

PGM-free Engineered Framework Nano-Structure Catalysts

2019 DOE Hydrogen and Fuel Cells Program Review Presentation

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Greenway Energy, LLC
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Project ID # FC173

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Project Overview

Timeline

- Project start date – 09/01/2017
- Project end date – 12/31/2020
- Percent complete – ~40%
(Q6 complete)

Budget

- Total project funding
 - \$2,000,000 (DOE share)
 - \$500,000 (Cost share)
- DOE funds spent
 - \$ 790k (as of 12/31/18)

Barriers

- A. Durability (Catalyst)
- B. Cost (Catalyst)
- C. Performance (Catalyst, MEA)

Partners and Collaborators

- Greenway Energy, LLC (Project Lead)
- Savannah River National Laboratory (Subcontractor)
- Northwestern University (Subcontractor)
- California State University-Northridge (Collaborator)
- Ballard Power Systems (No Cost Partner)
- Los Alamos National Laboratory (Core Lab)
- Oak Ridge National Laboratory (Core Lab)

Relevance

Overall Objective: Develop durable, highly active, PGM-free oxygen reduction electrocatalysts using rational design.

- This project addresses technical targets from DOE's FCTO Multi-Year R&D Plan to enable commercialization of fuel cell electric vehicles.
- This project is part of the ElectroCat Consortium for the advancement of PGM-free catalysts to reduce fuel cell costs.

FY2019 Objectives:

- Catalyst development based on high surface area polymers
- MEA optimization and fuel cell testing
- Achieve 25 mA cm⁻² in H₂/O₂ FC test (80°C and 100 kPa)

Metric	Units	Current Status	FY18 Target	FY19 Target	FY20 Target	2020 DOE Target
Fuel Cell test: Catalyst Activity	mA cm ⁻² @ 900 mV _{IR-free}	~30 ^b	≥ 20 ^b	≥ 25 ^b	≥ 30 ^b	≥ 44 ^a
Fuel Cell test: Catalyst Activity	mA cm ⁻² @ 800 mV	52.8	NA	NA	≥ 150 ^c	NA
RRDE test: Catalyst Activity	mA cm ⁻² @ 800 mV	2.78	≥ 1.5 ^d	≥ 2.0 ^d	NA	NA

^a 80°C H₂/O₂ MEA; fully humidified, total outlet pressure 150 kPa; anode stoich 2; cathode stoich 9.5

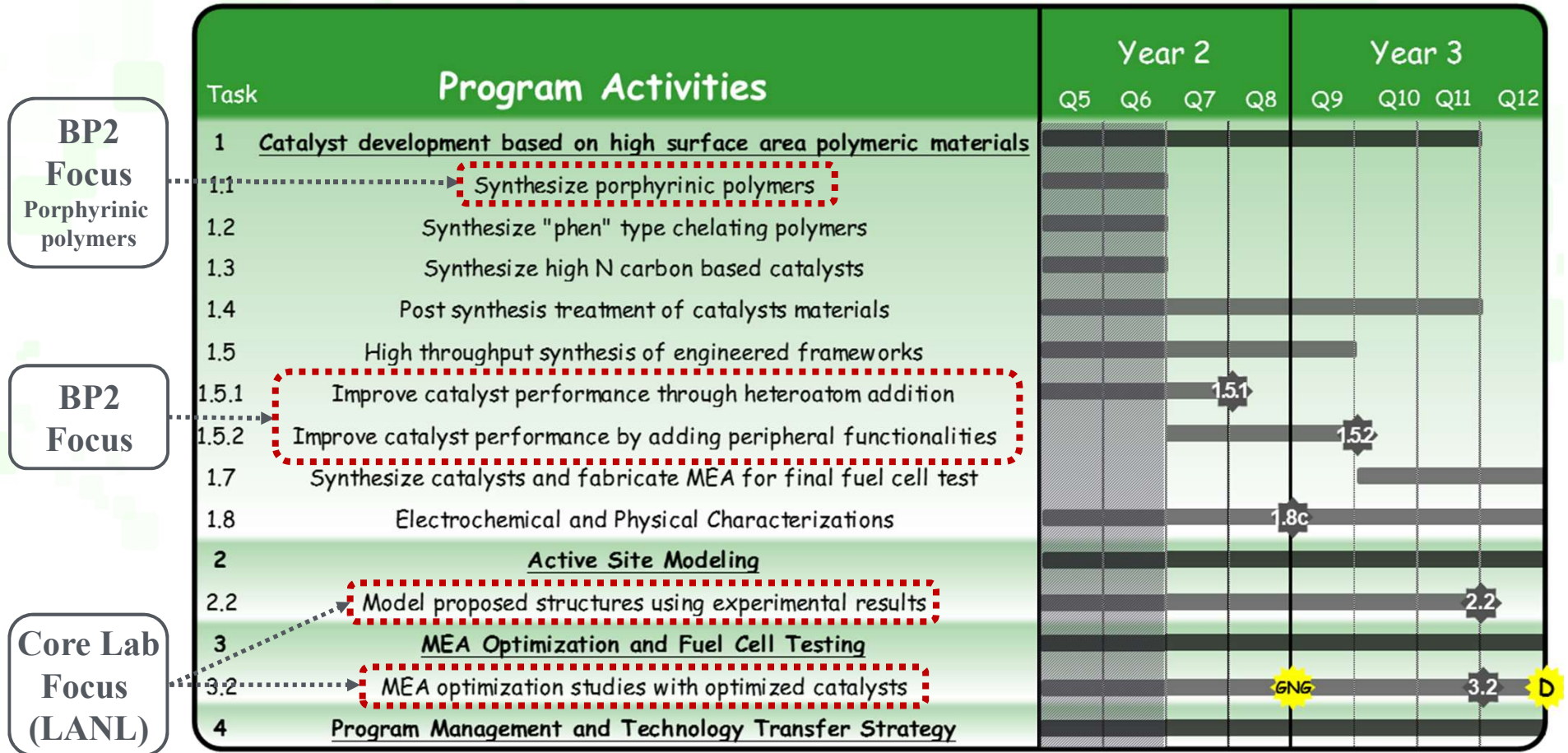
^b 80°C H₂/O₂ in an MEA; total outlet pressure of 100 kPa

^c 80°C H₂/Air in an MEA; total outlet pressure of 100 kPa

^d 0.1 M HClO₄ acid; catalyst loading of 0.6 mg cm⁻²

Approach

Overall Project View



Approach Milestones

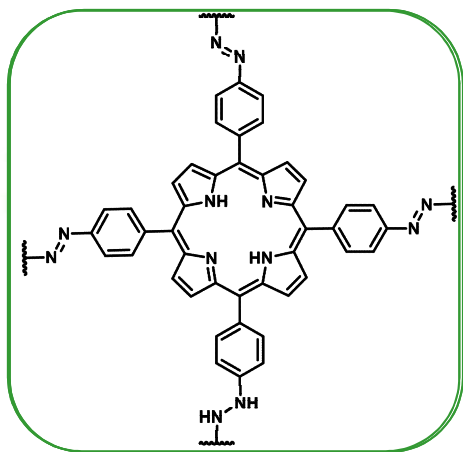
Milestone	Project Milestones	Type	Completion (Quarter)	%Complete	Progress Notes
1.1	Optimize synthesis protocol to prepare >400 mg of "phen" type chelating polymers per batch	Milestone	Q1	100%	Complete
1.2	Optimize synthesis protocol to prepare >400 mg of porphyrinic polymers per batch	Milestone	Q1	100%	Complete
1.3	Optimize synthesis protocol to prepare >400 mg of high N containing carbon based materials per batch	Milestone	Q1	100%	Complete
1.5	Down select polymeric materials for high throughput synthesis	Milestone	Q2	100%	Complete
1.8a	Demonstrate improved ORR activity through transition metal coordination.	Milestone	Q1	100%	Complete
1.8b	RRDE performance >1.5 mA cm ⁻² at 0.8 V vs. RHE	Milestone	Q3	100%	Complete
2.1	Align core lab modeling with experimental approach	Milestone	Q2	100%	Complete
GNG	Demonstrate H ₂ -O ₂ fuel cell performance that meets or exceeds 20 mA cm ⁻² at 0.90 V _{IR-free}	Go/No-Go	Q4	100%	Complete
1.8c	RRDE performance >2.0 mA cm ⁻² at 0.8 V vs. RHE	Milestone	Q5	100%	Complete
1.5.2	Initiate addition of peripheral functionalities on selected catalyst materials	Internal Milestone	Q6	10%	In Progress
1.5.1	Demonstrate improved catalyst performance through the addition of heteroatoms on selected catalyst materials	Milestone	Q7	10%	In Progress
GNG	Demonstrate H ₂ -O ₂ fuel cell performance that meets or exceeds 25 mA cm ⁻² at 0.90 V _{IR-free}	Go/No-Go	Q8	100%	Complete
2.2	Model proposed structures using experimental results	Milestone	Q10	50%	In Progress
Project Goal	Demonstrate H ₂ -O ₂ fuel cell performance that meets or exceeds 30 mA cm ⁻² at 0.90 V _{IR-free}	Milestone	Q12	100%	Complete
Project Goal	Demonstrate H ₂ -air fuel cell performance that meets or exceeds 150 mA cm ⁻² at 0.80 V, total absolute pressure of 1.0 bar and 80 °C	Milestone	Q12	0%	In progress

