U.S. DEPARTMENT OF ENERGY

# High Temperature, Low Relative Humidity Membrane Working Group

James M. Fenton
Coordinator for DOE’s HTMWG
University of Central Florida
December 6, 2006

# Working Group Members

## Led by University of Central Florida

Members with Current Funding

- Arizona State University
- Case Western Reserve U (2 projects)
- Clemson University
- Colorado School of Mines
- FuelCell Energy
- General Electric (GE Global Research)
- Giner Electrochemical Systems
- Pennsylvania State University
- U of Central Florida, FL Solar
- University of Tennessee
- Virginia Tech

New Participants

Arkema
3M
Lawrence Berkeley National Laboratory

Since 2000, over 140 organizations have participated in DOE’s Membrane Working Group

# Working Group Goal/Mission/Charge

- Develop materials that conduct protons under the conditions of low relative humidity and temperatures <120 $^{o}$C
- Provide state-of-the-art characterization of membranes
- Suggest studies to advance the high temperature, low humidity membrane field

# Working Group Objectives

Develop and fabricate membranes that meet all targets

- Reduce the cost of raw materials
- *Improve conductivity over entire temp and humidity range*
- Increase mechanical/chemical/thermal stability of ionomer over entire temp and humidity range
- Identify chemical and mechanical degradation mechanisms
- Develop strategies for mitigating degradation in performance and durability

# Working Group

Goal

Develop new polymeric electrolyte composite membranes with a conductivity of 0.1 S/cm with an inlet water vapor partial pressure of 1.5 kPa at 120 $^{o}$C

Budget for DOE Funded Members

- $19 million in federal funding
- $4.75 million in applicant cost sharing

# Three strategies for low $H_2O$ and high conductivity

- **Strategy 1 – phase segregation control** (*polymer & membrane*)

  *polymer* - conducting membranes with separate blocks of hydrophilic and hydrophobic phases within a single molecule to maintain the membrane's mechanical integrity.

  -A-A-A-A-A-B-B-B-B-B-
- *membrane* - composite membranes in which the physical form (geometry) of one of the materials causes the phase segregation (e.g., one polymer acts as a porous support while a second (ion-conducting) polymer is constrained in the pores).

- **Strategy 2 – non-aqueous proton conductors**

  incorporate inorganic oxides, heteropolyacids or ionic liquids, rather than water, to enhance conductivity

- **Strategy 3 – hydrophilic additives**

  create a membrane that will hold some water at the higher temperatures and still allow some bound water to be used for proton conduction.

# HTMWG projects span a variety of chemistries

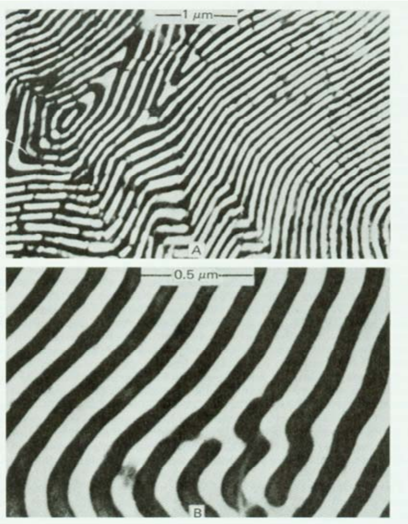
| | Strategy 1-Polymer | Strategy 1-Membrane | Strategy 2 Nonaqueous | Strategy 3-Hydrophilic additive |
|---|---|---|---|---|
| Principal Investigators | | | | |
| 🟥 Arizona State | | | X | |
| 🟥 Case Western I | X | | | |
| 🟥 Case Western II | | X | | X |
| 🟦 Clemson | X | | | |
| 🟩 Colorado School of Mines | | | X | |
| 🟦 Fuel Cell Energy | | X | | X |
| 🟥 GE Global Research | X | | | X |
| 🟦 Giner | | X | | |
| 🟦 Penn State | X | | X | |
| 🟥 University of Tennessee | X | | | |
| 🟥 Virginia Polytechnic | X | | | |
| 🟨 University of Central Florida | X | | | X |
| | | | | |
| Membrane type studied | Fluorocarbon | Hydrocarbon | Inorganic | Fluorocarbon and Hydrocarbon |
| | 🟦 | 🟥 | 🟩 | 🟨 |

# Strategy 1 – phase segregation

engineer the polymer’s molecular architecture

# Strategy 1 - phase segregation control

## Virginia Tech (James E. McGrath)



J.E. McGrath and A. Noshay, "Block Copolymers: Overview and Critical Survey," 520 pages, Academic Press, New York, January 1977, p.91.

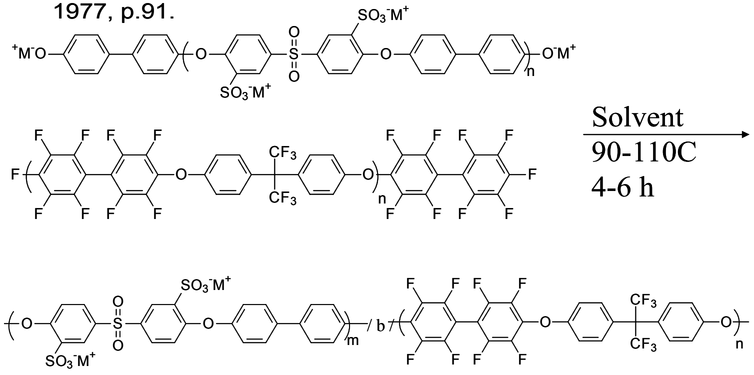


Fig. 7. Synthesis of Multiblock Perfectly Alternating Hydrophilic-Hydrophobic Multiphase Copolymers.

