Energy Materials Network
U.S. Department of Energy

HydroGEN
Advanced Water Splitting Materials

HydroGEN: High Temperature Electrolysis (HTE) Hydrogen Production

Michael Tucker, James O'Brien, Dong Ding, Andriy Zakutayev, Zhiwen Ma
Richard Boardman, Huyen Dinh, Adam Weber
Presenter: Richard Boardman
Date: June 13, 2018
Venue: 2018 Annual Merit Review, DC

Project ID # PD148B

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

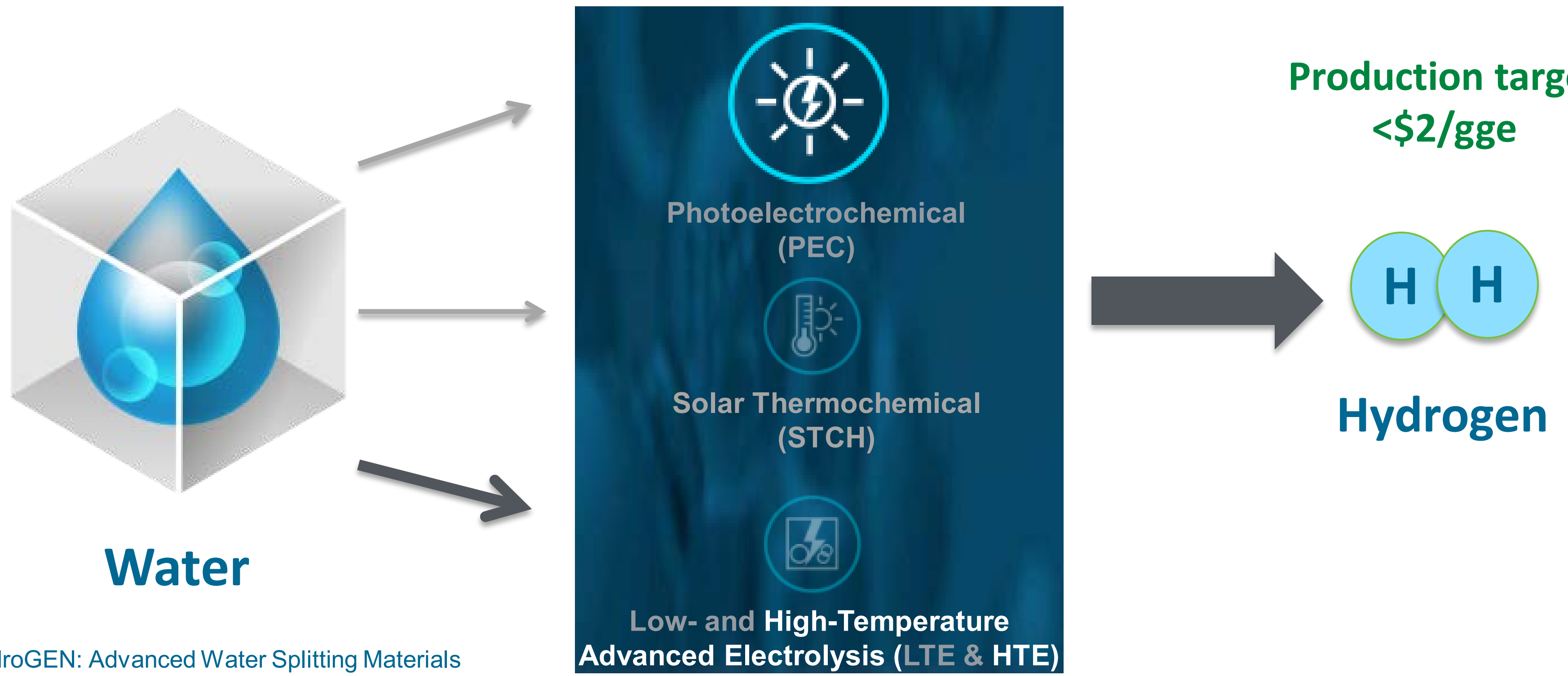
Advanced Water-Splitting Materials (AWSM)

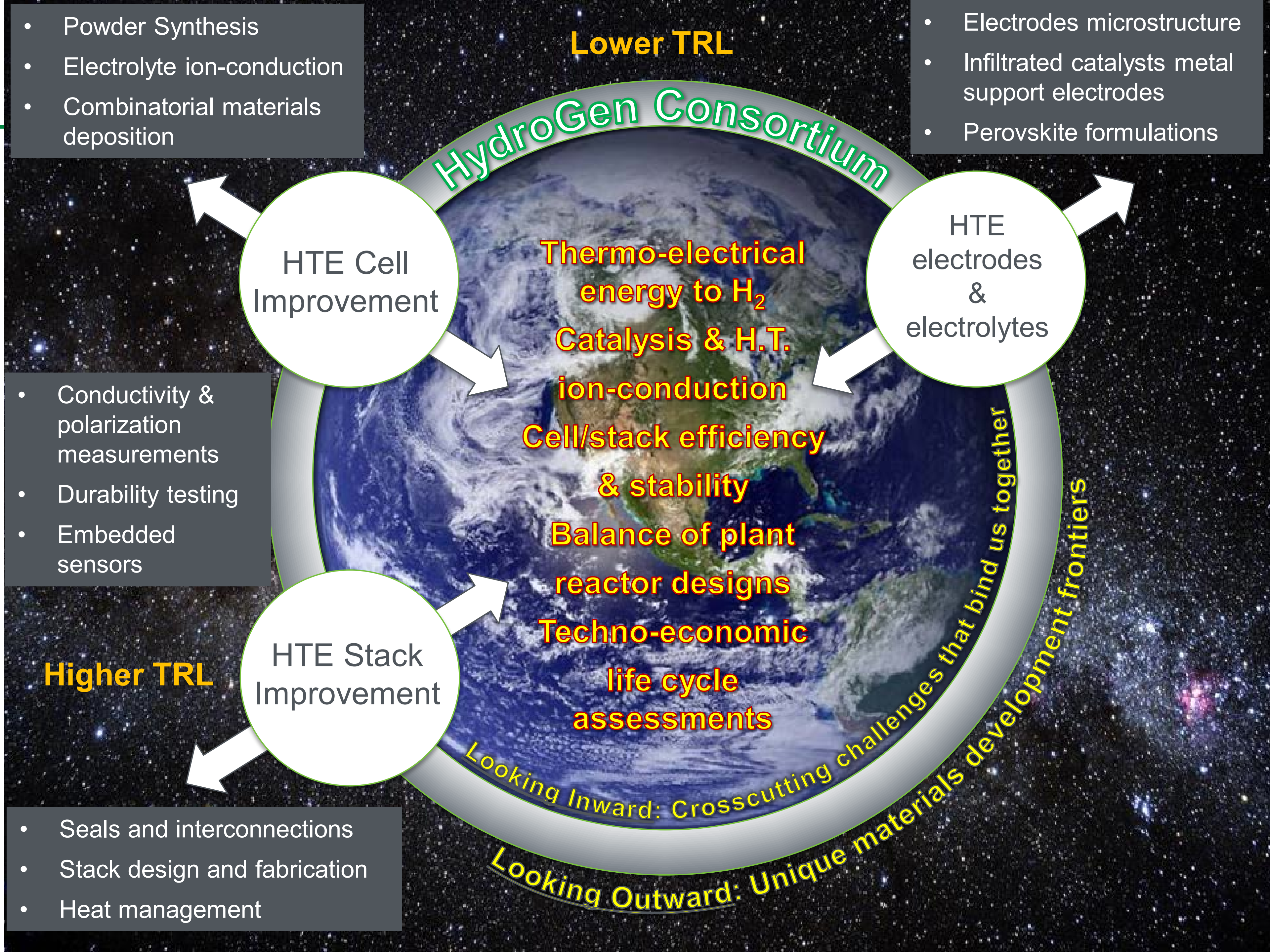
Relevance, Overall Objective, and Impact

AWSM Consortium
6 Core Labs:

NREL – National Renewable Energy Laboratory
Berkeley Lab
Sandia National Laboratories
INL – Idaho National Laboratory
Lawrence Livermore National Laboratory
SRNL

<u>Accelerating R&D</u> of innovative materials critical to advanced water splitting technologies for clean, sustainable & low cost H_2 production, including:



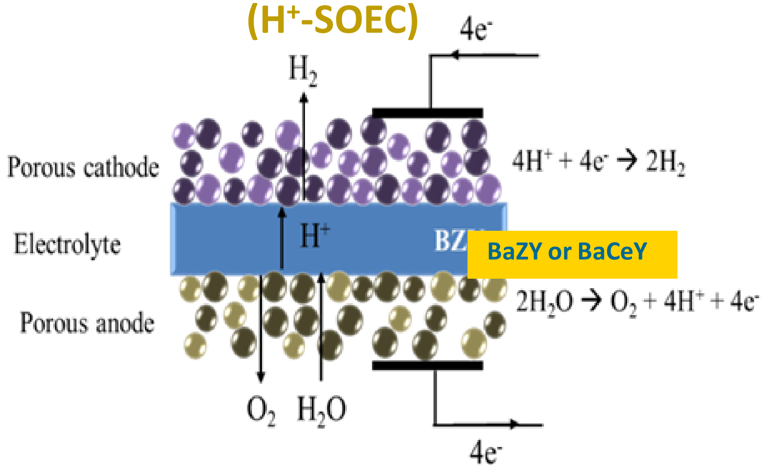


Powder Synthesis
Electrolyte ion-conduction
Combinatorial materials deposition
Lower TRL
Electrodes microstructure
Infiltrated catalysts metal support electrodes
Perovskite formulations
HydroGen Consortium
HTE Cell Improvement
HTE electrodes & electrolytes
Thermo-electrical energy to H_2
Catalysis & H.T.
ion-conduction
Cell/stack efficiency & stability
Balance of plant reactor designs
Techno-economic life cycle assessments
Conductivity & polarization measurements
Durability testing
Embedded sensors
Higher TRL
HTE Stack Improvement
Looking Inward: Crosscutting challenges that bind us together
Looking Outward: Unique materials development frontiers
Seals and interconnections
Stack design and fabrication
Heat management

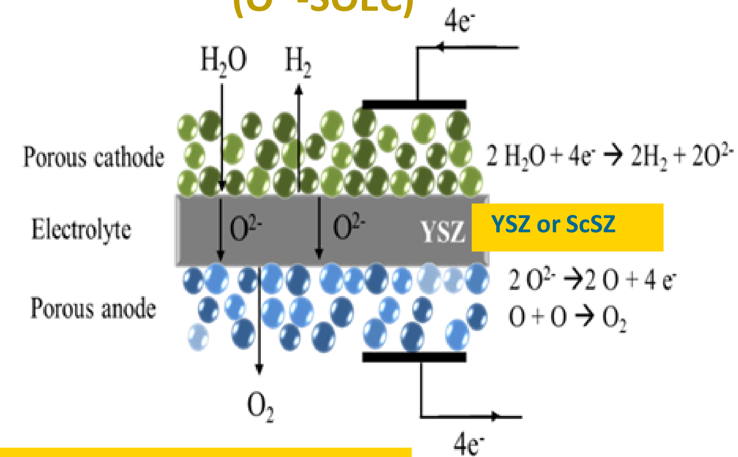
High Temperature Electrolysis (HTE) Technologies

Approach

Proton-Conducting Solid-Oxide Electrolysis (H^+-SOEC)



Oxygen Ion Transport Solid-Oxide Electrolysis (O^{2-}-SOEC)



Attributes	H^+- SOEC	O^{2-}- SOEC
Operating Temperature	550-750°C	650-850°C
Electrolyte Conductivity	0.01 $S.cm^{-1}$ at 650°C	0.015 $S.cm^{-1}$ at 850°C
Cathode Products	Pure H_2	$H_2O + H_2$
Anode Products	O_2 + sweep gas	$H_2O + O_2$

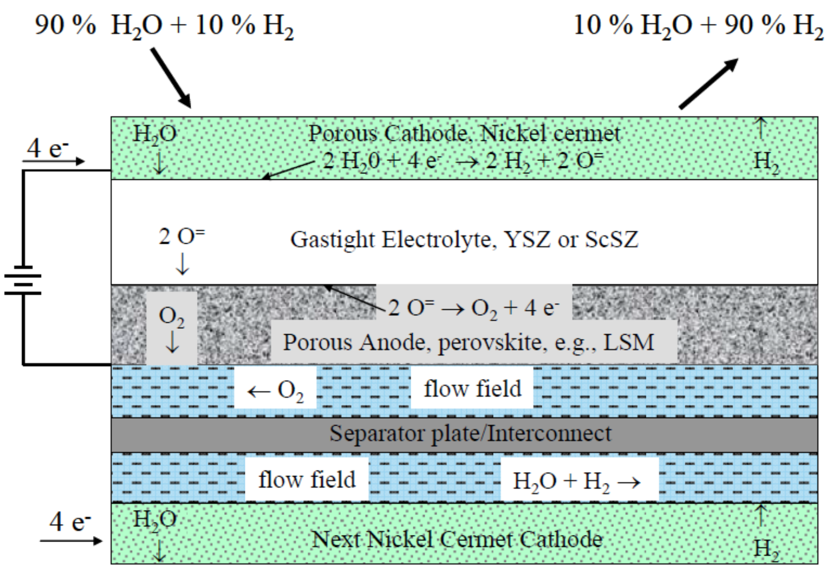
Figure and Table Adapted from: Singh and Hu, UConn

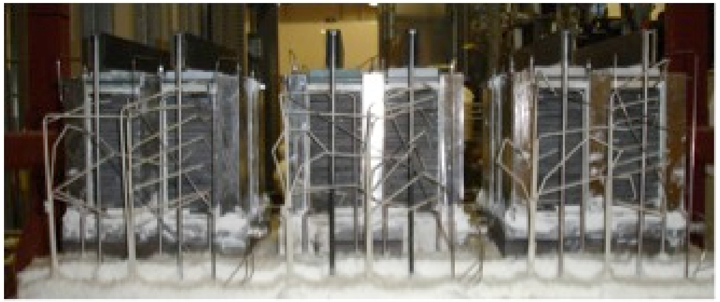
Trade-offs:

- **Thermodynamic efficiency increases at higher temperature**
- **Solid oxide conduction and kinetics increase with temperature**
- **Solid oxide is purely proton conducting < 600°C**
- **Materials durability decreases with higher temperatures**

Example: HTE Oxygen-Transporting Solid-Oxide Cell

Approach/Impact





- **Stacks must be tolerant to corrosion (Cr migration) and thermal cycling (discontinuous and dissimilar materials)**
- **Fabrication of SOECs cells require several steps and is energy intensive**

HydroGEN HTE Projects & Collaboration

Approach

High Temperature Electrolysis (HTE)
- Oxygen Conducting SOEC (o-SOEC)
- Proton Conducting SOEC (p-SOEC)

- Cost
- Efficiency
- Durability

HTE Node Labs

Idaho National Laboratory

BERKELEY LAB

NREL NATIONAL RENEWABLE ENERGY LABORATORY

Lawrence Livermore National Laboratory

Support through:

