2018 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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Newton, MA

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

June 13, 2018

Project #
FC170

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 $ 239, 075 (by 4/30/2018)

Giner Personnel

- Chao Lei and Magali Spinetta

Collaborators

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

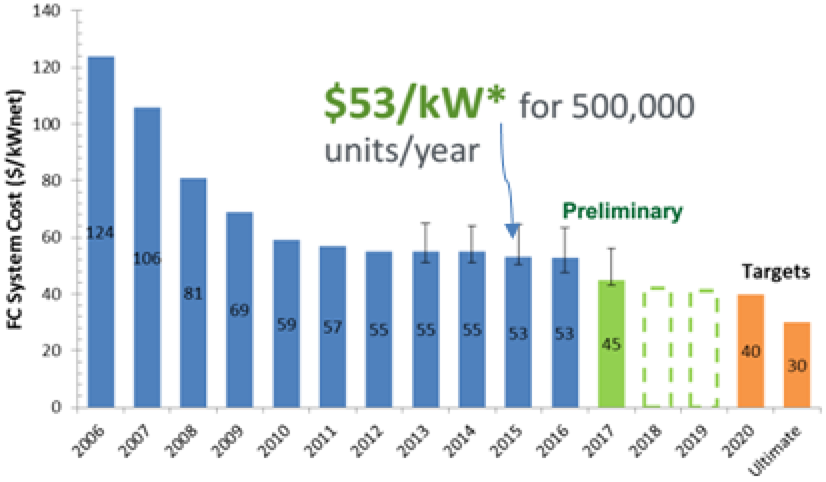
Barriers Addressed

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

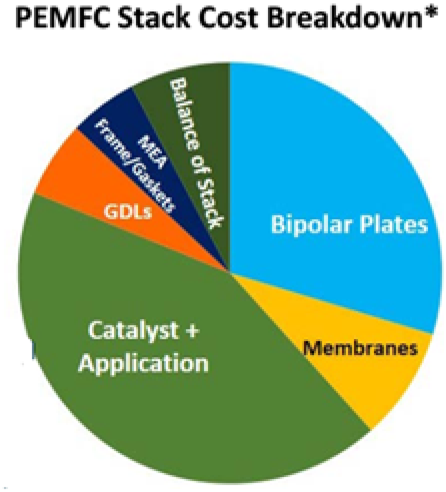
Technical Targets

- Design Mn-based PGM-free catalysts to meet DOE catalyst activity >0.044 A/cm2 @ 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%

Relevance



(From DOE FCTO website)



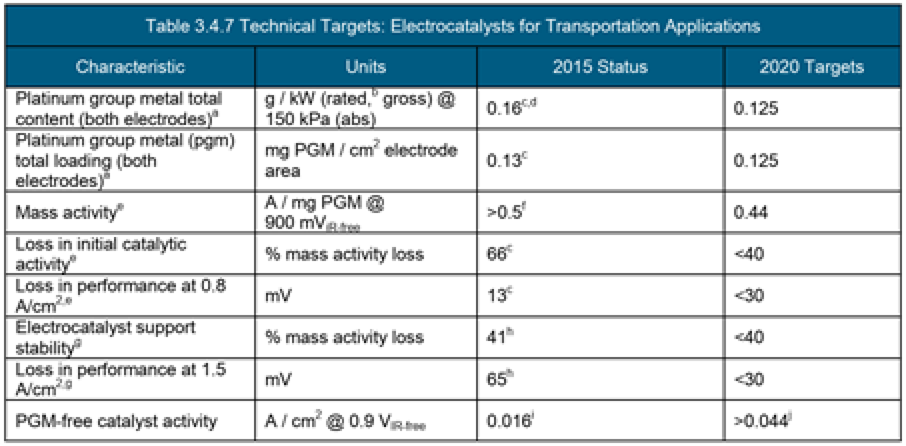


Table 3.4.7 Technical Targets: Electrocatalysts for Transportation Applications			
Characteristic	Units	2015 Status	2020 Targets
Platinum group metal total content (both electrodes)[a]	g / kW (rated,[b] gross) @ 150 kPa (abs)	0.16[c,d]	0.125
Platinum group metal (pgm) total loading (both electrodes)[a]	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[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^2 @ 0.9 $V_{iR\text{-}free}$	0.016[i]	>0.044[j]

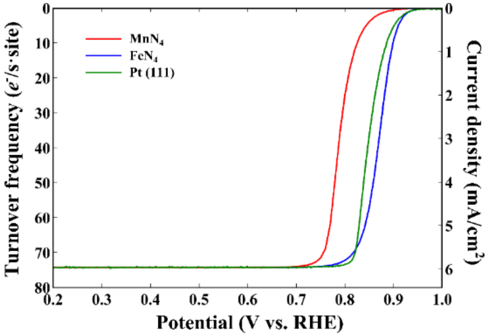
Ballard FCgen®-1040 prototype fuel cell stack, with Non Precious Metal Catalysts

- ❑ 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

Motivation

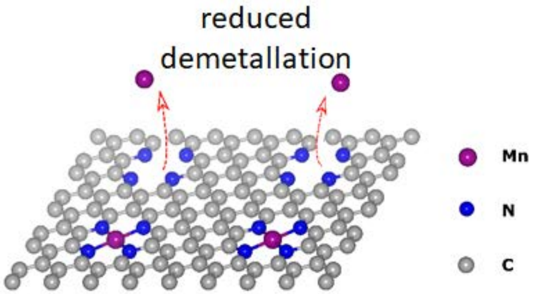
❑ PGM Catalyst
- High cost
- Scarcity
- Catalyst poisoning

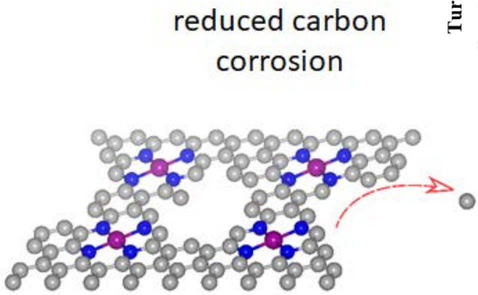
❑ Fe Based PGM-free Catalyst
- Insufficient stability
- Membrane degradation



