2019 DOE H_2 and Fuel Cell Annual Merit Review Meeting

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

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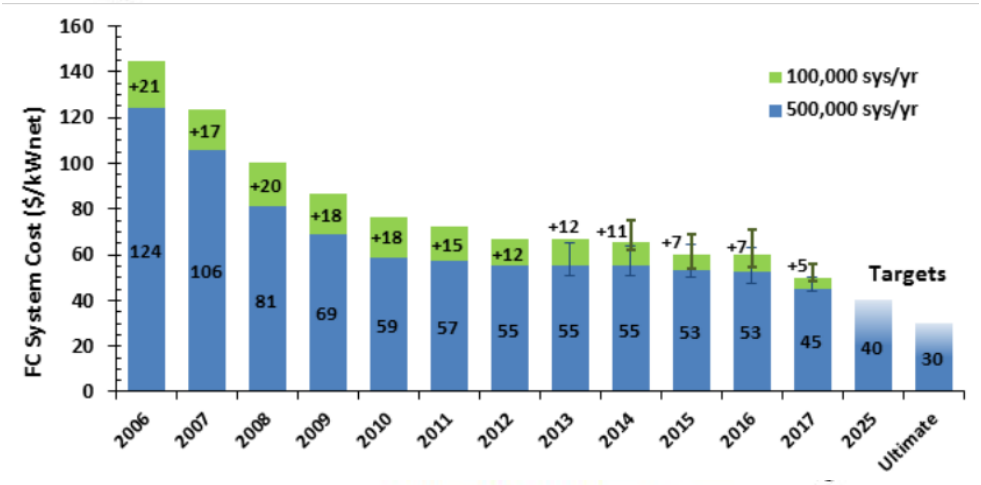
Subcontractors:
SUNY-Buffalo, Univ. Pittsburgh, and GM

April 29, 2019

Project #
FC170

Relevance



(From DOE FCTO website)

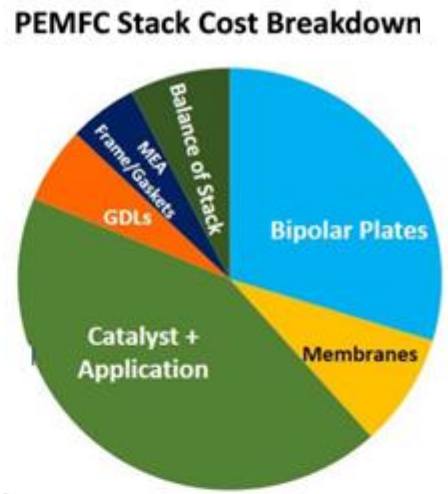


Table 3.4.7 Technical Targets: Electrocatalysts for Transportation Applications			
Characteristic	Units	2015 Status	2020 Targets
Platinum group metal total content (both electrodes)[a]	g / kW (rated,[b] gross) @ 150 kPa (abs)	0.16[c,d]	0.125
Platinum group metal (pgm) total loading (both electrodes)[a]	mg PGM / cm^2 electrode area	0.13[c]	0.125
Mass activity[e]	A / mg PGM @ 900 $mV_{iR\text{-}free}$	>0.5[f]	0.44
Loss in initial catalytic activity[e]	% mass activity loss	66[c]	<40
Loss in performance at 0.8 A/cm^2[g,e]	mV	13[c]	<30
Electrocatalyst support stability[g]	% mass activity loss	41[h]	<40
Loss in performance at 1.5 A/cm^2[g]	mV	65[h]	<30
PGM-free catalyst activity	A / cm^3 @ 0.9 $V_{iR\text{-}free}$	0.016[i]	>0.044[j]

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

- ❑ Catalyst cost still a major contributor to high fuel cell price
- ❑ Pt price volatility and supply shortage with mass production of fuel cells
- ❑ Development of non-PGM catalyst can likely resolve the issues

Project Overview

Timeline

- Project Start Date: Oct 1, 2017
  Project End Date: Sept 30, 2020

Budget

- Total $2.49 million
  - DOE share $1.99 million and cost sharing $500, 744
  - Spent $ 765, 075 (by 2/28/2019)

Collaborators

- SUNY-Buffalo: Prof. Gang Wu
- U. of Pitts.: Prof. Guofeng Wang
- GM: Dr. Anusorn Kongkanand
- Northeastern University: Dr. Sanjeev Mukerjee

Barriers Addressed

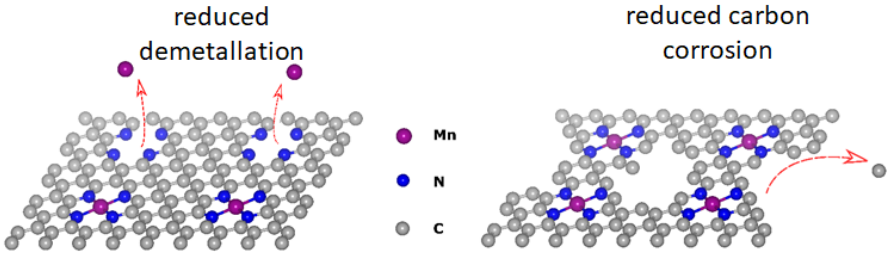
- Durability (catalyst; MEA)
- Cost (catalyst; MEA)

Technical Targets

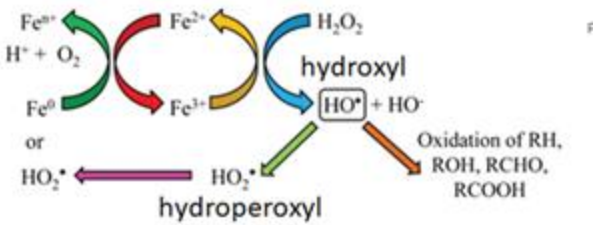
- Design Mn-based PGM-free catalysts to meet DOE catalyst activity >0.044 A/cm^2 @ 0.9 $V_{IR\text{-}free}$ in a MEA test
- The catalyst extends the durability by 50% (compared to state-of-the-art PGM-free catalyst)
- The catalyst mitigates membrane degradation caused by Fe-based catalysts by 50%

Motivation

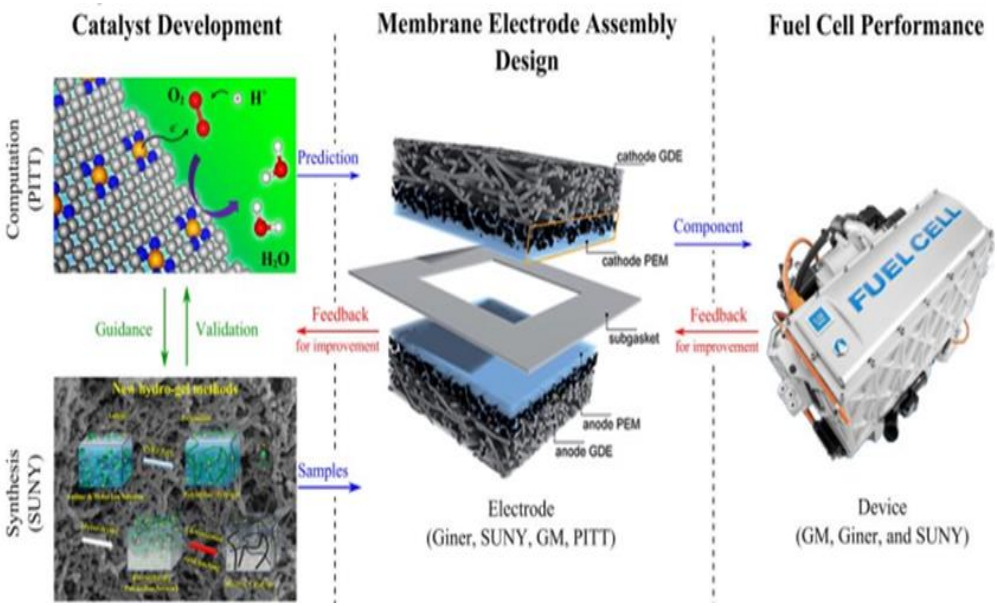
- PGM Catalyst
  - High cost
  - Scarcity
  - Catalyst poisoning
- Fe Based PGM-free Catalyst
  - Insufficient stability
  - Membrane degradation
- **Mn Based PGM-free Catalyst**
  - Catalyst Design: Improving Durability

