Novel Materials for High Efficiency Direct Methanol Fuel Cells

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

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June 8th, 2010

Project ID# FC063

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Overview

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

Barriers
- Durability
- Cost
- Performance

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

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

Organization

ARKEMA

Project Lead

PEM Development and testing

MEA diagnostics and durability

QUANTUM SPHERE

Catalyst development

MEA production and testing

ILLINOIS INSTITUTE OF TECHNOLOGY

Dr. Vijay Ramani's Research Group

Cutting-edge characterization of MEAs and development of composite membranes

ARKEMA

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	1-3·10^{-6} cm^2/s	5·10^{-8} cm^2/s
Areal resistance (Ωcm^2), 70 ºC	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 ºC.

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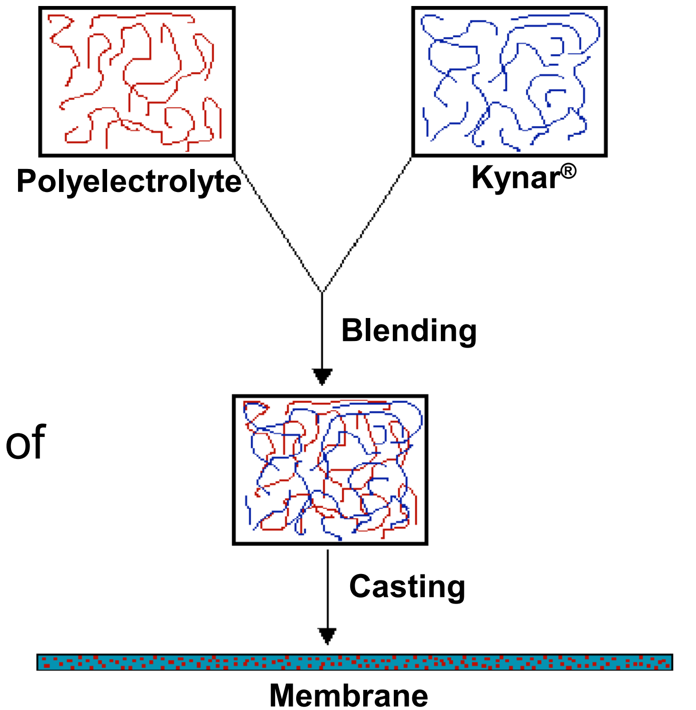
Approach: Membrane Development

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

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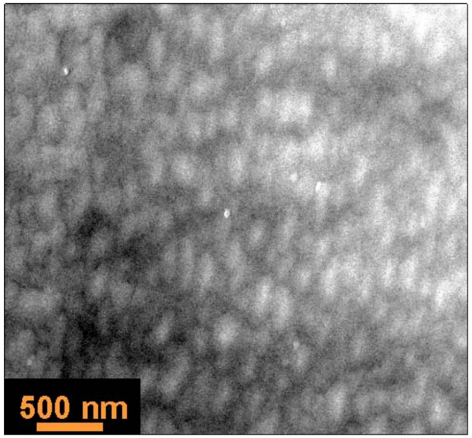
Approach: Membrane Development

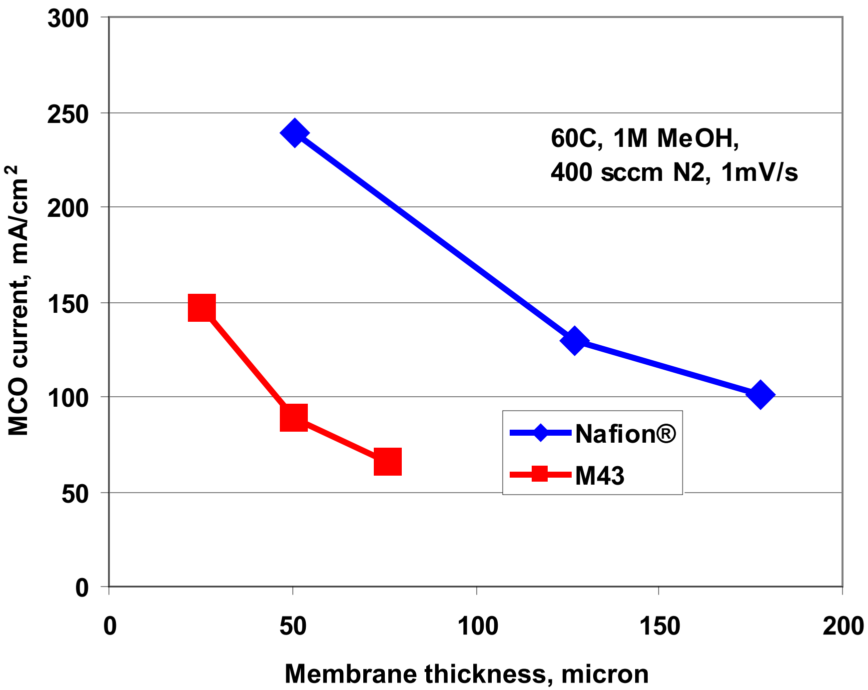
The key to the desired properties resides in careful control of composition, architecture, and morphology of the membrane components.

