

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

Project PI: Rod Borup¹

Daniel Leonard¹, K.C. Neyerlin², Sadia Kabir², David Cullen³

Los Alamos National Lab¹, National Renewable Energy Lab²,
Oak Ridge National Lab³

Monday, April 29th 2019



This presentation does not contain any proprietary, confidential, or otherwise restricted information.

Project - Overview

Timeline

Project start date: 10/01/2018

Project end date: 09/30/2020

< 5% complete

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

Budget

FY19 Project funding: \$500k

As proposed: 2-year

Total Expected Funding: \$1,000k

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

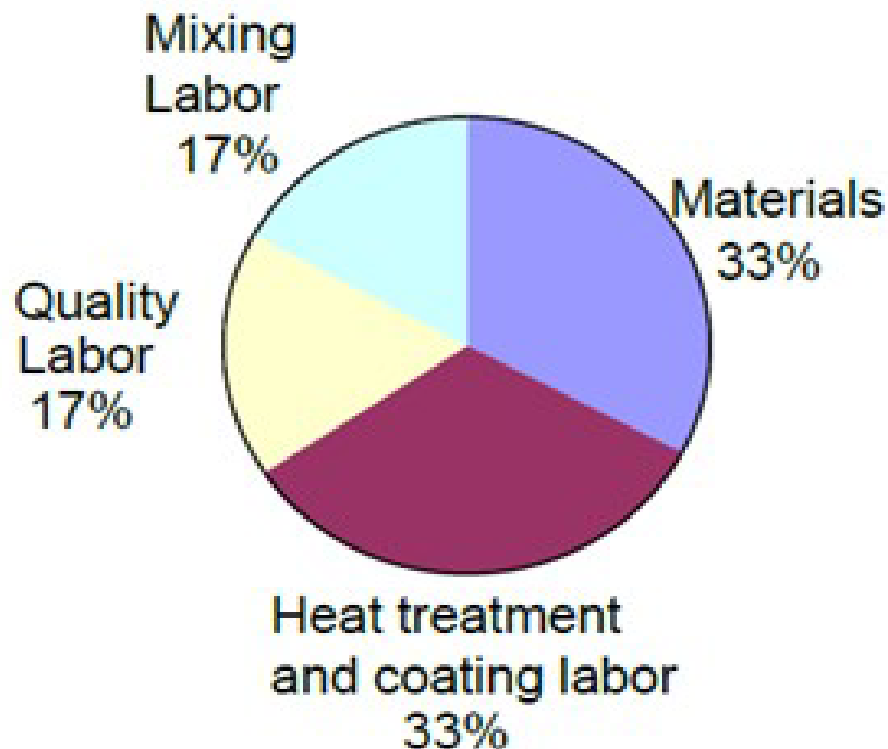
↳ This project will examine fibers which carbonize at lower temperatures, plus elimination/combination of these multiple processing steps.

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 enhance 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

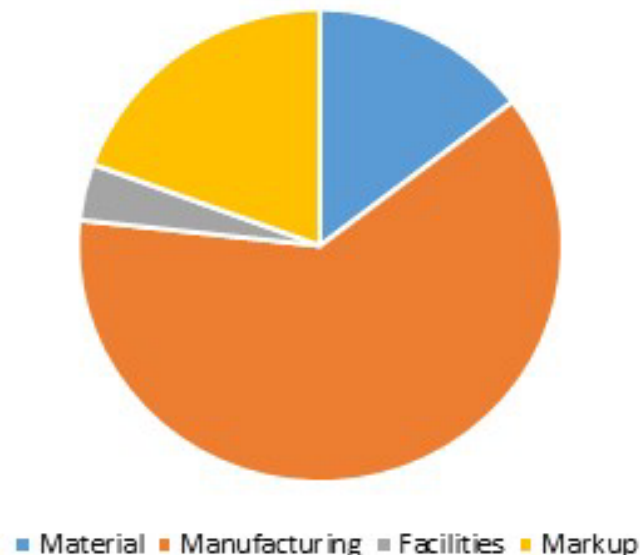
GDL Cost Breakdown Cost Studies



Ballard

Jason Morgan, Reduction in Fabrication Costs of Gas Diffusion Layers, Reduction in Fabrication Costs of Gas Diffusion Layers, DOE Hydrogen Program and Vehicle Technologies Annual Merit Review, May 2011