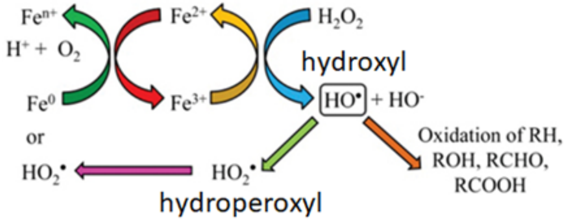
❑ **Mn Based PGM-free Catalyst**

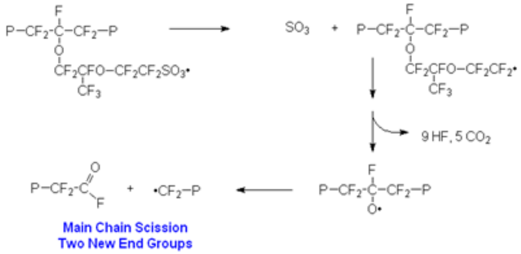
- Catalyst Design: Improving Durability



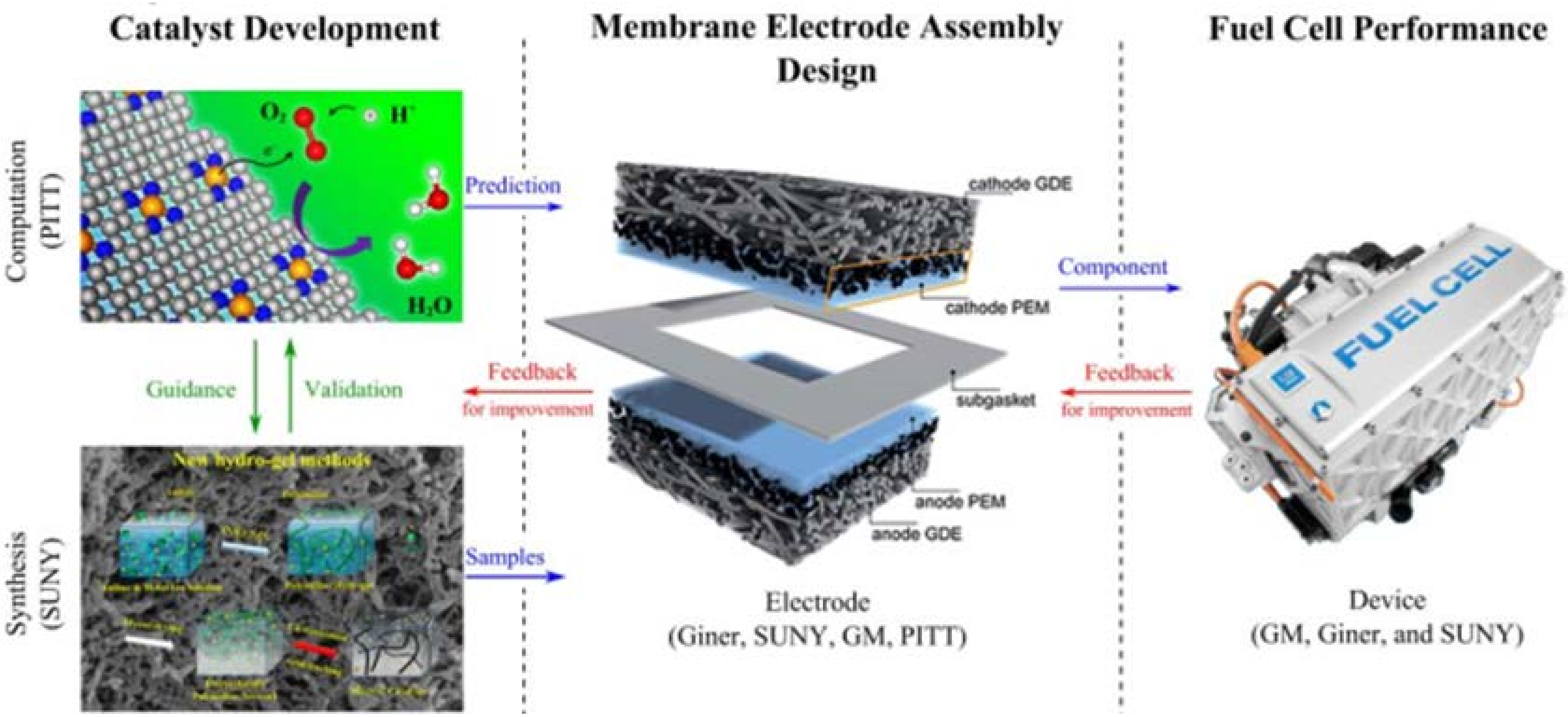


- MEA Design: Reducing PEM degradation





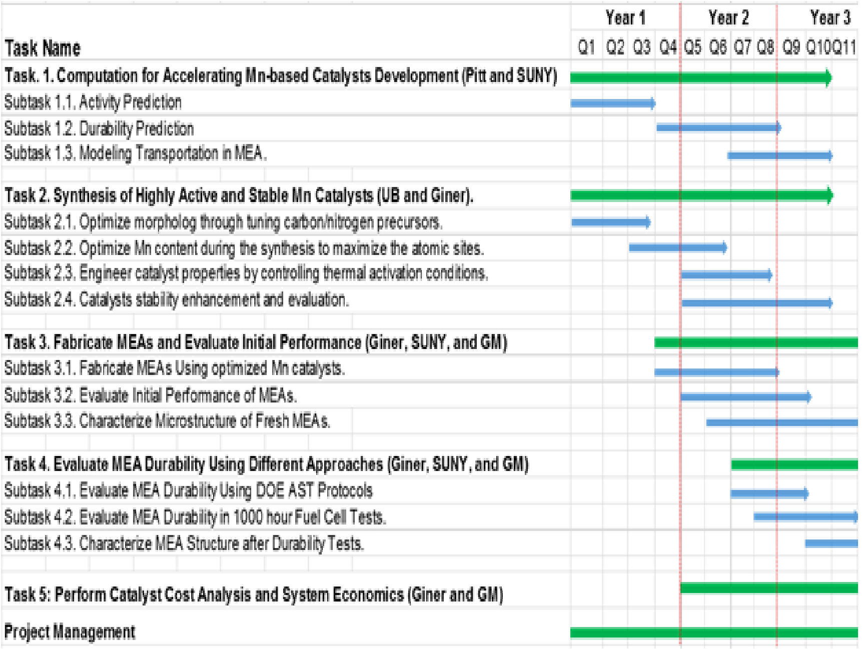
Technical Approach



A strong team was formed to transform the discovery of Mn-based catalyst into fuel cell application with expertise in the following areas:

☐ Catalyst modeling
☐ Catalyst synthesis
☐ MEA fabrication
☐ Fuel cell system integration

Tasks, Milestones, and Performance Period



Task Name

Task. 1. Computation for Accelerating Mn-based Catalysts Development (Pitt and SUNY)
Subtask 1.1. Activity Prediction
Subtask 1.2. Durability Prediction
Subtask 1.3. Modeling Transportation in MEA.

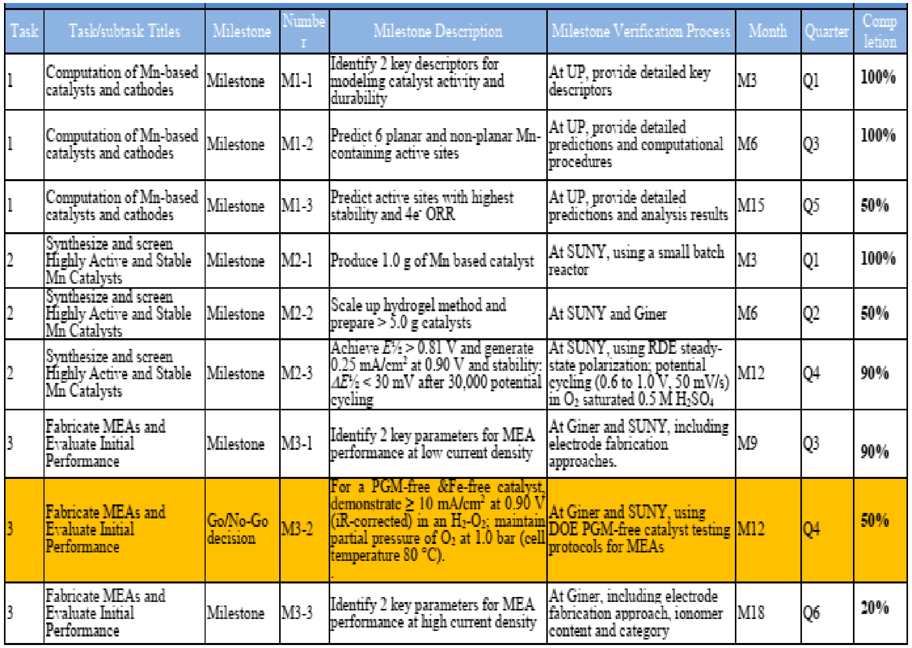
Task 2. Synthesis of Highly Active and Stable Mn Catalysts (UB and Giner).
Subtask 2.1. Optimize morpholog through tuning carbon/nitrogen precursors.
Subtask 2.2. Optimize Mn content during the synthesis to maximize the atomic sites.
Subtask 2.3. Engineer catalyst properties by controlling thermal activation conditions.
Subtask 2.4. Catalysts stability enhancement and evaluation.

Task 3. Fabricate MEAs and Evaluate Initial Performance (Giner, SUNY, and GM)
Subtask 3.1. Fabricate MEAs Using optimized Mn catalysts.
Subtask 3.2. Evaluate Initial Performance of MEAs.
Subtask 3.3. Characterize Microstructure of Fresh MEAs.

