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**University at Buffalo**  
*The State University of New York*

# ElectroCat: Durable Mn-Based PGM-Free Catalysts for Polymer Electrolyte Membrane Fuel Cells

**PI : Hui Xu (Giner, Inc.)**

2021 DOE H<sub>2</sub> and Fuel Cell Annual Merit Review Meeting

June 7-11, 2021

Project # FC170

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



## Timeline

- Project Start Date: 10/1/2017
- Project End Date: 8/30/2021

## Budget

- Total \$2.49 million
  - DOE share \$1.99 million cost sharing \$500K
  - Spent \$ 2.21 million (by April 23, 2021)

## Subcontractors

- U. Buffalo: Gang Wu
- U. Pitts.: Guofeng Wang
- GM: Anusorn Kongkanand

## Barriers Addressed

- Durability (catalyst; MEA)
- Cost (catalyst; MEA)

## Technical Targets

- Design Mn-based PGM-free catalysts to meet DOE catalyst activity  $>0.044 \text{ A cm}^{-2}$  @  $0.9 V_{\text{IR-free}}$  in a MEA test
- The catalyst extends the durability by 50% (compared to state-of-the-art PGM-free catalyst)
- The catalyst mitigates membrane degradation caused by Fe-based catalysts by 50%



# Milestones and Progress



University of Pittsburgh

## Milestone Summary

Recipient Name:

Giner, Inc.

Project Title:

Durable Mn-based PGM-Free Catalysts for Polymer Electrolyte Membrane Fuel Cells

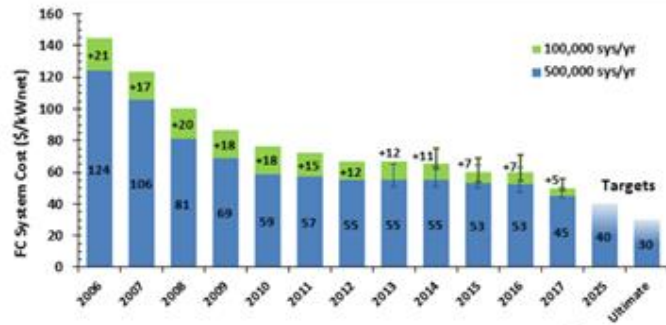
Task	Task/subtask Titles	Milestone	Number	Milestone Description	Milestone Verification Process	Month	Quarter	%Complete	Progress Notes
1	Computation of Mn-based catalysts and cathodes	Milestone	M1-4	Verify/refine the predicted active sites with highest stability and 4e <sup>-</sup> ORR	At UP, provide detailed comparison between predictions and RDE results	M27	Q9	100%	Completed
1	Computation of Mn-based catalysts and cathodes	Milestone	M1-5	Modeling mass transport process in the MEA with high-power	At UP, provide detailed predictions and analysis results	M30	Q10	100%	Completed
1	Computation of Mn-based catalysts and cathodes	Milestone	M1-6	Identify 2 key descriptors for modeling mass transport in the MEA	At UP, provide detailed comparison between predictions and MEA performance results	M33	Q11	100%	Completed
2	Synthesize and screen Highly Active and Stable Mn Catalysts	Milestone	M2-5	Achieve stability $\Delta E_{1/2} < 10$ mV after 30,000 potential cycling	At SUNY, potential cycling (0.6 to 1.0 V, 50 mV/s) in O <sub>2</sub> saturated 0.5 M H <sub>2</sub> SO <sub>4</sub>	M21	Q7	100%	Complete
2	Synthesize and screen Highly Active and Stable Mn Catalysts	Milestone	M2-6	Achieve $E_{1/2} \geq 0.85$ V; generate 0.75 mA/cm <sup>2</sup> at 0.90 V;	At SUNY, using RDE steady-state ORR polarization	M30	Q10	100%	Complete
3	Fabricate MEAs and Evaluate Initial Performance	Go/No-Go decision	M3-4	For a PGM-free & Fe-free catalyst, demonstrate $\geq 20$ mA/cm <sup>2</sup> at 0.90 V (iR-corrected) in an H <sub>2</sub> -O <sub>2</sub> ; maintain partial pressure of O <sub>2</sub> at 1.0 bar (cell temperature 80 ° C).	At Giner and SUNY, using DOE PGM-free catalyst testing protocols for MEAs	M24	Q8	100%	Completed
3	Fabricate MEAs and Evaluate Initial Performance	Milestone	M3-5	1.0 A/cm <sup>2</sup> at 0.50 V	At Giner, Using DOE PGM-free catalyst testing metrics	M33	Q11	100%	Completed
3	Fabricate MEAs and Evaluate Initial Performance	Go/No-Go decision	M3-6	For a PGM-free catalyst demonstrate $\geq 30$ mA/cm <sup>2</sup> at 0.90 V (iR-corrected) in an H <sub>2</sub> -O <sub>2</sub> fuel cell and 150 mA/cm <sup>2</sup> at 0.80 V in an H <sub>2</sub> -air fuel cell (measured); maintain partial pressure of O <sub>2</sub> + N <sub>2</sub> at 1.0 bar (cell T= 80 ° C).	At Giner and GM using DOE PGM-free catalyst testing protocols for MEAs	M36	Q12	80%	In Progress
4	Evaluate MEA Durability Using Different Approaches	Milestone	M4-1	MEA durability: $\Delta V < 30$ mV at 0.044 A/cm <sup>2</sup> ; activity loss < 100 mA/cm <sup>2</sup> at 0.6 V	At Giner and GM, using DOE MEA testing protocols after 30K voltage cycles (0.6 to 1.0 V) under H <sub>2</sub> -N <sub>2</sub> condition.	M36	Q12	80%	In Progress
5	Perform Catalyst Cost Analysis and System Economics	Milestone	M5-1	Deliver a 5-page cost analysis for the Mn-based PGM-free catalysts and cathodes.	At Giner and GM, using small-scale, short production	M36	Q12	30%	In Progress



# Project Goals



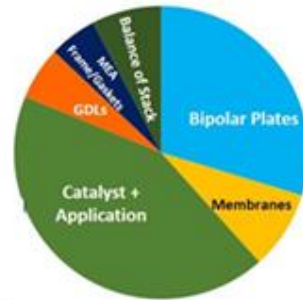
- ❑ Develop Mn-based catalysts that achieve sufficient activity ( $E_{1/2} > 0.85$ ) and stability in acidic media- Potential loss of  $E_{1/2} < 10$  mV after 30k potential (0.6 to 1.0 V) cycling tests in rotating disk electrode (RDE).
- ❑ Demonstrate fuel cell membrane electrode assemblies (MEAs) with a  $H_2/O_2$  mass activity of  $> 30 \text{ mA cm}^{-2}$  at  $0.9 \text{ V}_{\text{IR-free}}$ , and  $H_2/\text{air}$  performance  $> 350 \text{ cm}^{-2}$  @  $0.7 \text{ V}$  and  $> 1000 \text{ mA cm}^{-2}$  @  $0.5 \text{ V}$ , following DOE testing metrics.
- ❑ Limit reduction of catalyst activity in fuel cell MEAs ( $< 30$  mV after 30,000 potential cycles, 0.6-1.0 V in  $H_2/N_2$ ) following DOE's catalyst support durability testing protocols or any other protocols suggested from the *ElectroCat* Consortium.
- ❑ Develop a fundamental understanding of the structure-property-performance relationship of the novel Mn-N-C platinum group metal -free (PGM-free) catalysts. The relevant computational data, measurement data, and publications will be deposited into the database of *ElectroCat*.



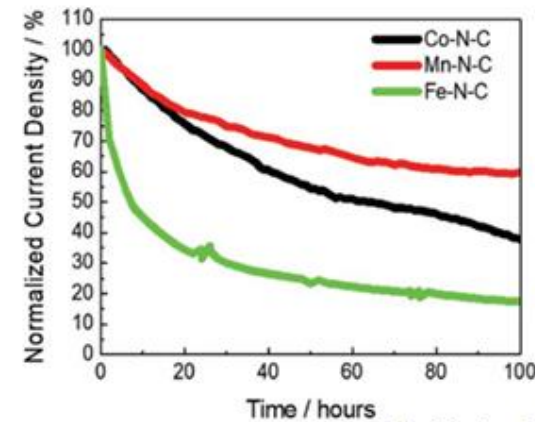
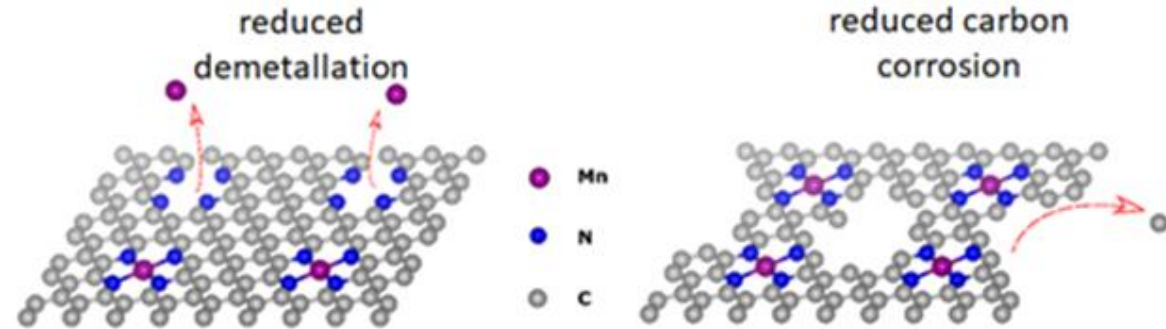
(From DOE FCTO website)

Characteristic	Units	2015 Status	2020 Targets
Platinum group metal total content (both electrodes) <sup>a</sup>	g / kW (rated, gross) @ 150 kPa (abs)	0.16 <sup>b</sup>	0.125
Platinum group metal (pgm) total loading (both electrodes) <sup>c</sup>	mg PGM / cm <sup>2</sup> electrode area	0.13 <sup>b</sup>	0.125
Mass activity <sup>d</sup>	A / mg PGM @ 900 mV <sub>RHE</sub>	>0.5 <sup>b</sup>	0.44
Loss in initial catalytic activity <sup>e</sup>	% mass activity loss	66 <sup>b</sup>	<40
Loss in performance at 0.8 A/cm <sup>2</sup> <sup>f</sup>	mV	13 <sup>b</sup>	<30
Electrocatalyst support stability <sup>g</sup>	% mass activity loss	41 <sup>b</sup>	<40
Loss in performance at 1.5 A/cm <sup>2</sup> <sup>h</sup>	mV	65 <sup>b</sup>	<30
PGM-free catalyst activity	A / cm <sup>2</sup> @ 0.9 V <sub>RHE</sub>	0.016 <sup>b</sup>	>0.04 <sup>f</sup>

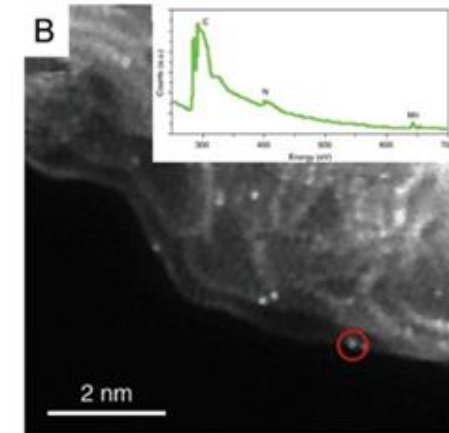
PEMFC Stack Cost Breakdown\*



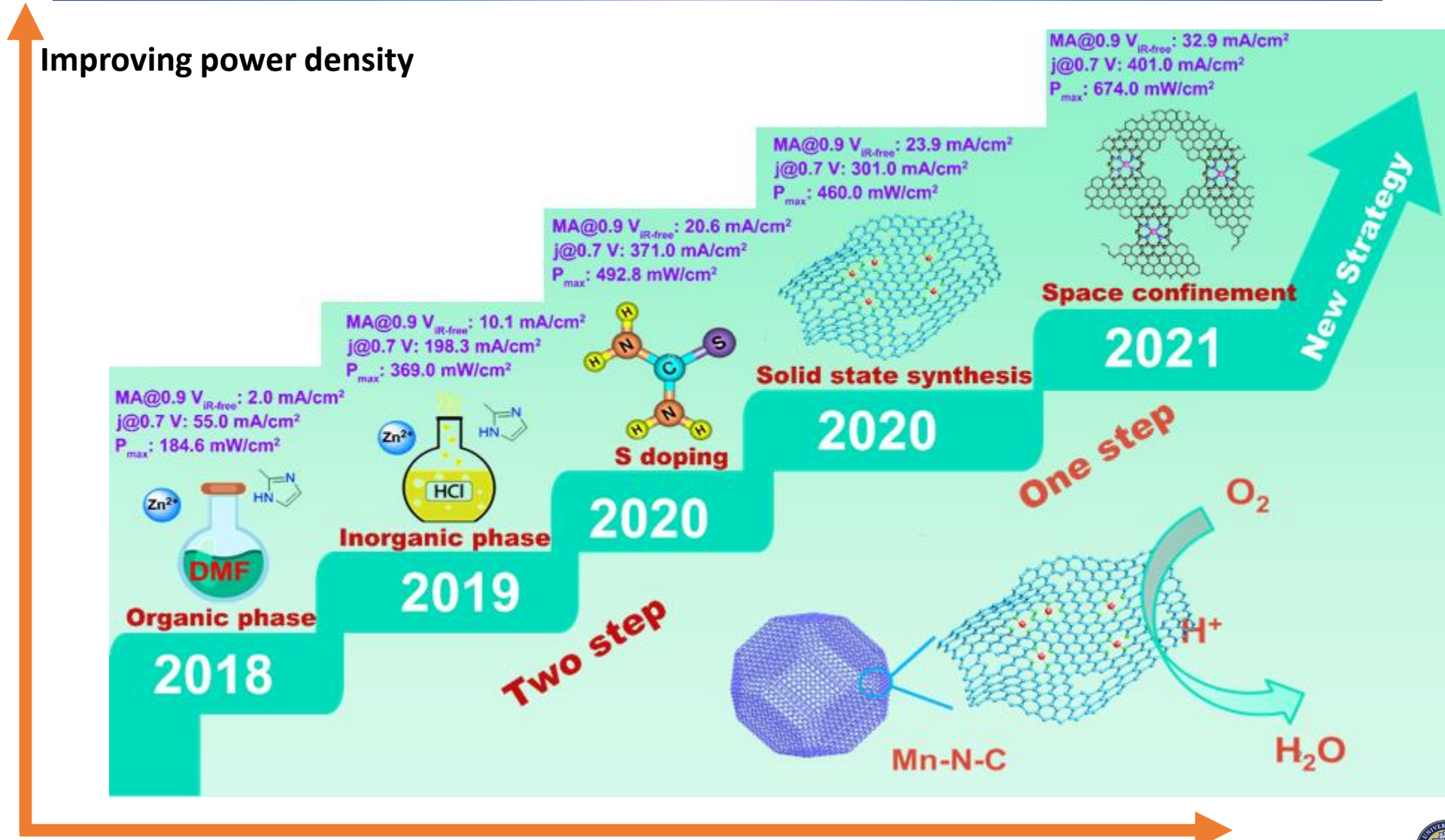
Ballard FCgen®-1040 prototype fuel cell stack, with Non Precious Metal Catalysts



Adv. Mater. 2020, 1908232

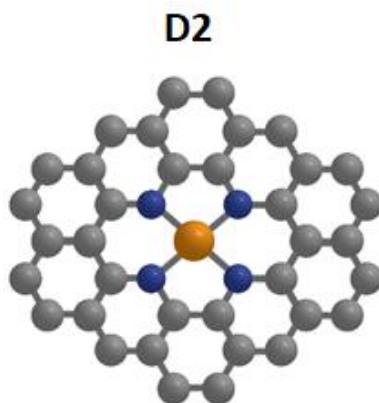
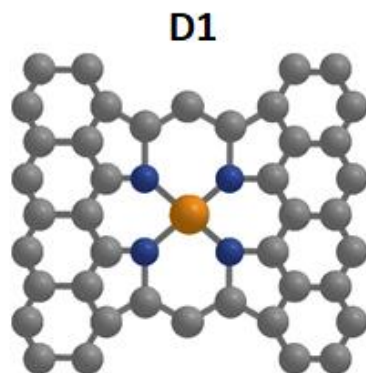


