High Temperature Membrane with Humidification-Independent Cluster Structure

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May 18th, 2012

Project ID # fc040

Overview

Timeline

- Project start date: Jun 2006
- Project end date: Aug 2012
- Percent complete: 96%

Budget

- Total project funding
  - DOE share: $1500k
  - Cost share: $600k
- Funding received in FY11: $168k
- Planned Funding for FY12: $65k

Barriers

A. Durability: Membrane and MEA durability

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

Partners

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

Relevance

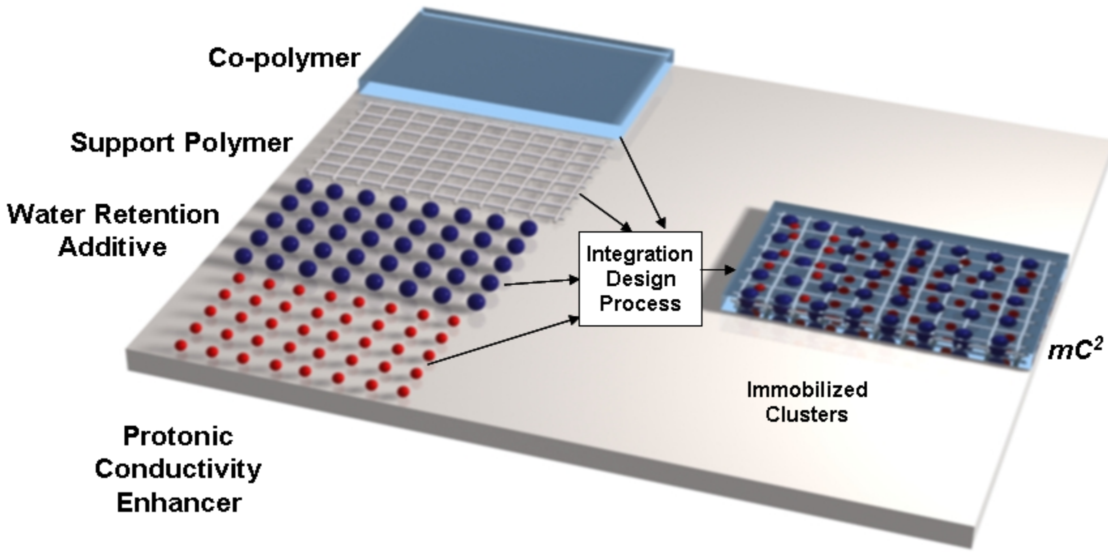
Development Objectives for Composite Membrane:

- **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 polymer, additives and composite membranes**
- **Scale-up considerations for cost reduction strategy**
- **Fabricate MEAs using promising membranes and characterize**

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, additives with highly mobile protons
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	Higher molecular weight polymer for stronger membrane structure
Minimum electrical resistance	1000 Ω cm^2	Improved membrane thickness tolerance and additive dispersion
Cost	20 $\$/m^2$	Simplify polymer processing
Performance @ 0.8 V (¼ rated power)	300 mA/cm^2	MEA with matching polymer in membrane and electrodes
Performance @ rated power	1,000 mW/cm^2	Optimized ionomer content in electrodes

Approach: mC^2 Concept



Improvements Made:

