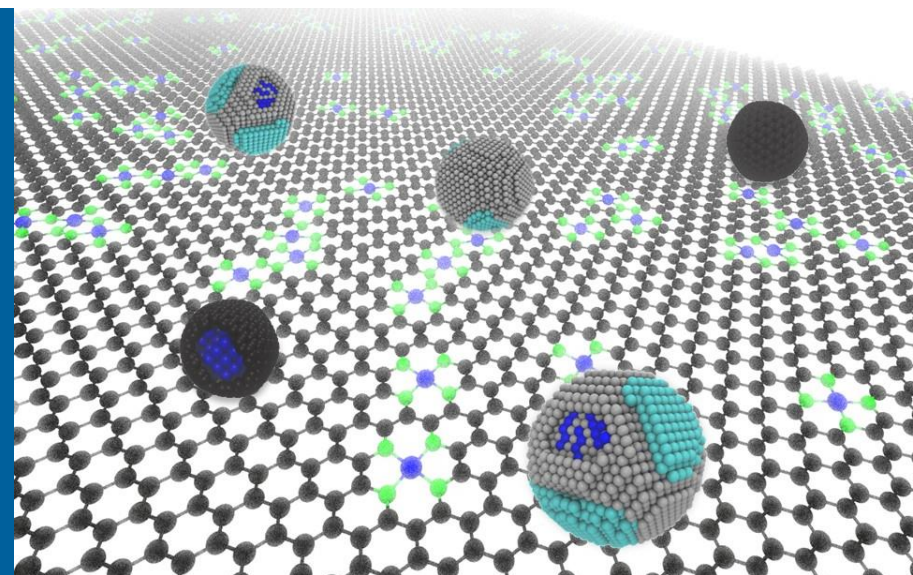


HIGHLY EFFICIENT AND DURABLE CATHODE CATALYST WITH ULTRALOW Pt LOADING THROUGH SYNERGETIC Pt/PGM-FREE CATALYTIC INTERACTION



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Project ID: fc174

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April 30 – May 1, 2019, Washington, D.C.

OVERVIEW

Timeline

- Project Start: April 2017
- Project End: September 2019

Budget

- FY2017 DOE Funding: \$ 300K
 - FY2018 DOE Funding: \$150K
 - DOE Fund Spent*: \$ 364 K
- * As of Jan/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

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

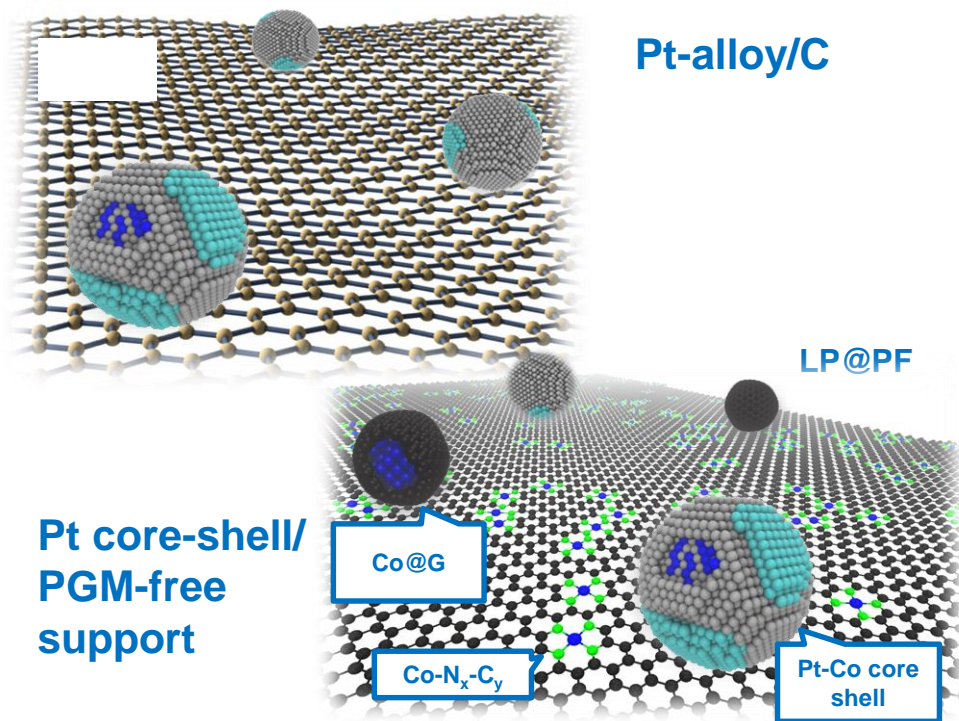
	Units	DOE 2025 Target	Project Inception	Current Status*
Pt mass activity @ 900 mV _{iR free}	A/mg _{PGM}	0.44	1.77	3.30
PGM total loading				0.033 (Cathode)
MEA performance @ 800 mV (1 bar air)	mA/cm ²	≥300	273	359
MEA performance @ 675 mV (1 bar air)	mA/cm ²			1005
Loss in catalytic (mass) activity	% 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

