



Novel Materials for High Efficiency Direct Methanol Fuel Cells

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Overview

Timeline

- Start: May 1st, 2010
- End: February 28th, 2013
- Percent Complete: 27%
(as of March 1st)

Budget

- Total Project Funding: \$3,472k
 - DOE: \$2,612k
 - Contractor: \$860k
- Funding Received for 2010: \$700k
- Funding for 2011: \$400k

Barriers

- Durability
- Cost
- Performance

Organization

- Project Lead
 - Arkema Inc.
- Partners (Subcontractors)
 - QuantumSphere Inc. (QSI)
 - Illinois Institute of Technology (IIT)

Relevance

● Project Objectives

- Develop ultra-thin membranes having extremely low methanol crossover, high conductivity, durability, and low cost
- Develop cathode catalysts that can operate with considerably reduced platinum loading and improved methanol tolerance
- Produce an MEA combining these two innovations and having a performance of at least 150 mW/cm² at 0.4 V and a cost of less than \$0.80/W for the membrane and cathode catalyst

● Targets*

Characteristic	Industry Benchmark	Project Target
Methanol Permeability	1-3·10 ⁻⁶ cm ² /s	5·10 ⁻⁸ cm ² /s
Areal resistance (Ωcm ²), 70 °C	0.120 (7 mil PFSA)	0.080 (2 mil thick film)
PGM Cathode Catalyst Specific Power (RDE) †	25 mW/mg PGM	≥50 mW/mg PGM
PGM Cathode Catalyst Loading	2.5 mg/cm ² PGM	≤2 mg/cm ²
MEA I-V Cell Characteristic	90 mW/cm ² @ 0.4 V	150 mW/cm ² @ 0.4 V
MEA Lifetime	> 3,000 h	5,000 h

* Targets based on a methanol concentration of 1M

† conditions at 0.45 V & 70 °C

Approach/ Milestones

Milestones & Go/No-go Decisions for 2011	Date	Progress
Membrane Milestone (Task 1) Generation 1 membrane with areal resistance $\leq 0.080 \Omega\text{cm}^2$ and a methanol perm. coeff. $\leq 1 \cdot 10^{-7} \text{ cm}^2/\text{s}$	June 2011	11 high potential candidates identified with the required areal resistance and a permeation coefficient $< 3 \cdot 10^{-7} \text{ cm}^2/\text{s}$
Catalyst Milestone (Task 2) 50 mW/mg _{PGM} RDE specific power in presence of 0.1M CH ₃ OH <i>(0.45V, 70°C, 50% Pt reduction)</i>	June 2011	115 mW/mg _{PGM} RDE specific power in presence of 0.1M CH ₃ OH <i>(0.45V, r.t, 50% Pt reduction)</i>
Go/No-go Decision: MEA performance of 120 mW/cm ² @ 0.4V (60°C, 1M methanol)	Dec 2011	120mW/cm ² achieved with Arkema membrane and a <i>commercial GDE</i>

Collaborations



PEM Development and testing
MEA diagnostics and durability



Kimberly McGrath - PI
Subcontractor

Catalyst development
MEA production and testing

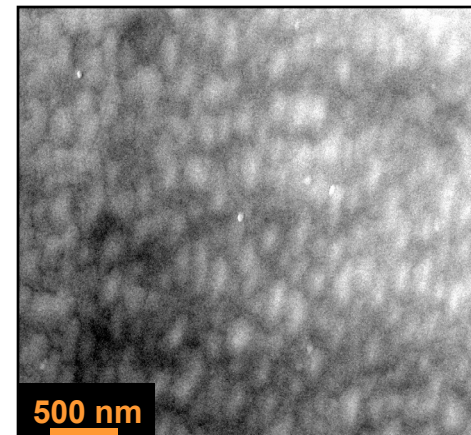


Development of composite membranes
and characterization/diagnostics of MEAs

Technical Approach:

Membrane Development (Task 1)

- Polymer blend comprised of PVDF and polyelectrolyte to minimize methanol permeation
 - Kynar® PVDF
 - Chemical stability and mechanical strength
 - Excellent barrier against methanol
 - Polyelectrolyte
 - H⁺ conduction
 - PVDF can be compatibilized with a range of polyelectrolytes
 - Latest generation taken to a pilot scale is M43 (baseline for this project)
- Key to the target properties: control of composition, architecture, and processing of the membrane components.
 - PVDF matrix optimization
 - Tailor the polyelectrolyte composition (minimize methanol permeation)
 - Morphology
 - Acidic inorganic additives



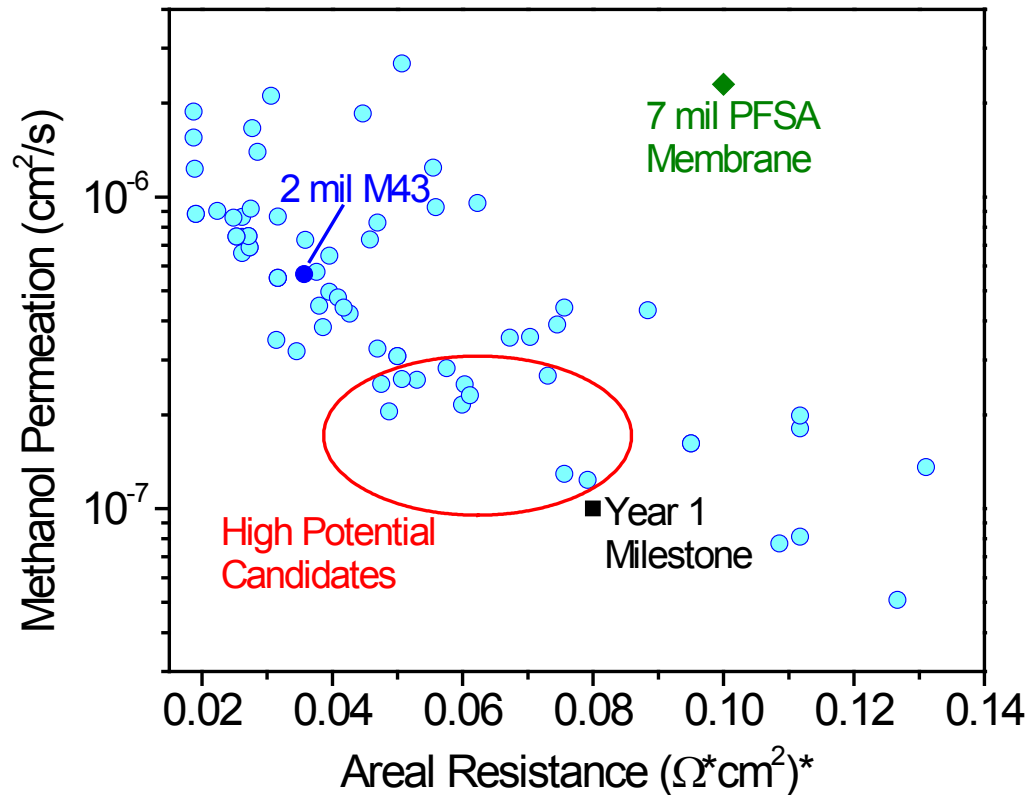
Membrane Development (Task 1)

