Thin-Film, Metal-Supported High-Performance and Durable Proton-Solid Oxide Electrolyzer Cell

Project ID # p154

Tianli Zhu
United Technologies Research Center
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**Project Overview**

**Thin-Film, Metal-Supported High-Performance and Durable Proton-Solid Oxide Electrolyzer Cell**

Tianli Zhu, United Technologies Research Center

Partner organizations: UConn, ElectroChem Ventures

**Project Vision**

Develop a highly efficient and cost competitive high-temperature electrolysis for H\textsubscript{2} generation, by a thin-film, high efficiency and durable metal-supported solid oxide electrolysis cell (SOEC) based on proton-conducting electrolyte at targeted operating temperatures of 550-650°C.

**Project Impact**

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

Project Motivation
Anode supported p-SOFC button cell (ARPA-E REBELs)

Key Impact

<table>
<thead>
<tr>
<th>Metric</th>
<th>State of the Art</th>
<th>Proposed</th>
</tr>
</thead>
<tbody>
<tr>
<td>SOEC Performance</td>
<td>1 A/cm² at 1.4 V at 800 °C</td>
<td>≥1 A/cm² at 1.4 V at 650 °C</td>
</tr>
<tr>
<td>SOEC Durability</td>
<td>(1-4)% per 1000 h (≈4 mV per 1000 h)</td>
<td>&lt;0.4% per 1000 h</td>
</tr>
<tr>
<td>H₂ production</td>
<td>&gt;$4/kg H₂</td>
<td>$2/kg H₂</td>
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</table>

Barriers
- Low cost deposition of ceramic layers: Deposition process without high T sintering: RSDT, SPS, LBNL co-sintering/metal infiltration
- Metal alloy durability
Proper selection of metal alloys and protective coatings through durability tests
- Steam electrode and electrolyte stability
INL’s high-throughput methodology; molecular dynamics modeling

Partnerships
- University of Connecticut (Prof. Radenka Maric): Cell Fabrication (RSDT)
- UTRC SPS Vendor/PW: Suspension Plasma Spray (SPS)
- ElectroChem Ventures (consultant): Metal-supported cell design
- EMS nodes: LBNL, INL & NREL
Phase 1 GO/NO GO: SOEC cell meets the performance target of >0.8A/cm² at 1.4 V, and <1%/1000h at T≤650 °C.

**Approach - Integrating Manufacturing, Material & Modeling**

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

**Metal alloy & coating selection**
- LBNL: oxidation study

**Co-sintered metal cell**
- LBNL

**Metal supported p-SOEC**
- Hydrogen electrode: $2H^+ + 2e^- \rightarrow H_2$
- Air electrode: $H_2O \rightarrow 2H^+ + 1/2O_2 + 2e^-$

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

**Electrochemical modeling**
- NREL
Relevance & Impact

Project Objectives
Develop highly efficient and cost competitive high temperature electrolysis for H₂ generation, by a high efficiency and durable metal-supported solid oxide electrolysis cell (SOEC) based on proton-conducting electrolyte at targeted operating temperatures of 550-650°C. Focus on developing a low cost, scalable fabrication of metal-supported cells and further material optimization for an efficient & durable p-SOEC.

Project Impact

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<tr>
<th>Metric</th>
<th>State of the Art</th>
<th>Phase 1</th>
<th>Project Target</th>
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<tr>
<td>SOEC Performance</td>
<td>1 A/cm² at 1.4 V at 800 °C</td>
<td>&gt;0.8 A/cm² at 1.4 V at 650 °C on button cells with SPS electrolyte</td>
<td>≥1.0 A/cm² at 1.4 V on button cells at T ≤ 650 °C;</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>≥0.8 A/cm² at 1.4 V at 650 °C on metal-supported cells by plasma spray fabrication</td>
</tr>
<tr>
<td>SOEC Durability</td>
<td>(1-4)% per 1000 h</td>
<td>&lt;1%/1000h</td>
<td>&lt;0.4% per 1000 h (≈4 mV per 1000 h)</td>
</tr>
<tr>
<td>H₂ production Cost</td>
<td>&gt;$4/kg H₂</td>
<td>$1.4/kg H₂</td>
<td>$2/kg H₂ based on cost analysis</td>
</tr>
</tbody>
</table>
H₂ electrode-supported button cells with **BZCY-based electrolyte + PBSCF or INL’s new steam electrode:** ≥ 1.0 A/cm² at 1.4 V and durability up to 200 h
Suspension plasma spray (SPS)-based deposition process provides a path to low cost stack.

Low cost cell fabrication
~$9/cell

Automated SPS process examples capable for multi cell and multilayer coating

- Electrolyte: Y and Yb-doped barium-zirconate-cerate (BZCYYb)
- Electrode: Ni+electrolyte and Lanthanum strontium cobalt ferrite (LSCF)
- 100 cm² cell

$1.35/kg H₂
(650°C, ASR=0.3 Ωcm², 1.0 A/cm², 100% Faraday efficiency
$0.039/kWh electricity)
Developed Electrolyte Fabrication by Suspension Plasma Spray (SPS)

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

Electrolyte BYZ 20 at% Ba (60 at%O) >90% density

H₂-electrode

Perovskite phase

- Barium zirconate perovskite structure
- Barium carbonate

2 theta (deg)
Demonstrated SPS Electrolyte Performance

Cell with SPS electrolyte exceeded Phase 1 performance target
(0.8 A/cm² at 1.4V & ≤650°C)

