Project ID: fc172

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

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04/30/2019

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*: $589,311

  * As of 03/04/19

Partners

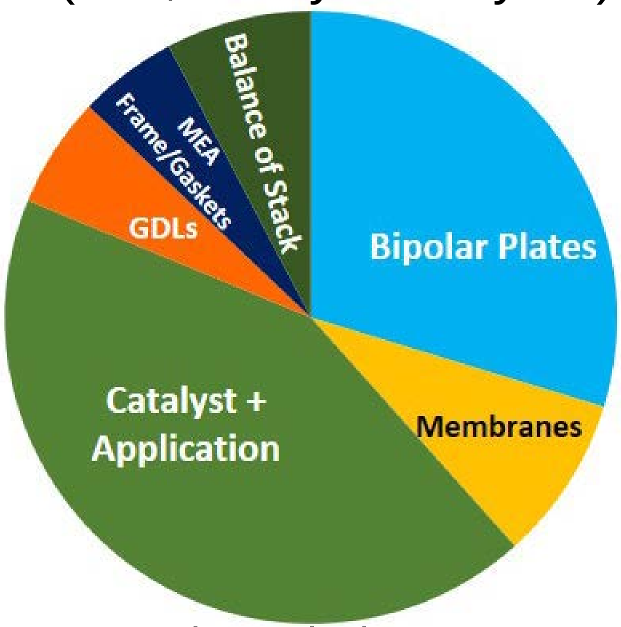
- Washington Univ. in St. Louis
- Univ. of Maryland, College Park
- Ballard Power Systems Inc.
- ElectroCat
- Project lead: PNNL

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

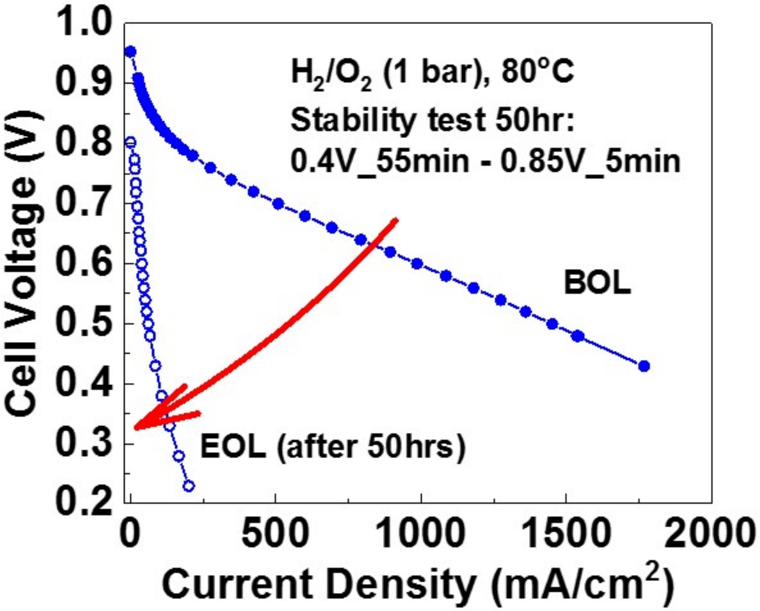
Relevance

PGM-free ORR catalysts could significantly decrease fuel cell cost, but the state-of-art activity and, particularly stability need 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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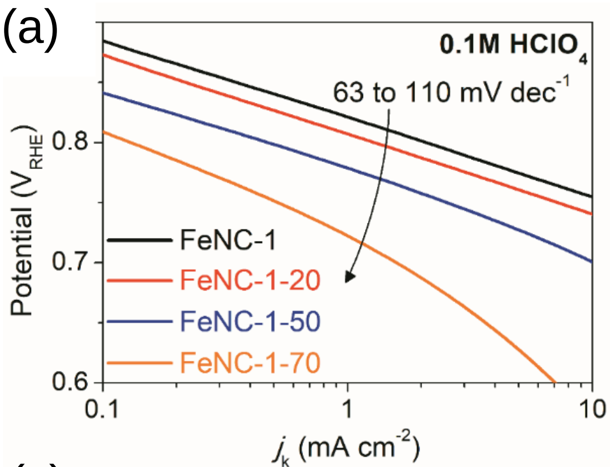
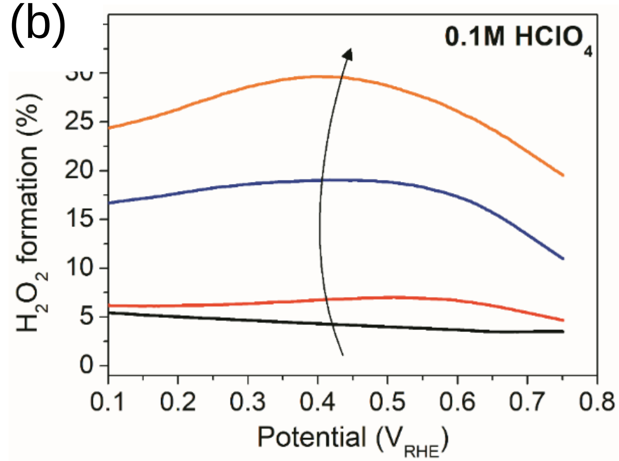
Relevance

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

(a)



(b)

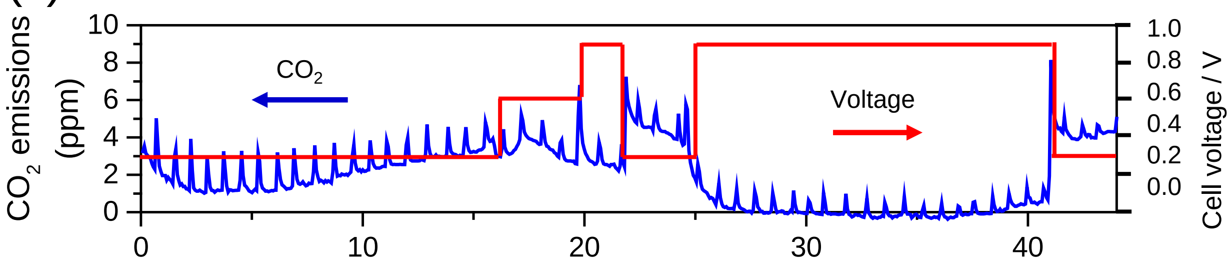


H_2O_2 (radicals) :

a) decrease ORR activity

b) increase H_2O_2 formation

(c)



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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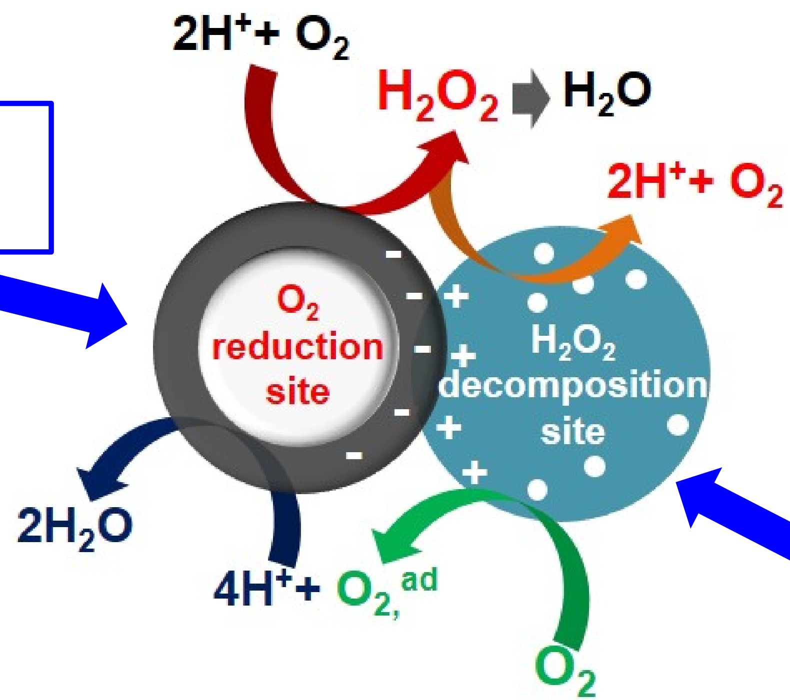
Approach

Dual active sites for ORR and H_2O_2: 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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Approach

Milestone	Milestone Description (Go/No-Go Decision)	Complete
GNG1 (Year 1)	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).	100%
M2.2	Identify O_2 reduction catalysts with $E_{1/2}$>=0.81V ($\Delta E_{1/2}$ < 50mV (vs. Pt/C)) under RRDE test (01/31/19)	100%
M1.2	Identify pathways to produce 20g catalysts using thermal shock activation technique (07/31/19)	50%
M3.3	Identify dual-site catalysts with $E_{1/2}$>=0.82V ($\Delta E_{1/2}$ < 45 mV (vs. Pt/C)) under RRDE test (07/31/19)	100%
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 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)	50%

