FuelCell Energy

High Temperature Membrane with Humidification-Independent Cluster Structure

Ludwig Lipp

FuelCell Energy, Inc.

June 18th, 2014

Project ID # fc040

Overview

Timeline

- Project Start Date: Jun 2006
- Project End Date: Dec 2013

Budget

- Total Funding Spent: $2,193,028*
- Total Project Value: $2,241,225
- Cost Share Percentage: 28.6%

* as of 3/31/14

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%).

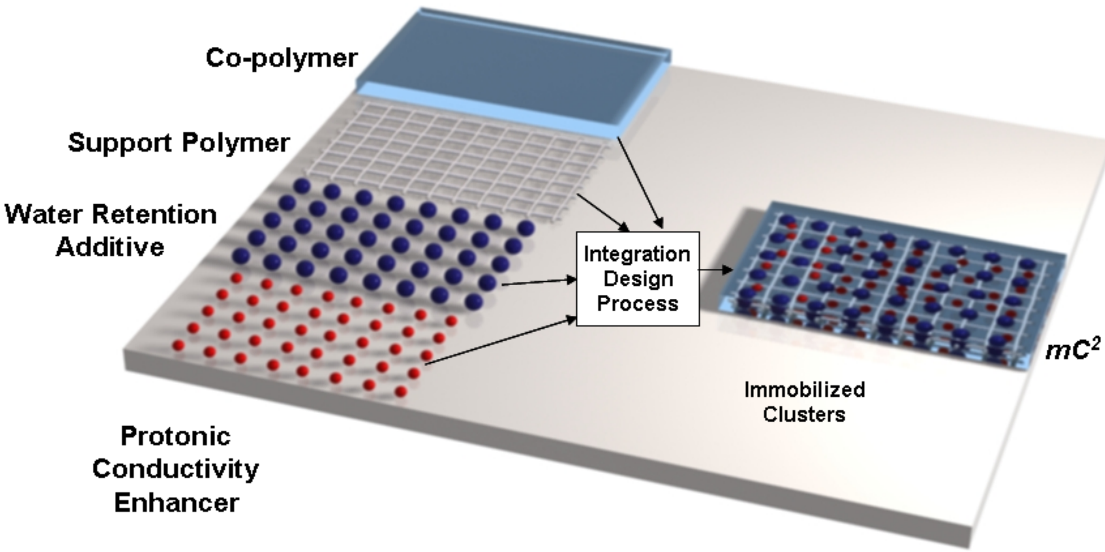
FY14 Obj.: Enhance durability using support polymer

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.**

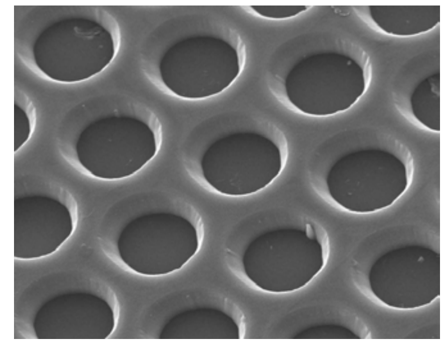
- **Lower EW (850 → 800-650)**
- **Higher Molecular Wt.**
- **Chemically stabilized polymer**
- **Smaller particle size (>80 → 30 nm)**
- **Increased proton density (1 → 2 mobile protons per molecule) and lower cost**

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

Approach

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

Benefits of 2DSM™ support polymer:



- **Short through-plane path**
- **Low tortuosity**
- **Suitable for thin membranes (≤ 25 micron)**
- **Suitable for higher current density**
- **Proven in electrolyzer applications**
- **Giner has shown it can be made very low cost**

Approach

Target Parameter	DOE Target (2017)	Approach
Area specific proton resistance at: 120°C 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)	>20,000	Mechanically strong support polymer for reduced swelling
Durability Chemical (hours)	>500	Chemically stabilized ionomer