Personnel

Equipment

Expertise

Capability

Materials

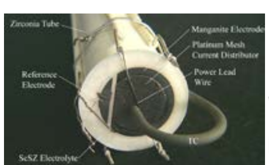
Data

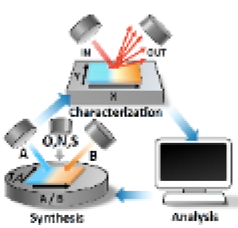
HTE Projects

United Technologies Research Center

UCONN

Northwestern

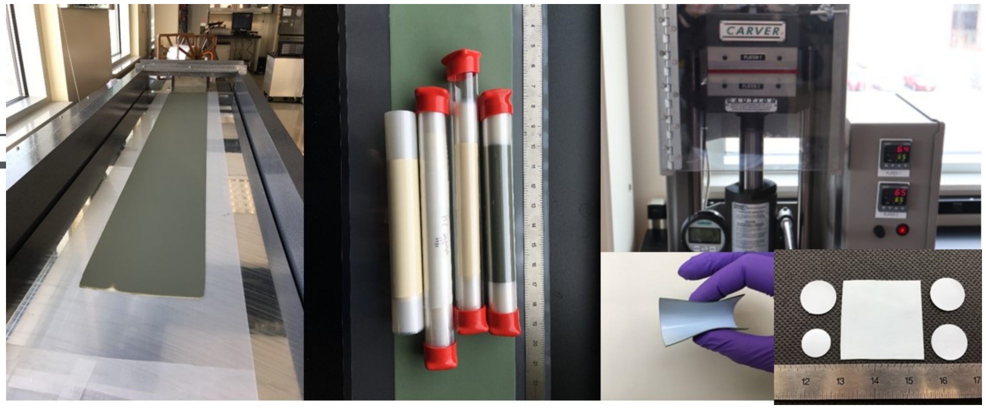




Example node: INL - HTE 1

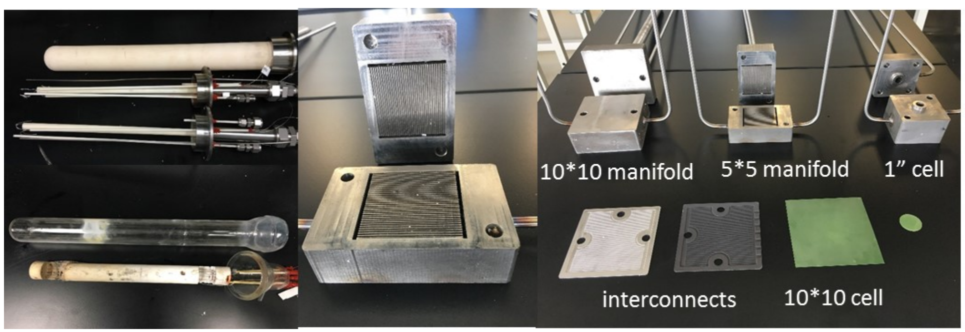
Advanced Materials for Elevated Temperature Water Electrolysis

HT Roll-to-Roll Manufacturing for button cells to large planar cells



Multi-functional sintering

High Throughput materials testing/screening



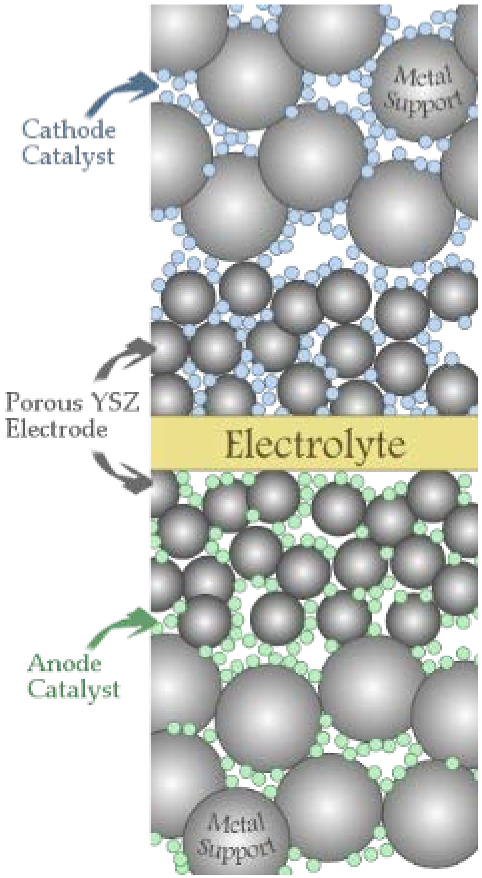
Testing fixtures for symmetrical cells, half cells, button cells, planar square cells and stacks (up to 19 channels)

Testing facilities for cells and stacks (17 channels with potentiostat and EIS)

Dong Ding, Node Expert

Example node: LBNL - HTE 3
Metal-Supported Solid Oxide Cells

Approach/Impact



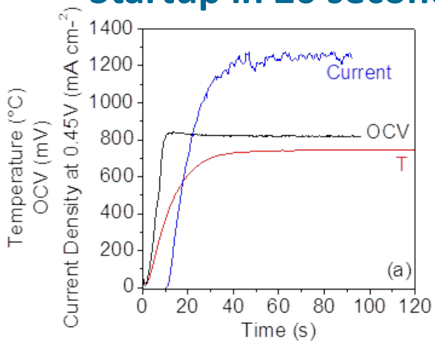
➢ Cost

- **Stainless steel order of magnitude less expensive than ceramics**
- **Single high-T sintering step**

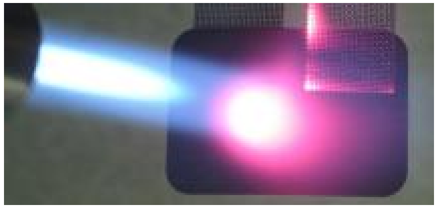
➢ Mechanical

- **Rugged, strong cell**
- **Welded electrical connections**
- **Tolerates rapid T-ramp**
- **Tolerates large T-gradient**

Startup in 20 seconds



>300° C/cm



➢ Operational

- **Very high performance**
- **T can vary quickly during operation (increase/decrease performance on the fly)**
- **Tolerates intermittent fuel/hydrogen (redox cycling)**
- **Imbalanced pressure acceptable**

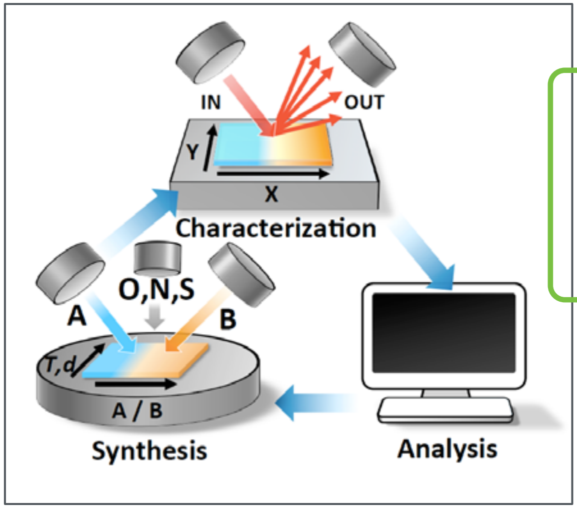
Michael Tucker, Node Expert

Example nodes: NREL - HTE 2 (also STCH and PEC)

High-Through Experiments Thin Film Combinatorial Capabilities

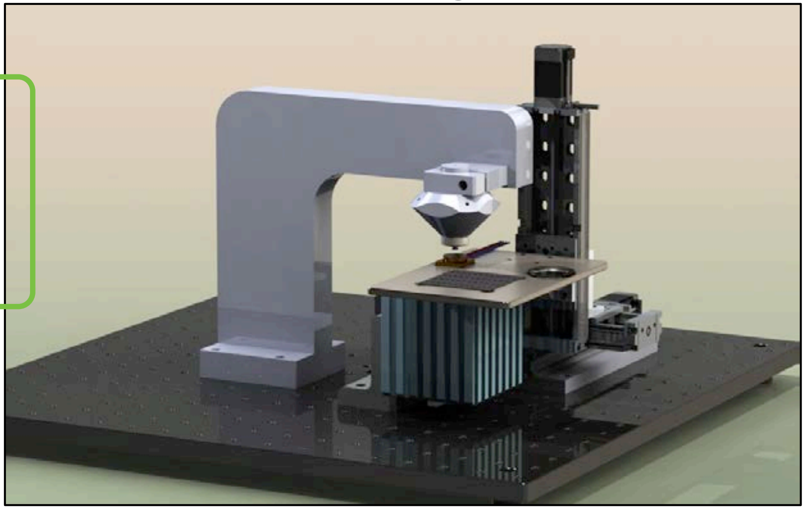
Approach/Impact

Existing: High-Throughput Experiments



Andriy Zakutayev, Node Expert

New: Scanning Droplet Cell



- 6 combinatorial synthesis chambers
- 14 spatially-resolved measurement tools
- Big data management and analysis

