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

- Project start date: April 1, 2006
- Project end date: May 31, 2012
- Percent complete: 99%

Budget

- Total project funding
  - DOE share: $2,650K
  - Cost share: $663K
- Funding received in FY11: $240K
- Planned funding for FY12: $75K

Barriers

A. **Durability:** Membrane and MEA durability

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

Partners

Scribner Associates – Through-plane and In–plane conductivity testing

High Temperature Membrane Working Group

Relevance

- Allows HTMWG Teams to concentrate on membrane development
- Membranes identified by supplier as promising are evaluated for in-situ performance
- Objectives:
  - Fabricate and test membrane electrode assemblies (MEAs) from Team membranes using standardized methodologies
  - Provide data and analysis to Teams to guide future development

Approach

- Evaluate proton conductivity
- Prepare and evaluate catalyst-coated membranes and MEAs
  - Performance, H_2 cross-over, and durability at high T, low RH
  - Pre- and post-test analysis including SEM, TEM, and cross-over/defect test
- Provide comprehensive report to supplier

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 < 2 mA/cm^2 (tested in MEA)

Desired Membrane Characteristics

High protonic conductivity

Low cross-over

Low electrical conductivity

Easily fabricated into an MEA

Good CCM performance

Good durability

Accomplishments
FuelCell Energy Membranes

High protonic conductivity

Low cross-over

Low electrical conductivity

Easily fabricated into an MEA

Good CCM performance

Good durability

Accomplishments FuelCell Energy Membranes

- Optimized electrode ionomer content (FCE ionomer) to maximize performance
  - Optimized electrode exhibited low cell resistance
  - *Observed a dependency of current interrupt resistance on electrode ionomer type and content*

