Developing Platinum Group Metal-Free Catalysts for Oxygen Reduction Reaction in Acid: Beyond the Single Metal Site

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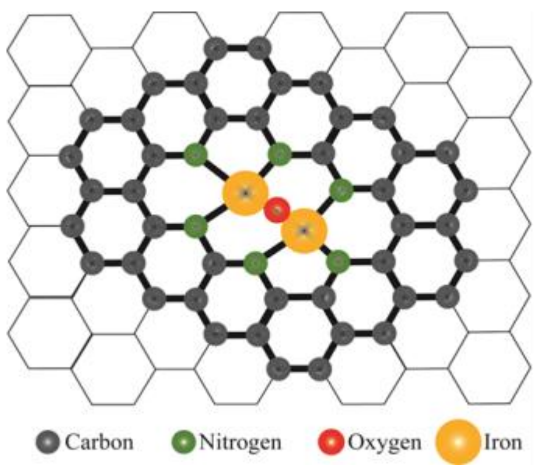
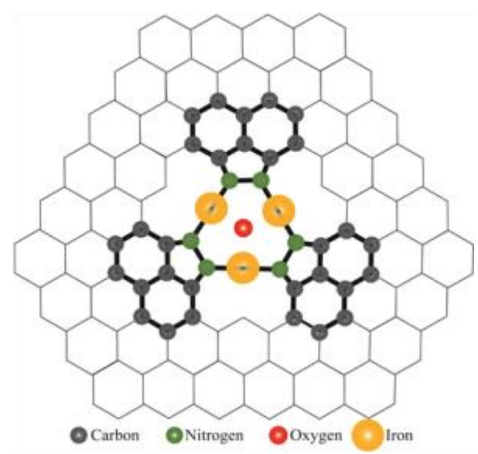
Northeastern University

Project ID# FC302

04/29/2019





Overview

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Timeline

- Project Start Date: 10/01/2018
- Project End Date: 09/30/2020

Barriers

- Performance in PEMFCs
- Durability in PEMFCs

Budget

- Total Project Budget: $1,020,000.00
  - Total Recipient Share: $250,000.00
  - Total Federal Share: $770,000.00
  - Total DOE Funds Spent*: $2,160.00

  * As of 03/01/2019

Partners

- Lawrence Berkeley National Laboratory
  Adam Weber
- Northeastern University
  Sanjeev Mukerjee

Relevance

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Objectives: Development of PGM-free ORR catalysts with high activity and durability in PEMFCs.

- Development of M_x-N-C catalysts featured with multiple metal centers (MMCs).
- Synthesis of $M_{(x)}$-N-C catalysts via surface deposition methods to bypass the necessity of pyrolysis.

Relevance: Our approaches move beyond the M-N-C catalysts featured with single metal sites while maintaining its beneficial configuration for the ORR. It is expected that the new catalysts may address the limited activity and durability of M-N-C catalysts, and thus meet the DOE targets.

Targets:

- 0.035 A/cm^2 at 0.9 V in a H_2/O_2 PEMFC (1.0 bar partial pressure, 80°C)
- Loss in activity ≤ 40% after 30,000 square wave cycles with steps between 0.6 V (3 s) and 0.95 V (3 s) .
- Power density of 0.5 W/cm^2 in a H_2/Air PEMFC with a MEA size ≥ 50 cm^2

Approach and Targets

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- **Synthesis**
  1. Ionothermal Carbonization
  2. Incorporation of pre-existing MMC sites into carbon substrate
  3. Surface deposition: dual IBAD, sputtering
- **Characterizations**
  Spectroscopy: in situ XAS, Mossbauer, XPS, NMR
  Microscopy: SEM, HAADF-STEM, HRTEM, X-ray images
- **MEA fabrication**
  electrospinning, IBAD
- **DFT modeling**
- **Mass transport modeling**
- **Milestones**
  1. 0.025 A/cm^2 at 0.90 V in a H_2/O_2 PEMFC (Period 1 Go/No-Go)
  2. Loss in activity ≤ 40% after 30,000 square wave cycles
  3. Power density of 0.5 W/cm^2 in a H_2/Air PEMFC

Accomplishments and Progress

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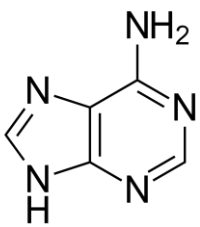
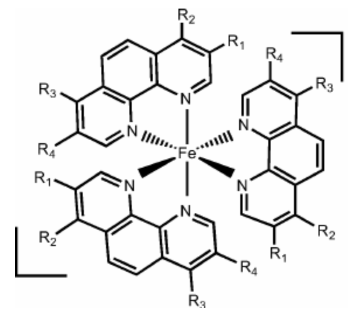
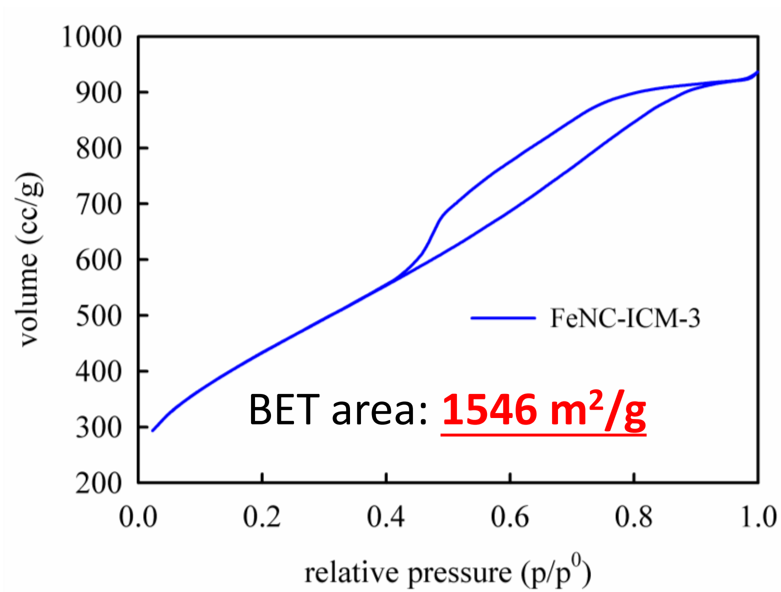
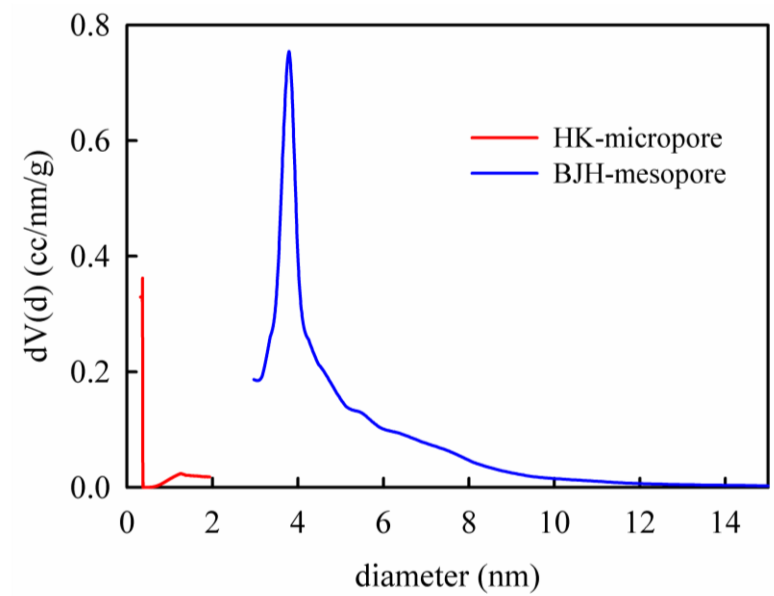
Ionothermal Carbonization synthesis



