Stationary Direct Methanol Fuel Cells Using Pure Methanol

PI and presenter: Xianglin Li / University of Kansas

Co-PI: Gang Wu/ University at Buffalo

Co-PI: Jun Li / Kansas State University

Co-PI: Shawn Litster / Carnegie Mellon University

Date: April 29, 2019

2019 DOE Hydrogen and Fuel Cells Program Review **Project ID # FC317**

Overview

Timeline

- **Project Start Date: 10/01/2018**
  - ***BP1: 10/1/2018 - 12/31/2019***
  - ***BP2: 1/1/2020 - 12/31/2020***
  - ***BP3: 1/1/2021 - 12/31/2021***
- **Effective Project Start Date: 01/03/2019**
- **Project End Date: 12/31/2021**

Budget

- **Total Project Budget: $ 1,249,449**
  - ***Recipient Share: $ 250,050***
  - ***Federal Share: $ 999,399***
- **Planned funding for Budget Period 1: $ 469,489**
- **Total DOE Funds Spent*: $ 13,283.93**

*** As of 3/1/2019**

Barriers Addressed

- **High platinum group metals (PGM) catalyst loading**
- **Catalyst poisoning by methanol**
- **High fuel crossover**

Partners

PI : Xianglin Li

University of Kansas (KU)

Co-PI: Gang Wu

University at Buffalo (UB)

Co-PI: Jun Li

Kansas State University (KSU)

Co-PI: Shawn Litster

Carnegie Mellon University (CMU)

Relevance/Impact

- **Objectives: The goal of this collaborative research is to develop stationary direct methanol fuel cells (DMFCs) using pure methanol as the fuel.**
- **Three critical challenges from material to system levels:**
  - **(1) Reduce noble catalyst loading and cost;**
  - **(2) Enhance cathode tolerance of methanol poisoning;**
  - **(3) Decrease methanol crossover.**
- **End of the Project Goal: The MEA and prototype delivered at the end of the project (50 cm^2 MEA) will produce peak power density of ≥ 300 mW/cm^2 with total loading of ≤ 3 $mgPGM/cm^2$.**
- **1^{st} BP target (10/1/2018 - 12/31/2019): The fuel cell prototype to be delivered at the first year (25 cm^2 MEA) will meet the milestone of ≥ 250 mW/cm^2 with 4 $mgPGM/cm^2$.**

Approach

This research integrates complementary *institutional expertise* on

- **Platinum group metals free (PGM-free) cathode catalyst (UB);**
- **Supported anode catalysts (KSU);**
- **Electrode fabrication, characterization, and optimization (CMU);**
- **Multi-phase mass transfer (KU):**

to

(1) Reduce noble catalyst loading and cost;

(2) Enhance cathode tolerance of methanol poisoning;

(3) Decrease methanol crossover.

The technical progress made by the H_2 fuel cell R&D greatly benefit this project:

- **The fabrication of advanced catalyst support materials;**
- **The design and development of PGM-free catalysts;**
- **The capability of electrode characterization and fabrication;**
- **The understanding of liquid-vapor mass transfer in porous electrodes.**

Approach

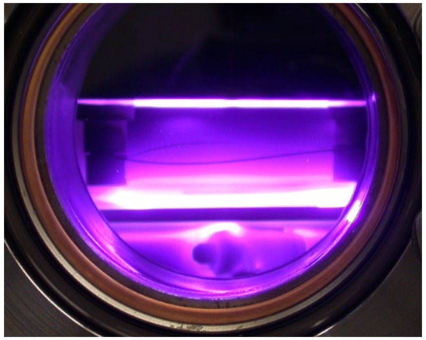
The planned milestones and Go/No-Go decisions for FY19

	Milestone Description	Status
Q1	Develop a testing platform to control fuel cell temperature, fuel and cathode flow rates, and relative humidity (KU). Develop a system to sputter PtRu onto VACNFs and evaluate catalytic activities using RDE (KSU). Develop a system to synthesize PGM-free cathode catalysts and evaluate catalytic activities using RDE (UB). Set up the sample preparation system, MicroCT facility, and data processing platform. (CMU)	100% completion
Q2	The fuel cell with commercial MEAs achieves about 125 mW/cm^2 peak power density with >3.0 M methanol solution (KU). Reconstruct nano-CT images of commercial electrodes (CMU). Establish correlation of RDE activity of pre-screened catalysts and MEA performance for DMFC (UB).	50% completion
Q3	Synthesize catalyst with $E_{1/2}$>0.80 V using dilute methanol solution (UB). Synthesize PtRu catalyst on VACNFs and evaluate its anodic MOR catalytic activity in dilute methanol solution (KSU). Incorporate customized anode and cathode catalysts into electrodes and generate nano-CT images of electrodes (CMU). The fuel cell with customized MEAs achieves a peak power of 175 mW/cm^2 with >3.0 M methanol solutions (KU&CMU).	20% completion
Q4	Go/No-GO Single cells with customized MEAs achieve a peak power of ≥ 250 mW/cm^2 with ≤4 mg_{PGM}/cm^2 using >3.0 M methanol solution.	10% completion

This project was not reviewed last year

Accomplishments and Progress – Anode Catalyst Support

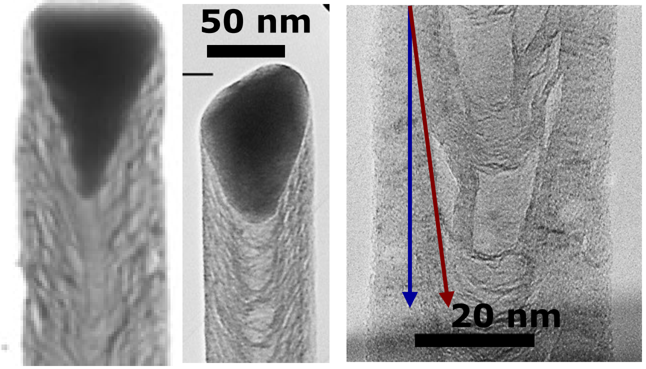
NH_3, C_2H_2



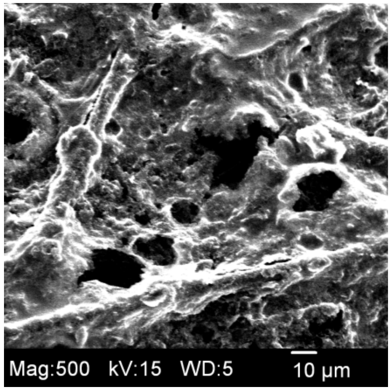
DC-biased Plasma Enhanced CVD (PECVD)

600-800°C

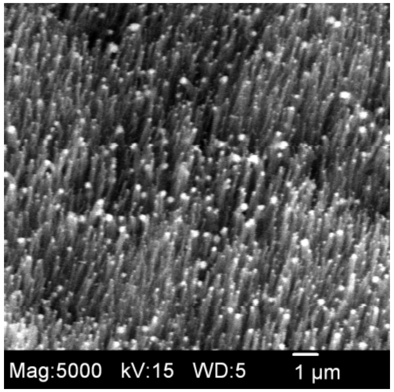
Carbon Nanofibers



Depending upon growth conditions, cone angles can vary between 5-30°.

