Graphite - Based Bipolar Plates for PEM Motive Fuel Cell Applications

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DOE Bipolar Plates Workshop
Feb 14th 2017
Outline

• Introduction to Advanced Energy Technologies LLC
• Review of Carbon & Graphite Bipolar Plate Technologies
  – Expanded/Flexible Graphite Materials
  – Molded/Filled/Particulate/Composite Graphite Materials
  – Carbon & Graphite Coated Metallic Plates
• R&D Needs
• Simon Farrington (AFCC) will talk later on forming and manufacturing issues in automotive bipolar plate production
Advanced Energy Technologies LLC (AET)

• A subsidiary of GrafTech International
• 100 year + company headquartered in Cleveland, Ohio
• Manufacturer of flexible graphite materials for electronic thermal management, fluid sealing, automotive gasket, fire retardant and fuel cell applications
• www.graftechchaet.com
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• R&D Needs
Expanded/Flexible Graphite Materials

- Expanded graphite materials are derived from naturally occurring flake graphite
- The flake is chemically intercalated and then heated to expand the graphite
- The expanded graphite is then gradually compressed into a mat form
- The mat blank is then compression molded into a half-plate comprising gas and coolant channels
- The graphite preform is then impregnated with resin and cured to form the finished half-plate
- Fuel and oxidant half-plates are adhesively bonded and cured to form the finished bipolar plate
- Bipolar plate/minimum web thickness
  - ~ 2.0 mm/0.45 mm current field use
  - ~ 1.6 mm/0.32 mm GrafTech/Ballard DOE project
  - ~ 1.1 mm/0.15-0.2 mm “State-of-the Art”
- More complex flow field designs possible vs corrugated metal plates

Screen shot courtesy of Ballard Power

US Patent 3,404,061 JH. Shane et al., Oct 1 1968
Expanded/Flexible Graphite Materials

- Expanded graphite materials retain the anisotropic structure of the starting flake with the result that in-plane (xy) and through thickness (z) properties are very different.
- Expanded graphite materials comprise a continuous graphite phase with resultant higher in-plane thermal & electrical conductivity than bulk molded compounds but lower through plane properties.
- Higher thermal conductivity exploited in higher current density designs.
- Lower density than steel and do not corrode.
- Lower strength and electrical conductivity than steel.

<table>
<thead>
<tr>
<th>Property</th>
<th>Expanded Graphite</th>
<th>Bulk Molded Compound (BMC 940)</th>
<th>Stainless Steel 316L (coated for corrosion results)</th>
<th>2020 DOE Target or Target impacted</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density g/cm³</td>
<td>1.7</td>
<td>1.89</td>
<td>8.0</td>
<td>Plate Weight &lt; 0.4 kg/kWnet</td>
</tr>
<tr>
<td>Thermal Conductivity W/mK (xy)</td>
<td>280</td>
<td>13</td>
<td>15</td>
<td>n/a</td>
</tr>
<tr>
<td>(z)</td>
<td>5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Electrical Conductivity S/cm (xy)</td>
<td>1100</td>
<td>70</td>
<td>13500</td>
<td>&gt; 100 S/cm</td>
</tr>
<tr>
<td>(z)</td>
<td>20</td>
<td>30</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CTE (µm)</td>
<td>1.0 (x,y) 90</td>
<td>30</td>
<td>16</td>
<td>n/a</td>
</tr>
<tr>
<td>(z)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tensile/Flexural Strength (MPa)</td>
<td>40/60</td>
<td>28/38</td>
<td>NA/480</td>
<td>Flex &gt; 34 (carbon plate)</td>
</tr>
<tr>
<td>Corrosion µA/cm²</td>
<td>None</td>
<td>None</td>
<td>&lt; 0.1</td>
<td>&lt; 1</td>
</tr>
</tbody>
</table>

Cross section of compressed expanded graphite sheet

Cross section of typical bulk molding compound
Expanded/Flexible Graphite Materials

- Ballard’s Mark 900 series liquid-cooled fuel cell stack introduced in January 2000 was the first to use resin impregnated expanded graphite for on-road vehicles.
- 2000-2006 Used in early generation automotive prototypes (Daimler-Chrysler NECAR Mercedes Benz A-Class, Ford Focus, Honda FCX, and bus programs (Daimler Chrysler Citaro)).
- Introduced into fork lift applications in 2005 with General Hydrogen. >13,000 Plug Power GenDrive® vehicles now in service.
- Used in current generation FCveloCity® modules for bus applications.
- >1,000,000 bipolar plates produced.
- Have accumulated:
  - >10 million km of road service in bus and automotive applications.
  - Millions of hours of run time in fork lift applications.

Field Information and photos courtesy of Ballard Power & Plug Power.
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Molded/Filled/Particulate Graphite Composite Materials

Manufacture, Properties & Field Performance

- Use bulk-molding compounds that comprise high fraction loadings (77-87 wt%) of natural and synthetic graphite particulates (d50 ~ 30-60 µm) and carbon fibers in thermoset resins typically epoxy/vinyl-ester/phenolic/bismaleimide resins
- Plates are typically compression molded with typical times of ~ 1-5 minutes at temperatures of 150-180°C at 20-50MPa
- Multiple suppliers of bulk molding compounds and finished plates
- Similar bipolar plate/web thicknesses to expanded graphite materials
  - ~ 1.5 mm/0.30 mm current field use
  - ~ 1.1 mm/0.15-0.2 mm “State-of the Art”
- Have been used successfully in motive applications since 2005 and favored for thicker plates/stationary power applications

Source: Nisshinbo website
Source: Composites World/BMCI
Screen shot courtesy of Ballard Power
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Carbon & Graphite Coated Metallic Plates

