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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°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°C: 100 mS/cm
  - At Room Temp.: 70 mS/cm
  - At –20°C: 10 mS/cm
- Cell Area Specific Resistance: 0.02 Ωcm^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 Ωcm^2	Improve bonding capability for MEA
Cost	<40 \$/m^2	Simplify polymer processing
Durability: - with cycling at >80°C - with cycling at $\leq$80°C	 >2000 hours >5000 hours	Thermo-mechanically compliant bonds, higher glass transition temperature
Survivability	-40°C	Stabilized cluster structure design

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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)

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

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

Grotthuss (requires free water)

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

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

Understanding the Role of Free and Chemically Bound Water is Needed

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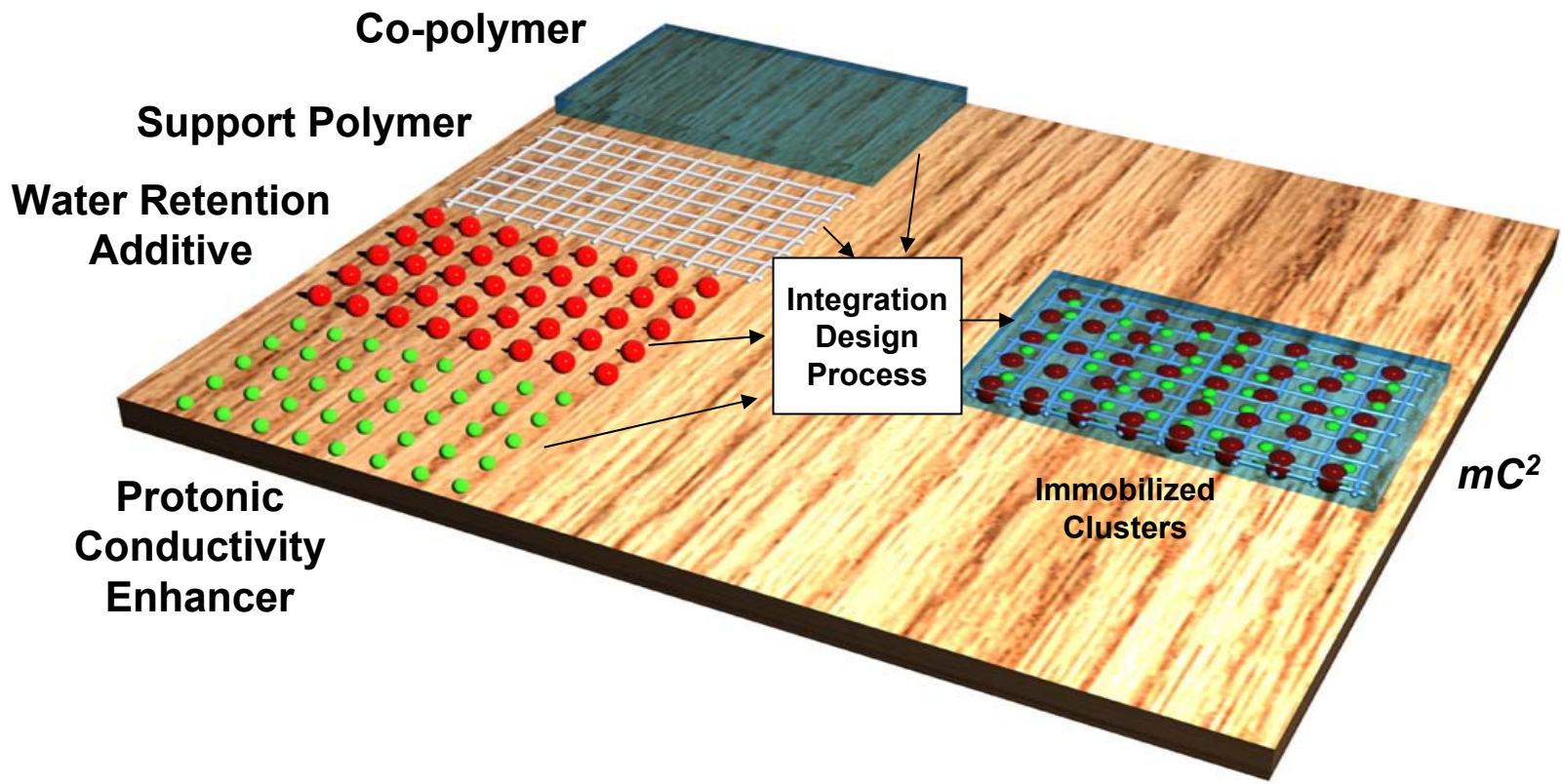
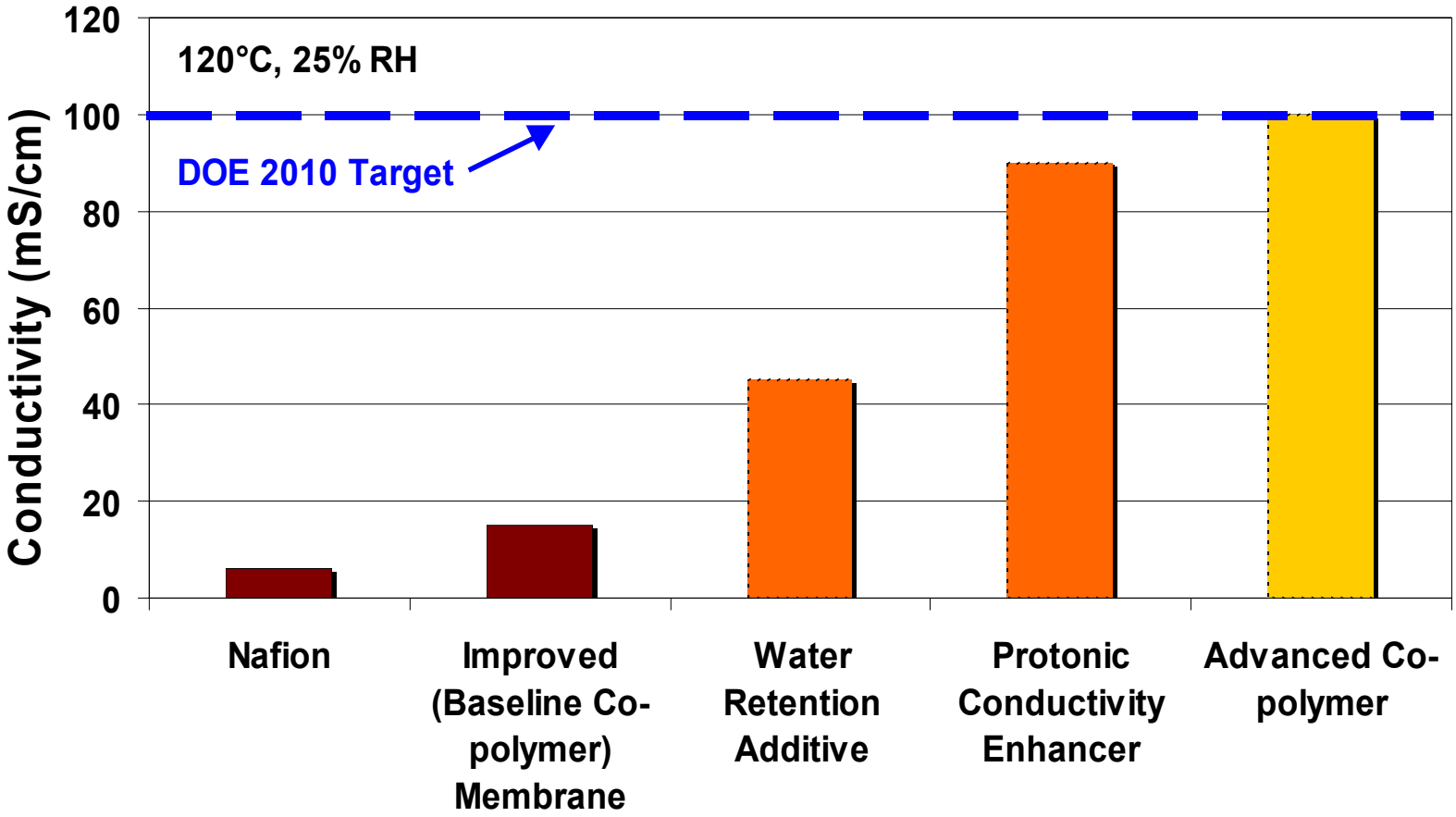
Composite Membrane Concept