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



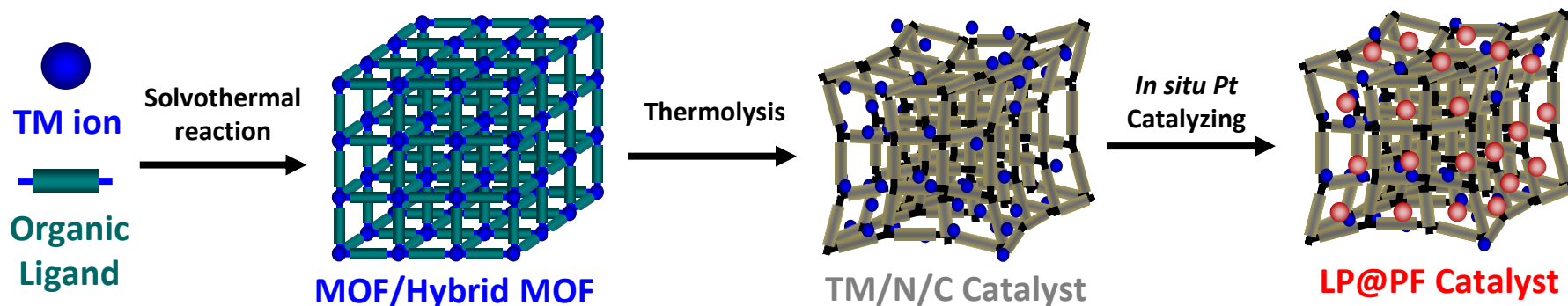
From conventional Pt/C to Pt/PGM free synergistic catalyst

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)

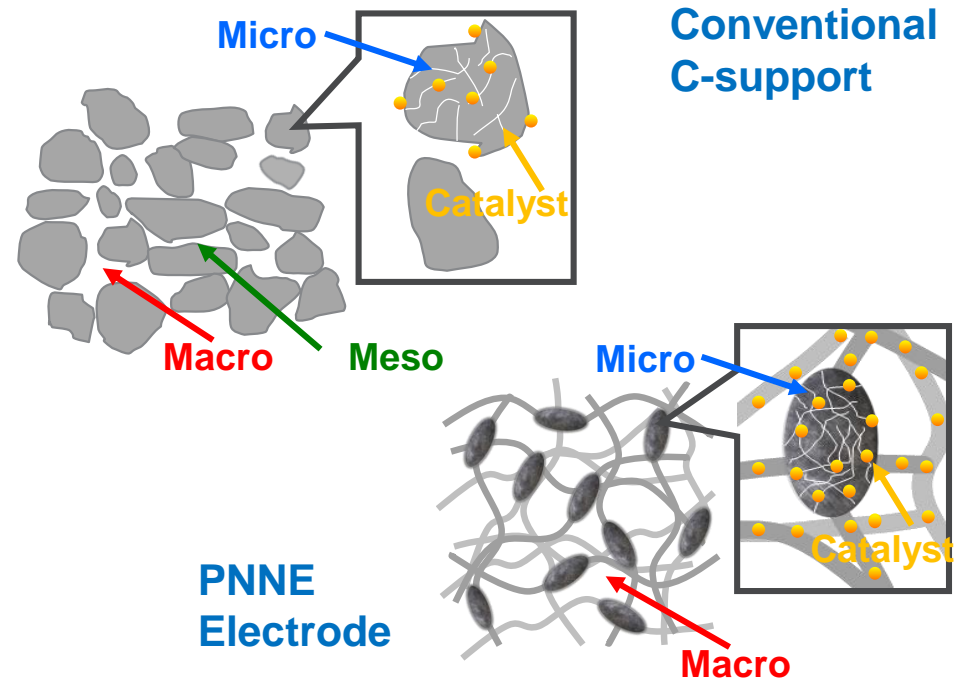
- Design and synthesis mono- and bimetallic MOFs containing ORR active TMs and organic ligand
- Thermal activation to convert MOF to PGM-free catalytically active support
- Catalyzing Pt precursor over TM NPs formed in PGM-free support
- In situ reduction to form Pt-TM core-shell structure over PGM-free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



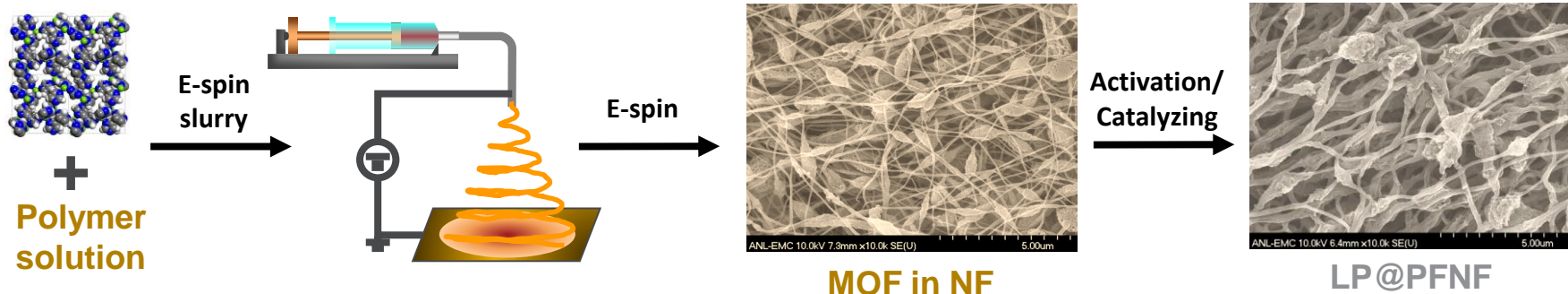
From conventional C-black to porous network electrode

