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

Project ID # p154

Tianli Zhu
United Technologies Research Center

5/1/2019

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, United Technologies Research Center

Partner organizations: UConn, ElectroChem Ventures

Award #	EE0008080
Start/End Date	10/1/2017 – 3/31/2021
Year 1 Funding	$0.31 M
Year 2 Funding	$0.57 M

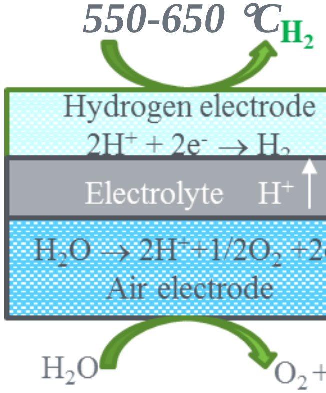
Project Vision

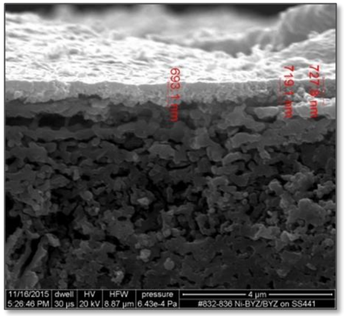
Develop a highly efficient and cost competitive high temperature electrolysis for H_2 generation, by a thin-film, high efficiency and durable metal-supported solid oxide electrolysis cell (SOEC) based on proton-conducting electrolyte at targeted operating temperatures of 550-650ºC.

Project Impact

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

Proton conducting electrolyzer 550-650 ℃





Thin film deposition for electrolyte

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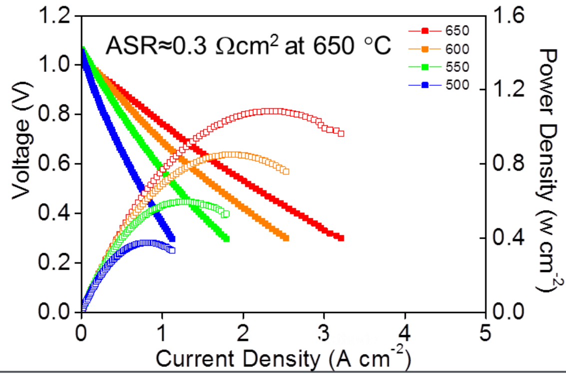
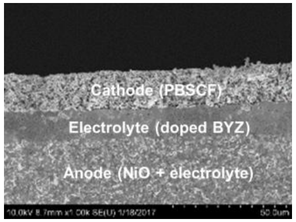
Approach- Summary

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

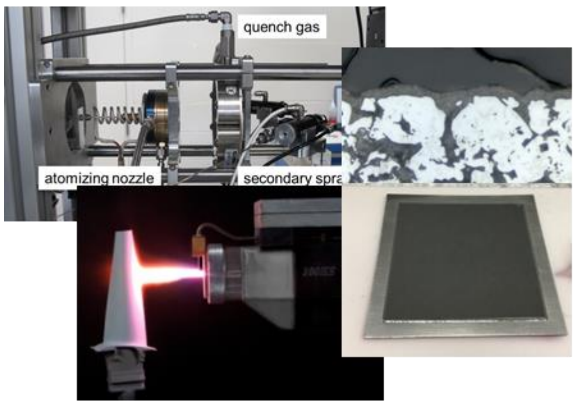
Partnerships

- 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

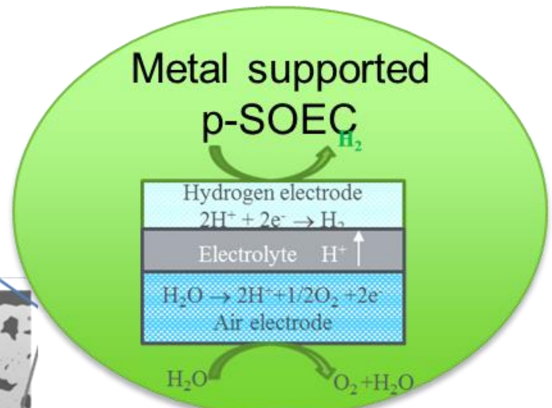
Approach- Integrating Manufacturing, Material & Modeling

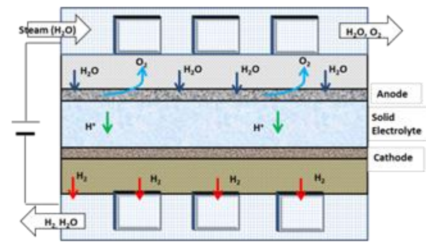
Phase 1 GO/NO GO: SOEC cell meets the performance target of >0.8A/cm^2 at 1.4 V , and <1%/1000h at T≤650 °C.

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



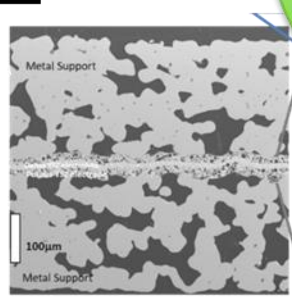
Metal alloy & coating selection
LBNL: oxidation study





