

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

DOE project award # DE-EE0008440

Date: June 6-8, 2022

DOE Hydrogen Program
2022 Annual Merit Review and Peer Evaluation Meeting

AMR Project ID # FC317

This presentation does not contain any proprietary, confidential, or otherwise restricted information.



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/cm² with total loading of ≤ 3 mgPGM/cm².

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 3/31/2023
- Effective Project Start Date: 01/03/2019
- **Project End Date: 3/31/2023**

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*: \$620,226

* As of 4/15/2022

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.
- **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 cm² MEA) will produce peak power density of ≥ 300 mW/cm² with total loading of ≤ 3 mg_{PGM}/cm².
- **3rd BP target (4/1/2021 - 3/31/2023):** A single cell (50 cm²) with MEA ≤ 3 mg_{PGM}/cm² achieves 300 mW/cm² using pure methanol.

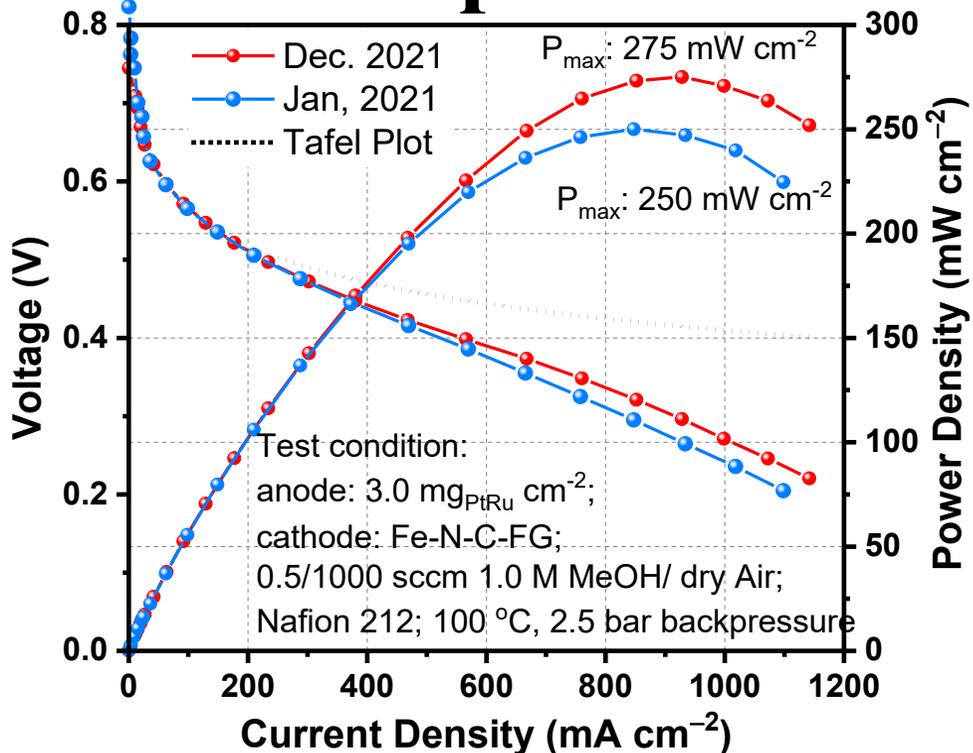
Review Criterion: Project Milestones and Status

This research integrates complementary institutional expertise on

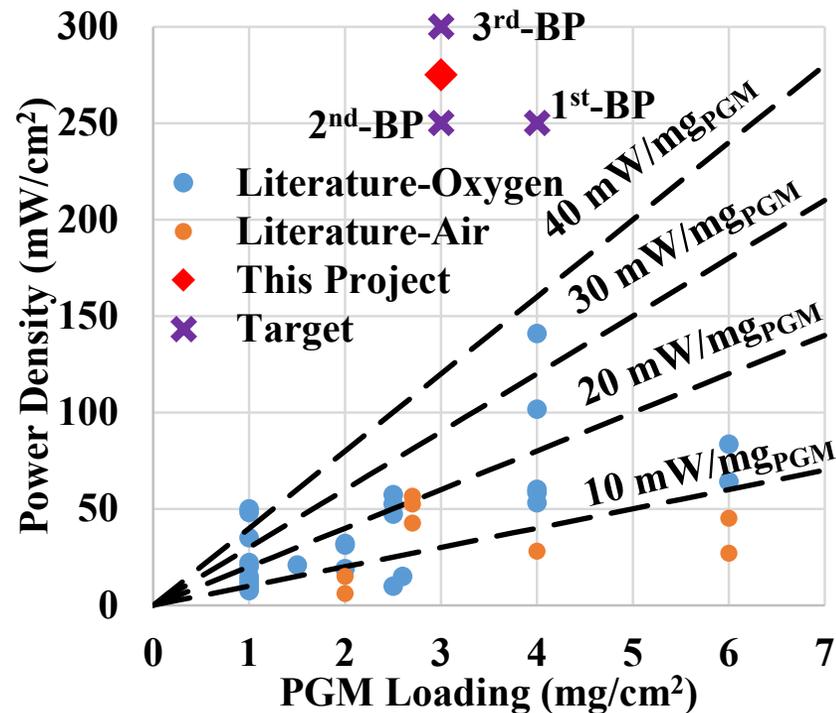
- Supported anode catalysts (KSU)
- Platinum group metals free (PGM-free) cathode catalyst (UB)
- Electrode fabrication, characterization, and optimization (CMU)
- Multi-phase mass transfer (KU)

	Milestone Description (Status as of 4/15/2022)	Status
Q9	<ul style="list-style-type: none"> • MEAs with ≤ 3 mgPGM/cm² can achieve 250 mW/cm² with ~16 M methanol solution. • Durability tests with ~1.0 M and ~16.0 M methanol solutions. • Measure the changes in particle size and morphology of catalysts using nano-CT. 	80%
Q10	<ul style="list-style-type: none"> • Cathode catalysts have $\Delta E_{1/2} < 30$ mV after 30 K cycles (0.6-0.95V) in ~3.0 M methanol. • Anode catalysts show higher stability than commercial JM HiSPEC® PtRu/C catalyst. • Understand the catalyst degradation mechanism following the ASTs test procedures. • Single cells achieve ≥ 300 mW/cm² with ≤ 3 mg_{PGM}/cm² using > 3.0 M methanol. 	70%
Q11	<ul style="list-style-type: none"> • Test anode and PGM-free cathode catalyst durability in > 3.0 M methanol. • Propose approaches to increase the durability of customized MEAs. • Single cells with ≤ 3 mgPGM/cm² can achieve 300 mW/cm² with ~16.0 M methanol. 	65%
Q12	<p>End of Project Goal: A single cell (50 cm²) with MEA ≤ 3 mg_{PGM}/cm² achieves 300 mW/cm² using pure methanol.</p>	50%

Accomplishments and Progress – Overview



The peak power density of 275 mW/cm^2 was achieved at high temperature of $100 \text{ }^\circ\text{C}$ at 2.5 bar back pressure of air (1000 sccm) and 1.0 M methanol (0.5 mL/min).

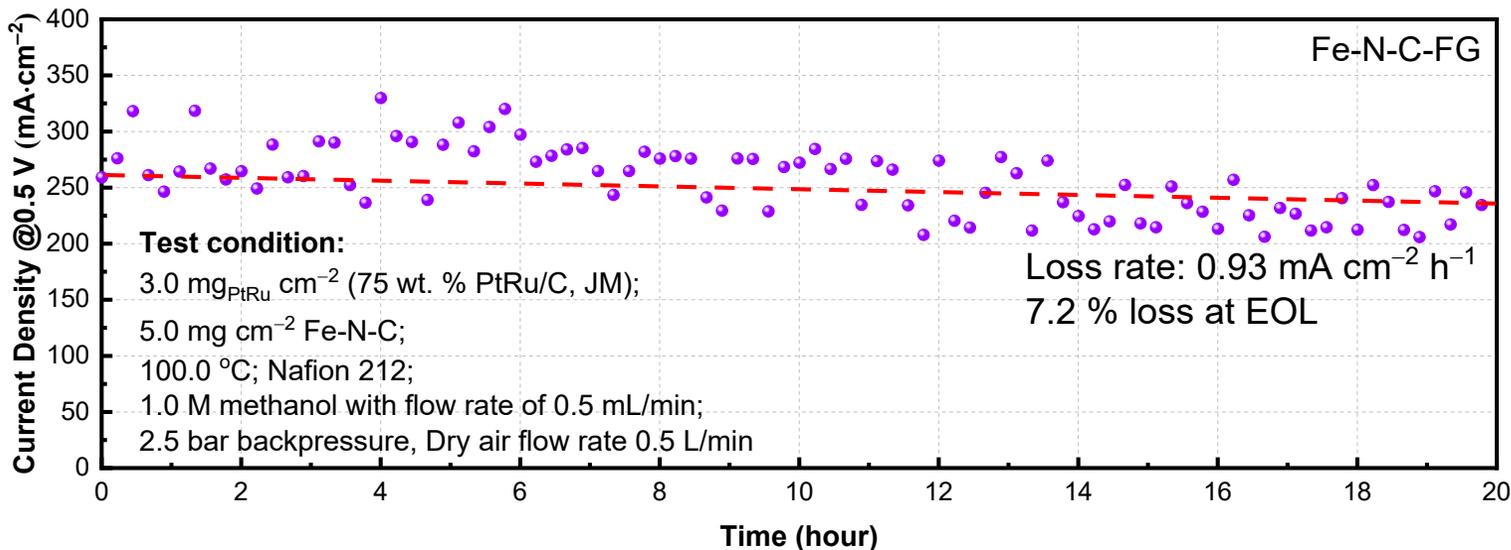


Power density versus anode PGM loading for DMFCs with PGM-free cathodes reported in the literature (circle), achieved by this research team (diamond), and project targets (cross).

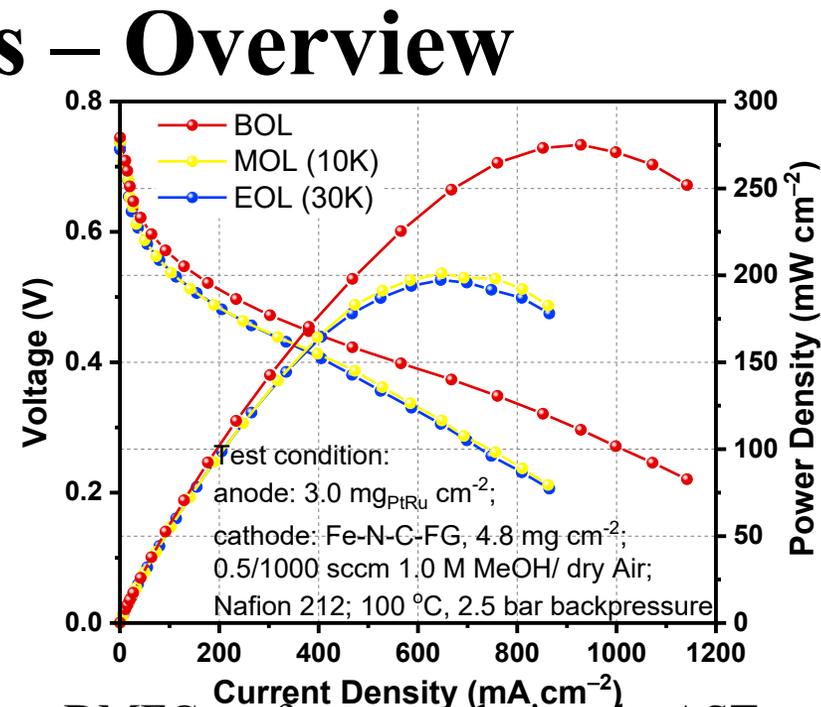
- Improvement of catalyst synthesis, MEA fabrication, and test system contribute to the peak power density;
- Tafel analysis indicates that the optimization of MEA structure is important to obtain 300 mW cm^{-2} .

The project team is on track to meet the final project goal: Achieve the peak power density of 300 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.

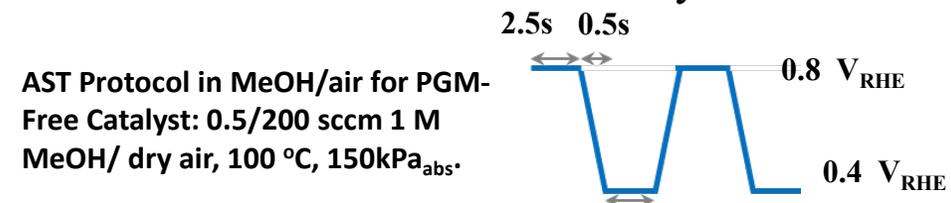
Accomplishments and Progress – Overview



Stability test of MEAs with PGM free cathode at 0.5V using 1 M methanol (0.5 mL/min) and Air (0.5 L/min, 2.5 bar BP) at 100°C.



DMFC performance during the AST test of Fe-N-C-FG catalyst.

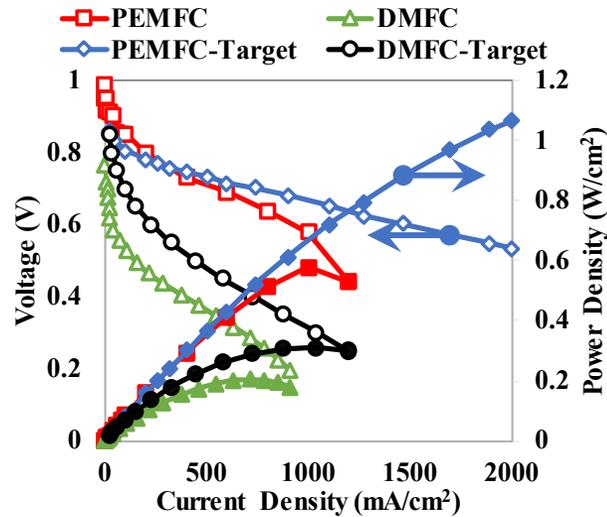


- Chronoamperometry @ 0.5 V manifests the stability of Fe-N-C in DMFC.
- Accelerated stress test (AST) of Fe-N-C has been attempted by applying square wave potential on cathode in DMFC operating condition;
- After first 10k of AST, the performance of Fe-N-C quickly dropped, in the following 20k test, the performance was nearly unchanged

UB Fe-N-C	Current density @ 0.50 V (MeOH/air, mA cm ⁻²)	Voltage @ 0.8 A cm ⁻² (mV)	Peak Power Density (MeOH/air, mW cm ⁻²)
BOL	225.4	337.2	274.9
10k	170.5	241.1	201.4
30k	170.5	234.1	197.3
Loss	24.4	30.6	28.2 %

Accomplishments and Progress

-Fuel Cells as the Power Source for Stationary Applications

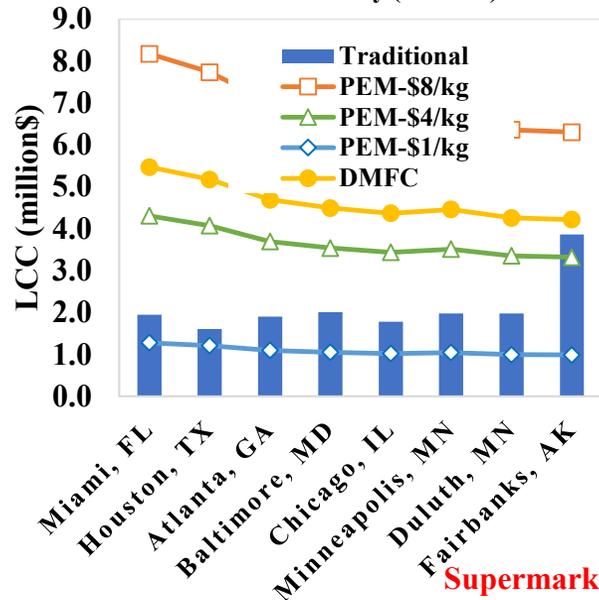


Fuel Cell Stack Cost Breakdown, 100 kW

	PEM	PEM-Target	DMFC	DMFC-Target
MEA Materials	\$12,701	\$5,828	\$372,813	\$129,003
Bipolar Plate and Sealing	\$6,015	\$3,656	\$17,810	\$11,913
Assembly and Testing	\$1,368	\$1,368	\$1,368	\$1,368
Balance of Plant (BOP)	\$35,258	\$35,258	\$35,258	\$35,258
Total	\$55,342	\$46,109	\$427,249	\$177,541
\$/kW	\$553.42	\$461.09	\$4,272.49	\$1,775.41

Fuel Cell Stack Cost Breakdown, 250 kW

	PEM	PEM-Target	DMFC	DMFC-Target
MEA Materials	\$31,563	\$14,484	\$926,106	\$320,469
Bipolar Plate and Sealing	\$15,035	\$9,161	\$44,403	\$29,719
Assembly and Testing	\$3,834	\$3,834	\$3,834	\$3,834
Balance of Plant (BOP)	\$74,725	\$74,725	\$74,725	\$74,725
Total	\$125,157	\$102,204	\$1,049,068	\$428,747
\$/kW	\$500.63	\$408.82	\$4,196.27	\$1,714.99



Parameters	PEMFC	DMFC
Life Time of the Fuel Cell (years)	10	
Fuel Price (\$/GGE)	8 [1-12]	0.43
Energy Content of Fuel (MJ/kg)	120.0	22.0

As the main power supply of supermarkets, DMFCs will have higher LCCs than the baseline cost using grid and natural gas in all weather conditions.

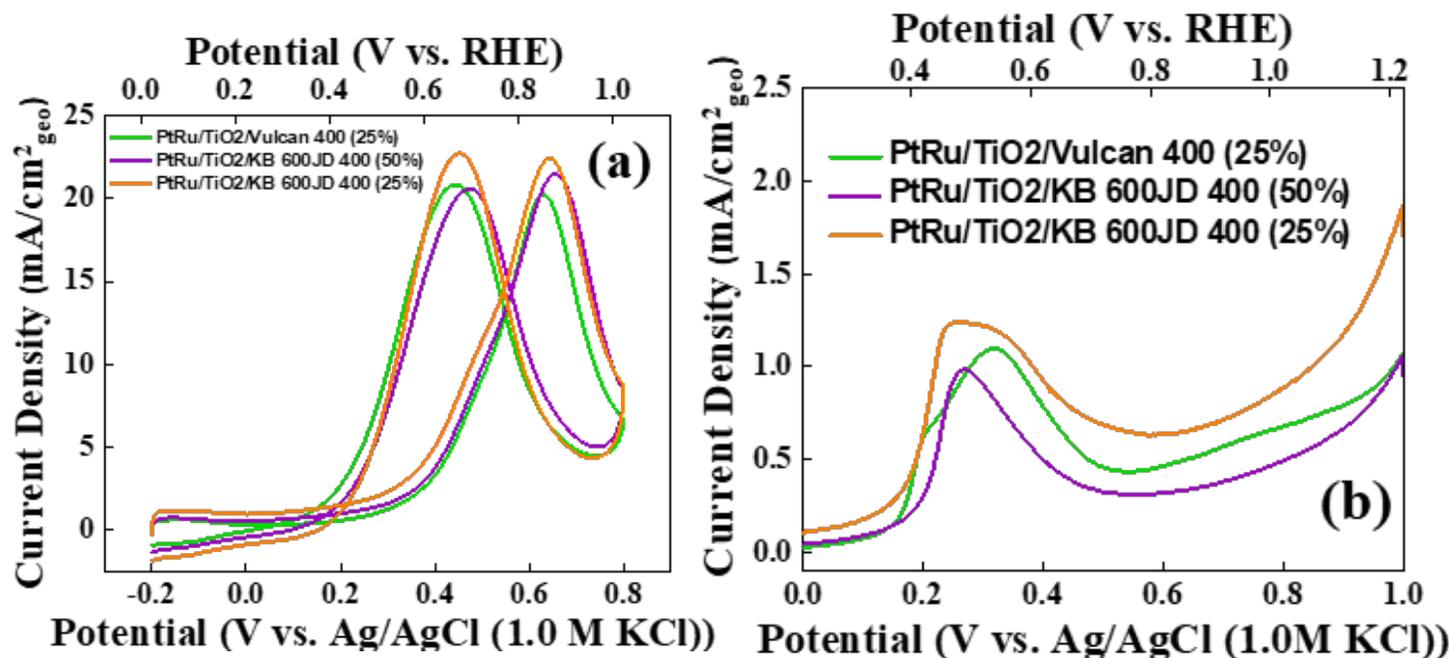
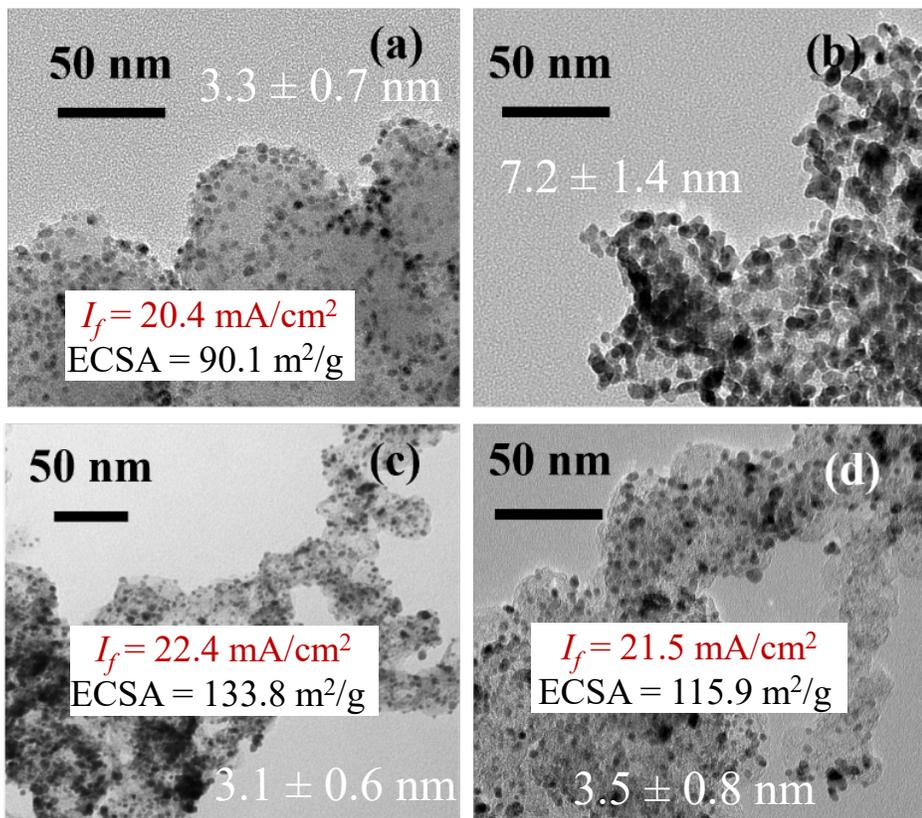
Baseline: Purchase electricity from grid and natural gas for the pipeline.

