

V.G.2 Novel Materials for High Efficiency Direct Methanol Fuel Cells

Chris Roger (Primary Contact), David Mountz, Wensheng He, and Tao Zhang

Arkema Inc.
900 First Ave.
King of Prussia, PA 19406
Phone: (610) 878-6707
E-mail: chris.roger@arkema.com

DOE Managers

HQ: Donna Ho
Phone: (202) 586-8000
E-mail: Donna.Ho@ee.doe.gov

GO: Reginald Tyler
Phone: (720) 356-1805
E-mail: Reginald.Tyler@go.doe.gov

Technical Advisor

John Kopasz
Argonne National Laboratory
Phone: (630) 252-7531
E-mail: kopasz@anl.gov

Contract Number: DE-EE0000474

Subcontractors:

- QuantumSphere Inc. (QSI), Santa Ana, CA
- Illinois Institute of Technology (IIT), Chicago, IL

Project Start Date: July 1, 2010

Project End Date: June 30, 2013

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 a membrane electrode assembly (MEA) combining these two innovations that has 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.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan for portable power devices:

- Durability
- Cost
- Performance

Technical Targets

This project is conducting focused research on next generation membrane and cathode catalyst materials for direct methanol fuel cells. Insights gained from these studies will be applied toward the design of an MEA for portable power applications that meet the DOE 2010 targets:

- Performance: specific power (100 W/kg), power density (100 W/l), and energy density (1,000 Wh/L)
- Cost: \$3/W
- Lifetime: 5,000 hours

In translating DOE-published targets, we have defined the following goals for the membrane, cathode catalyst, and MEA performance based on our modeling efforts (Table 1).

TABLE 1. Progress towards Meeting the Project Technical Targets for Portable Power Applications

Characteristic ¹	Units	Industry Benchmark	Project Target	Status
Methanol Permeability	cm ² /s	1-3x10 ⁻⁶	5x10 ⁻⁸	1.5x10 ⁻⁷
Areal Resistance, 70°C	Ωcm ²	0.120 (7 mil PFSA ³)	0.080	0.080
Cathode Catalyst Specific Power (rotating disk electrode, RDE) ²	mW/mg Platinum Group Metal (PGM)	25	>50	>100
MEA Cathode Catalyst Loading	mg/cm ² PGM	2.5	2	In progress
MEA Current-Voltage Cell Performance (0.4 V)	mW/cm ²	90	150	120 ⁴
MEA Lifetime	hours	>3,000	5,000	In progress

¹ Targets based on a methanol concentration of 1M

² Conditions at 0.45 V vs. standard hydrogen electrode and 70°C

³ Perfluorinated sulfonic acid

⁴ Measured with commercial gas diffusion electrode (GDE) with 1.5 mg/cm² Pt on the cathode and 4.5 mg/cm² Pt and Ru on the anode. This is intended to be a reference for MEA development work.

Fiscal Year (FY) 2011 Accomplishments

- Identified 15 high potential membrane candidates with the required areal resistance and a methanol permeation coefficient $\leq 3 \times 10^{-7}$ cm²/s. One candidate has a permeation coefficient of 1.5x10⁻⁷ cm²/s, slightly above the milestone target methanol permeation of 1x10⁻⁷ cm²/s.
- Successfully prepared composite membranes with a sulfonated silica additive with no visual indications of large-scale phase separation.

- Demonstrated a power of 120 mW/cm² from an MEA with an Arkema membrane and a commercial GDE.
- Successfully synthesized unsupported palladium and palladium-based nanocatalysts having a surface in excess of 90 m²/g (3-10 nm), both as admixtures and alloys.
- Initiated scale up of Pd catalyst production with an output of 1.2 kg/month at 60% recycling efficiency.
- Achieved a mass activity of 133 mW/mg_{PGM} at 0.45 V for Mn-promoted Pt/C + Pd, which fulfills the target for specific power. This includes an additional 20% reduction in PGM content. Corresponding cost of power is \$0.71/W, a 57% catalyst cost savings compared to commercial Pt/C.



Introduction

There is a tremendous need for small, efficient portable power sources. The explosive growth of the lithium-ion batteries market is fueled by the ever-growing demand for portable power used in consumer electronics. For the direct methanol fuel cell industry to emerge as an alternative to batteries, very difficult technical hurdles have to be overcome in terms of drastically reduced methanol cross-over in the membrane and improved anode and cathode catalyst efficiencies.

