Energy Materials Network
U.S. Department of Energy

HydroGEN
Advanced Water Splitting Materials

HydroGEN: High-Temperature Electrolysis

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Presenter: Richard Boardman, INL

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Venue: 2019 DOE Annual Merit Review

Project ID # P148B

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

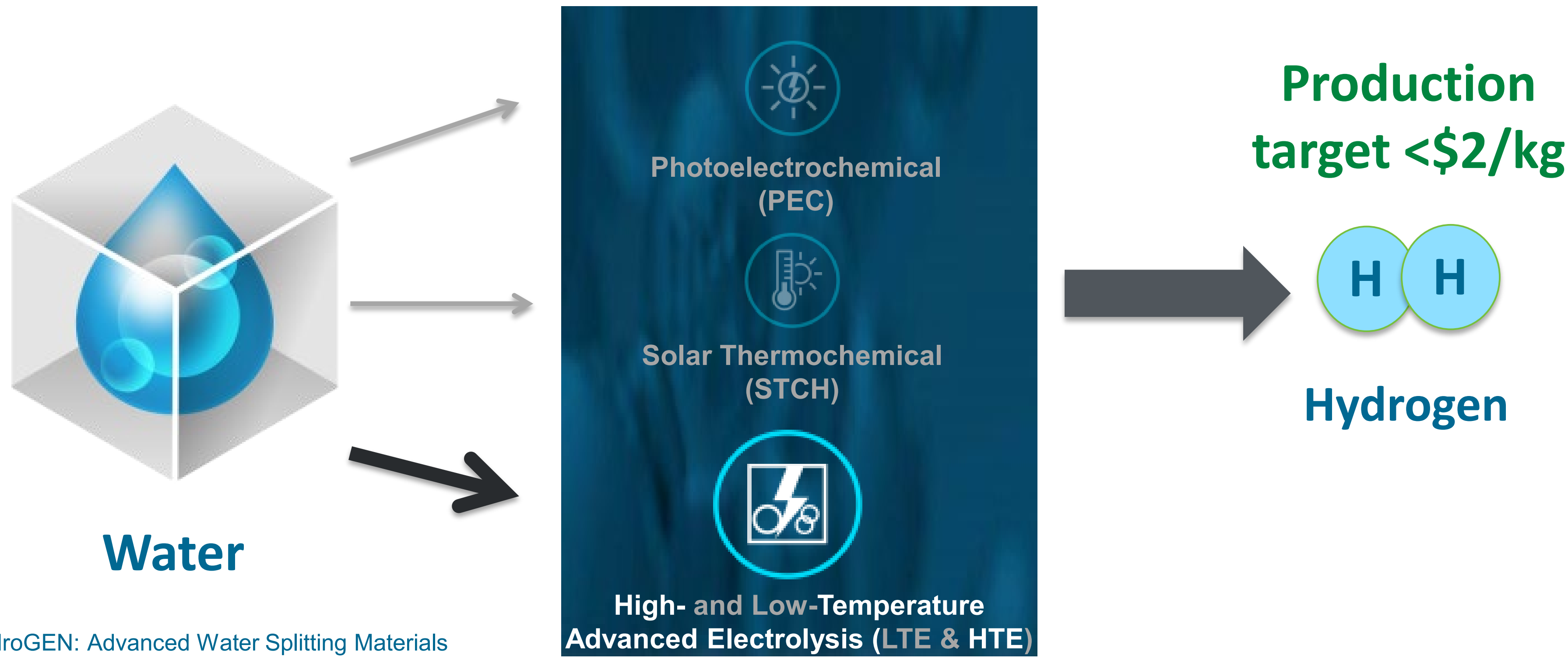
Advanced Water-Splitting Materials (AWSM)

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

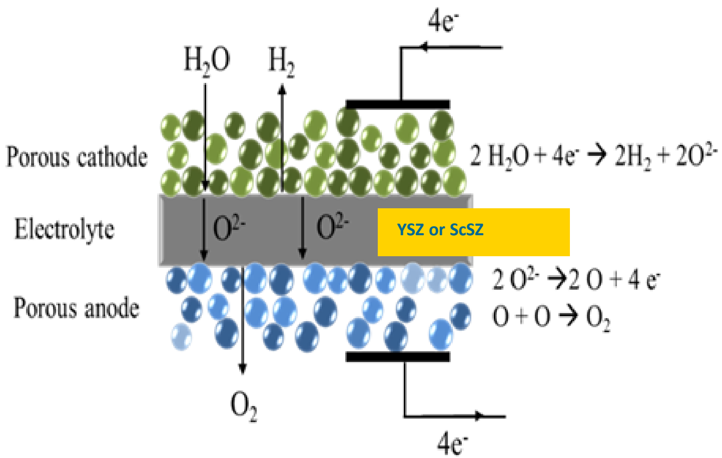
Accelerating R&D of innovative materials critical to advanced water splitting technologies for clean, sustainable & low cost H_2 production, including:



Overview – HTE Technology

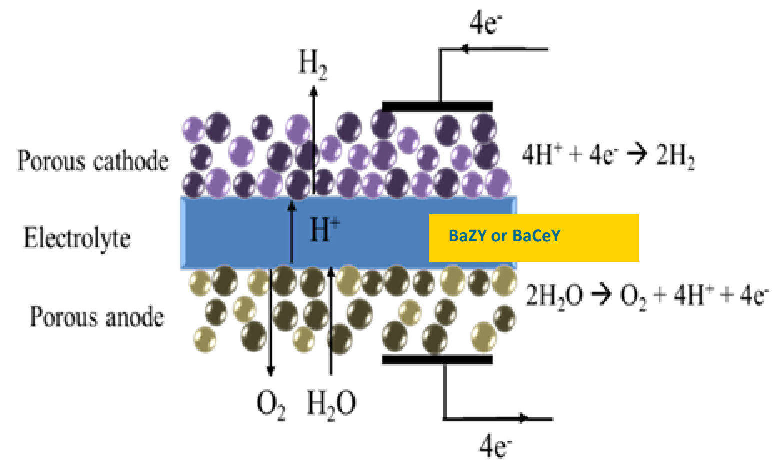
<u>Oxygen Ion Transport</u> **Solid-Oxide Electrolysis***

(O^{2-}–SOEC; Unresolved R&D Material Barriers Remain)



<u>Proton-Conducting</u> **Solid-Oxide Electrolysis***

(H^+-SOEC; Early-Stage Research Needed)