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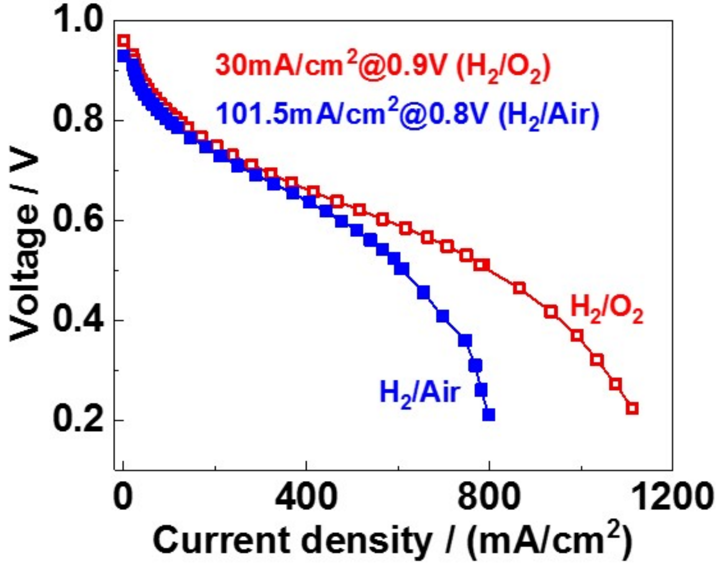
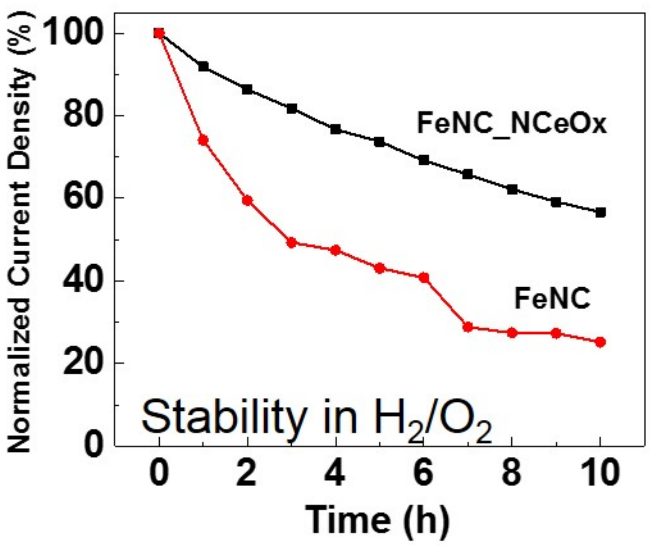
Accomplishments and Progress

Key updates: Dual active site catalyst FeNC_NCeOx exceeds Year 1 & Year 2 activity milestone and Year 1 performance milestone, improves catalyst stability.

Activity/performance



Improved stability



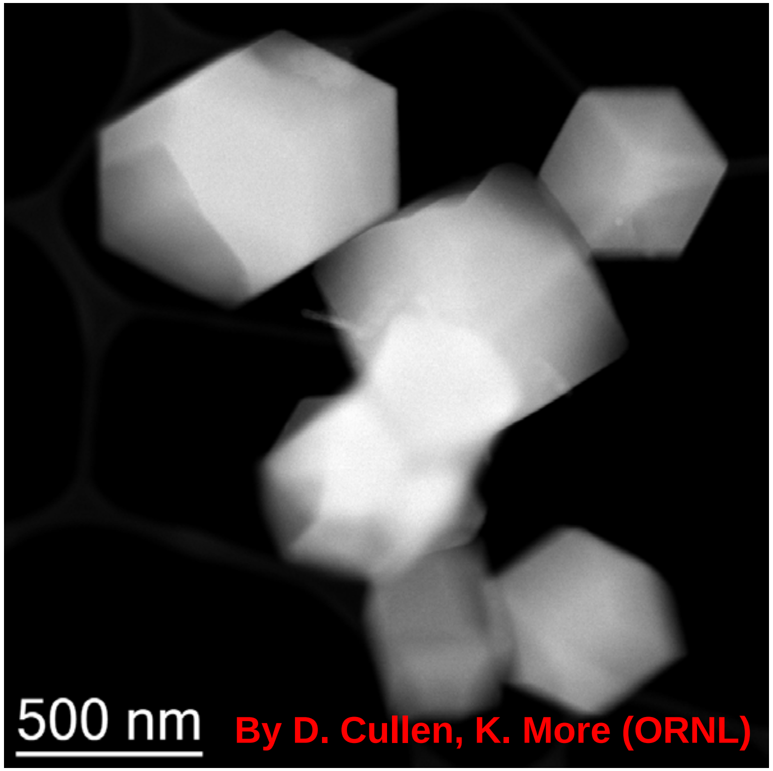
Anode: 0.2mg/cm² $_{Pt}$ 30wt% Nafion ionomer; Cathode: 4.5mg/cm² $_{PGM-free}$ (FeNC_5%NCeOx), 35wt% Nafion ionomer; Membrane: Gore (15μm); Active area: 5 cm²; 80%% RH, 80°C, O_2+N_2=1 bar. Stability test (in H_2/O_2): constant cell voltage at 0.4V for 55min and then 0.85V for 5min (0.4V_55min/0.85V_5min), record current density at 0.85V, repeat.

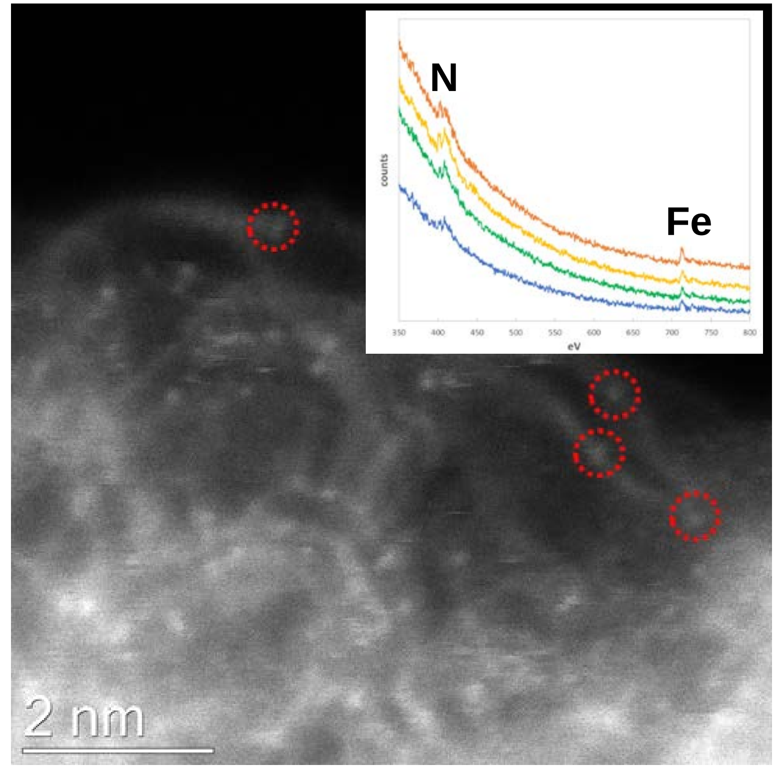
1. Radical scavenger NCeOx is directly loaded onto FeNC catalyst – more improvement possible with better integration.
2. Our stability test protocol is designed to maximize the negative effect of H_2O_2(radicals).

