GINER

University at Buffalo
*The State University of New York*

University of Pittsburgh

GM

2020 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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**Giner Inc.**
**Newton, MA**

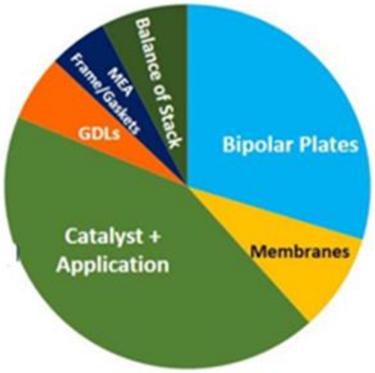
May 20, 2020

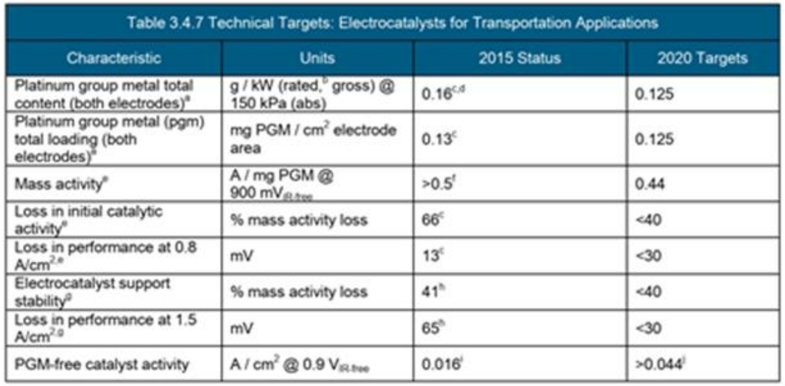
Project #
FC170

# Relevance

(From DOE FCTO website)

PEMFC Stack Cost Breakdown*





| 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

# Overview

## Timeline

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

## Budget

- Total $2.49 million
  - DOE share $1.99 million
    cost sharing $500K
  - Spent $ 1.73 million
    (by 5/14/2020)

## Collaborators

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

# Milestones and Project Progress

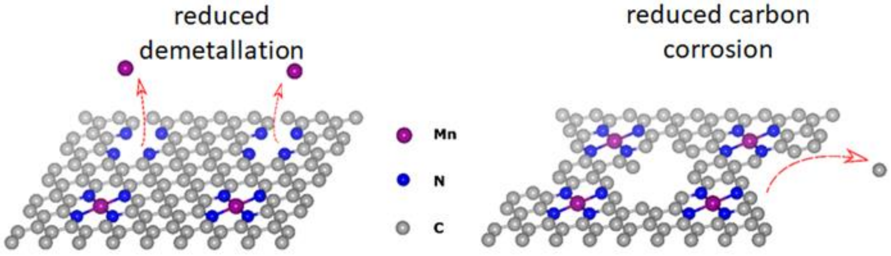
| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| **Milestone Summary** | | | | | | | | | |
| **Recipient Name:** | | | **Giner, Inc.** | | | | | | |
| **Project Title:** | | | **Durable Mn-based PGM-Free Catalysts for Polymer Electrolyte Membrane Fuel Cells** | | | | | | |
| Task | Task/subtask 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 $4e^-$ 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% | In Progress |
| 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% | In progress |
| 2 | Synthesize and screen Highly Active and Stable Mn Catalysts | Milestone | M2-5 | Achieve stability $\Delta E½ < 10$ 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 | 100% | Complete |
| 2 | Synthesize and screen Highly Active and Stable Mn Catalysts | Milestone | M2-6 | Achieve $E_{½} \geq$ 0.85 V; generate 0.75 mA/cm$^2$ at 0.90 V; | At SUNY, using RDE steady-state ORR polarization | M30 | Q10 | 40% | In Progress |
| 3 | Fabricate MEAs and Evaluate Initial Performance | Go/No-Go decision | M3-4 | For a PGM-free & Fe-free catalyst, demonstrate ≥ 20 mA/cm$^2$ 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 | 100% | Completed |
| 3 | Fabricate MEAs and Evaluate Initial Performance | Milestone | M3-5 | 1.0 A/cm$^2$ 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 ≥ 30 mA/cm$^2$ at 0.90 V (iR-corrected) in an $H_2$-$O_2$ fuel cell and 150 mA/cm$^2$ 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 | 50% | In Progress |
| 4 | Evaluate MEA Durability Using Different Approaches | Milestone | M4-1 | MEA durability: $\Delta V < 30\ mV$ at 0.044 A/cm$^2$; activity loss < 100 mA/cm$^2$ 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 | 100% | Completed |
| 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 | 0% | Not Started |

# Motivation

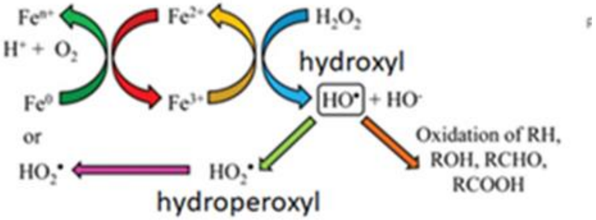
- ☐ PGM Catalyst
  - High cost
  - Scarcity
  - Catalyst poisoning