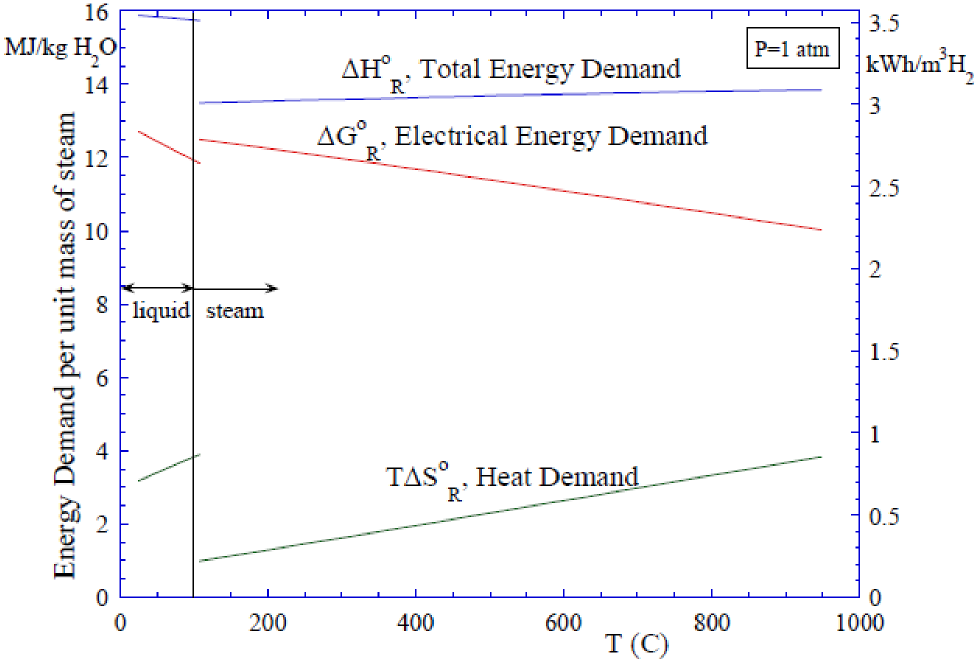
* **Figure and Table Adapted from: Singh and Hu, UConn**

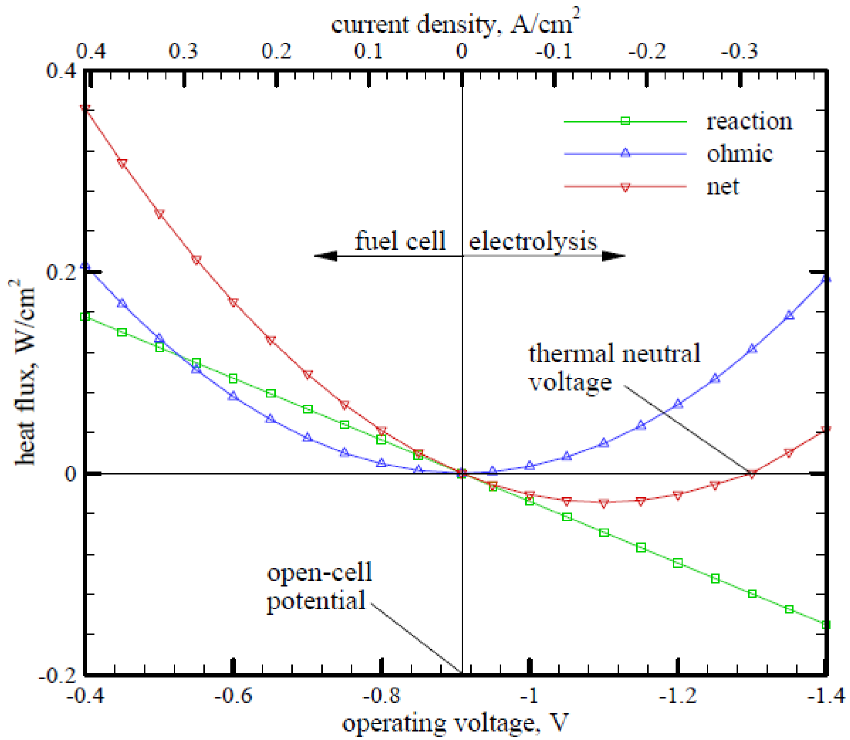
Attributes	H^+- SOEC	O^{2-}- SOEC
Operating Temperature	550-750°C	650-850°C
Electrolyte Conductivity	0.01 $S.cm^{-1}$ at 650°C	0.015 $S.cm^{-1}$ at 850°C
Cathode Products	Pure H_2	$H_2O + H_2$
Anode Products	O_2 + sweep gas	$H_2O + O_2$

- **Thermodynamic efficiency and solid oxide conduction and kinetics increase at higher temperature, but materials durability decreases due to progressive micro-structure evolution, thermal stresses, and chromium migration**

- **Solid oxide is purely proton conducting < 600°C, but kinetics are slower**
- **Electrode and electrolyte materials synthesis, densification, and enhancement for proton-conduction efficiency is in progress**