Accomplishments

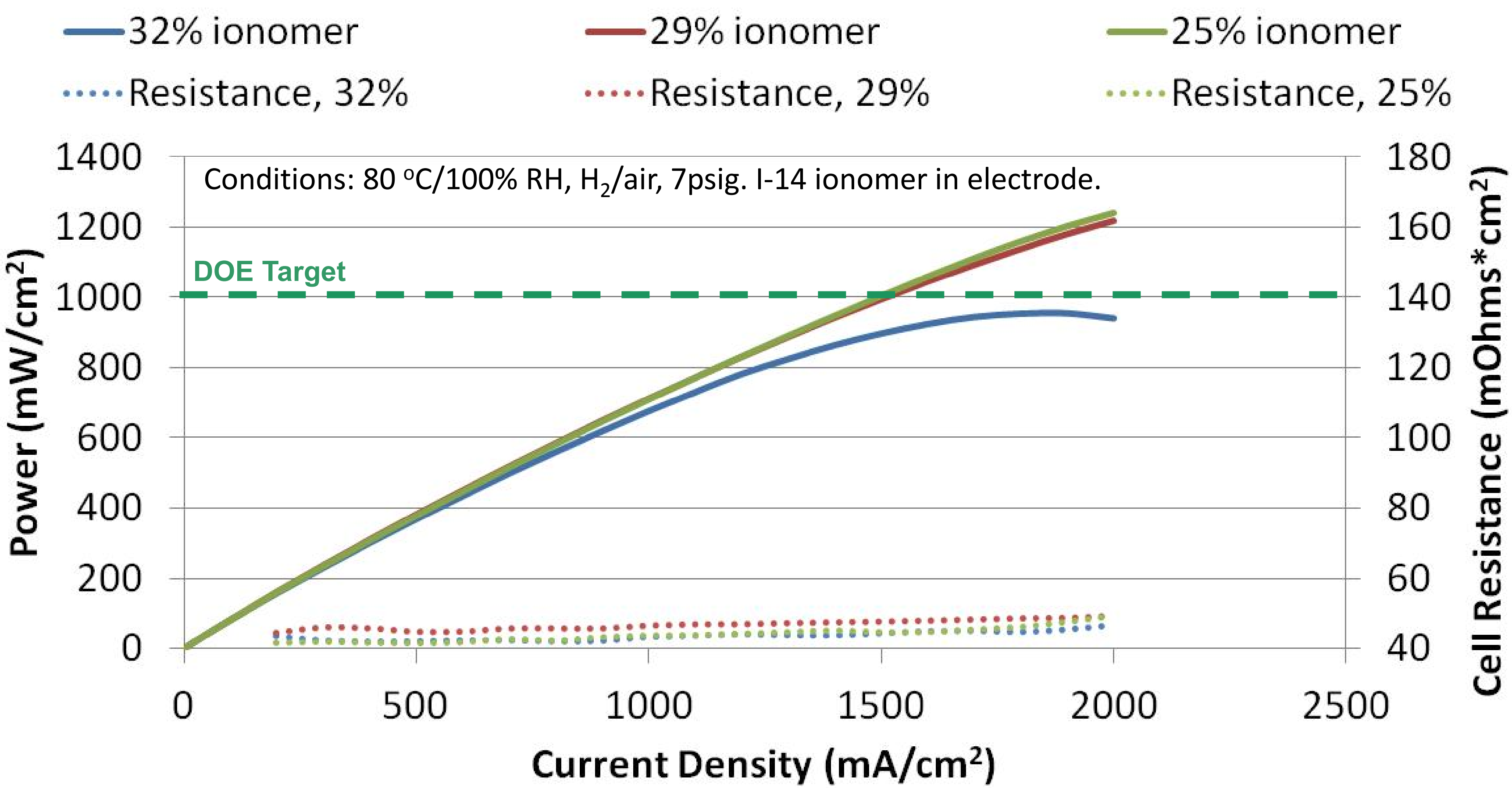
- **High protonic conductivity – 0.113 S/cm* (DOE Target: >0.1 S/cm)**
- **Low cross-over – 0.3 mA/cm^2 * (DOE Target: <2 mA/cm^2)**
- **Low electrical conductivity (high electrical resistance)**
  – 2,860 Ωcm^2 * (DOE Target: >1000 Ωcm^2)
- **Transferred MEA Fabrication Technology to UCF**
  - Easily 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**

FuelCell Energy

FLORIDA SOLAR ENERGY CENTER® A Research Institute of the University of Central Florida