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

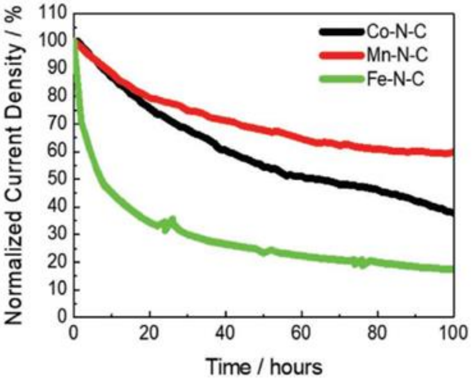
- ☐ **Mn Based PGM-free Catalyst**



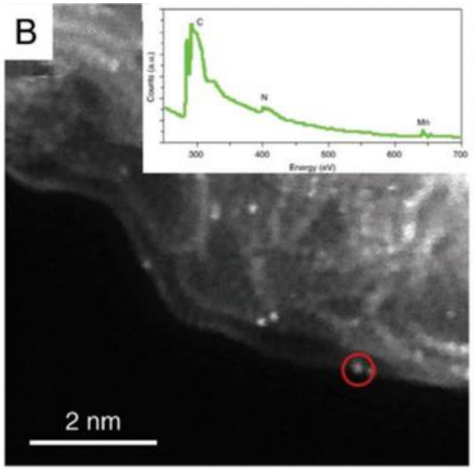
Catalyst Stability improvement



Fenton reaction mitigation

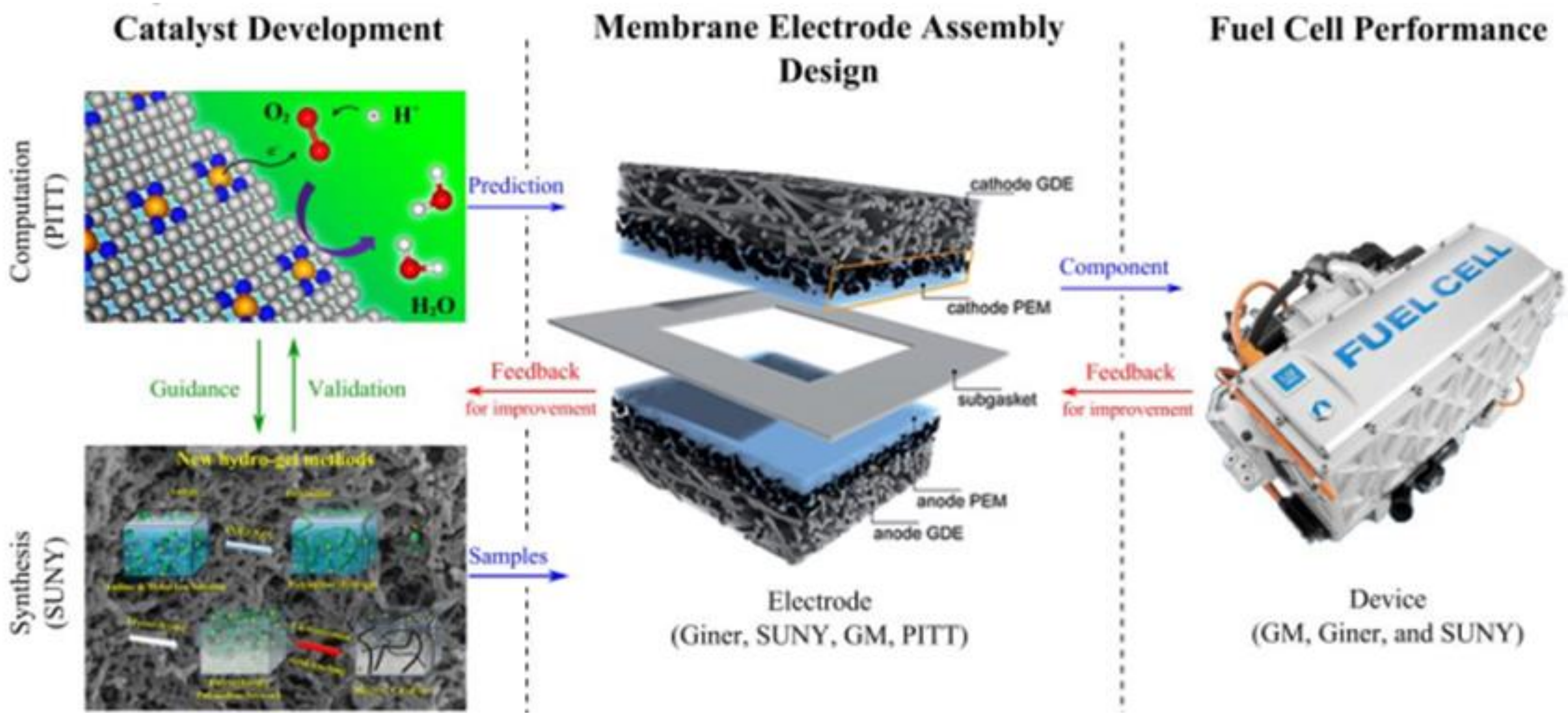


Improved MEA Durability



*Adv. Mater.* **2020**, 1908232

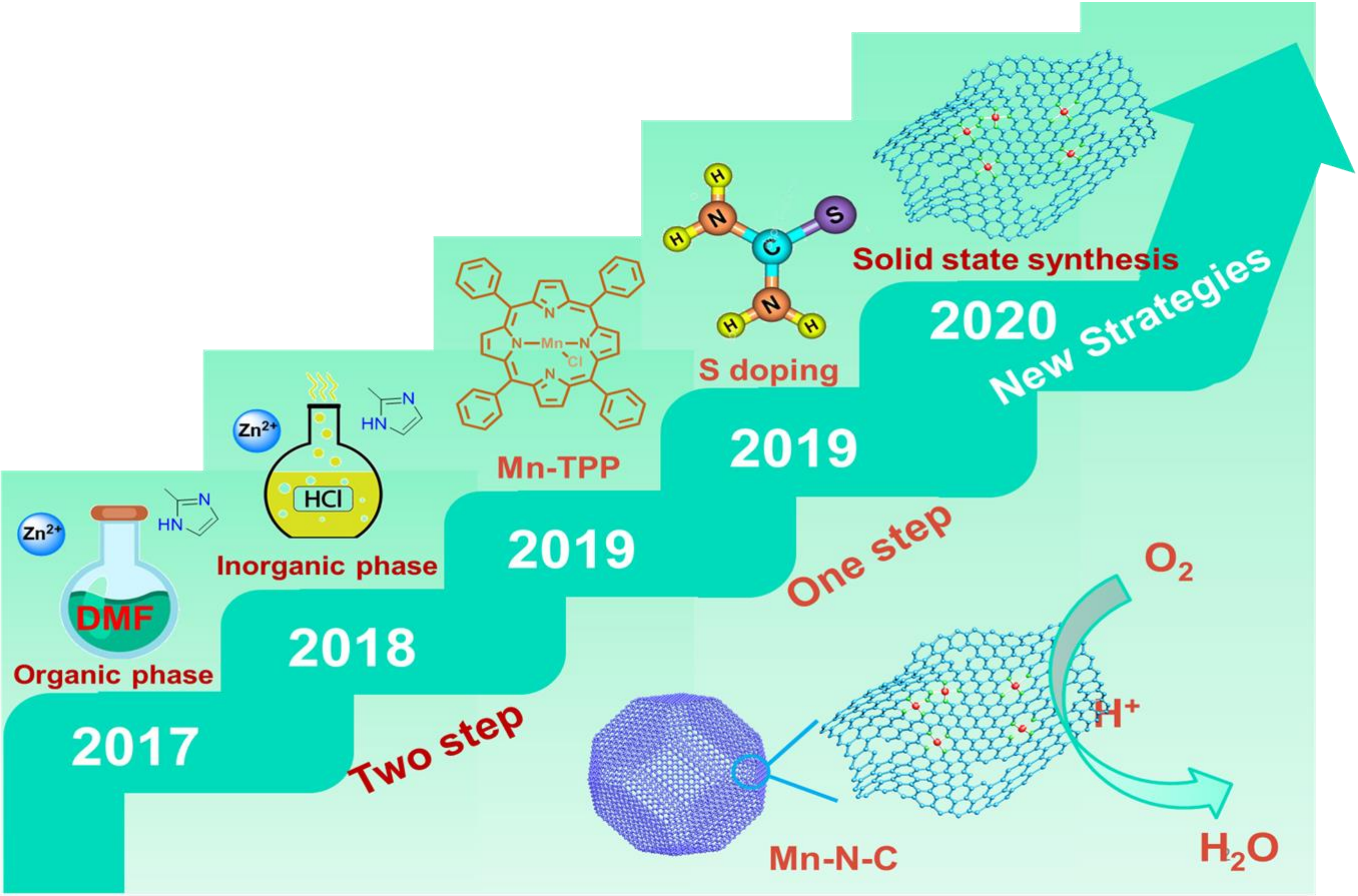
# Technical Approach



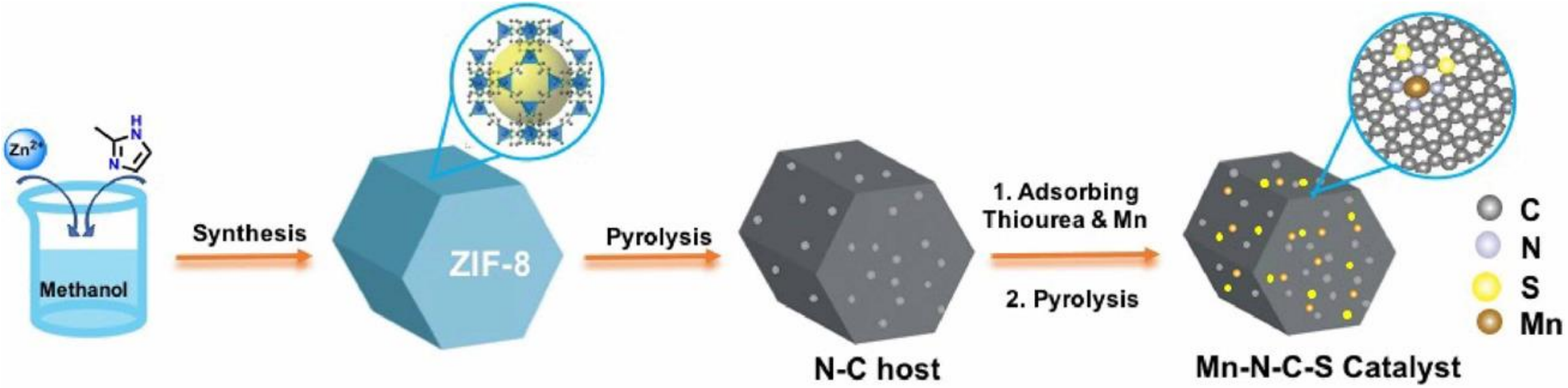
A strong team was formed to transform the discovery of Mn-based catalyst into fuel cell application with expertise in the following areas:

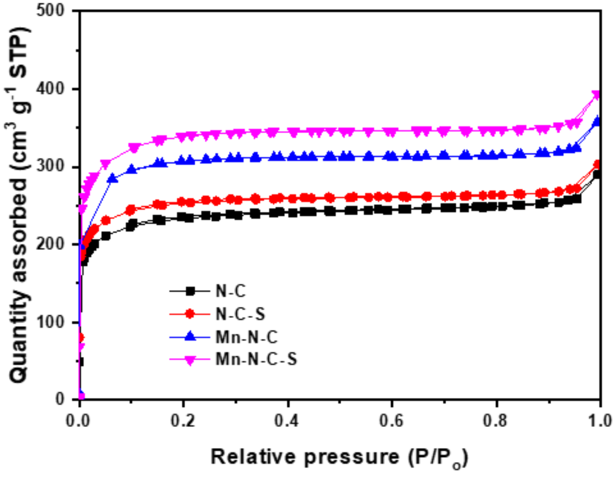
- ☐ Catalyst modeling
- ☐ Catalyst synthesis
- ☐ MEA fabrication
- ☐ Fuel cell system integration

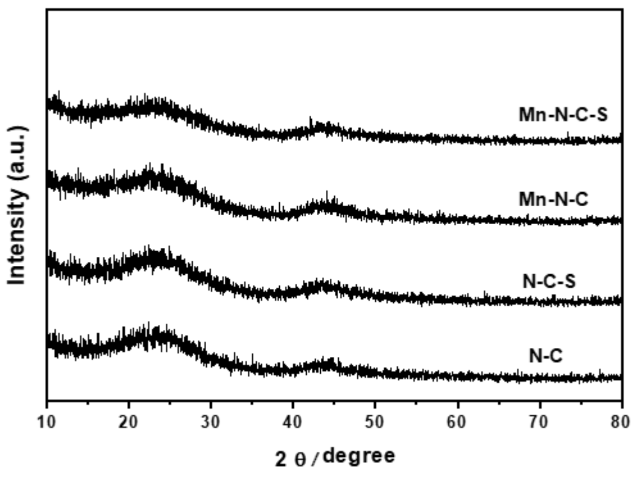
# Catalyst Synthesis



# Synthesis of Mn-N-C-S Catalyst

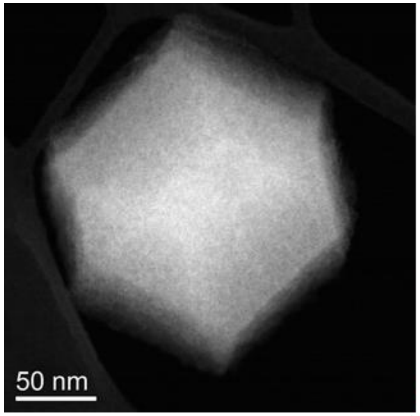


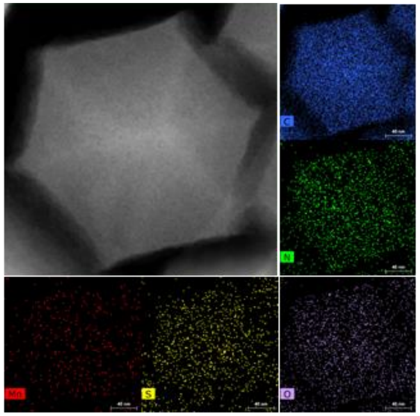


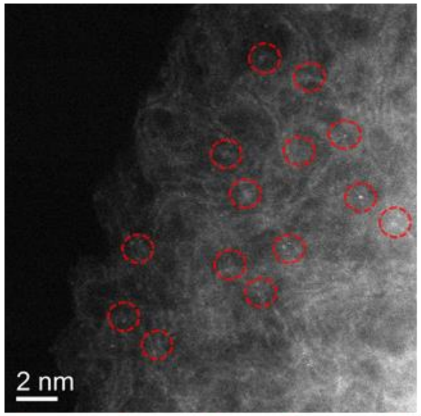


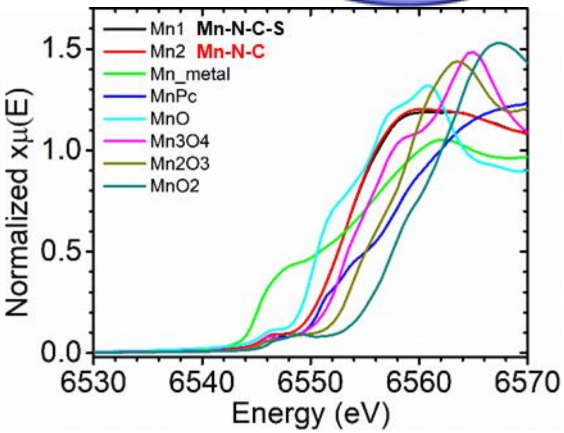
- ☐ **Sulfur-doping can introduce more defects on the carbon surface and increase surface area.**
- ☐ **Sulfur-doping didn't introduce MnS nanocrystal as shown in XRD pattern.**

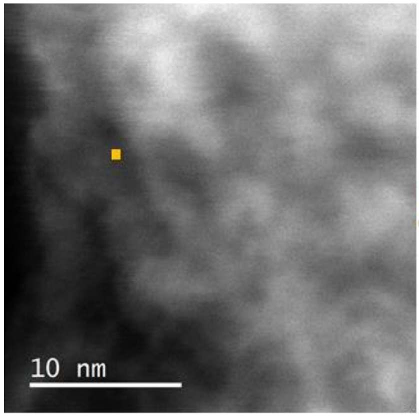
# Structure and Component of Mn-N-C-S Catalyst

