Final Report

Project Title: NEW MEA MATERIALS FOR IMPROVED DMFC PERFORMANCE, DURABILITY AND COST

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Overview

The University of North Florida (UNF), with project partners the University of Florida, Northeastern University, and Johnson Matthey, has recently completed the Department of Energy (DOE) project entitled “*New MEA Materials for Improved DMFC Performance, Durability and Cost*”. The primary objective of the project was to advance portable fuel cell MEA technology towards the commercial targets as laid out in the DOE R&D roadmap by developing a passive water recovery MEA.

Developers at the University of North Florida (UNF) identified water management components as an insurmountable barrier to achieving the required system size and weight necessary to achieve the energy density requirements of small portable power applications. UNF developed an innovative “passive water recovery” MEA for direct methanol fuel cells (DMFC) which provides a path to system simplification and optimization. The passive water recovery MEA incorporates a hydrophobic, porous barrier layer within the cathode electrode, so that capillary pressure forces the water produced at the cathode through holes in the membrane to the anode, as shown in Figure 1. By directly transferring the water from the cathode to the anode, the balance of plant is very much simplified; thus, the need for heavy, bulky water recovery components is eliminated.

Figure 1. Passive water recovery MEA for DMFCs.

Figure 2. UNF DM-1 and Nafion membrane vs. methanol crossover and cell resistance.

At the heart of the passive water recovery MEA is the UNF DM-1 membrane that utilizes a hydrocarbon structure to optimize performance in a DMFC system. The membrane has inherent performance advantages, such as a low methanol crossover (high overall efficiency), while maintaining a high proton conductivity (good electrochemical efficiency) when compared to perfluorinated sulfonic acid membranes such as Nafion. Critically, the membrane provides an extremely low electro-osmotic drag coefficient of ≈ 1 water molecule per proton (versus the 2-3 for Nafion) that minimizes flooding issues at the cathode which often fatally limit open cathode MEA performance. Moreover, because the membrane is a highly stable hydrocarbon based membrane it provides excellent mechanical characteristics and a low level of swelling, which enhances the durability.

By integrating the UNF DM-1 into a passive water recovery MEA, the balance of plant is significantly simplified. Figure 3 shows a schematic of the conventional DMFC system,

including the near impossible to miniaturize water management components such as the condenser heat exchanger. By comparison, Figure 4 shows the schematic of the simplified UNF system. The far fewer components are a result of integrating the UNF passive water recovery MEA, thus resulting in substantial weight and volume reductions.

Figure 3. Typical DMFC System Architecture

Figure 4. UNF Simplified DMFC Architecture

During this successfully completed DOE program the project team met all of the project goals. The team built and tested over 1,500 MEAs with a wide range of different manufacturing chemistries and process conditions. This project demonstrated that the UNF MEA design could be fabricated with a high degree of reproducibility and repeatability. Some specific achievements include:

- **Durability**

The UNF MEA has demonstrated over 11,000 hours continuous operation in a short stack configuration. The root cause of an off-state degradation issue was successfully mitigated by modifying the manufacturing process by changing the wetting agents used in the catalyst printing. The stability of the anode electrode was increased by replacing the anode electrodes with a stabilized PtRu/C catalyst. In addition, there was actually an improvement in overall MEA performance by carefully modifying the manufacturing process for the MEA. The overall degradation rate was significantly reduced through optimization of the MEA operating conditions. The voltage in the rest/recovery step was lowered to recover the cathode performance losses from the effects of short term or reversible degradation.

- **Performance**

The project team optimized the performance of the critical MEA components. By increasing the membrane thickness, the methanol crossover was reduced, thereby increasing the fuel utilization efficiency without sacrificing any electrochemical performance. The reduction in methanol crossover increased the fuel utilization efficiency by 25% from 78% to over 90%. The liquid barrier layer was optimized to provide improved reproducibility, thereby improving stack voltage uniformity and reliability. Additionally the barrier layer water permeability was lowered without sacrificing any power density, thereby enabling increased operating temperature. Improvements in the cathode catalyst selection and coating provided an additional 10% to 20% improvement in the MEA performance at the target operating range.

- Cost

Commercially scalable processes were developed for all of the critical MEA components which lead to improved yields and lower overall manufacturing costs. Furthermore, significant steps have been made in improving the process control which increases MEA uniformity and control of the transport properties to ensure reliable performance. MEAs that were made using these improved process controls showed excellent reproducibility in 40 cell stacks with as low as ± 6 mV voltage variation between the MEAs at the target 120 to 150 mA/cm² operating range. Given that the catalyst is an important driver of the MEA cost, the project team has successfully demonstrated that the catalyst loading can be lowered to 3 mg/cm² Pt and excellent durability still be achieved with over 2000 hours of operation.

UNF and its project partners have met all of the goals and milestones of this project. Additionally, MEA performance has been validated with a 20 W portable DMFC, as shown in Figure 5, which was developed in a separate DOE program. The performance of the DP4 system nearly meets the 2013 DOE goals.

Figure 5. DP4 power supply

Figure 6. DMFC stack from DP4

Table 1. System performance with 45 micron membrane

Technical Targets: Portable Power Fuel Cell Systems (10-50 Watts)					
Characteristic	Units	2011 Status	UNF DP4 2011 (25 W Net) ¹	2013 Targets	UNF 2013 (25 W Net) ²
Operational Time	hours		10		14.3
Specific Power ¹	W/kg	15	26.3	30	30.1
Power Density ¹	W/L	20	28	35	30.6
Specific Energy ¹	(W-hr)/kg	150	263	430	430
Energy Density ¹	(W-hr)/L	200	280	500	437

¹ Calculation includes weight and volume of hybrid battery and fuel as defined by the DOE.

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

Objectives

The project objective was to further develop direct methanol fuel cell (DMFC) MEAs to enable the advancement of portable fuel cell system technology towards the commercial targets as laid out by the DOE. The objective of this project, in conjunction with our partners the Johnson Matthey, Northeastern University and the University of Florida, is to examine and implement performance, durability and cost improvements in the UNF MEA design. The expected outcome of the project is a high performing, durable, low cost MEA that integrates into an advanced DMFC power supply for mobile computing with passive water recovery controlled within the MEA, thereby providing a significant system simplification.

Tasks

Task 1: Membrane Optimization

The membrane is the critical component at the heart of the UNF passive water recovery MEA. The UNF MEA is based on hydrocarbon membrane technologies acquired from former UNF partner PolyFuel. The hydrocarbon membrane chemistry provides a high level of flexibility in chemistry that can be applied to optimize the membrane physical and chemical properties. Furthermore, these membrane chemistries have been scaled up to reproducible roll-to-roll processes. Hydrocarbon membranes offer several benefits to DMFC technologies, including excellent mechanical and chemical stability, good ionic conductivity through the attached sulfonic acid groups, low methanol crossover, and low electroosmotic drag coefficients.

All of these factors are important to enhancing the performance of conventional DMFC systems, maximizing the efficiency, and minimizing flooding on the cathode by achieving low methanol and water crossover. For the UNF passive water recovery MEA architecture, in which water is recovered within the MEA, all of these membrane characteristics are important, however it is necessary to introduce additional areas of high water transport to allow the efficient return of the water produced on the cathode to the anode. The project team previously demonstrated that when combined with an efficient liquid barrier layer (Task 2), the post processing of the low methanol crossover hydrocarbon membrane by drilling a series of small holes using a UV laser provided efficient water recovery characteristics within the UNF MEA structure. These holes provide regions of high water transport by lowering the hydrostatic pressure required to drive water from the cathode layer to the anode layer, while maintaining the overall critical low methanol and water crossover characteristics of the underlying membrane structure. In this work, key membrane characteristics and post processing conditions required to both scale up the MEA production and optimize the MEA performance characteristics were investigated. The project team optimized the membrane and these post processing conditions to maximize the MEA performance characteristics. These results were examined both in short stacks and by confirming the performance characteristics in the DP4 system.

Optimization of the Membrane Post Processing

Membrane post processing was examined using full sheet MEA material (12 cm by 22 cm) using UNF's batch processing laser (Figure 7), which is capable of varying the laser pattern, intensity, and pulse duration.

Figure 7. UNF post processing equipment for full sheet MEA membrane pieces

Post Processing Conditions and Parameters

Baseline techniques were previously developed for the post processing conditions to control drilling of the holes and the hole spacing.

