Stationary Direct Methanol Fuel Cells Using Pure Methanol

PI and presenter: Xianglin Li / University of Kansas

Co-PI: Jun Li / Kansas State University

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

Co-PI: Shawn Litster / Carnegie Mellon University

Date: May 30, 2020

2020 DOE Hydrogen and Fuel Cells Program Review **Project ID # FC317**

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**

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*: $398,797**

*** As of 3/31/2020**

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: 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.**
- **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 $\leq$ 3 $mgPGM/cm^2$.**
- **1st BP target (10/1/2018 - 3/31/2020): The fuel cell prototype to be delivered at the first year (25 cm^2 MEA) will meet the milestone of $\geq$ 250 mW/cm^2 with 4 $mgPGM/cm^2$.**

Approach

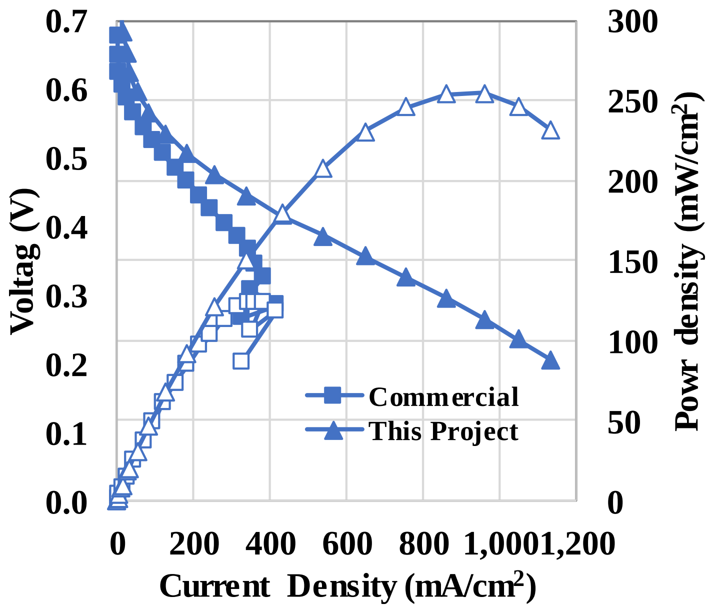
This research integrates complementary *institutional expertise* on

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

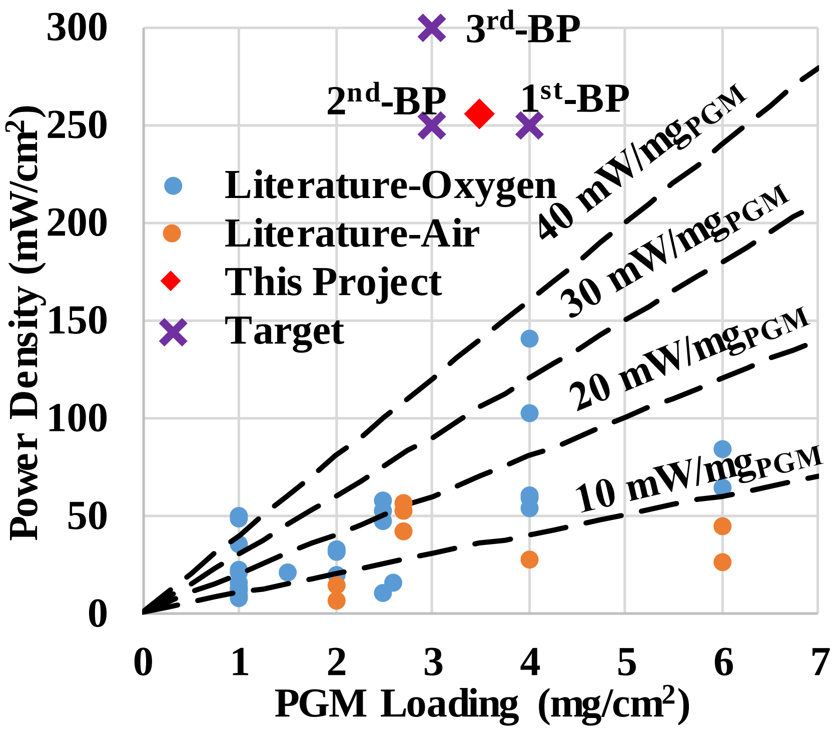
To meet planned milestones and Go/No-Go decisions for the 1st BP

	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).	100% 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).	100% 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.	95% completion

Accomplishments and Progress – Overview



Performance of MEA made from commercially available catalysts: 4.5 mg/cm² PtRu as anode and 1.25 mg/cm² Pt as cathode, tested with 1M methanol (1 mL/min) and air (1 bar, 0.1 L/min) at 80 ºC, and performance of MEA employing 3.5 mg/cm² commercial PtRu/C (72%) as anode and 4.2 mg/cm² Fe_2O_3-derived-Fe-N-C catalysts as cathode with 1M methanol (0.5 mL/min) and air (2.5 bar, 1 L/min) at 96.5 ºC.



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).

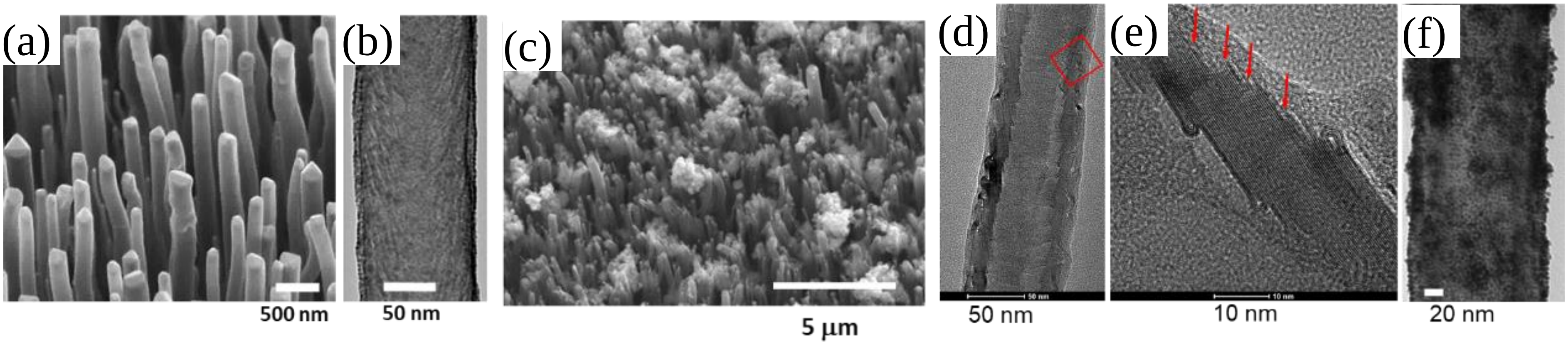
The project team has successfully met the Go/No-Go performance milestone of the 1st budget period (10/01/2018 to 03/31/2020): Achieve the peak power density of at least 250 mW/cm² with no more than 4.0 mg/cm² PGM catalyst loading. *Please note that both the air flow rate and air pressure are higher than proposed operating conditions.*

Accomplishments and Progress
– Anode Catalyst

Approach 1
Sputter PtRu Nanoparticles on VACNFs

Approach 2
Spray Commercial PtRu Nanoparticles on VACNFs

Approach 3
Microwave-Assisted Synthesis of PtRu Nanoparticles on Dispersed CNFs/CNTs

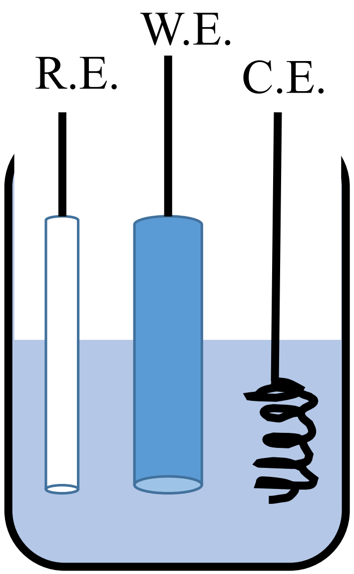


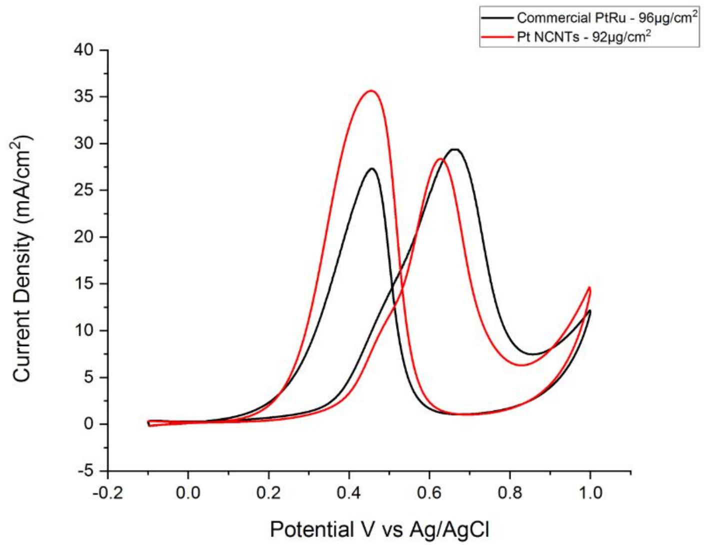
Approach 1 (a) SEM and (b) TEM images of PtRu (1:1 atomic ratio) sputtered onto the VACNFs grown on a graphite paper substrate. **Approach 2** (c) A SEM image of commercial PtRu nanoparticles (1:1 atomic ratio) airbrush spray-coated on a VACNF array grown on a graphite paper substrate. **Approach 3** TEM images of (d) a bare CNF at low magnification, (e) the high-resolution structure of the part highlighted by the red box showing the conically stacked graphitic CNF sidewall (indicated by red arrows) at high magnification, and (f) PtRu nanoparticles deposited on a CNF by the microwave process.