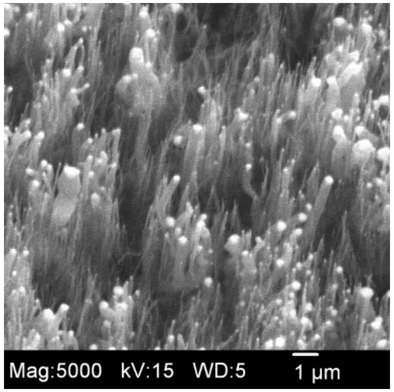


Bare AvCarbEP40T (0.2 mm thick, 13 wt%PTFE)



PECVD Growth of Vertically Aligned Carbon Nanofiber (VACNT) on AvCarbEP40T after 30 min.

&

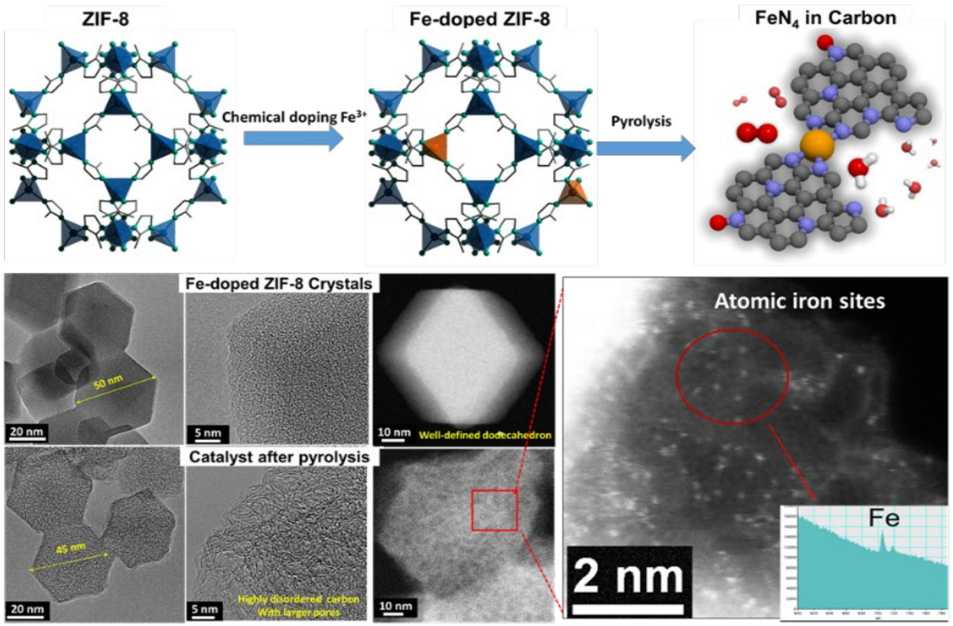


PECVD Growth of VACNT on AvCarbAvCarb P50 after 30 min.

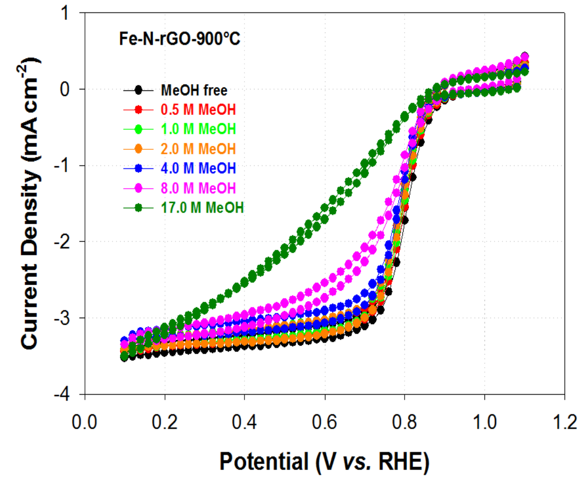
Initial VACNF growth was successful on several carbon cloth/paper with and without PTFE treatment.

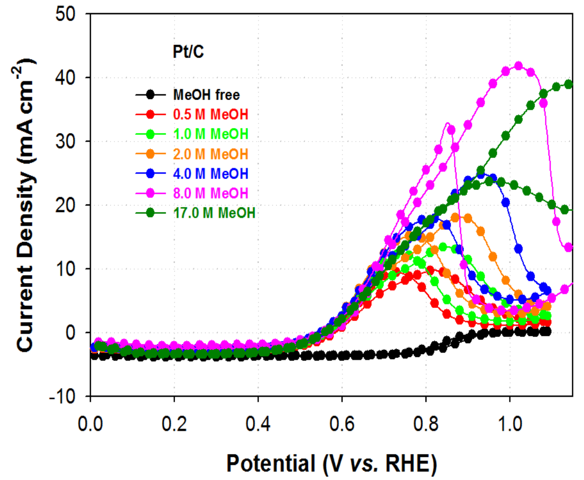
This project was not reviewed last year

Accomplishments and Progress – Cathode Catalysts

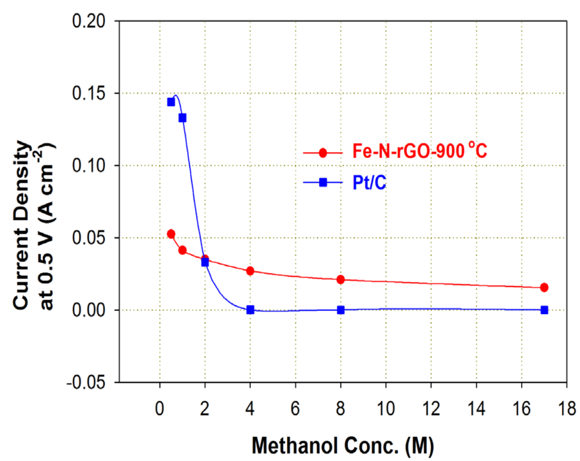


Fe-based PGM-free ORR catalysts



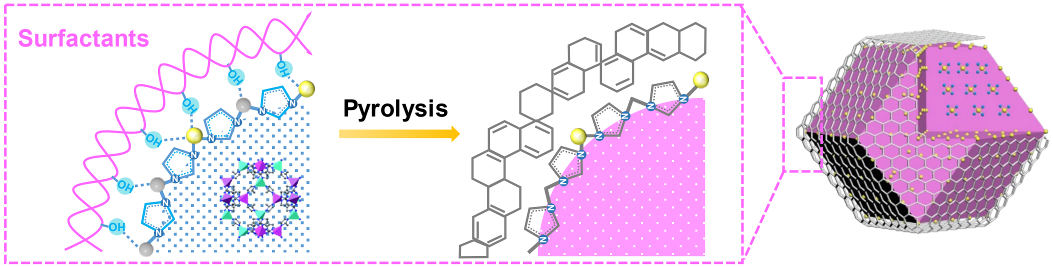


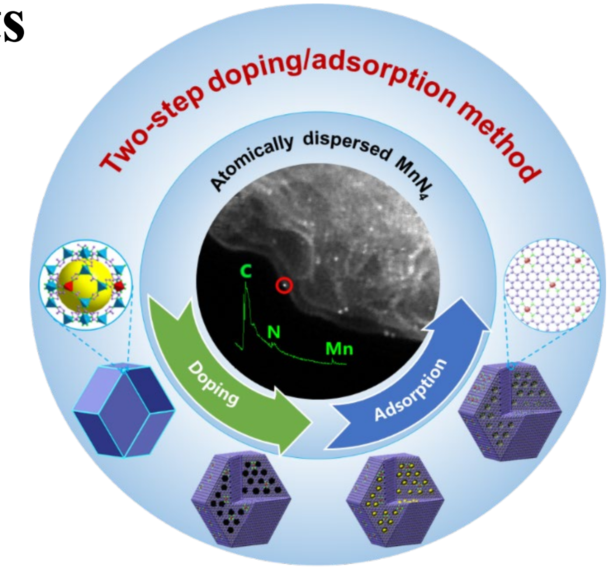
Fe-based PGM-free ORR catalysts show excellent methanol tolerance.

