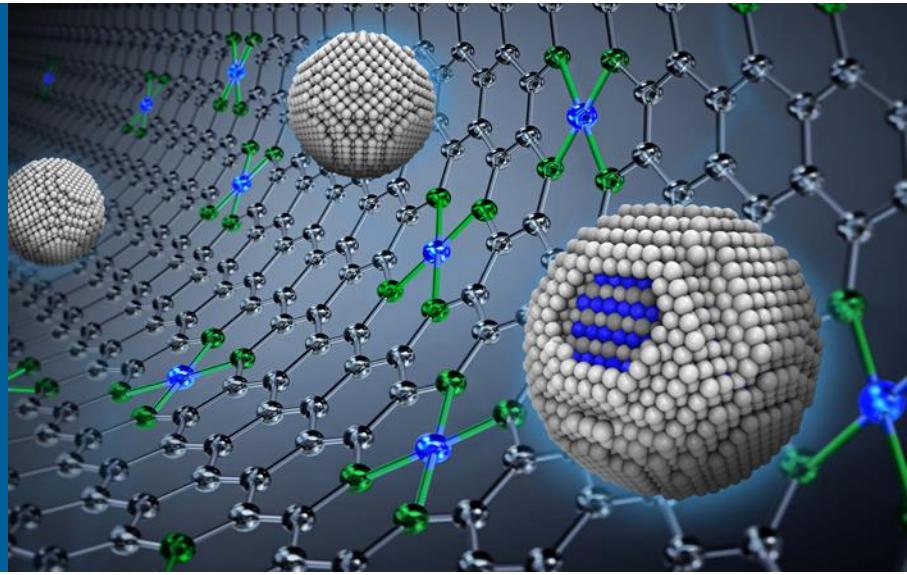
HIGHLY EFFICIENT AND DURABLE CATHODE CATALYST WITH ULTRALOW PT LOADING THROUGH SYNERGISTIC PT/PGM-FREE CATALYTIC INTERACTION



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2020 DOE Hydrogen and Fuel Cells Program Annual Merit Review and Peer Evaluation Meeting

FC174

Overview

Timeline

- Project Start: April 2017
- Project End: Under no-cost extension since December 31, 2019

Barriers

A. Insufficient fuel cell cathode catalyst durability
B. High cost due to high Pt loading in fuel cell cathode
C. Low performance at high fuel cell current density due to insufficient catalytic sites

Budget

- FY2017 DOE Funding: $ 480K
- DOE Fund Spent*: $ 480 K

* As of December 31, 2019

Collaborations

- Argonne National Lab (Lead)
- Purdue University
- Northern Illinois University
- Center for Nanomaterials, ANL

Objective - Relevance

Project Objective

To develop low-Pt@PGM-free (LP@PF) and low-Pt@PGM-free nanofiber (LP@PFNF) cathode catalysts that can meet or exceed DOE fuel cell catalyst and MEA performance metrics.

Relevance to Technology Barriers

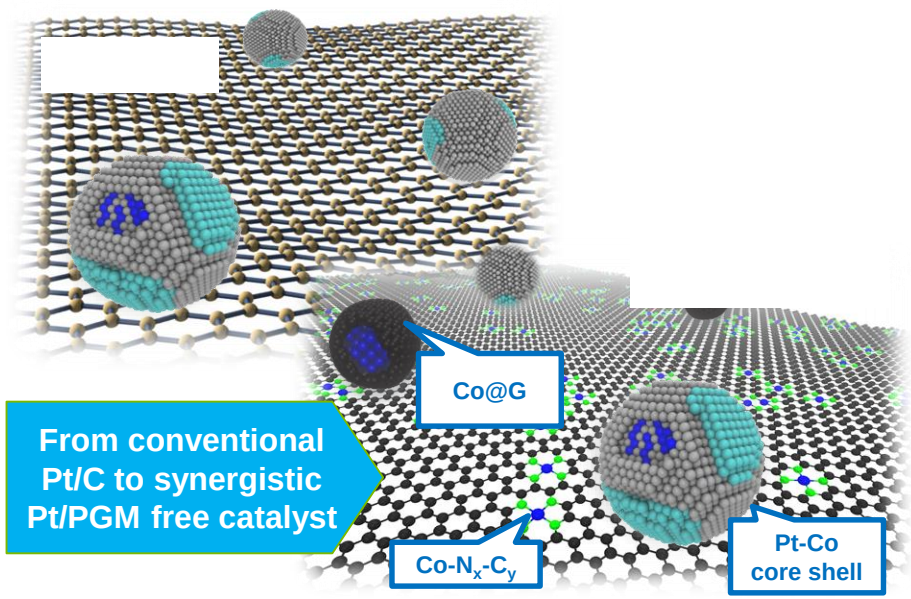
ANL LP@PF catalyst performance against DOE target

	Units	DOE 2025 Target	Current Status
Pt mass activity @ 900 $mV_{iR\ free}$	A/mg_{PGM}	0.44	1.1 - 1.9
PGM total loading	mg/cm^2	<0.125	<0.12
Loss in mass activity @ 900 $mV_{iR\ free}$	% loss	<40	7%
Loss in performance at 0.8 A/cm^2	mV	<30	30
Loss in performance at 1.5 A/cm^2	mV	<30	8

Approach – Platinum Usage Reduction Through Synergistic Interaction Between Ultralow Pt & PGM-free Sites

Activity Enhancement : Synergistic interaction between ultralow Pt over catalytically active PGM-free support