APPROACH – LP@PFNF 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

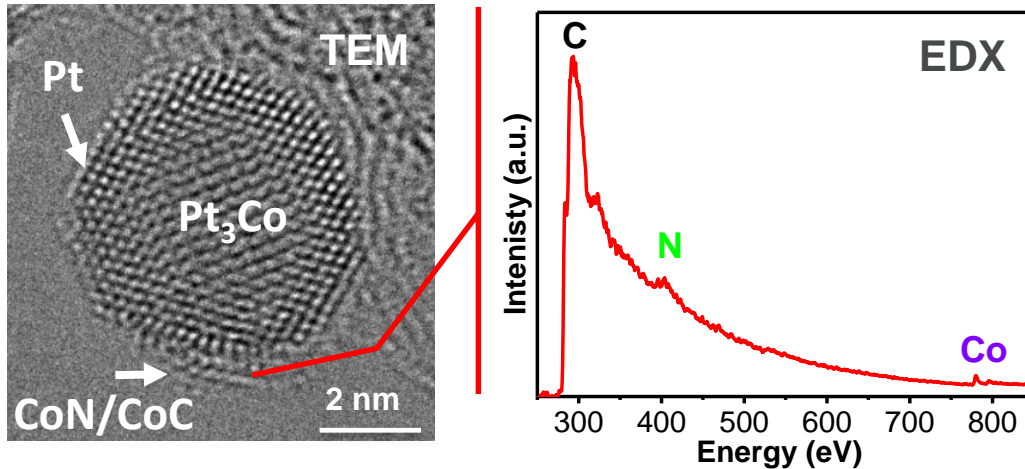
ANL's MOF-infused electrospin method can produce interconnected PFNF containing microporosity and specific surface area @ 800 m²/g or higher

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/cm ² .	(10/31/19)	On-going.
<p>Project Deliverable – Demonstrate a MEA with total Pt loading < 0.125 mg-Pt/cm² with improved activity (mass activity >0.44 A/mg-PGM, power density > 1 W/cm²) and durability (<40% loss of mass activity, <30 mV loss at 1.5 A/cm²). The new MEA/fuel cell will be delivered to NREL for evaluation. (10/31/18)</p>		

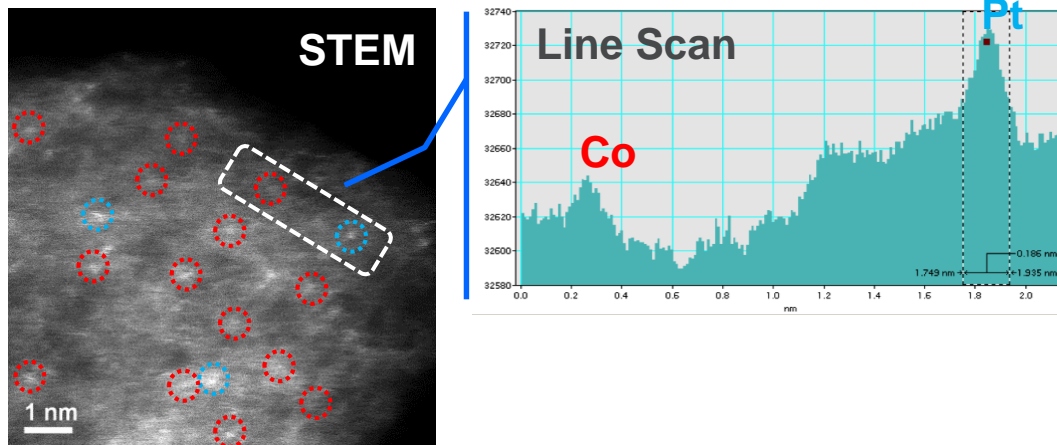
ACCOMPLISHMENT – UNDERSTANDING ALLOY CORE-SHELL STRUCTURE & PGM-FREE SUPPORT

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

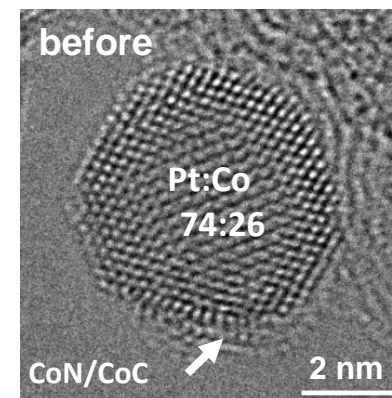
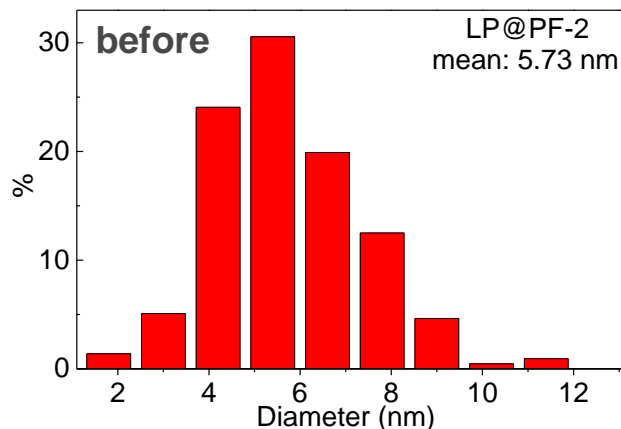
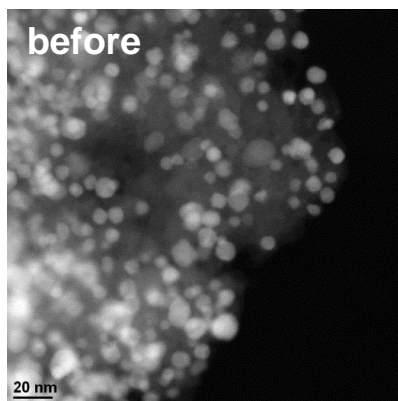
“PGM-free” Support



