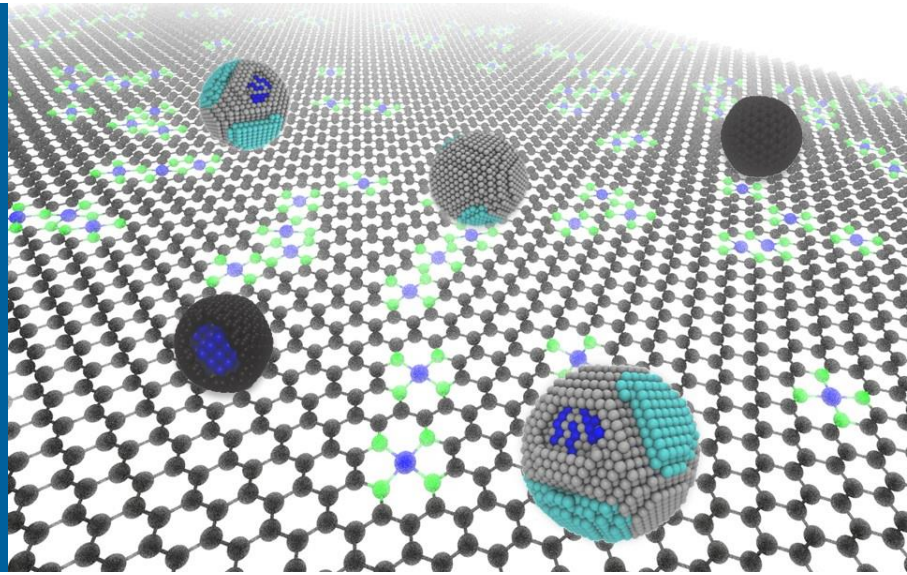
HIGHLY EFFICIENT AND DURABLE CATHODE CATALYST WITH ULTRALOW Pt LOADING THROUGH SYNERGETIC Pt/PGM-FREE CATALYTIC INTERACTION



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Project ID: fc174

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2019 DOE Hydrogen and Fuel Cells Program Annual Merit Review and Peer Evaluation Meeting
April 30 – May 1, 2019, Washington, D.C.

OVERVIEW

Timeline

- Project Start: April 2017
- Project End: September 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: $ 300K
- FY2018 DOE Funding: $150K
- DOE Fund Spent*: $ 364 K

* As of Jan/31/2019

Collaborations

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

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

	Units	DOE 2025 Target	Project Inception	Current Status*
Pt mass activity @ 900 $mV_{iR\ free}$	A/mg_{PGM}	0.44	1.77	3.30
PGM total loading				0.033 (Cathode)
MEA performance @ 800 mV (1 bar air)	mA/cm^2	≥300	273	359
MEA performance @ 675 mV (1 bar air)	mA/cm^2			1005
Loss in catalytic (mass) activity	% loss	<40	85%	7%
Loss in performance at 0.8 A/cm^2	mV	<30		1
Loss in performance at 1.5 A/cm^2			62	0

*** fuel cell performance measured over a single selected catalyst, LP@PF-1New**

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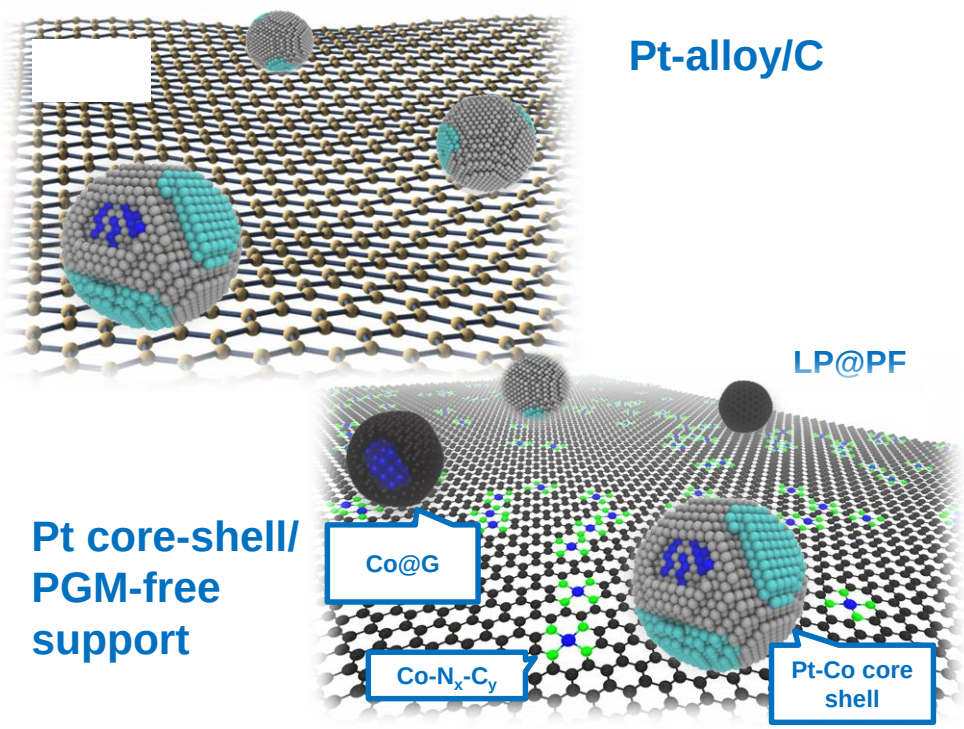
APPROACH – PLATINUM USAGE REDUCTION THROUGH SYNERGISTIC INTERACTION BETWEEN ULTRALOW Pt & PGM-FREE SITES

Activity Enhancement : Synergistic interaction between ultralow Pt over PGM-free catalyst support (LP@PF)

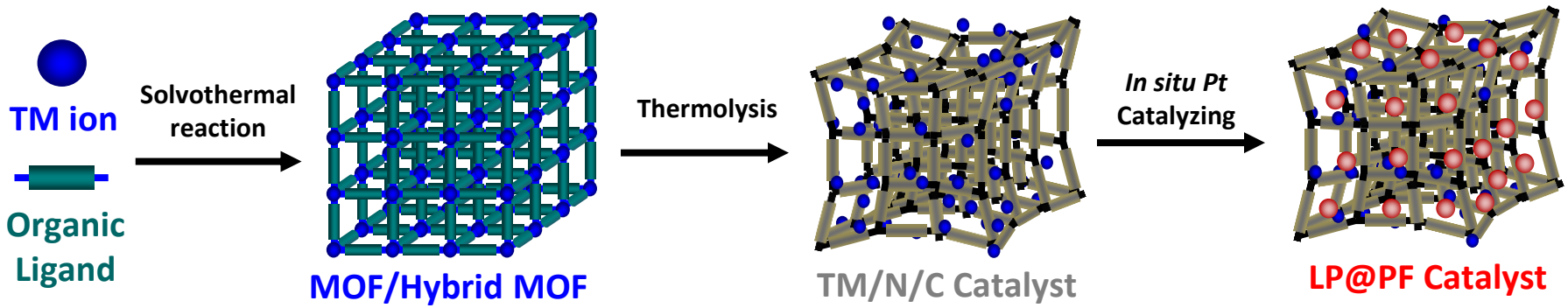
- Demands of both *activity* and *accessibility* of Pt sites limit the Pt loading reduction
- Synergistic catalysis between ultralow Pt & PGM-free sites (LP@PF) can improve Pt utilization and overall activity and durability
- PGM-free catalyst derived from metal-organic-framework (MOF) with uniformly distributed high density active sites serves as catalytically active support for Pt



