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: 03/31/21*

  * Project continuation and direction determined annually by DOE

  * No-cost extension for 6 months (Year 1: 10/01/17-03/31/19)

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*: $1,190,297

  * As of 05/20/19

Partners

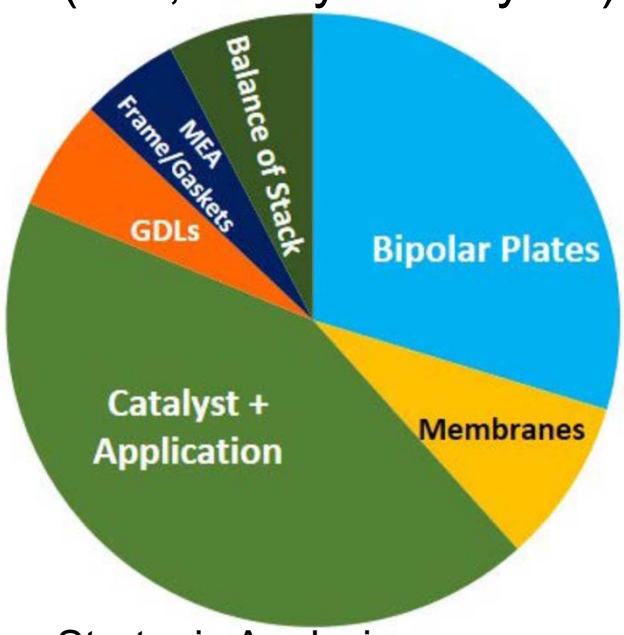
- Washington Univ. in St. Louis
- Univ. of Maryland, College Park
- Ballard Power Systems Inc.
- Oregon State Univ.
- ElectroCat Consortium
- Project lead: PNNL

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

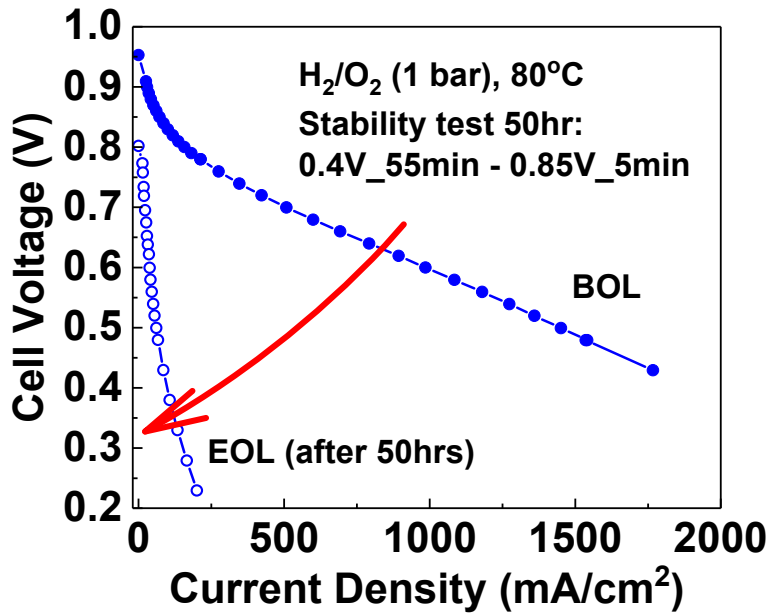
Relevance

PGM-free ORR catalysts could significantly decrease fuel cell cost, but their durability (and activity) needs improvement.

PEMFC Cost Breakdown
(500,000 systems/year)



Strategic Analysis



PGM-free cathodes typically degrades by 40–80% in the first 100 h of testing[1].

Ref.: 1) *Adv. Mater.* 2019, adma.201807615

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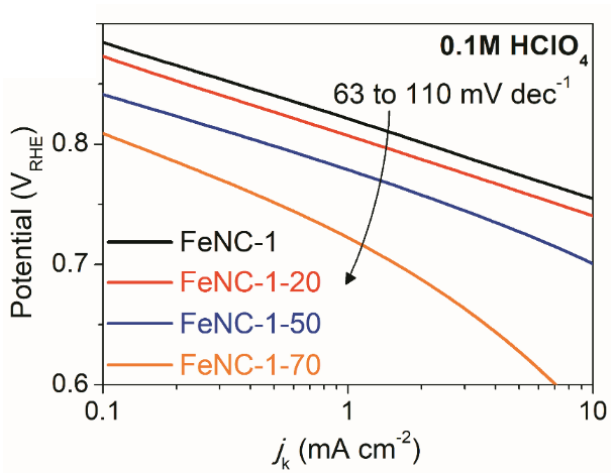
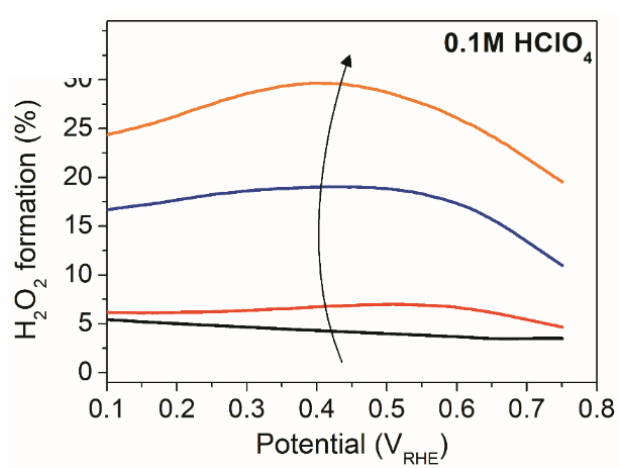
Relevance

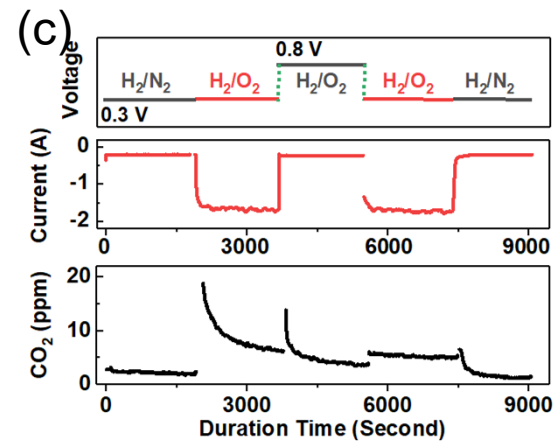
H_2O_2(radicals) play a significant role in PGM-free ORR catalysts degradation.



a) decrease ORR activity



b) increase H_2O_2 formation



c) Online CO_2 emission test (PNNL-LANL): CO_2 formation at 0.3V.

This project will decrease H_2O_2 (radical) formation through **dual active site** catalysts, doubling stability than baseline, while maintaining the high activity.

