High Performing and Durable Pyrophosphate Based Composite Membranes for Intermediate Temperature Fuel Cells

2018 DOE Annual Merit Review

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Operated by Los Alamos National Security, LLC for the U.S. Department of Energy's NNSA

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Overview

Timeline

- Project Start Date: January 2018
- Project End Date: January 2020*

* 2nd year continuation contingent on fulfillment of 1st year milestones.

Barriers addressed

- Early stage membrane concept that can:
  - Decrease system costs by operating at higher temperature (150–400 °C)
  - Achieve membrane ASR of ≤ 0.02 Ωcm^2
  - Achieve ASR ≤ 0.03 Ωcm^2 under low RH conditions
  - Achieve sufficient conductivity (0.2→ 0.02Ωcm^2) across entire range of operating temperatures

Budget

- Funding received in FY18: $150,000
- Total DOE Funds Spent**: $16,264

** As of 3/31/18

Partners

- University of New Mexico (Prof. Fernando Garzon)
  - No cost partner

Relevance

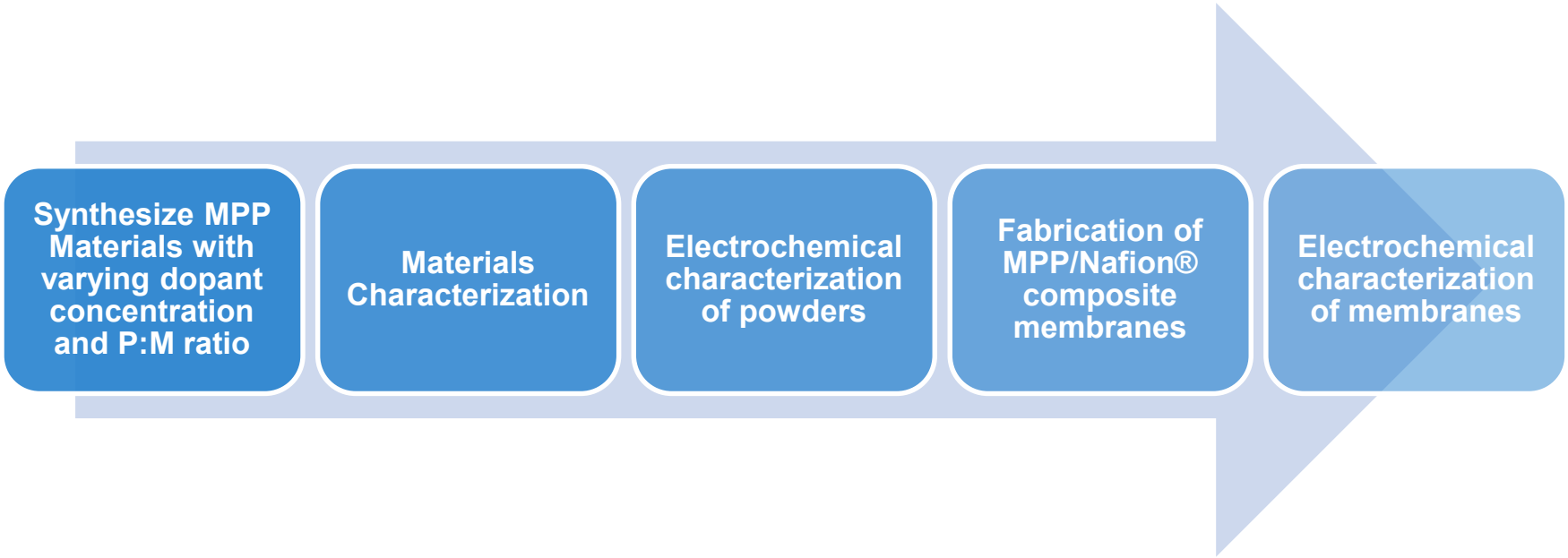
Objective: Develop membrane enabling system operation at higher temperature (200 °C) at low RH with conductivity across entire range of operating conditions for transportation applications.

- Tailor composition of MP_2O_7 (MPP)/polymer composite membranes to achieve DOE target for membrane ASR of ≤ 0.02 Ωcm^2.