Advantages/Disadvantages of HTE





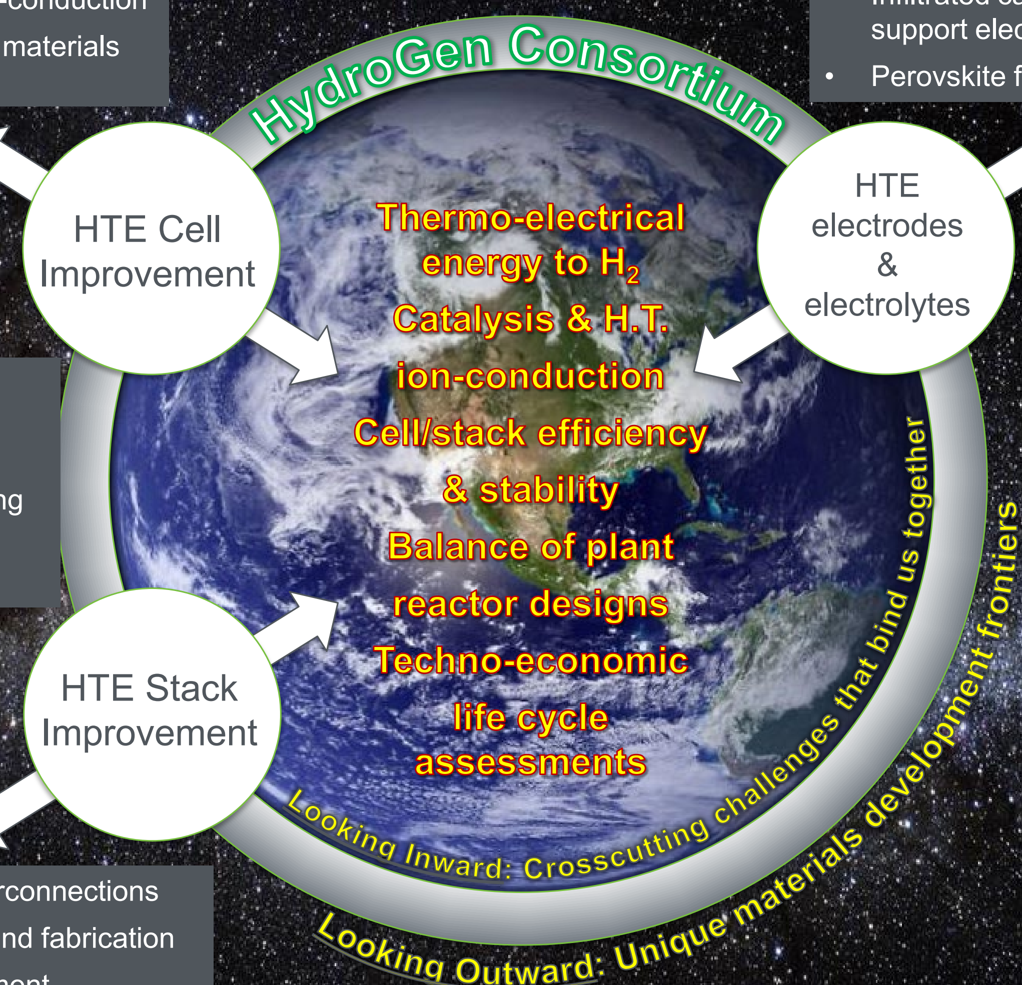
- 30-50% higher thermodynamic efficiency is possible for steam compared to water splitting (combined free energy and electricity use)
- Reversible operation is possible with optimal design of cells, stacks and modules
- Does not require highly precious metals
- Major concerns are rapid cell degradation (sintering, pore consolidation, Cr migration/poisoning, catalyst deactivation (Ni hydridation), delamination)

Overview - HTE Technology Relevance / Impact

- Powder Synthesis
- Electrolyte ion-conduction
- Combinatorial materials deposition

- Electrodes microstructure
- Infiltrated catalysts metal support electrodes
- Perovskite formulations

Lower TRL



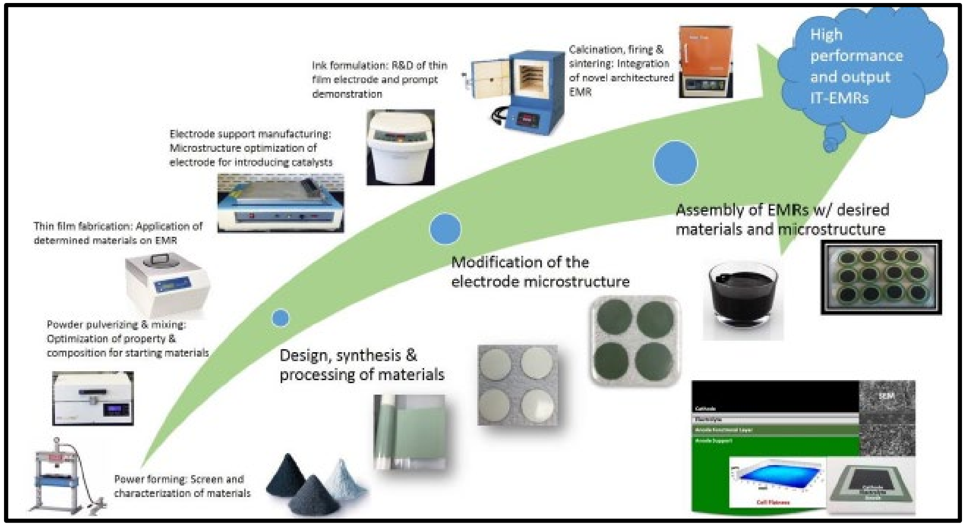
- Conductivity & polarization measurements
- Durability testing
- Embedded sensors

Higher TRL

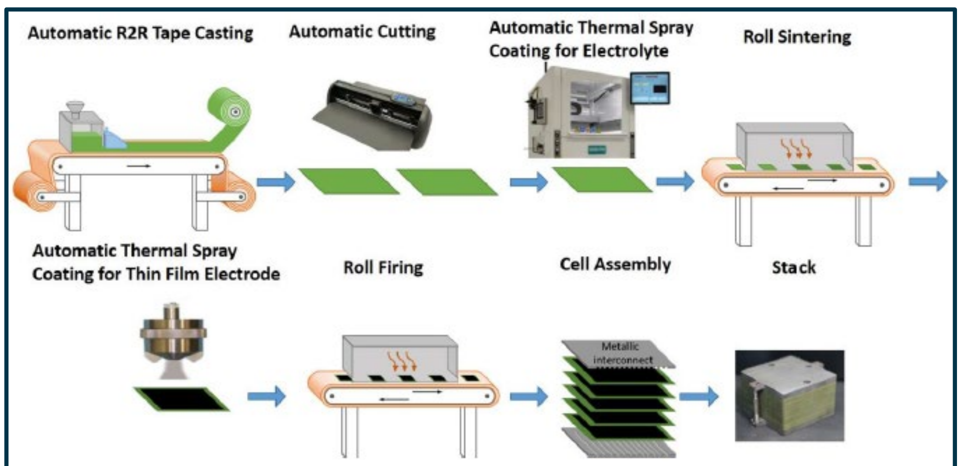
- Seals and interconnections
- Stack design and fabrication
- Heat management

- **Improvements in electrolyte and electrode materials will improve cell performance**
  - ✓ Increase cell conductivity
  - ✓ Enhance catalytic water splitting at triple point
  - ✓ Improve ion conductivity
  - ✓ Reduce area-specific resistance
- **Improvements in cell durability will increase stack longevity**
  - ✓ Reduce catalyst poisoning
  - ✓ Retard microstructure evolution
- **Improvement in stack materials design improve thermodynamic efficiency and reduce costs**
  - ✓ Achieves auto-thermal heat efficiency
  - ✓ Improves seals longevity
  - ✓ Interconnection with matched thermal expansion

