Accessible PGM-free Catalysts and Electrodes

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Los Alamos National Laboratory

Project ID FC318

May 30, 2020

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)

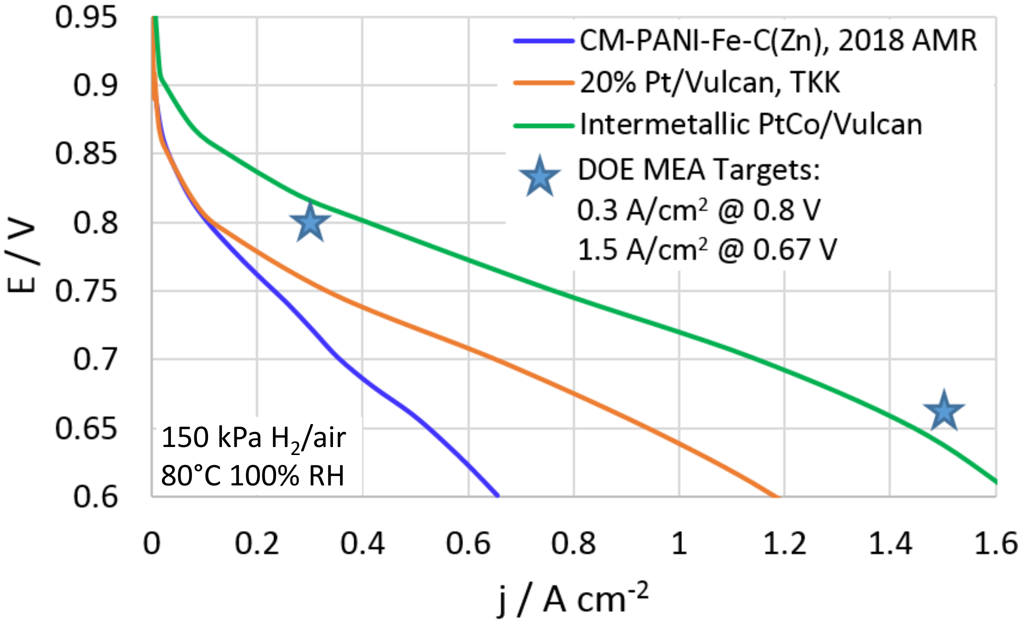
Barriers

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)

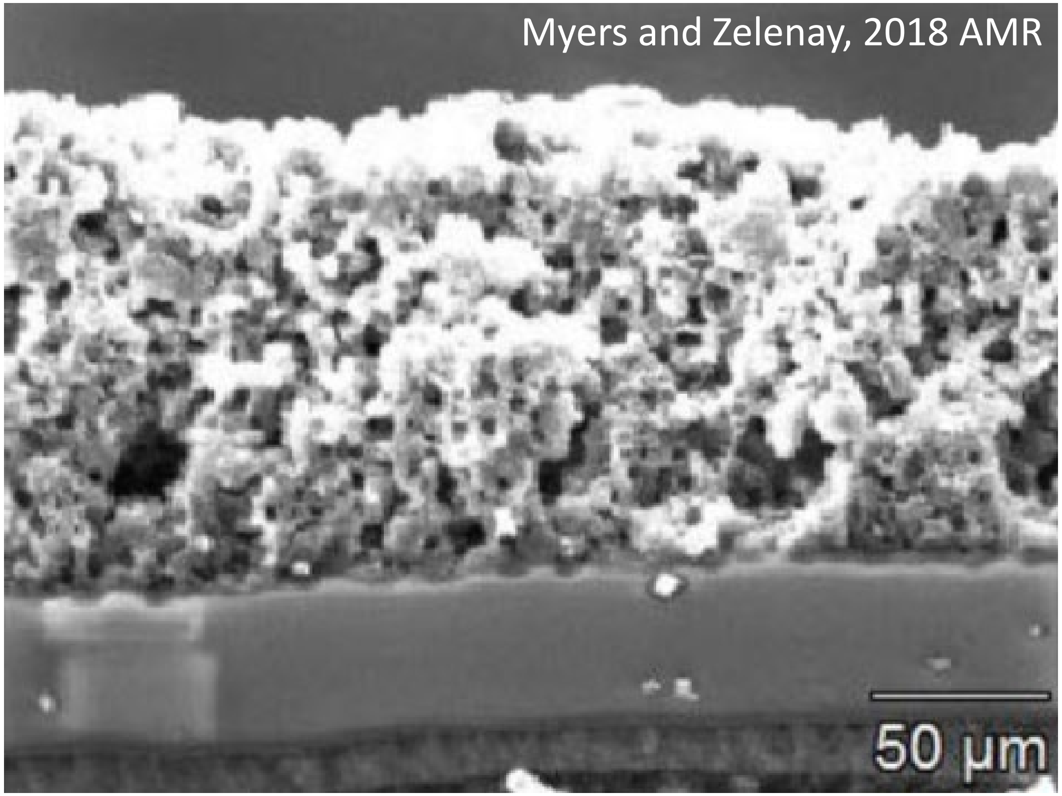
Relevance



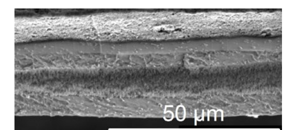
PGM-free at 0.67 V: **0.31 W/cm²**
DOE MEA target: **1 W/cm²**
Future MEA target: **1.5 W/cm²?**