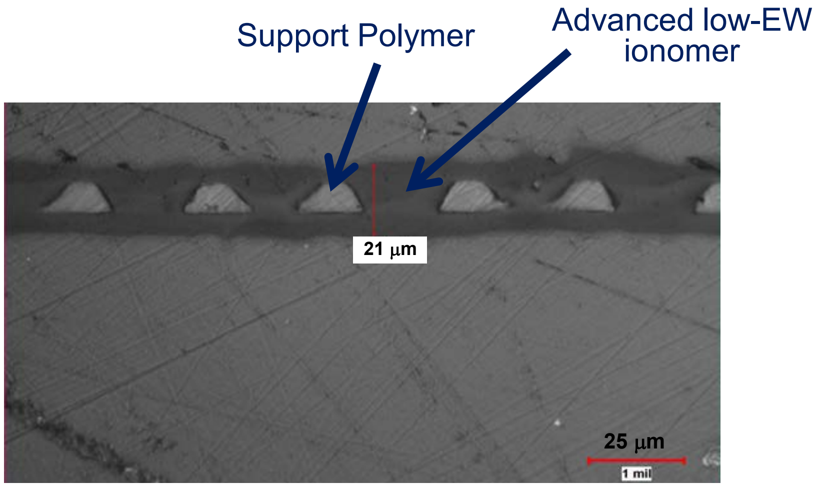
Accomplishments: mC^2 to MEA Development



Electrode Improvements Led to Higher Power

Accomplishments: Supported Membrane Fabrication

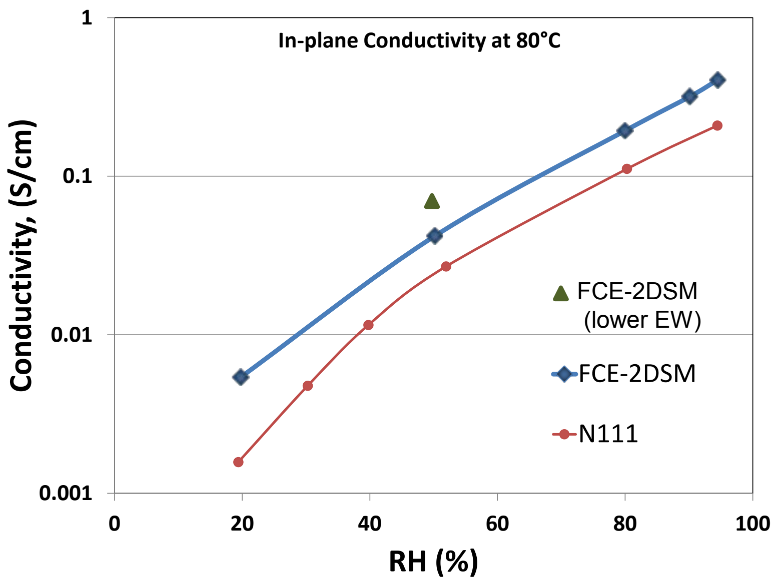
- **>23 fabrication trials using 2DSM™**
- **Challenges faced:**
  - **Dispersion solvent system**
  - **Uniformity – especially of thickness**
  - **Forming defect-free film for low gas cross-over**

