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

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Los Alamos NATIONAL LABORATORY

NREL NATIONAL RENEWABLE ENERGY LABORATORY

OAK RIDGE National Laboratory

Project - Overview

Timeline

Project start date: 10/01/2018

Project end date: 09/30/2021

~ 50% 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
FY20 Project funding: \$500k
As proposed: 2-year
Modified: 3-year project
(same total funding)
Total Expected Funding: \$1,000k

Partners

- **LANL –** Rod Borup, Daniel Leonard
- **ORNL –** David Cullen
- **NREL –** K.C. Neyerlin, Sadia Kabir

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:
  - Use of Teflon in the GDL substrate
  - 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.

Reasons for High Material and Manufacturing Costs

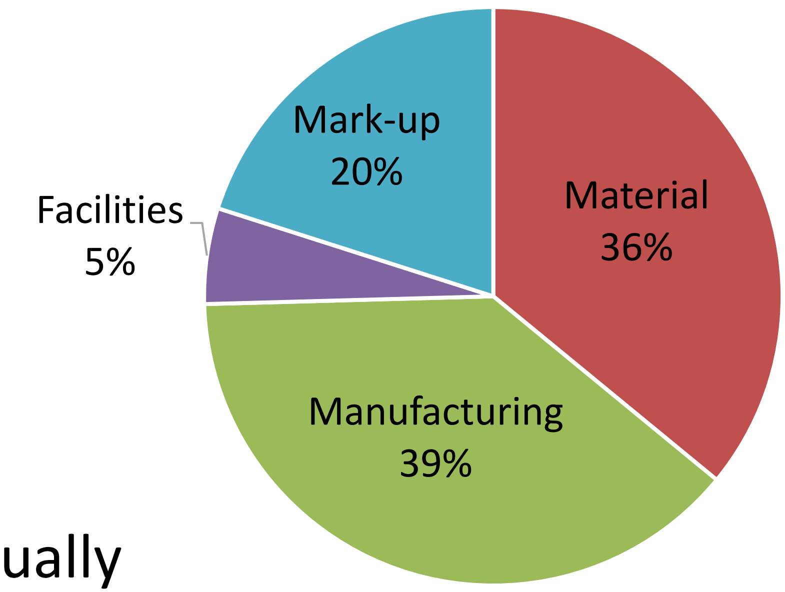
State-of-the-Art gas diffusion layers (GDLs) use Polyacrylonitrile (PAN) fibers.

- High Strength

Using PAN is expensive

- High cost of PAN
- High temperature processing
  - 1700°C → >2000°C
- Requires microporous layers (MPL)
- Requires hydrophobic treatment, usually PTFE

GDL Cost



Brian D. James, et al., Strategic Analysis, https://www.energy.gov/sites/prod/files/2017/06/f34/fctosa_2016_pemfc_transportation_cost_analysis.pdf, Jan 2017

Approach: Enhanced Performance

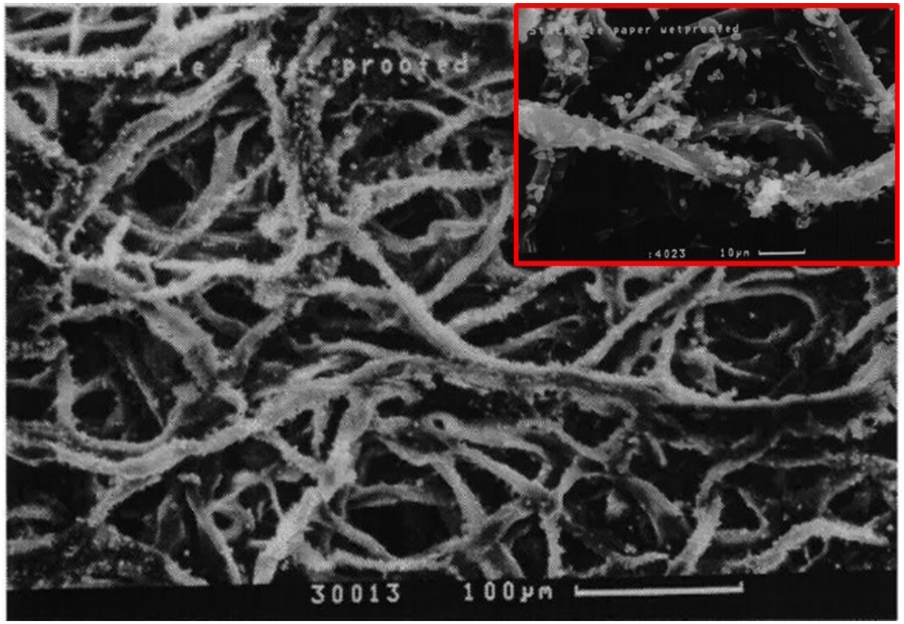
Enhanced Performance:

- 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
  - Biomimetic 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 Made of Cellulosic Fibers

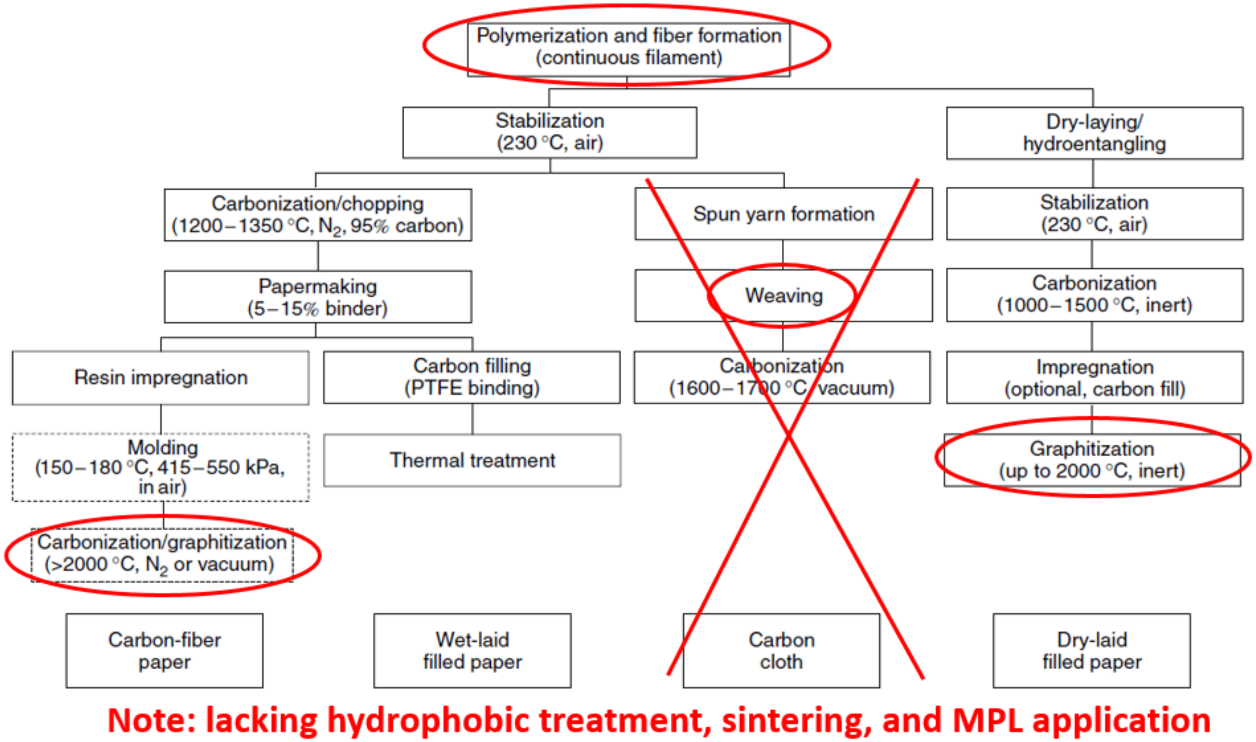


SEM image of Stackpole paper (100 micron bar) and higher magnification inset (10 micron bar)

GDL	BET Surface Area (cm2/g)	Calculated Fiber Diameter (micron)
Stackpole	15015	1.48
Toray 060	4265	5.21
Spectracarb (15mil, 0.28 g/cm3)	3427	6.48
Spectracarb (15mil, 0.45 g/cm3)	4403	5.05
Spectracarb (15mil, 0.45 g/cm3, 31% TFE)	6238	3.56

- 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)

