

# 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

## Budget:

- Total Project Budget:  
\$1.25M
- Total DOE Funds Spent:  
\$820K (05/30/2020)

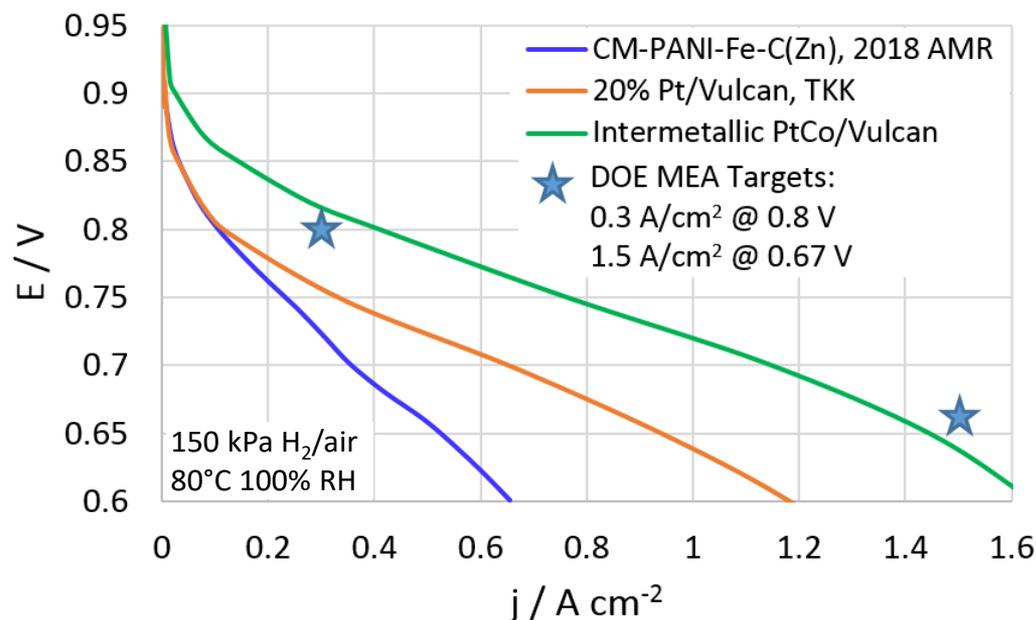
## Barriers

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

## Partners

- LANL (M. Aman Uddin, Xiaoxiao Qiao, Michael J. Workman, Siddharth Komini Babu, Rangachary Mukundan, Jacob S. Spendelow)
- University of Connecticut (M. Tanvir Alam Arman, Ugur Pasaogullari)
- Carnegie Mellon University (Shawn Litster)
- University at Buffalo (Yangua He, Gang Wu)
- Giner Inc. (Shuo Ding, Hui Zu)
- Pajarito Powder LLC (Alexey Serov, Barr Zulevi)
- ANL (Firat C. Cetinbas, Jui-Kun Pen, Xiaohua Wang, Rajesh K. Ahluwalia)

# Relevance

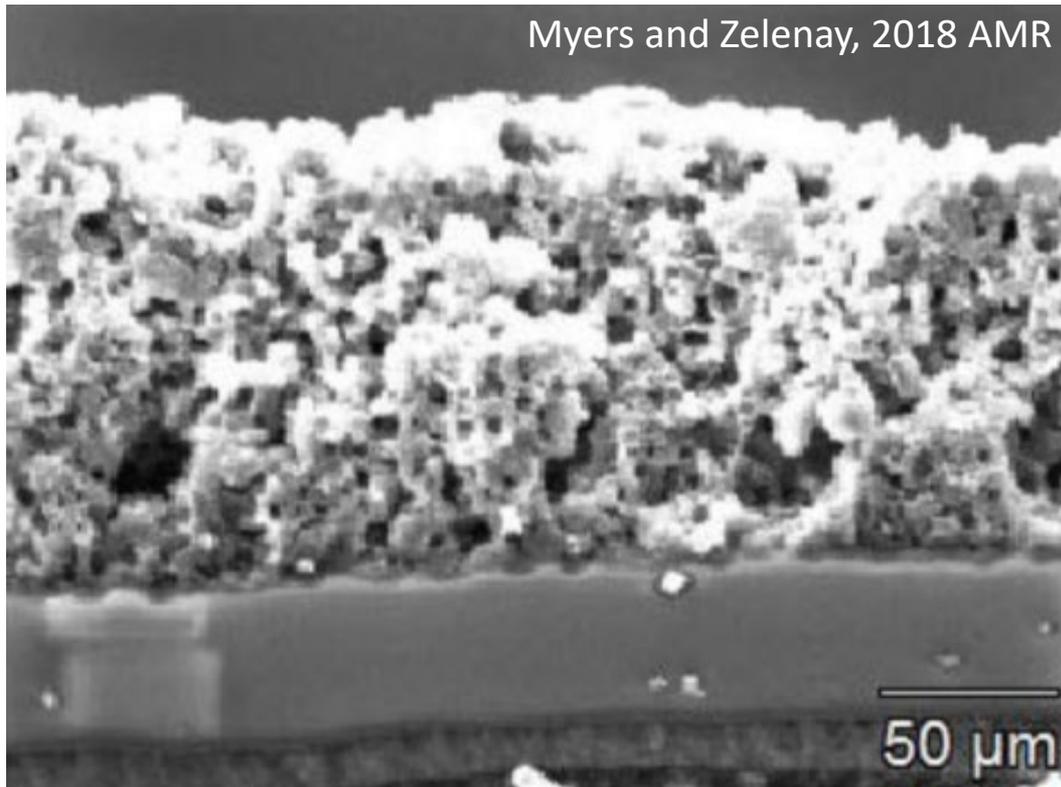


PGM-free at 0.67 V: **0.31 W/cm<sup>2</sup>**  
DOE MEA target: **1 W/cm<sup>2</sup>**  
Future MEA target: **1.5 W/cm<sup>2</sup>?**

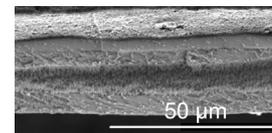
- To achieve target power densities, improvements in **electrode transport** and in **catalysis** are needed
- This project addresses both

