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DOE Hydrogen Program

High Temperature Membrane with Humidification-Independent Cluster Structure

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FuelCell Energy, Inc.

May 11th, 2011

Project ID # FC040

Overview

Timeline

- Start: June 2006
- End: May 2011
- 96% complete

Budget

- Total project funding
  - DOE share: $1500k
  - Contractor share: $600k
- Funding received in FY10: $300k
- Funding for FY11: $100k

Barriers

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

Partners

- Univ. of Central Florida
  - Membrane characterization, MEA fabrication & evaluation
- Oak Ridge National Lab
  - Membrane characterization, MEA fabrication & evaluation
- Polymer Partner
  - Polymer & membrane fabrication & characterization
- Additive Partners
  - Additives synthesis & characterization
- Consultants
  - Polymer, additives

Acknowledgements

- **DOE: Donna Ho, Kathi Martin, Jason Marcinkoski, Amy Manheim, Greg Kleen, Reg Tyler, Tom Benjamin and John Kopasz**
- **UCF: Jim Fenton, Darlene Slattery & Team (Testing protocols, membrane and MEA evaluation)**
- **ORNL: Kelly Perry, Karren More**
- **FCE Team: Pinakin Patel, Ray Kopp, Jonathan Malwitz**

Relevance

Objectives:

- **Develop membranes that meet the DOE performance, life and cost targets, including improved conductivity at up to 120°C and low relative humidity (25-50%)**
- **Develop membrane additives with high water retention and high proton conductivity**
- **Fabricate composite membranes (mC^2)**
- **Characterize polymer and composite membranes**
- **Fabricate MEAs using promising membranes and characterize (UCF)**

Relevance

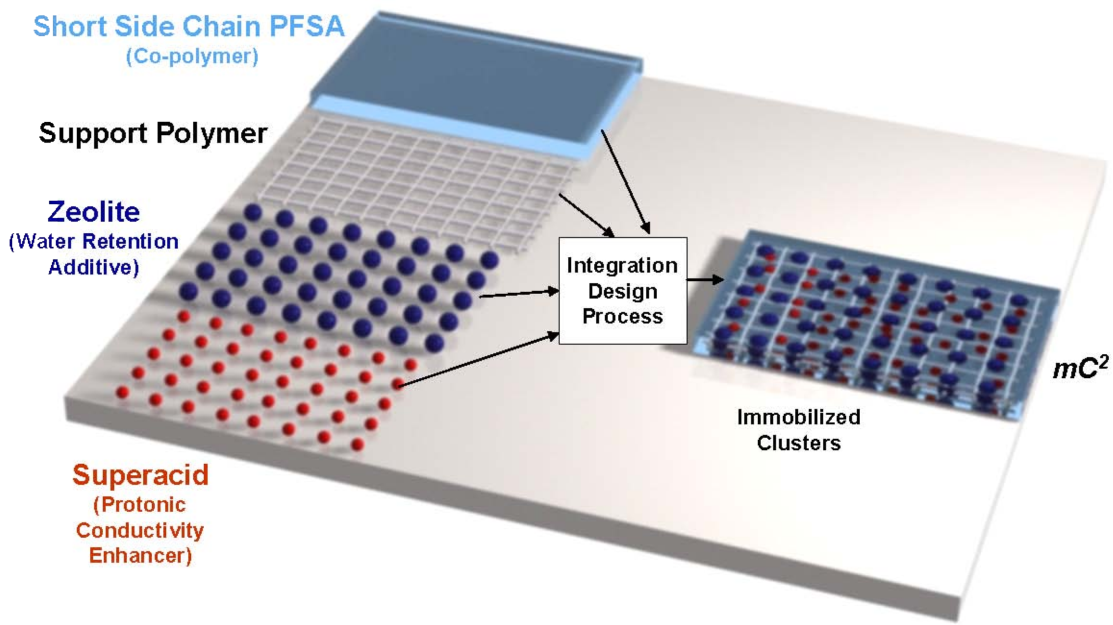
Impact of High Temperature Membrane:

- Higher conductivity membranes increase power density and efficiency of the fuel cell stack
- Operation at low relative humidity (RH) eliminates need for external humidification → simplifies the fuel cell system
- Operation at elevated temperatures simplifies thermal management (smaller radiator)
- Simpler system increases overall efficiency of fuel cell power plant → contributes to DOE 2015 cost target of $30/kW$_e$
- Reduced weight of automotive fuel cell system leads to higher fuel efficiency

Approach for the Composite Membrane

Target Parameter	DOE Target (2010)	Approach
Conductivity at: 120°C	100 mS/cm	Multi-component composite structure, lower EW, additives with highly mobile protons
: 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	MEA with matching polymer in membrane and electrodes
Cost	20 \$/m^2	Simplify polymer processing
Durability: - with cycling at >80°C - with cycling at ≤80°C	 >2000 hours >5000 hours	Thermo-mechanically compliant bonds, higher glass transition temperature
Survivability	-40°C	Stabilized cluster structure design

Composite Membrane Concept



Improvements Made:

- **Lower EW (850 → 800-650)**
- **Higher MW**
- **Chemically stabilized polymer**
- **Smaller particle size (>80 → 30 nm)**
- **Increased proton density (1 → 2 mobile protons per molecule) & lower cost**

Multi-Component System with Functionalized Additives

Technical Accomplishments

Major Achievements:

- **Met conductivity targets with polymer membrane and composite membrane**
- **Integrated lower-cost protonic conductivity enhancer (di-valent superacid, >80% lower cost)**
- **MEA Fabrication successful**
- **Met ASR target; cell performance progressing towards DOE targets**

Milestones

Milestone	FY09 Goal	FY10-11 Goal	Current Status
Screen Nano-additive Incorporation Options	complete	-	complete ✓
Characterize Advanced Membrane	complete	-	complete ✓
120°C Conductivity: Go/No-Go	100 mS/cm at 50% RH	-	100-148 mS/cm ✓
Provide membrane samples to UCF for MEA Fabrication	-	Advanced Polymer Lower cost mC^2	complete ✓ complete ✓
MEA Stability test by UCF	-	11-day test	complete ✓
Select low-cost, long life membrane design	-	High MW stabilized polymer	in progress
Cell testing at FCE	-	1,000 hr	in progress

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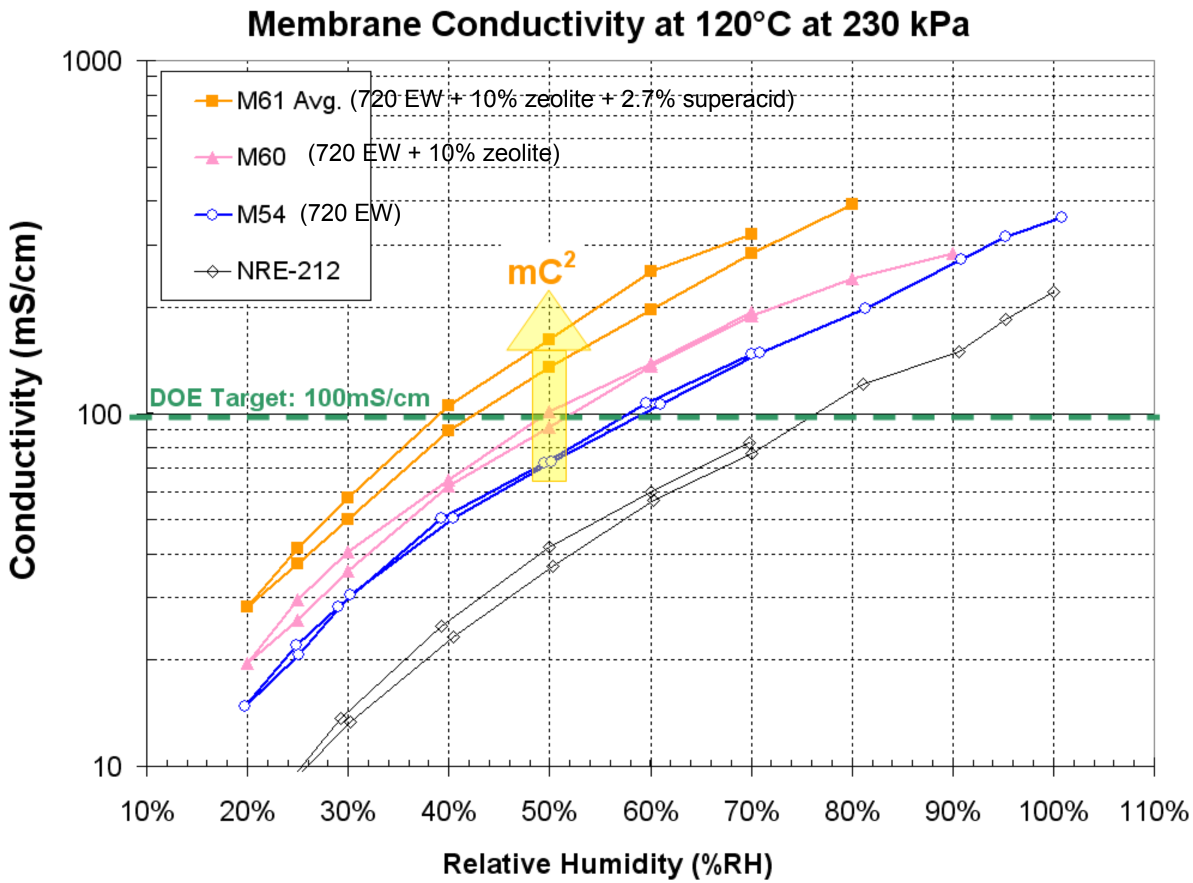
Data From 2009 AMR