DOE Technical Target	LANL Impact
Decrease system costs by operating at higher temperature (150–400 °C)	MP_2O_7/polymer composite membranes target operation temperature 200 °C
Achieve membrane ASR of ≤ 0.02 Ωcm^2	Achieve $\sigma \geq 100 mScm^{-1}$ at T ≥ 200 °C and RH<0.04bar while reducing MPP loading to cast membranes <40 μm thick. Y1 GNG: ASR of <0.04 Ωcm^2
Achieve ASR ≤ 0.03 Ωcm^2 under low RH conditions	Maintain target ASR under 0-0.04bar H_2O
Achieve activity (0.2→ 0.02Ωcm^2) across entire range of operating temperatures	MPP/polymer composite membranes do not rely on phase change or high RH for H+ transport extending operating temperature range

Approach: Tasks and Milestones (as of 4/17/18)

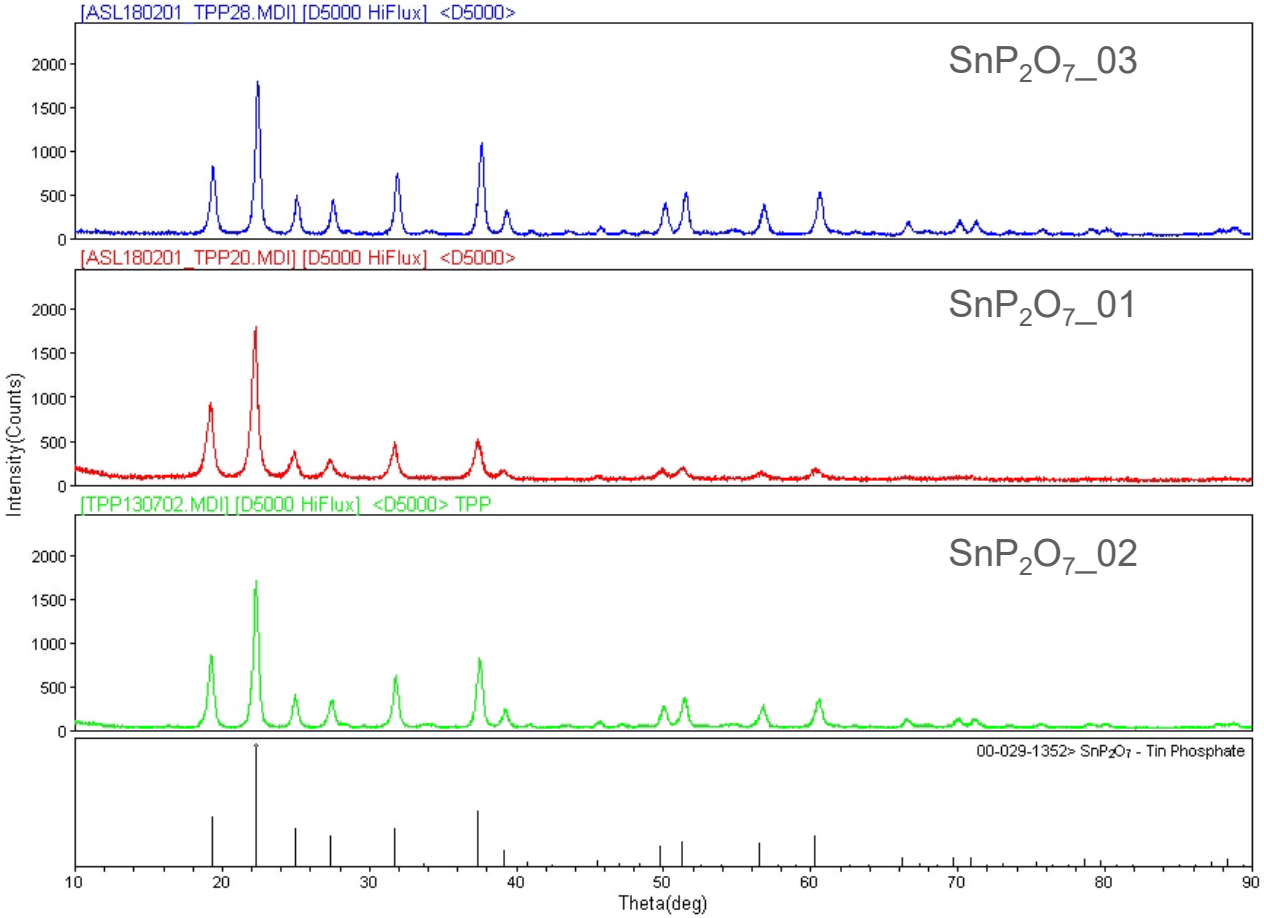
Q1: Synthesize and characterize 6 MPP materials with varying dopant concentration and P:M ratio	66%
Q2: Establish trends in conductivity with P:M ratio and cation dopant	10%
Q3: Fabricate membranes from MPP materials that exhibit high conductivities in powder form. Report membrane conductivities as a function of MPP loading and PA doping	5%
Q4: Minimize membrane thickness while retaining mechanical integrity	0%