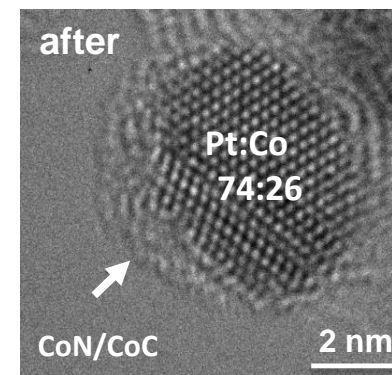
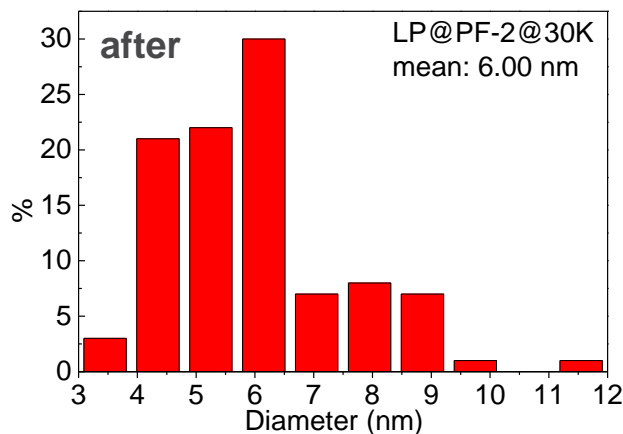
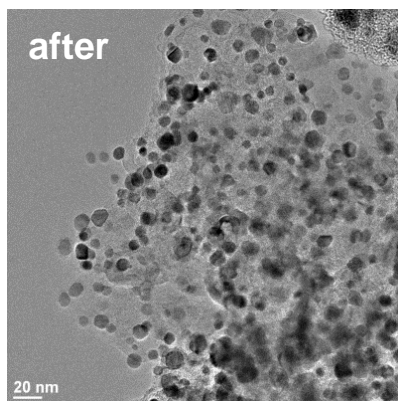
- Carbon surface can be amorphous or graphitized, decorated by atomically dispersed Co and trace Pt
- Atomic N is embedded in C matrix, similar to the PGM-free catalyst we previously reported (Chong, et. al. *ChemElecChem*, 2016)

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

Before AST



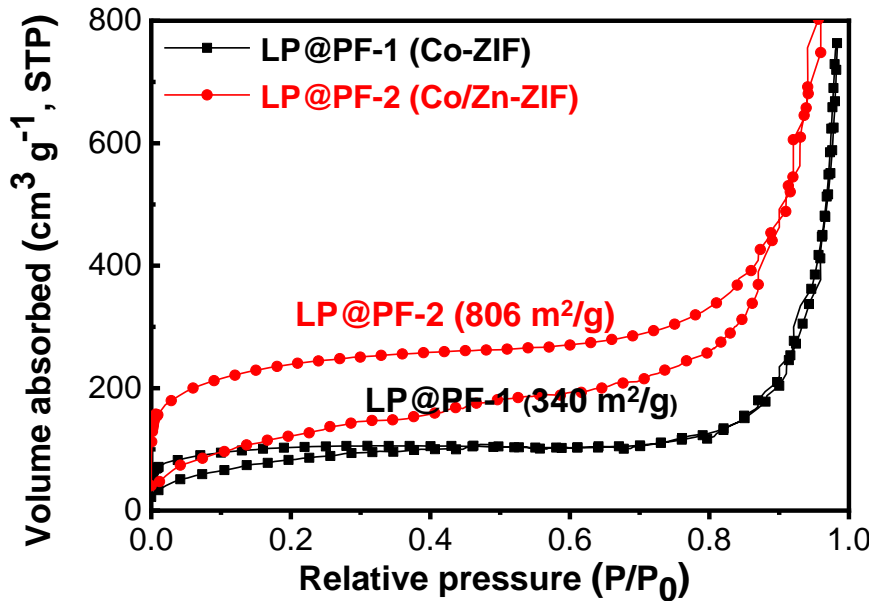
After AST



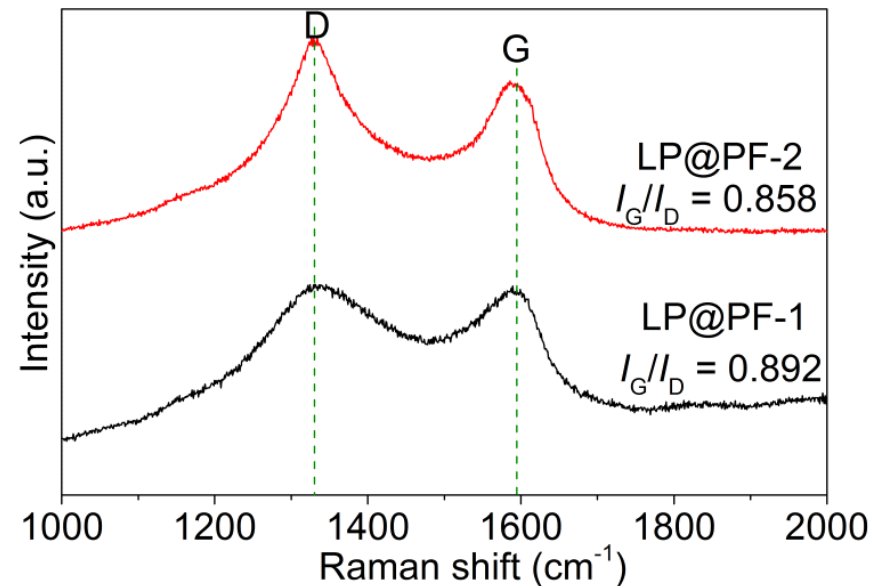
- Metal nanoparticles (NPs) by TEM shows a majority are Co wrapped by graphene, Co@G
- NP size distribution retains nearly the same after 30 K voltage cycle
- Pt-Co NP structure remains nearly the same covered by CoN/CoC terraces after AST

ACCOMPLISHMENT – UNDERSTANDING SURFACE PROPERTIES OF PGM-FREE “CATALYTIC SUBSTRATE”