mC^2 includes mono-superacid and zeolite in advanced polymer

>3x Improved Membrane Conductivity *vs.* NRE-212

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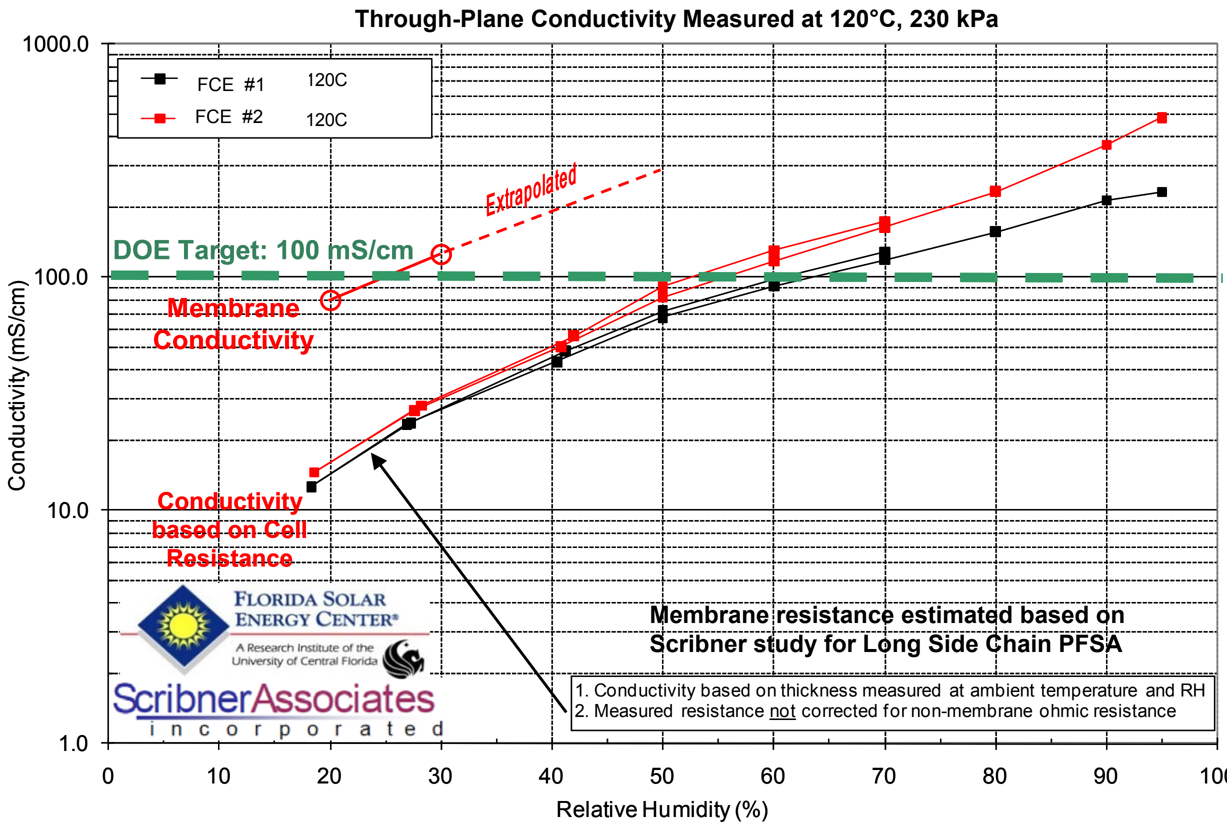
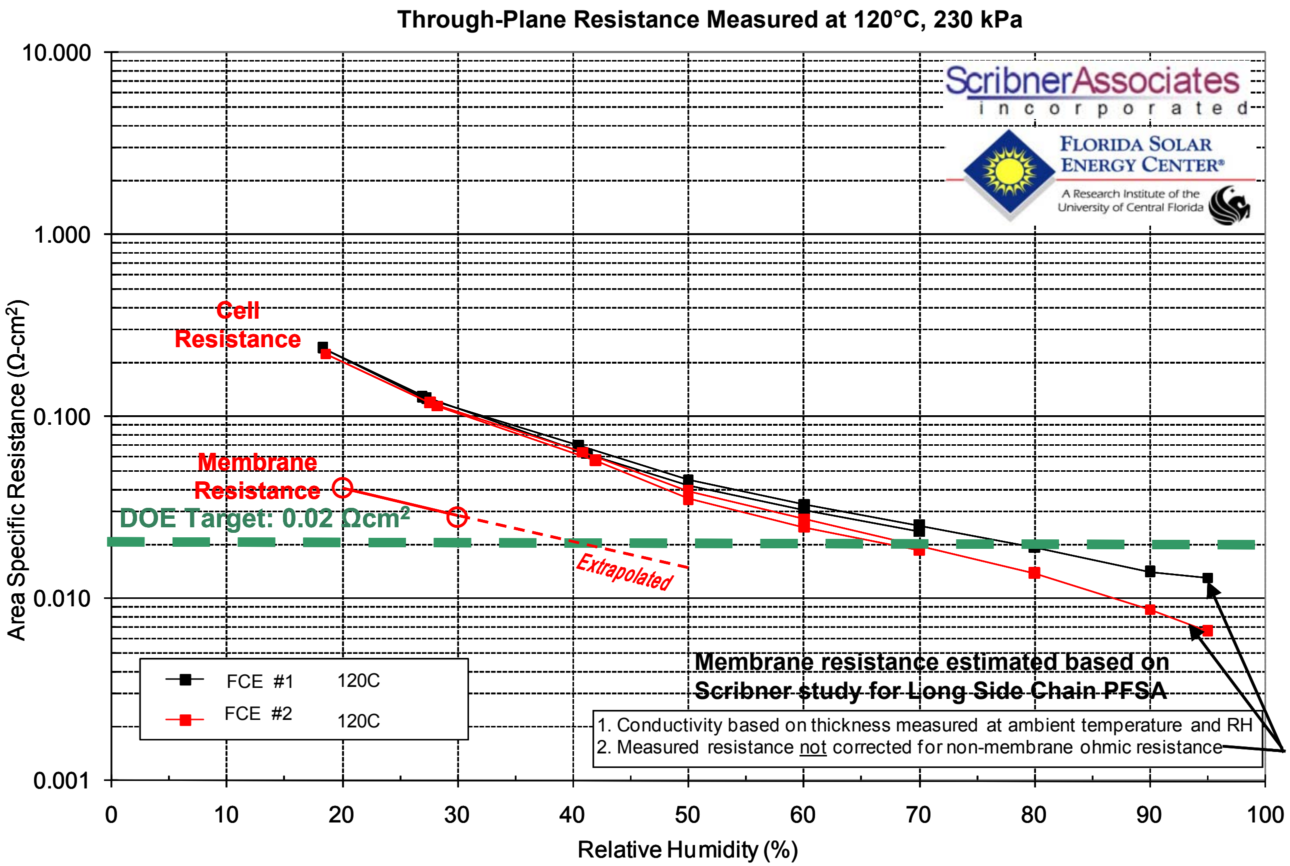
Membrane Conductivity FSEC Data