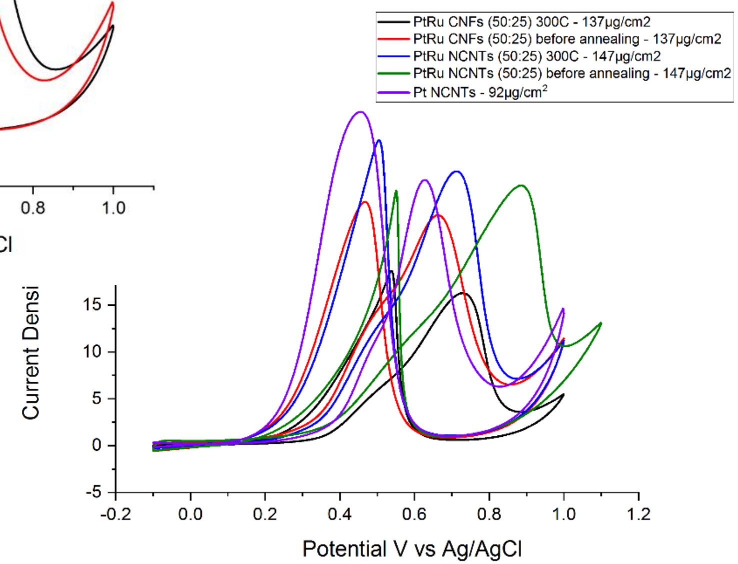
Approaches 1 and 2 are effective for low PtRu loading (<1 mg/cm^2). ***Approach 3*** **can synthesize PtRu particles with different sizes and mass ratio on CNTs or CNFs.**

Accomplishments and Progress
– Anode Catalyst (Half-Cell Studies of Methanol Oxidation)

0.5M H_2SO_4 + 3M MeOH
Final MeOH conc. = 0.75 M





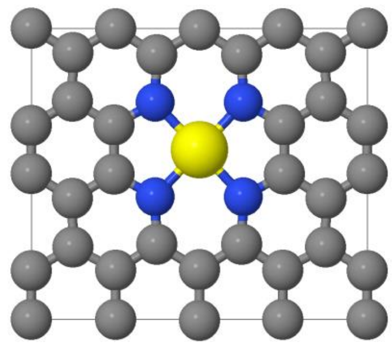


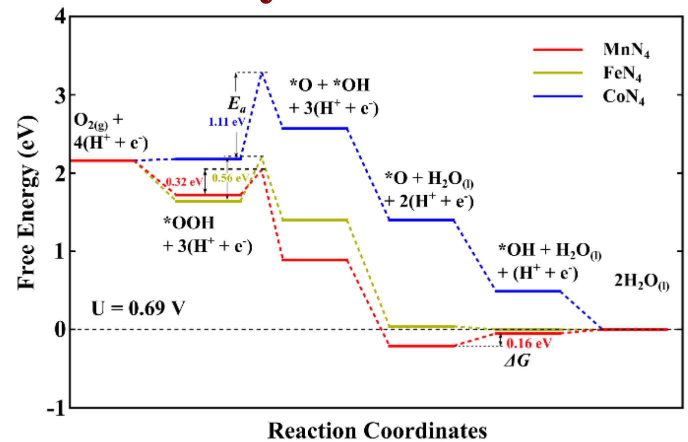
- A higher I_f/I_b ratio and lower peak potentials in cyclic voltammetry are preferred;
- The as-synthesized Pt/NCNTs (50) shows **comparable I_f with the commercial PtRu/C, but a lower peak potential at 0.62 V, though I_b is higher.**

Accomplishments and Progress
– Cathode PGM-free Catalysts

Activity Improvement of Fe-N-C Catalysts

Hypothesis **: Density functional theory (DFT) calculation suggested that the possible FeN_x sites could be as active as Pt for the O_2 adsorption and subsequent O=O bond disassociation during the ORR.**

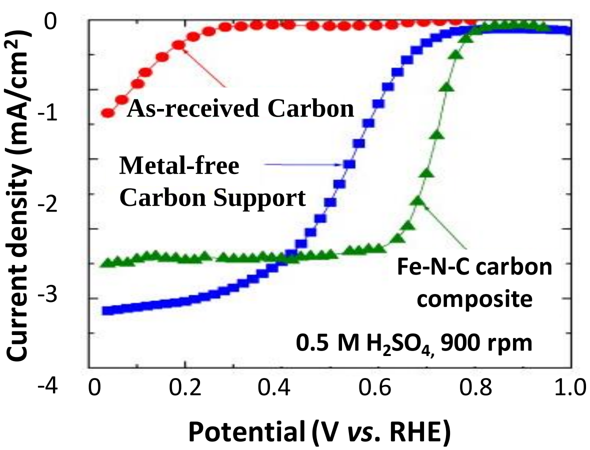


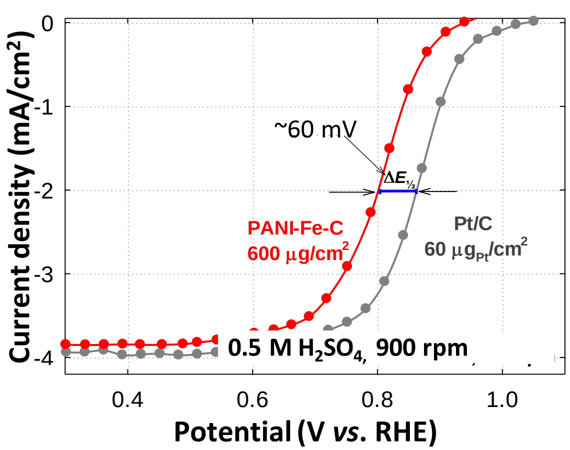


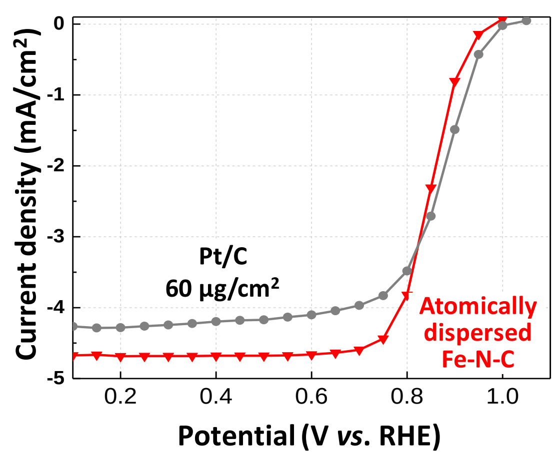
$E_{1/2}$= 0.72 V (2008)

$E_{1/2}$= 0.80 V (2011)

$E_{1/2}$= 0.87 V (2018)







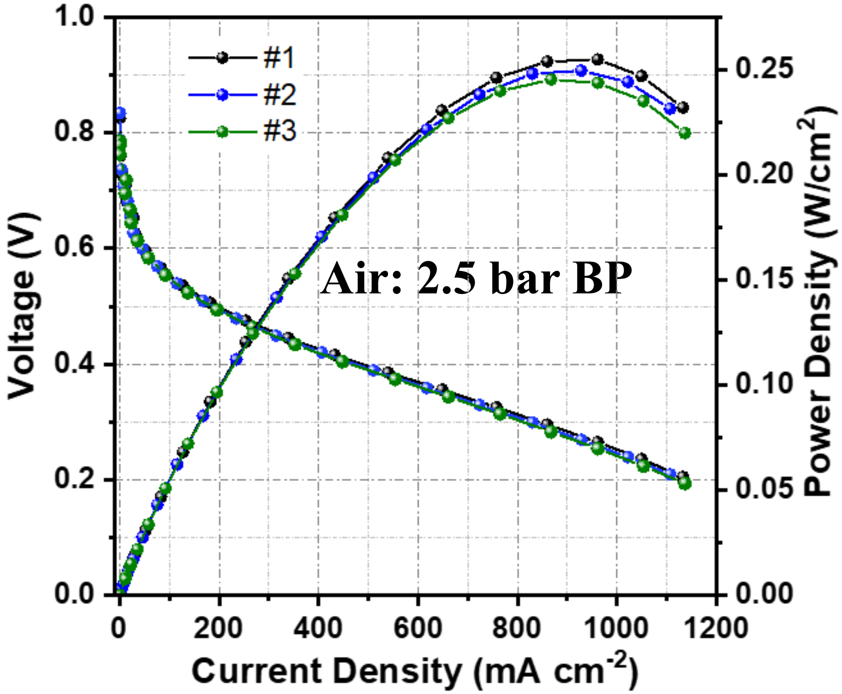
Popov, Wu, et al., *J. Power Sources*, **183**, 34, 2008.

