Final Technical Report

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“Reduction in Fabrication Costs of Gas Diffusion Layers”

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Work Performed Under
Award Number: DE-FG36-08GO18051

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Executive Summary

This final report to the Department of Energy (DOE) for Award Number: DE-FG36-08GO18051 covers the period of October 2008 through September 2011 and summarizes the work accomplished throughout the program. This project addresses the DOE Hydrogen Program's Manufacturing R&D for Hydrogen and Fuel Cell Systems objectives of improving manufacturing technologies to enable energy efficient, environmentally sustainable, high-volume processes, and creating a low-cost domestic supplier base necessary for market introduction and economic growth. Specifically, this project reduces the fabrication costs of high-performance Gas Diffusion Layer (GDL) products and demonstrates the means of achieving six sigma quality standards at high volume manufacturing.

Ballard Material Products (BMP) performed a pre-design technical and cost analysis of state of the art production technologies feasible for high volume GDL manufacturing. Based upon criteria that also included environmental health and safety, customer quality requirements, and future needs, BMP selected technologies that can be integrated into its current manufacturing process. These selections included Many-At-A-Time (MAAT) coating and continuous mixing technologies, as well as various on-line process control tools. These processes have allowed BMP to produce high performance GDLs at lower cost for near-term markets, as well as to define the inputs needed to develop a conceptual Greenfield facility to meet the cost targets for automotive volumes of 500,000 vehicles per year.

The end result of this program was a >50% reduction in the manufacturing costs of GDLs for near-term applications coupled with a four-fold increase in production capacity, since the program began. These results were achieved via improved manufacturing efficiencies, increased product yields, and improved product quality and are applicable to current GDL volumes, requiring no breakthrough technologies or projections of increased volumes. In addition, manufacturing process improvements (MAAT coating and continuous mixing) were implemented on a pilot scale. These processes were refined and successfully demonstrated to manufacture GDL material that was equivalent to standard production material. Implementation of these process steps will further increase production capacity (ten-fold from the start of the program) and provide additional cost savings (>65% from start of the program). Full implementation will require additional funding, however, for purchase of a full-width (800mm) MAAT coating head and improvements to the continuous mixing process for commercialization.

Throughout this program numerous on-line process control tools were implemented for both the commercial production and the new manufacturing processes. These on-line tools provide valuable insight into the production process and allow for the control of critical parameters throughout the process. A novel process to measure the chemical homogeneity of the GDL was also developed at the Pennsylvania State University. The measurement process utilized Raman scanning to detect PTFE concentrations on the surface of the GDL. Although this tool was not found to be useful for our production process, the knowledge gained will allow BMP to increase the processing speed of the PTFE coating step for production. A significant effort was also spent to determine the relationships between processing parameters and critical GDL properties. Empirical models were developed from these relationships, which allow BMP to control critical GDL properties and manufacture GDLs within tight specifications. This ability is critical for the production of GDLs for a wide range of applications (stationary, materials handling, portable, automotive, etc.) with the low-cost manufacturing process.

Finally, from the information gathered throughout this program, BMP put together a Greenfield Facility design that was capable of producing GDLs at volumes ($10,000,000 \text{ m}^2$) and costs ($<\$2/\text{kW}$) that are compatible with the 2015 DOE stack cost targets of $\$15/\text{kW}$. This facility design includes the low-cost processes developed in this program (MAAT coating and continuous mixing), but does not require any other breakthrough technologies or significant assumptions to implement. Further cost reductions may be possible through improved efficiencies or future improvements to the manufacturing process, but were not included in this analysis.

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1 - Comparison of Accomplishments with Goals and Objectives of the Project

1.1 Original Goals and Objectives

The overarching goal of this project was to reduce the fabrication costs of Gas Diffusion Layers (GDLs) through:

- (1) Development, implementation, & demonstration of novel manufacturing technology that reduces the number of process steps and enables a growth in product volumes & innovative product development to produce low-cost GDLs;
- (2) Development, implementation, and verification of real-time, on-line measurement tools to reduce/eliminate costly ex-situ characterization sampling and testing;
- (3) Development, implementation, and application of real-time, on-line process control tools to produce continuous high volume, low-cost GDLs to six sigma quality standards and maximize production yields;
- (4) Sustained development of an understanding of the relationships between process capabilities, GDL product properties, and fuel cell performance to direct process specifications that maximize production yields of high performance, low cost GDLs.

1.2 Accomplishments

The end-result of this project was a 56% decrease in the fabrication costs of the GDL along with a four-fold increase in production capacity. The equipment evaluated in this program could increase manufacturing capacity up to ten-fold (from the start of this program) in this current facility with additional capital investment.

These results were achieved by addressing each of the major topics described in the goals section. Verifying Many-At-A-Time (MAAT) coating technology will allow us to reduce the number of processing steps, if scaled up to production levels (800mm wide). Developing a continuous mixing process reduces manufacturing times and provides a versatile manufacturing process in the near-term, which could be scaled by adding mixing units or increasing the size of the mixer for volume increases in the future. Moving to full-width production enabled improved manufacturing efficiencies, reduced processing steps and helped reduce fabrication costs in the near-term. These accomplishments addressed the first key goal listed in section 1.1.

On-line process control tools, such as basis weight sensors and an on-line vision system on the coating line, improved product uniformity and reduced costly ex-situ processing, addressing the second key goal. Additional on-line process control tools, such as mass flow controllers and non-contact thermocouples, improved quality standards and maximized production yields, addressing the third key goal. Relationships between processing parameters and critical GDL properties were determined and these relationships led to the development of production models. These models allow for the control of critical GDL properties during production by adjusting process parameters as necessary. These controls have maximized production yields and enabled BMP to control the critical properties to produce high performance GDLs for various applications, addressing the final key goal. Additionally, more cost reductions will be realized once the new processes are fully integrated into our manufacturing process.

This program was successful in reducing the near-term GDL fabrication costs and, combined with BMP's modular manufacturing process, allows for the production of GDLs with significantly different physical properties. This allows BMP to supply GDL for various fuel cell platforms, regardless of cell design or end-use application. By combining the total volume from all of these applications, BMP is able to use economies of scale to reduce the costs of GDLs for the industry as a whole. Additionally the knowledge gathered through this program allows for the design of a production facility capable of meeting initial automotive production requirements within the 2015 DOE cost targets for MEAs.

2 - Introduction

2.1 Motivation for this project

A fuel cell is an electrochemical device that converts a fuel, typically hydrogen, directly into electricity in a chemical process. Since it does not involve burning the fuel, the efficiencies are typically much higher than most common energy generation techniques, which transform heat to kinetic energy and then to electricity. The most significant obstacle preventing the wide-spread use of fuel cells is the system cost, which can be 2-10 times the cost of other available options.

The most significant cost in the Polymer Electrolyte Membrane (PEM) fuel cell is the Membrane Electrode Assembly (MEA), which is comprised of two Gas Diffusion Layers (GDLs) and two catalyst layers sandwiched around a special ion conducting membrane, as shown in Figure 2.1. At the beginning of this program the cost to manufacture the GDL component alone was ~\$40/kW or almost 3 times the 2015 DOE cost target of \$15/kW for the entire fuel cell stack.

Figure 2.1 – Components of an MEA

Investigating the sources of cost in the GDL manufacturing process revealed that almost 70% of the costs were associated with labor, as shown in Figure 2.2. Based on these results it was determined that the cost of the GDL could be reduced most significantly by addressing the labor associated with the mixing and coating processes. Additional cost savings could be realized by improving the GDL quality, reducing the amount of ex-situ testing required, and improving product yields and manufacturing efficiencies.

Initial estimates indicated that GDL manufacturing costs could be reduced by as much as 65% at current production volumes, but that it would not be possible to reach costs required to meet the 2015 DOE cost targets at these volumes. The work done in this program would, however, be helpful in reaching the 2015 DOE cost targets, provided that volumes were sufficiently increased. A final deliverable from this program was the design of a Greenfield facility to produce GDLs using the BMP manufacturing process at volumes that could meet the 2015 cost target and support the initial automotive market penetration (500,000 systems/year).

Total GDL cost ~\$36/kW

Figure 2.2 – GDL Cost Breakdown

2.2 Background Information

2.2.1 – Many-At-A-Time Coating

Currently, the application of coating inks (e.g. carbon fiber paper matrix, GDL sublayers and GDE catalyst layers) occurs by multiple pass coating steps that include drying and rewinding with each pass. The replacement of these multiple passes with a single pass process is a key objective to reducing costs, improving quality, and manufacturing next generation GDL microstructures. The manufacturing costs, such as equipment setup times and labor costs, will be significantly reduced. In addition, product quality will be improved due to a lower probability of defects with the reduced number of process steps. Multilayer coating technology will give

GDL designers the ability to manufacture innovative substrate paper microstructures and engineered sublayer and catalyst interlayer microstructures in high volume at low cost. The prototype designs cannot be manufactured with multiple (or tandem) passes, but multilayer coating will open the design window for new concepts, such as graded microstructures, to be fabricated cost-effectively in high volume.

Advances in multilayer coating applicator technology have resulted in the commercial availability of several coating methods, which can simultaneously apply several uniform coating layers without the disadvantages of multiple passes or tandem coaters. The methods commercially available are multilayer slide coaters, multilayer curtain coaters, multilayer slot coaters, and multilayer extrusion coaters. Table 2.1 is a summary of the typical process window for these coating methods.

Table 2.1 - Typical Process Windows of Multilayer Coating Methods

Typical Operating Conditions	Multilayer Slot Coating	Multilayer Extrusion Coating	Multilayer Curtain Coating	Multilayer Slide Coating
Viscosity cP	15-20,000	50,000-300,000	5-5,000	1-500
Wet thickness um	10-250	15-525	5-500	25-250
Line speed fpm	20-1700	125-1825	400-3000+	20-1000
Accuracy % (max-min)/average	2	5	2	2
Characteristics	Wide operating window – low level vacuum can be used to extend	Similar to slot die but higher viscosity liquids required	Requires a minimum speed of 400 fpm to form a curtain	Stability of the process increases as the wet coating weight is increased up to the limit of coatability

A review of the technical requirements for coating based on the range of ink formulations (e.g. viscosity and solids content range), range of wet layer thickness, number of layers, coating weight accuracy and uniformity (particularly across wide rolls), substrate properties (roughness, permeability, stiffness, porosity), coating speed, maximum width of rolls, and so on was performed. Multilayer slot coating was down-selected as the only feasible method for this process. Essentially, the GDL ink viscosities are too high for slide coating, the minimum line speed required for curtain coating is too high, and the ink viscosities are too low for extrusion coating.

2.2.2 – Continuous Mixing

One of the major bottlenecks in the current production of GDLs is the ink manufacturing process. In this process, all of the components are weighed and added to the batch by hand. This process is slow and increases labor costs while also decreasing product uniformity due to operator error, such as imprecise measurements or inadequate mixing time. These errors may cause improper solids content or viscosity of the mixture, which increases processing costs due to material waste and decreased production yields. The batch mixing process requires approximately 8 hours, or one shift, per batch. There are also environmental hazards associated with the handling of some of these components, necessitating a considerable amount of protective equipment and cleaning time associated with each batch. This increases product cost due to employee training, safety equipment and labor costs for cleaning.

Implementing a new liquid and solids delivery system along with a high-shear continuous mixer can greatly reduce production time, while also improving the accuracy and uniformity of the mix. The solids can be stored in conical hoppers and fed to the continuous mixer at a constant rate using state of the art gravimetric feeders with external paddle agitation. The

liquids can be fed directly to the continuous mixer with a simple pumping system. This equipment can be combined with computer controls to ensure quick and accurate mix feeds, which can be easily adjusted for the different product requirements. The mixture could be pumped directly from the continuous mixer to the coating line or to a storage container for future use. These changes can reduce the current mixing time, and associated labor costs, by as much as 90%. In addition, the new system could ensure more accurate mixtures, thereby reducing wasted raw materials and increasing production yields, while also improving the health and safety of the operators.

There are many different options for continuous mixing, including dynamic and static in-line mixers and continuous extruders. Static in-line mixers have no moving parts and simply alter the flow pattern of the product by placing baffles in its path. Dynamic in-line mixers are distinguished from one another by the design of the mixing chamber. The mixing chamber design provides versatility, repeatable results, ease of setup and low maintenance. The speed and configuration of the mixing elements are easily modified to fine-tune the mixing process, which is important for processing a variety of products and products with variable raw materials. In-line mixers do not have the ability to process powders, however, and therefore require the formation of liquid slurry prior to entering the mixer.

A continuous extruder, however, can simultaneously process powder and liquid streams. Specially designed paddles are added to the mixing chamber and can be modified to control residence times and shear rates to alter the mix properties. The configuration of these paddles can be modified quickly and easily, providing a versatile mixing system. This increased versatility matches the needs of the modular BMP manufacturing process and was therefore selected as the mixing technology for this program.

2.2.3 – On-Line Process Control Tools

All of the process steps and support functions must operate correctly in order to achieve high quality GDL products at low cost. Failure in any one will lead to failure of the process, ending up with scrap, GDL products with defects, and/or increased equipment downtime. On-line process control and measurement systems are critical to ensuring the process variables and product properties are on target. The process control and measurement tools identified in this program can be categorized as either: (1) required for the new process technologies; (2) required for improved process specifications to achieve six sigma or better quality standards; (3) required for new control strategies arising from continued development of our understanding of the relationships between process variables, GDL properties and fuel cell performance. The on-line tools examined in this program are listed in Table 2.2 along with their primary GDL property and performance attributes as identified by BMP.

Table 2.2 - On-line Process Control and Measurement Tools

Process Step	On-line Process Control/Measurement Tool	Primary GDL Property / Performance Attribute
Heat Treatment	Non-contact Thermocouples	Allow for measurement of actual web temperature to assure process uniformity
	Tension Control system	Required to eliminate web breaks and assure product uniformity
Drying Coated Webs	Dew point sensors and non-contact thermocouples allow for controlled drying of PTFE and MPL coated substrates	Ability to adapt drying profile for different products (e.g. pore structures influence drying rate)
In-line ink mixing	Auto surface tension	Uniformity of sublayer coating, GDL interlayer adhesion – in cell degradation, low wet cell performance
	Auto viscometer Solids content	Uniformity of sublayer coating, pore structure, roughness – low cell performance, reduced CCM durability
Web Coating	Basis weight	Non uniform sublayer coating, interlayer mixing - low performance, reduced durability
	Surface Roughness (laser profilometry)	Continuously monitor surface roughness of GDL
	PTFE Distribution (Raman Scanning)	Evaluate content of PTFE on surface of the GDL as opposed to in the bulk – determine if changes influence GDL properties or cell performance
	Defect Inspection vision system	Real-time feedback of coating issues to operators to correct problems such as streaks or repeating defects

3 – Many-At-A-Time Coating Processes

3.1 Development of a MAAT Process

BMP began the process of selecting the proper type of continuous coating by consulting experts in the fields of general and multilayer coating, as well as fluid characterization. It was determined that continuous slot die coating was ideal based on the coating speeds, viscosity, and total loadings desired for this process. The key fluid properties for measurement were identified as surface and interfacial tension, visco-elastic properties, rheological properties and flow behavior. These properties were gathered for a variety of standard MPL inks and were used, in combination with coating thickness ranges, to establish key design parameters. These parameters include the hydrodynamics of the system, internal geometry for uniform coverage, flow behavior of the liquids, system shear stress(s), temperature, inertial effects, internal liquid pressure, and the prevention of vortices.

A total of six MPL ink designs were selected to be used in pilot laboratory tests in collaboration with the coating head manufacturer. These inks were tested over two days on both standard plastic films and a roll of standard anode substrate. These trials confirmed the coating head design and provided input into the requirements of the dispensing skids required to feed the coating head. These trials successfully demonstrated that the fluids could be applied using this MAAT coating process on BMP's GDL substrate, but some issues such as micro-cracking and drying defects were observed. It was determined that these issues could be addressed by modifying the drying process and, if necessary, the MPL inks.

With key inputs from the trial, such as slot heights, slot widths, coating gaps, bead vacuum, coating angle, and flow rates based on coverage aims, coupled with solution data, including solids % and viscosity, the key design parameters of the coating head were determined. With these specifications, the equipment was fabricated and purchased. A spare coating module from BMP's production coating line was retro-fitted to this new coating head to simplify the installation process. Since the standard manufacturing process only coated one layer at a time, two new dispensing skids were required and the original production dispensing skid was modified for this process. These dispensing skids included a dispensing vessel, pump, filter housing, and in-line viscometers. The vessel was pressure and vacuum rated, jacketed for temperature control, and equipped with a pneumatic agitator to prevent dissolution.

Prior to the installation of the new MAAT coating module, BMP began profiling the drying process in order to optimize it in anticipation of the higher wet loadings of GDLs with multilayer coatings. The web temperature was taken at designated locations throughout the oven and thermal profiles were generated. These thermal profiles were taken during production runs for each of the MPL coatings that would be used in the new MAAT coating process. The data helped to identify uncontrolled variables in the process and to create set-up sheets to establish controls on these variables thus making the profiles more reproducible. These controls were shown to improve product uniformity and provided critical knowledge required for the controlling the MAAT coating process.

3.2 Improvement of the MAAT Coating Process

Once the coating module and ink delivery skids were received and installed, the operators were trained to assemble and install the coating head, setup the ink delivery skids, perform necessary safety checks, and operate the equipment. The first trial on the line used a generic

polyester substrate and established that both the new delivery skids and the MAAT coating head were functioning properly. Each MPL was switched on and off and flow rates of MPL inks were related to pump speeds to control the overall loadings. These trials confirmed that all of the new equipment was functioning properly and three sublayers were successfully applied to the generic polyester base.

Once this work was complete, the polyester material was replaced with a generic paper GDL substrate. The multiple layers appeared to lie down well when wet, but some micro-cracking was noticed in the top layer after drying, as shown in Figure 3.1. There was evidence of similar micro-cracking during the pilot trials, however, and it was thought it could be eliminated by altering the fluid properties and/or the drying process. With the exception of the micro-cracking of the top layer, the trial was successful in confirming the performance of the new equipment and demonstrating MAAT coating on our GDL substrate with our production coating line.

Figure 3.1 – Example of MPL Cracking

Off-line testing was done on hand samples made with a standard K-coater. The results of this work indicated that both the fluid properties and the drying conditions contributed to the sublayer micro-cracking. Through experimentation it was observed that the micro-cracking could be minimized in these hand samples by adjusting the total wet loading, by increasing the percent solids in each solution, and by modifying the GDL drying process.

From these results the sublayer ink formulations were modified and the drying conditions altered for the next on-line MAAT coating trials. These trials were conducted with a sample roll of production material. A design of experiments screening was performed with the goal of varying the total coverage of each sublayer. This screening was done for both standard solution formulations with standard drying conditions and modified solution formulations with modified drying conditions. The results of this testing indicated that the solution formulation changes and modified drying conditions greatly reduced the sublayer micro-cracking. Additionally, changes in the total wet load of the GDL, as well as the coverage of the 3rd sublayer, also affected sublayer micro-cracking.

