Stationary Direct Methanol Fuel Cells Using Pure Methanol

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Co-PI: Jun Li / Kansas State University

Co-PI: Gang Wu/ University at Buffalo, SUNY

Co-PI: Shawn Litster / Carnegie Mellon University

DOE project award # DE-EE0008440

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DOE Hydrogen Program
2021 Annual Merit Review and Peer Evaluation Meeting

AMR Project ID # FC317

KU STATE UB Carnegie Mellon University

Project Goal

Project Goal

- Develop stationary direct methanol fuel cells (DMFCs) using pure methanol as the fuel.
- The DMFC prototype will produce peak power density of ≥ 300 mW/cm^2 with total loading of ≤ 3 $mgPGM/cm^2$.

Project Outcomes

The project will advance four novel concepts in parallel:

- 1. Cathode PGM-free Catalyst;
- 2. Anode Catalyst with Ultralow Loading PtRu on VACNFs Support;
- 3. Electrode fabrication and characterization;
- 4. Passive Fuel and water management.

Project Impacts

- Technical improvements and cost reductions would facilitate fuel cell market penetration in forklift and stationary power applications.
- The design and manufacture of cost-effective high performance PGM-free cathodes and ultralow PGM anodes will also have positive impacts on fuel cells for transportation and other portable applications.

Overview

Timeline

- **Project Start Date: 10/01/2018**
  BP1: 10/01/2018 to 3/31/2020
  BP2: 04/01/2020 to 3/31/2021
  BP3: 04/01/2021 to 3/31/2022
- Effective Project Start Date: 01/03/2019
- **Project End Date: 3/31/2022**

Barriers Addressed

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

Budget

- **Total Project Budget: $ 1,249,449**
  Recipient Share: $ 250,050
  Federal Share: $ 999,399
- Planned funding for
  Budget Period 1: $ 469,489
  Budget Period 2: $ 410,090
- Total DOE Funds Spent*: $596, 282

* As of 3/31/2021

Partners

PI : Xianglin Li
University of Kansas (KU)
Co-PI: Jun Li
Kansas State University (KSU)
Co-PI: Gang Wu
University at Buffalo (UB)
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.
- **The project will address 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 $\geq 300\ mW/cm^2$ with total loading of ≤ 3 $mgPGM/cm^2$.
- **2st BP target (4/1/2020 - 3/31/2021):** The fuel cell prototype to be delivered will meet the milestone of $\geq 250\ mW/cm^2$ with 3 $mgPGM/cm^2$.

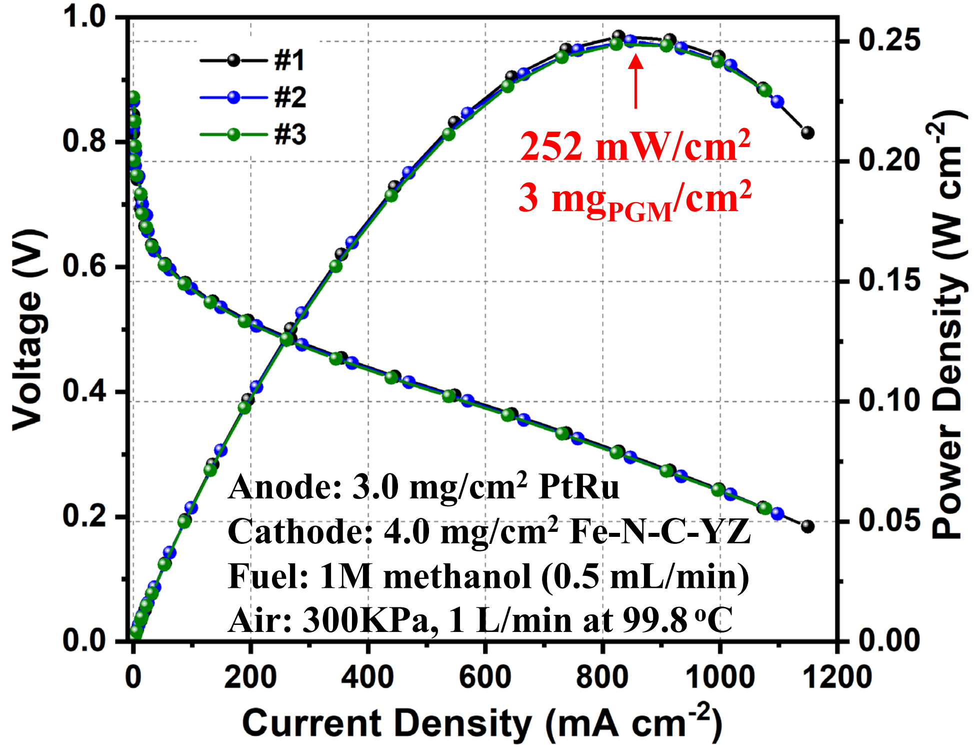
Approach: Project Milestones and Status

This research integrates complementary institutional expertise on

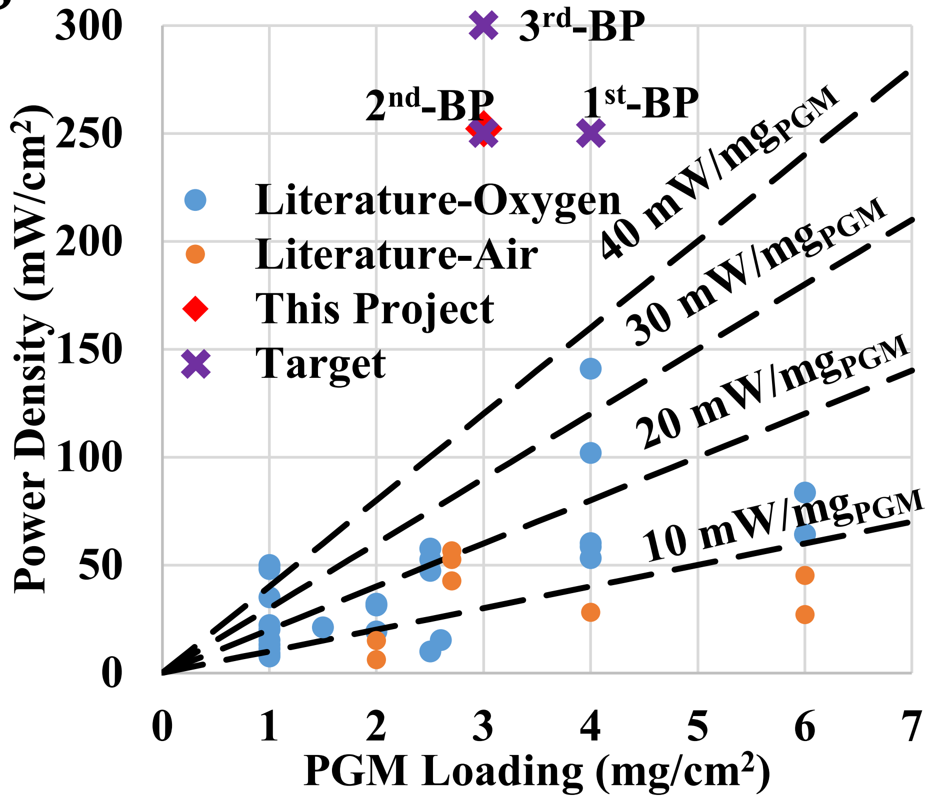
- Supported anode catalysts (KSU)
- Platinum group metals free (PGM-free) cathode catalyst (UB)
- Electrode fabrication, characterization, and optimization (CMU)
- Multi-phase mass transfer (KU)

	Milestone Description (Status as of 3/31/2021)	Status
Q5	• Integrate fuel and water regulations into MEAs and test by 16 M methanol solutions. • Optimize hierarchical particle size and electrode using reconstructed digital electrodes. • Determine procedures and parameters of ASTs.	100%
Q6	• Generate PGM-free cathode catalysts with $E_{1/2}$>0.85 V using dilute methanol solution. • Develop anode catalysts with lower degradation rate than HiSPEC® 10000 PtRu/C.	90%
Q7	• Perform particle-scale transport and reaction modeling to maximize catalyst utilization. • Single cells achieve ≥ 200 mW/cm^2 with ≤3 mgPGM/cm^2 and >3M methanol solution.	100%
Q8	**Go/No-GO Single cells achieve ≥ 250 mW/cm^2 with ≤ 3 mgPGM/cm^2.**	100%

Accomplishments and Progress – Overview



The peak power density of 252 mW/cm^2 was achieved at high temperature of 99.8 °C at 300 kPa back pressure of air (1000 sccm) and 1.0 M methanol (0.5 mL/min).

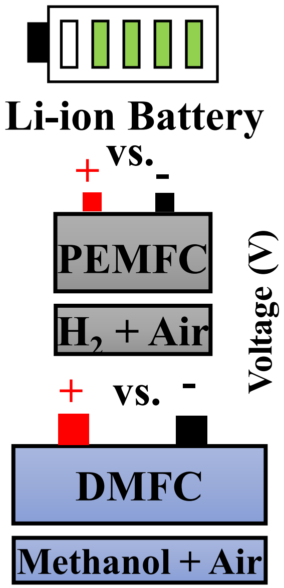


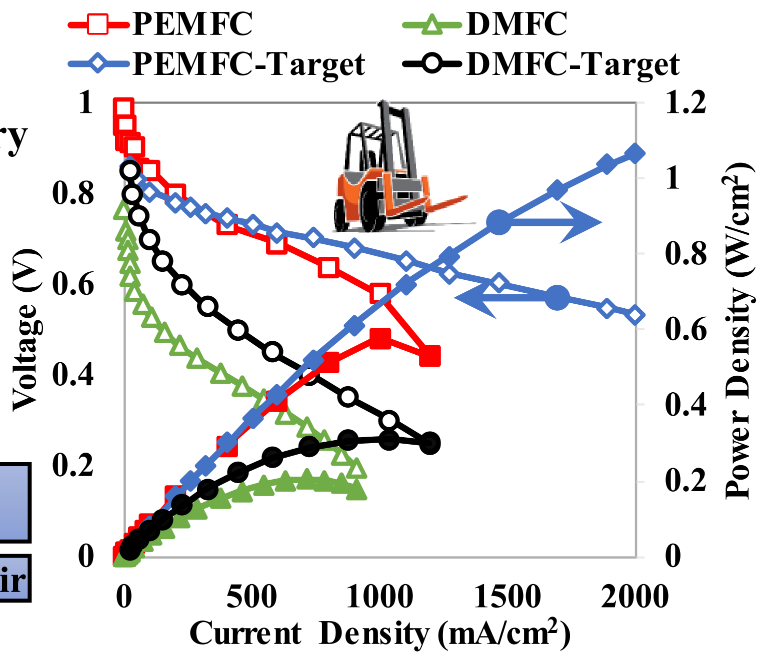
Power density versus anode PGM loading for DMFCs with PGM-free cathodes reported in the literature (circle), achieved by this research team (diamond), and project targets (cross).

