
Lab Call FY18 (Membrane): High Performing and Durable Pyrophosphate-Based Composite Membranes for Intermediate-Temperature Fuel Cells

Cortney Kreller (Primary Contact), Kannan Ramaiyan, Yu Seung Kim, Rangachary Mukundan, Mahlon Wilson
Los Alamos National Laboratory
PO Box 1663
Los Alamos, NM 87545
Phone: 505-665-5719
Email: ckreller@lanl.gov

DOE Manager: Donna Ho
Phone: 202-586-8000
Email: Donna.Ho@ee.doe.gov

Project Start Date: January 2018
Project End Date: July 2020

Overall Objectives

- Develop metal pyrophosphate (MPP)/Nafion composite membranes for operation at 200°C and low relative humidity (RH) for transportation applications.
- Optimize composition of MPP materials to achieve conductivities of 100 mS/cm.
- Fabricate membranes of <40 μm thickness to achieve membrane area specific resistance (ASR) of <0.04 Ω cm²
- Evaluate membrane durability in terms of crossover, shorting resistance, and open circuit voltage.

Fiscal Year (FY) 2019 Objectives

- Synthesize and characterize metal pyrophosphate materials with varying dopant concentration and phosphorous-to-metal (P:M) ratio.
- Establish trends in conductivity with P:M ratio and cation dopant.
- Fabricate membranes from MPP materials that exhibit high conductivities in powder form. Report membrane conductivities as a function

of MPP loading and phosphoric acid (PA) doping.

- Minimize membrane thickness while retaining mechanical integrity.

Technical Barriers

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

- Decrease system costs by operating at higher temperature (150°–400°C), allowing for use of lower purity fuel, simplification or removal of balance of plant components (e.g., smaller coolant loop, removal of shift reactor), and potential direct use of biofuels
- Demonstrate activity across the entire range of operating temperatures
- Achieve membrane ASR of ≤0.02 Ω cm²
- Mechanical/chemical durability.

Technical Targets

This project is developing a novel proton-conducting electrolyte operating at 200°C with conductivity $\sigma \geq 100$ mS/cm and RH <1%. Fabrication of membranes of less than 40 μm thickness will result in ASR <0.04 Ω cm². This membrane is at the initial stages of development to meet the following DOE membrane and MEA targets:

- ASR: ≤0.02 Ω cm²
- ASR: ≤0.03 Ω cm² under low RH conditions
- Max hydrogen crossover: 2 mA/cm²
- MEA performance: ≥300 mA/cm² @ 800 mV
- MEA performance: ≥1,000 mA/cm² @ 675 mV.

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

FY 2019 Accomplishments

- Established that Sn, In-doped Sn, and In-doped MP_2O_7 exhibited the highest conductivities in powder form, with the highest conductivity of 160 mS/cm observed for the In-doped material.
- Modified the synthesis procedure to determine the role of phosphate cation on conductivity and stability. Synthesis routes that did not include a phosphate cation yielded the highest conductivity, but it was not stable. Incorporating tetrabutylammonium as a stabilizing cation improved performance over diammonium cation.
- Achieved through-plane membrane conductivity of 95 mS/cm at 220°C and RH <1% in a 5-cm² cell using a SnP_2O_7 -tetrabutylammonium phosphate (TBAP)/Nafion composite membrane.
- Achieved ASR of 0.1 $\Omega \text{ cm}^2$ at 220°C and RH <1% in a 5-cm² cell using a 50- μm thick SnP_2O_7 -TBAP/Nafion composite membrane.
- Demonstrated fuel cell performance of 600 mW/cm² in H_2/O_2 at 220°C and RH <1% in a 5-cm² cell using a 50- μm thick SnP_2O_7 -TBAP/Nafion composite membrane.

