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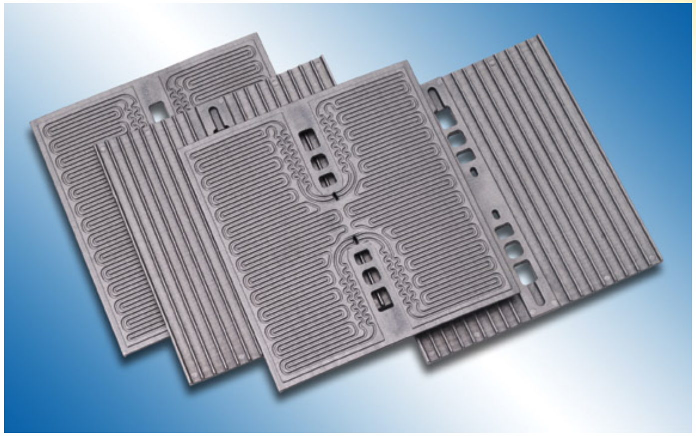
2007 DOE Hydrogen Program Review
Next Generation Bipolar Plates for Automotive PEM Fuel Cells



Orest Adrianowycz, Ph.D.
GrafTech International Ltd.
May 16th, 2007

DOE Hydrogen Program

Project ID # FCP10

GRAFTech
Advanced Energy Technology Inc.
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CASE
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Overview

Project Timeline

- Start date: March 1st, 2007
- End date: February 29th, 2009
- Percent complete: <5%

Budget

- Total project: $2.9 MM
  - DOE share: $2.3 MM
  - Contractor share: $0.6 MM
- Received in FY06: $0.00
- Funding for FY07: $200K

Barriers (bipolar plates)

- A - Durability
  - Improved corrosion resistance
  - Decrease weight and volume
- B - Cost
  - Lower material & production costs
  - Increased power density due to decreased thickness
- C - Performance
  - Improve gas impermeability
  - Improved electrical and thermal conductivity

Collaborators

GrafTech International Ltd.
Primary Contractor

- Orest L. Adrianowycz, Ph.D. Principle Investigator
- Expanded graphite selection
- Prepare and testing of intermediate polymer-graphite composites
- Final graphite/polymer composition selection
- Bipolar plate manufacturing

Ballard Power System

- Warren Williams, Team Leader
- Flow field plate design
- Fuel cell stack assembly
- Durability and freeze-start testing
- Post-test analysis of composite plates

Huntsman Advanced Materials

- Roger Tietze, Team Leader
- Preliminary screening of high temperature resin formulations
- Mold release agents and flow additives for the resin formulations
- Scale-up of resin production for full-size plates manufacturing

CWRU

- Professor Tom Zawodzinski, Team Leader
- High temperature membrane materials and testing protocol selection
- High temperature single cell testing of resin-graphite composite flow field plates
- Post-test analysis of high temperature single cell effluent/

Program Objectives

Overall Project Objective

- Develop next-generation automotive bipolar plates based on an engineered composite of expanded graphite and resin capable of operation at 120 °C

Goals Year 1

- Develop graphite/polymer composite to meet 120ºC fuel cell operating temperature
- Demonstrate manufacturing capability of new materials to a reduced bipolar plate thickness of 1.6 mm

Goals Year 2

- 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 $6/kW cost target through the use of low-cost materials amenable to high volume manufacturing

Approach

Task 1: Graphite Material Selection

- Raw Material Evaluation
- Natural Graphite Selection
- Intercalation Chemistry and Processing optimization

Task 2: Resin Screening, Testing and Selection

- Resin Evaluation
- Resin Selection
- Design Part Release Chemistry

Task 3: Small-Scale Composite Prep

- Develop Methods for Plate Manufacturing and Testing
- Evaluate Thermal and Mechanical Properties

Task 4: Machining and Embossment

- Machined Plates for Single Cell Testing
- Validate Properties of Composites
- Design, Fabricate, and Evaluate Small Embossed Test Plates

Approach (continued)

Task 5: Single Cell Testing

- Select High Temp Fuel Cell Components
- Develop Test Method for Analysis of Fuel Cell Leachates
- Perform 1000 hr Single Cell Testing
- Post Test Plate Analysis

Task 6: Design and Manufacture of Full-size Bipolar Plates

- Design Flow Field Plate Molds
- Fabricate Full Size Embossing Die Set
- Emboss Full-size Bipolar Plates

