Advanced Electro-Catalysts through Crystallographic Enhancement

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Project ID FC161

Overview

Timeline:

- Project Start Date: October 1, 2016*
- Project End Date: September 30, 2019

**Subcontracts in place February 2017*

Budget:

- Total Project Budget: $3.335M
  - Total Recipient Share: $335K
  - Total Federal Share: $3M
  - Total DOE Funds Spent: $2.80M*

**As of 05/30/2020*

Barriers

A. Durability
B. Cost
C. Performance

Partners

- LANL (J. Spendelow)
- Brown University (S. Sun, A. Peterson)
- University of Pennsylvania (C. Murray)
- SUNY University at Buffalo (G. Wu)
- IRD Fuel Cells (M. Odgaard)

Relevance

Objectives

- **Design active and durable nanoparticle ORR catalysts based on ordered intermetallic alloys on nitrogen-doped carbon supports**
  - Binary and ternary alloys of Pt with Co, Ni, other base metals (mostly Co)
  - Avoid Fenton-active metals ~~**Fe**~~
  - Incorporate new N-doped C supports
- **Demonstrate catalysts in high-performance, durable MEAs**

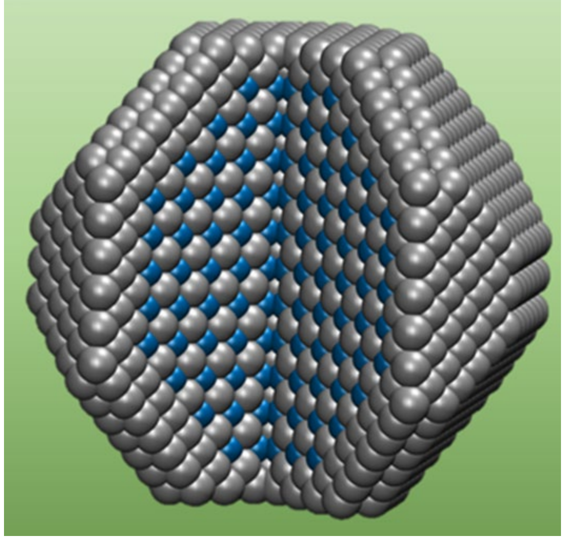
Project Targets:

- Mass activity > 0.44 A/mg$_{PGM}$ @ 0.9 V$_{iR\text{-free}}$
- <40% mass activity loss after catalyst AST
- <30 mV loss at 0.8 A/cm^2 after catalyst AST
- PGM total loading < 0.125 mg/cm^2
- Power density > 1 W/cm^2
- <40% mass activity loss after support AST
- <30 mV loss at 1.5 A/cm^2 after support AST

Approach: Synthesis

Use atomic-level ordering to increase performance and durability of Pt-based catalysts

- Synthesize intermetallic nanoparticles (CoPt, NiPt, ternaries)
  - Prepare ordered cores to stabilize base metal
  - Further protect core with Pt skin
  - Use theory and computation (DFT, machine-learning techniques) to guide nanoparticle design
- Support nanoparticles on Fe-free, N-doped graphitic carbon



Approach: Characterization and Testing

Use atomic-level ordering to increase performance and durability of Pt-based catalysts

- Integrate supported nanoparticles into MEAs, test initial performance and durability
- Perform MEA diagnostics (impedance, limiting current methods) to characterize loss mechanisms and guide electrode design
- Perform initial and post-mortem characterization (XRD, XAS, XRF, SEM-EDS, TEM, STEM-HAADF, STEM-EDS) to guide synthetic work and determine effect of structure and composition on performance and durability
- Scale-up and validate MEA performance (5 cm^2 → 50 cm^2)
- Scale-up catalyst synthesis (gram-scale batches)

Approach: Catalyst Structures

Ordered intermetallic catalysts

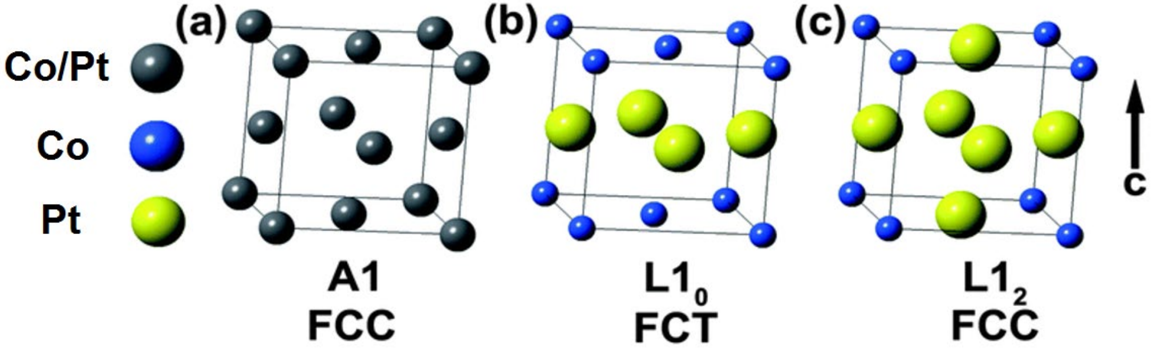
Primary material set:

1. $L1_0$-MPt (face-centered tetragonal, M = Co, Ni, etc.)
2. $L1_0$-M_1M_2Pt (ternaries)

Alternative materials (risk mitigation):

1. $L1_2$ structures (Pt_3M)
2. Doping with other elements
3. Other intermetallics

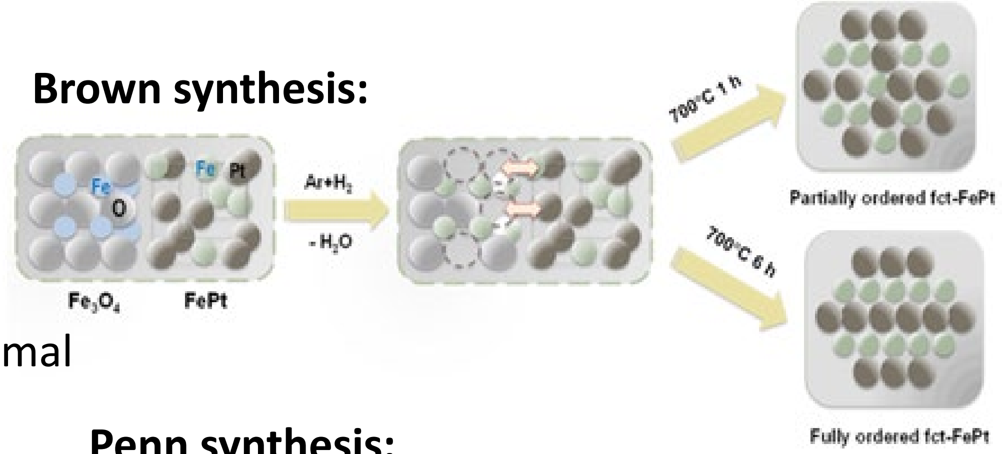
Adapted from Johnston-Peck et al., *Nanoscale*, 2011, **3**, 4142



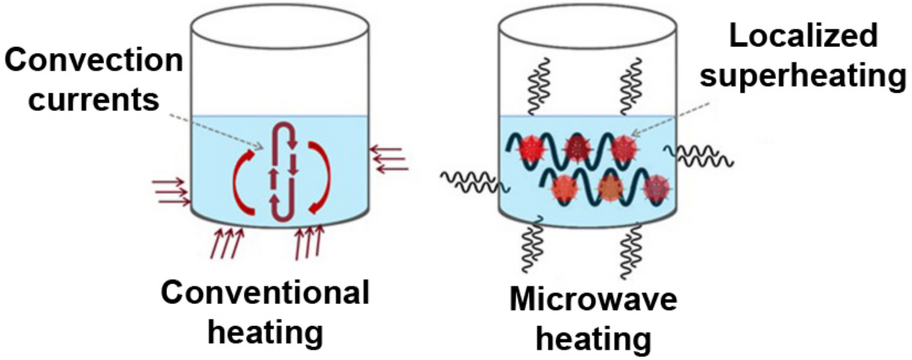
Approach: L1$_0$-MPt Synthesis

1. Brown: wet chemical synthesis of alloy nanoparticles in high-boiling solvents, followed by thermal annealing to create ordered structures (highest control, lowest scalability)
2. Penn: microwave synthesis and rapid thermal annealing (high risk, but may provide enhanced ordering, improved scalability)
3. LANL: seed-mediated synthesis by metal salt impregnation in Pt/C, followed by annealing to produce ordered structures (lowest control but highest scalability)

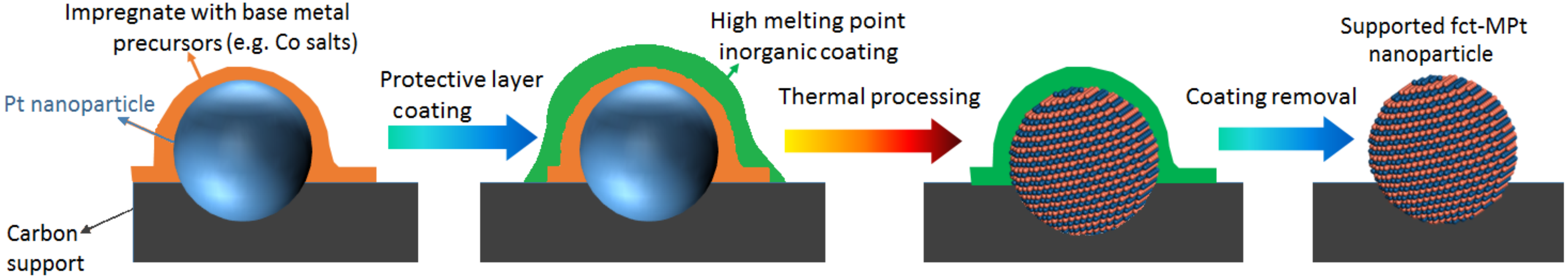
Brown synthesis:



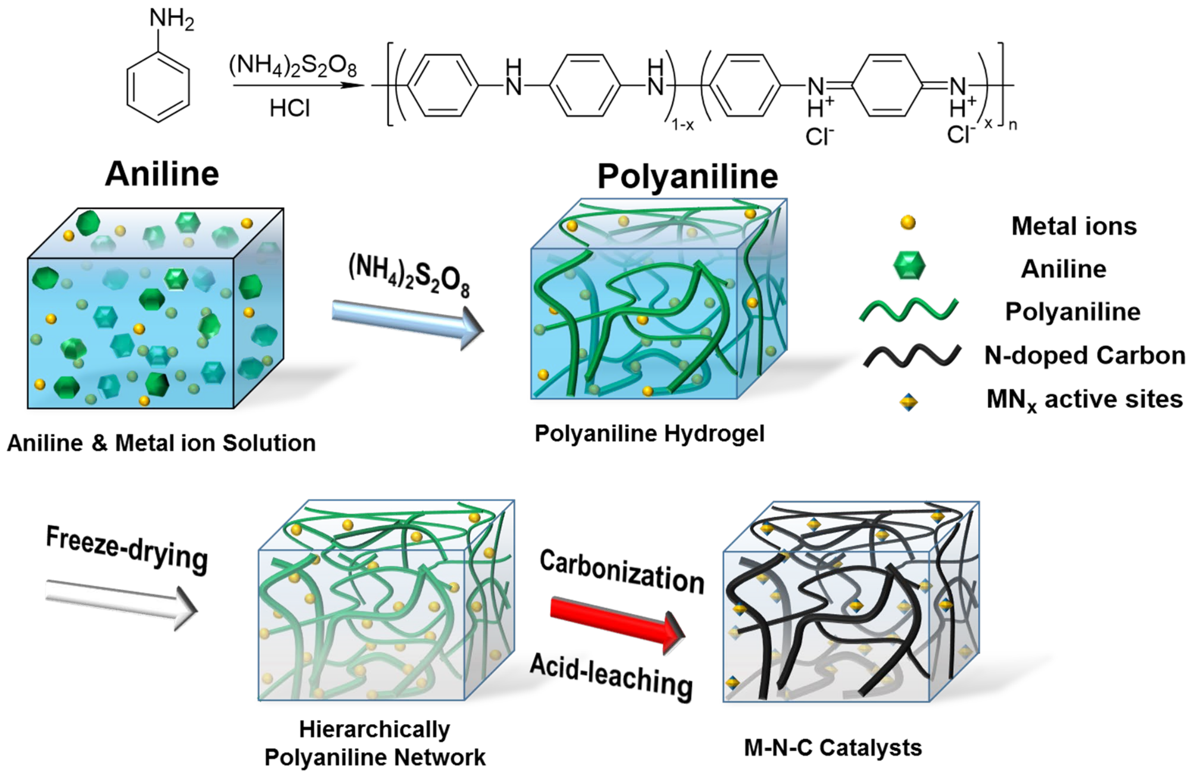
Penn synthesis:

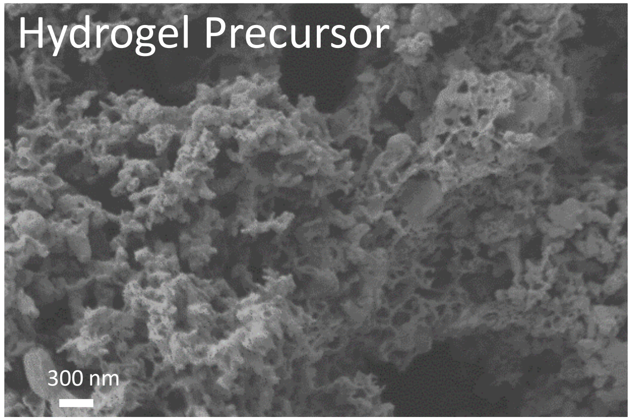


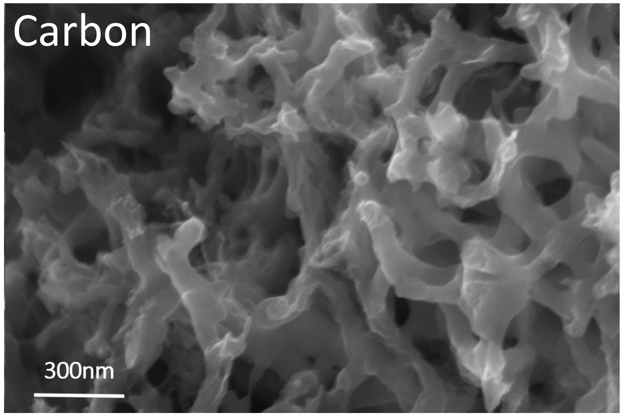
LANL synthesis:



Approach: N-doped Carbon Supports







Key attributes:

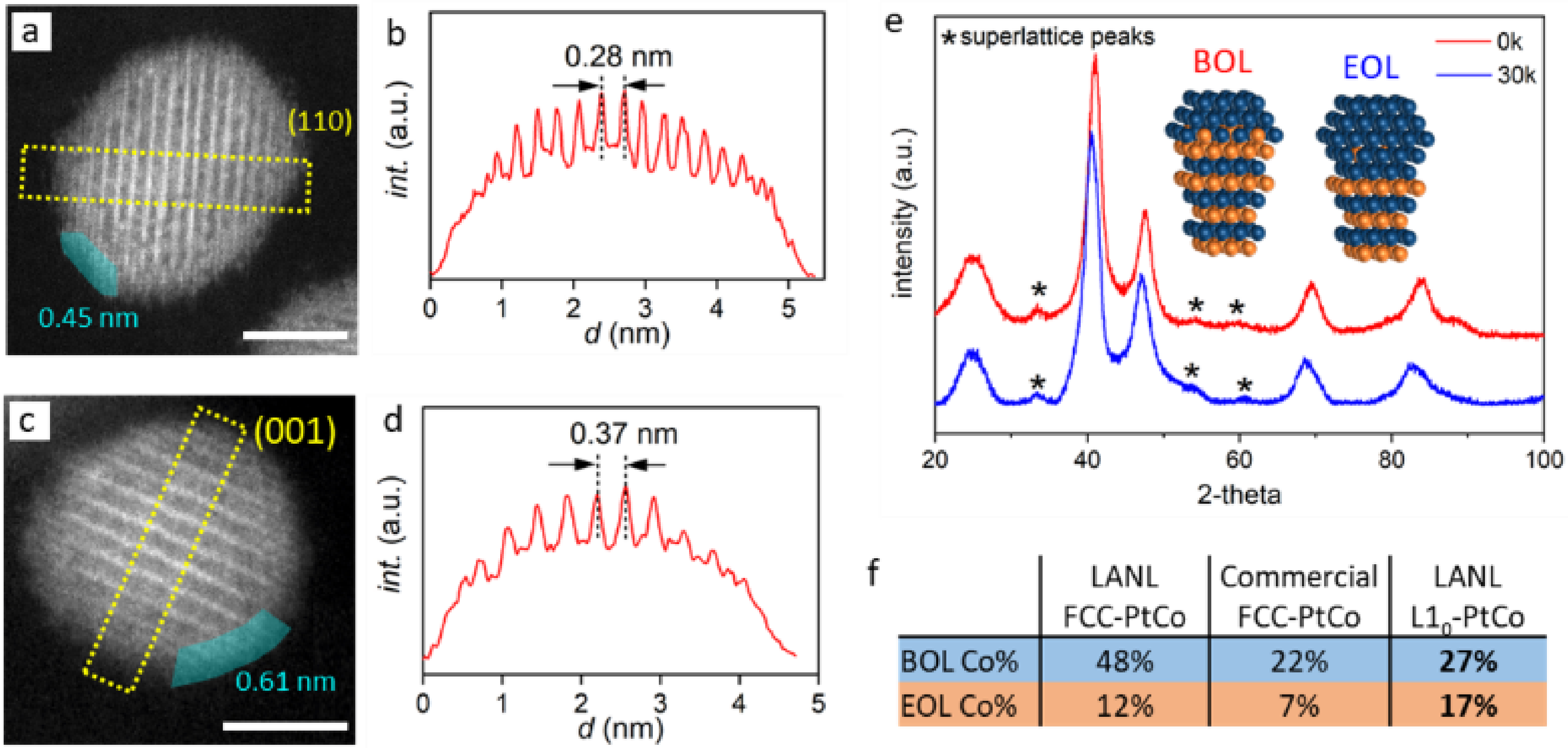
- **N-doped** - improved dispersion and stabilization of nanoparticle catalysts
- **Highly graphitized** - improved durability
- **Fe-free** - avoids Fenton degradation

Milestones

12/18	Demonstrate ordered intermetallic nanoparticle catalyst meeting mass activity and 30,000 cycle AST durability targets in 5 cm^2 MEA	100%
3/19	Demonstrate supported catalyst meeting 5,000 cycle support AST durability targets in 5 cm^2 MEA	100%
6/19	Demonstrate ordered intermetallic nanoparticle catalyst meeting mass activity and 30,000 cycle AST durability targets in 50 cm^2 MEA	80%*
9/19	Validate MEA performance of 1 W/cm^2 or greater and achievement of mass activity and durability targets in 50 cm^2 MEA	80%*
12/19	Measure effect of Zn doping on atomic level ordering of PtNi nanoparticle catalysts.	100%
3/20	Demonstrate face centered tetragonal PtCo nanoparticle catalyst with >20% Co content after 30,000 0.6-0.95 V cycles in an MEA.	100%

*Start of 50 cm^2 testing was delayed till 3/20. No cost extension for 50 cm^2 milestones.

