FC319: Low Cost Gas Diffusion Layer Materials and Treatments for Durable High Performance PEM Fuel Cells

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Project - Overview

Timeline

Project start date: 10/01/2018
Project end date: 09/30/2020
< 5% complete

Budget

FY19 Project funding: $500k
As proposed: 2-year
Total Expected Funding: $1,000k

Barriers

• Cost: $14/kW_{net} MEA
• Costs: Use of low-cost materials, and reduced processing costs
• Performance: Mitigation of transport Losses through improved water management

Partners

• LANL – Rod Borup
• ORNL – David Cullen
• NREL – K.C. Neyerlin
Relevance & Objectives

Cost Reduction:
• Develop lower cost GDLs
  ➤ Utilize lower cost fibers for reduced costs in materials
  ➤ Use lower carbonization temperatures to reduce processing costs
  ➤ Reduce manufacturing costs by developing low-cost gas phase surface treatments (to replace Teflon treatments)

Improved Performance:
• Develop GDLs with enhanced performance in terms of water management
  ➤ Improved water management by development of super-hydrophobicity coatings to prevent water flooding and transport losses
  ➤ Incorporation of hydrophilic pathways separate from hydrophobic domains to provide pathway for water removal
Approach: Cost Reduction

Cost reduction:
Three approaches will be employed to reduce the cost of GDL materials:
1. Utilize lower cost raw materials (fibers)
2. Develop hydrophobic surface treatments to replace Teflon
3. Lower processing costs (primarily graphitization temperature) and/or replacement of materials and processing steps.

• PAN (PolyAcryloNitrile) fibers are typically used in a GDL substrate; raw cost of $15 - $20/kg
  ➤ This project will develop the use of lower cost fibers in comparison to PAN

• Super-hydrophobic gas-phase surface treatments will be used to eliminate the use of Teflon in the GDL substrate, and possibly the Micro-Porous Layer (MPL) such as previously with cellulosic fiber GDLs.

• PAN fibers normally go through multiple high temperature processing steps
  ➤ This project will examine fibers which carbonize at lower temperatures, plus elimination/combination of these multiple processing steps.
Approach: Enhanced Performance

Enhanced Performance:

• New structures/surface treatments, primarily in the MPL, will be used to provide enhanced water transport to separate water transport from gas transport pathways.
  ➤ Hydrophobic treatments prevent water build-up and transport losses
  ➤ Hydrophilic fibers (e.g. CNT and aluminosilicate) in GDL MPLs have been shown to provide enhanced water transport

• Super-hydrophobic treatments will be examined to create the MPL hydrophobicity; the two methods to be examined include
  ➤ Gas phase surface treatments
  ➤ Biomimetics surface treatment for a lower-cost replacement for Teflon

• Hydrophilic fiber incorporation into GDL MPLs
  ➤ Non-fluorinated electrospun fibers
  ➤ Amorphous carbon fibers with a hydrophilic surfaces
GDL Cost Breakdown Cost Studies

**Ballard**


**Strategic Analysis**

GDL Made of Cellulosic Fibers

SEM image of Stackpole paper (100 micron bar) and higher magnification inset (10 micron bar)

- GDLs made of cellulosic fiber previously manufactured and successfully used in PEM fuel cells
- Higher surface area fibers were used with no additional MPL, in contrast to PAN fiber GDL substrates, which require MPL
- Issue with mechanical strength and intrusion into channels that no longer seems an issue with flowfields (e.g. Toyota Mirai 3D Fine Mesh)

<table>
<thead>
<tr>
<th></th>
<th>BET Surface Area (cm²/g)</th>
<th>Calculated Fiber Diameter (micron)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stackpole 15015</td>
<td>1.48</td>
<td></td>
</tr>
<tr>
<td>Toray 060</td>
<td>4265</td>
<td>5.21</td>
</tr>
<tr>
<td>Spectracarb (15mil, 0.28 g/cm³)</td>
<td>3427</td>
<td>6.48</td>
</tr>
<tr>
<td>Spectracarb (15mil, 0.45 g/cm³)</td>
<td>4403</td>
<td>5.05</td>
</tr>
<tr>
<td>Spectracarb (15mil, 0.45 g/cm³, 31% TFE)</td>
<td>6238</td>
<td>3.56</td>
</tr>
</tbody>
</table>
Microscopy of GDL Fibers Show Non-uniform Coating of Teflon

- Teflon solutions used to ‘coat’ GDL fibers to induce hydrophobicity
- Microscopy shows that Teflon does not wet the fibers; much of the Teflon agglomerate in localized areas
- Gas phase treatment should minimize quantities of hydrophobic material
Hydrophilic MPL Fibers Have Demonstrated Improved Water Management