FCE Membranes & DOE Targets

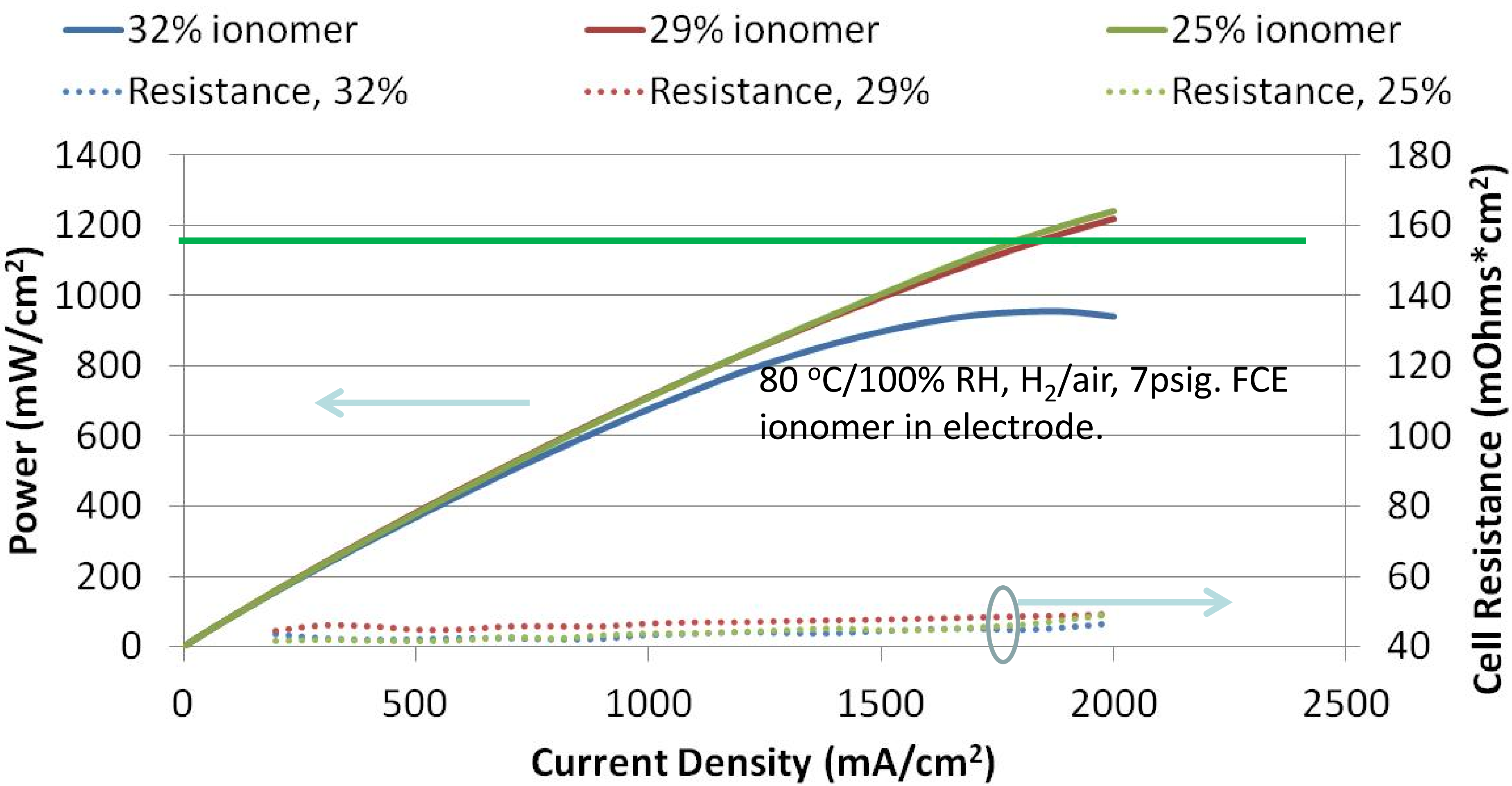
Characteristic	Units	Target 2017	B5 Opt.	B9 Opt.	NRE211 CCM
Area specific proton resistance at:					
120°C and 40 - 80 kPa H_2O partial pressure	Ohm cm^2	≤ 0.02	0.064*	0.110*	0.144*
80°C and 25 - 45 kPa H_2O partial pressure	Ohm cm^2	≤ 0.02	0.016‡	0.045‡	0.020‡
Contact Resistance (Interrupt – ASR)					
120°C and 70 kPa water partial pressure	Ohm cm^2		0.042	0.039	0.036
80°C and 38 kPa water partial pressure	Ohm cm^2		0.030	0.009	0.037
Maximum Hydrogen cross-over	mA / cm^2	2	1.6	<0.4	1.08
Minimum electrical resistance	Ohm cm^2	1000	417	855	526
Performance @ 0.8V	mA / cm^2	300	209	137	158
Performance @ rated power	mW / cm^2	1000	1239	577	936
Total fluoride emission during stability test	μmol	-	89	62	

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

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

- **Modifications to membrane to improve degradation may have led to increased resistance**
- **B5 CCM exhibited higher performance than DOE target**

Progress Towards DOE Power Target



Electrode optimization improved performance

FCE Summary

- FCE membranes show low proton resistance, even at high temp/low RH
- Electrode composition (with FCE ionomer) optimized through FSEC/FCE collaboration
  - Potential collaborative publication: capacitance vs. ionomer loading

Accomplishments
Case Western Membranes

High protonic conductivity

Low cross-over

Low electrical conductivity

Easily fabricated into an MEA

Good CCM performance

Good durability

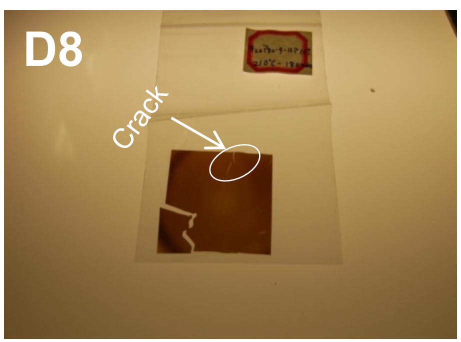
Accomplishments
Membrane Manufacturing

Brittle
- High Conductivity
- Fragile for CCM making

FSEC X-linking
- Avoided crack formation
- Successful CCM making

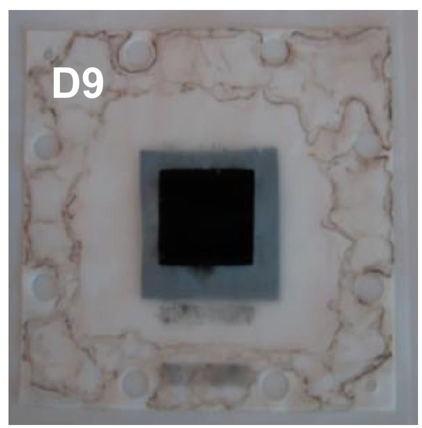
FSEC casting and X-linking
- ~1mil thick membrane
- Applied GDE

