Accessible PGM-free Catalysts and Electrodes

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Project ID FC318

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Overview

Timeline:

- Project Start Date: October 1, 2018
- Project End Date: September 30, 2020

Barriers

A. Durability

B. Cost

C. Performance

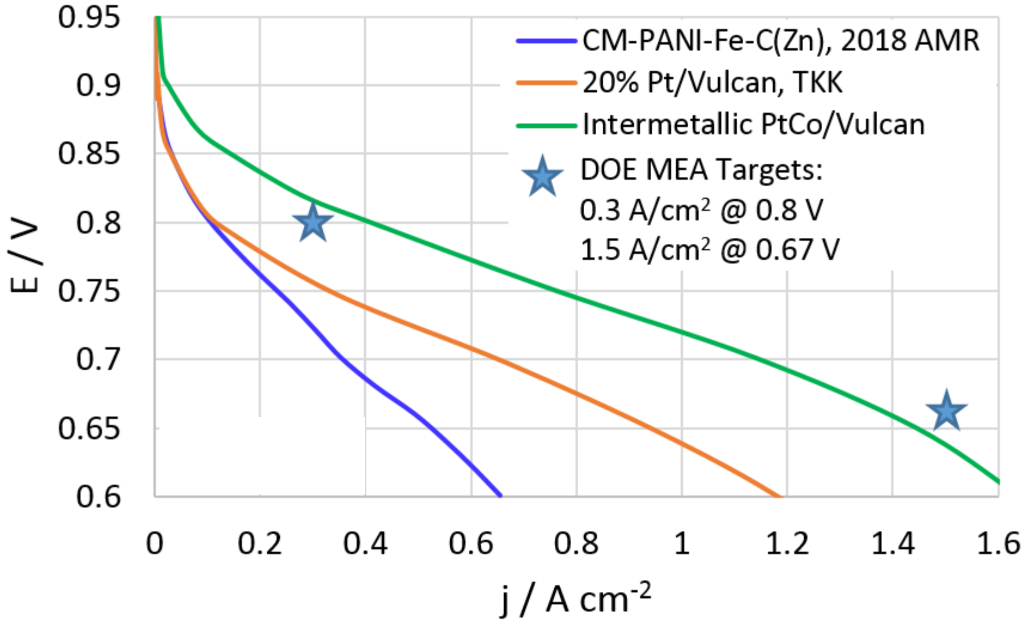
Budget:

- Total Project Budget: $1M
- Total DOE Funds Spent: $60K (03/01/2019)

Partners

- LANL (Jacob S. Spendelow, Mahlon Wilson, Siddharth Komini Babu, M. Aman Uddin)

Relevance



PGM-free at 0.67 V: **0.31 W/cm^2**
DOE MEA target: **1 W/cm^2**
Future MEA target: **1.5 W/cm^2?**

- **To achieve target power densities, improvements in electrode transport and in catalysis are needed**
- **This project will address both**