Accomplishments and Progress

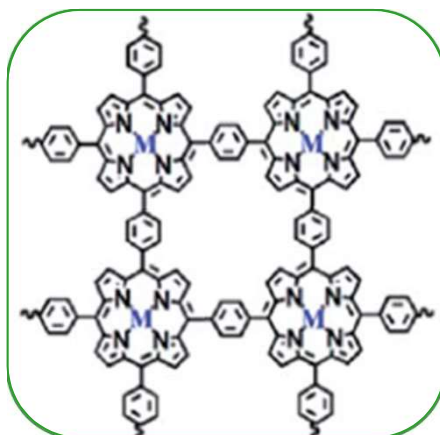
Experimental Approach: Materials of Focus

Catalyst Development Based on High Surface Area Polymers

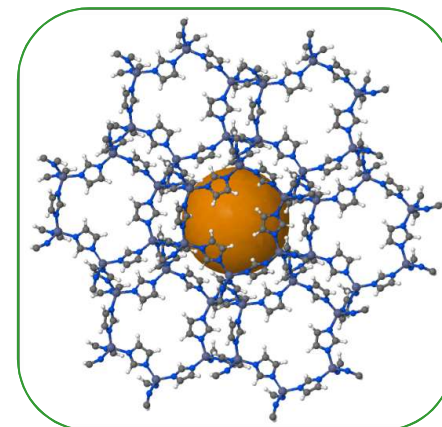
- Budget period 2 will focus on optimization and functionalization of down selected catalysts from 17 families
 - Polyporphyrin type of catalysts (unique catalyst in ElectroCat)
 - Study the effect of different linkers
 - Study the effect of incorporating heteroatoms
 - ZIF-8 type of catalyst selected (used as a baseline)



Poly-azoporphyrin



Poly-phenylporphyrin

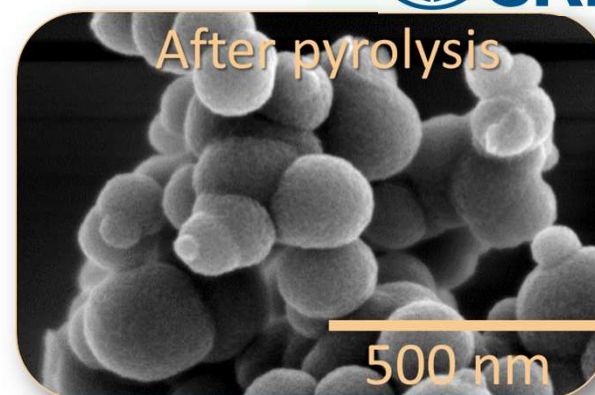
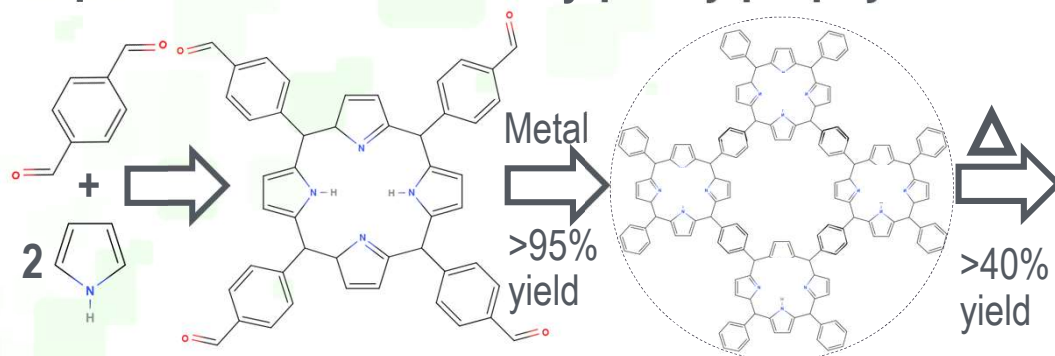


ZIF-8

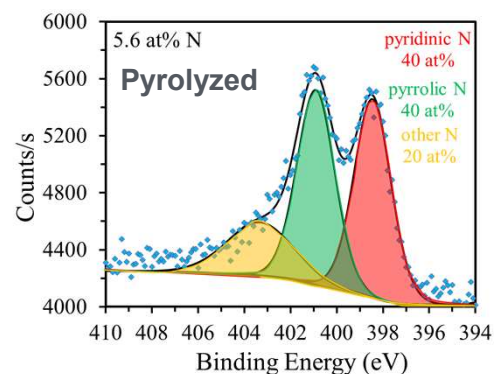
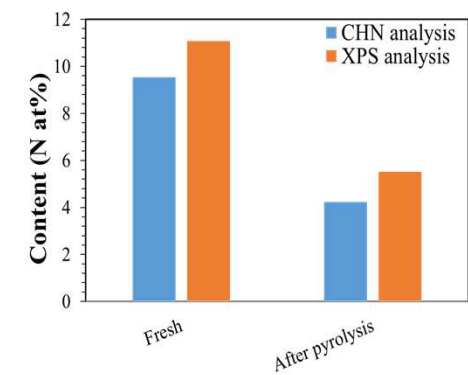
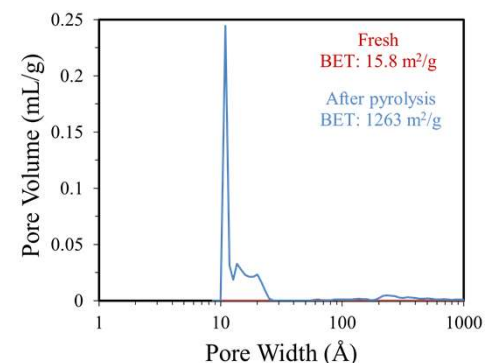
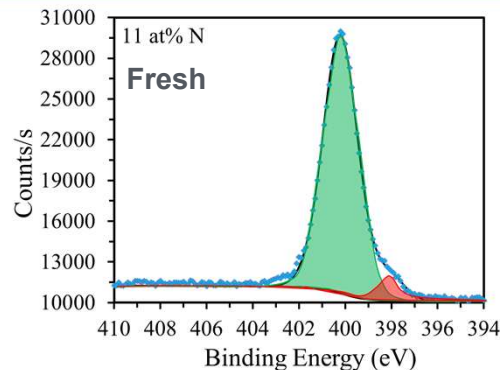
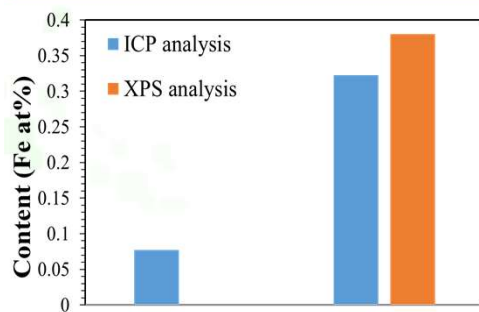


Accomplishments and Progress

Experimental Results: Poly-phenylporphyrin



- Synthesis has been developed and optimized to maximize catalyst performance
- Catalyst utilizes low cost precursors; simple to scale-up; requires minimal post synthesis treatments



