FuelCell Energy

DOE Hydrogen Program

High Temperature Membrane with Humidification-Independent Cluster Structure

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FuelCell Energy, Inc.

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Project ID # FC040

Overview

Timeline

- Project start date: Jun 2006
- Project end date: Dec 2013
- Percent complete: 92%

Budget

- Total project funding
  - DOE share: $1600k
  - Cost share: $641k
- Funding received in FY12: $0
- Funding received in FY13: $100k

Barriers

A. Durability: Membrane and MEA durability

C. Performance: High MEA performance at low RH & high T

Partners

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

Relevance

Overall Objective:

Develop mechanically stabilized membranes that meet the DOE performance, life and cost targets, including improved area specific resistance and durability at 95 to 120°C and low relative humidity (25-50%).

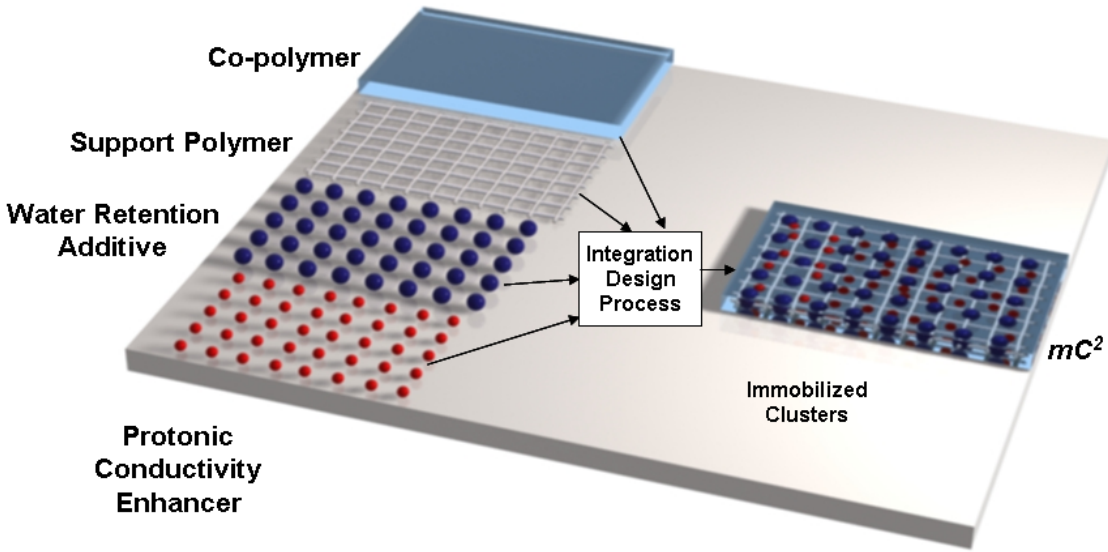
FY13 Obj.: Enhance durability using support polymer

Relevance

Development Objectives for Composite Membrane:

- **Fabricate mC^2 membranes with polymer support structure**
- Develop improved membrane polymer
- Develop membrane additives with high water retention (nano-zeolites)
- Develop membrane additives with high proton conductivity (superacids)
- Fabricate composite membranes (polymer + additives = mC^2)
- **Characterize supported membranes**
- **Scale-up considerations for cost reduction strategy**
- **Fabricate MEAs using promising membranes**
- **Characterize for chemical and mechanical stability**

Approach: mC^2 Concept



Improvements Made:

- **Introduced support polymer (2DSM™) from Giner, Inc.**

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

Multi-Component Composite Membrane (mC^2) with Functionalized Additives

Approach

DOE pursued a wide variety of approaches for High Temperature PEMFC membranes:

	Morphology	Molecular Approach			Additive Approach				Micro/nano engineering approach	
Conduction Mechanism		Other Polymer	Block Copolymer	Rigid Rods	ZrPhosphate	HPA	Zeolite	Other	Structured Support	Structured Ionomer
Aqueous										
	FC-SO3H	■			■	■		■	■	■
	HC-SO3H	■	■	■	■	■				■
	Hydrous Metal Oxides									
	sulfonyl imides	■						■		
Potential Non Aqueous										
	polyPOMs	■								
	Phosphates	■								
	Phosphonic acid	■								
	Phosphoric acids									
	Heterocyclic bases	■	■					■		
	Ionic liquids	■								

Reference: John Kopasz, HTMWG Meeting May 18, 2009

Membranes
3M, Arkema, DuPont, Plug Power, LANL, ANL, NREL, SNL, Colorado School of Mines, Penn State, Virginia Tech, Giner, U of Tenn, Case Western Reserve U (2), FuelCell Energy, Clemson U, GE Global Research, Arizona State U, U of Central Florida

Reference: Nancy Garland, 2006 AMR FC0

Approach

Build on Giner's parallel DOE program to manufacture low-cost high-strength membrane support structures

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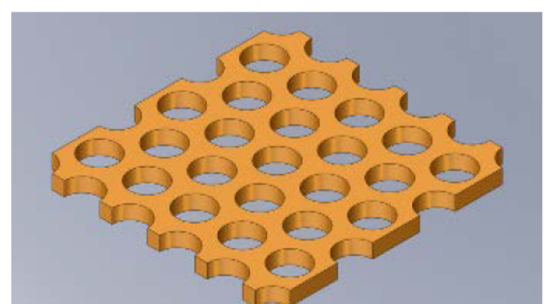
Approach: Criteria for DSM Manufacturing

