New MEA Materials for Improved DMFC Performance, Durability, and Cost

Dr. Jim Fletcher

Dr. Philip Cox

University of North Florida

School of Engineering

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Project ID
FC064

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Overview

Timeline

- Start date: January 1, 2010
- End date: June 30, 2012
- Percent complete: 90%
- Passed Go-NoGo milestone in July, 2011
  - Durability: >60 mW/cm^2 for 500 hours
  - No off-state degradation for one week (system compatible conditions)

Barriers

Characteristic	Requirement -2013
Specific Power	30 W/kg
Energy Density	500 Wh/L
Cost	< $10/W at system level
Durability	3000 hours

Budget

- Total project budget $3,112,850
  - DOE share: $2,490,078
  - Contractor share: $622,772
- Funding received FY 11 $709,100
- Funding planned FY 12 $380,978

Partners

- University of Florida (UF)
- Johnson Matthey Fuel Cells (JM)
- Northeastern University (NEU)

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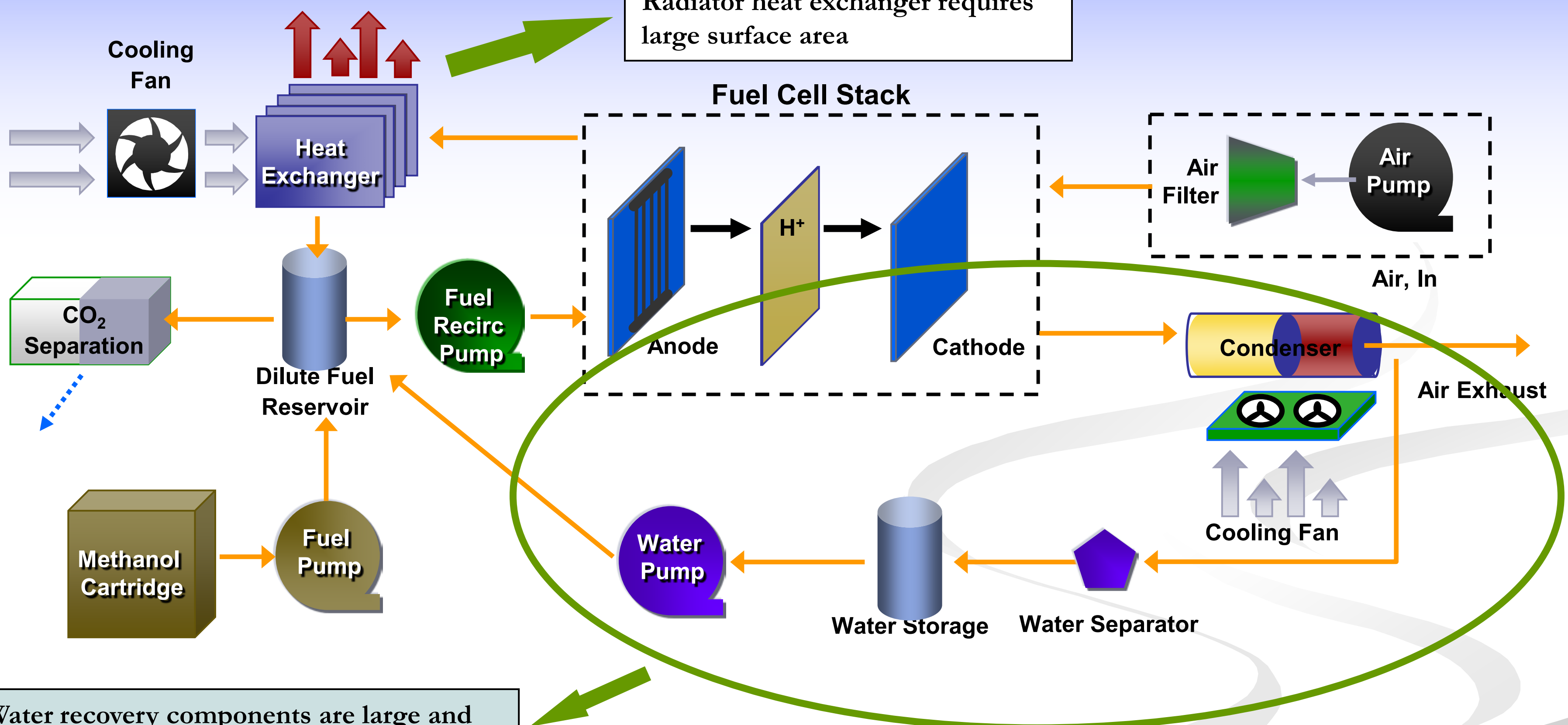
Relevance: Conventional DMFC System

Radiator heat exchanger requires large surface area



Water recovery components are large and cumbersome - also do not directly aid the electrochemical process

