# Novel Materials for High Efficiency Direct Methanol Fuel Cells

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Arkema Inc.

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Grant ID:
DE-EE0000474

Project ID# FC063

# Overview

**Timeline**

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

**Barriers**

- Durability
- Cost
- Performance

**Budget**

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

**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/cm$^2$ 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 | $1\text{-}3\cdot10^{-6}$ cm$^2$/s | $5\cdot10^{-8}$ cm$^2$/s |
| Areal resistance ($\Omega$cm$^2$), 70 ºC | 0.120 (7 mil PFSA) | 0.080 (2 mil thick film) |
| PGM Cathode Catalyst Specific Power (RDE) † | 25 mW/mg PGM | $\geq$50 mW/mg PGM |
| PGM Cathode Catalyst Loading | 2.5 mg/cm$^2$ PGM | $\leq$2 mg/cm$^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 |

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* Targets based on a methanol concentration of 1M

† conditions at 0.45 V & 70 ºC

# Approach/ Milestones

| **Milestones & Go/No-go Decisions for 2011** | **Date** | **Progress** |
| --- | --- | --- |
| Membrane Milestone (Task 1)<br>Generation 1 membrane with areal resistance $\leq$ 0.080 $\Omega cm^2$ and a methanol perm. coeff. $\leq 1 \cdot 10^{-7}$ $cm^2/s$ | June 2011 | 11 high potential candidates identified with the required areal resistance and a permeation coefficient < $3 \cdot 10^{-7}$ $cm^2/s$ |
| Catalyst Milestone (Task 2)<br>50 $mW/mg_{PGM}$ RDE specific power in presence of 0.1M $CH_3OH$<br>*(0.45V, 70ºC, 50% Pt reduction)* | June 2011 | 115 $mW/mg_{PGM}$<br>RDE specific power in presence of 0.1M $CH_3OH$<br>*(0.45V, r.t, 50% Pt reduction)* |
| Go/No-go Decision:<br>MEA performance of 120 $mW/cm^2$ @ 0.4V (60°C, 1M methanol) | Dec 2011 | 120$mW/cm^2$ achieved with Arkema membrane and a *commercial GDE* |

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# Collaborations

**Wensheng He - PI**
**Project Lead**

PEM Development and testing
MEA diagnostics and durability

**Kimberly McGrath - PI**
**Subcontractor**

Catalyst development
MEA production and testing

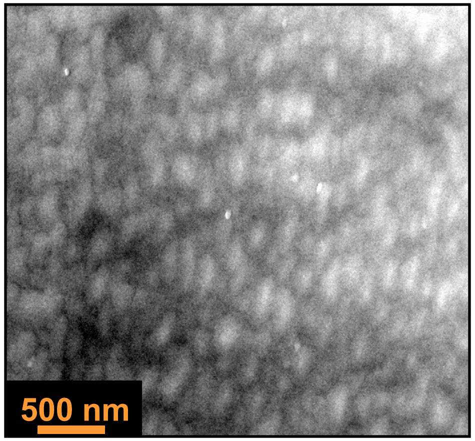
**Vijay Ramani - PI**
**Subcontractor**

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

*Technical Progress:*

# Membrane Development (Task 1)

## Progress versus Objectives

| Objectives of Task 1 | Progress Notes | % Complete (3/1/11) |
|---|---|---|
| Membrane Milestone #1<br>Generation 1 membrane: areal resistance $\leq$ 0.080 $\Omega cm^2$ and a methanol perm. coeff. $\leq 1 \cdot 10^{-7}$ $cm^2/s$ | 11 high potential candidates identified with the required areal resistance and a permeation coefficient < $3 \cdot 10^{-7}$ $cm^2/s$ | 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<br>Generation 2 membrane: areal resistance $\leq$ 0.080$\Omega cm^2$ and a methanol perm. Coeff. $\leq 5 \cdot 10^{-8}$ $cm^2/s$ | Work will build off of milestone #1. One composition displays the target perm. coefficient but resistance is 50% too high. | 22% |

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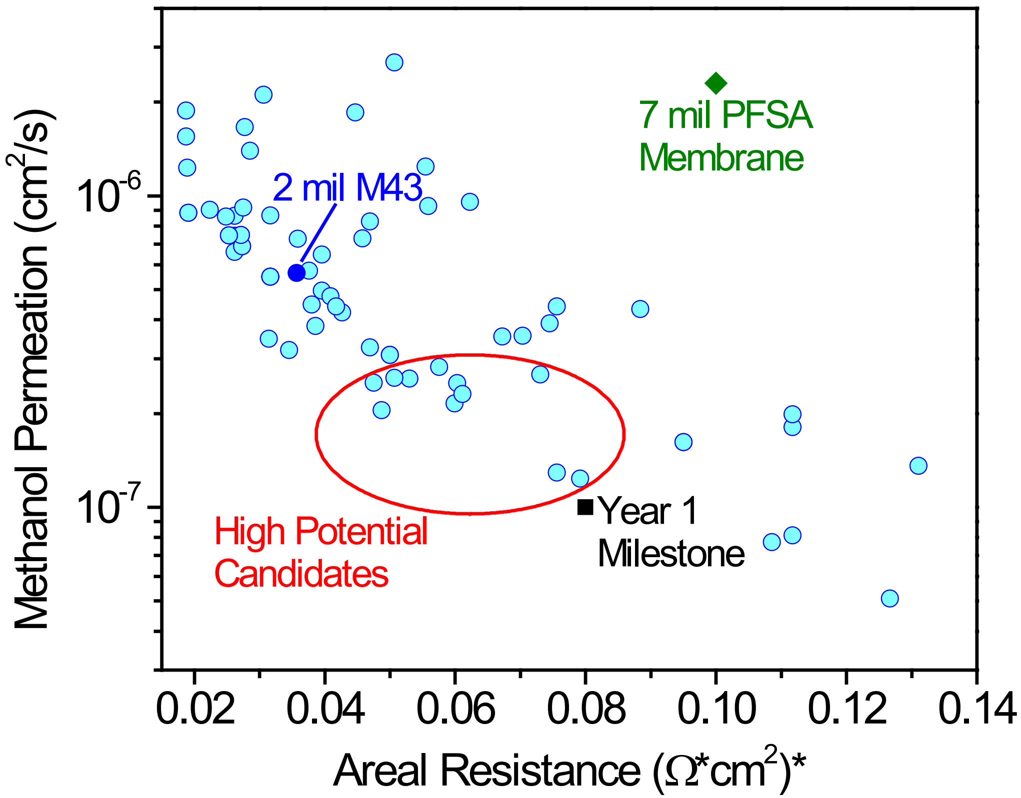
## *Technical Accomplishments:*

