

# Novel Approaches to Immobilized Heteropoly Acid (HPA) Systems for High Temperature, Low Relative Humidity Polymer-Type Membranes

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FCP 7



# Overview

## Timeline

- Start – April 2006
- Finish – March 2011
- 1.5% Complete

## Budget

- Total project funding
  - DOE - \$1,500K
  - Contractor - \$375K
- Funding received in FY06
  - \$150K
- Funding for FY07
  - \$300K

## Barriers

- A. Durability with cycling, 5000 h
- B. Cost, \$ 40 m<sup>-2</sup>
- C. Electrode Performance  
720 μAcm<sup>-2</sup> at 900mV
- Targets – Proton Conductivity, 0.1 S cm<sup>-1</sup>

	2004	2010
Temp./ °C	80	120
Inlet H <sub>2</sub> O P/kPa	50	1.5

Partners - 3M (1/3 of project effort)

# Objectives

<ul style="list-style-type: none"><li>• Overall</li></ul>	<ul style="list-style-type: none"><li>• Fabricate a hybrid HPA polymer from HPA functionalized monomers with:<ul style="list-style-type: none"><li>– <math>\sigma &gt; 0.1 \text{ S cm}^{-1}</math> at <math>120^\circ\text{C}</math> and <math>&lt; 1.5 \text{ kPa H}_2\text{O}</math></li></ul></li></ul>
<ul style="list-style-type: none"><li>• 2006</li></ul>	<ul style="list-style-type: none"><li>• Selection of most hydrolytically stable HPA to monomer linkage chemistry</li><li>• Synthesize free acids of HPA polymers</li></ul>
<ul style="list-style-type: none"><li>• 2007</li></ul>	<ul style="list-style-type: none"><li>• Synthesis and optimization of hybrid HPA polymers for RT conductivity</li></ul>

# Plan and Approach

- Task 1.1 Phenyl link stability

Phenyl HPA derivatives subjected to low pH/high temperatures to determine optimum chemistry for fuel cell stability

– A vast synthetic chemistry of hybrid organic/inorganic HPAs exists but none of it has been applied to fuel cell ready environments. (8% complete)

- Task 1.2 Ion exchange studies

Determination of most facile conversion of HPA polymers to proton conducting systems – Most published HPA chemistry is concerned with HPA salts. In order to conduct  $H^+$  we must learn how to convert these materials in to free acids. (8% complete)

- Task 1.3 Optimization of hybrid HPA polymers for RT

Morphology and structure of polymers controlled to optimize proton conductivity, HPA clustering or order

- Task 2.1 Optimization of hybrid HPA polymers for 120°C

Maximize  $H^+$  availability, exploit HPA dissociable  $H^+$  donor groups -  $>100^\circ C$   
HPA have fast  $H^+$  diffusion but not all  $H^+$  are available

