U.S. DEPARTMENT OF
ENERGY

Office of
ENERGY EFFICIENCY &
RENEWABLE ENERGY

Advanced Electrocatalysts through Crystallographic Enhancement

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Fuel Cell Technologies Office Webinar

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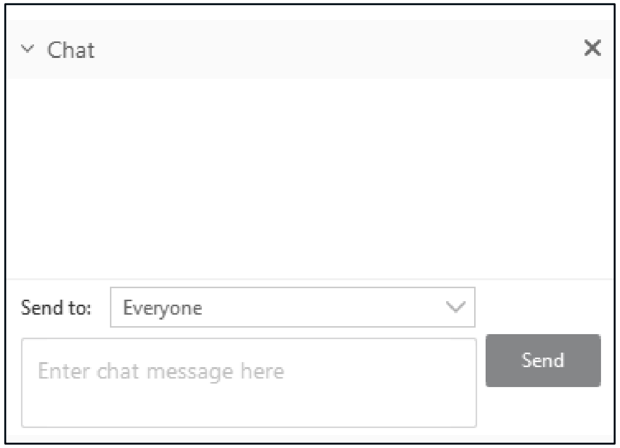
This presentation is part of the monthly webinar series provided by the U.S. Department of Energy's Fuel Cell Technologies Office (FCTO) within the Office of Energy Efficiency and Renewable Energy (EERE). Funding for research, development and innovation to accelerate progress in hydrogen and fuel cell technologies is provided by EERE FCTO.

During Q&A session:

Please type your questions to the chat box. **Send to: (HOST)**



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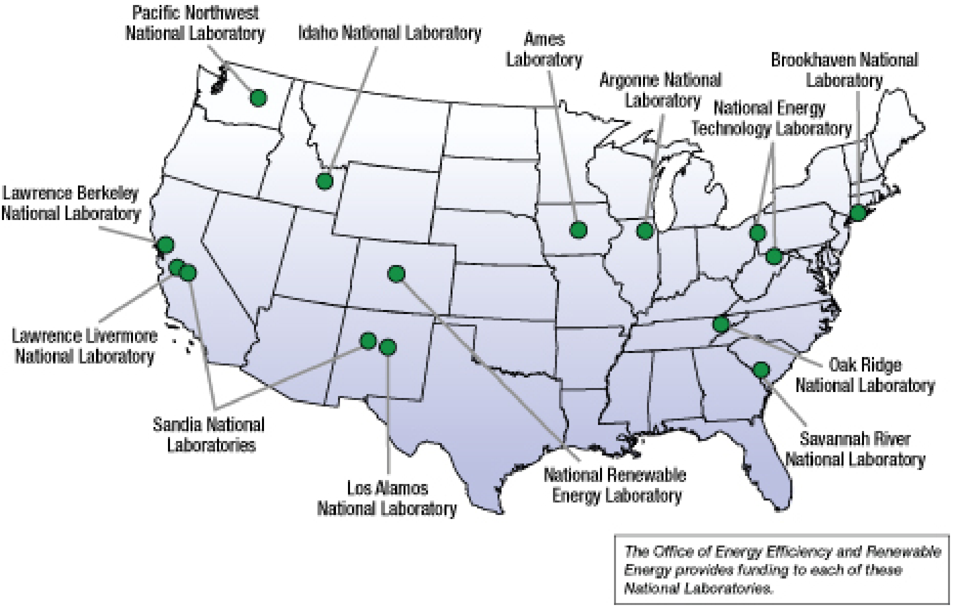


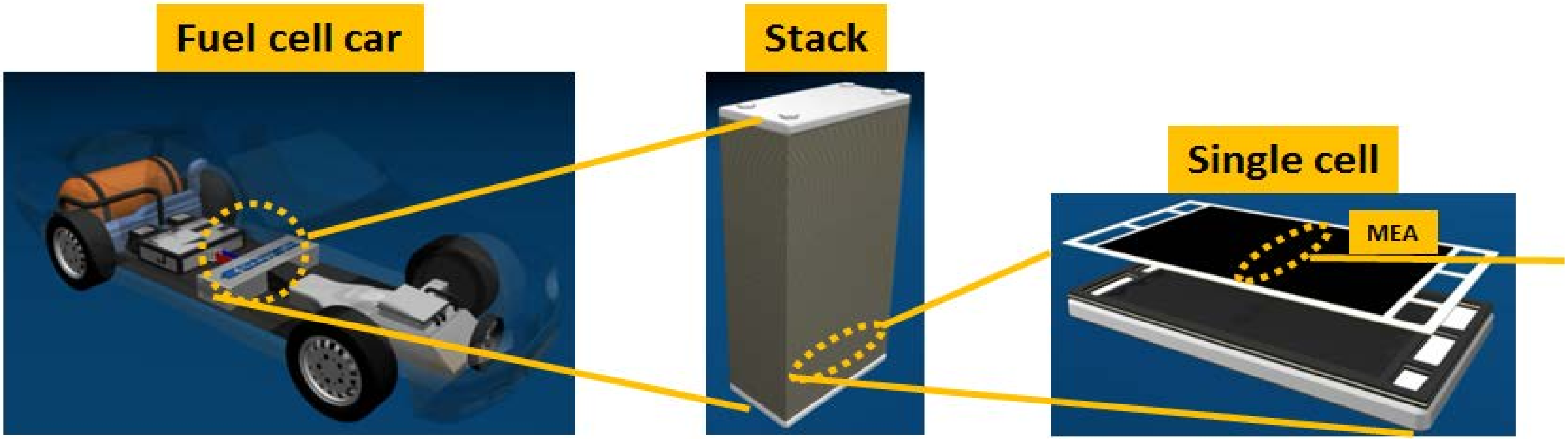
- Founded: 1943 for the Manhattan Project
- Location: Los Alamos, New Mexico
- $ 2.6B Budget, ~ 10,000 employees

Commercial Fuel Cell Vehicles

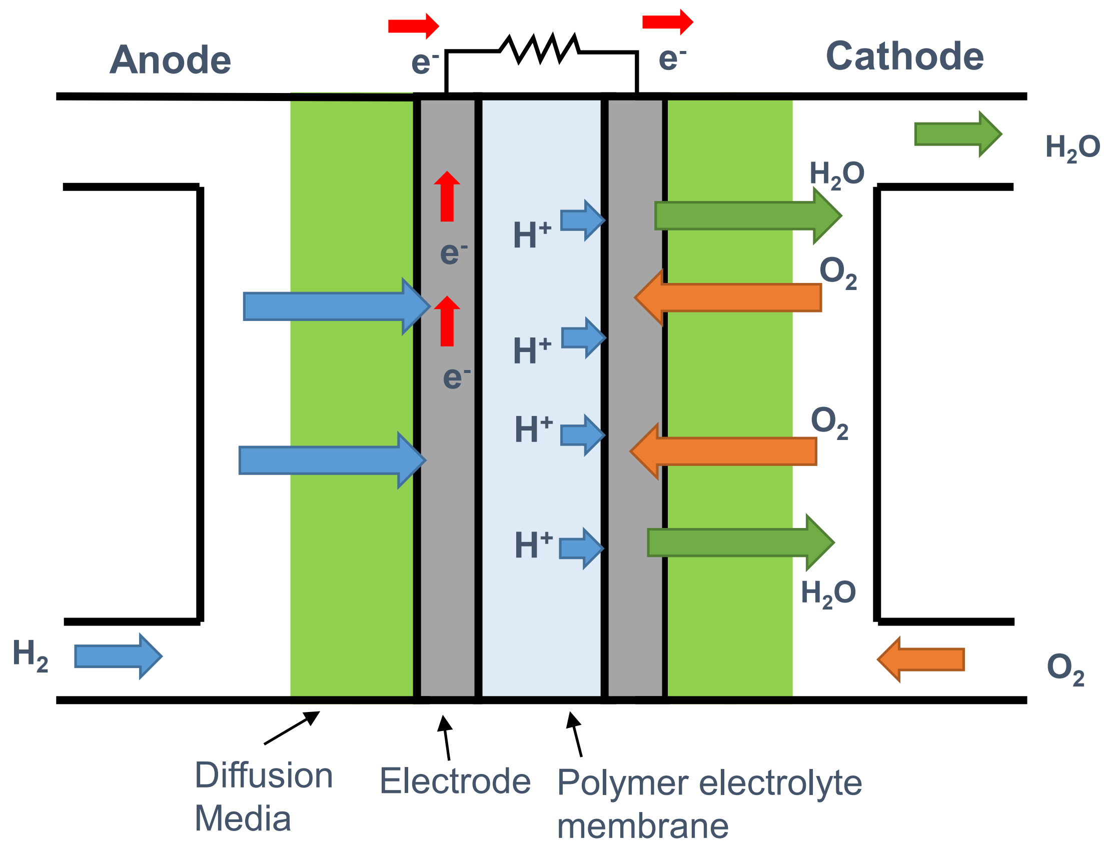
Toyota Mirai
MSRP: $58,365

Honda Clarity

Hyundai Nexo
Lease $399/mo.