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

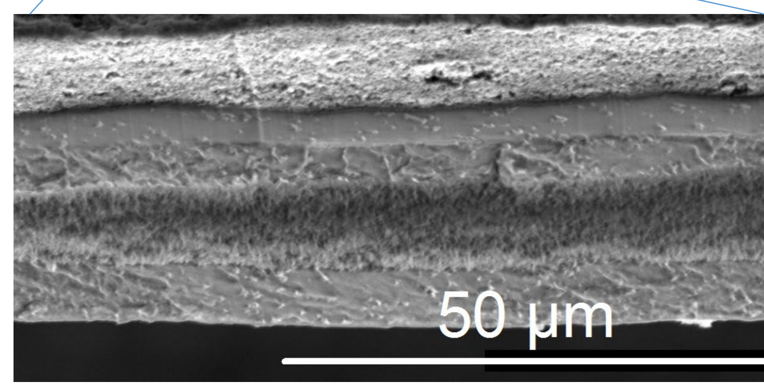
Background: Cathode Structure



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



PGM Cathode
[TEC10E40E]



PGM-free cathode is much thicker and coarser

O_2 Transport Limitations

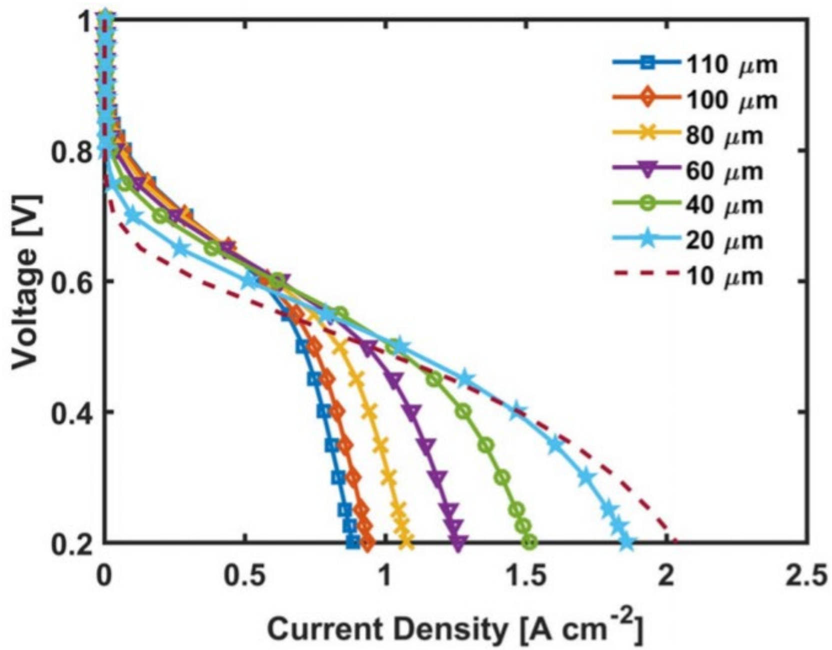


Figure 9. Effect of thickness on the 50 wt% Nafion loading CM-PANI-Fe electrode. The simulation was run at 80°C and 100% RH H_2 and air feed gas at 1 atm partial pressure.

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

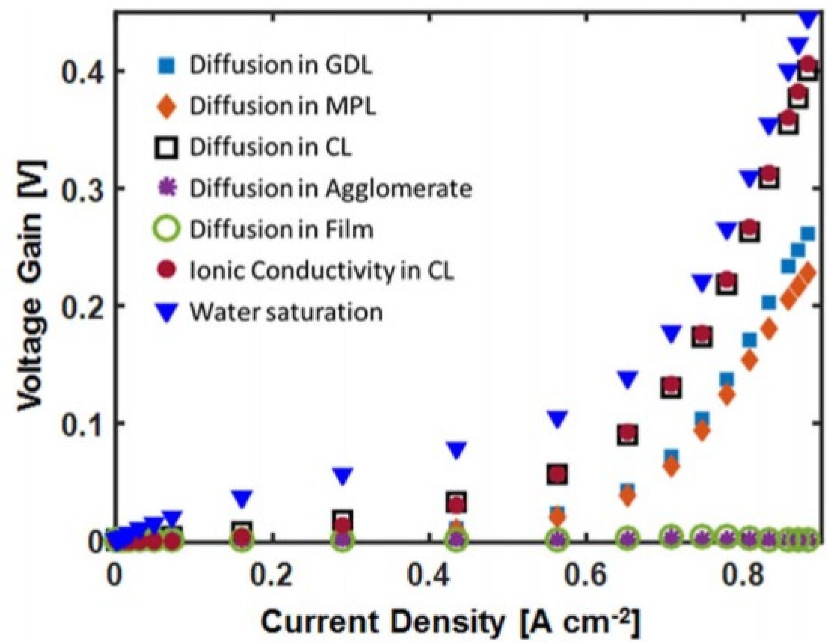


Figure 6. Voltage gain due to different resistance in the electrode for the 50 wt% Nafion electrode. The model was run with H_2 and air fully humidified gas at 80°C and 1 atm partial pressure.