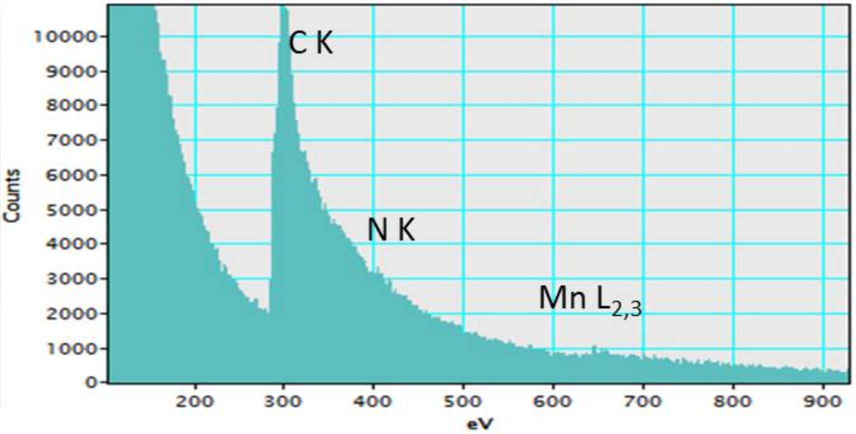


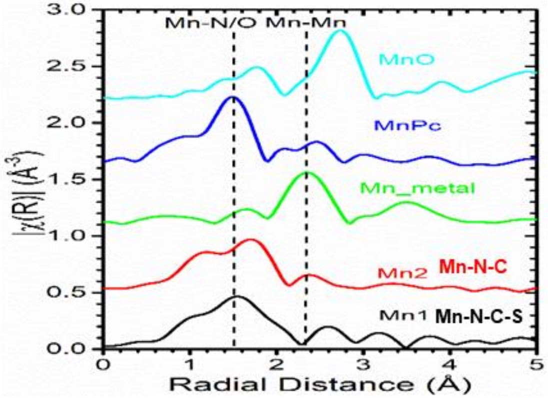






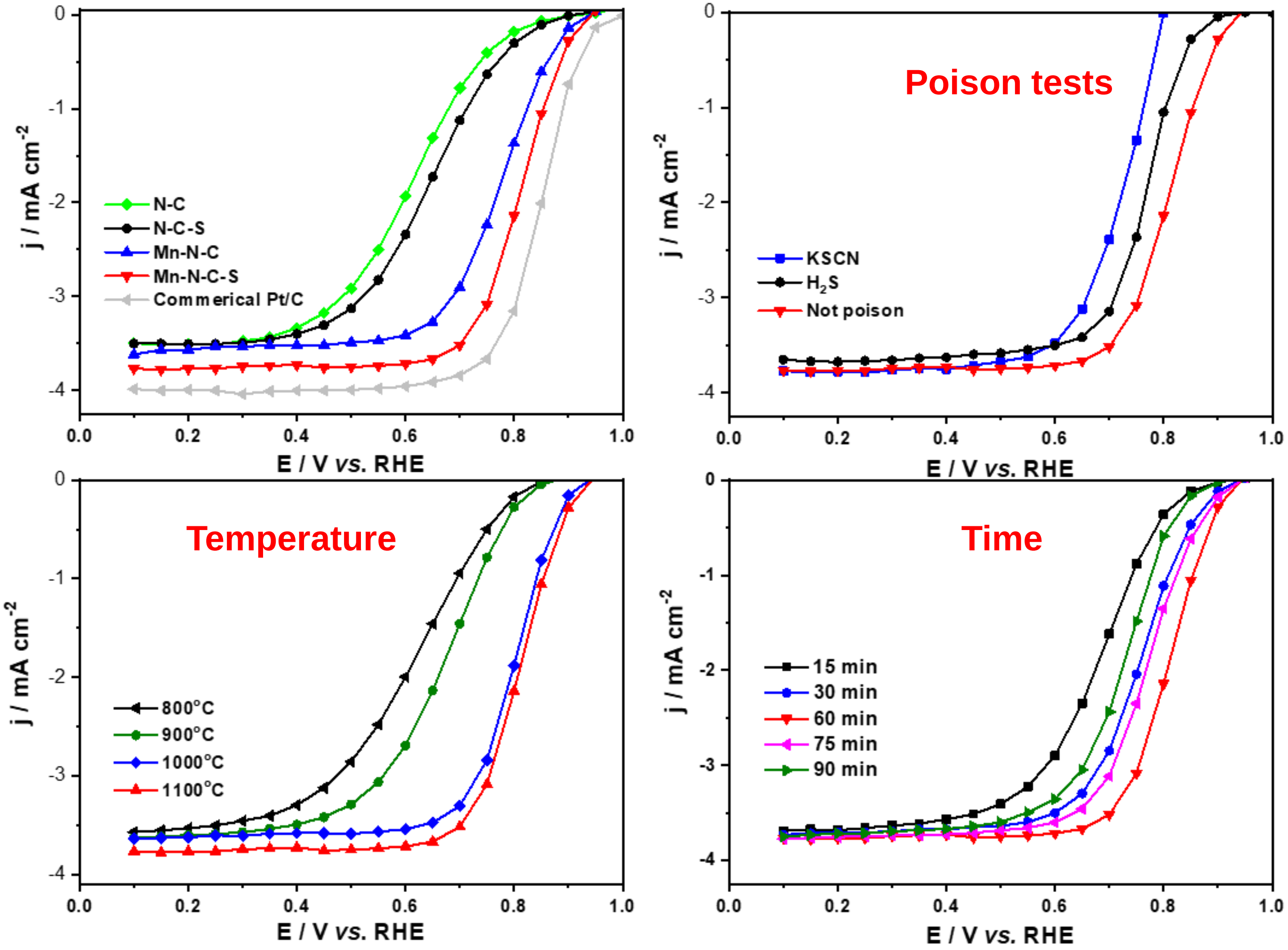






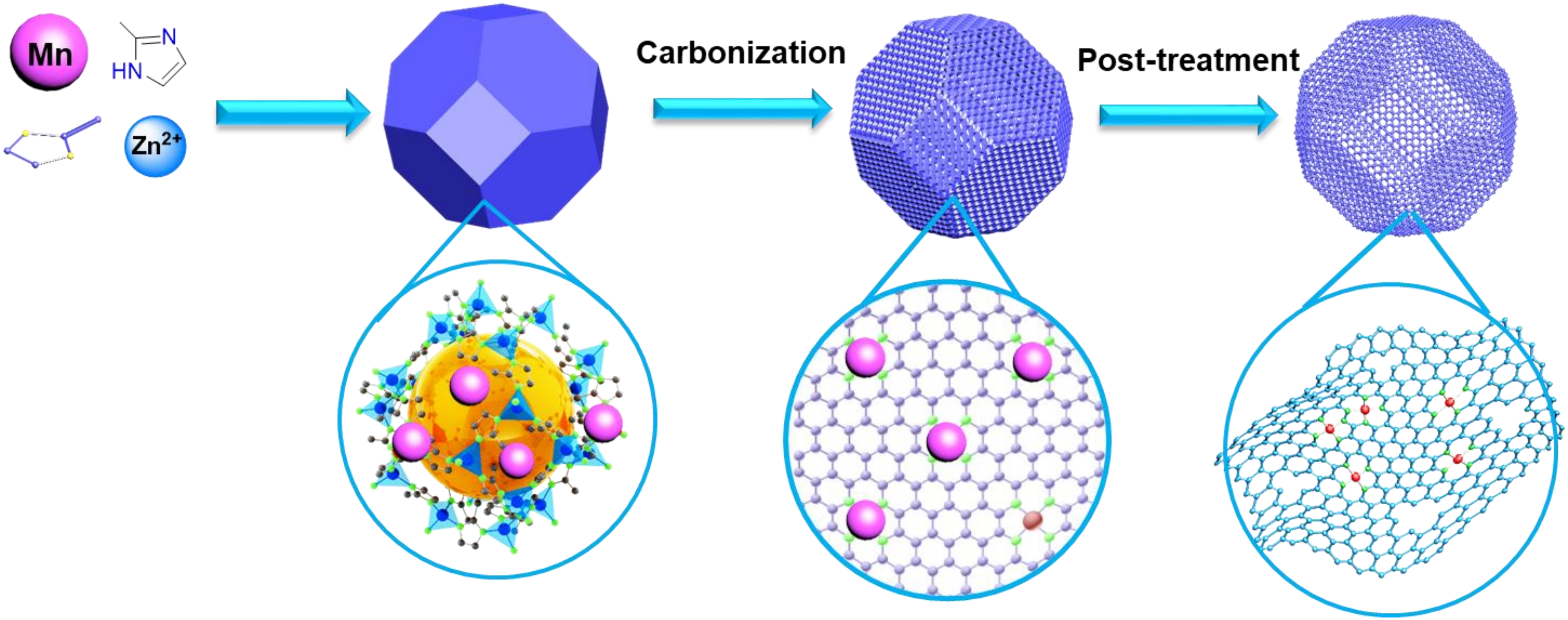
- ☐ **Mn, N and S elements have been successfully doped in the catalyst as shown in elemental mapping images.**
- ☐ **no Mn metal or Mn oxides particles can be found in STEM images, implying that Mn should exist as isolated single atom.**
- ☐ **XAS results show that the Mn samples are more like single atom materials which do not have strong Mn-Mn scattering.**

# The Effects of Temperature and Time on the ORR Activity of Mn-N-C-S Catalyst



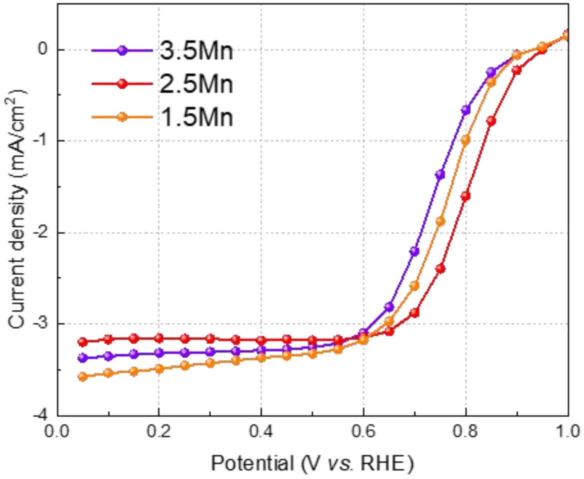
- ❑ **Mn-N-C-S shows higher half wave potential (~0.81 V) compare to other PGM-free catalyst.**
- ❑ **Poison tests demonstrate the active sites should be the Mn-N structure.**
- ❑ **Mn-N-C-S catalyst is very sensitive to treatment temperature and time.**

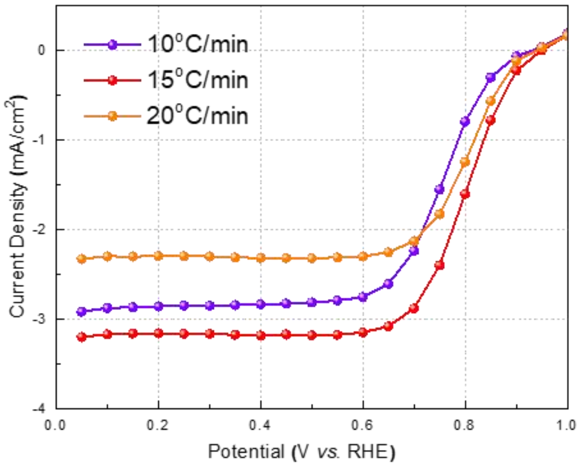
# Synthesis of Mn-N-C from Solid State Precursors