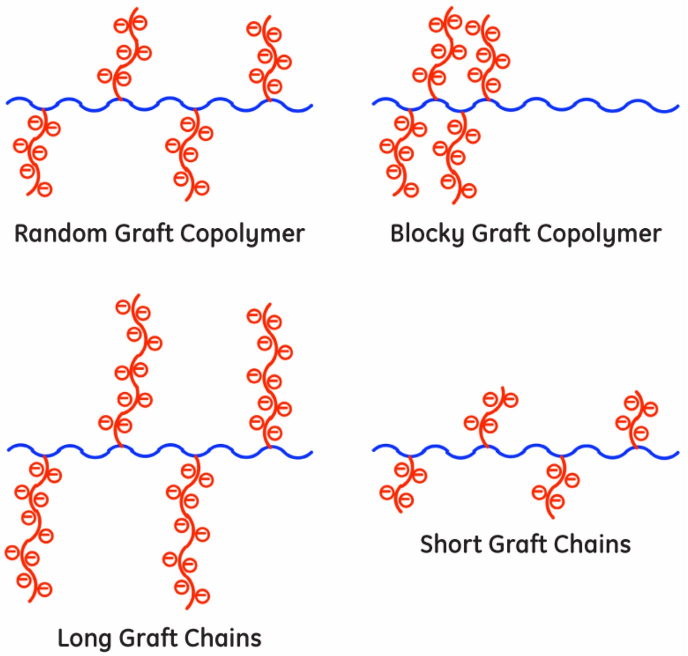
- Block copolymers can generate a co-continuous morphology with potentially an easier path for proton conduction
- Multiblock co-polymers are prepared using a hydrophilic aromatic oligomer and a perfluorinated hydrophobic material.

# Strategy 1 - phase segregation control

GE Global Research (Joyce Hung)

Controlled graft copolymer architecture

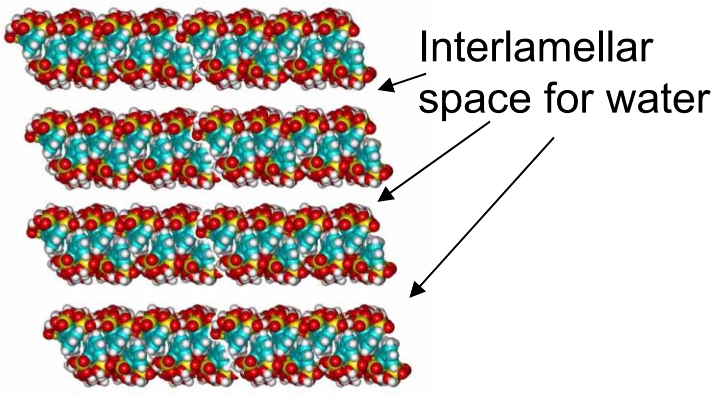
- Macromonomer graft chains with controlled length and low polydispersity will be made, and then copolymerized onto a polymer backbone
- Graft chains into the polymer backbone randomly or in blocks
- Establish structure-property correlations that will aid in subsequent polymer design and optimization

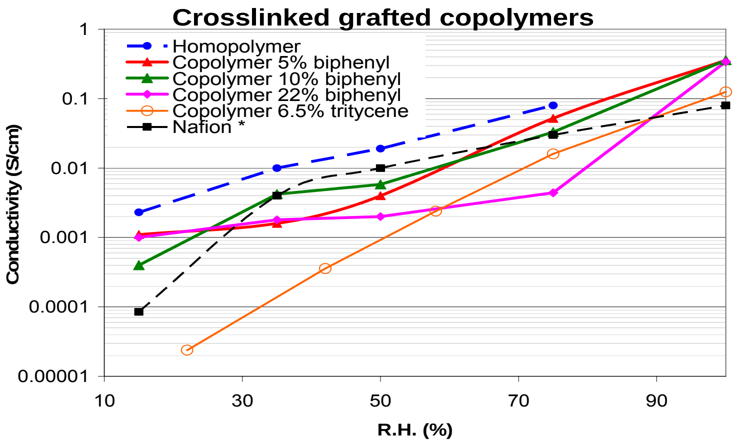


# Strategy 1 - phase segregation control

## Case Western Reserve U (Morton Litt)

- **Rigid aromatic structures with sulfonic groups attached.**
- **The bulky co-monomer units force the chains apart creating permanent pores with $SO_3H$ groups.**
- The nanoscale channels hold water very strongly, generating high conductivity even at low relative humidities.





