HIGH TECHNOLOGY MATERIALS & SERVICES

Development and Optimization of Porous Carbon Papers Suitable for Gas Diffusion Electrodes

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MP Dvorscak

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Mark P Dvorscak

Date

(630) 252-2393

E-mail: mark.dvorscak@ch.doe.gov

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Principal Investigator: Gerald J. Fleming (978) 682-1232, fax: (978) -3253, e-mail: spectragjf@aol.com

Contractor: Spectracorp Ltd., Lawrence, MA

Subcontractors: PSI, Andover, MA
Energy Partners, West Palm Beach, FL
H Power, Belleville, NJ

DOE Program Manager: Donna Ho (202) 586-2480, fax: (202) 586-9811, e-mail: donna.ho@hq.doe.gov

ANL Technical Advisor: James Miller (630) 252-4537, fax: (630) 252-4176, e-mail: millerj@cmt.anl.gov

Program Summary

Objectives

- The primary objectives of this program were improved performance and cost reduction in polymer electrolyte membrane (PEM) fuel cells through the optimization of the carbon based gas diffusion electrode (GDE) material. A matrix of numerous variations in the composition and processing of carbon fiber based papers was to be designed, manufactured, and fuel cell tested to determine the effect of performance enhancing and lower cost materials and processes.

Approach

- Various parameters in carbon/carbon GDE such as pore size distribution, electrical and thermal conductivity, and compression strength were to be changed by varying fiber types and lengths, heat treatment temperatures, density, and thickness (over 30 variants).
- Fuel cell performance testing was to be conducted on the manufactured GDE matrix. Subsequent analysis would correlate changes in GDE parameters to changes in fuel cell performance. The most promising GDE variants were to be subjected to longer term fuel cell testing to confirm initial results.
- The optimized paper(s) were to be manufactured on production equipment and made available for evaluation by laboratory and industry partners.

Accomplishments

- A matrix of over 30 GDE variants was designed, manufactured and tested for physical and electrical properties as well as pore size, pore size distributions and gas flow.
- Initial fuel cell testing eliminated most variants using cost and performance criteria. Several lower heat treatment (and hence lower cost) variants that were not anticipated to perform well equaled the fuel cell performance of industry standard GDE materials.
- Longer term fuel cell testing was performed on the more promising variants from initial screening tests. Initial results on the lower heat treatment materials were confirmed, demonstrating the feasibility of lower cost materials and manufacturing techniques, as well as the possibility of manufacturing carbon paper based GDE's in continuous rolls
- Based on the fuel cell testing results, a batch of a thinner, lower heat treatment GDE was manufactured utilizing production equipment and has been made available to DOE's government and industry partners.
- Several preliminary trials have been conducted towards the development of a continuous process resulting in a continuous roll of carbon fiber paper based GDE material. Initial results look promising and will be pursued in future development.

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Introduction

The objective of this program was to optimize the physical structure of porous carbon papers for use as gas diffusion electrodes (GDE) in membrane electrode assemblies for PEM fuel cells. This optimization was directed towards maximizing cell and stack performance with regard to such characteristics as mass transport (H_2O removal) and appropriate electrical conductivity, and reduced cost versus current state of the art materials.

Fuel cells of various sizes and power outputs have been under development for many years. Much of the recent efforts to increase the efficiency of polymer electrolyte membrane (PEM) cells has been involved with electrochemical aspects of the cell, such as catalysts, electrolytes and membranes, as well as operating conditions such as temperature, pressure and types of fuel. However, very little work has been performed on some of the carbon components, namely the GDE. The carbon papers being used in PEM cells were largely carried over from their application in phosphoric acid cells. Of particular interest was determining whether the high heat treatments ($\geq 2,000^\circ C$) that were carried over from phosphoric acid technology continued to be necessary given the less caustic environment of the PEM cell.

Due to the proprietary nature of fuel cell development, we had received very little feed back from customers on the relative performance of our papers and hence a definitive correlation between paper variants and fuel cell performance had been difficult to make, making optimization of the papers for fuel cells very difficult. For this program, we were able to subcontract with a number of fuel cell manufacturers, obtaining invaluable cell performance feedback based on the matrix of paper variants that we manufactured.