INTRODUCTION

Major hurdles to the development of fuel cell vehicles include the complexity of water management and the cost of precious metals, as well as the susceptibility of precious metals to poisoning by fuel impurities. A paradigm shift in automotive fuel cells can be achieved with an intermediate-temperature proton-conducting solid electrolyte that can operate above 150°C. This intermediate-temperature operation can greatly simplify thermal management and enable the use of non-precious metals or low loading of precious metal catalysts. The anhydrous electrolyte eliminates water management issues, thus dramatically simplifying the system and lowering costs. In addition, the less corrosive dry environment improves durability relative to current state-of-the-art polymer electrolyte membrane fuel cells. Furthermore, the 150°–250°C operation overcomes difficulties with carbon monoxide to allow the direct use of liquid alternatives to hydrogen (such as biofuels) or, at a minimum, reduce the stringent purity requirements of the hydrogen fuel stream. The goal of this project is to develop a novel proton-conducting electrolyte with conductivity ≥ 100 mS/cm at $\geq 200^\circ\text{C}$ and low RH to meet the DOE technical targets of decreasing system cost by operating at higher temperatures.

Two main tasks were conducted in Year 1 of this project. The first was to identify the composition of MPP materials that yielded the highest conductivity in powder form. We found that both crystalline cation dopants as well as the phosphate cation used in the synthesis impacted conductivity. We synthesized three MPP materials that exhibited conductivity ≥ 100 mS/cm in powder form and identified Sn, In-doped Sn, and Sc-doped Sn as the most promising crystalline composition and tetrabutylammonium as the phosphate cation that yielded the highest and most stable conductivity. The second task accomplished in Year 1 was incorporation of the MPP materials into composite MPP/Nafion membranes. Given that the intermediate-temperature proton-conducting MPP is a ceramic material, the polymer Nafion is required to fabricate thin, flexible, and mechanically robust membranes suitable for transportation applications [1]. Nafion is not conductive in the intermediate temperature range of interest, so it is desirable to maximize the MPP content while still retaining desired mechanical properties as well as minimizing membrane thickness. Membranes were fabricated with a composition of 90 wt % MPP/10 wt % Nafion as thin as 35 μm using a doctor blade process. Maximum membrane conductivity achieved to date is 95 mS/cm. Further improvement in conductivity and/or reduction in membrane thickness will enable this intermediate temperature membrane to achieve DOE technical targets of membrane ASR $\leq 0.02 \Omega \text{ cm}^2$ and ASR $\leq 0.03 \Omega \text{ cm}^2$ under low RH conditions.

APPROACH

MPP Synthesis and Characterization

We synthesized and characterized MPP materials of varying composition to investigate the impact of matrix effects between the crystalline phase and the proton-conducting excess polyphosphate phase. Materials were all synthesized via an aqueous solution precipitation process that provides good control over the ceramic

particle size and the amount of excess polyphosphate phase, obtaining small crystallites (15–30 nm) at a relatively low calcination temperature of 650°C [2]. $\text{Sn}_{(1-x)}\text{M}_x\text{P}_2\text{O}_7$ was synthesized with $\text{M} = \text{Zr}^{4+}$, Al^{3+} , Gd^{3+} , In^{3+} , Sc^{3+} , Sm^{3+} , and Mg^{2+} . Additionally, the influence of the composition of the excess polyphosphate phase was investigated by varying the phosphate precursor as phosphoric acid (PA), diammonium phosphate (DAP), and tetrabutylammonium phosphate (TBAP). X-ray diffraction was used to confirm the phase purity of the crystalline phase and thermogravimetric analysis and X-ray fluorescence were used to quantify the P:M ratio. Powder conductivity was measured by pressing bulk pellets in a uniaxially die and assembling into a spring-loaded compression setup with Pt-foil electrodes [3]. The frequency response was measured between 1 MHz and 0.1 Hz using an Amtek PARSTAT4000 potentiostat. The high frequency intercept of the Nyquist plot is attributed to the bulk pellet resistance.