- NaCl+$ZnCl_2$ (1:7 by wt) as molten salt
- Adenine as C and N precursor
- $Fe(Phen)_3(ClO_4)_2$ as Fe precursor (Fe-N_6)







By changing the salt precursor and the ratio, highly porous structure with selective mesopores or micropores can be obtained.

Accomplishments and Progress

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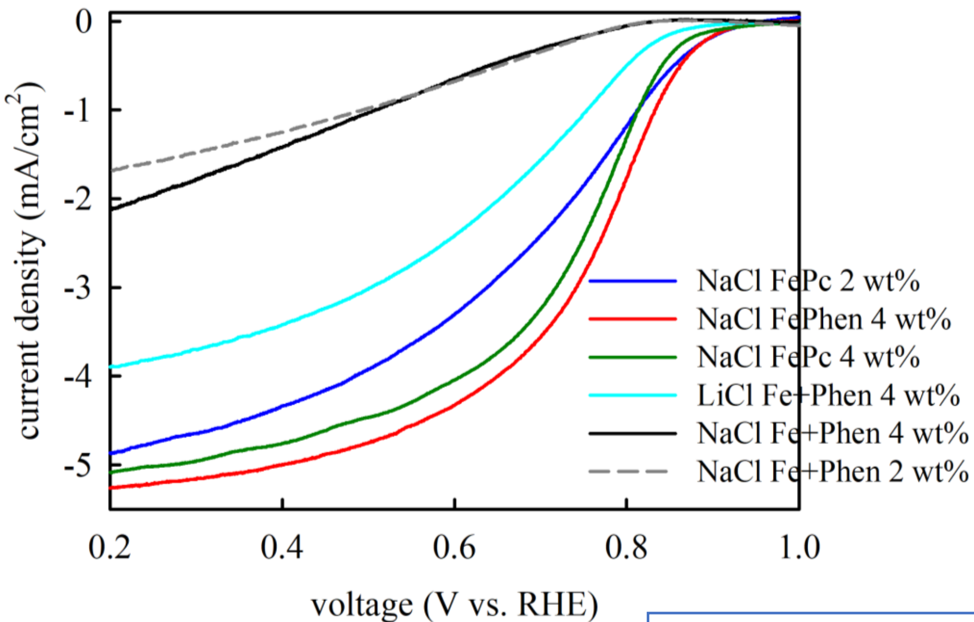
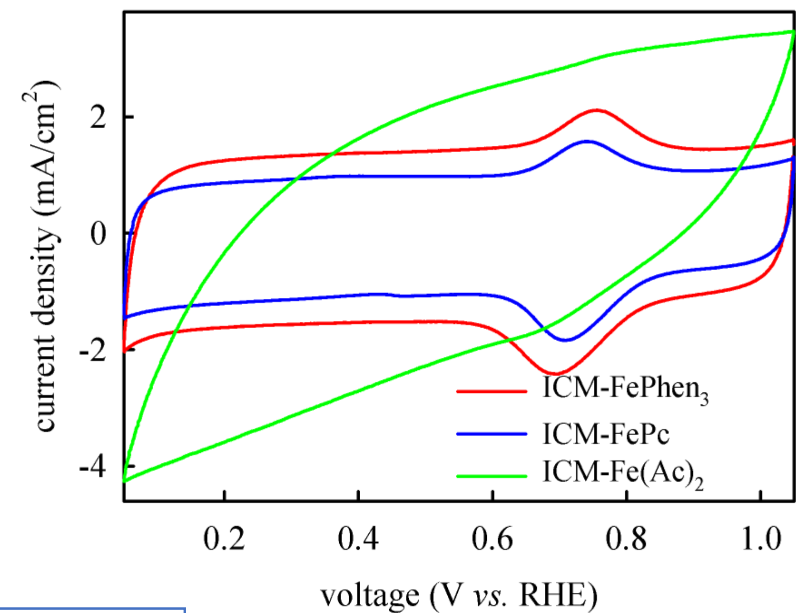
Electrochemistry





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The ORR performance is sensitive to the salt, Fe precursor, and Fe loading. The best performance in RDEs is comparable to the state-of-the-art. Further optimization is undergoing.

