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

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05/13/11

Project ID

FC064

Overview

Timeline

- Start date: January 1, 2010
- End date: June 30, 2012
- Percent complete: 50%

Budget

- Total project budget $3,112,850
  - DOE share $2,490,078
  - Contractor share $622,772
- Funding for FY 10/11 $1,400,000

Barriers

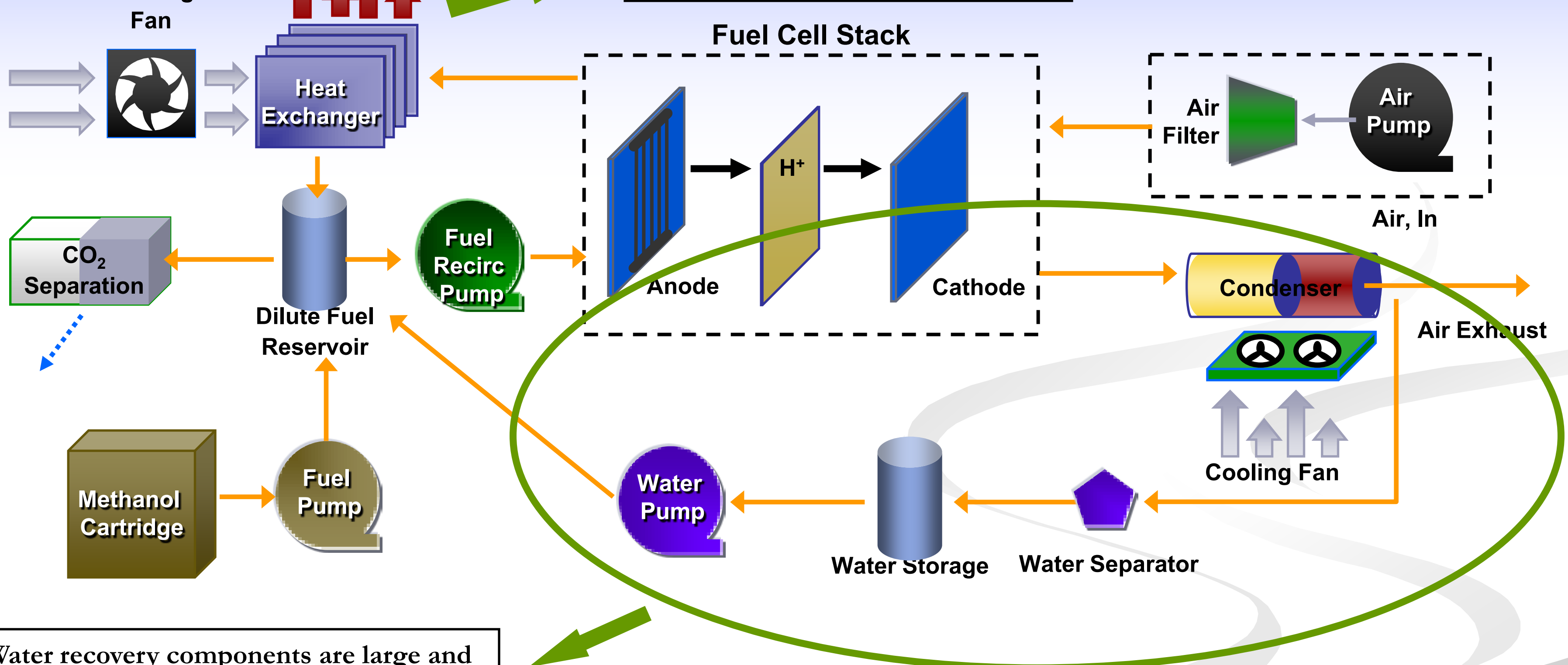
Characteristic	Requirement
Specific Power	100 W/kg
Energy Density	1000 Wh/L
Cost	< $3/W at the system level
Lifetime	2000 hours

Partners

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

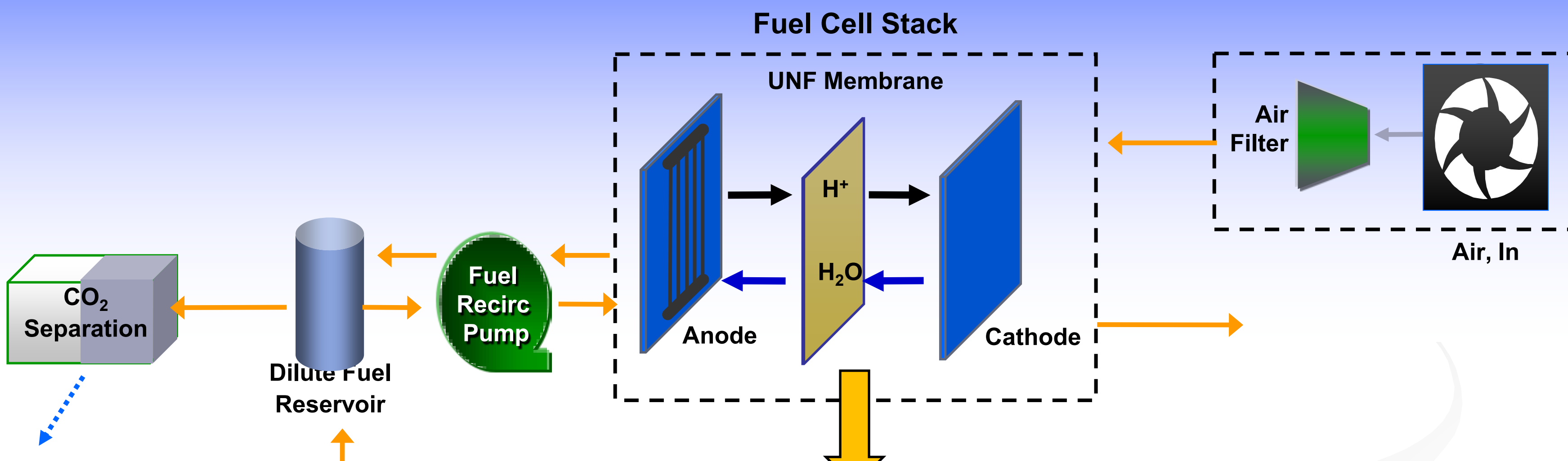
Relevance: Conventional DMFC System

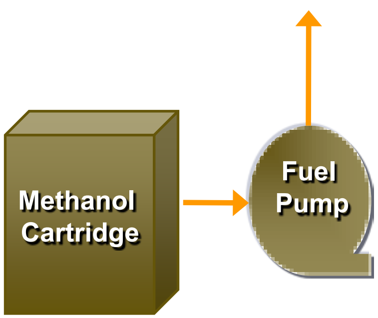
Radiator heat exchanger requires large surface area

