Florida Solar Energy Center

DOE Hydrogen Program

Lead Research and Development Activity for DOE's High Temperature, Low Relative Humidity Membrane Program

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Project ID #**FC035**

Overview

Timeline

- Start Date: April 1, 2006
- End Date: March 31, 2011
- 99% Complete

Budget

- Total project funding
  - DOE share - $2,500K
  - Contractor share - $625K
- Funding for FY10 - $500K
- Funding for FY11 - $165K

Barriers

- Barriers addressed
  - D. **Water Transport**: High Conductivity at Low RH & High T
  - C. **Performance:** High MEA Performance at Low RH & High T
  - A. **Durability:** Membrane and MEA durability
- Targets
  - Conductivity = 0.07 S/cm @ 80% relative humidity (RH) at room temp using alternate material – 3Q Yr 2 milestone
  - Conductivity >0.1 S/cm @ 50% RH at 120 ^{o}C – 3Q Yr 3 Go/No Go
  - H_2 and O_2 cross-over of 2 mA/cm^2 (tested in MEA)

Partners

- BekkTech LLC – In–plane conductivity protocols and testing
- Scribner Associates – Through-plane conductivity protocols and testing
- High Temperature Membrane Working Group

Relevance

Allows supported teams to concentrate on fabricating advanced membranes (with characterization input from neutral third party) to meet DOE targets for fuel cell membranes. Takes membranes that pass ex-situ tests and evaluates in-situ performance

- Objectives:
  - Fabricate membrane electrode assemblies (MEAs) from Team membranes
  - Test Team MEAs for fuel cell performance
  - Standardize methodologies for in-plane and through-plane membrane conductivity measurements

DOE Technical Requirements

Taken from Multi-Year Research, Development and Demonstration Plan: Planned Program Activities for 2005-2015

Characteristic	Units	2010 Target	2015 Target
Maximum operating temperature	°C	120	120
Area specific proton resistance at:			
Maximum operating temp and water partial pressures from 40 to 80 kPa	Ohm cm^2	0.02	0.02
80°C and water partial pressures from 25 - 45 kPa	Ohm cm^2	0.02	0.02
30°C and water partial pressures up to 4 kPa	Ohm cm^2	0.03	0.03
-20°C	Ohm cm^2	0.2	0.2
Maximum Oxygen cross-over[a]	mA/cm^2	2	2
Maximum Hydrogen cross-over[a]	mA/cm^2	2	2
Minimum electrical resistance[b]	ohm cm^2	1000	1000
Cost[c]	$\$/m^2$	20	20
Durability[d]			
Mechanical	Cycles w/<10sccm cross-over	20,000	20,000
Chemical	Hours	>500	>500

a. Tested in MEA at 1 atm O_2 or H_2 at nominal stack operating temperature, humidified gases at 0.5V DC.
b. Measure in humidified N_2/N_2 at 0.5V DC at 80°C .
c. Based on 2002 dollars and costs projected to high volume production (500,000 stacks per year).
d. Based on MEA Chemical Stability and Metrics

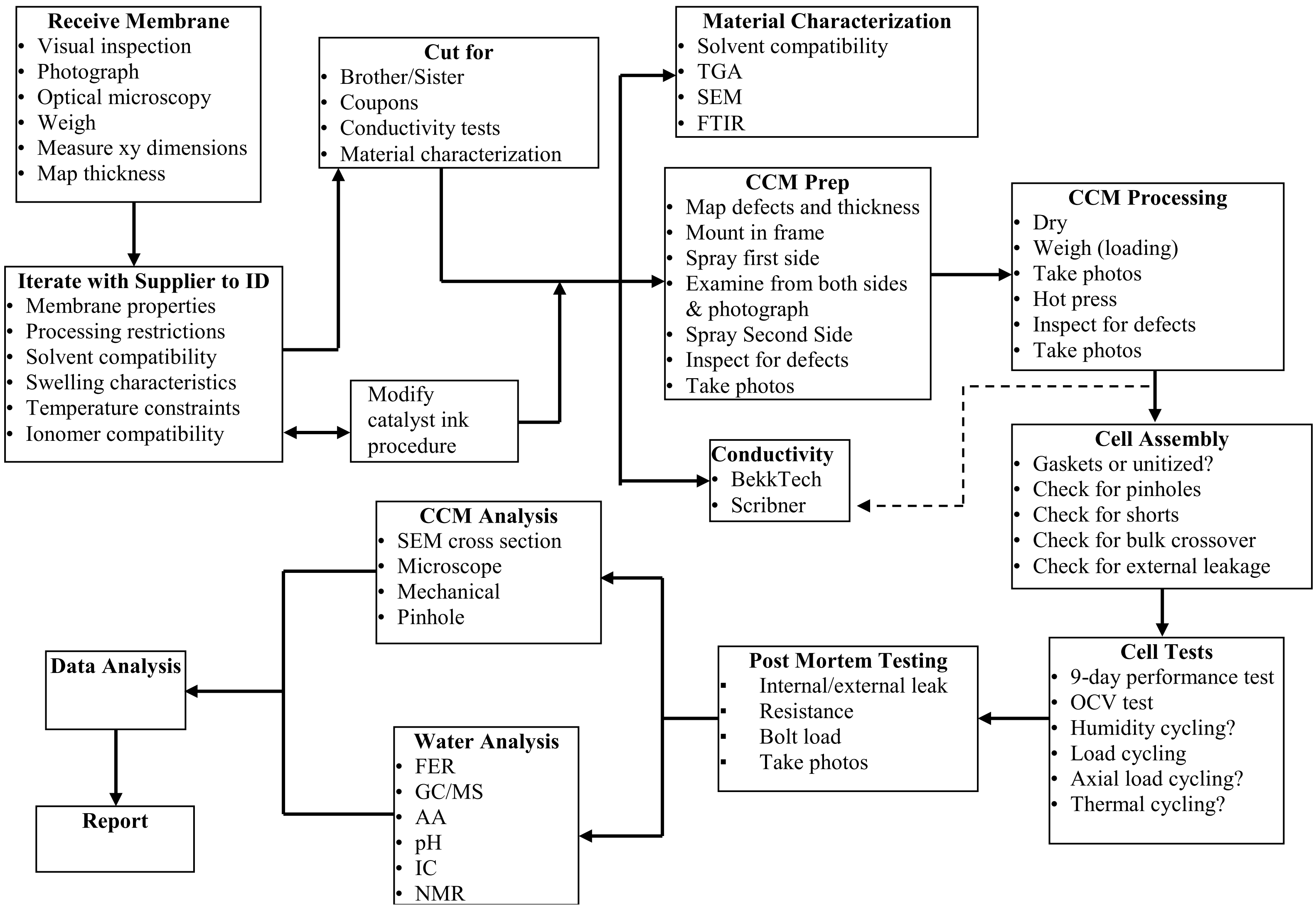
Approach

- Characterize the proton conduction (in- and through-plane) of the electrolytes, as well as mechanical, mass transport, and surface properties
- Prepare catalyst-coated membranes and MEAs based on promising new electrolyte materials from the working group membership
- Evaluate membranes as MEAs (as specified in DOE targets) at high temperature and low RH
  - Performance, H_2 cross-over, and durability
  - Post-test analysis including SEM, TEM, and cross-over/defect test
- Based on results of characterization tests, recommend most promising materials and down-selects

