V.B.2 Next Generation Bipolar Plates for Automotive PEM Fuel Cells

Orest L. Adrianowycz
GrafTech International Ltd.
12900 Snow Road
Parma, OH 44130
Phone: (216) 676-2381; Fax: (216) 676-2276
E-mail: orest.adrianowycz@graftech.com

DOE Technology Development Manager:
Terry Payne
Phone: (202) 586-9585; Fax: (202) 586-9811
E-mail: Terry.Payne@ee.doe.gov

DOE Project Officer: Reg Tyler
Phone: (303) 275-4929; Fax: (303) 275-4753
E-mail: Reginald.Tyler@go.doe.gov

Technical Advisor: Thomas Benjamin
Phone: (630) 252-1632; Fax: (630) 252-4176
E-mail: Benjamin@anl.gov

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Subcontractors:
- Ballard Power Systems (BPS), Vancouver, Canada
- Huntsman Advanced Materials (HAM), Woodlands, TX
- Case Western Reserve University (CWRU), Cleveland, OH

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Project End Date: February 28, 2009

Objectives

- Develop an expanded graphite/polymer composite to meet the 120°C fuel cell operating temperature target.
- Demonstrate manufacturing capability of new materials to a reduced bipolar plate thickness of 1.6 mm.
- Manufacture high-temperature flow field plates for full-scale testing.
- Validate performance of new plates under automotive conditions using a short (10-cell) stack.
- Show viability of $5/kW cost target through the use of low-cost materials amenable to high volume manufacturing.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section (3.4.4) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan [1]:

(A) Durability
- Improved corrosion resistance
- Decrease weight and volume

(B) Cost
- Lower material and production costs
- Increased power density due to decreased thickness

(C) Performance
- Improved gas impermeability
- Improved electrical and thermal conductivity

Technical Targets

The goal of this work is to develop bipolar plates for polymer electrolyte membrane (PEM) fuel cells which will meet the DOE high-temperature performance and low-cost manufacturing targets for 2010 and beyond. The targets are listed in Table 1. These goals will be met through a low-cost manufacturing process based on expanded graphite technology and the high-temperature performance of a new class of resins.

TABLE 1. DOE Technical Targets: Bipolar Plates (Table 3.4.14, Ref. 1)

Characteristic	Units	2010/2015	Project 2008 Status
Cost[a]	$/kW	5/3	TBD
Weight	kg/kW	<0.4	TBD
H_2 permeation flux	$cm^3\ sec^{-1}\ cm^{-2}$ at 80°C, 3 atm (equivalent to <0.1 mA/cm^2)	$<2 \times 10^{-6}$	TBD
Corrosion	$\mu A/cm^2$	<1[b]	<1[b]
Electrical conductivity	S/cm	>100	>1,000
Resistivity[c]	Ohm-cm	0.01	<0.010
Flexural Strength	MPa	>25	>55
Flexibility	% deflection at mid-span	3 to 5	TBD

[a] Based on 2002 dollars and costs projected to high volume production (500,000 stacks per year).
[b] May have to be as low as 1 nA/cm if all corrosion product ions remain in ionomer for metal plates. Corrosion of flexible graphite plates is not an issue.
[c] Includes contact resistance.
[d] Developers have used ASTM C-651-91 using four point loading at room temperature.
TBD - to be determined

Accomplishments

- All critical starting material evaluation and testing is complete and graphite mat and resin system for full-size plate fabrication have been selected.
- New composite systems have been shown to have equivalent or improved dimensional stability and mechanical and thermal properties over the current GRAFCELL®[1] composite.
- Gas impermeability has been demonstrated to a single plate thickness of less then 0.8 mm.
- Critical processing parameters for plate embossing have been identified and optimized.
- Basic plate architecture has been identified.
- Production press for fabrication of full-size plates has been identified, evaluated, and certified for use.
- Preliminary leachate, and glycol testing results are positive or do not indicate any significant problems with cell operations at elevated temperature.
- Single cell testing of machined resin-flexible graphite composite plates has demonstrated >1,000 hours of operation at 120°C with no evidence of failure.
- Project is on schedule to produce full-size flow field plates for high-temperature short-stack testing by Ballard in early 2009.

