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DOE Hydrogen Program

# High Temperature Membrane with Humidification-Independent Cluster Structure


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FuelCell Energy, Inc.


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Project ID# FC18

# Overview

## Timeline

- Start: July 2006
- End: May 2011
- 17% complete

## Barriers

- Low Proton Conductivity at 25-50% Inlet Relative Humidity and 120$^o$C

## Budget

- Total project funding
  - DOE share: $1500k
  - Contractor share: $600k
- Funding received in FY06: $150k
- Funding for FY07: $100k to date

## Targets

- Membrane Conductivity:
  - At 120$^o$C: 100 mS/cm
  - At Room Temp.: 70 mS/cm
  - At –20$^o$C: 10 mS/cm
- Cell Area Specific Resistance: 0.02 $\Omega cm^2$

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# Acknowledgements


- DOE: Amy Manheim, Reg Tyler, Tom Benjamin
- UCF: Jim Fenton & Team (Testing protocols, membrane conductivity workshop)
- BekkTech LLC: Tim Bekkedahl (In-plane conductivity measurement)
- FCE Team

# Approach for the Composite Membrane

| Target Parameter | DOE Target (2010) | Approach |
|---|---|---|
| Conductivity at: 120°C | 100 mS/cm | Multi-component composite structure, lower EW |
| : Room temp. | 70 mS/cm | Higher number of functional groups |
| : -20°C | 10 mS/cm | Stabilized nano-additives |
| Inlet water vapor partial pressure | 1.5 kPa | Immobilized cluster structure |
| Hydrogen and oxygen cross-over at 1 atm | 2 $mA/cm^2$ | Stronger membrane structure; functionalized additives |
| Area specific resistance | 0.02 $\Omega cm^2$ | Improve bonding capability for MEA |
| Cost | <40 $\$/m^2$ | Simplify polymer processing |
| Durability:<br>- with cycling at >80°C<br>- with cycling at ≤80°C | <br>>2000 hours<br>>5000 hours | Thermo-mechanically compliant bonds, higher glass transition temperature |
| Survivability | -40°C | Stabilized cluster structure design |

# Technical Accomplishments

- **Multi-Component Composite (mC$^2$) membrane concept defined**
- **Improved Baseline Polymer selected and characterized (6 month milestone met)**
- **Additives for water retention and protonic conductivity enhancement have been identified and fabricated.  Initial results are encouraging**
- **Measurements verified by BekkTech**
- **Conductivity is used as a “figure of merit”, mechanical properties are used as a check point**

# Proton Conductivity Model

**Surface (requires chemically bound water)**

$$\sigma_p = \sigma^{\Sigma}_{\mathrm{H}^+} + \sigma^{G}_{\mathrm{H}^+} + \sigma^{E}_{\mathrm{H}^+}$$