Wu and Zelenay *et al.*, *Science*, **332**, 443, 2011.

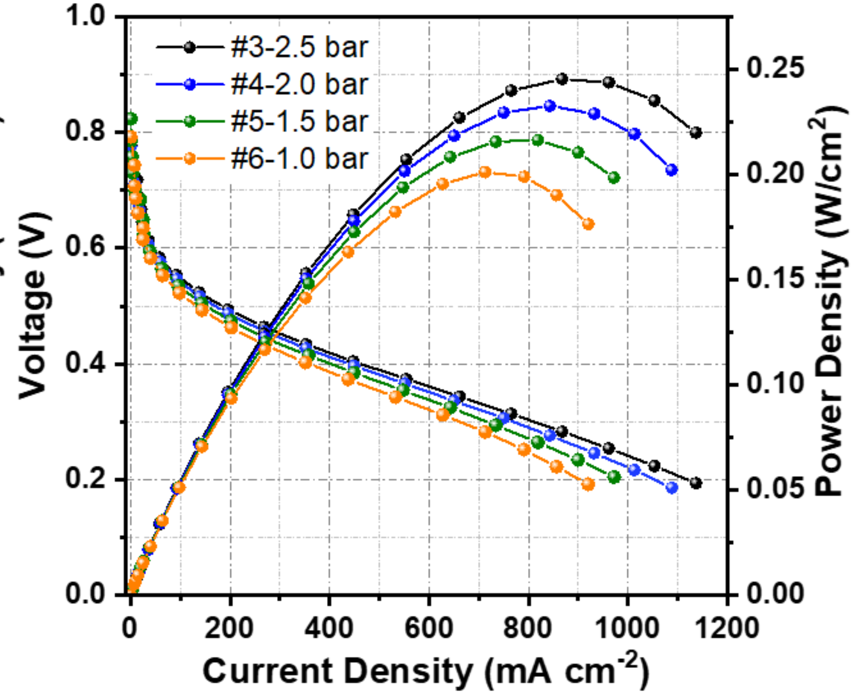
Wu, et al., *JACS*, **139**, 14143–14149, *2017*.

Accomplishments and Progress
– Cathode PGM-free Catalysts

Performance and Stability



Air Back Pressure



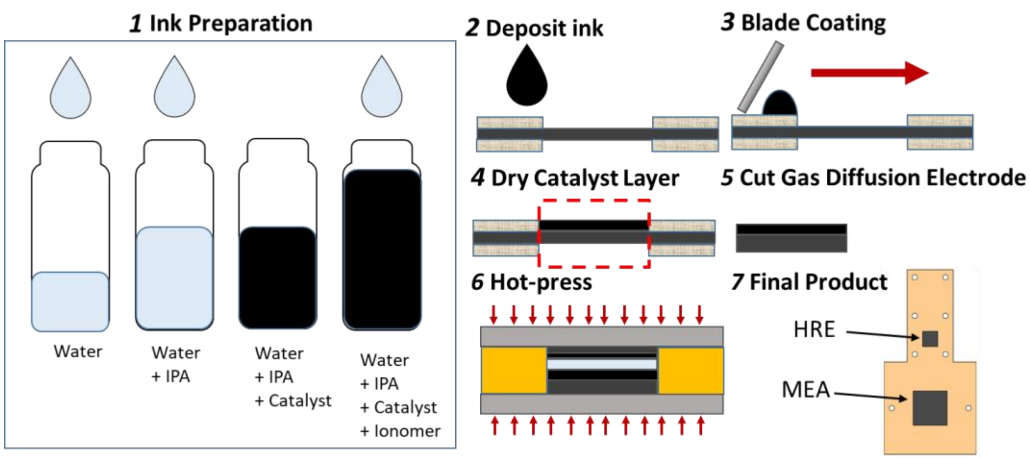
Anode: PtRu/C (72%): 3.5 mg/cm^2; Cathode: 10mg Fe-N-C:4.2 mg/cm^2
Nafion 212; 96.5 °C; 100%RH; 1M Methanol: 0.5 mL/min; Air: 1L/min

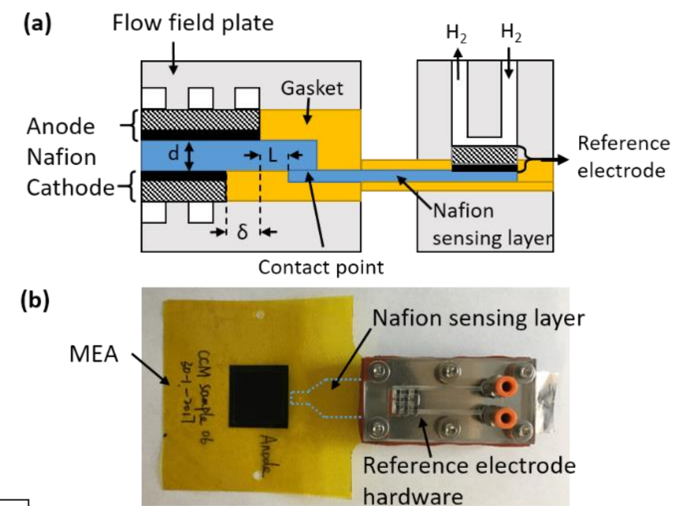
- **The maximum power density of 256 mW/cm^2 was obtained with good stability.**
- **The performance target was exceeded using high air backpressure and flow rates.**
- **Performance at reduced air backpressures and flow rates will be tested.**

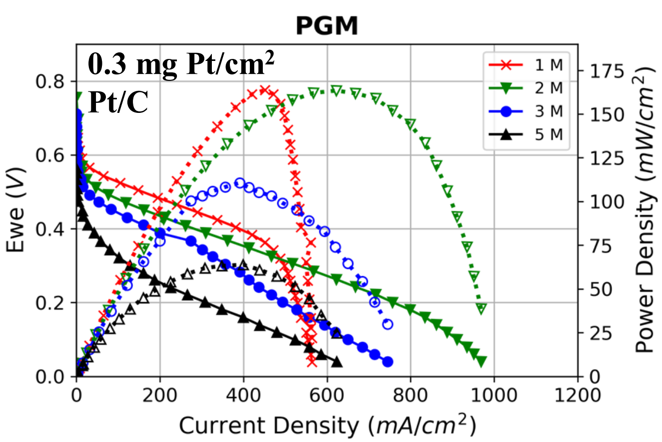
Accomplishments and Progress
- MEA development and diagnostics

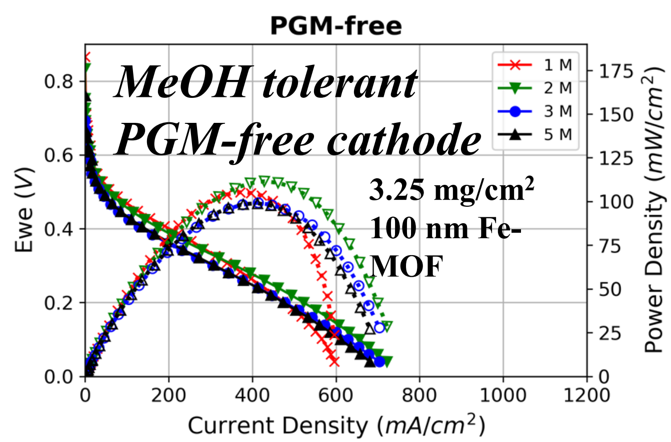
Carnegie Mellon University

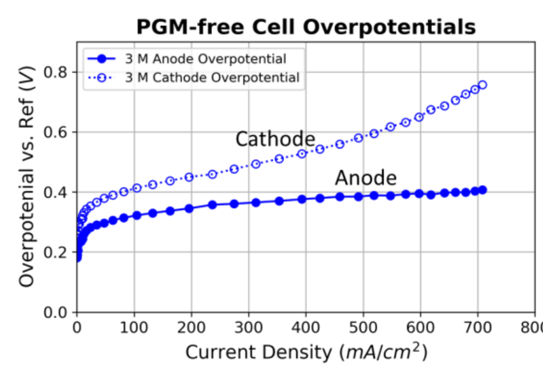
- Development of PGM-free cathode MEAs for DMFCs
- Integrated hydrogen reference electrodes to distinguish anode versus cathode overpotential
- Benchmarking of methanol tolerance of PGM-free cathode versus Pt/C PGM cathode
- **PGM-free cathode outperforms PGM at >3M MeOH with cathode overpotential ~50% higher than anode commercial JM PtRu/C GDE**











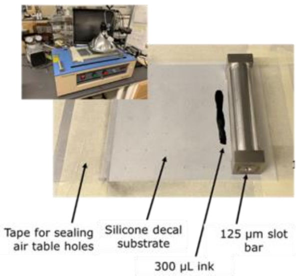
Nafion 212; 80 °C; Air: 100% RH, 150 kPa, 200 ml/min; MeOH: 2 ml/min

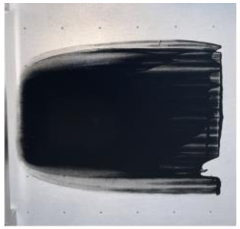
Accomplishments and Progress
-Anode Optimization: Ionomer and Ink

Carnegie Mellon University

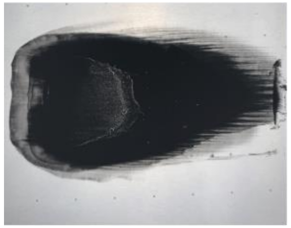
- Development of PGM anodes to support KSU catalyst integration and provide reference PtRu/C one-sided CCMs for the project
- Optimization of ionomer I/C and solvent for maximum MeOH oxidation activity
- Distinct transport requirements for MeOH oxidation versus ORR or HOR
- Best performing anodes featured lower I/C
- Development of automatic coating of high loading anode decals for preparing DMFC CCMs for higher activity and to facilitate anode porous transport layer studies in Year 2.