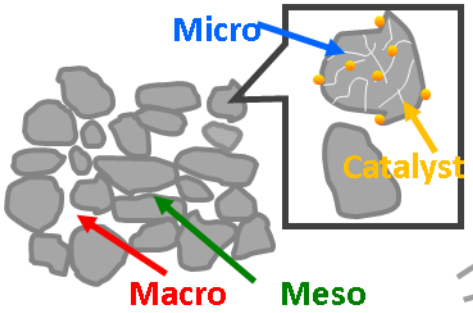
- Synergistic catalysis between ultralow Pt & PGM-free sites (LP@PF) can improve Pt utilization and overall activity/durability
- PGM-free catalyst derived from metal-organic-framework (MOF) with uniformly-distributed, high-density active sites can serve as catalytically active support for Pt



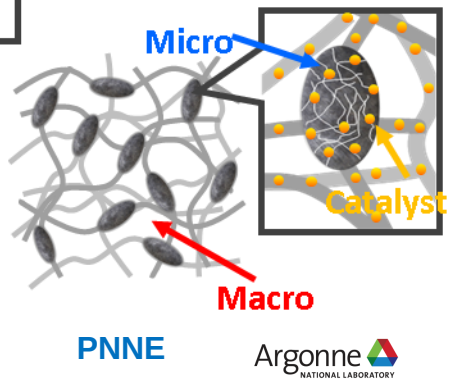
From conventional Pt/C to synergistic Pt/PGM free catalyst

Durability / Transport Improvements: Porous nano-network improves mass-charge transport against oxidative corrosion

- Conventional carbon supports are not optimized for efficient mass/charge transport and are vulnerable to oxidative corrosion
- ANL's LP@PFNF catalyst with porous nano-fibrous network (PNNE) offers combined high specific surface area (SSA), better connectivity to enhance mass/charge transfers and to increase stability through a hierarchical electrode architecture



From conventional carbon to porous network electrode



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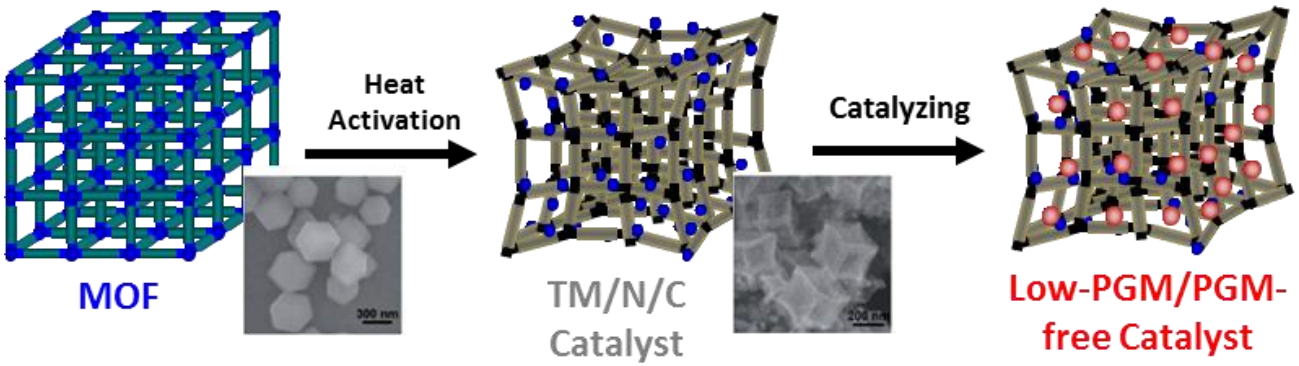
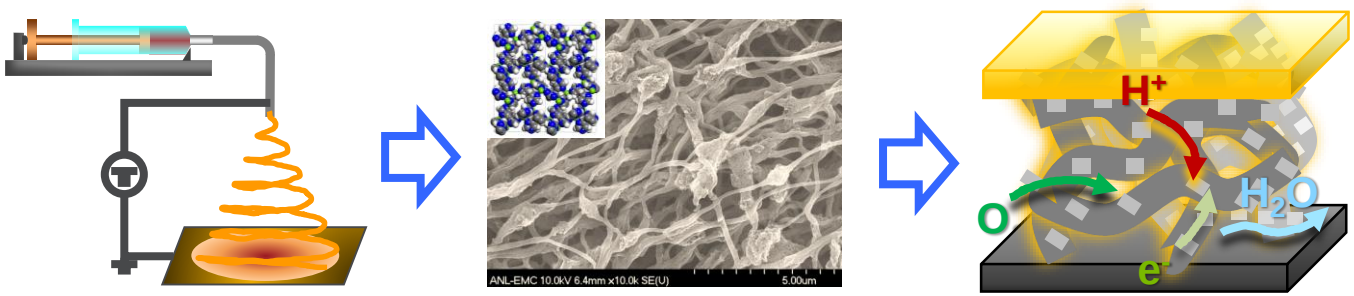
Approach - LP@PF & LP@PFNF Catalyst/MEA Design, Synthesis & Characterization

LP@PF & LP@PFNF Catalyst Syntheses → **Catalyst/MEA Testing & Optimization** → **Structural Studies & Computational Modeling**