DOE targets

- Conductivity = 0.07 S/cm @ 80% relative humidity (RH) at room temp using alternate material (milestone)
- Conductivity >0.1 S/cm @ 50% RH at 120 ^oC (Go/No-Go)
- H_2 and O_2 cross-over of 2 mA/cm^2 (tested in MEA)

Approach: Flow Chart for Membrane Testing



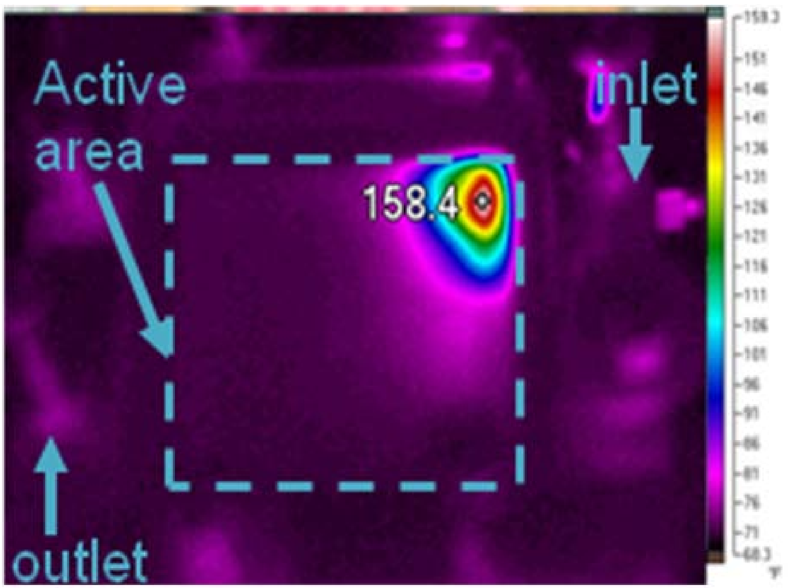
Approach: Electrode Fabrication

- Pt-Co/C from Tanaka (requested by DOE)
- 3M ionomer in electrode (requested by DOE)
  - Some teams preferred their ionomer instead
  - Each new ionomer required process modifications
- Team membranes
  - Optimization of electrode-membrane interface required to ensure best chance for membrane's true potential to be exhibited
- Electrode applied via spray process

Approach: Fuel Cell Performance Analysis

- Membrane resistance is only one factor influencing fuel cell performance
  - Others include electrode resistance, diffusion resistance, catalyst activity, and membrane/electrode interfacial resistance
- Performance curve analysis can identify electrode and diffusion resistances and catalyst activity

Approach: Cross-over/Defect Testing



- Allows detection, location, and quantification of membrane perforations/defects in an MEA
  - MEAs exposed to 4% H_2 on anode side
  - Cross-over H_2 reacts with air on cathode side, generating hot-spots
  - Infrared imaging identifies membrane defects
    - Defects can be thin spots, cracks, tears or pinholes

Can assist in diagnosis and analysis of degradation and failure mechanisms

Collaborations – Within Program

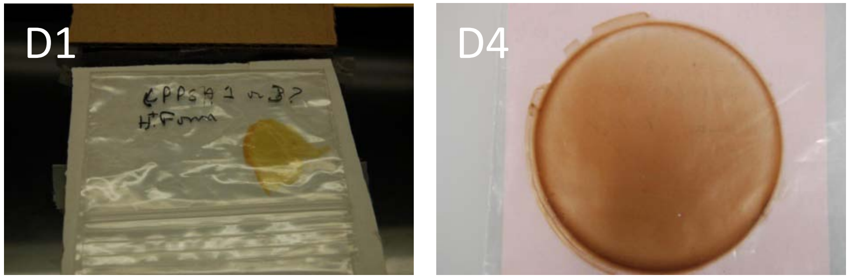
- Case Western Reserve – university
  - Supply membranes for MEA manufacture
- Giner Electrochemical Systems, LLC – industry
  - Supply membranes for MEA manufacture
- Fuel Cell Energy – industry
  - Supply membranes for MEA manufacture
- Colorado School of Mines – university
  - Supply membranes for MEA manufacture
- Vanderbilt University – university
  - Supply membranes for MEA manufacture
- *3M - industry*
  - *Supply ionomer for program*
- *BekkTech, LLC – industry*
  - *Subcontractor for in-plane conductivity*
- *Scribner Associates – industry*
  - *Subcontractor for through-plane conductivity*

Technical Accomplishments and Progress

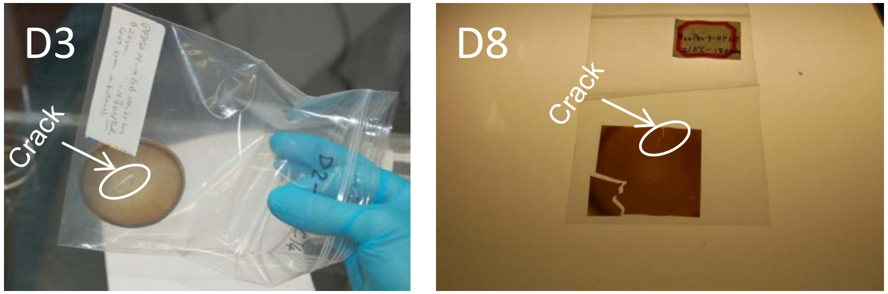
Case Western Reserve Membranes

CWR-D Membranes

- Total of 9 membranes and/or samples were received.
  - 3 cross-linked membranes too brittle for CCM development.
  - 2 cross-linked membranes dispatched for conductivity measurements.
- First few samples were very brittle
- All samples have very high proton conductivity