- **Conductivity of Polymer Alone Meets the DOE Target**
- **Study needed to accurately determine membrane resistance corrected for non-membrane ohmic resistance**

Membrane Area Specific Resistance (ASR)



Estimated Membrane Resistance meets the DOE Target

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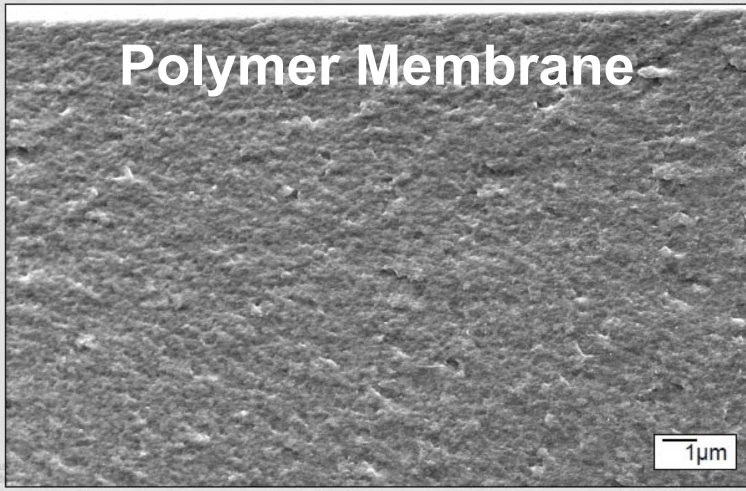
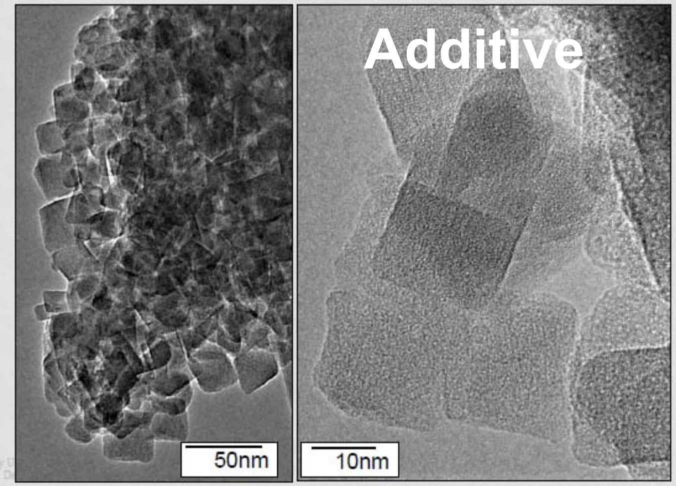
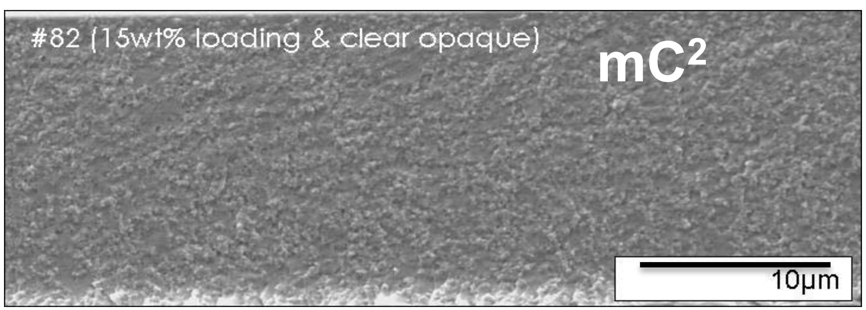
Microstructural Characterization

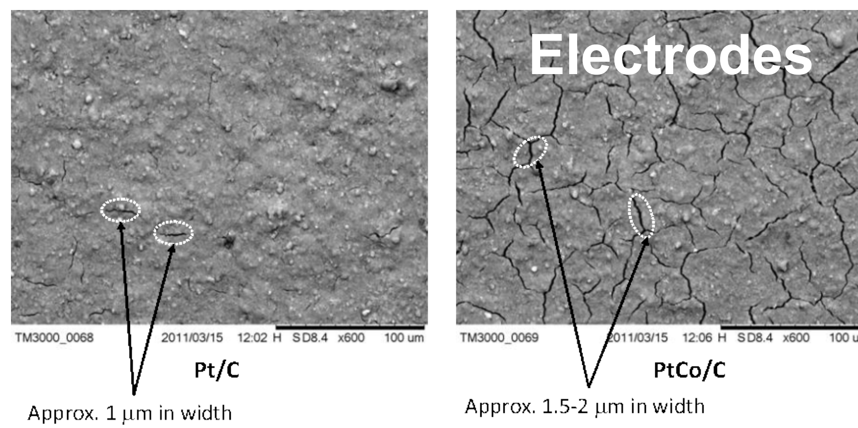
SEM image of a freeze-fracture cross-section of the blank membrane (#76) exhibited a dense, textured microstructure.