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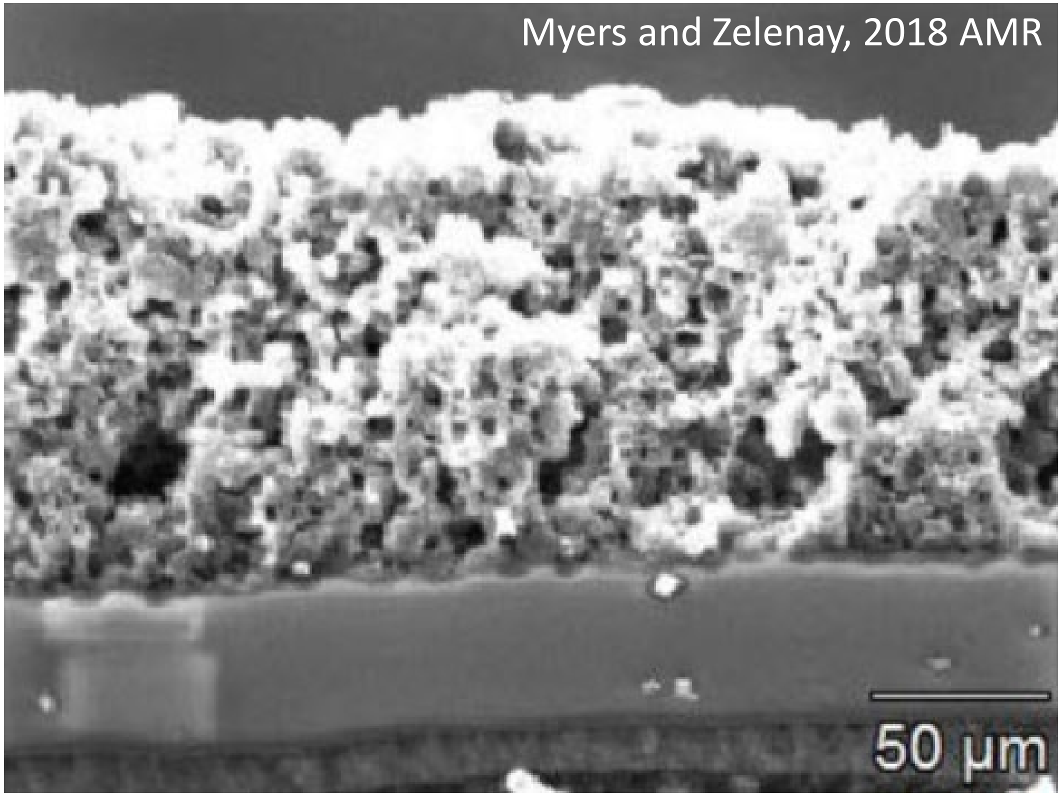
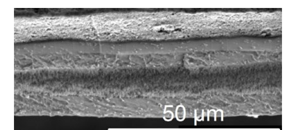
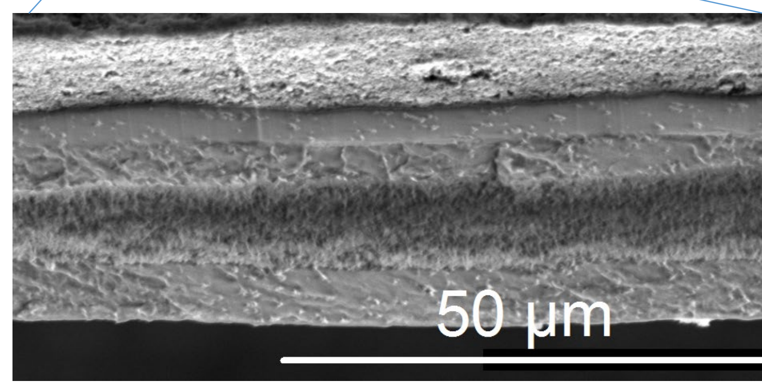
Background: Cathode Structure



PGM-free Cathode
[(CM+PANI)-Fe(Zn)-C]



PGM Cathode
[TEC10E40E]



PGM-free cathode is much thicker and coarser

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O_2 Transport Limitations

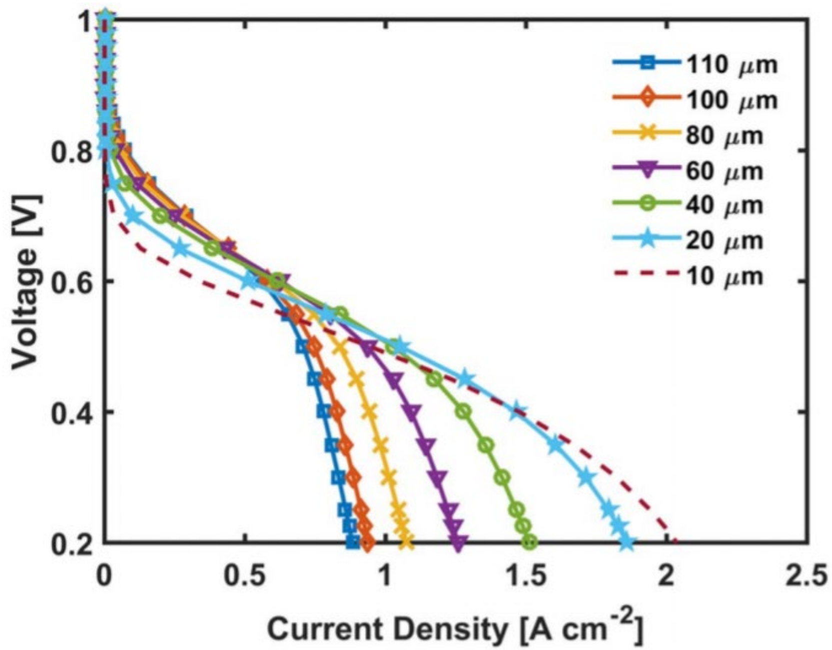

Figure 9. Effect of thickness on the 50 wt% Nafion loading CM-PANI-Fe electrode. The simulation was run at 80°C and 100% RH H_2 and air feed gas at 1 atm partial pressure.