5 cm^2



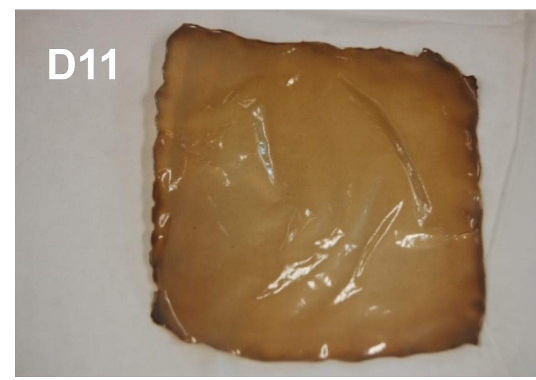
Brittle samples

5 cm^2



Sprayed x-linked membrane

25 cm^2



Recast and X-linked membrane

Accomplishments
MEA Manufacturing & Testing

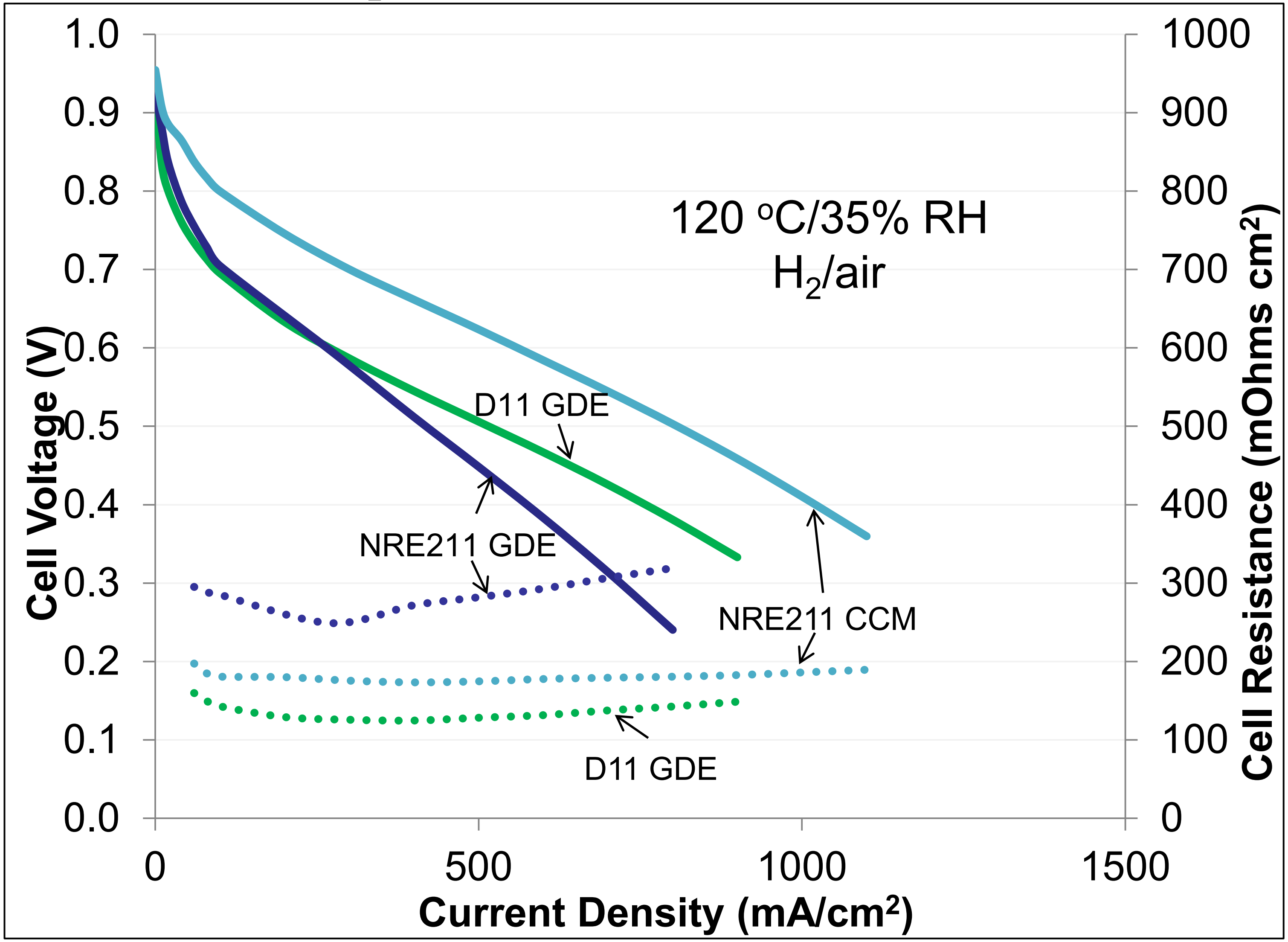
Modified test protocol in collaboration with CWR