- ❑ Catalyst cost still a major contributor to high fuel cell price
- ❑ Pt price volatility and supply shortage limit mass production of fuel cells
- ❑ Development of PGM-free Mn catalyst can likely resolve the durability issue of other PGM-free catalysts

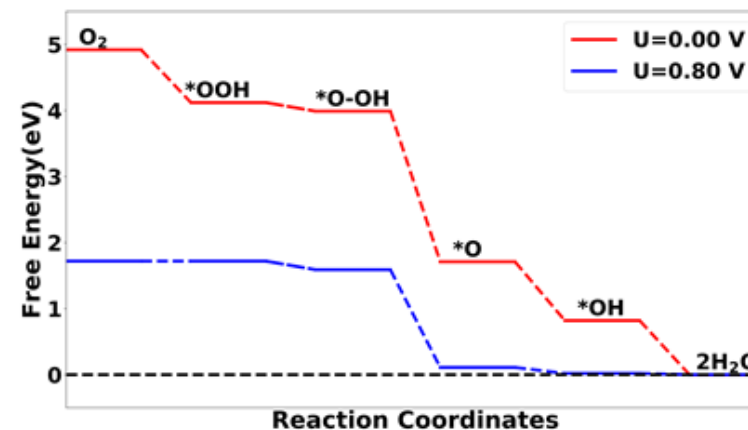


## Calculated free energy evolution for ORR

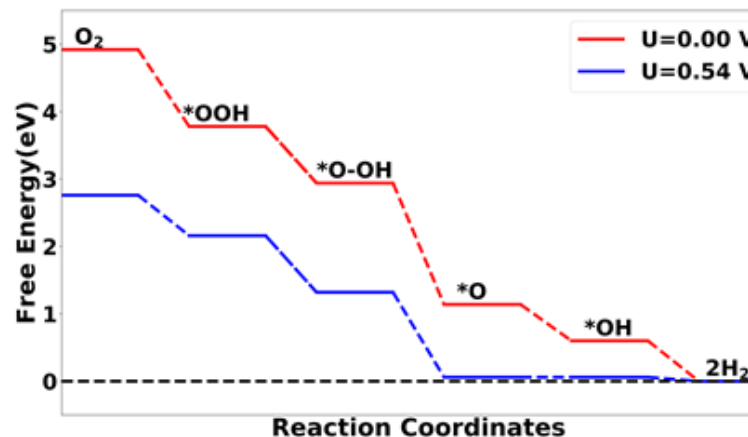
- Fe Mossbauer spectra on Fe-N-C catalyst indicates that  $\text{FeN}_4\text{C}_{12}$  (D1) and  $\text{FeN}_4\text{C}_{10}$  (D2) sites co-exist in this type of PGM-free catalyst. [from Li et al, Nature Catalysis 4 (2021) 10-1]



Note: The limiting potential is the predicted highest electrode potential for four-electron ORR to occur on the active sites. The higher the limiting potential, the higher the ORR activity.

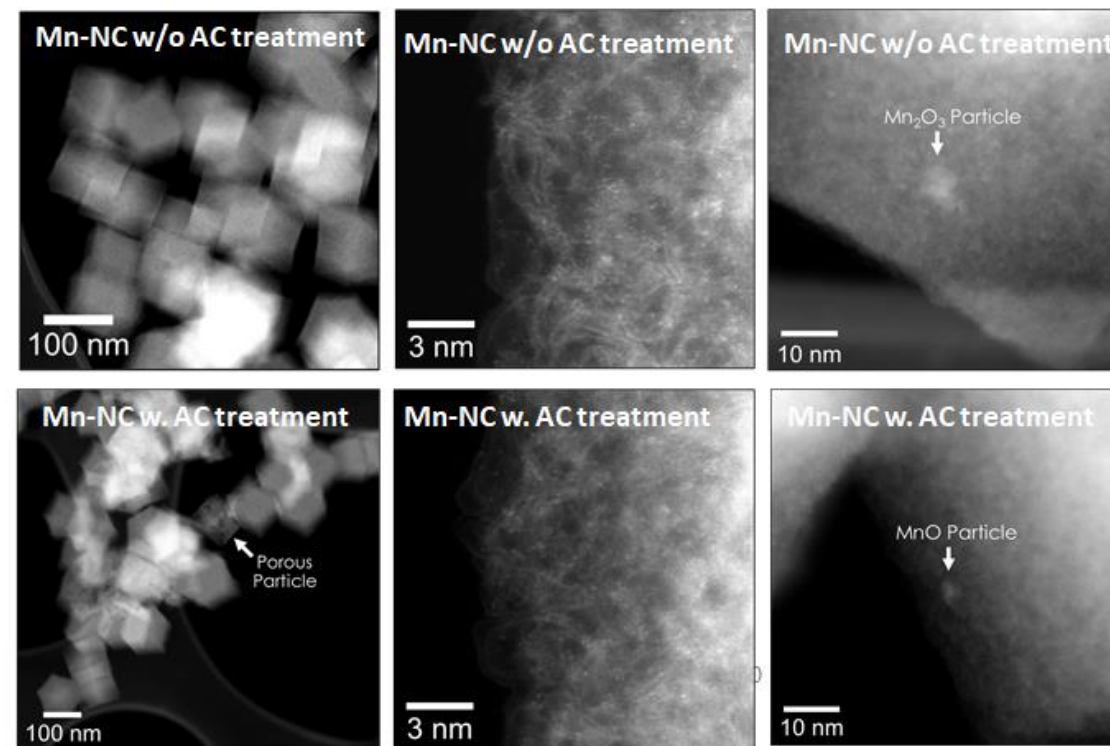
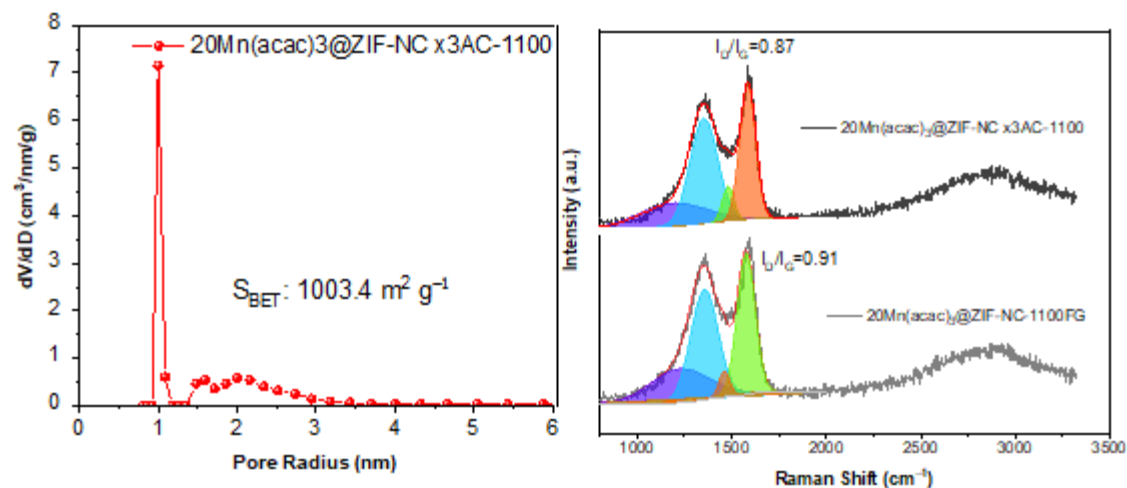
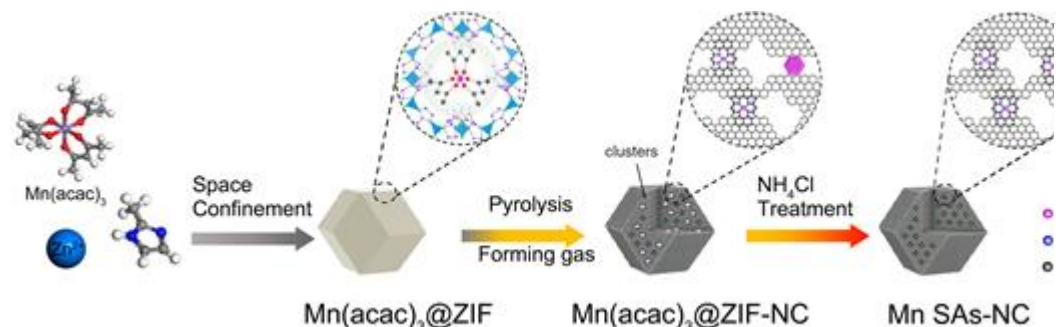


**D1 site ( $\text{MnN}_4\text{C}_{12}$ ) is predicted to have a limiting potential of **0.80 V****



**D2 site ( $\text{MnN}_4\text{C}_{10}$ ) is predicted to have a limiting potential of **0.54 V****

- Limiting potential used as an indicator to predict the activity of the two different  $\text{MnN}_4$  sites.
- DFT Prediction: Both  $\text{MnN}_4\text{C}_{12}$  (D1) and  $\text{MnN}_4\text{C}_{10}$  (D2) sites exhibit high ORR activity, whereas D1 is more active for ORR than D2 by having a higher limiting potential.

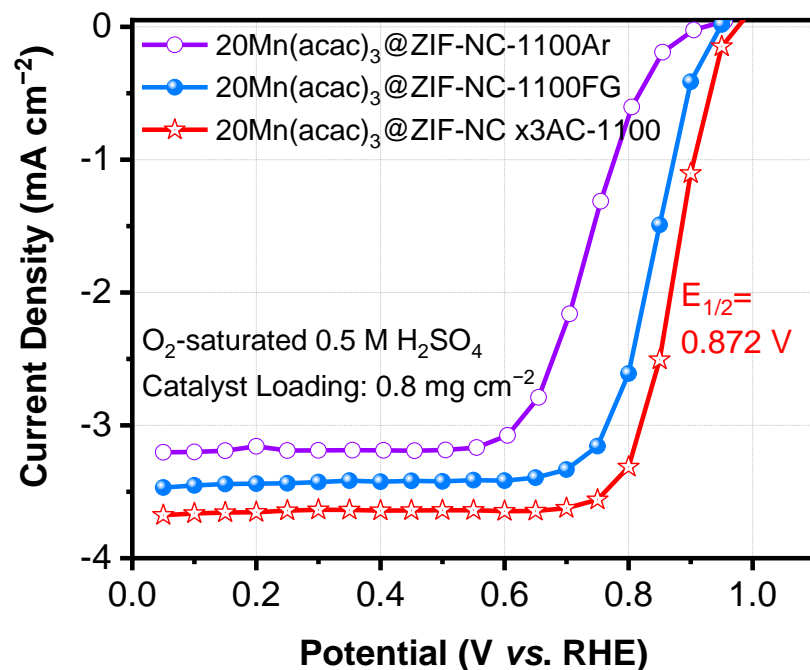


- ❑ A rational control of pyrolysis facilitates the construction of  $\text{MnN}_x$
- ❑ Carbon particles in catalysts present isolated morphology with a diameter around 100 nm;
- ❑ Atomically dispersed single Mn sites are uniformly dispersed in the carbon particle;

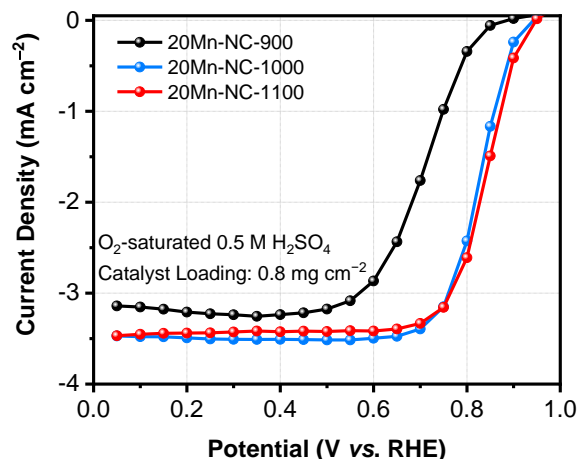


- Pyrolysis atmosphere, Mn content, heating temperatures, and ramping rates are crucial for achieving the optimal ORR activity;