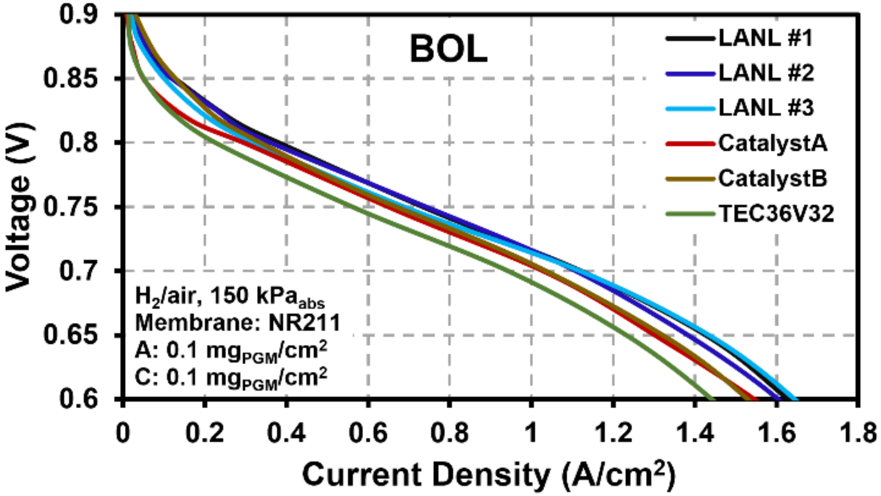
LANL L1$_0$-PtCo

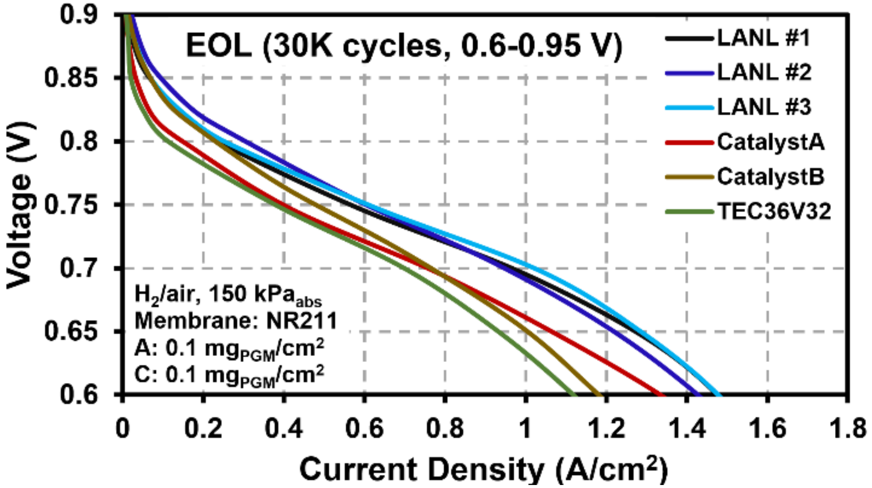


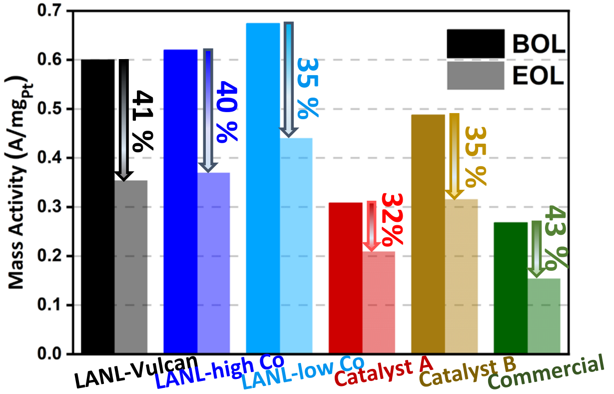
	LANL FCC-PtCo	Commercial FCC-PtCo	LANL L1$_0$-PtCo
BOL Co%	48%	22%	**27%**
EOL Co%	12%	7%	**17%**

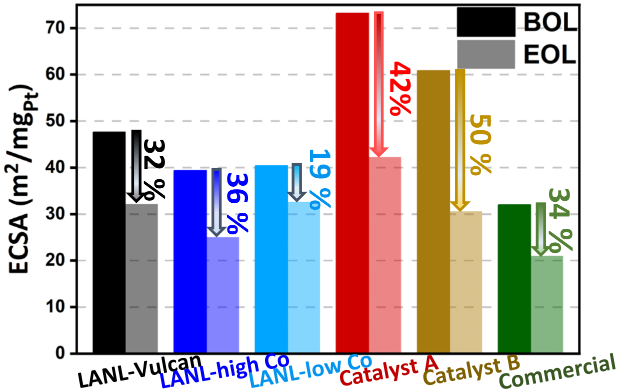
Crystallographic characterization of L1$_0$-PtCo. (a) STEM micrograph of as-prepared particle with a 0.45 nm Pt shell. (b) Intensity profile along the highlighted trajectory in (a). (c) STEM micrograph of post 30K tested catalyst particle with a 0.61 nm shell. (d) Intensity profile along the highlighted trajectory in (c). (e) XRD patterns of as-prepared and post 30K cycle tested catalysts. (f) Percentage of Co in PtCo catalyst tested at LANL.

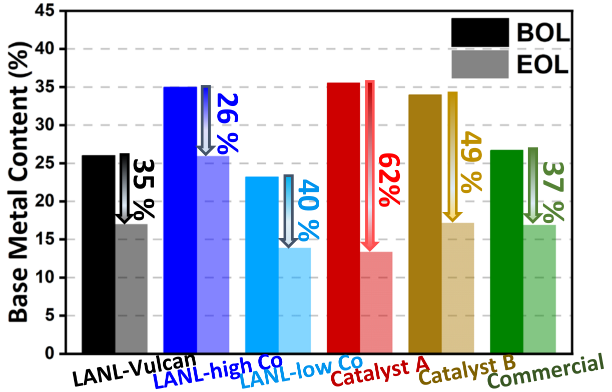
Accomplishment: High MEA Performance and Durability





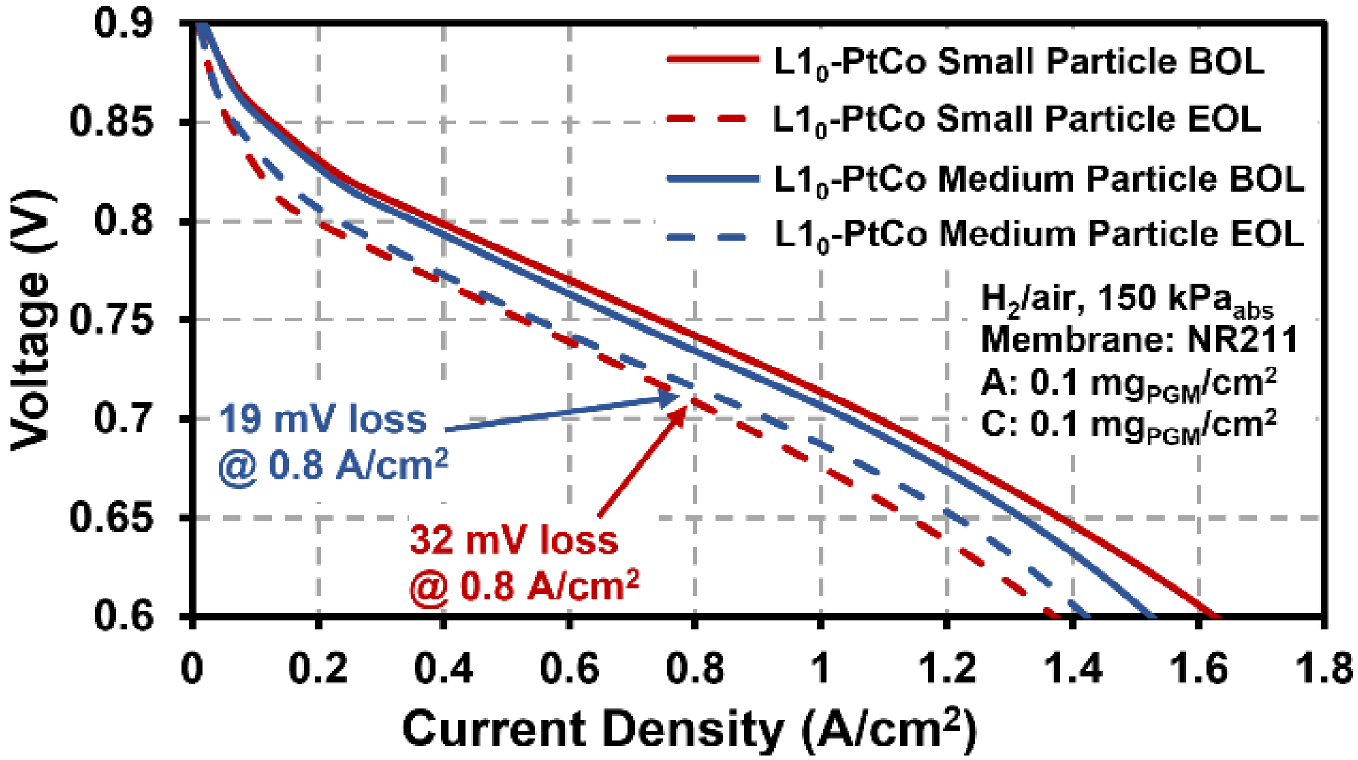






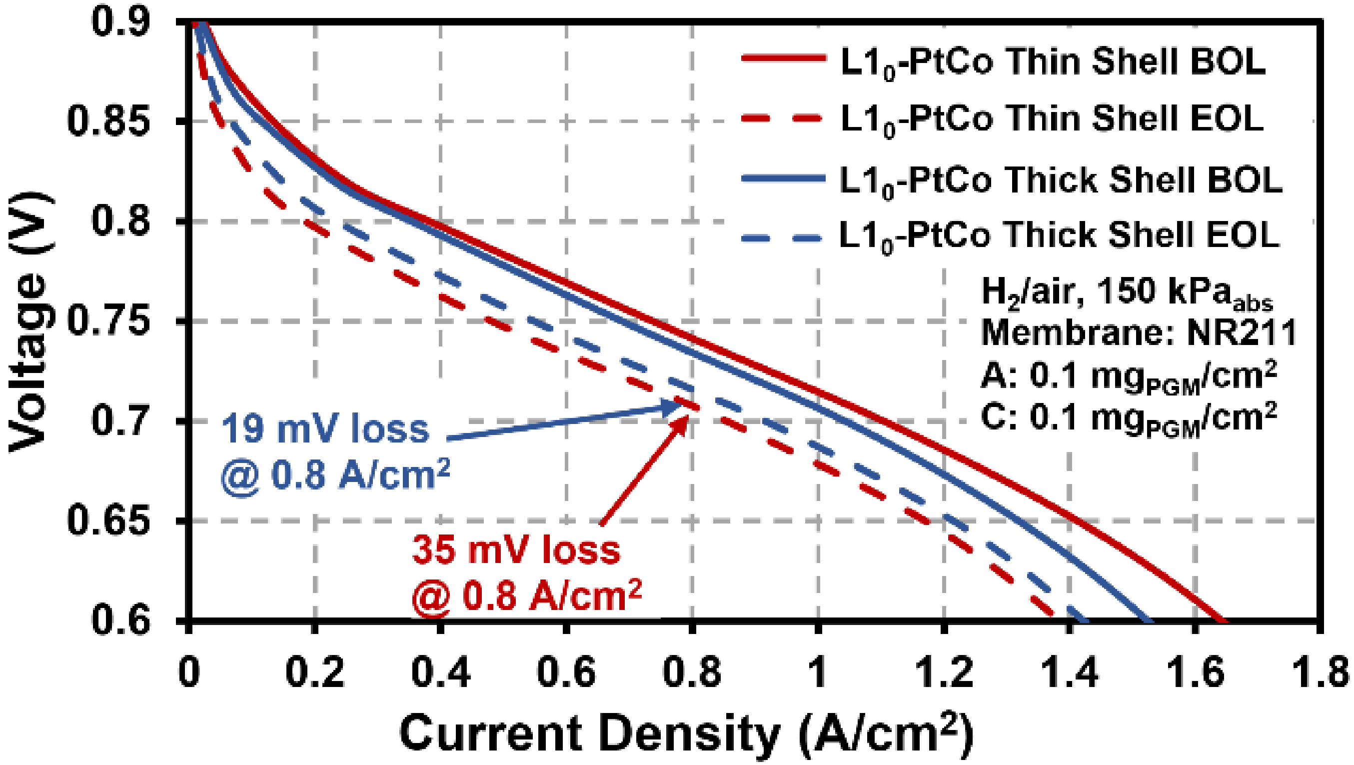
LANL L1$_0$-PtCo catalysts have high performance and durability, better than any other catalysts we've tested

Accomplishment: $L1_0$-PtCo Particle Size Effects



Small particle (3-4 nm, 65 m^2/g) $L1_0$-PtCo has slightly higher performance than medium particle $L1_0$-PtCo (4-5 nm, 48 m^2/g), but lower durability.