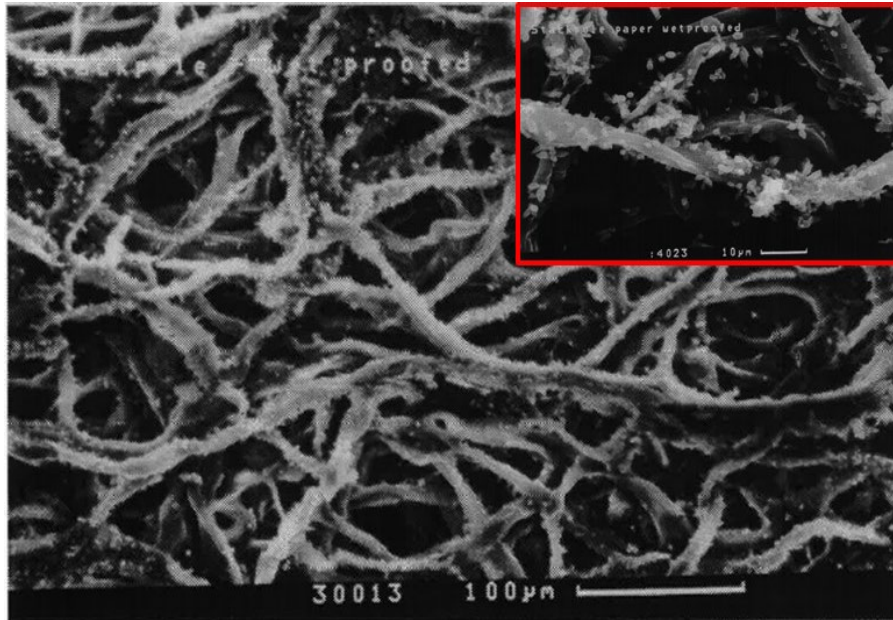
GDL Cost Breakdown



Strategic Analysis

Brian D. James, Jennie M. Huya-Kouadio, Cassidy Houchins, Daniel A. DeSantis, Mass Production Cost Estimation of Direct H₂ PEM Fuel Cell Systems for Transportation Applications: 2016 Update, https://www.energy.gov/sites/prod/files/2017/06/f34/fcto_sa_2016_pemfc_transportation_cost_analysis.pdf, Jan 2017

GDL Made of Cellulosic Fibers

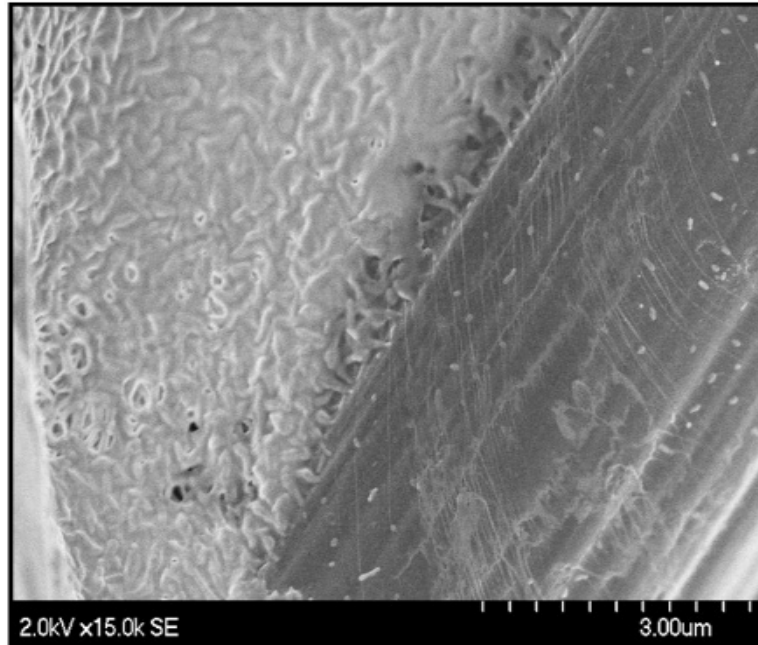


	BET Surface Area (cm ² /g)	Calculated Fiber Diameter (micron)