The project team has successfully met the Go/No-Go performance milestone of the 2nd budget period (04/01/2020 to 03/31/2021): Achieve the peak power density of at least 250 mW/cm^2 with no more than 3.0 mg/cm^2 PGM catalyst loading. ***Please note that both the air flow rate and pressure are higher than proposed operating conditions.***

Accomplishments and Progress

-Technical and Economic Analyses of Fuel Cells in Forklift Industry





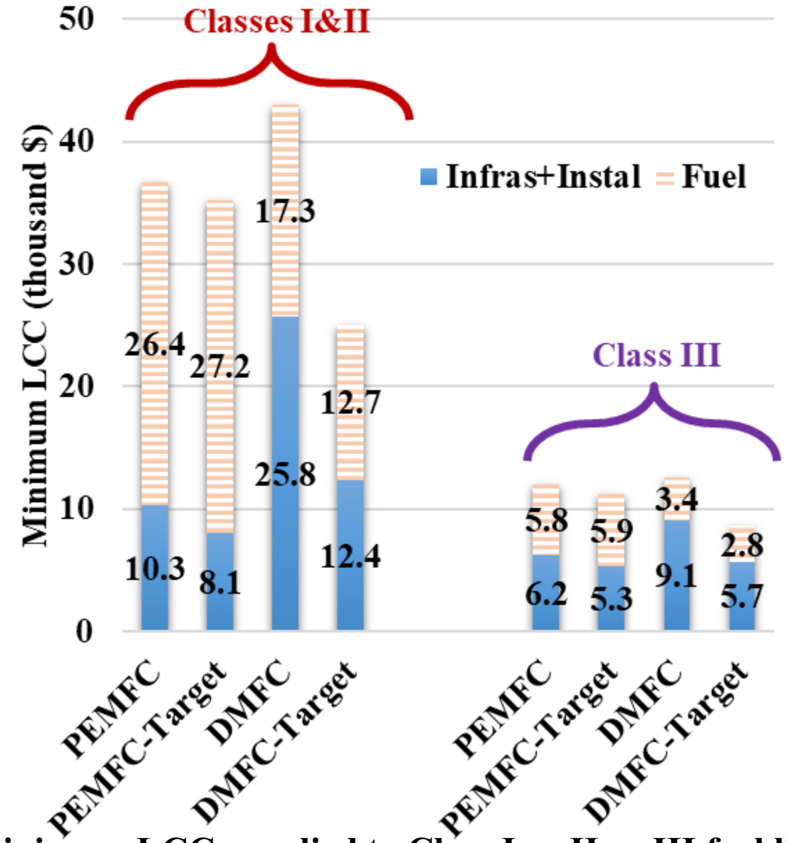
PEMFC: 0.6 W/cm^2; 0.4 mg$_{PGM}$/cm^2

PEMFC Target: 1 W/cm^2; 0.125 mg$_{PGM}$/cm^2

DMFC: 0.2 W/cm^2; 6 mg$_{PGM}$/cm^2

DMFC Target: 0.3 W/cm^2; 3 mg$_{PGM}$/cm^2

There Are Now More Than **35,000** Hydrogen Fuel Cell Forklifts (850,000 total) in Use Across the United States – DOE, Oct 2020



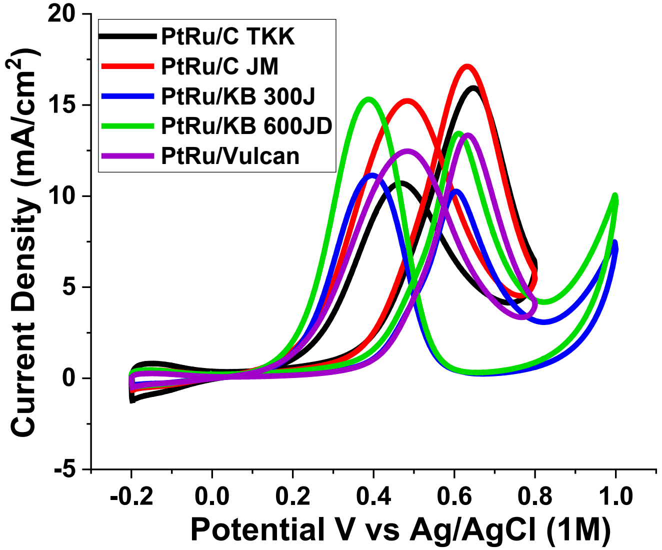
The minimum LCCs applied to Class I or II or III forklifts.

Comparing with PEMFC, DMFC has

- Lower infrastructure costs ($75k vs. ~$1M per site)
- Much lower fuel cost (~$0.64/GGE vs. $5-$22/GGE)
- Higher fuel cell cost (~$4,000/kW vs. ~$2,000/kW)

As power sources of forklifts, DMFCs could have up to 30% lower LCC (10 years) than PEMFCs.

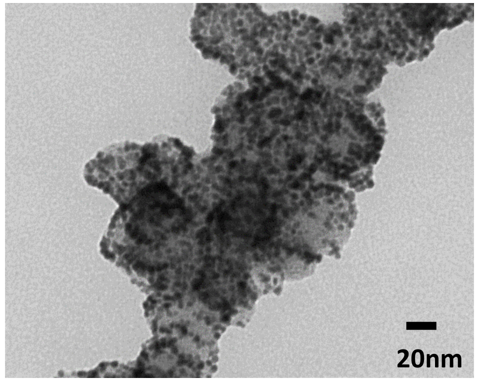
Accomplishments and Progress
– Anode Catalyst (PtRu deposited on commercial carbon supports)



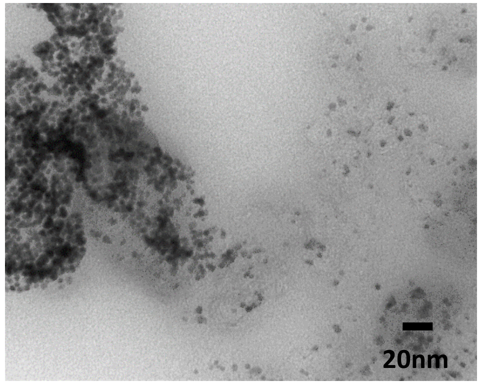
Deposit PtRu on commercial high-surface-area carbon supports:

- Vulcan carbon®(XR-72) (BET surface area – 250m^2/g)
- Ketjen Black® EC-300J (BET surface area – 800m^2/g)
- Ketjen Black® EC-600JD (BET surface area – 1400m^2/g)

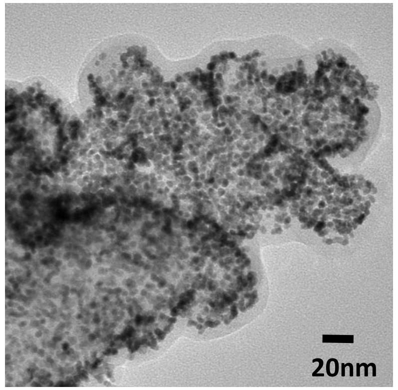
PtRu/KB 300J

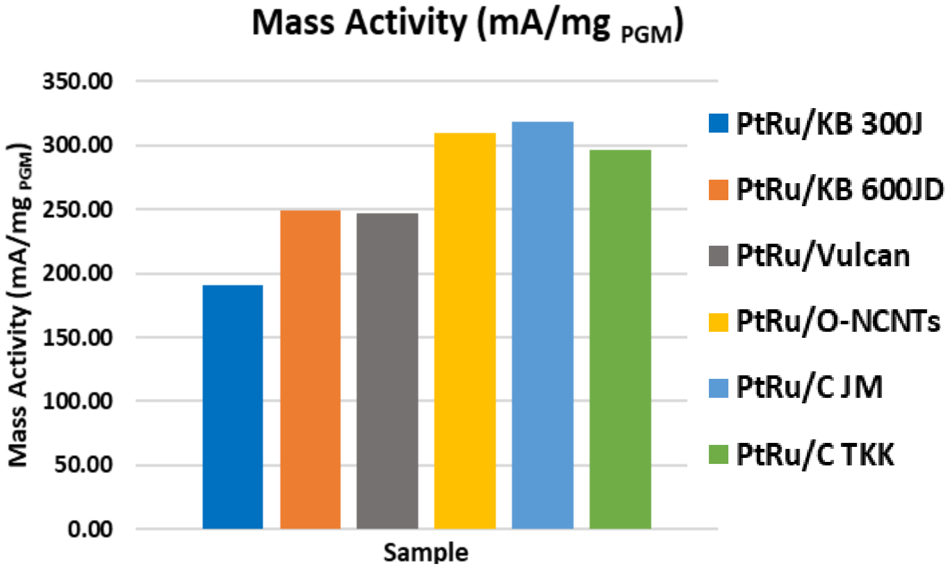


PtRu/KB 600JD



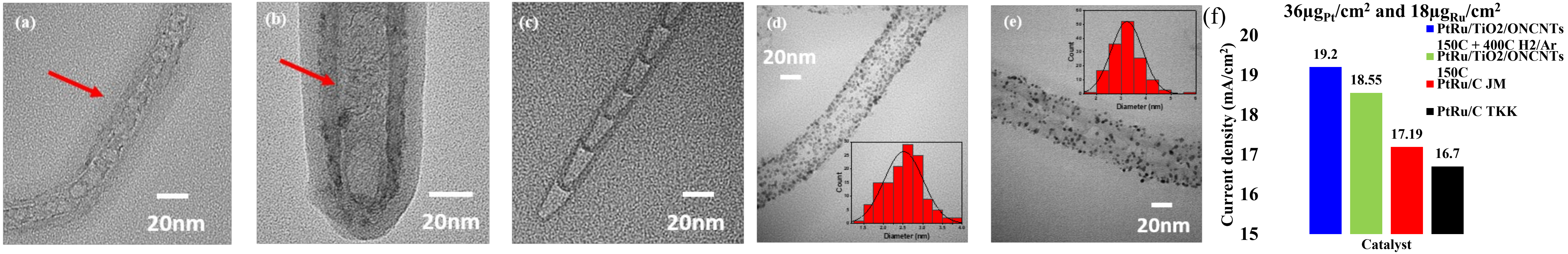
PtRu/Vulcan





Accomplishments and Progress
– Anode Catalyst Synthesized with Microwave-Assistant Approach