Tech Approach

Spectracorp has been developing and manufacturing PAN based porous carbon fiber papers since 1991, and its knowledge of the formation of carbon fiber papers for other uses dates back twenty years. Spectracorp has undertaken considerable internal R&D over the past six years to develop an understanding of pore sizes and distributions, paper densities, optimization of electrical conductivity and other properties of carbon fiber papers for use in fuel cells. These efforts produced a large amount of data upon which to base this program.

Currently, Spectracorp manufactures its papers on a commercial basis using full scale production equipment easily capable of manufacturing $500,000 \text{ m}^2/\text{year}$. The process and materials are tightly specified regarding carbon fiber type, lengths and binders, impregnating resins, resin content, degree of staging, molding conditions and graphitizing cycle. For the purpose of this program, these conditions were systematically modified to ascertain the effects upon fuel cell performance. In order to accomplish this for a large quantity of variants, the production process was brought back into the laboratory.

The basic approach for the program was to devise a matrix of porous carbon papers, utilizing our standard Spectracarb 2050-A paper as a baseline. One or more properties were changed for each matrix item and a series of fuel cell tests was conducted for each matrix item to determine the effect of changing each variable. The two main objectives were to optimize flow characteristics through changes in porosity and pore size and to reduce cost through reduced heat treatment temperature and material and process modification.

Experimental

The basic sequence of events for this program was as follows:

1. Devise GDE matrix
2. Specify, order, and install equipment
3. Manufacture and test GDE matrix
4. Fuel cell test GDE matrix (outsource)
5. Analysis of fuel cell testing
6. Production run of most promising material(s)
7. Conduct manufacturing feasibility study on most promising material(s), including possible continuous manufacturing and cost study

1. Devise GDE Matrix

As stated in the Tech Approach section earlier, we wanted to optimize flow characteristics through changes in porosity and pore size and to reduce cost through reduced heat treatment temperature and material and process modification. The following outline summarizes our approach:

I. Flow Characteristic Variants

- A. Resin Content (RC) Variants: a range of resin contents would delineate the trade-off between lower strength with higher porosity and higher strength with lower porosity.
- B. Multi-Ply Variants: past work indicated that flow characteristics differed when the same thickness and density material was produced with one, two or three plys.
- C. Density Variants: different areal weight papers would be molded to the same thickness to vary density while maintaining constant thickness to determine the effect of density.
- D. Thickness Variants: different areal weight papers would be molded to different thicknesses while maintaining constant density to determine the effect of thickness.
- E. Filler Variants: carbon and graphite fillers would be introduced during prepregging while maintaining constant thickness to determine the effect of fillers.
- F. Hydrophilic Variant: the naturally hydrophobic baseline material would be made hydrophilic through an electrochemical treatment in dilute acetic acid in an attempt to improve water management.

II. Cost Reduction Variants

- A. Material Variant: stainless steel fibers would be incorporated into the paper making process in an attempt to maintain conductivity while reducing heat treatment costs.

- B. Processing Variants: a series of carbonization and graphitization temperatures would be run to determine the lowest acceptable heat treatment that produced acceptable performance.

2. Specify, Order, and Install Equipment

A brief overview of the manufacturing process for the materials is as follows:

Figure 1: Gas Diffusion Electrode Manufacturing Steps

Carbon Fiber Paper Manufacture: The carbon fiber paper is manufactured in a wet laid paper process wherein the carbon fibers are suspended in water and, using commercial paper making equipment, are formed into a continuous roll of paper. Our original intent was to manufacture these papers in the laboratory using a hand sheet mold. However, budgetary and time constraints indicated that producing uniform hand sheets would require more time and expense than originally thought, so the hand sheet process was outsourced to a commercial paper manufacturer.

Impregnation: The paper is then impregnated with a specified phenolic resin by commercial prepreggers in a production mode. The paper travels through a dip tank, through squeeze rolls and then through an oven, where solvents are removed and the resin is partially cured – this is what is called "B – staging." We spent a fair amount of time in this program perfecting a laboratory prepreg method using a dip pan and squeeze rolls set to the desired thickness.

Molding: The impregnated paper is then molded in hydraulic presses. The papers are typically stacked with separators interleaved, then pressed to preset stops under temperature. After molding, the CF paper is significantly reduced in thickness. We obtained a 30 ton hydraulic press with 15" x 15" platens in order to mold the materials for this program.