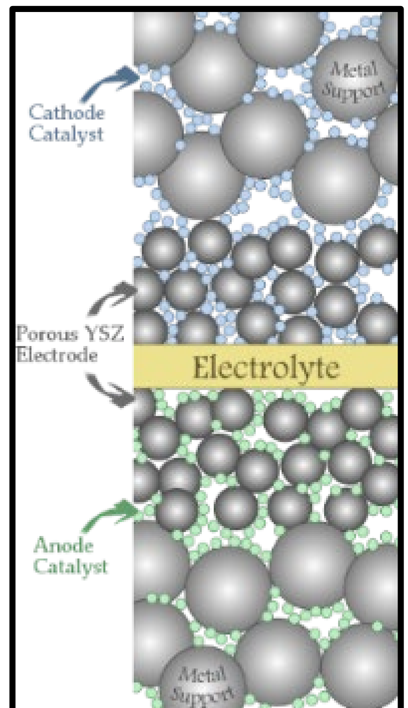
Overview - HTE Technology Relevance / Impact



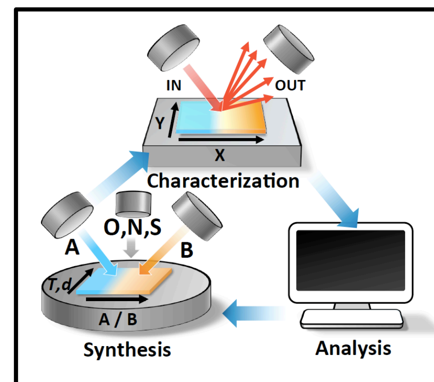
- Advanced HTE Electrode and Electrolyte Materials
- Fabricating cells for stack assembly
- Button Cell Fabrication and testing
- Metal-supported cells reduce cost while managing thermal transients and reducing fabrication steps
- Thermal Spray and Thin-Film Synthesis reduce defects and improve performance



INL Node for Process for Button Cell Fabrication (Upper)
INL Node for Super Proton-Conducting cells (Lower)

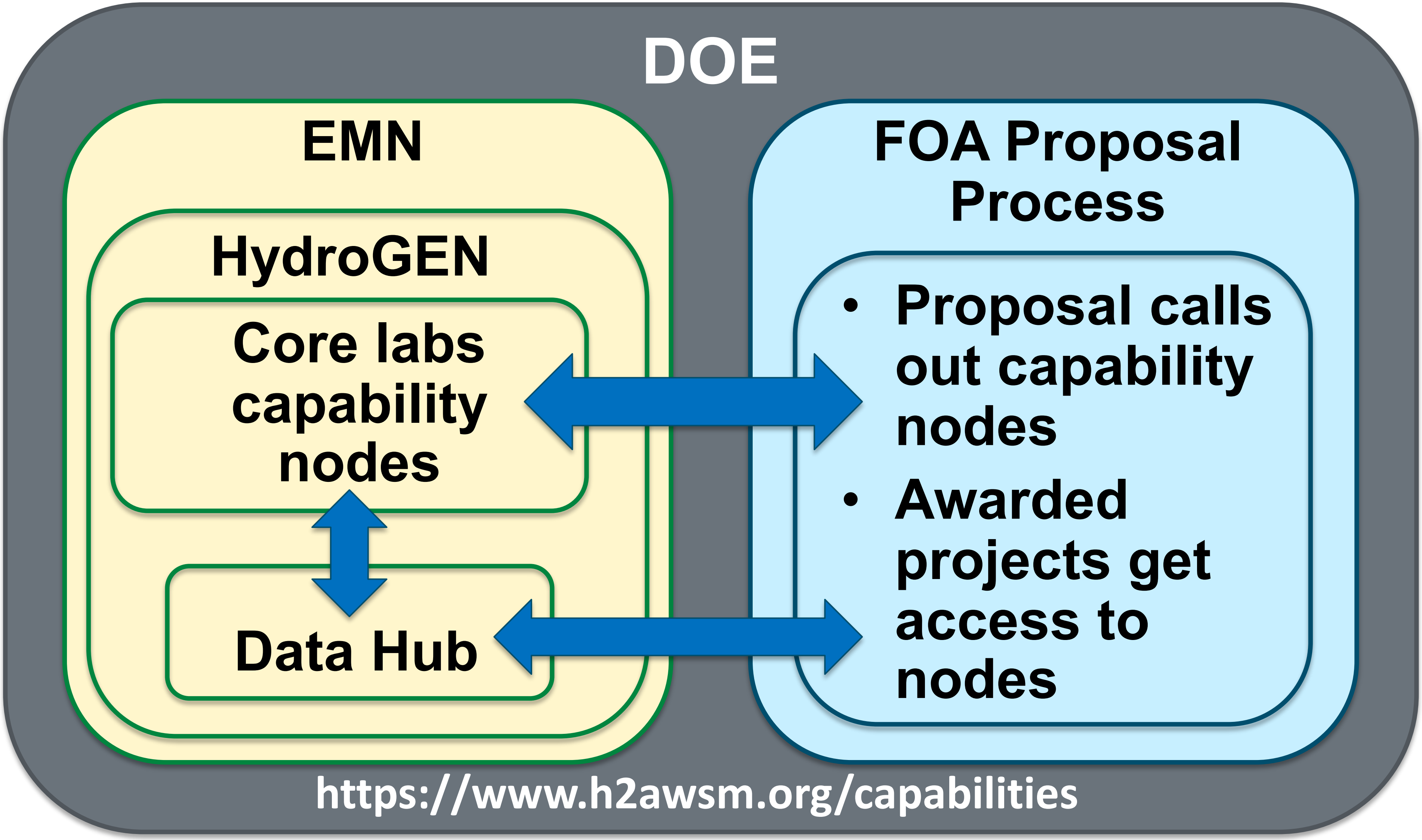


LBNL Node for Metal-Supported SOEC and Coatings (Left)



NREL Node for Thin Film Coatings and Combinatorial Testing (above)

Approach – HydroGEN EMN



Approach: HTE Projects & Collaboration

- Efficiency
- Yield
- **Cost**
- Durability
- Manufacturability

HTE Node Labs

Idaho National Laboratory

BERKELEY LAB

NREL
NATIONAL RENEWABLE ENERGY LABORATORY

Lawrence Livermore National Laboratory

Supernode

Support through:

Personnel

Equipment

Expertise

Capability

Materials

Data

HTE Projects

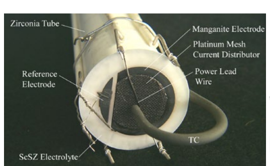
United Technologies Research Center

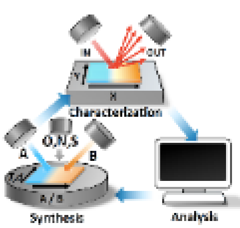
West Virginia University

Northwestern University

University of Connecticut

SAINT-GOBAIN



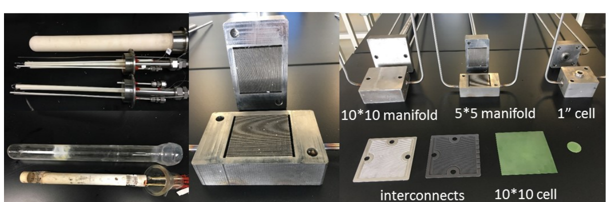


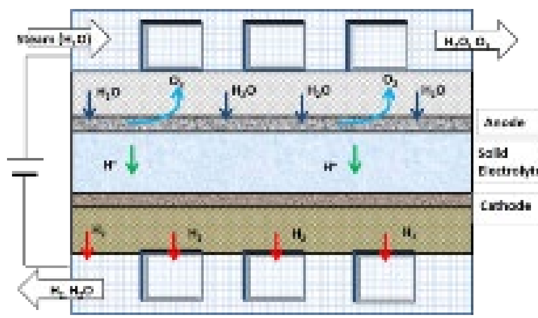
Accomplishments and Progress:
Established Nodes for Project Support

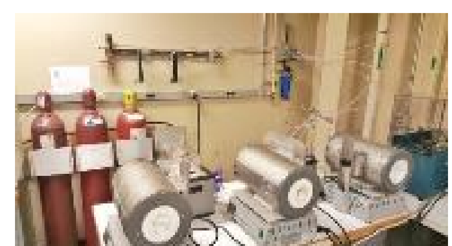
44 nodes for HTE
- 8x readiness level 1
- 24x readiness level 2
- 11x readiness level 3

7 nodes used by current HTE projects

Node Classification
6x Analysis
6x Benchmarking
20x Characterization
13x Computation
6x Material Synthesis
5x Process and Manufacturing Scale-Up
5x System Integration





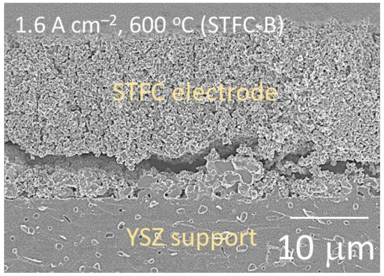


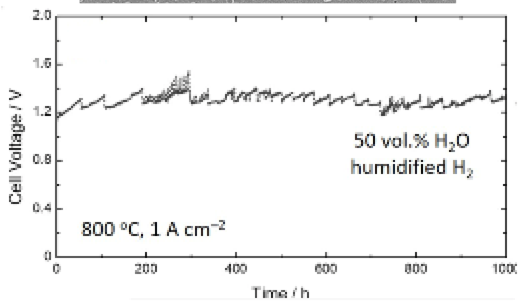
Accomplishments and Progress: Northwestern University P153

Characterization and Accelerated Life Testing of a new Solid Oxide Electrolysis Cell

Goal and approach

- Degradation mechanisms in solid oxide electrolysis cells (SOECs) are studied using accelerated life testing with varying conditions, materials, and cell designs
- Theory used with experimental data to develop a basic understanding of degradation mechanisms
- Development of improved SOECs that provide stable long term operation at high current density





Accomplishments in BP1

- Oxygen electrode overpotentials > 0.19 V shown cause cell fracture
- Theory predicts where internal oxygen pressure exceeds fracture strength solid oxide cells providing stable electrolysis operation at 1 A cm-2 have been demonstrated
- Novel metal-supported cells have been demonstrated for electrolysis

Focus of BP2

- Advanced solid oxide electrolysis cells will be life tested with electrochemical and microstructural characterization
- Achieving improved long-term stability
- Electrode and electrolyte degradation theory will be further developed by comparison with experiment
- Refine optimized cell designs for BP3

Accomplishments and Progress: **University of Connecticut:**

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

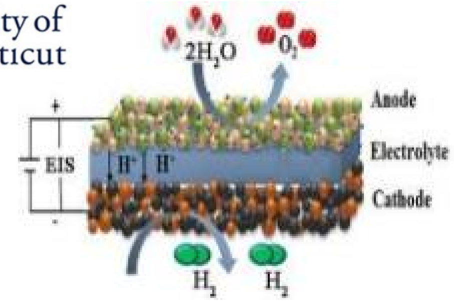
P152

Project Goals: 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 (< \$2/gge H_2) and performance targets (degradation rate <4 mV/1000 h at 1A/cm²), and electrical efficiency >95%.

PI: Prabhakar Singh
Co-PI: Boxun Hu
Partner: PNNL

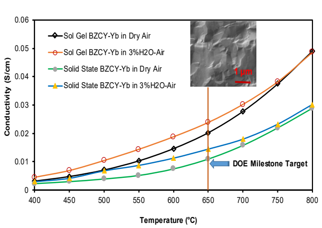
Approaches:

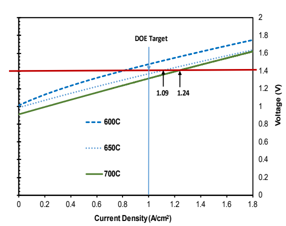
a) Develop electrolyte formulations capable of densification (96-98%) below 1400˚C;
b) Utilize tape cast multi-layer laminated electrolyte (10-20 µM) and electrode;
c) Optimize cell materials for densification, proton conductivity and structural stability;
d) Develop electrode poisoning and performance degradation mitigation approaches;
e) Utilize EMN core experimental and computational capabilities (INL & NREL).

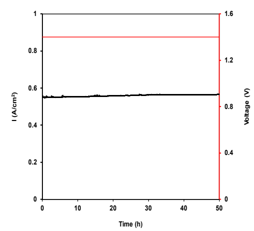


Accomplishments in BP1

- Sintered electrolyte at ≤1400˚C.
- Obtained electrical conductivity of 0.01 $S.cm^{-1}$ at 650˚C.
- Demonstrated cell performance of 1 A/cm² at 1.4 V and 650˚C.
- Achieved 50 hours cell performance stability.