Traditional GDL Production: Flow Diagram



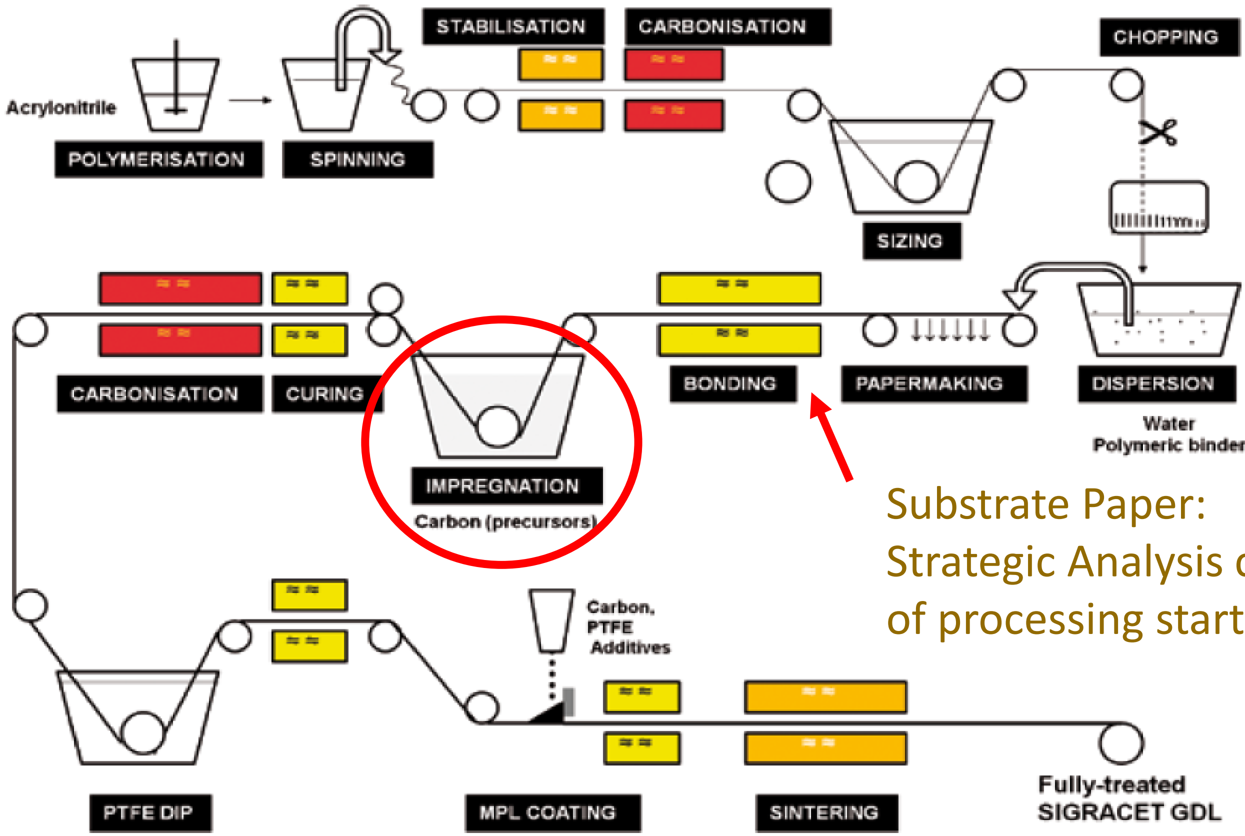
- Expensive process portions noted by circles
  - This project works to reduce cost modifying expensive processes
- Weaving typically expected (starting with PAN fibers) to be too expensive

- Natural low-cost fibers eliminates costly Polymer and Fiber Formation
- Fibers with lower carbonization temperatures reduces processing costs of Carbonization/Graphitization

M. Mathias, J. Roth, J. Flemming, W. Lehnert, Diffusion media materials and characterization, *Handbook of Fuel Cells – Fundamentals, Technology and Applications*, Edited by Wolf Vielstich, Hubert A. Gasteiger, Arnold Lamm. V. 3: *Fuel Cell Technology and Applications*. 2003

Jerry Flemming: Founder of SpectraCorp, and original Stackpole paper

Manufacturing Process of SIGRACET GDLs



From: Rudiger Schweiss, Christian Meiser, Tanja Damjanovic, Ivano galbati, Nico Haak, Sigracet Gas Diffusion Layers for PEM Fuel Cells, Electrolyzers and Batteries, SGL Group

Substrate Paper:
Strategic Analysis costs analysis of processing starts here

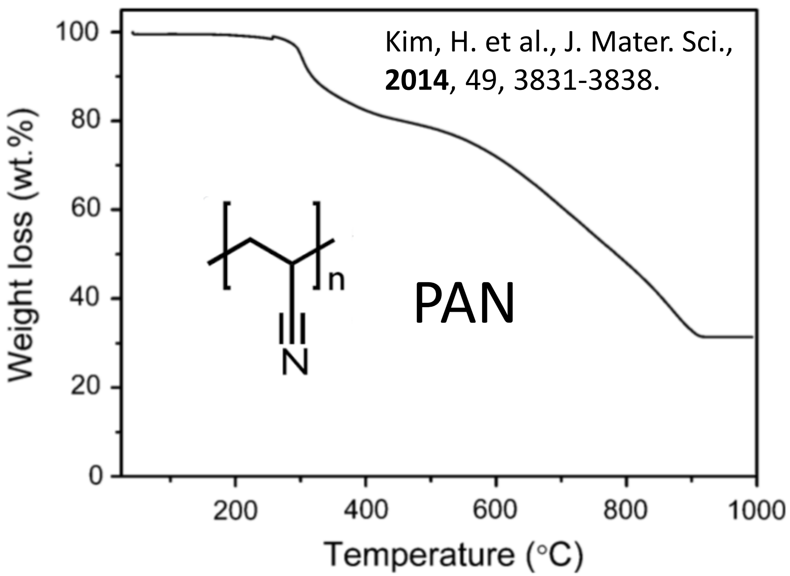
Project approach eliminates:

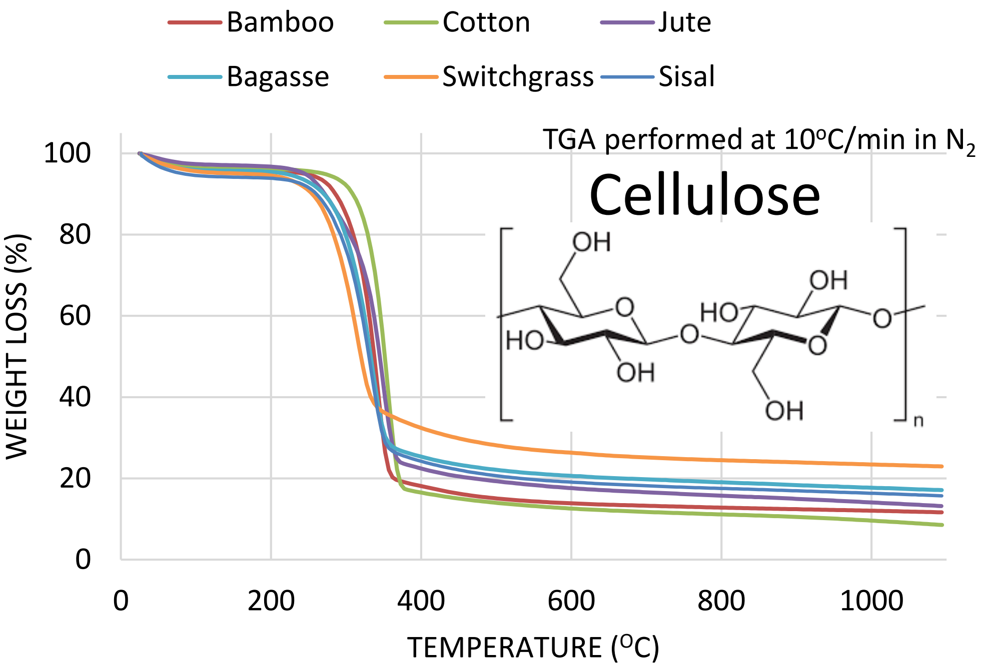
- Impregnation step (circled)
- Binder / bonding / curing

Reduces:

- Carbonization Temperature
- Cost of hydrophobic treatment

Thermo-Gravimetric Analysis (TGA) of Fibers to Evaluate Carbonization Temperature





Polyacrylonitrile (PAN)

- Density: 1.4 g/cm^3
- Carbon 67.91%
- Hydrogen 5.7%
- Nitrogen 26.4%

Cellulose (Jute)