Accomplishments and Progress

– Anode Catalyst (PtRu deposited on commercial carbon supports)

Specific surface area of carbon support:

Vulcan: $218 \text{ m}^2 \text{ g}^{-1}$ vs. KB600JD: $1270 \text{ m}^2 \text{ g}^{-1}$



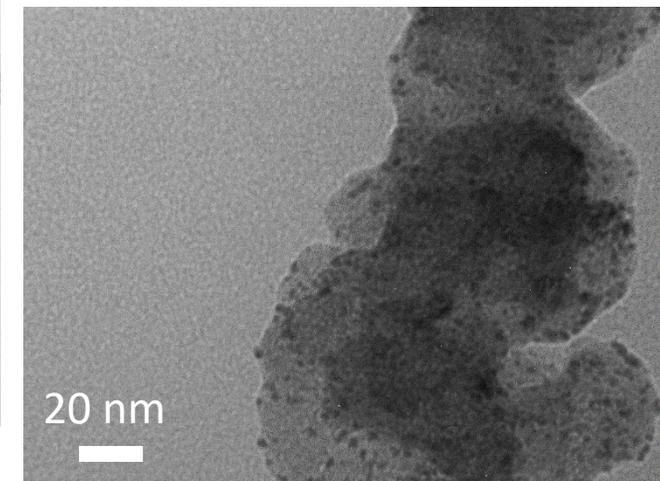
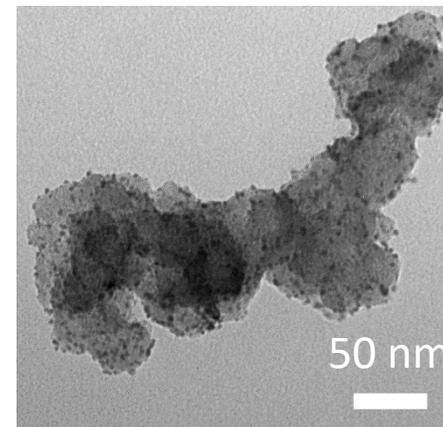
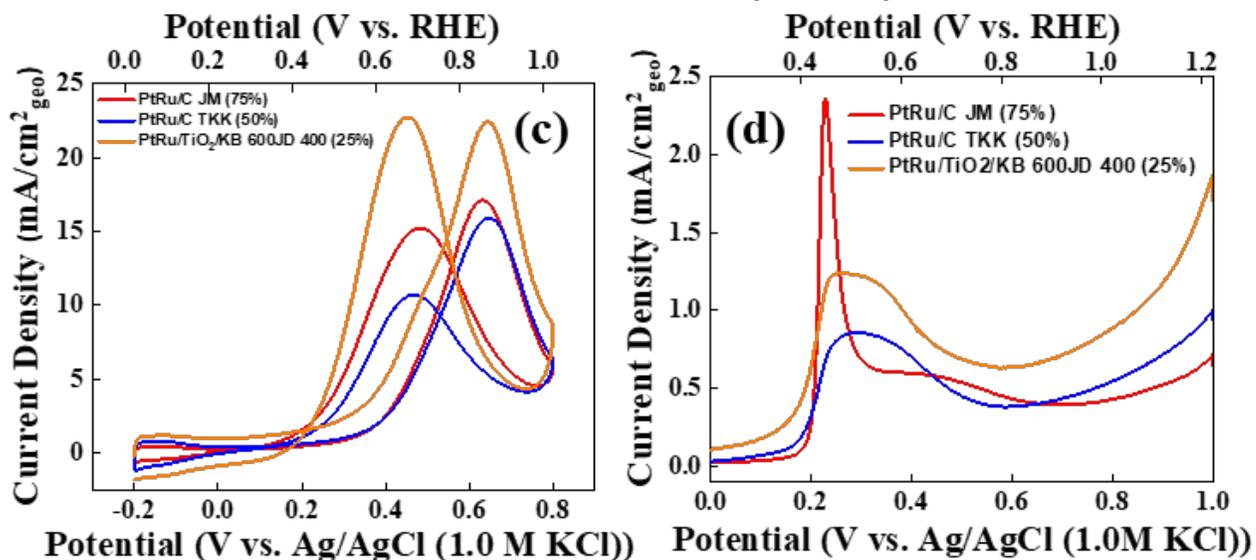
Comparison of PtRu/TiO₂/KB600JD-400 (25%) (orange line), PtRu/TiO₂/KB 600JD 400 (50%) (purple line) and PtRu/TiO₂/Vulcan-400 (25%) (green line): (a) CV (100th cycle) in Ar-purged $0.5 \text{ M H}_2\text{SO}_4$ solution containing 0.75 M methanol at a scan rate of 50 mV/s and (b) the first anodic scan of CO stripping curves in Ar-purged $0.5 \text{ M H}_2\text{SO}_4$ solution.

PtRu/TiO₂/KB600JD-400 (25%) has the highest I_f , the higher ECSA, and the lowest CO stripping onset potential.

Figure 5. TEM images of (a) PtRu/TiO₂/Vulcan-400 (25%), (b) PtRu/TiO₂/Vulcan-400 (50%), (c) PtRu/TiO₂/KB600JD-400 (25%) and (d) PtRu/TiO₂/KB600JD-400 (50%).

Accomplishments and Progress

– Anode Catalyst Synthesized with Microwave-Assistant Approach



Comparison of PtRu/TiO₂/KB600JD-400 (25%) (**orange line**) with commercial catalysts PtRu/C JM (75%) (**red line**) and PtRu/C TKK (50%) (**blue line**): (c) CV in Ar-purged 0.5 M H₂SO₄ solution containing 0.75 M methanol at a scan rate of 50 mV/s and (d) the first anodic scan of CO stripping curves in Ar-purged 0.5 M H₂SO₄ solution. The PGM loading in all catalysts were maintained at 54 μg/cm².

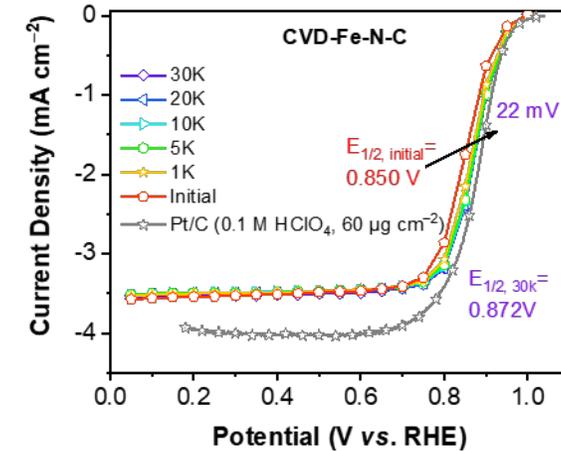
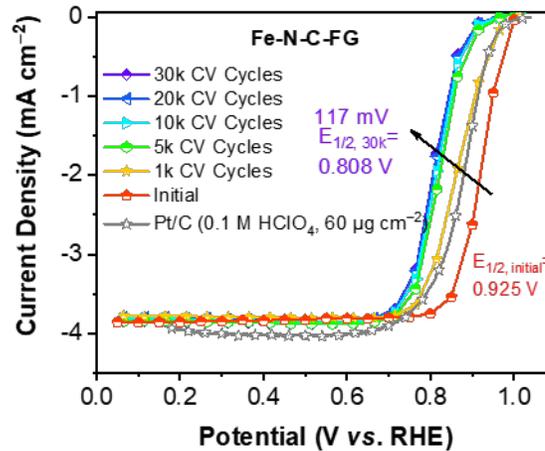
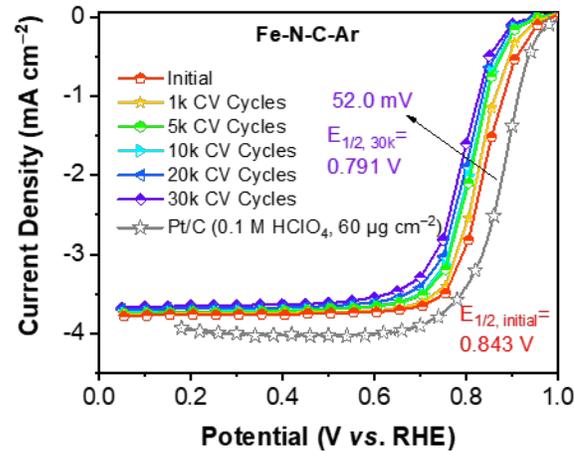
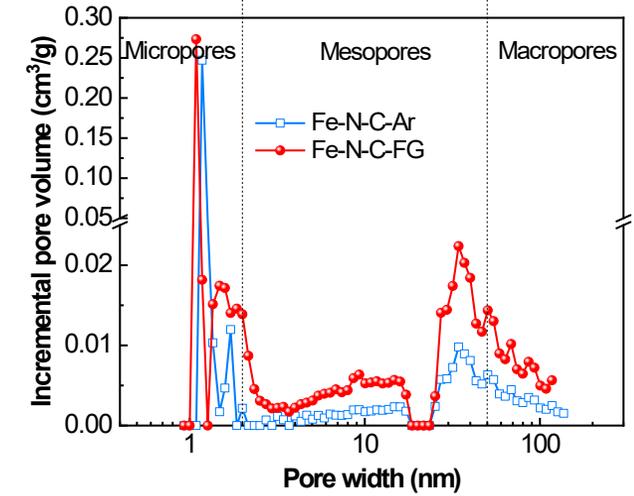
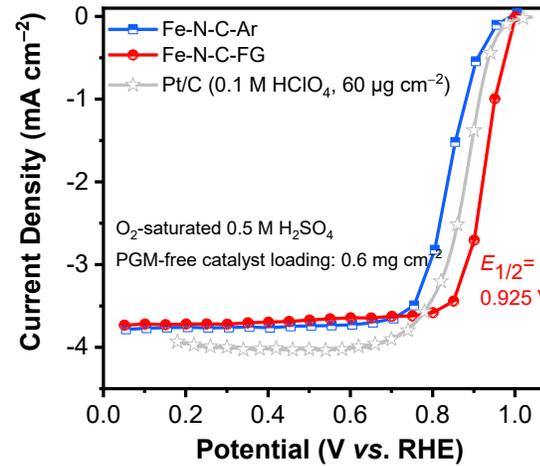
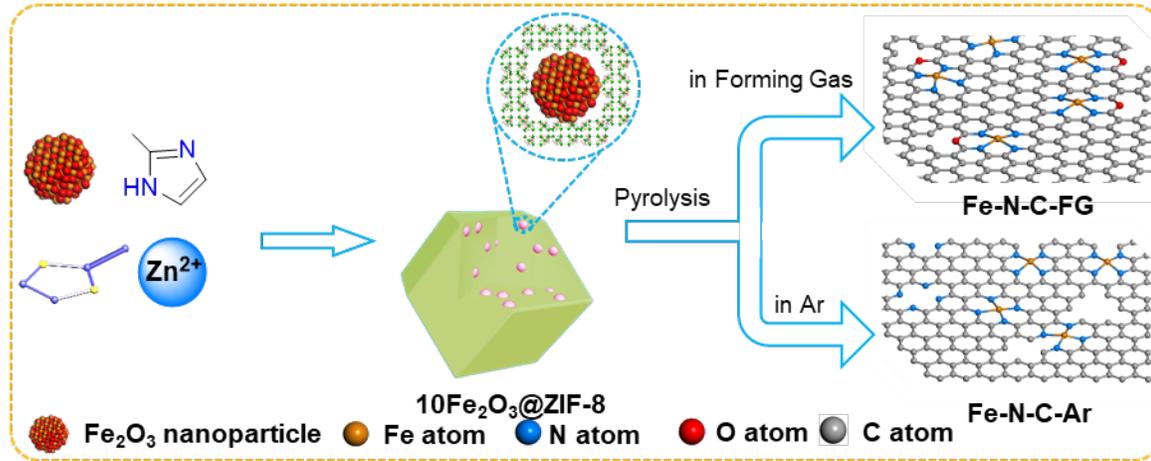
Apply RuO₂ as alternate metal oxide - SEM images of Ru deposited on Vulcan (Precursor: RuCl₃; Temp: 190 °C; Time: 2.5 min)

- PtRu/TiO₂/KB600JD-400 (25%) shows higher MOR I_f , higher ECSA, and earlier onset potentials for MOR and CO oxidation than commercial catalysts (JM and TKK).
- Ru nanoparticles (1 to 1.5 nm) were obtained. We are exploring different Ru precursors with different synthesis conditions to obtain thin shell of RuO₂ on carbon support.

Accomplishments and Progress



– Cathode PGM-free Catalysts

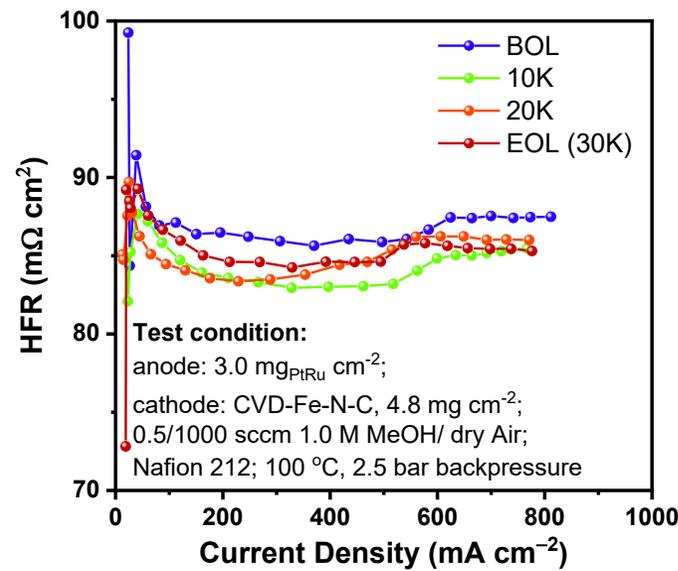
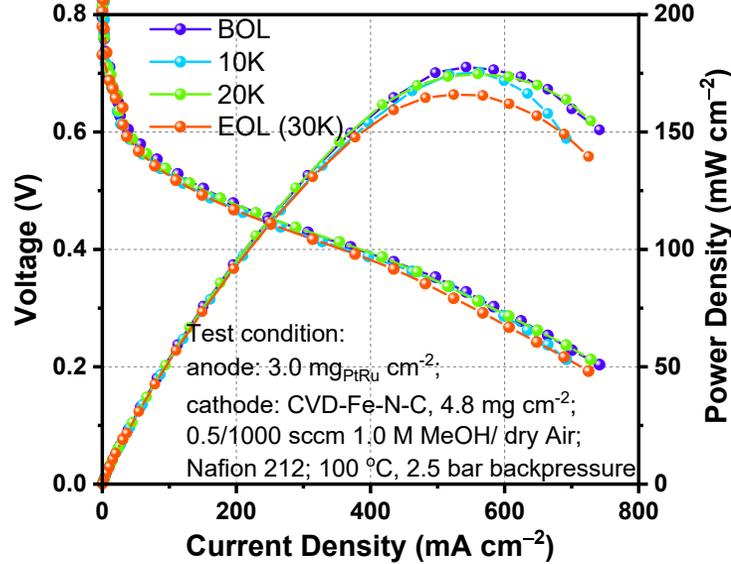


Durability improvement of Fe-N-C by CVD method

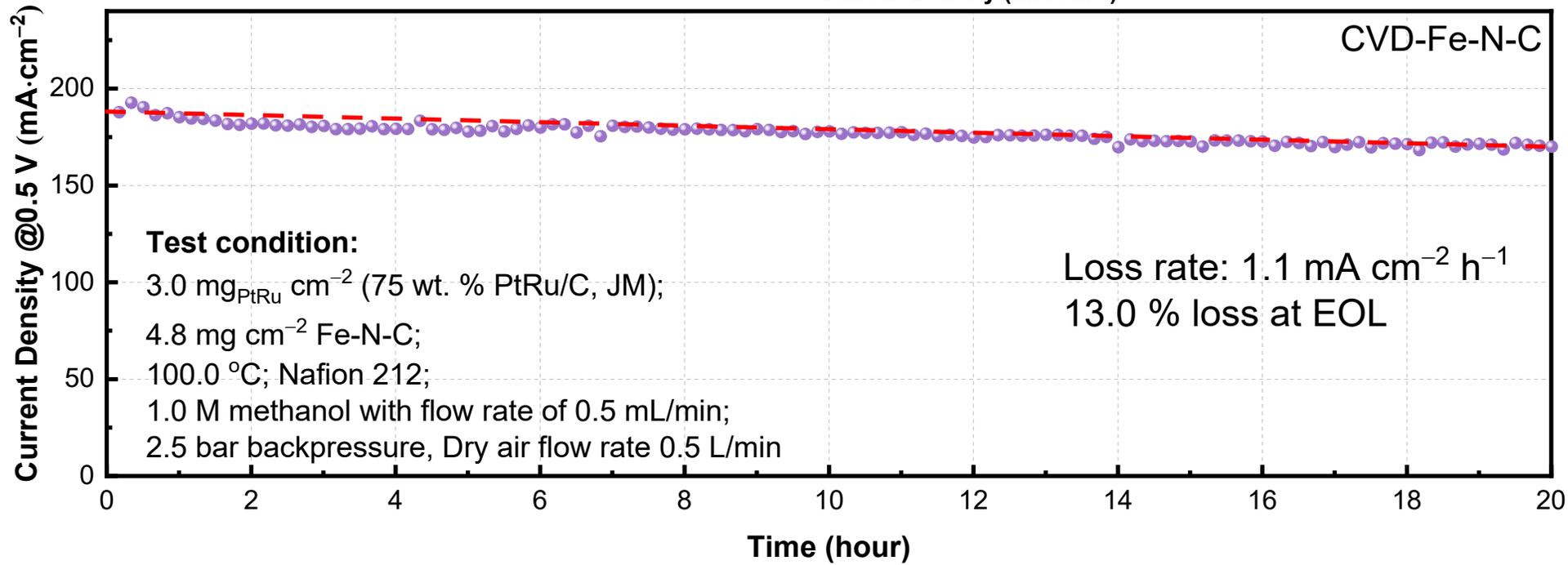
- Fe-N-C-FG achieved the highest recorded activity in acids ($E_{1/2} = 0.925 \text{ V}$), exceeding Pt/C ($60 \text{ } \mu\text{g}_{\text{Pt}}/\text{cm}^2$) by 50 mV.
- Fe-N-C-FG obtained by pyrolysis in forming gas has a higher BET surface area and a higher content of meso- and macroporosity.
- NH_4Cl treatment (AC) endows higher ORR activity by generating more defects.
- Chemical vapor deposition (CVD) boosts stability, study in RRDE verified that S2 site contributes most to the stability.

Accomplishments and Progress

Performance and Stability of Commercial Anode Catalyst and PGM-free Cathode Catalysts in DMFCs



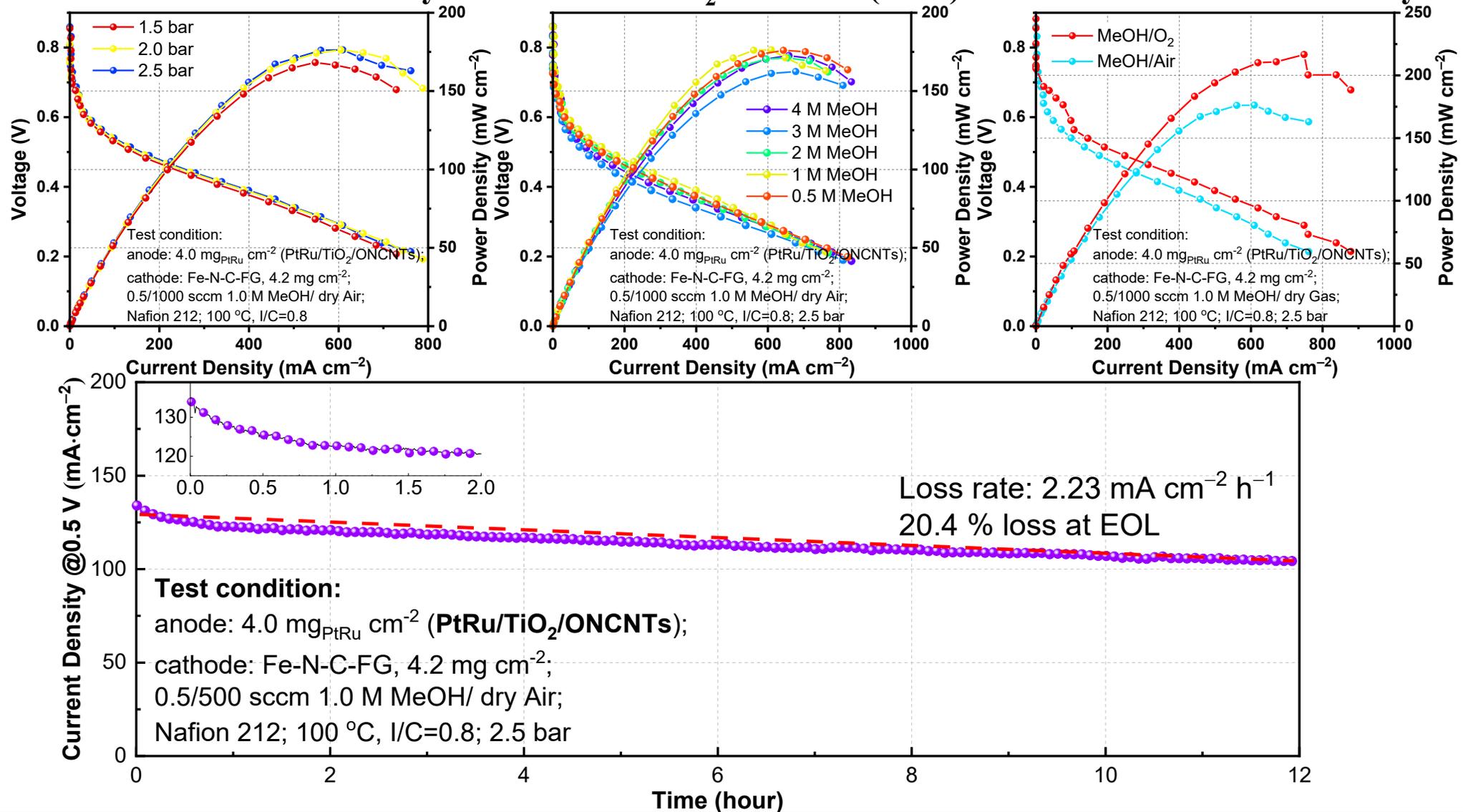
CVD-Fe-N-C	$i @ 0.50 \text{ V}$ (MeOH/air, mA cm^{-2})	Voltage @ 0.4 A cm^{-2} (mV)	p_{max} (MeOH/air, mW cm^{-2})
BOL	156.0	0.392	178.0
10k	151.9	0.387	175.7
20K	140.5	0.394	174.7
30k	136.0	0.382	165.7
Loss	12.8%	2.6%	6.9%



20h-stability test
AST indicates that
CVD-Fe-N-C has
promising stability
in DMFC
environment.