# 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

*Areal resistance was normalized to a membrane thickness of 1.5 mils. Sample thickness was typically 1.4-1.6 mils.

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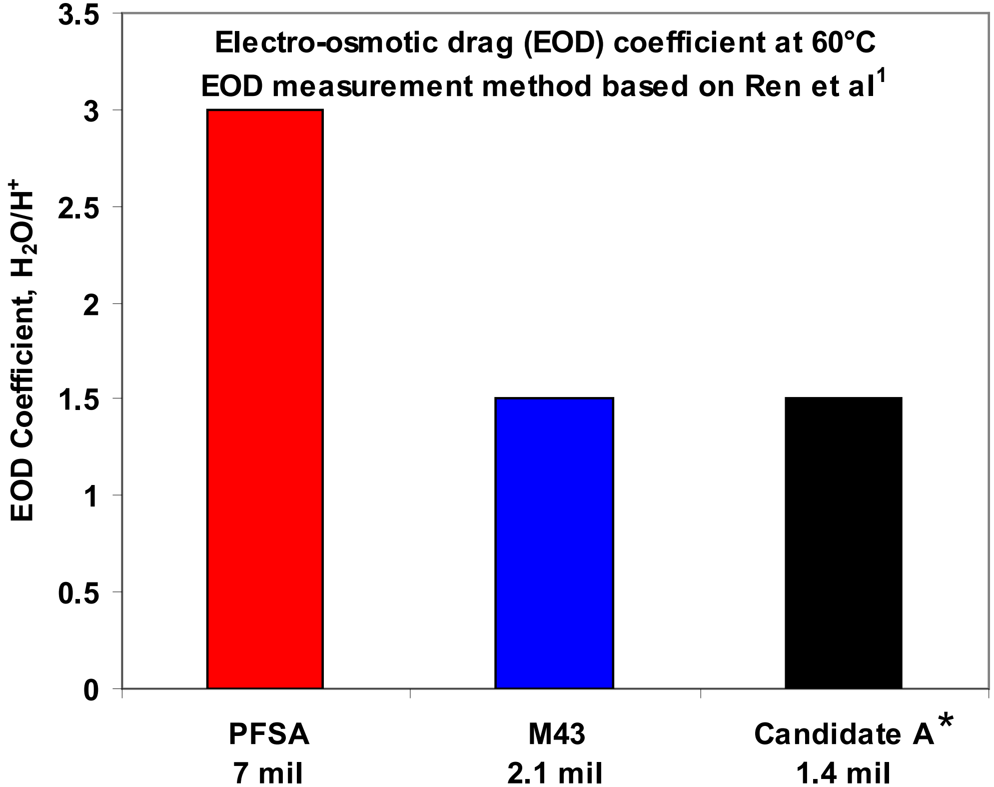
# Lower Electro-osmotic Drag Coefficient