Task 4. Evaluate MEA Durability Using Different Approaches (Giner, SUNY, and GM)
Subtask 4.1. Evaluate MEA Durability Using DOE AST Protocols
Subtask 4.2. Evaluate MEA Durability in 1000 hour Fuel Cell Tests.
Subtask 4.3. Characterize MEA Structure after Durability Tests.

Task 5: Perform Catalyst Cost Analysis and System Economics (Giner and GM)

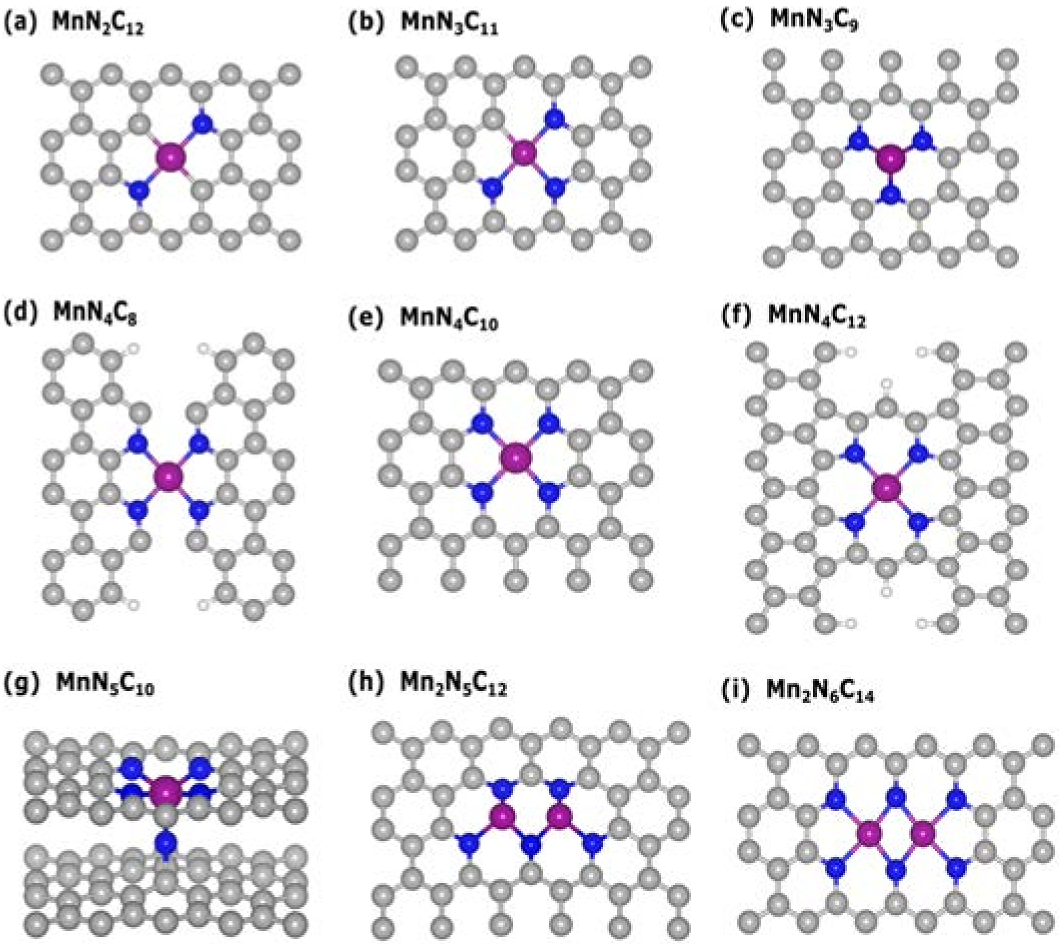
Project Management



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	**50%**
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	**50%**
2	Synthesize and screen Highly Active and Stable Mn Catalysts	Milestone	M2-3	Achieve $E_{½}$ > 0.81 V and generate 0.25 mA/cm^2 at 0.90 V and stability: $\Delta E_{½}$ < 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	**90%**
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	**90%**
3	Fabricate MEAs and Evaluate Initial Performance	Go/No-Go decision	M3-2	For a PGM-free &Fe-free catalyst, demonstrate ≥ 10 mA/cm^2 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	**50%**
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	**20%**

All the milestones are on track!

Model of Nine Possible Active Sites



- **(a) MnN_2C_{12} site**: single Mn with two N;
- **(b) MnN_3C_{11} site**: single Mn with three N;
- **(c) MnN_3C_9 site**: single Mn with three N;
- **(d) MnN_4C_8 site**: single Mn with four N; N are on six-carbon rings; at pore edge;
- **(e) MnN_4C_{10} site**: single Mn with four N; N are on six-carbon rings; inside basal plane;
- **(f) MnN_4C_{12} site**: single Mn with four N; N are on five-carbon rings;
- **(g) MnN_5C_{10} site**: single Mn with five N;
- **(h) $Mn_2N_5C_{12}$ site**: double Mn with five N;
- **(i) $Mn_2N_5C_{14}$ site**: double Mn with six N.

*** Gray, blue, purple, and white balls represent C, N, Mn, and H atoms, respectively**

Met Milestone 1-2: Predict 6 planar and non-planar Mn-containing active sites

Modeling Results

Adsorption Energy

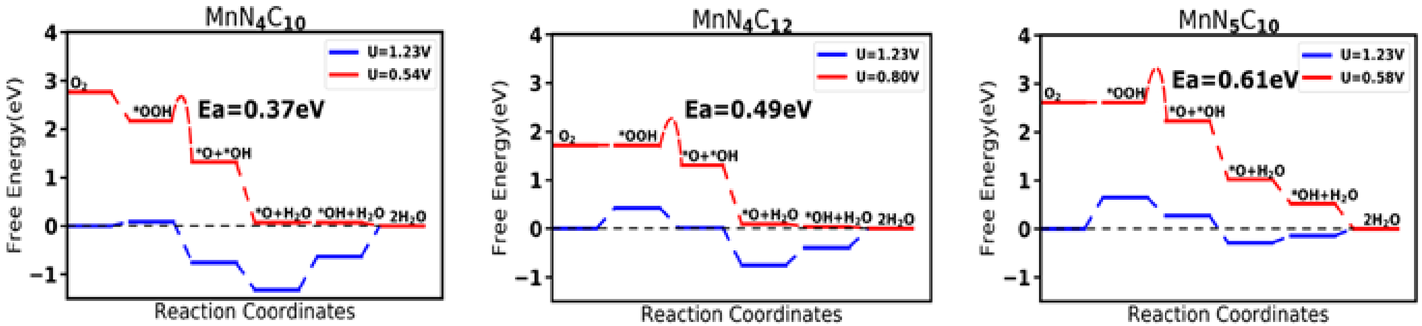
		E_{ad} (eV)	O_2	OOH	O	OH	H_2O
		MnN_2C_{12}	- 2.10	- 2.17	- 5.35	- 3.23	- 0.49
		MnN_3C_9	- 3.20	- 2.93	- 6.44	- 4.09	- 0.55
		MnN_3C_{11}	- 1.75	- 1.59	- 5.05	- 3.06	- 0.36
		MnN_4C_8	- 2.26	- 2.30	- 4.70	- 3.68	- 0.25
Single metal sites	✓	MnN_4C_{10}	- 1.27	- 1.62	- 4.40	- 2.77	- 0.26
	✓	MnN_4C_{12}	- 0.87	- 1.31	- 3.86	- 2.56	- 0.32
	✓	MnN_5C_{10}	- 2.26	- 1.08	- 3.37	- 1.75	- 0.02
		$Mn_2N_5C_{12}$	- 2.92	- 6.12	- 6.47	- 4.31	- 0.35
Double metal sites	✓	$Mn_2N_6C_{14}$	- 1.42	- 3.11	- 4.12	- 2.70	- 0.31