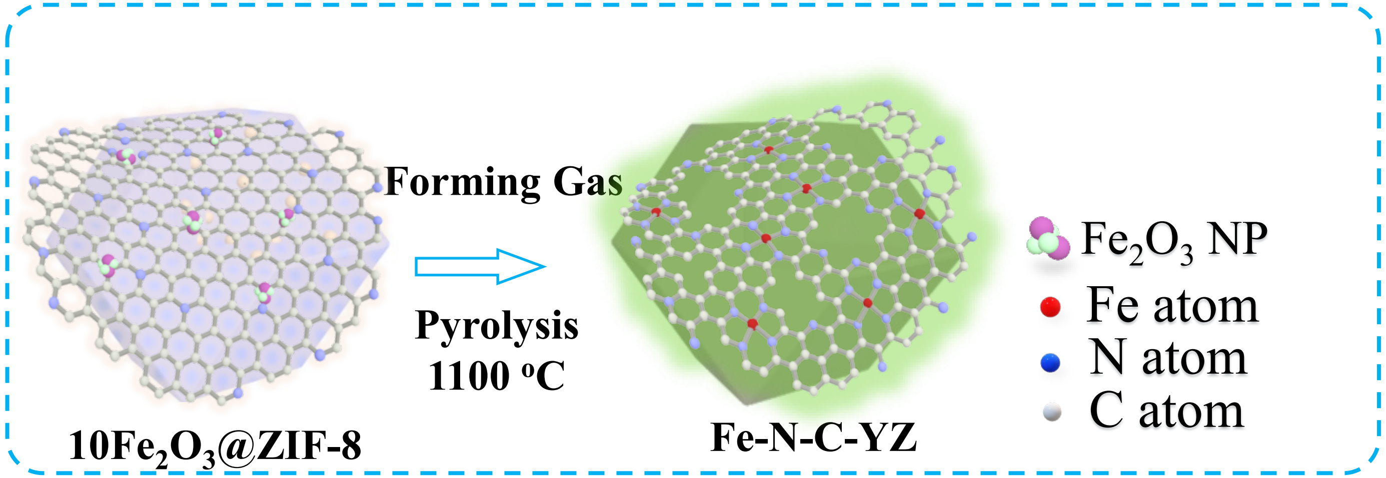
- **O-NCNTs** – Oxygenated nitrogen doped carbon nanotubes
- **PtRu/O-NCNTs** – Pt and Ru deposited on oxygenated nitrogen doped carbon nanotubes
- **TiO_2/O-NCNTs 150C** – Titanium dioxide deposited on O-NCNTs at 150C assisted by microwave (MW)
- **TiO_2/O-NCNTs 150C + 400C air** – TiO_2/O-NCNTs 150C MW samples + 400C annealing in air for 1hr
- **Pt/TiO_2/O-NCNTs 150C** – Pt deposited on TiO_2/O-NCNTs 150C MW
- **Pt/TiO_2/O-NCNTs 150C + 400C** – Pt deposited on TiO_2/O-NCNTs 150C MW + 400C annealing in air for 1hr
- **PtRu/TiO_2/O-NCNTs 150C** – PtRu deposited on TiO_2/O-NCNTs MW
- **PtRu/TiO2/O-NCNTs 150C + 400C H_2/Ar** – PtRu deposited on TiO_2/O-NCNTs + 400 C annealing inH_2/Ar.

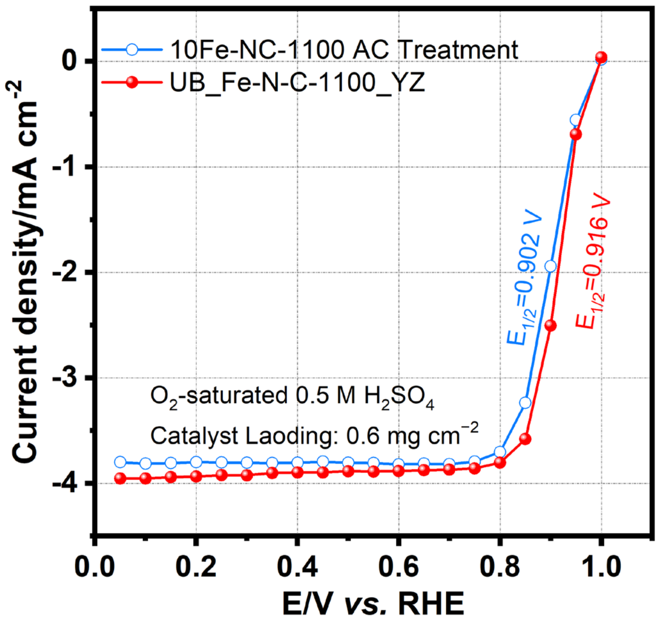


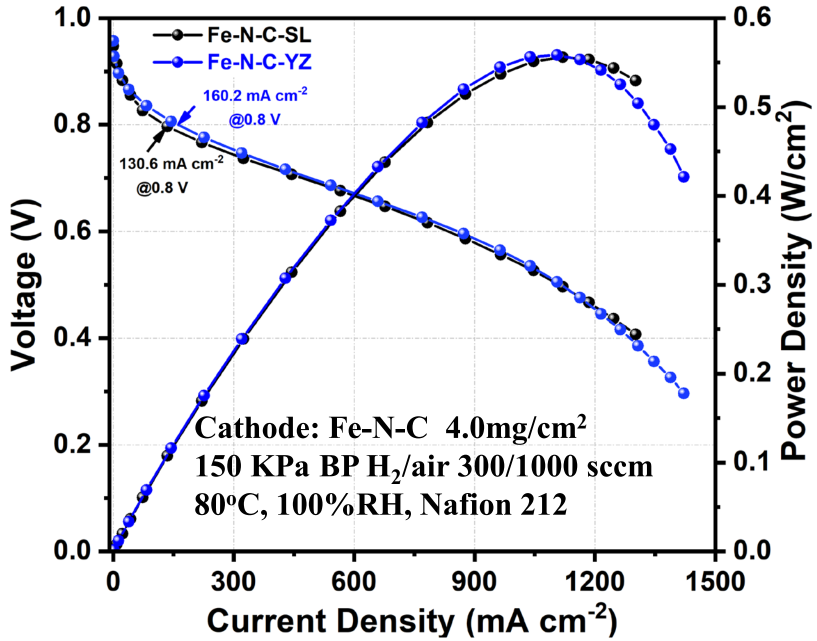
TEM images of (a) TiO_2/O-NCNTs 150 °C, (b) TiO_2/O-NCNTs 150 °C + 400 °C, (c) bare O-NCNTs, (d) Pt/TiO_2/O-NCNTs 150 °C and (e) Pt/TiO_2/O-NCNTs 150 °C + 400 °C. The insets of (d) and (e) show the corresponding histogram. (f) Half-cell current density (mA/cm^2) of best-performing catalysts.

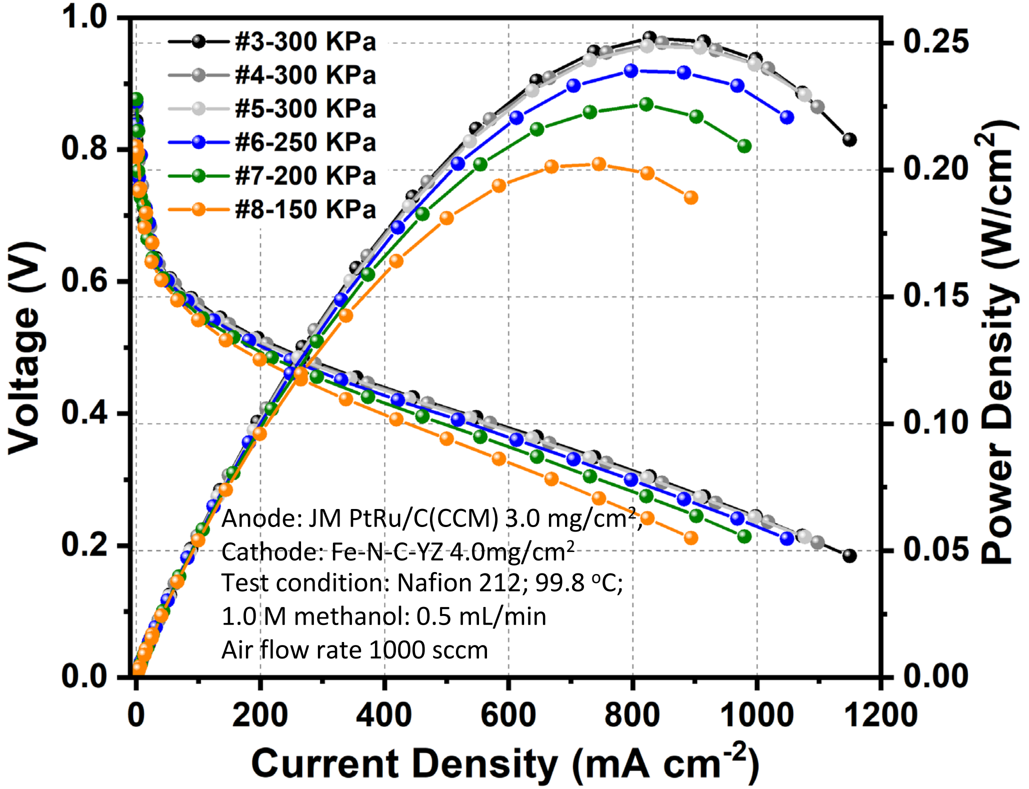
Customized PtRu/TiO2/O-NCNTs have higher current density than the best commercial PtRu/C catalysts.

Accomplishments and Progress
– Cathode PGM-free Catalysts



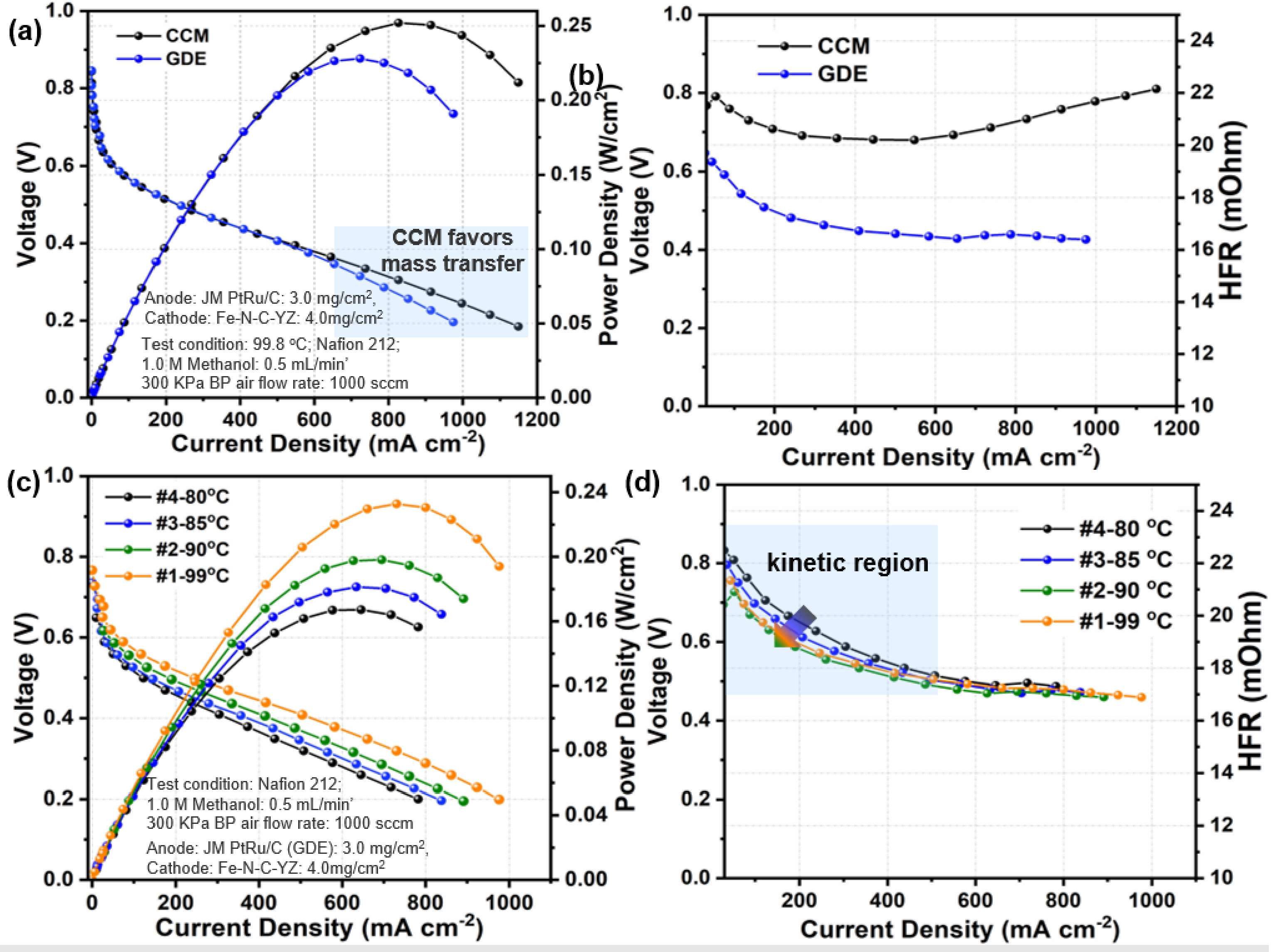






The MEA performance is stable and maintains the peak power density of 250 mW/cm^2 after three continuous scans from test #3 to 5. But the performance is sensitive to the applied back pressure with peak power density decreased to 204 mW/cm^2 when back pressure decreased to 150 KPa.

