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

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Project ID #**FC035**

Overview

Timeline

- April 1, 2006
- March 31, 2011
- 83% Complete

Budget

- Total project funding
  - DOE share - $2,500K
  - Contractor share - $625K
- Funding for FY09 - $450K
- Funding for FY10 - $500K

Barriers

- Barriers addressed
  - D. High Conductivity at Low RH & High T
  - C. High MEA Performance at Low RH & High T
  - A. 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 crossover 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

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

Relevance – 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
- Provide HTMWG members with standardized tests and methodologies
- Organize HTMWG bi-annual meetings

Relevance - Approach

Fuel Cell Performance:

Task 5. Characterize performance of MEAs for Team members

- MEA Test Protocol

Task 6. Characterize membrane & MEA durability for Team members

- MEA Durability Protocol

Standardized Testing

Task 3. In-Plane conductivity measurements by partner

Task 4. Through-Plane conductivity measurements by partner

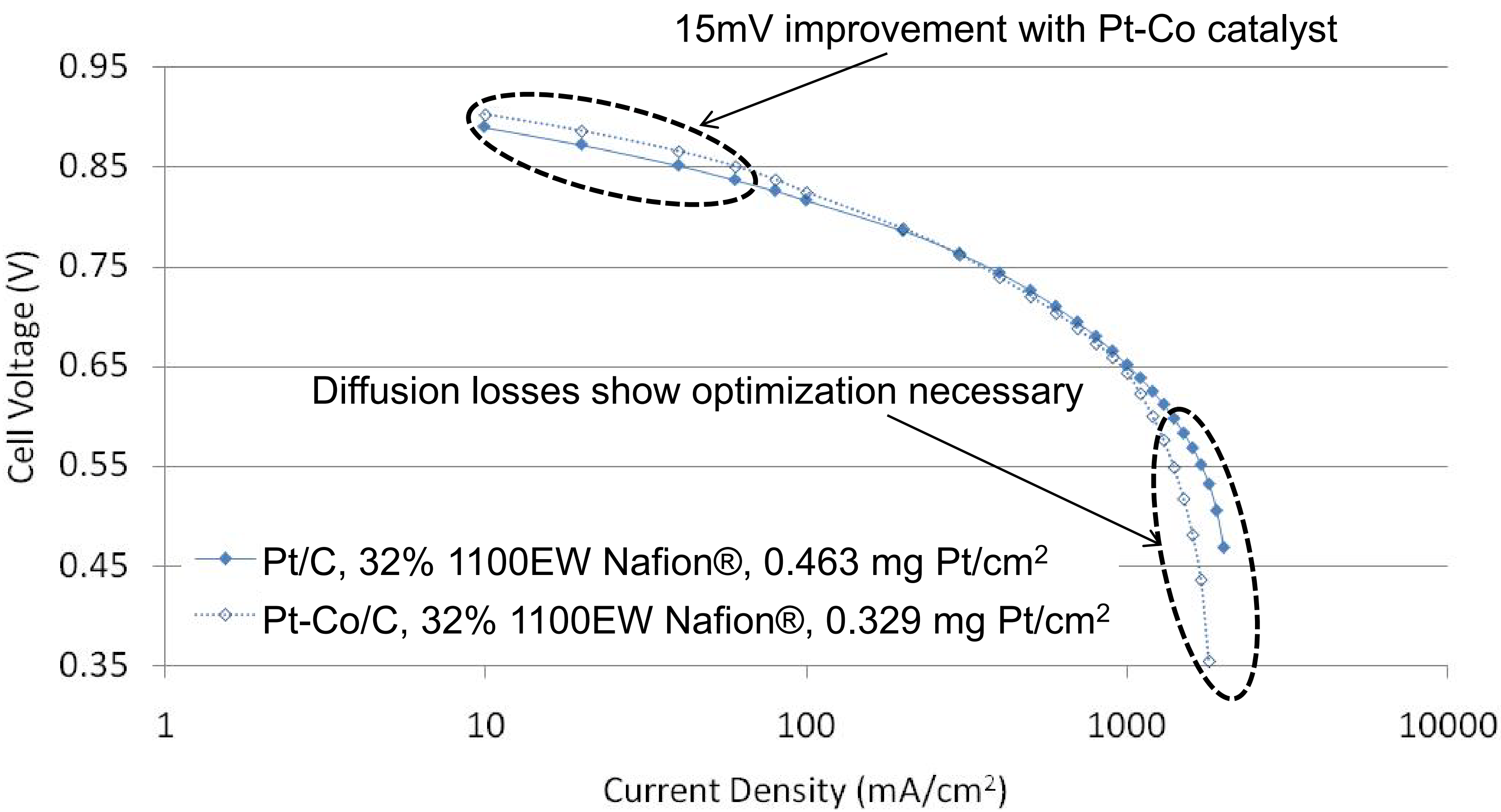
Task 7. Meetings and Activities of HTMWG