🟥 indicates too strong binding with H_2O

🟦 indicates too strong binding with OH

✓ indicates good active site candidates for ORR

Free Energy

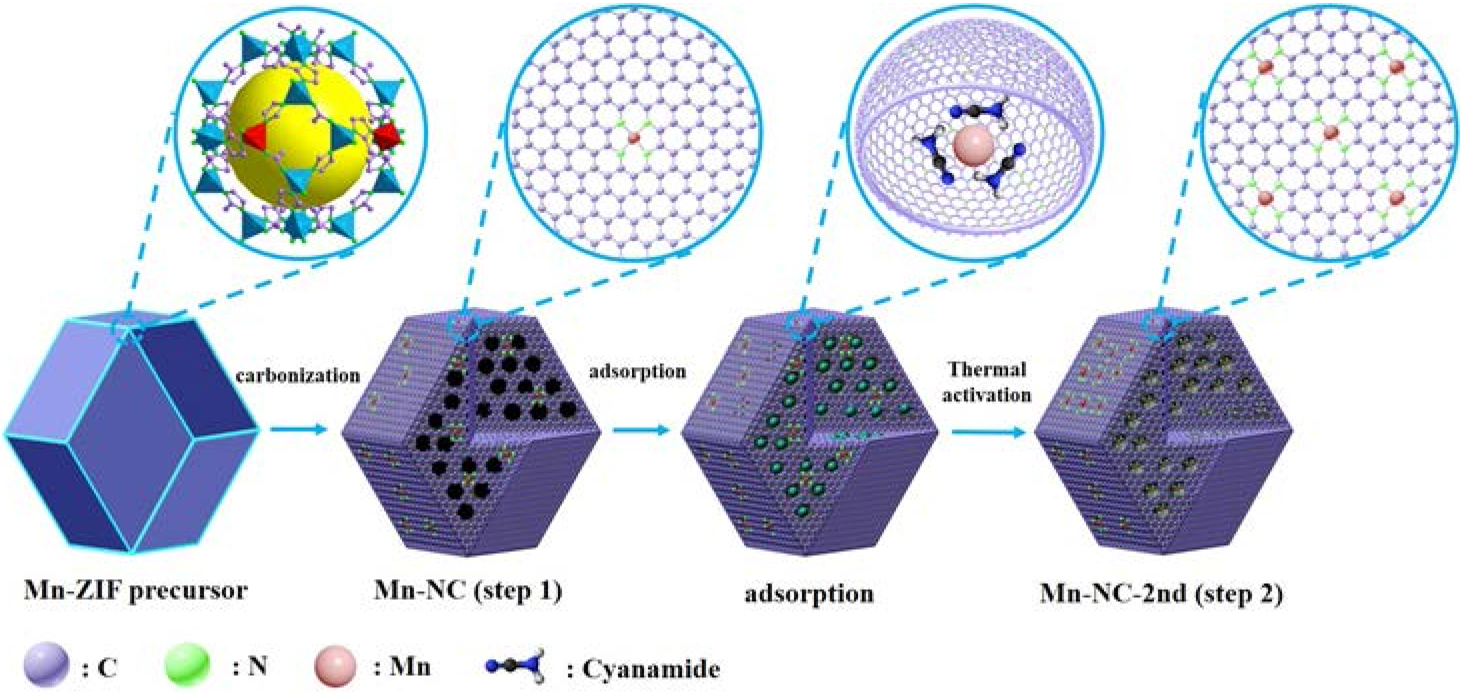


- ☐ Free energy keeps decreasing under the electrode potentials
  - Below 0.54 V on MnN_4C_{10}, 0.80 V on MnN_4C_{12} and 0.58 V on MnN_5C_{10}
- ☐ These three single metal sites all are active for ORR
- ☐ MnN_4C_{12} being the most promising one.

Met Milestone 1-1: Identify 2 key descriptors for modeling catalyst activity and durability

Two Step Approach to Introduce More Mn Ions

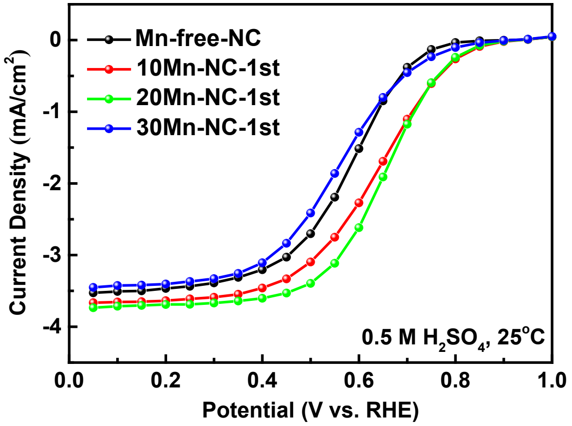
Schematic diagram for adsorbing method to introduce more Mn ions into the pore of Manganese-nitrogen doped carbon (Mn-NC)



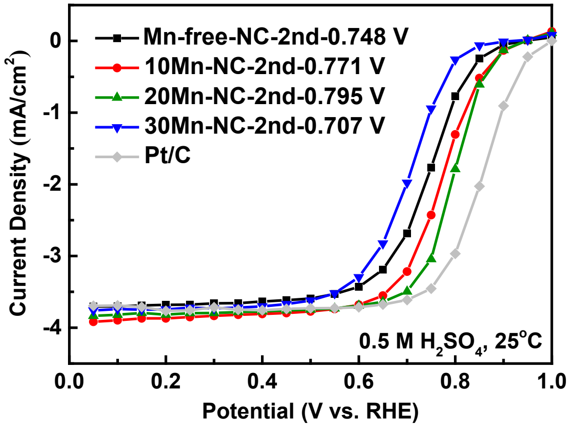
- ☐ **Unfavorable for Mn ions to replace original Zn, previous one-step chemical doping method is not efficient ($E_{1/2}$= 0.7 V).**
- ☐ **Mn-NC possesses abundant micropores doped with N, which enables the adsorption of additional Mn and N.**