LP@PF by MOF synthesis & in situ platinum reduction



LP@PFNF by electrospin, catalyzing & MEA fabrication

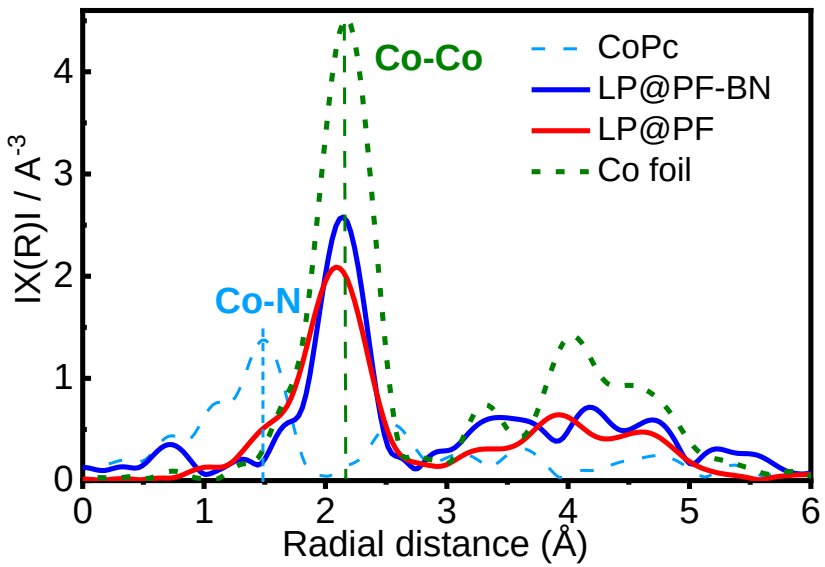


Electrospinning → Conversion to catalyst → MEA fabrication

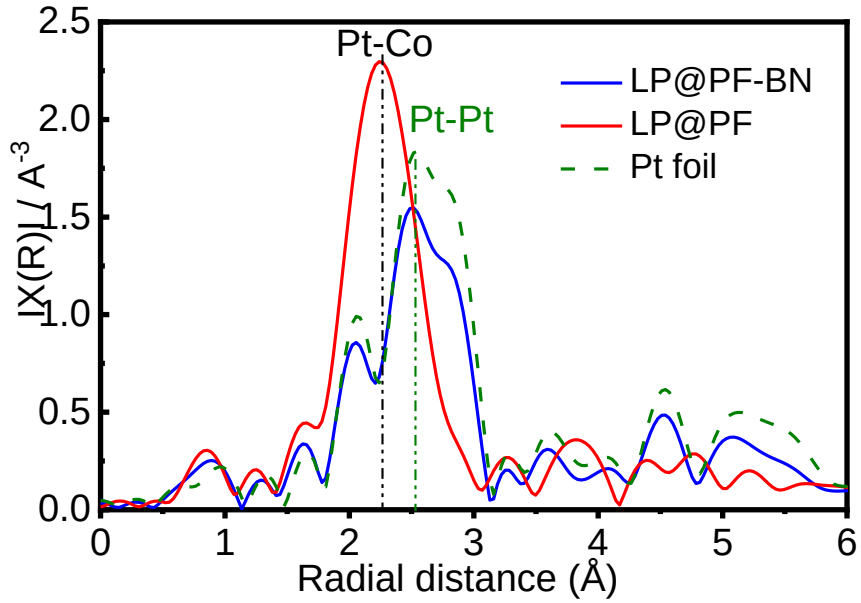
Two-step catalyst development with focus on MEA/fuel cell performance

Accomplishment – Identified Formation of PtCo Alloy & PGM-free Active Sites by X-ray Absorption Spectroscopy

EXAFS analysis shows a decrease of Co-Co peak and an increase of Co-N peak after NH_3 annealing indicating conversion of a fraction of metal Co to Co/N_4 sites



EXAFS at Pt K-edge shows decrease in the amount of Pt-Pt bonding and the formation of PtCo bonds after NH_3 annealing



XAS study identified formation of more PGM-free catalytic sites over the "support" and Pt-Co alloying during annealing, enhancing the synergistic catalysis

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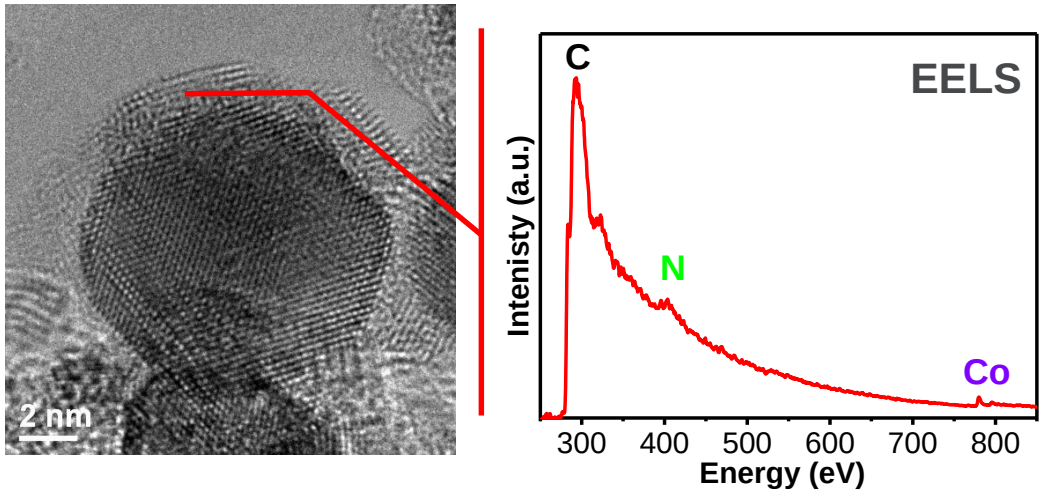
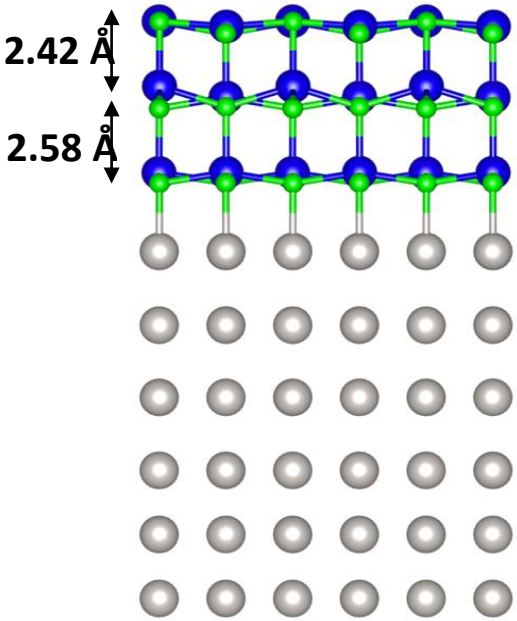
Accomplishment – Identified Cobalt Carbide/Nitride Lattice as Protective Layer for PtCo Core-shell Alloy

