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

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

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Project End Date: August 31, 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 of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan [1]:

(A) Durability
- Improved corrosion resistance

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

(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 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. [1])

Characteristic	Units	2010/2015	Program 2009 Status
Cost[a]	$/kW	5/3	TBD
Weight	kg/kW	<0.4	0.57
H_2 permeation flux	$cm^3\ sec^{-1}\ cm^{-2}$ @ 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	<0.01
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

- New resin impregnated flexible graphite 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.
- Single cell testing of machined resin-flexible graphite composite plates has demonstrated >1,100 hours of operation at 120°C with no evidence of plate degradation.
- Leachate, and glycol testing results do not indicate any significant problems with cell operations at elevated temperature.
- Bipolar plates have been pressed, cured, glued, leak tested and shipped to Ballard for stack testing.
- A short 10-cell stack of full-sized plates has been assembled and 1,000-hour testing at elevated temperatures initiated.
- Preliminary results on studies of high speed forming for resin impregnated bipolar plate production are positive.
- Cost analysis of the bipolar plate manufacturing process by Directed Technologies, Inc. is in progress.

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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.

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

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-flexible graphite composite materials will be measured, and flow field plates of the composites will be evaluated in high temperature (120°C) 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 cost target for bipolar plates of $5 per kW.

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 resin-flexible graphite 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 resin-flexible graphite 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, the first three of which were completed and reported in the previous annual report. Tasks four through six were completed in the past year. The major accomplishments of each of the tasks are summarized in the following sections.

Task 1: Natural Graphite Selection (Completed in 2008)

Natural graphite sources from a number of domestic and international suppliers were evaluated. The selected samples were characterized using a standard regimen of raw material tests. Evaluation of the selected graphites was done using a design of experiments methodology to identify the working range of intercalation chemistries and exfoliation methods. Based on the results three graphite mats, G1, G2 and G3 were down-selected for preliminary composite evaluation in Task 3.

Task 2: Resin Identification and Selection (Completed in 2008)

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 project goals were identified, formulated, and samples were evaluated on the laboratory-scale. Based on the results of the evaluation, three resin systems were down-selected for further evaluation in composites with the expanded graphite mats selected in Task 1.

Task 3: Small-Scale Composite Preparation and Evaluation (Completed in 2008)

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. Two resin systems, 2G and 2H, were selected for additional evaluation. Dynamic mechanical analysis of the composites showed glass transition temperatures >250°C; well in excess of the target 120°C operating temperature.

Composites of the two down-selected resin expanded graphite flat stock were temperature cycled in an environmental chamber using modified United States Council for Automotive Research - III Test Protocols for normal cycling and thermal shock cycle. 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 shows that composites prepared with the 2G resin were statistically identical to or better than, the unexposed samples for all properties evaluated. However, the 2H resin system composites did show mechanical property degradation.

Statistically designed experiments were completed to determine the effects of key process parameters on preparation of the flexible graphite resin composites. Nitrogen and helium 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 in Task 4.

Task 4: Machining and Embossment of Small-Scale Composites (Completed in 2009)

Mechanical testing samples were prepared, analyzed, and compared to results from comparable samples consisting of the incumbent GRAFCELL Flow Field Plate (FFP) standard resin composite system. Samples were analyzed in an environmental chamber at temperatures of -40, 23, 100, and 120°C in 50% relative humidity (RH). Statistical analysis of the mechanical testing results indicates that the flexural and tensile strengths and work-of-fracture 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 the benzoxazine resins are similar to, or indicate that both benzoxazine resins are similar to or significantly higher than the GrafCell composite at all temperatures tested in terms of flexural strength, modulus, and work-of-fracture. The improvements 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 (see Figure 1).

Additional physical and electrical property measurements have been made on the new benzoxazine resin systems composites. The measurements are summarized in Table 2 and 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 comparable to or better than those of the GRAFCELL FFP composite system.

Using a proprietary oxidant flow field die pattern, plates were molded from the composite materials. Figure 2 is a photo micrograph of a cross-section of one of the flow field plate channels showing the feature definition possible with the new resin-flexible graphite composites. Nitrogen gas permeability, in-plane and through-plane electrical resistance, and dimensional processing changes (growth factors) were measured for each plate. Nitrogen gas permeability results indicated that either of the two benzoxazine resins systems could 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.

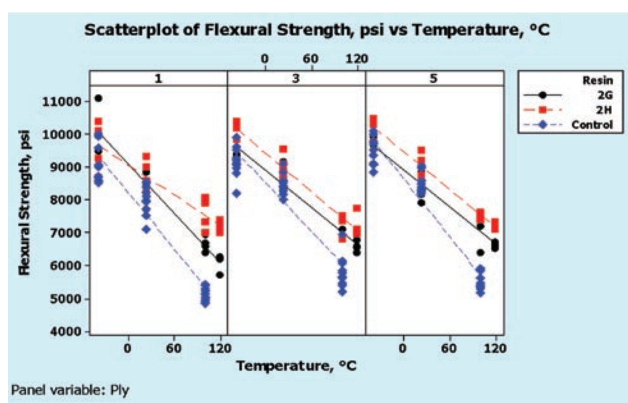

FIGURE 1. Mechanical Strength Testing Results

TABLE 2. Composite Property Comparison

Property	Method	Units	FFP Average	2G Resin Average	2H Resin Average
Bulk Density	ASTM C611	g/cm3	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	cm²/s	0.039	0.033	0.033
Electrical Resistivity (x,y)	ASTM C611	μΩm	7.8	8	11
Electrical Resistivity (x,y)	GTI Internal	μΩm	NA	10	9
Electrical Resistivity (z)	GTI Internal, 1-Ply	μΩm	NA	934	937
Contact Resistance	GTI Internal	μΩcm²	NA	2.1	3.0
Electrical Conductivity (x,y)	GTI Internal	S/cm	1470	1002	1111
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					