Electrochemical modeling
NREL

Co-sintered metal cell
LBNL



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

Relevance & Impact

Project Objectives

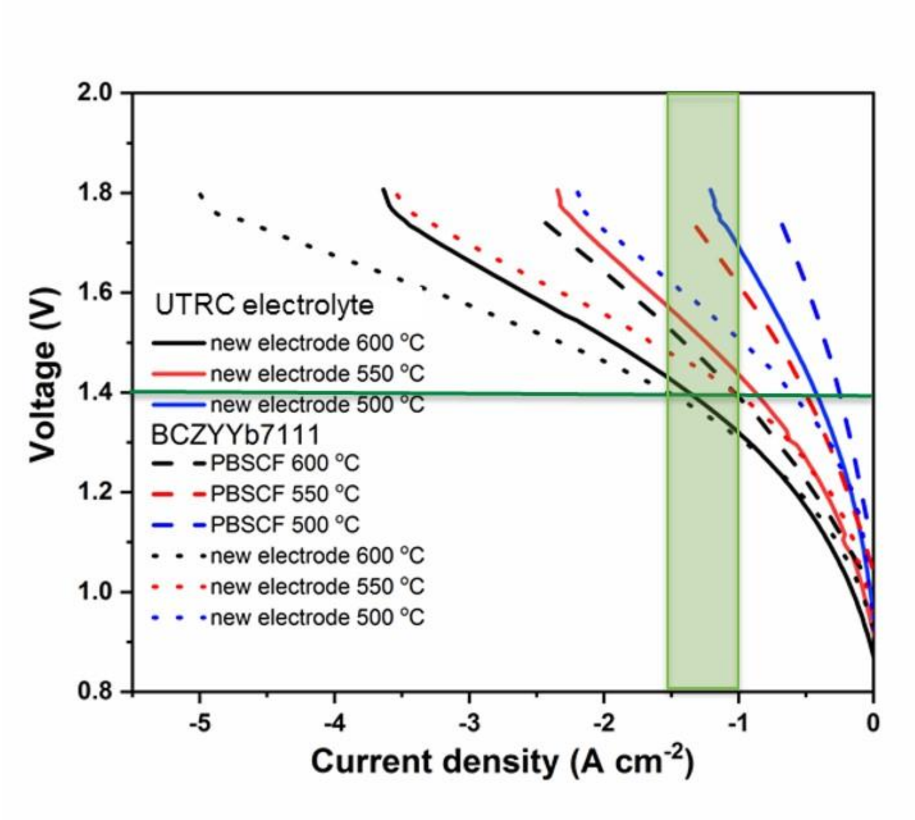
Develop highly efficient and cost competitive high temperature electrolysis for H_2 generation, by a high efficiency and durable metal-supported solid oxide electrolysis cell (SOEC) based on proton-conducting electrolyte at targeted operating temperatures of 550-650ºC. Focus on developing a low cost,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

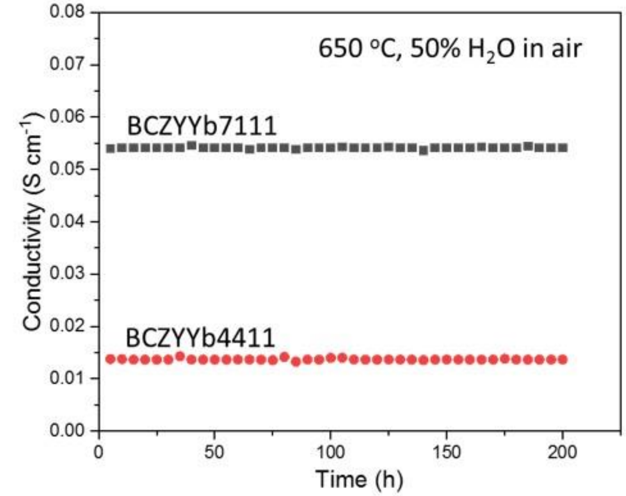
Project Impact

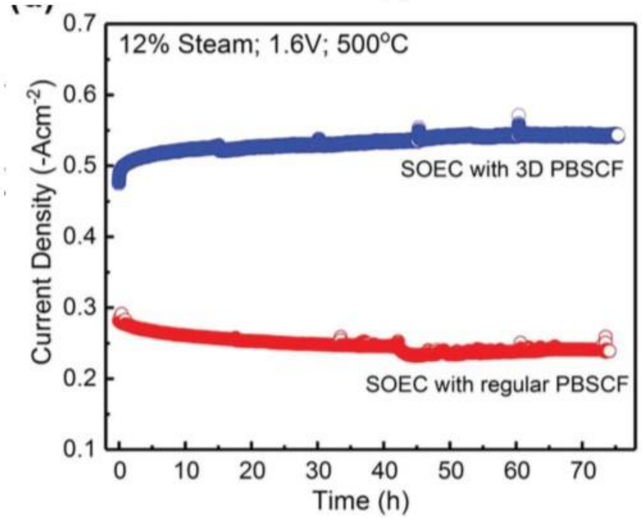
Metric	State of the Art	Phase 1	Project Target
SOEC Performance	**1 A/cm^2 at 1.4 V** at **800 ºC**	**>0.8 A/cm^2 at 1.4 V** at **650 °C** on button cells with SPS electrolyte	**≥1.0 A/cm^2 at 1.4 V** on button cells at T ≤ 650 ºC; **≥0.8 A/cm^2 at 1.4 V** at 650 ºC on metal-supported cells by plasma spray fabrication
SOEC Durability	(1-4)% per 1000 h	<1%/1000h	<0.4% per 1000 h (~4 mV per 1000 h)
H_2 production Cost	>$4/kg H_2	$1.4/kg H_2	$2/kg H_2 based on cost analysis

High Electrolysis Performance on p-Electrolyte and Electrode Materials (INL)

H_2 electrode-supported button cells with *BZCY-based electrolyte + PBSCF or INL's new steam electrode:* ≥ 1.0 A/cm^2 at 1.4 V and durability up to 200 h







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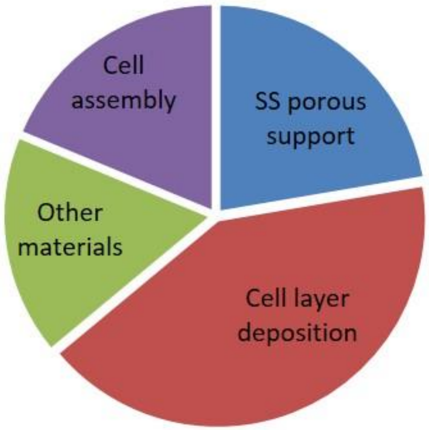
Low Cost Fabrication by Plasma Spray

Suspension plasma spray (SPS)-based deposition process provides a path to low cost stack.