# Background: Cathode Structure

Myers and Zelenay, 2018 AMR

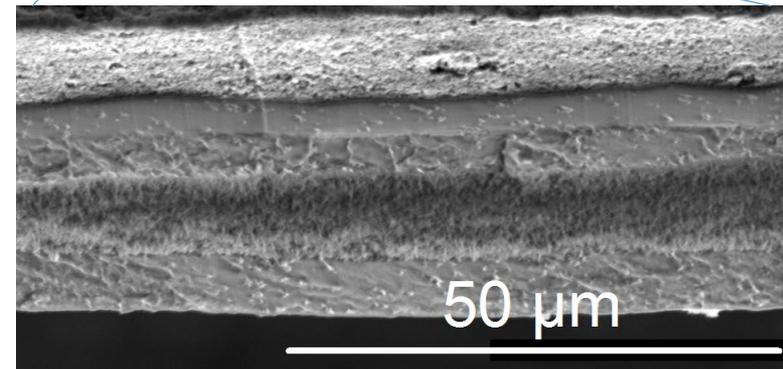


PGM-free Cathode  
[(CM+PANI)-Fe(Zn)-C]

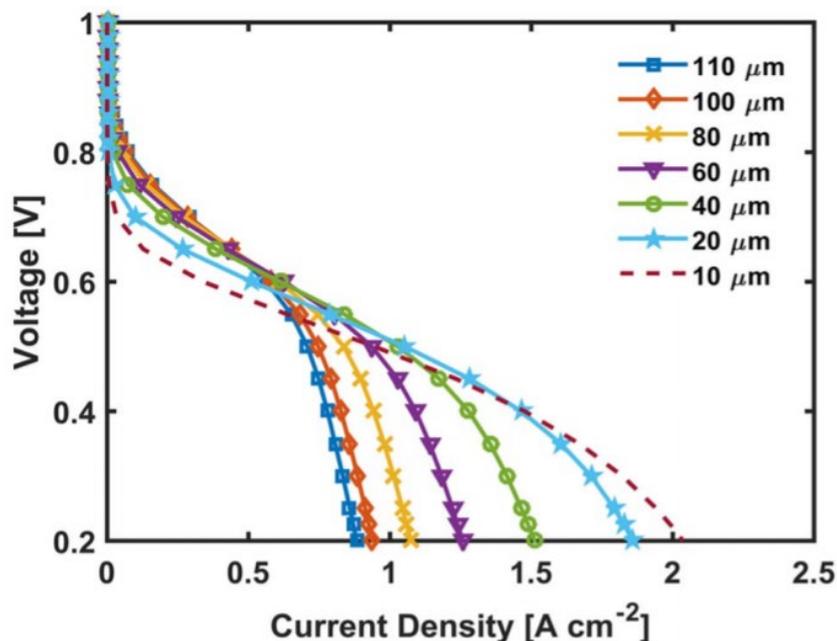


PGM Cathode  
[TEC10E40E]

PGM-free cathode is much thicker  
and coarser

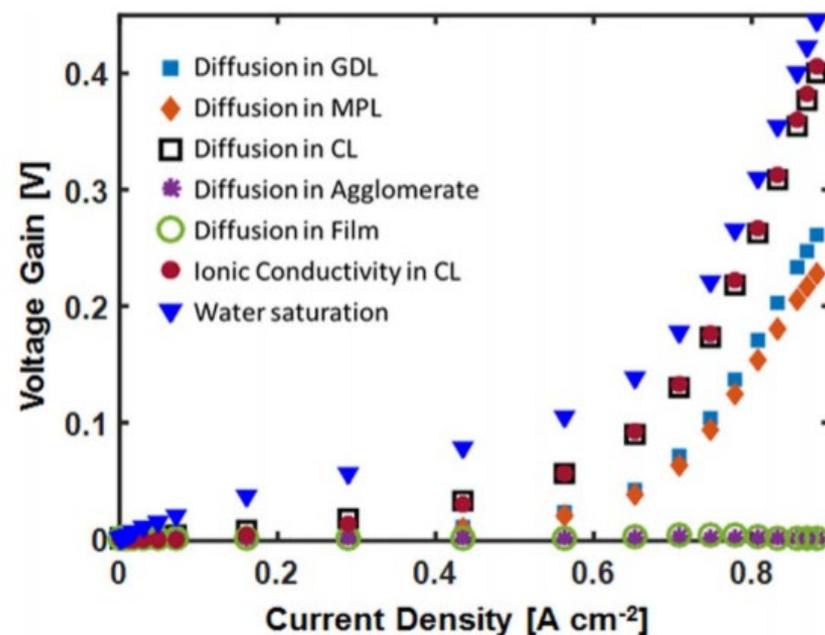


# O<sub>2</sub> Transport Limitations



**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<sub>2</sub> and air feed gas at 1 atm partial pressure.

S. Komini Babu et al. J ECS 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<sub>2</sub> and air fully humidified gas at 80°C and 1 atm partial pressure.

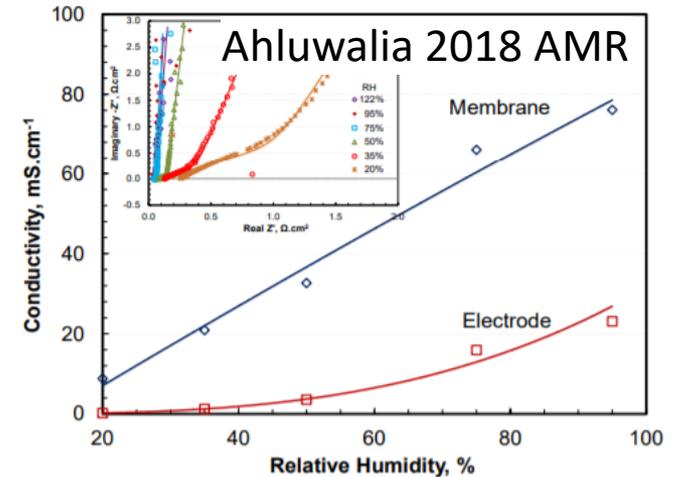
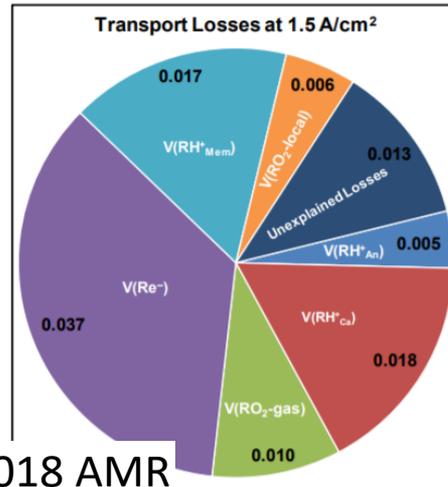
- Model calculations suggest significant effect of electrode thickness on O<sub>2</sub> transport
- O<sub>2</sub> transport in electrode causes several hundred mV loss at high currents

