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

2019 DOE Annual Merit Review

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Overview

Timeline

- Project Start Date: January 2018
- Project End Date: July 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 ($0.2 \rightarrow 0.02 \Omega cm^2$) across entire range of operating temperatures

Budget

- Funding received in FY18: $150,000
- Total DOE Funds Spent: $89,418

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 $\sigma \geq$ 100mScm^{-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

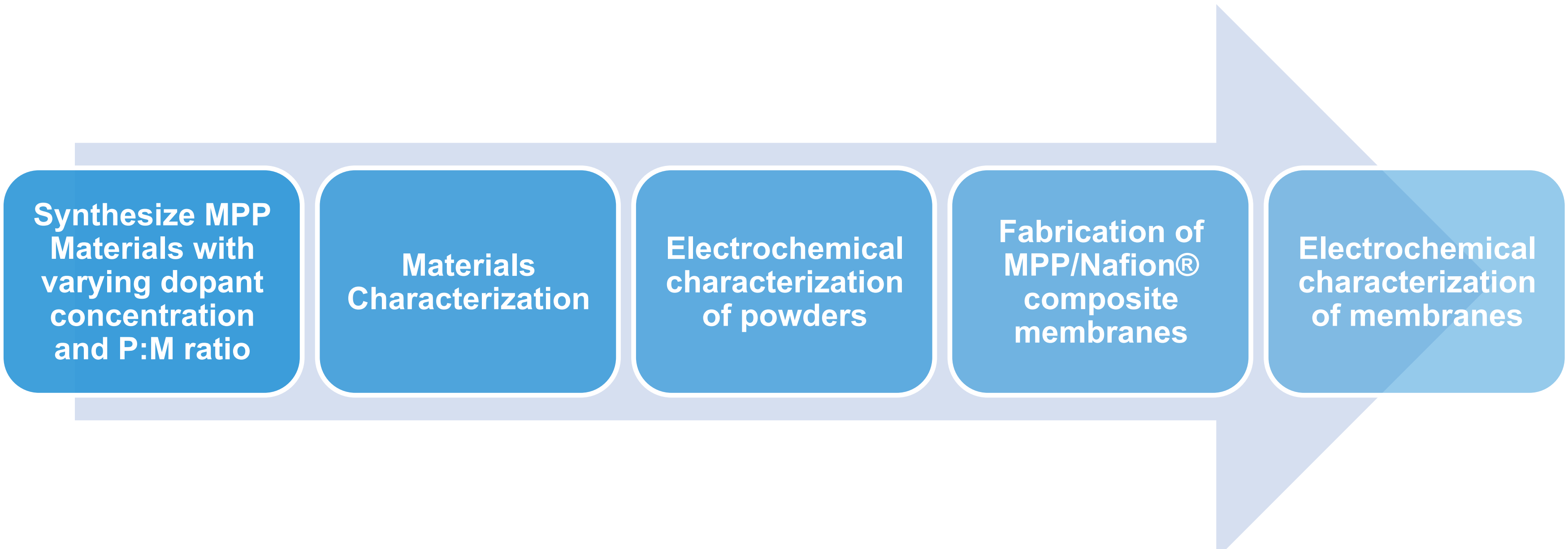
Approach: Tasks and Milestones

Q1: Synthesize and characterize 6 MPP materials with varying dopant concentration and P:M ratio — 100%

Q2: Establish trends in conductivity with P:M ratio and cation dopant — 100%

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 — 10%

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.

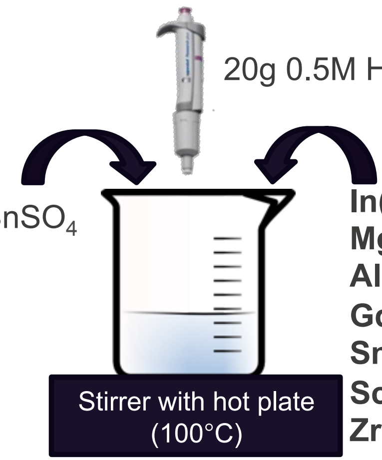
Specific Phase 2 quarterly milestones will be defined upon successful completion of Phase 1.