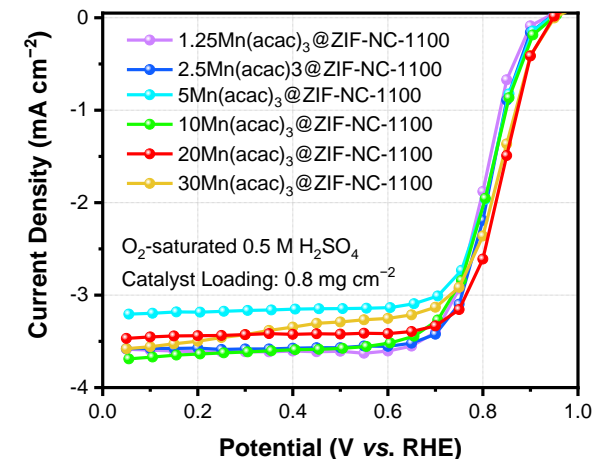
## Pyrolysis atmosphere



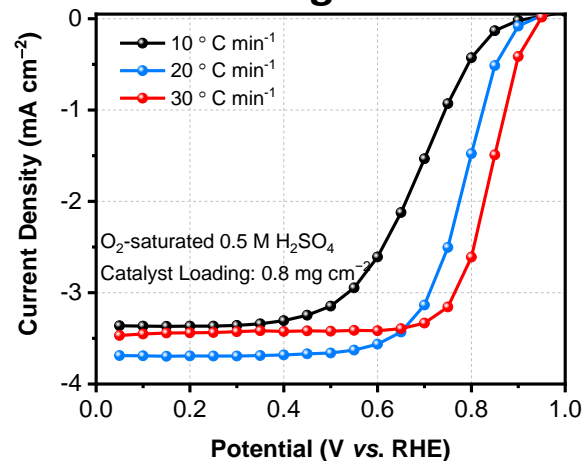
## Temperatures



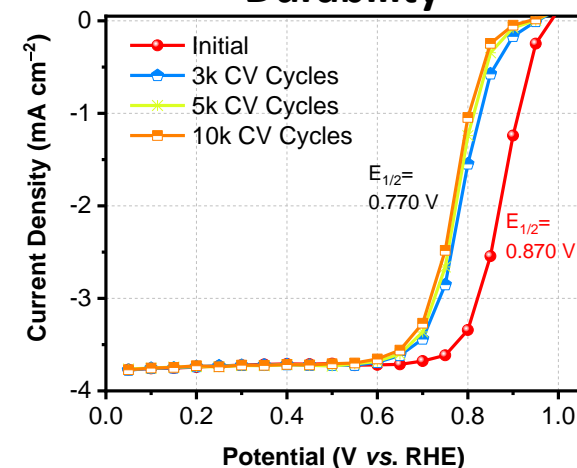
## Mn Content



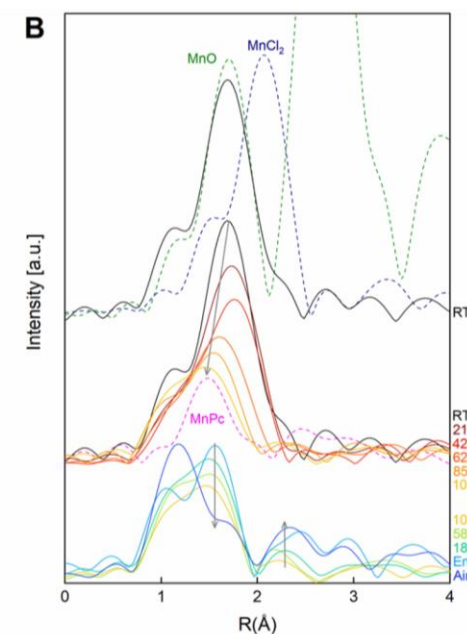
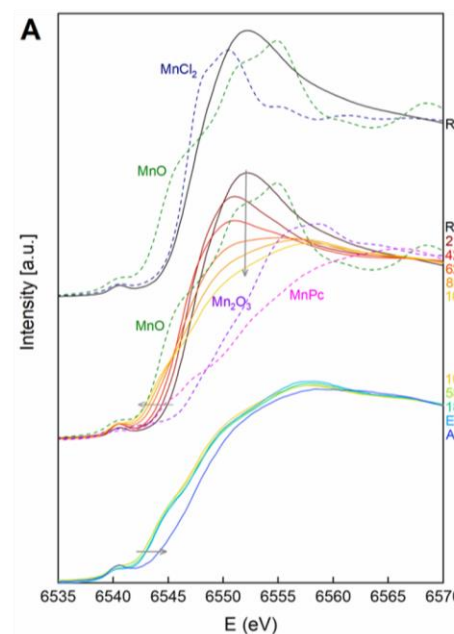
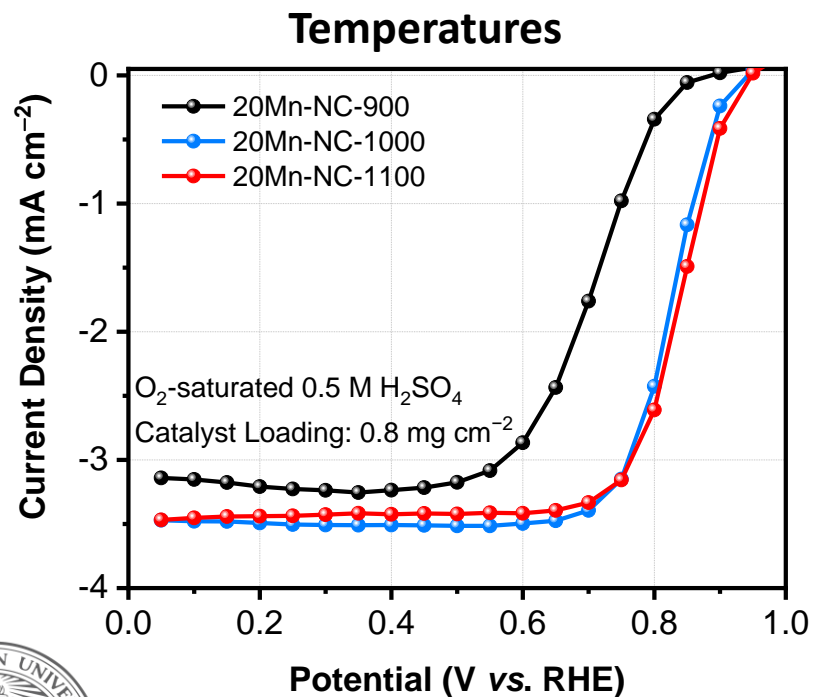
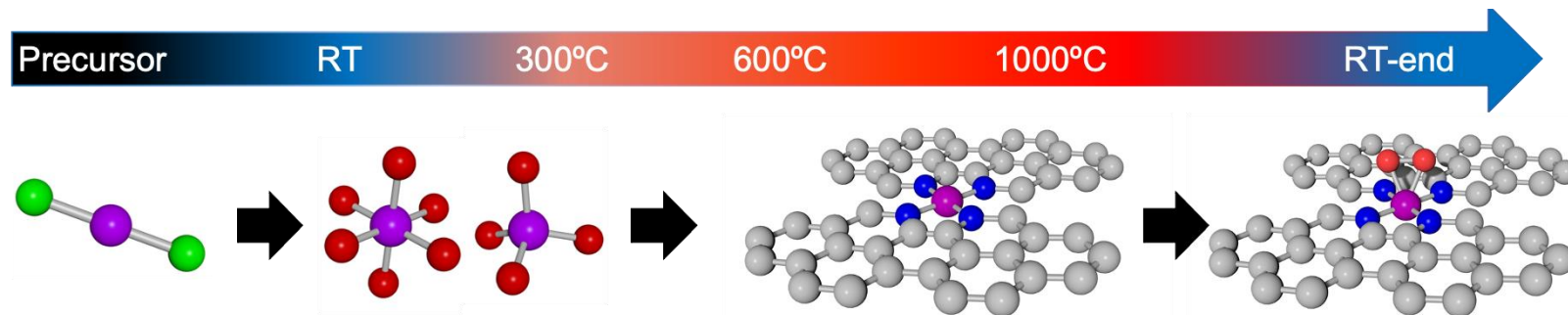
## Heating rates



## Durability

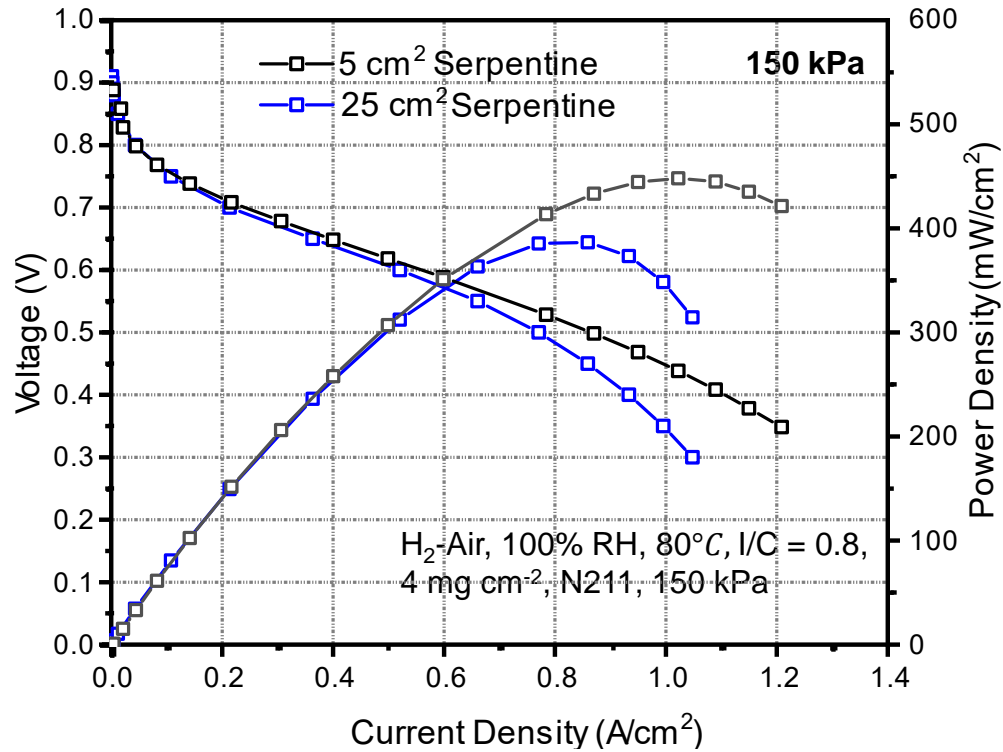


- Heat treatment under Forming Gas (FG) is crucial for active site formation and increasing ORR activity
- Second heat treatment step under Ammonia Chloride (AC) further improves half wave ( $E_{1/2}$ ) potentials
- The new Mn-N-C catalyst achieved recorded ORR activity in acids ( $E_{1/2} = 0.872 \text{ V}$ ;  $1.25 \text{ mA cm}^{-2}$  at  $0.9 \text{ V}$ )

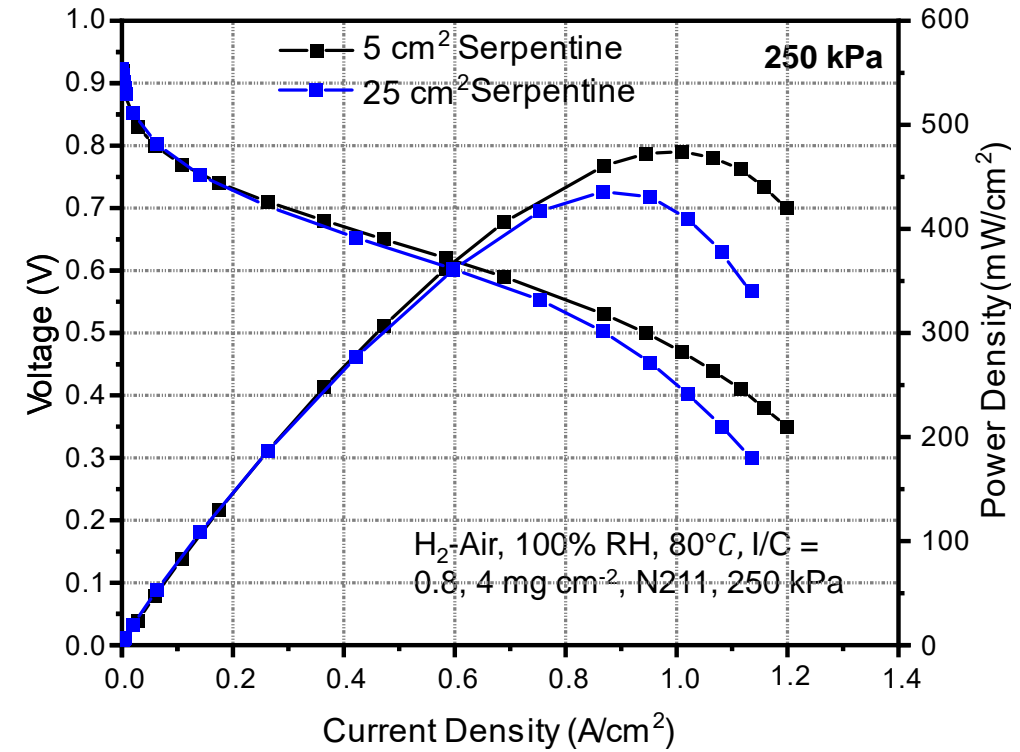


- ❑ In-situ high-temperature XAS measurements revealed the mechanism of MnN<sub>4</sub> site formation during the pyrolysis
- ❑ Due to the high oxophilicity of Mn, higher temperatures are required to push the reaction towards the active MnN<sub>4</sub> structure

# Accomplishment 3: Improving MEA Performance



150 kPa		
Flow Field	Current Density at 0.7 V	Maximum Power Density
5 cm <sup>2</sup> Serpentine	240 mA cm <sup>-2</sup>	450 mW cm <sup>-2</sup>
25 cm <sup>2</sup>	213 mA cm <sup>-2</sup>	386 mW cm <sup>-2</sup>

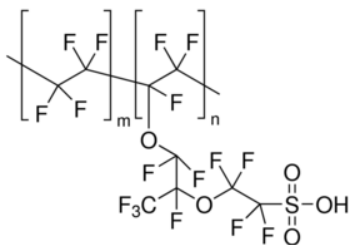


250 kPa		
Flow Field	Current Density at 0.7 V	Maximum Power Density
5 cm <sup>2</sup> Serpentine	300 mA cm <sup>-2</sup>	474 mW cm <sup>-2</sup>
25 cm <sup>2</sup>	264 mA cm <sup>-2</sup>	434 mW cm <sup>-2</sup>

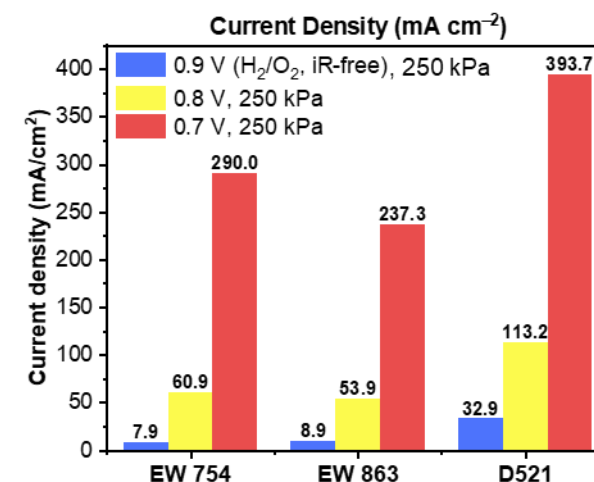
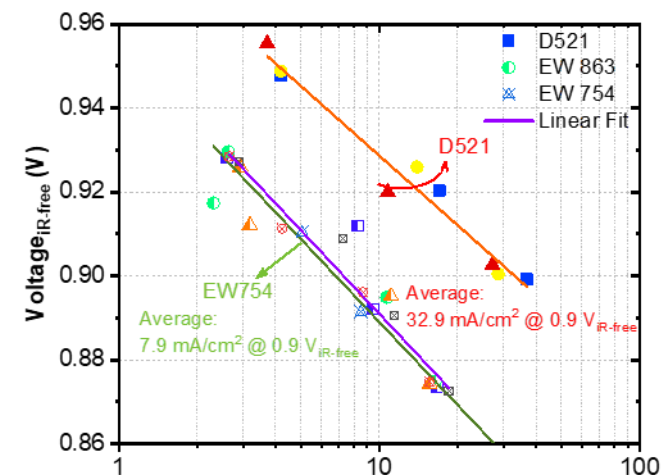
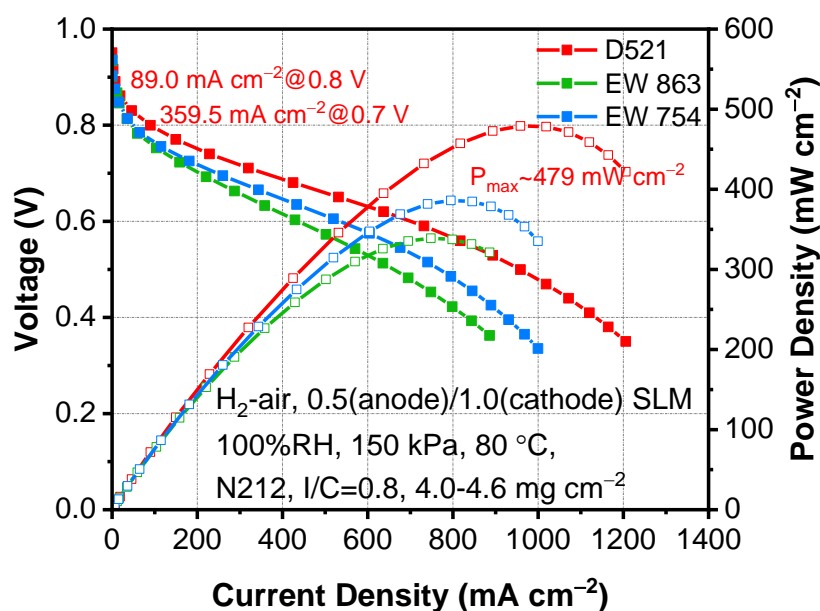
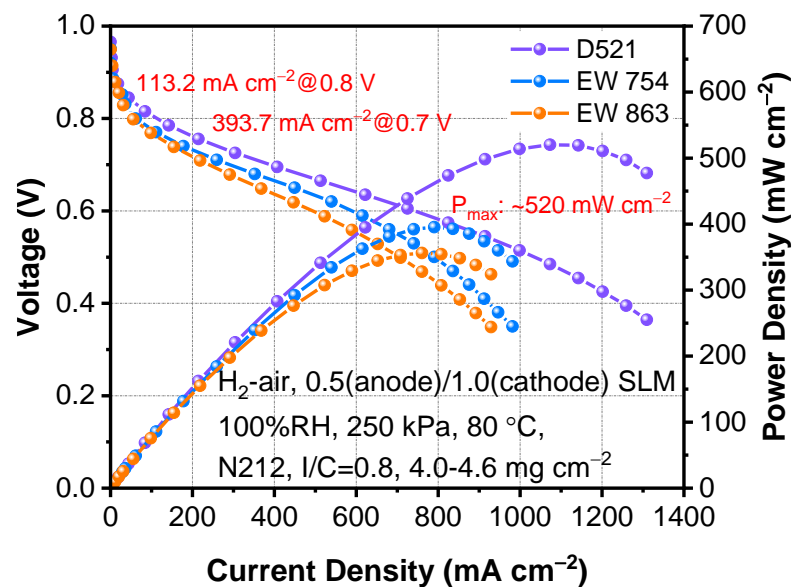
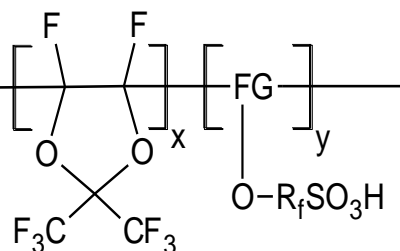
- ❑ 5cm<sup>2</sup> and 25 cm<sup>2</sup> MEAs were fabricated via the blade coating GDE approach
- ❑ Successfully scaled up to 25 cm<sup>2</sup> MEA without compromising performance, especially in kinetic voltage range.
- ❑ Difference arise in the high current density region (> 1 A cm<sup>-2</sup>) most likely due to water flooding