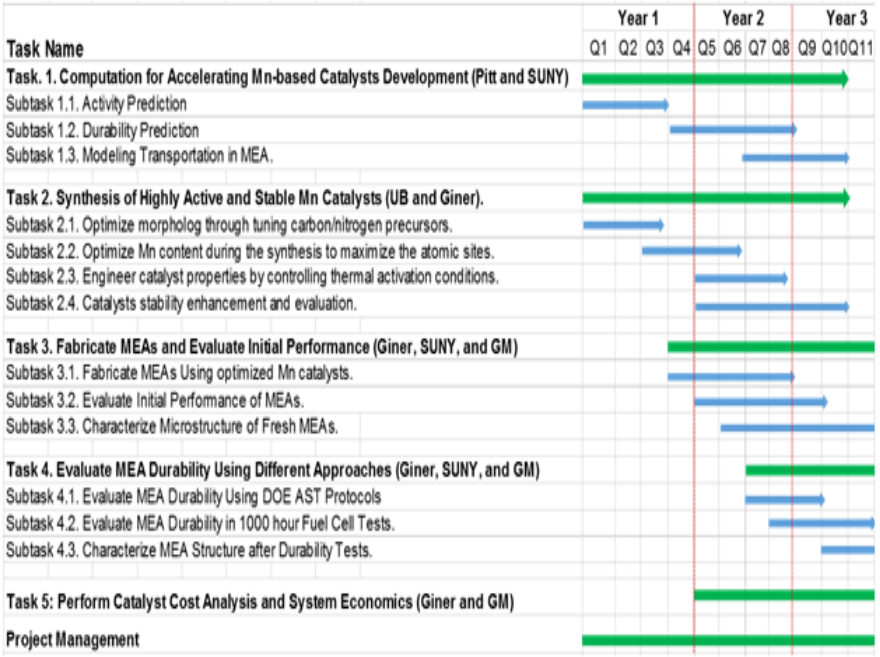


- MEA Design: Reducing PEM degradation by eliminating Fenton reaction



Technical Approaches and Tasks





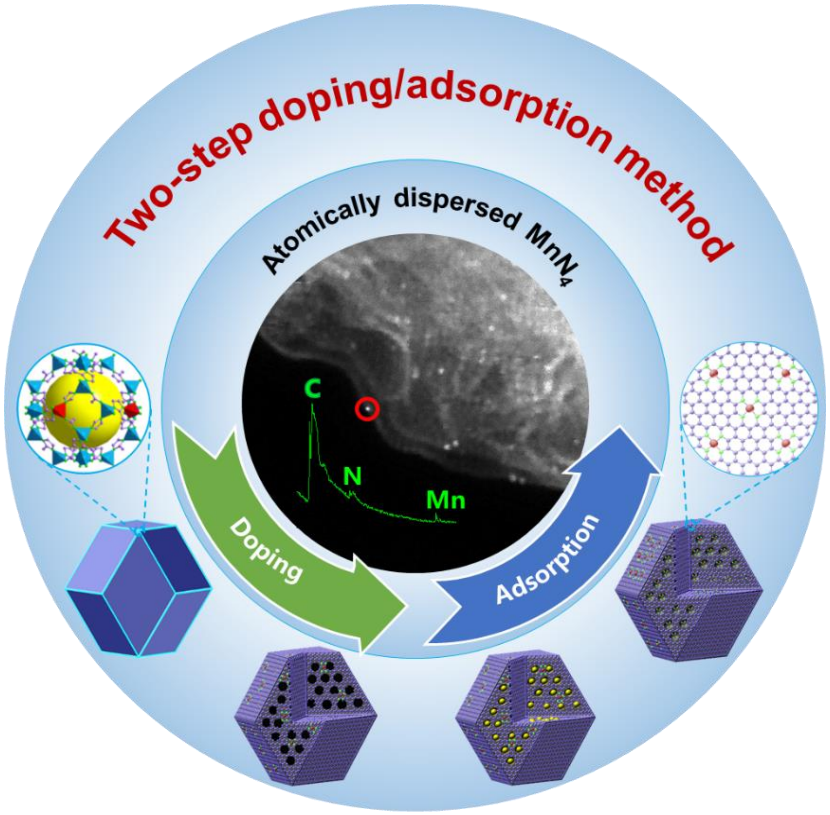
- ❑ **University of Pittsburgh: Catalyst Modeling**
- ❑ **University of Buffalo/SUNY: Catalyst Synthesis**
- ❑ **Giner: Electrode and MEA design**
- ❑ **GM: MEA validation**

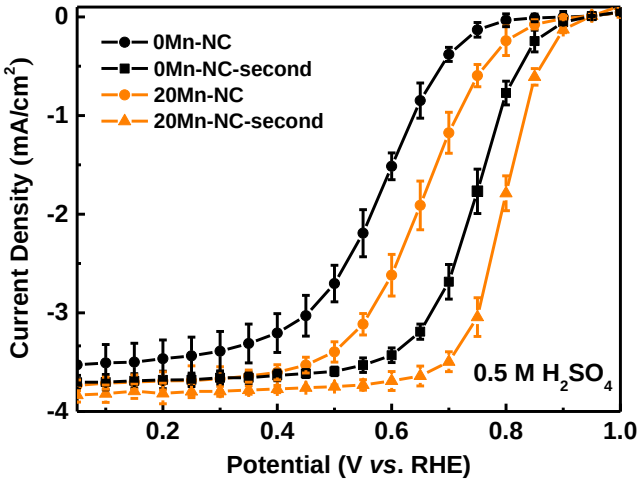
Milestones on Track

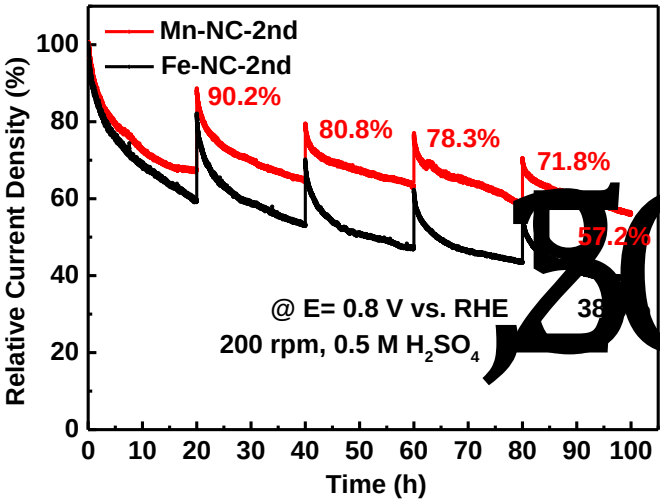
Task	Task/subtask Titles	Milestone	Number	Milestone Description	Milestone Verification Process	Month	Quarter	Completion
1	Computation of Mn-based catalysts and cathodes	Milestone	M1-1	Identify 2 key descriptors for modeling catalyst activity and durability	At UP, provide detailed key descriptors	M3	Q1	100%
1	Computation of Mn-based catalysts and cathodes	Milestone	M1-2	Predict 6 planar and non-planar Mn-containing active sites	At UP, provide detailed predictions and computational procedures	M6	Q3	100%
1	Computation of Mn-based catalysts and cathodes	Milestone	M1-3	Predict active sites with highest stability and 4e⁻ ORR	At UP, provide detailed predictions and analysis results	M15	Q5	100%
1	Computation of Mn-based catalysts and cathodes	Milestone	M1-4	Verify/refine the predicted active sites with highest stability and 4e⁻ ORR	At UP, provide detailed comparison between predictions and RDE results	M27	Q9	100%
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	30%
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	30%
2	Synthesize and screen Highly Active and Stable Mn Catalysts	Milestone	M2-1	Produce 1.0 g of Mn based catalyst	At SUNY, using a small batch reactor	M3	Q1	100%
2	Synthesize and screen Highly Active and Stable Mn Catalysts	Milestone	M2-2	Scale up hydrogel method and prepare > 5.0 g catalysts	At SUNY and Giner	M6	Q2	100%
2	Synthesize and screen Highly Active and Stable Mn Catalysts	Milestone Go/No-Go decision	M2-3	Achieve $E^{1}/_{2}$ > 0.81 V and generate 0.25 mA/cm² at 0.90 V and stability: $\Delta E^{1}/_{2}$ < 30 mV after 30,000 potential cycling	At SUNY, using RDE steady-state polarization; potential cycling (0.6 to 1.0 V, 50 mV/s) in O_2 saturated 0.5 M H_2SO_4	M12	Q4	100%
2	Synthesize and screen Highly Active and Stable Mn Catalysts	Milestone	M2-4	Achieve E_{N} ≥ 0.82 V and generate 0.50 mA/cm² at 0.90 $V_{IR-free}$	At SUNY, using steady-state ORR polarization	M18	Q6	100%
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_2 saturated 0.5 M H_2SO_4	M21	Q7	50%
2	Synthesize and screen Highly Active and Stable Mn Catalysts	Milestone	M2-6	Achieve E_{N} ≥ 0.85 V; generate 0.75 mA/cm² at 0.90 V;	At SUNY, using RDE steady-state ORR polarization	M30	Q10	30%
3	Fabricate MEAs and Evaluate Initial Performance	Milestone	M3-1	Identify 2 key parameters for MEA performance at low current density	At Giner and SUNY, including electrode fabrication approaches.	M9	Q3	100%
3	Fabricate MEAs and Evaluate Initial Performance	Go/No-Go decision	M3-2	For a PGM-free &Fe-free catalyst, demonstrate ≥ 10 mA/cm² at 0.90 V (iR-corrected) in an H_2-O_2; maintain partial pressure of O_2 at 1.0 bar (cell temperature 80 °C).	At Giner and SUNY, using DOE PGM-free catalyst testing protocols for MEAs	M12	Q4	100%
3	Fabricate MEAs and Evaluate Initial Performance	Milestone	M3-3	Identify 2 key parameters for MEA performance at high current density	At Giner, including electrode fabrication approach, ionomer content and category	M18	Q6	
3	Fabricate MEAs and Evaluate Initial Performance	Go/No-Go decision	M3-4	For a PGM-free & Fe-free catalyst, demonstrate ≥ 20 mA/cm² at 0.90 V (iR-corrected) in an H_2-O_2; maintain partial pressure of O2 at 1.0 bar (cell temperature 80 °C).	At Giner and SUNY, using DOE PGM-free catalyst testing protocols for MEAs	M24	Q8	
3	Fabricate MEAs and Evaluate Initial Performance	Milestone	M3-5	MEA performance: 0.044 A/cm² at ≥0.90 $V_{IR-free}$; 1.0 A/cm² at 0.50 V	At Giner, Using DOE PGM-free catalyst testing metrics	M33	Q11	
3	Fabricate MEAs and Evaluate Initial Performance	Go/No-Go decision	M3-6	For a PGM-free catalyst demonstrate ≥ 30 mA/cm² at 0.90 V (iR-corrected) in an H_2-O_2 fuel cell and 150 mA/cm² at 0.80 V in an H_2-air fuel cell (measured); maintain partial pressure of O_2 + N_2 at 1.0 bar (cell T= 80 °C).	At Giner and GM using DOE PGM-free catalyst testing protocols for MEAs	M36	Q12	
4	Evaluate MEA Durability Using Different Approaches	Milestone	M4-1	MEA durability: $\Delta V < 30\ mV$ at 0.044 A/cm²; activity loss < 100 mA/cm² 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_2-N_2 condition.	M36	Q12	
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	