Throughout the next several MAAT coating runs, tests were performed to try to fully eliminate the micro-cracking, while simultaneously producing a uniformly coated roll with proper coverages. In the course of modifying the coating inks, it was found that some changes to the coating head were also required. The increased viscosities of the higher solids solutions led to ribbing at the coating head and non-uniform coverages cross-web. These problems were rectified by altering the slot heights in the coating head for each of the solutions. There was also difficulty in controlling the overall basis weight of the GDL within production specification. Unfortunately, it was impossible to determine which of the sublayers did not have an accurate loading with the current setup. This problem was addressed by purchasing a mass flow meter for each of the sublayer inks to monitor and control the loading. With these mass flow meters, the flow rate for each solution was constantly controlled and the basis weight issues were eliminated. Additionally, the GDL drying profiles were optimized for the MAAT coating

3.3 Understanding the Microstructure of the GDL

Cross-sections of the most promising samples from this on-line testing were taken to be compared to baseline samples of the current product. The samples from the MAAT coating provide three distinct layers of particles as shown in Figure 3.2. The samples from the OAAT coating show a very similar structure as shown in Figure 3.3. These initial results give us confidence that the two coating methods should provide similar performance.

Although these images provide some assurance that the two processes are similar, it was important that we could verify this in a more substantial way. It was determined that the best way to determine the overall structure was to dope the MPL inks with different metals. These inks could then be used, in conjunction with non-doped inks, to produce hand samples of both OAAT and MAAT coatings. A procedure was developed to impregnate the GDL with resin to lock the sample in place and then the GDL was cut and polished for SEM images. The goal of this work would be to produce EDS scans of the sublayers of the doped samples to determine exactly where in the sublayer the dopants were located. If successful, this work would identify the degree of intermixing in the sublayers and would be used to verify that the MAAT coating process is similar to the OAAT coating process.

Figure 3.2 – Sample Image of GDL with new sublayer coating method (MAAT)

Figure 3.3 – Sample Image of GDL with standard sublayer coating method (OAAT)

For these doping trials, Copper (II) Acetate and Zinc (II) Acetate were chosen as the dopants and they were manually mixed, via mortar and pestle, and then heated to 350°C in a

nitrogen atmosphere. Initial work was able to demonstrate feasibility as both Cu and Zinc could be seen in EDS maps, as shown in Figure 3.4.

Figure 3.4 – EDS maps of (A) Carbon, Copper and Oxygen and (B) Carbon, Zinc and Oxygen from initial doping trials

Based on the results of these initial screening trials, it was determined that the amount of dopant should be increased from 1% to 10% to increase the signal. A new process, by which the graphite powders are washed with a solvent in which the metals are dissolved and then the powders are heat treated under nitrogen atmosphere, was also implemented. From these changes, we were able to see the copper attached to the carbon in SEM images and the EDS signals were vastly improved as shown in Figure 3.5. Initial coating trials were performed with these doped inks and the results are shown in Figure 3.6. The copper doping appears to be uniformly distributed among the carbon, but the zinc doping appears somewhat clumpy and non-uniformly distributed. Work was done to refine the ratio of metal to carbon for the zinc in order to get a more uniform distribution throughout the layer.

Figure 3.5 – SEM Image Showing Copper Attached to Carbon and EDS Maps of Carbon and Copper

Figure 3.6 – Backscatter images showing the location of A) copper and B) zinc throughout the sublayer

New samples of doped inks were manufactured with improved metal to graphite ratios. These inks were then hand coated in both OAAT and MAAT coating processes using a standard K-coating process as previously described. Each dopant was tried in both the first and second sublayers, with the results shown in Figure 3.7. Unfortunately it was found that regardless of how the dopants were set up, the metals migrate with the water during the drying process.

Figure 3.7 – Examples of OAAT coating demonstrating A) Zn migrating from SL1 to SL2 to form clumps and B) Cu migrating from SL1 to SL2 to form clumps

It was originally believed that the process developed for binding the metallic dopants to the carbon particles, before forming the inks, would prevent the metallic dopants from migrating with the water during the drying process. Since that process didn't work as expected, further work was done to find alternate dopants that would not alter the MPL properties or migrate towards the top MPL during drying. It was found that silica spheres could be added to the MPL ink to indicate the layers. The silica spheres do not interact with the carbon or water and should, therefore, be distributed evenly throughout the MPL.

By examining the particle size distributions of the carbon powders used in the MPLs, it was determined that 5 micron spheres would be small enough to not interfere, but large enough to easily be seen. Along the same lines, it was determined that Titanium dioxide (TiO_2) clay could be added in a similar fashion to the 2nd sublayer. Initial results were promising, as shown in Figure 3.8, but these dopants are not attached to the carbon particles in the MPL inks. They may be beneficial in better delineating one sublayer from the other, in order to understand thickness variations and other general properties, but they can not be used to understand if the carbon particles are intermixing during the multilayer coating process. Since the ultimate goal was to determine if the layers were intermixing in an effort to better understand the microstructure of the materials, it was determined that this would not be productive, so efforts on this activity were discontinued.

Figure 3.8 – Images showing A) Silica spheres dispersed throughout SL1 and B) TiO_2 clay dispersed through SL2

3.4 Initial Validation of Equipment

Four coating trials were conducted using standard coating inks to produce both Anode and Cathode material for single cell validation testing. The drying profiles were controlled during the tests in an attempt to prevent micro-cracking in the top sublayer. These trials provided key information about the optimal drying profile, the influence of viscosity and solids content of sublayer inks on both coating and drying, and the importance of controlling the temperature of the sublayer inks. The results of the tests were generally positive and samples were taken every 2m down the length of the material and the average and standard deviations were compared to standard materials, as shown in Table 1. The only property that significantly deviated from standard materials was the coating weights, which were higher than average in both cases. It was determined that controlling the pump speed alone was not adequate for controlling the basis weight and mass flow meters were purchased for each of the sublayer inks.

It is also important to note that although we were able to coat visually acceptable material, it was at a rate slower than normal production due to the top sublayer for these trials. The overall results were positive and the multilayer coating process has been shown to be viable for GDL production.

Table 3.1 - Comparison of MAAT Coating to Baseline Materials

Properties	Anode Material				Cathode Material			
	Baseline (Avg)	Baseline (StDev)	MAAT (Avg)	MAAT (StDev)	Baseline (Avg)	Baseline (StDev)	MAAT (Avg)	MAAT (StDev)
Basis Weight (g/m ²)	99.1	2	103.7	1.58	75.4	6	83	2.6
Thickness (mils)	8.73	0.21	8.67	0.18	9.09	0.29	9.2	0.22
Tensile Strength (N/m)	2280	508	2722	239	2616	514	2600	467
Bending stiffness MD	9.57	2.35	9.55	1.45	9.95	2.37	8.97	1.19
Bending stiffness CMD	7.11	2.99	5.29	1.36	6.33	2.05	7.31	1.31
Thickness @150psi	5.98	0.35	6.43	0.24	5.96	0.24	6.5	0.3
Resistivity (mΩ-cm ²)	11.01	1.88	11.78	0.41	9.99	0.97	11.14	0.33
Diffusivity	0.212	0.025	0.183	0.015	0.270	0.036	0.272	0.007

A new set of coating trials was conducted with the goal of eliminating the sublayer micro-cracking previously seen in the top layer of the cathode design when coated at normal production speeds. The ink formulations were modified and the drying conditions were optimized successfully and the sublayer micro-cracking was eliminated. All three mass flow meters were in place during these trials, which helped to ensure proper coat weights for each layer throughout the coating run. In addition, the in-line viscometers were re-spanned for the adjustments to the ink formulation and were also used in these trials. The result of these changes, shown in Figure 3.9, was a roll of cathode material that showed no sublayer micro-cracking in the top layer.

Figure 3.9 – Image of cathode GDL with A) sublayer micro-cracking and B) no sublayer micro-cracking

3.5 Evaluation of On-line Process Control Tools

A number of different process control tools were identified and investigated for improved quality control during the MAAT coating process. This section will identify the tools that were selected, discuss the operation and any conclusions drawn from their performance. It should be noted that all the details of the development of a tool to measure the PTFE distribution in the GDL is excluded from this section and can be found in Section 5.

3.5.1 – Dew Point Sensor

The partial pressure of water in the air stream, or Relative Humidity (RH), for each oven zone was identified as a key variable in the drying process. As such, there is a need to accurately measure the RH in the dryer to understand the degree of its variability and its affect on the final product. For this application, dew point measurement was determined to be the best method for determining RH. A set of requirements for a dew point measurement device was established based on dryer profile data and historical environmental data for the area. Multiple vendors were contacted to provide the best sensor based on estimated dew point range, sensor complexity (one, two or three stage cooling), cost and versatility. These sensors are based on the chilled mirror technique where a metallic surface is systematically chilled until dew begins to form. The advantages of this measurement are exceptional accuracy, durability and calibration stability.

A dew point sensor was purchased, sampling ports were setup for each oven zone and data was collected during the MAAT coating runs. Using the dew point data and the temperature in the zone the RH in that zone can be determined using a psychometric chart. As the dew point in the room increases so do the oven dew points. To maintain RH the supply temperatures can be increased. This is important to ensure that as the room conditions change throughout the year, the drying conditions in the oven (and thus the properties of the GDL) do not change. It was noted throughout the MAAT coating campaigns that once at steady state, dew points in the oven remained constant. Only extreme changes in room dew point affected zone dew points – thus in the summer when the dew points were higher, supply temperatures were increased to maintain RH, and in the winter, when the dew points were extremely low, supply temperatures were lowered to maintain RH.

During the multilayer coating runs, zone 3 had the highest dew point, which indicated where the majority of the drying was occurring in the oven. This data, combined with the oven profiles, enabled us to repeat drying conditions throughout the year.

3.5.2 – Basis Weight Sensor

A gamma gauge sensor was identified and down-selected as an on-line GDL coating weight measurement tool. This tool is capable of monitoring the basis weight in both the machine and cross-web (transverse) directions. The tool was set up and calibrated for the BMP coating line, including programming the data collection software, calibrating sensors and creating job reports. A demonstration of the basis weight data collected during a coating run is provided in Figure 3.10.

Figure 3.10 - First Run Web Scanning Data Collection

An evaluation of the accuracy of the coating weight tool for various products was performed and the results indicated that the tool will not require re-calibration for every product. This was a concern due to the non-uniformity of the GDL substrate (e.g. porous material with random fiber orientation), but the gauge factor for the process remains constant for our materials. The product recipes were updated for current specifications by inputting the appropriate gauge factors for all GDL configurations and these sensors are now fully functional for GDL coating operations.

It should be noted that although this tool gives an accurate overall basis weight, it is unable to determine the loading of each individual sublayer during multi-layer coating. For this reason, mass flow meters were deemed necessary to ensure that each sublayer had the correct coverage. These tools work together to validate the sublayer loadings and product uniformity of BMP GDLs.

3.5.3 – Mass Flow Meters

Mass flow meters were installed for each solution to monitor flow to the multilayer coating head. The coating line's PLC program was modified to accommodate input from the mass flow meter and the operator interface was modified to graph and log flow rate data. Consistent flow rates mean consistent coverage.

At the start of several campaigns, each solution, one at a time, was flowed into the multilayer coating head at a set flow rate. Solution was coated onto polyester. After drying and passing the basis weight tool, cutouts were weighed, the solution was washed off and the cutout was weighed again. The difference in weight is the basis weight. In every case, the actual basis weight was what the aim was (and the flow rate was based on) and it compared well with the basis weight tool. This gave us confidence, that if the flow rate was correct, then the individual coverage was correct.

In the process of monitoring our flow rates, we found that it took several minutes for the flow rate to reach steady state at start up. We finally attributed this to the loss of backpressure in the line whenever we stopped the flow. Thus we installed valves near the coating head to lock in the solution and maintain back pressure. This reduced the time it

took for the flow rates to reach steady state during stops and starts (usually only at the start of the run)

3.5.4 – In-Line Viscosity Sensors

In-line viscometers were installed on each of the three dispensing skids. The proper installation and calibration was checked by a company representative for the viscometers. Through the course of using our viscometers we did find some limitations that once we were aware of we could handle with proper usage instructions. The viscometers rely on a continuous flow of solution past the piston to keep the viscometer cool. We found if we ran at too low of a flow rate that the temperature of the solution would increase due to the friction of the piston moving up and down in the sample chamber. In addition, if we stopped flowing completely, then the material in the sample port would dry out and get stuck giving us subsequent false readings. To rectify this we turn off the viscometers whenever we stop and we make sure we are running at an adequate flow rate. Also, viscosity is dependent on temperature so it is important to maintain a consistent solution temperature. In general, once at steady state flow, the viscosity of each solution is rather consistent. Thus any significant changes to the viscosity of the solution should be picked up by the viscometer. In addition, the viscosity and temperature output from these viscometers were put into the PLC. With the upgraded operator interface, this information is now graphed real time and logged. The viscosity reading from the inline viscometer was compared with solution sampled post the in-line viscometer and tested using our standard lab bench Brookfield viscometer. The viscosities were linearly offset therefore a correlation was made to relate in-line viscosity to off-line measured viscosity.

3.5.5 – Non-Contact Thermocouples

Non-contact infrared thermocouples that can read web temperatures from 25°C to 300°C are needed for use in the drying oven and our first heat treatment step. This is a difficult process as most non-contact thermocouples can read and withstand the high temperature (>250°C) or read low temperature (<125°C) easily, but very few can do both, which is what we need. These thermocouples would allow for readings of the actual web temperature (as opposed to air temperature) and lead to improved drying process control.

A prototype unit was purchased and installed in the coating line oven. The thermocouple tested fine at all measurements below 125°C; however when the temperature was increased to 250°C, the unit was able to log for only 8 minutes before it failed. Since we were in the process of separating the low temperature and high temperature processes, we were able to use low temperature thermocouples in one oven and high temperature thermocouples in the higher temperature oven. We purchased additional low temperature thermocouples to continuously track the oven profile on the lower temperature coating line.

A final test was performed with both thermocouples and using contact thermocouples to verify the actual web temperature. The recalibrated thermocouple was consistently 20°C higher than actual temperature and the non-recalibrated thermocouple was 30°C higher. These tests were performed at three different temperatures within our possible process range. We conclude that these thermocouples can be used for our first heat treatment process but an offset will need to be figured in to determine actual web temperature.

3.5.6 – Surface Topology Tool

The selection of a surface topology sensor began with determination of the critical selection criteria. These criteria include accuracy, resolution, range (field of view), setup time (secondary), exposure time, scanning time, software image processing and data

processing time, price (secondary), ease of use and versatility (secondary). Three non-contact on-line surface topology measurement techniques were initially identified, which were: phase shifting interferometry, confocal laser, and white light axial chromatism. Representative GDL samples with a range of coated surface profiles were sent to representative equipment manufacturers for surface profile analysis. It was determined that GDL thickness was a significant product variable, so selecting a tool that was capable of monitoring both would be beneficial.

A suitable on-line surface topology demonstrated the ability to meet the evaluation criteria of ISO defined 2D profiles and 3D surface topography, and 2D & 3D parameters in accordance with international standards using advanced ISO 16610 filtering techniques. Long scan 2D profiles at a scanning speed representative of the web velocity were also demonstrated with an example of the measurement data received from this tool shown in Figure 3.11.

Figure 3.11 - Representative Data of Identified Surface Topology Sensor

The tool selected for this measurement technique consisted of two optical pens that would continuously monitor changes in distance, which correspond to peaks and valleys in the GDL surface. Initial trials, which were demonstrated on a moving table, were very promising for this technology. Unfortunately the system was unable to accurately monitor the GDL during the production process due to vibrations from the process equipment and fluttering of the moving web. These problems caused the sensors to inaccurately monitor the surface of the GDL and thus could not be used as originally designed. Efforts were made to test the pens as the GDL was passed over a roller to eliminate the web fluttering, but the vibrations caused from the equipment was still too much to be used effectively as a continuous process tool.

3.5.7 – On-Line Visual Inspection Station

An on-line visual inspection station was installed on the coating line with the goal of providing real-time feed back of coating defects, such as cracks, streaks or globs, to the operators. This addition enables longer coating run times by allowing operators to adjust processing parameters to prevent defects from occurring throughout an entire roll. The system consists of a line scan camera and software that will set off alarms to alert the

operators if certain defect thresholds have been met, with sample defects detected by the on-line system shown in Figure 3.12.

Figure 3.12 – Sample defects from on-line vision system on coating line

3.5.8 – Pressure Sensors

Air impingement velocity, as determined by the pressure drop across the nozzle plenum, and oven balance, the pressure difference between inside the oven and that of the room, were identified as process parameters that needed to be monitored and controlled. As such, digital pressure transmitters were ordered along with analog input cards and tied into the NI PLC system on the coating line in order to log these parameters. Fan speed and damper position control the air impingement velocity. Supply and exhaust damper positions affect oven balance. Setup sheets were established for each process indicating the desired values for these set points. By logging this data, there is now a record of these values during any particular run and they can be monitored in real time to ensure they are correct and don't vary throughout the run.

4 – Continuous Mixing Technology

4.1 Evaluation of Continuous Mixing Technologies

BMP began the process of implementing a continuous mixing process by developing a Process Failure Modes and Effects Analysis (PFMEA) and a conceptual process flow diagram. This work helped to identify critical process variables and potential pitfalls that would prevent successful mixing, such as improper material flow rates or inadequate mixing times. BMP then consulted experts in the field of continuous mixing, specifically considering both dynamic and static in-line mixers, continuous extruders, various gravimetric feeder designs and liquid pumping systems.

A total of three commercial vendors were consulted during the evaluation of various in-line mixer designs. Static mixers, which have no moving parts and simply alter the flow pattern of the product by placing baffles in its bath, were removed from consideration due to concerns about being able to vary the applied shear level. Dynamic in-line mixers vary mainly in the design of the mixing chamber with different mixing volumes, flow rates, mixing configurations, setup and maintenance requirements, and cost considerations. These dynamic mixers are not capable of processing powder feeds, however, and would require the additional step of generating a slurry prior to mixing and were therefore eliminated from consideration. The continuous extruder could process both solids and liquids simultaneously and consist of specially designed paddles to specify the mixing conditions. These paddles can be altered to modify the mixing process depending on the desired properties, providing significant flexibility. BMP's manufacturing process requires more than ten different MPL ink recipes, each of which may require slightly different processing conditions, so versatility was a significant factor in selecting the continuous extruder technology.

The critical considerations for the mixing design were ability to process and wet-out carbon powders, mixing shear rate range and versatility, bubble generation, ink flow pulsation and residence times. A continuous extruder was chosen based on these requirements, the properties of our raw materials, and the ability to scale the mixer easily by increasing the barrel size. Mixing trials were completed at a vendor to identify the optimal paddle configuration (mixing chamber design), flow rates, and fluid temperature to adequately mix the materials. Over twenty different trials were conducted over a two day period and the mixer was successful in mixing two different MPL configurations, which were chosen to represent the range of inks that are used in BMP's manufacturing process.

Once the mixing system was specified, focus shifted to the liquid delivery system. The major criteria considered for the liquid delivery system are provided in Table 4.1. Sine pumps were chosen for this application due to their low shear rates, high suction (important for our viscous fluids), low pulsation rates and easy maintenance. Pressurized tanks were chosen to house the fluids due to their highly viscous nature, which require some assistance (beyond gravity) to flow. Appropriate motors and VFDs were selected for these pumps and a pumping station was designed with capacity to hold the volume of each tank in case of a leak. Appropriate mass flow meters for each of the raw ingredients, as well as DI water, were purchased for these systems to ensure accurate feed rates.