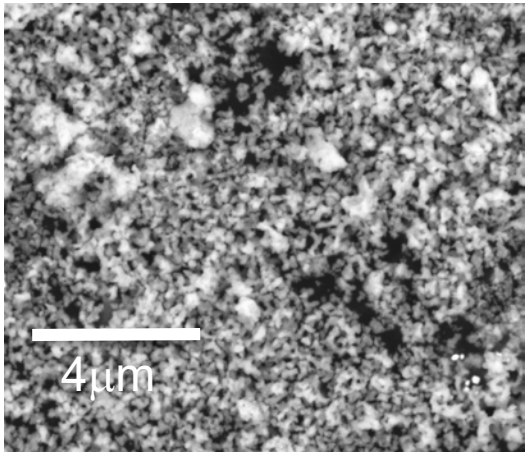


GNG end of Phase 1: Demonstrate in-plane membrane conductivity of ≥ 100mScm^{-1} at T > 200˚C and RH<0.04bar with a thickness ≤ 40 μm.

Specific Phase 2 quarterly milestones will be defined upon successful completion of Phase 1.

Accomplishments and Progress:
Synthesis and characterization of bulk powders

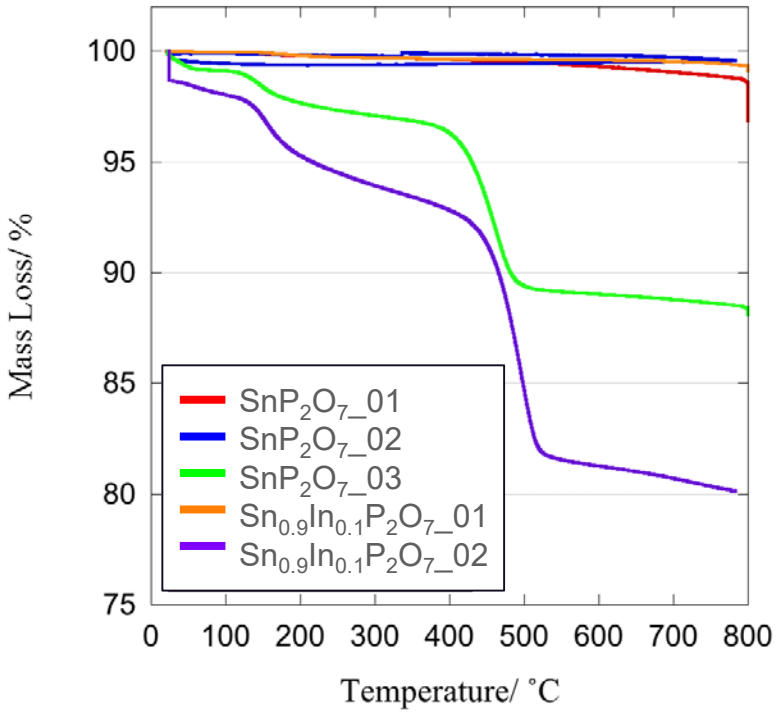




15-30nm crystallite size

Synthesized crystalline phase-pure SnP_2O_7 and $Sn_{0.9}In_{0.1}P_2O_7$

Accomplishments and Progress:
Synthesis and characterization of bulk powders

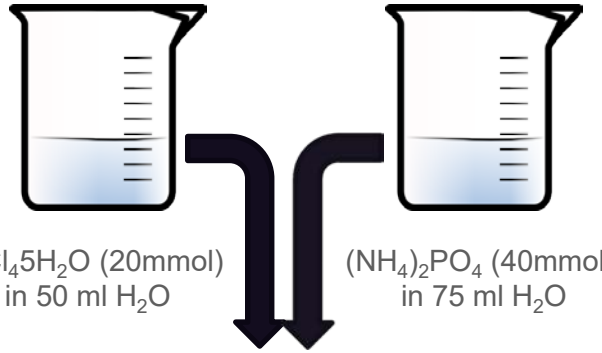


Sample	TGA Mass loss (%)	P:M	Log(σ) @200 °C dry/ 0.04 bar H_2O (Scm^{-1})
SnP_2O_7_01	3.14	2.10	< -7
SnP_2O_7_02	0.43	2.01	< -7
SnP_2O_7_03	11.91	2.40	-4.76/-4.18
$Sn_{0.9}In_{0.1}P_2O_7$_01	0.96	2.03	< -7
$Sn_{0.9}In_{0.1}P_2O_7$_02	19.96	2.74	-2.27/-1.98