Control of the hole size

Initial testing focused on optimizing the processing conditions and controlling the hole size, which affects the water flux and hydrostatic pressure requirements of the liquid barrier layer. This knowledge defines the manufacturing tolerances for the key capillary pressure requirement of the liquid barrier layer, discussed in more detail in Task 2. The target diameter for the holes based on initial modeling is 5 to 7 μm . To obtain holes of this dimension, it is necessary to drill the holes by using multiple pulses, thus the hole's size on the membrane side, where the laser is applied, is larger than on the distal side and the holes tend to be conical, in particular for the thicker membranes. The key manufacturing parameters, such as laser power or intensity, pulse duration, and number of pulses applied to drill an individual hole were investigated and optimized for a range of membrane thicknesses as part of this effort. The characteristics of the hole were investigated using scanning white light interferometer (SWLI). Figure 8 shows the images for both the laser application (side A) and the opposite or laser exit side (side B). It can be seen the holes are clearly conical with a significantly wider diameter on the laser entry side tapering down to the target 5-7 μm on the laser exit side. It was determined that the multiple pulse approach to drilling the hole resulted in no physical or chemical damages to the membrane area surrounding the drilled hole.

Figure 8. SWLI profiles of membrane holes. A) Top view of laser drilled hole which has an average diameter of 32 μm . B) Bottom view of hole, average diameter of 5 μm .

Membrane/ MEA Adhesion Optimization

During normal stack operation, particularly with the open cathode stack configuration used in the UNF system, the MEA will repeatedly go through wet-dry cycling which leads to expansion and contraction of the hydroscopic membrane--which can put significant stress on the catalyst to membrane interface. The quality of this ionic interface is very important for MEA performance and was considered a possible degradation mode for the MEA; therefore, membrane or MEA adhesion is a critical factor for the MEA.

The UNF passive water recovery MEAs are manufactured using a hot bond lamination of commercial DMFC anodes and UNF proprietary cathode electrodes onto the post processed hydrocarbon membrane. Since the UNF membrane is a hydrocarbon membrane with a high glass transition temperature, it cannot be laminated directly with sufficient bond strength, via a conventional hot press bonding process and provide sufficient durability for long term operation. Also, since the anode and cathode structures contain a Nafion fluorocarbon ionomer, there is a polymer incompatibility at the membrane to catalyst interface, which can lead to stresses and bonding issues. Therefore, to provide good physical and ionic interaction, the UNF membrane is treated with a hot bond layer on both sides of the membrane prior to the post processing step described above. MEA adhesion for freshly prepared and cycled MEAs are measured using a calibrated peel test, developed by UNF (see Figure 9). In this test the MEA is equilibrated at 50% relative humidity prior to the pull test so as to test the adhesion of the MEA in the wetted state, which typically exhibits the weakest bond strength situation in the MEA. In addition to the force at which the MEA separates, the amount of catalyst that has transferred to the membrane surface is estimated as a measure to the adhesion at the critical catalyst to membrane interface.

Figure 9. UNF Instron calibrated pull test. A. Instron Set up with prepared sample for Pull test. B. Sample prepared with Tape adhered to back side of the GDLs. C. Samples after pull test showing catalyst adhesion to the membrane surface.

Based on previous experience and the testing of MEAs discussed below, a peel strength of 1N force is considered adequate for adhesion for the MEA in operation. The typical adhesion of fresh, as prepared, passive water recovery MEAs is 2 to 5N. Additionally, the MEAs exhibit good transfer of the catalyst to the membrane surface with the MEA failure point during the peel test at the catalyst to GDL interface. Testing showed that the UNF optimized hot bond coating on the membrane provides an excellent electrochemical interface.

Since wet-dry cycling and MEA delamination was considered a potential degradation mechanism at the start of this development effort, the level of adhesion for the MEAs after wet-dry operational cycles in a fuel cell stack were examined. Testing the MEAs after cycling shows an adhesion level of 2N or better; it also shows good transfer of the catalyst to the membrane surface. In addition to the peel test on cycled MEAs, MEAs have been examined on more localized microscopic levels using scanning electron microscopy (SEM); insignificant delamination was observed. Additionally, high frequency resistance measurements at 8 to 10kHz show no change in the MEA resistance, thereby confirming that delamination is unlikely to be a significant degradation mechanism and that the UNF applied hot bond layer provides a durable ionic and physical adhesion for MEAs.

Alternative Membrane Pretreatment

Alternative treatments of the membrane have been investigated to determine the effect on performance as well as a method of obtaining improved adhesion. Figure 10 shows the effect on the durability and performance of a wet pressed membrane. The water present in the membrane during the pressing process acts as a plasticizer and improves the resulting electrochemical interface. However, since the membrane is pressed in a swollen state it tends to have a more open morphology, which leads to increased levels of methanol crossover and ionic conductivity, both of which, at the system level, lead to lower fuel utilization efficiency and lower energy densities. In Figure 10 it can be seen that there is no significant difference in the durability, i.e., both the wet and the dry pressed membrane yielding essentially no degradation. However, the wet pressed sample provided improved voltage characteristics, which need to be traded off against the increased methanol crossover. Additionally, wet pressing leads to significant difficulties in handling and obtaining manufacturing reproducibility due to the difficulties in controlling and maintaining a constant level of membrane hydration (or swelling) during the manufacturing process, especially at the point of hot pressing. Moreover, the methanol crossover increases and the values are significantly more variable, which moves the MEA away from the target of low methanol crossover, as discussed in the next section. Since this process did not provide a solution to the degradation issues discussed later in this report (Task 5) it was not investigated further.

Figure 10. The effect of wet pressed membrane on MEA performance and durability with standard cathode electrodes.

Membrane Selection and Thickness

The initial work on the passive water recovery MEA was performed using a 20 μm UNF DM-1 hydrocarbon membrane. While this membrane has a low methanol crossover, the crossover was still too high for optimum fuel cell efficiency, especially at higher operating temperatures. As discussed in more detail in Task 2, increased crossover leads to several potential performance consequences. In the passive water recovery MEA design, water loss is limited by the design of the barrier layer. However, limiting water loss has the consequence of also limiting the oxygen access which leads to a reduction in performance due to the competition on the cathode for the

limited oxygen between the crossover methanol (which also lowers the voltage) and the oxygen reduction reaction. Second, the methanol crossover leads to a lower stack and system efficiency due the methanol combusted on the cathode side, which, due to increased local temperature, also leads to increase water loss. The methanol crossover with the 20 μm membrane produces a fuel utilization efficiency of 78% at the 50°C and 120 mA/cm² stack operating point.

To lower the methanol crossover the project team investigated alternative membranes. In previous efforts, it was determined that thicker membranes lead to increased MEA resistance and delamination. However, during this project, it was shown that by improving the hot bond layers and MEA manufacturing, durable MEAs could be manufactured with the 45 μm membrane.

Figure 11 shows the improvement in crossover obtained from increasing the membrane thickness from 20 μm to 45 μm for the passive water recovery MEA under nominal operating conditions. The tradeoff associated with a thicker membrane is an increase in the membrane resistance, which typically leads to a lower level of electrochemical performance. However, as shown in Figure 12, through improvements in the MEA manufacturing process, the project team has been able to obtain electrochemical performance for the 45 μm membrane comparable to that of the 20 μm membrane, thereby gaining a significantly lower crossover without any significant voltage loss. Figure 13 shows the improvement in the overall stack performance from 78% fuel utilization efficiency for the baseline 20 μm membranes to over 90% fuel utilization efficiency for the optimized 45 μm MEA under nominal operating conditions. In addition to short cell stack testing, this improvement in efficiency has been further validated at the system level using the UNF DP-4 developed on a parallel DOE program, as shown in Table 1. Also, independent laboratory testing of the DP-4 over a 72 hour run-time test using a stack with the 45 μm membrane has shown an increase in the system energy density of 27%, i.e., from 632 wh/kg to 805 wh/kg.

Figure 11 Comparison of the methanol crossover measured at 120 mA/cm² nominal operating point for a 0.8 M methanol dilute fuel concentration

Figure 12 Comparison of the performance of UNF passive water MEAs using 20 micron and 45 micron membrane in 8 cell stacks. Cell temperature 50C and 0.8 M methanol concentration.