Accomplishments and Progress

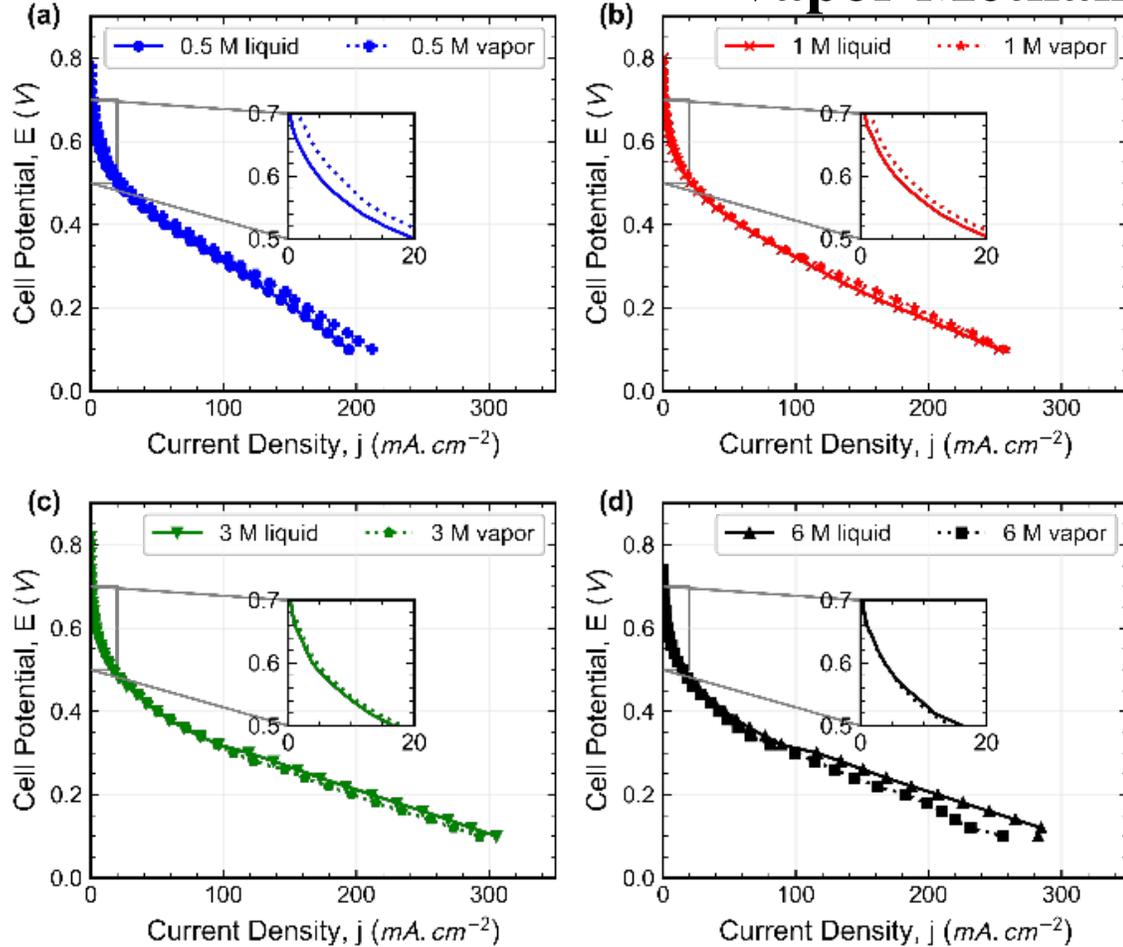
-Performance and Stability of 40% PtRu/TiO₂/ONCNTs (KSU) and PGM-free Cathode Catalysts



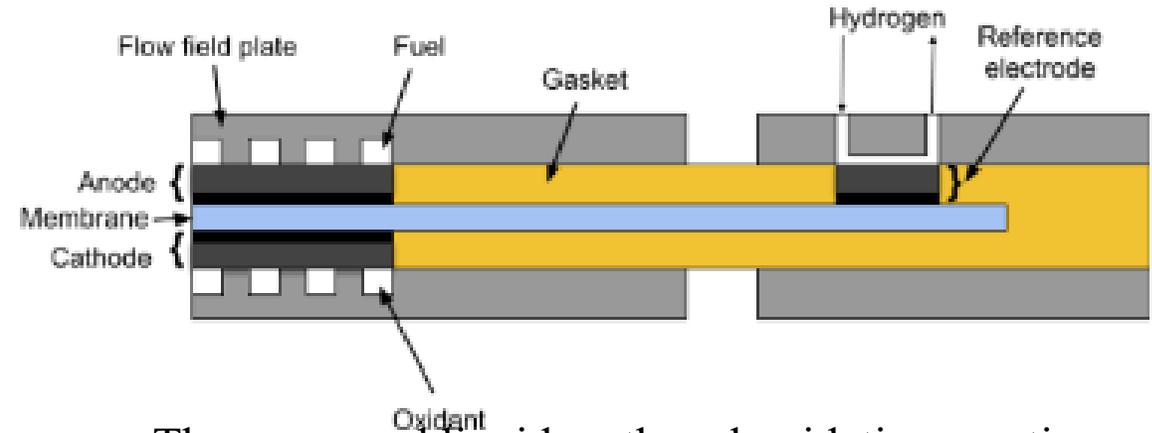
- Insignificant dependence of DMFC performance on operating parameters indicates that anodic polarization curve also governs the overall performance;
- Chronoamperometry @ 0.5 V manifests that PtRu/TiO₂/OCNTs has promising stability in DMFC.

Accomplishments and Progress

– Vapor Methanol Reaction Kinetics



Phase	Concentration, C (M)	Current Density @ 0.6 V, i (mA/cm ²)	Anode Overpotential, η @ 30 mA (V)	Max Power Density, P _d (mW/cm ²)
Liquid	0.5	4.80	0.223	32.3
	1	5.57	0.203	35.7
	3	3.82	0.218	42.3
Vapor	0.5	8.03	0.161	35.2
	1	7.20	0.179	38.7
	3	4.54	0.215	39.4
	6	3.73	0.203	36.5



The vapor and liquid methanol oxidation reaction of anode performance was measured by the reversible hydrogen reference electrode (RHE).

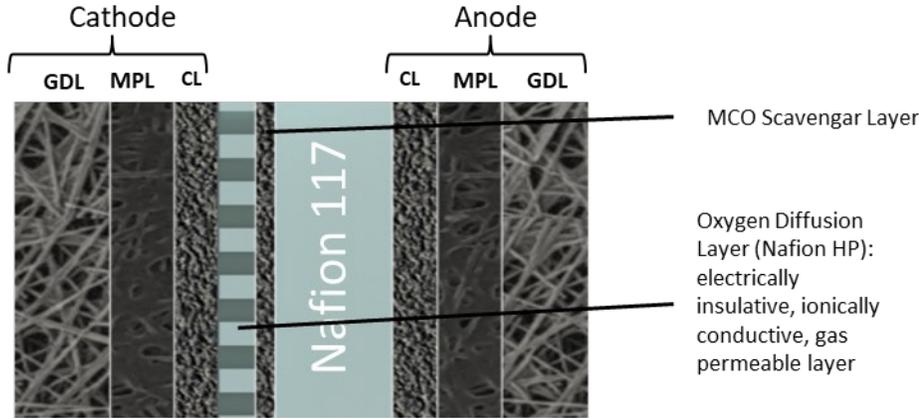
Polarizations scans of PGM-free MEA under liquid and vapor methanol operation, tested with (a) 0.5M; (b) 1M; (c) 3M; and (d) 6M methanol.

- Vapor-fed MOR has better reaction kinetics than liquid-fed MOR.
- The catalyst activity towards vapor-fed MOR decreased with methanol concentration, while the opposite trend was observed in liquid-fed MOR.
- The reaction order of vapor-fed MOR had a negative value of -0.53 while the reaction order of liquid-fed MOR had a positive value of 0.53.

Accomplishments and Progress

– Methanol crossover scavenger layer

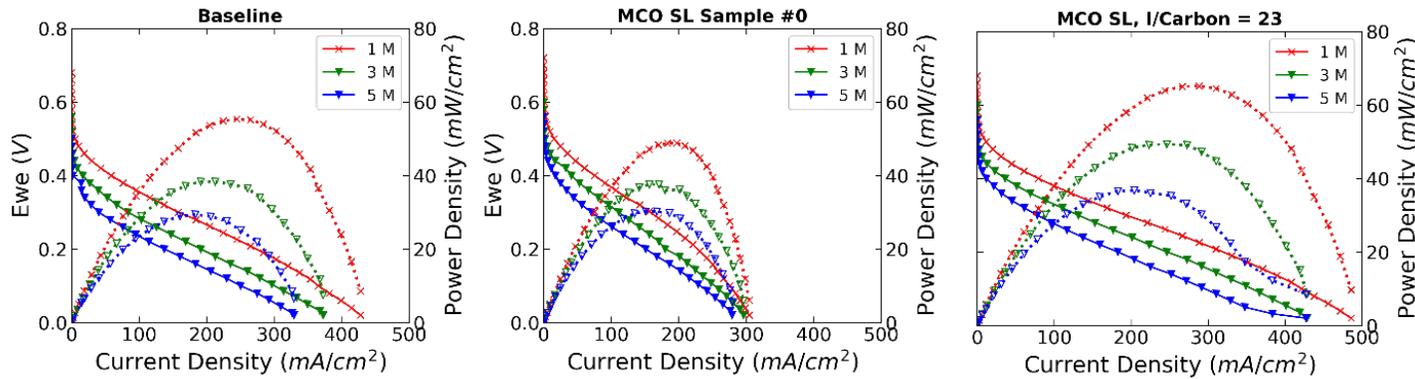
MEA fabrication details for MCO-SL experiments



	Anode	Cathode	MCO-SL	ODL	Electrolyte
Cell 72 (Baseline)	TKK50 PtRu/C, 2.26 mg/cm ²	Fuel Cell Etc. Pt/C 0.3 mgPt/cm ²	N/A		Nafion 117
Cell 71 (Sample #0)	TKK50 PtRu/C, 2.13 mg/cm ²		TTK50, decal transferred, I/C 1.5, 22 μm	Nafion HP	
Cell 73 (I/C 23)	TKK50 PtRu/C, 2.39 mg/cm ²		TTK50, spray-coated, I/C 23, 1.4 μm	Ionomer top-coat with 1.75 mg/cm ²	

Peak power density from polarization scan.

Architecture of the MEA with the scavenger layer, and oxygen diffusion layer (here depicted as Nafion HP).



Polarization scans done at 80 C, 100% RH in the cathode with anode/cathode: 1 M methanol/air, 2 ml·min⁻¹/200 ml·min⁻¹, 3 M methanol/air, 0.67 ml·min⁻¹/200 ml·min⁻¹, 5 M methanol/air, 0.4 ml·min⁻¹/200 ml·min⁻¹.

	Baseline PD (mW/cm ²)	Cell 71 PD (mW/cm ²)	Cell 73 PD (mW/cm ²)
1 M	55.4	48.8	65.1
3 M	38.3	37.6	49.2
5 M	29.4	30.2	36.7

Crossover rates measured from polarization scans at 80 C with methanol solution and humidified N₂.

Concentration (M)	Crossover rate, Baseline (mol/s)	Crossover rate, 71 (mol/s)	Crossover rate, 73 (mol/s)
1	1.67E-07	1.30E-07	1.47E-07
3	4.02E-07	3.08E-07	3.59E-07
5	5.37E-07	4.93E-07	5.23E-07

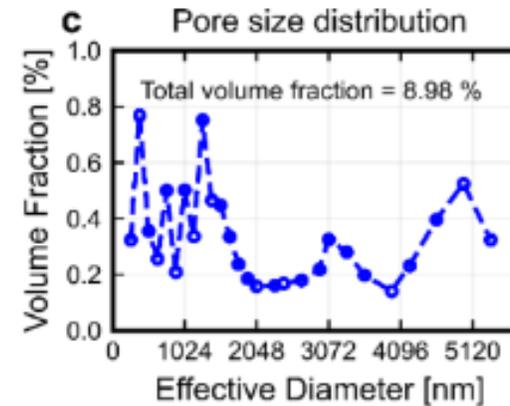
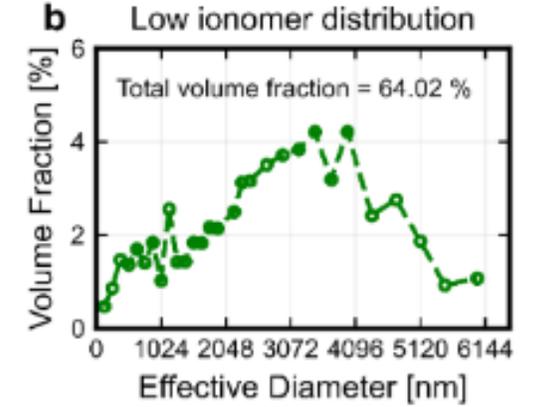
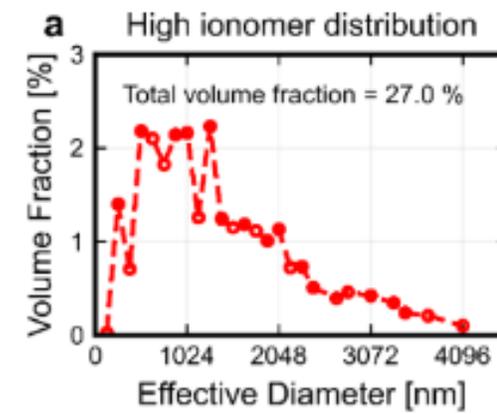
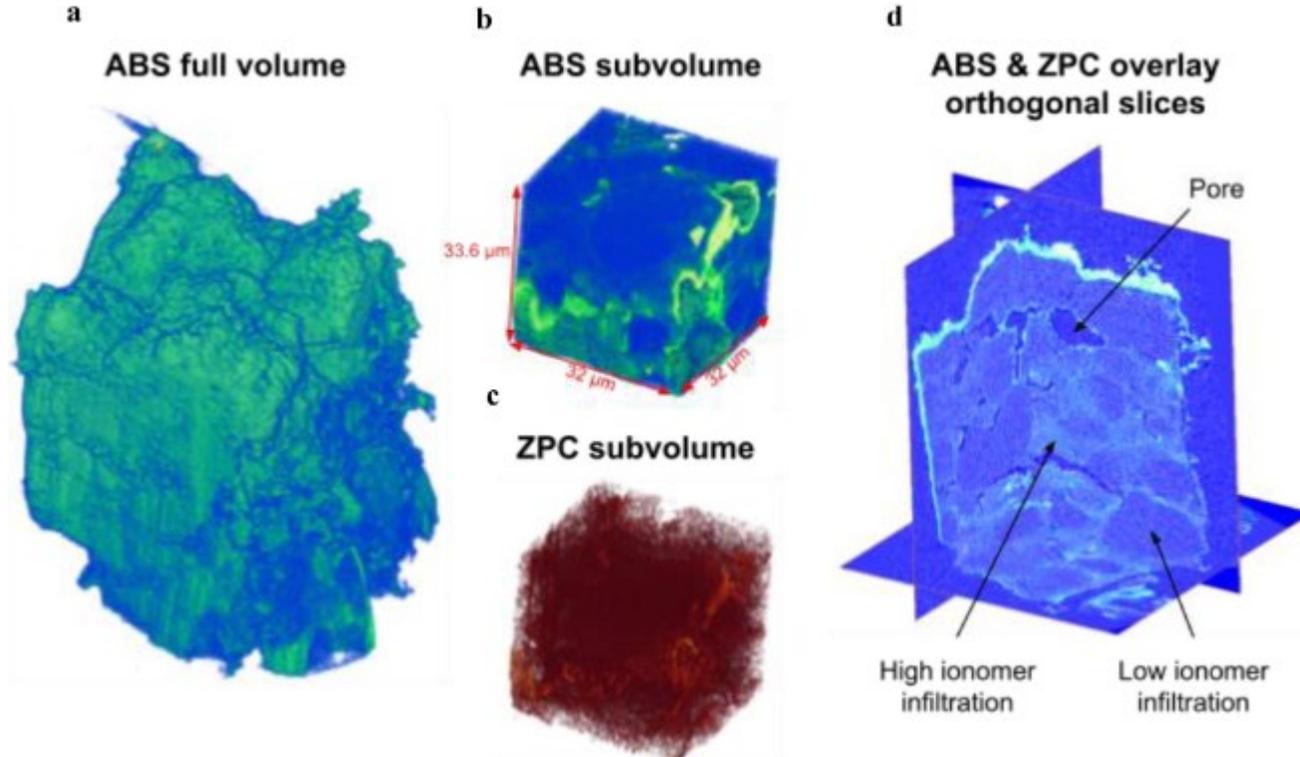
- The scavenger layer can successfully reduce the crossover rate of methanol.
- The reduction in crossover current could be overshadowed by the increase of high ohmic resistance (Cell 71).

Accomplishments and Progress

– Imaging and Microstructure Analysis

Green - Highly ionomer infiltrated regions

Blue - Poorly infiltrated ionomer regions



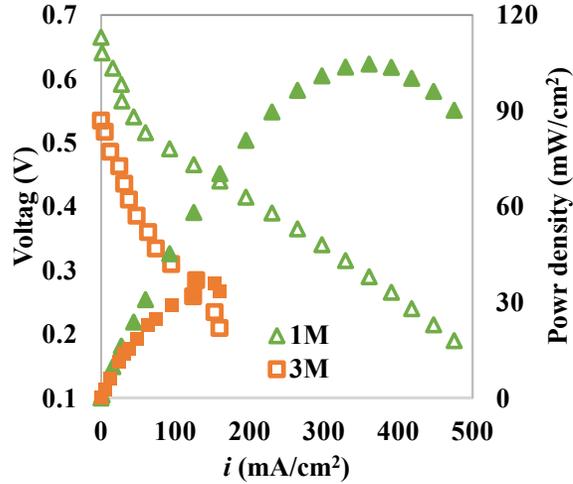
**The smallest resolvable feature is 150 nm. Therefore, a significant volume of micropores, mesopores, and small macropores could not be accounted for.*

Nano-CT images of cesium-stained Fe-N-C cathode using the absorption contrast technique (ABS): (a) 3D reconstruction of the full volume of dataset, (b) cropped ABS sub-volume for analysis, (c) cropped sub-volume using Zernike phase contrast technique (ZPC) for analysis, and (d) orthogonal slices of the masked image dataset.

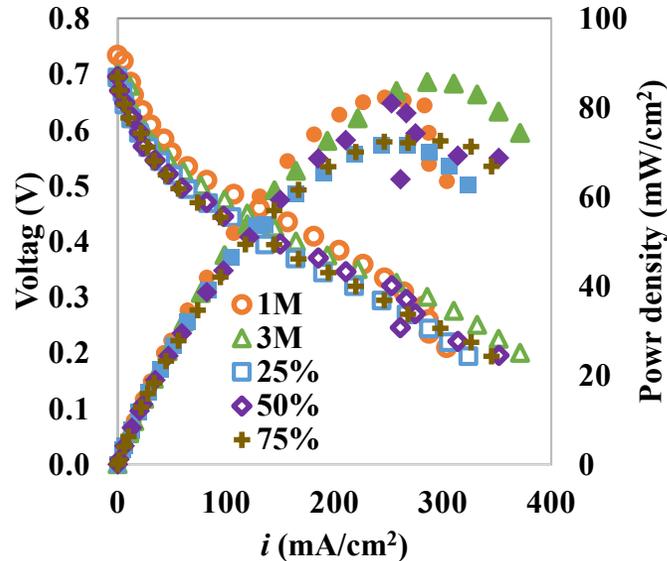
Size distributions* of the (a) high ionomer infiltration region, (b) low ionomer infiltration region, and (c) pore region.

Accomplishments and Progress

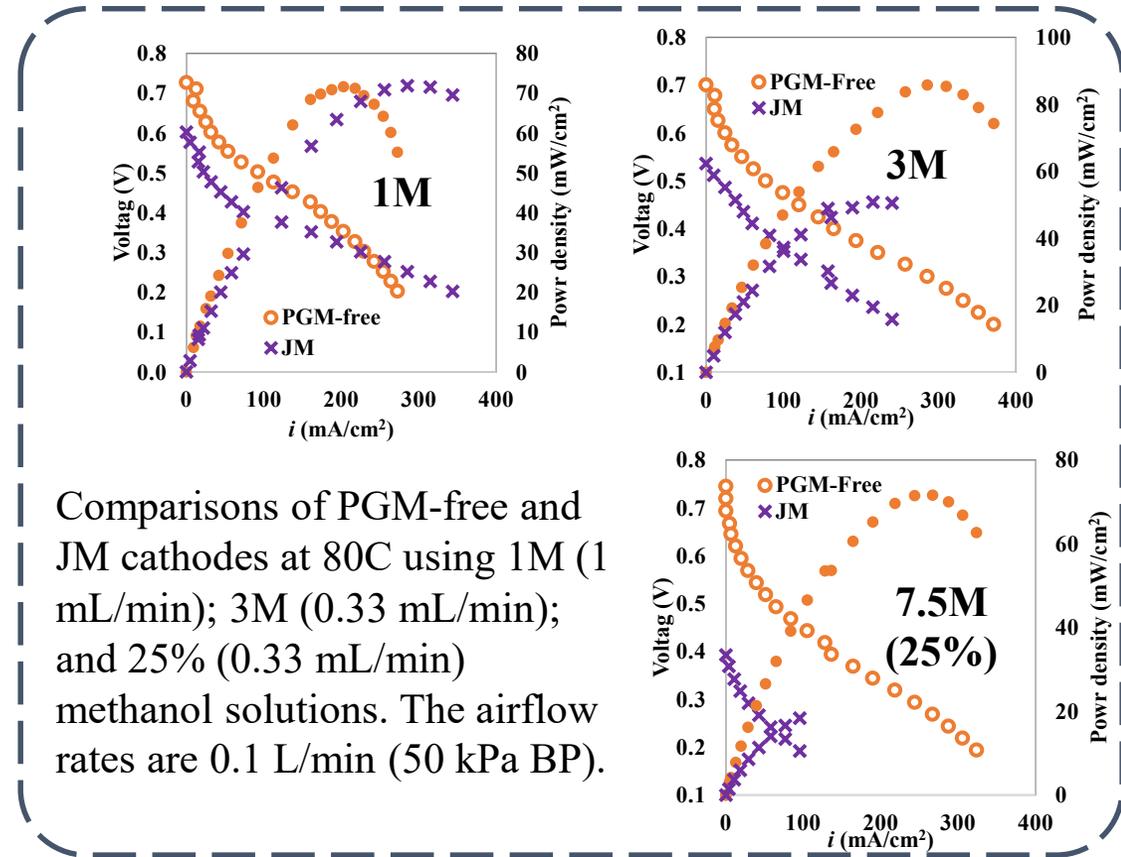
– PGM-Free Cathode Tested by Highly Concentrated Methanol Solutions



Polarization curves tested with methanol and air (0.1 L/min, 50 kPa) at 80C. Anode - 4.5 mg/cm² PtRu/C (TKK); Cathode – 1.5 mg/cm² Pt/C (JM).



Polarization curves and HFRs tested at 80C using varied concentrations; 0.5 L min⁻¹ air, 100 kPa BP. Anode - 4.33 mg/cm² PtRu/C (TKK); Cathode – 4.6 mg cm⁻² PGM-free (Fe-NC, Buffalo).