# MEA Performance (GDE): Effect of Ionomer Chemistry and EW

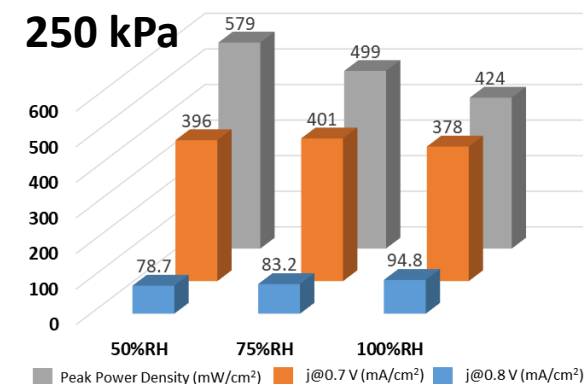
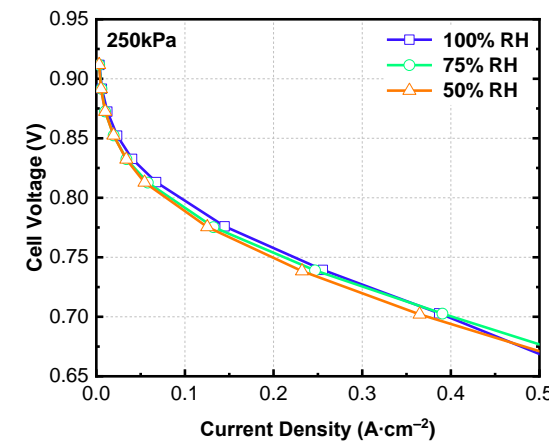
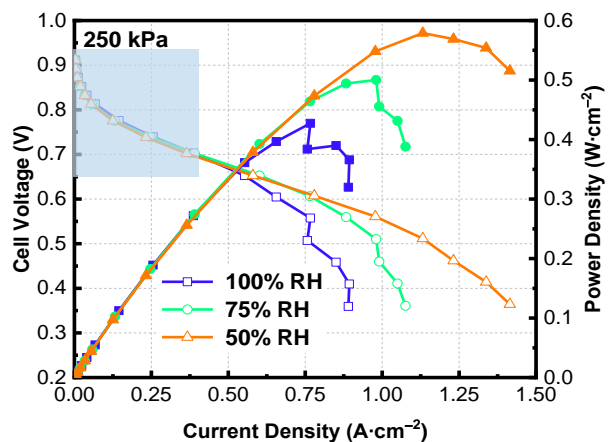
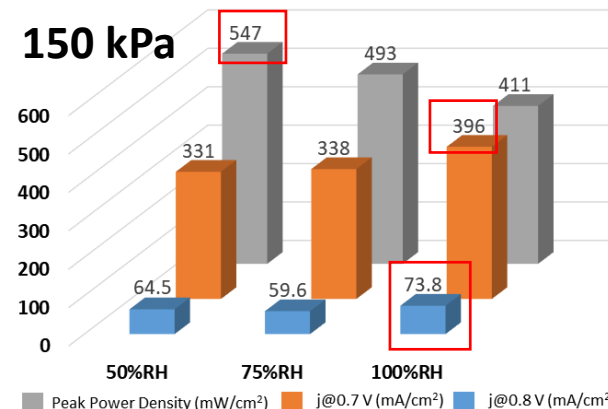
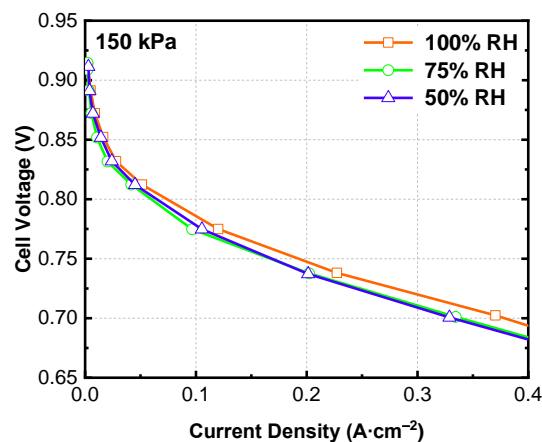
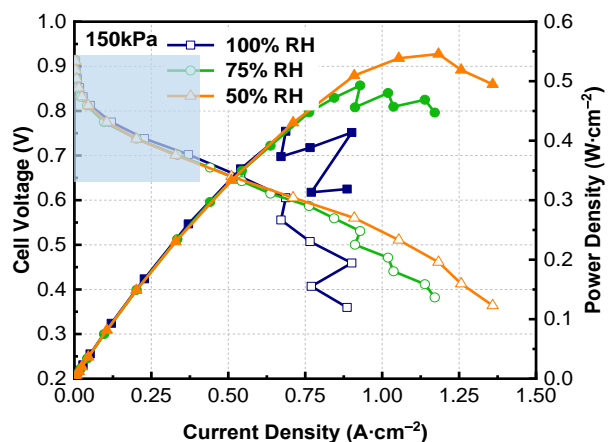
- D521 Nafion™ PFSA ionomer dispersion: 1100 EW



- High O<sub>2</sub> permeability ionomer (HOPI): 863 EW and 754 EW.



- ❑ D521 with higher hydrophobicity and equivalent weight (EW) is effective in achieving maximum performance
- ❑ The MEA yielded a current density @ 0.9V<sub>iR-free</sub> of 32.9 mA cm<sup>-2</sup> (H<sub>2</sub>/O<sub>2</sub>, 250 kPa) and a maximum power density of 520 mW cm<sup>-2</sup> (H<sub>2</sub>/air, 250 kPa) - **exceeded Year 3 key milestone**
- ❑ High O<sub>2</sub> permeability ionomer (HOPI) did not benefit PGM-free fuel cell electrodes

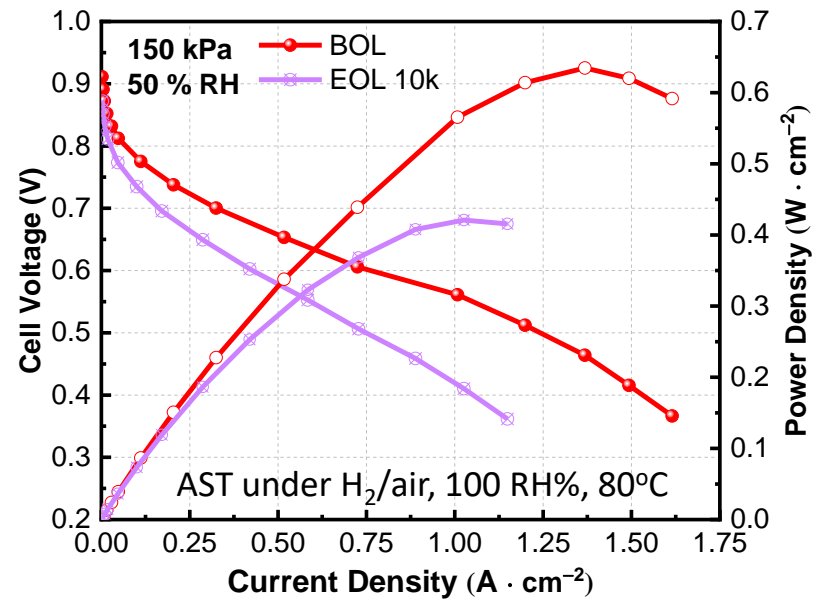


Test conditions: 80 °C; 0.92 V to 0.82 V in 20 mV steps; 0.82 V to 0.70 V in 40 mV steps; 45 s/step; 0.70 V to 0.35 V in 50 mV steps; 45 s/step.

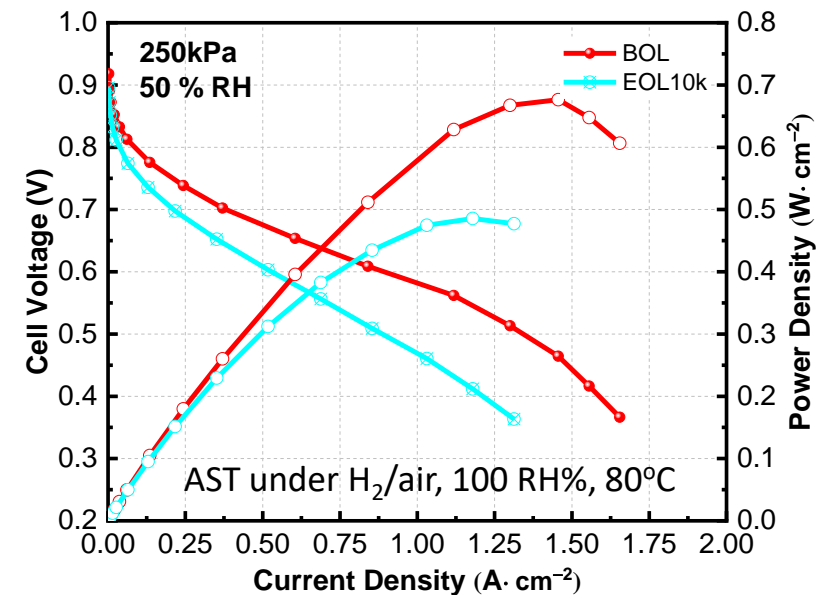
- ❑ The single cell performance was further improved by using a **thinner Gore membrane** and advanced sonication spray coating;
- ❑ The MEA at 100% RH generated 74 mA cm<sup>-2</sup> at 0.8 V and ~400 mA cm<sup>-2</sup> at 0.7 V, at 150 kPa, **comparable to most of Fe-N-C catalysts.**
- ❑ Optimal 50% RH achieved a record peak power density ( $P_{max}$ ) of ~550 mW cm<sup>-2</sup> at 150 kPa.

**Durability voltage cycling conditions:**  
hold OCV for square-wave cycle:  
steps between 0.60 V (3 s) and OCV  
(3 s); rise time of 0.5 s. During the  
cycling: anode:  $H_2$ , 200 sccm, 100  
 $kPa_{abs}$ , back pressure; Cathode: **Air**,  
400 sccm, 1.0 bar pressure

**MEA testing conditions:** Anode:  $0.1$   
 $mg_{Pt} cm^{-2}$  Pt/C  $H_2$ , 700 sccm; cathode:  
 $4.7 mg cm^{-2}$ , Mn-N-C. 1700 sccm, air;  
membrane: Gore; cell: differential,  $5$   
 $cm^2$  Test conditions:  $80\text{ }^\circ C$ ;  $0.92\text{ V}$  to  
 $0.82\text{ V}$  in  $20\text{ mV}$  steps;  $0.82\text{ V}$  to  $0.70$   
 $V$  in  $40\text{ mV}$  steps;  $45\text{ s/step}$ ;  $0.70\text{ V}$  to  
 $0.35\text{ V}$  in  $50\text{ mV}$  steps;  $45\text{ s/step}$ .

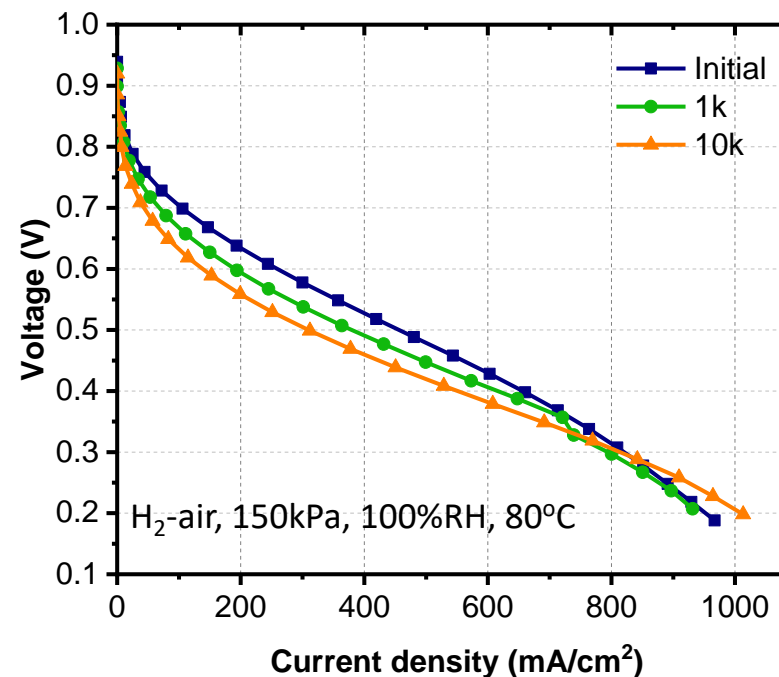
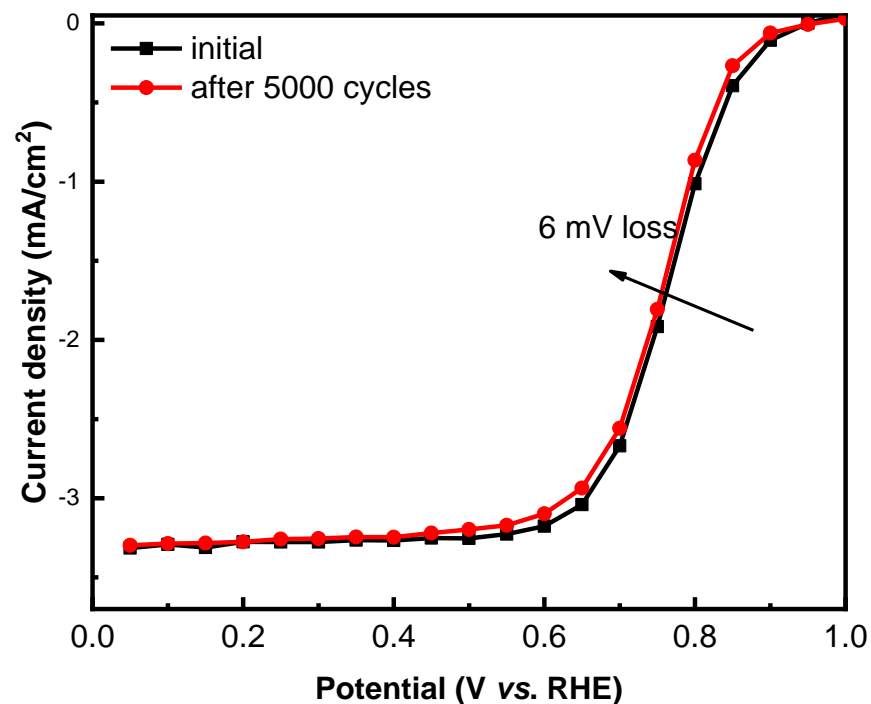


50 % RH 150 $kPa_{abs}$			
	Current Density @ 0.8V ( $mA cm^{-2}$ )	Current Density @ 0.7V ( $mA cm^{-2}$ )	Peak Power Density ( $mW cm^{-2}$ )
BOL	69.23	326	634
EOL	26.40	163	422