S. Komini Babu et al. JECS 2017 (164) F1037-F1049

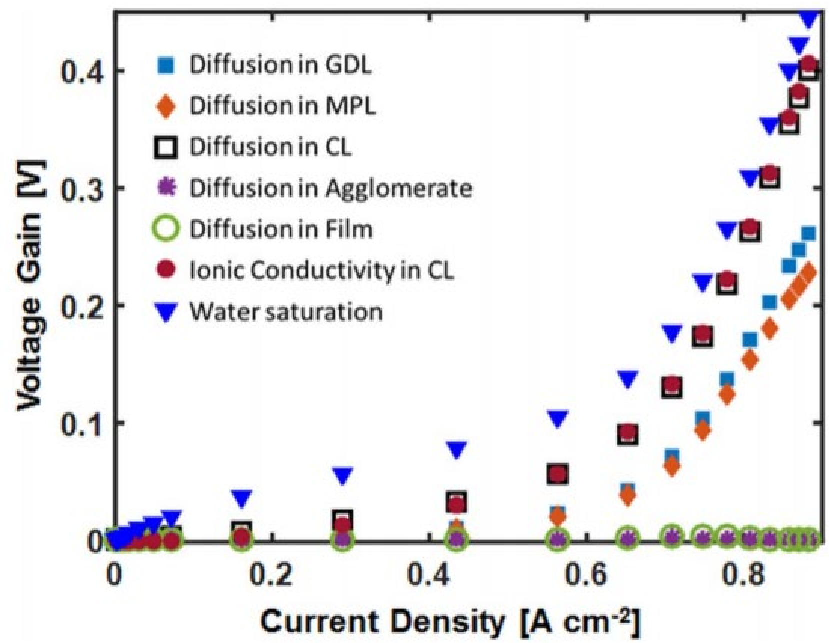

Figure 6. Voltage gain due to different resistance in the electrode for the 50 wt% Nafion electrode. The model was run with H_2 and air fully humidified gas at 80°C and 1 atm partial pressure.

- Model calculations suggest significant effect of electrode thickness on O_2 transport
- O_2 transport in electrode causes several hundred mV loss at high currents

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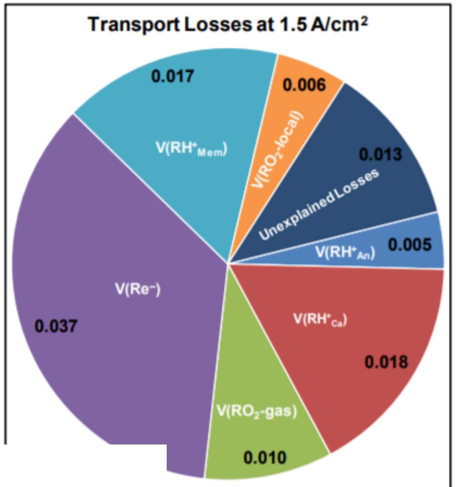
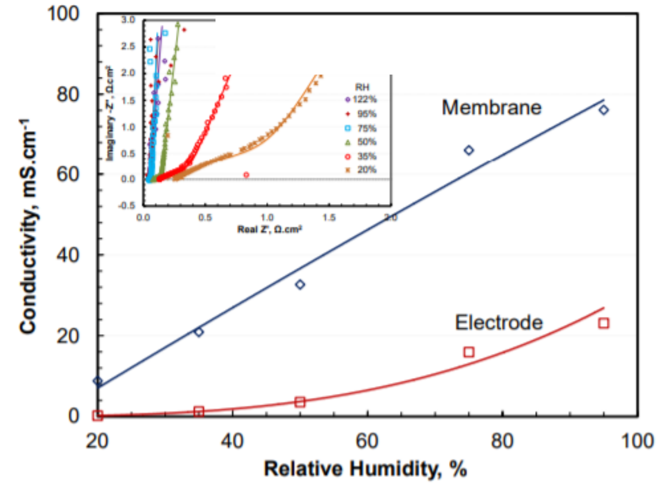
H^+ Transport Limitations