CASE
CASE WESTERN RESERVE UNIVERSITY

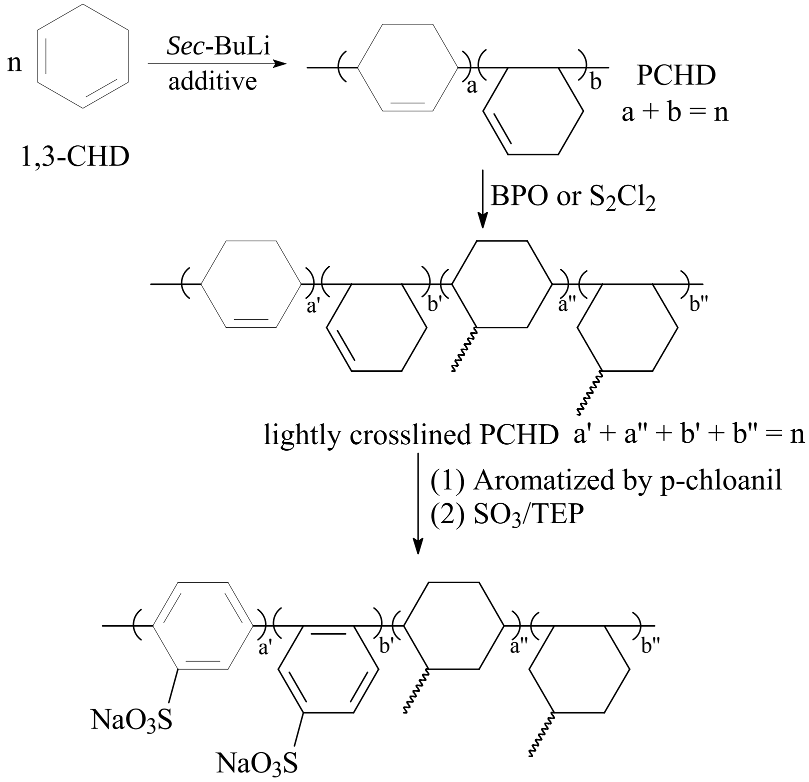
# Strategy 1 – phase segregation

engineer the membrane's structure by using separate polymers

# Strategy 1 - phase segregation control

## U Tennessee (Jimmy Mays)

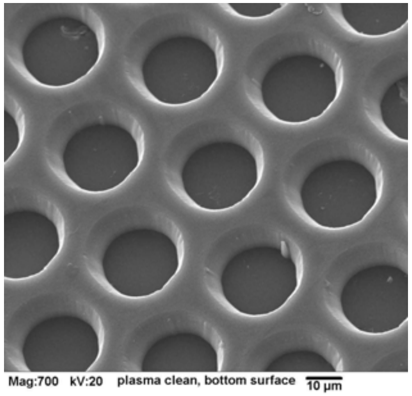
- A range of homopolymer and copolymer materials incorporating poly(cyclohexadiene) (PCHD) based membranes
- Optimization of molecular parameters including extent of aromatization and degree of sulfonation
- Sol-gel chemistry used to grow hydrophilic nanophase within the membrane

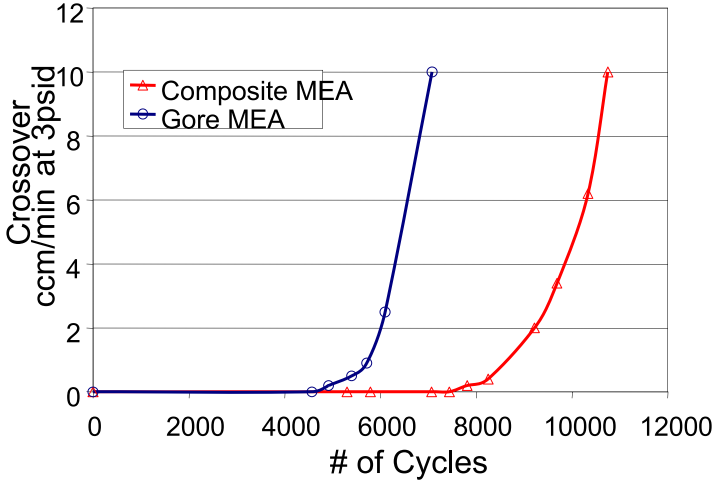


# Strategy 1 - phase segregation control

## Giner Electrochemical Systems (Cortney Mittelsteadt)

- Incorporate low EW ionomers in a high strength polymeric matrix
  - 2D matrix eliminates x-y swelling and improve freeze-thaw and wet-dry cycling durability, while improving conductivity
  - 3D matrix eliminates z-plane swelling
  - 3D matrices of polyimide and polysulfone with appropriate pore sizes (~100μm) are readily made and commercially available
  - Polymerization of PFSA in the matrix to fill pores





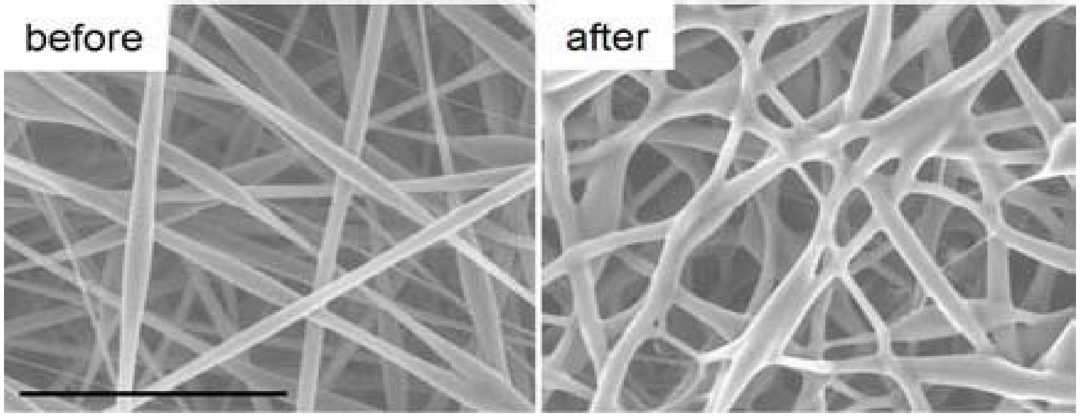
- Gas crossover during 2min/2min wet/dry cycling at 80°C

Giner, Incorporated and Giner Electrochemical Systems, LLC

# Strategy 1 - phase segregation control

## Case Western Reserve U (Peter Pintauro)

- 3-D network of nm-diameter proton-conducting polymer fibers embedded in an inert (uncharged) water/gas impermeable polymer matrix
- High density of fibers and low IEC ensure proton conductivity
- Inert matrix controls swelling and provides mechanical strength

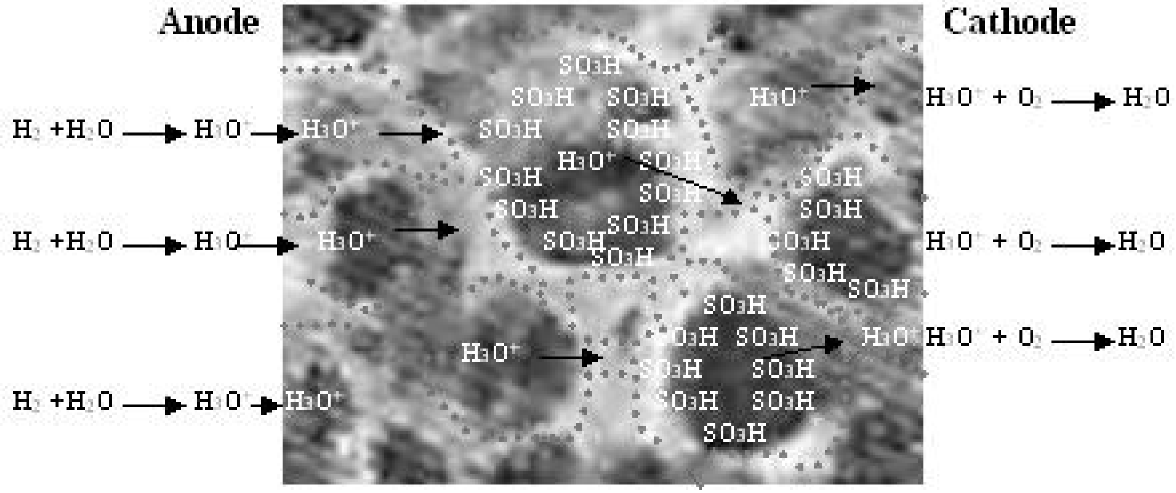


Solvent vapor welding of electrospun nanofibers.
Polycyclooctene exposed to THF vapor. Scale bar is 100 μm.