Ref.: 1) *Energy Environ. Sci.* 2018, DOI: 10.1039/C8EE01855C; 2) *Adv. Mater*. 2019, adma.201807615

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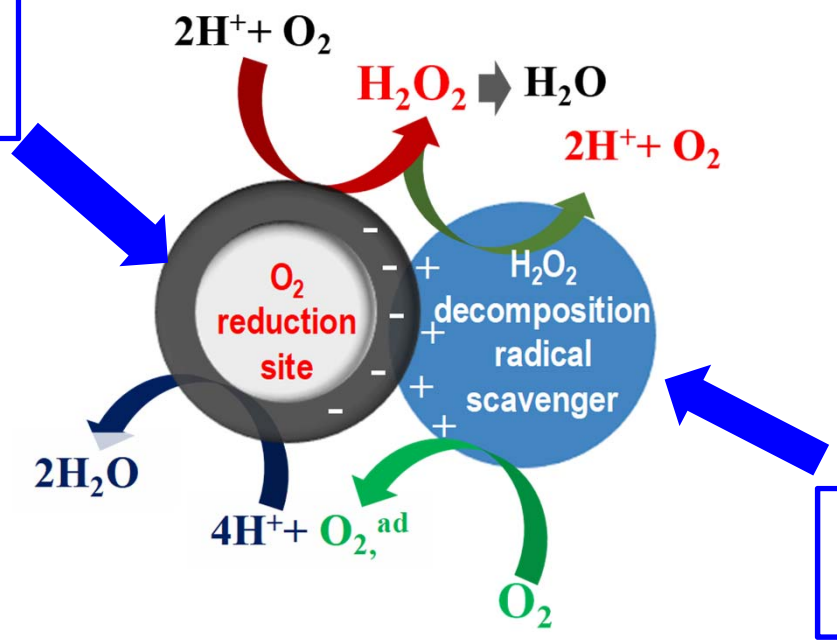
Approach

Dual active sites:
MNx & radical scavenger

Increase MNx active site density



Increase oxygen vacancy density

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

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Milestones

Milestone	Milestone Description (Go/No-Go Decision)	Due date	Status
GNG2 (Year 2)	Demonstrate a PGM-free catalyst ≥ 25 mA/cm^2 at 0.90 V (iR-corrected) in an H_2-O_2 fuel cell, maintain partial pressure of O_2 + N_2 at 1.0 bar (cell temperature 80 °C), demonstrate MEA 1.5X stability over baseline.	04/30/20	100%
M2.1	Identify dual-site catalysts with $\Delta E_{1/2}$ < 45 mV (vs. Pt/C) under RRDE test	07/31/19	100%
M2.2	Demonstrate ALD deposition of radical scavenger on PGM-free catalysts with < 5 nm particle size, and >50% decrease of H_2O_2 formation	10/31/19	100%
M2.3	Demonstrate AHD deposition of radical scavenger into micropores of PGM-free catalysts, >50% decrease of H_2O_2 formation	12/31/19	100%
M2.4	Identify dual-site catalysts with H_2O_2 generation less than half of Pt/C (2%) under RRDE test	01/31/20	100%
GNG3 (Year 3)	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.	04/30/21	On-going
M3.1	Demonstrate integrated ALD and AHD deposition of radical scavengers with >75% decrease of H_2O_2 formation and >50% decrease in carbon oxidation	07/31/20	On-going
M3.2	Demonstrate MEA 2X durability of dual-site catalysts over baseline	10/31/20	On-going

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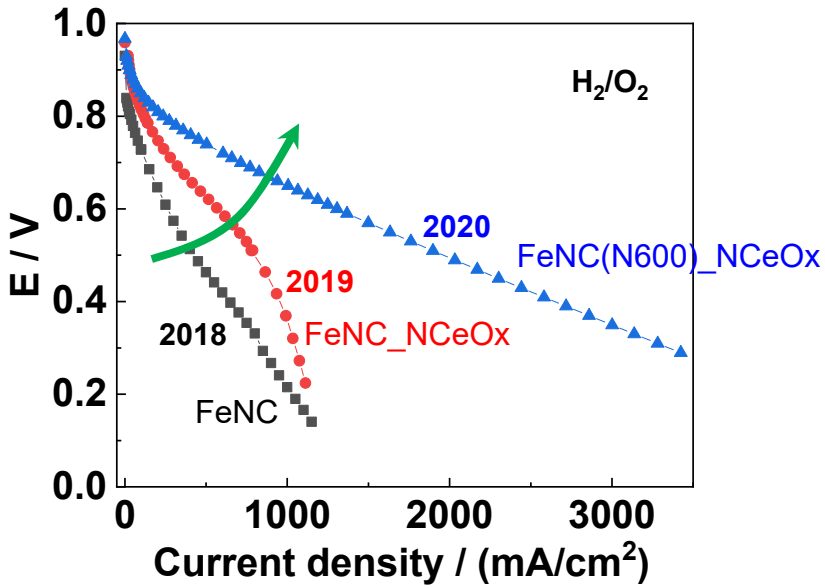
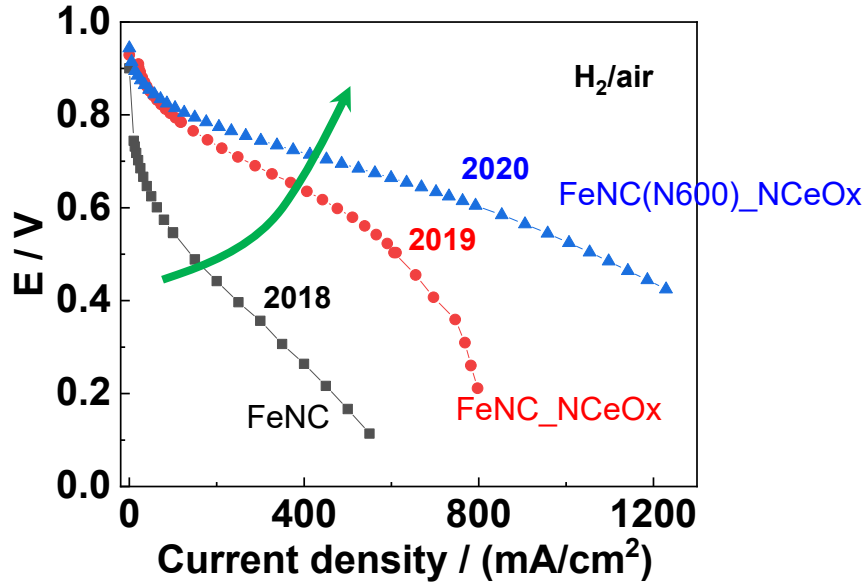
Accomplishments and Progress

Key update #1: MEA performance in both O_2 and air has been improved continuously in the past three years.





