Project ID: FC312

Molten Hydroxide Dual-Phase Membranes for Intermediate Temperature Anion Exchange Membrane Fuel Cells

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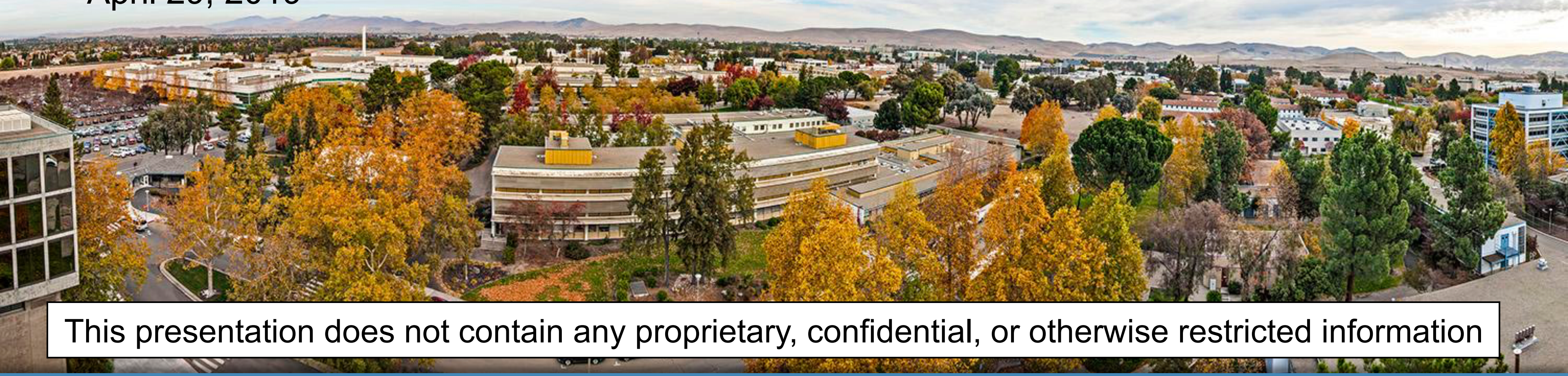
Lawrence Livermore National Laboratory
OxEon Energy, LLC

2019 DOE Hydrogen and Fuel Cells Program Annual Merit Review
April 29, 2019



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Overview

Barriers Addressed	
A. Durability	Dual-phase membranes consisting of molten salt supported by robust porous ceramic provide improved mechanical strength and thermal stability compared with polymer-based membranes in PEM and AEM fuel cells
B. Cost	Alkaline fuel cells can utilize PGM-free catalysts; Intermediate temperature operation has less stringent materials requirements and lower BOP cost compared with high-temperature fuel cells; Our dual-phase membranes are comprised of low-cost and abundant materials
C. Performance	Orders of magnitude improvement due to ultra-fast liquid-phase ion transport; Conductivity > 1 S/cm

- Timeline and Budget
  - Project Start Date: 10/01/18
  - Project End Date: 09/30/20
  - Total Project Budget: $1.25M
    - Total Recipient Share: $250k
    - Total Federal Share: $1M
    - Total DOE Funds Spent*: $208k

      *as of 03/01/19

- Industry Partner: OxEon Energy
  - A leader in high-temperature electrolysis technology
  - Developed Solid Oxide Electrolysis Stack for MOXIE, the Mars Oxygen ISRU (In Situ Resource Utilization) Experiment, for the 2020 NASA Curiosity class Mars rover

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Beyond Current Potential

Relevance

Objective: Demonstrate the performance of molten hydroxide dual-phase membranes as anion exchange membranes in intermediate temperature, air-oxidant compatible, hydrogen fuel cells

Project Aims:

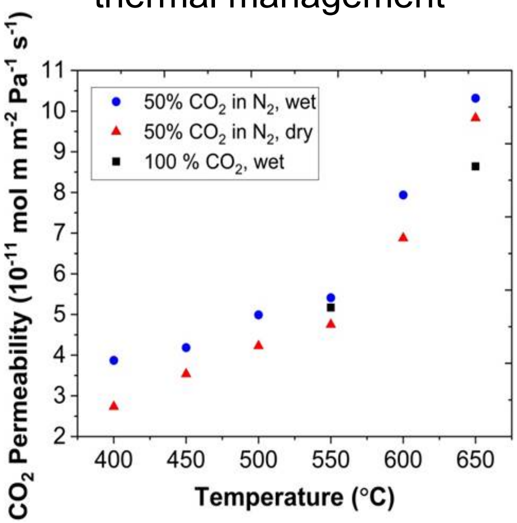
- Achieve ionic conductivity of >600 mS/cm
- Produce a complete fuel cell assembly (FCA) with a membrane area >50 cm^2
- Validate that steam-based carbonate management approach is effective during long-term operation
- Demonstrate high performance across the intermediate temperature range of 150-400 °C.