Two step approach to introduce more Mn ions

Two step doping/adsorption approach to producing MnN_4 active sites





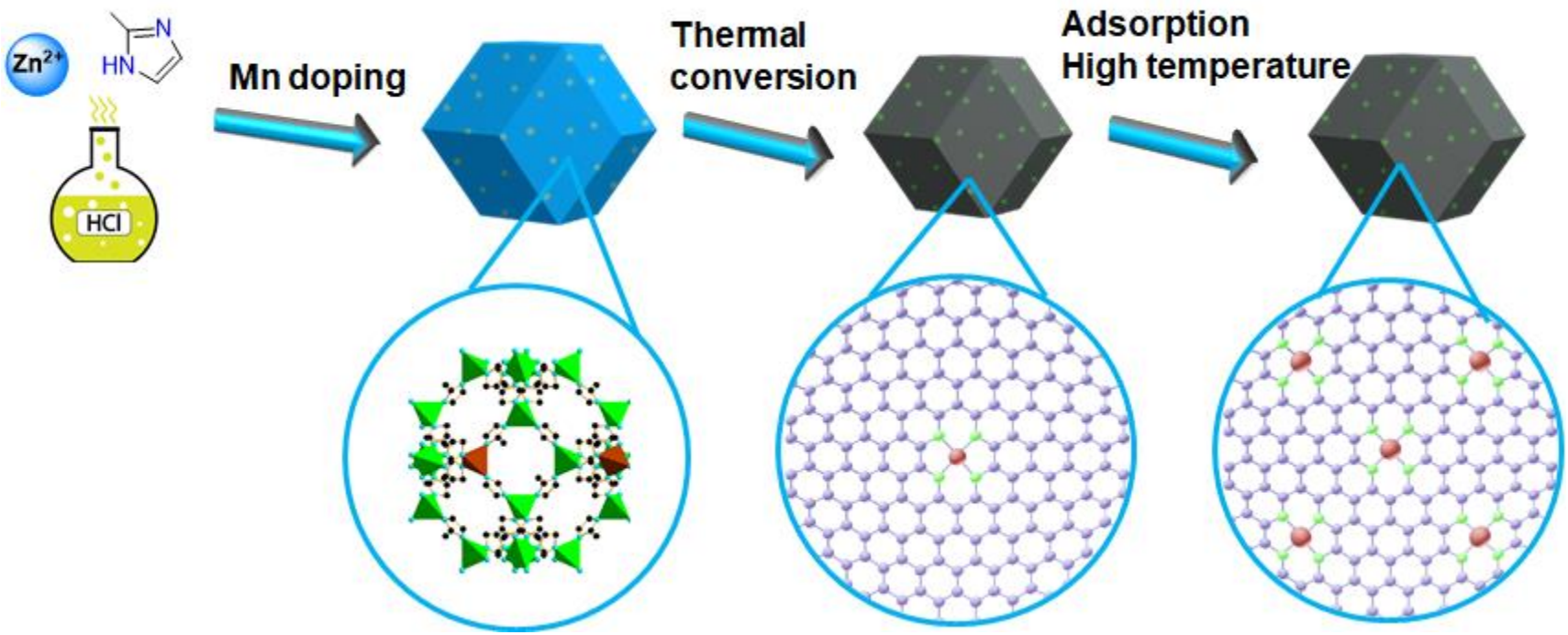


- The sequential doping and adsorption are effective to increase the density of MnN_4 active sites.
- The new Mn-N-C catalyst exhibited encouraging activity and stability.

This work has been published on *Nature Catalysis* (Vol 1. December 2018. 935-945)

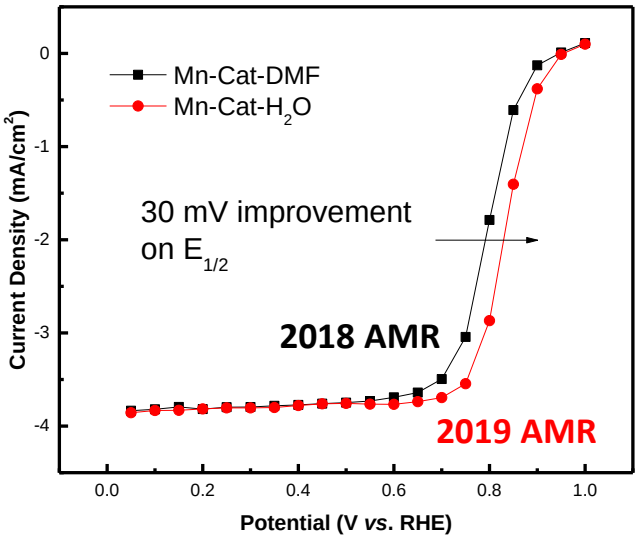
NATURE CATALYSIS

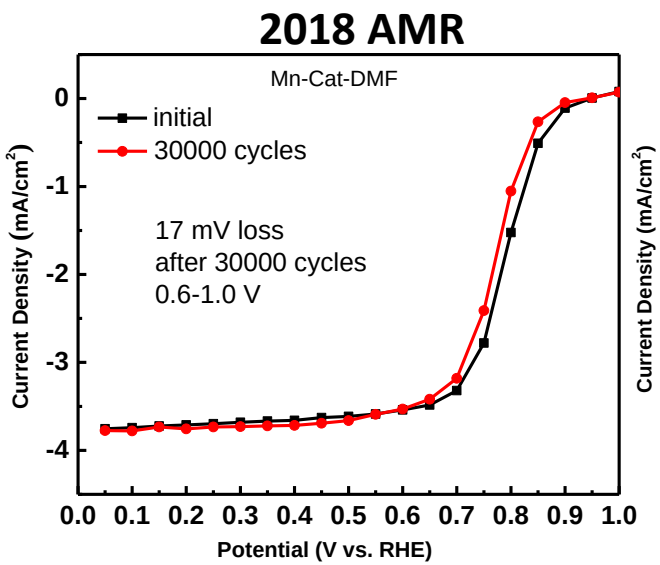
Innovative synthesis of Mn-N-C catalyst in low-cost and environmentally friendly aqueous system

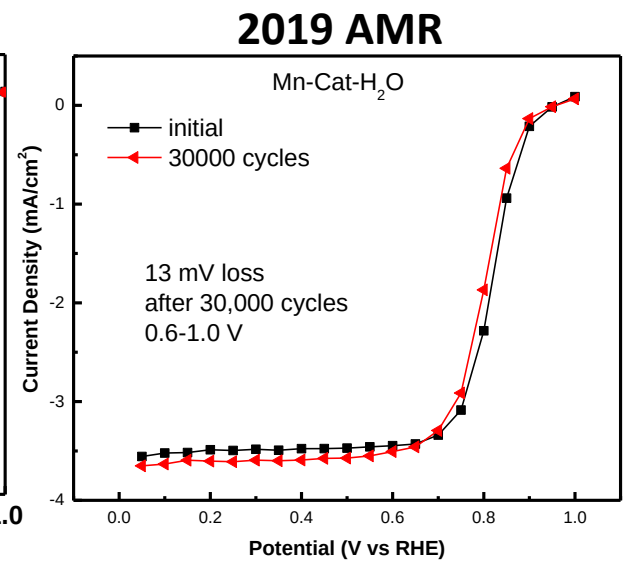


- Instead of organic solvents (e.g., DMF), aqueous synthesis methods are developed for Mn-N-C catalysts with enhanced activity.
- Acid was introduced for inhibiting the hydrolysis of Mn salts and increasing the doping content of Mn.

Progress on activity and stability improvement



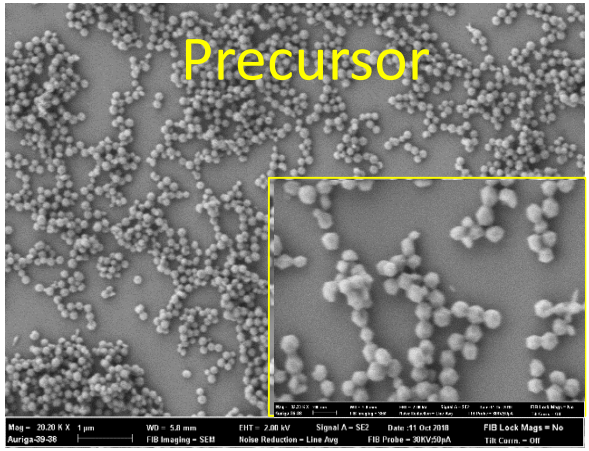


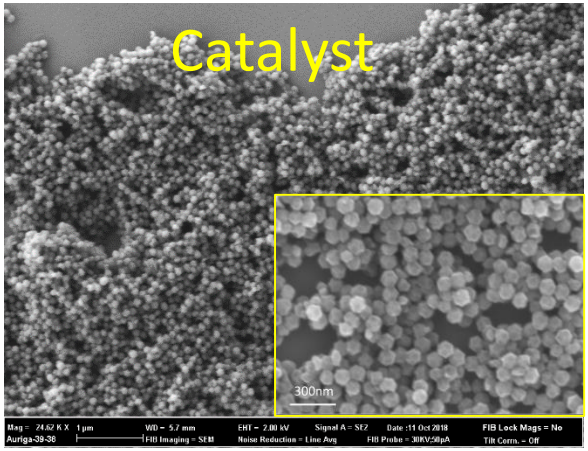


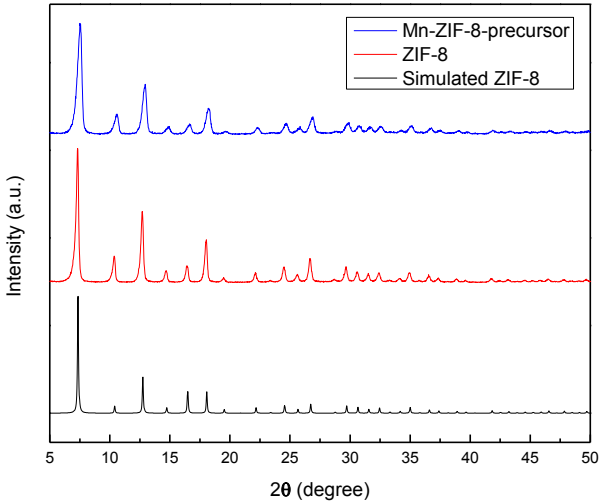
	2018 AMR	2019 AMR
Initial $E_{1/2}$	0.79	0.82
$\Delta E_{1/2}$ (30000 cycles from 0.6 to 1.0 V)	-17 mV	-13 mV

- **The $E_{1/2}$ is improved by 30 mV in RDE tests; met the milestone of $E_{1/2} \geq 0.82$ V)**
- **Stability of Mn-N-C catalyst synthesized from aqueous systems is enhanced as well, approaching the milestone of ($\Delta E_{1/2}$ < 10 mV after 30,000 potential cycling.)**

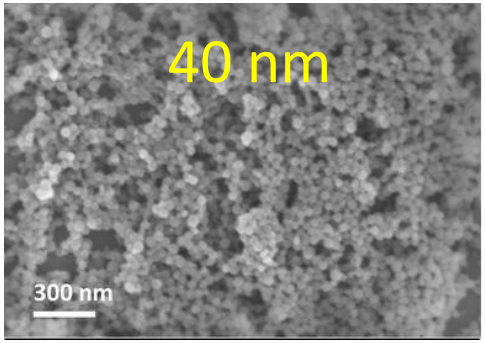
Morphologies of Mn-N-C catalyst and precursors