Anode: 0.1-0.2 mg/cm^2 $_{Pt}$; Cathode: 2.5-4.5mg/cm$^2_{PGM\text{-}free}$; Membrane: Gore (15µm)/NR211; Active area: 5 cm^2; 80-100% RH, 80°C, O_2+N_2=1 bar.

Performance improvement due to increased catalyst activity (increased active site density and accessibility (through porosity optimization)) and electrode fabrication.

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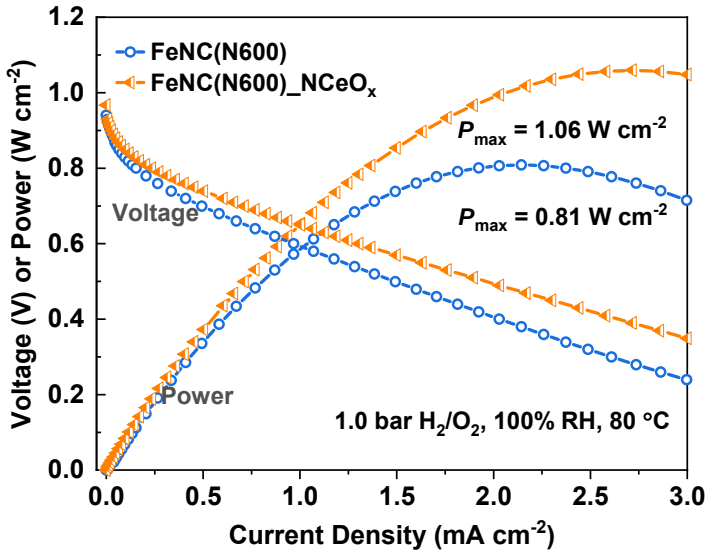
Any proposed future work is subject to change based on funding levels.

Accomplishments and Progress

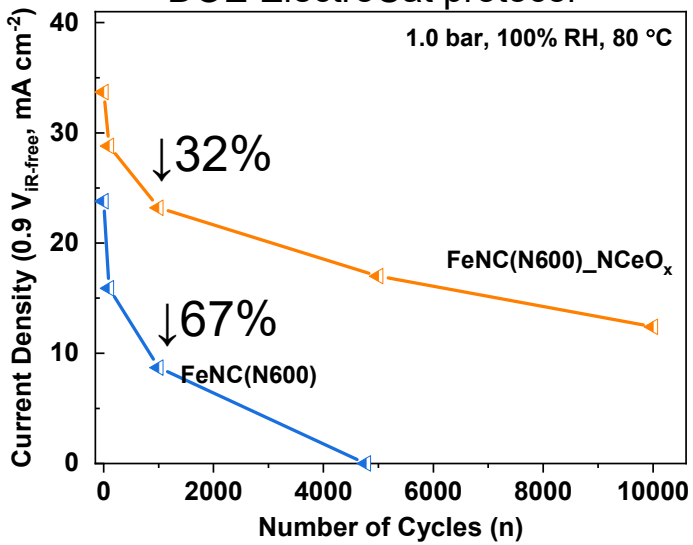
Key update #2: Dual active site catalyst FeNC_NCeOx exceeds Year 2 activity and durability milestones (i.e., ≥ 25 mA/cm^2 at 0.90 V (iR-corrected) in an H_2-O_2 fuel cell, 1.5X stability over baseline).

H_2/O_2



Durability

DOE ElectroCat protocol



Anode: 0.1 mg/cm^2 $_{Pt}$; Cathode: 2.6 mg/cm^2$_{PGM\text{-}free}$ (FeNC_NCeOx), 40 wt% Nafion ionomer; Membrane: NR211; Active area: 5 cm^2; 100% RH, 80°C, O_2+N_2=1 bar. DOE ElectroCat durability test protocol.

1. Initial MEA performance and activity (>30mA/cm^2 at 0.9V) in H_2/O_2 of dual-active site catalyst FeNC_NCeOx is better than baseline FeNC.
2. The retention of current density at 0.9V for FeNC_NCeOx is more than 100% of baseline.

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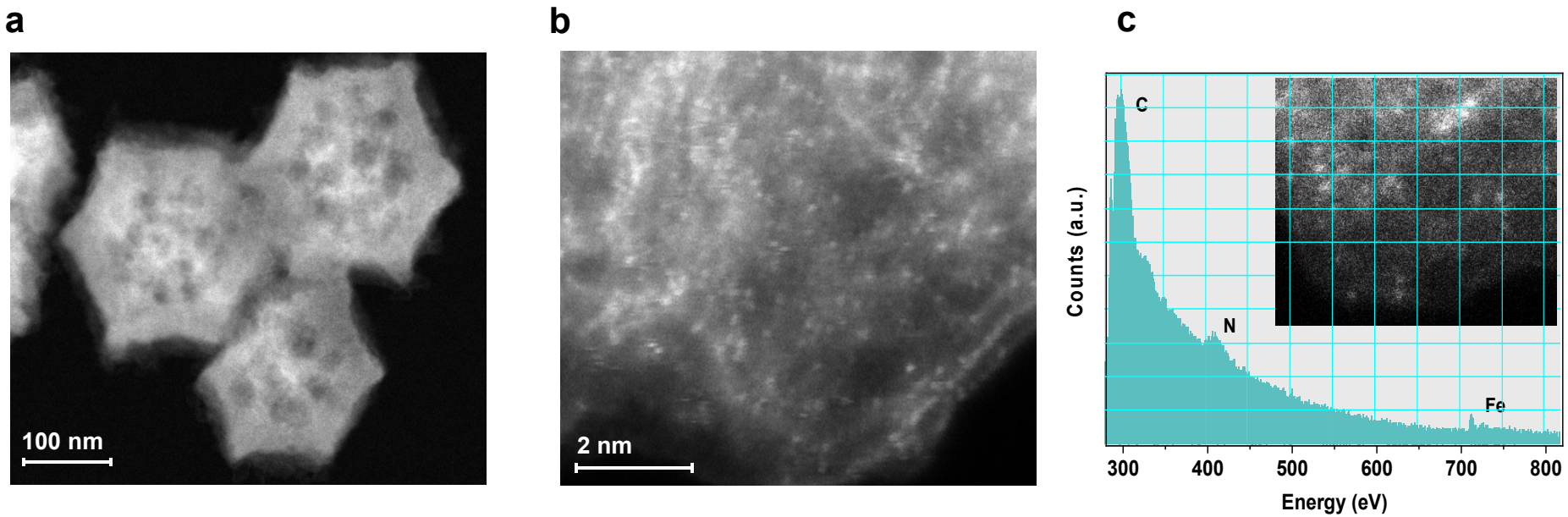
Accomplishments and Progress

