Project ID: p152

Energy Materials Network
U.S. Department of Energy

HydroGEN
Advanced Water Splitting Materials

Proton-Conducting Solid Oxide Electrolysis Cells for Large-scale Hydrogen Production at Intermediate Temperatures

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Olga Marina, Jeff Stevenson - Pacific Northwest National Laboratory

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Technical Contributors

UConn	Prabhakar Singh	Professor
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PNNL	Jeffery Stevenson	Laboratory Fellow
	Olga Marina	Chief Scientist
INL	Dong Ding	Senior Materials Engineer
	Henping Ding	Postdoctoral Fellow
NREL	Andriy Zakutayev	Staff Scientist
	David Ma	Staff Scientist

Program Manager: Dr. David Peterson, Department of Energy

Project Overview

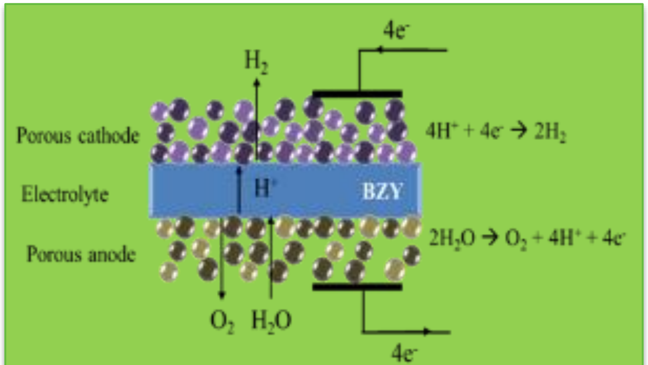
Project Partners

UConn: Prabhakar Singh (PI), Boxun Hu, Ugur Pasaogullari (Co-PI)
PNNL: Jeff Stevenson and Olga Marina (Co-PI)

Award #	EE0008078
Start Date Project End Date	10/1/2017 9/30/2020
Year 1 Funding* Year 2 Funding*	$312,500 $460,250

Project Vision

Identify novel materials and processing techniques to develop cost effective and efficient proton-conducting solid oxide electrolysis cells (H-SOECs) for large-scale hydrogen production at intermediate temperatures (600-800˚C) to meet DOE cost and performance targets.



- ➢ Higher conductivity (>0.01 s/cm) obtained
- ➢ Densification at <1400˚C achieved
- ➢ Uniform bulk phase composition obtained

Project Impact

(a) Innovation in materials chemistry – electrolyte and electrode formulations
(b) Use of non-noble and non-strategic cell and stack component materials
(c) Bulk, interface, and surface optimizations to achieve low ASR
(d) High proton-conductivity with a low sintering temperature (<1450˚C)
(e) Operating current density (>1 A/cm²) with the performance degradation rate not to exceed the DOE performance metric (< 4 mV/1000 h)

**this amount does not cover support for HydroGEN resources leveraged by the project (which is provided separately by DOE)*

Approach- Summary

Project Motivation

- Extensive background in HT/IT electrochemical systems
- Experience with functional ceramics, electrodics, electrochemical testing, performance degradation and data analysis
- Well established laboratory capabilities in materials processing and characterization
- On going research in SOFC,SOEC and H-SOEC

Key Impact

Metric	State of the Art	Proposed	Actual
Conductivity *(S/cm)*	*~10^{-3}*	*10^{-2}*	*4 x 10^{-2}*
Sintering temp. (˚C)	*>1450*	*≤1350*	*1350*
Thickness (µm)	>25	~15-20	20

Barriers

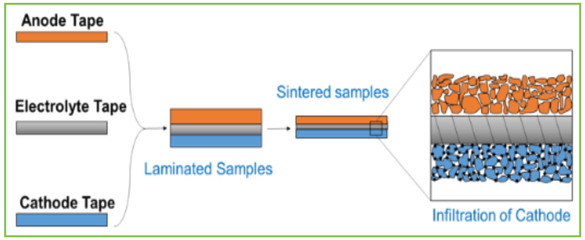
- High sintering temperature for electrolyte densification (>1400˚C)
- Decrease in conductivity during processing and operation
- High temperature gas sealing and operation with thermal cycling
- Complex processing and fabrication techniques
- Chemical and structural instability in presence of Cr, and Si contaminants

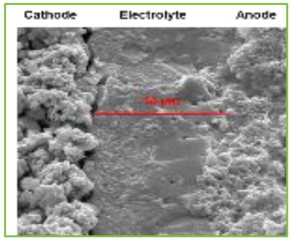
Partnerships

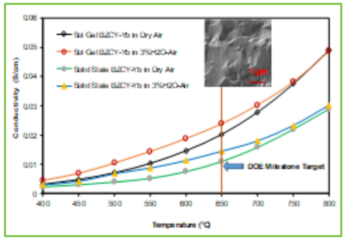
The research team collaborates with PNNL in developing and testing H-SOEC. Team will heavily leverage EMN network. We will work with NREL, INL and LBNL for the optimization of electrolyte chemistry.

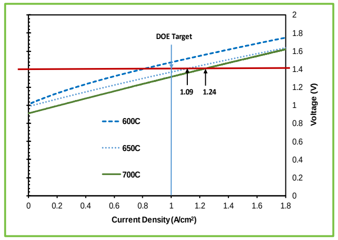
Approach- Innovation

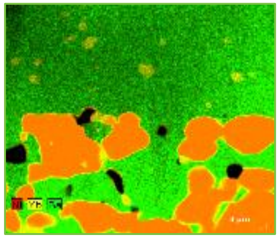
- Our approach for H-SOEC development leading to large scale manufacturing and commercialization will rely on utilizing EMN Network and core experimental and computational capabilities at NREL, INL and PNNL.
- Materials and Processes: Innovation in materials and processing techniques are anticipated to develop electrolyte formulations capable of densification (96-98%density) below 1400˚C in oxidizing atmospheres, meet electrical conductivity target (>0.01S/cm) and demonstrate bulk structural and chemical uniformity.
- Synthesis and fabrication processes: Cells utilizing tape cast multi-layer laminated electrolyte (10-20 µM) and electrode (integrated backbone, infiltration, thin film processing) will be sintered and electrically tested. Process will be optimized to achieve target ASR and current density to meet the overall project goals (1 A/cm^2 @1.4 V, 700˚C).
- Computational analysis: Electrolyte and electrode materials composition will be optimized for densification, proton conductivity and structural stability. Select electrode and electrolyte materials will be synthesized and electrochemically tested.
- Electrode poisoning and performance degradation mitigation: Electrode delamination and Cr assisted poisoning mechanisms will be developed. Mitigation approaches will be identified.











Relevance & Impact

- The proposed research program will develop cost effective and efficient solid oxide electrolysis cells consisting of novel thin film proton conducting electrolyte and tailored electrode materials for large-scale direct production of dry and pure hydrogen at intermediate temperatures using renewable energy. Developed materials will be electrically tested under SOEC systems operating conditions and mechanistic understanding for the performance degradation will be obtained.

- The research effort will benefit the global hydrogen producers, users and SOEC materials manufacturers. The developed technology will help the systems integrators to develop cost effective and stable materials, processing techniques and architectures for demonstrating and deployment of the SOEC technology for sustainable hydrogen production.

- Our approach for H-SOEC development leading to large-scale manufacturing and commercialization will rely on utilizing EMN Network and core experimental and computational capabilities at NREL, INL and PNNL.

- Key innovations include

  a) Computational materials design and optimization for chemically and structurally stable ceramic electrodes and electrolyte (NERL)

  b) Synthesis and fabrication processes for tailoring active components with enhanced catalytic sites and reduced area specific resistance (INL)

  c) Modelling and optimization of proton-conducting SOEC cell/stacks (NERL &PNNL).

  d) Mitigation of electrode delamination and chromium assisted poisoning (UConn).

Accomplishments

- Proton conducting- electrolyte and electrode materials have been selected and synthesized using sol-gel and conventional solid state ceramic processing methods. The powder synthesis process has been validated at 20 gram batch scale for BZY and BZCY-Yb proton-conducting powders.
- BZY and BZCY-Yb electrolyte discs have been prepared using reactive / fugitive sintering aids (nanosized ZnO). Sintering of BZCY-Yb at 1350˚C in oxygen show the densification (>97% density), which is 100˚C lower than the state of the art (1450˚C). The conductivity of sintered BZY and BZCY-Yb measured by 4-probe technique are ~ 0.01 and 0.04 S/cm, respectively.
- H-SOEC full cells with low area specific resistance have been fabricated using thin dense electrolyte (15-20 µm) and porous electrodes using INL node.
- Button cell testing of steam electrolysis in the temperature range of 600-800˚C have been conducted. Electrochemical performance meet the program milestones (1.4 V@1 A/cm^2 and 50-hour performance stability).
- Technical progress and accomplishments meet the program milestones (M1-1, 2-1, M3-1, M4-1 and GNG-BP1).
- The overall program goals of the Budget Period-1 and Go/No-Go Decision have been achieved.