Introduction - Polymer Electrolyte Fuel Cell



Anode:

$$H_2 \rightarrow 2H^+ + 2\,e^-$$

Cathode:

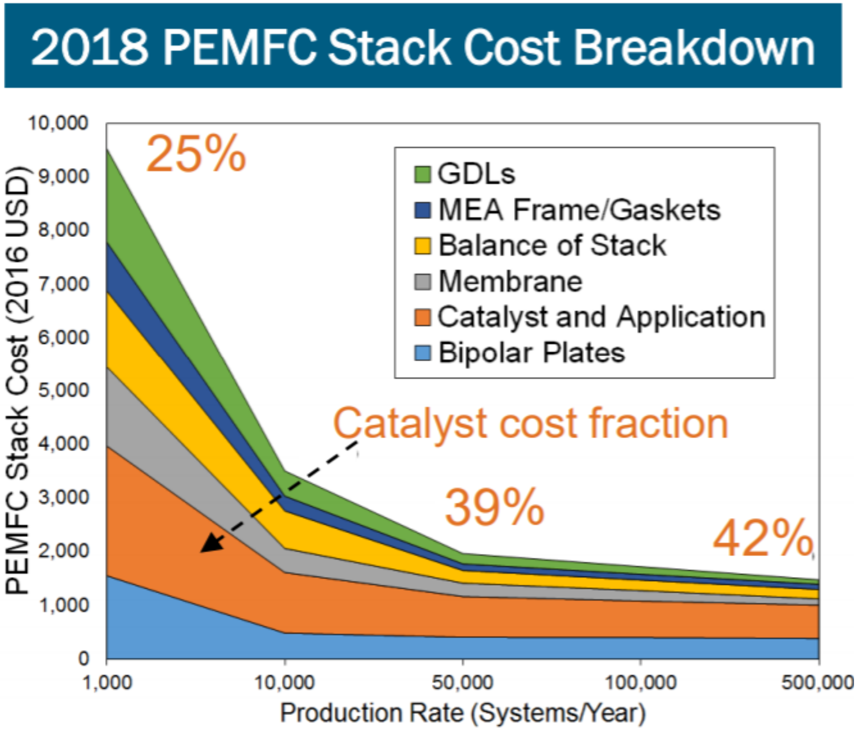
$$\frac{1}{2}O_2 + 2H^+ + 2\,e^- \rightarrow H_2O$$

Overall Reaction:

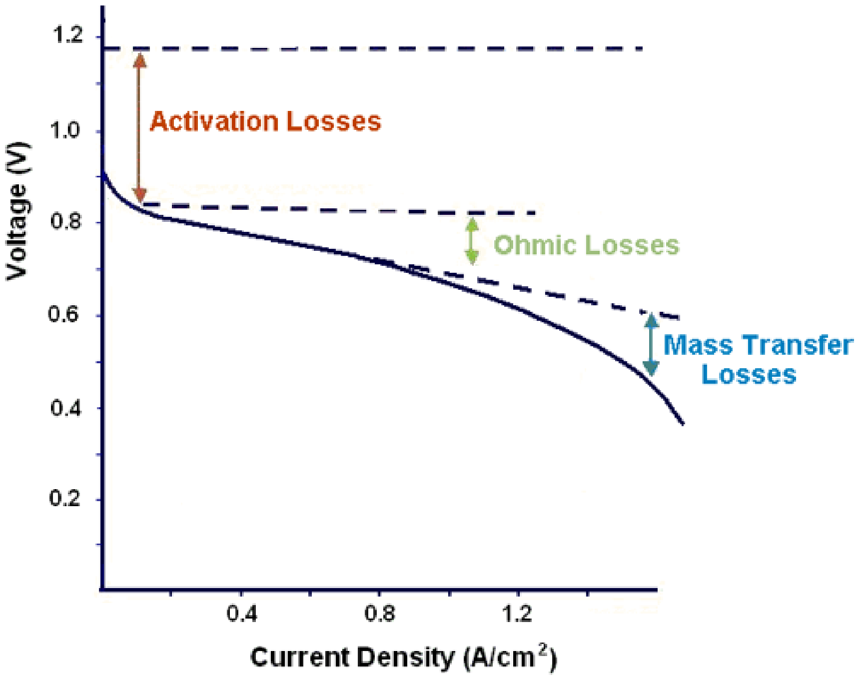
$$H_2 + \frac{1}{2}O_2 \rightarrow H_2O + \text{Electricity}$$

- **Slow O_2 reduction on the cathode is the main barrier to increased performance**
- **Platinum alloy catalysts (PtCo, PtNi) are used to improve O_2 reduction kinetics, but cost and durability are issues**

Cost Reduction



D. Papageorgopoulos, FCTO Annual Merit Review., 2019



Fuel cells need to be cheaper!

Strategies:

1. Better catalyst → less Pt → reduced cost
2. Higher performance → smaller fuel cell → reduced cost

Relevance

Objectives

- **Design active and durable nanoparticle ORR catalysts based on fully-ordered intermetallic alloys on highly graphitized nitrogen-doped carbon supports**
  - Binary and ternary alloys of Pt with Co, Ni, other base metals
  - Project will avoid Fenton-active metals
  - Commercial supports used initially; N-doped C supports later
- **Demonstrate catalysts in high-performance, durable MEAs and scale up to 50 cm^2**

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: Catalyst Structures

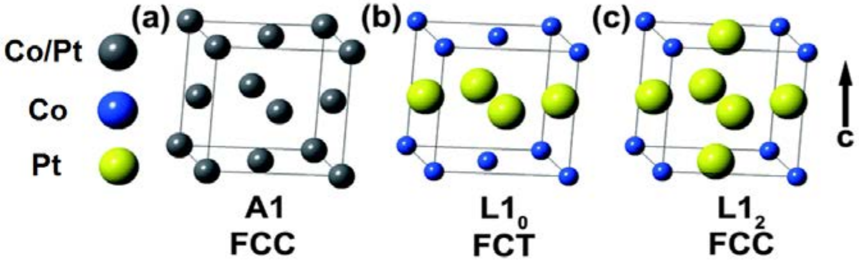
Ordered intermetallic catalysts

Primary material set:

1. $L1_0$-MPt (also known as face-centered tetragonal) M = Co, Ni, other transition metals
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

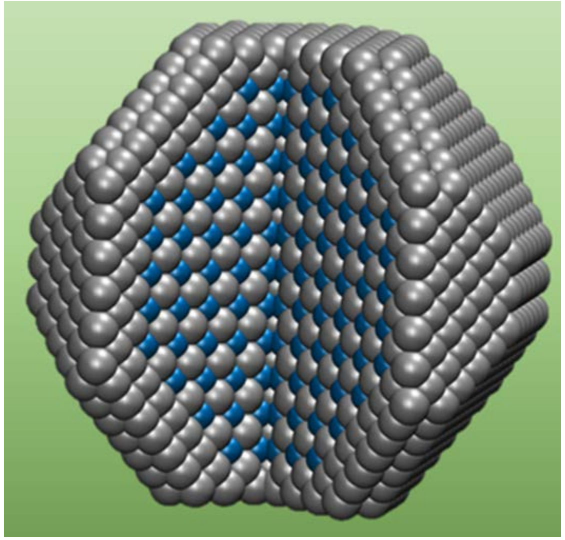


Adapted from Johnston-Peck et al., *Nanoscale*, 2011, **3**, 4142

Approach: Synthesis

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

- Synthesize intermetallic nanoparticles (CoPt, NiPt, ternaries)
  - Prepare fully-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

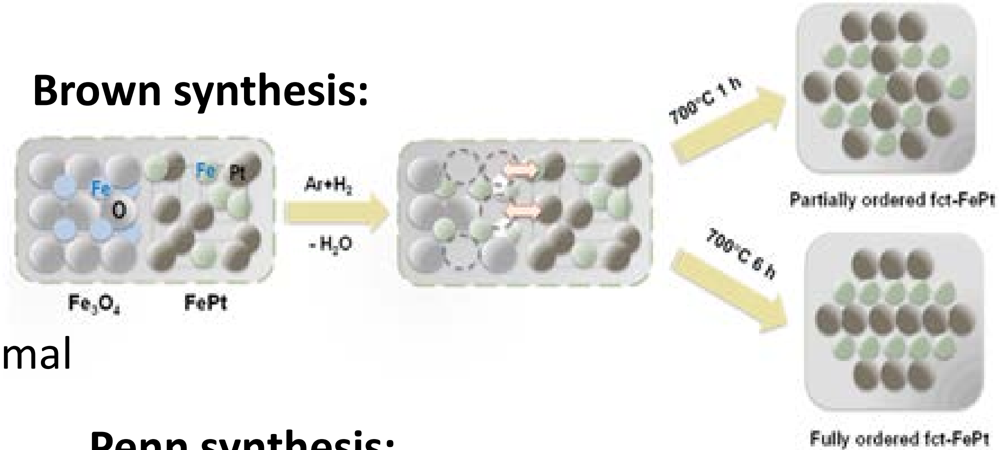
Use atomic-level ordering to increase performance and durability of Pt-based catalysts

- 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)