Atomically dispersed, highly porous FeNC catalysts

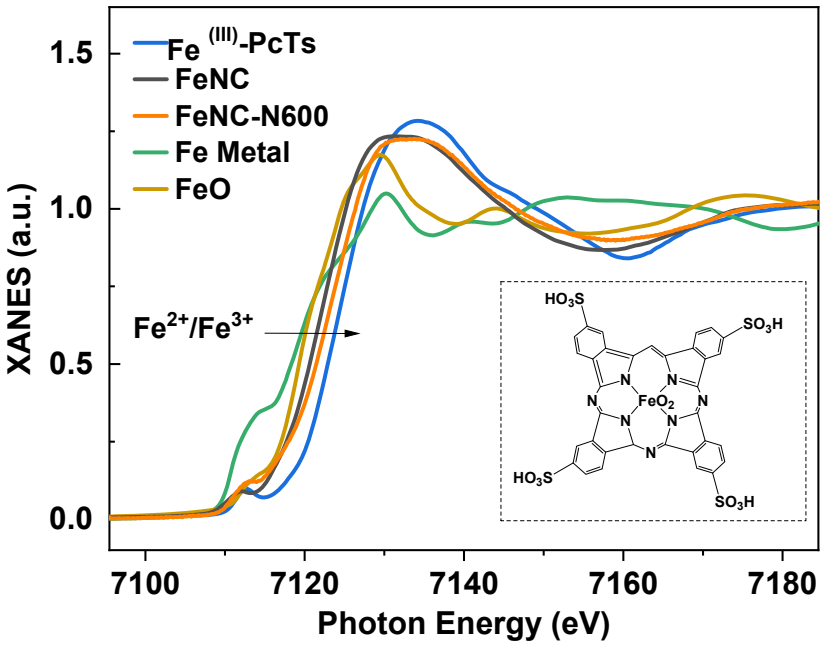


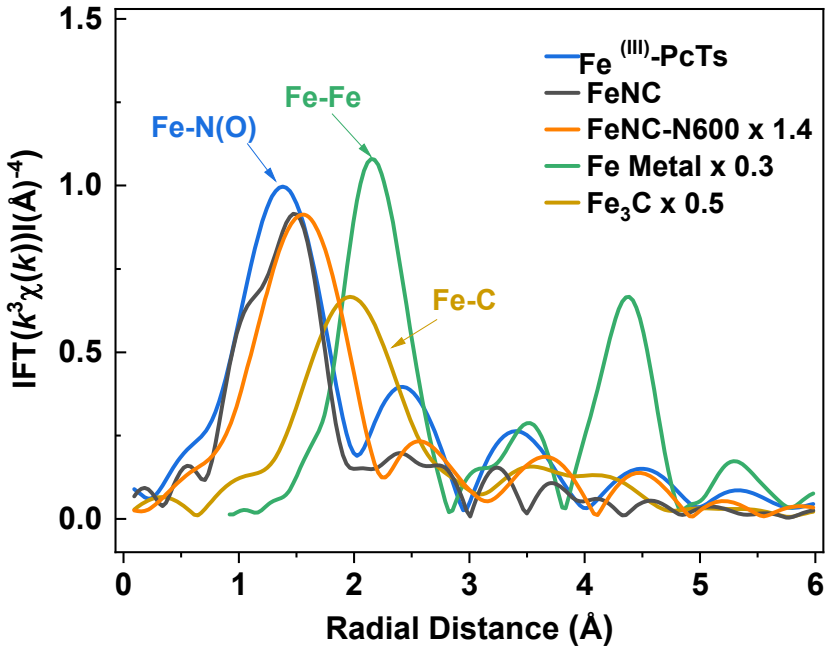
STEM/EELS confirm high-density, atomically dispersed Fe and most likely FeNx moieties. The catalyst shows highly porous structure.

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

Accomplishments and Progress

Atomically dispersed FeNC catalysts





XANES and EXAFS confirm atomic dispersion of Fe (no Fe-Fe and Fe-C).

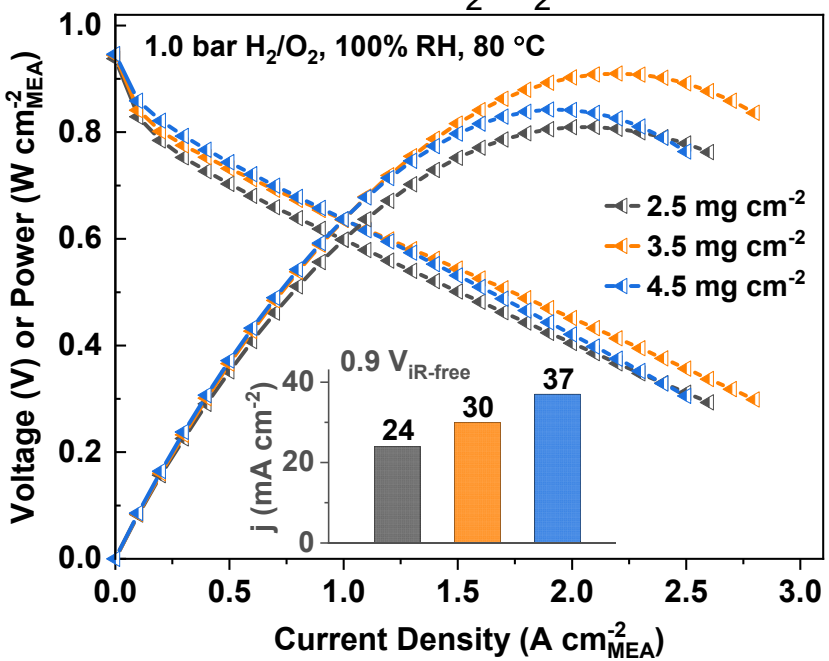
Any proposed future work is subject to change based on funding levels.