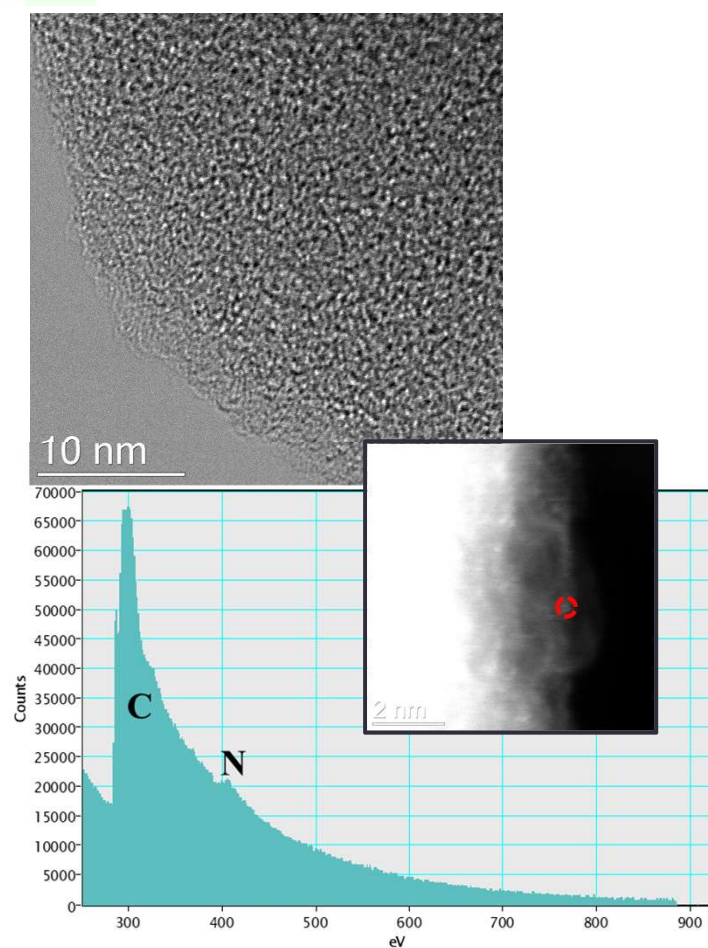
- Fresh material shows a high nitrogen content, corresponding to the theoretical amounts
- After pyrolysis, the nitrogen content decreases by half as confirmed by CHN and XPS analysis
- Metal content increases from 0.08 at% to about 0.35 at% after pyrolysis
- BET analysis shows surface area increases from 16 m²/g to 1263 m²/g after pyrolysis

Accomplishments and Progress

Experimental Results: Poly-phenylporphyrin

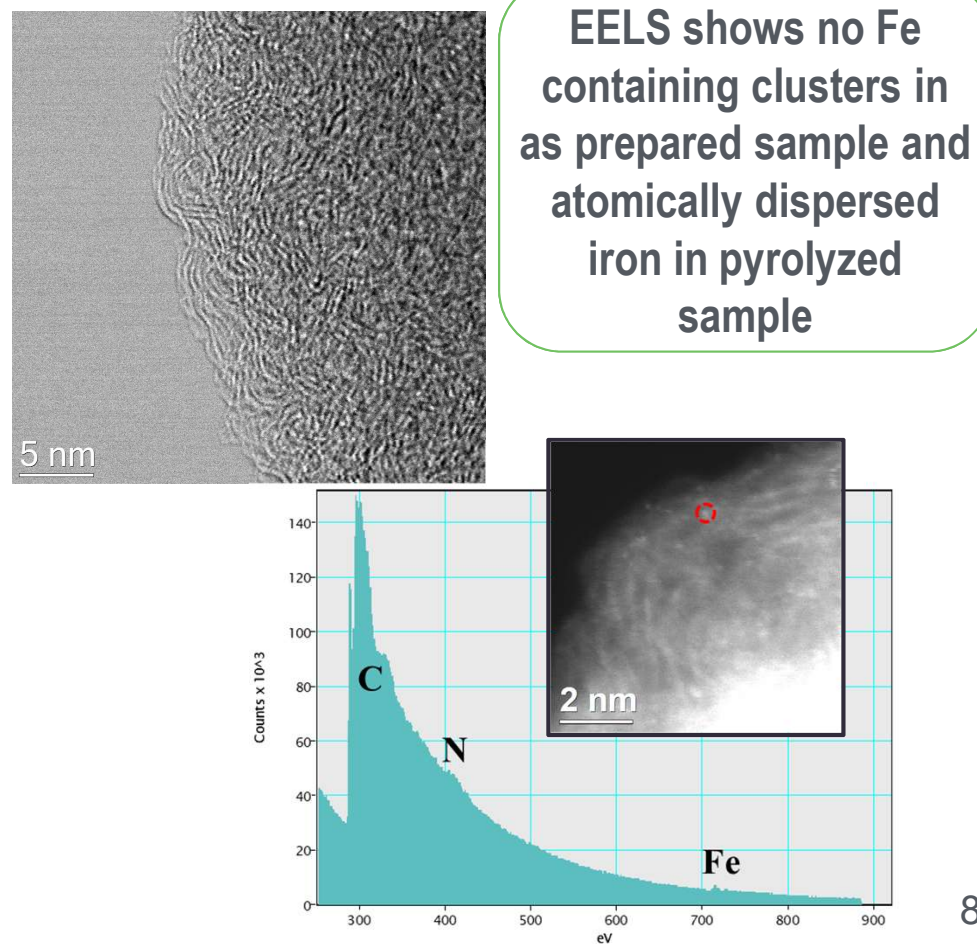
As prepared

- As prepared particles are dense, have smooth surfaces and are mostly amorphous
- No Fe containing clusters or particles observed



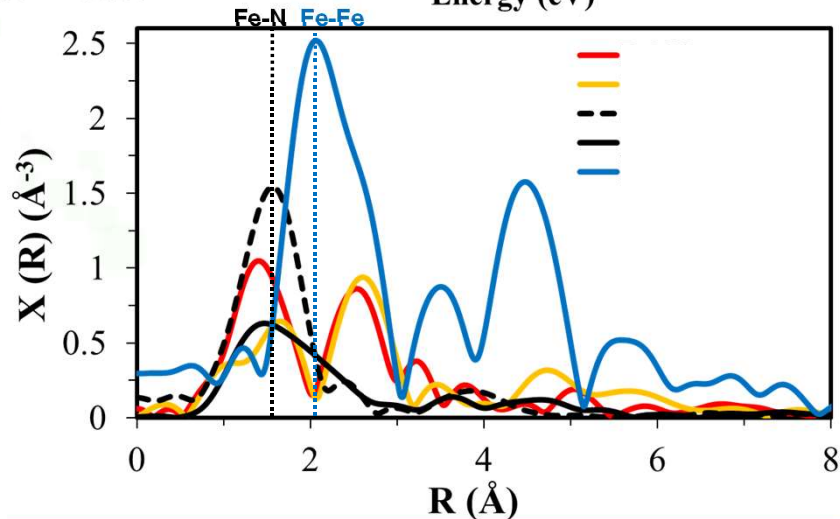
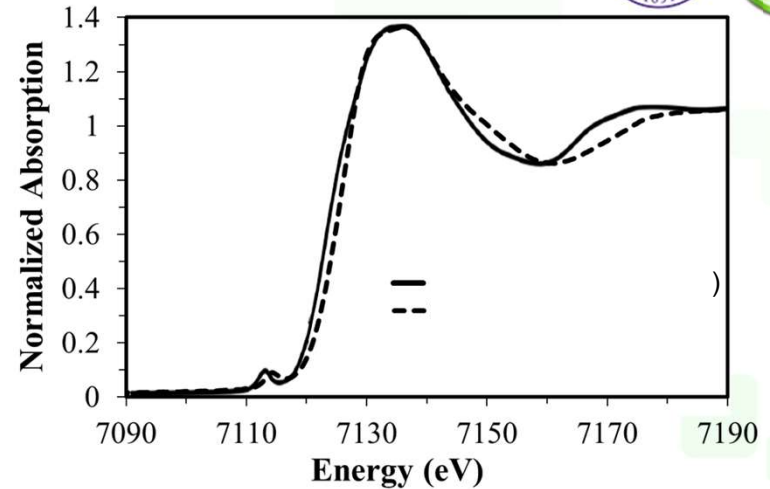
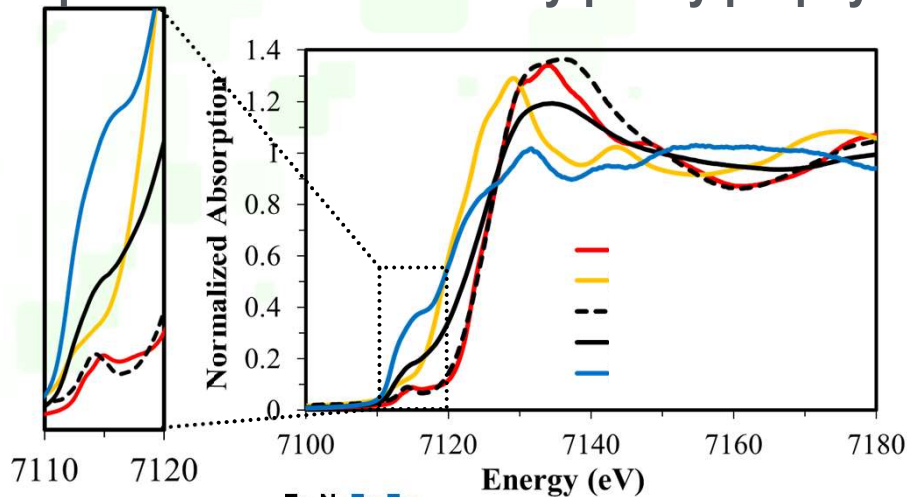
After Pyrolysis