Figure 13. Measured Stack Efficiency for 20 µm and 45 µm membrane based passive water recovery MEA under typical operating conditions using 8 cell short stacks.

Task 2: Barrier Layer Process Development

The UNF MEA shown in Figure 1 includes the post processed membrane engineered to provide a high level of water transport through the laser-generated holes while also providing a low crossover through the bulk of the membrane structure. The second key part of the UNF MEA design is the incorporation of a liquid barrier layer/diffusion layer which forms part of the cathode GDL (gas diffusion layer) structure. This layer has been developed to have two key characteristics: First, the liquid barrier layer must have a capillary pressure sufficiently high to prevent water ingress into the layer and to allow sufficient hydrostatic pressure to develop in the

cathode layer, which drives water through the small holes engineered into the membrane. Second, the barrier layer must have a low water vapor permeability, which is required to minimize the water loss. During this program, UNF, with its project partners Johnson Matthey and University of Florida, has optimized the barrier layer performance characteristics, increased the reproducibility of the barrier layer and thus the MEA production, as well as developing commercially scalable productions processes for the barrier layer and the resulting MEA.

Ink Formulation and Mixing

Ink formulation and mixing were determined to be critical parameters in obtaining reproducible layers. The coating contains graphite powder and Teflon, together with a surfactant, to maintain adequate dispersion. It was determined that by controlling the ratio of these components, together with the level of dispersion, the barrier layer properties could be controlled and adjusted as required. Several key factors were determined including the level of surfactant to carbon in the initial dispersion, which was particularly important as the carbon materials or batch was adjusted.

Barrier Ink production scale up

Lab scale production of the barrier layer uses ultrasonic mixing to obtain a good dispersion. This process is difficult to scale to commercial levels. For large scale production, inks were produced in a dual asymmetric centrifuge mixer which allows a high throughput and provides the additional benefit of minimizing the opportunity for contamination and minimizing the chances of sonicator damage to glassware by using single-batch containers.

The initial batches of ink produced using the dual centrifuge mixer contained a large number of bubbles due to incorporated air. The barrier layer inks were improved by using a more aggressive vacuum degassing prior to coating; reducing the pressure to 200mbar absolute was found to remove the bubbles adequately. Figure 14 shows the improvement in layer quality resulting from the improved bubble removal.

Figure 14: Left, initial ink production show evidence of incorporated air in the form of bubbles on the coating surface. Right, a later ink batch after more aggressive vacuum treatment.

Coating Process Development and Coating Uniformity

The baseline prototype process uses a multilayer hand painting process; typically eight layers are used to obtain the target loading to deposit barrier layer ink onto the GDL substrate. To investigate the barrier layer coating process and obtain improved coating reproducibility and coating uniformity, sintering conditions and coating technique were investigated.

Non-contact thickness measurements

Both the thicknesses and the thickness uniformity are important parameters in the performance of the final barrier layers in the MEA. To understand the coating variability as well as optimize the coating parameters the project team developed a non-contact capacitive thickness measurement technique capable of mapping the full sized barrier sheets (12 cm by 22 cm) as shown in Figure 15. The vacuum stage was optimized to provide maximum suction without introducing localized distortion to the sample.

Figure 15. Non-contact capacitive probe and automated stage for thickness profiling of full sized barrier sheets (12 cm by 22 cm)

An example thickness profile from typical barrier (#2214) is shown in Figure 16. Six sample barrier layers of nominally the same composition were measured. The mean thickness was determined to be 277.9 μm with a standard deviation of 12.1 μm .

Figure 16. Thickness profile from a typical barrier layer showing the even distribution of the sample thickness and no clear high or low spots. The scale indicates the units in μm .

To verify the validity of the capacitance probe setup, a sample of the barrier was measured using scanning white light interferometry (SWLI). This device provided topography data that compared favorably to the capacitance probe results. A 7.5 mm by 10 mm sample of barrier #2214 was measured (see Figure 17) and is comparable to the capacitance probe data -- see Table 2. The resolution of the surface topographical data compared well with the capacitance probe developed for measuring the full barrier sheets.

Figure 17. SWLI surface map. The peak-to-valley difference is 97.14 μm .

Table 2. Comparison of measurement results for barrier 2214.

Measurement	Peak-to-valley (μm)	Percent difference (%)
SWLI	97.14	
Capacitance probe	91.25	6.06

The 6.06% difference in measurements is most likely related to the sensing diameter (3.2 mm) of the capacitance probe as the capacitance probe averages over the entire area the thickness of the sample beneath it. SWLI uses a microscope objective to focus the light over a much smaller area, thereby obtaining a higher level of resolution. SWLI is not an applicable technique for the full sheet samples because data can only gathered over a restricted area and does not provide information on the sample thickness. The standard deviation for the samples was found to be 12 to 14 μm , which is acceptable because the value is comparable to the carbon fiber paper used as a substrate for the coatings.

Optimization of the Liquid Barrier Layer

The main advancements in initial MEAs were improved barrier layer and MEA reproducibility and control, which were the result of the improved manufacturing process and process control, as outlined above for the barrier layer and for the MEA discussed in Task 4. These MEAs utilized a 20 μm hydrocarbon membrane that had been modified by drilling holes to provide areas of high water transport. The project team developed a method for quantifying both the water vapor transport or permeability ($K_{\text{H}_2\text{O}}$) and the capillary pressure of the liquid barrier layer. The key

parameter for the system design for water balance is the K_{H_2O} (mm/s) value, which is a lumped constant for the diffusion coefficient of water vapor in air and the barrier layer process parameters, as shown below

$$K_{H_2O} = \frac{[Diffusion\ Coefficient_{H_2O\ in\ Air}] * [Barrier\ Layer\ Porosity] * [Tortuosity]}{[Thickness\ of\ Liquid\ Barrier\ Layer]}$$

The K value for the liquid barrier layer (LBL) is a measure of the ability of the MEA to retain water vapor; the lower the K_{H_2O} value of the MEA, the more water vapor that is retained within the MEA. Figure 18 shows the performance of the baseline MEA in a short stack (8 cell test stack). With the improved manufacturing processes, the standard deviation of the cell voltages was very low (± 6 mV), similar cell to cell variation was achieved in a 40 cell stack integrated into a packaged system.

Figure 18. MEA performance with 0.8 M methanol, 50°C Stack temperature, anode flow rate 1.4 cm³/cell/min. Cathode flow rate controlled to maintain a stack temperature of 50°C (> 20times stoichiometric levels).

The baseline LBL values of the MEAs used at the start of this program had an ex-situ measured K_{H_2O} value of 1.65 mm/s. At the system level, this value required adding water to the fuel to maintain water balance, thereby significantly affecting the system energy density. The manufacturing process of the barrier layer was optimized in order to reduce the K values further. The trade off with reducing the K value for water loss is that the oxygen access to the MEA is also reduced, which in previous studies has shown decreased MEA performance. Through an improved manufacturing process, UNF has achieved lower K-values. The lower K value leads to less water loss and with a higher operating temperature and voltage thus better efficiency, as highlighted in Figure 13. Figure 19 shows there is no loss in electrochemical performance as the K_{H_2O} value is reduced to 1.27 mm/s. These lower K values not only reduce water loss but allow the removal of water from the fuel and thus increase the system energy density. However, if the K value is reduced too far, the performance is reduced due to the mass transport limitation of oxygen reaching the catalyst layer. The stack performance is reduced, as can be seen in the figure when the K_{H_2O} value is reduced to 1.0 mm/s. The performance of these MEAs were

verified in a 40 cell stack within a system which resulted in a significant increase in the system level energy density by removing the water that was typically mixed with the fuel.

Figure 19. Optimization of the liquid barrier layer properties to maximize MEA water retention and MEA performance trade off.

In addition to the ex-situ measurement of the barrier layer K value, the project team performed extensive measurements of the effects of operating conditions on the water loss. Figure 20 shows the net water production for an 8 cell stack under a range of temperatures and operating conditions. In this plot, the stack operates in water balance (no net loss or gain of water in the recirculation system) under a range of conditions. Clearly, higher current density operation is advantageous for water production.

Figure 20. Water loss at various operating conditions for a typical MEA.

Commercially Scalable Process for Barrier Layer Manufacture

To deliver a barrier layer target loading, six to eight brush coats are required. Given that this method is not suited to large scale manufacturing, two scalable commercial coating processes to produce the barrier layer were investigated.

