Microstructured Electrodes and Diffusion Layers for Enhanced Transport in Reversible Fuel Cells

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Project ID FC181

Overview

Timeline:

- Project Start Date: January 1, 2018
- Project End Date: December 31, 2019

Barriers

A. Durability

B. Cost

C. Performance

Budget:

- Total Project Budget: $400K
- Total DOE Funds Spent: $110K (03/01/2019)

Partners

- LANL (Jacob S. Spendelow, Siddharth Komini Babu, Zachary R. Brounstein, Aman Uddin)

Relevance

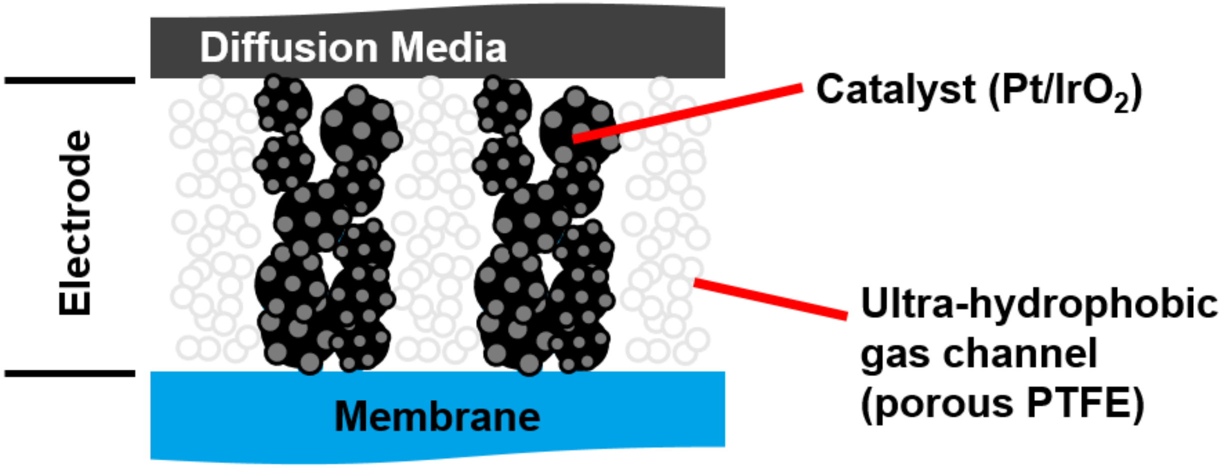
Objectives

- **Enhance transport performance of unitized reversible fuel cells (URFCs) using arrays of interspersed hydrophobic and hydrophilic channels in electrodes, MPLs, and GDL substrates**
- **Fabricate, test, and validate URFCs with high performance and durability**

- URFCs could address energy storage challenges of intermittent renewable power sources and **could be instrumental in realizing the vision of H2@Scale**
- Achieving high performance in both fuel cell and electrolyzer mode is a critical challenge due to conflicting water management requirements:
  - Electrolyzers perform best with high liquid water saturation (rapid transport of H_2O reactant to catalyst)
  - Fuel cells perform best with low liquid water saturation (rapid transport of O_2 reactant to catalyst)
- **Amphiphilic electrode structures and diffusion media are the key to overcome this H_2O and O_2 transport challenge**

Approach: Amphiphilic Catalyst Layers

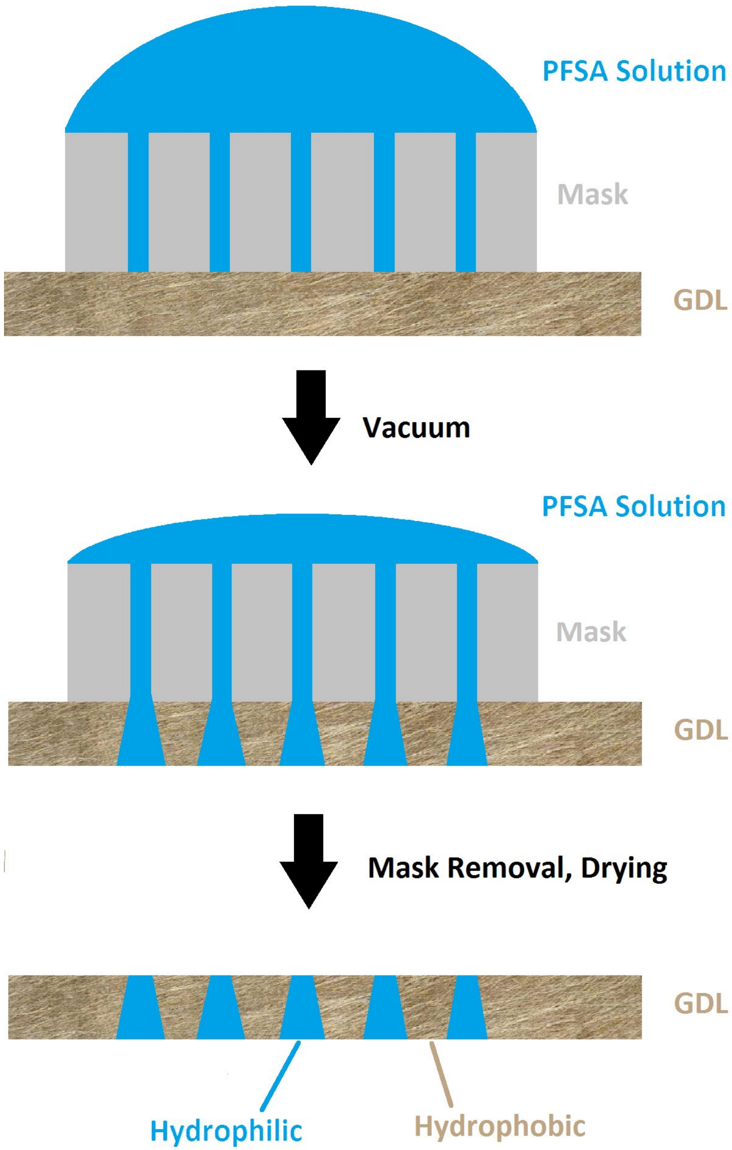
Interspersed arrays of hydrophobic and hydrophilic through-plane channels provide enhanced O_2 and H_2O transport, enabling high performance in both fuel cell and electrolyzer mode