Automated SPS process examples capable for multi cell and multilayer coating

- Electrolyte: Y and Yb-doped barium-zirconate-cerate (BZCYYb)
- Electrode: Ni+electrolyte and Lanthanum strontium cobalt ferrite (LSCF)
- 100 cm^2 cell

Low cost cell fabrication ~$9/cell

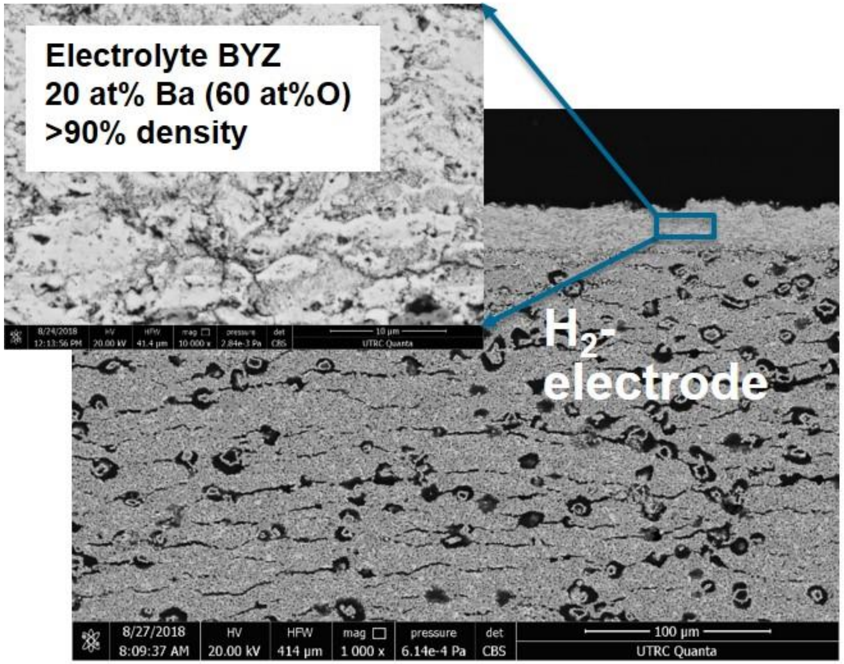


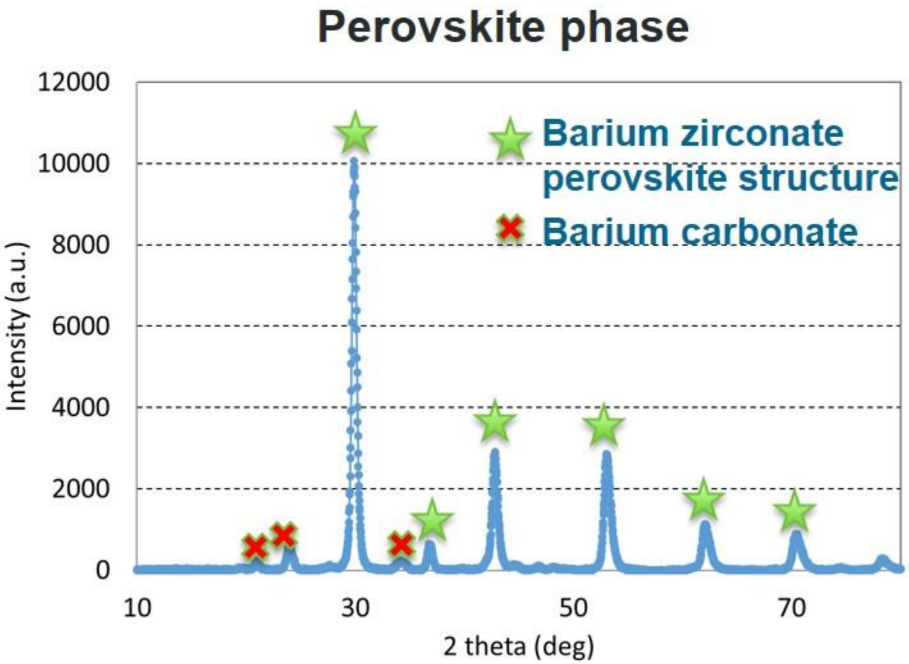
<u>$1.35/kg H_2</u>

(650°C, ASR=0.3 Ωcm^2, 1.0 A/cm^2, 100% Faraday efficiency $0.039/kWh electricity)

Developed Electrolyte Fabrication by Suspension Plasma Spray (SPS)

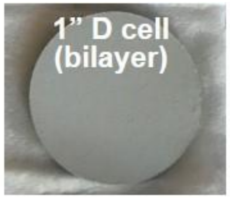
Demonstrated BYZ-based perovskite structure, AND stoichiometric amount of Barium content in electrolyte layer