- Heat treated particles are porous/rough, meso-graphitic, exhibit some nano-porosity
- Atomically dispersed iron



Accomplishments and Progress

Experimental Results: Poly-phenylporphyrin



- Single atom Fe sites in polyporphyrins
- Fe-N₄ present in “as prepared” polyporphyrin, good match to Fe-porphine reference
- Lower symmetry in pyrolyzed polyporphyrin, some Fe-N_x (x<4) present

Fe K-edge XANES analysis

- Rising edge absorption energy indicates Fe in 3+ oxidation state for both “as prepared” and pyrolyzed polyporphyrin samples
- Pre-edge peak at ~7114 eV shows
 - high symmetry (fingerprint of D_{4h}) for “as prepared” sample indicating Fe-N₄
 - lower symmetry for pyrolyzed sample indicating some Fe-N_x (x<4)
- “as prepared” sample absorption energy is a good match to Fe-porphine reference

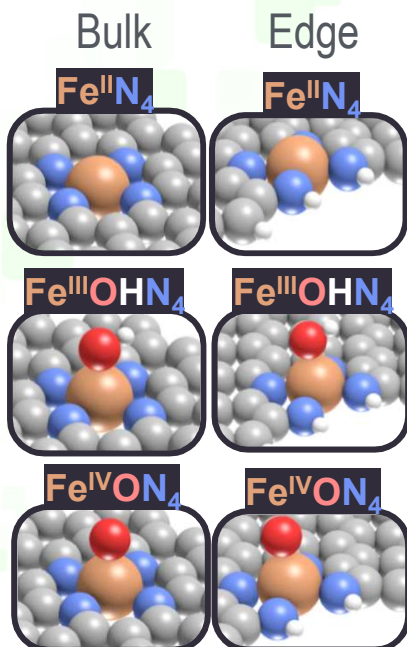
Fe K-edge EXAFS analysis

- Both samples show absorption at ~1.5 Å which is attributed to Fe-N scattering path
- Neither sample shows a Fe-Fe signal at 2.13 Å₉

Accomplishments and Progress

Modeling Results: Active site modeling

Active sites considered



Assumed Reaction Mechanism

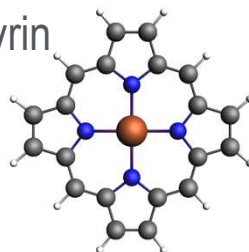
1. $O_2(g) + H^+(aq) + e^- \rightarrow OOH(ads)$
2. $OOH(ads) + H^+(aq) + e^- \rightarrow O(ads)$
3. $O(ads) + H^+(aq) + e^- \rightarrow OH(ads)$
4. $OH(ads) + H^+(aq) + e^- \rightarrow H_2O(l)$
5. $O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$

During 2018 AMR

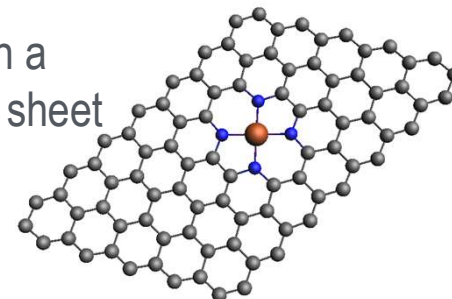
- Quantify the impact of various theoretical methods
 - computational hydrogen electrode (CHE)
 - linear Gibbs energy relation (LGER)
- Adsorption energies and reversible potentials were calculated for various species on Fe-bulk and Fe-edge sites based on four electrochemical steps
 - Fe^{III} and Fe^{IV} are closer to the ideal values and are able to catalyze the 4e⁻ reduction at the operating potentials
- OH is stable when bonded on bulk Fe^{II}, producing a stable bulk Fe^{III} site
- Fe^{III} edge site is stable and is predicted to be active for the 4 e⁻ reduction

FY19- Using both the OH and O ligand on the FeN₄, a new reaction pathway for the ORR is proposed and applied to Fe-porphyrin and FeN₄ present in a graphene sheet

Fe-porphyrin

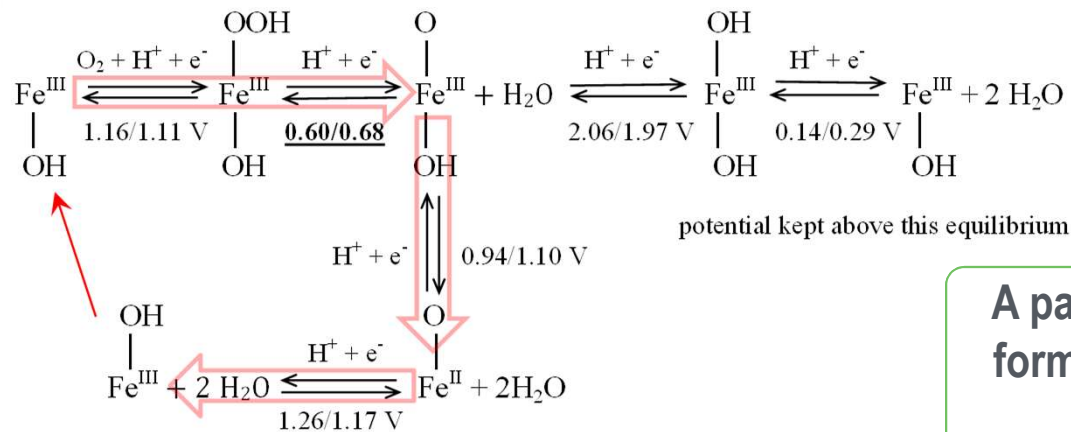
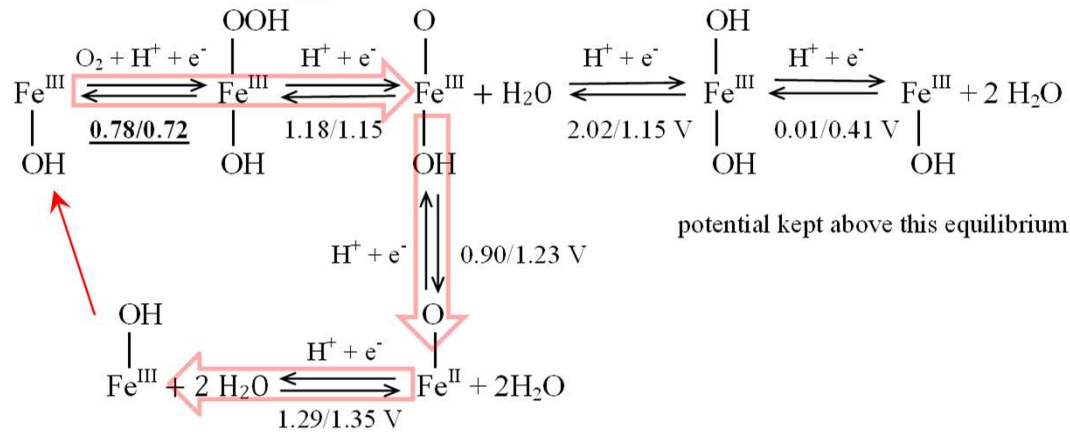


FeN₄ in a graphene sheet



Accomplishments and Progress

Modeling Results: Reaction Pathway (Fe-porphyrin)