Collaboration: Effectiveness

INL Advanced Materials for Water Electrolysis at Elevated Temperatures (Expert: Dr. Dong Ding)

The INL-UConn collaboration spanned over the topics for the development of dense electrolyte and performance improvement of the anode. Technical discussions have been held with Dr. Ding with focus on materials selection, processing techniques and electrochemical performance evaluation. The tasks for BP1 include:

Task 1: Development of electrolyte densification technique and determination of corresponding ionic conductivities (Q1-Q2).
UConn have received proton-conducting half-cells and full cells (1 cm diameter) from INL for SOEC testing and characterization. The measured conductivity and thickness (~20 µm) of dense electrolyte meets the project milestones. INL also provided large size full cells (1.3 cm) and electrode materials for SOEC testing.

Task 2: Anode microstructural modification for performance improvement (Q3-Q4).
UConn have discussed the use of INL capability to fabricate full cells with porous electrodes and thin electrolyte using HT-R2R technique with UConn-made electrode and electrolyte materials). A UConn researcher visited INL labs for two weeks. The samples fabricated by (High Temperature Roll-to-Roll, HT-R2R) have been sintered and tested, using INL's (High Throughput Materials Testing, HTMT) to achieve target ASR and current density to meet the overall project goals.

The tasks for BP2 include:
Task 3. Fabricate multilayer cells using roll to roll tape casting and sintering (2"X2").

Task 4: Optimize electrode chemistry and structure.

Collaboration: Effectiveness

NERL High-Throughput Experimental Thin Film Combinatorial Capabilities (Experts: Drs. Andriy Zakutayev, John Perkins, David Ginley, David Ma)

Technical discussion held with Dr. Andriy Zakutayev has identified scope of work for the development of electrolyte materials for sintering and conductivity optimization.

The tasks for BP1:

Task 1: The HTE combinatorial node at NREL is responsible for the investigation of combinatorial libraries of Y-substituted $BaZrO_3$ (BZY). Other minor additives (e.g. transition metals, alkali earth, rare-earth) that have a potential to improve BZY's sinterability without inducing secondary phases or impeding protonic and electronic charger transport.

Task 2: The films are characterized at NREL for composition, structure, morphology, and electrical properties at room temperature. These NREL thin film results have been compared to the UConn bulk synthesis results, in order to determine how thin film morphology and ceramic sinterability correlate with each other. At later phases of the project, optimized thin film compositions may be deposited at NREL on ceramic or metallic supports provided by UConn.

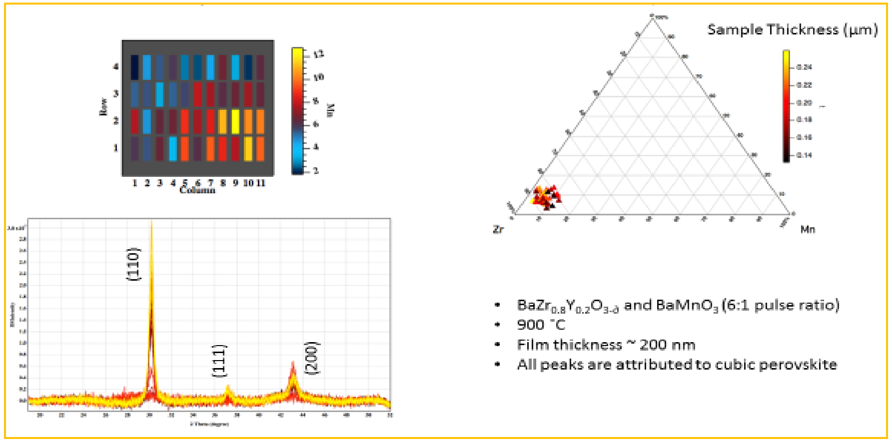
The tasks for BP2:

Task 3: Using NREL combinatorial node, develop sintering aids to decrease sintering temperature.

Task 4: Conduct diffusion couple study to establish interfacial stability

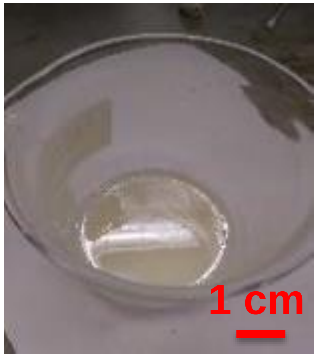
Task 5:Develop and calibrate a SOEC electrochemical model based on cell materials and single cell testing data.

Task 6: Economic model by predicting performance parameters including temperature, current density, and species distributions.



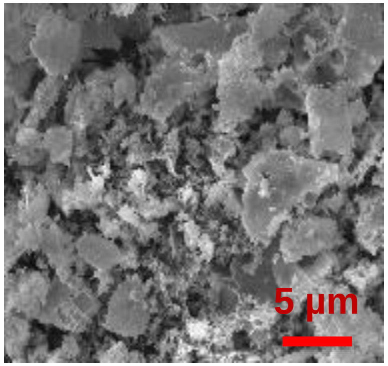
Synthesis of Electrolyte/Electrode Materials

Synthesis of BZCY-Yb by Sol-gel method



BZCY-Yb gel

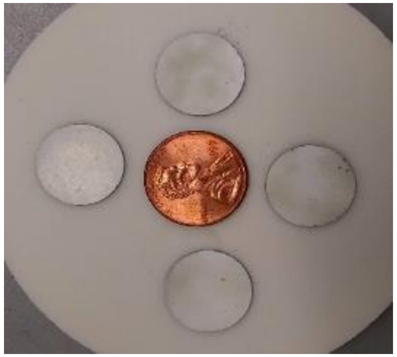
BZCY-Yb Powder

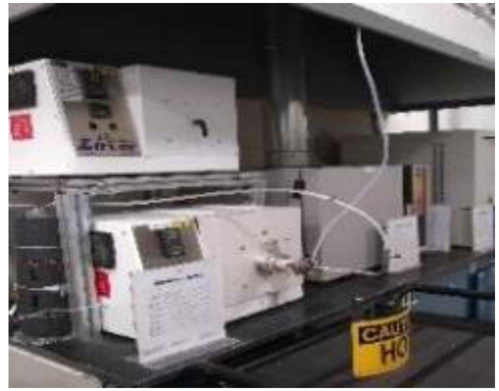


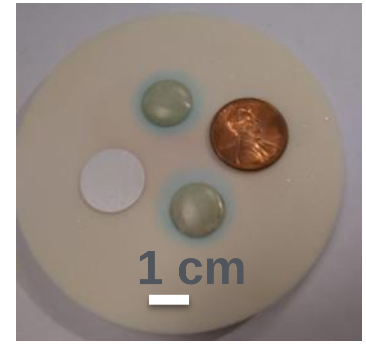
SEM image

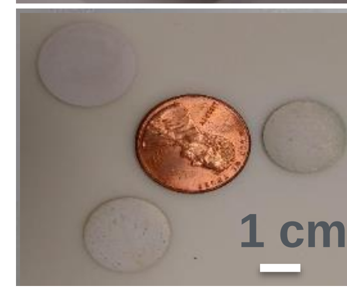
20-gram batch synthesis of BZCY-Yb proton-conducting materials has been validated using Sol-gel method.

Lower Temperature Sintering of BZY Electrolyte

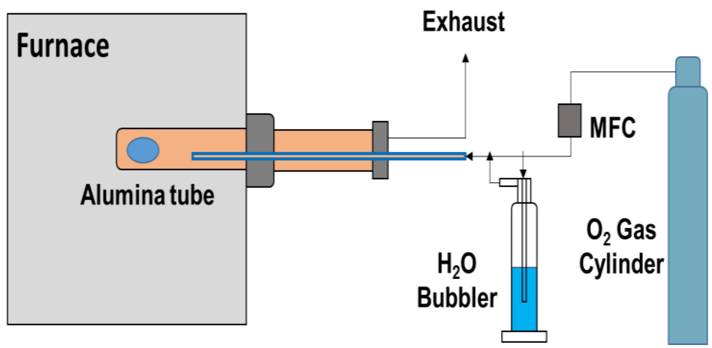








BZCY-Yb pellet by isostatic pressing (1.6 cm diameter)