# H<sup>+</sup> Transport Limitations

Comparison with PGM-based MEAs suggests major H<sup>+</sup> transport limitations

Item	Description
Cathode catalyst	30% PtCo/HSC-a 0.1 mg <sub>Pt</sub> /cm <sup>2</sup>
Cathode ionomer	Mid side chain 0.9 I/C (EW825)
Membrane	12 μm PFSA
Anode catalyst	10% Pt/C 0.025 mg <sub>Pt</sub> /cm <sup>2</sup>
GDL thickness	235 μm

Kumaraguru 2018 AMR



- H<sup>+</sup> 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<sup>+</sup> 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**

# Approach

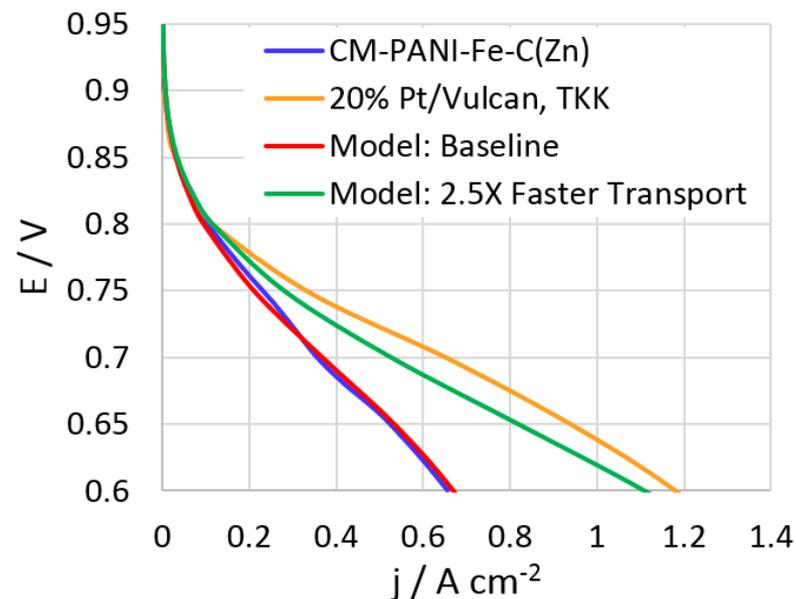
Develop PGM-free MEAs with facile transport of  $O_2$ ,  $H^+$ ,  $H_2O$ , and  $e^-$  at

- **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

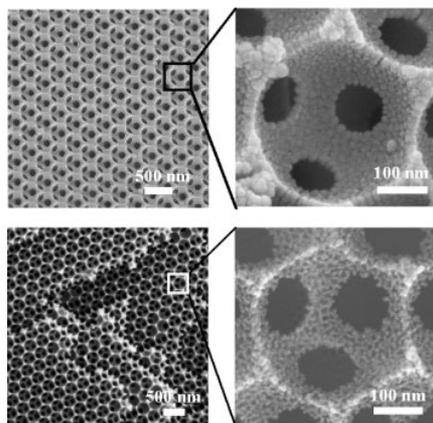
**Objective:** create innovative catalyst and electrode structures that enable PGM-free electrodes to have high-current performance approaching that of PGM-based electrodes



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

# Approach: Accessible Catalysts

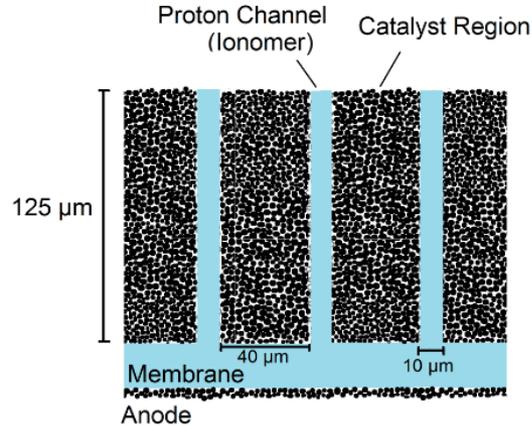
- Template assisted synthesis of PGM-free catalysts with long range order
  - Synthesize catalysts within anode aluminum oxide (AAO) templates
    - Direct synthesis from precursors within the templates
    - Coat templates with aniline and then polymerize and introduce nitrogen and iron
- Develop long-range hierarchical PGM-free catalysts
  - Use silica and polystyrene to provide hierarchical template
    - Synthesize PGM-free catalyst around sacrificial template to maintain hierarchical porosity
    - Synthesize hierarchical carbon to utilize in PGM-free catalyst synthesis



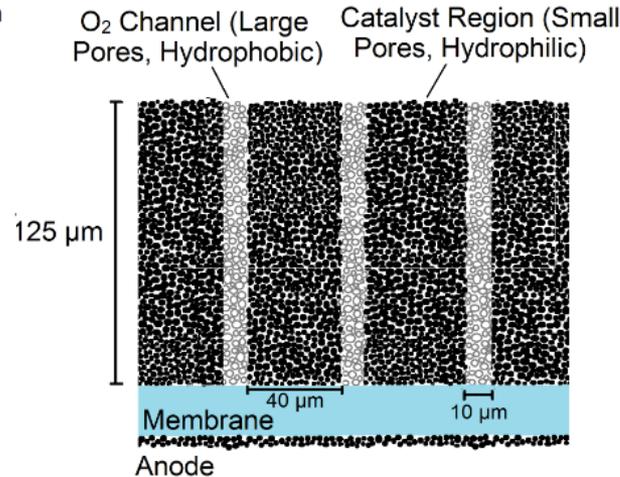
Geun Seok Chai, et al. *Adv. Mater.* 16. No 22 (2004): 2057-2061.