Task 7: Short Stack Test of Full-size Plates

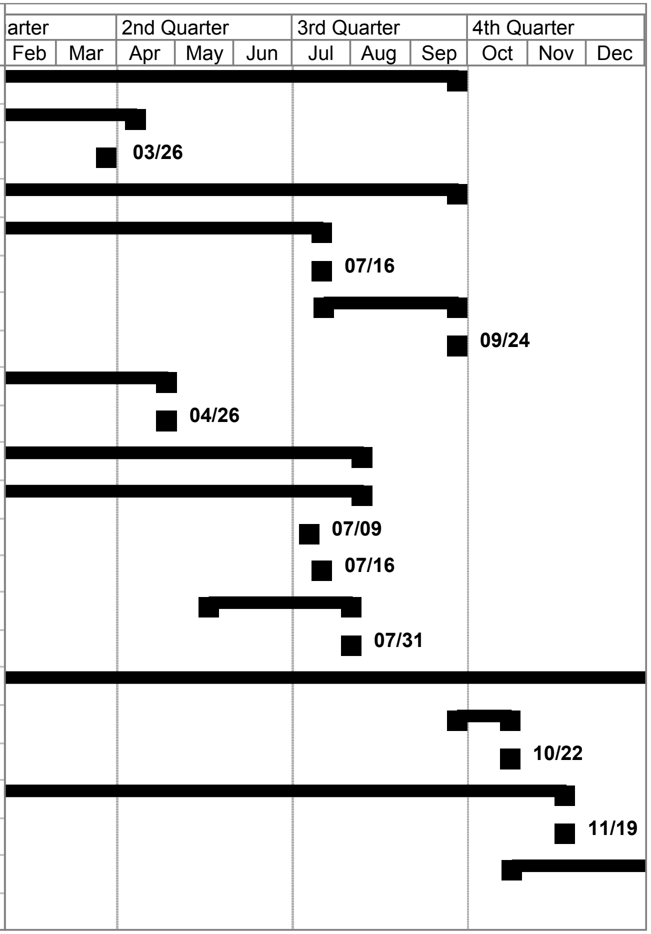
- Short stack plate assembly
- Test Cells in Short-Cell Stack
- Post-Test Analysis
- Deliver Full Size Plate Stack to DOE

Task 8: Economic Assessment of New Technologies

- Perform economic assessment of the selected raw material and manufacturing processing