Progress versus Objectives

Objectives of Task 1	Progress Notes	% Complete (3/1/11)
Membrane Milestone #1 Generation 1 membrane: areal resistance $\leq 0.080 \Omega\text{cm}^2$ and a methanol perm. coeff. $\leq 1 \cdot 10^{-7} \text{ cm}^2/\text{s}$	11 high potential candidates identified with the required areal resistance and a permeation coefficient $< 3 \cdot 10^{-7} \text{ cm}^2/\text{s}$	67%
Deliverable: Scaleup of composition from milestone #1 for MEA development work	M43 produced on a pilot scale several times; process recently extended to lower temperatures	50%
Membrane Milestone #2 Generation 2 membrane: areal resistance $\leq 0.080 \Omega\text{cm}^2$ and a methanol perm. Coeff. $\leq 5 \cdot 10^{-8} \text{ cm}^2/\text{s}$	Work will build off of milestone #1. One composition displays the target perm. coefficient but resistance is 50% too high.	22%

Technical Accomplishments:

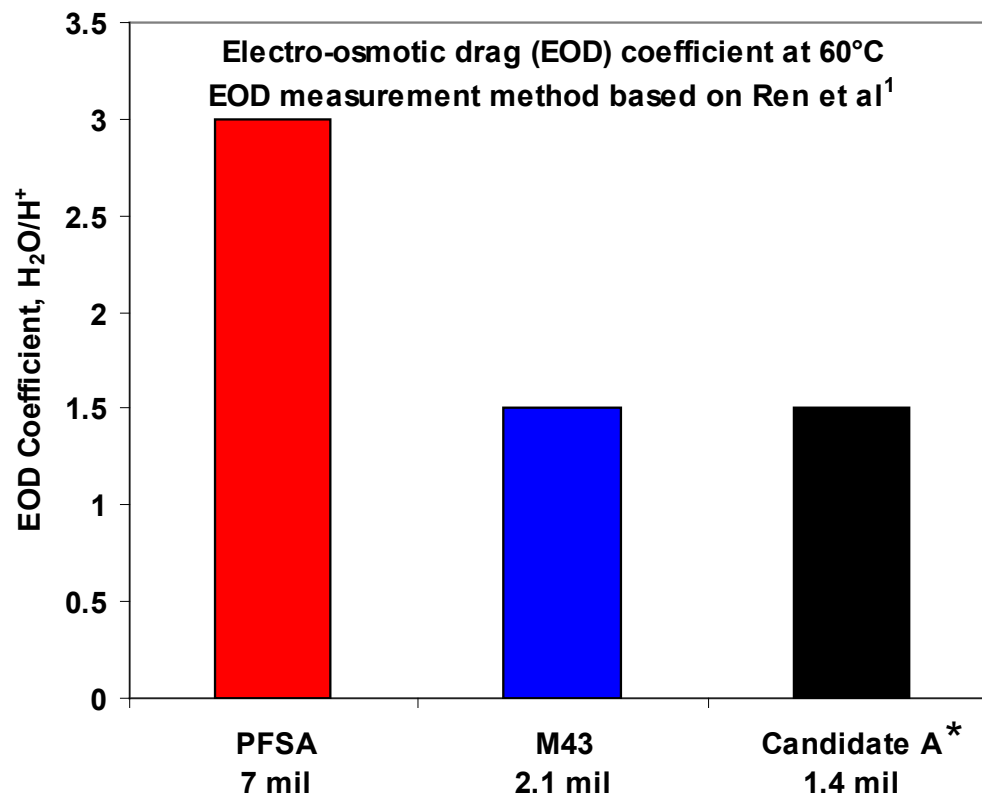
Membrane Screening



- Ex-situ properties of over 75 compositions tested → 11 of them identified as high potential candidates to reach the milestone
- Most of the testing has focused on PVDF grade, polyelectrolyte compositions, and polyelectrolyte loading

Technical Accomplishments:

Lower Electro-osmotic Drag Coefficient



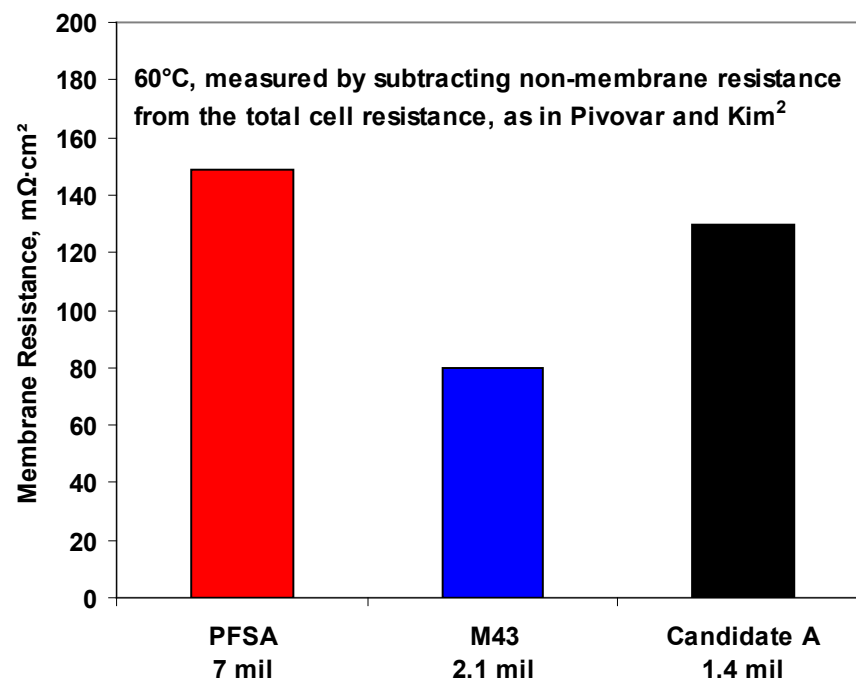
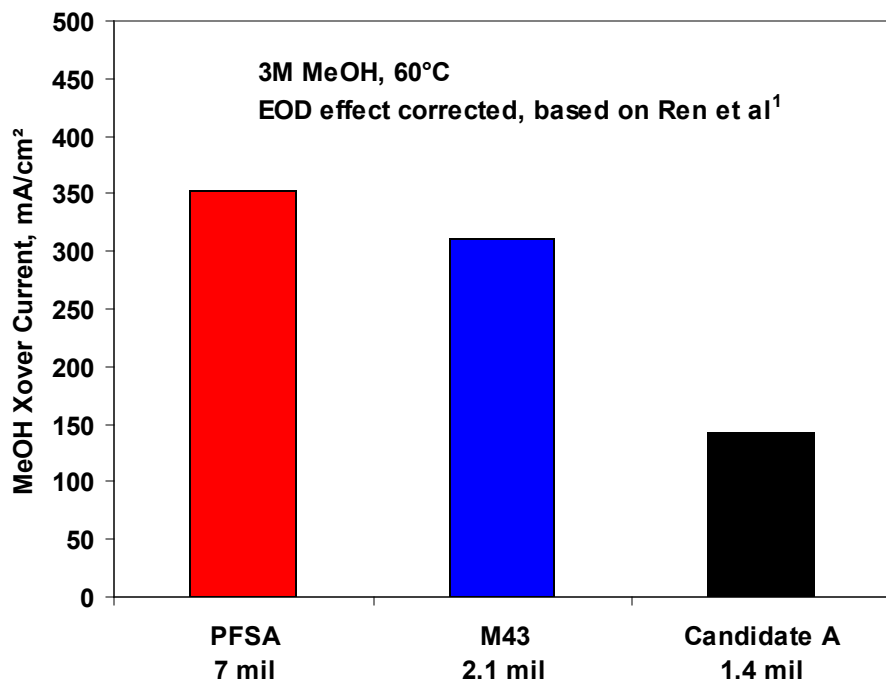
- 50% lower EOD coefficients for Arkema membranes than PFSA
- Lower EOD coefficient is advantageous for DMFC applications
 - Less cathode flooding, and easier water management
 - Reduced methanol crossover