Carbonization and Graphitization: Carbonization ($> 700^{\circ}\text{C}$) and subsequent graphitization ($\geq 2000^{\circ}\text{C}$) is done in one step in a furnace under an inert atmosphere (Nitrogen or Argon). This carbonizes the phenolic resin, resulting in a nominal weight loss of 50% for the resin. The carbon fiber loses only about 5% of its weight, since it has already been carbonized. We obtained a graphitization furnace (2000°C capability, 8" x 8" x 2.5" heating zone) for this program in order to quickly and economically heat treat the numerous iterations of GDE produced.

3. Manufacture and Test GDE Matrix

Following equipment set-up, the GDE matrix was manufactured according to the processes previously described. Following manufacture, we conducted a series of physical and electrical tests to characterize the materials and to ensure the materials met certain minimum standards before proceeding with fuel cell testing. The manufactured matrix and test results are presented in Table 1.

Table 1: GDE Matrix and Physical Test Results

Category	Variant	Thickness (mils)	Density (g/cc)	In-Plane Resist ($\Omega \cdot \text{cm}$)	Flexural Strength (psi)	Gas Flow (cfm)	PSD (μ)
Baseline	None	10.5	0.50	0.007	5064	47.5	28.0
Flow	Low RC1	12.0	0.36	0.014	4465	93.5	30.7
	Low RC2	12.0	0.39	0.012	4245	85.3	30.0
	Std RC1	11.5	0.44	0.011	5486	75.7	30.7
	Std RC2	11.0	0.48	0.011	4686	68.6	28.0
	High RC1	11.0	0.52	0.010	6539	63.7	28.6
	High RC2	11.0	0.63	0.008	6140	43.9	28.2
Flow	Ply (2)	11.5	0.48	0.009	5989	80.2	29.7
	Ply (3)	11.0	0.50	0.008	5732	76.1	30.8
Flow	Density	10.5	0.33	0.012	3603	205.6	39.5
	Density	11.0	0.41	0.009	5028	83.5	32.4
	Density	12.0	0.53	0.007	5785	51.2	29.7
	Density	11.5	0.65	0.006	7526	33.5	28.0
Flow	Thickness	5.0	0.48	0.008	5644	64.6	N/A
	Thickness	8.0	0.44	0.007	4833	70.8	28.6
	Thickness	11.0	0.50	0.009	5836	79.4	30.8
Flow	Filler C15	11.0	0.63	0.009	5293	53.4	28.8
	Filler C30	11.0	0.71	0.008	5377	31.4	27.8
	Filler G15	11.0	0.55	0.008	5230	58.2	28.6
Flow	Hydro	11.0	0.48	0.012	5434	66.4	28.2
Cost	SS 30%	11.0	0.50	N/A	N/A	N/A	N/A
	HT1	12.0	0.47	0.027	2474	44.8	26.0
	HT2	8.0	0.46	0.022	4233	48.4	N/A
	HT2	11.5	0.50	0.018	3565	74.2	24.5
	HT3	11.0	0.47	0.012	6261	65.8	25.2
	HT4	11.5	0.47	0.011	5249	47.5	25.2
	HT5	9.5	0.56	0.002	4089	47.6	24.5

The only variant which was not successfully manufactured was the variant utilizing stainless steel fibers. Satisfactory hand sheets were not able to be produced, and given feedback that the steel fibers could compromise cell performance, this variant was dropped from the matrix.

4. Fuel Cell Testing of GDE Matrix

We contracted with several outsource vendors to perform fuel cell testing on the GDE variants. It was quickly determined that the different fuel cell designs, membrane electrode assembly techniques, and cell operating conditions had a dramatic effect on the performance of the electrodes, to the extent that it was initially difficult to obtain results that were repeatable enough to differentiate the effect of the GDE variants. We subsequently conducted extensive work with several fuel cell manufacturers to ensure stable performance on industry standard baseline materials. During the course of this work we determined that we would have to sacrifice some raw fuel cell performance in order to obtain reproducible results across the broad range of GDE variants. Raw performance was sacrificed solely for achieving the program's purpose of evaluating variations in the GDE under similar cell conditions and does not reflect the GDE's potential in an optimized cell. A summary of representative fuel cell testing results by variant is presented in Table 2.