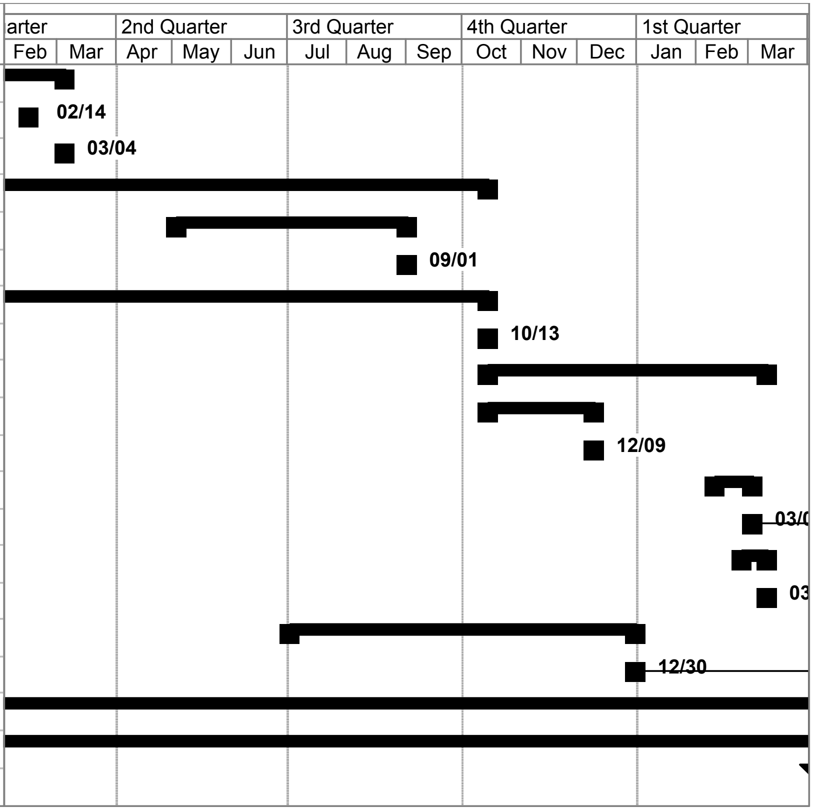
Program Milestones Tasks 1 through 4

ID	Task Name
1	**1 Expanded Graphite Material Selection**
2	**1.1 Natural Graphite Selection**
9	1.1.7 Select Final Flake Sources
11	**1.2 Intercalation Chemistry and Exfoliation Methods**
12	**1.2.1 Execute and Analyze Screening Experimental Design**
28	1.2.1.14 Identify and Finalize Key Processing Variables
29	**1.2.2 Execute and Analyze Response Surface Statistical Experiment**
41	1.2.2.12 Optimized Expanded Graphite Identified
42	**2 Resin Identification and Selection**
49	2.7 Ten Resin Formulations Downselected
50	**3 Small-Scale Composite Preparation and Evaluation**
51	**3.1 Design Experiment and Execute Screening DOE**
58	3.1.7 Contingency Point Resin Reformulation
61	3.1.10 Optimum Composite Compositions for Minimum Thickness Identified
65	**3.3 Evaluate Thermal and Mechanical Properties**
69	3.3.4 A Few Resin Candidates Downselected
70	**4 Machining and Embossment of Small-Scale Composites**
71	**4.1 Fabricate New Composite Materials**
75	4.1.4 New Composites Ready for Embossed and Machined Plates
76	**4.2 Machined Plates for Single Cell Testing**
80	4.2.4 Machined Plates Completed
83	**4.4 Design, Fabricate, and Evaluate Small Embossed Test Plates**
93	4.4.10 New Composites Embossability Characterized



Program Milestones Task 5 through 9

ID	Task Name
94	**5 Single Cell Testing**
99	5.5 Single Cell Test Completed
102	5.8 Primary Resin/Composite Candidate Downselected
103	**6 Design and Manufacture of Full-size Bipolar Plates**
113	**6.3 Fabricate Full Size Embossing Die Set**
119	6.3.6 Full Size Tool and Leak Check Device Ready
120	**6.4 Emboss Full-size Bipolar Plates**
130	6.4.10 Full Size Plates Ready for Short Stack Testing
131	**7 Short Stack Test of Full-size Plates**
132	**7.1 Part and Test Station Preparation**
137	7.1.5 Short Stack Ready for Testing
141	**7.3 Post-Test Analysis of Parts and Performance**
144	7.3.3 Final Review of Short Stack Test Results Completed
145	**7.4 Deliver Full Size Plate Stack to DOE**
147	7.4.2 Plates Delivered to DOE
148	**8 Economic Assessment of New Technologies**
150	8.2 Complete Economic Assessment
151	**9 Team Meetings and Reports**
171	**9.4 Final Report**
173	**9.4.2 Final Report Complete**



DOE Bipolar Plates Technical Targets (Table 3.4.14)

Characteristic	Units	2005 Status	2010	2015
Cost	\$/kW	10	5	3
Weight	kg/kW	0.36	<0.4	<0.4
H_2 permeation flux	$cm^3 sec^{-1} cm^{-2}$ @ 80°C, 3 atm (= <0.1 mA/cm^2)	$<2 \times 10^{-6}$	$<2 \times 10^{-6}$	$<2 \times 10^{-6}$
Corrosion	$\mu A/cm^2$	<1	<1	<1
Electrical conductivity	S/cm	>600	>100	>100
Resistivity	Ohm-cm	<0.02	0.01	0.01
Flexural Strength	MPa	>34	>25	>25
Flexibility	% deflection at mid-span	1.5 to 3.5	3 to 5	3 to 5

Flow Field Plate Technologies Comparison

Technology	Advantages	Disadvantages
Graphite-filled polymers	Known fabrication techniques Molded-in flow fields Density	Thermal conductivity Electrical conductivity Temperature (thermoplastics) Brittleness Molding with high filler content
Carbon/carbon composites	Electrical conductivity Strength Chemically inert Density	Unproven volume manufacturing Thermal conductivity Thickness
Metals	Electrical conductivity Strength Temperature Thin Known fabrication techniques	Corrosion Contact resistance Thermal conductivity Density Expensive alloys and coatings
Expanded graphite	Chemically inert Electrical conductivity Contact resistance Thermal conductivity Thin Cost Proven performance	Permeability Temperature Strength

