# V.G.2 New MEA Materials for Improved Direct Methanol Fuel Cell (DMFC) Performance, Durability, and Cost

James Fletcher (Primary Contact), Philip Cox University of North Florida (UNF) 1 UNF Drive Jacksonville, FL 32224 Phone: (904) 620-1844 Email: jfletche@UNF.edu

#### DOE Managers

HQ: Donna Ho Phone: (202) 586-8000 Email: Donna.Ho@ee.doe.gov GO: Katie Randolph Phone: (720) 356-1759 Email: Katie.Randolph@go.doe.gov

#### Contract Number: DE-EE0000475

#### Subcontractors:

- University of Florida, Gainesville, FL
- Northeastern University, Boston, MA
- Johnson Matthey Fuel Cells, Swindon, UK

Project Start Date: January 1, 2010 Project End Date: June 30, 2012

# Fiscal Year (FY) 2012 Objectives

The primary objective of this project is to optimize the functionality and internal water recovery features of the UNF passive water recovery membrane electrode assembly (MEA) to facilitate overall system simplicity, thereby increasing power and energy density and lowering the cost at the system level to address DOE's fuel cell target goals for consumer electronics applications.

- Optimize the UNF MEA design:
  - Improve durability and reliability
  - Increase power and energy density
  - Lower cost
- Develop commercial production capabilities:
  - Scale up the process to commercial batch operation level
    - Improve performance and increase reproducibility
    - Lower cost
- Increase catalyst stability and lower loading:
  - Increase the anode catalyst stability
  - Lower MEA cost

### **Technical Barriers**

This project addresses the following technical barriers for consumer based electronic applications of less than 50 Watt from the Fuel Cells section of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) Durability
- (B) Cost
- (C) Performance

# **Technical Targets**

**TABLE 1.** Comparison of the status of the UNF 25-W DMFC power supply based on the passive water recovery MEAs optimized in this project versus the DOE technical targets for portable fuel cell power supplies

Technical Targets: Portable Power Fuel Cell Systems (10-50 Watts)				
Characteristic	Units	UNF 2011 (25 W Net) <sup>1</sup>	2013 Targets	UNF 2013 (25 W Net) <sup>2</sup>
Operational Time	Hours	10.0	-	14.3
Specific Power	W/kg	26.3	30	30.1
Power Density	W/L	28.0	35	30.6
Specific Energy	(W-hr)/kg	263	430	430
Energy Density	(W-hr)/L	280	500	437

<sup>1</sup> System data include weight and volume of hybrid battery and fuel as defined by the DOE.

<sup>2</sup>Calculation assumes reduction in weight and volume based on component and brassboard (unpackaged) test results. Current MEA performance is used.

# FY 2012 Accomplishments

- Optimized the membrane properties to minimize methanol cross-over and improve overall MEA performance.
- Continued optimization and characterization of the properties of the liquid barrier layer integrated into the passive water recovery MEA.
- Integrated the new Johnson Matthey anode, the optimized membrane, and improved cathode into the passive water recovery MEA which resulted in >20% increase in efficiency.
- Minimized the off-state degradation through change in wetting agents used in the cathode electrode.
- Continued optimization of rest/rejuvenation profile to minimize on-state degradation and achieved nearly 10,000 hours of durable MEA operation.

• In collaboration with Johnson Matthey, continued development of commercially viable processes for production of the passive–water recovery MEA technology.

 $\diamond$   $\diamond$   $\diamond$   $\diamond$   $\diamond$ 

#### Introduction

Typical DMFC systems use bulky condensers and other components to recover water at the system level. These system components occupy a large volume and weight within the system design and have a significant impact on the system power and energy density. The UNF passive water recovery MEA (Figure 1) has been designed to incorporate novel passive water recycling features within the MEA to provide water recovery and management. This approach enables a significant simplification and miniaturization of the DMFC at the system level and facilitates substantial progress towards the DOE goals for power and energy density in small portable power systems as shown in Table 1.

# Approach

The approach was to optimize the performance of the UNF passive water recovery MEA and to transition the technology to commercially viable processes, thereby lowering the cost and increasing the durability of the MEA. The MEA performance was improved through better anode catalysts, improved membrane properties, and optimization of the liquid barrier layer in the cathode--specifically the water retention capability. By improving the anode catalyst structure to enhance the stability of the ruthenium, the MEA durability will be significantly enhanced. Optimizing the membrane physical properties, such as thickness, can improve overall efficiency by minimizing methanol crossover. Optimizing the cathode barrier layer parameters will maximize the oxygen content at the cathode catalyst and thus improve the MEA performance.

Scale up of the manufacturing process for the different MEA layers is expected to enhance the performance and reliability as well as reduce the overall cost. Optimizing the manufacturing process will move beyond the prototype operation by developing batch manufacturing processes that will minimize the MEA-to-MEA variability. The methodology also includes evaluation of the MEA both on the test stand as well as integrated into the lightweight, compact DMFC system developed in a related project at UNF.