- Synthesized stoichiometric and excess polyphosphate containing material for SnP_2O_7 and $Sn_{0.9}In_{0.1}P_2O_7$ composition
- Stoichiometric SnP_2O_7 materials do not exhibit significant conductivity below ~600 °C
- Increasing P:M ratio with increasing excess polyphosphate phase will improve conductivity of bulk material

Accomplishments and Progress:
Method of preparing MPP and MPP/Nafion® composite membranes

TPP Particle Synthesis



$SnCl_4 5H_2O$ (20mmol) in 50 ml H_2O

$(NH_4)_2PO_4$ (40mmol) in 75 ml H_2O

Co-precipitation

↓

Dehydration 140 °C, overnight

↓

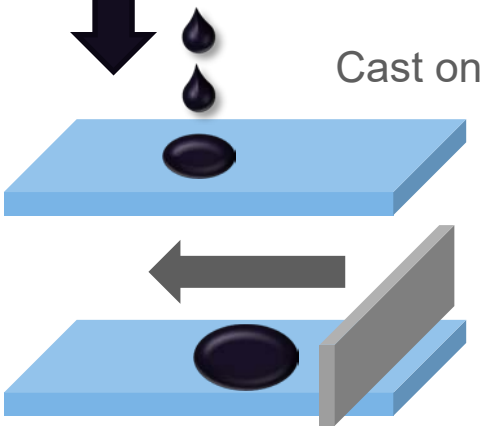
Calcination in air 650 °C, 2.5h

Composite Membrane Fabrication

5 wt% Nafion® 212 Dispersion in 1,2-pentanediol + TPP powder (9:1 wt:wt TPP:Nafion®) sonicated with probe sonicator 3 x 5 min increments.

↓

Cast on glass slide



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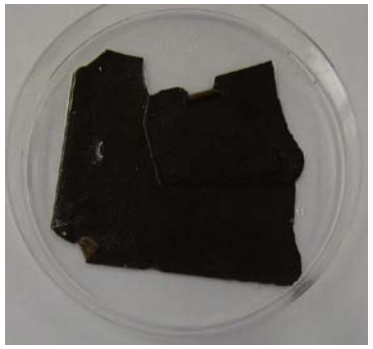
- Dry at 120 °C 4hr, then at 160 °C under vacuum overnight
- Soak in 85wt% phosphoric acid 10h

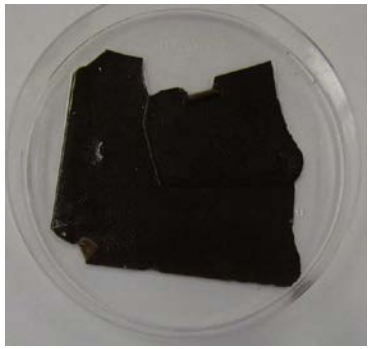
Accomplishments and Progress:
Quantifying PA uptake of membranes