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Introduction

PEM fuel cells that can operate at higher temperatures can deliver more power and have a more efficient balance-of-plant. Accordingly, the 2010 Department of Energy targets for membrane and balance-of-plant components call for fuel cells that can operate at temperatures up to 120°C. Today's plate materials are typically used and tested at temperatures between 80 and 90°C. Although excellent performance has been demonstrated by fuel cells operating under these conditions in cars and buses around the world, vehicle manufacturers are already demanding higher operating temperatures to increase power and efficiency. It is clear that new bipolar plate materials must be developed that can meet DOE's targets for cost, corrosion, and other characteristics, as well as operate at higher temperature.

Approach

In this project, a continuous expanded natural graphite structure will incorporate new thermoset resin systems that can improve the high temperature performance and properties of PEM fuel cells. Physical properties of resin/graphite composite materials will be measured, and flow field plates of the composites will be evaluated in high temperature (120ºC) single-cell testing. Full-size automotive plates of the preferred composite will be molded and tested in a 10-cell stack under automotive conditions. A material and manufacturing cost estimate will be completed to show how the new bipolar plate composite can meet the DOE 2010 target for bipolar plates of $5 per kilowatt, thereby contributing to the goal of reduced system cost.

The use of polybenzoxazine polymers, a new class of resin system with higher glass transition temperatures, will be explored to provide the necessary improvement in high-temperature performance. Other bipolar plate physical properties will be addressed by further modification and formulation of the new resin system. Forming of bipolar plates from the new composites depends primarily on the graphite/resin composite, but also on specific processing conditions of the forming method and on the design and geometry of the part. Aspects of the molding operation will be investigated through the use of small-scale die sets. Ballard Power will supply specific geometric features pertinent to automotive-style bipolar plates, and these will be molded on a small-scale to understand the processing limitations of the new graphite/resin material. A full-scale die set will be made to mold bipolar plates for a 1,000-hour stack test at Ballard Power.

Results

The project plan consists of eight major tasks, six of which have started. The major accomplishments of each of the six tasks that have begun are summarized in the following sections.

Task 1: Natural Graphite Selection

Natural graphite sources from a number of domestic and international suppliers were evaluated. Candidate flakes from these sources were selected based on data contained in a proprietary GrafTech database. The selected samples were characterized using a standard regimen of raw material tests. Included in this analysis was an evaluation of the flakes for their suitability in expanded graphite production. Evaluation of the selected graphites was done using a design of experiments methodology to identify the working range of intercalation chemistries and exfoliation methods. An initial screening experiment was conducted to identify key graphite materials and processing variables. After completion of the screening experiment, a response surface experiment was initiated to focus on those key variables to more clearly identify interactions, as well as the usable range of materials. Preliminary statistical analysis of the response surface data identified optimum properties for graphite mat production. Based on these

[1] GRAFCELL is a registered trademark of GrafTech International Holdings Inc.

results three graphite mats, G1, G2 and G3 were down-selected for preliminary composite evaluation in Task 3.

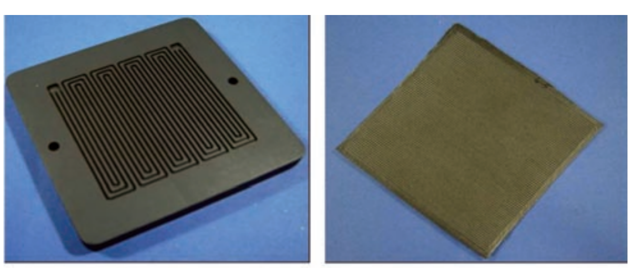
Task 2: Resin Identification and Selection

Fuel cell performance characteristics, and resin specifications based on these characteristics, were defined. Using the resin specifications, a number of benzoxazine and epoxy resin systems that are potentially capable of meeting the program goals were identified. New resin chemistries, including catalyzed systems were formulated and laboratory-scale samples of these resin systems were evaluated. Three resin systems were down-selected for evaluation in composites with the expanded graphite mats selected in Task 1.

