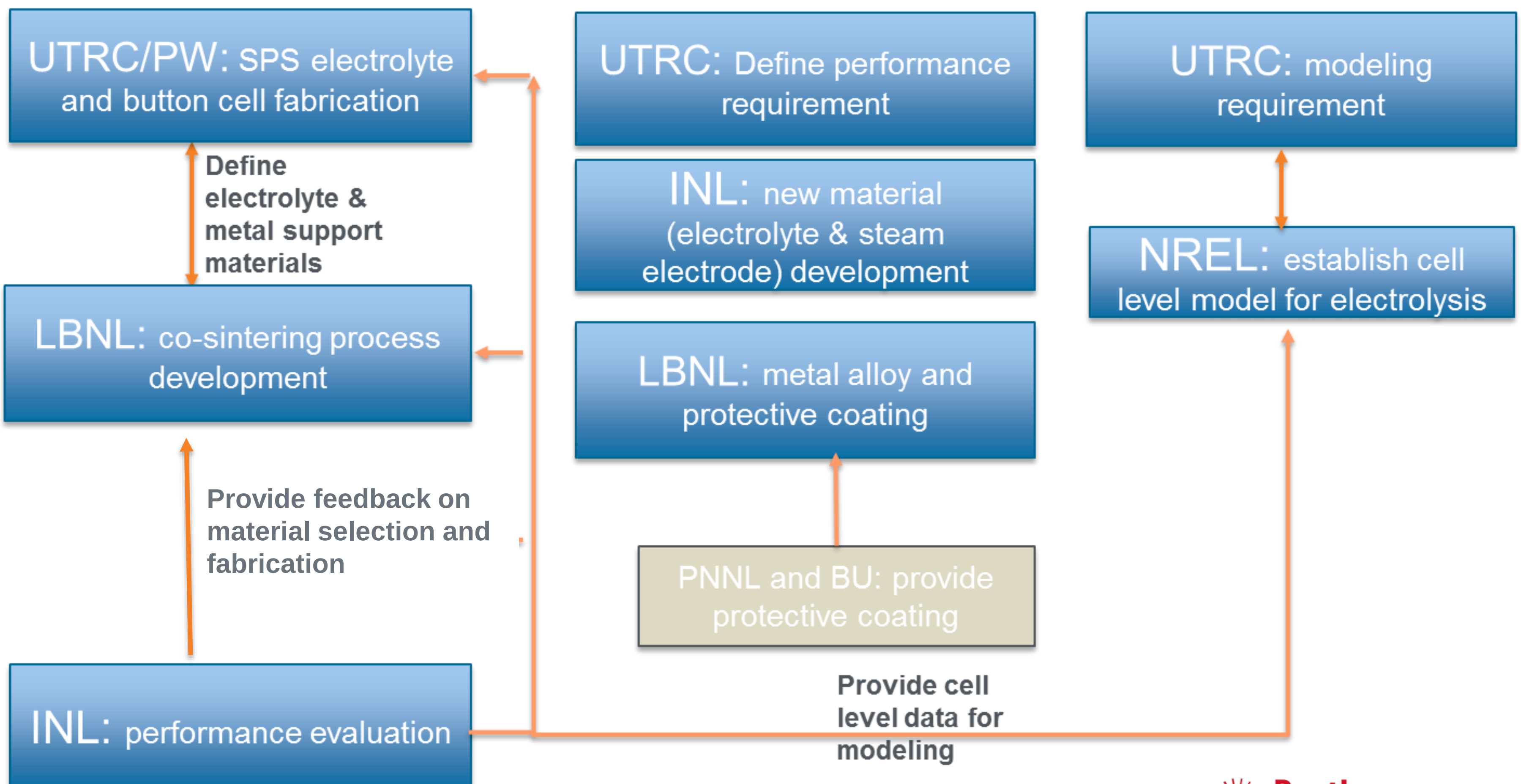
Collaborations

Monthly telecom to exchange ideas and results

Low cost cell fabrication

Material development for performance and durability

Establish Electrochemical modeling



Proposed Work

- Metal-supported cell fabrication (UTRC/LBNL)
  - Continuing optimization of SPS process for a fully dense electrolyte.
  - Fabricate co-sintered bilayer and full button cells with tapecasting for thinner and crack-free layers.
  - Fabricate metal cells and demonstrate performance

