

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

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Project ID FC181

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Overview

Timeline:

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

Budget:

- Total Project Budget:
\$400K
- Total DOE Funds Spent:
\$335K (05/30/2020)

Barriers

- A. Durability
- B. Cost
- C. Performance

Partners

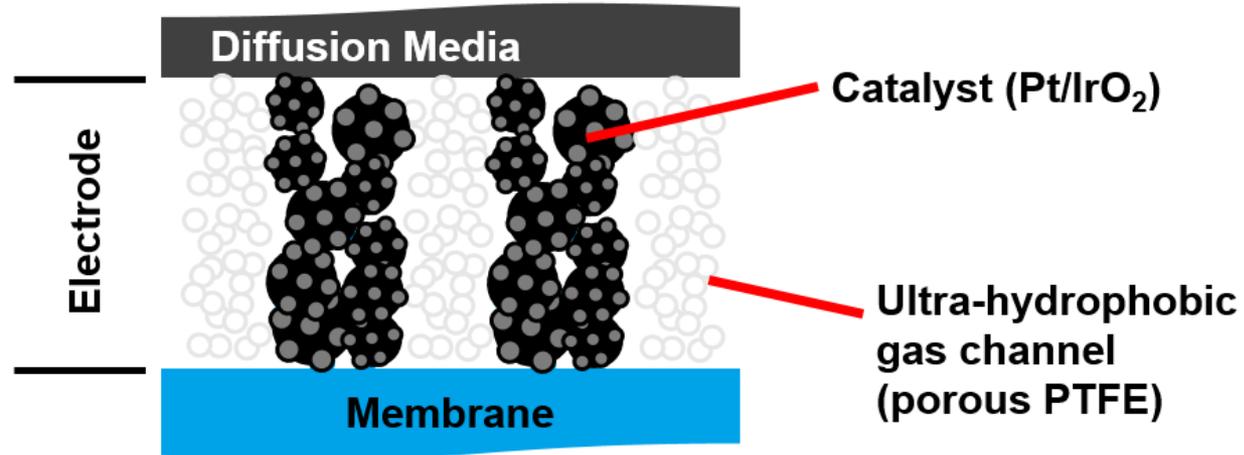
- LANL (Jacob S. Spendelow, Siddharth Komini Babu, Zachary R. Brounstein, Aman Uddin)

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 H₂O reactant to catalyst)
 - Fuel cells perform best with low liquid water saturation (rapid transport of O₂ reactant to catalyst)
- **Amphiphilic electrode structures and diffusion media are the key to overcome this H₂O and O₂ transport challenge**

Approach: Amphiphilic Catalyst Layers

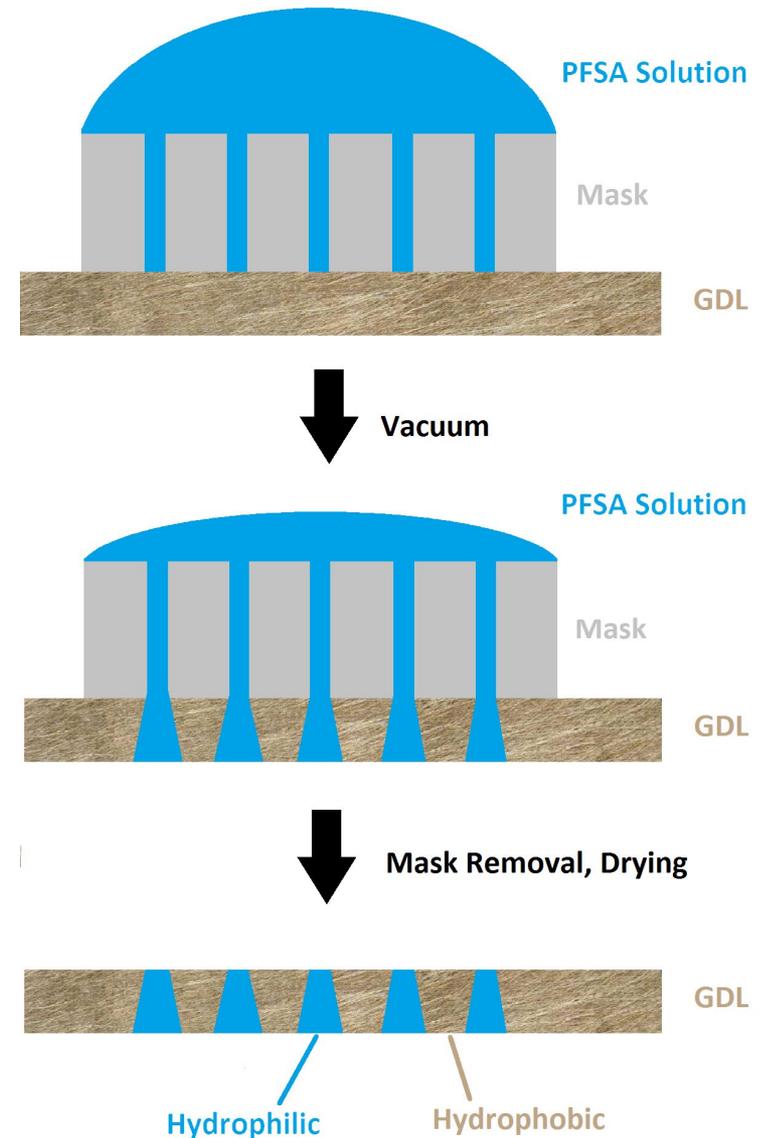
Interspersed arrays of hydrophobic and hydrophilic through-plane channels provide enhanced O_2 and H_2O transport, enabling high performance in both fuel cell and electrolyzer mode