Table 2: Fuel Cell Test Results on GDE Matrix

Category	Variant	Fuel Cell Resistivity ($\text{m}\Omega\cdot\text{cm}^2$)	Volts @ (mA/cm^2)			
			OCV	600	1000	1600
Baseline	None	128	0.97	0.73	0.64	0.46
Flow	Low RC1	121	0.97	0.73	0.64	0.48
	Low RC2	120	0.97	0.66	0	0
	Std RC1	118	0.98	0.74	0.65	0
	Std RC2	127	0.98	0	0	0
	High RC1	131	0.96	0	0	0
	High RC2	139	0.98	0	0	0
Flow	Ply (2)	N/A	0.98	0.68	0.54	0.36
	Ply (3)	108	0.98	0.55	0	0
Flow	0.33 g/cc	127	0.97	0.71	0.53	0
	0.65 g/cc	N/A	0.98	0.58	0	0
Flow	5 mil	N/A	0.97	0.65	0.49	0.35
	8 mil	137	0.97	0.73	0.63	0.45
Flow	Filler C15	125	0.98	0.69	0.52	0
	Filler C30	152	0.96	0	0	0
	Filler G15	N/A	0.96	0.68	0.58	0.38
Flow	Hydro	N/A	0.96	0.3	0	0
Cost	HT1	170	0.98	0.68	0.39	0
	HT2 (std)	121	0.97	0.74	0.64	0.46
	HT2 (thin)	N/A	0.98	0.73	0.60	0.47

The original matrix contained thirty variants. Initial fuel cell testing enabled us to trim costs by eliminating cell testing of some variants which were anticipated to be poor performers.

5. Analysis of Fuel Cell Testing

Analysis of the above results is as follows:

Flow Characteristic Variants

Resin Content: It was quickly determined that there is a diminishing return with increasing resin content. Standard and low resin contents provided acceptable fuel cell results, while higher resin contents tended to choke off the surface of the electrode, resulting in flooding and poor results. SEM photomicrographs shown in Figures 2 and 3 demonstrate this effect. At a resin content of 50%, the resin saturates the fibers while leaving the pore structure intact. At a resin content of 75%, the excess resin has begun to web on the surface of the electrode, blocking a significant amount of the pore structure.

Figure 2: Resin Saturation at 50% Resin Content (50x)

Figure 3: Resin Webbing at 75% Resin Content (50x)

Multi-Ply: The two ply material approached the performance of the baseline material, but the increased cost associated with manufacturing twice as much base paper to produce the finished product eliminated this material from further consideration.

Density: The high density material flooded at higher voltages due to reduced porosity. The lower density material performed well except at the highest voltages, but merely matching baseline performance did not compensate for the reduced strength of this material.

Thickness: Thinner materials matched or approached the baseline performance. This information proved valuable, as thinner GDE's can produce higher power densities due to thinner stacks and are also more conducive to continuous production, as will be discussed later in this report.

Fillers: A high filler content (30%) tended to fill pores and hence resulted in flooding. Lower filler contents (15%) provided adequate performance, but once again the results did not justify the expense of additional materials and manufacturing steps.

Hydrophilic: The hydrophilic material performed adequately under dry conditions, keeping the membrane hydrated, but quickly flooded under wet conditions. As other materials provided more balanced performance at lower cost, no further tests were performed.

In summary, while the resin content studies proved useful in defining the resin content limits for whatever GDE material is used, none of the flow characteristic variants produced significantly better results than the baseline material and hence did not merit further evaluation at this time.

Cost Reduction Variants

Heat Treatment: The heat treatment matrix provided the most promising data. As the data shows, the fuel cell resistance was fairly high for the HT1 (lowest heat treatment) material, and performance began to suffer at higher voltages. However, at HT2, the paper's conductivity had increased to the point where the fuel cell resistance was comparable to higher heat treatment materials, and cell performance matched or improved upon the baseline. This was thought to be an anomalous result at first, but subsequent screening and long term testing duplicated the initial results.

Figure 4 shows cell voltages at discrete amperages for several materials that were tested in a 13 cell short stack. The lower cost (HT2) Spectracorp variant is equal or better to the industry standard material at the high voltages that many companies are utilizing for high efficiencies and is very close to matching the industry standard material at lower voltages. Figure 5 shows the performance of the lower cost (HT2) Spectracorp material versus industry standard materials across the full polarization curve.