Membrane / electrolyte type	PEM	Alkaline	High-temp SOFC	Intermediate-temp hydroxide (this study)
Operating temperature (°C)	<100	<100	>500	✓ **150-400**
Ionic conductivity (mS/cm)	<200	Up to 1000	<50	✓ **>600**
PGM-free catalyst?	No	Depends	Yes	✓ **Yes**
Air-oxidant compatible?	Yes	No	Yes	✓ **Yes**

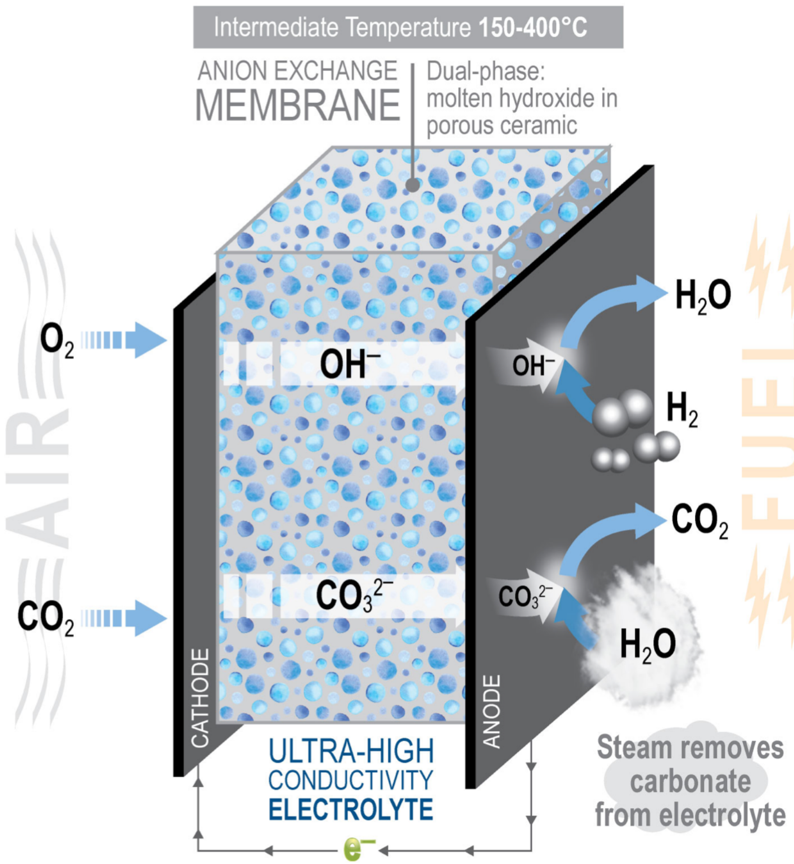
Approach: Novel Membrane Concept

Our dual-phase **molten hydroxide/ceramic support** membrane utilizes **steam-based carbonate management** and works at intermediate temperature to enable superior fuel cell performance and simplified operation

- Alkaline fuel cells (AFCs): oldest FC technology, enables high performance with PGM-free catalysts
- Typical AFCs require pure O_2 due to CO_2 poisoning of electrolyte
- Intermediate temperature (150-400 °C) enables higher air/fuel impurity tolerance and simplified water and thermal management



- High CO_2 permeability (i.e., reversible CO_2 uptake and release) in molten hydroxide membranes was demonstrated at temperatures <400 °C in recent work from LLNL on CO_2 separation from flue gas [1]



1. Cerón, M. R.; Campbell, P. G. et al. *J. Membr. Sci.* **2018**, *567*, 191–198.

Approach: Phases and Milestones

1. Optimize electrolyte conductivity across intermediate temp. (M1 – M9)

- ✓ EIS-based method established and verified
- ✓ Porous ceramic supports produced
- ❑ Hydroxide mixtures and additives evaluated from 150-400 °C