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

Accomplishments and Progress

Atomically dispersed FeNC catalysts



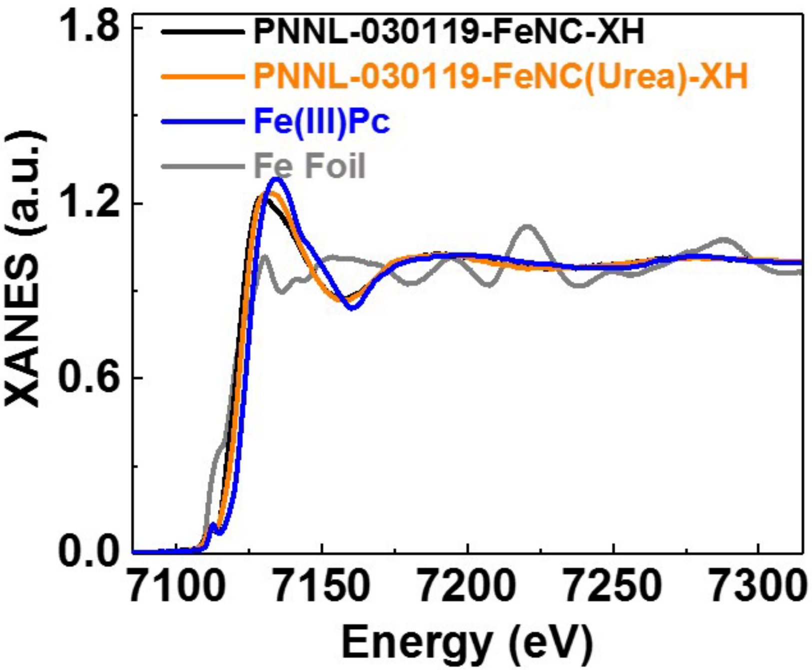


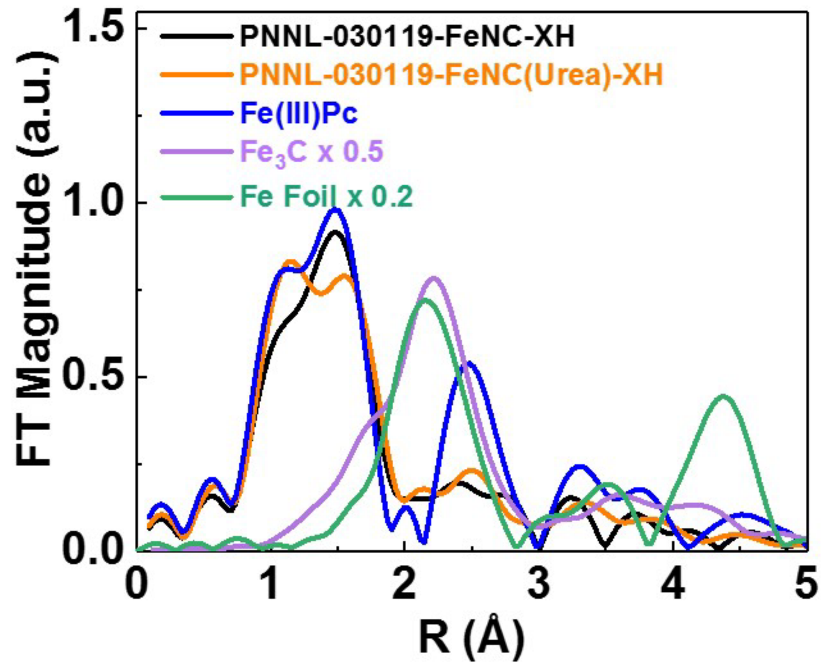
STEM/EELS confirm atomic dispersion of Fe and very common FeNx moieties (most atoms probed showed Fe and N).

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

Accomplishments and Progress

Atomically dispersed FeNC catalysts





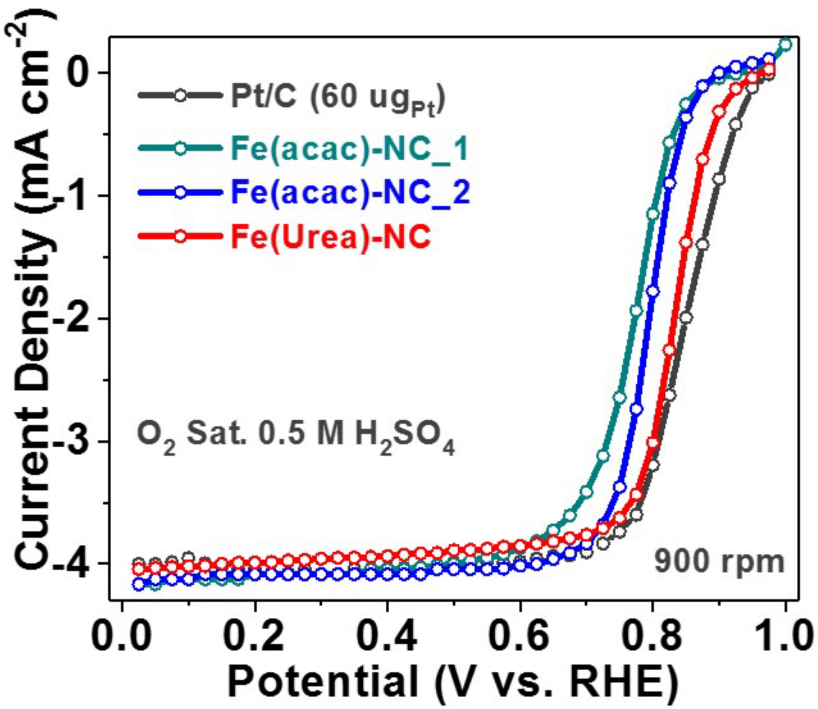
Measured by D. Myers et al. (ANL)

XANES and EXAFS confirm Fe valence between 2+ and 3+, and FeNx (with some Fe-O bonds), but free of Fe-Fe and Fe-C.

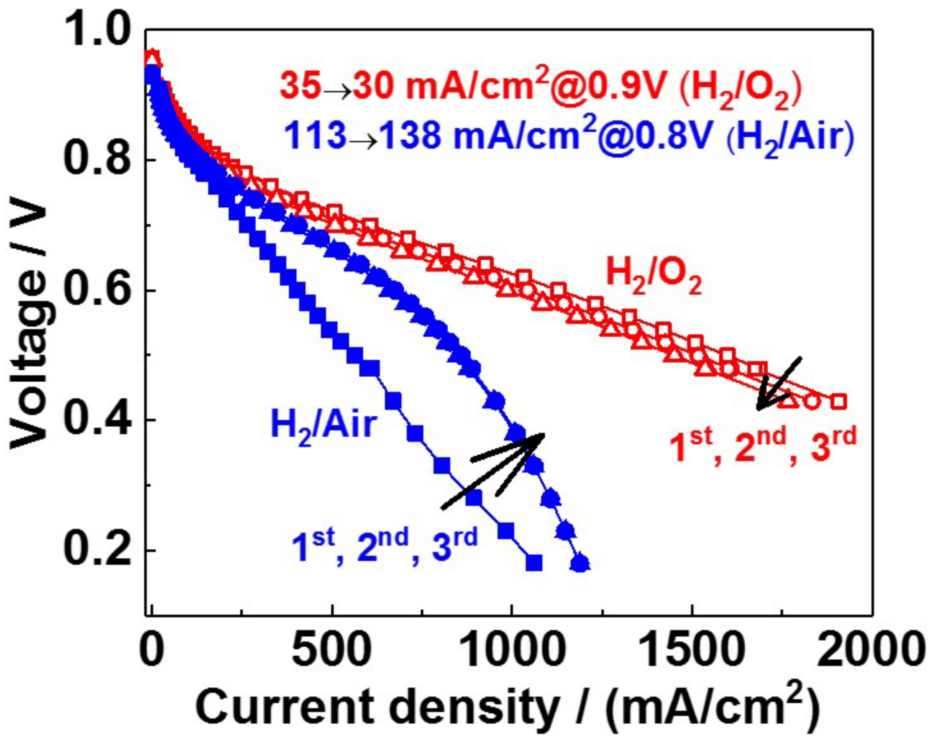
Any proposed future work is subject to change based on funding levels.

Accomplishments and Progress

FeNC catalyst exceeds Year 2 activity and performance milestones



Best FeNC show $E_{1/2}$=0.84V.



MEA – Anode: 0.2mg/cm$^2_{Pt}$ 30wt% Nafion ionomer; Cathode (single layer): 4.0mg/cm$^2_{PGM\text{-}free}$ (012319-Fe(acac)3-1000C-xh), 35wt% Nafion ionomer; Membrane: Gore (15μm); Active area: 5 cm^2; 80%% RH, 80°C, O_2+N_2=1 bar
RDE – PGM-free in 0.5M H_2SO_4, 600ug/cm^2; Pt/C (60ug_{Pt}/cm^2) in 0.1M $HClO_4$.

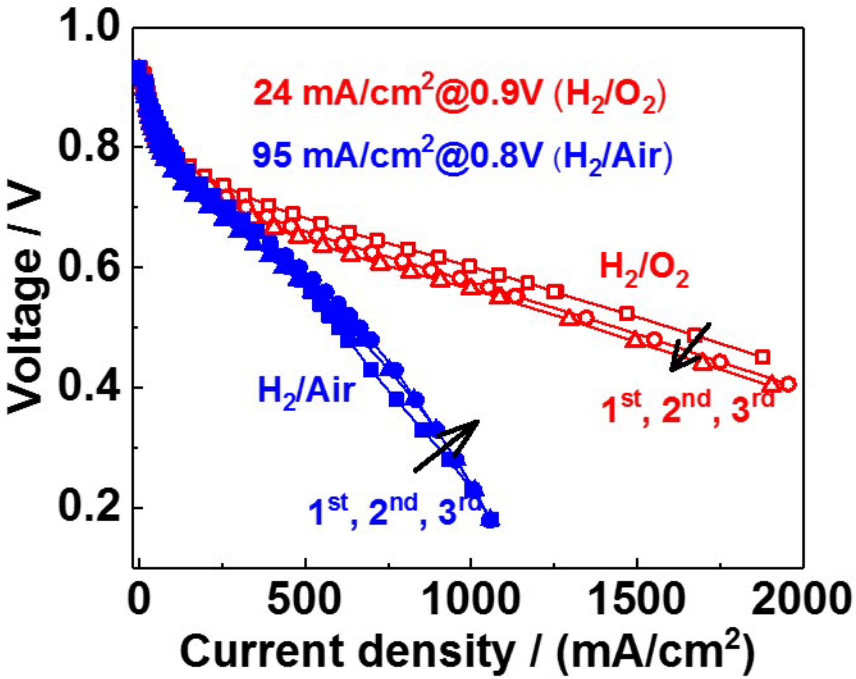
1. High activity in both RDE and MEA tests
2. Max power density 0.43W/cm^2 (H_2/Air)