# Approach: Accessible Electrodes

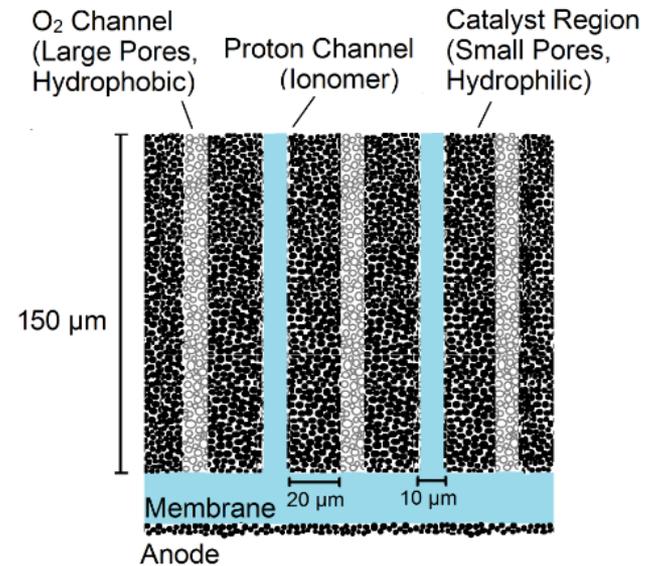
## Proton Channel Electrode



## Oxygen Channel Electrode



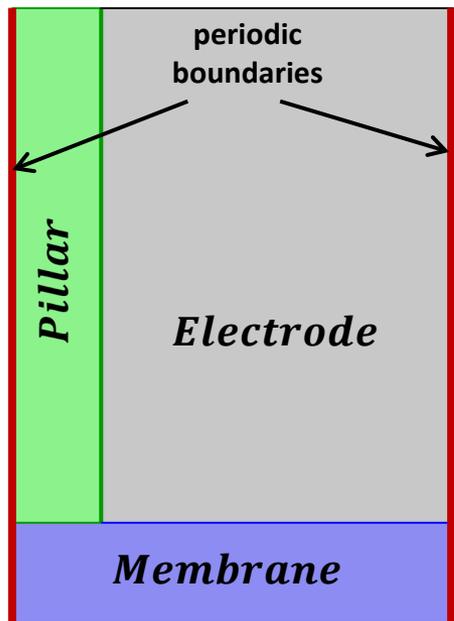
## Multi Channel Electrode



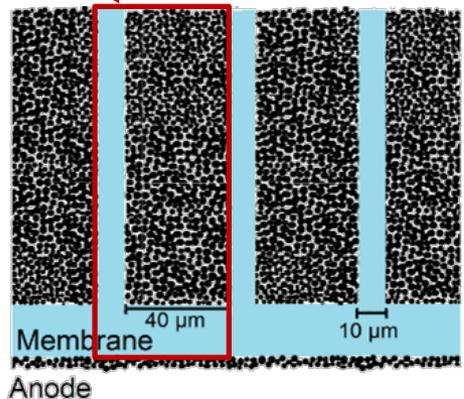
- Design of electrode structures with dedicated transport channels
  - PFSA-based channels for transport of  $H^+$
  - Carbon/PTFE-based channels for transport of  $O_2$
  - Electrodes with both types of transport channels
- Transport channels can be tailored to their specific transport function, and can provide non-tortuous pathways

# Milestones

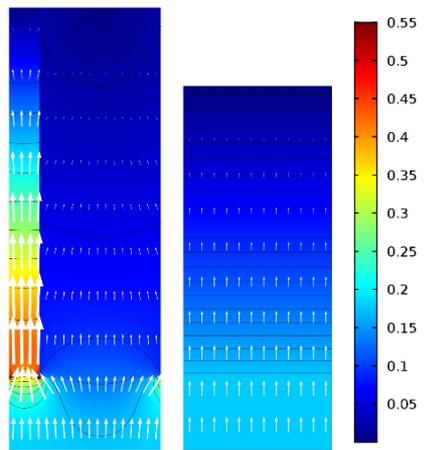
<b>12/18</b>	Fabricate H <sup>+</sup> channel electrodes and perform initial testing.	
<b>3/19</b>	Perform initial templated catalyst synthesis.	
<b>6/19</b>	Provide initial multiscale modeling results to guide electrode design.	
<b>9/19</b>	Demonstrate MEA performance of 0.025 A/cm <sup>2</sup> at 0.9 V H <sub>2</sub> /O <sub>2</sub> and 0.5 A/cm <sup>2</sup> at 0.67 V H <sub>2</sub> /air (150 kPa <sub>abs</sub> ) (Go/No-go)	
<b>12/19</b>	Demonstrate H <sup>+</sup> transport in catalysts without ionomer.	
<b>3/20</b>	Demonstrate ionomer channels that enable H <sup>+</sup> transport in electrodes with reduced ionomer content.	
<b>6/20</b>	Demonstrate multi channel electrode structures in MEA testing.	
<b>9/20</b>	Demonstrate MEA performance of 0.025 A/cm <sup>2</sup> at 0.9 V H <sub>2</sub> /O <sub>2</sub> and 0.75 A/cm <sup>2</sup> at 0.67 V H <sub>2</sub> /air (150 kPa <sub>abs</sub> ).	