- Assembled D11 into **GDE**-based cell
- RH maintained at 35% at request of CWR

• Assembled NRE 211 GDE and tested to same conditions as D11

- D11 out performed and out lasted NRE 211

GDE Impact on Performance



D11 membrane shows much lower resistance than NRE but performance could be improved with CCM

CWR Cell: GDE versus CCM

Characteristic	Units	Target 2017	D11 GDE 35%*	NRE211 GDE 35%*	NRE211 GDE	NRE211 CCM
Cell resistance at:						
120 °C and 70 kPa water partial pressure	Ohm cm^2		0.193	0.287	0.275	0.180
80 °C and 38 kPa water partial pressure	Ohm cm^2		0.100	0.158	0.064	0.057
Contact resistance						
120 °C and 70 kPa water partial pressure	Ohm cm^2		---	0.142	0.131	0.036
80 °C and 38 kPa water partial pressure	Ohm cm^2		---	0.048	0.044	0.037
Maximum hydrogen cross-over	mA / cm^2	2	<0.4	0.8	1.20	1.08
Hydrogen cross-over at EOT	mA / cm^2	2	<0.2	short	0.72	1.48
Minimum electrical resistance	Ohm cm^2	1000	1648	1101	1310	526
Performance @ 0.8 V (¼ power)	mA / cm^2	300	15	62	190	158
Performance @ rated power	mW / cm^2	1000	280	380	855	936

*Membranes tested at low RH as requested by CWR

Contact resistance is much higher for the GDEs than the CCM

D11 membrane showed better durability after testing in harsh conditions

CWR Summary

- FSEC assistance in casting and crosslinking has solved early issues
  - Crosslinking has eliminated solubility issues
  - Membrane thickness reduced to 1 mil
- Resistance from cell interrupt good
  - Membranes are highly conductive
- Cell performance is dominated by interfacial resistance with GDE
- Membrane integrity maintained even at harsh conditions