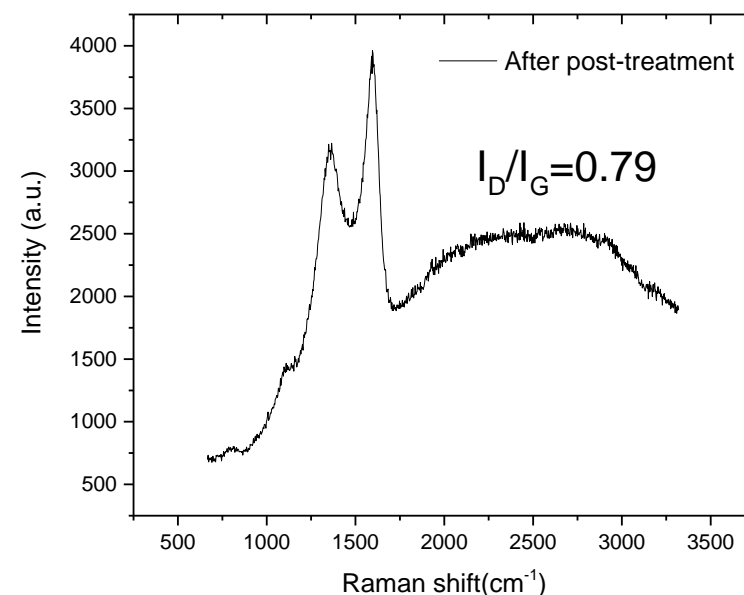
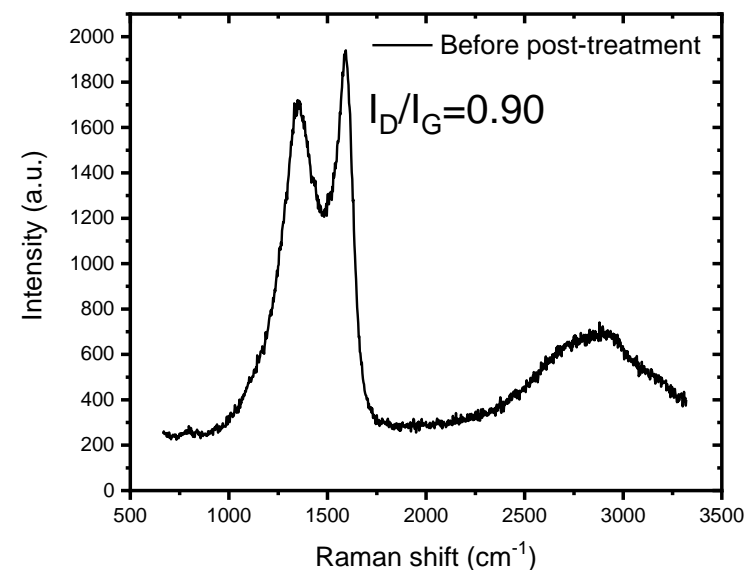
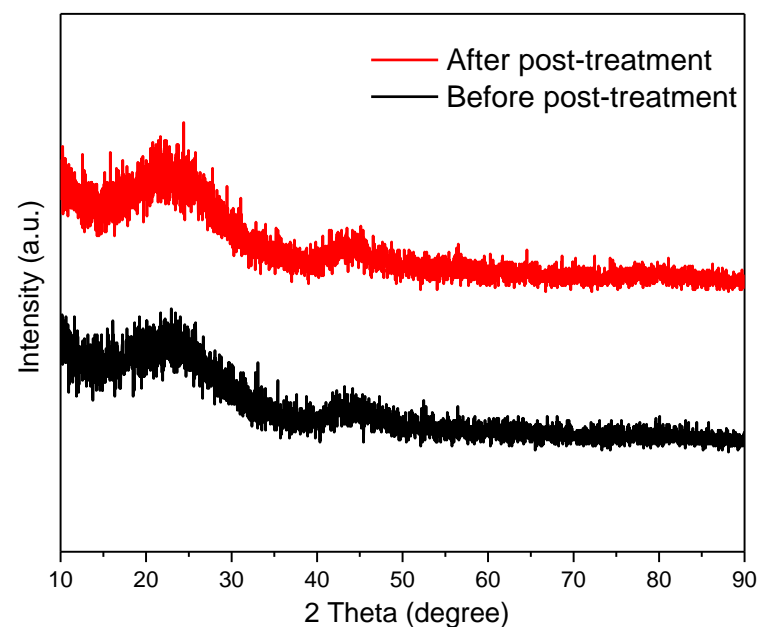
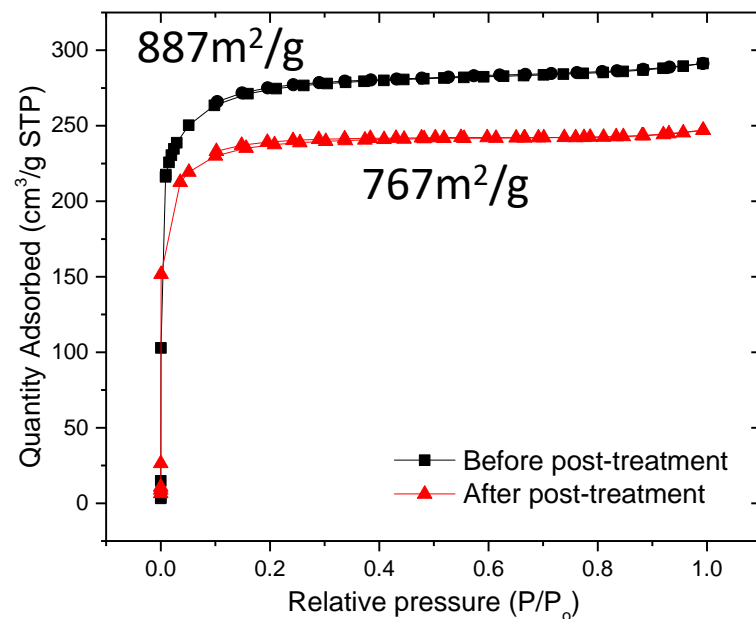


50 % RH 250 $kPa_{abs}$			
	Current Density @ 0.8V ( $mA cm^{-2}$ )	Current Density @ 0.7V ( $mA cm^{-2}$ )	Peak Power Density ( $mW cm^{-2}$ )
BOL	86.46	381	674
EOL	38.28	211	486

- An ever-recorded power density ( $634\text{ mW cm}^{-2}$  at  $150\text{ kPa}$ ) was obtained after optimization of operation parameters (50% RH, Differential  $5\text{ cm}^2$  hardware);
- The MEA still suffered initial performance degradation following the trend of Fe-N-C catalysts.
- Engineering carbon structures to enhance Mn-N-C catalyst stability is ongoing (*see preliminary results the next slide*).

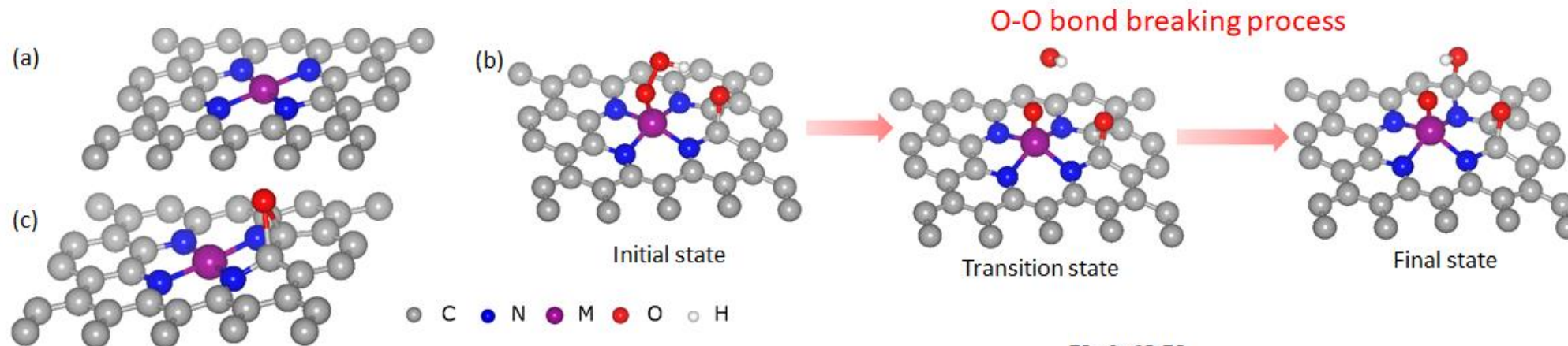


- ❑ Post-treatment with small hydrocarbon compounds (e.g., **benzimidazole**) after catalyst synthesis led to durable RDE activity and MEA performance, but with lower initial performance
  - Tradeoff between performance and durability
- ❑ Further tuning carbon structures and local environment are demanded to simultaneously achieve the optimal activity and stability.



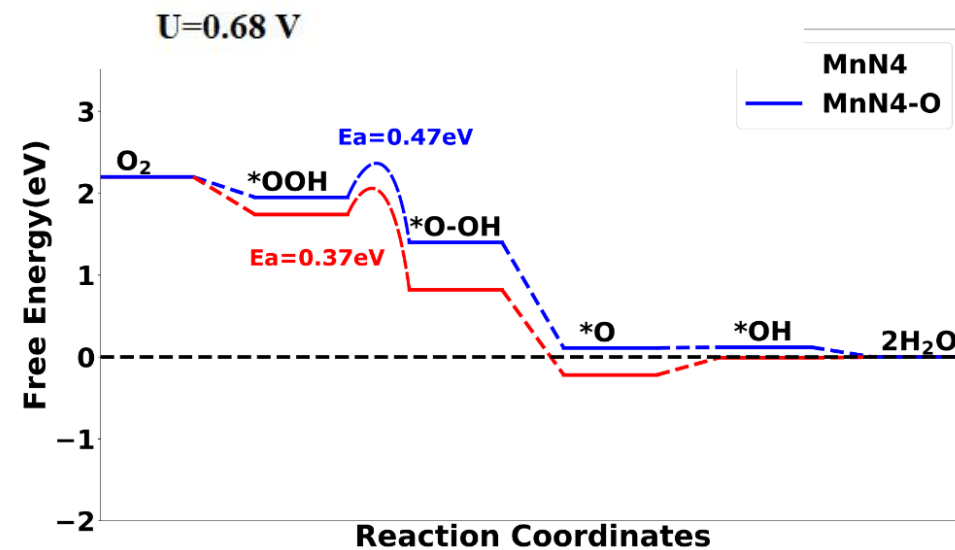
- ❑ Catalyst surface areas are slightly decreased after the post-treatment using benzimidazole;
- ❑ XRD show insignificant change in crystalline structure of catalysts.
- ❑ Raman spectra indicate a major difference in the dominant G peak and lower intensity of D peak, suggesting that the carbon structure becomes more graphitized after the post treatment.



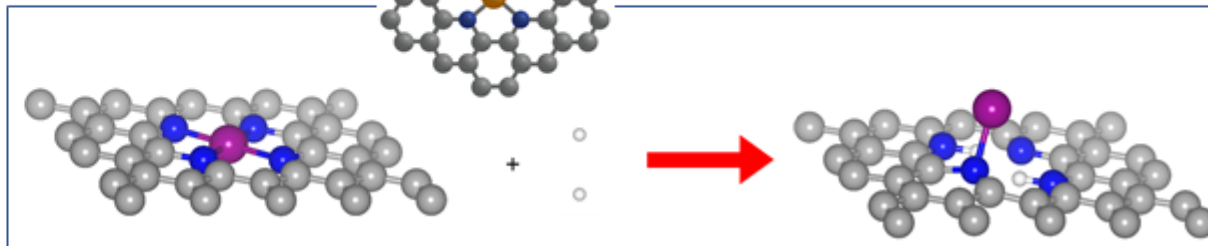
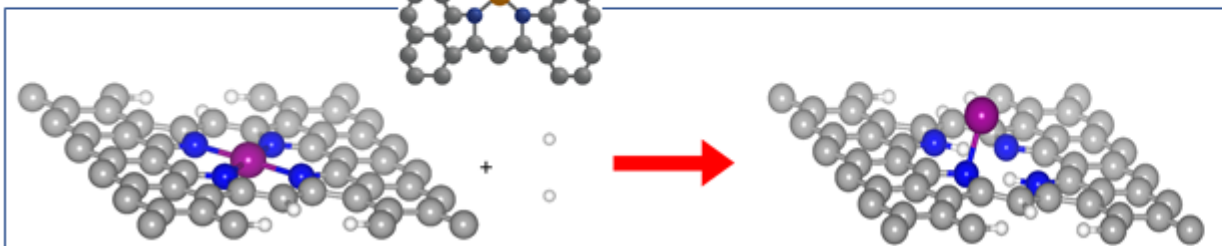


Activation energy (eV)	Non oxidized	oxidized
D1 site ( $\text{MnN}_4\text{C}_{12}$ )	0.49	0.84
<b>D2 site (<math>\text{MnN}_4\text{C}_{10}</math>)</b>	<b>0.37</b>	<b>0.47</b>
D1 site ( $\text{FeN}_4\text{C}_{12}$ )	0.72	0.86
<b>D2 site (<math>\text{FeN}_4\text{C}_{10}</math>)</b>	<b>0.59</b>	<b>1.05</b>

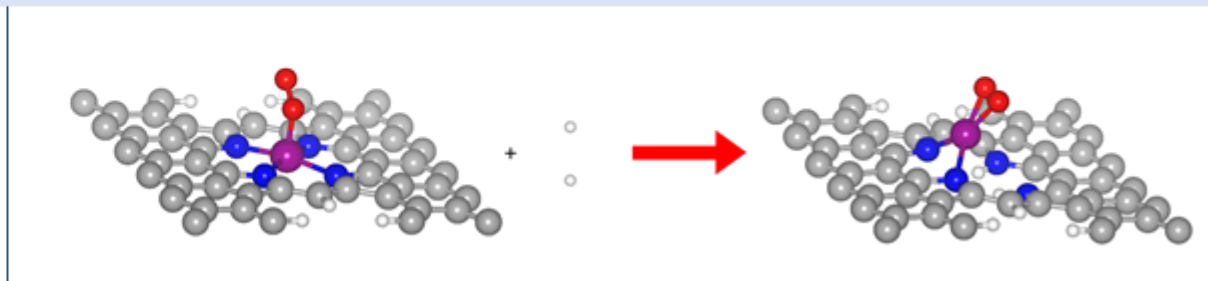
increase



- ❑ Carbon oxidation degrades ORR activity of the catalysts by increasing the activation energy for O-O bond breaking.
- ❑  **$\text{MnN}_4$  sites are predicted to have better resistance to carbon oxidation degradation than  $\text{FeN}_4$  sites.**



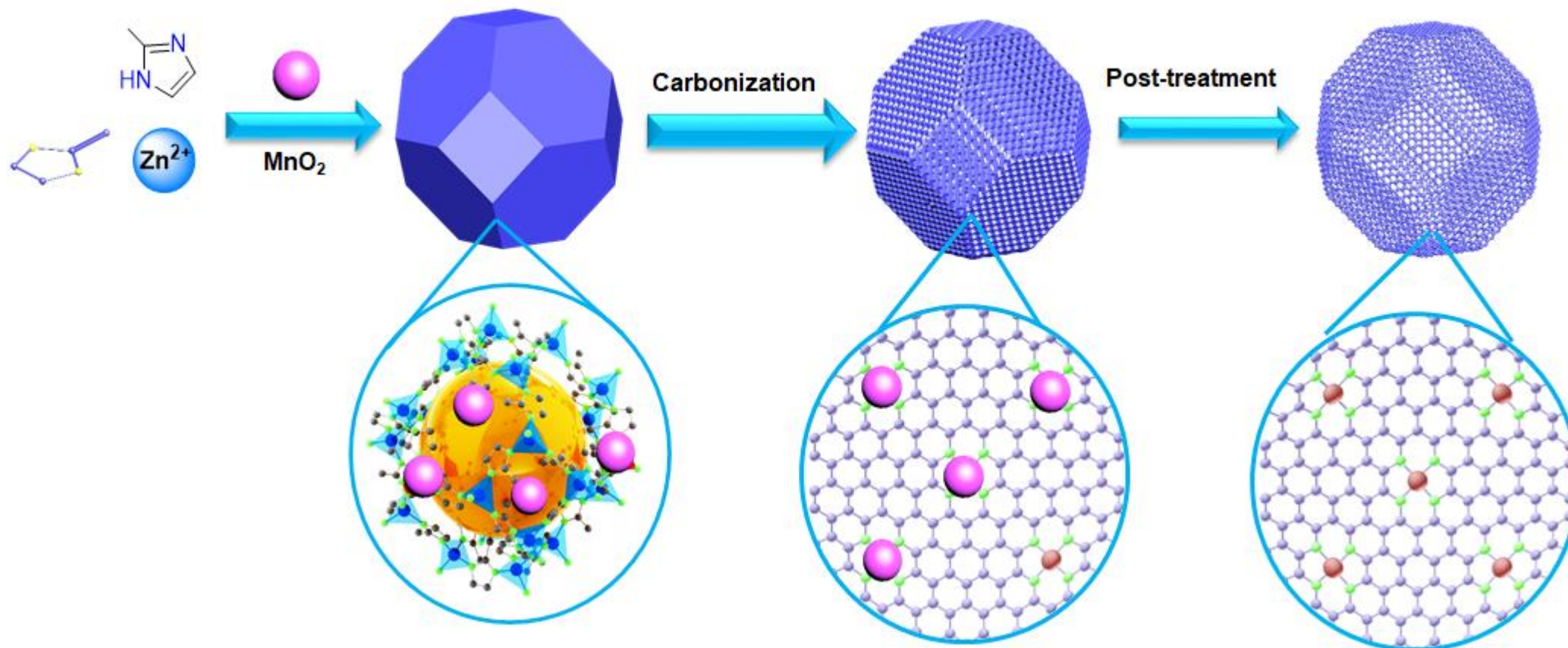
- In inert environment, both D1 ( $MnN_4C_{12}$ ) and D2 ( $MnN_4C_{10}$ ) sites are predicted to be thermodynamically stable. (M= Mn, Fe)