Flow Field Plate Property Comparison

		Filled Polymer	Filled Polymer	Carbon / Carbon Composite	Machined Graphite	Metal - 316 Stainless Steel	Resin Flexible Graphite
Property	**Units**	**BMC 900**	**SGL 900**	**Porvair**	**POCO AXD 5Q**		**GRAFCELL® Composite**
Density	g/cm^3	1.82	1.84	1.25	1.78	8	1.6
Electrical Conductivity	S/cm	100 (x,y) 50 (z)	56 (x,y) 18 (z)	>500	680	13500	1470 (x,y) 1-3 (z)
Thermal Conductivity	W/m-K	NA (x,y) 18 (z)	14	35 (x,y)	95	16	200 (x,y) ~ 5 (z)
Thermal Expansion Coefficient	1 x 10E-6	30	50	2	8	16	0 (x,y) 27 (z)
Flexural Strength	MPa	40	35	41	86	460-860 (Tensile)	70
Corrosion		No	No	No	No	Yes	No
Projected Cost		Medium	Medium	High	Very High	High	Low
NA - Not Available							
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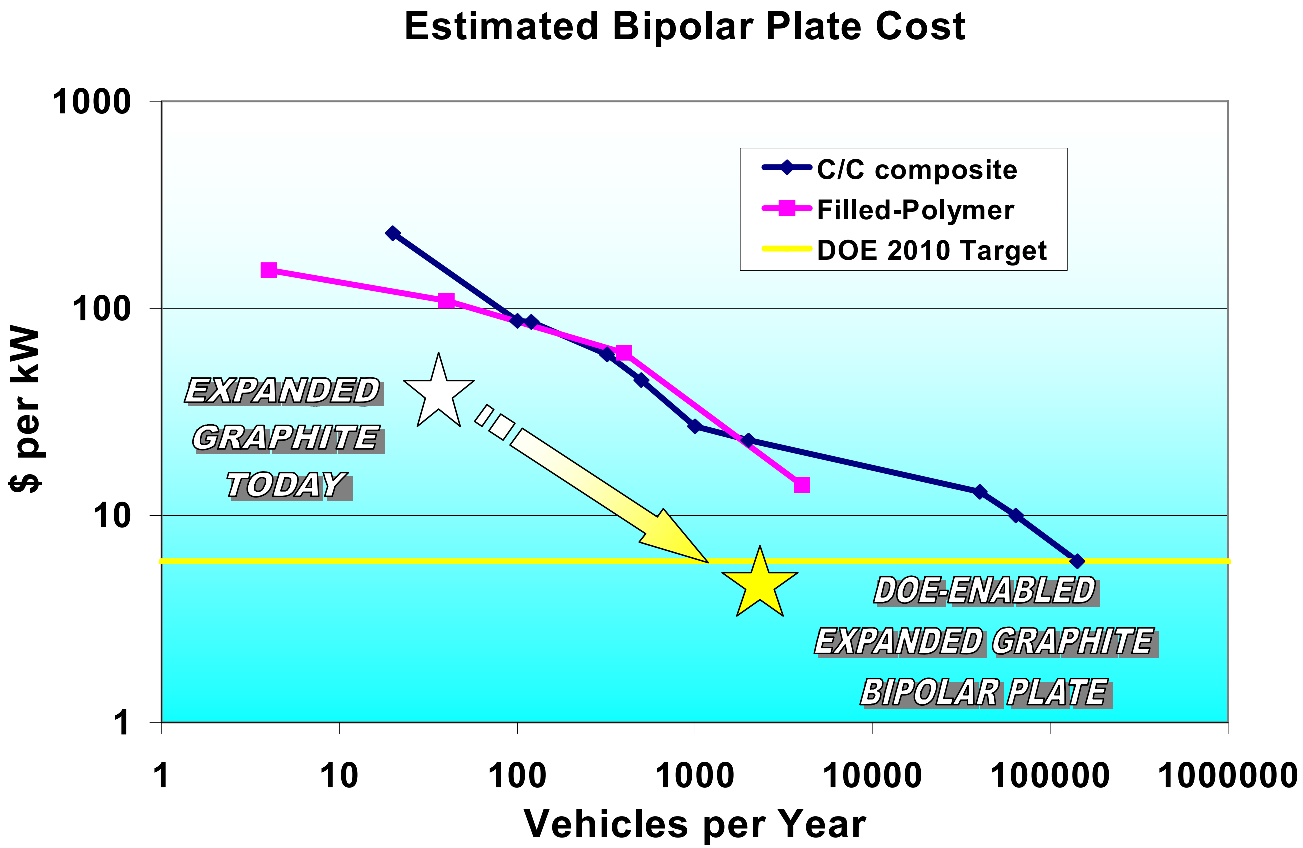
Bipolar Plate Cost Projection Comparisons



1. Graphite Filled Polymer Estimate: A. Mueller, et. al.; “Injection Molded BPP – A Big Step to Cost Reduction of PEMFC”, 2004 Fuel Cell Seminar
2. Carbon/Carbon Composite Estimate: D. Haack; “Scale-up of Carbon/Carbon Composite Bipolar Plates”, Porvair Advanced Materials, Inc. final report to the DOE, May 2005, Contract Number: DE-FC04-02AL67627
3. Resin Filled Expanded Graphite Composite Estimate: E. Carson, et. al.; “Cost Analysis of PEM Fuel Cell Systems for Transportation”, Subcontract Report NREL/SR-560-39104, 2005

Accomplishments Task 1 – Graphite Selection

Graphite

- Primary domestic production flake (G-1)
- Alternative imported production flake (G-2)
- Purified domestic production flake (G-3)
- Purified imported flake (G-4)
- Alternative imported intercalated flake (G-5)
- Experimental imported alternative flake (G-6)

Accomplishments Task 1 – Graphite Selection

Treat Chemistry

- Current treat process (TP1).
- Alternative routine process higher expansion (TP2)
- Experimental process (TP3)