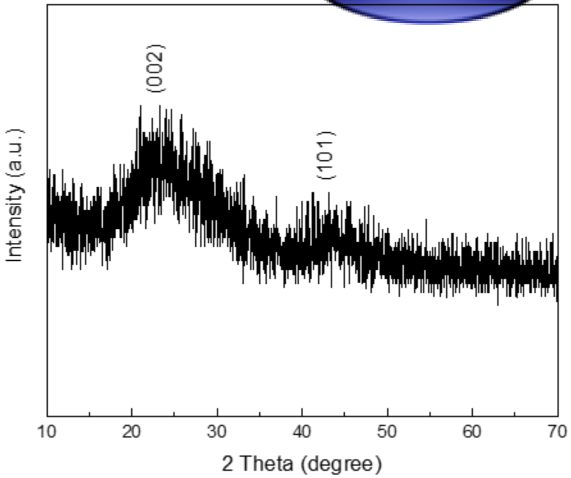


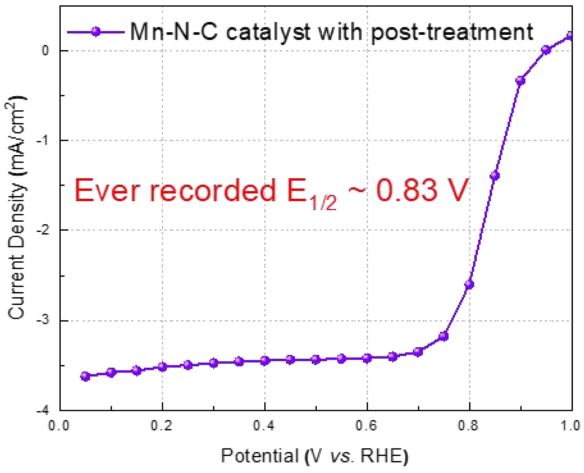
- ☐ Solid-state precursor methods are developed for Mn-N-C catalysts, which can be **easily scaled up** for MEA studies.
- ☐ More porous structure and higher activity can be obtained by **post treatment**, facilitating the intrinsic activity and mass transport.

# Mn-N-C from Solid State Precursors

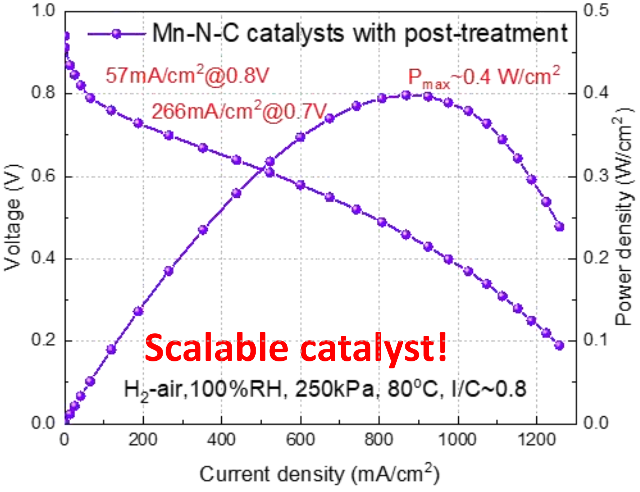






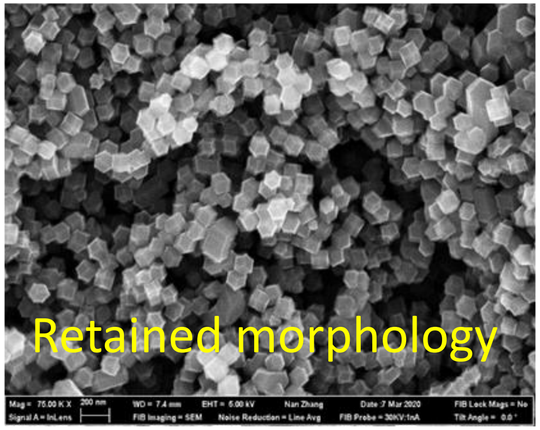


Ever recorded $E_{1/2}$ ~ 0.83 V



**Scalable catalyst!**

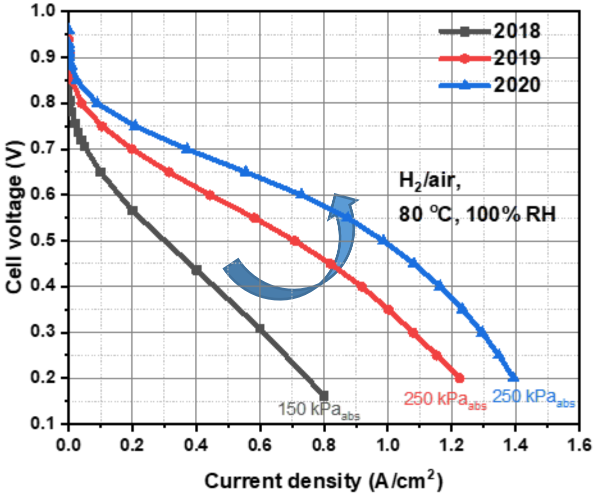
$H_2$-air, 100%RH, 250kPa, 80°C, I/C~0.8



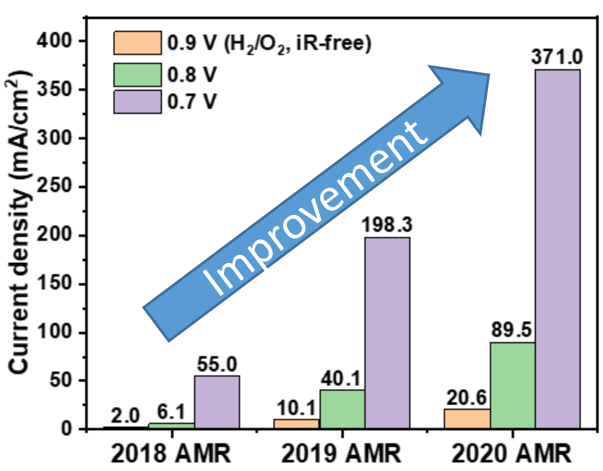
Retained morphology

- ❑ **High half-wave potential *$E_{1/2}$* ~ 0.83 V is achieved by post-treatment on such Mn-N-C catalyst derived from solid state precursor, maintaining the original morphology.**
- ❑ **Mn-based catalyst from such method is sensitive to the Mn content and ramping rate.**

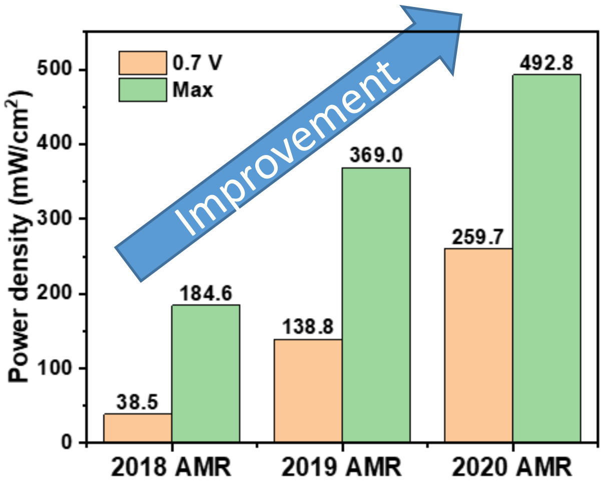
# Performance Improvement



MEA polarization curve



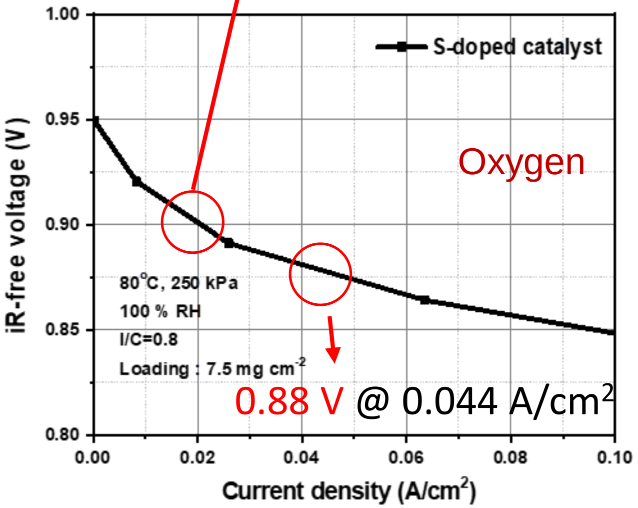
Current density



Power density

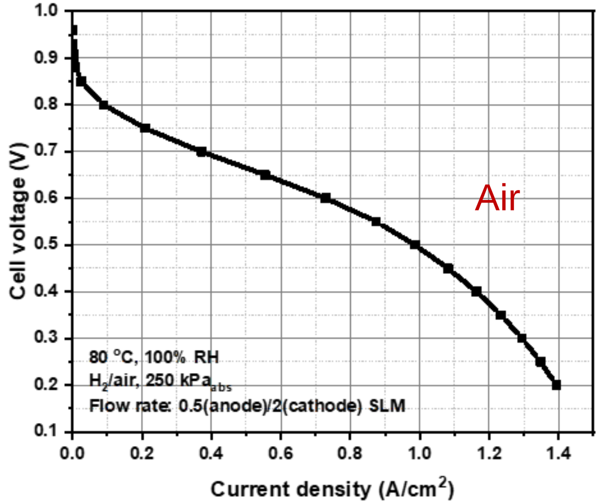
- ☐ **Consistent improvements have demonstrated over time**
- ☐ Initial (2018) MEAs utilized catalyst prepared via one step-NMP synthesis
- ☐ MEA performance was improved in 2019 by using 2-step water synthesis catalyst and optimizing electrode structure
- ☐ The MEA performance was further improved this year due to the development of S-doped catalyst and optimized electrode fabrication