Automatic coater





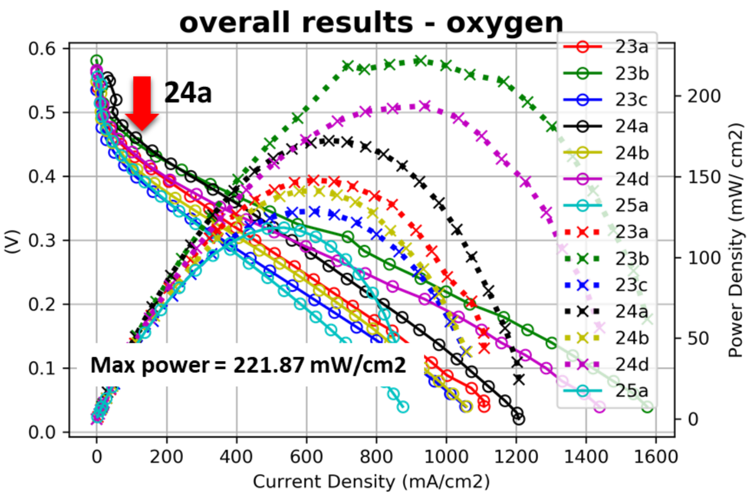
8 wt %, IPA:H2O 5:1
1.02 mg/cm2, 6 passes

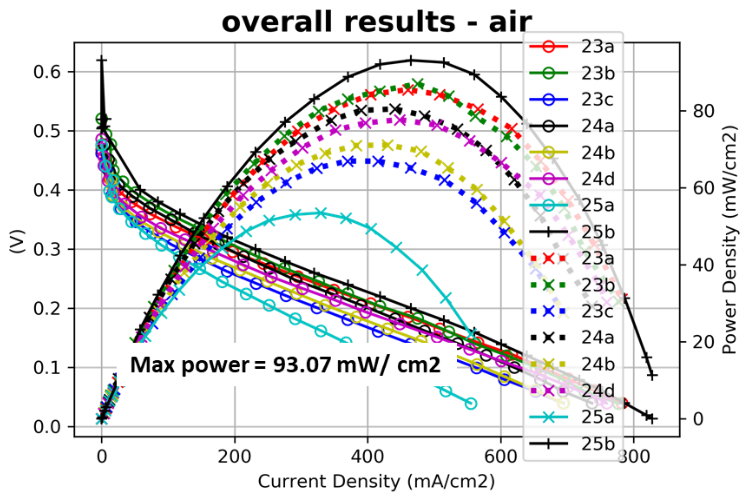


10 wt % solids, IPA:H2O 1:1
0.73 mg/cm2, 3 passes

5 wt %, IPA:H2O 5:1
0.42 mg/cm2, 28 passes

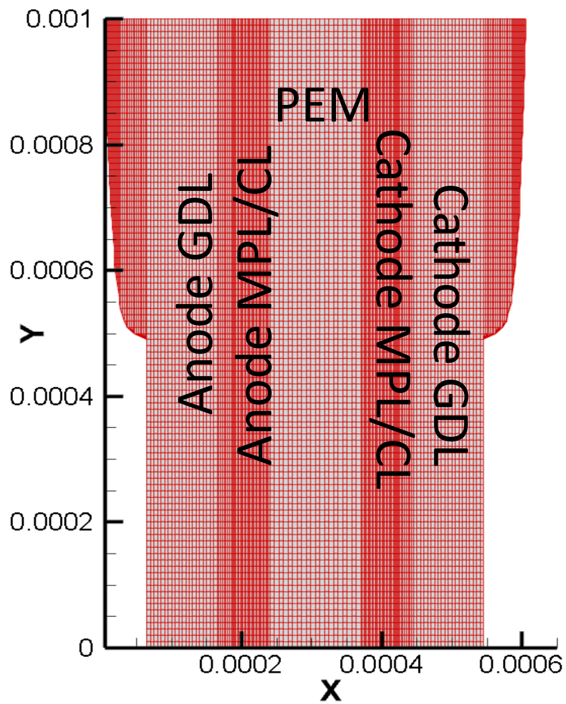
Broad parametric study of anode ink composition



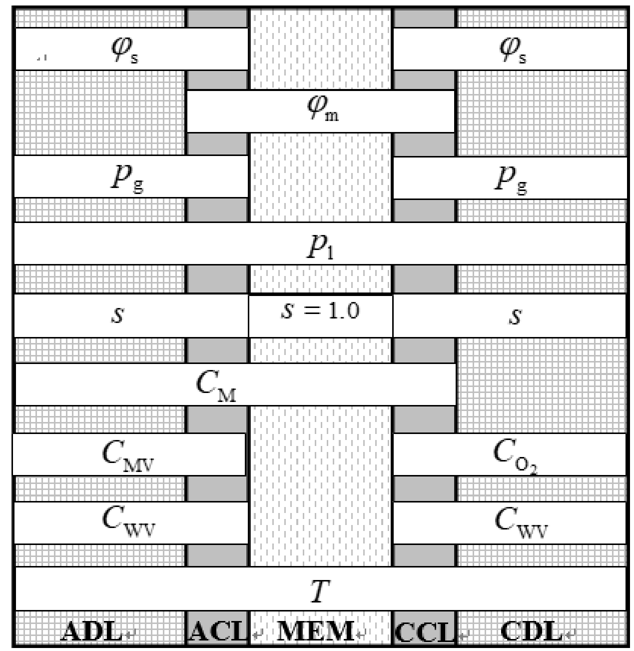


Nafion 212; Commercial cathode Pt/C GDE; 80 °C; Air: 100% RH, 150 kPa, 200 ml/min; MeOH: 2 ml/min

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



The computational domain and mesh.



