FuelCell Energy

DOE Hydrogen Program

# High Temperature Membrane with Humidification-Independent Cluster Structure

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# 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

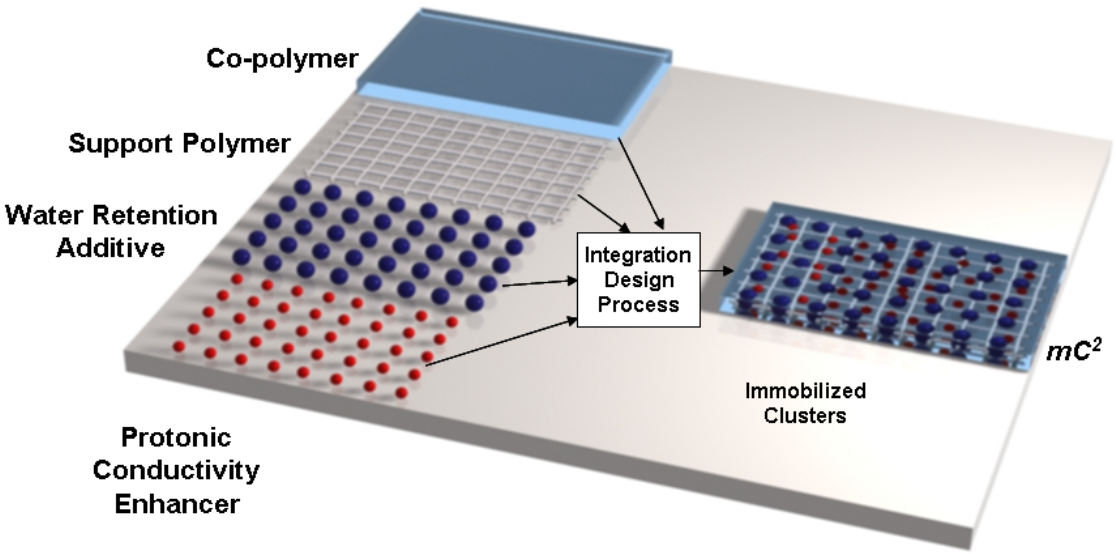
**Development Objectives for Composite Membrane:**

- **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

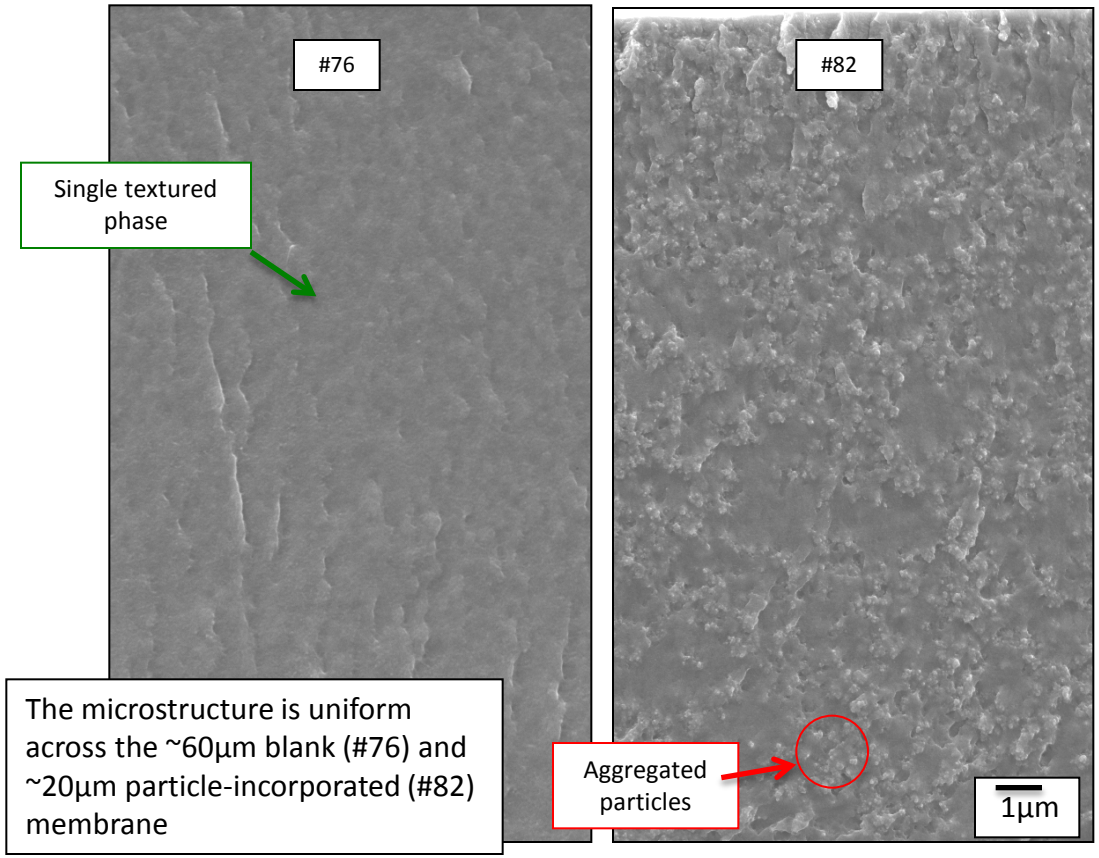
| Issues | Resolution |
|---|---|
| Produce Stable Nanozeolites | Completed |
| Produce Nanozeolite Superacid Composites | Completed |
| Produce $mC^2$/Polymer Composites | Completed |
| Increase Production Capacity of Nanozeolite | Completed |
| Decrease Cost of Superacids | Completed |
| Demonstrate 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