Accomplishments and Progress:
Synthesis and characterization of bulk powders

TPP Particle Synthesis

20g 0.5M H_2SO_4

$SnSO_4$



$In(NO_3)_3.xH_2O$
$Mg(CH_3COO).4H_2O$
$Al(NO_3)_3.9H_2O$
$Gd(CH_3COO)_3.xH_2O$
$Sm(NO_3)_3.6H_2O$
$Sc(NO_3)_3.xH_2O$
Zr(IV) acetate hydroxide

1. 5g Oxalic Acid
2. 10g H_3PO_4
3. Heat (120°C)

140°C overnight

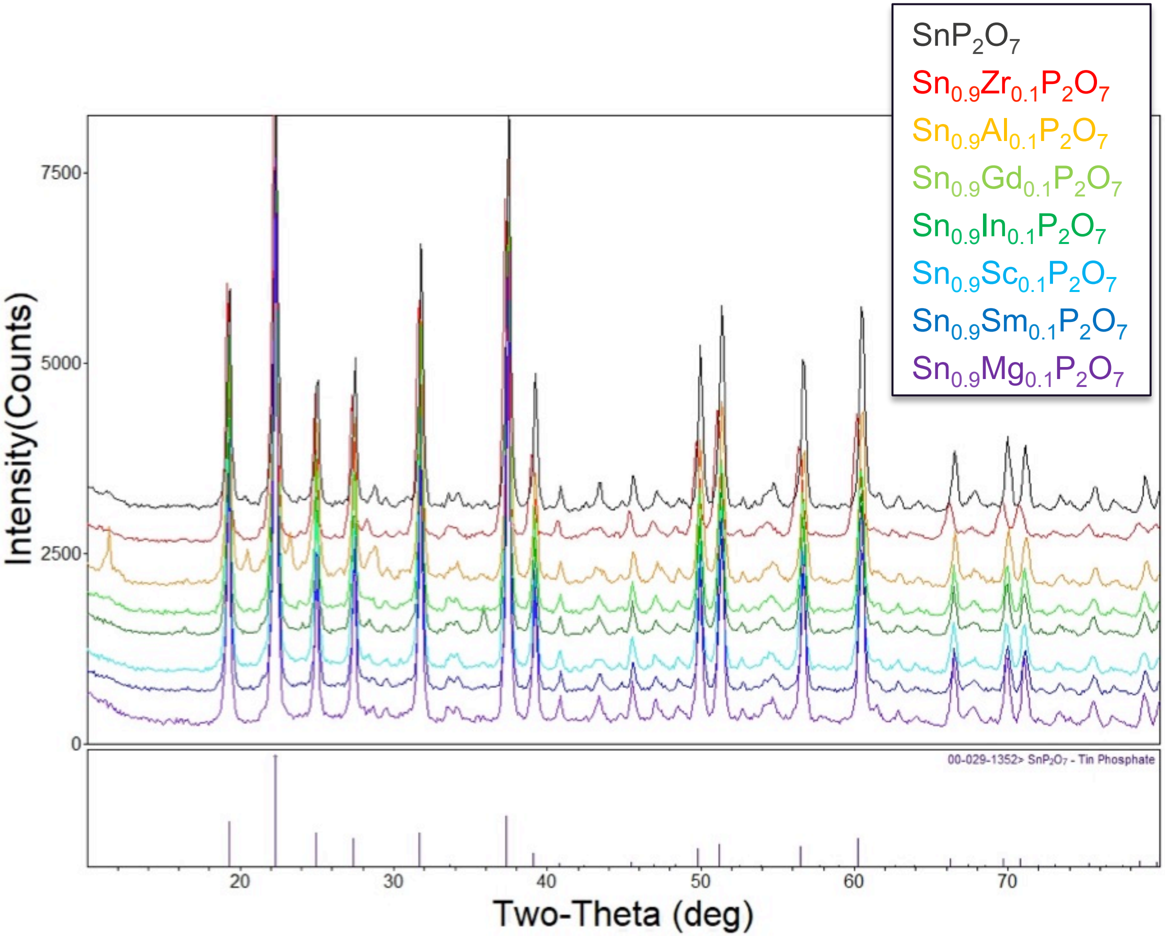
650°C – 2 hours

Mass loss measured by TGA to 800˚C

$Sn_{(1-x)}M_xP_2O_7$		Weight loss (%)	P:M
M	x		
-	0	24.10	2.80
Zr^{4+}	0.1	30.05	3.07
Al^{3+}	0.1	21.99	2.69
Gd^{3+}	0.1	25.34	2.87
In^{3+}	0.1	23.06	2.76
In^{3+}	0.1	44.23	4.00
Sc^{3+}	0.1	22.93	2.73
Sc^{3+}	0.1	30.39	3.29
Sm^{3+}	0.1	19.48	2.62
Mg^{2+}	0.1	15.76	2.46
Mg^{2+}	0.1	23.30	2.74

- Assumed volatile phase H_3PO_4+H_2O to calculate Phosphorous to Metal (P:M) ratio