- 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

Major Accomplishments

- **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: Risk Resolution

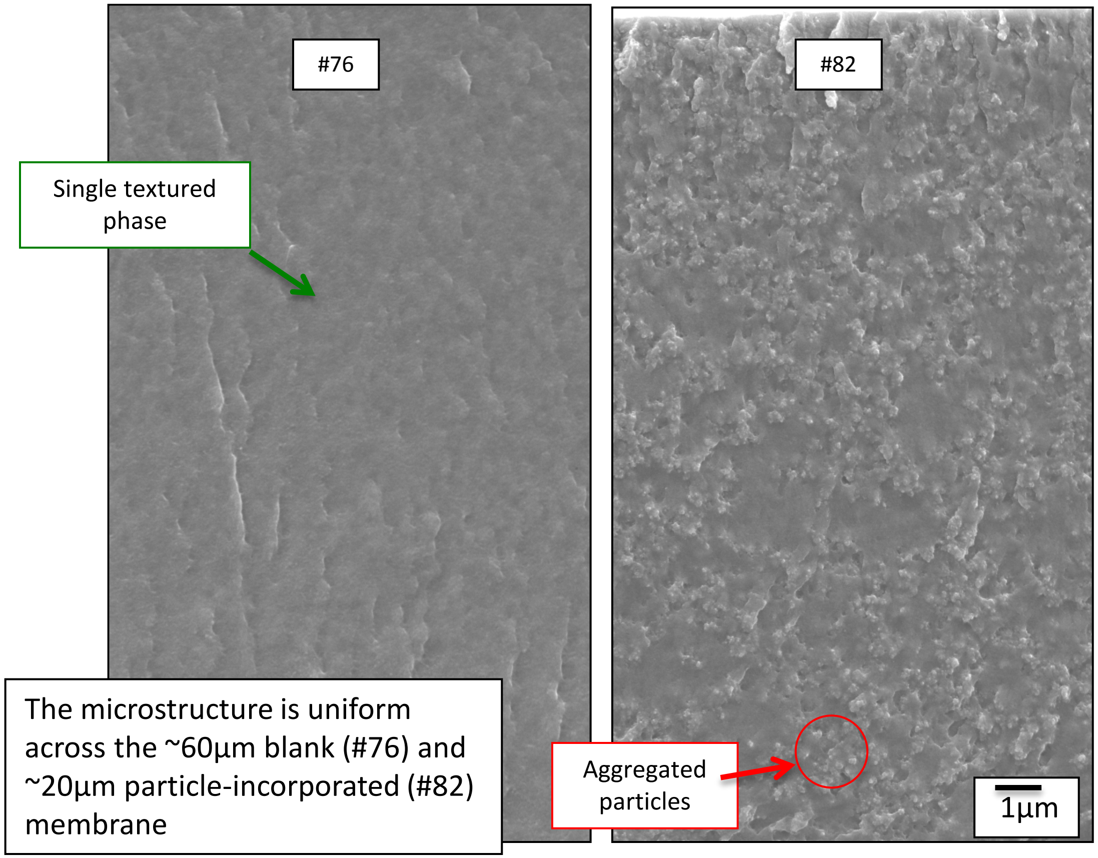
Issues	Resolution
Produce Stable Nanozeolites	Completed
Produce Nanozeolite Superacid Composites	Completed
Produce mC^2/Polymer Composites	Completed
Increase Production Capacity of Nanozeolite	Completed
Decrease Cost of Superacids	Completed
Demonstrate Improved Conductivity	Completed
Demonstrate Reproducibility 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

Accomplishments: IP Discoveries

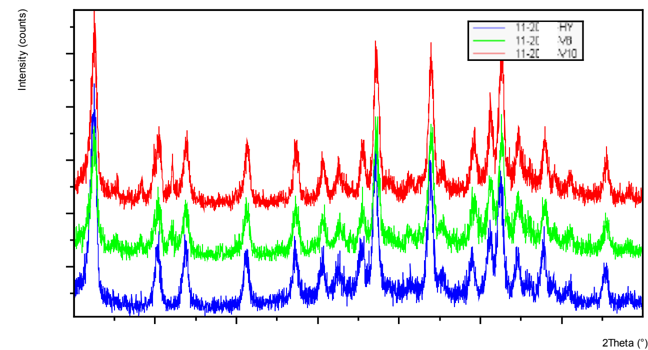
- The key factor to maintain nanoparticle zeolites indefinitely
- The adsorption of superacids on zeolite without affecting the zeolite structure
- The use of novel superacids in fuel cells
- The use of superacids adsorbed on zeolites in fuel cells
- The potential use of superacids adsorbed on zeolites as new H^+ acid catalysts
- The key fact that casting solvents can reduce measured conductivities by an order of magnitude but can be removed by acid wash or time in high RH gas streams

Accomplishments: mC² 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.



