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

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Project Start Date: October 1, 2018
Project End Date: September 30, 2020

Overall Objectives

- Improve ionic conductivity compared with existing intermediate temperature membranes by developing a high ionic conductivity molten phase electrolyte supported by porous ceramic (hydroxide ceramic dual phase [HCDP]) membrane that provides ionic conductivity >600 mS/cm across the intermediate temperature range (150°–400°C).
- Manage/mitigate carbonate in the molten phase by developing an anode-side humidification protocol to facilitate CO₂ removal from the HCDP membrane.
- Develop operational prototype fuel cell assembly (FCA) with membrane area up to 50 cm².
- Determine the long-term stability and performance of the FCAs by performing relevant testing, evaluating component failures, and designing improvements to maximize reliability, stability, and lifetime.

Fiscal Year (FY) 2019 Objectives

- Integrate electrodes with HCDP membrane for electrochemical characterization (ionic conductivity, fuel cell operation).
- Optimize hydroxide ion transport across the dual-phase membrane; target: >600 mS/cm.
- Evaluate electrode, catalyst, and packaging materials for potential use in the prototype FCA.
- Construct small-scale FCA prototype to measure performance and reliability before design and construction of full-scale FCA.
- Implement humidification of fuel cell gases for carbonate mitigation.

Technical Barriers

This project addresses the following technical barriers identified in the Fuel Cells section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan¹:

- (C) Performance
- (A) Durability
- (B) Cost.

Technical Targets

During our 2-year project, we will show that HCDP membranes can achieve:

- Ionic conductivity: >600 mS/cm
- Membrane area: >50 cm²
- Intermediate temperature range: 150°–400°C
- Long-term air-oxidant operation with effective steam-based carbonate management approach.

¹ <https://www.energy.gov/eere/fuelcells/downloads/fuel-cell-technologies-office-multi-year-research-development-and-22>

FY 2019 Accomplishments

- Demonstrated very high ionic conductivity with molten hydroxide mixture in porous ceramic support: 1.4 S/cm at 250°C.
- Developed new routes to thinner, defect-free ceramic membrane support materials.
- Developed methods for reliable electrical contact and sealing of fuel cell components to prevent leaks and hydrogen crossover.
- Designed and produced prototype small-scale FCA.
- Implemented gas humidification for carbonate mitigation.

INTRODUCTION

Alkaline fuel cells (AFCs) are among the oldest fuel cell technologies. They have traditionally used porous media saturated with aqueous alkaline hydroxide electrolyte as the ion-conducting electrode separator. However, AFCs suffer from CO₂ poisoning when air is used as the oxidant. One approach to address the limitations of traditional AFCs is to use polymeric anion exchange membranes, which can be immune to CO₂ poisoning. The highest performing polymer membranes have ionic conductivity of 100–200 mS/cm. However, polymer membranes have several drawbacks, including (1) limited chemical stability at high pH due to hydroxide ion attacks of the main chain and functional groups of the polymer; (2) limited diffusion/ionic conductivity rates, and (3) poor mechanical performance leading to short lifetimes. Solid-state hydroxide ion-conducting electrolytes have good mechanical properties and chemical resistance but suffer from limited ionic conductivity of ~10 mS/cm at 100°–200°C.

The most promising hydroxide ion-conducting electrolytes in the intermediate temperature range are molten alkaline hydroxide mixtures, which can have melting points below 150°C when hydrated. Molten hydroxide electrolytes operating at intermediate temperature offer exceptional ionic conductivity (>1,000 mS/cm), which is nearly two orders of magnitude higher than the best solid-phase intermediate temperature electrolyte. However, molten hydroxides suffer from the same carbonate poisoning effect as aqueous hydroxides and are difficult to package as membranes due to the corrosivity and reactivity of molten hydroxides. Therefore, they have been overlooked as potential electrolytes in air breathing fuel cells.