Technical Accomplishments and Progress

FSEC Electrode Fabrication

- Catalyst
  - Pt/C and Pt-Co/C
- Ionomer
  - PFSA, supplied as a dispersion in a mixture of water and alcohols
  - Equivalent weights = 1100, 950, 825, 750
  - Optimized loading ~ 25% to 32%, by weight
- Ink
  - Ionomer
  - Ethanol, propanol, methanol, water
  - Catalyst
- Ink application method
  - Spraying

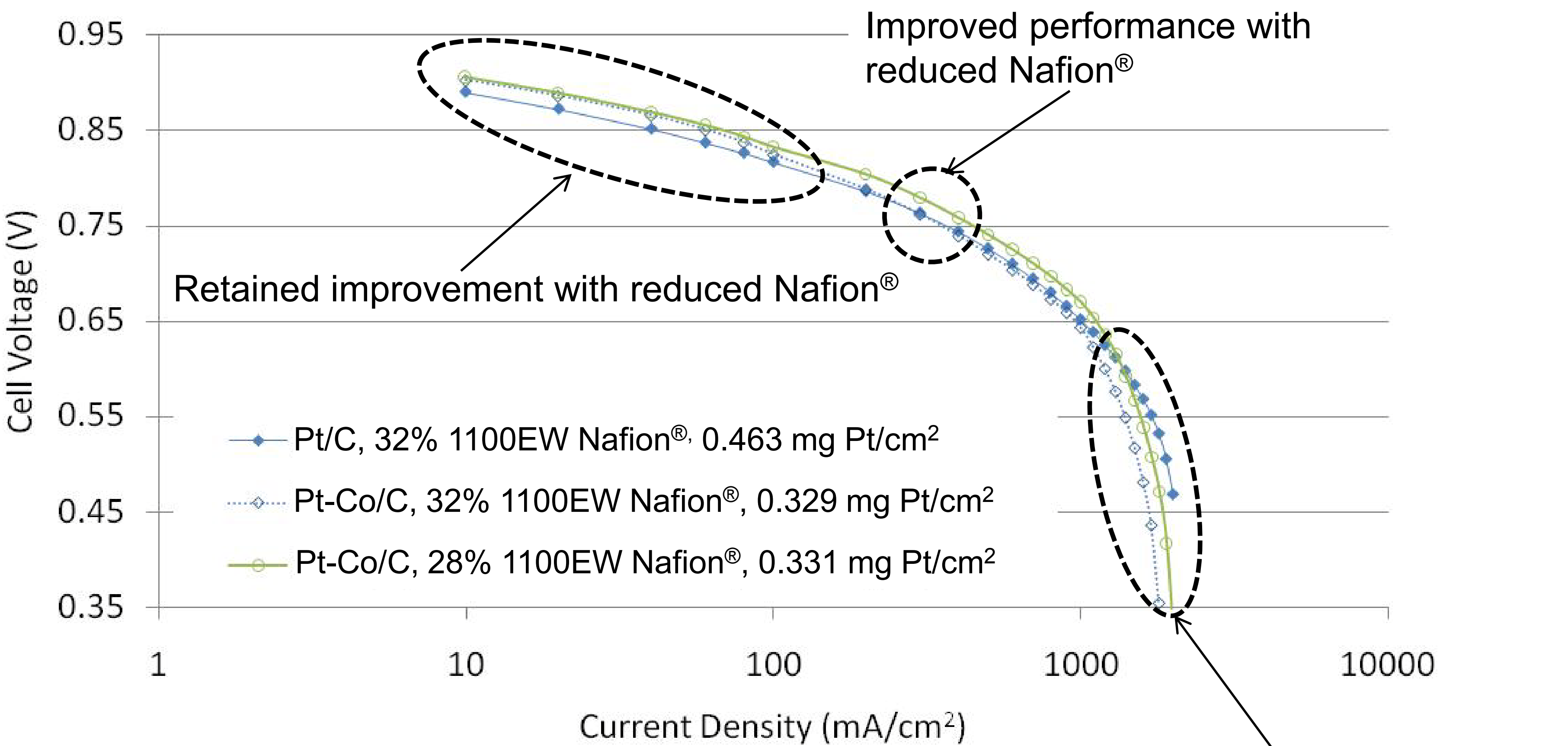
Higher Catalyst Activity for Pt-Co



80 ^{o}C/100% RH, H_2/air, 7 psi, PEM Test Protocol

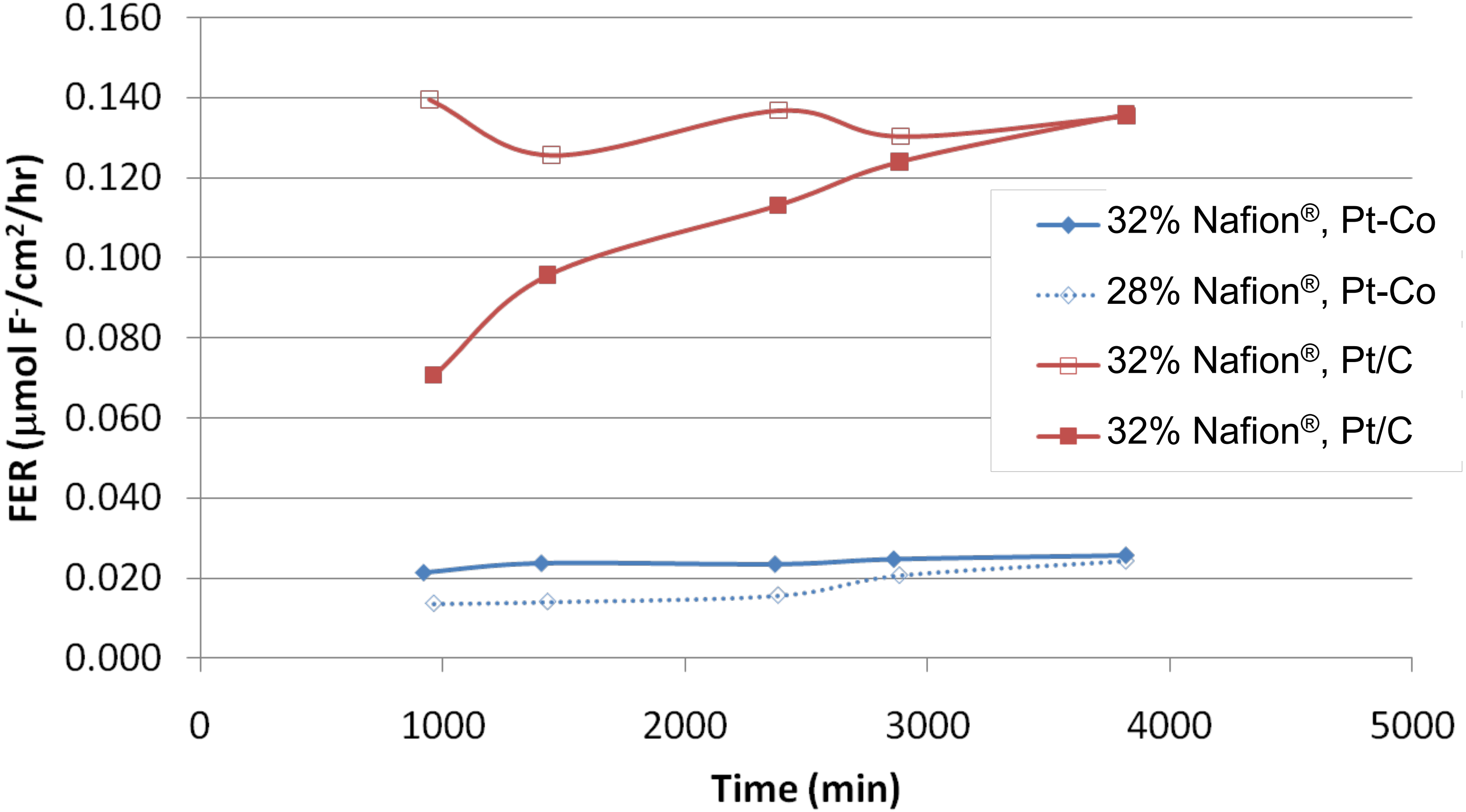
Pt-Co/C Electrode Improvement

(change in ionomer loading)