- 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

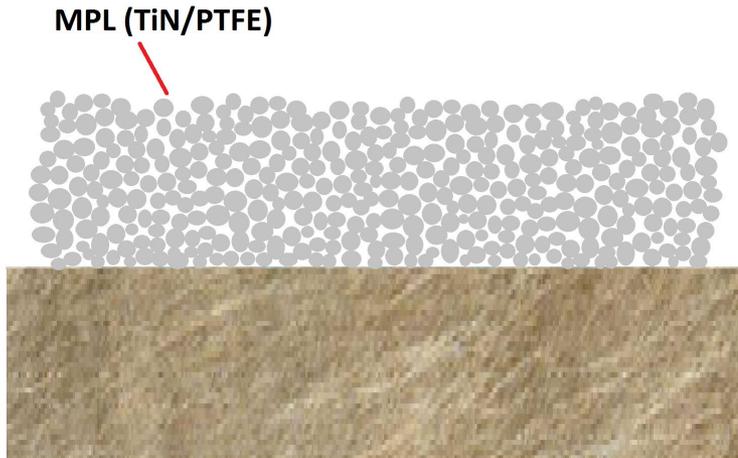
Approach: Patterned GDL Substrates

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

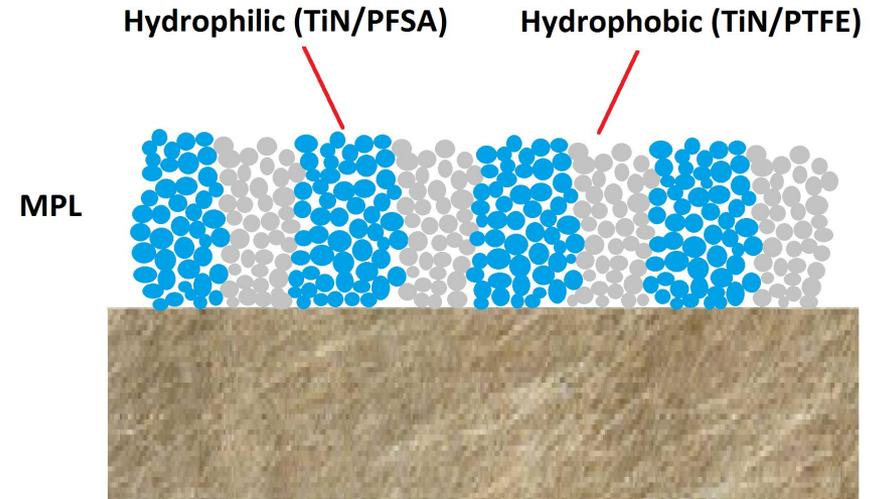


Approach: Microporous Layers

Gen 1 MPL (Hydrophobic)



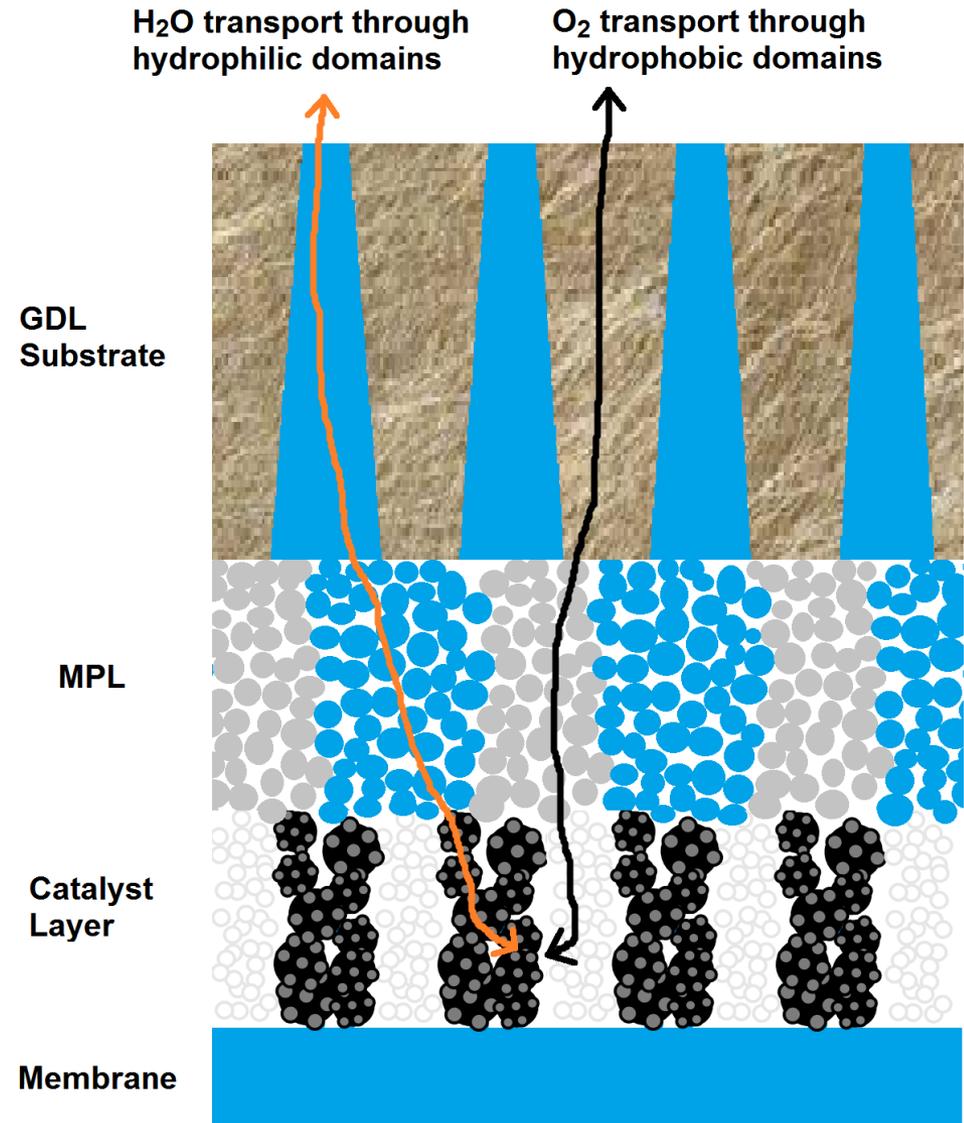
Gen 2 MPL (Amphiphilic)