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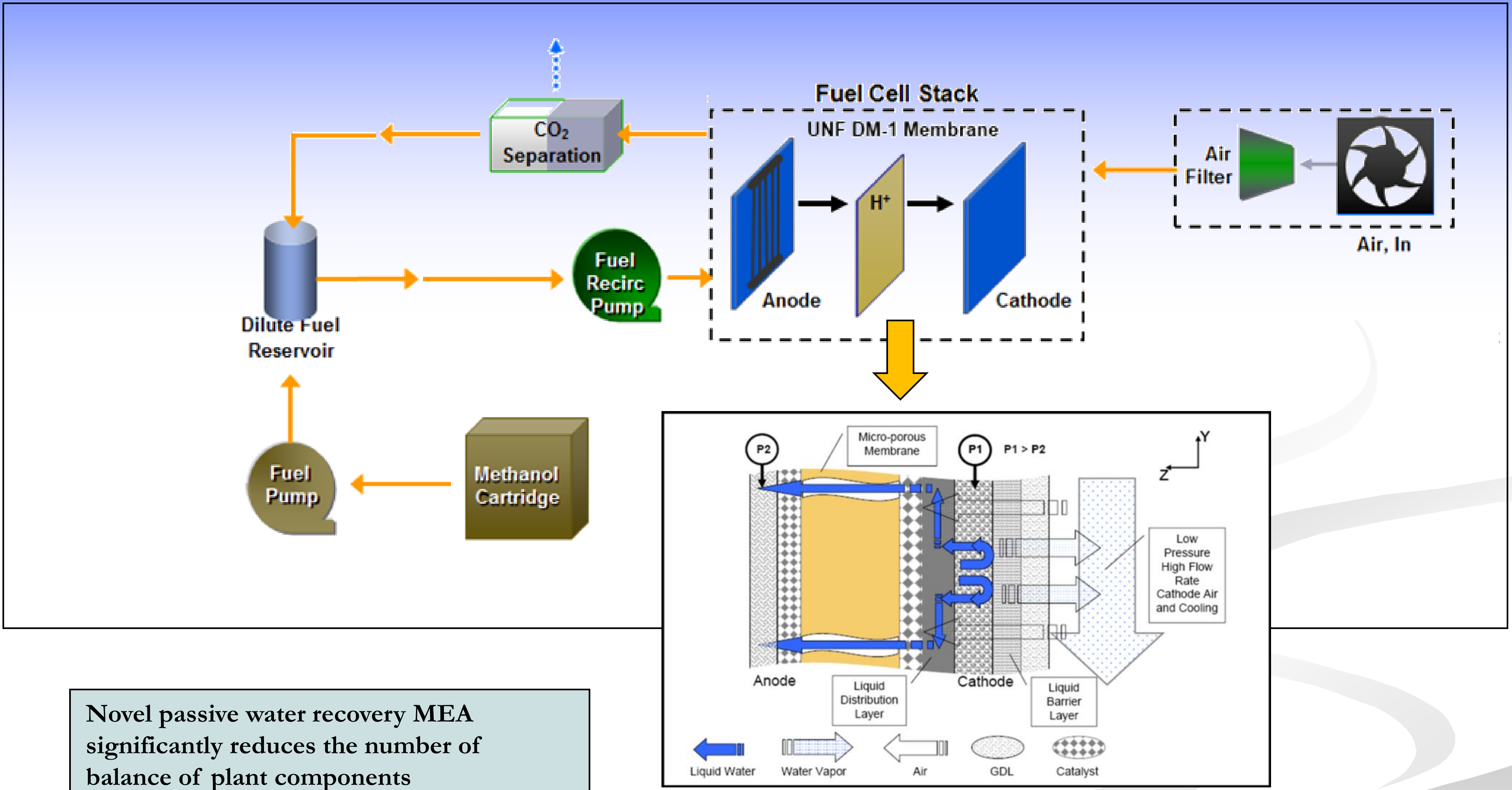
Relevance: UNF's Simplified DMFC System



Novel passive water recovery MEA significantly reduces the number of balance of plant components

UNF Passive Water Recovery MEA Design

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Relevance: Objective

- The project objective is to increase MEA functionality and internal water recovery to facilitate system simplicity, increased power and energy density, and reduced cost to address DOE's consumer electronics goals.
  - Improve the performance and durability of the UNF MEA to increase power, increase energy density, and lower the cost
  - Development of commercial production capabilities to improve performance and lower cost
  - Increase catalyst stability to lower degradation rates and lower catalyst loadings to reduce MEA cost

Relevance: Impact

- UNF Baseline Membrane Electrode Assembly (MEA) provides path to system simplification and increased power and energy density, with lower system cost.

DOE Technical Targets: Portable Power Fuel Cell Systems (10-50 Watts)					
Characteristic	Units	2011 Status	UNF DP4 Status 2011 (25 W Net)[1]	2013 Targets	2015 Targets
Specific Power	W/kg	15	26.3	30	45
Power Density	W/L	20	28.0	35	55
Specific Energy	(W-hr)/kg	150	263	430	650
Energy Density	(W-hr)/L	200	280	500	800
Cost	$/system	15	--	10	7
Durability	hours	1500	--	3000	5000
Mean time between failures	hours	500	--	1500	5000

[1] UNF values based on 10 hours operation

Continued improvement required for commercialization.

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Approach: Milestones

90% Complete

➢ Membrane Optimization
- Membrane Post-processing
- Commercial & Experimental Membranes
- Reversible Wet/Dry Cycling

95% Complete

➢ Barrier Layer Process Development
- Barrier Layer Ink Production
- Deposition of Barrier Layers
- Barrier Layer Optimization
- Quality Control Techniques

75% Complete

➢ Catalyst Development
- Commercial Catalyst Screening
- Ultra-stable Anode Catalyst
- EtOH Catalyst Development

90% Complete

➢ MEA Development
- Cathode Catalyst Layer Composition
- Cathode Catalyst Layer Deposition
- Anode Structure
- Catalyst Loading Optimization
- Delamination Mitigation

90% Complete

➢ MEA Performance and Durability Testing
- Short Stack Fuel Cell Testing
- Small-Volume Recirculated Fuel Loop Test

➢ Program Management
- Quarterly & Annual Reports
- Go /No-Go Decision - Passed
  - > 60 mW/cm^2 for 500 hours
  - Stable for one week in DP3 compatible rest

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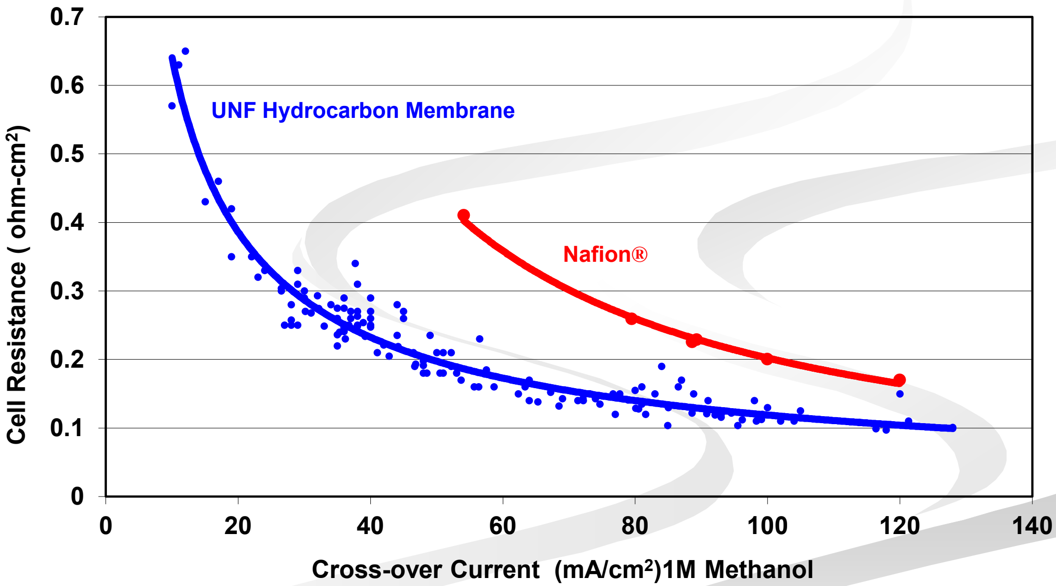
UNF DM-1 Membrane