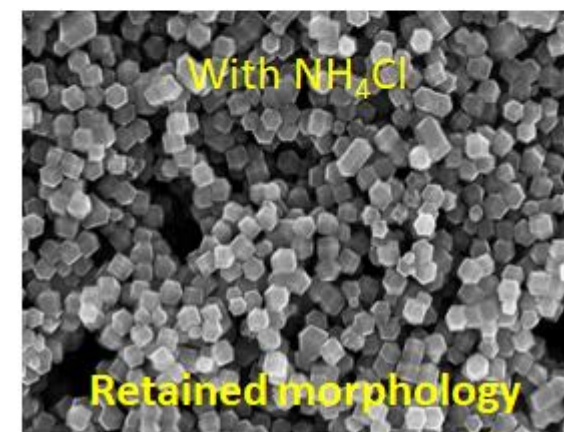
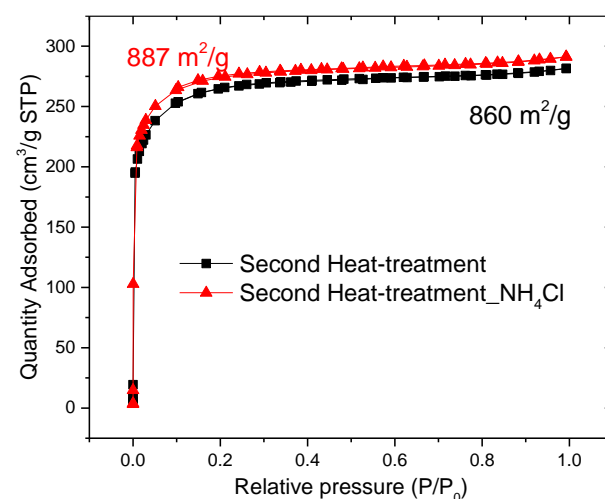
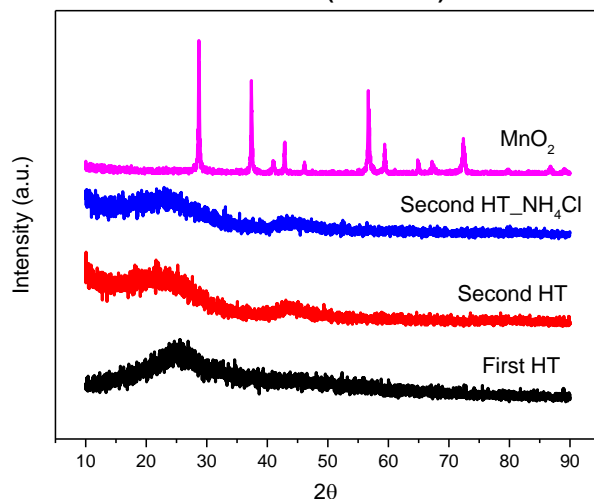
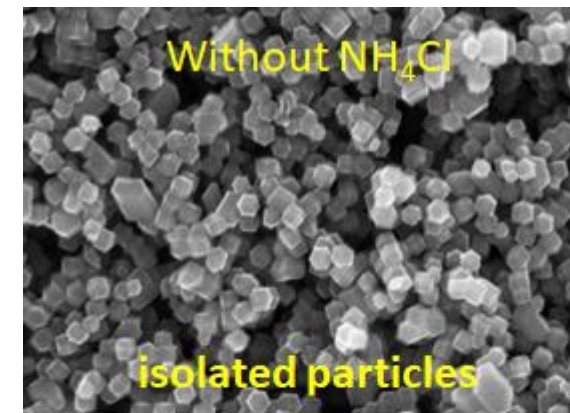
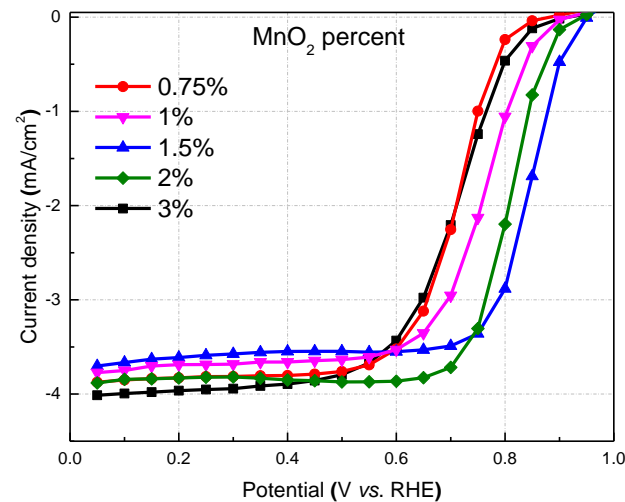
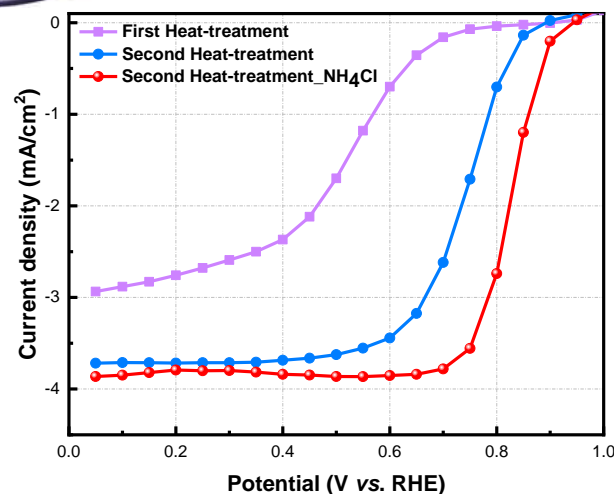
- In  $O_2$ -containing electrochemical environment, D1 ( $MnN_4C_{12}$ ) is predicted to exhibit worse resistance to demetallation than D2 ( $MnN_4C_{10}$ ).

Free energy change (eV)	Clean	Oxygen molecule adsorbed
D1 site ( $MnN_4C_{12}$ )	3.23	0.52
D2 site ( $MnN_4C_{10}$ )	3.40	1.41
D1 site ( $FeN_4C_{12}$ )	3.46	0.46
D2 site ( $FeN_4C_{10}$ )	3.88	1.31

Note: the free energy change for the transition from an active  $MnN_4$  site to an inactive  $MnN_2$  site is calculated to predict the demetallation tendency. The lower the free energy change, the higher chance of demetallation.

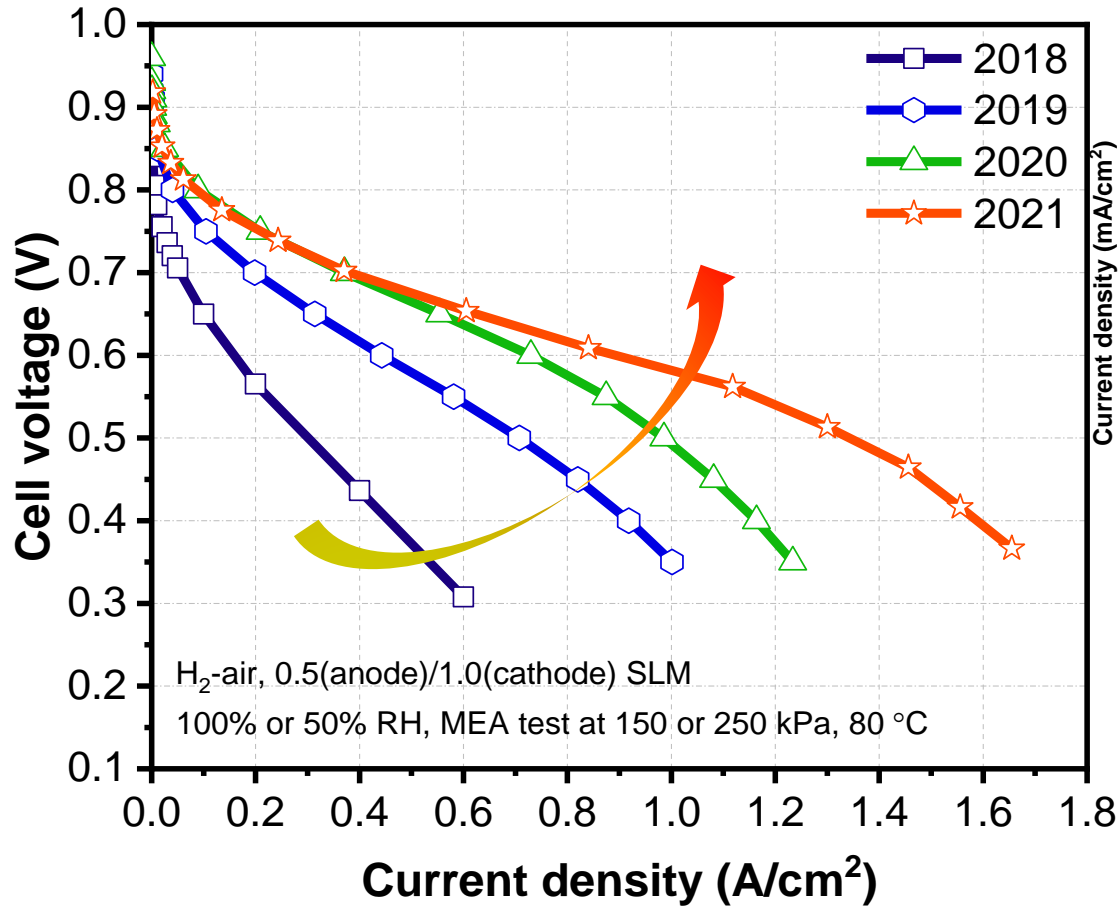


- Unlike traditional wet-chemistry synthesis, we are developing a scalable solid-state synthesis approach by using  $MnO_2$  as a precursor, rather than Mn ions in solution.
- The solid-state synthesis methods can be easily scaled up for large quantity synthesis.

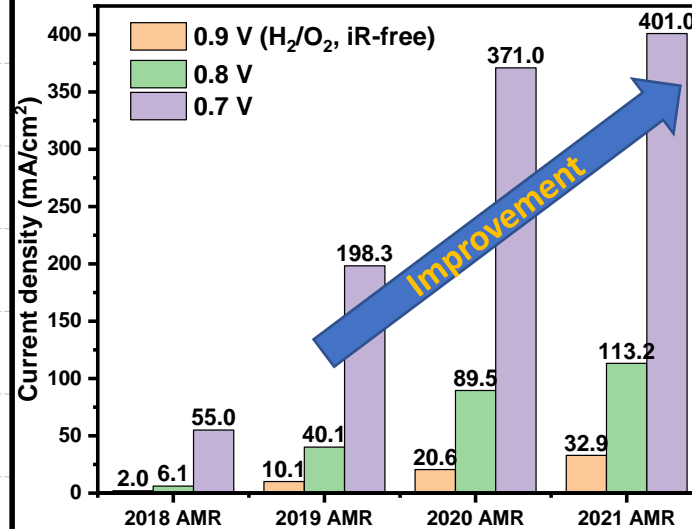


- Solid-state manganese oxide can be converted to MnN<sub>4</sub> sites through a controlled high-temperature treatment.
- The morphology of carbon is isolated particles, which is retained from ZIF-8 precursors.
- The NH<sub>4</sub>Cl post-treatment can improve the intrinsic activity of catalyst without changing surface areas or morphologies

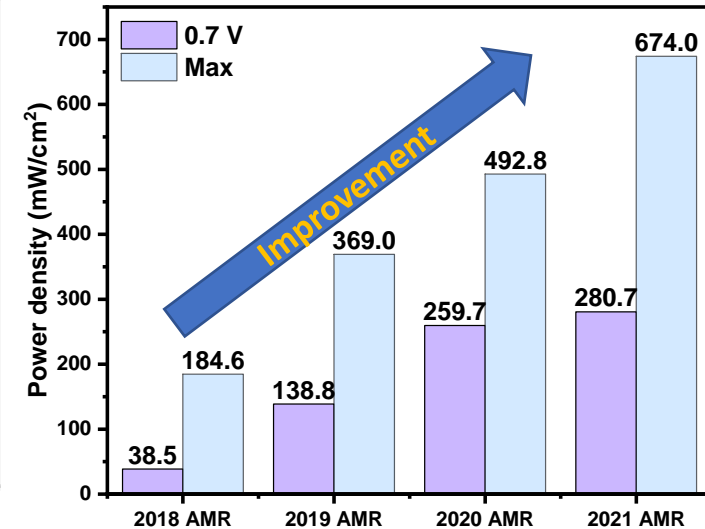
MEA VI polarization curves



Current density



Power density



- Consistent improvements have demonstrated throughout the project
- Improvements are due to new catalyst synthesis guided by DFT predictions, innovative electrode design and MEA integration

- ❑ Insufficient catalyst durability persists as a primary challenge
  - Most active catalysts decayed ~ 50% after 10k voltage cycling
  - Improving durability caused the activity and stability trade-off
  
- ❑ Water flooding issues of thick electrodes using PGM-free catalysts
  - Electrode fabrication strategies used for PGM catalysts have been adapted for PGM-free catalysts
  - Unique PGM-free catalyst morphologies and structures need to be considered for electrode design

- ❑ **Further understand the degradation mechanisms of Mn-N-C catalysts**
  - Mn oxidation could be more complex than other metals
  - Operating voltage, temperature and RH effects on the MEA durability using in situ XAS
  - Differentiating recoverable and non-recoverable decay
- ❑ **Develop strategies to achieve high performance and durability simultaneously**
  - Catalyst design: reduce Mn oxidation and demetallation
  - Increase more D2 sites of the catalyst
  - Electrode design and fabrication (e.g., thick electrode design to avoid flooding)
  - Optimize MEA break-in, operating and recovery procedure

- ❑ Used DFT calculations predict catalyst activity and durability and guide catalyst design
  - Both  $\text{MnN}_4\text{C}_{12}$  (D1) and  $\text{MnN}_4\text{C}_{10}$  (D2) sites exhibit high ORR activity:
  - Under  $\text{O}_2$ -containing environment, D1 exhibits lower resistance to demetallation than D2.
  - $\text{MnN}_4$  sites are predicted to have better resistance to carbon oxidation than  $\text{FeN}_4$  sites.
- ❑ Developed space confinement strategy to synthesize highly active Mn-N-C catalysts.
  - High-temperature treatment under controlled atmosphere leads to improved atomic active site dispersion
  - Optimal post-treatment increased the active sites density
- ❑ Improved MEA Performance by optimizing cell components and operating conditions
  - Varying Ionomer, membrane and RH%
  - Current density  $> 32 \text{ mA cm}^{-2}$  @0.9V ( $\text{H}_2/\text{O}_2$ );
  - Current density  $> 400 \text{ mA cm}^{-2}$  at 0.7 V; peak power density  $> 630 \text{ mW cm}^{-2}$  ( $\text{H}_2/\text{air}$ )
- ❑ Identified strategies to further Improve catalyst durability
  - A post-treatment step with small hydrocarbon compounds led to more durable MEAs
  - A trade-off between initial performance and durability
- ❑ Developed solid-state synthesis approach to enabling scalability of the Mn-N-C catalysts
  - Environmentally benign aqueous synthesis, rather than toxic organic solvent;
  - One step synthesis to improve catalyst reproducibility



Table 3.4.7 Technical Targets: Electrocatalysts for Transportation Applications

Characteristic	Units	2015 Status	2020 Targets
Platinum group metal total content (both electrodes) <sup>a</sup>	g / kW (rated, <sup>b</sup> gross) @ 150 kPa (abs)	0.16 <sup>c,d</sup>	0.125
Platinum group metal (pgm) total loading (both electrodes) <sup>a</sup>	mg PGM / cm <sup>2</sup> electrode area	0.13 <sup>c</sup>	0.125
Mass activity <sup>e</sup>	A / mg PGM @ 900 mV <sub>IR-free</sub>	>0.5 <sup>f</sup>	0.44
Loss in initial catalytic activity <sup>e</sup>	% mass activity loss	66 <sup>c</sup>	<40
Loss in performance at 0.8 A/cm <sup>2,e</sup>	mV	13 <sup>c</sup>	<30
Electrocatalyst support stability <sup>g</sup>	% mass activity loss	41 <sup>h</sup>	<40
Loss in performance at 1.5 A/cm <sup>2,g</sup>	mV	65 <sup>h</sup>	<30
PGM-free catalyst activity	A / cm <sup>2</sup> @ 0.9 V <sub>IR-free</sub>	0.016 <sup>i</sup>	>0.044 <sup>j</sup>

This Work
NA
PGM-free loading of 4 mg cm <sup>-2</sup>
NA
NA (no mass activity)
53% loss at 0.7 V after 10K cycles
NA (no mass activity)
NA (no rated power)
0.033

### Milestones met in this project

- 32.9 mA cm<sup>-2</sup> @0.9V (H<sub>2</sub>/O<sub>2</sub>)
- 400 mA cm<sup>-2</sup> at 0.7 V; peak power density = 634 mW cm<sup>-2</sup> (H<sub>2</sub>/Air)

- ❑ M. Chen, X. Li, F. yang, B. Li, T. Stracensky, S. Karakalos, S. Mukerjee, Q. Jia, D. Su, G. Wang, G. Wu, H. Xu, “Atomically Dispersed  $\text{MnN}_4$  Catalysts via Environmentally Benign Aqueous Synthesis for Oxygen Reduction: Mechanistic Understanding of Activity and Stability Improvements”, *ACS Catalysis* 10, 10523-10534 (2020)
- ❑ L. Guo, S. Hwang, B. Li, F. Yang, M. Wang, M. Chen, X. Yang, S. Karakalos, D. A. Cullen, Z. Feng, G. Wang, G. Wu, H. Xu, “Promoting Atomically Dispersed  $\text{MnN}_4$  Sites via Sulfur Doping for Oxygen Reduction: Unveiling Intrinsic Activity and Degradation in Fuel Cells”, *ACS Nano* 15, 6886-6899 (2021).