# Strategy 1 - phase segregation control

## Fuel Cell Energy (Ludwig Lipp)

- Composite membrane: support polymer for greater stability at 120°C and lower EW ionomer for higher σ
- Ionomer forms "clusters" for proton transport that are immobilized in the porous support polymer for low RH operation
- Nano-sized additives will further improve the water retention and proton conductivity.



++++++++ : **Back bone of ionomer covalently bonded onto the frame network**

# Strategy 2- non-aqueous proton conductors

proton conduction does not rely on water

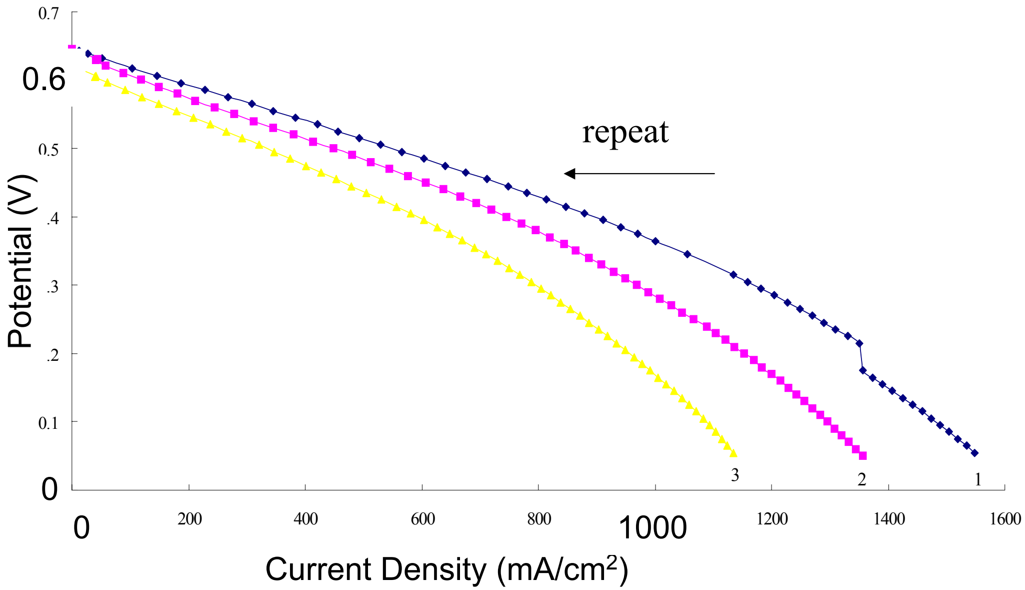
- Proton "hopping"
- Non-evaporating "vehicle" for $H^+$ transport

# Strategy 2 – non-aqueous proton conductors

Colorado School of Mines (Andrew M. Herring)

**Immobilized Heteropolyacids**

- Heteropolyacids (HPAs) are a large class of inorganic proton conductors with high σ at RT.
- New hybrid organic/inorganic materials with HPAs immobilized by covalently attaching to an organic moiety e.g., a polymer.



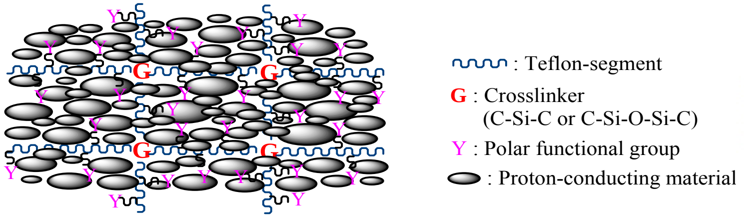
Polarization curve for a membrane composed of 1:1 by weight $H_3PW_{12}O_{40}$/PVDF-HFP, 30 μm, dry $H_2/O_2$ at 0.5 L min$^{-1}$, RT, Pt-ELAT electrodes, no Nafion®.

# Strategy 2 – non-aqueous proton conductors

Pennsylvania State U (Serguei Lvov)

- Hydrophilic inorganic particulate materials with structural or surface proton conductivity as a major component (up to 80 wt.%) for fuel cell membranes
- Inorganic particles linked to end-chain functionalized Teflon-based polymer by inorganic functional groups
- A number of new inorganic materials will be carefully selected and synthesized based on their transport and surface properties.

Proposed structure of the inorganic/polymer composite

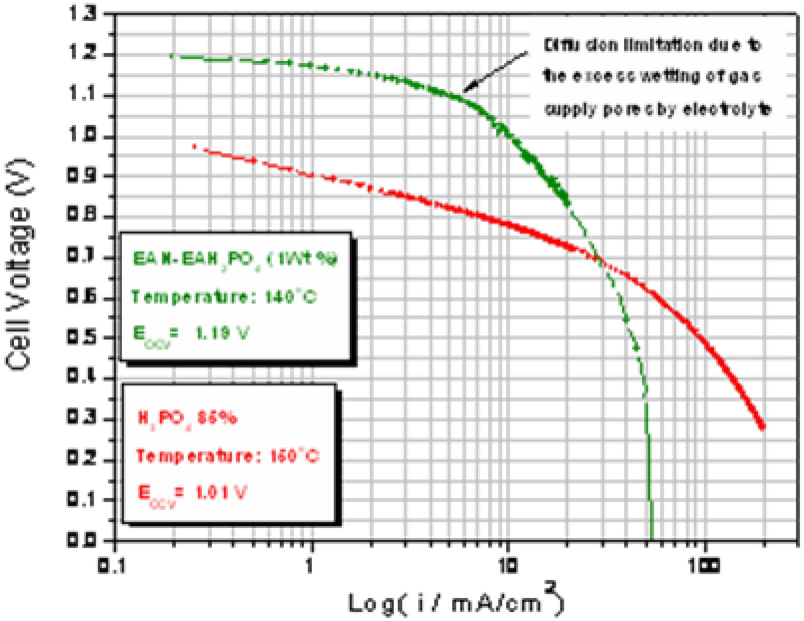


# Strategy 2 – non-aqueous proton conductors

Arizona State U (D. Gervasio)