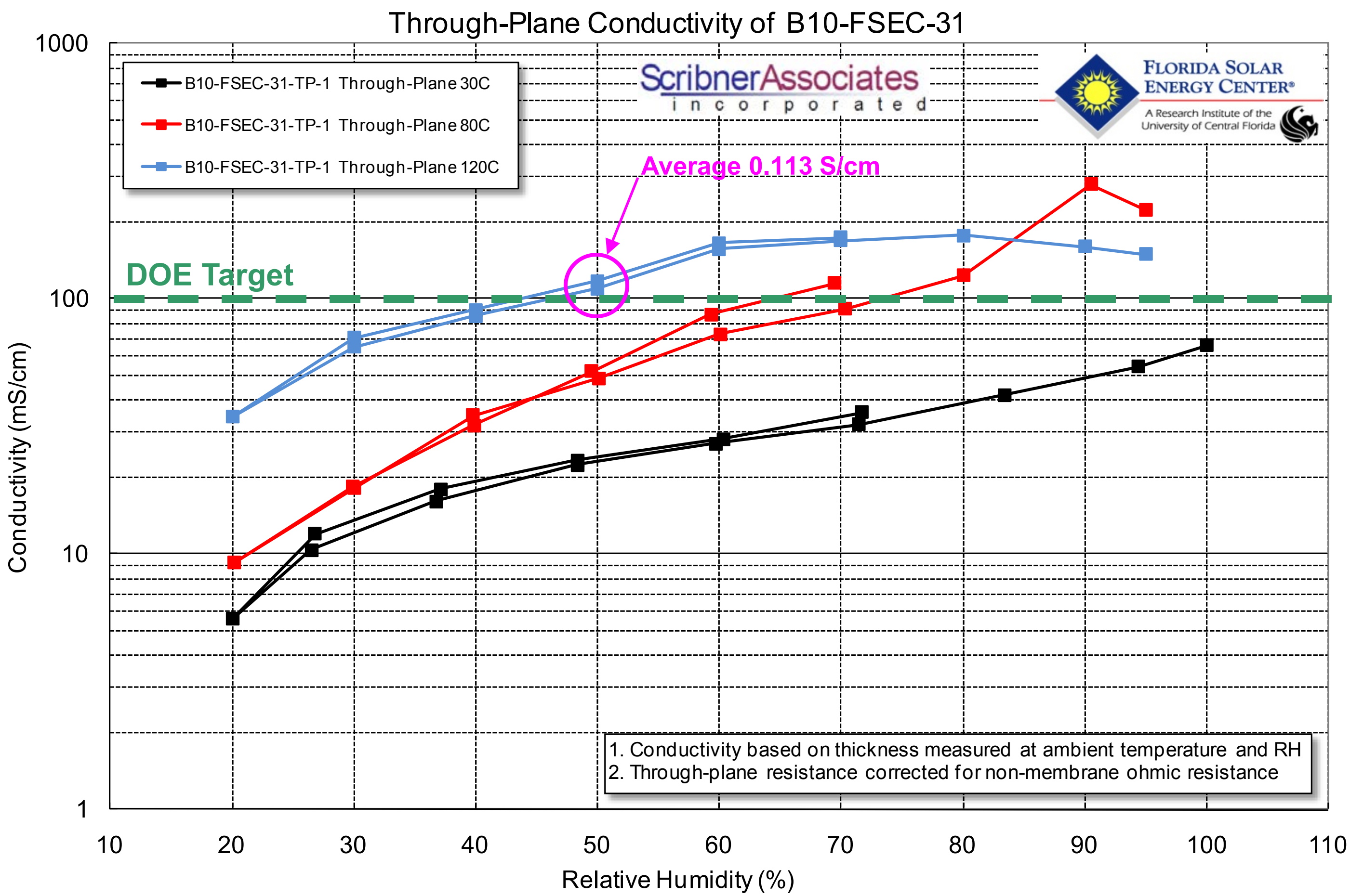
The microstructure is uniform across the ~60µm blank (#76) and ~20µm particle-incorporated (#82) membrane