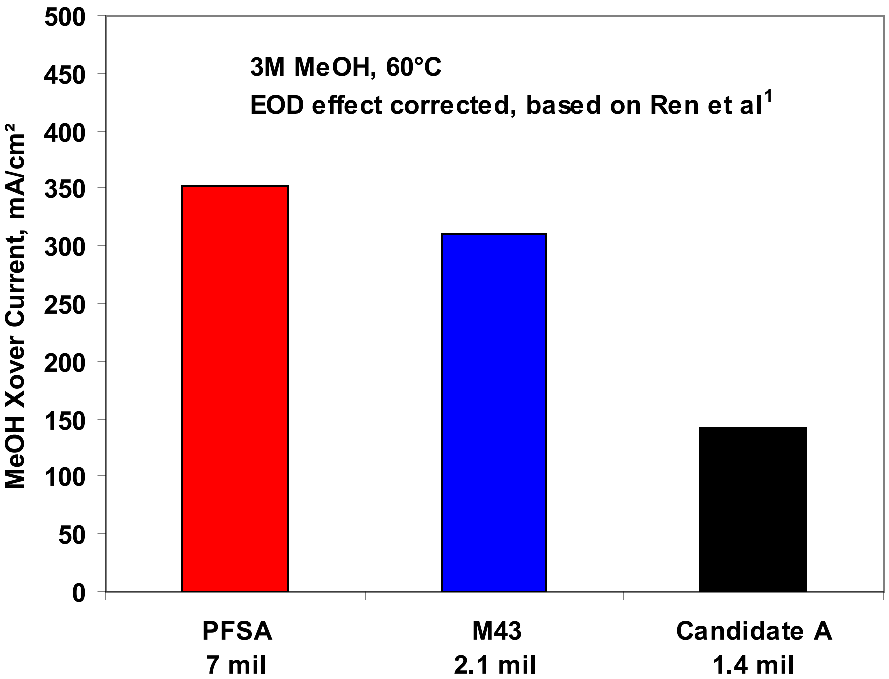


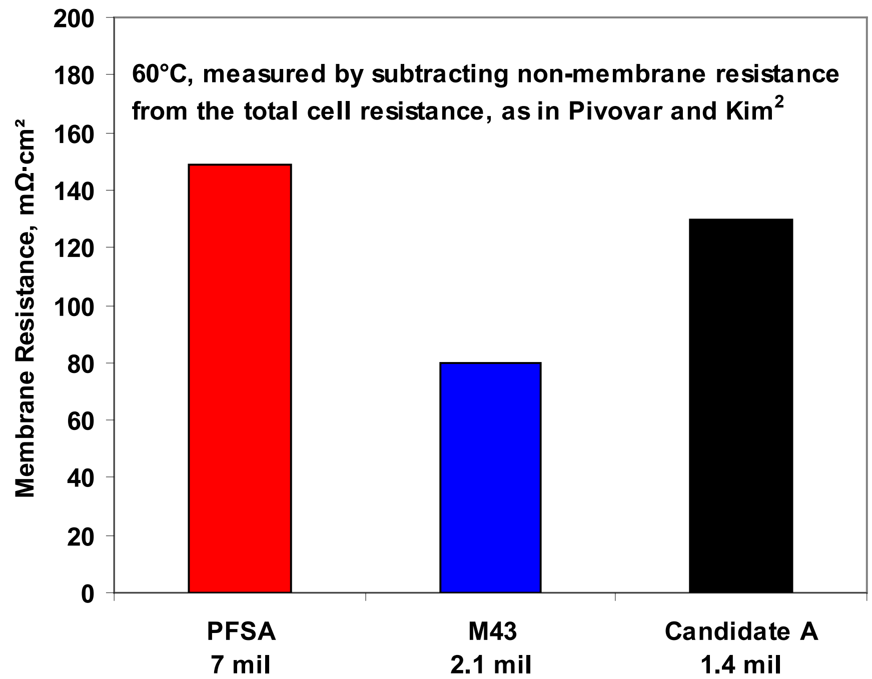

- 50% lower EOD coefficients for Arkema membranes than PFSA
- Lower EOD coefficient is advantageous for DMFC applications
  - Less cathode flooding, and easier water management
  - Reduced methanol crossover

