Designing Highly Durable Ternary PtCoM Intermetallic Catalysts on Advanced Support for Heavy-Duty MEAs

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University at Buffalo, The State University of New York (SUNY)

DOE project award #: DE-EE0010750

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AMR Project ID #: FC369

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Project Goals

- Develop and scale up highly active and stable innovative **PGM catalysts** (*e.g.*, highly ordered PtCo(Ni)M ternary intermetallic) with well-controlled nanoparticle (NP) size (< 4 nm), composition, and strengthened support-metal interactions, aiming to significantly improve MEA performance and durability for HDVs.
- Integrate the scaled-up **PGM** cathode catalysts with **advanced support** (carbon, oxide or/and carbon/oxide nanocomposite) and **ROS-removal scavengers** to significantly improve MEA performance and durability.
- Identify the optimal variables for preparing inks, constructing electrodes, and **fabricating large-scale MEAs** (>50 cm^2) using the newly developed scaled-up catalysts to increase power density and long-term durability.
- Meet or exceed DOE targets:
  - PGM loading in MEA: **< 0.3 mg/cm²**
  - Sufficient activity and long-term Durability: > **1.07 A/cm²** at 0.7 V and 2.5 kW/g_{PGM} after equivalent 25,000-hour operations based on the *M2FCT* protocols.

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Overview

Timeline

- Project Start Date: 09/01/2023
- Project End Date: 08/31/2026

Budget

- Total Project Budget: $3.3 M
  - Federal share: $2.67 M
  - Cost share: $0.63 M

Teams and Partners

- **University at Buffalo, SUNY (**Project Leader): *PGM catalysts and carbon support*
- **Washington University St. Louis:** *Non-carbon support or oxide/carbon composite*
- **Pacific Northwest National Laboratory**: *Effective scavengers into support*
- **Ballard Power System Inc:** *MEA design, fabrication and testing*

Barriers Addressed

- Insufficient performance and durability of heavy-duty fuel cell MEAs
- Scale-up of catalyst synthesis
- Scalable MEA design and fabrication

M2FCT Consortium:

LANL, ORNL, ANL, NERL and LBNL.

- MEA performance verification
- Electrode design, diagnosis, and multiple-scale simulation
- Advanced spectroscopy and microscopy characterization

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Relevance and Impact

Hydrogen Fuel Cells for Heavy-Duty Vehicles

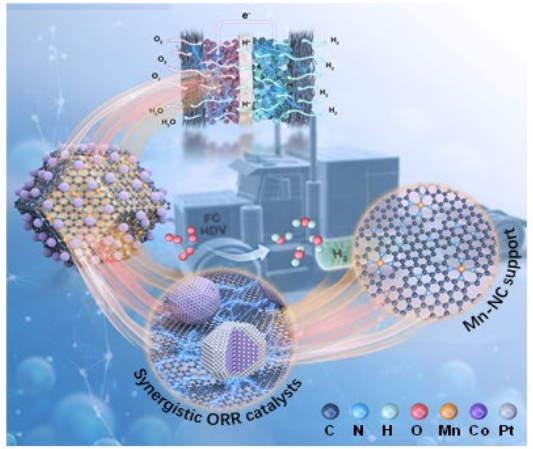
Weight: Hydrogen is significantly more energy dense than batteries

Distance: Longer driving ranges due to high energy density of hydrogen and quick refueling time

Downtime: Refueling takes minutes over battery recharging for hours

Cost: Lowest-cost to decarbonize heavy-duty road transport; R&D advances, newer fuel cells require less precious metals

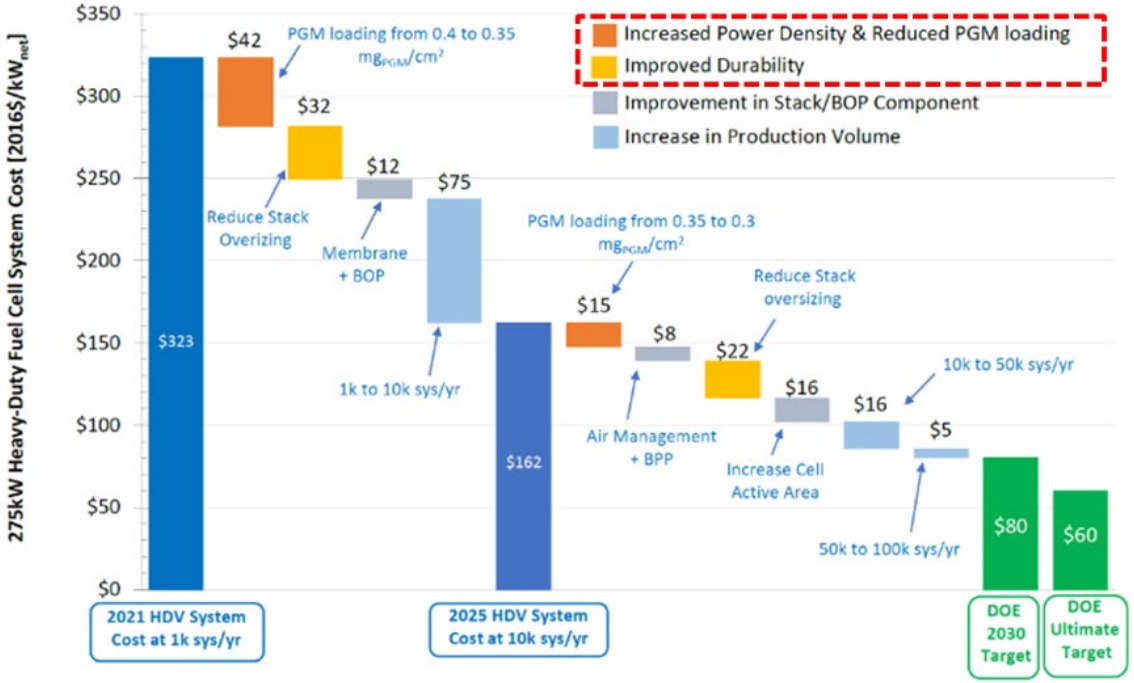
Infrastructure: Less demands for H_2 infrastructures due to pre-determined routes and stops.



Impact and Significance

- **2.5 kW/g_{PGM}** power (**1.07 A/cm² at 0.7 V**) with lifetime up to **25,000** hours.
- Meet DOE cost target of **$80/kW$_{net}$**
- Developing **high-performance catalysts** can significantly reduce the cost and improve energy efficiencies.

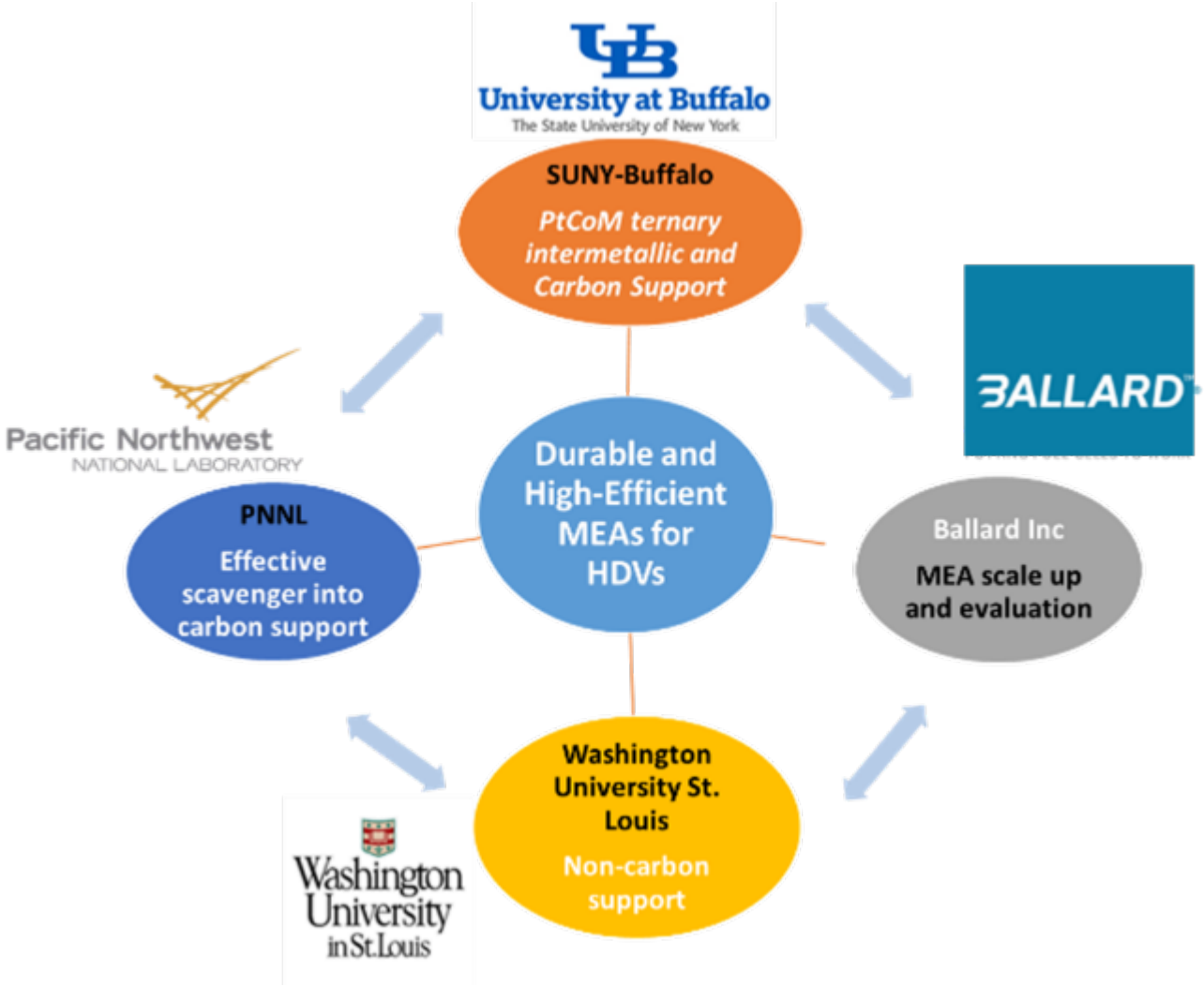
Catalyst is the Key to Performance and Durability



https://www.umicore.com/en/newsroom/fuel-cells-battery-difference/

Technical Approaches and Teams

Integrate highly durable and scalable **PGM catalysts** with **advanced support** and **scavengers**, aiming to design high-efficient and durable MEAs for HDVs



- **SUNY-Buffalo** will develop innovative ternary PtCoM intermetallic catalysts and MOF-derived carbon to improve catalyst and support stability under HDV conditions (Profs. Gang Wu, Hao Zeng, and Jim Zheng).
- The proposed project will further expand current carbon support to other promising non-carbon or oxide/carbon composite support by leveraging the substantial expertise of *Prof. Vijay Ramani*'s team at **Washington University St. Louis (WUST)**.
- The project will benefit from the **PNNL** (*Dr. Yuyan Shao*)'s new strategy to incorporate effective scavengers into support to mitigate carbon and catalyst corrosion under HDV conditions.
- Importantly, **Ballard Power System Inc** *(Dr. Lijun Yang* and *Alan Young)* will leverage Ballard's substantial expertise in ink preparation and electrode design to achieve further enhanced performance and durability of MEAs consisting of ternary PGM catalysts and advanced support.

