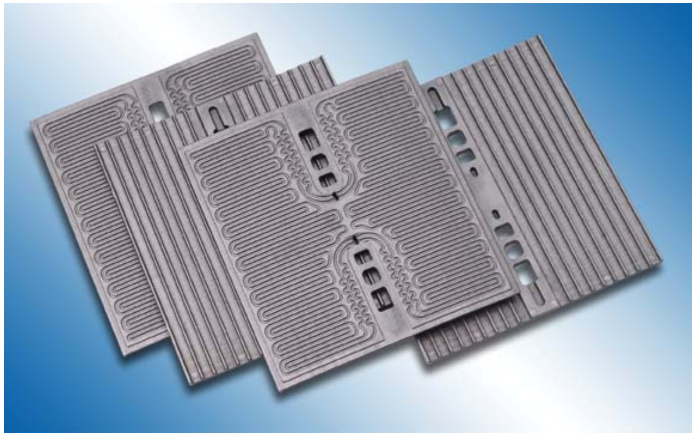
Next Generation Bipolar Plates for Automotive PEM Fuel Cells

2009 Department of Energy Hydrogen Program Annual Merit Review



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Project ID # FC_41_Adrianowycz

DOE Hydrogen Program

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CASE
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GRAFTech International

Overview

Collaborators

- GrafTech International Ltd.
  - Primary Contractor
  - Composite fabrication
- Ballard Power Systems
  - Fuel Cell design
  - Stack Testing
- Huntsman Advanced Materials
  - Resin Selection
- Case Western Reserve University
  - Single cell testing, HT MEA

Project Timeline

- Start date: March 1st, 2007
- End date: February 29th, 2009
- Extension date: August 31, 2009
- Percent complete: 90%

Budget

- Total project: $2.9 MM
  - 20 % Cost Share
- Spending FY07: $760 K
- Spending FY08: $1,550 K
- Budgeted FY09: $590 K

Barriers (bipolar plates)

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

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 published cost target through the use of low-cost materials amenable to high volume manufacturing

Approach

Task 1: Graphite Selection
- Raw Material Evaluation
- Intercalation Chemistry and Processing Optimization

Task 2: Resin Selection
- Resin Evaluation
- Resin Selection

Task 3: Small-Scale Composite Prep
- Develop Methods for Composite Plate Manufacturing and Testing
- Evaluate Properties
- Environmental Chamber Testing

Task 4: Composite Machining and Embossing
- Machined Plates for Single Cell Testing
- Validate Composite Properties
- Evaluate Small Embossed Test Plates
  - GO-no-GO Decision point

Task 5: Single Cell Testing
- Select High Temp Cell Components
- Develop Test Method for Leachates
- Perform Single Cell Testing and Analysis

Task 6: Design and Manufacture Full-size Bipolar Plates
- Design Flow Field Plate Molds
- Fabricate Full Size Embossing Die Set
- Manufacture Full-size Bipolar Plates

Task 7: Full-size Plate Short Stack Testing
- 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

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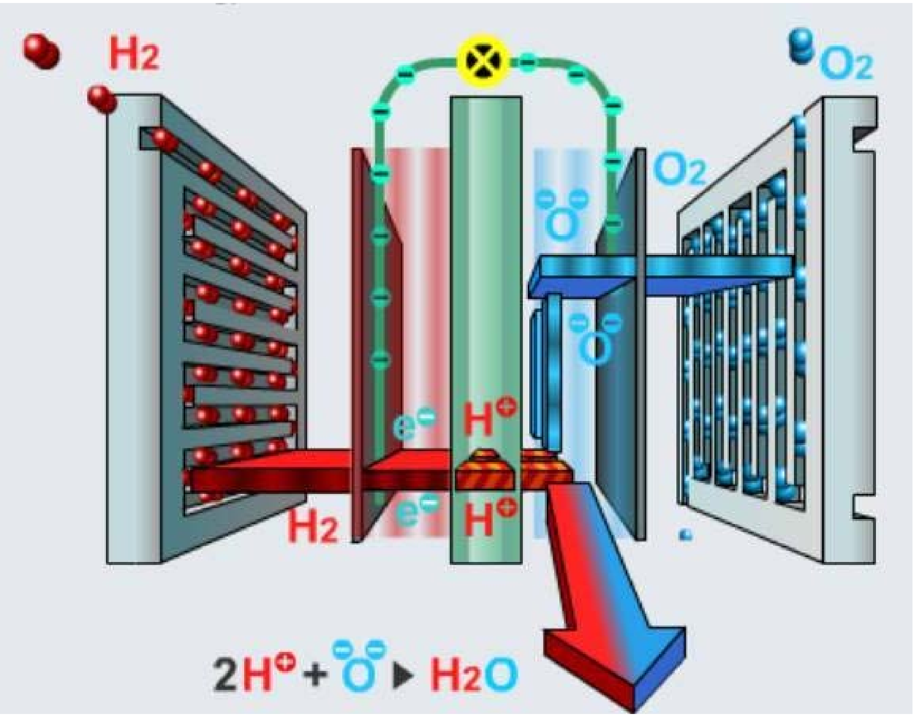
Flow Field Plate Functions