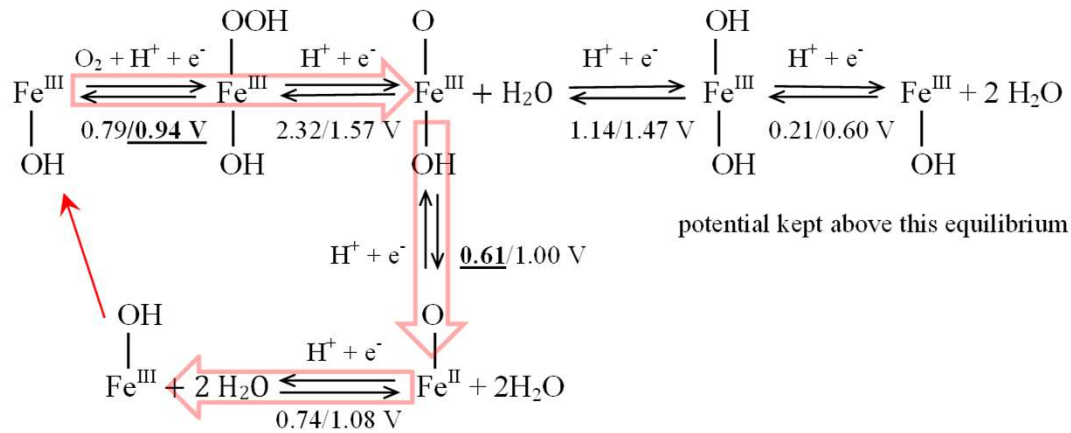


- ORR pathways were evaluated where both axial positions of an Fe atom as well as the neighboring C-binding site are included for a variety of FeN₄-type structures.
- Both O and OH intermediates can possibly act as ligand modifiers.
- In this pathway, a spontaneously evolved OH ligand is formed (as previously proposed) and then acts as an intermediate with the OH/O ligation effectively changing sides of the complex during cycles of ORR.
- For Fe-porphyrin, neighboring carbon was not found to be a stable binding site, unlike in the bulk hosted FeN₄

A pathway is proposed where OH/O ligands form and change sides on the Fe-porphyrin complex during cycles of ORR.

* Fe porphyrin pathways are analyzed using LGER and CHE thermochemical approaches with two different exchange-correlation functionals (PBE and RPBE).

Modeling Results: Reaction Pathway (FeN₄ in graphene)



- New multi-valent reaction pathway proposed based on calculations of multiple structures and multiple methods
- Catalyst synthesis design should target open Fe axial sites

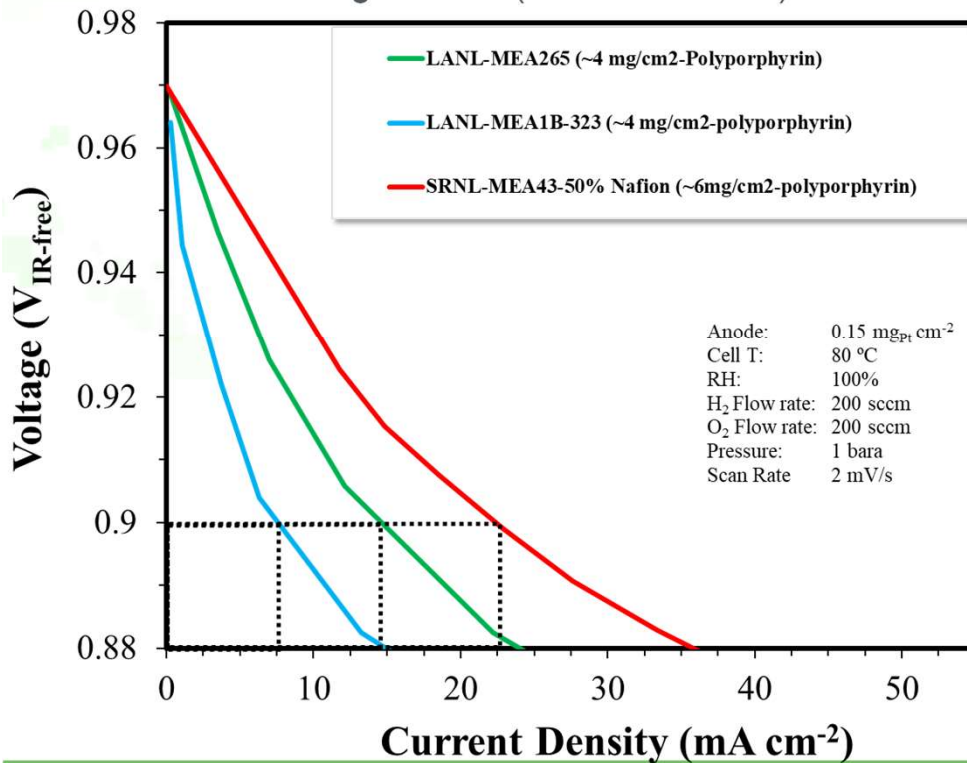
- Graphene hosted FeN₄ structure is likewise shown to have a fairly high ORR activity for this newly proposed pathway.
- The new approach only utilizes Fe binding and thus is not susceptible to C-based poisoning as suggested in literature.
- For such pathways to occur, both axial positions of the Fe must remain accessible to the environment and not form stacked layers that could sterically block these high activity pathways.
- Theoretical input to the experimental effort suggests using polymerization approaches that maintain the open 2D nature after pyrolysis to enable such pathways and to obtain high ORR activities.

Accomplishments and Progress

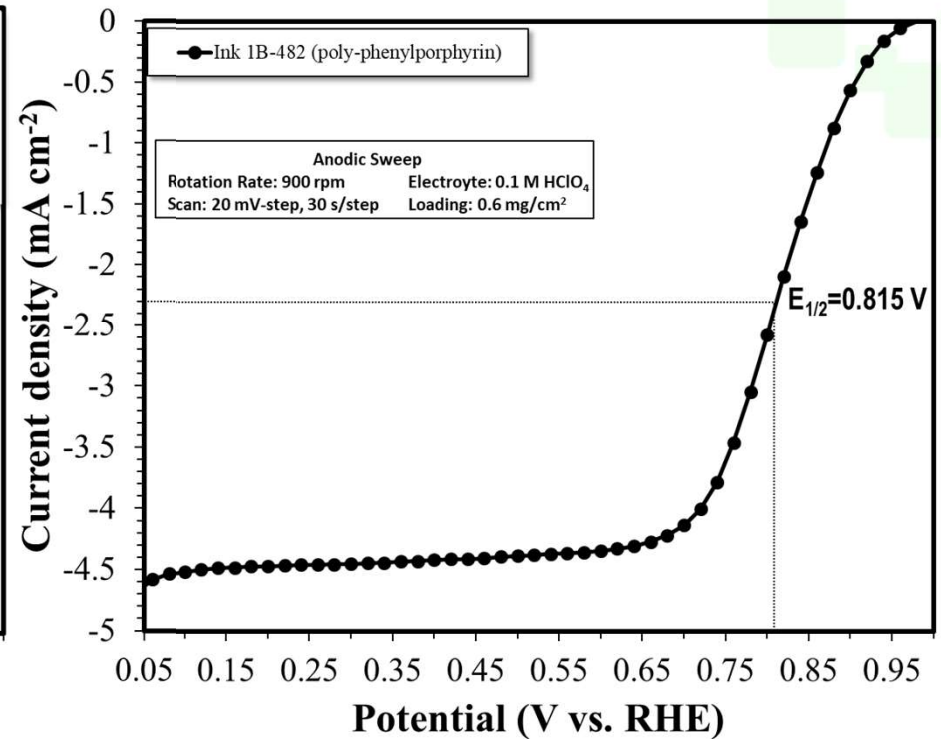
Experimental Results: Poly-phenylporphyrin



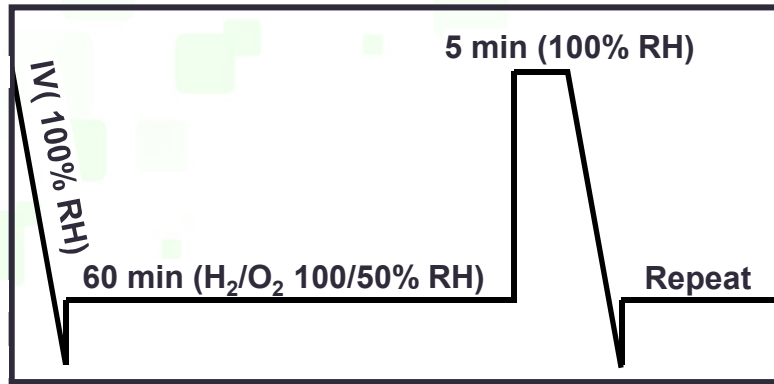
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-
- MEAs show high OCPs (0.965 - 0.986 V)