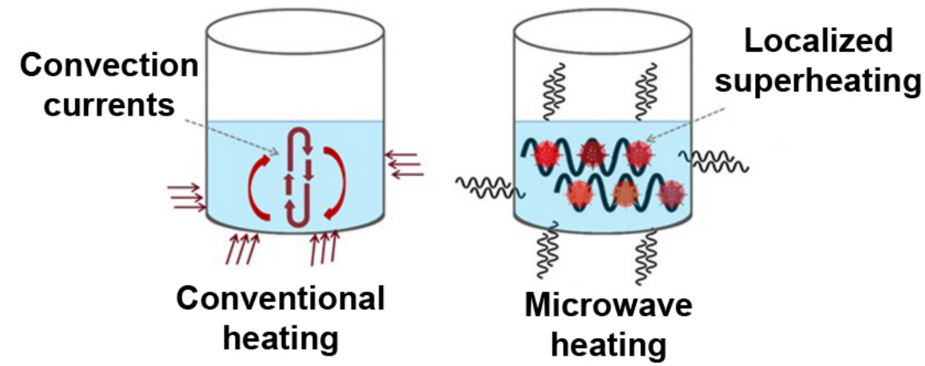
Approach: $L1_0$-MPt Synthesis

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)

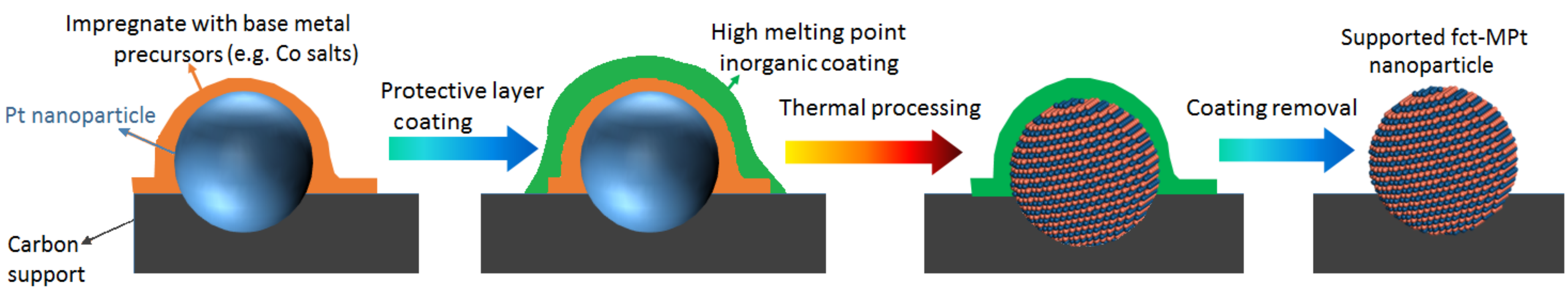
Brown synthesis:



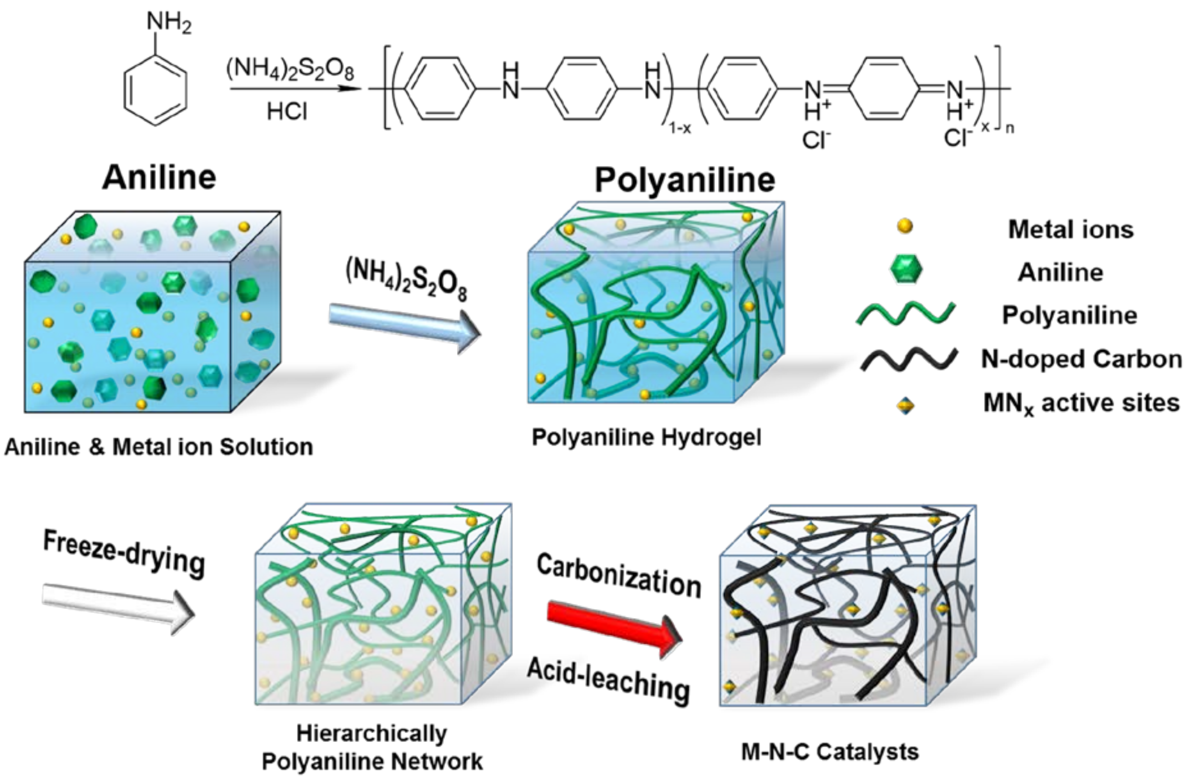
Penn synthesis:

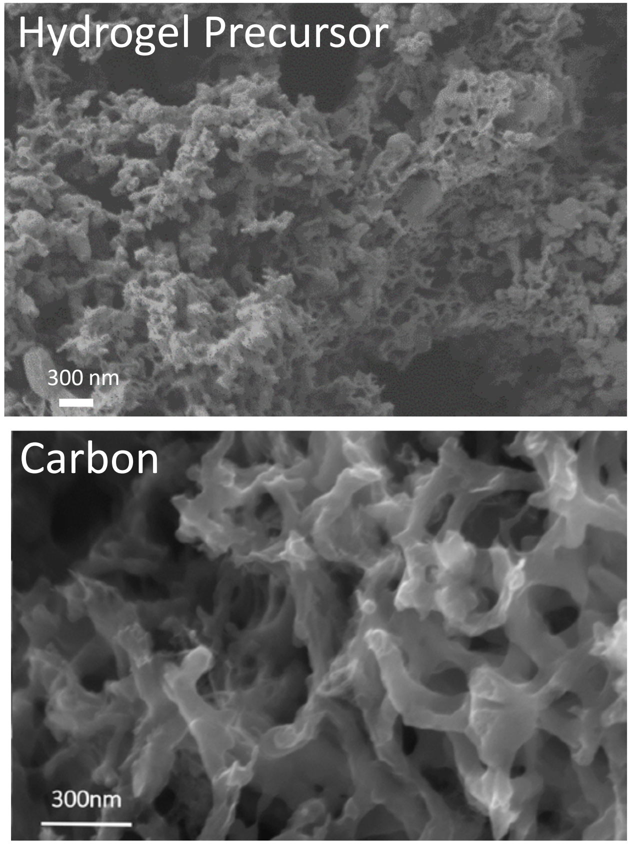


LANL synthesis:



Approach: N-doped Carbon Supports

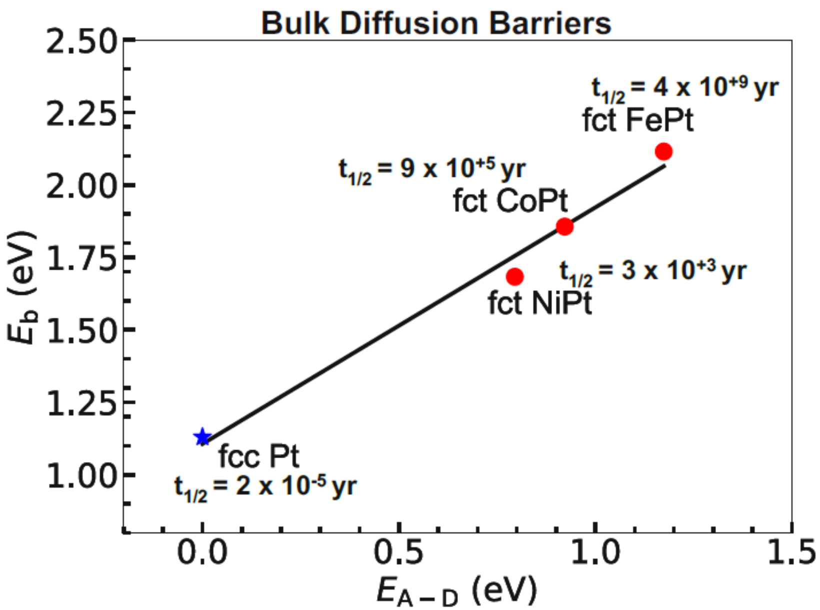


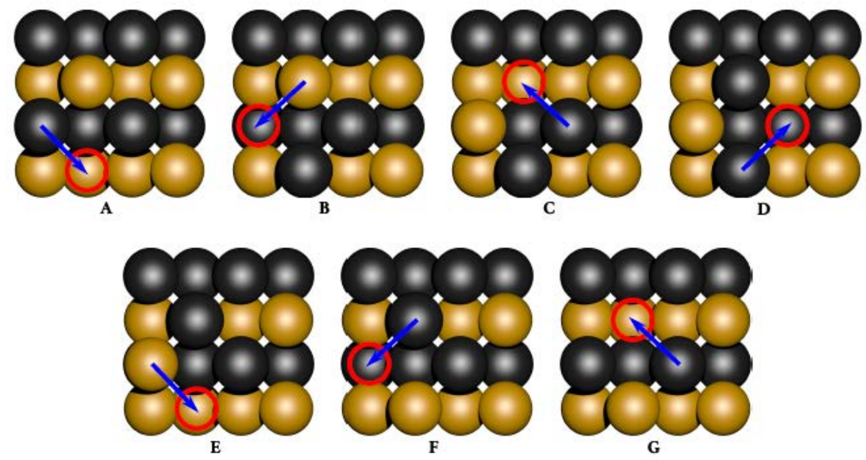


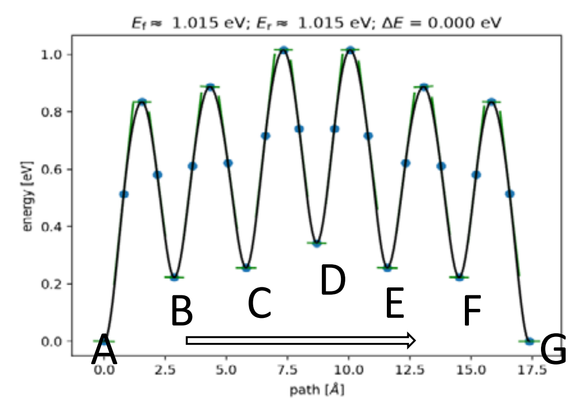
Key attributes:

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

Accomplishments and Progress: DFT Computation







- Bulk diffusion barrier correlates strongly with potential energy difference between states A and D
- $L1_0$ intermetallics show much larger diffusion barriers than fcc Pt
- Results suggest that **alternative mechanisms (e.g., oxygen place exchange) are more important in controlling base metal leaching** – work is ongoing in this area

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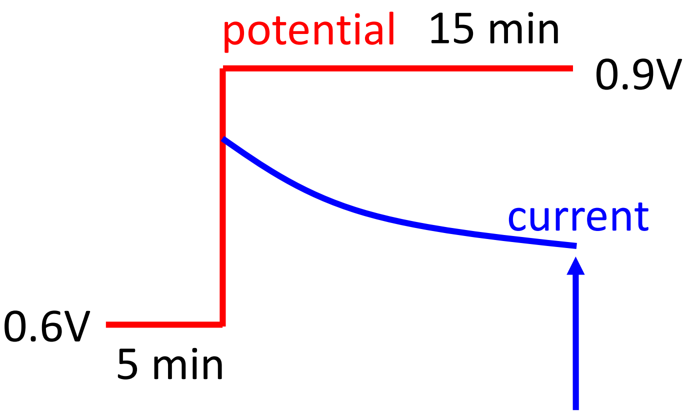
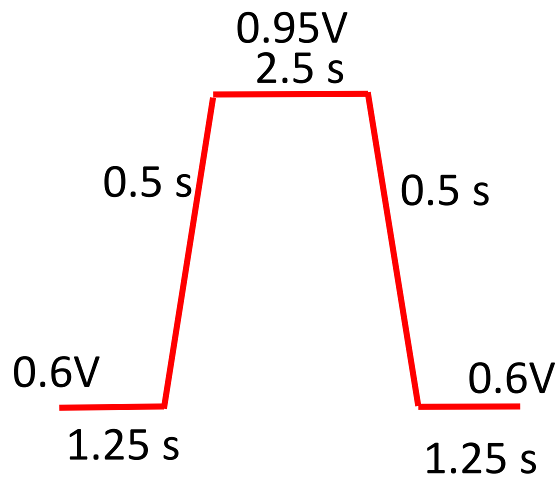
MEA Testing Protocols

Mass Activity: 15 min hold at 0.9 V

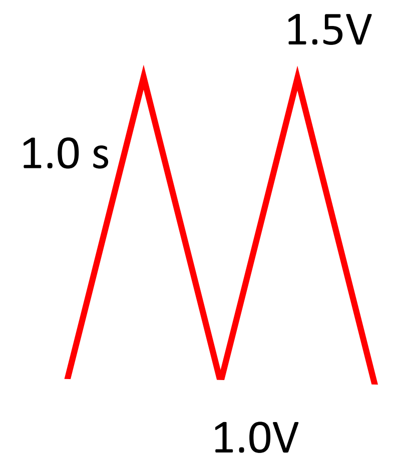


Mass activity measured during last 1 min of 15 min hold

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

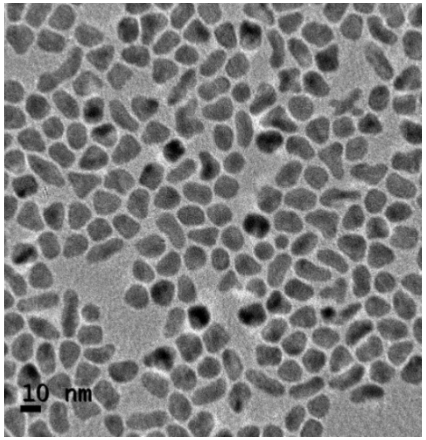
MEA Preparation and Testing

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 500/2000 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**

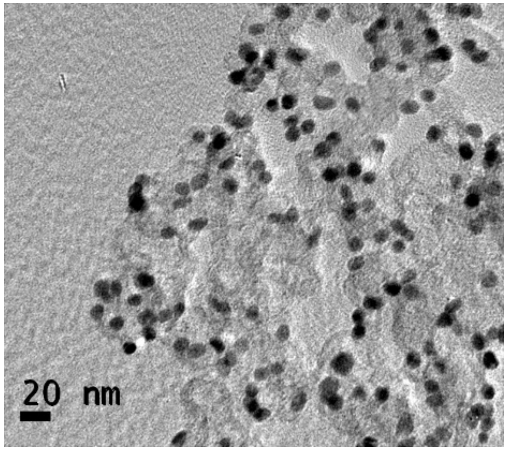
Large Particle $L1_0$-PtCo

Large Particle $L1_0$-CoPt with Pt Shell

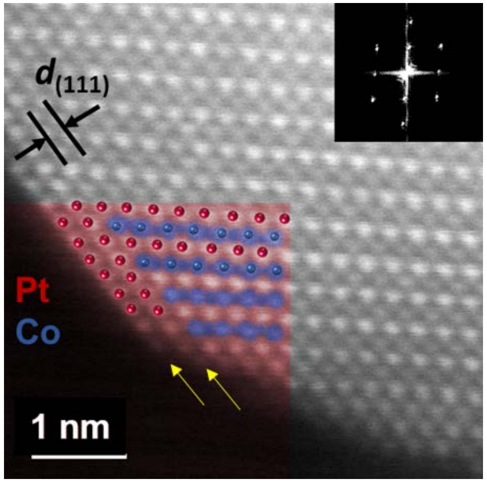


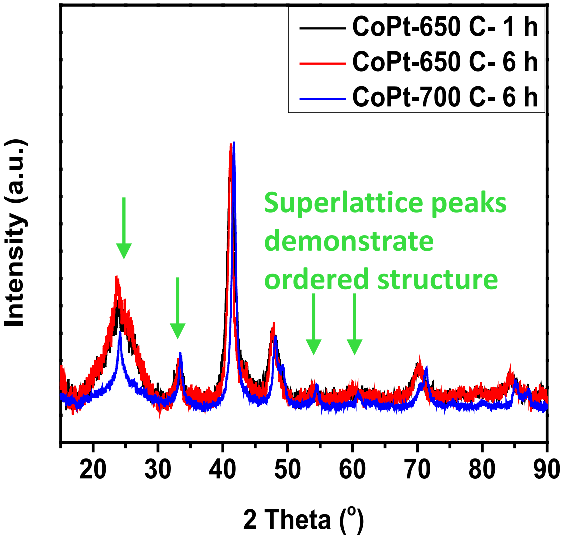
9 nm $Co_{49}Pt_{51}$

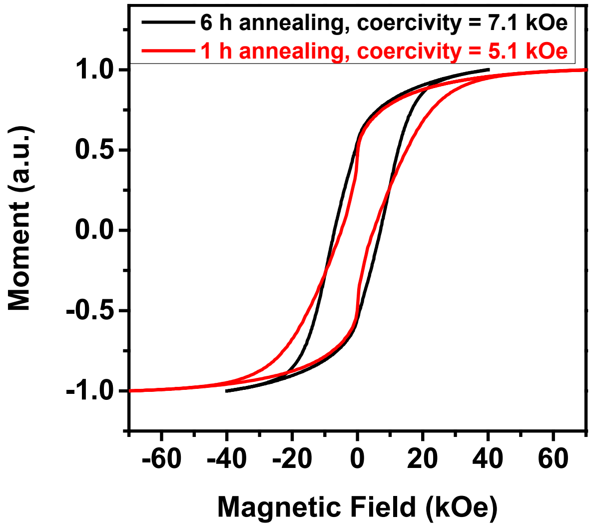
Loaded on carbon, annealed at 650°C for 6 h in 5% H_2/Ar