- Bi-phasic porous matrices filled with:
  - water-immiscible ionic liquids immobilized by capillary forces
  - ionic liquids sorbed in polymers

- Non-leachable PEMs consisting of novel polymers and polymer blends with no plasticizers that allow all acid and base moieties to be immobilized by covalent and electrostatic binding



86% $H_3PO_4$ EAN-EA$H_2PO_4$

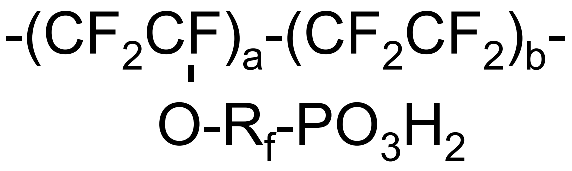
I-V curve for neat EAN-EA-$H_2PO_4$ and 85% $H_3PO_4$ in Teflon cell. Flow $H_2$ = 40 sccm, $O_2$ = 30 sccm, E-TEK electrode area = 0.5 cm$^2$ Pt loading = 0.5 mg/cm$^2$.

# Strategy 2 – non-aqueous proton conductors

Clemson U (Stephen Creager )

- Fluoroalkylphosphonic acids stronger than phosphoric and alkylphosphonic acids
  - readily self-dissociates to allow both vehicular (hydronium ion) and hopping (Grotthus) proton transport yielding high σ under wet & dry conditions
- Weak adsorption on Pt to diminish electrocatalyst poisoning and promote higher oxygen reduction activity
- Higher oxygen solubility to promote high oxygen reduction activity
- Robust and should have very long life in a PEMFC power system operating under high-temperature, low-humidity conditions

Structure of proposed phosphonic acid trifluorovinylether/tetrafluoroethylene copolymer ionomers



$$-(CF_2\underset{\displaystyle O-R_f-PO_3H_2}{CF})_a-(CF_2CF_2)_b-$$

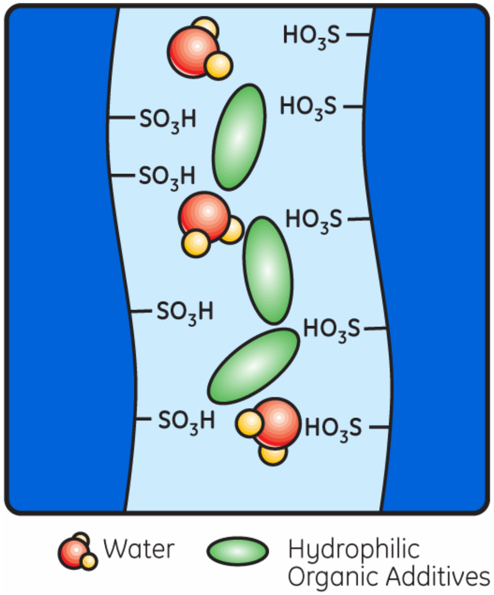
# Strategy 3 - hydrophilic additives

- hydrophilic additives can provide some water at high T, low RH
- additives provide structural or surface proton conduction
- can be added to proton-conducting ionomer (Nafion®, etc.)

# Strategy 3 – hydrophilic additives

## GE Global Research (Joyce Hung)

- Additives based on organic materials known to be extremely hygroscopic
- Hydrolytically stable organic additives hydrogen bond and possess several exchangeable acidic protons
- To avoid leaching from membrane, organic additives can also be oligomerized or directly incorporated into polymer matrix.
- The additives can crosslink the membranes to improve mechanical properties



# Strategy 3 – hydrophilic additives

## U of Central Florida (James M. Fenton)

- Poly[perfluorosulfonic acid] - Teflon® -phosphotungstic acid membrane fabrication
  - Low eq. wt. PFSA
  - Smaller particle phosphotungstic acid
  - Increase stabilization of membrane
- Sulfonated poly(ether ketone ketone), SPEKK, or sulfonated poly(ether ether ketone), SPEEK, membranes
  - Smaller particle phosphotungstic acid added
- Conductivity measurements
  - Apparatus and protocols defined and verified
  - Commercially available membrane samples and baseline NTPA tested

FLORIDA SOLAR ENERGY CENTER®
A Research Institute of the University of Central Florida

# UCF focus

- New polymeric electrolyte membranes
- Standardized Characterization Methodologies
  - Conductivity f(RH, T, Phys. Props.) {Through & In Plane; As MEA}
  - Characterize mechanical, mass transport and surface properties of membranes
  - Predict durability of membranes and MEAs fabricated from other eleven HT Low RH Membrane Programs
- Provide team members with standardized tests and methodologies (Short Courses)
- Organize HTMWG bi-annual meetings

# HTMWG First Year Activities

- Ability to measure conductivity established
- Calculations performed to determine appropriate RH levels for testing
- 2-D potential distribution modeling performed to study electrode geometry for through-plane conductivity testing

# HTMWG First Year Activities cont.

- Cell chamber for through-plane conductivity measurements developed
- Document developed to explain in-plane conductivity testing
- Two meetings of the HTMW group organized and held