*A is one of the most promising candidates identified from the screening study



Technical Accomplishments:

Lower Methanol Crossover & Membrane Resistance



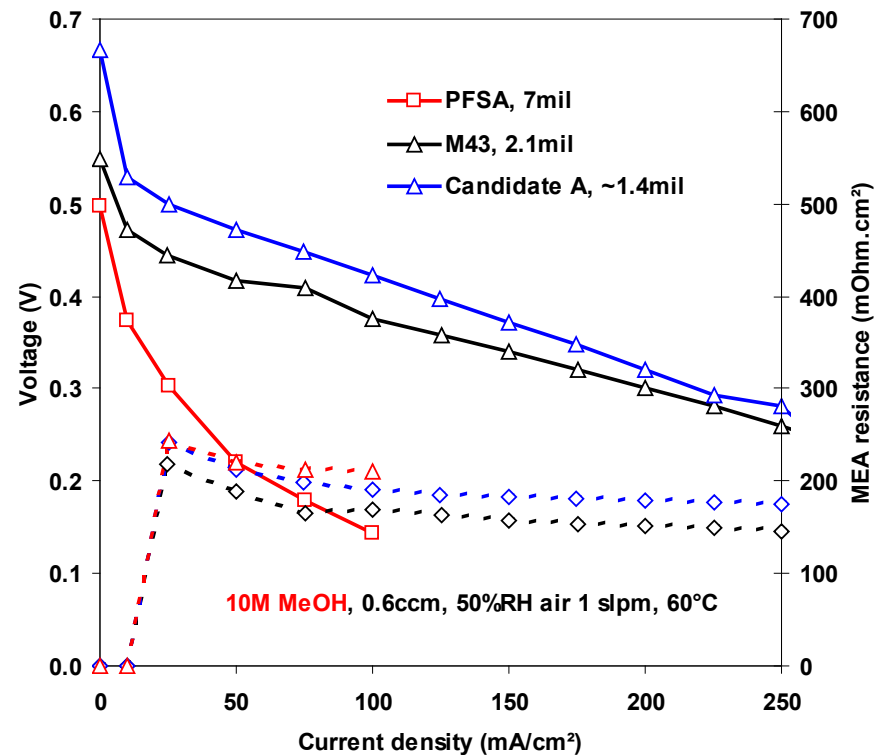
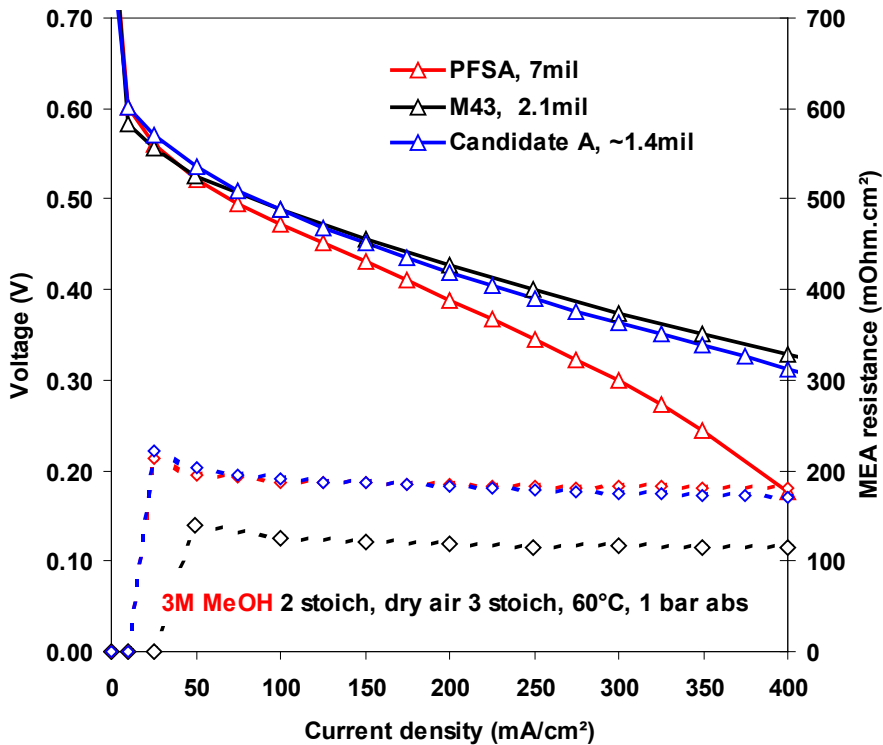
- Arkema membranes showed substantially lower methanol crossover lower membrane resistance than 7mil PFSA
- Membrane Candidate A showed 60% lower crossover and 10% lower resistance than a 7mil PFSA membrane