- 
- ❑ Wu, G., Chen, M., Yang, C and Xu, H., “Atomically Dispersed  $\text{MnN}_4$  Catalysts via Environmentally Benign Aqueous, provisional patent filed August 20, 2020
  - ❑ Wu, G., Liu, S., Ding, Suo, and Xu, H, “Chemical Vapor Deposition for Atomically Dispersed and Nitrogen Coordinated Single Metal Site Catalysts, provisional patent filed August 20, 2021
  - ❑ Wu, G., Xu, H, Liu, S., Ding, S., “Solid-State Synthesis and Carbon structure Engineering for M-N-C, provisional patent filed August 20, 2021



# Collaborations



Institutions	Roles
<b>Giner Inc. (Giner)</b> Hui Xu (PI), Sadia Kabir, Fan Yang, Shuo Ding, and Shirley Zhong	Prime, oversees the project; MEA design and fabrication; performance and durability tests; cost analysis
<b>University of Buffalo(UB)</b> Gang Wu (Co-PI), Yachao Zeng, Mengjie Chen, and Lin Guo	Mn-based non-PGM catalyst synthesis; characterization; RDE screening; MEA test;
<b>University of Pittsburgh (Pitt)</b> Guofeng Wang (Co-PI), Boyang Li	Catalyst and electrode modeling using DFT; molecular dynamics and pore network
<b>General Motors (GM)</b> Anusorn Kongkanand (Co-PI)	Fuel cell system integration; cost analysis
<b>Indiana University–Purdue University Indianapolis (IUPUI)</b> Jian Xie, Chenzhao Li	MEA testing and fabrication using Gore membrane and CCMs
<b>Compact Membrane Systems (CMS)</b> Dan Lousenberg	High O <sub>2</sub> Permeability Ionomer (HOPI) development
<b>Northeastern University (NEU)</b> Sanjeev Mukerjee, Qingying and Jia and Thomas Stracensky (collaborator)	XAS Characterizations and ORR mechanisms





# ElectroCat Integration



University at Buffalo  
The State University of New York

Priority order	Lab	Description
1	ORNL	High resolution TEM and STEM, for catalyst, electrode and MEA before and after durability tests. In-situ TEM to observe MEA under operating conditions
2	ANL	Ex-situ X-ray absorption spectroscopy (XAS) to determine Mn-related active sites; X-ray tomography to study Nano- and micro-structure of materials and cell layers; in-operando electrochemical XAS as a function of potential and potential cycling in an aqueous electrolyte and in a MEA
3	LANL	MEA design and fabrication to maximize the fuel cell initial performance and durability, which include: (i) catalyst ink optimization, (ii) catalyst layer deposition
4	ORNL	High angle annular dark field (HAADF) STEM tomography to elucidate the interaction between catalyst and ionomer.
5	NREL	Operando differential cell measurements of electrochemical kinetics and transport, providing insight into the reaction mechanisms and transport resistance measurements



University of  
Pittsburgh



# Response to Year 2019 Reviewer Comments

- ❑ *The project's weaknesses include the poor performance demonstrated in MEA testing. It is hard to envision that any of the PGM-free systems would be able to meet expectations in real systems.*

**We have demonstrated that Mn-based catalysts have comparable MEA performance with Fe-based catalyst. Given the cost effectiveness of transition metal catalysts and ability to scale up their synthesis, is it reasonable to vision that PGM-free catalysts have demonstrated viability for real world applications.**

- ❑ *As of yet, the project has not placed sufficient emphasis on addressing durability.*

**In both 2020 and 2021 , we have evaluated the durability of the MnNC catalysts using multiple approaches (RDE, MEA) and under multiple conditions (RH, cycles etc.). Some Durability studies were already included in 2020 AMR presentation.**

- ❑ *The claim of improved stability is not supported by any sufficient datasets. There is a lack of statistical data from the catalyst batches and no inductively coupled plasma data on the main leaching elements.*

**Post-treatment with benzimidazole after catalyst synthesis led to significant enhancements in RDE and MEA durability. We did perform ICP and did not detect Mn species.**

- ❑ *It is not clear whether the project is on track to hit its year 2 performance goal. No MEA durability has been shown yet, although it looks like this is not yet a milestone. The team should consider whether the DFT modeling is proving helpful for the synthesis and durability efforts.*

**Stability against demetallation of MnN<sub>4</sub> D1 and D2 active sites in inert and O<sub>2</sub>-containing electrochemical environment was extensively studied. DFT predicted limiting potential studies were useful in identifying the corrosion resistant active sites.**

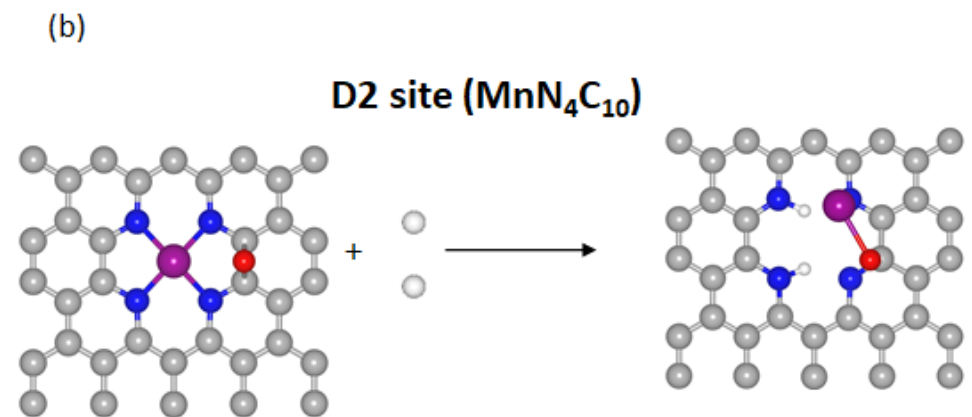
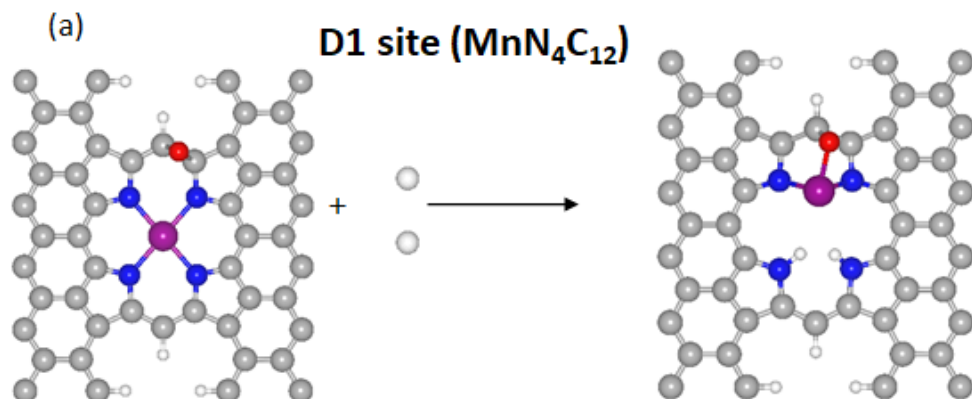
- ❑ *The project has presented many misreported, inconsistent, and "optimistic" conclusions. It also has unclear differentiation from other projects, except for the Mn approach. The DFT contribution is also lacking. Is this true?*

**The property of Mn-based catalyst is unique and has many aspects that are different from Fe-based catalysts. DFT predictions were important for understanding the active site configuration and their ability to break oxygen bonds for ORR. The combination of experimental and computational approach was important for designing high performance MnNC catalysts for fuel cell applications.**



- Financial support from DOE HFTO Fuel Cell Program under award # DE-EE0008075
- Program Manager
  - Dr. Nancy Garland (retired)
  - Dr. William Gibbons
- ElectroCat Consortium
  - Drs. Piotr Zelenay, Debbie Myers, ave Cullen and K.C. Neyerlin
- NEU: Thomas Stracensky, Drs. Sanjeev Mukerjee a
- IUPUI: Drs. Jie Xie and Chenzhao Li
- CMS: Dr. Dan Lousenberg

# Back-up Slides



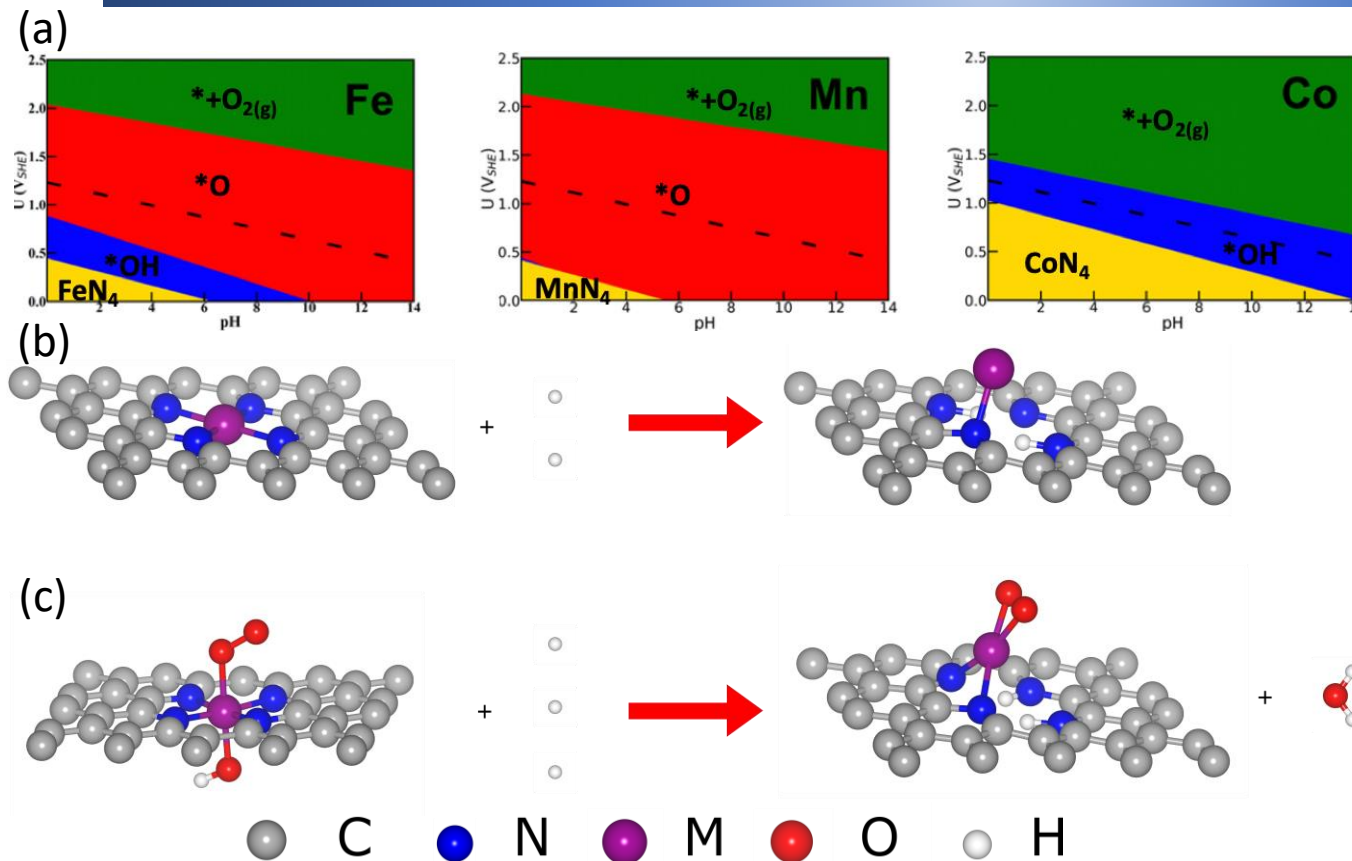
Free energy change (eV)	Non oxidized	Oxidized
D1 site ( $MnN_4C_{12}$ )	3.23	0.52
D2 site ( $MnN_4C_{10}$ )	3.40	1.26

Note: Large positive values of free energy change indicate high resistance to demetallation. Free energy changes were calculated under T of 298K. The higher the free energy change, the better resistance to the ORR activity degradation.

### DFT Prediction:

- The stability against demetallation on both D1 ( $MnN_4C_{12}$ ) and D2 ( $MnN_4C_{10}$ ) becomes worse if the carbon near  $MnN_4$  sites is oxidized.
- Moreover, oxidized D2 ( $MnN_4C_{12}$ ) is found to be more stable than oxidized D1 ( $MnN_4C_{10}$ ).
- Combination of carbon oxidation and demetallation make the catalyst less stable.
- Reducing carbon oxidation will improve durability of the catalysts.