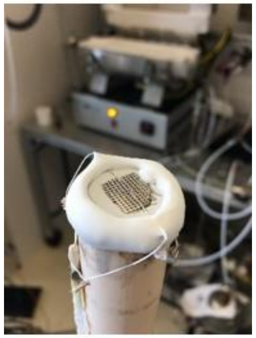




Demonstrated SPS Electrolyte Performance

SPS Electrolyte on sintered Hydrogen-electrode

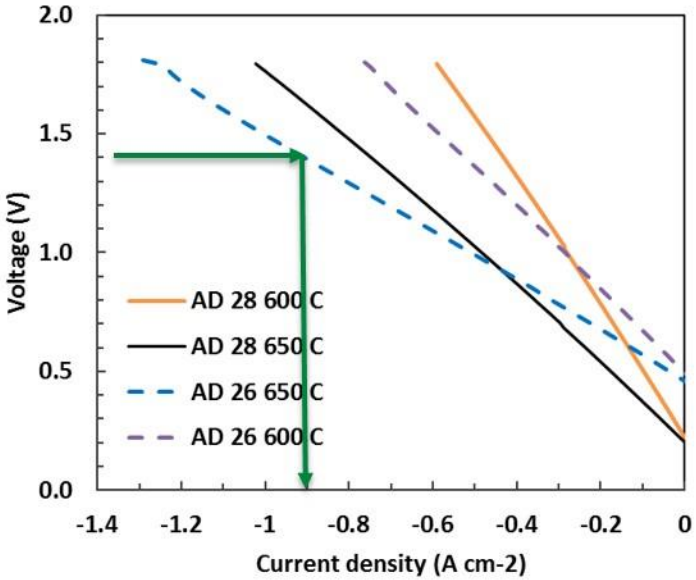




Test at INL

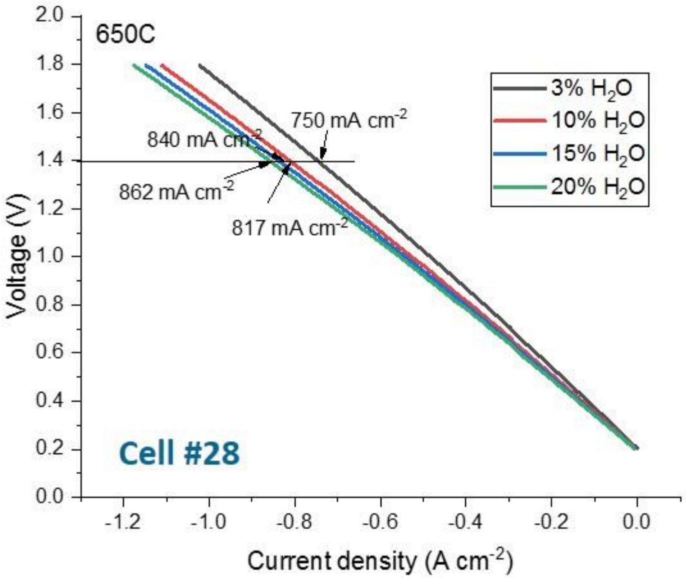
Cell with SPS electrolyte exceeded Phase 1 performance target (0.8 A/cm^2 at 1.4V & ≤650°C)

Cell performance, 3% Steam



3%Steam/Oxygen, 20%H2 as sweeping gas

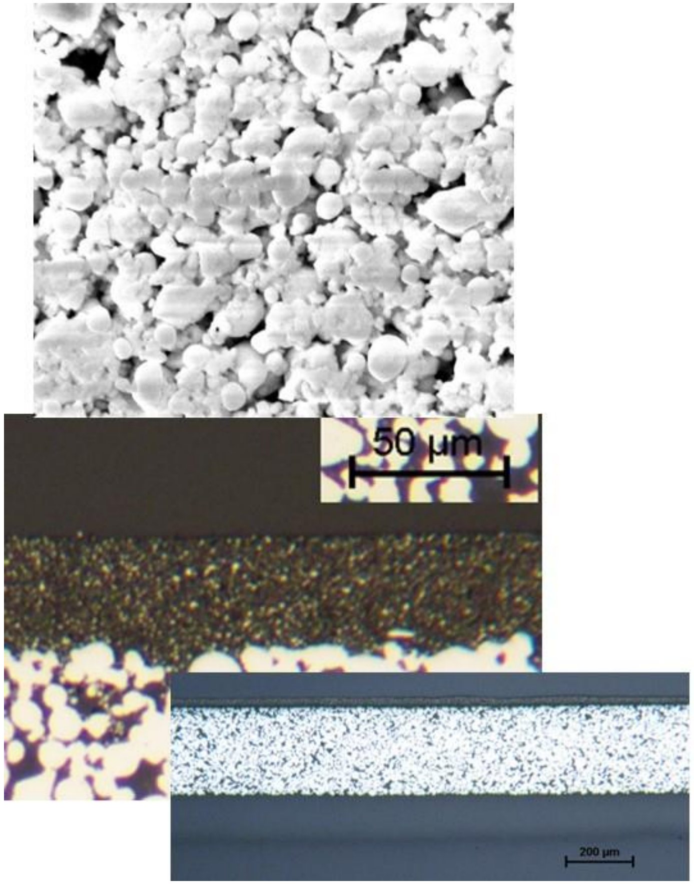
Steam concentration effect



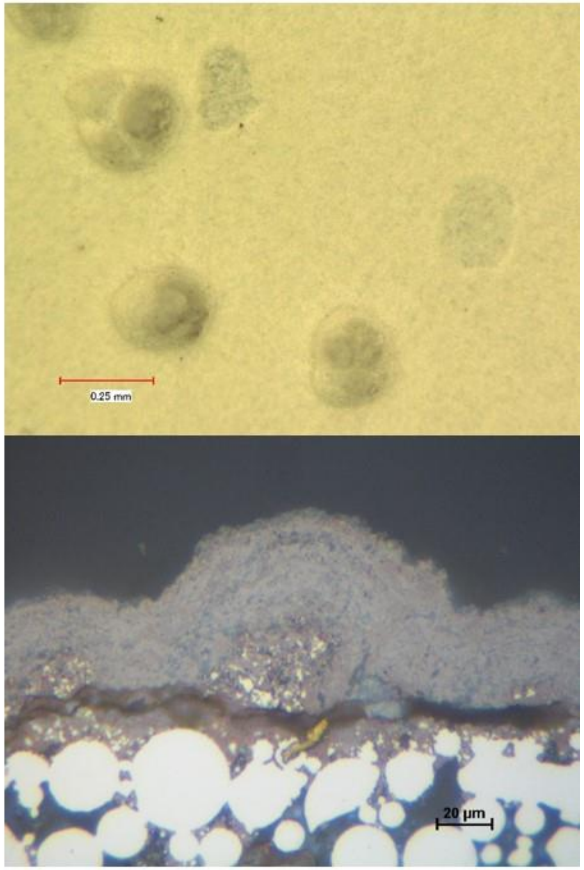
Metal Supported Cell Fabrication Process (SPS)