Capabilities developed using BES and SETO

- Electrochemical measurement under light
- 44 spots tested on 1 sample library
- 1-2 mm spatial sample resolution

Capabilities developed using HydroGen EMN

https://www.h2awsm.org/capabilities/high-throughput-experimental-thin-film-combinatorial-capabilities

HydroGEN EMM projects:

- **CSM**: Accelerated Discovery of Solar Thermochemical Hydrogen Production Materials
- **Rutgers**: Best-in-class PGM-free Catalyst Integrated Tandem Junction (PEC) Devices
- **UConn**: Proton-Conducting Solid Oxide Electrolysis Cells at Intermediate Temperatures
- **HNEI**: Novel Chalcopyrites For Advanced Photoelectrochemical Water Splitting

Overview:
FOA Seedling Projects

5 Nodes utilized
7 Lab PIs engaged
6 samples exchanged
Files being compiled for Data Hub

Approach

Northwestern University (NWU, Scott Barney PD153):
Characterization and Accelerated Life Testing of a New Solid Oxide Electrolysis Cell

United Technologies Research Center (UTRC, Tianli Zhu; PD154):
Thin-Film, Metal-Supported High-Performance and Durable Proton-Solid Oxide Electrolyzer Cell

University of Connecticut (Uconn, Prabhakar Singh; PD15X):
Proton-Conducting Solid Oxide Electrolysis Cells for Large-scale Hydrogen Production at Intermediate Temperatures

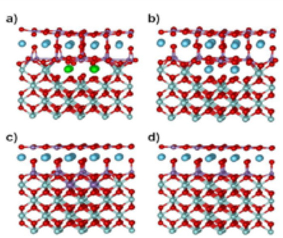
- **Interact with the HTE Working Group and 2B** (PNNL, Olga Marina)

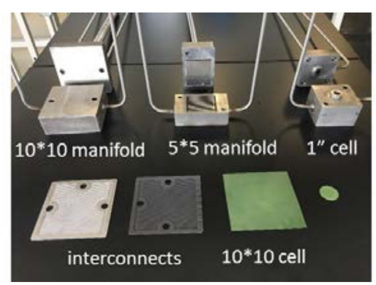
Collaboration: HydroGEN HTE Node Utilization

Approach

Lab	Node	Node PI	NWU	UConn	UTRC
NREL	Engineering of Balance of Plant (BOP) for High-Temperature Systems	Ma, Zhiwen Martinek, Janna			✓
LBNL	Metal-Supported SOEC	Tucker, Michael Wang, Ruofan	✓		✓
INL	Advanced Materials for Elevated Temperature Water Electrolysis	Ding, Dong	✓	✓	✓
INL	SOEC Characterization	O'Brien, James Stoots, Carl	✓		
NREL	High-Throughput Experimental Thin Film Combinatorial Capabilities	Zakutayev, Andriy		✓	

Computation **Material Synthesis** **Characterization**





NWU Accomplishments
Prepared Cells for NWU

See Poster PD153

PI: Scott Barnet

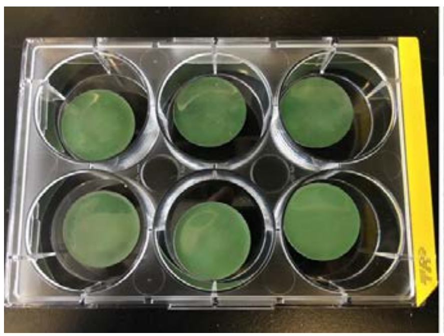
Project Vision

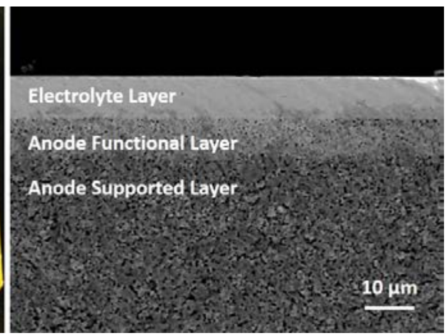
Collaboration

Study degradation mechanisms in solid oxide electrolysis cells operated at high current density using accelerated testing closely coupled with theory and modeling.

- INL prepared materials for NWU testing
- Testing at NWU and INL
- Student from NMU supporting testing at INL (Summer, 2018)

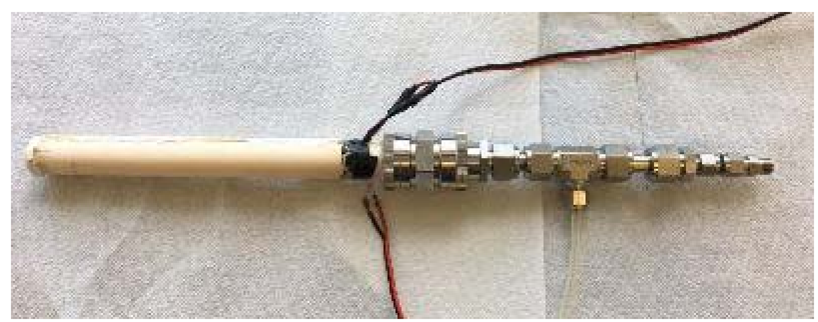
Fabricated YSZ-based SOECs as requested (ongoing)





Anode-supported cell with YSZ electrolyte

Metal-supported cell mounted on ceramic tube with current collector



Button cell test fixture prepared

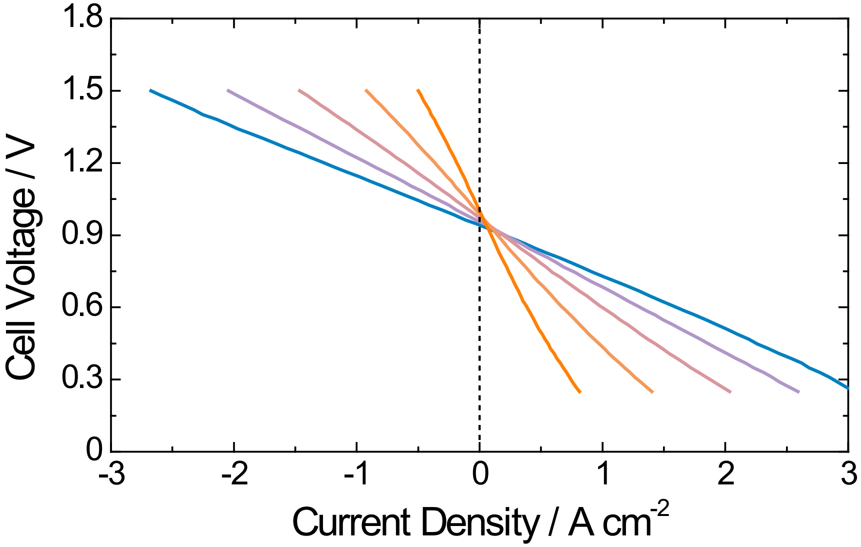
NWU Accomplishments
Test Results at NWU

See Poster PD153

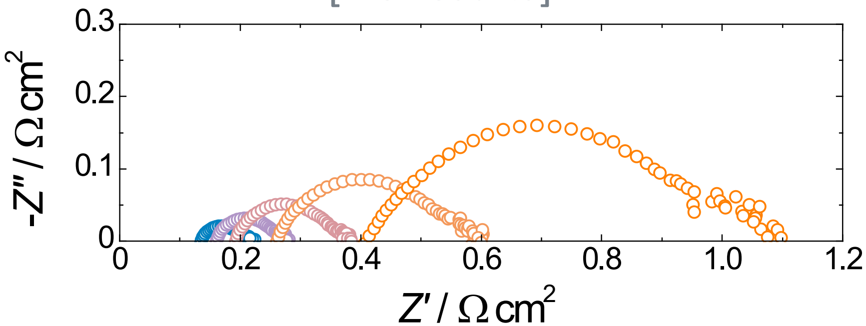
Collaboration

- Cell performance has been fully characterized
- Cell current density at expected electrolysis voltage, and cell resistance, are as desired
- The performance results meet the second part of
  - Milestone 1.1: < 1.3 V at 1.0 A/cm^2 (800^{o}C, in air and humidified hydrogen)

[I–V curves with different temperatures]



[EIS results]



- The SOEC indicates the cell voltage of ~1.15 V at 1 A cm^{-2} (800 ^{o}C).