- Density: 1.3–1.46
- Carbon 44.4%
- Hydrogen 6.2%
- Nitrogen 49.4%

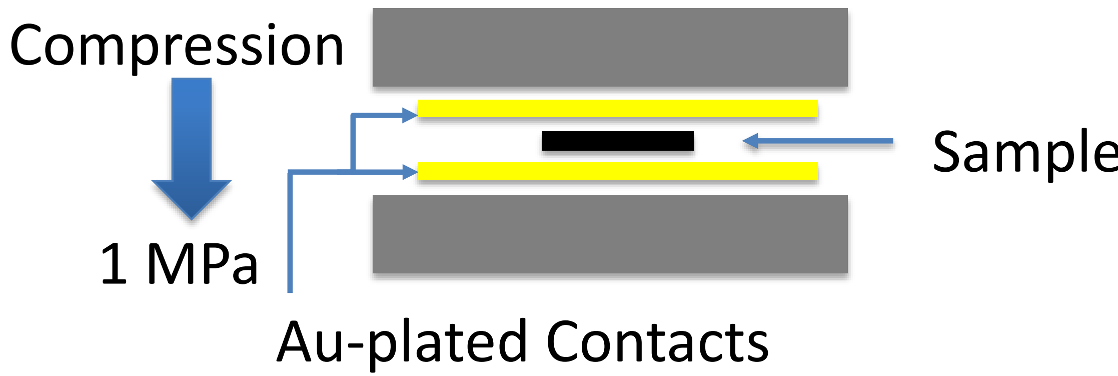
- **Graphitization of cellulose is somewhat self-oxidizing and does not require breaking of triple CN bonds**
- Cellulose fibers undergo > 90% of ultimate mass loss by 600°C

Good Conductivity of Lower-cost fibers met with carbonization at 1200 °C

Similar Contact Resistance to Commercial GDLs

GDL Sample	ASR (Ohm-cm^2)
SGL 29BC	0.0092
Toray 060BC	0.0071
Jute	0.0140
Bagasse	0.0096
Sisal	0.0105
Switchgrass	0.0106

Pyrolyzed @ > 1700°C



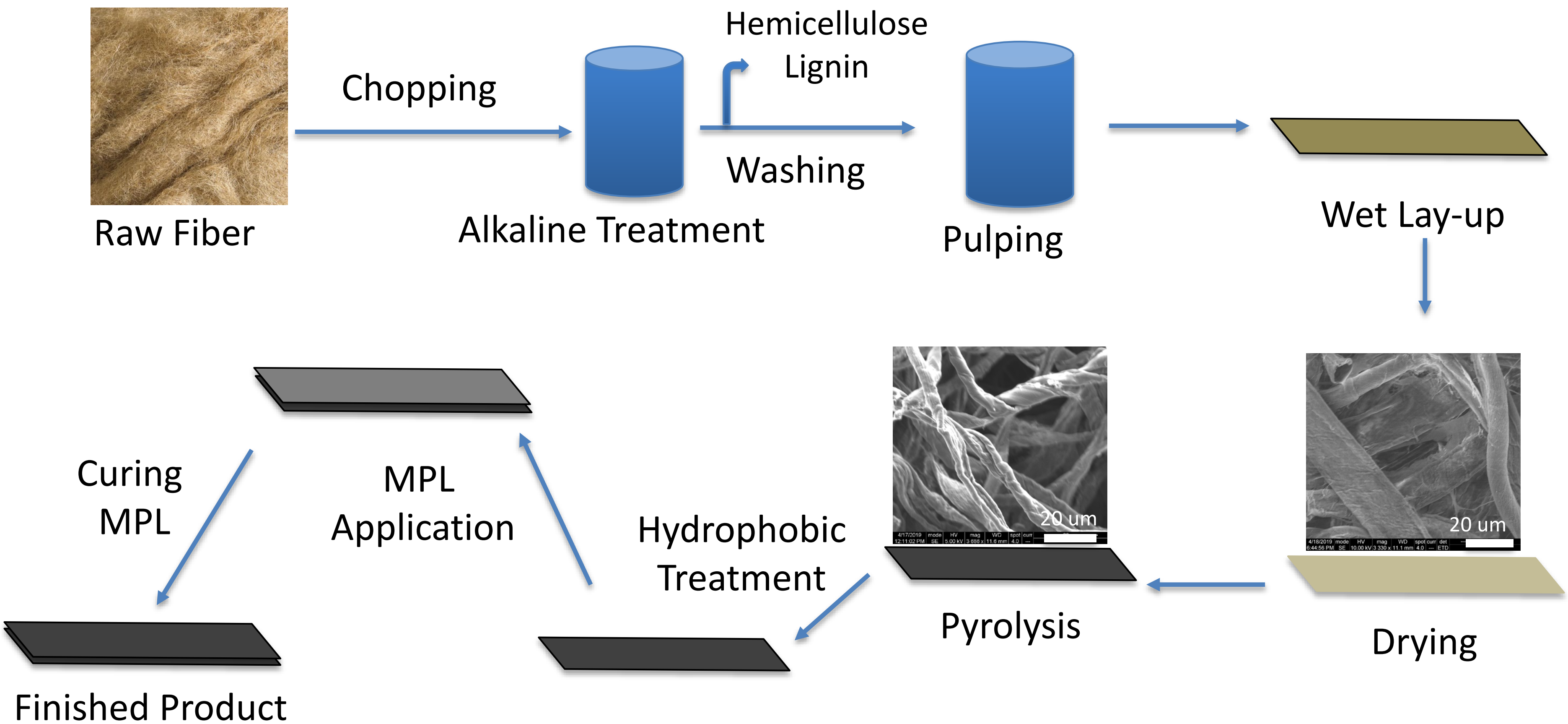
- *Conductivity sufficient with graphitization at 1200 °C*

→ With lower cost fibers

→ Lower cost in terms of graphitization temperature

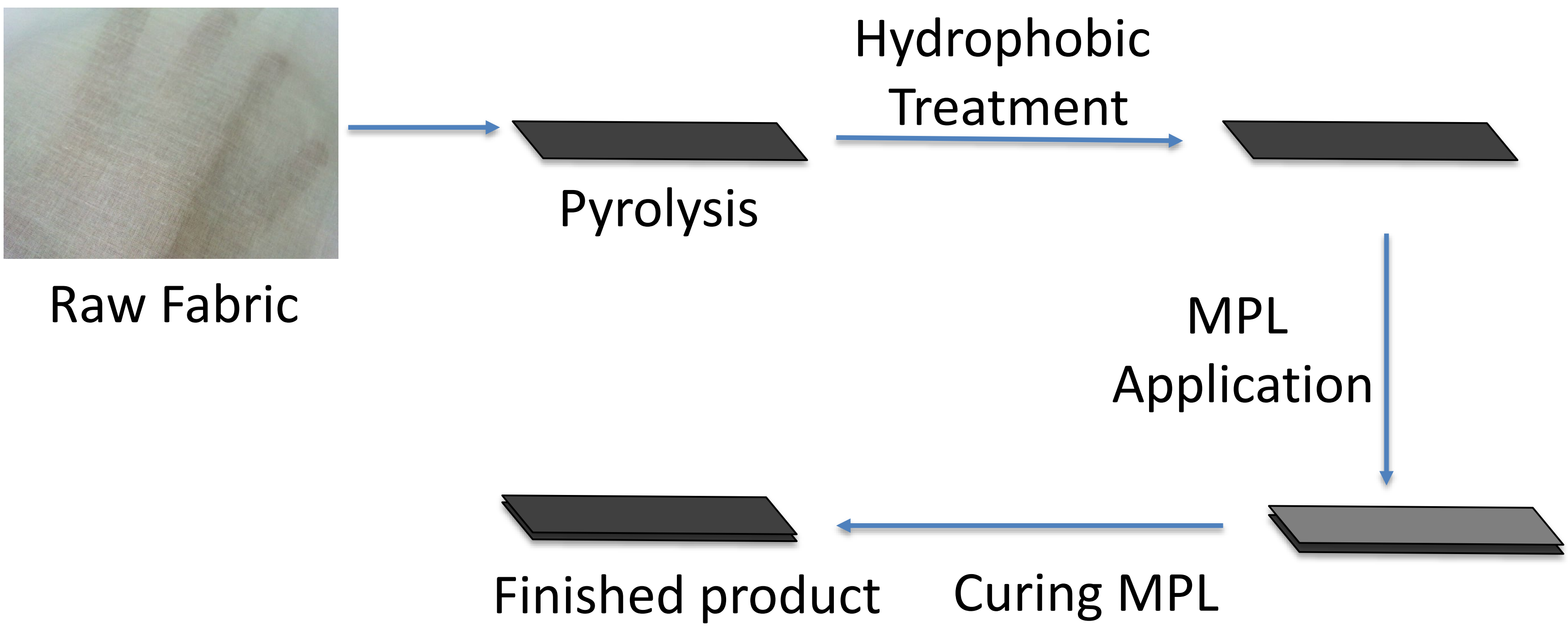
- We estimate 50% reduction in manufacturing cost (removing impregnation step and lower pyrolysis temperature)
- We estimate 25% reduction in materials cost due to low cost fibers