- 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

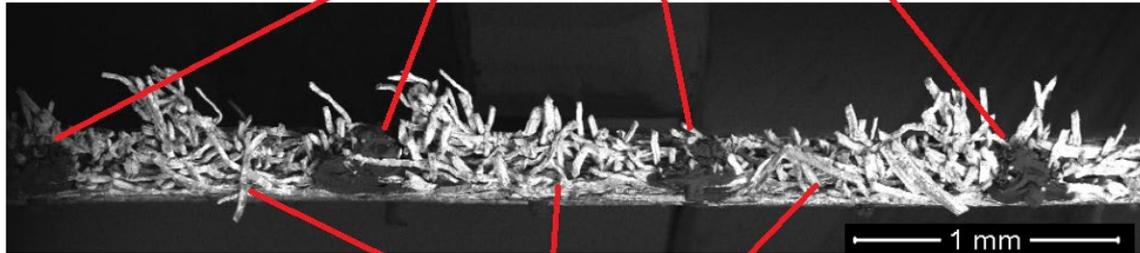


Milestones

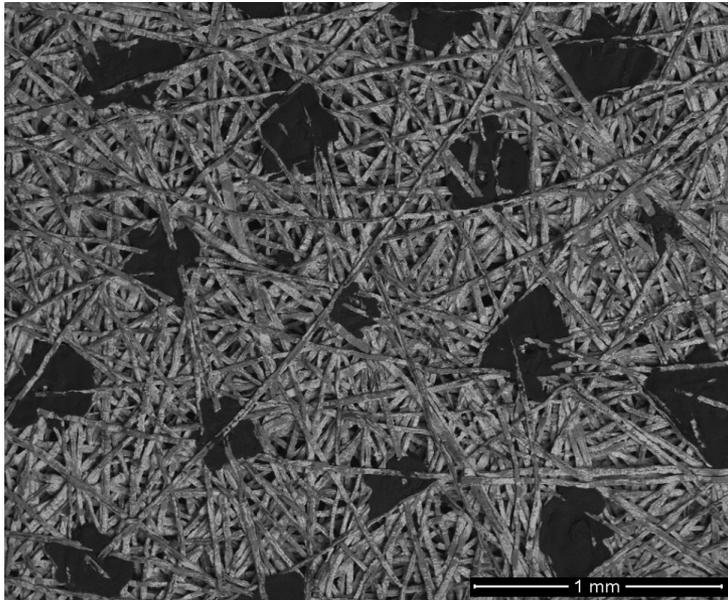
| | | |
|--------------|--|---|
| 3/18 | Perform modeling to determine optimal hydrophobic channel size and spacing for GDLs and electrodes |  |
| 6/18 | Prepare GDL templates and use them to demonstrate fabrication of local hydrophobic GDL microstructures |  |
| 9/18 | Prepare 4 different electrode 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 | Use patterned Ti felt GDLs to demonstrate E-FC voltage difference at 0.6 A/cm^2 of < 1.05 V |  |

Patterned Ti Felt GDLs (2019)

Hydrophilic Channels (Nafion-Rich)



Hydrophobic Regions (PTFE/Ti)

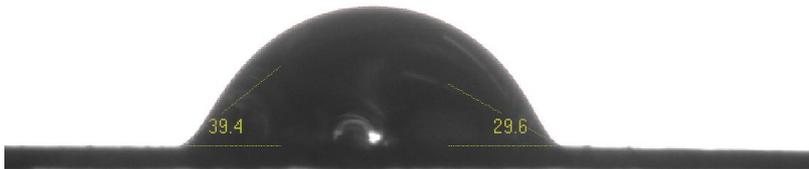


- Hydrophobic treatment (7-15 wt.% PTFE) of Ti felt GDL to prevent global flooding
- Local impregnation with Nafion to create hydrophilic channels through GDL, enabling effective water transport in fuel cell and electrolyzer mode

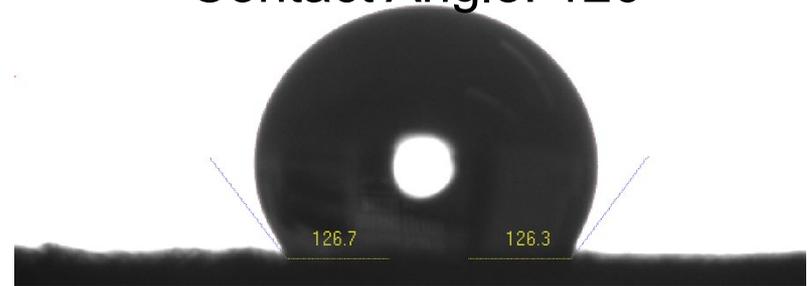
First demonstration of hydrophobic/hydrophilic GDL patterning via PTFE/Nafion segregation