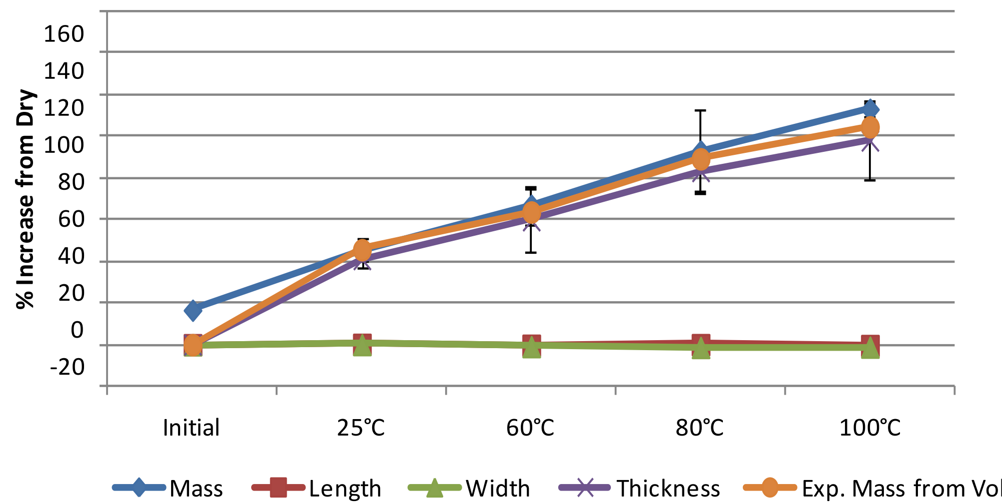


Supported Membrane cross-section

Supported membrane samples fabricated – promising properties

Accomplishments: Conductivity and Swelling





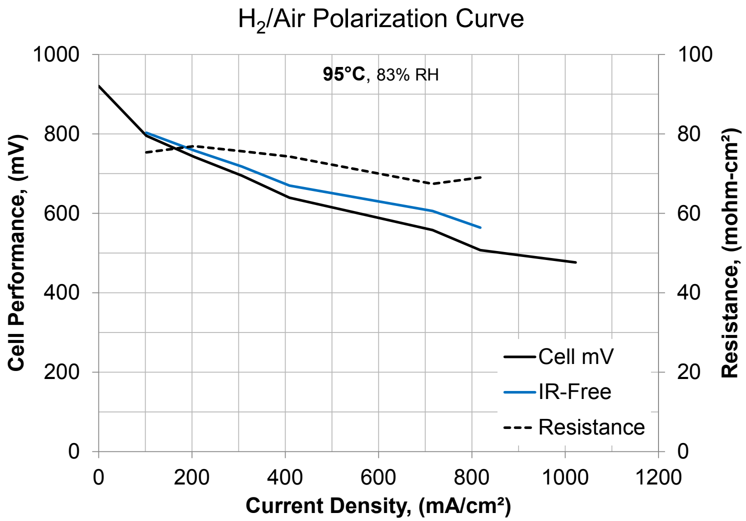
High conductivity achieved with lower-EW supported membrane

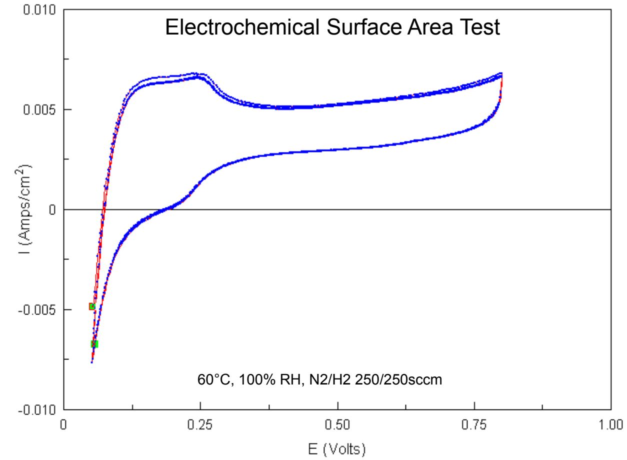
Negligible in-plane swelling for enhanced stability in automotive cycling conditions