RDE Activity for ORR during Synthesis Steps

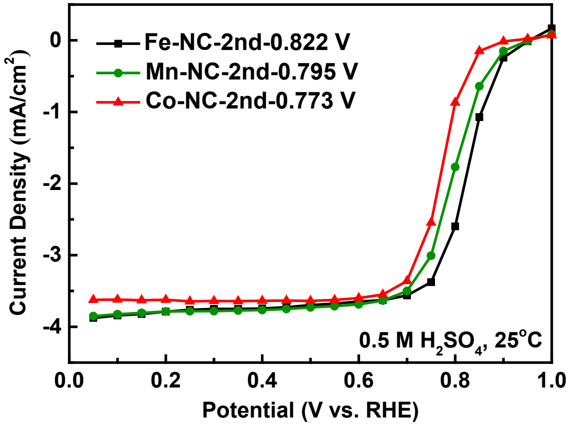
Step 1

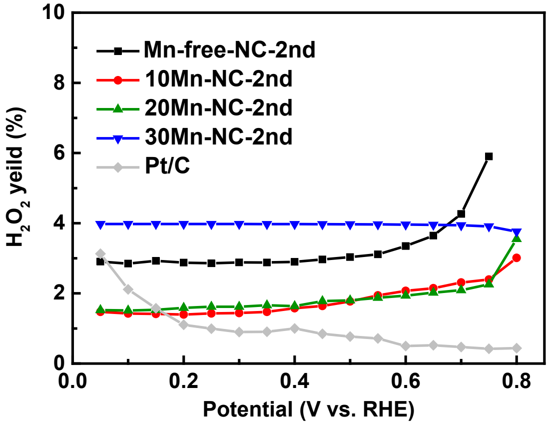


Step 2



Comparison: Fe, Co, and Mn



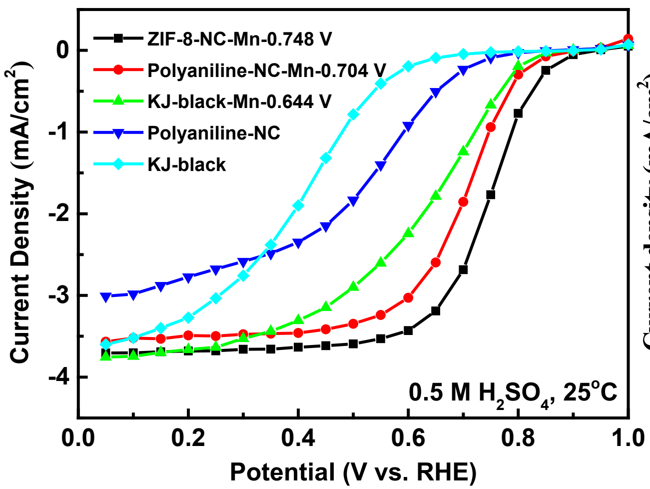


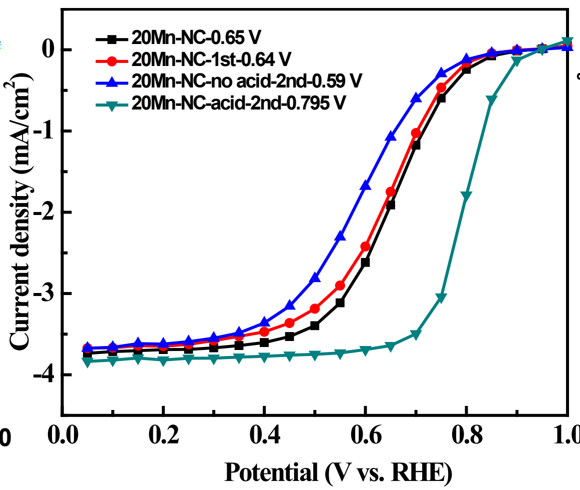
Electrolyte: 0.5 M H_2SO_4, 25 °C, 900 rpm, catalyst loading: 0.8 mg/cm^2

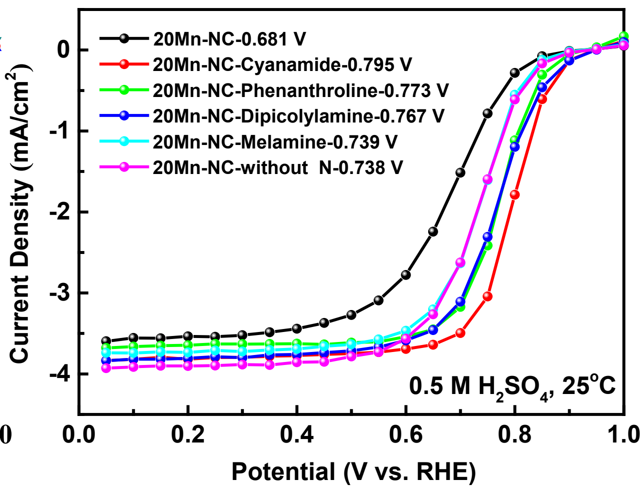
- **Using Mn-NC derived from Mn-doped ZIF as precursors, the performance shows a significant enhancement after the secondary adsorption step, indicating that the adsorption method is efficient to introduce more active sites.**
- **Pre-doping content of Mn during the *step 1* was found critical for catalyst performance after *step 2* adsorption; 20 wt. % Mn precursor exhibit the best activity close to a half-wave potential of 0.80 V.**

Technical Accomplishment

Effect of Carbon /Acid Leaching/Nitrogen Precursors

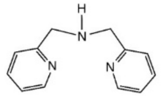

Effect of carbon support


Effect of acid leaching

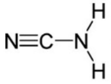

Effect of nitrogen precursors

- ❑ N-doping and micropores are crucial for ***step 2*** adsorption with enhanced activity.
- ❑ Acid leaching after ***step 1*** doping doesn't change the activity, it's essential for ***step 2***.
- ❑ The best performance was obtained from cyanamide as nitrogen source due to its smaller geometry and/or C≡N structures

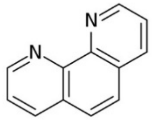
Dipicolylamine



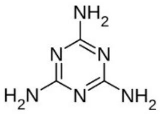
Cyanamide



phenanthroline



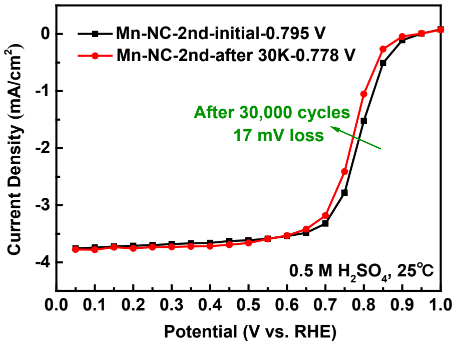
Melamine

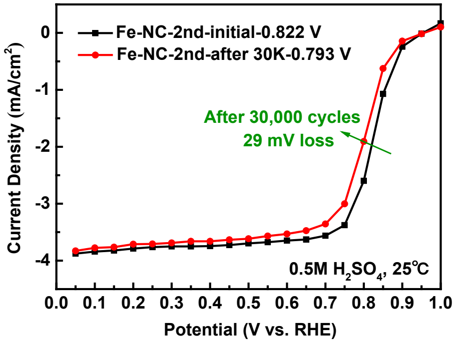


RDE Constant and Cycling Potential Stability

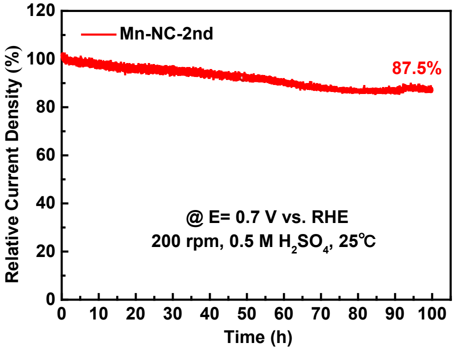
* After each 20 hours test, potential cycling from 0 to 1.0 V about 10 cycles was performed to refresh the electrode. Partial activity is recovered due to possible adsorption oxygen functional groups on active sites.

