



Novel Materials for High Efficiency Direct Methanol Fuel Cells

2010 U.S. DOE HYDROGEN PROGRAM AND VEHICLE TECHNOLOGIES
PROGRAM ANNUAL MERIT REVIEW AND PEER EVALUATION MEETING

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Project ID# FC063

Overview

Timeline

- Proposed Start: May 1, 2010
- Proposed End: April 30, 2012
- Percent Complete: 0%

Funding

- Total Project Funding: \$3,501k
 - DOE: \$2,634k
 - Contractor: \$867k
- Funding Received FY09: \$0
- Proposed Funding FY2010: \$780k

Barriers

- Durability
- Cost
- Performance

Organization

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



Organization



PEM Development and testing
MEA diagnostics and durability



Catalyst development
MEA production and testing



Cutting-edge characterization of
MEAs and development of composite
membranes



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 (Nafion [®] 117)	0.080 (2 mil thick film)
Catalyst Mass Activity (RDE) †	22.5 mW/mg Pt	> 100 mW/mg Pt
MEA Cathode Catalyst Loading	4 mg/cm ²	1.5 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

† conditions at 0.45 V & 70 °C.

Approach: Membrane Development

- Polymer blend

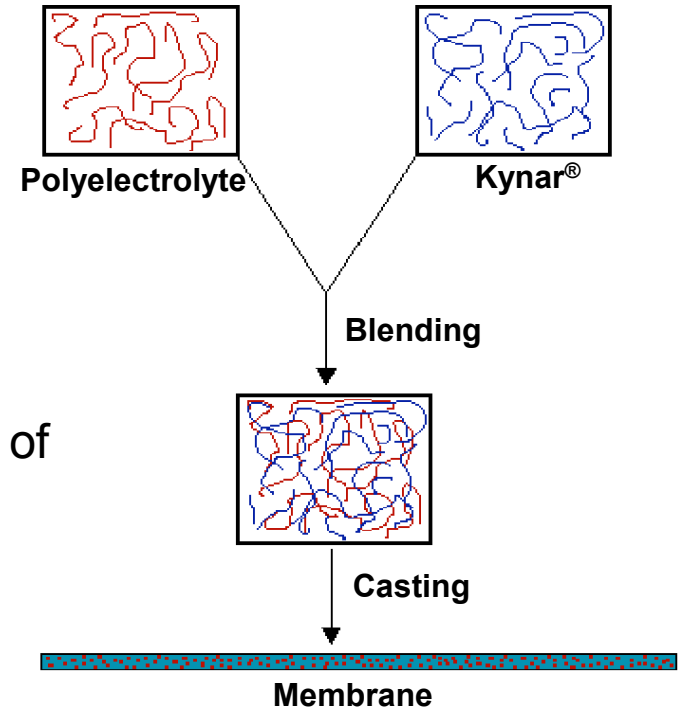
- Decouples conductivity from other requirements
- Kynar® PVDF
 - Chemical and electrochemical stability
 - Mechanical strength
 - **Excellent barrier against methanol**
- Polyelectrolyte
 - H⁺ conduction and water uptake

- Robust blending process

- PVDF can be compatibilized with a large range of polyelectrolytes
 - Latest generation taken to a pilot scale is M43, which is a baseline for this project
- Morphology and physical property control
 - Phase separation on a scale of 10-100s of nm

- Potential lower cost approach compared to PFSA

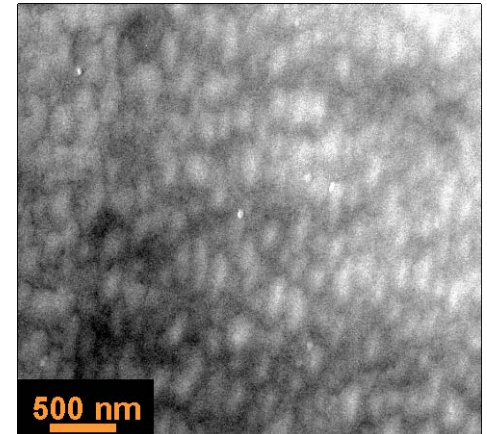
- Kynar® PVDF - commercial product
- Polyelectrolyte – hydrocarbon based