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

APPROACH – LP@PF CATALYST DESIGN & SYNTHESIS

MOF Synthesis & Pt Catalyzing → **Catalyst / MEA Testing & Optimization** → **Structural Studies & Computational Modeling**



L. Chong, *et. al*. *Science* 362, 1276–1281 (**2018**)

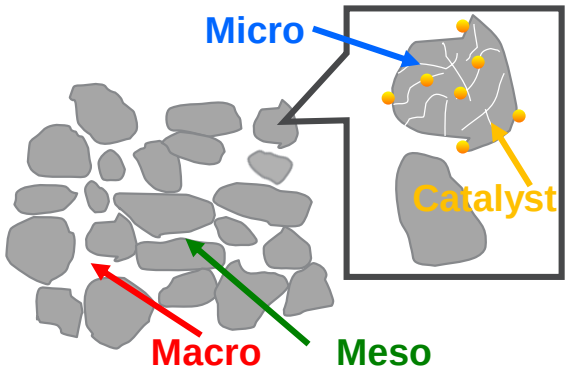
- Design and synthesis mono- and bimetallic MOFs containing ORR active TMs and organic ligand
- Thermal activation to convert MOF to PGM-free catalytically active support
- Catalyzing Pt precursor over TM NPs formed in PGM-free support
- In situ reduction to form Pt-TM core-shell structure over PGM-free catalyst support

The MOF-based synthesis offers versatile and industrial scalable approach to prepare LP@PF catalysts of different core-shell alloys

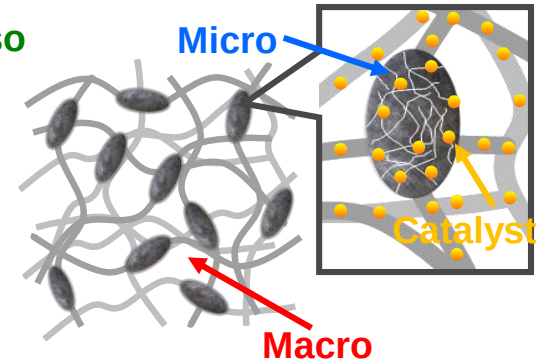
APPROACH – DURABILITY & MASS/CHARGE TRANSPORT IMPROVEMENT THROUGH POROUS NANOFIBROUS NETWORK

Durability / Transport Improvements: Ultralow Pt over PGM-free catalytic support in porous nano-network (LP@PFNF)

- Conventional C-supports are not optimized for mass/charge transports 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
- It also improves catalyst stability against corrosion



Conventional C-support

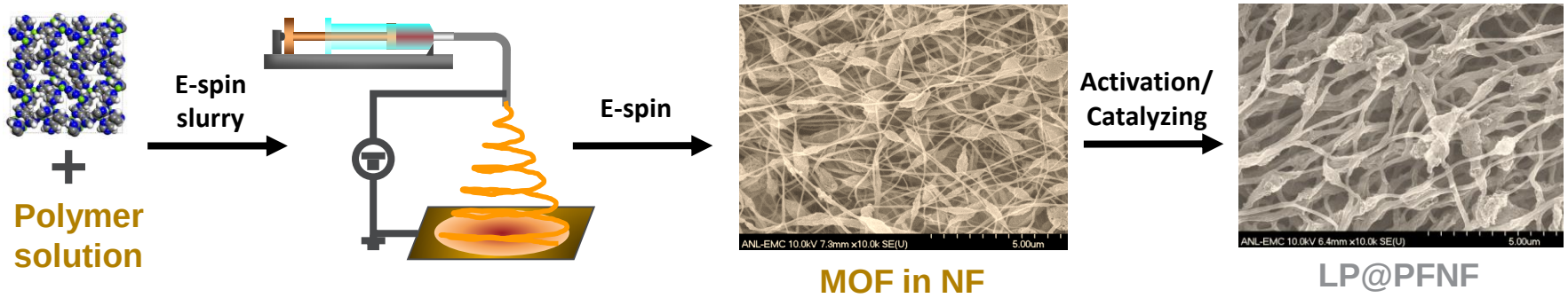


PNNE Electrode

From conventional C-black to porous network electrode

APPROACH – LP@PF IN NANOFIBER ELECTRODE DESIGN & FABRICATION

LP@PFNF Catalyst Electrode Preparation → **Electrode / MEA Testing & Optimization** → **Structural Characterization**



Shui, *et. al*. *PNAS*, **2015**, vol. 112, no. 34, 10629

- Mixing and suspending MOFs in polymer solution to form electro-spinning slurry
- Electrospinning to form nanofibers followed by heat-curing and conversion to PFNF
- Catalyzing Pt precursor over ORR active PGM-free PFNF
- *In situ* reduction to form LP@PFNF

ANL's MOF-infused electrospin method can produce interconnected PFNF containing microporosity and specific surface area @ 800 m^2/g or higher