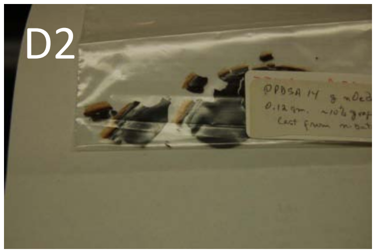


Samples dispatched for conductivity measurements



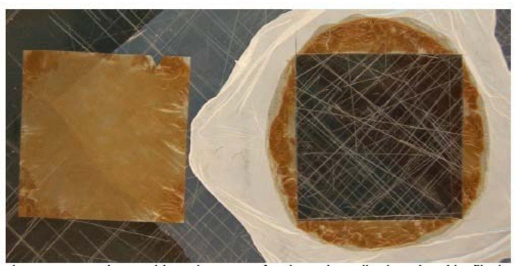
Brittle samples

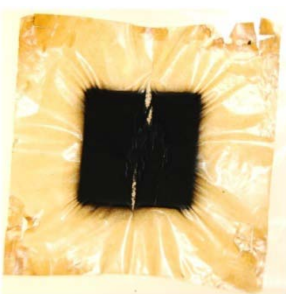
D2 - Membrane Casting & CCM via Spraying



As Received

Recast from MeOH/DMF with Teflon® support



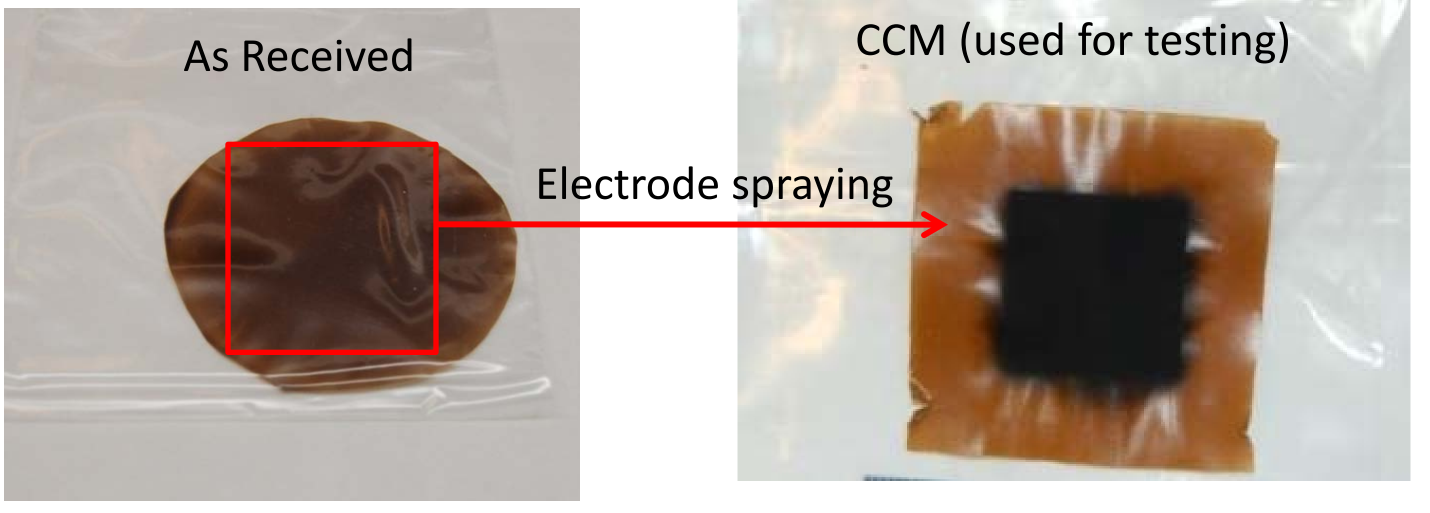


After Spraying

- A membrane was cast with a Teflon support
- The CCM developed two major cracks after spraying process

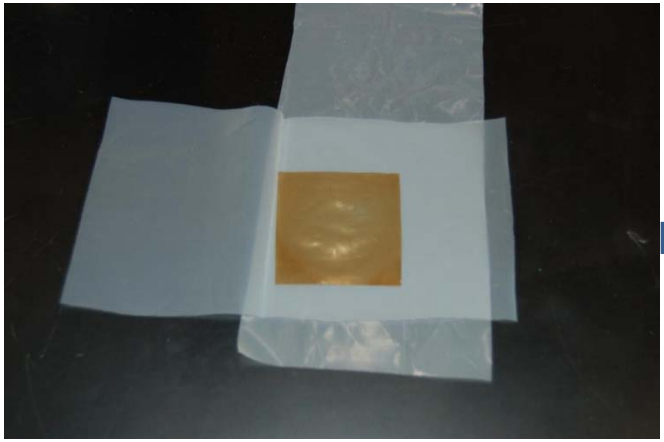
CWR polymers show promise for development, with additional research, as reinforced membranes