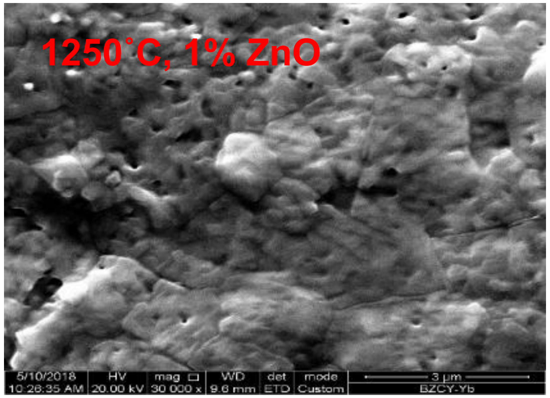


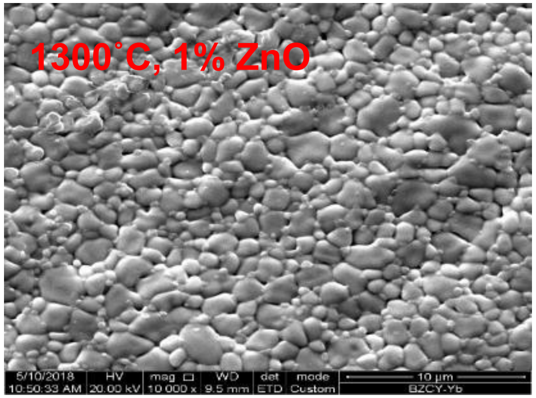
Dense electrolyte (~1.3 cm diameter)

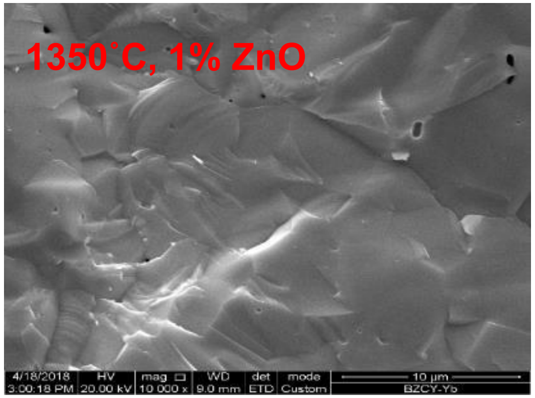
Sintering BZCY-Yb at different gases/PO_2

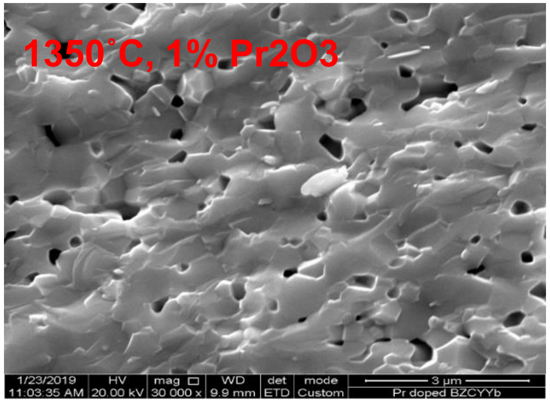
BZCY-Yb electrolyte has been fabricated using isostatic pressing and reactive sintering methods at temperatures <1450˚C with sintering aids namely ZnO, Mn_2O_3, and Pr_2O_3.

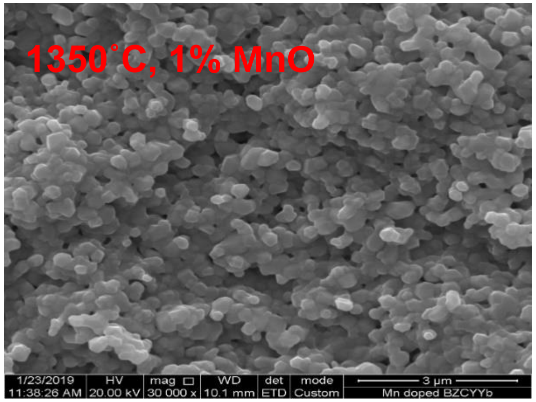
Effect of Sintering Temperature

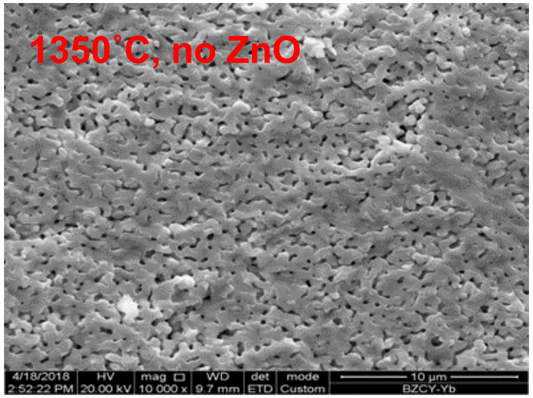








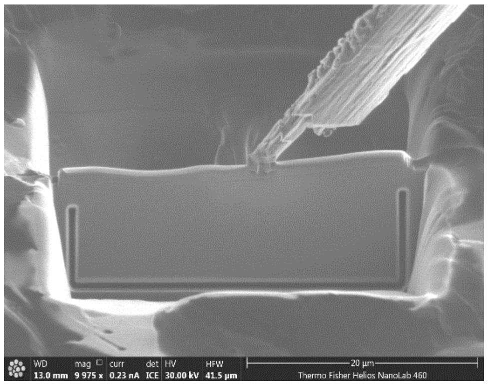


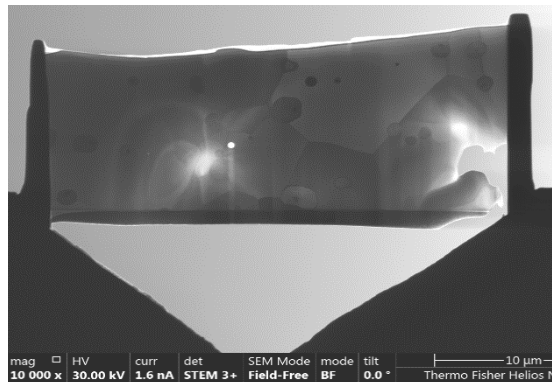


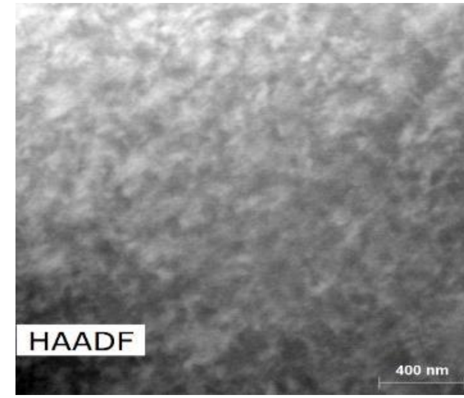
Full densification achieved at 1350˚C with ZnO sintering additive

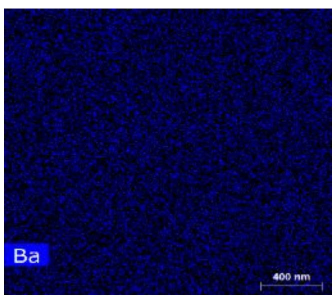
FIB-STEM Characterization

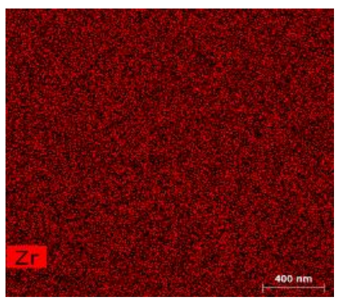
BZCYYb was synthesized by sol-gel synthesis technique.