Task 3: Small-Scale Composite Preparation and Evaluation

Resin-impregnated expanded graphite composites from the three expanded graphite mats and three down-selected resin systems were prepared. Cured resin expanded graphite composites were fabricated as blank stock with a target thickness of 0.60 mm. This base stock was used to prepare samples for all subsequent testing. During the composite preparation process the decision was made to eliminate the epoxy resin due to a number of processing issues. The two remaining resin systems are coded as 2G and 2H. Dynamic mechanical analysis of the 2G composite shows a glass transition temperature of 260°C; well in excess of the thermal stability required for operation at 120°C.

Composites of the two down-selected resin expanded graphite flat stock were temperature cycled in an environmental chamber using modified USCAR - III Test Protocols for normal cycling and thermal shock cycle. The exposure conditions are given in Figure 1. Results of the mechanical testing on these samples were compared to the results obtained on samples which were not environmentally cycled. Analysis of the data show that composites prepared with the 2G resin were statistically identical to or better than, the unexposed samples for all properties evaluated. However, the resin



Machined GRAFCELL Composite Single Cell Flow Field Plate **Molded GRAFCELL Composite Corrugated Flow Field Oxidant Plate**

FIGURE 1. Composite Plate Photographs

TABLE 2. Long-Term Environmental Cycling Protocol

USCAR - III Environmental Test Protocol (Modified)					
	Shock Test		Normal Cycle		
Cycles	100		40		
Step	1	2	1	2	3
Temperature, °C	125	-40	-40	87.5	125
Dwell, hrs	0.5		0.5		
Ramp Rate, °C/min	-328	328	4.25	1.25	-2.75
Hold Temp, °C	-40	125	87.5	125	-40
Relative Humidity, %	50	NA	80-90	NA	NA
Dwell, hrs	0.5	0.5	4	1.5	0.5

NA - not applicable

composites prepared with the 2H resin system did show degradation in both flexural and tensile properties for some samples.

Statistically designed experiments were completed to determine the effects of key process parameters on preparation of the flexible graphite resin composites. Nitrogen leak testing of the flat composite stock showed no detectable leaks for any of the un-embossed sheets under all combinations of process parameters tested. Final optimum processing conditions were determined as part of the embossing designed experiments planned in Task 4.

Task 4: Machining and Embossment of Small-Scale Composites

Additional samples of the new resin-expanded graphite composites were fabricated using the two down-selected resin systems and three expanded graphite materials. Mechanical testing samples were analyzed and compared to results from comparable samples consisting of the incumbent GRAFCELL® FFP standard resin composite system. Test methods used were ASTM D790 for flexural testing and ASTM D638 for tensile testing. Samples were analyzed in an environmental chamber at temperatures of -40, 23, 100, and 120°C in 50% relative humidity (RH).

Statistical analysis of test results indicates that the flexural and tensile strengths of the 2G and 2H benzoxazine resin systems were not significantly different from each other. However, comparisons of results between each resin system and the incumbent GRAFCELL® FFP composite system indicate that both resins are similar to, or significantly higher, in flexural strength and modulus than the GRAFCELL® composite at all temperatures tested. The improvements in mechanical testing properties are most pronounced at elevated temperatures (100 and 120°C) where both benzoxazine resin systems are significantly stronger than the incumbent material and have significantly higher modulus. The tensile strength results are consistent with the flexural results showing that the benzoxazine resins are significantly higher in tensile strength than the GRAFCELL® FFP composite resin system. The results for the tensile modulus are less conclusive. Additional major physical and electrical property measurements have been made on the new benzoxazine resin systems composites. The measurements available to date are summarized in Table 3. These measurements are compared to similar results for the GRAFCELL® FFP material where available. In general, physical properties on the new resin composites are similar to each other and very comparable to or better than those of the GRAFCELL® FFP composite system.