After acid leach:







- XRD, coercivity measurements, and TEM all demonstrate high degree of ordering
- Pt shell (~2 atoms thick) after acid leach

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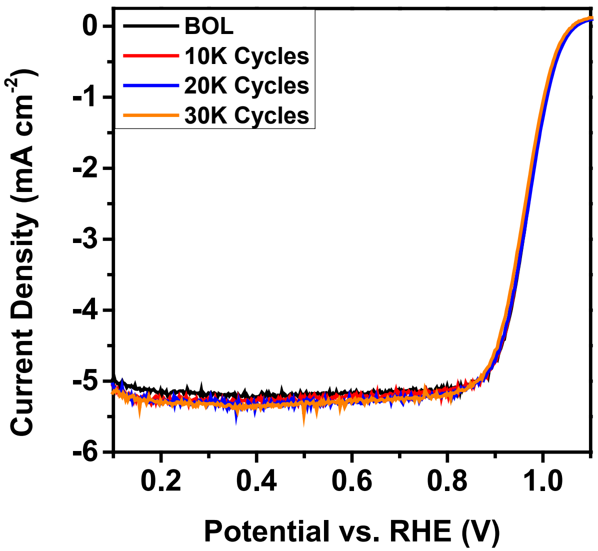
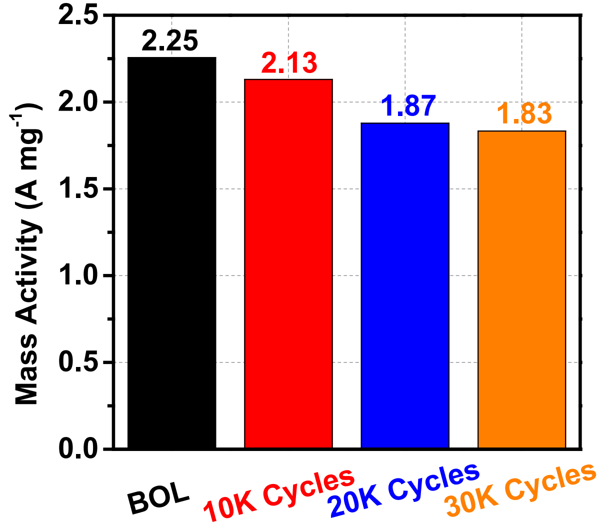
Large Particle $L1_0$-CoPt with Pt Shell

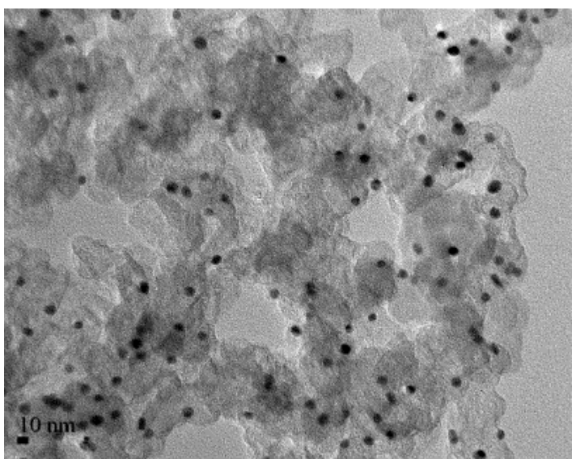
AST at 60°C, ORR measured at 25 °C



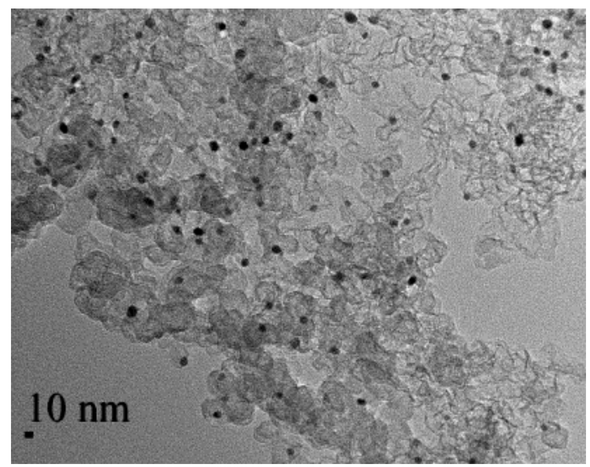


18.6 % loss in MA

BOL



$Co_{43}Pt_{57}$



$Co_{39}Pt_{61}$

EOL:
After 30 K Cycles

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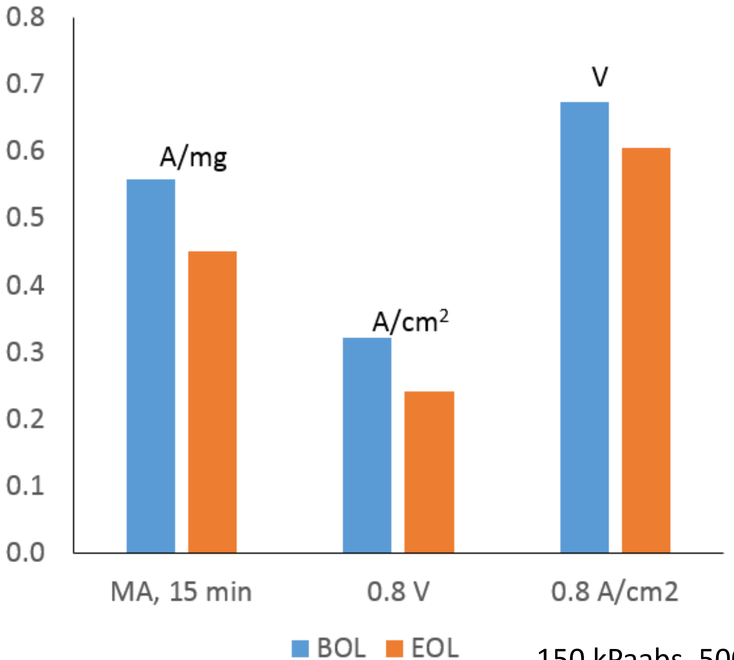
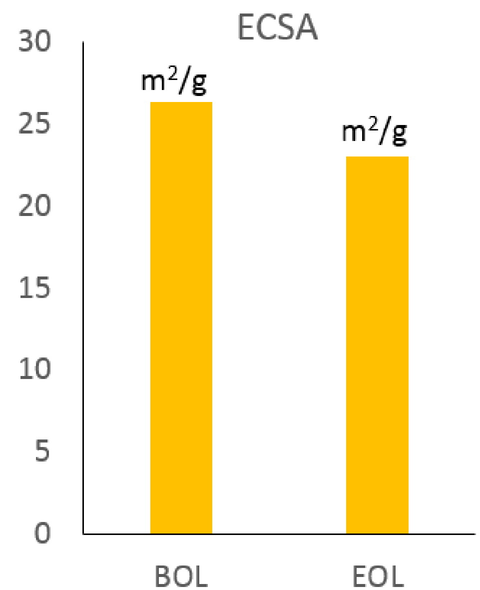
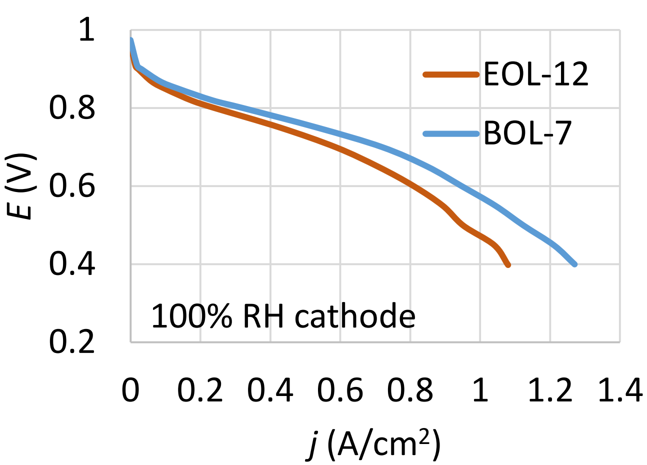
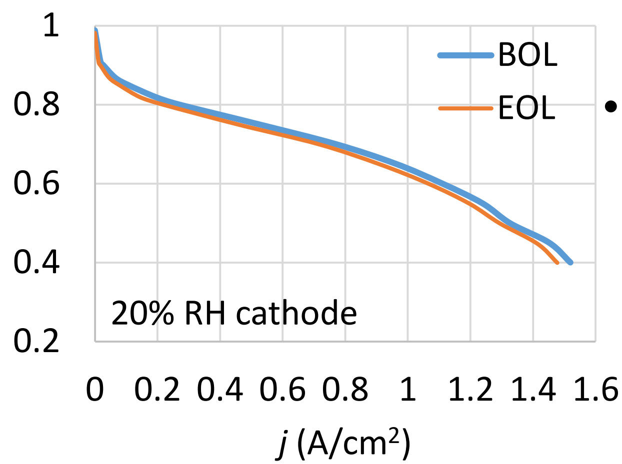
Large Particle L1$_0$-CoPt@Pt: MEA Testing