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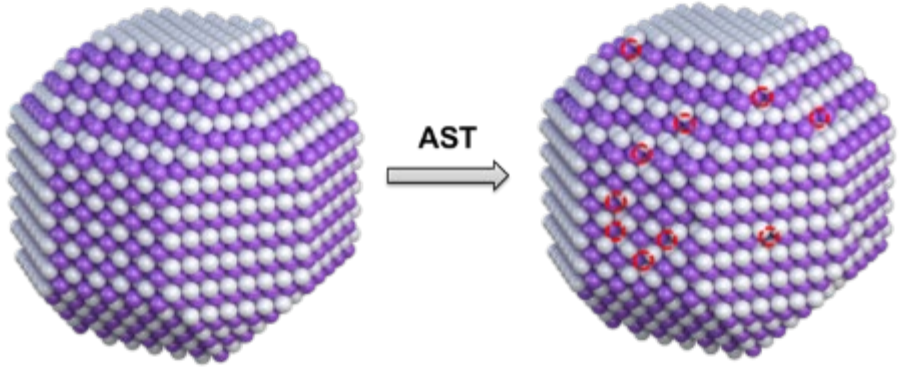
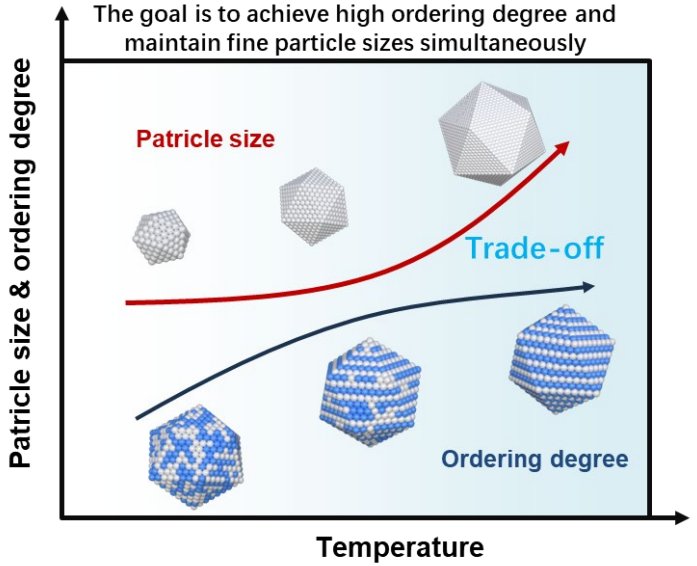
Approaches: Ordered PtCoM Intermetallic Catalysts

Relative to **traditional PtCo solid solutions**, highly **ordered PtCo intermetallics** have been clearly identified as advanced catalysts with intrinsically enhanced activity and stability.

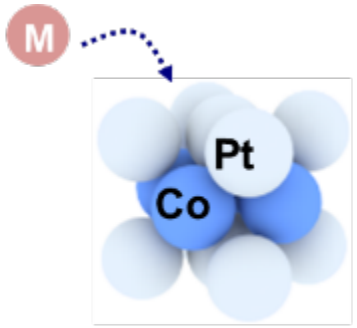


- **Higher ordering degree is demanded for improved stability.**
- **Ordering process requires high-temperature treatments, challenging size control (3-5 nm desired).**

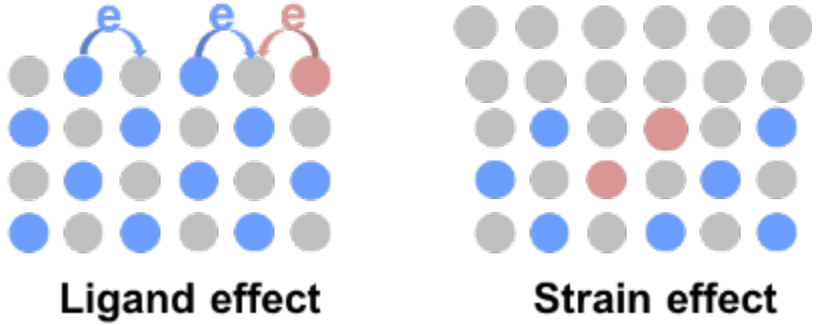
Trade-off between particle size and ordering degree



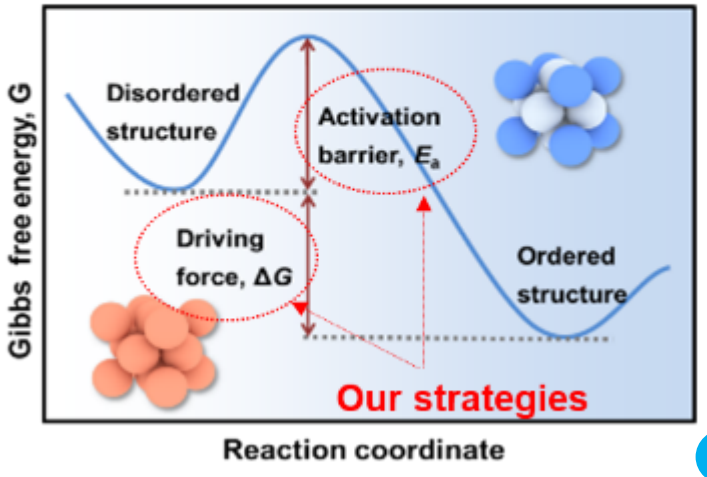
Innovative Ternary PtCoM Catalysts



Better opportunities for modulations



Introducing the third metal to increase order degree while maintaining fine particle sizes



Introducing M in PtCo to achieve higher ordering degree is beneficial for activity and stability enhancement

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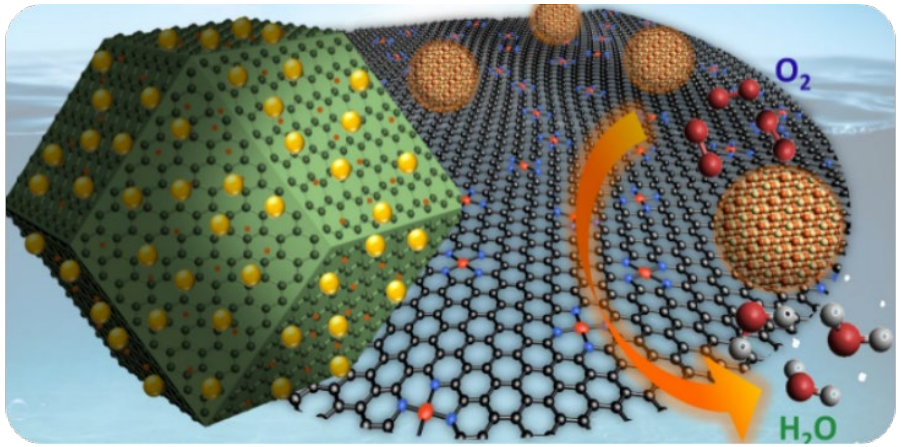
Approaches: Critical Role of Carbon Support

Importance and Challenges of Carbon Support

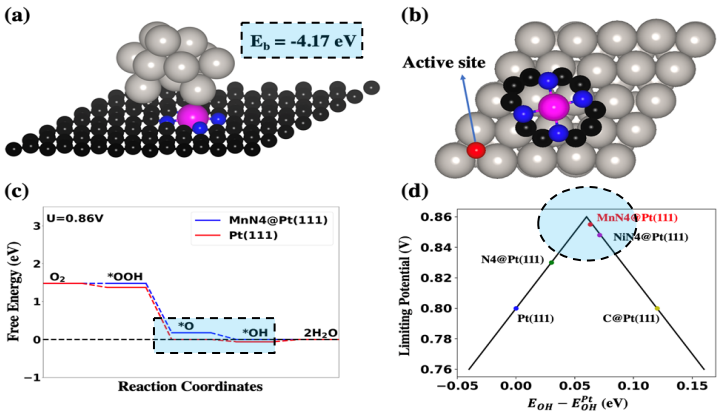
- Carbon is the primary component in catalyst layers by volume and weight, crucial for PGM catalyst activity and durability in MEAs.
- Current high-surface-area **amorphous carbon black** supports are not electrochemically stable.
- **Graphitized carbons** suffer from low surface areas and weak metal-support interactions causing significant aggregation of PGM nanoparticles.

Solutions and Innovations: PGM-free M-N-C carbon (M: Mn, Co, Ni, or Ce) containing atomic metal sites and nitrogen dopants may provide a new opportunity to design advanced carbon with favorable **physical** and **chemical** properties.



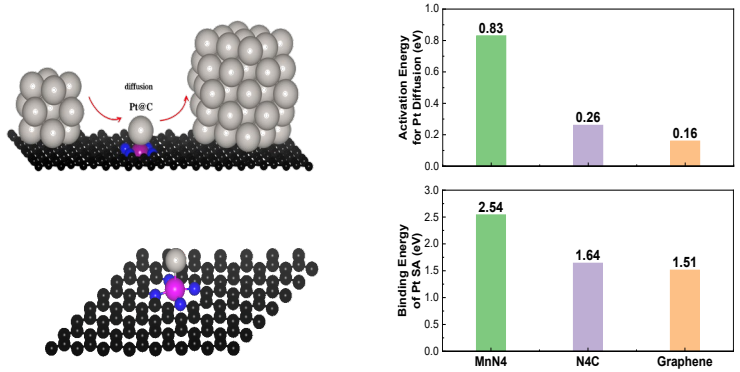
Theoretical Predictions

The integration of MnN_4 sites in carbon and Pt (111) yields the **enhanced intrinsic ORR activity** and **stability**.



Zeng et al, J. Am. Chem. Soc., 145, 17643, 2023.

MnN_4 site shows **stronger interaction** with Pt single atom, increased the **energy barrier** for the Pt dissolution.



Zeng et al, ACS Catalysis, 13, 11871, *2023.*

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Approaches: Safety Planning and Culture

UB and **Ballard** teams will be using moderate amounts of hydrogen (H_2) (<10 slpm) for fuel cell experiments, whereas **PNNL** and **WUST** will use very low amounts of H_2 (<0.1 slpm) for testing catalysts by rotating disk electrode.

- During the fuel cell tests, only one hydrogen cylinder is used in the laboratory. The hydrogen is plumbed to the test stand through braided stainless-steel tubing with a flame arrestor located directly after the regulator. An audible hydrogen alarm is placed at the test stand.
- The maximum hydrogen flow rate is 0.5 slpm with a pressure ranges from 0-15 psig in the experiments. the hydrogen enters the fuel cell that consists of a polymer electrolyte membrane with platinum or platinum-substitute electrodes on either side. The fuel cell features heaters and thermocouples. The cell is typically operated at 80°C and no more than 90°C. The electrochemical reactions generate a voltage and a current that is controlled by the electronic load in the test stand. The gases are sealed from each other within the cell and do not mix.
- Typical levels of use for each test stand are 5 days/week, 8 hours per day with 0.2 slpm H_2 flow rate.