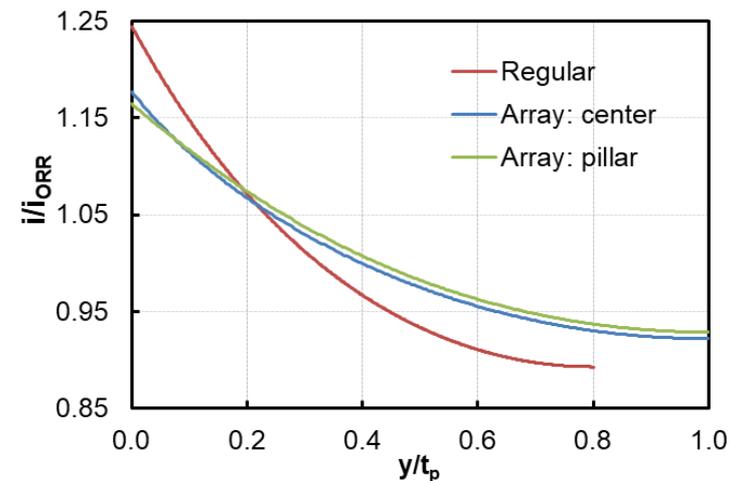
$$\sigma_i \frac{dV_i}{dy} = Vi/R_{ct}$$



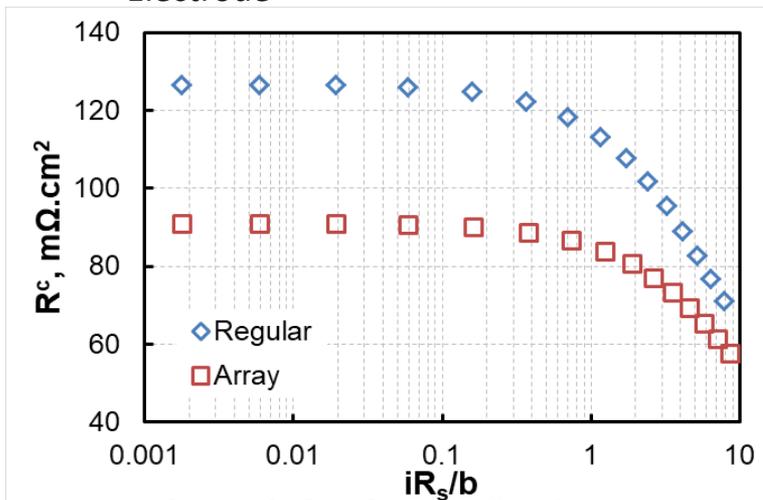
**Ionic Current Density,  $A \cdot cm^{-2}$**



Array Electrode      Baseline Electrode



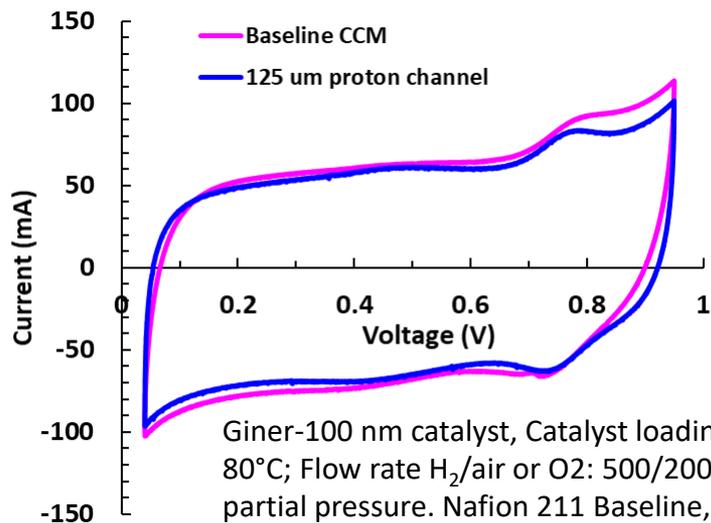
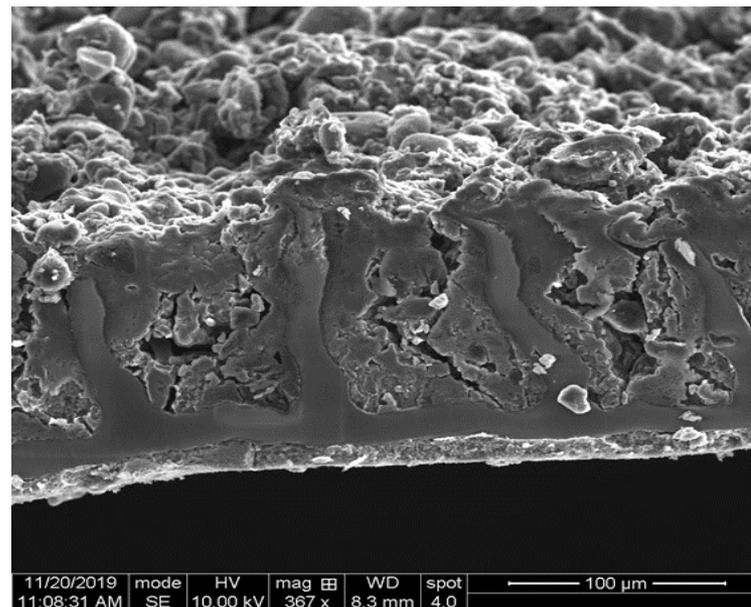
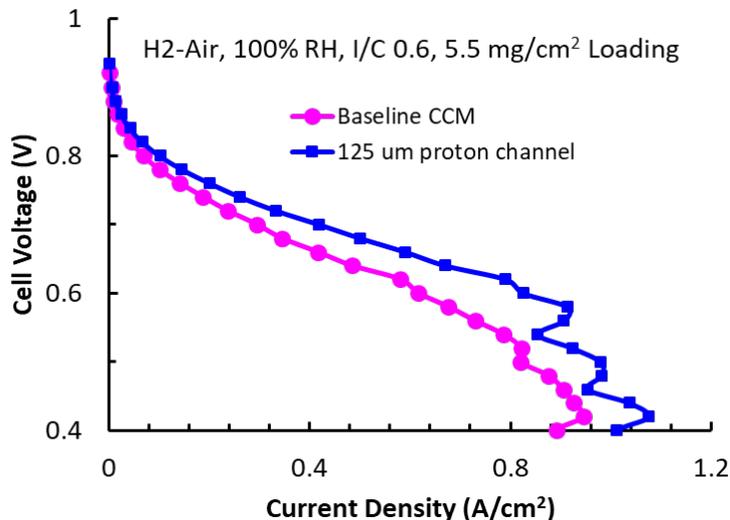
**Array electrode enables more uniform catalyst utilization**