Accomplishment: $L1_0$-PtCo Shell Thickness



$L1_0$-PtCo with thick Pt shell layers (>0.5 nm) has slightly lower performance than $L1_0$-PtCo with thin Pt shells (<0.5 nm), but higher durability.

Accomplishment: DFT Studies on Co Leaching

BROWN

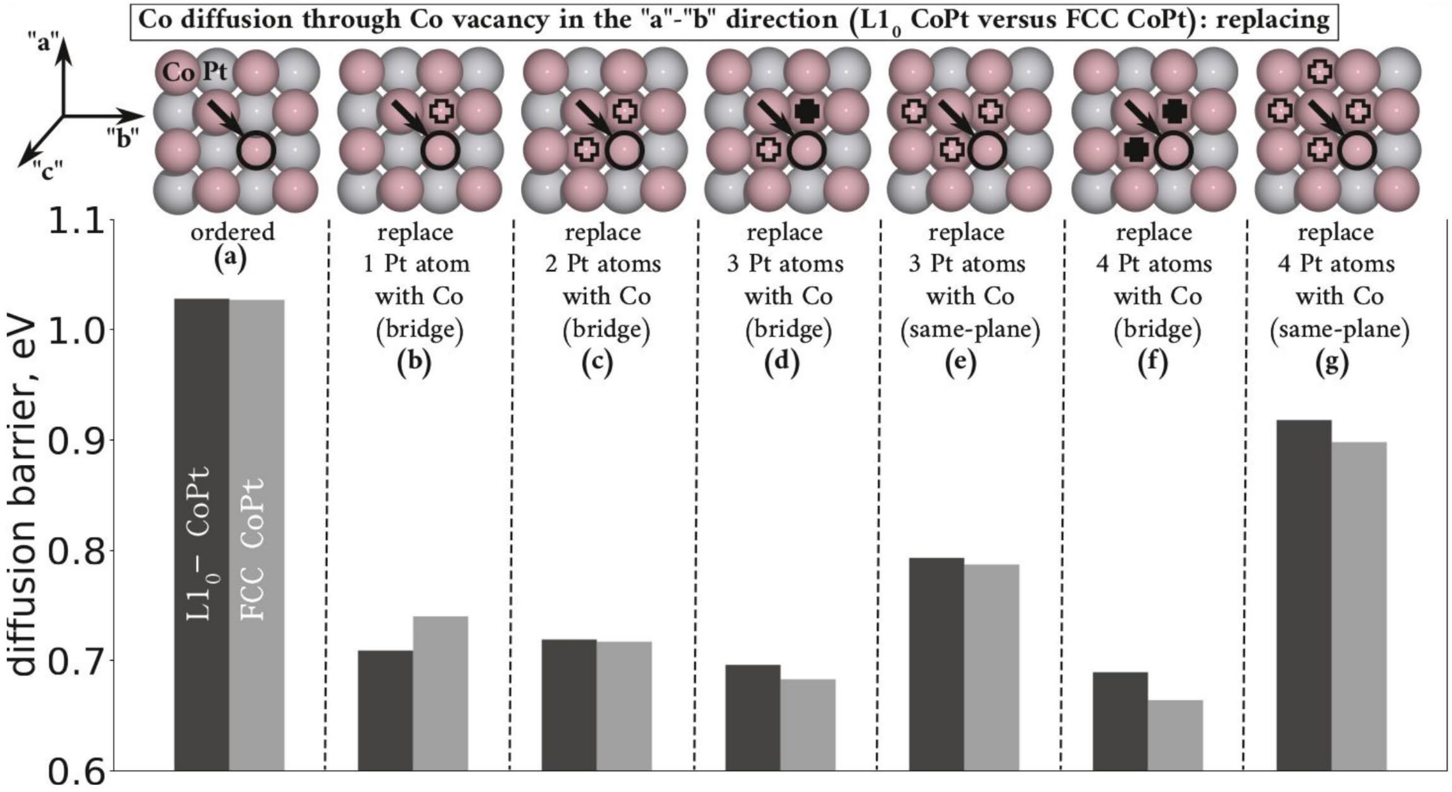
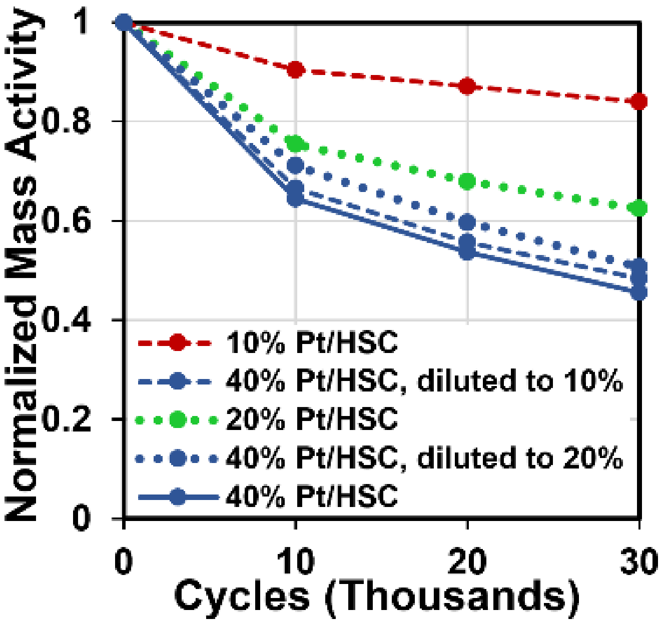
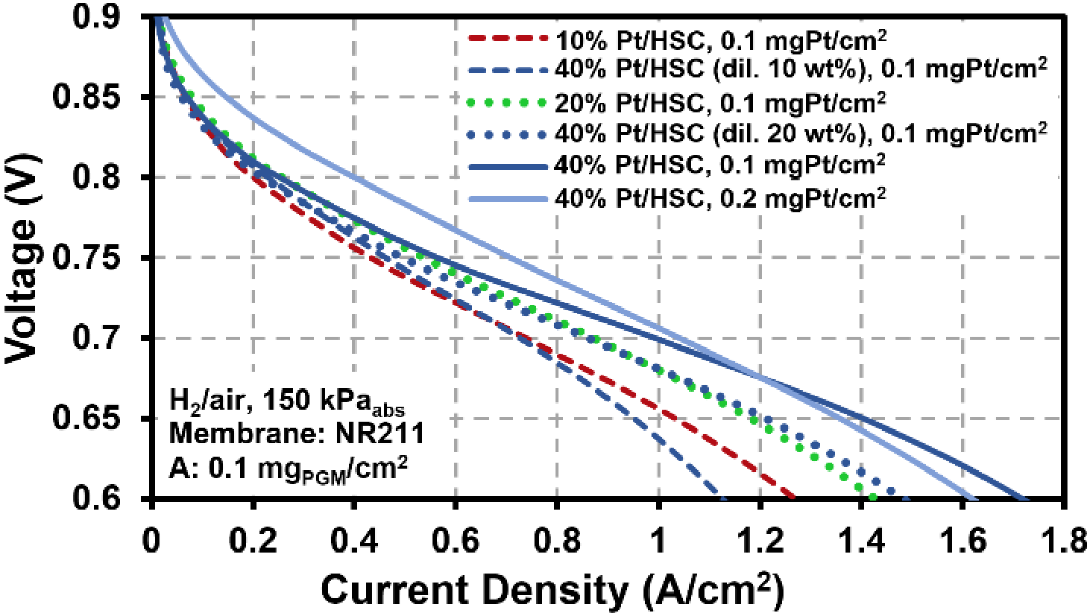


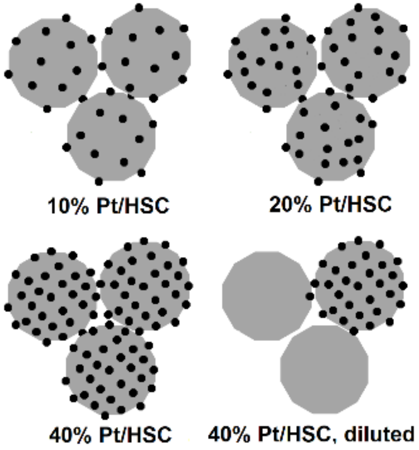
Figure 1: $L1_0$ versus FCC comparison of Co diffusion barrier (eV) through Co vacancy in the "a"-"b" direction as a function of Pt to Co replacement. The hollow circle represents a Co vacancy. The arrow shows the direction of Co atom diffusion. The "hollow plus" represents a replacement of Pt atom to Co. The "filled plus" symbol represents the replacement of two Pt atoms to Co (one visible in the schematic and the one periodically above it in the "c" direction). Note: Bridge denotes the four atoms through which Co diffuses.