150 kPaabs, 500/1000 sccm H_2/air, 5 cm^2, 0.105 mgPt/cm^2 cathode, Nafion 211





- BOL mass activity: **0.56 A/mgPGM** (Target: >0.44 A/mgPGM)
- Post-30K cycle mass activity (measured at 15 min): **0.45 A/mgPGM**
- Loss after 30K cycles: **20%** (Target: <40%)
- Loss at 0.8 A/cm^2 after 30K cycles: **69 mV** (Target: <30 mV), but mostly due to flooding
- Power density: **0.58 and 0.73 W/cm^2** at 150 and 250 kPa (Target: 1 W/cm^2)

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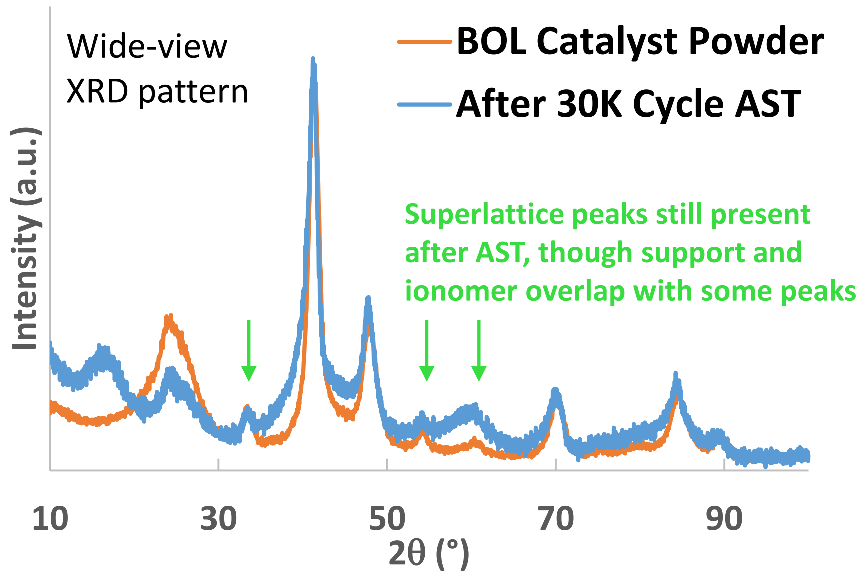
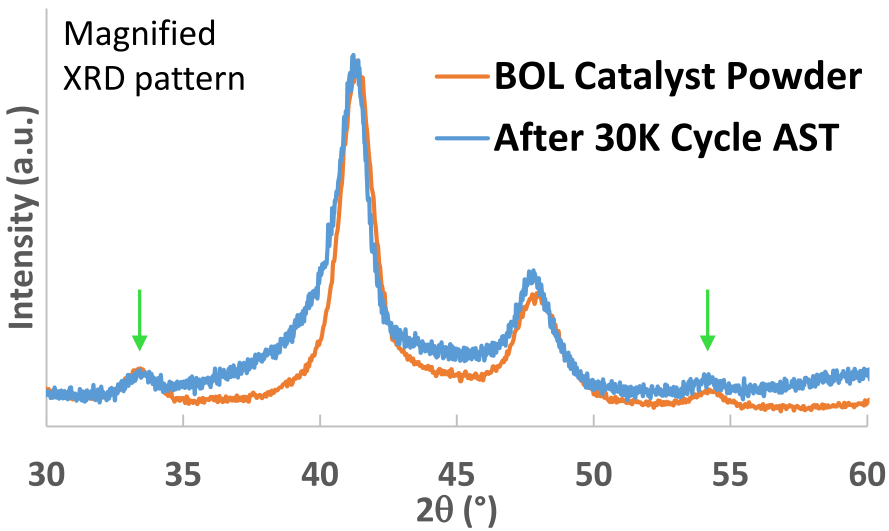
Large Particle $L1_0$-CoPt@Pt: XRD and XRF





- XRD superlattice peaks are slightly smaller after 30K cycle AST, suggesting surface leaching
- Insignificant shift in peak position, indicating **lattice established by ordered core remains unchanged**
- XRF indicates composition change ($Pt_{0.61}Co_{0.39} \rightarrow Pt_{0.71}Co_{0.29}$), indicating 36% of Co was lost

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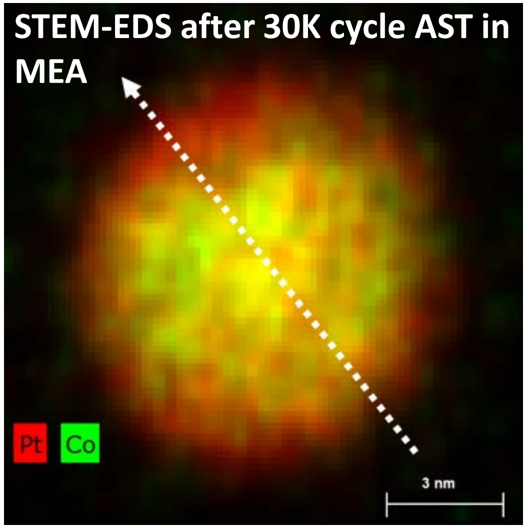
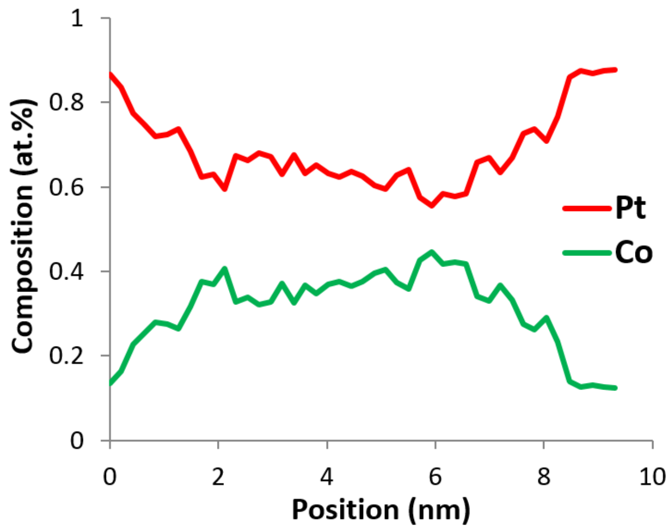
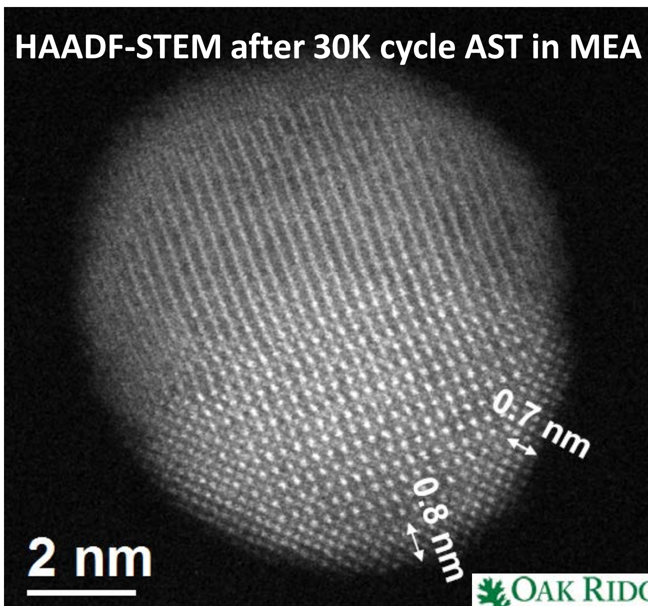
Brown $L1_0$-CoPt/Pt: STEM





- STEM-EDS shows ~1 nm Pt shell surrounding $Pt_{50}Co_{50}$ core after AST (total particle composition $Pt_{70}Co_{30}$)
- HAADF-STEM shows highly ordered core remains after AST, coated with a ~0.7-1.0 nm Pt shell (3-4 atoms thick)



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Key conclusions:

- Ordered core remains intact even after AST
- Co leaching occurs only from surface, forming Pt shell that protects particle interior from further leaching
- Pt shell is too thick for significant ligand enhancement after AST, but **kinetic enhancement due to strain remains even after 30K cycles**

J Li et al., Joule 2018

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Large Particle $L1_0$-CoPt@Pt Status vs. Targets