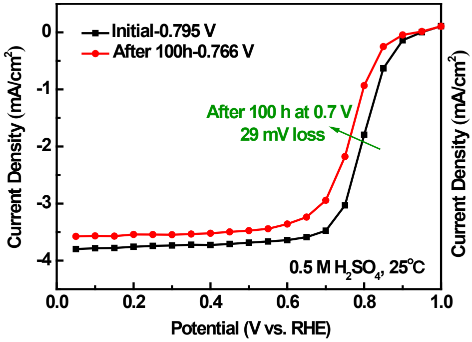
Potential cycling: 0.6-1.0 V, 30 k



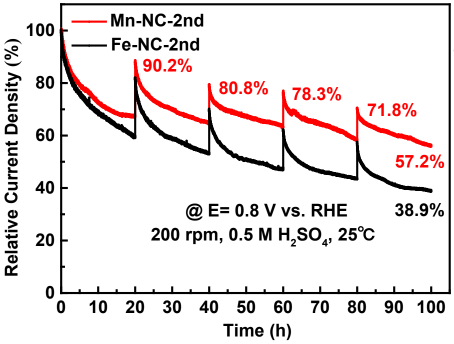


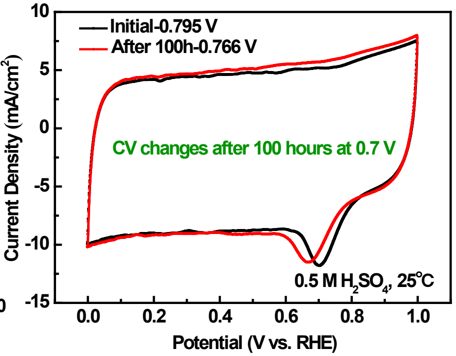
Constant *E* at 0.7 V



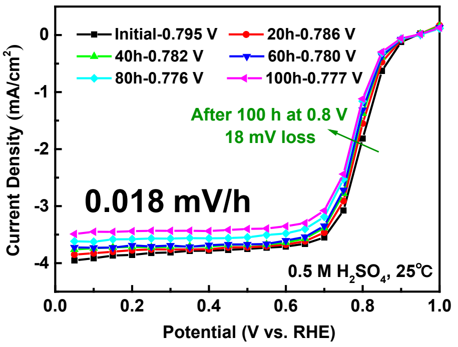


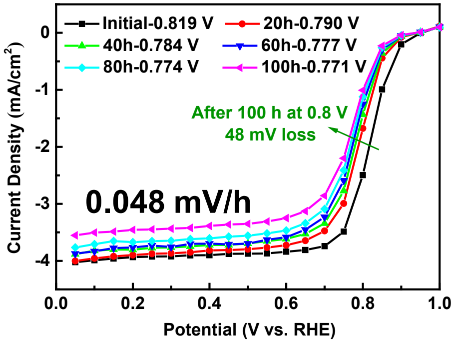
Constant *E* at 0.8 V*





ORR polarization plots

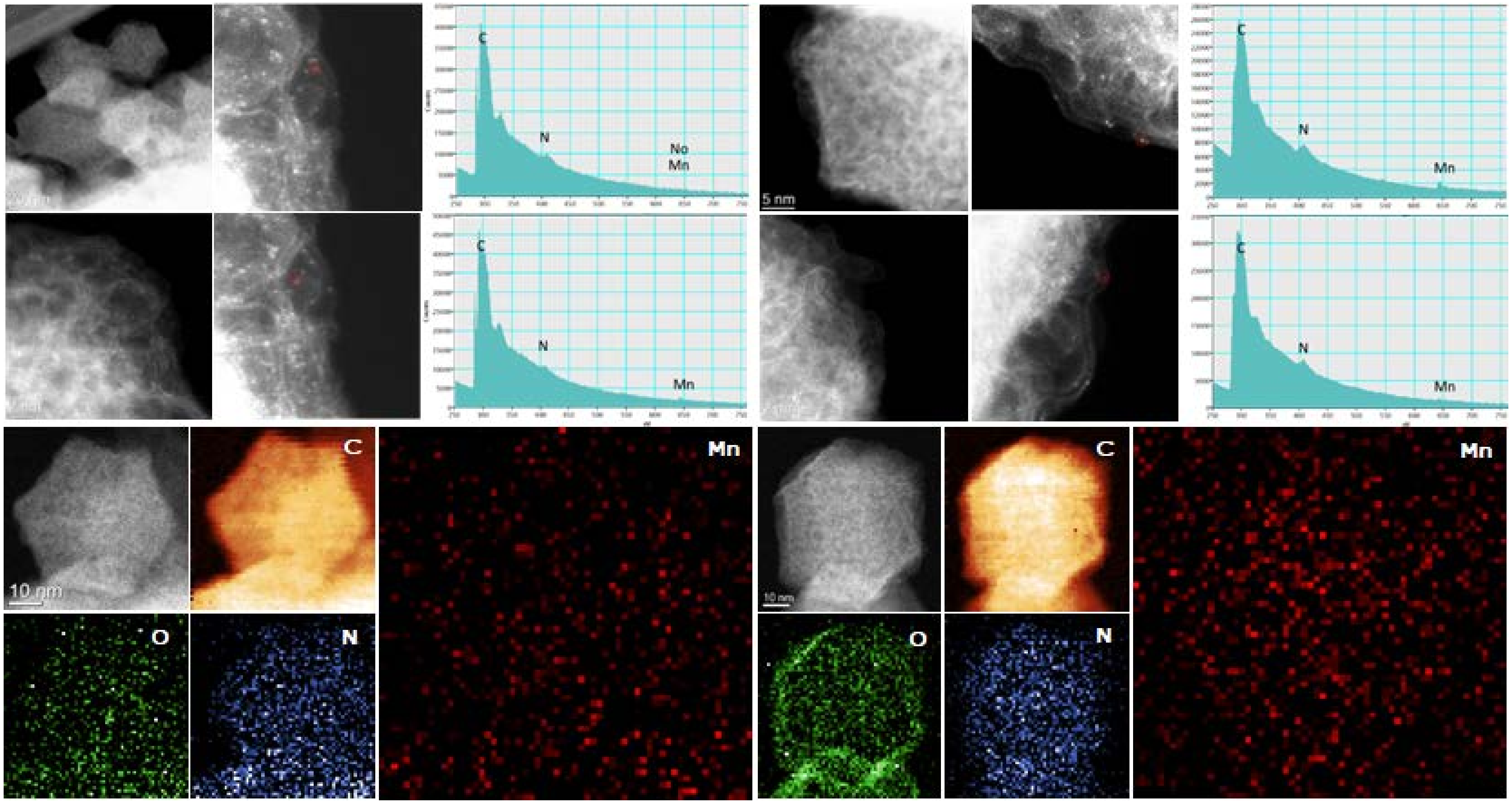




- ☐ With stable Mn-N_x active sites and corrosion-resistant structure, Mn-NC catalyst showed enhanced stability compared to Fe-NC .

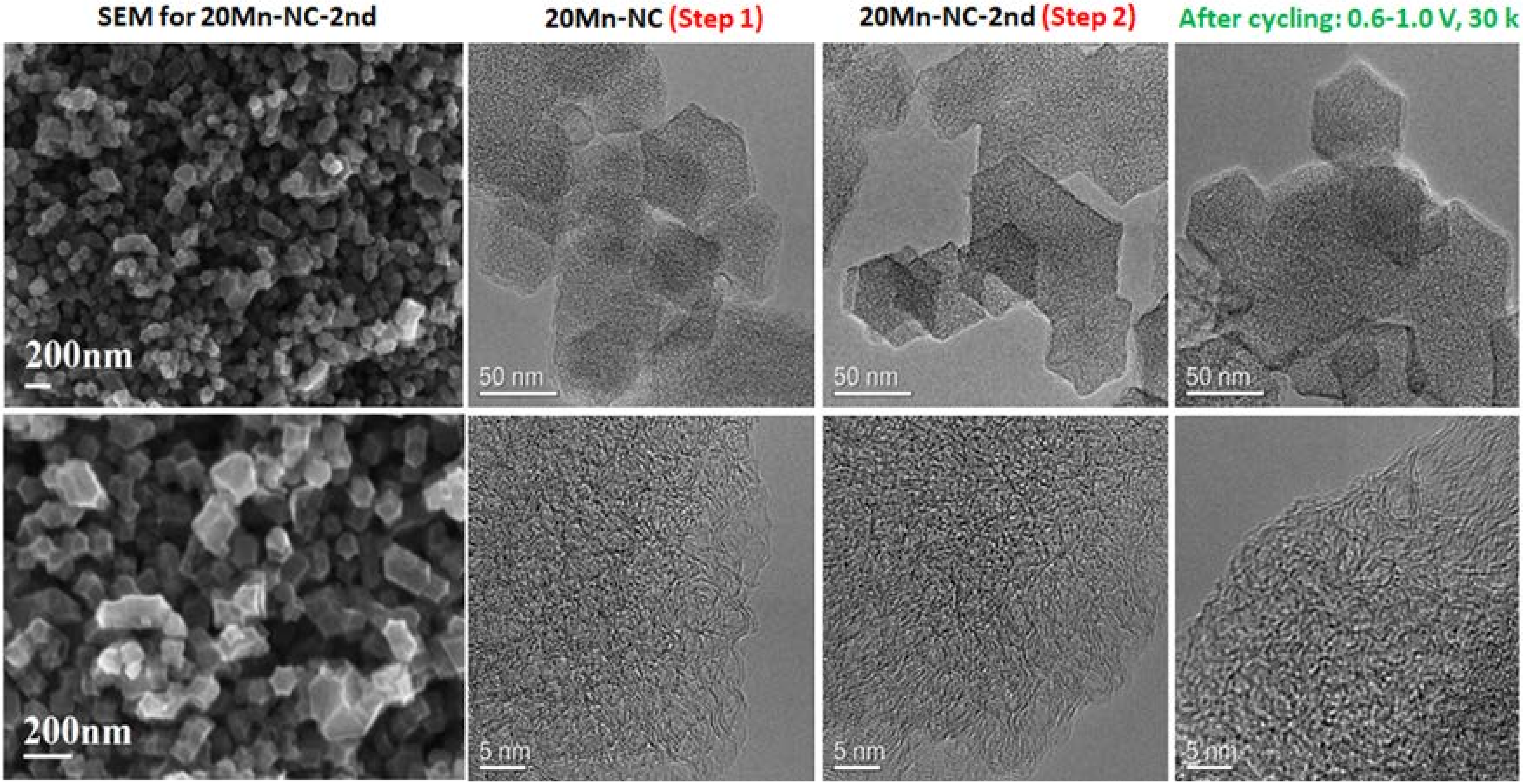
Mostly Met Milestone 2-3: achieve *E½* > 0.81 V and generate **0.25 mA/cm^2** at 0.90 V and stability: ***ΔE½* < 30 mV** after 30,000 potential cycling