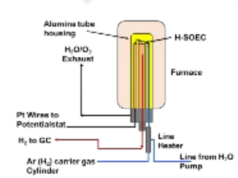


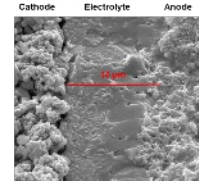


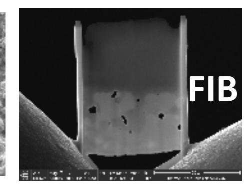


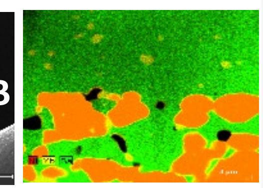
Focus of BP2

- Develop 50-gram batch proton-conducting electrolyte with conductivity of at least 0.02 $S.cm^{-1}$ at 650°C.
- Develop and test 1-inch diameter cells with stable electrolysis performance (<25 mV/1000 h) for at least 200 hours.
- Obtain current density above 1 A/cm² at ≤ 1.4 V and temperature of ≤ 650°C.









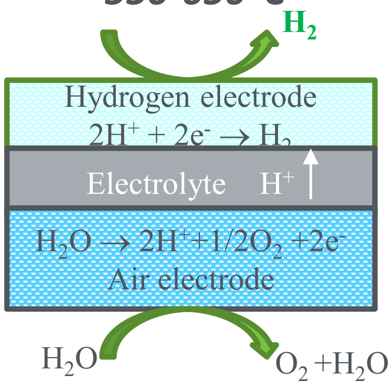
Accomplishments and Progress: **United Technology Research Center**
Thin-Film, Metal-Supported High-Performance and Durable Proton-Solid Oxide Electrolyzer Cell

P154

Concept

Proton conducting electrolyzer

550-650 ℃



Approach

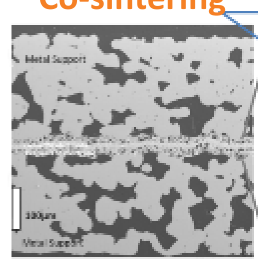
Integrate low cost fabrication, material optimization and modeling

Target performance >1.0 A/cm² at 1.4 V and ≤650 ℃

Plasma Spray

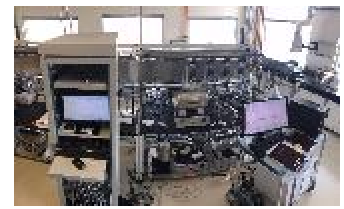
UTRC

Co-sintering



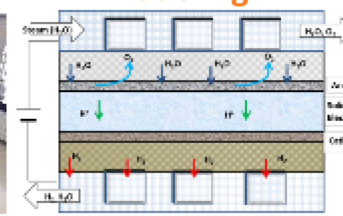
LBNL

Material optimization



INL

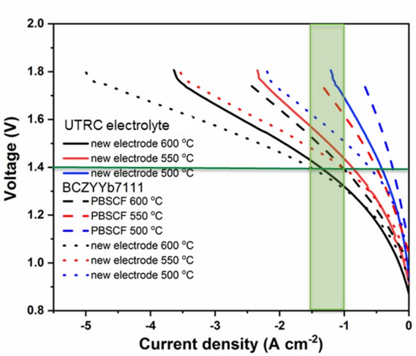
p-SOEC cell modeling



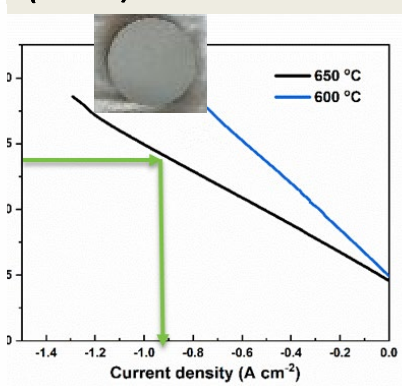
NREL

BP1 Main Accomplishments

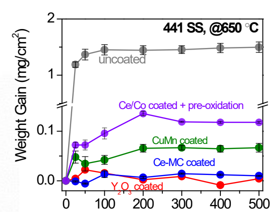
High performance material identified for p-SOEC (>1.0 A/cm² at 1.4V & <650°C)



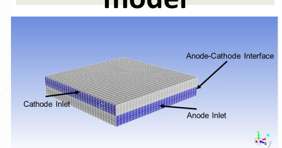
Button cell with SPS electrolyte exceeded BP1 target (>0.8 A/cm² at 1.4V & 650°C)



Protective coatings for SS alloys, 500h no oxidation



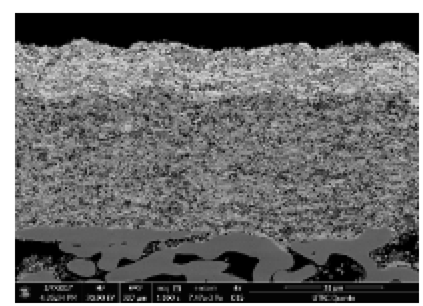
Establish cell model



BP2 Focus

- Metal cell fabrication by plasma spray
- Material optimization and durability
- Cell performance modeling

Half cell on metal support by plasma spray



Accomplishments and Progress:
West Virginia University (New project, in BP 1)

West Virginia University

P175

Goal: IT H-SOECs for simultaneous H_2O splitting and H_2 separation with high current densities > 1.0 A/cm^2 at 1.4 V/cell while operating at ~700 °C (BP1).

Approach:

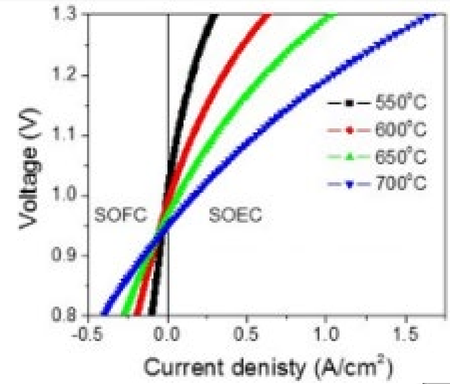
Electrode and full cell @ WVU
- Modeling driving
  - H_2O-splitting reaction kinetics
  - Anode structural and composition
- Candidate anodes development
- Conformal catalyst layer coating
- Cell fabrication and performance measurements