Approach

Arkema and IIT are developing a new generation of membranes with very low methanol cross-over and high conductivity. The membranes are formed from blends of poly(vinylidene fluoride) (PVDF) with a variety of highly sulfonated polyelectrolytes, technology that was developed in DE-FC36-04GO14051 and DE-FC36-07GO17008. A number of variables can be easily adjusted in the blending process to tailor the membrane properties, such as conductivity and methanol permeation. The key to obtaining the desired properties resides in control of composition, architecture, and morphology of the membrane components. These are controlled on a practical level through polyelectrolyte chemistry, processing, and use of inorganic materials, which are being systematically investigated and correlated with properties.

QSI is developing a new series of cathode catalysts with improved mass activity obtained by suppressing methanol oxidation. The QSI catalyst has demonstrated higher specific activity for oxygen reduction in the presence of methanol compared to commercially used Pt/C. The scope of work in the first year included development of the synthesis and electrochemical characterization of nanoscale Pd-based catalysts, methods to increase catalyst production yield, and basic MEA testing in anticipation of extensive MEA development and testing for the rest of the project.

Results

Membrane Development

Over 100 membrane compositions were fabricated at Arkema with varying polyelectrolyte compositions, PVDF grades, ratios of sulfonated polyelectrolyte to PVDF, and crosslinking agents. Testing for the compositions focused on ex situ conductivity and methanol permeation. Other testing (crystallinity measurements, microscopy, and mechanical testing) was also carried out on a small number of candidates to understand structure-property relationships and morphology. In-cell testing was also done on about 1/3 of the candidates to validate the ex situ property data.

Data from a majority of the samples is shown in Figure 1, along with PFSA and M43 references. The M43 membrane was developed for H₂ fuel cells and is used as a baseline for this project. All of the variables affected performance, but the polyelectrolyte chemistry had the most influence on membrane permselectivity through changes in polarity, equivalent weight, and molecular weight. The polyelectrolyte:PVDF ratio and PVDF grade, which alter equivalent weight and percent crystallinity respectively, also had a significant impact on membrane conductivity and permeation. Fifteen high potential candidates from the group have the required areal resistance and a methanol permeation coefficient $\leq 3 \times 10^{-7}$ cm²/s. The most promising of these candidates has a permeation of 1.5×10^{-7} cm²/s, slightly above the year one milestone target of 1×10^{-7} cm²/s. Efforts are now focused at refining these high potential candidates to meet the milestone requirements.

The MEA performance of the most promising high potential candidate (Candidate A) and M43 in 3M and 10M

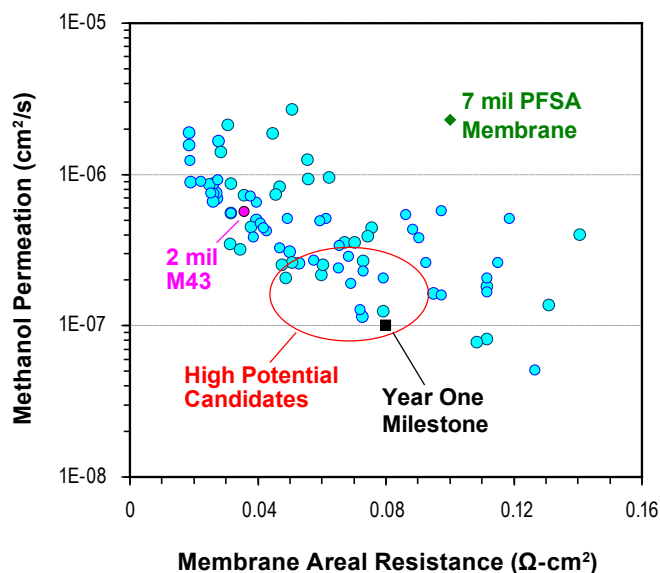


FIGURE 1. Conductivity versus Permeation for the Membrane Compositions Screened at Arkema

methanol is shown in Figure 2. Both materials outperform the PFSA reference at both methanol concentrations. Compared to M43, Candidate A shows slightly higher performance with 10M, and exhibits superior durability due to its mechanical properties. Both Arkema membranes have also demonstrated 120 mW/cm² at 0.4 V with 1M methanol using a commercial GDE from Johnson Matthey, which will be used as a baseline in the next stage of the project where QSI's catalyst and Arkema's membrane are incorporated into an MEA.