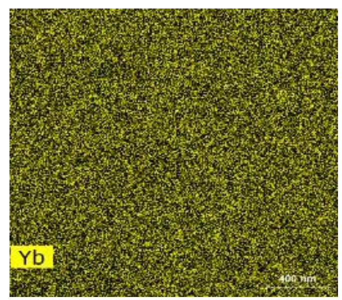


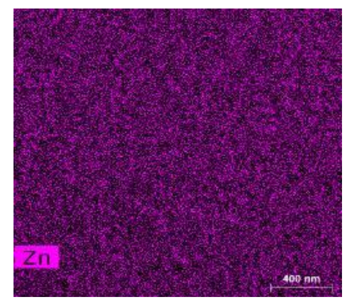


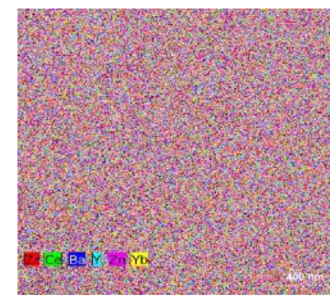






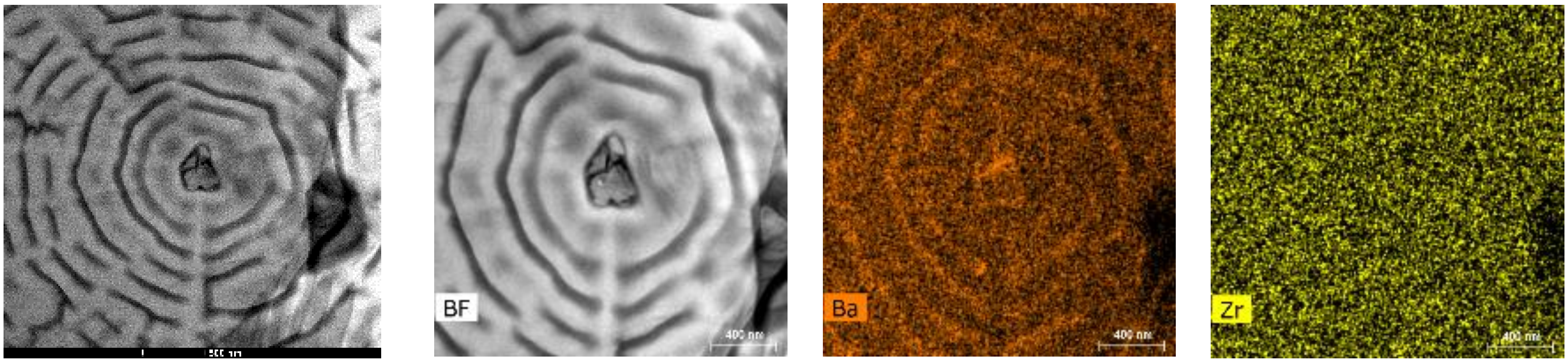




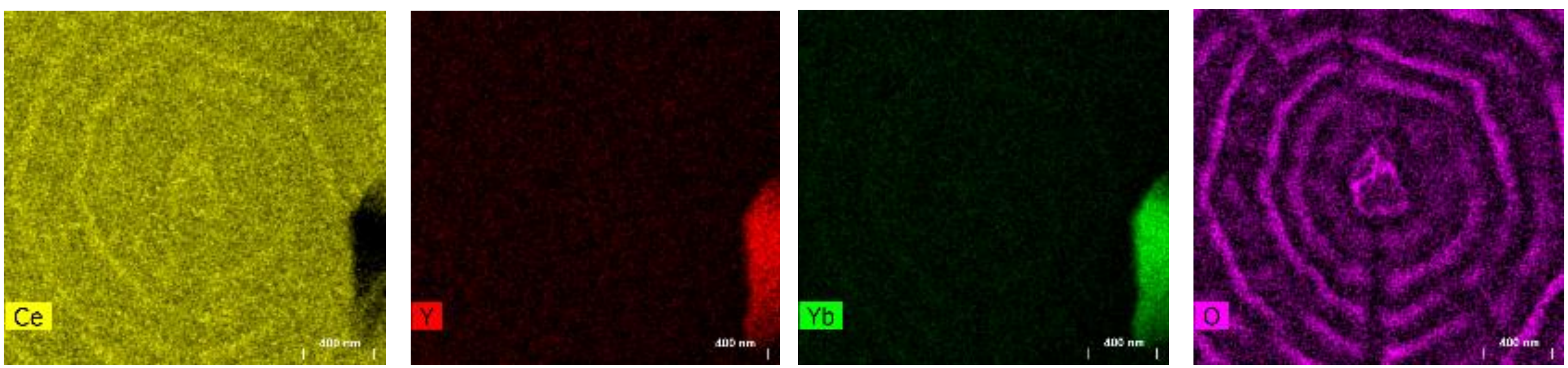


FIB-TEM maps show uniform elemental distribution.

FIB-STEM map of BZCYYb electrolyte cross-section

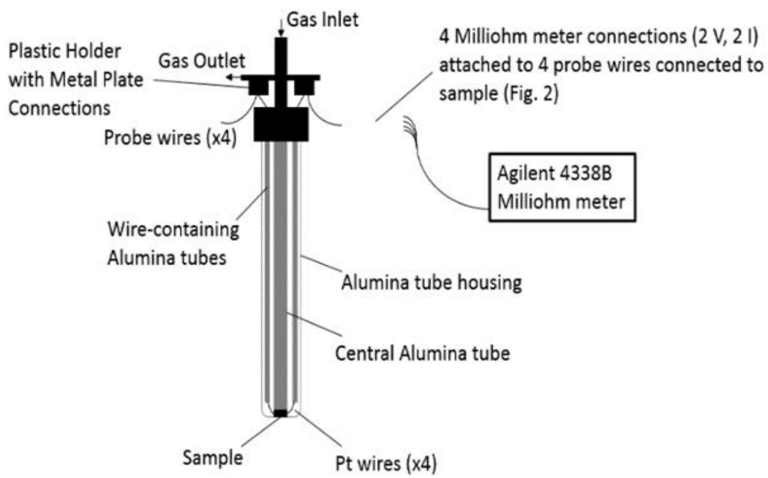


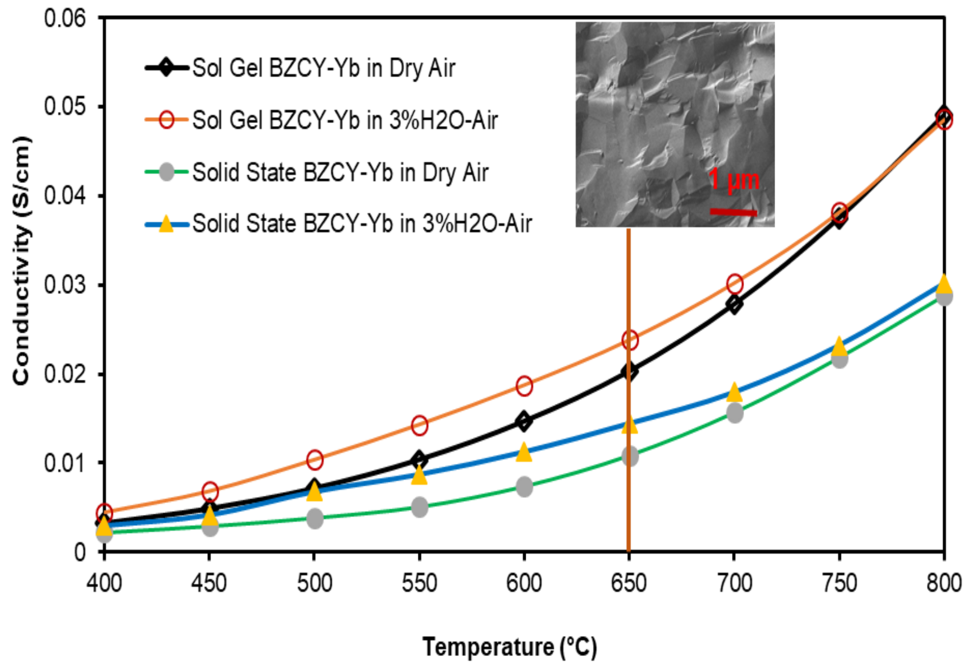
BZCYYb was synthesized by solid state synthesis method.



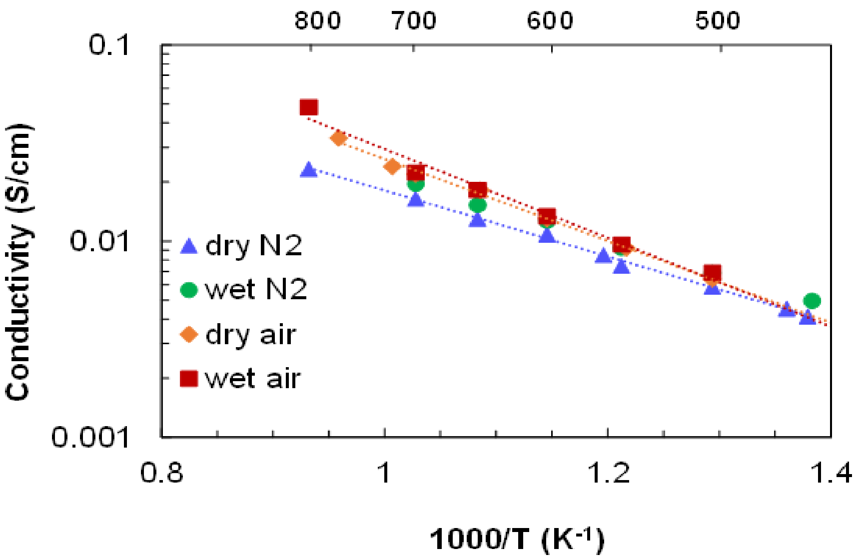
Oxygen rich rings and center particle - $BaCeO_3$.

