Membranes and MEA's for Dry, Hot Operating Conditions

DE-FG36-07GO17006

Steve Hamrock

3M Company

May 17, 2007

Project ID #
FCP 32

Partners

- Case Western Reserve Univ.
  - *Professors T. Zawodzinski and D. Schiraldi*
- Colorado School of Mines
  - *Professor A. Herring*
- University of Detroit Mercy
  - *Professor S. Schlick*
- University of Alabama Huntsville
  - *Professor S. Paddison*

Overview

Timeline

- Project start 4/1/07
- Project end 3/31/11
- 0.9 % complete

Budget

- Total Project funding $11.4 million
  - $8.9 million - DOE
  - $2.5 million - contractor cost share (22%)
- Received in FY07: $ 0

Barriers

A. Durability

C. Performance

DOE Technical Targets *(2010)*

- Durability w/cycling: > 5000 hrs,
- Conductivity 0.1 S/cm @120ºC
- Cost: $20/m^2

3M Contacts

- PI Steven Hamrock
  Phone (651) 733-4254
- FAX (651) 737-5335

- Contract Administrator Steven L. Kays
- Phone (651) 737-0853
- FAX (651) 736-4777

Technical Targets

Material Targets

Membrane Conductivity	Temperature	%RH
0.1 S/cm	120ºC	≤ 25-50*
0.07 S/cm	20ºC	≥ 100
0.01 S/cm	-20ºC	≥ 100

O_2 Crossover	**2 mA/cm²**
H_2 Crossover	**2 mA/cm²**
Cost	**$20/m²**

MEA/Stack Targets

- **Lifetime** **>5000 hours**

(in DOE specified accelerated durability test)

- **Membrane area specific resistance** **≤0.02 ohms-cm²**

(fuel cell w/ ≤ 1.5 kPa inlet water vapor pressure)

- **Membrane must be stable to liquid water**

*Estimate for testing %RH which gives membrane humidification level equal to stack running w/ ≤ 1.5 kPa inlet water vapor pressure.

Project Objectives

- The objective of this project is to develop a new proton exchange membrane with higher proton conductivity under hotter, dryer conditions and improved durability compared to state of the art membranes today.

    - The target for this membrane is to operate and be stable under high and low humidification conditions and at temperatures ranging from -20ºC to 120ºC in order to meet DOE HFCIT 2010 commercialization targets for automotive fuel cells.

    - Membranes developed in this project may also have improved durability and performance characteristics making them useful in stationary fuel cell applications.

Project Approach -Scope of Work

- New polymers, fluoropolymers, non-fluorinated polymers and composite/hybrid systems with increased proton conductivity and improved chemical and mechanical stability
- Developing new membrane additives for both increased conductivity and improved stability/durability under these dry conditions
- Experimental and theoretical studies of factors controlling proton transport both within the membrane and at the catalyst interface, mechanisms of polymer degradation and membrane durability in an MEA
- Focus on materials which can be made using processes which are scalable to commercial volumes using cost effective methods
- Integration of new membranes into MEA's
- Testing performance and durability. Tests will be performed in conductivity cells, single fuel cells and short stacks using realistic automotive testing conditions and protocols.

Project Approach

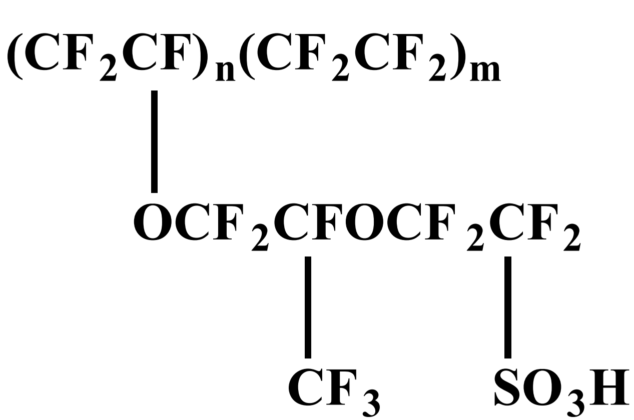
- **Task 1** Membrane Subcomponent Development
  - **Subtask** Materials Development (Polymer development, conductivity enhancing additive development and stabilizing additive development)
  - **Subtask** Studies for Downselection (conductivity, membrane physical properties, failure and degradation mechanisms)
  - **Subtask** Membrane Fabrication Process Development
- **Task 2** MEA Fabrication and Testing (MEA fabrication, performance and durability test method development, initial performance testing, accelerated durability testing)
- **Task 3** Final MEA Design and Integration (membrane fabrication, catalyst interface optimization and integration, final MEA optimization and fabrication)
- **Task 4** Final Fuel Cell Testing (stack fabrication and testing, durability and performance testing)
- **Task 5** Project Management, Deliverables and Reporting (building and testing short stack, reporting)