BET surface area analysis



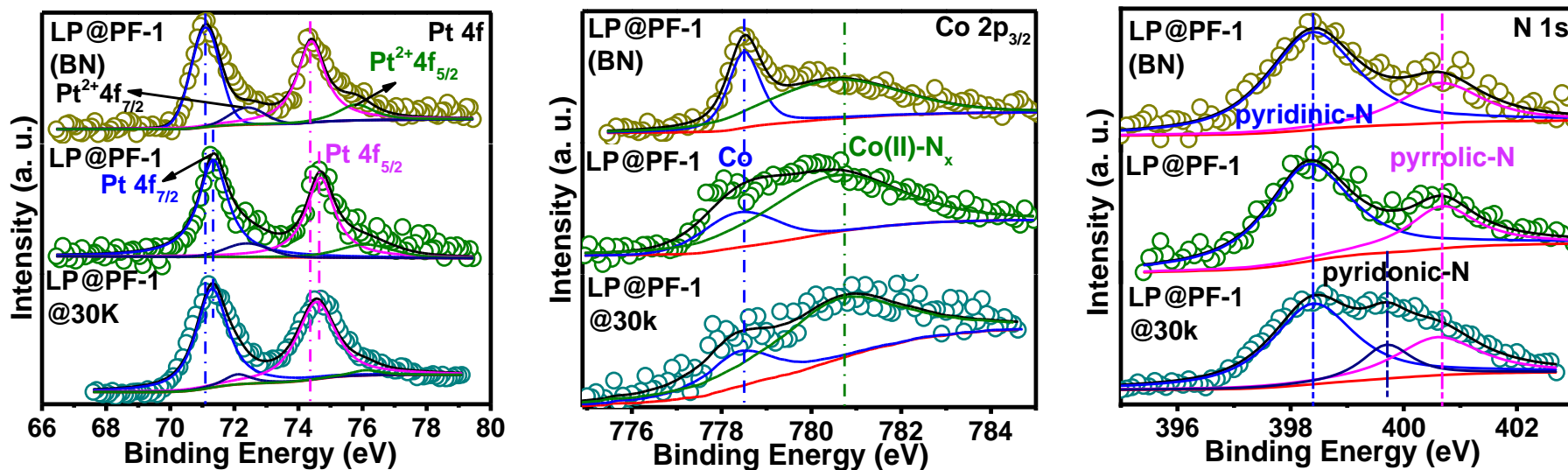
Raman surface area analysis



- 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

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

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

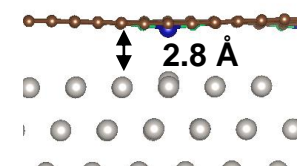


BN = Before NH₃ annealing

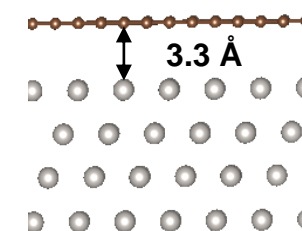
- Pt and Co showed significant peak energy and intensity shifts after ammonia annealing, indicating Pt-Co alloy and more Co-N₄ active site formation
- No significant Pt and Co peak shifts or intensity re-distribution were observed after AST, indicating no major changes in Pt or Co core-shell structure
- New pyridonic nitrogen peak detected after 30 K voltage cycle, suggesting oxidation of C adjacent to pyridinic nitrogen

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

Enhanced binding b/w Pt NP & PF substrate

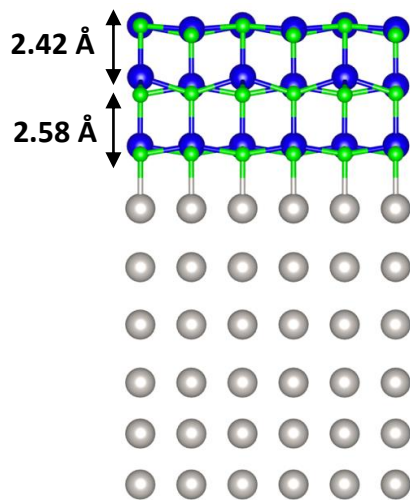


Pt/Co-N₄-graphene

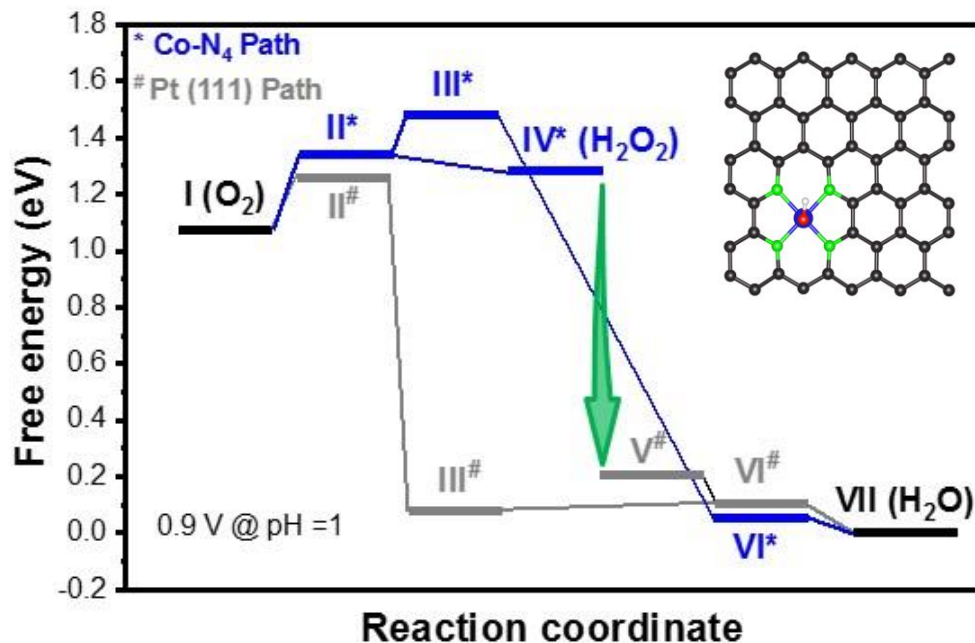


Pt/graphene

Preferential growth of CoN/CoC over Pt (10)