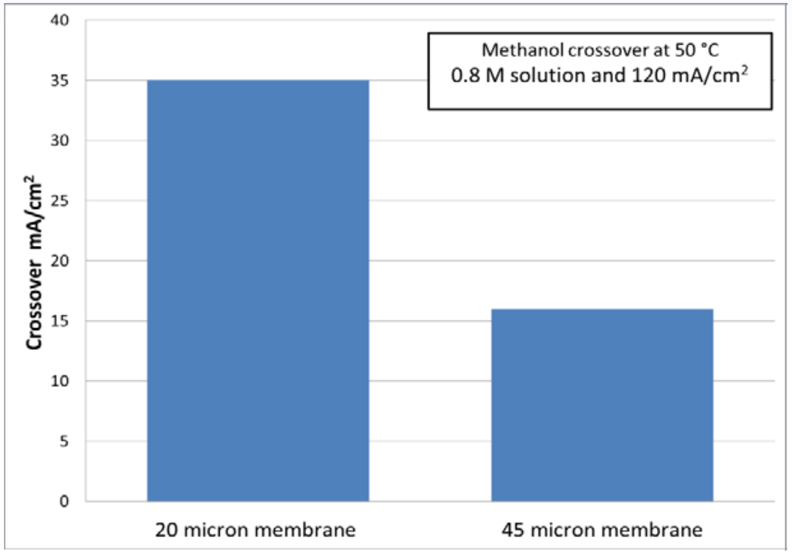
- Hydrocarbon polymer with sulfonic acid ion exchange groups – good control of membrane chemistry/properties
- Technology acquired from former partner PolyFuel
- Benefits for Passive Water Recovery MEA
  - Good chemical and mechanical stability in alcohol solutions
  - Low methanol crossover
  - Good ionic conductivity
  - Low level of water crossover - EOD

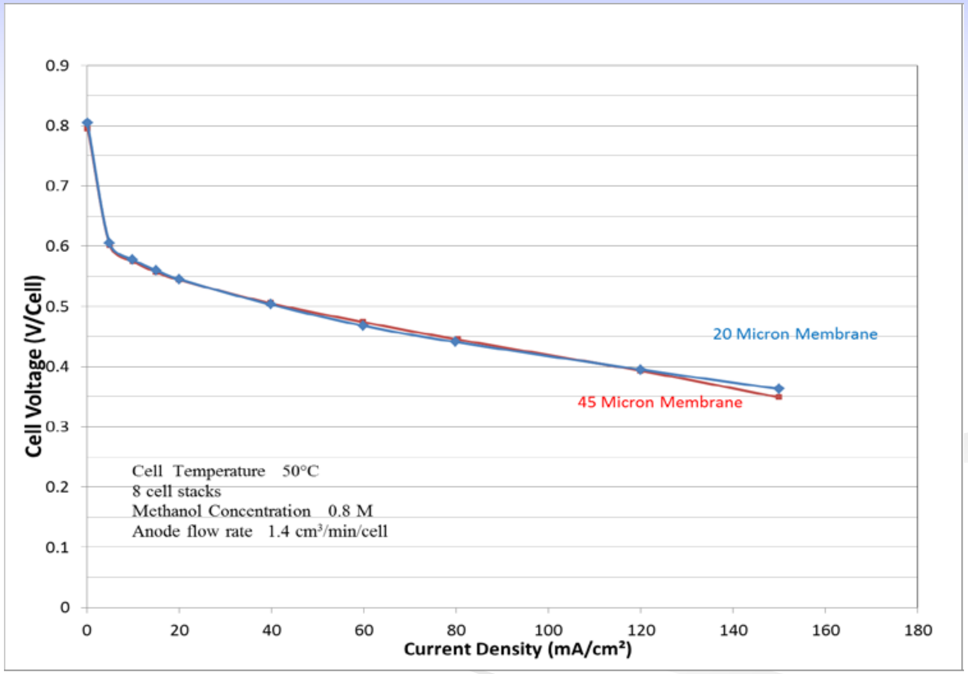


Technical Accomplishments:

Membrane Development and Optimization

- Increased membrane thickness to lower methanol crossover
- Improved Hot Bond coating and MEA fabrication





Significant reduction in methanol consumed in cross-over

Similar electrochemical performance between 20 μm and 45 μm membrane

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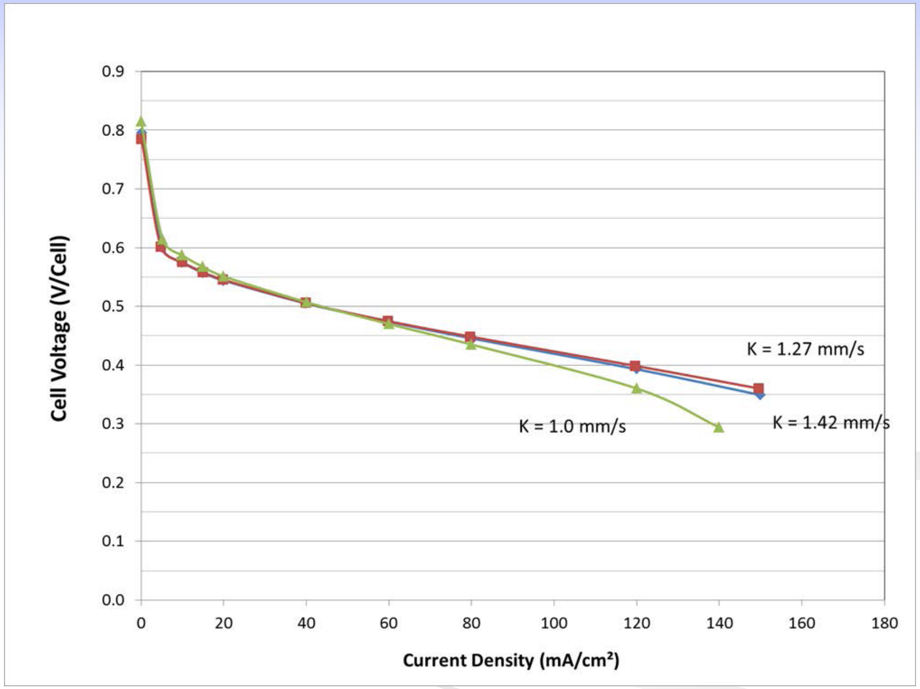
Technical Accomplishments:

Liquid Barrier Optimization

- Extensive effort to control barrier layer properties (thickness, materials, etc.)
- K-Value (K_{H2O}): Experimentally determined permeability (mm/s) of water through the liquid barrier layer
- Investigation underway to determine what parameters (operating temperature, barrier thickness, etc.) affect the K-value



UNF has achieved lower K-values without loss in performance
-Lower K-value = less water loss = higher operating temperature = better efficiency
-However there is a point where the reduced oxygen levels reduce performance