Relevant Prior Work

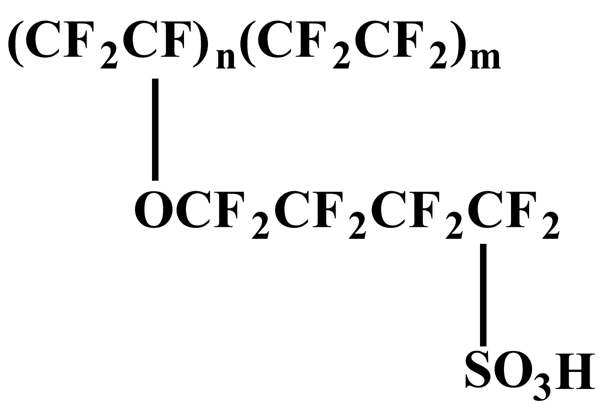
The new 3M ionomer has a slightly shorter side chain than standard PFSA membrane ionomer without the pendant -CF3 group:

Gives:
- higher degree of crystallinity,
- higher modulus,
- higher Tg at a given equivalent weight (EW).

Allows:
- lower EW membranes with higher conductivity,
- improved mechanical properties and durability under hot, dry conditions.



Standard PFSA



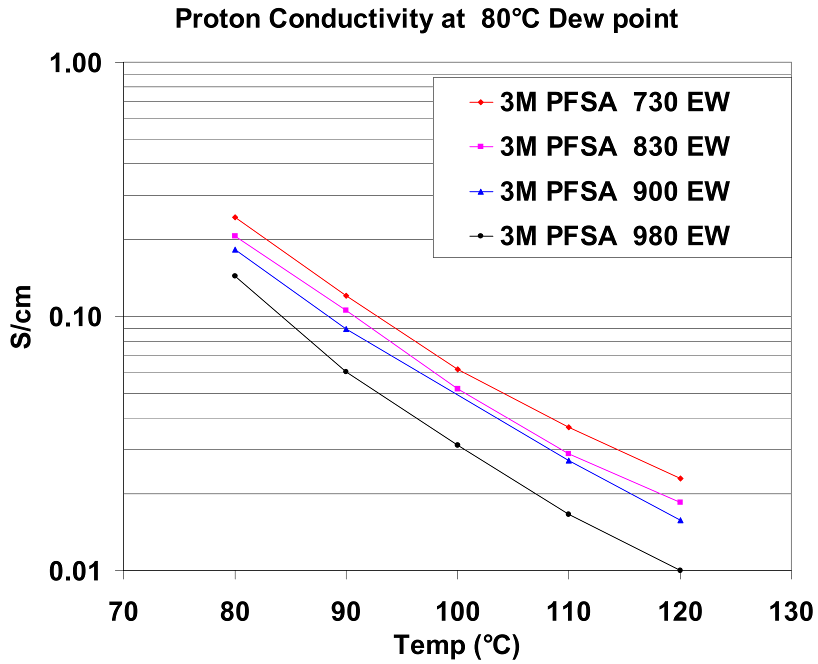
New 3M Polymer

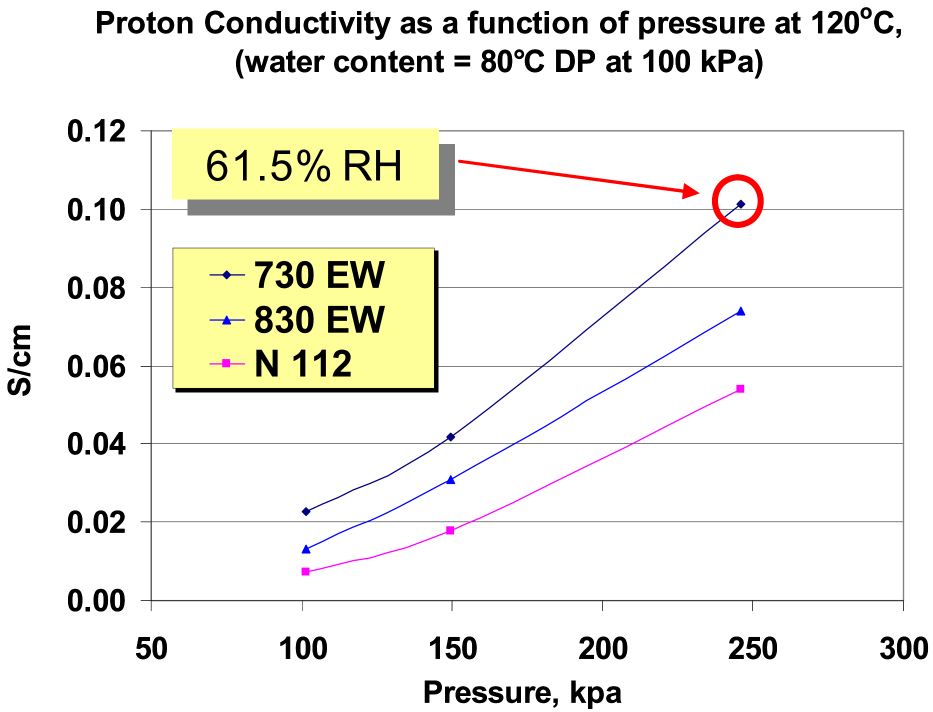
Relevant Prior Work

3M membranes with multiple EW's have been evaluated.

- Conductivity vs. temperature for EW ionomers in 730 – 980 EW range.
- The lowest EW ionomer tested so far, 730 EW, shows a conductivity of about 25 mS/cm at 120° C, 80° C DP, ambient pressure, very dry conditions.

AC 4-point probe measurement.

