

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

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DE-PS36-05GO95020  
5/19/06

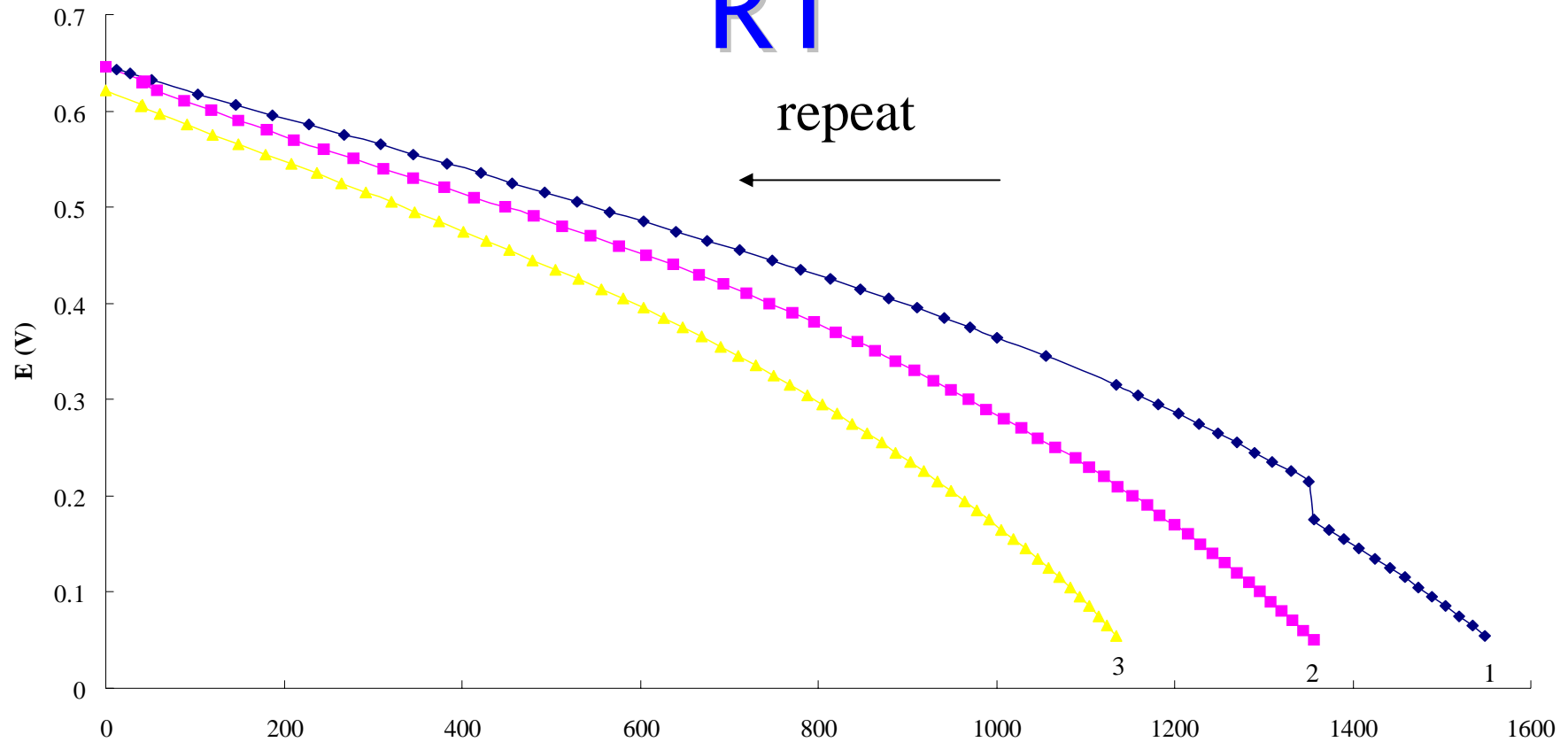
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# Unique Approach