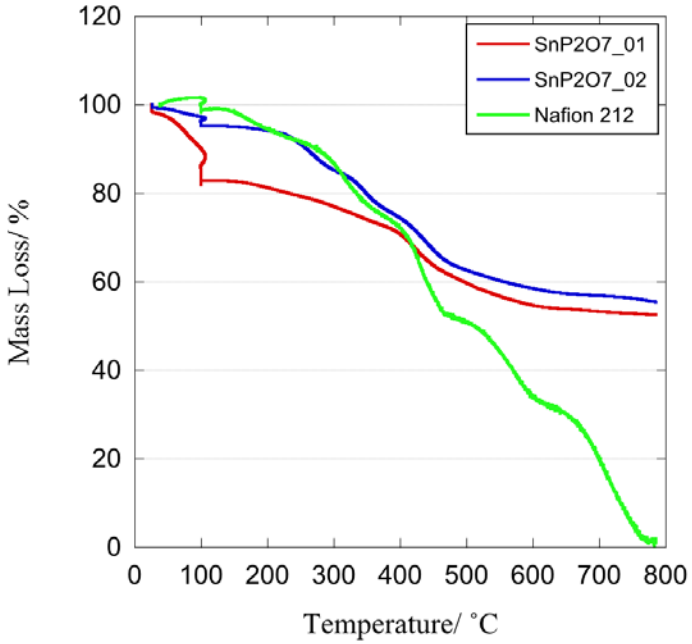
SnP_2O_7_01

SnP_2O_7_02



Nafion

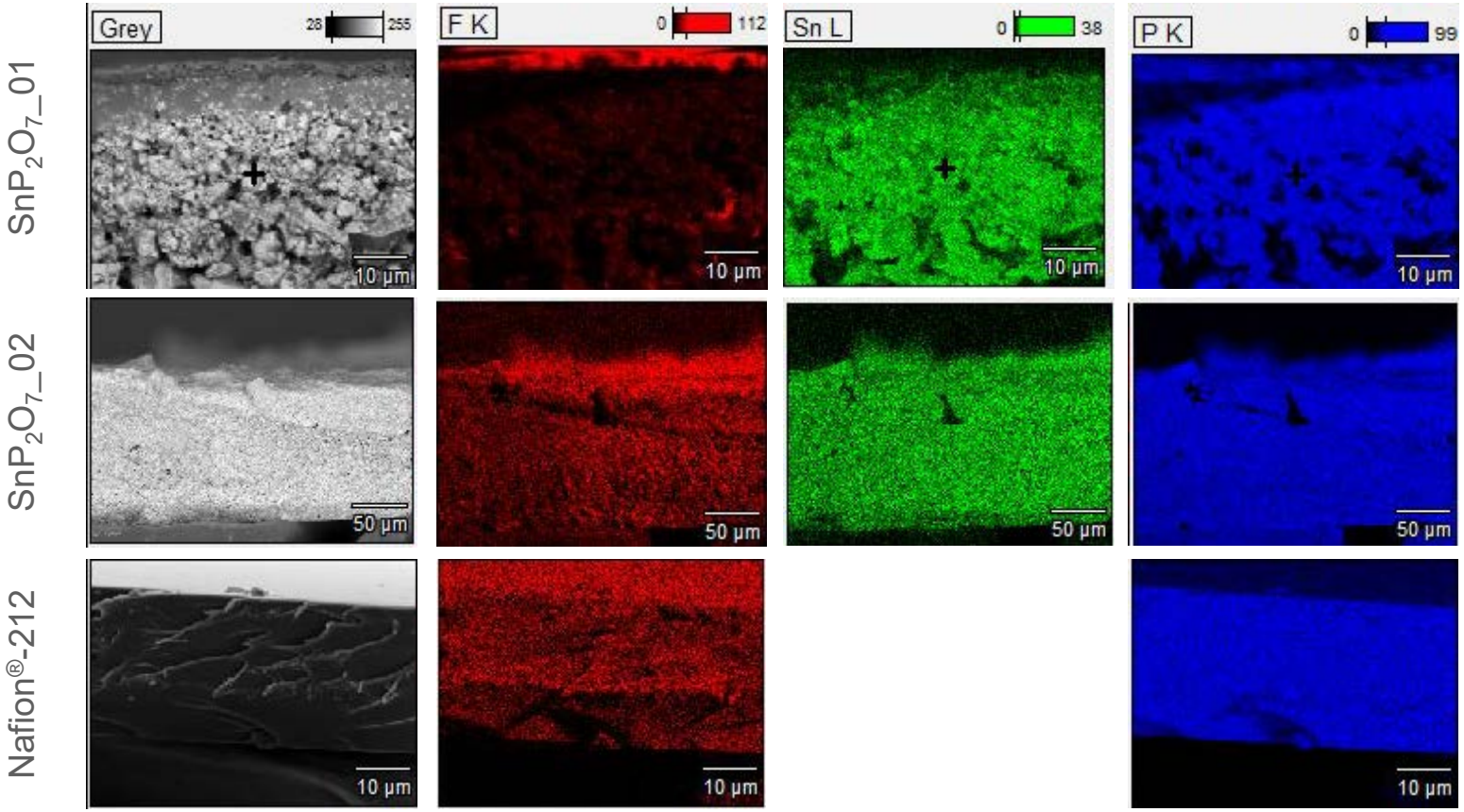




- First membranes prepared from stoichiometric SnP_2O_7 powder ~120μm thick
- TGA mass loss used to calculate H_3PO_4 uptake
- PA uptake similar for all membranes