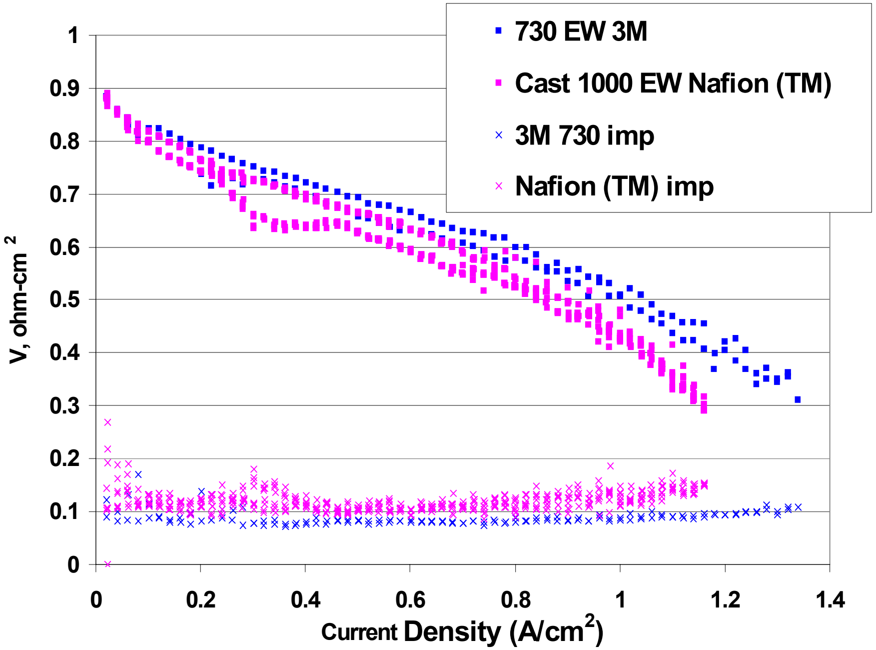




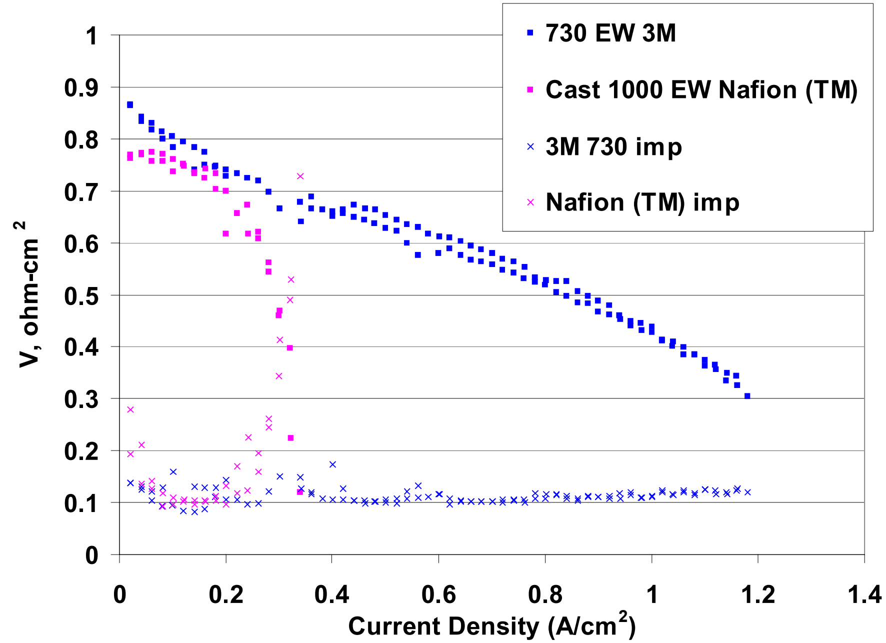
Relevant Prior Work

- *3M/DOE Cooperative Agreement No. DE-FC36-02AL67621*
  - *"Advanced MEA's for Enhanced Operating Conditions"*

Fuel cell performance is higher for lower EW membranes under hot, dry conditions.



730 EW ionomer, 120˚ C, 250 kPa, **20 % RH**



730 EW ionomer, 120˚ C, 250 kPa, **10 % RH**

3M

Relevant Prior Work

- 3M membrane with additives shows >15 X increase in lifetime (4 cell average ~ 4100 hrs) vs. 50 micron extruded standard PFSA membrane under load cycling tests at 90ºC, w/60ºC dewpoints.
- Accelerated durability testing was stopped periodically and sample was tested at 70˚C 100%RH.

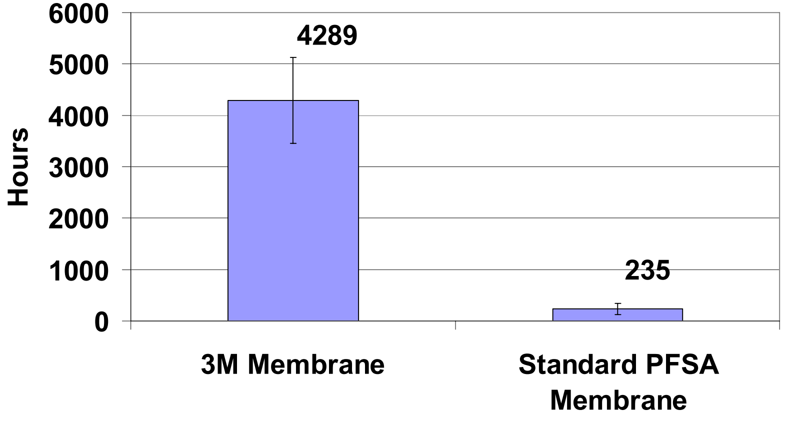
- No increase in crossover or shorting was detected before 3500 hours.