80 ^oC/100% RH, H_2/air, 7 psi, PEM Test Protocol

Lower Fluoride Emission Rate (FER) with Pt-Co



NRE 211 membranes with 1100EW Nafion® in electrode and Pt-Co or Pt/C catalyst. Durability Test 100 ^{o}C/70% RH, H_2/air, 7psi, constant current (10A) for 64 hrs

Electrode Fabrication for Program

- Pt-Co/C from Tanaka
- 3M™ ionomer in electrode
  - Some teams prefer their ionomer instead
  - Each new ionomer requires process modifications
- Team membranes
  - Optimization of electrode-membrane interface required

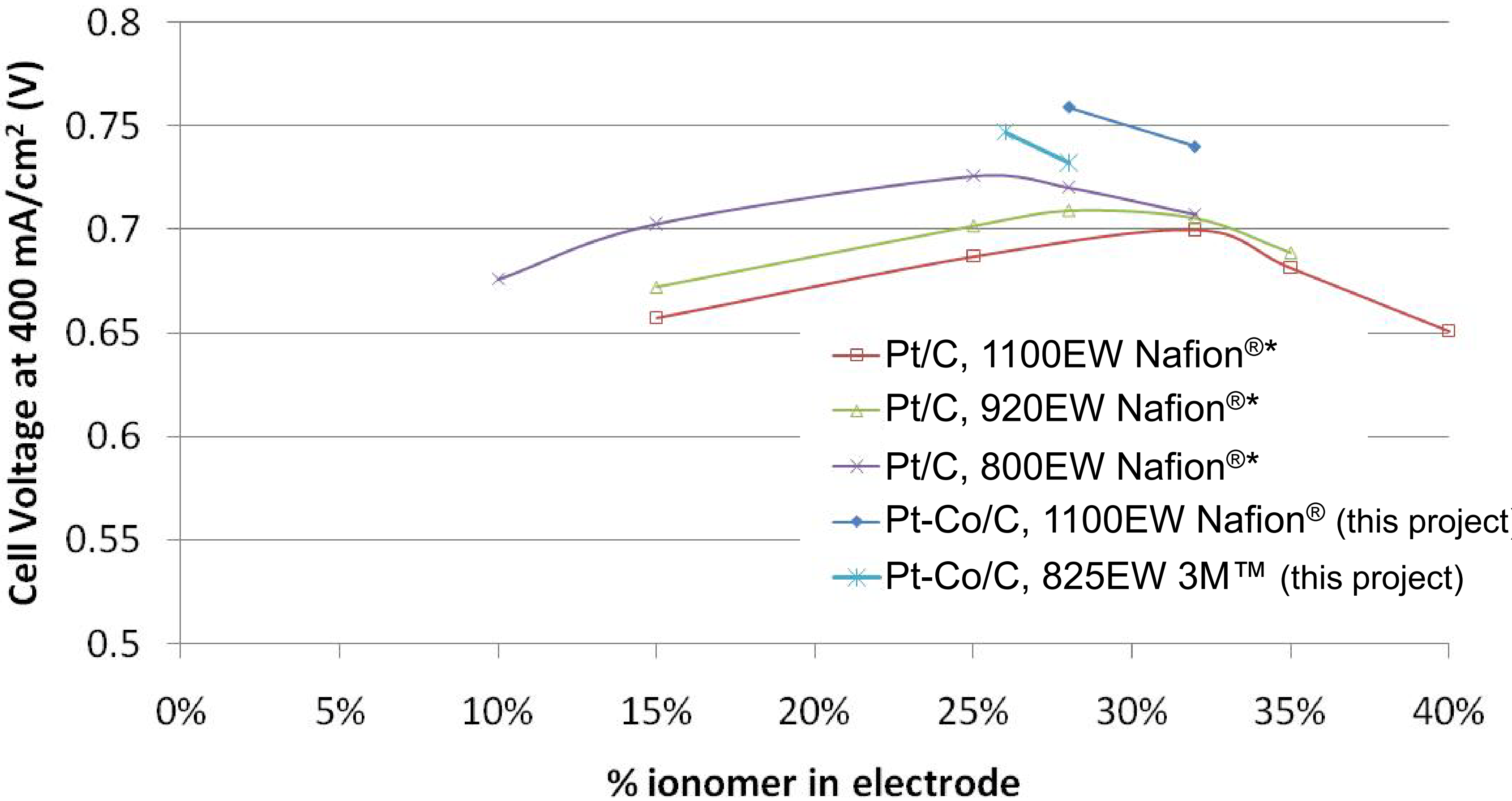
3M Ionomer in Electrodes

- Ionomer loading is known to have an impact on cell performance
  - Based on the EW of the 3M™ ionomer, 28% was chosen as a starting point*
- Higher ionomer concentration in dispersion means a slightly modified ink formulation

Electrode Formulations	
Using 5% Nafion® dispersion	Using 18% 3M™ dispersion
0.72 g Pt/C catalyst	0.72 g Pt/C catalyst
3.158 g water	3.158 g water
20 g methanol	20 g methanol
5.93 g Nafion® dispersion	1.56 g 3M™ dispersion

*H. Xu, H.R. Kunz, L.J. Bonville, and J.M. Fenton. "Improving PEMFC Performance Using Low Equivalent Weight PFSA Ionomers and Pt-Co/C Catalyst in the Cathode" /J. Electrochem. Soc./, vol. 154 (2), pp. B271-B278 (2007).

Optimization of Ionomer Loading is Dependent Upon EW and Catalyst



80 ^{o}C/100% RH, H_2/air, ambient

*H. Xu, H.R. Kunz, L.J. Bonville, and J.M. Fenton. "Improving PEMFC Performance Using Low Equivalent Weight PFSA Ionomers and Pt-Co/C Catalyst in the Cathode" /J. Electrochem. Soc./, vol. 154 (2), pp. B271-B278 (2007).

CCMs Sprayed

CCM Name	Membrane	Electrode ionomer Type	Electrode ionomer Loading	Electrode catalyst Type	Pt Loading (mg Pt/cm^2)	Post-Spraying Processing steps	Cell #
092509B	NRE 211	1100EW Nafion®	32%	Pt-Co	0.329	Cs, 180 °C HP, Prot	B414
092509S	NRE 211	1100EW Nafion®	32%	Pt-Co	0.355	Cs, 180 °C HP, Prot	
101309B	NRE 211	1100EW Nafion®	28%	Pt-Co	0.331	Cs, 180 °C HP, Prot	B415