See Poster PD153

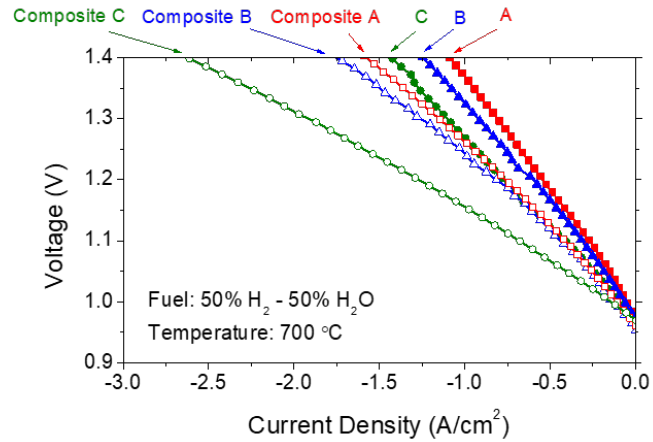
Collaboration

Technology Innovation & Accelerated Testing

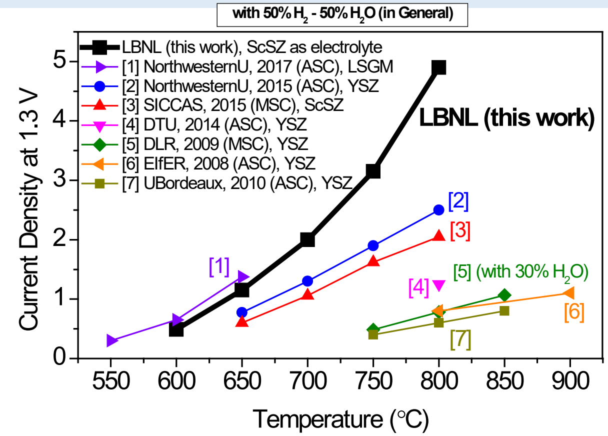
- M-SOEC cell testing underway at LBNL
  - ✓ Information exchange is on-going between Node and PI
  - ✓ Consistent test matrix has been established
  - ✓ First time testing of well-developed metal supported solid-oxide cells in electrolysis mode
- Optimizing cell catalysts for SOEC
- Technical manuscript is being prepared by Tucker, et al.

Zirconia oxide-conducting

High Performance of OER catalysts



Comparison with other oxygen-conducting SOECs



See Poster PD154

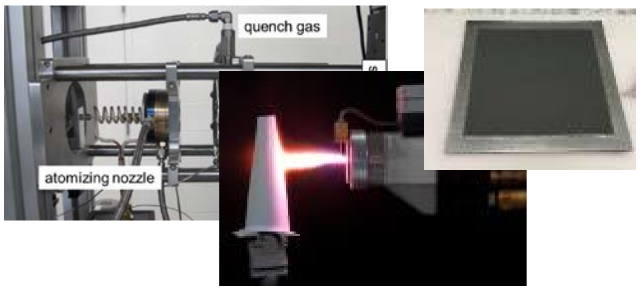
Collaboration

PI: Tianli Zhu
Partner: University of Connecticut

Project Vision

Develop low cost, scalable fabrication of metal-supported cell, and further material optimization for an efficient & durable proton conducting SOEC (p-SOEC) at 550-650°C.

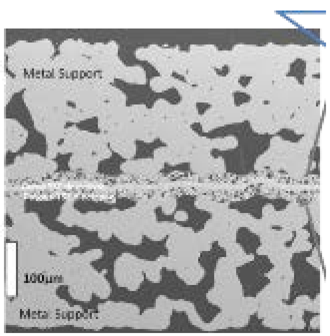
UTRC low cost cell fabrication



Metal supported p-SOEC

UTRC stack & system testing (up to 10kWe)

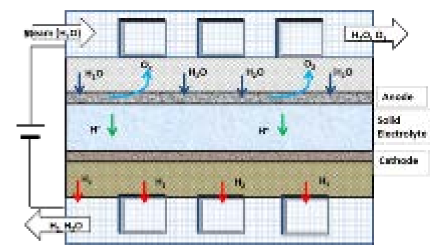
Reactive Spray Deposition (<10μm)
Suspension plasma spray (<15 μm)



Co-sintered metal cell LBNL

Metal alloy selection: oxidation rig at LBNL

Material optimization: high throughput testing stands at INL



Electrochemical modeling at NREL

United Technologies Research Center

This material is based upon work supported by the U.S. Department of Energy's Office of Energy Efficiency and Renewable Energy (EERE) under the Fuel Cells Technology Office (FCTO) Award Number DE-EE00080808

Partnerships: UCONN and Electrochem

UTRC Project Accomplishments

See Poster PD154

Collaboration

PI: Tianli Zhu
Partner: University of Connecticut

- **UTRC:** Hydrogen electrode deposition on porous metal support is complete
- **UTRC:** Electrolyte deposition by Reactive Spray Deposition Technique (RSDT) and Suspension Plasma Spray (RSD) in progress, focus on optimization
- **UTRC:** Open circuit voltage (OCV) results of the electrolyte indicate density of electrolyte needs improvement
- **LBNL:** Co-Sintering doped BZY compatible stainless steel support material
- **LBNL:** Selection of interconnect alloy and coating through oxidation study
  - Severe oxidation of uncoated SS metal alloy in 50% steam-air (650 °C)
  - Minimal oxidation observed with coated metals in 50% steam-air (650 °C)
- **INL:** Electrolyte and electrode material optimization
  - Tested BaZrCeY proton-conducting based ceramics in high steam
  - Evaluated the conductivities of different electrolytes and their stability in high water content at operating temperatures
- **NREL:** Thermal/Electrochemical modeling of Solid Oxide Electrolysis Cell (SOEC)
  - Extended the fundamental mathematical description of the cell electrochemical process for the proton-conducting SOEC.

UConn Project Accomplishments

See Poster PD152

Collaboration

UConn: Prabhakar Singh, Boxun Hu
and Ugur Pasaogullari
PNNL: Jeff Stevenson

Project Vision

Develop innovative, cost effective and efficient proton-conducting solid oxide electrolysis cells (H-SOECs) for large-scale hydrogen production at intermediate temperatures (600-800C).

Development of electrolyte densification technique and determination of corresponding ionic conductivities.

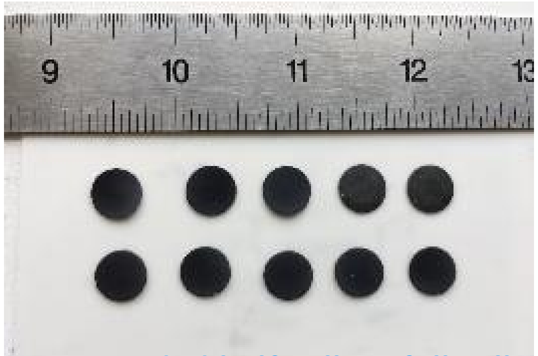
- INL provided proton-conducting half-cells and full cells (1 cm diameter) for SOEC testing and characterization.
    - ➢ The measured conductivity and the thickness (~20 μm) of dense electrolyte at elevated temperature
    - ✓ Electrical conductivity >0.01 S/cm below 700°C

      ⇒ **Meets Program Milestone**
    - ➢ INL will provide large size full cells (1.3 cm or 2.5 cm diameter) and electrode materials for SOEC testing

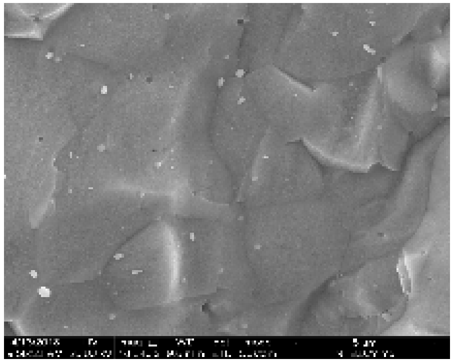
Anode microstructural modification for performance improvement and develop mechanisms for polarization losses.