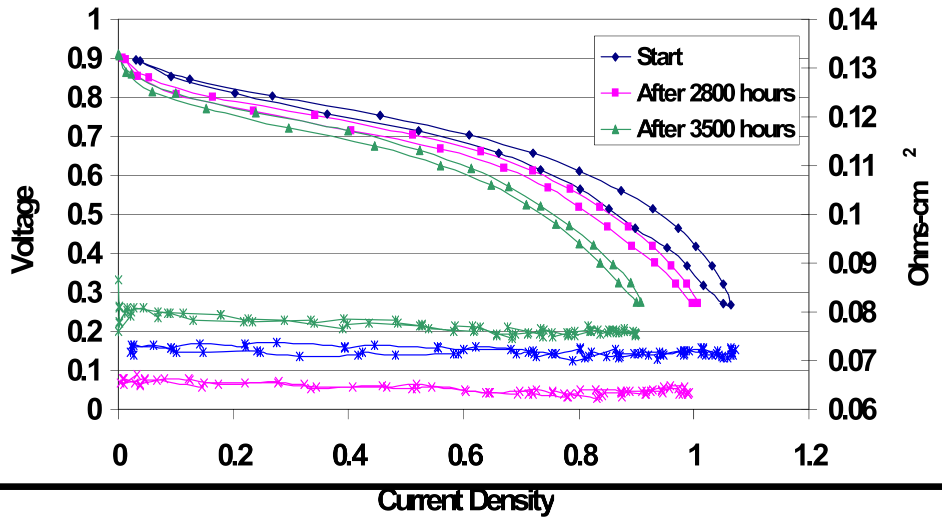
-IR change of PEM was minimal.

- Most performance loss due to loss of catalyst surface area or mass transport.

Pt surface area ratio (M^2/M^2)	H_2 Crossover (mA/cm^2)	Short Resistance ($OHM\text{-}CM^2$)	Testing Time
178.3	4.2	>500	0
102.9	3.4	>500	2800
78.1	17.0	>500	3500