**Array electrode has lower effective CCL resistance**

- Modeling suggests that accessible electrode approach can decrease effective CCL resistance and improve catalyst utilization
- Next step: optimize proton channel shape/size/spacing

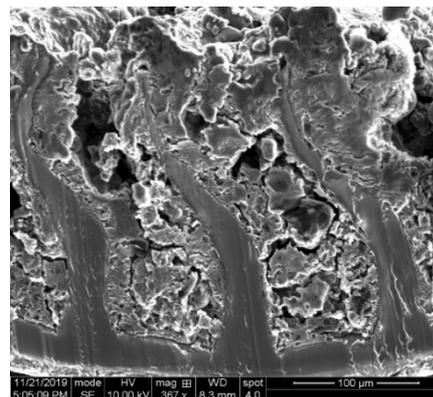
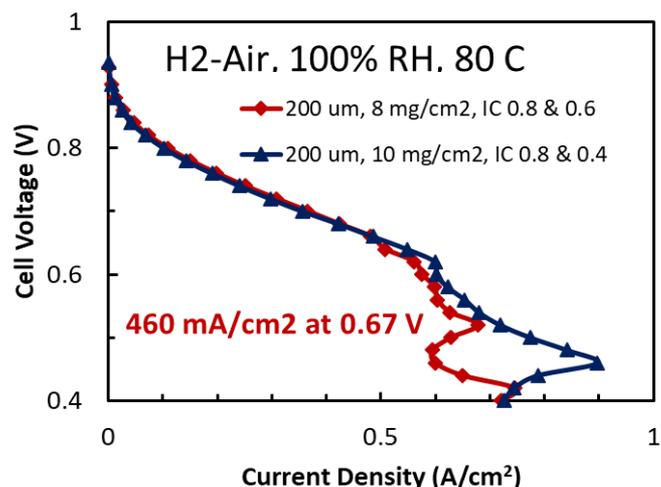
# Accomplishments and Progress: Proton Channels



Giner-100 nm catalyst, Catalyst loading: 5.5 mg/cm<sup>2</sup>, Cell temperature: 80°C; Flow rate H<sub>2</sub>/air or O<sub>2</sub>: 500/2000 sccm, RH: 100%, 1 bar H<sub>2</sub>/air or O<sub>2</sub> partial pressure. Nafion 211 Baseline, Nafion 212 for patterned membrane, \*Spray coated (1.5 mg/cm<sup>2</sup>) & Blade coated (4 mg/cm<sup>2</sup>)

- Baseline CCM: **385 mA/cm<sup>2</sup> at 0.67 V**, 290 mA/cm<sup>2</sup> at 0.7 V, 66 mA/cm<sup>2</sup> at 0.8 V
- Accessible Electrode: **545 mA/cm<sup>2</sup> at 0.67 V**, 420 mA/cm<sup>2</sup> at 0.7 V, 100 mA/cm<sup>2</sup> at 0.8 V

# Accomplishments and Progress: Increased Catalyst Loading



Carnegie  
Mellon  
University

UB  
University at Buffalo  
The State University of New York



Giner-100 nm catalyst, Cell temperature: 80°C;  
Flow rate H<sub>2</sub>/air or O<sub>2</sub>: 500/2000 sccm, RH: 100%,  
1 bar H<sub>2</sub>/air or O<sub>2</sub> partial pressure. Nafion 212+211  
for patterned membrane  
\*I/C 0.8 (spray coating) and 0.4 or 0.6 (blade  
coating)

- Increasing catalyst loading increases 0.9 V performance, but high-current performance suffers
- Next steps:
  - Tailor proton channel dimensions
  - Optimize I/C
  - Add O<sub>2</sub> channels

MEA performance, mA/cm<sup>2</sup>

	Baseline, 5.5 mg/cm <sup>2</sup> Aman12032019	Proton Channel, 5.5 mg/cm <sup>2</sup> Aman11072019	Proton Channel, 10 mg/cm <sup>2</sup> Aman11212019	Year 1 Target	Year 2 Target
0.67 V, air	385	545	460	500	750
0.7 V, air	290	420	360		
0.8 V, air	66	100	100		
0.9 V, O <sub>2</sub>		18	25	25	25

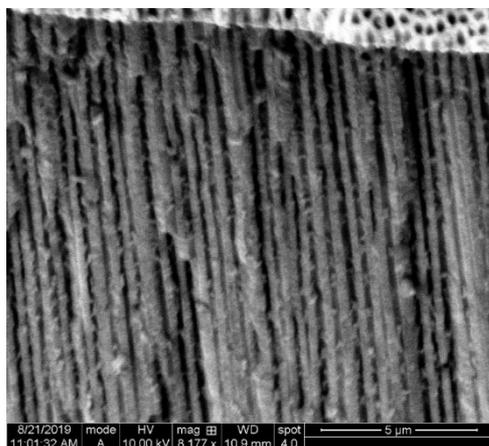
# Accomplishments and Progress: Tubular Structured Catalysts

Multiple techniques investigated for PANI-based catalyst synthesis using AAO templates:

- PANI hot-pressing into AAO template unsuccessful ❌
- Aniline coating onto untreated AAO template unsuccessful ❌
- Succeeded in making uniform PANI tubes using pre-silanization of template – this method down-selected for further development ✅