Nano-zeolite structure remains intact after superacid deposition

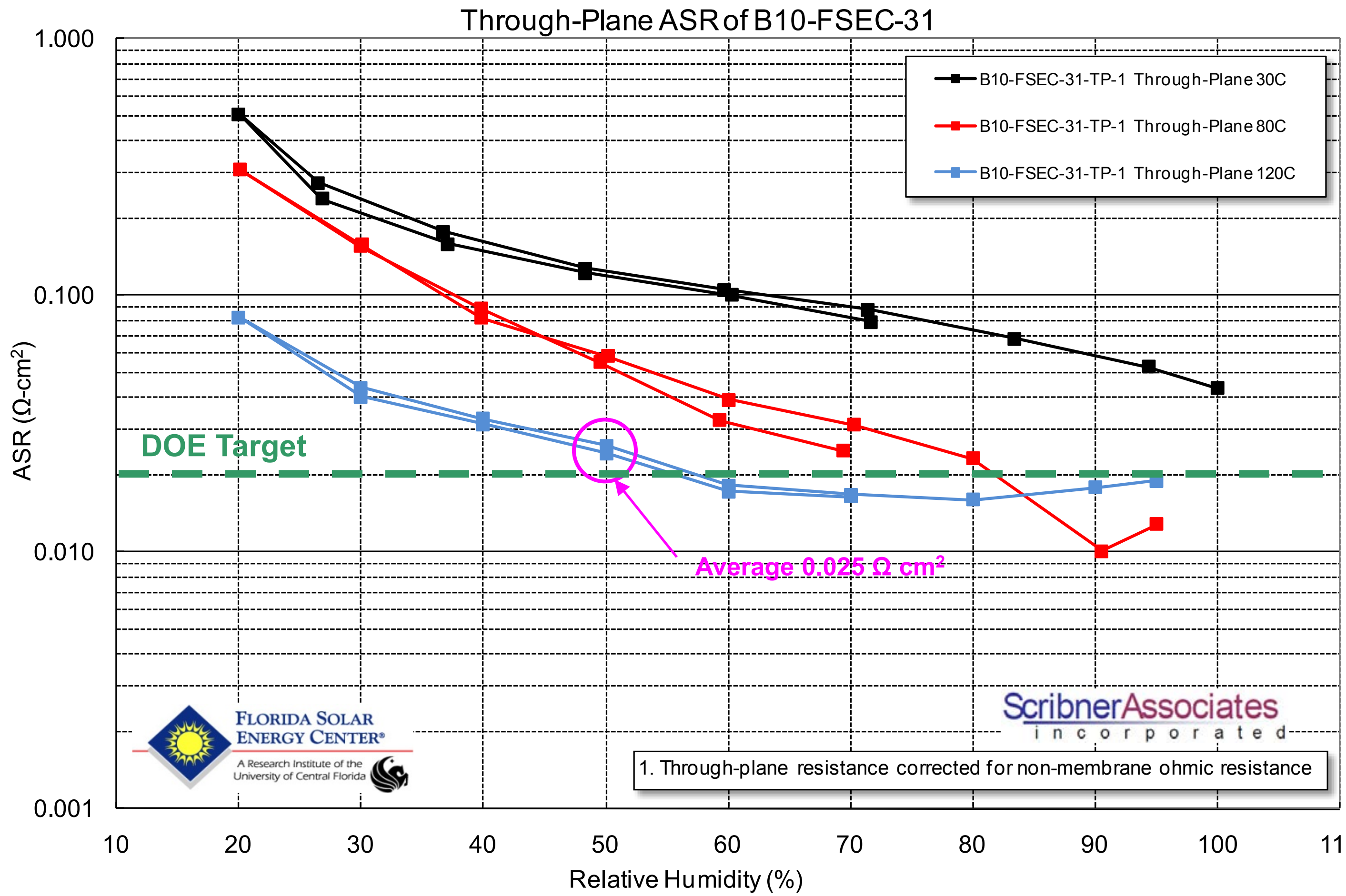
Achieved good distribution of additives in mC²