Performance and lifetime during accelerated durability testing

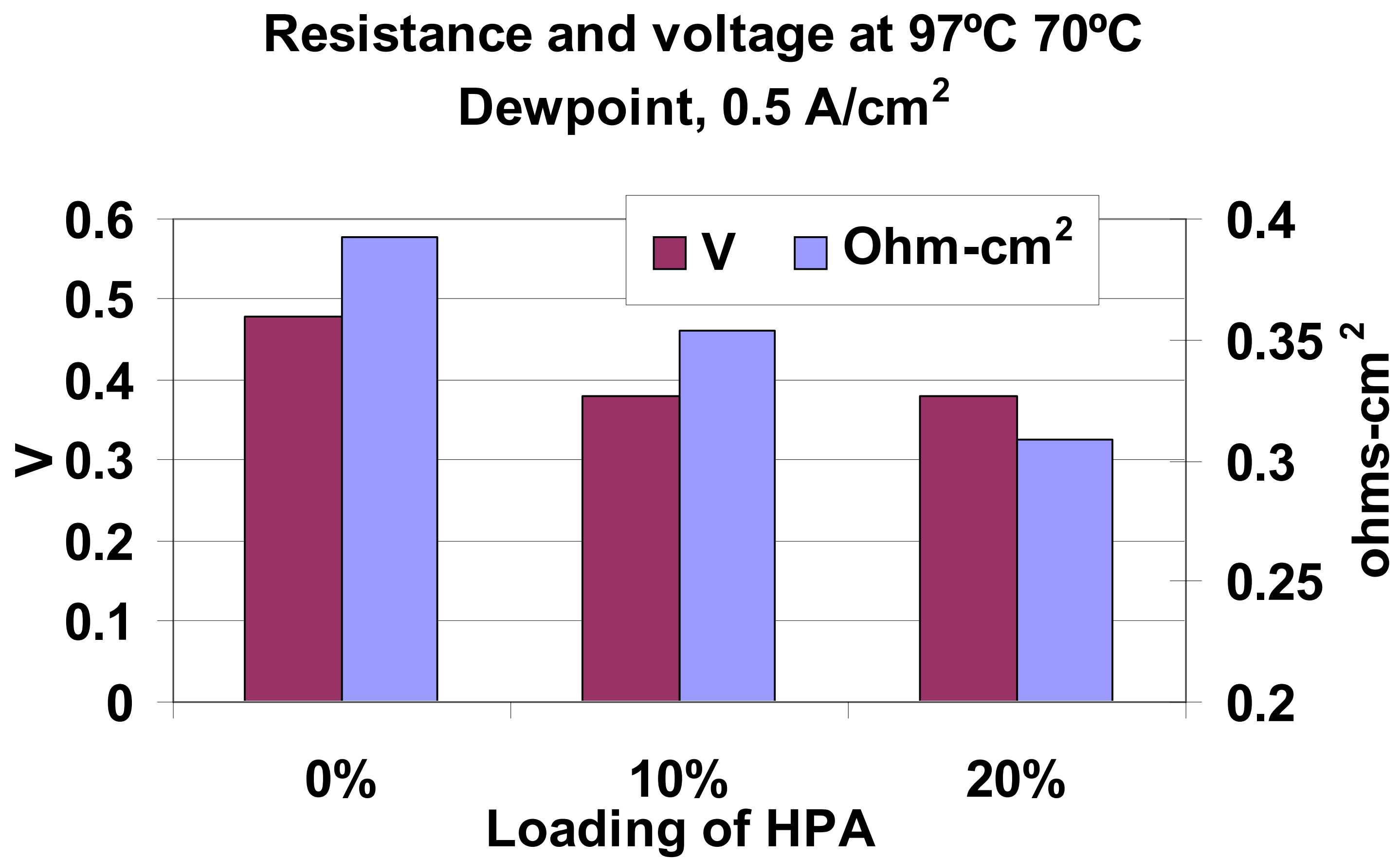




3M

Relevant Prior Work