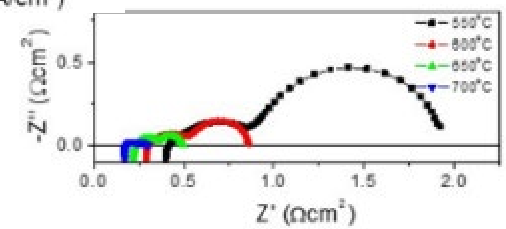
Electrocatalyst @ CSM&NREL
- Appropriate electrocatalyst compositions
  - High-throughput screening
- Catalysis & local surface activity
  - Operando ambient-pressure XPS

H-electrolyte @ INL:
- Advanced powder synthesis techniques
  - sol-gel and nitrate-combustion
- Post analysis
  - SEM/EDX, TEM and XPS
- Conductivity improvements

Accomplishment of BP1

- Established framework of H_2O-splitting reaction kinetics modeling
- Development of highly performing triple conducting anode, ~1A/cm^2 at 1.3V 700^{o}C
- Initial testing of reference samples on Scienta-Omicron HIPP Lab System at Mines
- Reference samples are being characterized with E-XPS, high throughput screen of anode and catalyst has started
- Initiated study on improving conductivity, stability and sinterability of BCZYYb system by adjusting Zr/Ce ratio in INL





Accomplishments and Progress:
Saint-Gobain (New project, in BP 1)

P176

SAINT-GOBAIN

Project Goal

Develop oxygen electrode materials with high performance which solve the issue of electrode delamination in order to produce hydrogen below the DOE target of $1.87/kg and to test this electrode in a stack platform that has shown degradation rates <0.2%/1000 hrs in SOFC mode.

Approach

Novel chemistries of nickelate-based materials showing enhanced oxygen hyperstoichiometry will be developed. These materials will be co-sintered in button cells and stacks to be tested for performance and durability.

Barriers to be overcome

1) Phase stability/performance: Identification of stability boundaries with target electrochemical properties

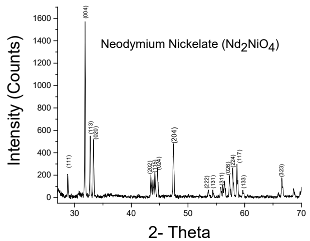
2) Co-sintering with balance of cell: Incorporate materials with stacks ensuring porosity & activity

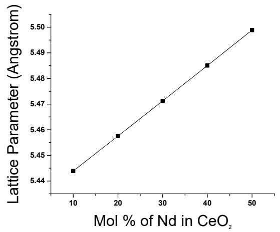
3) Accelerated testing: Protocol development to probe dominant degradation mechanism

BP1: 10/18 – 9/19

Saint-Gobain, Boston University, PNNL & INL refined testing protocol, project plan, and responsibilities

- Neodymium nicklate (NNO) and neodymium doped ceria (NDC) chosen as 1st material set to produce
- Synthesis procedures developed resulting in phase purity
- Phase pure NNO prepared
- Lattice parameter shift correlates very will with degree of Nd doping in CeO2





Remainder of BP1: 3/19 – 9/19

- Complete synthesis of remaining target compositions
- Utilize high-temp XRD & TGA @ SNL to quantify oxygen hyperstoichiometry
- Quantify phase stability of target material systems
- Prepare button cells of baseline and new compositions
- Test baseline SOEC performance and degradation
- Down-select material compositions based on lab tests
- Test top performers in SOEC mode to show enhanced performance and durability
- Utilize microstructural analysis including CT scanning to determine degradation mode

BP2 10/19 – 9/20 Proposed Plan

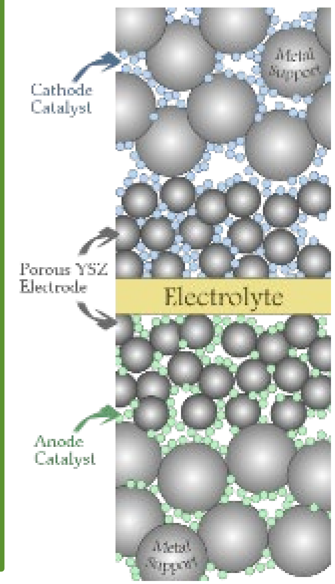
- Scale testing from button cells to stacks
- Optimize stoichiometry of high performing material

HTE Supernode : Characterization of Solid Oxide Electrode Microstructure Evolution

Challenge:

Degradation mechanisms in solid oxide electrolysis cells (SOECs), which are poorly understood at present, will be studied using accelerated testing at high current density, closely coupled with theory.

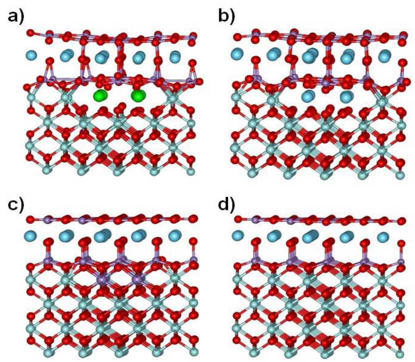
A deeper understanding of high temperature electrolysis (HTE) electrode microstructure evolution as a function of local solid-oxide composition and operating conditions is needed to develop more active, longer-life electrodes.



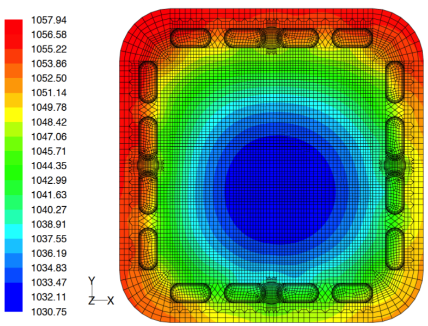
Catalyst particle coarsening

Solid-oxide electrode & electrolyte sintering

Electrical currents and ion forces lead to inter-crystalline structure forces



High temperatures and thermal gradients cause non-uniform grain boundary stresses



Goal: *Combine HTE nodes to establish achieve a deep understanding of high temperature electrolysis (HTE) electrode microstructure evolution as a function of local solid-oxide composition and operating conditions.*

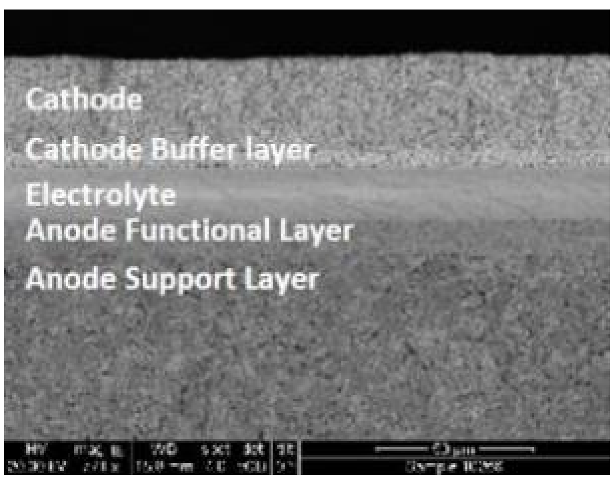
HTE Supernode : Characterization of Solid Oxide Electrode Microstructure Evolution

Accomplishments

- ✓ Supernode team established; R&D plan has been initiated
- ✓ First batch of YSZ-based SOEC fabricated using high-purity precursors.
- ✓ Sintering aid used in cathode buffer layers.
- ✓ Electrolyte thickness: 10-15 um.