**Grotthuss (requires free water)**

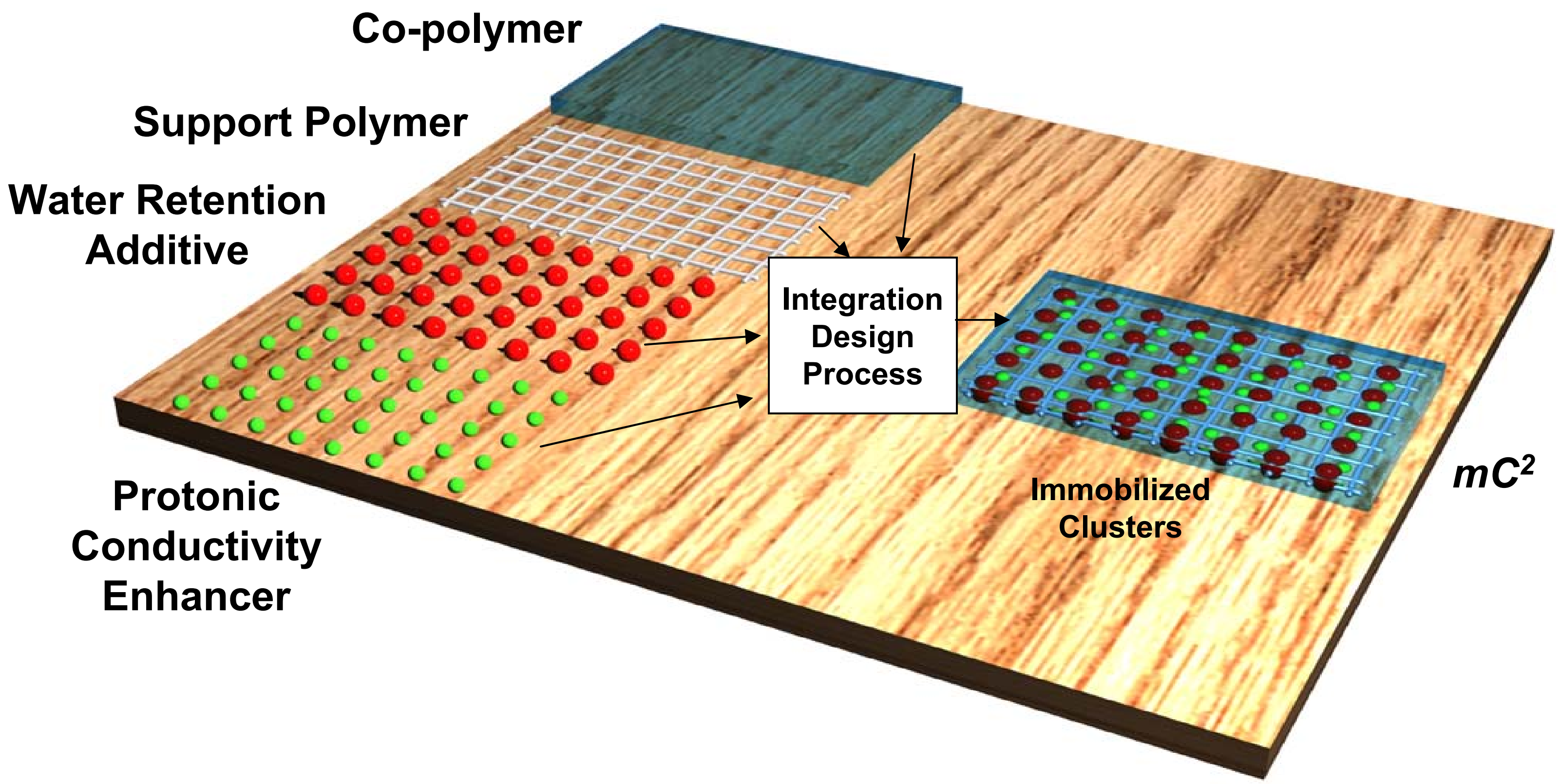
$$\sigma^{\alpha}_{\mathrm{H}^+} = \frac{F^2}{RT} D^{\alpha}_{\mathrm{H}^+} C^{\alpha}_{\mathrm{H}^+}$$

$$\sigma_p = \frac{\varepsilon}{\tau}\left[\frac{F^2}{RT}\left\{D^{\Sigma}_{\mathrm{H}^+} C^{\Sigma}_{\mathrm{H}^+} + \left(D^{G}_{\mathrm{H}^+} + \frac{D_{\mathrm{H}^+\mathrm{W}}}{1+\delta}\right) C_{H^+}\right\}\right]$$

$C^{\Sigma}_{\mathrm{H}+}$ and $C_{\mathrm{H}+}$ obtained from sorption thermodynamics

