High Temperature, Low Relative Humidity Membrane Working Group

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Coordinator for DOE’s HTMWG
University of Central Florida
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This presentation does not contain any proprietary or confidential information
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 °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 °C

Budget for DOE Funded Members
• $19 million in federal funding
• $4.75 million in applicant cost sharing
Three strategies for low H$_2$O 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-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

<table>
<thead>
<tr>
<th>Principal Investigators</th>
<th>Strategy 1-Polymer</th>
<th>Strategy 1-Membrane</th>
<th>Strategy 2 Nonaqueous</th>
<th>Strategy 3-Hydrophilic additive</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arizona State</td>
<td></td>
<td></td>
<td></td>
<td>X</td>
</tr>
<tr>
<td>Case Western I</td>
<td>X</td>
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<tr>
<td>Case Western II</td>
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<td>Clemson</td>
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<td>Colorado School of Mines</td>
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<tr>
<td>Fuel Cell Energy</td>
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<td>GE Global Research</td>
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<td>Giner</td>
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<tr>
<td>Penn State</td>
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<tr>
<td>Virginia Polytechnic</td>
<td></td>
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<tr>
<td>University of Central Florida</td>
<td></td>
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<td></td>
<td>X</td>
</tr>
</tbody>
</table>

- 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)

- 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.


Fig. 7. Synthesis of Multiblock Perfectly Alternating Hydrophilic-Hydrophobic Multiphase Copolymers.
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
• Rigid aromatic structures with sulfonic groups attached.

• The bulky co-monomer units force the chains apart creating permanent pores with SO$_3$H groups.

• The nanoscale channels hold water very strongly, generating high conductivity even at low relative humidities.
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
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 $\sigma$

- 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.

![Diagram of fuel cell reaction](image-url)

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
Immobilized Heteropolyacids

- Heteropolyacids (HPAs) are a large class of inorganic proton conductors with high $\sigma$ 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 $\mu$m, 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

▲ ▲ ▲ : Teflon-segment
G : Crosslinker
(C-Si-C or C-Si-O-Si-C)
Y : Polar functional group
• : Proton-conducting material
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% H₃PO₄   EAN-EAH₂PO₄

I-V curve for neat EAN-EA-H₂PO₄ and 85% H₃PO₄ in Teflon cell. Flow H₂ = 40 sccm, O₂ = 30 sccm, E-TEK electrode area = 0.5 cm² Pt loading = 0.5 mg/cm².
• **Fluoroalkylphosphonic acids** stronger than phosphoric and alkylphosphonic acids
  
  – readily self-dissociates to allow both vehicular (hydronium ion) and hopping (Grotthus) proton transport yielding high $\sigma$ 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

\[ -(\text{CF}_2\text{CF})_a-(\text{CF}_2\text{CF}_2)_b- \text{O-R}_f\text{-PO}_3\text{H}_2 \]
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
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 °C
– Conductivity >0.1 S/cm with an inlet water vapor partial pressure of 1.5 kPa at 120 °C
Membrane Conductivity

\( \sigma \) 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 \( \sigma \) for 95 °C initial fuel cell commercialization
0.1 S/cm at ~ 50% RH

ideal \( \sigma \) for 120 °C long term targets
0.1 S/cm at ~ 25% RH

3Q Yr 3 Go/No Go
\( \sigma >0.1 \) 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
Bipolar Plates

Electrodes
Seals

Membrane Electrode Assemblies
Balance-of-plant Components

Gas Diffusion Layers
Innovative Concepts

Analysis, Characterization and Benchmarking
Not Just Conductivity of Membrane but MEA and GDL

Test Protocols are Needed

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

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Units</th>
<th>2005 Status</th>
<th>2010</th>
<th>2015</th>
</tr>
</thead>
<tbody>
<tr>
<td>Membrane conductivity at inlet water vapor partial pressure and:</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Operating temperature</td>
<td>S/cm</td>
<td>0.10</td>
<td>0.10</td>
<td>0.10</td>
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<tr>
<td>20°C</td>
<td>S/cm</td>
<td>0.07</td>
<td>0.07</td>
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<tr>
<td>-20°C</td>
<td>S/cm</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
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<tr>
<td>Operating temperature</td>
<td>°C</td>
<td>≤80</td>
<td>≤120</td>
<td>≤120</td>
</tr>
<tr>
<td>Inlet water vapor partial pressure</td>
<td>kPa</td>
<td>50</td>
<td>≤1.5</td>
<td>≤1.5</td>
</tr>
<tr>
<td>Oxygen cross-over</td>
<td>mA/cm²</td>
<td>5</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Hydrogen cross-over</td>
<td>mA/cm²</td>
<td>5</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Area specific resistance</td>
<td>Ohm/cm²</td>
<td>0.03</td>
<td>0.02</td>
<td>0.02</td>
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<tr>
<td>Cost</td>
<td>$/m²</td>
<td>25⁹</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>Durability with cycling</td>
<td>hours</td>
<td>~2,000⁹</td>
<td>5,000⁷</td>
<td>5,000⁷</td>
</tr>
<tr>
<td>At operating temp of ≤80°C</td>
<td>hours</td>
<td>na⁸</td>
<td>2,000</td>
<td>5,000⁷</td>
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<tr>
<td>At operating temp of &gt;80°C</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Unassisted start from</td>
<td>°C</td>
<td>-20</td>
<td>-40</td>
<td>-40</td>
</tr>
<tr>
<td>Thermal cyclability in presence of condensed water</td>
<td></td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Metric</th>
<th>Frequency</th>
<th>Cut-off Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>F release or equivalent for non-fluorine membranes</td>
<td>At least every 24 h</td>
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</tr>
<tr>
<td>Hydrogen Crossover (mA/cm²)</td>
<td>Every 24 h</td>
<td></td>
</tr>
<tr>
<td>OCV</td>
<td>Continuous</td>
<td>20% loss in OCV</td>
</tr>
<tr>
<td>High-frequency resistance</td>
<td>Every 25 h at 0.2 A/cm²</td>
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## Membrane Mechanical Cycle and Metrics

<table>
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<th>Metric</th>
<th>Frequency</th>
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</thead>
<tbody>
<tr>
<td>Crossover</td>
<td>Every 24 h</td>
<td>&gt;10 sccm at 20 kPa deltaP</td>
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</tbody>
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> Taken from DOE CELL COMPONENT DURABILITY TEST PROTOCOL FOR 2010 Status PEM FUEL CELLS (Electrocatalysts, Supports, Membranes, and Membrane Electrode Assemblies) Draft November 2006

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<table>
<thead>
<tr>
<th>Cycle</th>
<th>Cycle RH 0 (2m) to 90°C dewpoint (2m), single cell 50cm²</th>
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</thead>
<tbody>
<tr>
<td>Total time</td>
<td>Until crossover &gt;10 sccm at 20 kPa ΔP or 20,000 cycles</td>
</tr>
<tr>
<td>Temperature</td>
<td>80°C</td>
</tr>
<tr>
<td>Relative Humidity</td>
<td>Cycle from 0% RH (2 m) to 90°C dewpoint (2 m)</td>
</tr>
<tr>
<td>Fuel/Oxidant</td>
<td>Air/Air at 2 slpm on both sides</td>
</tr>
<tr>
<td>Pressure</td>
<td>0 kPa gauge</td>
</tr>
</tbody>
</table>

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<table>
<thead>
<tr>
<th>Metric</th>
<th>Frequency</th>
<th>Cut-off Value</th>
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</tbody>
</table>
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 °C for 20 - 100 %RH; What other temperatures?
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?