Accomplishment: Effect of Hydrophilic Channels on Wetting

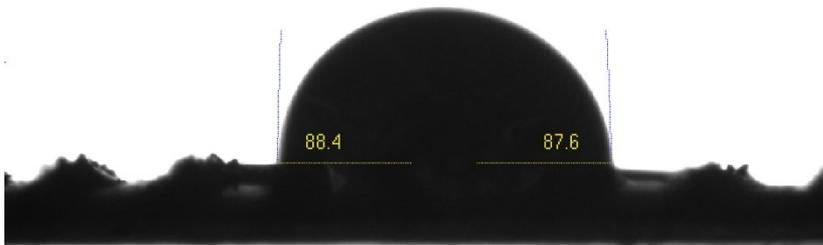
Untreated
Contact Angle: 35°



Hydrophobic Treated
Contact Angle: 126°



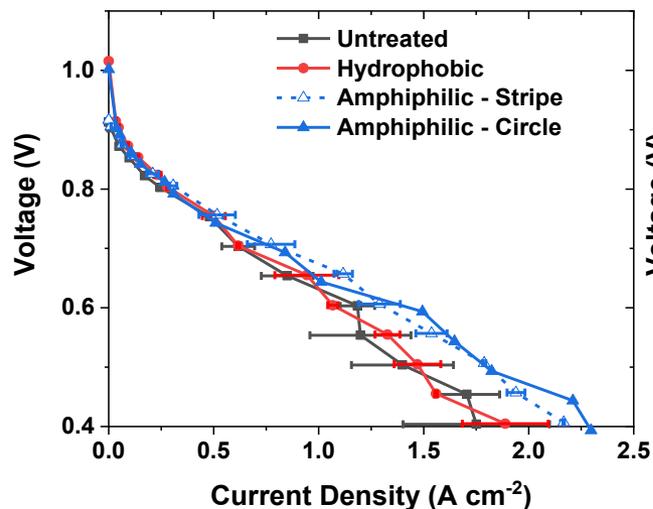
Hydrophobic/Hydrophilic
Contact Angle: 88°



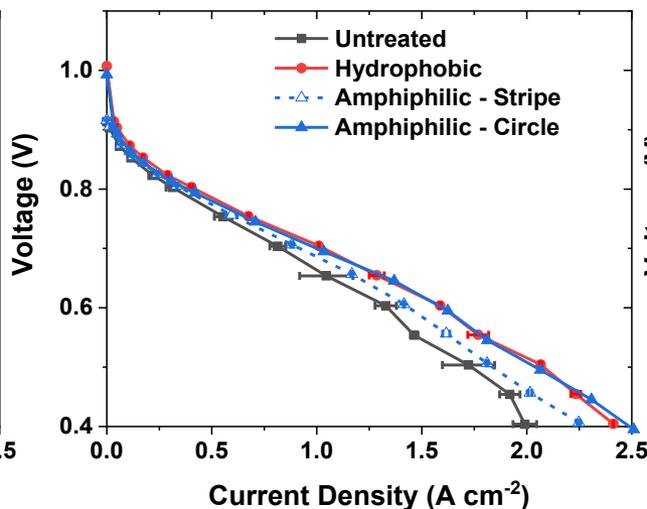
Hydrophobic/hydrophilic patterning maintains high bulk hydrophobicity of GDL, while still providing local water transport pathways