**Understanding the Role of Free and Chemically Bound Water is Needed**

# Composite Membrane Concept




**Multi-Component System with Functionalized Components**

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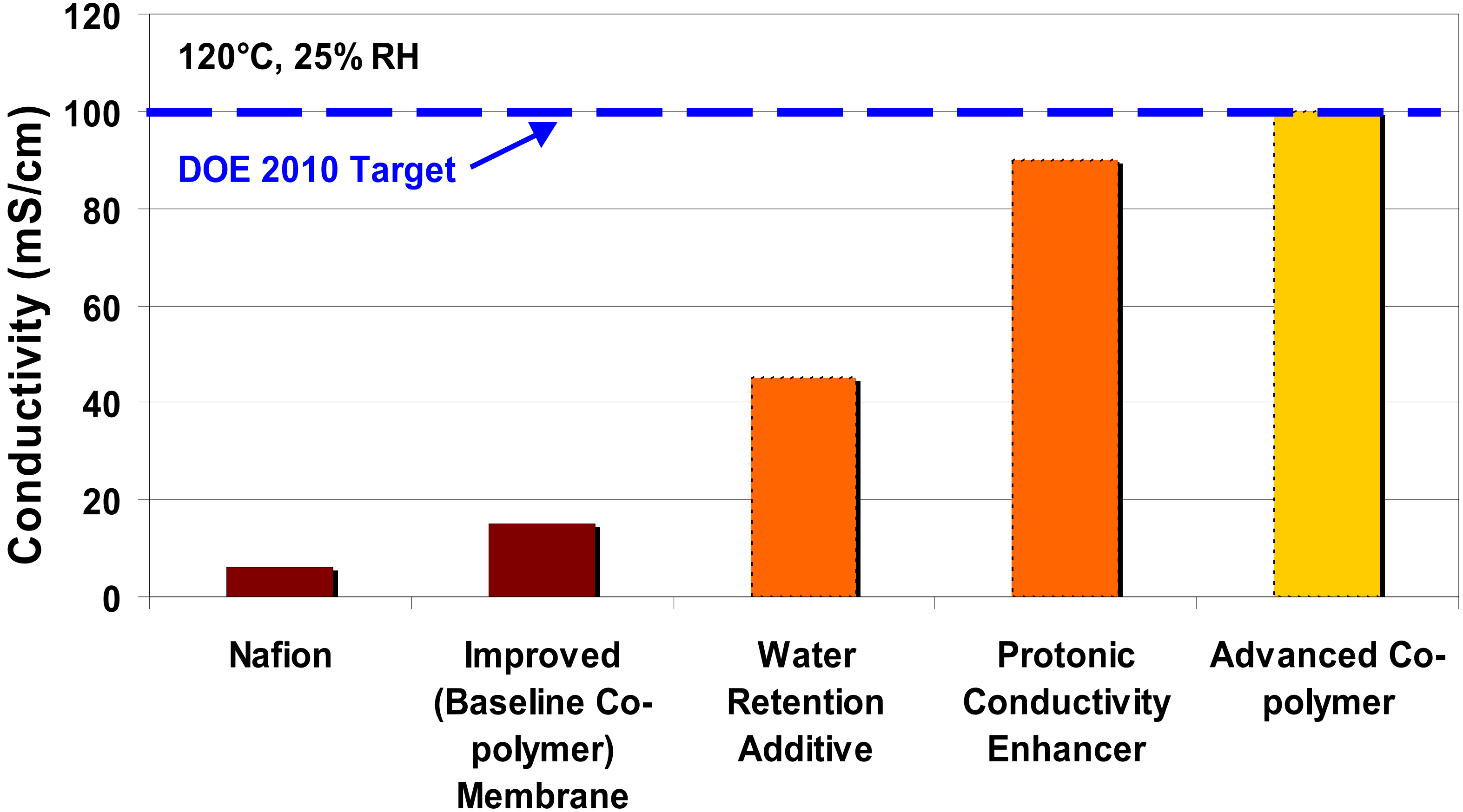
# Development Steps to Conductivity Goal