Table 4.1 - Liquid Pump Selection Criteria

Potential Concerns	Pump Design Requirements
Durability/Leaking of fluids	Chemical compatibility of wetted parts
Viscosity of fluid	Suction lift, pressure capabilities
Liquid ingredients vary based on mix design	Flexibility to pump more than 1 fluid type
Shear rate & pump speed	Low-shear, VFD controls
Digital/Analog inputs/outputs	Installation Requirements
Air Entrainment	Pulse Less Flow
Run Dry	Self Priming

The final major concern for the continuous mixing system is the solids delivery system. There are many different kinds of powders that are used based on the ink design, so it was important that the chosen powder feed system was versatile. Based on the estimated flow rates, it was determined that there were two very different solids types that should be evaluated separately. Three different vendors conducted testing of each powder type over the expected feed rate range for the system. The technologies considered included single screw, twin screw and rotating disc gravimetric feeders. Each of these designs evaluated the powder types over the operating range with a sample of the evaluation results provided in Figure 4.1. The requirements for each powder design were very different and each technology had strengths and weaknesses for our system. Each of the options was evaluated based on six criteria (listed in order of importance) which were:

- 1) Feed Accuracy
- 2) Unit Cost
- 3) System Versatility
- 4) Manufacturability (ease of scale-up)
- 5) Support (technical support availability)
- 6) Reliability (company history/size)

Based on this evaluation, single screw gravimetric feeders were chosen for this process. These feeders showed high accuracy over the range of expected flow rates, provided versatile design with fast set-ups, are available in various designs and sizes for easy scale-up, and the supply company has a solid technical support group with a long history of success.

Figure 4.1 - Representative continuous solids delivery equipment evaluation test results

4.2 Installation of Equipment

All of the equipment for the in-line mixing system was received at the end of the first year. An engineer was assigned to design an appropriate layout for the in-line mixing equipment accounting for: operator safety, spatial and electrical requirements and cost. Based on these requirements, a support for the gravimetric feeders was designed to attach to the in-line mixer, allowing them to be safely held above the mixer inlet. A metallic funnel was designed to fit over the mixer inlet and reach the appropriate height of the feeders to ensure that the powders will get into the mixer as they are fed. The entire area was enclosed with Plexiglas thereby eliminating operator exposure to airborne carbon particles during refilling. The enclosure opens at the top to allow for simple and safe re-filling and will open on either side for easy removal and cleaning of the gravimetric feeders.

The liquid delivery system consists of three pressurized tanks, each set in a metallic tray, which can act as primary containment in the event of a liquid leak. Each of the delivery systems consists of a pressurized tank, a sine pump, a 0.5HP motor and piping to the in-line mixer. A DI water line is being run to the in-line mixer and electricity and compressed air lines are being run to all of the individual components, which have been set in their final location. A heat exchanger was sized and added to the system, along with thermocouples along the mixer barrel, to allow for precise control of the fluid temperature during the mixing process. The completed continuous mixing process is shown in Figure 4.2.

The system has been fully automated using LabVIEW to provide complete control over the system by a single user. This system utilizes PID control loops along with mass flow controllers to ensure accurate feed of each raw ingredient. The system has the ability to stop the process in the event of a processing error, thereby preventing the production of bad product. This process has the potential to reduce the manufacturing time in half, improve the variability of the mixing process, both from batch to batch and within a single batch and provide a simple, efficient clean/changeover process enabling production of ink on demand.

Figure 4.2 – In-line mixing system setup

4.3 Characterization of Ink Properties

Work has been done to characterize the rheological properties of the various batch produced sublayer inks. Critical information, including the ink particle size distribution, viscosities, viscoelasticity, and solids % have been measured and will be used as a bench mark for the in-line produced ink formulations. A sample graph showing the particle size distribution (psd) of various inks is shown in figure 4.3.

Figure 4.3 – Image displaying typical particle size distribution for various sublayer inks

For this analysis a rotational steady state, controlled shear stress/ controlled shear rate, rheometer was used. The measuring sample was positioned in the measuring gap between a stationary measuring cup and a rotating, serrated measuring bob. The

rheometer can run either a controlled stress test or a controlled rate test. Based on which option is used, several curves can be generated from the results of these tests.

In general, many tests were conducted specifically to determine the impact of adjusting certain variables. For these tests, ink samples were taken and each of the different tests was run on the rheometer. The curves generated from these tests were compared and the impact of these variables was determined from the observed differences. In order to utilize statistical software packages, certain aspects of these curves had to be quantified, such as slope, maximum points, and y-intercepts. These values were used to identify key process variables, with some examples described below.

The yield stress (YS) is the applied stress that must be exceeded in order to make a fluid flow. The higher the yield stress the less likely the ink is to change at rest or in storage, thereby impacting the shelf-life of the fluid.

The yield modulus (G) is the gradient of stress vs strain in a constant rate test. A steeper curve indicates a stiffer solution, which corresponds to an improvement in the quality of the mixing of our fluids.

The Ostwald power law index (n) gives an indication of how Newtonian a fluid is. As the Ostwald index approaches 0 it indicates a more shear thinning fluid. The equation is:

$$\eta = \kappa \dot{\gamma}^{(n-1)}$$

η = Viscosity

$\dot{\gamma}$ = Shear rate

κ = Consistency factor – viscosity at shear rate = 1 (1/s).

n = Power law index

Understanding this relationship is key to assessing the quality of the ink and ensuring performance in the MAAT process.

4.4 Validation of Continuous Mixing Process

The first step in the initial validation of the continuous mixing process was producing significant volumes (>5 gallons) of three standard ink designs that are used in the GDL designs being verified in this program. The second step was verifying the liquid and solid feed rates to the continuous mixer by measuring the solids percentage of the continuous inks. After completing the demonstration and verifying the properties of the inks, the final step was verifying performance by coating the inks (one at a time) using the standard coating process to verify functionality. The results of this coating trial, coupled with ex-situ measurement of critical GDL properties such as thickness and basis weight, demonstrate the feasibility of the continuous mixing technologies. Additional in-situ analysis (single cell) is used to verify the performance of the GDL made with continuous inks.

After this initial validation, subsequent work focused on improving the mixing uniformity for all six of the inks used in this program (anode and cathode materials), improved filtering/de-gassing of the inks, matching the physical properties of the standard batch

made inks and then integrating these inks into the new MAAT coating process. Both ex-situ and in-situ (10+ cell stacks) testing will verify the performance of these GDLs.

4.4.1 – Initial Validation of Continuous Inks

The three inks used in the production of the anode material were selected for the initial manufacturing trials. These inks were representative of the different types of carbon/graphite particles that are used in various MPL ink designs and had a significant production history that could be used for comparison. The first two sublayer inks both mixed adequately in the continuous mixer with the configuration determined during the mixer trials at the vendor. The third sublayer ink, which contained a different style of carbon powder, did not mix adequately during this first trial.

It was determined that the residence time in the mixing chamber was not adequate to wet-out the powders and the result was an unusable ink. Some efforts were made to reduce the output of the continuous mixer, thereby increasing residence to improve the uniformity of the ink. Additional efforts examined the location of the liquid injection ports, the barrel temperature and the ratio of surfactant to viscosity agent was modified in an attempt to improve the ink quality. The end result was a useable sublayer ink that appeared to have similar properties to the standard formulation.

The inks generated on the two inch continuous extruder were coated one at a time using standard coating practices to create an Anode roll. There were no significant problems with coating the first two sublayer inks with our standard process and the material appeared normal. The third sublayer ink did appear to be somewhat different from the standard ink, although it could be processed and coated on the paper. These differences were considered minor (e.g. difficulty pumping/filtering, particulates in the ink, etc.) and were attributed to the modifications made to continuously mix this ink design. Additional focus (discussed in section 4.4.2) was spent on improving the quality of this ink design for subsequent testing.

This anode roll was cut into one meter long pieces and each piece was tested on both the left and right sides. Charts showing the down-web and cross-web uniformity of both thickness and basis weight for Anode material are shown in Figure 4.4. The consistency and uniformity of the difference in basis weight (left to right) led to the conclusion that it was a setup issue and not related to the in-line ink itself. The overall conclusion from this work is that the continuous mixing process can adequately mimic the standard batch process and that the continuous inks can be coated via our standard process to make GDLs.

Figure 4.4 – Thickness and basis weight of left vs. right side as a function of distance down-web of anode material processed with in-line ink

Single cell testing, performed on a 50cm² single cell test unit, was completed under three different sets of conditions to determine any performance variations. Each performance curve is the average of a 6 individual tests, which should help remove variability due to the catalyst coated membrane (CCM) or differences in setup. The results from dry conditions (<20% RH), medium conditions (<60% RH) and wet conditions (>75% RH) can be seen in Figure 4.5. The results from this single cell testing showed that there was no significant performance loss due to the new inks vs. the standard baseline. These data, combined with the ex-situ measurements, validated the continuous ink mixing process.

Figure 4.5 – Single cell performance curves under various operating conditions with GDL manufactured with continuous inks and standard (baseline) inks.

4.4.2 – Improving the Ink Mixing Process and Short Stack Validation

After the initial validation of the continuous mixing process, efforts focused on manufacturing two rolls of anode and two rolls of cathode GDL, utilizing inks made with the new continuous mixing technology in conjunction with the multilayer coating system.

Both of these technologies had been validated independently, but to this point had not been run in conjunction. This material would be validated through ex-situ and in-situ (10 cell stack) performance and compared to baseline materials. One anode and one cathode roll would be processed on day one, followed by a complete clean-up and finally another roll of anode and cathode materials. Each of these rolls would be run with a different set of continuously made inks to verify repeatability of the mixing process.

The microporous layer (MPL) inks (six designs) used in these trials were manufactured over a 10-day period using the continuous mixing equipment. Both the anode and cathode GDLs consist of a carbon paper substrate with three MPL coatings. Ex-situ testing was performed on each of the continuous MPL inks to be sure that they were within specification limits for our normal product process. All of the materials were produced successfully with no apparent issues.

During the first MAAT coating trials with these continuous inks, an issue was found with the 3rd MPL ink on the anode. This ink caused many streaks and defects in the top MPL, producing poor quality GDL. Initial analysis determined that these defects were caused by increased air content within the ink, as well particulates passing through the filter to reach the coating head. Based on these findings, the MPL inks for the anode were drained and replaced with the cathode inks. The 3rd sublayer ink for the anode was then filtered and degassed to remove the air and particulates that were causing the problems.

Focus then shifted to manufacturing a roll of cathode material. The coating trials were a success in that the loadings matched the target and few coating defects or streaks were observed in the material. After this cathode roll was finished, the coating head and dispensing skids were completely disassembled and cleaned by the operators as planned. Next, the coating head was reassembled and the equipment was set-up for another anode material run with a different lot of continuous inks. As this material was run, we discovered that there was an incompatibility with the 1st MPL ink. It was then decided that the coating inks should be switched from anode to cathode. The focus then shifted to producing a roll of cathode material, which was manufactured with no issues.

Overall these coating trials were successful in that we were able to utilize both the continuous mixing and multilayer coating technologies in conjunction with each other. We also learned that there were issues with the anode inks that were made continuously, which need to be addressed. These issues were related to the modifications to the ink formulations that were required for multilayer coating to eliminate micro-cracking in the top layer. During the anode coating trials, it was also discovered that all continuously made coating inks require thorough filtering and degassing prior to utilizing the multilayer coating head. Any entrained air or particulate matter will create coating defects, especially in the 3rd MPL, which contains very small carbon particles.

Based on these findings, a process was developed to thoroughly filter and degas the inks prior to being transferred to the coating skids for MAAT coating. The coating skids were fit with an additional filter, such that the inks are filtered twice prior to reaching the coating head. The issue encountered with the 1st anode MPL ink appears to be related to the shelf life. This was determined by an examination after use, during which it appeared that a significant amount of the solids had fallen out of solution. The ink in question was made approximately 6 weeks prior to use. It was determined that the shelf

life of the continuously made inks could be extended via remixing, but using the materials quickly after they are made is preferable to remixing the inks.

At the conclusion of these coating trials, the mixing equipment was disassembled as part of the standard maintenance procedures. At this time, it was observed that oxidation was present on several of the mixing paddles. Figures 4.6-4.8 show images of this oxidation, as well as paddles that appear to be unaffected. This oxidation was surprising because the paddles were specified as solid 316 SS, which should not oxidize under our mixing conditions. Fuel cells, particularly the catalysts, are extremely sensitive to metallic contaminants. This discovery calls into question the material manufactured during these trials, which makes the use of these materials undesirable for single cell and short stack testing, as originally planned.

The manufacturer of the continuous mixer was contacted and shown the images of the oxidation seen on the paddles. They assured us that they would fix the problem and manufactured replacement paddles. The inks and coated materials made during these coating trials were evaluated for metal contaminants with the results provided in Table 4.2. Although the contamination level was low, new material was manufactured for the final verification trials to give the most representative performance.

Figure 4.6 – Images showing oxidation of some paddles in the continuous mixer

Figure 4.7 – Close up of paddle oxidation seen during PM

Figure 4.8 – Close up of paddles showing no signs of oxidation

Samples of each MPL ink manufactured before and after the paddles were replaced were sent for analysis. The standard range is a best guess based on analysis of similar inks manufactured in the standard batch mixing process. Since the design of the MPL inks was modified for the continuous mixing process, the comparison is not ideal, but it does give a good feel for what can be expected. The results are presented in Table 4.2, with MPL 1A referring to the first sublayer manufactured with the oxidized paddles and MPL 1B referring to the first sublayer manufactured with the replacement paddles. The values highlighted in red are the values that fall outside of the expected range. The overall results of this analysis showed that there was no significant difference in metals content in the inks made with the oxidized paddles.

Table 4.2 – Analysis of Metals Content of Various Continuous MPL Inks

Sample	Al	Cr	Cu	Fe	Mg	Ni	Pb	Si	Zn
Standard Range	0-10	0-2	0-2	0-5	0-2	0-10	0-1	0-3	0-2
MPL 1A	5.7	<1	<1	3.7	<1	6.7	<1	<1	<1
MPL 1B	7.4	<1	<1	11.3	1.1	9	<1	3	1.7
MPL 2A	11	<1	<1	4.2	<1	5.2	<1	2.7	<1
MPL 2B	5.3	<1	<1	3.6	<1	5.5	<1	<1	1.1
MPL 3A	4.3	<1	<1	1.5	5.2	4.5	<1	1.3	2.5
MPL 3B	<1	<1	<1	<1	<1	3.2	<1	<1	<1

* All results in ppm

4.4.3 – Final Manufacturing Trial

Efforts then began on repeating the manufacturing of two anode rolls and two cathode rolls using both the continuous mixing and MAAT coating technologies. Microporous layer (MPL) inks were manufactured in the continuous mixer over a 10-day period for these coating trials. In an effort to minimize shelf life issues, the anode inks were made first, followed by the cathode inks, to mimic the order in which they are coated. The result was about an 8 day delay between the time the inks were manufactured and when they were used for MAAT coating. Based on the observations from the previous coating trials, special care was taken to ensure the inks were sufficiently filtered and degassed, especially the ink for the 3rd sublayer. Once the inks were manufactured with the continuous mixer, the unit was disassembled and we saw no indication of further oxidation of the paddles.

It should be noted that there are some significant differences between the standard inks and the inks manufactured for these trials. These modifications were necessary to eliminate issues, such as micro-cracking, that were previously observed when using the MAAT coating process. The solids percentage in each mixture was increased in an effort to reduce the overall wet-load. This increase in solids leads to a more viscous ink, as shown in the results from Table 4.3. These changes make direct comparison vs. standard inks difficult, but the inks fell within the expected ranges and were therefore approved for use in the MAAT coating trials.

Table 4.3 – Physical Properties of Standard and Test Inks

Type of Ink	Standard Material		Trial Material	
	Viscosity	% Solids	Viscosity	% Solids
Anode SL 1	6,600	13	10,000	15
Anode SL 2	6,800	13	9,800	15
Anode SL 3	5,500	10	7,500	11
Cathode Sublayer 1	7,300	13	10,700	15
Cathode Sublayer 2	7,000	13	9,600	15
Cathode Sublayer 3	5,500	10	7,500	11

The MAAT coating trials began with the operators assembling the coating head, setting up the mass flow meters, on-line viscometers and basis weight sensors, and adjusting the oven to the proper drying profile. The inks were first coated onto a polyester film to ensure that the flow rate targets from the mass flow meter gave the proper coverage and to provide data to confirm that the basis weight sensor was performing correctly. Next, the anode substrate was coated using the continuously made inks and the MAAT coating head and some issues were encountered with the filtering of the ink during the trial.

The filter on the pump cart of the 1st sublayer ink became clogged quickly and after the filter was changed, an obstruction was discovered in the coating head. This obstruction led to a continuous coating streak down one side of the material. This obstruction could not be removed, despite repeated efforts. It was decided that the impact of the obstruction was minimal and that the coating could continue. The same streak was visible throughout the second roll as well. Towards the end of the second roll some additional agglomerations reached the coating head causing some additional streaks and other coating blemishes. The mass flow meters ensured the proper loading for each sublayer; the drying conditions prevented any sublayer micro-cracking and the basis weight sensors were used to monitor the uniformity throughout the roll.

Once coating of the anode material was completed, the coating head and dispensing skids were completely disassembled and cleaned by the operators. The obstruction in the coating head appeared to be a clump of solids that got past the filter, which was not easily dissolved. The operators then re-assembled the head and the dispensing skids and prepared for the cathode coating trials. Again the on-line control tools were set up and the drying profile was set by the operators with minimal engineering support. The cathode rolls were then successfully coated without pumping or filtration problems.

There were, however, what appeared to be very small particulates in the top sublayer. These particulates seem to be small agglomerates that are either found in the carbon powder or created during the continuous mixing process. These particulates did cause a few minor streaks and blemishes randomly throughout the coating run. The powder that is used in the making of sublayer 3 is often clumped due to compaction during packaging/shipping and the continuous mixer may not acceptably break up these clumps during mixing. Even with these minor issues, these trials can be considered generally successful. We were able to coat the continuously made ink with the MAAT coating head, the loadings were controlled and there was no cracking in the layers. The material was then cut up for ex-situ and in-situ testing to compare to our standard baseline materials, the results of which are reported in section 7.2.

4.5 Process Control Tools

In addition to surface tension, viscosity, solids content, and bubble content, additional variables have been identified for process control and measurement. These include pH, particle size distribution, and temperature. Two types of viscometers have been evaluated; constant shear rate and variable shear rate. The advantages of the constant shear rate tools are their simplicity and low cost. However, their shear rate is generally very low while the shear rates in the coating processes are very high & variable, and the viscosity-shear rate relationship is non-linear. The advantages of variable shear rate viscometers are the ability to measure viscosities at the shear rates of interest over a wide range of temperatures, and measure solution changes that cannot be captured with a single-point measurement. The disadvantages are their complexity of operation and high cost.

4.5.1 – Surface Tension

Surface tension measurement techniques and equipment were evaluated. Static methods based on the DuNouy ring & Wilhelmy plate techniques have been eliminated from consideration since the coating solutions are not pure liquids and their surface tension is not constant. Dynamic measurements more accurately reflect the practical, in-process, state of the inks. Dynamic techniques under assessment include oscillating jet, drop volume, and bubble pressure. The advantage of the oscillating jet technique is that the surface age can be determined whereas the surface age from the drop technique is often unknown. The main disadvantages of the oscillating jet technique are the complicated orifice, and the high cost due to the need for sophisticated equipment to measure wavelengths and jet radii. The drop volume technique determines surface tension from calculating physical drop characteristics as it forms at the end of a capillary tip of known external radius. The bubble pressure method is based on the maximum pressure in a capillary necessary to produce and detach a bubble from the capillary tip immersed in the test solution. The advantages of both the drop volume and bubble pressure techniques are their simplicity. The drop volume instruments have been adapted for in-line sampling but the bubble pressure instruments are limited to ex-situ QC testing. Samples of inks were assembled and sent to manufacturers of both the drop volume and bubble pressure instruments for capability testing.