Accomplishments and Progress

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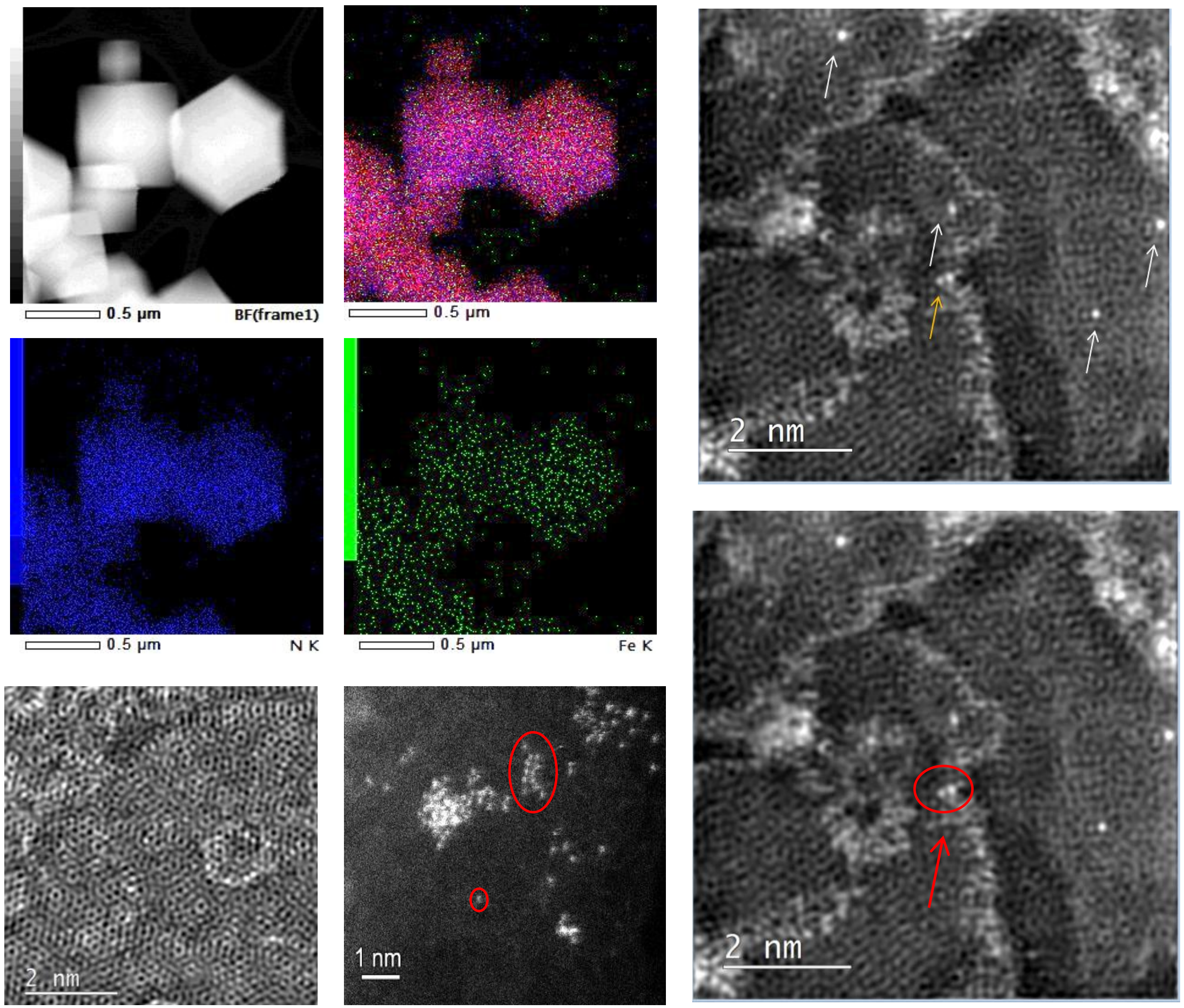
Microscopy



- Both single and multiple iron atoms center directly observed.
- Nicely shaped crystals with size from 100 – 500 nm
- Graphene-like carbon

Accomplishments and Progress

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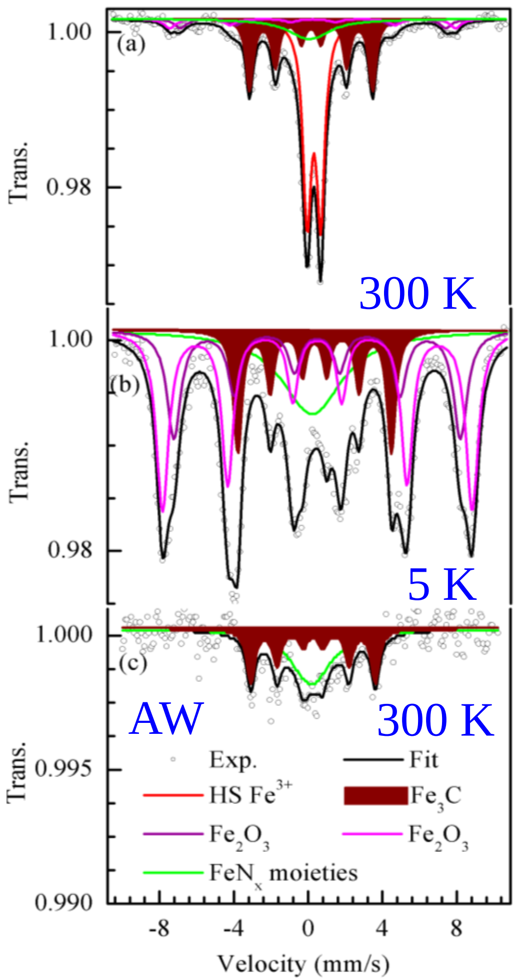
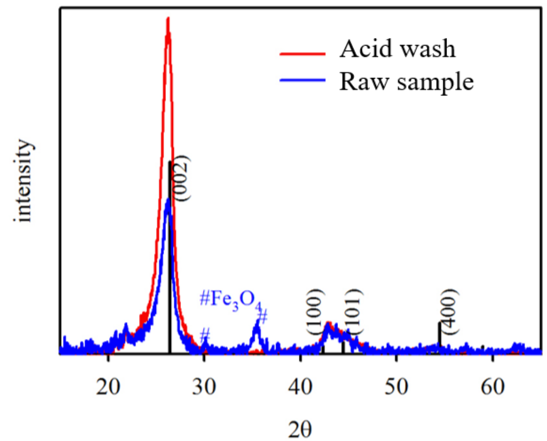
Spectroscopy





Sample	Mössbauerco mponent	Mössbauer RA % (300 K)	Mössbauer RA % (5 K)
ICM $FePhen_3$	Singlet	12	22
	Fe_2O_3 (1)	58	62
	Fe_3C	30	16
ICM $FePhen_3$ AW	Singlet	55	NA
	Fe_2O_3 (1)	0	NA
	Fe_3C	45	NA

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One species unseen before is stable in acid, tentatively assigned to MMC.