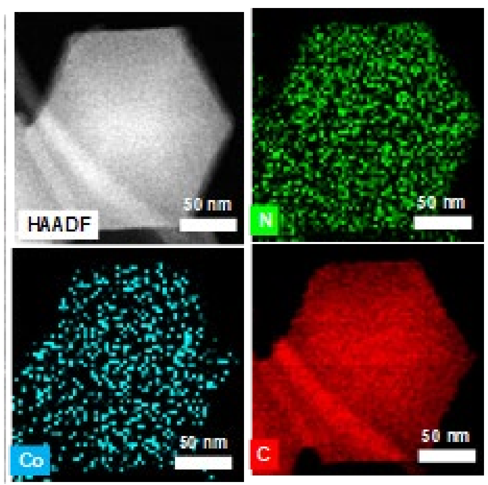


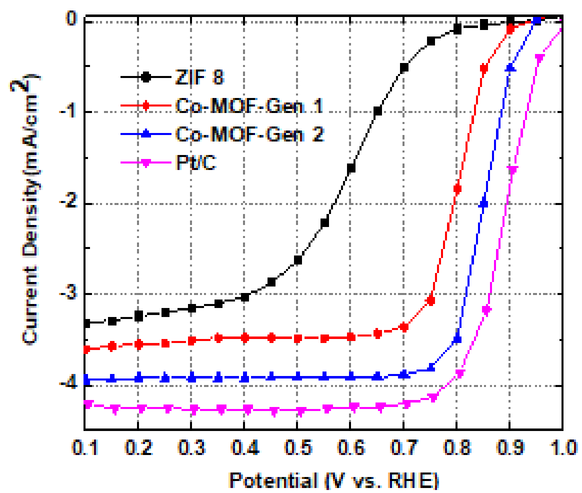
This project was not reviewed last year

Accomplishments and Progress
– Cathode Catalysts

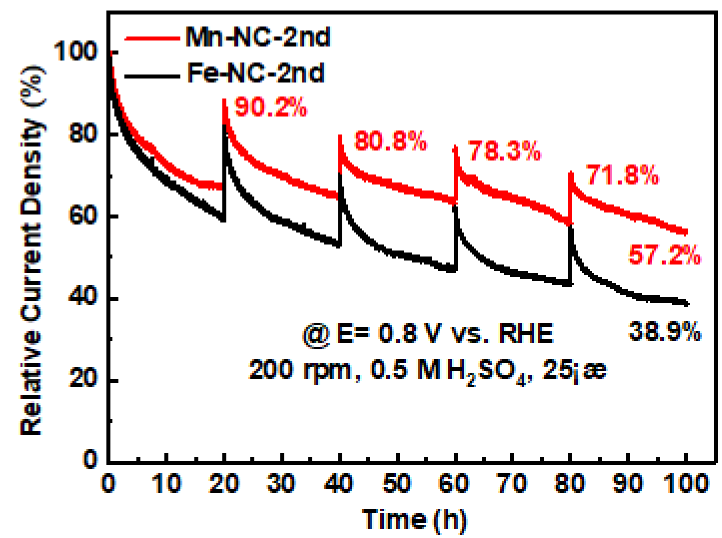








Co-based PGM-free ORR catalysts



Mn-based PGM-free ORR catalysts

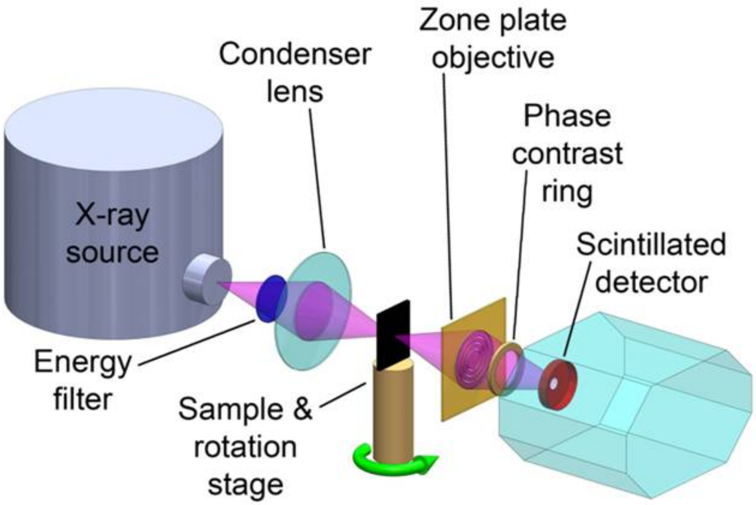
High-performance PGM-free and Fe-free catalysts show enhanced performance and stability

This project was not reviewed last year

Carnegie Mellon University

Accomplishments and Progress – Electrode Characterization

Xradia UltraXRM-L200 nano-CT



Schematic representation of nano-CT

- Two levels of resolution- (a) 50 nm resolution (16 nm pixels) for a 16 µm field of view & (b) 150 nm resolution (65 nm pixels) for a 65 µm field of view;
- Conventional absorption contrast imaging mode at 8 keV to generate the contrast by the X-ray absorptivity of the sample (a function the local atomic number and density)
- Zernike phase contrast mode to enhance imaging of low-contrast, soft materials (e.g., carbon and organic materials) with low Z.

The research team has a unique Nano-CT to measure the detailed pore-scale structures of fuel cell electrodes.