- Current collector
- Deliver and uniformly distribute fuel and oxidant over cell active area
- Facilitate membrane water management
- Maintain impermeable hydrogen barrier across membrane for higher power
- Stack structural support
- Heat removal & distribution
- Most bulky component in the PEM fuel cell stack by weight and volume



Technical Targets: Bipolar Plates, Table 3.4.14

Characteristic	Units	2005 Status [a]	2010 Targets	2015 Targets
Cost [b]	$ / kW	10 [c]	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 (equivalent to <0.1 mA / cm²)	$<2 \times 10^{-6}$	$<2 \times 10^{-6}$	$<2 \times 10^{-6}$
Corrosion	$\mu A / cm^2$	<1 [d]	<1 [d]	<1 [d]
Electrical conductivity	S / cm	>600	>100	>100
Resistivity [e]	Ohm-cm	<0.02	0.01	0.01
Flexural Strength [f]	MPa	>34	>25	>25
Flexibility	% deflection at mid-span	1.5 to 3.5	3 to 5	3 to 5

[a] First year for which status was available. 2005 status is for carbon plates, except for corrosion status which is based on metal plates.

[b] Based on 2002 dollars and costs projected to high volume production (500,000 stacks per year)

[c] Status is from 2005 TIAX study and will be periodically updated.

[d] May have to be as low as 1 nA / cm2 if all corrosion product ions remain in ionomer

[e] Includes contact resistance

[f] 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.

Flow Field Plate Technologies Comparison

Technology	Advantages	Disadvantages
GRAFCELL® Resin Impregnated Flexible Graphite	Chemically inert Electrical conductivity Contact resistance Thermal conductivity Thin Lower Cost Proven performance	Strength Not as thin as metals
Graphite-Filled Polymers	Known fabrication techniques Molded-in flow fields Low Density	Thermal conductivity Electrical conductivity Temperature capability Brittleness Molding with high filler content
Metals	Electrical conductivity Strength Temperature Thin Known fabrication techniques	Corrosion Poisoning of MEA Contact resistance Thermal conductivity Density Expensive alloys and coatings

Property Status for New Expanded Graphite FFPs

Material Property	DOE Target Need	Status
Electrical Conductivity	Plate	Meets DoE 2015 Target
Thermal Conductivity	Balance of Plant	Meets DoE 2015 Target
Contact Resistance	Plate	Meets DoE 2015 Target
Temperature (120 ºC)	MEA, Balance of Plant	R&D needed
Gas Impermeability	Plate	R&D needed
Mechanical Strength	Plate	R&D needed
Corrosion	Plate	Meets DoE 2015 Target
Ion Leachability	System Durability	R&D needed
Thickness	System Power Density	R&D needed
Manufacturability	Technology Viability	R&D needed
Flexibility	Plate	Meets DoE 2015 Target
Weight	Plate	Meets DoE 2015 Target
Cost	All	R&D needed