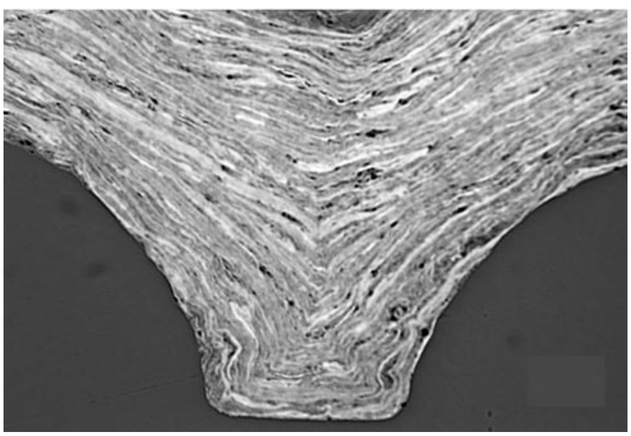

FIGURE 2. Test Tool Plate Cross Section

Task 5: Single Cell Testing (Completed in 2009)

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

Single cell testing of the 2G resin flexible graphite composite is complete. As was anticipated, periodic disassembly of the cell, inspection of the flow field plates and replacement of the membrane electrode assembly (MEA) was necessary. There was no evidence of degradation or contamination of the composite after more than 1,120 hrs of operation at 120°C. Similar testing was initiated for the 2H resin composite and over 200 hrs of operation were completed with no evidence of plate degradation. Unfortunately, additional testing of the 2H plates was suspended due to consumption of the supply of high temperature MEAs. Additional MEAs could not be obtained and the decision was made to discontinue any additional single cell testing. Analysis of the effluent that was collected during testing is in progress.

Task 6: Design and Manufacture Full-size Bipolar Plates (Completed in 2009)

Ballard selected an FFP design based on a modification of a plate from a previous design for use in final full-size plate production. This modified plate design has a plate assembly thickness below 1.6 mm and a plate area greater than 250 cm² which meet the project requirements.

The final selection of graphite and resin for full sized plate fabrication was made and consisted of the 2G benzoxazine resin system and G3 graphite. The 2G resin-composite demonstrated better performance than the 2H resin composite in a significant majority of the evaluation criteria. The final graphite selection was based primarily on flake availability. Using the selected starting materials, approximately 60 fuel and 60 oxidant plates were fabricated. All of the plates were within the target thickness of <0.8 mm and with length and width measurements within Ballard's specifications.

Task 7: Short Stack Test of Full-Size Plates (In progress)

In a change from the original project plan, GrafTech was responsible for gluing the individual flow field plates to form the bipolar plate. The new glue dispensing equipment was delivered, installed and used to glue the anode and cathode plates and end-plate assemblies. All the glued assemblies were successfully cured.

Using the initial GTI shipment of bipolar plates, Ballard assembled one 10-cell stack and started testing in early June. The stack developed problems with cell six at higher temperatures and was taken off-test and disassembled. Preliminary evaluation indicated that the problem with the cell was due to degradation of the MEA seals at high temperatures. A modified seal capable of operation at higher temperatures was substituted and the stack operating temperature reduced to 110°C. The stack is in the process of being reassembled and tested. Two additional stacks will be assembled; one for testing by a group at Argonne National Laboratory and the second for freeze testing by Ballard. The Argonne group was selected by the DOE to perform verification of the bipolar plates.

Task 8: Economic Assessment of New Technologies (In Progress)

Bipolar plate manufacturing cost analysis of the new resin systems and associated processes has been initiated. Costs of raw materials and production processes for the anticipated manufacturing processes have been obtained or estimated. To ensure consistency with previous bipolar plate manufacturing cost estimates, the DOE has requested that the manufacturing cost estimate is made using the methodology employed by Directed Technologies, Inc. (DTI). DTI has been contacted, a non-disclosure agreement executed, and cost data exchanged.

Conclusions and Future Directions

Conclusions

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 then 0.8 mm which is adequate for fuel cell operation under the proposed design.
- 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.
- Critical processing parameters for plate embossing have been identified, optimized and full size bipolar plates embossed, sealed and glued.
- A short 10-cell stack has been assembled and placed in test using a standard duty cycle.
- Manufacturing cost analysis data has been obtained and submitted to DTI for evaluation.

Future Directions

- Complete durability testing targeting 1,000 hours on a 10-cell stack.
- Conduct freeze start testing.
- Post test analysis, results and review including plate inspection.
- Assembly and delivery of a full size 10-plate stack to Argonne National Laboratory.

Special Recognitions & Awards/Patents Issued

1. "Fuelling Great Opportunities: Resin Development Program for Fuel Cell Applications", JEC Composites Raw Materials Award and presentation, Paris France, March 2009.

FY 2009 Publications/Presentations

1. "Flexible Graphite-Resin Composite Bipolar Plates for High Temperature High Energy Density PEM Fuel Cells", Fuel Cell Symposium Presentation #: 1481.

2. Oral presentation before the members of the Department of Energy and the FreedomCAR and Fuel Partnership's Fuel Cell Technology Team (FCTT) on November 20, 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, Oct 2007.