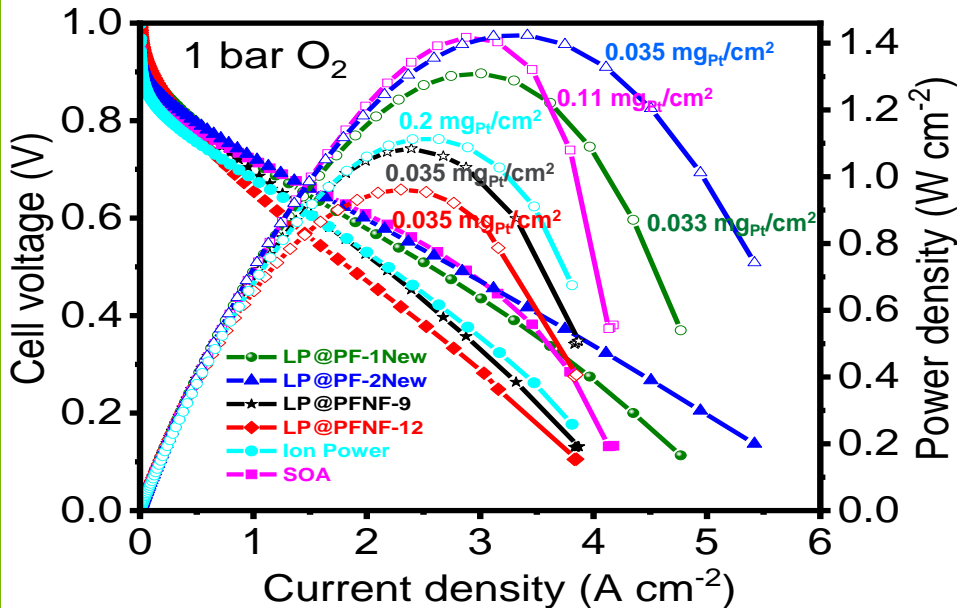
Calculation of binding energy as descriptor for ORR reveals the synergistic catalysis paths



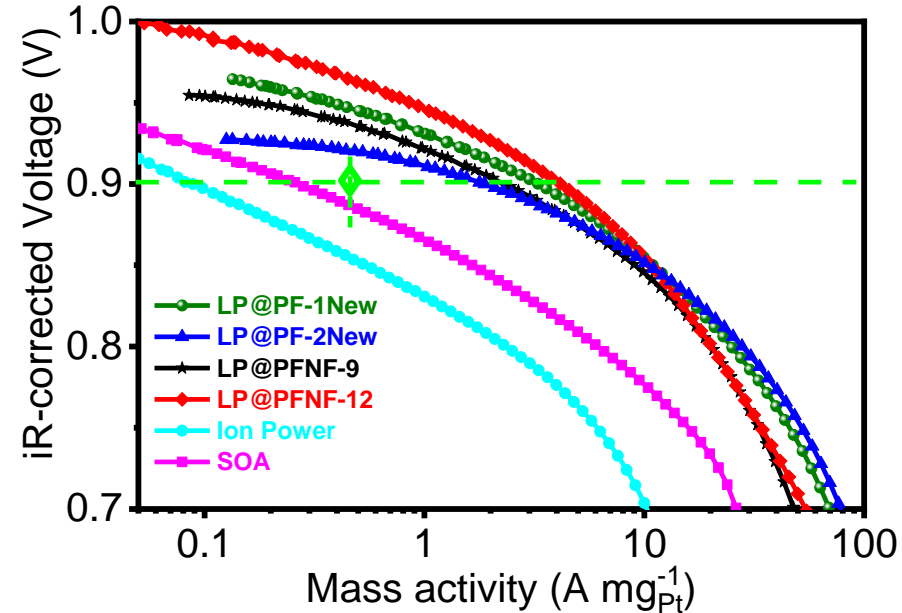
- CoN₄ brings Pt NP closer to carbon support and improves binding and charge transfer
- CoN/CoC terraces tend to grow over and protect Pt(100) facet, which is the least catalytically active and most vulnerable to acidic dissolution
- Unbounded H₂O₂ from Co-N_x-C_y site migrates to nearby Pt NP represents a critical step in facilitating catalytic activity and preserving stability