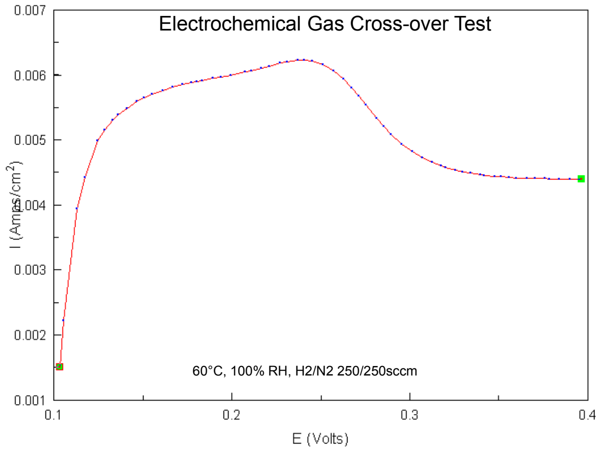
FuelCell Energy

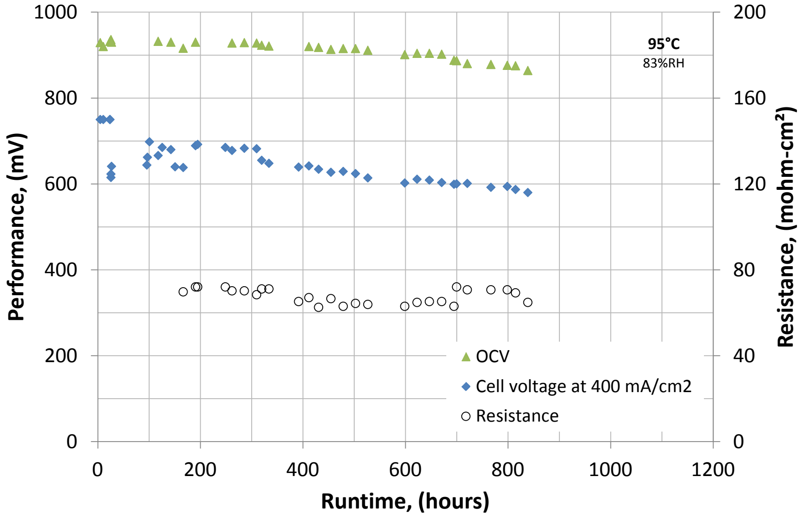
GINER

Accomplishments: Cell Performance









- **Performance at 95°C promising**
- **H_2 cross-over primary cause of performance degradation**
- **>5,000 RH cycles to date**

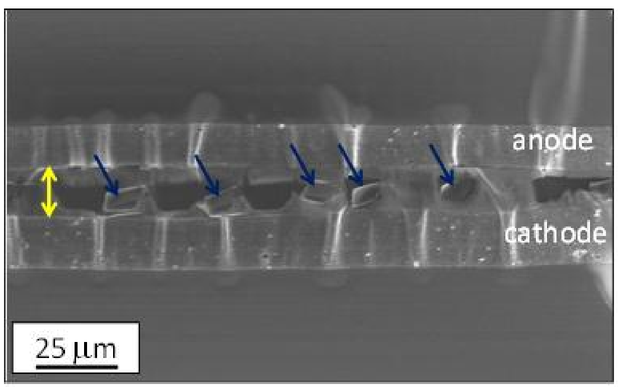
FuelCell Energy

GINER

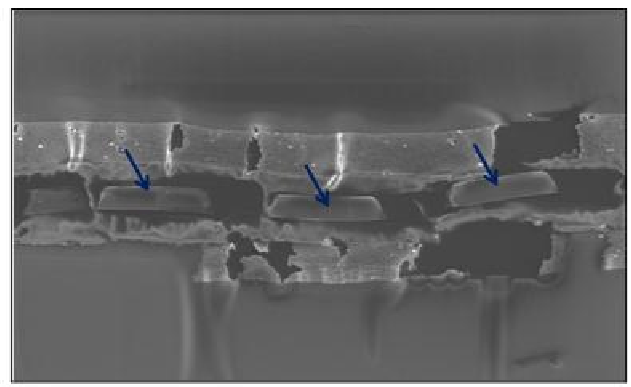
Accomplishments: Supported Membrane Microstructural Analysis

- **2DSM™ support enabled fabrication of ultra-thin (16 μm) membranes**
- **MEA successfully fabricated using Pt/C electrodes**
- **High mechanical strength of support polymer affected the ability to uniformly section the MEAs via microtomy, causing tearing and dragging of the support polymer within the membrane**
- **Aged MEA shows weakened cathode, suggesting local loss of contact**