1. Ren, X.; Springer, T.E., Zawodzinski, T.A., and Gottesfeld, S., *J. Electrochem. Soc.*, **2000**, 147, 466

2. Pivovar, B.S. and Kim, Y.S., *J. Electrochem. Soc.*, **2007**, 154, B739-B744

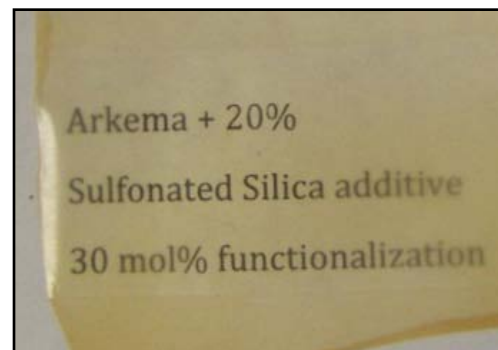
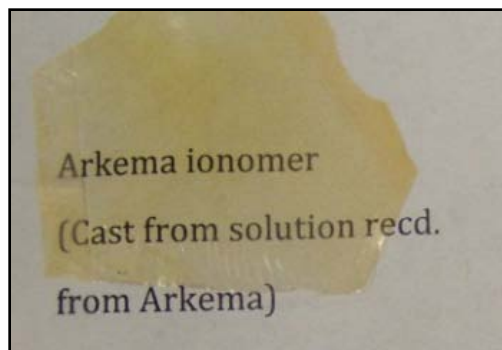
Technical Accomplishments: DMFC Performance



- Arkema membranes outperform 7mil PFSA membrane in both 3M and 10M methanol tests, especially in 10M
- Candidate A (1.4mil) achieved the better performance in 10M methanol testing, due to lower crossover rate

Technical Accomplishments:

Sulfonic Acid Functionalized Silica Additive



Membrane + silica with 30% sulfonation	Conductivity @70°C, mS/cm	Permeability @ R.T., $\times 10^{-7}$ cm ² /s	Conductivity/Perm Selectivity
Arkema membrane	125 ± 7	6.7 ± 0.2	18.6
With 15 wt% silica	75 ± 4	5.7 ± 0.4	13.1
With 20 wt% silica	49 ± 1	3.4 ± 0.1	14.4
With 25 wt% silica	58 ± 9	3.2 ± 0.2	18.1

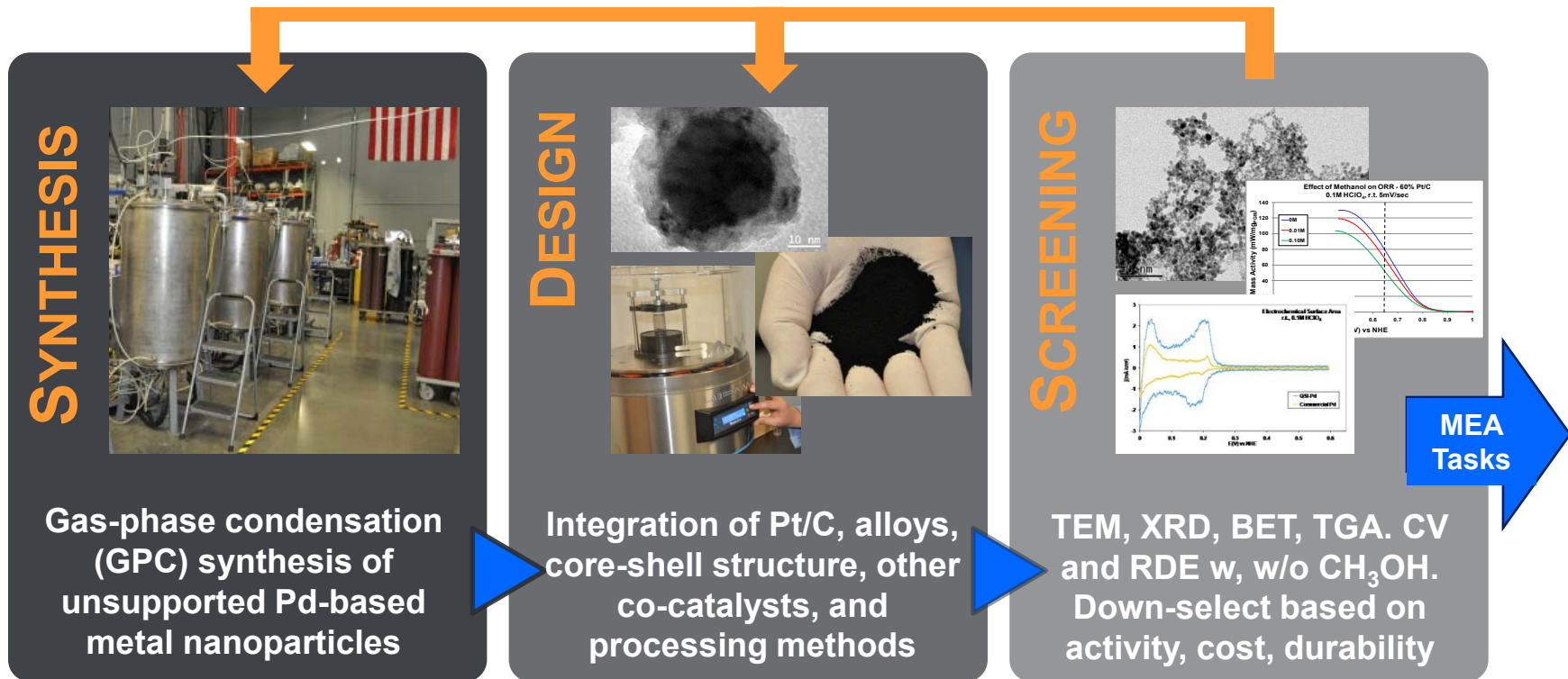
- No large scale phase separation observed from forming the composite
- Permeability and conductivity lowered as the silica is added. Selectivity increases with higher silica contents
- Conductivity may be improved by using a higher sulfonation level in silica

Technical Approach:

DMFC Cathode Catalyst Development (Task 2)

Utilize Pd-based nanoscale catalysts with Pt/C to:

- Increase $\text{mW}/\text{mg}_{\text{PGM}}$ by suppressing methanol oxidation
- Reduce Pt content \rightarrow decrease $\$/\text{W}$