CCM Development

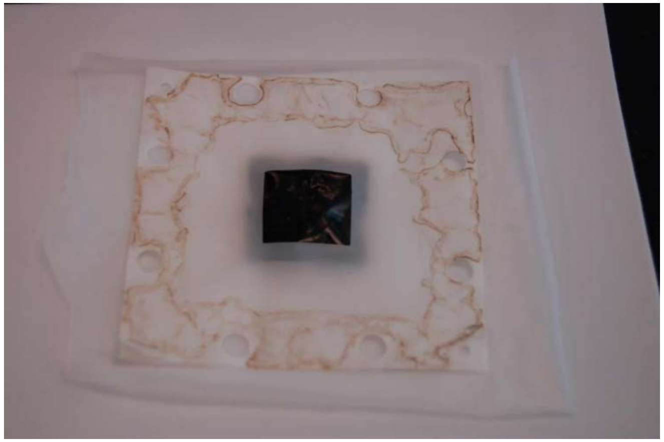


CCM development was successful using FSEC's standard spraying protocol

D9 - Cross-linked at FSEC



As received – before cross-linking



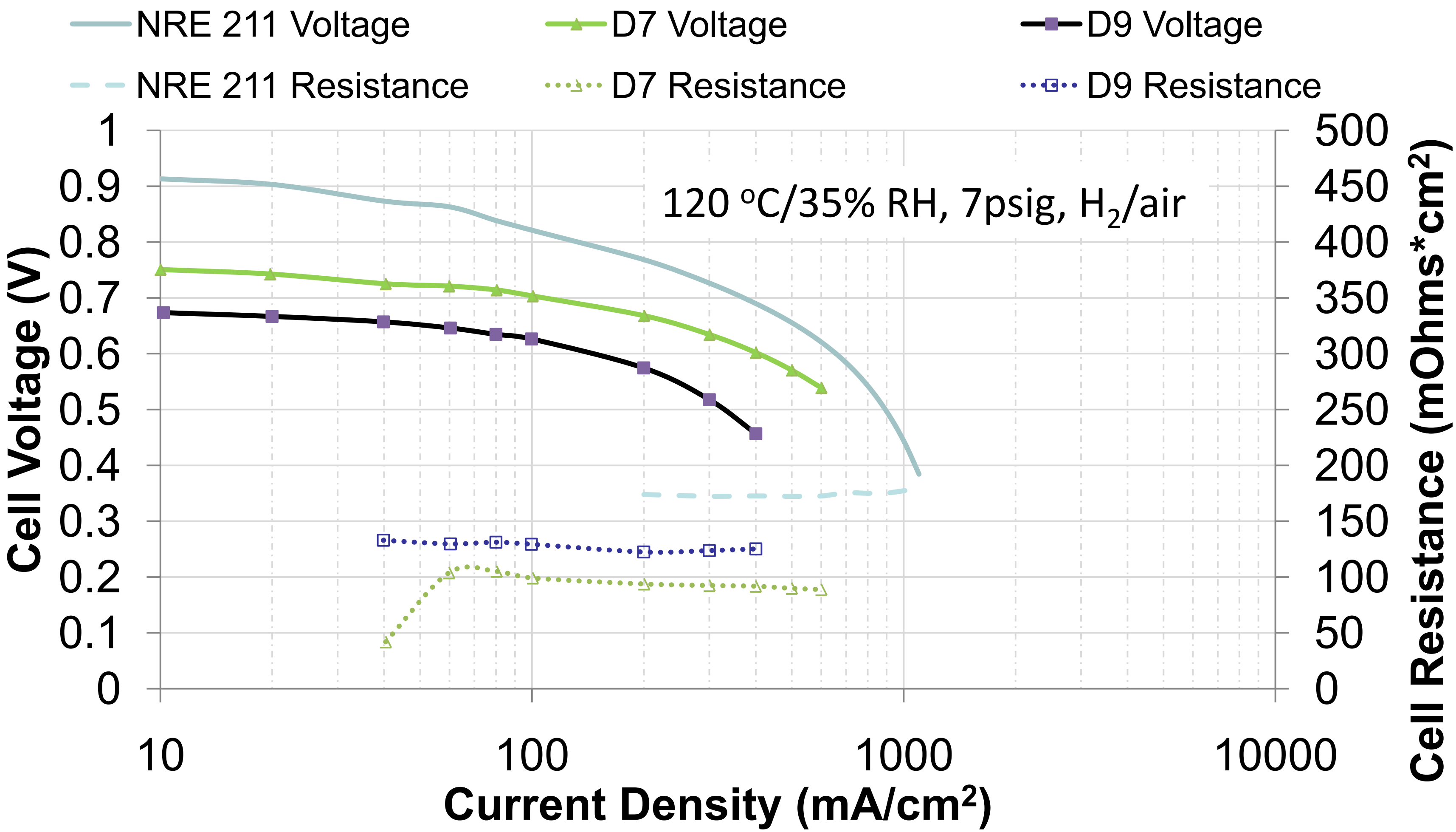
After cross-linking

Sprayed Cross-linked membrane

- Membranes with adequate level of cross- linking were being damaged during shipping process
- D9 membrane was shipped uncross-linked
- Cross-linking was accomplished at FSEC

Crack formation avoided by cross-linking at FSEC

CWR Performance



D7 and D9 exhibit lower resistance than NRE211, in spite of being thicker

CWR Membranes Compared to DOE Targets

Characteristic	Units	Target 2015	D6	D7	D9	NRE211
Area specific proton resistance at:						
120 ° C and 70 kPa water partial pressure	Ohm cm^2	≤ 0.02	N/D	0.05	0.097	0.15
80°C and 38 kPa water partial pressure	Ohm cm^2	≤ 0.02	0.055	0.02	0.018	0.02
Maximum Hydrogen cross-over [a]	mA / cm^2	2	10.8	1.9	136	0.76
Minimum electrical resistance [b]	Ohm cm^2	1000	8.4	31	14	2100
Performance @ 0.8 V (¼ power)	mA / cm^2 mW / cm^2	300 250	N/D N/D	34 27	N/D N/D	151 120
Performance @ rated power	mW / cm^2	1000	N/D	108	N/D	480

*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

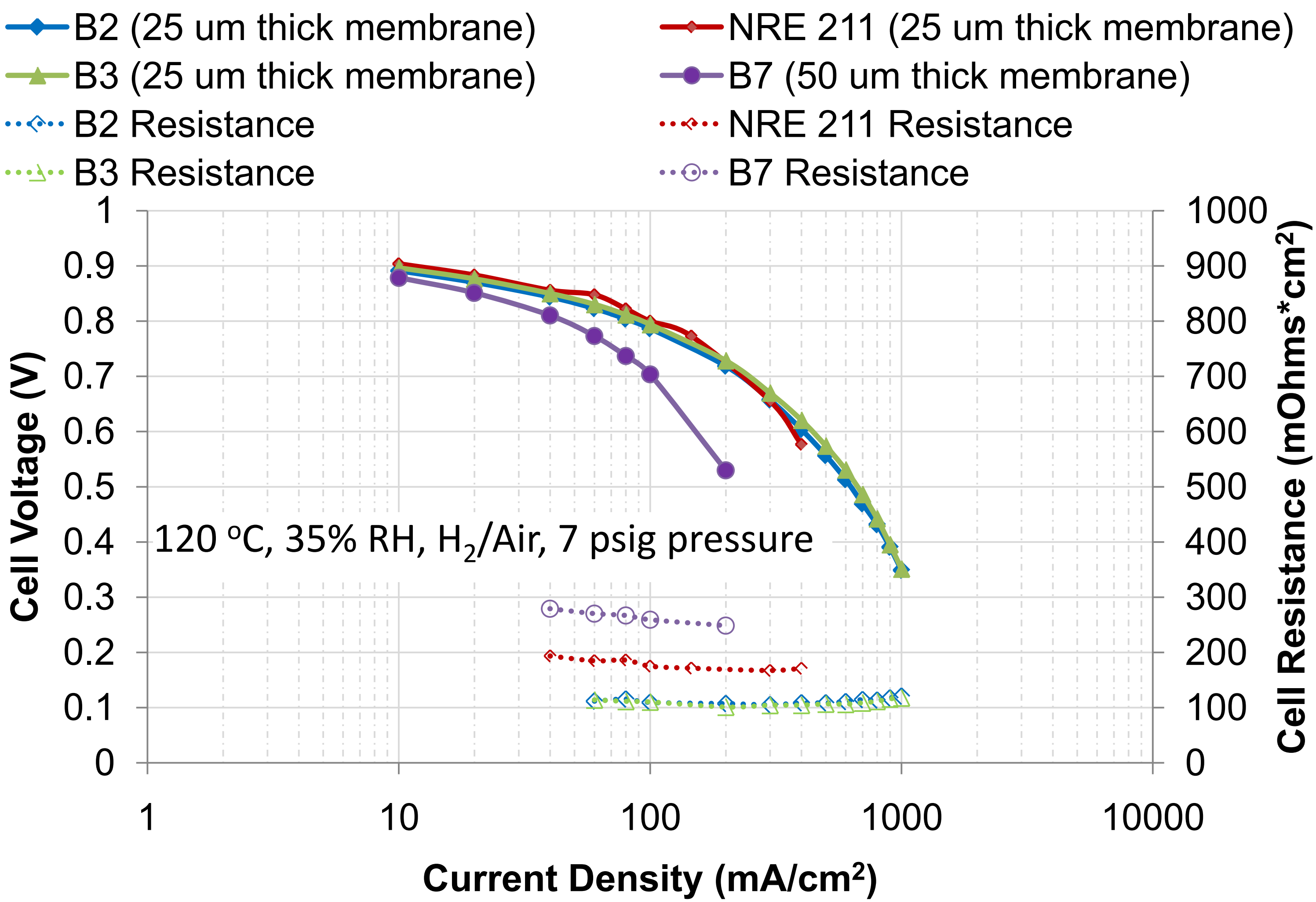
CWR membranes show promise to meet DOE ASR targets