LANL Process for Making Cellulosic Paper GDLs



Industrial papermaking uses similar methodology

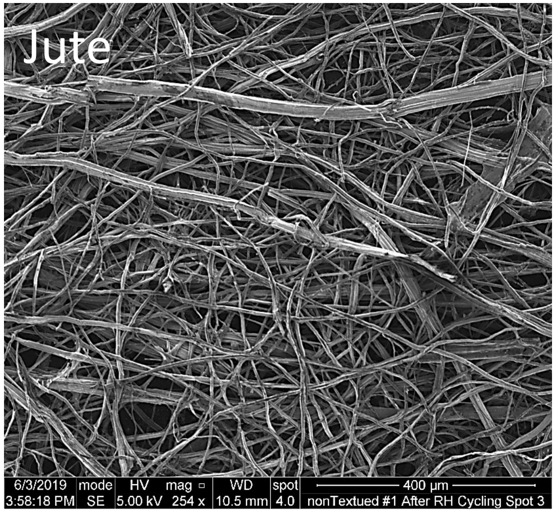
LANL Process for Making Cellulosic Fabric GDLs

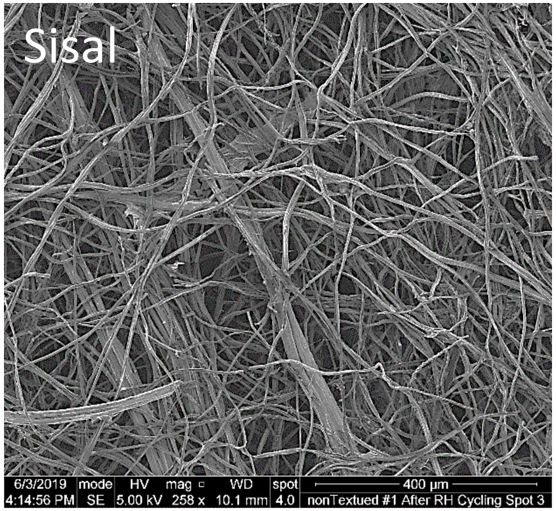


4 processing steps for fabrics vs. 10 processing steps for papers

Fabric GDLs are flexible and less fragile than paper GDLs

Higher Porosity and Surface Area than Commercial GDLs



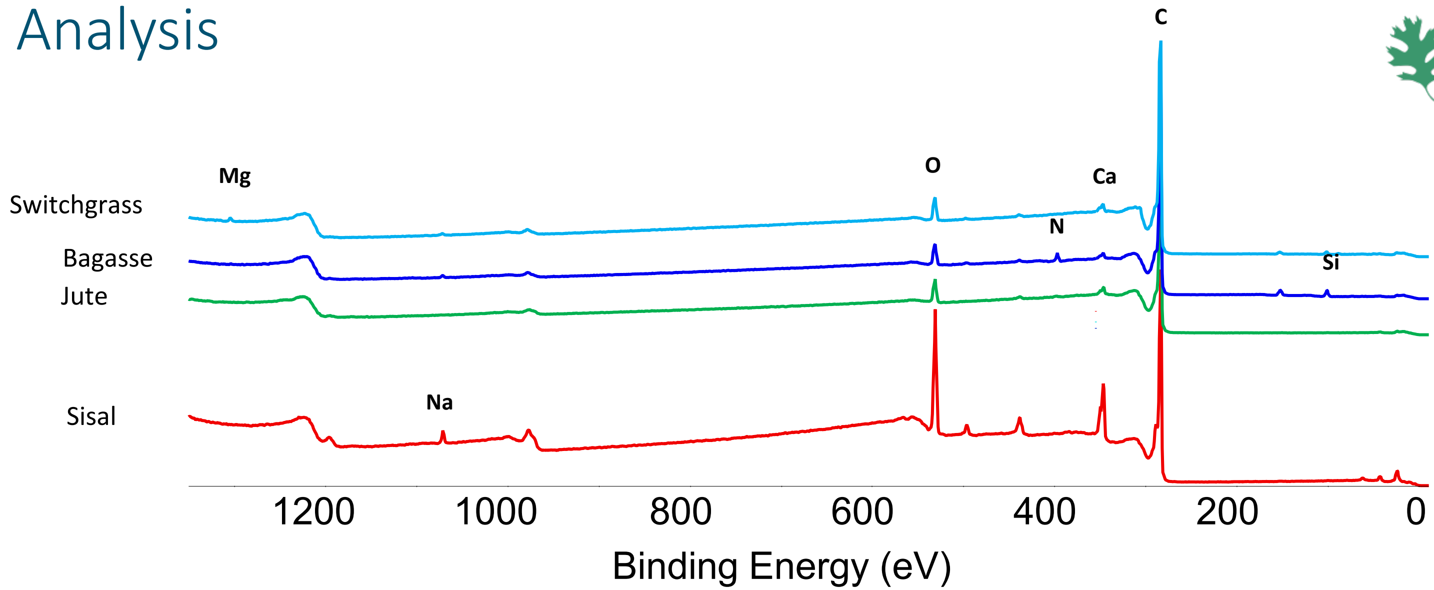


Fiber	% Porosity*	BET Surface Area (m^2/g)
Toray 060	78	0.427
Jute	89.8	6.76
Sisal	88.8	105.8
Bagasse	82.8	84.63
Switchgrass	90.0	106.9

*Porosity estimated from density of amorphous carbon

Elemental Composition after Carbonization

XPS Analysis

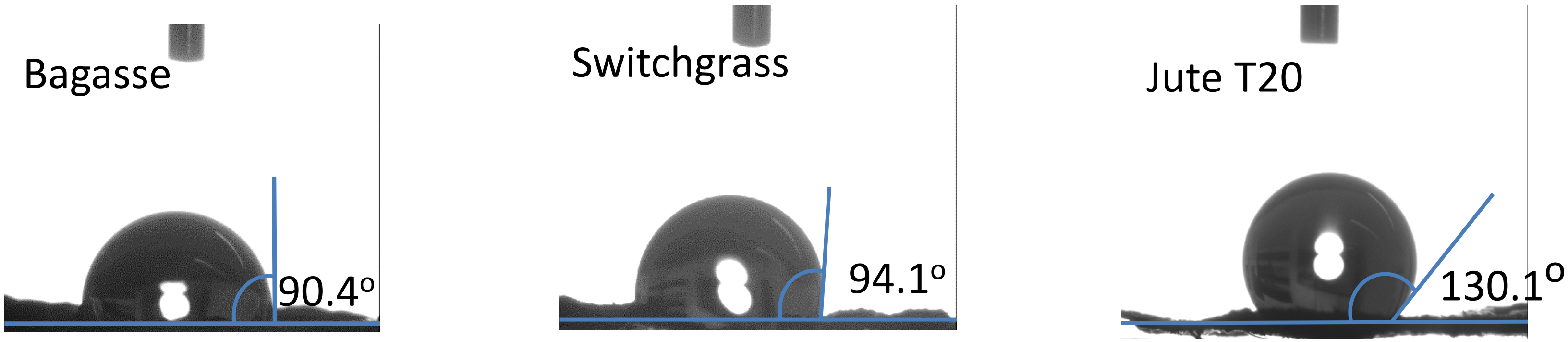


Surface Composition (at.%)	C	O	N	Si	Ca	Na	Mg
Sisal	77.1	17.4	0.0	0.2	4.5	0.8	0.0
Jute	94.0	4.6	0.5	0.1	0.8	0.0	0.0
Bagasse	90.9	3.9	1.9	2.5	0.5	0.2	0.1
Switchgrass	93.3	4.4	0.0	1.0	0.8	0.2	0.3

- Minor presence of contaminants post carbonization
- Sisal might need higher Temp carbonization (to remove oxygen) for good long-term durability

Water Contact Angles with Natural Fibers

Contact Angle



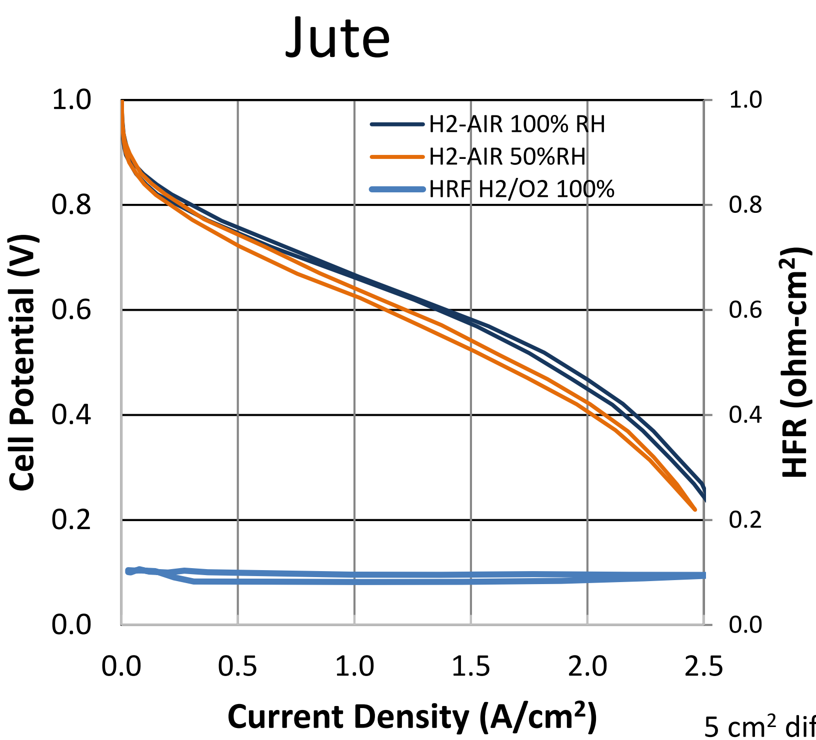
Fiber	Contact Angle
Jute	0^{o}
Sisal	0^{o}
Bagasse	90.4^{o}
Switchgrass	94.1^{o}
Jute T20	130.1^{o}