- 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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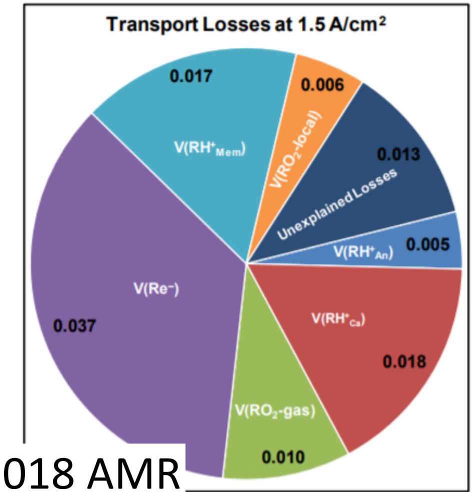
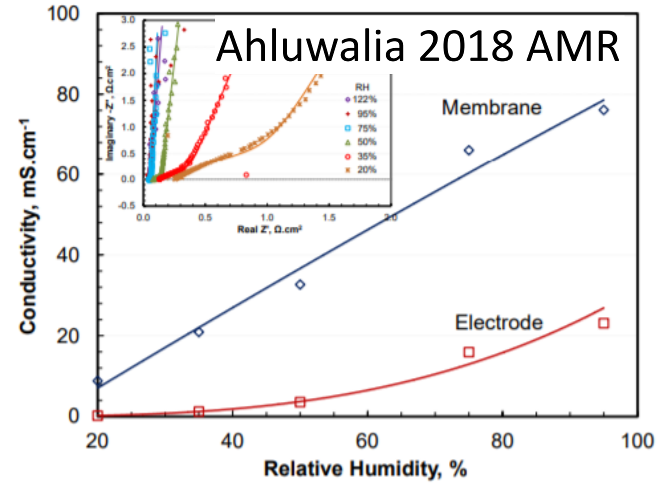
H^+ Transport Limitations

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



Kumaraguru 2018 AMR



- 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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Approach

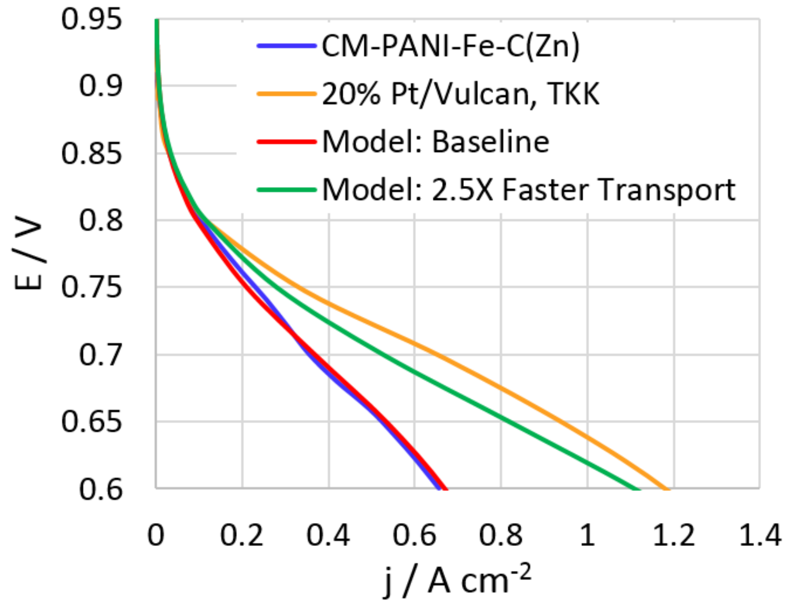
Develop PGM-free <u>MEAs</u> with facile transport of O_2, H^+, H_2O, and e^- at

- **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

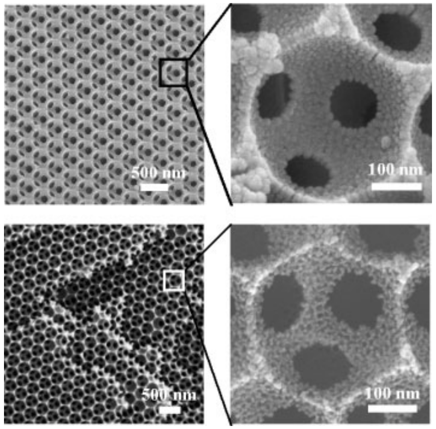
Objective: *create innovative catalyst and electrode structures that enable PGM-free electrodes to have high-current performance approaching that of PGM-based electrodes*