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

H₂-O₂ fuel cell performances



Mass activity (MA) Tafel plots

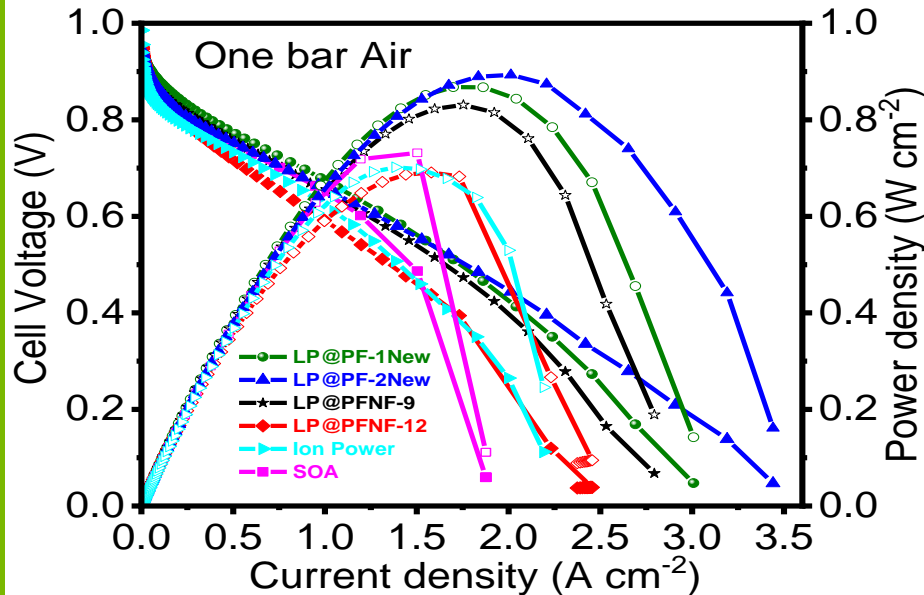


Test condition: Cathodic Pt loading, LP@PF/LP@PFNF = 0.033 ~ 0.035 mg_{Pt}/cm², Ion Power (Pt/C) = 0.2 mg_{Pt}/cm², State-of-the-art SOA (Pt/Co) = 0.11 mg_{Pt}/cm², Nafion 211, T = 80 °C, P_{H₂} = P_{O₂} = 100 kPa @ 100% RH (back pressure = 50 kPa), flow rate = 200 mL min⁻¹ Conditioning time: 15 to 20 hours

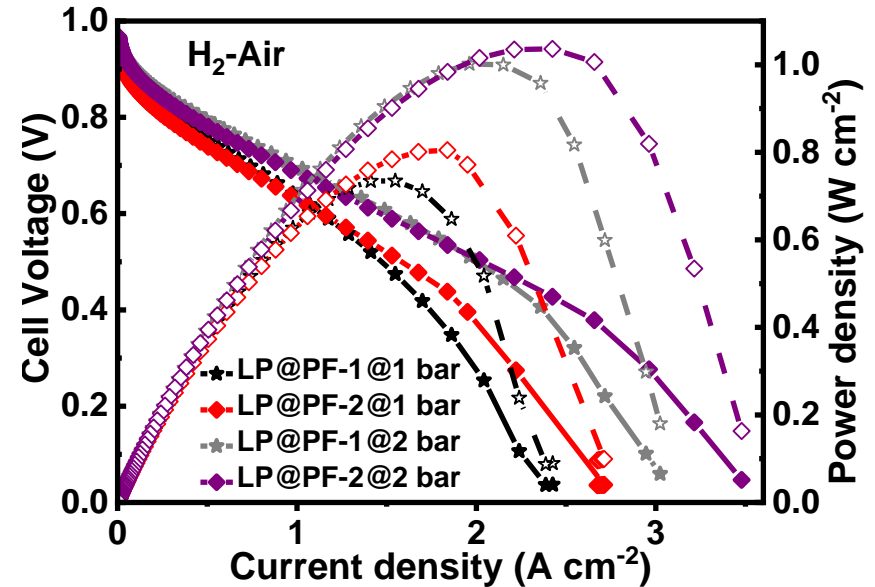
- LP&PF and LP@PFNF catalysts improved the fuel cell mass activities, exceeded DOE target of 0.44 A/mg_{Pt} at beginning of life (BOL)
- LP@PF cathode catalysts outperformed commercial Pt/C and the state-of-the-art Pt₃Co/C catalysts at high voltage and high current domains with lower Pt loading

ACCOMPLISHMENT – EXCELLENT POLARIZATIONS OF LP@PF & LP@PFNF IN H₂-AIR MEA/FUEL CELL

H₂-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}/cm², Ion Power (Pt/C) = 0.2 mg_{Pt}/cm², SOA (Pt/Co) = 0.11 mg_{Pt}/cm², Nafion 211, Temperature = 80 °C, P_{H₂} = P_{air} = 1 bar or 2 bar as marked @ 100% RH, Stoch = 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 O₂ reduction by PGM-free site

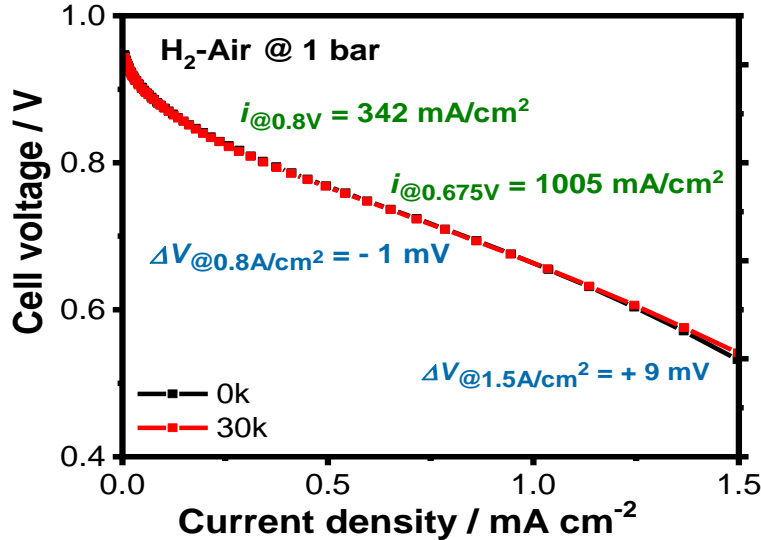
ACCOMPLISHMENT – FUEL CELL ACTIVITY COMPARISON OF SELECTED LP@PF & LP@PFNF CATALYSTS WITH BENCHMARK

Catalyst	Type of Cathode Catalyst	Cathode Pt loading (mg/cm ²)	MEA Mass Activity @0.9 V (A·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 ₃ Co (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 ₃ Co/C	0.11	0.28	220	877