Accomplishments and Progress
– GDE vs. CCM using PGM-free Catalysts



- CCM technique is benefit for mass transfer as it straightforward presented the catalysts advantageous porous structure separated from GDL.
- Additional spray in GDE offsets the ohmic loss.

- High temperature increased reaction kinetic.
- Methanol evaporation was accelerated at higher temperature .

Accomplishments and Progress
– MEA Optimization: Spray vs. Blade Coating

(a)

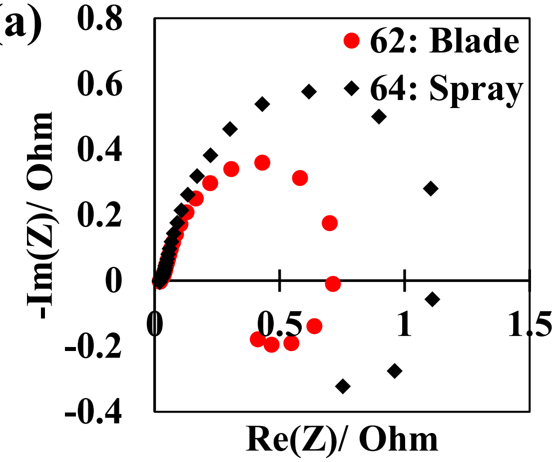
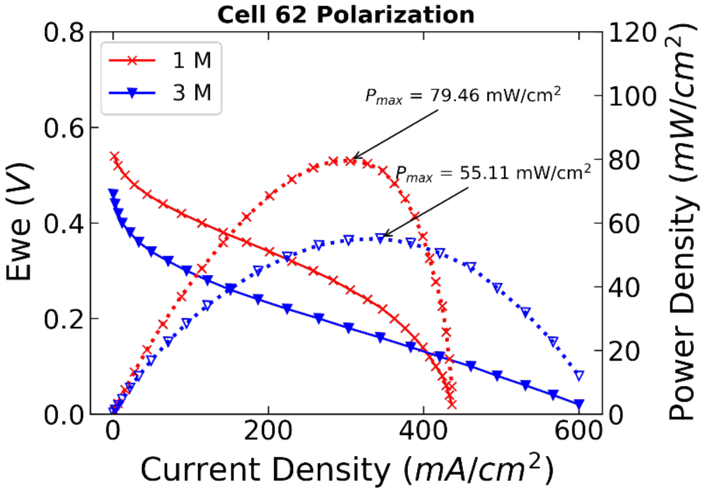


Table 1 Values of parameters fitted by the EIS results

	Cell 62: Blade Coated	Cell 64: Spray Coated
C_d (F)	0.4958	0.5526
R_{ct}(Ohm)		1.2139
R_o (Ohm)	0.2928	0.3237
L (H)		

Lower resistances with blade coated anode



(b)

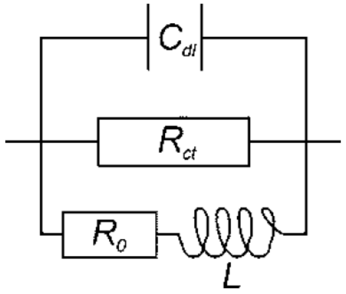
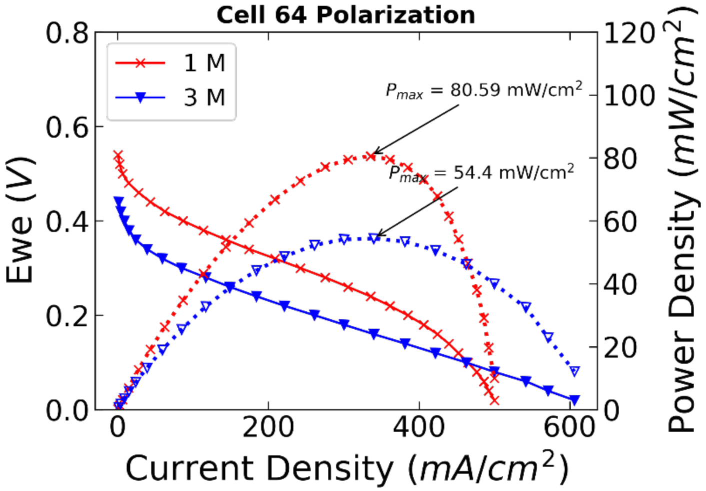


Figure 8. (a) EIS results and (b) equivalent circuit model

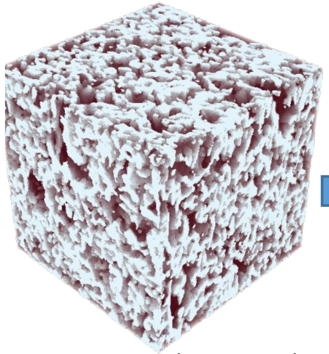
- **L** is due to the slowness of CO_{ads} coverage. It takes some time after a potential perturbation before the new steady state coverage is established and the corresponding current (leading to a phase delay)
- $\mathbf{R_o}$ serves to modify the phase delay according to the reaction scheme
- $\mathbf{R_{ct}}$ is associated with the current response that occurs without change in coverage
- $\mathbf{C_d}$ is not only related to the double layer capacitance because values are typically 0.001 – 0.01 F/cm². It is believed to be associated with the redistribution of charge at the anode



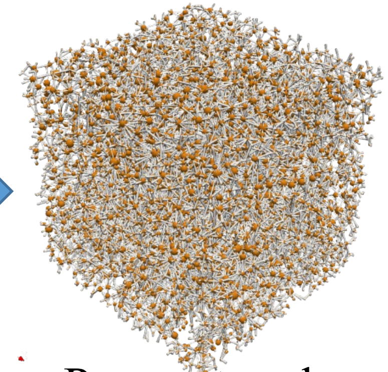
Operating conditions: 80 ̊C, 100%RH Anode: 1 M MeOH 2 mL/min Cathode: H_2 200 mL/min
Cell Parameters: Anode: 2 mg_{pgm}/cm^2 Alfa Aesar 75 wt% PtRu/C Cathode: 0.3 mg/cm² Fuel Cell Etc. Pt/C

Differences in anode resistance were not significant enough to impact DMFC performance.