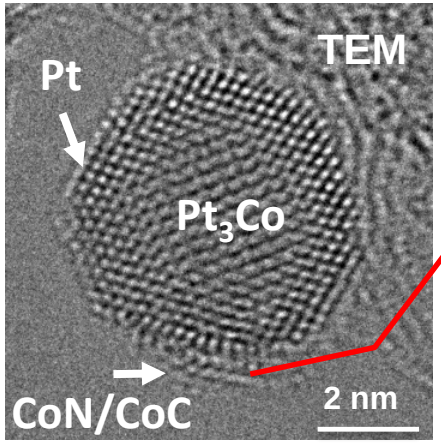
APPROACH – FY19 MILESTONES

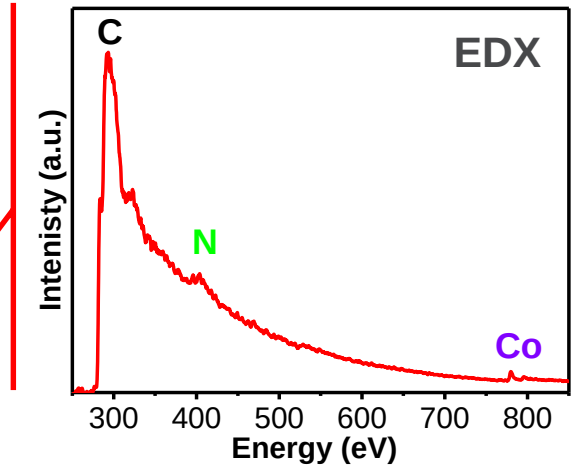
Milestones	Month/ Year	Status Update
Complete synthesis of nanofibrous LP@PF catalyst and MEA/fuel cell performance evaluation.	(10/31/18)	**100% completed.** Two more LP@PNEF catalysts were fabricated into MEA and tested in a single fuel cell. All demonstrated very good fuel cell performance.
To complete evaluation of at least two new membranes for LP@PF catalyst MEA	(1/31/19)	**60% Completed:** New thin membrane and high T membrane have been procured. Method for MEA fabrication is under development
To complete synthesis and evaluation of at least three trimetallic catalysts and catalytic electrode for LP@PF MEA	(4/30/19)	**75% Completed:** Over 8 MEAs with ANL's catalysts were prepared with two being tested. MEAs with the-state-of-art industrial catalyst were also evaluated and compared
To complete investigation of reducing anode Pt loading in MEA fabrication	(7/31/19)	**15% Completed:** The state-of-the-art anode catalysts were acquired after NDA with an industrial supplier.
To complete the optimization of anode / cathode Pt distribution and to demonstrate MEA with total Pt loading < 0.125 mg/cm2.	(10/31/19)	**On-going.**

Project Deliverable – Demonstrate a MEA with total Pt loading < 0.125 mg-Pt/cm^2 with improved activity (mass activity >0.44 A/mg-PGM, power density > 1 W/cm^2) and durability (<40% loss of mass activity, <30 mV loss at 1.5 A/cm^2). The new MEA/fuel cell will be delivered to NREL for evaluation. (10/31/18)

ACCOMPLISHMENT – UNDERSTANDING ALLOY CORE-SHELL STRUCTURE & PGM-FREE SUPPORT

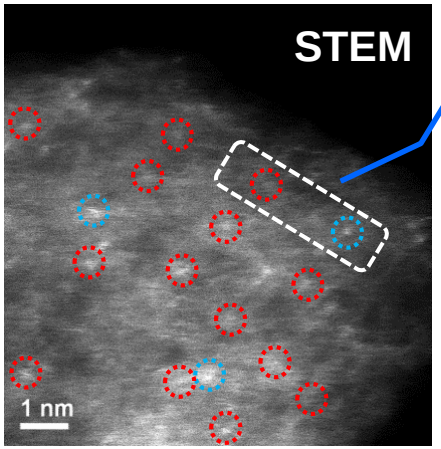
Pt-Co Core-Shell Structure

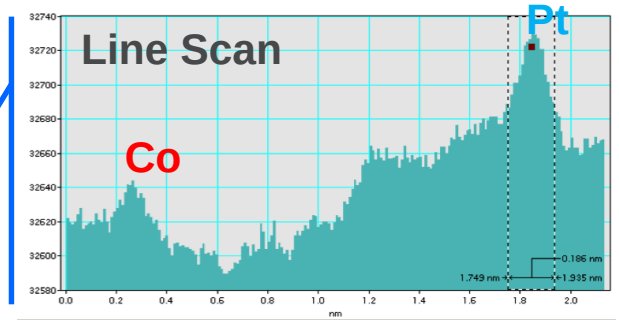




- Well defined core-shell structure with super-lattice Pt-Co core and 2-3 layer Pt shell is found
- Pt shell lattice is highly strained (3~4%)
- Pt shell is partially protected by terraces of CoN/CoN layers

"PGM-free" Support





- Carbon surface can be amorphous or graphitized, decorated by atomically dispersed Co and trace Pt
- Atomic N is embedded in C matrix, similar to the PGM-free catalyst we previously reported
(Chong, et. al. *ChemElecChem*, 2016)

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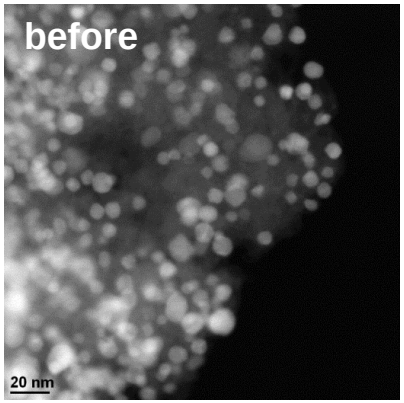
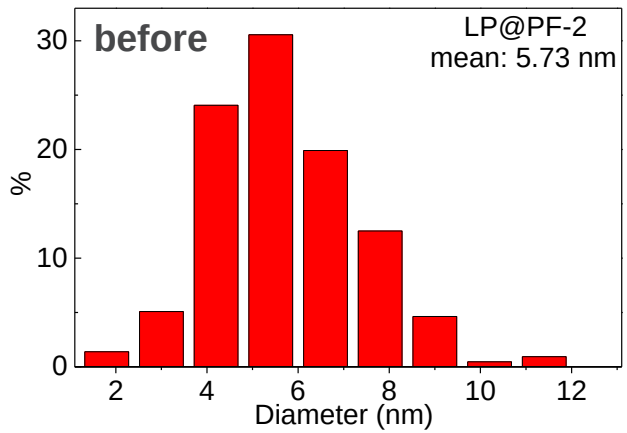
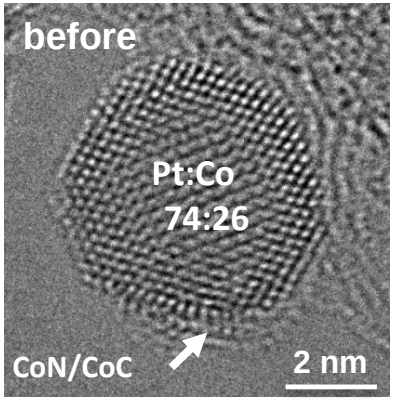
ACCOMPLISHMENT – UNDERSTANDING CATALYST NANOPARTICLE DISTRIBUTIONS BEFORE/AFTER ACCELERATED STRESS TEST