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

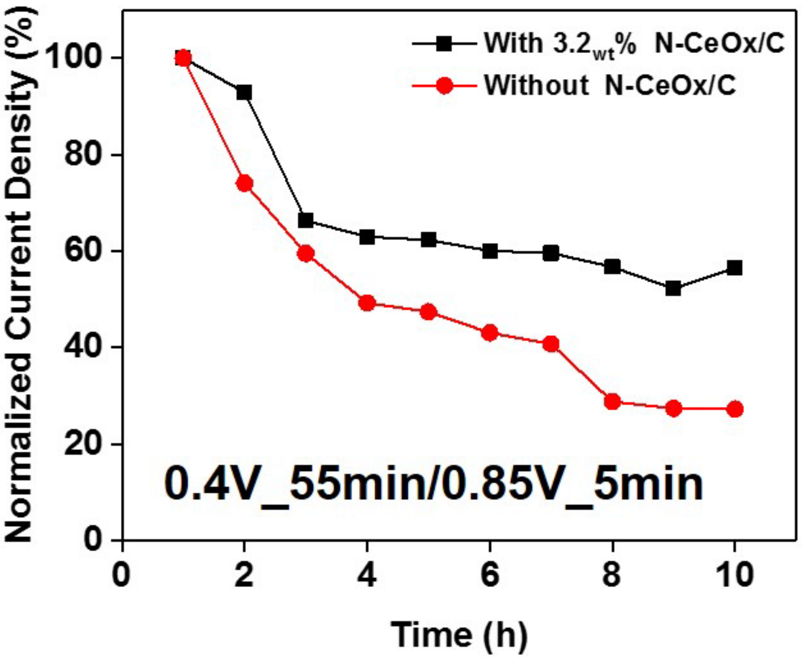
Accomplishments and Progress

Dual active site catalyst: FeNC+NCeOx (physical mixing)

Performance/activity



Stability



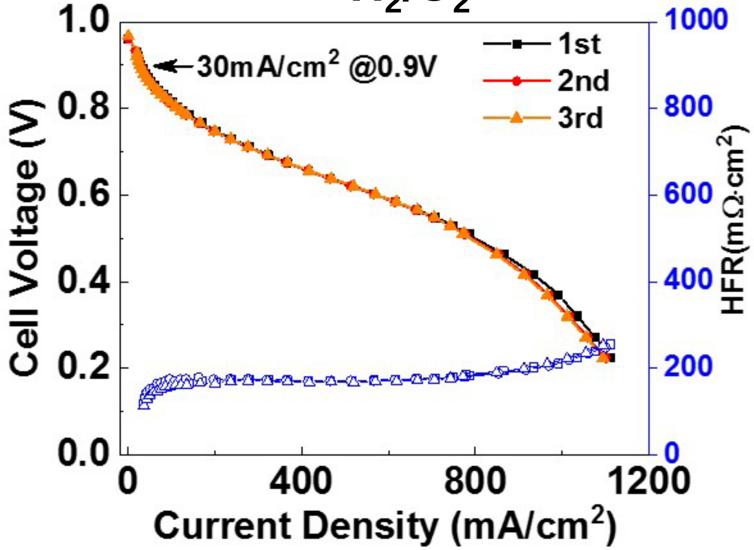
Anode: 0.2mg/cm² $_{Pt}$ 30wt% Nafion ionomer; Cathode: 4.1mg/cm² $_{PGM-free}$ (012319-Fe(acac)3-1000C-xh+3.5%NCeOx/C), 35wt% Nafion ionomer; Membrane: Gore (15μm); Active area: 5 cm²; 80%RH, 80°C, O_2+N_2=1 bar Stability test (in H_2/O_2): constant cell voltage at 0.4V for 55min and then 0.85V for 5min (0.4V_55min/0.85V_5min), record current density at 0.85V, repeat.

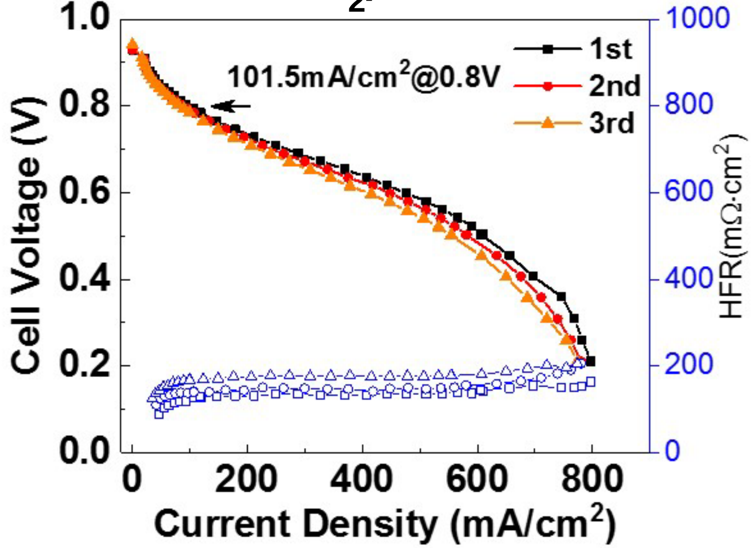
1. Improved stability with NCeOx
2. Adding NCeOx decreases performance and activity, still nearly hitting Year 1 GNG.

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

Accomplishments and Progress

Dual active site catalyst: FeNC_NCeOx (direct loading) Improved activity and performance





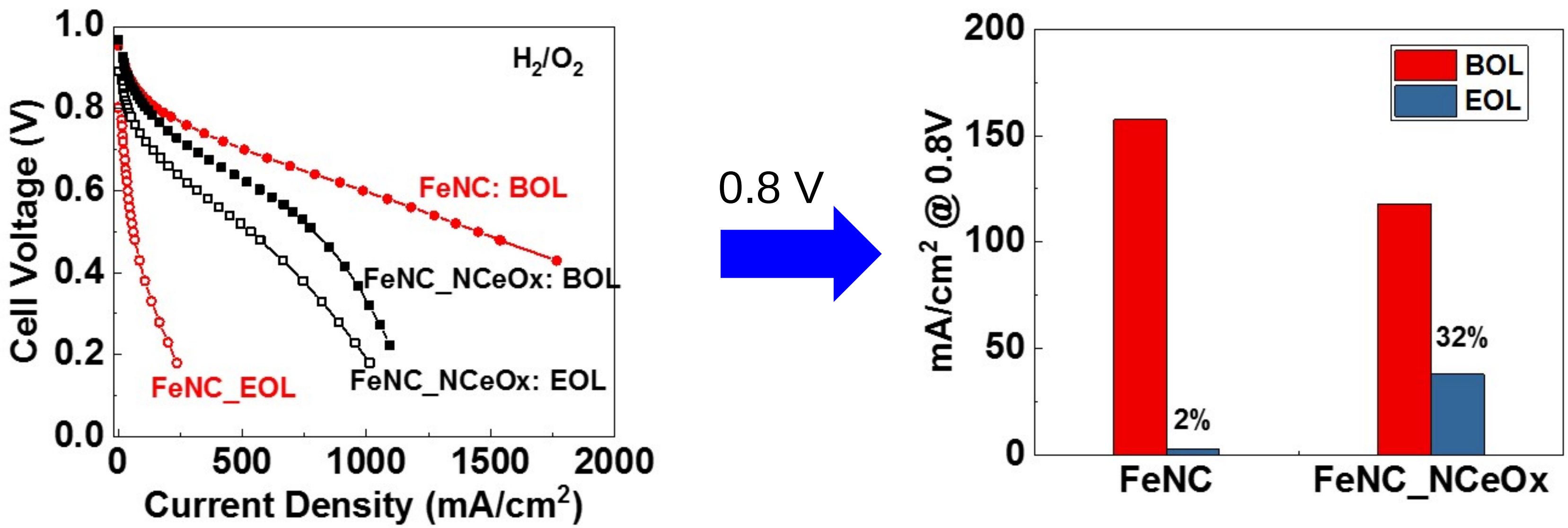
Anode: 0.2mg/cm^2 $_{Pt}$ 30wt% Nafion ionomer; Cathode: 4.5mg/cm$^2_{PGM\text{-}free}$ (FeNC_5%NCeOx), 35wt% Nafion ionomer; Membrane: Gore (15µm); Active area: 5 cm^2; 80%% RH, 80°C, O_2+N_2=1 bar. Stability test (in H_2/O_2): constant cell voltage at 0.4V for 55min and then 0.85V for 5min (0.4V_55min/0.85V_5min), record current density at 0.85V, repeat.

1. FeNC_NCeOx activity and performance exceed Year 1 GNG milestone (and Year 2 activity milestone); maximum power density 0.31W/cm^2 (H_2/Air).
2. Needs to identify the reason for high HFR and decrease it.

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

Accomplishments and Progress

Dual active site catalyst: FeNC_NCeOx (direct loading) Improved stability



Anode: 0.2mg/cm^2 $_{Pt}$ 30wt% Nafion ionomer; Cathode: 4.5mg/cm$^2_{PGM\text{-}free}$ (FeNC_5%NCeOx), 35wt% Nafion ionomer; Membrane: Gore (15μm); Active area: 5 cm^2; 80%% RH, 80°C, O_2+N_2=1 bar. Stability test (in H_2/O_2): constant cell voltage at 0.4V for 55min and then 0.85V for 5min (0.4V_55min/0.85V_5min), record current density at 0.85V, repeat.