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


1. Ren, X.; Henderson, W. and Gottesfeld, S., *J. Electrochem. Soc.*, **1997**, 144, L267.

# Lower Methanol Crossover & Membrane Resistance



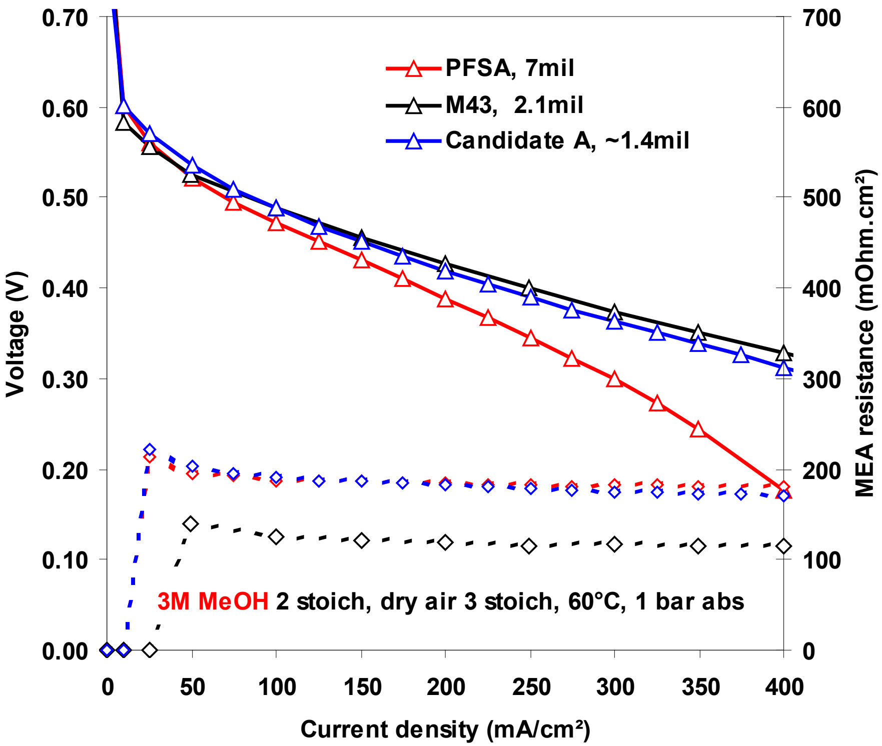



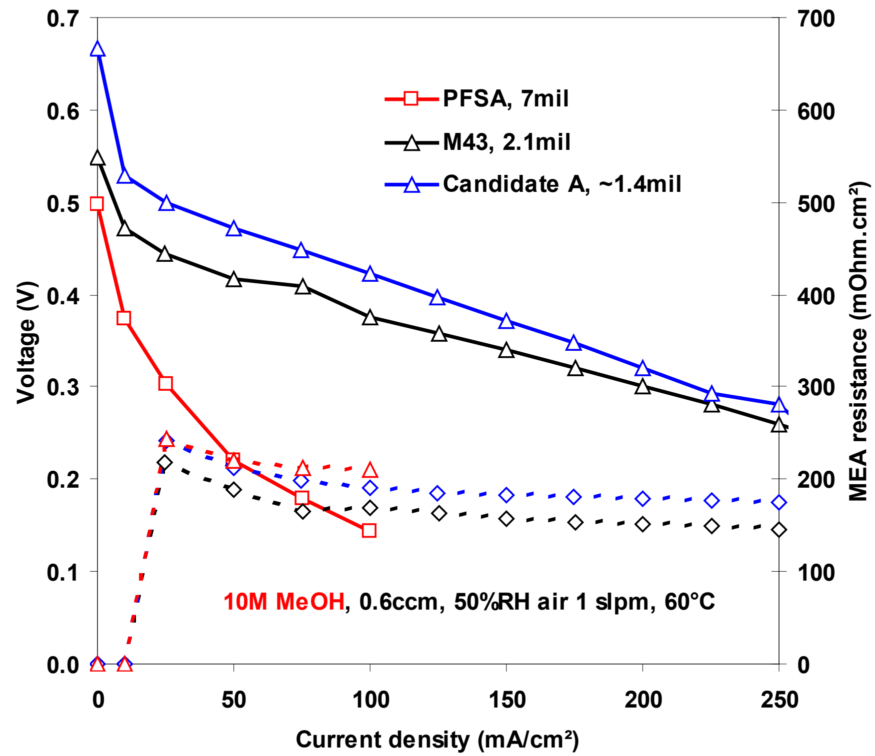

- Arkema membranes showed substantially lower methanol crossover lower membrane resistance than 7mil PFSA
- Membrane Candidate A showed 60% lower crossover and 10% lower resistance than a 7mil PFSA membrane

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

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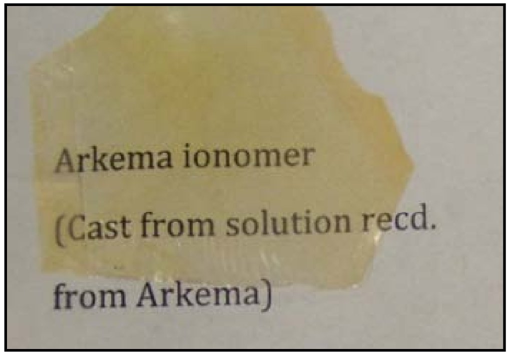
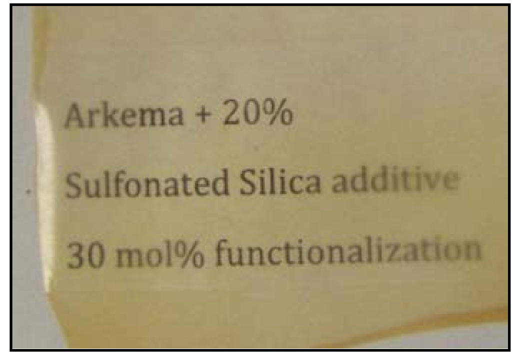
# Sulfonic Acid Functionalized Silica Additive




| Membrane + silica with 30% sulfonation | Conductivity @70°C, mS/cm | Permeability @ R.T., $x10^{-7}$ $cm^2/s$ | 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

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*Technical Approach:*

# DMFC Cathode Catalyst Development (Task 2)

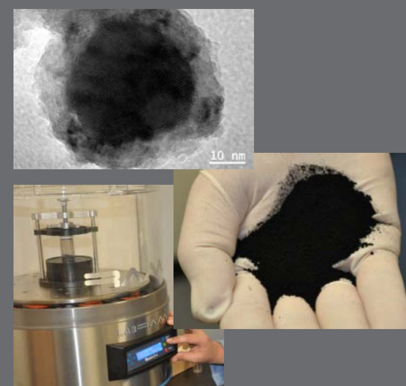