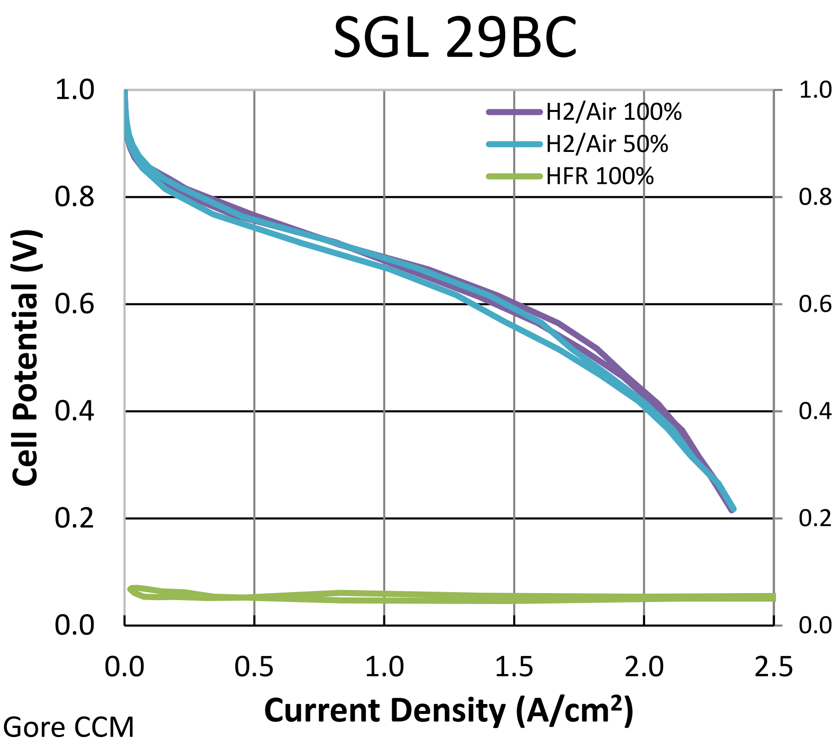
Jute and Sisal papers too hydrophilic for angle measurement

← Teflonated Jute (Jute T20)

Surface Area (Jute) = 6.759 m^2/g
Surface Area (PAN) = 0.42 m^2/g
Surface Area (Sisal) = 105.817 m^2/g

Jute GDL Performance on Fuel Cell Anode

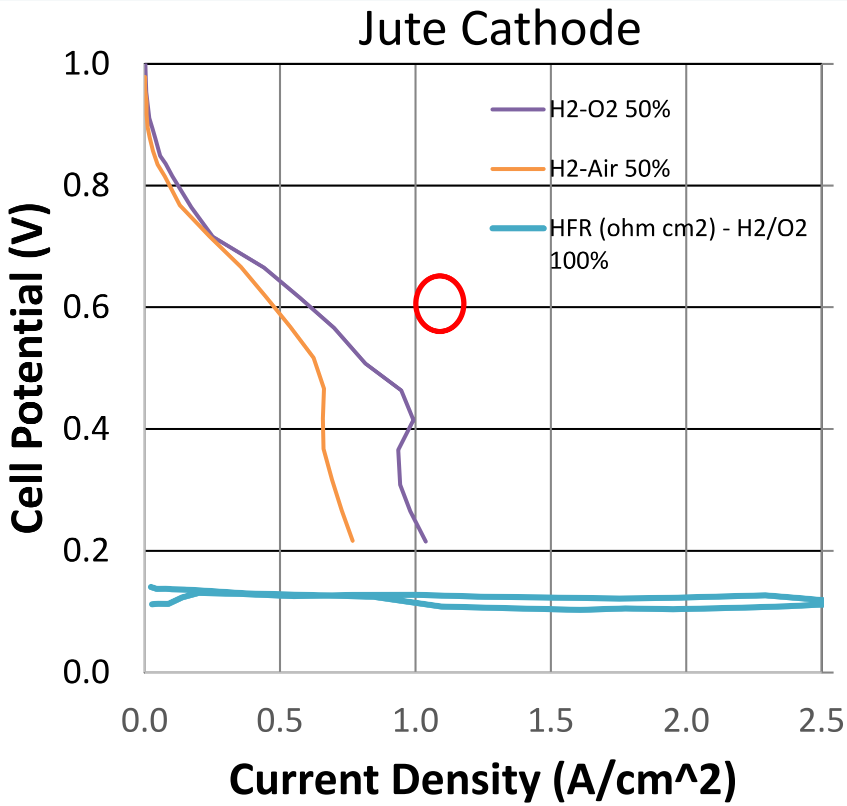


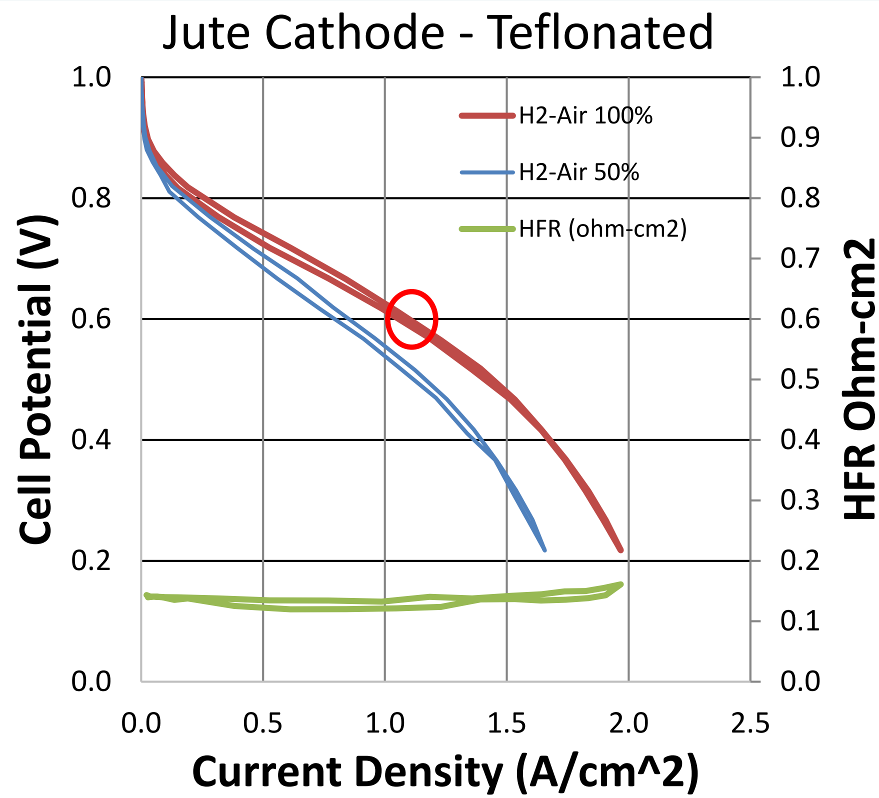


5 cm^2 differential cell, Gore CCM
18 um, 0.1/0.4 mg_{Pt}/cm^2
200/500 sccm, 150 kPa

- Initial performance with cellulosic GDL on anode within 30 mV at 1.5 A/cm^2
  - HFR slightly higher, which correlates to 10 mV.
- Cellulosic GDL shows better performance at > 2.0 A/cm^2
- Performance close to commercial but with lower cost material, no hydrophobic treatment and no optimization to date