IIT has been developing novel sulfonated silica materials for use as conductors in the formulation of composite membranes. Addition of inorganic additives to membranes has been shown to lower methanol permeability, but this is usually combined with a reduction in conductivity [1]. This deficiency may be addressed by functionalizing the silica with sulfonic acid groups.

Mesoporous sulfonated silica particles are made by hydrolyzing tetraethyl orthosilicate with HCl and reacting it with (3-mercaptopropyl) trimethoxysilane. The materials were sulfonated over a range of 30-67% (ion exchange capacity = 1.4-2.1 mmol/g). All of them display high conductivity: 100 mS/cm at 60°C and 100% relative humidity.

Thirty percent sulfonated silica was incorporated into an Arkema formulation and cast into composite membranes. The membranes were transparent with no visual indication of particle aggregation. Data from the composites is shown in Table 2. Permeability and conductivity are lowered as the silica is added. Selectivity is more complex, initially decreasing compared to the reference at the lowest silica loading and then increasing with higher silica contents. The composite properties may be improved by using silica with higher sulfonation and this work is in progress.

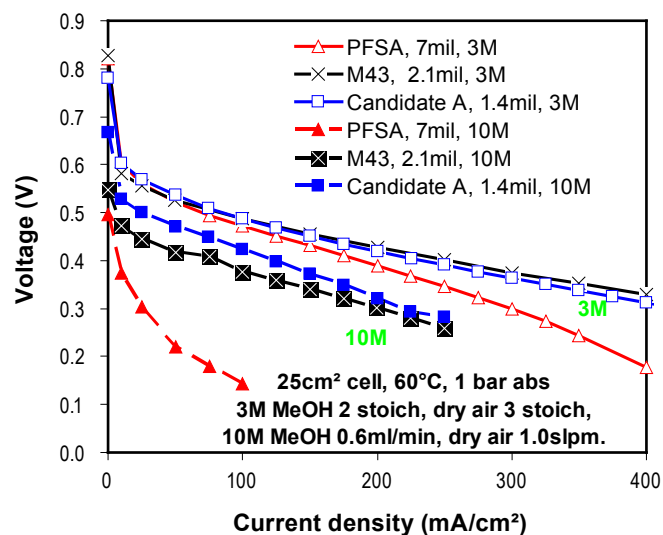


FIGURE 2. Performance of Two Arkema Membranes and a PFSA Benchmark in 3M and 10M Methanol

TABLE 2. Conductivity and Permeation Data for a Membrane Composites Series made with Sulfonated Silica

Membrane + Silica with 30% Sulfonation	Conductivity @ 70°C, mS/cm	Permeability @ Room Temperature, $\times 10^{-7}$ cm ² /s	Conductivity/Perm Selectivity
Arkema membrane	125 ± 7	6.7 ± 0.2	19
With 15 wt% silica	75 ± 4	5.7 ± 0.4	13
With 20 wt% silica	49 ± 1	3.4 ± 0.1	14
With 25 wt% silica	58 ± 9	3.2 ± 0.2	18

Catalyst Development

QSI successfully fabricated Pd and Pd-M (M= Ni, Co, Mn, Fe, Cr, Ag, Au, Se) nanocatalysts with high surface area (>90 m²/g). Catalyst particle sizes are in 3-10 nm range, as illustrated in Figure 3. The oxygen reduction reactivity of Pd-M + Pt/C catalysts (i.e. a mixture) was evaluated using RDE with and without methanol in the electrolyte. The Pd + Pt/C blended catalyst showed doubled mass activity (>100 mW/mg PGM) compared to Pt/C alone in the presence of 0.1M methanol. The resulting PGM costs per watt of various cathode catalysts (assuming cost of \$54.00/g for QSI nano-Pd and \$128.00/g for 60% Pt/C) are shown in Figure 4. Up to 57% cost savings (M = Mn) is realized when a Pd-M co-catalyst is used with Pt/C.