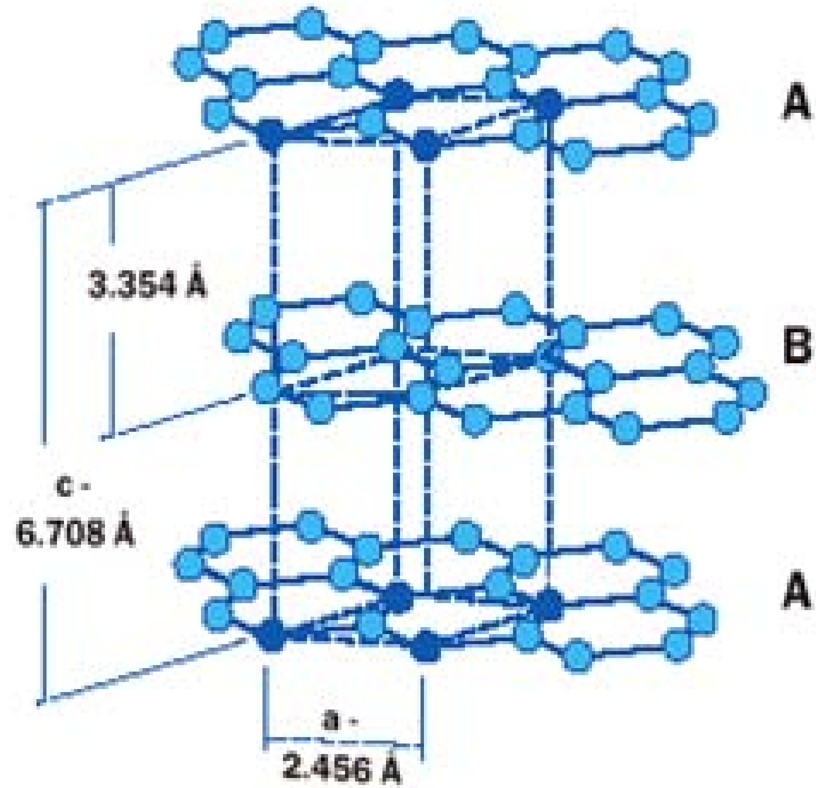
Approach to Meeting Remaining DOE FFP Targets

The "4 T's":

- Temperature
  - New higher temperature resin systems
- Thickness
  - Enabled through a combination of flake sourcing, flake processing, and composite processing
- Toughness
  - Enhanced through resin-reinforcement
- Throughput
  - Viable path to commercialization brought about by low cost manufacturing methodologies

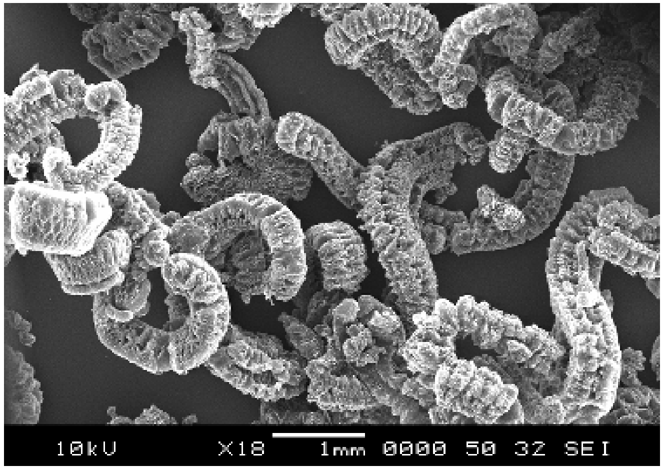
Natural Graphite – Starting Material

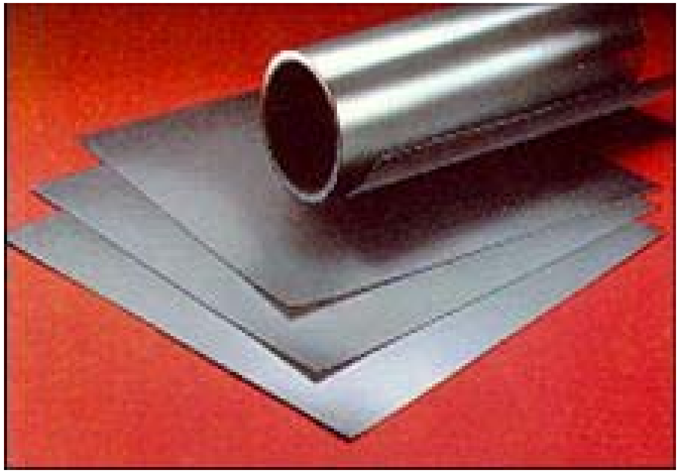
- Mineral form of graphite
- Abundant deposits worldwide
  - 200 Sources
  - 800 MM Tons
- Secure source for high-quality deposits
- Graphitized "by nature"
  - Avoid high-temperature heat treatments.
  - Lower Cost
- Anisotropy (<u>not</u> isotropic)
  - Properties are directionally dependent.