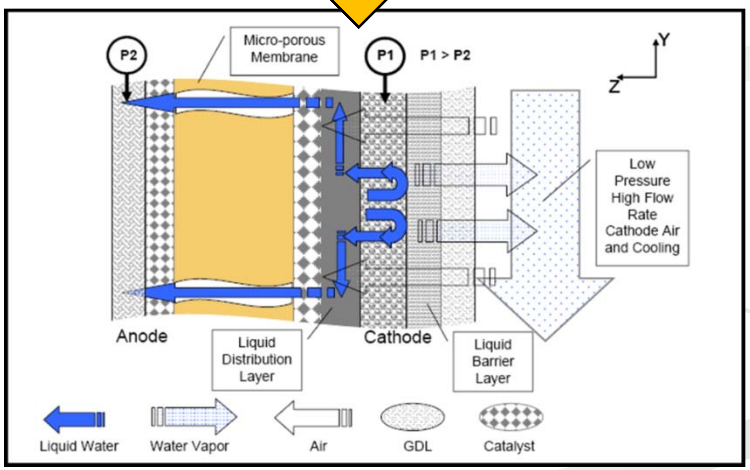


Water recovery components are large and cumbersome - also do not directly aid the electrochemical process

Relevance: UNF's Simplified DMFC System







UNF Passive Water Recovery MEA Design

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

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Relevance: Objective

- The project objective is to increase MEA functionality and internal water recovery which facilitates system simplicity, increases power and energy density as well as reduce 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.

Characteristic	Units	UNF 15 W DP3 2008 Status	DOE 2010 Target	UNF Proposed 20W System Design
Specific Power [a]	W / kg	35	100	41.5
Power Density [a]	W / L	48	100	55.6
Energy Density	W-hr / L	250 (1 x 100ml)[b] 396 (1 x 200ml)[b]	1000	193(1 x 100ml) 321 (1 x 200ml) 575 (3 x 200 ml)
	W-hr/kg	155 (1 x 100ml)[b] 247 (1 x 200ml)[b]	N/A	162 (1 x 100 ml) 307 (1 x 200 ml) 638 (3 x 200 ml)
Lifetime [c]	Operating Hours	1,000 hrs in single cell	5,000	2,500 Integrated System
Cost	$ / Watt	11 (est. in volume)	<3	< 10 (est. in volume)

[a] Beginning of life, 30°C, sea level,50% R.H., excluding hybrid battery, power module alone
[b] Normalized from DP3 data from 150 ml cartridge to either 100ml or 200ml for comparison purposes
[c] Lifetime measured to 80% of rated power

Marked improvement on the road towards commercialization.

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Approach: Milestones

25% Complete

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

45% Complete

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

50% Complete

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

35% Complete

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

45% 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
  - $>$ 60 mW/cm^2 for 500 hours
  - Stable for one week in DP3 compatible rest

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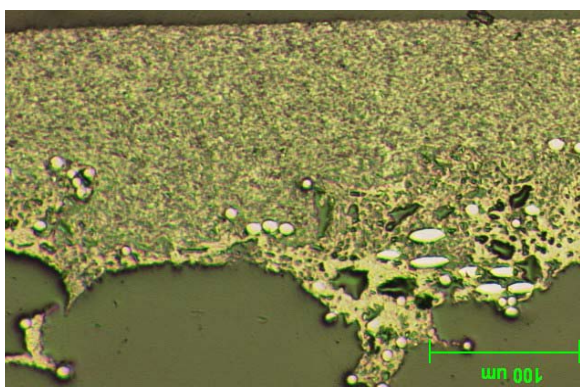
Technical Accomplishments:

Barrier Layer Scale Up

- Baseline MEA design transferred to JM and commercially scalable batch processes introduced
  - High throughput dual centrifuge mixer to eliminate small scale ultrasonic mixing
  - K-bar coating process introduced for ink deposition - higher throughput coating and increased repeatability

Carbon fiber substrate



K-bar coated barrier layer with good uniformity and impregnation of the substrate

Cross section microscope picture of barrier layer coating

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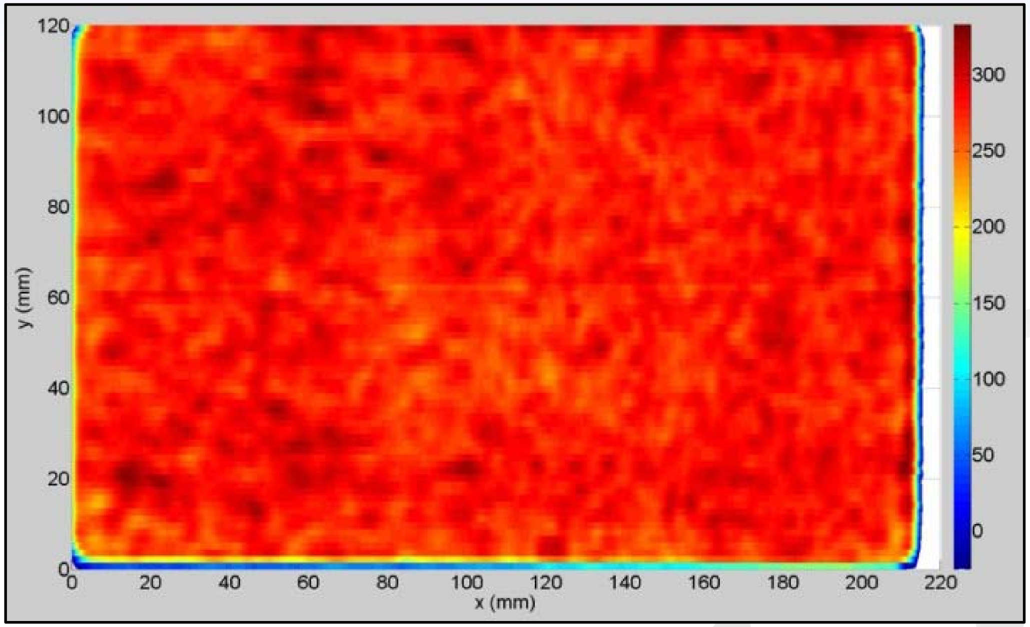
Technical Accomplishments:

Barrier Layer Scale Up

- Non-contact thickness measurement developed to measure process uniformity – Liquid barrier layer thickness improved by process optimization



Thickness variation of coated barrier same as original carbon fiber substrate (Standard Deviation ~18 μm)

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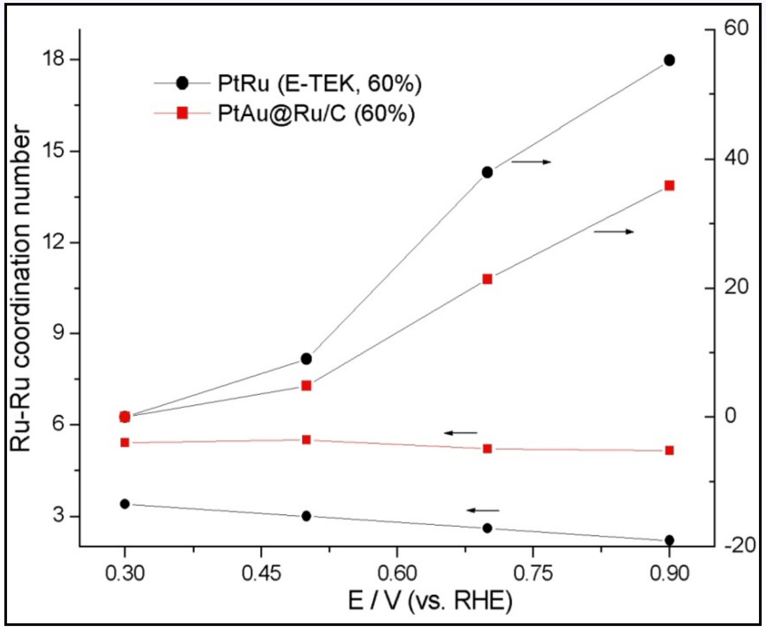
Technical Accomplishments:

Ultra-stable Anode Catalyst Development

- PtAuRu/C has excellent surface area retention under accelerated testing
- Commercial PtRu/C lost more than 10% due to catalyst dissolution.



Δμ-XANES and EXAFS data indicates the oxide growth on the PtAuRu is lower indicating increased stability and lower tendency to dissolution

	Change in overall ECA (-%)	Increased Pt coverage (+%)	Initial Pt coverage (%)
PtRu/C (60%, E-TEK), room T, *24* hours	11.9	4.9	69.4
PtRu/C (60%, E-TEK), at 50 , *4* hours	11.3	7.3	69.5
PtAuRu/C (60%, micro-emulsion), room T, *24* hours	1.7	2.0	74.4
PtAuRu/C (60% micro-emulsion) , at 50 , *4* hours	0.5	1.7	75.7

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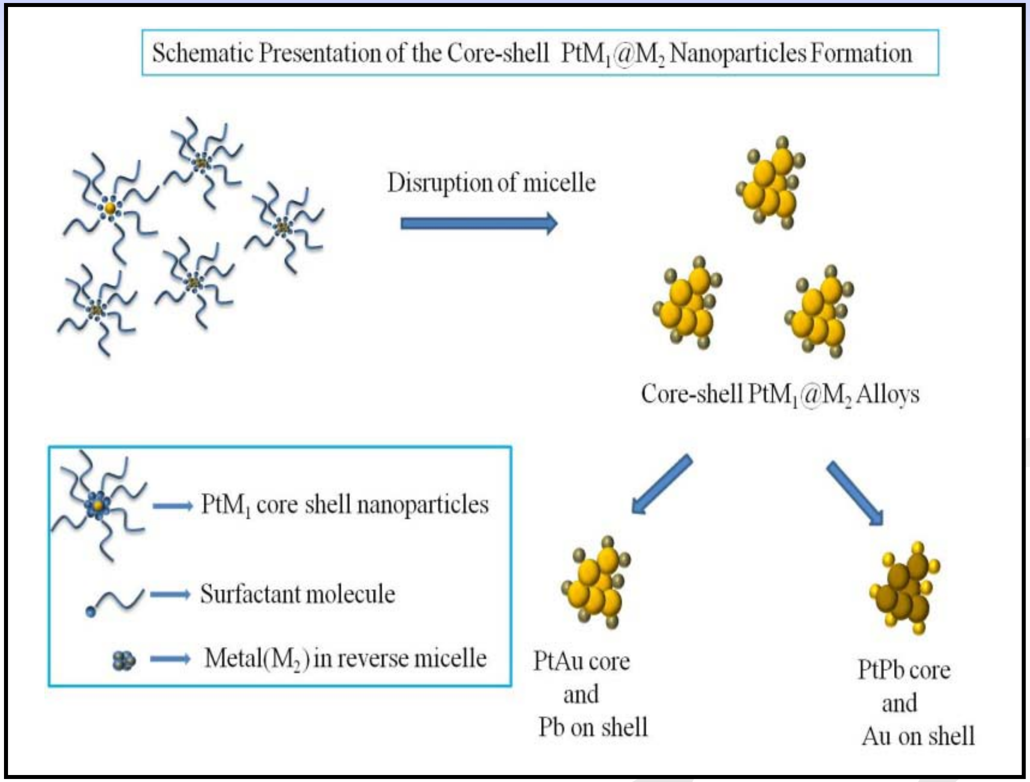
Technical Accomplishments:

Ultra-stable PtRu Catalyst Scale Up

- Reversed micelle method doubled in scale - but still in the gram scale (<1g/week)
- Reverse micelle method scale is limited due to the size of micelle.
- A new approach to increase catalyst throughput – new solvent and smaller chain length surfactants to increase the production rate



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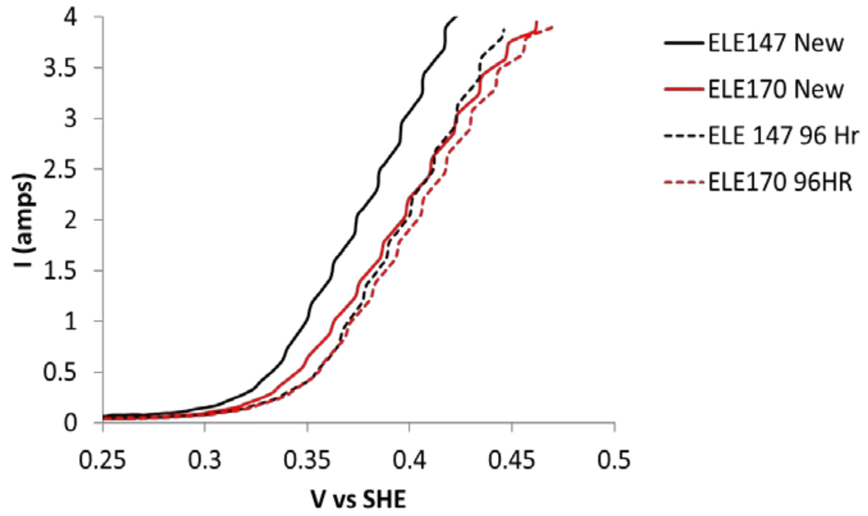
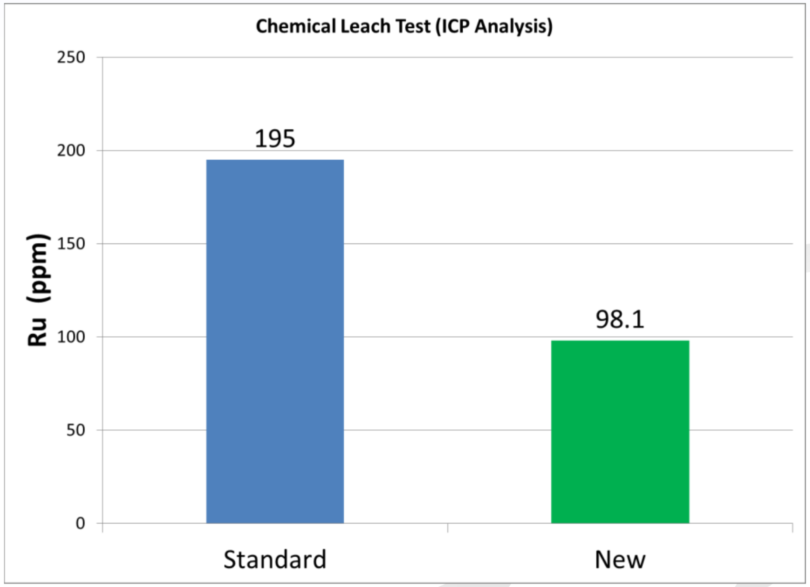
Technical Accomplishments:

Improved Durability with Commercial Catalyst

- JM's new anode shows improved stability in UNF MEA
  - Slightly lower beginning of life performance for the new anode, but improved ruthenium stability – increased MEA lifetime performance



Anode polarization measurements show improved stability



Ex-situ tests showed lower Ruthenium loss.