# Milestones

**3Q Yr 2 milestone**

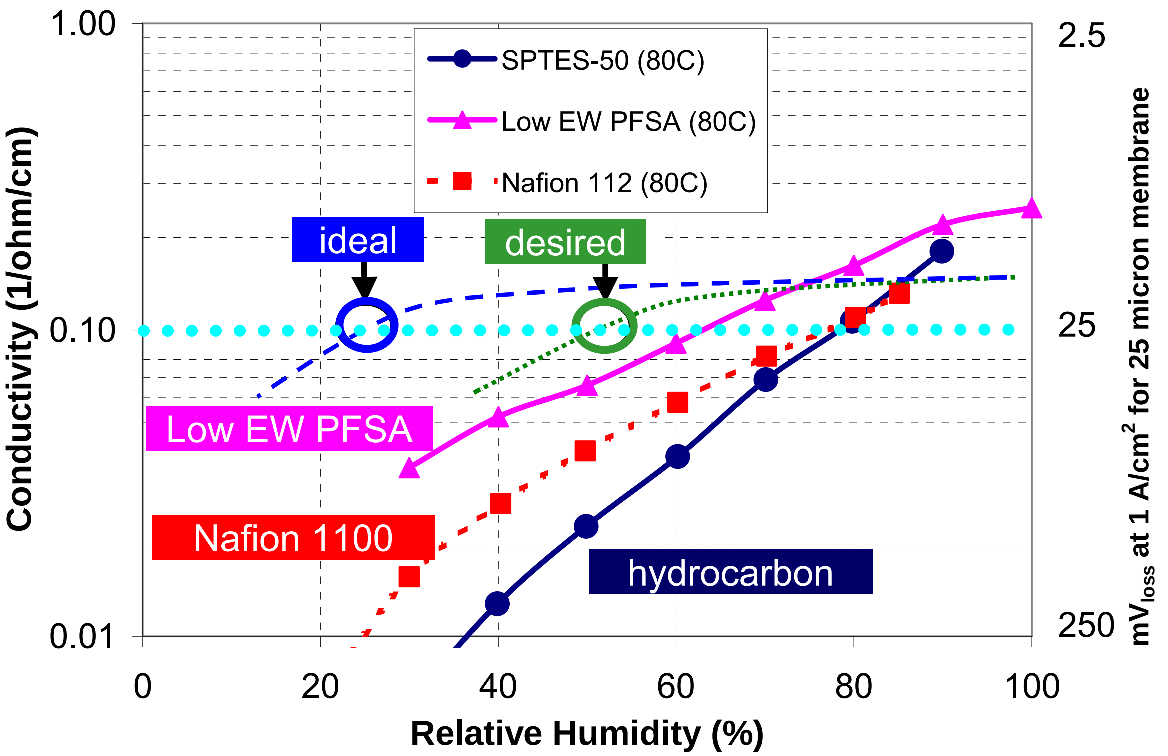
- Conductivity = 0.07 S/cm at 80% relative humidity (RH) at room temp using alternate material

**3Q Yr 3 Go/No Go (2010 Target)**

- ~~Conductivity > 0.1 S/cm at 50% relative humidity and 120~~ $^{o}$C
- Conductivity >0.1 S/cm with an inlet water vapor partial pressure of 1.5 kPa at 120 $^{o}$C

# Membrane Conductivity

**σ Target: 0.1 S/cm**



Low EW PFSA meets target at >65% RH
Nafion® 1100 meets target >80% RH
Low EW PFSAs meet near term performance targets.

desired σ for 95 °C initial fuel cell commercialization
0.1 S/cm at ~ 50% RH

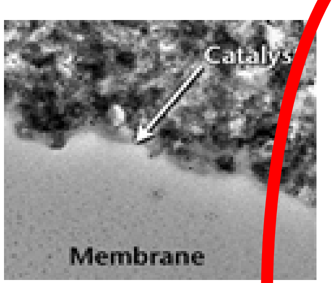
ideal σ for 120 °C long term targets
0.1 S/cm at ~ 25% RH

**3Q Yr 3 Go/No Go**
σ >0.1 S/cm inlet water vapor partial pressure 1.5 kPa at 120 °C (membrane sees ~ 25% RH)

Taken from slide 8 “Membrane Performance and Durability Overview for Automotive Fuel Cell Applications,” by Tom Greszler (GM) September 2006 HTMWG Meeting

# US DOE Strategy

- **Primary focus is on fuel cells for transportation applications**
- **R&D is focused on components rather than systems**



**Membranes**

**Electrodes**

**Membrane Electrode Assemblies**

**Gas Diffusion Layers**

**Bipolar Plates**

**Seals**

**Balance-of-plant Components**

**Innovative Concepts**

**Analysis, Characterization and Benchmarking**

**Not Just Conductivity of Membrane but MEA and GDL**

*Taken From:* *Valri Lightner DOE – Fuel Cell R&D Presentation 2006 DOE Hydrogen Program Merit Review and Peer Evaluation Meeting May 16, 2006*