Approach: Membrane Development

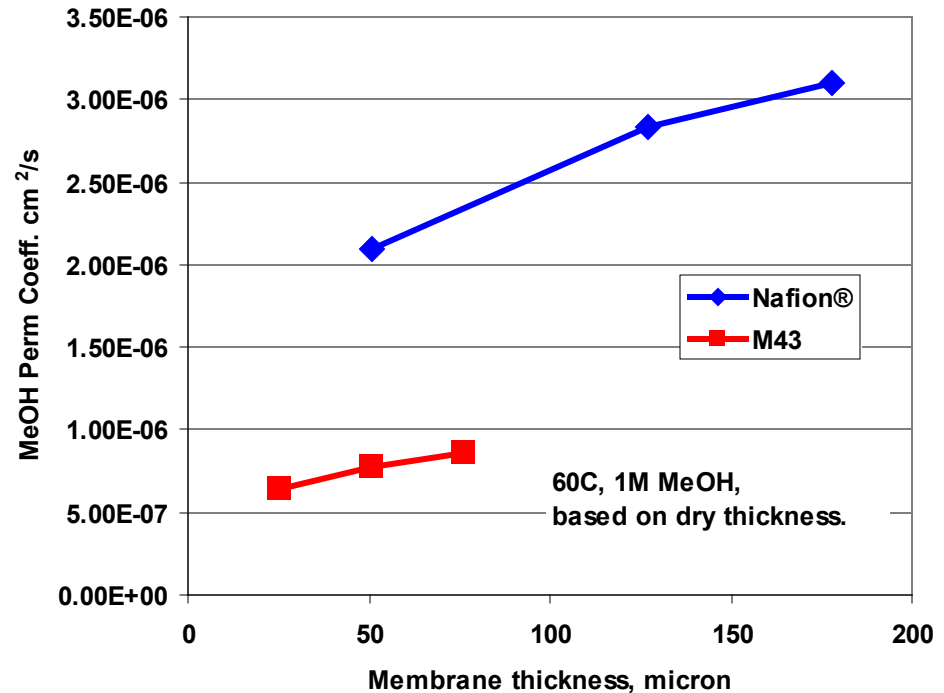
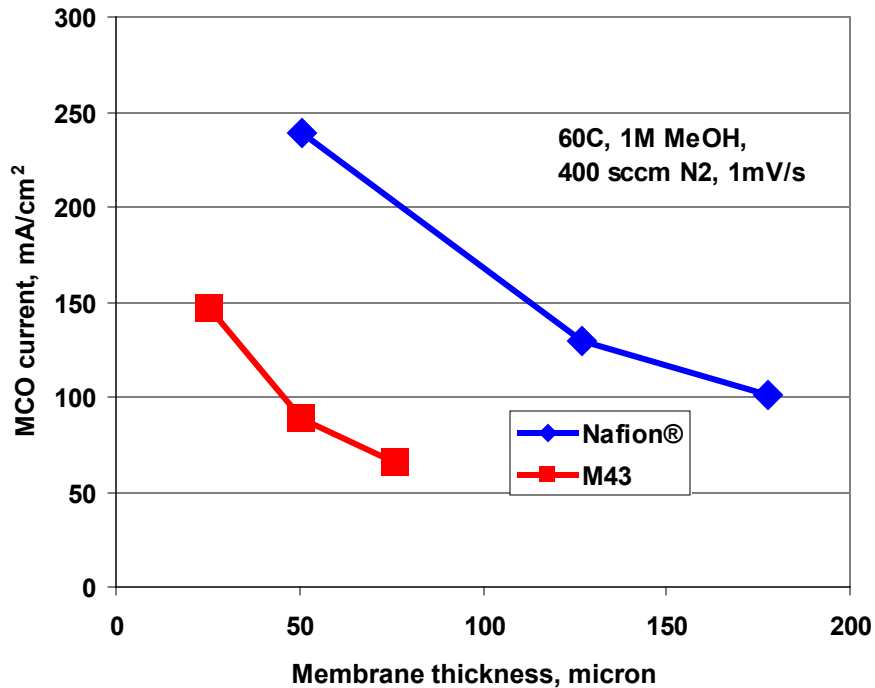
The key to the desired properties resides in careful control of composition, architecture, and morphology of the membrane components.

- Phase separation on the order of 10s of nm
 - Polymer architecture, composition, and type of compatibilizer
- PVDF matrix optimization
 - Degree of crystallinity (barrier against methanol permeation)
- Tailor the polyelectrolyte composition to minimize methanol permeation in this phase
 - Different acid and ion-containing groups
- Acidic inorganic additives
 - Reduce swelling in the membrane while maintaining conductivity