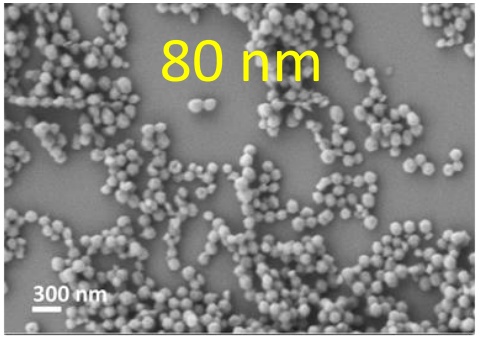


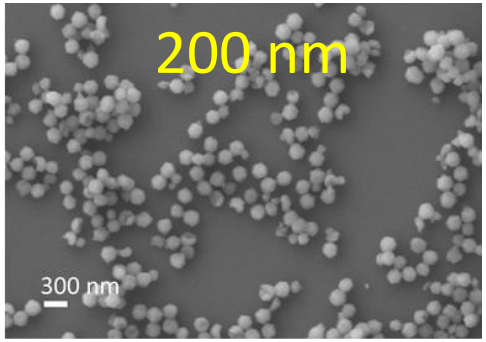




Particle size control



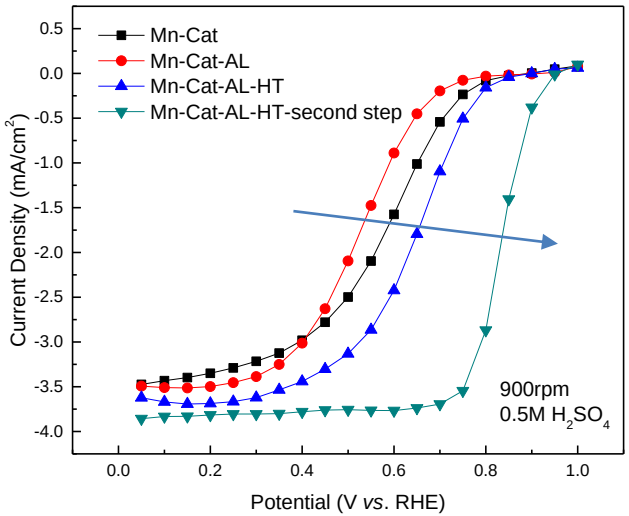




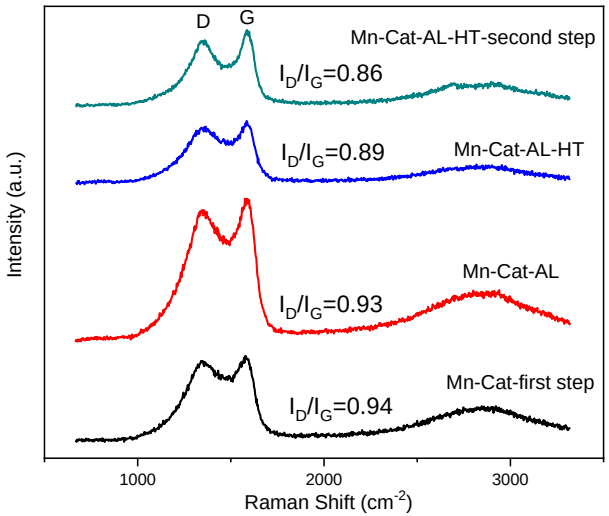
- **Polyhedron structure was observed for the Mn-N-C catalysts from aqueous solution; the particle size can be well controlled by tuning the concentration of metal salts.**
- **XRD shows that the Mn doping does not affect the crystal structure of ZIF-8; no obvious Mn oxides were detected.**
- **Particles were well isolated and not fused together; the particle morphology was maintained after high-temperature treatment.**

RDE activity and catalyst structure evolution for the aqueous Mn-N-C catalyst (Gen2-Mn-Cat)