2. Incorporate dual-phase membrane into FCA with compatible materials (M4 – M15)

- ✓ FCA test station and cell hardware
- ❑ Membrane sealing via dense edge

GO/NO-GO 1: Satisfactory membrane and cell component performance (M12)

3. Implement steam-based carbonate mitigation strategy and FC operation (M7 – M18)

- ❑ Resistance measurements and gas analysis performed at LLNL
- ❑ Field testing performed at OxEon

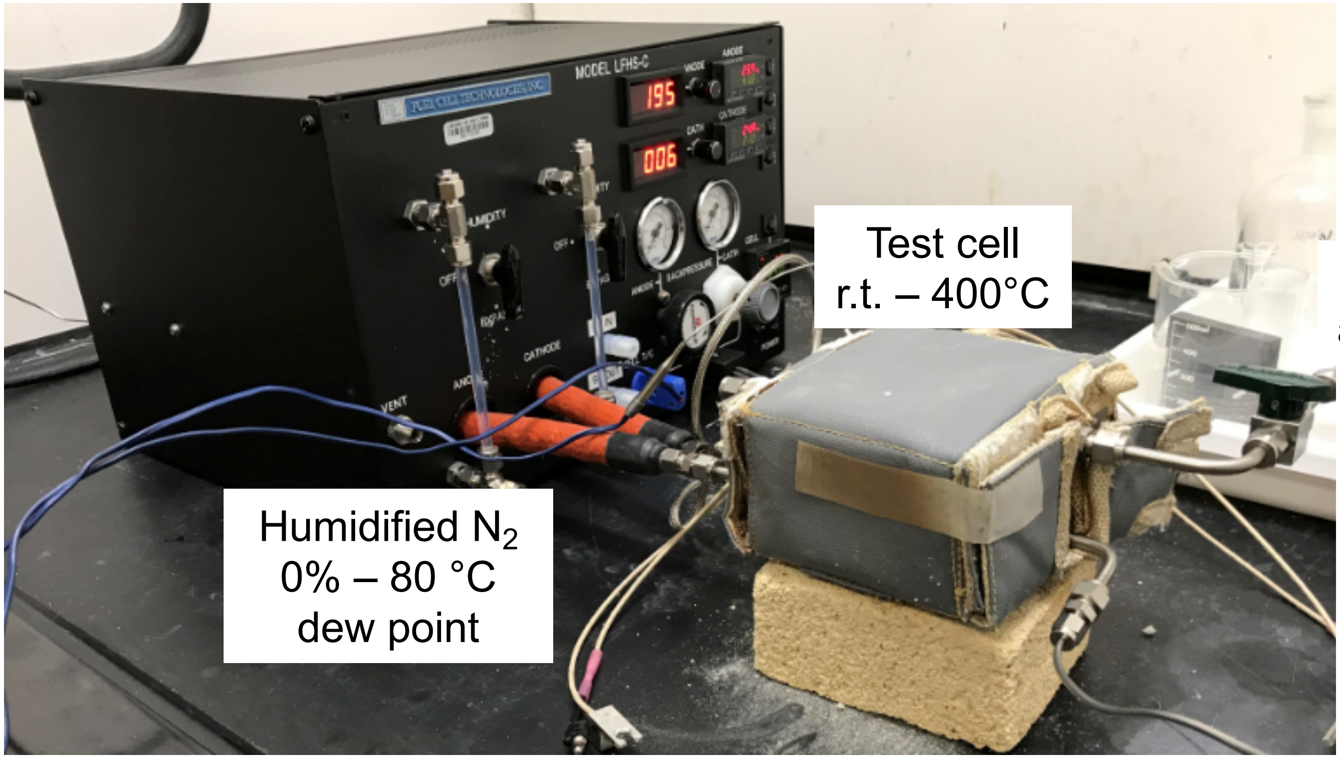
4. Scale and test membrane and carbonate management in full-size FCA (M12 – M24)

- ❑ 50 cm^2 membrane area; ionic conductivity >600 mS/cm
- ❑ Long long-term stability, prevention of carbonate buildup

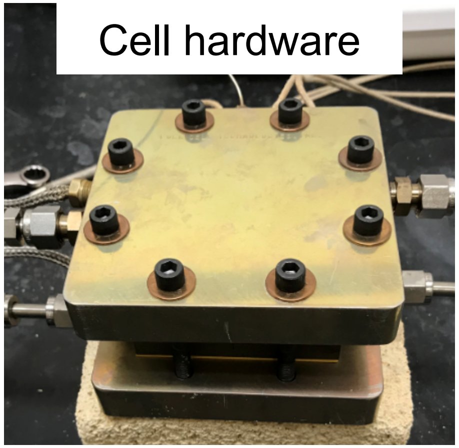
GO/NO-GO 2: Determine viability of molten hydroxide dual-phase membranes in intermediate temperature fuel cells (M24)