# MEA Activity Improvement



20.6 mA/cm² @0.9V iR-free

0.88 V @ 0.044 A/cm²



371 mA/cm² @ 0.7 V; 89 mA/cm² @ 0.8 V

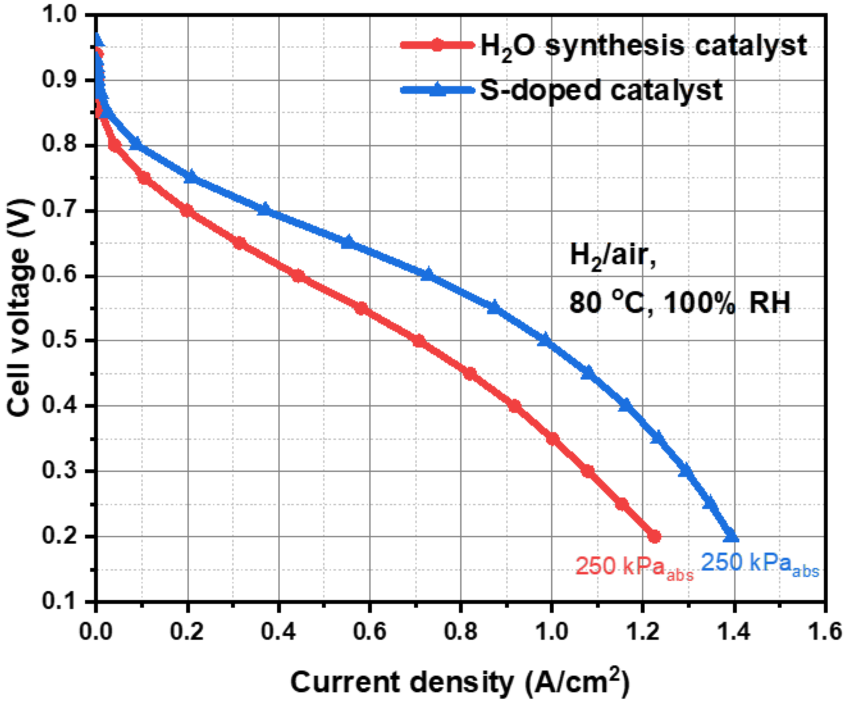
**Performance comparison between Mn and Fe based catalysts**

| | 0.7 V power density ($H_2$/air) | 0.8 V Current density ($H_2$/air) | iR-free V @ 0.044 A/cm² |
|---|---|---|---|
| **Mn (250 kPa)** | **371 mW/cm²** | **89.5 mA/cm²** | **0.88 V** |
| **Fe (150 kPa)** | **471 mW/cm²** | **113 mA/cm²** | **0.89 V** |

- ☐ Using UB's S-doped catalyst, the performance has been tremendously improved.
- ☐ 0.9 V $H_2/O_2$ performance (20.6 mA/cm²) has met 2nd year Go/NoGo milestone.
- ☐ 0.7 V power density of Mn-based catalyst is 260, closed to Fe-based catalyst.
- ☐ 0.8 V current density of Mn-based catalyst is 89 mA/cm², closed to Fe (113 mA/cm²)

**S-doping improves catalyst activity tremendously.**

# Performance Improvement



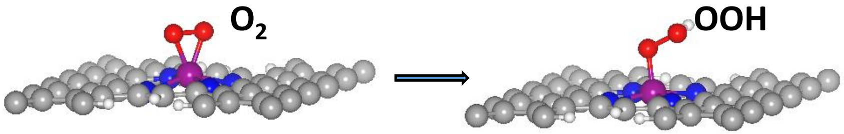
- ❑ S-doped catalyst demonstrates improved RDE and MEA performance over two-step water synthesis catalyst reported last year.
- ❑ The performance enhancement is due to the effect of sulfur doping.

**S-doping improves catalyst activity tremendously.**

# Computational Modeling

The first-principles density functional theory (DFT) calculations were performed using software ***VASP***

### 1. Adsorption of ORR species on Mn active sites

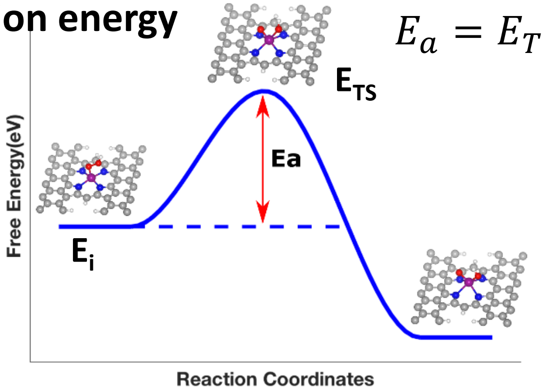


**Adsorption energy** $\Delta E = E_{system} - E_{catalyst} - E_{molecule}$

**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

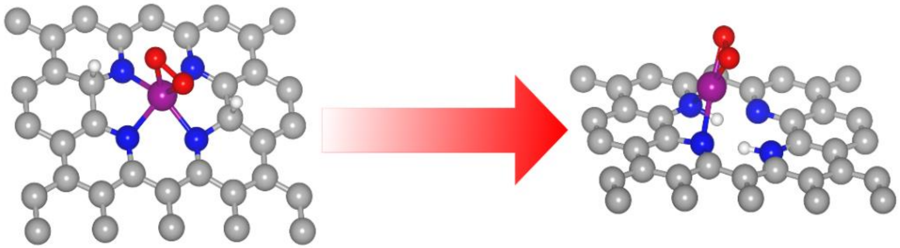
$$k_- = \frac{k}{K} \text{ and } K = \exp(-\frac{\Delta G(\mathrm{U})}{k_B \mathrm{T}})$$

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 ($MO_2$)

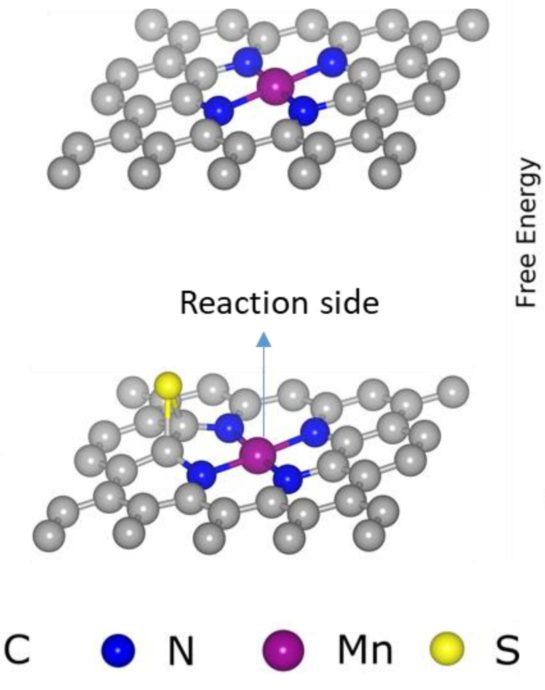
$$MN_4RO_2 + 2H^+ + 2e^- = H_2N_4R - MO_2$$

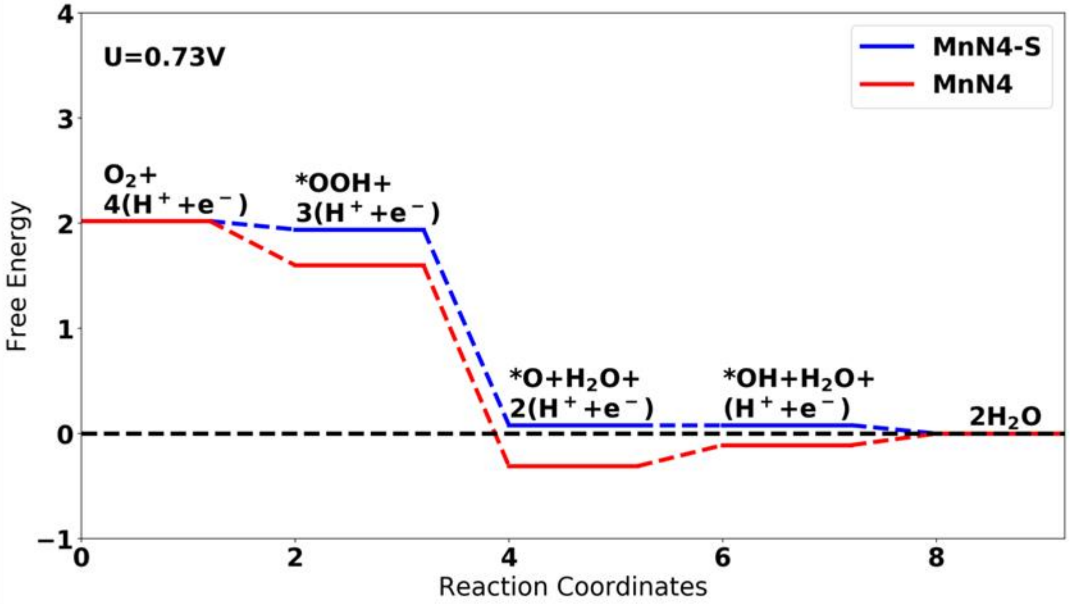


# Free Energy Evolution for ORR on S doped $MnN_4$

$MnN_4$

$MnN_4$-S

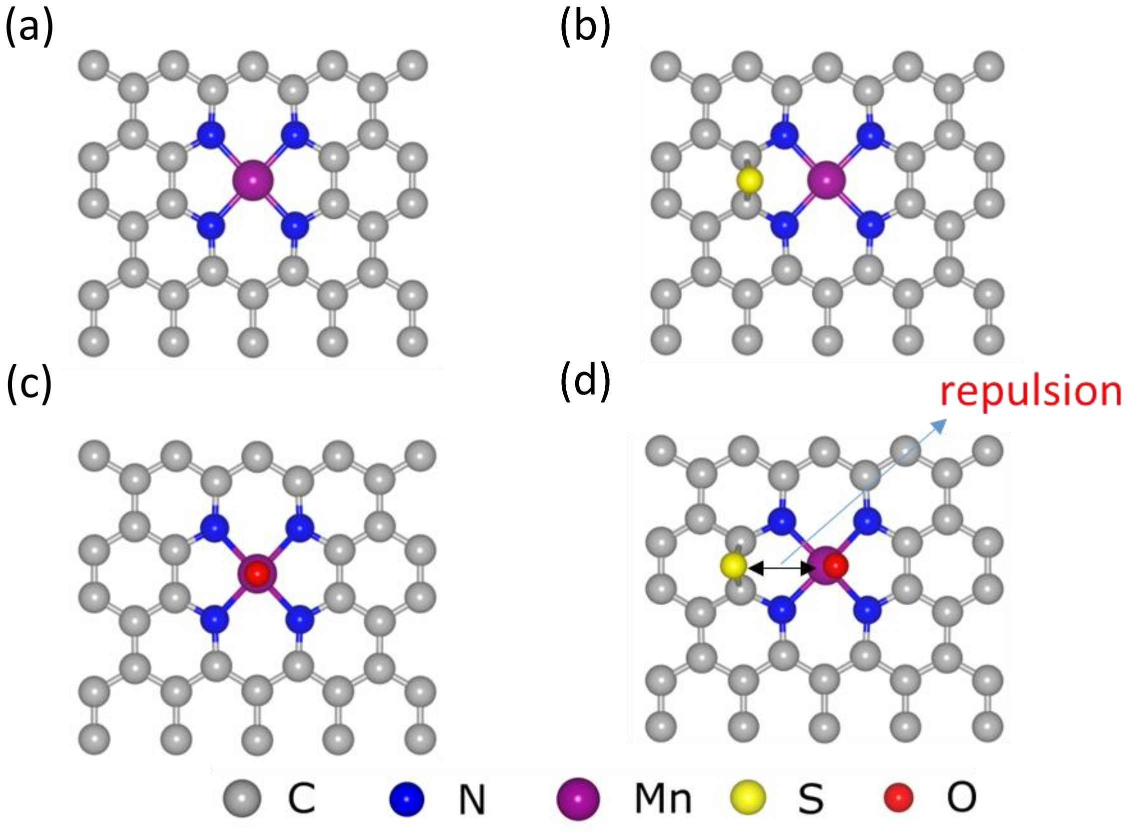




| | **Limiting potential** |
|---|---|
| $MnN_4$ | 0.53 V |
| $MnN_4$-S | 0.73 V |
| **Enhancement** | **+0.20 V** |