Accomplishments and Progress

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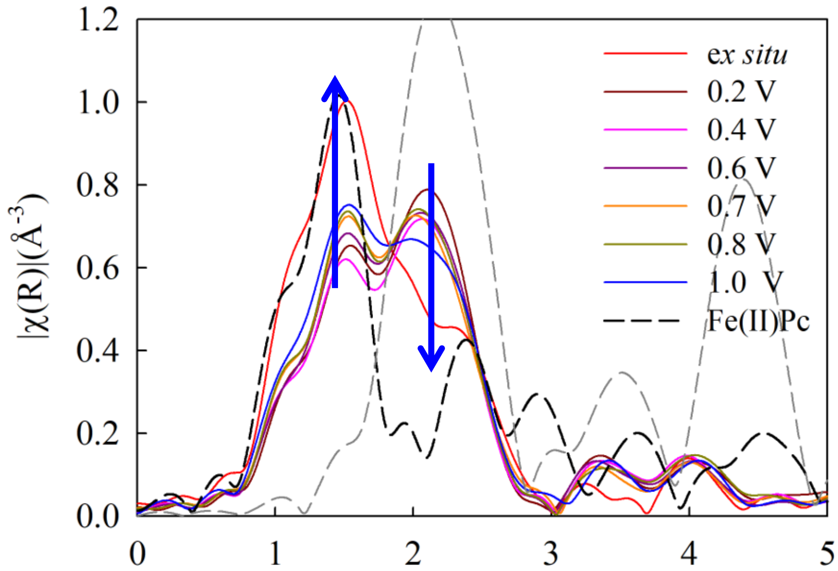
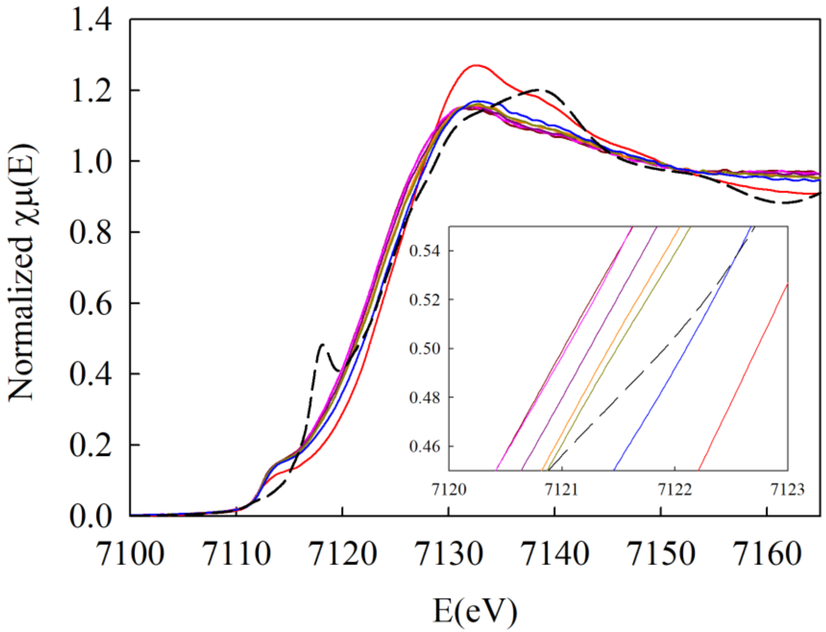
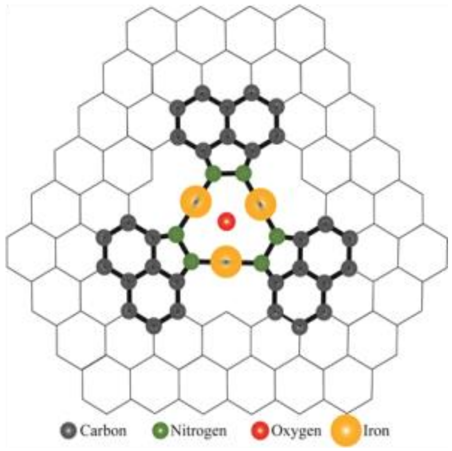
In situ XAS



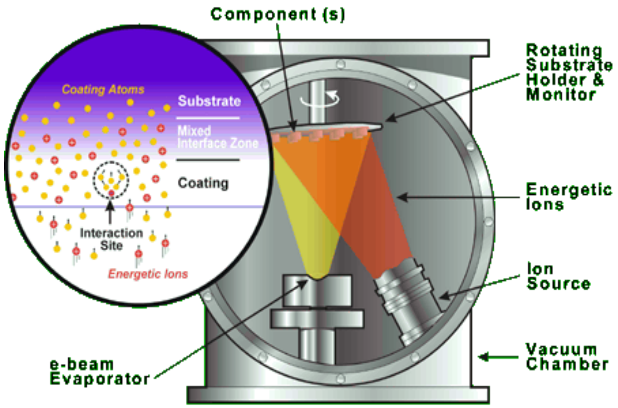


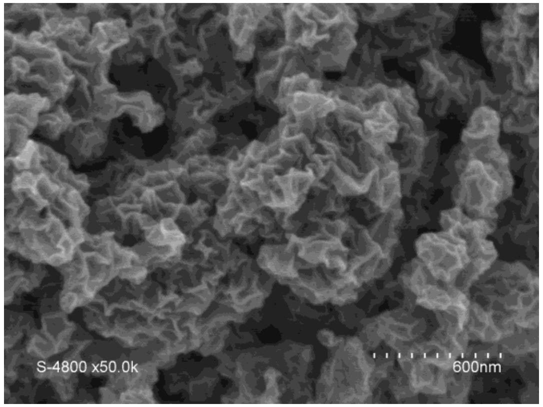


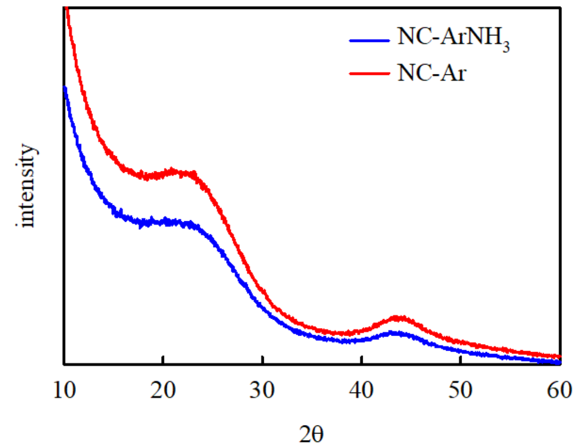
In situ XAS clearly shows the presence of short range Fe-Fe bonds that are stable and electroactive in acid solutions, suggesting the presence MNC sites participating in the ORR.