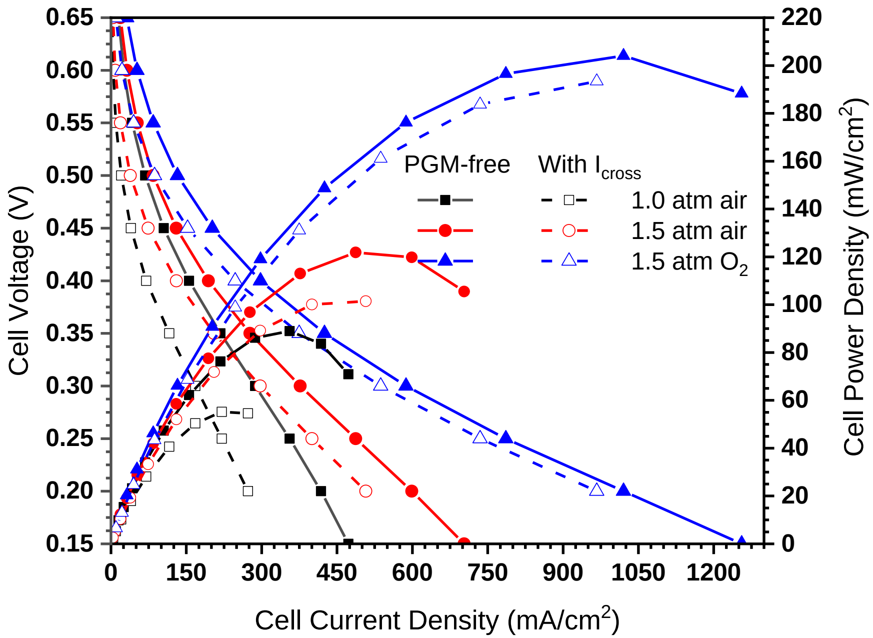
Specified sub-domains for all variables

Governing Equations Solved

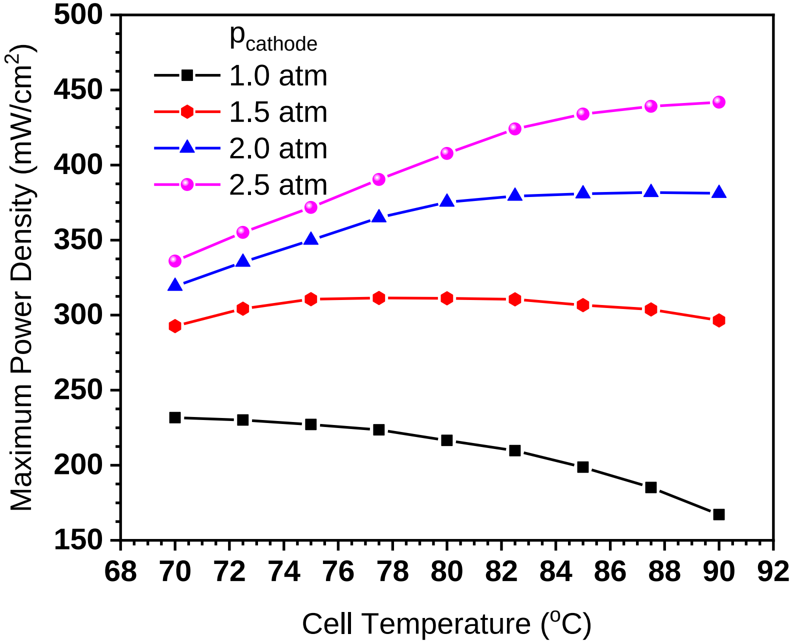
Solid potential (φ_s); Membrane potential (φ_m); Gas pressure (p_g); Liquid saturation (s)

- Velocity of liquid phase (u_l); Velocity of gas phases(u_g)
- Concentration of liquid MeOH (C_M); Concentration of MeOH vapor (C_{MV})
- Concentration of H_2O Vapor (C_{WV})

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



Effects of the methanol crossover on the DMFC performance.



Effect of the operation temperature and cathode back pressure (keep the relative humidity of air as 100%).

- **Although the PGM-free catalyst is methanol tolerant, the crossover of liquid methanol will hinder the oxygen transfer.**
- **The humidification of air will reduce the partial pressure of oxygen pressure. Liquid water in the methanol solution is sufficient to hydrate the membrane, therefore, the cathode air may not need to be humidified.**

Responses to Previous Year Reviewers' Comments

Comment: ***"… there is no clear reason a direct methanol fuel cell is needed…without an application, uncertainty will remain around the objectives, which will lead to milestones and targets that relate more to what can be achieved rather than what needs to be achieved."***

- **The team is carrying out technical and economic analyses of DMFCs applied to the forklift industry. Preliminary results show economic benefits of DMFC compared with PEMFC in many operating scenarios. Further analysis will recommend performance targets of DMFCs in several case studies.**

Comment: ***"…the team needs to concentrate on improvements to the anode, rather than ill-conceived reductions in methanol crossover and methanol tolerance and unsubstantiated benefits of the use of high methanol feed concentration (there are some benefits, but overall, they are quite minimal). Improving the anode is easier said than done, but it is the right primary focus of any research aimed at changing DMFC status in a major way."***

- **We agree that the performance of anode catalyst is critical. The team is applying several different approaches to improve the catalytic activities of the anode catalyst. Using high-concentration methanol solutions will be the focus of the 3rd BP after developing high-performance MEAs tested with dilute methanol solutions.**

Comment: ***"The way the PGM-free catalyst development has been carried out to date appears not to be DMFC-specific and is largely a duplication of the effort in other projects."***

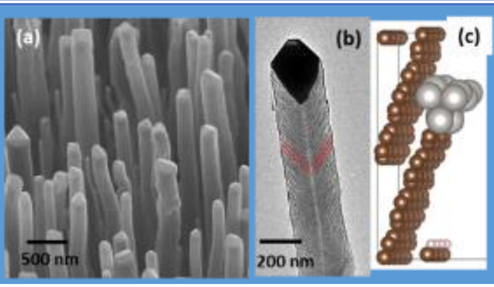
- **Advance of PGM-free catalysts will benefit both PEMFC and DMFC. The different reaction kinetics and mass transfer properties between PEMFC and DMFC results in slightly different requirements on the cathode catalyst design. The team is planning to apply knowledge learned from existing studies and model simulations to further improve the DMFC performance using PGM-free cathode catalyst.**

Collaboration and Coordination

Sub: Jun Li (KSU)

Anode Catalyst

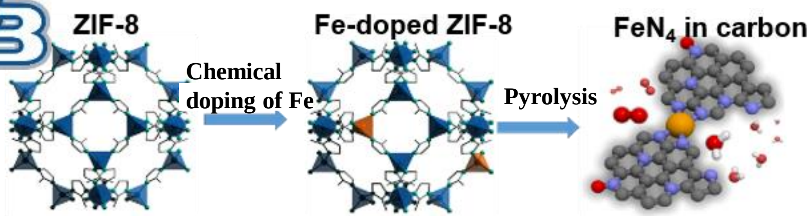
- Sputter PtRu onto VACNFs;
- Spray coat commercial PtRu nanoparticles on VACNFs;
- Microwave-assisted synthesis of PtRu nanoparticles on CNFs/CNTs



Sub: Gang Wu (UB)

Cathode PGM-free Catalyst

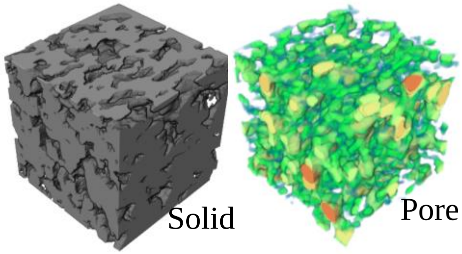
- Fe-MOF catalysts with controllable particle sizes;
- Co-N-C catalysts and FeCo-N-C catalyst;
- Methanol tolerance studies.



Sub: Shawn Litster (CMU)

Electrode characterization

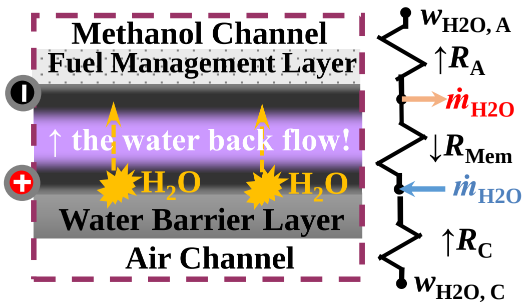
- Ionomer/Catalyst ratio;
- Optimized solvent to prepare the catalyst inks;
- Tomography of commercial electrodes and PGM-free electrodes.



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.



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.**

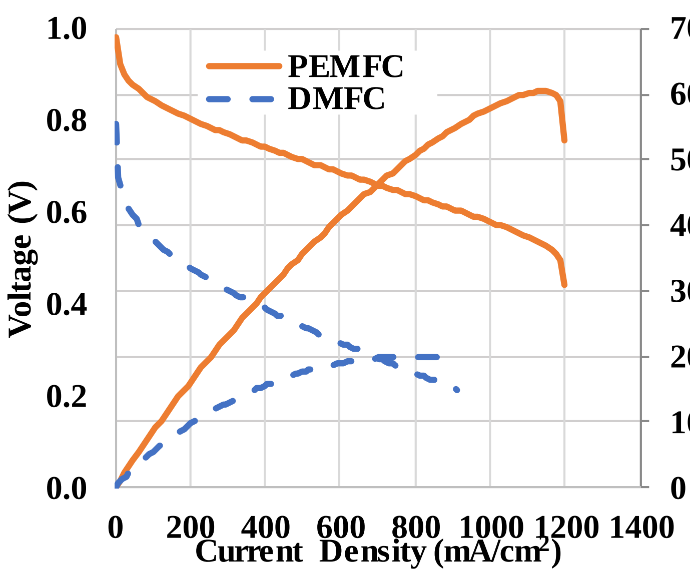
Planned Resolution:

- **Select, design and synthesize catalysts and catalyst support materials based on existing knowledge and successful progress.**
- **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.**