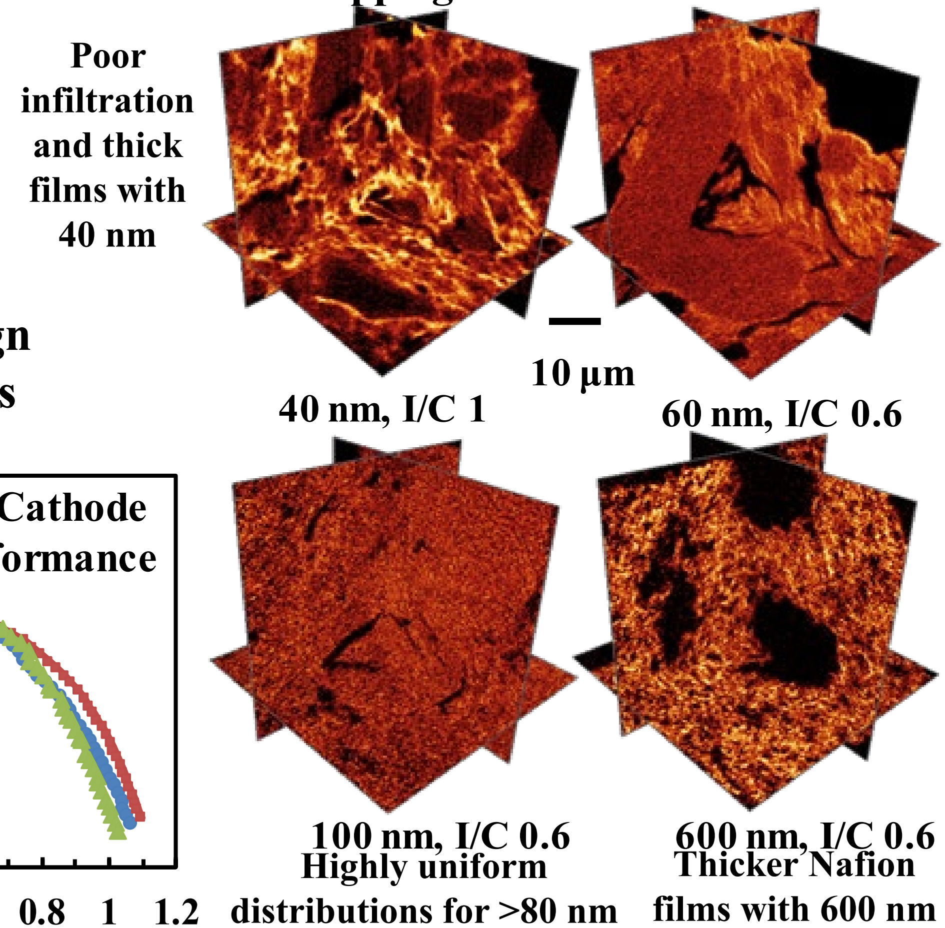
This project was not reviewed last year

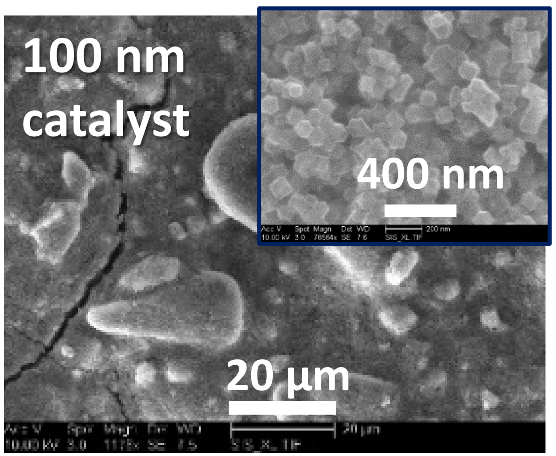
Carnegie Mellon University

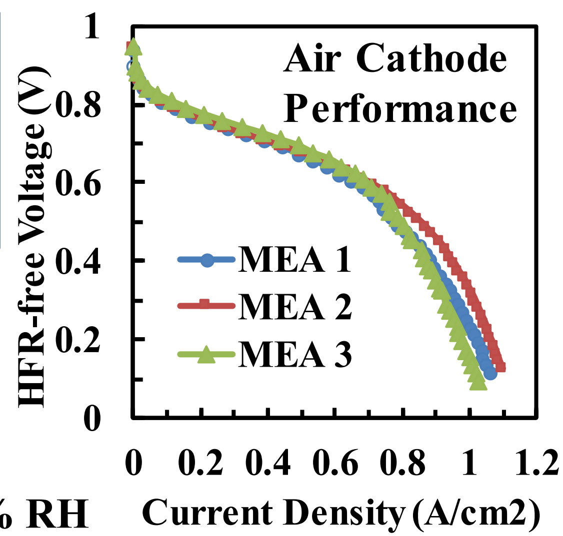
Accomplishments and Progress – Electrode Characterization

- **Prior development of PGM-free cathodes with Fe-MOF PGM-free catalyst in CMU's FC171 project**
- **Optimized particle size and ionomer integration for repeatable, high air performance**
- **Applying CMU's PGM-free cathode design principles to DMFC cathode requirements**

Nano-CT: 3D Mapping of Cs+ stained Ionomer







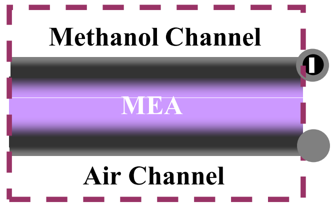
80^oC, Air/H_2, 1.5 atm, 100% RH

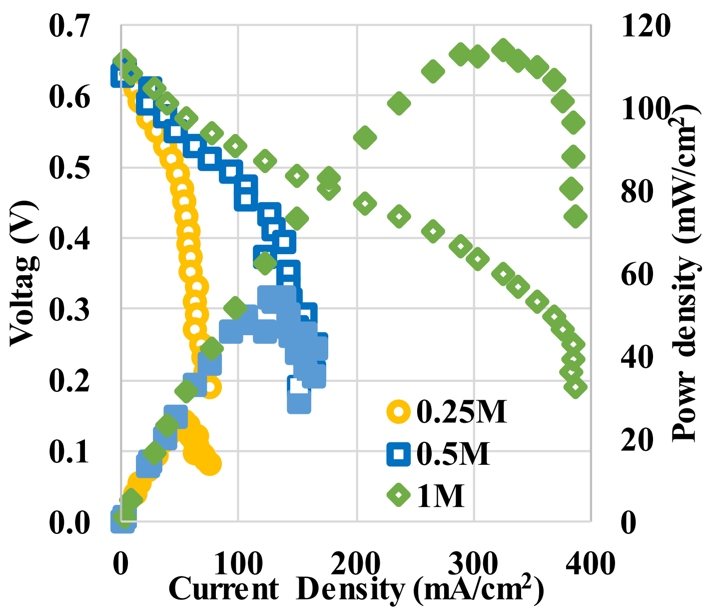
Primary particle size and ionomer loading should consider trade-offs between activity, conductivity, and mass transport.

This project was not reviewed last year

Accomplishments and Progress – Fuel and Water Management

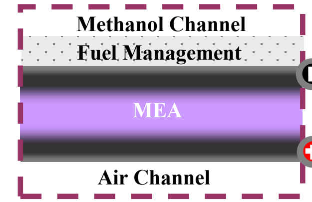
5 cm^2 commercial MEAs, 80^oC
no fuel management layer
no water management layer

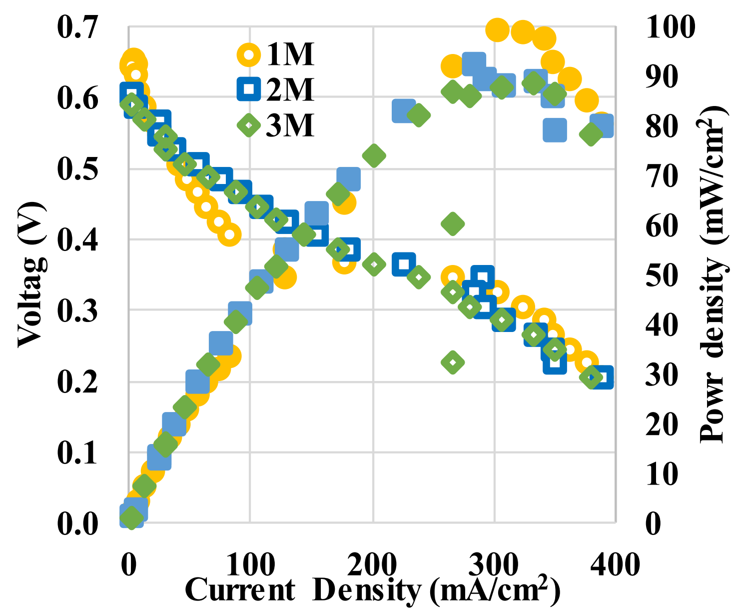




Commercial electrodes
1 ml/min MeOH, 0.2 l/min Air

5 cm^2 commercial MEAs, 80^oC
AN: Fuel Management Layer
no water management layer