The nanozeolite is predominantly 20-50nm crystalline cuboidal particles.







Highly dispersed particles in mC²

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Oak Ridge National Laboratory

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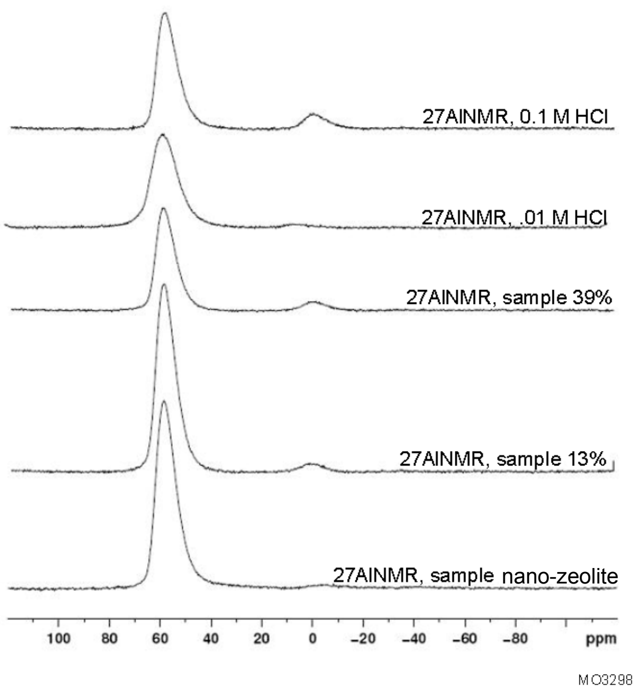
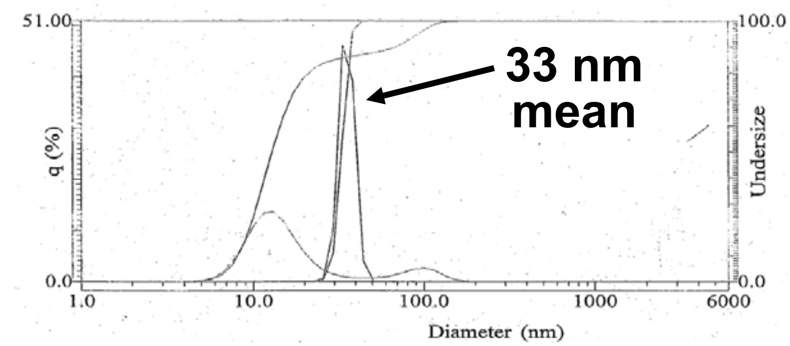
Ex-situ Characterization

^{27}Al Solid State Magic Angle Spinning NMR (^{27}Al SS MAS/NMR) measurements were preformed with a Bruker 400 spectrometer spinning at 100 MHz. Aluminum nitrate was used as reference and a total of 1024 scans were collected.



Adsorption of di-valent superacid on nano-zeolite does not have a negative interaction



Demonstrated long-term (1 yr) nano-zeolite particle size stability

Tensile Test ASTM D638 (23°C – 50% RH):

Sample#	Module [Mpa]	Yield Stress [Mpa]	Deformation [%]	Stress at break [Mpa]	Deformation at break [%]
850EW Blank	255 (7)	12 (0.2)	7.3 (0.2)	28.2 (0.8)	172 (11)
850EW + 2.7% Zeolite	242 (5)	12 (0.1)	9 (0.2)	30.3 (1.6)	204 (16)
850EW + 10% Zeolite	298 (10)	12.6 (0.3)	7.6 (0.2)	27.2 (1.5)	178 (8)

Values are average of three tests, with standard deviation in parenthesis

No significant effect observed on membrane mechanical properties induced by the presence of the zeolite