### Results

The overall efficiency of the UNF passive water recovery MEA was improved by more than 20%, as shown in Figure 2. The efficiency improvement was achieved through improvements in the membrane properties and in the liquid barrier layer characteristics of the cathode. The UNF DM1 membrane was extensively tested to optimize the passive water recovery MEA performance. Increasing the membrane thickness to 45 micron from 20 micron reduced the methanol cross-over by more than 50% with minimal increase in the membrane resistance. Extensive effort was undertaken to

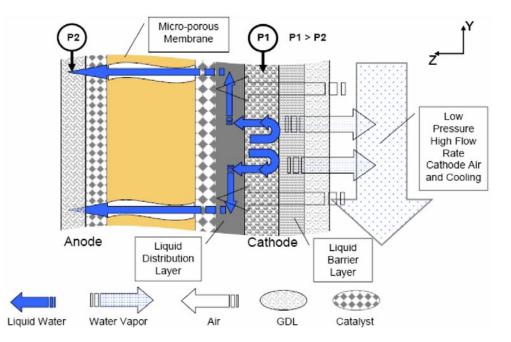


FIGURE 1. Water Transport characteristics optimized to internally recycle water to anode compartment

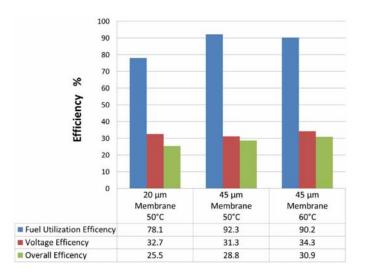
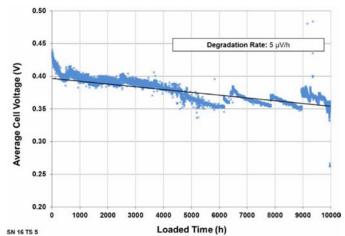


FIGURE 2. Improvement in overall MEA efficiency

evaluate the performance of the liquid barrier layer, while focusing on the trade-off between retaining water within the MEA versus ensuring adequate oxygen access to the cathode catalyst reaction zone. Through careful material selection and thorough investigation of manufacturing processes and physical properties of the barrier layer such as thickness, the MEA operating temperature at which water balance is achieved was increased from approximately 45°C to 55°C.

MEA durability is a critical factor in system durability. In addition to investigating the MEA and its sub-components to improve MEA performance characteristics, extensive optimization was undertaken to remove impurities and improve the durability both in the on-state, as well as the offstate. The current MEA design continued to exhibit excellent durability in continuous operation, with MEAs achieving nearly 10,000 hours of operation (Figure 3). The off-state degradation was significantly improved through changes in wetting agents used during the manufacturing process, which led to a significant reduction of the quantity and influence of organic impurities. Testing has now shown a substantial reduction in the off-state degradation to acceptable levels for system operation and life. Investigation continued into optimizing the rest/rejuvenation cycle, specifically into the air starve step which is particularly challenging in an opencathode MEA. Changes to the voltage during the air-starve has resulted in more thorough reduction in oxides on the cathode catalyst and lowered on-state degradation.

Anode stability is a particular concern for long-term durability due to the loss of ruthenium from the anode. To address this issue, new Johnson Matthey anode electrodes were studied with testing indicating reduced degradation and improved lifetime. In addition, new ultra-stable ternary anode catalyst inks, developed by project partners, which incorporates a third metal in order to both stabilize the ruthenium and enhance the catalyst activity were



**FIGURE 3.** Passive water recovery MEAs show excellent durability under continuous operation (eight-cell stack operating at 120 mA/cm<sup>2</sup>, 50°C, and at 0.8M methanol).

investigated. Project personnel scaled up the production process of these catalysts and MEA testing is underway.

During the past year, the UNF and Johnson Matthey have continued to optimize the formulation and mixing process to enhance the barrier layer reproducibility, as well as improve control of the key barrier layer properties of capillary pressure and permeability. By utilizing dual centrifuge mixing, a commercially applicable, scalable batch mixing processes, the project team has optimized the formulation. We have applied it to a knife coating process to provide a commercially scalable manufacturing process for the liquid barrier layer. Additionally, Johnson Matthey has developed a scalable coating process for the deposition of the cathode catalyst layer ink onto the liquid barrier layer to produce a well adhered, high performing cathode catalyst layer.

# **Conclusions and Future Directions**

Research conducted during the past year has:

- Improved the overall efficiency of the UNF passive water recovery MEA by more than 20% by improving the membrane properties and the performance of the liquid barrier layer within the cathode electrode.
- Increased the MEA operating temperature at which water balance is achieved from approximately 45°C to 55°C, primarily through improved manufacturing techniques.
- Improved the durability of MEA in both the on-state and off-state. Continuous testing showed acceptable performance for nearly 10,000 hours.

Future efforts include:

- Continue to optimize the manufacturing techniques and formulations for the liquid barrier layer to maximize performance and durability.
- Improve the MEA performance by increasing the operating temperature and improving the oxygen access to the cathode catalyst.
  - Optimize the cathode structures for water management and power density.
  - Optimize the anode for durability and performance in the passive water recovery MEA.
- Continue the investigation of the rest/rejuvenation cycle and optimize for the open cathode structure of the passive water recovery MEA.