

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.graftech.aet.com

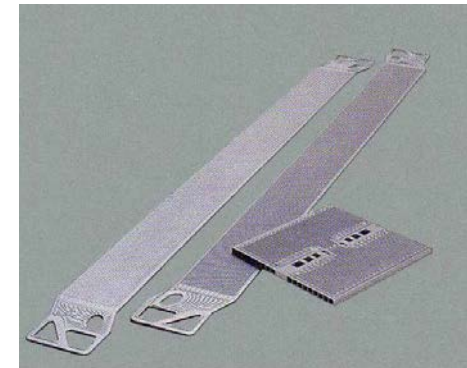
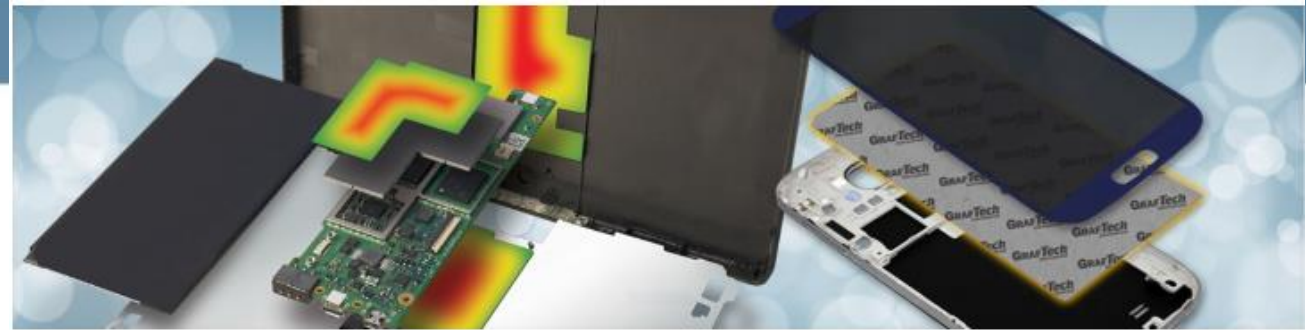
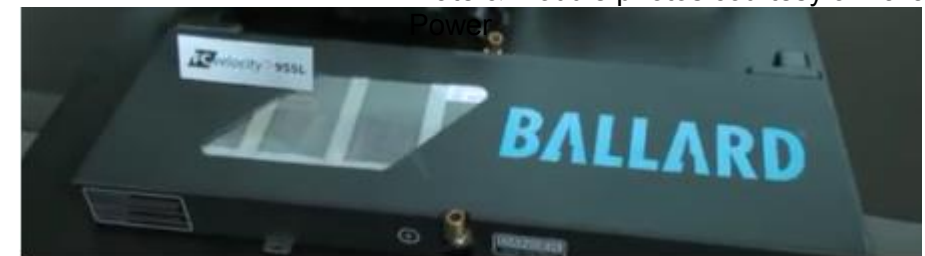