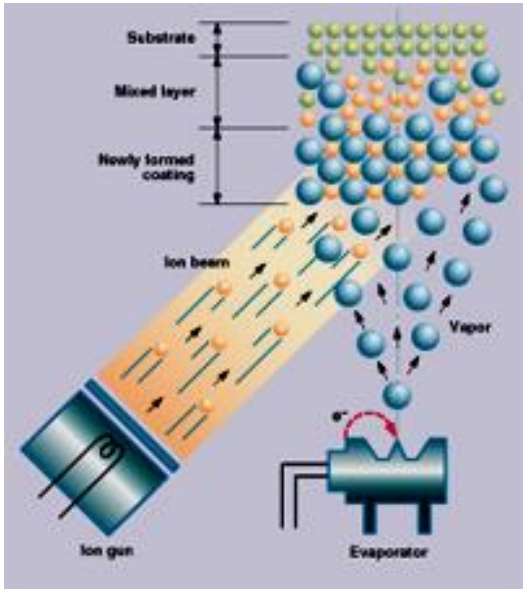
Accomplishments and Progress

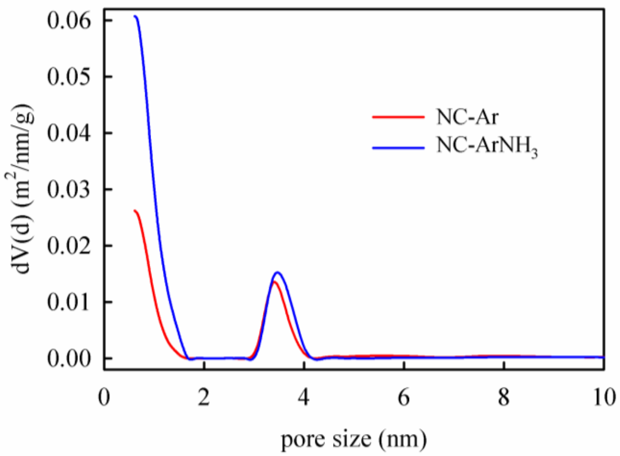
IBAD: N-doped carbon substrate optimization

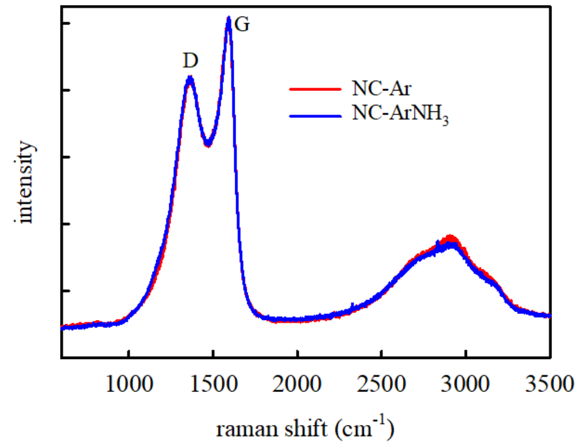








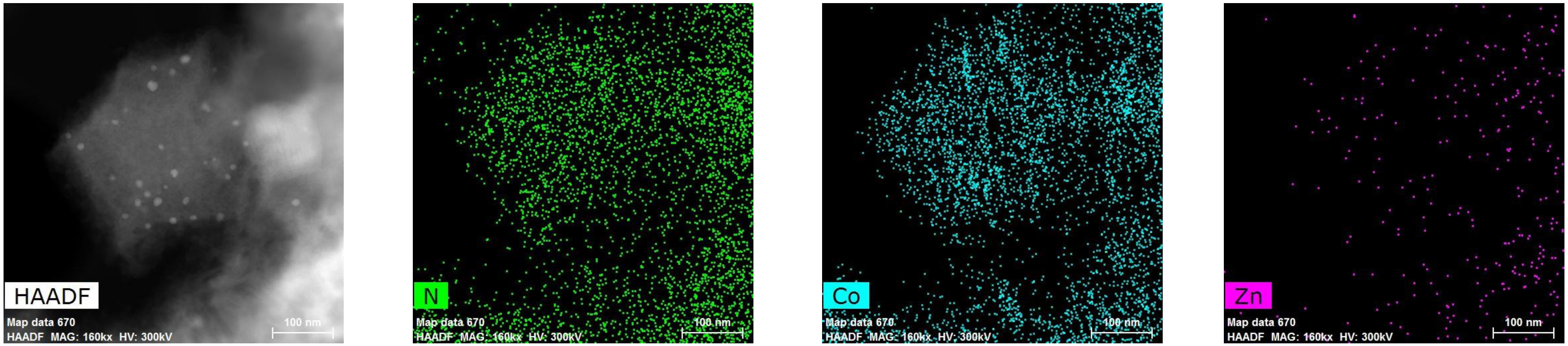




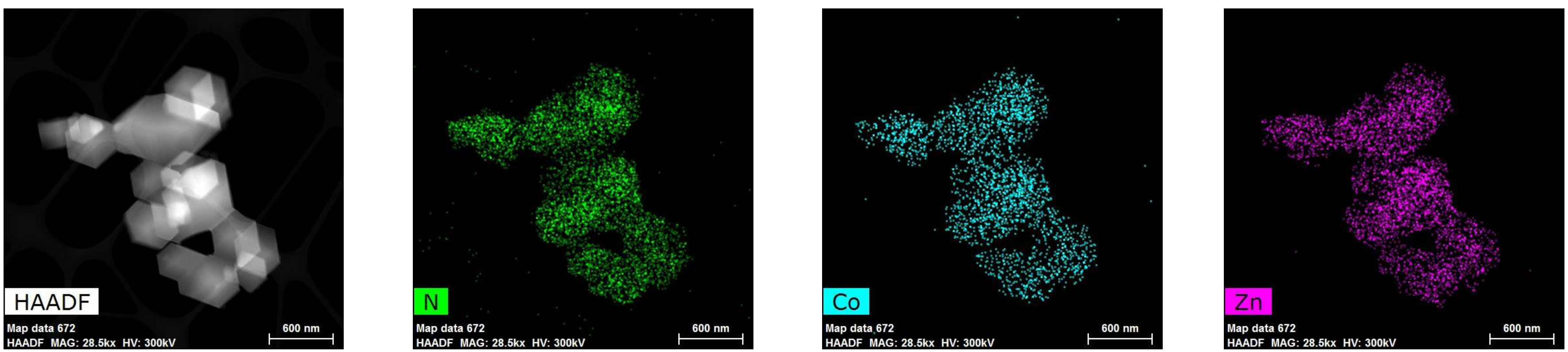
Porous and amorphous N-doped carbon with abundant micropores achieved.

