V.G.1 Novel Materials for High Efficiency Direct Methanol Fuel Cells

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Subcontractor:
Illinois Institute of Technology (IIT), Chicago, IL

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Project End Date: June 30, 2013

Fiscal Year (FY) 2012 Objectives

- Demonstrate membrane electrode assembly (MEA) performance of 120 mW/cm^2 at 0.4 V with an Arkema membrane in 1M methanol (Go/No-Go decision - January 2012).

- Obtain a specific power ≥50 mW/mg precious group metal (PGM) in an MEA with 50% Pt reduction.

- Develop a second generation membrane with an areal resistance ≤0.0375 Ωcm^2 and a methanol permeation coefficient ≤1x10^{-7} cm^2/s (deliverable – September 2012).

- Demonstrate an MEA performance of 135 mW/cm^2 @ 0.4 V with a composite membrane in 1M methanol (Go/No-Go decision – September 2012).

Technical Barriers

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

(A) Durability
(B) Cost
(C) 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 a MEA for portable power devices that meet the DOE 2013 targets:

- Performance: specific power (30 W/kg), power density (35 W/L), specific energy (430 Wh/kg), and energy density (500 Wh/L)

- Cost: $10/W

- Lifetime: 3,000 hours

In translating DOE targets, the following goals for the membrane and MEA performance were defined (Table 1). The progress towards meeting these goals is also summarized.

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

Characteristic[1]	Units	Industry Benchmark	Project Target	Status
Methanol Permeability	cm^2/s	1-3·10^{-6}	1x10^{-7}	1x10^{-7}
Areal Resistance, 70°C	Ωcm^2	0.120 (7 mil PFSA[2])	0.0375	0.080
MEA Cathode Catalyst Loading	mg/cm^2 PGM	2.5	2	~1.3
MEA I-V Cell Performance (0.4 V)	mW/cm^2	90	150	120[3]
MEA Lifetime	Hours	>3,000	5,000	In progress

[1] Targets based on a methanol concentration of 1M.
[2] Perfluorinated sulfonic acid
[3] Measured with commercial gas diffusion electrode (GDE) with 1.5 mg/cm^2 Pt on the cathode. The anode contains a Pt loading of 3.0 mg/cm^2 and a Ru loading of 1.5 mg/cm^2. This is intended to be reference for MEA development work.

FY 2012 Accomplishments

- Met the January 2012 Go/No-Go MEA performance target using an Arkema membrane and either a commercial GDE or a lab-made cathode.

- Obtained a specific power of 80-100 mW/mg PGM in a MEA with a cathode Pt loading in the range of 1.0-1.3 mg/cm^2.

- Demonstrated a technique to deconvolute performance loss from individual components and sources in direct methanol fuel cell (DMFC) operation.

- Started durability test in 2M methanol. MEAs failed earlier than expected and major performance loss came from degradation in both electrodes.

- Synthesized 23 different polyelectrolytes to develop a second generation DMFC membrane. The membrane is being designed to have higher performance and a lower cost than the first generation. All second generation membranes have unacceptably high polyelectrolyte loss after a brief immersion in water. Strategies to reduce the polyelectrolyte loss are being explored.

- Evaluated composite membranes containing sulfonated silica and rare-earth triflates. The most promising candidates are showing higher conductivity than the ones prepared last year.

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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 reduced methanol cross-over in the membrane and improved catalyst efficiencies.

Approach

Arkema and IIT are developing new DMFC membranes with lower fuel cross-over and high conductivity. The membranes are formed from blends of poly(vinylidene fluoride) with a variety of highly sulfonated polyelectrolytes. A number of variables can be easily adjusted in the blending process to tailor 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.

Arkema completed the development of the first generation of polyelectrolytes this past year and began work on a new generation of polyelectrolyte technology that can be used in membranes to form different microstructures than the ones used in the current technology. These microstructures may be potent factor to increase membrane performance. The new technology may also have a potentially lower cost stemming from the use of less expensive, commercially available monomers and reducing the number of steps in the membrane fabrication process. IIT continued work on the addition of sulfonated silica and rare-earth triflate additives to Arkema's membranes, which have been shown to lower methanol permeability. IIT's efforts are now focused on improving membrane conductivity while keeping the methanol permeability low.

Results

Go/No-Go Decision

After the down-selection of membranes that have met the first year milestone requirements in July 2011, efforts focused on the development and testing of MEAs from these membranes to meet the Go/No-Go decision in January 2012. The membranes down-selected produced lower than expected MEA performance, and we identified that conductivity has a higher contribution on performance than methanol permeation in 1-2M methanol. The Go/No-Go milestone was met using a membrane composition containing slightly more polyelectrolyte than a down-selected candidate from the milestone and either a commercial GDE or a lab-made cathode[1]. Data collected using the lab-made cathode and Arkema membrane in 2M methanol is shown in Figure 1 with a specific power of 92 mW/mg PGM.

The use of palladium-based cathode co-catalysts being developed in the project reduced MEA performance when it was added to the cathode ink formulations. The cause of the lower performance is, at least, partially attributed to the palladium catalyst agglomerating, causing poor catalyst distribution. Various strategies were explored (e.g. ink mixing method), but none of them were effective. The work on the Pd based co-catalyst was stopped after the Go/No-Go project review.