**Utilize Pd-based nanoscale catalysts with Pt/C to:**

- **Increase $mW/mg_{PGM}$ by suppressing methanol oxidation**
- **Reduce Pt content → decrease \$/W**

## SYNTHESIS

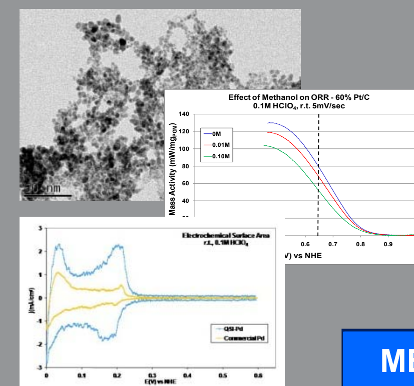
Gas-phase condensation (GPC) synthesis of unsupported Pd-based metal nanoparticles

## DESIGN




Integration of Pt/C, alloys, core-shell structure, other co-catalysts, and processing methods

## SCREENING




TEM, XRD, BET, TGA. CV and RDE w, w/o $CH_3OH$. Down-select based on activity, cost, durability

**MEA Tasks**

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*Technical Progress:*

# DMFC Cathode Catalyst Development (Task 2)

## Progress versus Objectives

| Objectives of Task 2 | Progress | % Complete (3/1/11) |
|---|---|---|
| Milestone: 50 $mW/mg_{PGM}$<br>RDE specific power in presence of 0.1M $CH_3OH$<br>*(0.45V, 70ºC, 50% Pt reduction)* | 115 $mW/mg_{PGM}$<br>RDE specific power in presence of 0.1M $CH_3OH$<br>*(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% |