- ➢ Uconn made electrode and electrolyte materials
- ➢ Tape cast and sintered multi-layer laminated
- ✓ Full densification below 1400°C

  ⇒ **Meets Program Milestone**
- ➢ TEM analysis at PNNL showed no grain boundaries or secondary phases



INL provided half-cells & full cells



Dense electrolyte at 1350°C

Engagement with 2B Benchmarking Team
Olga Marina, PNNL

Collaboration

- Completed preliminary assessment of the EMN Node capabilities
- Developed HTE Test Framework and HTE Benchmark Questionnaire.
  - Drafts sent to node experts for critical review.
  - The framework is categorized into Materials Property Testing, Cell Testing and Stack Testing.
    - Looking at INL to support SOEC stack testing
  - Assembled a list of experts who should be participating in this survey.
  - Both test matrix and questionnaire have been sent out to community for inputs.

Future Work

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

- Leverage HydroGEN Nodes at the labs to enable successful Go/No-Go of Phase 1 projects
  - New SOEC electrodes, new $O^{=}$ and H^{+} conduction electrolytes, new robust metal-support materials and coatings
  - Increased durability and lifetime at optimum cell temperatures
  - Increased production rates
- Enable research in Phase 2 work for some projects and enable new seedling projects
- Work with the 2B team and HTE working group to establish testing protocols and benchmarks
- Utilize data hub for increased communication, collaboration, generalized learnings, and making digital data public
- Leverage related projects, particularly projects of similar objectives and scope (e.g., Strategic Partnerships Projects)

Summary

- Supporting 3 FOA projects with 5 nodes and 7 PIs
  - Synthesis, benchmarking, modeling, characterization
- Working closely with the project participants to advance knowledge and utilize capabilities and the data hub
- Projects demonstrate improvements in durable, less expensive materials with high performance
- Future work will include continuing to enable the projects technical progress and develop & utilize lab core capabilities

Acknowledgements

Energy Materials Network
U.S. Department of Energy

HydroGEN
Advanced Water Splitting Materials

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Carl Stoots
Andriy Zakutayev

HTE Project Leads

Scott Barnet
Tianli Zhu
Prabhakar Singh

Research Teams

UCONN
United Technologies Research Center
Northwestern
Pacific Northwest National Laboratory
ElectroChem Ventures

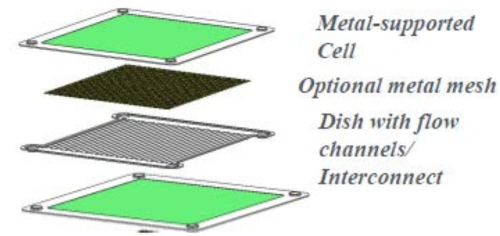
NREL National Renewable Energy Laboratory
Berkeley Lab
Sandia National Laboratories
INL Idaho National Laboratory
Lawrence Livermore National Laboratory
SRNL

Technical Backup Slides

UTRC Project Accomplishments
Testing of materials (LBNL Node)

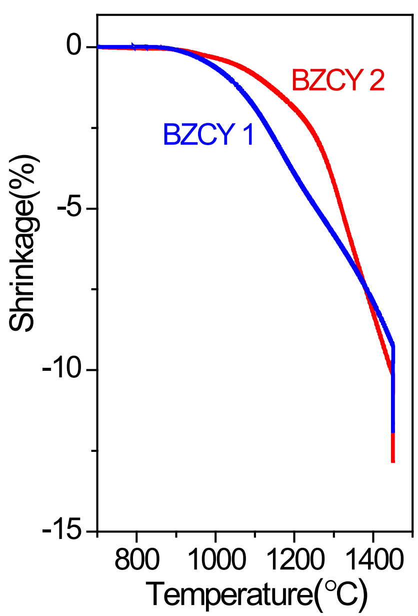
See Poster PD154

- Testing oxidation rates of various metals and metals coating < 650°C
- BaZrCeY proton-conducting based ceramics in high steam

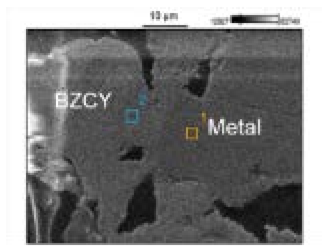


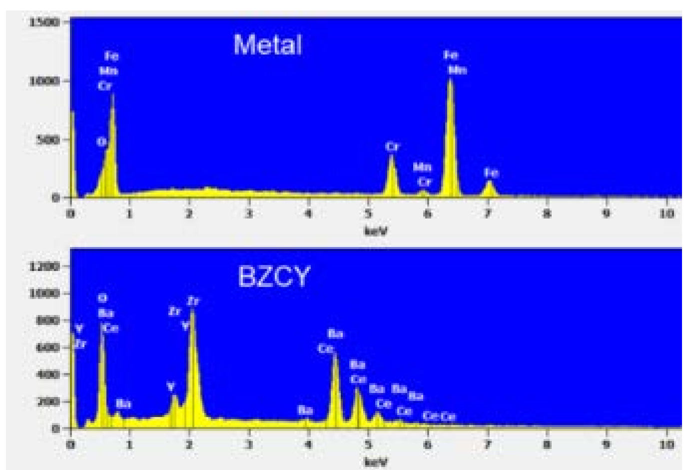
Assessing compatibility with stainless steel and processing conditions

Sintering in H_2 atmosphere

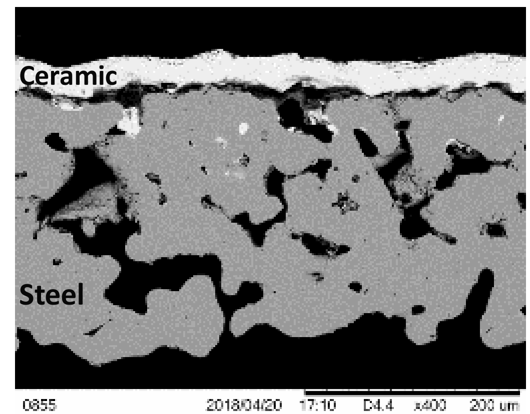


Inter-diffusion avoided





Stainless steel and BZCY-based co-sintered in H_2 atmosphere

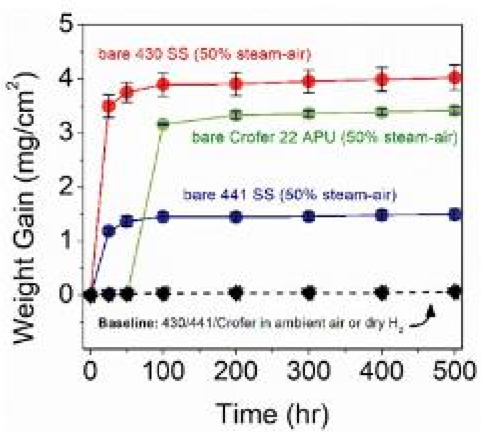


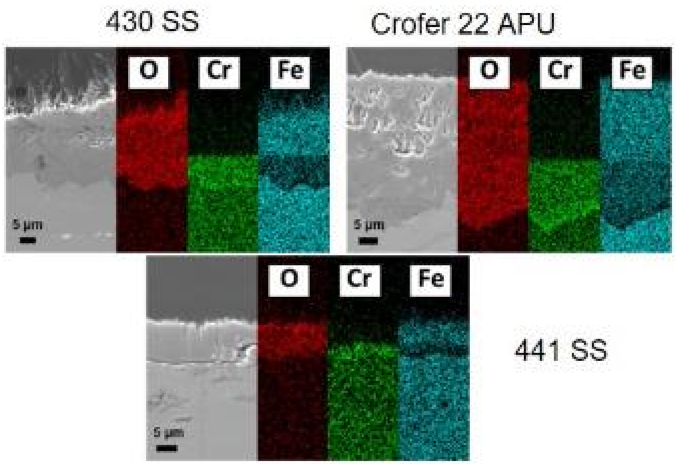
See poster for current project test outcomes