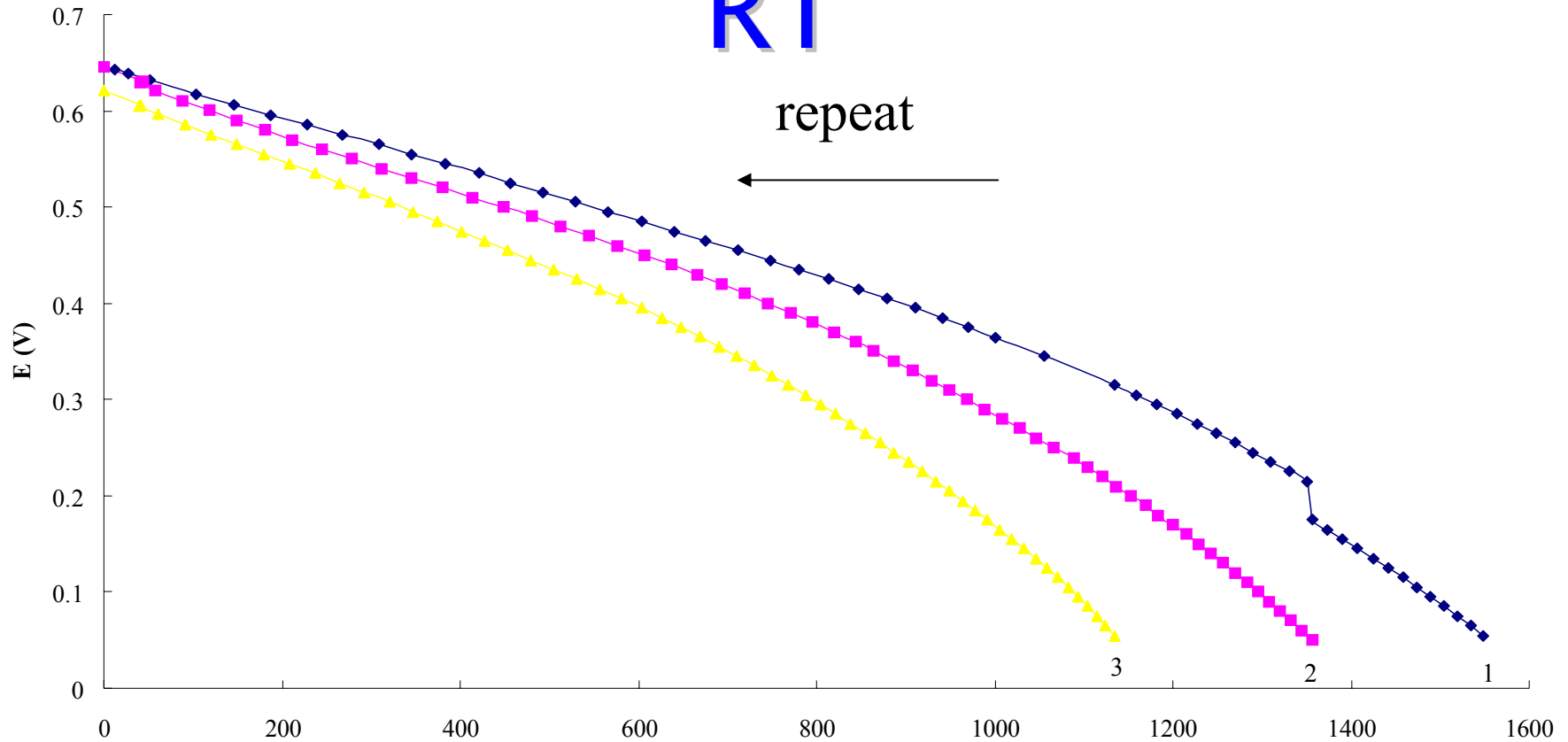
- Task 3.2 Optimize oxidative stability

Use oxidatively stable organic chemistry, exploit HPA peroxide catalysis

# Unique Approach

- Materials Synthesis based on HPA Monomers
- Novel “High and Dry” proton conduction pathways mediated by organized HPA moieties
- 3M will bring additional synthetic expertise and direct later stages of project towards manufacturability.