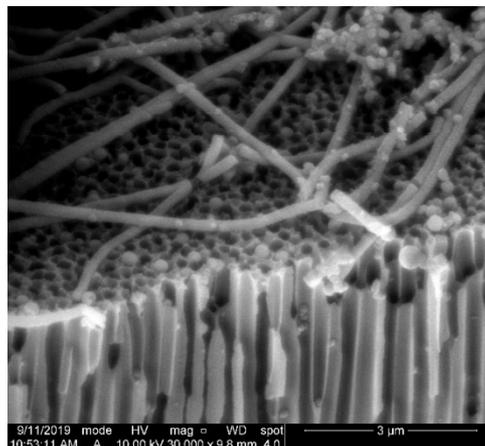
## Untreated AAO

Granular PANI  
inside AAO pores



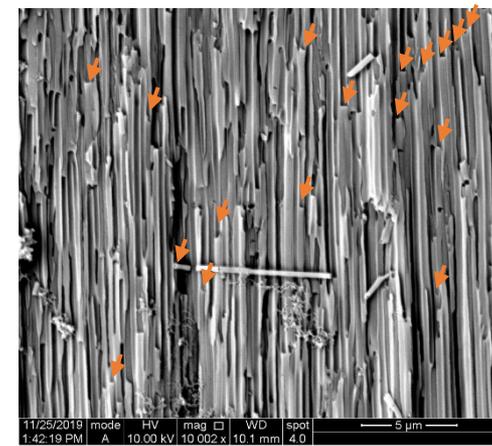
## Untreated AAO

PANI tubes outside AAO  
pores



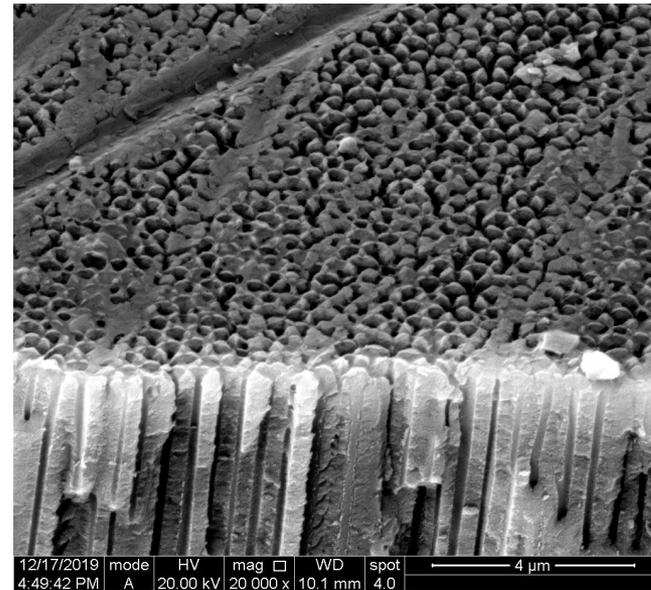
## Silanized AAO

Two-step oxidation  
PANI Tubes



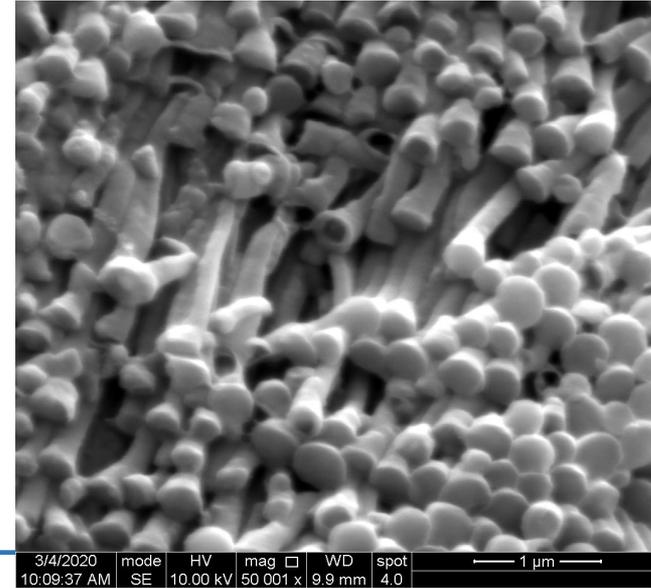
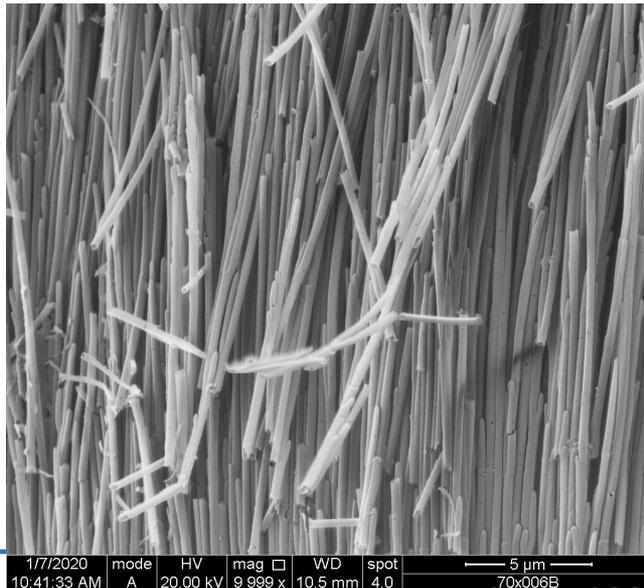
# Accomplishments and Progress: Tubular Structured Catalysts

- Heat treatment to form PGM-free catalyst within tubes
- Nafion impregnation into tubes (solution method better than hot pressing)
- Template dissolved to yield coaxial structure with PGM-free catalyst shell and Nafion core



Heat treated PGM-free catalyst tubes within AAO template

PGM-free catalyst tubes :  
AAO template dissolved @  
160 °C with  
85% H<sub>3</sub>PO<sub>4</sub>