Historically, the high electrical and thermal conductivity and corrosion resistance needed for phosphoric acid cells was obtained by heat treating to 2800°C. However, heat treating to this temperature is quite expensive due to furnace component deterioration. Most carbon fiber papers used in PEM cells are still heat treated to > 2000°C. Reducing this temperature to 1600°C or lower (carbonizing temperatures) would result in significant cost savings due to energy and furnace design considerations. The heat treatment matrix results demonstrated that carbonizing temperatures (HT2, $\leq 1600^{\circ}\text{C}$) produce acceptable material. Such temperatures not only allow for much less expensive furnaces but also make continuous production feasible. In summary, the heat treatment data demonstrates that the material produced under this program can match the performance of current state of the art GDE materials at a lower cost and can be feasibly produced in a continuous fashion, as will be discussed later in this report.

Figure 4: Gas Diffusion Electrode Performance at Discrete Amperages

Figure 5: Polarization Curves for Low Cost Gas Diffusion Electrode

6. Production Run

Based on the confirmed results from the fuel cell testing which demonstrated that a thinner, lower heat treated material could match or improve upon the performance of current state-of-the-art materials, we manufactured a small production run of the thin, low heat treat (8.5 mils, HT2 heat treat) material. The run consisted of approximately (500) 15" x 15" sheets manufactured using commercial paper making, prepregging, molding, and carbonization equipment. This material has been made available to DOE's commercial fuel cell partners for initial testing in their respective fuel cell systems.

7. Manufacturing Feasibility Analysis

Following the successful production run we were able to begin a manufacturing feasibility analysis, including some preliminary processing trials, on a large volume, continuous manufacturing process for low cost GDE.

Most fuel cell manufacturers state that they will need a continuous roll of GDE material in order to make an affordable continuous MEA in large volume production. The only continuous material currently in commercial use is woven carbon fiber cloth, which will

remain nearly twice as expensive as non-woven carbon fiber papers in large volumes. Papers are currently made in batch processes due to the technical complexities and expense of continuous molding and high temperature heat treating. The data obtained in this program has demonstrated that lower temperature heat treatments still produce viable GDE material, significantly simplifying the final manufacturing process and allowing for further investigation of continuous production.

The first two stages of manufacturing (paper manufacture and impregnation) are already continuous processes. The impregnated paper is currently sheeted because the material is currently batch molded, but we have already had prepreg rolled continuously on a 6" core for purposes of continuous process evaluation. We are also evaluating the possibility of eliminating a separate impregnation step by using a hot melt phenolic prior to molding.

The difficulty in continuously molding these paper-based GDE materials is in maintaining the required temperature and pressure for a sufficient time to uniformly cure the prepreg. Most of the continuous methods have discrete pressure and temperature zones, so the phenolic resin has to be heated quickly to temperatures greater than 150°C in order to cure in a reasonable amount of time. Numerous continuous molding trials have already been conducted. One early trial used an indexing press, a variant of existing hydraulic presses which compression molds a discrete section of a continuous roll, advances the roll, and molds the next section. However, waste was produced at the edges of the mold, where the material sees temperature without pressure. The difficulty in obtaining simultaneous temperature and pressure is touched upon on the following pages, which discuss several different technologies which are being evaluated.

Figure 6: Flatbed laminating systems

Pressure is applied by heated rolls. Initial trials indicated insufficient time at temperature and pressure to produce sufficient molding.

Figure 7: Heated continuous stainless steel belts

Material is continuously molded between the belt and a heated drum. Discrete pieces have been successfully run through this process under several conditions. Trials are now being run on continuous rolls.

Figure 8: Continuous pressure flatbed system

Discrete pieces have been successfully run. We are awaiting scheduling for a continuous run.

We are confident that we will soon have a continuously molded material employing one of the continuous technologies presented. We will then further evaluate the economics of each technology before proceeding.

Continuous carbonization technology currently exists and has been employed to successfully carbonize discrete samples of up to one square meter in size. Further trials on continuous rolls awaits successful production of continuously molded material.

Conclusions/Future Direction

We have demonstrated that it is possible to manufacture a high performance carbon paper based GDE material at a lower cost than existing materials. In addition, the GDE material developed in this program is highly suited to continuous production resulting in a roll product, which is essential for large volume production of multi-layer MEA's. Our initial projections indicate that commercial pricing for the new material (2050-L) should be at least 20% less than our baseline material (2050-A), with continuously produced material perhaps $\geq 30\%$ less expensive. A volume price projection is presented in Figure 9.

Figure 9: Volume Price Projections for Continuous Carbon Fiber Papers

Following initial evaluation of the batch manufactured GDE resulting from this program, we will continue to work with DOE fuel cell stack partners in order to accelerate the transition to continuous commercial scale production.