Bar coating

A method more suited to larger scale production uses a wire-wound bar coater. The ability to deposit from a range of wire wound bars, both close-wound and spiral wound (with gaps between wires), means a range of loadings can be deposited.

Initial concerns that bar coating might force ink through the substrate rather than depositing the ink on the surface were assessed by examining cross sections under an optical microscope. Sections of the GDL and barrier layer sheets were mounted in resin, polished and photographed under the microscope. Figure 21 shows a single coated barrier layer; Figure 22 shows a similar section where the bar has removed a section of a lower layer, with a clear gap in the layer. A two-coat layer may be possible if the second layer is coherent across the whole surface and fills any gaps in the layer below. Figure 23 shows a twin-coated layer with a boundary between layers. Despite successes in depositing a hydrophobic barrier layer, attempts to use wire wound bars with a large diameter wire did not deliver the required ex-situ properties with few coats -- see Figure 24. Early attempts at bar coating led to poor surface quality with clear lines for the bar coater in the barrier layer surface. Modifications in the coating technique led to improvements in uniformity and visual appearance -- see Figure 24. Even the optimized smoother layers typically had insufficient capillary pressure, most likely due to residual small ridges and surface defects. This process did not produce commercially scalable process to meet the target performance specifications.

Figure 21: Single coat of graphite/PTFE barrier layer ink on SGL24BA. The substrate is towards the top of the images – the bright patches are the carbon fibers in cross section. The barrier layer is the flecked layer throughout the middle of the image – the dark region below is the paper support holding the cross-section in place while the resin sets.

Figure 22: Evidence of the removal of a section of barrier layer following a second pass of the wire-wound bar without ink.

Figure 23: Twin-coated layers on the surface of a SGL 24BA substrate, total loading 24 mg cm^{-2} graphite/PTFE

Figure 24. Improvements in the bar coating

Blade-guided barrier layer deposition

A guided or Doctor Blade method was evaluated, in order to replicate the deposition step in a roll-to-roll slot coating method. Figure 25 below illustrates the process.

Figure 25. View of guided blade showing micrometer gauge controls to raise or lower the blade height. Supporting structure needs to maintain contact on unprinted substrate margin, leading to difficulties controlling loading. An area sampling procedure to assess the loading had to be developed.

Using the bladed guided deposition technique the target graphite/PTFE loading was achieved with a single layer; however, the layer was uneven due to ink pooling on the substrate. Workable loadings could be deposited using two coats; this approach produced usable barrier layers via a commercially scalable process. Figure 26 displays the performance of MEAs prepared using the commercially scalable guided blade process. The MEAs have comparable properties to the hand painted samples. There is a small increase in the performance over the time, which could be attributed to the removal of impurities from the catalyst printing process; this observation is discussed in more detail in the discussion of the cathode catalyst coating process in Task 4.

Figure 26. Blade coated barrier layer MEA performance is comparable to optimized lab batch scale

Task 3: Catalyst Development

UNF's passive water recovery MEA employs commercial anode electrodes and an internally-designed cathode electrode using commercial cathode catalysts. Catalyst deactivation, whether by poisoning, surface area loss, flooding, etc., is a major area of concern in all fuel cell electrodes. For the DMFC application, the PtRu anode catalyst stability is a major concern and is the major focus of this task. The objective was to develop and select the best anode catalyst for maximizing the performance and stability of the DMFC system.

Commercial Catalyst Screening

Anode catalyst and, when available, fabricated anode electrodes were tested from three manufactures (Johnson Matthey (JM), Tanaka, and Cabot). Testing was conducted on both assembled MEAs and in half cells.

Anode Half Cell Reaction Comparison

Anode catalysts from Cabot and Tanaka were compared in half cell measurements at temperatures and methanol concentrations similar to those employed in the system. To eliminate possible effects of production methods upon performance, the Tanaka and Cabot catalysts were examined ex-situ to an MEA with cyclic voltammetry in a half cell. For comparison, a JM anode catalyst, JM Hi-spec 10100, was also analyzed. In the half-cell rig, catalyst was deposited onto a 5mm glassy carbon disk with 20% Nafion as a binder. The catalyst was then placed in a 0.8 M methanol solution with 0.5 M H₂SO₄ as an electrolyte. The half-cell was jacketed allowing the temperature of the solution to be adjusted in a range of 40 to 60 °C as shown in Figure 27.

Figure 27. Half Cell Experimental Set Up

Figure 28. Linear sweep voltammogram (20 mV/s) of commercial anodes. 20 μ g Catalyst in 0.5 M H_2SO_4 , 0.8 M Methanol, conditioned at 60 $^\circ\text{C}$. Nominal Metal Loadings: JM 60%, Cabot 60%, Tanaka 54.2%

Figure 28 shows a linear sweep voltammogram of the three commercial catalysts at 50 $^\circ\text{C}$ after conditioning by cyclic voltammetry at 60 $^\circ\text{C}$. The Cabot catalyst gave the lowest activity for all temperatures (40, 50 and 60 $^\circ\text{C}$). The Tanaka catalyst had good performance at 60 $^\circ\text{C}$, outperforming the JM catalyst when conditioned at higher temperatures; but the JM Hi Spec had the best activity at 50 $^\circ\text{C}$ and below. Additionally, the JM anode gave the most reproducible results, was the least sensitive to break-in conditions, and generally deactivated less over the course of experiments compared with the other commercial catalysts. The JM catalyst gave the best overall reproducibility and performance in the initial screening.

Accelerated aging comparison

Accelerated aging was performed to compare MEAs with alternate commercial anodes for use in the MEA. Single cells were cycled for 96 h at low voltage (0.05 V) with a low concentration of methanol (0.3 M) in the fuel feed. The alternates were compared to previous generation MEAs that contained the Johnson Matthey anode (ELE 147). An anode polarization measurement was performed on each MEA before, during, and after accelerated aging (Figure 29). In this test the ELE-147 had the best beginning of life performance of all the MEAs, including the JM ELE 170 anode. However, subsequent optimization of MEA fabrication led to increased performance from the ELE-170. Furthermore, the ELE 170 anode gave the best stability to ruthenium leaching of all the anodes tested. ELE-170 was chosen as the anode for the new generation MEA because it gives the best combination of activity and deactivation resistance.

Figure 29. Accelerated aging: anode polarization

Using anode polarization, the project team calculated active surface area relative to a freshly broken-in ELE 147 anode used in the first generation MEAs. The results are shown in Table 3.

Table 3. Fraction of active surface area of anodes at 120 mA/cm² relative to ELE 147 after break-in at 50 °C in 0.8 M methanol solution after low-voltage cycling

	Break In	48 Hr	96 Hr
ELE 147	1	0.72	0.70
ELE 170	0.87	0.72	0.70
Cabot	0.73	0.62	0.57
Tanaka	0.72	0.65	0.54

In initial testing, none of the anodes produced activities superior to the ELE-147 at break-in. However, the ELE-170 has comparable activity after 48 hrs of low-voltage degradation, indicating that it is more stable than the ELE-147. Subsequent optimization of MEA fabrication for ELE 170 showed comparable performance with the ELE 147. The Cabot and Tanaka catalysts were inferior to the two Johnson-Matthey anodes in terms of active surface area in this initial screening. To further confirm the stability, the two Johnson Matthey anodes were compared using a chemical leaching test to determine the relative Ruthenium stability. Figure 30 shows the ELE170 loses approximately half the amount of Ruthenium compared to previous generation ELE 147 anodes. The Johnson Matthey ELE 170 anode electrode was chosen as the most promising commercially available anode catalyst and was selected to replace the baseline ELE 147 anodes.

Figure 30. Ru dissolution after ex-situ acid leaching of catalyst in 2M methanol and 0.5M sulphuric acid at 60 °C for 2 hours.

Northeastern Ultrastable Ternary Anode Catalyst

While the ELE 170 is the most promising commercially available catalyst, it is still desirable to increase the anode stability and to improve the performance of the anode. One goal of this project was to synthesize ternary catalysts for increased ruthenium durability. Dissolution of both Pt and Ru has been shown to cause detrimental effects, such as severe decay of the anodic activity and increase of the ohmic resistance. Also, studies have shown that Ru may migrate through the membrane and to cathode of the DMFC (Ru crossover), which can severely affect the oxygen reduction reaction kinetics with the presence of even micro molar concentrations of Ru. This PtAu@Ru/C catalyst is found to be remarkably resistant to Ru dissolution and, therefore, quite stable during long term chronoamperometric measurements. The enhanced stability is attributed to both a size-effect and the composition; more specifically, the stability is due to the alloying with Au which stabilizes the surface composition of the nanoparticles. This study also leads to the idea that using lead (Pb) in a controlled amount in PtRu@Pb ternary catalysts for DMFC application is indeed a useful one.