Conclusions and Future Directions

- Identified 15 high potential membrane candidates with the required areal resistance and a permeation coefficient $\leq 3 \times 10^{-7}$ cm²/s.
- Composite membranes with a sulfonated silica additive were successfully prepared. Higher sulfonation

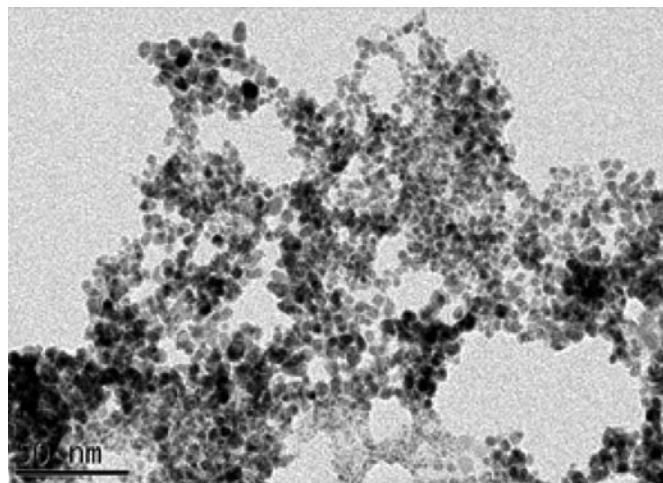


FIGURE 3. Transmission Electron Microscope Image of Pd-Mn Nanocatalysts (The scalebar represents 50 nm.)

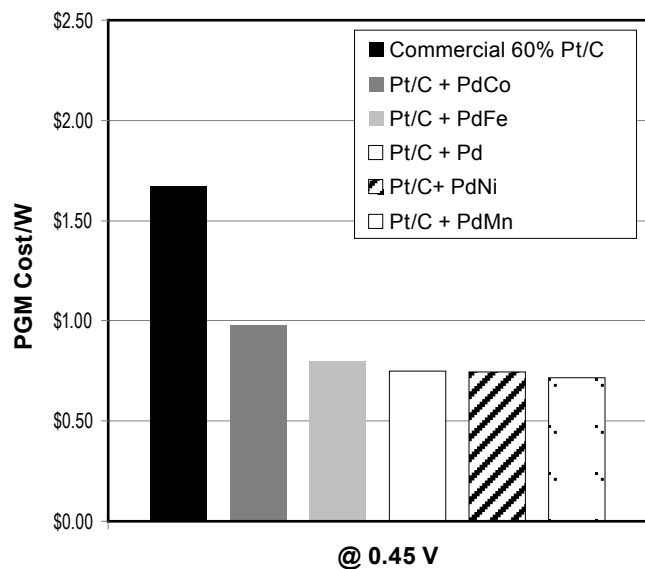


FIGURE 4. Cost of Power at 0.45 V for Cathode Catalyst in the Presence of 0.1M Methanol to Simulate Crossover

levels and better dispersion of the inorganic particles are needed to improve conductivity and decrease permeation, which will be pursued in the future.

- A catalyst containing a mixture of Pt/C + Pd-Mn achieved a mass activity of 133 mW/mg_{PGM} at 0.45 V, which fulfills the target for specific power.

- Down-select membrane and catalyst candidates that meet the year one milestone, refine their properties, and produce target compositions on a pilot-scale for MEA development.
- Initiate MEA development for 50% reduction in PGM content at the cathode to meet the goal of ≤ 2 mg/cm² total PGM loading with the target cell performance.

Patents Issued

1. Goldbach, J.; Mountz, D. "Blend of ionic (co)polymer resins and matrix (co)polymers." U.S. Divisional Patent #7,781,529, Aug 24, 2010.
2. Goldbach, J.; Gaboury, S.; Umpleby, R.; Parvole, J.; Mountz, D. "Blend of ionic (co)polymer resins and matrix (co)polymers." U.S. Divisional Patent #7,815,986, Oct 19, 2010.

FY 2011 Publications/Presentations

1. Poster presentation at the 2010 DOE Hydrogen Program and Vehicle Technologies Program Annual Merit Review and Peer Evaluation Meeting, D. Mountz, W. He, and C. Roger.

References

1. R. Jiang, Kunz, H.R., and Fenton, J.M., Journal of Membrane Science, 272, 116 (2006).