- Catalyst layer is composed of interspersed arrays of catalyst domains and gas transport domains
- Hydrophilic catalyst domains are flooded during normal operation, while hydrophobic gas transport domains serve as channels for O_2 transport
- Since the hydration state of amphiphilic catalyst layer is similar in fuel cell and electrolyzer modes, rapid switching between fuel cell mode and electrolyzer mode without gas purging is possible

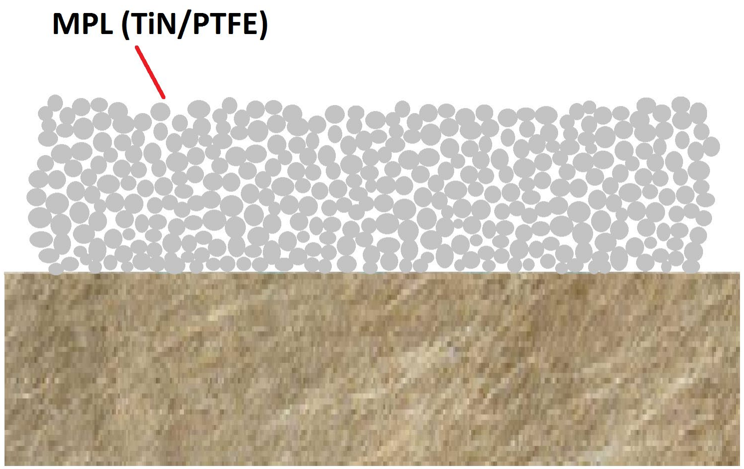
Approach: Patterned GDL Substrates

GDL substrates (Ti fiber, Nb-doped Ti fiber, or Ti sinter) can be locally patterned with hydrophilic (PFSA) and hydrophobic (PTFE) agents to create channels for rapid transport of H_2O and O_2

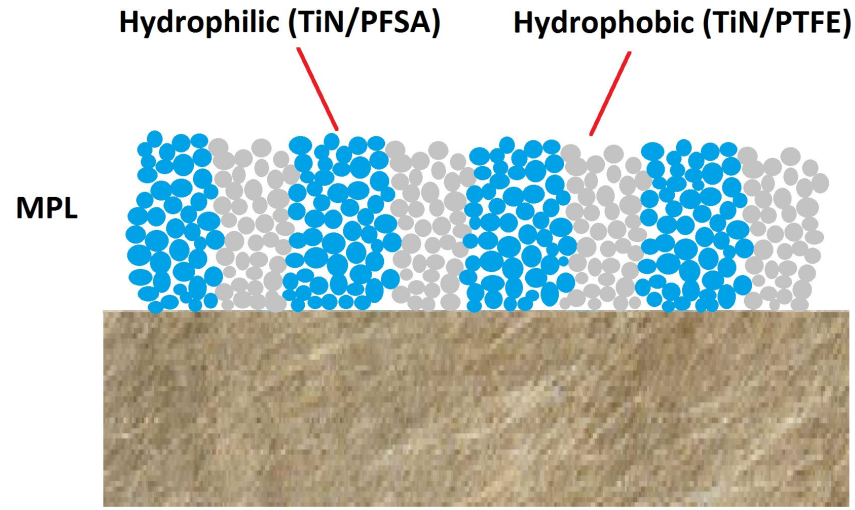


Approach: Microporous Layers

Gen 1 MPL (Hydrophobic)