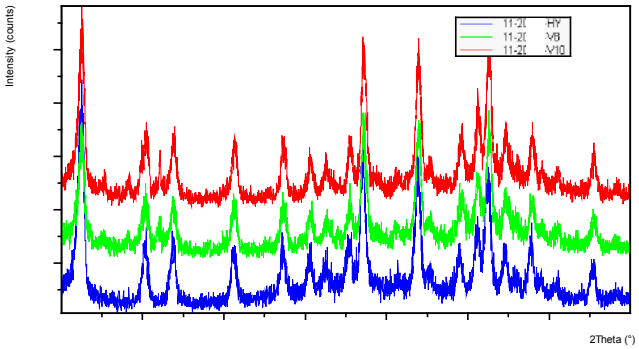
- The key factor to maintain nanoparticle zeolites indefinitely
- The adsorption of superacids on zeolite without affecting the zeolite structure
- The use of novel superacids in fuel cells
- The use of superacids adsorbed on zeolites in fuel cells
- The potential use of superacids adsorbed on zeolites 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: $mC^2$ 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.



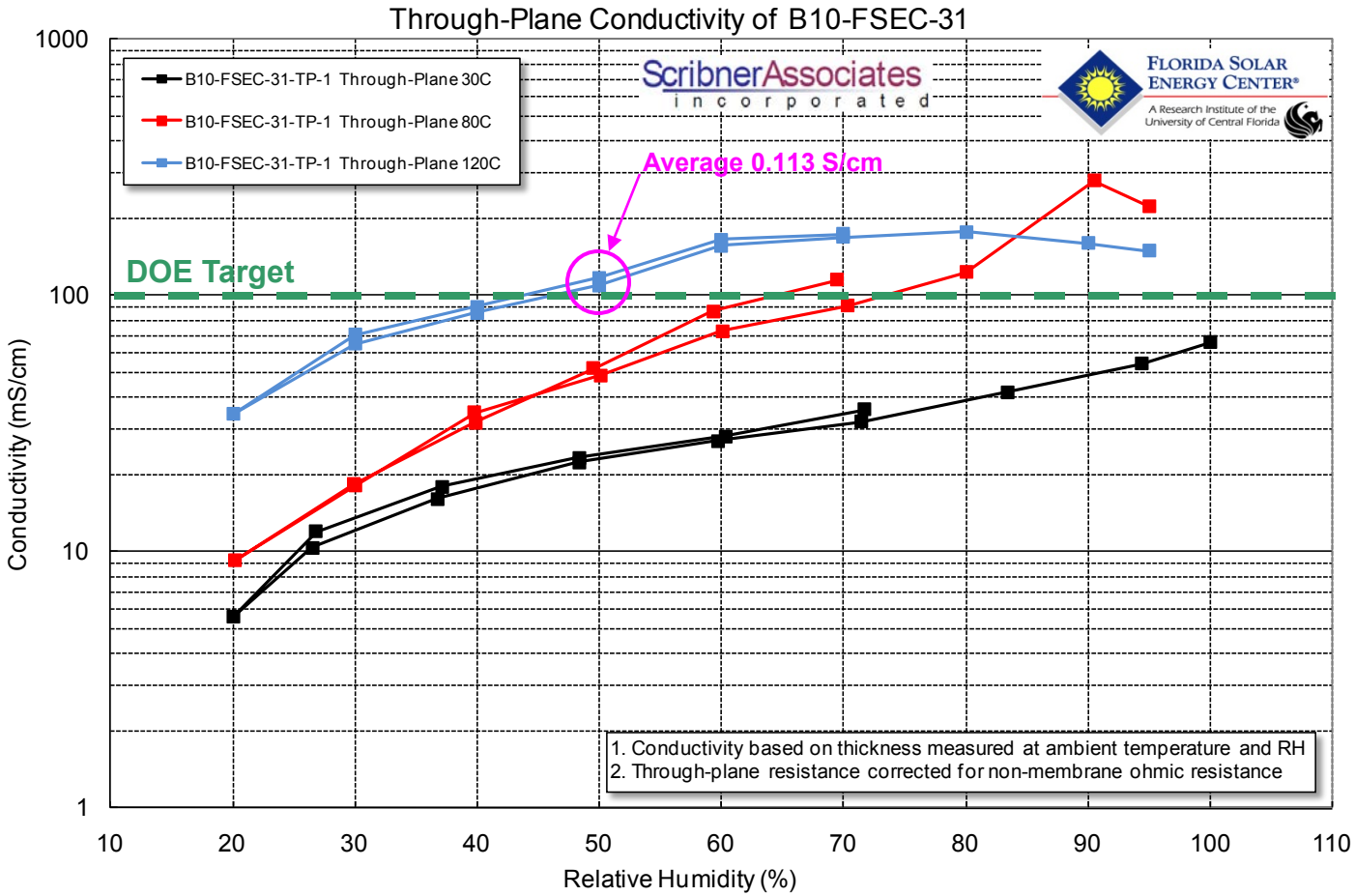

The microstructure is uniform across the ~60µm blank (#76) and ~20µm particle-incorporated (#82) membrane