APPROACH

Lawrence Livermore National Laboratory (LLNL) developed a novel HCDP membrane technology that can be used in anion exchange membrane fuel cells (Figure 1). This technology overcomes the CO₂ poisoning issue by shifting the chemical equilibrium of the undesired carbonate ions toward hydroxide and CO₂ in the presence of water, thus releasing CO₂ from the electrolyte in situ during operation [1]. LLNL's novel dual-phase molten hydroxide membrane works at intermediate temperatures and eliminates the need for CO₂ removal from the air feed. Our HCDP-based fuel cell will achieve higher performance, increased reliability, and lower cost compared with current state-of-the-art fuel cells. Anionic transport allows for the use of platinum group metal (PGM)-free catalysts, while intermediate temperature operation enables greater impurity tolerance, faster startup, and simplified packaging. In order to realize the promise of HCDP-based fuel cells, this project will:

- Improve ionic conductivity by optimizing electrolyte composition and ceramic support geometry.
- Manage/mitigate carbonate in the molten phase by developing an anode-side humidification protocol.
- Design and build a prototype FCA, guided by testing and commercialization requirements.
- Determine the long-term stability and performance of the FCAs under realistic operating conditions.

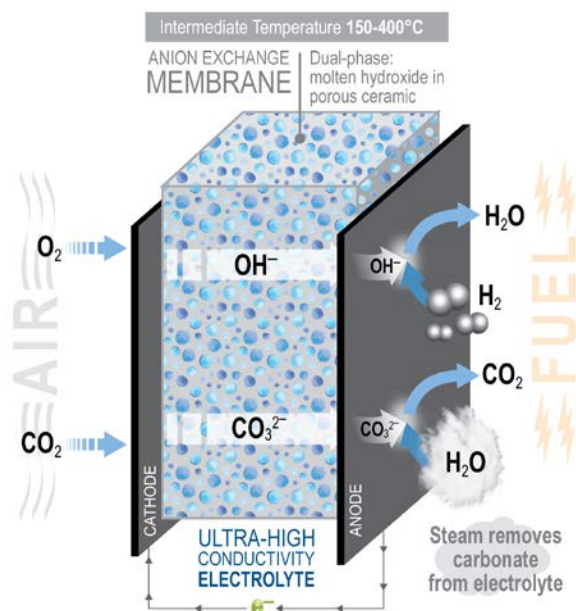


Figure 1. LLNL's HCDP membrane technology, which uses steam to limit carbonate in the molten phase

RESULTS

To produce a dual-phase membrane with liquid-phase ion transport, a support material that can maintain the molten hydroxide phase within the pores via capillary pressure is required. The support must be stable to extremely corrosive molten alkali hydroxide mixtures and, for intermediate temperature applications, must withstand temperatures up to 400°C. Based on prior work at LLNL evaluating various carbide and oxide based ceramic materials as membrane supports, we established that 3% yttria-stabilized zirconium oxide (YSZ) is stable to prolonged exposure to hydroxide melts at elevated temperatures [1]. We improved our existing methods to produce ceramic materials with tunable porosity and enabled production of thinner ceramic materials (Figure 2).