Using a proprietary oxidant flow field die, plates were molded from the composite materials. Photographs of the embossed and machined plates are shown in Figure 1. Nitrogen gas permeability, in-plane and through plane electrical resistance, and dimensional processing changes (growth factors) were measured for each plate. During the permeability testing, composites made using one of the G2 graphite mat materials were observed to be significantly higher in permeability than all others and were removed from additional consideration. Nitrogen gas permeability results indicate either of the two down-selected benzoxazine resins systems can be successfully fabricated into full-size flow field plates that can survive the short-stack testing that is planned for Tasks 6 and 7. With these results, the project contingency point was satisfied.

A processing optimization designed experiment was conducted with the composite dimensional changes (growth factors) as dependent variables. The results indicate that both of the benzoxazine resins exhibit significantly less growth in length and width than the comparable GRAFCELL® resin system. Comparison of the results for the two resin systems indicate than the growth factors in the length direction are statistically the same for the two resins. However, the growth factor difference in the width direction is statistically significant. In both directions, the 2G resin grew less then the 2H resin.

Task 5: Single Cell Testing

High-temperature cell components have been identified and procured from a proprietary source by Professor Tom Zawodzinski of CWRU. The single cell testing protocol selected involves more severe conditions than standard procedures, including potential cycling between 0.5V, 0.8V and open circuit voltage (OCV). The final single cell testing protocol is as follows: 114 hrs at 80°C (70% RH); 86 hrs at 120°C (24% RH). Cells were constructed using an ETEC 1500 gas diffusion layer; conditioned 24-48 hrs at 80°C and liquid samples were collected throughout operations. Cell resistance was as follows: 0.23 ohm-cm^2 after 114 hrs at 80°C; 0.55 ohm-cm^2 after 71 hrs at 120°C; and 0.54 ohm-cm^2 after 86 hrs at 120°C.

Because severe operating conditions are also known to accelerate membrane electrode assembly (MEA) degradation, eight MEAs have been consumed in the course of testing the 2G flow field plate. To date the cell has been in operation for more then 1,000 hours at 120°C. Diagnostic chemical and electrochemical tests are planned to differentiate between MEA degradation and flow field plate degradation. Ex situ tests of bipolar plate materials will be used to develop a profile of possible organic and inorganic leachate. These tests will be used in the post-test analysis of the plates and test effluents.

Task 6: Design and Manufacture Full-size Bipolar Plates (In Progress)

Calibration and certification of the GrafTech AFGF TMP press has been completed. The results indicate that the press flatness characteristics are adequate for use in the final pressing of full size plates. Ballard has approved use of this press for final plate fabrication. Ballard has evaluated their tooling and fuel cell testing equipment inventories and selected a flow field plate design based on modification of a previous plate design for use in final full size plate production. The proposed design has a plate assembly thickness below 1.6 mm and a plate area greater than 250 cm². Test tools of the proposed design have been fabricated and are being used to press test plates for evaluations of growth factors prior to final plate fabrication.

Ballard has developed a glycol permeation test based on ASTM D739-99a to evaluate the permeation of ethylene glycol across the resin expanded graphite composite. Composite plates with the 2G resin showed significantly better performance than those made with the 2H resin. Based on this result and those discussed previously, the 2G benzoxazine resin system has clearly demonstrated better performance over the 2H resin composite and was selected for final plate fabrication. The selection of graphite mat was less obvious since the results for most of the criteria were statistically inconclusive. The final decision was made in favor of the G3 graphite based on the fact that this material is a purified grade. Manufacture of 2G resin for full size plate production has been scheduled by Huntsman and should be available in time for final full plate production.

Conclusions and Future Directions

The following are tasks which will be completed in the next year.

