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**Office of
Science**
U.S. DEPARTMENT OF ENERGY

A U.S. Department of Energy laboratory
managed by UChicago Argonne, LLC

HTMWG
May 18, 2009

Welcome!

Agenda

9:00 am	Welcome	Nancy Garland, DOE
9:05 am	Update on Membrane Approaches	J. Kopasz, ANL
9:25 am	Integration of non-traditional membranes into MEAs	Yu Seung Kim, LANL
10:10 am	MEA Testing Issues and Fabrication from team members	Jim Fenton FSEC
10:55 am	OEM perspective	Craig Gittelman GM
11:40	Open discussion	

Membrane Project Presentations at the DOE H₂ Program Annual Merit Review

■ Poster Session—Crystal Gateway
Grand Ballroom 6-9 PM,
FCP 10 K. Mauritz

Tuesday AM Fuel Cell Session
Crystal Gateway Salon IV
8:30 FC 01 J. Fenton UCF/FSEC
9:00 FC02 C.Mittelsteadt Giner
9:30 FC03 S. Lvov Penn State
10:00 FC04 J. Mays U. of Tennessee
10:30 Break
11:00 FC05 J. McGRath Virginia Tech
11:30 FC06 D. Gervasio Arizona State
12:00 FC07 S. Creager, Clemson

Tuesday PM Fuel Cell Session

1:45 FC08 M. Litt Case Western
2:15 FC09 P. Pintauro, Vanderbilt
2:45 FC10 L. Lipp, FCE
3:15 FC11 A. Herring Colorado
School of Mines
3:45- Break
4:15 FC12 J. Goldbach Arkema
4:45 FC13 S. Hamrock, 3M
5:15 FC14 J. Kerr, LBNL

Wednesday AM Fuel Cell Session
Crystal Gateway Salon IV

8:30AM FC 15 S. Das, Kettering



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Membrane Classification Scheme – Update with some results

High Temperature Membrane Working Group

May 14, 2007

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***



A wide variety of approaches for High temperature PEMFC membranes are being pursued

		Molecular Approach			Additive Approach				Micro/nano engineering approach	
		Morphology								
Conduction Mechanism		Other Polymer	Block Copolymer	Rigid Rods	ZrPhosphate	HPA	Zeolite	Other	Structured Support	Structured Ionomer
Aqueous										
	FC-SO ₃ H									
	HC-SO ₃ H									
	Hydrous Metal Oxides									
	sulfonyl imides									
Potential Non Aqueous										
	polyPOMs									
	Phosphates									
	Phosphonic acid									
	Phosphoric acids									
	Heterocyclic bases									
	Ionic liquids									

A wide variety of approaches for High temperature PEMFC membranes are being pursued

	Morphology	Molecular Approach			Additive Approach				Micro/nano engineering approach	
Conduction Mechanism		Other Polymer	Block Copolymer	Rigid Rods	ZrPhosphate	HPA	Zeolite	Other	Structured Support	Structured Ionomer
Aqueous										
	FC-SO3H									
	HC-SO3H									
	Hydrous Metal Oxides									
	sulfonyl imides									
Potential Non Aqueous										
	polyPOMs									
	Phosphates									
	Phosphonic acids									
	Phosphoric acid									
	Heterocyclic bases									
	Ionic liquids									
	DOE/EERE									
	Other									

DOE Membrane Targets

Characteristic	Units	2006 status	2005 target	2010 target	2015 target
Maximum operating temperature	°C	80	120	120	120
Area specific proton transfer 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	2	2
Hydrogen cross-over ^a	mA/cm ²		5	2	2
Cost ^b	\$/m ²	^c		20	20
Durability					
mechanical ^e	5 cycles w<10 secm crossover	200		20,000 ^e	20,000 ^e
chemical ^f	H2 crossover<15 < 2mA/cm ²			500 h	500 h
Minimum Electrical resistance	Ohm cm ²			1000	1000

Targets in numbers we're familiar with

- 0.02 ohm-cm² corresponds to a conductivity of 0.1 S/cm for a 20 micron thick membrane
- $P_{\text{H}_2\text{O}}$ 25-45 kPa at 80°C ~ 50-95%RH
- $P_{\text{H}_2\text{O}}$ 40-80 kPa at 120C ~ 20-40% RH