Accomplishments and Progress: Membrane Conductivity, FCA Test Station

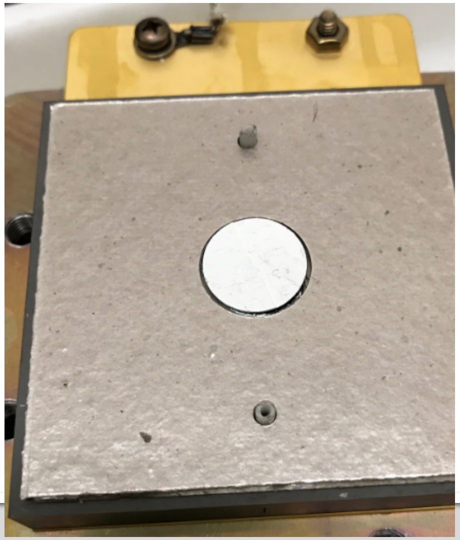
Humidification/temperature control system
Fuel Cell Technologies, Inc.



Cell hardware



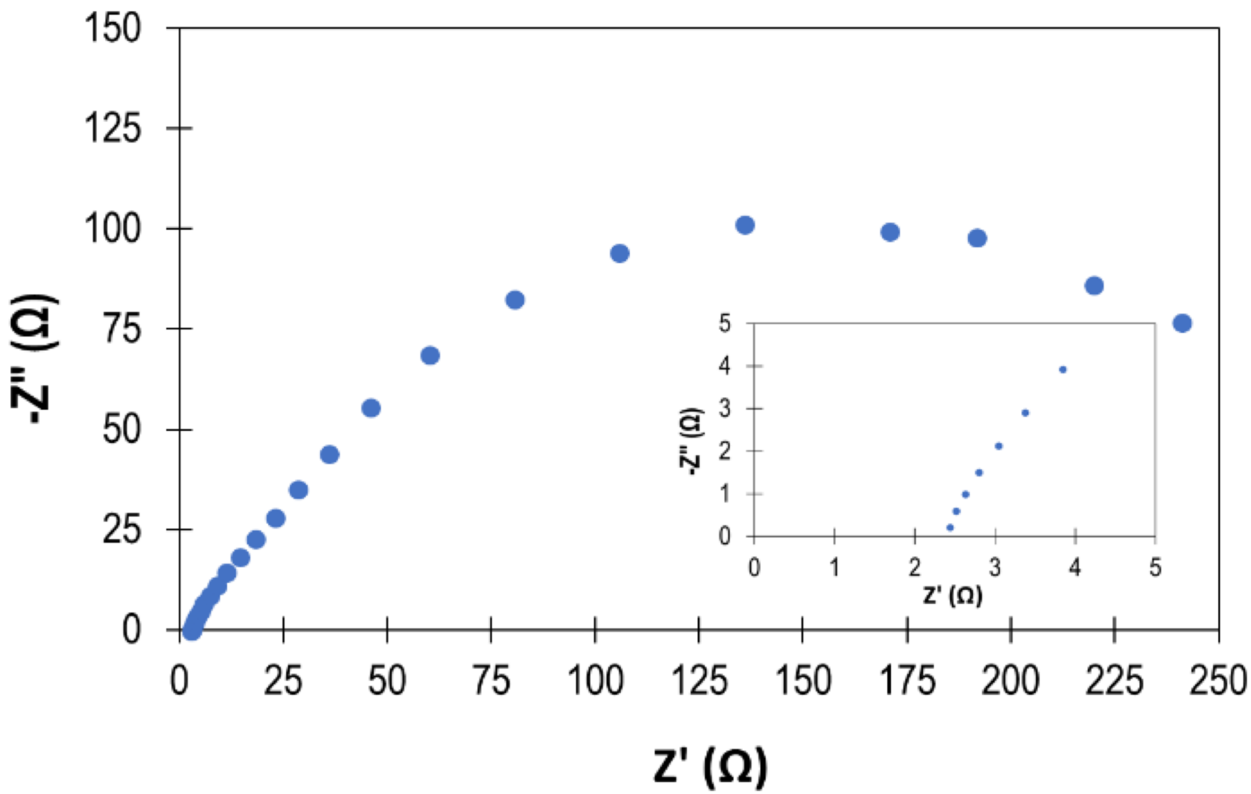
Membrane-electrode assembly inside mica gasket