Jute GDL Performance on Fuel Cell Cathode



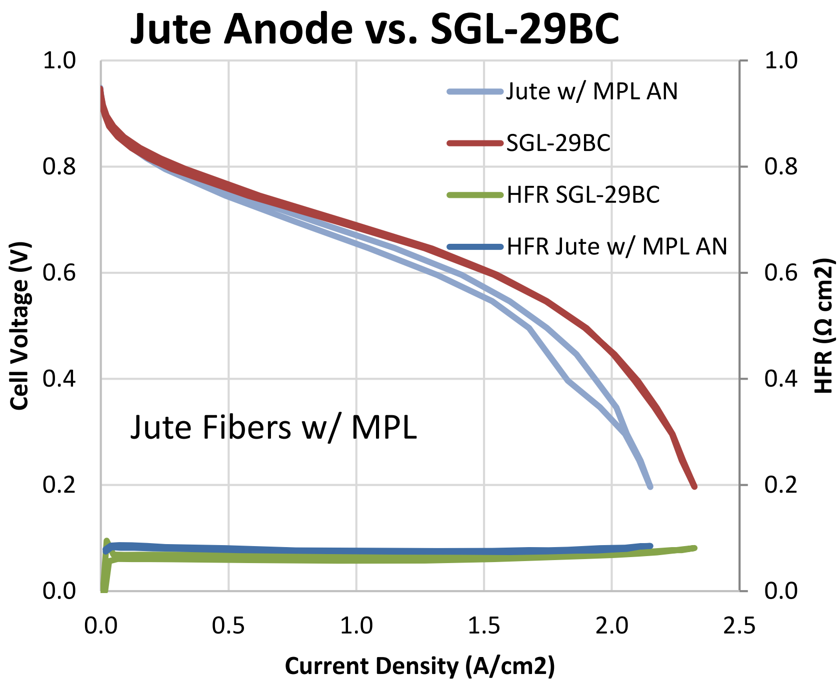


- Hydrophobic treatments of Jute GDL clearly required on cathode
  - Hydrophobicity greatly improves performance
  - Still below performance of commercial materials

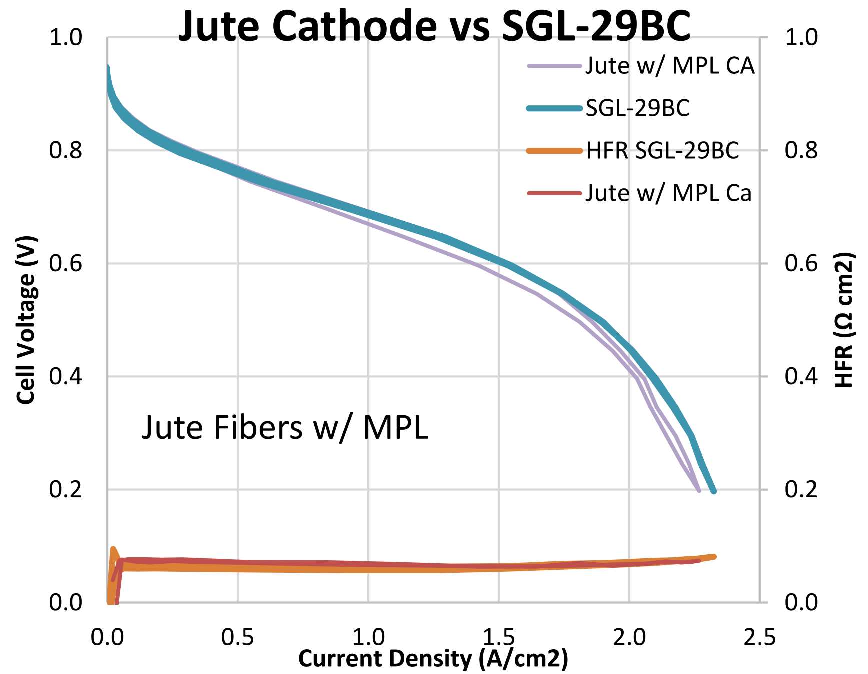
Gore 0.1/0.4 18 micron CCM, 5 cm^2

Jute GDL Fuel Cell Performance Comparison

Jute Anode



Jute Cathode

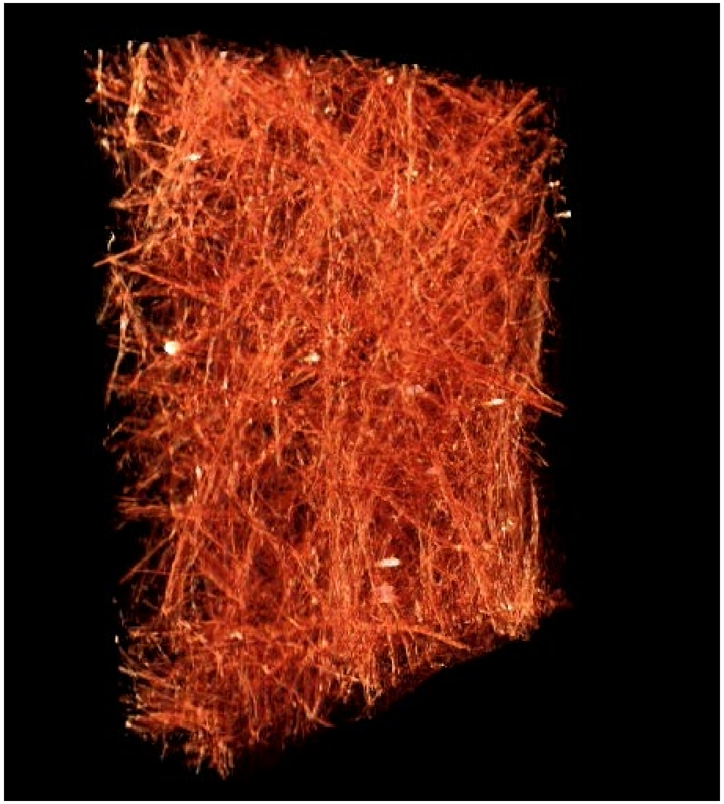


- Jute GDL on anode within 30 mV at 1.5 A/cm^2
  - HFR slightly higher, which correlates to 10 mV.
- Jute GDL on cathode has identical performance at 1.5A/cm2 (forward sweep), but more hysteresis, and losses at higher current densities