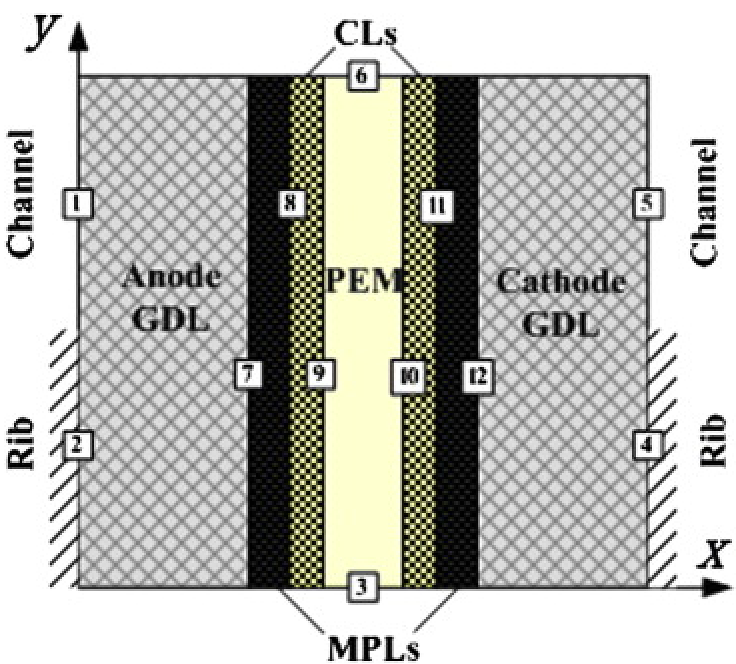


1/C ml/min MeOH, 0.2 l/min Air
AN: micro porous layer on Carbon Cloth

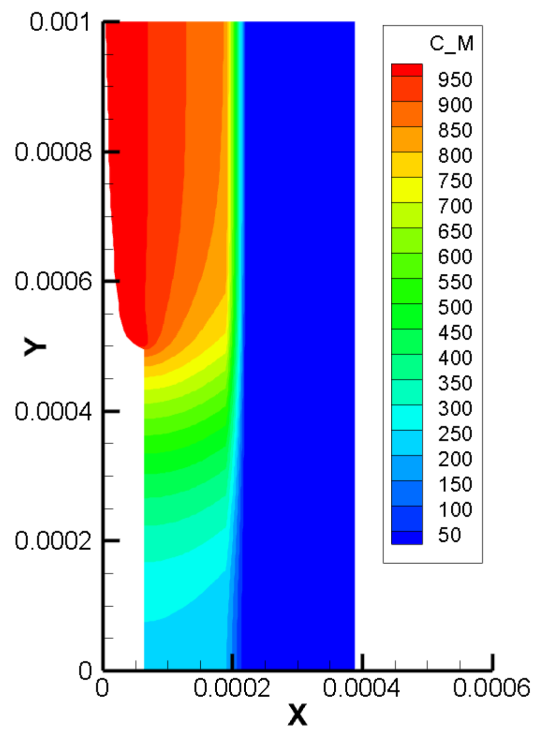
The fuel management is critical for the high-performance operation of fuel cells with concentrated methanol solutions

This project was not reviewed last year

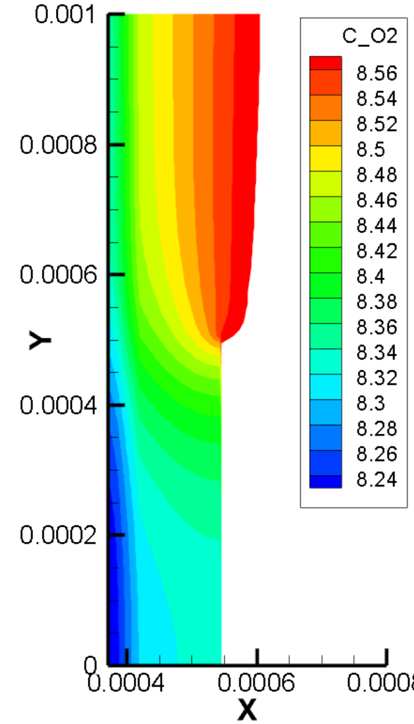
Accomplishments and Progress – Fuel and Water Management



Computational domains of the fuel cell model



Methanol concentration



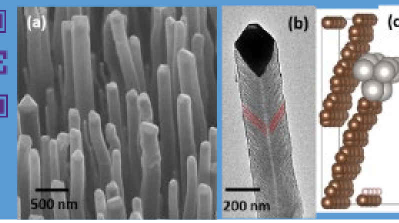
O_2 concentration

The fuel cell models can help understand the liquid-vapor two-phase flow within the MEA.

Collaboration and Coordination

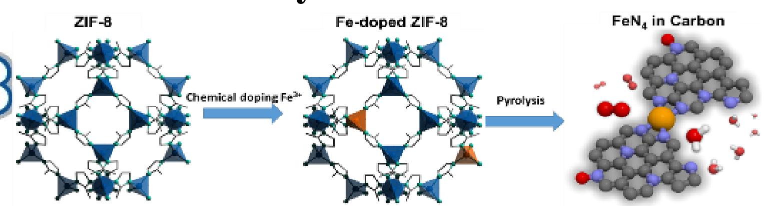
Sub: Jun Li
Kansas State University
Anode Catalyst

Anode catalyst on vertically aligned carbon nanofibers with ultralow PGM loading.



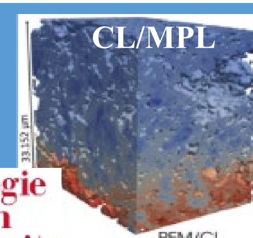
Sub: Gang Wu
University at Buffalo
Cathode PGM-free Catalyst

Cathode catalyst: highly methanol-tolerant and low-cost PGM-free catalysts.



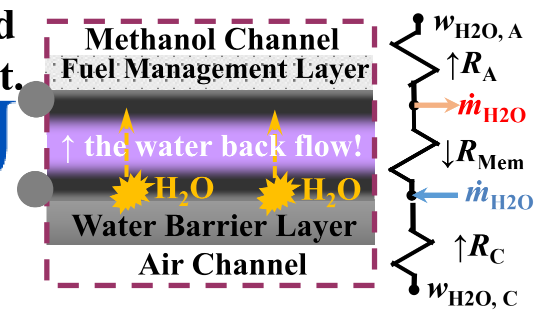
Sub: Shawn Litster
Carnegie Mellon University
Electrode characterization

Electrode fabrication, characterization and optimization using high-resolution X-ray CT imaging and simulation.



Prime: Xianglin Li
University of Kansas

System integration and prototype development. Fuel and water management to enable DMFCs using pure methanol.