Accomplishments: mC^2 Conductivity



Conductivity Milestone at 120°C has been Independently Validated

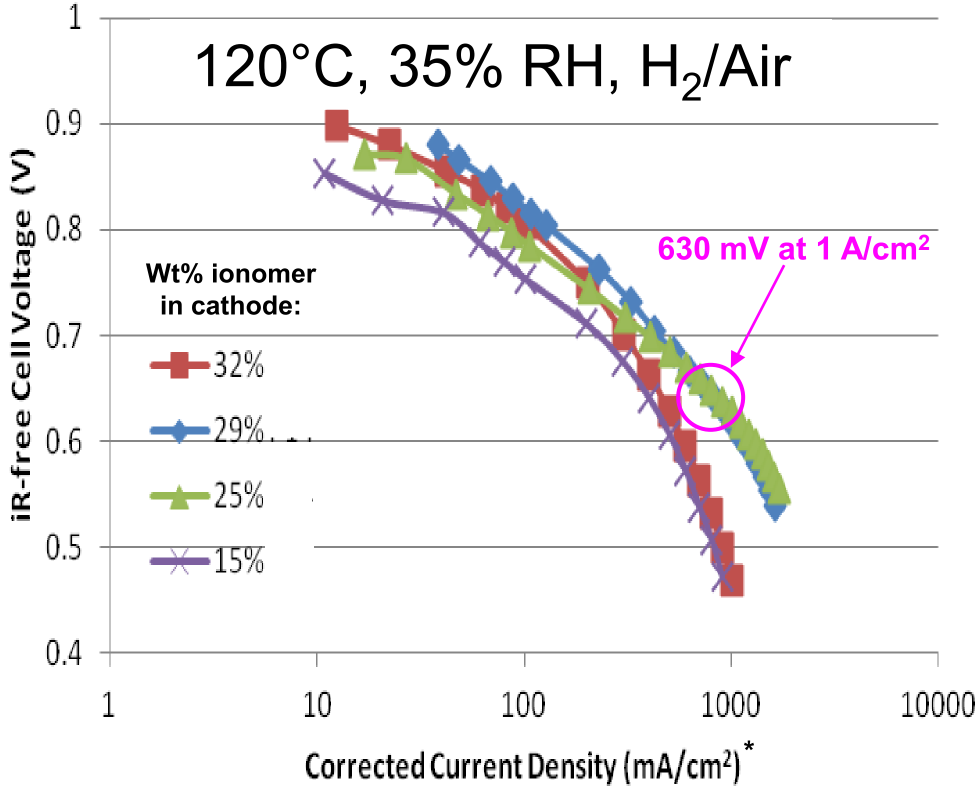
Accomplishments: Area Specific Resistance