Multi-Component System with Functionalized Components

Development Steps to Conductivity Goal



Each Individual Component Contributes to Conductivity Improvements

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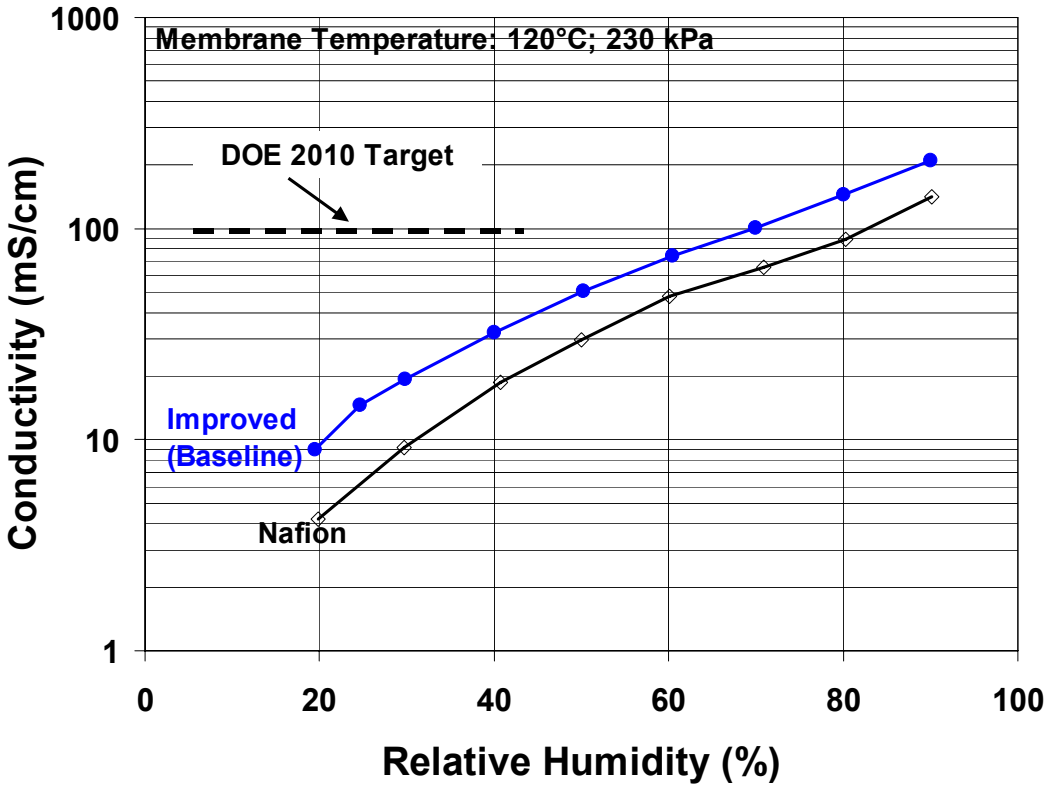
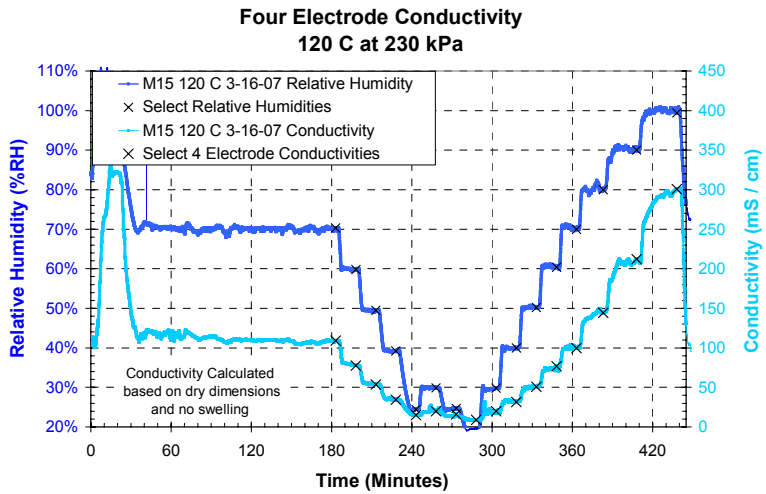
Improvements in the Polymer Membrane