Accomplishments and Progress
– Pore-Scale Liquid-Vapor Two-Phase DMFC Model

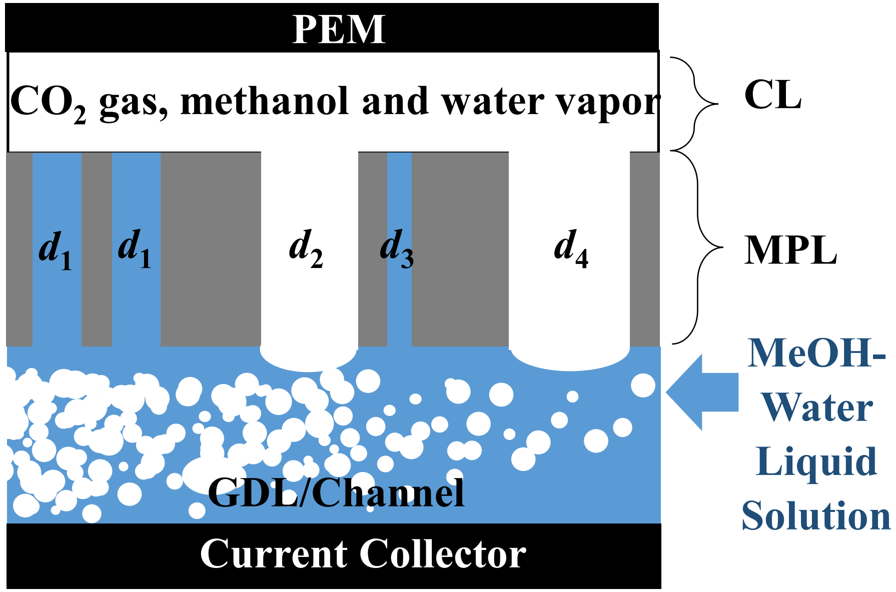


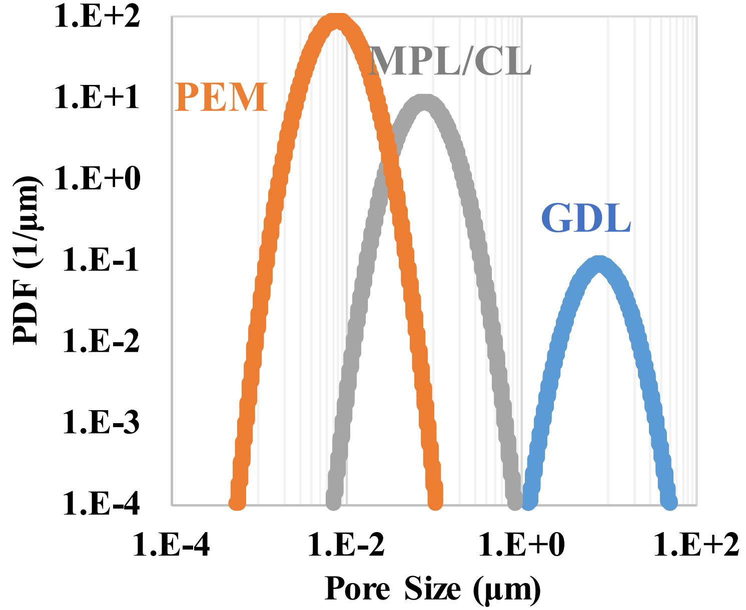
Segmented Anode p-FIB data

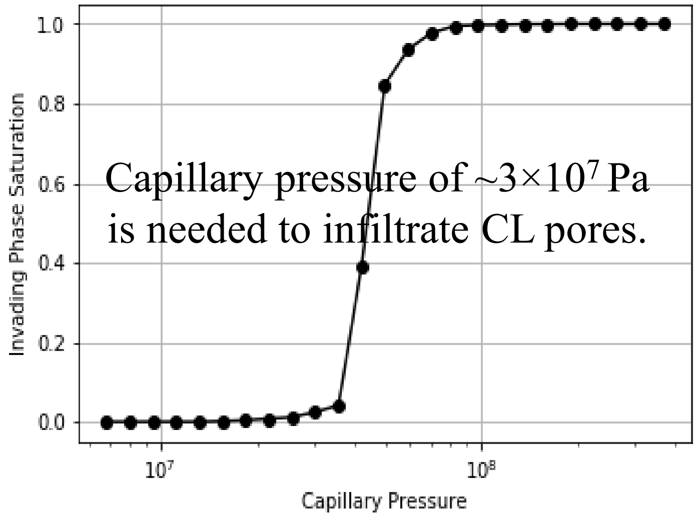


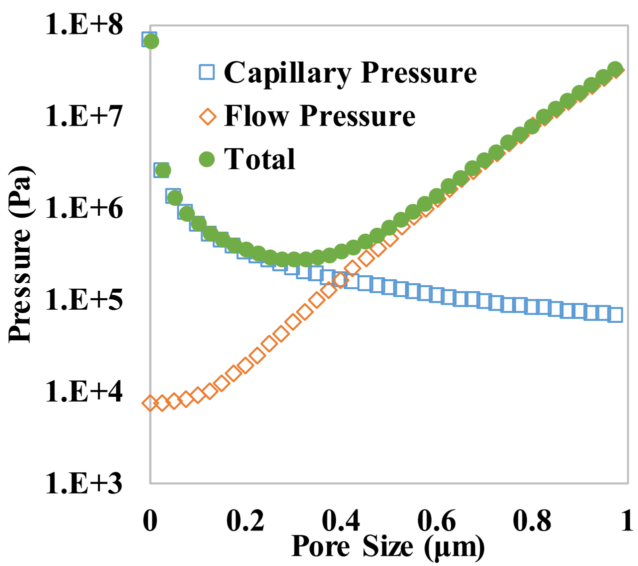
Pore-network extraction

Gaussian blur with sigma = 0.4
Initial number of peaks: 25872
After trimming saddle points and nearby peaks: 9958







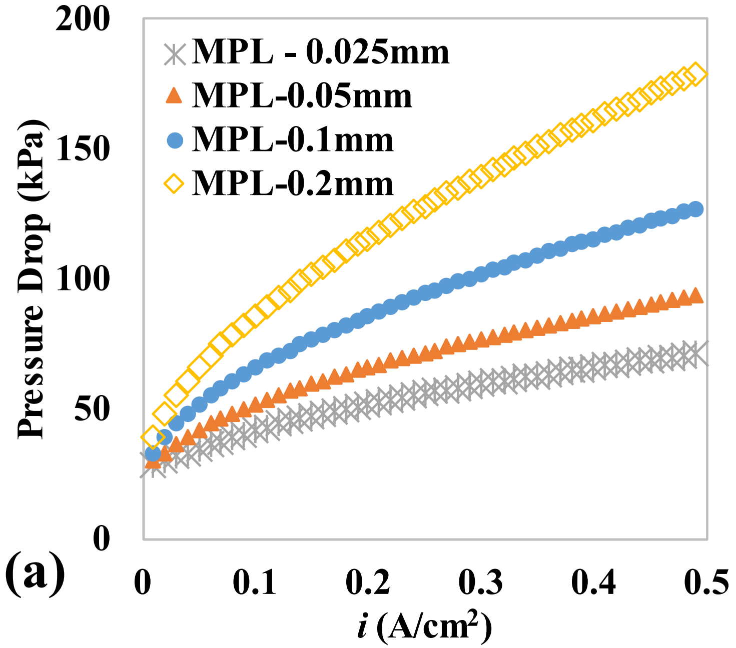


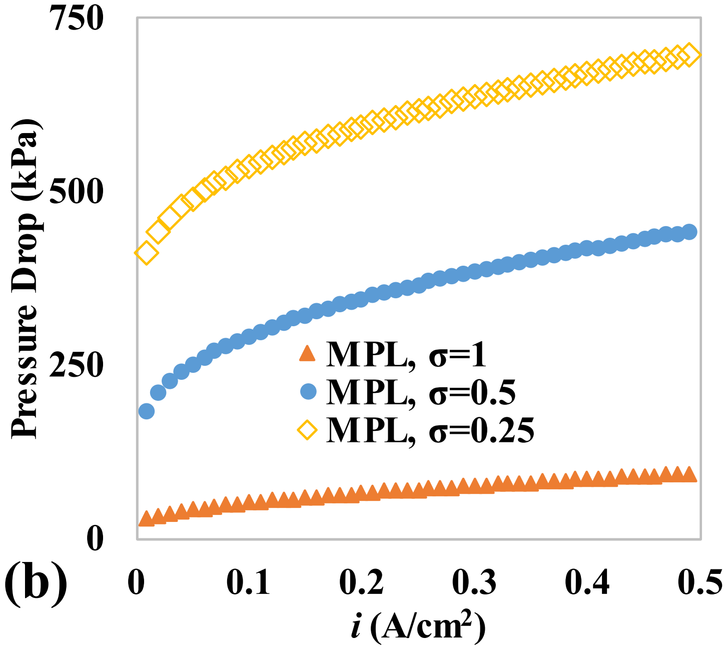
The gas flow pressure balances the capillary pressure and the flow resistance:

$$p_g = \frac{4 \cdot \sigma \cdot \cos\theta}{d} + \frac{150\mu}{d_{avg}^2}\frac{(1-\varepsilon)^2}{\varepsilon^3} \times \frac{i}{6F} \times \frac{R_u T}{p_g} \times \frac{\delta}{(1-\mathrm{CDF}(d))}$$

The pore size distribution has significant impacts on the capillary pressure and liquid-vapor two-phase flow.

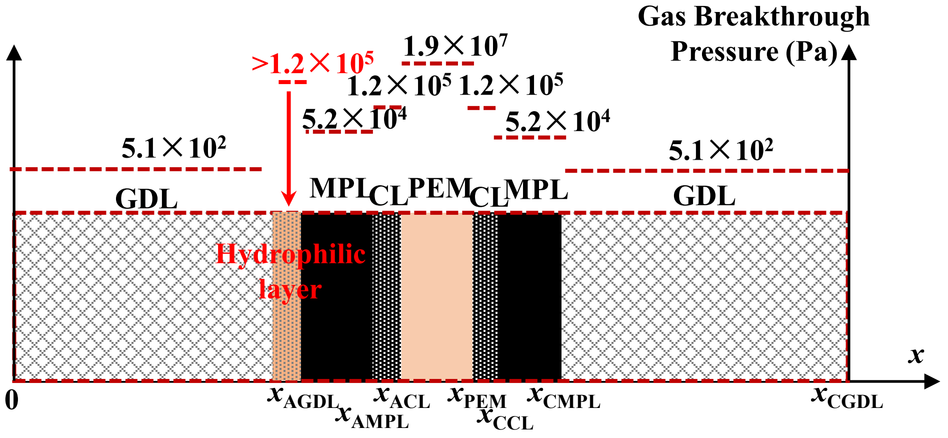
Accomplishments and Progress
– Pore-Scale Liquid-Vapor Two-Phase DMFC Model



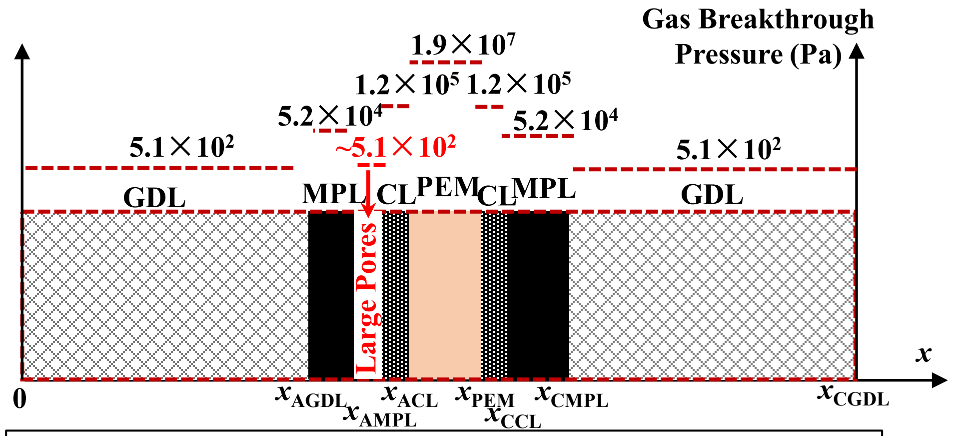


Total gas pressure drops through MPLs with (a) different thicknesses at the shape factor of 1.0 and (b) different shape factors at the thickness of 50 μm.

Changing the pore size distribution and minimizing the micro cracks is more effective than changing the thickness in order to regulate the liquid and gas flow in MEAs.



The strongly hydrophilic layer can create additional resistance for gas flow and decrease the methanol crossover.



The layer with large pores has minimum capillary pressure and can reduce the liquid flow rate.

Accomplishments and Progress
– Responses to Previous Year Reviewers' Comments

This project has NOT been previously reviewed at an AMR.

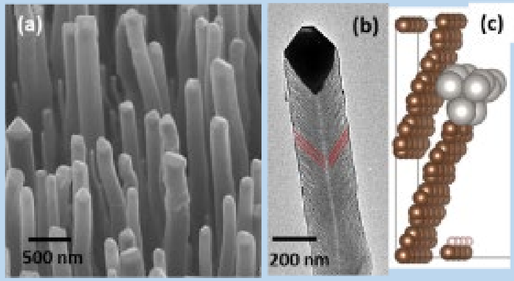
Collaboration and Coordination

Team Members

Sub: Jun Li (KSU)

Anode Catalyst

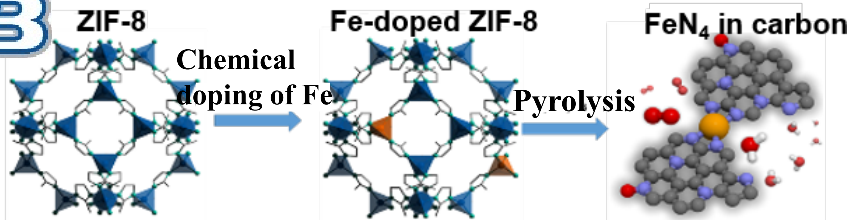
- Sputter PtRu onto VACNFs;
- Spray coat commercial PtRu nanoparticles on VACNFs;
- Microwave-assisted synthesis of PtRu nanoparticles on CNFs/CNTs



Sub: Gang Wu (UB)

Cathode PGM-free Catalyst

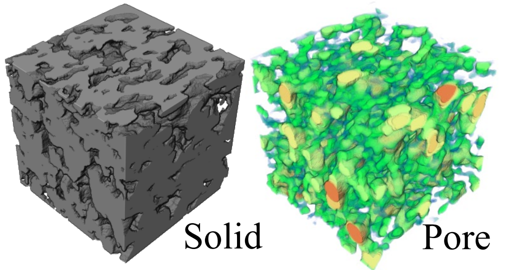
- Fe-N-C catalysts development via oxides doping;
- Dual-site FeCo-N-C catalyst;
- Methanol tolerance studies.