**Each Individual Component Contributes to Conductivity Improvements**

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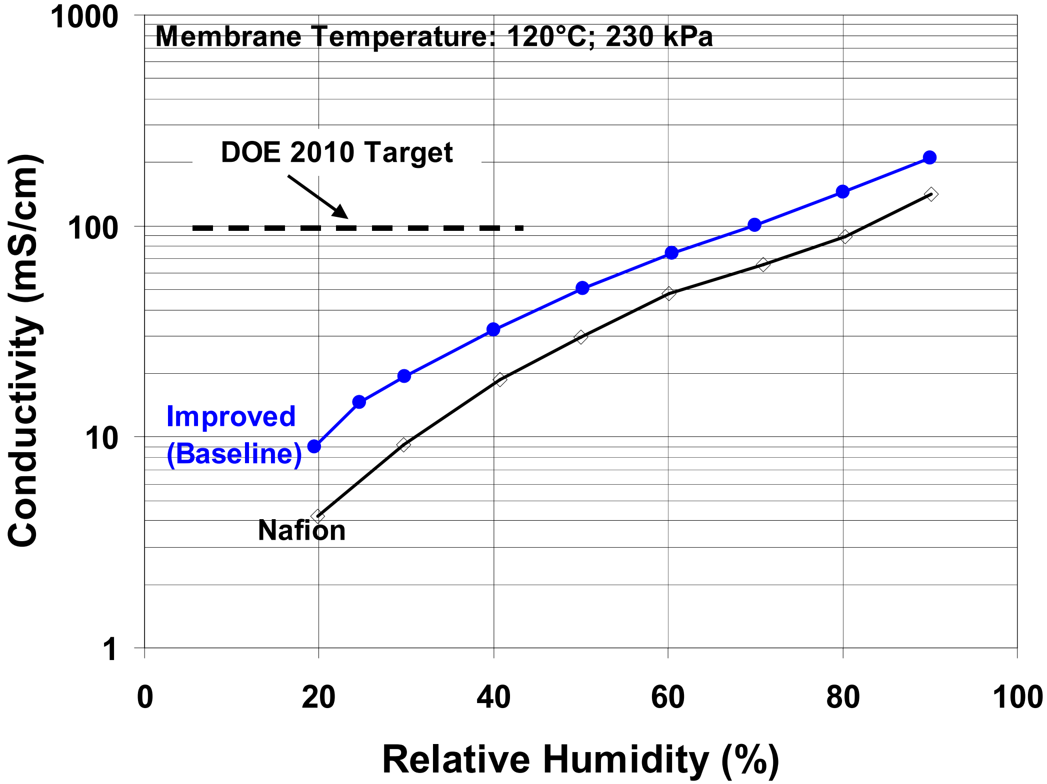
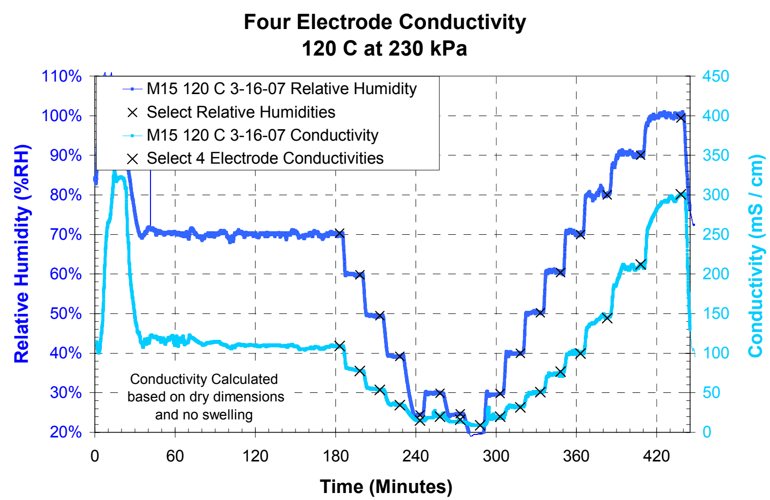
# Improvements in the Polymer Membrane

- In-plane 4-electrode Measurement used to Determine Conductivity
- BekkTech has Developed a Reliable In-plane Conductivity Measurement