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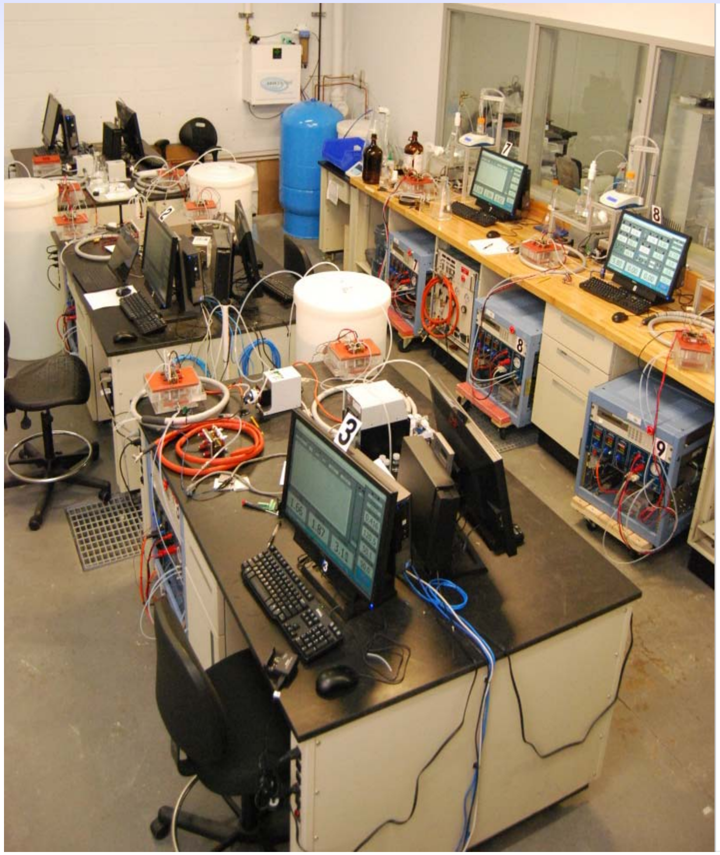
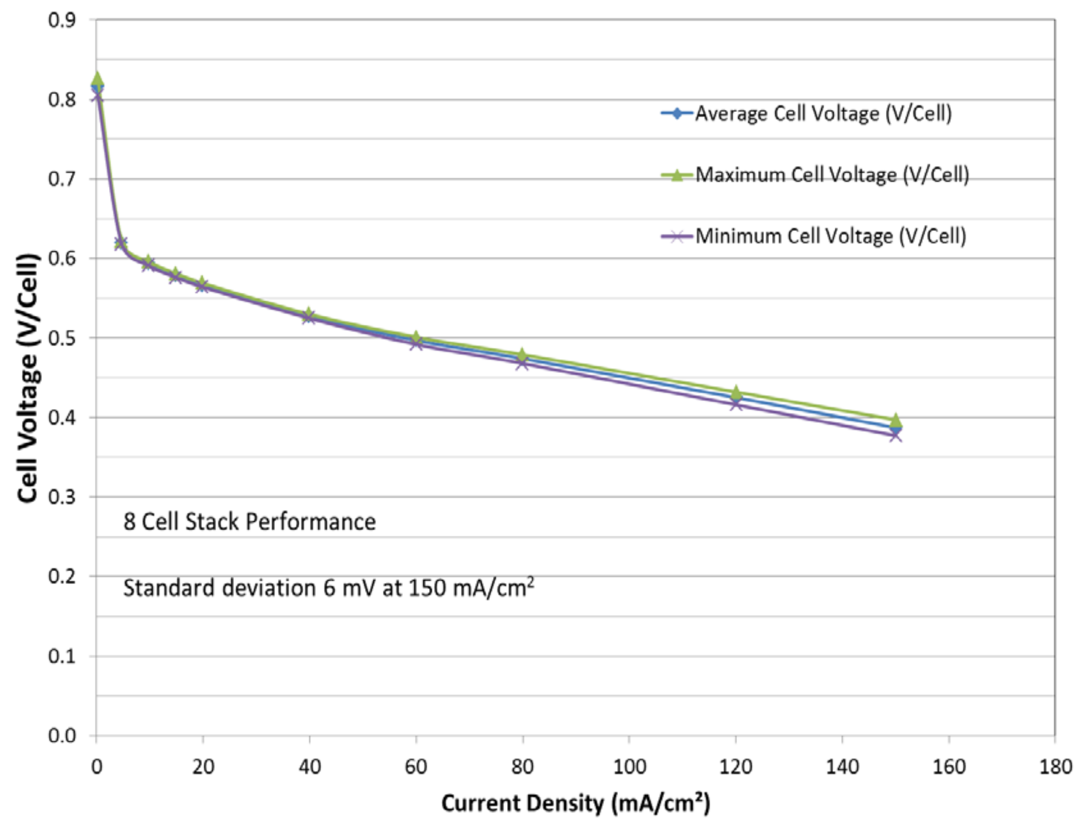
Technical Accomplishments:

MEA Performance

- Good performance obtained with low cell to cell variability





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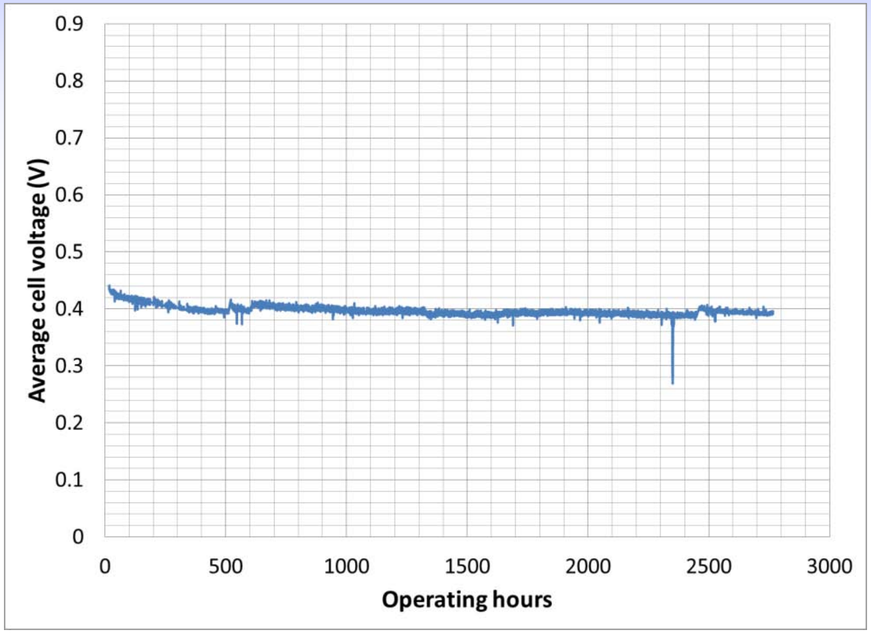
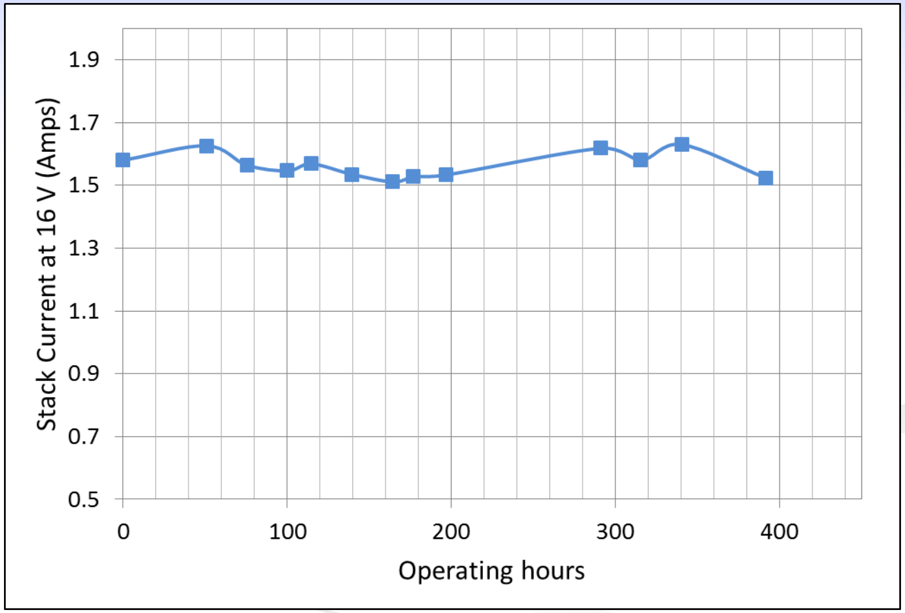
Technical Accomplishments:

MEA Durability

- MEAs shows excellent durability in continuous operation testing



Durability measurement on the test stand . Average cell voltage at 120 mA/cm^2, 0.8 M methanol and 50°C for an 8 cell stack



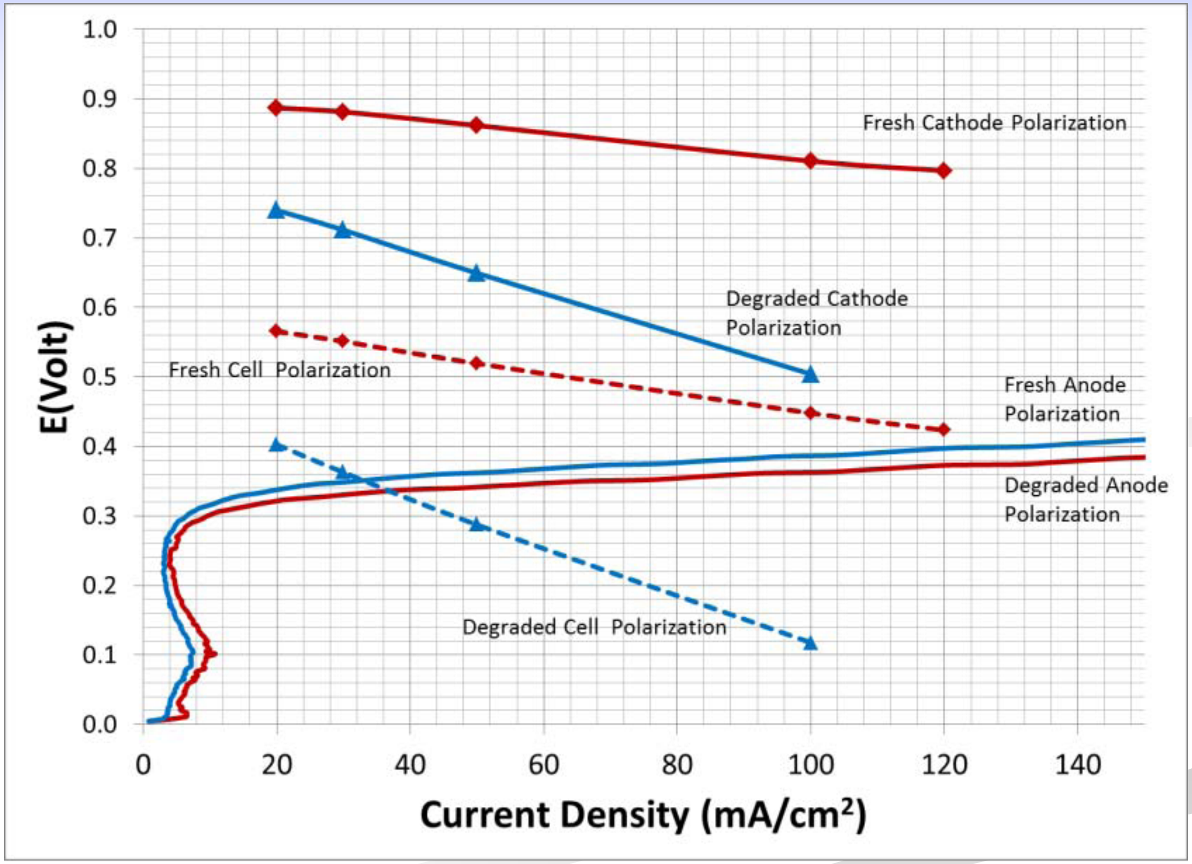
DP4 brassboard durability. Stack current at 0.4 V/cell, 50°C, 0.8 M methanol.

Technical Accomplishments:

Electrochemical Analysis of Degraded MEAs

- Periodic operation shows unexpected increased degradation during the off time

Resistance compensated anode, cathode and cell polarization curves show the overall performance loss is due to significant performance loss in the cathode



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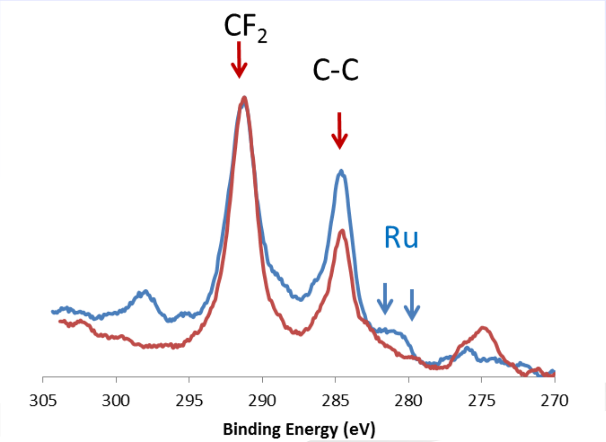
Technical Accomplishments:

Ex-situ Analysis of Degraded MEAs

- SEM/EDAX
  - No delamination observed
  - No significant presence of Ru on the cathode
- XPS (X-ray Photoelectron Spectroscopy)
  - No significant levels of Ru on the cathode
  - No formation of platinum oxide films on the cathode
  - A small increase in the presence of aliphatic carbon on the catalyst
- Initial infrared spectroscopy shows potential presence of low levels of organic species in the cathode catalyst layer – under further investigation