Sub: Shawn Litster (CMU)

Electrode characterization

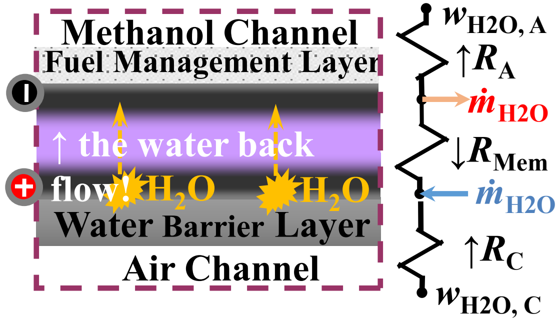
- Ionomer/Catalyst ratio;
- Optimized solvent to prepare the catalyst inks;
- Tomography of commercial electrodes and PGM-free electrodes.



Prime: Xianglin Li (KU)

System integration and prototype development.

- MEA fabrication and testing;
- Fuel and water management;
- Liquid-vapor two-phase models;
- Technical and economic analyses of DMFCs.



Research Collaboration

GENERAL GRAPHENE

NM STATE — Dr. Ivan Vlassiouk, Prof. Sergei Smirnov (Gr coating on membrane)

KU — Prof. Gibum Kwon (Polymer coating on membrane)

IUPUI — Prof. Jian Xie (CCM manufacture)

Remaining Challenges and Barriers

Challenge:

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

Planned Resolution:

- Use half-cell tests to guide the selection, design and synthesis of catalysts and catalyst support materials.
- 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.

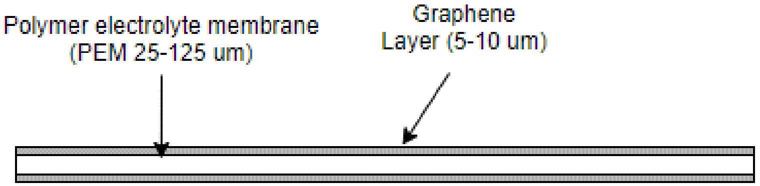
Proposed Future Work

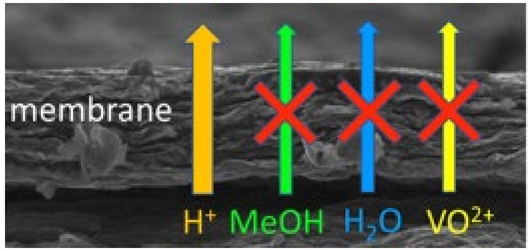
Membranes with Extremely Low Water and Methanol Crossover

GENERAL GRAPHENE

NM STATE

Dr. Ivan Vlassiouk
Prof. Sergei Smirnov
(Graphene coating)



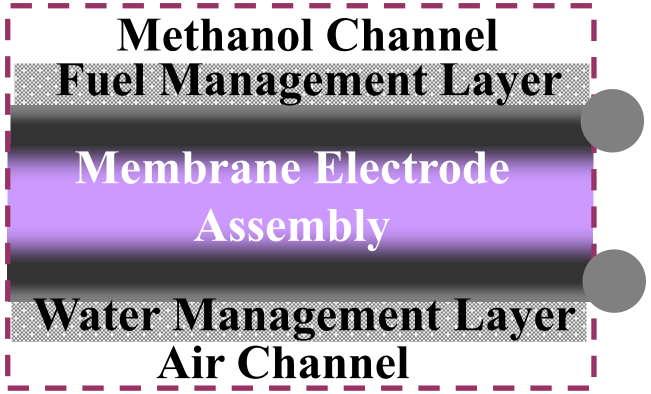


KU

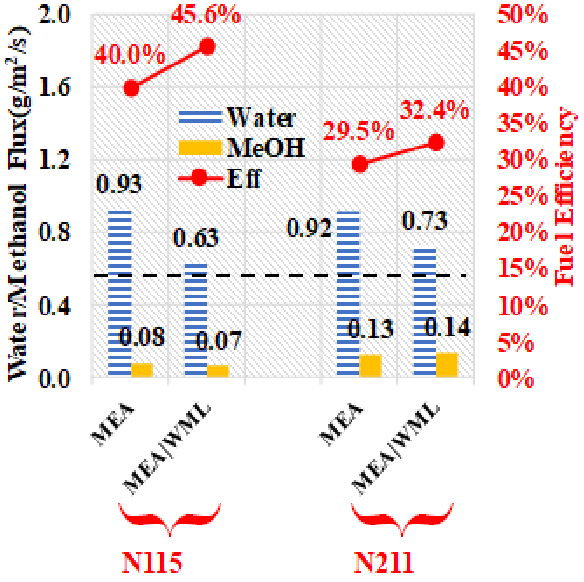
Prof. Gibum Kwon
(Polymer coating)

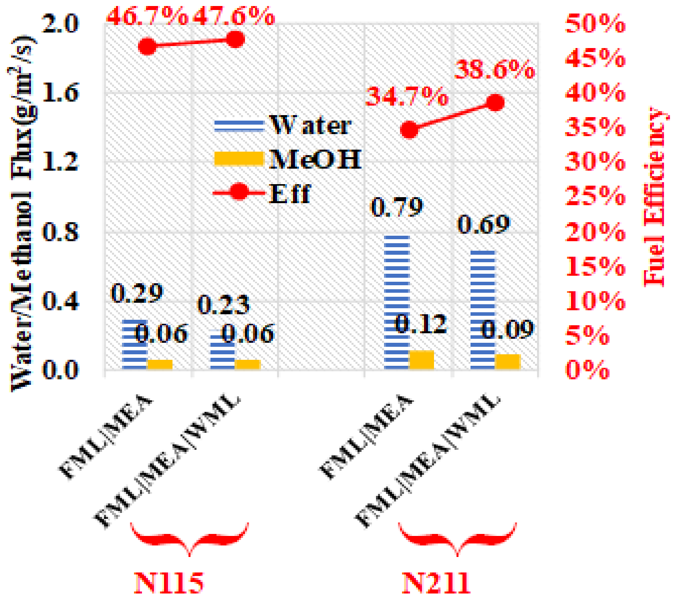
We are also collaborating with Dr. Gibum Kown's lab at KU to develop Nafion membrane coated with fluorinated silica to engineer the surface characteristics.

Regulating Water and Methanol by Capillary Pressure



FML: Fuel Management Layer
WML: Water Management Layer





Summary

2^{nd} Budget Period Go/No-Go Decision Point

Single cell achieved the peak power density of ≥250 mW/cm^2 with ≤3.0 mg_{PGM}/cm^2 catalyst.

2^{nd} Budget Period Accomplishments and Significant Findings

1) DMFC single cell achieved 252 mW/cm^2 peak power with 3.0 mgPGM/cm^2.
2) The latest Fe-N-C catalysts delivered an $E_{1/2}$ of 0.912V and conveyed a current density of 160.2 mA/cm^2 at 0.8 V and peak power density of 558 mW/cm^2 at 80 °C and 150 KPa back pressure with H_2/air.
3) The Fe-N-C catalyst had $E_{1/2}$ > 0.80 V after 30K potential cycling between 0.6 and 0.95 V.
4) The FIB-SEM images of anode electrode were transferred to the pore network model and pore-scale model to simulate liquid-vapor two-phase flow and guide the fuel cell component design.
5) A simple AST protocol to cycle the potential between 0.3 and 0.5V is proposed.
6) Analysis of technical and economic feasibility of DMFC as the power source of electric forklifts.
7) Customized PtRu/TiO_2/O-NCNTs showed higher activity than the best commercial anode catalysts in half-cell tests.
8) Experimentally measured the reaction order of vapor-feed MOR.

ACKNOWLEDGEMENT

DOE EERE: Energy Efficiency and Renewable Energy Fuel Cell Technologies Office (FCTO)

DOE Program Manager: Donna Ho

Project Team

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Kansas State University
- **Prof. Jun Li**
- **Archana Sekar**

Carnegie Melon University
- **Prof. Shawn Lister**
- **Mohamed Abdelrahman**

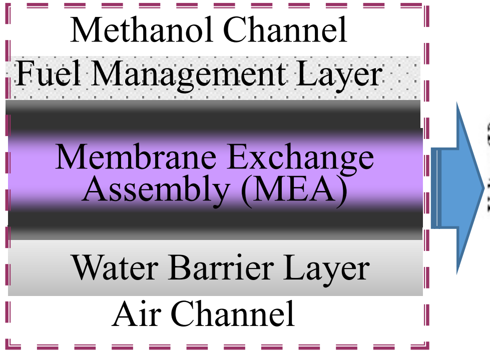
Technical Backup and Additional Information

Maximum 20 slides

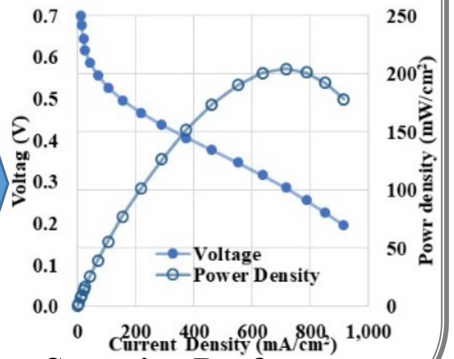
Technology Transfer Activities

Technical Feasibility of DMFCs

➔ **Fuel Cell Size and Cost + Fuel Cost**



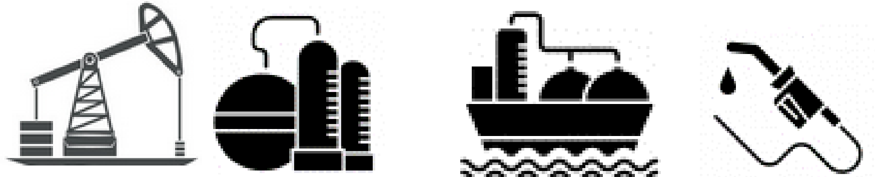
The New DMFC Design



Superior Performance

Full Fuel Cycle Analyses of Fuels

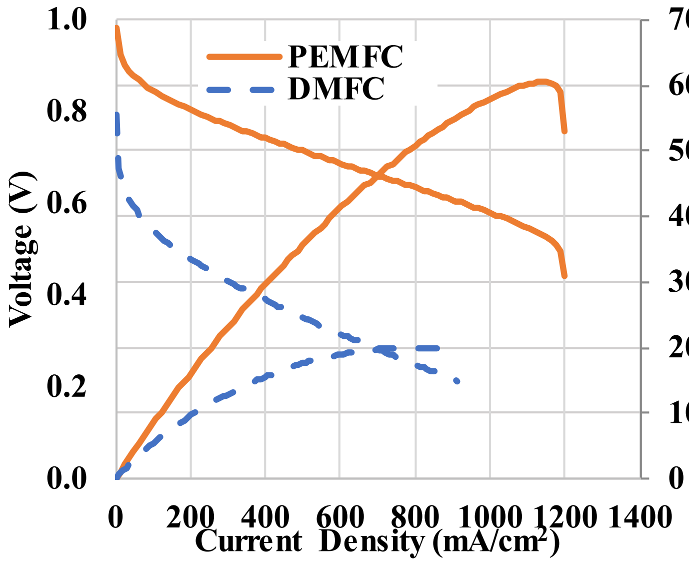
➔**GHG Emissions + PM Emissions**



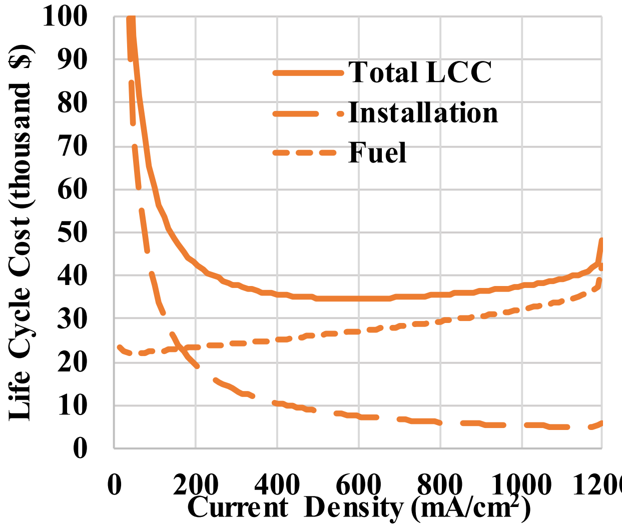
Extraction | Processing | Transportation | End User

Technical, economic and environmental analyses of DMFCs as the power source for forklifts.