Comparison with PGM-based MEAs suggests major H^+ transport limitations

Item	Description
Cathode catalyst	30% PtCo/HSC-a 0.1 mg_{Pt}/cm^2
Cathode ionomer	Mid side chain 0.9 I/C (EW825)
Membrane	12 μm PFSA
Anode catalyst	10% Pt/C 0.025 mg_{Pt}/cm^2
GDL thickness	235 μm





- H^+ resistance in cathode causes ~20 mV loss in ~5 μm PGM-based CCL
    - First approximation: **~400 mV loss** in ~100 μm PGM-free CCL
- H^+ resistance in 12 μm membrane causes ~15 mV loss
    - Suggests that electrode with 5-10X higher thickness and 5-10X lower conductivity could cause **several hundred mV loss**

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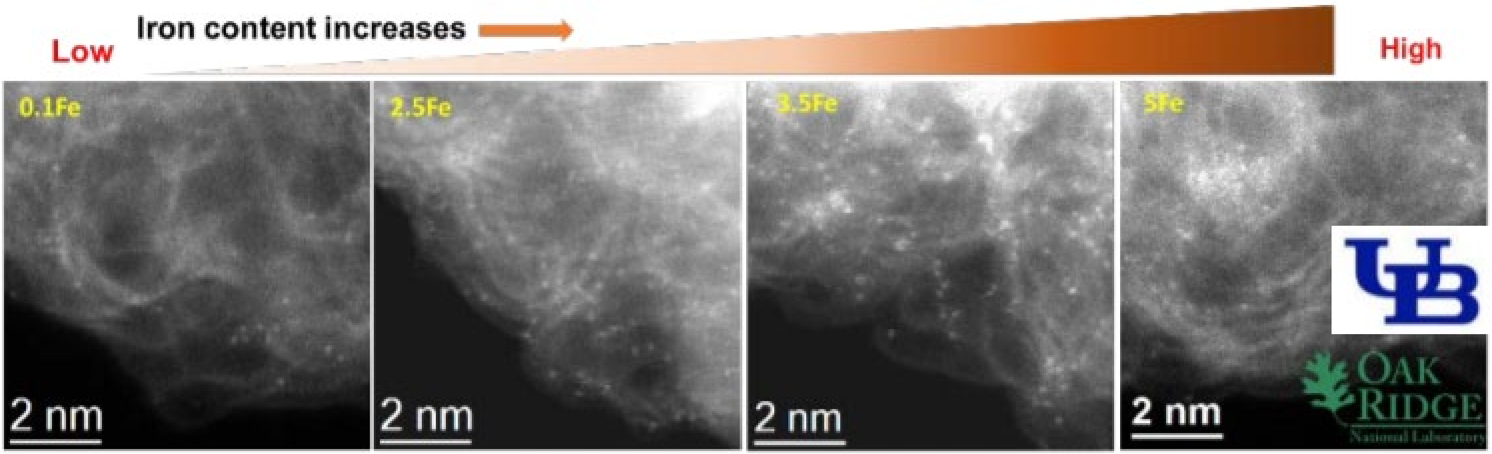
Active Site Density



Litster, 2018 AMR

- Active site density is low: ~3×10^{12} sites/cm^2 on atomically-dispersed Fe-N-C (Myers and Zelenay, 2018 AMR), vs. ~10^{14} sites/cm^2 on 20%Pt/Vulcan
- Increasing Fe loading causes clustering and decrease of ORR activity

Approach

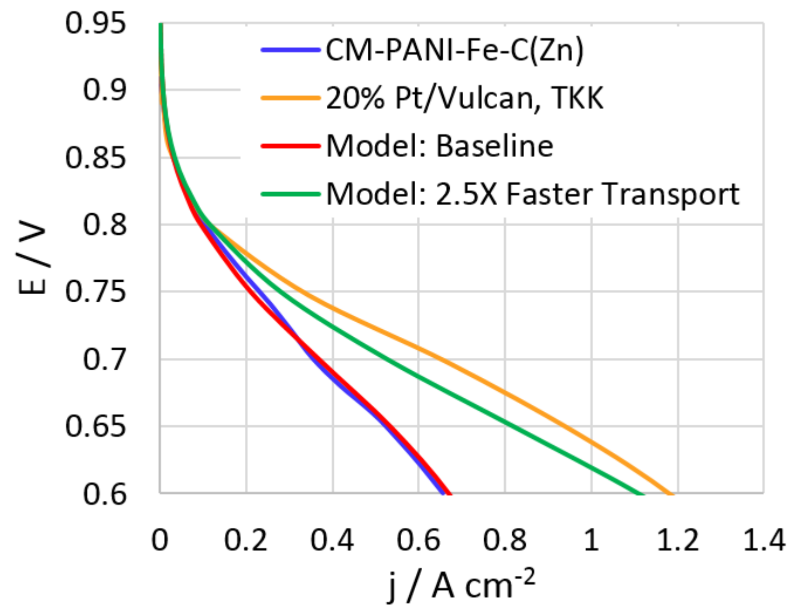
Develop PGM-free <u>MEAs</u> with facile transport of O_2, H^+, H_2O, and e^- at