Nano-zeolite structure remains intact after superacid deposition

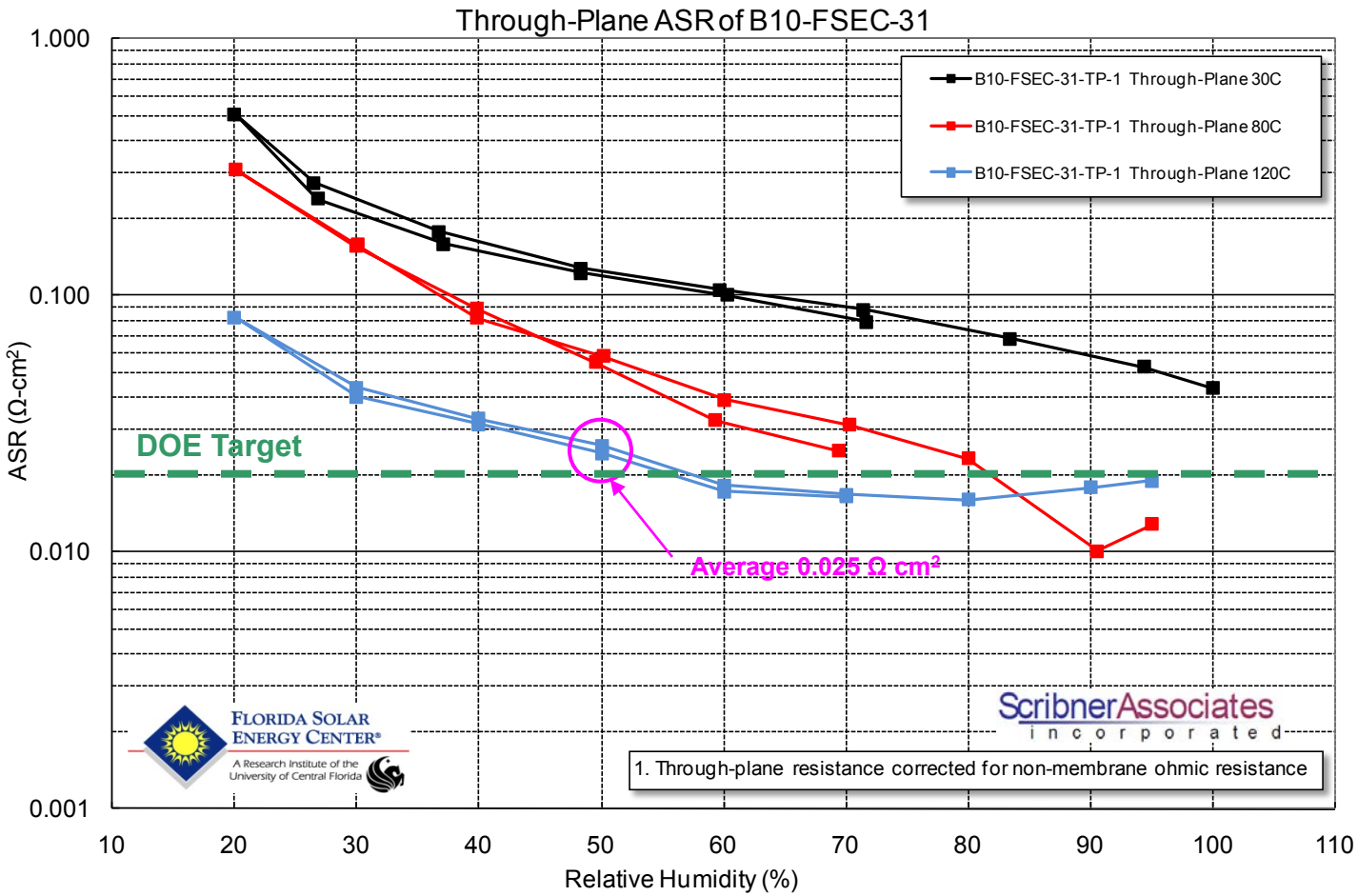
**Achieved good distribution of additives in $mC^2$**

# Accomplishments: mC$^2$ Conductivity




**Conductivity Milestone at 120°C has been Independently Validated**

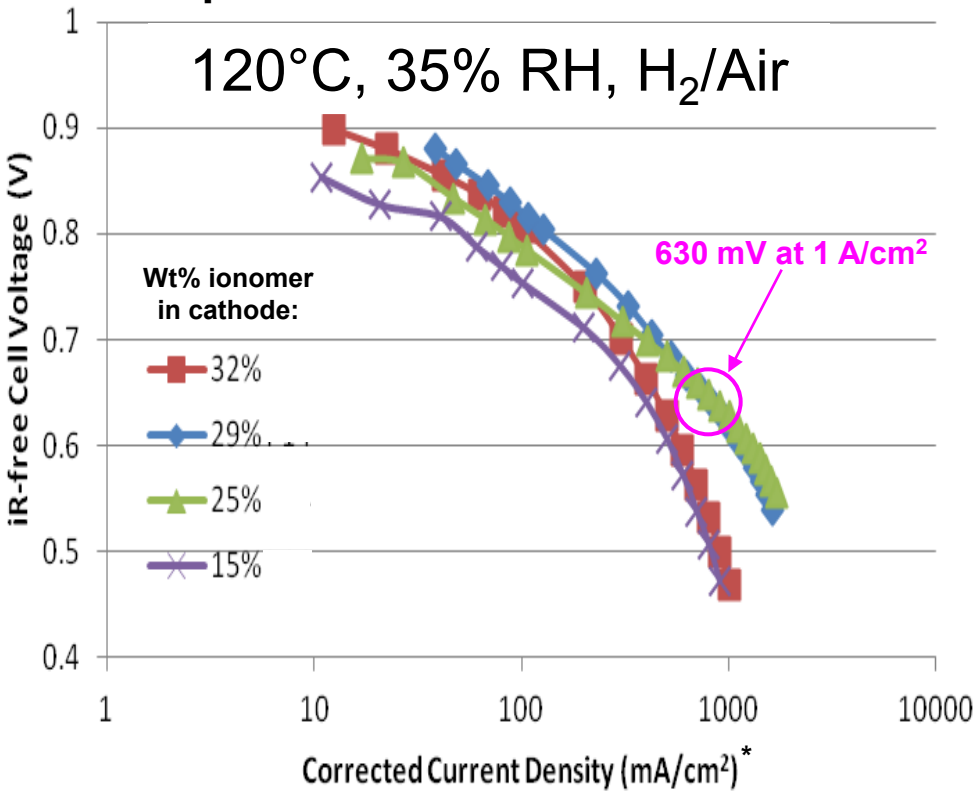
# Accomplishments: Area Specific Resistance