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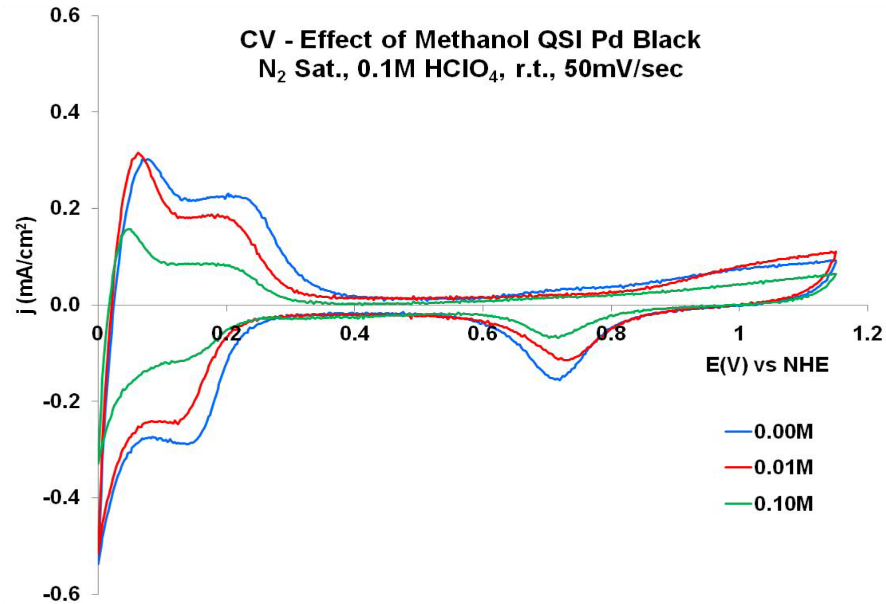
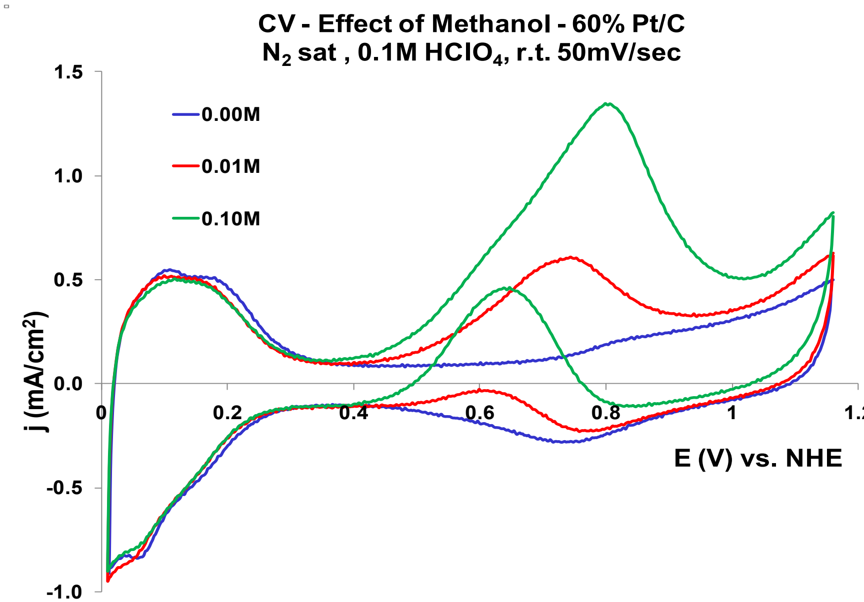
# Demonstration of Methanol Tolerance




QSI nano-Pd only




Commercial Pt/C

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

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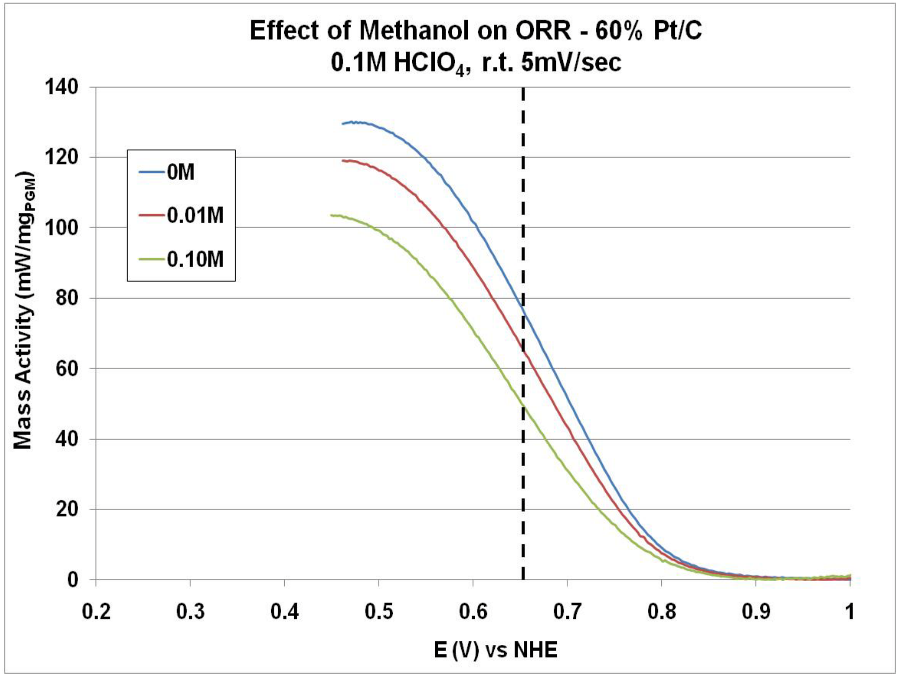
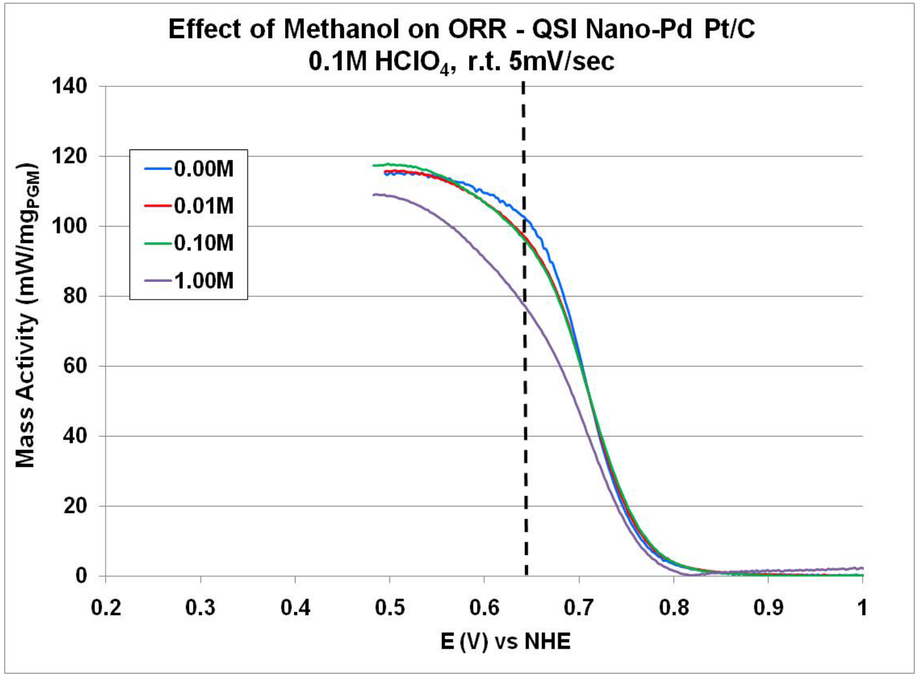
# Increased Specific Power (RDE Measurement)