- **Design:** 6-8 μm thick support structures with 8-20 μm diameter holes and 50% porosity to accommodate ionomers.
- **Process:** High tensile strength to handle in a roll-to-roll system without tearing and breaking
- **Performance:** Negligible expansion in the XY plane and preserved modulus when exposed to wet/dry cycles.
- **Durability:** High durability to survive 20,000 wet/dry cycles without crack failure.
- **Stability:** High-temperature stability in the range of -30 to 120°C

DSM support design with 20 μm hole diameter and 50% open area



Reference: fc036_mittelsteadt_2012_o

Approach

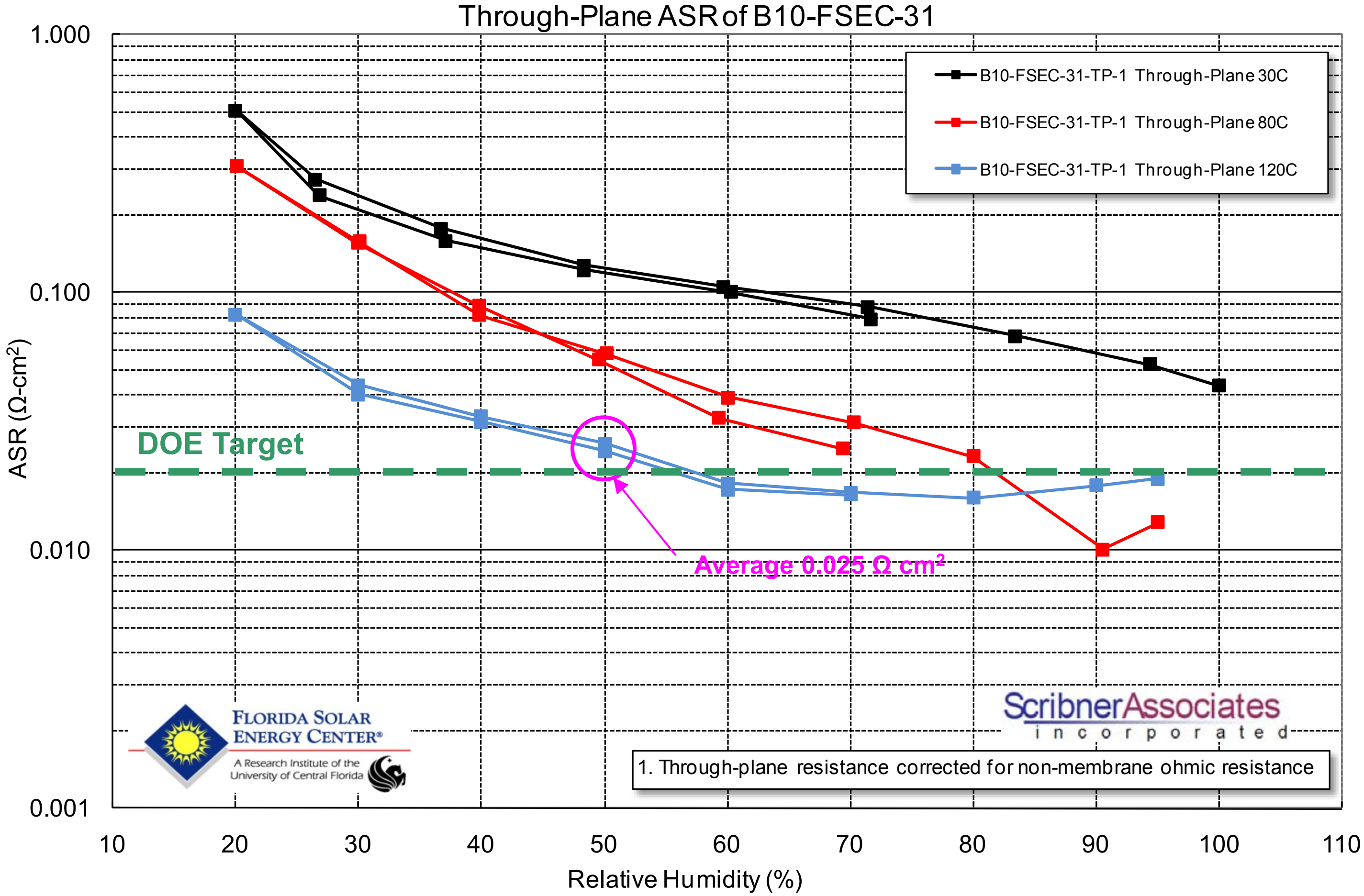
Target Parameter	DOE Target (2017)	Approach
Area specific proton resistance at: 120ÁC and 40-80 kPa water partial pressure	0.02 Ω cm^2	Multi-component composite structure, lower EW, polymer support for thinner membrane
80°C and 25-45 kPa water partial pressure	0.02 Ω cm^2	Higher number of functional groups
Hydrogen and oxygen cross-over at 1 atm	2 mA/cm^2	Support polymer for mechanically stronger membrane structure
Minimum electrical resistance	1000 Ω cm^2	Improved membrane thickness tolerance and additive dispersion
Cost	20 $\$/m^2$	Simplify polymer processing
Durability Mechanical (Cycles with <10 sccm crossover hrs)	>20,000	Mechanically strong support polymer for reduced swelling
Durability Chemical (Cycles with <10 sccm crossover hrs)	>500	Chemically stabilized ionomer