Remaining Challenges and Barriers

Challenge:

- **Performance of customized non-PGM catalysts and anode catalyst supports.**
- **Production scale-up of customized catalysts and catalyst supports for 25 cm^2 and 50 cm^2 MEAs;**
- **Fuel management of fuel cells running with highly concentrated methanol solutions or pure methanol.**
- **Development of accelerated stress test (AST) procedures for DMFC.**

Planned Resolution:

- **Select, design and synthesize catalysts and catalyst support materials based on successful progress made by hydrogen fuel cells research.**
- **Explore different methods for catalyst deposition: sputtering, microwave-assisted synthesis, atomic layer deposition, etc.**
- **Understand pore-scale liquid-vapor two-phase transfer assisted by advanced imaging technologies (micro- and nano-CT) and model simulations.**
- **Develop DMFC's AST by modifying established AST protocols for hydrogen fuel cells.**

Technology Transfer Activities

This project just started at the beginning of the year, the research team is ***planning*** to carry out the following technology transfer activities during and beyond this project

- **Feasibility studies and economic analyses of DMFCs:**
  - Research on a few early market applications for DMFCs
  - Evaluate domestic and international markets to identify possible beneficiaries of the project's DMFC technologies
  - Identify key manufactures or fuel cell vendors for specific applications/markets
  - Carry out case studies or economic analyses
- **Potential future funding**
  - ARPA-E
  - NSF Partnerships for Innovation: Research Partnership
- **Patent or potential licensing**
  - Non-provisional patents on the new materials, electrode designs, fuel cell systems and their derivatives validated in this project will be filed.

Proposed Future Work

Remainder of FY19

- ***Pre-screen PGM-free ORR catalysts*: Establish correlation of RDE activity several pre-screened catalysts and MEA performance for DMFC.**
- ***Synthesize high-performance PGM-free ORR catalysts*: Synthesize at least 5 g catalyst with $E_{1/2}$>0.80 V and a peak power of 250 mW/cm^2 using dilute (<3.0 M) MeOH.**
- ***Sputter PtRu onto VACNFs* and evaluate its anodic MOR catalytic activity in 3.0 M MeOH.**
- ***Measure pore-scale electrode structure* using nano-CT.**
- ***Develop liquid-vapor two-phase models* to simulate mass transfer coupled with reactions.**
- ***Manage fuel and water in fuel cells* to achieve 250 mW/cm^2 peak power density with ≤ 4 mgPGM/cm^2 (Go/No-Go #1).**

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

Proposed Future Work

FY20

- ***Synthesize high-performance PGM-free ORR catalysts***: Synthesize 5 g catalyst with $E_{1/2}$>0.80 V and a peak power of 250 mW/cm^2 using >3.0 M MeOH.
- ***Test PGM-free ORR catalysts stability and durability***: The catalyst has $E_{1/2}$ loss of <30 mV after 30K potential cycling 0.6-0.95 V in 3.0 M methanol.
- ***Test anode catalysts in fuel cells***: The fuel cell obtains the maximum power density of 250 mW/cm^2 using <4 $mgPGM/cm^2$ in 3.0 M MeOH.
- ***Develop electrochemical models*** using reconstructed digital electrodes.
- ***Optimize hierarchical particle size and electrode*** based on reconstructed electrodes.
- ***Develop two-phase pore-scale models*** to simulate mass transfer coupled with reactions.
- The single cell achieves ≥ 250 mW/cm^2 peak power with ≤ 3 $mgPGM/cm^2$ (Go/No-Go #2).

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

Summary Slide

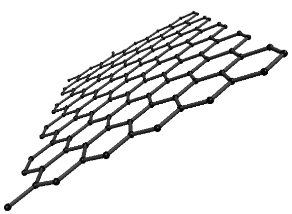
- The high energy content of liquid methanol (4.67 kWh/L) makes DMFC an ideal technology for stationary applications (1-25 kW).
- Since the start of the project, KU, KSU, UB, and CMU have all built capable research teams and setup the research platform as planned.
- The four participating research teams have worked closely with the program manager to share information, update progress, and discuss technical challenges and feasible plans to reach the project goal.
- The advanced catalyst support material as well as the PGM-free show promising performance and methanol tolerance in RDE/CV tests.

Technical Backup Slides

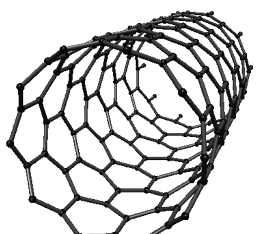
This project was not reviewed last year

Technical Backup Slides – Anode Catalyst Support

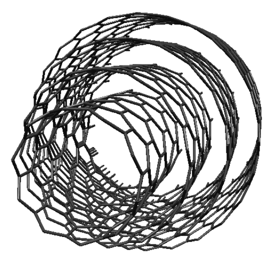
Aixtron PECVD system in Li lab, KSU



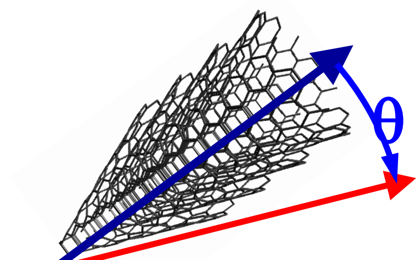
Graphene



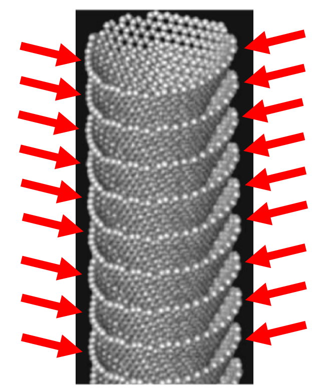
Single-walled Carbon Nanotube



Multi-walled carbon nanotube



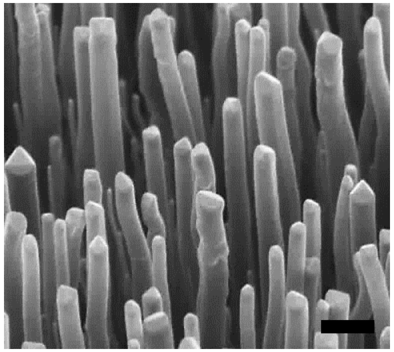
Carbon Nanofiber



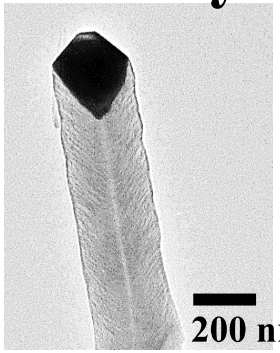
Vertically Aligned Carbon Nanofiber

The research team has the equipment and experience to grow vertically aligned carbon nanofiber as the catalyst support.