Accomplishments and Progress

Zn_1/Co_1-MOF



Zn_9/Co_1-MOF

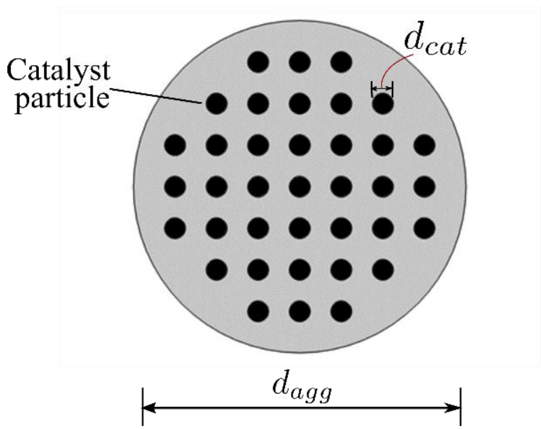


Porous and amorphous N-doped carbon with abundant micropores and no particles achieved. Further optimization undergoing.

Accomplishments and Progress

Mass transport modeling

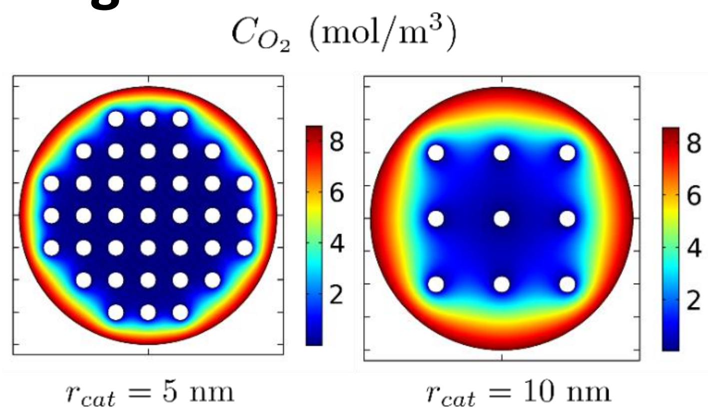
Microscale Studies

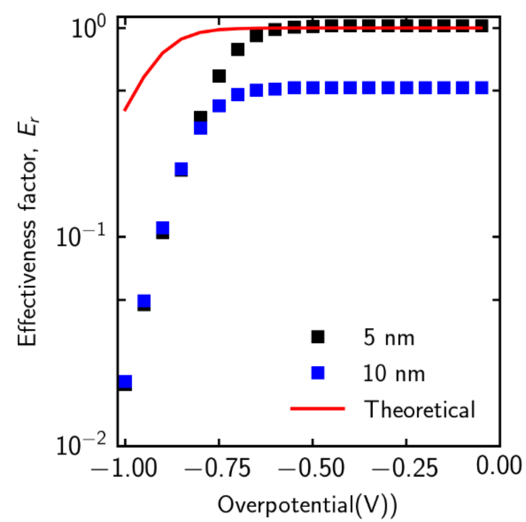


- **Microscale model of agglomerate**
- **Larger catalyst particles compared to Pt based**
  - Effect of local diffusion
  - Reactant limitation/ flooding

Microscale Studies

- **Smaller particles result in better utilization**
- **Discrete catalyst particles result in lower effectiveness factor at higher overpotential (transport limited behavior)**

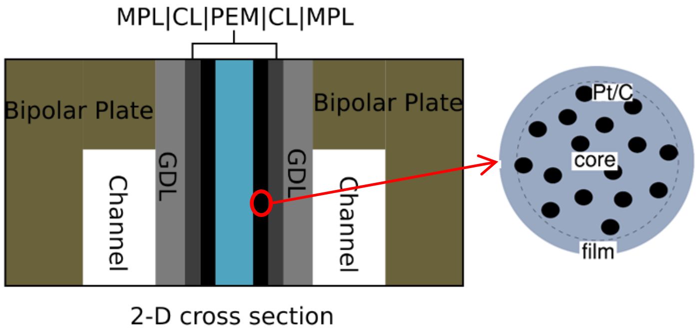


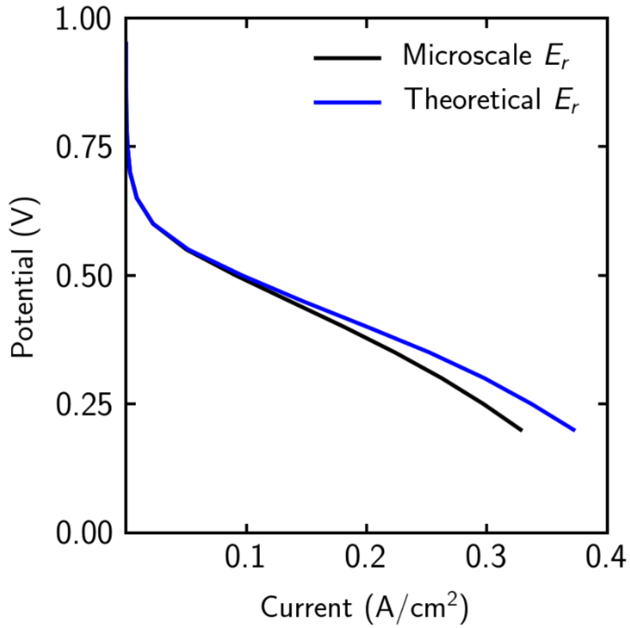


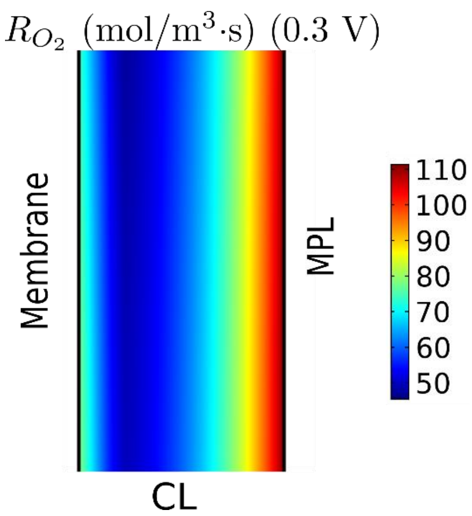
Quantified reduction in catalyst utilization due to discrete catalyst particles.