Membrane Fabrication and Testing

MPP materials prepared by the solution precipitation method were ball-milled prior to mixing with 1 g PA and 5 wt % Nafion in 1,2-pentanediol. The solution was then ball-milled for 24 hours to form a uniformly dispersed slurry. Initially, a second 2-hour sonication step was included, but it was found that this resulted in excessive porosity in the final membranes. Removal of the sonication step and application of vacuum to the slurry prior to casting greatly reduced membrane porosity. Thicker membranes (>100 μm) were formed by casting on glass slides while thinner membranes were cast with a doctor blade. All membranes were dried at 120°C for 3 hours then under vacuum at 160°C for 4 hours. Scanning electron microscopy images were used to evaluate membrane density and confirm thickness. The performance of the membranes was evaluated by measuring the high frequency resistance in a 5 cm^2 cell. Gas diffusion electrodes were fabricated by painting Pt catalyst ink onto carbon cloth or carbon paper. The TPP composite membranes were sandwiched between gas diffusion electrodes and fixed in a fuel cell setup into an MEA without hot pressing.

RESULTS

Figure 1 shows the conductivity at 200°C measured in bulk pellet form of $\text{Sn}_{(1-x)}\text{M}_x\text{P}_2\text{O}_7$ with varying M dopants. The conductivity increases with increasing P:M ratio, so the conductivity is plotted vs. P:M ratio in order to more accurately compare the influence of crystalline composition. Zr and Gd resulted in poor conductivities even at relatively high P:M ratios, whereas the undoped material, and the dopants In and Sc, yielded higher conductivities, with an In-doped material exhibiting a conductivity of 160 mS/cm —the highest conductivity reported for these materials to date.

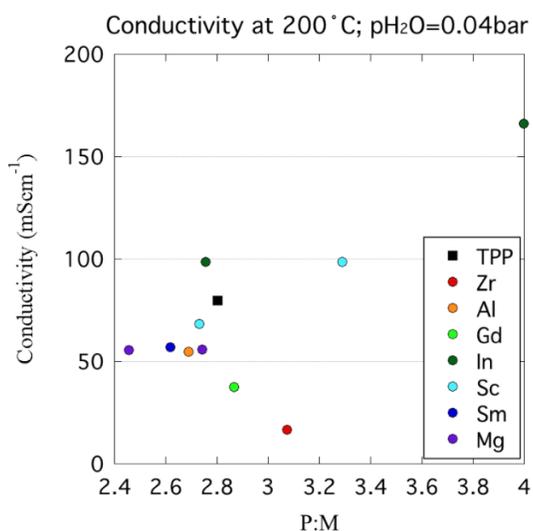


Figure 1. Conductivity vs. P:M ratio for $\text{Sn}_{(1-x)}\text{M}_x\text{P}_2\text{O}_7$ with varying M dopants

The fuel cell performance of three 5- cm^2 cells at 220°C in H_2/O_2 is shown in Figure 2. Each of these membranes was fabricated from SnP_2O_7 with varying phosphate precursor, namely PA, DAP, and TBAP. The TBAP-based membrane provided the highest open circuit voltage and power density and the lowest ASR.

Given that it was also the thickest among the three, we fabricated a 50- μm membrane to verify that we were observing a compositional effect rather than a thickness effect. The data comparing the performance of the thick and thin TBAP membranes are shown in Figure 3. The open circuit voltage of the thinner membrane matched that of the thicker membrane and exhibited a peak power density of 600 mW/cm^2 . We believe that the phosphate cation is playing a role in the uptake and retention of phosphoric acid and that the larger-molecular-weight cation serves to stabilize the excess polyphosphate phase.

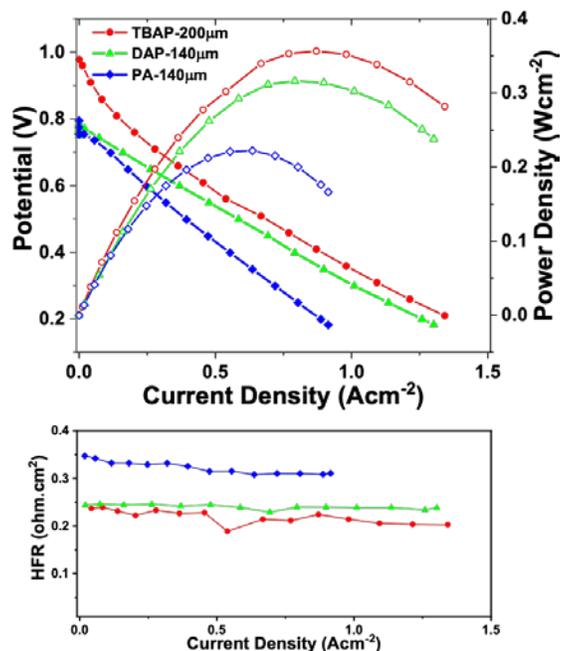


Figure 2. Performance at 220°C in H_2/O_2 of $\text{SnP}_2\text{O}_7/\text{Nafion}$ composite membrane fabricated from MPP with three different phosphate precursors