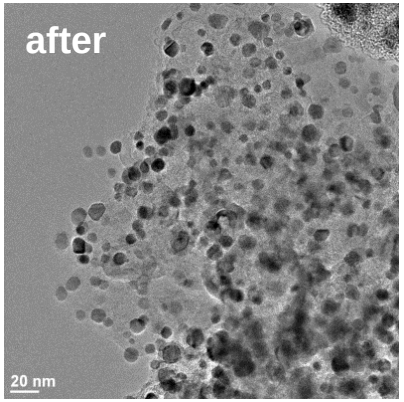
Before AST

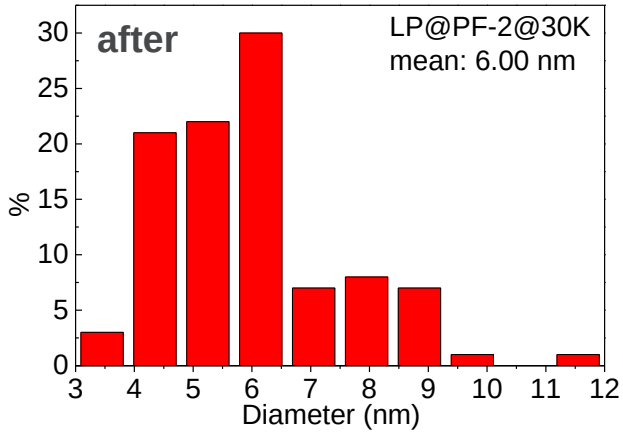


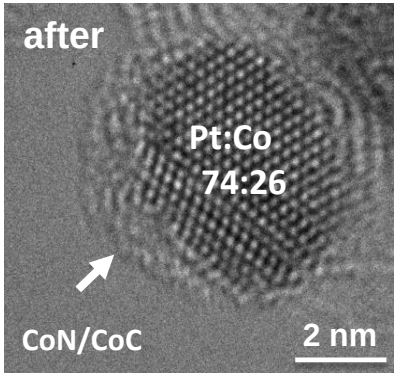




After AST



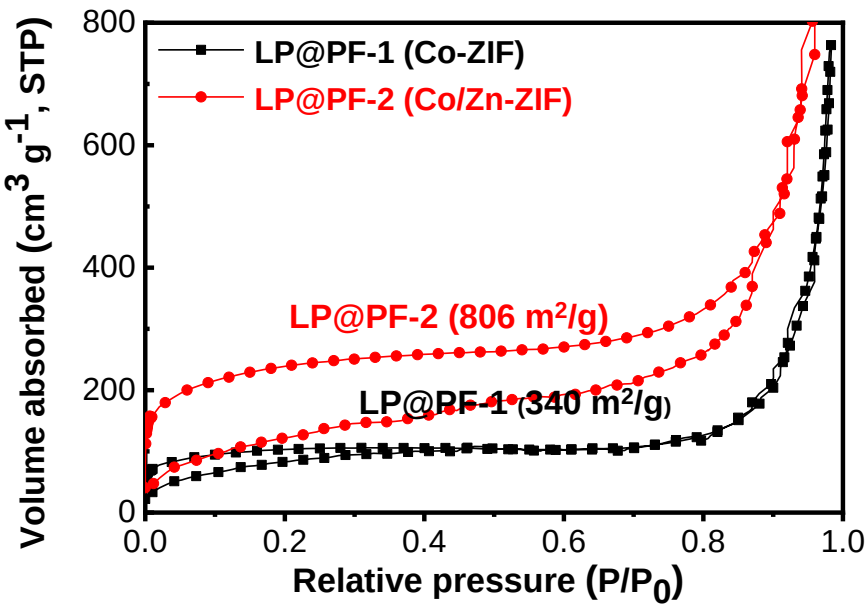




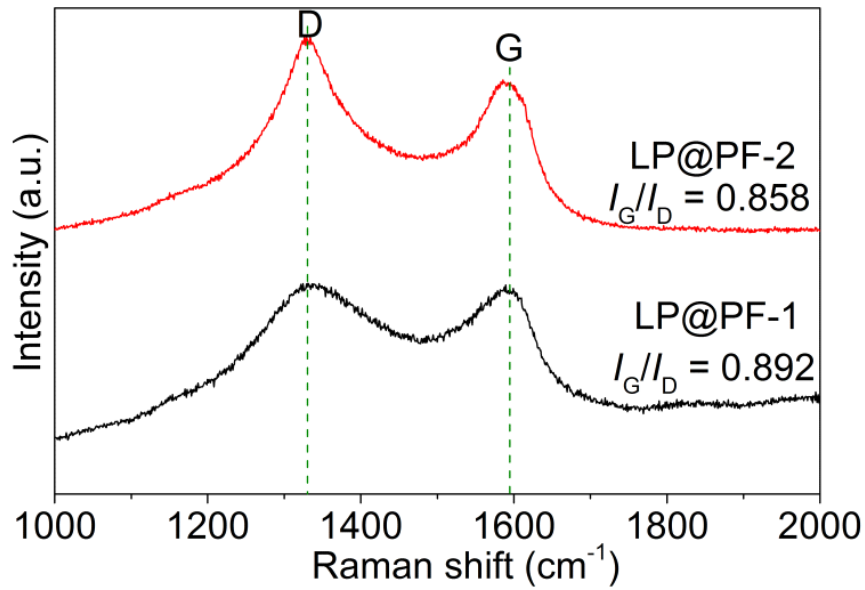
- **Metal nanoparticles (NPs) by TEM shows a majority are Co wrapped by graphene, Co@G**
- **NP size distribution retains nearly the same after 30 K voltage cycle**
- **Pt-Co NP structure remains nearly the same covered by CoN/CoC terraces after AST**

ACCOMPLISHMENT – UNDERSTANDING SURFACE PROPERTIES OF PGM-FREE "CATALYTIC SUBSTRATE"

BET surface area analysis



Raman surface area analysis



- **BET analysis shows that specific surface area (SSA) of PGM-free substrate can be controlled by MOF precursor composition**
- **Raman analysis indicates that surface graphitization (I_G:I_D) also can be controlled by MOF's makeup and is inversely correlated with SSA.**
- **SSA and I_G:I_D ratio directly impact the catalyst activity & durability**