Conductivity Measurement of BZCY-Yb Electrolyte





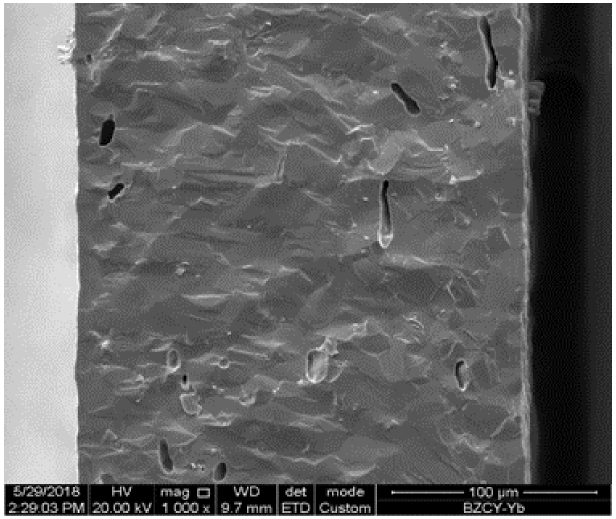
Conductivity measured at UConn

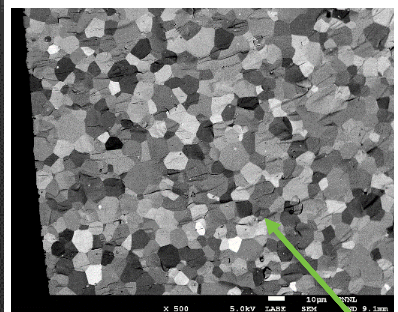


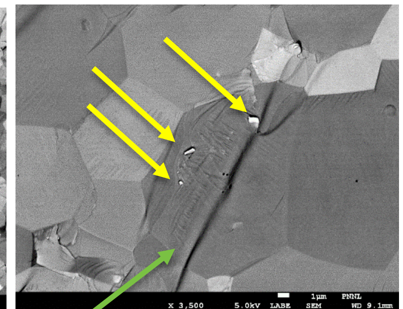
Conductivity measured at PNNL

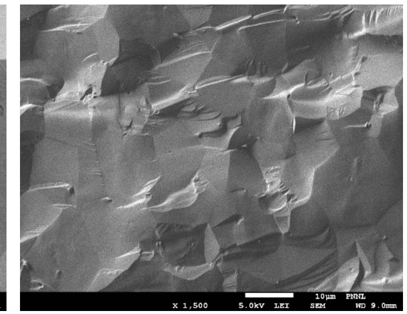
BZCY-Yb prepared by sol-gel method has higher proton conductivity than that prepared by solid-state method.

Characterization of Sintered BZCYYb Electrolyte



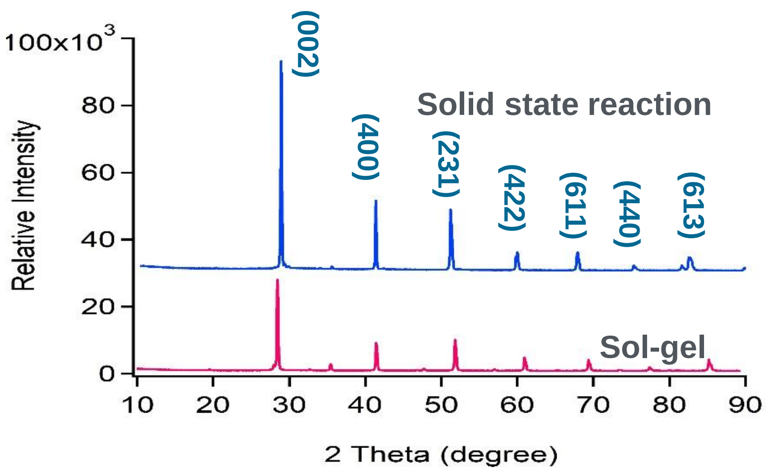




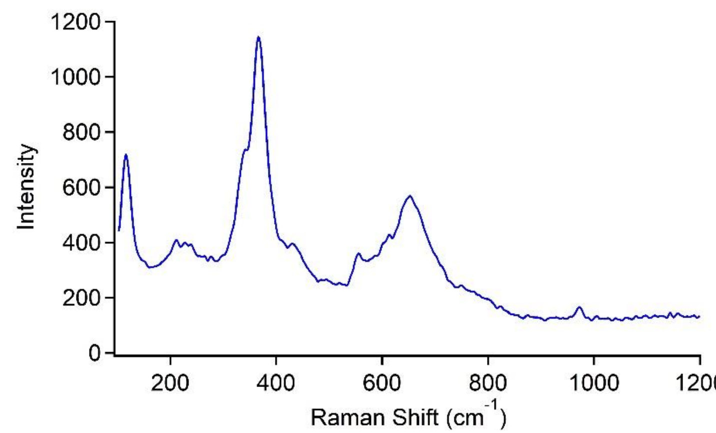


SEM Images taken at PNNL

Gray scale differences are due to orientation contrast

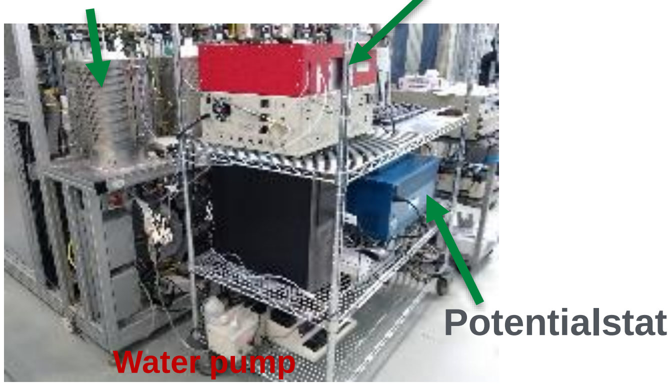


XRD Patterns of sintered 1% ZnO-BZCYYb pellets at 1350ºC. Smaller crystallite size for sol-gel BZCYYb powder.

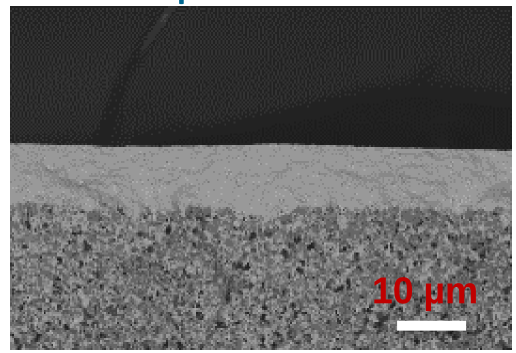


Raman spectra show a single perovskite phase of BZCY-Yb sintered at 1350˚C .

