V.B.1 Next Generation Bipolar Plates for Automotive PEM Fuel Cells

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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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Objectives

- Develop an expanded graphite/polymer composite to meet the 120ºC 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
- Decrease weight and volume

(B) Cost
- Lower material & 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 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 low cost manufacturing processes based on expanded graphite technology and the high temperature performance of a new class of resins.

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Units</th>
<th>2005 Status*</th>
<th>2010</th>
<th>2015</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cost</td>
<td>$/kW</td>
<td>10$^4</td>
<td>5</td>
<td>3</td>
</tr>
<tr>
<td>Weight</td>
<td>kg/kW</td>
<td>0.36</td>
<td>&lt;0.4</td>
<td>&lt;0.4</td>
</tr>
<tr>
<td>H₂ permeation flux</td>
<td>cm³ sec⁻¹ cm⁻² @ 80ºC, 3 atm (equivalent to &lt;0.1 mA/cm²)</td>
<td>&lt;2 × 10⁻⁴</td>
<td>&lt;2 × 10⁻⁴</td>
<td>&lt;2 × 10⁻⁴</td>
</tr>
<tr>
<td>Corrosion</td>
<td>µA/cm²</td>
<td>&lt;1$^4$</td>
<td>&lt;1$^4$</td>
<td>&lt;1$^4$</td>
</tr>
<tr>
<td>Electrical conductivity</td>
<td>S/cm</td>
<td>&gt;600</td>
<td>&gt;100</td>
<td>&gt;100</td>
</tr>
<tr>
<td>Resistivity</td>
<td>Ohm-cm</td>
<td>&lt;0.02</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>Flexural Strength</td>
<td>MPa</td>
<td>&gt;34</td>
<td>&gt;25</td>
<td>&gt;25</td>
</tr>
<tr>
<td>Flexibility</td>
<td>% deflection at mid-span</td>
<td>1.5 to 3.5</td>
<td>3 to 5</td>
<td>3 to 5</td>
</tr>
</tbody>
</table>

* This is the first year for which status is available. 2005 status is for carbon plates, except for corrosion status which is based on metal plates.

¹ Based on 2002 dollars and costs projected to high volume production (500,000 stacks per year).

² Status is from 2005 TIAx study and will be periodically updated.

³ May have to be as low as 1 nA/cm if all corrosion product ions remain in ionomer.

⁴ Includes contact resistance.

⁵ Developers have used ASTM C-651-91 Standard Test Method for Flexural Strength of Manufactured Carbon and Graphite Articles Using Four Point Loading at Room 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. The chemistry of the resin system and graphite raw material will be chosen in order to improve the interaction between the resin and graphite. Physical properties of resin/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 target for bipolar plates of $5 per kilowatt, thereby contributing to the goal of reduced system cost.

- The sourcing and chemical processing of natural graphite flake will be studied in order to understand and control the flake properties that most affect the final composite properties. The objective is to identify a working range of acceptable properties so as not to limit options for flake sourcing and eventual large-scale commercialization. Additionally, the edge plane chemistry of the expanded natural graphite flake will be characterized to help identify potential modifications that can improve graphite-resin bonding. This approach should improve composite properties while expanding the scope of usable natural graphite flake sources.
- 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. The interaction of the resin with graphite in general and graphite edge-plane functional groups in particular will be investigated.
- 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.

Accomplishments

The project plan consists of eight major tasks. In the short period of time since the beginning of the project, work has been performed on portions of Tasks 1 through 5. The major accomplishments of each task are summarized in the following sections.

Task 1: Natural Graphite Selection

- Natural graphite sources from a number of domestic and international suppliers have been evaluated. Candidate flakes from these sources have been selected based on data contained in a proprietary GrafTech database.
- The selected natural graphite flakes are listed in Table 2. They include a variety from domestic and imported sources, flakes that are thermally and chemically purified, and a commercially available intercalated flake.
- The selected samples have been 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. Based on the results of this evaluation, four materials have been down selected for further evaluation with resins.