	Units	Measured	Target
Mass Activity	A/mgPGM	**0.56**	**0.44**
Mass Activity after Catalyst AST	A/mgPGM	**0.45**	**0.264**
Degradation at 0.8 A/cm^2 (Catalyst AST)	mV	**69**	**30**
Current Density at 0.8 V	A/cm^2	**0.32**	**0.3**
Power at 0.67 V, 150 kPa_{abs}	W/cm^2	**0.58**	**1**
Power at 0.67 V, 250 kPa_{abs}	W/cm^2	**0.73**	**1**
Cathode PGM Loading	mg/cm^2	**0.105**	**0.125**
Robustness, Cold		**0.64**	**0.7**
Robustness, Cold Transient		**0.68**	**0.7**
Robustness, Hot		**0.19**	**0.7**
ECSA	m^2/gPt	**26**	
ECSA after Catalyst AST	m^2/gPt	**23**	
Crystallite Size (XRD)	nm	**7.8**	
Crystallite Size after Catalyst AST	nm	**9.6**	
Particle Size (TEM)	nm	**8.9**	
Particle Size after Catalyst AST	nm	**8.7**	
Composition	%	**Pt61Co39**	
Composition after Catalyst AST	%	**Pt71Co29**	

- High mass activity at BOL; only 20% loss after AST
- Excellent ECSA retention (but low ECSA from the start)
- Degradation at 0.8 A/cm^2 due to increased flooding after AST
- High power performance is too low – probably due to thick electrode (~25 µm)

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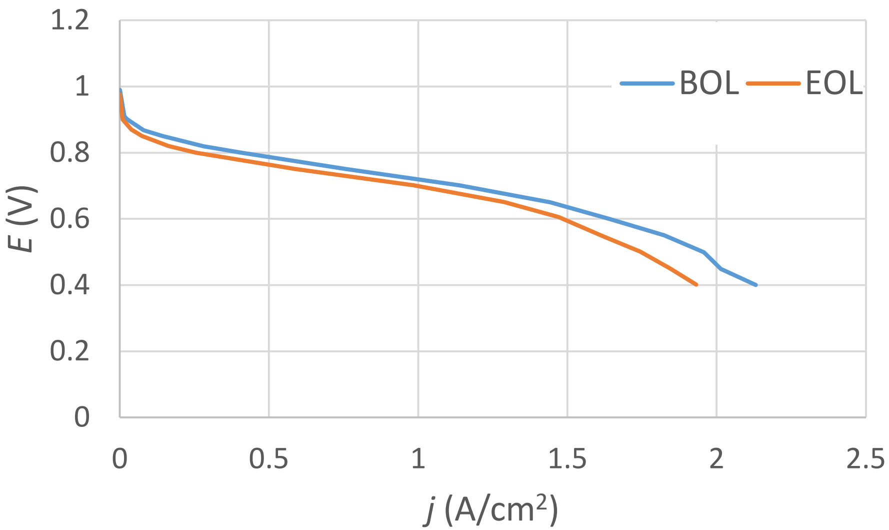
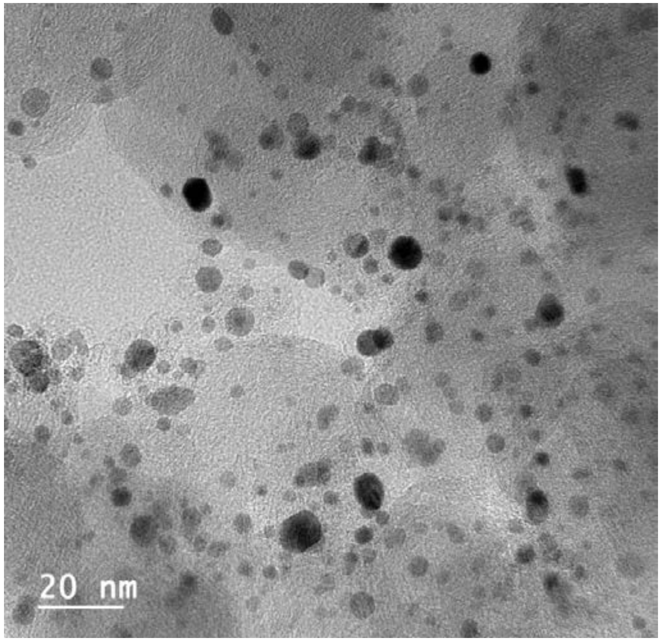
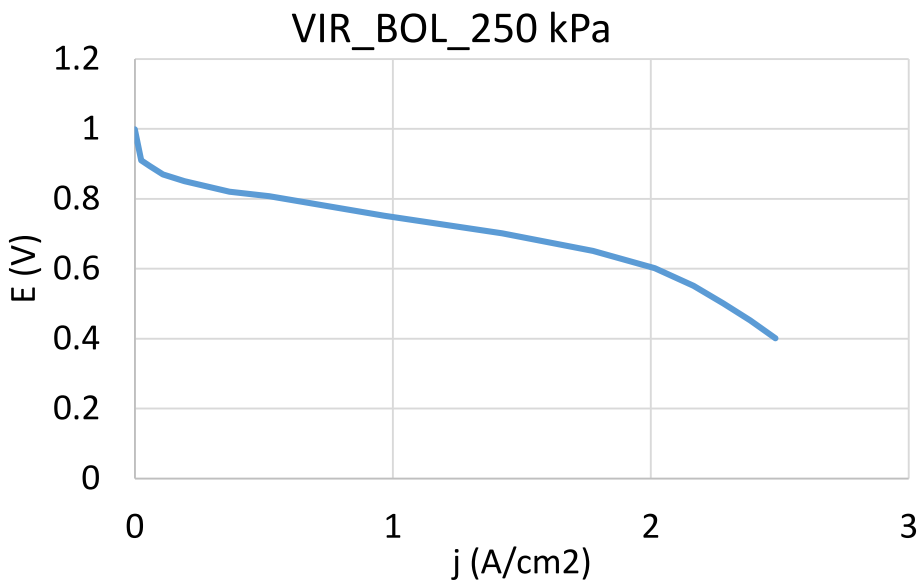
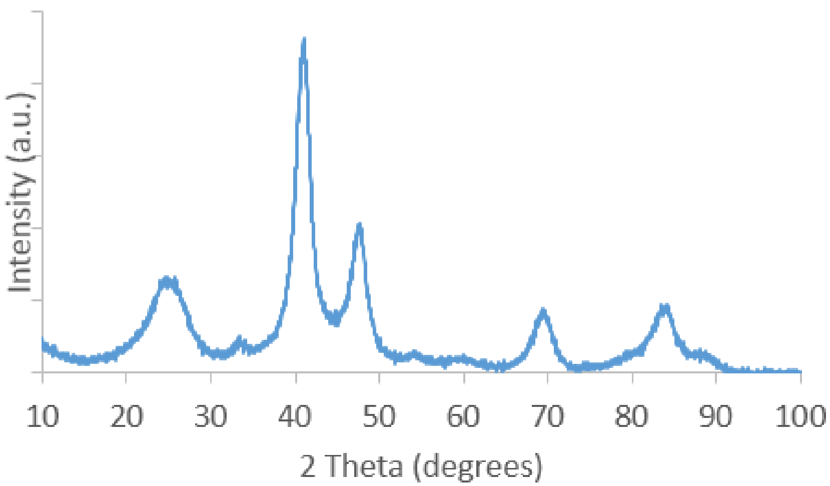
Small Particle $L1_0$-PtCo