- 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

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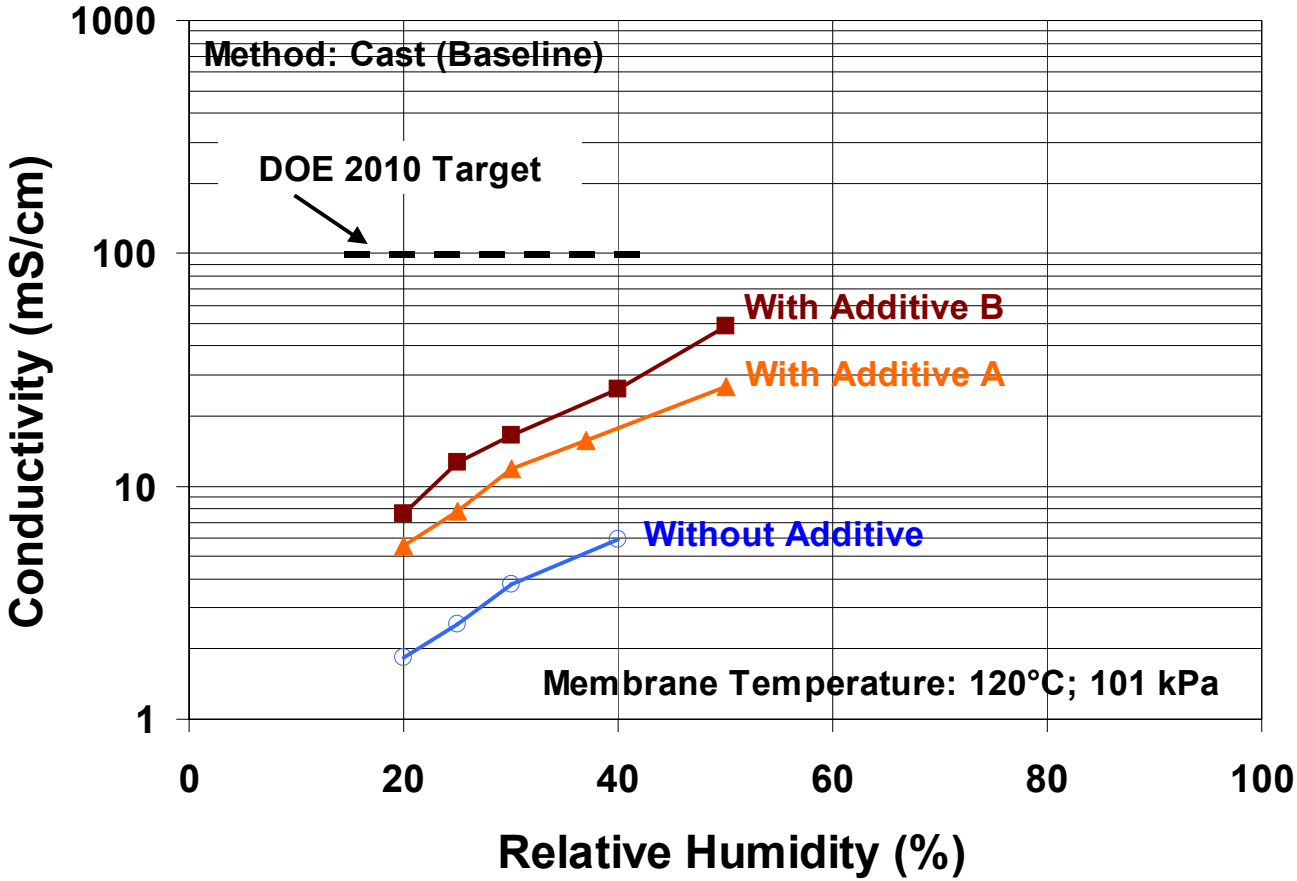
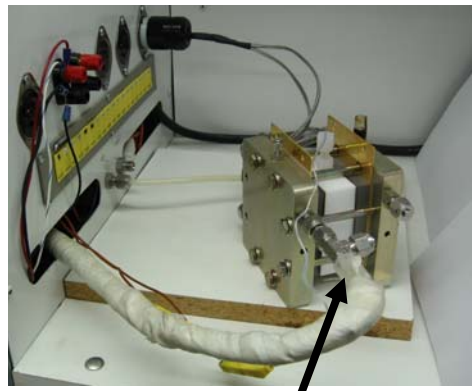
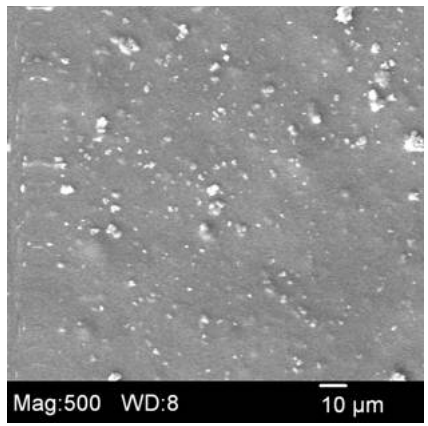
Conductivity Improvements Due To Additives