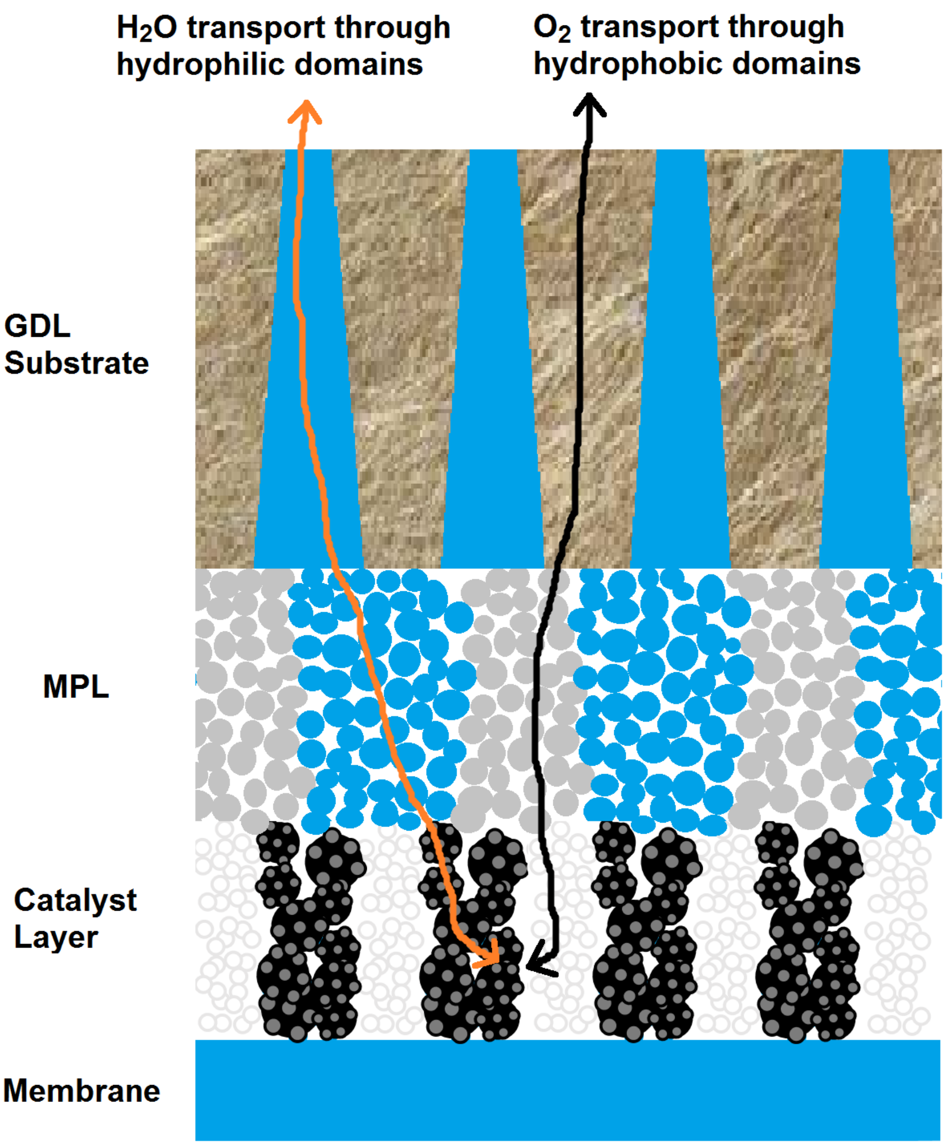
Gen 2 MPL (Amphiphilic)



- Microporous layers (MPLs) are a critically important component of diffusion media in conventional fuel cells, but most URFC designs lack an MPL
- MPLs help with water management, keeping GDL substrate from flooding while catalyst layer stays well-hydrated
- MPLs will be fabricated using stable and conductive metal or ceramic powders (Ti, TiN, Nb-doped Ti) with PTFE binder (Gen 1)
- Patterned hydrophilic/hydrophobic MPLs will further enhance water management for effective transport in both fuel cell and electrolyzer modes (Gen 2)