- **Micron scale (accessible electrodes)**
- **Nanometer scale (accessible catalysts)**

Accessible electrodes will be fabricated using non-tortuous transport channels

Accessible catalysts will be fabricated using structural control at nanoscale

Objective: *create innovative catalyst and electrode structures that enable PGM-free electrodes to have high-current performance approaching that of PGM-based electrodes*



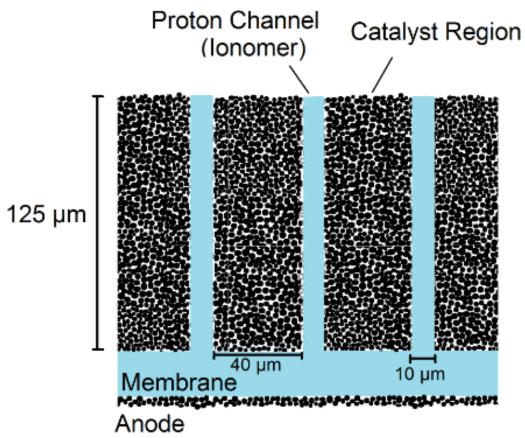
Model: S. Komini-Babu et al. JECS 164 (2017) F1037-F1049

Milestones

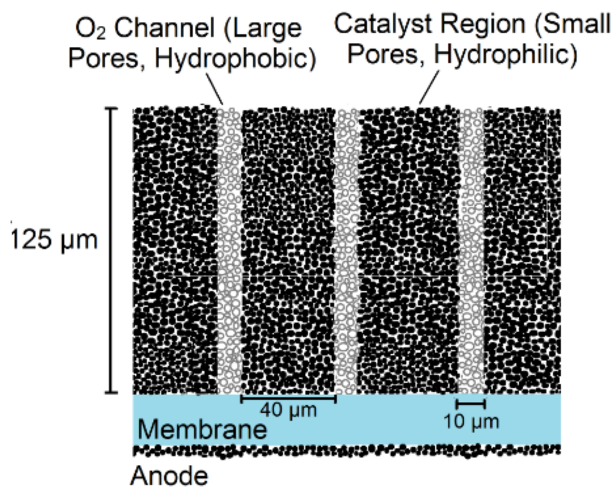
12/18	Fabricate H^+ channel electrodes and perform initial testing.
3/19	Perform initial templated catalyst synthesis.
6/19	Provide initial multiscale modeling results to guide electrode design.
9/19	Demonstrate MEA performance of 0.025 A/cm^2 at 0.9 V H_2/O_2 and 0.5 A/cm^2 at 0.67 V H_2/air (150 kPa$_{abs}$) (Go/No-go)
12/17	Demonstrate H^+ transport in catalysts without ionomer.
3/18	Demonstrate multi channel electrode structures in MEA testing.
6/18	Test durability on drive cycle for 500 hours.
9/18	Demonstrate MEA performance of 0.044 A/cm^2 at 0.9 V H_2/O_2 and 0.75 A/cm^2 at 0.67 V H_2/air (150 kPa$_{abs}$).