Plate & module photos courtesy of Ballard



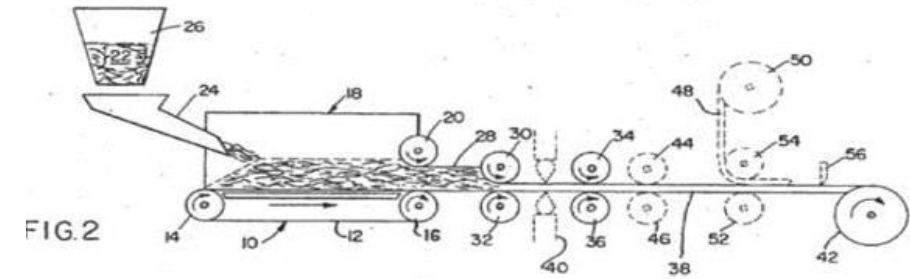
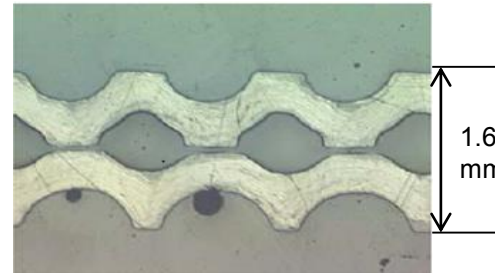
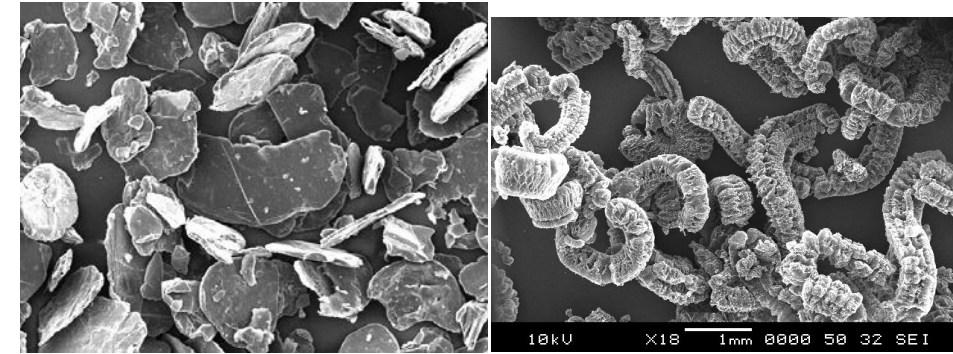
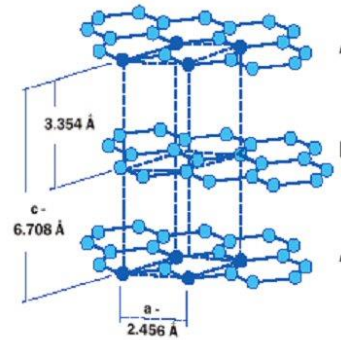
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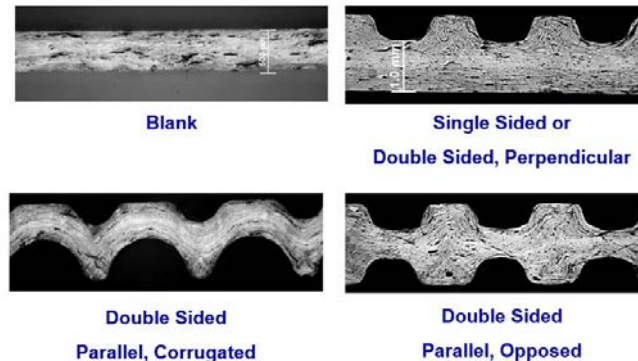
Expanded/Flexible Graphite Materials

Manufacture

- 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



US Patent 3,404,061 JH.Shane et al., Oct 1 1968

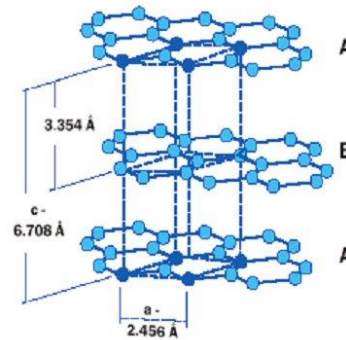


Screen shot courtesy of Ballard Power

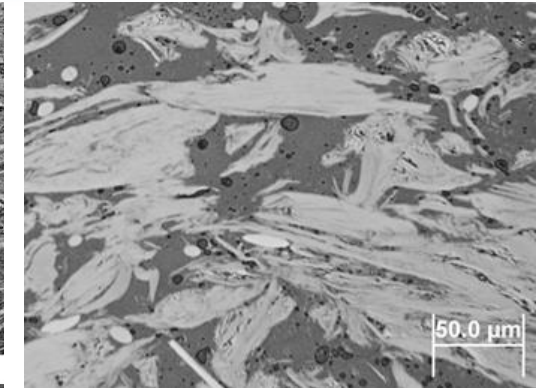
Expanded/Flexible Graphite Materials

Properties

- 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



Cross section of compressed expanded graphite sheet



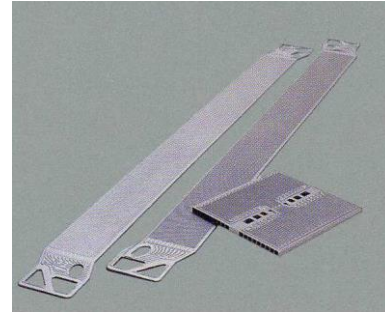
Cross section of typical bulk molding compound

| Property | Expanded Graphite | Bulk Molded Compound (BMC 940) | Stainless Steel 316L (coated for corrosion results) | 2020 DOE Target or Target impacted |
|---------------------------------|---------------------|--------------------------------|---|------------------------------------|
| Density g/cm ³ | 1.7 | 1.89 | 8.0 | Plate Weight < 0.4 kg/kWnet |
| Thermal Conductivity W/mK | 280 (xy) 5 (z) | 13 | 15 | n/a |
| Electrical Conductivity S/cm | 1100 (xy) 20 (z) | 70 (xy) 30 (z) | 13500 | > 100 S/cm |
| CTE (μm) | 1.0 (x,y) 90 (z) | 30 | 16 | n/a |
| Tensile/Flexural Strength (MPa) | 40/60 | 28/38 | NA/480 | Flex > 34 (carbon plate) |
| Corrosion μA/cm ² | None | None | < 0.1 | < 1 |

