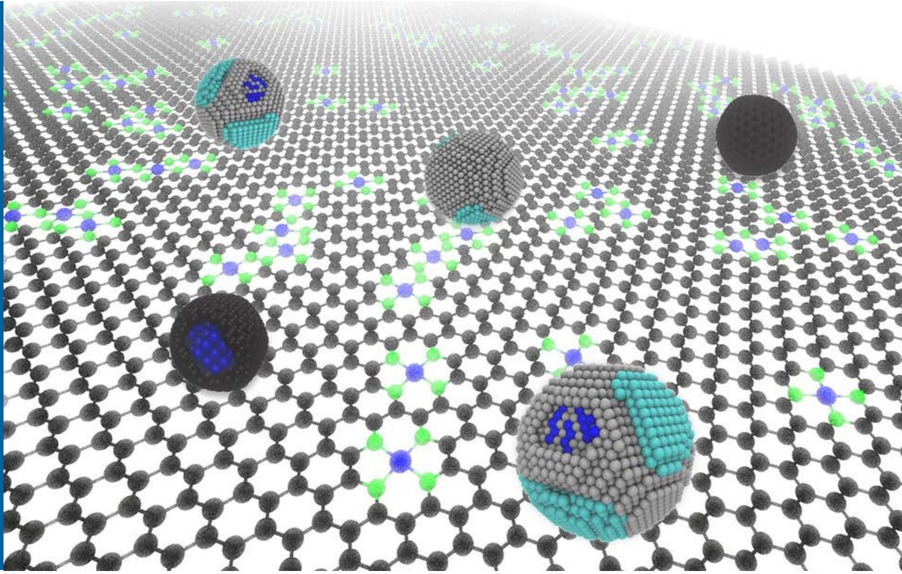
HIGHLY EFFICIENT AND DURABLE CATHODE CATALYST WITH ULTRALOW PT LOADING THROUGH SYNERGETIC PT/PGM-FREE CATALYTIC INTERACTION



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Project ID: fc174

2018 DOE Hydrogen and Fuel Cells Program Annual Merit Review and Peer Evaluation Meeting
June 13-15, 2018, Washington, D.C.

OVERVIEW

Timeline

- Project Start: April 2017
- Project End: September 2018

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: $ 300K
- DOE Fund Spent*: $ 195 K

  * As of 3/31/2018

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 achieve all DOE fuel cell catalyst / MEA performance metrics, particularly at high current/power density region.

Relevance to Technology Barriers

ANL LP@PF catalyst performance against DOE target

	Units	DOE 2025 Target	ANL LP@PF-1	ANL LP@PF-2
Pt mass activity @ 900 $mV_{iR\text{-}free}$	A/mg_{PGM}	0.44	1.08	1.77
PGM total loading (both electrodes)	mg/cm^2	<0.125	0.033 (Cathode)	0.035 (Cathode)
MEA performance @ 800 mV (air)	mA/cm^2	≥300	270	273
MEA performance @ 675 mV (air)	mA/cm^2	≥1000	717	754
Loss in catalytic (mass) activity	% loss	<40	38	85
Loss in performance at 0.8 A/cm^2	mV	<30	8	50
Loss in performance at 1.5 A/cm^2	mV	<30	3	62

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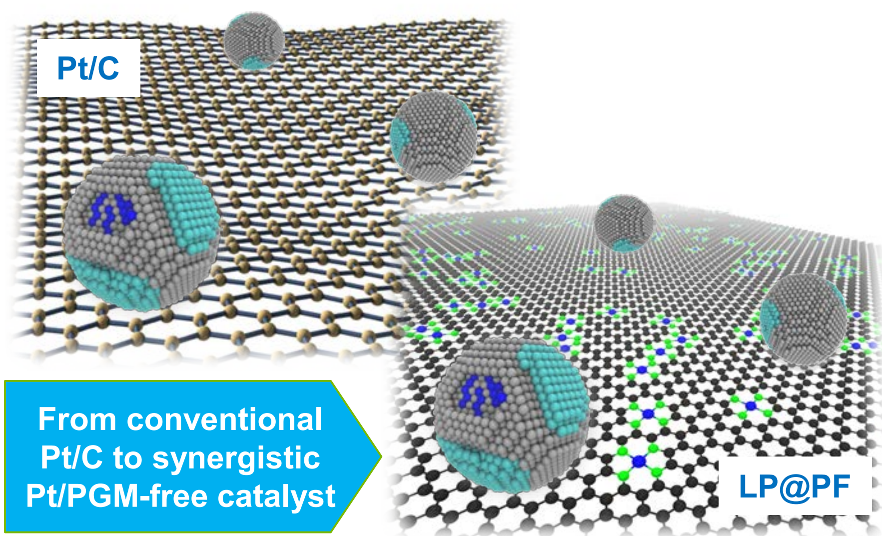
APPROACH – PLATINUM USAGE REDUCTION THROUGH SYNERGISTIC INTERACTION BETWEEN ULTRALOW PT & PGM-FREE SITES

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

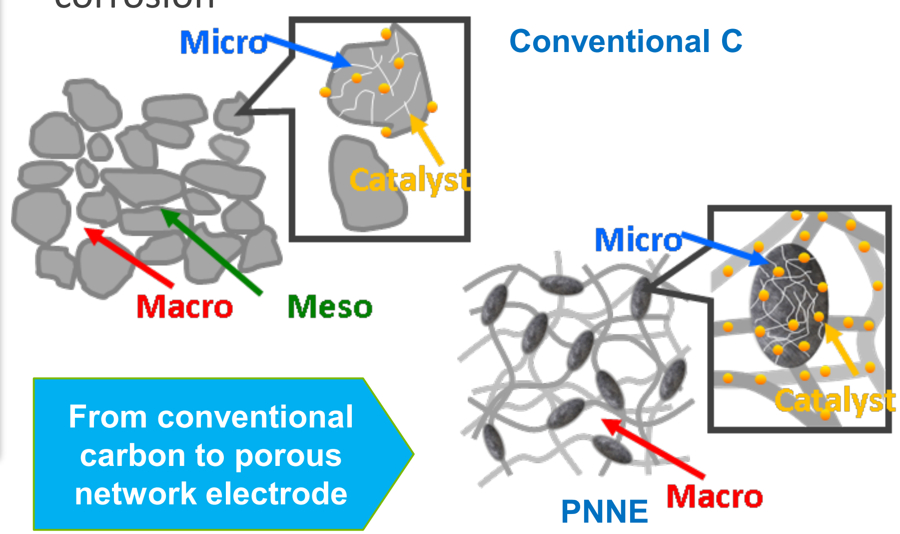
- Demands of both *activity* and *accessibility* of Pt sites limit the potential for Pt loading reduction
- Synergistic catalysis between ultralow Pt & PGM-free sites (LP@PF) can improve Pt utilization and overall activity/durability
- PGM-free catalyst derived from metal-organic-framework (MOF) with 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 C-supports are not designed for ideal mass/charge transport and are venerable to oxidative corrosion
- ANL's LP@PFNF catalyst with porous nano-fibrous network (PNNE) offers combined high specific surface area (SSA) and connectivity for better mass/charge transfers through hierarchical electrode architecture
- It also improves catalyst stability against corrosion