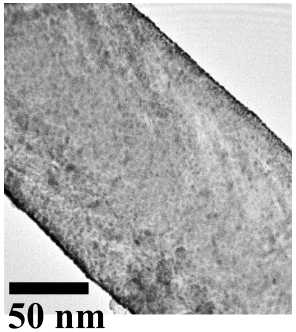
Technical Backup Slides
– Anode Catalyst Support



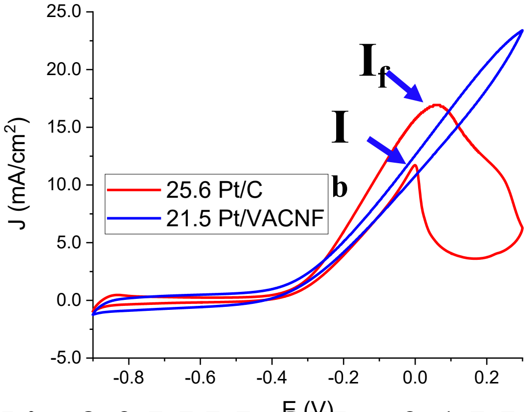
Length variable from 3 –10 mm
The average spacing ~400 nm



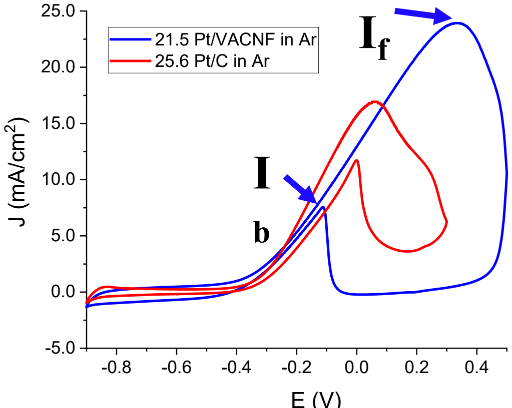
Well-defined graphitic edge sites at the sidewall



Pt sputtered on VACNFs
-Avg. Pt size: ~ 3 nm



CV in 3.0 M MeOH + 0.1 M KOH in O_2



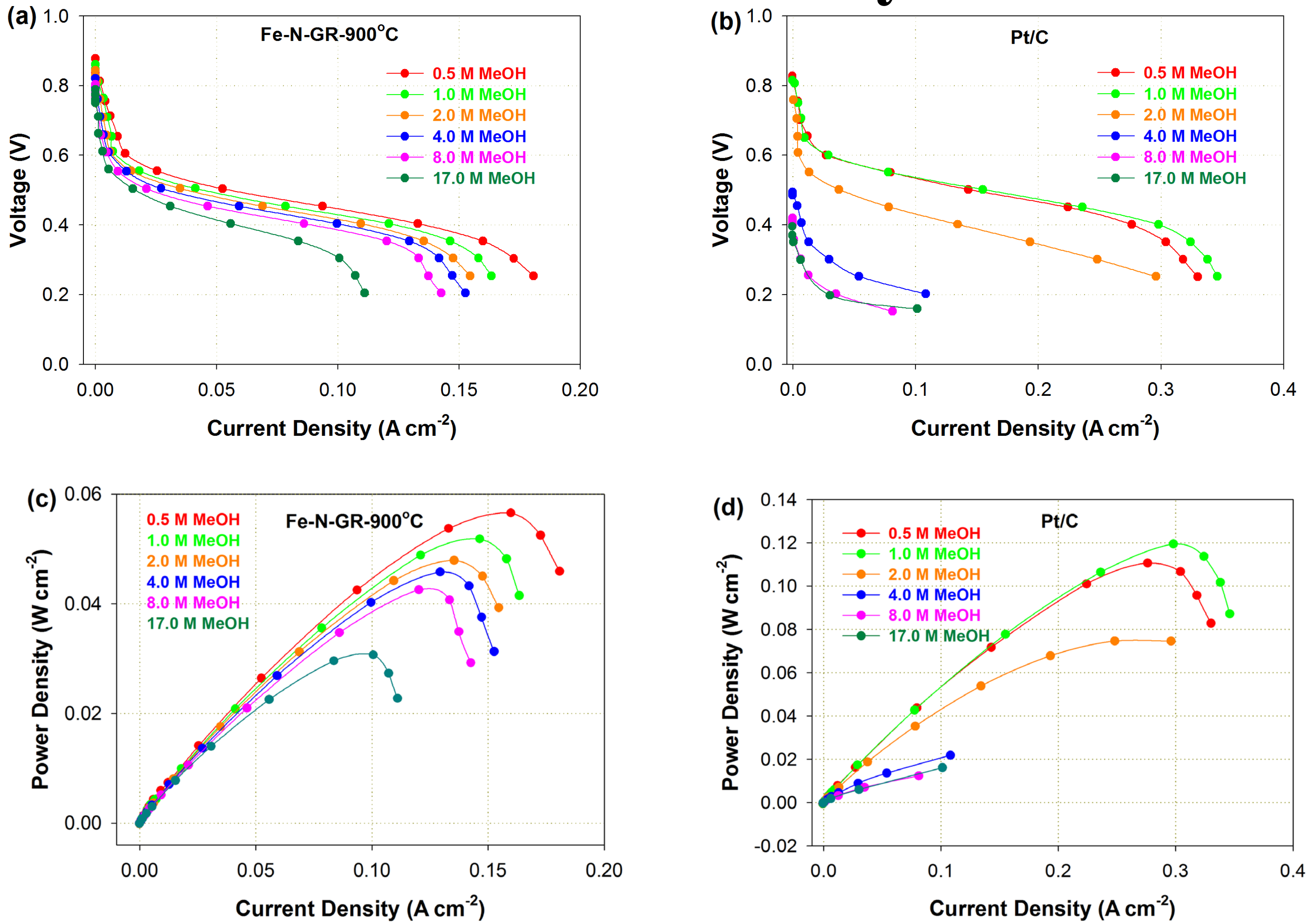
CV in 3.0 M MeOH + 0.1 M KOH in Ar

3 nm Pt/VACNF for methanol oxidation reaction

Suppressed I_b/I_f indicates reduced carbonaceous deposit on Pt (at ~20-25 μg/cm^2) using VACNF as the catalyst support. The durability of Pt/VACNF is likely higher. Similar behavior observed at lower Pt loading (~10-13 μg/cm^2).