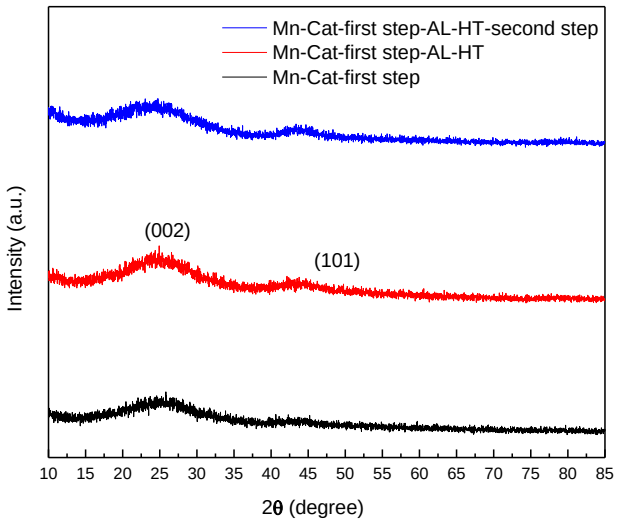
Activity during synthesis



Raman spectra



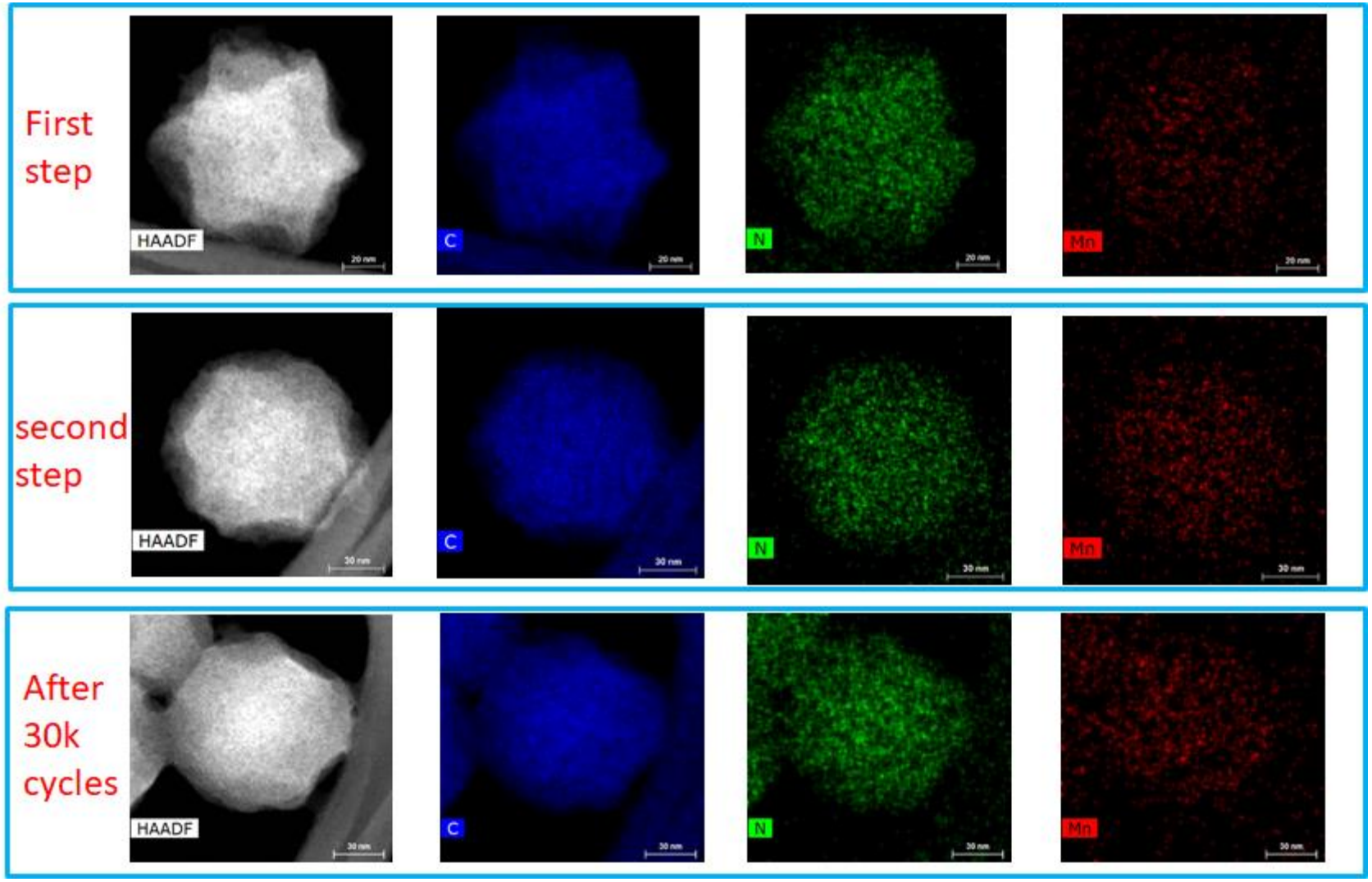
XRD patterns



AL: acid leaching; HT: heat treatment

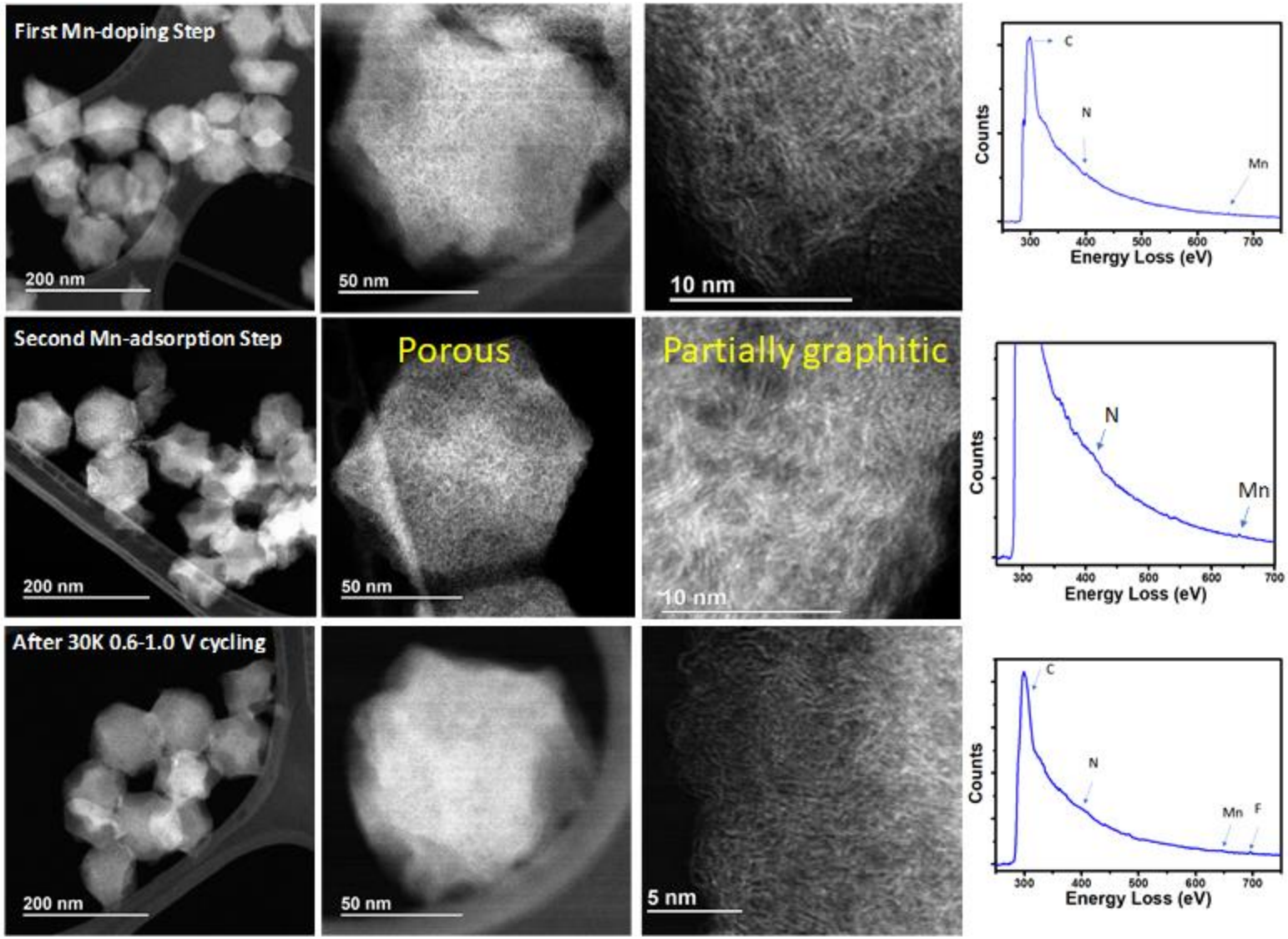
- **Relatively low carbonization temperature (900℃) producing MnN_x leads to a low performance ($E_{1/2}$=0.6 V) after Step 1; however, higher nitrogen content could be obtained, benefiting adsorption step and density of MnN_x.**
- **Raman spectra evolution indicates that the graphitization degree of Mn-doped nanocarbon is increasing with the number of heat treatment. However, nitrogen content also decreased according to G' peaks around 2800 cm^{-1} indicating less defects.**
- **Amorphous carbon structure was detected by XRD. No obvious Mn oxide signals were detected.**

Structure and Morphology Evolution



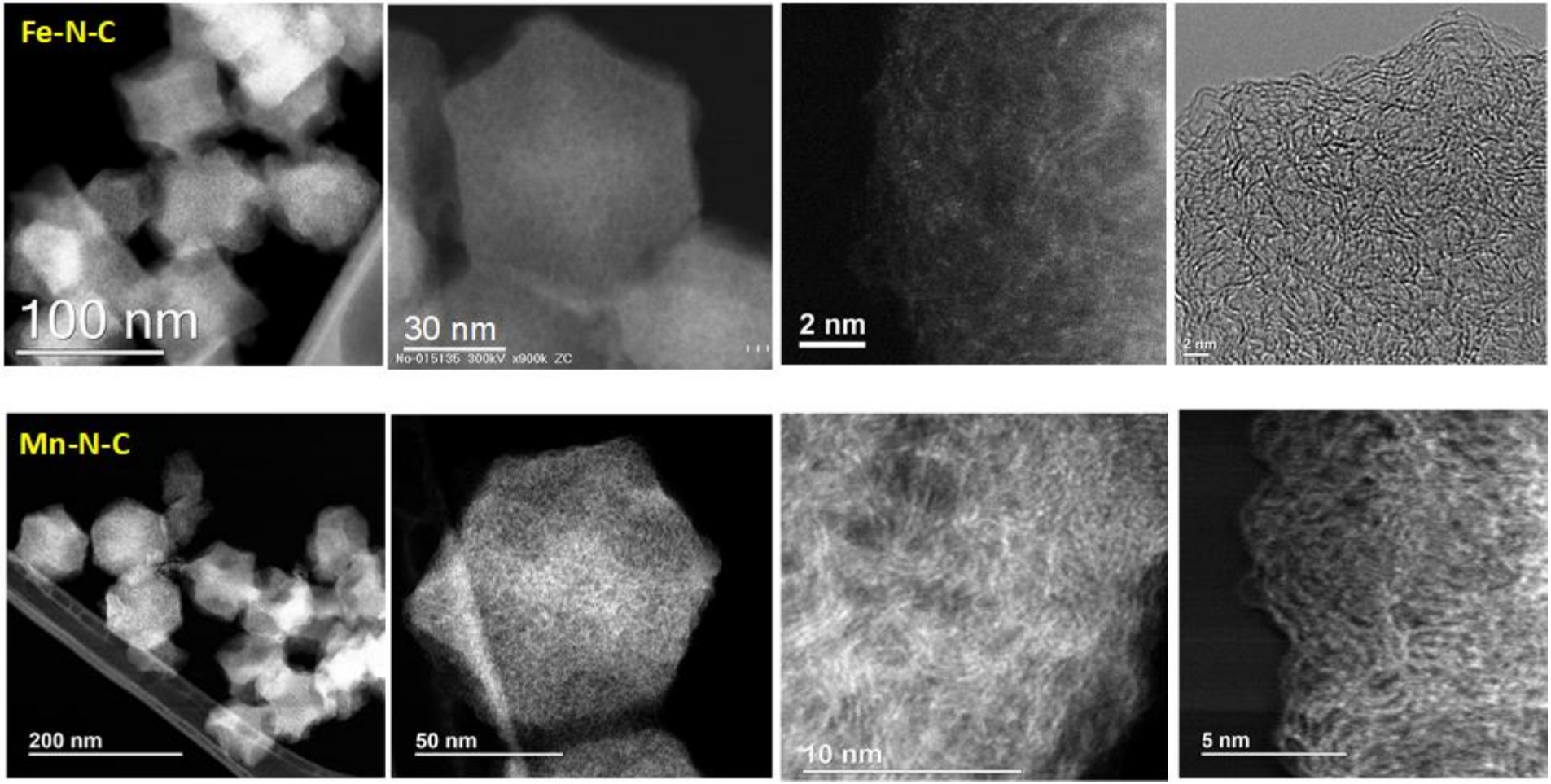
- Mn signals became much stronger after the second step, indicating the increased active site density.
- Morphology and Mn signals of catalysts were well maintained after the potential cycling, indicating the robust MnN_x structure.

Structure and Morphology Evolution



Atomically dispersed and N coordinated Mn sites along with porous and partially graphitic carbon in the Mn-N-C catalysts are well retained after potential cycling tests.

Comparison between Mn-N-C and Fe-N-C catalysts

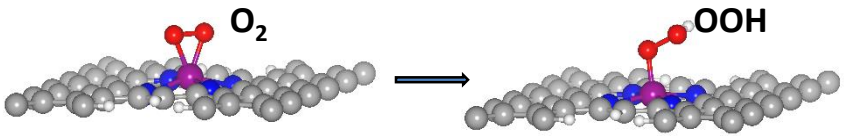


The Mn-N-C catalyst has a relatively higher degree of graphitization relative to Fe-N-C catalysts based on these STEM images, which may explain the enhanced stability.

Computational Modeling

The first-principles calculations were performed using software ***VASP***

1. Adsorption of ORR species on Mn active sites

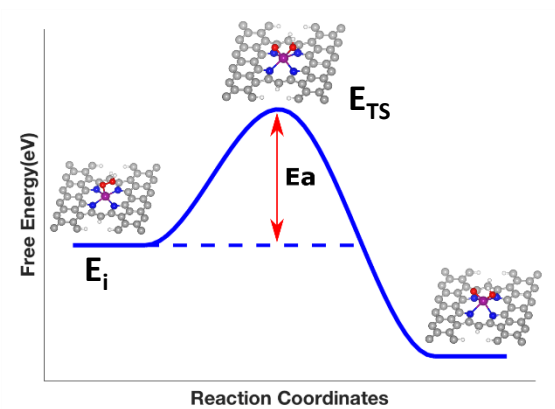


Adsorption energy $\Delta E = E_{system} - E_{catalyst} - E_{molecule}$

Free energy change $\Delta G = \Delta E + \Delta E_{solv} + \Delta E_{ZPE} - T\Delta S + neU$

2. Transition state calculation of ORR

Activation energy $E_a = E_{TS} - E_i$



3. Microkinetic modeling of ORR on Mn active sites

For each ORR elementary reaction,
the forward reaction constant is calculated as

$$k = A \cdot \exp(-\frac{E_a(\mathrm{U})}{k_B \mathrm{T}})$$

here, $E_a(\mathrm{U})$ is the activation energy
the backward reaction constant is calculated as

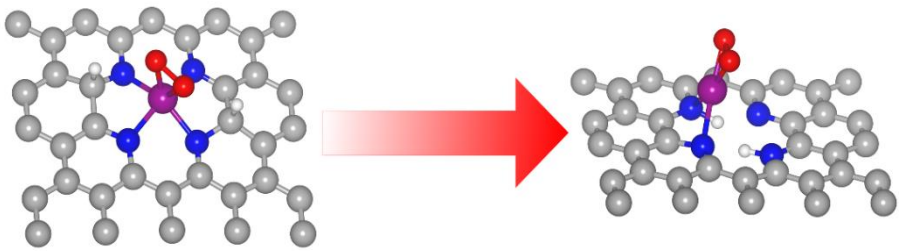
$$k_- = \frac{k}{K} \text{ and } K = \exp(-\frac{\Delta G(\mathrm{U})}{k_B \mathrm{T}})$$

here, $\Delta \mathrm{G}(U)$ is the free energy change
The outputs include polarization curves:

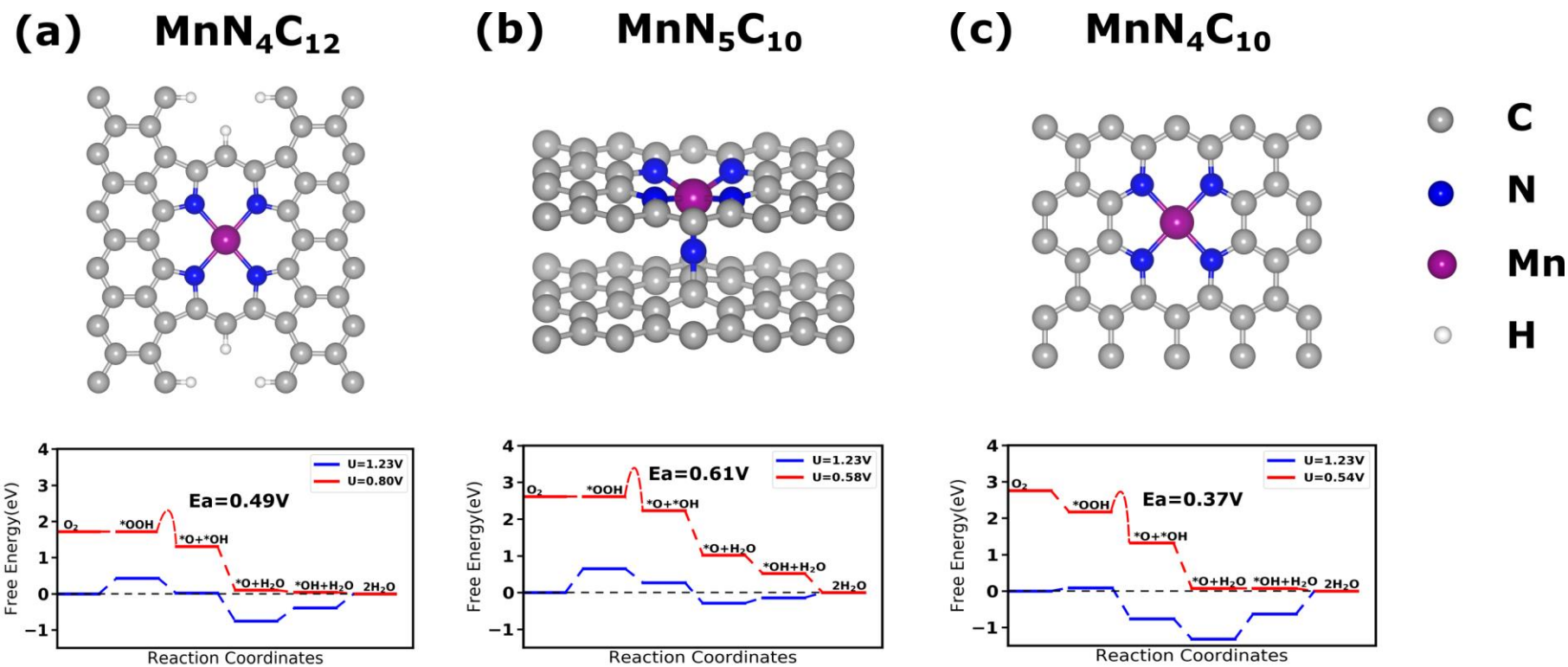
4. Thermodynamic prediction of active site stability

Metal Leaching in form of metal-oxide (MO_2)

$$MN_4RO_2 + 2H^+ + 2e^- = H_2N_4R + MO_2$$



Summary of Activity Predictions



- Three Mn-N_4 sites are predicted to promote 4e- ORR.
- After considering free energy and activation energy, the MnN_4C_{12} is predicted to have the highest activity for oxygen reduction reaction.

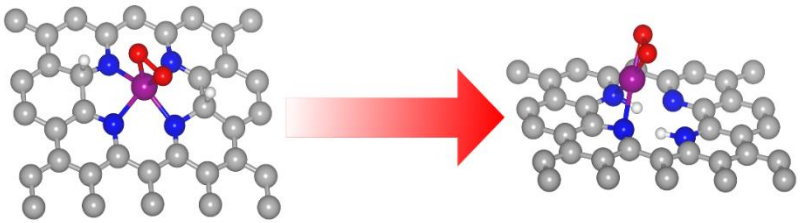
Interplay Between Catalyst Computation and Synthesis

- **In this project, our computational study provides guidance to the catalyst development. Conversely, experimental measurements offers verification and validation to the computational predictions.**

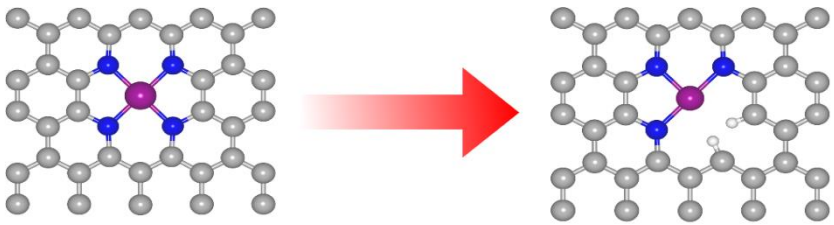
Catalyst Computation	Catalyst Synthesis
Predict that Mn-based PGM-free catalysts exhibit ORR activity	Verified by experimental RDE measurements
Predict that Mn-based PGM-free catalysts catalyze $4e^-$ ORR	Verified by experimental finding of very low H_2O_2 yield
Predict that MnN_4 sites have better ORR activity than MnN_2, MnN_3, and MnN_5 sites	Guide the MOF based catalyst synthesis to maximize the number of MnN_4 sites in the catalysts
Predict that graphitic N doping adjacent to MnN_4 sites could enhance their ORR activity	Guide the catalyst synthesis to include more N-containing precursors
Predict that MnN_4 sites near micropores have enhanced ORR activity	Guide the catalyst synthesis to introduce more micropores in the catalysts
Predict that Mn-based PGM-free catalysts have better stability than Fe-based catalysts	Verified by experimental durability tests

Stability Prediction on Metal Leaching

Metal leaching occurs during O_2 adsorption $MN_4RO_2 + 2H^+ + 2e^- = H_2N_4R + MO_2$

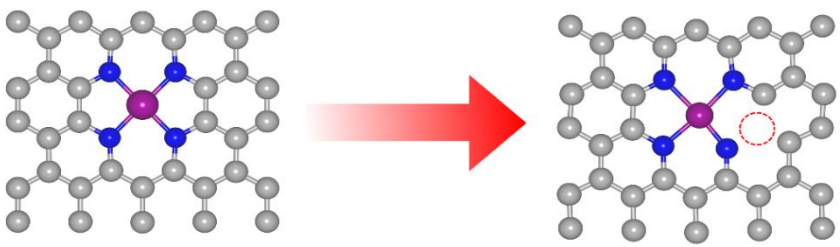


N corrosion reaction: $MN_4R + 5H^+ + 5e^- = NH_3 + MH_2N_3R$



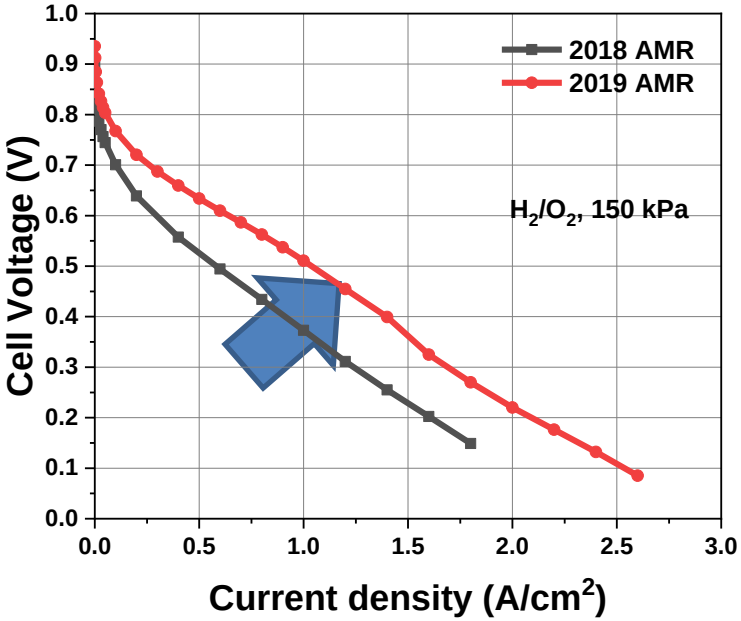
ΔG (kJ/mol)	Mn	Fe	Co
Metal leaching	77.3	16.7	79.8
N-corr	179.4	146.1	100.2
C-corr	126.3	109.5	98.8

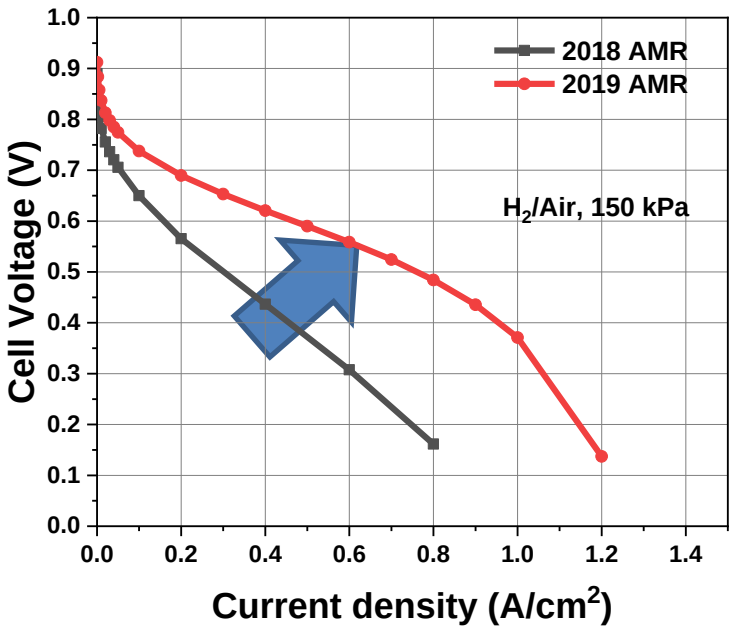
C corrosion reaction: $MN_4R + O_2 = CO_2 + MN_4R'$



- **The metal leaching in the form of MO_2 is found most possible. The trend of resistance to metal leaching is: Co ≈ Mn > Fe**
- **The trend of resistance to N and C corrosion is: Mn > Fe > Co**

Performance Improvement from 2018 to 2019





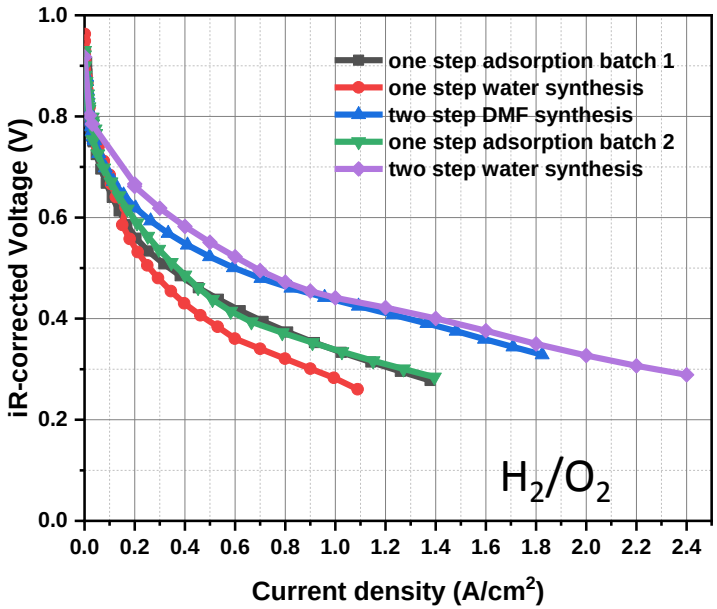
CD (mA/cm^2)	2018 Mn	2019 Mn	Year 1 milestone	Year 2 milestone	Fe catalyst
CD @0.9 V (H_2/O_2)[a, b]	2.0	10.1	10	20	25
CD@0.7V (H2/Air)[a]	55	~ 200	N/A	N/A	330