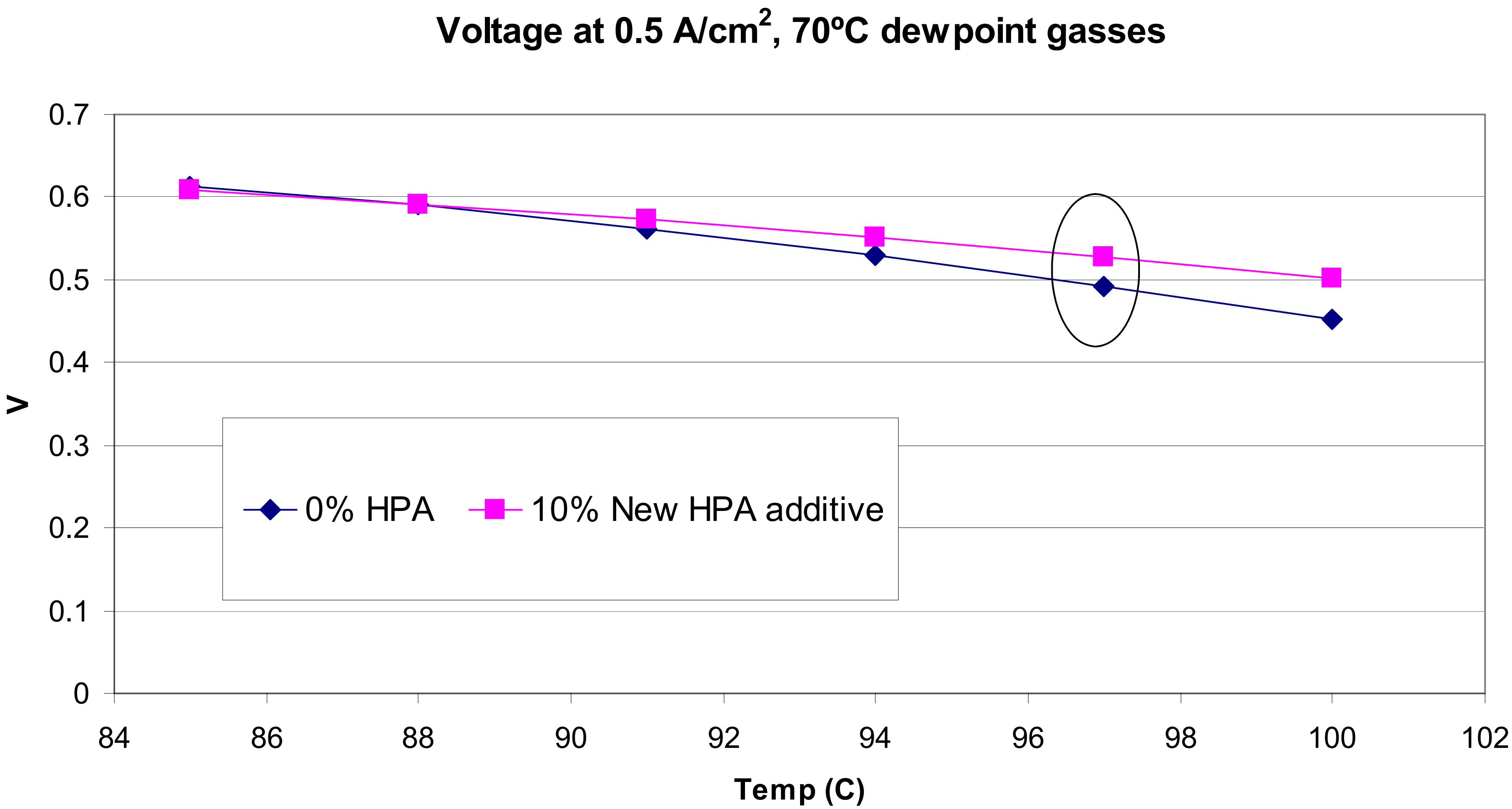
- *3M/DOE Cooperative Agreement No. DE-FC36-02AL67621*
  - *"Advanced MEA's for Enhanced Operating Conditions"*