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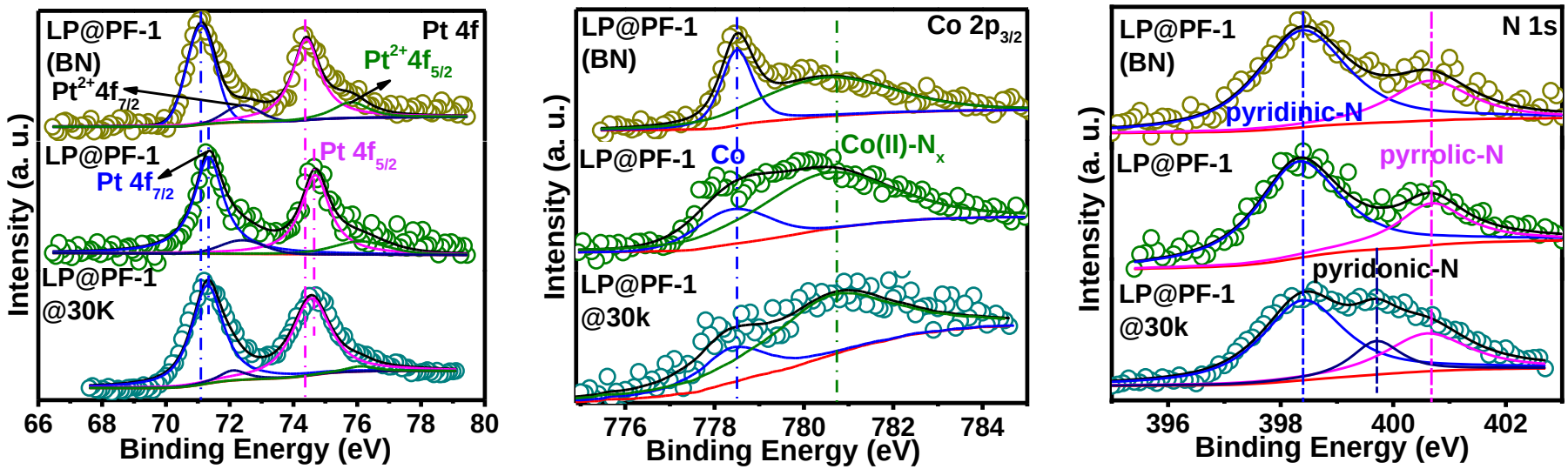
ACCOMPLISHMENT – UNDERSTANDING ELECTRONIC STRUCTURAL CHANGES OF KEY ELEMENTS IN LP@PF

XPS analysis on Pt, Co and N during synthesis & after AST



BN = Before NH_3 annealing

- Pt and Co showed significant peak energy and intensity shifts after ammonia annealing, indicating Pt-Co alloy and more Co-N_4 active site formation
- No significant Pt and Co peak shifts or intensity re-distribution were observed after AST, indicating no major changes in Pt or Co core-shell structure
- New pyridonic nitrogen peak detected after 30 K voltage cycle, suggesting oxidation of C adjacent to pyridinic nitrogen

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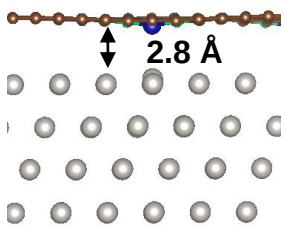
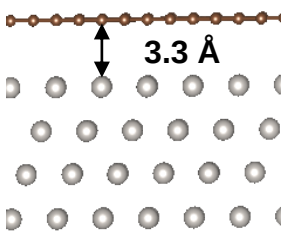
ACCOMPLISHMENTS – MODELING ON Pt/PGM-FREE INTERACTION & SYNERGISTIC CATALYSIS

Enhanced binding b/w Pt NP & PF substrate

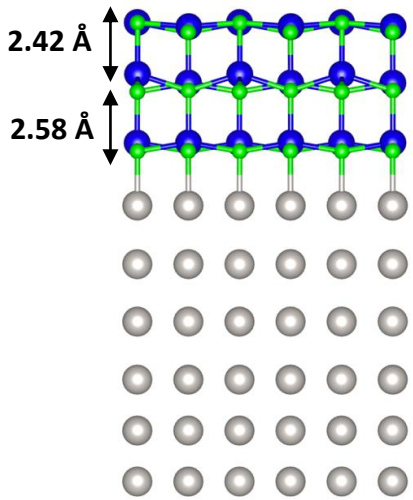


Pt/Co-N_4-graphene

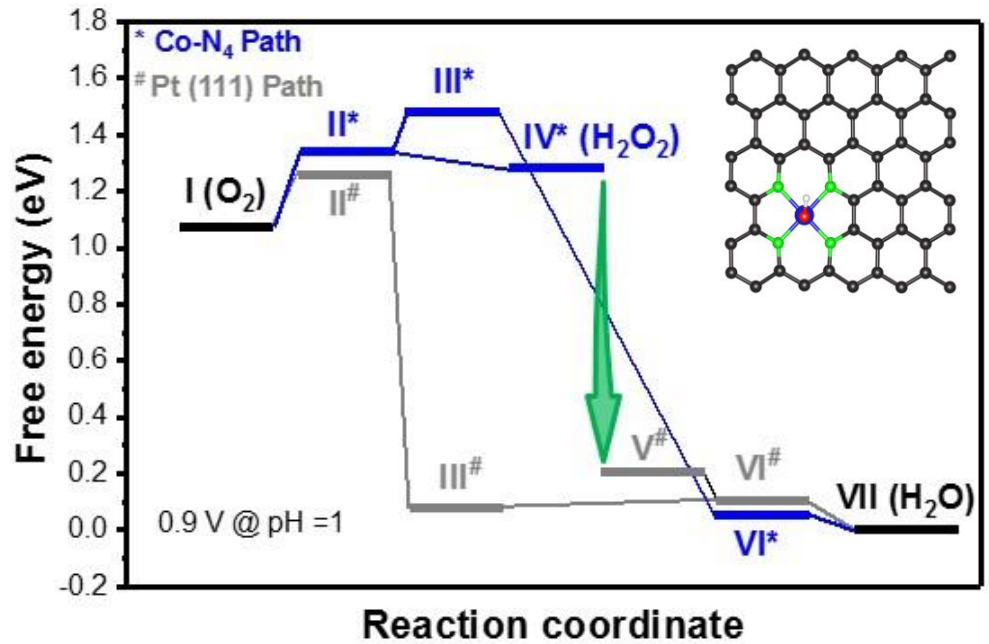


Pt/graphene

Preferential growth of CoN/CoC over Pt (10



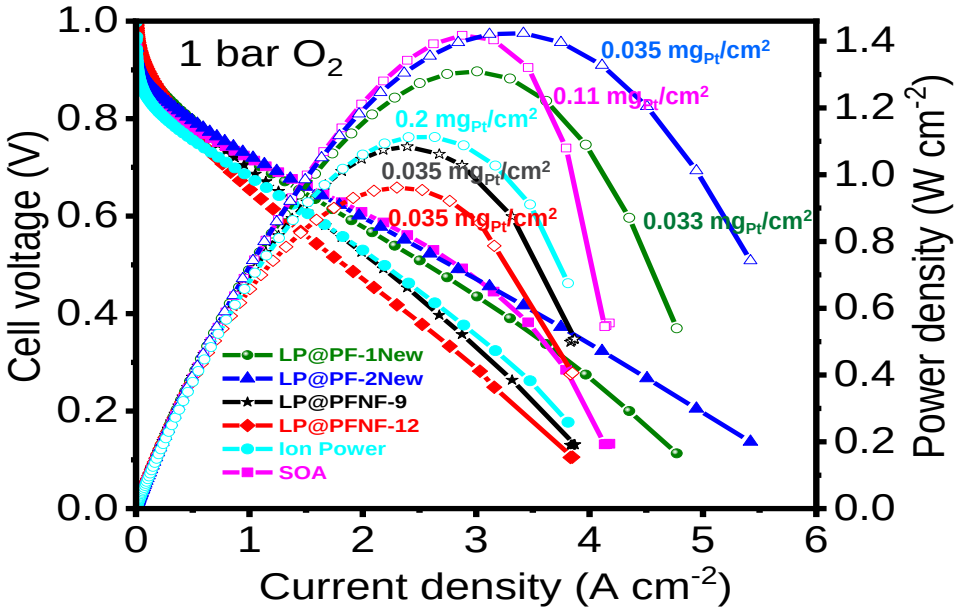
Calculation of binding energy as descriptor for ORR reveals the synergistic catalysis paths