Preliminary Data





Conductivity Cell



Range of Conductivity Improvement: 3 to 5x

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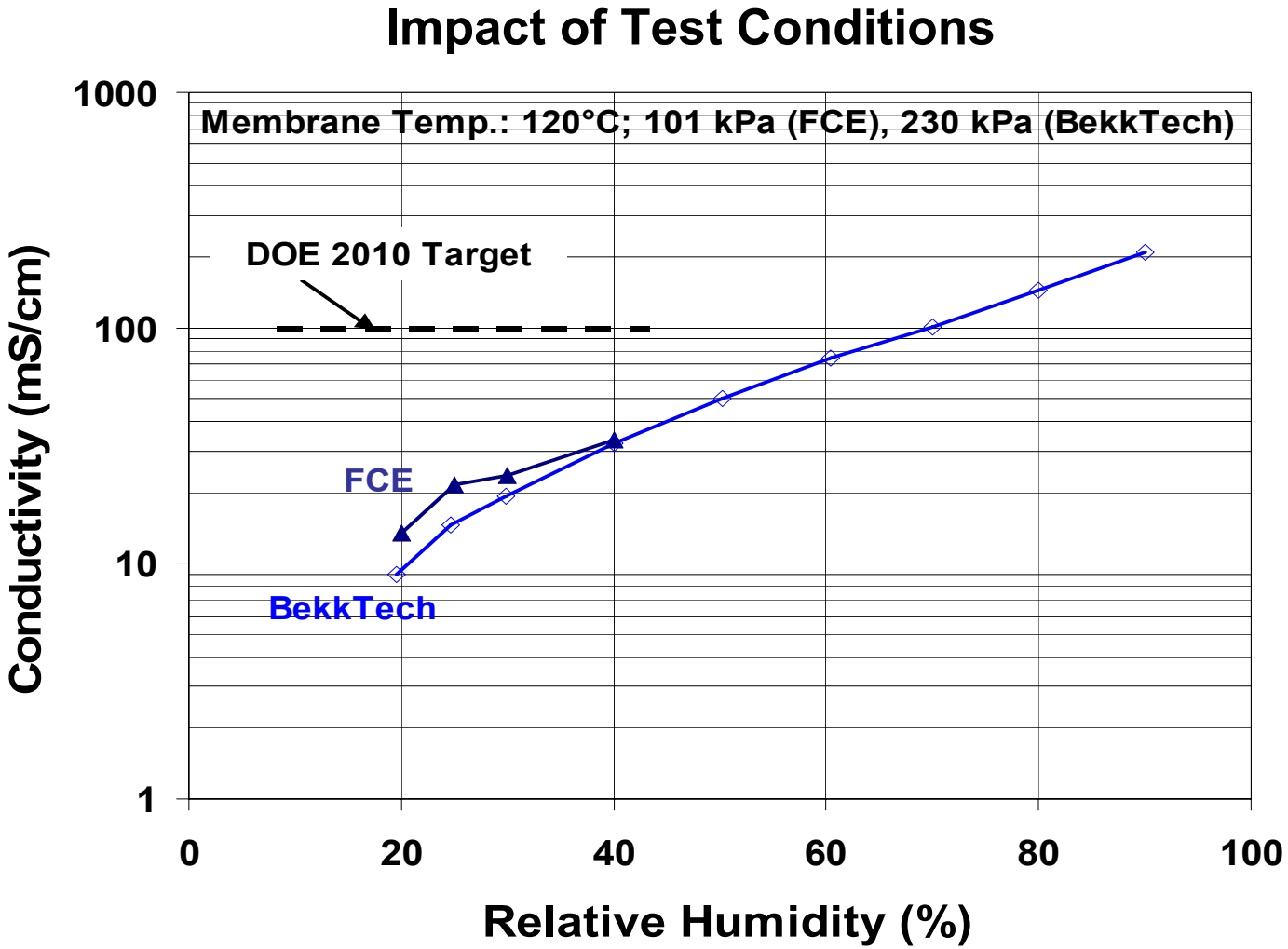
Reproducibility of Conductivity Data