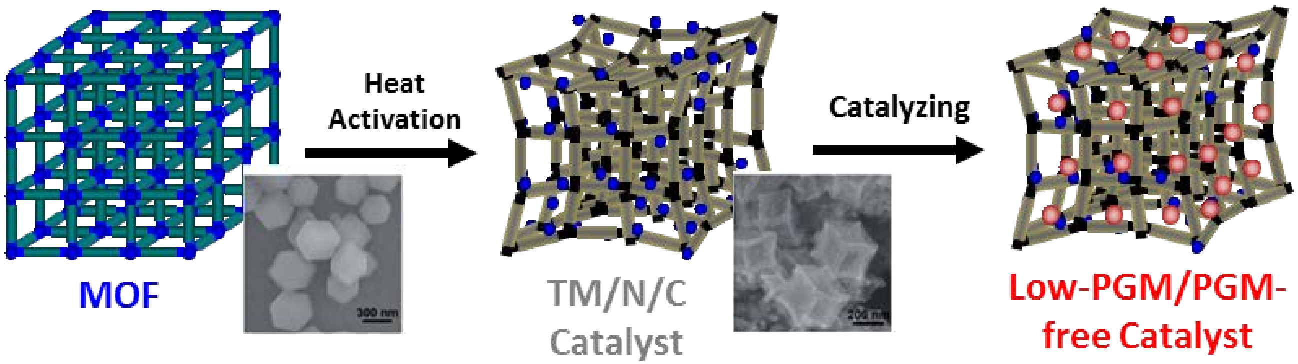


From conventional carbon to porous network electrode

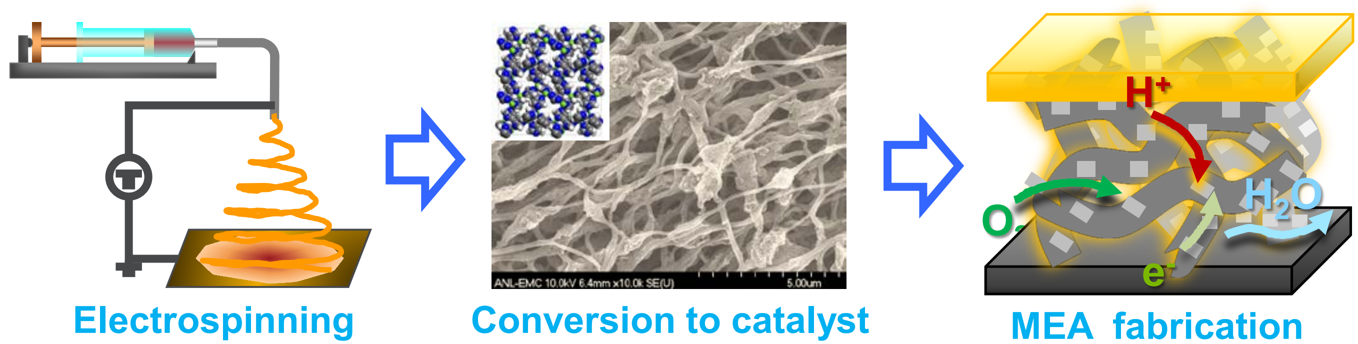
APPROACH – LP@PF & LP@PFNF CATALYST/MEA DESIGN, SYNTHESIS & CHARACTERIZATION

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



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

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APPROACH – MILESTONES

Milestones	Month/ Year	Status Update
Complete ZIF synthesis, post-treatment and catalyzing at least four active LP@PF catalysts with demonstrated E½ ≥ 0.96 V	(10/31/17)	**100% completed**. Six different LP@PF catalyst s were designed and prepared. Two of them achieved E½ = 0.96 V measured by RDE in O_2 saturated $HClO_4$ solution (0.1M).
To complete preparation and testing of at least four MEAs containing LP@PF cathode catalysts.	(4/30/18)	**60% complete.** MEAs preparation is completed. The testing is delayed due to restoration of test stand
G/NG Point: Demonstrate a MEA at single cell with current density > 300 mA/cm^2 @ 0.8 V and < 40% loss of mass activity	(4/30/18)	**In process.**
Complete LP@PF catalyst structural characterization with XRD, BET, SEM, TEM, etc.	(7/31/18)	**100% completed.** Extensive studies using XRD, BET, SEM, TEM have been carried out and wealth of structural information obtained.
Complete LP@PF catalyst structural study using synchrotron XAS techniques.	(7/31/18)	**70% completed**. Initial EXAFS and XANES completed. Conversion from Pt to Pt alloy observed
Complete synthesis of nanofibrous LP@PF catalyst and MEA/fuel cell performance evaluation.	(10/31/18)	**50% completed.** Optimization of MOF-embedded LP@PFNF catalyst is nearly completed
Final demonstration: a MEA/fuel cell with cathode loading < 0.05 mg-Pt/cm^2, mass activity >0.44 A/mg-Pt, performance at rated power >1 W/cm^2 in activity; and <40% loss of mass activity, <30 mV loss at 1.5 A/cm^2 in durability, following the accelerated test protocol by DOE	(10/31/18)	**In process**

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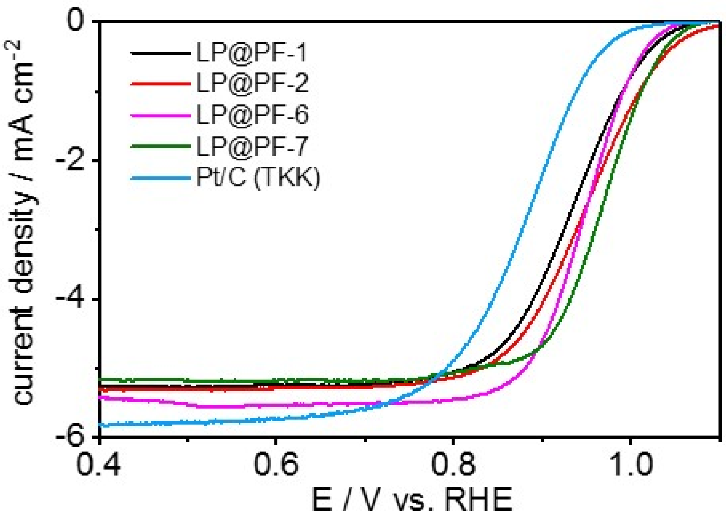
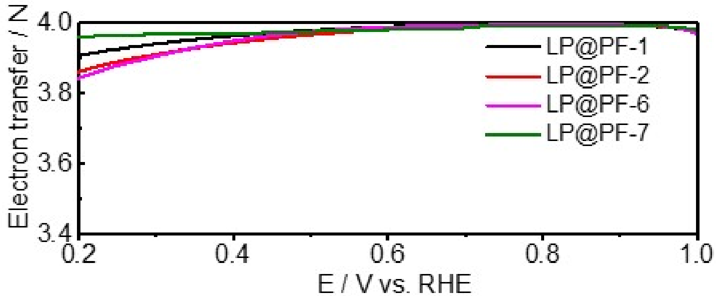
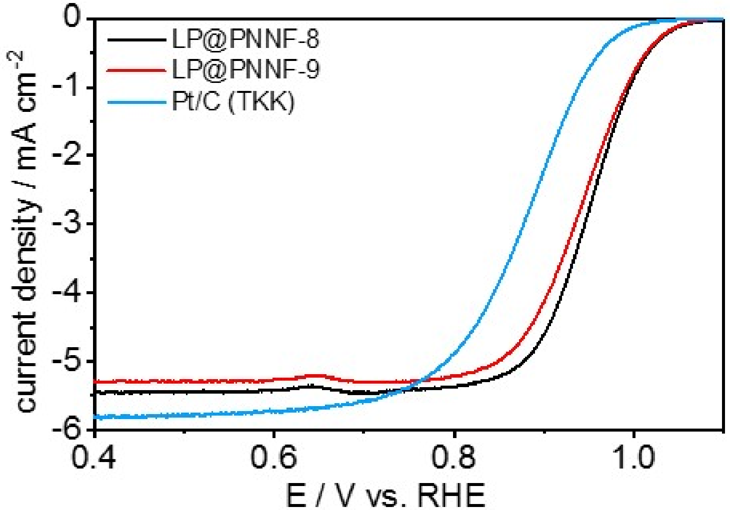
ACCOMPLISHMENTS – SYNTHESES & ACTIVITY STUDY OF NEW LP@PF & LP@PFNF CATALYSTS