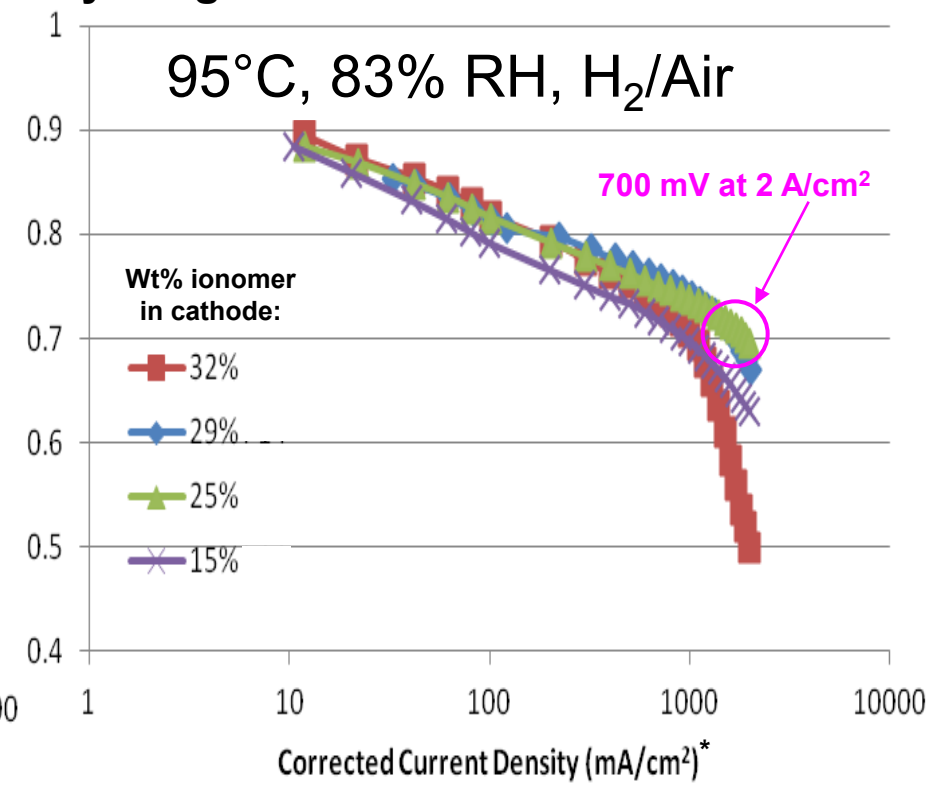



**ASR almost meets the DOE target at 120°C and 50% RH**

# Accomplishments: Electrode Improvements

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

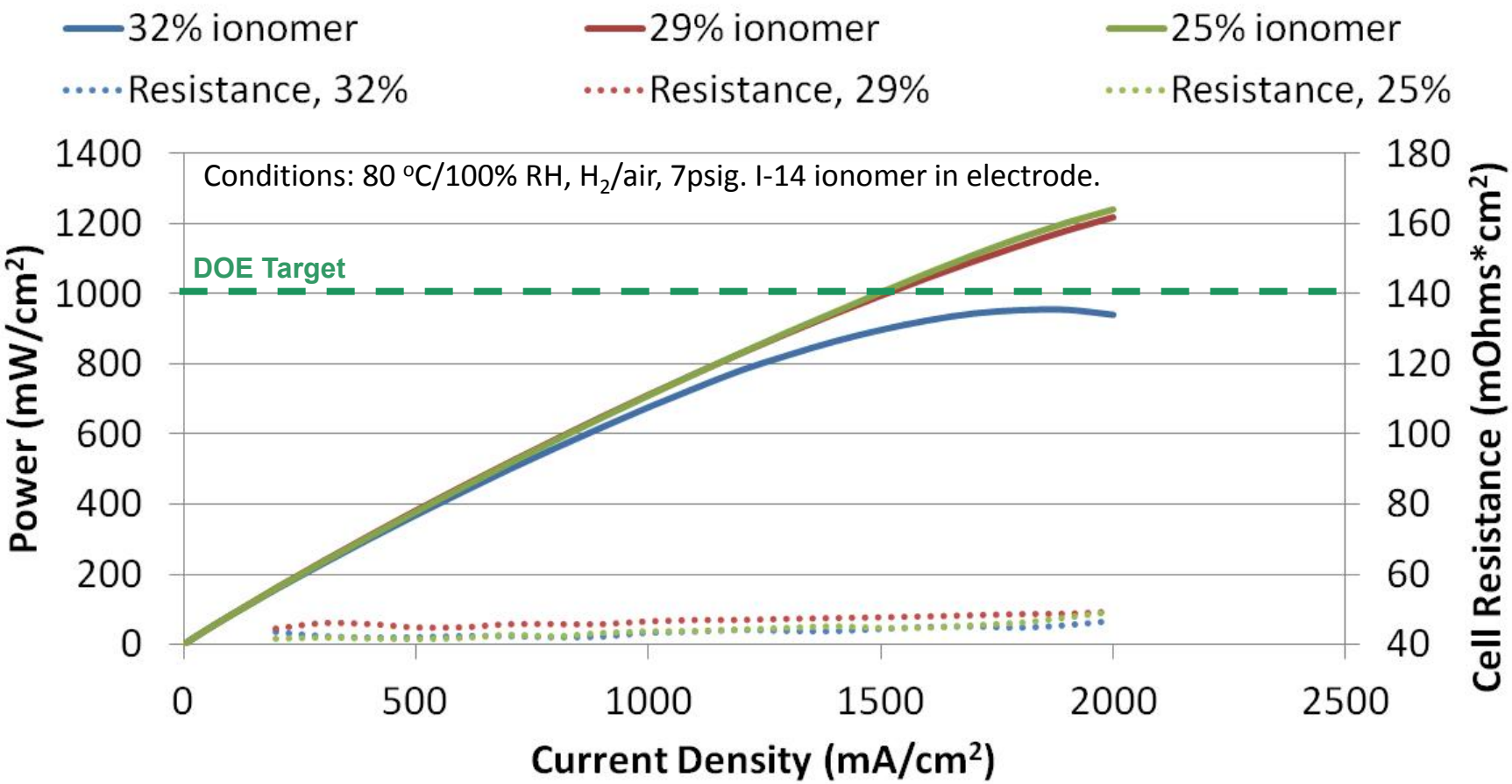



* Corrected for Crossover $H_2$: Limiting current density in the Linear