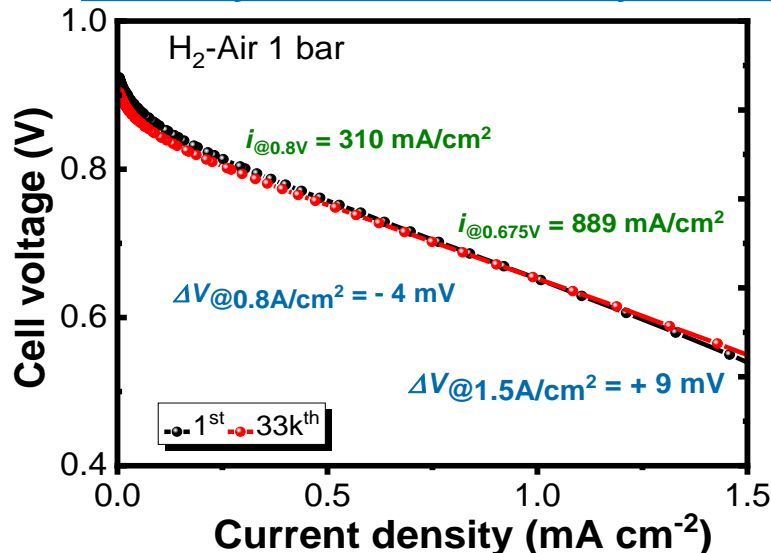
NF = Nanofiber

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

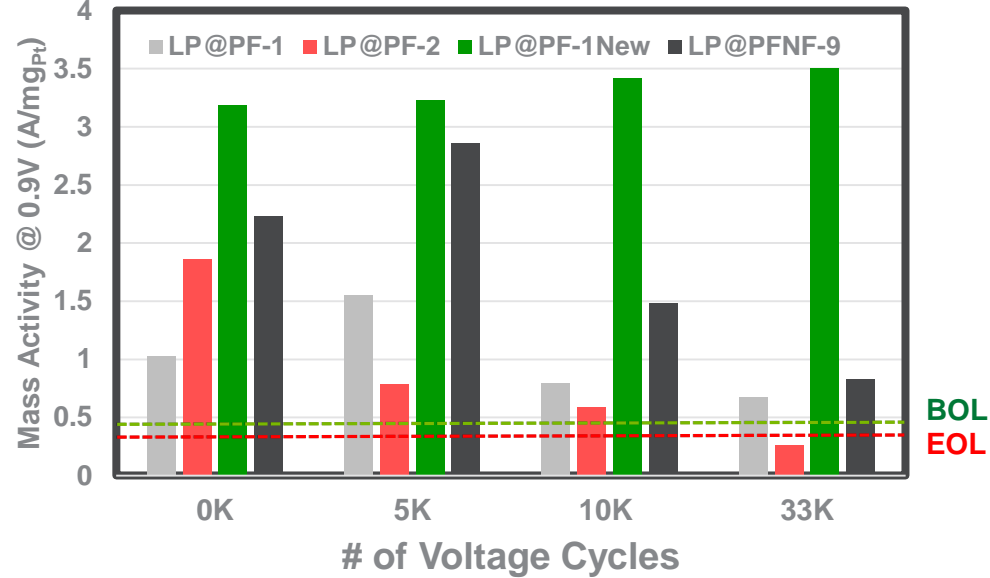
Durability of a LP@PF catalyst in AST



Durability of a LP@PFNF catalyst in AST



Fuel cell mass activity (MA) change during AST



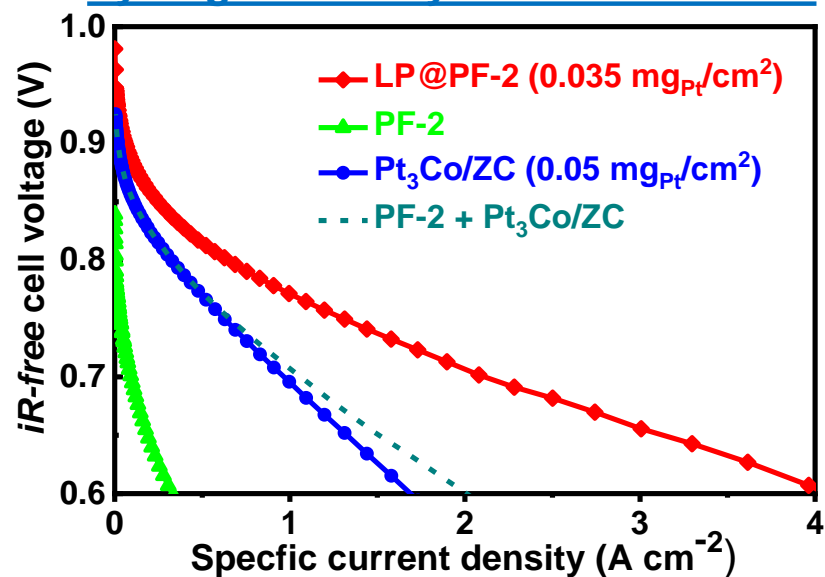
AST condition: Voltage cycling from 0.6 V to 1.0 V @ 50 mV/sec, Anode = H_2 @ 100% RH, Cathode = N_2 @ 100% RH, Temperature = 80 °C, P = 100 kPa (backpressure = 50 kPa)

- 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



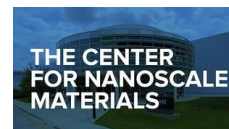
Cathode catalyst weight ~ 1.1 mg/cm², N 211, T = 80 °C, P=100 kPa @ 100% RH, flowrate = 200 ml/min; LP-2 = heat activated Co/Zn-ZIF; Pt₃Co/ZC = Pt₃Co core-shell added over heat activated Zn-ZIF with similar surface area to LP-2 but absent of Co-N₄ site

- Specific activity of LP@PF-2 > twice the sum of LP-2 and Pt₃Co/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)



Northern Illinois
University



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 H₂-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/cm²
- 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/cm² 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
- H₂-air fuel cells with ANL's LP@PF & LP@PFNF cathode catalysts exhibited low voltage drops at 0.8A/cm² and 1.5A/cm² 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

ACKNOWLEDGEMENT

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