TEM/EELE study found CoC/CoN terraces partially cover PtCo Core-Shell crystallite



DFT calculation showed CoC/CoN preferentially grow over Pt (100)

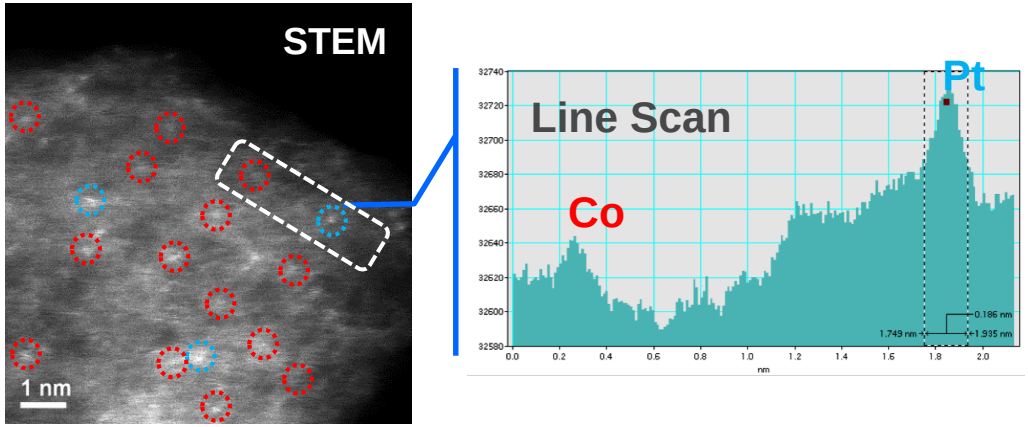


- **Well defined core-shell structure with super-lattice PtCo core and 2-3 layer Pt shell is observed**
- **Pt shell is partially protected by terraces of CoC/CoN layers, which serve as bridge for synergistic catalysis**
- **CoC/CoN terrace grow preferentially over unstable Pt (100) lattice instead of catalytically active Pt (111)**

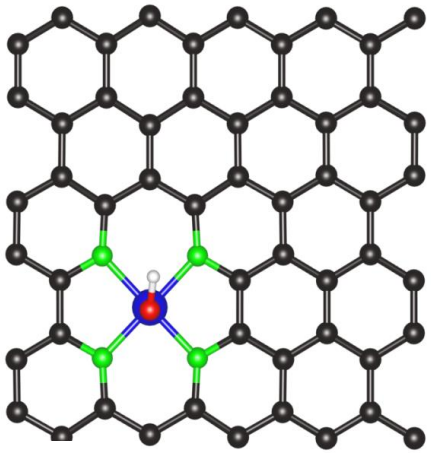
Computational modeling predicts the corrosion prone Pt lattice (100) being covered by CoC/CoN lattices consistent with experimental observation

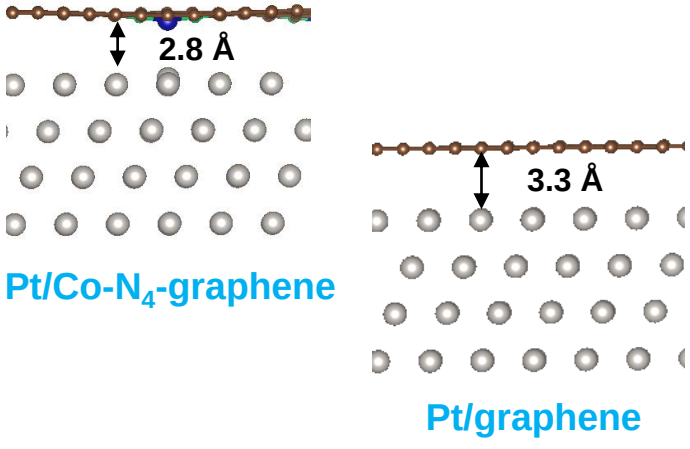
Accomplishment – Identified Structure & Interaction between PGM-free Support and Pt Alloy

PGM-free substrate consists of atomically dispersed Co and N embedded in C



DFT calculation shows that Co/N_4/C enhances the binding with Pt with shorten Pt-support distance and improves charge transfer