Expanded Graphite – Composite Matrix

- Intercalation by “inserting” compounds between graphene planes
- Exfoliation by rapid heating to decomposes intercalant forcing graphene layers apart
- Calendaring, embossing, pressing
  - No binder required
- Compression re-aligns expanded graphite layers
  - Structurally anisotropic
- Conformable & sealable
- Light weight
- Thermally and electrically Conductive
- Near-zero in-plane CTE
- Chemically inert





Accomplishments

Task 1: Graphite Selection

Contributors: GrafTech, Ballard, Huntsman

- Define FFP specifications
- Potential natural graphite sources evaluated
- Candidate flakes selected
- Graphite processing response surface experiment completed

Task 2: Resin Selection

Contributors: GrafTech, Huntsman

- Resin specification table developed

Task 2: Resin Selection (cont)

- Resins selected for initial evaluation
  - Lab scale resin samples formulated
  - Neat resin properties evaluated
  - Mold release chemistry incorporated
  - Benzoxazine (9) & Epoxy (6) formulation evaluated
- Resin formulations down selected
  - Benzoxazine (2)
  - Epoxy (1)

Accomplishments - Task 2: Neat Resin Systems

				DMA Tg		TMA		TGA	
System	Catalyst	Gel Time @ 200°C	Softening Point	Tan Delta	Storage Modulus	Tg	CTE	Decomp Temp	Weight Loss
		s	°C	°C	°C	°C	µm/m°C	°C	%
Benzoxazine Resin									
1	No	>600	70.5	215	185	183	64	339	2.2
2	No	>600	84.8	171	137	128	82	319	1.9
2A	No	>600	Liquid	232	198	216	85	351	3.1
2B	No	>600	Liquid	225	183	195	159	343	2.6
2G	No	364.9	88.1	282	252	247	61	343	3.8
2H	No	440.9	74.6	282	255	261	52	347	3.8
3	No	>600	80.5	298	183	175	67	317	2.5
4	No	420	98	148	120	114	75	NA	NA
5	No	>600	87	183	148	104	65	NA	NA
Epoxy Resin									
1	Yes	30.3	Liquid	205.0	178.0	172.0	82.0	336.0	3.8
2	Yes	170/150°C	Liquid	208.0	191.0	184.0	81.0	309.0	3.5
3	Yes	100/150°C	Liquid	242.0	210.0	197.0	72.0	341.0	3.5
4	No	155/150°C	Liquid	156.0	125.0	NA	NA	NA	NA
5	Yes	31.3	Liquid	143.0	96.0	NA	NA	286.0	3.2
6	No	>600	Liquid	95.0	88.0	NA	NA	NA	NA
	Selected Systems								

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Resin Candidate

Benzoxazines

- Reaction product of amine, phenol, and formaldehyde
- High purity : No halogens
- Thermosetting chemistry
- High Tg (Glass Transition Temperature)
  - Selected Resins have T_g >250 °C
- Low coefficient of thermal expansion
  - <70 µm/m-°C
- Low moisture absorption.
- Electrical properties better than the epoxy analog
- Can react with epoxies and other thermoset resins

Accomplishments

Task 3 Composite Preparation

Contributors: GrafTech, Huntsman

- Un-embossed composites successfully fabricated
  - Molding temperature
- Gas impermeability verified
- Resins selected for single cell and embossing studies
  - Epoxy resin system eliminated due to processing issues
- Temp cycle and shock testing
  - 2G resin system - no significant changes
  - 2H resin composite - some degradation
- Key process variables identified

Task 4 Embossed Composites

- Contributors: GrafTech, Huntsman, Ballard
- Mechanical and physical properties
  - ≥ Incumbent system
- Single cell plates machined
- Embossed plates evaluated
  - Molded to single plate thickness < 0.8 mm.
  - Nitrogen & helium gas permeability measured
  - In-plane and through plane electrical resistance
  - Dimensional processing changes (growth factors)
- One graphite eliminated based on high gas permeability results