CWR Summary

- FSEC assistance in casting and crosslinking has solved early issues
  - Crosslinking has eliminated solubility issues
- Resistance from cell interrupt good
  - Membranes are highly conductive
- Cell performance improving but dominated by high H_2 cross-over
- Durability data needed

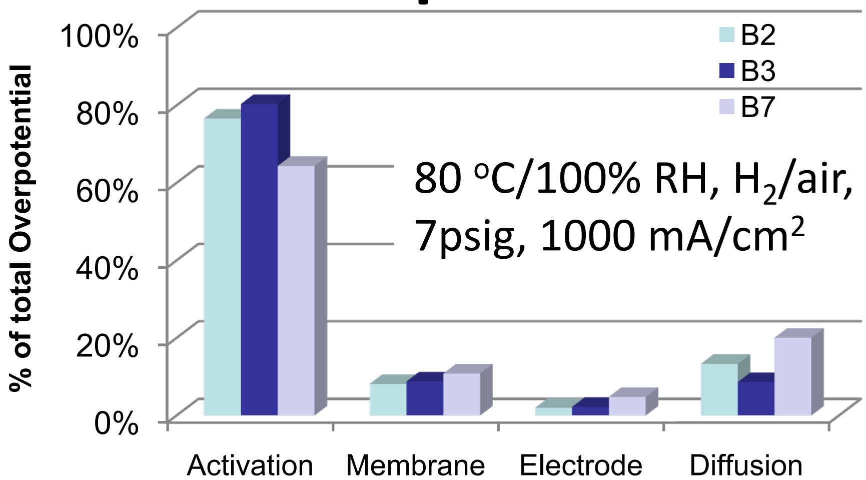
Fuel Cell Energy Membranes

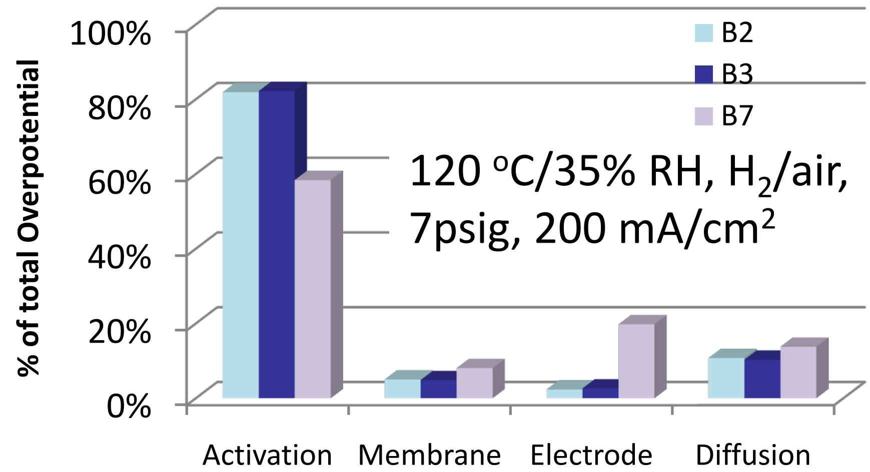
FCE Performance Summary



B2 and B3 have lower resistance than NRE211

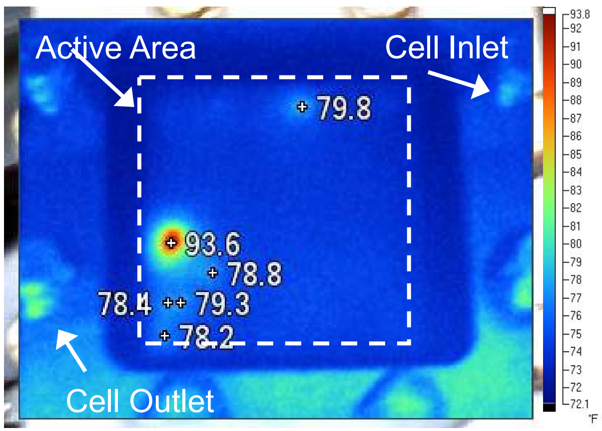
Data Analysis Reveals MEA Optimization is Required



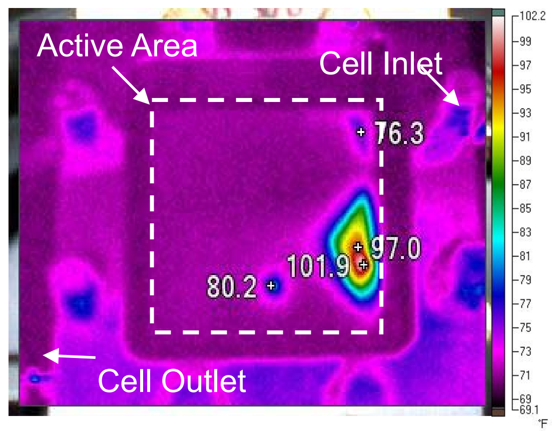


- These cells used the same ionomer in the membrane as in the electrode
  - This approach minimizes membrane/electrode interfacial resistance
- Because catalyst layer structure was not optimized, combined electrode and diffusion resistances exceeded that of the membrane
- Full characterization of the B7 membrane was not possible because fuel cell performance was limited by catalyst layer resistances
- Once MEA optimization has been accomplished, the true performance of these membranes can be ascertained