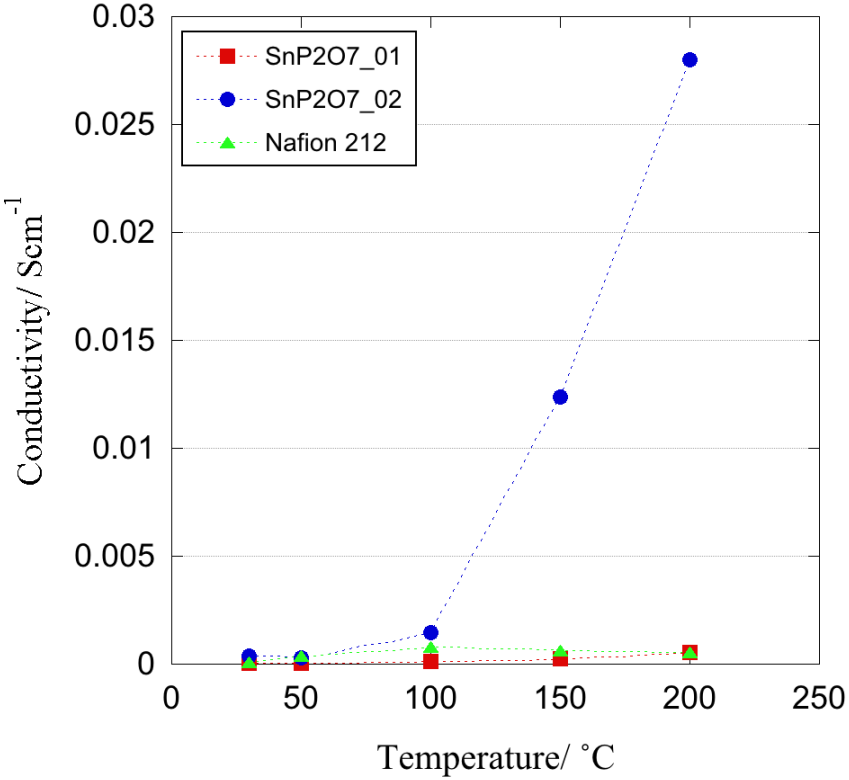
Sample	TGA Mass loss (%)	Calculated H_3PO_4 uptake	P:M
SnP_2O_7_01	47.4	64%	4.10
SnP_2O_7_02	44.7	59%	3.94
Nafion®	~100%	-	-

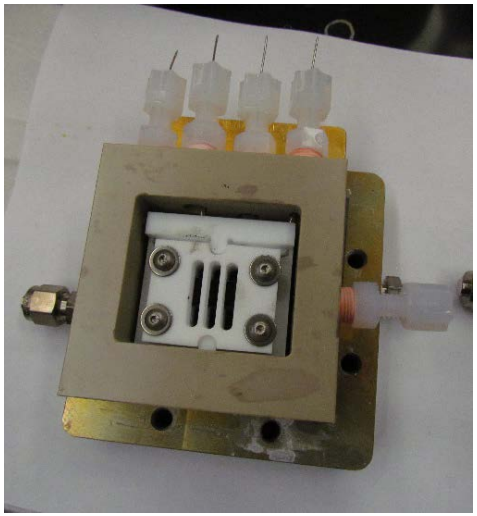
Accomplishments and Progress:
EDS mapping of membranes imbibed with phosphoric acid (PA)



- Un-milled SnP_2O_7_01 shows large distribution in particle size with phase separated Nafion® layer on top and large crystallites on bottom
- Milled SnP_2O_7_02 shows uniform distribution of Sn, F and P throughout membrane thickness
- PA doped Nafion® also shows uniform distribution of F and P

Accomplishments and Progress:
In-plane conductivity of PA-imbibed MPP/Nafion® membranes





- SnP_2O_7_02 exhibited highest conductivity of 0.028 Scm-1 at 200 °C in dry N_2
- While PA uptake was similar for all membranes, SnP_2O_7_02 exhibited most uniform dispersion of stoichiometric SnP_2O_7 crystallites
- Nafion® did not contribute to total conductivity due to anhydrous conditions
- Retention of PA in commercial Nafion® probably poor due to high density of membrane

Collaboration & Coordination

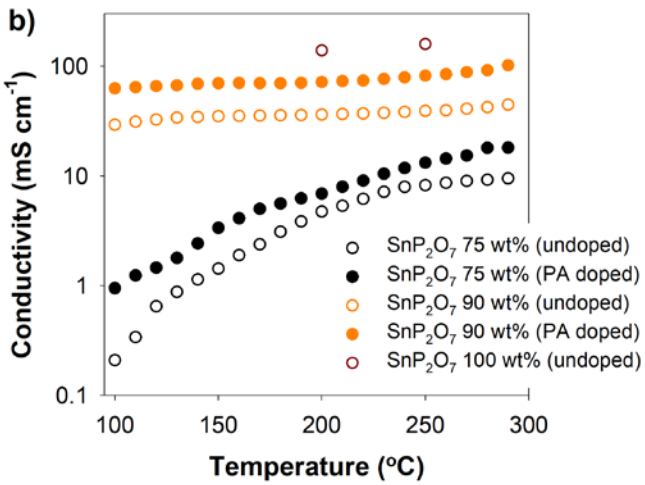
- Lab call project open to National Labs only- no official collaborators
- University of New Mexico- no cost partner interested in evaluating membranes for fuel electrosynthesis reactors
- Will solicit more partners once proof of concept is established