Accomplishments: Proof-of-concept Accessible Electrode Structures

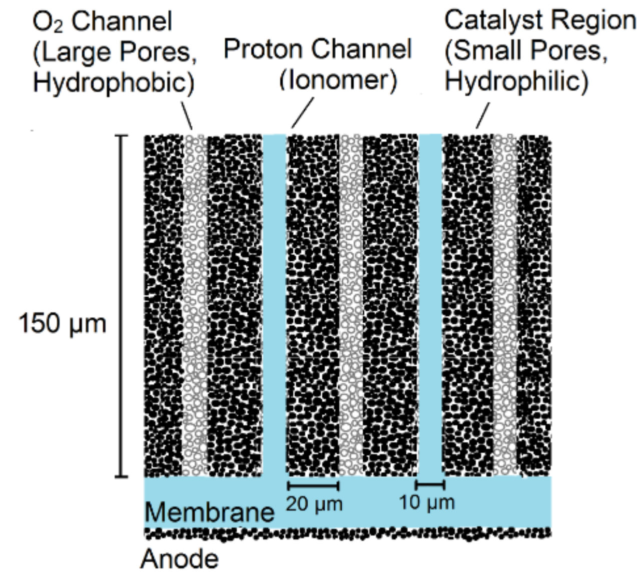
Proton Channel Electrode

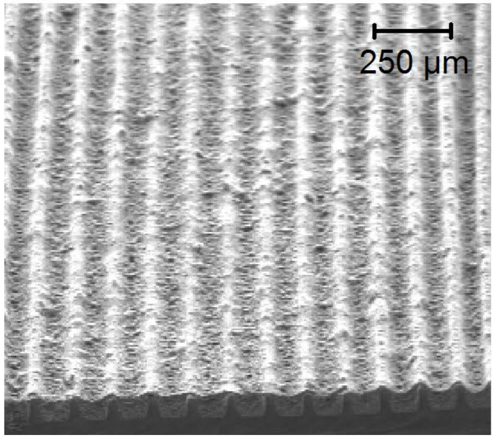


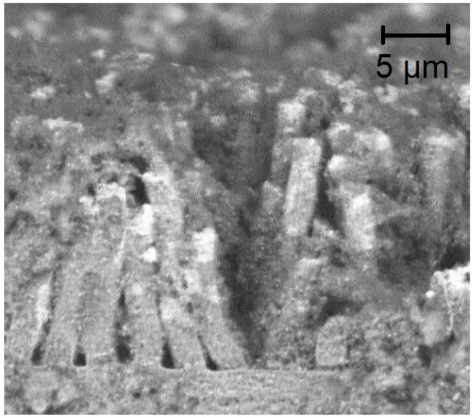
Oxygen Channel Electrode

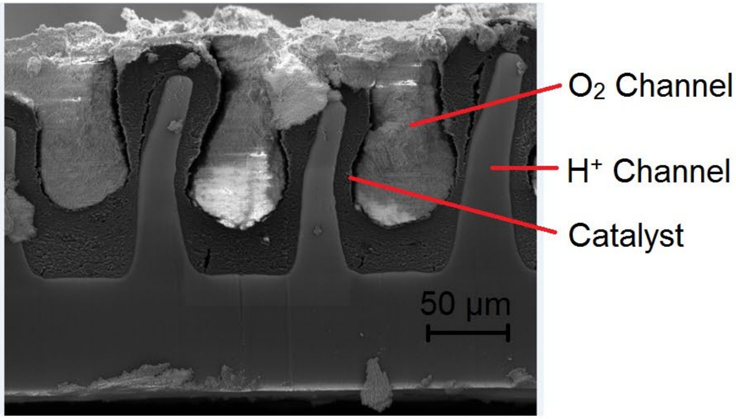


Multi Channel Electrode









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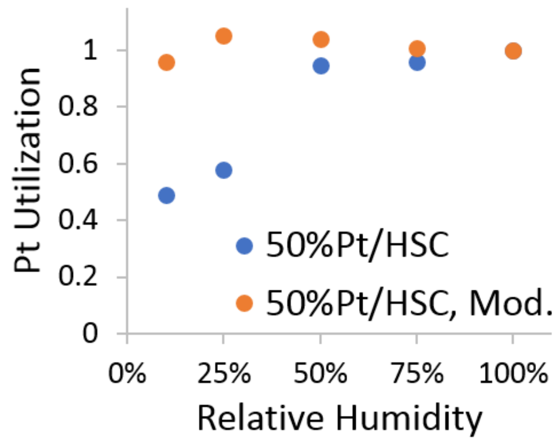
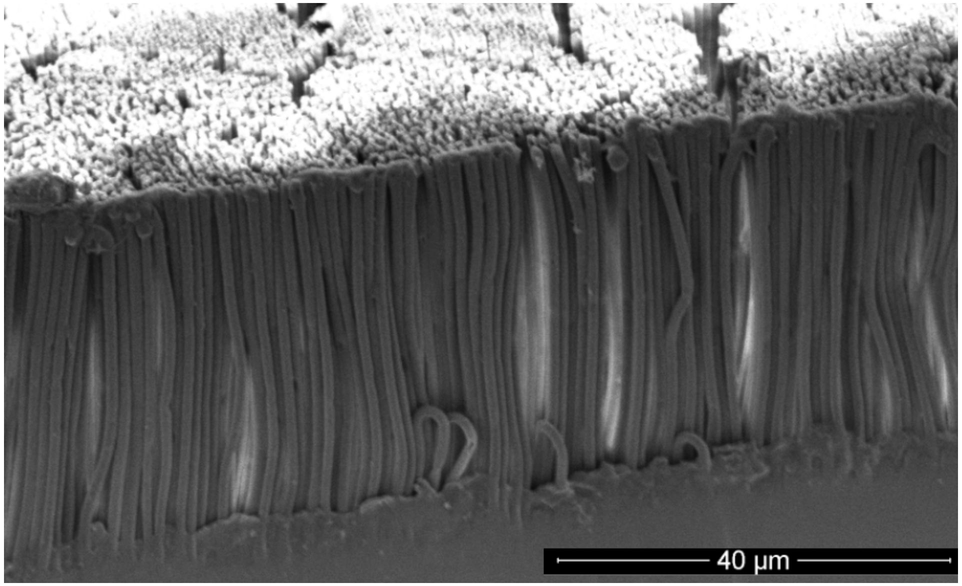
Accessible Catalysts

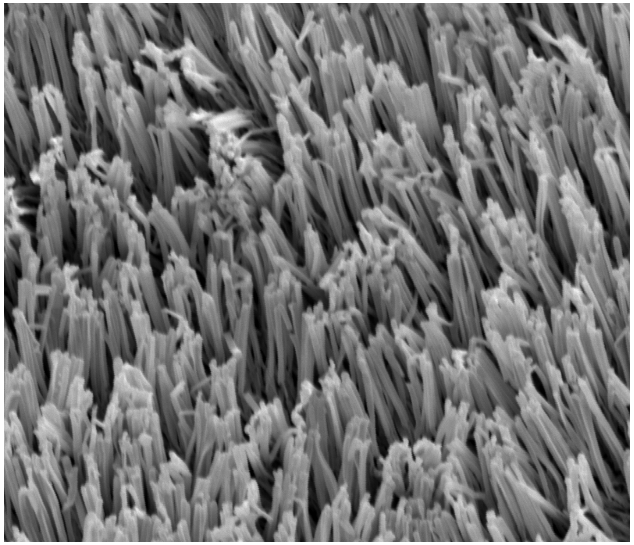
- Control of hierarchical electrode structure to enable effective O_2 transport at nanoscale