This project was not reviewed last year

Technical Backup Slides – Cathode Catalysts

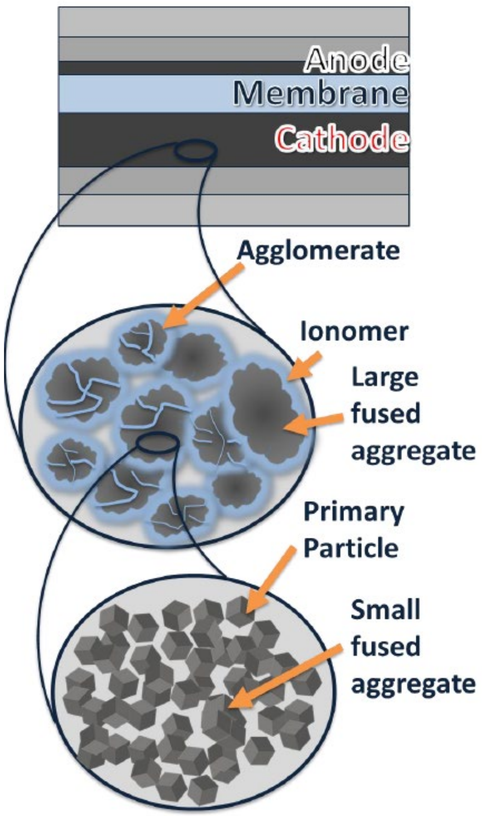


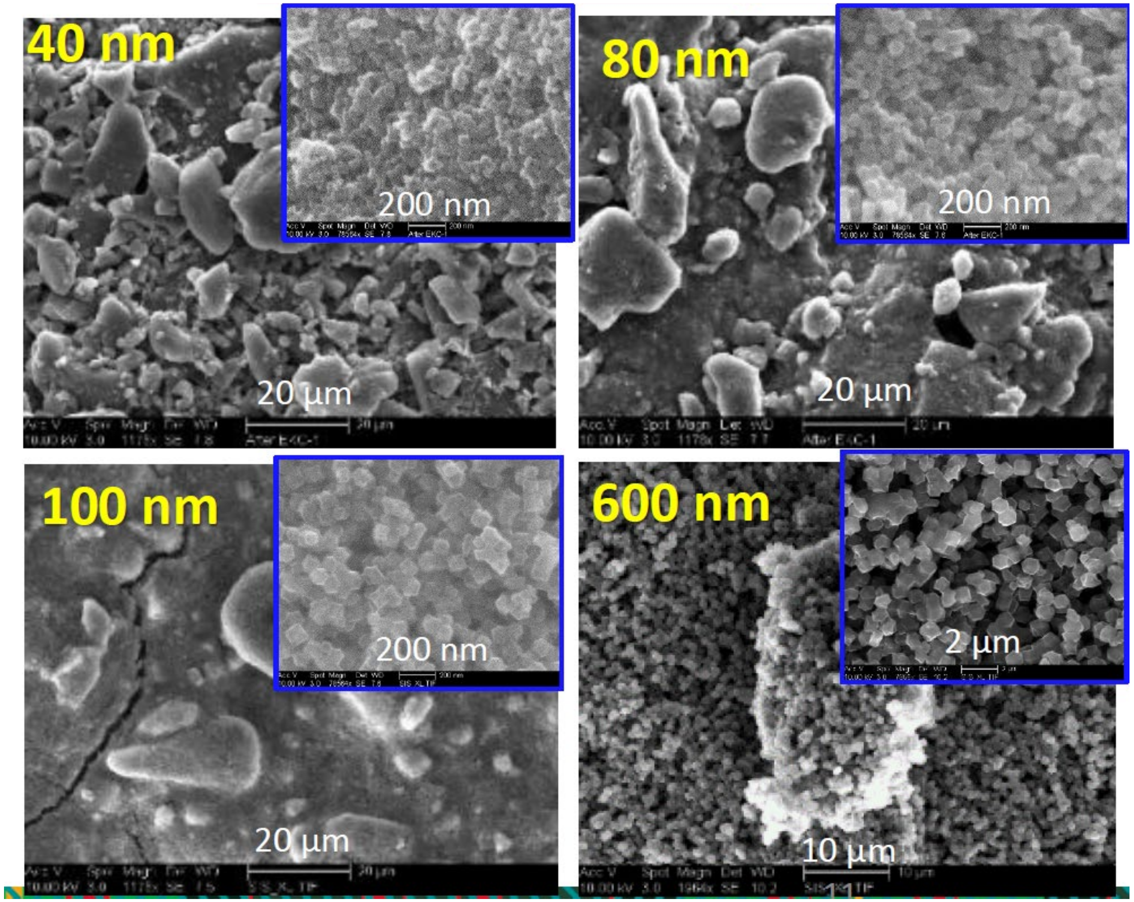
When methanol concentration is above 2M, PGM-free cathode performs better than PGM cathode

This project was not reviewed last year

Carnegie Mellon University

Technical Backup Slides – Electrode Characterization



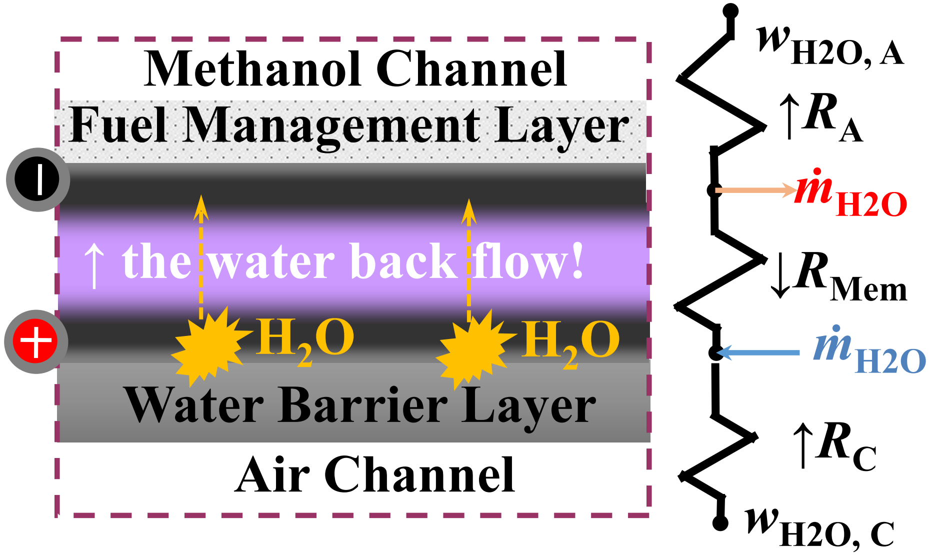


Fe-MOF Catalyst with Different Primary Particle Sizes

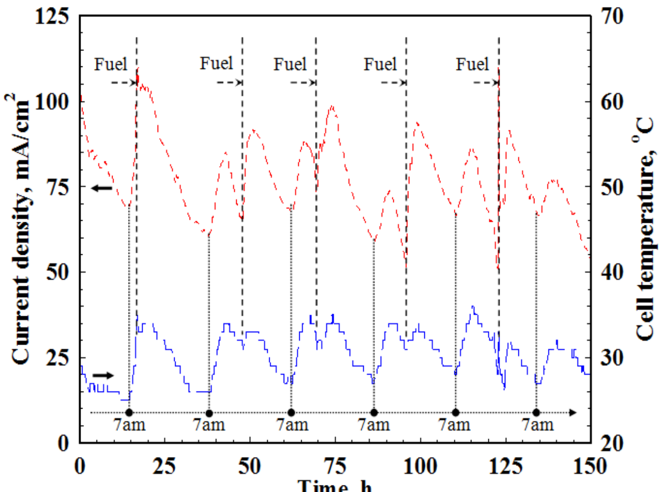
- **40 nm: Agglomerated primary particles and large fused aggregates**
- **60 nm to 100 nm: Less large agglomerates and more distinct primary particles**
- **600 nm: Few large agglomerates and more dispersed primary particles.**

This project was not reviewed last year

Technical Backup Slides
– Fuel and Water Management



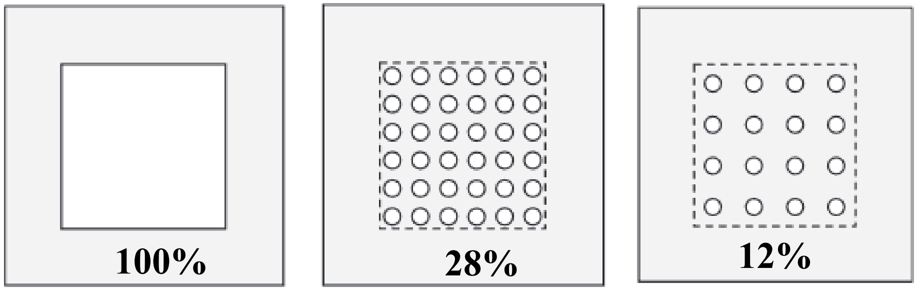
Performance in passive systems



Current density and temperature changes of a passive DMFC using pure methanol at 0.2 V and room temperature.

Preferred materials to regulate water and fuel in MEA:

- Strongly hydrophobic;
- High mass transfer resistance;
- Highly electric conductive;
- Thin and lightweight.



Sample structures with controllable open ratios