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

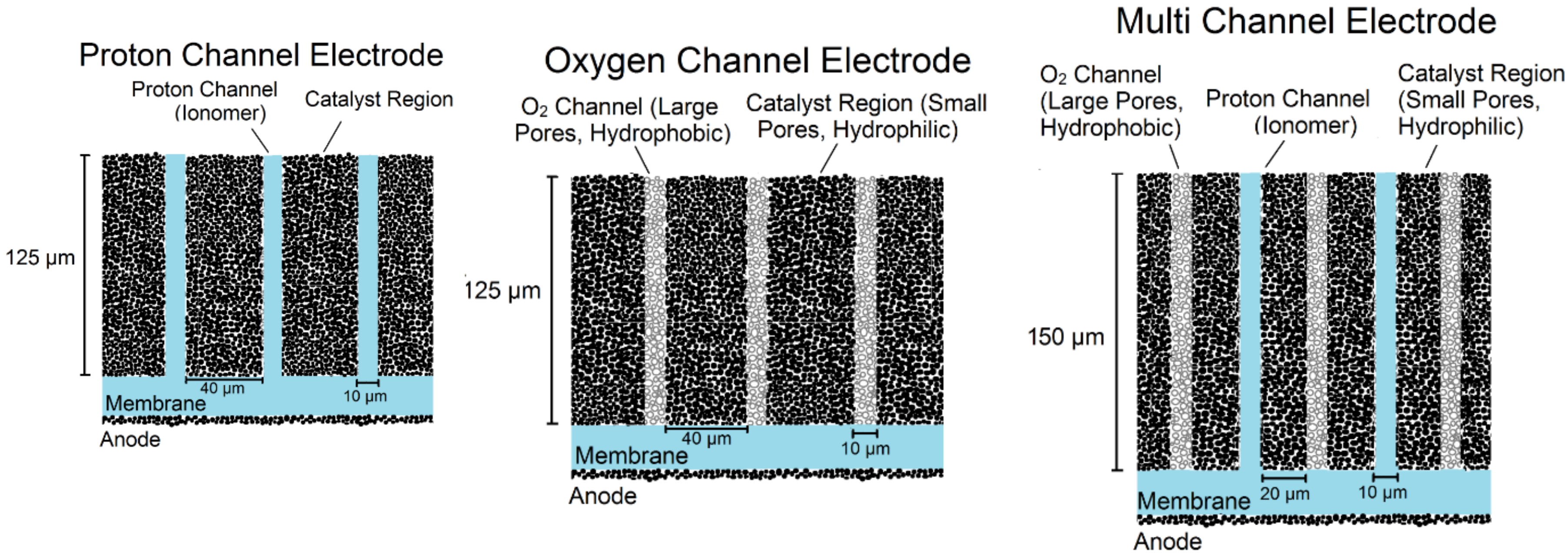
Approach: Accessible Catalysts

- 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



- 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

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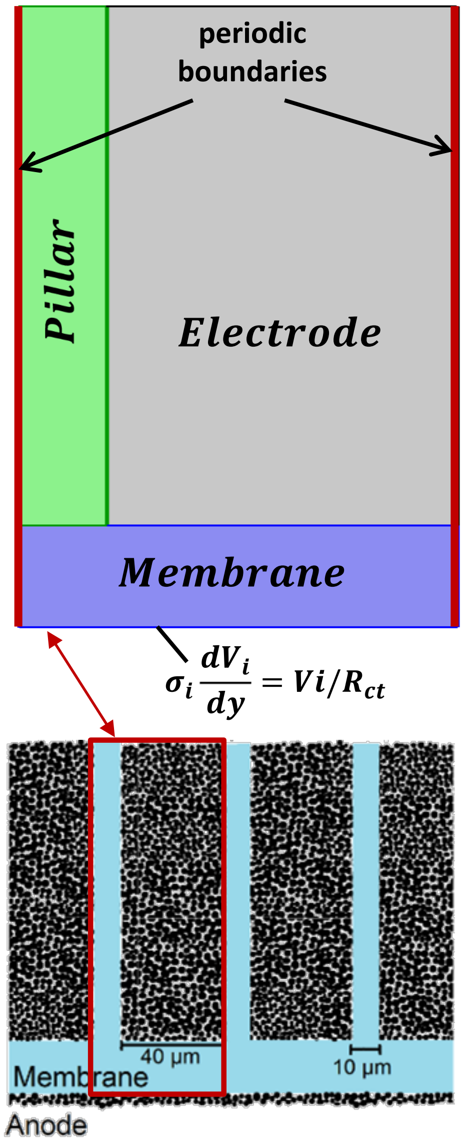
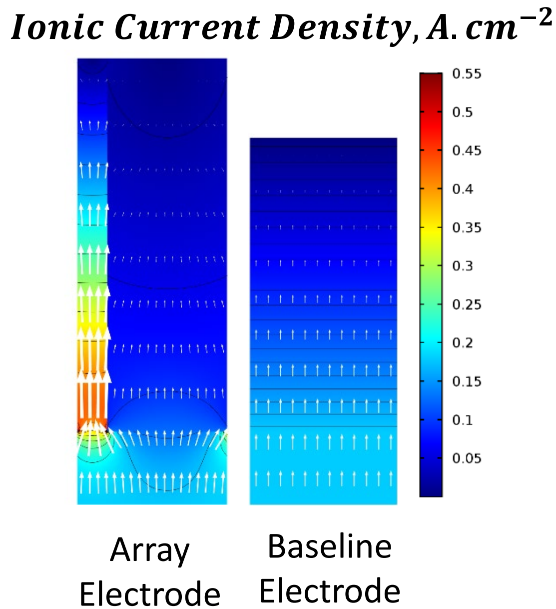
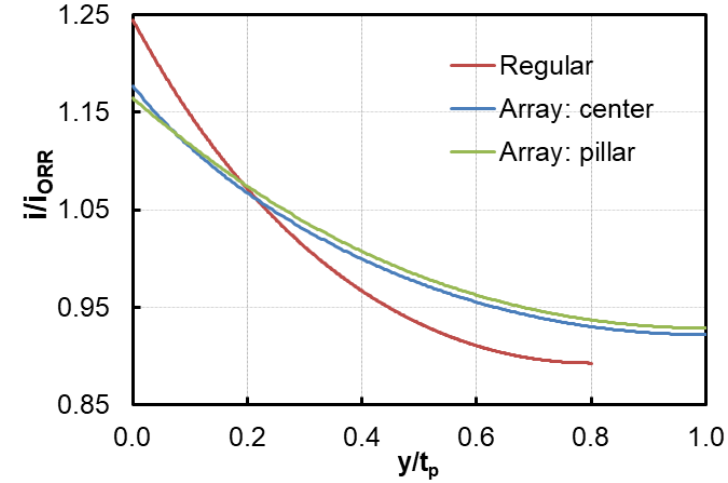
Milestones