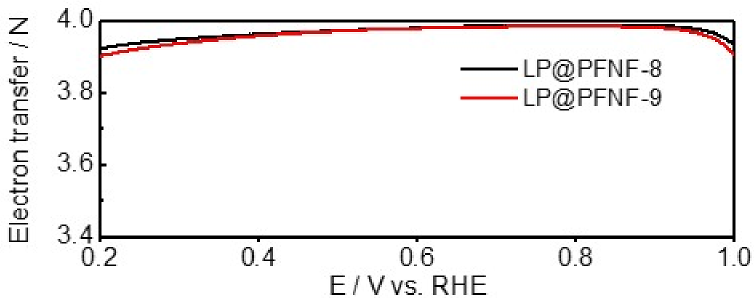
RRDE results of selected MOF-based LP@PFs





RRDE results of selected nanofiber LP@PFNFs



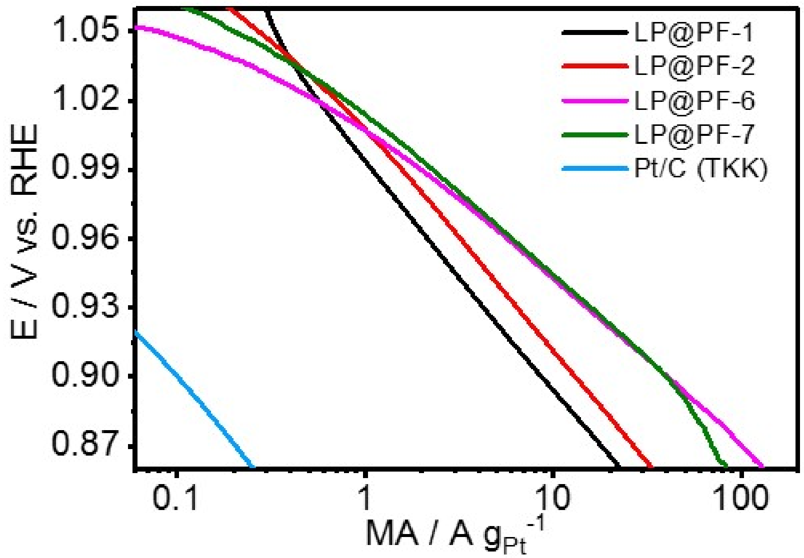


ORR catalytic activities were measured by RRDE method in O_2 saturated $HClO_4$ (0.1M) at RT;
Pt loading for LP@PF/LP@PFNF 3~4 μg/cm^2; Pt loading for Pt/C (TKK) = 17 μg/cm^2

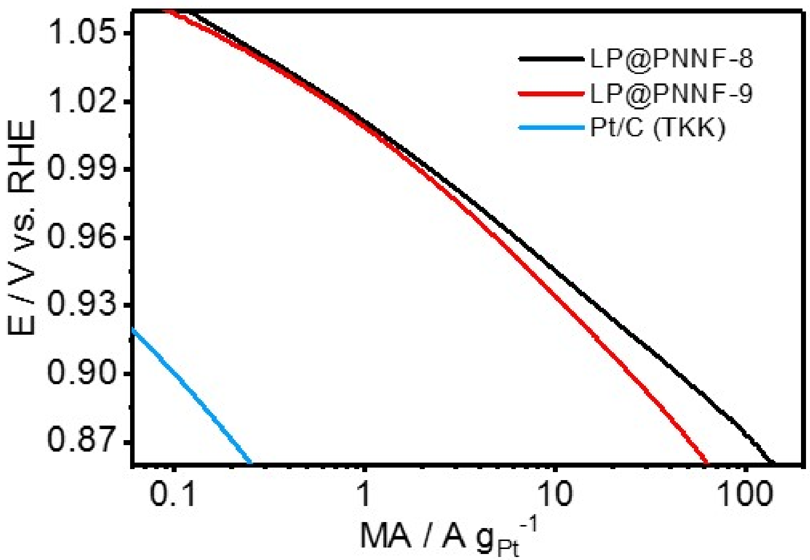
Over 30 LP@PFs/LP@PFNFs were synthesized and tested, several showed significantly better ORR activities than commercial Pt/C catalyst even at much lower Pt loading