Pt/C only

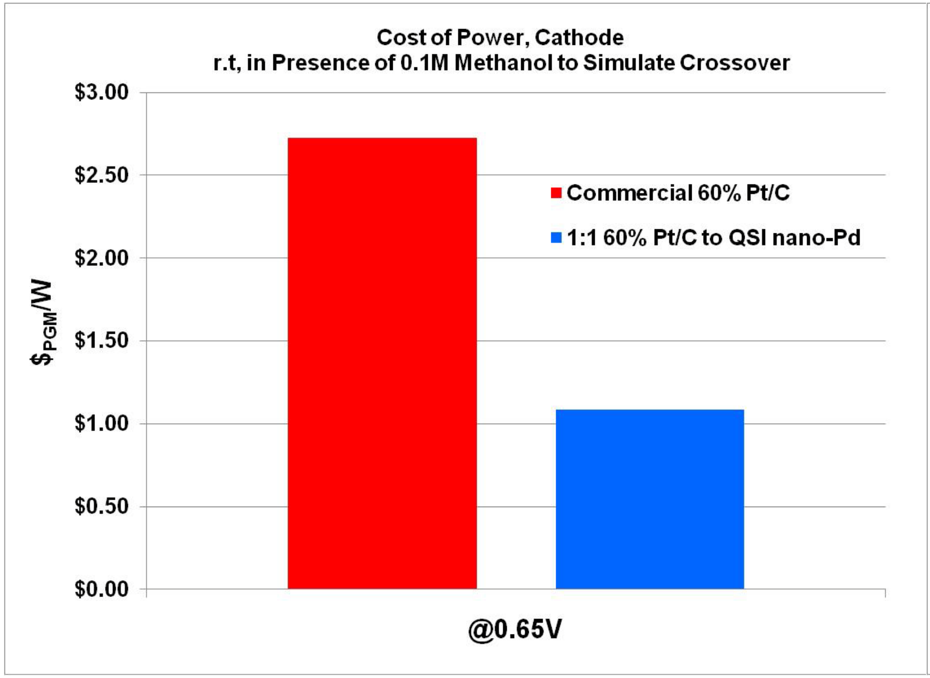
Pt/C and nano-Pd

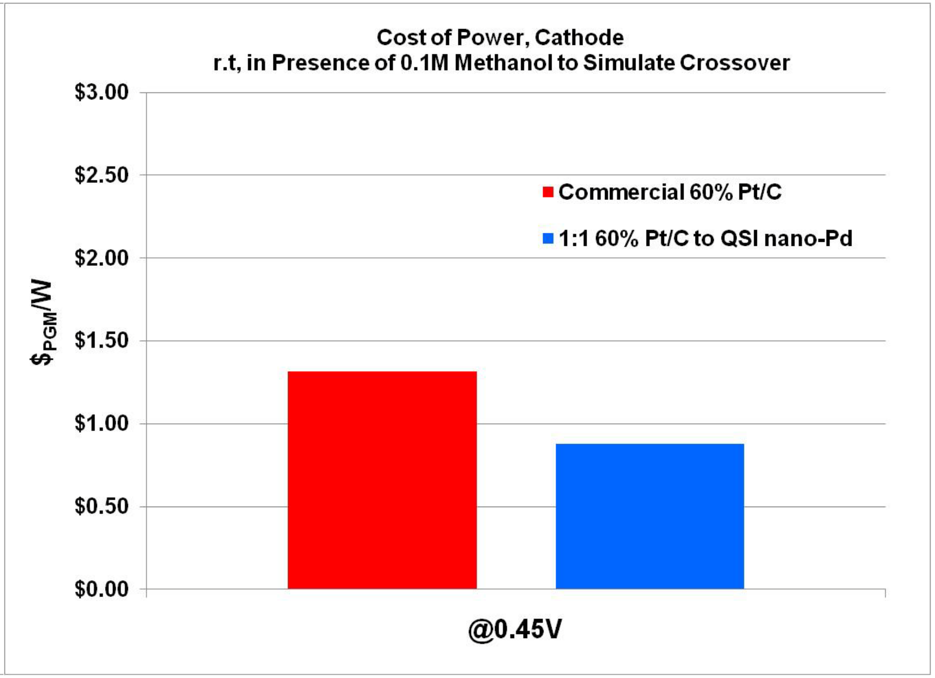
50% of Pt substituted with Pd

- >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

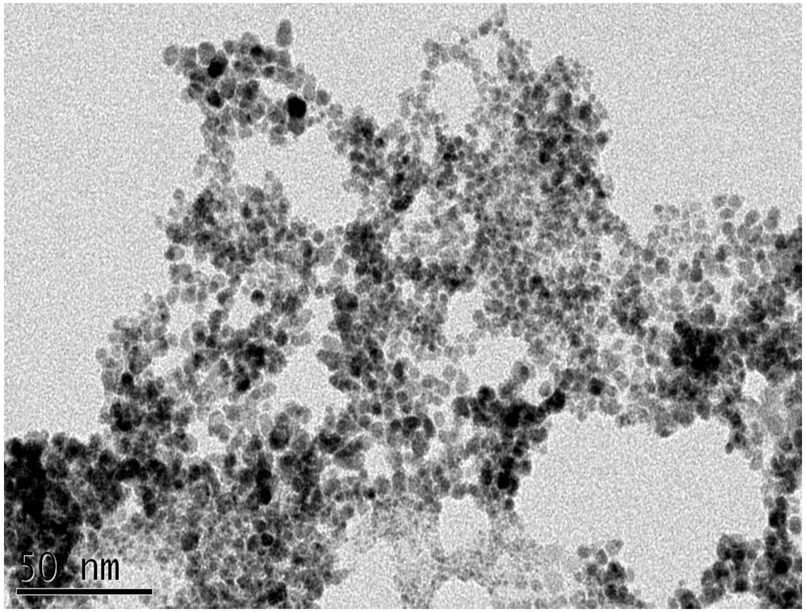



- 60% cost reduction at 0.65V (Cathode catalyst = $\$1.08_{PGM}$/W, low volume)
- 33% cost reduction at 0.45V (Cathode catalyst = $\$ 0.88_{PGM}$/W, low volume)

*Technical Accomplishments:*

# 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.

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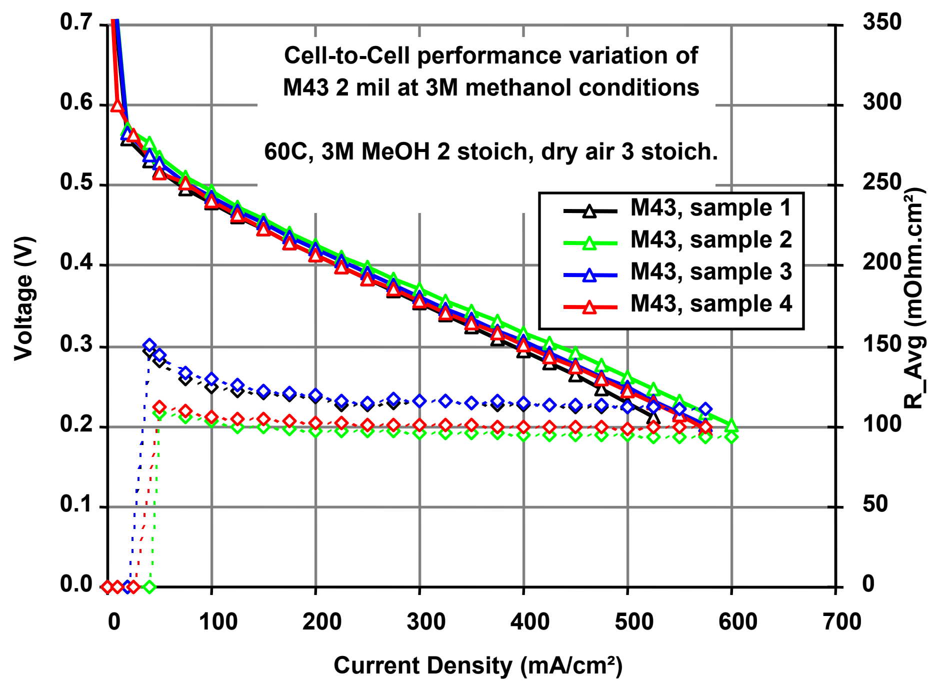
Technical Back-Up Slides