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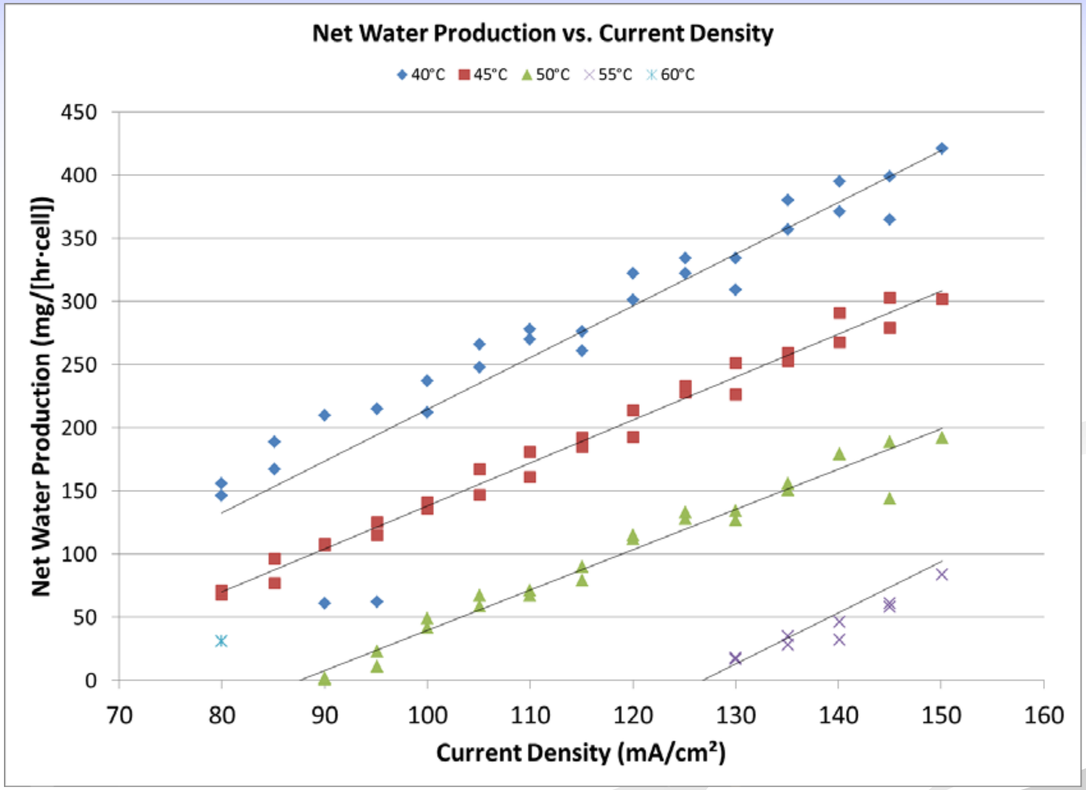
Technical Accomplishments:

Barrier Optimization

- Improved membrane/barrier properties have increased operating temperature (~45°C to ~55°C)
- Complicated interaction between methanol cross-over and barrier performance
  - Methanol combustion creates localized issues such as high temperatures
- Increased performance with more optimization

45 μm membrane, K_{H20} = 1.1 mm/s, MeOH = 0.8 M



Increased current density key to water balance

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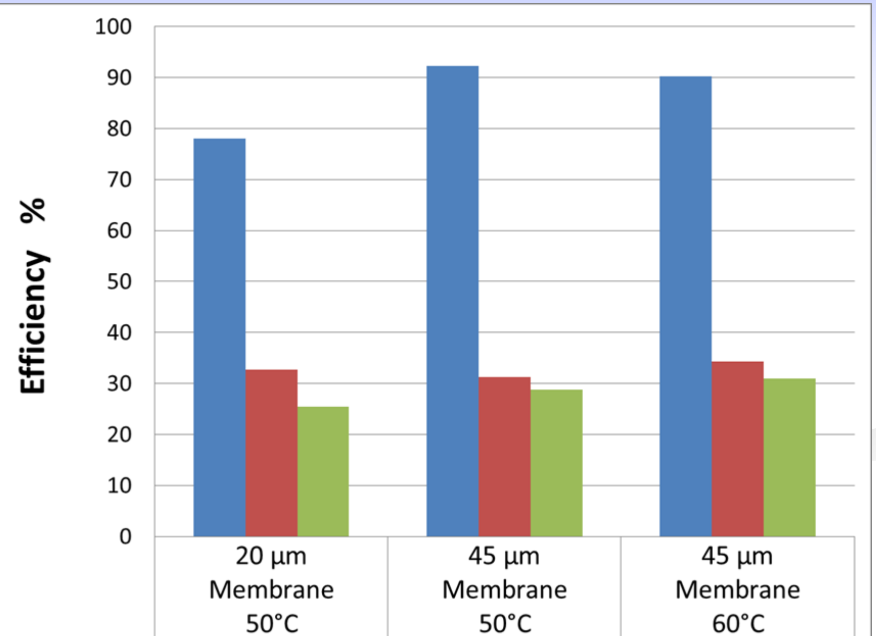
Technical Accomplishments:

MEA Optimization

- MEA optimization has resulted in significant improvements in performance
- Membrane improvements have resulted in fuel utilization efficiencies >90%
- Improved barrier performance has resulted in increased operating temperature and higher electrochemical efficiency



	20 µm Membrane 50°C	45 µm Membrane 50°C	45 µm Membrane 60°C
Fuel Utilization Efficency	78.1	92.3	90.2
Voltage Efficency	32.7	31.3	34.3
Overall Efficency	25.5	28.8	30.9