101309S	**A1_FSEC1**	**1100EW Nafion®**	**28%**	**Pt-Co**	**0.343**	**No Cs, 136 °C HP, Prot**	**B342**
102809B	NRE 211	3M™	28%	Pt/C	0.437	No Cs, 136 °C HP, Prot	B340
102809S	NRE 211	3M™	28%	Pt/C	0.438	Cs, 150 °C HP, Prot	B417
110609B	NRE 211	3M + 4.4g PrOH	28%	Pt/C	0.348	No Cs, 136 °C HP, Prot	B344
110609S	NRE 211	3M + 4.4g PrOH	28%	Pt/C	0.331	Cs, 150 °C HP, Prot	
122209B	**A2_FSEC2**	**1100EW Nafion®**	**32%**	**Pt/C**	**0.439**	**No Cs, 136 °C HP, No Prot**	**B345**
122209S	NRE 211	1100EW Nafion®	32%	Pt/C	0.434		
010710B	NRE 211	3M + 4.4g PrOH	28%	Pt/C	0.342	Cs, 150 °C HP, Prot	B354
010710S	NRE 211	3M + 4.4g PrOH	28%	Pt/C	0.349		
011310B	NRE 211	3M + 4.4g PrOH	28%	Pt-Co	0.362	Cs, 150 °C HP, Prot	B355
011310S	NRE 211	3M + 4.4g PrOH	28%	Pt-Co	0.359		
012010B	NRE 211	Team B + PrOH	32%	Pt/C	0.402	Cs, 180 °C HP, Prot	B418
012010S	NRE 211	Team B + PrOH	32%	Pt/C	0.401	No Cs, 136 °C HP, Prot	B419
012210B	NRE 211	Team B + PrOH	32%	Pt/C	0.367		
012210S	**B1_FSEC4**	**Team B + PrOH**	**32%**	**Pt/C**	**0.383**	**Cs, 180 °C HP, Prot**	
020410B	NRE 211	Team B + PrOH	32%	Pt-Co and Pt/C	0.343 and 0.451		
020410S	**B2_FSEC5**	**Team B + PrOH**	**32%**	**Pt-Co and Pt/C**	**0.343 and 0.451**	**No Cs, 150 °C HP, no Prot**	**B358**
020510B	NRE 211	Team B + PrOH	32%	Pt-Co and Pt/C	0.371 and 0.432		
020510S	**B3_FSEC6**	**Team B + PrOH**	**32%**	**Pt-Co and Pt/C**	**0.371 and 0.432**	**No Cs, 180 °C HP, no Prot**	**B360**
021110B	NRE 211	3M + 4.4g PrOH	26%	Pt-Co	0.331	Cs, 150 °C HP, Prot	B357
021110S	NRE 211	3M + 4.4g PrOH	26%	Pt-Co	0.327		
022410B	**A3_FSEC3**	**3M + 4.4g PrOH**	**28%**	**Pt-Co**	**0.366**	**No Cs, 136 °C HP, no Prot**	**B359**
022410S	NRE 211	3M + 4.4g PrOH	28%	Pt-Co	0.362		
022610Up	**C2_FSEC15**	**1100EW Nafion®**	**32%**	**Pt/C**			
032410B	**A4_FSEC8**	**3M + 4.4g PrOH**	**28%**	**Pt-Co**	**0.396**		
032410S	**A4_FSEC8**	**3M + 4.4g PrOH**	**28%**	**Pt-Co**	**0.402**		