Expanded/Flexible Graphite Materials

History of Field Performance

- 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

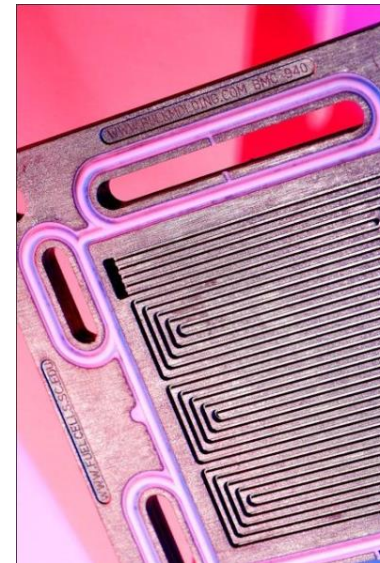
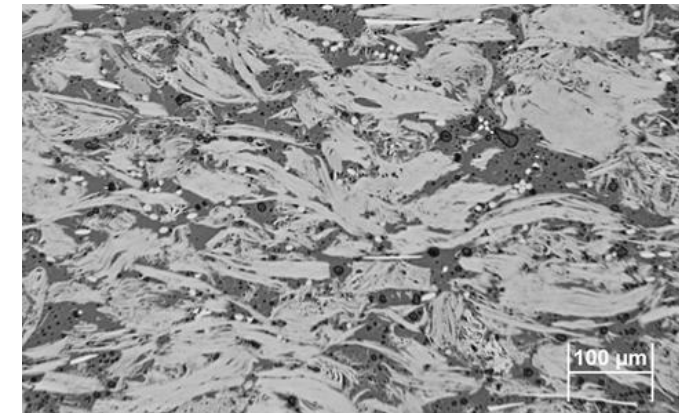
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Molded/Filled/Particulate Graphite Composite Materials

Manufacture, Properties & Field Performance

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



Source:- Composites World/BMCI



Source:- Nisshinbo website



Screen shot courtesy of Ballard Power

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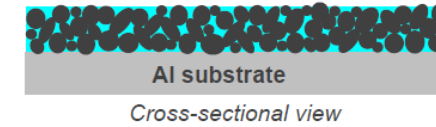
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Carbon & Graphite Coated Metallic Plates

Manufacture & Properties

- 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

- Filler: Metal carbide, boride or silicide, **graphite**, and/or **carbon black**
- Fluoropolymer: Ethylene tetrafluoroethylene (ETFE) or Polychlorotrifluoroethylene (PCTFE)



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- 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)

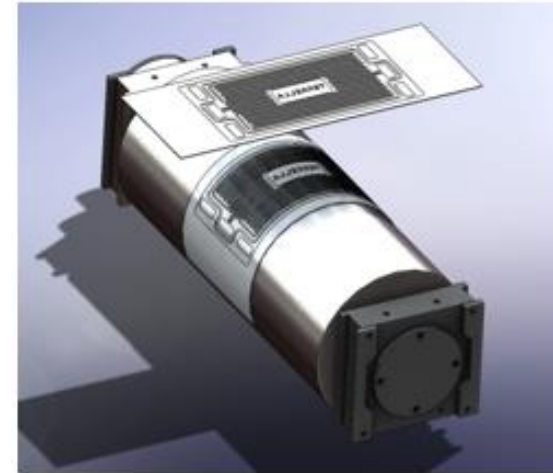
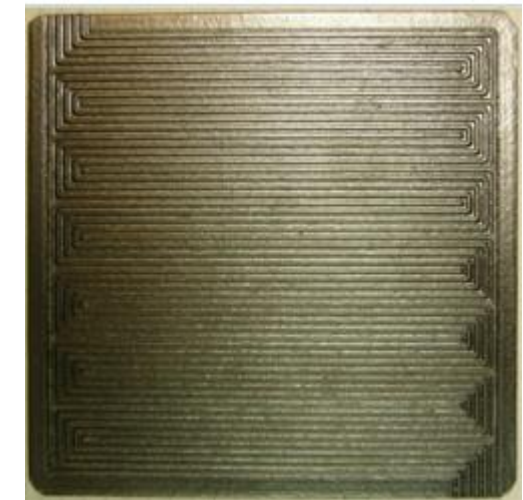
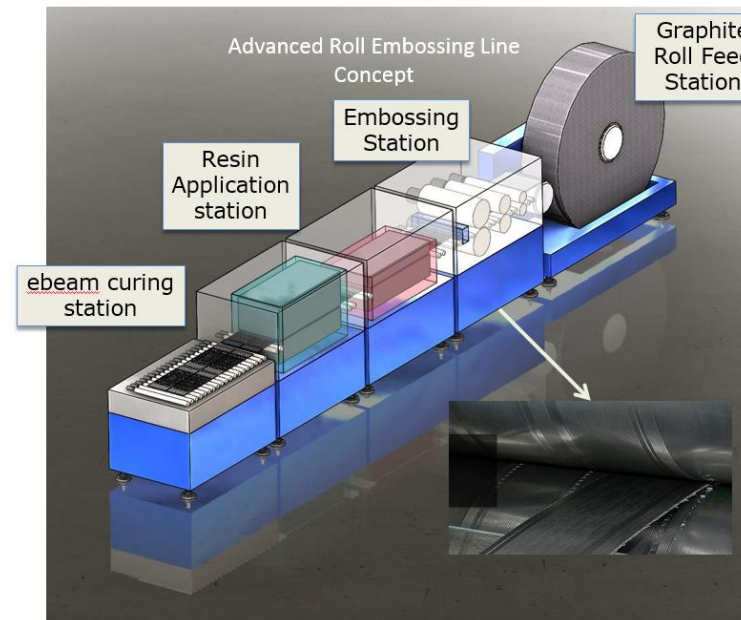