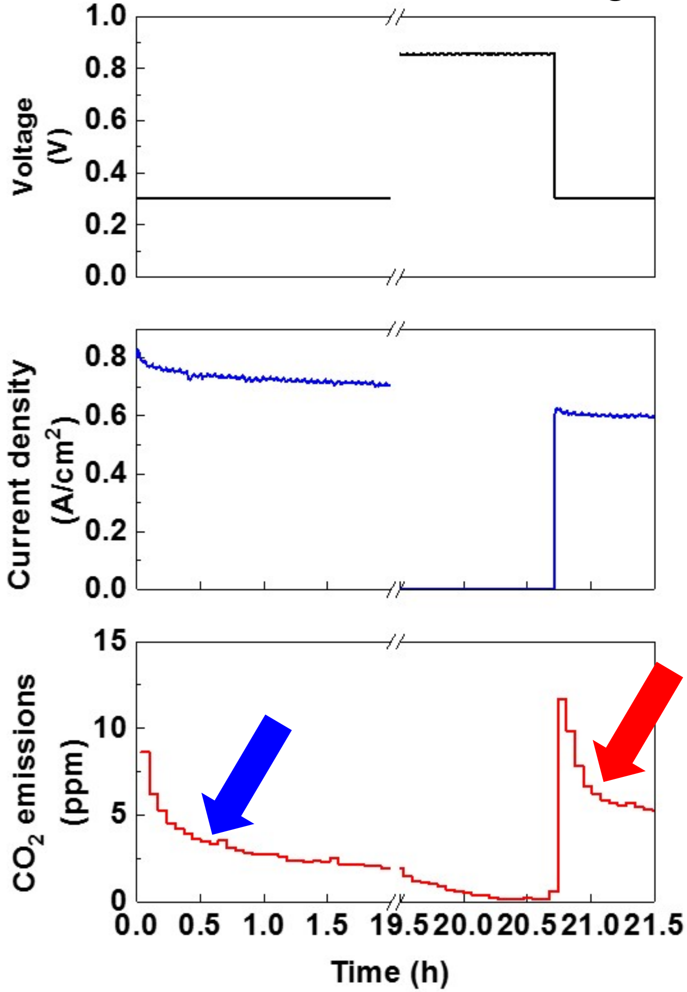
1. Improved stability of dual active site catalyst FeNC_NCeOx.
2. FeNC_NCeOx activity/performance is slightly lower than FeNC.

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

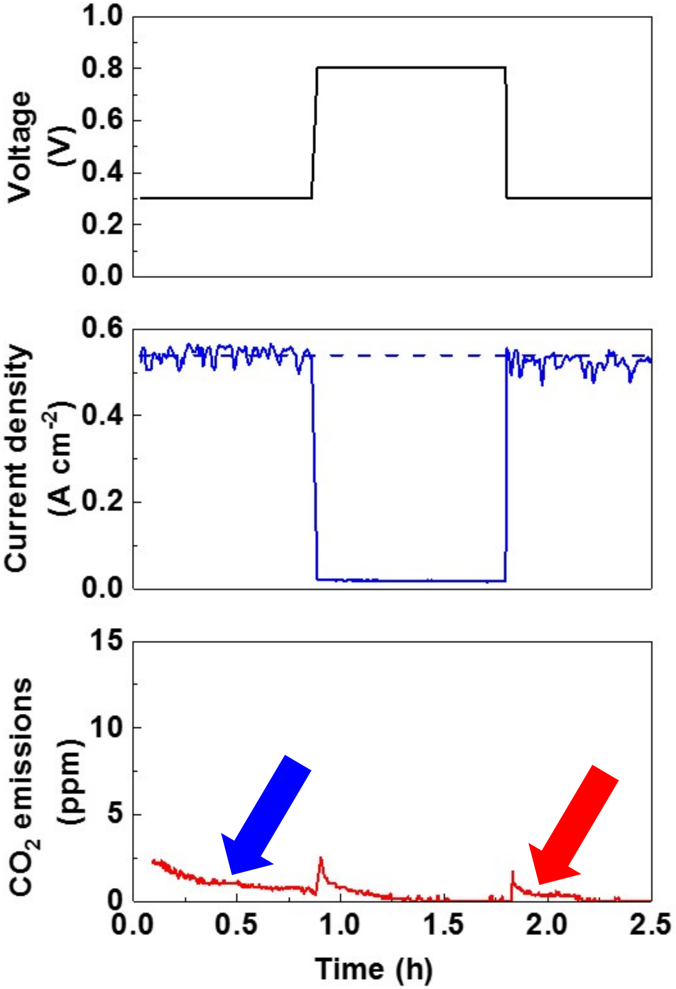
Accomplishments and Progress

Dual active sites decrease CO_2 emission, increase stability
Tested with LANL (CM+PANI)-Fe-C(Zn) catalyst (physical mixing)

Without radical scavenger



With radical scavenger

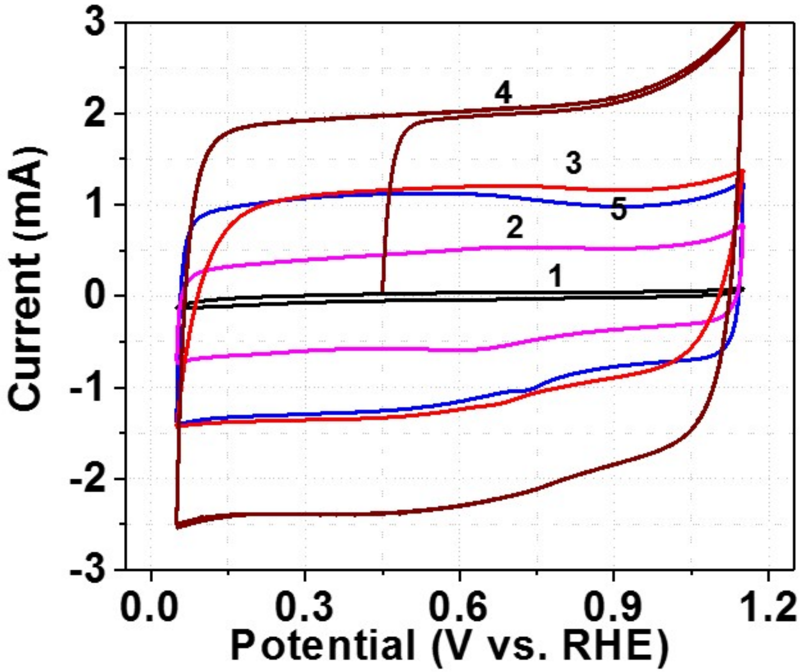


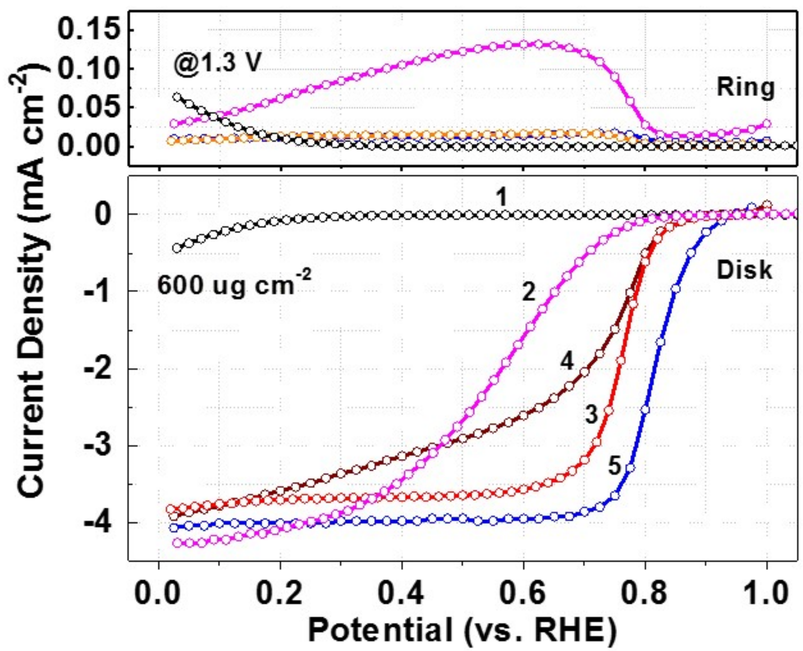
by U. Martinez (LANL)

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

Accomplishments and Progress

Thermal shock activation synthesis of CoZIF catalysts.