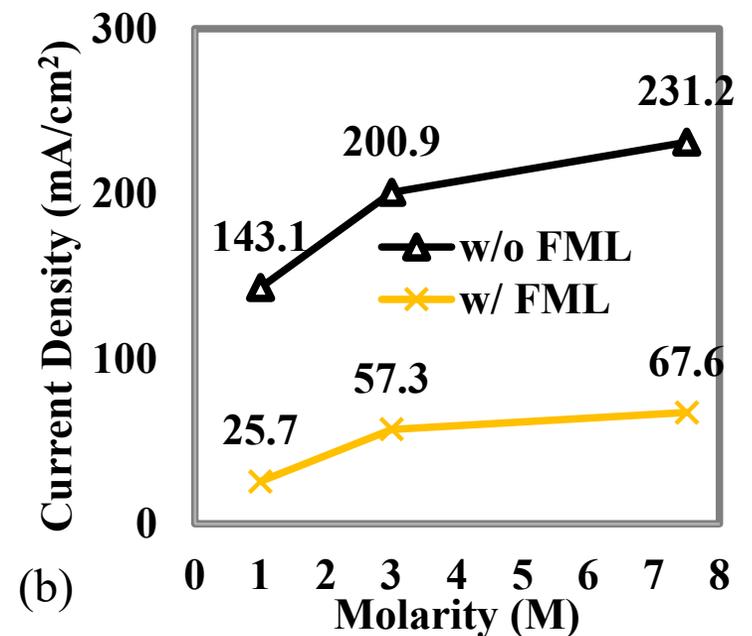
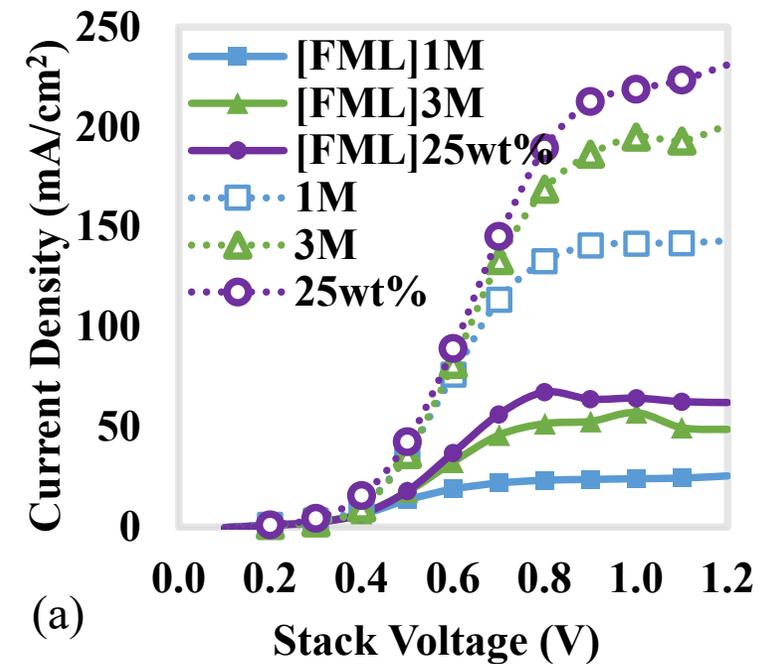
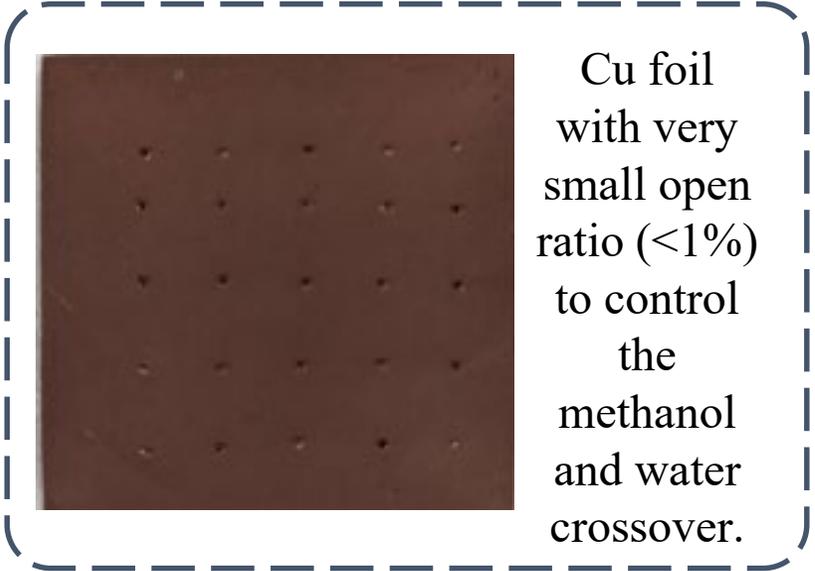


Comparisons of PGM-free and JM cathodes at 80C using 1M (1 mL/min); 3M (0.33 mL/min); and 25% (0.33 mL/min) methanol solutions. The airflow rates are 0.1 L/min (50 kPa BP).

- The peak power density of commercial cathode catalysts quickly decreased with increased methanol concentration. The peak power density was <math>< 20 \text{ mW/cm}^2</math> once the methanol concentration is 25% (7.5 M) or higher.
- The peak power density of PGM-free cathode is insensitive to the methanol concentration. The peak power densities are 82.2 (1M), 85.7 (3M), 71.6 (25% or 7.5 M), 81.0 (50% or 14.1M), and 72.5 (75% or 20.2 M) mW/cm², respectively.

Accomplishments and Progress

– Effects of the Fuel Management Layer (FML)

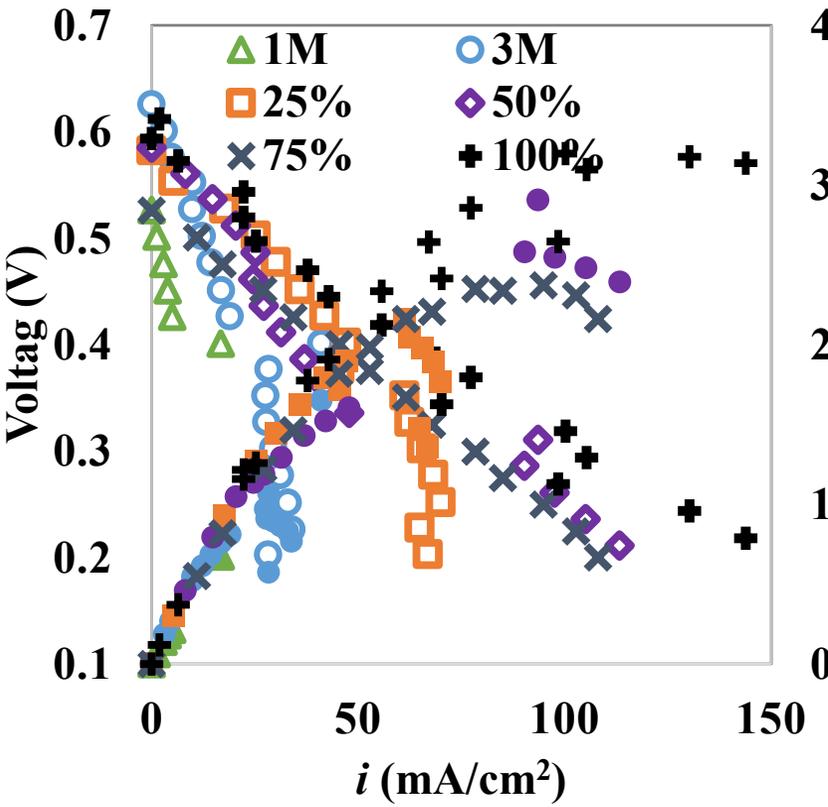


(a) Crossover current density at different voltages and (b) the maximum crossover current density of MEA59 with FML and without FML tested using 1M (1 mL/min), 3M (0.33 mL/min), and 25wt% (0.33 mL/min) methanol and N₂ (0.1 L/min, 50 kPa back pressure) at 80°C.

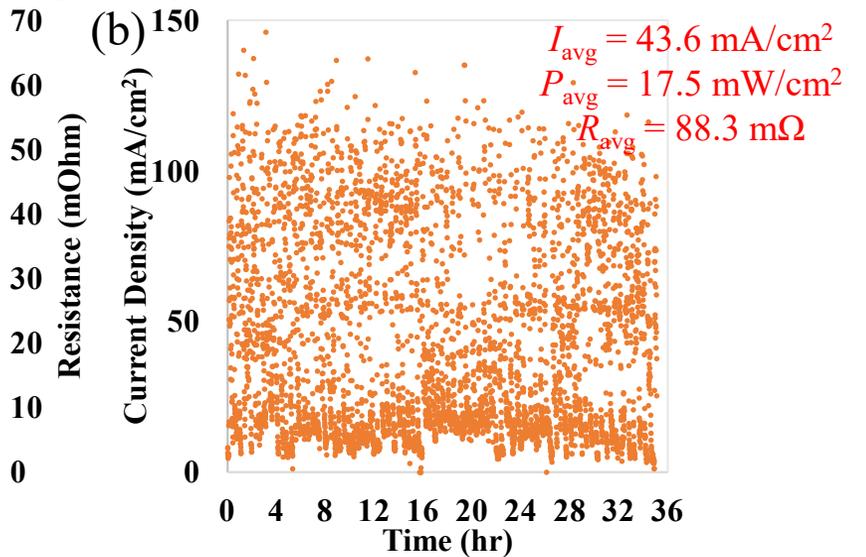
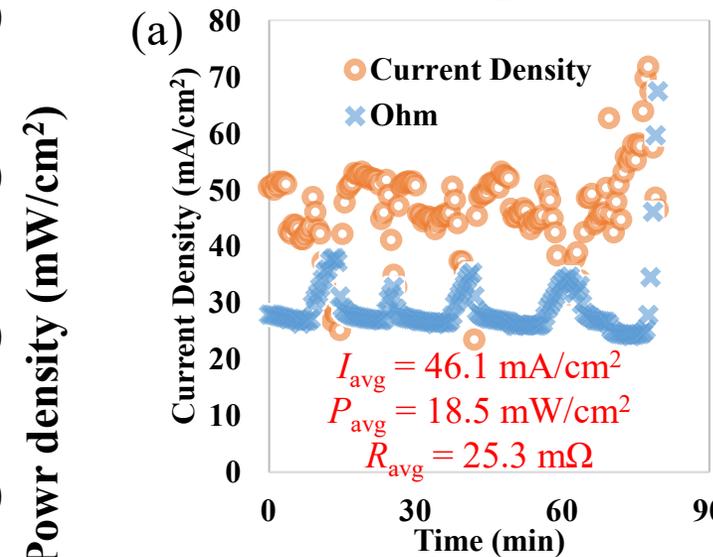
The maximum crossover current density with the FML has been reduced to less than 30% of the maximum crossover current density without FML under the methanol concentrations tested (1M, 3M, and 7.5M or 25 wt%).

Accomplishments and Progress

– Effects of the Fuel Management Layer (FML)

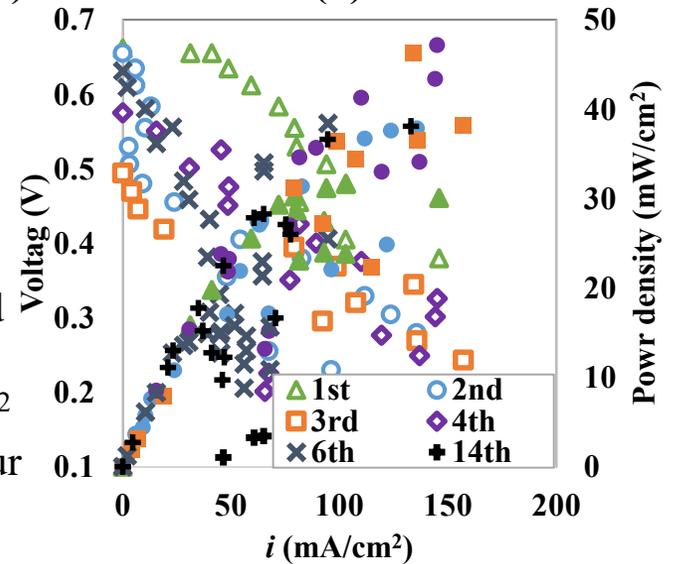


Polarization curves tested with methanol and air (0.1 L/min, 50 kPa) at 80C. Anode - 4.5 mg/cm² PtRu/C (TKK); Cathode – 1.5 mg/cm² Pt/C (JM). **FMLs with controlled open ratio were used to reduce the crossover rate.**



Current density and HFR of the MEA with FML at 0.4V tested with methanol (0.1 ml/min) and air (0.1 L/min, 50 kPa) at 80C: (a) **75% methanol** (b) **100% methanol**.

Polarization curves of the MEA with FML tested with **100% methanol** (0.1 ml/min) and air (0.1 L/min, 50 kPa) at 80C. Anode - 4.5 mg/cm² PtRu/C (TKK); Cathode – 1.5 mg/cm² Pt/C (JM). Each scan was separated by a 4-hour constant voltage (0.4V) discharge.



Accomplishments and Progress

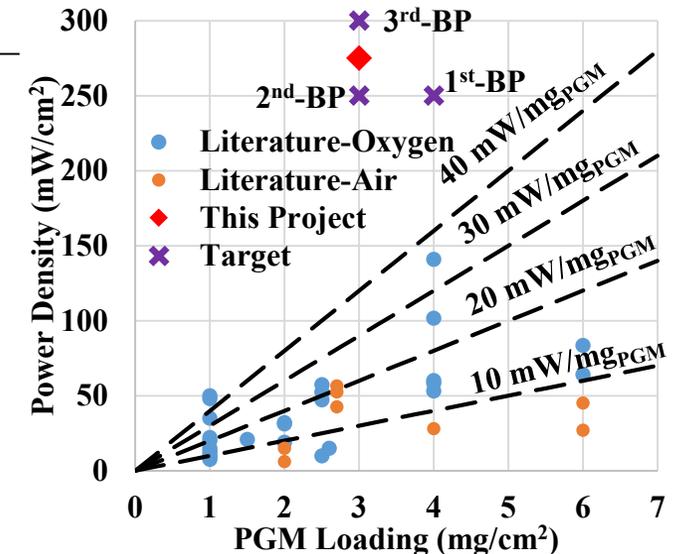
– Responses to Previous Year Reviewers' Comments

The project exceeded the target performance while maintaining the PGM at the targeted level. Chart 6 shows the project surpassed literature-reported DMFCs with PGM-free cathodes. The chart was difficult to read because of the overlap of the performance and the target. The authors report that the air flow rate and the pressure are higher than the proposed operating conditions.

Jan 2021 – The peak power density of 252 mW/cm² was achieved at 99.8 °C, 300 kPa back pressure of air (1000 sccm), and 1.0 M methanol (0.5 mL/min).



Dec 2021 - The peak power density of 275 mW/cm² was achieved at 100 °C, 2.5 bar back pressure of air (1000 sccm), and 1.0 M methanol (0.5 mL/min).



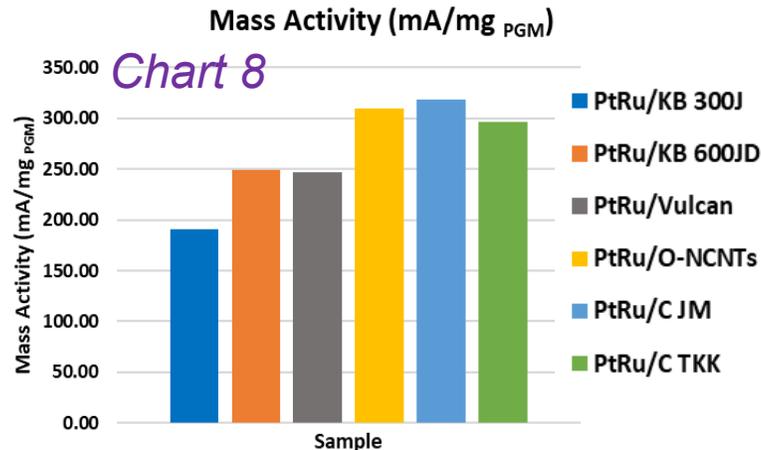
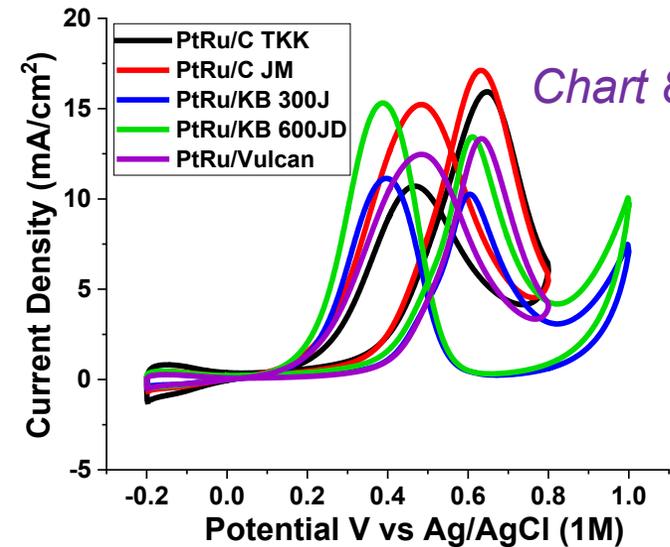
The project is focused primarily on performance metrics but does not quantify all loss metrics, such as methanol crossover or parasitic power/water requirements, and does not address durability at all, which is certainly the most difficult hurdle in terms of making DMFCs relevant.

This project mainly focuses on the performance, as instructed by the FOA and SOPO. Obtaining attractive performance is a critical first step to make DMFC relevant and practical. The research teams are quantifying fuel efficiency and crossover rates and have started the durability tests on the cathode PGM-free catalysts. We will be more than happy to focus on challenges related to durability and loss in future projects.

Accomplishments and Progress

– Responses to Previous Year Reviewers' Comments

The researchers report Pt/Ru/TiO₂/O-NCNTs (nitrogen-doped carbon nanotubes with open-ended channels) have greater current density than commercial PtRu/C catalysts, but the experimental conditions were not reported. It is unclear at what voltage these data were collected. In chart 8, the Johnson Matthey (JM) PtRu/C has a greater mass activity than the Pt/Ru/TiO₂/ONCNTs. Why the Pt/Ru/TiO₂/O-NCNTs have a greater current density, as claimed in Chart 9, could be better explained.



All mass Activities are calculated using the peak current density in the CV scans.

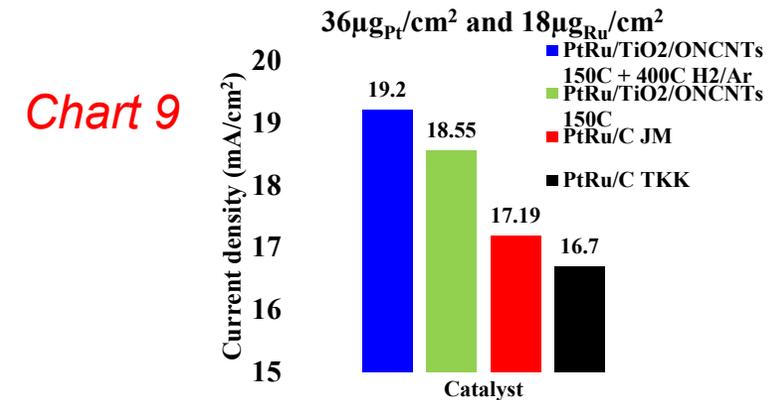


Chart 8 compares commercial catalysts with PtRu on various carbon supports (no TiO₂ layer) and Chapter 9 compares commercial PtRu with Pt/Ru/TiO₂/O-NCNTs

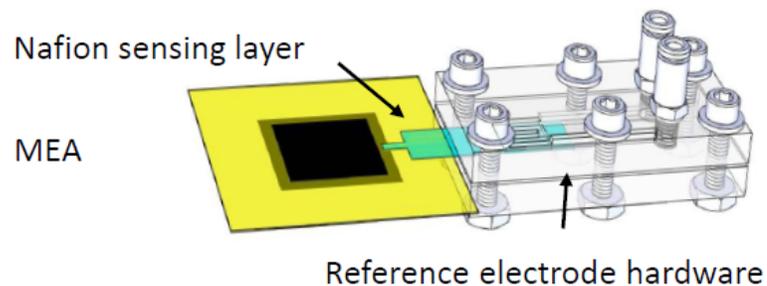
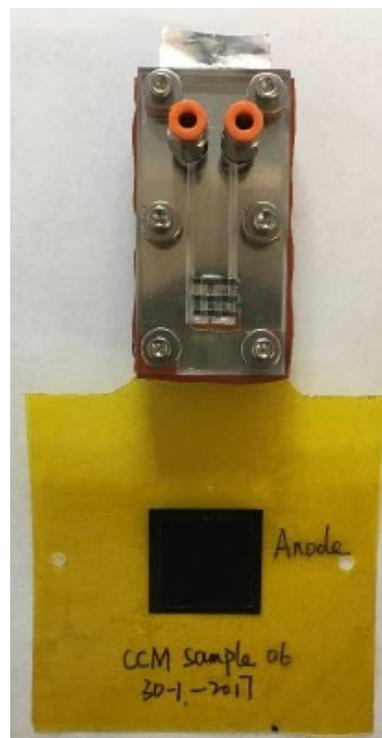
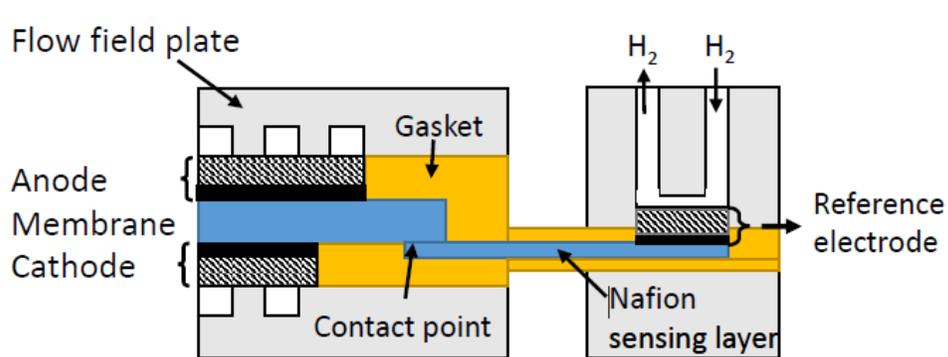
It is unclear whether the sensitivity of the MEA in chart 10 to applied back pressure is unique to the MEA or cathode. If a platinum or platinum alloy catalyst on carbon replaced the PGM-free catalyst, it is unclear whether the same dependence on back pressure would be observed. It would be helpful to know if the back pressure dependence is a product of the MEA design.

The sensitivity of the MEA to applied back pressure also applies to Pt cathodes. The back pressure and flow rate generally impact mass transfer of oxygen and water in the cathode of MEA, regardless of the catalyst used.

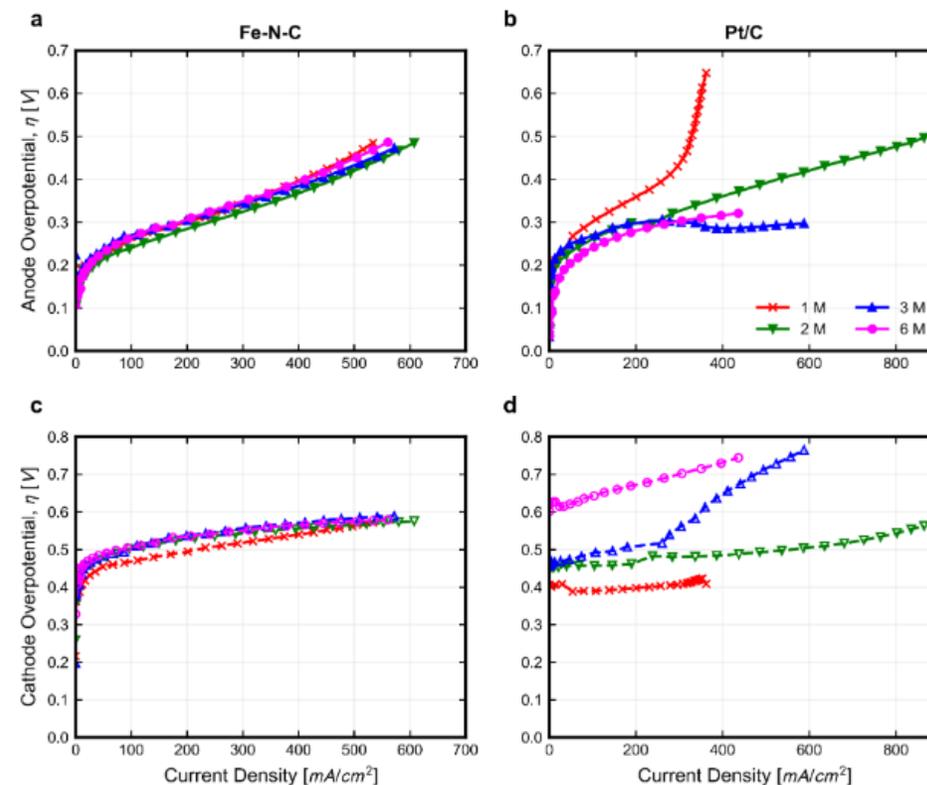
Accomplishments and Progress

– Responses to Previous Year Reviewers' Comments

Perhaps one of the team members could attempt to do a voltage loss breakdown analysis to understand the contribution of losses from anode kinetics, cathode kinetics, methanol crossover, transport losses, etc.