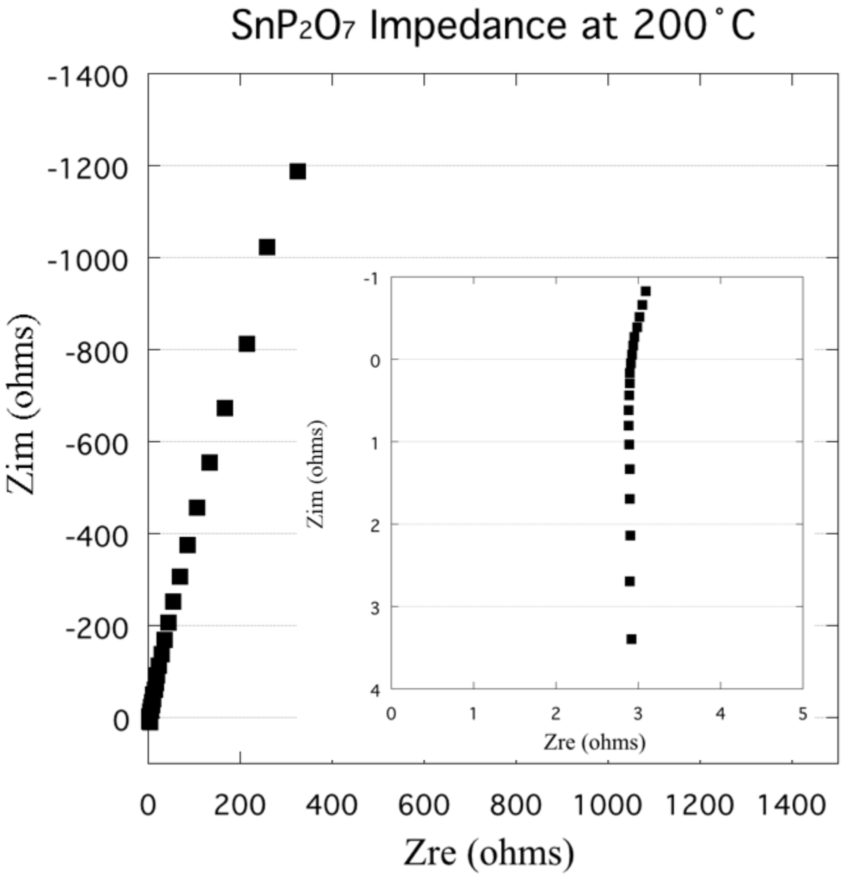
Accomplishments and Progress:
Synthesis and characterization of bulk powders

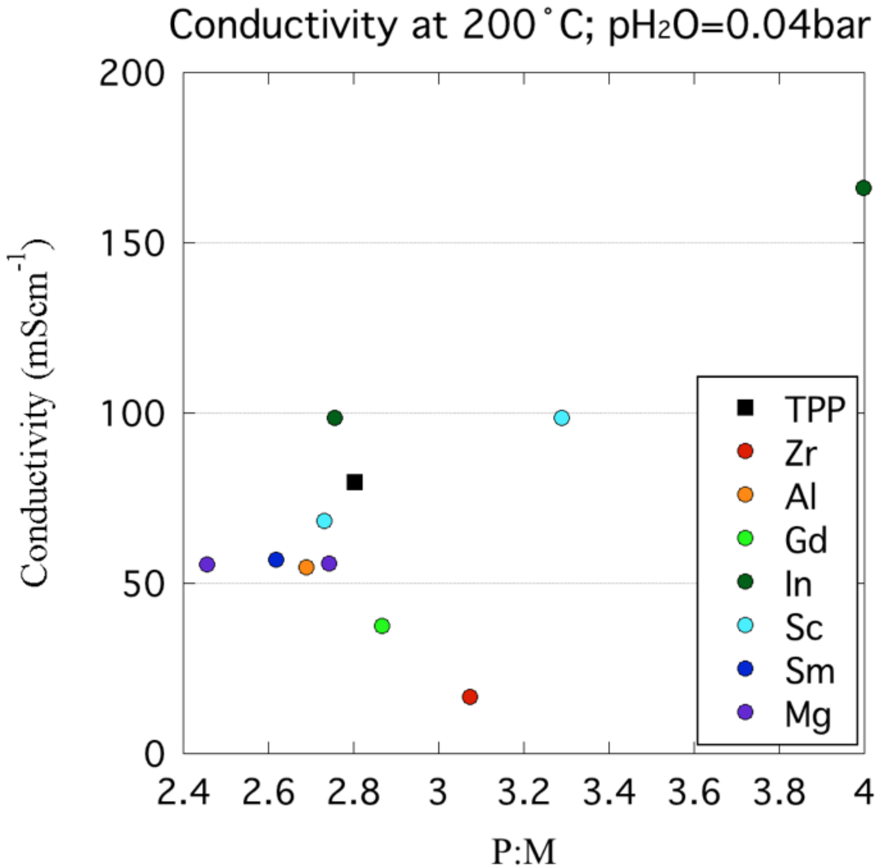


$Sn_{(1-x)}M_xP_2O_7$ M	x	Lattice Parameter (Å)	± error	Crystallite size (Å)
-	0	7.9453	0.001366	51
Zr^{4+}	0.1	7.9637	0.001708	34.1
Al^{3+}	0.1	7.9366	0.001827	42.6
Gd^{3+}	0.1	7.9479	0.001254	50.8
In^{3+}	0.1	7.9494	0.001244	52
Sc^{3+}	0.1	7.9509	0.001433	37.6
Sm^{3+}	0.1	7.9512	0.001212	54.4
Mg^{2+}	0.1	7.9483	0.001472	40.5

