Lab Call FY19: Low-Cost Gas Diffusion Layer Materials and Treatments for Durable High-Performance Polymer Electrolyte Membrane Fuel Cells

Rod L. Borup1 (Primary Contact), Daniel P. Leonard,1 R. Mukundan,1 K.C. Neyerlin,2 Sadia Kabir,2 David Cullen3

1Los Alamos National Laboratory
MS D429, P.O. Box 1663
Los Alamos, NM 87545
Phone: 505-667-2823
E-mail: Borup@lanl.gov

DOE Manager: Donna Ho
Phone: 202-586-8000
Email: Donna.Ho@ee.doe.gov

Subcontractors and Collaborators:
• 2National Renewable Energy Laboratory, Golden, CO
• 3Oak Ridge National Laboratory, Oak Ridge, TN

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Overall Objectives
This project is developing new gas diffusion layer (GDL) materials to reduce cost of GDL materials in polymer electrolyte membrane fuel cells.

Develop materials and processes for low-cost GDLs
• Reduce the initial material cost
• Process the materials with lower-cost processes (e.g., lower carbonization temperature).

Meet performance objectives with low-cost GDLs
• Electrical conductivity >100 S/cm
• Areal specific resistance (ASR) <0.01 Ohm-cm²
• Performance equivalent to that of SGL Carbon’s 29BC at 40% and 100% RH, 80°C at 1.5 A/cm² with identical membrane electrode assemblies (MEAs).

Technical Barriers
This project addresses the following technical barriers from Table 3 of the Fuel Cell Technical Team Roadmap:
• **Cost:** $14/kWnet MEA.
• **Cost:** Use low-cost materials and reduce processing costs. Reduce the cost compared to current state-of-the-art GDL materials.
• **Performance:** Meet equivalent performance of GDL materials with lower-cost materials. Potentially, mitigate transport losses through improved water management for higher performing fuel cell MEAs.

Technical Targets
There are few targets related to GDLs. This is in part because the GDL performance metrics are complicated and the science of two-phase transport is ill-defined. The role of the GDL can also vary by the fuel cell’s bipolar plate flow field design. There are no performance or durability protocols related to GDL materials, thus there are no (few) technical targets to be compared against.

Several performance metrics can be adopted from bipolar plate materials:
• Electrical conductivity >100 S/cm
• ASR <0.01 Ohm-cm².
Performance target:
- Meet performance equivalent to that of SGL Carbon’s 29BC at 40% and 100% RH, 80°C, at 1.5 A/cm² with identical MEAs.

FY 2019 Accomplishments
- Identification and procurement of base fiber materials.
- Evaluation of carbonization of raw fibers—defined carbonization temperature to meet conductivity targets.

INTRODUCTION
The GDL is the fuel cell component used to enhance gas transport to the electrodes and water removal from the electrodes, conduct electrical current from the electrodes to the bipolar plates, and provide mechanical support plus compression distribution to the membrane/electrode assembly. This project is developing new GDL materials and structures to enhance water transport in PEM fuel cells and reduce the cost of GDL materials. The project concentrates on development of lower-cost materials and processes to result in lower-cost GDLs. Different physical structures are being developed to enhance water removal with different surface treatments used to simultaneously enhance water removal from and gas transport to the catalyst layer.

APPROACH
Three methods are being employed to reduce the cost of GDL materials: (1) lower-cost raw materials (fibers), (2) lower processing costs (primarily graphitization temperature) and/or replacement of processing steps, and (3) surface treatments to replace hydrophobic treatments by Teflonation.

Polyacrylonitrile (PAN) fibers are typically used in a GDL substrate; this project is developing the use of lower-cost fibers. The PAN fibers normally go through multiple high-temperature processing steps—by using lower-cost fibers, which are more easily converted into amorphous carbon due to the lack of nitrile groups, a lower graphitization temperature can be used. In addition, natural fibers intertwine, which potentially eliminates the need for binders during the paper making process. Super-hydrophobic surface treatments will be developed to eliminate the use of Teflon in the GDL substrate and possibly the micro-porous layer (MPL).

