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

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Subcontractors:
- IRD Fuel Cells, LLC, Albuquerque, NM
- Illinois Institute of Technology, Chicago, IL

Project Start Date: May 1, 2010
Project End Date: September 30, 2013

Overall Objectives

- Develop a membrane technology having low methanol crossover, high conductivity, and increased durability.
- Develop cathode catalysts that can operate with considerably reduced platinum loading and improved methanol tolerance.
- Combine the cathode catalyst and membrane into a membrane electrode assembly (MEA) having a performance of 150 mW/cm^2 at 0.4 V and a cost of less than $0.80/W for the two components.

Fiscal Year (FY) 2013 Objectives

- Develop a Generation 2 membrane with an areal resistance <0.0375 Ω∗cm^2 and a methanol permeation coefficient ≤1x10^{-7} cm^2/s.
- Demonstrate MEA performance with a developmental membrane of 150 mW/cm^2 @ 0.4 V (60°C, 1M methanol).
- Demonstrate an MEA with an Arkema membrane with ≥5,000 hours of durability testing.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section (Portable Power) of the Fuel Cell Technologies Office 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 (DMFCs). Work on the cathode catalysts was stopped after a Go/No-Go decision in January 2012 and remaining work focused on membrane development and testing these materials in MEAs. Insights gained from these studies will be applied toward the design of an MEA for portable power devices that meet the DOE 2013 targets for a 10-50 W system:

- 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 towards meeting the project technical targets for portable power applications. All targets were based on a methanol concentration of 1M.

Characteristic	Units	Industry Benchmark	Project Target	Status
Methanol Permeability	cm^2/s	3x10^{-6}	1x10^{-7}	5x10^{-7}
Areal Resistance, 70°C	Ω∗cm^2	0.120 (7 mil PFSA)	0.0375	0.03
MEA I-V Cell Performance (0.4 V)	mW/cm^2	90	150	140
MEA Lifetime	Hours	>3,000	5,000	1,500-3,000

I-V – current-voltage; PFSA – perfluorinated sulfonic acid

FY 2013 Accomplishments

- Achieved a 140 mW/cm^2 MEA power density using an optimized Generation 1 membrane and commercially available gas diffusion electrodes (GDEs).
- Optimized a Generation 1 membrane to have a 0.030 Ω*cm^2 areal resistance (AR) and a 5 x 10^{-7}cm^2/s methanol permeation coefficient.
- Continued work on the Generation 2 membranes to decrease their high water solubility.
- Obtained 1,500-3,000 hrs of MEA durability with Generation 1 membranes and commercial GDEs.
- IRD completed initial 600-hour durability evaluations of Arkema's reference MEAs.
- Based on findings from the reference MEA testing, and in conjunction with internal IRD knowledge regarding electrodes, catalyst loading, and gas diffusion layers (GDLs), IRD has fabricated a short stack and initiated testing.

INTRODUCTION

There is a tremendous need for efficient portable power sources. The explosive growth of the lithium-ion battery market is fueled by the ever-growing demand for portable power used in consumer electronics. For the DMFC industry to emerge as an alternative to batteries, difficult technical hurdles have to be overcome. One hurdle is developing inexpensive membranes with reduced methanol cross-over and areal resistance that will contribute to more efficient DMFCs.

APPROACH

Arkema is developing new DMFC membranes with lower fuel 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 initially developed in previous DOE-funded projects. 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 processes, which are being systematically investigated.

In the past year, work has focused on refining the first and second membrane generations. These membranes were durability tested in MEAs with several different commercial GDEs. IRD was brought into the project at the end of 2012 to assist in evaluating the performance of Arkema membranes in MEAs and short stacks.

RESULTS

MEA Performance

MEA development work focused on screening commercial electrodes in 2012. Johnson Matthey ELE170/171 electrodes were used as the standard electrodes in this project. Two new sets of commercial electrodes were evaluated and the details of the electrodes are shown in Table 2.

TABLE 2. Details of commercial Johnson Matthey GDEs evaluated in this project.

Anode/ Cathode Series	Anode Catalyst Loading	Cathode Catalyst Loading	Remarks
ELE 170/171	3 mg Pt/cm² 1.5 mg Ru/cm²	1.5 mg Pt/cm²	Standard electrodes used in most of the testing to date.
ELE 156/157	2.5 mg Pt/cm² 1.25 mg Ru/cm²	1.0 mg Pt/cm²	Lower catalyst loadings. Same catalyst ink formulation as standard.
ELE 196/197	3 mg Pt/cm² 1.5 mg Ru/cm²	1.5 mg Pt/cm²	GDE designed for hydrocarbon membranes.