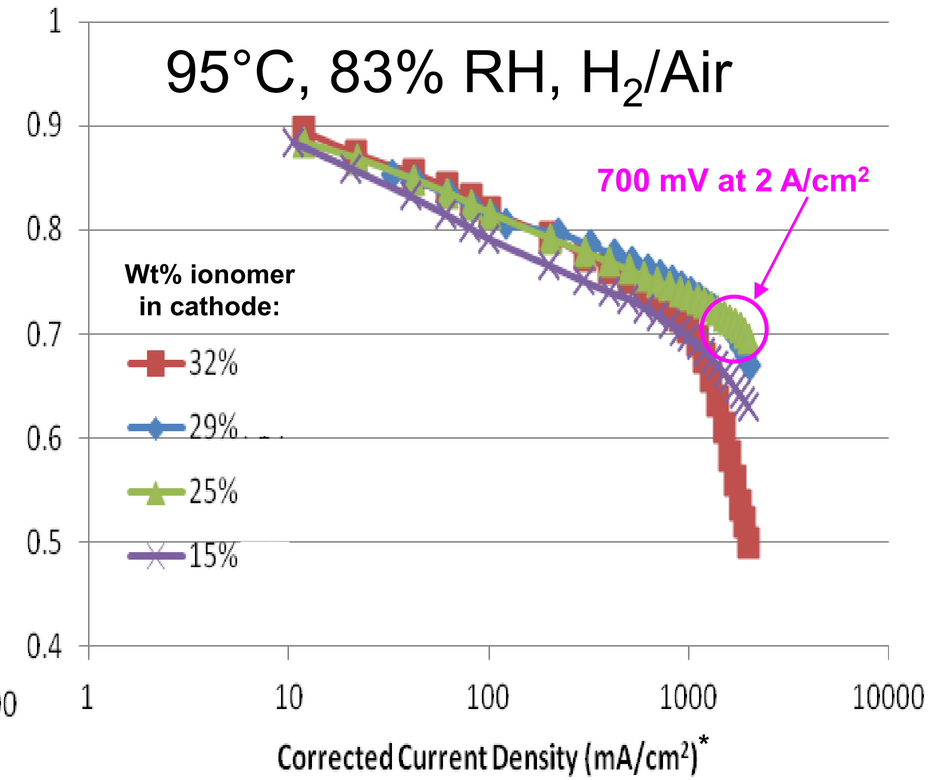


ASR almost meets the DOE target at 120°C and 50% RH

Accomplishments: Electrode Improvements

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

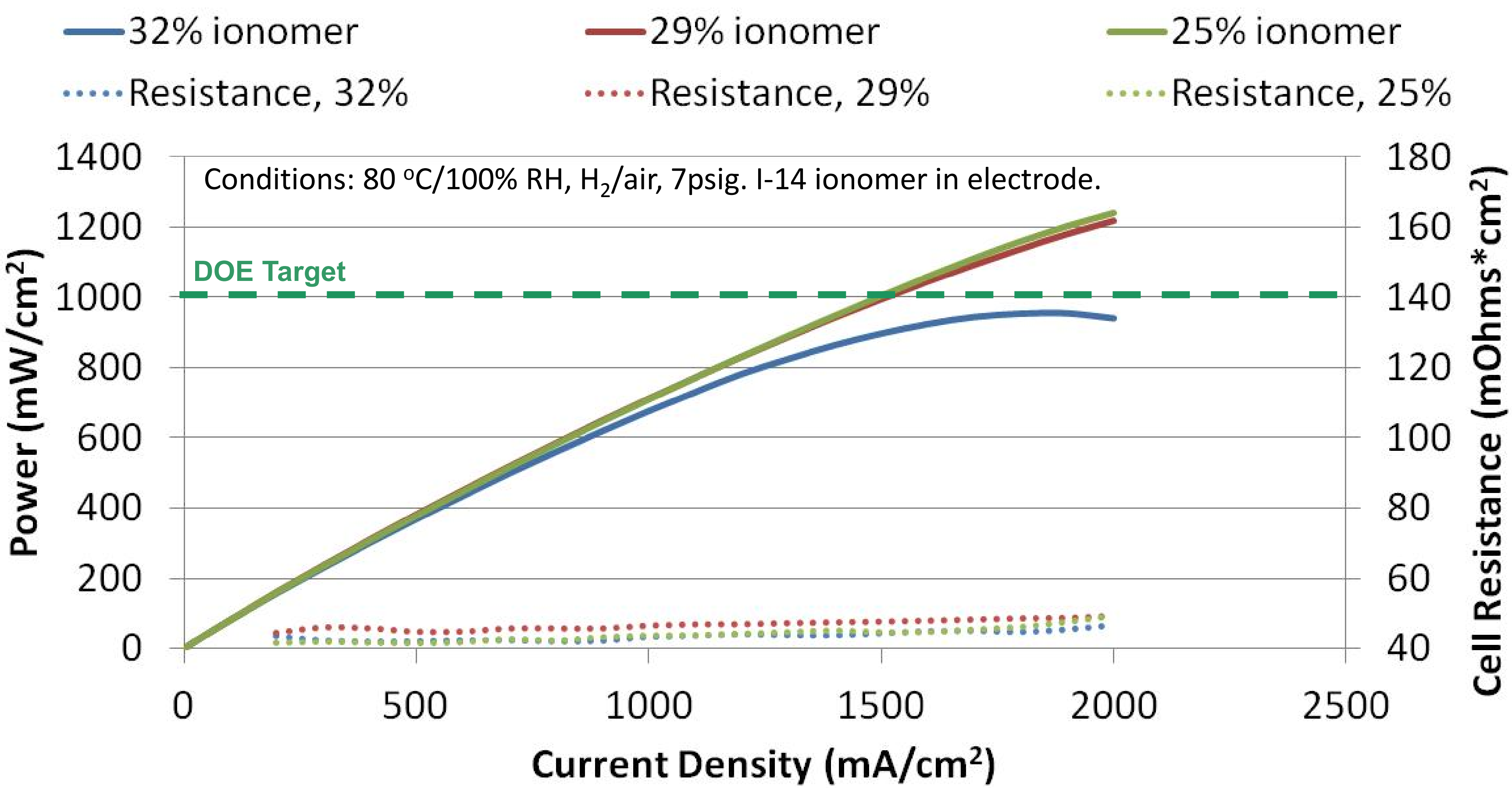




* Corrected for Crossover H_2: Limiting current density in the Linear Sweep Voltammogram was deducted from the measured current densities in the polarization curves to isolate the effect of ionomer content in the cathode.