1-4: radiation heating samples, 5: traditional furnace sample

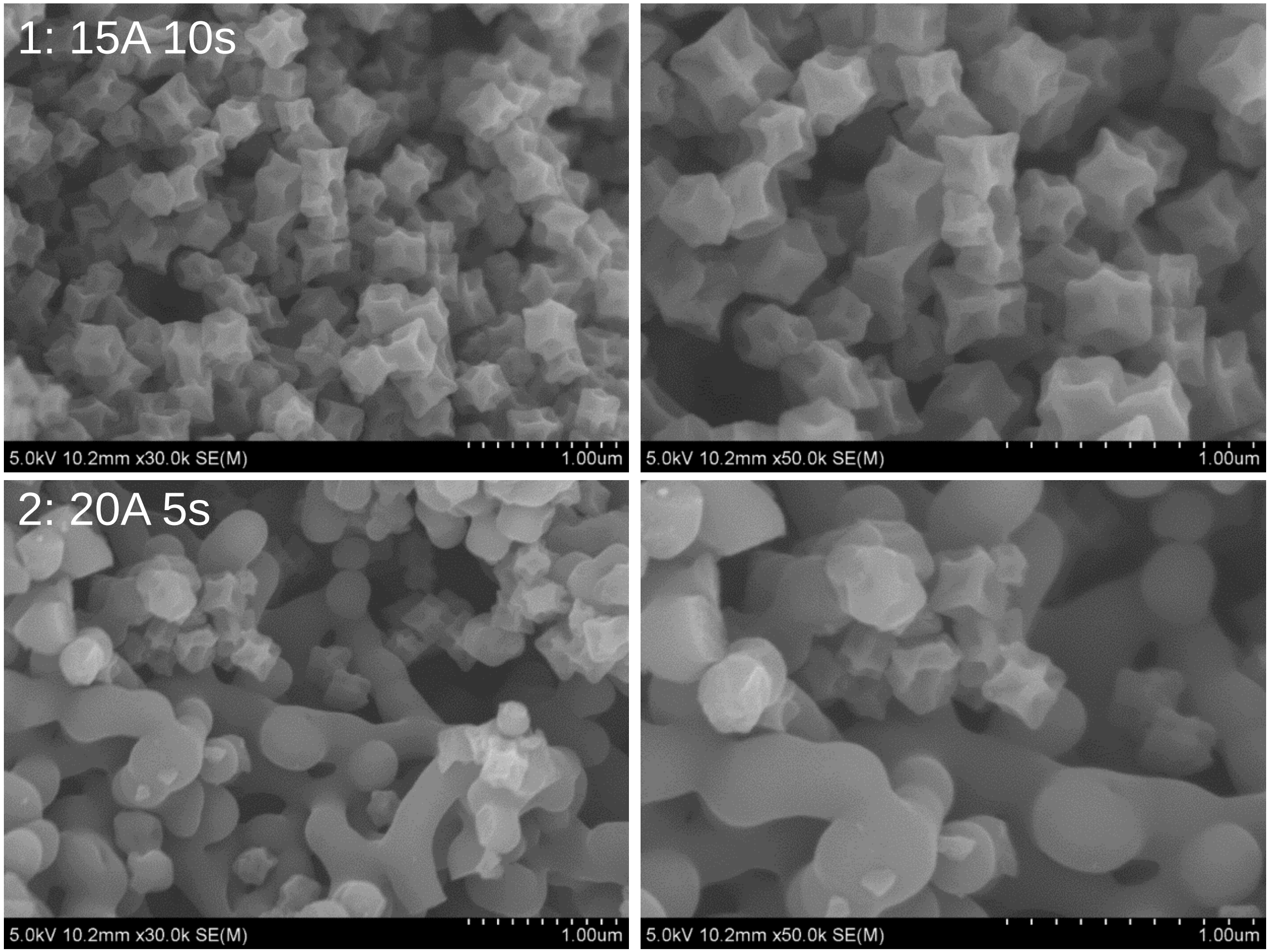
Test condition: 0.5M H_2SO_4, 50mV/s CV, ORR staircase potential step of 0.025 V at intervals of 25 s from 1.0 to 0.0 V vs RHE. Catalyst loading: 0.6mg/cm^2.

Optimized thermal shock increases surface area (from double layer capacitance), but ORR activity increase is limited.

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

Accomplishments and Progress

Thermal shock is not effective enough to remove Zn.



Element	**[norm. wt.%]**	**[norm. at.%]**
N	**33.3**	**42.9**
C	25.9	39.0
O	7.8	8.9
Zn	**29.5**	**8.1**
Co	3.4	1.04
Cl	0.06	0.03
	100	100

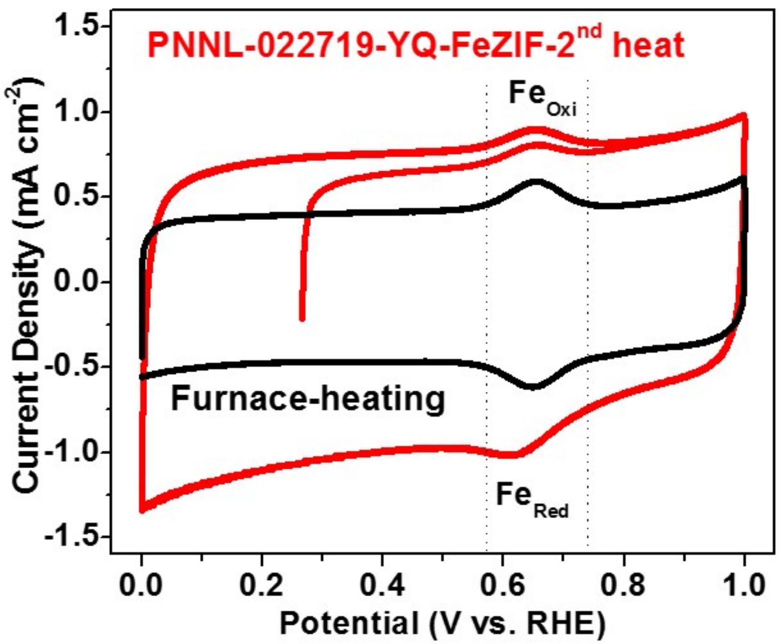
Element	[norm. wt.%]	[norm. at.%]
N	**34.1**	**45.6**
C	21.8	34.1
O	8.5	9.9
Zn	**32.9**	**9.4**
Co	2.7	0.8
Cl	0.08	0.04
	100	100

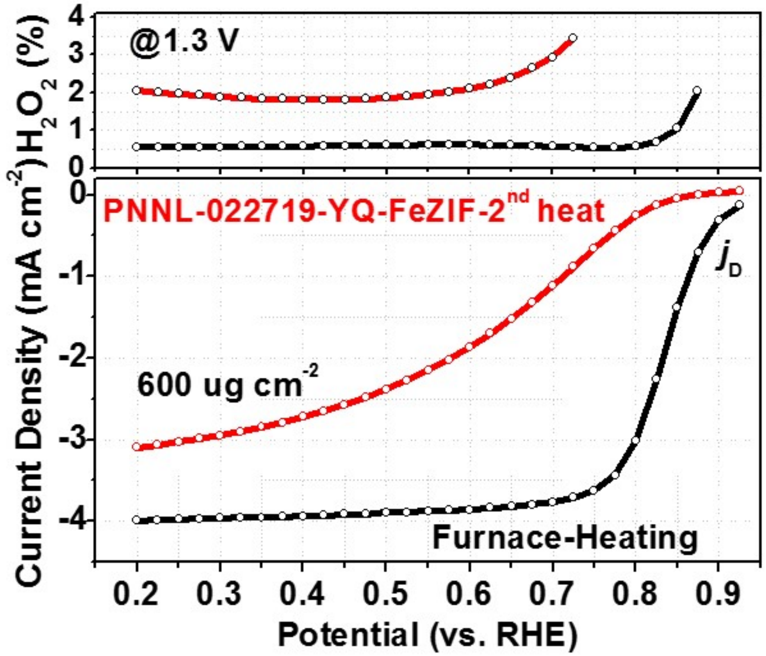
(also see Review comments #5)

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

Accomplishments and Progress

Thermal shock activation synthesis of FeZIF catalysts (radiation heating)





Optimized thermal shock increases surface area (from double layer capacitance), but not for ORR activity of FeZIF catalyst (after 2nd heat-treatment).

Test condition: 0.5M H_2SO_4, 50mV/s CV, 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.