Accomplishments - FY12

- **High protonic conductivity – 0.113 S/cm* (DOE Target: >0.1 S/cm)**
- **Low cross-over – 0.3 mA/cm^2 * (DOE Target: <2 mA/cm^2)**
- **Low electrical conductivity (high electrical resistance)**
  – 2,860 Ωcm^2 * (DOE Target: >1000 Ωcm^2)
- **Transferred MEA Fabrication Technology to UCF**
  - Easily fabricated into an MEA (in UCF's Experience)
- **Good CCM performance – 1247 mW/cm^2 at rated power***
  (DOE Target: >1000 mW/cm^2)
- **Good durability in UCF 11-day test protocol**

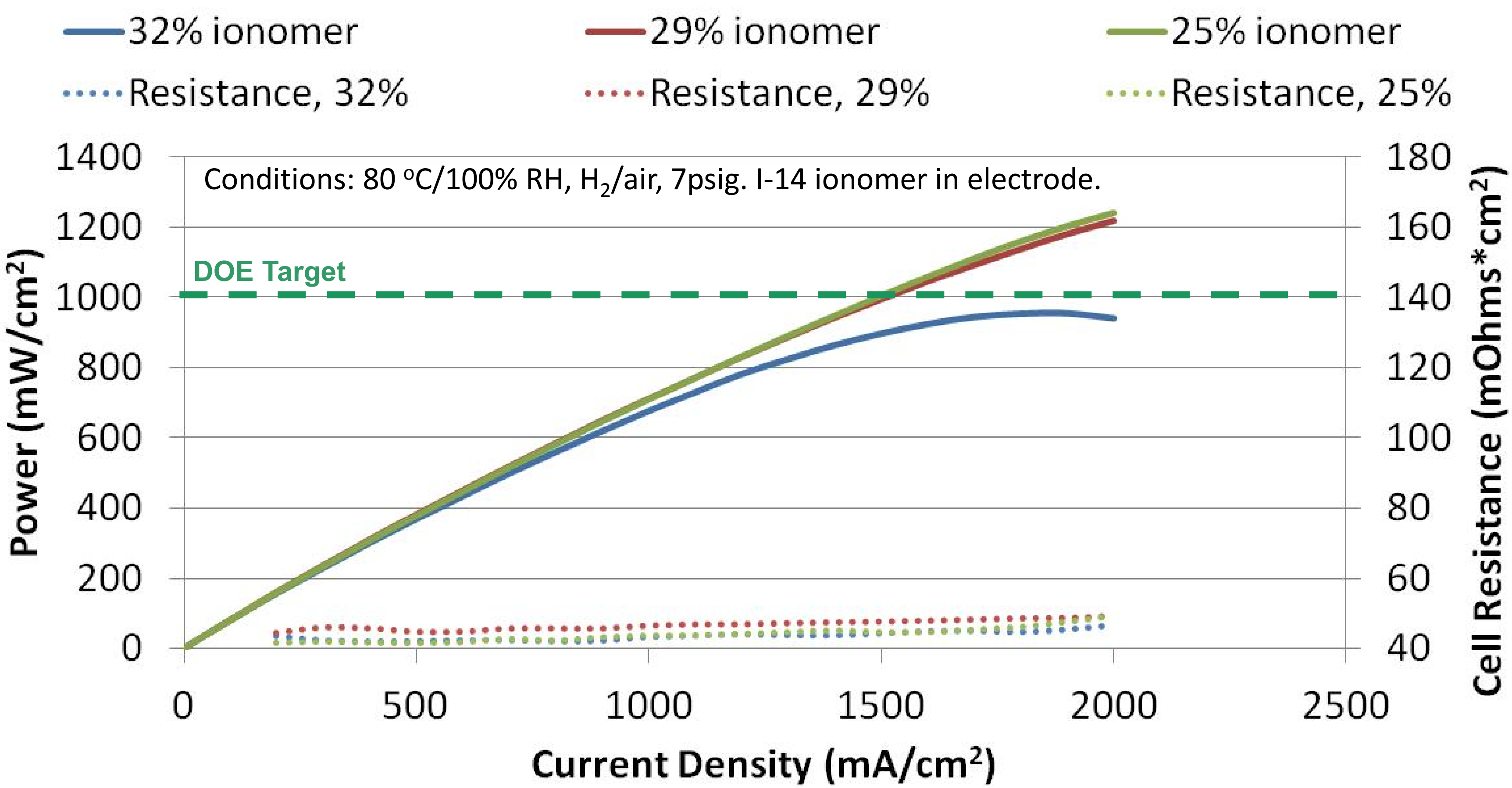
*** UCF Data**

Accomplishments: Area Specific Resistance



ASR almost meets the DOE target at 120°C and 50% RH

Accomplishments: mC^2 to MEA Development



Electrode Improvements Led to Higher Power

Accomplishments: MEA Comparison to DOE Targets

Characteristic	Units	Target 2017	B2	B3	B5	B7	B9	B10	NRE 211
Area specific proton resistance[c] at:									
120°C and 40 - 80 kPa pH_2O	Ohm cm²	≤ 0.02	0.08*	0.08*	0.064*	0.23*	0.110*	0.025*	0.15*
80°C and 25 - 45 kPa pH_2O	Ohm cm²	≤ 0.02	0.02‡	0.02‡	0.016‡	0.05‡	0.045‡	0.056‡	0.02‡
Maximum Hydrogen cross-over [a]	mA / cm²	2	1	0.95	1.6	0.48	<0.4	0.3	0.76
Minimum electrical resistance [b]	Ohm cm²	1000	1200	800	417	500	2,860	1,836	2100
Performance @ 0.8V (¼ Power)	mA/cm²	300	104	177	209	150	137	206	113
Performance @ rated power	mW/cm²	1000	334	567	1239	482	577	1247	363