16 μm



As-prepared MEA:
good bonding of electrodes to membrane

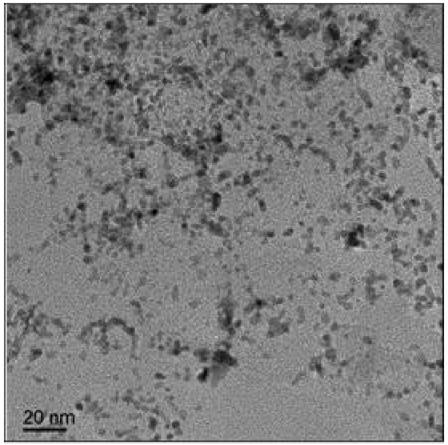


Aged MEA after 850 hr test at 95°C:
the support remains structurally intact

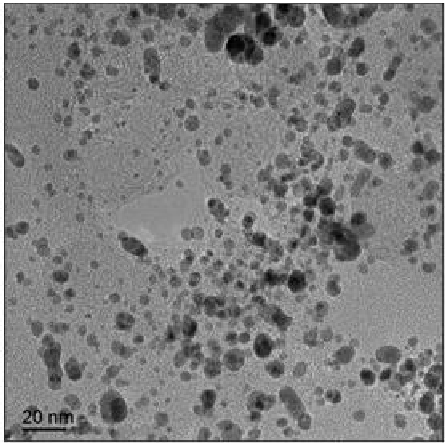
Blue arrows point to support polymer

Fabricated MEA with ultra-thin supported membrane

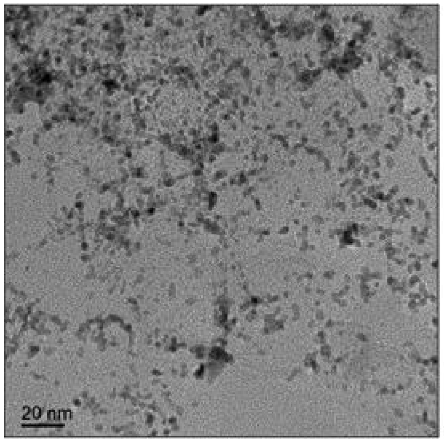
Accomplishments: Supported Membrane Microstructural Analysis



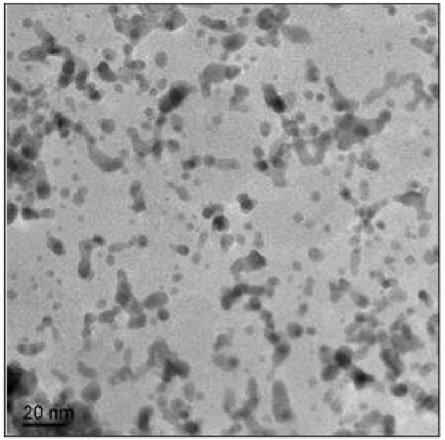
As-prepared cathode



Cathode after 850 hr at 95°C



As-prepared anode



Anode after 850 hr at 95°C

- **Carbon support remains graphitic, indicating little carbon corrosion**
- **Did not observe Pt migration into membrane**
- **Aged electrodes exhibit significant coarsening of Pt catalyst particles → improved catalyst support needed for higher temperature fuel cell operation**

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. (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

Current project has ended. Suggestions for follow-on efforts:

- Further improve supported membrane fabrication to reduce gas cross-over and extend life
- Improved catalyst support materials are needed for demanding higher temperature and low relative humidity operation
- Optimize ionomer properties for high compatibility with support polymer and best combination of conductivity and durability
- Optimize additives developed earlier in the program to further increase performance and life

Progress Summary

- **Fabrication Improvement:**
  - **Fabricated supported membrane using advanced ionomers and Giner, Inc.'s 2DSM™ polymer support material**
  - **Fabricated MEAs using supported membrane**
  - **Cell fabrication**
- **Characterization:**
  - **Swelling <3% in-plane swelling → good mechanical support**
  - **Conductivity: Increased in-plane conductivity to three times that of conventional Nafion®**
  - **Promising RH cycling data: >5,000 RH cycles**
- **Cell Testing: nearly 1,000 hr life at 95°C**

Project Summary Table

Characteristic	Units	DOE 2017 Target	Program 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	1,000	2,860 ✓
Performance @ 0.8V (¼ Power)	mA / cm^2	300	209
Performance @ rated power	mW / cm^2	1,000	1247 ✓
Durability, mechanical	Cycles with <10 sccm crossover	20,000	>5,000

*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.)
- ORNL: Karren More (Microstructural analysis)
- 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)
- LGC Consultant LLC: Larry Christner
- FCE Team: Pinakin Patel, Ray Kopp, Jonathan Malwitz, Paul Pinard, Chao-Yi Yuh, Adam Franco, Al Tealdi