MEA Diagnostics

Electrochemical diagnostic techniques were employed to understand how the electrocatalyst, electrode, and MEA properties affect performance and durability. These diagnostic techniques are currently used in the membrane

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[1] Lab-made cathode made with JM Hispec™ 9100 Pt/C catalyst with a loading between 1.0-1.5 mg/cm^2. Anode was a commercial material from Johnson Matthey (same as described in in Table 1 - note #3).
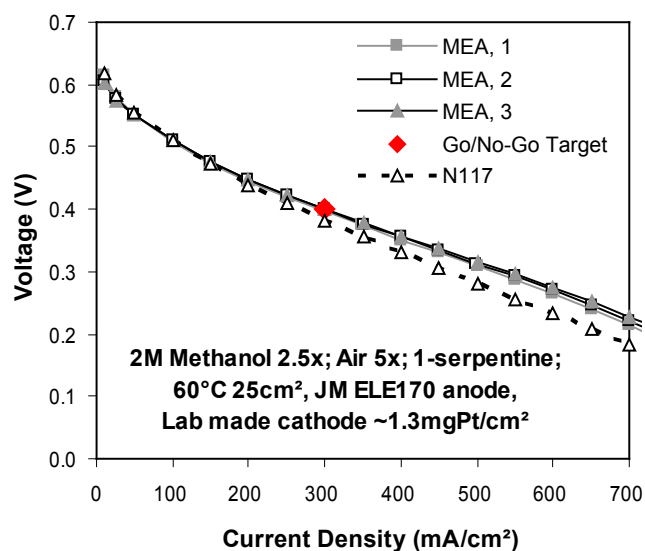
FIGURE 1. Polarization curves of Arkema membranes and lab-made cathodes in 2M methanol at 60°C. Each curve shown represents a sample replicate. This data also shows that MEA exhibited a specific power of 92 mW/mg PGM.

FIGURE 2. Contribution of the different losses in the actual performance of a 25 cm^2 MEA fabricated using Arkema M43 membrane and Johnson Matthey commercial electrodes. The polarization curve was acquired at 60°C using 3M methanol (2 stoichiometry) as fuel and air, oxygen, and helox as oxidants (3.5 stoichiometry). Cathode contributions from the electrode ohmic loss and binder-liquid phase mass transfer loss are negligible compared to the other losses plotted.

and MEA developments in both Arkema and IIT facilities. IIT can also perform in situ alternating current impedance spectroscopy and that can be used to gain further insights into MEA performance analysis by using an in-cell reference electrode.

IIT has recently demonstrated a useful technique based on the procedure described by Williams and coworkers to enable detailed breakdown of all the major contributions in MEA performance losses. One example of voltage loss breakdown of an MEA with Johnson Matthey standard electrodes and M43 membrane is shown in Figure 2. This technique does not account for methanol crossover on cathode performance in its current form. However, work is planned to account for this effect in coming year.

MEA Durability Testing

Several samples of the membrane developed for the Go/No-Go work were tested and most failed within 500-1,000 hours due to overall performance degradation (>20% voltage loss at 0.2 A/cm^2). During the life testing, significant losses at the anode and cathode were also observed. An example of the distribution of voltage losses over the lifetime of an MEA using the Go/No-Go membrane, Johnson Matthey anode and Arkema cathode is shown in Figure 3. This data shows that the majority of the performance loss stems from the electrodes, especially the cathode. The MEAs also developed much higher (~50%) resistance and lower methanol crossover current over the cell lifetime. It is worth noted that despite the significant resistance increase, the resultant performance loss is still
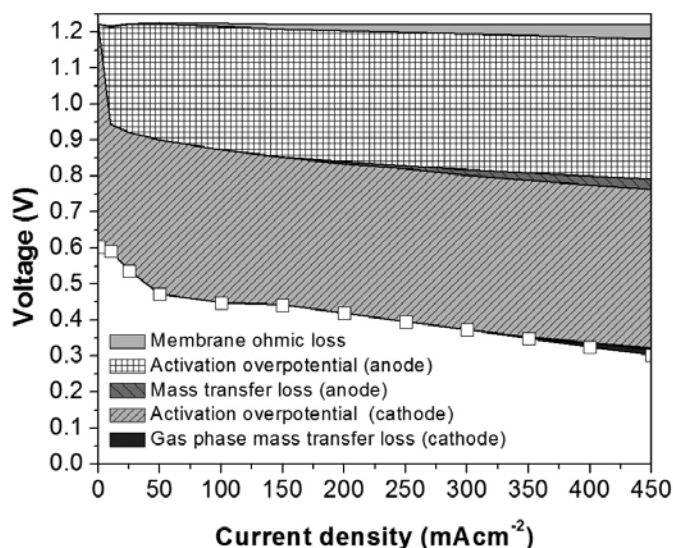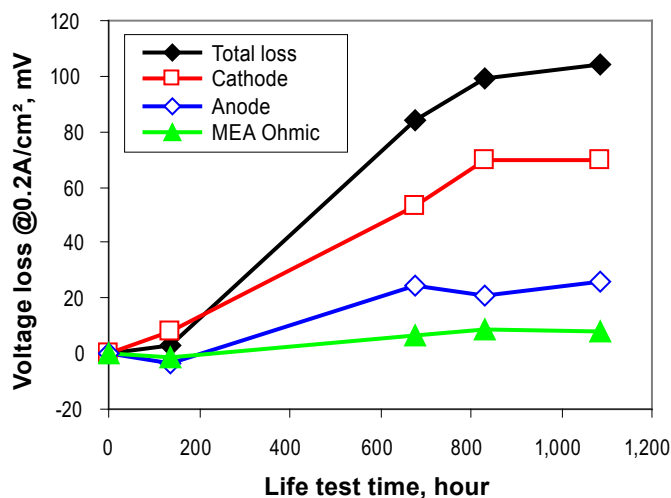