ACCOMPLISHMENTS – THE STATE-OF-THE ART ORR ACTIVITIES BY SELECTED LP@PFs & LP@PFNFs

Mass activities (MA) of MOF-based LP@PFs



Mass activities (MA) of nanofiber LP@PFNFs

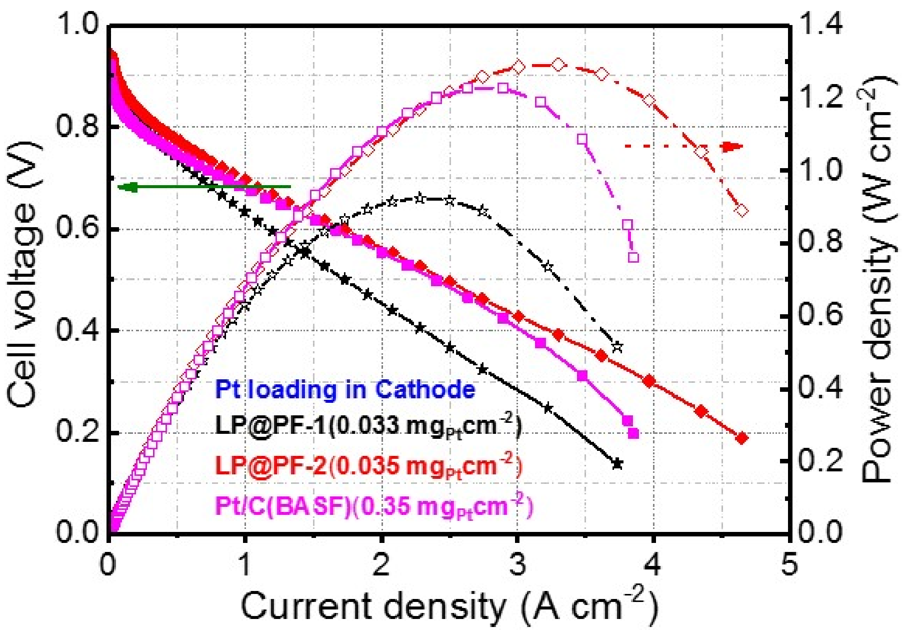


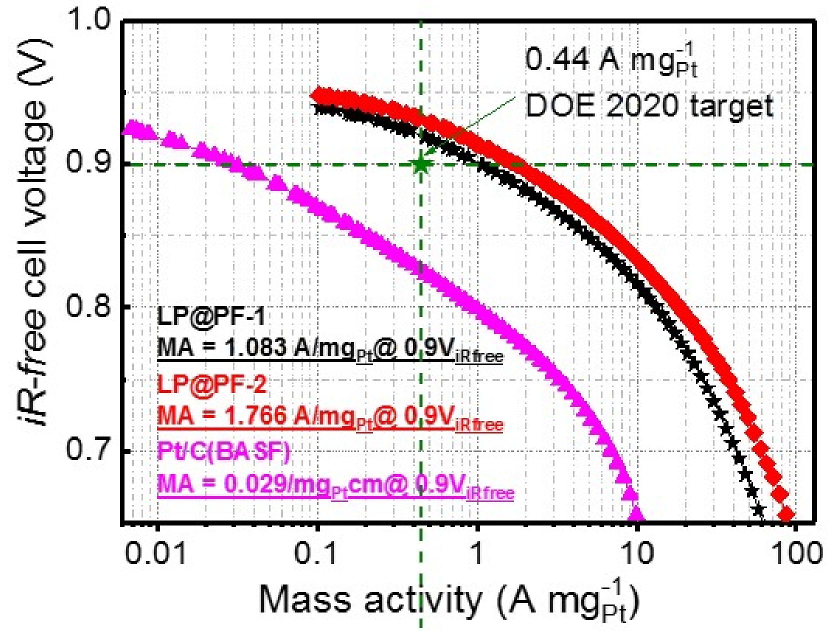
Catalyst	E_0 (V)*	$E_{1/2}$ (V)	# of electron transfer	Mass Activity @0.95 V ($A \cdot mg_{Pt}^{-1}$)	Mass Activity @0.9 V ($A \cdot mg_{Pt}^{-1}$)
LP@PF-1	1.06	0.94	3.91~3.99	2.68	8.64
LP@PF-2	1.09	0.96	3.90~3.99	3.95	12.4
LP@PF-6	1.05	0.95	3.85~3.99	7.85	40.5
LP@PF-7	1.07	0.97	3.96~3.99	8.28	40.0
LP@PFNF-8	1.07	0.95	3.92~3.99	8.63	44.0
LP@PFNF-9	1.06	0.94	3.90~3.99	6.46	24.7
47%Pt/C	1.00	0.88	3.90-3.97	0.023	0.100

* Potential measured at current density of 0.05 mA/cm^2

ACCOMPLISHMENTS – INVESTIGATION OF LP@PF CATHODIC ACTIVITY IN H_2-O_2 FUEL CELL

Performances of MEA/fuel cell with ANL's LP@PF cathodic catalysts vs. commercial Pt/C in H_2/O_2



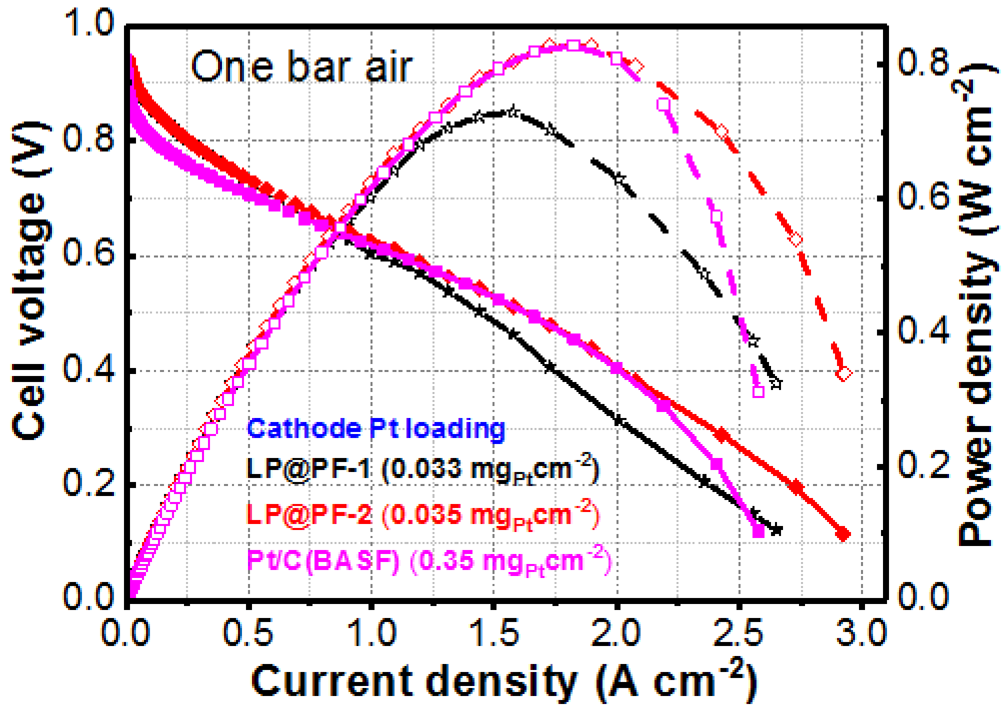


Test condition: membrane = Nafion 211, Temperature = 80 °C, $P_{H2} = P_{O2}$ = 100 kPa @ 100% relative humidity (RH) (back pressure = 50 kPa), flow rate = 200 mL min^{-1}

- **At high voltage domain, LP@PF catalysts demonstrate higher OCVs and current densities than commercial MEA, suggesting a synergistic catalysis**
- **At high current domain, LP@PF-2 outperforms commercial MEA without "mass transport limit" tail, indicating continuous conversion of O_2 by PGM-free site**

ACCOMPLISHMENTS – INVESTIGATION OF LP@PF CATHODIC ACTIVITY IN H_2-AIR FUEL CELL

Performances of MEA/fuel cell with ANL's LP@PF cathodic catalysts vs. commercial Pt/C in H_2/Air



Test condition: membrane = Nafion 211, Temperature = 80 °C, P_{H2} = P_{AIR} = 100 kPa @ 100% relative humidity (RH) (back pressure = 50 kPa), flow rate = 1000 mL min^{-1}.