Expansion Method

- Current process (EP1)
- Experimental process (EP2)
- Alternative Experimental process (EP3)

Sizing

- Production sizing (SZ-1)
- Experimental sizing (SZ-2)

Thickness

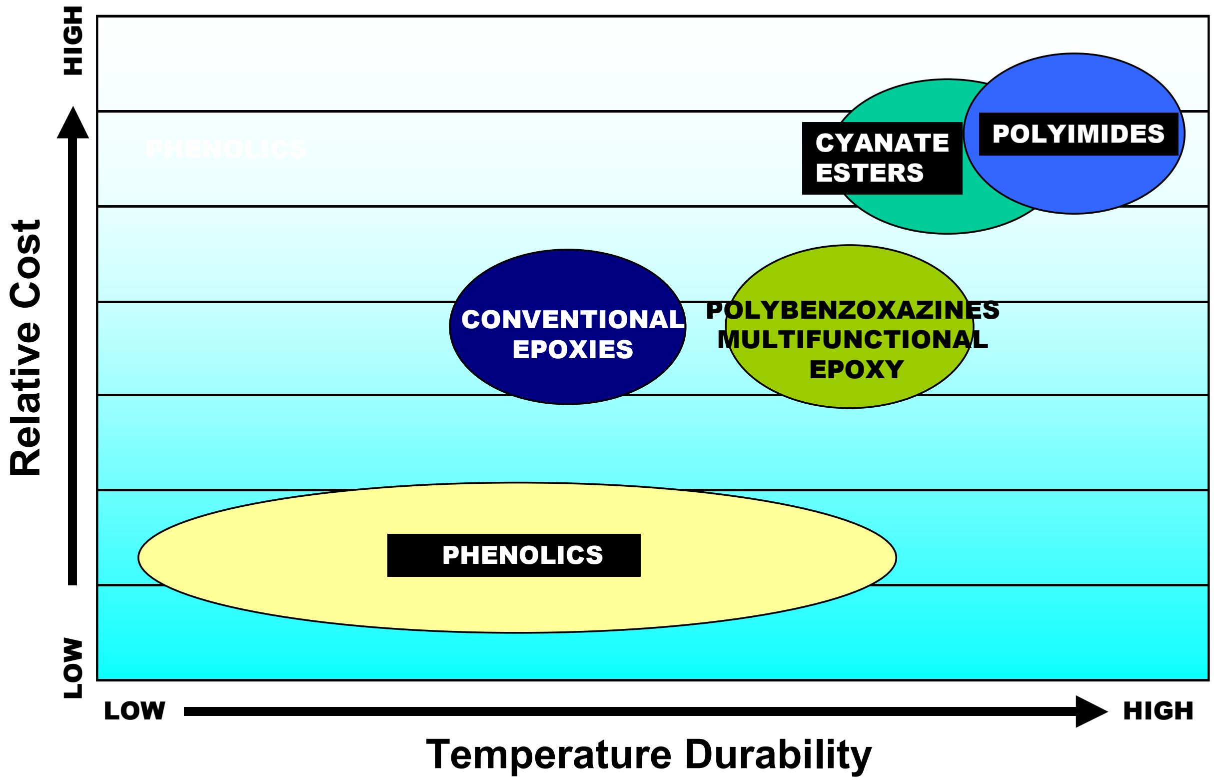
- Current thickness (MT-1)
- Target thickness (MT-2)

Accomplishments Task 1 – Graphite Testing Protocol

Test Description	Raw Flake	Treated Flake
Surface Acid		X
Graphite Flake Fluorine Content		X
pH		X
Oxidation Rate		X
Taber Stiffness		X
Flake Expansion		X
Tap Density	X	
Sizing	X	
Leco Sulfur %	X	
TMA In tumescence Temperature		X
Moisture		X
Volatiles		X
Ash		X
X-Ray Diffraction Lattice Parameters	X	X
ICP-AES	X	
XRF		X