Changes in Humidification Play an Important Role

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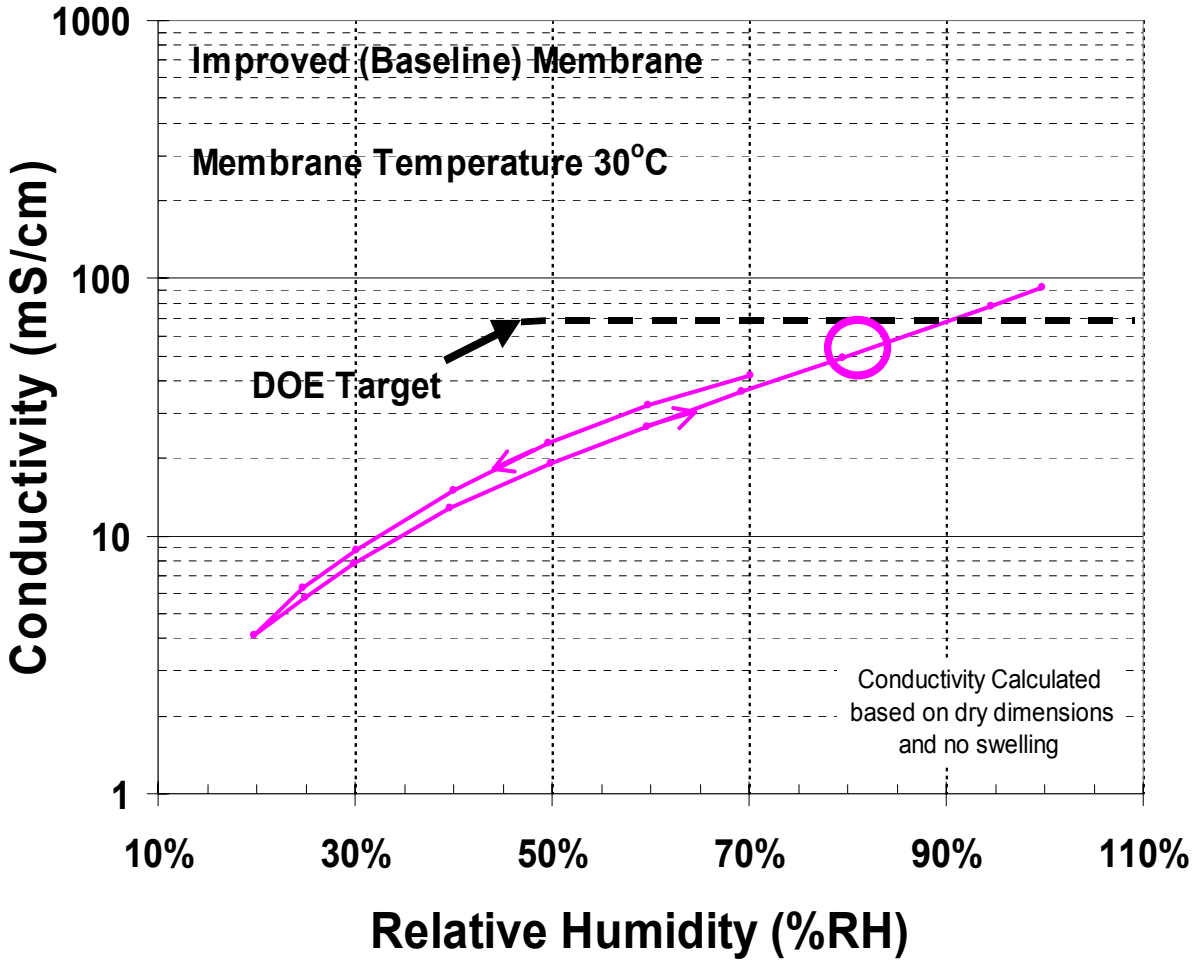
Lower Temperature Conductivity