Evaluation of the dynamic surface tension meter was completed and a multiple probe, maximum differential bubble pressure method surface tensiometer with full automation and a patented viscosity compensating design was purchased and received. It was set up and a procedure for calibration and operation was put together. A group of samples of each type of ink was collected and analyzed on the tool to better understand the measurement accuracy and repeatability. A procedure that provided repeatable curve results could not be established, however, due to the properties of our inks. Instead, a curve was generated by creating a subroutine that would systematically change the bubble rates based on specific parameters, wait for equilibrium and then measure the surface tension at those conditions. By running several test conditions one after another, a curve could be generated.

The problem with our inks was two-fold. First, it seems to be our material is so viscous that the fluid clogs in the sampling tube, providing a false high surface tension reading, especially at slow bubble rates. When the bubble rates were high enough to avoid clogging the sampling tube, the surfactant would deposit on the outside of the probe and create a false low surface tension over time. We were able to address these issues by

running one condition at a time and cleaning the tube between each run. This process was much more time consuming, however, and could not be done continually. As such, this tool was used to characterize the inks, but was not a standard measurement for every batch of ink that was produced. These limitations indicated that for our process it would not be feasible to use this as an in-line measurement tool.

From the results of our characterization studies, we found that all of our MPL inks had a similar surface tension. Since these inks only had a few components in common, it became easy to determine which of the raw materials influenced the surface tension of the inks. By performing multiple dynamic surface tension curves on this raw material, it was possible to determine specifications for alternative products that could replace the original raw material. Fortunately, it was found that this was not necessary because it was possible to successfully MAAT coat our inks without further modifications.

4.5.2 – In-line Viscosity

Multiple in-line viscometers were evaluated, including: rotational, falling piston, shear wave, and electromagnetic. Vendors of each type of viscometer were contacted to determine equipment cost and measurement feasibility with our inks. Lab-scale testing was performed with various ink samples. The in-line rotational (flow through) viscometer was eliminated because the required flow rate was greater than the ink delivery process flow rates. Falling piston viscometers were eliminated due to their inability to handle the particles present in the solutions.

Two sensor technologies, shear wave and electromagnetic, were short-listed for detailed analysis. The shear wave technology utilizes significantly higher shear rates than our ink delivery process, does not fall in the shear rate range of current quality control ex-situ measurement practice, and does not measure temperature. The electromagnetic viscometer employed too low of a shear rate than the ink delivery process; however, the shear rate was in the range of ex-situ measurement and the sensor measured the ink temperature. Working with the manufacturer, the electromagnetic sensor was modified to increase the shear rate to a value that was suitable for both ex-situ quality control verification and ink delivery process control.

Electromagnetic viscometers were chosen based on the fluid properties and system requirements. See section 3.5.4 for details on the installation and debug of the sensors in our process as well as the limitations we found with these sensors.

Viscosity readings from the inline viscometers used during the MAAT coating trials were compared with solution sampled post the in-line viscometers and tested using our standard lab bench Brookfield viscometer. The viscosities were, in general, linearly offset therefore a correlation was made to relate in-line viscosity to off-line measured viscosity. It appears that the correlation is stable and the offset is a constant, as shown in Figure 4.9.

Figure 4.9 – Comparison of In-Line and Lab Viscosity Measurements

4.5.3 – Flow Meters

Two different flow controllers were chosen for this process. For the DI water a FloCat® was installed, which determines the flow rate by measuring a pressure drop across a unique internal restriction. This restriction is designed such that the water molecules are forced to move in parallel paths along the entire length of the passage. This establishes laminar flow over the entire range of operation of the device. The Poiseuille Equation can be used to determine the volumetric flow rate, provided that the fluid viscosity is known. This is a simple design that accurately controls the volumetric flow rate of water over the range of flow rates required for the mixing system.

For the other liquids, an Intek Rheotherm flow meter was chosen due to the highly viscous nature of these fluids. These sensors use a thermal sensing technique that accurately measures the flow rate using two temperature sensors. The first sensor is in thermal equilibrium with the incoming fluid while the second sensor is located near a heater and is, therefore, at a slightly higher temperature. The rate that the heat is removed from the second sensor is directly related to the flow rate of the fluid and the temperature difference between the two sensors correlates directly to the fluid flow rate.

4.5.4 – Rheometer

For this analysis a rotational steady state, controlled shear stress/ controlled shear rate, rheometer was selected, as discussed in section 4.3. The measuring sample was positioned in the measuring gap between a stationary measuring cup and a rotating, serrated measuring bob. The rheometer can run either a controlled stress test or a controlled rate test. Based on which option is used, several curves can be generated from the results of these tests.

4.5.5 – Particle Size Distribution

Three different measurement techniques were evaluated for determining the particle size distribution, including laser light scattering, electrical sensing and ultrasonic spectroscopy (acoustic scattering). The laser light scattering technique requires a heavily diluted sample and is prone to particle agglomeration and skewed distributions for our inks. Similarly, the electrical sensing zone method also requires high levels of dilution and is subject to agglomeration. These two techniques were eliminated from consideration based on these evaluations.

The ultrasonic spectroscopy method is a relatively new technology that is capable of analyzing concentrated, multi-component mixtures without requiring dilution. Samples were sent to a vendor's lab for ex-situ particle size distribution analysis. It was found that the accuracy of the distributions was highly dependent upon the accuracy of the volume concentration of the solids. Based on this analysis the ultrasonic spectroscopy method was selected for analyzing our inks.

Particular attention was given to the dependence of the PSD accuracy on the variation of volume percentage of solids, such that it was possible to accommodate the widest range of ink rheologies. For our inks, it was found that with low volume percentages of solids (e.g. <6%), there will be significant errors in the measured PSD by the tool. When the inks have high volume percentages of solids (e.g. >30%), the error associated with the PSD measurement will be very small unless there are variations greater than 10% volume percentages of solids. The various inks made in this program all have moderate volume percentages of solids (>10%) with fairly minimal variation and are therefore adequate for use with this tool.

Ultimately the ultrasonic particle size distribution tool was not selected as an on-line tool for this program. Although the trials showed that the tool would work properly with our material, it was determined that the costs of the tool far outweighed the benefits. This is because the particle size distribution does not change significantly from batch to batch as currently prepared. Samples of the inks made with the in-line mixer will instead be sent out to independent labs to determine the particle size distribution as part of the ink qualification.

5 – Substrate Processing Improvements

The GDL substrate, or paper base layer, is critical to producing GDLs that are optimized for a specific application. The substrate sets the range of many critical GDL parameters such as thickness, basis weight, porosity, water vapor diffusivity, and thermal/electrical properties. The substrate design is chosen for an application and then modified through hydrophobic (PTFE) coatings and the addition of one or more microporous layers (MPLs) for optimal performance in a fuel cell system. As such, there are a limited number of base substrates that are used to form many different GDL designs.

One way to help reduce the fabrication costs of GDLs for near-term markets is to increase the manufacturing efficiency and product yields of the GDL substrates. Since these substrate designs are used in multiple final products, small improvements can have a big impact on overall cost. Another way to improve the GDL costs is to improve the understanding of how process parameters affect GDL properties, thereby improving product uniformities and eliminating product failures.

In this program, BMP first focused on improving the substrate manufacturing process by evaluating process variables on each of the five process steps involved in manufacturing the GDL substrate. Developing an understanding of how changes in operational variables, such as web speed, and set-up variables, such as process temperature, influence critical GDL properties is important in improving manufacturing efficiencies. If a variable is found to have a critical impact, then improving controls will help improve product uniformities, whereas a variable that has little or no impact can be modified to improve efficiency.

The secondary focus in this program was to transfer from half-width (400mm) to full-width (800mm) production. At the beginning of this program, all materials were run at half-width due to web breaks and inconsistent properties both across-web and down-web when materials were run at full-width. This severely limited production capacity and increased the GDL costs, but was required in order to meet production specifications. Process scrap rates were higher than necessary due to inefficient manufacturing, product yields were low due to multiple web breaks, and GDL costs were high due to a significant rate of product failures due to inability to meet tight customer specifications.

The tertiary focus in this program was to implement on-line processing and control tools where possible to improve the manufacturing process. This includes processing tools, such as tension control systems to eliminate web breaks, and control tools, such as non-contact thermocouples to control web temperature throughout a process. Additional tools, which did not fit in the scope and/or budget of this program, have been identified to improve the manufacturing process and reduce the fabrication costs further.

5.1 Evaluation of Processing Parameters

The evaluation of the impact of processing parameters on critical GDL properties began by identifying critical GDL parameters and why they are important to success. The list of properties identified for consideration is presented in Table 5.1, but the level of importance and reason for their selection have been omitted due to the proprietary nature of the process.

Table 5.1 – Critical Variables for GDL Production

GDL Variables	
Basis Weight	Diffusivity
Flexural Stiffness	Hydrophobicity
MPL Composition	MPL Thickness
Permeability	Porosity
Surface Roughness	Thickness
Thermal Conductivity	Electrical Resistivity

Once the critical GDL properties have been determined, the key process variables at each production step were identified. The substrate production process consists of five critical steps as described in the process flow diagram shown in Figure 5.1. Each step was examined and a list of process variables, such as web speed, process temperature or system pressure, was established and each variable was ranked by importance.

Figure 5.1 – Substrate Manufacturing Process

After the critical GDL properties were identified and the process variables were determined, the focus moved to implementing a data collection system. An on-line database system was developed and implemented to gather data during actual production runs. A second database was used to collect information on the critical GDL properties as measured during quality inspection at the end of the substrate production process.

After collecting a significant amount of data on each process, the data were analyzed using JMP® statistical software to identify potential links between process variables and critical GDL properties. Based on this analysis, a set of experiments was designed to test the impact of key process parameters on GDL properties. In some cases, as shown in Figure 5.2, strong relationships were found between a process parameter and a critical property. In other cases, as shown in Figure 5.3, there was no significant

relationship. These relationships are not explained in detail due to their proprietary nature, but they are critical to understanding the GDL manufacturing process, improving product quality and reducing GDL costs.

Figure 5.2 – Impact of A) Process Variables on GDL Diffusivity and B) Process Variables on GDL Tensile Strength

Figure 5.3 – Impact of Process Variables on Flexural Stiffness

Once the relationships between process parameters and critical GDL properties were determined, the focus moved towards improving production controls. Empirical models were constructed based around these relationships, which allow BMP to adjust parameters throughout the production process to control the final GDL properties. These improved process controls significantly reduce the GDL production costs by severely reducing rejection rates and part failures. An example of the process capability of meeting a tight specification window before and after the implementation of the empirical models is shown in Figure 5.4. It should be noted that the lower specification limit (LSL) and upper specification limit (USL) shown in Figure 5.4a and 5.4b are the same values.

Figure 5.4 – Process Capability A) without and B) with Empirical Control Models

5.2 Full-Width Production

The transition from half-width (400mm) to full-width (800mm) production was inhibited by web breaks and product non-uniformities, particularly during the heat treatment process. The first step in understanding these issues was to improve the understanding of the heat treatment process, which was done in a standalone furnace. Work then focused on improving the tension controls and unwind/rewind systems on the production heat treatment process. The final step was to improve the process controls on the heat treatment equipment. After all of these changes were implemented, a full-width production roll was manufactured and dissected to determine cross-web and down-web uniformity.

The ex-situ analysis began with an understanding of the impact of critical parameters including: temperature, heating rates, thermal soak times, and type atmosphere conditions. The first goal was to understand how these parameters influenced the rate of volatilization and, thereby, the carbon yields of the process. These properties greatly influence the strength of the paper, which should help to eliminate web breaks. The initial results, shown in Figure 5.5, indicate that modifying the first heat treatment step has a significant impact on constituent A, but less so on constituents B or C. Further efforts, not included due to their proprietary nature, allow for the improved control over the rate of the other constituents as well.

The understanding of how these modifications influence the volatilization rates of the constituents of our GDL substrate is important in predicting how the structure will be formed and setting the back-bone of the substrate. These modifications allow for a stronger material with the same overall pore structure. This is very important because other changes to improve the strength of the paper would have a negative impact on the performance of the GDL, while these changes do not.

Figure 5.5 - TGA Results of Substrate Paper Precursor Pyrolysis

Once the impact of modifying the conditions of the heat treatment step were completed, focus turned to improving carbon yields to strengthen the paper further. A set of experiments was conducted where different blends of our constituents were combined with other solids and then subjected to the heat treatment process. By adjusting the ratio of the constituents, incorporating solids and modifying the process conditions of the first heat treatment step, the volatilization rate at the higher heating rate was below the sooting threshold for this process, as shown in Figure 5.6. Additionally, the overall carbon yields through the process were increased with the higher heating rate, as shown in Figure 5.7.

Figure 5.6 - TGA Results of Substrate Paper Precursor Pyrolysis

Figure 5.7 - TGA Results of Substrate Precursor Carbon Yield

These results were very encouraging, but they were not significant enough to eliminate the problem of web breaks by themselves. Additional work was required to improve the tension controls through the roll-to-roll heat treatment processes. An outside vendor was contacted and a new system was designed and installed on the heat treatment line. Additional efforts were spent on controlling the rewind tension to allow for larger rolls (>300m in length) and, therefore, longer run times. These changes allowed BMP to move from production 400mm wide, <300m long rolls to producing 800mm wide, >700m long rolls through the heat treatment process.

The ability to process rolls of these size is a step in the right direction, but they must also be uniform both across-web and down-web. Understanding how the process parameters impact the GDL properties was critical to ensuring uniform properties. The machine setup was modified to ensure that the key process parameters were uniform across-web throughout the oven. Additionally, process control checks were used to ensure that the process remained within the specified windows throughout the entire run, ensuring uniform down-web properties.

A controlled experiment was designed in order to test the uniformity of the GDL after these modifications to the oven. A roll of GDL substrate was run through the first two process steps as a full-width (800mm) roll. Prior to entering the second heat treatment step (where the full-width non-uniformity was occurring), the master roll was split into three 100m long smaller rolls. The first of the 100m rolls was left as is at full width. The second of the 100 m long rolls was then rewound to have the opposite orientation as the first roll in order to account for cross-web variations in the raw material. The last of the 100m long segments was then slit into two half-width rolls.

The first half-width roll was run through the process, followed by the first full-width roll. Next, the second half-width roll was run and lastly the rewound full-width roll was run. These rolls were then sampled every 2m for the length of the roll. The first half-width roll was the left side, while the second half-width roll was the right side. The full-width rolls were split into four samples across to ensure uniformity. The results of this experiment, shown in Figures 5.8 and 5.9, confirm that the new full-width processing is uniform both across-web and down-web with the properties falling in line with the standard half-width

processing. Further testing was completed by BMP's customers, who found no performance issues with using the full-width materials. All GDLs are now run full-width through the GDL manufacturing process.

Figure 5.8 – Basis Weight Measurements for A) Half-Width and B) Full-Width GDL production

Figure 5.9 – Thickness Measurements for A) Half-Width and B) Full-Width GDL production

5.3 On-line Process Control Tools

After determining the relationship between process parameters and critical GDL properties, it is important to be able to control the processes through the different manufacturing steps. Some of the process control tools introduced in the MAAT coating section (Chapter 3), such as basis weight sensors, also apply to the saturation coating step in the substrate production process. These tools will not be included in this section for that purpose. It should also be noted that some process control tools have been identified, but were outside the scope and budget of this program. These tools will not be included here due to the proprietary nature of the manufacturing process and their exclusion from this project.

5.3.1 – Tension Control System

After examining the cause of the web breaks in the continuous heat treatment process line, it was determined that an improved web handling and tension control system was required. A specification was written for a new web handling and tension control system. Included in this specification were special considerations for the properties of our paper. Also, three isolated tension zones were called out; unwind, process, and rewind.

An outside consultant was brought in to design and install a new system based upon the specification. The result was a system that could handle full width, full length rolls without web breaks through the heat treatment process. The unwind could handle all rolls, including rolls with incoming issues (e.g. telescoping). The rewind was able to wind rolls consistently to prevent issues during subsequent process steps. The line speed and tension controls were significantly improved, which led to more consistent product.

Obvious benefits of this system are the ability to process full width, full length rolls through the heat treatment process. This capability more than doubled the material throughput on this process and, by extension, all subsequent processes. Other benefits include improved uniformity due to better control of line speed and tension in the process. This was a significant accomplishment that had a major impact on the near-term volumes and costs of GDL manufacturing.

5.3.2 – Non-Contact, High Temperature Thermocouples

Two high temperature thermocouples were purchased for the substrate manufacturing process, which were similar to the non-contact thermocouples described in section 3.5.5. These had special optic lenses rated to 300°C and fiber optic cabling. These enabled us to put these thermocouples into the oven without the need of cooling. Initial testing showed the measured temperature vs. the supply temperature was about 15°C higher. After further investigation it was determined the thermocouple needed to be recalibrated and it needed to be recalibrated at the temperature in which it operated. One of the thermocouples was sent back to the factory to be recalibrated. In doing so, the factory discovered a film on the optic, which they determined to be from the gasketing in the thermocouple. They replaced the gasket and the optic and recalibrated. However, they do not have the means to calibrate the thermocouple at operating temperature so they calibrated it at room temperature.

5.3.3 – Automated Visual Inspection Station

One of the most labor-intensive portions of the substrate manufacturing process was the final inspection. Prior to this program an operator was required to manually watch a roll rewind and record any visual defects, along with the location on the roll, and provide a defect history to the customer. This was a very slow process, often at speeds between 5-10m/min, and was subject to discrepancies due to operator experience and opinions on what constituted a defect.

A solution to this problem was to install a two-camera system that could automatically detect and log defects in the roll. This process was much more efficient with one camera focused on surface defects, such as lumps, cracks or scrapes, and the other camera focused on through-holes. These cameras can operate at speeds over 20-30 m/min, and provide a full map of defect sizes and locations. Another major advantage is that in addition to actual defects, the system can detect much smaller issues and provide feedback to the manufacturing engineers for each product. This helps to improve the

process and eliminate issues during production that are not necessarily defects today, but could potentially cause product failures in the field.

The increased speed and accuracy significantly reduces the cost required for inspecting the GDL on the substrate level and provides critical feedback to the manufacturing team. The system allows for the detection of defects that are within specification tolerances and can generate a roll report for customers listing the size and location of such defects. Additionally, the system can detect blemishes that are beneath the specification tolerance, which allows us to better understand the production quality of various rolls. This information can provide valuable insight into how various process changes can influence the material, even when it is not considered a defect. This should help further improve GDL quality in the future.

6 – Development of a PTFE Distribution Measurement Tool

In addition to modifying the current process to increase capacity and reduce fabrication costs, one of the program goals was to develop on-line process control tools for the GDL manufacturing process. Many of the key GDL properties can be measured by adapting existing technologies for our production process, as described in the on-line tools sections in Chapters 4 and 5. One GDL property that was believed to be critical for GDL performance, which couldn't be measured with currently available tools, was the chemical homogeneity or the uniformity of the distribution of PTFE in the substrate.

It is simple to determine the total loading of PTFE on the GDL substrate by measuring the basis weight before and after coating, but determining where that PTFE is located in the GDL is much more difficult. The Pennsylvania State University, under the direction of Dr. Michael Hickner, was given the task of determining the best method to measure the PTFE distribution in the GDL. The method must be able to determine the difference in PTFE loading on the surface of the GDL versus the PTFE loading in the center of the GDL.