*Measured at 120°C and 70 kPa water partial pressure

‡Measured at 80°C and 38 kPa water partial pressure

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

Most targets met, good progress towards remaining targets

→ Incorporating support to reach remaining targets

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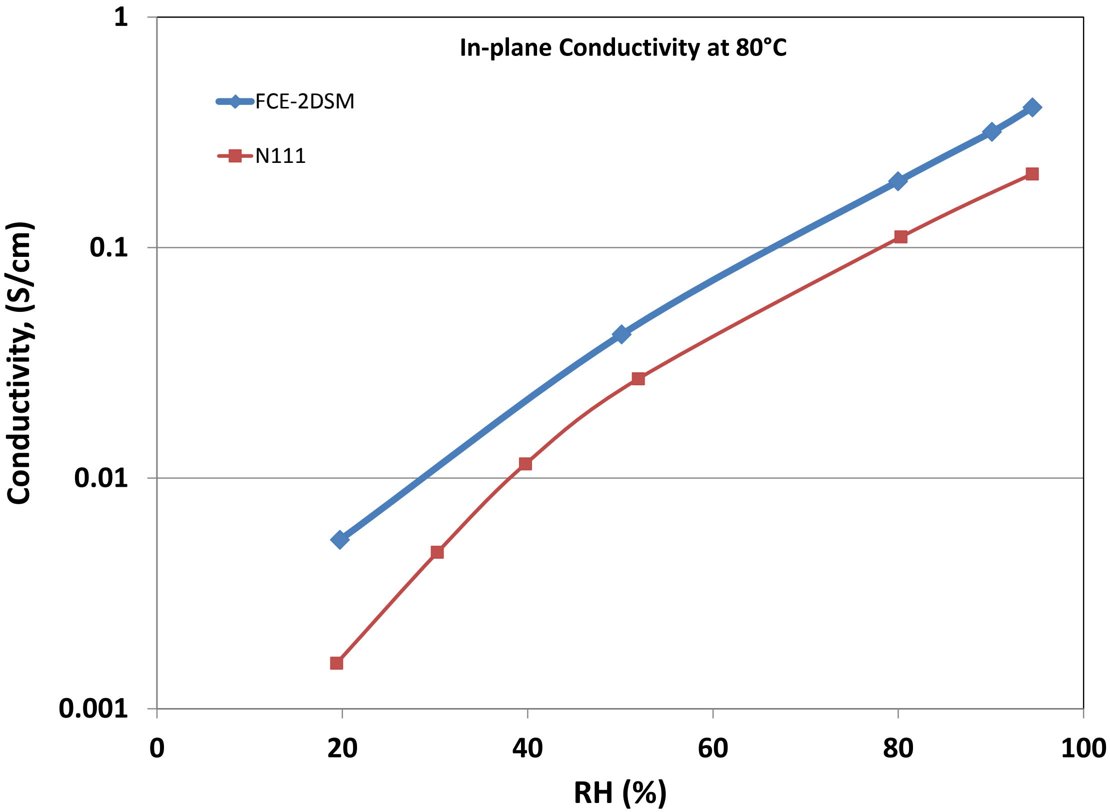
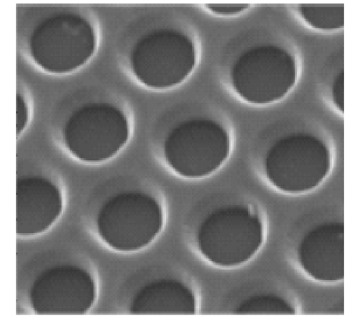
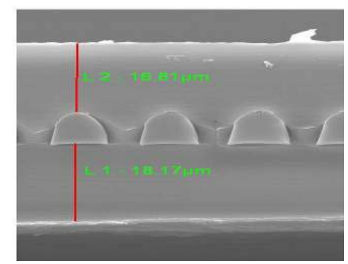
Accomplishments - FY13: Supported Membrane Conductivity





Giner, Inc. 2DSM™
Support Polymer



Giner, Inc. 2DSM™
Composite Membrane
cross-section

Initial sample fabricated successfully – conductivity promising

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Collaborations

Prime

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

Partners

- **Giner, Inc.: Supported membrane fabrication and characterization**
- University of Central Florida (University):
  - Membrane characterization, MEA fabrication & evaluation
- Scribner Associates, Inc. and BekkTech LLC (Industry):
  - Membrane through-plane and in-plane conductivity
- **Oak Ridge National Lab (Federal Laboratory):**
  - **Membrane and additive microstructural and chemical characterization**
- **Polymer Company (Industry):**
  - **Polymer and membrane fabrication, initial characterization**
- Additive Partners (Industry/University):
  - Additives synthesis, functionalization and characterization
- **LGC Consultant LLC (Industry):**
  - **Additive synthesis and integration into mC^2**

FuelCell Energy GINER OAK RIDGE National Laboratory ScribnerAssociates incorporated FLORIDA SOLAR ENERGY CENTER® A Research Institute of the University of Central Florida