Electrolyte deposition by SPS feasible, defects due to H_2 electrode erosion

As sintered H_2 Electrode (Ni-Electrolyte) by doc blade

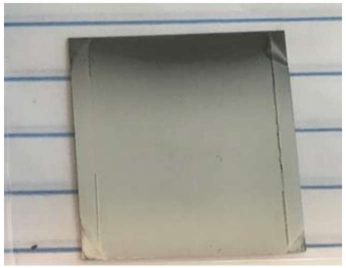


Electrolyte deposition
Defects due to anode erosion

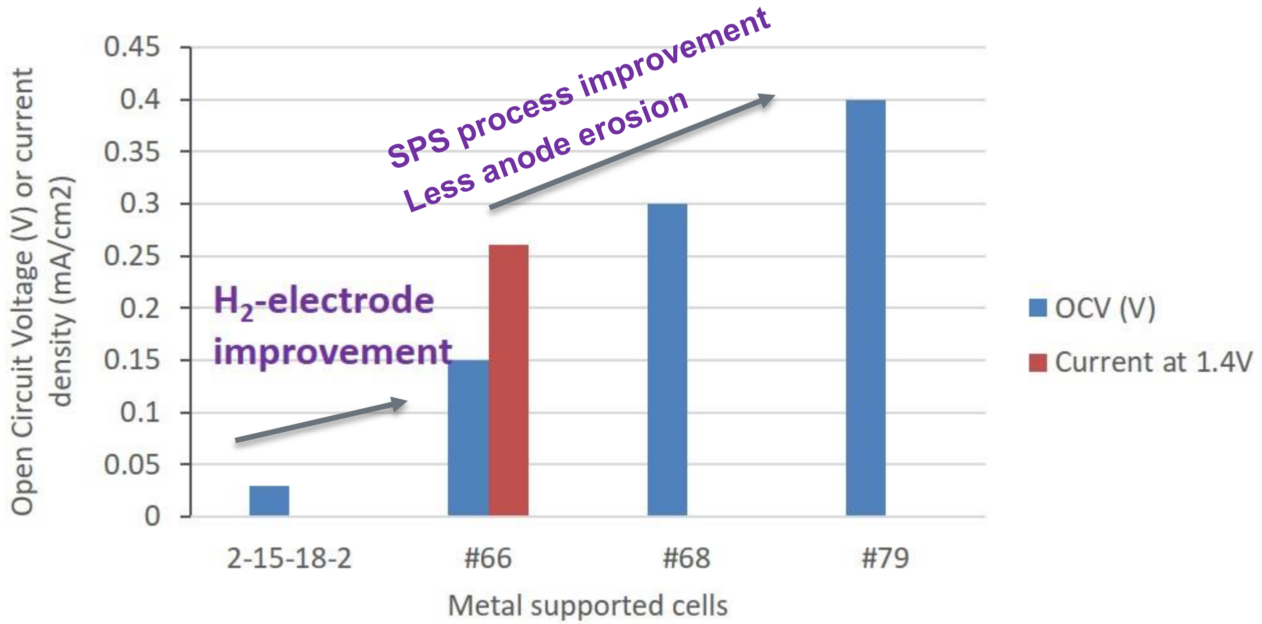


Progress in Metal Supported Cell Fabrication

3cmx 3cm
cell (bilayer)



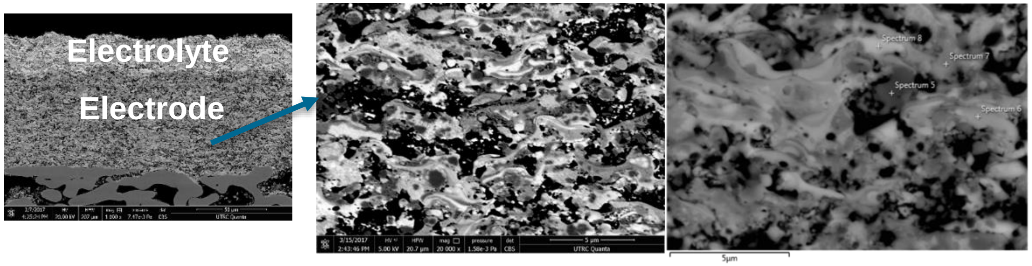
Use same SPS processes for ceramic cells



Path forward: SPS electrode and electrolyte

0.25 A/cm² at 1.4V → **Target: ≥ 0.8 A/cm² at 1.4V, 1.0 OCV**

- *Stronger H_2-electrode*
- *Optimized electrolyte*



NiO+doped barium zirconate, 60 micron, ~20% porosity, well adhered to metal support

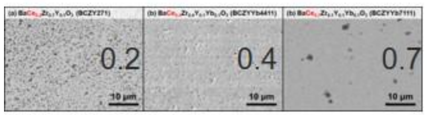
BZCY-steel Co-Sintering (LBNL)

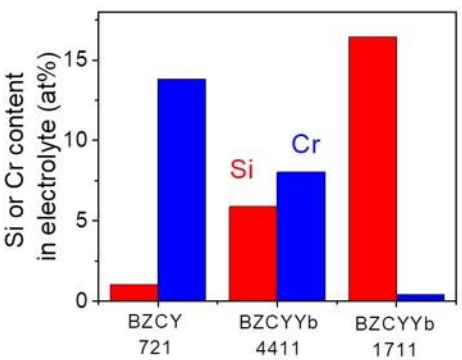
Challenges:

Processing conditions dictated by stainless steel: 2% Hydrogen, 1450°C

Si migration from steel to BZCY → $BaSiO_3$

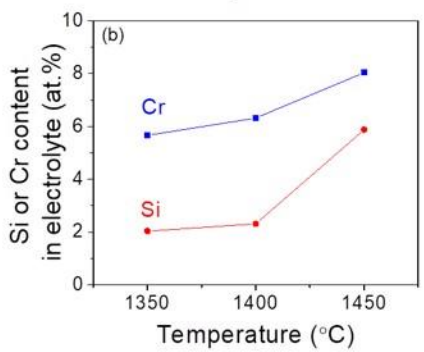
Ce/Zr ratio



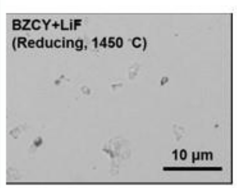


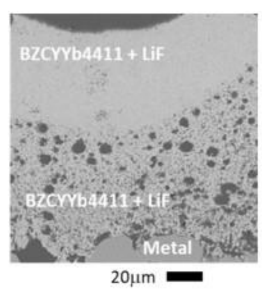
Reduce sintering temp

Si, Cr migration is sensitive to temperature



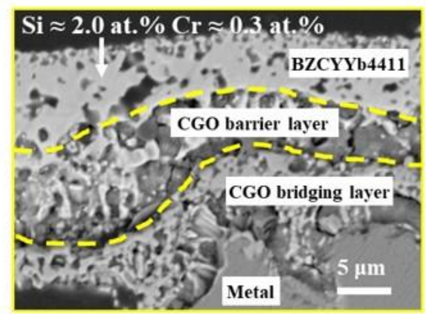
Need sintering aids



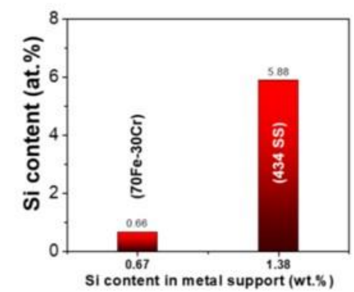


Barrier layer

Reduces Si, Cr migration



Low-Si metal



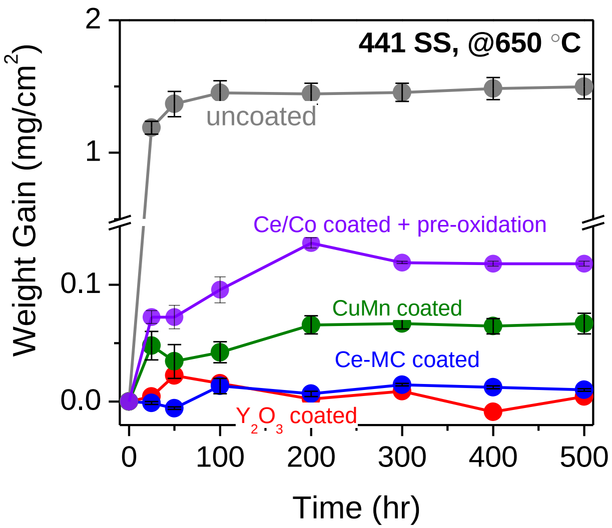
BP2: Combine these approaches to:
- limit Si content in metal
- limit migration of Si

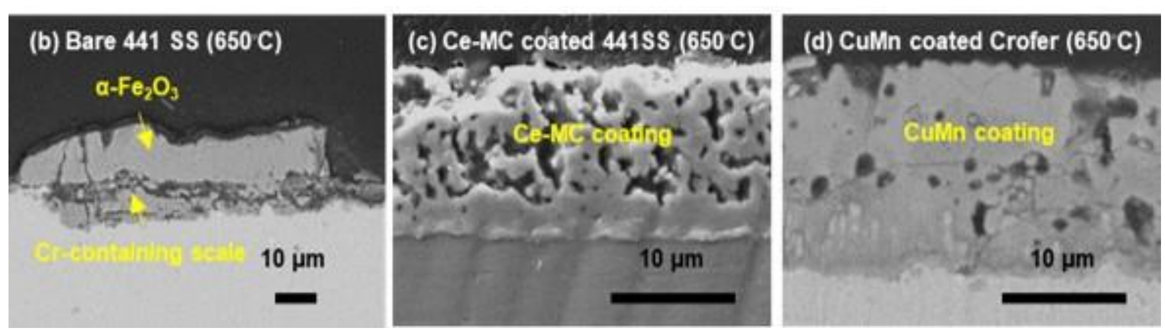
Oxidation for Interconnect Stainless Steel (LBNL)

Various coating/steel combinations are acceptable

50% steam/air 650°C

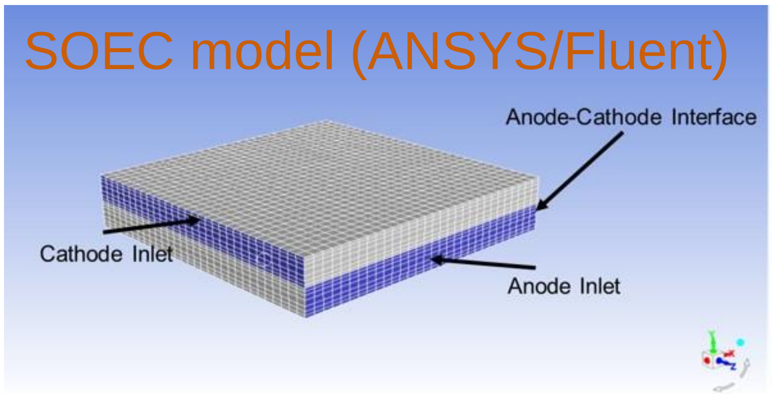
Coating condition	Rapid breakaway oxidation?		
	430 SS	441 SS	Crofer 22
Uncoated	Yes	Yes	Yes
Pre-oxidized	Yes	Yes	Yes
Y_2O_3-coated	No	No	Yes
Ce-MC-coated	Yes	No	No
$CuMn_{1.8}O_4$-coated	No	No	No
Ce/Co-coated	-	No	-





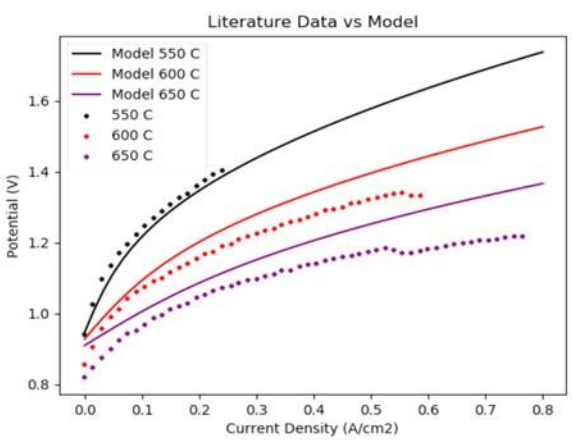
Thermal/Electrochemical Modeling of SOEC (NREL)

Developed electrochemical model and cell model ready for SOEC characterization and simulation, and able to model cell/stack performance for material scale up

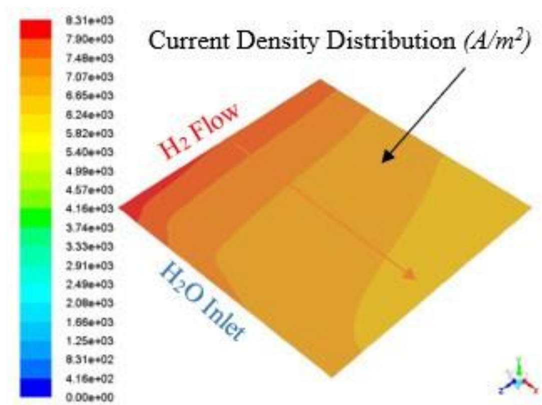


- Focused on proton-conducting SOEC modeling with reference to broad SOEC/SOFC modeling works.
- Calibrated various cell overpotentials vs. operating conditions.
- Modeled the variation of V-I curves.