# Excellent H<sup>+</sup> Conductivity at RT

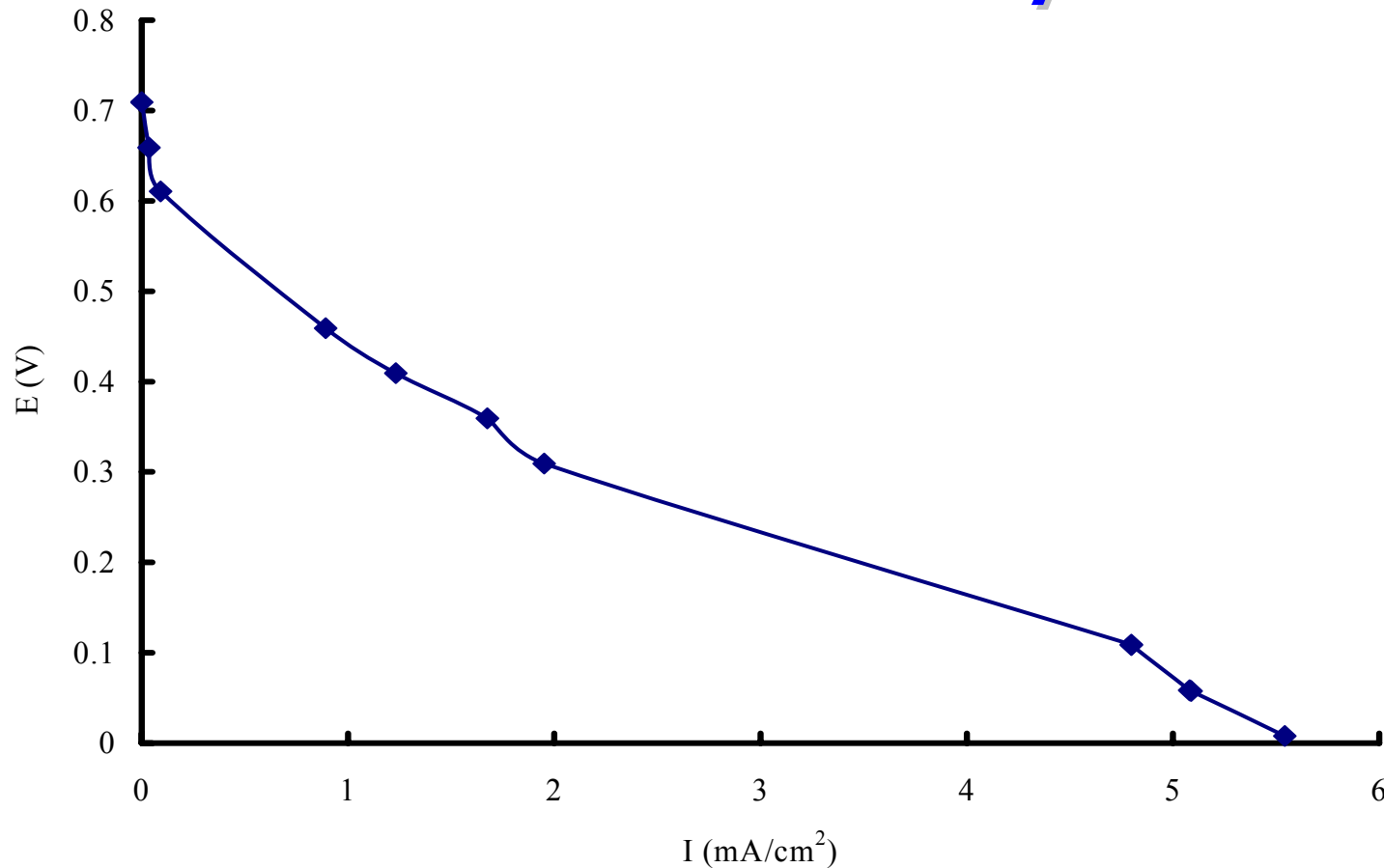


- 12-HPW/PVDF-HFP, 30  $\mu\text{m}$ , **Dry Gases**, 0.5 l min<sup>-1</sup>, H<sub>2</sub>/O<sub>2</sub>, **RT**.

Previous results from DE-FC02-0CH11088



# Poor H<sup>+</sup> Conductivity > 100°C



- 18-HP<sub>2</sub>W/PVDF-HFP, 30 μm, 25% RH, 0.5 l min<sup>-1</sup>, H<sub>2</sub>/O<sub>2</sub>, 120°C.