**The Improved (Baseline) Membrane Offers 2.5x Better Conductivity over Nafion®**

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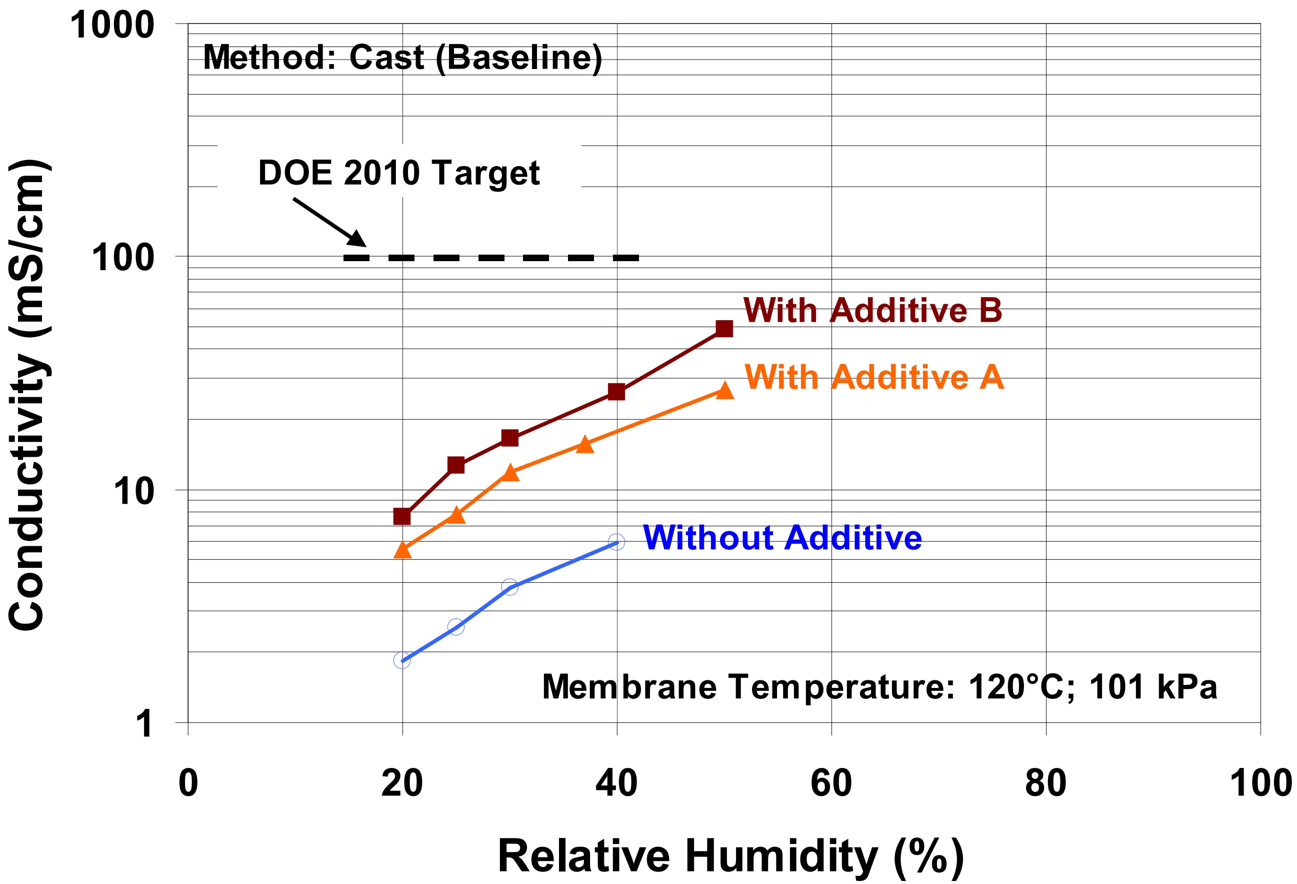
# Membrane Additive Development

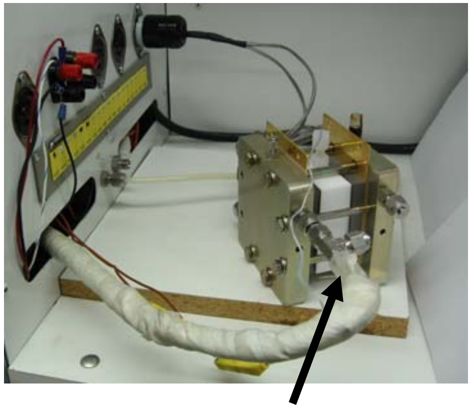
**Benefits:**
- Conductivity less dependent on RH
- Conductivity at subfreezing temp.
- Potentially lower cost
- Design for mechanical strength

**Anticipated Issues:**
- Water solubility
- Electrochemical stability
- Compete for “real estate”
- Non-uniform dispersion

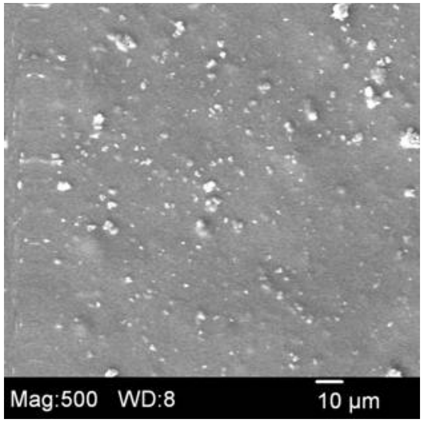
# Conductivity Improvements Due To Additives