- Synthesized $Sn_{1-x}M_xP_2O_7$ powders with aliovalent dopants and varying amounts of excess polyphosphate phase

Accomplishments and Progress:
Bulk pellet conductivity





- Highest conductivities observed for SnP_2O_7, $Sn_{0.9}In_{0.1}P_2O_7$ and $Sn_{0.9}Sc_{0.1}P_2O_7$

Responses to Previous Year Reviewer's Comments

Project was not reviewed last year

Collaboration & Coordination

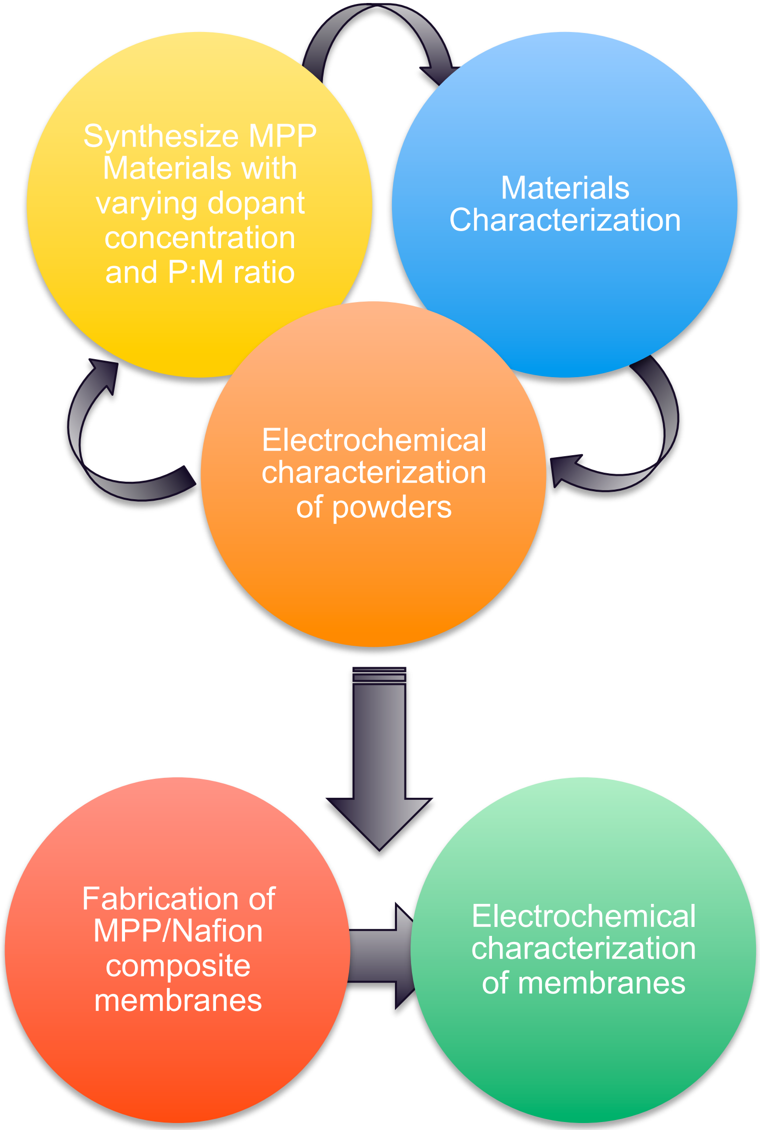
- Lab call project open to National Labs only- no official collaborators
- University of New Mexico- no cost partner interested in evaluating membranes for fuel electrosynthesis reactors
- Will solicit more partners once proof of concept is established

Proposed Future Work

- Fabricate membranes with $Sn_{1-x}M_xP_2O_7$ ($M=In^{3+}$, Sc^{3+})
- 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:Nafion) 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 $\leq$ 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.
- Highest conductivities were observed for SnP_2O_7, $Sn_{0.9}In_{0.1}P_2O_7$ and $Sn_{0.9}Sc_{0.1}P_2O_7$.
- Future work will identify trends in PA uptake and conductivity with MPP stoichiometry and amount of excess polyphosphate phase in composite membranes. The most promising materials will be used to optimize membrane composition.

Technical Back-up Slides

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