FY18 FC activity target met

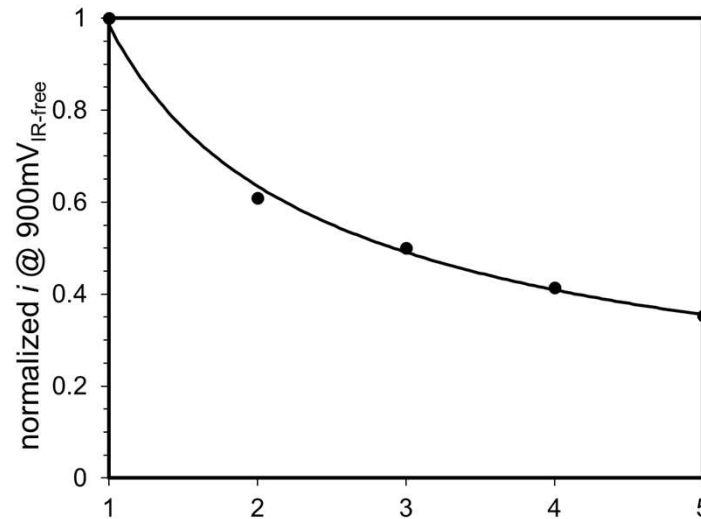
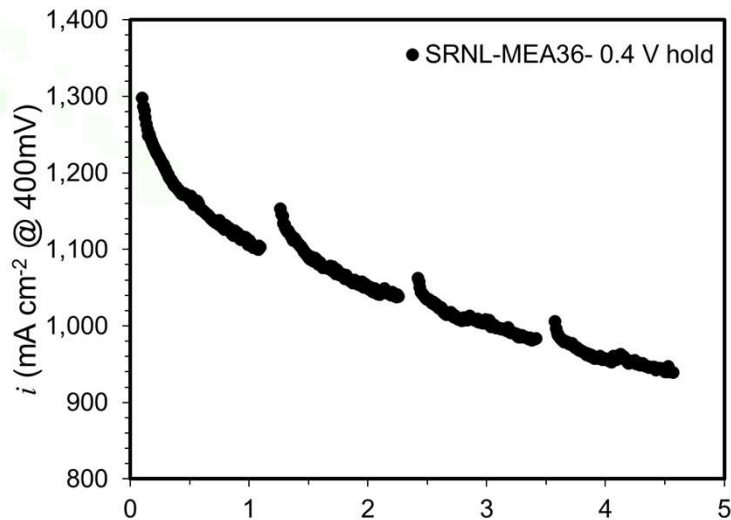


Experimental Results: Poly-phenylporphyrin FC stability testing



- Water flooding observed as performance recovers after polarization

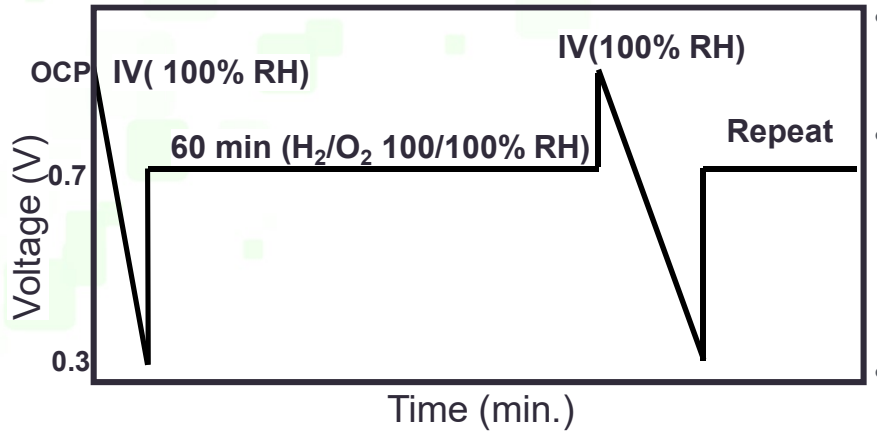
RH
decay



High degradation rate is observed during potential hold at 0.4 V

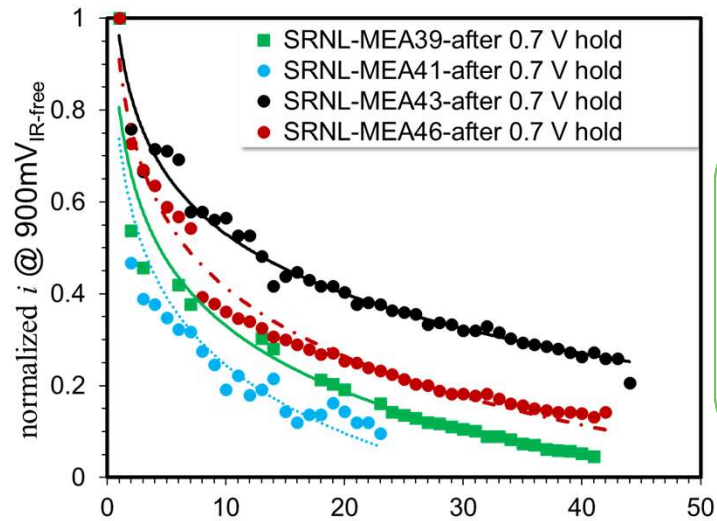
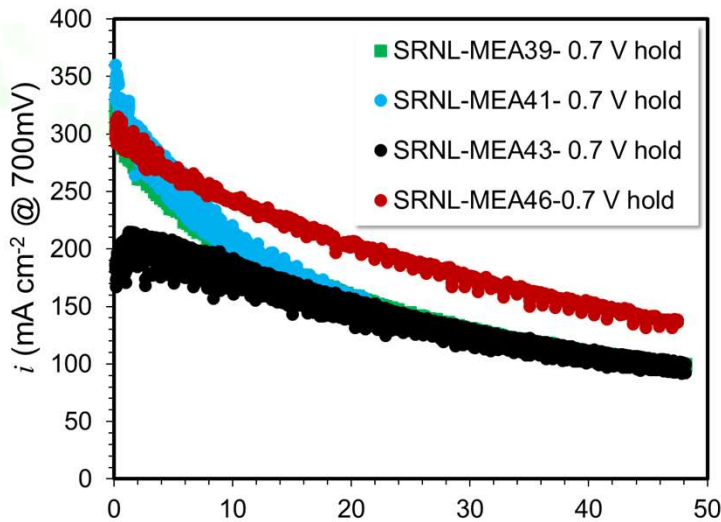
Accomplishments and Progress

Experimental Results: Poly-phenylporphyrin FC stability testing



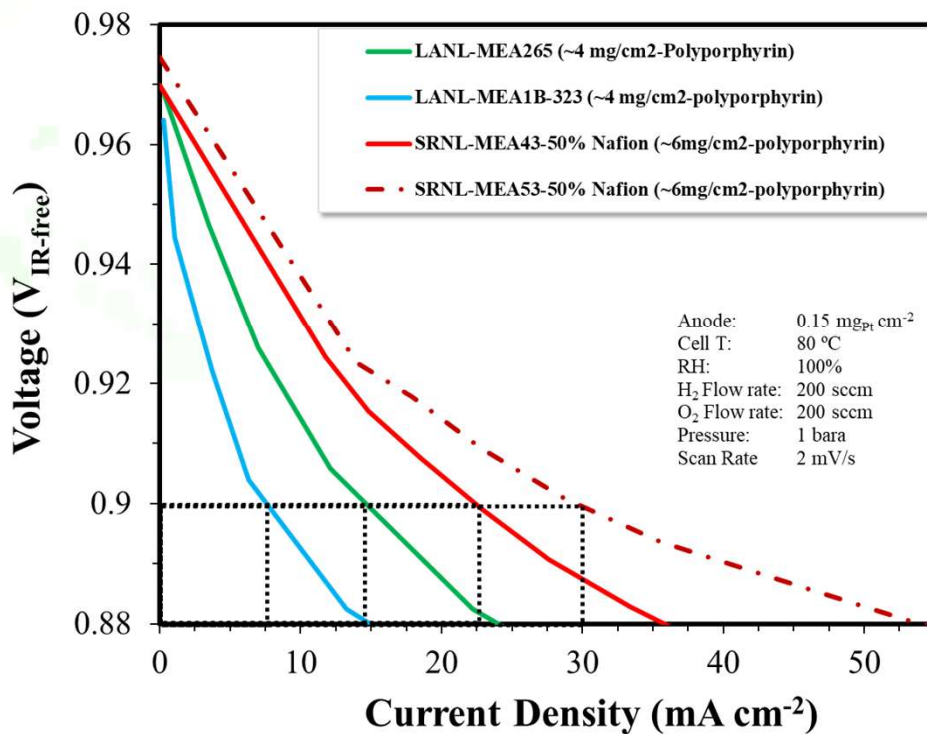
and 100% RH

Various modifications in the catalysts synthesis are investigated to increase durability