Accomplishments – Giner Membranes

High protonic conductivity

Low cross-over

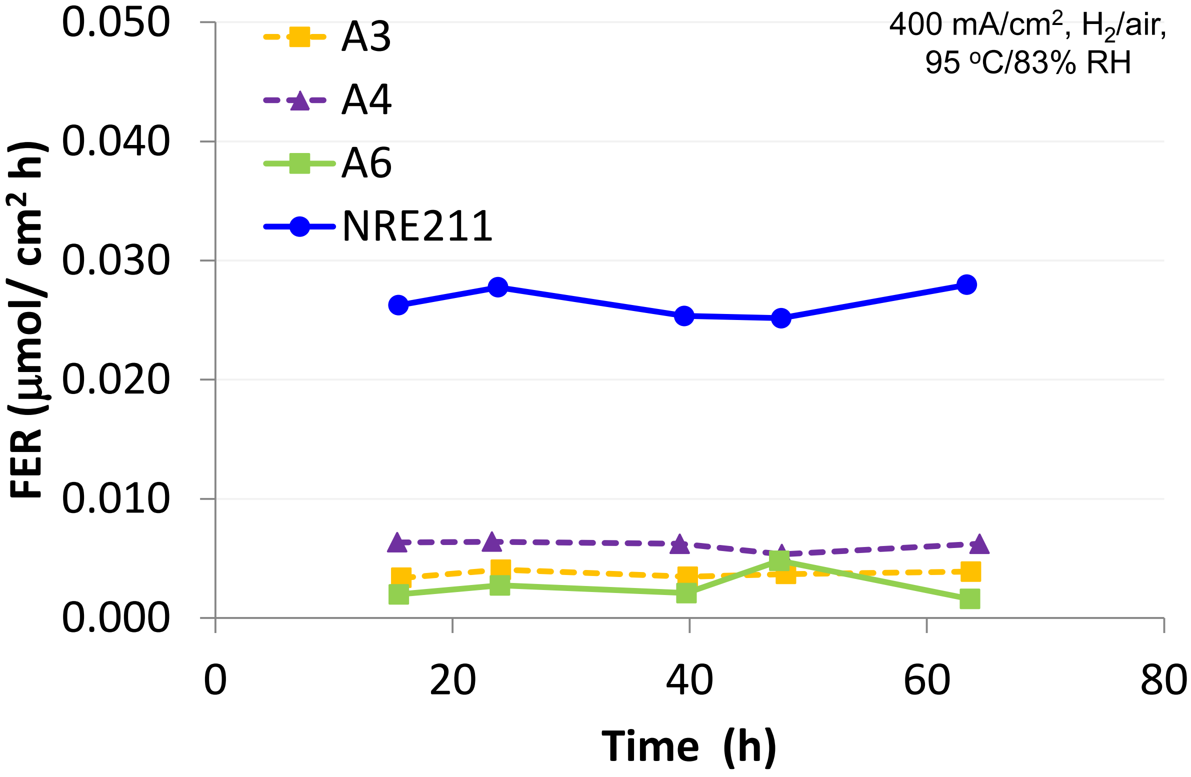
Low electrical conductivity

Easily fabricated into an MEA

Good CCM performance

Good durability

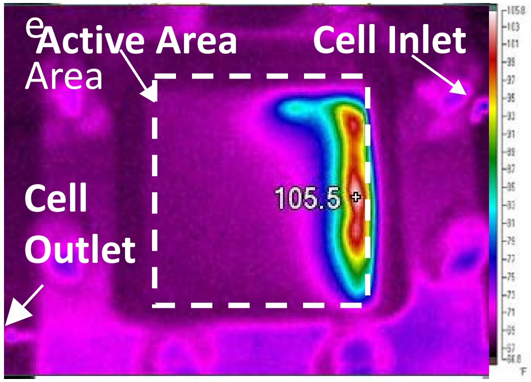
Giner Membrane Stability



Giner membranes consistently show FER that is an order of magnitude lower than NRE 211

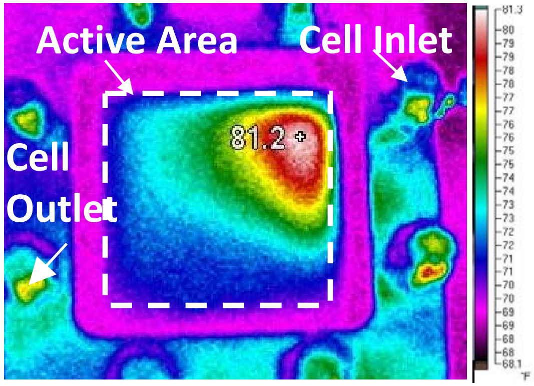
Localized Defects

A2



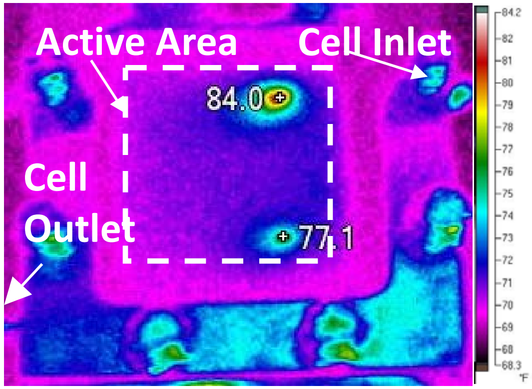
Large defect.