Plate Design wrapped onto a drum



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)

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 - Warren Williams & Bevan Moss Ballard
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References

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- 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

| Characteristic | Units | 2015 Status | 2020 Targets |
|--|--|---------------------------------|--------------------------|
| Cost ^a | \$/kW _{net} | 7 ^b | 3 |
| Plate weight | kg/kW _{net} | <0.4 ^c | 0.4 |
| Plate H ₂ permeation coefficient ^d | Std cm ³ /(sec cm ² Pa) @ 80°C, 3 atm, 100% RH | 0 ^e | <1.3x10 ^{-14,f} |
| Corrosion, anode ^g | μA/cm ² | no active peak ^h | <1 and no active peak |
| Corrosion, cathode ⁱ | μA/cm ² | <0.1 ^c | <1 |
| Electrical conductivity | S/cm | >100 ^j | >100 |
| Areal specific resistance ^k | ohm cm ² | 0.006 ^h | <0.01 |
| Flexural strength ^l | MPa | >34 (carbon plate) ^m | >25 |
| Forming elongation ⁿ | % | 20–40 ^o | 40 |

^a Costs projected to high volume production (500,000 80 kW systems per year), assuming MEA meets performance target of 1,000 mW/cm².

^b Cost when producing sufficient plates for 500,000 systems per year. DOE Hydrogen and Fuel Cells Program Record 15015, "Fuel Cell System Cost—2015."

^c C.H. Wang (Treadstone), "Low-cost PEM Fuel Cell Metal Bipolar Plates," 2012 Annual Progress Report.

^d Per the standard gas transport test (ASTM D1434).

^e C.H. Wang (Treadstone), private communication, October 2014.

^f Blunk, et al., J. Power Sources 159 (2008) 533–542.

^g pH 3 0.1ppm HF, 80°C, peak active current <1x10⁻⁵ A/cm² (potentiodynamic test at 0.1 mV/s, -0.4V to +0.6V (Ag/AgCl)), de-aerated with Ar purge.

^h Kumar, M. Ricketts, and S. Hirano, "Ex-situ evaluation of nanometer range gold coating on stainless steel substrate for automotive polymer electrolyte membrane fuel cell bipolar plate," Journal of Power Sources 195 (2010): 1401–1407, September 2009.

ⁱ pH 3 0.1ppm HF, 80°C, passive current <5x10⁻⁸ A/cm² (potentiostatic test at +0.6V (Ag/AgCl) for >24h, aerated solution).

^j O. Adrianowicz (GrafTech), "Next Generation Bipolar Plates for Automotive PEM Fuel Cells," 2009 Annual Progress Report.

^k Includes interfacial contact resistance (on as received and after potentiostatic test) measured both sides per Wang, et al. J. Power Sources 115 (2003) 243–251 at 200 psi (138 N/cm²).

^l ASTM-D 790-10 Standard Test Method for Flexural Properties of Unreinforced and Reinforced Plastics and Electrical Insulating Materials.

^m D. Haack et al. (Porvair), "Carbon-Carbon Bipolar Plates," 2007 Annual Progress Report.

ⁿ Per ASTM E8M-01 Standard Test Methods for Tension Testing of Metallic Materials, or demonstrate ability to stamp generic channel design with width, depth, and radius.

^o M. Brady et al. (Oak Ridge National Laboratory), "Nitrided Metallic Bipolar Plates," 2010 Annual Progress Report.