More than 20% improvement in MEA performance

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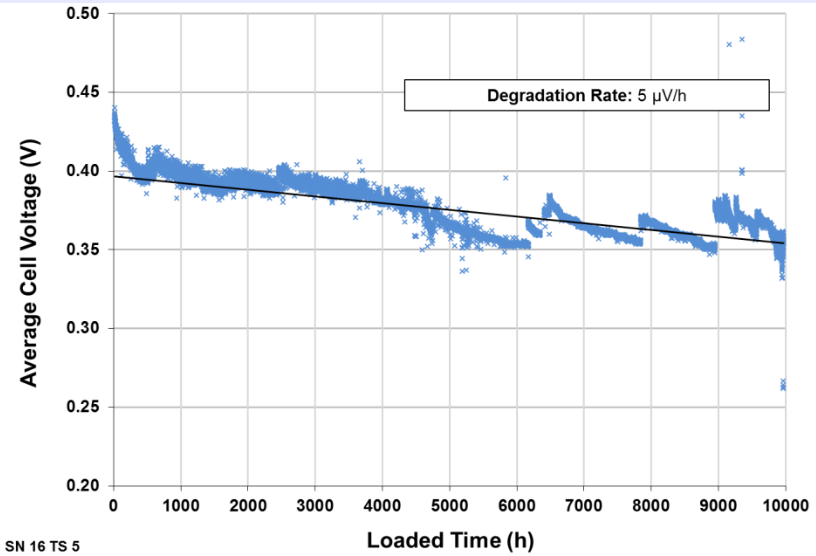
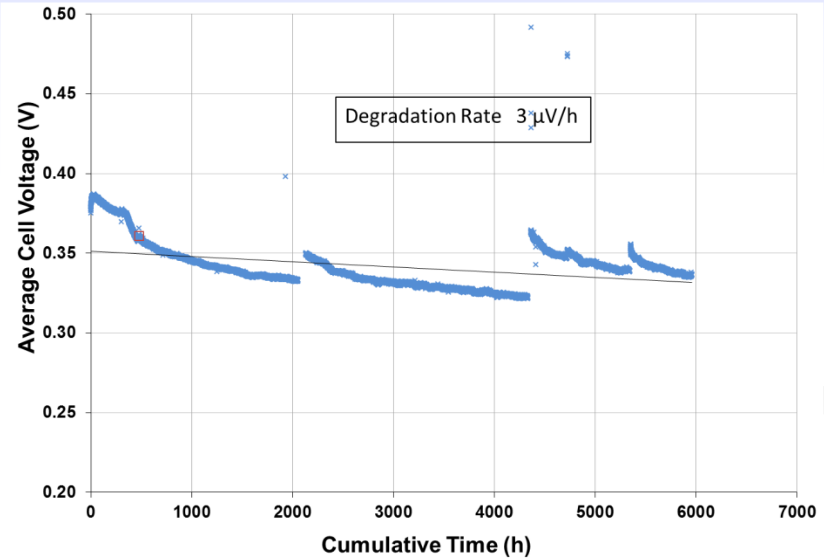
Technical Accomplishments:

MEA Durability

- MEAs shows excellent durability in continuous operation testing



Test stand durability. Average cell voltage at 120 mA/cm^2, 0.8 M methanol and 50°C for an 8 cell stack

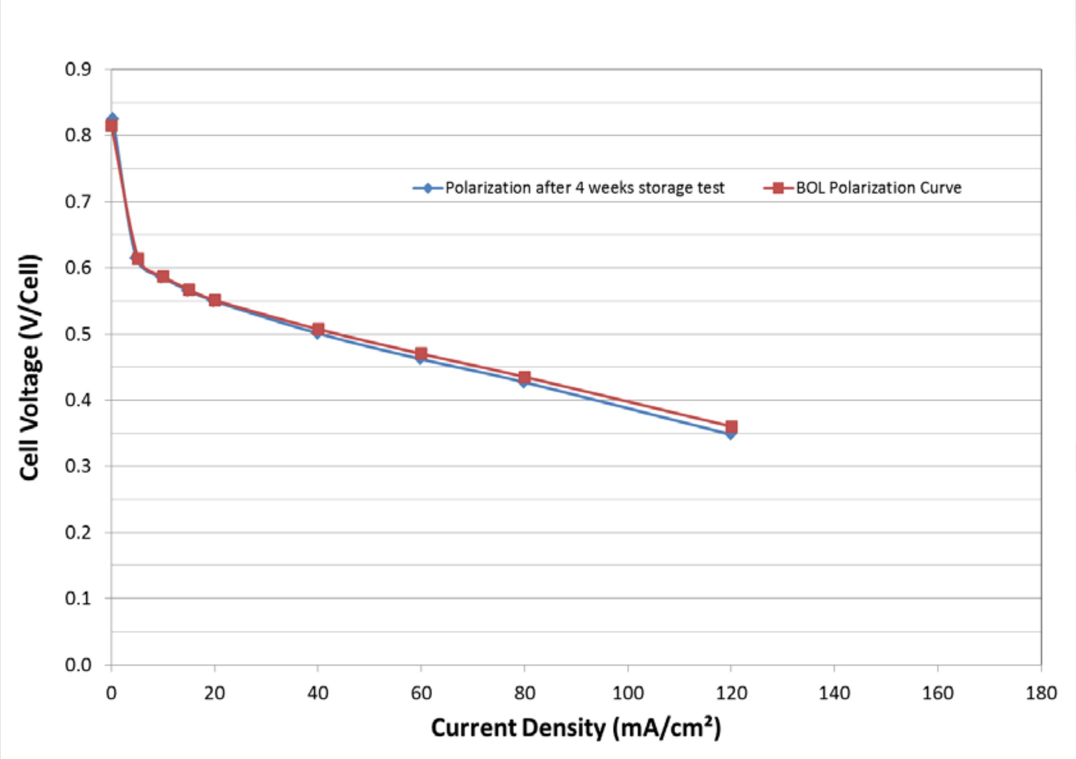


Test stand durability. Average cell voltage at 160 mA/cm^2, 0.8 M methanol and 50°C for an 8 cell stack

Technical Accomplishments:

Off-State Degradation

- Series 100 UNF MEAs displayed significant off-state degradation
- Root cause was the wetting agent for the cathode catalyst application
  - Series 200 MEAs use new wetting agent
- Series 200 MEAs show no activation loss in storage tests



Eliminating off-state degradation has allowed for better MEA performance analysis

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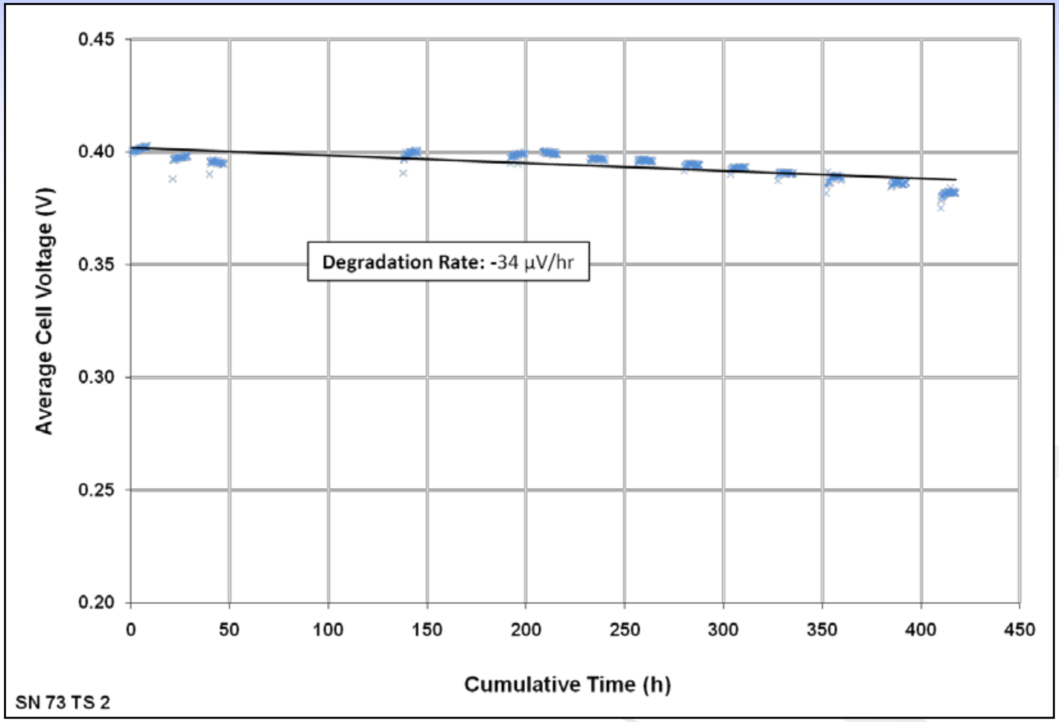
Technical Accomplishments:

Start/Stop Degradation

- Although Series 200 MEAs do not exhibit off-state degradation, daily operation (8 hours on/16 hours off) results in increased degradation
- Degradation in daily operation is "recoverable" and possibly due to oxide formation on the cathode catalyst

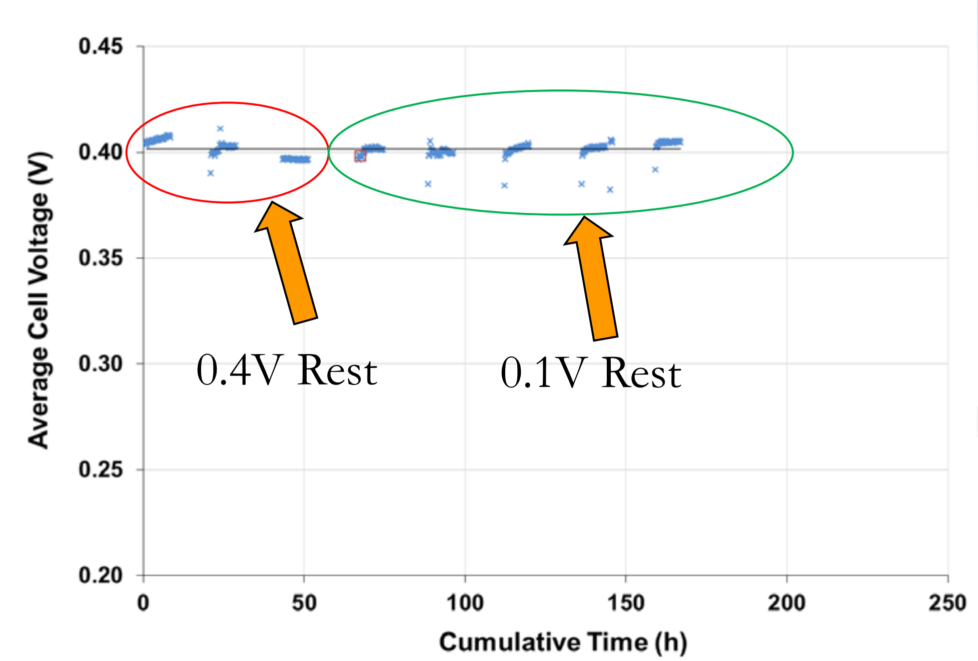


Data shows that the off-state degradation has been mitigated.

Technical Accomplishments:

Mitigation of Start/Stop Degradation

- Rest/rejuvenation in the "Passive Water Recovery" MEA challenging due to very short oxygen diffusion path
- Reducing the voltage during the air starve rest from 0.4 V to 0.1 V mitigates much (but not all) of the degradation during start/stop operation.
- Further optimization of rest profile underway.



Rest profile significant factor in mitigating degradation.

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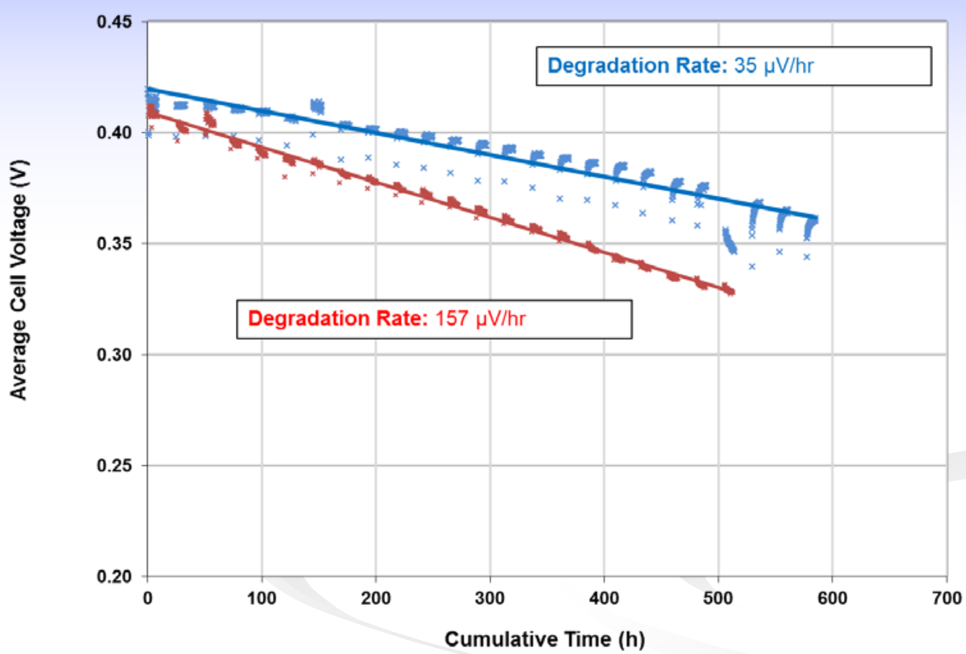
Technical Accomplishments:

MEA Improved Operating Profiles

- On/Off degradation has been significantly reduced
- Mitigation techniques include:
  - Changes to rest profile
  - Limiting oxygen access during shutdown
  - Pre-soak during start-up
- Mechanically "Sealing" the cathode has shown promise



Degradation rate increases with operating time.