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

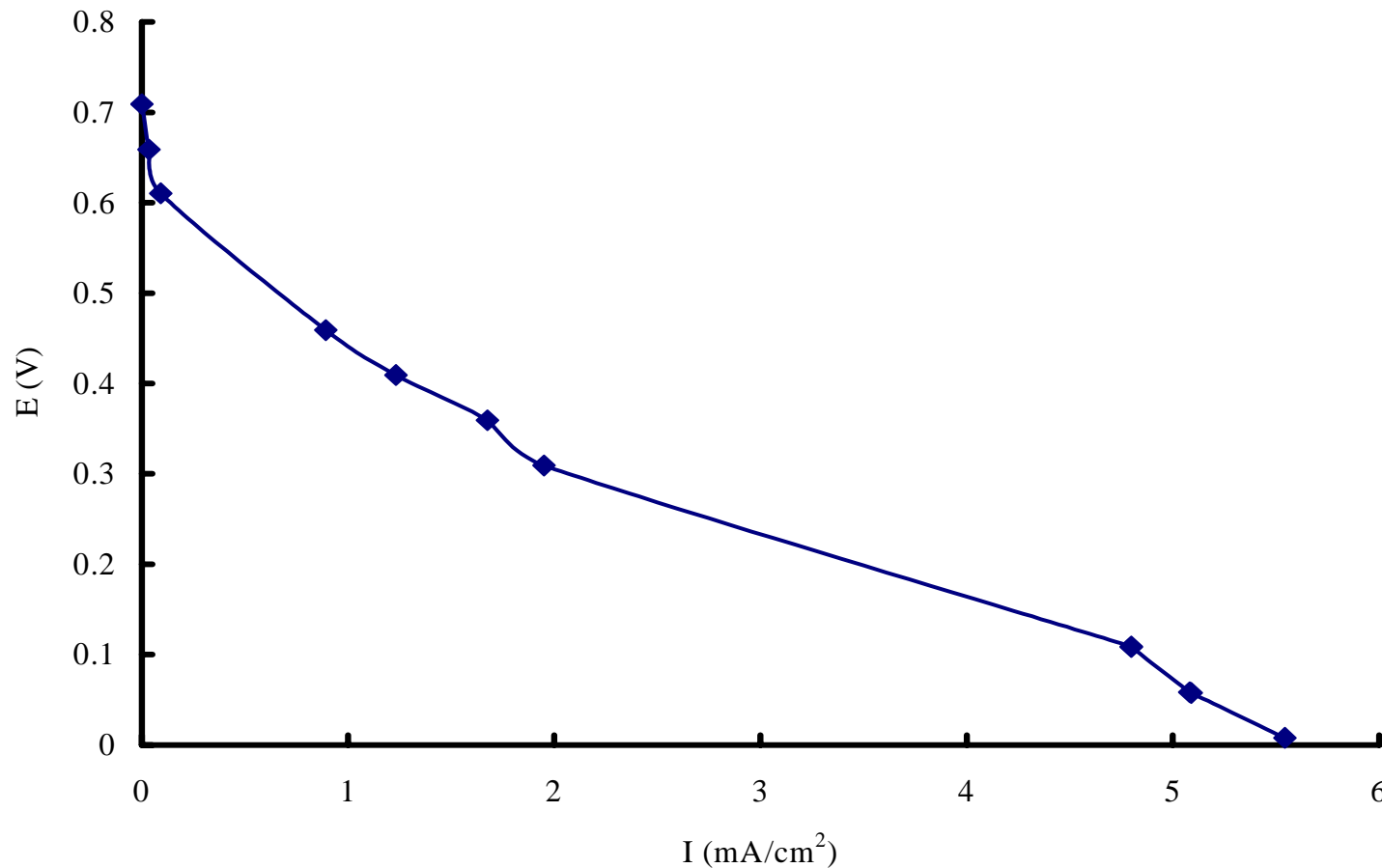
# Excellent $\text{H}^+$ Conductivity at RT



- 12-HPW/PVDF-HFP,  $30 \mu\text{m}$ , **Dry Gases**,  $0.5 \text{ l min}^{-1}$ ,  $\text{H}_2/\text{O}_2$ , **RT**.