Risk Mitigation plans:

Each team has regular employee training , safety reviews, self-audits, and emergency response plans. This vulnerability study uses a Failure Mode Analysis to determine the primary risks associated with the Hydrogen Fuel Cell Project. Each part of the system has been assessed for likely failures and mitigation measure are provided to minimize the impact, or likelihood of failur The primary failure modes of this system would be: *(i) l*oss of power, (ii) leak at the hydrogen tank, or hydrogen lines, (iii) leak i the hydrogen fuel cell test system, (iv) fire inside the hydrogen fuel cell test system, and (v) impact from outside force, nearby work.

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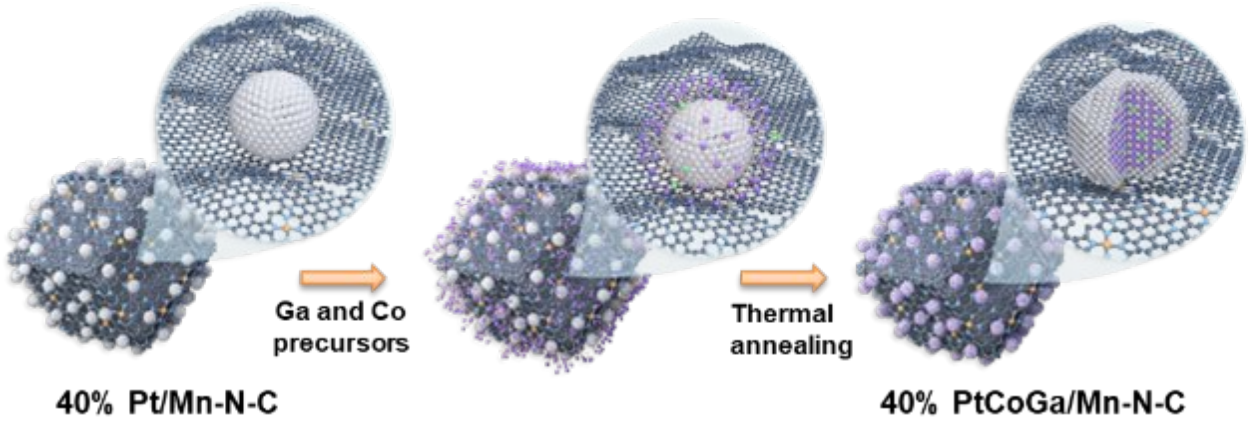
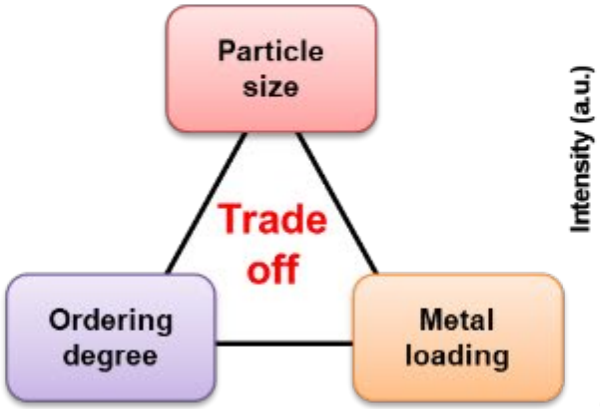
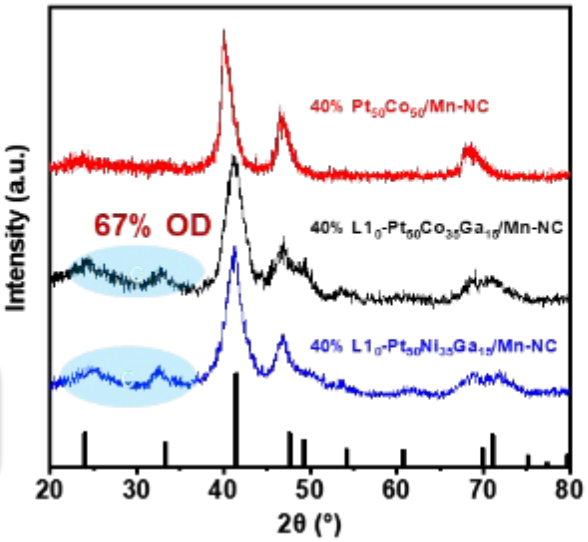
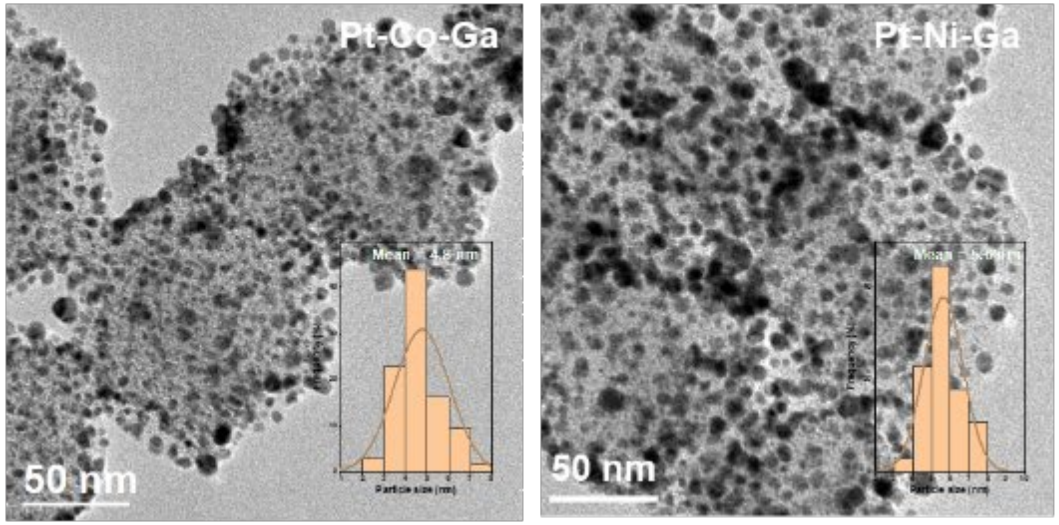
Accomplishments and Progress

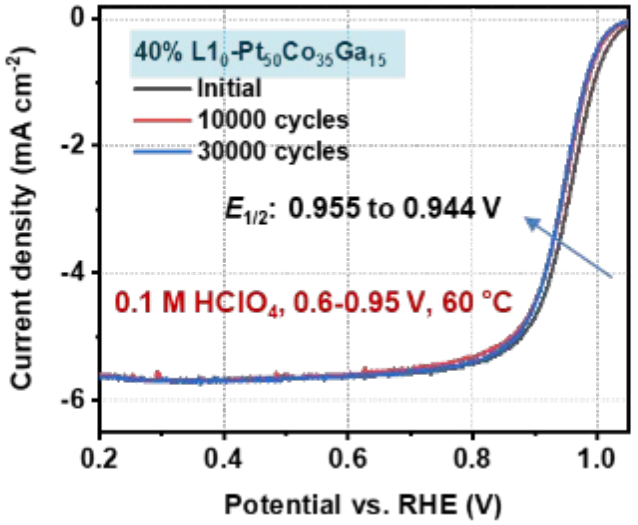
PtCo(Ni)Ga Intermetallic Catalysts

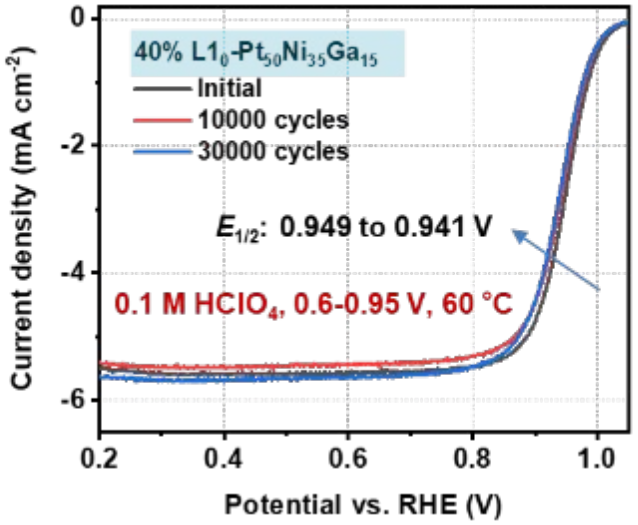












- Adding Ga can promote the ordering process, generating **small particles with high ordering degree**
- Promising activity and stability during the RDE tests at 60°C (~10 mV loss in $E_{1/2}$ after 30,000 potential cycles).

PtCo(Ni)Ga Intermetallic Catalysts: MEA Performance (5 cm²)

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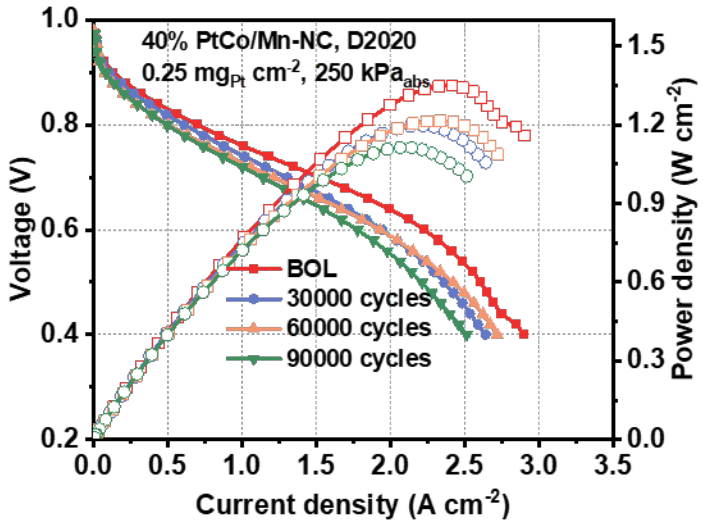
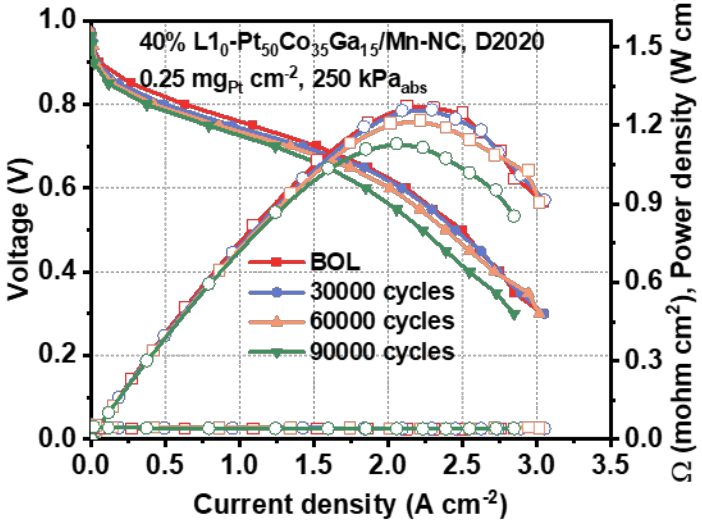
PtCo