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

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

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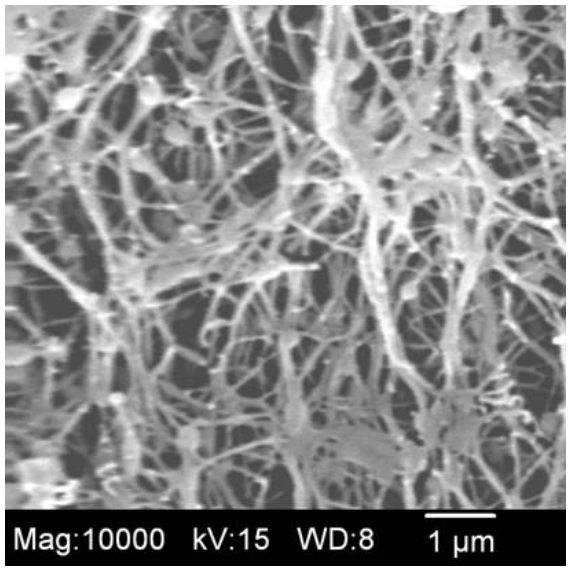
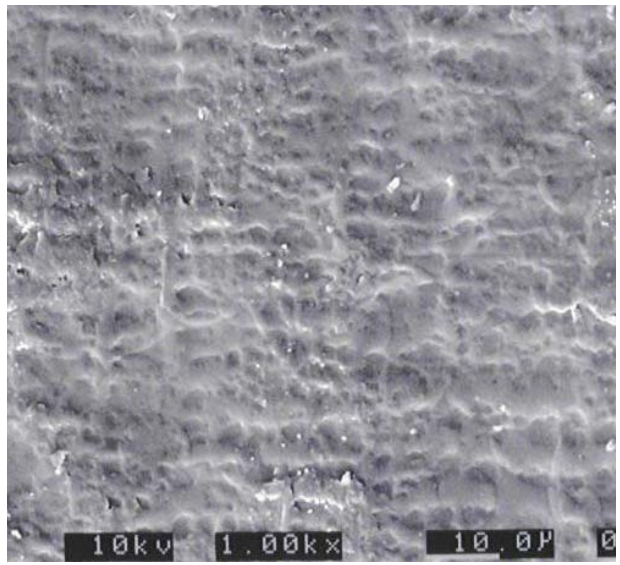
Composite Membrane Fabricated

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**

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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

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