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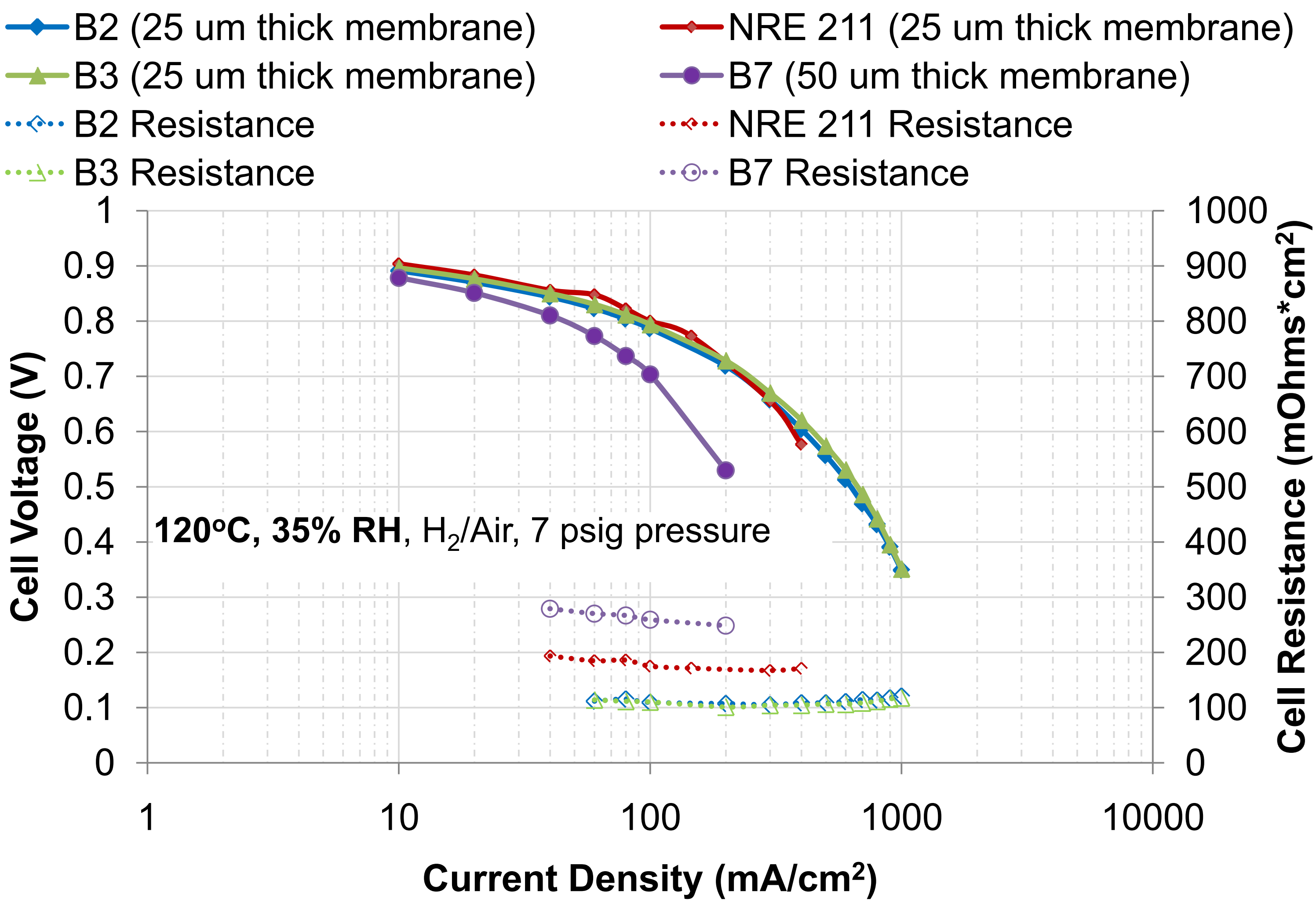
Cell Performance at 120°C



B2 and B3 have lower cell resistance than NRE211

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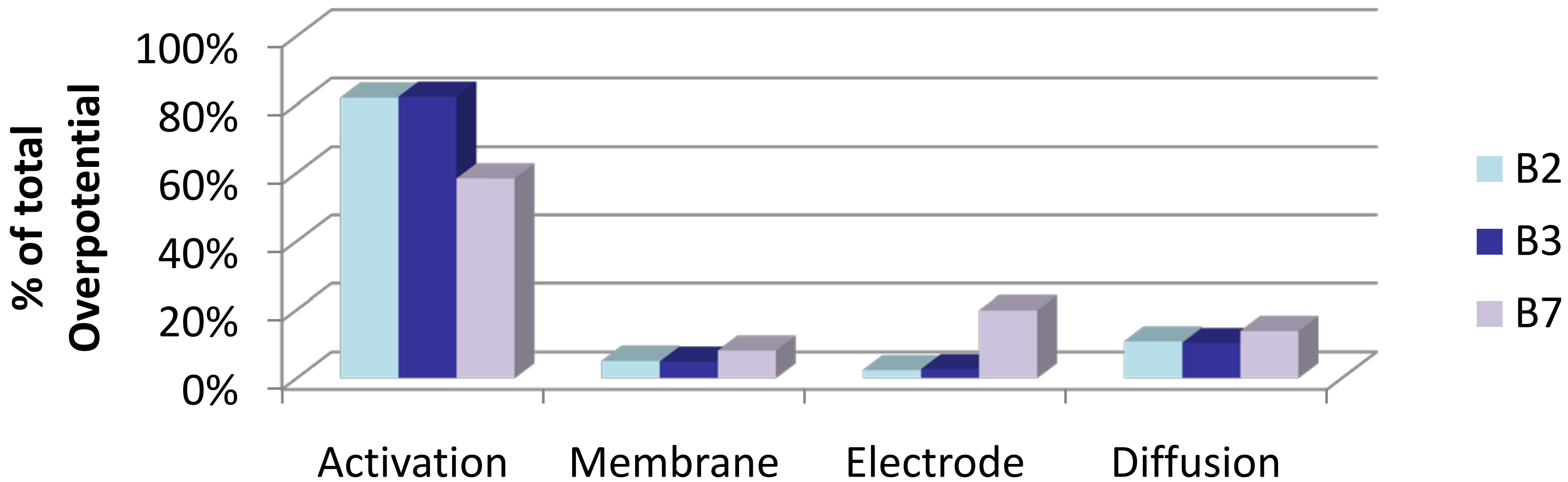
Fuel Cell Performance Analysis