- Carbon surface is decorated by atomically dispersed Co and some single-atom Pt
- Atomic N is embedded in C matrix, similar to the PGM-free catalyst derived from Co-doped ZIF we previously published (Chong, *et. al. ChemElectroChem*, 2016)
- Co/N/C enhances binding and charge transfer between substrate and Pt

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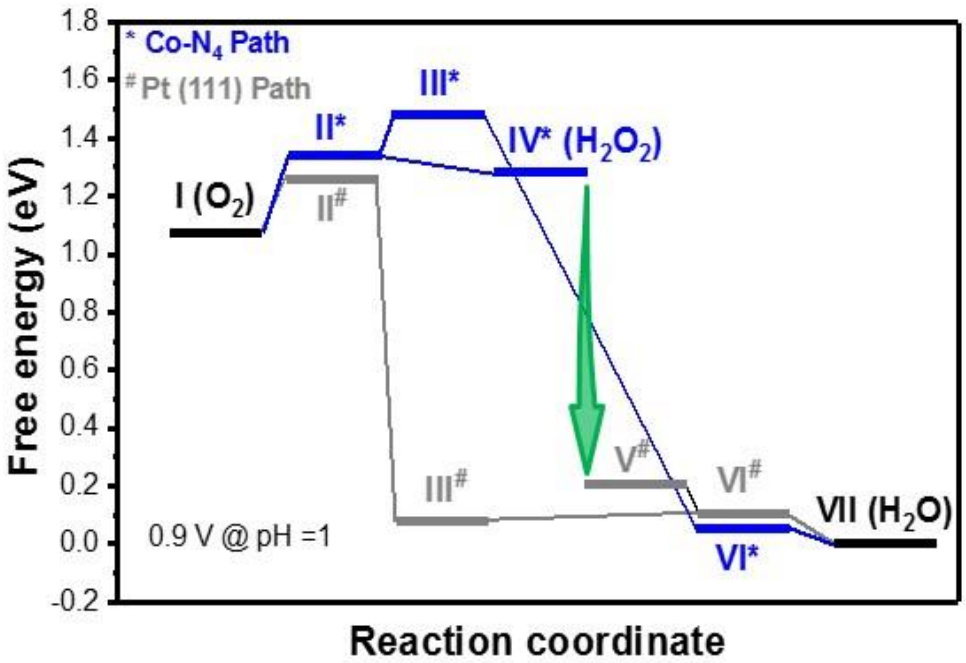
Accomplishment – Computational Modeling Identified Pt/PGM-free Interaction & Synergistic Catalysis Path

- Binding energy of ORR intermediate to active site can serve as the descriptor for predicting catalysis pathway
- DFT calculation showed two parallel paths over Pt and PGM-free sites



$4(H^+ + e^-) + * + O_2 \rightarrow 3(H^+ + e^-) + OOH^*$

$3(H^+ + e^-) + OOH^* \rightarrow 2(H^+ + e^-) + O^* + H_2O$

$2(H^+ + e^-) + O^* + H_2O \rightarrow (H^+ + e^-) + OH^* + H_2O$

$(H^+ + e^-) + OH^* + H_2O \rightarrow * + 2H_2O$

Same path for Pt site #

H_2O_2 transfer from Co-N_4 to Pt: a key step in synergistic catalysis

$H^+ + e^- + OOH^* \rightarrow * + H_2O_2$ (l) (II* → IV*)

$H_2O_2(l) + 2^\# \rightarrow 2OH^\#$ (IV* → V#)

$H^+ + e^- + 2OH^\# \rightarrow OH^\# + {}^\# + H_2O$ (V# → VI#)

$H^+ + e^- + OH^\# \rightarrow {}^\# + H_2O$ (VI# → VII)

- **Migration of unbounded H_2O_2 from Co-N_x-C_y site to nearby Pt NP represents a critical step in synergistic catalysis**
- **Fast H_2O_2 reduction over Pt improves platinum usage by reducing non-catalytic dwell time, facilitates overall catalytic efficiency**