Effect of 3M™ Ionomer

Collaboration with Steven Hamrock

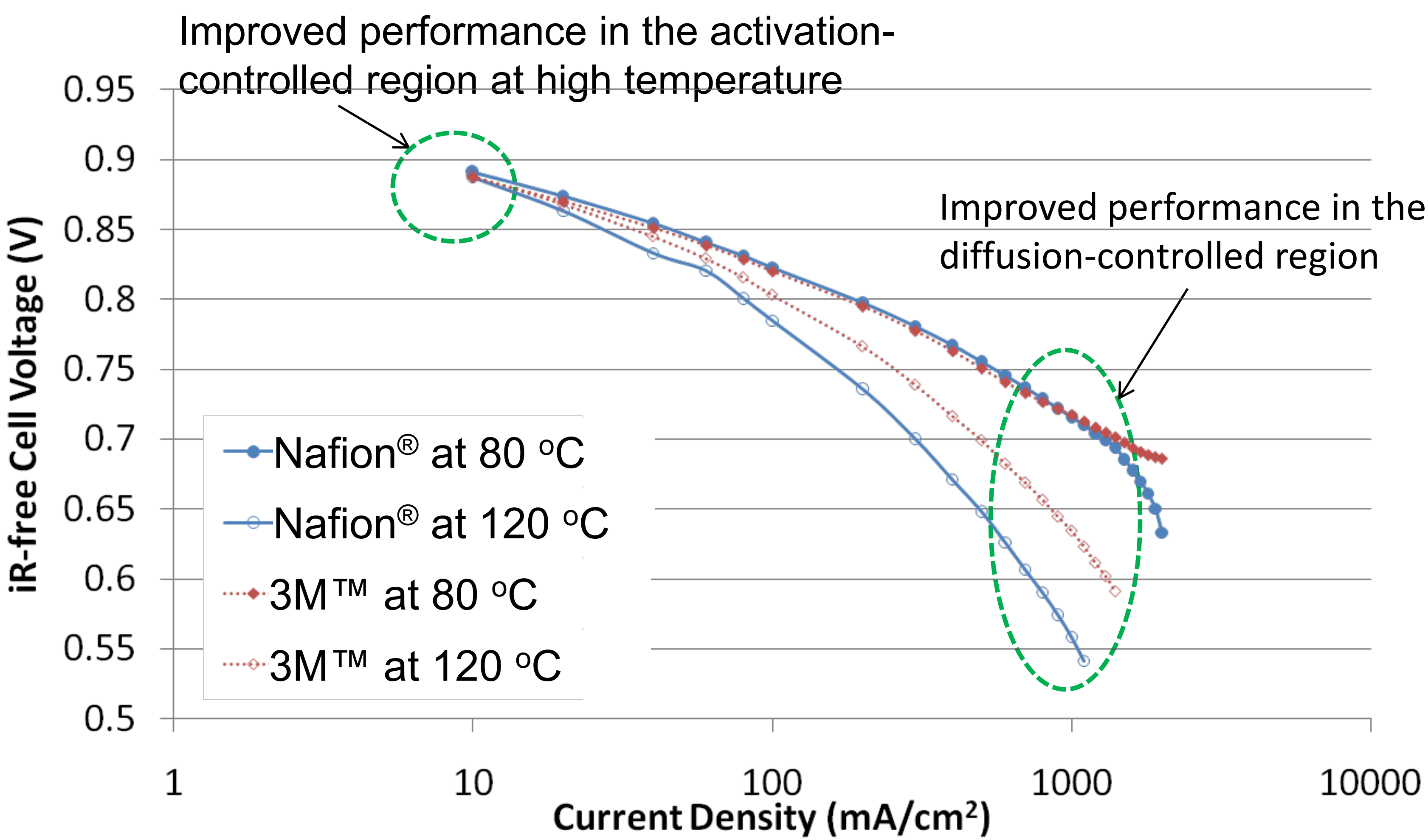
Comparison of Electrodes

- NRE 211 membranes
- All CCMs have been processed the same
  – Cesium treatment, hot press, protonated
- Difference in ionomer
  – 28% 3M™ ionomer chosen for low EW