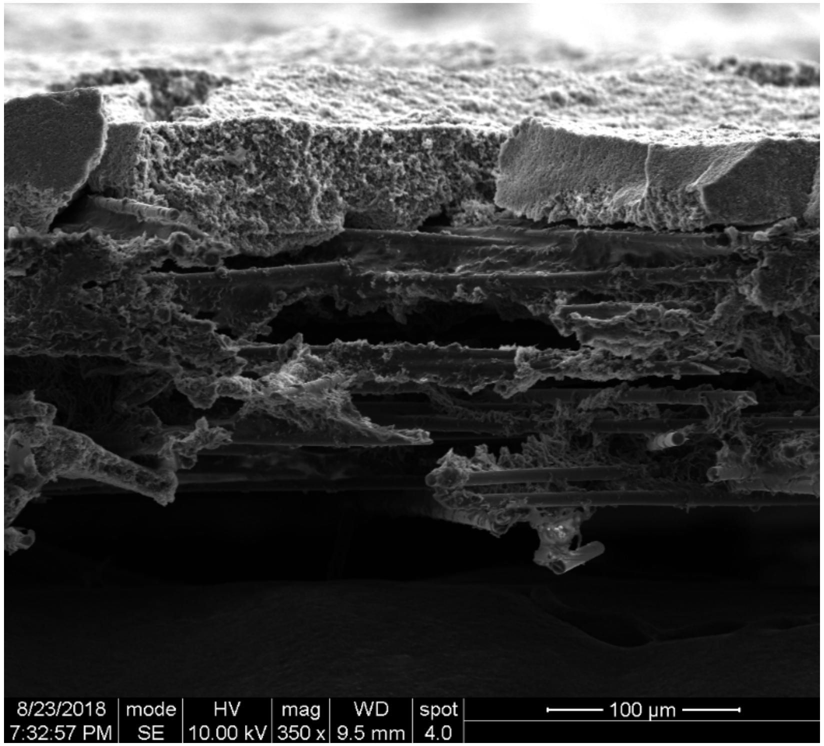
Approach: Patterned MEA

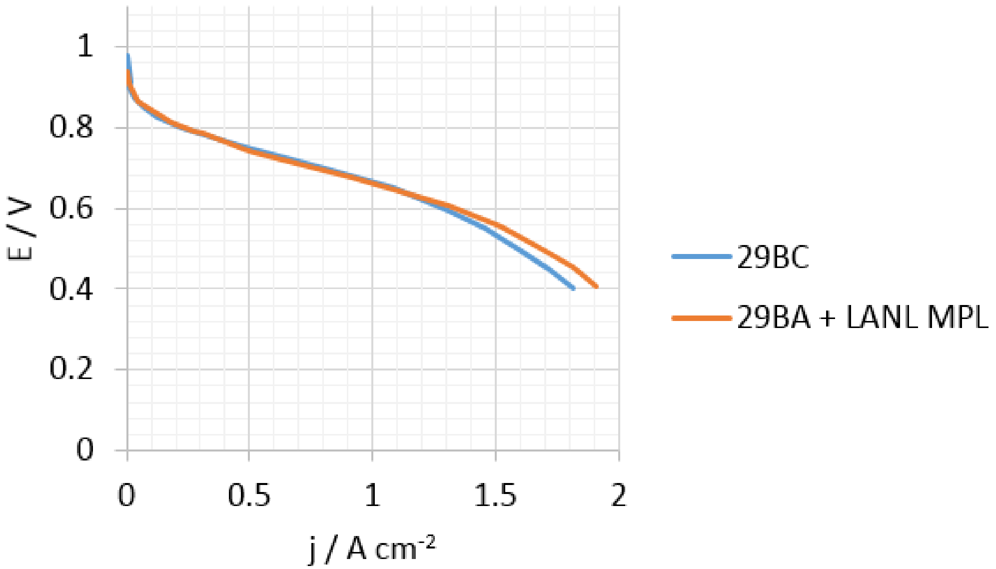
- Patterned hydrophilic/ hydrophobic GDL substrates, MPLs, and catalyst layers will be combined to produce a patterned MEA with enhanced H_2O and O_2 transport characteristics
- This amphiphilic MEA is expected to enable:
  - Improved performance in fuel cell and electrolyzer modes
  - Rapid switching between modes



Accomplishment: PEMFC MPLs

- First step in designing an MPL: can we reproduce existing PEMFC MPLs?
- Standard SGL GDL is 29BC
    - Carbon paper/PTFE substrate (29BA)
    - SGL MPL (acetylene black + PTFE)
- **LANL MPL deposited on 29BA gives similar or better performance**