Lower ordering (modeled by replacing one or more Pt atoms with Co) leads to locally Co-rich areas, with lower barrier for Co diffusion (faster Co leaching)

Accomplishment: Effect of Pt Weight Percent

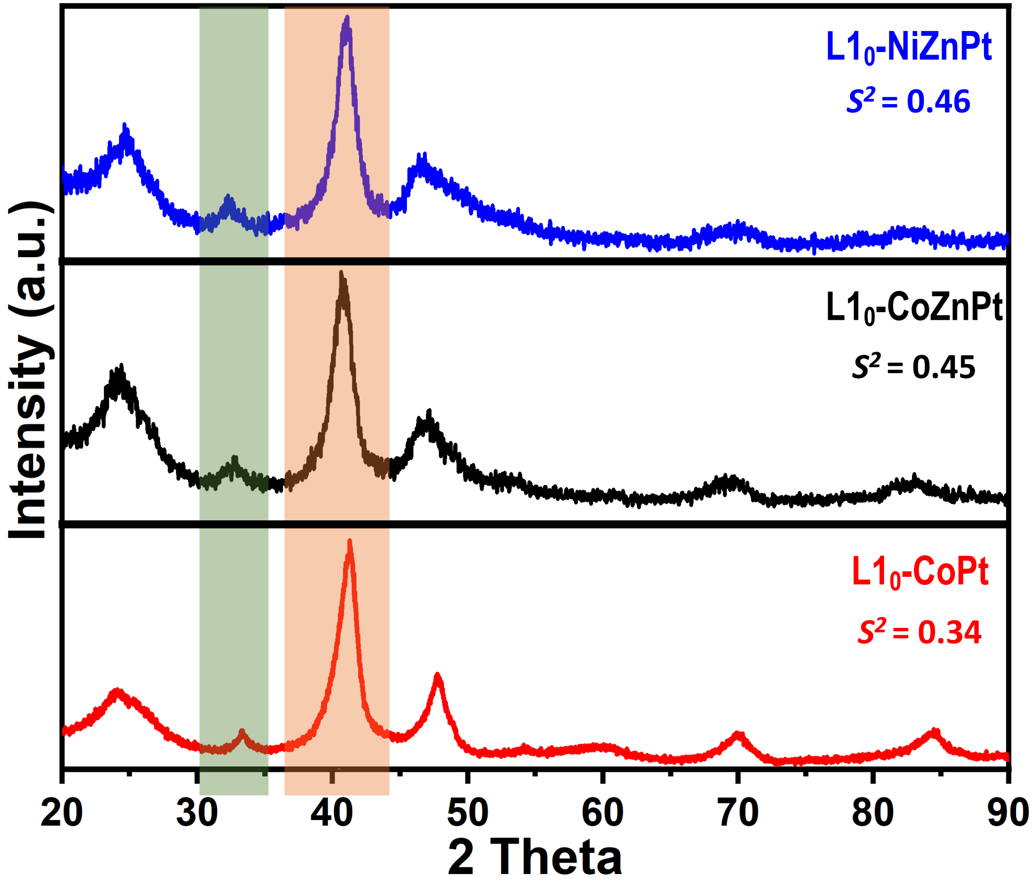






- Pt/HSC durability increases with decreasing Pt wt%
- Local Pt density seems to be key factor – dilution does not improve durability
- MEA performance of different Pt/HSC catalysts is similar in kinetic region, but lower wt% has worse transport due to thicker electrodes

Accomplishment: Zn doping for improved ordering



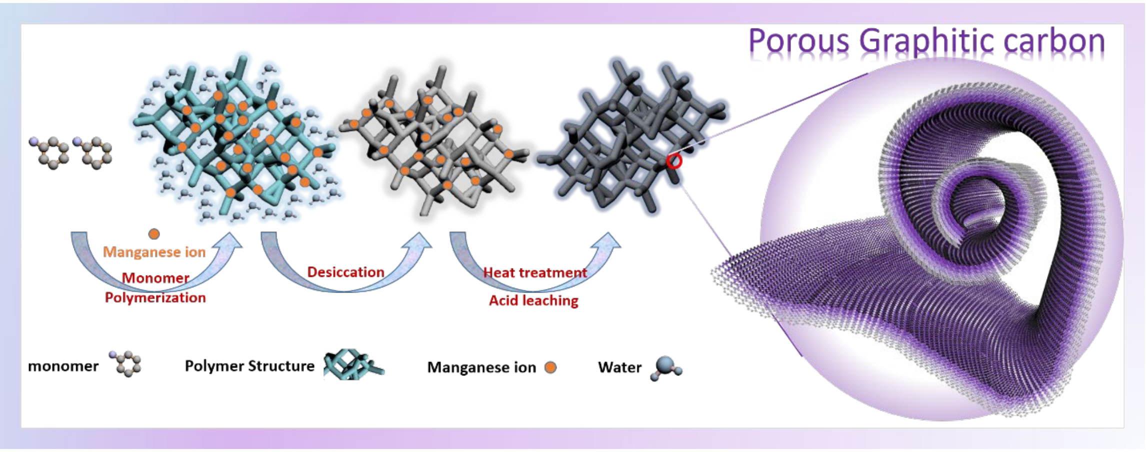
❖ **Quantifying Ordering**

S^2 = Degree of ordering

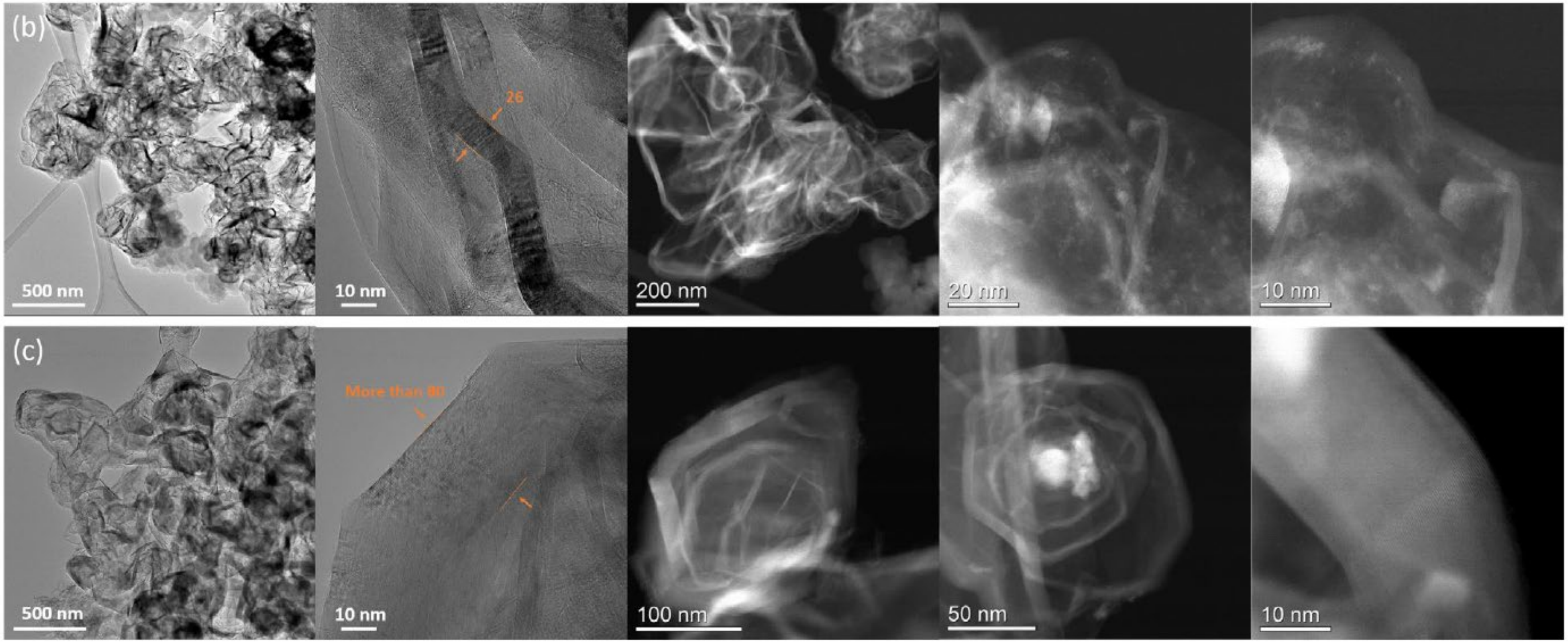
$$S^2 = \frac{\{I_{(110)}/I_{(111)}\}_{\text{measured}}}{\{I_{(110)}/I_{(111)}\}_{\text{ordered}}}$$

- Addition of Zn enables improved ordering
- Nanoscale PtNi is difficult to order at all without Zn, so role of Zn is crucial

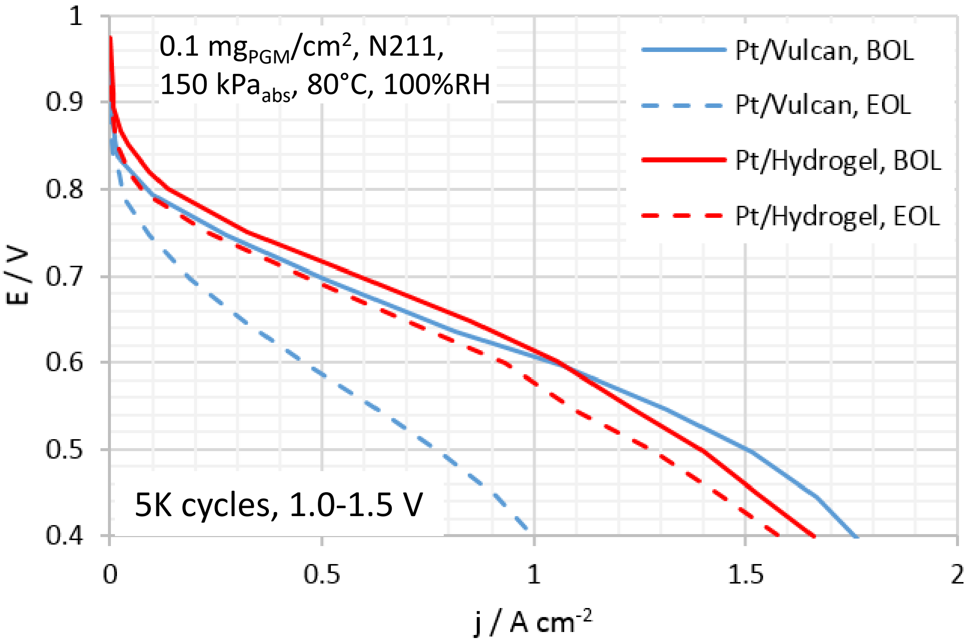
Buffalo Mn-Hydrogel Supports

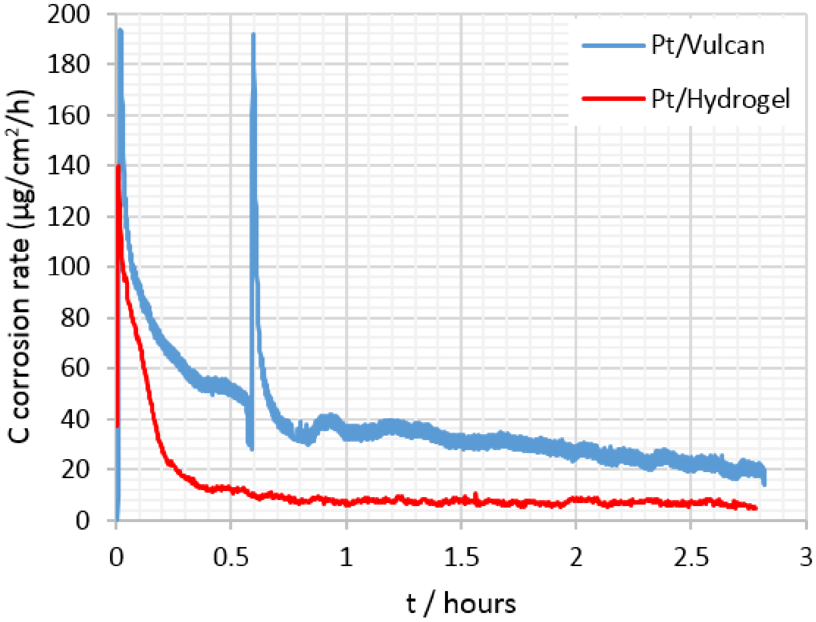


- Polymer hydrogels carbonized in presence of Mn have highly graphitic structure
- Graphitic structure prevents C corrosion, enhancing fuel cell stability