Parameters	PEMFC	DMFC
Average Power of Class I&II Forklifts (kW)	2.75	
Annual Energy Consumption of Class I&II Forklifts (MJ)	23,760	
Average Power of Class III Forklifts (kW)	0.55	
Annual Energy Consumption of Class III Forklifts (MJ)	4,752	
Life Time of the Fuel Cell (years)	10	
Fuel Cell Cost ($/kW)	1,868	3,772
Fuel Price ($/GGE)	8 [4-22]	0.43
Energy Content of Fuel (MJ/kg)	120.0	22.0



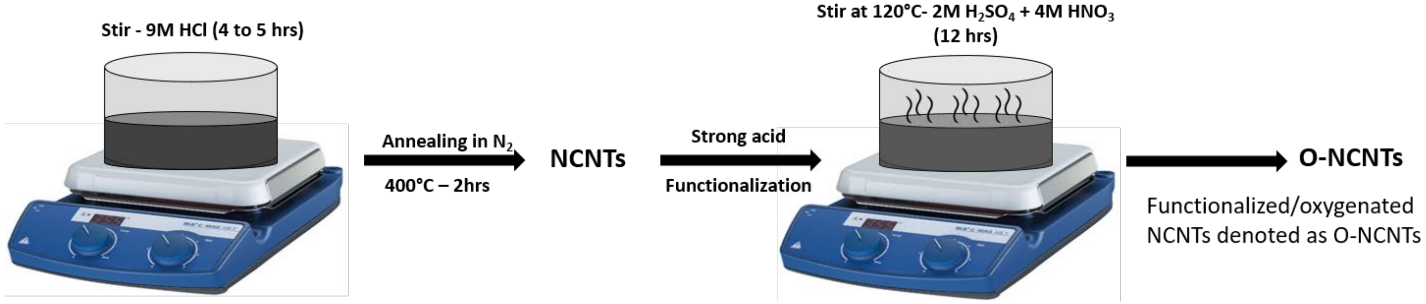
Performance of the PEMFC and DMFC technologies used in the analyses.



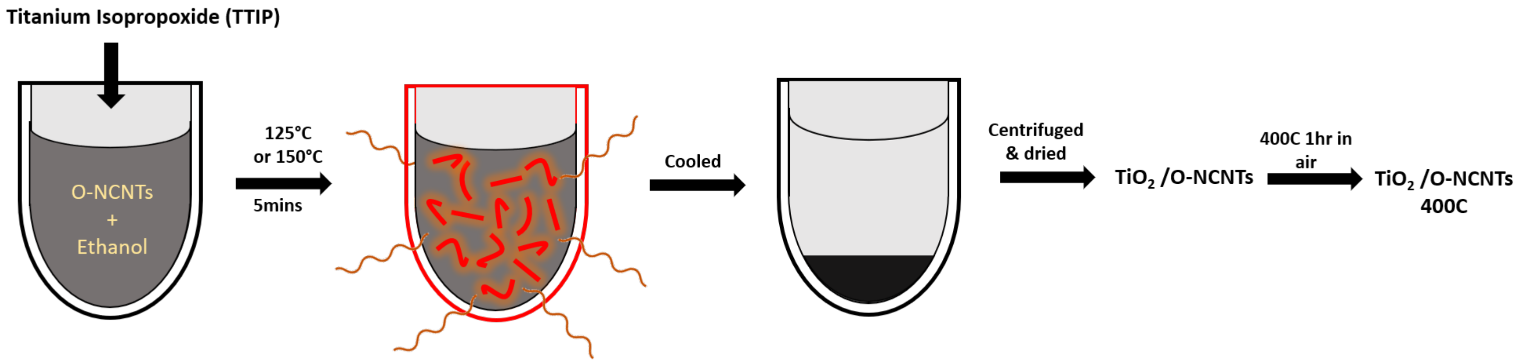
Example of life cycle cost of a PEMFC that drives Class I&II forklifts ($8/GGE hydrogen price, 10-year lifetime).

Technical Backup – Anode Catalyst Synthesis

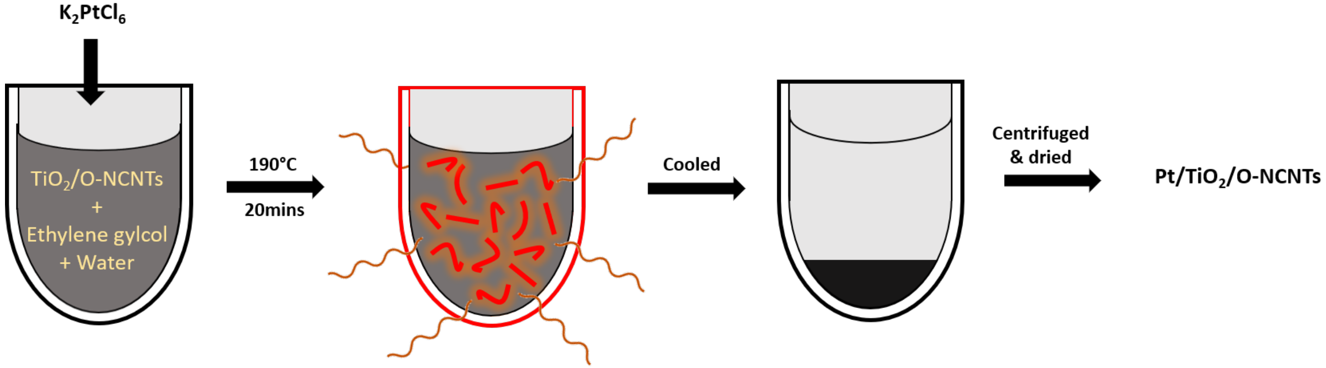
Step 1: NCNTs functionalization



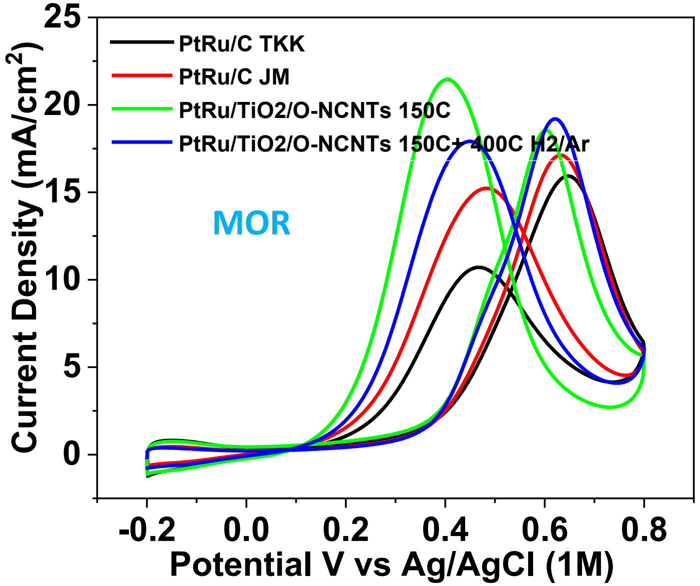
Step 2: TiO_2 deposition on O-NCNTs by Microwave Assisted Synthesis

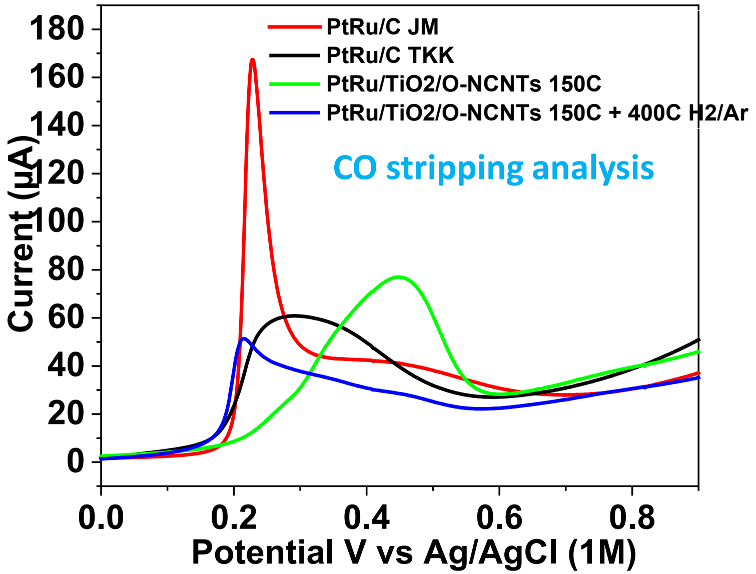


Step 3: Pt deposition on TiO_2/O-NCNTs by Microwave Assisted Synthesis



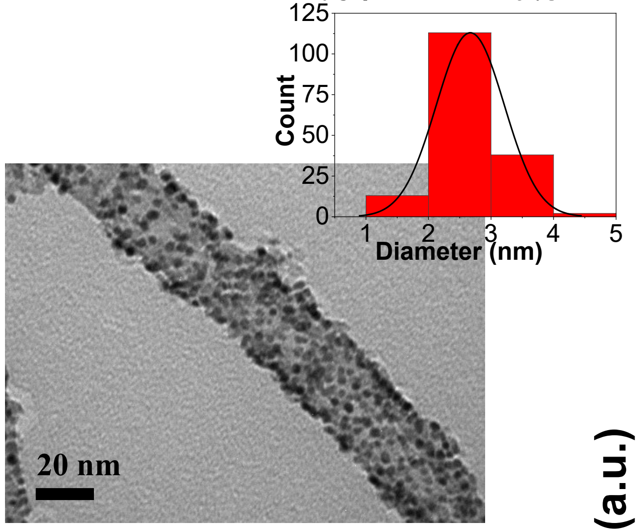
Half-Cell CV tests with 0.75 M Methanol ($36\ \mu g_{Pt}/cm^2$ and $18\ \mu g_{Ru}/cm^2$)