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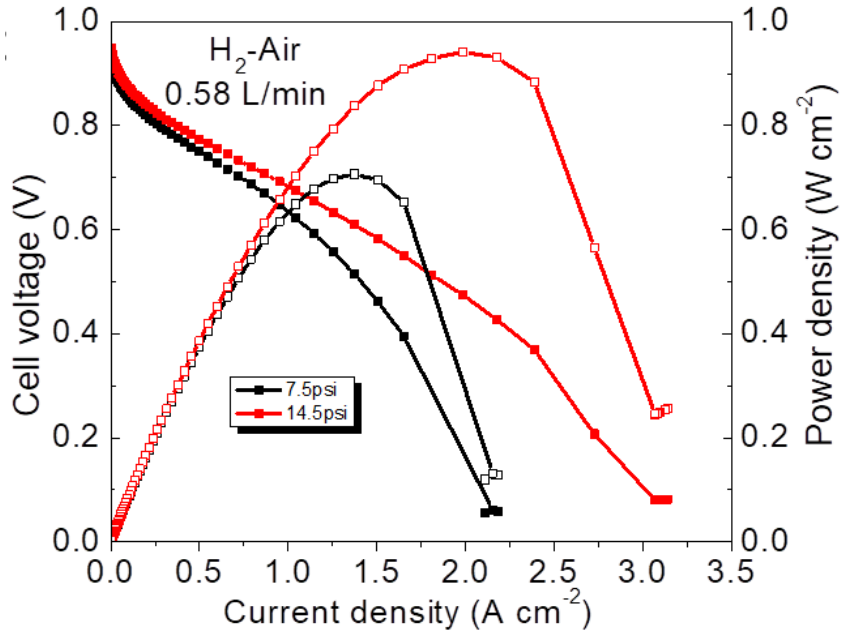
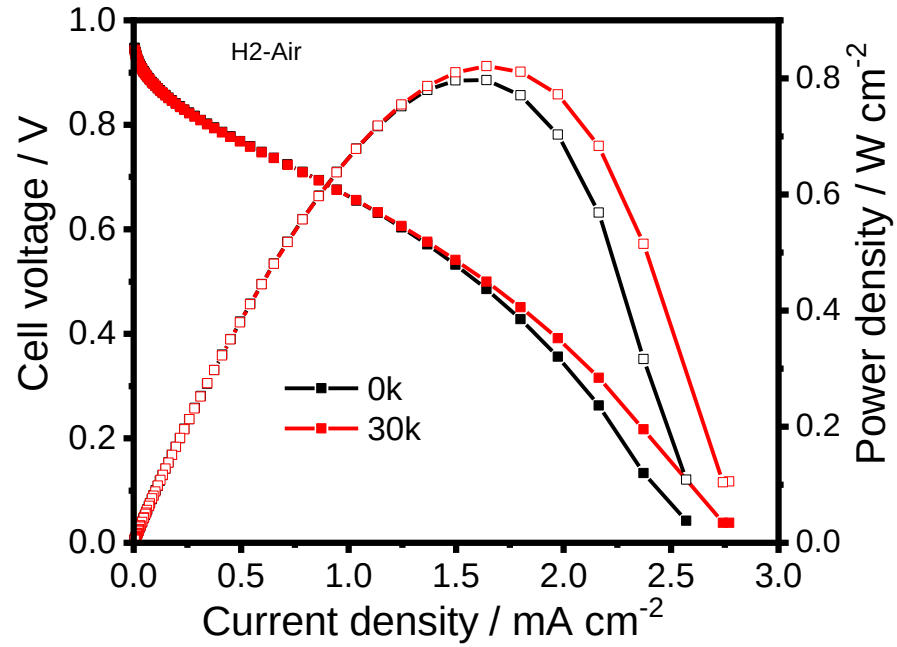
Accomplishment – LP@PFNF Offers Improved MEA/Fuel Cell Performance Compared to LP@PF

LP@PFNF shows high polarization current and power densities in fuel cell under different H_2-air pressures



LP@PFNF also demonstrates excellent fuel cell durability after 30k cycles in the accelerated stress test



Anode = H_2 @ 100% RH, 200 ml/min Cathode = air @ 100% RH, 580 ml/min, T = 80 °C, P = 100 to 150 kPa, Anode Pt/C = 0.3 mg_{Pt}/cm^2 , Cathode, LP@PF = 0.05 – 0.06 mg_{Pt}/cm^2

- LP@PFNF catalyst showed a better batch-to-batch consistency than LP@PF, presumably due to more effective Co core size control by nanofiber isolation and improved conductivity through the fiber's graphitic skin

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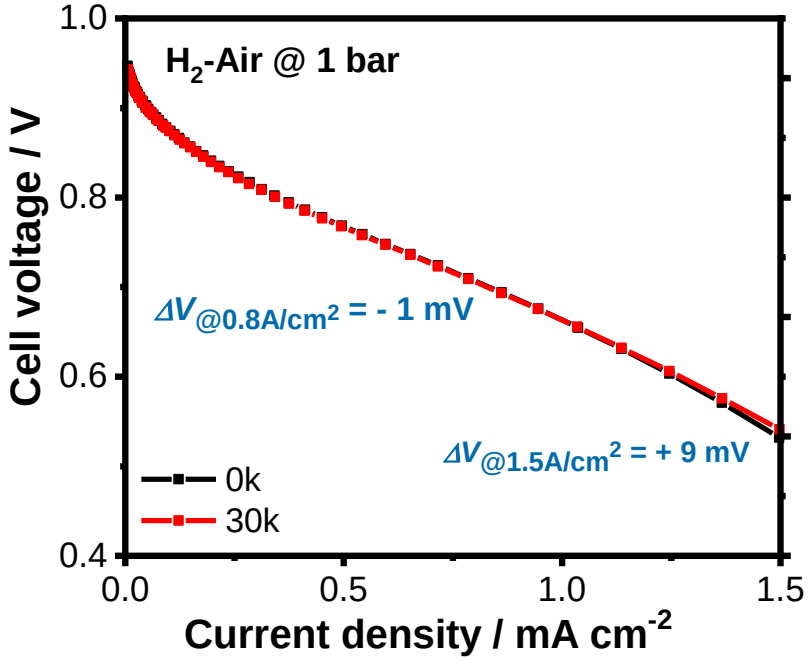
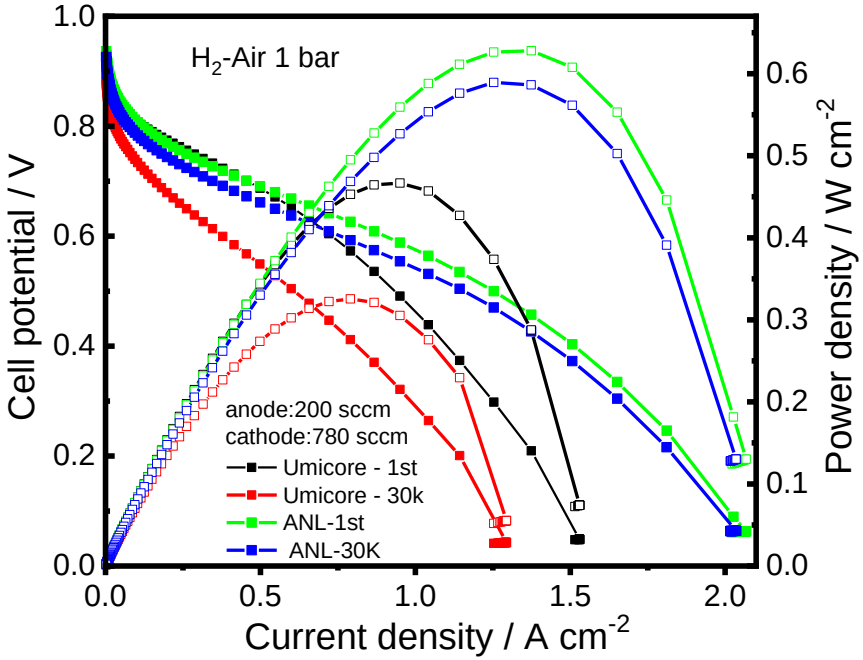
Accomplishment – LP@PF Catalysts Surpass Durability Target under Accelerated Stress Test (AST)