Proposed Future Work

- Supported membrane fabrication: process improvements, ionomer optimization
- Ex-situ membrane characterization (dimensional stability, gas permeability, membrane conductivity as function of T and RH, mechanical properties)
- MEA testing: Meet ASR target of 0.02 Ω cm^2 at 120°C and 50% RH and cross-over target of 2 mA/cm2
- Complete mechanical and chemical stability characterization per DOE protocols
- 25 cm^2 cell testing for durability at 95°C and 120°C up to 1000 hrs

Progress Summary

- **Developed technology to synthesize mC² components and to integrate them**
- **mC² exceeds DOE 120°C conductivity target at 50% RH and approaches ASR target**
- **Developed MEA fabrication process with UCF that is compatible with mC²**
- **Preliminary optimization of ionomer content in cathode led to good 120°C MEA performance of 510 mV at 1 A/cm², 35% RH (UCF)**
- **Cell data exceeds DOE power density target (UCF)**
- **Fabricated initial supported membrane samples**

Project Summary Table

Characteristic	Units	DOE 2017 Target	FY12 Result
Area specific proton resistance at:			
120°C and 40-80 kPa water partial pressure [c]	Ohm cm^2	≤ 0.02	0.025
80°C and 25-45 kPa water partial pressure [c]	Ohm cm^2	≤ 0.02	0.016✓
Maximum Hydrogen cross-over [a]	mA / cm^2	2	0.3 ✓
Minimum electrical resistance [b]	Ohm cm^2	1000	2,860 ✓
Performance @ 0.8V (¼ Power)	mA / cm^2	300	209
Performance @ rated power	mW / cm^2	1000	1247 ✓

*Values are at 80°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

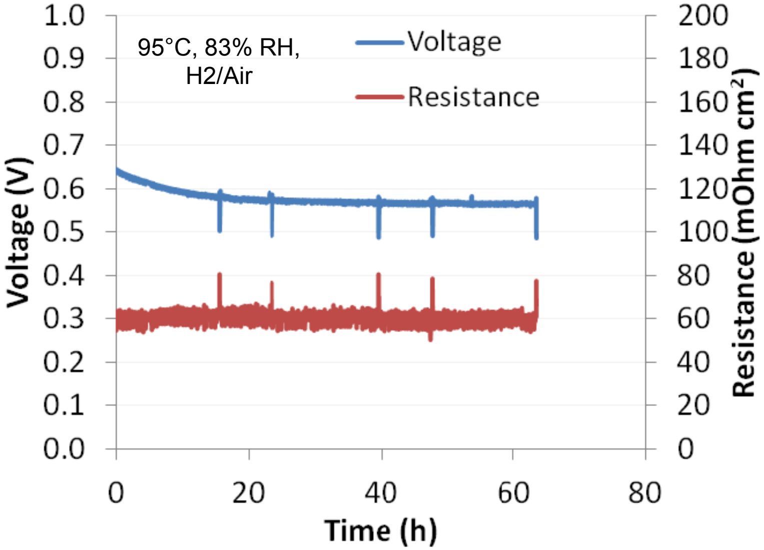
c. Determined by subtracting contact resistances from cell current interrupt values

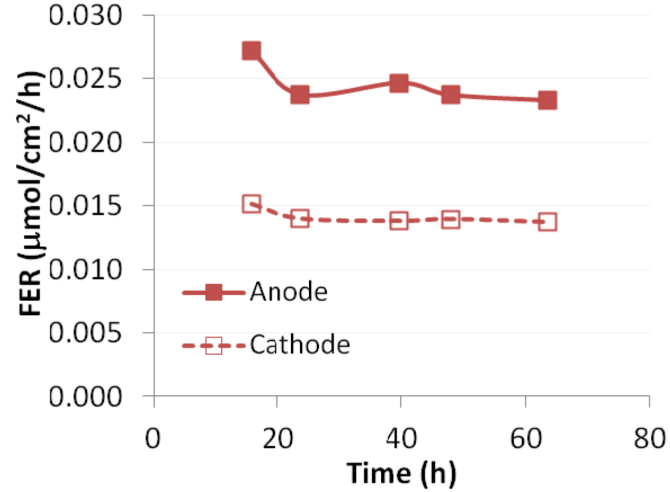
Acknowledgements

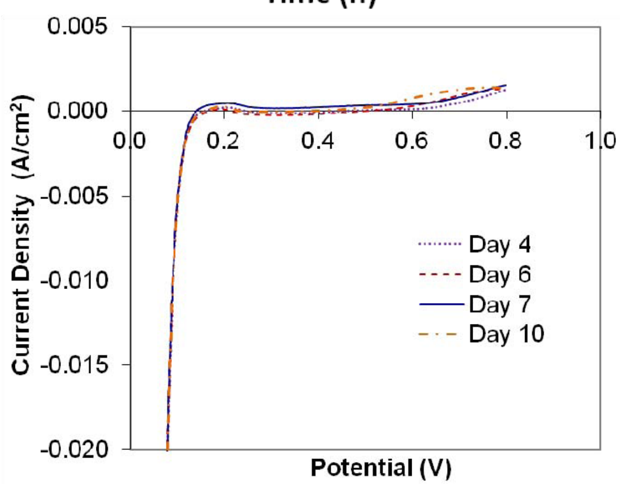
- DOE: Donna Ho, Greg Kleen, Tom Benjamin, Kathi Epping Martin, Jason Marcinkoski, Amy Manheim, Reg Tyler and John Kopasz
- Giner, Inc.: Cortney Mittelsteadt, Shelly Brawn (DSM fab. & charact.)
- UCF: Jim Fenton, Darlene Slattery, Marianne Rodgers, Paul Brooker, Nahid Mohajeri, Len Bonville, Russ Kunz (Testing protocols, membrane and MEA evaluation)
- Scribner Associates, Inc.: Kevin Cooper (Conductivity measurements)
- BekkTech LLC: Tim Bekkedahl (In-plane conductivity)
- ORNL: Kelly Perry, Karren More (Microstructural characterization)
- LGC Consultant LLC: Larry Christner
- FCE Team: Pinakin Patel, Ray Kopp, Jonathan Malwitz, Chao-Yi Yuh, Nikhil Jalani, Adam Franco, Al Tealdi