120°C, 35% RH, H_2/air, 7 psig, 200 mA/cm²



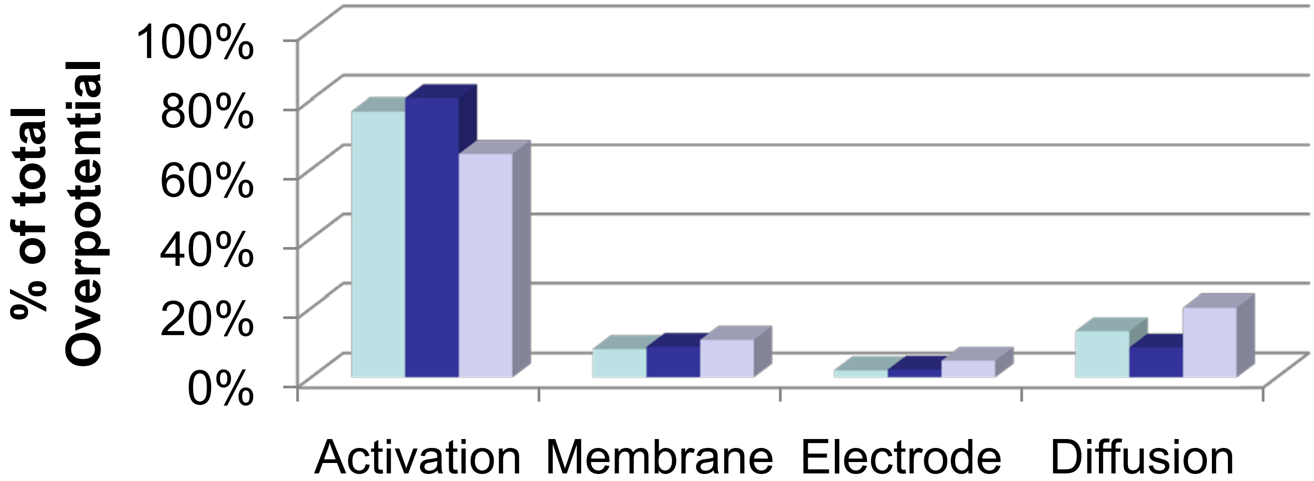
Calculated using a method described in reference: M.V. Williams, H.R. Kunz, J.M. Fenton, J. Electrochem. Soc., Vol. 152 (3) A635-A644 (2005)

B7 used different ionomer in electrodes (5% lower EW, chemically stabilized) than B2 and B3, leading to increased electrode and diffusion resistance

→ Electrode optimization required

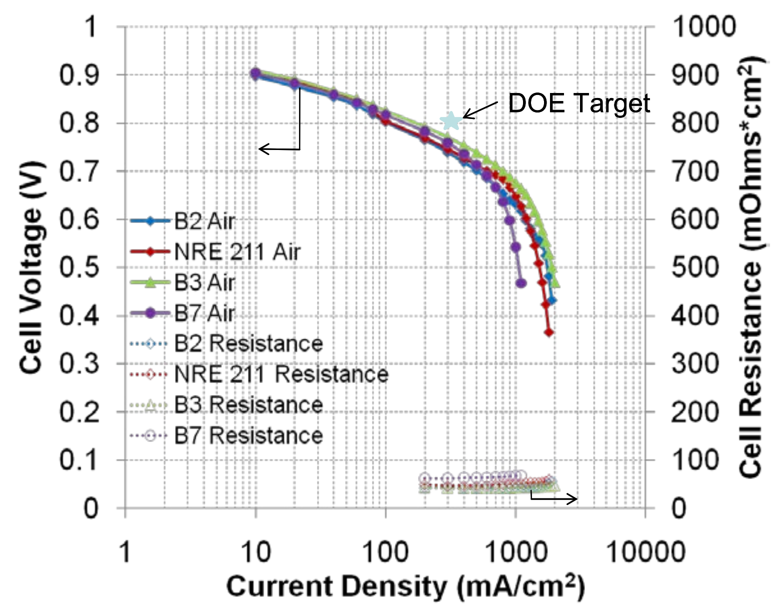
Fuel Cell Performance Analysis

80°C, 100% RH, H_2/air, 7 psig, 1000 mA/cm²



Calculated using a method described in reference:

M.V. Williams, H.R. Kunz, J.M. Fenton, J. Electrochem. Soc., Vol. 152 (3) A635-A644 (2005)



B7 diffusion losses dominate performance more than membrane resistance

→ Illustrates importance of electrode ionomer optimization

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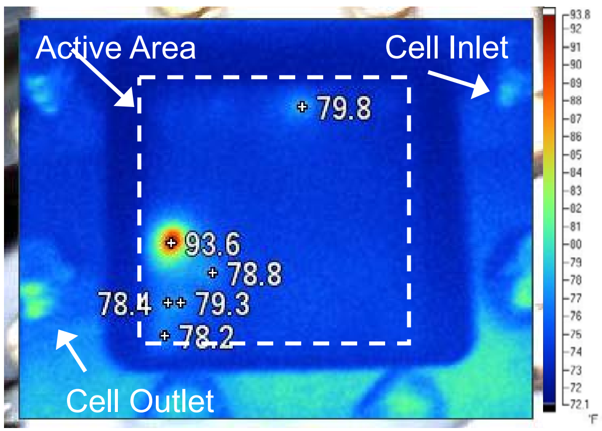
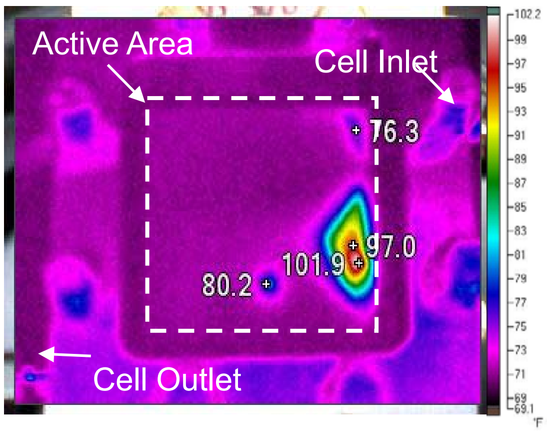
MEA Post-Test Analysis