Synthesis of Platinum-Gold@ Ruthenium (PtAu@Ru) Core-shell Nanoparticles

Microemulsion Technique: All the syntheses were carried out under an argon atmosphere using a Schlenk line technique. This reverse micelle method is a sequential procedure of two major steps. In the first major step, the core of PtAu alloys had been prepared by the reverse micelle method and in the second major step, the reverse micelle of Ruthenium chloride was reduced by another reverse micelle of sodium borohydride. Reduced metallic ruthenium was decorated as a shell on the core of PtAu alloys. The final heat treatment was done in hydrogen/Argon (5% H₂) gas at a ramp rate of 5° C min⁻¹ to the desired temperature (220°C) and soaked at the specified temperature for 6 hours.

Ultrastable Ternary Anode Catalyst Scale Up

The major limitation of the initial micro-emulsion catalyst synthesis technique developed by NEU under this program is the small batch size. As part of this program, NEU developed a new sequential multi-step process to increase the catalyst production capability. In the first step platinum-gold nanoalloys are prepared and, in the second step, these PtAu nanoalloys are used as the nucleation sites for third metal, ruthenium, to form a shell surrounding the PtAu alloys – see Figure 31. This change in the syntheses process improves the NEU production capability from less than 1g/week to around 10g/week. The process can be further increased to 1 kg scale, with the major limitation on current capabilities being the furnace size. Additionally, this process is applicable to all the ternary core shell catalyst, which shows improved properties for methanol oxidation and potentially ethanol oxidation developed under this program.

Figure 31. Synthesis route and process steps for the micro-emulsion method of catalyst preparation and the new scalable production method for core shell catalyst structures.

Development of Lead-based Ternary Catalysts

Synthesis method of Ternary PtPb@Ru Catalysts: The synthesis of PtRu@Pb is very similar to the synthesis of PtRu@Au, except instead of using gold, lead nitrate was used. The synthesis of PtPb@Au core shell nanoparticles is very similar to PtAu@Pb, but the difference is in the order of the addition of metal salts.

Synthesis of PtPb@Au alloys: The first step of synthesis involves the addition of an aqueous mixture solution lead acetate and chloroplatinic acid in the surfactant solution of AOT and the subsequent reduction of them by sodium borohydride solution. The visible color change in the metal solution indicates the formation of nanoparticles. The second step involves the slow addition and reduction of chloroauric acid on the pre-synthesized PtPb alloys. Thus, this ternary metal catalyst has inner PtPb core with the outer shell of gold.

Synthesis of PtAu@Pb alloys: The synthesis protocol of PtAu@Pb is quite similar to PtPb@Au, except the sequences of addition of metal salts are different. In case of PtAu@Pb, the initial step involves the synthesis of PtAu alloys; the second step involves the reduction of lead salt on the pre-synthesized gold-platinum alloys. The complete reduction of lead results in the formation of gold-platinum core and outer layer shell of lead metal. In both the cases of PtPb@Au and PtAu@Pb, after synthesis the nanoparticles are dispersed in the carbon support. The product is dried under vacuum for 8 hours at 70°C. The heat treatment of the samples has been done at 220°C under the mixture of H₂/Argon for 6 hours.

The XRD of both of the catalysts confirms the presence of different type of lead oxide formation, though the major peaks are from the intermetallic alloys of platinum and lead. The absence of peaks of metallic platinum and lead confirms the formation of core PtPb alloys.

Electrochemical Activity: Electrochemical activity of the carbon-supported catalysts was studied by using cyclic voltammetry in a rotating disk electrode setup. The electrode was activated by cycling it for several times until stable cyclic voltammogram was obtained. The methanol oxidation was performed in a mixture of 1 M methanol and 0.1 M HClO₄. The current density obtained by the PtRu@Au catalysts was found to be four times higher than the commercial PtRu ETEK catalysts; onset potential for the PtRu@Au catalysts is also slightly lower than the commercial PtRu. While the current density for JM PtRu catalysts is highest in terms of stability and durability, PtRu@Au is much better in performance. Table 4 shows the comparison of electrochemical performance of all the catalysts.

Table 4. Shows the comparison of electrochemical performance of all the catalysts synthesized in the project

Catalysts	Peak potential for methanol oxidation (V)	Current density $A\text{ gm}^{-1}\text{cm}^{-2}$	On set potential for CO oxidation (V)
PtRu Johnson Matthey	0.730	110	0.43
PtRu@Au microemulsion	0.750	60	0.42
PtRu@Au large scale	0.730	80	0.40
PtRu@Pb	0.75	200	0.32
PtPb@Au	0.89	340	0.66
PtAu@Pb	0.96	278	0.68

The steady state current measurements were completed in 1M methanol and 0.1 M HClO_4 to understand the kinetic pathways of the catalysts activity. The total amount of catalysts loading was constant at $15\mu\text{gm per cm}^2$. The onset potential for methanol oxidation by PtPb@Au is roughly 100 millivolts lower than by PtAu@Pb. The current density for methanol oxidation by PtPb@Au initially increases on repeated cycling, then slowly decreases; after a certain scan it remains constant for several repeated scans. On the other hand, the first scan for methanol oxidation by PtAu@Pb shows a very high current density. In case of PtAu@Pb, the stable current density could not be achieved even after prolonged scans. The reason for the difference in their electrochemical behavior is completely dependent upon the dissolution of lead oxide from the catalysts surface.

In case of PtPb@Au, a definite amount of lead oxide was dissolved in the electrolyte and increased the current density; however after cycles the dissolution of lead oxide gets inhibited by the surface gold on the shell of core-shell structure, thereby resulting in a stable current density. The situation is distinctly different in the case of PtAu@Pb where the lead oxide dissolution with repeated cycles is continuous.

To understand the mechanism behind the higher current density obtained by the ternary PtRu@Pb catalysts, the CO adsorption experiment was carried out when the electrode surface was saturated with CO at a potential of 0.1 V in 0.1 M HClO_4 medium. The CO stripping experiment shows that the onset potential for CO stripping of PtRu@Pb 220 is lower than the commercial PtRu-JM catalysts; the highest peak potential for CO stripping has been shifted by almost 60 mV.

The electrode surface was cleaned of pre-adsorbed methanol decomposition products by stepping potential from a potential in the hydrogen region 0.085 V to 0.855V for 10 s to oxidize all the

pre-adsorbed products. The transient currents were recorded from 0.3 to 0.9 V with a potential step increase of 50mV per experiment for a time interval of 180 s. The steady-state current recorded at each potential is plotted against the potential; it clearly shows that the onset potential for methanol oxidation was nearly the same for the PtPb@Au and commercial PtRu ETEK catalysts. The potential step experiment also indicates that at all the potential ranges the current obtained by PtPb@Au is much higher in magnitude than the commercial PtRu. The cyclic voltammetry measurement shows that at 0.750 V the current obtained by PtPb@Au is 4 times higher than commercial PtRu.

In situ X-ray Absorption Spectroscopy Study

All the catalysts have been characterized by X-ray absorption spectroscopy in Brookhaven National Laboratory. To understand the role of lead in the ternary catalysts and to explain the higher current density of the new catalysts, the in situ X-Ray absorption spectroscopy(XAS) of the catalysts has been performed. The small changes in coordination number (N) or bond distance (R), mean square-disorder term (commonly referred as Debye-Waller factor), and oxidation state can be detected during an electrochemical reaction by analyzing the extended X-ray absorption fine structure (EXAFS) and X-ray absorption near edge structure (XANES). A FEFF 8.0 calculation on a Pt_4Ru_2 “Janin cluster” was imported to model the Pt-Pt and Pt-Ru paths at the Pt edge. Figure 32 shows the analysis of the XANES white lines at the L_3 edge can yield information on the d band vacancies. The L_3 edge is due to the excitation of $2p_{3/2}$ electrons. These electrons can undergo transitions to empty states in the vicinity of Fermi level. The intensity of L_3 increases with the increase in the d band. The magnitude of the white line intensity for the ternary alloys is found to be less than that of pure Pt foil, which signifies that there is a decrease in the d band vacancy of Pt (5 d -orbital).