# Test Protocols are Needed

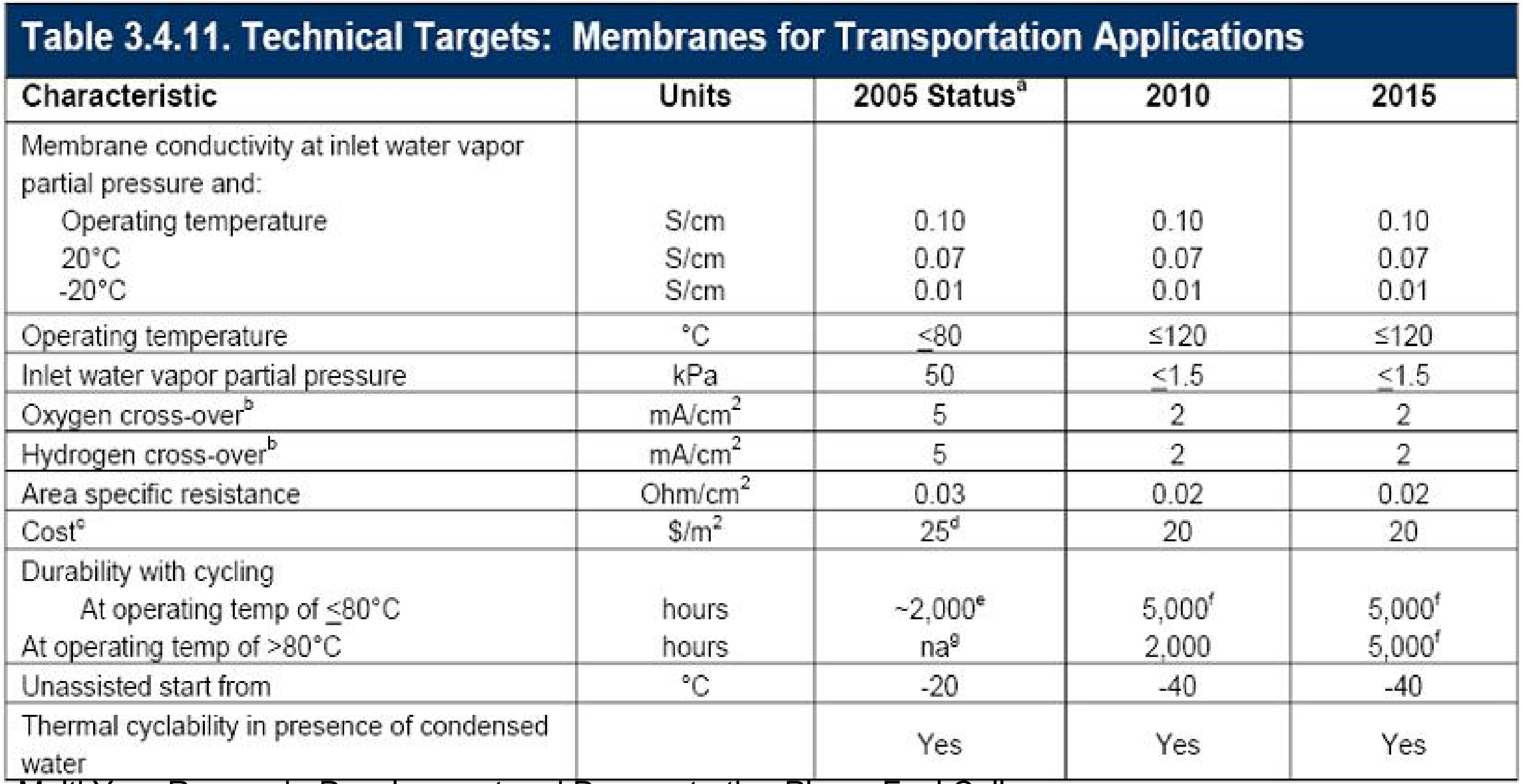


**Table 3.4.11. Technical Targets: Membranes for Transportation Applications**

| Characteristic | Units | 2005 Status[a] | 2010 | 2015 |
|---|---|---|---|---|
| Membrane conductivity at inlet water vapor partial pressure and: | | | | |
| Operating temperature | S/cm | 0.10 | 0.10 | 0.10 |
| 20°C | S/cm | 0.07 | 0.07 | 0.07 |
| -20°C | S/cm | 0.01 | 0.01 | 0.01 |
| Operating temperature | °C | ≤80 | ≤120 | ≤120 |
| Inlet water vapor partial pressure | kPa | 50 | ≤1.5 | ≤1.5 |
| Oxygen cross-over[b] | $mA/cm^2$ | 5 | 2 | 2 |
| Hydrogen cross-over[b] | $mA/cm^2$ | 5 | 2 | 2 |
| Area specific resistance | $Ohm/cm^2$ | 0.03 | 0.02 | 0.02 |
| Cost[c] | $\$/m^2$ | 25[d] | 20 | 20 |
| Durability with cycling | | | | |
| At operating temp of ≤80°C | hours | ~2,000[e] | 5,000[f] | 5,000[f] |
| At operating temp of >80°C | hours | na[g] | 2,000 | 5,000[f] |
| Unassisted start from | °C | -20 | -40 | -40 |
| Thermal cyclability in presence of condensed water | | Yes | Yes | Yes |

Multi Year Research, Development and Demonstration Plan – Fuel Cells

http://www1.eere.energy.gov/hydrogenandfuelcells/mypp/pdfs/fuel_cells.pdf

Conductivity Protocols

UCF FSEC with subcontractors

- BekkTech LLC – In–plane conductivity protocols
- Scribner Associates – Through-plane conductivity protocols