CMU has applied their customized H₂ reference electrode to measure the losses from anode, and cathode kinetics (figures on right). The methanol crossover loss is also measured as described in previous slides.



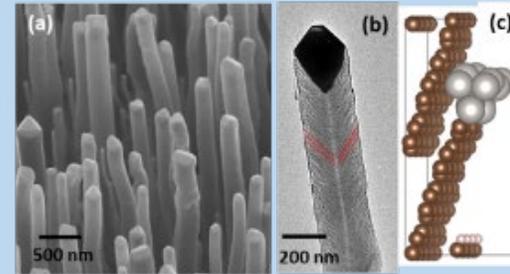
Anode overpotentials (a and b), and cathode overpotentials (c and d) measured by the RHE for the Fe-N-C cathode (a and c) and the Pt/C cathode (b and d).

Collaboration and Coordination

Team Members

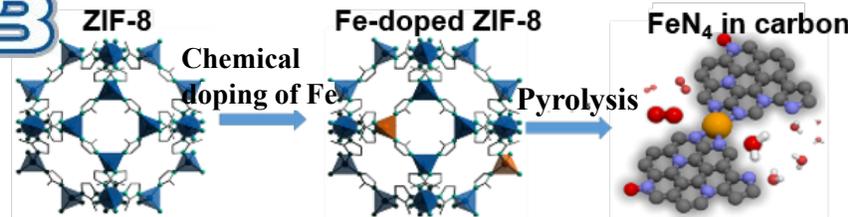
Sub: Jun Li (KSU)
Anode Catalyst

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



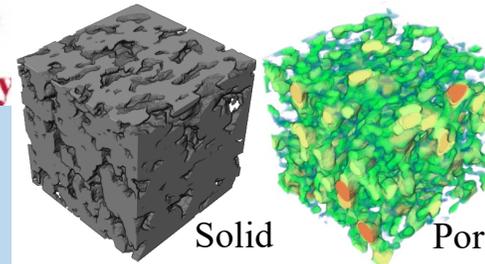
Sub: Gang Wu (UB)
Cathode PGM-free Catalyst

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



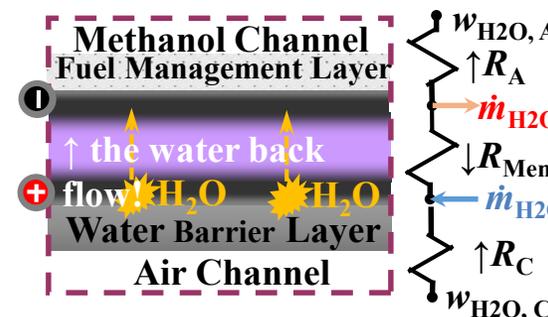
Sub: Shawn Litster (CMU)
Electrode characterization

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

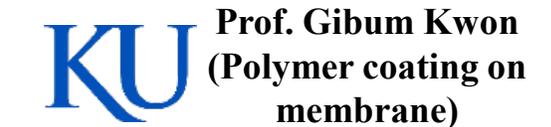
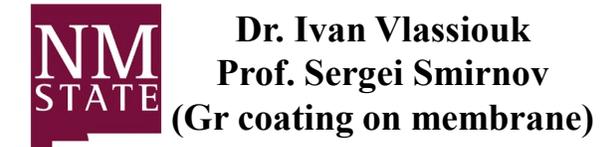


Prime: Xianglin Li (KU)
System integration and prototype development.

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



Research Collaboration

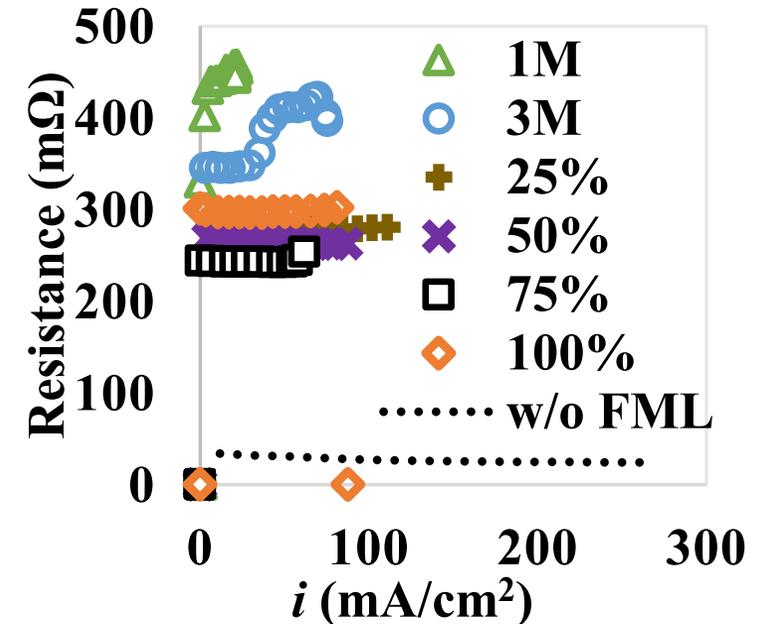


Prof. Jian Xie
 (CCM manufacture)

Remaining Challenges and Barriers

Challenge:

High ohmic resistance of fuel cell when the fuel management is applied to operate with highly concentrated methanol solutions or pure methanol. The HFR in fuel cell without FML is on the order of 20 m Ω , once the FML is applied, the HFR could be an order of magnitude higher (>300 m Ω).



Planned Resolution:

- Design and develop composite porous structures (under patent application) to improve the water management in the fuel cell. The water retention within the MEA is critical to reduce the ohmic resistance and increase the peak power density when highly-concentrated methanol solution is applied.
- Use PGM-free catalysts in MEAs so the fuel management layer doesn't have to reduce the methanol crossover too aggressively. Since the water and methanol managements are correlated, it will partially mitigate the water management challenges.

Proposed Future Work

- Incorporate newly developed highly active and stable Fe-N-C catalyst into DMFCs and test with pure methanol, concerning the types of ionomers (Nafion, Aquivion, or HOPI), temperatures, and RH.
- Study methanol tolerance on these new Fe-N-C catalysts.
- Develop AST protocols for evaluating PGM-free catalyst stability in DMFCs.
- Deployment of ultrasonicating spray coating to mitigate cracking in the catalyst layer fabrication.
- Improve the designs of FMLs and WMLs to further improve water transfer and performance stability.
- Atomize liquid methanol and methanol solutions and test vapor-feed DMFCs.
- Further optimization of the scavenge layer to balance the decrease of methanol crossover and decrease of ionic conductivity.
- Apply Nano-CT or Plasma-FIB imaging to characterize structure changes of electrodes after long-term tests.
- Computational exploration of trade-offs between durability and performance mitigated of PGM-free catalysts by optimized control strategies for a given drive cycle.
- Carry out full MEA studies on customized anode catalysts: PtRu/TiO₂/KB 600JD-400; PtRu/TiO₂/OCNT-400; PtRu/TiO₂/MnNC-400.
 - Use customized catalyst support (Manganese Nitrogen-doped Carbon, MnNC) for anode catalysts and conduct half-cell electrochemical characterization and materials characterization on control samples such as PtRu/MnNC-MW and PtRu/MnNC-400 to have more insights on MnNC support effect in MOR.
 - Optimize thin-film deposition of SnO₂ on carbon supports to study the effect of SnO₂ in improving the activity and stability of PtRu nanoparticles.
 - Synthesis core-shell Pt-Ru nanoparticles using microwave assisted methods.

Summary

End of the Project Goal

A single cell (50 cm²) with MEA ≤ 3 mgPGM/cm² achieves 300 mW/cm² using pure methanol.

3rd Budget Period Accomplishments and Significant Findings

- 1) DMFC achieved 275 mW/cm² peak power with 3.0 mgPGM/cm², tested with 1M methanol.
- 2) Developed Accelerated stress test (AST) by applying square wave potential between 0.4V and 0.8V in DMFC operation.
- 3) Fe-N-C catalyst stabilized after first 10k of AST, the performance was nearly unchanged between 10k and 30k cycles.
- 4) CVD-Fe-N-C cathode showed promising stability in DMFC: 7.2% loss at EOL (0.93 mA/cm²/h) after 24 hours of Chronoamperometry @ 0.5 V.
- 5) Developed PtRu/TiO₂/KB600JD-400 (25%) catalyst that shows higher MOR If, higher ECSA, and earlier onset potentials for MOR and CO oxidation than commercial catalysts (JM and TKK).
- 6) Customized anode (PtRu/TiO₂/ONCNTs) and Fe-N-C-FG cathode showed 20.4% loss (2.23 mA/cm²/hr) after 12 hours of Chronoamperometry @ 0.5 V.
- 7) Experimentally measured the reaction order of vapor-feed and liquid-feed MOR.
- 8) Developed the scavenger layer to reduce the methanol crossover.
- 9) Experimentally measured the over-potentials from anode and cathode kinetics using a customized H₂ reference electrode.
- 10) Customized fuel and water management layers to enable stable DMFC operation using pure methanol for more than 36 hour at constant voltage of 0.4V.
- 11) Analysis of technical and economic feasibility of DMFC to power commercial buildings.

ACKNOWLEDGEMENT

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

DOE Program Manager: Donna Ho

Project Team



University of Kansas

- Prof. Xianglin Li
- Nathaniel Metzger



University of Buffalo

- Prof. Gang Wu
- Dr. Yachao Zeng



Kansas State University

- Prof. Jun Li
- Archana Sekar



Carnegie Mellon University

- Prof. Shawn Lister
- Mohamed Abdelrahman

Technical Backup and Additional Information

Technology Transfer Activities

Patent and licensing.

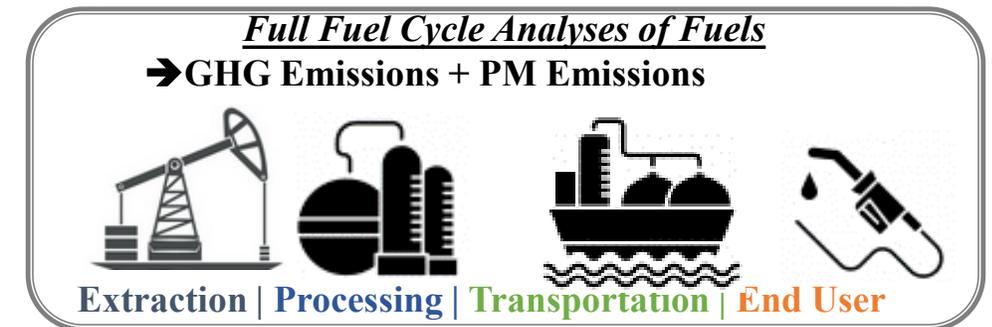
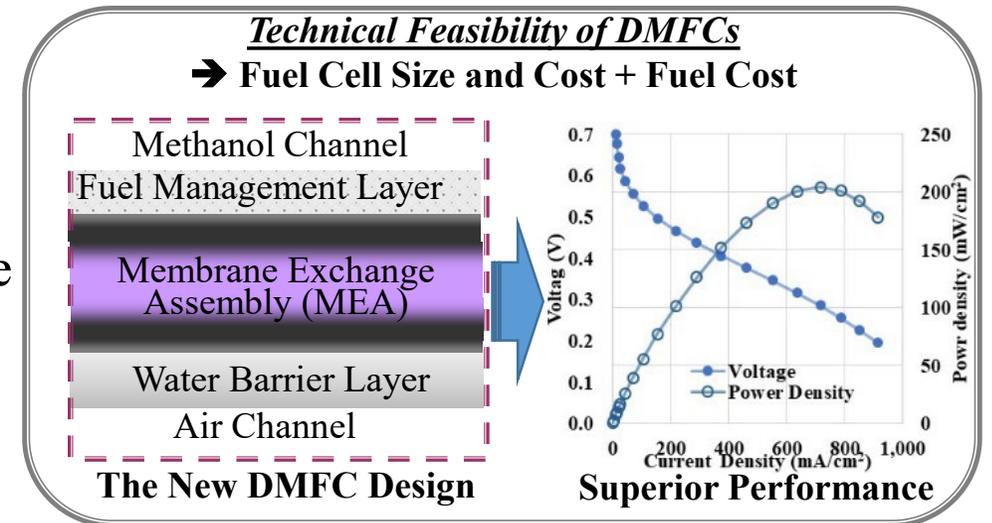
- We are applying a patent related to the fuel and water management layers.

Technology transfer plans and strategies.

- Demonstrate single cells using pure methanol and measure the efficiency and specific energy;
- Develop DMFC stacks using pure methanol and show the specific energy;
- Conduct economic analysis to analyze the feasibility of applying DMFCs for portable applications;
- Integrate DMFC stacks with UAVs and other portable devices.

Plans for future funding from alternative sources as well as marketing strategies and options.

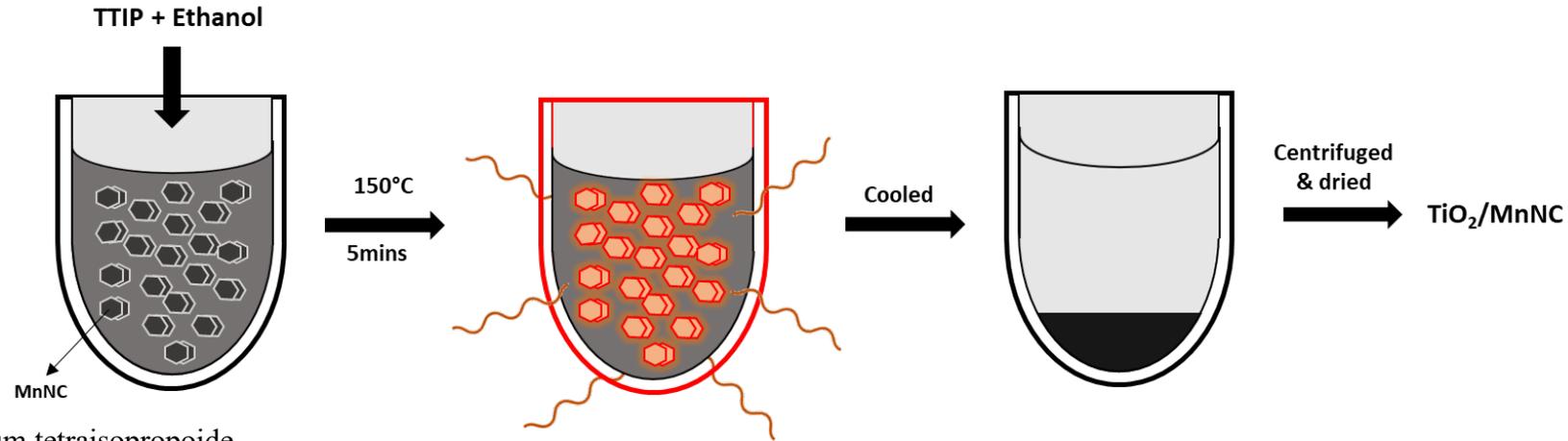
- ARPA-E and DOD for portable DMFCs using pure methanol.
- Collaborating with industry to identify potential users of high-energy power sources and develop prototypes.



Technical, economic and environmental analyses of DMFCs as portable power sources.

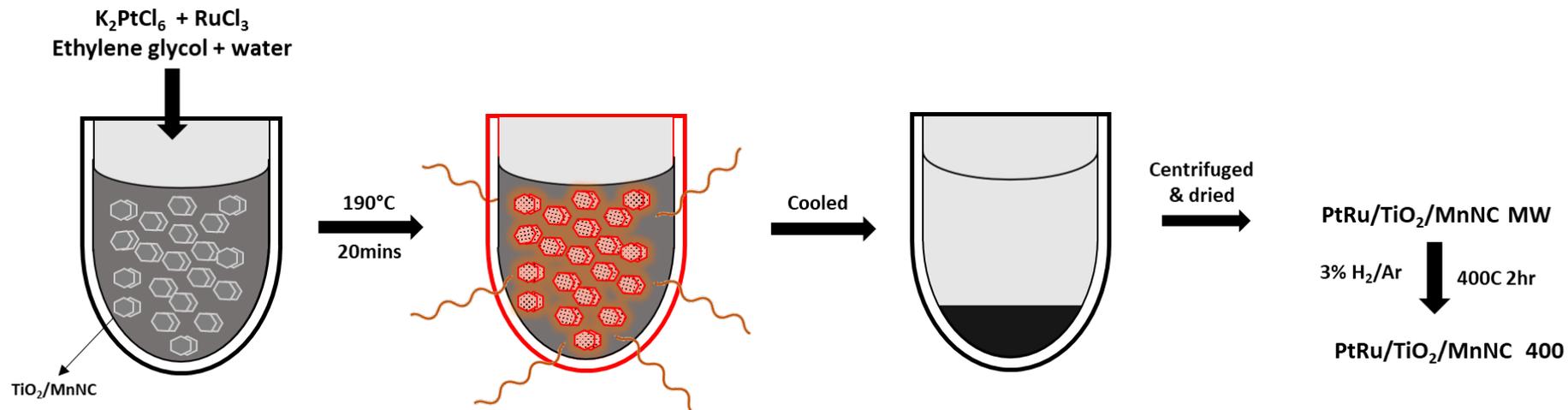
Materials Synthesis: PtRu/TiO₂/MnNC 400

Step 1: TiO₂ deposition on MnNC



TTIP: Titanium tetraisopropoxide
MnNC: 10 mg; TTIP: 10 µl; Ethanol: 6 ml

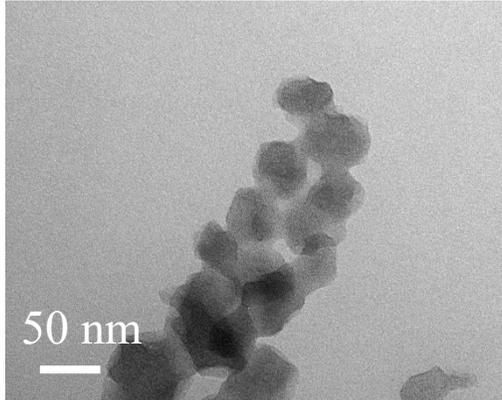
Step 2: PtRu deposition on TiO₂/MnNC



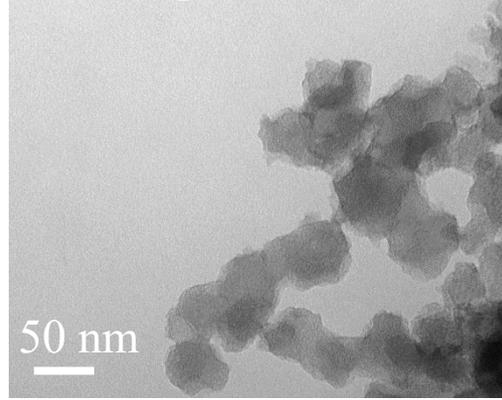
K₂PtCl₆: 12.1 mg; RuCl₃.xH₂O: 5.2 mg; TiO₂/MnNC: 16 mg
Ethylene glycol + water: 16 ml + 4ml

Materials Characterization: TEM and TGA

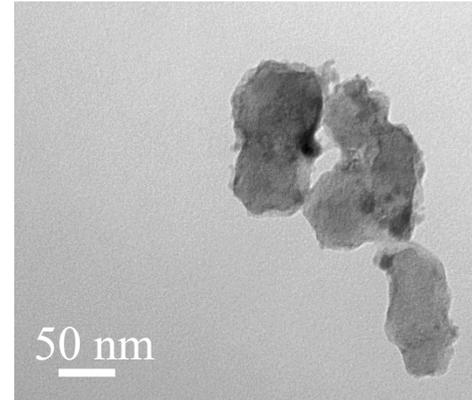
MnNC support



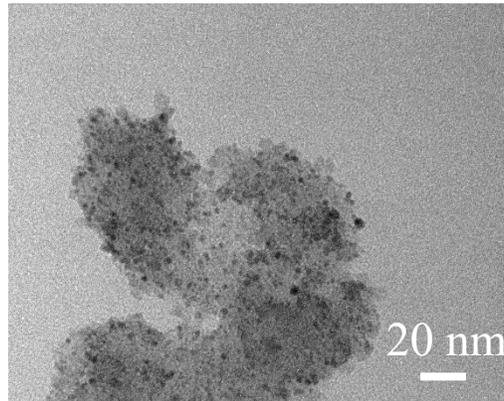
TiO₂/MnNC MW



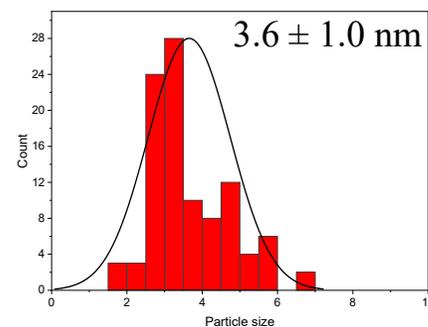
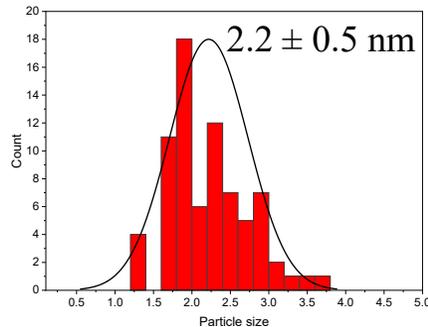
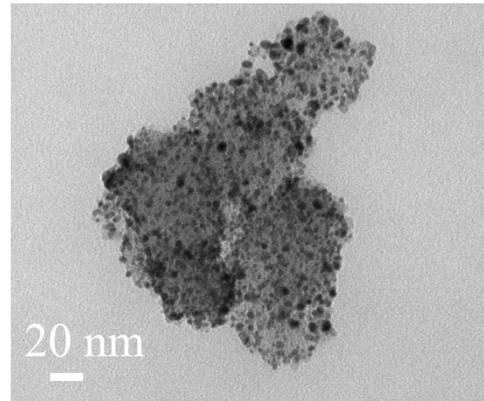
TiO₂/MnNC 400