- ☐ **DFT Prediction: With adsorbed sulfur nearby, the limiting potential of $MnN_4$ for ORR increases from 0.53V to 0.73V. Hence, the ORR activity in Mn-N-C catalysts can be enhanced by S doping.**

# Elucidation of Effects of S Doping



| Charge effect | Bader charge of Mn |
|---|---|
| (a) without S | +1.36 |
| (b) With S | +1.42 |
| difference | +0.06 |

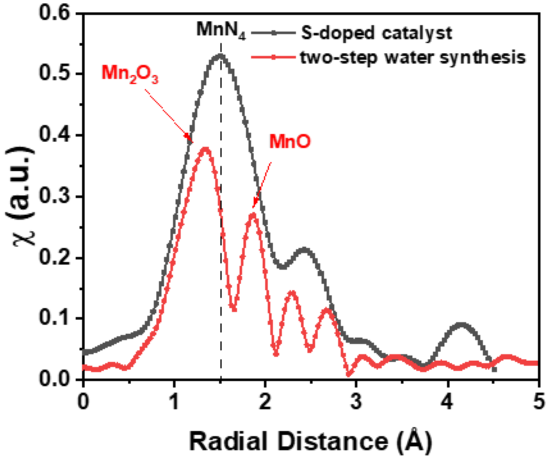
| Spatial effect | O adsorption energy (eV) |
|---|---|
| (c) without S | -6.29 |
| (d) with S | -5.90 |
| difference | +0.39 |

- **DFT Prediction:** **The adsorbed S only induces very little change in the charge of central Mn atom and hence the charge effect is insignificant. More importantly, the repelling interaction between S and ORR intermediates leads to weaker adsorption of ORR intermediates and enhanced ORR activity at the MnN$_4$ site.**

*Technical Accomplishment*

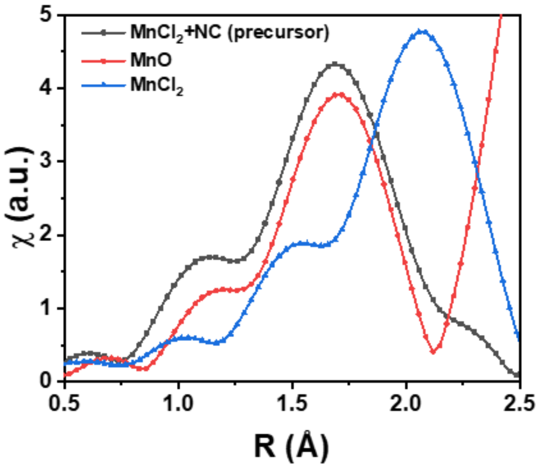
# XAS Study of Active Site Formation

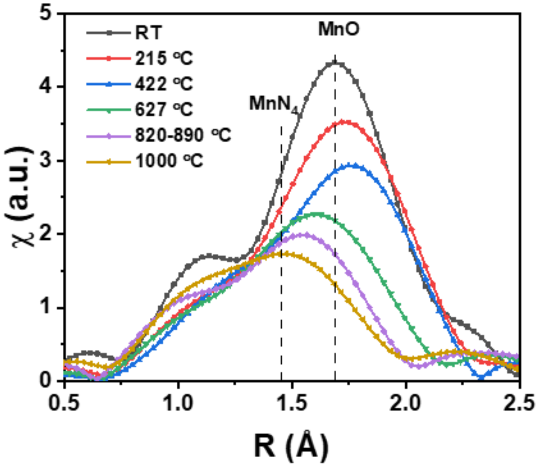
Argonne NATIONAL LABORATORY

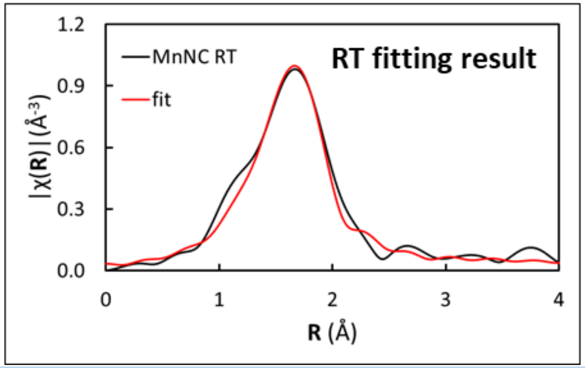


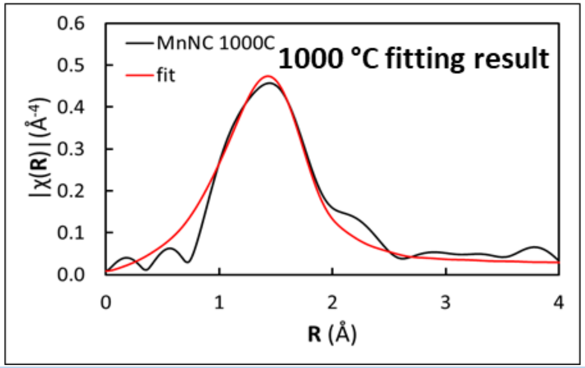
Fourier transform XAFS spectra of as-synthesis catalysts

In-temperature XAS study ($MnCl_2$+NC synthesis)







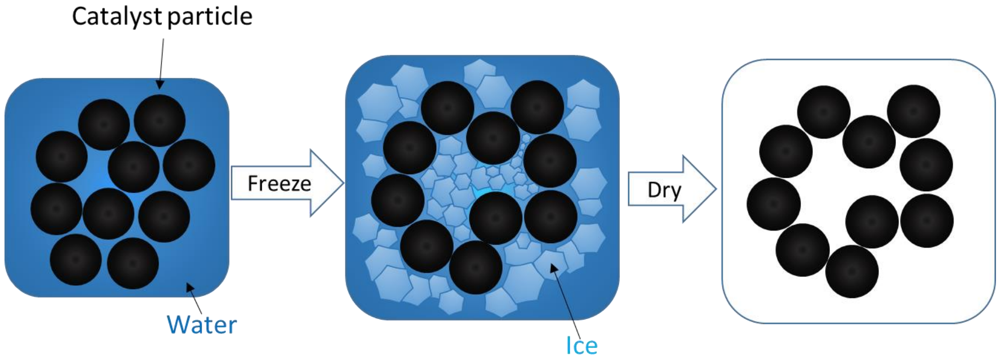


- ☐ Water synthesized catalyst is the combination of MnO and $Mn_2O_3$.
- ☐ S-doped catalyst possesses more $MnN_4$ structure which accounts for higher activity.
- ☐ For the CVD approach, balling milling of $MnCl_2$ with NC results in the formation of amorphous MnO.
- ☐ The precursor started to form in-plane $MnN_4$ from 627 °C.
- ☐ The fitting result of the XAFS confirms that the bonding length decrease from 2.17 Å to 2.00 Å. This is the indication of the phase transformation to in-plan $MnN_4$ structure.

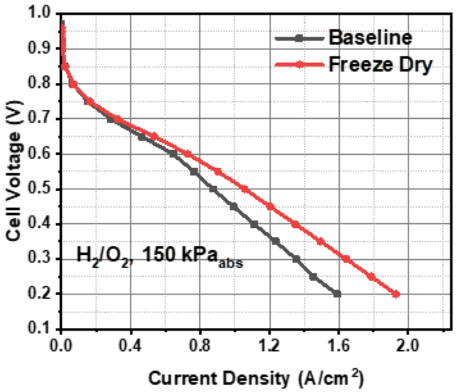
# Electrode Structure Optimization

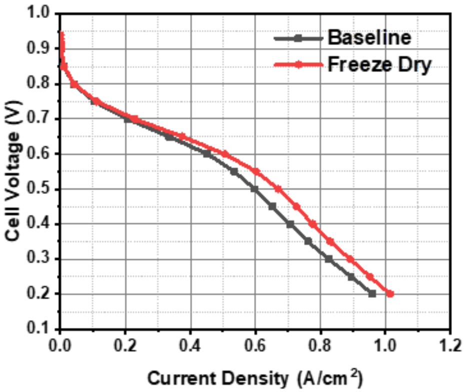
## Freeze Drying Approach to Improve the Transport in Electrode

**Dense Electrode Structure**



**More Porous Electrode Structure**

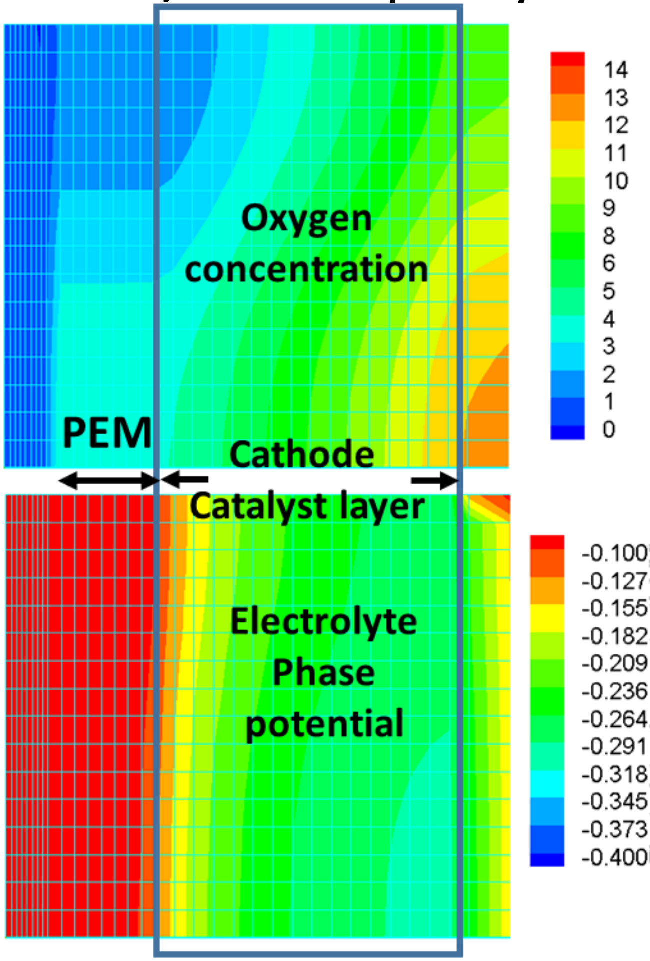




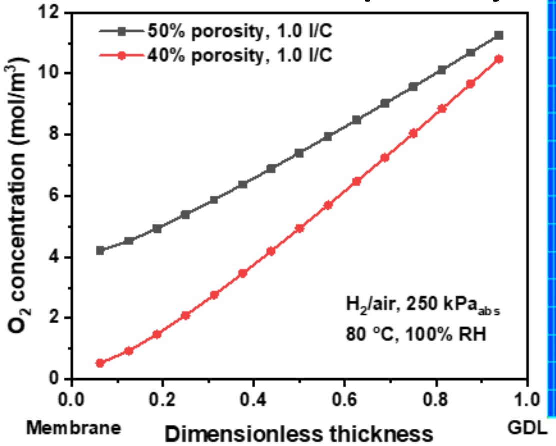
- The volume expansion of the water during freeze drying process will increase the pore volume in the electrode which will facilitate the oxygen and water transport.
- The MEA made from freeze drying approach shows better performances at high current density region due to better transport.
- The results agree well with the electrode modeling result that higher porosity will increase the oxygen concentration and electrolyte phase potential, which enhance the MEA performance.