Previous results from DE-FC02-0CH11088

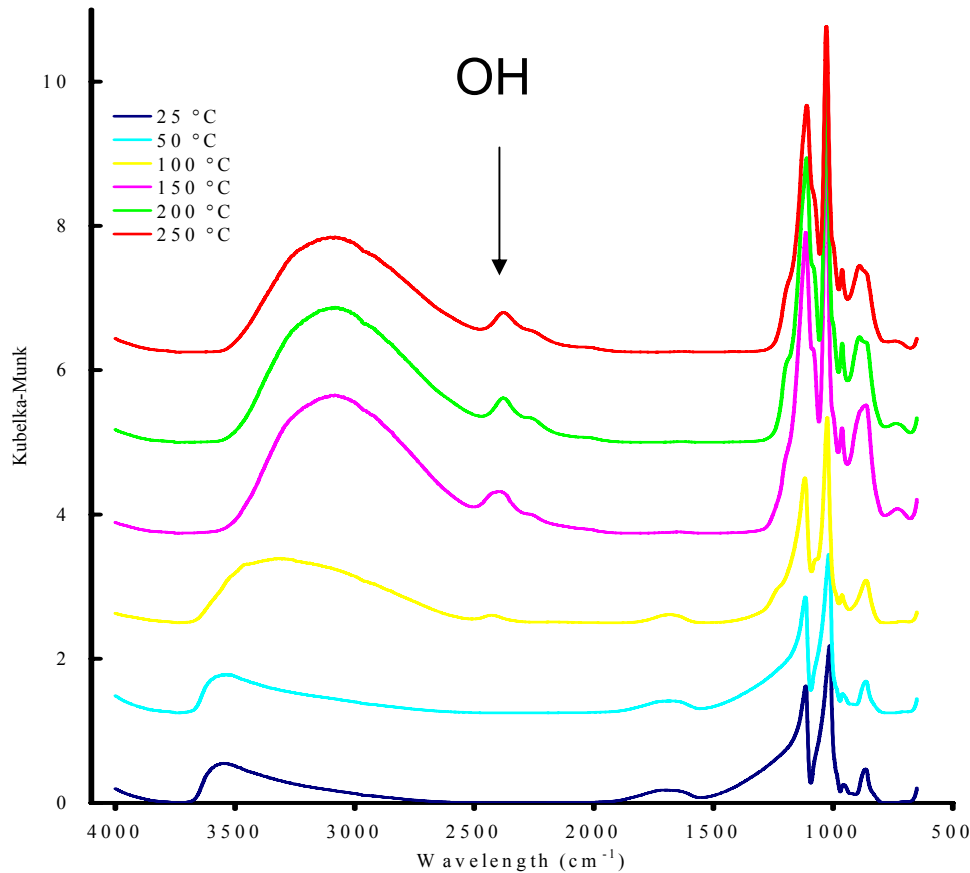
# Fast H<sup>+</sup> Diffusion > 100°C

HPA	Max diffusion coefficient x 10 <sup>-6</sup> cm <sup>2</sup> s <sup>-1</sup>	Temperature of maximum D, °C	E <sub>a</sub> before Max T, kJ mol <sup>-1</sup>	Secondary structure	
12-HPW	25	117	13	H <sup>+</sup> (H <sub>2</sub> O) <sub>x</sub>	cubic
12-HSiW	30	130	20	H <sup>+</sup> (H <sub>2</sub> O) <sub>x</sub>	cubic
12-HZnW	2	108	27	H <sub>5</sub> O <sub>2</sub> <sup>+</sup> , OH	cubic
12-HGeW	0.7	90	35		cubic
11-SiW11	3	108	6	H <sub>5</sub> O <sub>2</sub> <sup>+</sup> , OH	cubic
39-HB3W	7	128	8	H <sup>+</sup> (H <sub>2</sub> O) <sub>x</sub>	sheets
18-HP2W	1.2	>150	20	H <sub>3</sub> O <sup>+</sup>	triclinic
21-HAs2W	3.7	>150	18	H <sub>5</sub> O <sub>2</sub> <sup>+</sup>	
21-H <sub>2</sub> Rb <sub>4</sub> As <sub>2</sub> W	30	25	-	H <sup>+</sup> (H <sub>2</sub> O) <sub>x</sub>	channels
21-HP2W	2.3	110	24	H <sub>3</sub> O <sup>+</sup>	

- For Keggin anions E<sub>a</sub> increases and D decreases as the heteroatom becomes heavier
- More complex for less symmetrical anions