Accomplishments and Progress

Mass transport modeling







- **2-D MEA cross-section model**
- **Incorporated physics:**
  - Non-isothermal, two-phase model
  - Multicomponent diffusion
  - Electronic and protonic conduction
  - BV kinetics in anode, Tafel with PtOH coverage in Cathode
  - Agglomerate model uses micro-scale simulated effectiveness factor

- Very low kinetic performance due to low ECSA
- Microscale-based model shows lower performance at lower potential due to discrete catalyst particles
- Low CL utilization due to larger thickness
- Local flooding effects due to higher reaction rates need to be captured using microscale model

Modeled non-PGM catalyst-layer performance showing importance of transport.

Accomplishments and Progress

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Response to Reviewers' Comments

This is the first year of our project. There is no previous comments from reviewers.

Collaboration & Coordination

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Center for Renewable Energy Technology

Catalyst design and characterization, MEA fabrication and testing, project management:
Qingying Jia (Project Lead), Sanjeev Mukerjee (Co-PI), Lynne LaRochelle Richard, Ershuai Liu, Li Jiao, Thomas Stracensky

Berkeley Lab

Mass transport modeling:
Adam Weber, Lalit Pant

EMN Consortium Members

PEMFC testing

STEM- HAADF

Synchrotron microscopy and tomography

Multi-scale modeling

Remaining Challenges and Barriers

- Improve the activity and durability of $M_{(x)}$-N-C catalysts in PEMFCs.
- Densify multiple metal sites in M-N-C catalysts synthesized by ionothermal carbonization.
- Incorporate and densify MMC sites into carbon substrate via surface deposition method.
- Escape pyrolysis for synthesis of M-N-C catalysts via surface deposition methods.
- Refine MEA fabrication (electrospinning, IBAD).
- Understand the degradation mode of $M_{(x)}$-N-C catalysts and electrodes in PEMFCs.

Proposed Future Work

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- <u>Improve the activity and stability of ionothermal carbonization synthesized M-N-C catalysts</u>.
  Densify MMC sites.
  Optimize precursors and pyrolysis parameters.
  Tuning the pore distributions.
- <u>Incorporate precursors with pre-existing MMC sites into N-doped carbon substrate</u>.
  Pyrolysis (short time)
  Surface deposition (IBAD and sputtering)
- <u>Optimize the deposition approach (IBAD and sputtering)</u>.
  Improve N-doped carbon substrate with abundant N-C cavities.
  Optimize metal targets.
- <u>MEA fabrication</u>
  Conducting IBAD and electrospinning for MEA fabrication.
- <u>Systematic PEMFC testing</u>

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

Summary

Progress and Accomplishments

- Multiple metal centers (MMCs) directly observed in Fe-N-C catalysts.
- In situ spectroscopy shows MMCs are electroactive for the ORR in acid.
- Porous N-doped carbon substrates for deposition achieved.
- Initial mass-transport model coded and working including multiscale, multiphase physics.
  - Developed microscale model to account for discrete particles in the non PGM CL.

Technical Back-Up Slides

Technical Back-Up

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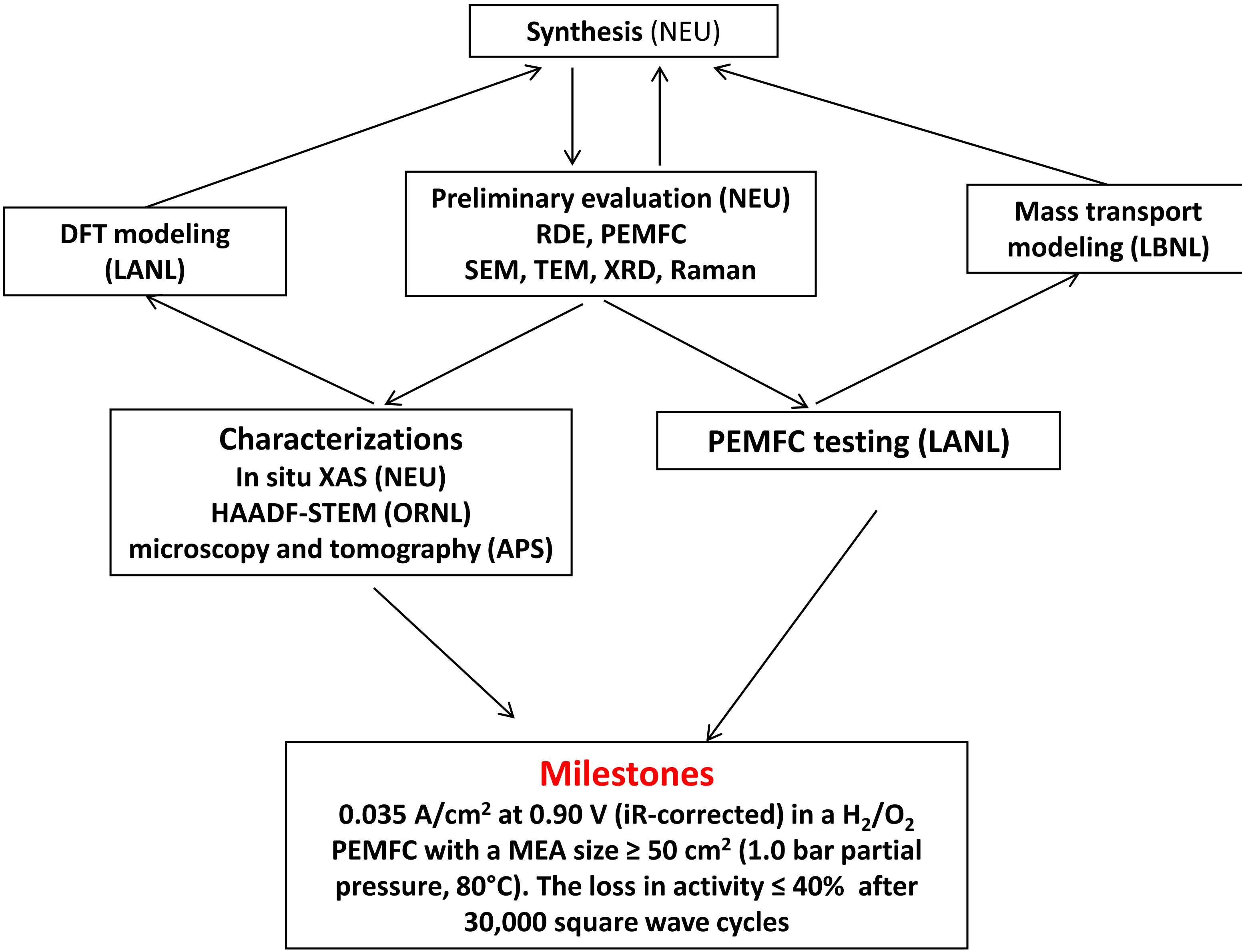