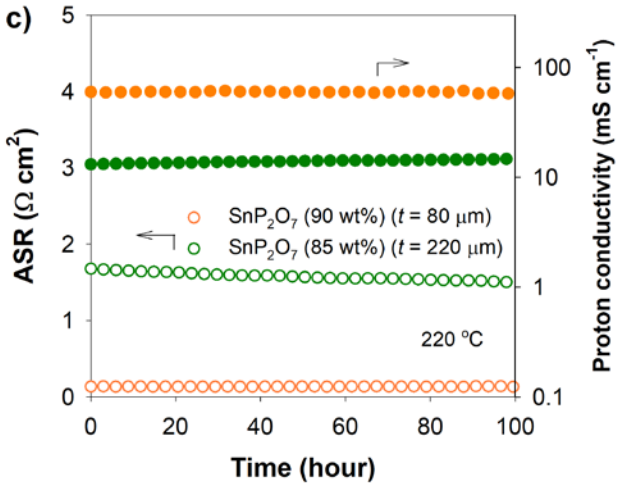
Remaining Challenges and Barriers

Challenge: Maintain high conductivity with decreased MPP loading in order to decrease membrane thickness to meet ASR targets

Planned resolution: Evaluate materials with different crystalline nonstoichiometry as well as varying amounts of excess polyphosphate phase to identify composite that improves PA uptake/retention or conductivity of grain boundary phase

- ***State-of-the-art achieved previously yielded 80μm thick membranes with conductivity of ~100mScm^{-1}***
- ***Need to reduce MPP loading in order to reduce membrane thickness while maintaining sufficient mechanical integrity***
- ***In this work, our goal is to modify the MPP phase such that we maintain $\sigma \geq$ 100mScm^{-1} while reducing the membrane thickness to $\leq$ 40μm***



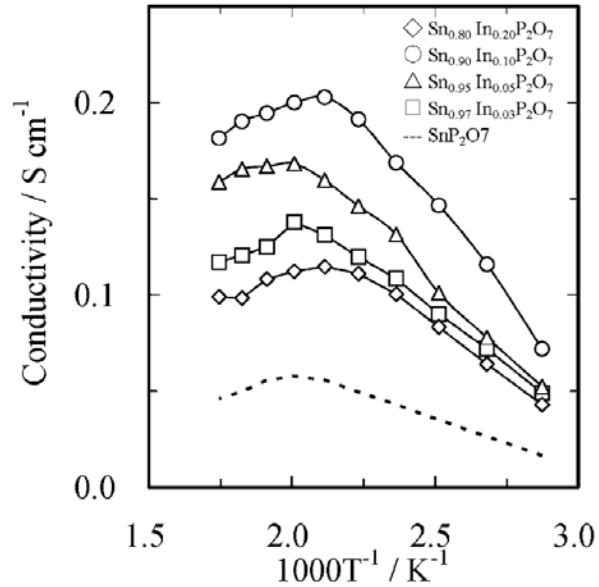


Lee, Kwan-Soo, *Energy & Environmental Science* 11, no. 4 (2018): 979-87

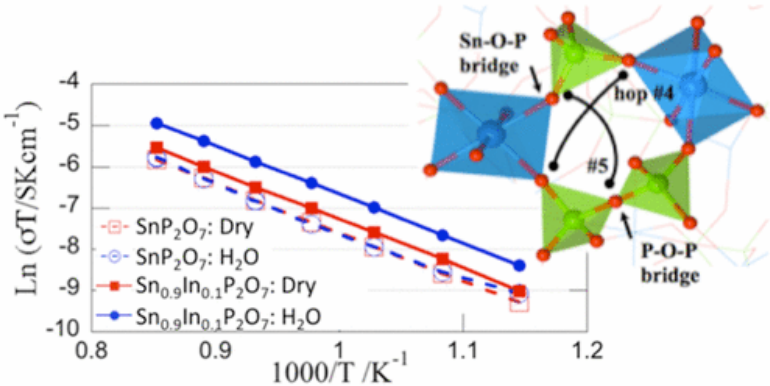
Proposed Future Work

- Initial publications on MP_2O_7 showed that conductivity at low-to-intermediate temperatures improved with introduction of lattice oxygen vacancies via aliovalent doping.
- Our subsequent work found that the crystalline MP_2O_7 material exhibited negligible conductivity in the low-to-intermediate temperature range, and an amorphous grain boundary polyphosphate phase is required for IT proton conduction.
- Crystalline MP_2O_7 phase may induce matrix effects on conductivity (space charge effects) and/or retention (basicity of MP_2O_7 varies with composition) of polyphosphate phase responsible for IT conduction.
- Matrix effect may extend to PA. Excess polyphosphate phase may also influence uptake/retention of PA.