Preliminary Data: M43 Methanol Crossover

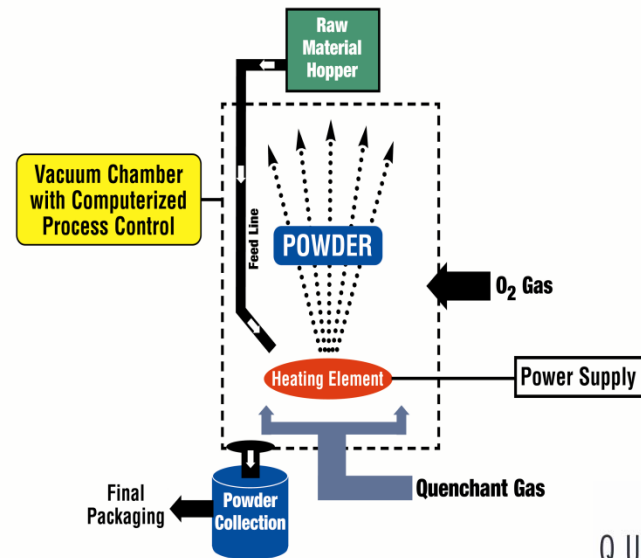
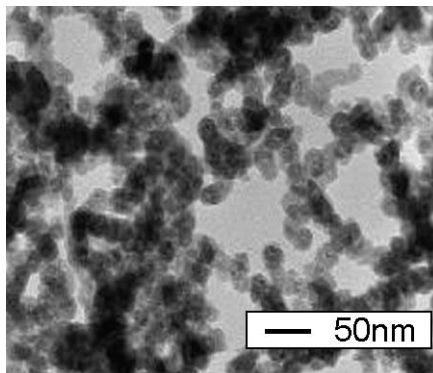
Conductivity: 140 mS/cm (1 mil) @ 70 °C (in DI Water)



- M43 was developed for hydrogen applications
- Without any development, M43 is already a good methanol barrier

Approach: Methanol Tolerant Cathode Catalyst

- Pd based alloy nanocatalyst mixed with Pt/C
 - Improved mass activity by suppressing methanol oxidation
 - Significant cost reduction by lower Pt content
 - Particle size = 3-10nm
- Pd-based nanocatalysts prepared using gas phase condensation
 - Control of particle size, alloy ratio, and core-shell structure
- Catalysts screening by rotating disk voltammetry, in presence and absence of methanol