## Preliminary Data



Conductivity Cell




**Range of Conductivity Improvement: 3 to 5x**

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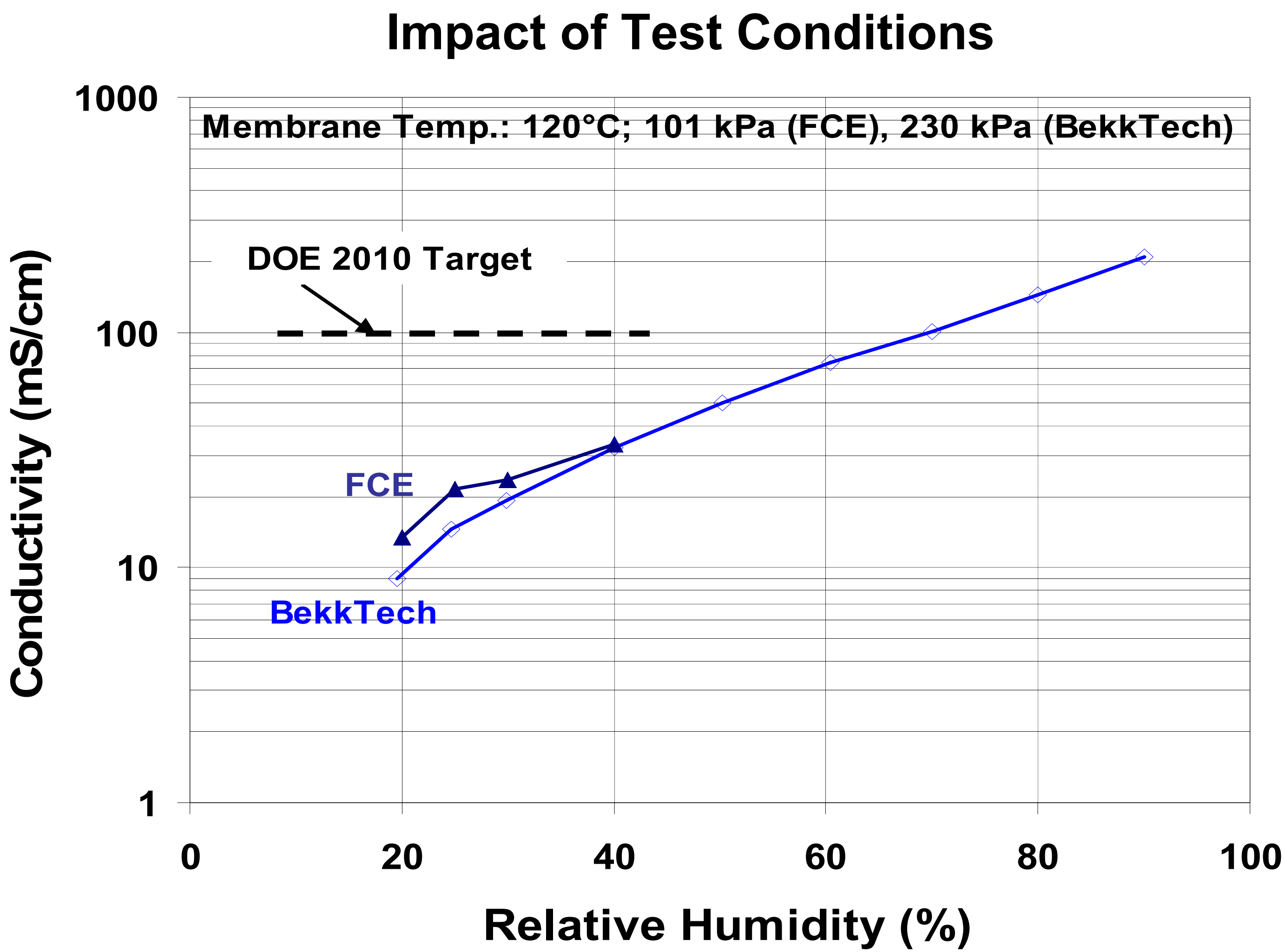
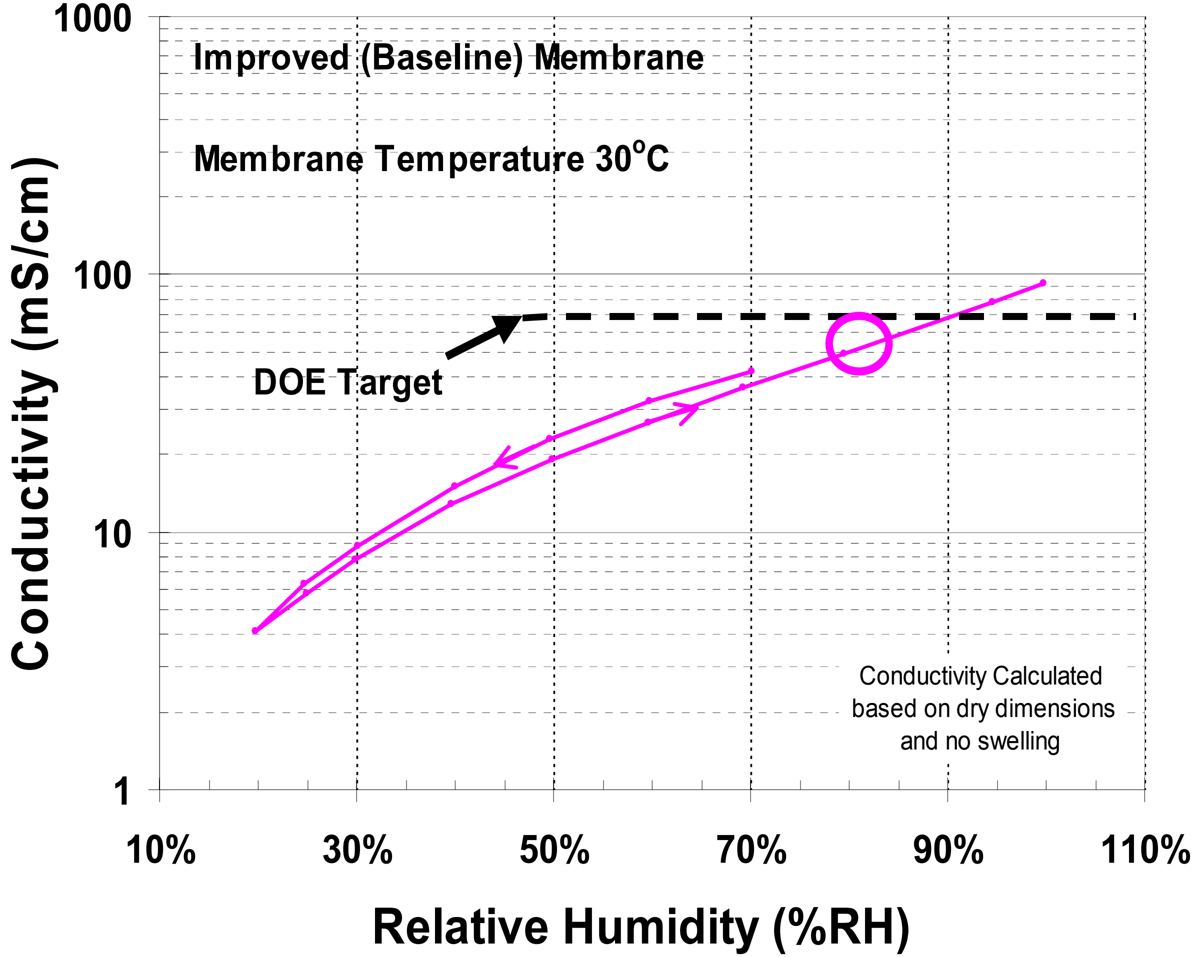
# Reproducibility of Conductivity Data