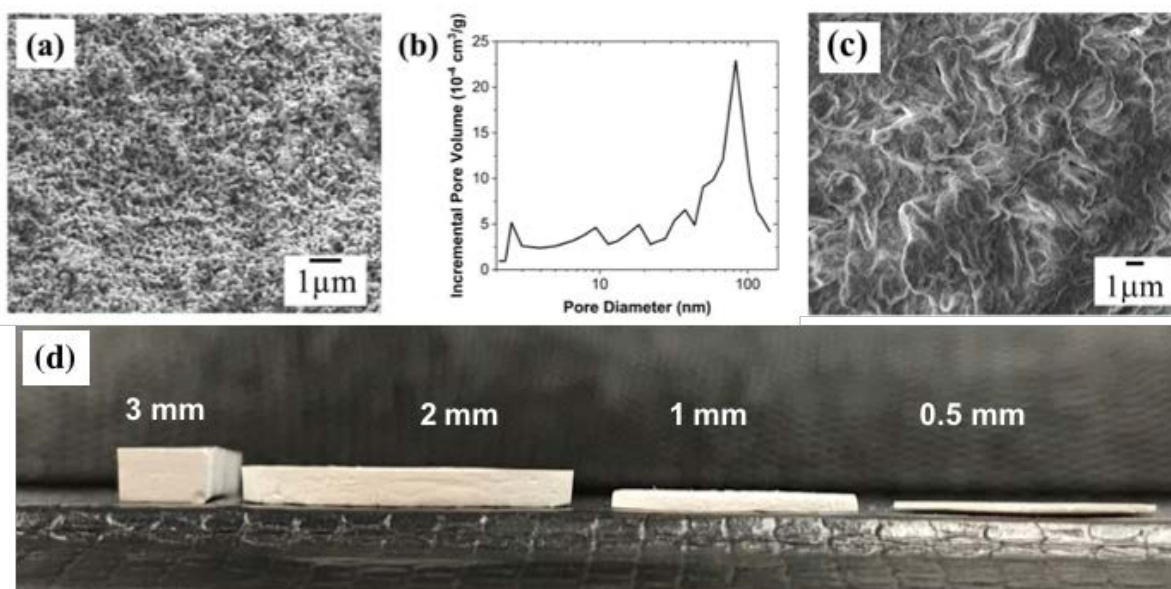


Figure 2. 3% yttria-stabilized zirconia porous ceramic support materials: (a) scanning electron microscope (SEM) micrograph of unfilled porous ceramic; (b) pore size distribution; (c) SEM micrograph of cross-section of hydroxide infilled ceramic showing complete infilling with no voids or pinholes; d) photograph of YSZ supports of various thickness

We evaluated porous ceramic membrane support materials fabricated from a new YSZ feedstock with higher sintering temperature that enables thinner supports with increased mechanical strength and minimal defects. We also evaluated porous supports derived from YSZ/NiO composite, which demonstrate superior mechanical properties and may enable even thinner (<100 μm) membrane supports. Composite-derived porous ceramic materials have lower overall porosity compared with existing materials, and studies are underway to measure the impact of porosity and pore volume on ionic conductivity of the dual-phase membrane.

Forming reliable, high-temperature, and corrosives-compatible seals between the membrane and other components in the FCA remains a critical challenge to this project. We have developed two new methods to produce fully dense ceramic regions in our porous support to enable sealing with gasket material (e.g., mica) while preventing contact between gasket and hydroxide. The newly developed YSZ feedstock sinters at higher temperature, which enables secondary coatings to be applied to form a dense perimeter region. The composite ceramic can be co-sintered with a dense YSZ tape, which demonstrates good bonding and remains adhered during reduction and etching (Figure 3, top). Additional pore-formers can be incorporated into the composite ceramic formulation, creating larger pores on the order of 10s of μm which can enable more efficient gas diffusion to the membrane surface (Figure 3, bottom).