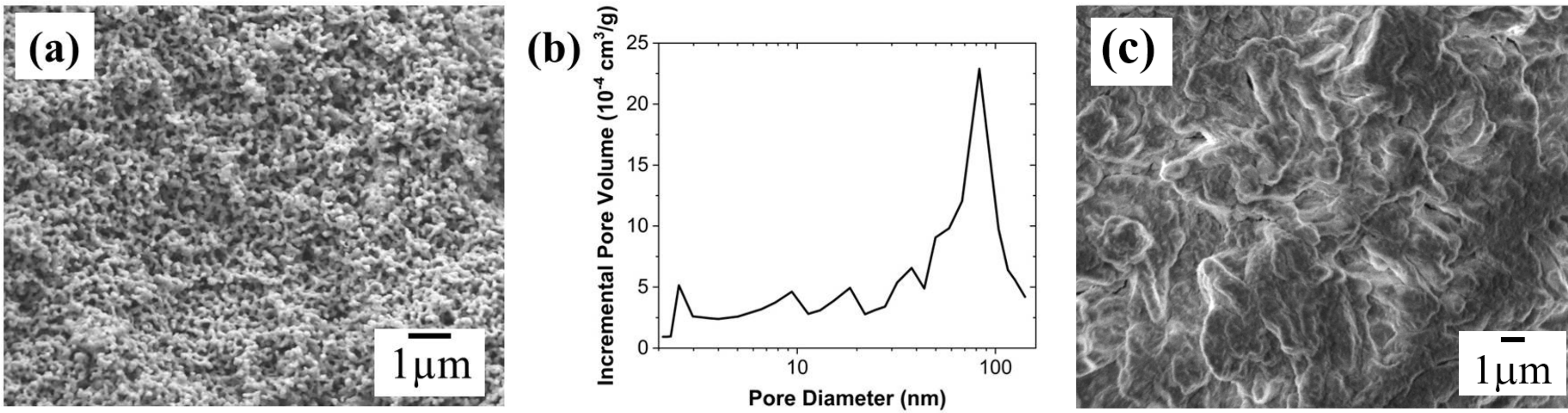
Accomplishments and Progress: Optimizing Electrolyte Conductivity

- Electrochemical Impedance Spectroscopy (EIS) is used to determine ionic conductivity of HCDP membranes with various hydroxide mixtures at temperatures 150-400 °C

- Preliminary measurements with 1:1 NaOH-KOH at 200°C: conductivity 196 mS/cm, area specific resistance 0.5 Ω



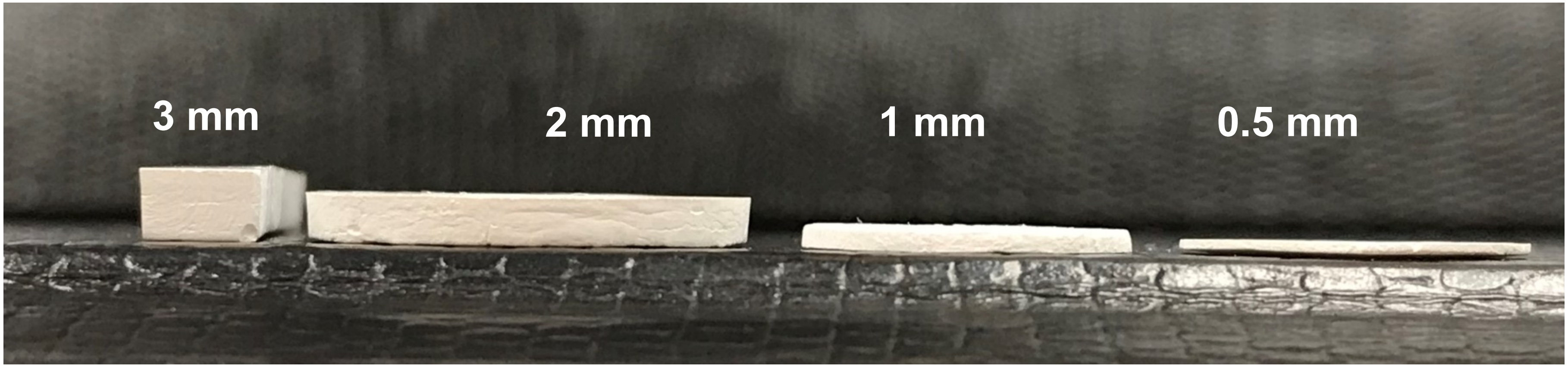
Accomplishments and Progress: Hydroxide Electrolyte in Ceramic Support