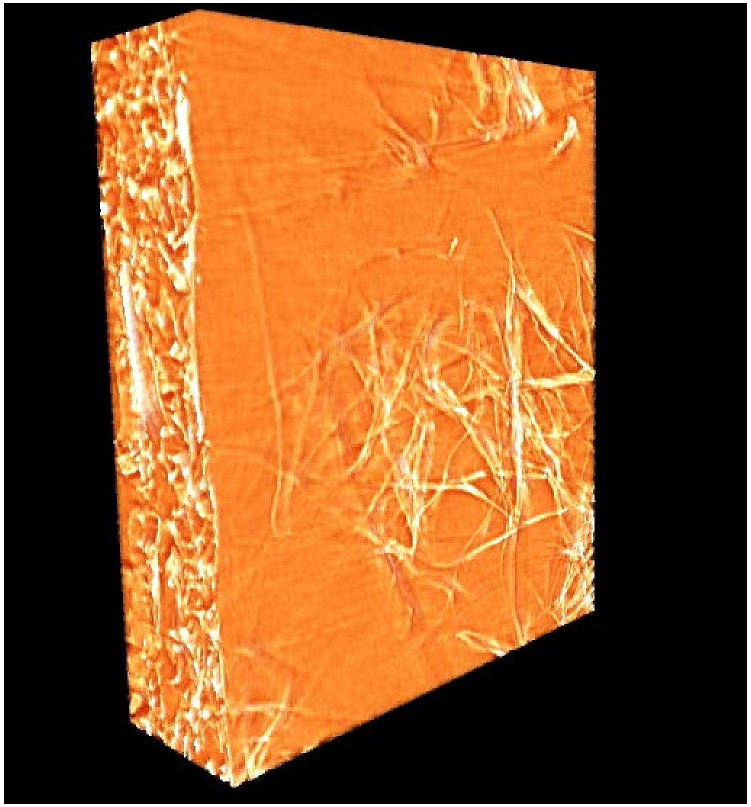
Gore 0.1/0.4 18 micron CCM, 5 cm^2

X-Ray Computed Tomography of Jute GDL

Jute GDL

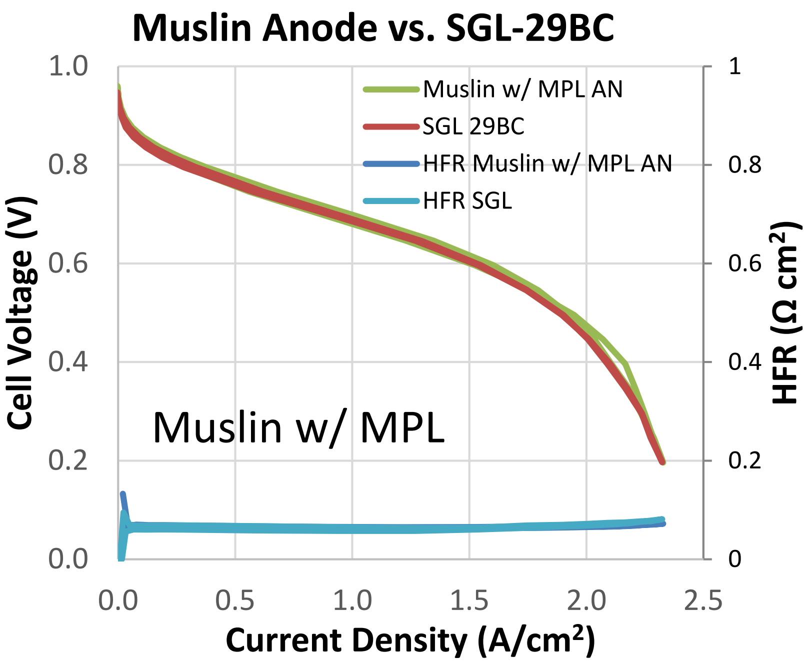


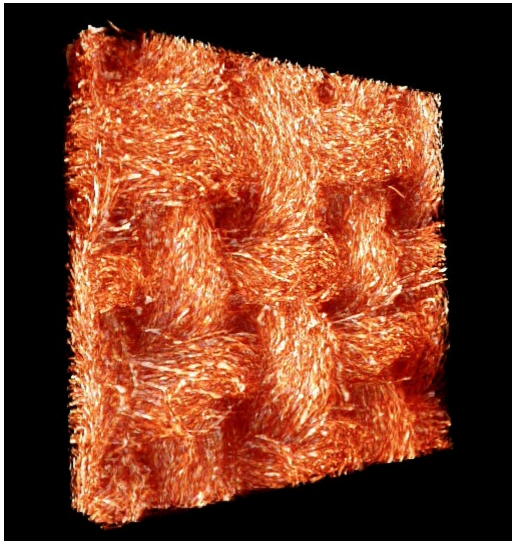
Jute GDL with MPL



- MPL infiltrates the Jute less than the Muslin.
- Jute MPL has more cracks than Muslin MPL; also less smooth
    - Porosity of the fibers: 0.85 +- 0.05
    - Porosity of full GDL with the MPL: 0.65 +- 0.05

Muslin GDL Fabric Performance





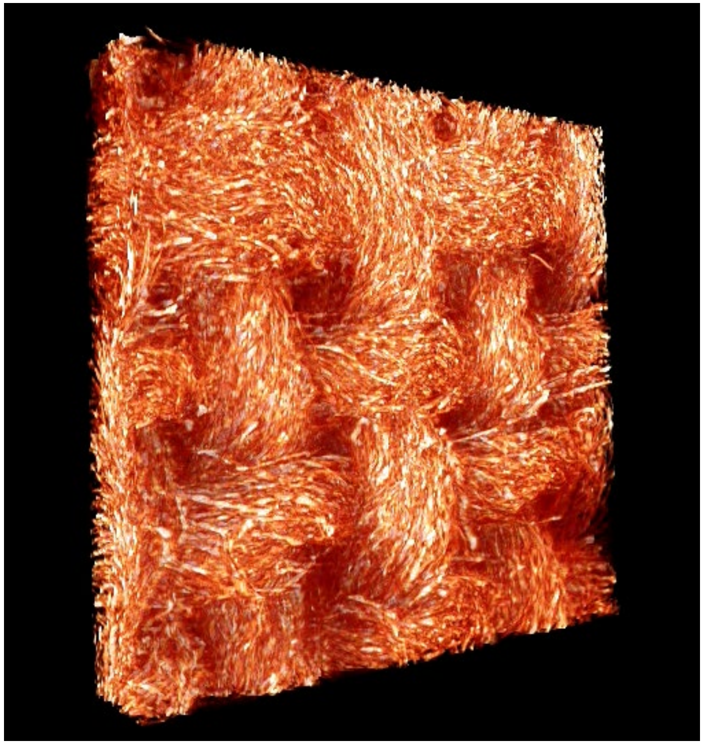
- Muslin anode GDL shows equivalent performance across the polarization range to commercial materials

- Muslin is a cotton fiber woven mat
- Similar material cost savings as other natural fibers: \$3.5-5/kg.
- Requires no additional processing other than pyrolysis

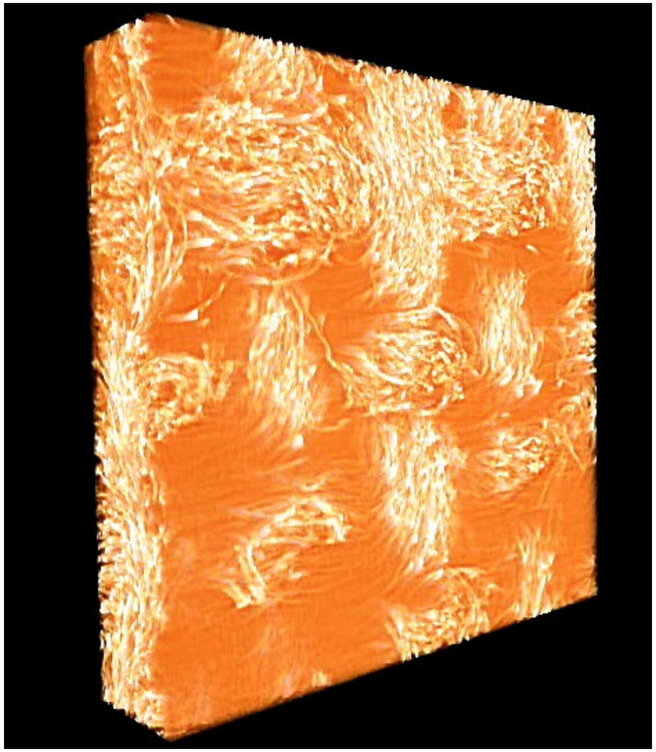
GM Differential Cell
100% RH; 200/500 sccm, 150 kPa
Gore 0.1/0.4 18 micron CCM, 5 cm^2

X-Ray Computed Tomography of Muslin GDL

Muslin GDL



Muslin GDL with MPL



- Little of the MPL (very thin layer) is deposited on top of the threads
- Thicker layers in the portions between the threads.
- MPL thickness changes from 0-10 μm in thin areas, to 40-50 μm in thick areas
- Future work: Compare MPLs applied by spray coater, versus doctor bladed layers on the woven Muslin to see if a uniform, or thick/thin layer is better.

Cellulosic Fibers are Inherently Low Cost

https://en.wikipedia.org/wiki/bagasse

https://en.wikipedia.org/wiki/switchgrass

Fiber Source	Est. Cost $/kg
PAN (carbon paper)	$10.90*
Cotton	$1.57
Muslin (cotton fabric)	~ $3.50 - $5.00
Jute	$0.50 - $1.50
Bagasse (waste cane)	$0.08 – $0.22
Sisal	$1.01-$2.1
Switchgrass	Target: $0.07

https://en.wikipedia.org/wiki/cotton

https://en.wikipedia.org/wiki/jute

https://en.wikipedia.org/wiki/Sisal

- Reducing raw materials can result is large reduction in overall cost
- Additional reduction in processing costs:
    - Impregnation step
    - Binder / bonding / curing
    - Carbonization Temperature
    - Cost of hydrophobic treatment

* Cost estimate based on Strategic Analysis report. PAN cost refers to PAN paper prior to other treatments.

Cost-Reduction Expectations to Manufacturing Cost from Strategic Analysis Report

(Brian James, et al., SA, Dec 2017 report, 2018 report)

Low Volume Estimates			GDL		GDL	
	Annual GDL Production	m2/year	200,000	700,000	2,000,000	10,000,000
Paper Making		$/m2	$3.85	$1.60	$1.66	$0.80
	Material	$/m2	$0.55	$0.55	$0.55	$0.55
	Manufacturing	$/m2	$3.30	$1.05	$1.11	$0.26
Impregnation Coating (Porosity)		$/m2	$1.76	$1.00	$0.90	$0.61
	Material	$/m2	$0.49	$0.49	$0.49	$0.49
	Manufacturing	$/m2	$1.28	$0.51	$0.41	$0.13
Oxidation/Carbonization/Graphitization		$/m2	$5.69	$3.68	$1.15	$1.01
	Material	$/m2	$0.29	$0.29	$0.29	$0.29
	Manufacturing	$/m2	$5.40	$3.39	$0.86	$0.72
Impregnation Coating (Hydrophobicity)			$1.52	$0.75	$0.65	$0.37
	Material	$/m2	$0.25	$0.25	$0.25	$0.25
	Manufacturing	$/m2	$1.27	$0.50	$0.40	$0.12
MPL Coating		$/m2	$1.54	$1.17	$0.76	$0.55
	Material	$/m2	$0.31	$0.31	$0.31	$0.31
	Manufacturing	$/m2	$1.23	$0.86	$0.45	$0.24
Sintering		$/m2	$5.12	$1.69	$0.86	$0.57
	Material	$/m2	$0.00	$0.00	$0.00	$0.00
	Manufacturing	$/m2	$5.12	$1.69	$0.86	$0.57
Real Estate		$/m2	$1.56	$0.50	$0.89	$0.28
Markup		%	25%	25%	23%	23%
	Material	$/m2	$1.88	$1.88	$1.88	$1.88
	Manufacturing	$/m2	$17.60	$8.00	$4.10	$2.02
	Facilities	$/m2	$1.56	$0.50	$0.89	$0.28
	Total Cost Without Markup	$/m2	$21.04	$10.38	$6.87	$4.18
	Total Cost With Markup	$/m2	$26.30	$12.98	$8.58	$5.23

3 zones

- Graphitization cost 35% high volume
- 1200C should require 1 fewer zone

Material costs irrelevant at low volume, but ~ half at high volume

- Projected 50% cost reduction of manufacturing costs based on eliminating impregnation and reducing carbonization temperature (1200C should require 1 fewer heating zone, removed graphitization portion)
- Projected 25% cost reduction of material costs based on raw fiber material costs

Cost Savings by Reducing Graphitization Temperature plus Potential Elimination of Raw Materials & Processes

Lower temperature graphitization

- Conductivity met at graphitization at 1200 ^{o}C
- Traditional GDL processing: Carbonization/graphitization(>2000 ^{o}C)

[ref. Mathias/Fleming publication, SGL Samples]

[Note: personal communication with Peter Wilde, SGL Carbon, ~ 10 years ago indicated SGL using lower graphitization temperature than Freudenberg; leading to lower strength, lower conductivity, but lower cost GDLs.]