<table>
<thead>
<tr>
<th>Code</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>G1-SZ1</td>
<td>Current production flake</td>
</tr>
<tr>
<td>G1-SZ2</td>
<td>Current production Thermally Purified</td>
</tr>
<tr>
<td>G1-SZ3</td>
<td>Current production Thermally Purified</td>
</tr>
<tr>
<td>G2-SZ1</td>
<td>Imported Current Production</td>
</tr>
<tr>
<td>G3-SZ1</td>
<td>Thermally Purified Domestic</td>
</tr>
<tr>
<td>G4-SZ1</td>
<td>Chemically Purified Imported</td>
</tr>
<tr>
<td>G4-SZ2</td>
<td>Chemically Purified Imported</td>
</tr>
<tr>
<td>G5-SZ1</td>
<td>Imported Intercalated</td>
</tr>
<tr>
<td>G6-SZ1</td>
<td>Alternative Imported</td>
</tr>
</tbody>
</table>

Task 2: Resin Identification and Selection

- GrafTech, Ballard Power Systems, and Huntsman Advanced Materials have agreed on the key fuel cell performance characteristics and developed detailed resin specifications based on these characteristics. Testing procedures and technical targets have been identified and prioritized for every property. When available, common testing protocols have been specified. These specifications are listed in Table 3.
- Based on the resin specifications, Huntsman Advanced Materials has identified a number of benzoxazine and epoxy resin systems that are
potentially capable of meeting the program goals. New resin chemistries, including catalyzed systems have been defined and formulated.

- Preparation of laboratory-scale resin samples has begun and properties on the uncured and cured resins have been obtained. Three of the resin systems have been down selected and evaluation of them in composites has begun using expanded graphite mats from the starting flakes identified in Task 1.