AST using original voltage cycling protocol (Saw-tooth, 0.6 V to 1.0 V)



AST using updated voltage cycling protocol (Square-wave, 0.6 V to 0.95 V)



AST : Anode = H_2 @ 100% RH, Cathode = air @ 100% RH, T = 80 °C, P = 100 kPa,, Anode Pt/C = 0.3 mg_{Pt}/cm^2 , Cathode, LP@PF = 0.06 mg_{Pt}/cm^2 (left); or Anode Pt/C = 0.035 mg_{Pt}/cm^2, Cathode, LP@PF or Umicore = 0.06 mg_{Pt}/cm^2 (right)

LP@PF catalysts showed excellent durability with less than 30 mV cell voltage drops at 0.8 A/cm² and 1.5 A/cm² after AST, meeting DOE durability targets and outperforming the a commercial benchmark catalyst

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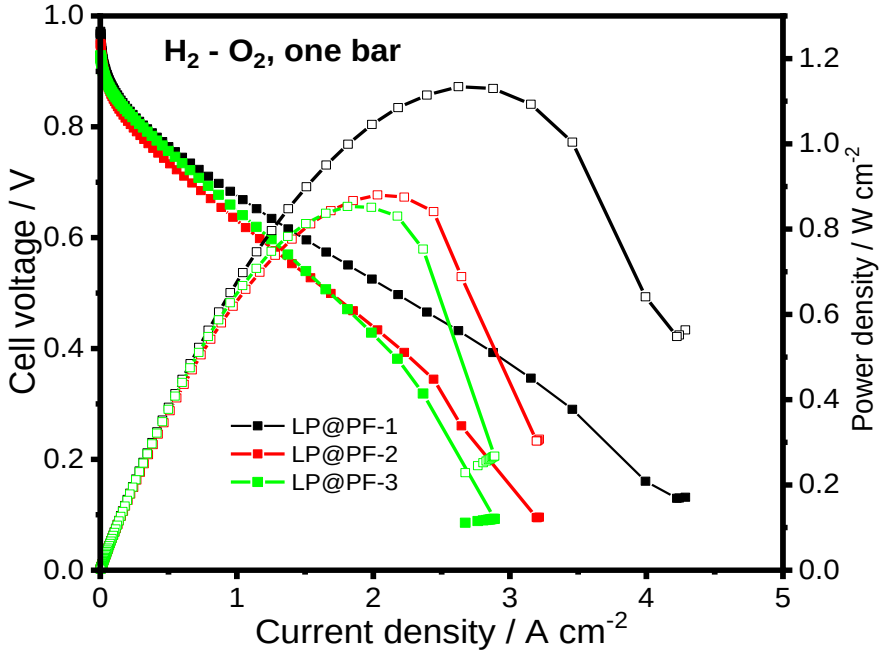
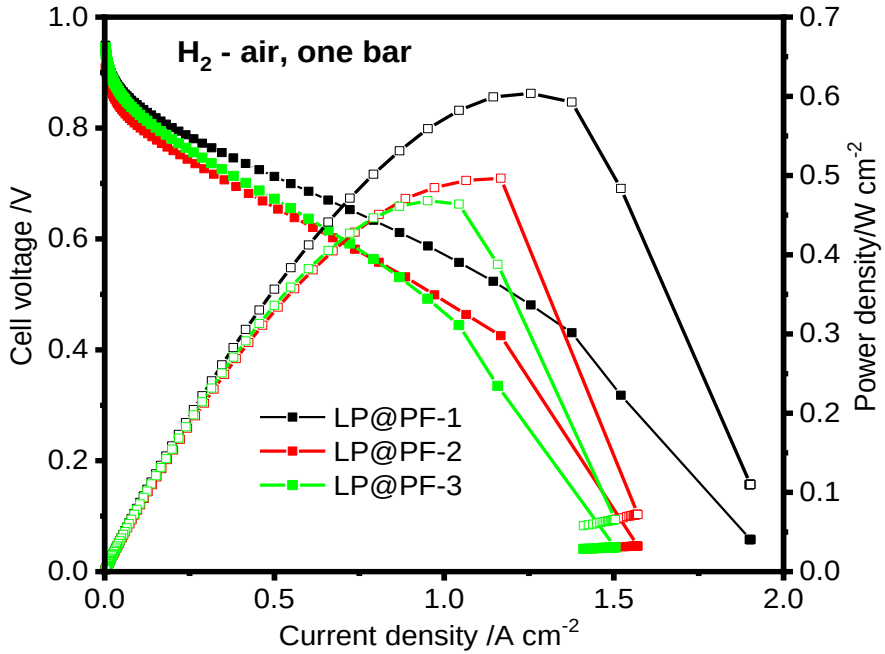
Accomplishment – Lessons Learned on LP@PF Synthesis