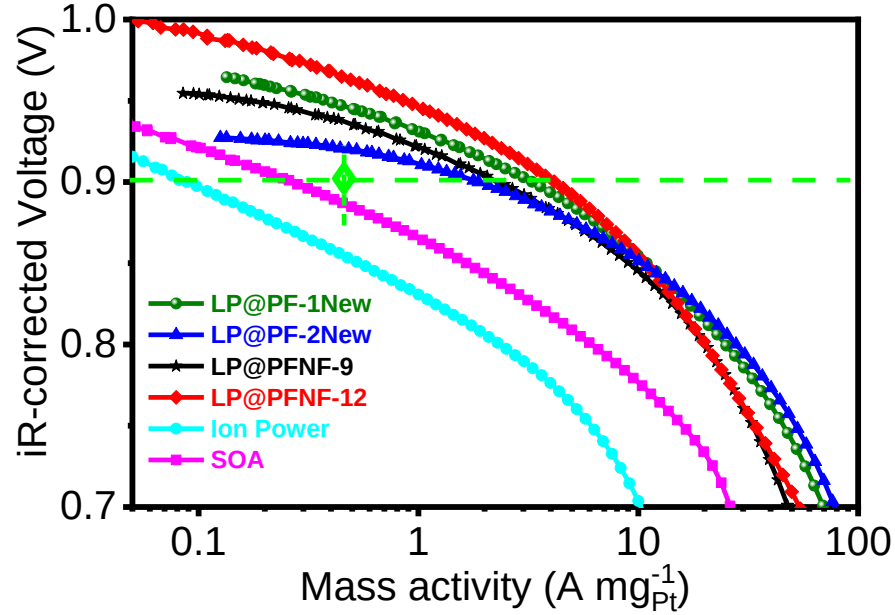
- CoN_4 brings Pt NP closer to carbon support and improves binding and charge transfer
- CoN/CoC terraces tend to grow over and protect Pt(100) facet, which is the least catalytically active and most vulnerable to acidic dissolution
- Unbounded H_2O_2 from Co-N_x-C_y site migrates to nearby Pt NP represents a critical step in facilitating catalytic activity and preserving stability

ACCOMPLISHMENT – ACTIVITY OF SELECTED LP@PF & LP@PFNF CATALYSTS IN MEA / FUEL CELL

H_2-O_2 fuel cell performances



Mass activity (MA) Tafel plots

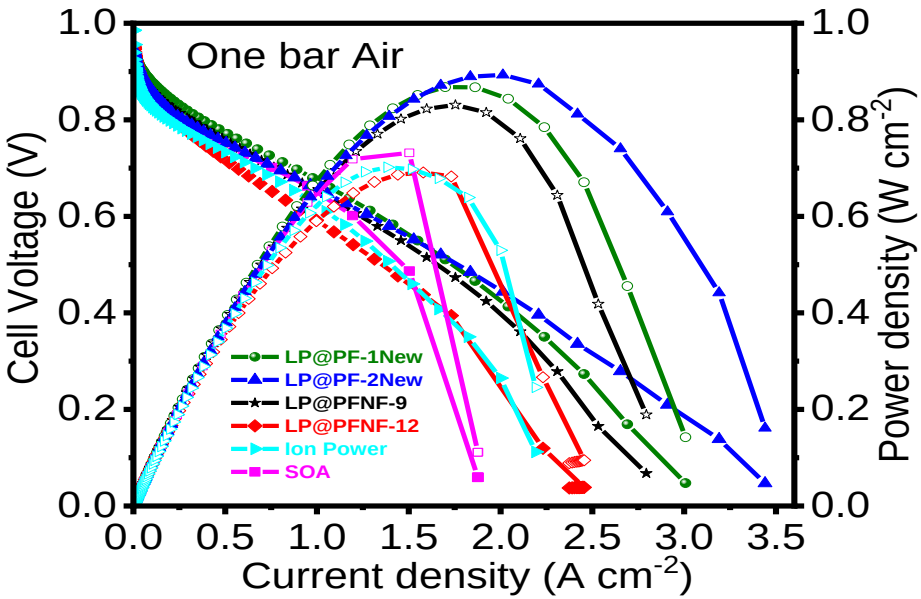


Test condition: Cathodic Pt loading, LP@PF/LP@PFNF = 0.033 ~ 0.035 mg_{Pt}/cm^2, Ion Power (Pt/C) = 0.2 mg_{Pt}/cm^2, State-of-the-art SOA (Pt/Co) = 0.11 mg_{Pt}/cm^2, Nafion 211, T = 80 °C, P_{H2} = P_{O2} = 100 kPa @ 100% RH (back pressure = 50 kPa), flow rate = 200 mL min^{-1} Conditioning time: 15 to 20 hours

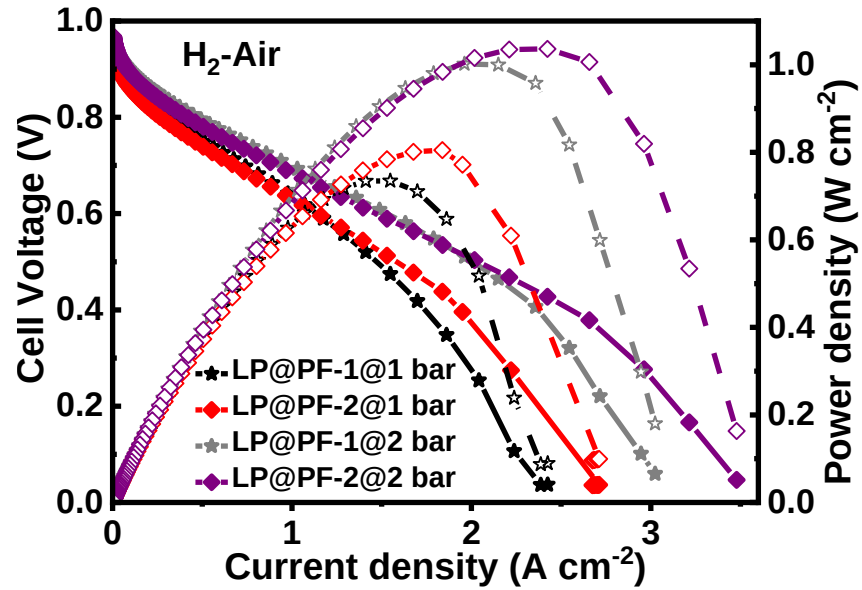
- LP&PF and LP@PFNF catalysts improved the fuel cell mass activities, exceeded DOE target of 0.44 A/mg_{Pt} at beginning of life (BOL)
- LP@PF cathode catalysts outperformed commercial Pt/C and the state-of-the-art Pt_3Co/C catalysts at high voltage and high current domains with lower Pt loading

