Project ID: fc172

Highly Active and Durable PGM-free ORR Electrocatalysts through the Synergy of Active Sites

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Overview

Timeline

- Project Start Date: 10/01/17
- Project End Date: 09/30/20*

*Project continuation and direction determined annually by DOE

Barriers

- Barriers addressed
  - Cost (catalyst)
  - Activity (catalyst; MEA)
  - Durability (catalyst; MEA)

Budget

- Total Project Budget: $2,223,776
  - Total Recipient Share: $223,776
  - Total Federal Share: $2,000,000
  - Total DOE Funds Spent*: $211,249

* As of 04/06/18

Partners

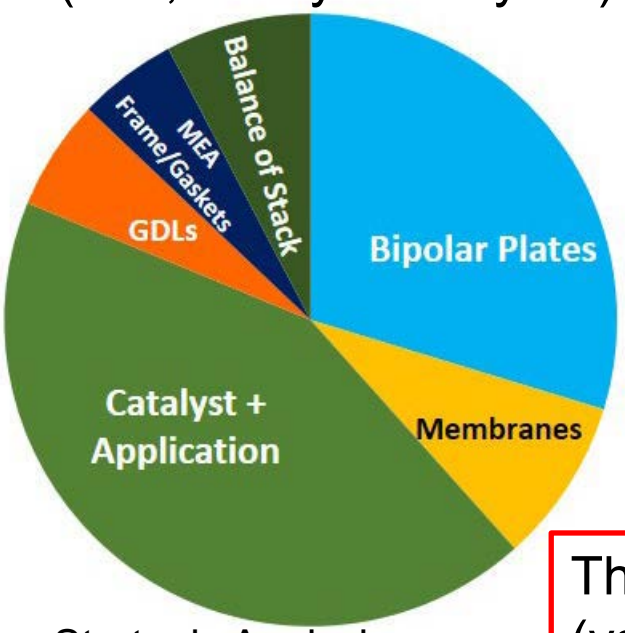
- Washington Univ. in St. Louis
- Univ. of Maryland, College Park
- Ballard Power Systems Inc.
- ElectroCat
- Project lead: PNNL

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

Relevance

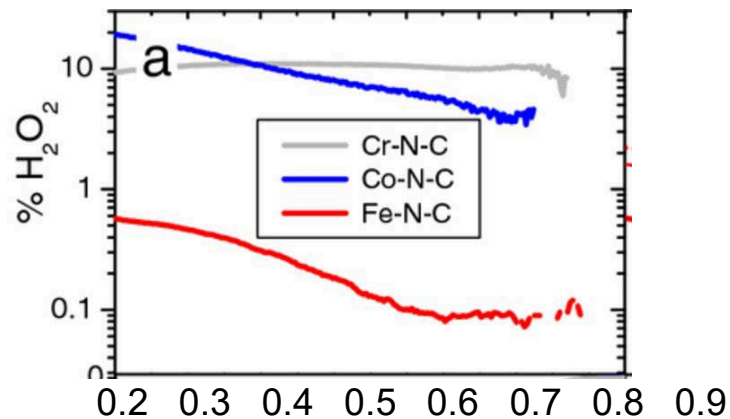
Objective: Improve the activity and durability of PGM-free oxygen reduction reaction (ORR) catalysts through dual active sites for enhanced O_2 reduction and H_2O_2 decomposition.

PEMFC Cost Breakdown
(500,000 systems/year)



Strategic Analysis

Less Fenton-active transition metals based ORR catalysts produce considerable amount of H_2O_2.



JES, 162 (6) H403-H414 (2015)

This project will cut H_2O_2 formation by half (vs. Pt catalysts), while maintaining the same activity and doubling durability than baseline.

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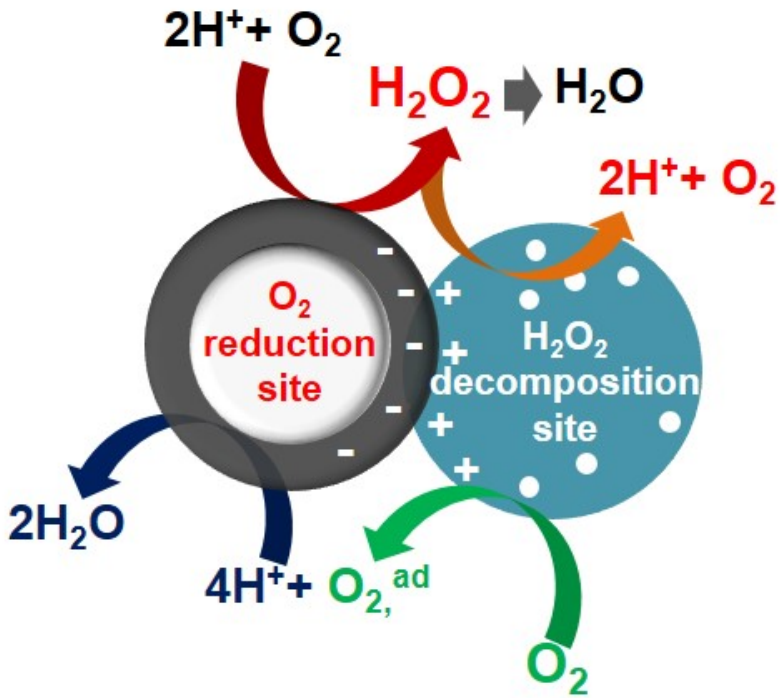
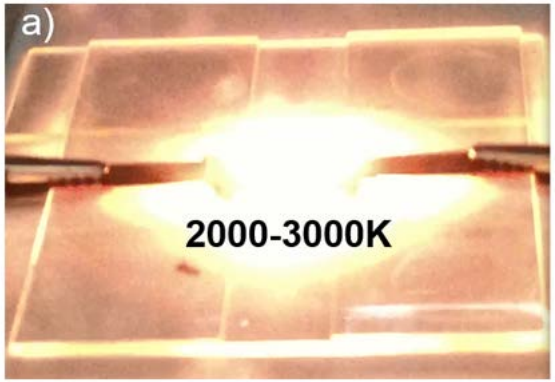
Approach

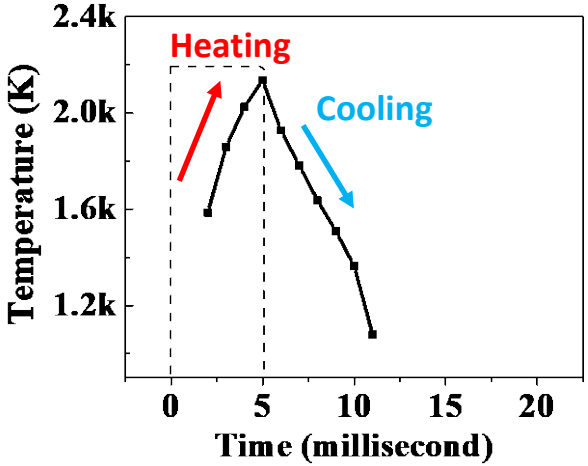
Material and synthesis innovation

Dual active sites for ORR and H_2O_2



Thermal shock activation for high activity by increasing active site density.





Fundamental understanding using ElectroCat capabilities includes HR-STEM, synchrotron X-ray, *In situ* degradation measurement/detection, and MEA diagnosis.