- Porous yttria-stabilized zirconia (YSZ) material previously developed for CO_2 separation membrane
- Pore size distribution: majority of pores <100 nm to maintain liquid hydroxide phase in pores via capillary force
- Cross section of hydroxide-infilled membrane; YSZ is stable in ultra-high pH environment

Cerón, M. R.; Campbell, P. G. et al. *J. Membr. Sci.* **2018**, *567*, 191–198.

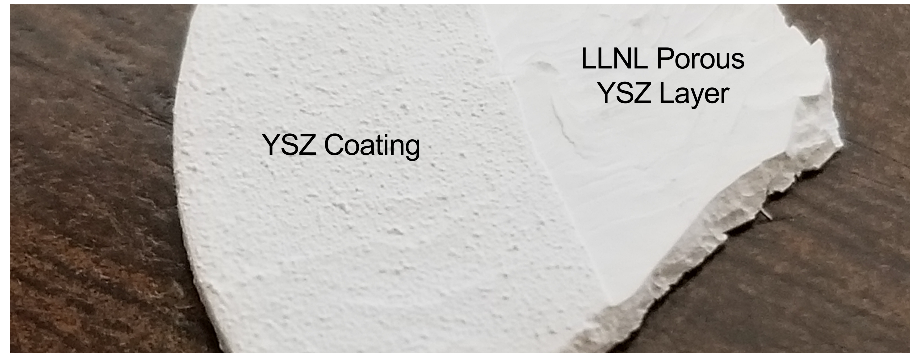
Accomplishments and Progress: Improving Porous Ceramic Support

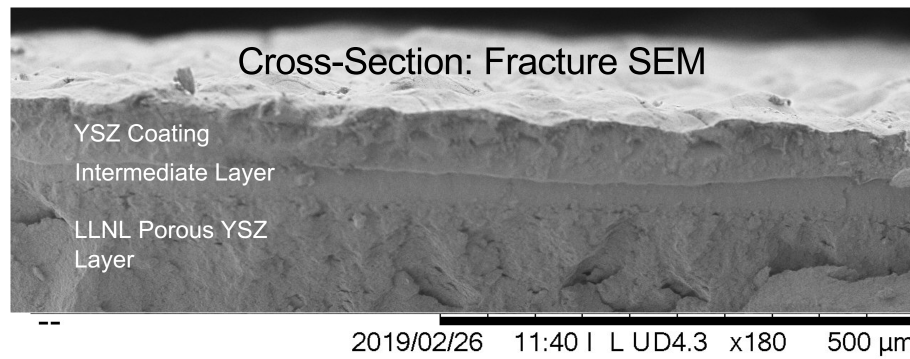


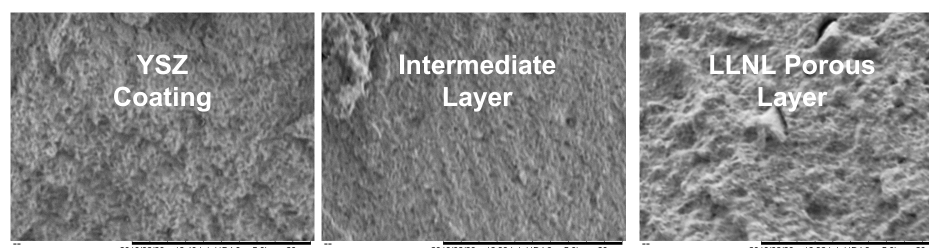
- Porous YSZ supports can now be fabricated free from pinholes and other defects at thicknesses of 0.5 mm
- Advances to the production method will enable <100 µm supports for optimal fuel cell performance

Accomplishments and Progress:
Dip Coated Dense Edge, OxEon Preliminary Trial

- Dip coating slip derived from OxEon's tape casting formulation
- Sintering temperature limited to prevent densification of LLNL's porous layer
- Coating thickness = 50-80 µm
- SEM on fractured cross-section reveals an intermediate layer (~40 µm) possibly from YSZ powder fines infiltrating into porous layer
- Coating and intermediate layers exhibit very fine pores but densified well considering the limited sintering temp
- Polished cross-section SEM is planned for better understanding of layers' porosity; plan to optimize process conditions to achieve a thinner, denser, and more uniform coating







Responses to Previous Year Reviewers' Comments

- This project was not reviewed last year

Collaboration and Coordination

Highly collaborative project led by LLNL, inventors of the dual phase membrane technology. Procurement subcontract to OxEon Energy who bring expertise in high-temperature fuel cell and electrolyzer operation to the project.