- *No information available on cost savings by reducing graphitization temperature*

Binder: No binder (PAA) being used with natural fibers - intertwined

- binder cost of $1.8 - $2/kg (5−15% binder) represents costs of 1 kg material
  - $0.20 savings per kg of GDL (from no binder)
  - Equates to ~ 8% savings by SA Report

High surface area fibers (e.g. stackpole paper) required no MPL

- Equates to ~ 27 – 32% savings by SA Report

2019 Go/No-Go Criteria

QTR	Type	Progress Measures, Milestones, Deliverables	Comments
2019 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.	✓ Completed

FY2020 Milestones

QTR	Type	Progress Measures, Milestones, Deliverables	Comments
Q1	Milestone	***Low-Cost GDL Fiber mats*** Demonstrate complete fabrication of fiber GDL mats (utilizing lower-cost and more easily carbonized fibers), including MPL and hydrophobic treatment. Measure fuel cell operation over a range of conditions.	✓ Completed
Q2	Milestone	***MPL / Hydrophilic fiber Incorporation*** Demonstrate MPL/hydrophilic fiber performance on water removal. Compare MEA performance with hydrophilic fibers incorporated into GDL/MPL with baseline SGL 29BC over range of RHs. Measure Mass Transport resistance by EIS and HeLOx as function of current density.	✓ NREL has demonstrated electrospun PAN fibers • Behind schedule
Q3	Milestone	***Gas-phase hydrophobic treatment*** Compare hydrophobicity of low-cost gas phase treatment to conventional Teflon treatment	✓ Materials acquired • Delayed due to COVID-19
Q4	Milestone	***Demonstrate S.O.A. equivalent GDL Performance*** Demonstrate equivalent or better fuel cell performance using lower-cost GDLs e than baseline GDL (SGL 29BC). Lower cost to be defined by lower cost processing conditions (i.e. lower carbonization temperature), lower cost base materials and/or fewer processing steps.	✓ In progress ✓ Anode performance demonstrated equivalent ✓ Cathode GDL shows small hysteresis; within 20 mV • Delayed due to COVID-19

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.

Recommendations for additions/deletions to project scope:

• The team should explain the reasons (based on technical evidence) for expecting cost reduction with the new hydrophobic treatments. More details should be given about how new, lower-cost component structures should lead to improved properties and/or performance. ……….. also clarify in more detail how durability is being addressed, including whether there is a possibility to maintain or improve water or gas transport properties and their stability, as well as what the risk is regarding the hydrophilicity/phobicity stability of the new materials.

Based on material cost. Most GDLs have 15-20 wt% PTFE. A thin coating is less material.
Materials can/will be durability tested. → noting that current materials do show loss of hydrophobicity.

• It is recommended that the team add a thermal conductivity target, something necessary to mitigate potential high-temperature, high-current-density MEA degradation. The researchers should pursue coating stability testing if they successfully identify a candidate that meets initial life targets.

GDL targets are lacking. I've only seen one OEM inquire about thermal conductivity. My assumption here, is they want high thermal conductivity. FCTT/DOE generally sets targets…..… 2nd comment?

• The team should add a task for cost analysis based on the final performance of the developed GDL. Otherwise, this whole activity is meaningless.

We can, (and have been) make use of existing cost analysis, with multiple discussions with SA (Brian James, Cassidy Hutchins). Using lower cost materials, and processes surely equates to lower cost GDLs. I don't see LANL doing an extensive cost analysis; don't see it as necessary.

• The project could be improved by introducing a systematic framework for understanding, along with complete characterization.

More characterization presented here….. Not sure I get systematic framework; seems like fundamental understanding.

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

Subtask 1.2: Carbonization/graphitization of raw fibers

Subtask 1.3: Characterization of carbonized raw fibers

Subtask 1.4: Fabrication and carbonization/graphitization of fiber mat

Task 2: Hydrophilic highway

Subtask 2.1: MPL Modification: Hydrophilic Treatment

Subtask 2.2: Impregnation of Amorphous Carbon through GDL Structure

Subtask 2.3: Gas Phase Treatments: Hydrophilic

Task 3: Super-hydrophobicity Surface Modification

Subtask 3.1: Gas Phase Treatments: Hydrophobic

Subtask 3.2: Biomimetic Surface Treatment

Subtask 3.3: Characterization of surface treatments

Task 4: GDL Fabrication, in situ Measurements

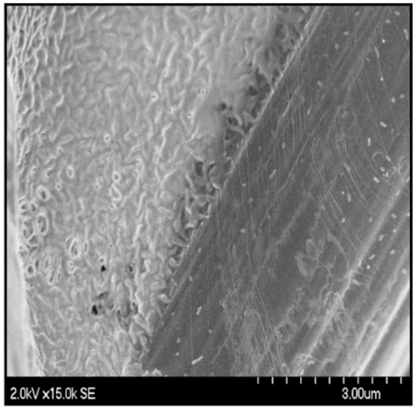
Subtask4.1: Fabrication of Modified GDLs

Subtask 4.2: MEA testing of GDLs

Subtask 4.3: Durability of low cost GDLs

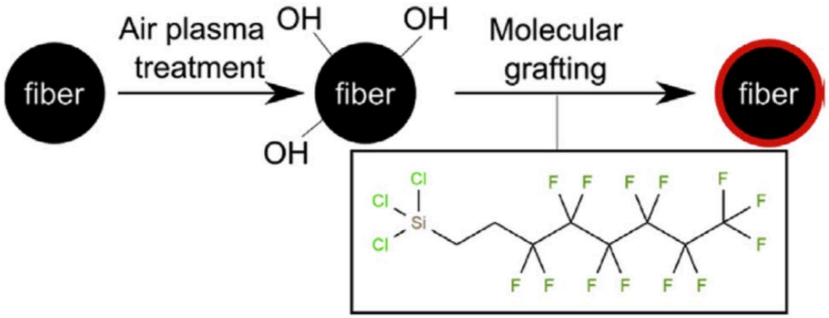
Subtask 4.4: Neutron imaging of water profiles in GDLs

Gas Phase Treatments for Hydrophobicity



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 Teflon agglomerates in localized areas



S. Chevalier et al., J. Power Sources, 352, **2017**, 272-280.

- Silane covalently bonds to surface oxygen groups
- Perfluorinated group provides hydrophobicity
- Coating thickness should be on molecular scale

Publications and Presentations

- Daniel P. Leonard, Rod Borup, R. Mukundan, K.C. Neyerlin, Sadia Kabir, David Cullen, Low Cost Gas Diffusion Layer Materials and Treatments for Durable High Performance PEM Fuel Cells, 236th ECS Atlanta, GA, October 16, 2019
- Daniel P. Leonard, Siddharth Komini-Babu, Rod Borup, LANL Patent Disclosure "Cellulosic Gas Diffusion Layers"
- Daniel P. Leonard, Siddharth Komini-Babu, R. Mukundan, David Cullen and Rod Borup, Low Cost Gas Diffusion Layer Materials and Treatments for Durable High Performance PEM Fuel Cells, in preparation

Summary of Technical Accomplishments

<u>Muslin Anode GDL</u>

- Equivalent performance across the polarization range compared to commercial materials
- Muslin GDL made from lower cost material, no binder, lower temperature pyrolysis

<u>Jute Anode GDL</u>

- Jute GDL on anode within 30 mV at 1.5 A/cm^2

<u>Jute Cathode GDL</u>

- Equivalent performance at 1.5A/cm^2 (forward sweep)
- Additional hysteresis/losses at higher current densities

<u>Cost Reduction</u>

- 50% material cost reduction in terms of low-cost fibers meeting conductivity targets at lower-graphitization temperature
  - Conductivity met with low temperature pyrolysis @ 1200^{o}C (0.01 Ohm.cm2 ASR)
- Lower cost manufacturing processes used.
  - Difficult to quantitate temperature reduction impact on cost; reduction of 1 temperature zone
  - Process minimization cost reductions are greater 30%

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