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)
12/19	Demonstrate H^+ transport in catalysts without ionomer.
3/20	Demonstrate ionomer channels that enable H^+ transport in electrodes with reduced ionomer content.
6/20	Demonstrate multi channel electrode structures in MEA testing.
9/20	Demonstrate MEA performance of 0.025 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$_{abs}$).

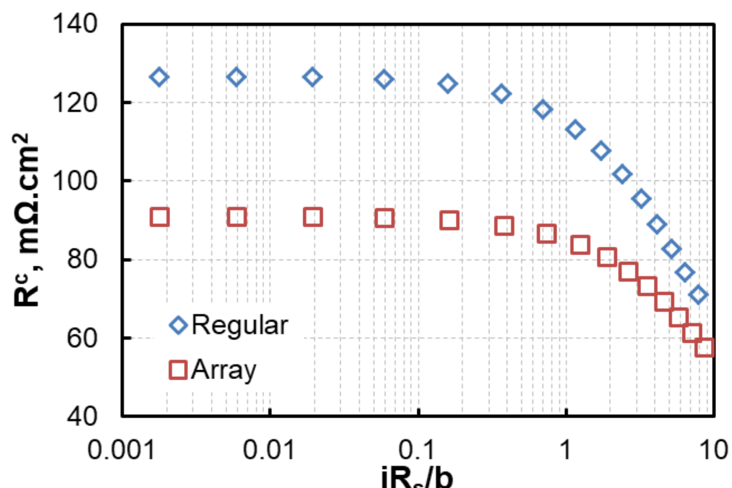
Accomplishments and Progress: Accessible Electrode Modeling







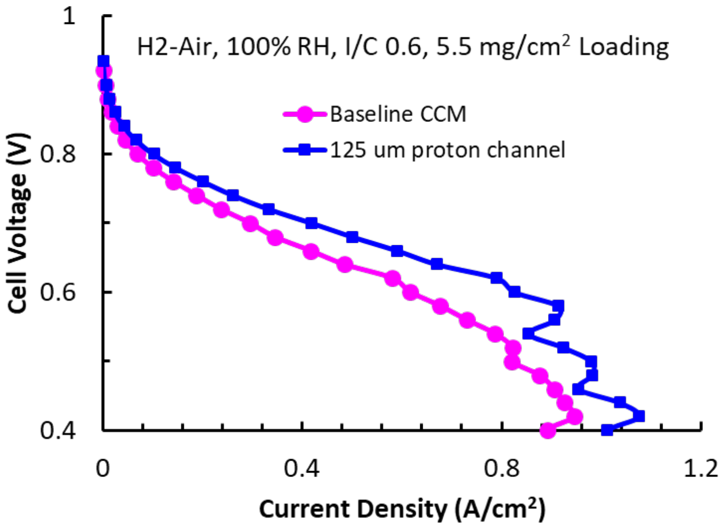
Array electrode enables more uniform catalyst utilization