Lower degradation rate is observed during potential hold at 0.7 V

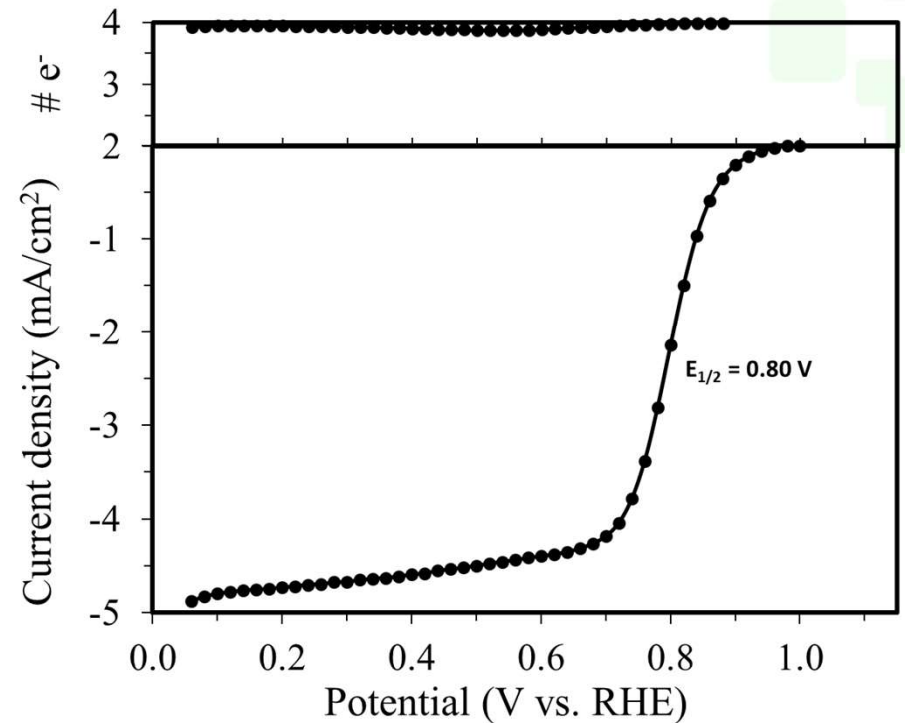
End of project FC activity target met



RDE Performance

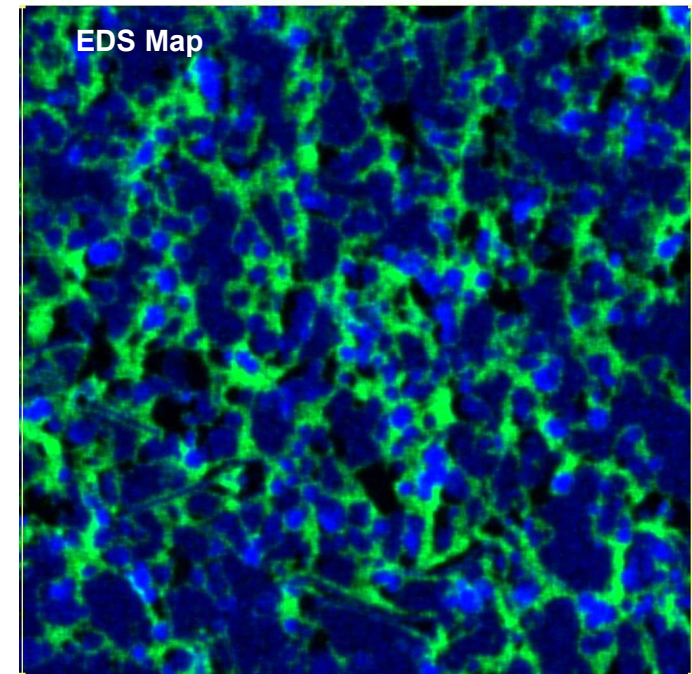
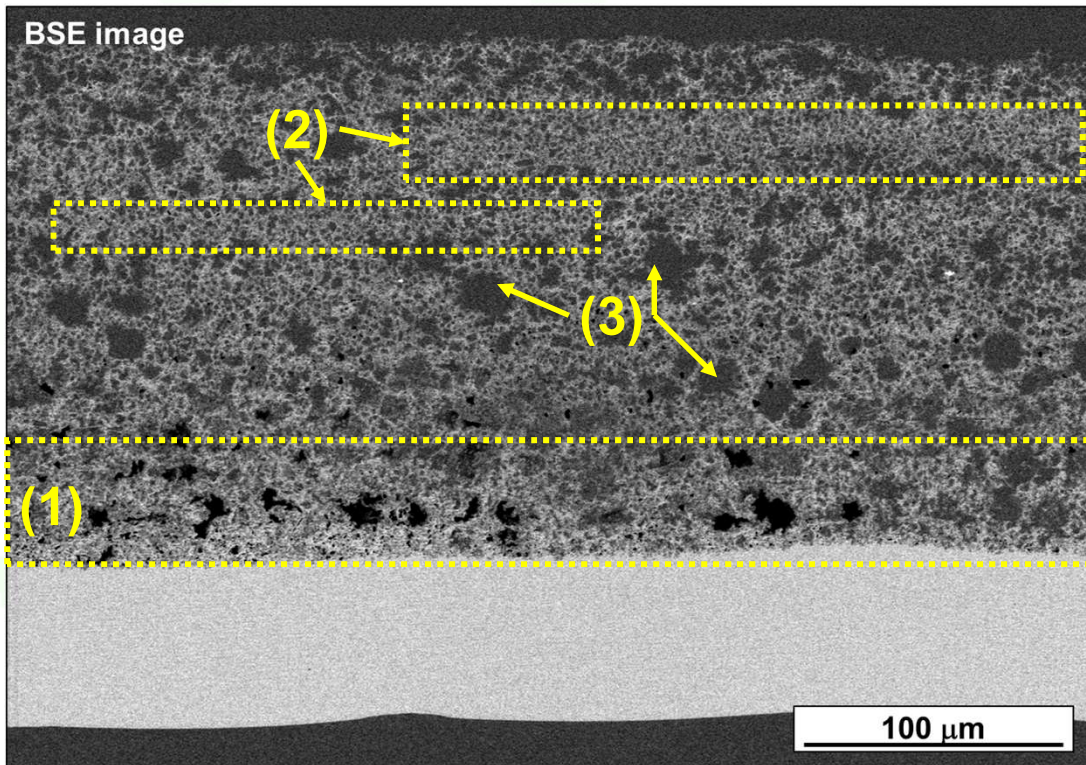
- RDE performance did not change significantly

shows #e⁻ transferred ~ 3.88



Accomplishments and Progress

Experimental Results: Modified Poly-phenylporphyrin



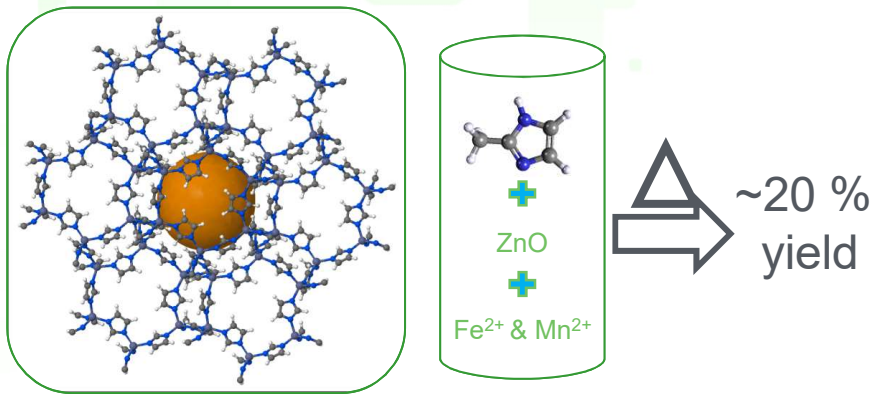
- Large pockets of ionomer (green) between aggregates of catalyst (blue)

- Heterogeneous catalyst layer structure
 - (1) Highly porous layer close to membrane
 - (2) Dense bands of catalyst/ionomer parallel to membrane
 - (3) Large pores observed throughout the layer