A3



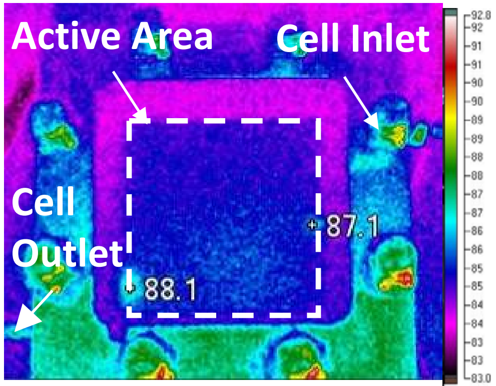
Large defect.

A4



Two defects.

A6



Two small defects present.

Membranes show fewer cracks and pinholes, after testing, in their more recent materials

Giner Summary

- Membrane durability shows good progress towards meeting DOE targets
  - Fluoride emission reduced
  - Defects reduced
- Giner membrane performance shows good progress towards meeting DOE targets
  - Membranes are less than 30 µm
  - Low H_2 cross-over
  - High electrical resistance

Accomplishments Vanderbilt Membranes

High protonic conductivity

Low cross-over

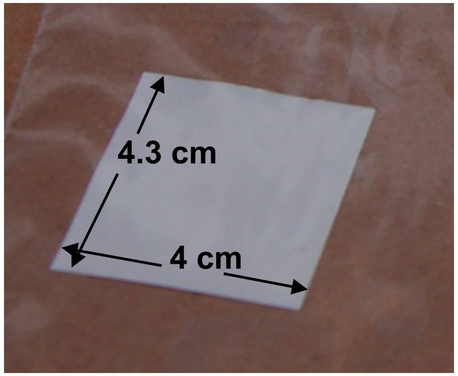
Low electrical conductivity

Easily fabricated into an MEA

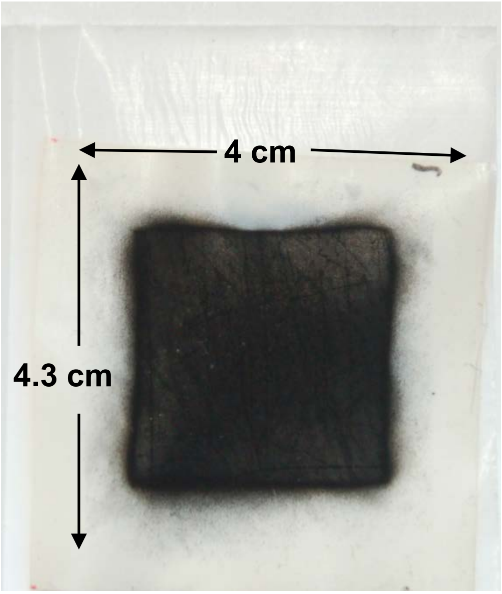
Good CCM performance

Good durability

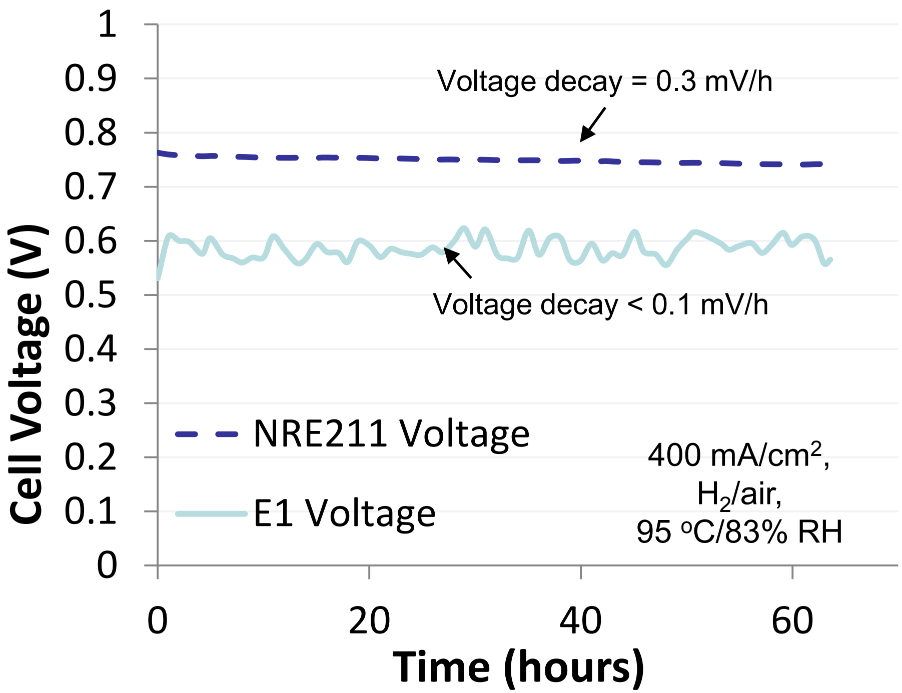
Accomplishments CCM Manufacture

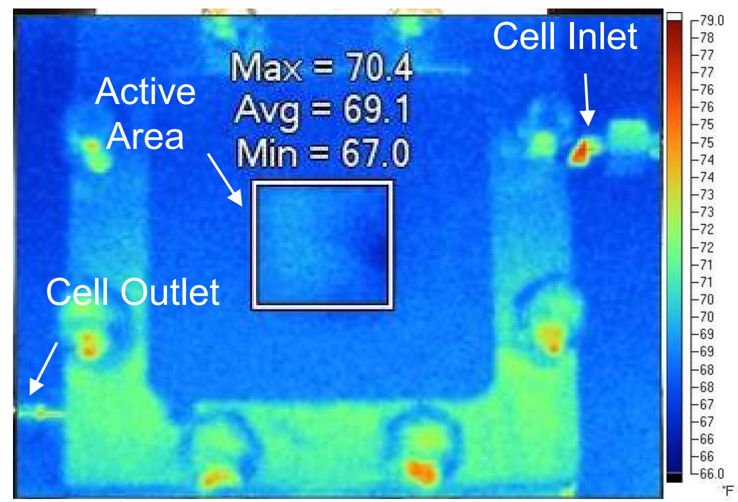


- Too small for standard cell
- Prepared CCM for 5 cm^2 cell



VU Stability & Defect Formation





E2 Cross-over ≈ 0 mA/cm^2 at end of test. No significant defects present.

- **Completed test protocol with second membrane**
- **Low cross-over should lead to good durability**
- **Few defects observed after testing**

Vanderbilt Summary

- **Easily constructed MEA**
- **Excellent stability**
- **Low cross-over**
- **Few cracks and pinholes**

Collaborations – Within Program

- Case Western Reserve – university
  - Supply membranes for MEA manufacture
- Giner Electrochemical Systems, LLC – industry
  - Supply membranes for MEA manufacture
- FuelCell 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*
- *Scribner Associates – industry*
  - *Subcontractor for through-plane and in-plane conductivity*

Proposed Future Work

- Continue to support teams
  - Prepare FCE MEA using newest membrane with optimized electrode
  - Validate CWR performance in 25 cm^2 cell at standard conditions
  - Prepare and test 25 cm^2 MEAS for Vanderbilt
  - Improve performance on Giner MEAs while maintaining high durability

- Examine membrane /electrode interface
  - Study interfacial resistance
    - Examine CWR MEAs by SEM to determine degree of contact between membrane and GDE
    - Decrease interfacial resistance of CWR MEAs by alternative electrode application methods
    - Focus on interfacial resistance for MEAs made with FCE ionomers Understand interfacial resistance for MEAs made with 3M ionomer and with Team member's ionomer
  - Determine differences in swelling rates between team member membranes and Nafion®
- Investigate mechanical properties as a function of degradation

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 show promise and should be pursued
- Improving one parameter may cause decrease in another
- Collaboration between FSEC and Teams guided CCM development
  - Excellent model for future DOE membrane development programs