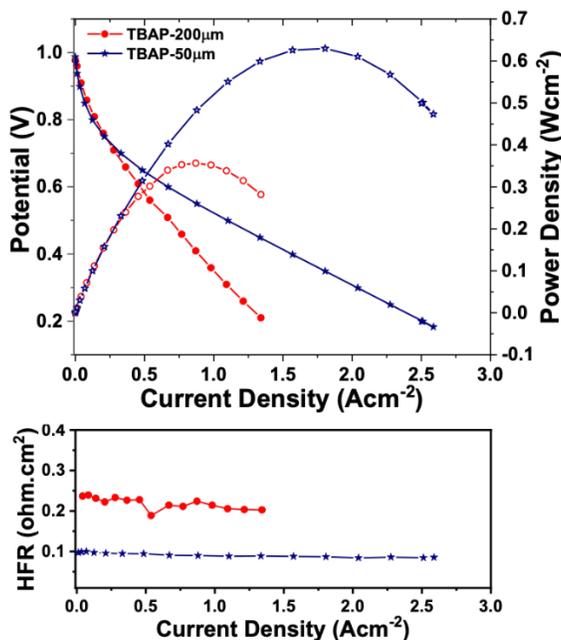


Figure 3. Performance at 220°C in H_2/O_2 of $\text{SnP}_2\text{O}_7\text{-TBAP}/\text{Nafion}$ composite membrane of 200- μm and 50- μm thickness

CONCLUSIONS AND UPCOMING ACTIVITIES

The first year of the project successfully identified the most promising MPP compositions for maximizing intermediate-temperature proton conductivity. MPP/Nafion composite membranes were fabricated and tested in 5-cm² fuel cells. The membrane fabrication procedure was modified and optimized to reduce porosity and membrane thickness. In FY 2020, we will turn our focus to membrane performance and durability under fuel cell operating conditions. We have demonstrated conductivity of 95 mS/cm at 220°C in a 5-cm² fuel cell using undoped SnP₂O₇ and anticipate increasing to >100 mS/cm by utilizing In-doped SnP₂O₇ and increasing the P:M ratio of the MPP material. An ASR of <0.04 Ω cm² will be achieved by reducing the thickness of the membrane to 40 μm using the MPP material with the highest conductivity. Durability will be evaluated against DOE technical targets for hydrogen crossover, shorting resistance, and open circuit voltage.

FY 2019 PUBLICATIONS/PRESENTATIONS

1. Cortney Kreller, Kannan Ramaiyan, Yu Seung Kim, Rangachary Mukundan, and Mahlon Wilson, “High Performing and Durable Pyrophosphate Based Composite Membranes for Intermediate Temperature Fuel Cells,” presented at the DOE Hydrogen and Fuel Cells Program Annual Merit Review and Peer Evaluation Meeting, Crystal City, VA, May 1, 2019.

REFERENCES

1. K.S. Lee, S. Maurya, Y.S. Kim, C.R. Kreller, M.S. Wilson, D. Larsen, S.E. Elangovan, and R. Mukundan, “Intermediate Temperature Fuel Cells Via an Ion-Pair Coordinated Polymer Electrolyte,” *Energy & Environmental Science* 11, no. 4 (Apr 2018): 979–987.
2. M. Einsla, R. Mukundan, E.L. Brosha, and F.H. Garzon, *ECS Transactions* 16 (2008): 2165.
3. C.R. Kreller, M.S. Wilson, R. Mukundan, E.L. Brosha, and F.H. Garzon, *Electrochemical and Solid-State Letters* 2 (2013).