Structures and Morphologies During Synthesis



☐ Atomically dispersed Mn-N sites were observed by EELS, and Mn signals become much stronger after adsorption

Structures and morphologies during Synthesis and Stability Test



SEM for 20Mn-NC-2nd

20Mn-NC (Step 1)

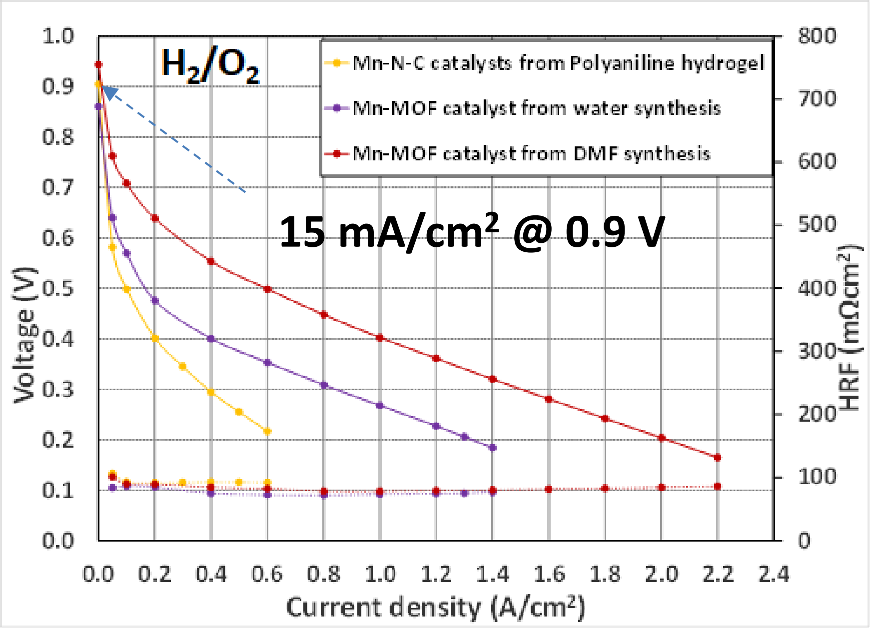
20Mn-NC-2nd (Step 2)

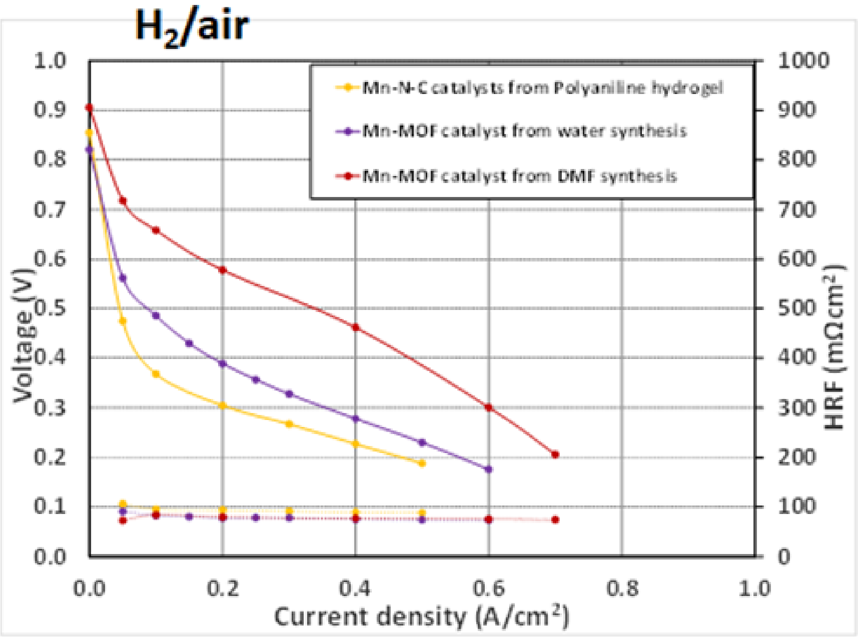
After cycling: 0.6-1.0 V, 30 k

- ❑ **Homogeneous polyhedron carbon particles with abundant micropores appeared on surface.**
- ❑ **Microstructures exhibited excellent carbon corrosion resistance during the potential cycling.**

MEA Performance- Synthesis Route Impact

Anode: 0.25 mg_{Pt} cm^{-2} Pt/C H_2, 200 sccm, **1.0 bar** H_2 partial pressure; **Cathode:** *ca.* 4.0 mg cm^{-2} O_2, 200 sccm, **1.0 bar** O_2 partial pressure; **Membrane: Nafion®212**; **Cell:** 80°C, 100%RH



