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Universal Membrane Classification Scheme

How can DOE maximize the return on High Temperature PEM Membrane Research Efforts?

High Temperature Membrane Working Group

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U.S. Department of Energy

UChicago Argonne LLC

Huge variety of possible polymer membranes to investigate

- Hydrocarbon, Fluorocarbon, Inorganic
- Branched, Comb, hyperbranched, dendritic,,
- With additives
- With structural supports,

What avenues should be pursued?

Which are dead ends?

How do we decide?

Need a way to organize/manage information gathered

- We are developing a membrane classification scheme to help
  - Track different types of approaches
  - Determine which strategies are most fruitful
  - Determine which strategies are dead ends
  - Improve our understanding of proton transport
  - Help maximize our return on HTM research

Contributors

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Categorized based on Strategies for conduction and membrane morphology

- 1) Type of conduction mechanism
  - Aqueous
  - Non-aqueous

- 1) Plan to control the membrane structure/morphology
  - Molecular
  - Additive
  - Micro/nanoengineering

Morphology approaches

- Molecular approach- use molecular design to provide phase separation to improve mechanical properties and proton conduction under low RH conditions by concentrating acid groups in hydrophilic phase

- Additive approach- use of additives to maintain some water at additive surfaces at high temperatures, allowing for conduction at high temperature-low RH,

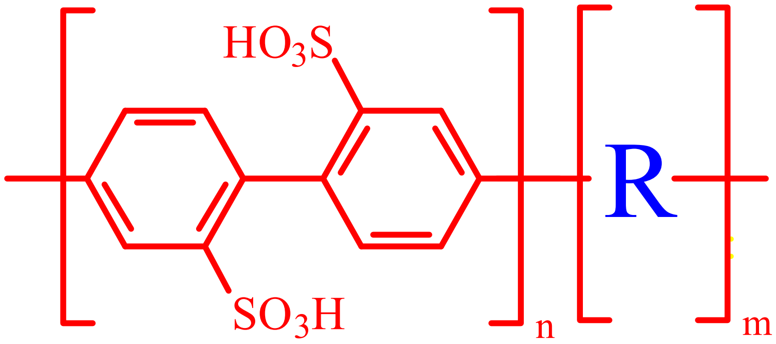
- micro/nano-engineering approach - by designing physical structure of materials (ie pores, or fibers) engineer material to provide domains of high-conductivity, which will operate at high-temp low RH (and be freed of requirements for mechanical integrity/strength) and separate domains of high-strength.

Level 1 Categorization

Conduction Mechanism	**Morphology**	Molecular approach	Additive approach	micro/nano-engineering approach
Aqueous Conduction-				
Non aqueous conduction				

Molecular approach example

Poly (p-Phenylene Sulfonic acids)
Case Western Reserve University Approach: Use Rigid Rod, Liquid Crystalline polymers with the acid groups directly attached to the backbone**.** Use poly(p-phenylene sulfonic acid); it can't hydrolyze. Use bulky comonomers to generate free volume.