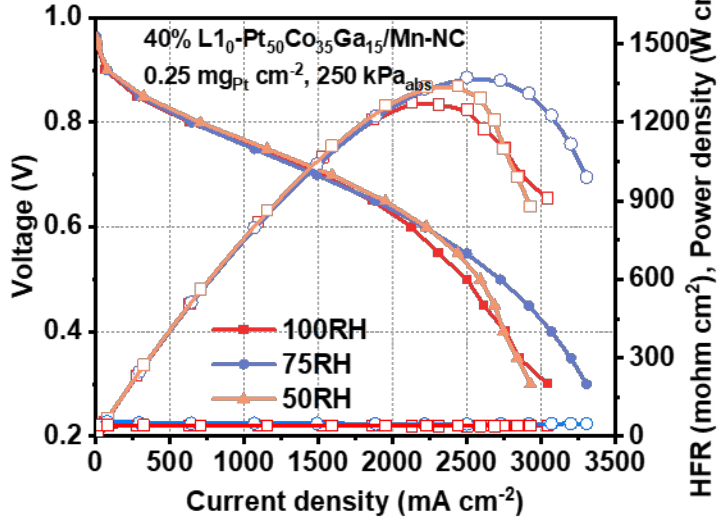
1.53 A cm^{-2} at BOL; 1.14 A cm^{-2} at 90k cycles

PtCoGa

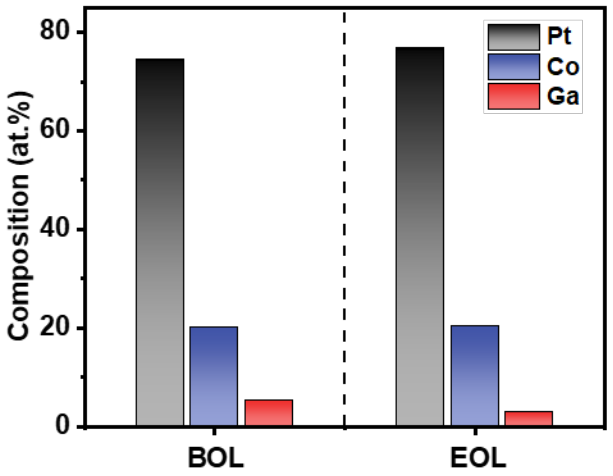


1.53 A cm^{-2} at BOL; 1.24 A cm^{-2} at 90k cycles

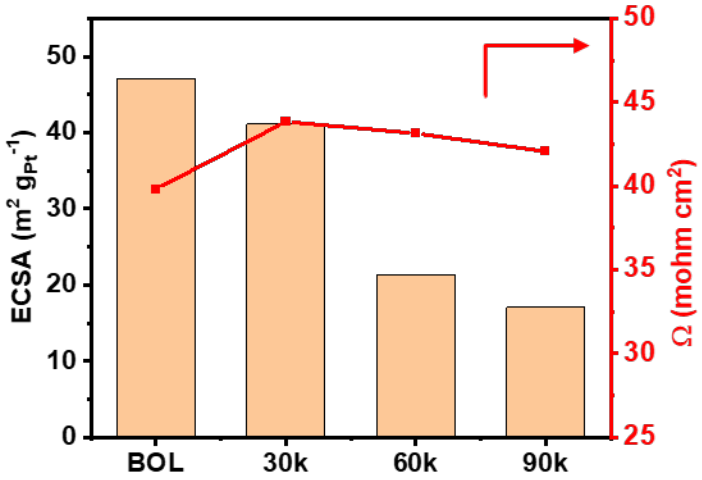
PtCoGa



Elemental content by XRF



ECSA and HFR

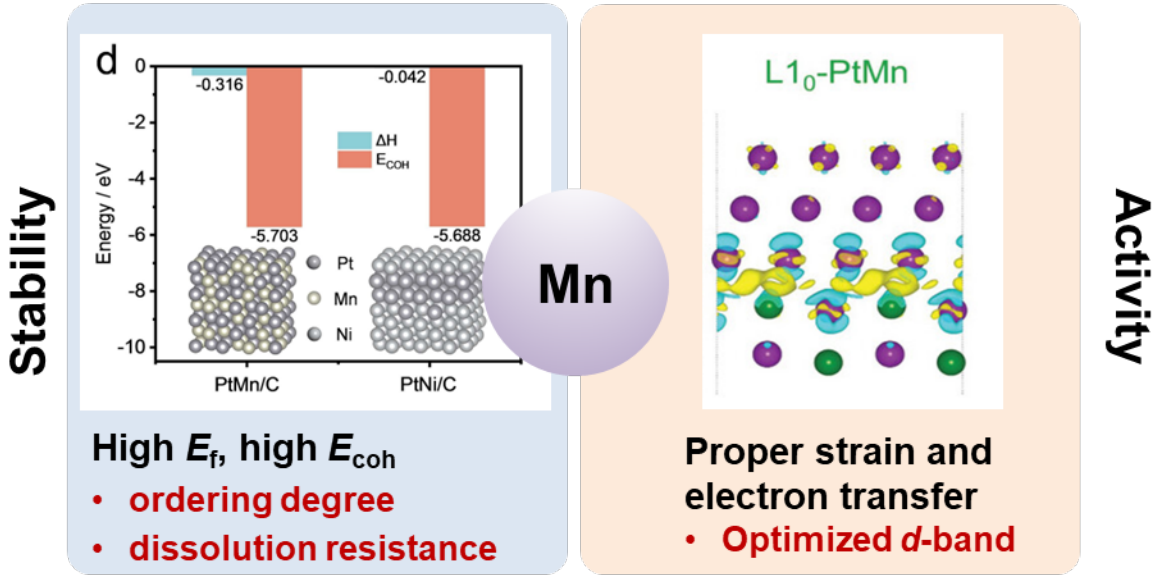


- PtCoGa catalysts exhibited improved durability under HDV conditions, relative to traditional PtCo catalysts.
- After 90,000 voltage AST, the MEA performance tended to be stabilized, retaining **1.24 A/cm² at 0.7 V (18% loss).**
- HFR values remain nearly the same during the AST, suggesting insignificant membrane/ionomer contamination with dissolved Co or Ga ions.

Accomplishments and Progress

PtCoMn Intermetallic Catalysts

Rational catalyst design

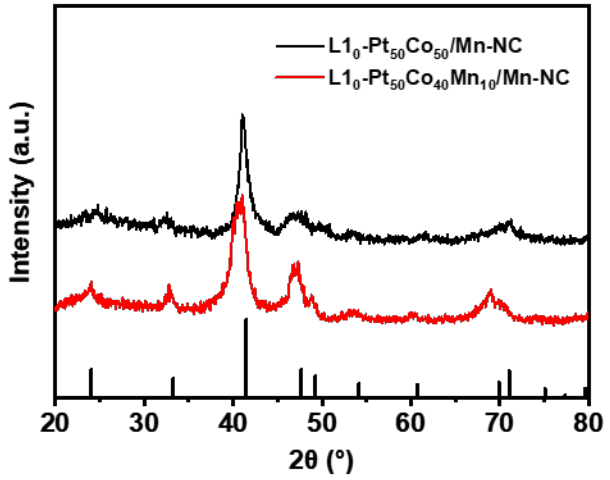


High E_f, high E_{coh}
- ordering degree
- dissolution resistance

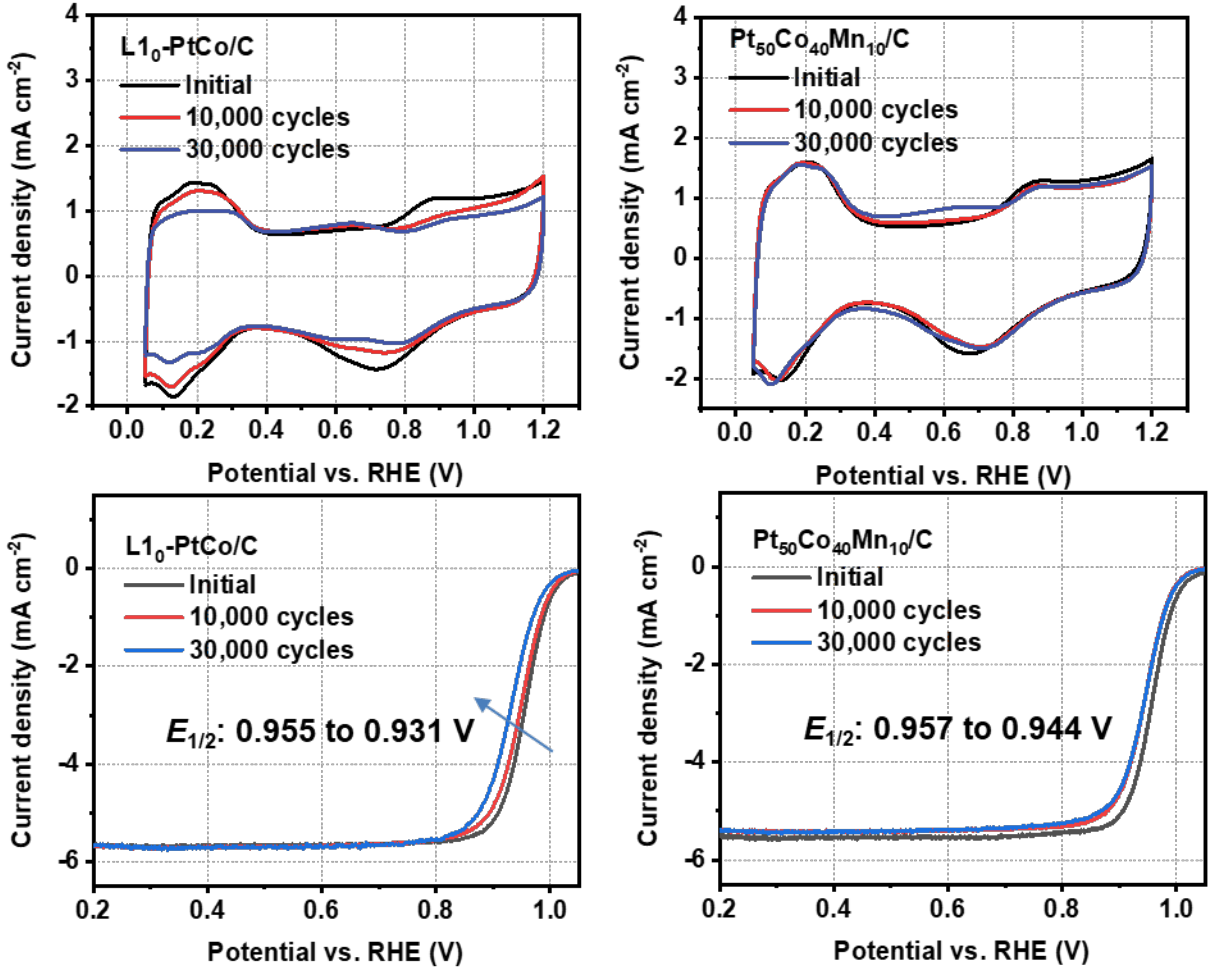
Proper strain and electron transfer
- Optimized *d*-band

Guo et al., *Angew. Chem.Int. Ed.* 2024, e202317987.