Accomplishments and Progress

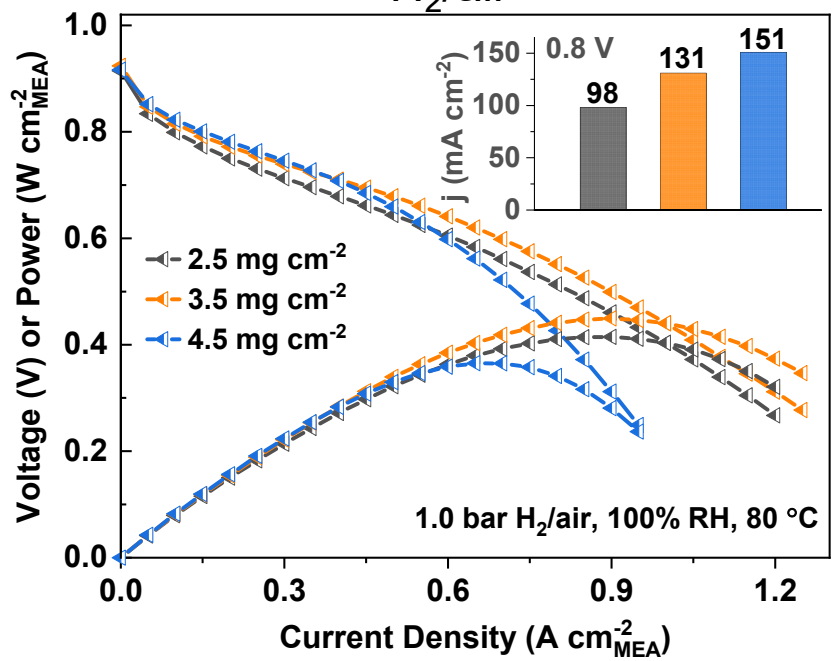
FeNC catalyst exceeds Year 3 activity and performance milestones

(i.e.,>30mA/cm^2 at 0.9V in O_2 and >150mA/cm2 at 0.8V in air)

H_2/O_2



H_2/air



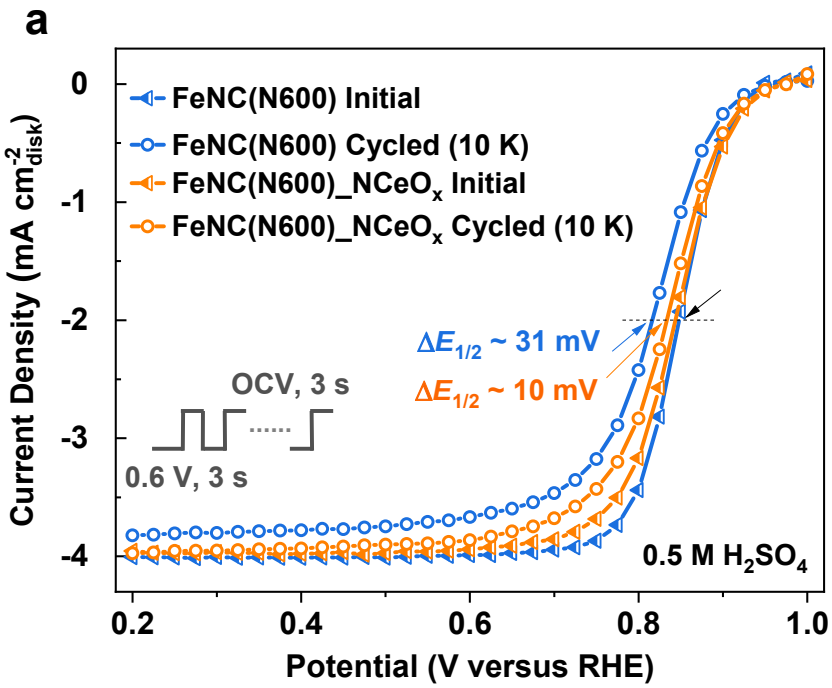
Anode: 0.1 mg/cm^2 $_{Pt}$; Cathode: 2.6 mg/cm^2$_{PGM-free}$ (FeNC), 40 wt% Nafion ionomer; Membrane: NR211; Active area: 5 cm^2; 100% RH, 80°C, O_2+N_2=1 bar.

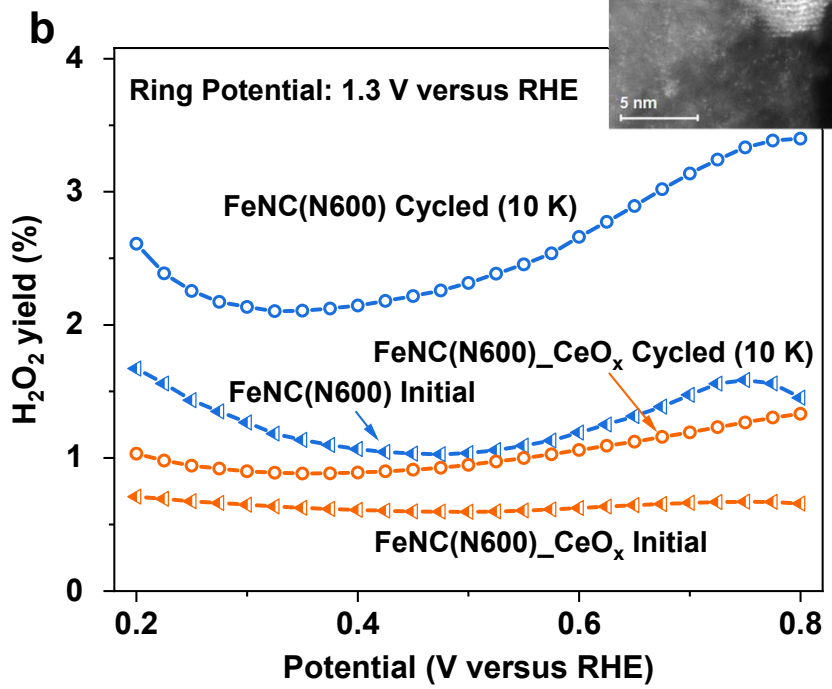
1. MEA performance depends on catalyst loading, achieving 37mA/cm^2 at 0.9V in O_2 and 151mA/cm^2 at 0.8V in air at 4.5mg/cm^2 catalyst loading (read from I-V curves).
2. High catalyst loading decreases performance at high current density region – low catalyst loading (2.5mg/cm^2) was chosen for comparison.

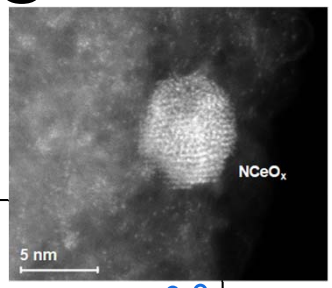
Any proposed future work is subject to change based on funding levels.

Accomplishments and Progress

Dual active sites: FeNC_NCeOx – improved durability







Test condition: 0.5M H_2SO_4, ORR staircase potential step of 0.025 V at intervals of 25 s from 1.0 to 0.0 V vs RHE. Catalyst loading: 0.6mg/cm^2. 25°C.