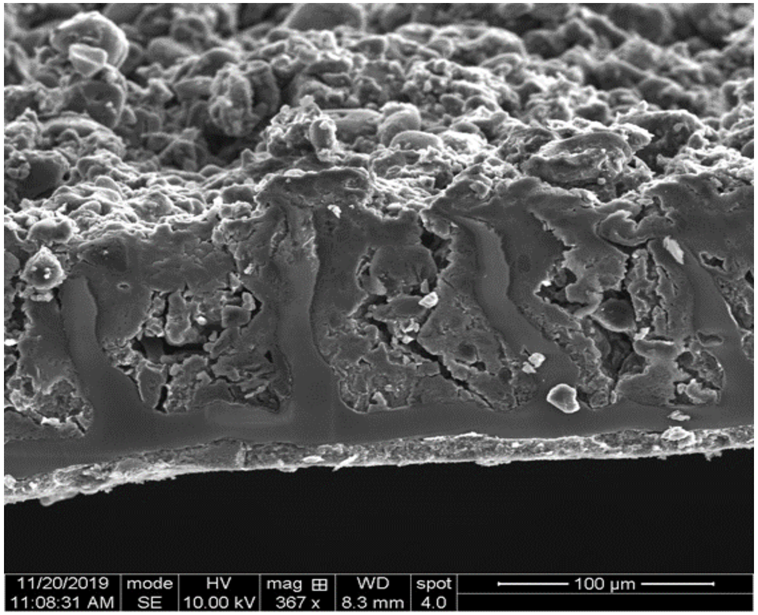


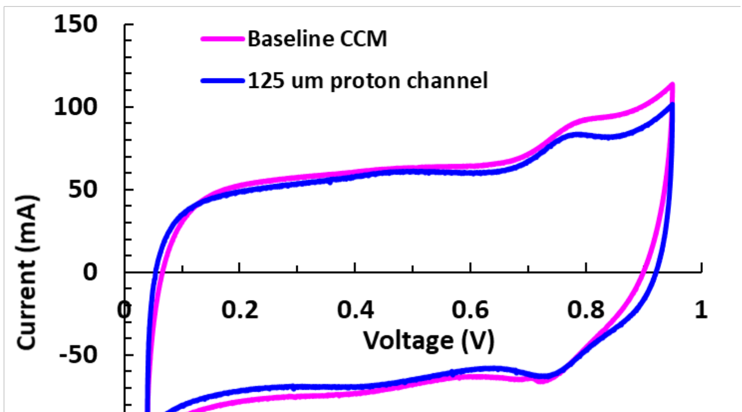
Array electrode has lower effective CCL resistance

- **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







- Baseline CCM: **385 mA/cm² at 0.67 V**, 290 mA/cm² at 0.7 V, 66 mA/cm² at 0.8 V
- Accessible Electrode: **545 mA/cm² at 0.67 V**, 420 mA/cm² at 0.7 V, 100 mA/cm² at 0.8 V

Giner-100 nm catalyst, Catalyst loading: 5.5 mg/cm², Cell temperature: 80°C; Flow rate H_2/air or O2: 500/2000 sccm, RH: 100%, 1 bar H_2/air or O2 partial pressure. Nafion 211 Baseline, Nafion 212 for patterned membrane, *Spray coated (1.5 mg/cm2) & Blade coated (4 mg/cm2)

Carnegie Mellon University
University at Buffalo The State University of New York
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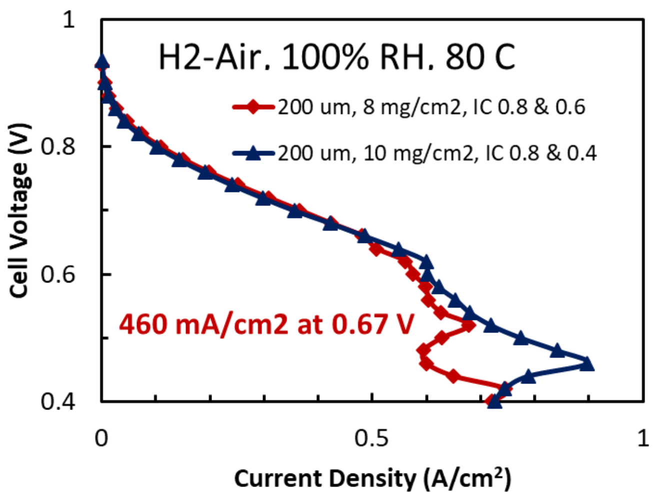
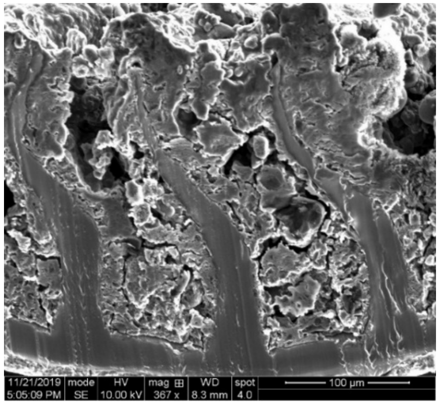
Accomplishments and Progress: Increased Catalyst Loading



Giner-100 nm catalyst, Cell temperature: 80°C; Flow rate H_2/air or O2: 500/2000 sccm, RH: 100%, 1 bar H_2/air or O2 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_2 channels**