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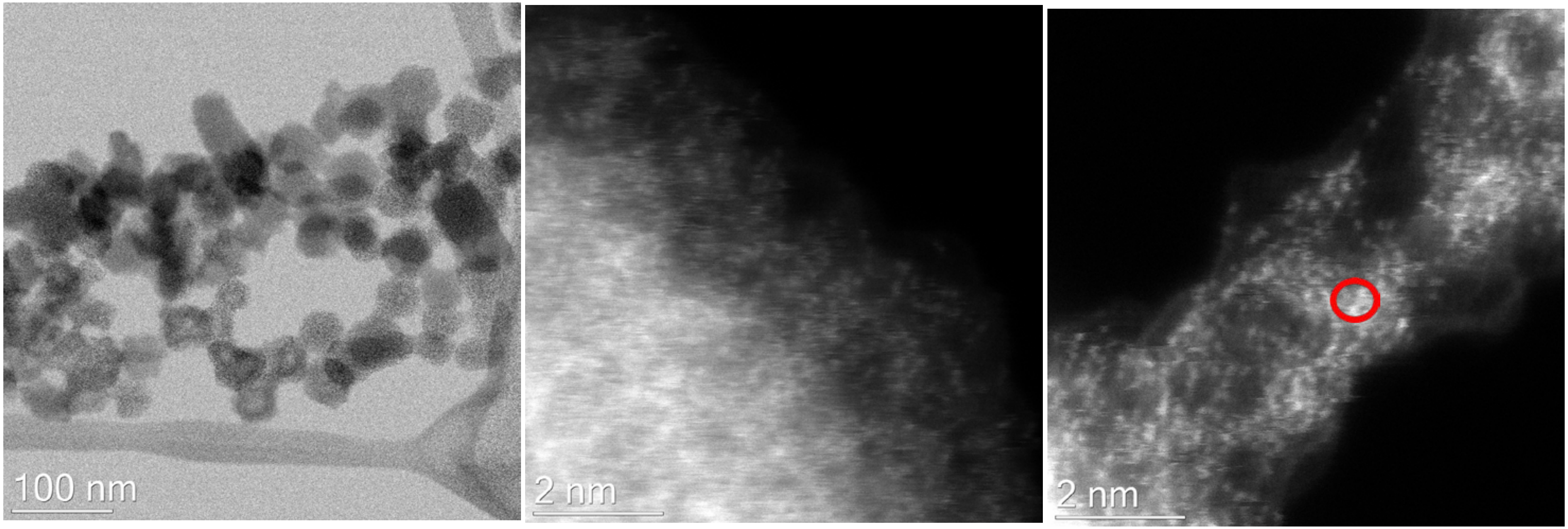
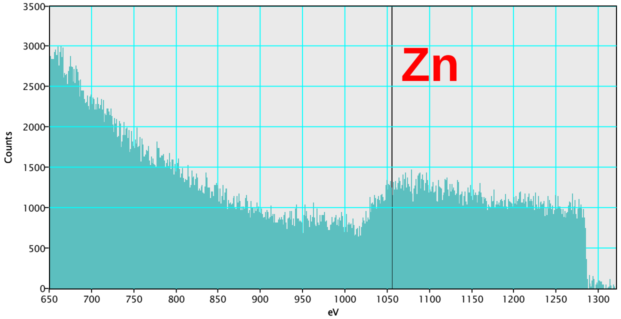
Accomplishments and Progress

Thermal shock activation did not fully pyrolyze FeZIF precursor



- Surfaces coated with Zn with usually high N content (20 at.%), but without Fe particles
- Carbon EELS edge did not look highly graphitic
- Not fully pyrolyzed.



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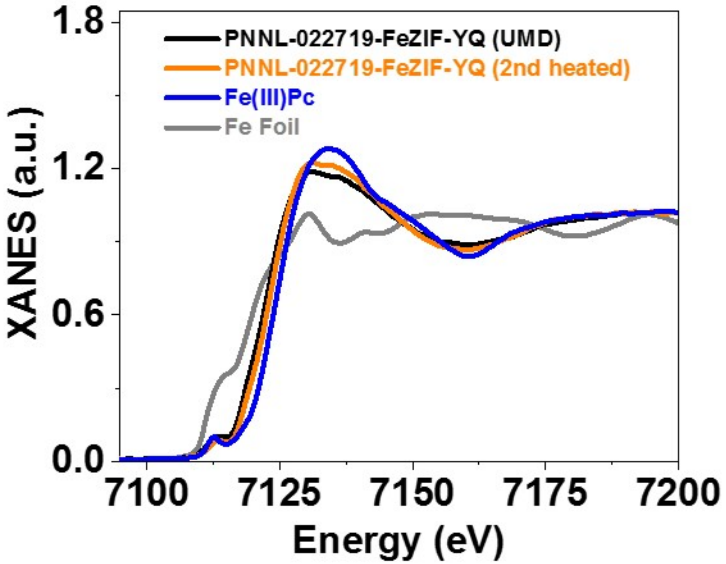
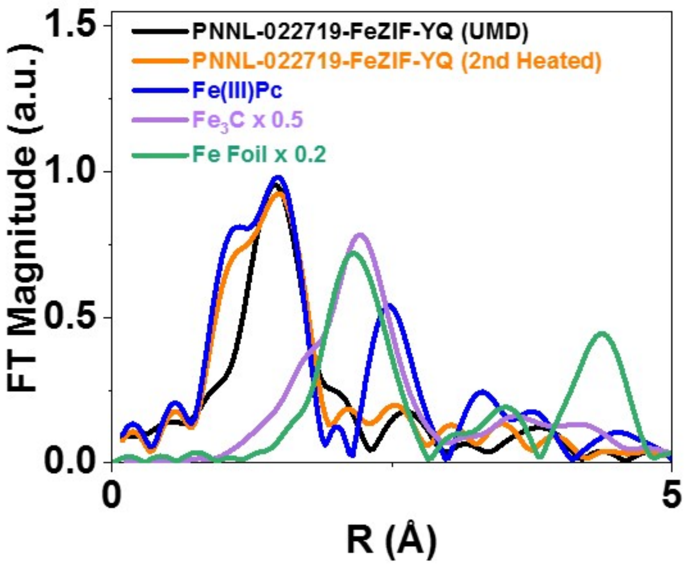
Accomplishments and Progress

Thermal shock activation synthesis of FeZIF catalysts (radiation heating)



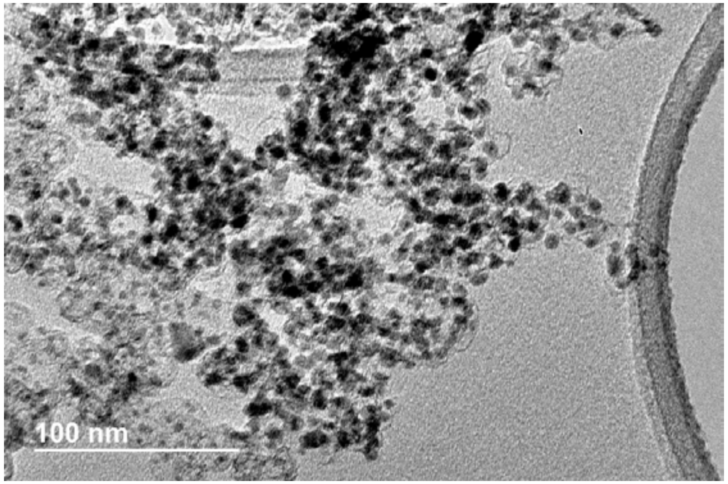


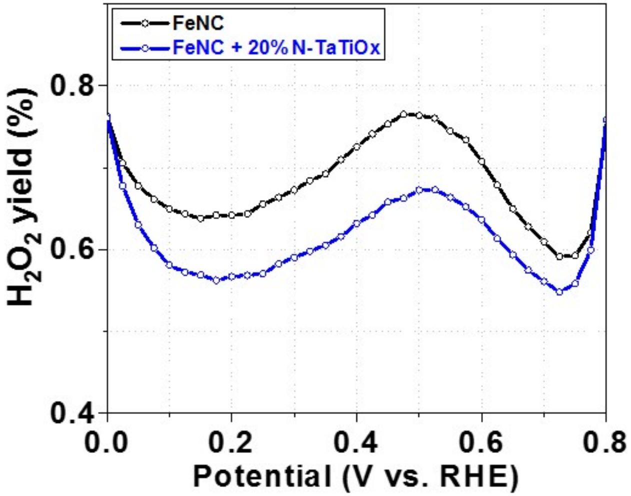
By Debbie Myers et al (ANL)

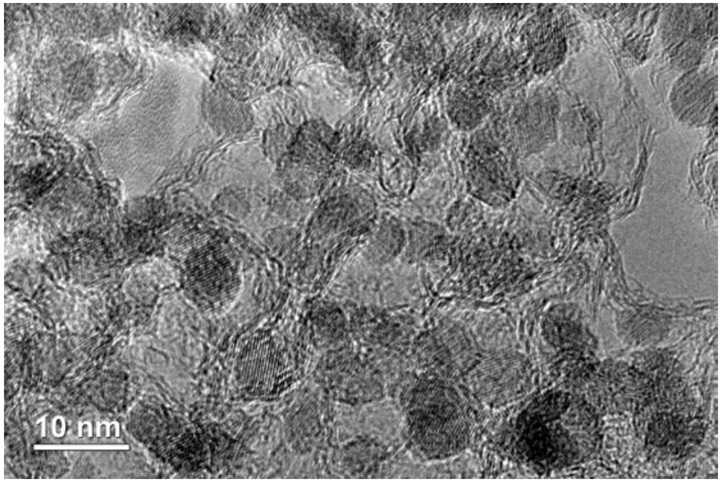
1. Thermal shock sample has lower oxidation state (than regular FeN4 samples), likely due to incomplete pyrolysis of precursor; it also likely has carbide (high shock temperature may convert FeN4 to carbide?)
2. No Fe-Fe bonds observed.
3. Lower active site density leads to lower ORR activity? – need to confirm.