Technical Back-Up

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Sample	Comp.	RA %	IS mm/s	QS mm/s	LW mm/s	H Tesla	Assignment
ICM $FePhen_3$ 300 K	Singlet	12	0.1	-	2.7	-	Unresolved
	Doublet	46	0.34	0.74	0.54	-	Nano-Fe_2O_3
	Sextet 1	6	0.31	-	0.7	44.4	Fe_2O_3
	Sextet 2	6	0.31	-	0.7	47.8	Fe_2O_3
	Sextet 3	30	0.19	-	0.48	20.6	Fe_3C
ICM $FePhen_3$ 5 K	Singlet	22	0.21	-	4.0	-	Unresolved
	Sextet 1	23	0.48	-	0.77	47.9	Fe_2O_3
	Sextet 2	39	0.49	-	0.67	51.7	Fe_2O_3
	Sextet 3	16	0.33	-	0.49	25.7	Fe_3C
ICM $FePhen_3$ AW 300 K	Singlet	55	0.17	-	2.6	-	Unresolved
	Sextet	45	0.26	-	0.5	20.8	Fe_3C

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Technical Back-Up

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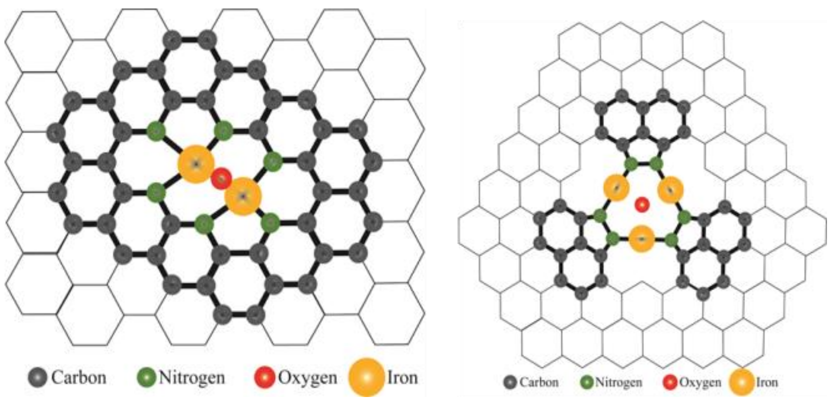
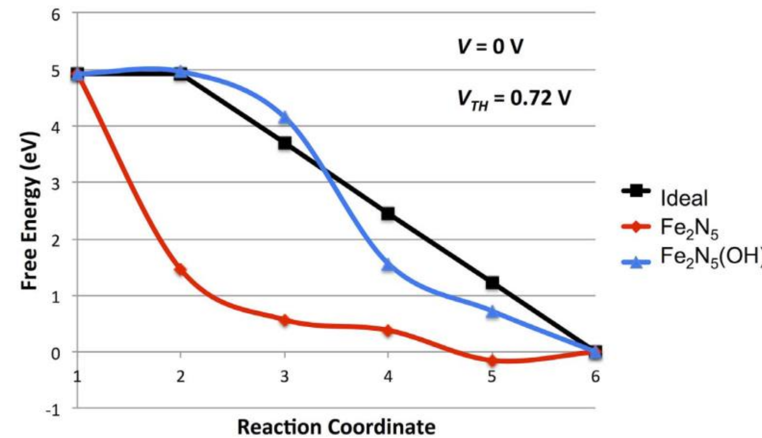
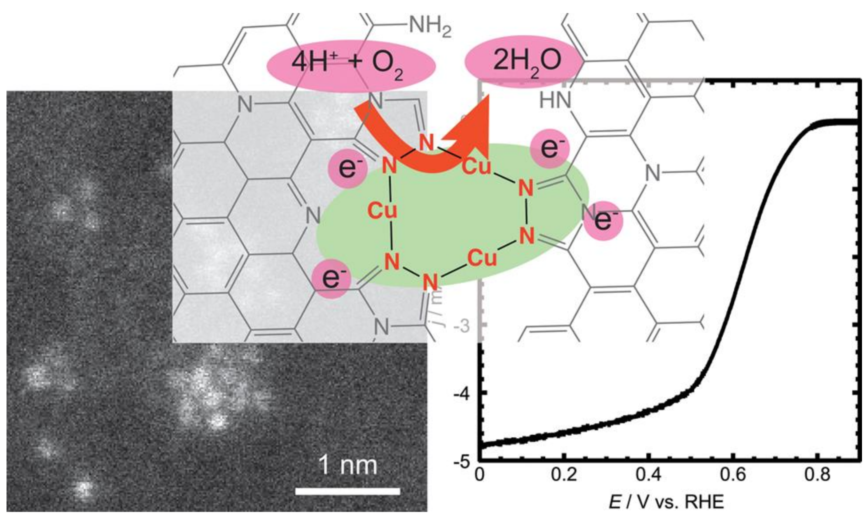


Schematic illustration of MMC sites.

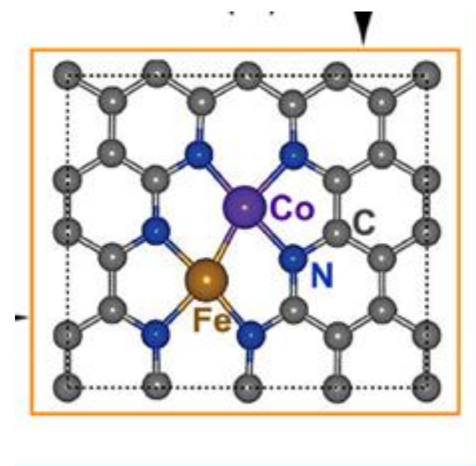


Holby, E. F.; Taylor, C. D. *Sci. Rep.* **2015**, *5*.

Desired ORR kinetics of MMC sites by DFT



ACS Appl. Energy Mater. **2018**, 1, 2358–2364



J. Am. Chem. Soc. **2017**, 139, 17281

Literature evidence for the presence of MMC sites.