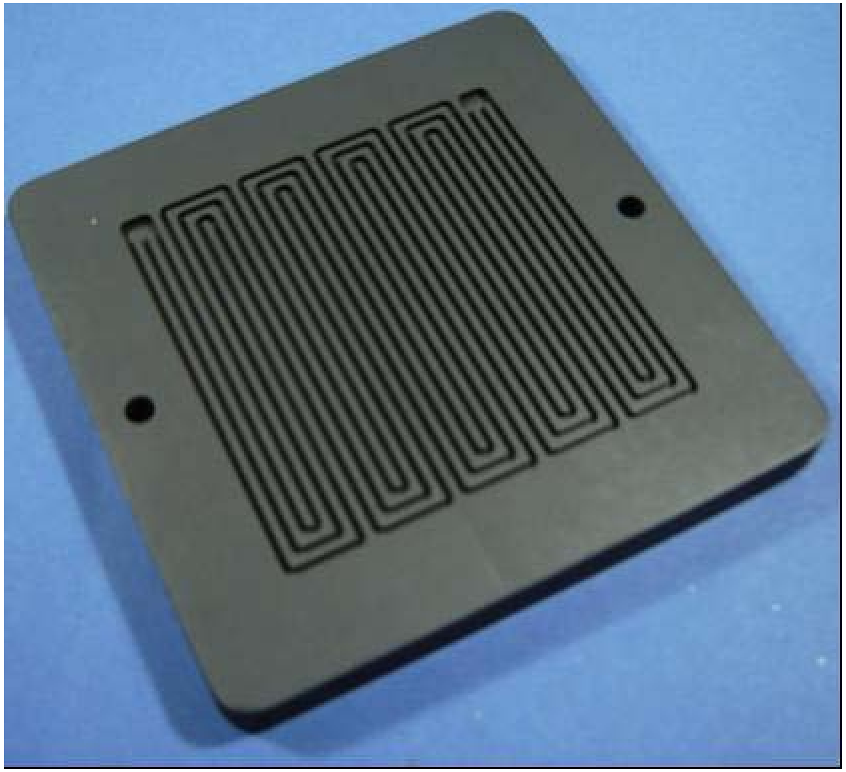
Composite Property Comparison

			FFP	2G Resin	2H Resin
Property	Method	Units	Average	Average	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	cm^2/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	$\mu\Omega cm^2$	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					

Temperature Cycling Studies

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

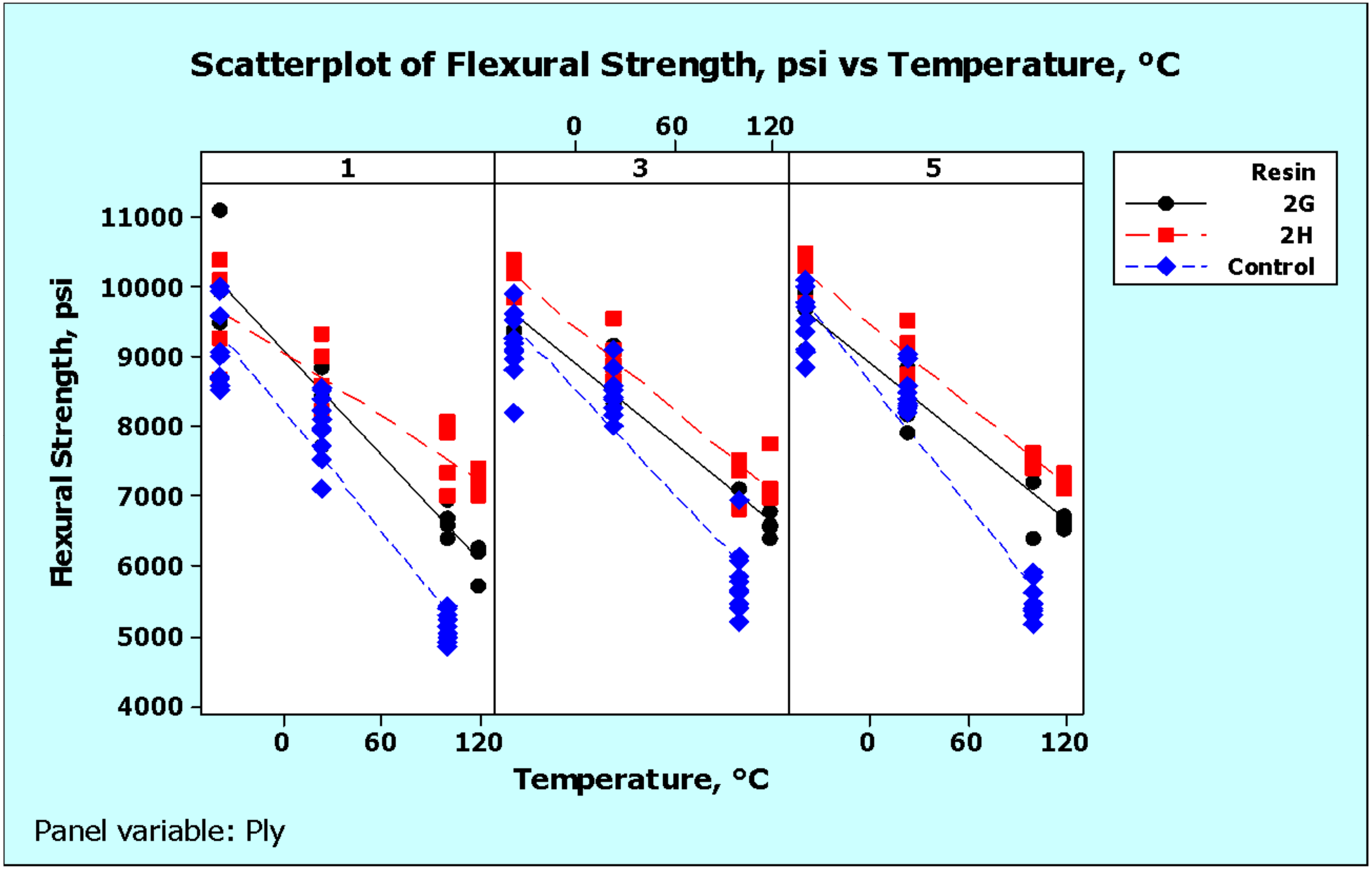
Benzoxazine Resin GRAFCELL® Composite Plates