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

Accomplishments: mC^2 to MEA Development



Electrode Improvements Led to Higher Power

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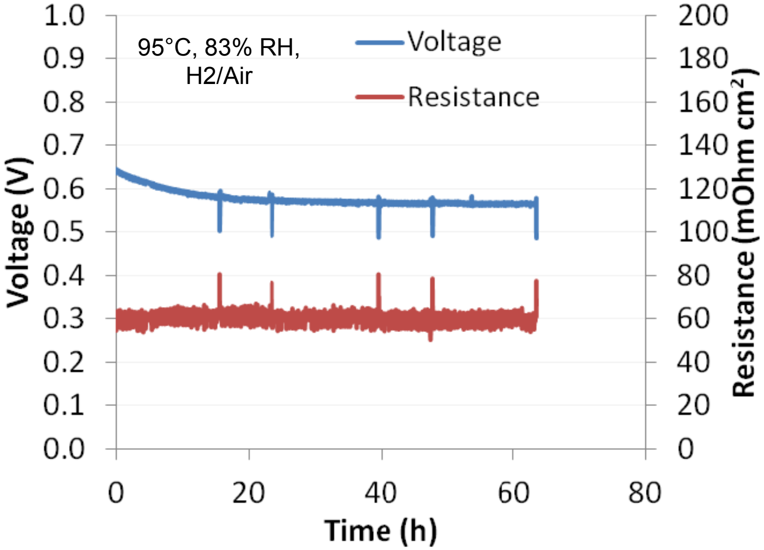
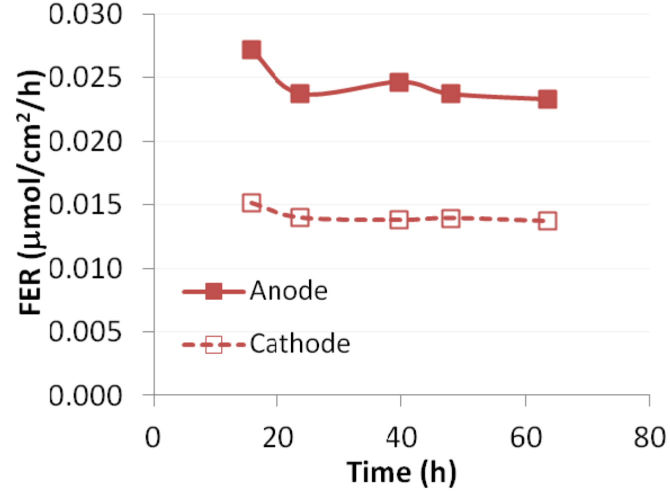
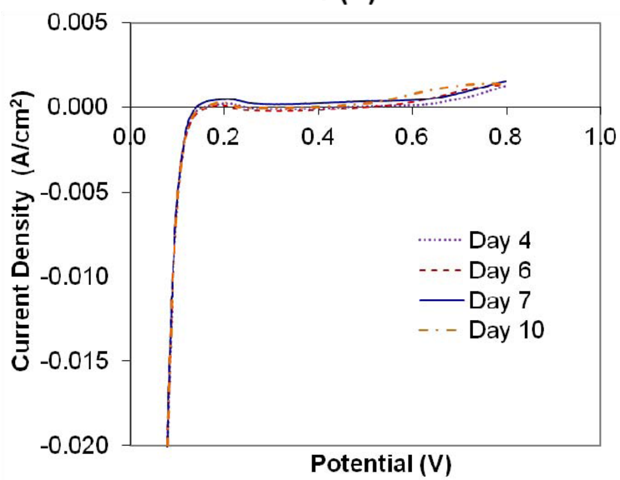
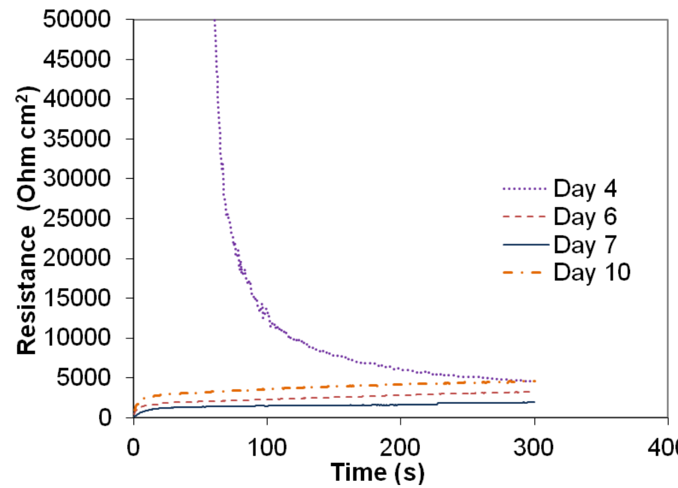
Accomplishments: mC² Performance Stability