LP@PF catalyst outperformed commercial MEA in the entire fuel cell polarization span with only 1/10 of Pt loading at cathode

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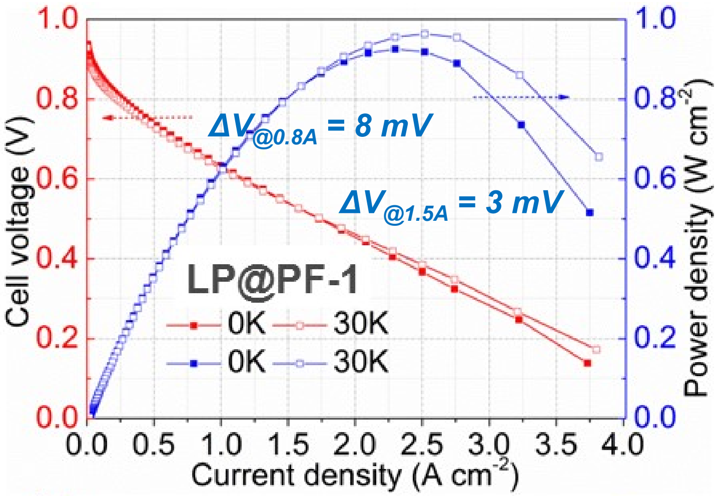
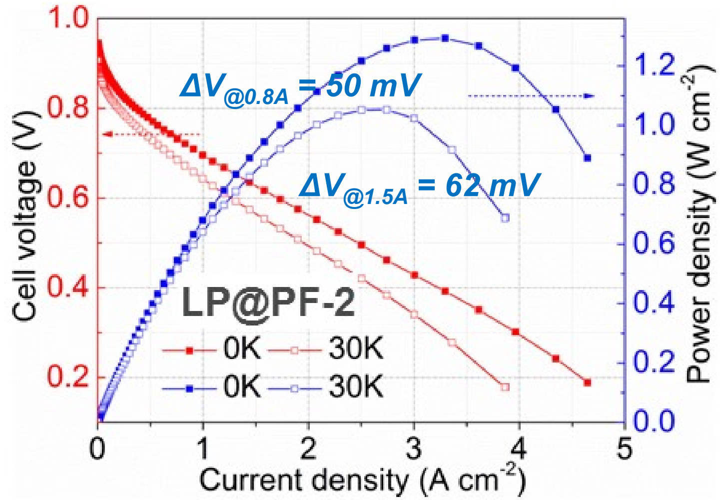
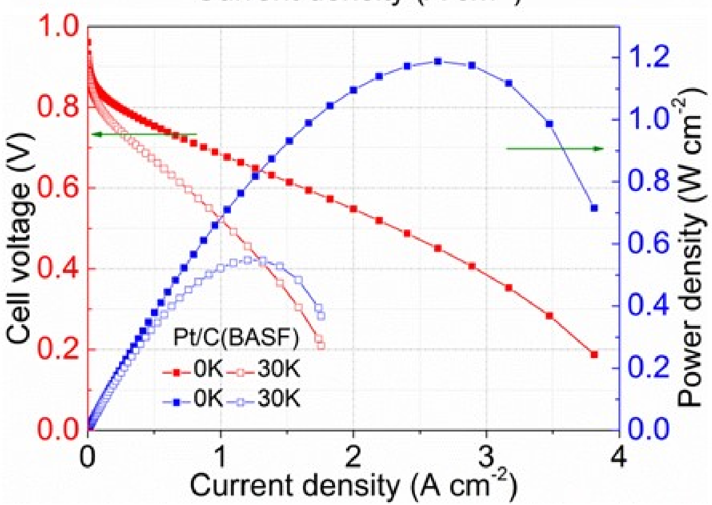
ACCOMPLISHMENTS – INVESTIGATION OF LP@PF CATALYST DURABILITY IN FUEL CELL

Performances of MEAs/fuel cells with LP@PF cathodic catalysts vs. commercial Pt/C before & after 30,000 voltage cycles in the accelereated stress tests (AST)





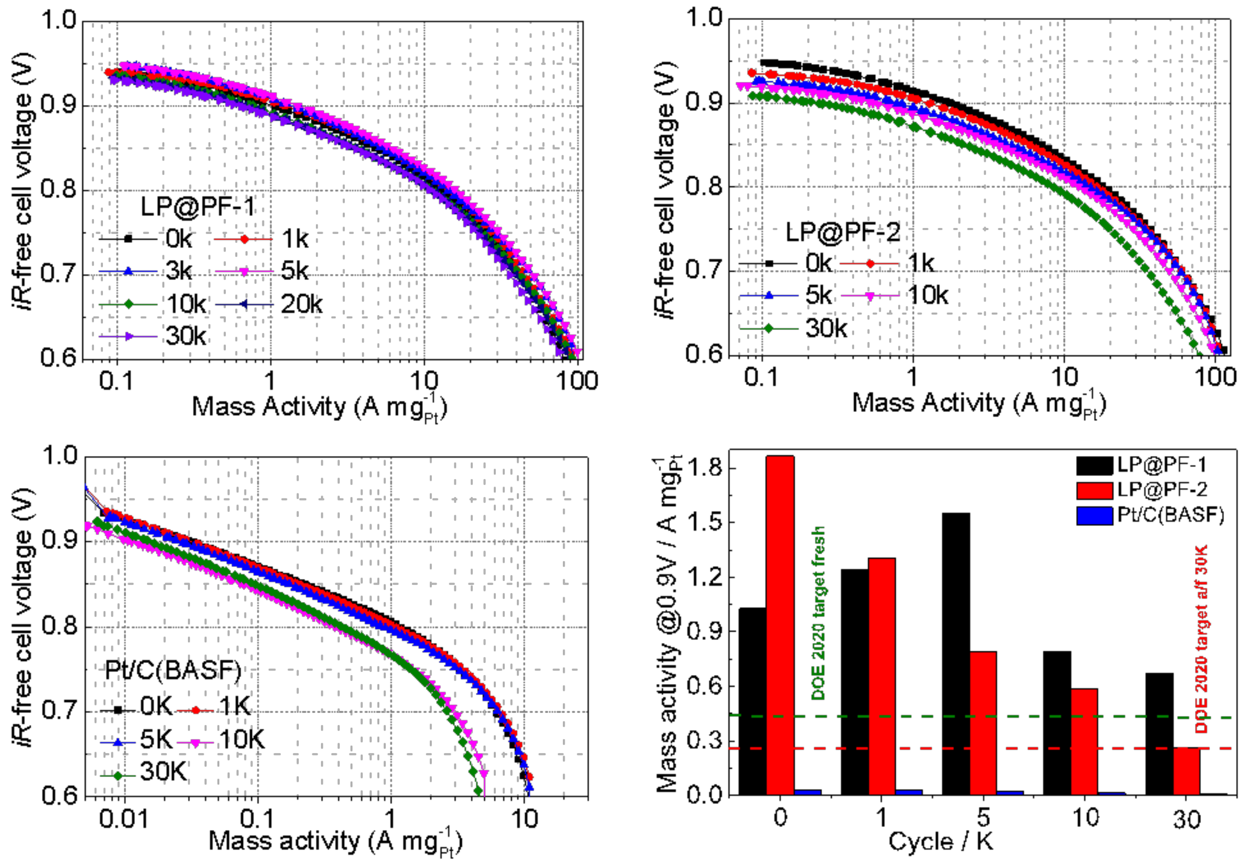


AST condition: Voltage cycling from 0.6 V to 1.0 V @ 50 mV/sec, Anode = H_2 @ 100% RH, Cathode = N_2 @ 100% RH, Temperature = 80 °C, P = 100 kPa