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



Nagao, M. et. al, ESSL 9(3) 2006.



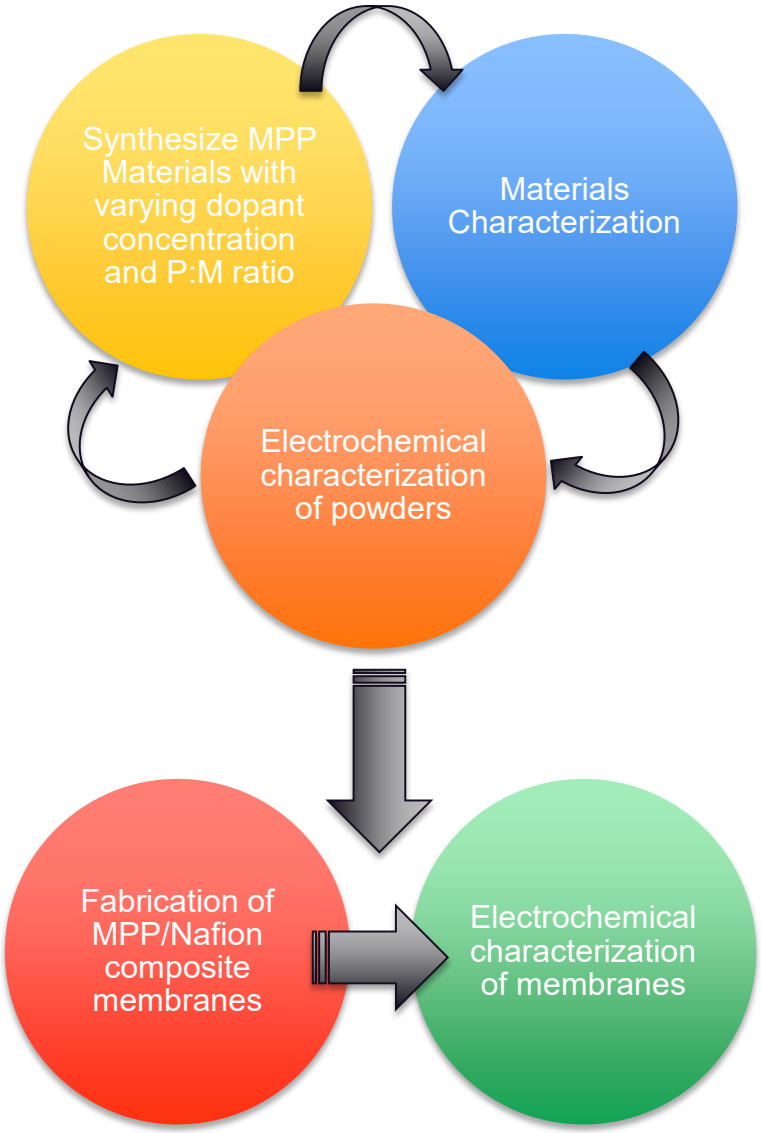
Kreller, C.R. et. al, J. Phys Chem. C 121,43, 2017.

Proposed Future Work

- Synthesize MP_2O_7 powders (M=Sn, Ce) with aliovalent dopants (i.e., In^{3+}, Al^{3+}, Mg^{2+}, Sc^{3+}) and varying amounts of excess polyphosphate phase
- Identify trends in PA uptake and total conductivity with dopant and with amount of excess polyphosphate phase
- For most promising conductors, identify optimum membrane composition (MPP:polymer) for maximizing conductivity while minimizing thickness.
- Any proposed future work is subject to change based on funding levels.

Year 1 GNG: *In-plane $\sigma \geq 100 mScm^{-1}$ while reducing the membrane thickness to ≤ 40μm at T>200˚C and humidity <0.04bar*

Year 2: *Incorporate membranes into MEAs and demonstrate durability and start-up performance*



Summary

- MPP materials of composition $Sn_{1-x}In_xP_2O_7$ have been synthesized with x=0,0.1 and P:M ratio of 2.0 (stoichiometric) and >2 (excess polyphosphate phase).
- Bulk pellet conductivity of P:M>2 materials was measured to be in reasonable agreement with prior results for MPP materials with comparable excess polyphosphate phase.
- Stoichiometric SnP_2O_7 powders were incorporated into membranes for the first time. When MPP material was uniformly dispersed in composite membrane imbibed with PA, conductivity of $30mScm^{-1}$ was obtained at 200˚C.
- Future work will identify trends in PA uptake and conductivity with MPP stoichiometry and amount of excess polyphosphate phase. The most promising materials will be used to optimize membrane composition.