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- Project lead
- Ion conductivity optimization
- Humidification/carbonate mitigation strategy development
- Laboratory evaluation of FCA performance
- Optimization of operating modes
- Technoeconomic analysis and planning for next stage of research

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- FCA design and component fabrication
- Membrane sealing
- Field testing of FCA and carbonate mitigation
- Scale-up and long-term performance evaluation

Remaining Challenges and Barriers

Challenge	Mitigation Strategy
High-temperature, high-pH compatible seals in FCA	1) Full density edge via dip-coating 2) Glue porous support to full density outer ring/sealing edge
Controlling fuel-side humidity beyond 80 °C dew point, if necessary	Add external steam generator; already have quote for bench scale laboratory steam generator
Producing large-area, thin membranes	Flexibility in ceramic feedstock formulation and casting techniques (e.g., variable binder/ceramic ratio, tape casting vs molding)

Ongoing Challenge:

- Accurate characterization of water content in electrolyte; stability during fuel cell operation with carbonate mitigation

Proposed Future Work

Remainder of FY2019

Electrolyte Optimization

- Evaluate binary and ternary hydroxide mixtures, water and other additives
- Fuel and oxidant side humidity conditions

Fuel Cell Assembly and Testing

- Continue to develop dense edge sealing technique
- Test cell components for compatibility with temperature and pH conditions

Carbonate Mitigation Strategy

- Begin testing FCA operation with air-oxidant

FY2020

Fuel Cell Assembly and Testing

- Produce membrane at 50 cm^2
- Scale up fuel cell components

Carbonate Mitigation Strategy

- Optimize steam operation across intermediate temperature range
- Transfer protocol to OxEon, acquire necessary equipment

Long-Term and Accelerated Stress Testing

- Performed at OxEon to determine suitability of hydroxide based dual-phase membrane and carbonate mitigation strategy
- Evaluate areas for future research, commercialization

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

Technology Transfer Activities

Patents and patent applications related to this membrane technology

- Campbell, et al. “Molten Hydroxide Dual-Phase Membranes for Intermediate Temperature Fuel Cells.” Provisional Application Number 62/682,729 (USPTO). Filing Date: 08-Jun-2018
- Ceron Hernandez, et al. “Porous Ceramic Membrane Support Materials” Provisional Patent Application Number 62/457,087 (USPTO). Filing Date 09-Feb-2017
- Campbell, et al. “MOLTEN HYDROXIDE FOR SEPARATION OF ACID GASES FROM EMISSIONS” (app no: 15/159,681 filed 05/19/2016) (Foreign Filing PCT 3/22/17) Granted 5/4/17: PCT US2017/031155, International application filed 11/23/17: WO2017200764A1, PENDING: 2016-05-19 US15159681, Status: Pending

Summary

Objective: Demonstrate the performance of molten hydroxide dual-phase membranes as anion exchange membranes in intermediate temperature, air-oxidant compatible, hydrogen fuel cells.

Relevance: Achieve order-of-magnitude improvement in ionic conductivity compared to existing intermediate temperature membranes.

Produce a complete fuel cell assembly with a membrane area >50 cm^2.

Validate that steam-based carbonate management approach is effective during long-term operation.

Approach: Dual-phase molten hydroxide/ceramic support membrane with steam-based carbonate management; works at intermediate temperature to enable superior fuel cell performance and simplified operation.

Accomplishments: Equipment and protocols were established for evaluating membrane/electrolyte conductivity.

Produced porous ceramic support at <500 μm without pinholes or other defects.

Began study of dip-coating method to produce dense edge for reliable high-temperature sealing.

Collaborations: Highly collaborative project with commercial partner, OxEon Energy, providing fuel cell and electrolyzer expertise, FCA design consulting, and testing capabilities.