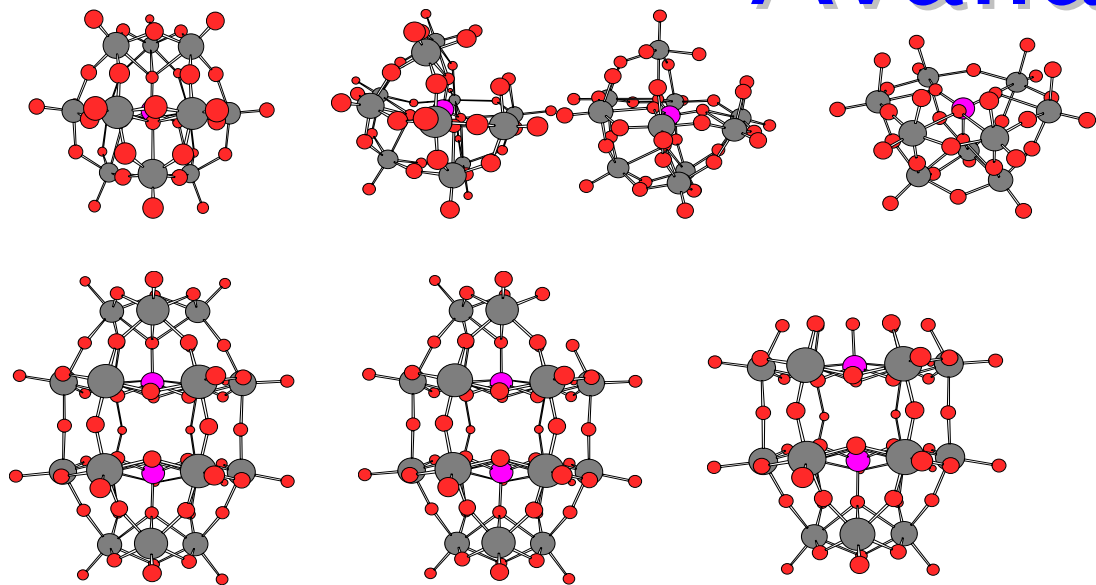
# Low $H^+$ Availability $> 100^\circ C$