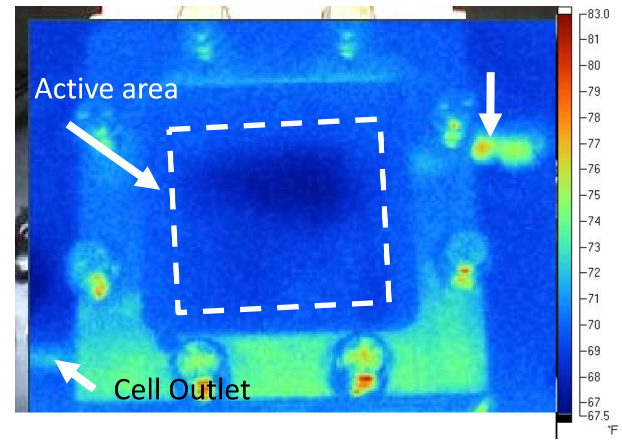
FCE Cross-over/Defects



B2
After testing
Cross-over = 1.0 mA/cm^2



B3
After testing
Cross-over = 77 mA/cm^2



B7
After testing
Cross-over = 0.5 mA/cm^2

Defect formation and hydrogen cross-over are lower in B7

FCE Membranes Compared to DOE Targets

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

*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

‡Membrane thickness double that of others in series

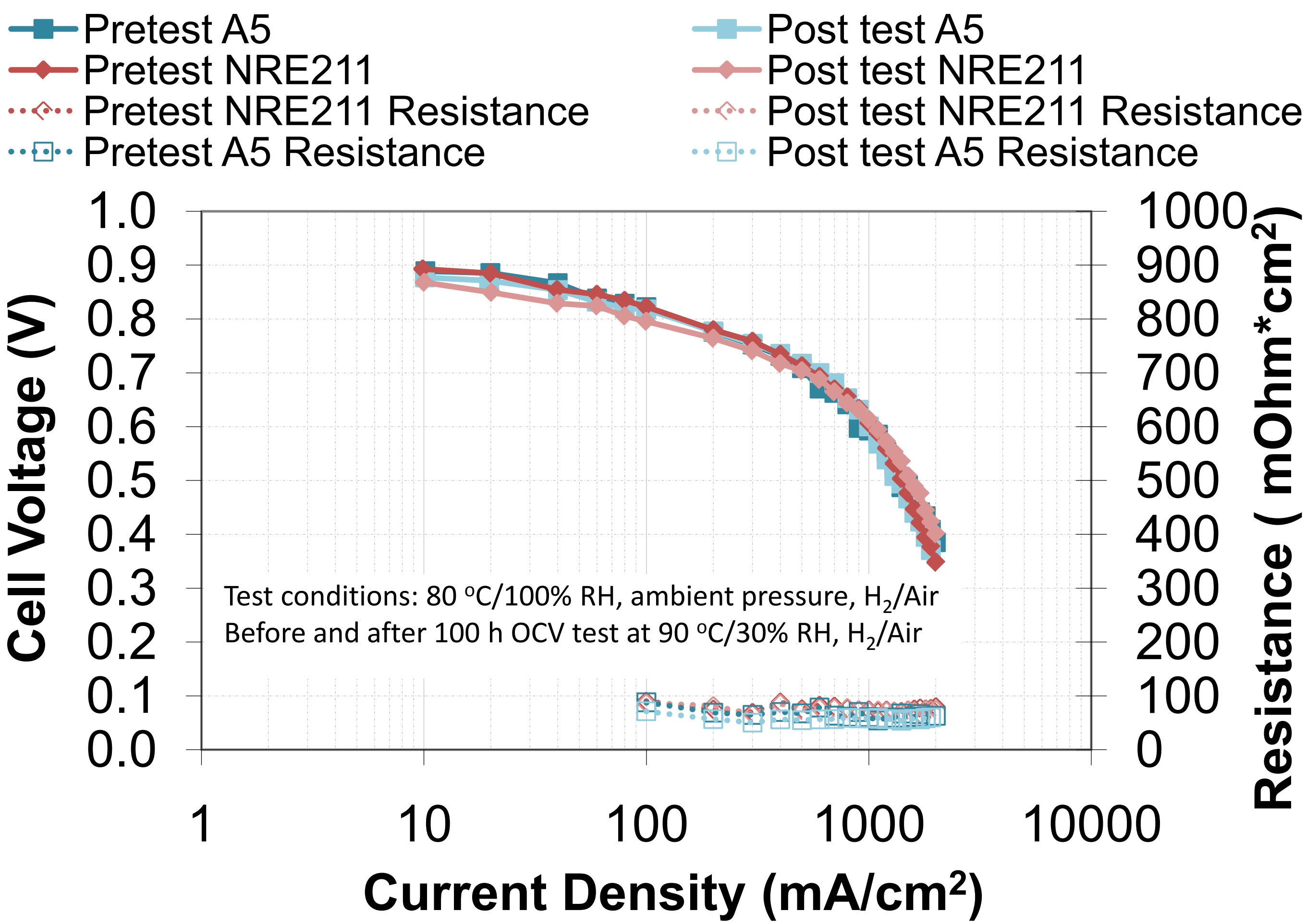
Membranes are showing progress towards the DOE resistance and H_2 cross-over targets.

FCE Summary

- B2 and B3 show progress towards the DOE resistance targets
  - Higher resistance in B7 is a result of the membrane being twice as thick as B2 and B3
- B7 shows improved membrane conductivity, but catalyst layer resistances significantly influence fuel cell performance
  - Electrode optimization with FCE ionomer is required