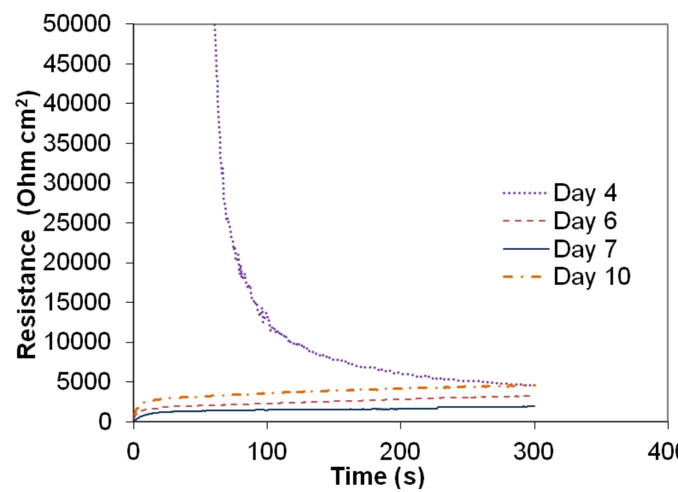
Technical Back-Up Slides

Accomplishments: mC^2 Performance Stability









Promising Stability at 95°C

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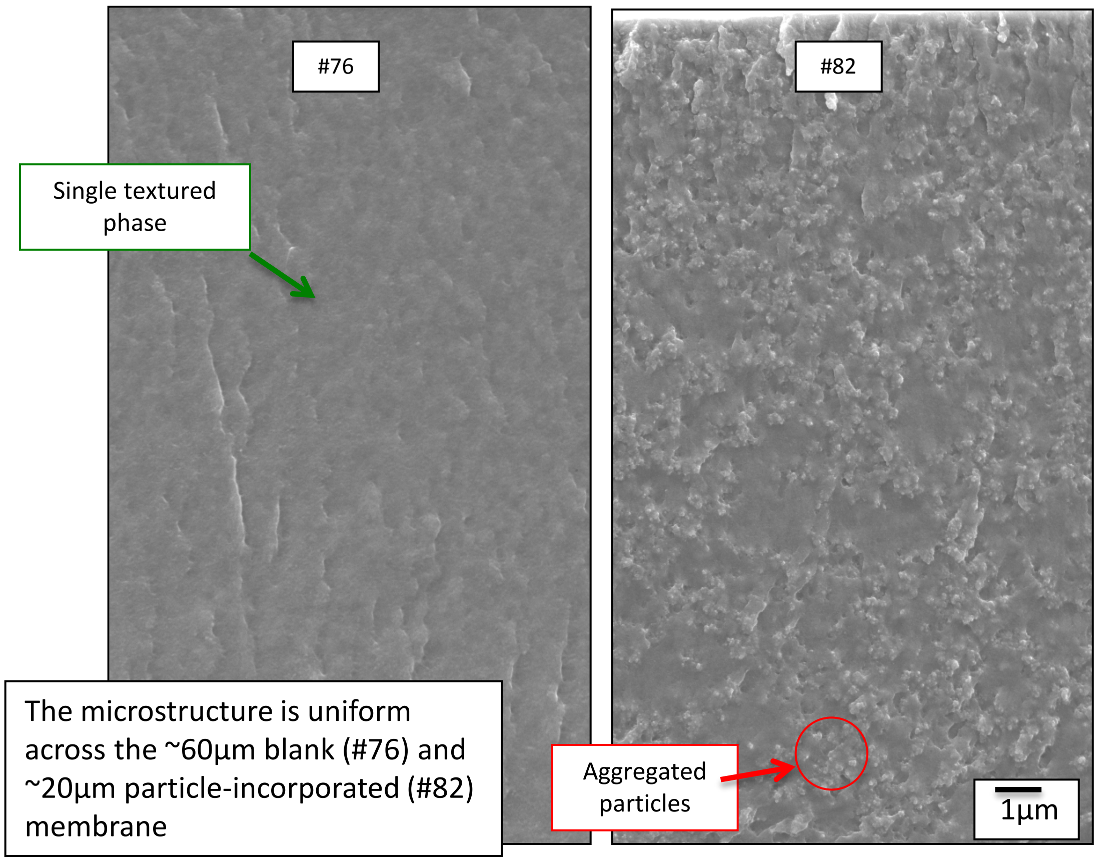
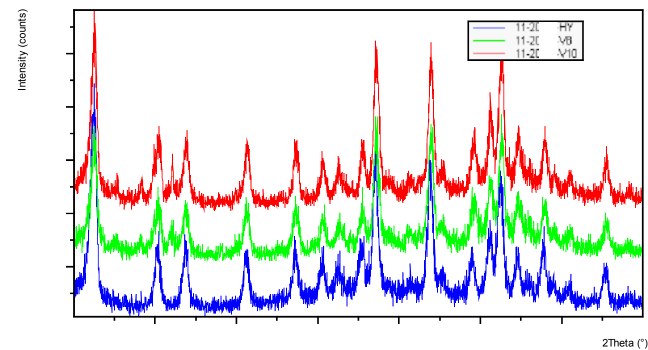
Accomplishments: mC^2 Characterization