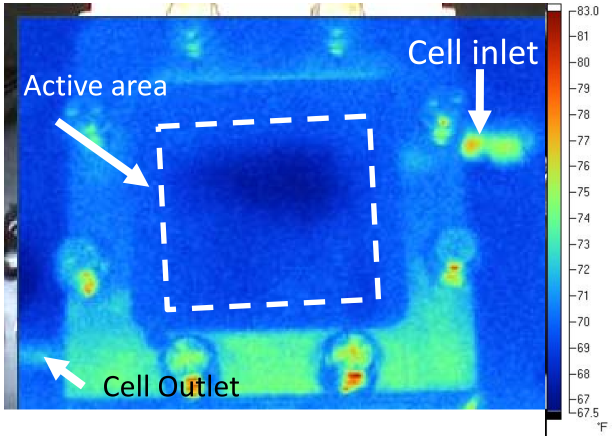
Pinhole Data



B2
After testing
crossover = 1.0 mA/cm^2



B3
After testing
crossover = 77 mA/cm^2



B7
After testing
crossover = 0.5 mA/cm^2

Defect formation and hydrogen cross-over are lower with chemically stabilized polymer (B7)

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Comparison to DOE Targets

Characteristic	Units	Target 2015	B1	B2	B3	B7	NRE 211
Area specific proton resistance[c] at:							
120°C and 70 kPa water partial pressure	Ohm cm^2	≤ 0.02	N/D	0.08	0.08	0.23	0.15
80°C and 38 kPa water partial pressure	Ohm cm^2	≤ 0.02	N/D	0.02	0.02	0.05	0.02
Maximum Hydrogen cross-over [a]	mA / cm^2	2	N/D	1	0.95	0.48	0.76
Minimum electrical resistance [b]	Ohm cm^2	1000	N/D	1200	800	500	2100
Performance @ 0.8V (¼ Power)	mA / cm^2 mW / cm^2	300 250	N/D N/D	104 84	177 142	150 120	113 91
Performance @ rated power	mW / cm^2	1000	N/D	334	567	482	363

* Values are at 80^{o}C unless otherwise noted

a. Measure in humidified H_2/N_2 at 25°C

b. Measure in humidified H_2/N_2 using LSV curve from 0.4 to 0.6 V at 80°C

c. Determined by subtracting contact resistances from cell current interrupt values

Some targets met, good progress towards remaining targets

Collaborations

Prime

- **FuelCell Energy, Inc.* (Industry):**
  - **Leading fuel cell developer for over 40 years**

Partners

- **University of Central Florida (University):**
  - **Membrane characterization, MEA fabrication & evaluation**
- **Oak Ridge National Lab (Federal Laboratory):**
  - **Membrane microstructural characterization**
- **Polymer Company* (Industry):**
  - **Polymer and membrane fabrication, initial characterization**
- **Additive Partners* (Industry/University):**
  - **Additives synthesis and characterization**
- **Consultant* (Industry):**
  - **Additive synthesis and integration into mC^2**

*** Within DOE H_2 Program**

Proposed Future Work

- **Fabricate most advanced polymer sample (lower EW, high MW, chemically stabilized)**
- **Use microstructural analysis data to guide mC^2 formulations and treatment**
- **Explore reproducibility of the casts that show improvements exceeding the goals**
- **Support UCF in electrode optimization using FCE ionomer**
- **Conduct longer-term single cell testing at 95 and 120°C (up to 1,000 hrs)**

Proposed Future Work

Upcoming Key Milestones:

- **Select low-cost, long life membrane design**
- **Readiness to meet DOE targets (durability tests)**
- **Final Membrane/MEA evaluation by DOE**

Project Summary

- **Developed MEA fabrication process with UCF that is compatible with mC^2**
- **Microstructural analysis shows highly dispersed particles in mC^2**
- **Improved membrane meets DOE conductivity and ASR targets at 120°C**
- **MEA has met targets for ASR (80°C), cross-over and electrical resistance**
- **Chemical stabilization results in improved membrane durability**
- **Cell performance analysis has identified electrode optimization opportunity**

Project Summary Table

Characteristic	Units	DOE 2015 Target	FY10-11 Result
Area specific proton resistance[c] at:			
120°C and 70 kPa water partial pressure	Ohm cm^2	≤ 0.02	0.08
80°C and 38 kPa water partial pressure	Ohm cm^2	≤ 0.02	0.02 ✓
Maximum Hydrogen cross-over [a]	mA / cm^2	2	0.95 ✓
Minimum electrical resistance [b]	Ohm cm^2	1000	1200 ✓
Performance @ 0.8V (¼ Power)	mA / cm^2 mW / cm^2	300 250	177 142
Performance @ rated power	mW / cm^2	1000	567

*Values are at 80^{o}C unless otherwise noted

a. Measure in humidified H_2/N_2 at 25°C

b. Measure in humidified H_2/N_2 using LSV curve from 0.4 to 0.6 V at 80°C

c. Determined by subtracting contact resistances from cell current interrupt values