Accomplishment: Improved URFC Performance

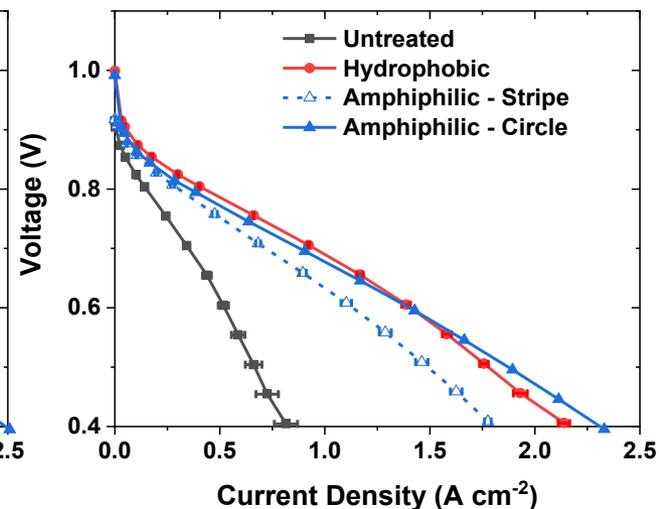
75% RH



100% RH



150% RH

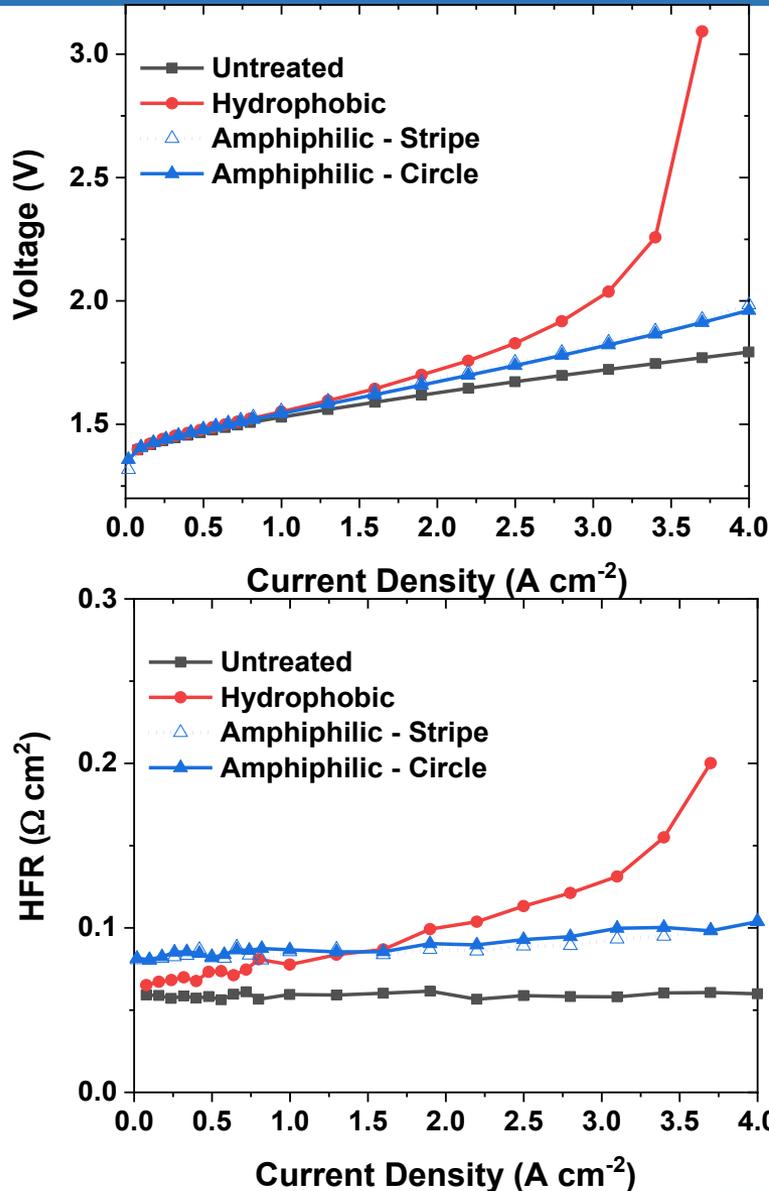


- Hydrophobic treatment (15 wt.% PTFE) of Ti felt GDL enables improved fuel cell performance
- Further performance improvement demonstrated using combination of PTFE treatment with local Nafion treatment to produce patterned hydrophobic/hydrophilic Ti felt GDL

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

80°C, H₂/O₂, 150 kPa_{abs}
1 mg/cm² Pt, 1 mg/cm² 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

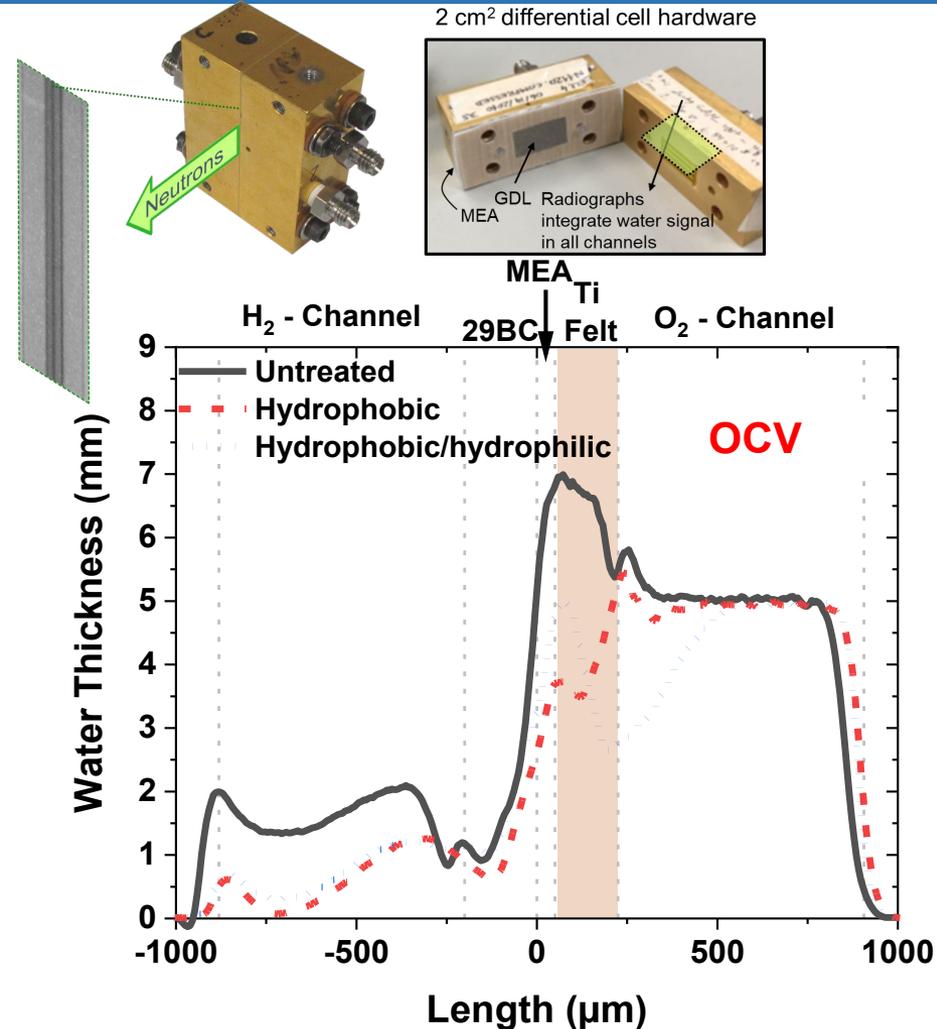
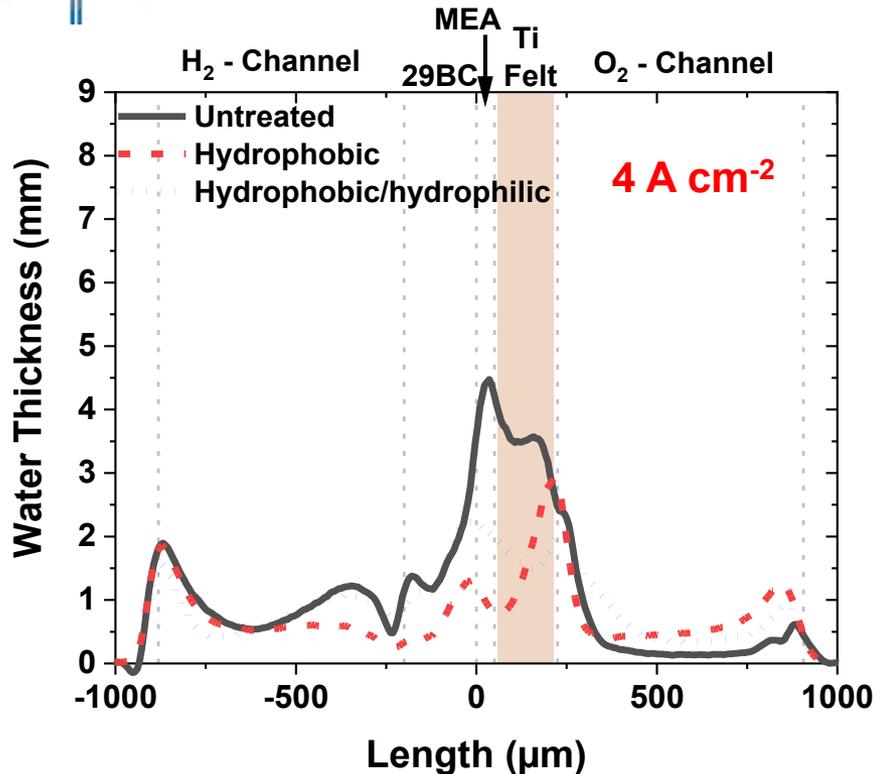
Hydrophobic/hydrophilic patterning enables enhanced URFC performance under a wide range of hydration conditions