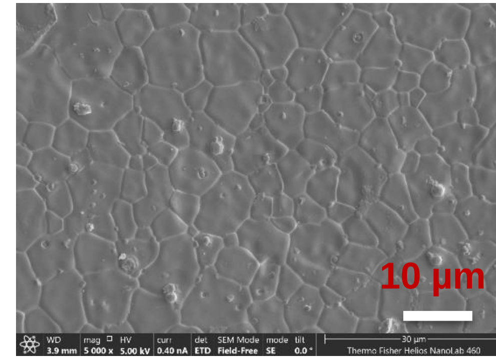
H-SOEC Cell Preparation & Testing



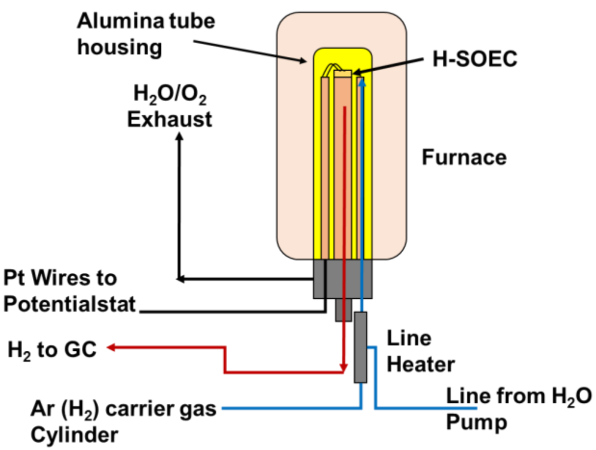
Prepared at INL

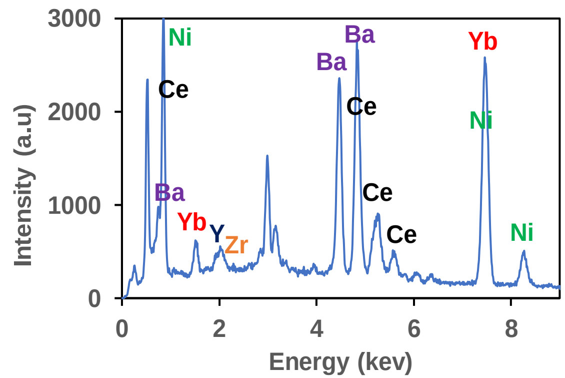


~20 μm thickness of electrolyte

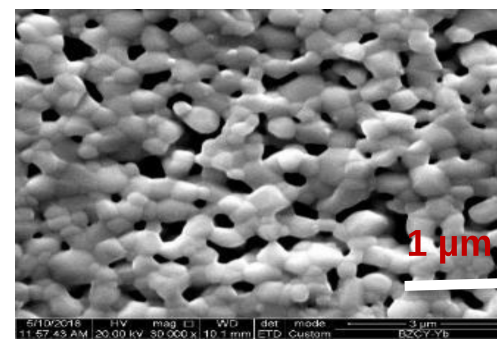


Dense electrolyte at 1350˚C





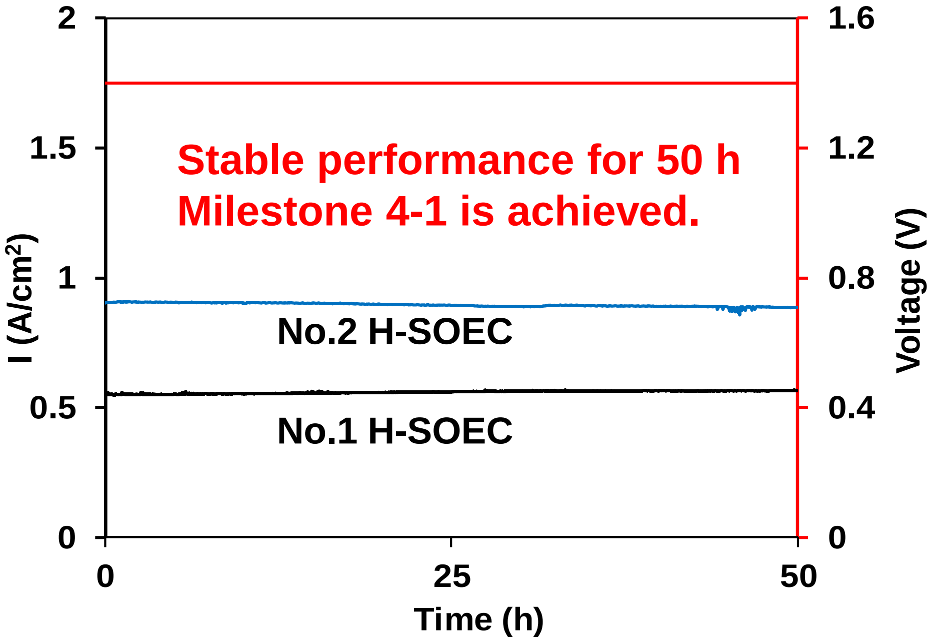
EDS spectra of hydrogen electrode



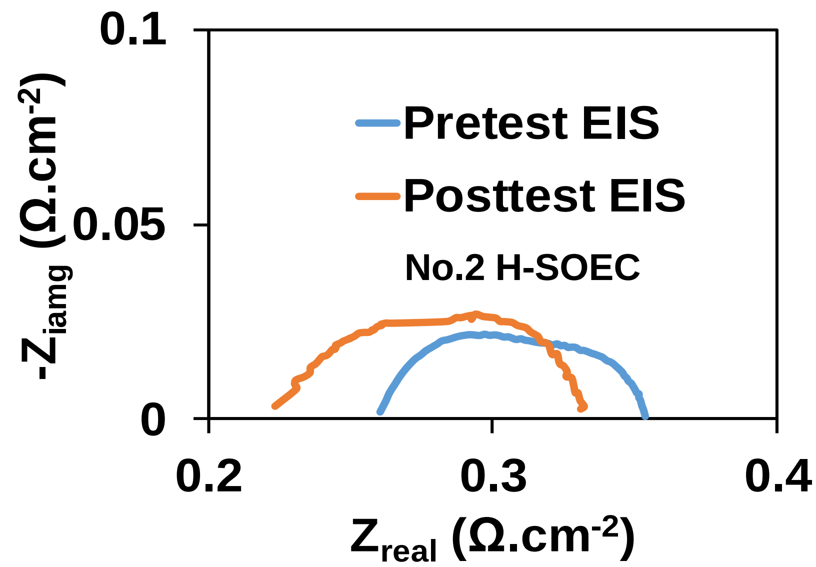
Porous oxygen electrode

H-SOEC full cells have been fabricated with thin dense electrolyte (15-20 μm). Above SEM images show a typical Ni-BZCY-Yb||BZCY-Yb half cell.

Performance Stability during Steam Electrolysis

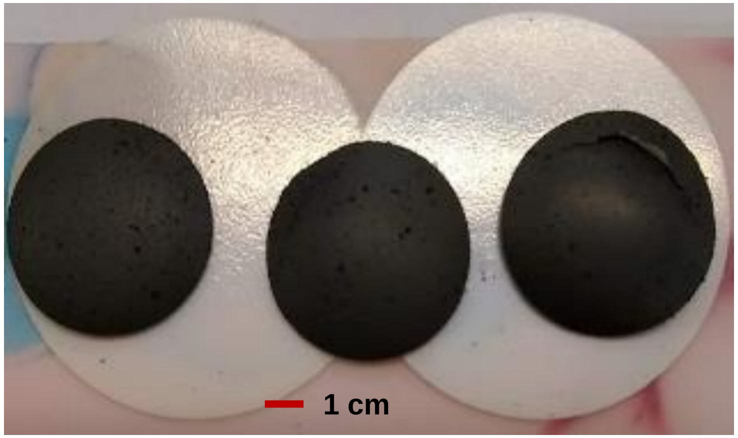


Low ASR was achieved by cell optimization.

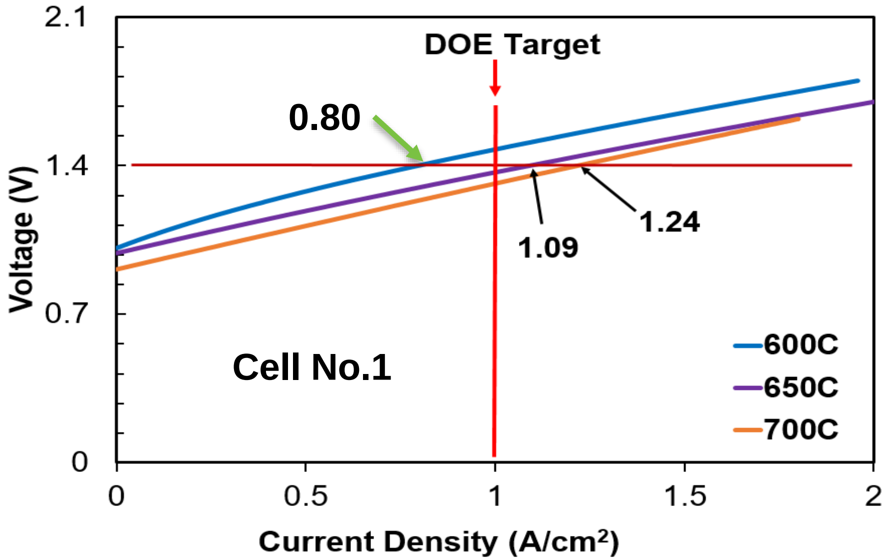


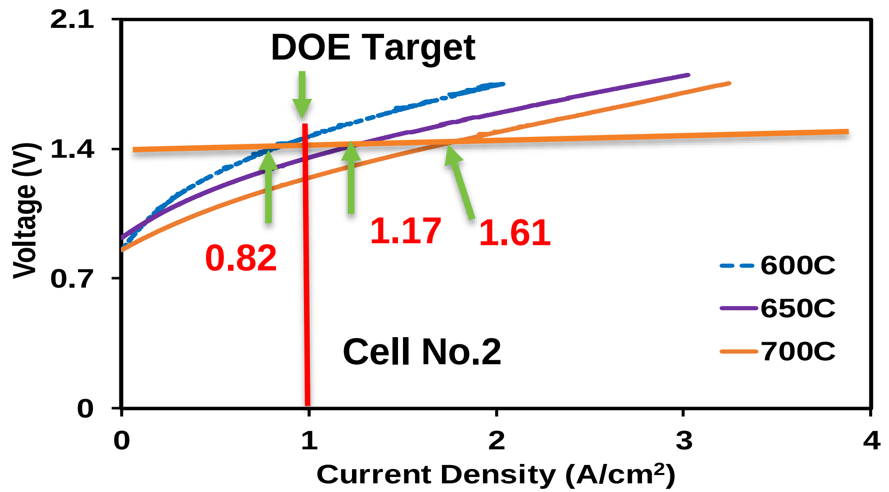
- Cell #1 : I-t curve of steam electrolysis at 700˚C at 1.4 V
  H electrode flow rate: 40 sccm of 50% H_2/Ar, O electrode: 60 sccm of 3% H_2O/air
- Cell #2: I-t curve of steam electrolysis at 600ºC at 1.4 V
  H electrode flow rate: 40 sccm of 80% H_2/Ar, O electrode: 120 sccm of 3% H_2O/air
- Both cells use Ni-BZCY-Yb//BZCY-Yb//PBSCF cell configuration
  Cell #2 has thinner PBSCF electrode.

