V.G.3 New MEA Materials for Improved Direct Methanol Fuel Cell (DMFC) Performance, Durability, and Cost

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• Northeastern University, Boston, MA
• Johnson Matthey Fuel Cells, Swindon, UK

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Fiscal Year (FY) 2011 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 lower 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 W 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

A comparison of the UNF DMFC power supply versus the DOE technical targets for portable fuel cell power supplies is shown in Table 1.

FY 2011 Accomplishments

• Optimized open cathode MEA fabrication processes to provide excellent MEA-to-MEA reproducibility in stack testing.
• Developed MEAs with low on-state degradation <50 µV/h under a range of operating conditions and obtained over 4,000 hours of operation for an eight cell short stack.
• Improved the off-state durability of the MEAs by optimizing the cathode electrode and barrier layer formulation and processing conditions.
• Incorporated system operating conditions to improve MEA off-state durability.
• Scaled up barrier layer coating process from hand production to commercially applicable mixing and coating processes.
• Submitted revised Hydrogen Safety Plan.

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Introduction

Typical DMFC systems use bulky condensers and other heat exchangers 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

TABLE 1. Comparison of the status of the UNF 20 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.

Characteristic	Units	UNF 15 W DP3 2008 Status	DOE 2010 Target	UNF Proposed 20W System Design
Specific Power[a]	W / kg	35	100	41.5
Power Density [a]	W / L	48	100	55.6
Energy Density	W-hr / L	250 (1 x 100ml)[b] 396 (1 x 200ml)[b]	1000	193 (1 x 100ml) 321 (1 x 200ml) 575 (3 x 200 ml)
	W-hr/kg	155 (1 x 100ml)[b] 247 (1 x 200ml)[b]	N/A	162 (1 x 100 ml) 307 (1 x 200 ml) 638 (3 x 200 ml)
Lifetime [c]	Operating Hours	1,000 hrs in single cell	5,000	2,500 Integrated System
Cost	$ / Watt	11 (est. in volume)	<3	< 10 (est. in volume)

[a] Beginning of life, 30°C, sea level, 50% R.H., excluding hybrid battery, power module alone
[b] Normalized from DP3 data from 150 ml cartridge to either 100ml or 200ml for comparison purposes
[c] Lifetime measured to 80% of rated power
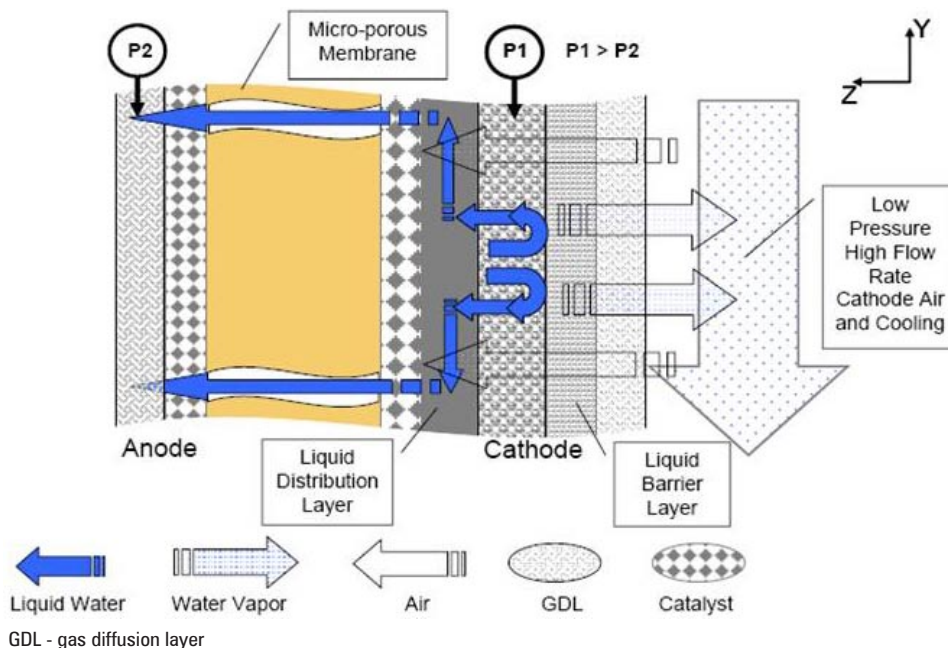
FIGURE 1. Water Transport Characteristics Optimized to Internally Recycle Water to Anode Compartment

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. This progress has been demonstrated in the UNF system design.

Approach

The approach is to optimize the performance of the UNF passive water MEA and transition the technology to commercially viable processes, thereby lowering the cost and increasing the durability of the MEA. The MEA performance will be improved through better anode catalysts

and optimization of the cathode barrier layer 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 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 MEA layers is expected to enhance both performance and reliability as well as reduce the overall cost. Optimizing the manufacturing process will move beyond the prototype operation by developing a batch manufacturing process which will improve the MEA-to-MEA reproducibility, increase the durability, and reduce the cost of the overall MEA. The methodology also includes an evaluation of the MEA produced at both the single cell and the system level against system operating conditions required for a small compact DMFC system developed in a related project at UNF.