Model calibration using literature data



Model simulation of parameter distribution (2"X 2" cell)

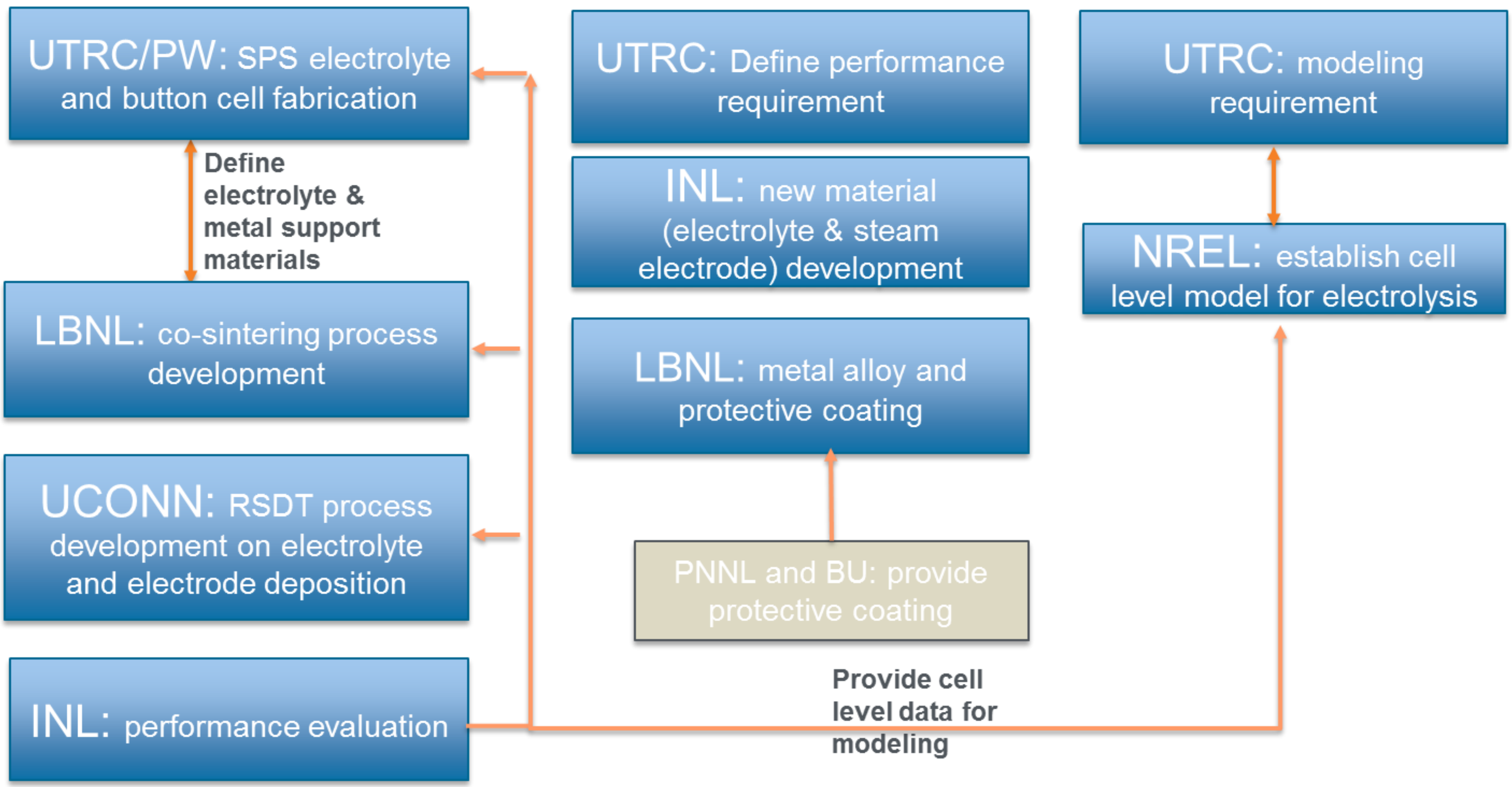


Collaborations

Low cost cell fabrication

Material development for performance and durability

Establish Electrochemical modeling

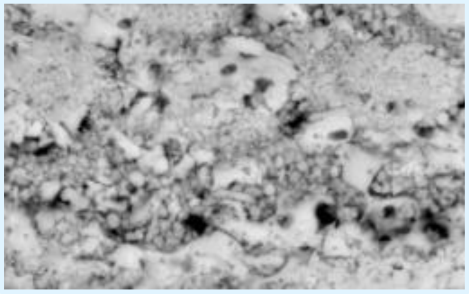


Remaining Challenges

- Challenges:
  - Further densification of the electrolyte by SPS

    Achieve fully dense layer while obtaining desirable composition;