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)

Microscopy of GDL Fibers Show Non-uniform Coating of Teflon

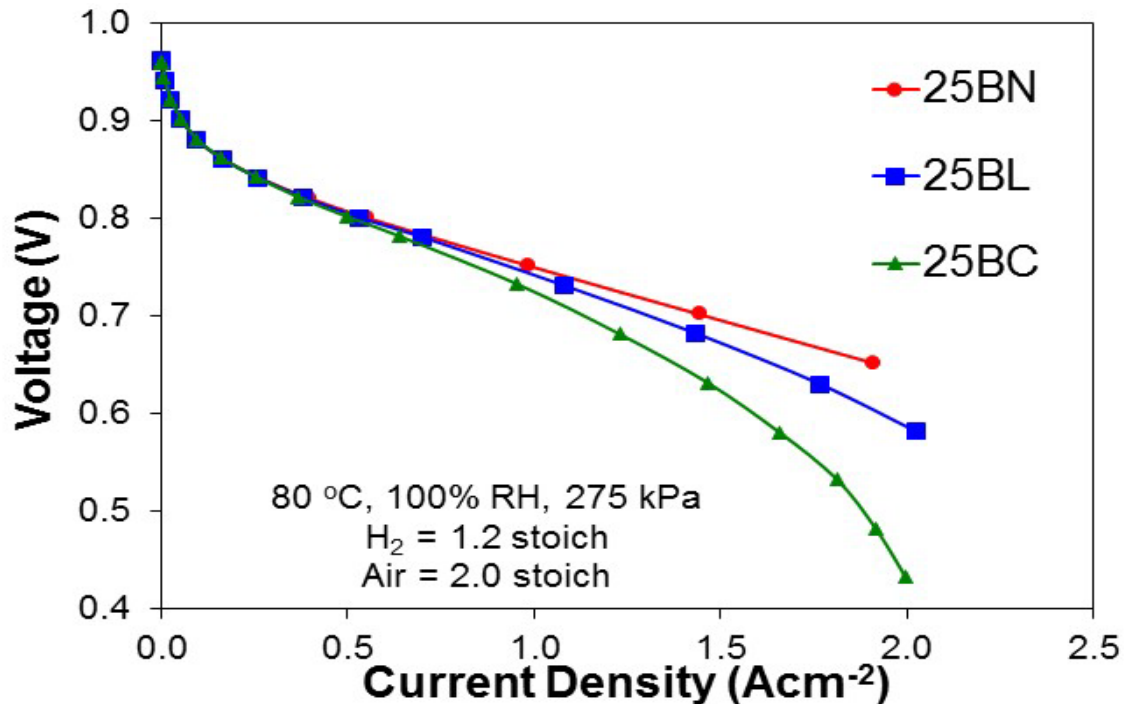


SEM of a fiber in a GDL showing Teflon coating (left) and uncoated fiber (right)

- 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 aluminosilicate fibers)
 - 25BN (with carbon nanotube (CNT) fibers)
 - 25BC has a traditional MPL

FY2019 Milestones

QTR	Type	Progress Measures, Milestones, Deliverables	Comments
Q1	Milestone	Identify and procure at least 3 sets of fibers for carbonization/graphitization measurements.	✓ Completed
Q2	Milestone	Incorporate hydrophilic fiber into MPLs on base GDL substrate. Demonstrate improved Mass Transport resistance by EIS and HeLOx at 2 A/cm ² of at least 30 mV over 29BC.	
Q3	Milestone	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	
Q4	Milestone	Complete characterization of graphitized fibers; electrical conductivity, fiber strength	
Q4	Go/No-Go	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.cm ² 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.	
Q4	Decision Go/No-Go	Demonstrate improve MEA performance with hydrophilic fibers incorporated into GDL/MPL. Performance at 1.5 A/cm ² , compared to SGL 29BC.	
Q4	Decision Go/No-Go	Demonstrate higher contact angle compared to graphitized carbon using gas phase treatment with estimated cost reduction compared to Teflon treatment.	