Results

The UNF baseline passive water recovery MEA design has been successfully transferred to Johnson Matthey. The baseline process for the liquid barrier layer is based on a tedious multilayer, hand painted process to obtain the key water retention properties of water and oxygen diffusion and retention while recycling the liquid water to the cathode. Research during the past year has optimized the formulation and mixing process to enhance the barrier layer reproducibility, as well as improve control of the key barrier layer properties. Johnson Matthey has incorporated dual centrifuge mixing, a commercially applicable, scalable batch mixing processes, to replace the small scale ultrasonic mixing used in the baseline process. The formulation and processing has been further optimized to provide highly reproducible barrier layers leading to excellent MEA-to-MEA reproducibility in short stack testing.

The baseline ink application process requiring layer-by-layer hand painting has been scaled up to a commercially applicable automated coating process. This approach has now introduced rod coating where an excess of the coating is deposited onto the substrate. The wire-wound metering rod, sometimes known as a Meyer Rod, allows the desired quantity of the coating to remain on the substrate. The amount of material deposited is determined by the diameter of the wire used on the rod and the solids loading and viscosity of the coating solution. Using a large diameter wire on the metering rod and optimization of the coating ink characteristics has reduced the number of coatings required, improved reproducibility and reduced production costs. Single layer coatings (Figure 2) with good surface coverage and uniformity have been produced showing comparable baseline performance in MEA testing compared to the multilayer hand painted liquid barrier layers.

MEA durability is a critical factor in system durability. An extensive investigation and optimization of the MEA, liquid barrier layer and catalyst layer production has been
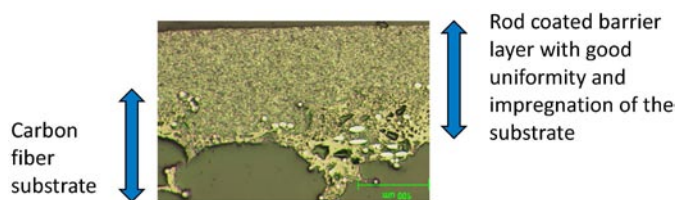

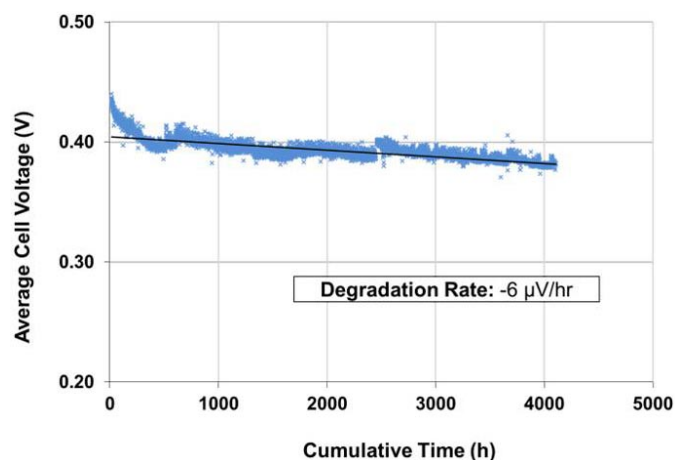**FIGURE 2.** Cross-Section of Single Layer Barrier Layer Coating

FIGURE 3. Passive water recovery MEAs show excellent durability under continuous operation. Eight cell stack operating at 120 mA/cm^2, 50°C, and 0.8 M methanol.

conducted in order to remove impurities and optimize the performance and durability both in the on-state as well as the off-state. The current MEA design exhibits excellent durability in continuous operation tests achieving over 4,000 hours of operation in an ongoing test (Figure 3). However, off-state testing has revealed significant degradation. Ex situ analysis of degraded MEAs indicated the presence of an organic impurity in the cathode catalyst structures. Optimization of MEA fabrication methods and improved operating parameters has 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.

Anode stability is a particular concern for long-term durability due to the loss of ruthenium from the anode. To address this issue, an ultra-stable ternary anode catalyst has been developed by project partners which incorporates a third metal to both stabilize the ruthenium and enhance the catalyst activity. This new catalyst provides improved durability and a reduction of cost at the system operation level. Project personnel are now in the process of scaling up the production of these catalysts for MEA testing. Additionally, the testing of commercially available catalysts has led to an improved anode catalyst showing significantly improved durability in methanol starvation accelerated testing.

Conclusions and Future Directions

Research conducted during the past year has:

- Successfully scaled up the passive water recovery MEA and improved the MEA-to-MEA reproducibility.
- Produced MEAs with excellent durability with projected life of over 5,000 hours of operation life.
- Identified significant steps in lowering the off-state durability by optimizing both the MEA fabrication and the operational parameters such that the overall MEA durability is in acceptable range for long term operation of the fuel cell system.

Future efforts include:

- Optimization of manufacturing techniques and formulations for the liquid barrier layer to maximize performance and durability.

- Improve MEA performance:
  – Optimization of the cathode structures for water management and power density.
  – Optimize the anode for durability and performance in the passive water recovery MEA.
- Optimization of the fuel cell operational parameters of startup, shut down and operation to maximize MEA performance and durability over the system operating life.
- Continued MEA durability testing to evaluate durability under a range of in-specification and out-of specification conditions.