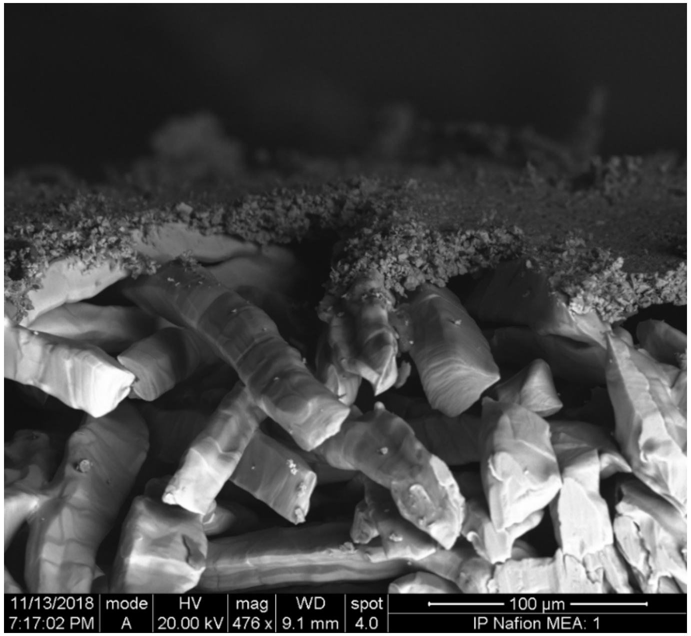


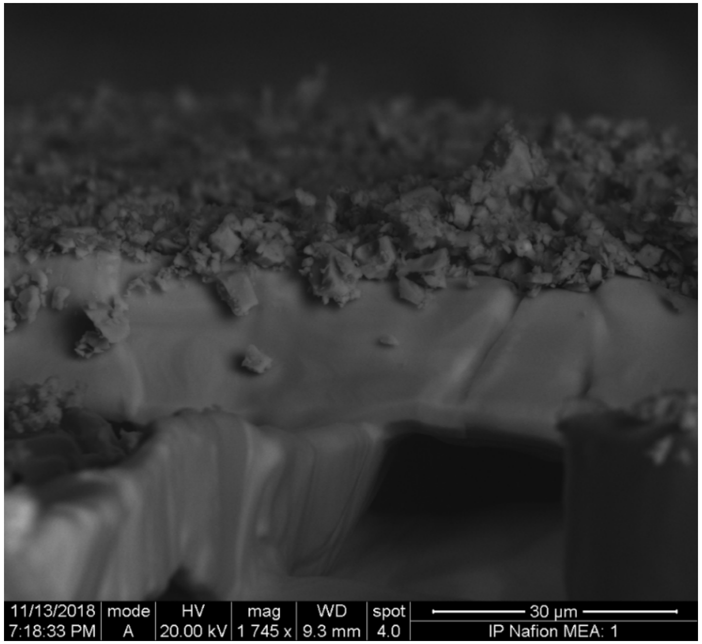


80°C, H_2/air, 100%RH, 150 kPa_{abs}
0.1 mg/cm² Pt, N211

Accomplishment: Ti Felt GDL with TiN MPL

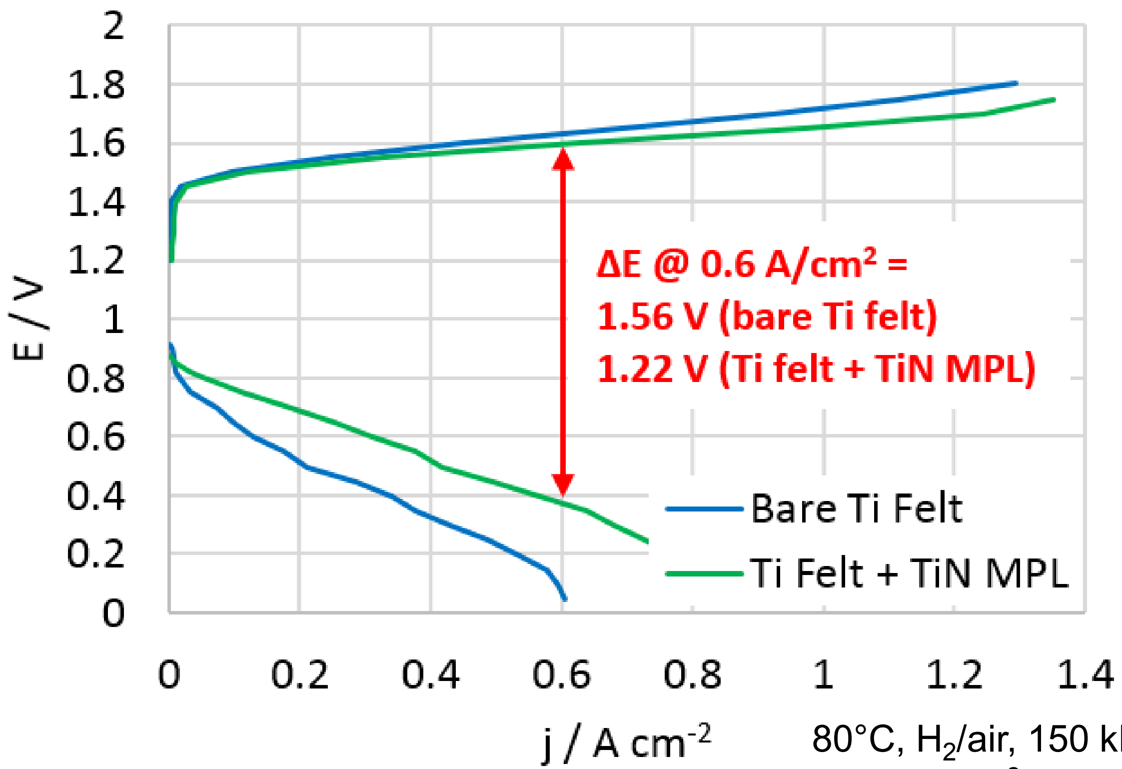
- LANL URFC MPL being developed to provide improved water management
- MPL based on TiN powder dispersed with PTFE, deposited from ink and sintered
- Two deposition methods demonstrated:
  - Direct blade coating onto Ti felt (high penetration into felt)
  - Decal transfer to Ti felt surface (low penetration into felt)





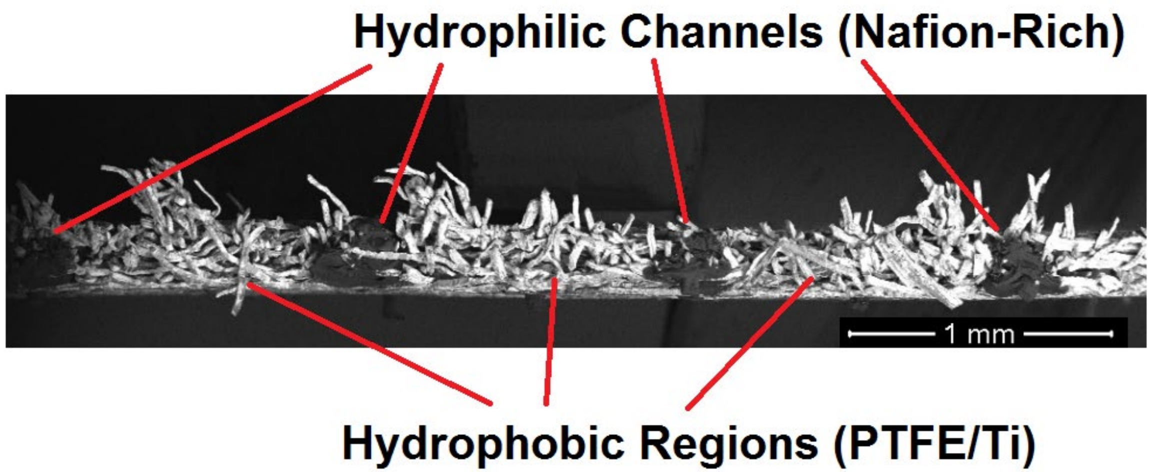
Accomplishment: URFC MEA Testing

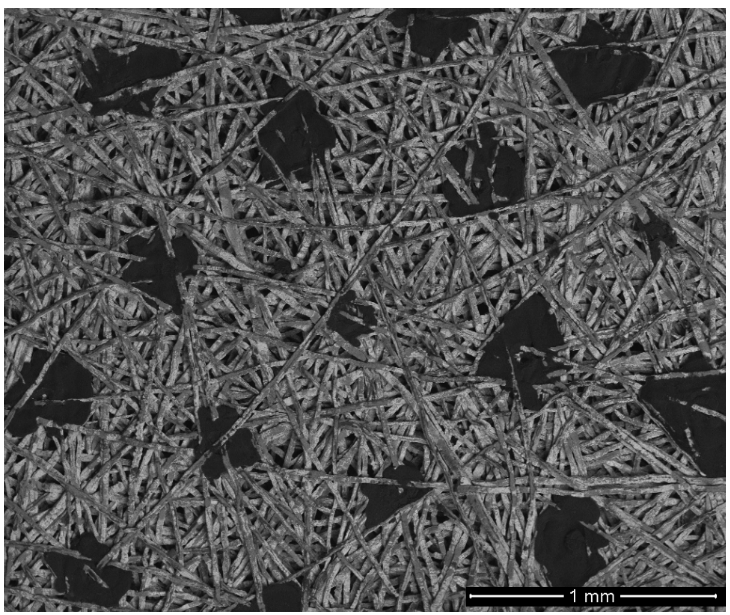
- Project Go/No-Go: 1.4 V difference between fuel cell and electrolyzer voltage at 0.6 A/cm^2
- 12/18/18 Status: 1.56 V (baseline Ti felt), 1.22 V (Ti felt + LANL MPL)
- Go/No-Go criteria met ☑



