CONTINUOUS GRAPHITE MATRIX COMPOSITES FOR HIGH TEMPERATURE PEM FUEL CELLS

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Introduction

The defining characteristic of GrafTech's patented GRAFCELL® materials technology platform is the continuous matrix of expanded natural graphite. The graphite matrix is impregnated with thermoset resins to form a fluid impermeable, composite prepreg sheet for molding fuel cell components. GRAFCELL materials eliminate the electrochemical corrosion issues inherent with metal plates while providing higher strength, flexibility, thermal conductivity and electrical conductivity than graphite-filled polymer composites. Today, GrafTech's GRAFCELL fuel cell components are operating in polymer electrolyte membrane (PEM) fuel cell stacks in automotive, materials handling and backup power applications.

GrafTech's current epoxy-filled GRAFCELL "FFP-Series" materials provide excellent performance in low-temperature perfluorosulfonic acid (PFSA) membrane type PEM fuel cells, but new, improved materials were needed to provide adequate performance in the challenging environments presented by emerging high temperature PEM fuel cell applications. The U. S. Department of Energy target for *Next Generation Automotive* PEM fuel cell operating temperature is 120 °C. Components for high temperature PEM fuel cells utilizing a phosphoric acid doped polybenzimidazole (PBI) membranes must be able to survive operation at temperatures up to 200 °C in a concentrated phosphoric acid environment. In response to the technical challenges presented by the high temperature PEM fuel cell environments, GrafTech International has developed two new grades of composite materials.

Experimental

Properties of the graphite matrix were optimized according to a designed experiment, as reported by Adrianowycz and colleagues [1].

Polymer resins meeting the performance and cost requirements for both the *Next Generation Automotive* and the PBI membrane type high temperature PEM applications were selected by Huntsman Advanced Materials [2] and modified to be compatible with GrafTech's patented manufacturing process.

The graphite matrix and polymer resins were combined to form prepregs, which were then compression molded to form flat plates and cured. The relevant mechanical, thermal, electrical and chemical properties of the resulting composite materials were evaluated according to the respective standardized test procedures.

Moldability was evaluated by forming prepregs into bipolar plates utilizing both conventional and experimental molding techniques.

The performance and durability of the new composites was demonstrated in ex-situ, single cell and short stack testing.

Results and Discussion

Two new grades of bipolar plate materials were developed. The first, "DOE-2G" utilizes a benzoxazine based resin to meet the performance targets of the next generation automotive application. The key performance improvement of DOE-2G is its greater strength at high temperature. The second new composite, "TG-728" utilizes a bismaleimide based resin system to satisfy requirements of the PBI membrane fuel cell application. In addition to high temperature tolerance, TG-728 provides resistance to concentrated phosphoric acid. The relevant material properties of the new composites are presented alongside GrafTech's FFP series material in Table 1.

Molding trials showed that both DOE-2G and TG-728 composites were able to form fine features and hold the dimensional tolerances required for bipolar plates. Experimental molding trials yielded thin (<1.5 mm), leak-free composite plates with high density (>1.7 g/cc) and excellent feature definition. Single and double sided plates (with flow channels on opposite faces in both parallel and perpendicular configurations) were formed in a single pressing operation.

Full-size automotive plates with internal cooling channels were molded from DOE-2G material, then joined and gasketed to form bipolar plates. The finished plate assemblies had an active area greater than 250cm^2, a total thickness of 1.6mm and a minimum web of 320µm between reactant and coolant channels.

TG-728 and three competitor's materials were subjected to a 2000 hour immersion test in concentrated phosphoric acid at Plug Power. Three-point flex and tensile strength of TG-728 remained above 50 MPa and 30 MPa, respectively throughout the duration of the test, far exceeding competitor's materials, which were lower initially and lost strength as a function of time.