RESULTS
The initial approach at reducing GDL costs is to utilize lower-cost materials. PAN fiber use in GDLs is ubiquitous; while PAN fibers are strong, they are also expensive. Natural fibers are significantly less expensive. Table 1 shows the costs of PAN fibers versus the costs of various natural fibers. Utilizing natural fibers can be a significant cost reduction at high-volume manufacturing. Using the cost study by Brian James et al. (SA), lower-cost fibers reduce GDL cost by up to 13% at high volumes [1].
Table 1. Comparison of Natural Fiber Costs versus PAN Fiber Costs

<table>
<thead>
<tr>
<th>Fiber Source</th>
<th>Est. Cost ($/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAN (pyrolyzed)</td>
<td>$15.00–$20.00</td>
</tr>
<tr>
<td>PAN (chopped)</td>
<td>$3.20 (SA $10.9)</td>
</tr>
<tr>
<td>Jute</td>
<td>$0.50–$1.50</td>
</tr>
<tr>
<td>Bagasse (waste cane)</td>
<td>$0.0035–$0.00118</td>
</tr>
<tr>
<td></td>
<td>(Alibaba: $0.08–$0.22)</td>
</tr>
<tr>
<td>Sisal</td>
<td>$1.01–$2.1</td>
</tr>
<tr>
<td>Switchgrass</td>
<td>Target: $0.07</td>
</tr>
</tbody>
</table>

An important contributor to cost is the carbonization/graphitization of the carbon fibers. Figure 1 shows the mass loss during carbonization as measured by thermal gravimetric analysis for various natural fibers. Over 95% of the carbonization is complete by 800°C. In contrast, PAN fibers still have about 45% of their weight remaining at 800°C [2]. To meet the electrical conductivity target, 1,200°C was used to carbonize the fibers. The measured electrical conductivity of the natural fibers is compared to measured electrical conductivity of commercial GDLs (SGL 29BC and Toray 060), which are carbonized to what is believed to be a much higher temperature of >2,000°C. Note that furnace costs are greatly reduced below ~1,400°C [3].

![Thermal gravimetric analysis of natural fibers cotton, bamboo, and coconut](image)

The measured electrical resistance of GDLs after carbonization at 1,200°C is shown in Table 2, along with commercial GDLs by SGL and Toray for comparison. The electrical conductivity was measured by the same methodology as listed on the specification sheets for SGL Carbon GDL 24DC: 2-point measurement, 5 cm², gold-plated contacts with 1 MPa contact pressure. The listed resistivity of 24DC is listed as 0.0131 Ohm*cm², although we measured a lower resistance of 0.009 Ohm*cm². The resistance measurements of the natural fibers, carbonized only to 1200°C, were mostly below the listed resistance of 24DC, and in most cases similar to the measured resistance of 24DC.
Table 2. Measured Electrical Resistance of Commercial GDLs and Natural Fibers Carbonized to a Temperature of 1,200 °C

<table>
<thead>
<tr>
<th>Sample</th>
<th>V</th>
<th>A</th>
<th>Area</th>
<th>Ohm*cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>SGL 29BC</td>
<td>0.0092</td>
<td>5</td>
<td>5</td>
<td>0.0092</td>
</tr>
<tr>
<td>Toray 060BC</td>
<td>0.0071</td>
<td>5</td>
<td>5</td>
<td>0.0071</td>
</tr>
<tr>
<td>Bagasse</td>
<td>0.0116</td>
<td>5</td>
<td>4.15</td>
<td>0.0096</td>
</tr>
<tr>
<td>Switchgrass</td>
<td>0.0128</td>
<td>5</td>
<td>4.15</td>
<td>0.0106</td>
</tr>
<tr>
<td>Sisal</td>
<td>0.0126</td>
<td>5</td>
<td>4.15</td>
<td>0.0105</td>
</tr>
<tr>
<td>Jute</td>
<td>0.0169</td>
<td>5</td>
<td>4.15</td>
<td>0.0140</td>
</tr>
</tbody>
</table>

For good transport, GDLs require high porosity. PAN fibers have excellent uniformity in terms of fiber diameter, which is approximately 8 microns. Natural fibers, of course, have a much wider variability in terms of fiber diameter, length and geometry. Figure 2 shows SEM micrographs of GDL papers from PAN fibers, jute fibers, sisal fibers, and bagasse fibers. The variability in fiber diameter of the natural fibers is obvious in the SEM micrographs. Jute fibers, as an example, were measured to range from 1 micron to 65 micron in diameter. In terms of porosity, SGL-29AA is specified to be 78%, whereas the jute, sisal and bagasse were measured to be 90%, 89%, and 83%, respectively. Note that PAN fiber GDL papers undergo an impregnation process, which reduces their porosity, which is apparently intentional during the fabrication process [4].