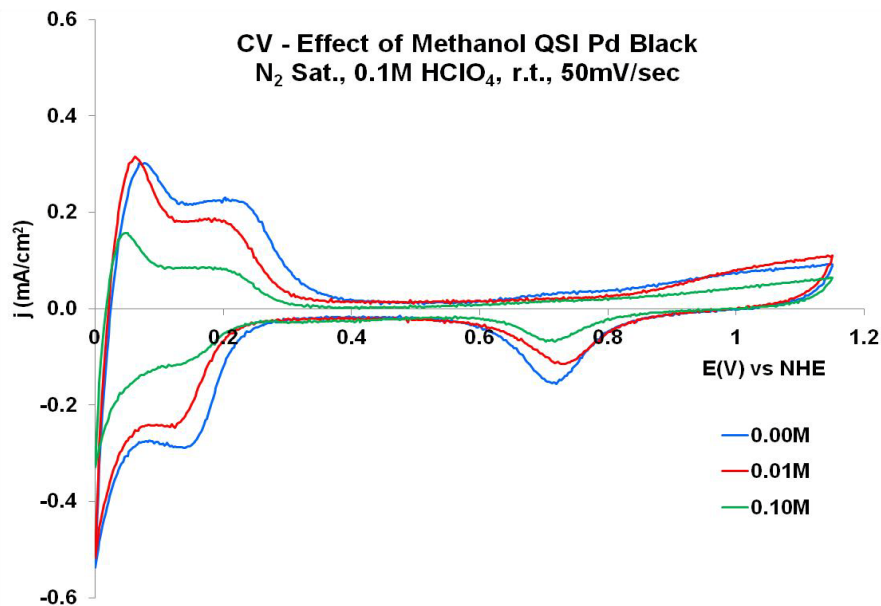
DMFC Cathode Catalyst Development (Task 2)

Progress versus Objectives

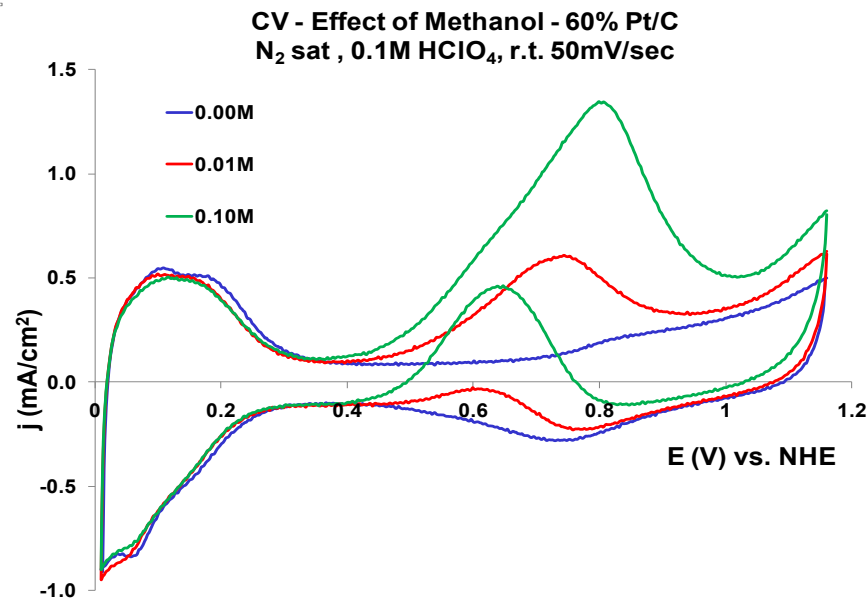
Objectives of Task 2	Progress	% Complete (3/1/11)
Milestone: 50 mW/mg _{PGM} RDE specific power in presence of 0.1M CH ₃ OH (0.45V, 70°C, 50% Pt reduction)	115 mW/mg _{PGM} RDE specific power in presence of 0.1M CH ₃ OH (0.45V, r.t., 50% Pt reduction)	67%
Deliverable: Catalyst scale up for MEA development work, 1.2 kg/month, 60% Pd recycling efficiency	Nano-Pd production rate @ 1kg/month, 85% Pd recycling efficiency	53%
Deliverable: MEA specific power of 40 mW/mg _{PGM} , 50% Pt reduction	MEA testing initiated	41%

Technical Accomplishments:

Demonstration of Methanol Tolerance



QSI nano-Pd only

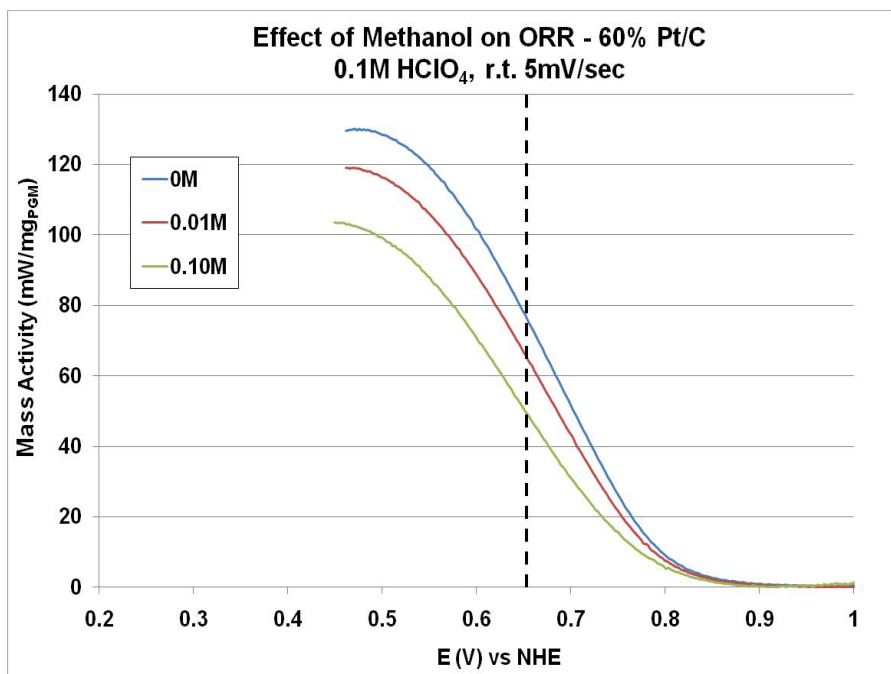


Commercial Pt/C

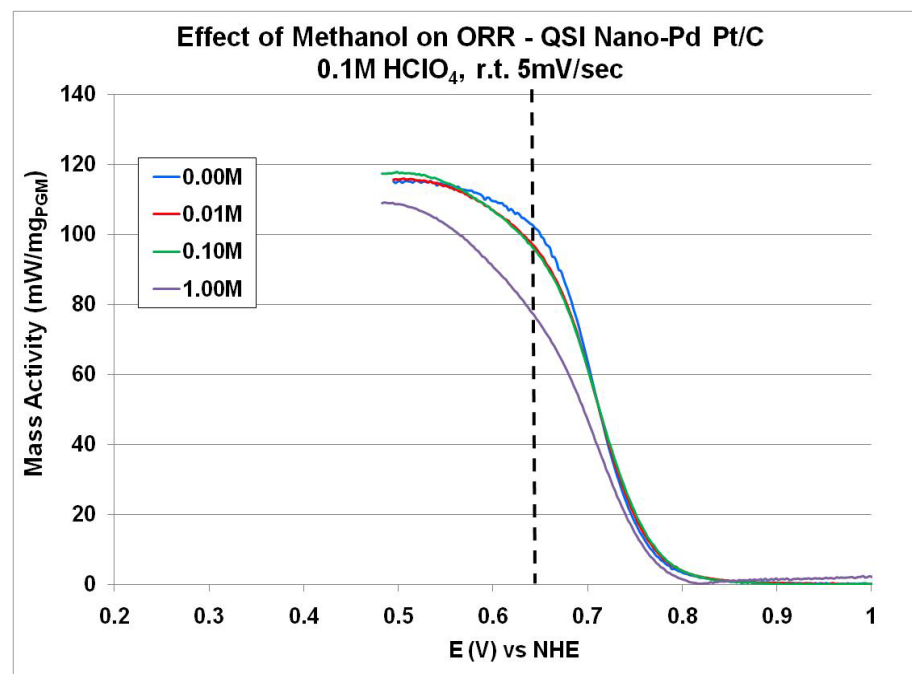
- Cyclic Voltammetry: Methanol is not oxidized on nano-Pd, regardless of concentration

Technical Accomplishments:

Increased Specific Power (RDE Measurement)



Pt/C only



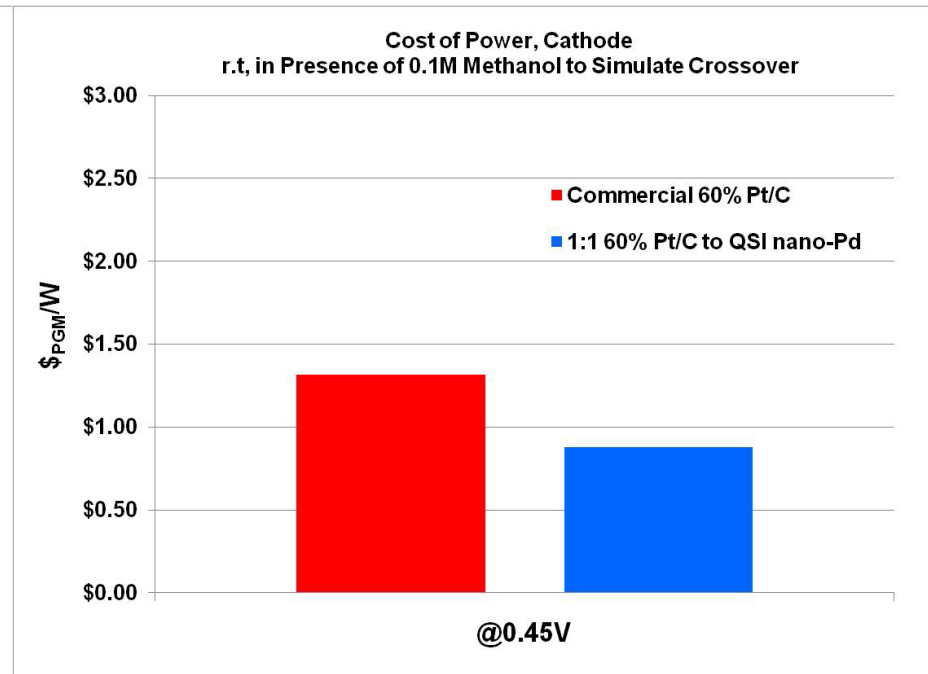
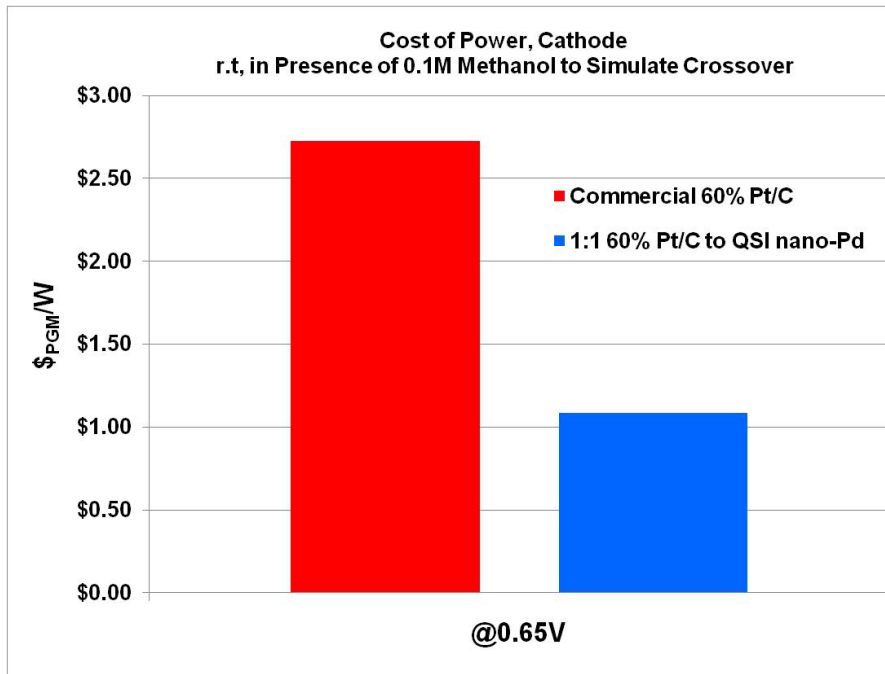
Pt/C and nano-Pd

50% of Pt substituted with Pd

- >2x mass activity increase in presence of 0.1M Methanol @ 0.65V
- 10% mass activity increase in presence of 0.1M Methanol @ 0.45V