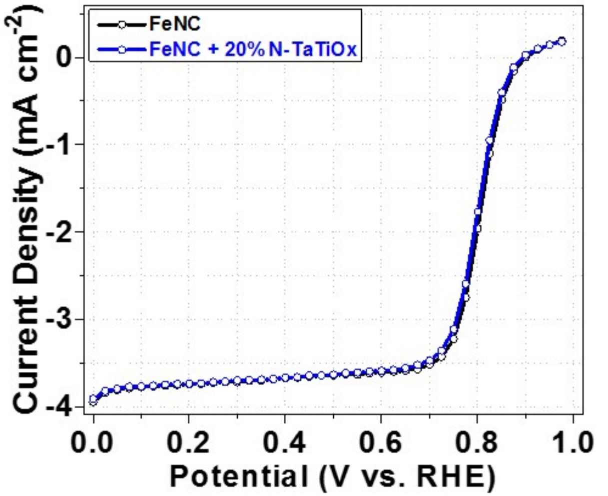
Accomplishments and Progress

Thermal shock synthesis of new radical scavenger NTaTiOx: Small and uniform particles, decreased H_2O_2 formation









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Accomplishments and Progress: Responses to Previous Year Reviewers' Comments

1. **Comments:** "…show a clear side-by-side comparison of MEA degradation …, vs. …catalyst without peroxide decomposer…" **Response:** MEA test results on durability w/wo H_2O_2 decomposers have been reported (FY19 AMR slides).
2. **Comments:** "… the team should … attain reasonable ORR activities…." **Response:** we have improved ORR activity to >30mA/cm^2@0.9V in H_2/O_2 (FY19 AMR slides).
3. **Comments:** "…not demonstrated that peroxide decomposition will protect the active sites, ionomer, and membrane sufficiently." **Response:** we have demonstrated decreased CO_2 (related to catalyst stability) and F release (related to ionomer and membrane stability) (FY18 and FY19 AMR slides).
4. **Comments: "**… the team's uncertainty in how to achieve molecular-level integration of the two types of active sites." **Response:** we have demonstrated direct loading of NCeOx onto PGM-free ORR catalyst which shows good activity/performance and improved stability (FY19 AMR slides).
5. **Comments:** "…it is likely that the proper removal of Zn, …is not possible with this (thermal shock) technique." **Response:** we did observe incomplete removal of Zn, and lower ORR activity for thermal shock samples; and thermal shock technique shows promising results in synthesizing uniform small metal oxide nanoparticles as H_2O_2 decomposer (radical scavenger) (FY19 AMR slides).

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

Collaboration & Coordination

Partner	Project roles
PNNL – Lead (Y. Shao, X. Xie, V. Prabhakaran, J. Liu)	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

- Maintain high activity of PGM-free catalysts while improving its stability through dual active sites.
- Improve synergy of dual active sites.
- Determine catalyst material systems that thermal shock activation synthesis works for improved catalyst performance.
- MEA engineering for performance improvement in both H_2/O_2 and H_2/Air at high current density.

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

Proposed Future Work

- Optimize dual active site catalysts by direct loading radical scavengers to PGM-free catalysts (better dispersion and more uniform small particles of radical scavenger, new radical scavengers like NTaTiOx).
- Optimize PGM-free catalysts including active site density, morphology (e.g., particle size), surface property (e.g., hydrophobicity) to improve MEA performance (in combination with MEA engineering).
- Optimize thermal shock synthesis: 1) determine if MOF catalysts can be improved through thermal shock, 2) improve new radical scavenger synthesis, e.g., NTaTiOx.
- MEA diagnostics to evaluate sources and distribution of polarization within the MEAs.

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

Summary Slide

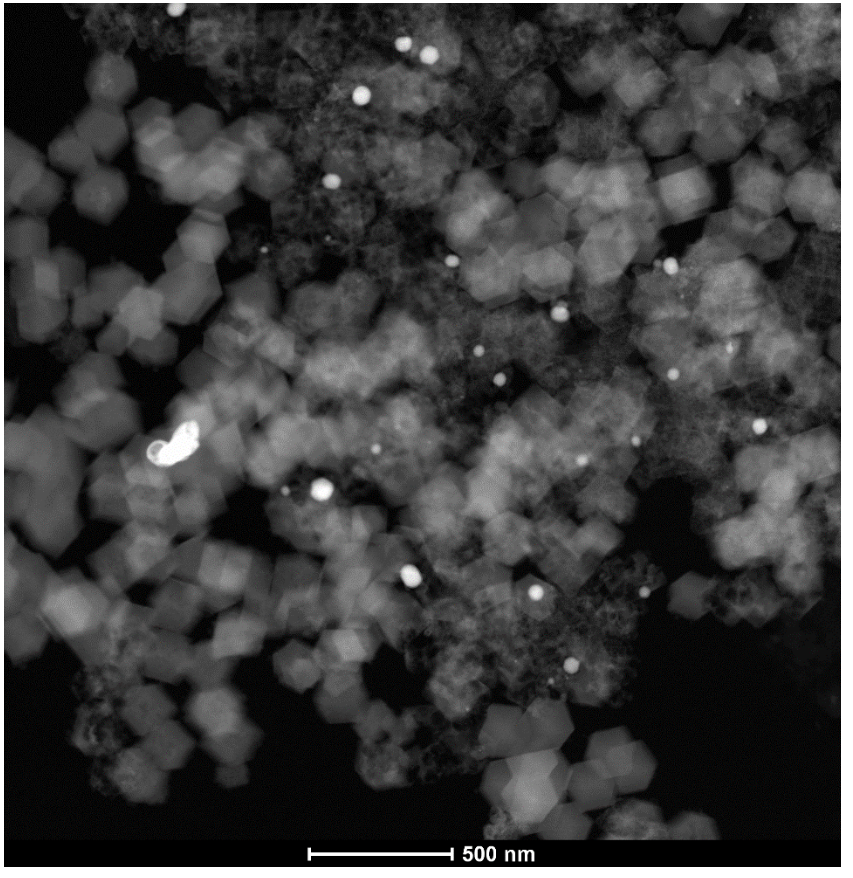
- Dual active site catalyst FeNC_NCeOx exceeds Year 2 activity milestones (30mA/cm^2, 0.9V in H_2/O_2) and Year 1 performance milestone (101.5mA/cm^2, 0.8V in H_2/Air).
- FeNC catalyst exceeds Year 3 activity milestone (35mA/cm^2, 0.9V in H_2/O_2) and Year 2 performance milestone (138mA/cm^2-2nd test, 0.8V in H_2/Air).
- Dual active site catalyst improves catalyst stability. Direct loading of radical scavenger functions better than physical mixing method.
- Collaboration with ElectroCat helped deep understand our catalysts (chemistry, active sites).
- Need improvement and understanding on thermal shock synthesis.

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

Technical Back-Up Slides

Accomplishments and Progress

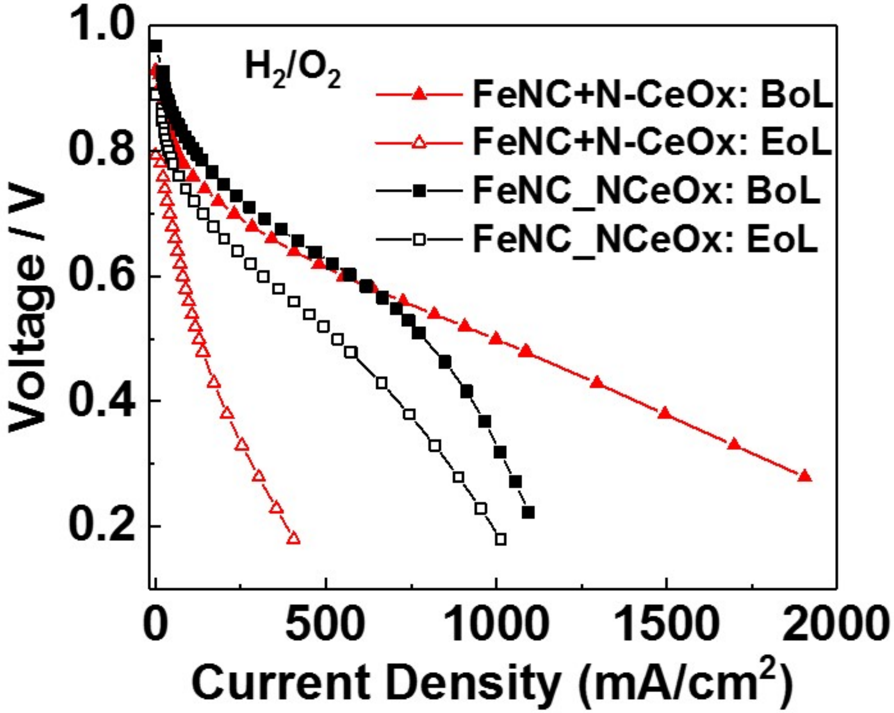
Dual active site catalyst: FeNC_NCeOx (direct loading)



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

Accomplishments and Progress

FeNC_NCeOx (direct loading) vs. FeNC+NCeOx (physical mixing)



Anode: 0.2mg/cm^2 $_{Pt}$ 30wt% Nafion ionomer; Cathode: 4.5mg/cm^2$_{PGM\text{-}free}$ (FeNC_5%NCeOx), 35wt% Nafion ionomer; Membrane: Gore (15µm); Active area: 5 cm^2; 80%% RH, 80°C, O_2+N_2=1 bar. Stability test (in H_2/O_2): constant cell voltage at 0.4V for 55min and then 0.85V for 5min (0.4V_55min/0.85V_5min), record current density at 0.85V, repeat.

FeNC_NCeOx show better activity and stability than FeNC+NCeOx, indicating NCeOx and its loading (dispersion) matters which points to potential room for improvement.