- Use of mesoporous templates to control particle size and aspect ratio, while limiting metal clustering

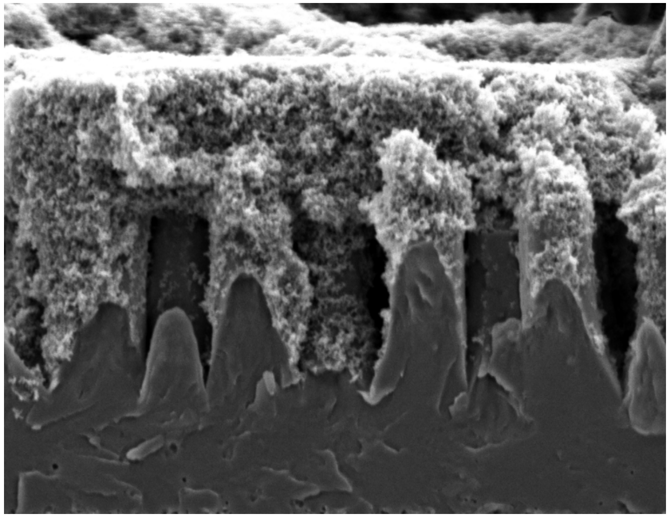


- Modification of pore structure and surface properties to control agglomeration and enable effective H^+ transport at nanoscale

Leveraging Electrode Work







- Advanced electrode structures developed in FC-PAD and in LANL URFC project will be adapted for this project

Characterization and Modeling

Characterization techniques including:

- SEM
- TEM/STEM
- XCT
- XAS
- USAXS
- BET
- Neutron imaging

Modeling of kinetics and transport to guide design of accessible catalysts and accessible electrode structures