# Test Protocols are Needed

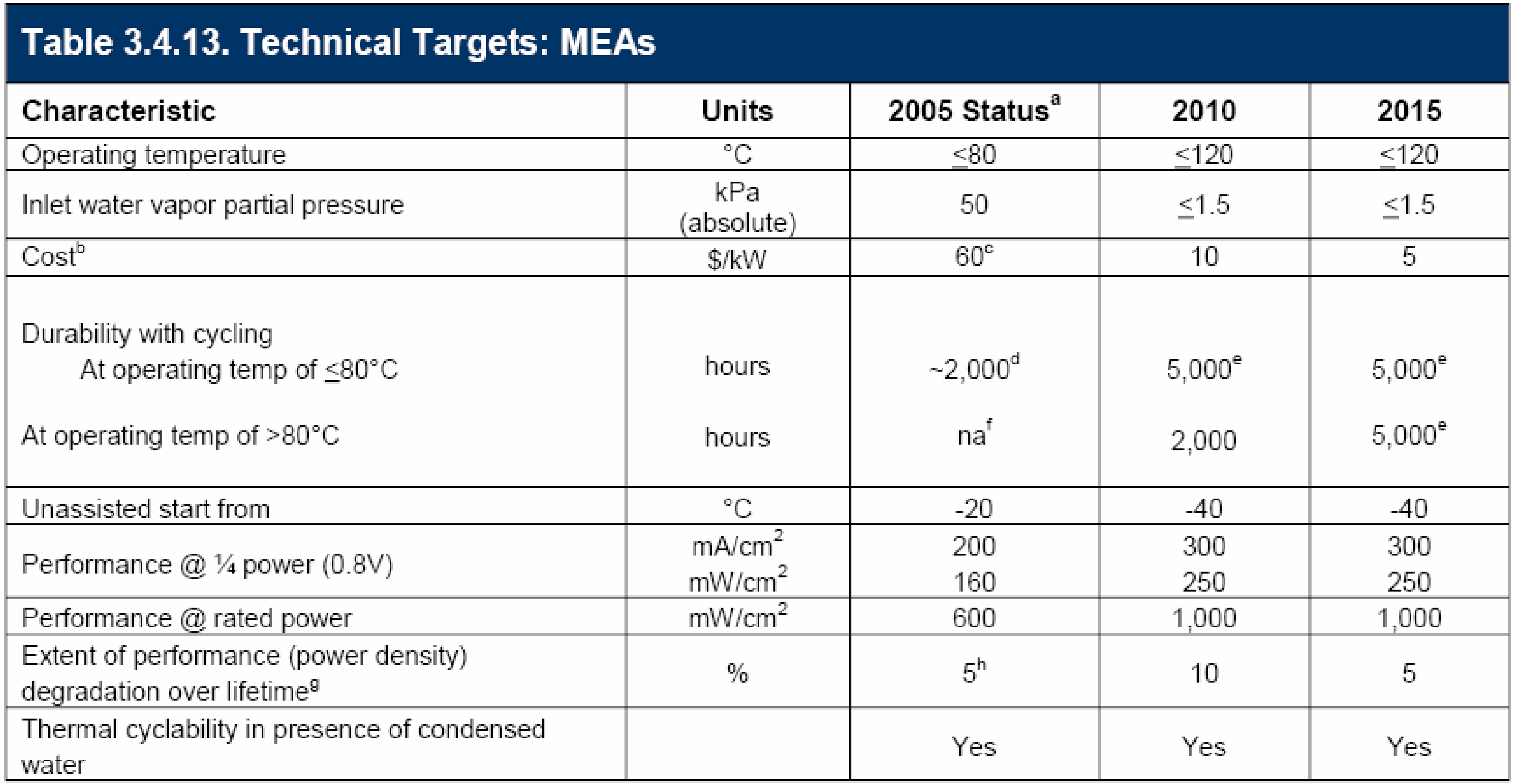


**Table 3.4.13. Technical Targets: MEAs**

| Characteristic | Units | 2005 Status[a] | 2010 | 2015 |
|---|---|---|---|---|
| Operating temperature | °C | ≤80 | ≤120 | ≤120 |
| Inlet water vapor partial pressure | kPa (absolute) | 50 | ≤1.5 | ≤1.5 |
| Cost[b] | $/kW | 60[c] | 10 | 5 |
| Durability with cycling | | | | |
| At operating temp of ≤80°C | hours | ~2,000[d] | 5,000[e] | 5,000[e] |
| At operating temp of >80°C | hours | na[f] | 2,000 | 5,000[e] |
| Unassisted start from | °C | -20 | -40 | -40 |
| Performance @ ¼ power (0.8V) | mA/cm$^2$<br>mW/cm$^2$ | 200<br>160 | 300<br>250 | 300<br>250 |
| Performance @ rated power | mW/cm$^2$ | 600 | 1,000 | 1,000 |
| Extent of performance (power density) degradation over lifetime[g] | % | 5[h] | 10 | 5 |
| Thermal cyclability in presence of condensed water | | Yes | Yes | Yes |

Multi Year Research, Development and Demonstration Plan — Fuel Cells

http://www1.eere.energy.gov/hydrogenandfuelcells/mypp/pdfs/fuel_cells.pdf

# Membrane and MEA Durability – Test Protocols

| MEA Chemical Cycle and Metrics | | |
|---|---|---|
| **Cycle** | **Steady state OCV, single cell 50cm$^2$** | |
| **Total time** | 200 h | |
| **Temperature** | 90ºC | |
| **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** | **Cut-off Value** |
| **F release or equivalent for non-fluorine membranes** | At least every 24 h | |
| **Hydrogen Crossover (mA/cm$^2$)** | Every 24 h | |
| **OCV** | Continuous | 20% loss in OCV |
| **High-frequency resistance** | Every 25 h at 0.2 A/cm$^2$ | |

| Membrane Mechanical Cycle and Metrics | | |
|---|---|---|
| **Cycle** | **Cycle RH 0 (2m) to 90ºC dewpoint (2m), single cell 50cm$^2$** | |
| **Total time** | Until crossover >10 sccm at 20 kPa $\Delta$P or 20,000 cycles | |
| **Temperature** | 80ºC | |
| **Relative Humidity** | Cycle from 0% RH (2 m) to 90ºC dewpoint (2 m) | |
| **Fuel/Oxidant** | Air/Air at 2 slpm on both sides | |
| **Pressure** | 0 kPa gauge | |
| | | |
| **Metric** | **Frequency** | **Cut-off Value** |
| **Crossover** | Every 24 h | >10 sccm at 20 kPa deltaP |

Taken from **DOE CELL COMPONENT DURABILITY TEST PROTOCOL FOR 2010 Status PEM FUEL CELLS** (Electrocatalysts, Supports, Membranes, and Membrane Electrode Assemblies) **Draft November 2006**

# Membrane Questions

- Conductivity = 0.1 S/cm, RH = ?
  - In-plane, through-plane
  - *In-situ, ex-situ*
- What is effective RH that membrane sees?
  - RH inlet stack ≠? RH inlet membrane
  - Inlet RH, Exit RH, Average RH, Log Mean RH?
- Voltage drop across the membrane
  - Current density, membrane thickness, area specific resistance?
- Membrane thickness?
  - Voltage drop
  - Cross over
- 120 $^{o}$C for 20 - 100 %RH;  What other temperatures?

# Questions for discussion

The material used to produce a membrane must also provide electrolyte for the electrodes. This means that additional properties are needed.

- How will the electrolyte affect the rate of the electrode reactions? (The cathode kinetics for Nafion® are strongly dependent on relative humidity.)
- Will the electrodes need a new electrolyte material?
- How well will that material interact with the membrane?
- Will the electrode fabrication procedures need to be modified to obtain optimum electrode performance? (This is a certainty.)
- Will the stability of the cathode, in terms of Pt and carbon corrosion, be affected?

# Questions for discussion

- Will platinum recrystallization be affected?
- Will the electrolyte be electrochemically stable? (Sulfuric acid is reduced at the anode.)

In addition, cell design may require some modification.

- Will structural (swelling, liquid component) characteristics require new cell design?
- Will cell fabrication procedure need modification because of membrane properties?

# Questions for discussion

- Are special GDL properties required?
- Does MEA need to be pre-conditioned before cell assembly?
- Does cell assembly procedure have additional requirements?
- Are there special cell start up requirements?
- Are there special conditioning requirements?
- Are there special operating limits?
- Are there special shut down limits?