Single cell plates machined from both DOE-2G and TG-728 were both tested for greater than 1000 hours at 120 °C with a PFSA membrane and 180 °C with a PBI membrane, respectively. Although the 120 °C test was interrupted several times by MEA failures, no evidence of plate degradation was found during or after either test.

Final verification of DOE-2G performance was carried out by Ballard Power Systems. 10-cell stacks of full-size

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automotive plates were assembled and demonstrated excellent performance under a simulated drive cycle protocol. No evidence of reactant or coolant leakage was detectable after either high temperature operation or freeze-thaw cycling.

Stacks of both machined and molded TG-728 plates have been tested by customers in PBI membrane applications. The extremely high thermal conductivity of TG-728 has enabled stacks with improved thermal management and has led to a commercial molding program.

Conclusions

Expanded graphite composite bipolar plate materials incorporating two new polymer resin systems have been developed to meet the requirements for high temperature PEM and PBI membrane fuel cell applications. High temperature performance of the new composites is achieved with the added benefits of improvements in strength, modulus, and dimensional stability over the incumbent resin systems. The resulting composite materials can be thin, lightweight and flexible. Electrical and thermal conductivity are largely independent of resin type and loading, indicating that these properties are determined by the continuous graphite matrix. Other properties including maximum use temperature and acid compatibility are determined by the polymer resin reinforcement. The performance and durability of both new composites has been demonstrated in ex-situ testing, single cell testing and stack testing of full-sized, compression molded plates. High-volume manufacturing techniques have been demonstrated successfully and are being scaled up to satisfy future demands for fuel cell bipolar plates and related components for next generation energy conversion and storage devices.

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New GRAFCELL materials were developed in collaboration with Ballard Power Systems, Case Western Reserve University, Huntsman Advanced Materials and Plug Power.

References

[1] Adrianowicz, O.L. et al., Flexible graphite-resin composite bipolar plates for high temperature, high energy density PEM fuel cells. Fuel Cell Seminar and Exposition 2008. Abstract GHT34-3.

[2] Nguyen, Y-L. H. et al., High temperature thermoset resin system for composite bipolar plates. Fuel Cell Seminar and Exposition 2009. Abstract LRD25-26.

Table 1. Typical Properties of GRAFCELL Materials

Property	Method	Units	FFP	DOE-2G	TG-728
Acid Compatibility			Dilute Sulfuric	Dilute Sulfuric	100% Phosphoric
Resin Glass Transition Temperature	DSC, TMA	°C	125	> 200	> 200
Bulk Density	ASTM C559	g/cm^3	1.68	1.68	1.61
Thermal Conductivity (x,y)	ASTM D5470	W/m-K	275	286	285
Thermal Conductivity (z)	ASTM C714	W/m-K	4.67	4.03	4.24
Thermal Diffusivity	ASTM C714	cm^2/s	0.039	0.033	0.035
Contact Resistance (at 0.69 MPa)	GTI Internal	mΩcm^2	1.9	2.2	6.7
Contact Resistance (at 1.75 MPa)	GTI Internal	mΩcm^2	1.2	1.9	3.8
Electrical Conductivity (x,y)	GTI Internal	S/cm	1240	1002	1053
Electrical Conductivity (z)	GTI Internal	S/cm	23	17.5	23
Thermal Expansion (x,y)	ASTM E1545	µm/m-K	1.31	0.95	1
Thermal Expansion (z)	ASTM E1545	µm/m-K	97.2	81.8	80
Flexural Strength, -40 °C	ASTM D790	MPa	63.9	67.3	66.9
Flexural Strength, 23 °C	ASTM D790	MPa	57.5	58.7	59.4
Flexural Strength, 120 °C	ASTM D790	MPa	NM	44.3	47
Tensile Strength, -40°C	ASTM D638	MPa	41.9	41.3	42
Tensile Strength, 23°C	ASTM D638	MPa	38.6	37.4	40
Tensile Strength, 120°C	ASTM D638	MPa	NM	32.6	35