Sweep Voltammogram was deducted from the measured current densities in the polarization curves to isolate the effect of ionomer content in the cathode.

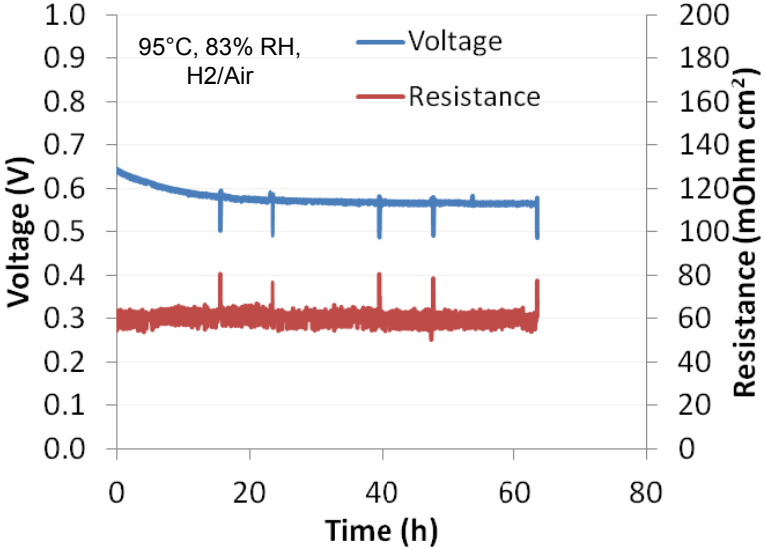
- **$mC^2$ Required Re-optimization of the MEA**
- **Achieved High Performance at High Temp. and High Current Density**