    Feedstock suppliers



Non-ideal feedstock resulted in less dense area

  - Low cost and robust H_2-electrode fabrication

    Traditional sintering process limited by metal support

  - Durability of BYZ-based cells

Proposed Future Work

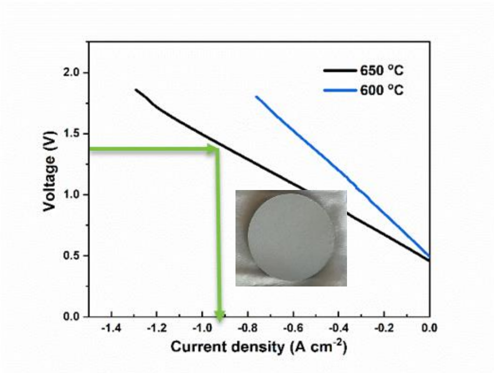
- Continue development in metal supported cell fabrication
  - Further optimization of electrolyte by SPS
    - Feedstock optimization (working with suppliers)
    - Process optimization with PW and SPS Vendor
  - Evaluate low cost H_2-electrode fabrication
  - LBNL: further development of co-sintering process; infiltration for performance improvement of plasma sprayed cell
- Durability of BYZ-based cells (INL)
  - Material optimization
  - Durability test of PBSCF|BYZ-based cells
- Establish p-SOEC model parameters based on cell performance data; characterize cell performance, and guide cell design (NREL)
- Update cost analysis of the cell manufacturing process

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

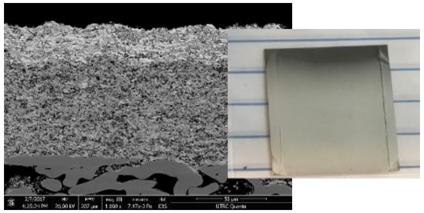
Project Summary

Low cost cell fabrication

- ✓ ***Demonstrated SPS Electrolyte process and performance***
  Identified paths to further improvement



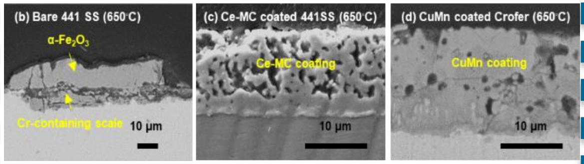
- ***Metal cell fabrication***
  - ***Path forward: Mechanically strong anode***



- ***Identified paths to Co-sintering of BYZ-based cell***

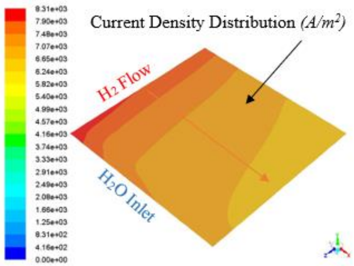
Metal alloy & coating selection

- ✓ ***Identified potential combination of alloys and protective coatings***



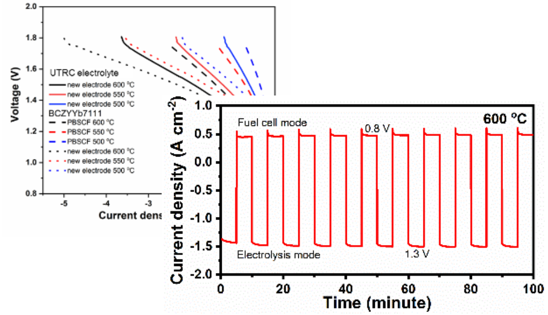
Electrochemical modeling
NREL

- ✓ ***Established cell level model***



Material optimization & cell testing

- ✓ ***Demonstrated short term stability of PBSCF|BCZYYb cells***
- ✓ ***Optimized steam electrode performance***
- ✓ ***Demonstrate reversibility of p-SOEC cell***



Acknowledgement

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Organization	Team Members
UTRC	Tianli Zhu, Justin Hawkes, Mike Humbert, Sean Emerson
ElectroChem Ventures	John Yamanis
UCONN	Radenka Maric, Leonard Bonville, Ryan Ouimet
LBNL	Mike Tucker, Ruofan Wang, Conor Byrne
INL	Dong Ding, Hanping Ding
NREL	Zhiwen Ma

Publications & Presentations

Presentations:

- Ruofan Wang, Conor Byrne, Michael C Tucker, "Proton-Conducting Ceramics for Metal-Supported Solid Oxide Cells", 19th International Conference on Solid State Protonic Conductors, 9/21/2018, Stowe, VT
- Dong Ding, Hanping Ding, et al. "A New Triple-Conducting Material for Efficient Hydrogen Production in Proton Conducting Solid Oxide Electrolysis Cells", 234^{th} ECS conference, Cancun, Mexico, Sept 30 – Oct 4, 2018
- Hanping Ding, Dong Ding, et al. "Novel Triple Conducting Electrode for Fast Hydrogen Production in Protonic Ceramic Electrochemical Cells", 43^{rd} international conference and exposition on advanced ceramics and composites, ICACC 2019, Daytona Beach, FL, Jan 27 – Feb 1, 2019

Publications:

- Ruofan Wang, Grace Y. Lau, Dong Ding, Tianli Zhu, Michael C Tucker, "Approaches for Co-Sintering Metal-Supported Proton-Conducting Solid Oxide Cells with Ba(Zr,Ce,Y,Yb)O3 Electrolyte", International Journal of Hydrogen Energy, accepted
- Ruofan Wang, Conor Byrne, Michael C Tucker, "Assessment of Co-Sintering as a Fabrication Approach for Metal-Supported Proton-Conducting Solid Oxide Cells", Solid State Ionics 332 (2019) 25–33
- Ruofan Wang, Michael C Tucker, "Oxidation of metallic interconnects for proton-conducting electrolysis cells", J. Power Sources, in preparation
- Wei Wu, Hanping Ding, Dong Ding, et al. "Hydrogen Production: 3D Self-Architectured Steam Electrode Enabled Efficient and Durable Hydrogen Production in a Proton-Conducting Solid Oxide Electrolysis Cell at Temperatures Lower Than 600 °C" Advanced Science, 2018 https://doi.org/10.1002/advs.201870070
- Hanping Ding, Dong Ding, et al. "Superior Self-Sustainable Protonic Ceramic Electrochemical Cells Using a Novel Triple-Phase Conducting Electrode for Hydrogen and Power Production", Advanced Materials, under review

Submitted NREL Record of Invention: Ma, Z., A novel electrochemical stack design for electrolysis or fuel cells, NREL Record of Invention ROI-18-65. 2018.