Relatively homogeneous dispersion of aggregated particles are observed in the membrane (#82) with a higher loading. The aggregated particles may have achieved a continuous 3-dimensional network.





Nano-zeolite structure remains intact after superacid deposition

Achieved good distribution of additives in mC^2

Oak Ridge National Laboratory

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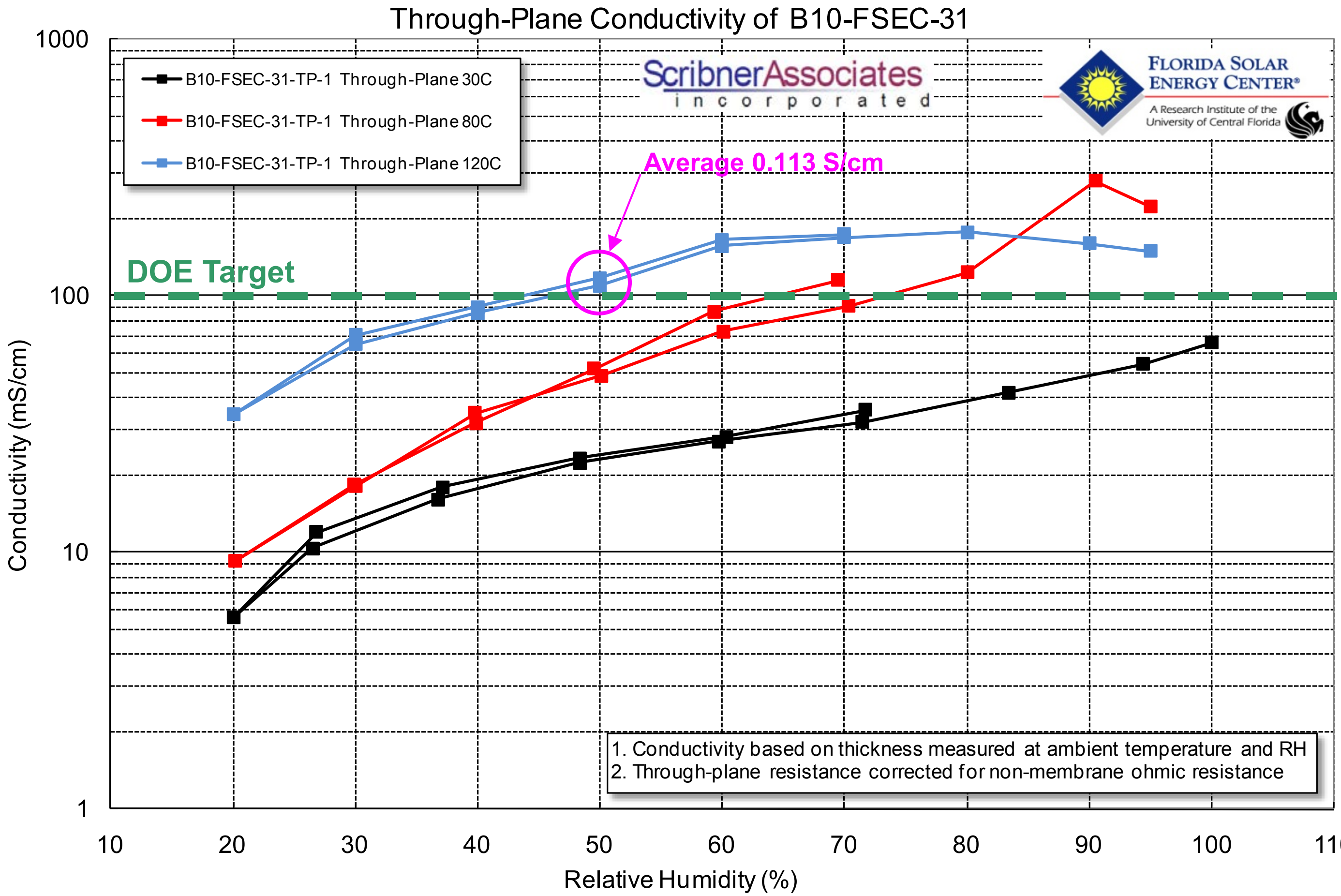
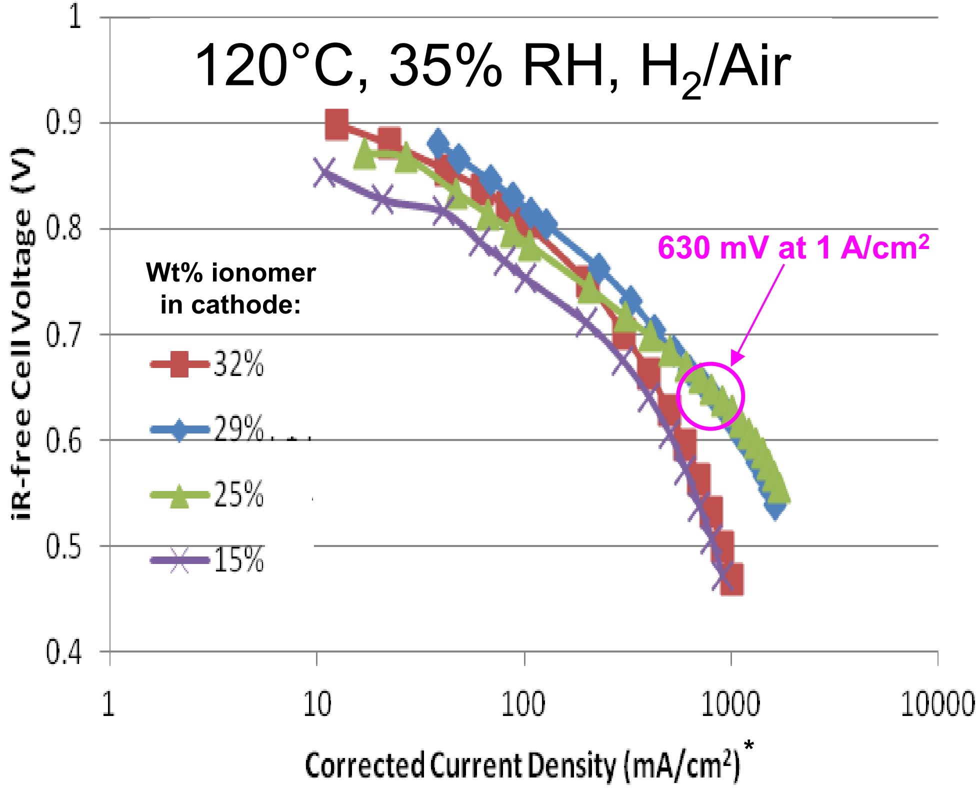
Accomplishments: mC² Conductivity