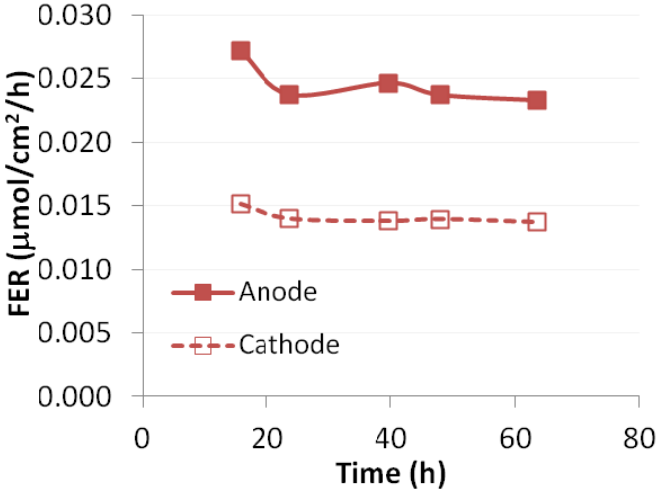
# Accomplishments: $mC^2$ to MEA Development

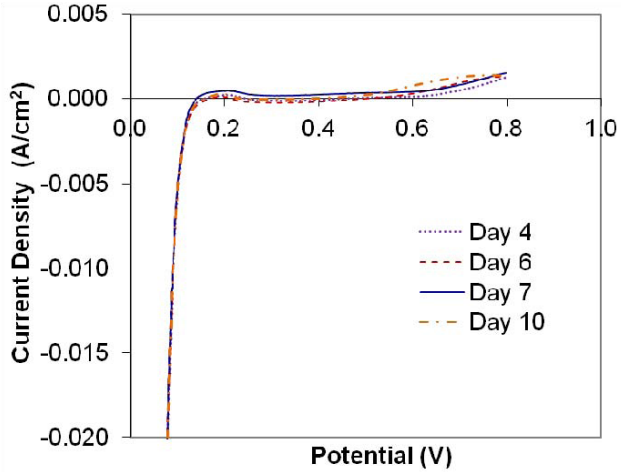


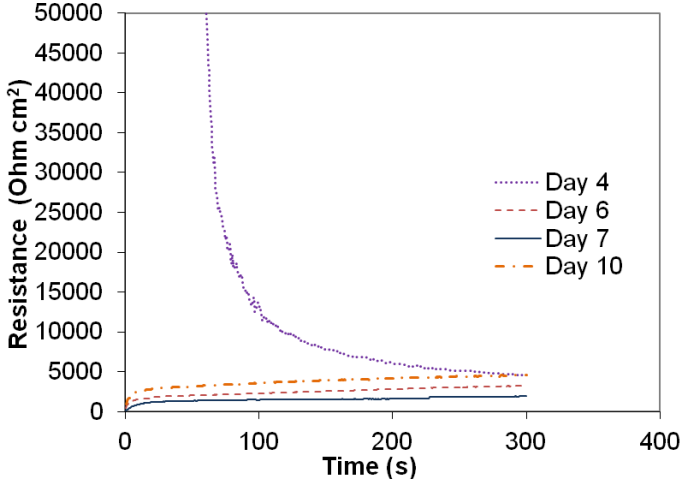

**Electrode Improvements Led to Higher Power**

# Accomplishments: mC$^2$ 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**

# 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 $mC^2$**

# 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°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**