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

Approach

Milestone	Milestone Description (Go/No-Go Decision)	Complete
M3.1	Identify at least two stable H_2O_2 decomposers (01/31/18)	100%
M1.1	Identify pathways to produce 200mg catalysts using thermal shock activation technique (04/30/18)	50%
M2.1	Identify at least two O_2 reduction catalysts with $\Delta E_{1/2} < 65$mV (vs. Pt/C) under RRDE test (07/31/18)	100%
M3.2	Identify dual-site catalysts with H_2O_2 generation comparable to Pt/C (4%) under RRDE test (10/31/18)	100%
GNG1	Demonstrate a PGM-free catalyst ≥ 20 mA/cm^2 at 0.90 V (iR-corrected) in an H_2-O_2 fuel cell and 100 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 temperature 80 °C). (10/31/18)	20%
M2.2	Identify O_2 reduction catalysts with $\Delta E_{1/2} < 50$mV (vs. Pt/C) under RRDE test (01/31/19)	Started
M1.2	Identify pathways to produce 20g catalysts using thermal shock activation technique (07/31/19)	
M3.3	Identify dual-site catalysts with $\Delta E_{1/2} < 45$ mV (vs. Pt/C) under RRDE test (07/31/19)	
GNG2	Demonstrate a PGM-free catalyst ≥ 25 mA/cm^2 at 0.90 V (iR-corrected) in an H_2-O_2 fuel cell and 125 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 temperature 80 °C). (10/31/19)	
M3.4	Identify dual-site catalysts with H_2O_2 generation less than half of Pt/C (2%) under RRDE test (01/31/20)	
M4.3	Demonstrate MEA 2X durability of dual-site catalysts over baseline (04/30/20)	
GNG3	Demonstrate a PGM-free catalyst ≥ 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 temperature 80 °C). Provide six 50cm^2 MEAs to DOE while showing a reasonable pathway to achieve DOE performance and durability targets. (10/31/20)	

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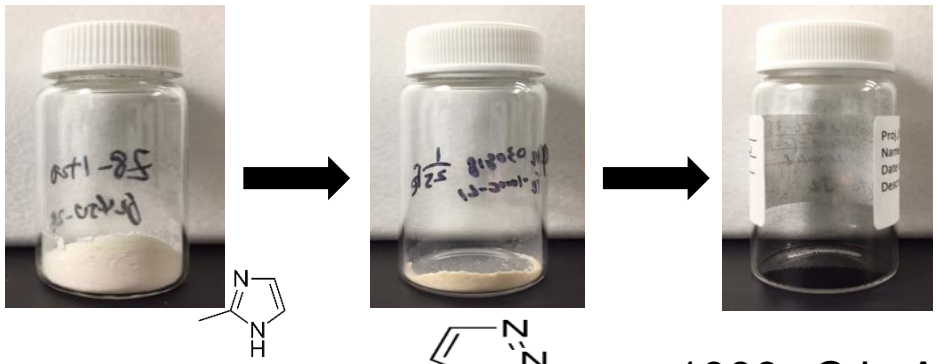
Accomplishments and Progress

Atomically dispersed Fe catalysts

MOF-1 → MOF-2 → Catalyst



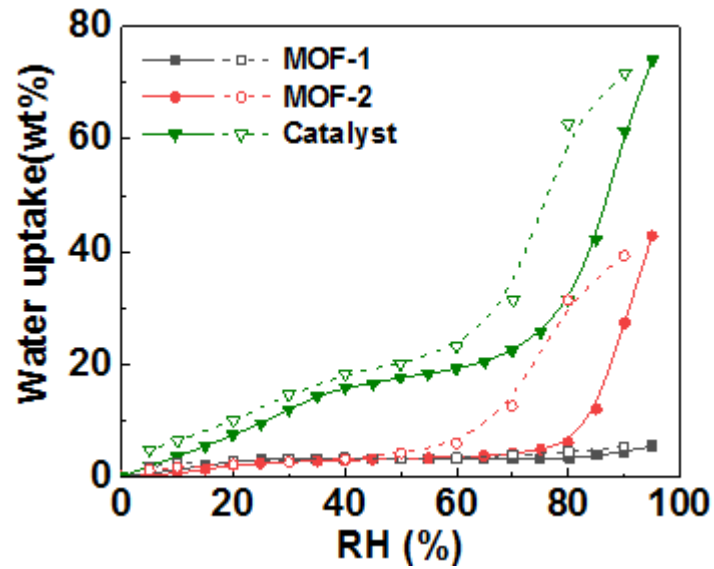
ZIF-8 synthesized in DMF

+ $Fe(acac)_3$

1000 °C in Ar for 1h

Sample	BET area (m^2/g)	Pore (cc/g)	Micropore (cc/g)
MOF-1	1823	1.1	0.64
MOF-2	643	0.52	0.16
Catalyst	935	1.2	0.14

Water adsorption isotherm



Hysteresis in the water adsorption isotherm for the catalyst confirms the mesoporous structure.

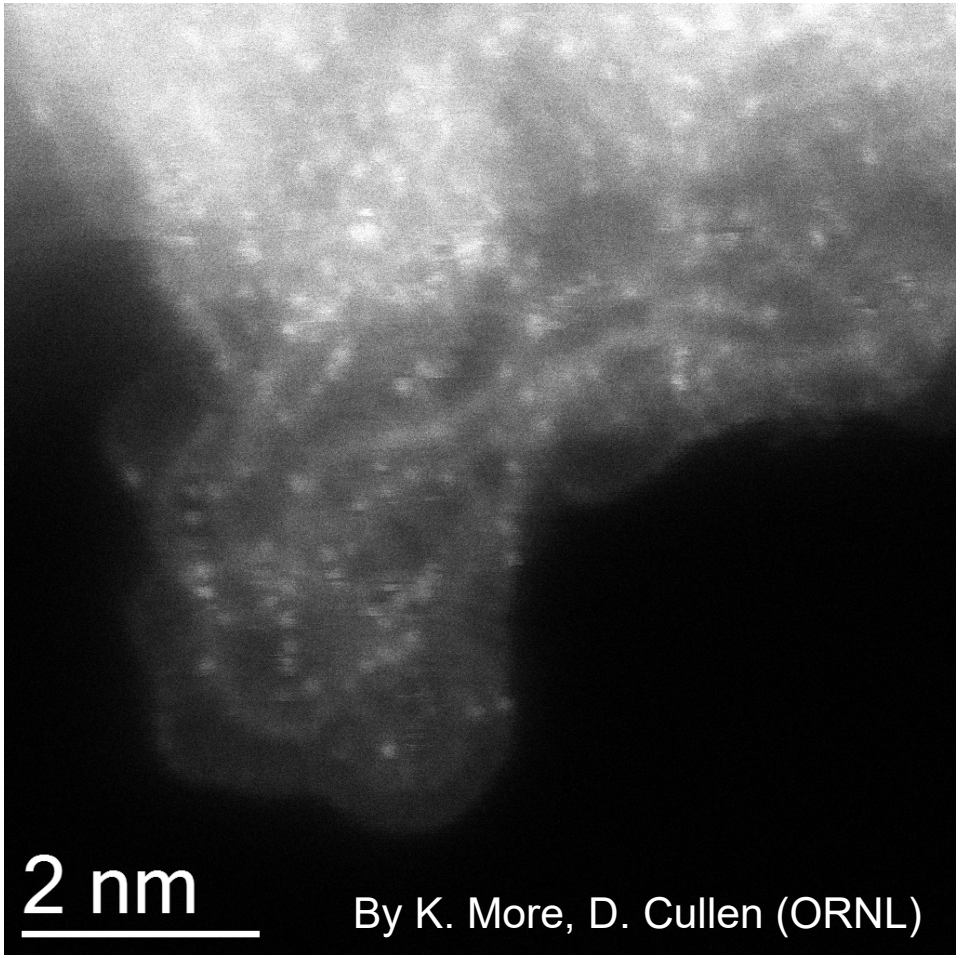
➡ Mass transport

Metal exchange and ligand exchange successful; Porous structure for good mass transport; micropores need improvement for active sites.