R = bulky comonomer

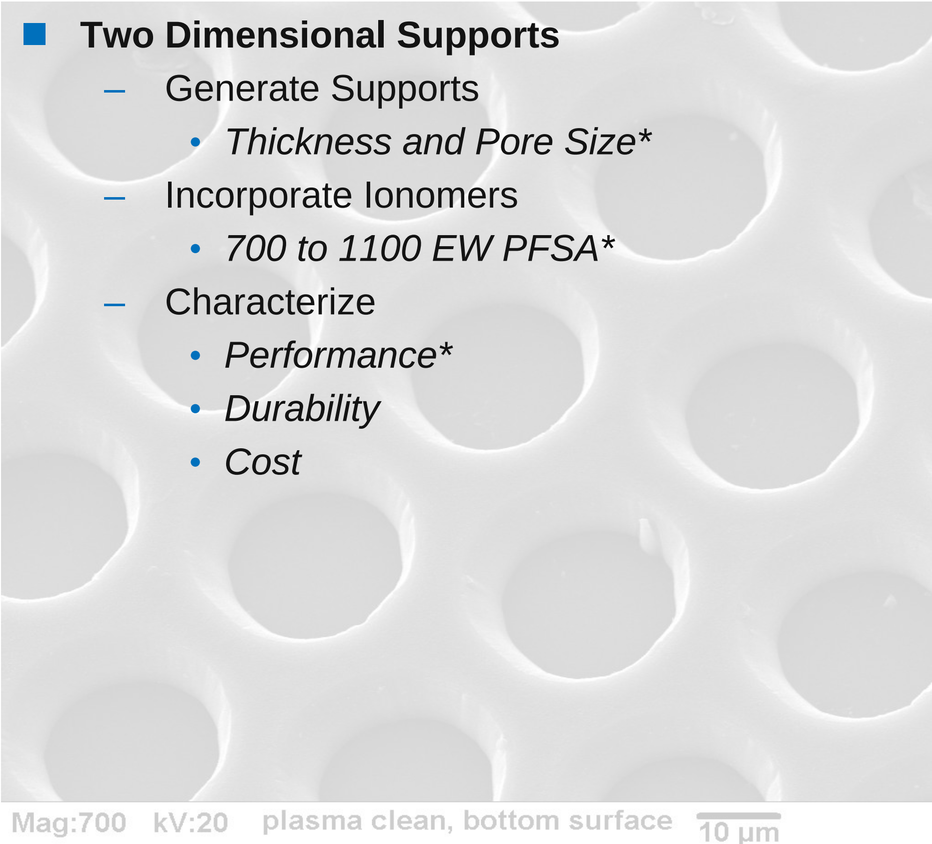
Additive approach example

- **Florida Solar Energy Center Approach**

SPEEK and SPEKK-based PTA Composite Membranes

Poly[perfluoro-sulfonic acid] - Teflon® -phosphotungstic acid (PTA) membranes

Micro/nanoengineering approach example



- **Two Dimensional Supports**
  - Generate Supports
    - *Thickness and Pore Size**
  - Incorporate Ionomers
    - *700 to 1100 EW PFSA**
  - Characterize
    - *Performance**
    - *Durability*
    - *Cost*

Giner Electrochemical Systems Approach: Lower EW of perfluorosulfonic acid ionomers to increase low RH conductivity and support the ionomer with two and three-dimensional non-ionic materials

Level 2

Conduction Mechanism	Morphology	Molecular approach		Additive approach		micro/nanoengineering approach	
Aqueous Conduction-		Structured polymers	Random polymers	Organic additive	Inorganic additive	Structured support	Structured ionomer
Sulfonic acids							
hydrous metal oxides							
Sulfonyl imides							
Non aqueous conduction							
Inorganic oxides							
P-acids							
Heterocyclic bases							
Ionic liquids							

Categorization- Level 3

Conduction Mechanism	Morphology		Molecular approach					Additive approach						micro/nano-engineering approach			
			Random Polymer		*Structured Polymer*			*Organic additive*	*Inorganic additive*					*Structured support*		*Structured ionomer*	
			Mono Polymer	Polymer blends	Graft	Block	Self assembling domains		SiO2	TiO2	ZrHPO4	HPA	Zeolite	Porous	Fibrous	Porous	Fibrous
Aqueous Conduction-																	
	Sulfonic acids																
		Fluorosulfonic acids															
		HC-Sulfonic acids															
	Hydrous Metal oxides																
		SiO2															
		TiO2															
	Sulfonyl imides																
		Fluorosulfonyl imides															
Non aqueous conduction																	
	Inorganic oxides																
		HPAs															
		Metal Oxides															
		ZrHPO4															
	P-acids																
		Phosphoric acids															
		Phosphonic acids															
	heterocyclic bases																
		imidazoles															
		triazoles															
		oxazoles															
	ionic liquids																
		imidazolium salts															
		quaternary ammonium salts															