2019 Result: Mn-Hydrogel Supports





	Units	Measured	Target
Mass Activity	A/mgPGM	**0.18**	**0.44**
Mass Activity Loss [1]	%	**39**	**40**
Degradation at 1.5 A/cm^2 [1]	mV	**9**	**30**
Current Density at 0.8 V	A/cm^2	**0.14**	**0.3**
Power at 0.67 V, 150 kPa_{abs}	W/cm^2	**0.49**	**1**
Power at 0.67 V, 250 kPa_{abs}	W/cm^2		**1**
PGM Loading [2]	mg/cm^2	**0.13**	**0.125**

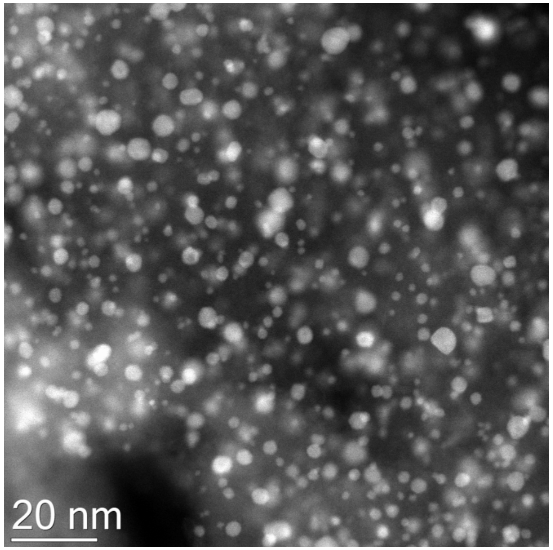
[1] 5K triangle wave cycles, 1.0-1.5 V

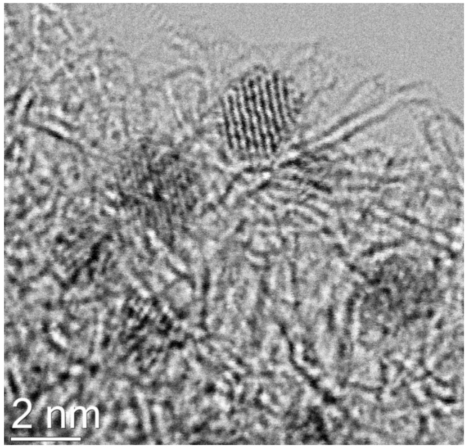
[2] Cathode

Qiao et al., Energy Environ. Sci., 2019

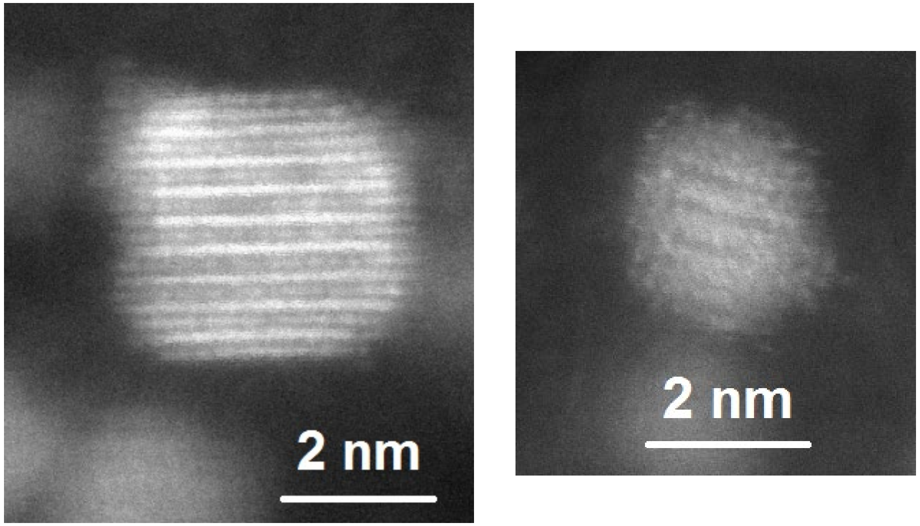
- Graphitic structure reduces corrosion
- **Hydrogel supports meet support durability targets**
- Need more active catalyst for performance targets

Accomplishment: L1$_0$-PtCo/Hydrogel





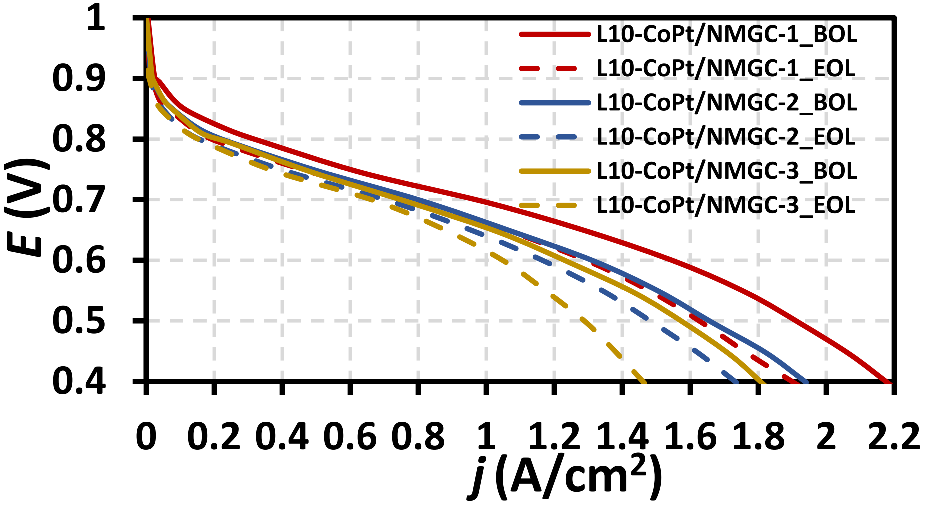
PtCo particles on folded graphene sheets



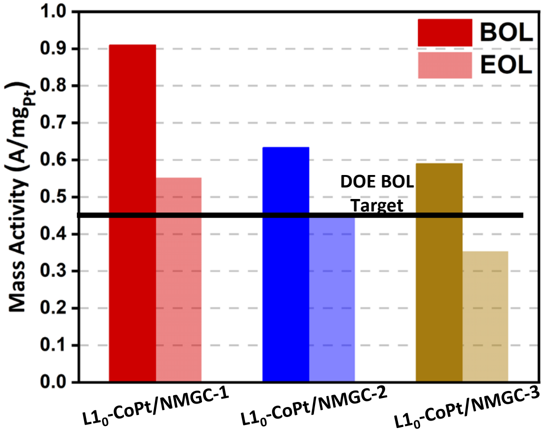
Small L1$_0$ ordered PtCo

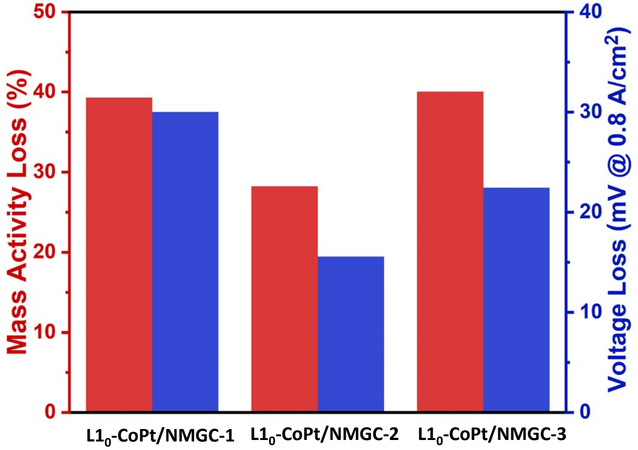
Hydrogel-based support enables improved dispersion of 2-4 nm L1$_0$-PtCo

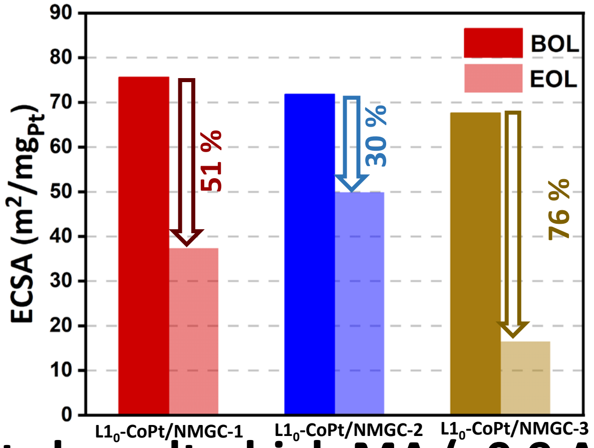
Accomplishment: $L1_0$-PtCo/Hydrogel



From 1 to 3, graphitization of carbon supports increases.