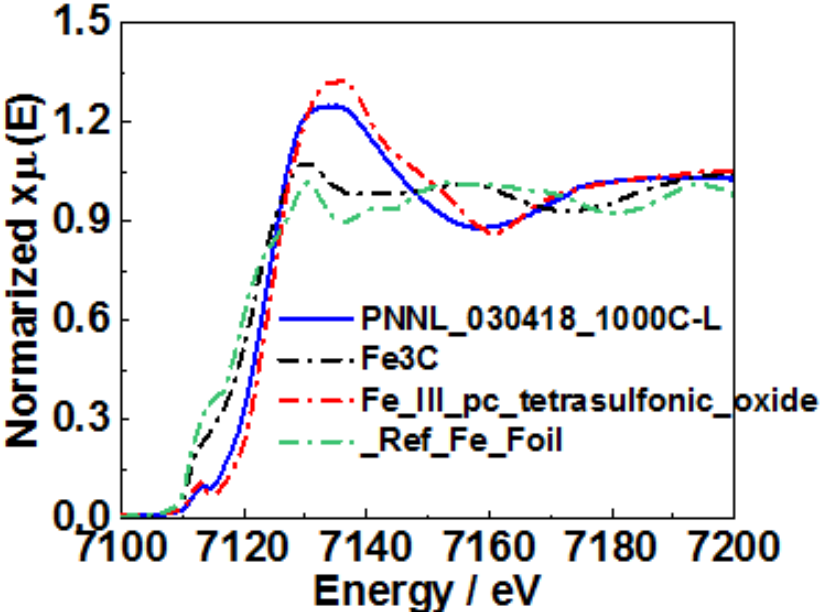
Any proposed future work is subject to change based on funding levels.

Accomplishments and Progress

Atomically dispersed Fe catalysts



Fe-N_4 structure



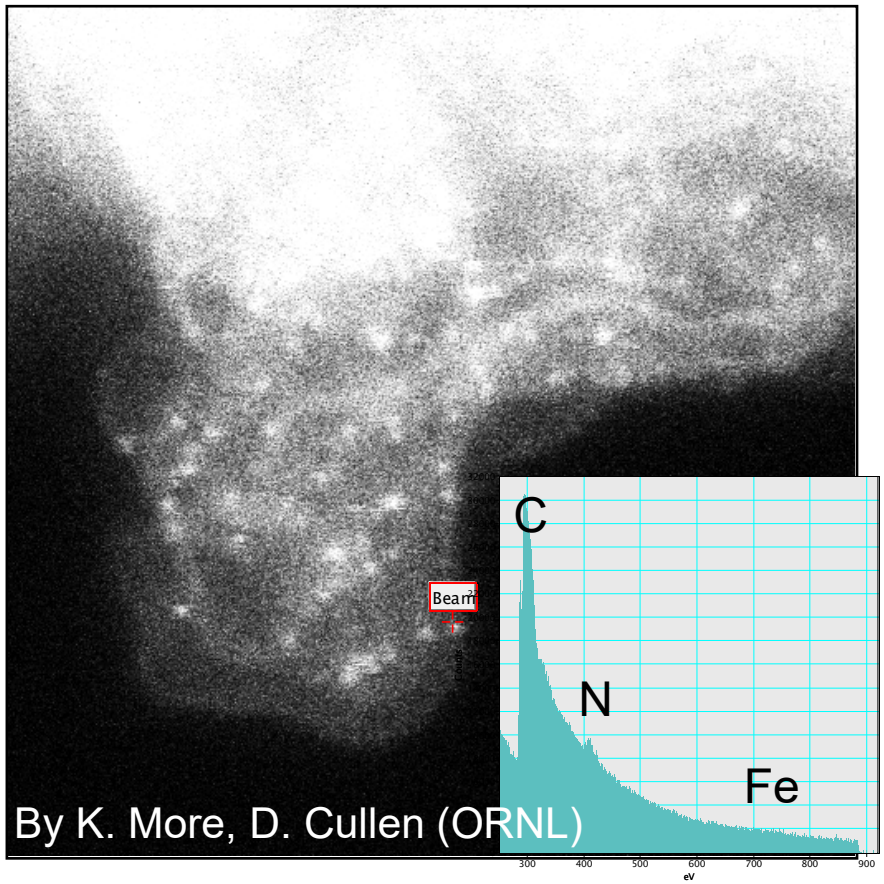
By D. Myers et al. (ANL)

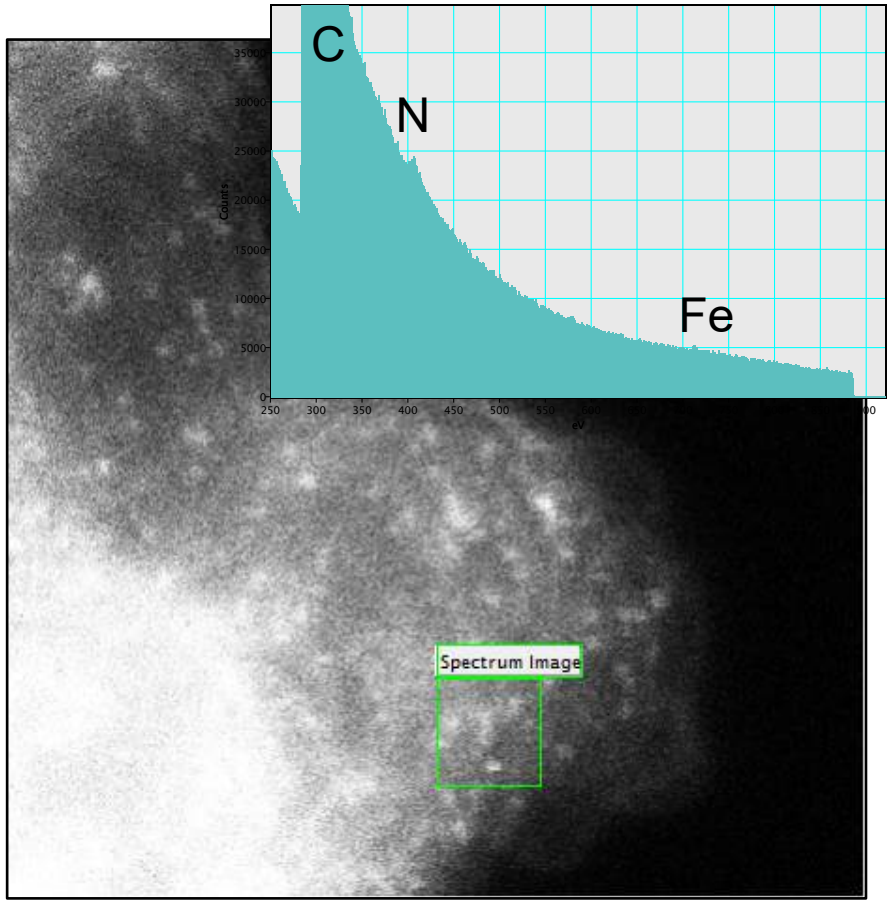
STEM and XANES confirm atomic dispersion of metal, Fe in Fe-N_4 structure.

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

Accomplishments and Progress

Atomically dispersed Fe catalysts



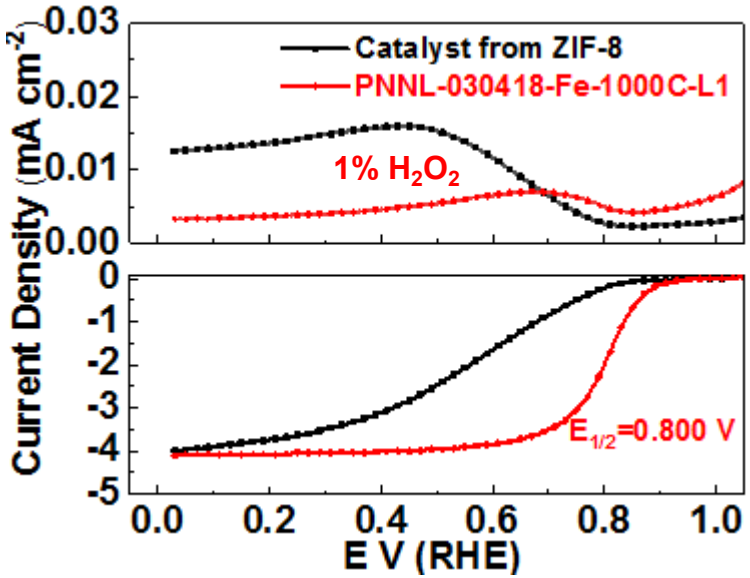


1. Most Fe and Zn are associated with the graphitic basal plane edges;
2. Fe are highly mobile under electron beam most likely because they are not strongly bonded to carbon. The underlying reasons are under investigation.