- Mn may improve stability by forming strong bond with Pt/Co or increasing ordering degree
- The $L1_0$-$Pt_{50}Co_{40}Mn_{10}$ shows high ordering degree of **~78 %** (I_{110}/I_{111})
- Smaller particle size compared to traditional $L1_0$-PtCo (**4.8 vs. 7.2 nm**)



RDE activity and stability



- Adding Mn does not compromise the high ORR activity of PtCo catalysts ($E_{1/2}$ ~0.955 V).
- The optimal 10% Mn doping into PtCo catalysts can improve the stability, with **only 12% ECSA** and **13 mV $E_{1/2}$ loss**.

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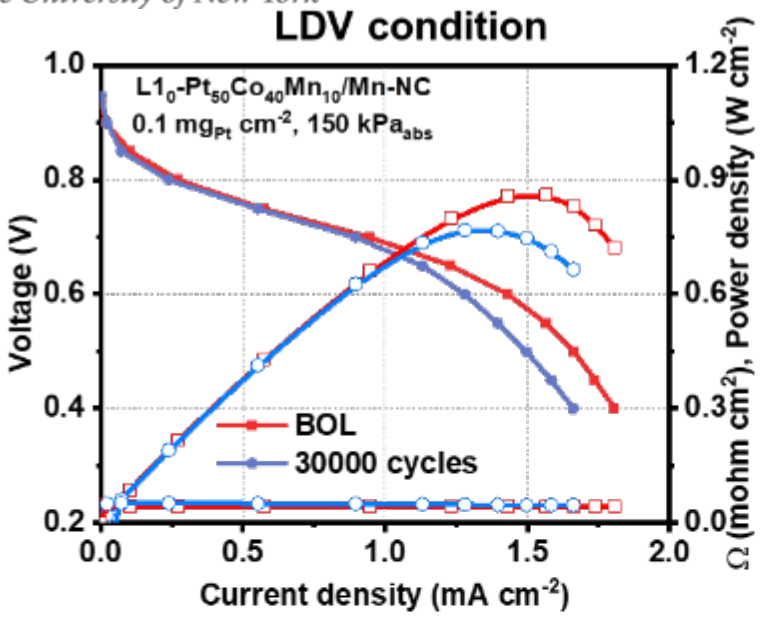
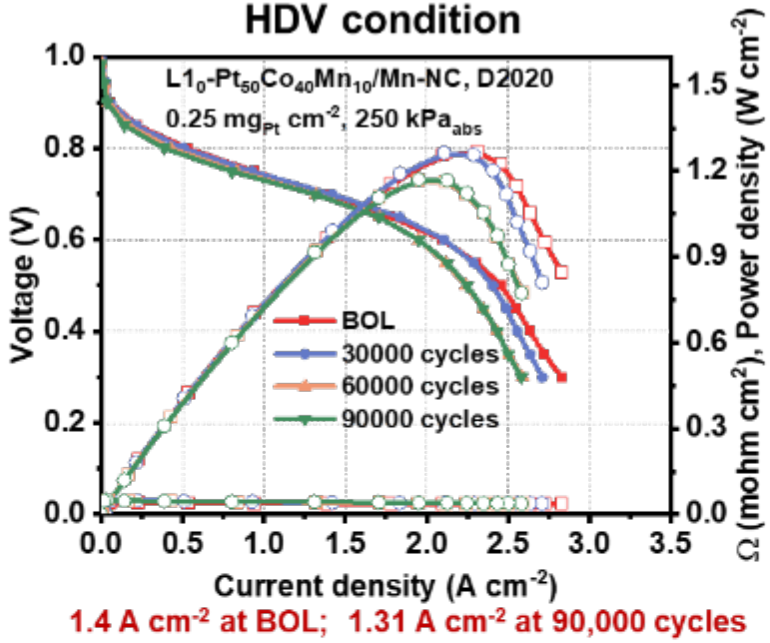
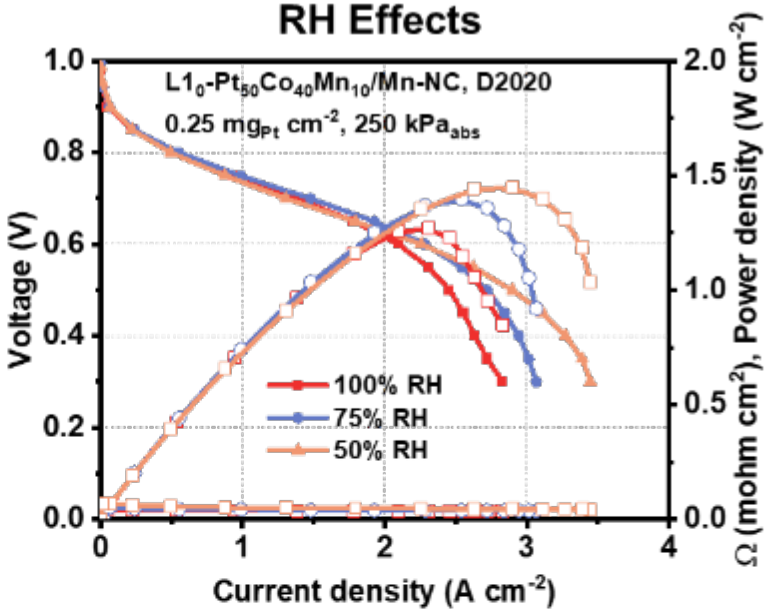
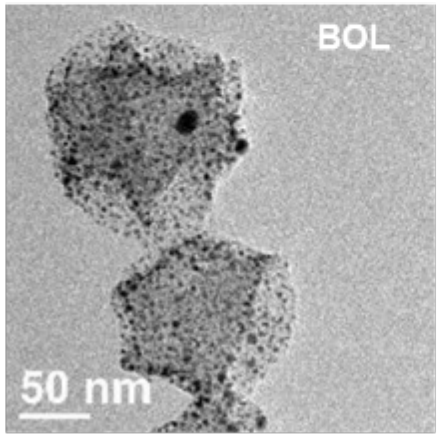
PtCoMn Intermetallic Catalysts: MEA Performance (5 cm^2)

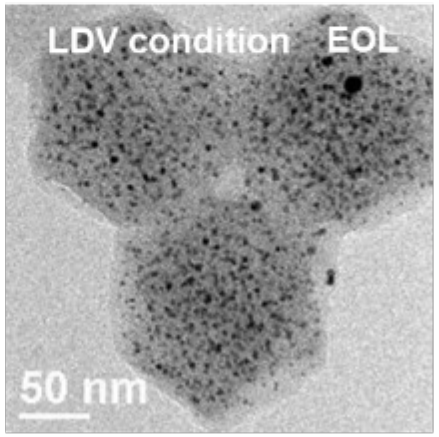


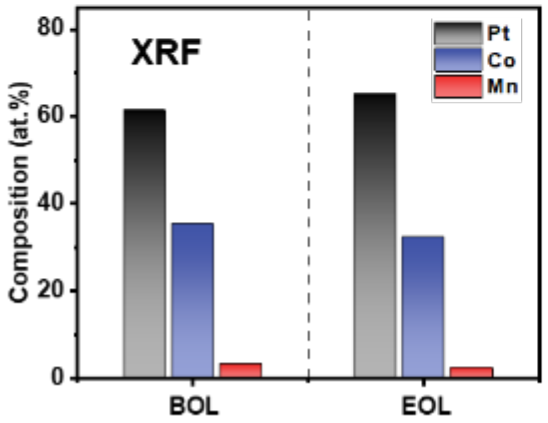


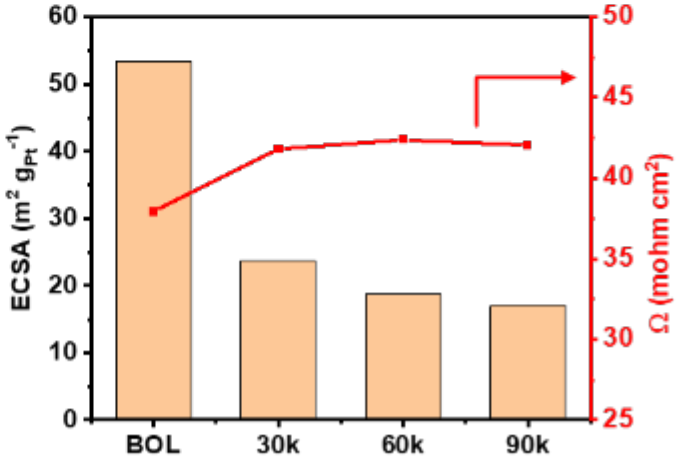
1.4 A cm^{-2} at BOL; 1.31 A cm^{-2} at 90,000 cycles











- Good stability under both of LDV and HDV conditions
- After the 90,000 voltage AST, the MEA performance tended to be stabilized, retaining **1.31 A/cm^2 at 0.7 V (5% loss)**
- Similar particle size and negligible Co/Mn leaching after the 30,000-cycle AST under LDV conditions.

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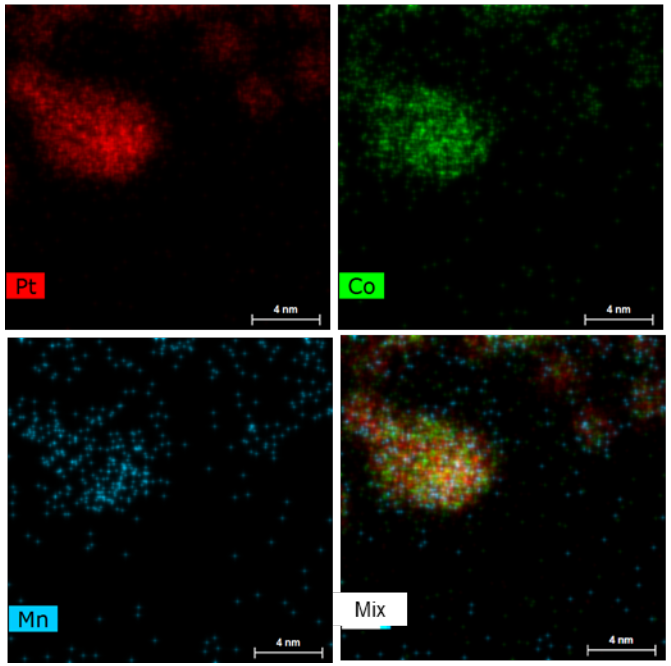
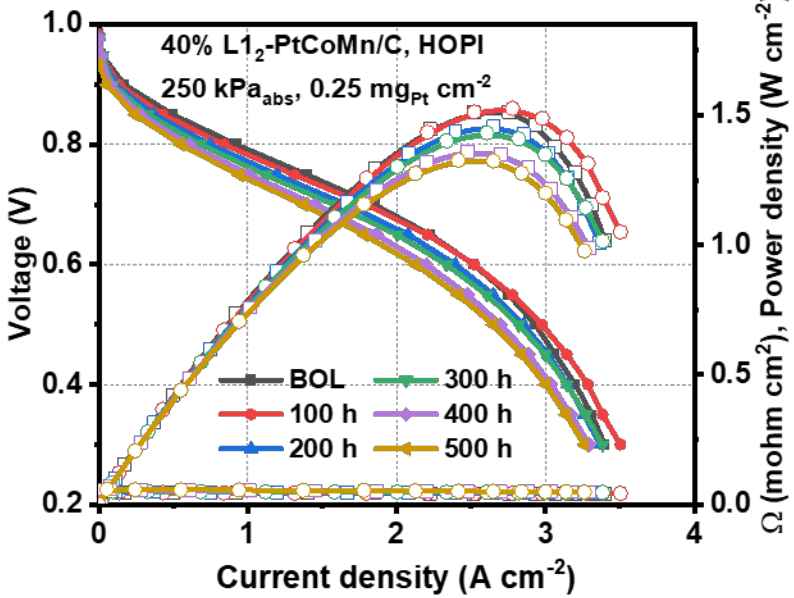
M2FCT AST Protocol Studies