LP@PF catalyst/MEA showed considerably higher stability than commercial MEA over 30K voltage cycles during AST

ACCOMPLISHMENTS – MASS ACTIVITY VARIATION OF LP@PF CATALYST DURING FUEL CELL AST

Change of MEA/fuel cell cathodic mass activity during 30 K voltage cycles



0.44 A/mg$_{Pt}$

0.264 A/mg$_{Pt}$

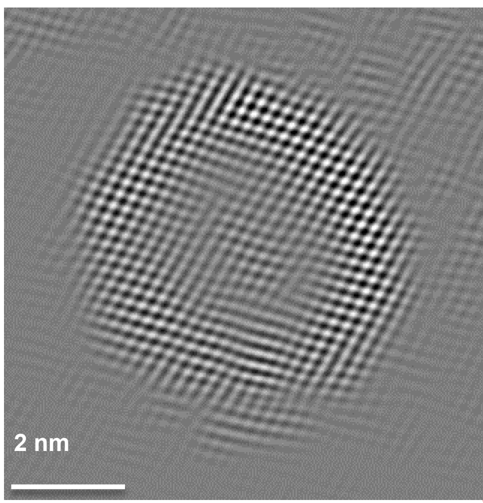
Although performance loss was observed during AST, the mass activities of both LP@PF catalysts still met or exceeded 0.264 A/mg$_{Pt}$, or 60% of initial 0.44 A/mg$_{Pt}$ of DOE 2020 target at the end of 30 K cycles

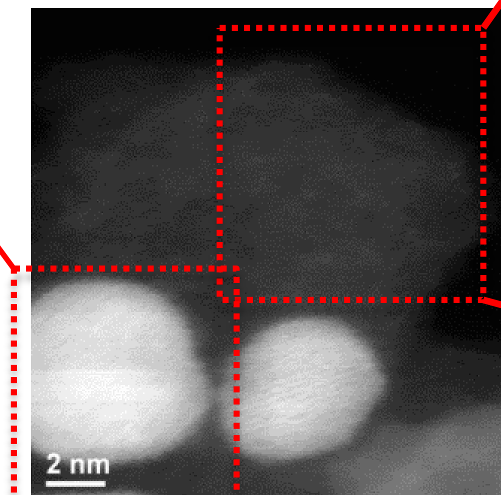
ACCOMPLISHMENTS – INVESTIGATION OF LP@PF CATALYST STRUCTURE & MORPHOLOGY

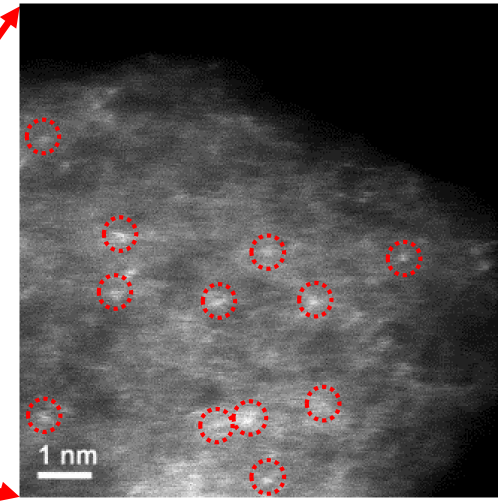
Electron microscopic study of a representative LP@PF catalyst

Pt-Co alloy NPs are situated over $Co/N_x/C_y$ catalytic support

Pt-Co NP has core-shell structure with average diameter of 5~6 nm and super-lattice inside







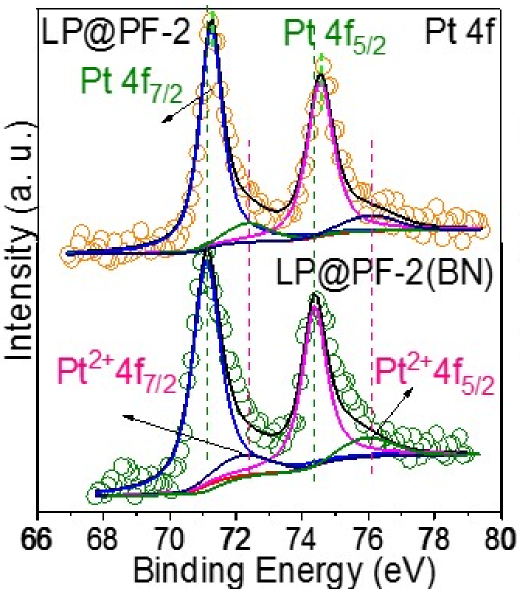
Atomic Co is embedded in N/C composite in PGM-free substrate

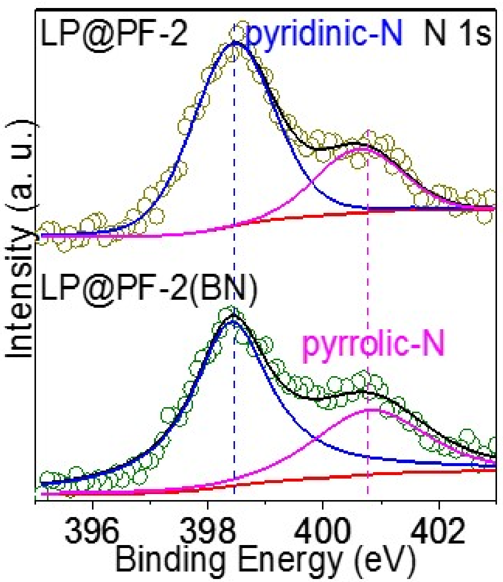
LP@PF catalyst structure offers close interaction between Pt-TM NPs and PGM-free site for improved synergistic catalysis

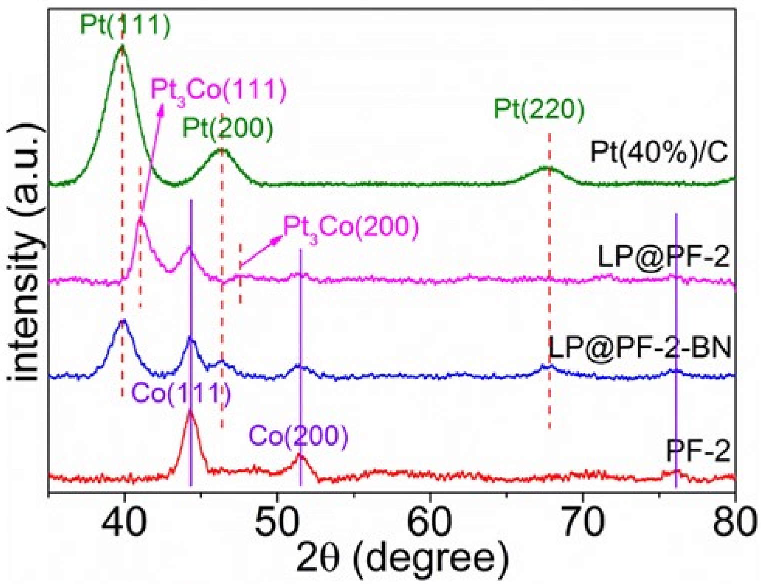
ACCOMPLISHMENTS – INVESTIGATION OF LP@PF CATALYST LATTICE & ELECTRONIC STATES

XPS study clearly shows the change of Pt electronic state and N population redistribution in PGM-free site during in situ reduction…