A performance of 140 mΩ/cm² was demonstrated with a 1.3-mil Arkema membrane and a combination of ELE156/197 electrodes, as shown in Figure 1. For comparison, a performance of 110 mΩ/cm² was typically obtained with

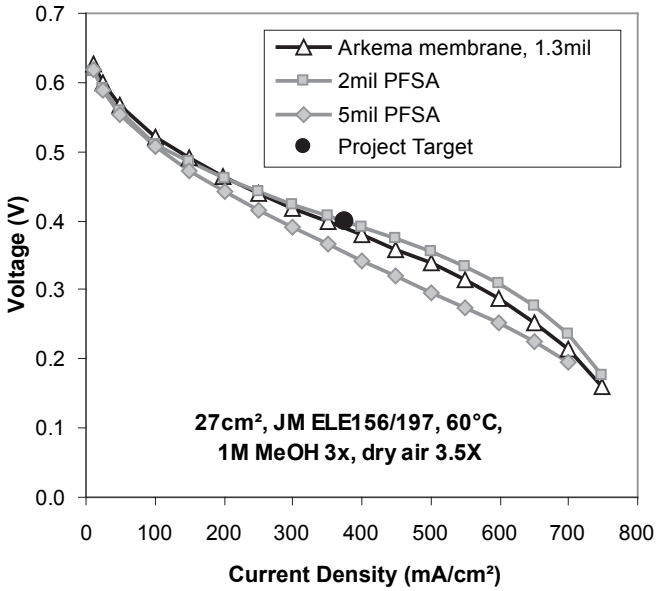

FIGURE 1. Beginning-of-life MEA performance of Arkema and PFSA membranes with the ELE156/197 electrodes.

ELE 170/171 electrodes in 1M methanol testing. The significant performance increase was attributed to improved mass transport in the new electrodes over the ELE170/171 electrodes. The performance using the ELE156/197 electrodes is close to the final project target of 150 mW/cm². We attempted to further increase the MEA performance by adjusting membrane composition and thickness, but no performance increase was observed. At this stage, the MEA performance is dominated by other variables such as the electrodes.

MEA Durability

A summary of the durability testing is shown in Table 3. There is some variation in the data due to several unexplained failures recently. The results suggest that MEAs with the Arkema membrane have less durability than ones with 2-mil PFSA. A comparison of MEA property changes between the two longest-lasting Arkema and PFSA MEAs is shown in Figure 2. The MEA with the Arkema membrane shows a steady increase in MEA resistance over time, while the PFSA membrane-based MEA show little to no increase. The result is consistent with that of Kim, et al., who compared the durability of MEAs based on PFSA and BPSH membranes [1]. They attributed the MEA resistance increase to the deterioration of the membrane/electrode interface.

TABLE 3. Summary of MEA durability test results and status. The failure criterion is a 20% in voltage loss at 0.2 A/cm^2 from the polarization curves. Arkema membranes have a thickness of 1-1.3 mils.

Membrane	# of Samples	Total Hours/comments
2-mil PFSA	1	4,500 hrs
Arkema (28-30 wt% PE)	5	1,000-2,000 hrs.
Arkema (35 wt% PE)	4	One ran 3,000 hrs and another <1,000 hrs. Two repeat tests started recently.
5-mil PFSA	3	1,400-2,600 hrs. Failed earlier than expected.

PE – polyelectrolyte

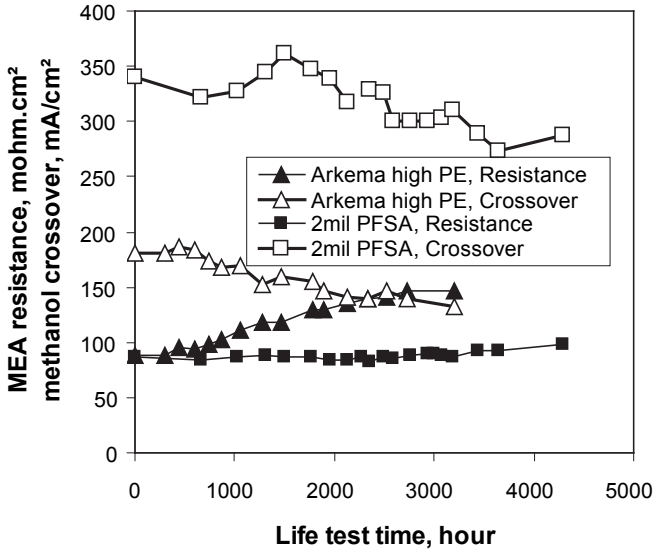

FIGURE 2. Change of MEA properties in durability testing for MEAs with Arkema high-PE and 2-mil PFSA membranes.

The Arkema membrane with a higher polyelectrolyte loading showed increased durability in one test, and more samples are running to validate the result. The higher loading may give more durability by providing a larger buffer for electrolyte degradation and lower MEA resistance.