Polarization curves for GDLs with different MPLs

- 25BL and 25BN MPLs have hydrophilic fibers
  - 25BL (with alumosilicate fibers)
  - 25BN (with carbon nanotube (CNT) fibers)
- 25BC has a traditional MPL
## FY2019 Milestones

<table>
<thead>
<tr>
<th>QTR</th>
<th>Type</th>
<th>Progress Measures, Milestones, Deliverables</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Q1</td>
<td>Milestone</td>
<td>Identify and procure at least 3 sets of fibers for carbonization/graphitization measurements.</td>
<td>✓ Completed</td>
</tr>
<tr>
<td>Q2</td>
<td>Milestone</td>
<td>Incorporate hydrophilic fiber into MPLs on base GDL substrate. Demonstrate improved Mass Transport resistance by EIS and HeLOx at 2 A/cm² of at least 30 mV over 29BC.</td>
<td></td>
</tr>
<tr>
<td>Q3</td>
<td>Milestone</td>
<td>Complete series of carbonization/graphitization of fibers at series of temperatures ranging from: Carbonization from 1000 °C to 1700 °C and graphitization from 1700 °C to 2700 °C</td>
<td></td>
</tr>
<tr>
<td>Q4</td>
<td>Milestone</td>
<td>Complete characterization of graphitized fibers; electrical conductivity, fiber strength</td>
<td></td>
</tr>
<tr>
<td>Q4</td>
<td>Go/No-Go</td>
<td>Demonstrate materials replacement (e.g. carbon fiber) sufficient for 50% materials cost reduction or elimination of MPL by higher surface area cellulosic fibers. Demonstrate lower cost graphitized fibers with electrical conductivity capable of meeting 0.01W.cm² ASR. Demonstrate lower cost manufacturing processes (e.g. temperature reduction, gas phase) or elimination of processing step(s) (one-step carbonization/graphitization rather than two) sufficient for 30% cost reduction.</td>
<td></td>
</tr>
<tr>
<td>Q4</td>
<td>Decision Go/No-Go</td>
<td>Demonstrate improve MEA performance with hydrophilic fibers incorporated into GDL/MPL. Performance at 1.5 A/cm², compared to SGL 29BC.</td>
<td></td>
</tr>
<tr>
<td>Q4</td>
<td>Decision Go/No-Go</td>
<td>Demonstrate higher contact angle compared to graphitized carbon using gas phase treatment with estimated cost reduction compared to Teflon treatment.</td>
<td></td>
</tr>
</tbody>
</table>
Accomplishments: Initial Work

- Project work started end of January 2019 (< 5% complete)
- Kick-off meeting held with NREL and ORNL Jan 28
  - Rod Borup, Daniel Leonard (LANL)
  - David Cullen (ORNL)
  - K.C. Neyerlin, Sadia Kabir (NREL)
- Initial cost reduction strategy is to obtain low-cost natural fibers and carbonize, for example:
  - Cotton fiber
  - Coconut fiber
  - Bamboo-pulp paper
- Initial results examine fibers by:
  - TGA
    - Determine carbon content, carbonization temperature
  - pyrolysis experiments
    - Post-XRD used to determine graphitic content
    - Conductivity measurements
Evaluate/compare

- Cost of natural fibers versus GDL traditional fibers
- Pyrolysis in terms of temperature, fiber structure and post-fiber mass

<table>
<thead>
<tr>
<th>Fiber Source</th>
<th>Est. Cost $/kg</th>
<th>Mass Post Pyrolysis %</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAN</td>
<td>$15.00 - $20.00</td>
<td>32.0</td>
</tr>
<tr>
<td>PAN (chopped)</td>
<td>$3.20</td>
<td>32.0</td>
</tr>
<tr>
<td>Cotton*</td>
<td>$1.57</td>
<td>19.4</td>
</tr>
<tr>
<td>Bamboo*</td>
<td>$2.10 - $2.90</td>
<td>14.7</td>
</tr>
<tr>
<td>Coconut*</td>
<td>$0.25 - $0.32</td>
<td>38.1</td>
</tr>
<tr>
<td>Jute</td>
<td>$0.50 - $1.50</td>
<td>No Data</td>
</tr>
<tr>
<td>Bagasse</td>
<td>$0.0035 - $0.00118</td>
<td>No Data</td>
</tr>
<tr>
<td>Flax</td>
<td>$2.85-15/kg</td>
<td>No Data</td>
</tr>
<tr>
<td>Hemp</td>
<td>$1.90-2.30/kg</td>
<td>No Data</td>
</tr>
</tbody>
</table>