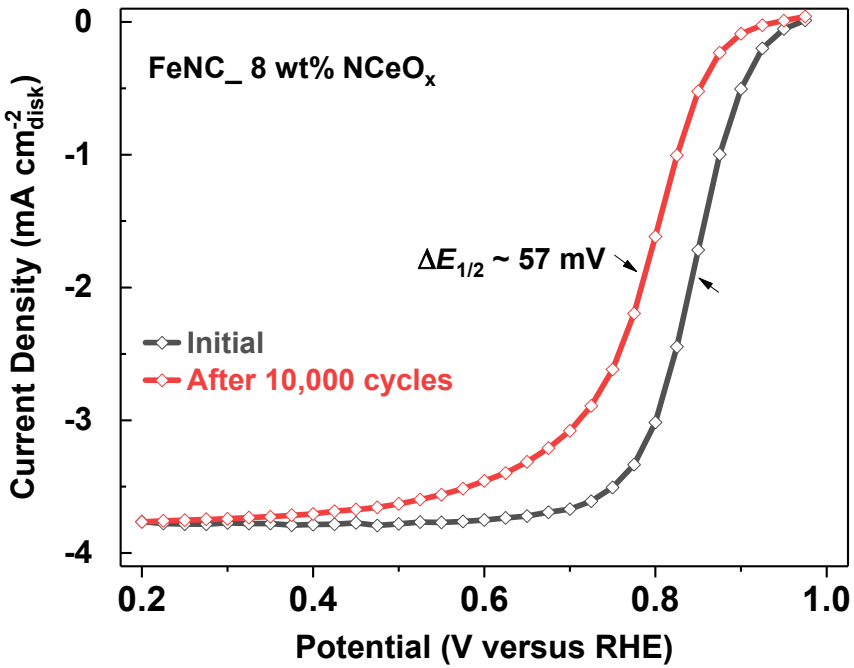
1. Improved ORR stability with NCeOx
2. H_2O_2% increases after durability testing – much smaller increase with NCeOx – indicating a self-catalyzed degradation for FeNC.
3. MEA performance and durability in Slide #8.

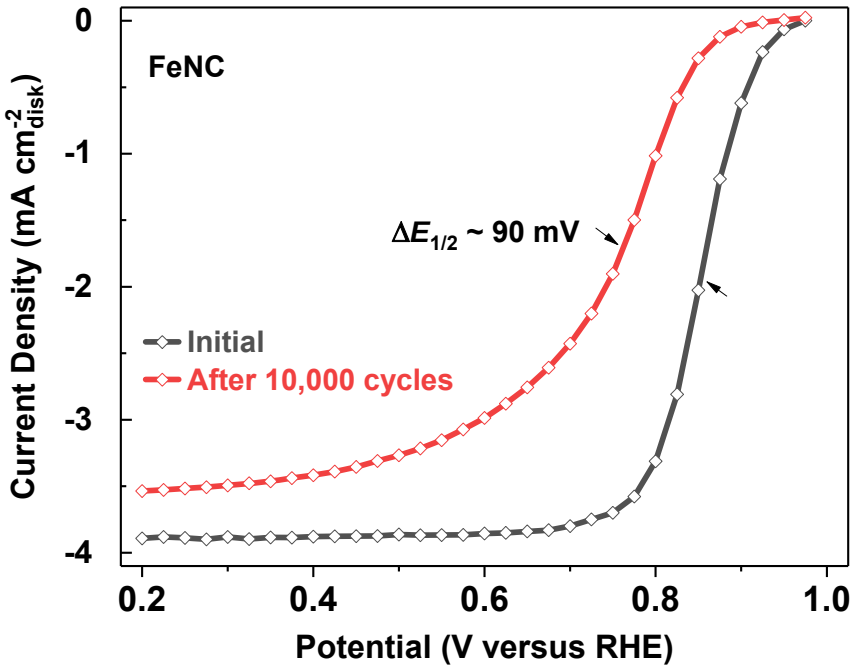
Any proposed future work is subject to change based on funding levels.

Accomplishments and Progress

Dual active site catalyst: FeNC(N600)_NCeOx – improved durability

80°C





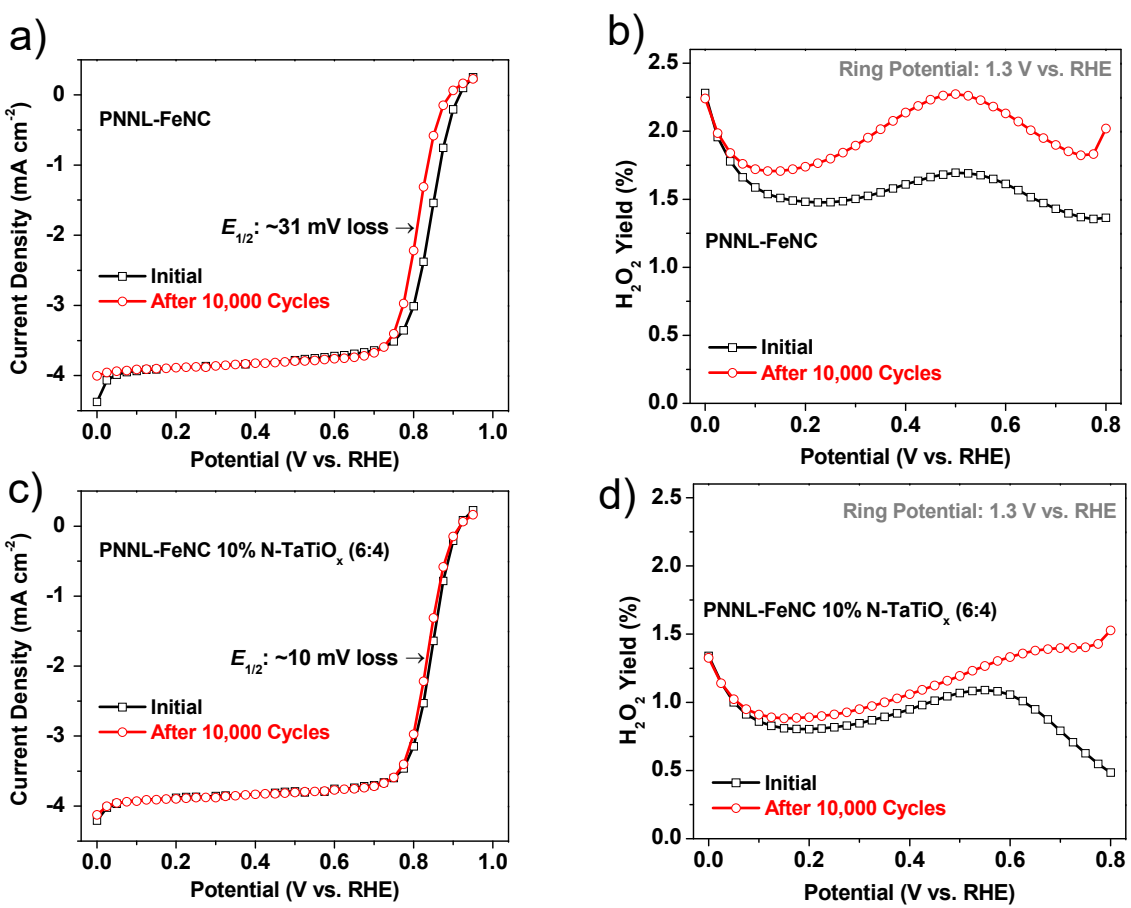
Test condition: 0.5M H_2SO_4, ORR staircase potential step of 0.025 V at intervals of 25 s from 1.0 to 0.0 V vs RHE. Catalyst loading: 0.6mg/cm^2. 80°C.