Figure 32 Comparison of Pt L_3 XANES for Pt foil, PtRu and ternary PtRu@Pb catalysts in 0.54 V in 0.1M HClO₄ (a) theoretical model and (b) experimental data.

NEU has previously published data about the relationship between the d-band vacancy of Pt-based alloy and the activity of the enhanced CO tolerant catalysts like PtMo. Traditional Fourier Transform (FT) EXAFS analysis was performed to understand the true electrochemical nature of the ternary PtRu@Pb catalyst. The bond lengths $R_{\text{Pt-Pt}}$ and $R_{\text{Pt-Ru}}$, obtained by EXAFS analysis, remained unchanged within uncertainties over different potentials; thus they were restricted to be constant over potentials to refine the fittings. This enabled us to perform the $\Delta\mu$ analysis that heavily relies on a crystallographic model with unchanging bond length.

For comparison, the corresponding $\Delta\mu$ amplitude collected on PtRu(ETEK) by Ramaker et al. and $\Delta\mu$ amplitude for Pt/C with similar particle size are also included. As shown, at higher potential range (0.8 V or above), the O(H) coverage decrease in the direction PtRu > Pt > PtRu@Pb (see Figure 33)

Figure 33 Pt L_3 edge $\Delta\mu$ spectra for PtRu@Pb sample in clean 0.1 M HClO_4 using 0.50 V as the reference. The

The positive shift of the onset potential for PtRu@Pb compared to PtRu shown in Figure 33 affirms the stronger O(H) inhibition on PtRu@Pb than PtRu. Therefore, while alloying with Ru increases the binding energy between O(H) and Pt, the further deposition of Pb on surface significantly weakens the chemisorption of O(H), which makes the enhanced CO tolerance mechanism of PtRu@Pb completely different from that of PtRu. Specifically, for PtRu, a significant amount of CO survives from bifunctional mechanism (Eq. 2, below) due to the increased Pt-CO bond strength. This bond not only decelerates the following reaction rate, but heavily impedes CO migration across the surface to react with OH.

Afterwards, the remaining CO is continuously removed by the adsorption of O(H) on Pt near and far away from Ru. Accordingly, Ramaker et al.^{1,2} claimed the ligand effects between Pt and Ru arise primarily from increased activation with water to form OH rather than weakening of the CO-Pt bond. The CO coverage on PtRu is still significant and reduces continuously at 0.4-0.8V, along with the increase of O(H) coverage. On the other hand, the weaker O(H) chemisorptions

on PtRu@Pb promotes the bifunctional mechanism by accelerating the reaction rate and facilitating the CO migration. As a result, much lower CO coverage with a smaller decreasing slope between 0.4-0.6V is observed; the sharper decrease beyond ~ 0.65 V is due to the adsorption of O(H) on Pt. Since bifunctional mechanism is widely acknowledged as the dominant effect in CO tolerance, it is believed that the better performance of PtRu@Pb can be mainly attributed to the weakening of the Pt-CO bond induced by the deposited Pb. Combining the result from the theoretical evidence with our in situ EXFAS study, the conclusion was drawn that lead plays a significant role in the enhanced performance of PtRu@Pb catalysts.

Four novel ternary core-shells, PtRu@Au, PtRu@Pb, PtPb@Au and PtAu@Pb, have been synthesized and their complete structural and microstructural analyses have been done. It has been found that PtPb@Au shows better stability than PtAu@Pb due to the presence of Au on the core. Gold reduces the oxidation of lead in the air and imparts more durability. In addition, with respect to methanol oxidation, PtPb@Au oxidizes methanol at much lower potential than PtAu@Pb. In comparison to commercial PtRu catalysts, PtPb@Au produces four times higher current density at the highest peak potential for PtRu. In summary, the PtPb@Au is a stable and durable catalyst. Enhanced and improved methanol oxidation properties were found despite the larger size of the PtAu@Ru catalyst. This sample shows significant enhancement of the kinetic performance in comparison with commercial PtRu/C catalyst. Both the experimental and theoretical calculations suggest lead helps for the better activity of the platinum in the ternary catalysts by changing the d-band state of Pt in PtRu@Pb.

Performance of the Ultrastable Anode Catalyst in an MEA

Numerous attempts were made at fabricating anodes and MEAs from the NEU ternary anode catalyst, with minimal success. Although the catalyst showed excellent properties in the solution based electrochemical tests, it did not produce a good anode and performed poorly in MEA testing. Figure 34 shows the polarization with a typical comparison polarization curve for the ELE 170 anode based MEA. The anode catalyst loading was comparable in both cases. The NEU catalyst MEA exhibited an area specific resistance of 0.9 ohm.cm^2 which was caused by high impedance in the anode layer.

Figure 34. MEA Performance for NEU ultrastable anode

Task 4: MEA Development

The UNF internal water management strategy requires rigorous hydrophobicity control of the cathode, as discussed in Task 2, in order to avoid cathode flooding. MEA composition and manufacturing factors were examined in order to develop an understanding of the relationship between MEA structures water transport and flooding to optimize the performance. The optimization of two critical components of the UNF MEA design, the low methanol crossover membrane and the liquid barrier layer, has been discussed in detail in Tasks 1 and 2.

Catalyst Coating and Formulation

UNF has performed significant testing and optimization of the MEA processing conditions as the subcomponents of the system have changed. Much of the effort was directed at optimizing the catalyst ink and in deposition conditions to provide a good layer on the highly hydrophobic liquid barrier layers described in Task 2. Figure 35 shows issues with coating the ink onto the liquid barrier layers. In Task 5, the performance consequences of the wetting agents selected for the printing ink are discussed.

Figure 35. Ink wetting characteristics

Catalyst Ink Deposition with Wire-Wound Bar.

JMFC developed experience in catalyst deposition methods that do not require printing, including bar, blade, and slot controlled deposition of ink. A wire-wound bar coating method for cathode catalyst deposition was also investigated. Work at JMFC suggested that standard inks required dilution to a lower solid content before successful bar coating. Similarly the previous work on screen printing cathode catalyst layers had suggested the addition of water and n-propanol to dilute the ink. However, this strategy alone did not deliver layers of sufficient quality, as Figure 36 shows. As with the screen-printed electrodes described previously, a pre-treatment of the hydrophobic surface is required. Spraying a dilute solution of isopropanol with water onto the surface significantly improved the subsequently applied cathode catalyst layer

quality – see Figure 37. It is anticipated that production-scale deposition would involve the movement of the substrate in a roll-to-roll process under a wire-wound bar.

Figure 36. Poor quality bar-coated layers deposited without GDL wetting pre-treatment.

Figure 37. Superior quality bar-coated layers due to isopropanol/water spraying of surface.

Figure 38. Wire-wound bar-drawn cathode catalyst deposition process. With 30% isopropanol in water pretreatment, the catalyst ink successfully wets the highly hydrophobic surface. This cathode was printed with a Pt loading of 1.5 mg cm^{-2} , and laminated into an MEA.

MEA Manufacturing Optimization

The JM ELE 170 anode based MEAs clearly produce improved anode stability, the MEAs also showed a lower level of performance. The MEA lamination conditions were optimized. Figure 39 shows the performance of an MEA with 20% decrease in lamination pressure, which resulted in a 20 mV increase in cell voltage at 120 mA/cm² without an increase in the degradation rate.

Figure 39. Optimization of the lamination conditions for performance and durability using ELE 170 MEAs.

Improved Manufacturing and Cathode Catalyst

Significant additional optimization of the catalyst dispersion and coating was performed at UNF using a screen printing technique to deposit the catalyst and ink containing wetting agents. Much of the work throughout this effort was performed with JM Hi-spec 8000 catalyst as a baseline. Figure 40 shows the significant improvement in the electrochemical performance of the MEA from an MEA fabricated with an improved cathode catalyst (JM Hi-Spec 9100) using the same Pt loading.