80°C, H_2/air, 150 kPa$_{abs}$
0.15 mg/cm^2 Pt, 0.15 mg/cm^2 Ir black, N212

Accomplishment: Patterned Ti Felt GDLs

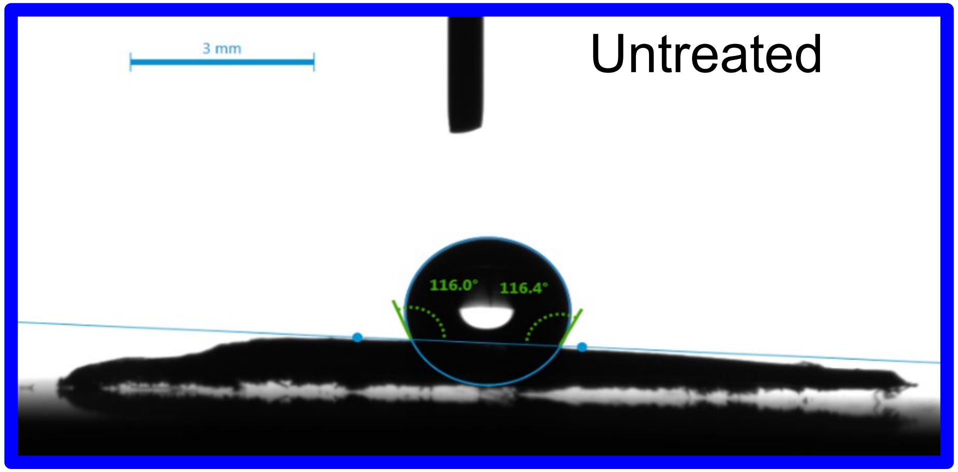


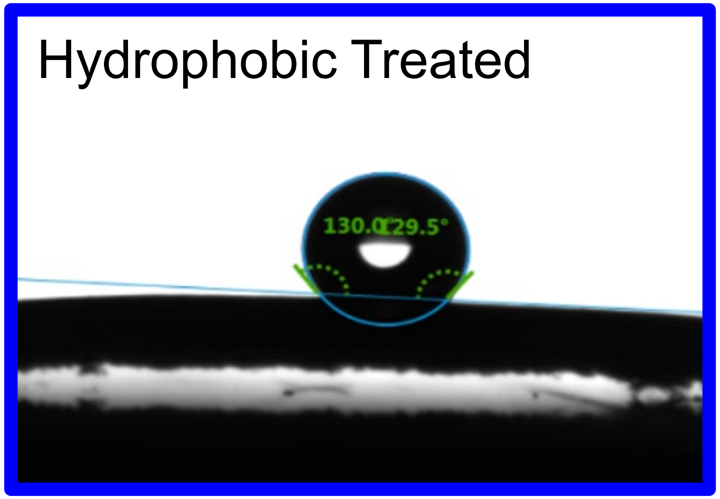


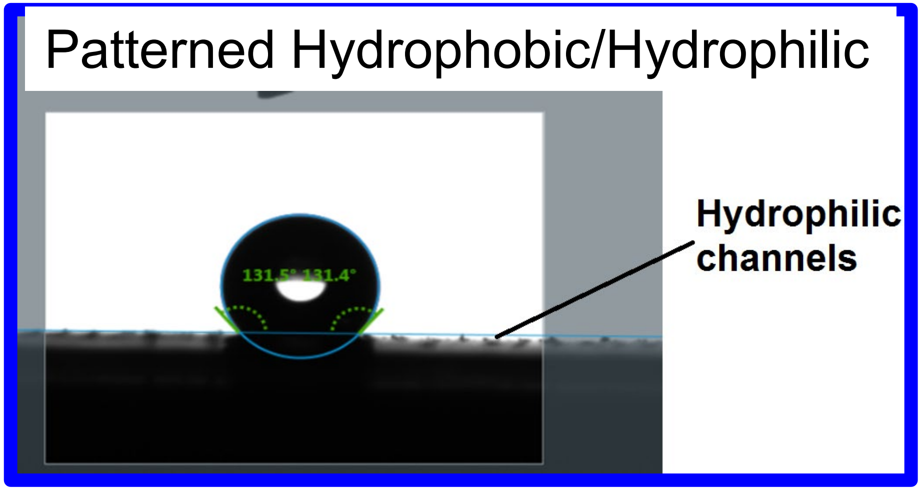
- Hydrophobic treatment (7 wt.% PTFE) of Ti felt GDL to prevent global flooding
- Local impregnation with Nafion to create hydrophilic channels through GDL, enabling effective water transport in fuel cell and electrolyzer mode

First demonstration of hydrophobic/ hydrophilic GDL patterning via PTFE/Nafion segregation