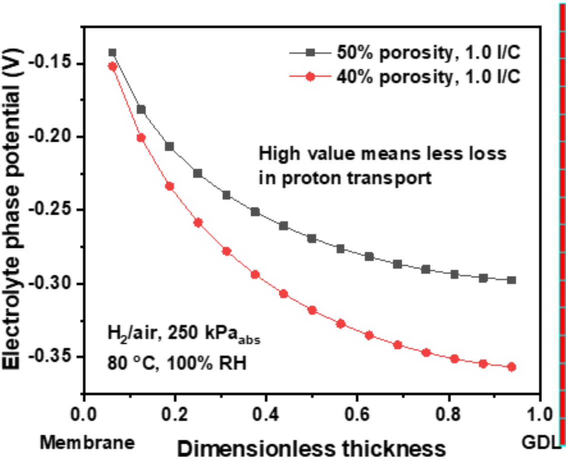
# Electrode Modeling

**1.0 I/C with 50% porosity**

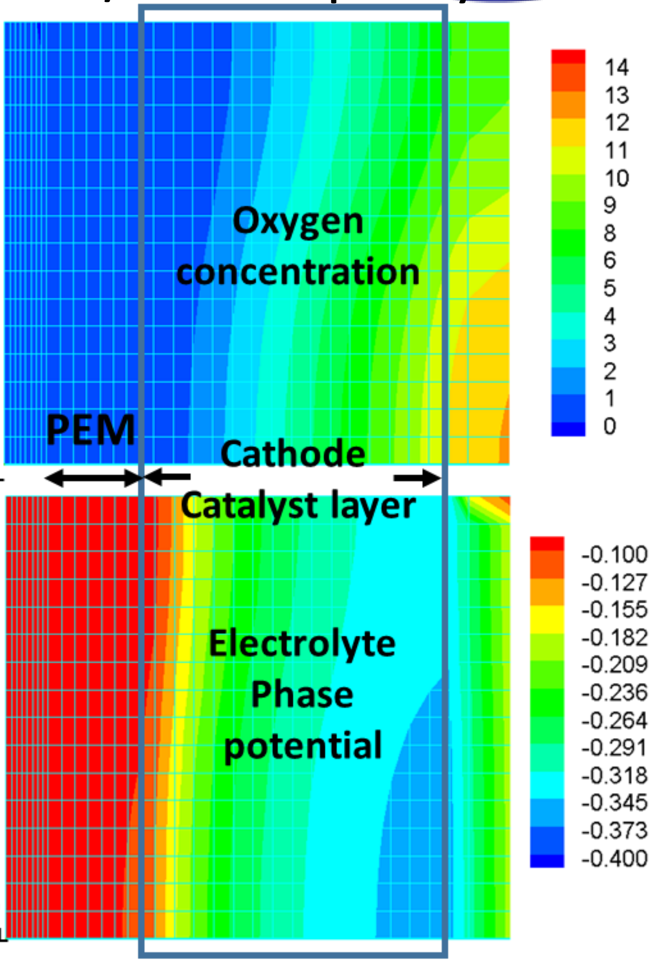


**Comparison between 50% and 40% porosity**



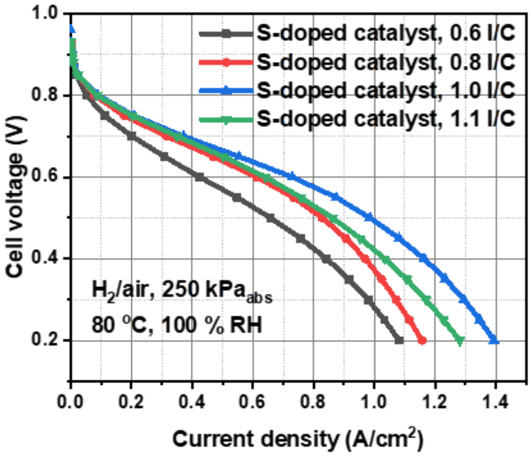


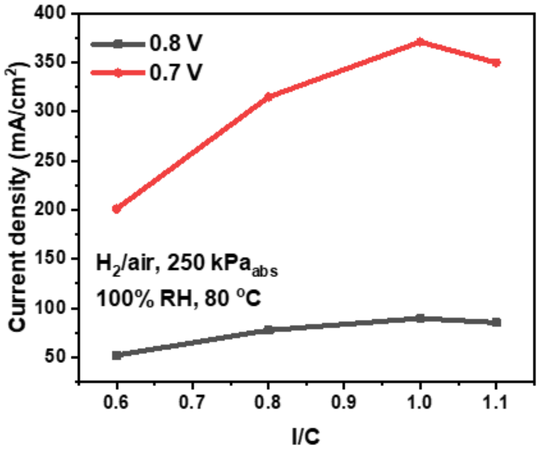
**1.0 I/C with 40% porosity**

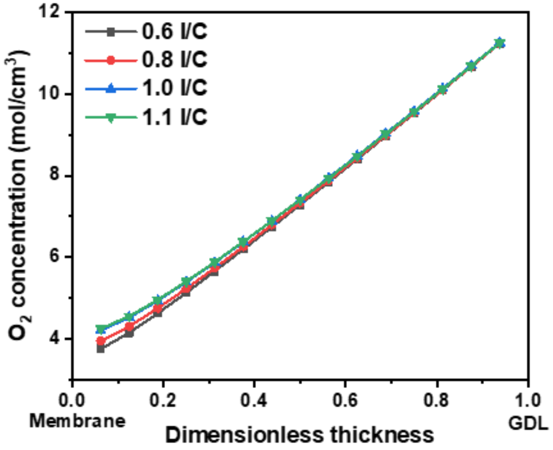


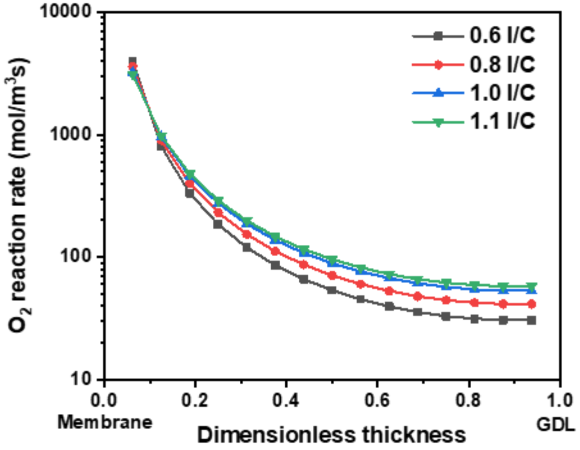
- ☐ $O_2$ concentration will be increased with higher porosity due to better $O_2$ transportation in the catalyst layer.
- ☐ The electrolyte phase potential will also increase with higher porosity. The higher electrolyte phase potential reflects less proton transport loss in the catalyst layer. The difference is more significant in the region close to the GDL.

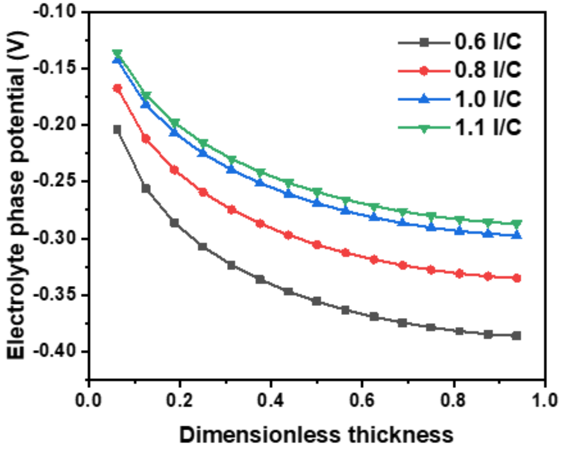
# I/C Ratio Effect on MEA Performance









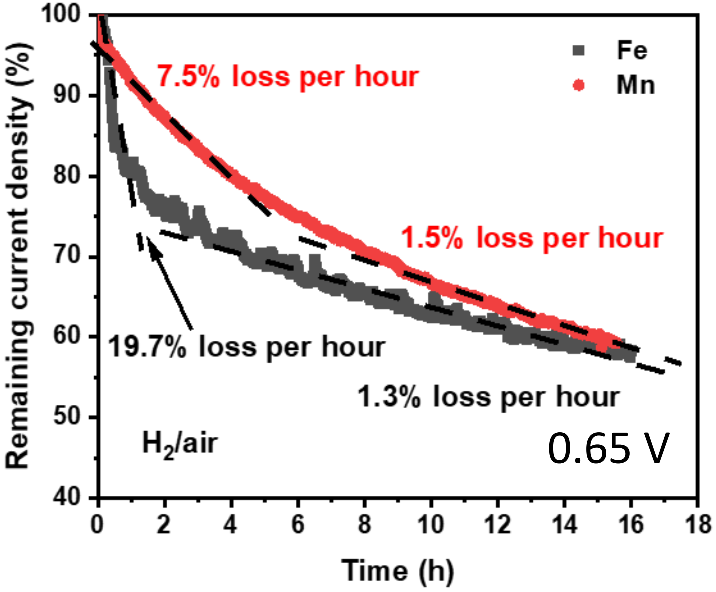


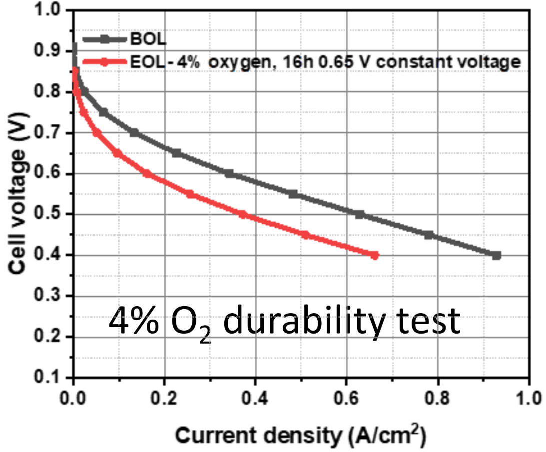
- ❑ 1.0 I/C is optimal for S-doped catalyst MEA.
- ❑ Samples with 1.0 I/C and 1.1 I/C demonstrate slightly higher oxygen concentration and oxygen reaction rate.
- ❑ The advantage of higher I/C is the higher electrolyte phase potential which is the indication of less loss in proton transport.
- ❑ Transport through ionomer is not considered in this model.