- LP@PF demonstrated better RDE/fuel cell performance using ZIF8@ZIF67 rather than ZIF67 as the MOF precursor, even though both precursors resulted in catalysts with similar surface area
- Best PGM-free catalyst for ORR is not necessarily the best support for the synergistic catalyst. The catalysts promoting intermediate (e. g. H_2O_2), such as high loading Co catalyst in this study and those reported by the others in recent publications, may serve as better PGM-free supports
- The performance of MEA containing LP@PF cathode showed a strong correlation to the length of “break-in” time, indicating the importance in establishing connection between Pt and PGM-free sites during conditioning
- Thermal activation parameters of MOF such as temperature, duration, etc., have profound effects in the catalyst conductivity and performance

Challenge & Barrier – Controlling Variability of Synthesizing LP@PF Catalyst Remains a Challenge

LP@PF synthesis exhibits high batch-to-batch variability, as shown by the differences in performance of three fuel cells containing the LP@PF catalysts prepared under "identical conditions"





Anode = H_2 @ 100% RH, 200 ml/min Cathode = O_2 or air @ 100% RH, 580 ml/min, T = 80 °C, P = 100 kPa, Anode Pt/C = 0.3 mg_{Pt}/cm^2 , Cathode, LP@PF = 0.05 – 0.06 mg_{Pt}/cm^2

- Current success rate for LP@PF synthesis is ~ 25%, a better process control on the variability is clearly needed
- Variability probably occurs during the conversion of the MOF to PF support during the high temperature heat treatment

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Responses To AMR Reviewers' Comments

- Industrial partnerships should be added to understand robustness needs under realistic mobile application operation.
  - Agreed. Our current effort focuses on catalyst development addressing Table 3.4.7 of MYRDD instead of MEA and its robustness is addressed. We are hoping to tackle robustness issues in future MEA focused study.
- Electrode stability by FC-PAD is needed to confirm the issues others reported with this approach.
  - Agreed. We have been discussing with FC-PAD/NREL on MEA fabrication and test protocol and are preparing samples to be tested at NREL.
- The proposed mechanism should involve generation of desorbed peroxide to be measured by RRDE.
  - Agreed. We have re-directed some effort to RRDE study with focus on wide voltage polarization. We are also developing a SPP agreement with an automotive OEM.
- The future work plan can be improved by focus on mechanistic understanding and reduced consideration of MEA issues. …Validating the low Pt loading and the high performance through collaboration with automotive OEMs
  - We are developing a Strategic Partnership Project (SPP) agreement with an automotive OEM with the focus on fundamental understanding of synergistic catalysis.

Collaborations

- **Purdue University**
  - **Computational modeling of synergistic catalysis mechanism**

- **Center for Nanoscale Materials, Argonne National Laboratory**
  - **DFT calculation on Pt/PGM-free site interaction**
  - **High resolution electron microscopic studies**

- **Northern Illinois University**
  - **Joint training of a guest graduate student providing the catalyst development and test support**

- **FC-PAD (ANL, NREL)**
  - **Consultation on catalyst/MEA testing and for providing a sample of the benchmark catalyst from Umicore**

Proposed Future Work

The project was concluded by Q2FY2020. The results of this study revealed some potential directions for further improving ORR activity through synergistic catalysis. Specifically, we identify the following opportunities:

- LP@PF catalyst can be further improved through multi-metallic (beyond just cobalt…) synthesis by taking advantage of MOF's porous structure and exchangeable framework
- The catalyst stability and mass transport robustness can be further enhanced through protective coating, higher graphitization level and nano-network architecture.
- Fundamental understanding on Pt and PGM-free site interaction is essential to producing highly effective catalyst beyond the limit of "scaling relationship" over single site catalyst

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

SUMMARY

- High resolution imaging and X-ray absorption spectroscopy revealed formation of the synergistic catalyst at different steps of synthesis
- Computational modeling identified importance of cobalt carbide and nitride in preserving PtCo core-shell alloy particle stability during ORR catalysis
- LP@PF and LP@PFNF catalysts demonstrated high Pt mass activities in MEA/fuel cell tests
- LP@PF & LP@PFNF catalysts also demonstrated excellent stabilities during the accelerated stress test, meeting DOE's targets of less than 30 mV voltage drops measured at 0.8 A/cm^2 and 1.5 A/cm^2 in H_2-air fuel cells
- High batch-to-batch variability during LP@PF catalyst synthesis was observed. The cause and control strategy are yet to be fully understood and developed at present

ACKNOWLEDGEMENT

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  - Dimitrios Papageorgopoulos (Program Manager, Fuel Cells)
  - Simon Thompson (ORISE Fellow)