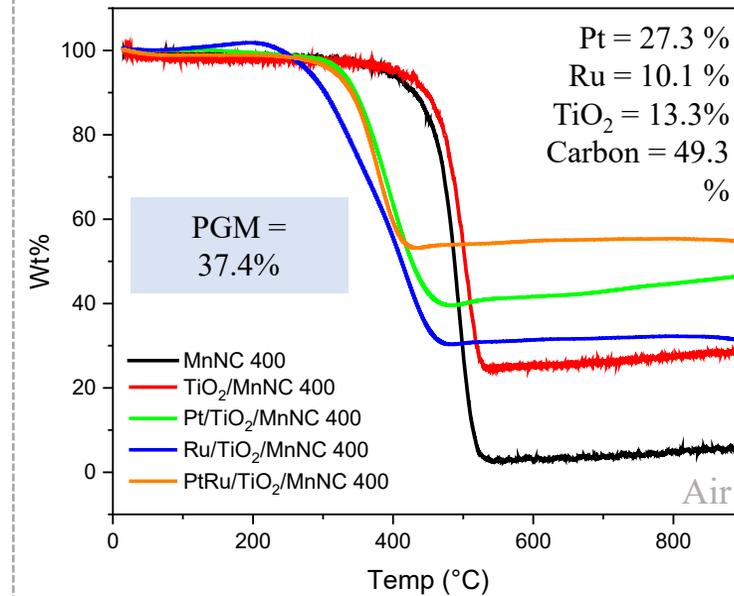
PtRu/TiO₂/MnNC MW



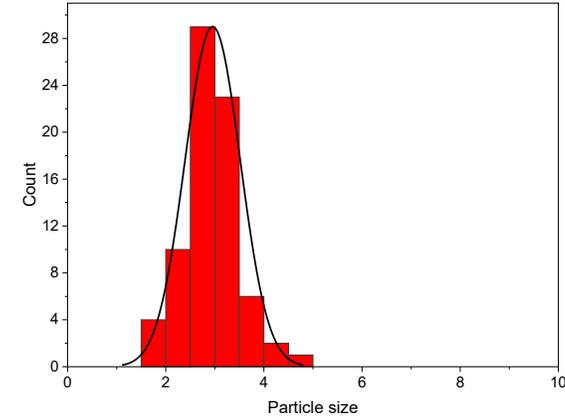
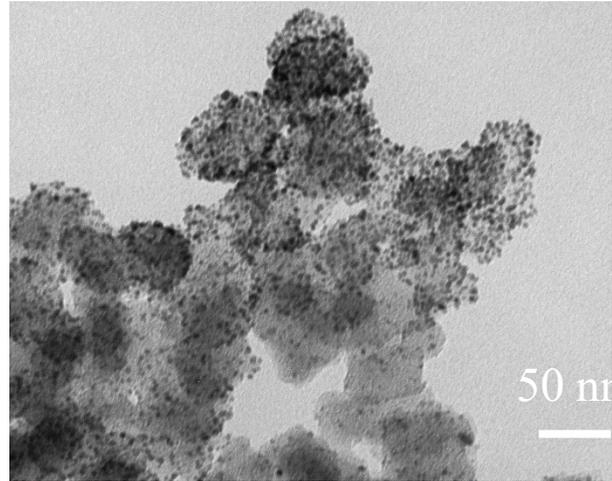
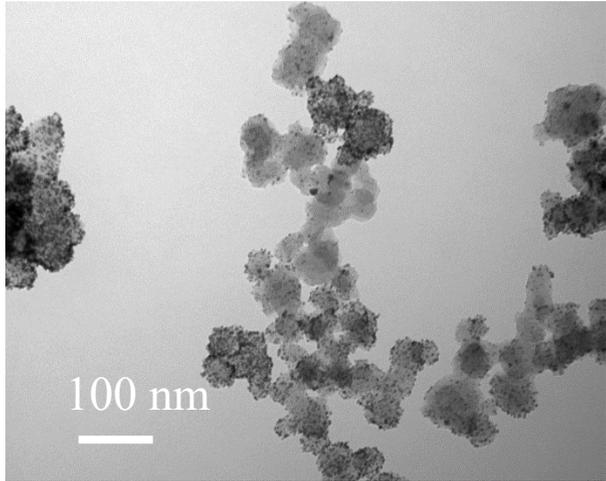
PtRu/TiO₂/MnNC 400



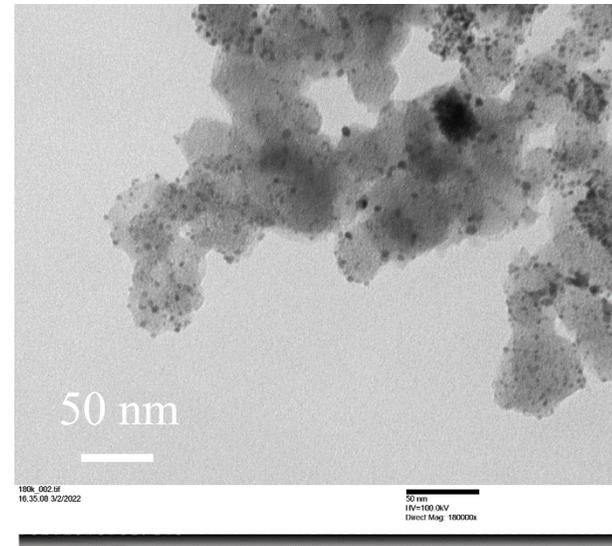
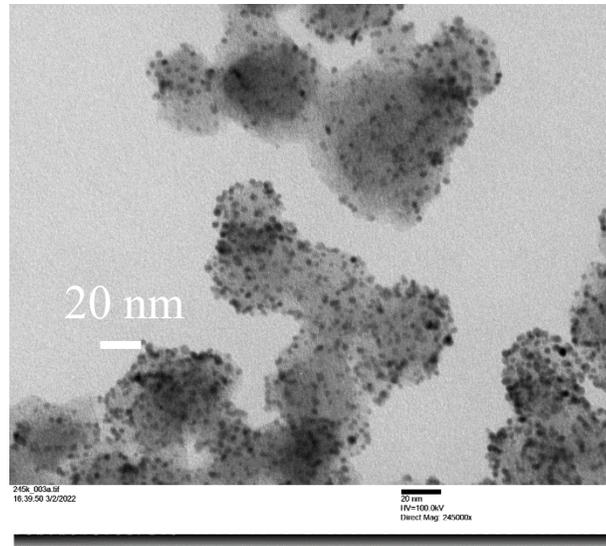
PtRu/TiO₂/MnNC 400



PtRu/Mn-NC MW (w/o TiO₂)



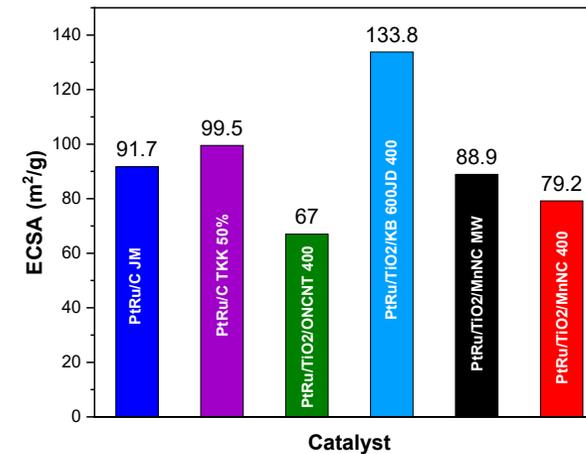
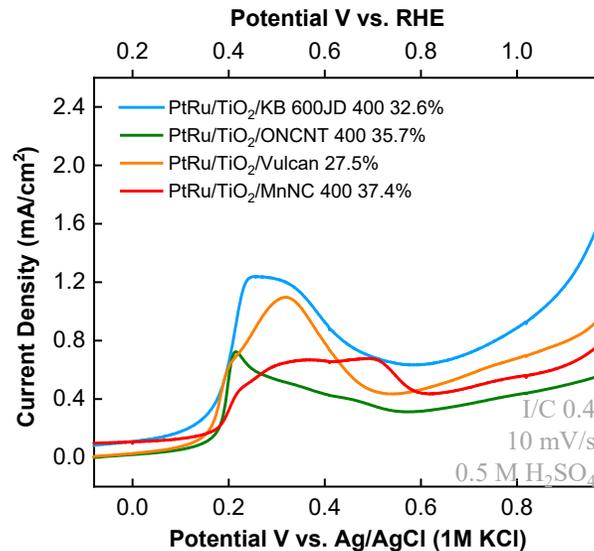
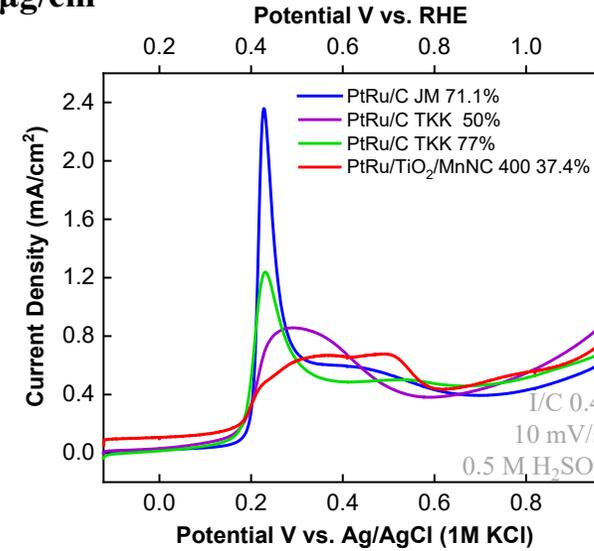
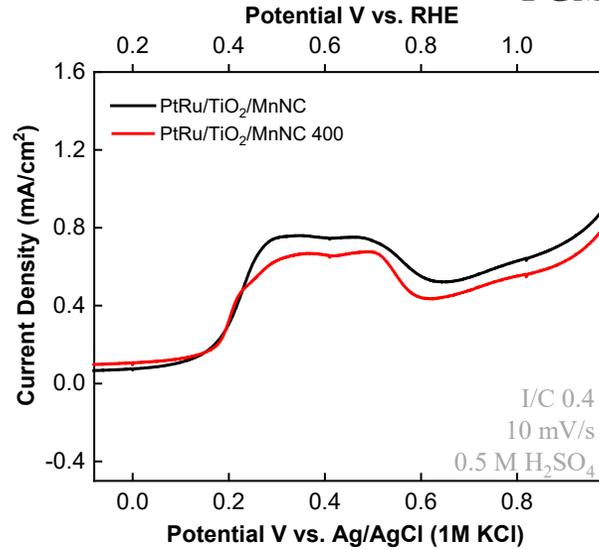
Avg. Particle size = 3.0 ± 0.6 nm



- Non-uniformity in nanoparticle deposition. Surface functionalities may affect the dispersion on the catalyst surface.

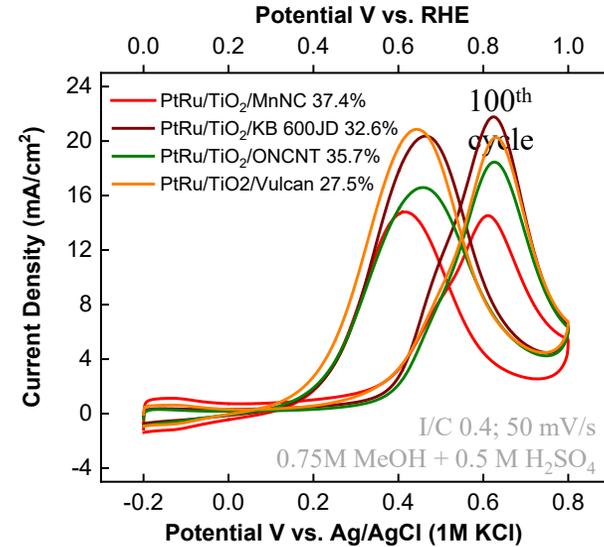
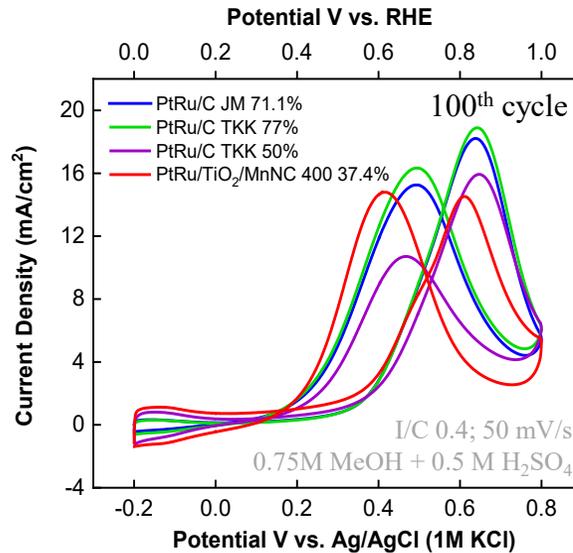
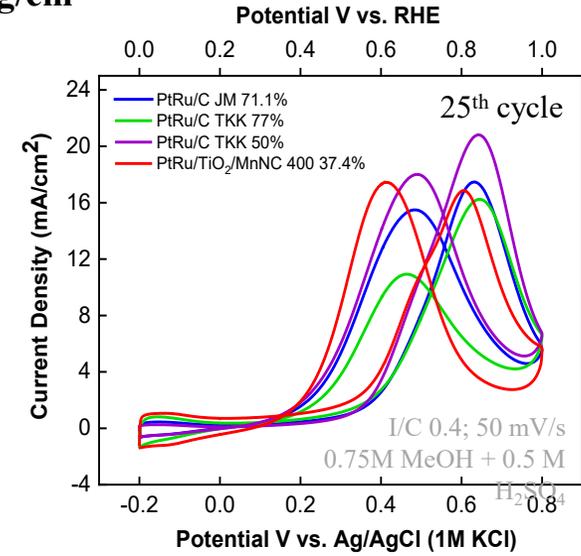
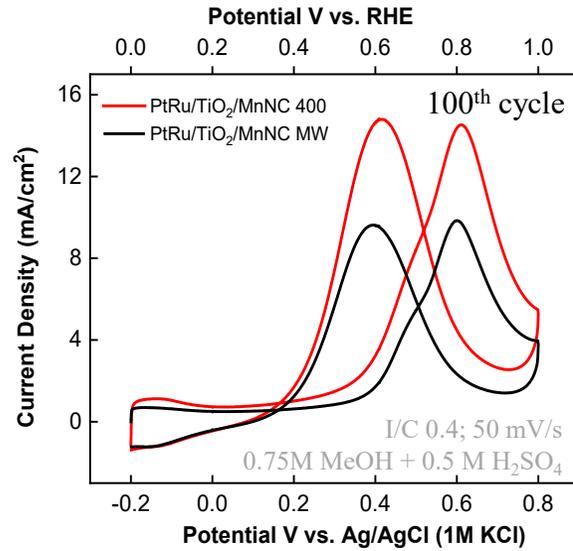
Half-Cell Evaluation: CO Stripping Analysis

PGM loading = $54 \mu\text{g}/\text{cm}^2$

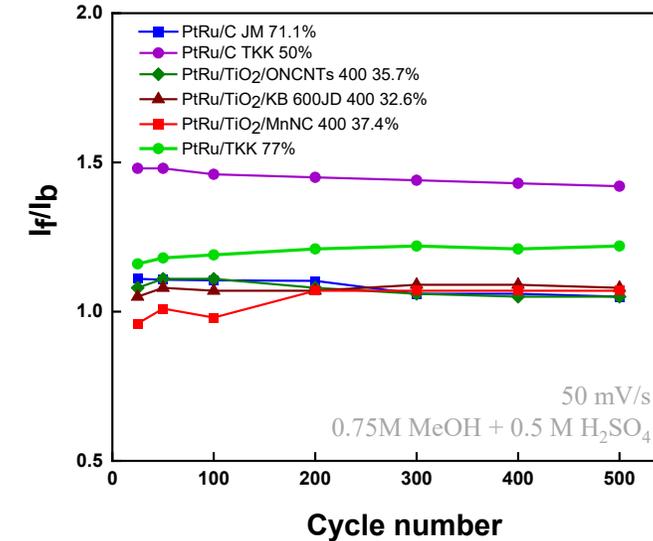
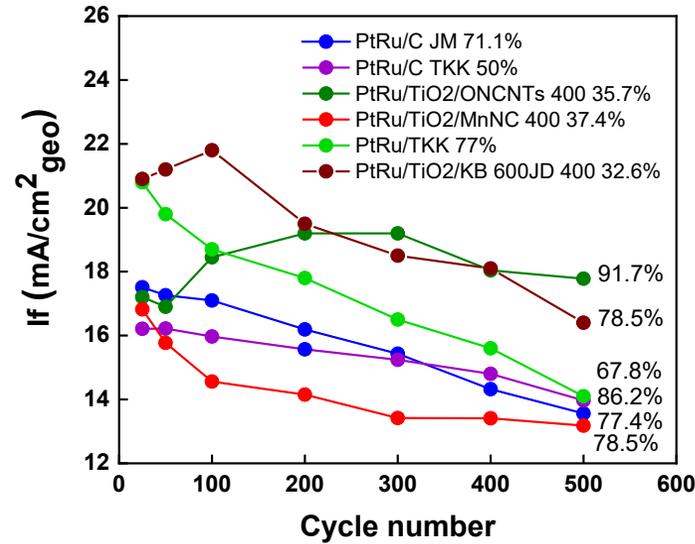


Half-Cell Evaluation: MOR Kinetics

PGM loading = 54 $\mu\text{g}/\text{cm}^2$



Half-Cell Evaluation: MOR Durability



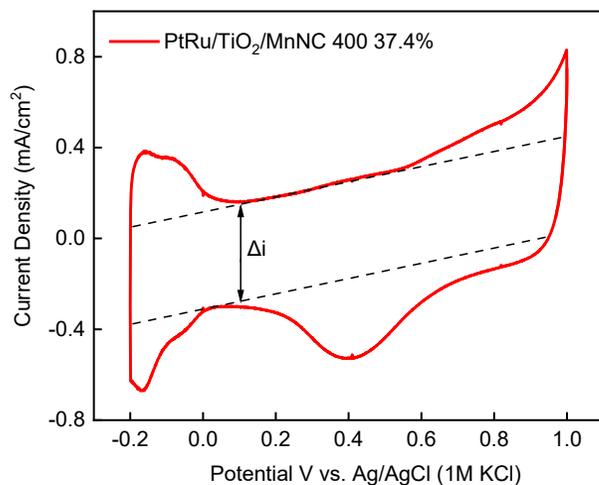
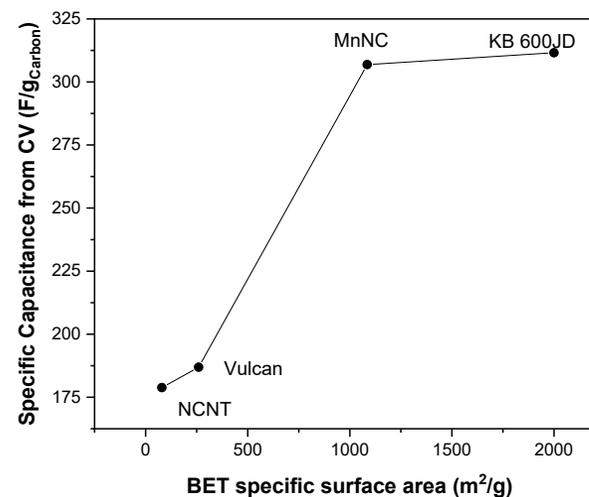
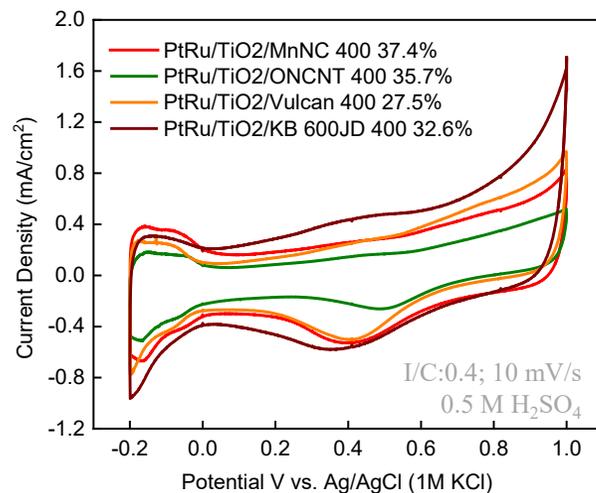
Inference:

- The PtRu/TiO₂/MnNC-400 catalyst had much earlier onset for MOR when compared to commercial anode catalysts and other custom catalysts made from KSU.
- The PtRu/TiO₂/MnNC-400 had 78.5 % retention in peak I_f after 500 continuous CV cycles which is comparable to commercial PtRu/C JM 71.1% and better than commercial PtRu/C TKK 77.7%.
- The initial I_f at 25th cycle was comparable to commercial catalysts, however, inferior to KSU-custom made catalysts with other carbon supports such as NCNTs, KB 600JD and Vulcan.