Accomplishment: Water Imaging in UFRC



Electrolysis Mode

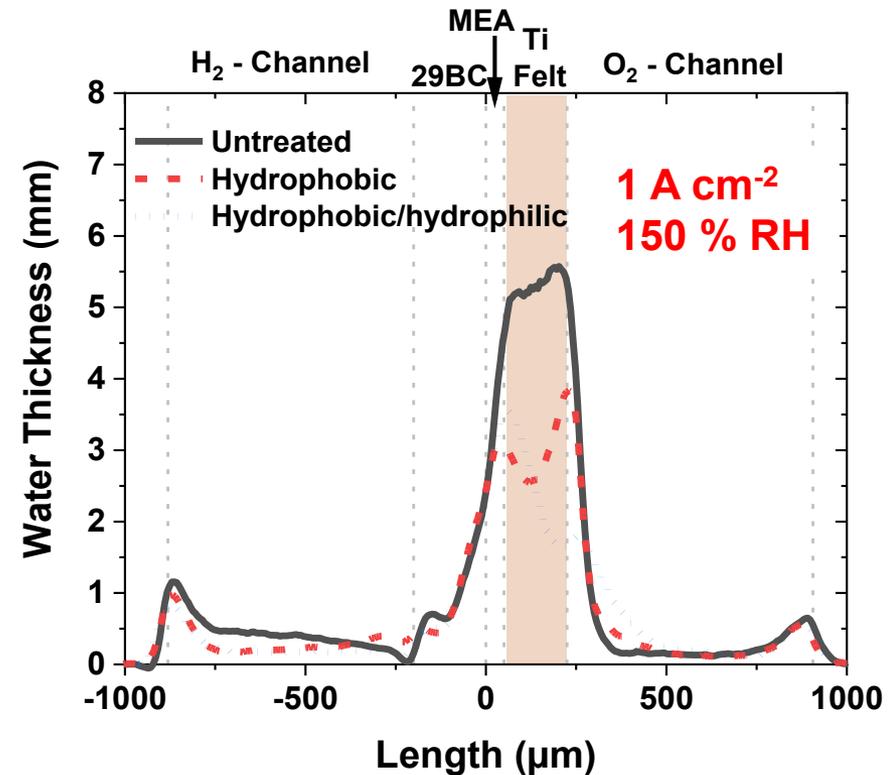
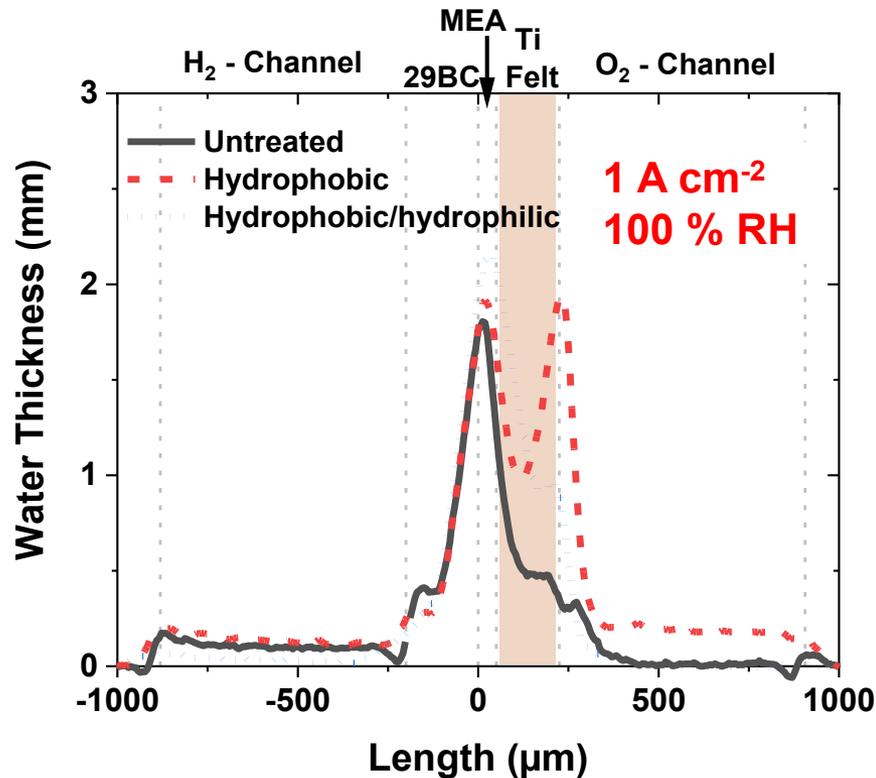
Jacob LaManna, Eli Baltic, Dan Hussey, David Jacobson