- Continue performance optimization of BYZ-based cells (INL)

- Further improving p-SOEC current leakage model and validating model prediction with the experiment results (NREL/INL)

Summary

- Metal-supported cell fabrication
  - Demonstrated porous electrode layer with desired porosity and composition by SPS.
  - Further optimization of SPS electrolyte is in progress.
  - Sintering aid for lower T co-sintering was identified.
  - Co-sintered bilayer and full button cells to be fabricated with tapecasting for thinner and crack-free layers.

- Performance optimization of BYZ-based cells (INL)
  - FE decreased with increasing Ce doping in BYZ. There is probably an optimum Ce concentration to achieve high performance and high efficiency.
  - A higher FE can be achieved through higher steam concentration, composition optimization, and cell layer design.

- Established p-SOEC current leakage model, model predicted FE vs. current density trend was consistent with the experiment results.

Selected Publications & Presentations

Publications:

- R. Wang, Z. Sun, J.-P, Choi, S. N. Basu, J.W. Stevenson, M.C. Tucker,Ferritic stainless steel interconnects for protonic ceramic electrochemical cell stacks: Oxidation behavior and protective coatings, International Journal of Hydrogen Energy, 47 (2019) 25297-25309 https://doi.org/10.1016/j.ijhydene.2019.08.041
- E. Dogdibegovic, F. Shen, R. Wang, I. Robinson, G.Y. Lau, M.C. Tucker, Progress in Metal-Supported Solid Oxide Fuel Cells and Electrolyzers With Symmetric Metal Supports and Infiltrated Electrodes, ECS Transactions, 91 (1) 877-855 (2019) 10.1149/09101.0877ecst
- R. Wang, E. Dogdibegovic, G.Y. Lau, M.C. Tucker, Metal-Supported Solid Oxide Electrolysis Cell with Significantly Enhanced Catalysis, Energy Technology, 7 (2019) 1901154 https://doi.org/10.1002/ente.201801154
- R. Wang, G.Y. Lau, D. Ding, T. Zhu, and M.C. Tucker, Approaches for co-sintering metal-supported proton-conducting solid oxide cells with Ba(Zr,Ce,Y,Yb)O3-δ electrolyte, International Journal of Hydrogen Energy, 44 (2019) 13768-13776 doi.org/10.1016/j.ijhydene.2019.03.181
- Hanping Ding, Wei Wu, Dong Ding et al. “Self-Sustainable Protonic Ceramic Electrochemical Cells Using A Triple-Phase Conducting Electrode for Hydrogen and Power Production”. Nature Communications. Accepted manuscript.
- Hanping Ding, Wu Wu, Dong Ding. “Advancement of Proton-Conducting Solid Oxide Fuel Cells and Solid Oxide Electrolysis Cells at Idaho National Laboratory (INL)”. ECS Transactions. 91 (2019) 1029-1034.

IPs:

- He Ting, Dong Ding, Wei Wu. Methods and systems for hydrogen gas production through water electrolysis, and related electrolysis cells. US Patent Application (16/483,631), 2019.
- Dong Ding, Hanping Ding, Wei Wu and Chaojiang. Electrochemical cells for hydrogen gas production and electricity generation, and related structures, apparatuses, systems, and methods. PCT Application (PCT/US19/58287), 2019
- Dong Ding, Hanping Ding, Wei Wu and Chaojiang. Reversible Solid oxide Cell Operated with A High-Performing and Durable Anode Material for hydrogen and power generation at intermediate temperatures. US Patent Application (16/560, 719), 2019.

Acknowledgement

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ElectroChem Ventures	John Yamanis
LBNL	Mike Tucker, Grace Y. Lau
INL	Dong Ding, Hanping Ding
NREL	Zhiwen Ma, Jacob Wrubel