Cycle: square wave between 0.675 V (30s) and 0.925V (30s), single cell **5 cm²**
Duration: 500 hours and 30,000 cycles
Each cycle time: 1 minute
Temperature: 90 °C
Relative Humidity: 50%/50% anode/cathode
Fuel/oxidant: H_2/air (500 and 2500 sccm)
Pressure: 250 Kpa

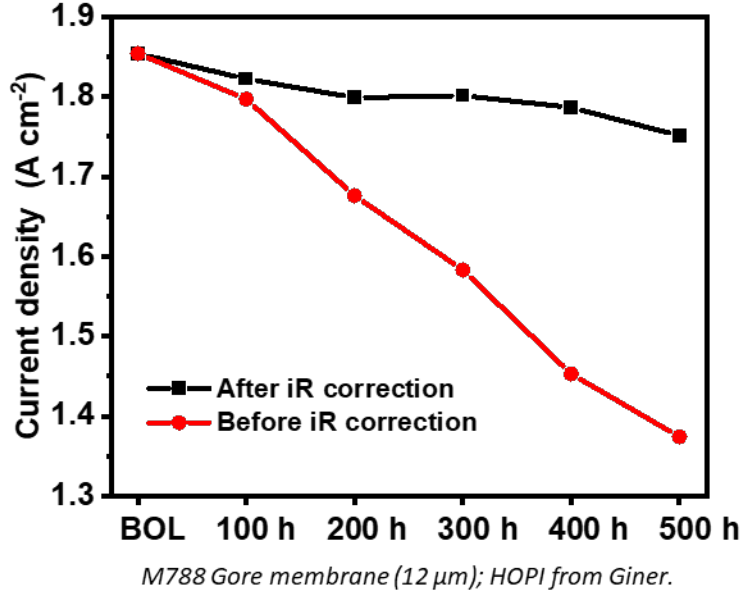
PtCoMn/ZIF-NC



VI Polarization Plots

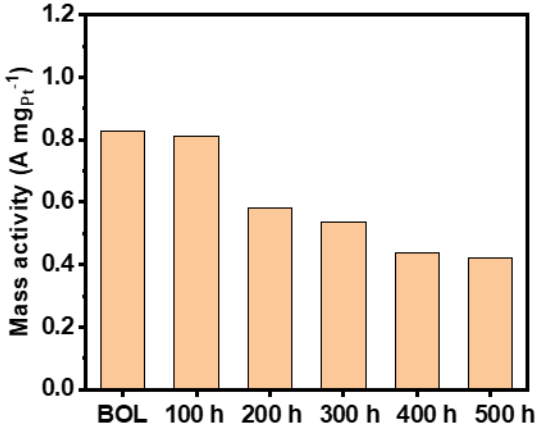


Performance at 0.7 V

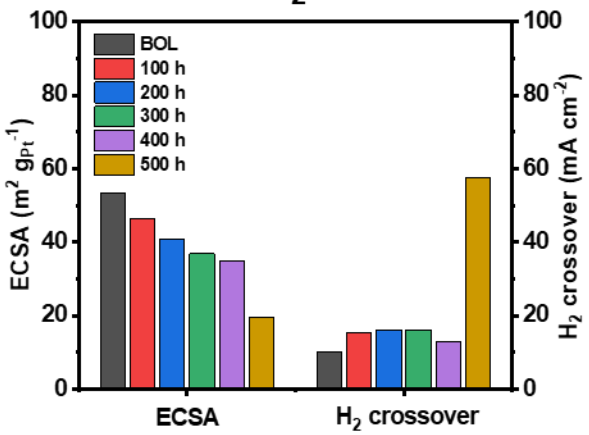


M788 Gore membrane (12 µm); HOPI from Giner.

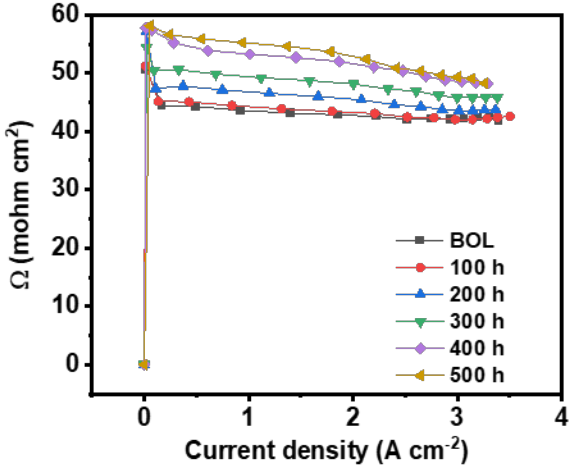
Mass Activities



ESA and H_2 Crossover



HFR



- After the **500-hour AST (30,000 voltage cycles)**, the MEA retained **1.37 A/cm² at 0.7 V.**
- Performance decay partially was caused by **HFR increment** and **increased H_2 crossover**; only 5% loss after IR correction.

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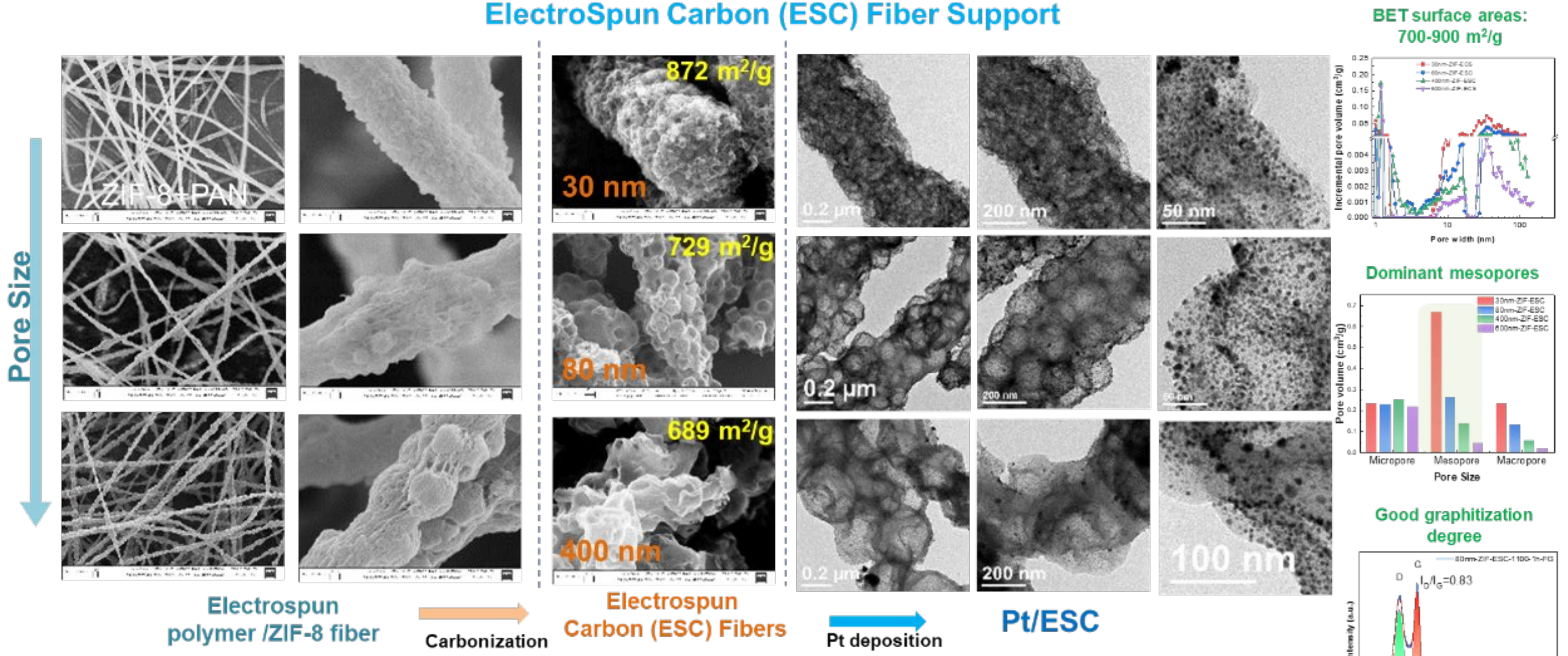
Accomplishments and Progress

ElectroSpun Carbon (ESC) Fiber Support



BET surface areas: 700-900 m^2/g

Dominant mesopores

Good graphitization degree

- Adding ZIF-8 precursors with different sizes to electrospun fibers, the **size-controllable mesopores** can be created.
- The **BET surface** area and **O_2 mass transport** can be boosted with the obtained ESC carbon support.
- Pt NPs present a **uniform distribution** on the ESC fiber support, ensuring sufficient ECSA of the Pt catalysts.

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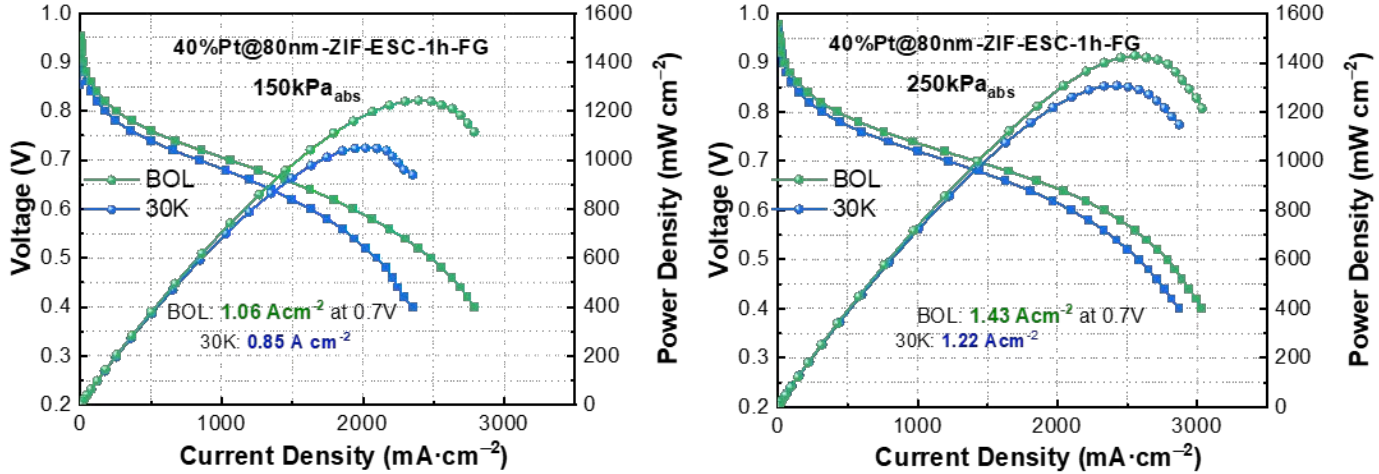
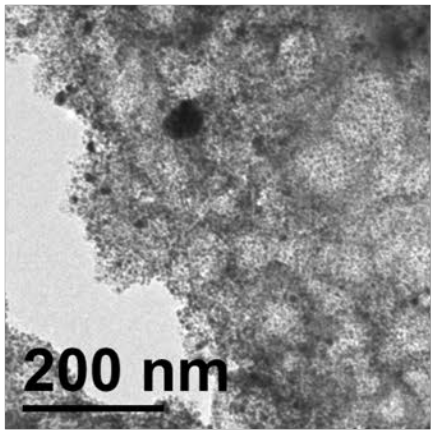
PGM Catalysts on the ESC Fiber Support (MEA 5 cm²)