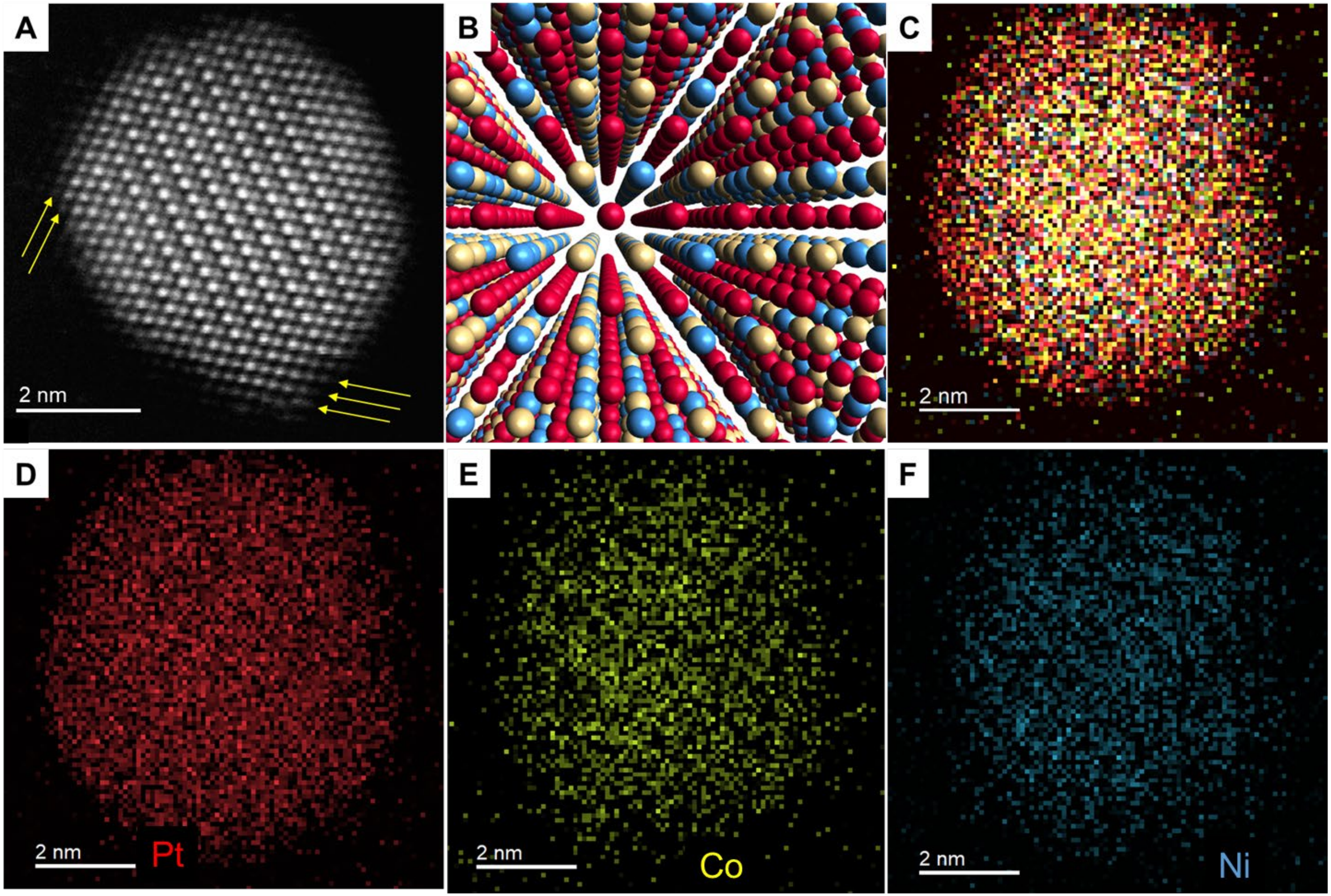






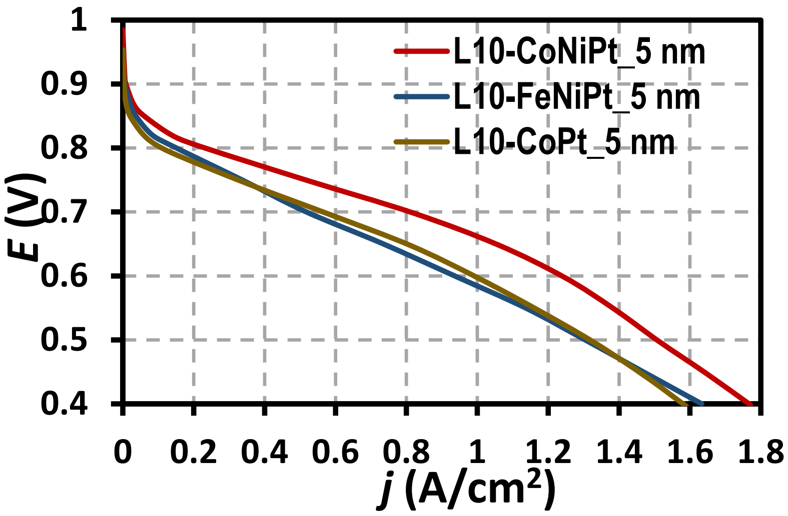
- **$L1_0$-PtCo on hydrogel-based supports has ultrahigh MA (>0.9 A/mg_{PGM} in MEA)**
- **Tuning graphitic content required to balance performance and durability**

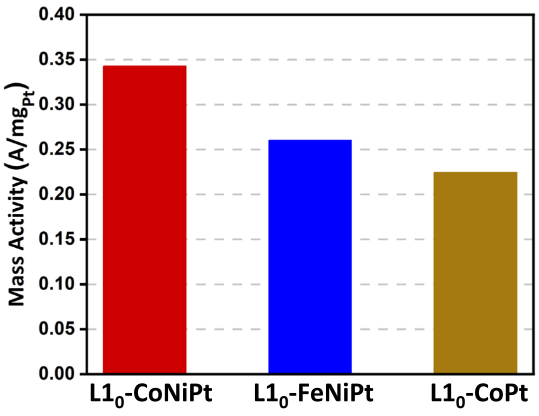
L1_0-PtCoNi STEM

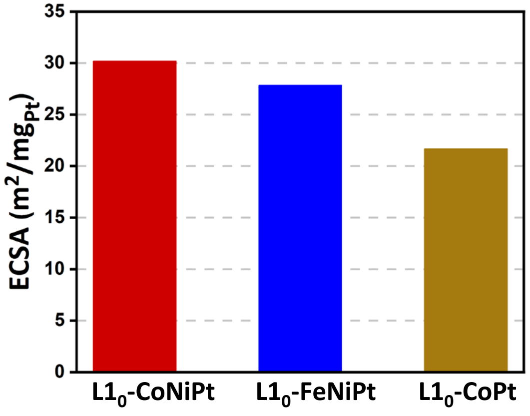


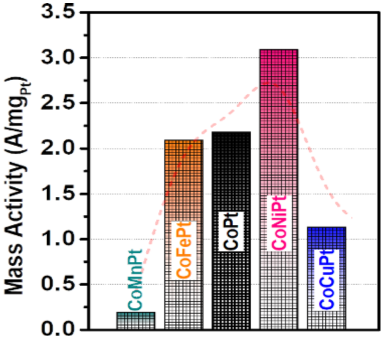
OAK RIDGE National Laboratory

L1$_0$-Ternaries: MEA Testing

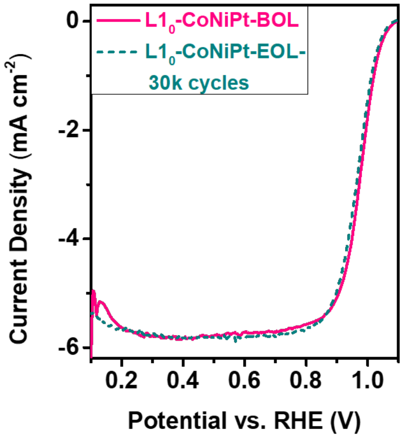


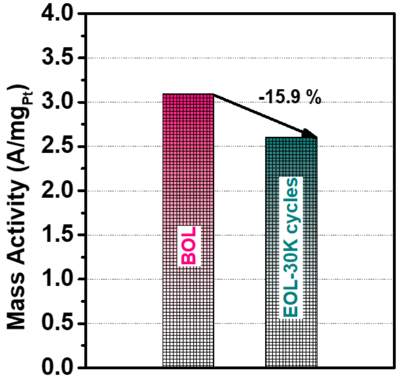






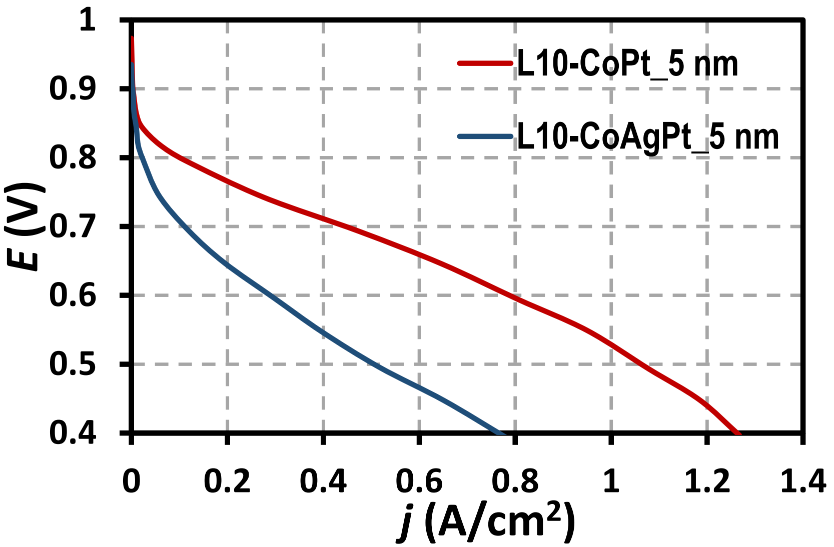
RDE mass activity of 5 nm L1$_0$ nanoparticles.

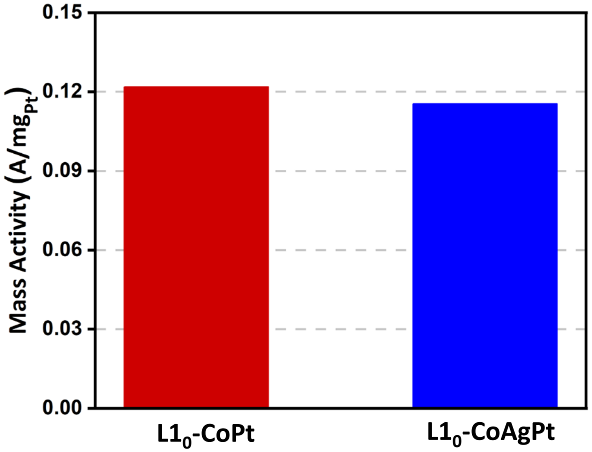


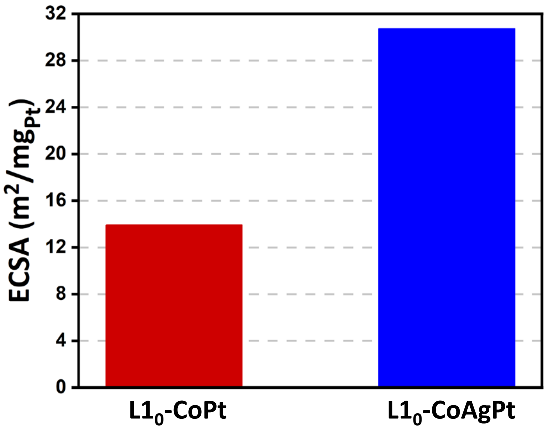


- Poor MEA-RDE agreement could be a result of the residual surfactants on nanoparticles.
- The ECSA values for these 5 nm catalysts are comparable to or even lower than that for 9 nm catalyst, due to the surface contamination.