Once the measurement technique is established, the work focused on determining if the PTFE distribution could be significantly modified by altering process parameters in the production process. Efforts then focused on establishing if the measurement technique could be adapted to an online measurement process. Additional work was done to determine if changes in the distribution affected critical ex-situ properties or in-situ performance of the GDL. If the PTFE distribution could be modified by altering process parameters in BMP's GDL production process and those modifications influenced ex-situ properties or in-situ performance, then an on-line measurement process would be developed.

6.1 Evaluating Measurement Techniques

The development of a tool to characterize the chemical homogeneity of the GDL began by evaluating methods including: Near Infrared, Raman and X-Ray Fluorescence spectroscopy. Performing these measurements on GDL samples proved difficult, however, with challenges including: high surface roughness, micro vs. macro spatial resolution and interference from constituents in the GDL not under detection (binder, fill materials, etc.). Raman spectroscopy showed the most promise of these techniques as a PTFE Raman peak is distinguishable from a carbon peak, as shown in Figure 6.1. This allows us to construct a chemical image map by using Raman scanning over a defined area, as shown in Figure 6.2.

PENNSTATE MATERIALS SCIENCE and ENGINEERING
Raman Spectra of P50T & Standards

Figure 6.1 - Raman Spectra of Teflonated Substrate and Standards

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Carbon & Teflon data divided by Total intensity

Figure 6.2 - Raman Chemical Image Map of Carbon and PTFE® Distribution

Additional testing found the FTIR spectroscopy could also be viable as an on-line technique to measure the chemical composition of the GDL, as shown in Figure 6.3. The Raman spectroscopy is preferred, however, as it can accurately detect both carbon and PTFE, while the FTIR is only capable of detecting PTFE. Additionally, chemical mapping of PTFE on the surface of the GDL was not possible with FTIR due to the absorption of IR radiation by carbon in the GDL. It was determined that both of these techniques should be pursued, however, because it was possible that FTIR can provide complementary information that may be missed with Raman scanning alone. It is possible, for instance, to detect water with FTIR, but not with Raman scanning. If there is a desire to examine the water distribution in a flooded GDL, FTIR may provide critical information that could not be determined by Raman alone.

Figure 6.3 - Raman and FTIR Vibrational spectroscopy imaging to determine surface PTFE distribution of GDLs

GDL samples were prepared with PTFE loadings of 5, 10, 15, 20, 30 and 50 percent by weight. These samples were then used to generate large-area Raman maps in an effort to determine how the imaging data corresponds to the overall change in PTFE loading. It is expected that increased PTFE loadings will show higher PTFE signals in the Raman scanning, but it is unclear how the PTFE signal will scale with increased loadings. From these trials, it was clear that the data is fairly linear above 10-15% PTFE, as shown in Figure 6.4. When the loading was below 10%, the signal appeared to be constant indicating that at low loadings the Raman technique may not be able to distinguish a difference in PTFE distribution.

Other ways of normalizing the data sets will be investigated going forward, such as examining frequency histograms of the PTFE intensity for each of the maps. The carbon fiber network can be discerned in the carbon maps indicating that the spatial resolution chosen (10 μm) to perform these mapping experiments is reasonable for resolving the salient GDL features. Also, no noticeable differences in the carbon fiber network were seen as PTFE loading was increased. Carbon does not seem to have a noticeable trend, which is probably due to the fact that the carbon content of the substrate is not changing in these experiments.

Figure 6.4 - Normalized average total intensity of the PTFE maps vs. PTFE loading of the GDL substrate.

A second set of GDL samples was fabricated with 2, 12, 16, 24 and 44 weight percent PTFE both with and without an MPL coating. Raman scanning was used to examine these samples before and after being sintered, both with and without an MPL (which contains PTFE). The results of this work, shown in Figure 6.5, indicated that for the plane GDL substrate, there was no difference in PTFE concentration before and after sintering for PTFE values below 24 weight percent. Above 24 weight percent, however, there was a dramatic drop in PTFE signal. When the MPL was added to the GDL, there appeared to be a significant difference before and after sintering above 16 weight percent, perhaps due to the additional PTFE located in the MPL.

Figure 6.5 – Total sum of PTFE counts A) without and B) with MPLs in both sintered and un-sintered GDLs of various PTFE loadings

These results imply that the PTFE located on the surface of the GDL after coating migrates to the center of the material during sintering, when the PTFE content exceeds a certain threshold. Preliminary experiments were conducted on a cross-section of the GDL with 44 wt % PTFE. The GDL was mounted perpendicular to the beam and a Raman map was generated over an area of ~1500 x 150 μm . The sum of the integrated PTFE peak and cross-section scans, which are colored according to Raman intensity with the same color map, are shown in Figure 6.6. The total amount of PTFE detected increased significantly on the cross section of the GDL, further supporting the notion that

the PTFE migrates to the center of the GDL during sintering. Other possibilities for these results include PTFE detection limit issues or sampling issues.

Figure 6.6 – Cross-sectional analysis of the GDL showing A) total sum of PTFE counts and B) color maps indicating an increased presence of PTFE in the center of the GDL upon sintering

To confirm the results of this finding, samples were prepared using a doping agent (tungsten salt) in an effort to increase the PTFE signal on the Raman imaging. These samples were prepared from the same base material with the same PTFE solution and pieces were either sintered, un-sintered or partially sintered (an un-sintered section was removed and marked from the sintered sample). Scanning electron microscopy (SEM) with energy dispersive spectroscopy (EDS) was used to characterize the surface of the GDLs that were doped with this tungsten salt. A set of three samples were analyzed with PTFE loadings of 13, 17 and 23 wt % PTFE, as shown in Figure 6.7. In all three cases carbon, fluorine and tungsten are easily detected, and EDS maps were generated. Figure 6.8 shows a sample EDS map along with its corresponding SEM image and a superimposed triangle was used to highlight the area where PTFE is expected.

Figure 6.7 - EDS spectra of a) GDL with 13 wt % b) 17 wt % & c) 23 wt % PTFE

Figure 6.8 - The left image shows an EDS map of Tungsten while the right image is the corresponding SEM image.

6.2 Examining the Impact of Sintering with Continuous Measurements

Raman scanning has been shown to effectively measure the PTFE loading on the surface of a GDL through 2D scanning. A method must be developed, therefore, to use continuous line scan measurements to simulate on-line measurement and analysis. A 514nm Ar ion laser at 11.5 mW was used for all experiments and spectra were collected every 50μm over a distance of 6mm at a collection rate of 0.5s per spot. After Raman collection, each data set was examined and corrected to eliminate cosmic ray hits or significant fluorescence. The intensity of PTFE at 735 cm^{-1} was extracted from each spectrum and Figures 6.9 and 6.10 show the average and summed peak intensities, respectively. It is clear from this work that the unsintered (green) GDL samples correlate much better to differences in loading than the sintered samples.

Figure 6.9 – Average intensity of green and sintered samples versus PTFE weight %

Figure 6.10 – Summed intensity of green and sintered samples versus PTFE weight %.

Previous work had demonstrated that the PTFE content on the surface of the GDL was different before and after sintering. Initial results indicated that this was due to the PTFE migrating from the surface towards the center of the GDL during sintering. Additional tests were designed to examine the different sides of the GDL to determine if the differences can be associated with the side of the GDL being measured. Continuous line scan measurements of green (un-sintered) and sintered GDLs were performed on both sides of the GDL with PTFE loadings ranging from 11 to 29 wt%, as shown in Figure 6.11. In general, more PTFE is detected on the green surface than on the sintered surface (regardless of side) and more PTFE is detected on the convex (top side during coating) side of the GDL than on the concave side (bottom side during coating).

Figure 6.11 - Line scanning measurements of green and sintered GDLs with 11 to 29% PTFE for convex and concave side of GDL.

Optical images of the cross section of these green and sintered GDLs were taken as shown in Figures 6.12 and 6.13. The PTFE can be clearly seen in the green GDLs and qualitatively, it can be seen that most of the PTFE appears to be closer to the convex

(top) side of the GDL. These micrographs further support the line scanning data shown in Figure 6.11. It should be noted that the bright spots that are seen on the sintered cross-section GDL does not indicate PTFE; when Raman spectra are gathered from that area there is a significant amount of reflected light from the sample.

Figure 6.12 - Cross sectional optical images of green GDL with 28% PTFE. Convex side of GDL is labeled.

Figure 6.13 - Cross sectional optical images of sintered GDL with 28% PTFE. Convex side of GDL is labeled.

The green optical images of the GDLs show that the PTFE is firmly held in place by the carbon fiber network, as shown in Figure 6.14. The probability that most of the PTFE migrates to the bulk upon sintering seems unlikely. While cross sectional Raman mapping proved to be difficult to achieve, single spectrum were collected in a variety of spots throughout the thickness of the GDL. PTFE was detected throughout the bulk and showed no visible preference of being in the bulk or the surface.

Figure 6.14 - Optical image of a green GDL with the PTFE clearly seen as being white/blue (due to the color of the microscope lamp).

From this investigation, two general trends have been established with regards to PTFE loading and the GDL. First, more PTFE is detected on the convex side of the GDL than on the concave side. Second, more PTFE is detected on the surface of the GDL before sintering. The initial theory that the PTFE migrates from the surface of the GDL towards the center of the GDL upon sintering was not confirmed. Rather, the PTFE distribution in high resolution Raman maps of green and sintered GDLs show that the high concentration of PTFE on the surface of the green GDL seems to spread across the surface of the material during sintering. All samples will be taken on green GDLs to prevent inaccuracies due to this spreading of PTFE concentration on the surface of the GDL.

6.3 Developing an On-Line Tool

A new idea, based on the finding that the PTFE spreads over the surface of the GDL after sintering, was proposed to develop a 1D scanning method. In this method, scans could be used to determine average PTFE agglomerate sizes on GDLs on green GDLs. Differences in agglomerate size could relate to changes in the distribution of PTFE in the GDL. Since it is known in the general literature that modifying the drying conditions will influence the distribution of PTFE in the GDL, the goal of this work will be to modify the drying conditions and then examine the PTFE agglomerate size on the surface of the GDL.

The problem was finding a method of 1D scanning that could be used to accurately determine the PTFE agglomerate size. A novel concept was proposed to use the peak widths from the 1D intensity plots to determine the average PTFE agglomerate size. A sample of scans of both 13 and 23 wt % PTFE are shown in Figure 6.15. It is clear from this data that the width of the peaks is significantly different and previous area scans have shown that the PTFE clustering is significantly different. A computer program was developed to automatically define a minimum measurement point (indicated by the blue line in Figure 6.15), which is used as a cut-off for standard noise, and then compute the width of the peaks.

Figure 6.15 – 1D intensity plots of 13 and 23 wt% PTFE loadings, with samples of peak to peak measurements

High resolution maps of green 12, 24, and 29 wt % PTFE GDLs were collected of a 1000 x1000 μm area with a resolution of 10 μm in both the x & y directions. Line scans

were then extracted from each graph and the distance between peaks was used to determine the PTFE agglomerate size histogram plot, shown in Figures 6.16, 6.17 and 6.18.

Figure 6.16 – Areal map, line scan and frequency histogram for green GDL with 12% PTFE taken at $y = 400\mu\text{m}$

Figure 6.17 – Areal map, line scan and frequency histogram for green GDL with 24% PTFE taken at $y = 300\mu\text{m}$

Figure 6.18 – Areal map, line scan and frequency histogram for green GDL with 29% PTFE taken at $y = 500\mu\text{m}$

The high resolution maps can be visually correlated to the line scans and frequency histogram, demonstrating that the process should work. There might, however, be an issue with the resolution, if the system were to be utilized in a continuous fashion. The scan rate would have to match the line speed of the equipment, which means that for a resolution of $10\mu\text{m}$, the power of the laser must be increased to very high levels to process the image at a high enough rate. The required increase in power will subsequently damage the product, unless the measurement area was significantly increased. In other words, we need to reduce the resolution, or spot size, of the laser in order to process the data fast enough to be used on our process line.

Work was done on green GDLs with 17.5 wt% PTFE to determine the influence of the spot size on the accuracy of the frequency histogram. Three different spot sizes were used (25, 50 and $100\mu\text{m}$) and both area maps and histograms were generated as

shown in Figures 6.19 and 6.20, respectively. The resolution in the area maps is degraded as the spot size is increased and the frequency histograms are significantly altered as well. Even with these differences, however, the frequency histogram of agglomerate size, although being dependent on the spot size being measured, could still correlate to PTFE distribution in the GDL.

Figure 6.19 – Areal maps for green GDL with 17.5% PTFE taken at 25μm, 50μm and 100μm spot sizes

Figure 6.20 – Frequency histograms for green GDL with 17.5% PTFE taken at 25μm, 50μm and 100μm spot sizes

An effort was made to determine whether drying conditions would influence the PTFE distribution and thereby the agglomerate size. In support of this effort, three identical samples of GDL with a PTFE loading of 18% were dried under different conditions. One sample was allowed to air dry overnight with no outside influence. The second sample was hand dried with a heat gun over a period of 10 minutes. The third sample was placed in a 140°C oven to dry as quickly as possible. The area maps, shown in Figures 6.21 and 6.22, show the PTFE distribution on the surface of the GDL for both green and sintered GDLs respectively. It is clear from these images that the slow, air dried sample has significantly less PTFE on the surface than the samples that were dried much faster.

Figure 6.21 – Area map of green GDL with 18% PTFE loading that is A) air dried B) hand dried and C) oven dried

Figure 6.22 – Area map of sintered GDL with 18% PTFE loading that is A) air dried B) hand dried and C) oven dried

An image analysis program was used to segment the PTFE groupings to determine what fraction of the surface is covered by PTFE. The results of this analysis are presented in Table 6.1. These results show that the slow air dried samples have roughly half concentration of PTFE on the surface compared to the faster hand and oven dried samples. It is also interesting to note that there seems to be no discernible difference between the hand and oven dried samples. This indicates that although drying speed may influence PTFE distribution on the surface of the GDL, it may not be possible to control this distribution by adjusting the dryer settings on the commercial coating line. Since these were just hand-made samples, however, it is difficult to be sure that the hand dried and oven dried samples were truly different. A controlled drying test on the line needs to be done in order to better differentiate between a “fast” and “medium” drying rate.

Table 6.1 – Area fraction of PTFE on the surface of the GDL

Areal Fraction of PTFE %	Air Dried	Hand Dried	Oven Dried
Dry	45.2	72.7	71.3
Sintered	10.3	19.9	20.0

The air dried samples were investigated using four different spot sizes (25 μm , 50 μm , 100 μm and 200 μm) to determine if the accuracy was reduced by moving to a smaller spot size. The results of this work, presented in Table 2, indicate that although the resolution of the area maps is reduced as the spot size increases, the distribution of PTFE remains constant. This is encouraging as a 200 mm spot size would be required to translate this measurement technique to an on-line tool. Additional work is necessary

to determine if the drying conditions on the coating line can be modified enough to alter the distribution of PTFE on the surface.

Table 6.2 – Areal fraction of PTFE on the surface of green and sintered, air dried GDL

Sample	Areal Fraction of PTFE
Air Dry - 25 μ m resolution	41%
Air Dry - 200 μ m resolution	45%
Air Dry Sintered - 25 μ m resolution	11%
Air Dry Sintered - 200 μ m resolution	11%

Further analysis of these samples was done to determine if the change on the surface could be seen when examining the cross-section of the GDL samples. Sample cross-sections of the air-dried (Figure 6.23) and the oven-dried (Figure 6.24) GDLs showed that the amount of PTFE changed not only on the surface, but in the bulk of the GDL. These results appear to confirm that the PTFE distribution throughout the GDL can be modified by altering the drying conditions.

Figure 6.23 – PTFE distribution throughout the GDL that was air-dried, showing high concentration in the center of the GDL and less on the surface

Figure 6.24 – PTFE distribution throughout the GDL that was oven-dried, showing high concentration on the surface and minimal concentration in the center

This work has shown that radical changes in the GDL drying conditions, such as air drying vs. oven drying, can have an impact on the PTFE distribution throughout the GDL. It was not clear, however, that slight modifications, such as drying in the second vs. third zones of the oven, would impact the GDL distribution. Three samples of GDL were fabricated on our commercial line in an effort to determine the impact such modifications could have on the PTFE distribution. These samples were run under normal drying conditions, with only the location of the drying being modified. One sample was dried immediately upon entering the oven, one sample around the middle of the oven and one sample at the very end of the drying oven. The samples were then randomized and sent to Penn. State for evaluation to determine which sample was run under each condition. Two dimensional Raman maps were taken of each sample, as shown in the color maps shown in Figure 6.25. It should be noted that the orange in Figure 6.25 corresponds to PTFE on the surface of the GDL with lighter spots representing higher concentrations.

Figure 6.25 – 2D Raman Maps of the Surface of each GDL Sample

From examining the surface maps displayed in Figure 6.25, it is clear that Sample 2 has the highest amount of PTFE on the surface. Since each of these samples has the same overall PTFE loading, this indicates that samples 1 and 3 have a higher PTFE loading in the bulk vs. on the surface. An imaging program (ImageJ) was used to quantify the surface coverage of PTFE in an objective manner. The drying conditions, apparent surface coverage (determined optically) and measured surface content (from ImageJ) are presented in Table 6.3. From these results, it is not apparent that there is a significant difference between the slowest drying and the middle drying for our oven, but there is a clear difference between the fastest drying and the other two.

Table 6.3 – Drying Conditions and PTFE Surface Coverage for Trial Samples

Sample #	Drying Conditions	Apparent Amount of PTFE on Surface	Measured Surface Content
Sample 1	Slow	Lowest	63%
Sample 2	Fast	Highest	70%
Sample 3	Medium	Middle	63%

These results are interesting and confirm that the drying conditions in our oven could potentially have enough effect to alter the PTFE distribution in the GDL and subsequently influence cell performance. Unfortunately this type of 2D surface analysis is too slow to be used as an online tool and as such, efforts were undertaken to determine how this 2D surface data can be related to 1D line scan data.

After extensively analyzing the data it was determined that the raw line scan data compared favorably to the surface plot yields from the imaging software, even though the data sets were significantly different sizes (~1000 points in the surface plot vs. ~50 points for the line scan), as shown in Figure 6.26. Even though the line scan is significantly faster than the 2D analysis and records only 5% of the amount of data, it can be used to estimate the overall area fraction of PTFE on the surface. This is done by first selecting an offset (values will be different for both the line scan and surface plot data, but should be material dependent), and then measuring the area under the curve for each peak, as shown in Figure 6.27.

Figure 6.26 – Comparison of Line Scan Data vs. Surface Plot Yields over Various GDL Samples

Figure 6.27 – Examples of Calculation of Area from Line Scan Data

6.4 Evaluating PTFE Distributions on Commercial Samples

These results are promising; however, the data set used is extremely small. A new set of GDL samples was fabricated with different PTFE loadings, under a range of different

drying conditions on our coating line. Table 6.4 shows the 8 sets of conditions that were used in these trials, which included 2 different drying speeds, 2 different line speeds and 2 different PTFE loadings. Approximately 15m of each sample was fabricated on our commercial coating line and the set of experiments was run with 2 sets of GDL substrate ("L" and "R") to ensure that any conclusions were repeatable (a total of 16 samples).