Amphiphilic patterned Ti felt provides sufficient water for electrolysis, unlike hydrophobic treated Ti felt, which starves the O₂ electrode

Accomplishment: Water Imaging in UFRC

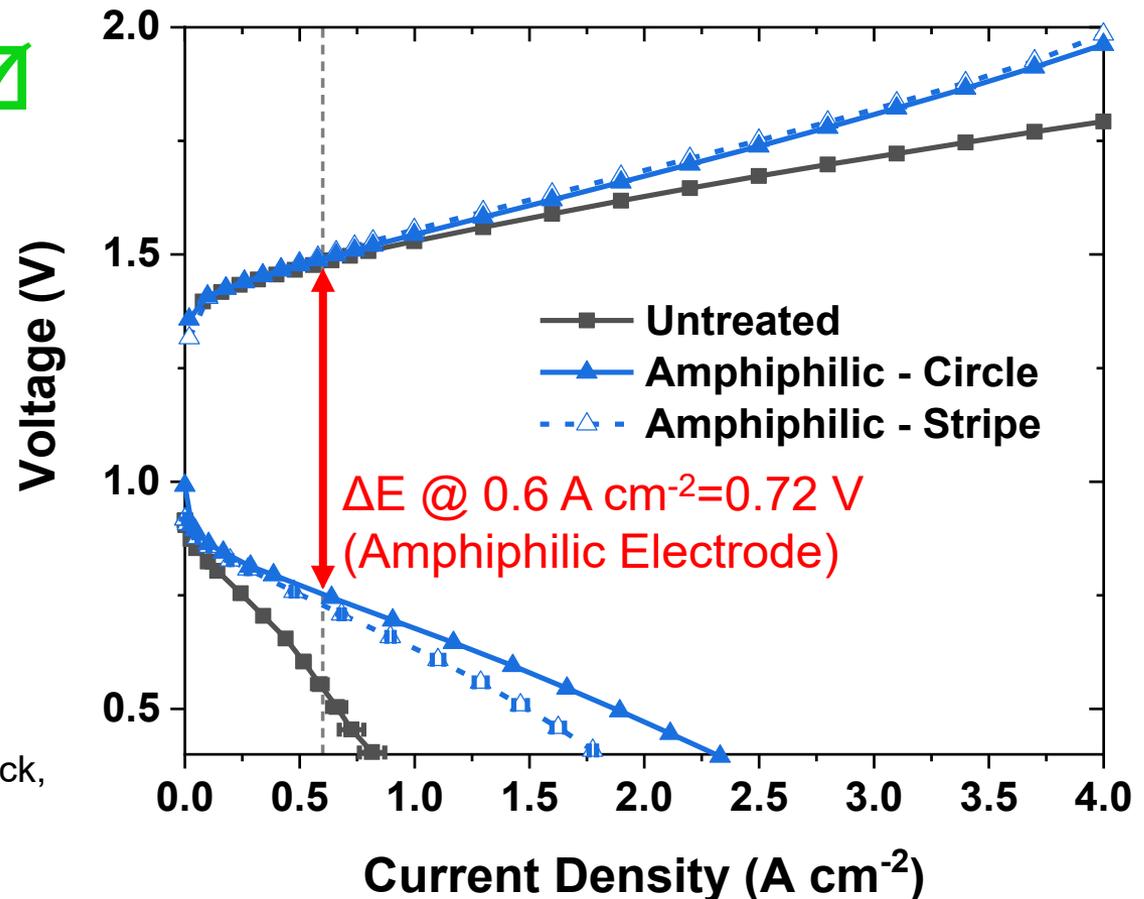
Fuel Cell Mode



Hydrophobic/hydrophilic and the hydrophobic Ti felt prevents flooding in the CL and the GDL unlike the untreated Ti felt