Machined GRAFCELL® Composite Single Cell Flow Field Plate

Molded GRAFCELL® Composite Corrugated Flow Field Oxidant Plate

Mechanical Strength Testing Results



Accomplishments

Task 5: Single Cell Testing

Contributors: GrafTech, CWRU

- Leachate analysis method developed
- High Temp components selected and procured
  - MEAs delayed start
- Single Cell Testing results
  - 2G resin >1100 hrs at 120 °C
    - Multiple MEAs used
    - Typical MEA lasts approximately 100 hrs
  - 2H resin >200 hrs at 120 °C
    - Operation terminated due to MEA supply
- Post-test plate and effluent analysis still in progress

Protocol

- ETEK 1500 GDL
- 114 hrs @ 80 °C
  - 70% RH
- 86 hrs @ 120 °C
  - 24% RH
- Cells conditioned 24-48 hrs @ 80 °C
- Liquid samples collected

Cell Resistance

- 114 hrs @ 80 °C: 0.23 Ohm cm^2
- 71 hrs @ 120 °C: 0.55 Ohm cm^2
- 86 hrs @ 120 °C: 0.54 Ohm cm^2

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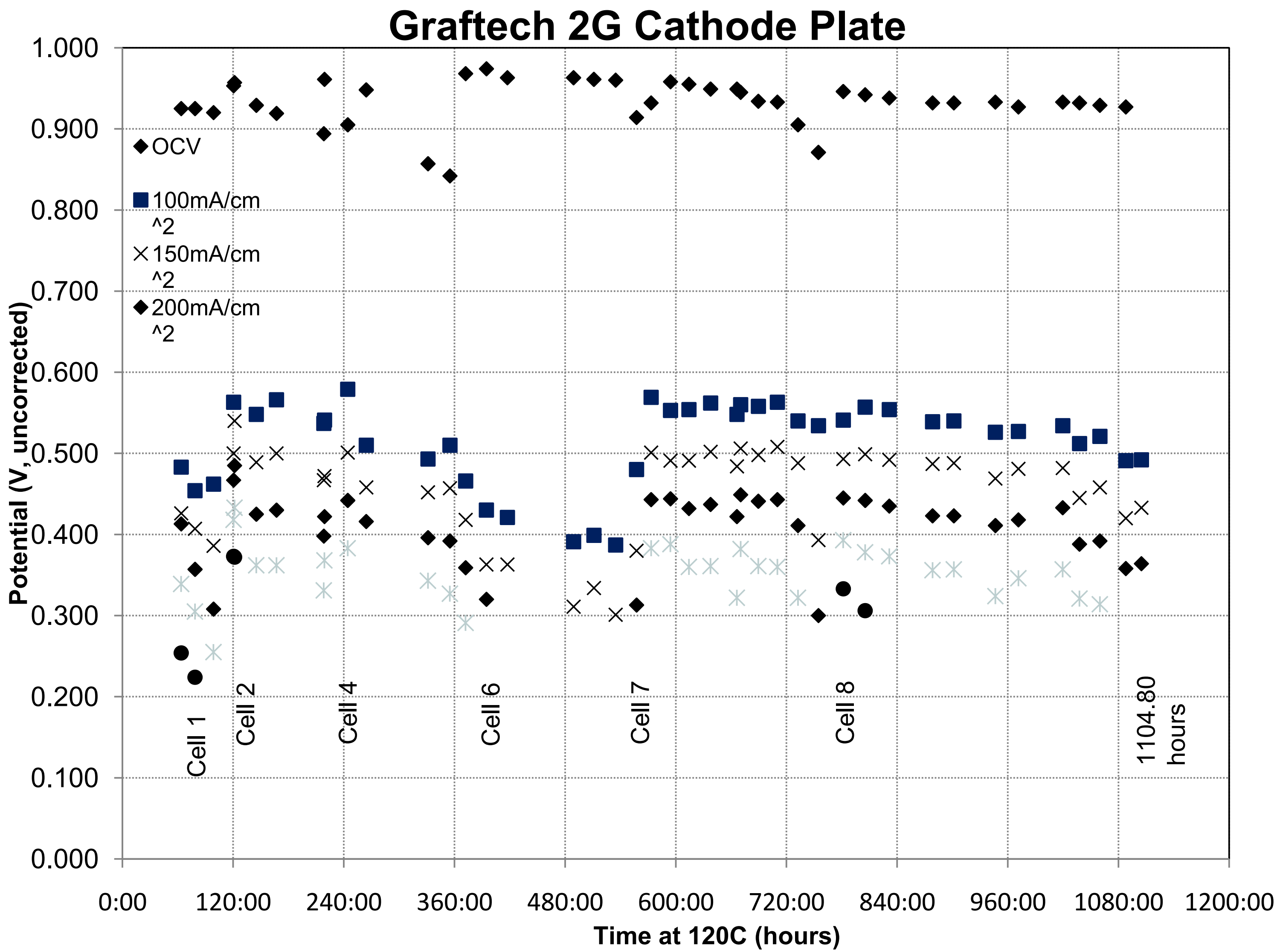
High Temperature Single Cell Testing Results