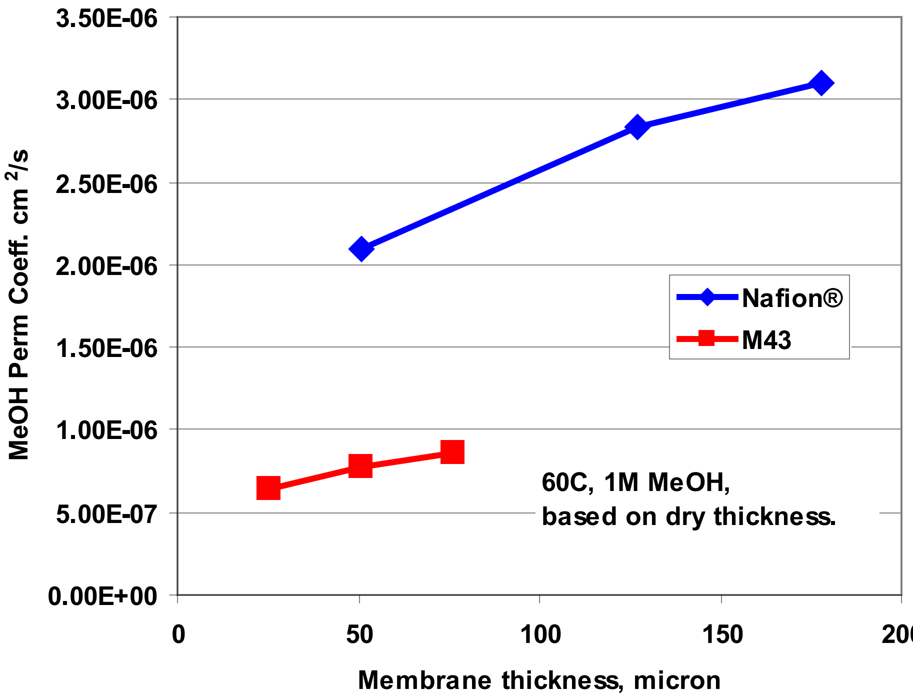
- Phase separation on the order of 10s of nm
  - Polymer architecture, composition, and type of compatibilizer
- PVDF matrix optimization
  - Degree of crystallinity (barrier against methanol permeation)
- Tailor the polyelectrolyte composition to minimize methanol permeation in this phase
  - Different 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)

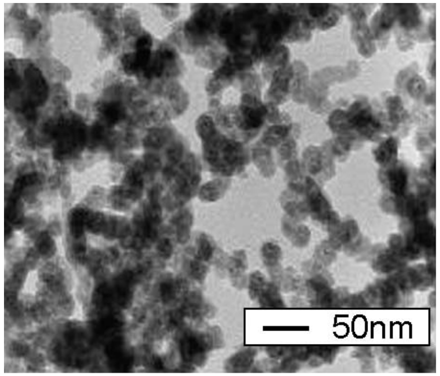


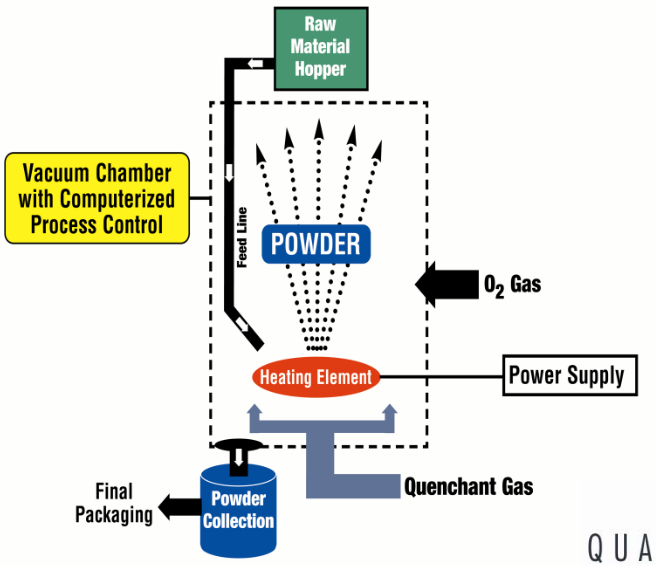


- M43 was developed for hydrogen applications
- Without any development, M43 is already a good methanol barrier