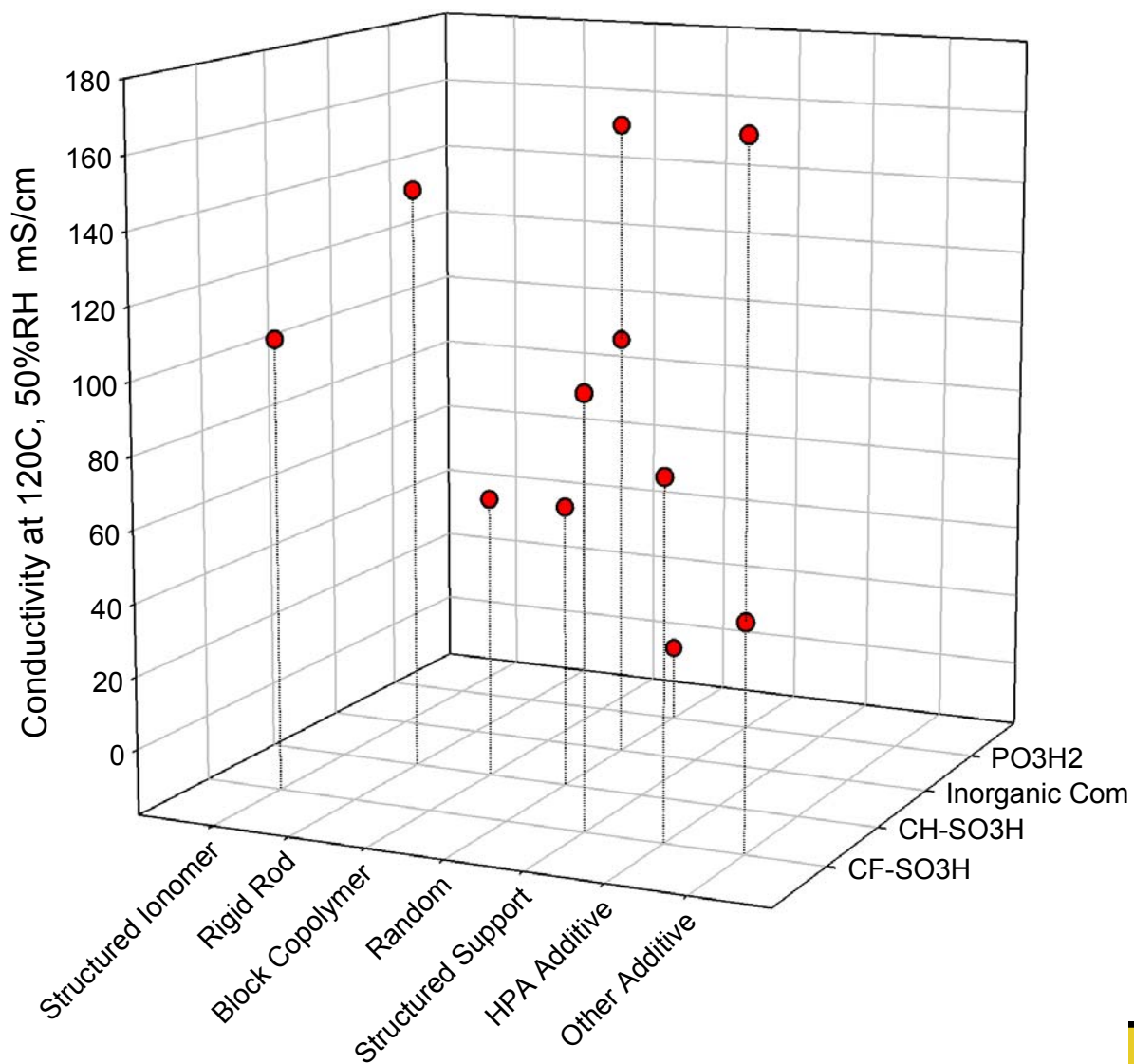
Conductivity Results at 80°C and 80% RH

Aqueous										
	FC-SO ₃ H									
	HC-SO ₃ H									
	Hydrous Metal Oxides									
	sulfonyl imides									
Potential Non Aqueous										
	polyPOMs	*								
	Phosphates									
	Phosphonic acids									
	Phosphoric acid									
	Heterocyclic bases									
	Ionic liquids									
		>200 mS/cm								
		100-200 mS/cm								
		Less than 100 mS/cm								
	*	measured in house and by a second party (not FSEC/BekkTech)								

DOE Projects have achieved high conductivity at 120°C 50% RH with a variety of approaches