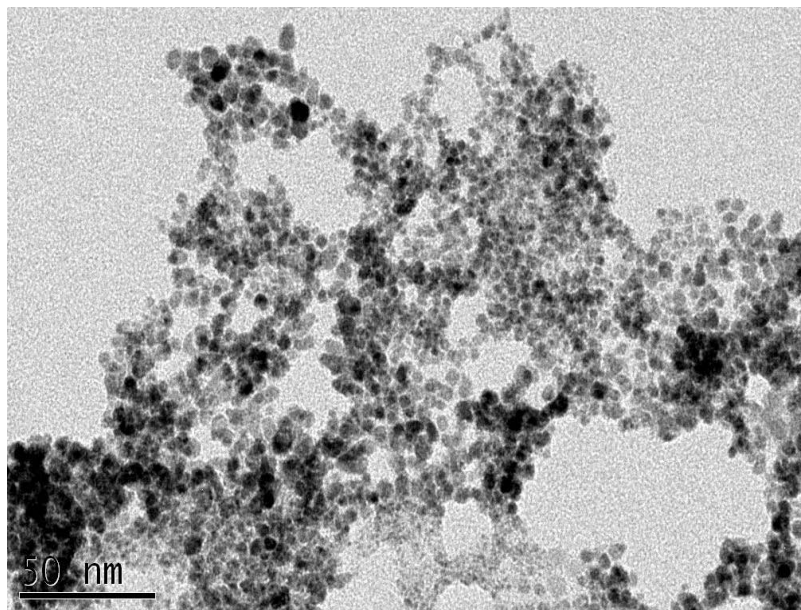
Technical Accomplishments:

Reduced Cost of Power



- 60% cost reduction at 0.65V (Cathode catalyst = \$1.08_{PGM}/W, low volume)
- 33% cost reduction at 0.45V (Cathode catalyst = \$ 0.88_{PGM}/W, low volume)

Pd-based Catalyst Synthesis



Catalyst Pd, Pd-"M"	Surface Area (m ² /g)
QSI-Nano Pd black (ref)	57.4
Other Commercial Pd black	7.3
QSI-Nano Pd-Cr	65.8
QSI-Nano Pd-Ag	38.3
QSI-Nano Pd-Mn	94.5
QSI-Nano Pd-Co	80.6
QSI-Nano Pd-Fe	134.2
QSI-Nano Pd-Ni	99.8
QSI-Nano Pd-Sn	65.4
QSI-Nano Pd-Se	82.9

- High surface area nanoscale metals successfully produced, currently been screened by *BET*, *TEM*, *elemental analysis*, *CV*, *RDE*
- Electrochemical impact of alloying (Pd-M) vs. bimetallic (Pd + M) is under investigation

Future Work

- **Membrane Development (Task 1)**
 - Down-select membrane candidates that pass YR 1 milestone and begin refining their properties (Q2 2011)
 - Produce pilot scale membrane quantities of best membrane candidate, perform cost analysis, and deliver material to QSI & IIT (Q3 2011)
- **Catalyst Development (Task 2)**
 - Down-select cathode catalyst composition, perform *ex-situ* durability evaluation (Q2 2011)
 - Increase reactor production rate, collect cost metrics, deliver catalyst to Arkema, IIT (Q3 2011)
 - Evaluation of catalyst at MEA level (Q4 2011)
 - Demonstrate 50% Pt reduction at MEA-level (Q1 2012)
- **MEA Development (Task 3)**
 - Initiate development of MEAs with Arkema membrane and QSI catalyst (Q4 2011)
- **MEA Testing and Durability (Task 4)**
 - Initiate testing of MEAs from Task 3 (Q1 2012)

Summary

Primary project objective is to develop new materials for DMFC that can be the basis for a device to meet the DOE's technical targets for consumer electronics.

- 11 membrane compositions identified as high potential candidates to reach the year 1 milestone.

The Arkema membrane technology showed lower methanol permeation and electro-osmotic drag coefficients than 7 mil PFSA, while maintaining lower membrane areal resistance .

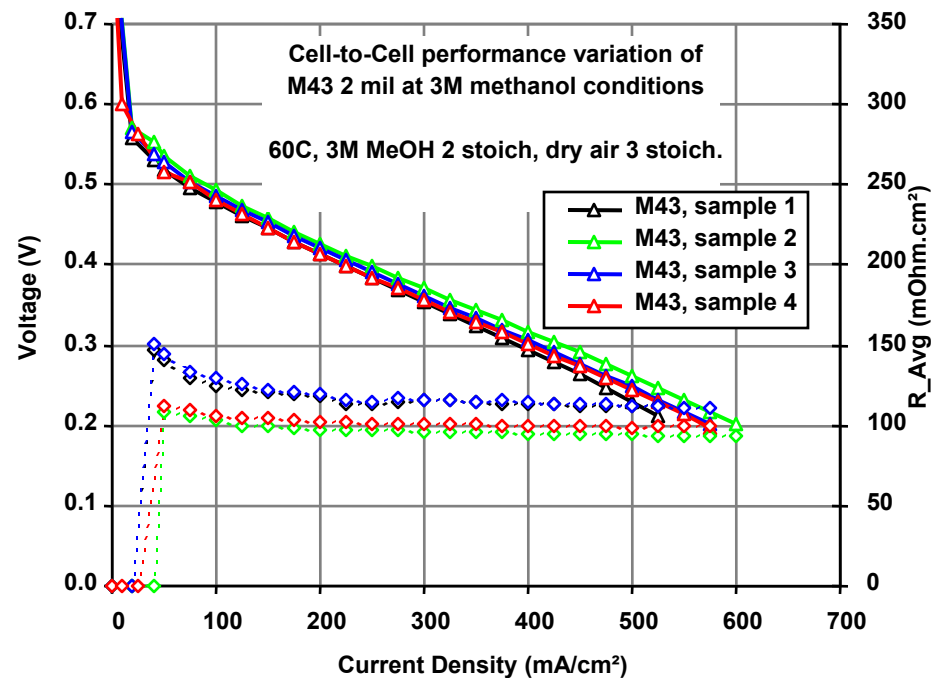
- Composite membranes with a sulfonated silica additive were prepared. Higher sulfonation level is needed to improve conductivity.
- Nano-Pd mixed with Pt/C catalyst showed 2x mass activity over Pt/C (on total PGM basis) at 0.65V, in presence of 0.1M methanol.