MEA performance, mA/cm^2

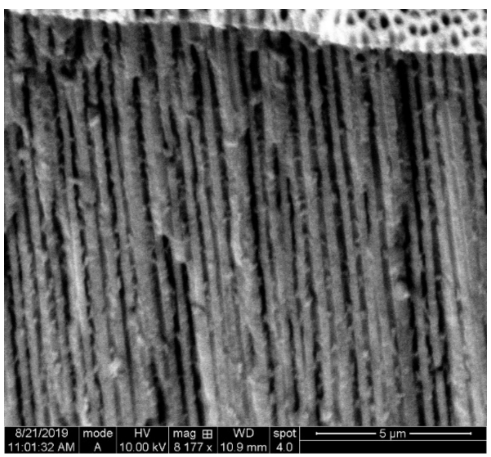
	Baseline, 5.5 mg/cm² Aman12032019	**Proton Channel, 5.5 mg/cm² Aman11072019**	**Proton Channel, 10 mg/cm² Aman11212019**	**Year 1 Target**	**Year 2 Target**
0.67 V, air	385	545	460	500	750
0.7 V, air	290	420	360		
0.8 V, air	66	100	100		
0.9 V, O2		18	25	25	25

Accomplishments and Progress: Tubular Structured Catalysts

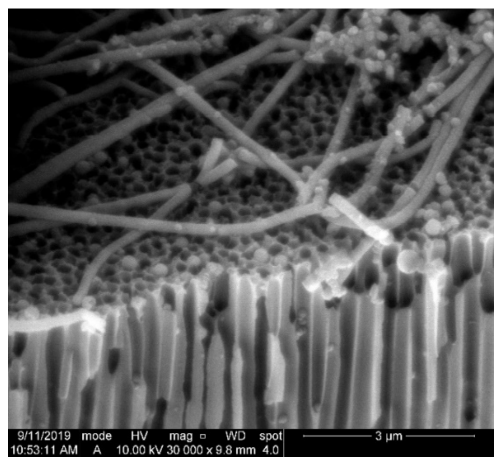
Multiple techniques investigated for PANI-based catalyst synthesis using AAO templates:

- 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 ☑

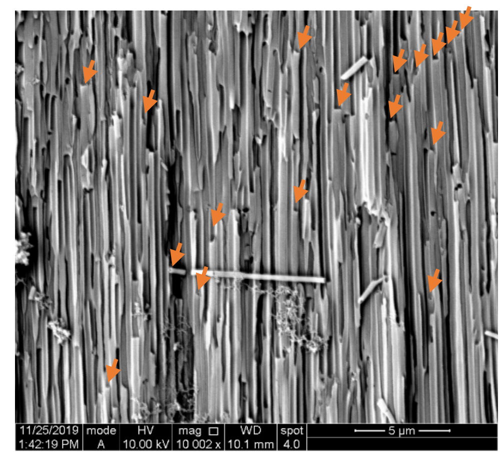
Untreated AAO
Granular PANI inside AAO pores



Untreated AAO
PANI tubes outside AAO pores



Silanized AAO
Two-step oxidation PANI Tubes



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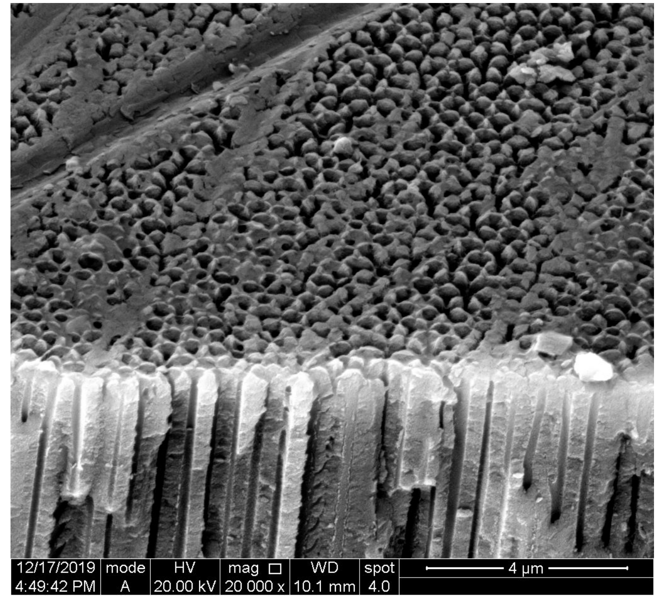
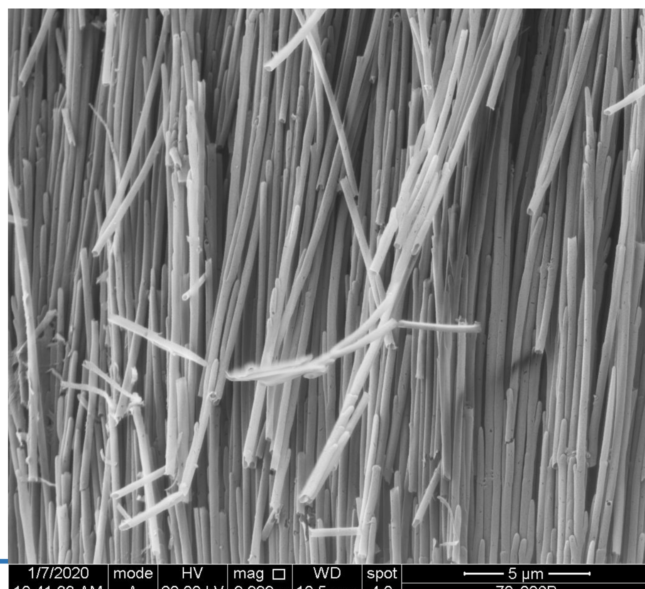
Accomplishments and Progress: Tubular Structured Catalysts