Figure 40. Optimized MEA with 45 micron and 9100 catalyst

Catalyst Loading Reduction

The cost of the platinum is a significant cost driver for the MEA. As part of the effort to drive MEA costs down, the durability and baseline performance of reduced loading anodes and cathodes were examined. Figure 41 shows the performance of a low loading MEA. The peak power density after 2000 hours of continuous operation is 60 mW/cm^2 . This MEA was prepared using the Hi-Spec 8000 catalyst so improved performance is expected using the Hi-Spec 9100 as described above. The use of reduced catalyst loading's appears promising for durability, however further improvement in the performance is needed as well as a detailed examination of the durability of these lower loading anodes under on/off operation as described below.

Figure 41. Performance of low catalyst loading sample ($\sim 3 \text{ mg/cm}^2 \text{ Pt}$) after 2000 hours of continuous operation. Peak power $\sim 60 \text{ mW/cm}^2$.

Task 5: MEA Performance and Durability Testing

Testing of the UNF passive water recovery MEAs was performed in short stacks. The impact of optimizing various components of the MEA on the beginning of life performance is presented in the preceding tasks. In this section, the stability and durability of the MEAs is discussed. The following three types of degradation were observed at the on-set of this study: on state, off state and on-off cycling. Each of these durability characteristics will be discussed separately

On State/ Continuous Operation Degradation Testing

The UNF passive water recovery MEAs show excellent performance, as discussed previously, and high level of durability for continuous operation, with testing over 10,000 hours. Figure 42 shows the performance of an eight-cell, first generation baseline MEA under continuous operation at 120 mA/cm^2 . The stack shows excellent durability with an average degradation rate of $5 \mu\text{V/h}$. Figure 43 shows the performance of the second generation of MEA with the ELE 170 anodes and a $20 \mu\text{m}$ membrane. The stack is being operated at 160 mA/cm^2 constant current and has over 11,000 hours of continuous operation with a similar degradation rate of $5 \mu\text{V/h}$.

Figure 42. First generation MEAs with old wetting agent. Continuous operation at 120 mA/cm², 50°C cell operation. 10,000 hours of operation.

Figure 43. Second generation MEAs with the modified wetting agent continuous operation at high power density. Over 11,500 hour operation.

Off State Degradation Analysis of Used MEAs

While the UNF MEAs exhibit promising levels of degradation in the on or loaded operating state, as illustrated in the previous section, the project team found an unexpectedly high level of degradation when the stack was not being used. Additionally, the degradation was linear with the amount of time the cell was off and was not related to the cycling frequency or number of on/off cycles. Typically, commercial DMFC MEAs do not exhibit this type of degradation during the off state. As a major part of this program, an extensive analysis of this off state degradation was to determine the underlying cause and mitigate it.

Analysis of Degraded MEAs from 40 Cell Stack

To determine which component(s) of the MEA was the root cause of this degradation, polarization curves, impedance measurements and cross-over measurements were performed on MEAs from a degraded 40-cell stack that had been exposed to significant off state time. The results were compared to the performance of a new MEA. Changes to the membrane or MEA resistance and methanol crossover were determined to be within the experimental variation of the measurements. Therefore, changes to the membrane transport properties (proton or methanol transport) or delamination were not likely to be a major contributor to the MEA degradation. The absence of delamination as the cause was confirmed using the adhesion measurements discussed above in Task 1 and scanning electron microscopy (SEM) on degraded MEAs.

To examine if one electrode was the major contributor to the degradation, polarization curves for the MEA cathode and anode were collected under controlled operating conditions. Figure 44 shows a typical iR compensated polarization curve for the degraded MEA compared to a fresh MEA operated under identical conditions. Clearly, from the overall cell polarization curves, there is a significant degradation in the MEA performance after the extended storage or off state. Examination of the anode polarization data indicates little or no degradation of the anode performance. However, examination of the cathode polarization indicates a significant degradation in the cathode performance. In particular, a significant activation loss on the cathode can be observed as a major contributor to the cell performance loss.

Figure 44. IR-corrected polarization curves for off state degraded stack MEA versus a fresh MEA (No significant changes were observed in the membrane of MEA resistance).

Ex-situ Characterization of Off State Degraded Cathodes

The degraded MEAs were also subjected to a series of chemical and physical characterization techniques to determine the source of degradation.

Scanning electron microscopy (SEM) / energy dispersive analysis of x-ray for used MEAs

SEM-EDS was performed on typical anode and cathode samples from fresh (unused) and degraded stacks. The SEM micrographs did not indicate any physical deterioration of the cathode or anode layers. A small but noticeable ruthenium (Ru) signal is seen on the degraded cathode (Figure 45). While deposition of ruthenium leached from the anode is a mechanism for cathode degradation, the amount of ruthenium seen is not sufficient to be consistent with the large amount of cathode degradation observed in the MEAs, so ruthenium leaching is unlikely to be the major contributor to the off-state degradation.

Figure 45. EDS of Cathode from degraded MEA.

X-ray photoelectron spectroscopy of typical cathode

X-ray photoelectron spectroscopy (XPS) was used to probe the chemical states of the cathode and look for contaminants. A negligible sulfur signal indicates that there is little degradation of the Nafion binder. A high resolution scan of the Pt 4f region (Figure 46) shows no significant platinum oxide formation. Additionally, there is no significant Ru deposition, which is consistent with the SEM/EDS results. The most significant difference is seen in the C1's region of the XPS spectra obtained from the fresh and degraded MEA cathodes (Figure 46). The ratio of graphitic and aliphatic carbon to CF₂ carbon from the Nafion binder is increased in the degraded MEA. While some amount of graphitic and aliphatic carbon is expected, there is unexpectedly more of these species in the degraded versus fresh cathode layers. Integration of the XPS spectra indicates an approximately 25% increase in the ratio of organic or graphitic carbon to Nafion carbon (CF₂ bonded). No corresponding decrease in fluorine signal was detected, which is consistent with additional carbon being deposited onto the catalyst. The presence of an organic contaminant was further confirmed using IR measurements, which indicates an organic material or contaminant present with a signal wave numbers ~1600 to 1750 cm⁻¹; this result is consistent with the presence of an alkene or ketone organic species on the surface.

Figure 46. C1s spectra of fresh unused (red line) and spent (blue line) cathodes

Stack performance analysis

As part of the root cause analysis, all of the components and process steps were systematically examined to identify the cause of the off-state degradation. The following section highlights the key steps in the analysis.

Membrane, seals, plates and open cathode design

Control samples with JMFC standard cathode and anode electrodes on the UNF membrane were produced. These MEAs were evaluated in the UNF open cathode slack design using edge sealed MEAs and the UNF membrane. Figure 47 shows the performance of the MEA which does not exhibit any off state degradation, and also in this case, exhibits a low on state degradation. This performance indicates that the membrane, stack design, edge sealed MEA design, MEA seals, and open cathode operation is not at the root cause of the off state degradation. Therefore, the project team focused on the key difference between our MEA design and the conventional MEA design in particular the liquid barrier layer and the cathode catalyst layer structure.

Liquid barrier layer

The liquid barrier layer is fabricated from a mixture of graphite and Teflon with surfactants. As part of the manufacturing of these components the Teflon must be sintered and the surfactants burned off. A possibility is that the surfactants were not totally removed, especially from the dense diffusion barrier layer. An extensive investigation of the barrier layer chemistry and firing conditions were performed, including both removing components and increasing components, to evaluate the effect on the degradation rate. Additionally, MEAs were produced using the same ink without the barrier layer. None of the changes to the liquid barrier layer composition and chemistry provided a change in the off state degradation characteristic of the MEA, thus the liquid barrier layer was not at the root of the off state degradation -- see Figure 48.

Figure 47. Degradation perofamcne of JM standard DMFC anode and cathode in UNF MEA and stack configuration

Figure 48. Typical data for changes to the liquid barrier layer is not at the root cause of the degradation

Wetting agents in the cathode catalyst ink

As discussed above, to print the catalyst layer, organic solvents are needed to wet out the barrier layer. Additionally, these solvents may be difficult to remove completely from the catalyst layer which could potentially absorb in the graphite of the barrier layer requiring higher temperatures to remove them from the cathode electrode structure (catalyst layer on liquid barrier layer). Catalyst ink chemistries on the off state degradation were investigated. The UNF baseline in chemistry uses a ketone as the major organic component. Since the XPS analysis shows the presence of the ketone groups in the degraded cathode layers, investigation into the ink and replacement of the ketone with an alcohol Figure 49 shows the degradation profile for an eight cell stack prepared with no ketone in the ink. There is a clear change in the degradation profile from previous measurements as the degradation levels in longer off periods and does not

continue linearly. The IPA used in the ink may also react in the ink to form a ketone so it was further replaced with an alternative alcohol. Figure 50 shows the performance of an initial eight cells stack with this new ink chemistry and improved stability is observed in the off state after a one week test.