**Changes in Humidification Play an Important Role**

# Lower Temperature Conductivity




**Close to Meeting Conductivity Target of 70 mS/cm @ 80% RH @ RT (Reached 70% of Target)**

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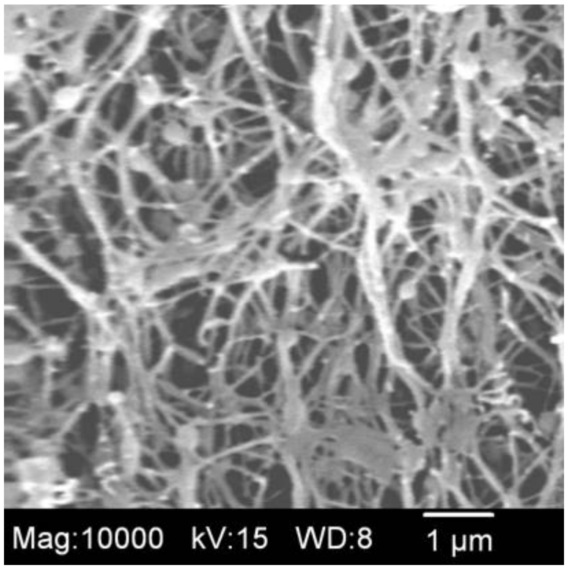
# Mechanical Properties: Nafion vs. Improved (Baseline)

| Membrane (Dry state, 50μm thick) | Baseline-M15 | Baseline-M15 | N112 | N112 |
|---|---|---|---|---|
| Test direction | MD | TD | MD | TD |
| Tensile Modulus, MPa | 182 | 188 | 232 | 208 |
| Tensile Strength, MPa | 34 | 24 | 38 | 23 |
| Elongation at Break, % | 162 | 214 | 117 | 228 |

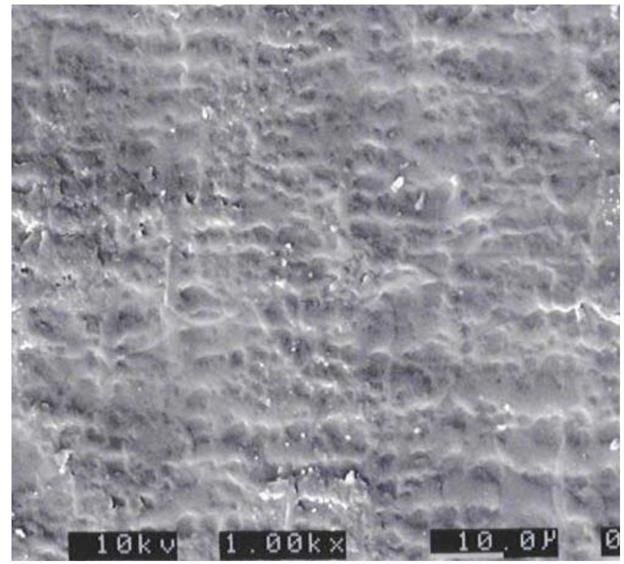
**No Apparent Loss in Mechanical Strength**

# Composite Membrane Fabricated

**Porous Support**




**Composite Membrane**




Pore-free membrane successfully fabricated; conductivity measurements in progress; mechanical testing planned

**Benefits:** **- Higher Mechanical Strength**

**- Thinner Membrane (25 μm)**

# Future Work

- Fabricate and Characterize mC$^2$ Improved Baseline Membrane Process
- Improve Functionality of Individual Components
- Initiate Materials/Compositions/Processing for Advanced Membrane Polymer Development
- Upcoming Key Milestones:
  - Define materials/compositions/processing for advanced membrane (Nov 07)
  - Meet conductivity target of 70 mS/cm @ 80% RH @ RT (Feb 08)
  - Select preferred design for the composite membrane (May 08)
  - Conductivity testing by DOE (annually)

# Project Summary

- **Multi-component composite membrane design identified for high temperature and low relative humidity operation**
- **Demonstrated conductivity > 2.5x higher than Nafion, without loss in mechanical properties**
- **Functionalized additives show promise to further increase conductivity by 3 to 5x to approach DOE goal**
- **Initial composite membrane fabricated**

# Project Summary Table

| DOE 2010 Technical Targets for Membranes for Transportation Applications# | | | | |
|---|---|---|---|---|
| Performance Parameter | Units | 2010 Target | Commercial Membrane (Nafion® 112) | FY06-07 Result |
| Conductivity at 120°C and 25% RH | mS/cm | 100 | 6 | 15* Membrane Only |
| $H_2$ Cross-over at 1 atm | $mA/cm^2$ | 2 | ≤1 | ~1 expected |

# From DOE Multi-Year RD&D Plan, Technical Plan - Fuel Cells, Table 3.4.12., April 2006

* Anticipated with the Additives: >45 mS/cm