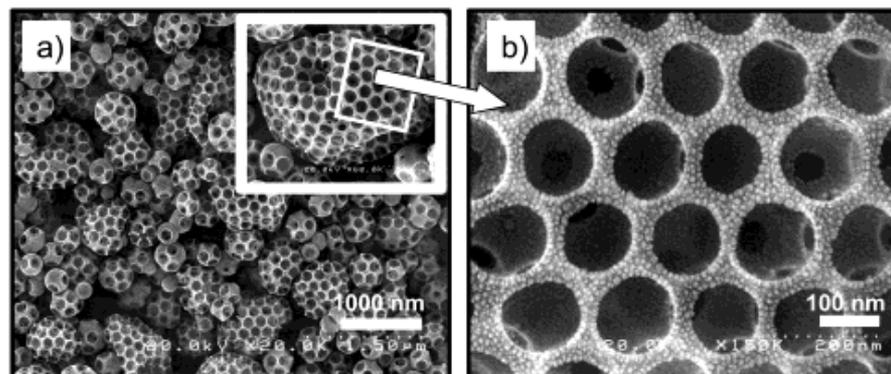
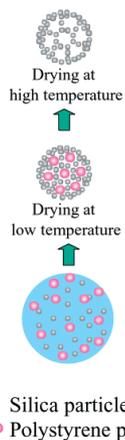
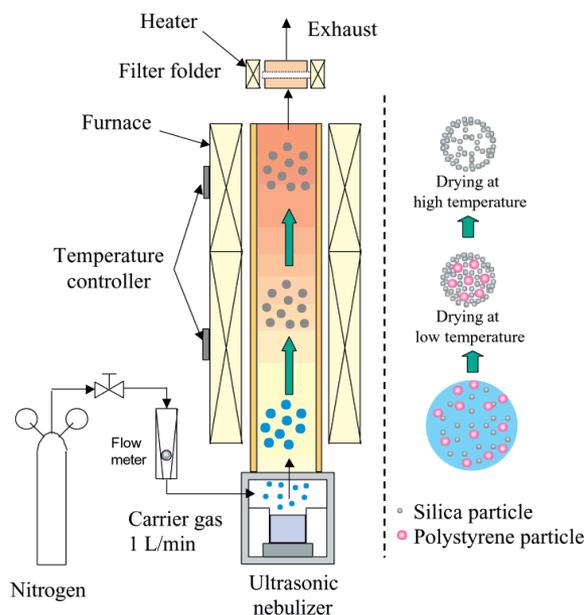
Nafion impregnated PANI tubes

# Next Steps: Tubular Structured Catalysts

- Activity testing of PGM-free catalyst tubes
  - Decrease pyrolysis temperature from 900 °C to 750 °C (Prevent conversion of AAO into stable  $\alpha$ -alumina)
  - Will enable more benign dissolution of AAO template (replace 85%  $\text{H}_3\text{PO}_4$  at 160°C with 10%  $\text{H}_3\text{PO}_4$  at room temperature)
- Nafion impregnation of active catalyst and incorporate electrode on a Nafion membrane
- Activity testing of spray-pyrolyzed hierarchical PGM-free catalysts and incorporation into MEA

# Next Steps: Hierarchical Templated Catalysts

- Next step for polystyrene/silica templating method: spray pyrolysis
  - Spraying the polystyrene/silica mixture into a controlled multi-zone temperature furnace has been used to create Silica nano-structures
  - Then use the silica templates to prepare PGM-free catalysts



Iskandar, Ferry, Mikrajuddin, and, and Kikuo Okuyama. "In situ production of spherical silica particles containing self-organized mesopores." *Nano Letters* 1.5 (2001): 231-234.

# 2019 Reviewer Comments

**“There was a lack of consideration of the catalyst.”**

During the past year we have tested accessible electrodes based on catalyst provided by five suppliers: Giner Inc. and University at Buffalo (in collaboration with the CMU ElectroCat FOA project), Pajarito Powder, the LANL core ElectroCat team, and our own LANL lab call team

**“The approach is based on catalyst and electrode structuring to improve transport in PGM-free electrodes. The project has little emphasis on catalyst synthesis.”**

Electrode development work began earlier in the project and is farther ahead, but catalyst development work has ramped up in FY20

# Collaboration and Coordination

- **University of Connecticut**
  - This project supports a UConn Ph.D. student for R&D on accessible electrodes. The student works full time at LANL.
- This project collaborates with multiple catalyst developers. Partners provide catalyst, our team incorporates the catalyst in accessible electrodes, and we provide characterization, performance, and durability data in return. Partners include:
  - **Giner Inc. (CMU ElectroCat FOA project)**
  - **University at Buffalo (CMU ElectroCat FOA project)**
  - **Pajarito Powder LLC**
  - **LANL core ElectroCat team**
- **ANL**
  - Modeling of transport and MEA performance using accessible electrode designs

# Remaining Challenges and Barriers

- Fabricating accessible electrode structures with high design fidelity
  - Significant progress made in FY20 on improved electrode fabrication, but further work required to maximize transport enhancements
- Synthesizing PGM-free catalysts with high nanoscale accessibility
  - Synthetic challenges remain for making hierarchical structured catalyst with long range order based on silica/polystyrene templates
  - Nanotubular catalysts based on AAO templates need further development for high activity and accessibility

# Proposed Future Work

- Further improve design fidelity for proton channel, oxygen channel, and multichannel electrodes
- Demonstrate further performance improvement at high and low current through achievement of improved transport in high-loaded electrodes
- Further develop accessible PGM-free catalysts based on silica/polystyrene templates and AAO templates
- Perform MEA testing of accessible PGM-free catalysts
- Continue modeling of transport and kinetics in accessible electrodes

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

# Technology Transfer Activities

- LANL team works with Feynman Center for Innovation on IP protection

# Summary

- Objective:** Design accessible PGM-free catalysts and electrodes with facile transport of H<sup>+</sup> and O<sub>2</sub>, and demonstrate in high-performance, durable MEAs.
- Relevance:** Project directly addresses cost, durability, and performance through key DOE targets:
- MEA performance > 44 mA/cm<sup>2</sup> @ 0.9 V<sub>iR-free</sub>, H<sub>2</sub>/O<sub>2</sub>, 150 kPa<sub>abs</sub>
  - MEA performance > 300 mA/cm<sup>2</sup> @ 0.8 V, H<sub>2</sub>/air, 150 kPa<sub>abs</sub>
  - Power density > 1 W/cm<sup>2</sup>
  - Cost < \$40/kW (near-term), < \$30/kW (ultimate)
- Approach:** Develop PGM-free electrodes with rapid micron-scale transport of O<sub>2</sub> and H<sup>+</sup> using non-tortuous transport channels and control of local hydrophobicity/hydrophilicity. Develop PGM-free catalysts with rapid nanometer-scale transport of O<sub>2</sub> and H<sup>+</sup> through control of nanostructure, including metal site clustering and particle agglomeration
- Accomplishments:** Advanced electrode designs developed in this project have enabled improved transport, resulting in power density as high as 545 mA/cm<sup>2</sup> at 0.67 V. Transport and kinetic modeling has guided electrode design work. Proof-of-concept accessible catalyst structures have been developed.
- Collaborations:** Extensive collaboration and utilization of ElectroCat consortium capabilities