Figure 49. Changes in the wetting agent lead to change in the linear degradation rate

Figure 50. Off state degradation

Daily Operation (8 hours on/16 hours off)

The third mode of fuel cell operation is periodic start/stop operation. Figure 51 shows the period operation of a stack with the improved cathode ink wetting agent. The stack shows no degradation during extended off periods but there is still a significant degradation during the daily stop start operation. An extensive investigation of the operation and process parameters was performed to find the root cause.

Figure 51. Modified wetting agent in the ink composition shows a lower rate of degradation

Effect of the operating profile on the degradation rate

The effect of the operating profile was evaluated, in particular the rest rejuvenation step. DMFC fuel cells typically show short term reversible degradation that can be reduced by applying some sort of air starvation, which brings the cathode voltage down and strips off the platinum oxides that build up on the catalyst surface. Since the UNF system is an open cathode system the cathode voltage is pulled down using a combination of removing the air feed and actively pulling the cathode voltage down by applying a constant voltage load the fuel cell stack. A typical air starve rest is shown below in Figure 52. Previous tests on continuous operation have shown the voltage applied had no significant effect on the degradation rate. However, screening tests on the behavior of the MEAs during daily 8hr on/16 hr off operation shows there is a significant effect of the load portion of the rest/rejuvenation step. Figure 53 shows the effect of various rest rejuvenation steps on the improvement of the performance through improved stripping of the oxides from the cathode. Clearly, the lower voltage which pulls the cathode voltage down sufficiently gives improved recovery. Figure 54 shows a comparison of the degradation rate using two different voltages; the lower the value in the rest clearly gives a lower degradation rate.

Figure 52. Typical air starve profile used in UNF MEA testing.

Figure 53. Effect of rest voltage on recovery of surface oxides

Figure 54. Effect of rest voltage

Conclusion

All research goals and objectives were met or exceeded during this successfully completed DOE program. Over 1,500 MEAs were built and tested in fuel cell stacks using a wide range of different MEA manufacturing chemistries and process conditions. The project demonstrated that the UNF MEA design could be fabricated with a high degree of reproducibility and repeatability. Improved scalable manufacturing processes have increased the performance and lowered the catalyst loading to reduce the MEA cost. In addition to short stack testing, the MEA performance has been validated in 40-cell stacks in the UNF 20+ W DMFC system.

The program exceeded the initial durability requirements and Go/No decision point by demonstrating over 500 hours with an MEA power density greater than 60 mW/cm^2 . In fact, the project team has demonstrated over 11,000 hours of continuous operation in a short stack, which significantly exceeds the system end of life power criteria required to produce 20+ W net power. Additionally, through improved manufacturing processes and the removal of impurities, the project team was able to mitigate an off state durability issue that affected the baseline MEAs used at the start of the program and satisfy the go/no-go milestone. Through optimization of the MEA operating conditions, the overall degradation rate in periodic on-off operation was significantly reduced by lowering the voltage in the rest/recovery step thereby recovering the cathode performance from the effects of short term or reversible degradation.

The membrane properties were optimized, including down selecting the UNF DM-1 $45 \mu\text{m}$ membrane. Optimizing the post processing lowered the methanol crossover by over 50%, which increased the fuel utilization efficiency from 78% to 90%. Furthermore, improved MEA manufacturing and post processing afforded this improvement without any loss of power density. In independent system level testing, this approach increased the system efficiency from 17% to 24%.

As part of the MEA development, the project team investigated a range of commercially available anode and cathode catalysts, as well as novel ternary alloy anode catalysts developed as part of this program. Ultimately, the Johnson Matthey anode electrode (ELE 170) was selected. This electrode provided optimal performance in the MEA, with significantly improved durability by improving Ru stability. Ru instability is a known mechanism of DMFC performance degradation. After optimization of the MEA manufacturing process, the ELE 170 gave comparable electrochemical performance to the ELE 147 anode but with better stability. The Johnson Matthey Hi-Spec 9100 catalyst performed 10-20% better than the other cathode catalysts tested. The JM 9100 catalyst was selected late in the program and system level data presented in Table 1 does not reflect these improvements.

The catalyst loading was reduced to 3 mg/cm^2 of platinum and successfully met the final program goal of 60 mW/cm^2 at 1000 hours of operation. To date, the goal has been met at over 2000 hours of operation. This performance was achieved using the baseline cathode catalyst and further improvements are expected with the Hi Spec 9100 catalyst.

Lowering the catalyst loading, improving the MEA durability, and implementing the scalable, commercial manufacturing processes developed in this program provides a path to lower MEA and system cost. As a result of these efforts, the UNF passive water MEA provides a path to meet the DOE 2013 system level goals for the 10-50 W application, as shown in Table 1.

Task / Milestone Schedule

Task #	Project Milestones	Milestone Completion Date				DOE Funding		Progress Notes
		Original Planned	Revised Planned	Actual	Percent Complete	Original Planned	Cumulative Actual	
1	Membrane	3/30/2012			100%	\$474,556	\$474,556.00	
2	Barrier Layer	6/30/2012			100%	467,282	\$467,282.00	
3	Catalyst Development	3/30/2012			100%	497,282	\$420,930.50	
4	MEA Development	6/30/2012			100%	436,407	\$436,406.50	
5	MEA Durability	6/30/2012			100%	614,553	\$599,424.86	

Project Spending and Estimate of Future Spending							
Quarter	From	To	Federal Share of Outlays*	Recipient Share of Outlays*	Cumulative Federal Share of Outlays*	Cumulative Recipient Share of Outlays*	Cumulative for Project*
1Q10	1/1/2010	3/31/2010	\$0.00	\$0.00	\$0.00	\$0.00	\$0.00
2Q10	4/1/2010	6/30/2010	\$126,307.96	\$0.00	\$126,307.96	\$0.00	\$126,307.96
3Q10	7/31/2010	9/30/2010	\$170,892.21	\$0.00	\$297,200.17	\$0.00	\$297,200.17
4Q10	10/1/2010	12/31/2010	\$226,378.80	\$0.00	\$523,578.97	\$0.00	\$523,578.97
1Q11	1/1/2011	3/31/2011	\$319,232.09	\$42,144.47	\$842,811.06	\$42,144.47	\$884,955.53
2Q11	4/1/2011	6/30/2011	\$317,385.53	235,829.58	\$1,160,196.59	\$277,974.05	\$1,438,170.64
3Q11	7/1/2011	9/30/2011	\$399,581.19	\$111,798.65	\$1,559,777.78	\$389,772.70	\$1,949,550.48
4Q11	10/1/2011	12/31/2011	\$200,733.17	\$89,202.95	\$1,760,510.95	\$478,975.65	\$2,239,486.60
1Q12	1/1/2012	3/31/2012	\$129,352.64	\$22,628.68	\$1,889,863.59	\$501,604.33	\$2,391,467.92
2Q12	4/1/2012	6/30/2012	\$139,942.26	\$38,588.46	\$2,029,805.85	\$540,192.79	\$2,569,998.64
2Q12	7/1/2012	9/28/2012	\$368,794.01	\$112,156.16	\$2,398,599.86	\$652,348.95	\$3,050,948.81
Totals			\$2,398,599.86	\$652,348.95			

* Update quarterly – previous quarters should show actual expenditures and should coincide with the SF425 numbers; future quarters should show estimates. Estimates need to be provided for the entire project. If spending for a given quarter is different than estimated, then the remaining quarter's estimates should be updated to account for the difference. Total DOE and Cost Share amounts should be the same as the Award amount.

General Notes: 1) DOE Laboratory partner spending should not be included in the above table. 2) The information in this table should be consistent with the information provided in section 10 of the quarterly financial status reports (SF425).

¹ C. Roth, N. Benker, T. Buhrmester, M. Mazurek, M. Loster, H. Fuess, D.C. Koningsberger, D.E. Ramaker, *Journal of the American Chemical Society*, 127 (2005) 14607-14615.

² F.J. Scott, S. Mukerjee, D.E. Ramaker, *The Journal of Physical Chemistry C*, 114 (2009) 442-453.