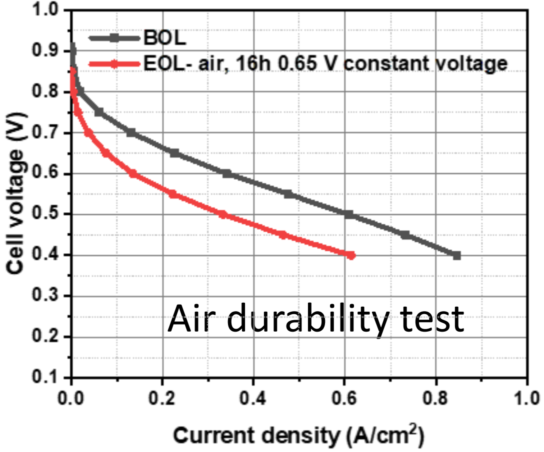
# Durability Study

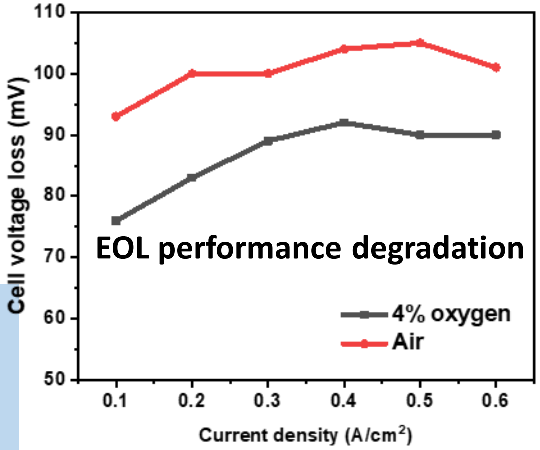
**Testing conditions: 250 kPa, 80C, 100%RH**
**Durability: 16 h 0.65 V constant voltage**

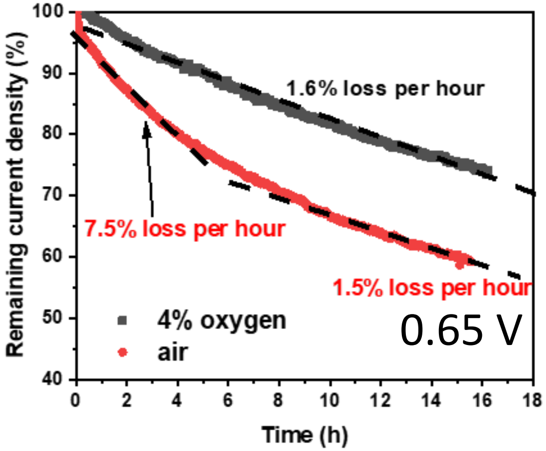
## $O_2$ concentration effect







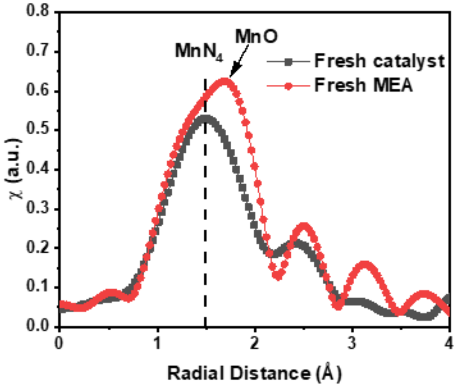




- ❑ The MEA degrades more in higher concentration of $O_2$.
- ❑ Under air condition, the MEA shows a two-stage degradation behavior.

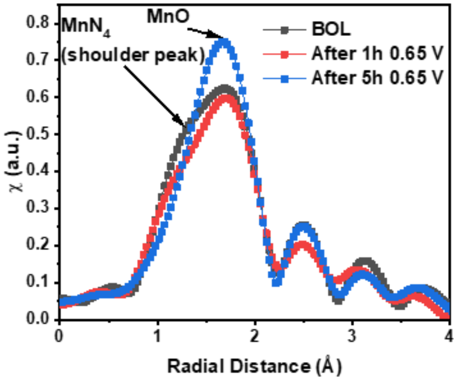
- ❑ For both 4% $O_2$ and air cases, the voltage drops after durability at different current densities are the same. Indicating the mechanism is dominated by the catalyst activity degradation.
- ❑ The cell voltage loss of the MEA under air durability condition is more than the one under 4% $O_2$ condition, indicating $O_2$ can accelerate the catalyst activity degradation.
- ❑ Fe catalyst decays much faster at the initial stage.

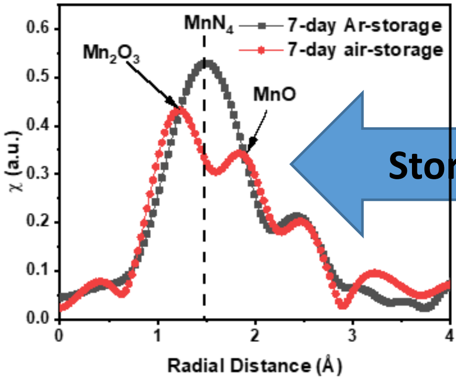
# Study of MEA Degradation Mechanism



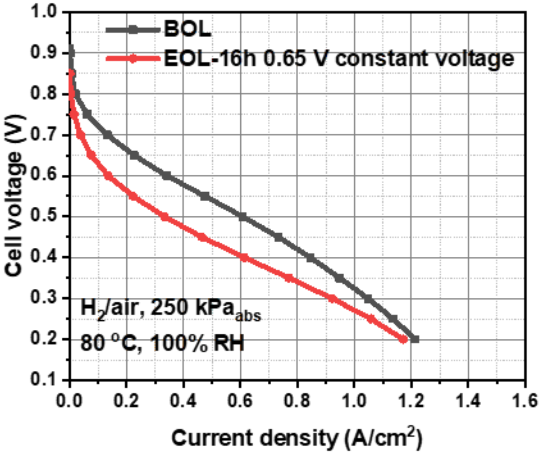
**MEA fabrication**

**Active site oxidation during test**

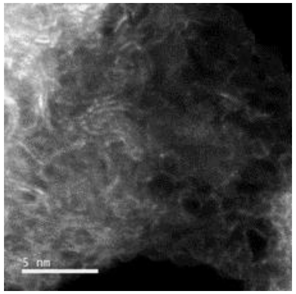




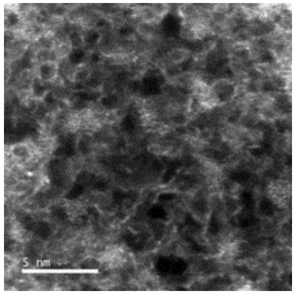
**Storage**



**BOL**



**After 5h 0.65 V**



- ☐ Initial degradation is caused by two aspects:
  - Storage degradation- $MnN_4$ was oxidized to MnO and $Mn_2O_3$.
  - Catalyst degradation during the MEA fabrication (Hot pressing and ink preparation)- $MnN_4$ was partially oxidized to MnO.
- ☐ During MEA durability test, more active $MnN_4$ sites change to MnO.
- ☐ Active site agglomeration is another mechanism for the performance decay during durability test.

# Summary

- S-doping has been applied to Mn-based catalyst for a better catalytic activity. The DFT calculations predict that S-dopants will help to weaken the adsorption of ORR intermediate on $MnN_4$ active site and thus enhance its ORR activity.
- Solid state synthesis approached has been developed with great potential for catalyst synthesis scaling-up and the post-treatment of this catalyst is comparable with other Mn-based catalysts
- Electrode modeling is helpful to understand the effect of porosity and I/C ratio on the MEA performance and to guide the MEA design.
- Freeze drying approach has been developed to improve the porosity of the electrode and enhance MEA performance.
- Testing protocol, oxygen concentration both have impacts on MEA durability of Mn-based catalyst.
- In-situ XAS was used to study the active site formation and change in order to better understand MEA durability and degradation mechanisms, which include active site oxidation and agglomeration.

# Collaborations

| Institutions | Roles |
|---|---|
| **Giner Inc. (Giner)**<br>Hui Xu (PI), Fan Yang, Shuo Ding, and Shirley Zhong | Prime, oversees the project; MEA design and fabrication; performance and durability tests; cost analysis |
| **University of Buffalo(UB)**<br>Gang Wu (Co-PI), Mengjie Chen, and Lin Guo | Mn-based non-PGM catalyst synthesis; RDE screening; MEA test |
| **University of Pittsburgh (Pitt)**<br>Guofeng Wang (Co-PI) | Catalyst and electrode modeling using DFT; molecular dynamics and pore network |
| **General Motors (GM)**<br>Anusorn Kongkanand (Co-PI) | MEA optimization; fuel cell system integration and cost analysis |
| **University of California, Irvine (UCI)**<br>Yun Wang (collaborator) | Electrode and transport modeling |
| **Northeastern University (NEU)**<br>Sanjeev Mukerjee, Qingying and Jia and Thomas Stracensky (collaborator) | XAS Characterizations and ORR mechanisms |

# ElectroCat Integration

| 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 |

# Future Work

- Sulfur doping to improve the performance of Mn-N-C catalyst synthesized from solid state precursors.
- Hollow structure control on Mn-N-C catalyst for performance improvement.
- *In-operando* Study of the MEA degradation in real-time. This information will be used for the guidance for MEA durability improvement.
- DFT modeling of various degradation processes.
- Temperature, relative humidity and voltage effects on the MEA durability.
- More electrode fabrication study for MEA performance enhancement.

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

# Responses to Previous Year Reviewer's 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 catalyst has comparable performance with Fe-based catalyst.**

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

  **Tremendous efforts have been made on the MEA durability study this year.**

- ☐ 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.

  **The stability test has been carried out in this year and the degradation mechanism studied by combining TEM and XAFS characterizations. ICP analysis has also been conduced.**

- ☐ 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.

  **Year 2 performance goal has been met. MEA durability has been extensively studied in this year. The DFT modeling has been used to model S-doping synthesis approach and predict the metal leaching tendency of the MnN4 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 many aspects are different from those of Fe-based catalysts. DFT calculation was focusing on the active site prediction and durability. In this year, DFT has elucidated the performance enhancement mechanism of S-doping thus providing guidance for catalyst synthesis.**

# Acknowledgements

- ☐ Financial support from DOE HFTO Fuel Cell Program under award # DE-EE0008075
- ☐ Program Manager
  - Dr. Nancy Garland
- ☐ ElectroCat Consortium
  - Drs. Piotr Zelenay, Debbie Myers, Karren More, Dave Cullen and K.C. Neyerlin
- ☐ NEU: Drs. Sanjeev Mukerjee and Qingying Jia
- ☐ CMY: Dr. Shawn Litster
- ☐ UCI: Dr. Yun Wang
- ☐ Brookhaven National Labs: Dr. Eli Stavitski