Accomplishments Task 2 - Resin Selection

Resin Cost and Temperature Overview



Accomplishments Task 2 – Resin Selection

Benzoxazines

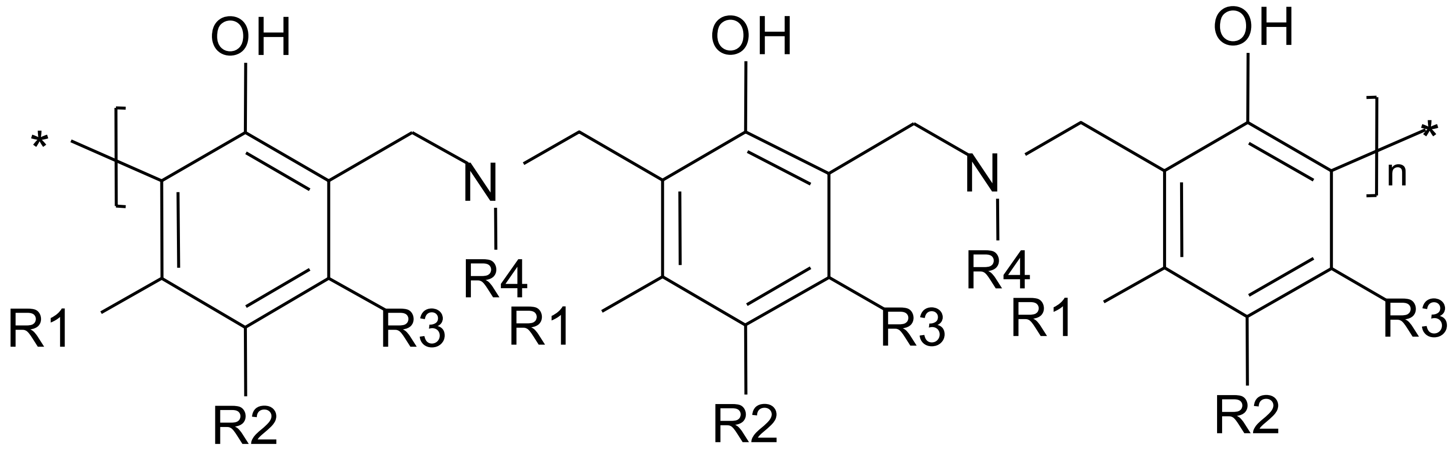
- Reaction product of amine, phenol, and formaldehyde
- High purity : No halogens [ie; Epichlorohydrin]
- Thermosetting chemistry
- High T_g
- Low coefficient of thermal expansion
- Low moisture absorption.
- Electrical properties better than the epoxy analog
- Can react with epoxies and other thermosets.

Epoxy

- Standard Chemistry offering many well proven products
- Thermosetting chemistry
- Multifunctional epoxies will provide high T_g properties
- Good mechanical properties

Accomplishments Task 2 – Resin Selection

Polymer Backbone of Polybenzoxazine



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Accomplishments Task 2 - Resin Selection

DSC Date Resin Systems

			Peak Onset Temperature	Exotherm Peak Temperature	Exothermic Heat
Resin	**Formulation**	**Catalyst**	**°C**	**°C**	**J/g**
Benzoxazine	1	No	239.1	260.7	187.4
	2	No	239.4	262.5	186.9
	3	No	242.8	263.8	219.2
	4	No	202.2	205.5	150.9
	5	No	245.4	266	249.6
Epoxy	1	Yes	137.2	175.9	249.9
	2	Yes	NA	NA	NA
	3	Yes	140.5	169.5	187.5
	4	No	154.3	193.5	220.5
	5	No	141.9	178.4	168.5
	6	No	130.7	194.3	118.3

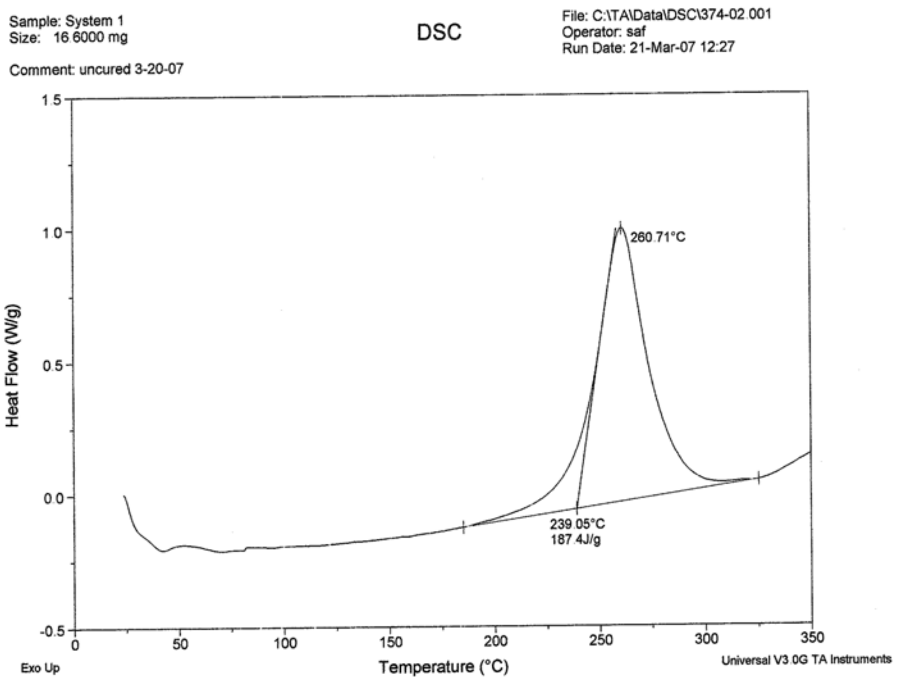
Accomplishments Task 2 - Resin Selection