	Morphology	Molecular Approach			Additive Approach				Micro/nano engineering approach	
Conduction Mechanism		Other Polymer	Block Copolymer	Rigid Rods	ZrPhosphate	HPA	Zeolite	Other	Structured Support	Structured Ionomer
Aqueous										
	FC-SO ₃ H									
	HC-SO ₃ H									
	Hydrous Metal Oxides									
	sulfonyl imides									
Potential Non Aqueous										
	polyPOMs	*								
	Phosphates	**								
	Phosphonic acids									
	Phosphoric acid									
	Heterocyclic bases									
	Ionic liquids									
		≥ 0.1 S/cm at 120C and 50%RH								
		> 50% of target								
		Less than 50% of target			NRE 212 < 50% of target					
	*	Measured in-house and by a second party								
	**	Measured in-house								

Conductivity Results at 120°C, 50%RH



conductivity at 120°C, 25% RH with a variety of approaches

	Morphology	Molecular Approach			Additive Approach				Micro/nano engineering approach	
Conduction Mechanism		Other Polymer	Block Copolymer	Rigid Rods	ZrPhosphate	HPA	Zeolite	Other	Structured Support	Structured Ionomer
Aqueous										
	FC-SO ₃ H									
	HC-SO ₃ H									
	Hydrous Metal Oxides									
	sulfonyl imides									
Potential Non Aqueous										
	polyPOMs	*								
	Phosphates	**								
	Phosphonic acids									
	Phosphoric acid									
	Heterocyclic bases									
	Ionic liquids									
		met conductivity target of 0.1 S/cm								
		30-50% of target								
		20-30%				NRE 212 < 50% of target				
		Less than 20% of target								
	*	Measured in-house and by a second party								
	**	Measured in-house								

What is the impact on mechanical properties?

	Morphology	Molecular Approach			Additive Approach				Micro/nano engineering approach	
Conduction Mechanism		Other Polymer	Block Copolymer	Rigid Rods	ZrPhosphate	HPA	Zeolite	Other	Structured Support	Structured Ionomer
Aqueous										
	FC-SO ₃ H									
	HC-SO ₃ H									
	Hydrous Metal Oxides									
	sulfonyl imides									
Potential Non Aqueous										
	polyPOMs									
	Phosphates									
	Phosphonic acids									
	Phosphoric acid									
	Heterocyclic bases									
	ionic liquids									
		improvement								
		neutral or unknown								
		decrease								

Mechanical Durability Test

Table 4 Membrane Mechanical Cycle and Metrics (Test using a MEA)		
Cycle	Cycle 0% RH (2 min) to 90°C dewpoint (2 min), single cell 25-50 cm ²	
Total time	Until crossover >2 mA/cm ² or 20,000 cycles	
Temperature	80°C	
Relative Humidity	Cycle from 0% RH (2 min) to 90°C dewpoint (2 min)	
Fuel/Oxidant	Air/Air at 2 SLPM on both sides	
Pressure	Ambient or no back-pressure	
Metric	Frequency	Target
Crossover*	Every 24 h	≤2 mA/cm ²
Shorting resistance	Every 24 h	>1,000 ohm cm ²

* Crossover current per USFCC “Single Cell Test Protocol” Section A3-2, electrochemical hydrogen crossover method

Chemical Durability Test (requires MEA)

Table 3
MEA Chemical Stability and Metrics

Test Condition	Steady state OCV, single cell 25-50 cm ²	
Total time	500 h	
Temperature	90°C	
Relative Humidity	Anode/Cathode 30/30%	
Fuel/Oxidant	Hydrogen/Air at stoics of 10/10 at 0.2 A/cm ² equivalent flow	
Pressure, inlet kPa abs (bara)	Anode 250 (2.5), Cathode 200 (2.0)	
Metric	Frequency	Target
F ⁻ release or equivalent for non-fluorine membranes	At least every 24 h	No target – for monitoring
Hydrogen Crossover (mA/cm ²)*	Every 24 h	≤2 mA/cm ²
OCV	Continuous	≤20% loss in OCV
High-frequency resistance	Every 24 h at 0.2 A/cm ²	No target – for monitoring
Shorting resistance	Every 24 h	>1,000 ohm cm ²

*Crossover current per USFCC “Single Cell Test Protocol” Section A3-2, electrochemical hydrogen crossover method

Room for improvement

- Using a 2D grid to try to simplify a higher-dimensional system
 - Is there a more useful representation?
 - Is there a better way to deal with projects that use multiple approaches?
- Incomplete data set

Need a way to organize/manage information gathered

- 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

Conductivity Results at 120°C, 25%RH

Conductivity 120C, 25%RH