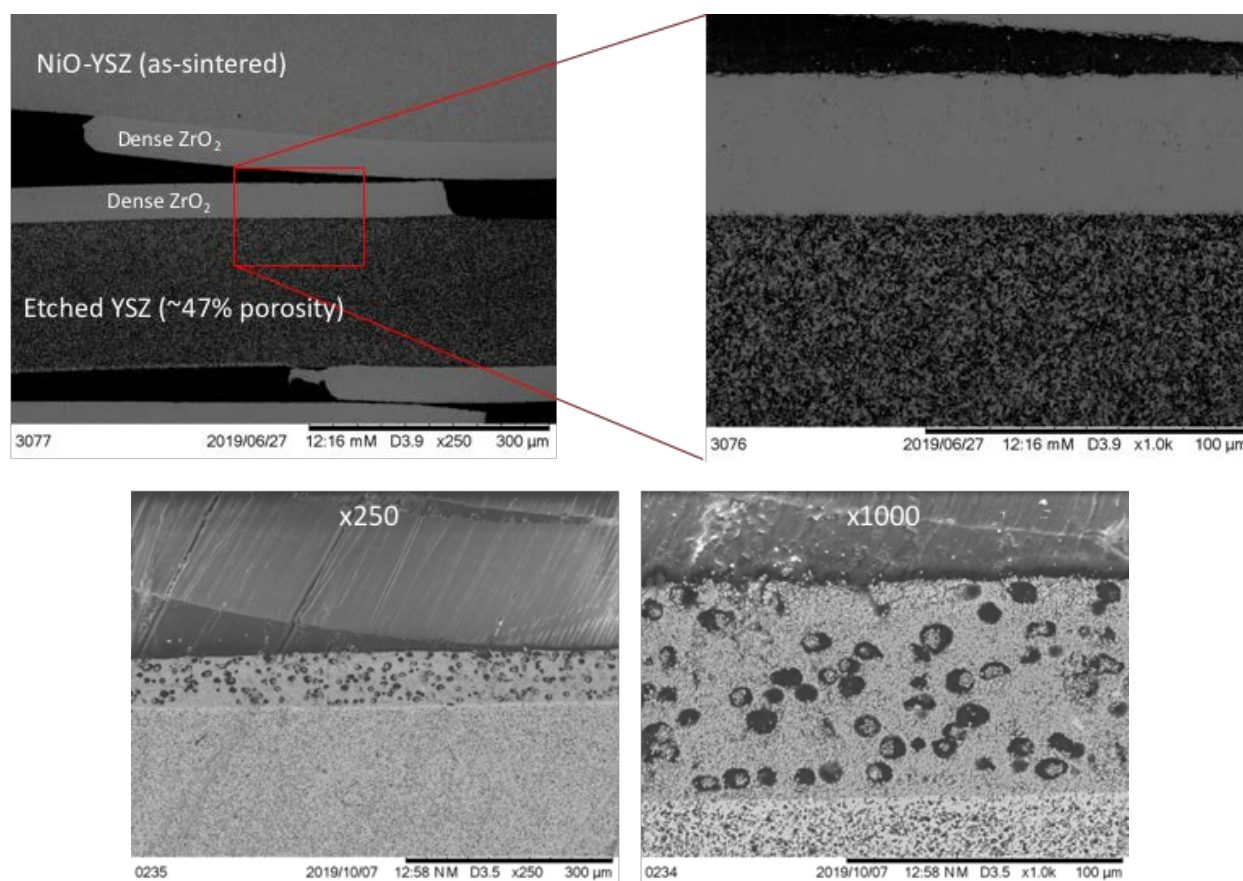


Figure 3. (Top) SEM micrograph of dense with composite ceramic co-sintered ZrO_2 tape, which shows good adhesion after the etching step. (Bottom) SEM micrograph of porous YSZ co-sintered with layer containing additional pore former for >10 μm pores to be used as gas-diffusion layer.

Stable, low-resistance electrical contact between the membrane and electrode/current collector is a requirement for good fuel cell performance. Dual-phase membranes can present additional challenges, in part due to volume change of the electrolyte during heating and varied humidity conditions. By painting the surface of hydroxide-infilled membranes with silver paint, we were able to establish good electrical

contact and measure ionic conductivity as a function of temperature. However, performance degrades fairly rapidly as the silver paint is corroded by the hydroxide electrolyte. Nickel is stable under operating conditions, and results from preliminary experiments using nickel paint between the membrane and current collector are promising. Work is continuing to optimize the sintering profile of nickel paint with the YSZ support to ensure good adhesion and to evaluate other current collector/catalyst materials such as platinum paint.

We measured the ionic conductivity of hydroxide infilled membranes and successfully achieved our Q3 milestone of >0.6 mS/cm. In fact, we measured ultra-high conductivity, 1.4 S/cm, under humidified conditions at 250°C (Figure 4). However, extended dwell time at high temperature (>200 °C) led to reduction of conductivity as water loss from the electrolyte could not be countered by humidified gas flow. Our current humidification system is limited to saturated N_2 at <100 °C. We are developing a modified protocol to increase the water concentration in the gas streams. We are also investigating the effect of temperature, carbonate concentration, water content, and alkali cation ratio on conductivity using 4-point measurements in bulk hydroxide melts.

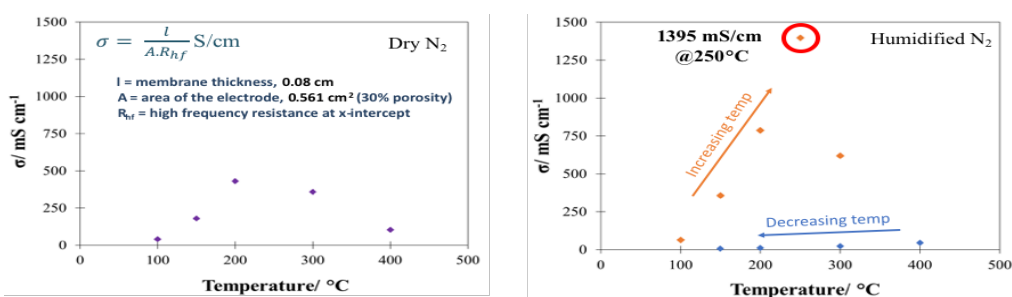


Figure 4. Conductivity measurements for hydroxide infilled, 800 μm dual phase membrane under dry (left) and humidified (right) conditions. Maximum value of 1.4 S/cm was achieved at 250°C, but electrolyte stability was limited by loss of water at higher temperatures.