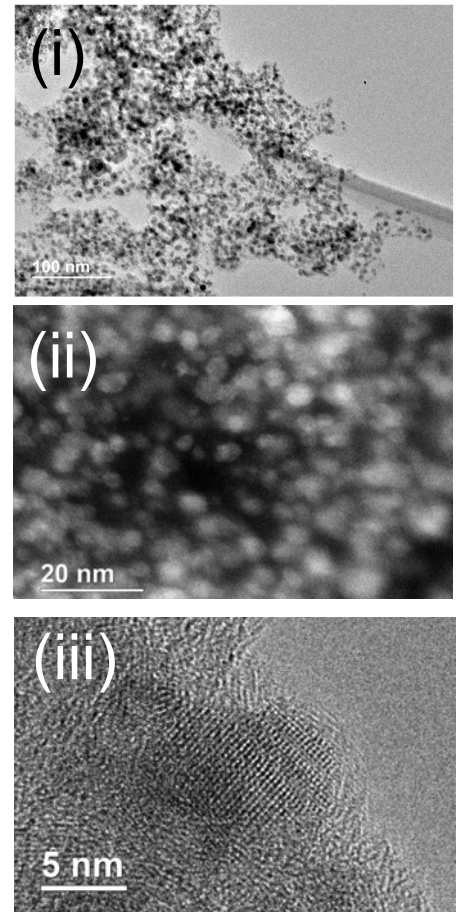
1. Increasing temperature for durability testing accelerates catalyst degradation.
2. Improved ORR stability with NCeOx

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

Accomplishments and Progress

New radical scavenger NTaTiOx improves catalyst durability





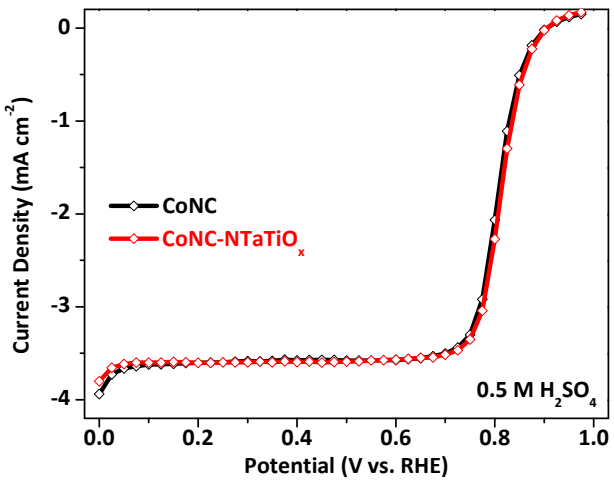
Test condition: 0.5M H_2SO_4, ORR staircase potential step of 0.025 V at intervals of 25 s from 1.0 to 0.0 V vs RHE. Catalyst loading: 0.6mg/cm^2. 25°C.

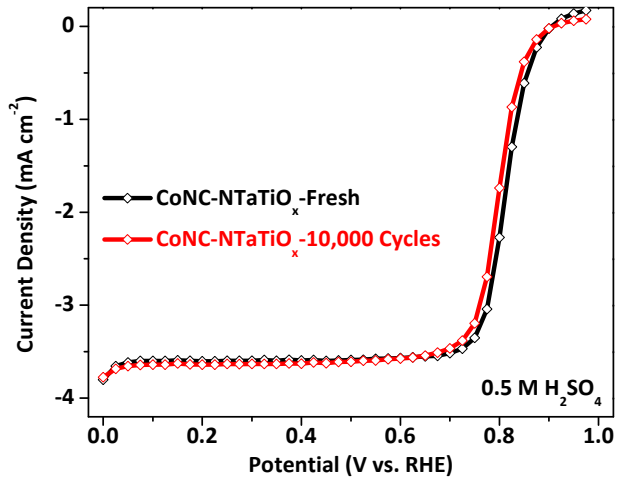
With NTaTiOx, both ORR activity and H_2O_2% change much less than baseline.

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

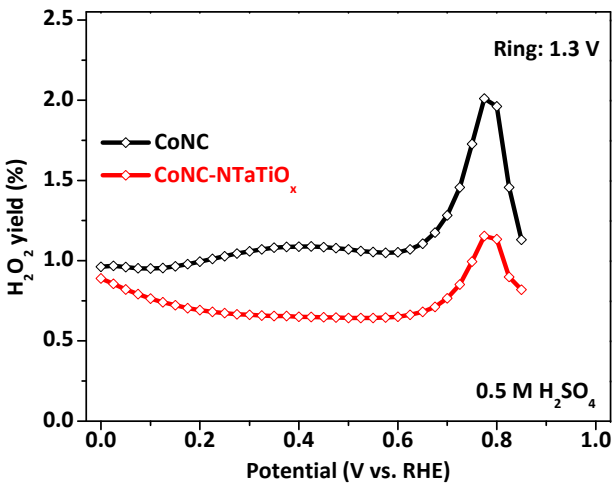
Accomplishments and Progress

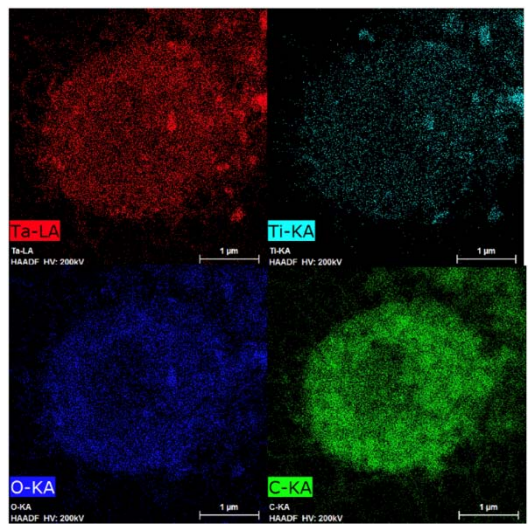
Successful loading of NTaTiOx using ambient hydrolysis deposition method





1. Improved durability for CoNC catalyst – indicating applicable to non-Fe catalyst
2. Decreased H_2O_2%





Test condition: 0.5M H_2SO_4, ORR staircase potential step of 0.025 V at intervals of 25 s from 1.0 to 0.0 V vs RHE. Catalyst loading: 0.6mg/cm^2.