- Argonne National Lab has reported work (Project ID #FC024) on composite fluoropolymer/graphite coatings on aluminum bipolar plates
  - Orion panels show no corrosion; a single cell stack was tested with improved performance vs uncoated aluminum

- Chung et al and Fukutsuka et al. both utilized carbon-coated 304SS in single and three-cell PEM fuel cells respectively
  - CVD carbon film on Ni-coated 304 SS plates demonstrated chemical stabilities comparable to Poco graphite
  - Plasma assisted CVD carbon film on 304SS – exhibited higher electrical conductivity than uncoated material while maintaining an acceptable level of corrosion resistance
  - Both studies were relatively short term so further study required
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R&D Needs

• For expanded flexible graphite materials, the recommended main focus area needs to be high speed forming, sealing, curing, gluing & cutting operations to meet the automotive volume and cost targets
• Per DE-FC36-07GO17012 Roller Embossing & Adiabatic Forming have been identified as candidate high speed forming routes to 100k-500k stacks/yr
• Some encouraging R&D/pilot scale scoping work performed on roller embossing & adiabatic forming
  – Roller embossing demonstrated at 9 meters/min by Terrella Energy – translates into 1 plate/3 seconds. Very high density graphite parts demonstrated which reduces resin content facilitating sealing vs impregnation approach, faster curing, enabling a continuous operation
  – Adiabatic forming - Double sided 160 cm² test half-plate formed in < 0.1 s using high velocity impact unit. Improved material flow and feature definition. Less energy than identical metal part.
  – Need to update cost analysis to incorporate these new manufacturing scenarios
  – For particulate graphite materials we are suggesting a similar focus on high speed forming and property improvements for high current density (particularly thermal)

Focus on High Speed Forming

Plate Design wrapped onto a drum

Demonstration for 9 meters/min process

Double sided 160 cm² test plate produced by adiabatic forming (< 0.1s)
Summary

• Expanded flexible graphite plates have been used successfully in full-scale motive applications for > 15 years with >10 million km of road service in bus and automotive applications and millions of hours of run time in fork lift applications.
  – Recent high-speed forming work, particularly roller embossing, has demonstrated a path to automotive scale cost and volumes at the current densities required by the industry. This is a recommended area for additional R&D

• Filled/particulate/molded graphite composite plates have been used successfully in full-scale motive applications for > 10 years.
  – R&D needs identified include a focus on high speed forming methods and property improvements (particularly thermal)
Acknowledgements

• The presenter would like to acknowledge the assistance of the following individuals in preparing the presentation
  – Warren Williams & Bevan Moss Ballard
  – Simon Farrington of AFCC
  – John Kenna of Terrella Energy
  – Dave Stuart, Ryan Wayne and Matt Getz and of Advanced Energy Technologies LLC.
References

- Typical Data BMC 940 Vinyl Ester BiPolar Plate Material BMC inc
- A review of Metallic BiPolar Plates for Proton Exchange Membrane Fuel Cells; Materials & Fabrication Methods, Karimi et al., Advances in Materials Science and Engineering Volume 2012 (2012), Article ID 828070
- Metallic Bipolar plates with Composite Coatings, Mawdsley et al. Argonne National Laboratory Project ID # FC024, May 11, 2011
Appendix Slides – DOE Bipolar Plate Targets
### DOE Bipolar Plate Targets

**Technical Targets: Bipolar Plates for Transportation Applications**

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Units</th>
<th>2015 Status</th>
<th>2020 Targets</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cost</td>
<td>$/kW·yr</td>
<td>y^8</td>
<td>3</td>
</tr>
<tr>
<td>Plate weight</td>
<td>kg/kW·yr</td>
<td>0.4</td>
<td>0.3</td>
</tr>
<tr>
<td>Plate H2 permeation coefficient</td>
<td>std cm^3/(sec·cm·Pa) @ 50°C, 3 atm, 100% RH</td>
<td>0.9</td>
<td>&lt;1.3x10^-14.1</td>
</tr>
<tr>
<td>Corrosion, anode^2</td>
<td>µA/cm^2</td>
<td>no active peak^b</td>
<td>&lt;1 and no active peak</td>
</tr>
<tr>
<td>Corrosion, cathode^1</td>
<td>µA/cm^2</td>
<td>&lt;0.1</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Electrical conductivity</td>
<td>S/cm</td>
<td>&gt;100</td>
<td>&lt;100</td>
</tr>
<tr>
<td>Anode specific resistance^5</td>
<td>ohm·cm</td>
<td>0.059</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Flexural strength^3</td>
<td>MPa</td>
<td>24 (carbon plate)^m</td>
<td>25</td>
</tr>
<tr>
<td>Running elongation^3</td>
<td>%</td>
<td>20-40^c</td>
<td>40</td>
</tr>
</tbody>
</table>

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1. Costs projected to high-volume production (100,000 50 kW systems per year), assuming MEA costs performance target of 1,000 m²/kW².
4. Per the standard gas transport test (ASTM D 149).
5. C.F. Wang (Thetford), private communication, October 2014.
7. pH 0.01M HF, 87°C, peak amperage current (10s/20s A/cm²) (steady-state test at 0.1 mV/H, 0.4 V to +0.15V (Ag/AgCl)), de-aerated with Ar purge.
9. pH 0.01M HCl, 87°C, passive current (10s/20s A/cm²) (steady-state test at +0.15V (Ag/AgCl), de-aerated solution.
11. Includes interfacial contact resistance (on as received and after pretreatment) measured both sides per Wang, et al., J. Power Sources 115 (2003): 243-251 at 200 pa (1.05 H2O).
14. Per the ASTM D5856 Standard Test Methods for Tensile Testing of Metallic Materials, or demonstrate ability to withstand channel design with width, depth, and radius.