XPS Spectra of fresh and highly degraded MEAs

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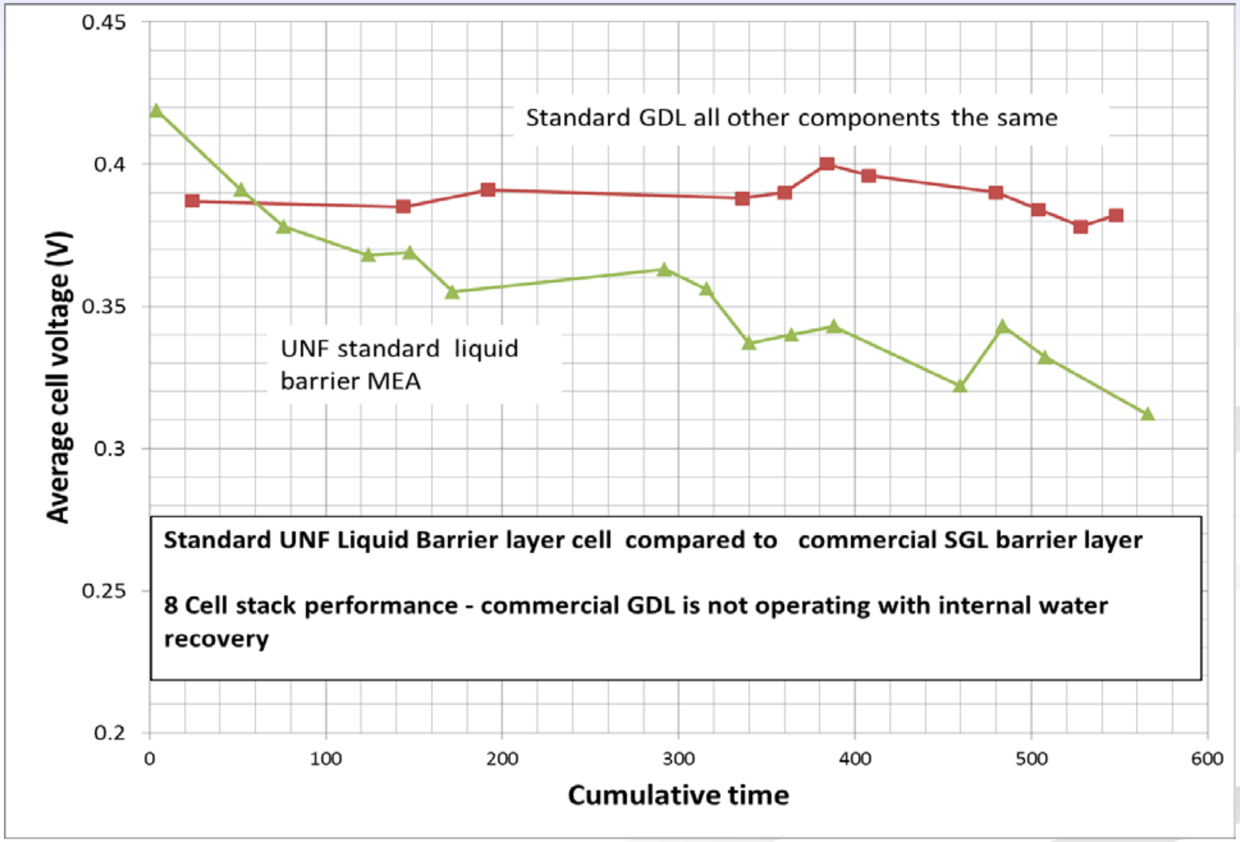
Technical Accomplishments:
Good Open Cathode MEA Durability

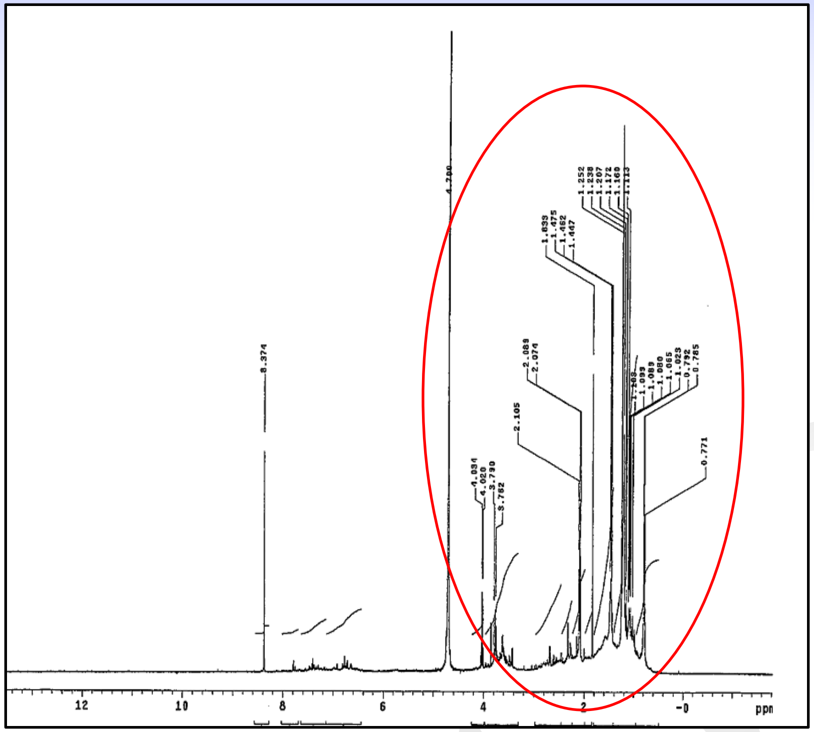
- No off-state degradation seen with Commercial GDL in place of liquid barrier layer - suggests barrier layer components are the root cause



Technical Accomplishments:

MEA Durability

- Extraction and analysis of the liquid barrier layer shows the presence of organic water soluble impurities
  - NMR analysis of the extracted material shows a mixture of hydrocarbon species
  - Possible barrier layer surfactant residue or processing chemicals



Peaks highlighted in red circle represent hydrocarbon contaminants.