7 nodes combined:

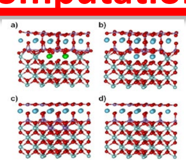
INL, NREL, LBNL, LLNL, Sandia



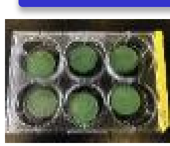
Collaboration: HTE Node Utilization

Lab	Node	Node PI	NWU	UConn	UTRC	Super-Node
NREL	Multi-Scale Thermochemical and Electrochemical Modeling for Material Scale-Up to Component and System Design	Ma, Zhiwen Martinek, Janna		✓	✓	
LBNL	Metal-Supported SOEC Cell	Tucker, Michael Wang, Ruofan	✓		✓	
INL	Advanced Materials for Elevated Temperature Water Electrolysis	Ding, Dong		✓	✓	✓
NREL	Controlled Materials Synthesis and Defect Engineering	Ginley, David Parilla, Philip Bell, Robert				✓
NREL	High-Throughput Experimental Thin Film Combinatorial Capabilities	Zakutayev, Andriy		✓		
INL	SOEC Characterization	O'Brien, James	✓			✓
NREL	Secondary Ion Mass Spectrometry (SIMS)	Harvey, Steven	✓			
SNL	Advanced Electron Microscopy	Sugar, Josh				✓
LLNL	Multi-Scale Modeling of Solid-Sate Interfaces and Microsructures in High-Temperature Water Splitting Materials	Wook, Tase Wood, Brandon Frolov, Timofey				✓

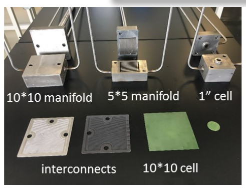
Computation

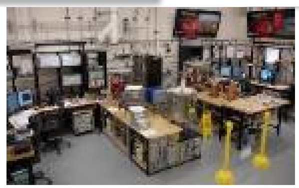


Material Synthesis

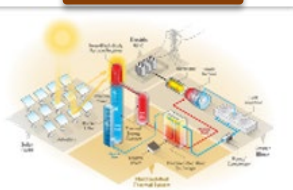


Characterization

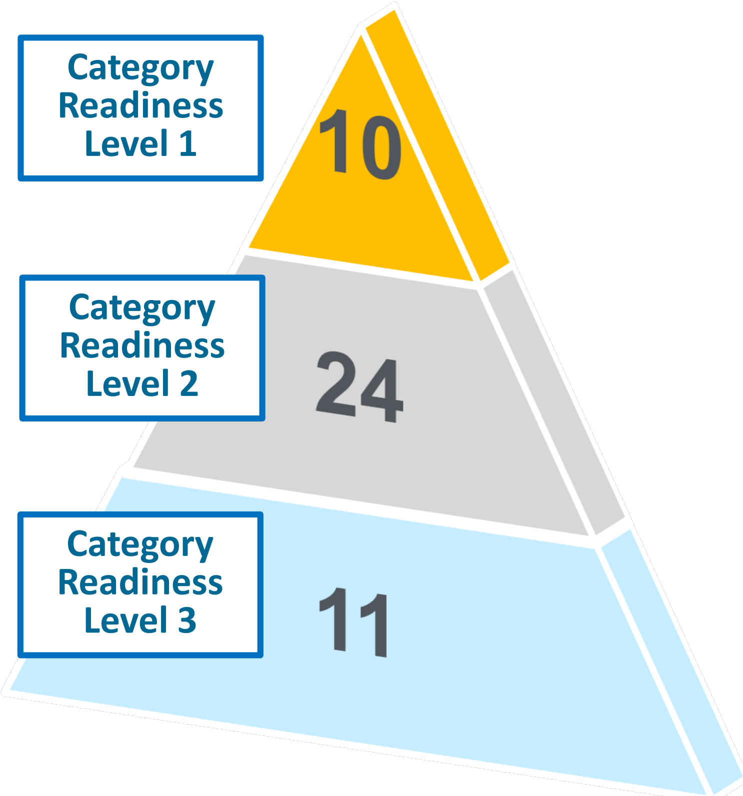




Analysis



Collaboration: 44 HTE Nodes



Analysis: 2	Characterization: 5
Computation: 1	Synthesis: 2

Analysis: 2	Characterization: 9
Computation: 10	Synthesis: 3

Analysis: 2	Characterization: 6
Computation: 2	Synthesis: 1

- Nodes comprise equipment and expertise including uniqueness
- Category refers to availability and readiness and not necessarily the expense and time commitment
- Note that many nodes span classification areas

Data Hub & Engagement with 2B Benchmarking Team (Olga Marina, PNNL – HTE Lead)

BENCHMARKING

- **Ongoing assessment of the EMN Node capabilities**
- **Collaborated with HydroGEN Benchmarking Project**
- **Leadership role in developing path forward for harmonized protocols, hardware, and materials**
- **Benchmarking working groups and annual meeting**
- **Disseminated benchmarking information**

DATA HUB

- **HTE data metadata definitions in development**
- **Several datasets uploaded to hub**

Summary - HydroGEN LTE Projects

- **HydroGEN HTE is:**
  - Supporting 5 FOA projects with 9 nodes
  - Leading a Supernode with 6 nodes
- **Projects demonstrate improvements in Proton-Conducting and Oxygen Ion Transport Electrodes / Electrolytes**
- **Working closely with the project participants and benchmarking activities to advance knowledge and utilize capabilities**

Future Work

- Continue to enable and support research of Phase 2 Projects through lab nodes and expertise
- Enable new FOA awarded seedling projects (Fall 2019)
- Continue to develop HTE supernode to attain deeper understanding of microstructure functionality and evolution
- 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

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HydroGEN
Advanced Water Splitting Materials

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