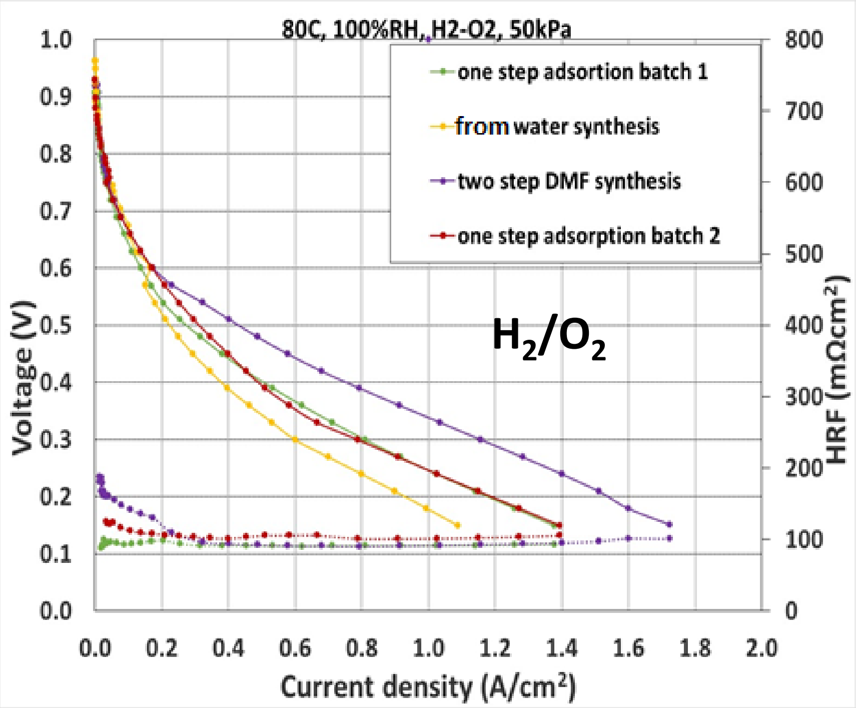


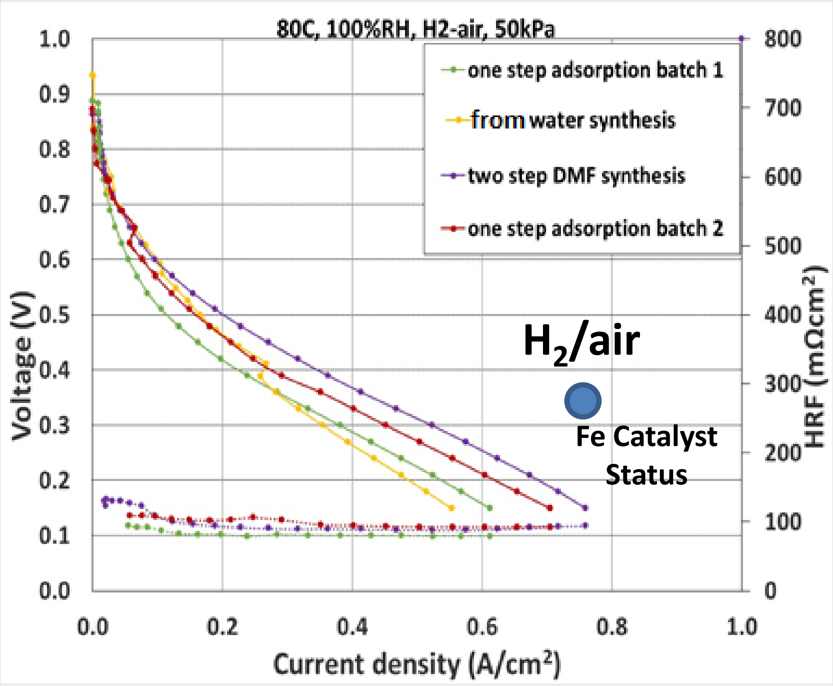
- ❑ **Performance ranking: DMF synthesis > Water synthesis > Polyaniline hydrogen synthesis**
- ❑ **Benefits of using MOF to produce highly active Mn-N-C catalysts for ORR, likely due to their well-defined structure, high surface area and porous structure.**

Met Year 1 GO/NO GO decision point: 10 mA/cm² @ 0.9 V

MEA Performance- Synthesis Route Impact

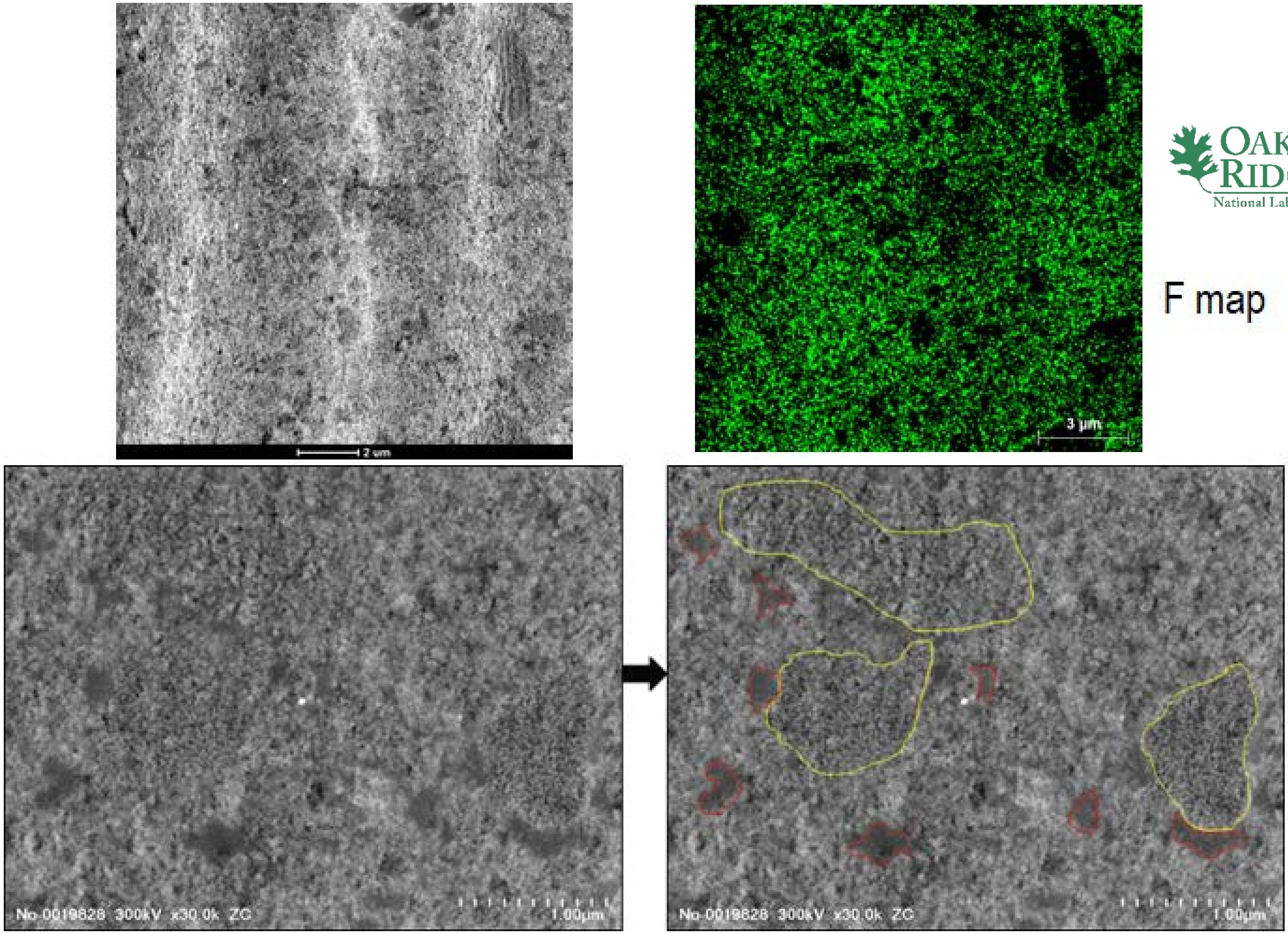
Anode: 0.25 $mg_{Pt}\,cm^{-2}$ Pt/C H_2, 200 sccm, **1.0 bar** H_2 partial pressure; **Cathode:** *ca.* 4.0 mg cm^{-2} O_2 or air, 200 sccm, **1.0 bar** O_2 or air partial pressure; **Membrane:** **Nafion®·212**; **Cell:** 80°C, 100%RH





- ☐ Performance ranking: Two–step from DMF > One step adsorption > from Water synthesis:
  - Two step introduced more Mn active sites
  - Consistent with RDE results
- ☐ Still Big gap from Fe-Based Catalyst
  - Catalyst activity improvement needed
  - MEA design to maximize the utilization of active sites

Electrode Structure: HAADF-STEM Image



F map

OAK RIDGE
National Laboratory

MEA #7-4: UB-Mn-ZIF-8-ZQ (one step adsorb method) catalyst

- ☐ Agglomerated ZIF particles observed in catalyst layer with little ionomer infiltration
- ☐ F map shows lack of ionomer within ZIF agglomerates

Summary

❑ **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
- Free energy evolution for four-electron
- Activation energy for the ORR elementary steps

❑ **Change in Mn-MOF catalyst synthesis led to significantly improved catalyst activity and durability in RDE studies**

- Importance of carbon precursors for adsorption
- Importance of post treatment for adsorption
- Effect of secondary nitrogen precursors
- Role of pre-doped Mn in the first step

❑ **MEA evaluation validated RDE results and performance, and performance depended on electrode fabrication and approach**

- Ink preparation and electrode fabrication impacts electrode microstructures
- MEA conditioning can lead to catalyst structuring
- Inefficient ionomer interaction without catalyst observed by TEM

Future Work

☐ Catalyst Modeling

- Catalyst: To achieve high activity and durability simultaneously
- Electrode: Structure affects MEA performance

☐ 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
- Ionomer effect
- New electrode design(e.g., Ionomer -less or -free electrode design)
- Thick electrode transport studies (O_2 and water)

☐ Electrode in-situ and ex-situ characterizations

- To correlate electrode microstructures with performance

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

Team Collaborations/Project Management

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

☐ Biweekly meeting
☐ Biannual visit

☐ Quarterly report/project review
☐ Meeting with ElectroCat Consortium

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

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- Collaborators
  - Dr. Guofeng Wang (UP)
  - Dr. Gang Wu (UB)
  - Dr. Anusorn Kongkanand (GM)
- Giner Personnel
  - Drs. Chao Lei, Shuai Zhao and Cortney Mittelsteadt