Accomplishments and Progress

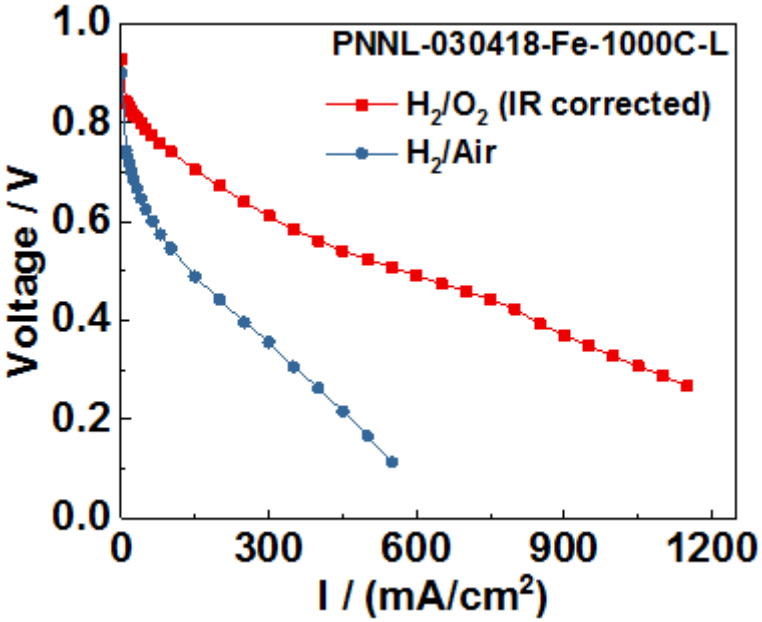
Atomically dispersed Fe catalysts

Ex situ RRDE



$E_{1/2}$=0.82V (20ugPt/cm^2)
$E_{1/2}$=0.86V (60ugPt/cm^2), Adv. Mater. 2018, 30, 1706758

MEA (1st try)



Cathode: 3.8mg/cm^2, 35$_{wt}$% Nafion@;
anode: 0.3mgPt/cm^2;
Atm. Pressure. 75%RH. 80°C.

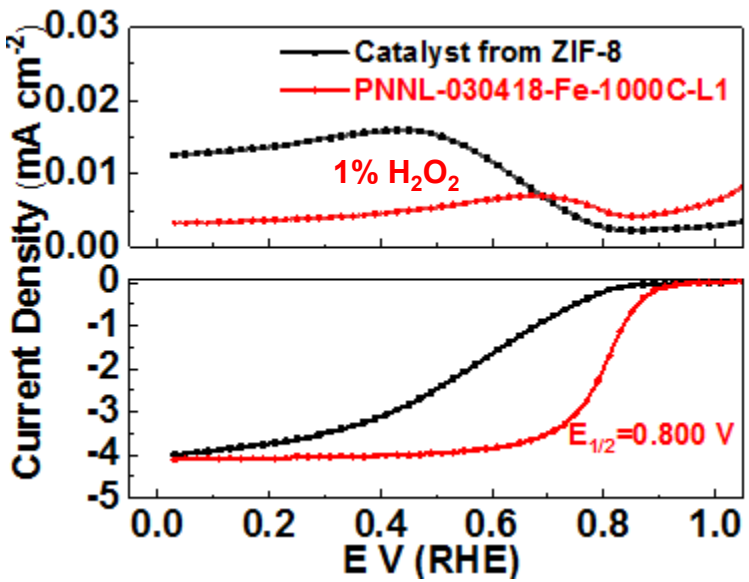
1. Atomically dispersed Fe catalyst performance meets the milestone ($\Delta E_{1/2}$ <65mV vs Pt).
2. MEA performance needs improvement (both H_2/O_2 and H_2/Air).

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

Accomplishments and Progress

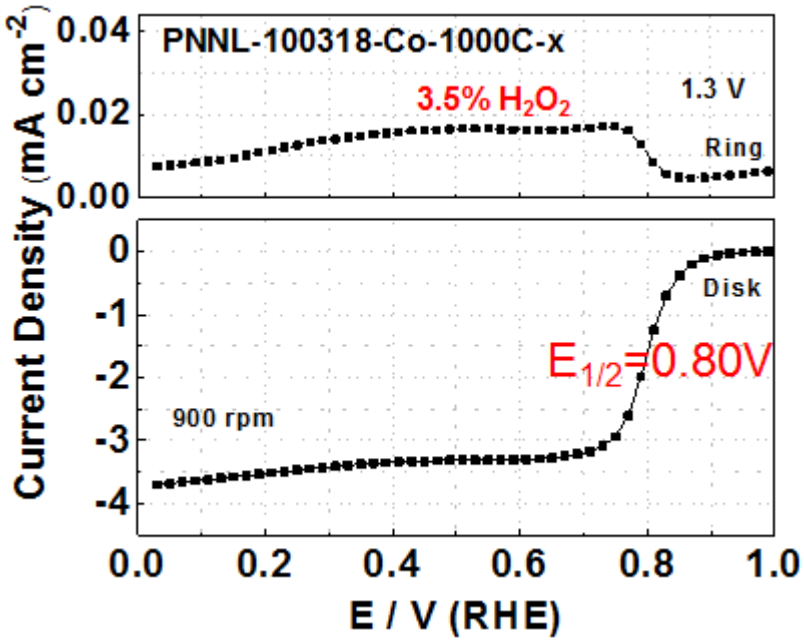
Two catalysts with $E_{1/2}$ no less than 0.80V

Atomically dispersed Fe catalysts



$E_{1/2}$=0.82V (20ugPt/cm^2)
$E_{1/2}$=0.86V (60ugPt/cm^2), Adv. Mater. 2018, 30, 1706758

Co catalysts



Co catalyst characterization underway

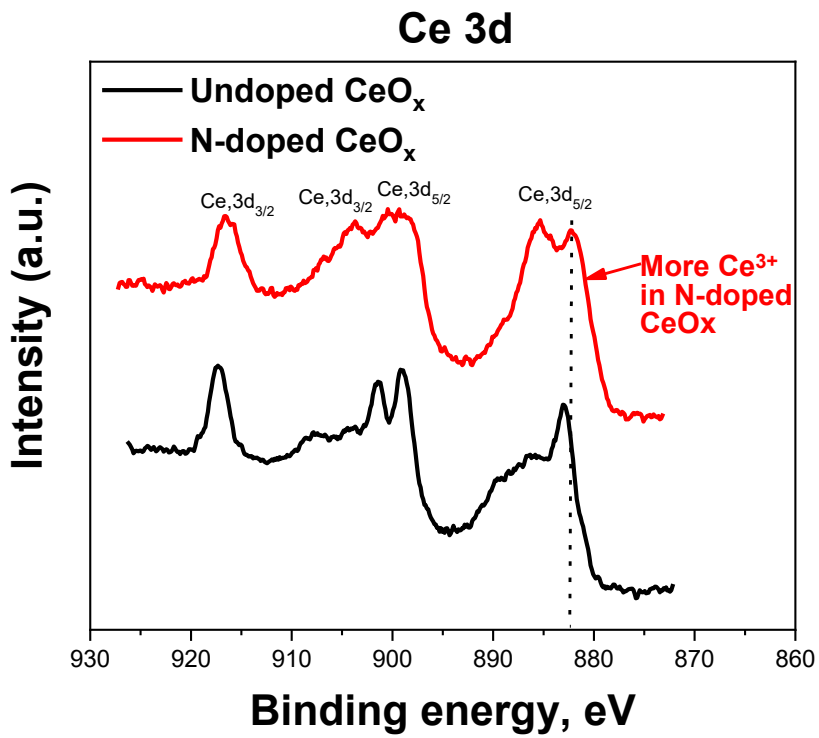
M2.1	**Identify at least two O_2 reduction catalysts with $\Delta E_{1/2}$ < 65mV (vs. Pt/C) under RRDE test**