IRD MEA Evaluation

IRD was contracted to complete a brief MEA development project and perform durability testing on the optimized MEA. Variations in MEA components and constructions were evaluated, inclusive of the Arkema membrane(s). Variations such as the air permeability of the GDLs, catalyst loadings, and modifications to the gasketing in the MEA were evaluated. Representative data for the Arkema membrane testing at IRD is provided in Figure 3, which shows how the changes in air permeability of the GDL can be used to improve the performance of the MEA. More specifically, increased air permeability provided better performance.

The results of the testing above led IRD to describe the Arkema membranes as being more similar to hydrocarbon membranes than to PFSA membranes. They felt this would allow them to select combinations of conditions, materials, and fabrication techniques to obtain improved performance of MEAs including Arkema membranes. From the results obtained, IRD created cells using the Arkema membranes (with IRD's knowledge of best MEA parameter choices) to fabricate short stacks and initiate performance and durability testing. Initial results are promising and the evaluations should be completed by the end of August 2013.

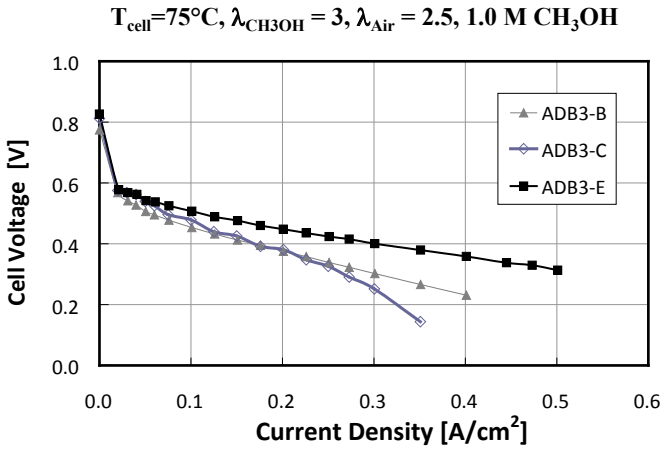

FIGURE 3. Performance of MEAs fabricated at IRD with different GDLs.

Membrane Development

The best performance was obtained with Generation 1 membranes that were modified from the work done last year. Specifically, the PVDF:PE ratio and thickness were optimized to produce lower AR at the expense of slightly raising the methanol permeability. The optimized membrane AR is 0.03 $\Omega*cm^2$ and the methanol permeability coefficient is 5 x 10^{-7} cm^2/s at 1.2 mils. This meets the AR project target, but not the methanol permeability coefficient target. Due to the inherent limitations with this membrane chemistry, both targets cannot be met with one composition. As discussed in an earlier report, the AR has a greater impact than methanol crossover on MEA performance which was factored into the membrane design.

Efforts also continued on the second generation of PE technology that can be used in membranes to form different microstructures than the ones used in the first generation. The microstructure may be a potent factor to increase membrane performance through changes in morphology. Various crosslinking technologies were employed in an attempt to reduce leaching of the water-soluble PE from the membrane after immersion in water. The approaches to crosslinking have not been effective at reducing leaching of the PE, which is leading to high AR values and poor performance.

CONCLUSIONS AND FUTURE DIRECTIONS

140 mW/cm² was demonstrated with an Arkema membrane and a combination of commercial electrodes, which is close to the project target. The best MEA durability results with an Arkema membrane is 3,000 hrs, which is lower than the 5,000 hr project target, but meets the DOE 2013 portable power target. Remaining project work includes completing on-going durability tests and performing post-mortem analysis.

FY 2013 PUBLICATIONS/PRESENTATIONS

1. Hou, J.; Mountz, D.; Hull, M.; Madsen, L. "Correlating Morphology, Proton Conductivity, and Water Transport in Polyelectrolyte-Fluoropolymer Blend Membranes," Accepted to the Journal of Membrane Science in August 2013.

2. "Novel Materials for High Efficiency Direct Methanol Fuel Cells," David Mountz, Wensheng He, Tao Zhang, and Steve Carson. Presentation at the 2012 DOE Hydrogen Program and Vehicle Technologies Program Annual Merit Review and Peer Evaluation Meeting, May 15.

3. He, W.; Mountz, D.; Zhang, T.; Roger, C. "Polyvinylidene Fluoride-Based Membranes for Direct Methanol Fuel Cell Applications," Presented at the Department of Energy Webinar on Fuel Cells for Portable Power, July 17th.

REFERENCES

1. Yu Seung Kim, Melinda Einsla, James E. McGrath, and Bryan S. Pivovar, "The Membrane–Electrode Interface in PEFCs II. Impact on Fuel Cell Durability", *J Electrochem. Soc.*, 2010, **157**, B1602-B1607.