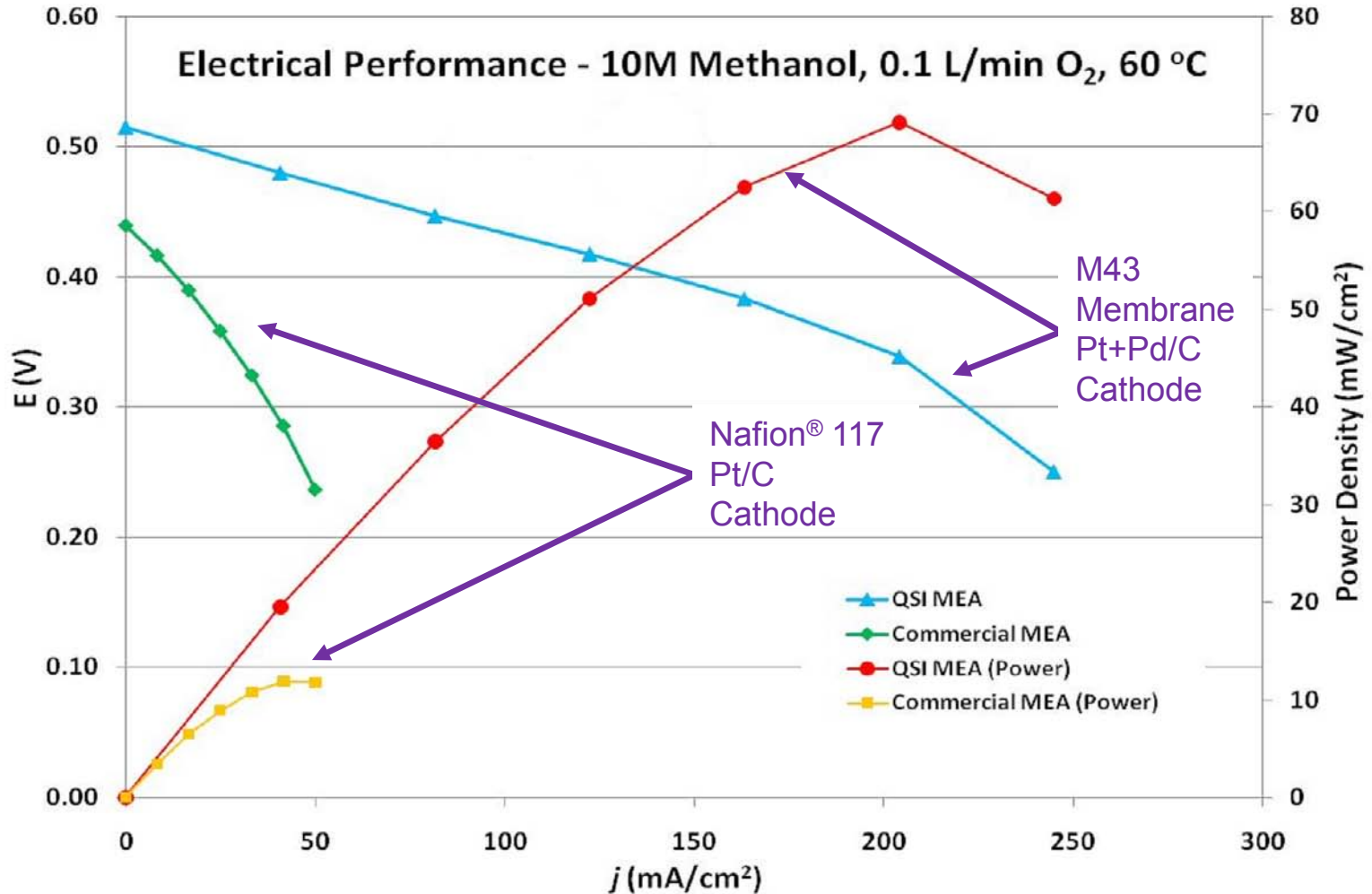


Approach: MEA Testing

- MEA development and characterization (QSI)
 - Optimize catalyst layer composition/construction
 - Ionomer content
 - GDE vs CCM
- MEA diagnostics (IIT, Arkema, QSI)
 - Single cell polarization with 1-10M methanol/air
 - Anode and cathode half-cell polarization measurement using reference electrode
 - Linear sweep voltammetry and CO₂ sensor to monitor methanol crossover
 - Cyclic voltammetry for catalyst active area
 - In-situ AC impedance for MEA resistance and transport resistances.
- MEA durability testing (Arkema, IIT, QSI)
 - Constant current mode, monitoring voltage loss over time.

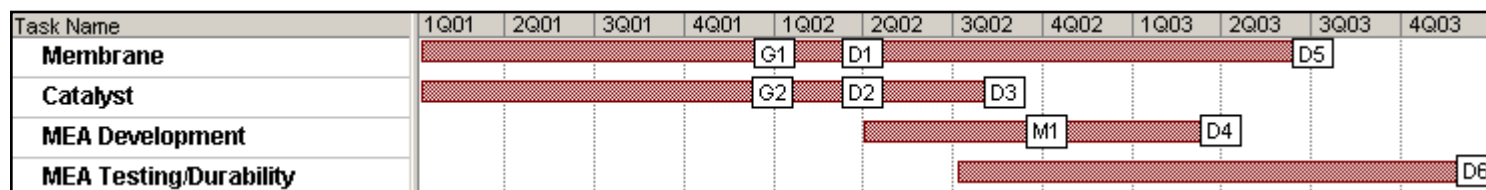
Preliminary Results: MEA Performance

Arkema M43 Low Crossover Membrane, QSI-Nano[®] Methanol Tolerant Cathode



Approach/Milestones

Project start: May 2010



- G1: Membrane w/ areal resistance $\leq 0.080 \Omega\text{cm}^2$ and a permeation coefficient $\leq 1 \cdot 10^{-7} \text{ cm}^2/\text{s}$
- G2: Catalyst w/mass activity $> 70 \text{ mW/mg}$
- D1: Membrane scale-up for MEA development
- D2: Catalyst scale-up for MEA development
- D3: MEA w/ 50% Pt reduction and mass activity $> 100 \text{ mW/mg}$
- M1: MEA w/ ohmic resistance $< 0.12 \Omega\text{cm}^2$ (determined from impedance)
- D4: MEA performance of 150 mW/cm^2 @ 0.4 V ($60 \text{ }^\circ\text{C}$, 1 M methanol)
- D5: Membrane w/ areal resistance $\leq 0.080 \Omega\text{cm}^2$ and a permeation coefficient $\leq 5 \cdot 10^{-8} \text{ cm}^2/\text{s}$
- D6: MEA passes 5,000 h durability testing

Summary

- The primary project objective is to develop new materials for DMFC that be the basis for a device to meet the DOE's technical targets for consumer electronics.
 - A multi-pronged approach will be taken to address the reduction of methanol cross-over through the membrane (morphology, membrane composition, polyelectrolyte chemistry, and additives).
 - Pd based nanocatalysts for the cathode will be developed that can operate with considerably reduced platinum loading and improved methanol tolerance.
- Preliminary data on a MEA containing Arkema's M43 membrane and QSI's methanol tolerant cathode catalyst shows good performance in 10M methanol at 60°C.
- Proposed project start in May 2010.