Cell performance, 3% Steam

Steam concentration effect

3%Steam/Oxygen, 20%H₂ as sweeping gas
Metal Supported Cell Fabrication Process (SPS)

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

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

Electrolyte deposition
Defects due to anode erosion
Progress in Metal Supported Cell Fabrication

Use same SPS processes for ceramic cells

Path forward: SPS electrode and electrolyte

- **Stronger H$_2$-electrode**
- **Optimized electrolyte**

**Target:** $\geq 0.8$ A/cm$^2$ at 1.4V, 1.0 OCV

**NiO+doped barium zirconate, 60 micron, ~20% porosity, well adhered to metal support**
**BZCY-steel Co-Sintering (LBNL)**

**Challenges:**
Processing conditions dictated by stainless steel: 2% Hydrogen, 1450°C
Si migration from steel to BZCY → BaSiO₃

- **Ce/Zr ratio**
- **Reduce sintering temp**
- **Barrier layer**
- **Low-Si metal**

**BP2: Combine these approaches to:**
- limit Si content in metal
- limit migration of Si
Various coating/steel combinations are acceptable

50% steam/air 650°C

<table>
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<tr>
<th>Coating condition</th>
<th>Rapid breakaway oxidation?</th>
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<tbody>
<tr>
<td></td>
<td>430 SS</td>
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<tr>
<td>Uncoated</td>
<td>Yes</td>
</tr>
<tr>
<td>Pre-oxidized</td>
<td>Yes</td>
</tr>
<tr>
<td>$\text{Y}_2\text{O}_3$-coated</td>
<td>No</td>
</tr>
<tr>
<td>Ce-MC-coated</td>
<td>Yes</td>
</tr>
<tr>
<td>CuMn$_{1.8}$O$_4$-coated</td>
<td>No</td>
</tr>
<tr>
<td>Ce/Co-coated</td>
<td>-</td>
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Thermal/Electrochemical Modeling of SOEC (NREL)

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

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

Model calibration using literature data

Model simulation of parameter distribution (2”X 2” cell)
Collaborations

**Low cost cell fabrication**
- **UTRC/PW**: SPS electrolyte and button cell fabrication
- **LBNL**: co-sintering process development
- **UCONN**: RSDT process development on electrolyte and electrode deposition
- **INL**: performance evaluation

**Material development for performance and durability**
- **UTRC**: Define performance requirement
- **INL**: new material (electrolyte & steam electrode) development
- **LBNL**: metal alloy and protective coating
- **PNNL and BU**: provide protective coating

**Establish Electrochemical modeling**
- **UTRC**: modeling requirement
- **NREL**: establish cell level model for electrolysis

**Provide cell level data for modeling**
Remaining Challenges

• Challenges:
  – Further densification of the electrolyte by SPS
    Achieve fully dense layer while obtaining desirable composition;
    Feedstock suppliers

  – Low cost and robust H₂-electrode fabrication
    Traditional sintering process limited by metal support

  – Durability of BYZ-based cells

Non-ideal feedstock resulted in less dense area
Proposed Future Work

• Continue development in metal supported cell fabrication
  – Further optimization of electrolyte by SPS
    • Feedstock optimization (working with suppliers)
    • Process optimization with PW and SPS Vendor
  – Evaluate low cost H₂-electrode fabrication
  – LBNL: further development of co-sintering process; infiltration for performance improvement of plasma sprayed cell

• Durability of BYZ-based cells (INL)
  – Material optimization
  – Durability test of PBSCF|BYZ-based cells

• Establish p-SOEC model parameters based on cell performance data; characterize cell performance, and guide cell design (NREL)

• Update cost analysis of the cell manufacturing process

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

**Low cost cell fabrication**
- Demonstrated SPS Electrolyte process and performance
- Identified paths to further improvement

**Metal alloy & coating selection**
- Identified potential combination of alloys and protective coatings

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

- **Electrochemical modeling**
  - NREL
  - Established cell level model

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

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

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

Presentations:

• Ruofan Wang, Conor Byrne, Michael C Tucker, "Proton-Conducting Ceramics for Metal-Supported Solid Oxide Cells", 19th International Conference on Solid State Protonic Conductors, 9/21/2018, Stowe, VT
• Hanping Ding, Dong Ding, et al. “Novel Triple Conducting Electrode for Fast Hydrogen Production in Protonic Ceramic Electrochemical Cells”, 43rd international conference and exposition on advanced ceramics and composites, ICACC 2019, Daytona Beach, FL, Jan 27 – Feb 1, 2019

Publications:

• Ruofan Wang, Grace Y. Lau, Dong Ding, Tianli Zhu, Michael C Tucker, “Approaches for Co-Sintering Metal-Supported Proton-Conducting Solid Oxide Cells with Ba(Zr,Ce,Y,Yb)O3 Electrolyte”, International Journal of Hydrogen Energy, accepted
• Ruofan Wang, Michael C Tucker, "Oxidation of metallic interconnects for proton-conducting electrolysis cells", J. Power Sources, in preparation
• Hanping Ding, Dong Ding, et al. “Superior Self-Sustainable Protonic Ceramic Electrochemical Cells Using a Novel Triple-Phase Conducting Electrode for Hydrogen and Power Production”, Advanced Materials, under review

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