*Technical Accomplishments:*

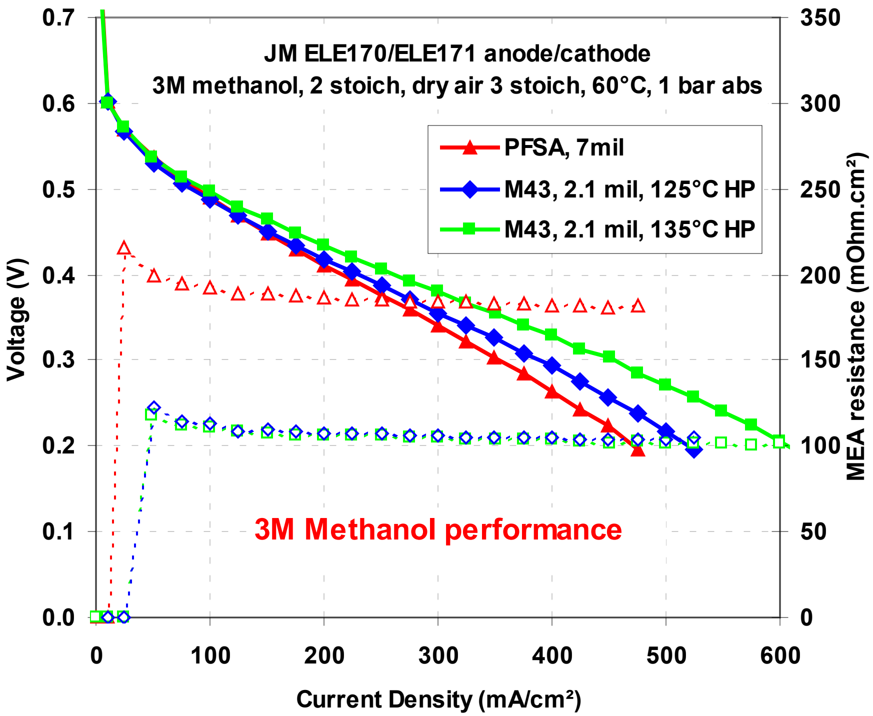
# DMFC Conditioning

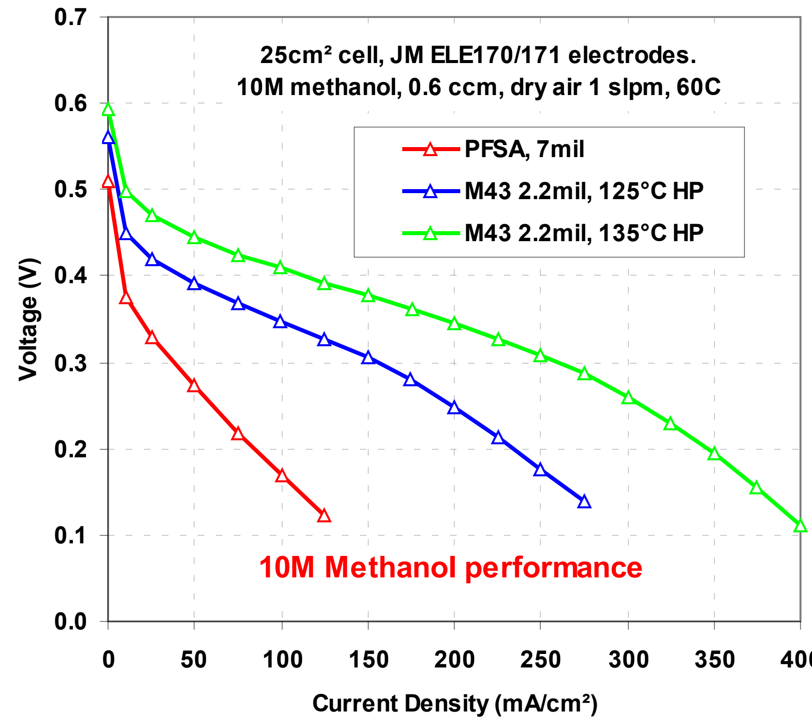
- Objective: Achieve optimal and repeatable performance in minimal time
- Challenge:
  - Arkema M43-based MEAs condition slower than PFSA
  - Common conditioning methods were developed based on PFSA, and do not work effectively on Arkema membranes
- Arkema conditioning method
  - Quick voltage cycling 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



*Technical Accomplishments:*

# 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.

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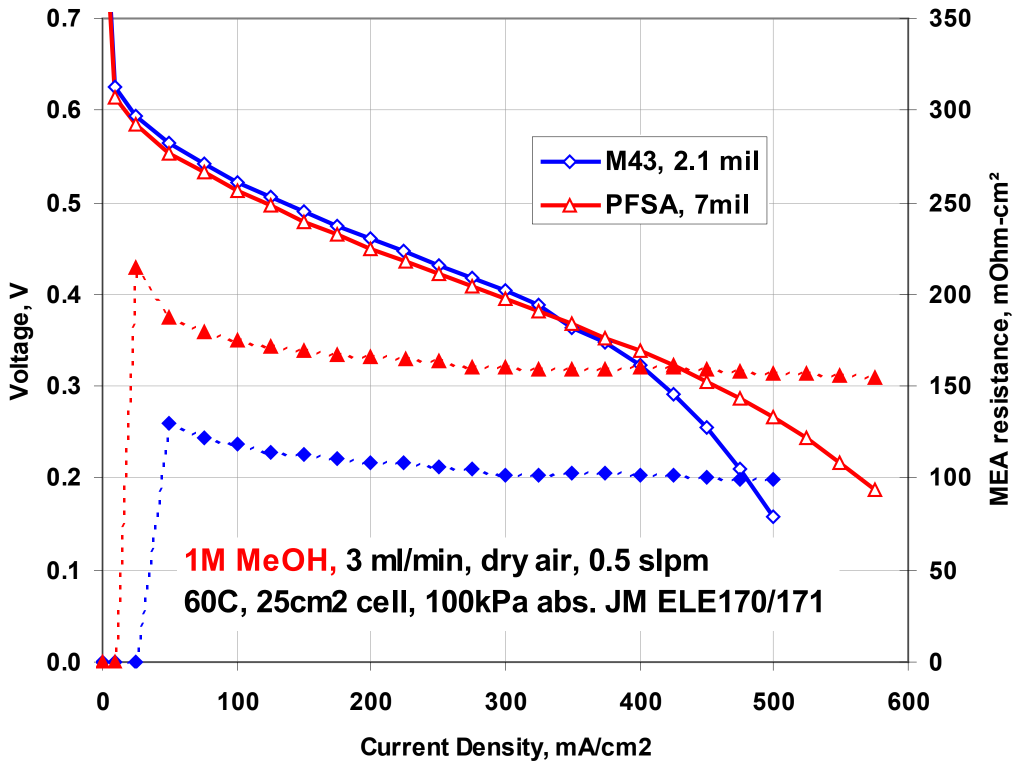
*Technical Accomplishments:*

# M43 MEA Performance: 1M Methanol




At 0.4V, M43 reaches 300mA/cm$^2$, or 120mW/cm$^2$ power, with commercial Johnson Matthey gas diffusion electrodes.

*Technical Approach:*

# Synthesis of Sulfonic Acid Functionalized Silica

Tetraethyl orthosilicate (TEOS)

↓ **Hydrolisis step** + HCl

$Si(OH)_4$

↓ **Condensation step**

+ Pluronic® 123 (template)

+ (3-mercaptopropyl) Trimethoxysilane (MPTMS) *Functionalization precursor*

+ $H_2O_2$

$SiO_2$-$SO_3H$(mesoporous silica)

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