*Initial fibers procured to evaluate pyrolysis/carbonization by TGA/XRD
Accomplishments: Thermo-Gravimetric Analysis (TGA) of Fibers to Evaluate Carbonization Temperature

TGA comparison of PAN versus natural fibers:
• 90% of weight loss complete by 370 °C for Bamboo & Cotton; 550 °C for PAN
• Weight loss not fully complete (>99%) until ~ 800 °C for all fibers
Accomplishments: Fibers after Carbonization

- Fiber structures left intact after carbonization
  - Cotton fibers appear more easily fabricated into GDL

- XRD did not show distinguishable difference in fiber crystallinity.
- Post carbonization suggests carbon filaments are primarily amorphous (or sample sizes too small for definitive diffraction)
- Need to evaluate conductivity, hydrophobicity
Collaborations & Coordination

Partner Laboratories
• ORNL (Oak Ridge National Lab) – David Cullen
• NREL (National Renewable Energy Lab) – K.C. Neyerlin
• National Institute of Standards and Technology (No-Cost) - Dan Hussey

Coordination with Industry
• No formal collaboration with GDL suppliers or OEMs
  • Formal collaboration was not eligible in National Lab Call DE-LC-000L062
  • Discussions were held with GDL supplier about project
• Contacts and prior collaborations exist with both GDL suppliers and OEMs
  • When GDL performance is equivalent to standard commercial materials with lower cost materials, industrial interactions will be initiated.
2018 Reviewer Comments

• This is a new project awarded through the National Lab Call DE-LC-000L062; official start date of Oct 1, 2018 - work commenced in Jan 2019

• Project was not reviewed last year
Future Work: Task Break-down

Task 1: Low Cost Material Fibers and Reduction in Graphitization Temperature
- Subtask 1.1: Identification and procurement of base fiber materials (Q1) (LANL)
- Subtask 1.2: Carbonization/graphitization of raw fibers (Q2-Q3) (LANL)
- Subtask 1.3: Characterization of carbonized raw fibers (Q2-Q4) (LANL, ORNL)
- Subtask 1.4: Fabrication and carbonization/graphitization of fiber mat (Q4-Q7) (LANL)

Task 2: Hydrophilic highway (LANL, NREL)
- Subtask 2.1: MPL Modification: Hydrophilic Treatment (Q1-Q4) (LANL, NREL)
- Subtask 2.2: Impregnation of Amorphous Carbon through GDL Structure (Q3-Q5) (LANL, NREL)
- Subtask 2.3: Gas Phase Treatments: Hydrophilic (Q6-Q8) (LANL)

Task 3: Super-hydrophobicity Surface Modification (Q4-Q6) (LANL)
- Subtask 3.1: Gas Phase Treatments: Hydrophobic (Q3-Q6) (LANL)
- Subtask 3.2: Biomimetic Surface Treatment (Q1-Q8) (LANL)
- Subtask 3.3: Characterization of surface treatments (Q1-Q8) (LANL, ORNL)

Task 4: GDL Fabrication, in situ Measurements
- Subtask 4.1: Fabrication of Modified GDLs (LANL, NREL)
- Subtask 4.2: MEA testing of GDLs (LANL, NREL)
- Subtask 4.3: Durability of low cost GDLs (LANL)
- Subtask 4.4: Neutron imaging of water profiles in GDLs (NIST)

Any proposed future work is subject to change based on funding levels.
Future Work: Task Timeline

Any proposed future work is subject to change based on funding levels.
Summary

Relevance/Objective:
- Develop lower cost GDLs and enhanced performance in terms of water management

Approach:

Cost reduction:
- Three approaches will be employed to reduce the cost of GDL materials:
  1. Utilize lower cost raw materials (fibers)
  2. Develop hydrophobic surface treatments to replace Teflon
  3. Lower processing costs (primarily graphitization temperature) and/or replacement of processing steps.

Enhanced Performance:
- Super-hydrophobic treatments and hydrophilic fibers will be examined:
  1. New structures/surface treatments, primarily in the MPL, will be used to provide enhanced water transport to separate water transport from gas transport pathways.
  2. Hydrophilic fiber incorporation into GDL MPLs

Technical Accomplishments:
- Initial comparison of natural fiber cost and procurement
- TGA and carbonization of fibers

Future Work:
- Project work recently started. Future work laid out in project approach.
Acknowledgements

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Fuel Cell Technologies Office (FCTO)

• Fuel Cells Technology Manager & Program Team Leaders:
  ¦ Donna Ho
  ¦ Dimitrios Papageorgopoulos