We utilized commercial fuel cell hardware to measure preliminary fuel cell performance with the HCDP membrane and Pt/carbon electrodes (Figure 5, left). While the carbon electrodes are not stable at elevated temperatures or under long-term exposure to molten hydroxide electrolyte, the initial results indicate modest performance under these non-optimized conditions (current density of 25 mA/cm² at 70% open circuit voltage). We are currently investigating alternatives to Pt/carbon, which, along with the use of thinner membranes, will allow us to exceed our current-density goal of 100 mA/cm². Additionally, we built the first prototype of a custom FCA designed to meet the unique requirements of intermediate temperature operation and hydroxide-based electrolyte (Figure 5, right). This small-scale FCA will allow us to evaluate the performance of individual fuel cell components before we scale up to 50 cm² membrane area.

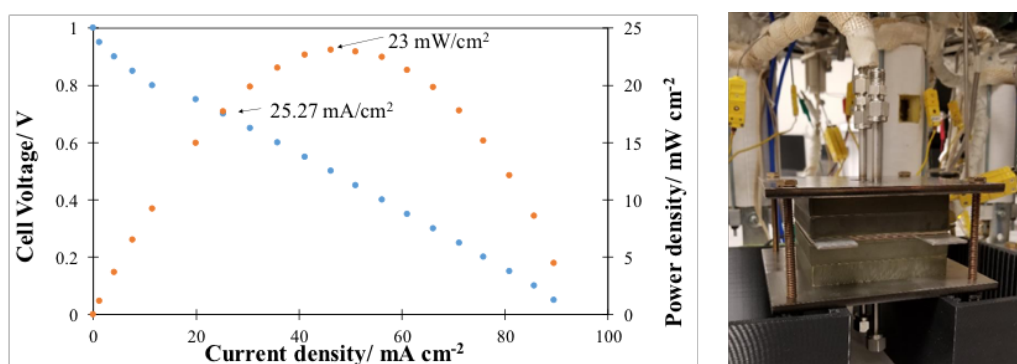


Figure 5. (Left) Preliminary full cell performance measurements using Pt/carbon electrode. (Right) Photograph of custom designed fuel cell assembly with integrated temperature control.

CONCLUSIONS AND UPCOMING ACTIVITIES

In conclusion, we were able to satisfy our FY 2019 objectives and deliverables and set the stage for success in FY 2020. In the upcoming year, we will demonstrate carbonate mitigation during fuel cell operation by using humidified sweep gas on the anode/hydrogen side to maintain low, steady-state concentration of carbonate and thus good ionic conductivity in the electrolyte. We will validate the performance of the small-scale FCA components in order to design the large-scale FCA, which will include demonstrating reliable membrane sealing, good electrode contact with low resistance, and satisfactory catalyst/fuel cell performance with air oxidant. We will design, procure components, and fabricate the large-scale FCA. Lastly, we will determine viability of the HCDP membrane concept for intermediate temperature fuel cells. Evaluation criteria will include accelerated stress testing, long-term testing, and business case analysis using $>50 \text{ cm}^2$ membrane area, air oxidant operation, and current density $>100 \text{ mA/cm}^2$ at 70% open circuit voltage.

SPECIAL RECOGNITIONS AND AWARDS/PATENTS ISSUED

1. “Molten Hydroxide Dual-Phase Membranes for Intermediate Temperature Fuel Cells,” Provisional Application Number 62/682,729 (USPTO), file date: June 8, 2018.
2. “Molten Hydroxide Dual-Phase Membranes for Intermediate Temperature Fuel Cells,” US Nonprovisional Application No. 16/435,131, file date: June 7, 2019. PCT Application, International Application No. PCT/US19/35872, file date June 6, 2019.

FY 2019 PUBLICATIONS/PRESENTATIONS

1. “Molten Hydroxide Dual-Phase Membranes for Intermediate Temperature Anion Exchange Membrane Fuel Cells,” poster, 2019 DOE Hydrogen and Fuel Cells Program Annual Merit Review and Peer Evaluation Meeting.
2. Face to face meeting with OxEon collaborators and Greg Kleen from DOE at LLNL (June 11, 2019): presentations from LLNL and OxEon.

REFERENCES

1. M.R. Cerón, L.S. Lai, A. Amiri, M. Monte, S. Katta, J.C. Kelly, M.A. Worsley, M. Merrill, S. Kim, and P.G. Campbell, *Journal of Membrane Science* 567 (2018): 191–198.