ACCOMPLISHMENT – EXCELLENT POLARIZATIONS OF LP@PF & LP@PFNF IN H_2-AIR MEA/FUEL CELL

H_2-air fuel cell polarizations compared to benchmark MEAs



LP@PF fuel cell polarizations at different pressures



Condition: LP@PF & LP@PFNF = 0.033 ~ 0.035 mg_{Pt}/cm^2, Ion Power (Pt/C) = 0.2 mg_{Pt}/cm^2, SOA (Pt/Co) = 0.11 mg_{Pt}/cm^2, Nafion 211, Temperature = 80 °C, $P_{H2} = P_{air}$ = 1 bar or 2 bar as marked @ 100% RH, Stoich = 1.5/1.8

- At high voltage domain, ORR activity contributed from synergistic interaction between Pt-Co and PGM-free sites led to higher current densities than commercial and SOA MEA
- At high current domain, LP@PF catalysts extended current density beyond "mass transport limit", indicating continuous O_2 reduction by PGM-free site

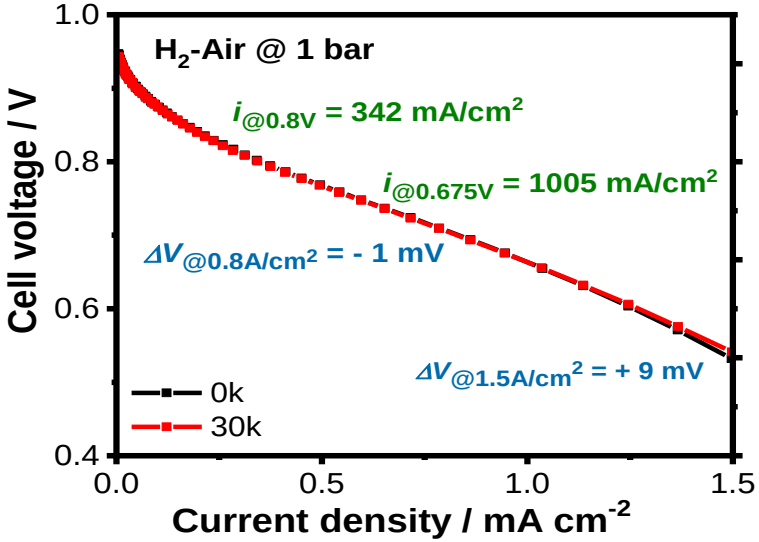
ACCOMPLISHMENT – FUEL CELL ACTIVITY COMPARISON OF SELECTED LP@PF & LP@PFNF CATALYSTS WITH BENCHMARK

Catalyst	Type of Cathode Catalyst	Cathode Pt loading (mg/cm^2)	MEA Mass Activity @0.9 V ($A \cdot mg_{Pt}^{-1}$)	FC current density @ 800 mV 1 bar air (mA/cm^2)	FC current density @ 675 mV 1 bar air (mA/cm^2)
LP@PF-1 New	PtCo (ZIF67)	0.033	3.29	360	1005
LP@PF-2 New	Pt_3Co (ZIF67/ZIF8)	0.035	1.78	280	890
LP@PFNF-9	PtCo (ZIF67/NF)	0.035	2.39	310	889
LP@PFNF-12	PtCo (ZIF67/NF)	0.035	4.16	223	660
Ion Power	Pt/C	0.2	0.09	200	770
SOA	Pt_3Co/C	0.11	0.28	220	877