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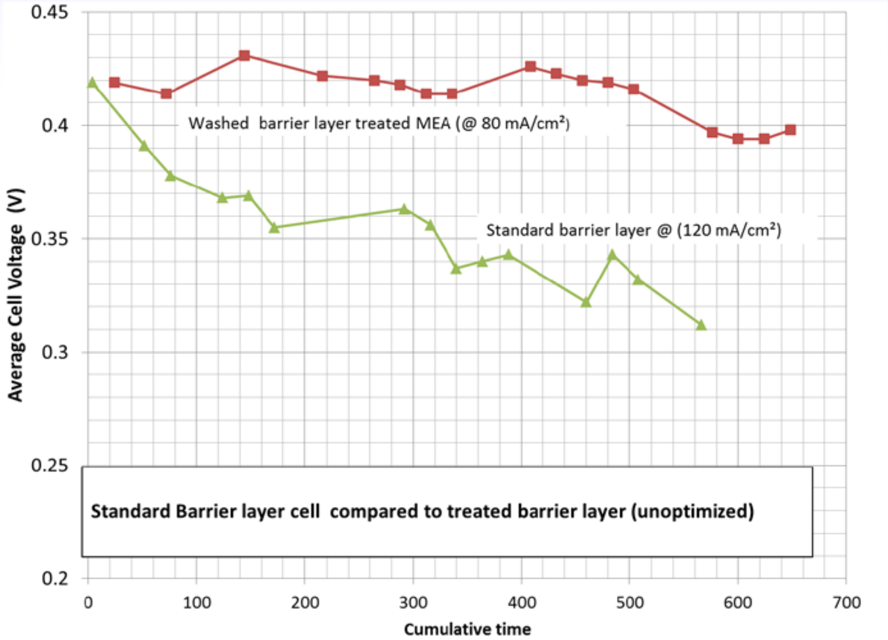
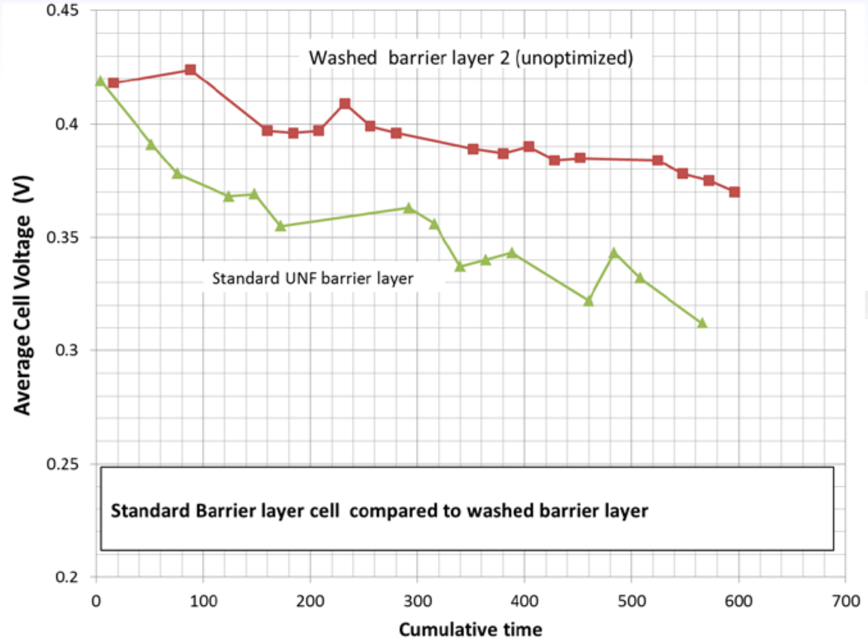
Technical Accomplishments:

MEA Durability of Cleaned Barriers

- Post treated barriers show lower off-state degradation - further optimization underway





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Collaborations

Subcontractors

- University of Florida
  - Dr Tony Schmitz / Dr. William Lear
    - Manufacturing development and quality control measurement development
  - Dr. Jason Weaver/Dr. Helena Weaver
    - Catalyst development and MEA characterization
- Northeastern University
  - Dr Sanjeev Mukerjee –Anode catalyst development and fuel cell testing
- Johnson Matthey Fuel Cells
  - Dr. Angus Dickinson –Liquid barrier layer and MEA scale up and optimization

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Proposed Future Work : FY11

- Optimization manufacturing techniques for the liquid barrier layer (JM, UNF, UF)
  - Optimize barrier layer cleaning and firing process - to remove any residual contaminants
  - Optimize commercial applicable coating process to produce contaminate free barrier layers
- Ultra-stable Anode
  - Scale up of anode catalyst production capability (NEU)
  - MEA testing of high stability anode catalyst (NEU, UNF)
- Improve MEA Performance
  - Optimize coating conditions and porosity of cathode and anode for the UNF MEA design
- MEA Durability Testing
  - Evaluate both on and off state durability to determine the root cause of degradation

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Proposed Future Work: FY 12

- Optimization of high stability anode catalyst MEAs and durability testing (NEU, UNF)
  - Improve lifetime and performance for scaled up catalyst
- MEA development (UNF, JM, UF)
  - Improve performance to increase power density and energy density
  - Improve lifetime
- Stack testing (UNF)
  - Determine durability under system operating profiles for both on and off state degradation

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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 2010 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. Developed MEAs with low on state degradation $< 50\ \mu V/h$ under a range of operating conditions. Improved the off state degradation by post treating the liquid barrier layer prior to MEA fabrication.
- **Collaborations:** In process of transferring baseline technology for the liquid barrier layer MEA to project partner JM.
- **Proposed Future Work:** Develop improved liquid barrier layer processing to remove the impurities responsible for the off-state degradation. Continue the transfer to commercially applicable processes.

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