FIGURE 3. Distribution of voltage losses (relative to beginning of life) during life test of a MEA using Arkema Go/No-Go membrane and Johnson Matthey ELE170 anode and Arkema lab-made cathode. Life test conditions are 60°C, 2M methanol 3 stoichiometry, air 3.5 stoichiometry, at constant current of 0.2 A/cm^2.

smaller than the contribution by both electrodes. Detailed diagnostics and more controlled durability experiments will be conducted next year to understand why and how electrode degradation occurs.

Generation 2 Membrane Development

Twenty-three different polyelectrolytes were synthesized this past year to develop the current membrane generation. All membranes showed >30% sulfur loss and low conductivity after a short period of immersion in water, which is originating from polyelectrolyte leaching from the membrane. The leaching was traced back to inadequate crosslinking/tethering of the polyelectrolyte in the membrane. Without adequate crosslinking, the polyelectrolytes are quickly removed from the membrane since they are water soluble. Various strategies to improve crosslinking and limit polyelectrolyte water solubility are being explored.

Composite Membrane Development

Most inorganic additives screened reduced both methanol permeability and conductivity, as shown in Figure 4. There is a correlation between conductivity and permeability with most materials prepared with lower additive loadings (highlighted area of Figure 4) showing
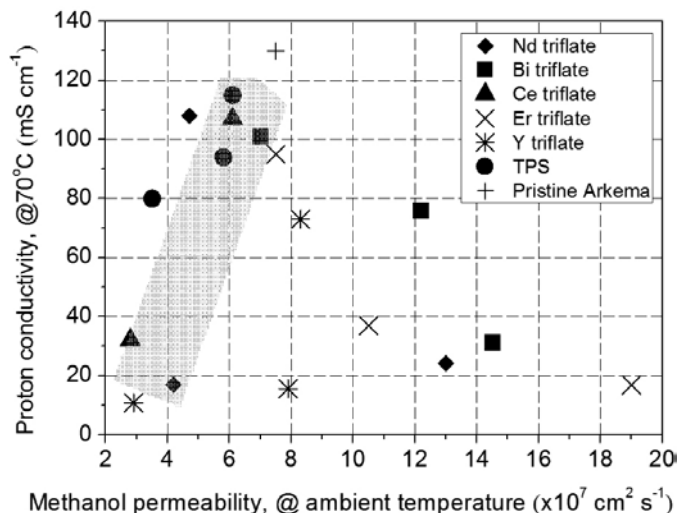

FIGURE 4. Relationship between proton conductivity and methanol permeability for composite membranes prepared with several inorganic fillers and loadings between 5-30 wt%.

only slight changes in selectivity. The most promising candidates were prepared with 5 wt% 3-(trihydroxysilyl)-1-propane-sulfonic acid (TPS) or neodymium triflate, which showed more selectivity than the unfilled Arkema membrane reference and have higher conductivity than the composites prepared last year (conductivity of composites last year was 58-75 mS/cm). The higher selectivity has not yield better performance in MEA testing thus far. Work is continuing on developing membrane composites with higher conductivity.

Conclusions and Future Directions

- Met the January Go/No-Go MEA performance target using an Arkema membrane and either a commercial GDE or a lab-made cathode in 1-2M methanol. Work on the cathode co-catalyst was stopped at this point due to low performance.
- Demonstrated a technique to deconvolute performance loss from individual components and sources in DMFC operation.
- Initiated durability testing. MEAs have failed earlier than expected; major performance losses have come from degradation in the electrodes.
- Continued development of membrane composites at IIT. Initiated the work on the second membrane generation at Arkema.
- Future work includes continuing the investigation of the failure modes in DMFC durability testing; understanding the effect of key factors such as membrane chemistry, methanol concentration, and catalyst loading, on durability; and continuing development of the second generation Arkema membrane and membrane composite materials.

FY 2012 Publications/Presentations

1. "Novel Materials for High Efficiency Direct Methanol Fuel Cells," David Mountz, Wensheng He, Tao Zhang, and Chris Roger. Presentation at the 2012 DOE Hydrogen Program and Vehicle Technologies Program Annual Merit Review and Peer Evaluation Meeting, May 16.