Effect of Hydrophilic Channels on Wetting

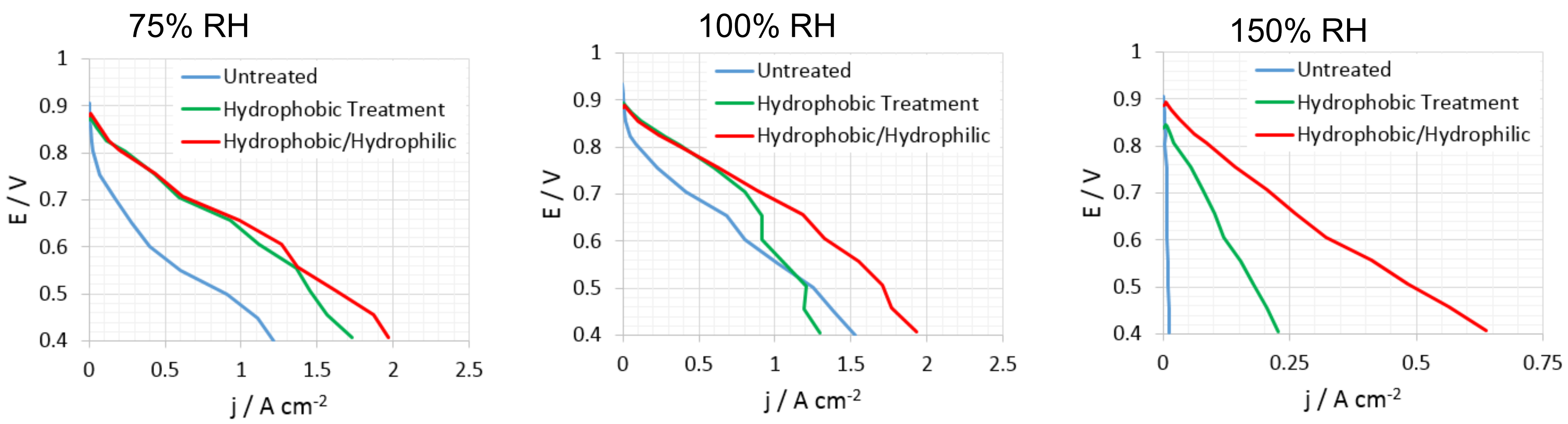






Hydrophobic/hydrophilic patterning maintains high bulk hydrophobicity of GDL, while still providing local water transport pathways

Accomplishment: Improved URFC Performance

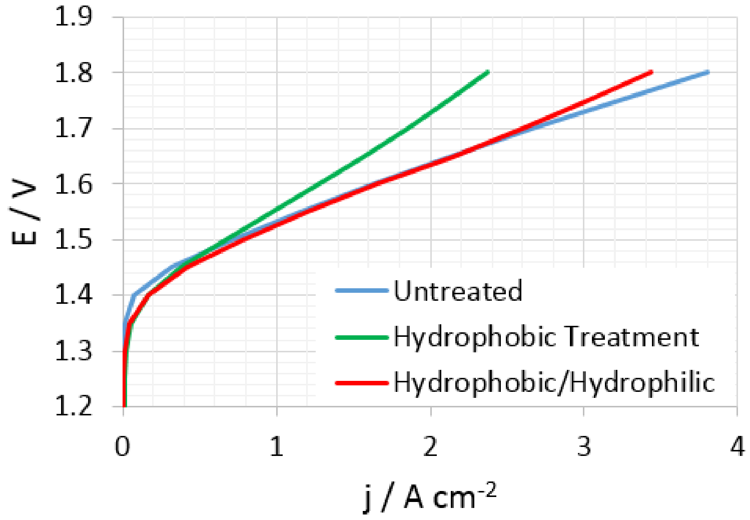


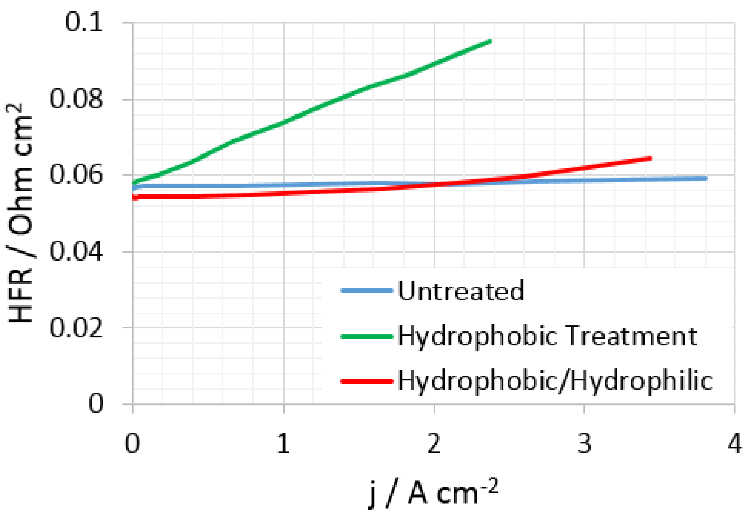
- Hydrophobic treatment (7 wt.% PTFE) of Ti felt GDL enables improved fuel cell performance
- Further performance improvement demonstrated using combination of PTFE treatment with local Nafion treatment to produce patterned hydrophobic/hydrophilic Ti felt GDL

Hydrophobic/hydrophilic patterning provides major enhancement in performance, especially under highly flooded conditions

80°C, H_2/air, 250 kPa_{abs}
1 mg/cm^2 Pt, 1 mg/cm^2 Ir black, N212

Accomplishment: Improved URFC Performance





- Hydrophobic GDL treatment is needed for good fuel cell performance, but it hurts electrolysis performance by impeding water transport
- Water starvation causes mass transport loss and Ohmic loss due to membrane dry-out
- Hydrophobic/hydrophilic patterned Ti felt provides channels for water transport, preventing water starvation