MEA Testing: L1_0-CoPt and L1_0-CoAgPt



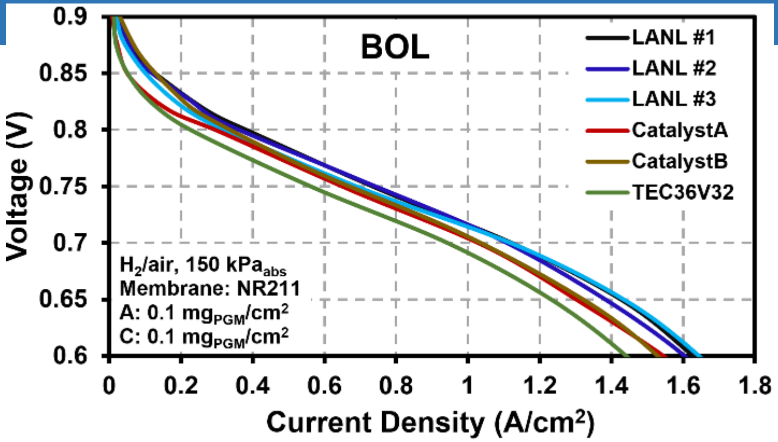


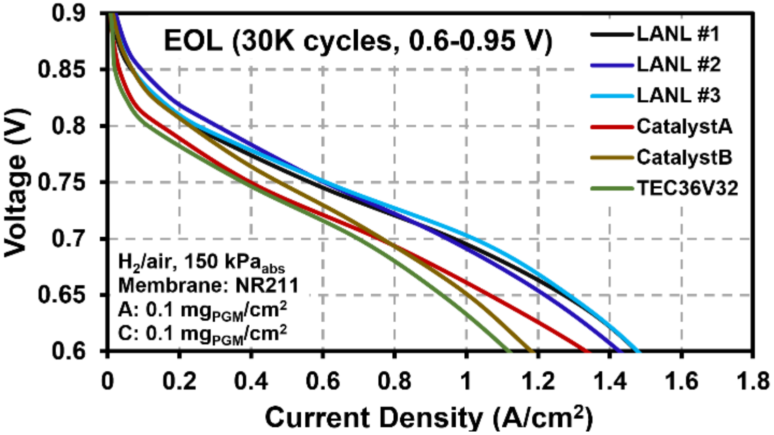


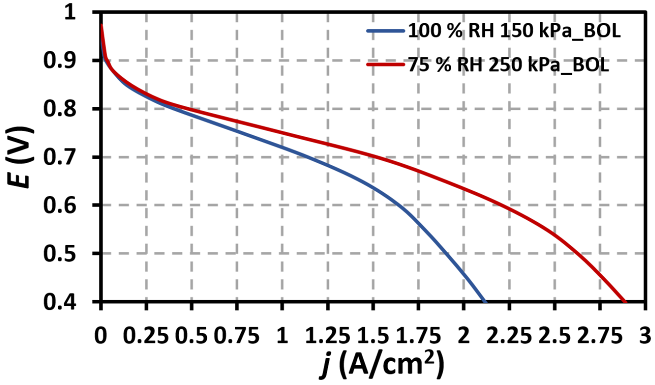
More examples of solvothermal-synthesized catalysts that worked well in RDE, but not MEA…

Project Status

- Intermetallic PtCo catalysts provide high activity and durability in MEAs
- Ordered catalysts with Pt skins can keep high Co content even after durability testing
- $L1_0$ ordering still apparent even after 30,000 voltage cycles
- Best catalysts can meet DOE performance and durability targets
- Role of support is critical in determining durability and power density







	Units	LANL #1	LANL #2	LANL #3	Target
Mass Activity	A/mg_{PGM}	0.60	0.62	0.67	0.44
Loss of Mass Activity	%	41	40	35	40
Power at 0.67 V, 150 kPa	W/cm^2	0.87	0.85	0.88	1
Power at 0.67 V, 250 kPa	W/cm^2			1.17	1
Voltage Loss at 0.8 A/cm^2	mV	26	21	10	30
Current Density at 0.8 V	A/cm^2	0.38	0.40	0.32	0.30

2019 Reviewer Comments

It is not clear what is preventing Co from leaching.

DFT studies in FY20 revealed the critical role of local Co content. High ordering prevents formation of locally Co-rich regions, which are especially vulnerable to Co leaching due to lower diffusion barriers.

The project is focused on only transition metals to provide ordered structure, even for M_1M_2Pt alloys. It is suggested that the team explore the possibility of other metals to provide stability to the ordered PtM structure.

We have performed studies using non-transition metals in FY20. Zn appears to be a promising dopant to increase degree of ordering and decrease base metal leaching.

It would be good to see comparisons to commercial PtCo catalysts.

We have provided these comparisons this year (slide 11).

Collaboration and Coordination

LANL

- Coordinate project
- Synthesize, characterize, and test catalysts
- Produce and test MEAs

Brown

- Solvothermal catalyst synthesis
- Characterize catalysts and supply to partners
- Provide theory-based design principles

Buffalo

- Synthesize and characterize supports; supply to partners

Penn

- Alternative catalyst synthesis based on microwave and rapid thermal annealing
- Characterize catalysts and supply to partners

IRD

- Scale up MEA production
- Catalyst/MEA validation

Other collaborators:

- **ANL** (Synchrotron X-Ray studies)
- **ORNL** (TEM, STEM)

Remaining Challenges and Barriers

- Tune particle size and Pt shell thickness for improved durability and efficiency in heavy duty applications
- Extend gram-scale synthesis to multi-gram batches that match performance of small batches
- Tailor support N-doping and graphitization for optimal durability and high-current performance

Proposed Future Work

- Increase high-current performance and durability through improved $L1_0$-PtCo dispersion – to be achieved via improved control of synthesis, improved N doping in supports
- Further improve performance and durability through ternary catalyst development
- Scale up MEA testing from 5 cm^2 to 50 cm^2
- Develop improved synthesis for high-volume manufacturing
- Tailor $L1_0$-PtCo for heavy duty vehicle applications

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

Tech Transfer Activities

- Engaged a US catalyst supplier (Pajarito Powder LLC) to discuss possible licensing and scale-up activities

Summary

Objective: Design active and durable ORR catalysts based on $L1_0$ ordered intermetallic alloys on graphitized nitrogen-doped carbon supports, and demonstrate in high-performance, durable MEAs.

Relevance: Project directly addresses cost, durability, and performance through key DOE targets:

- MEA mass activity > 0.44 A/mg_{PGM} @ 0.9 ViR-free
- <40% MEA mass activity loss after catalyst and support ASTs
- <30 mV loss at 0.8 A/cm^2 and 1.5 A/cm^2 after catalyst and support ASTs
- PGM total loading < 0.125 mg/cm^2
- Power density > 1 W/cm^2

Approach: Ordered intermetallic Pt alloy catalysts supported on graphitized N-doped carbon supports are being developed and tested in MEAs. Synthetic work is guided by computational ORR kinetic studies. Feedback from MEA testing and from characterization studies guides each round of synthetic development.

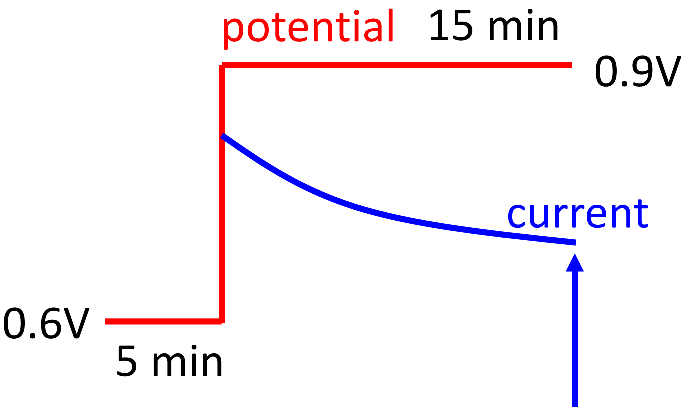
Accomplishments: Intermetallic $L1_0$-CoPt catalyst meets mass activity and durability targets. New N-doped supports enable high mass activity and meet support durability targets. Ordered $L1_0$ structure was demonstrated to decrease Co leaching, improving durability.

Collaborations: Strong team consists of a national lab with extensive catalyst synthesis, MEA testing, and characterization capabilities, three universities with excellent synthetic and computational capabilities, and an industrial partner with experience in MEA validation and scale-up. External collaborators provide additional characterization capabilities.

Technical Backup Slides

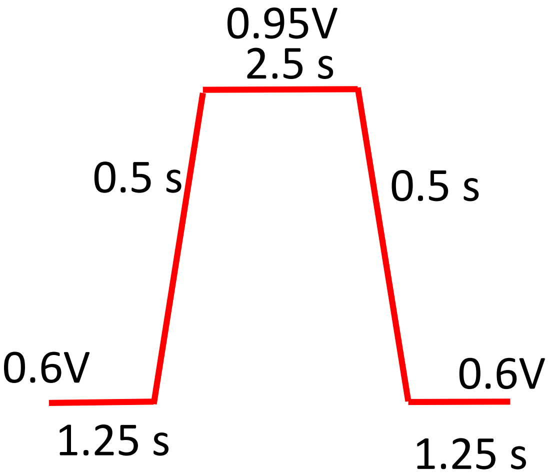
MEA Testing Protocols

Mass Activity: 15 min hold at 0.9 V

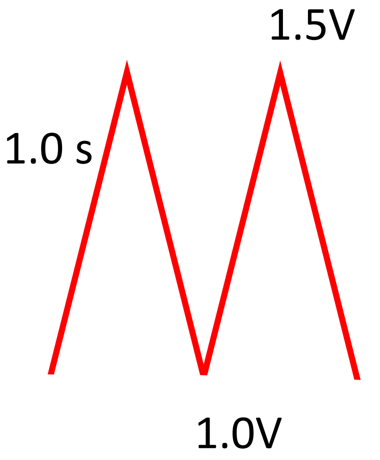


Mass activity measured during last 1 min of 15 min hold

Catalyst AST: square wave between 0.6 and 0.95 V with 0.5 s rise time



Support AST: triangle wave between 1.0 and 1.5 V at 500 mV/s



H_2/O_2, 500/1000 sccm; 80°C; 100% RH; 150 kPa_{abs}; cathode: 0.1 mg_{Pt}/cm^2 ; anode: 0.1mg_{Pt}/cm^2

H_2/N_2, 200/200 sccm; 80°C; 100% RH; 150 kPa_{abs}; cathode: 0.1 mg_{Pt}/cm^2 ; anode: 0.1mg_{Pt}/cm^2

MEA Preparation and Testing

All MEA testing reported here uses MEAs made using standard techniques:

- **Water/n-propanol inks, with catalyst and ionomer dispersed by sonication, and deposited by ultrasonic spray**
- **I/C = 0.9 for high surface area carbon or 0.5 for Vulcan carbon**
- **GDLs are 29BC (SGL), compressed by 20-25%**
- **Membranes are Nafion 211**
- **Testing used 5 cm^2 differential cells at 500/1000 sccm anode/cathode**
- **Target electrode loading 0.1 mg Pt/cm^2 (some sample-to-sample variation as reported in the test results)**
- **All testing was performed at 150 kPa_{abs} and 100% RH unless noted otherwise**