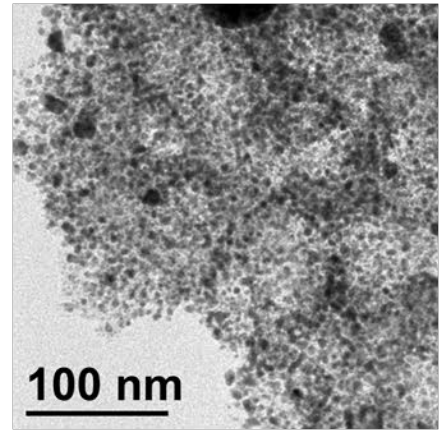
Pt catalysts

MEA Performance and Durability



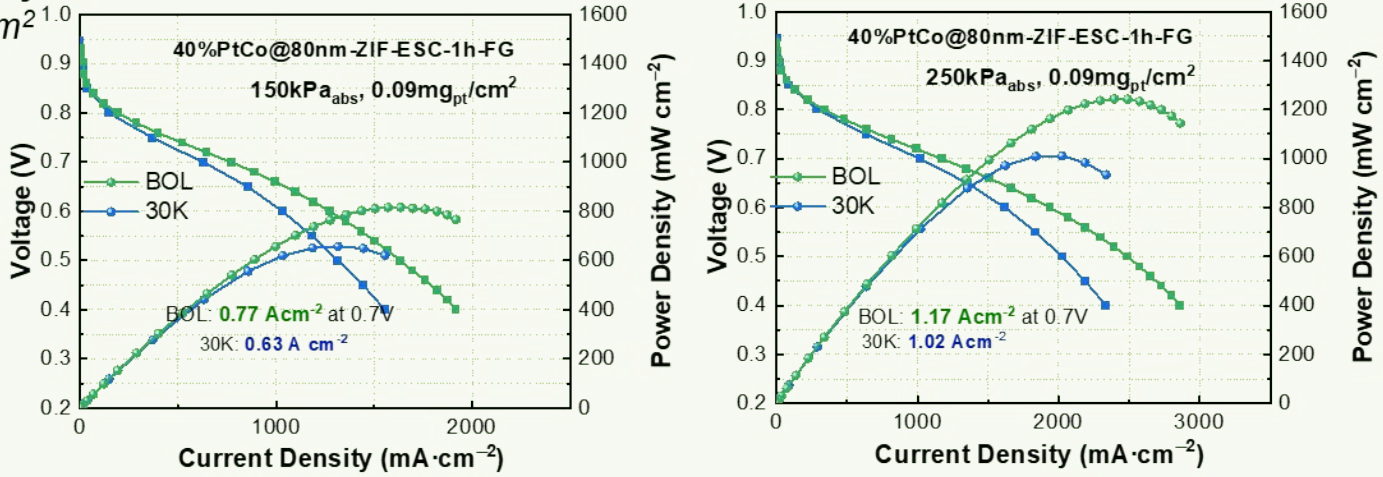
Morphologies

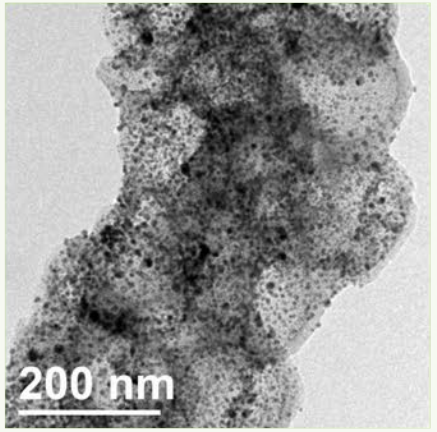


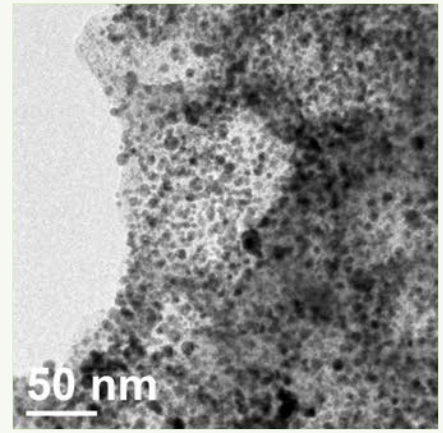


PtCo catalysts

0.09mg/cm²





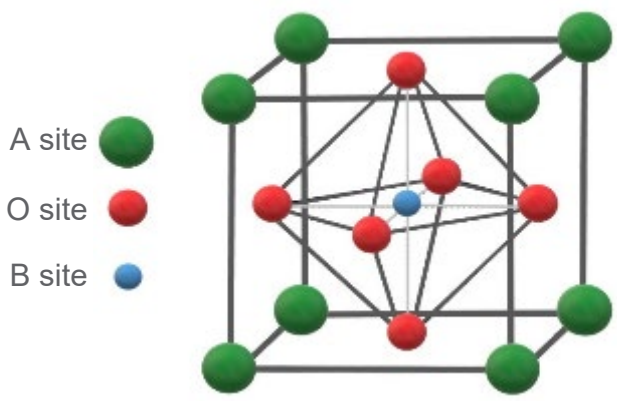


Initial effort indicated that the electrospun carbon fiber supported Pt and PtCo catalysts presented promising performance and durability at a low Pt loading.

Accomplishments and Progress

Integration of ROS Scavengers in PGM Catalysts

Perovskite oxide (ABO_3) for ROS scavenger



- A is for alkali metal to achieve high pK_a
- B is for radical scavenger

A metal candidate: Ba, Sr, and La
B metal candidate: Ce, Zr, and Mn

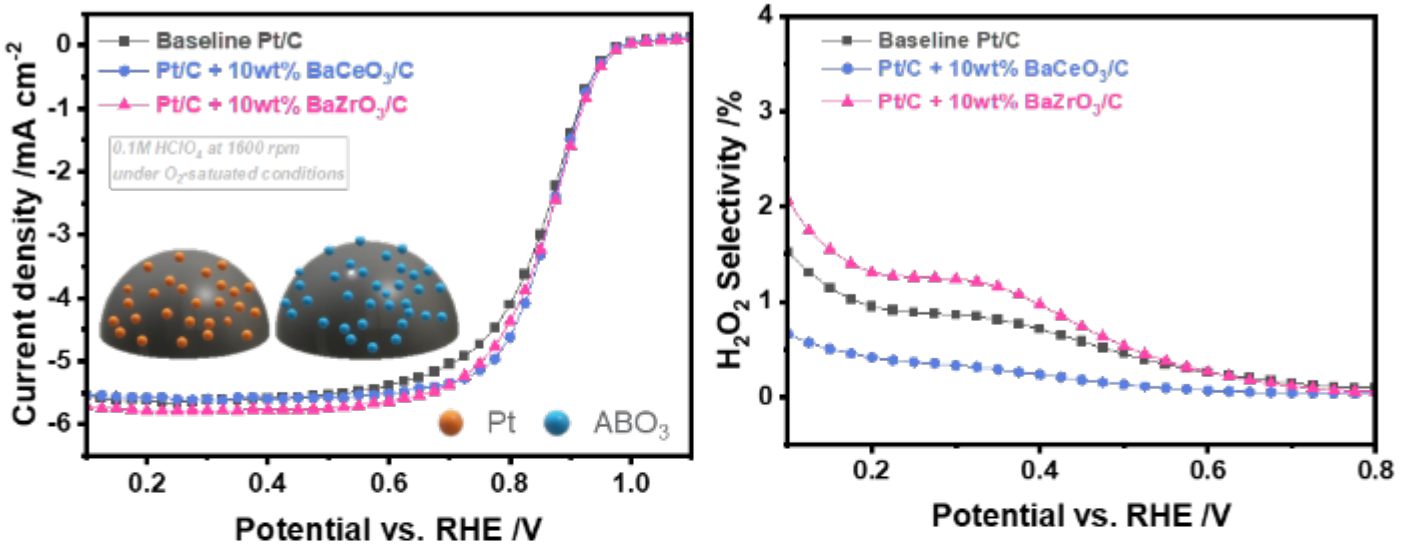
Innovation

- ORR activity was evaluated using different ROS loading methods. (toward 4.3)
- $BaCeO_3$ nanoparticles not only had lower H_2O_2 selectivity than baseline Pt/C but also improved ORR activity.

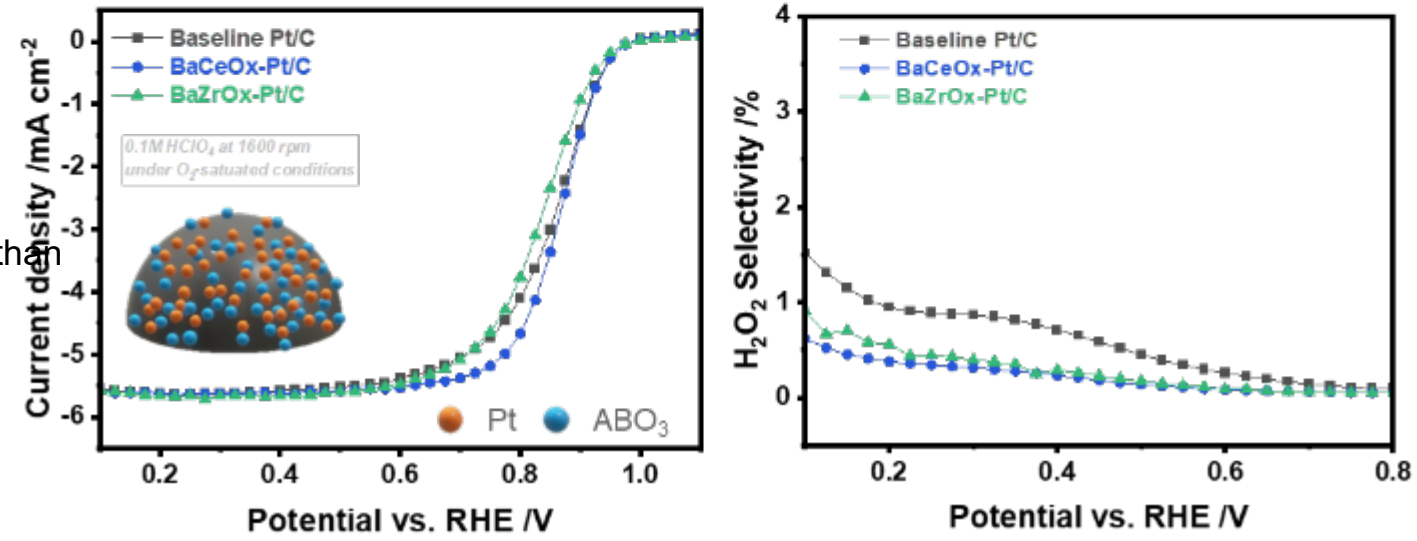
Next plan

- Assessment pK_a and stability of perovskite.
- Apply PtCo alloy catalyst using this approach

