HydroGEN: High-Temperature Electrolysis

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Advanced Water-Splitting Materials (AWSM)
Relevance, Overall Objective, and Impact

Accelerating R&D of innovative materials critical to advanced water splitting technologies for clean, sustainable & low cost H₂ production, including:

**Photoelectrochemical (PEC)**
**Solar Thermochemical (STCH)**
**High- and Low-Temperature Advanced Electrolysis (LTE & HTE)**

Production target <$2/kg

Hydrogen
Overview – HTE Technology

Oxygen Ion Transport Solid-Oxide Electrolysis*  
(O\textsuperscript{2−}-SOEC; Unresolved R&D Material Barriers Remain)

Proton-Conducting Solid-Oxide Electrolysis*  
(H\textsuperscript{+}-SOEC; Early-Stage Research Needed)

- 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

<table>
<thead>
<tr>
<th>Attributes</th>
<th>H\textsuperscript{+}- SOEC</th>
<th>O\textsuperscript{2−}- SOEC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Operating Temperature</td>
<td>550-750°C</td>
<td>650-850°C</td>
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<tr>
<td>Electrolyte Conductivity</td>
<td>0.01 S.cm\textsuperscript{-1} at 650°C</td>
<td>0.015 S.cm\textsuperscript{-1} at 850°C</td>
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<tr>
<td>Cathode Products</td>
<td>Pure H\textsubscript{2}</td>
<td>H\textsubscript{2}O + H\textsubscript{2}</td>
</tr>
<tr>
<td>Anode Products</td>
<td>O\textsubscript{2} + sweep gas</td>
<td>H\textsubscript{2}O + O\textsubscript{2}</td>
</tr>
</tbody>
</table>

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

Lower TRL

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

Higher TRL

- Conductivity & polarization measurements
- Durability testing
- Embedded sensors

HTE Cell Improvement

- Thermo-electrical energy to H₂
- Catalysis & H.T. ion-conduction
- Cell/stack efficiency & stability
- Balance of plant reactor designs
- Techno-economic life cycle assessments

HTE electrodes & electrolytes

- 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

HydroGEN: Advanced Water Splitting Materials
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
Approach – HydroGEN EMN

- HydroGEN
  - Core labs capability nodes
  - Data Hub

DOE

FOA Proposal Process
- Proposal calls out capability nodes
- Awarded projects get access to nodes

https://www.h2awsm.org/capabilities
HydroGEN: Advanced Water Splitting Materials

Support through:
- Personnel
- Equipment
- Expertise
- Capability
- Materials
- Data

HTE Node Labs
- INL
- Berkeley Lab
- NREL
- Lawrence Livermore National Laboratory

Supernode

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
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
**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 H₂) and performance targets (degradation rate < 4 mV/1000 h at 1 A/cm²), and electrical efficiency > 95%.

**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.
Concept
**Proton conducting electrolyzer**

550-650 °C

Hydrogen electrode

2H⁺ + 2e⁻ → H₂

Electrolyte

H₂O → 2H⁺ + 1/2O₂ + 2e⁻

Air electrode

H₂O → H₂ + O₂

Approach

Integrate low cost fabrication, material optimization and modeling

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

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)

BP2 Focus

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

Half cell on metal support by plasma spray

Protective coatings for SS alloys, 500h no oxidation

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

Goal: IT H-SOECs for simultaneous \( \text{H}_2\text{O} \) splitting and \( \text{H}_2 \) separation with high current densities > 1.0 A/cm\(^2\) at 1.4 V/cell while operating at \( \sim 700 \, ^\circ\text{C} \) (BP1).

Approach:

**Electrode and full cell @ WVU**
- Modeling driving
  - \( \text{H}_2\text{O} \)-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

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**Accomplishment of BP1**

- Established framework of \( \text{H}_2\text{O} \)-splitting reaction kinetics modeling
- Development of highly performing triple conducting anode, \( \sim 1\text{A/cm}^2 \) at 1.3V 700\(^\circ\text{C}\)
- 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)

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
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.

Goal: Combine HTE nodes to establish 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 µm.

7 nodes combined:

INL, NREL, LBNL, LLNL, Sandia

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Cathode
Cathode Buffer layer
Electrolyte
Anode Functional Layer
Anode Support Layer
# Collaboration: HTE Node Utilization

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<tr>
<th>Lab</th>
<th>Node</th>
<th>Node PI</th>
<th>NWU</th>
<th>UConn</th>
<th>UTRC</th>
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<td>NREL</td>
<td>Multi-Scale Thermochemical and Electrochemical Modeling for Material Scale-Up to Component and System Design</td>
<td>Ma, Zhiwen Martinek, Janna</td>
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<td>LBNL</td>
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<td>Tucker, Michael Wang, Ruofan</td>
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<td>LLNL</td>
<td>Multi-Scale Modeling of Solid-State Interfaces and Microstructures in High-Temperature Water Splitting Materials</td>
<td>Wook, Tase Wood, Brandon Frolov, Timofey</td>
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## HydroGEN: Advanced Water Splitting Materials

- **Computation**
- **Material Synthesis**
- **Characterization**
- **Analysis**
Collaboration: 44 HTE Nodes

- 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
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
Acknowledgements

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Node Experts

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