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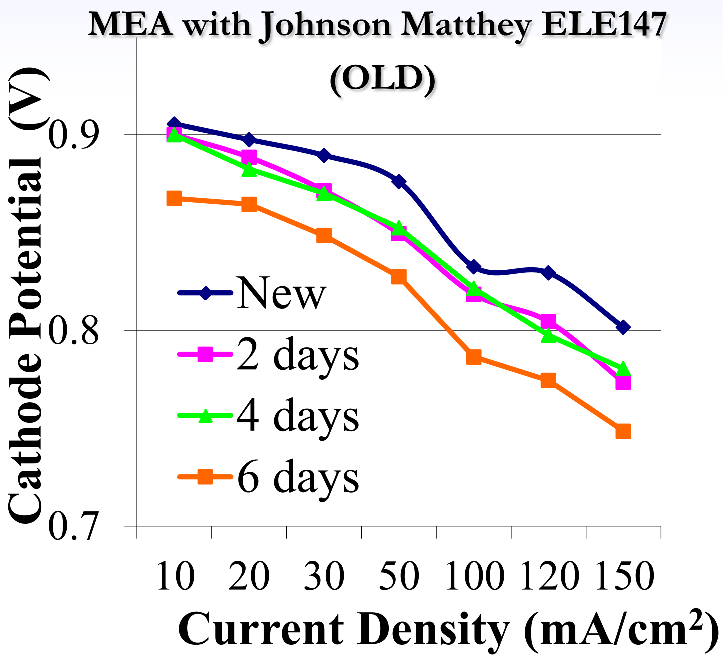
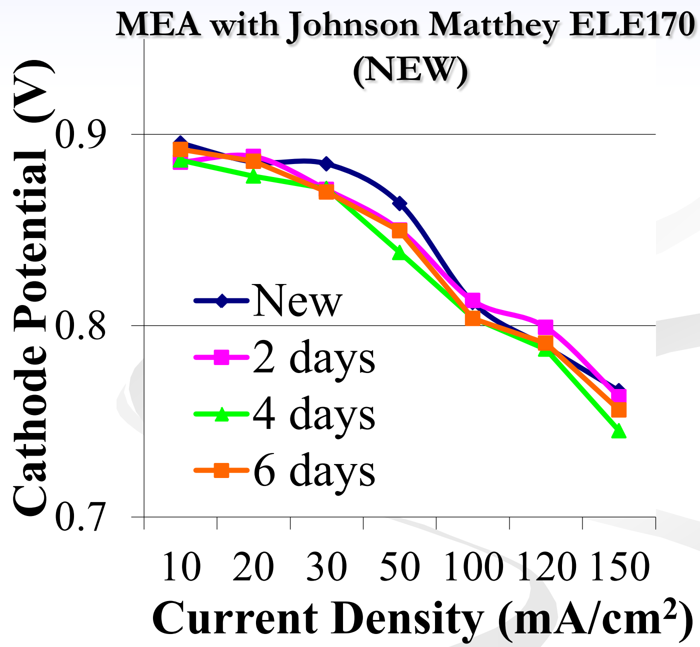
Technical Accomplishments:

Johnson Matthey: Improved Anode Stability

Anode stress test of commercially-available anodes: Cathode performance after continuous MEA testing under fuel starvation conditions (low methanol concentration, low operating voltage) to accelerate anode Ruthenium loss. (Voltage corrected for changes in resistance)





Similar performance with better stability using JM ELE170 anode electrode

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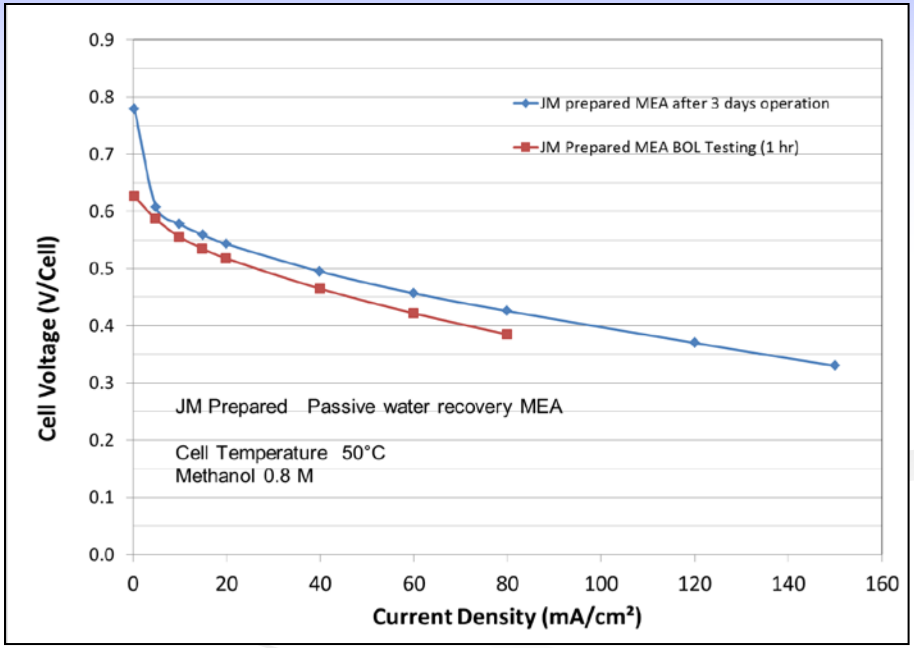
Technical Accomplishments:
Johnson Matthey: Barrier Layer Scale Up

- Knife coating technique allows for controlled, even application
  - Similar to continuous slot-coater for large scale production.
- Initial JM MEAs perform similar to UNF manufactured MEAs
- Provides a path to commercial production of the UNF Passive Water Recovery MEA



Performance improves with operation – more work required on MEA break-in procedure

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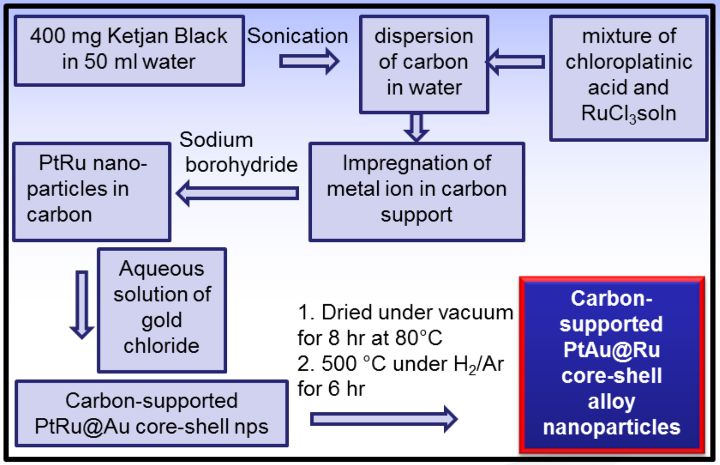
Technical Accomplishments:

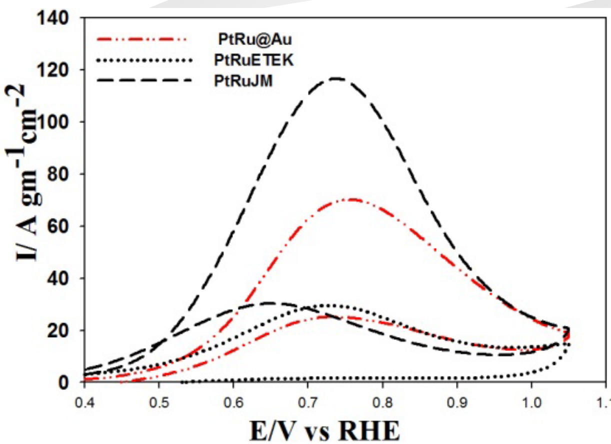
Northeastern University: Ultra-stable Anode Catalyst

- NEU achieved comparable electrochemical performance for new scaled-up production catalyst process
    - Ex-situ tests have demonstrated good stability against Ru loss

- Catalyst electrochemical performance better than ETEK catalyst but lower than the JM commercial catalyst



Scaled-up catalyst production process



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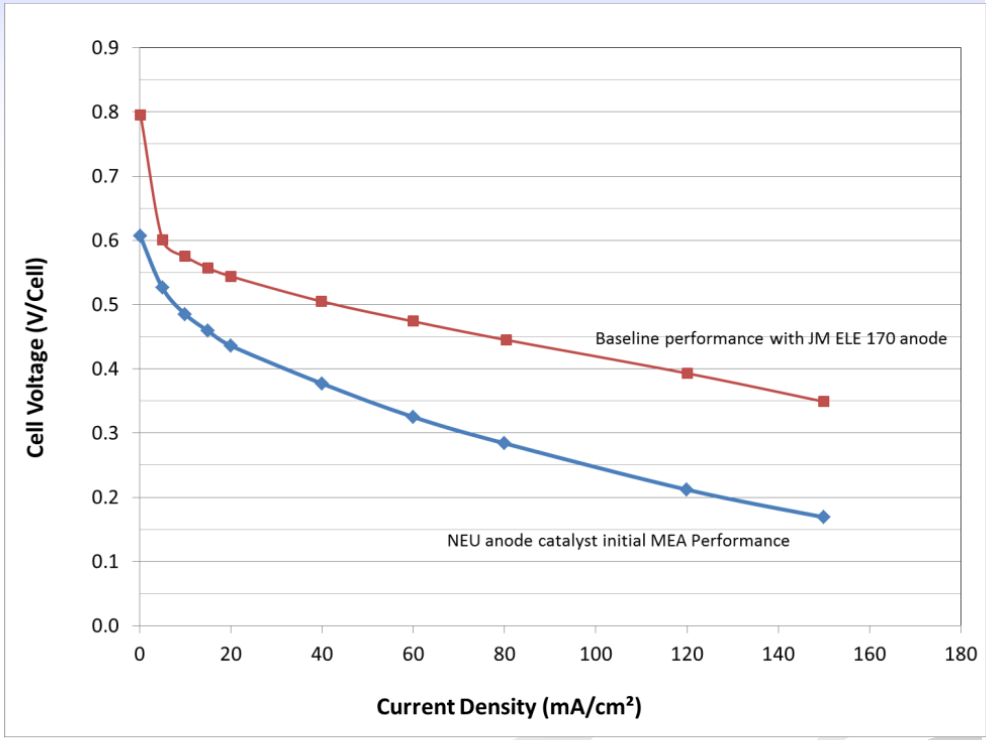
Technical Accomplishments:

Northeastern University: Ultra-stable PtRu MEA Tests

- Initial MEA Test show poor electrochemical performance
  - High area specific resistance - 0.9 ohm.cm^2
  - Catalyst loadings similar for both sets of MEAs
- Further MEA optimization is underway
  - Optimizing ionomer content to improve conductivity



JM ELE170 Anode shows best overall performance to date

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Technical Accomplishments

System Status

Technical Targets: Portable Power Fuel Cell Systems (10-50 Watts)					
Characteristic	Units	2011 Status	UNF DP4 2011 (25 W Net)[1]	2013 Targets	UNF 2013 (25 W Net)[2]
Operational Time	hours		10		14.3
Specific Power[1]	W/kg	15	26.3	30	30.1
Power Density[1]	W/L	20	28	35	30.6
Specific Energy[1]	(W-hr)/kg	150	263	430	430
Energy Density[1]	(W-hr)/L	200	280	500	437

[1] Calculation includes weight and volume of hybrid battery and fuel as defined by the DOE.

[2] Calculation assumes reduction in weight and volume based on component and brassboard (unpackaged) test results. Current MEA performance is used.

Present UNF DMFC technology nearly meets 2013 Technical Targets

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Collaborations

- University of Florida
  - Dr Tony Schmitz / Dr. William Lear: Manufacturing processes and quality control measurement development
  - Dr. Jason Weaver/Dr. Helena Weaver: Catalyst development, MEA characterization, and failure analysis
- Northeastern University
  - Dr Sanjeev Mukergee – Anode catalyst development and MEA testing /failure analysis
- Johnson Matthey Fuel Cells
  - Dr. Angus Dickinson – Anode structure development, liquid barrier layer process, cathode catalyst ink production, and MEA Fabrication Scale-Up:
  - <u>Commercialization</u> of UNF Passive Water Recovery MEA technology

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Proposed Future Work: FY 12

- MEA development (UNF, JM, UF)
  - Focus on catalyst reduction – reduce costs
- Stack testing (UNF)
  - Continued developing system compatible rest/rejuvenation and start-up/shutdown operating profiles to mitigate degradation
- Commercialize the UNF MEA (JM, UNF)
  - Continue technology transfer to JM including latest MEA sub-components
- Continued in-situ MEA tests to optimize ultra-stable NEU anode catalyst (NEU, UNF)
  - Improve performance with NEU "scaled-up" catalyst

Project Summary

- **Project Relevance:** The novel passive water recovery MEA technology allows for simplified balance-of-plant which results in a DMFC power supply approaching the DOE Technical Targets.
- **Approach:** Optimize the performance of the UNF MEA and transition the technology to commercially-viable processes. Integrate the advanced MEA into an advanced system architecture.
- **Technical Accomplishments:** Developed open cathode MEA fabrication processes to provide excellent MEA-to-MEA reproducibility. Optimized membrane and barrier properties. Developed MEAs with low on state degradation < 50 μV/h under a range of operating conditions. Eliminated the off state degradation by altering cathode catalyst ink wetting agent.
- **Collaborations:** In process of transferring baseline technology for the liquid barrier layer MEA to project partner JM.
- **Proposed Future Work:** Continue optimization of MEA performance and system operating profiles, start up and shut down to maximize durability and performance. Continue the transfer to commercially applicable processes.

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