Cure Data Resin Systems

System	Catalyst	Cure Temperature	Cure Time	Gel Time @ 200 °C	DMA Tan Delta T_g	DMA Storage Modulus T_g	TMA T_g	TMA CTE
		°C	hr	s	°C	°C	°C	µm/m -°C
Benzoxazine								
1	**No**	230°C/2	2.0	>600	215	185	183	64
2	**No**	205°C/2	2.0	>600	171	137		82
2A	**No**	205°C/1.5	1.5	>600	232	198		74
2B	**No**	205°C/2	2.0	>600	225	183		97
3	**No**	205 hold ramp to 230 230 hold	2 1 1	>600	208	183	175	67
4	**No**	205°C/2	2.0	420	148	120	114	75
5	**No**	205 hold ramp to 230 230 hold	2 1 1	>600	183	148	104	65
6	**Yes**							
Epoxy	**Yes**							
1	**Yes**			30.3				
2	**Yes**							
3	**Yes**			64.3				
4	**No**			135.7				
5	**Yes**			31.3				
6	**No**			181.2				

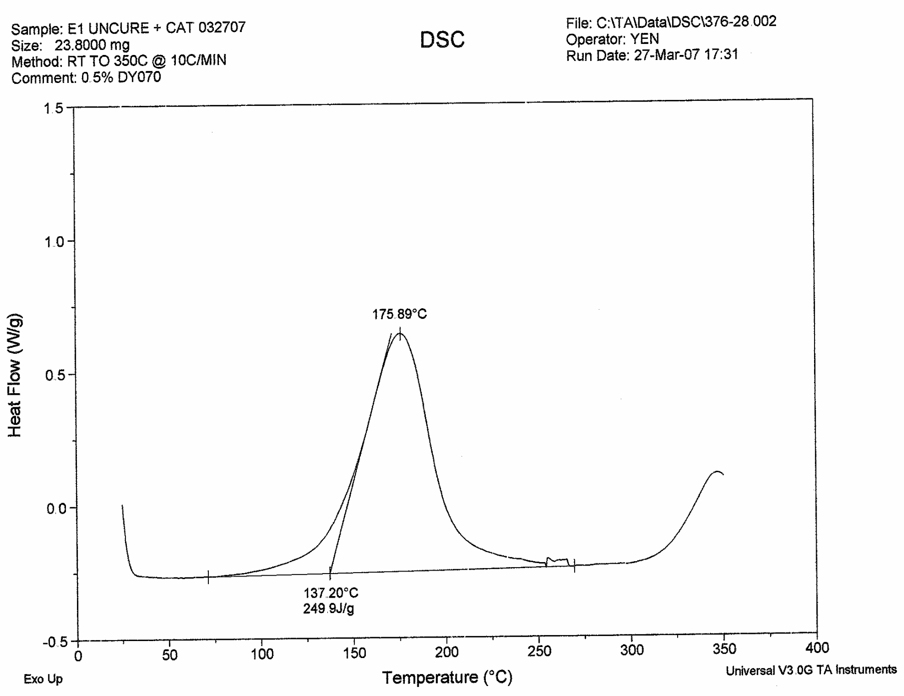
Accomplishments Task 2 - Resin Selection

Resin DSC Plots



Sample: System 1
Size: 16.6000 mg
Comment: uncured 3-20-07

File: C:\TA\Data\DSC\374-02.001
Operator: saf
Run Date: 21-Mar-07 12:27



Sample: E1 UNCURE + CAT 032707
Size: 23.8000 mg
Method: RT TO 350C @ 10C/MIN
Comment: 0.5% DY070