Ionomer type	Ionomer loading	Catalyst type	Catalyst loading
3M™ ionomer	28%	Pt/C	0.437 mgPt/cm^2
1100EW Nafion®	32%	Pt/C	0.463 mgPt/cm^2

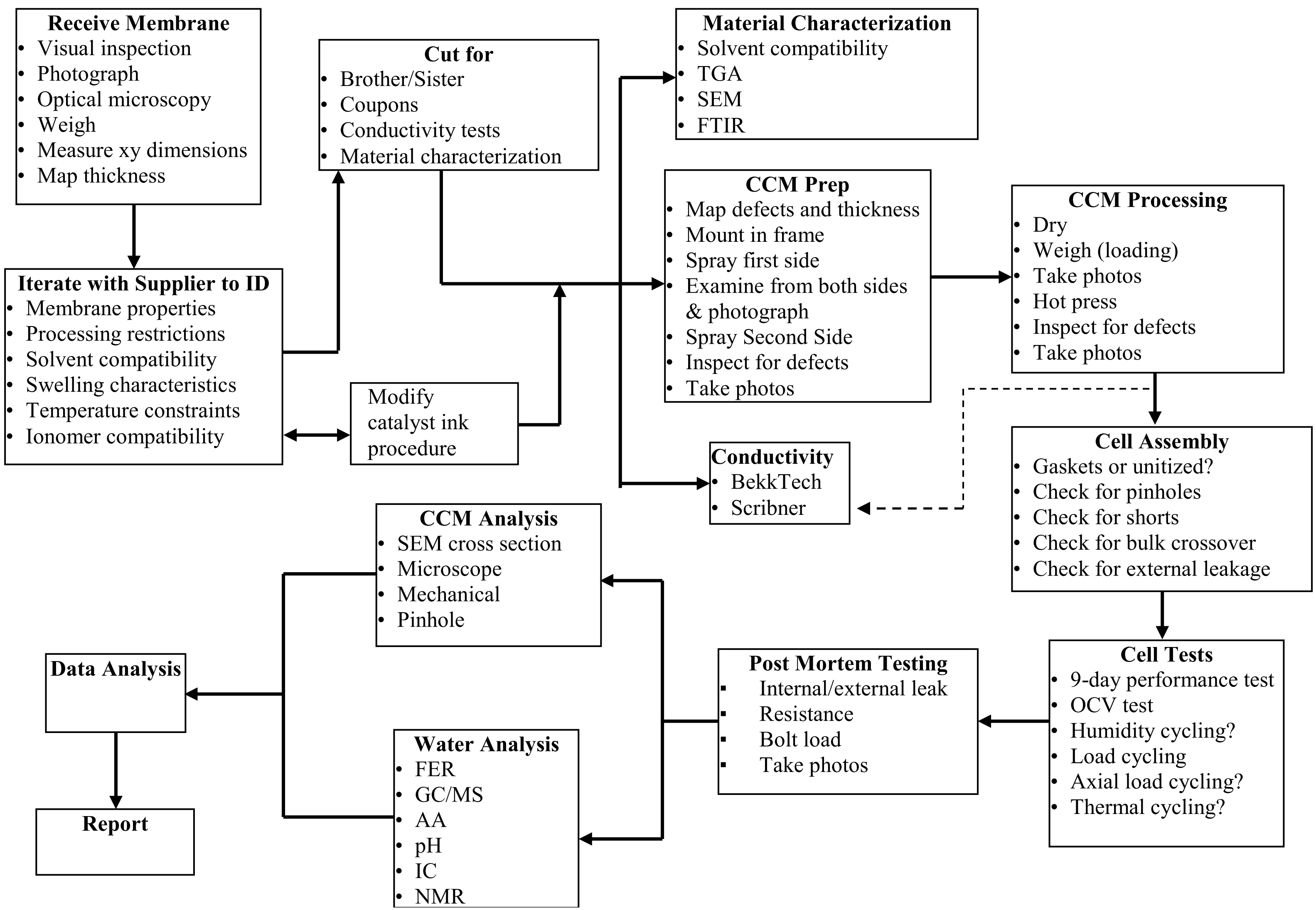
- Compared performance at 80 ^{o}C/100% RH, 100 ^{o}C/70% RH, and 120 ^{o}C/35% RH, all at 7psi