![Figure 2. SEM micrographs of GDL papers of (a) SGL-29AA (graphitized PAN fibers)—78% porosity, (b) jute fibers—90% porosity, (c) sisal fibers—89% porosity, and (d) bagasse fibers—83% porosity](image)

Of course, the ultimate test of any GDL is its performance in an operating fuel cell environment. Initial measurements were made to compare the jute GDL against state-of-the-art baseline materials (SGL 29BC). The natural fiber GDLs were first examined on the anode side of a fuel cell, as that is typically less demanding. A fuel cell polarization curve is shown in Figure 3a for a jute GDL on the anode side and compared to the baseline in Figure 3b; all fuel cell measurements were made with identical W.L. Gore MEAs (0.1/0.4 18 micron catalyst coated membrane, 5 cm²). At 1.5 A/cm², the jute anode showed performance within 30 mV of the baseline (circled in red). At much higher current densities, close to 2.5 A/cm², the jute anode GDL actually outperforms the baseline materials; however, this is not a realistic operating voltage. The high-frequency-resistance (HFR) of the jute GDL was slightly higher, but that only equates to about 10 mV of the performance difference. To date, no optimization has been performed of the jute GDL related to anode testing, including a hydrophobic treatment.
Figure 3. Polarization curves for (a) jute anode GDL and (b) SGL-29BC anode. MEA: W.L. Gore 0.1/0.4 mg Pt/cm$^2$ anode/cathode, 5 cm$^2$ differential cell, cathode GDL: SGL-29BC.

The more challenging application of GDLs is on the cathode side of the fuel cell. Figure 4 compares the GDL performance on the fuel cell cathode between a jute GDL and the baseline. While the cell with the jute GDL shows respectable performance (0.48 V at 1.5 A/cm$^2$), the jute underperformed the baseline materials by over 100 mV at 1.5 A/cm$^2$. In this case, the jute GDL was treated to make it hydrophobic by a Teflonation treatment. Impedance analysis shows a much higher resistance; this suggest an MPL is required for the cathode GDL. Regardless, the jute GDL requires optimization of its properties to make the performance competitive with that of commercial baseline materials; the first step in this optimization will be to add an MPL. Other methods include adjusting the paper porosity, increasing the electrical conductivity, and adjusting the hydrophobicity.

Figure 4. Polarization curves for (a) jute cathode GDL and (b) SGL-29BC cathode. MEA: W.L. Gore 0.1/0.4 mg Pt/cm$^2$ anode/cathode, 5 cm$^2$ differential cell, anode GDL: SGL-29BC.

**CONCLUSIONS AND UPCOMING ACTIVITIES**

This project has concentrated on developing lower-cost GDL materials and processing costs. To date we have demonstrated that lower-cost materials and reduction in processing conditions are valid methods to reduce cost. Testing lower-cost GDLs on a fuel cell anode showed performance close to that of the baseline materials.
Similar testing on a fuel cell cathode indicates the GDL requires substantial optimization to have competitive performance.

Future work will continue to develop methods to reduce processing costs and materials. The current materials described in this report will be modified with MPLs and the performance will be compared. Impedance analysis, and potentially other analyses (such as water concentration measurements by neutron imaging), will be done to determine the appropriate material optimization strategies.

The following tasks will commence during Year 2 of the project.

**Hydrophilic highway for enhanced water removal**
- MPL modification: hydrophilic treatment
- Impregnation of amorphous carbon throughout GDL structure
- Gas phase treatments: hydrophilic.

**Super-hydrophobicity surface modification**
- Gas phase treatments: hydrophobic
- Biomimetic surface treatment
- Characterization of surface treatments.

**FY 2019 PUBLICATIONS/PRESENTATIONS**

**REFERENCES**