UTRC Accomplishments: Selection of Interconnector Alloy and Coating through Oxidation Study in SOEC Conditions (LBNL)

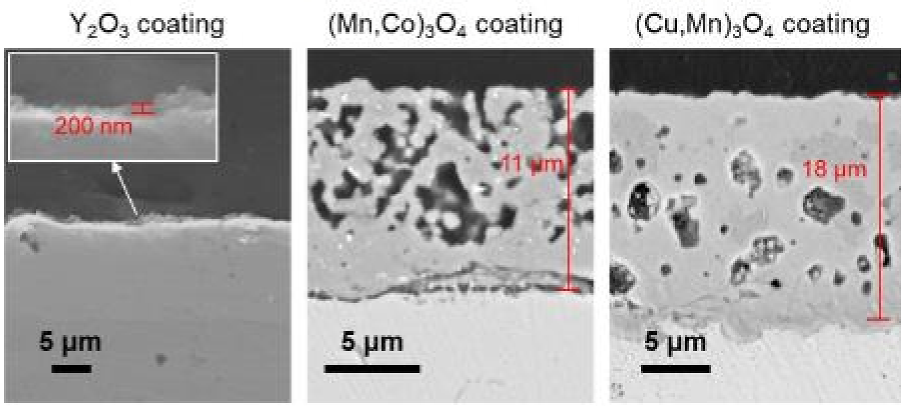
- Severe oxidation of uncoated SS metal alloy in 50% steam-air (650 °C)
- Minimal oxidation observed with coated metals in 50% steam-air (650 °C)

50% steam-air, 650 °C, 500 h

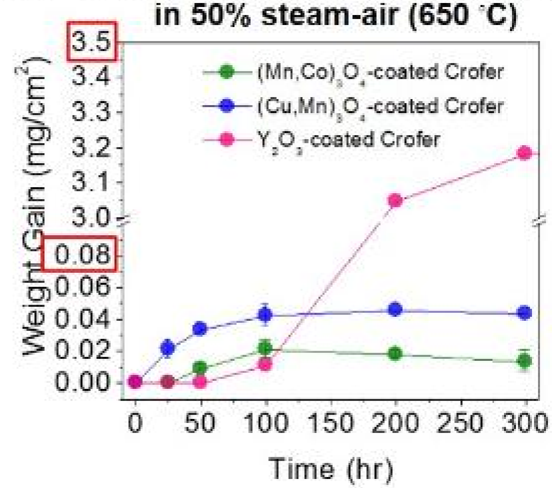




Potential protective coating



Minimal oxidation for MnCo- and CuMn-coated metals in 50% steam-air (650 °C)



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

UTRC Accomplishments
Materials synthesis and testing (INL Node)

See Poster PD154

- Evaluated the conductivities of different electrolytes and their stability in high water content at operating temperatures
- Helped test 1” metal-supported electrolysis cells

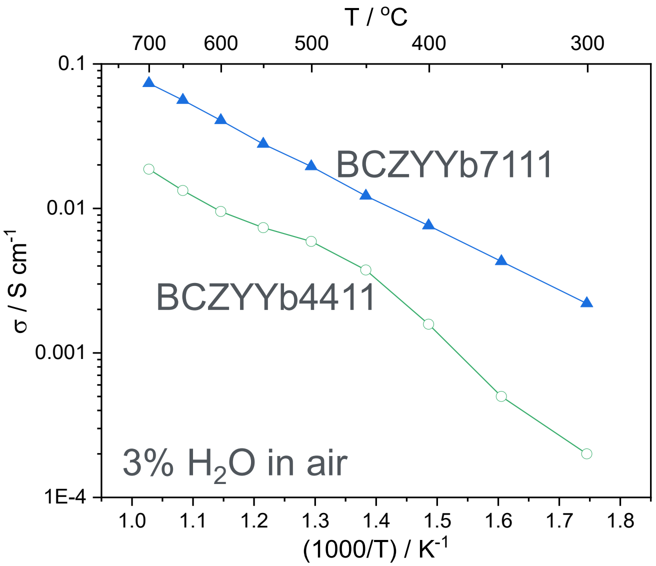


Figure 1a: The temperature dependence of electrical conductivities of BCZYYb7111 and BCZYYb4411 pellets measured by four-probe method in wet air.

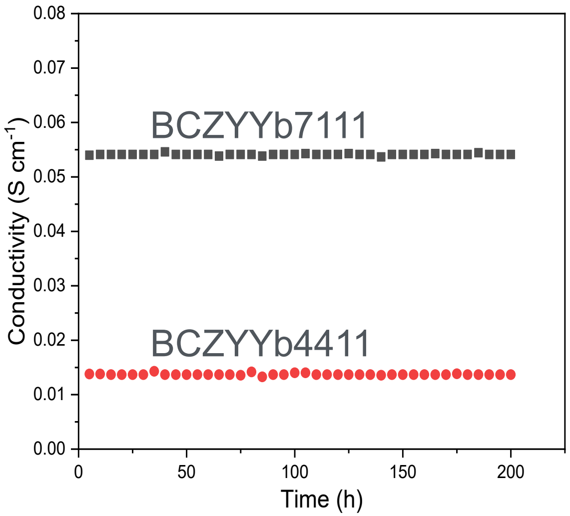
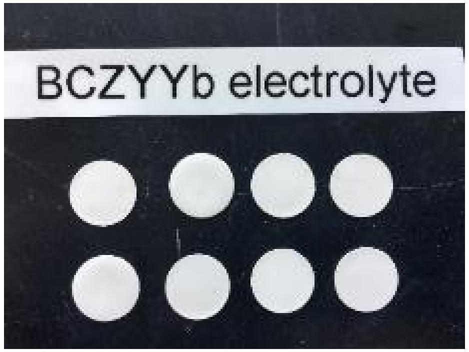


Figure 1b: The stability test of two proton conducting electrolytes in 50% H_2O (carried by air) at 650 °C.



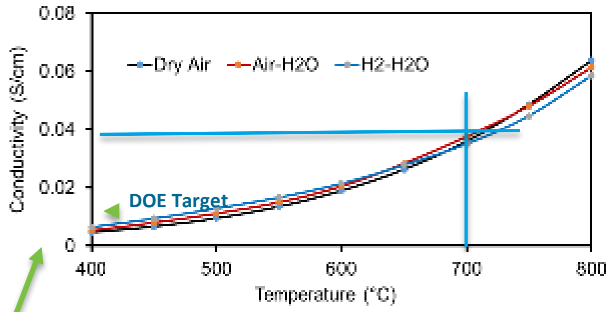
1” cell on testing fixture

UConn Project Accomplishments
Conductivity Measurements and Densification Studies

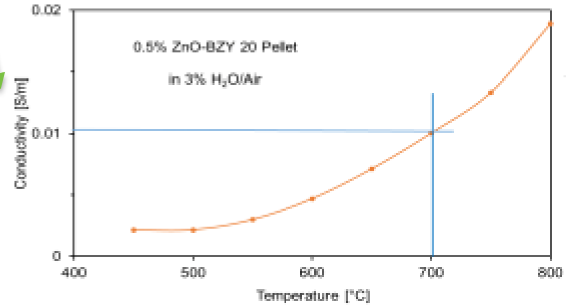
See Poster PD 152

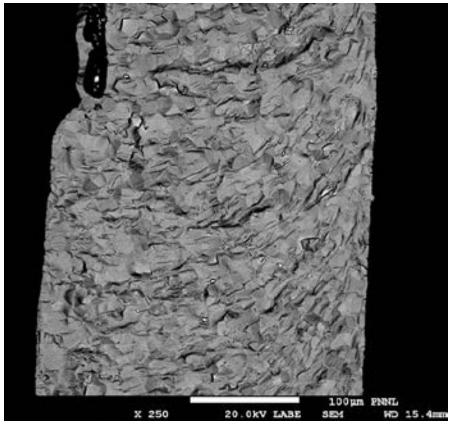
Four-probe Conductivity Test setup Assembled at UConn