Accomplishments – Task 6

Design and Manufacture Full-size Bipolar Plates

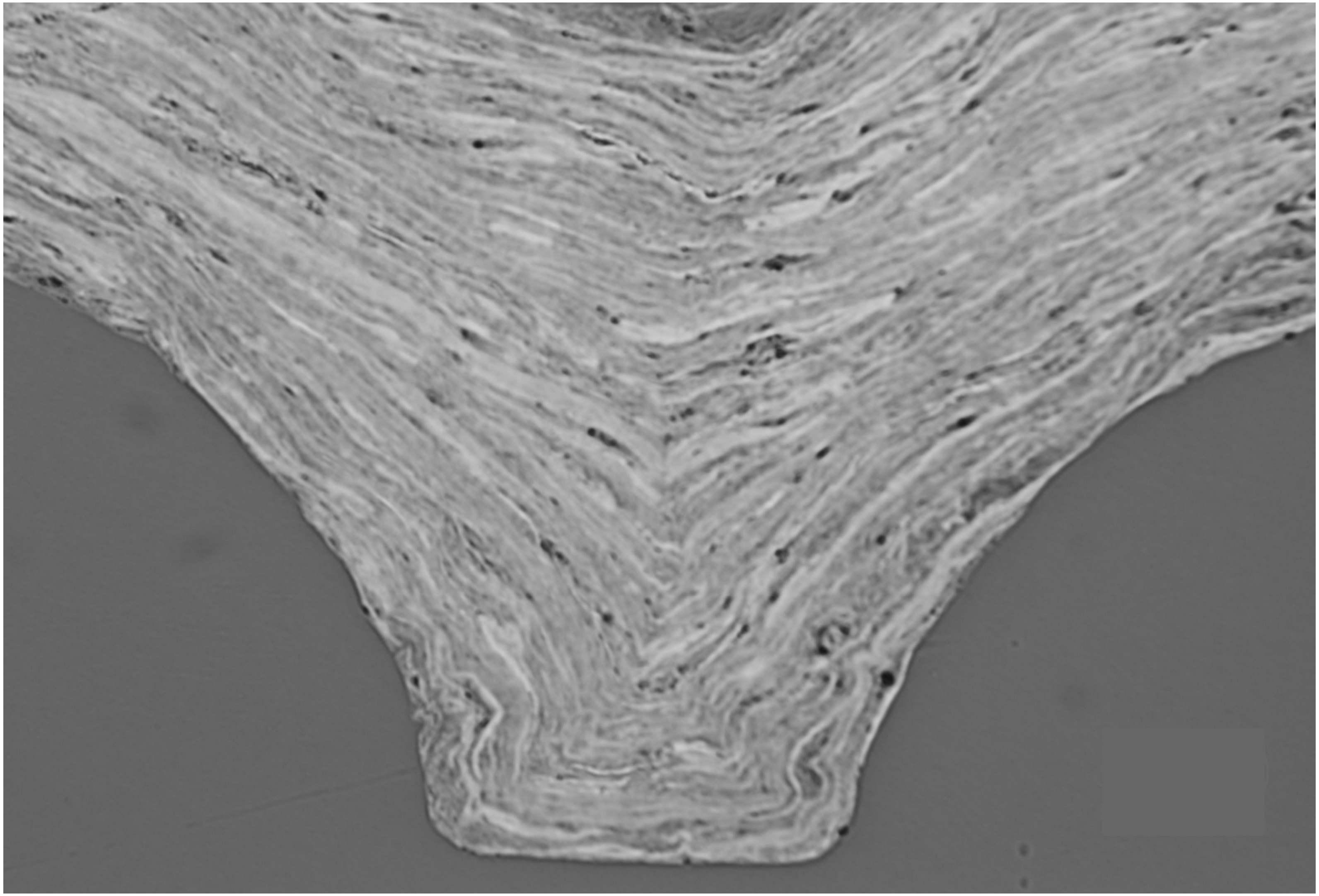
Contributors; GrafTech, Ballard

- Tested plate coolant durability
  - ASTM D739-99a permeation
  - Ethylene glycol coolant
  - 2G better than 2H
- Final review and selection of graphite, resin and processing conditions
  - 2G resin system and G3 graphite mat selected
- Selected and evaluated press for full-size plate fabrication
- Plate design approved
  - Bipolar plate assembled thickness below 1.6 mm
  - Plate area greater than 250 cm^2.
- Small test tools fabricated
  - Growth factors evaluated
  - Feature formation
- Full size embossing die sets fabricated
- Resin and graphite for full size plate produced
- Leak check device and glue fixtures fabricated
- Glue equipment commissioned
- Full-size bipolar plates embossed
- Compression stack hardware fabricated
- Membrane Electrode Assembly (MEA) and seal equipment selected and prepared
- Bipolar plate assemblies glued and inspected

Summary of Composite Testing Results

Property	Preferred Graphite	Preferred Resin
Thermal Properties	No preference	Benzoxazine
Mechanical Properties	No preference	Benzoxazine
Nitrogen Permeability	G1P2S1T1E1	2G Benzoxazine
Growth Factor Analysis	G3P1S1T1E1	2G Benzoxazine
Preliminary Coolant Compatibility	No preference	2G Benzoxazine
Preliminary Leachate Analysis	No preference	2G Benzoxazine
Preliminary Single Cell Testing	No preference	2G OK
Preliminary Environmental Cycling	No preference	No preference