Promising Stability at 95°C

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 cm^2	≤ 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 cm^2	≤ 0.02	0.02‡	0.02‡	0.016‡	0.05‡	0.045‡	0.056‡	0.02‡
Maximum Hydrogen cross-over [a]	mA / cm^2	2	1	0.95	1.6	0.48	<0.4	0.3	0.76
Minimum electrical resistance [b]	Ohm cm^2	1000	1200	800	417	500	2,860	1,836	2100
Performance @ 0.8V (¼ Power)	mA/cm^2	300	104	177	209	150	137	206	113
Performance @ rated power	mW/cm^2	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

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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**
- **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

Oak Ridge National Laboratory

Scribner Associates incorporated

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Collaborations: Team Efforts

- **Polymer: Synthesized >20 batches of polymer and ionomer dispersion**
- **Water-retaining Additive: Synthesized and purified >30 batches of nano-zeolite**
- **Protonic Conductivity Enhancer: Synthesized >5 batches of 1 and 2-proton molecules**
- **Functionalized Additive: Fabricated 3 batches of Protonic Conductivity Enhancer deposited on Water-retaining Additive**
- **Membrane and mC^2 Fabrication: >15 batches of polymer membrane film and >30 batches of mC^2 membrane film**
- **Microstructural Characterization: ORNL characterized >10 membrane samples and >10 additive samples**
- **MEA: UCF fabricated 13 MEAs**
- **Cell Testing: >30 cells tested, including 12 cells at UCF**

Proposed Future Work

- Durability: Characterization of mC^2 mechanical and chemical stability per DOE protocols (UCF – funding permitting)
- Complete invention disclosure
- Complete final report

Progress Summary

- **Developed technology to synthesize mC^2 components and to integrate them**
- **Membrane exceeds DOE 120°C conductivity target at 50% RH and approaches ASR target**
- **Developed MEA fabrication process with UCF that is compatible with mC^2**
- **Preliminary optimization of ionomer content in cathode led to good 120°C MEA performance of 510 mV at 1 A/cm^2, 35% RH (UCF)**
- **At near-term target of 95°C: 585 mV at 2 A/cm^2, 83% RH (UCF)**
- **Cell data exceeds DOE power density target (UCF)**

Project Summary Table

Characteristic	Units	DOE 2017 Target	FY11-12 Result
Area specific proton resistance[c] at:			
120°C and 40-80 kPa water partial pressure	Ohm cm^2	≤ 0.02	0.025
80°C and 25-45 kPa water partial pressure	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^{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

Acknowledgements

- **DOE: Donna Ho, Greg Kleen, Tom Benjamin, Kathi Martin, Jason Marcinkoski, Amy Manheim, Reg Tyler and John Kopasz**
- **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)**
- **FCE Team: Pinakin Patel, Ray Kopp, Jonathan Malwitz, Chao-Yi Yuh, Nikhil Jalani, Adam Franco, Al Tealdi**