Table 6.4 – Process Conditions for PTFE Distribution Variations

Sample Number	Line Speed	Drying Speed	PTFE Loading
1	Slow	Slow	Low
2	Fast	Slow	Low
3	Fast	Fast	Low
4	Slow	Fast	Low
5	Slow	Fast	High
6	Fast	Fast	High
7	Fast	Slow	High
8	Slow	Slow	High

The focus of this work is to determine both the maximum difference in PTFE distribution attainable in our drying oven, as well as the impact this difference will have on key ex-situ and in-situ GDL properties. To achieve these goals our industry partner, Ballard Power Systems (BPS), evaluated the ex-situ and in-situ properties of the samples, while our educational partner, the Pennsylvania State University (Penn. State), evaluated the PTFE distribution differences. BPS has state-of-the-art testing facilities and extensive experience working with our GDL. Penn. State has previously demonstrated capability in accurately determining the PTFE distribution in the GDL with their Raman Scanning technology. The result of this work should indicate one of three things:

- 1) Altering the drying conditions of our commercial oven significantly alters the PTFE distribution and these differences influence critical properties and fuel cell performance
- 2) Altering the drying conditions of our commercial oven significantly alters the PTFE distribution, but these differences have minimal impact on critical GDL properties and fuel cell performance
- 3) The PTFE distribution cannot be significantly altered under the most extreme conditions in our commercial oven and do not, therefore, require on-line process control tools

BPS, under the direction of Julie Bellerive, measured key ex-situ properties of these samples as well as in-situ limiting current density. The results of these ex-situ measurements, which are shown in Table 6.5, show a correlation between both line speed and drying conditions. Looking at the through-plane and in-plane permeability (TTP, IPP), it appears that the line speed is the dominating factor. Samples 1 and 4, which are both slow line speeds, are significantly higher than samples 2 and 3, which are fast line speeds. The same holds true, albeit to a lesser extent, on the high PTFE loadings with samples 5 and 8 being higher than samples 6 and 7. Resistivity under compression (RUC), however, shows a stronger correlation with the drying conditions. Samples 1 and 2, which were slow drying, have significantly lower RUC values than samples 3 and 4, which were dried much faster. The same is true with the higher PTFE loading as samples 5 and 6 (fast drying) were significantly higher than samples 7 and 8 (slow drying).

Table 6.5 – Ex-situ Properties of GDL Samples with Various PTFE Distributions

Sample #	TPP	IPP	7.3psi TUC	150psi TUC	7.3psi RUC	150psi RUC	234psi RUC
1L	846.2	126.4	151.0	111.7	1.590	0.366	0.310
2L	645.2	121.2	147.3	108.3	1.620	0.382	0.323
3L	651.9	120.2	146.4	108.3	1.803	0.394	0.340
4L	766.0	121.4	147.9	109.1	1.702	0.401	0.342
5L	518.2	130.7	148.1	120.7	2.560	0.576	0.491
6L	501.4	123.1	147.7	121.6	2.331	0.539	0.446
7L	452.0	116.2	155.6	128.2	2.005	0.497	0.417
8L	502.8	119.0	153.6	127.1	1.918	0.472	0.390

Based on these ex-situ measurements, it is expected that the in-situ limiting current density tests should be balanced between two factors. Increased TPP/IPP measurements should be better for mass transport, while lower resistivity is better for ohmic performance. This would lead us to expect that the limiting current density would be highest with samples 1 and 8 and lowest with samples 3 and 6. The results, shown in Table 6.6, generally follow the expected trends, but with a few key exceptions. The trends move as expected for the low PTFE loading samples (1-4), but not for the higher PTFE loadings (5-8). This is likely true because at high PTFE loadings, mass transport dominates and higher TPP/IPP values outweigh the higher resistivity values. Therefore sample 5, having the highest TPP/IPP values, shows the best performance while sample 7, having the lowest TPP/IPP values, shows the worst.

Table 6.6 – Wet Limiting Current Density Values

Sample #	Wet Limiting Current Density
1L	3.341
2L	3.260
3L	2.952
4L	3.214
5L	2.239
6L	1.865
7L	1.790
8L	2.106

From these results we can conclude that there are subtle differences in final GDL properties based on GDL drying conditions and that these variations might influence GDL performance. Further work is required to determine if these differences could be detected with an on-line tool.

The Pennsylvania State University, under the direction of Dr. Michael Hickner, performed area Raman scans at 3 different locations in each sample. The average results of these Raman scans, presented in Table 6.7, show differences in PTFE distributions on the surface of the GDL, but do not necessarily show the expected results. It is clear that line speed has an influence on the surface content with slow line speeds showing lower PTFE distribution on the surface than fast line speeds, but the impact of drying speed is less clear. For the low PTFE loadings, sample 4 (slow line speed, fast drying) shows the lowest concentration of PTFE on the surface, while for the high PTFE loadings, sample 8 (slow drying, slow line speed) shows the lowest concentration on the surface.

Table 6.7 – Average Raman Counts on the Surface of “L” GDL Samples

Sample #	Average Raman
1L	9.37
2L	14.03
3L	13.57
4L	6.97
5L	20.47
6L	25.63
7L	21.87
8L	18.33

Color maps of these samples are presented in Figure 6.28. It is clear from these images, along with the average Raman counts, that there is more PTFE on the surface of the GDL in samples 2L and 3L compared to samples 1L and 4L. Since the total PTFE loading for each of these samples is the same, the higher loading on the surface of the GDL must correlate to a lower loading throughout the GDL. These results indicate that line speed plays a significant role in the distribution of PTFE in the GDL.

Figure 6.28 – Raman Maps of GDL Samples (L1-L4) with Different Drying Profiles

After the work on this set of samples was completed, the second set of samples was tested to confirm these results. The average Raman counts for these samples are presented in Table 6.8. These results did not confirm the previous results and actually showed almost the opposite trend, where slow drying/slow line speed had a higher concentration on the surface when compared to fast drying/fast line speed, at least for low PTFE concentrations.

Table 6.8 – Average Raman Counts on the Surface of “R” GDL Samples

Sample #	Average Raman
1R	10.47
2R	11.70
3R	9.70
4R	11.63
5R	21.43
6R	16.60
7R	20.77
8R	18.37

After analyzing all of the samples, it was found that there was no consistent difference between the various samples. In some cases, line speed correlated to PTFE concentration, while in others drying speed correlated. Overall the results indicated that neither of these factors strongly related to the PTFE distribution in the GDL. This led us to the conclusion that we cannot significantly alter the PTFE distribution in the GDL with our current production process. Due to these results, no further efforts were made to develop or install an on-line tool for our production process. This result is not negative, however, as we will be able to adjust our process to maximize throughput without the concern of altering the GDL performance. This should help further reduce the manufacturing costs of the GDL in future products.

7 – Evaluation of Low Cost GDLs

The final evaluation of the low cost GDLs manufactured in this program involves examining the results of the final integration of MAAT coating and continuous mixing, and evaluating the ex-situ GDL properties and in-situ performance. The main focus of the final integration of MAAT coating was on the performance of the MAAT coating using continuous inks with all of the on-line process control tools fully functional. The ex-situ analysis will examine the properties of the anode and cathode GDL materials, both across-web and down-web, for the integrated system. The in-situ performance will consider short stack (10 cells) and full stack (110 cells) testing. Additional work will examine sensitivities in short stack performance including reactant stoichiometries and system pressure.

7.1 Integration of MAAT Coating and Continuous Mixing

Previous trials for integrating the MAAT coating and continuous mixing processes had some minor issues, such as streaks and agglomerates, which did not affect performance, but were not acceptable by production standards. Significant efforts were spent to improve the continuously mixed inks to remove agglomerates and improve uniformity. Additional work was focused on modifying the MAAT coating head to improve the flow distribution and uniformity of the coating. A final coating run of anode material was made at the end of this process, which will be used to establish the validity of these new process methods for production purposes.

7.1.1 – Improving the Continuous Inks

Much of these efforts focused on modifying the continuous mixing process, such that the continuous ink properties more closely resembled the batch ink properties and the frequency of agglomerate formation in the inks could be reduced. In support of this effort, key process variables (e.g. mixer speed, solution temperature, paddle configuration, order of addition, residence time, % solids, and others) were modified and samples were collected and analyzed in the rheometer. It was found that the solids percentage and thickening agent percentage had the strongest correlation with key rheological properties (e.g. yield stress) and agglomerate formation. Additionally, the shear stress of the continuously made inks was lower than that of their batch-made counterparts and continuous inks with higher solids are less stable under high shear rates, as shown in Figure 7.1. This instability may account for the filtration and shelf-life issues that we have seen during our previous manufacturing trials.

Figure 7.1 - Shear Stress vs. Shear Rate Curves for Standard & High Solids Continuous Inks and Standard Batch Inks

After examining potential causes of the agglomerates seen in the top sublayer, efforts were made to sift the incoming carbon powder to break up compacted clumps of powder prior to mixing. Contact was made with a local company and multiple sizes of mesh screens were evaluated for potential use. A 140 mesh screen was down selected for use with our powder and a total of 10kg of powder was processed. This powder was then used in the continuous mixing process and the frequency and size of agglomerates was compared to standard materials. The sifted powder showed vast improvements, as shown in Figure 2, when compared to the standard materials and was used in the subsequent production run trial. The results from the production run trial indicated the size of the agglomerations was reduced but they were still in the solution at about the same frequency.

Figure 7.2 – Standard Ink (A), Sifted Carbon (B) and Un-sifted Carbon (C) Continuous Ink Coatings

A consultant was brought in from the company who supplied the continuous mixer to help eliminate the formation of agglomerates in the continuous inks. This consultant provided additional paddle designs and sizes, allowing for more aggressive paddle configuration changes. Based on the results of the previous testing, order of addition, port location (residence time between component adds) and solids percentage were modified in addition to these paddle configuration changes.

This work focused exclusively on the third sublayer ink, which has been shown to have the highest percentage of agglomerates. A method was developed to de-gas and coat a thin layer of each ink onto a plastic sheet, as a way to quantify the amount of agglomerates in each ink. Ratings of the agglomerate level were subjective and based on size and frequency after each coating. Rheological properties were also measured to determine how the modifications would impact the other coating properties of the inks. The results of this work indicated that using a paddle configuration with mostly high shear paddles, combined with some paddles to increase residence time in the mixer, had an order of magnitude decrease in the size and frequency of agglomerations. In addition, more residence time prior to the addition of certain components also helped in minimizing agglomerations. Specifically, increasing the amount of time that the powder, thickening agent and PTFE had to mix, prior to the addition of water, was critical to reducing the degree of agglomerate formation. From these experiments, it is believed that increasing the overall mixing time of the inks will lead to a more stable, better performing ink.

A new mixing process was developed, therefore, which included passing the ink mixture through the continuous mixer twice. The first pass would focus on mixing the powder, viscosity agent, and PTFE which aids in breaking down the agglomerations due to the high viscosity of this premix and the new high shear paddle configuration. The second pass is where the final water add is made and the final solution is given time to thoroughly mix.

Ideally, this process would be run in a single mixer with approximately twice the barrel length of the current mixer. A secondary option would be to add a second continuous mixer and have the output from the first mixer directly enter the second mixer. Neither of these options was within the scope and budget of this process, but they provide a path to continuously produce agglomerate free inks. This same process was then used to make the 1st sublayer ink that had been shown to have shelf-life and filtering issues. The ink made using this process settled out less quickly than earlier continuously made inks with the same formulation. This process was used to manufacture the 1st and 3rd sublayer inks for the final manufacturing trial. There was no filtration or settling problems with the 1st ink, even though the ink was 2 weeks old when the ink was coated, and the 3rd layer had no agglomerations when coated.

7.1.2 – Improving the MAAT Coating

When we combined the MAAT coating with the inks made on the continuous mixer several issues came to light. First, the 1st sublayer appeared to have a shelf life and filterability issue. In addition, our top sublayer, the carbon black layer, had many fine agglomerates that left bumps on what was supposed to be a smooth top surface. Though this did not affect the fuel cell performance we were concerned this could potentially lead to premature failure in the fuel cell stack over time. Refer to section 7.1.1 to understand how these issues were eliminated.

Once the mixing issues were resolved, we ran another MAAT coating run to verify the combined processes produced good material. The result was a roll of Anode material made without any shelf-life or filtration issues and agglomeration free in the top layer. No other modifications were required for the use of the MAAT coating process.

7.1.3 – Final Manufacturing Trial

After the modifications to the continuous mixing process and MAAT coating were complete, a final production length run (>300m) of anode material was performed to assess the final capabilities at the end of the program. All of the on-line process control tools were functional for this trial and all of the equipment was set up and run exclusively by the operators with minimal engineering supervision. The vision system at the end of the coating line was used to detect the presence of coating streaks and agglomerates throughout the coating run.

The entire roll was processed successfully with no significant issues and sample images of the material are included, along with a sample of the anode material from the full-stack testing, in Figure 7.3. The pumping skids did not experience any filter plugs or require any changes during the run. The sublayers were coated uniformly across the web with no micro-cracking or intermixing of the layers. There were very few, if any, agglomerates on the surface of the final GDL. This is a true validation for the continuous processing of the sublayer inks and the MAAT coating for BMP's GDL designs.

Figure 7.3 – Comparison of Anode Materials Made with Integrated MAAT and Continuous Mixing Technologies for A) Full-Stack Trial and B) Final Manufacturing Trial

The only significant issue that remains to be addressed is the removal of entrained air from the continuously made inks. At current production rates the inks can be de-gassed in batch format, but as the production demands increase, an in-line processing method will have to be developed. A list of potential solution ideas has been generated, but was not addressed through this program. The most significant issue with current options for continuous de-gassing methods is the high viscosity and solids content of our coating inks.

7.2 Ex-Situ Evaluation

The ex-situ evaluation was performed for two separate demonstration trials of the integrated continuous mixing and MAAT coating processes. The first evaluation was for the short rolls that were used in the short stack (10 cell) testing. The second evaluation was for the production length (>300m) anode and cathode rolls that were produced for full stack (110 cell) testing. Some additional data is provided for the final manufacturing roll of anode material as described in Section 7.1.3.

7.2.1 – Short Stack Validation

Two rolls of anode and two rolls of cathode material of moderate length (<100m) were produced for the short stack validation process. Critical ex-situ properties were measured both down-web and across-web to establish uniformity. A full list of critical ex-situ properties, including the average and standard deviations for the baseline and each of the demonstration rolls is provided in Table 7.1 (anode) and Table 7.2 (cathode). The basis weight (Figure 7.4) and thickness (Figure 7.5) of the anode rolls was well within production specifications (marked with black lines). Other than a minor dip around 15 meters into the first roll, the values were very consistent both across-web & down-web.

Figure 7.4 – Cross-Web and Down-Web Data for Basis Weight on Anode Rolls

Figure 7.5 – Cross-Web and Down-Web Data for Thickness on Anode Rolls

The basis weight (Figure 7.6) and thickness (Figure 7.7) of the cathode rolls was similarly consistent both across-web & down-web. The overall basis weight for roll 1 was near the high end of the specification limit, but only two data points were outside the specifications as the values were very consistent. The thickness was uniform and consistent throughout the whole roll.

Figure 7.6 – Cross-Web and Down-Web Data for Basis Weight on Cathode Rolls

Figure 7.7 – Cross-Web and Down-Web Data for Thickness on Cathode Rolls

Table 7.1 – Average and Standard Deviations for Critical Anode Properties

	Anode Material					
	Baseline	Baseline	MAAT 1	MAAT 1	MAAT 2	MAAT 2
	average	stdev	average	stdev	average	stdev
Basis Weight (g/m ²)	99.1	4	96.9	1.27	94.5	3.5
Thickness (mils)	8.73	0.21	8.65	0.16	8.31	0.27
Tensile Strength (N/m)	2280	508	1998	380	2229	414
Bending stiffness MD	9.57	2.35	8.61	1.44	9.81	1.50
Bending stiffness CMD	7.11	2.99	6.49	1.17	4.37	0.94
Thickness @150psi	5.98	0.35	6.08	0.38	6.03	0.31
Resistivity (mΩ-cm ²)	11.01	1.88	12.2	0.31	10.9	0.34
Diffusivity	0.212	0.025	0.194	0.009	0.235	0.009

Table 7.2 – Average and Standard Deviations for Critical Cathode Properties

	Cathode Material					
	Baseline	Baseline	MAAT 1	MAAT 1	MAAT 2	MAAT 2
	average	stdev	average	stdev	average	stdev
Basis Weight (g/m ²)	75.4	6	80.4	1.12	77.1	1.61
Thickness (mils)	9.09	0.29	8.9	0.22	8.95	0.25
Tensile Strength (N/m)	2616	514	3368	371	2984	470
Bending stiffness MD	9.95	2.37	9.78	3.89	10.7	1.96
Bending stiffness CMD	6.33	2.05	3.89	0.88	5.4	1.2
Thickness @150psi	5.96	0.24	5.97	0.38	5.52	0.40
Resistivity (mΩ-cm ²)	9.99	0.97	11.4	1.5	12.1	1.9
Diffusivity	0.270	0.036	0.318	0.017	0.242	0.008

Overall the properties for the anode and cathode materials manufactured with the integrated MAAT coating with continuously made inks were in line with standard production averages. The standard deviations for most properties were significantly improved, particularly in the basis weight and diffusivity values. These improved standard deviations are likely attributed to the on-line process control tools that were added to the process, but could also be random variation due to limited sample size. None of the ex-situ data was significantly different than the standard production values, so these trials were considered a successful demonstration of the viability of these new processes.

7.2.2 – Full Stack Validation

With the success of the short roll manufacturing demonstration, it was determined that a full-scale demonstration was needed. Past experiences have shown that issues arise when transitioning from production of short rolls (<100m) to production of longer rolls (>300m). Therefore, one production length roll (>300m) of anode and cathode was produced to demonstrate performance under actual manufacturing conditions.

The anode production roll was not completed due to issues with the coating inks, particularly in the 3rd sublayer, so the total length (~100m) was significantly less than planned. The uniformity of the coated portion was acceptable, however, with basis weight (Figure 7.8) and thickness (Figure 7.9) included in this report. Table 7.3 has a summary table with the average and standard deviations for all the critical GDL properties, compared to average baseline materials.

Figure 7.8 – Cross-Web and Down-Web Data for Basis Weight on Anode Roll

Figure 7.9 – Cross-Web and Down-Web Data for Thickness on Anode Roll

Table 7.3 – Average and Standard Deviations for Critical Anode Properties

Anode Material				
	Baseline	Baseline	MAAT	MAAT
	average	stdev	average	stdev
Basis Weight (g/m ²)	99.1	4	100.1	3.58
Thickness (mils)	8.73	0.21	8.81	0.25
Tensile Strength (N/m)	2280	508	2173	216
Bending stiffness MD	9.57	2.35	7.51	1.19
Bending stiffness CMD	7.11	2.99	6.02	1.36
Thickness @150psi	5.98	0.35	N/A	N/A
Resistivity (mΩ-cm ²)	11.01	1.88	N/A	N/A
Diffusivity	0.212	0.025	0.177	0.006

The cathode production roll was completed with the total length (~300m) with uniform properties both across-web and down-web with basis weight (Figure 7.10) and thickness (Figure 7.11) data provided. Although the full-length of material was coated, there was still an issue with some coating streaks and agglomerations during this run. The properties of the rolls were within specification, as shown in Table 7.4, and therefore used in the full stack validation testing, but one more commercial coating roll will be manufactured to demonstrate that these issues can be resolved.