Carbon Support Structure Property Correlation



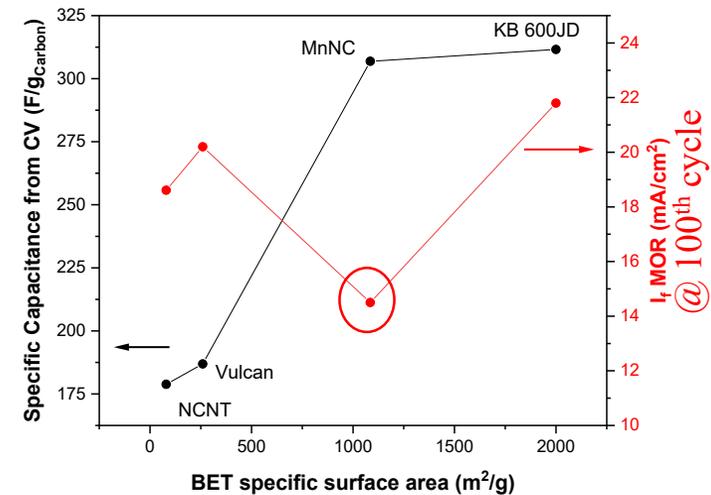
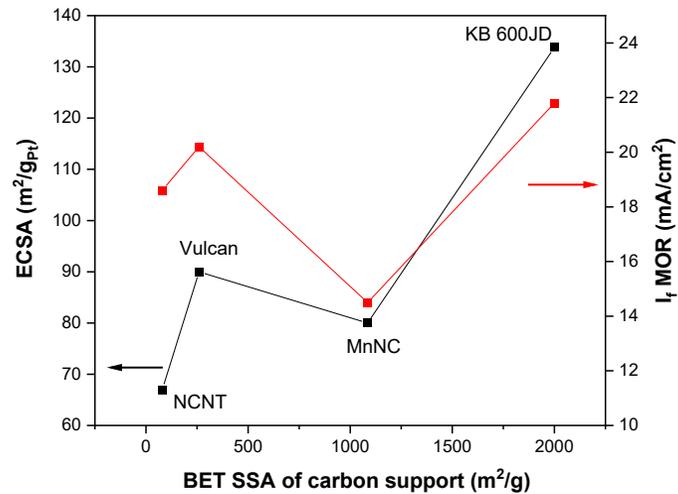
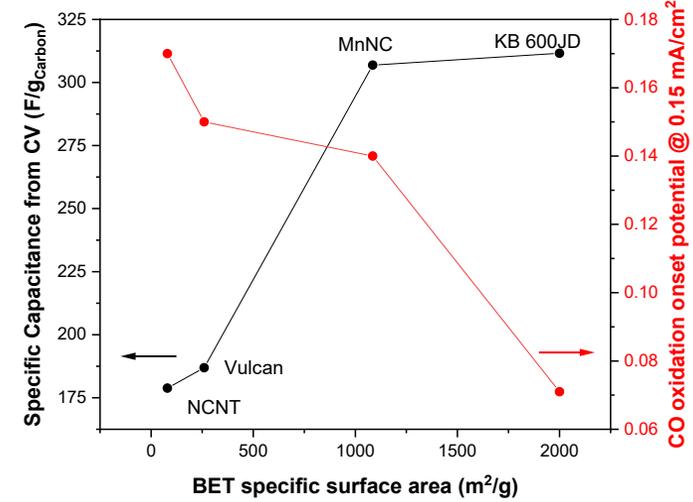
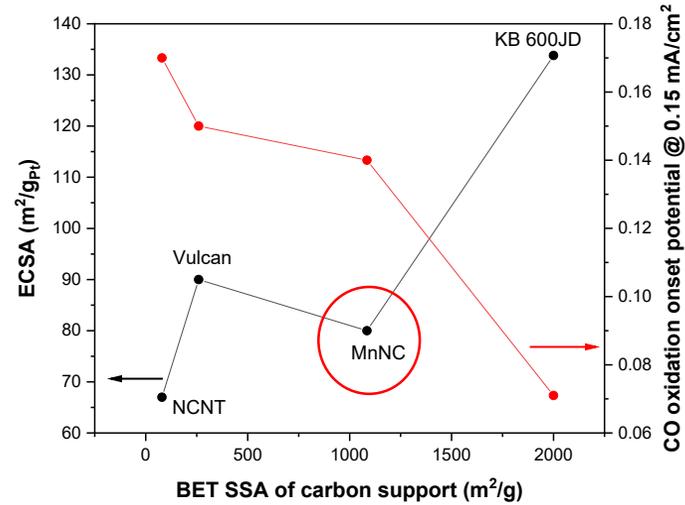
PGM loading = 54 $\mu\text{g}/\text{cm}^2$



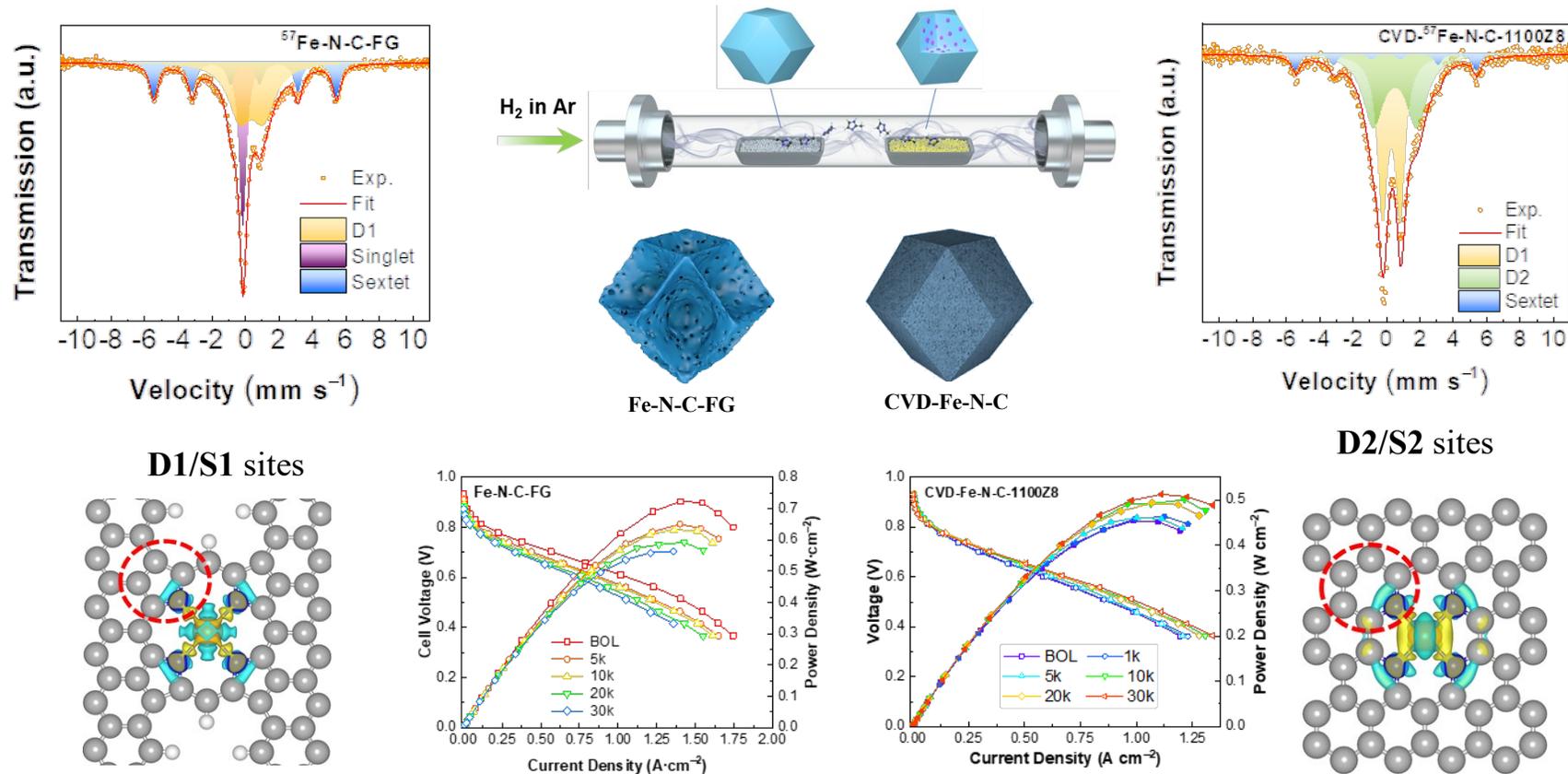
Catalyst	Specific Capacitance (F/g _{Carbon})
PtRu/TiO ₂ /ONCNT 400 35.7%	178.8
PtRu/TiO ₂ /Vulcan 400 27.5%	186.9
PtRu/TiO ₂ /MnNC 400 37.4%	306.9
PtRu/TiO ₂ /KB 600JD 400 32.6%	311.6

$$\text{Specific Capacitance } \left(\frac{F}{g}\right) = \frac{\left(\frac{\Delta i}{2}\right) \cdot \Delta V}{\Delta V \cdot \frac{V}{s} \cdot \text{mass of carbon}}$$

Carbon Support Structure Property Correlation

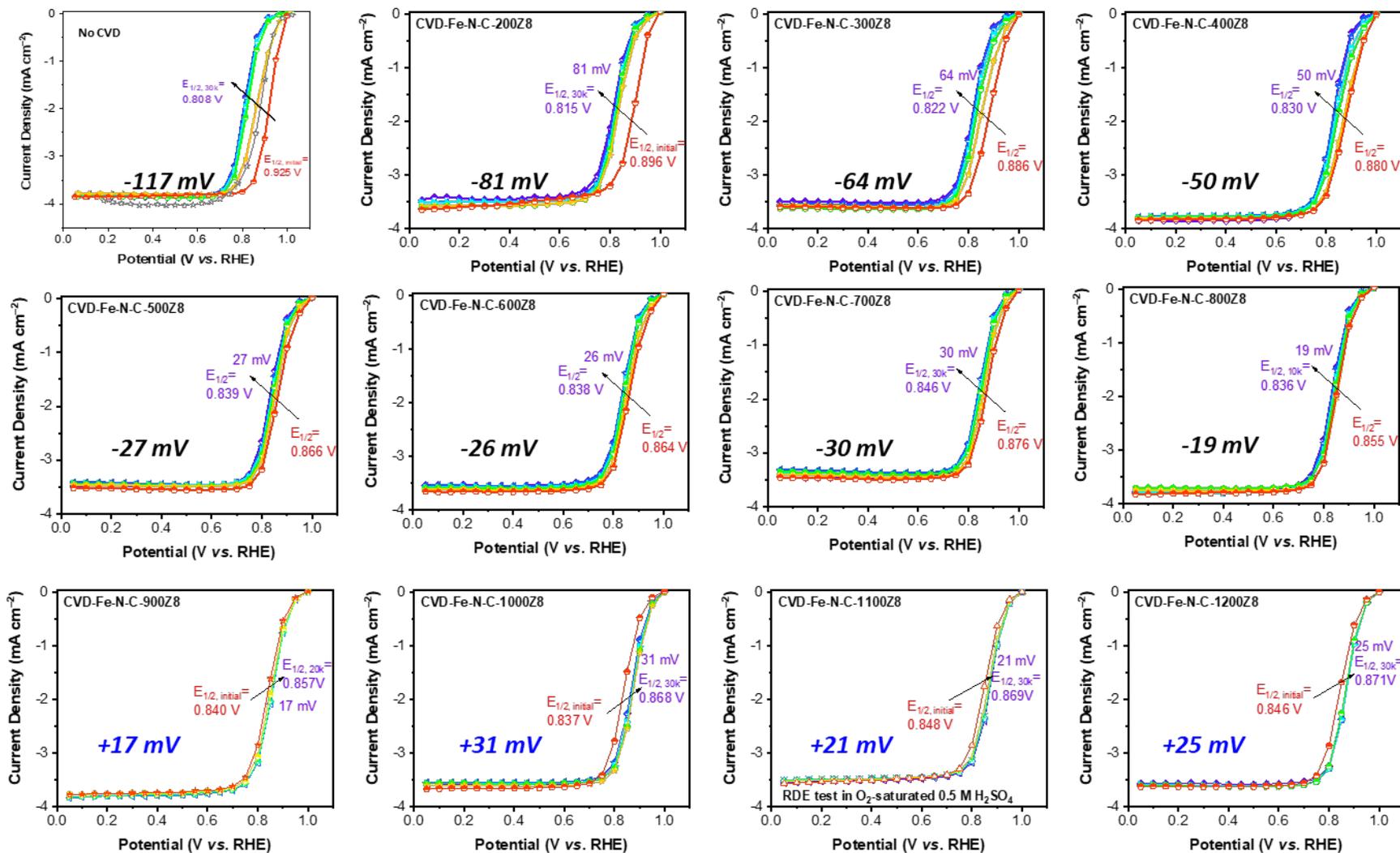


High Performance PGM-free Catalysts with Trade-off Activity and Stability



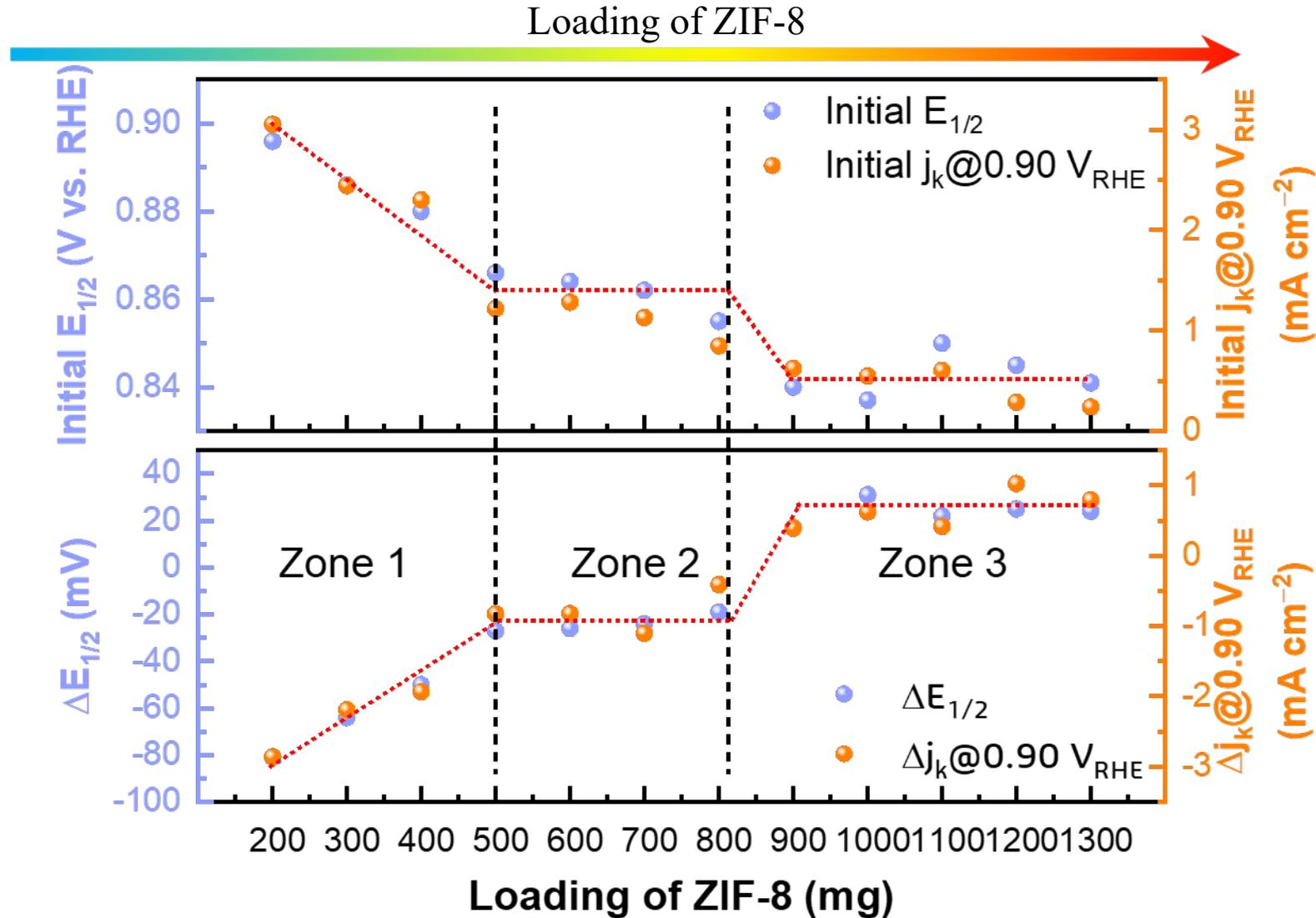
- Mössbauer spectroscopy explain that the enhanced stability is due to changes in the local carbon structure around the FeN_4 sites associated with the **conversion** of unstable **S1** sites to more stable **S2** sites through deposition of a **thin layer of nitrogen-doped carbon around FeN_4 sites**.
- DFT calculations clearly predict S1 sites are intrinsically more active, but less stable than S2 sites.
- AST in H₂-air fuel cells verified the feasibility of stability enhancement by CVD.

Tuning CVD Conditions to Trade Off Activity and Stability



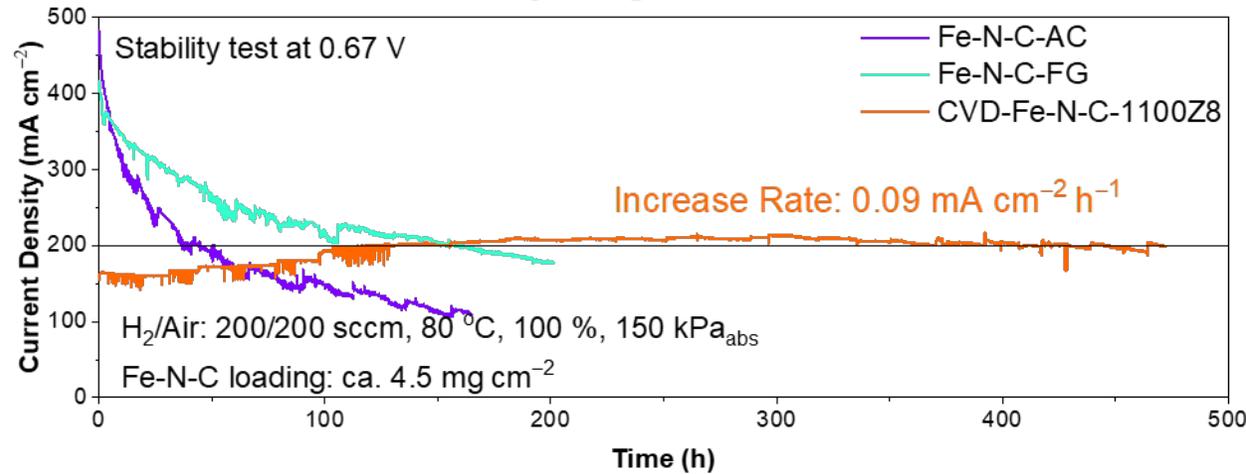
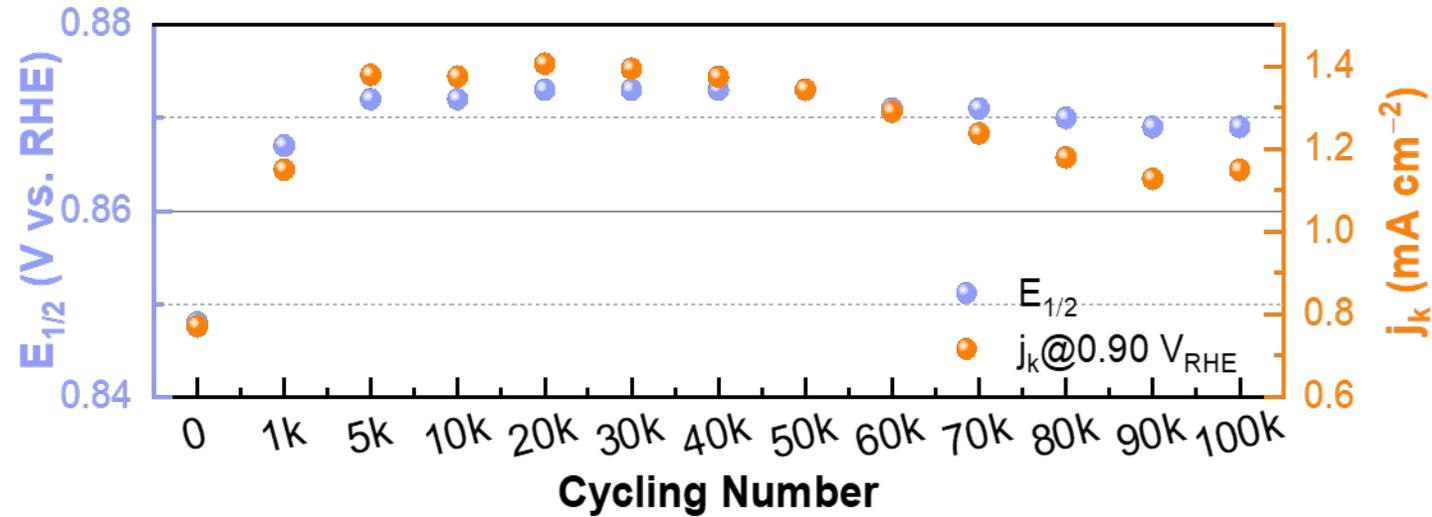
Increasing CVD content improves stability but mitigates initial activity.

Balancing Activity and Stability



Optimizing CVD conditions to improve stability and maintain adequate activity.

Long-term stability test in RDE and H₂-air fuel cells



- 100,000 cycles of AST of CVD-Fe-NC-1100Z8 in rotatory disk electrode demonstrated the improvement in the intrinsic stability.
- Long-term stability test in H₂-air fuel cells verified the feasibility of deployment of CVD-treated catalysts in real applications.

Evaluation of Degradation Acceleration Factors

Goals

- Determine impact of operating point on degradation rate in MEAs
- Perform time-efficient evaluation of degradation acceleration factors (k_i) on a single MEA

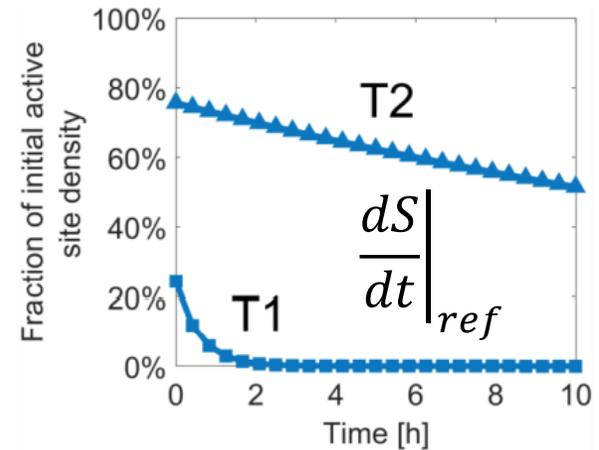
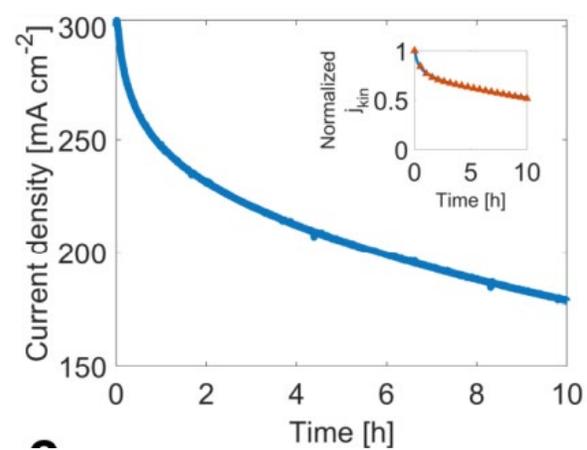
Impact

- Identify operating points that optimize performance and durability trade-off
- Apply empirical degradation correlations into drive-cycle models for PGM-free catalysts for simulation-based lifetime performance forecasting

Two-site double exponential model:

$$j_{k,normal} = C \exp(-k_1 t) + (1 - C) \exp(-k_2 t)$$

$$C = K_1[X_1]_{s,t=0} / (K_1[X_1]_{s,t=0} + K_2[X_2]_{s,t=0})$$

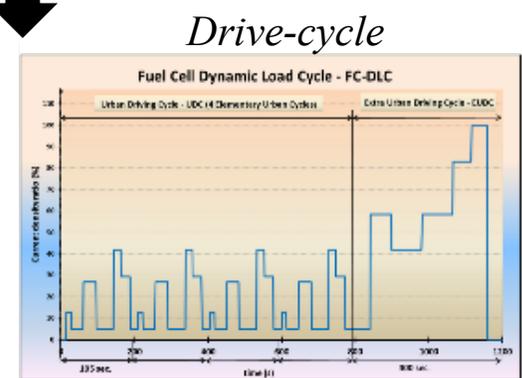
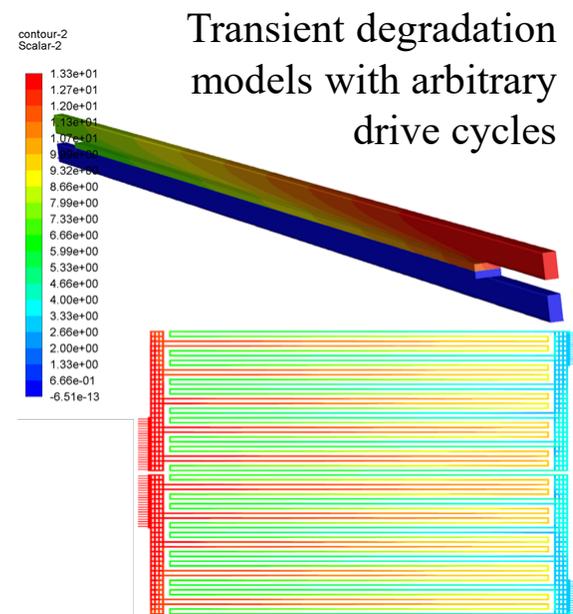


Empirical active-site density (S) loss model

$$\frac{dS}{dt} = \underbrace{k_T k_{RH} k_V}_{\text{Acceleration factors}} \frac{dS}{dt} \Big|_{ref}$$