Hydrophobic/hydrophilic patterning enables enhanced URFC performance under a wide range of hydration conditions

Collaborations & Coordination

We are collaborating with multiple projects and organizations, including:

- Electrolysis Rocket Ignition System (LANL LDRD project)
- FC-PAD consortium (complementary efforts in electrode microstructure development for fuel cells)

Milestones

3/18	Perform modeling to determine optimal hydrophobic channel size and spacing for GDLs and electrodes
6/18	Prepare GDL templates and use them to demonstrate fabrication of local hydrophobic GDL microstructures
9/18	Prepare 4 different electrode templates and use them to demonstrate fabrication of local hydrophobic electrode microstructures with characteristic lengths of < 1 micron
12/18	Go/No-Go: Incorporate microstructured GDLs and electrodes into functional URFCs and demonstrate E-FC voltage difference at 0.6 A/cm^2 of < 1.4 V
3/19	Use characterization tools to determine effect of local microstructure on water management
6/19	Use diagnostics to determine effect of local microstructures on gas transport
9/19	Tailor URFC structures based on characterization and diagnostic results to achieve an E-FC voltage difference at 0.6 A/cm^2 respectively of < 1.1 V
12/19	Tailor URFC structures to limit the transport-related degradation to less than 50 mV after 1,000 E-FC mode cycles

Remaining Challenges and Barriers

- Improvement of fabrication techniques by:
  - Increasing control and quality of deposited structures
  - Improving positioning and alignment of transport channels
- Improvement of techniques for controlled and reproducible integration of multiple layers of controlled transport structures into an MEA
- Adaptation of fabrication techniques to low-cost and scalable processes compatible with high volume manufacturing

Proposed Future Work

FY19:

- Improve fabrication methods to enable higher aspect ratios and smaller feature sizes in patterned diffusion media
- Combine hydrophobic/hydrophilic patterned Ti felt GDL (demonstrated already) with patterned MPL and electrode (under development) to further enhance water transport while reducing flooding
- Continue using performance diagnostics (impedance, limiting current methods, helox measurements) to characterize transport resistances
- Use characterization techniques including *in operando* X-ray computed tomography and neutron radiography to quantify effects of patterned structures on water transport (neutron radiography scheduled for August 2019)

FY20:

- Perform durability studies and characterize and mitigate degradation modes

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

Technology Transfer Activities

- We are developing IP related to patterned hydrophoibic/hydrophilic structures for URFC applications
- If successful, we will pursue licensing of technology to URFC developers
- We will pursue tech transfer opportunities leveraging resources of LANL Feynman Center for Innovation

Summary

Objective: Enhance transport performance of unitized reversible fuel cells (URFCs) using arrays of interspersed hydrophobic and hydrophilic channels in electrodes, MPLs, and GDL substrates.

Relevance: URFCs could address energy storage challenges of intermittent renewable power sources and could be instrumental in realizing the vision of H2@Scale, but achieving high performance in both fuel cell and electrolyzer mode is a critical challenge due to conflicting water management requirements. Amphiphilic electrode structures and diffusion media are the key to overcome this H_2O and O_2 transport challenge.

Approach: Interspersed arrays of hydrophobic and hydrophilic through-plane channels provide enhanced O_2 and H_2O transport, enabling high performance in both fuel cell and electrolyzer mode. Hydrophilic domains are flooded during normal operation, while hydrophobic domains serve as channels for O_2 transport.

Accomplishments: We have demonstrated TiN-based MPLs and patterned hydrophilic/hydrophobic diffusion media based on Ti felts. We have met our year 1 go/no-go (< 1.4 V difference between fuel cell and electrolysis voltages at 0.6 A/cm^2) using novel materials developed in this project.

Collaborations: Coordination with Electrolysis Rocket Ignition System LDRD project and FC-PAD, as well as InRedox and Smart Membranes (microstructure fabrication)

Reviewer-Only Slides

Critical Assumptions and Issues

1. Assumption: patterned electrodes and diffusion media can be fabricated successfully. This risk has been mitigated by the identification of multiple fabrication routes to produce the desired pattering:
    a. Templating: transport channels can be fabricated by materials impregnation in porous templates such as anodized aluminum oxide and macroporous Si, followed by template removal
    b. Stamping: void spaces in electrodes and MPLs can be created by imprinting with a stamp, with subsequent materials deposition in the void space
    c. Masking: hydrophobic or hydrophilic components can be deposited selectively in predetermined locations through use of a reusable mask
2. Assumption: prototype patterned electrodes and diffusion media can be scaled up for manufacturing
    a. We will conduct scalability analysis and develop low-cost and scalable methods such as stamping and self-assembly
3. Assumption: patterned structures will be durable
    a. During the next year we will test durability and develop methods to mitigate any observed degradation modes

Publications and Presentations

- Jacob Spendelow, Siddharth Komini Babu, Zachary Brounstein, Rangachary Mukundan, Rod Borup, "Transport Structures in Fuel Cell Electrodes and Diffusion Media," poster at the 2018 Fuel Cell GRC.
- Jacob S. Spendelow, Siddharth Komini Babu, Zachary Brounstein, Rangachary Mukundan, Rod Borup, Dave Cullen, Karren More, "Fuel Cell Electrodes based on Functional Meso-Structured Arrays," presentation at the 234th ECS meeting.