Stability: 0.6 V _ 3 s; 0.95 V _ 3 s, 10,000 cycles, O_2 saturation. 25°C.

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Accomplishments and Progress: Responses to Previous Year Reviewers' Comments

1. **Comments:** "…The radical scavenger approach is good, and the results are promising. The team needs to further improve membrane electrode assembly (MEA) performance.…" **Response:** we have improved MEA performance continuously, especially in FY20. (Slide #7).
2. **Comments:** "… whether the dual-site catalyst is really more stable or only appears more stable because it starts at lower performance. …." **Response:** We have demonstrated that, with the initial activity and performance of dual-site catalyst being higher than baseline, the durability is better than baseline (Slide #8).
3. **Comments:** "…What is missing in the logic chain is direct evidence showing that the improved durability in PEMFCs is indeed related to the reduced H2O2 yield." **Response:** in the past years (FY18, FY19), we showed the correlation between catalyst degradation – H_2O_2 yield – CO_2 formation; we are designing experiment to confirm the direct relationship between improved durability and reduced H_2O_2 yield.
4. **Comments: "**… It is strongly recommended that the project team design experiments or perform modeling to determine the extent to which this approach will work.." **Response:** This is critical for overall durability study. We have seen different degradation in liquid vs. MEA and we are working to quantify the degradation and dual-site effect.

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

Collaboration & Coordination

Partner	Project roles
PNNL – Lead (Y. Shao, X. Xie, L. Yan, V. Prabhakaran)	Project lead, management and coordination; catalysts design and synthesis.
Ballard (L. Yang)	MEA design, test and analysis
Univ. Maryland(L. Hu)	New radical scavenger, atomic layer deposition
WashU (V. Ramani)	Electrode design and MEA assembly, MEA test and analysis
Oregon State U. (X. Ji)	New radical scavenger, ambient hydrolysis deposition

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

- Understand degradation mechanisms of PGM-free catalysts under various conditions;
- Improve synergy of dual active sites for further enhanced durability;
- MEA performance and durability.

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Proposed Future Work

- Quantify each degradation pathway (e.g., radical oxidation, demetallation,…) and identify mitigation strategy for each of them;
- Develop and optimize new radical scavenger (e.g., NTaTiOx) and new synthesis method (e.g., ALD and AHD) for further enhanced durability;
- Optimize PGM-free catalysts including active sites and active site density, porosity, particle size.
- Optimize MEA fabrication (e.g., interaction between catalyst – radical scavenger – ionomers).

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

Summary Slide

- Dual active site catalyst FeNC(N600)_NCeOx exceeds Year 2 activity milestones (>25mA/cm^2, 0.9V in H_2/O_2) and durability milestone (1.5X durability improvement).
- FeNC catalyst exceeds Year 3 activity milestone (>30mA/cm^2, 0.9V in H_2/O_2) and performance milestone (>150mA/cm^2, 0.8V in H_2/Air) – high catalyst loading.
- Dual active site catalyst improves catalyst durability while achieving higher activity than baseline.
- Collaboration with ElectroCat helped understand the catalysts (chemistry, active sites, functional mechanisms,…).
- Need improvement on catalyst degradation understanding.

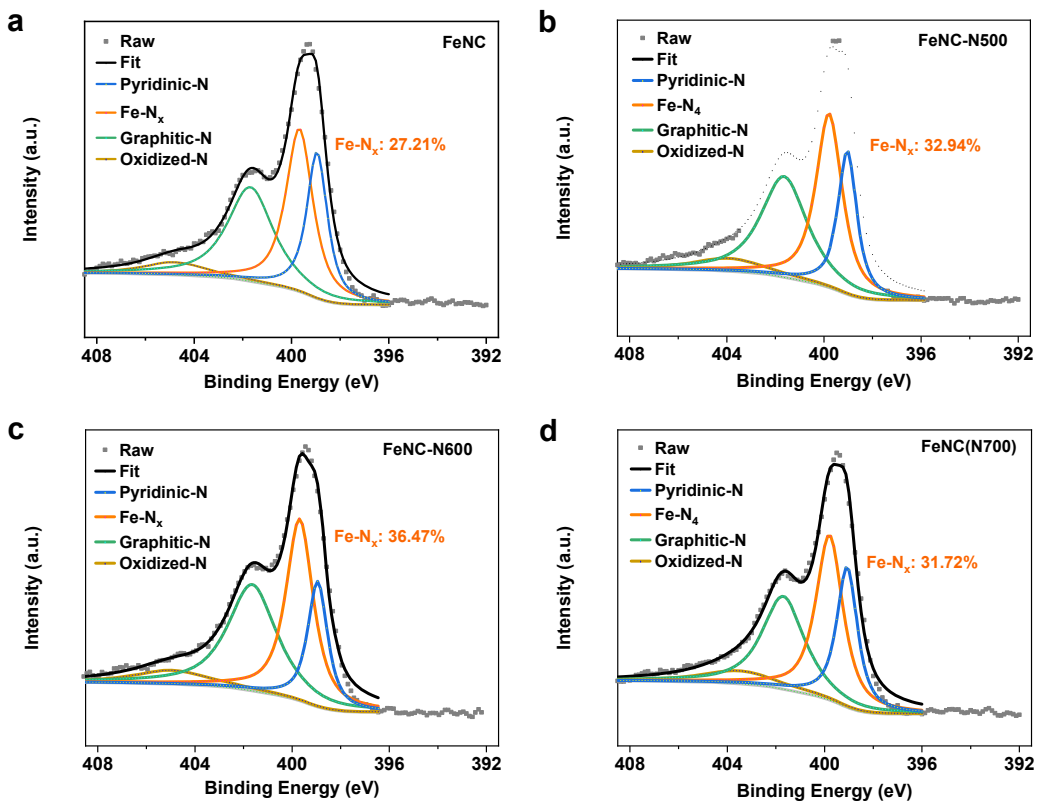
Any proposed future work is subject to change based on funding levels.

Technical Back-Up Slides

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

Accomplishments and Progress

XPS shows the increase of Fe loading with optimal synthesis.



Element content in catalysts

Catalyst	C 1s (wt%)	N 1s (wt%)	O 1s (wt%)	Fe 2p3 (wt%)
FeNC	81.31	12.76	4.17	1.76
FeNC(N400)	81.12	12.84	4.23	1.81
FeNC(N500)	79.68	12.39	4.69	3.24
FeNC(N600)	79.05	12.47	4.28	4.20
FeNC(N700)	79.42	12.36	4.95	3.27

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