1%ZnO BZCY-Yb sintered at 1350˚C for 6 h

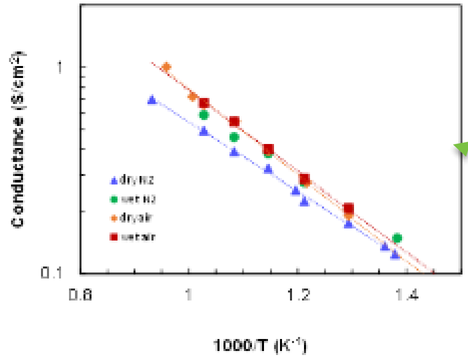


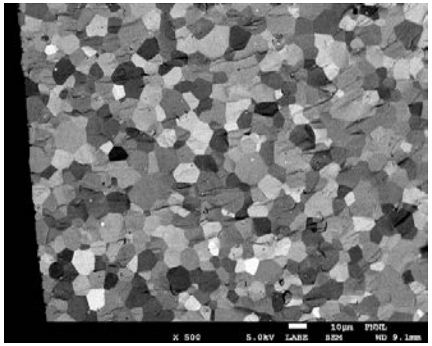
0.5%ZnO BZY sintered at 1450˚C for 6 h

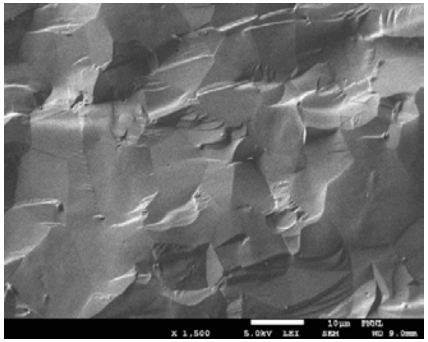




Fractured dense sample





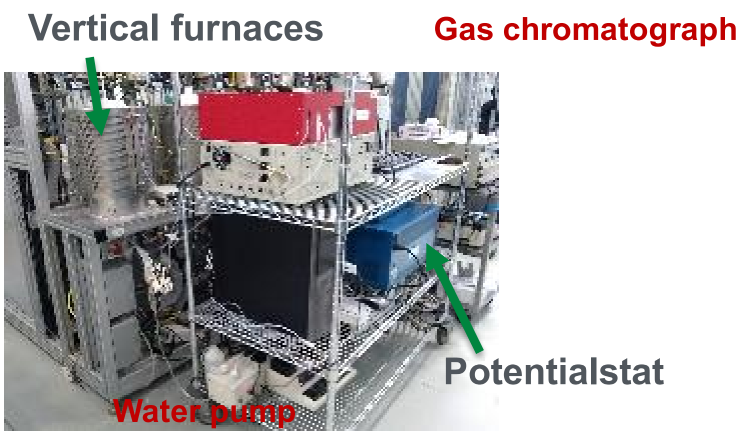


Analyzed by PNNL

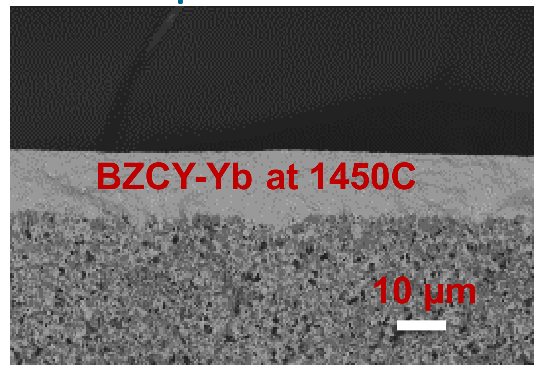
- Measurements obtained at UConn and PNNL show that the conductivity of dense BZCY-Yb (0.04 s/cm) and BZY (0.01 s/cm) electrolyte meets with the DOE Target of Milestone 3-1 (0.01 s/cm at 700˚C).
- Experiments and characterization performed at UConn and PNNL show full densification at 1350°C after sintering in air. The bulk phase remains free of GB precipitates

UConn Project Accomplishments
H-SOEC Cell Preparation & Testing

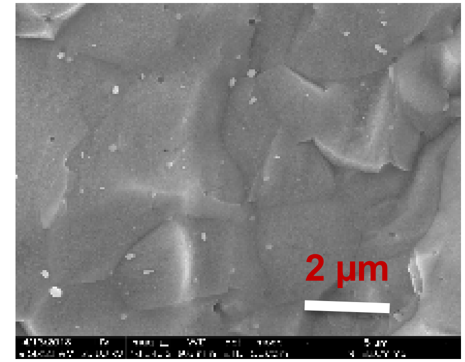
See Poster PD 152



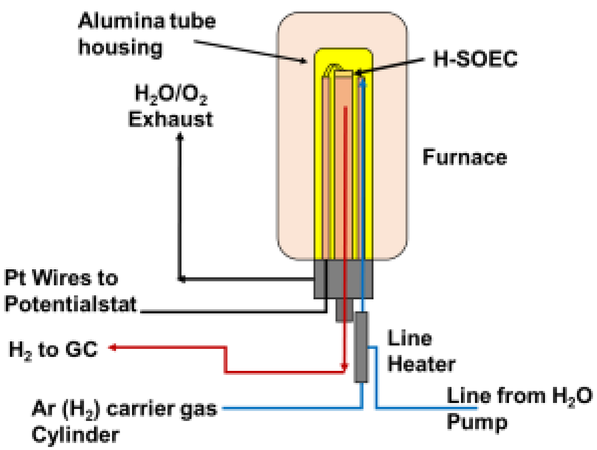
Prepared at INL

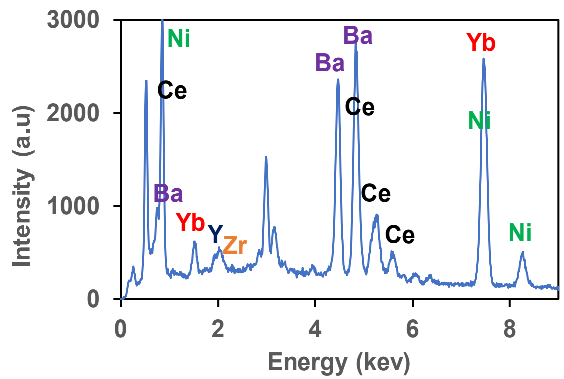


~15 µm thickness of electrolyte

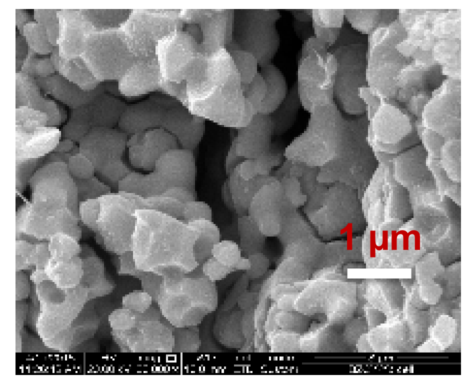


Dense electrolyte at 1350˚C





EDS spectra of electrode



Porous electrode

UConn and INL have fabricated and characterized H-SOEC cells with thin dense electrolyte (15-40 µm). Above SEM images shows a typical Ni-BZCY-Yb||BZCY-Yb half cell. Ni-BZY||BZY||LSCF-BZY cell are being fabricated. Both H-SOEC cells will be tested in Q3 and Q4.