Performance Comparison with Pt/C 1100EW Nafion® vs. 3M™ Ionomer



All tests were conducted with H_2/air with 7psi backpressure
3M™ electrode used 28% 3M ionomer with Pt/C on an NRE 211 membrane.
Nafion® electrode used 32% 1100EW ionomer with Pt/C on an NRE 211 membrane.

Membrane Flow Chart



Collaborations

- Arizona State University
  - Don Gervasio
- Case Western
  - Morton Litt
- Colorado School of Mines
  - Andy Herring
- Fuel Cell Energy
  - Ludwig Lipp
- Giner Electrochemical Systems, LLC
  - Cortney Mittlesteadt
- Vanderbilt University
  - Peter Pintauro
- *3M*
  - *Stephen Hamrock*

Arizona State University

- ASU to supply MEA in hardware
- Agreement to try to use Flow Chart on ASU MEA hardware - February
- Subsequent Email communications exchanged

Case Western

- Agreement on Flow Chart for testing reached - February
- Multiple emails exchanged regarding the supplying of samples
- Preliminary samples received
  – Recasting of one sample
  – Another sample sent for through-plane conductivity testing
  – Coupon sized MEA prepared

Colorado School of Mines

- Agreement on Flow Chart for testing reached – October
- Preliminary sample received - February
- Iterating on In-Plane and Through-Plane conductivity
- MEA development ongoing

Fuel Cell Energy

- Agreement on Flow Chart for testing reached – October
- Received membrane sample (for baseline study) and ionomer solution - late December
  - Agreement to use FCE ionomer in ink
  - Ink with FCE ionomer sprayed on NRE 211
- Agreement to use Pt/C on anode and Pt-Co/C on cathode
  - MEAs fabricated
  - Flow Chart Tests ongoing

Giner

- *Preliminary sample* received - September
  - MEA tested following Preliminary Flow Chart
  - Results supplied and MEA returned to team
- Agreement on Flow Chart for subsequent testing reached - October
- Three additional samples received
- MEAs fabricated
  - Flow Chart Tests ongoing

Vanderbilt

- Agreement on Flow Chart for testing reached – February
- Discussion ongoing as to if MEA or membrane will be provided

Data Supplied to Membrane Provider

- All data supplied only to membrane provider
  - Detailed reports with analysis
  - Fuel cell data
    - Performance
    - CO/CV
    - Stability
  - Photos
    - Incoming membrane
    - Spraying process
    - CCM processing
    - Post test
  - FT-Ir spectra
  - Conductivity data
  - TG and DSC thermograms
  - Sister CCM and coupon

Proposed Future Work

- Continue to work closely with team members to
  - Characterize membranes
  - Prepare MEAs
  - Test MEAs in fuel cell hardware
- Collaboration with 3M on electrode development and characterization (should lead to publication next year)
- Comparison of area specific resistance measurements *in cell*, in-plane and through-plane are needed
- Need direction from DOE on area specific resistance controversy (in- and through- plane, actual cell, homogeneous and non-homogeneous)