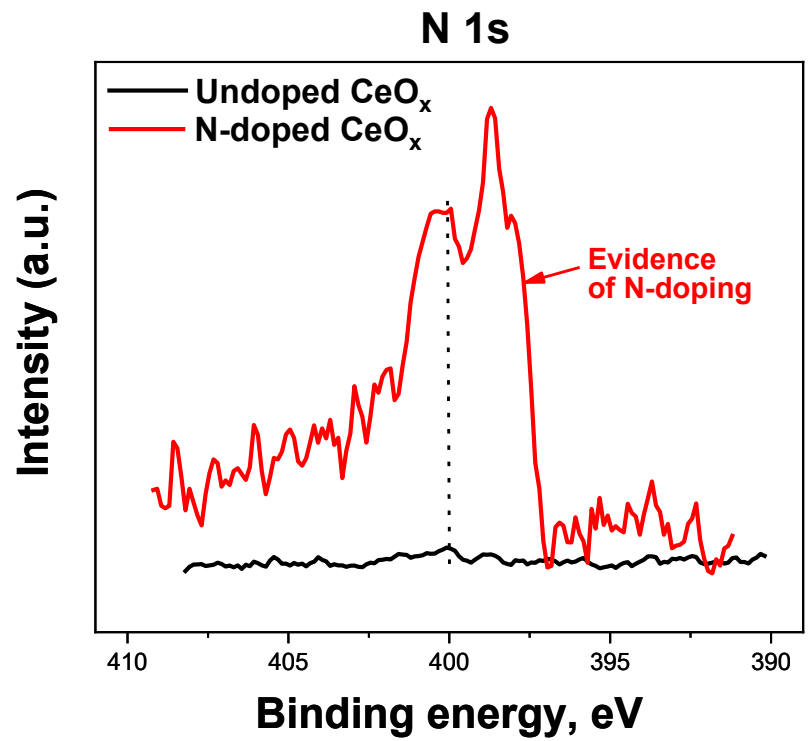
Any proposed future work is subject to change based on funding levels.

Accomplishments and Progress

Dual active site catalysts – Non-stoichiometric H_2O_2 decomposer

N-CeOx as an example





N-doping promotes more non-stoichiometricity (Ce^{3+}) → oxygen vacancies → more peroxide scavenging ability → higher stability of PGM-free catalysts

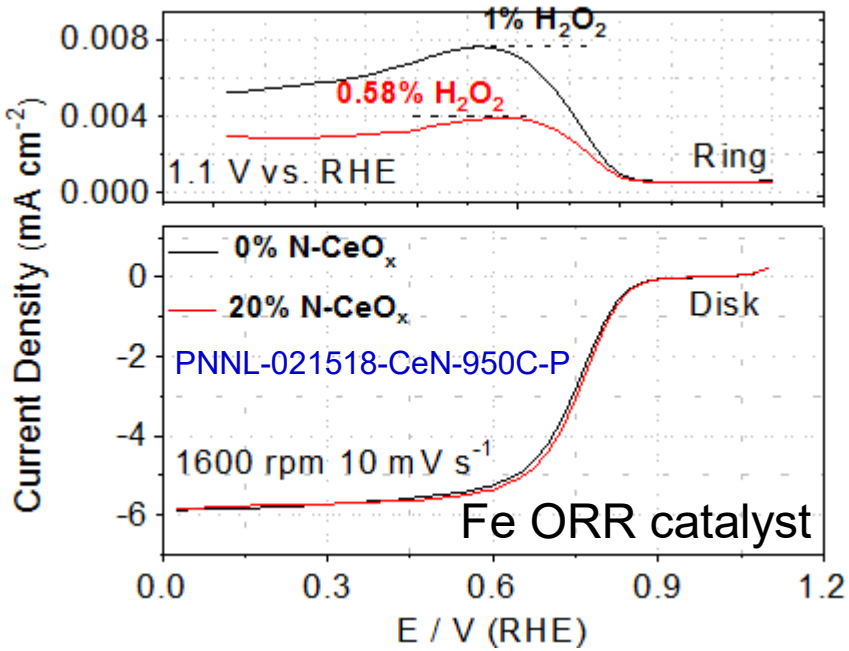
Any proposed future work is subject to change based on funding levels.

Accomplishments and Progress

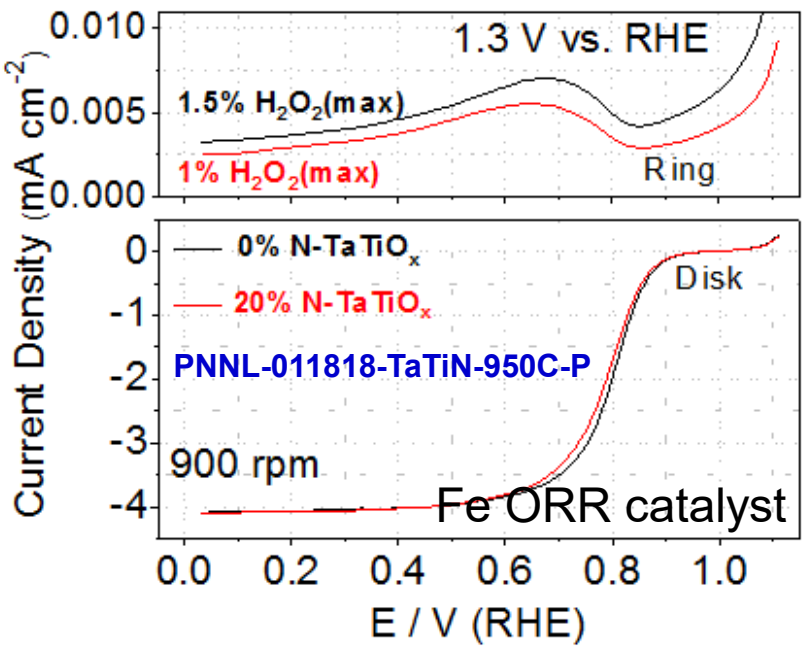
Dual active site catalysts – H_2O_2 decomposer N-CeO_x ,N-$TaTiO_x$