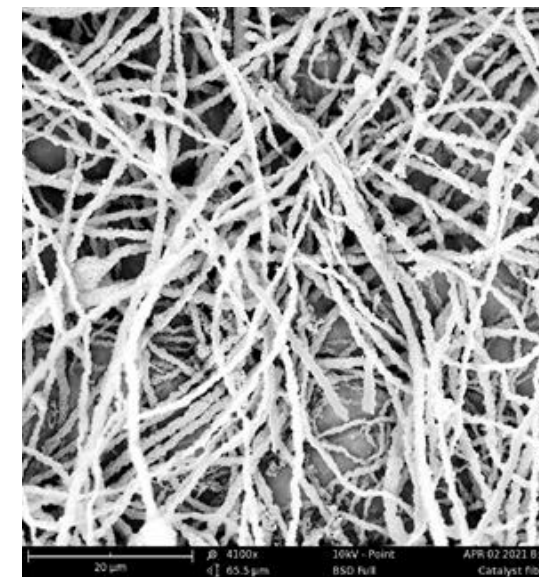
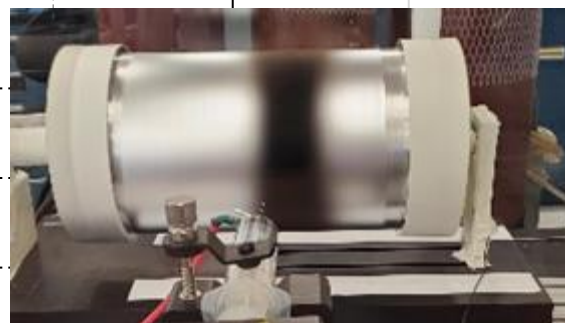
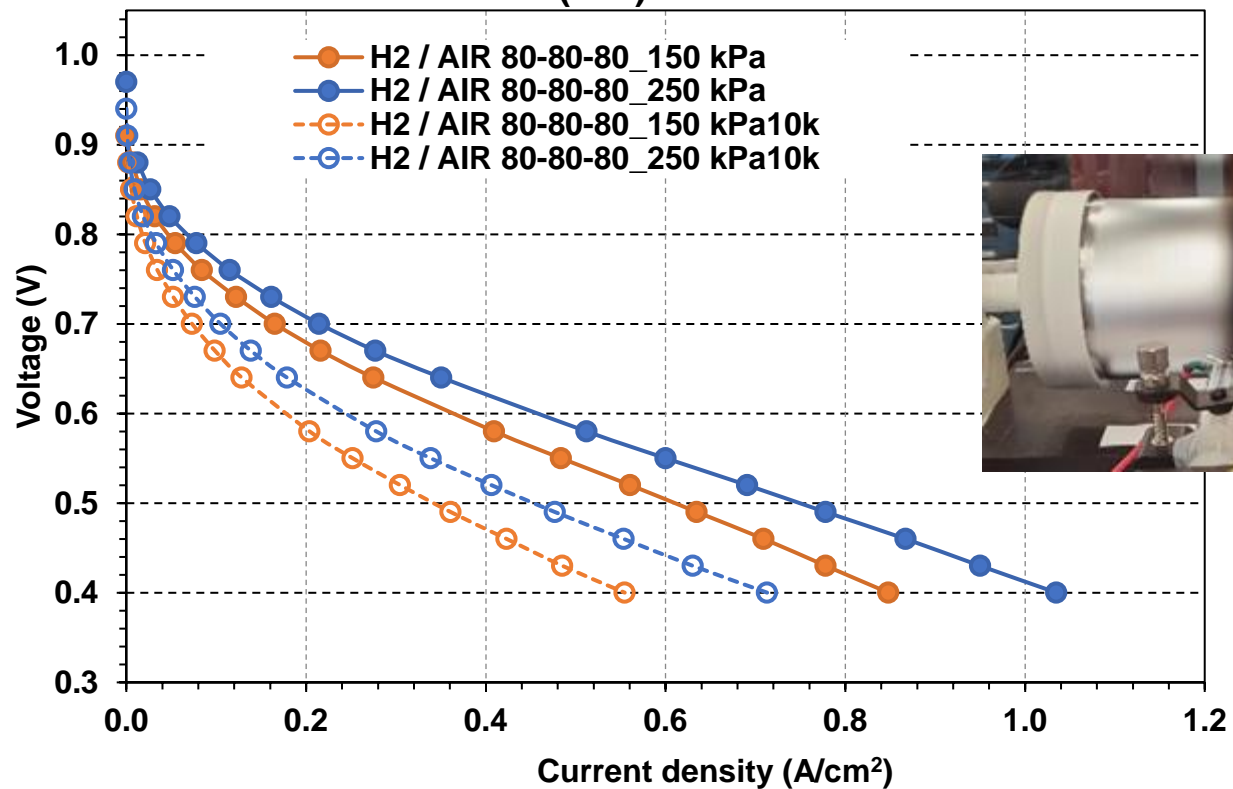


**DFT Prediction:** The DFT predicted Pourbaix diagram suggests that at high electrode potential, FeN<sub>4</sub> and MnN<sub>4</sub> site are covered by O-species, whereas there are no chemical adsorbates at CoN<sub>4</sub> site.

In oxygen-containing electrochemical environment, the stability of MN<sub>4</sub> site would further decrease owing to the O-species covered at FeN<sub>4</sub> and MnN<sub>4</sub> site

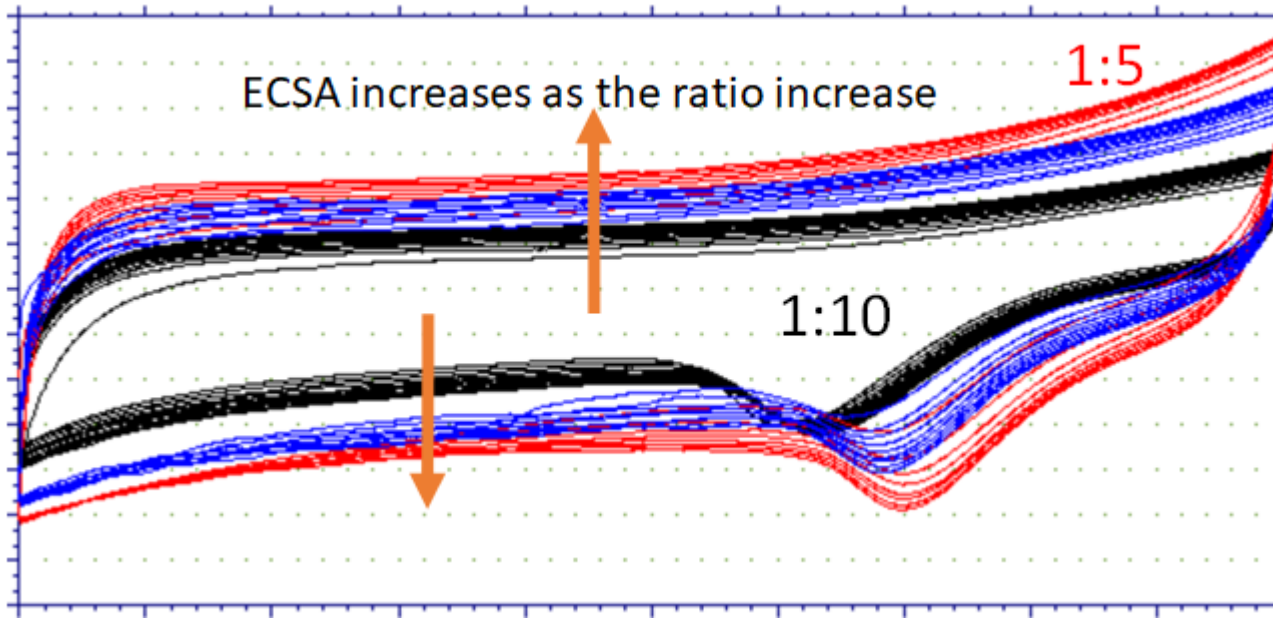
Free energy change (eV)	Inert environment (b)	Oxygen-containing environment (c)
MnN <sub>4</sub>	3.40	0.35
FeN <sub>4</sub>	3.88	0.18

Mn(acc) Nanofibers

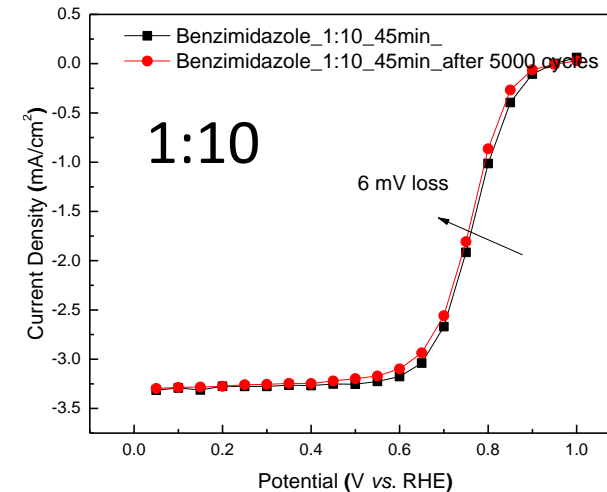
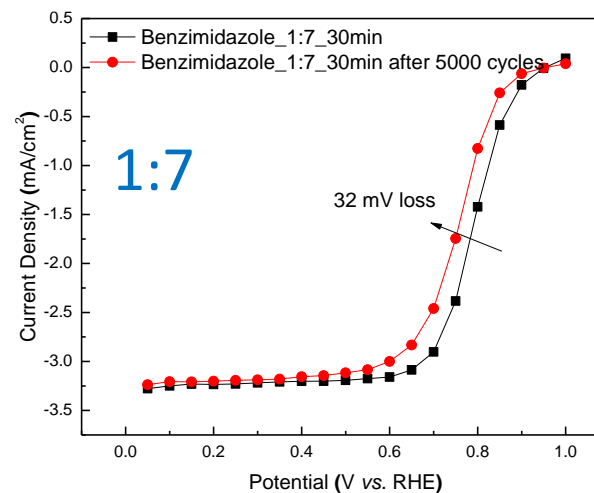
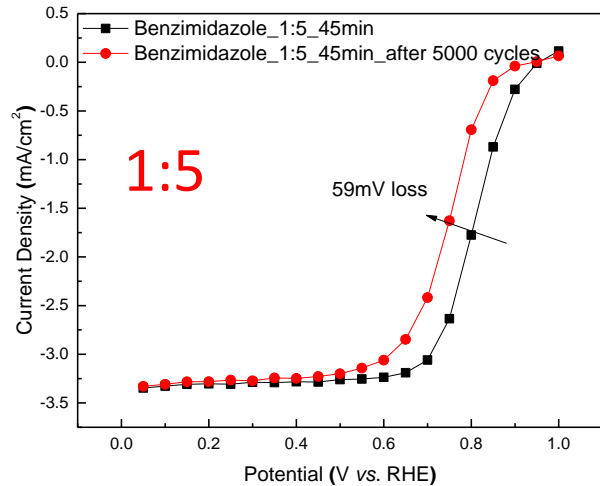


100 % RH			
Pressure	Current Density at 0.7 V, BOL (mA cm <sup>-2</sup> )	Current Density at 0.7V, EOL (mA cm <sup>-2</sup> )	% Retention
250 kPa	130	70	54%
150 kPa	90	50	55%

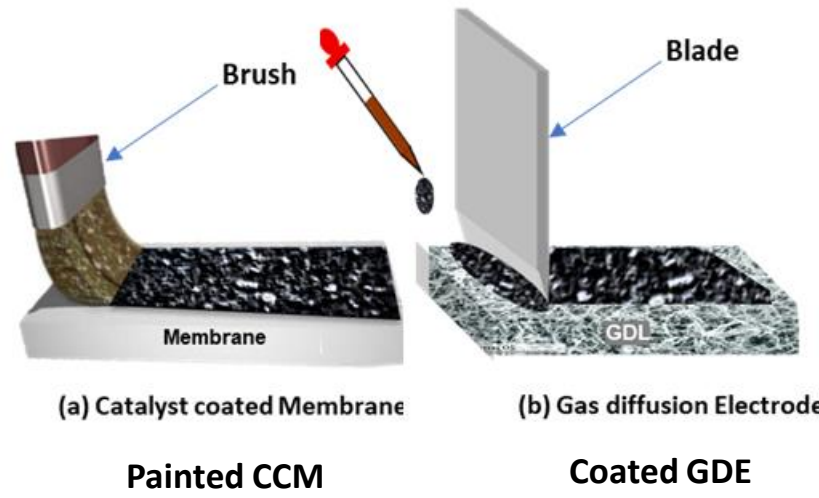
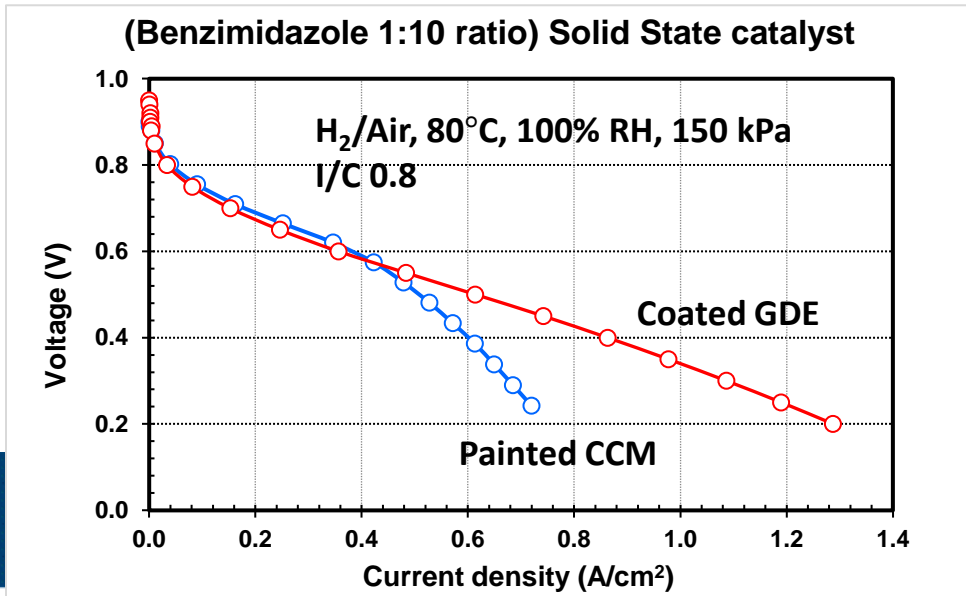
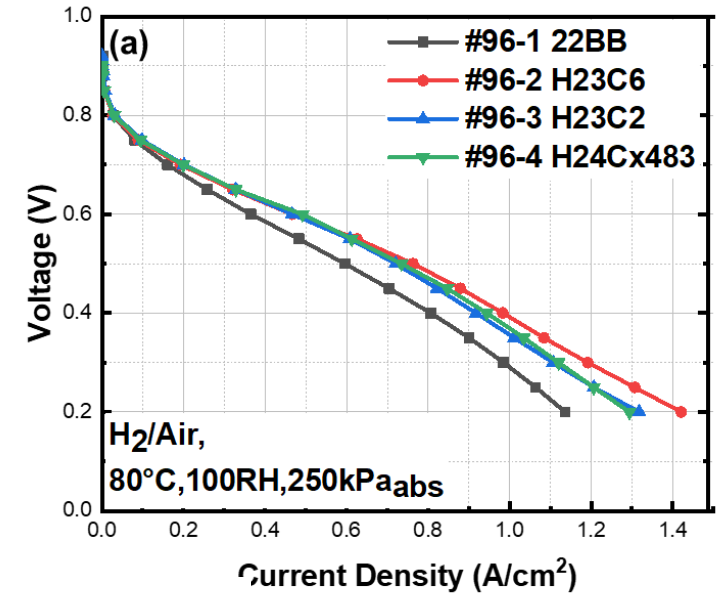
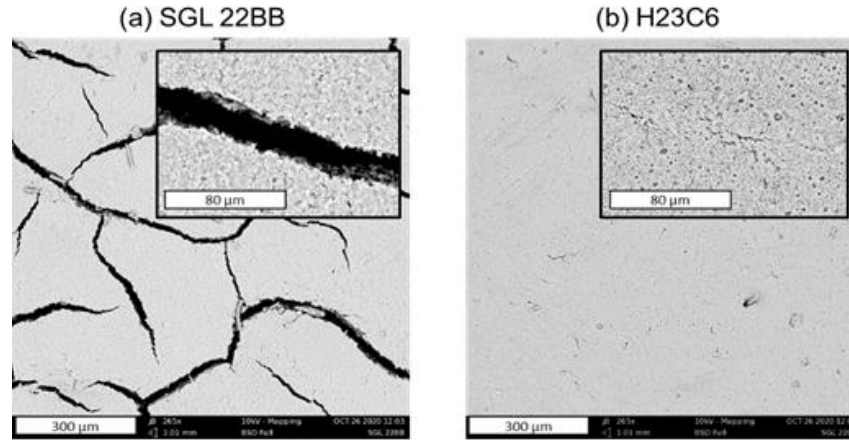
- Mn(acc)-N-C catalysts synthesized using the space confinement strategy were electrospun into a fiber using a mixture of catalyst, Nafion ionomer and carrier polymer, poly(acrylic)acid PAA.
- The nanofiber electrodes demonstrated enhanced active site retention of (54-55%) compared to blade coated GDEs (42%)



- Ratio of precursor ( $MnO_2$ )/ benzimidazole (BIM) and its effect on capacitance and RDE durability
- Increasing the ratio from 1:5, 1:7 and 1:19 improves RDE durability
- An increasing capacitance suggests the benzimidazole can cover the pores and protect active sites from degradation.



- Utilized Freudenberg GDL materials (H23C6, H23C2 and H23Cx483) significantly improved MEA performances in comparison to SGL 22BB GDLS
- Improved water management and gas diffusion in uniform cathode catalyst layers



Fabricating painted CCM electrodes with BIM (1:10) ratio catalysts leads to reduced high current density performance (likely due to flooding) in comparison to blade coated GDEs