- As Temperature increases more  $H^+$  become strongly associated with anion

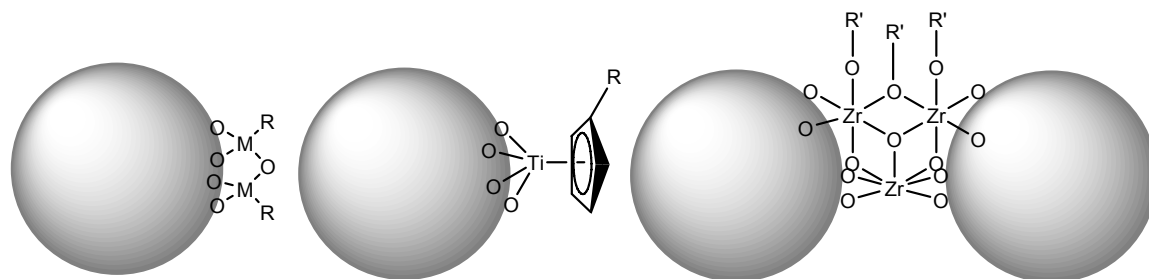
Previous results from DE-FC02-0CH11088

# Extensive HPA Chemistry Available



- Lacunary HPA allow easy attachment points

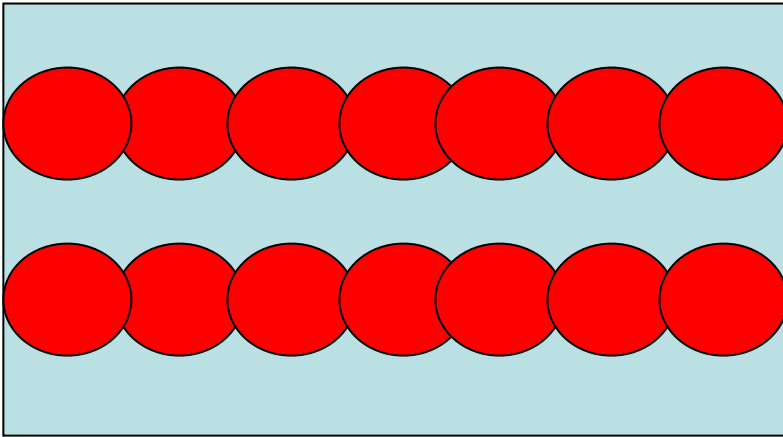
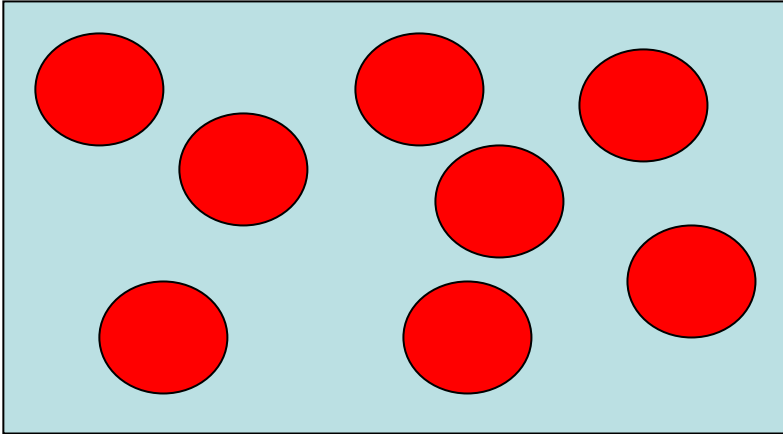
- Extensive linkage chemistry available
- $M = P, Si, Ge, Sn$
- $R, R' = \text{monomer}$



# Ion Exchange

- Almost of all of the hybrid HPA chemistry to date has been for diverse applications including biochemistry, catalysis and materials science where the free acid form of the molecule was not desired and so all of this chemistry is based on salts, the cation being chosen to allow the use of diverse solvents
- The challenge here is to exploit the salt chemistry to achieve the desired materials but to perform ion-exchange at the appropriate synthetic point to deliver a proton conducting material

# HPA Self Templating



- HPA will be strongly attracted to one another and will aggregate
- Must co-polymerize HPA monomers with hydrophobic monomers to affect correct phase separation and formation of H<sup>+</sup> conduction pathways.

# Oxidative Stability

- Use of aromatic monomers without aliphatic C-H bonds will be explored
- The well known interaction of HPA with peroxide either as activation or decomposition catalyst will be exploited

# Optimize Mechanical Properties

- High proton conductivity and oxidative stability are not enough on their own.
- Working closely with our partners at 3M we will optimize the final membranes for mechanical stability, minimal swelling, creep and defects.

# Technical Accomplishments / Progress / Results – Month 1

- Task 1.1 We have begun to synthesize a library of Phenyl HPA molecules for the stability study
- Task 1.2 We have successfully ion-exchanged the tetra-butyl ammonium salt from a poly(methylmetacrylateHPA) polymer

# Future Work

- **FY06**

- Synthesize Phenyl derivatives and asses stability under fuel cell relevant conditions (CSM)
- Optimize Ion-exchange of HPA materials (CSM)
- Synthesize HPA materials (CSM/3M)

- **FY07**

- Milestone 1: Selection of most hydrolytically stable HPA linkage chemistry (CSM)
- Milestone 2: Post- or Pre- ion exchange strategy identified (CSM)
- Milestone 3: Demonstrate Conductivity of  $0.07 \text{ Scm}^{-1}$  at 80% RH and RT (CSM/3M)



# Summary

•Relevance	•Fabricate membranes that will run under hot ( $\leq 120^{\circ}\text{C}$ ) and dry ( $< 1\text{KPa H}_2\text{O}$ ) conditions
•Approach	•Use unique polymeric materials based on hybrid HPA monomers
•Technical Accomplishments	•Project only 1 month old •First proton conducting materials synthesized
•Collaborations	•3M subcontract for 1/3 project effort
•Future Research	•Address HPA immobilization/hybrid HPA stability and synthesis issues with fabricating proton conductors •Synthesis optimized proton conducting systems

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