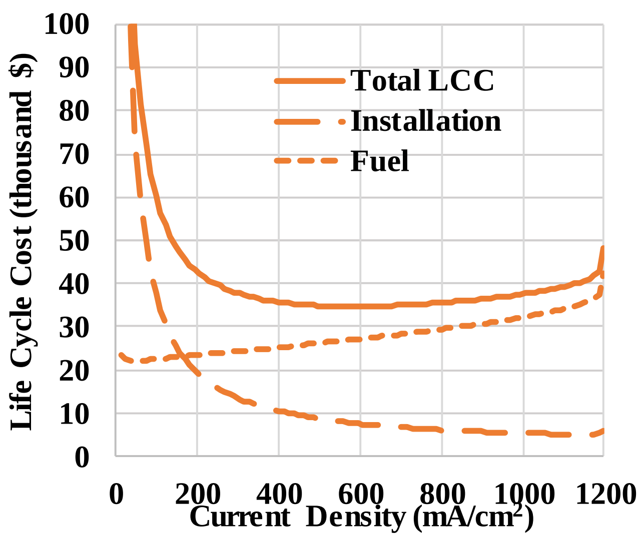
Technology Transfer Activities

-Technical and Economic Analyses of Fuel Cells in Forklift Industry

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



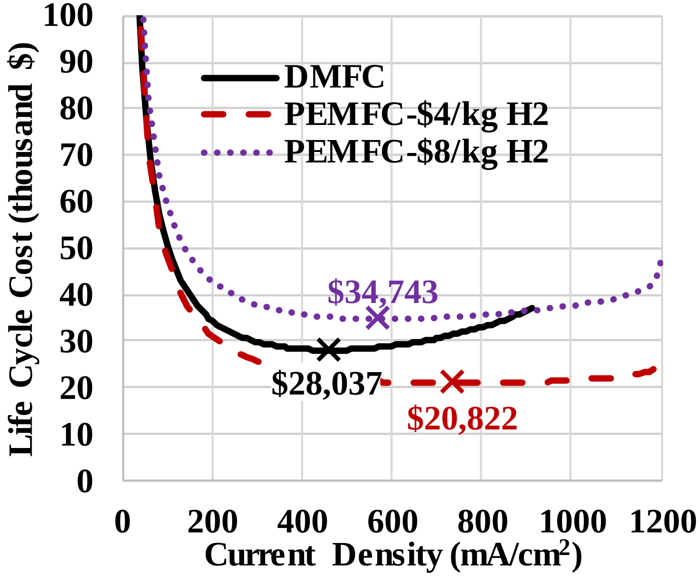
Performance of the PEMFC and DMFC in the analyses.



The life cycle cost (LCC) of a PEMFC that drives Class I&II forklifts ($8/GGE H_2, 10-year lifetime).

Technology Transfer Activities

-Technical and Economic Analyses of PEMFC vs. DMFC



Estimated LCC of fuel cells that power Class I&II forklifts.

Future Plans

- **Extend the analyses to Class III forklifts.**
- **Include the cost of hydrogen ($500,000 to $1M per site) and methanol infrastructure (~$75,000 per site) into the analyses.**
- **Use the latest DMFC performance obtained by this project.**
- **Carry out sensitivity analyses of hydrogen cost, fuel cell cost, lifetime etc.**
- **Compare the LCC of forklifts driven by batteries and maybe internal combustion engine.**

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 1st Budge Period (10/01/2018 to 3/31/2020)

- ***Fabricate and test 25-cm^2 MEAs*** **to achieve 250 mW/cm^2 peak power density with $\leq$ 4 mgPGM/cm^2 (Go/No-Go #1).**

2nd Budge Period (04/01/2020 to 3/31/2021)

- ***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.**
- ***Synthesize and Test anode catalysts*****: 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 DMFC models*** **to simulate mass transfer coupled with reactions.**
- **Single cell achieves $\geq$ 250 mW/cm^2 peak power with $\leq$ 3 mg$_{PGM}$/cm^2 (Go/No-Go #2).**

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

Summary Slide

1^{st} Budget Period Go/No-Go Decision Point

Single cell achieves the peak power density of ≥250 mW/cm^2 with ≤4.0 mg$_{PGM}$/cm^2 catalyst.

1^{st} Budget Period Accomplishments and Significant Findings

1. **Developed reliable protocols to evaluate the methanol tolerance of PGM-free cathode catalysts and catalytic activities using Rotating Disk-Electrode (RDE). Established correlation of RDE activity of pre-screened catalysts and MEA performance.**
2. **Synthesized and selected several PGM-free catalysts (FeCo-N-C) with $E_{1/2}$ > 0.87 V in solutions containing methanol up to 3 M.**
3. **Developed a system to sputter PtRu onto VACNFs and evaluate catalytic activities using Cyclic Voltammetry (CV).**
4. **Obtained nano-tomography of commercial and customized electrodes with 3 nm voxel resolution.**
5. **The MEAs made from one of the best performing PGM-free cathode catalyst achieved the peak power density of 256.2 mW/cm^2 with 1.0 M methanol solution (0.5 mL/min) and air (1 L/min) at 96.5 ^oC.**
6. **Developed a microwave assisted system to synthesize PtRu on carbon nanofiber (CNFs) as the anode fuel cell catalyst.**
7. **Developed two-phase continuous models to simulate mass transfer coupled with reactions.**
8. **Started the economic analyses of DMFC-driven forklifts (Class I, II, and III).**

Acknowledgement

DOE Fuel Cell Technologies Office

- Brian Hunter (Program Manager)
- Donna Ho (Program Manager)
- Dan Berteletti
- John Kopasz

University of Kansas

- Zheng Miao (Visiting Scholar, North China Electric Power University)
- Nathaniel Metzger
- Isaac Blankenau
- Lauren Marten

University of Buffalo

- Gang Wu (UB PI)
- Qiurong Shi

Kansas State University

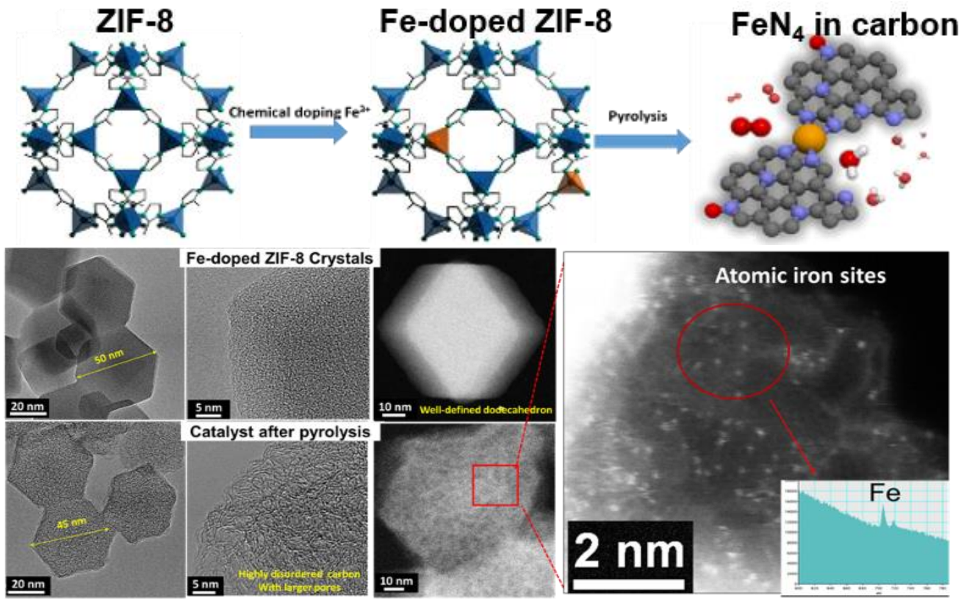
- Jun Li (KSU PI)
- Ayyappan Elangovan
- Archana Sekar

Carnegie Mellon University

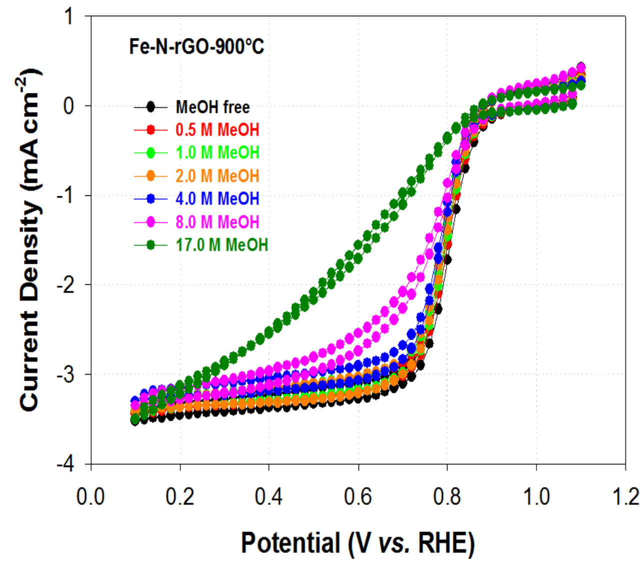
- Shawn Litster (CMU PI)
- Mohamed Abdelrahman

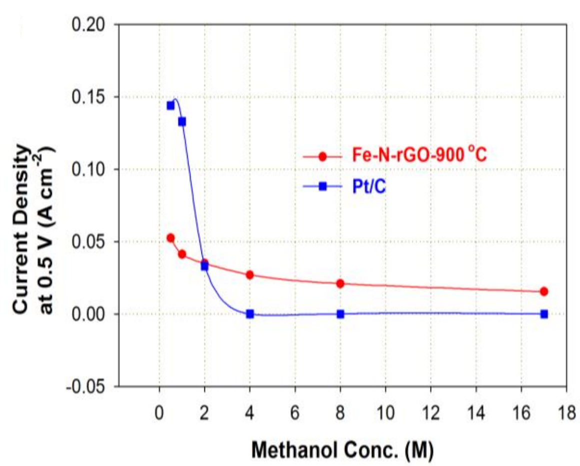
Technical Backup Slides

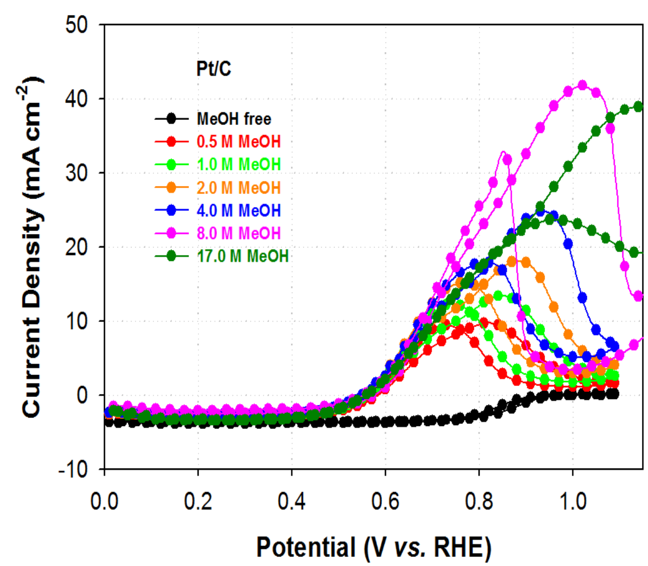
Technical Backup Slides
– Cathode PGM-free Catalysts