File: C:\TA\Data\DSC\376-28.002
Operator: YEN
Run Date: 27-Mar-07 17:31

Accomplishments Task 2 - Resin Selection

Resin / Thermoset Requirements for Next Generation Bipolar Plates

Property	Priority	Test	Technical Target
Processing			
Resin viscosity (in acetone)	1	Shear/Brookfield, 25ºC	0.8 cp (Max 2.0 cp)
Curing conditions	1	DSC	205ºC, 1 h (Max. 230ºC, 2 h)
Polymerization volatiles	1	TGA	No detectable change
Resin latency			
Ambient	1	DSC/Thermosel	Indefinite
Thermal cycle	1	One cycle to 85ºC with 45-min. hold	Indefinite (Min. one month shelf life)
Resin softening point	1	DMA/TMA	50ºC (Max. 100 ºC)
Shrinkage (linear, volumetric)	2	Huntsman internal	
Thermal			
Glass transition (T_g)	1	DMA/TMA	210ºC (Min. 150ºC)
Dimensional stability	1	TMA (z-axis)	40 ppm ºC^{-1} (Max. 70 ppm ºC^{-1})
Mechanical			
Flexural			
Strength	2	ASTM D790 – Method 1 – Procedure A	8700 psi (25ºC), 6100 psi (130ºC)
Modulus	2	ASTM D790 – Method 1 – Procedure A	2.1 Mpsi (25ºC), 1.4 Mpsi at (130ºC)
Flexural strength, modulus retention			
Thermal shock cycling	1	USCAR III (100 cycles, -40ºC to 130ºC)	No detectable change
Thermal cycling	1	USCAR III (10 cycles -40ºC to 130ºC)	No detectable change
Freeze start up	2	30 d at -40ºC	No detectable change
Hot and humid conditions	1	48 h in air at 130ºC and 100% RH	50%
Tensile			
Strength	2	ASTM D638 – Type 1	5500 psi (25ºC), 3900 psi (130ºC)
Modulus	2	ASTM D638 – Type 1	5 Mpsi (25ºC), 7 Mpsi (130ºC)
Compressive			
Strength	2	ASTM F36 (Procedure J)	13,700 psi (25ºC), 10,800 psi (130ºC)
Modulus	2	ASTM F36 (Procedure J)	

Accomplishments Task 2 - Resin Selection

Resin / Thermoset Requirements for Next Generation Bipolar Plates			
Property	**Priority**	**Test**	**Technical Target**
Toughness	2	ASTM D5045-99	
Creep	2	ASTM D2990 (modified)	0 at 200 psi, 130ºC
Chemical/Purity			
Leaching treatment (50 h, 90ºC) in Water 1 mM H2SO4 (aq) 2 wt. % MeOH (aq) 60 wt. % MeOH (aq) Glycol	1	HPLC (amines, aromatics)	Not detectable
Leaching treatment (50 h, 90ºC) in Water 1 mM H2SO4 (aq) 2 wt. % MeOH (aq) 60 wt. % MeOH (aq) Glycol	1	Ionic Conductivity	Not detectable
Primary Metals	2	ICP (Ba, Br, B, Cl, Cr, Cu, Fe, Ti, V, Zn) FTIR (Br, Cl)	Not detectable
Secondary Metals	2	ICP (Ag, Al, As, Be, Bi, Ca, Cd, Co, K, Li, Mg, Mn, Mo, Na, Ni, P, Sb, Si, Sn, Sr, Tl, U, V, Zr)	Not detectable
Other			
Fluid absorbance	2	Incorporated into leachables testing	No detectable fluid uptake
Flammability	2	UL94	V-0
Electrical	3	Huntsman internal	
Environmental friendliness	3	International Material Data System (IMDS)	

Future Work - 2007

Tasks scheduled for completion in 2007
Corresponding Milestones Shown with Target Dates

1. Expanded Graphite Material Selection
   - Optimized Expanded Graphite Identified, 10/9/07
2. Resin Identification and Selection
   - Resin Formulations Down selected, 5/24/07
3. Small-Scale Composite Preparation and Evaluation
   - Optimum Composite Compositions Identified, 8/31/07
   - Evaluate Thermal and Mechanical Properties, 9/5/07
   - Final Resin Candidates Down selected, 9/5/07
4. Machining and Embossment of Small-Scale Composites
   - Composites Ready for Embossed and Machined Plates, 10/17/07
   - Machined Plates for Single Cell Testing Completed, 11/14/07

Future Work - 2008

Tasks scheduled for completion in 2008
Corresponding Milestones Shown with Target Dates

5. Single Cell Testing
   - **Single Cell Test Completed, 2/11/08**
   - **Primary Resin/Composite Candidate Down selected, 2/28/08**
6. Design and Manufacture of Full-size Bipolar Plates
   - **Full Size Tool and Leak Check Device Ready, 8/6/08**
   - **Full Size Plates Ready for Short Stack Testing, 11/5/08**
7. Short Stack Test of Full-size Plates
   - **Short Stack Ready for Testing, 12/11/08**
   - **Final Review of Short Stack Test Results, 2/27/09**
   - **Full Size Plate Stack Delivered to DOE, 3/9/09**
8. Economic Assessment of New Technologies
   - **Complete Economic Assessment, 12/15/08**

Summary

- Expanded Graphite – Resin Based composites have a history of success as PEM Flow Field Plate materials under current operating requirements
  - Performance and cost projections indicate that these plates have an overall advantage over competing technologies
- The goal of this work is to develop plates which will deliver on the DOE high temperature performance and low manufacturing cost targets for 2010 and beyond.
- These goals will be met through the low cost manufacturing processes based on expanded graphite technology and the high temperature performance of a new class of resins.