Figure 7.10 – Cross-Web and Down-Web Data for Basis Weight on Cathode Roll

Figure 7.11 – Cross-Web and Down-Web Data for Thickness on Cathode Roll

Table 7.4 – Average and Standard Deviations for Critical Cathode Properties

Cathode Material				
	Baseline	Baseline	MAAT	MAAT
	average	stdev	average	stdev
Basis Weight (g/m²)	75.4	6	79.7	1.3
Thickness (mils)	9.09	0.29	9.05	0.15
Tensile Strength (N/m)	2616	514	2515	336
Bending stiffness MD	9.95	2.37	8.1	1.19
Bending stiffness CMD	6.33	2.05	6.7	0.97
Thickness @150psi	5.96	0.24	N/A	N/A
Resistivity (mΩ-cm²)	9.99	0.97	N/A	N/A
Diffusivity	0.270	0.036	0.276	0.009

7.2.3 – Final Manufacturing Trial

As previously mentioned, although the properties of the produced materials were within specifications, there was a concern over the coating quality. Agglomerates present in the ink created streaks in the coating by blocking flow from the coating head and formed a rough surface that may impact durability of fuel cells. The cause of these agglomerations was related back to the processing of the 3rd sublayer ink in the continuous mixer.

A two-step mixing process was implemented in an effort to reduce the production of agglomerates in the ink. A final coating trial was run at the end of the program with inks manufactured with this new two-step mixing approach. A total of 300m of anode material was processed with only one coating streak and limited agglomerations on the surface. This step verified that the MAAT and continuous mixing processes introduced in this program can successfully be implemented in BMP's GDL manufacturing process.

A complete analysis of this roll was not possible due to the time frame of the coating run, which took place during the last week of the program. A 1m sample was taken from both the beginning and end of the roll and subjected to the standard GDL testing. This process is similar to the quality check that is given to actual production material. The properties as measured at the beginning and end of the roll are included in this report in Table 7.5. Since these processes have now been validated, it is possible to add them to the manufacturing process with some additional funding.

The addition of the MAAT coating process will take a moderate amount of funding as a full-width (800mm) MAAT coating head will need to be purchased and installed on the coating line. Modifications, such as extending the barrel length or adding a second unit, are required to bring the continuous mixing equipment online for production purposes. Overall the result of this program is successful demonstration of equipment modifications that can quickly increase production capacity and further reduce manufacturing costs when the demands for production warrant the investment.

7.3 In-Situ Evaluation

In addition to the extensive ex-situ validation of the materials generated during these manufacturing demonstrations, in-situ testing in the form of short stack and full stack

testing was completed. The short stack validation included up and down polarization curves, fuel and air stoichiometric sensitivities and pressure drop as a function of current density for each of the stacks manufactured. A comparative baseline performance was included for reference purposes. The full-stack validation work included performance curves and cell-to-cell variability studies at various current densities.

7.3.1 – Short Stack Validation

For the short stack validation two rolls of anode and two rolls of cathode were produced continuously. A total of two short stacks were built, each using material from one roll of anode and one roll of cathode. The up and down polarization curves, shown in Figure 7.12 and 7.13 respectively, show that the performance of the low-cost stacks is slightly below baseline performance at low currents, but showed improvement at higher currents due to reduced mass transport losses, as shown in Figure 7.14.

Figure 7.12 – Up Polarization Curve for Both 10-Cell Short Stacks and a Baseline Reference

Figure 7.13 – Down Polarization Curve for Both 10-Cell Short Stacks and a Baseline Reference

Figure 7.14 – Breakdown of Voltage Losses in Low Cost and Baseline 10 Cell Stacks

The fuel and air stoichiometric sensitivity plots, shown in Figure 7.15 and 7.16 respectively, indicate that the low cost stacks are slightly less sensitive to reduced flow rates. This improvement may be related to improved uniformity of the GDL due to the on-line process controls, but the sample size is too small to be sure. The oxidant pressure drop is shown to be slightly higher with the low cost stacks than with the baseline, as shown in Figure 7.17. This increase in oxidant pressure drop may offset the improved mass transport seen with the low-cost materials. It is possible that the increased pressure drop is related to differences in the physical strength (i.e. flexural stiffness) of the low-cost GDL, but the sample size is too small to be sure.

Figure 7.15 – Fuel Stoichiometric Sensitivity for Low Cost and Baseline Stacks

Figure 7.16 – Oxidant Stoichiometric Sensitivity for Low Cost and Baseline Stacks

Figure 7.17 – Oxidant Pressure Drop Analysis for Low Cost and Baseline Stacks

From these testing results we can conclude that there is no performance loss associated with the low cost manufacturing process. There may or may not be slight improvements in the mass transport losses corresponding to a slight increase in oxidant pressure drop, but the differences are not significant enough to warrant concern at this stage.

7.3.2 – Full Stack Validation

For the full stack validation trial, one roll of anode material and one roll of cathode material was manufactured with the low cost GDL process. These materials were processed as a normal production roll and tested in a 110 cell stack. The performance of the low cost GDL, shown in Figure 7.18, was very similar to the baseline performance, with a slight increase in performance at 1A/cm². This increase may be related to the

decreased variability in GDL properties or could be associated with the improved mass transport with the low cost GDLs as seen in the 10 cell stack testing. It is impossible to be sure due to small sample size, but regardless, there was no performance loss associated with the low cost processing. These results validate that the low cost GDL manufacturing process has no negative impact on ex-situ or in-situ GDL properties.

Figure 7.18 – Performance and Power Curves for Low Cost and Baseline Stacks

Figure 7.19 – Cell to Cell Variability with Low Cost GDLs at Various Current Densities

8 – Evaluation of Process Capabilities

The process capability index (Cpk values) is a standard measure for determining the manufacturability of critical components. The Cpk value is dependent on the material specifications and higher Cpk values represent improved control with 1 being the low end of acceptability and 2 being required for six sigma processes. The Cpk value for each of the critical GDL properties was estimated, using current manufacturing specifications, for the new manufacturing process and compared to our baseline manufacturing procedure. It should be noted that these values are only estimates based on the two rolls of anode and cathode measured for the short stack validation testing. Although the true Cpk values for this new process cannot be determined based off such limited data, it is useful to estimate how we compare to the standard materials. Table 8.1 presents the values of the trial anode material, as well as the baseline for anode material, and Table 8.2 presents the values of the trial cathode material, as well as the baseline for cathode material.

It is clear from Table 8.1 that the new integrated processes compare favorably to the standard manufacturing process. The only significant differences are the nominal thickness (@ 7.3 psi) and the water vapor diffusivity. The diffusivity value is higher than standard because the material made in these trials had higher than typical diffusivity values. Since the specification limit only contains a lower value, the higher diffusivity leads to a higher Cpk value. The nominal thickness appears to be lower due to the substrate paper being slightly higher in thickness than normal. The compressed thickness (@150 psi), which is a much more important property, compares favorably to the standard manufacturing process.

The values in table 8.2 show that the trial cathode material compares just as favorably with standard production processes as the anode material. The nominal thickness (@7.3 psi) for the roll is significantly below the standard materials, but may be attributed to the starting substrate, similar to the anode. It is important to note that the Cpk of the compressed thickness (@150 psi) for the trial material is actually higher than that of the baseline. Further testing will be required to confirm that these values are accurate for the trial material, but initial results are positive.

Table 8.1 – Cpk Values for Short Stack Trial and Commercial Anode Materials

Trial Material					
Anode Design					
Basis Weight (g/m ²)	Thickness (7.3 psi)	Taber Stiffness	Tensile Strength	Thickness @ 150 psi	Water Vapor Diffusivity
1.34	0.41	1.1	0.8	0.9	1.9
Commercial Material					
Anode Design					
Basis Weight (g/m ²)	Thickness (7.3 psi)	Taber Stiffness	Tensile Strength	Thickness @ 150 psi	Water Vapor Diffusivity
1.64	1.1	0.9	1.0	1.0	1.4

Table 8.2 – Cpk Values for Short Stack Trial and Commercial Cathode Materials

Trial Material					
Cathode Design					
Basis Weight (g/m ²)	Thickness (7.3 psi)	Taber Stiffness	Tensile Strength	Thickness @ 150 psi	Water Vapor Diffusivity
0.99	0.43	0.9	1.4	1.1	1.1
Commercial Material					
Cathode Design					
Basis Weight (g/m ²)	Thickness (7.3 psi)	Taber Stiffness	Tensile Strength	Thickness @ 150 psi	Water Vapor Diffusivity
1.40	1.1	1.0	1.3	0.8	1.3

Additional Cpk values for the critical GDL properties were estimated based on the anode and cathode rolls measured for the full stack validation testing. Again, the true Cpk values for this process cannot be determined based off such limited data, but it is useful to estimate how we compare to the standard materials. Table 8.3 presents the values of the full stack anode material, as well as the baseline for anode material, while Table 8.4 presents the values of the full stack cathode material, as well as the baseline for cathode material. As you can see from these results, the Cpk values are roughly the same or better than the commercial standard values. The basis weight and thickness values are slightly lower than commercial ratings due to the slightly high loadings seen in the uniformity charts presented in section 7.2.

Table 8.3 – Cpk Values for Full Stack Trial and Commercial Anode Materials

Trial Material					
Anode Design					
Basis Weight (g/m ²)	Thickness (7.3 psi)	Taber Stiffness	Tensile Strength	Thickness @ 150 psi	Water Vapor Diffusivity
0.99	0.92	2.1	2.3	0.9	1.8
Commercial Material					
Anode Design					
Basis Weight (g/m ²)	Thickness (7.3 psi)	Taber Stiffness	Tensile Strength	Thickness @ 150 psi	Water Vapor Diffusivity
1.64	1.1	0.9	1.0	1.0	1.4

Table 8.4 – Cpk Values for Full Stack Trial and Commercial Cathode Materials

Trial Material					
Cathode Design					
Basis Weight (g/m ²)	Thickness (7.3 psi)	Taber Stiffness	Tensile Strength	Thickness @ 150 psi	Water Vapor Diffusivity
1.20	0.97	2.5	2.2	2.3	1.3
Commercial Material					
Cathode Design					
Basis Weight (g/m ²)	Thickness (7.3 psi)	Taber Stiffness	Tensile Strength	Thickness @ 150 psi	Water Vapor Diffusivity
1.40	1.1	1.0	1.3	0.8	1.3

Overall, the results from this testing are very positive in that the low cost manufacturing process does not negatively impact the GDL properties. These values are only estimates of the capability, but they fall in-line with the expected values inherent in the GDL design. Capability box plots were made for some of the key properties and presented in Figure 8.1. It is clear from these results that the variability in these properties is low and the averages, for the most part, are centered on the target values. This gives us confidence that moving to the low cost production process will not negatively impact our ability to manufacture GDLs within specification limits.

Figure 8.1 – Capability Box Plots of Critical GDL Properties

9 – Development of a Greenfield Facility

BMP has undertaken an engineering study to determine an estimated cost to build a Greenfield manufacturing facility within the United States to support the production of 500,000 automotive fuel cell systems per year. This amount of automotive systems would require approximately 10,000,000 m² of GDL per year (assuming 70kW per automotive system with a power density of 0.65 W/cm²). BMP's philosophy for GDL design and development, since entering the market back in 2001, has been to only move forward with material systems and processes that are readily scalable. As such, the current GDL manufacturing process, incorporating the manufacturing methods developed as part of this DoE program (MAAT coating & continuous mixing), is used in this study.

BMP is obtaining energy requirements, run rates, operating temperatures and other pertinent processing parameters from the current manufacturing process. The current bill of materials for a GDL design used in the materials handling segment is being used to determine raw material volumes and requirements. This design has been chosen as it is believed that the ultimate GDL design for automotive applications will be very similar in formulation as the current material handling GDL design. It should be noted that all of the processes used in this Greenfield study have been commercially demonstrated, scale-up in a reasonable, cost-effective fashion and that no breakthrough technology or exotic equipment designs are required.

9.1 Location

One of the major cost drivers to the production of GDL materials is energy, specifically electricity in this case. BMP has found over many years of producing carbon materials that electric fired ovens and furnaces are preferable. Although these systems are typically more expensive to operate than gas fired units, the temperature uniformity and process controls are much better and there is no chance of contamination from natural gas by-products. In addition to the electricity, an abundant source of clean water is also required to support the paper making activity.

Niagara Falls, New York was selected for this type of facility based on these constraints. Not only are the electricity rates some of the lowest in the country, but the electricity is clean and renewable, being generated from hydro-electric plants. In addition, industrial sites are abundant, inexpensive and readily available. Numerous Universities and Colleges are in the area and many large manufacturing facilities were once based in this region. This region also has an ample supply of skilled work force including both professional and non-professional workers.

9.2 Facilities & Equipment

The facility for this study will be newly built and will have capacity to store enough raw materials and final product for one month of full operations. This facility will house all of the process steps required, including paper making, to produce rolls of finished GDL products at an annual rate of at least 10,000,000 m². The facility will be located within the state of New York, ideally in the Niagara Falls region.

The cost of construction in upstate New York is estimated to be \$100/ ft², including both basic construction and standard utilities. BMP is estimating that the cost to accommodate the installation of the processing equipment and supply adequate utilities to them will be \$150 per square foot. A 20 MW electric service will be required to feed the site.

Process run rates have been determined from current process throughputs and provide the residence times required to produce the desired GDL structures. Based on these run rates, process equipment has been appropriately sized to maximize throughput rates without compromising the properties of the final product. From this equipment size analysis, along with determining the number of process lines necessary to meet the production volumes, it is estimated that a 110,000 square foot facility will be required to house the processing equipment and support staff. The process equipment details (run rates, capacity, etc...) are provided in table 9.1 below. These data were used to generate a simplified manufacturing plant layout to provide a representation of what the floor plan for such plant would resemble, as shown in Figure 9.1.

9.3 Raw Materials

BMP has obtained cost estimates from its supply chain for annual material quantities required to support production of 10,000,000 m² annually of GDL materials. The current supply chain has the capacity to support these volumes within the current infrastructure, with the potential exception of one supplier (DuPont for PTFE solution). BMP wasn't able to get a cost estimate for the required volume of PTFE from DuPont nor would any capacity / scale-up requirements be shared. As such, BMP has simply applied a 20% reduction to the cost of PTFE from the current price paid. It is believed that this is a conservative number and hopefully the cost will be significantly less when the volumes are actually realized.

The cost of carbon fiber in 2011 is at an all time high, as demand is surging to support the production of airline composites, wind turbine blades and numerous other applications. Additionally, the cost of the raw material to produce the fiber (PAN) is also near an all time high, as it is directly tied to the cost of crude oil. For this study, BMP is using the current high price of carbon fiber (currently at \$33/kg). Hopefully the prices will be significantly lower once additional carbon fiber capacity comes on-line within the next few years. Fortunately BMP's GDL design incorporates only a small amount of carbon fiber on a square meter basis. Carbon fiber, even at this high price, only accounts for 10% of the final GDL cost. A break out of the material cost components is provided in Figure 9.2.

Table 9.1 – Detailed Breakdown of Process Equipment

Assumption		Calculations	
Annual qty	10,000,000 m2	Hourly output	2367 m2
		Daily output from factory	45455 m2
		Annual output of factory	10,000,000 m2
weeks/year	44 weeks	effective Throughput	
Days/ week	5 days		
shifts/day	3 shifts		
hrs/shift	8 hours		
equipment up time	0.8		
		paper making	54.400 m2/min
		Saturation coating	40.000 m2/min
		Oxidation	40.133 m2/min
		heat treatment (CGX)	40.200 m2/min
		coating	53.600 m2/min
# of processing lines		effective line length	
paper making	1		
Saturation coating	2		
Oxidation	3		
heat treatment (CGX)	3		
coating	2		
		paper making	68 m
		Saturation coating	100 m
		Oxidation (7 pass)	301 m
		heat treatment (CGX)	67 m
		coating	67 m
Processing line width(s)		Capital equipment cost	
paper making	4 m		
Saturation coating	2 m		
Oxidation	2 m		
heat treatment (CGX)	2 m		
coating	2 m		
		paper making \$	6,000,000
		Saturation coating \$	4,000,000
		Oxidation \$	6,000,000
		heat treatment (CGX) \$	12,000,000
		MPL coating \$	4,000,000
Capital equipment cost		Total equipment \$	32,000,000
paper making \$	6,000,000	Facilities (Sq footage requirements)	
Saturation coating \$	2,000,000		
Oxidation \$	2,000,000		
heat treatment (CGX) \$	4,000,000		
coating \$	2,000,000		
Facilities		paper making	11,696.00 sq ft
cost/ft2 \$	250	Saturation coating	17,200.00 sq ft
		Oxidation	11,094.00 sq ft
		heat treatment (CGX)	17,286.00 sq ft
		coating	11,524.00 sq ft
		offices/ storage	41,280.00 sq ft
		total	110080 sq ft
		\$	27,520,000
		0	
		total capital investment \$	59,520,000

Figure 9.1 – Layout of Proposed Greenfield Facility

Figure 9.2 – Breakdown of GDL Material Costs

9.4 Labor

This Greenfield facility is assumed to be a stand alone facility, with a dedicated management team. This includes support functions such as purchasing, finance, HR, EH&S among others. It is also being assumed that this is strictly a manufacturing facility and no R&D or marketing activities are based out of this location. A breakdown of the labor grades, number of employees and estimated salaries (based on data obtained from the US department of Commerce) is provided in Table 9.2. These numbers are representative of an experienced work force should cost today. The labor requirements are based on a five day (three shifts per day) work schedule.

Table 9.2 – Labor Breakdown for Facility Operation

Labor Category	Average Labor rate (\$/hr)	Fringe (\$@ 40% rate)	Annual cost (\$/yr)	Average Annual Salary (\$/yr)	# of employees	Total cost (\$/year)
Management	\$ 70.00	\$ 28	\$ 203,840	\$ 145,600	4	\$ 582,400
Administrative	\$ 40.00	\$ 16	\$ 116,480	\$ 83,200	6	\$ 499,200
Engineering	\$ 44.85	\$ 18	\$ 130,603	\$ 93,288	8	\$ 746,304
Quality	\$ 31.25	\$ 13	\$ 91,000	\$ 65,000	10	\$ 650,000
Maintenance	\$ 23.50	\$ 9	\$ 68,432	\$ 48,880	15	\$ 733,200
Production	\$ 17.25	\$ 7	\$ 50,232	\$ 35,880	21	\$ 753,480
Totals					64	\$ 3,964,584

9.5 Utilities

In order to obtain accurate power consumption numbers, BMP measured the energy consumption rate on each piece of processing equipment throughout every step of the current manufacturing process. From this data, an energy consumption value per square meter was determined and then a 20% efficiency value was incorporated and

used to estimate the scale-up consumption values, as shown in Table 9.3 and Figure 9.3. Based on these estimates, the facility will require an electrical service of 20MW to support full production requirements.

Table 9.3 – Power Requirements by Process Step

Process	Measured Power consumption (kWh/hr)	Throughput m2/hr	power usage (kWh/m2)	power cost (\$/kWh) **	Electrical power cost (\$/m2)
Paper making*	130	320	0.4063	\$ 0.045	\$ 0.015
Saturation coating	150	240	0.6250	\$ 0.045	\$ 0.023
Oxidation	170	35	4.8571	\$ 0.045	\$ 0.175
carbonization	168	146.3	1.1483	\$ 0.045	\$ 0.041
graphitization	271	170	1.5941	\$ 0.045	\$ 0.057
PTFE coating	105	240	0.4375	\$ 0.045	\$ 0.016
MPL coating	127	127.5	0.9961	\$ 0.045	\$ 0.036
Sintering	280	180	1.5556	\$ 0.045	\$ 0.056
Pollution control	45.8	146.3	0.3131	\$ 0.045	\$ 0.011

* paper making numbers provider by supplier

** Energy numbers based on Niagara Falls electric rate of \$0.045/kWh

Figure 9.3 –Breakdown of Electrical Costs for GDL Manufacturing Process

In addition to electrical requirements the facility will also need a supply of natural gas to support the operation of pollution control devices (in this case thermal oxidizers). Thermal oxidizers are required to destroy the by-products being generated during the heat treatment processes. The amount of natural gas required to operate these thermal oxidizers is based on actual measurements made in the existing BMP manufacturing facility. The natural gas requirements are shown in table 9.4, and the current cost of natural gas is being used to determine the cost requirements.