Fe-based PGM-free ORR catalysts

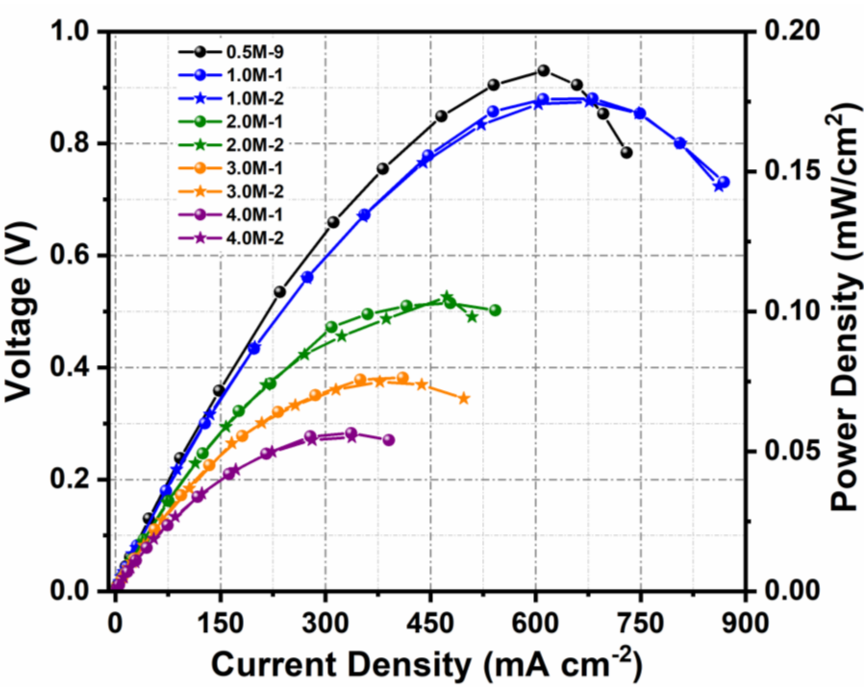




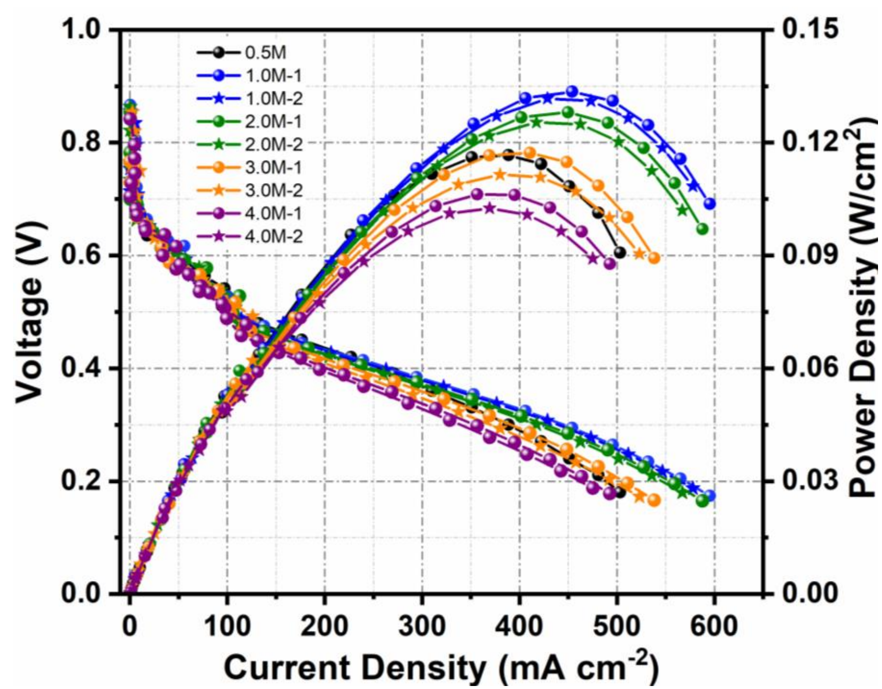


Fe-based PGM-free ORR catalysts show excellent methanol tolerance.

Technical Backup Slides
– Effect of Methanol Crossover on PGM-free Cathodes



Anode: Pt_2Ru/C(72%) 3.10 mg/cm^2
Cathode: Pt/C (80%) 2.56 mg/cm^2



Anode: Pt_2Ru/C(72%) 4.00 mg/cm^2
Cathode: FeCo-N-C 5.00 mg/ cm^2

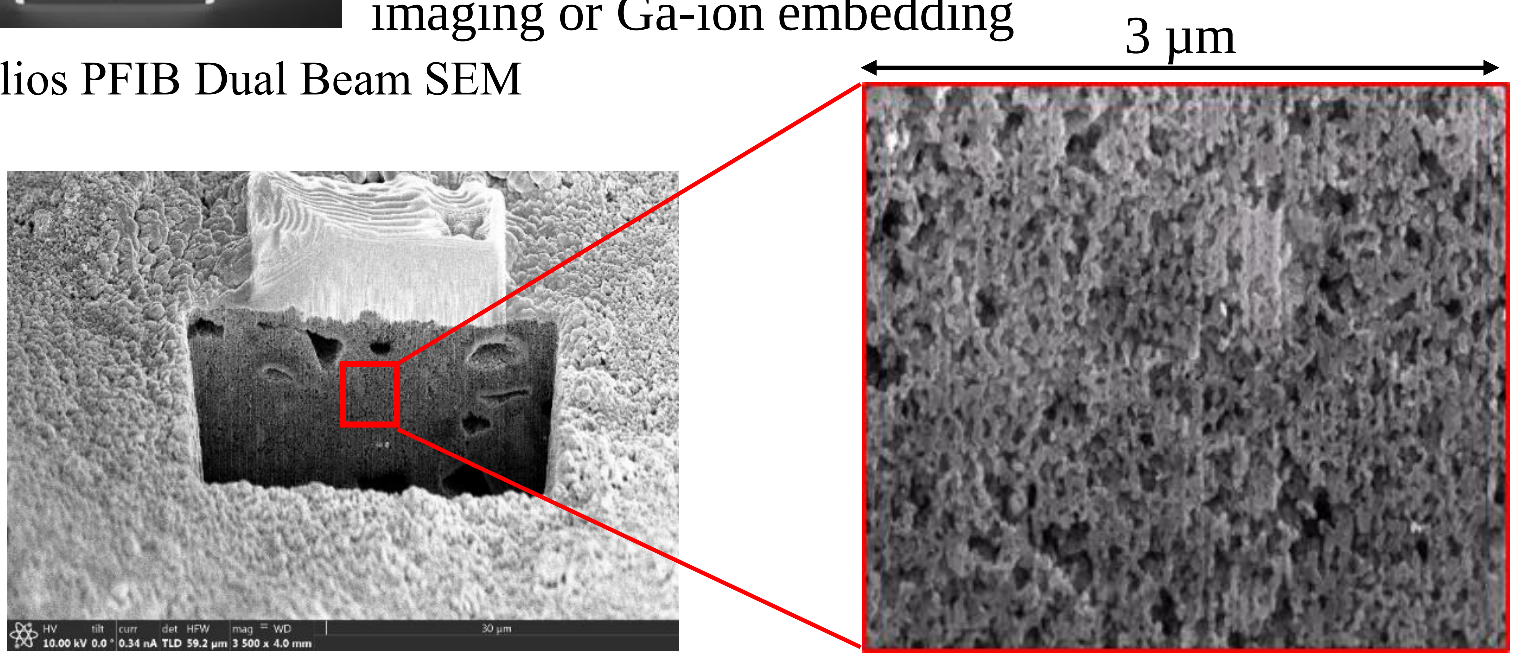
Test condition: 80 °C; 100% RH; Nafion 212; methanol: 0.5 mL/min; 1.0 bar air: 1.0 L/min

- **With pure Pt/C in the cathode, the power density shows significant difference under different methanol concentrations, indicating a serious methanol crossover and easily poison by methanol.**
- **PGM-free catalysts demonstrate a higher methanol poison resistance than Pt/C.**