MEA Testing

- MEA-oriented project; little if any RDE work
- Initial work in 5 cm^2 differential cells
- Operating conditions ranging from hot and dry to cold and wet to determine performance under real world conditions
- Use of helox and impedance transport diagnostics
- Successful catalysts/electrodes scaled up to 50 cm^2 testing
- Durability testing using steady-state holds and drive-cycle testing

Schedule

	Task/Subtask	FY 2019				FY 2020			
		Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4
T1	**Accessible Electrode Structures**								
T1.1	Proton Channel Electrodes	M1							
T1.2	Oxygen Channel Electrodes								
T1.3	Multi Channel Electrodes						M6		
T1.4	Catalyst Porosity								
T1.5	Novel Proton Conductors								
T2	**Accessible Catalyst Structures**								
T2.1	Control of Particle Size		M2		M4/GNG				
T2.2	Control of Agglomerate Size								
T2.3	Enhanced Transport in Particles/Agglomerates					M5			
T3	**Characterization and Modeling**								
T3.1	Characterization								
T3.2	Multiscale Modeling			M3					
T4	**MEA Testing**								
T4.1	Performance Testing								M8
T4.2	Durability Testing							M7	

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Collaboration and Coordination: Interactions with ElectroCat

- *PGM-free Catalyst Synthesis, Analytical Characterization, and Electrochemical and Fuel Cell Testing (LANL).* SOA catalysts supplied by ElectroCat will be used for accessible electrode development, while synthesis procedures will be adapted in collaboration with ElectroCat for accessible catalysts.
- *Segmented Cell and Neutron Imaging (LANL).* Neutron imaging will be used to assess local water saturation in accessible electrodes.
- *X-Ray Characterization Techniques (LANL).* Micro-XCT will be used to characterize microscale electrode structure.
- *Electrode Microstructure Characterization and Simulation; In situ and Operando Atomic, Nano, and Micro-structure Characterization (ANL)*. Nano-XCT will be used to characterize nanoscale electrode structure. In situ nano-XCT will enable direct visualization of water distribution with the electrode. USAXS will provide catalyst agglomerate measurements.

Collaboration and Coordination: Interactions with ElectroCat

- *Kinetics and Transport (NREL).* Transport diagnostics will be used to measure electrode transport limitations.
- *Modeling Kinetic and Transport Processes in PGM-free Electrodes (ANL).* Multiscale modeling will be instrumental in guiding design of accessible catalyst and electrode structures.
- *In situ Fluoride and Carbon Dioxide Emission Measurements (LANL).* In situ diagnostics will be used to characterize the relationship between transport and durability.
- *High-resolution Analytical Scanning Transmission Electron Microscopy; Electron Tomography (ORNL).* These techniques will be used to characterize accessible catalyst structures.

Remaining Challenges and Barriers

- Fabricating accessible electrode structures with high design fidelity
- Synthesizing PGM-free catalysts with high nanoscale accessibility

Proposed Future Work

This project has just begun, so almost all work is future work

- Designing, fabricating, and demonstrating accessible PGM-free electrode structures
- Synthesizing accessible PGM-free catalysts
- Modeling transport and kinetics in PGM-free catalysts and electrodes
- Characterizing PGM-free catalysts and electrodes and performing in situ and in operando diagnostics
- Fuel cell testing, including durability

Summary

Objective: Design accessible PGM-free catalysts and electrodes with facile transport of H^+ and O_2, and demonstrate in high-performance, durable MEAs.

Relevance: Project directly addresses cost, durability, and performance through key DOE targets:

- MEA performance > 44 mA/cm^2 @ 0.9 $V_{iR\text{-}free}$, H_2/O_2, 150 kPa_{abs}
- MEA performance > 300 mA/cm^2 @ 0.8 V, H_2/air, 150 kPa_{abs}
- Power density > 1 W/cm^2
- Cost < $40/kW (near-term), < $30/kW (ultimate)

Approach: Develop PGM-free electrodes with rapid micron-scale transport of O_2 and H^+ using non-tortuous transport channels and control of local hydrophobicity/hydrophilicity. Develop PGM-free catalysts with rapid nanometer-scale transport of O_2 and H^+ through control of nanostructure, including metal site clustering and particle agglomeration

Accomplishments: Project just started. Accomplishments to date are limited to procuring materials, preparing test infrastructure, and producing proof-of-concept structures

Collaborations: Extensive collaboration and utilization of ElectroCat consortium capabilities