3M

Accomplishments

- New additive shows increased performance under hotter, drier conditions



Partner Goals/Responsibilities

3M

- Prepare stable low EW perfluorinated polymers and composite fluorinated/hydrocarbon polymer membranes (with CWRU).
- Develop new stabilizing / conductivity enhancing additives (with CSM).
- Develop membrane fabrication techniques for improved properties.
- Test membrane properties including conductivity and physical/mechanical properties.
- Design, prepare and test MEA's and final short stack.
- Fuel cell performance and durability testing.

Case Western Reserve University

- Prepare polymers and membranes with high acidity based on aromatic backbone polymers and composite fluorinated/hydrocarbon polymer membranes (with 3M).
- Characterize the water uptake and transport properties of these and other materials prepared in the project.
- Participate in work (with UAH) to explore the impact of high acid site density.
- Perform studies of the degradation products and relative rates of degradation of experimental membranes and small molecule model compounds.

Partner Goals/Responsibilities

University of Detroit Mercy

- Study the stability of new membrane materials when exposed to reactive oxygen radicals.
- Perform studies to determine the effect of various stabilizers on membrane stability.
- The major methods of study will be *direct* ESR and *spin trapping*.

University of Alabama in Huntsville

- Perform first principles based modeling of both the perfluoro and hydrocarbon ionomer systems and conductivity enhancing additives.
- Participate in the elucidation of failure and degradation mechanisms of the ionomers through first principles based calculation.

Colorado School of Mines

- Preparation and characterization of immobilized HPA and other inorganic super acids on nano-particles using SiO_2, TiO_2, etc. and tethered to a polymer backbone.
- Participate with team in the development of composite membranes incorporating these materials.

Future Work – Year 1

- Complete the development of all pertinent testing methods and install and modify new equipment as appropriate. Begin screening of new materials.
- Initial molecular modeling protocol for quantifying effects of polymer chemistry, morphology, and additive(s) developed and validated for existing membrane materials.
- Begin study and screening of heteropolyacids and other inorganic proton conductors.
- Begin screening methods for immobilization of the HPA.
- Prepare low EW PFSA's for evaluation.
- Choose hydrocarbon polymer scaffold for modification and begin polymer development with fluorochemical materials.
- Select model compound suite for initial degradation testing designed.
- Begin *ex situ* degradation studies.
- Characterize degradation pathways of current 3M membranes by ESR and other analytical techniques.

Summary

- This new program will focus on the development a new membrane comprised of:
  - New polymers, fluoropolymers, non-fluorinated polymers and composite/hybrid systems with increased proton conductivity and improved chemical and mechanical stability.
  - New membrane additives for both increased conductivity and improved stability/durability under these dry conditions.

- The goal for this membrane is to operate under both high and low humidification conditions and at temperatures ranging from -20ºC to 120ºC in order to meet DOE targets for automotive fuel cells. Membranes developed in this project may also have improved durability and performance characteristics making them useful in stationary fuel cell applications.

- The new membrane will be integrated into MEA's and tested for performance and durability.