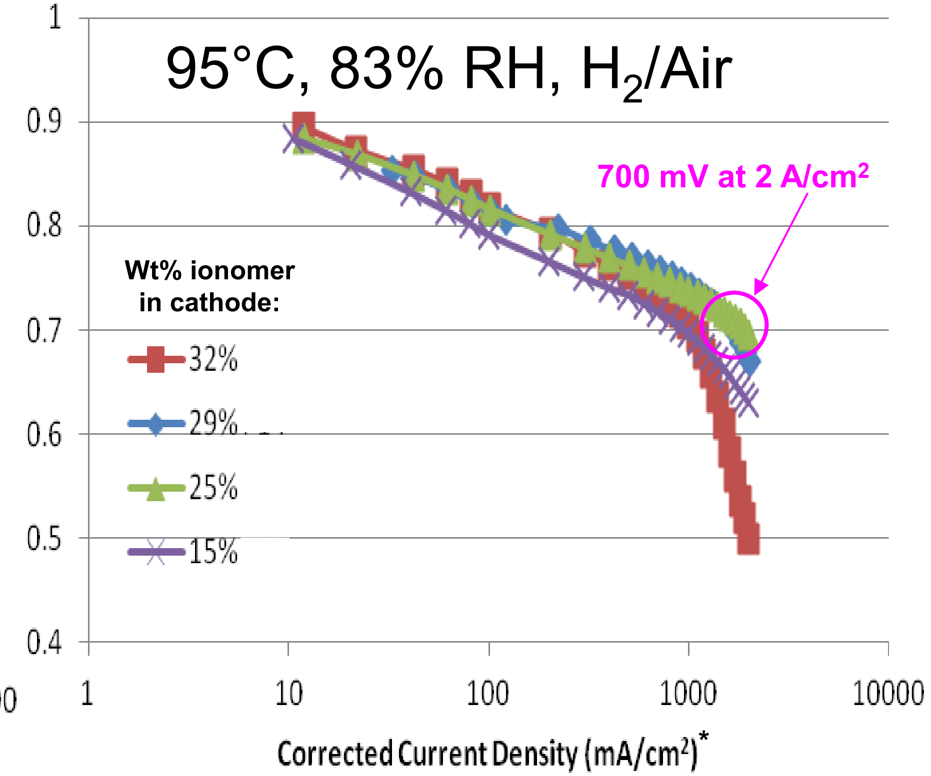


Conductivity Milestone at 120°C has been Independently Validated

Accomplishments: Electrode Improvements

MEA performance as function of ionomer dry weight in the cathode electrode





* Corrected for Crossover H_2: Limiting current density in the Linear Sweep Voltammogram was deducted from the measured current densities in the polarization curves to isolate the effect of ionomer content in the cathode.

- **mC^2 Required Re-optimization of the MEA**
- **Achieved High Performance at High Temp. and High Current Density**

Accomplishments: Risk Resolution

Issues	Resolution
Produce Stable Nanozeolites	Completed
Produce Nanozeolite Superacid Composites	Completed
Produce mC^2/Polymer Composites	Completed
Increase Production Capacity of Nanozeolite	Completed
Decrease Cost of Superacids	Completed
Demonstrate Improved Conductivity	Completed
Demonstrate Reproducibility of Select Systems	Completed
Identify Best Slurry Compositions, Casting Substrates and Treatment Conditions that give Improved Conductivity	Completed
In-cell characterization and durability	In progress