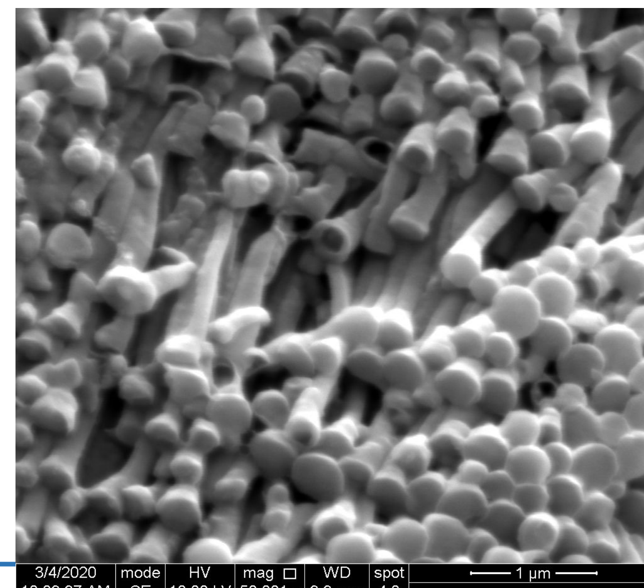
- Heat treatment to form PGM-free catalyst within tubes
- Nafion impregnation into tubes (solution method better than hot pressing)
- Template dissolved to yield coaxial structure with PGM-free catalyst shell and Nafion core



Heat treated PGM-free catalyst tubes within AAO template

PGM-free catalyst tubes : AAO template dissolved @ 160 ^{o}C with 85% H_3PO_4





Nafion impregnated PANI tubes

Next Steps: Tubular Structured Catalysts

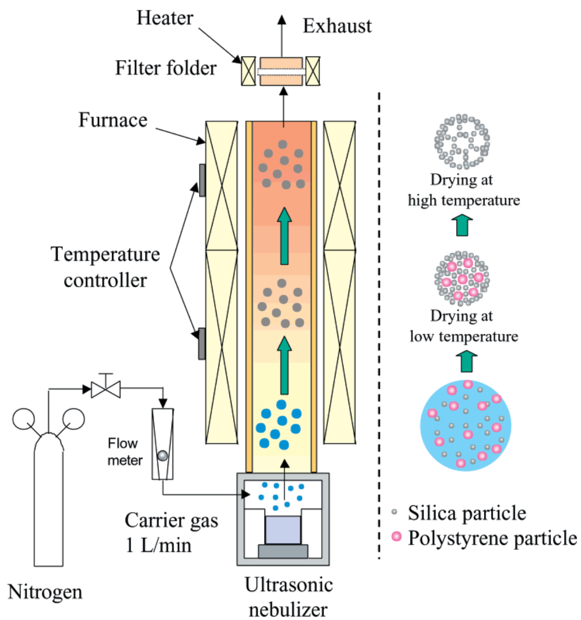
- Activity testing of PGM-free catalyst tubes
  - Decrease pyrolysis temperature from 900 ^{o}C to 750 ^{o}C (Prevent conversion of AAO into stable α-alumina)
  - Will enable more benign dissolution of AAO template (replace 85% H_3PO_4 at 160^{o}C with 10% H_3PO_4 at room temperature)

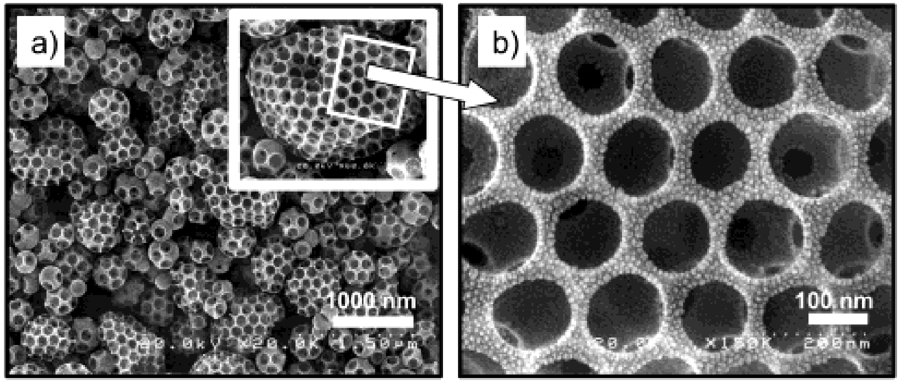
- Nafion impregnation of active catalyst and incorporate electrode on a Nafion membrane

- 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

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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 rang 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 catalyts
- 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^+ 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: Advanced electrode designs developed in this project have enabled improved transport, resulting in power density as high as 545 mA/cm2 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