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





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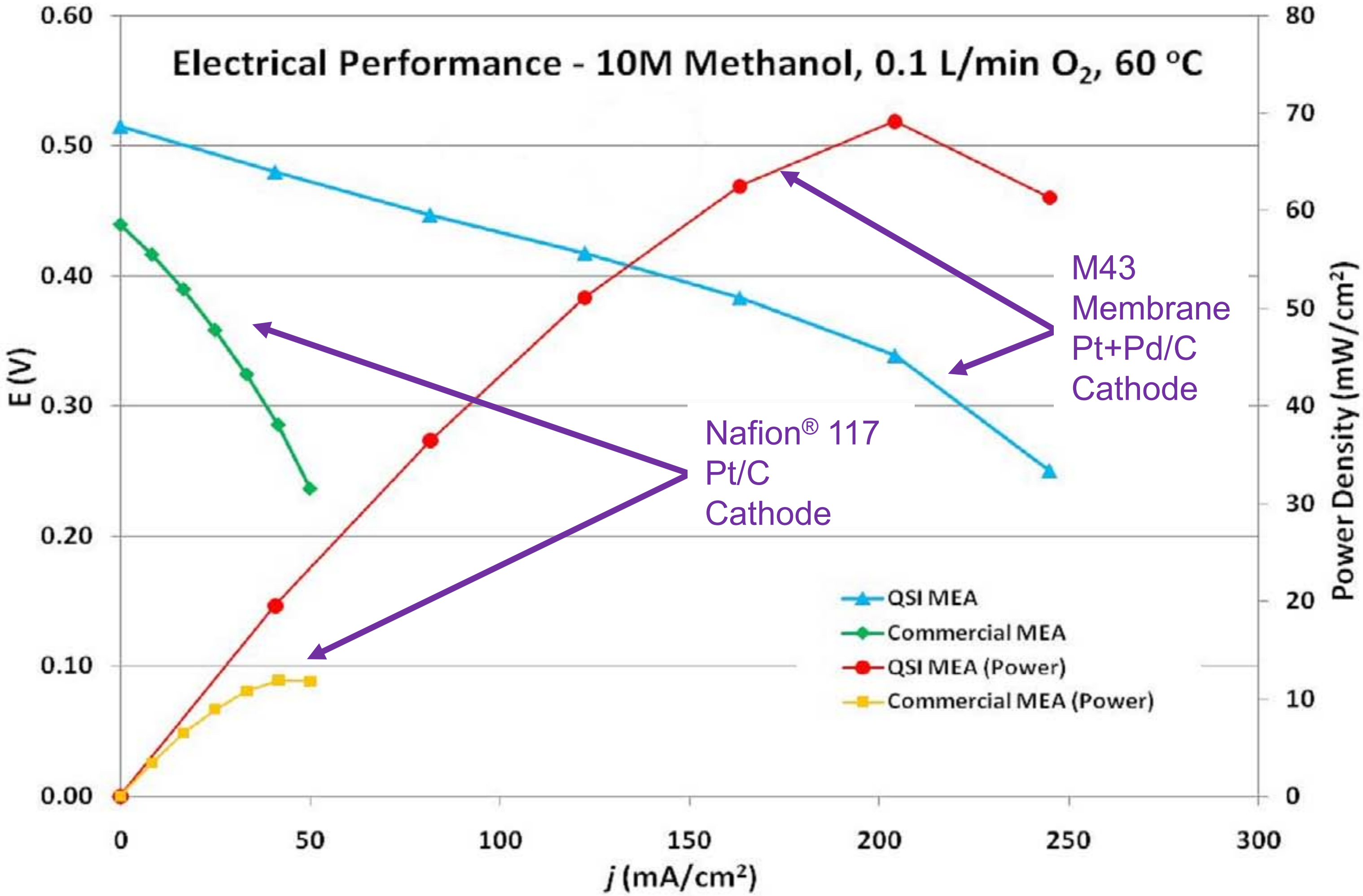
Approach: MEA Testing

- 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 CO_2 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



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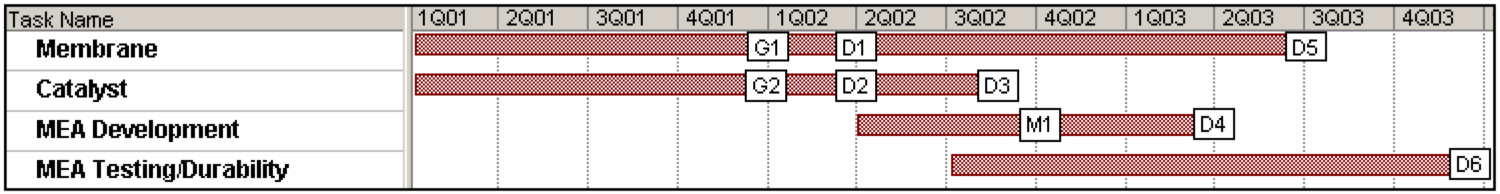
Approach/Milestones

Project start: May 2010



G1: Membrane w/ areal resistance $\leq 0.080\ \Omega cm^2$ and a permeation coefficient $\leq 1 \cdot 10^{-7}\ cm^2/s$

G2: Catalyst w/mass activity > 70 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 mW/mg

M1: MEA w/ ohmic resistance $< 0.12\ \Omega cm^2$ (determined from impedance)

D4: MEA performance of 150 mW/cm^2 @ 0.4 V (60 C, 1 M methanol)

D5: Membrane w/ areal resistance $\leq 0.080\ \Omega cm^2$ and a permeation coefficient $\leq 5 \cdot 10^{-8}\ cm^2/s$

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.

ARKEMA