Giner Membranes

Giner - A5 Performance Before and After Durability Test

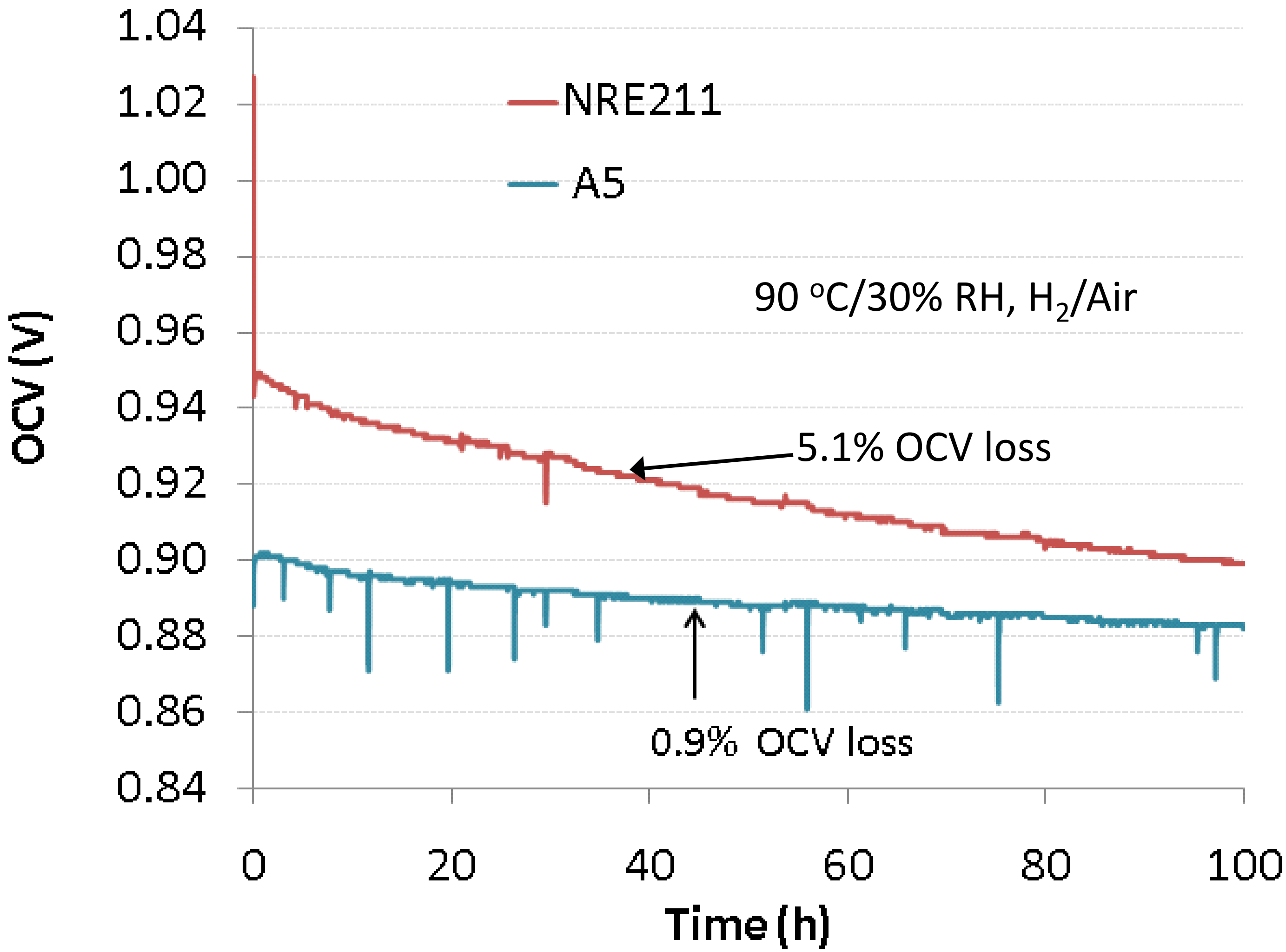


Durability Test

OCV hold, 100 h, 90 °C/30% RH, H_2/Air

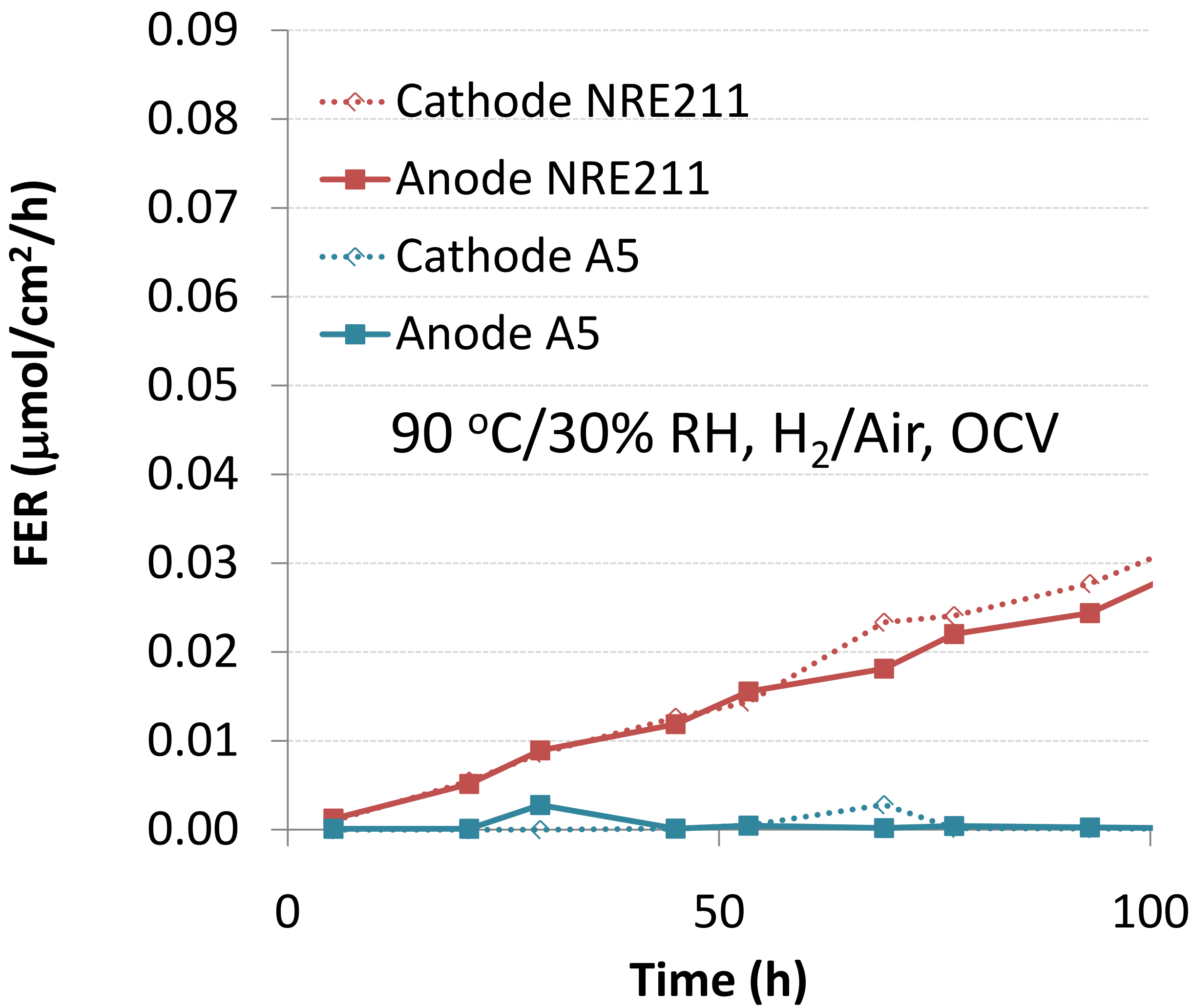
A5 had and maintained performance better than NRE211