N-CeO_x ,N-$TaTiO_x$ catalyst characterization underway

N-CeO_x



N-$TaTiO_x$



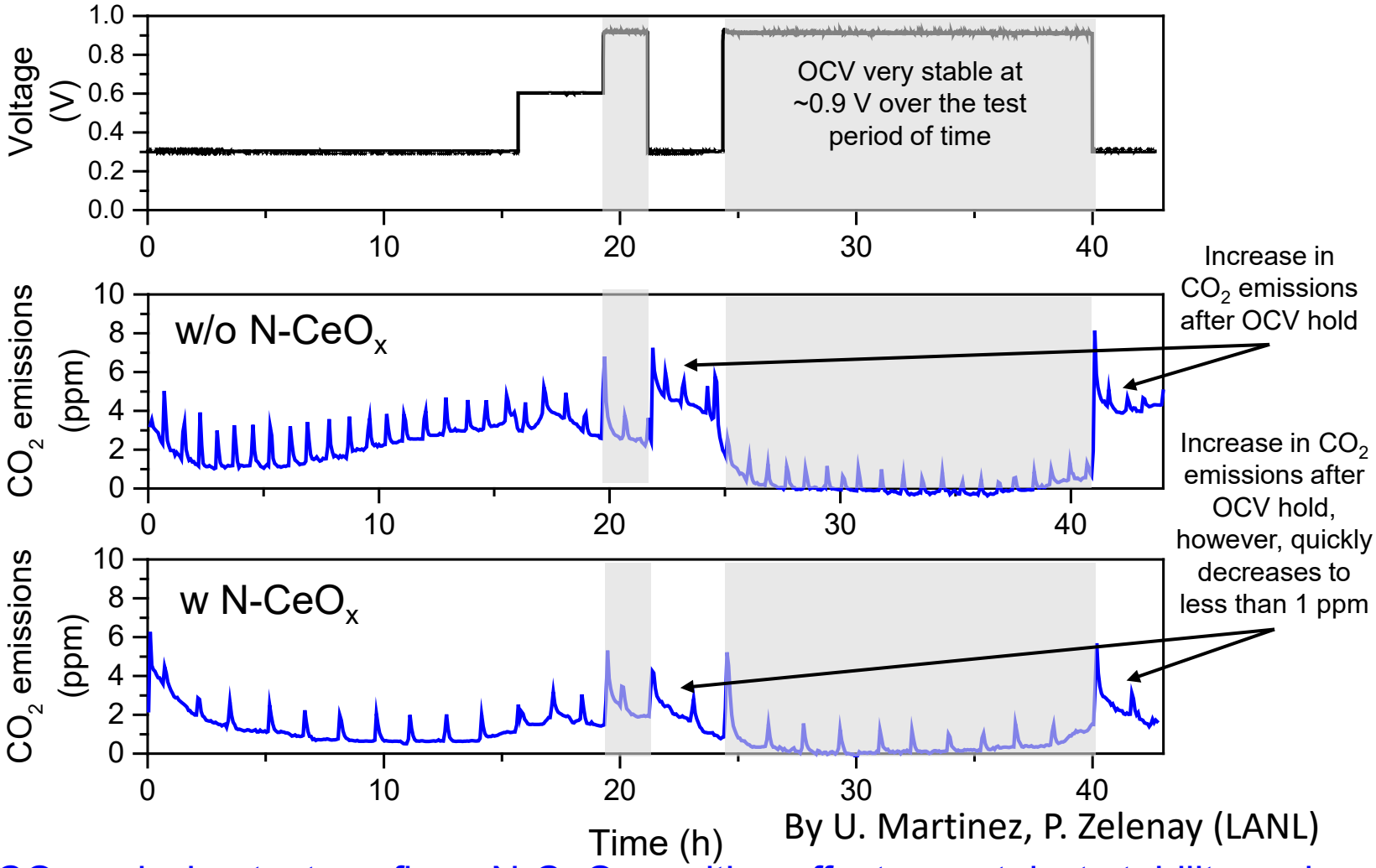
Radical scavengers N-CeO_x and N-$TaTiO_x$ significantly decrease H_2O_2 formation.

M3.1	Identify at least two stable H_2O_2 decomposers

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

Accomplishments and Progress

In situ CO_2 emission: N-CeO_x effect and degradation mechanisms



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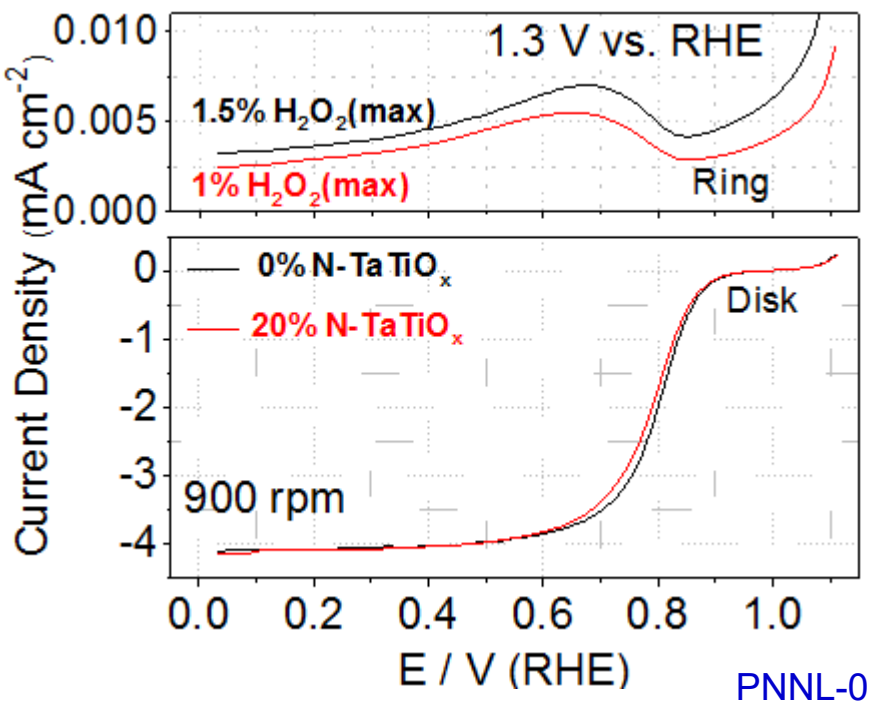
In situ CO_2 emission test confirms N-CeO_x positive effect on catalyst stability and reveals one degradation mechanism: hydroperoxyl radical attack.

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

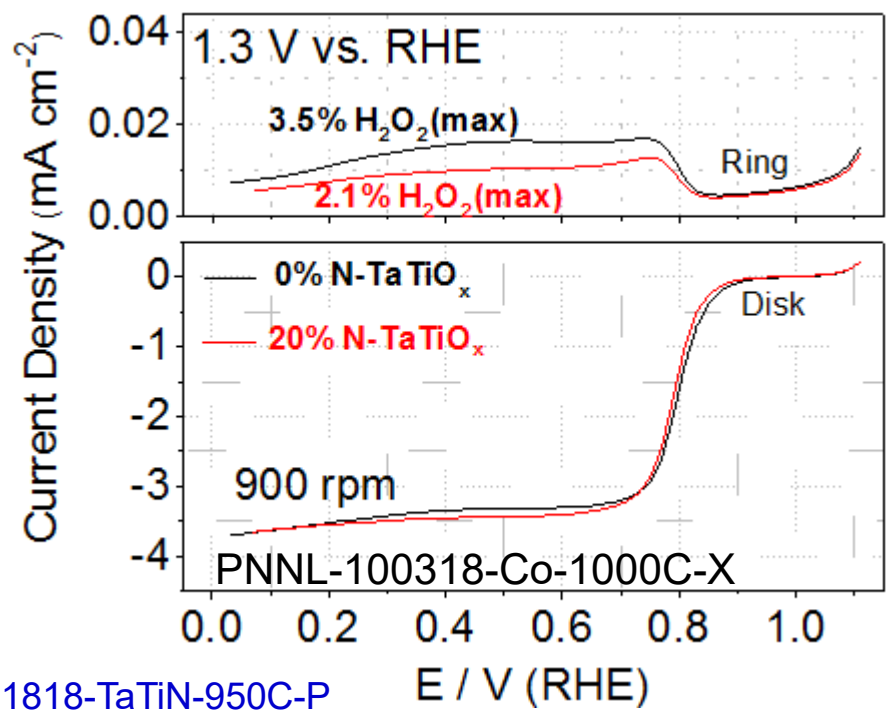
Accomplishments and Progress

Developed two dual active site catalysts (w/ N-$TaTiO_x$)