The temperatures reached in the heat treatment equipment used in the GDL manufacturing process are extremely high, which means that the processing must be done in an inert atmosphere. This is required to prevent oxidation of the carbon fiber and matrix in the GDL. In this process, inert gas is used to displace the air in the furnaces and provide an inert atmosphere. The cost of the inert gas required is based on actual consumption numbers, similar to the natural gas analysis, and the requirements are shown in Table 9.5.

Table 9.4 – Natural Gas Consumption

Process	Natural gas usage (SCFH)	Natural gas usage (SCFH/m ²)	Natural gas cost (\$/SCFH)	Natural Gas cost (\$/m ²)
Pollution control	2000	13.671	\$ 0.008	0.104

Table 9.5 – Inert Gas Consumption

Process	Inert gas (N ₂) usage (SCFH)	Inert gas usage (SCFH/m ²)	Inert gas cost (\$/SCFH)	Inert gas cost (\$/m ²)
carbonization	8000	54.68	\$ 0.004	\$ 0.191
graphitization	17500	3.22	\$ 0.004	\$ 0.011

A tornado chart was put together to examine the sensitivity of the cost estimates on the final cost of the GDL. Low, medium and high costs are assumed based on the values provided in Table 9.6. A plot of the results showing the low, medium and high price brackets are provided in the tornado chart in Figure 9.4. Additionally, estimates for the cost were determined based on an electricity cost of \$0.10/kW. The total cost for the GDL in this very high scenario (assuming the high values for everything else listed in Table 9.6) is ~\$5.80/m² or \$1.80/kW, which is still below the required target of \$2/kW.

Table 9.6 – Cost Ranges used for the Tornado Chart in Figure 9.4

	Low	Medium	High
Nitrogen (\$/SCF)	\$ 0.0015	\$ 0.0035	\$ 0.0065
Natural gas (\$/SCF)	\$ 0.0045	\$ 0.0075	\$ 0.0115
Labor (\$/kW)	\$ 0.06	\$ 0.12	\$ 0.20
Electricity (\$/kWh)	\$ 0.0200	\$ 0.0450	\$ 0.0650
Maintenance (\$/kW)	\$ 0.08	\$ 0.15	\$ 0.20
Raw Materials (\$/kW)	\$ 0.58	\$ 0.77	\$ 0.84

Figure 9.4 – Tornado chart of GDL Costs in \$/kW

9.6 Depreciation

The manufacturing process of the GDL product is capital intensive, as is the case with most carbon products. High temperature furnaces and process lines are required and the facilities required to support their operations are very costly. Expensive equipment, such as cooling towers, high power switch gears and pollution control device are all

required. As such, two of the main cost drivers of the GDL products are the costs of the equipment and facilities required to support the manufacturing process. In order to determine a cost/m² of GDL for equipment and facilities, depreciation schedules of 10 years were used for equipment and a 20 year schedule was used for the facility. The individual contributing components of the depreciation cost are given in Figure 9.4.

Figure 9.5 – Breakdown of Depreciation Costs for GDL Manufacturing Process

9.7 Summary

Based on the achievements of this DOE program combined with the results of the Greenfield facility study, BMP is confident that the goal of producing high quality, high performance GDL for \$4.50 per m² is obtainable. This study identifies the cost of GDLs at high volume to be \$4.45 per m² or approximately \$1.37 per kW. The processes identified in the Greenfield facility are either currently used or have been demonstrated in BMP's current manufacturing process and facility.

In high volume production the three top cost components to the GDL are:

- 1) Raw Materials at 57% of the cost
- 2) Maintenance/Labor at 19% of the cost
- 3) Electricity at 9 % of the cost.

A complete breakdown of the GDL costs at high volume is provided in Figure 9.5.

Figure 9.6 – Breakdown of Total GDL Costs at High Production Volume (10MM m²/year)

10 – Conclusions

Overall this program was successful in meeting the goals set forth including:

- 1) Reducing the fabrication costs of the GDL by >50% for near-term applications by improving manufacturing efficiencies and product yields
- 2) Increasing production capacity four-fold through modifications allowing for full-width processing and improved manufacturing efficiencies
- 3) Demonstrating a process for Many-At-A-Time (MAAT) coating of GDLs to eliminate multiple passes through the coating line
- 4) Developing a process to manufacture sublayer inks continuously to eliminate slow batch processes
- 5) Establishing relationships between process parameters and critical GDL properties and developing models to control these properties within specification limits
- 6) Developing an on-line method to characterize the PTFE distribution in the GDL, although it was found that changes in the distribution had minimal impact within actual production ranges
- 7) Evaluated short-stack and full-stack performance with new low-cost GDL to establish that there was no reduction in performance
- 8) Demonstrated process capability similar to current standards for production with new low-cost manufacturing process
- 9) Gathered necessary inputs to design a Greenfield Facility capable of producing GDLs at volumes (10,000,000 m²) and costs (<\$4/kW) that are compatible with 2015 DOE targets

This final chapter will address the lessons learned throughout the program, presented in the same order as this report, followed by an overall summary of the key parts of the program and recommendations for future work.

10.1 Lessons Learned

There were many important lessons learned throughout this program, although some important lessons are deemed proprietary and will not be discussed in detail in this report.

10.1.1 – Many-At-A-Time Coating

Throughout the installation of the MAAT coating process, there were many critical lessons learned for our application including:

Drying Parameters

The drying parameters are critical for applying multiple sublayers to GDL substrate. Drying properties, such as the dew point and web temperature in a given zone, are important to monitor and control to ensure consistent drying. Process parameters, such as line speed and tension control, are critical for maintaining coating uniformity with increased wet loads. Determining the most appropriate drying profile will help to minimize surface imperfections and flocculating of the particles of the sublayers, while preventing common issues such as micro-cracking.

Critical Fluid Properties

The fluid properties, such as viscosity and surface tension, play an important role in determining how well multiple layers will coat on a GDL substrate. Modifying the solids in the solutions, for instance, will dramatically alter the required wet-load, thereby

influencing the drying profile as well as the viscosity of the solution potentially requiring, at a minimum, changes in coating head slot heights but may potentially require redesign of the internal channels. Modifications to surface tension of various fluids will alter the interface between the liquid layers and may lead to poor wetting out or surface defects such as cracking.

Mass Flow Meters

When applying multiple liquid layers, it becomes increasingly important that mass flow meters are incorporated in the system to control the individual sublayer loading. Other tools, such as basis weight sensors, can determine the overall loading, but not the loading of the individual layers. Utilizing a simple relationship, such as pump speed, allows for significant differences in individual loadings within the same total loading profile.

Programming Requirements

Automated controls are significantly more important with MAAT coating due to increased sensitivity to process shifts. A standard coating process can have a much larger window of acceptable values, whereas in MAAT coating even a slight shift can result in micro-cracking or non-uniform sublayers. Proper process control tools and set-up parameters are critical to ensuring the success of a MAAT coating process for GDL manufacturing.

10.1.2 – Continuous Mixing

Transitioning from a batch mixing to a continuous mixing process was much more difficult than initially believed due to the difficulty of wetting out carbon powders, the increased shear rate on raw materials and the reduced overall residence time of the mixing process. Important lessons learned through this program included:

Influence of Barrel Temperature

The barrel temperature has a significant impact on the quality of a continuously processed sublayer ink, especially for the carbon powders. Modifying the barrel temperature, coupled with adjustments to the mixer speed, allowed for better control over the amount of work applied to the fluid. Controlling this parameter is critical to obtaining the proper fluid properties, such as the yield stress, of our coating inks.

Wetting Out Carbon Powder

One of the most difficult aspects of continuously mixing fluids for sublayer inks is wetting out the carbon powder. Through this program it was determined that controlling the order of addition, as well as the residence time allowed with each ingredient, is critical to completely wetting out the carbon powder. Adjusting the paddle configuration to control the amount of back-mixing can also have a significant impact on the ability to wet out the carbon black.

Eliminating Agglomerate Formation

The most significant issue encountered with the continuously made inks was the creation of agglomerates, which caused coating defects, such as bumps and streaks. It was found that pre-processing the carbon powder to remove clumps helped to reduce the size of the agglomerates, but it was time consuming and increased processing costs. It was determined, however, that modifying the paddle configuration and increasing the residence times with specific raw materials could eliminate the agglomerates. This was accomplished by implementing a two-pass process in this program, but could be

addressed by increasing the barrel length of one unit or feeding the outlet of the current mixer into a second mixer. One of these options would need to be selected in order to implement continuous mixing into the current production process, but will require some additional capital investments.

Removing Entrained Air from Continuous Mixes

After successfully eliminating the agglomerate formation in the continuous inks, the final barrier to implementing continuous mixing is removing the entrained air. A large amount of air is introduced into the inks through the chosen mixing process, from both the powder entrance and the collection method. For this program, the air was removed by pulling a vacuum during a secondary filtering step, but this solution will not be adequate for true continuous processing. Additional concepts, such as drawing a vacuum on the mixing chamber or utilizing specialty equipment to de-gas the mixture as it leaves the extruder, will need to be explored for full implementation.

10.1.3 – Substrate Processing Improvements

While converting the substrate manufacturing process from half-width (400mm) to full-width (800mm), many important lessons were learned including:

Tension Control & Web Handling

As the process shifted from half-width to full-width, it was critical that the proper tension control system be put in place. It was particularly important that the unwind, process and rewind tensions were separate to eliminate web breaks in the process zone, to have a good package for further processing in the rewind zone, and to provide the ability to handle slightly imperfect incoming rolls in the unwind zone. In addition, the proper web guiding system minimized twisting of the web, which can lead to web breaks, and produced an evenly wound, non-telescoped roll. Proper control of the tension also improved the uniformity by eliminating variability from roll to roll.

The shift to full-length (>700m) and full-width (800 mm) rolls also placed a greater emphasis on the ability to wind the rolls. If the roll telescopes at any point, the material can slip off the core or be damaged during subsequent processes. It is critical that the roll tension is controlled throughout the windup process to maintain a firm wrap and that the material is centered to prevent telescoping.

Cross-web uniformity

One of the biggest concerns in the shift from half-width to full-width production was the impact on cross-web uniformity of the GDL. Through extensive process analysis, multiple key parameters that impact GDL properties were determined. It was found that improving the control of these properties was critical to maintaining cross-web uniformity. This is especially true for the beginning and end of the roll where process variability is at a maximum.

10.1.4 – Relationships Between Process Parameters and Critical GDL Properties

While the relationship between process parameters and key GDL properties were established, there were many lessons learned. The details of these lessons cannot be provided within this report, but some of the key highlights are addressed in general terms.

GDL Diffusivity

The diffusivity of the GDL is one of the most critical parameters as it has a significant impact on the water management of a fuel cell. Throughout this program BMP was able to develop a process model that allows for full control over the diffusivity of the GDL by modifying critical process parameters. This allows the same basic manufacturing concept to be used regardless of the application for which the GDL is used (e.g. stationary vs. automotive fuel cell stacks).

Tensile Strength

The tensile strength of the GDL is very important, not for the performance of the GDL in a fuel cell, but rather for the manufacturability. As key GDL properties are modified, the inherent tensile strength of the GDL is changed and can become unsuitable for roll-to-roll production. Through this program we have identified key process parameters that allow BMP to modify the tensile strength to improve the manufacturability of the GDL.

Thickness

The thickness of the GDL is one of the most important factors as variation has a significant impact on the sealing of the MEA. Throughout this program BMP has evaluated key process parameters and determined their influence on the thickness of the GDL under compression. This knowledge helps improve the overall uniformity of the GDL and should improve the quality moving forward.

10.1.5 – On-Line Process Control Tools

Throughout this program there were multiple on-line process control tools implemented on BMP's manufacturing process. Some of these tools, such as the mass flow meter, were successfully implemented, while others, such as the surface topology tool, would not work with our equipment. The lessons learned from the key process control tools are discussed in this section.

Mass Flow Meters

Mass flow meters were incorporated on both the MAAT coating process line and the continuous mixing process. In both cases, these tools provided key information that improved uniformity and consistency of the product. In the case of the MAAT coating process the mass flow meters controlled the feed rate of each of the sublayer loadings to ensure consistent GDL production. For the continuous mixing process, the mass flow controllers ensured uniform mix by controlling the flow of the raw ingredients to the mixer. It was determined that incorporating mass flow meters provides critical control and ensures uniformity for any application.

Basis Weight Sensor

The basis weight sensor employed on BMP's coating line was successful in monitoring the down-web uniformity, but struggled to provide good data on the cross-web uniformity. The reason for this was due to the inability to scan the GDL at appropriate speeds, which limited the data collection rate. For this application, using multiple stand-alone gauges would be beneficial rather than a transversing gauge.

Surface Topology Tool

The surface topology tool that was selected for this program used two optical pens that would record differences in the distance between the stationary head and the paper. Unfortunately, these pens did not work well due to the vibrations caused on the process line as well as the fluttering of the GDL. Some efforts were made to transition the pen to observe the material as it passed over a roller, thereby eliminating the web fluttering, but

this was unsuccessful due to the machine vibrations. Other process technologies may have been more suitable, but this system is not recommended for continuous processing on a web-line.

On-line Visual Inspection Station

The key parameters in an on-line visual inspection system are the camera angle and the light intensity. Having the camera positioned at a 30-45° angle allows for easy detection of surface defects, such as cracks or bumps, while a camera located perpendicular to the web allows for the detection of through-holes. The key lesson learned through the installation of this equipment is that identification and classification of defects are the most challenging aspects. This work should be done as thoroughly as possible upfront to eliminate problems once the system is installed.

10.2 Summary of Results

The end result of this program is a >50% reduction in the manufacturing costs of GDLs for near-term applications. Additionally, the current production capacity for GDL manufacturing has been increased four fold from the start of the program. These cost savings and capacity increases are applicable to current GDL volumes and requires no breakthrough technologies or projections of increased volumes. These improvements were achieved by shifting from half-width (400mm) to full-width (800mm) production, improving manufacturing efficiencies and increasing product yields.

In addition, further improvements to the manufacturing process (MAAT coating and continuous mixing) were demonstrated utilizing prototype equipment. These processes were refined and successfully demonstrated to manufacture GDL within current production specifications and with the same quality level as standard production material. Implementation of these process steps will further increase production capacity (ten fold from the start of the program) and provide additional cost savings (>65% from start of the program). Full implementation will require additional funding, however, for purchase of a full-width (800mm) MAAT coating head and improvements to the continuous mixing process for commercialization.

Throughout this program numerous on-line process control tools were implemented for both the commercial production and the new manufacturing processes. These on-line tools provide critical feedback that improve the uniformity of the GDL and provide operator feedback for critical process parameters. In addition, a novel process was developed to measure the chemical homogeneity of the GDL at the Pennsylvania State University. The measurement process utilized Raman scanning to detect PTFE concentrations on the surface of the GDL. This process was refined and shown to be capable of determining the PTFE content on the surface vs. the total loading. The drying conditions were shown to influence the PTFE distribution in the GDL with slow drying having a higher concentration of PTFE in the center and fast drying having a higher concentration on the surface. Trials were run utilizing the commercial drying oven and it was determined that the PTFE distribution could not be significantly altered, such that this tool could detect any variations. Although this tool was unsuccessful, this knowledge will allow BMP to increase the processing speed of the PTFE coating step without concern of altering the GDL properties.

Along with the development and implementation of on-line process control tools, a significant effort was spent to determine the relationships between processing parameters and critical GDL properties. From these evaluations, empirical models were

developed to allow BMP to control critical GDL properties by altering the key processing parameters. This ability allows BMP to manufacture GDLs to within tight specification windows and utilize the same base manufacturing process for the production of GDLs with significantly different properties. This ability will be critical for the production of GDLs for a wide range of applications (stationary, materials handling, portable, automotive, etc.) with BMP's low-cost manufacturing process.

Finally, from the information gathered throughout this program, BMP put together a Greenfield Facility design that was capable of producing GDLs at volumes (10,000,000 m²) and costs that are compatible with the 2015 DOE stack cost targets of \$15/kW. DTI estimated that the GDL costs were ~12% of the stack costs at these volumes, which equates to \$2/kW, while our projected costs is below \$2/kW. This facility design includes the low-cost processes developed in this program (MAAT coating and continuous mixing), but does not require any other breakthrough technologies or significant assumptions to implement. Further cost reductions may be possible through improved efficiencies or future improvements to the manufacturing process, but were not included in this analysis.

10.3 Future Work

BMP has developed a novel, green (VOC free) manufacturing process that is capable of producing GDLs at high-volumes and low costs for the fuel cell industry. BMP is currently the only domestic supplier of GDLs and supplies a wide variety of domestic MEA and stack manufacturers for a variety of fuel cell platforms (PEMFC, PAFC, DMFC, etc.). Substantial progress has been made throughout this program to harden the GDL manufacturing process, however, there are still many challenges ahead, as would be expected for the scale-up to automotive volumes. A breakdown of some of these critical challenges is included, along with a brief description of why they are necessary.

Implementation of Low-Cost Processes

Although the new low-cost processes were demonstrated throughout this program, additional investments will be required to bring these technologies to a commercial level. The MAAT coating process will require a full-width coating head, as well as improved ink delivery skids capable of holding larger volumes of fluid (>30 gallons) for full-length production runs. Additional work will also be required to control the drying conditions to accommodate the additional wet-load associated with the larger widths. The continuous mixing process will require a modified barrel length or the addition of a second continuous mixer to accommodate the increased residence time required to eliminate the agglomerate formation. Additional gravimetric feeders and pumping systems will also be required for the production of all coating designs used in BMP's manufacturing process. Finally, a novel method for the continuous removal of entrained air is required to bring this mixing process to production levels. These challenges are expected to take 12-14 months and require ~\$1.3MM to complete.

Reduction of Energy Consumption

The production process is currently very energy intensive and estimates for energy consumption for the production of 20,000,000 m² of GDL exceed 900 billion BTUs per year. One way to significantly reduce the cost of the GDL is to reduce one of the slow, energy intensive heat treatment steps with a novel less energy intensive step. One such process, which utilizes high intensity radiation processes (such as gamma ray or electron beam) has been identified, but significant work would be required to develop and implement such a system. This novel manufacturing process would potentially

provide a significant reduction in energy consumption (~250 billion BTUs per year), as well as provide additional cost savings (~20%). Successful implementation of such a system would give BMP a significant technological advantage over GDL competitors for future GDL production. This work is expected to require 2-3 years and ~\$2-2.5MM for completion.

Further Process Improvements

After the implementation of the low-cost production processes developed in this program, the manufacturing process will be limited by the secondary heat treatment steps. These heat treatment steps also create some minor issues with the handling of the GDL for certain customers. There would be a significant advantage to combining these two separate heat treatment steps into a single step by developing a new continuous high temperature heat treatment line. This would help reduce energy consumption, allow for increased throughput rates, and provide significantly more control over the final GDL properties. Such a novel heat treatment system would provide a competitive advantage for BMP in the commercial GDL market. Implementation of such a process would require 2-3 years and ~\$3.5 MM for completion.