### TABLE 3. Resin Property Specifications

<table>
<thead>
<tr>
<th>Property</th>
<th>Priority</th>
<th>Test</th>
<th>Technical Target</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Processing</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Resin viscosity (in acetone)</td>
<td>1</td>
<td>Shear/Brookfield (25ºC)</td>
<td>0.8 cP (Max. 2.0 cP)</td>
</tr>
<tr>
<td>Curing conditions</td>
<td>1</td>
<td>DSC</td>
<td>205ºC, 1 h (Max. 230ºC, 2 h)</td>
</tr>
<tr>
<td>Polymerization volatiles</td>
<td>1</td>
<td>TGA</td>
<td>Not detectable</td>
</tr>
<tr>
<td>Resin latency</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ambient</td>
<td>1</td>
<td>DSC/Thermosel</td>
<td>Indefinite</td>
</tr>
<tr>
<td>Thermal cycle</td>
<td>1</td>
<td>One cycle to 85ºC with 45-min. hold</td>
<td>Indefinite (Max. one month shelf life)</td>
</tr>
<tr>
<td>Resin softening point</td>
<td>1</td>
<td>DMA/TMA</td>
<td>50ºC (Max. 100ºC)</td>
</tr>
<tr>
<td>Shrinkage (linear, volumetric)</td>
<td>2</td>
<td>Huntsman internal</td>
<td></td>
</tr>
<tr>
<td><strong>Thermal</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Glass transition (Tg)</td>
<td>1</td>
<td>DMA/TMA</td>
<td>210ºC (Min. 150ºC)</td>
</tr>
<tr>
<td>Dimensional stability</td>
<td>1</td>
<td>TMA (z-axis)</td>
<td>40 ppm ºC-1 (Max. 70 ppm ºC)</td>
</tr>
<tr>
<td><strong>Mechanical</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Strength</td>
<td>2</td>
<td>ASTM D790 (Method 1, Procedure A)</td>
<td>8,700 psi (25ºC), 6,100 psi (130ºC)</td>
</tr>
<tr>
<td>Modulus</td>
<td>2</td>
<td></td>
<td>2.1 Mpsi (25ºC), 1.4 Mpsi (130ºC)</td>
</tr>
<tr>
<td>Retention of flexural strength and modulus</td>
<td>2</td>
<td>ASTM D790 (Method 1, Procedure A)</td>
<td>8,700 psi (25ºC), 6,100 psi (130ºC)</td>
</tr>
<tr>
<td>Thermal shock cycling</td>
<td>2</td>
<td>USCAR III (100 cycles, -40ºC to 130ºC)</td>
<td>No detectable change</td>
</tr>
<tr>
<td>Thermal cycling</td>
<td>2</td>
<td>USCAR III (10 cycles, -40ºC to 130ºC)</td>
<td>No detectable change</td>
</tr>
<tr>
<td>Freeze start up</td>
<td>2</td>
<td>30 d at -40ºC</td>
<td>No detectable change</td>
</tr>
<tr>
<td>Hot and humid conditions</td>
<td>1</td>
<td>48 h in air at 130ºC and 100% RH</td>
<td>50%</td>
</tr>
<tr>
<td><strong>Tensile</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Strength</td>
<td>2</td>
<td>ASTM D638 (Type 1)</td>
<td>5,500 psi (25ºC), 3900 psi (130ºC)</td>
</tr>
<tr>
<td>Modulus</td>
<td>2</td>
<td></td>
<td>5 Mpsi (25ºC), 7 Mpsi (130ºC)</td>
</tr>
<tr>
<td><strong>Compressive</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Strength</td>
<td>2</td>
<td>ASTM F36 (Procedure J)</td>
<td>13,700 psi (25ºC), 10,800 psi (130ºC)</td>
</tr>
<tr>
<td>Modulus</td>
<td>2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Toughness</td>
<td>2</td>
<td>ASTM D5045-99</td>
<td></td>
</tr>
<tr>
<td>Creep</td>
<td>2</td>
<td>ASTM D2990 (modified)</td>
<td>0 at 200 psi, 130ºC</td>
</tr>
<tr>
<td><strong>Chemical/Purity</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Amine, aromatic, and ionic leaching</td>
<td>1</td>
<td>HPLC (amines, aromatics) and solution conductance (ions) following treatment (50 h, 90ºC) with water, 1 mM H₂SO₄ (aq), 2 wt. % MeOH (aq), 60 wt. % MeOH (aq), or Glysantin® FC G 20</td>
<td>Not detectable</td>
</tr>
<tr>
<td>Maximum potential for specific elements</td>
<td>2</td>
<td>ICP-AES (metals), FTIR (Br, Cl)</td>
<td>Not detectable</td>
</tr>
<tr>
<td>Fluid absorbance</td>
<td>2</td>
<td>Incorporated into leachables testing</td>
<td>No detectable fluid uptake</td>
</tr>
<tr>
<td>Flammability</td>
<td>2</td>
<td>UL94</td>
<td>V-0</td>
</tr>
<tr>
<td>Electrical</td>
<td>3</td>
<td>Huntsman internal</td>
<td></td>
</tr>
<tr>
<td>Conformance with IMDS</td>
<td>3</td>
<td>International Material Data System</td>
<td></td>
</tr>
</tbody>
</table>
Task 3: Small-Scale Composite Preparation and Evaluation

- The most promising resins selected from Task 2 will be evaluated in a series of statistically designed experiments intended to determine the effects of key process parameters for preparation of bipolar plates. The independent and dependent variables of these experiments have been defined. The independent variables include two chemical parameters (resin content and type of graphite flake) and one process variable (molding pressure). The dependent variables include composite properties of interest.

- GrafTech has started work on designing and implementing a new small-size test die to quickly screen impregnated materials. This will permit direct comparison of permeability, mechanical, electrical, and physical properties as a function of material and press operating parameters prior to embossment of features. This test die can later be modified to add flow field plate features. These plates will be used to determine growth rates (dimensional stability) which are critical for final part design.

- New techniques/equipment to more quickly screen for permeability have been investigated and will be refined for use with Task 3 related work.

Task 4: Machining and Embossment of Small-Scale Composites

- Expanded graphite mat to be used in the initial screening of new resins has been prepared.

- The design of the machined flow field plate that will be used to standardize comparison of the new graphite/resin composites with the control plates during the single fuel cell testing has been selected.

Task 5: Single-Cell Testing

- A meeting was held between GrafTech and Case Western Reserve University to initiate the selection of fuel cell components suitable for high temperature testing.

FY 2007 Publications/Presentations


References