Previous results from DE-FC02-0CH11088

# Poor $H^+$ Conductivity $> 100^\circ C$



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

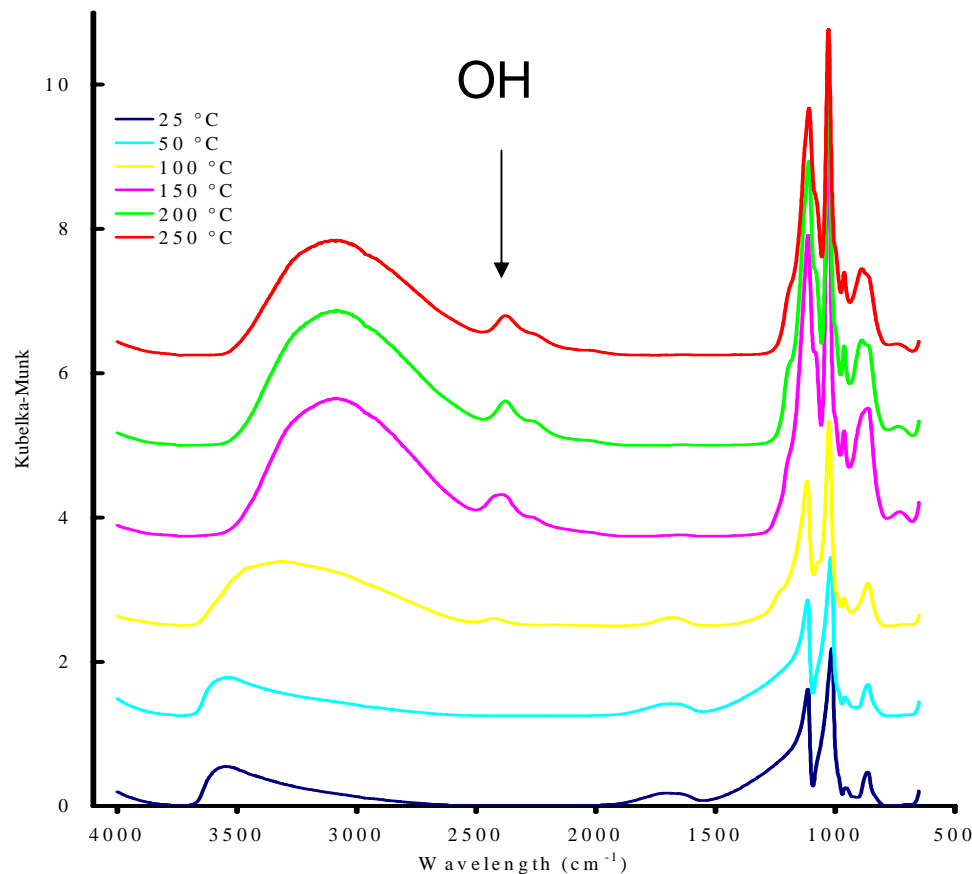
Previous results from DE-FC02-0CH11088

# 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> As2W	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

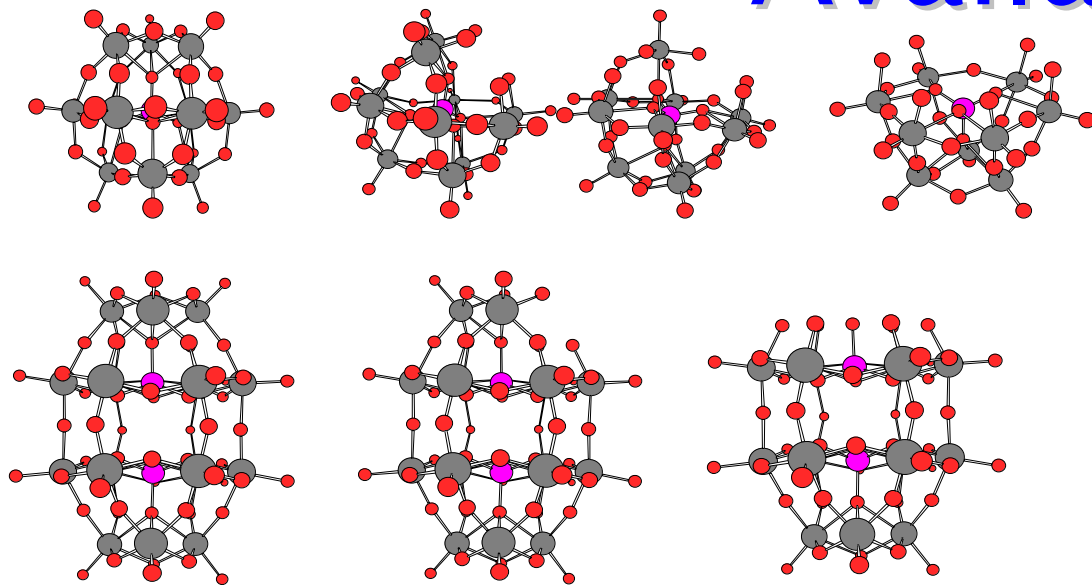
# Low $H^+$ Availability $> 100^\circ C$



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