… XRD demonstrates Pt-TM alloy formation in NPs during in situ reduction







XPS and XRD further confirm the Pt-TM NP alloy formation and distribution of carbonaceous nitrogen during in situ reduction

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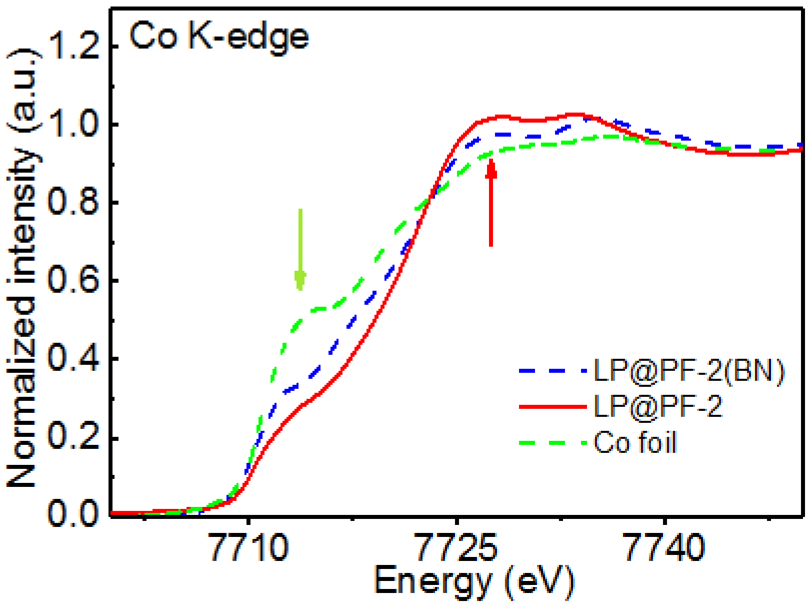
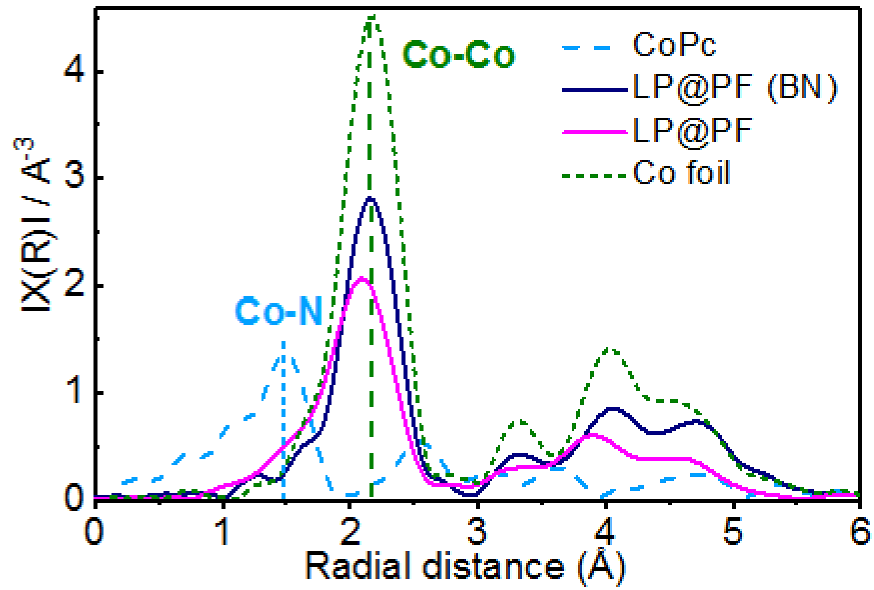
ACCOMPLISHMENTS – INVESTIGATION OF LP@PF CATALYST Co COORDINATION & OXIDATION STATE

X-ray absorption near edge structure (XANES) indicates cobalt metallic to ionic transition after post-treatment…



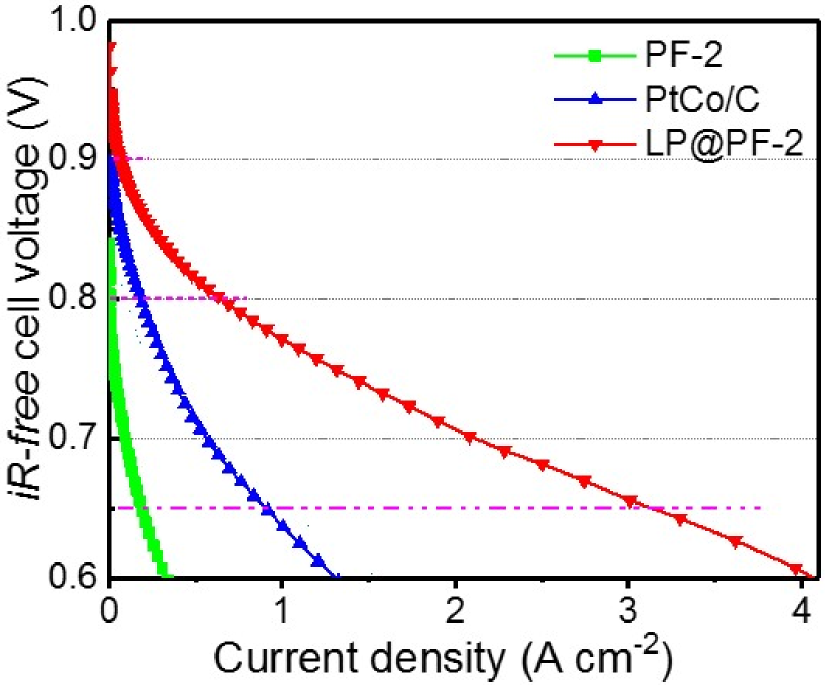
…corroborated by extended X-ray absorption fine structure (EXAFS) showing increased Co-N_x ligation



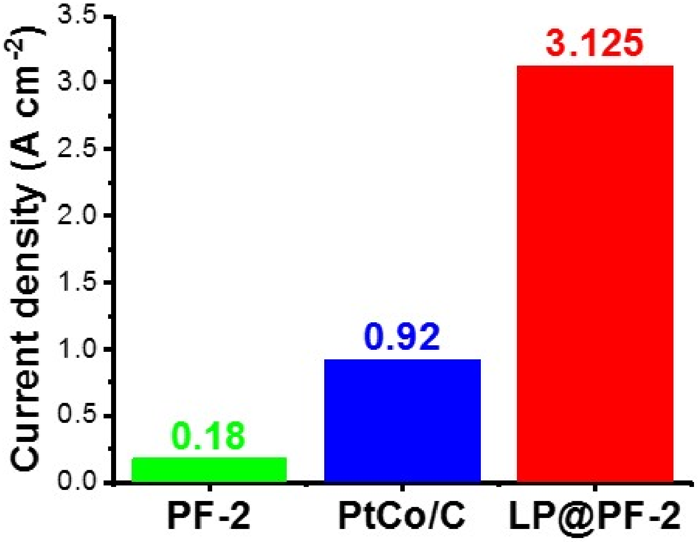
X-ray absorption spectroscopies identified formation of additional PGM-free catalytic sites over the "support" during the post-treatment, enhancing the synergistic catalysis

ACCOMPLISHMENTS – UNDERSTANDING OF SYNERGISTIC INTERACTION IN LP@PF CATALYST

To better understand the synergistic interaction between Pt-TM and PGM-free site, a low PtCo/C and a PGM-free catalysts were individually prepared and studied in fuel cell.