Task 6: Design Flow Field Plate Using Existing Architectures (Q3 2008)

TABLE 3. Composite Property Comparison

			FFP	2G Resin	2H Resin
Property	**Method**	**Units**	**Average**	**Average**	**Average**
Bulk Density	ASTM C611	g/cm^3	1.68	1.68	1.72
Thermal Conductivity (x,y)	ASTM D5470 Modified	W/m-K	275	286	294
Thermal Conductivity (z)	ASTM C714	W/m-K	4.67	4.03	4.03
Thermal Diffusivity	ASTM C714	cm^2/s	0.039	0.033	0.033
Electrical Resistivity (x,y)	ASTM C611	$\mu\Omega$m	7.8	8	11
Electrical Resistivity (x,y)	GTI Internal	$\mu\Omega$m	NA	10	9
Electrical Resistivity (z)	GTI Internal, 1-Ply	$\mu\Omega$m	NA	934	937
Contact Resistance	GTI Internal	$\mu\Omega$cm^2	NA	2.1	3.0
Electrical Conductivity (x,y)	GTI Internal	S/cm	1,470	1,002	1,111
Electrical Conductivity (z)	GTI Internal, 1-Ply	S/cm	NA	10.7	10.7
Thermal Expansion Coefficient (x,y)	ASTM E1545	μm/m-K	1.31	0.95	0.98
Thermal Expansion Coefficient (z)	ASTM E1545	μm/m-K	97.2	81.8	74.1
Flexural Strength, -40°C	ASTM D790	MPa	63.9	67.3	69.0
Flexural Strength, 23°C	ASTM D790	MPa	57.5	58.7	61.8
Flexural Strength, 100°C	ASTM D790	MPa	37.8	47.8	51.3
Flexural Strength, 120°C	ASTM D790	MPa	NM	44.3	49.7
Tensile Strength, -40°C	ASTM D638	MPa	41.9	41.3	44.6
Tensile Strength, 23°C	ASTM D638	MPa	38.6	37.4	43.8
Tensile Strength, 100°C	ASTM D638	MPa	29.2	32.8	36.4
Tensile Strength, 120°C	ASTM D638	MPa	NM	32.6	37.4
NA - Not Available					
NM - Not Measured					

- Finalize plate design with material selection and growth factors incorporated.
- Build full-size embossing tool and leak testing device followed by final material fabrication.
- Commission glue equipment.
- Build compression stack hardware including all supporting components.
- Select MEA and modify seal equipment.
- Fabricate, inspect and glue plate assemblies.

Task 7: Short-Stack Test of Full-size Plates (Q4 2008 and Q1 2009)

- Fabricate and seal MEAs.
- Assemble plates with sealed MEAs in compression stack hardware.
- Commission test station with duty cycle.
- Conduct durability testing targeting 1,000 hours on a 10-cell stack.
- Conduct freeze start testing.
- Post test analysis, results and review including plate inspection.
- Deliver full-size plate stack to DOE.

Task 8: Economic Assessment of New Technologies (Q3 and Q4 2008)

The following are conclusions based on the work completed to date.

- New expanded graphite-resin composite systems have superior thermal stability and equivalent or improved dimensional stability and mechanical properties over the current GRAFCELL® composite.
- Gas impermeability for these materials has been demonstrated to a single plate thickness of less than 0.8 mm which is adequate for fuel cell operation under the proposed design.
- Critical processing parameters for plate embossing have been identified and optimized.
- Preliminary leachate, glycol and single-cell testing results on the new composite systems are positive

or do not indicate any significant problems with cell operations at elevated temperature.

FY 2008 Publications/Presentations

1. A presentation of the project results to-date was given at the Third Annual MEA Manufacturing Symposium in Dayton, Ohio on August 21, 2007.

2. A presentation of the project status was given before the United States Council for Automotive Research (USCAR) Fuel Cell Technical Team in Detroit on October 10th, 2007.

3. Project results were presented at the U.S. Department of Energy (DOE) Annual Fuel Cell Program Merit Review in Washington, D.C. on June 11th, 2008.

References

1. "Hydrogen, Fuel Cells and Infrastructure Technologies Multi-Year Research, Development and Demonstration Plan", U.S. Department of Energy, Hydrogen, Fuel Cells & Infrastructure Technologies Program, DOE/GO-102003-1741, October 2007.