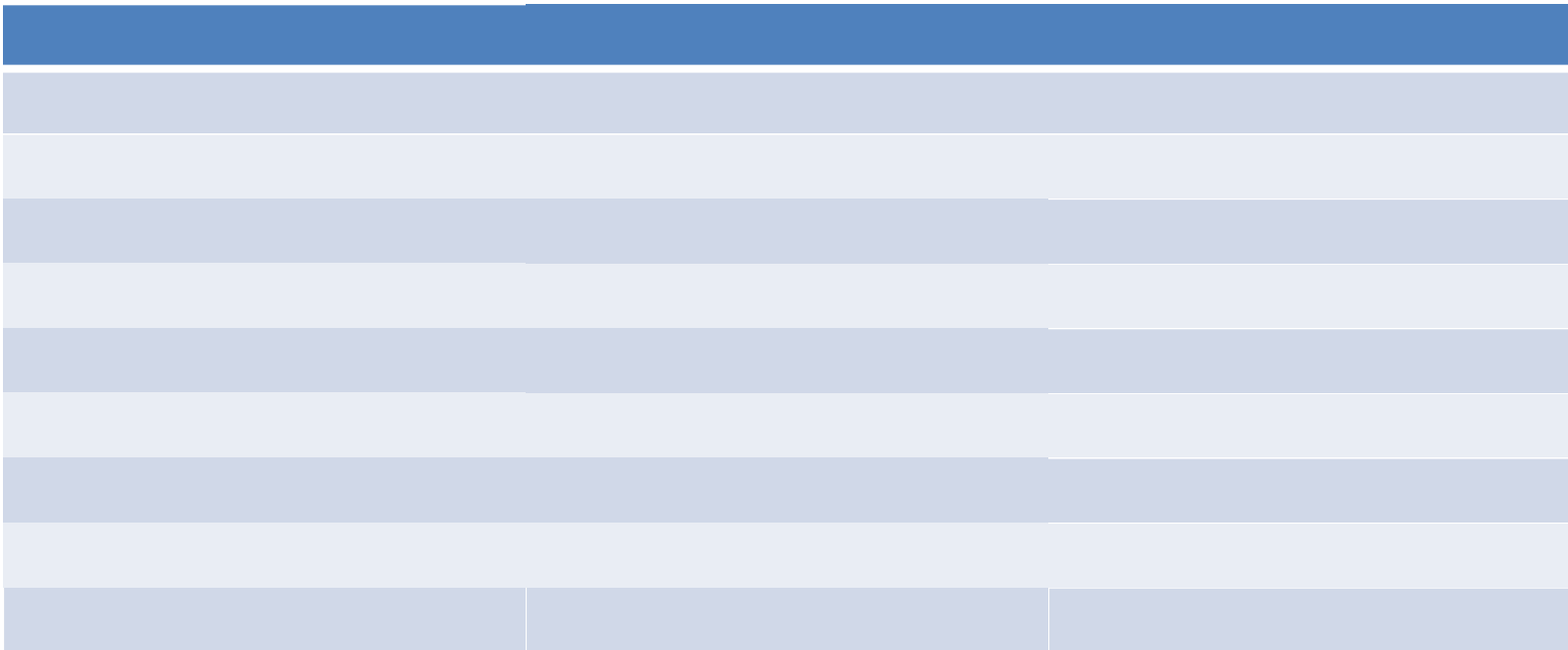
Accomplishments: Initial Work

- 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

Initial Accomplishments: Fiber Cost Comparison

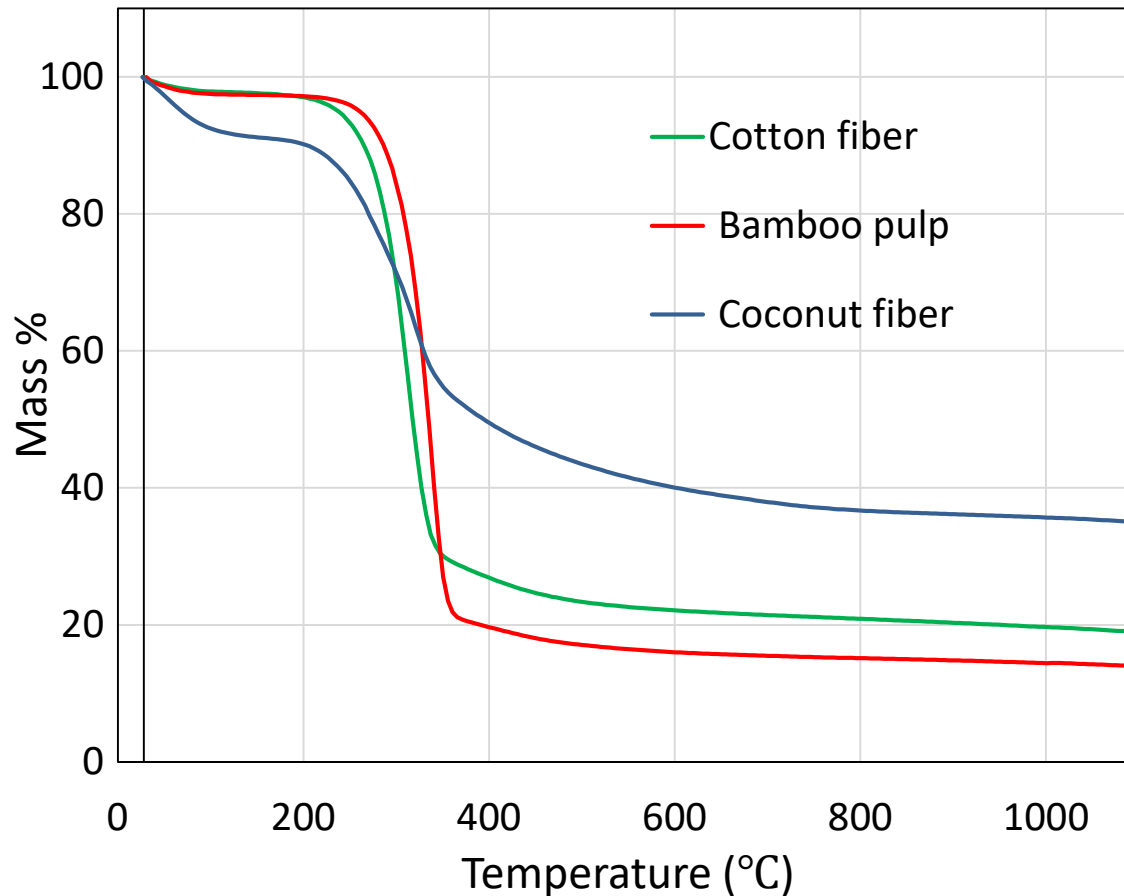
Evaluate/compare

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



*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

Cotton



Bamboo



- 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

Task #	Task/Subtask	Yr 1 (Q)				Yr 2 (Q)				
		1	2	3	4	5	6	7	8	
Low Cost Material Fibers and Reduction in Graphitization Temperature										
1	1. Identification and procurement of base fiber materials	M1								
	2. Carbonization of raw fibers			M3						
	3. Characterization of carbonized raw fibers				M4 G1					
	4. Fabrication and carbonization/graphitization of fiber mat							M7		
Creation of the Hydrophilic Highway: Material Synthesis and Modification										
2	1. Incorporation of hydrophilic fibers into MPLs				G2					
	2. Amorphous carbon path					M5				
	3. Gas-phase treatments: hydrophilic									
Super-hydrophobicity Surface Modification										
3	1. Gas-phase Treatments: Hydrophobic				G3		M6			
	2. Biomimetics surface treatment									
	3. Characterization of surface treatments									
GDL Fabrication, MEA Measurements and Water Imaging										
4	1. Fabrication of Modified GDLs									
	2. MEA testing of GDLs							M8		
	3. Durability of low cost GDLs									
	4. Neutron imaging of water profiles									

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

DOE EERE: Energy Efficiency and Renewable Energy Fuel Cell Technologies Office (FCTO)

- Fuel Cells Technology Manger & Program Team Leaders:
 - ↳ Donna Ho
 - ↳ Dimitrios Papageorgopoulos