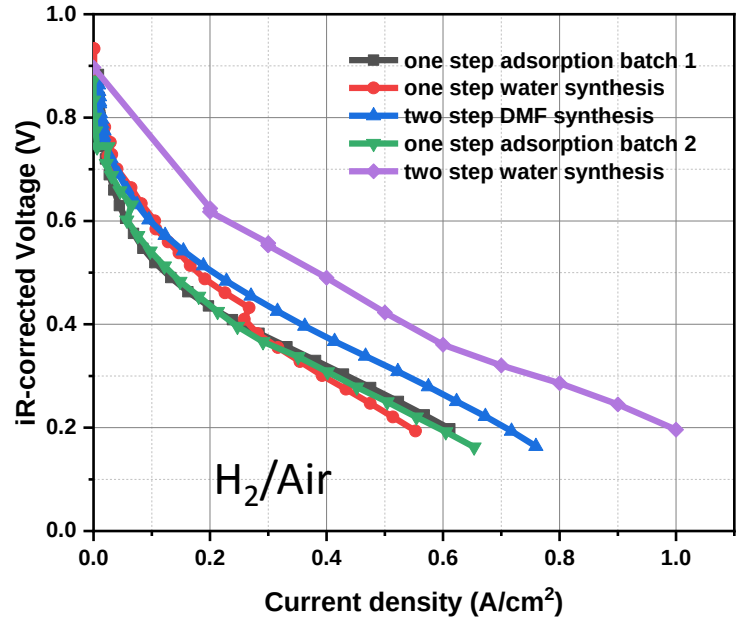
a: 80°C, 100% RH, 0.6 I/C Aquivion, 150 kpa (abs) b: Using Nafion 117 and high catalyst loading (6 mg/cm^2)

- **Significantly performance improvement achieved from 2018 to 2019;**
  - Catalyst synthesis, electrode design and MEA fabrication
- **A gap still exists compared to state-of-the-art Fe catalysts**
  - Low Mn content in catalyst active sites
  - Possible formation of MnOx

Impact of Catalyst Synthesis Route

80°C, 100% RH, 0.6 I/C Aquivion, 150 kpa (abs)

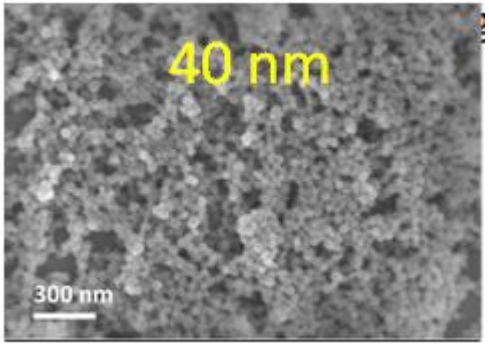


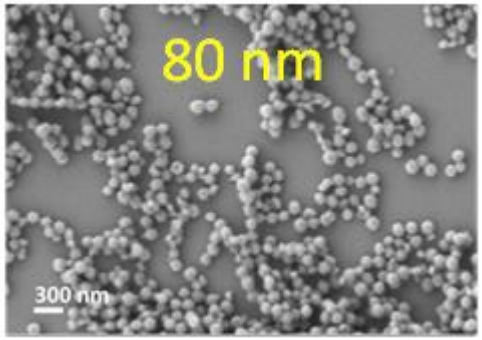


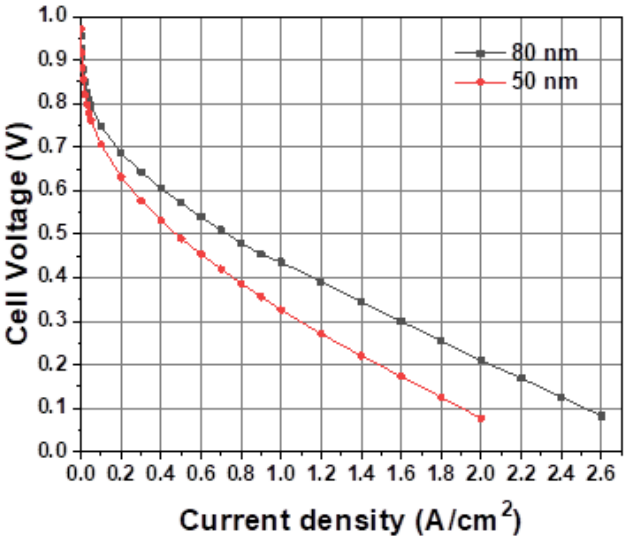
- ❑ Two-step water synthesis > Two–step from DMF > One step adsorption > one step water synthesis
- ❑ Two step introduced more Mn active sites

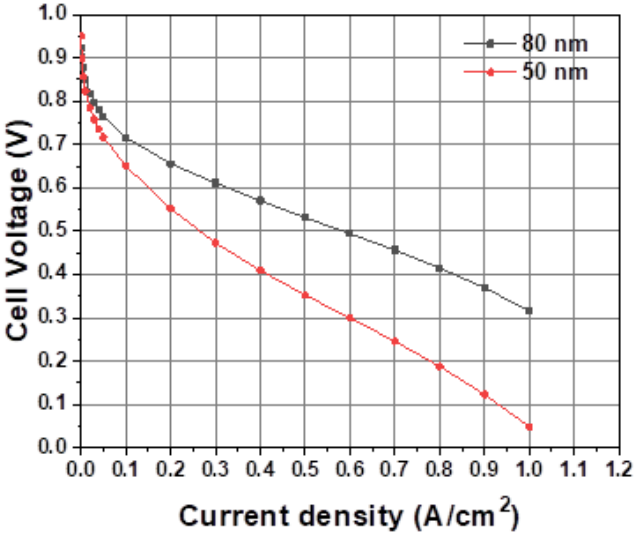
Water-based synthesis not only produces the best performance, but also leads to more environmentally benign process

Impact of Catalyst Particle Size









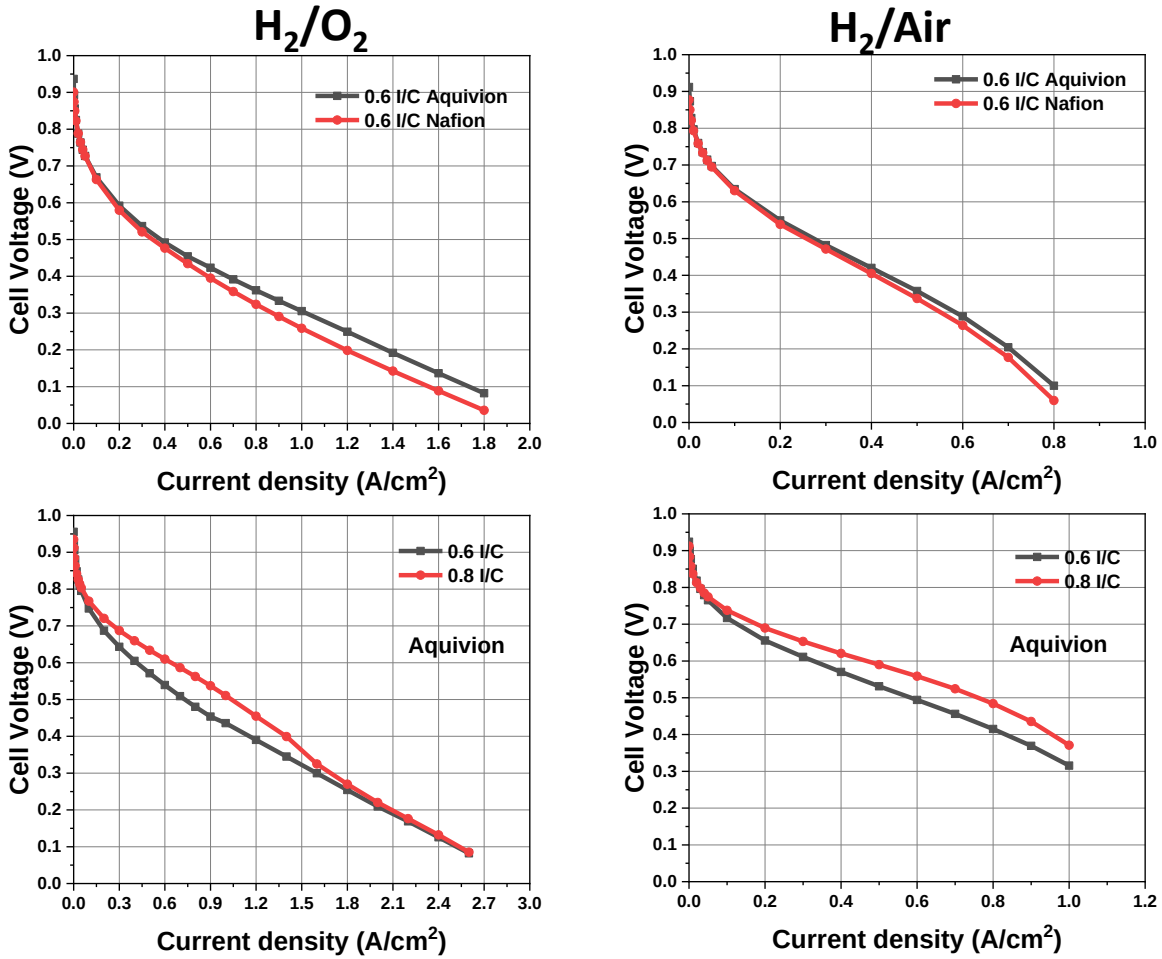
- ❑ Particle size largely impacts performance
  - 80 nm catalyst performs better than 50 nm catalyst
- ❑ Large particles tend to form optimal electrode pore structure

Impact of Ionomers

N211 membrane, 4mg/cm^2 catalyst loading, 0.6 or 0.8 I/C, 150 kPa

I: Ionomer variation (50nm)