Steam Electrolysis Performance of H-SOECs



H-SOEC cells
Half cell sintered at 1350˚C
PBSCF sintered at 950˚C





Fabricated H-SOECs meet budget period 1 GO/ No-Go decision point (I> 1 A/cm^2 at ≤1.4 V at a < 700^{o}C)

Proposed Future Work

The overall objective of the proposed development efforts under phase II includes

(a) Optimize materials chemistry and processing conditions utilizing the NERL node.
- Lower electrode polarization and resistive losses (ASR< 0.4 Ω/cm^2 at 650ºC).
- Increase proton conductivity(>0.02 S.cm^{-1} at 650ºC) (Milestone M5-1, Q6)
- Identify contributions from proton, oxygen ion and electronic conductivities, measure transference number.
- Decrease the cell degradation rate using Cr getters (M6-1, Q7)

(b) Fabricate large button cells(25 cm^2) and 3 cell stacks using tape casting utilizing the INL node (M8-1, Q10).

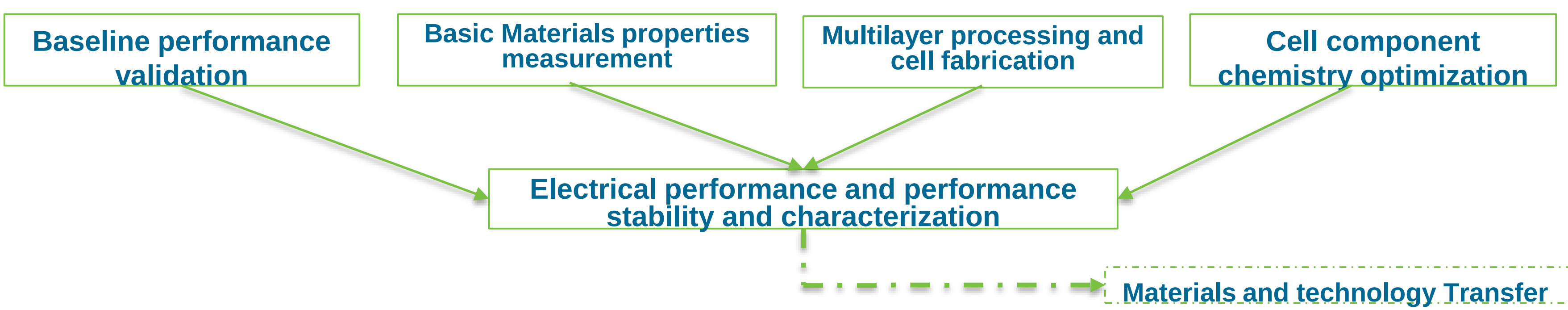
(c) Test 1-inch cell for 200 h (<10 mV/1000h) and characterize cell components (M7-1, Q8, Go/No GO decision point)

(d) Examine and validate long term (>500 h) chemical and structural stability of cell component materials, large cells, and 3 cell stacks in the high temperature steam electrolysis (M9-1, Q11).

(e) Demonstrate performance stability and validate project target: degradation rate <4 mV/1000 h at 1 A/cm^2, electrical efficiency >95%, and cost of hydrogen production < \$2/gge H_2 (M10-1, Q12, GO/No go decision point).

(f) Develop mechanistic understanding of electrochemical / electrodics processes

(g) Modelling and economic analysis of large-scale hydrogen production using NERL node (Dr. Zhiwen Ma).
- Develop and calibrate a SOEC electrochemical model based on cell materials and single cell testing data.
- Economic model by predicting performance parameters including temperature, current density, and species distributions (M10-1, Q12).



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

Project Summary

Technical progress and accomplishments **meet the program milestones (M1-1, 2-1, M3-1, M4-1 and GNG-BP1).** The overall program goals of the Budget Period-1 have been achieved.

- Candidate electrolyte and electrode material compositional space for H-SOECs have been selected based on guidance from advanced modeling tools and analytical techniques. (M1-1)
- Proton conducting electrolyte has been synthesized with a density of >90% and its proton conductivity (0.025 S/cm at 700^{o}C) reach Milestone M2-1.
- Selected H-SOEC electrolyte and electrode materials electrolysis performance have been measured and have demonstrated relatively stable (<10 mV/1000 h) for 50-hour test in real-world electrolyzer operating conditions, meeting with milestone 4-1.
- Selected H-SOECs has demonstrated 1.20 and 1.32 A/cm^2 at ≤1.4 V at a temperature of and 650˚C and 700^{o}C in steam electrolysis. Optimized H-SOECs with thin electrodes has demonstrated 1.17 and 1.81 A/cm^2 at ≤1.4 V at a lower temperature of and 600˚C in steam electrolysis. Both H-SOEC tests have meeting with budget Period 1 Go/No-Go Decision Point.
- Computational materials design and optimization for chemically and structurally stable ceramic electrodes and electrolyte are suggested. Long-term tests at cell and SOEC stack levels are needed to validate the DOE overall project target.

Technical Back-Up Slides

Reviewer-Only Slides

Publications & Presentations

List of publications and presentations that have resulted from work on this project:

- Boxun Hu, Ashish N Aphale, Michael Reisert a, Seraphim Belko, Olga A Marina, Jeffry Stevenson, and Prabhakar Singh, Solid Oxide Electrolysis for Hydrogen Production: From Oxygen Ion to Proton Conducting Cells, 233rd ECS Meeting, Seattle, WA, May 13 -17, 2018.

- Boxun Hu, Michael Reisert, Ashish Aphale, Seraphim Belko, Olga Marina, Jeff Stevenson, Dong Ding and Prabhakar Singh, Barium Zirconate Based Electrolyte Densification Using Reactive Sintering Aids, 43rd International Conference and Exposition on Advanced Ceramics and Composites (ICACC 2019), Daytona FL, Jan. 25-31, 2019.

- Boxun Hu, Olga A Marina, Ashish N Aphale, Dong Ding, Hanping Ding, Andriy Zakutayev, Jeffry Stevenson, Prabhakar Singh, Stable Proton-conducting Solid Oxide Electrolysis Cells for Pure Hydrogen Production at Intermediate Temperatures, 2019 Materials Research Society Spring Symposia on Advanced Water Splitting, April 22–26, 2019, Phoenix, Arizona.

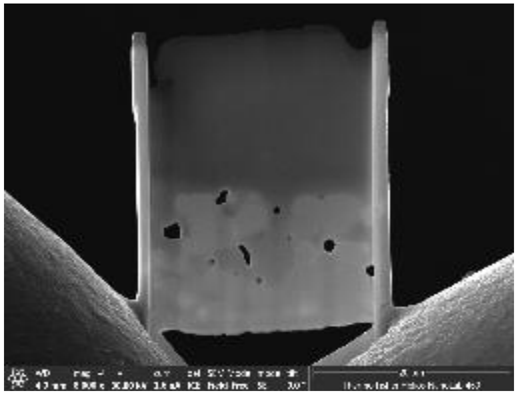
- Boxun Hu, Michael Reisert, Ashish Aphale, Seraphim Belko, Olga Marina, Henping Ding, Jeff Stevenson, Dong Ding, and Prabhakar Singh, “Stable Hydrogen Production by intermediate temperature steam electrolysis using Proton-conducting Solid Oxide Electrolysis Cells” in preparation