Accomplishment: High Performance

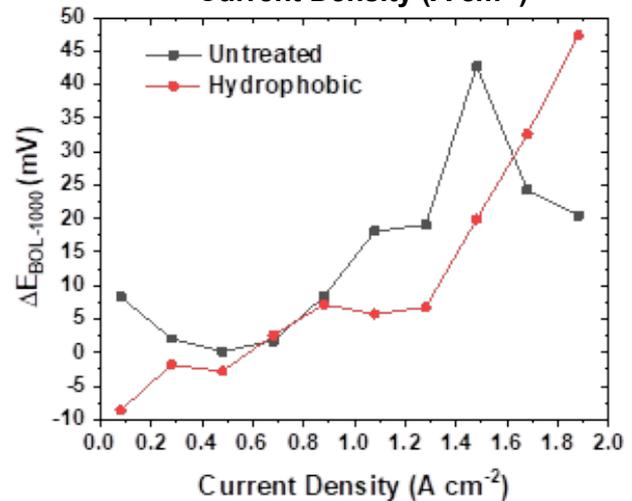
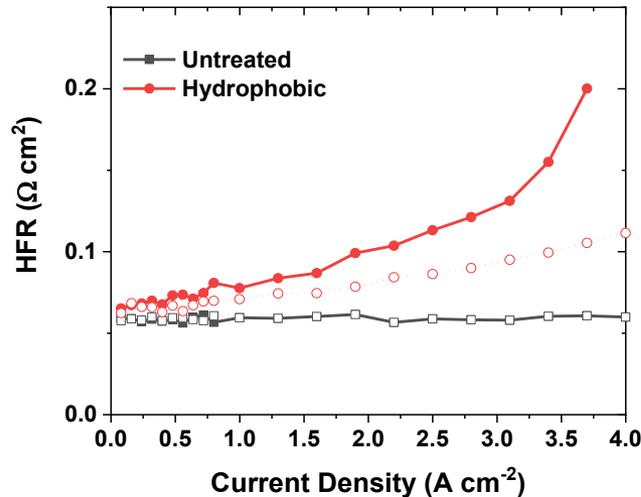
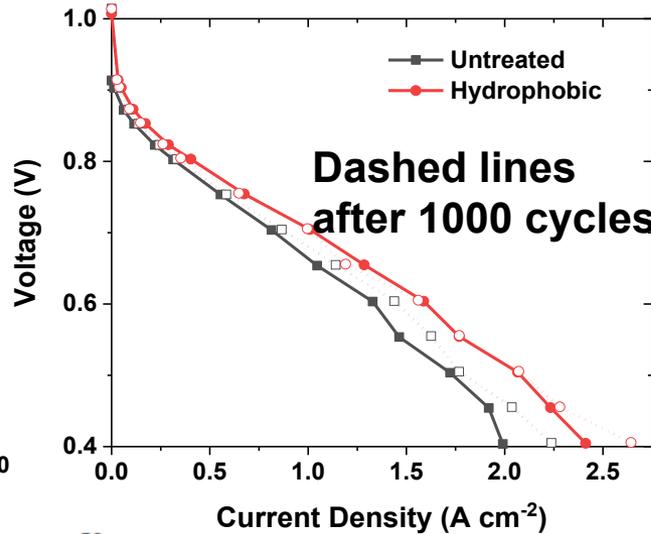
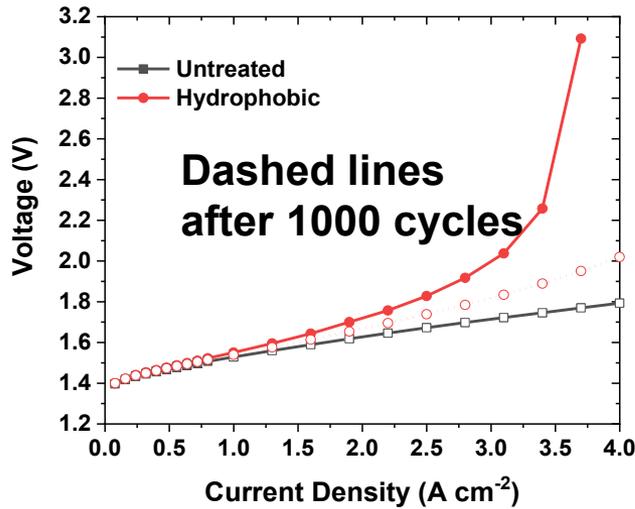
- **Project Goal #1:** 1.1 V difference between fuel cell and electrolyzer voltage at 0.6 A/cm²
- 5/30/19 Status: O₂ – 0.72 V, Air – 0.78 V (Amphiphilic Electrode with circle pattern)
- Project Milestone met 



80°C, H₂/O₂, 150 kPa_{abs}
1 mg/cm² Pt, 1 mg/cm² Ir black,
N212

Accomplishment: High Durability

- **Project Goal #2:** Tailor URFC structures to limit the transport-related degradation to less than 50 mV after 1,000 E-FC mode cycles 



- Performance of untreated Ti felt showed no losses in E mode while a slight improvement in FC mode at high current density
- Performance of hydrophobic-treated GDL increases significantly in E mode and slight improvement in FC mode during durability testing

- 0.6V to 1.6 V with 2.5 s hold and rise time of 0.5 s
- 80 °C, 150 kPa, Anode: H₂ @100 % RH, Cathode: liquid water

2019 Reviewer Comments

It is recommended that the team consult with an industrial partner.

We have now partnered with Giner Inc. and will work with them going forward.

A greater focus on confirming the major role of water–gas transport in achieving these results, perhaps via computational models that were apparently used at the start of the project, would be helpful.

In addition to the modeling work, we have also conducted neutron imaging that confirmed the role of liquid water transport in amphiphilic diffusion media in controlling performance.

Technoeconomic analysis of the proposed patterned MEA and stacks should be added to the work scope.

Project resources are insufficient to cover this, but we are interested in collaborating with others on TEA.

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)

In FY20, we began partnering with Giner Inc. in a new project that will continue this work

Remaining Challenges and Barriers

- Amphiphilic GDLs show significant advantages, but thus far have shown high HFR. HFR reduction is needed to fully realize the benefits of the amphiphilic approach.
- 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

- Continue using performance diagnostics (impedance, limiting current methods, helox measurements) to characterize transport resistances for amphiphilic patterned MEA
- Use characterization techniques including *in operando* X-ray computed tomography and neutron radiography to quantify effects of amphiphilic patterned MEA on water transport
- Complete GDL substrate work and move focus to MPL

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

Technology Transfer Activities

- We are developing IP related to patterned hydrophobic/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 H₂O and O₂ transport challenge.
- Approach:** Interspersed arrays of hydrophobic and hydrophilic through-plane channels provide enhanced O₂ and H₂O 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 O₂ transport.
- Accomplishments:** We have demonstrated TiN-based MPLs and patterned hydrophilic/hydrophobic diffusion media based on Ti felts. We have met project milestone (< 1.1 V difference between fuel cell and electrolysis voltages at 0.6 A/cm²) 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), and new collaboration with Giner Inc. to continue this work in a new project.