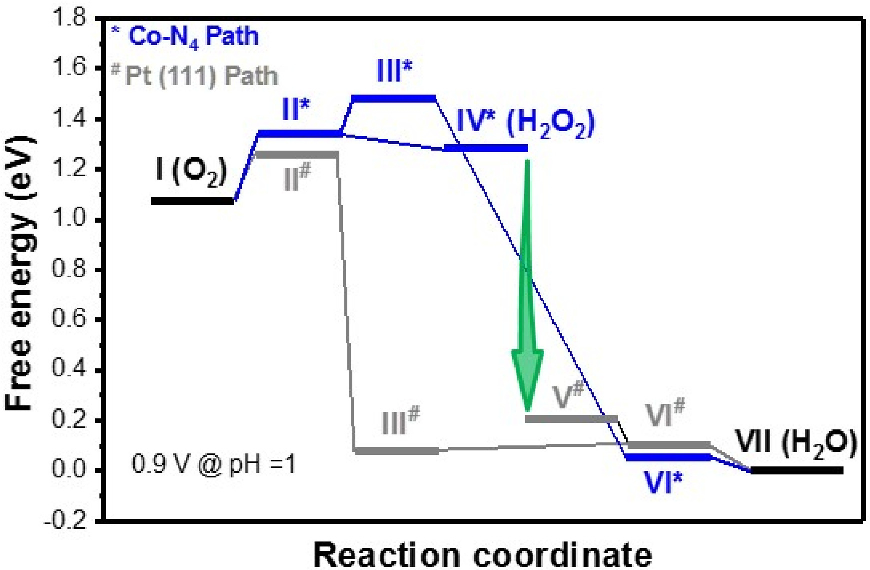
Synergistic Interaction:
Activity of LP@PF > LP + PF

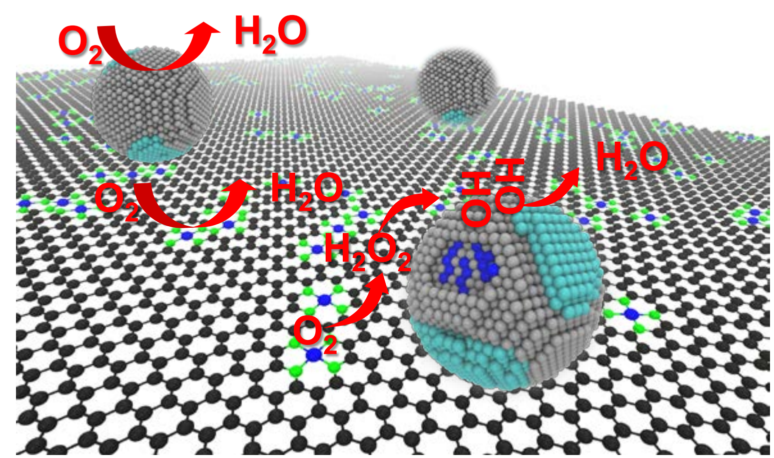


- At any given voltage, LP@PF activity (current density) is higher than the sum of individual contribution from Pt and PGM-free catalysts.
- Synergistic catalysis also significantly improved the catalyst durability.

ACCOMPLISHMENTS – COMPUTATIONAL MODELING OF PT/PGM-FREE SITE INTERACTION

DFT calculation to simulate synergistic ORR catalysis over LP@PF catalyst was performed by ANL/Purdue theorists





In addition to parallel catalysis at both sites, sequential reactions between PGM-free and Pt sites improve overall kinetics:

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

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

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

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

Unbounded H_2O_2 from Co-N_x-C_y site migrates to nearby Pt NP followed by decomposition to H_2O – a critical step in facilitating overall catalytic activity and preserving catalyst stability

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RESPONSES TO PREVIOUS YEAR REVIEWERS' COMMENTS

- This project was not reviewed last year.

COLLABORATIONS

- Purdue University (Collaborator)
  - Computational modeling of synergistic catalysis mechanism
- Center for Nanoscale Materials, Argonne National Laboratory (Collaborators)
  - DFT calculation on Pt/PGM-free site interaction
  - High resolution electron microscopic
- Northern Illinois University (Collaborator)
  - Experimental support through a joint guest graduate student

Supports on modeling/simulation and advanced microscopic imaging prove to be invaluable to the fundamental understanding on the new catalytic mechanism!

PROPOSED FUTURE WORK

Remaining project tasks & milestones

- Complete LP@PF catalyst and MEA optimizations, producing fuel cell performance with current density > 300 mA/cm^2 @ 0.8 V and < 40% MA loss.
- Complete the catalyst characterization with improved understanding on synergistic catalysis.
- Complete LP@PFNF catalyst and MEA optimizations, demonstrate a MEA/fuel cell with mass activity >0.44 A/mg-PGM, >1 W/cm^2 in activity; and <40% loss of mass activity, <30 mV loss at 1.5 A/cm^2 in durability, following AST protocol.

Future directions

- What is the lowest Pt level one can achieve to maintain an effective synergistic catalysis with PGM-free site? (Pt NP size, PGM-free site density, etc.)
- How to facilitate the interaction between Pt and PGM-free active site through catalyst structural improvement and electrode/MEA optimization? (intermediate migration/transport, water management)

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

SUMMARY

- ANL's new LP@PF catalysts demonstrated high Pt mass activities in fuel cell tests (1.08 A/mg_{Pt} to 1.77 A/mg_{Pt}), surpassing DOE target
- Fuel cells containing ANL's LP@PF cathode catalyst with ultralow Pt loading showed promising current densities under one bar air at 0.8 V and 0.65 V, respectively.
- Fuel cells containing ANL's LP@PF cathode catalyst with ultralow Pt loading showed promising durability in 30,000 voltage cycles during AST, approaching to DOE target.
- Structural characterizations using various techniques identified LP@PF catalysts having Pt-Co core-shell nanoparticles (5-6 nm), situating over Co-N_x-C_y catalytically active support.
- DFT modeling revealed the synergistic catalytic mechanism involving both parallel and sequential ORRs between Pt-Co nanoparticles and PGM-free catalytic sites.

ACKNOWLEDGEMENT

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