A5 Durability results



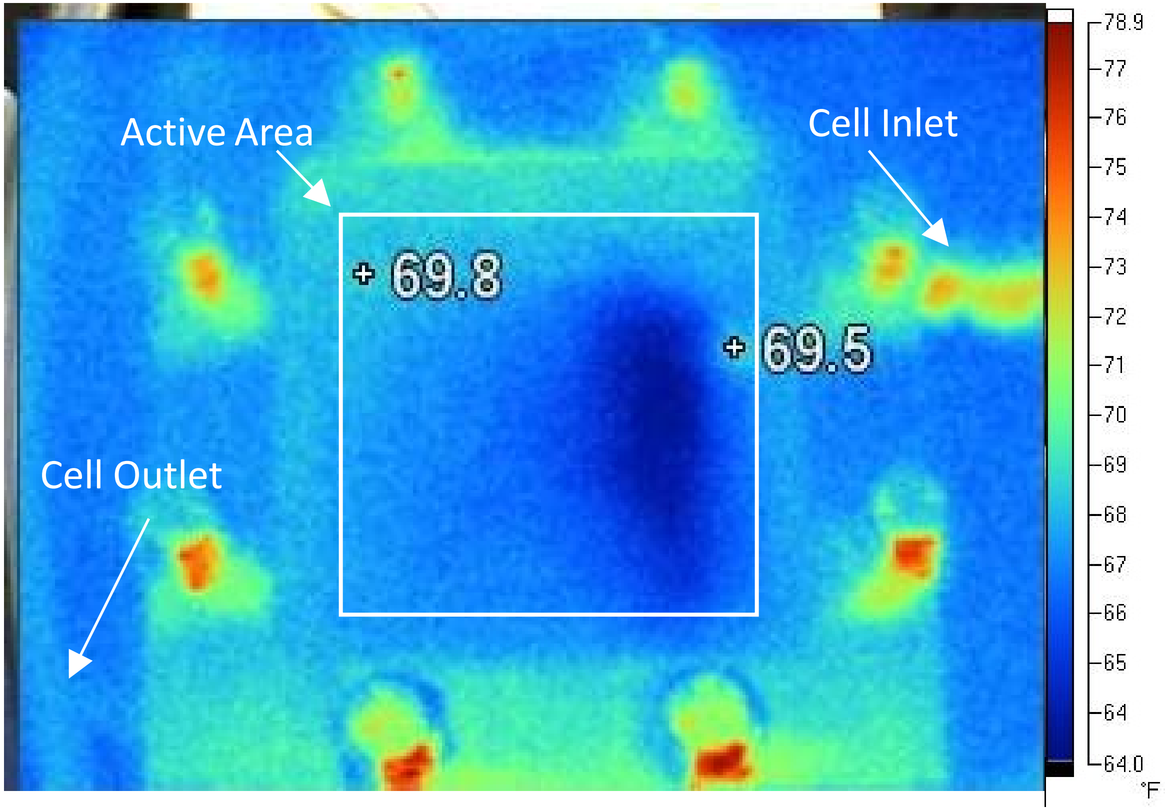
A5 approaches DOE Target, which is 20% OCV loss over 500 h

A5 FER Durability Results



A5 has much lower fluoride emission rate than does NRE211

A5 Cross-over/Defects



Cross-over = 1.5 mA/cm^2 at end of test. No significant defects present

Giner Membranes Compared to DOE Targets

Characteristic	Units	Target 2015	A1	A2	A3	A4	NRE211
Area specific proton resistance at:							
120 ° C and 70 kPa water partial pressure	Ohm cm^2	≤ 0.02	0.26	0.24	0.32	0.14	0.15
80°C and 38 kPa water partial pressure	Ohm cm^2	≤ 0.02	0.05	0.03	0.04	0.01	0.02
Maximum Hydrogen cross-over [a]	mA / cm^2	2	0.75	1.6	0.61	0.70	0.76
Minimum electrical resistance [b]	Ohm cm^2	1000	65	358	1073	813	2100
Performance @ 0.8V (¼ Power)	mA / cm^2 mW / cm^2	300 250	94 75	222 177	112 89	81 65	151 120
Performance @ rated power	mW / cm^2	1000	300	708	356	260	480

*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

Giner membranes show good progress toward meeting DOE resistance and cross-over targets

Giner Summary

- Giner membrane OCV durability shows good progress towards meeting DOE targets
  - Extrapolated OCV losses are ¼ of DOE targets
  - 40 fold decrease in F^- emission
  - Low defect formation after durability test
- Giner membrane performance shows good progress towards meeting DOE targets
  - Resistance is reduced by 30% of the initial value
  - Membranes are less than 30 μm yet still exhibit lower H_2 cross-over than DOE targets

HTM Program Summary

- Eleven teams initially funded to develop high conductivity membranes
  - Six teams selected to continue after go/no-go
- Conductivity, stability and performance improved over course of program
  - Many membranes showed promise and should be pursued
- Collaboration between FSEC and Teams guided CCM development
  - Excellent model for future DOE membrane development programs
- Significant progress made toward developing a membrane suitable for fuel cell use

Proposed Future Work

- Continue to work closely with team members to
  - Characterize membranes
  - Prepare MEAs
  - Test MEAs in fuel cell hardware
- FCE is requesting additional support in electrode optimization
- CWR requires additional support in reducing cross-over

FSEC Project Tasks and Team

- Project Management
  - Dr. Darlene Slattery and Leonard Bonville
- Fabrication of catalyst coated membranes
  - Dr. Paul Brooker
- Performance testing
  - Dr. Paul Brooker and Dr. Marianne Rodgers
- Durability testing
  - Dr. Marianne Rodgers
- Conductivity testing
  - Tim Bekkedahl, (in-plane) and Dr. Kevin Cooper (through-plane)
- Technical Advisor/Data Analysis
  - Dr. H. Russell Kunz
- Material Science (SEM, TEM, EDAX, FTIR, TGA)
  - Dr. Nahid Mohajeri, Dr. Marianne Rodgers and Graduate Students