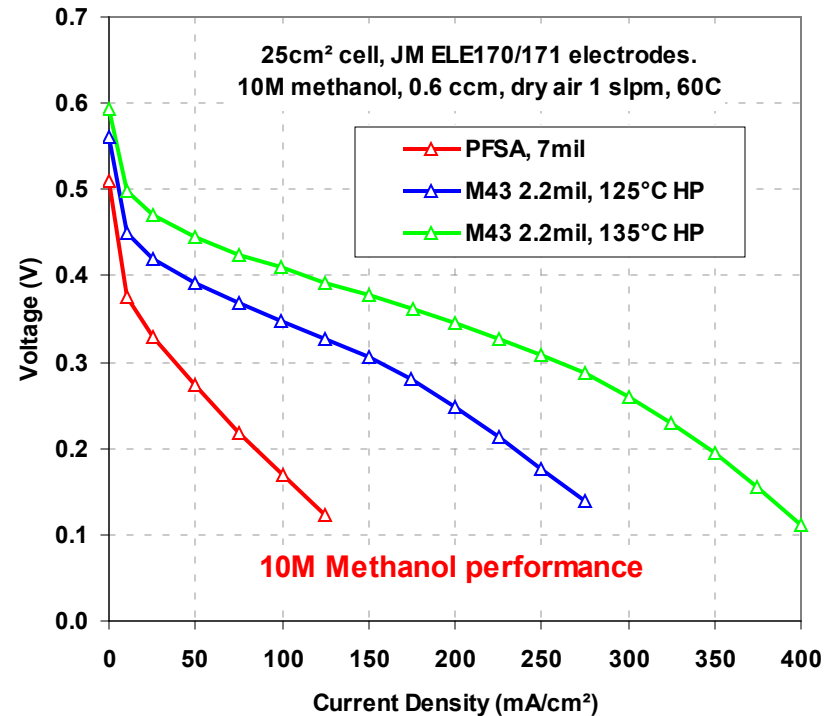
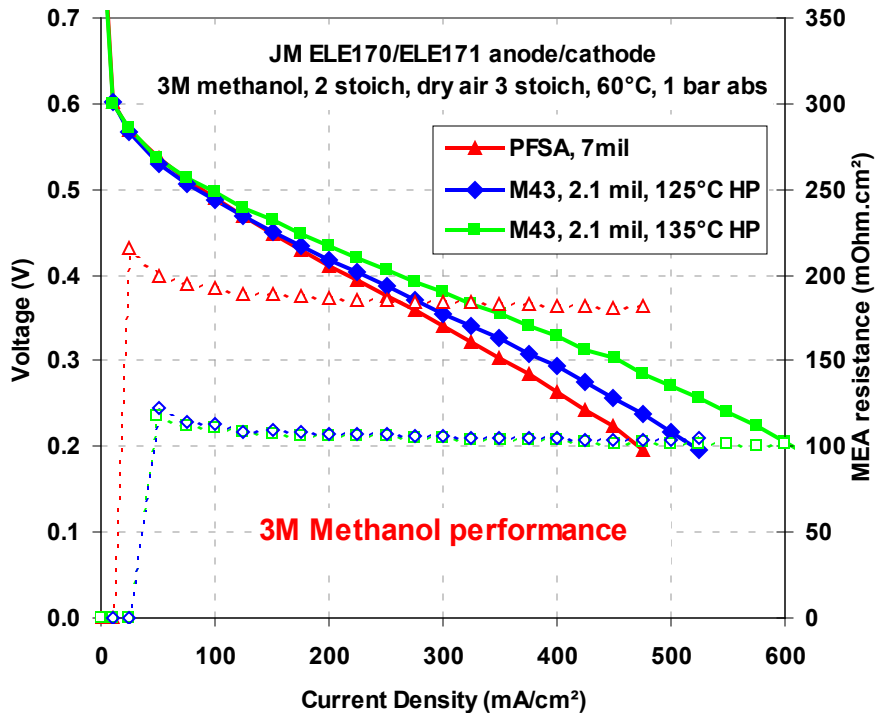
Technical Back-Up Slides

DMFC Conditioning

- Objective: Achieve optimal and repeatable performance in minimal time
- Challenge:
 - Arkema M43-based MEAs condition slower than PFSA
 - Common conditioning methods were developed based on PFSA, and do not work effectively on Arkema membranes
- Arkema conditioning method
 - Quick voltage cycling between OCV/0.4/0.2V
 - Air starvation during part of OCV time
 - Runs on Methanol/air only, no hydrogen conditioning needed
- Cell fully conditioned within 18 hours
- Consistent performance (<10% variation) from cell to cell



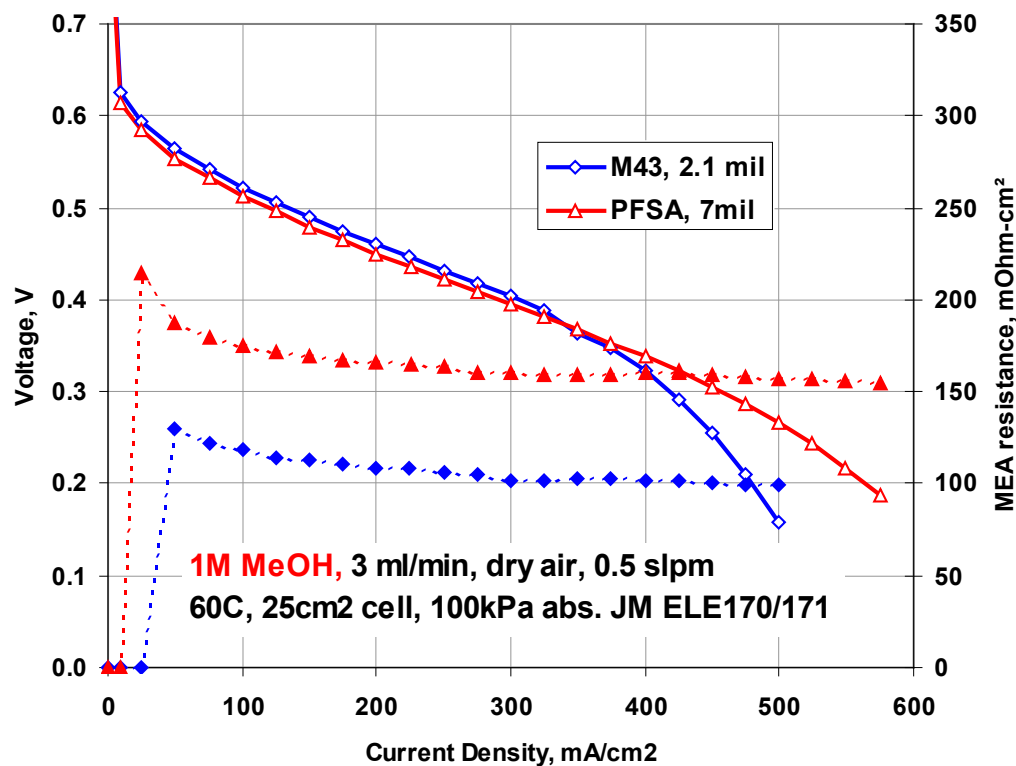
M43 Performance Improvement



- Heat treatment of M43 membranes at 135°C significantly increased the DMFC performances, especially at 10M methanol.
- No such effect was observed on PFSA 7mil membrane.

Technical Accomplishments:

M43 MEA Performance: 1M Methanol



At 0.4V, M43 reaches 300mA/cm², or 120mW/cm² power, with commercial Johnson Matthey gas diffusion electrodes.

Synthesis of Sulfonic Acid Functionalized Silica