Technical Backup Slides
– High-throughput 3D Imaging: PFIB-SEM at CMU

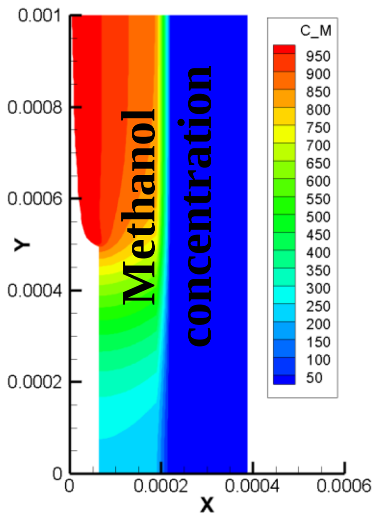
CMU's Helios PFIB Dual Beam SEM

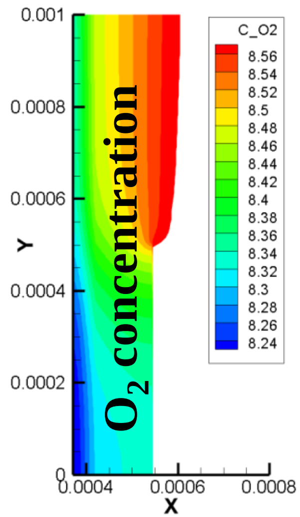
- The sub-10 nm resolution to accurately resolve primary particles is outside of either X-ray CT or Ga FIB-SEM capabilities
- PFIB cross-section significantly higher through-put versus conventional gallium ion FIB-SEMs
- No intrusive damage artifacts to electrode structure imaging or Ga-ion embedding

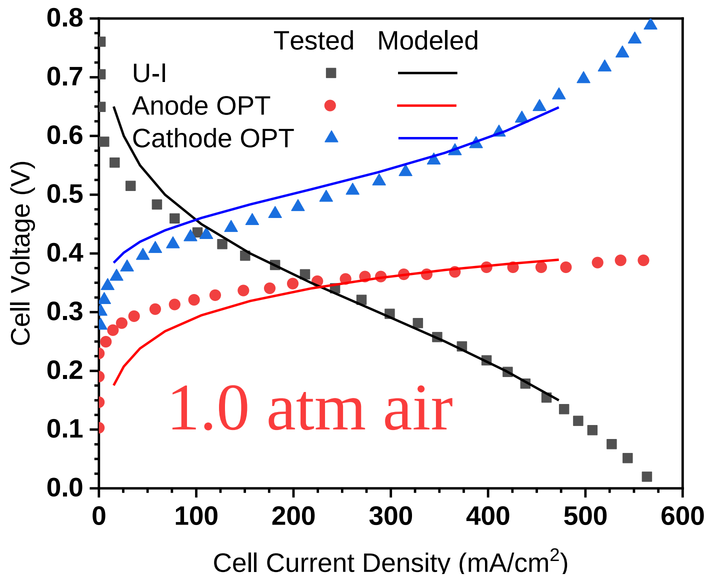


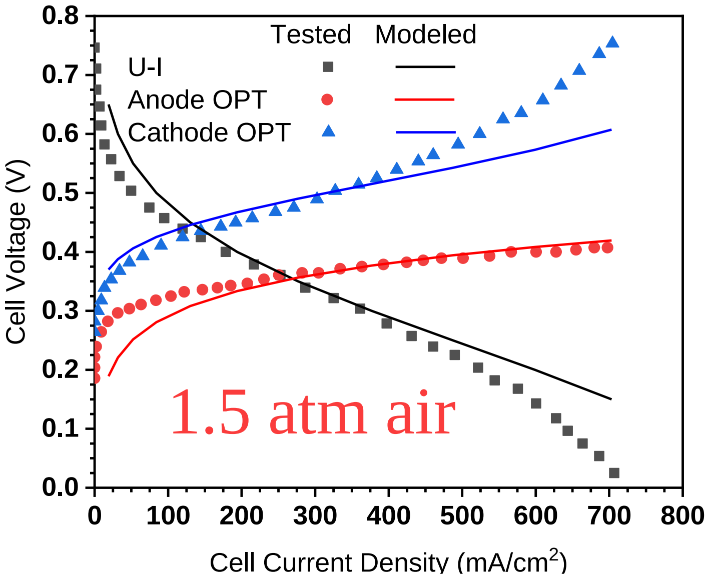
Area of cut before imaging

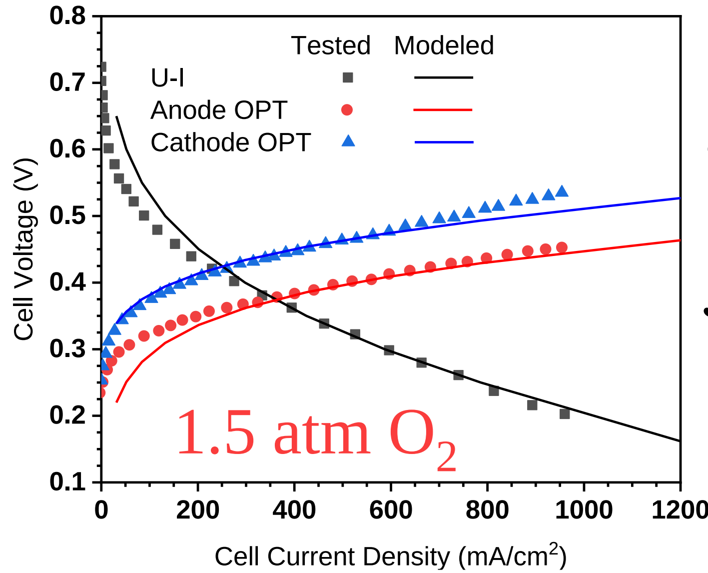
Technical Backup Slides
– Liquid-Vapor Two-Phase DMFC Model Validation





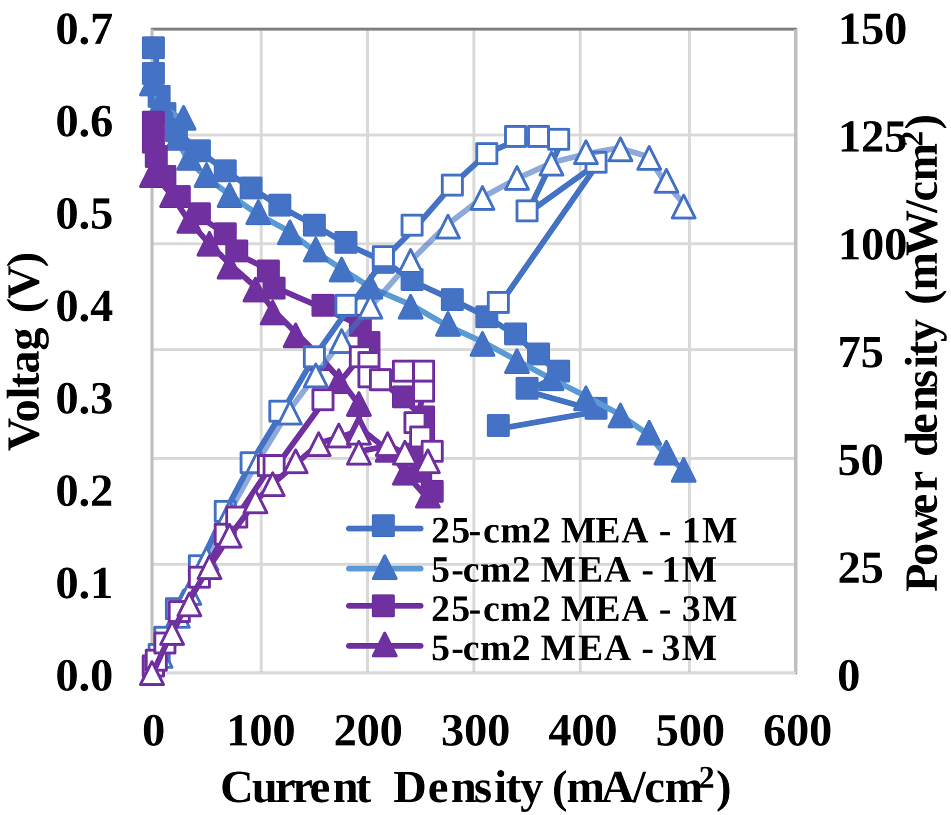






Validation of the model based on CMU's experimental data tested with MEA made from JM's anode electrode and PGM-free cathode catalyst. 1M methanol at 80°C.

Technical Backup Slides
– MEAs Made from Commercial GDEs



The fuel cells were both tested at 80°C with fully hydrated air at atmospheric pressure.

5-cm² MEA: 1 mL/min 1M MeOH or 0.33 mL/min 3M MeOH; 0.2 l/min Air.

25-cm² MEA: 3 mL/min 1M or 1 mL/min 3M MeOH; 0.5 L/min Air. (λ_{MeOH} = 2.9; λ_{O2} = 3.0)

MEAs with 5-cm² and 25-cm² sizes showed similar performance!