Fe catalyst + N-$TaTiO_x$



Co catalyst + N-$TaTiO_x$



PNNL-011818-TaTiN-950C-P

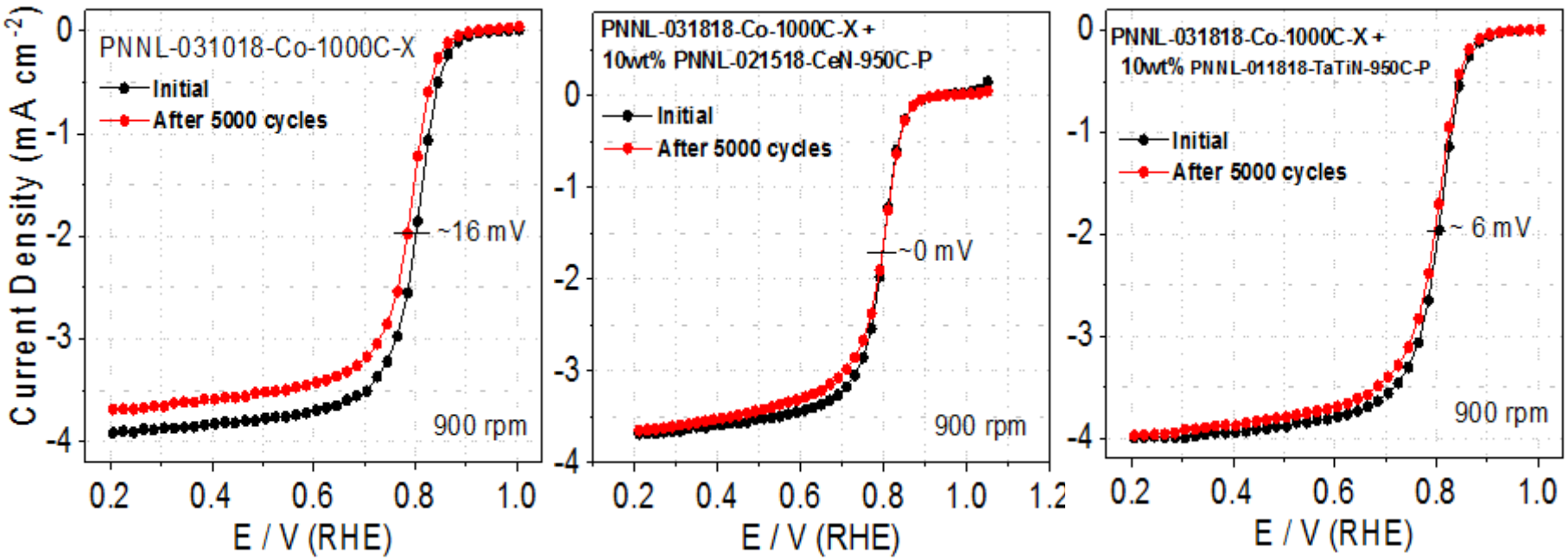
M3.2	**Identify dual-site catalysts with H_2O_2 generation comparable to Pt/C (4%) under RRDE test (10/31/18)**

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

Accomplishments and Progress

Dual active site catalysts – durability improvement

Baseline | W/ N-CeOx | W/ N-TaTiOx



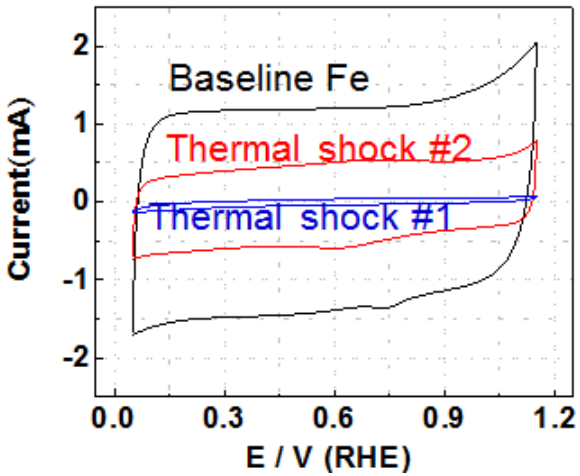
Stability test protocol: potential steps between 0.6 V (3 s) and 0.95 V (3 s) with rise time of ~1 s in O_2 saturated 0.5M H_2SO_4.

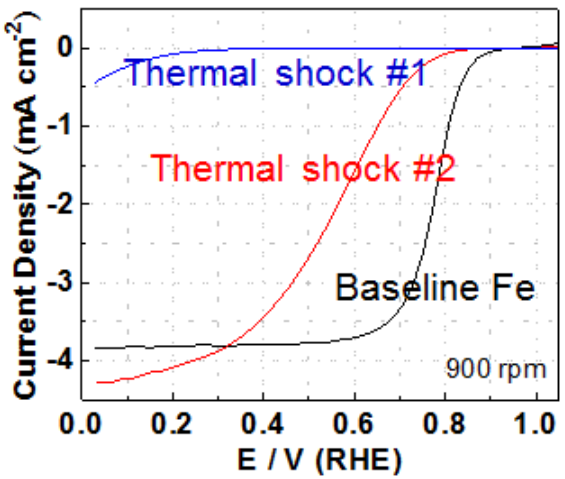
Dual active site catalysts improve durability.

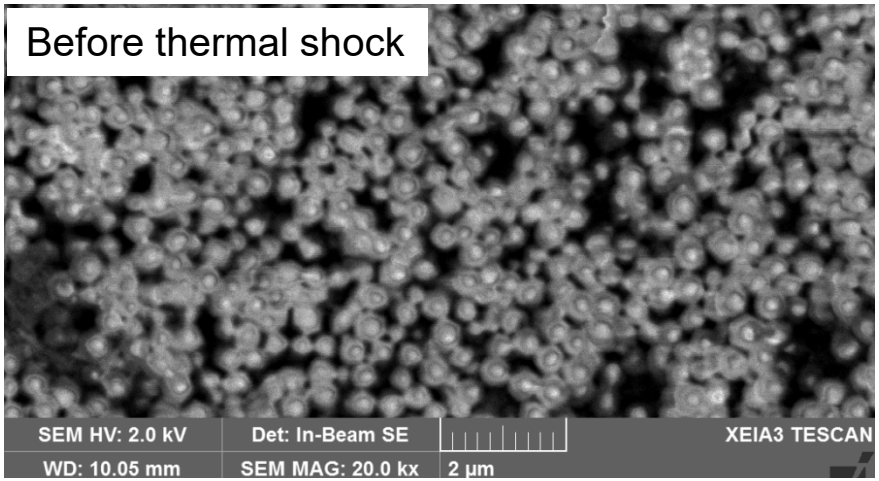
Any proposed future work is subject to change based on funding levels.

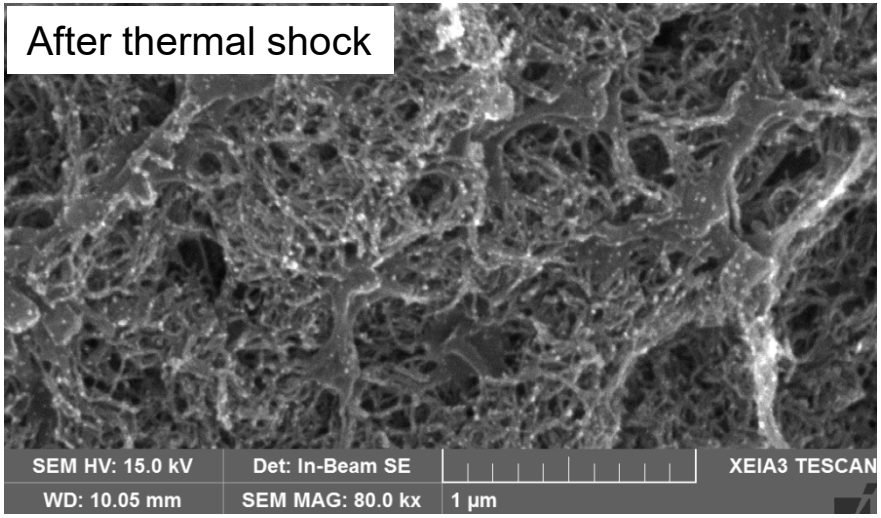
Accomplishments and Progress

Thermal shock activation synthesis









Highly porous structure; Performance needs improvement.