Milestones for Proposed BP-2 Work

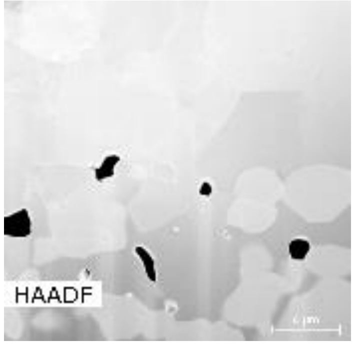
Milestone Summary Table (Phase 2)						
Recipient Name:		University of Connecticut, Prabhakar Singh				
Project Title:		Proton-Conducting Solid Oxide Electrolysis Cells for Large-scale Hydrogen Production at Intermediate Temperatures				
Task Number	**Task or Subtask Title**	**Milestone Type**	**Milestone Number***	**Milestone Description**	**Milestone Verification Process**	**Anticipated Quarter**
1	Program management and plan	Milestone	M1-1	Program priorities are established in consultation with program manager. Statement of work for selected HydroGEN nodes is identified.	Verify and consult with program manager	5
5	Optimization of proton conducting electrolyte/electrode materials	Milestone	M5-1	Scaled up synthesis process provides consistent powder quality in terms of phase chemistry, particle size and electrical properties (proton conductivity of >0.02 S/cm at 650 oC), low Area Specific Resistance (ASR) (< 0.4 Ω/cm2 at 650° C).	Experimental validation through testing and reporting	6
6	Characterization of electrolyte/electrode materials	Milestone	M6-1	Contributions of proton, oxygen ion and electrical conductivities in the electrolyte are identified with preferred proton transference in excess of 90%. Select electrode materials chemical and structural changes and related performance degradation, if any, are identified under electrochemically active steam electrolysis conditions with initial rationale for the degradation developed.	Verification through laboratory testing and peer-reviewed publications	7
7	Design, fabricate and evaluate large area H-SOECs	Milestone	M7-1	Electrolysis performance of selected 1-inch diameter H-SOEC cell is measured and is relatively stable (<25 mV/1000 h) for 200-hour test in real-world electrolyzer operating conditions.	Verification through report review.	8
		Go/No-Go Decision point	Phase 2, period 1	The decision points for the Go/No-go decision include: (a) Scaled up synthesis process for proton-conducting electrolyte (50 g batch) with conductivity of at least 0.02 S.cm-1 at 650° C, (b) Developed 1-inch diameter H-SOEC cells demonstrate high current density of > 1 A/cm2 under a bias of 1.4 V at a temperature of ⩽ 650 °C, (c) The SOEC cells show a lower degradation rate of < 25 mV/1000 h during 200-hour durability tests (under thermal neutral voltage; minimum current density of 0.5 A/cm2) and cell electrical energy efficiency great than 98%.	Test at least 2 SOECs at UCONN or PNNL to verify.	8

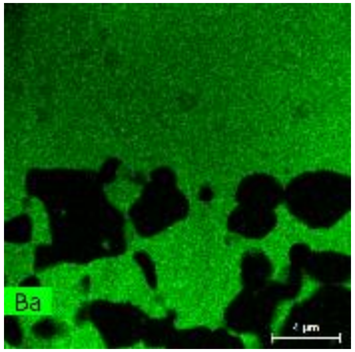
FIB-TEM Analysis of BZCYYb/NiO-BZCYYb half-cell

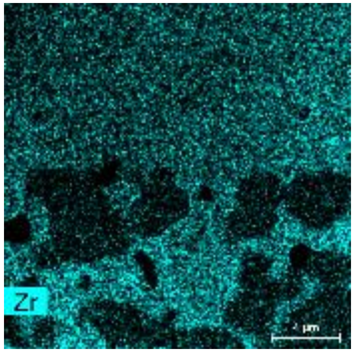
FIB sample of sintered BZCY-Yb Disc at 1350˚C in O_2

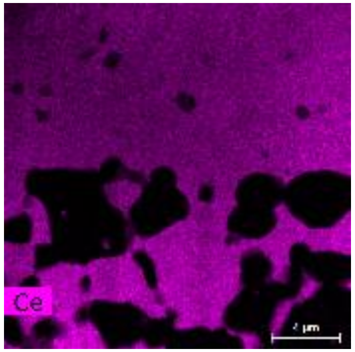


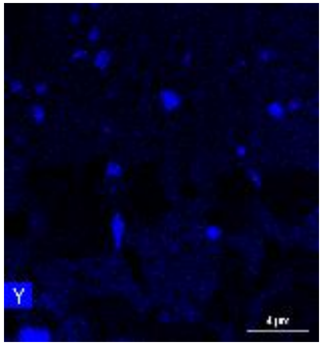
Electrolyte/H electrode interface

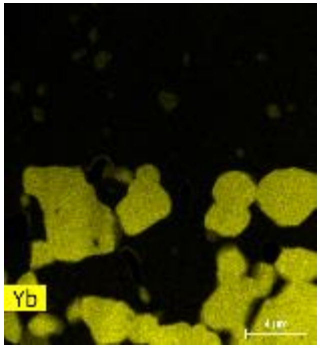


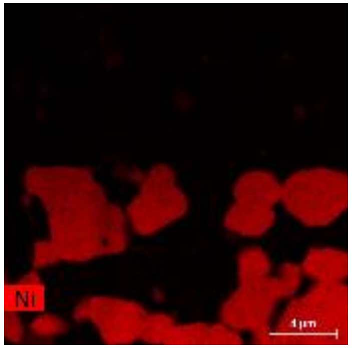


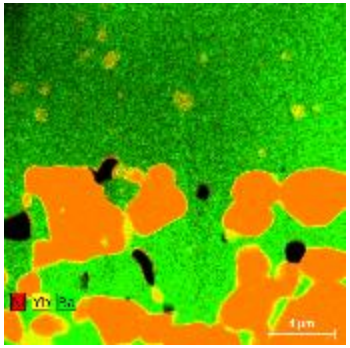






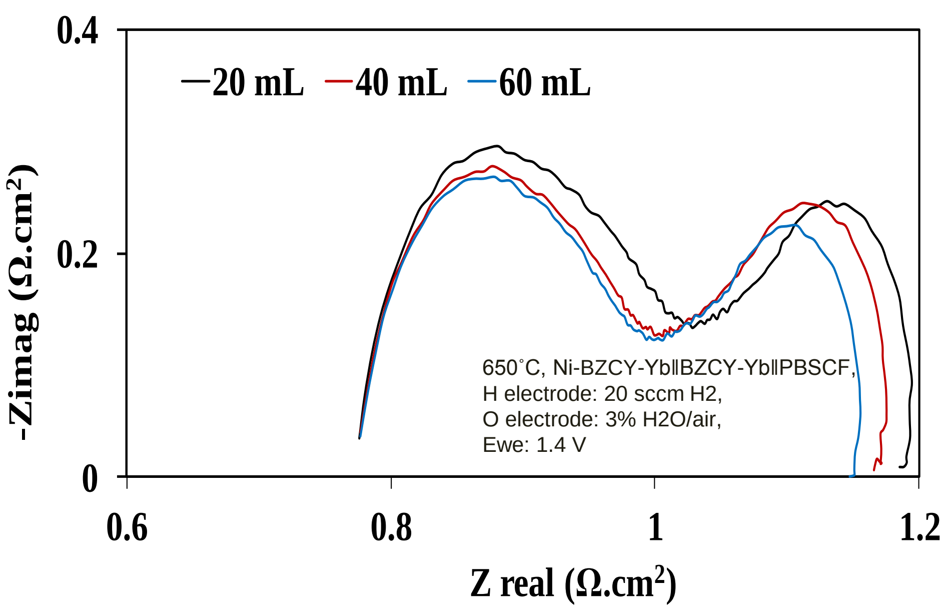


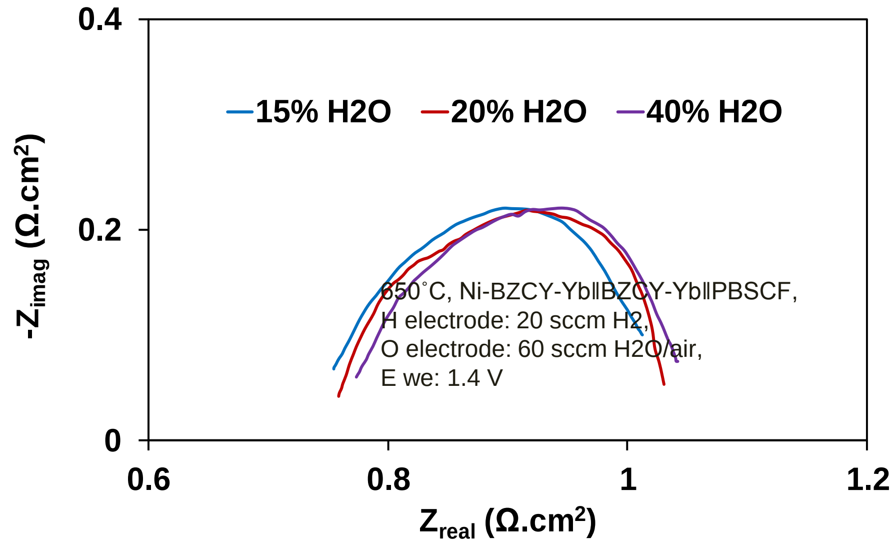




FIB-STEM images show dense BZCY-Yb electrolyte and porous NiO-BZCY-Yb electrode in pretest BZCYYb/NiO-BZCYYb half-cell. Yb and Ni maps are matched well.

Electrolysis under varying Steam Flow/ Concentration





Increased steam flow leads to improved current density due to lower diffusional resistance

- Relatively stable performance observed in 15-40% steam concentration.
- Long term chemical/ structural stability in high H_2O% needs to be investigated.

Thank you

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