II: Ionomer content (80nm)

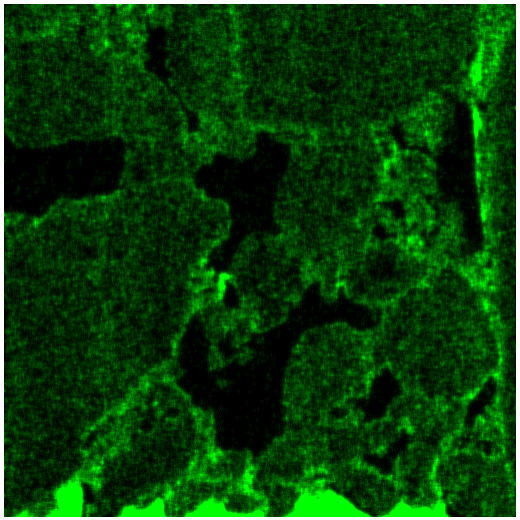


- Ionomer variation and content influences the performance
- Performance difference b/t I and II due to catalyst in various batches

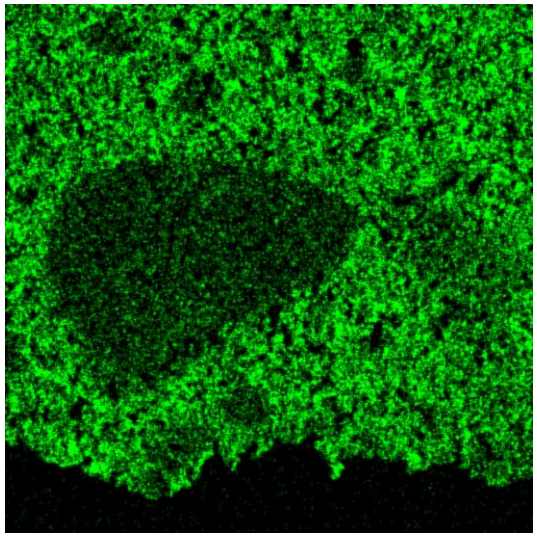
Best performance achieved with 80nm catalyst, Aquivion ionomer and I/C=0.8

Ionomer Distribution in Electrode

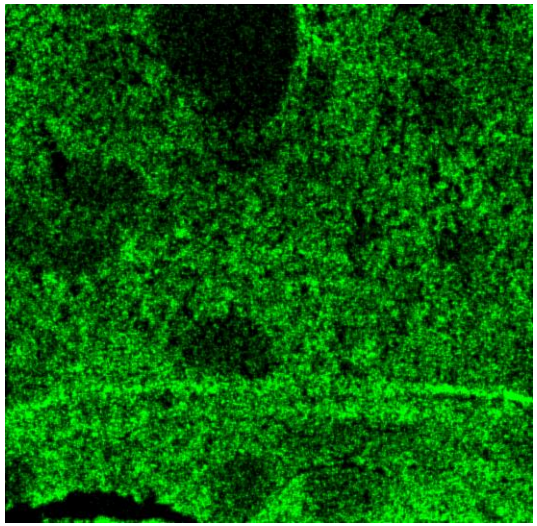
I: MeOH based, Aquivion ionomer



II: Water based, Aquivion ionomer



III: Water based, Nafion ionomer



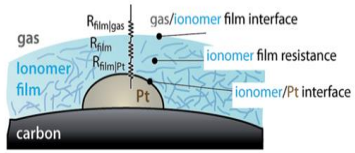
Picture taken by Dr. Karren More @ ORNL

- Left shows large pores between large catalyst agglomerates with ionomer highly concentrated between **large agglomerates**
  - –Little "loose" MOF/ZIF particles between large agglomerates.
  - - Evidence for ionomer within the large agglomerates.
- Middle and right show catalyst agglomerate size is smaller with a lot of "loose" ZIF/MOF particles between larger agglomerates. Ionomer is located primarily in regions with loose catalyst particles (between larger agglomerates).

Strategies to Improve Electrode Structures

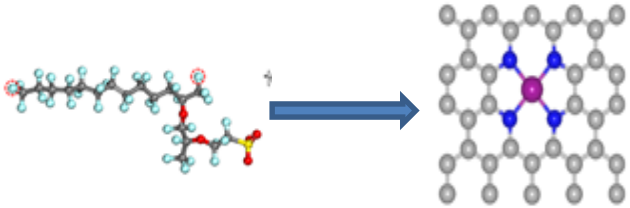
- ❑ Ionomer with higher gas permeability
- ❑ Optimal electrode pore structures for gas and water transport
- ❑ Ionomer utilization

PGM



Weber and Kusoglu ., J. Mater. Chem, 2014: 2, 17207-17211

PGM -free



- **M-N_x active sites are internally embedded in the carbon matrix, likely inaccessible by most ionomer**
- **Over-increasing ionomer content may not help, but may cause transport loss**
- **Ionomer-less (free) electrode concept is being pursued**

Summary

- **Change in Mn-MOF catalyst synthesis led to significantly improved catalyst activity and durability in RDE studies**
  - **Half-wave potential reached 0.82V**
  - Importance of carbon precursors for adsorption
  - Importance of post treatment for adsorption
  - Effect of secondary nitrogen precursors

- **Completed the first-principles DFT calculations to predict nine types of possible active sites in the Mn catalysts**
  - Optimized atomic structural configurations
  - Stable adsorption of O_2, OOH, O, OH and H_2O
  - **Metal leaching and carbon and nitrogen corrosion reduced**

- **MEA evaluation validated RDE results and performance, and performance depended on electrode fabrication and approach**
  - **MEA performance improved to 200 mA/cm^2 at 0.7 V (H_2/air)**
  - Ink preparation and electrode fabrication impacts electrode microstructures
  - MEA conditioning can lead to catalyst structuring
  - Inefficient ionomer interaction without catalyst observed by TEM

Team Collaborations/Project Management

Institutions	Roles
Giner Inc. (Giner) Hui Xu (PI), Fan Yang, Magali Spinetta, and Shirley Zhong	Prime, oversees the project; MEA design and fabrication; performance and durability tests; cost analysis
SUNY -Buffalo(SUNY) Gang Wu (Co-PI), Mengjie Chen, and Jiazhan Li	Mn-based non-PGM catalyst synthesis; RDE screening; MEA test
University of Pittsburgh (UP) Guofeng Wang (Co-PI)	Catalyst and electrode modeling using DFT; molecular dynamics and pore network
General Motors Companies (GM) Anusorn Kongkanand (Co-PI)	MEA optimization; fuel cell system integration and cost analysis

- ❑ Biweekly meeting
- ❑ Biannual visit
- ❑ Quarterly report/project review
- ❑ Meeting with ElectroCat Consortium

Future Work

- **Catalyst Modeling**
  - Catalyst activity: Improve the intrinsic MnN_4 activity and the density of MnN_4 active sites
  - Catalyst durability: Understand the degradation process of Mn-based PGM-free catalyst.
- **Further improve catalyst synthesis**
  - Increase effective Mn doping (current Mn content is low ~ 0.1 at%)
  - Improve catalyst synthesis reproducibility
  - Scale up catalyst synthesis
- **Optimize electrode and MEA design**
  - Ink preparation (different solvent/ionomer)
  - MEA fabrication (spray/brush painting/blade coating)
  - New electrode design (Ionomer -less or -free electrode/pore former)
  - Thick electrode transport studies (O_2 and water)
- **Electrode in-situ and ex-situ characterizations**
  - To correlate electrode microstructures with performance
- **MEA durability test of Mn based catalyst**

Acknowledgments

- Financial support from DOE FCTO Fuel Cell Program under award # DE-EE0008075
- Program Manager
  - Dr. Nancy Garland
- *ElectroCat* Consortium
  - Drs. Piotr Zelenay, Debbie Myers, Karren More and K.C. Neyerlin
- NEU: Drs. Sanjeev Mukerjee and Qingying Jia
- CMY: Dr. Shawn Litster

Collaboration with ElectroCat Electrocatalysis Consortium

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

Responses to Reviewers' Comments from Last AMR

Comment: The main weakness of the project is significant disintegration between the proposed tasks, milestones, and go/no-go decision points. Tasks are not logically connected, and results of milestones do not effect progress toward project goals. As an example, up to now the project did not benefit from DFT calculations.

Response: In this year, we have improved the interplay between Task 2 (synthesis) and Task 1 (computation). For example, the DFT predicts that introducing micropore and more N doping enhances the intrinsic activity of the catalysts. These suggestions have been employed in synthesis. On the other hand, the DFT calculations help to explain the choice of optimal pyrolysis temperature of the synthesis. Mainly, the DFT calculations are used to understand the experimental findings and suggest synthesis targets in this project.

Comment: The project design is based on DFT modeling, which does not take into account the real fuel cell environment, such as the presence of water molecules on the surface and potential. So far, DFT modeling has succeeded mostly in interpreting experimental results rather than in predicting new catalysts.

Response: We have been working on the DFT modeling of the catalyst in real fuel cell operation environment and will report the result in the Year-2 reports (Slide 16)

Comment: Evidence for the need to use Mn-based PGM-free catalysts is somewhat lacking. While Fe is a Fenton's catalyst, it is still unclear whether Fe in current Fe-based PGM-free catalysts really causes increased degradation . The MEA performance of the Mn-based catalyst is concerningly low. Significant improvements are required in the coming months.

Response: Significant performance improvement has been made for both RDE and MEA using newly developed two-step water synthesized Mn-catalyst and optimal electrode design (Slide 19)

Comment: Additional focus should be placed on assessing durability (potential cycling, carbon corrosion) in the MEA to determine the feasibility of the approach for commercial applications**.**

Response: Since highly-active Mn-based catalyst has just been achieved, we will certainly focus on MEA durability in Year-2.

Comment: The computational portion contribution, rigor, and ability to predict are unclear. Since stability and intrinsic performance for Mn systems is unknown, there should be a better effort on this side of things.

Response: Following this suggestion, the DFT calculations have focused on predicting the stability and intrinsic activity of MnN4 active sites in this year. Specifically, we modelled the processes of N corrosion, C corrosion, and metal leaching in the catalysts. Comparing our predictions for Mn, Fe, and Co –based catalysts, we gained mechanistic understanding of the performance degradation of PGM-free catalysts.

Comment: This project has ambitious goals and a substantial breadth of materials options to investigate in a rather limited period of time. The probability of undesirable reactions of the Mn species still seems quite high.

Response: We are aware of the complex challenges of the Mn system and have developed strategies to mitigate MOx formation by controlling Mn-precursor and synthesis conditions