Physical mixing with ROS



Direct loading onto the PGM catalyst

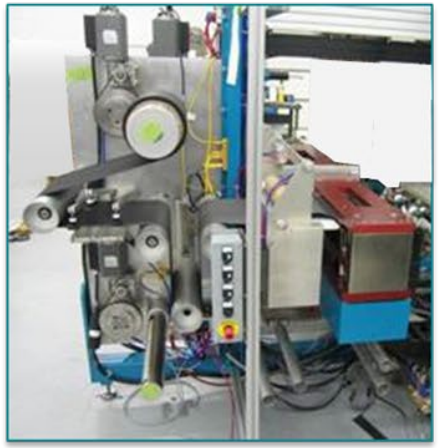


Accomplishments and Progress

Ballard Power Systems Task Plan and Work Progress

MEA Fabrication

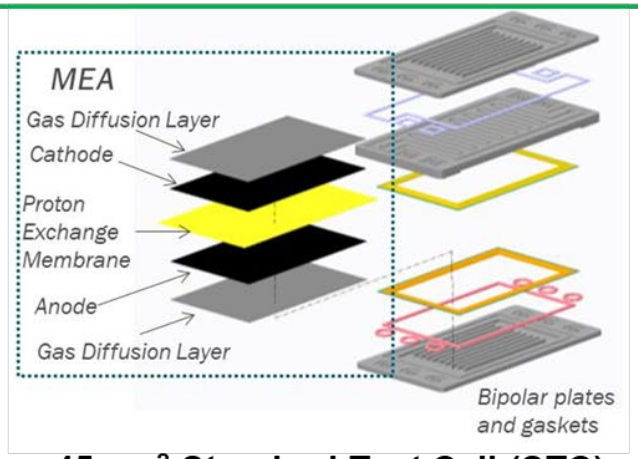
- Material characterizations
- Ionomer optimization
- Scalable ink mixing and coating



Roll-to-roll coating

MEA Evaluations

- 45 cm^2 MEA in-situ diagnostics
- Pt dissolution AST development
- Membrane durability impact
- New catalyst Go/ No-Go decision



45 cm^2 Standard Test Cell (STC)

Degradation Mechanism Understanding

EOT diagnostics

+

Ex-situ failure analysis

↓

Voltage degradation model

↓

Lifetime forecast

In the progress of benchmarking commercial Pt/C and PtCo/C catalysts in 45 cm^2 MEA

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Responses to Previous Year Reviewers' Comments

This project is a **new** one and was not previously reviewed last year

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Collaboration and Coordination

- **Technical Manager and advisor from DOE**
  - **-- Dr. William Gibbons**
  - **-- Dr. Bryan Dreyfus**

- **Collaborators**
  - **-- Collaborations with the M2FCT Consortium:**
    - *MEA performance verification carbon corrosion (**LANL**)*
    - *Electrode design, diagnosis, and multiple-scale simulation (**NERL** and **LBNL**)*
    - *Advanced spectroscopy and microscopy characterization (**ANL** and **ORNL**)*
    - *Develop AST protocol between Ballard and M2FCT (**LANL, NERL,** and **LBNL**)*
  - **-- DFT calculations (no cost): Prof. Guofeng Wang at University of Pittsburg**
  - **-- Innovative HOPI ionomers (no cost): Giner Inc.**

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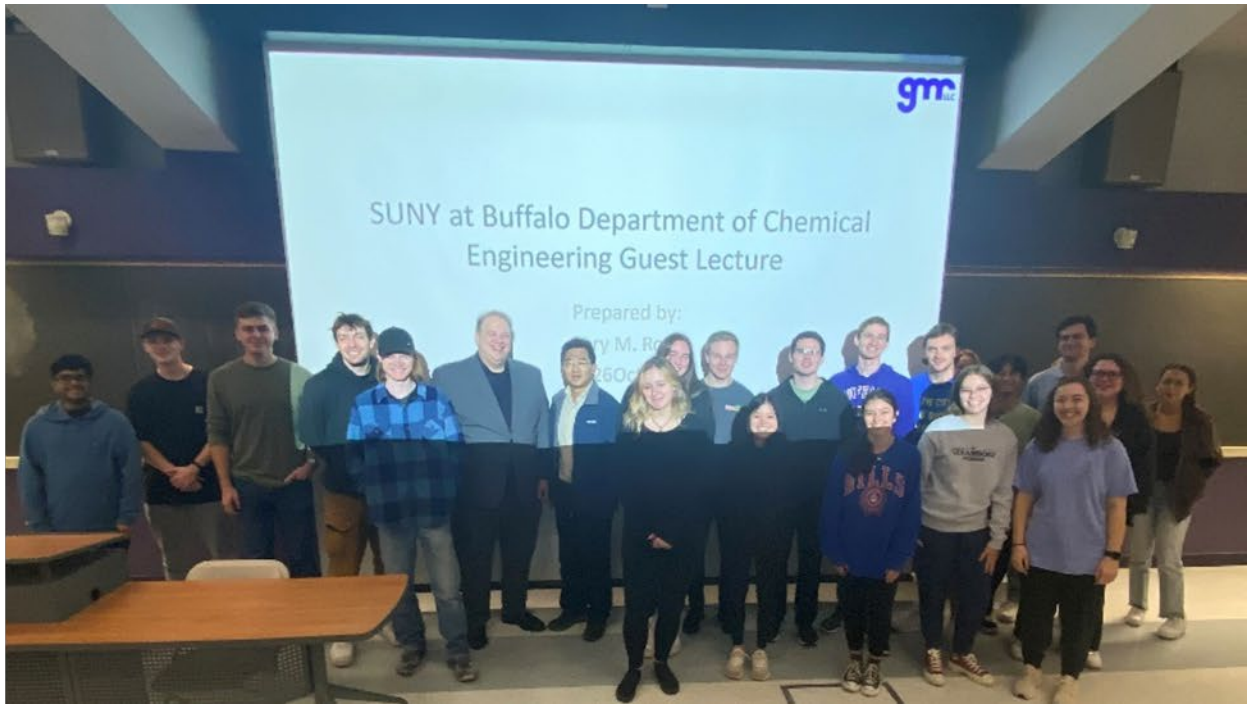
DEIA/Community Benefits Plans and Activities

- **The SUNY-Buffalo team has hired two Ph.D. students and one postdoc for the DOE project. One is a female Ph.D. student (Sarah Hamdan, U.S. citizen) originally from the Mideast for the DOE project (*left*). Currently, she is in Dr. Wu's group and has learned catalyst synthesis, characterization, and applied electrochemistry for fuel cell technologies.**
- **Dr. Wu at SUNY-Buffalo organized a seminar and invited Gary Robb, who is a consultant to the DOE/Hydrogen and Fuel Cell Technologies Office with over 25 years' experience in the clean energy sector, to give a lecture about the perspective of hydrogen and fuel cell technologies to undergraduate students at SUNY-Buffalo from majority underrepresented groups (*right*).**



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Remaining Challenges and Barriers

- Further increasing high ordering degree of PtCoM intermetallic structures (>80%) to enhance intrinsic stability while maintaining fine particle sizes (3-4 nm) for sufficient ECSAs.
- Design and synthesize advanced carbon supports with optimal balance among micro, meso, and macro porosities for performance and durability improvements under HDV conditions.
- Improve oxygen transfer and Pt utilization within catalyst layers by identifying optimal ionomers and engineering electrode structures.
- Further strengthening the catalyst and support interaction to improve catalyst stability by regulating chemical and physical properties of support.
- Performing large MEA tests (>50 cm^2) remains a great challenging due to catalyst scale up and MEA fabrications.

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Proposed Future Work

- Explore effective M elements and significantly improve activity and durability of current PtCo and PtNi catalysts.
- Further optimizing the promising PtCoGa and PtCoMn *via* optimizing synthetic methods, annealing temperature, duration, the resulting ordering degree, and establishing their structure-performance relationship.
- Explore new metal site and heteroatom dopants in innovative carbon support to strengthen intrinsic Pt and support interactions.
- Further develop novel fiber 1D carbon support, carbon/oxide composite support, and effective scavengers, aiming to significantly enhance long-term durability while maintaining adequate performance .
- Elucidate mechanisms of stability enhancement via *in-situ* and MEA characterization at BOL, 30k, 60k, 90k etc during the AST under HDV conditions.
- Perform New M2FCT protocol to elucidate the stability.
- MEA performance in larger active area (>50 cm^2).

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Summary

- **The SUNY team synthesized two ternary catalysts (PtCoGa and PtCoMn), demonstrating high initial $E_{1/2}$ >0.955 V and insignificant loss < 10 mV after 30,000 potential cycles in RDE tests (60 °C). Met the following critical milestone:**

  Q2 Milestone: Develop ordered PtCoM catalysts, showing BOL $E_{1/2}$ > 0.92 V vs. RHE; EOL $E_{1/2}$ loss < 50 mV at 60 °C in RDE.

- **In MEA tests, the ternary PtCoMn catalyst retained a current density of 1.31 A cm^{-2} at 0.7 V after extensive 90,000 AST voltage cycles. The new results met the primary milestones below:**

  Q4 Milestone: MEAs (0.3 mgPt/cm^2) achieve current density at 0.7 V > 1.07 A/cm^2 (air, 250 kPa) after AST tests (equivalent to 10,000 hours).

- **Developed innovative electrospun porous fiber carbon for PGM catalysts, showing promising performance and durability in both RDE and MEA tests. Alao, a gradient-structured buckypaper electrode was successfully developed and met the following milestone**

  Q2 Milestone: surface areas > 300 m^2/g and electric conductivity> 0.5 S/cm.

- **PNNL team developed two perovskite oxide (ABO_3) for ROS scavengers for Pt catalyst showing promising initial activity in RDE and partially met the following milestone:**

  Q2 Milestone: Synthesize three types of $TaTiO_x$; $E_{1/2}$ > 0.88 V in RDE.

- **Ballard team develop MEA testing protocol and started testing Pt/C and PtCo/C baseline catalysts**

- **SUNY Buffalo team hired a female Ph.D. student for the DOE project. SUNY Buffalo team invited Gary Robb to give a guest lecture for undergraduate students in Buffalo from majority underrepresented groups about clean hydrogen and fuel cell technology overview. The following milestones were partially met.**

Q4 Milestone: Each team will support at least one Ph.D. student or postdoc from underrepresented groups.

Q12 Milestone: Organize at least one workshop for underrepresented researchers.