Final Selection	G3P1S1T1E1	2G Benzoxazine

Test Tool Plate Cross Section



Remaining Work – 2009

Task 7: Short Stack Test of Full-size Plates

- **Final full stack testing preparations**
  - **MEAs fabricated and sealed (Complete)**
  - **Test station commissioned, duty cycle identified (Complete)**
  - **Assemble bipolar plates with sealed MEAs in compression stack hardware**
- **10-Cell short stack testing**
  - **Durability testing targeting 1000 hours**
  - **Freeze testing**
- **Post test analysis**
  - **Cell Performance**
  - **Effluent stream leachate**
  - **Bipolar plate post mortem**
- **Deliver Full Size Plate Stack to DOE**

Task 8: Economic Assessment of New Technologies

Summary

- All critical starting material evaluation and testing is complete
  - Graphite and resin system for plate fabrication selected.
- New composite systems shown to have equivalent or improved dimensional stability and mechanical and thermal properties over the incumbent GRAFCELL® composite.
- Gas impermeability demonstrated to a single plate thickness of less then 0.8mm.
- Leachate, glycol and single cell testing results are positive or do not indicate any significant problems with cell operations at elevated (120 °C) temperature
- Critical processing parameters identified and optimized.
- Full-size embossing dies and leak-check device fabricated
- Full size bipolar plates embossed, sealed and glued
- Stack MEAs, hardware, and sealing device ready for assembly