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

Accomplishments and Progress: Responses to Previous Year Reviewers' Comments

- This is a new-start project and was not reviewed last year.

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

Collaboration & Coordination

Partner	Project roles
PNNL – Lead (Y. Shao, V. Prabhakaran, J. Liu, X. Xie)	Project lead, management and coordination; catalysts design, development and characterization, H_2O_2 decomposer development and integration.
Univ. Maryland(L. Hu)	Synthesis protocol – thermal shock activation, catalyst synthesis
WashU (V. Ramani)	Electrode design and MEA assembly, MEA test and analysis
Ballard (D. Banham)	MEA design, test and analysis

ElectroCat	Capabilities
ANL	*In situ* and Operando Atomic, Nano-, and Micro-structure Characterization (X-ray adsorption, including *ex-situ, in-situ* in liquid/MEA) Electrode Microstructure Characterization and Simulation (X-ray Nano CT)
LANL	*In situ* fluoride and carbon dioxide emission measurements (including F/metal/CO_2 detection simultaneously)
NREL	Kinetics and Transport (Operando differential cell measurements of electrochemical kinetics and transport)
ORNL	Electron microscopy

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

Remaining Challenges and Barriers

- Demonstrate thermal shock activation synthesis for improved catalyst performance.
- Catalyst degradation mechanisms.
- Improve synergy of dual active sites.
- Catalyst performance and catalyst scale-up synthesis for MEA engineering and test ($50cm^2$).
- MEA engineering for performance improvement in both H_2/O_2 and H_2/Air.

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

Proposed Future Work

- Optimize and develop alternative thermal shock activation (e.g., microwave) for improved synthesis at relevant scale.
- Understand catalyst degradation under various conditions through collaboration with ElectroCat (CO_2 emission, metal leaching, metal-nitrogen coordination, etc.).
- Improve catalyst performance through chemistry, structure, morphology innovation (MOF precursors, nanowires, etc.).
- Molecular level integration of dual active sites for enhanced synergy between ORR and H_2O_2 decomposition.
- Enhance MEA performance through electrode engineering, specifically by optimizing the loading and distribution of ionomer.
- MEA diagnostics to evaluate sources and distribution of polarization with the MEAs.

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

Technology Transfer Activities

- An invention report filed “Dual-site PGM-free cathodes for proton exchange membrane fuel cells technology” (IPID=31334-E).

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

Summary Slide

- Two PGM-free catalysts including one Co-based catalyst have been developed with $E_{1/2}$=0.80V, meeting project milestone (M2.1).
- Two H_2O_2 decomposers have been developed and successfully integrated into ORR catalysts and reduced the formation of H_2O_2 below 2.1%, meeting project milestones (M3.1, M3.2).
- Collaboration with ElectroCat helped deep understand our catalysts (chemistry, degradation mechanisms).
- Need improvement on new synthesis (thermal shock activation) and MEA performance.

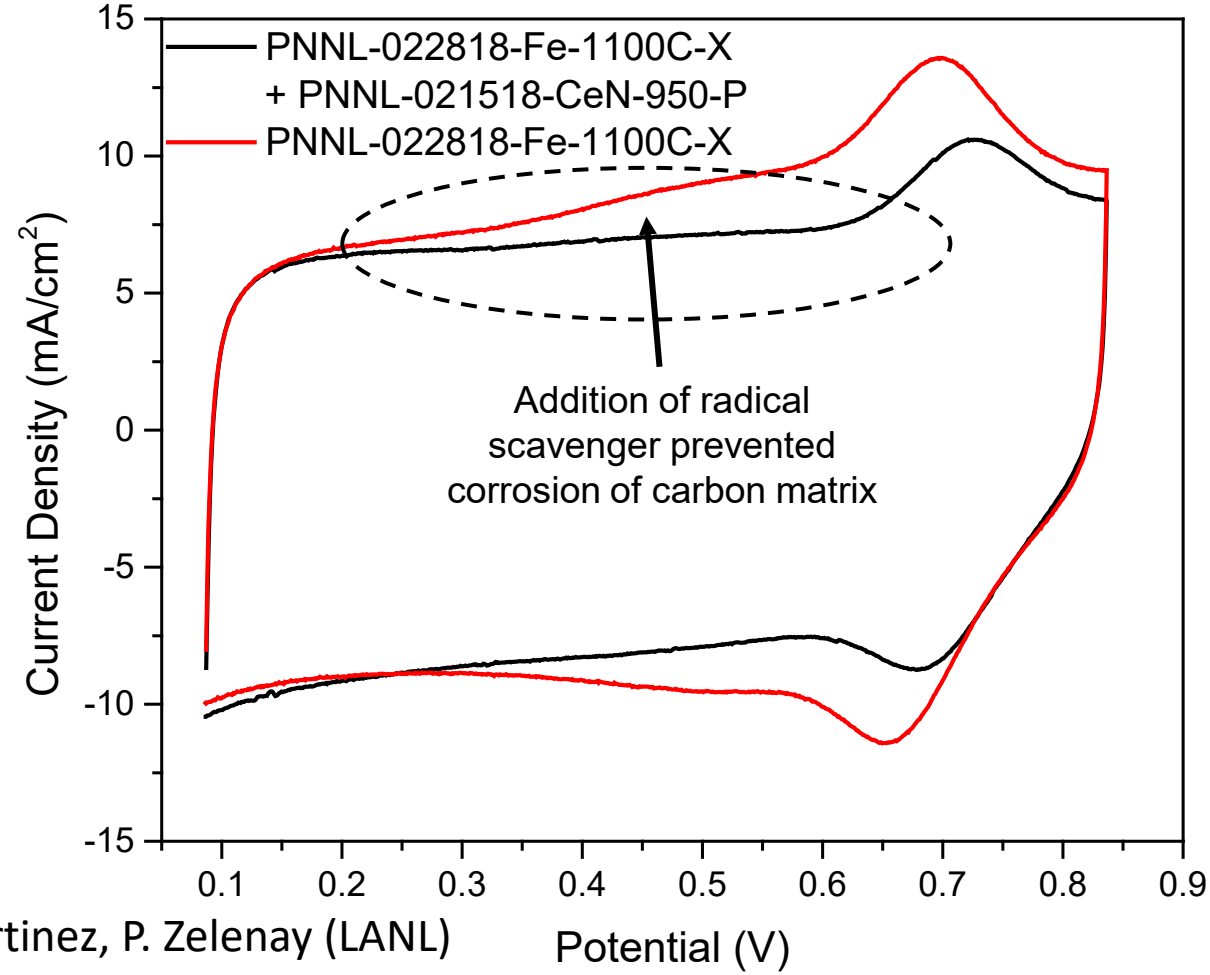
Any proposed future work is subject to change based on funding levels.

Technical Back-Up Slides

Technical Back-Up

Comparison of Cyclic Voltammograms at EOL

Anode: 0.2 mg_{Pt} cm^{-2} Pt/C H_2, 200 sccm; Cathode: *ca.* 3 mg cm^{-2}, N_2, 500 sccm; Membrane: Nafion®,212; Cell: 80°C; 100% RH. Cyclic voltammogram: 20 mV/s at EOL.



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