Local oxygen reduction reaction model

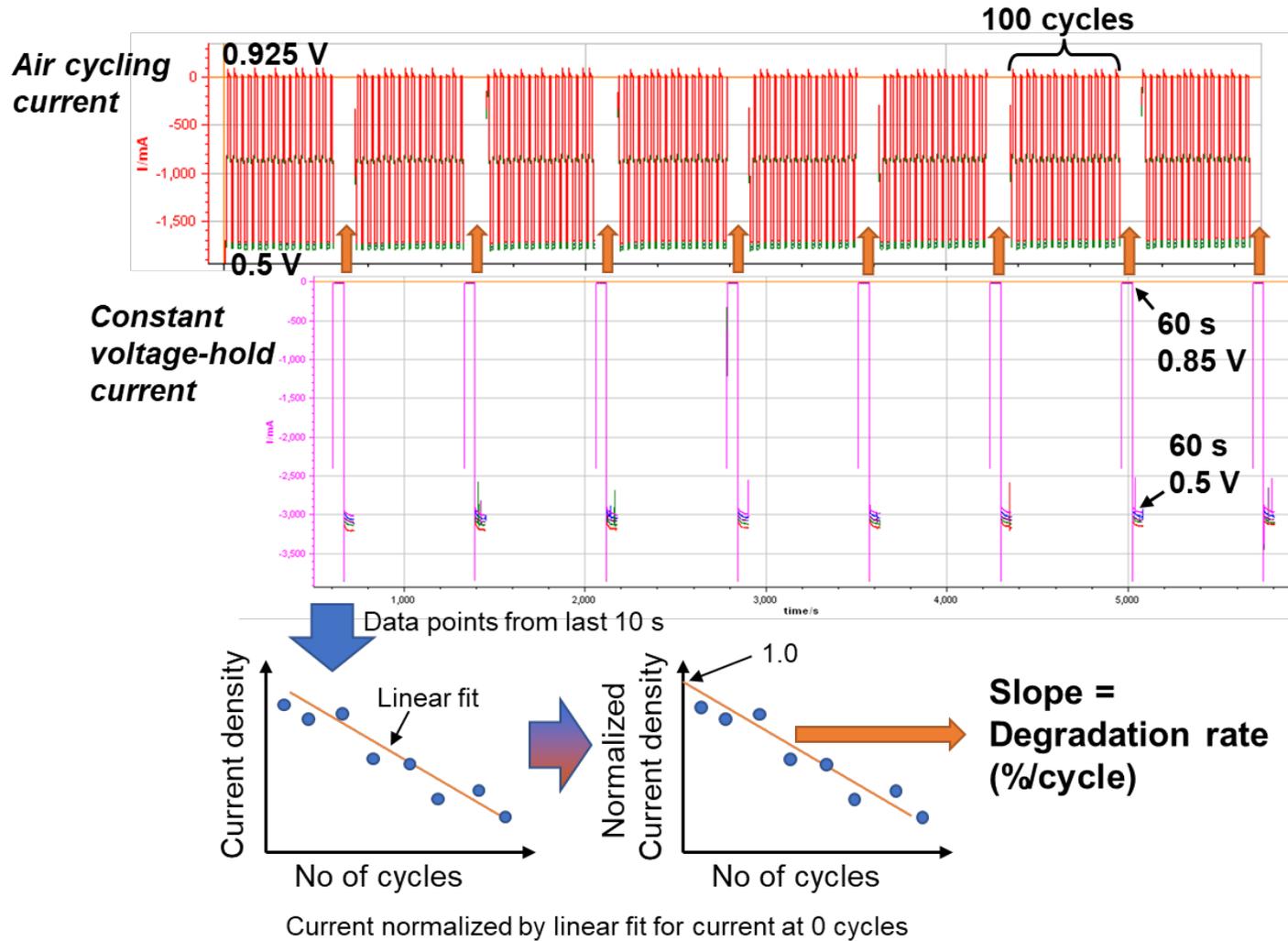
$$j_{ORR} = RS \frac{C_{O_2}}{C_{O_2}^{ref}} \exp\left(\frac{\alpha F}{RT} \eta\right)$$



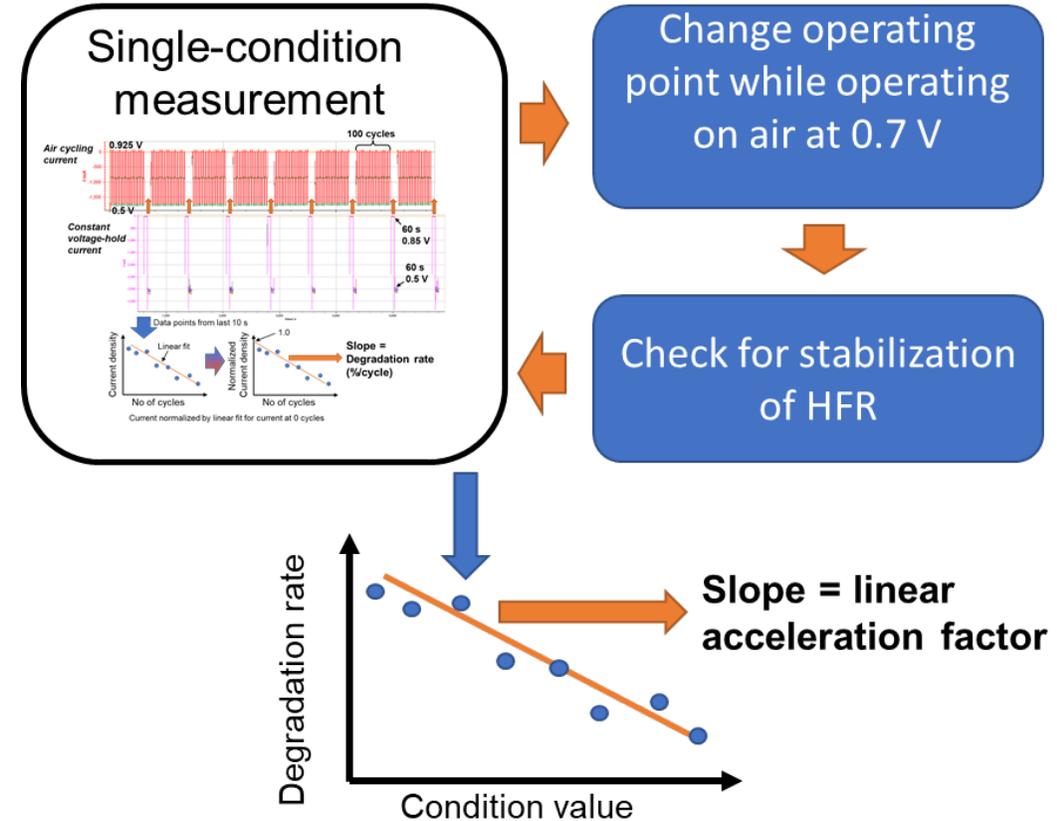
Beltrán et al, *Advanced Energy and Sustainability Research*, 2021

Measurement Protocol

Evaluating degradation rate at a single condition



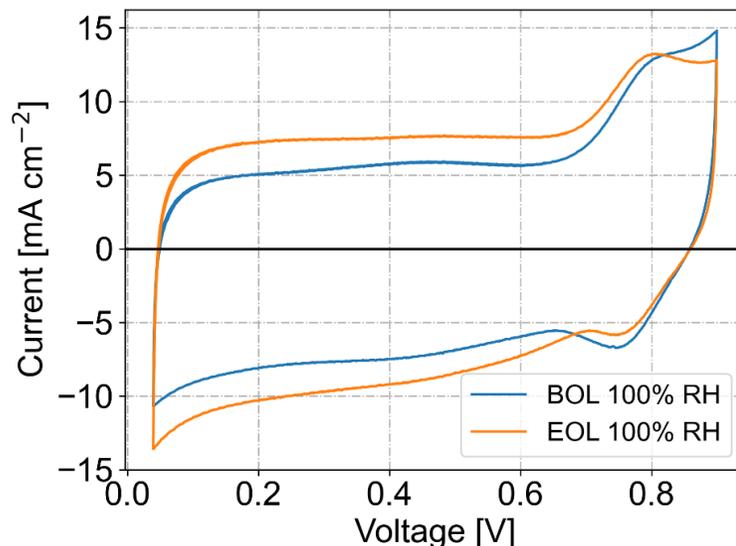
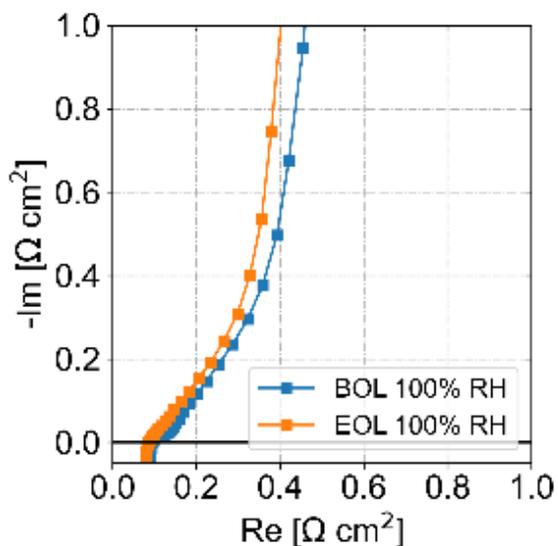
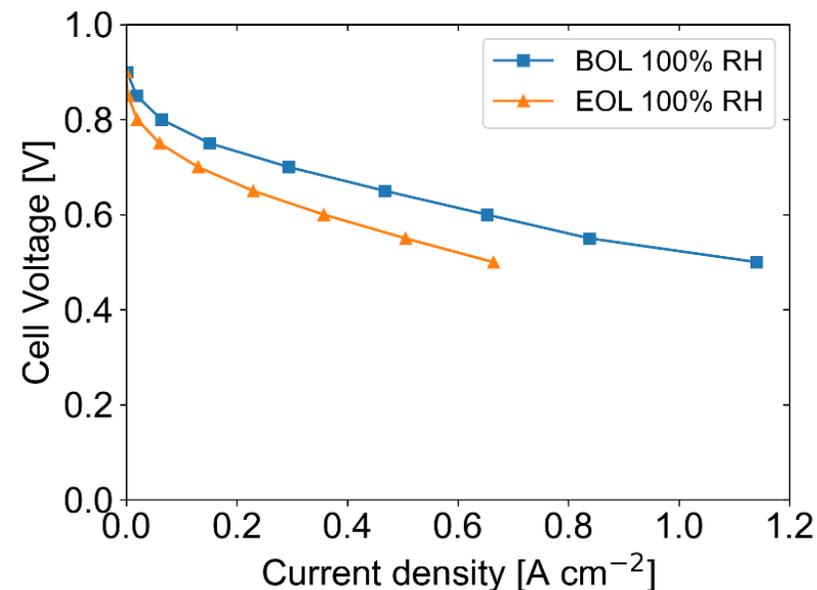
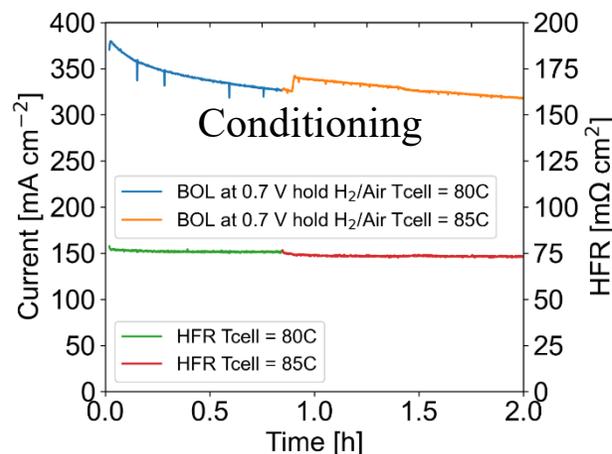
Evaluating acceleration factor



- Relative humidity
- Temperature
- Upper potential limit (UPL)

Beginning and End of Test Characterization

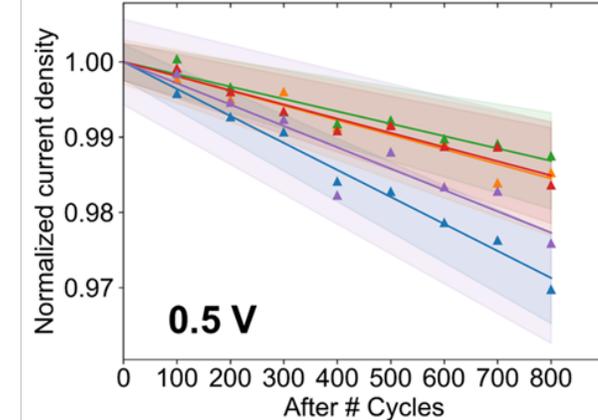
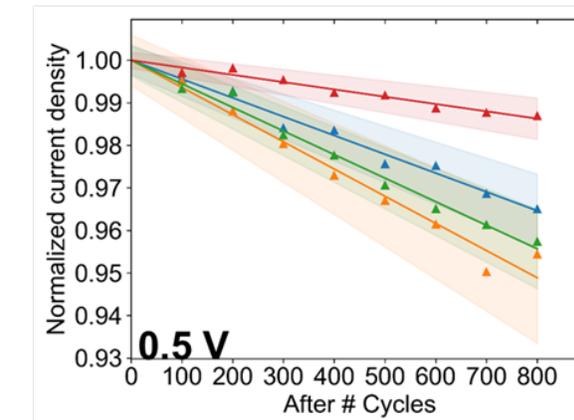
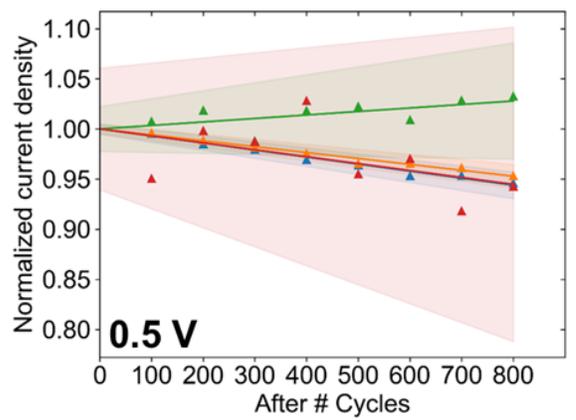
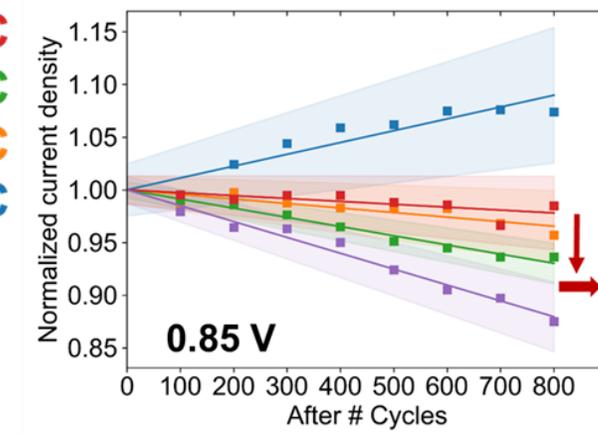
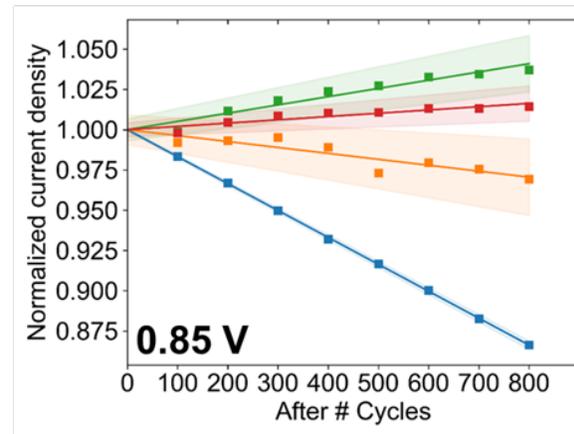
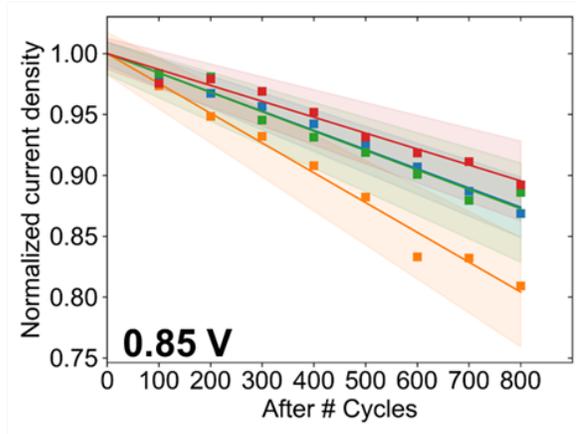
- Characterization before and after all air cycling
- ~13,000 cycles at more aggressive conditions than standard AST (85°C, 0.925 V UPL)
- Significant reduction in performance
 - 85% loss at 0.85 V
 - 39% loss at 0.55 V
- No change in electrode H⁺ conduction resistance
- 20% increase in CV double layer current



Membrane electrode assembly

- Catalyst: UB Fe-N-C-AC-CVD
- GDE Cathode: 4 mg/cm², D2020 I/C 0.6 with D2020 overcoat
- GDLs: Freudenberg H23C6
- Membrane: Nafion HP
- Anode: 0.1 mg/cm² Pt/C

Degradation Rates for RH, T, and UPL Studies

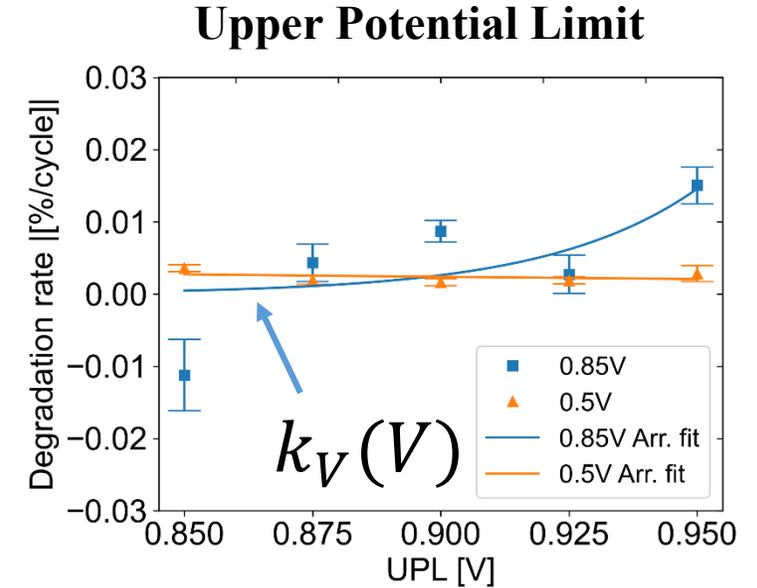
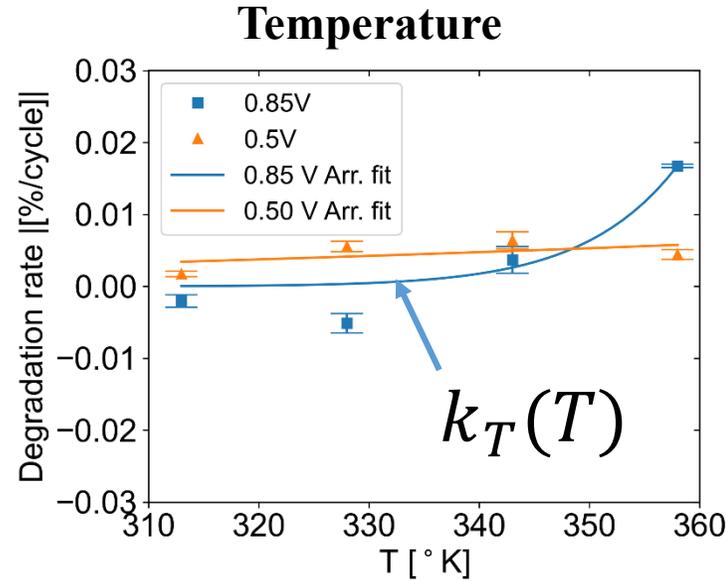
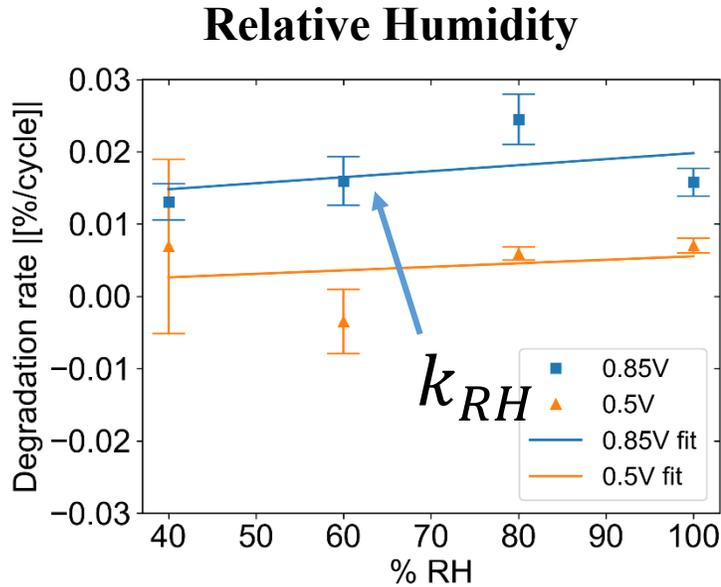


Shading is 95% confidence intervals for linear fits

- Consistent 0.85 V baseline rate in all three studies
- Rate is sufficiently independent of absolute cell degradation
- 0.5 V exhibits low sensitivity due to other overpotentials

- Minor effect of RH on degradation rate
- Negligible degradation at 40°C and 55°C and significant increased degradation at >70°C
- Significant reduced degradation with UPL <0.9 V

Degradation Acceleration Factors



- Slope of curves for sensitivity to operating point and acceleration factor

$$\frac{dS}{dt} = \underbrace{k_T k_{RH} k_V}_{\text{Acceleration factors}} \frac{dS}{dt} \Big|_{ref}$$

- Relative humidity has lowest relative impact on degradation rate. However, relative humidity may significantly reduce performance
- Degradation rate significantly reduced at <70°C. Reducing temperature from 85°C to 70°C reduces degradation rate by ~75%
 - ~25% reduction in 0.85 V current at 70°C versus 85°C
 - ~15% reduction in 0.5 V current at 70°C versus 85°C
- Degradation rate with UPL < 0.875 V is difficult to resolve in 800 cycles at 85°C
- At most benign conditions (low temperature, low UPL), the 0.85 V current density increases 3-7% for first 400 cycles

Publications and Presentations

Journal Publications

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, Xianglin Li. "Technical and Economic Analysis of Fuel Cells for Material Handling Applications", *ACS OMEGA*, **Under Revision**.
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*, (2021) JEECS-21-1038.
6. Archana Sekar, Nathaniel Metzger, Sabari Rajendran, Ayyappan Elangovan, Yonghai Cao, Feng Peng, Xianglin Li, Jun Li, "Enhancing Methanol Oxidation Reaction of Precious Metal Catalysts on Nitrogen-doped Carbon Nanotubes using Ultrathin Conformal Hydrogenated TiO₂ Shells", *ACS Appl. Nano Materials* (cover image), 5 (2022) 3275–3288.
7. Mohamed Abdelrahman, Hanguang Zhang, Gang Wu, Xianglin Li, Shawn Litster, "Half-cell electrode assessments of a crossover-tolerant direct methanol fuel cell with a platinum group metal-free cathode", *Electrochimica Acta*, 416 (2022) 140262.