Level 4

Aqueous Conduction-			
	Sulfonic acids		
		Fluorosulfonic acids	
			aromatic backbone
			non-aromatic backbone
		HC-Sulfonic acids	
			aromatic backbone
			non-aromatic backbone

Level 5

Aqueous Conduction-				
	Sulfonic acids			
		Fluorosulfonic acids		
			aromatic backbone	
				Sulfonated ring
				linear sidechain
				branched sidechain
			non-aromatic backbone	
				linear sidechain
				branched sidechain
		HC-Sulfonic acids		
			aromatic backbone	
				Sulfonated ring
				linear sidechain
				branched sidechain
			non-aromatic backbone	
				linear sidechain
				branched sidechain

Categorization- Level 3

Morphology		Molecular approach					Additive approach						micro/nano-engineering approach			
		Random Polymer		*Structured Polymer*			*Organic additive*	*Inorganic additive*					*Structured support*		*Structured ionomer*	
		Mono Polymer	Polymer blends	Graft	Block	Self assembling domains		SiO2	TiO2	ZrHPO4	HPA	Zeolite	Porous	Fibrous	Porous	Fibrous
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s conduction																
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P-acids																
	Phosphoric acids															
	Phosphonic acids															
heterocyclic bases																
	imidazoles															
	triazoles															
	oxazoles															
ionic liquids																
	imidazolium salts															
	quaternary ammonium salts															

We need your help!

- Identify where your projects belong in the scheme
  - Share as much information as possible!
- Identify testing concerns

Why should you help?

- Input in to possible testing requirements
- Eliminate need to develop individual tests for each membrane
- Identify subgroups for collaboration

Needs/concerns may be different for different categories.

- Micro/nano-engineering approach
  - can be highly nonisotropic
  - need thru plane measurements of conductivity?
- Additive approach
  - migration of additives could be problematic
  - concerns about additive leaching
  - additives may affect peroxy radical formation, decomposition

Effects of Strategy on membrane properties

- How does the membrane strategy affect conductivity?
- Transport properties – water, O_2, H_2 ?
- Chemical durability?
- Mechanical durability?
- Integration with catalyst and catalyst layer?

How does strategy affect testing?

Do we need new/different tests for some of the strategies?

Why should DOE continue to look at multiple approaches?

- Different risks/benefits for the different conduction mechanisms
  - Aqueous mechanisms-less risky for improving conductivity at moderately lower RH and moderate temperatures, more risky at very low RH and higher temperatures. Likely to provide some intermediate benefits
  - Nonaqueous mechanisms – Potential for water-free conduction so conductivity at extremely low RH possible, higher risk

New Targets Proposed for Membranes

Characteristic	Units	2006 status	2005 target	2010 target	2015 target
Maximum operating temperature	°C	80	120	120	120
Area specific resistance at:					
Maximum operating temp and water partial pressures from 40 – 80 kPa	Ohm cm^2	0.03	0.02	0.02	0.02
80°C and water partial pressures from 25 - 45 kPa	Ohm cm^2	0.03	0.02	0.02	0.02
30°C and water partial pressures up to 4 kPa	Ohm cm^2	0.04	0.03	0.03	0.03
-20°C and water partial pressures up to 0.1 kPa	Ohm cm^2	0.3	0.2	0.2	0.2
Oxygen cross-over[a]	mA/cm^2	5	5	2	2
Hydrogen cross-over[a]	mA/cm^2	5	5	2	2
Cost[b]	$\$/m^2$	15[c]	200	20	20
Durability with cycling					
At operating temp ≤80°C	hours	~2000[d]	2000	5000[e]	5000[e]
At operating temp >80°C	hours	(not avail.[f])		2000	5000[e]
Unassisted start from	°C	-20	-30	-40	-40
Thermal cyclability in presence of condensed water		Yes	Yes	Yes	Yes

What we want a membrane to do

Thank you for your attention!