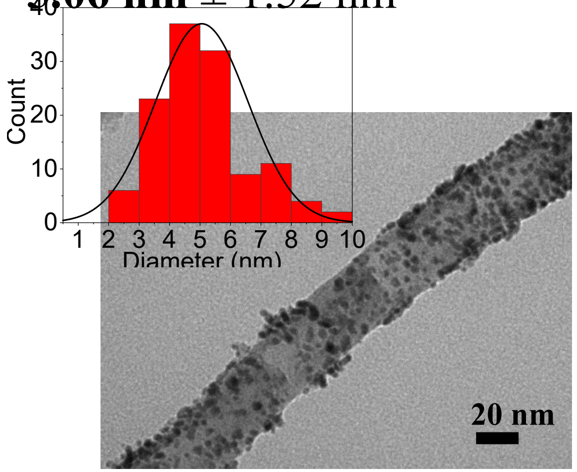
Technical Backup – Anode Catalyst Synthesis

2.67 nm ± 0.54 nm

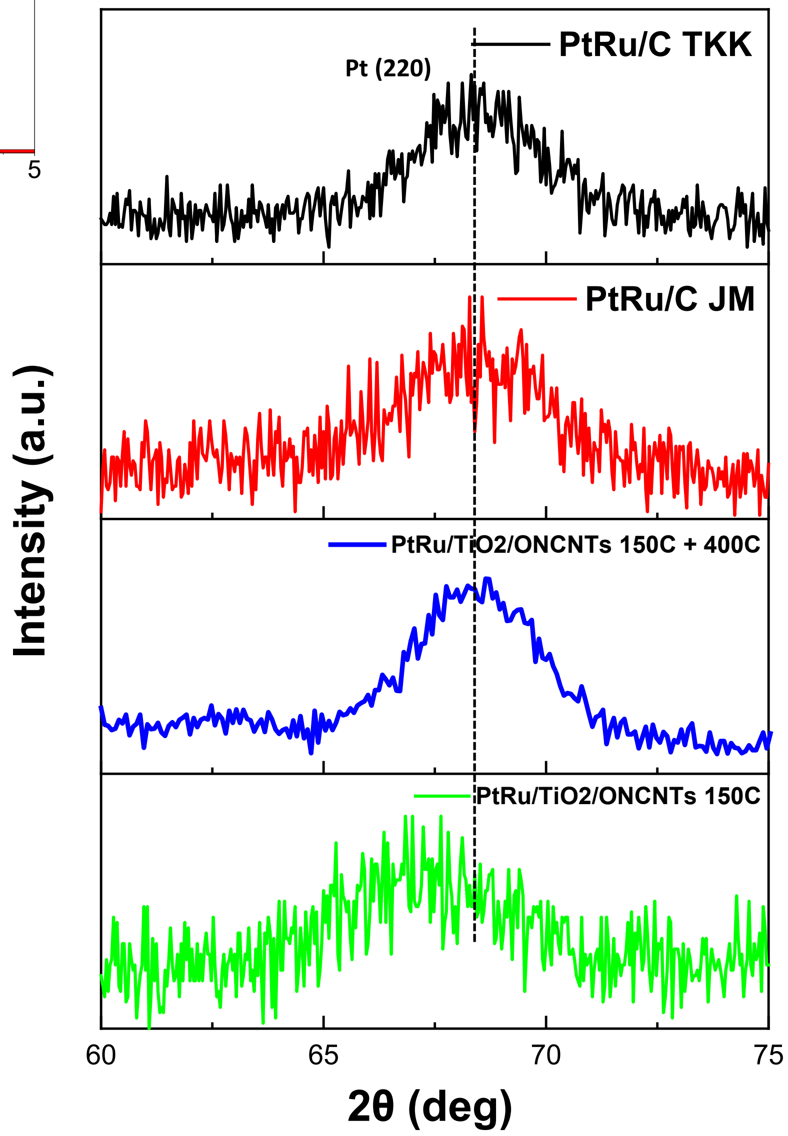


PtRu/TiO_2/O-NCNTs

5.06 nm ± 1.52 nm



PtRu/TiO_2/O-NCNTs 400C



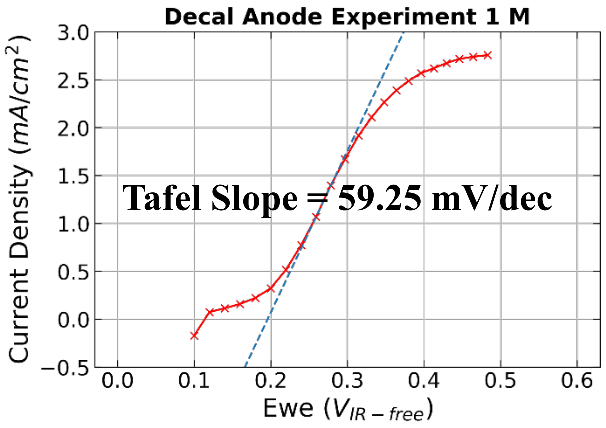
Inference:

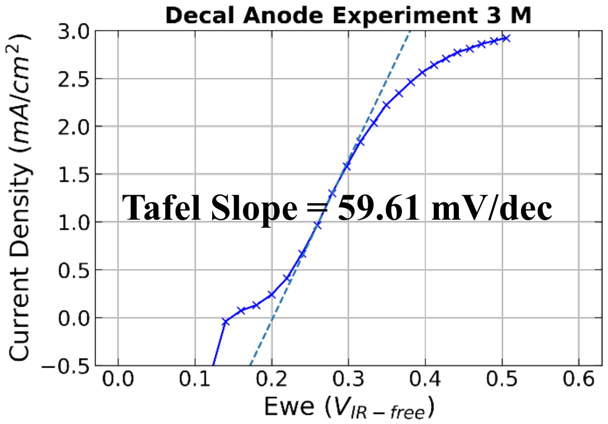
- The 400C annealed sample showed 2θ shifts in Pt diffraction planes which suggest that Ru has alloyed with Pt.
- Calculated the alloying degree in the annealed sample using Vegard's law.
- PtRu/TiO2/O-NCNTs 400C H2/Ar showed a significant shift in the 2θ at Pt (220) and Pt (311) plane.
- Alloying degree (or atomic fraction in alloy formation) was found to be 1.5:1, which is close to commercial PtRu alloy in JM/TKK.

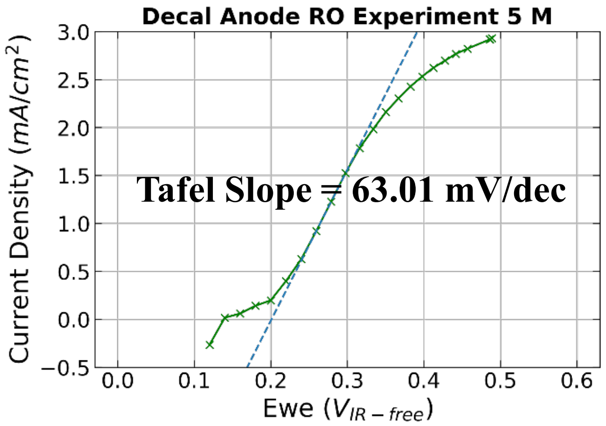
Catalyst	X_{Pt}	X_{Ru}	Atomic fraction (Pt:Ru)
PtRu/TiO2/O-NCNTs	100 %	0 %	**Only Pt (no alloy)**
PtRu/TiO2/O-NCNTs 400C H2/Ar	44.5 %	55.5 %	**1.5 : 1**
PtRu/C TKK	55%	45%	**~1 :1**
PtRu/C JM	56%	44%	**~1: 1**

Carnegie Mellon University

Technical Backup – Vapor-fed MOR Reaction Order

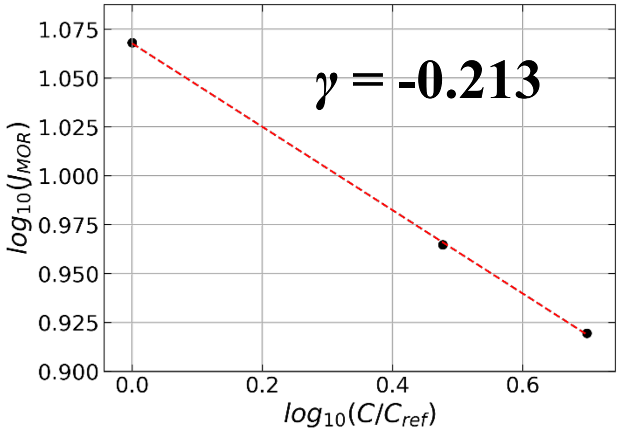






Current increases slightly with lower MeOH concentrations

Tafel slopes are consistent with an ideal two-electron rate determining step



The current density at 0.26 V vs. RHE

The reaction is likely to be zero-order. However, there may be some effects of methanol crossover.

MEA with Alfa Aesar PtRu/C anode and JM Pt/C cathode

Anode: vaporized methanol; Cathode: 200 mL/min hydrogen; 80°C.

Progress toward DOE Targets or Milestones

Go/No-Go Criteria at the end of 2nd Budge Period (4/01/2020 to 3/31/2021)

Fabricate and test MEAs to achieve 250 mW/cm^2 peak power density with ≤ 3 $mgPGM/cm^2$

Characteristic	**Units**	**2nd BP Targets**	**Project Status**
Peak Power Density	mW/cm^2	250	252
Catalyst Loading	mg_{PGM}/cm^2	3	3
MEA Size	cm^2	50	5
Temperature	^oC	~80	99
Pressure	kPa	~100	300
Stoichiometric ratio, Methanol	/	≤2.0	1.0
Stoichiometric ratio, Air	/	≤3.0	34.8

Publications and Presentations

1. Qiurong Shi, Yanghua He, Xiaowan Bai, Maoyu Wang, David A Cullen, Macros Lucero, Xunhua Zhao, Karren L. More, Hua Zhou, Zhenxing Feng, Yuanyue Liu, Gang Wu. “Methanol tolerance of atomically dispersed single metal site catalysts: mechanistic understanding and high-performance direct methanol fuel cells”, *Energy Environmental Science*, 13 (**2020**) 3544-3555.
2. Nathaniel Metzger, Archana Sekar, Jun Li, Xianglin Li. "Understanding Carbon Dioxide Transfer in Direct Methanol Fuel Cells Using a Pore-Scale Model", *Journal of Electrochemical Energy Conversion and Storage*, (**2021**) JEECS-20-1185.
3. Xianglin Li, Zheng Miao, Lauren Marten, Isaac Blankenau. “Experimental measurements of fuel and water crossover in an active DMFC”, *International Journal of Hydrogen Energy*, 46 (**2021**) 4437-4446.
4. Nathaniel Metzger, Samuel Hong, Sangwon Kang, Jianan Zheng, Tylor Bachet, Kelvin Feuerborn, Thomas DeAgostino, Xianglin Li. "Technical and Economic Analysis of Fuel Cells for Material Handling Applications", *Renewable and Sustainable Energy Reviews*, **Under Review**.
5. Zheng Miao, Zihang Li, Ya-Ling He, Jinliang Xu, Xianglin Li, "A Liquid-Vapor Two-Phase Model of Direct Methanol Fuel Cells with PGM-Free Cathode Catalyst", *Journal of Electrochemical Energy Conversion and Storage*, **Under Review**.