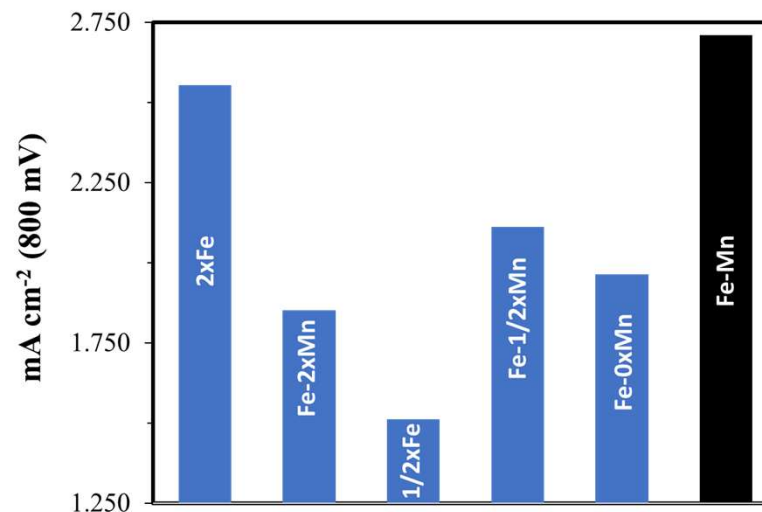
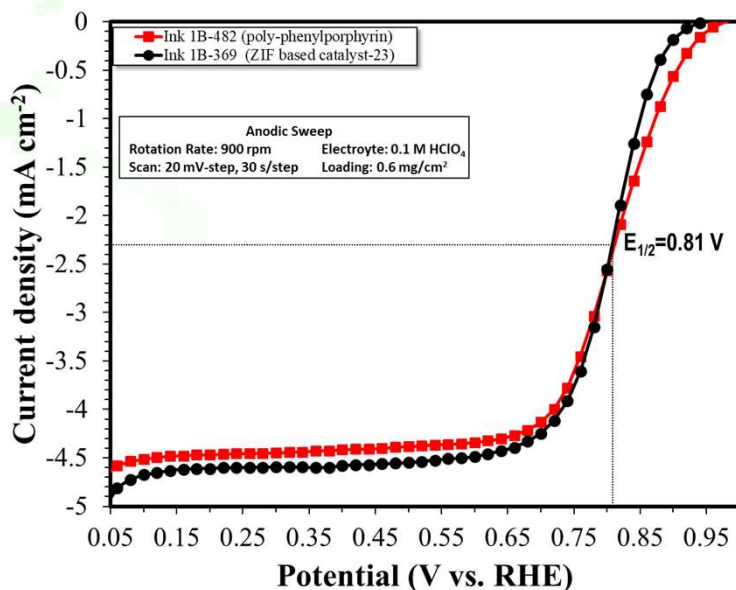
MEA catalyst layer needs optimization to improve ionomer distribution, increase porosity, and decrease catalyst layer thickness

Accomplishments and Progress

Experimental Results: ZIF based catalyst



- Solid state synthesis
 - Large scale reaction
- High surface area
- Mn can be introduced
- Metal loading optimization is on-going
 - Various Fe/Mn ratios are being tested
- $E_{1/2} = 0.81 \text{ V}$
- Lower currents observed at high potentials (kinetic region) as compared to poly-phenylporphyrin



Synergistic effect observed for Mn addition to Fe based catalyst

Accomplishments and Progress Response to Previous Year Reviewer's Comments

Reviewer's Comment	Response to Comment
Lack of durability data	We initiated and presented the stability testing under H ₂ /O ₂ using input from our industrial and ElectroCat partners.
Collaboration not clear	Contributing entities added to each progress slide
The current FC performance status seems significantly short of performance target	We increased our FC testing and met end of project H ₂ /O ₂ performance target.
It is unclear at the present time whether the model results will direct future experiments.	Our computational studies are currently evaluating possible ORR active sites and reaction pathways to narrow the gap between model and experimental results. We initiated the study of Fe-porphyrin as active sites using novel reaction pathways for the ORR.
Porphyrinic compounds have been examined in the past.	We consider our catalyst system to be unique with respect to previous and current funded projects. We incorporate porphyrinic functional groups into the catalyst, but that is the extent of the similarities with previous work.

Team

GreenWay Energy (Project Lead, Small Business)

- Prabhu Ganesan – material characterization, MEA fabrication, fuel cell testing, and project management
- Mark Elvington – rational design, synthesis, and development of engineered framework nano-scale electrocatalysts
- Alfred Anderson – direct the active site modeling

SRNL (Subcontractor, FFRDC)

- Héctor Colón-Mercado – electrochemical characterization, catalyst activation, and fuel cell testing

Northwestern University (Subcontractor, University)

- Joseph Hupp – manage NU polymer electrocatalyst design and synthesis
- Omar Farha – direct NU polymer electrocatalyst design and synthesis

Ballard Power Systems (OEM, Industry)

- Shanna Knights – evaluation of promising electrocatalysts

California State University-Northridge (University, Collaborator)

- Joseph Teprovič – synthesis of ZIF based catalysts

Collaborations with ElectroCat Consortium

Los Alamos National Laboratory (ElectroCat Core Lab)

- Piotr Zelenay, Hoon Taek Chung
 - Membrane electrode assembly fabrication
 - PGM-free catalyst synthesis, analytical characterization, and electrochemical and fuel cell testing
- Edward Holby
 - Multi-scale modeling for rational design of PGM-free catalysts

Oak Ridge National Laboratory (ElectroCat Core Lab)

- Karren More
 - Analytical electron microscopy and/or electron tomography

Remaining Challenges and Barriers

- Catalyst Durability – catalyst stability requires significant attention during BP2
- Catalyst Performance – current catalyst performance meets RRDE targets, however, improved MEA performance is still needed meet end of project H₂/air fuel cell performance (150 mA/cm² @ 800 mV)
 - Optimize catalysts' physical properties and increase electrochemical surface area

Task 2 – Active site modeling

- The kinetic treatment on the combined electron transfer and bond rearrangement presents a challenge. This form of OOH_{ads} may be important to understanding active site degradation and poisoning.

Task 3 – MEA optimization and fuel cell testing

- MEA performance – Optimize MEA fabrication to:
 - lower high frequency resistance
 - increase catalyst distribution and utilization
 - Increase high current density performance

Proposed Future Work

Task 1 – Catalyst development based on high surface area polymers

- Study the effect of heteroatom substitution and peripheral groups addition
- Explore the use of different polyporphyrin linkers
- Explore the use of different transition metal centers
 - Mn, Co, Ni
- Continue to improve the electrochemically active surface area
- Continue to improve the electronic conductivity of the catalyst

Task 2 – Active site modeling

-

Task 3 – MEA optimization and fuel cell testing

- Continue in-house FC screening of prepared catalyst
- Continue MEA optimization at LANL
- Initiate FC catalyst evaluation in H₂/air

Summary of work performed to date

- PGM-free Engineered Framework Nano-Structure Catalysts selected from were prepared using a rational catalyst design with well defined structures and functional groups. 17 families of catalysts based on MOFs, COFs, and POPs were prepared and characterized
 - XAS analysis shows single atom Fe sites in polyporphyrins with Fe-N₄ sites in “as prepared” polyporphyrin, and similar absorption energy to Fe-porphine reference. Lower symmetry observed in pyrolyzed polyporphyrin, some Fe-N_x (x<4) present.
 - Electron microscopy studies show “as prepared” particles are dense, have smooth surfaces, are mostly amorphous, and contain no Fe clusters or particles. Heat treated particles are porous/rough, meso-graphitic, exhibit some nano-porosity and atomically dispersed iron.
- New multi-valent reaction pathway proposed based on calculations of multiple structures and multiple methods – synthesize materials to keep both Fe axial sites open.
- Electrochemical characterization of polyporphyrin catalysts developed during BP1 shows high performance for the ORR (see table).
 - End of project catalyst activity target (30 mA/cm² at 0.9 V_{IR-free}) achieved.

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RRDE test: Catalyst Activity	mA cm ⁻² @ 800 mV	2.78	≥ 1.5 ^d	≥ 2.0 ^d	NA	NA

^a 80°C H₂/O₂ MEA; fully humidified, total outlet pressure 150 kPa; anode stoich 2; cathode stoich 9.5

^b 80°C H₂/O₂ in an MEA; total outlet pressure of 100 kPa

^c 80°C H₂/Air in an MEA; total outlet pressure of 100 kPa

^d 0.1 M HClO₄ acid; catalyst loading of 0.6 mg cm⁻²

Acknowledgements



Donna Ho, DOE

Simon Thompson, DOE

Dimitrios Papageorgopoulos, DOE

John Kopasz, ANL

Hoon Chung, LANL

Piotr Zelenay, LANL

Edward Holby, LANL

Karren More, ORNL

ElectroCat Steering Committee and Experts

ElectroCat Project PIs