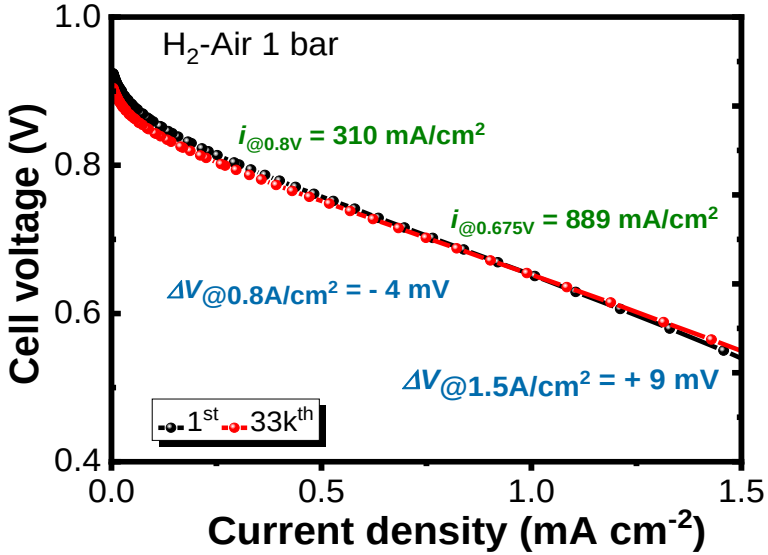
NF = Nanofiber

ACCOMPLISHMENT – DURABILITY STUDY OF SELECTED LP@PF & LP@PFNF CATALYSTS IN FUEL CELL

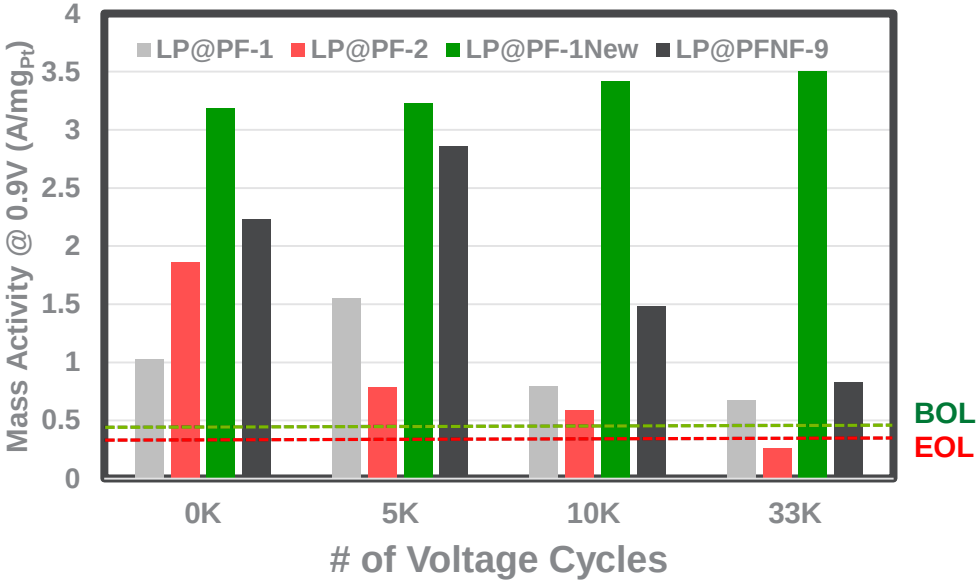
Durability of a LP@PF catalyst in AST



Durability of a LP@PFNF catalyst in AST



Fuel cell mass activity (MA) change during AST



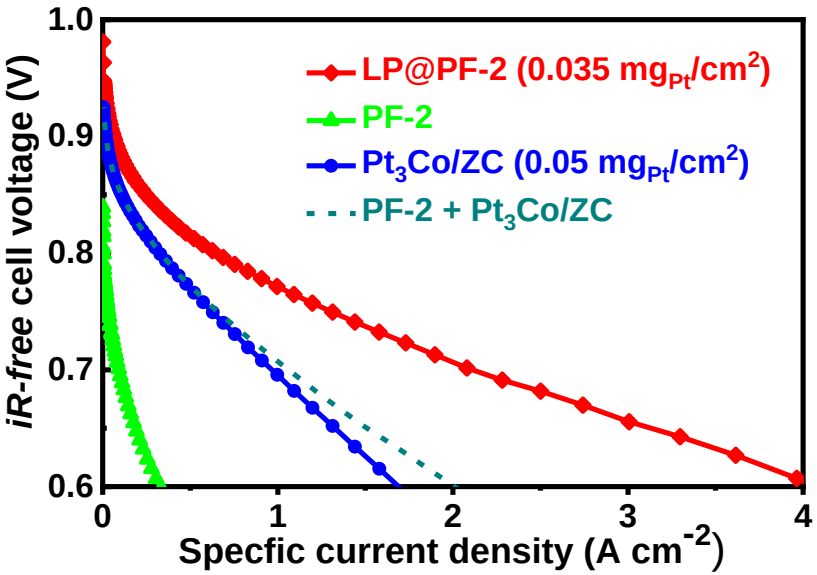
AST condition: Voltage cycling from 0.6 V to 1.0 V @ 50 mV/sec, Anode = H_2 @ 100% RH, Cathode = N_2 @ 100% RH, Temperature = 80 °C, P = 100 kPa (backpressure = 50 kPa)

- **Two LP@PF and LP@PFNF catalysts showed excellent durability with small or no cell voltage drops at 0.8 A/cm² and 1.5 A/cm² after AST, meeting DOE targets**
- **Multiple LP@PF and LP@PFNF catalysts exceeded DOE 2025 MA durability targets at both BOL (0.44 A/mg$_{Pt}$) and EOL (0.264 A/mg$_{Pt}$)**

ACCOMPLISHMENT & PROGRESS – RESPONSES TO PREVIOUS YEAR REVIEWERS' COMMENTS

- "Confirmation on the synergistic effect between two active sites is necessary…"
  - New comparative catalysts were synthesized and tested, the result supports the enhancement at kinetic & mass transport regions
- "PtCo-based SOA catalysts need to be selected as a reference for comparison…"
  - A state-of-the-art (SOA) catalyst was tested and the result is compared with LP@PF in this presentation
- "need of a catalyst or catalyst-coated membrane supplier for collaboration"
  - We initiated discussion with automotive OEMs for potential collaboration
  - Argonne Tech Transfer is currently exploring technology transfer / licensing opportunities

Synergistic catalysis demonstration



Cathode catalyst weight ~ 1.1 mg/cm^2, N 211, T = 80 °C, P=100 kPa @ 100% RH, flowrate = 200 ml/min; LP-2 = heat activated Co/Zn-ZIF; Pt3Co/ZC = Pt3Co core-shell added over heat activated Zn-ZIF with similar surface area to LP-2 but absent of Co-N_4 site

- Specific activity of LP@PF-2 > twice the sum of LP-2 and Pt_3Co/ZC at any voltage
- Lower peroxide formation found in RDE experiment

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 sample exchange of benchmark catalyst**

Collaboration from multiple institutions led to a high impact joint publication (Chong, et. al. *Science*, 2018)

PROPOSED FUTURE WORK

- To complete trimetallic LP@PF catalyst and MEA optimizations to further improve the performance at fuel cell level
- To integrate commercial high temperature membrane in MEA fabrication and to evaluate the fuel cell performance at higher temperature
- To apply thin membrane to MEA and to improve both current & power densities in H_2-air fuel cell using LP@PF cathode catalyst
- To rebalance the platinum amount by increasing the cathode loading (thinner cathode) and decreasing anode amount, leading to improved fuel cell performance with total Pt loading less than 0.125 mg/cm^2
- To develop a better understanding on the interaction between Pt and PGM-free active site through catalyst structural improvement and electrode/MEA optimization (peroxide/transport, water management)
- To deliver one or more MEAs with total Pt loading < 0.125 mg/cm^2 to NREL for MEA/fuel cell evaluation

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

SUMMARY

- ANL's new LP@PF and LP@PFNF catalysts demonstrated high Pt mass activities in fuel cell tests, exceeded DOE target
- The best LP@PF cathode catalyst showed improvement in fuel cell current densities, reaching DOE targets at 0.8 V and 0.65 V under one bar air
- Fuel cells with ANL's LP@PF & LP@PFNF cathode catalysts maintained excellent BOL and EOL mass activities durability during AST, exceeded DOE's targets
- H_2-air fuel cells with ANL's LP@PF & LP@PFNF cathode catalysts exhibited low voltage drops at 0.8A/cm^2 and 1.5A/cm^2 after AST, meeting DOE's targets
- Characterizations identified the catalyst containing strained Pt-Co core-shell nanostructure covered by protective CoC/CoN and Co@graphene nanoparticles
- The MOF-derived "catalytic support" contains Co-N_x-C_y ORR active sites with variable surface area and graphitization level
- DFT modeling revealed the synergistic catalytic mechanism involving both parallel and intercepted ORR reaction paths between Pt-Co nanoparticles and PGM-free catalytic sites.

More investigations are needed to improve catalyst performance through better understanding on the synergistic catalysis

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