L1_0-CoPt@Pt/Vulcan

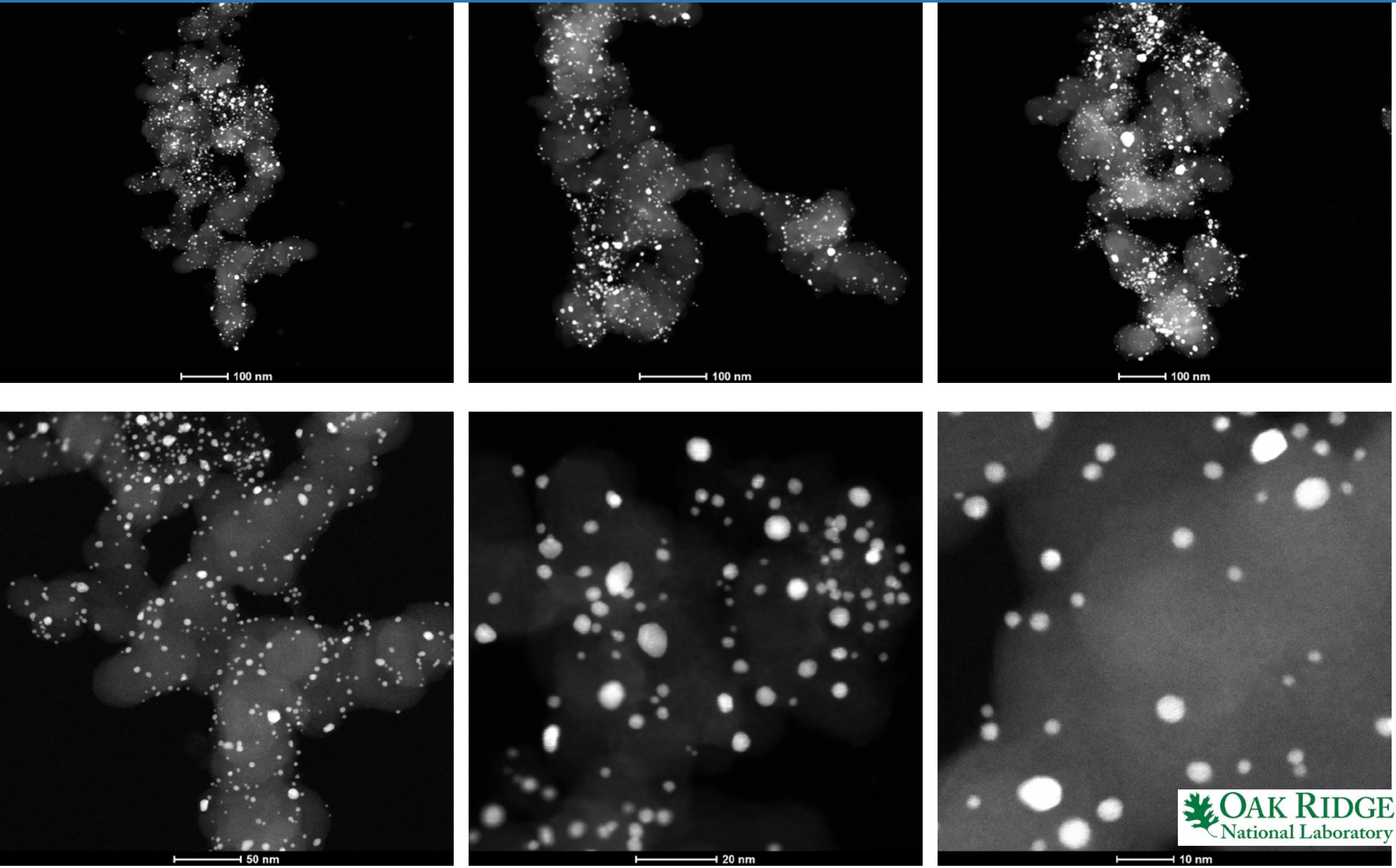






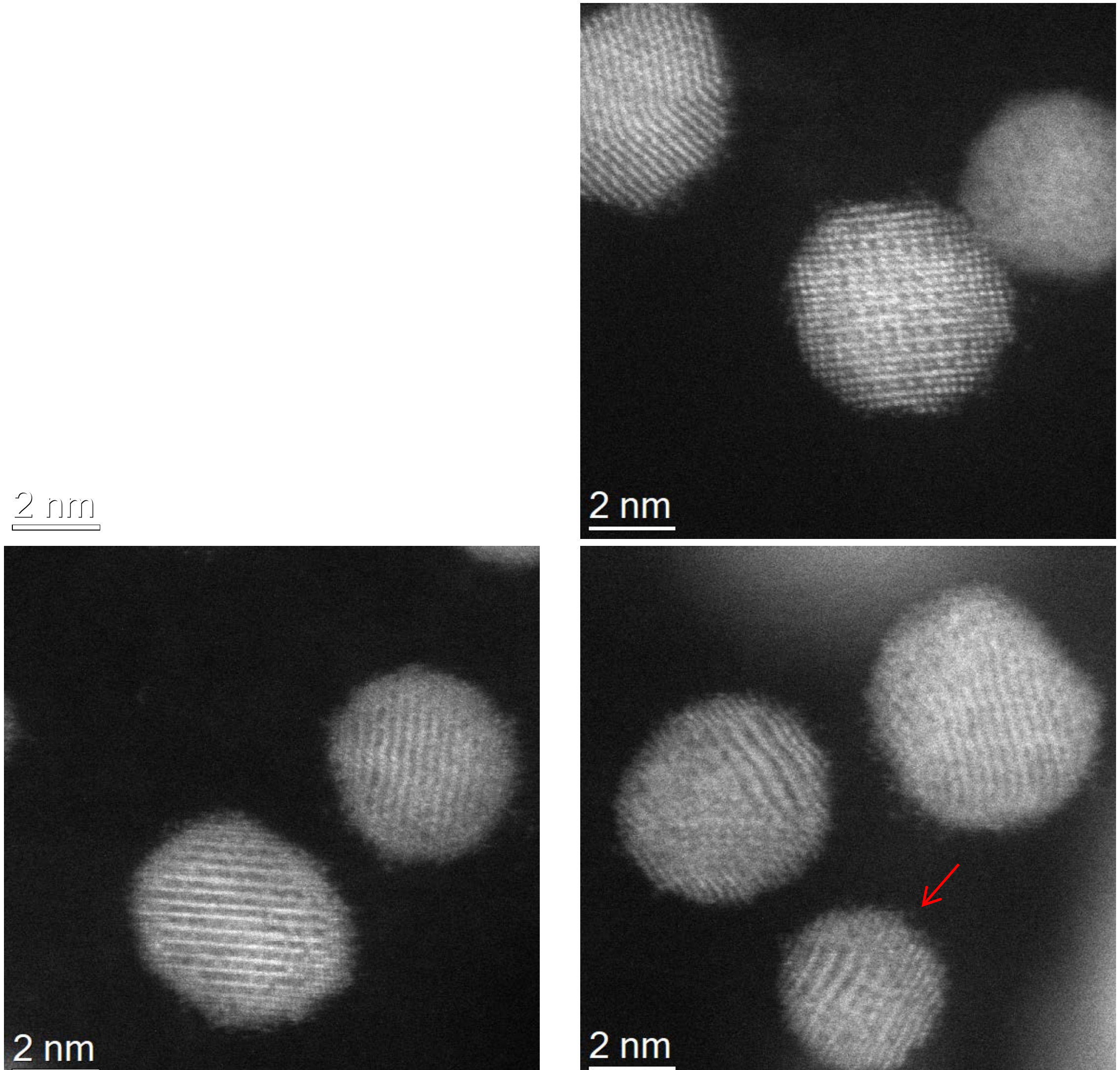


$L1_0$-CoPt@Pt/Vulcan

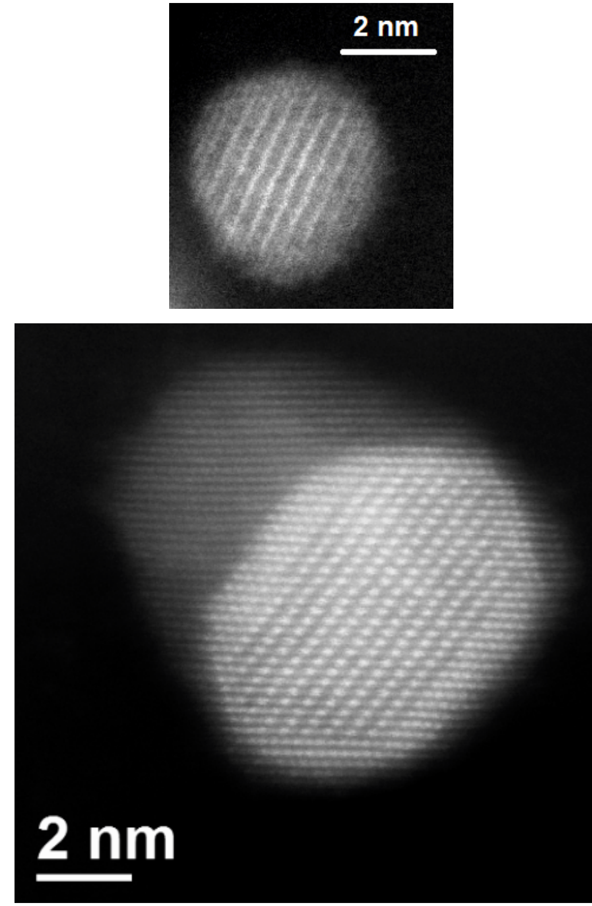


L1$_0$-CoPt@Pt/Vulcan (#19g)

BOL Powder

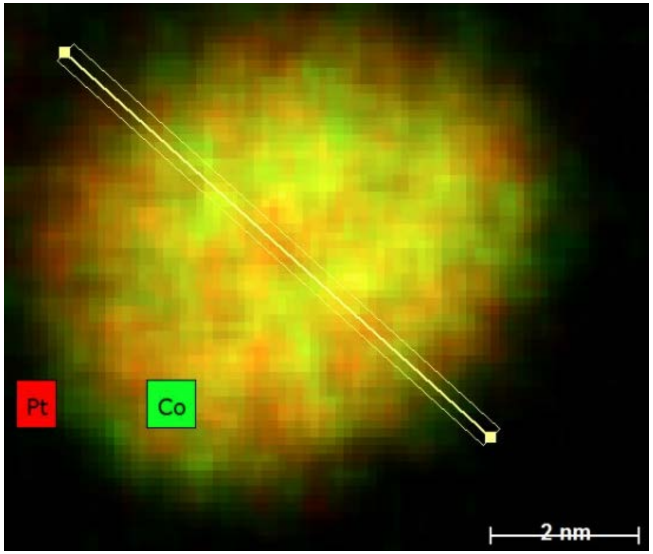


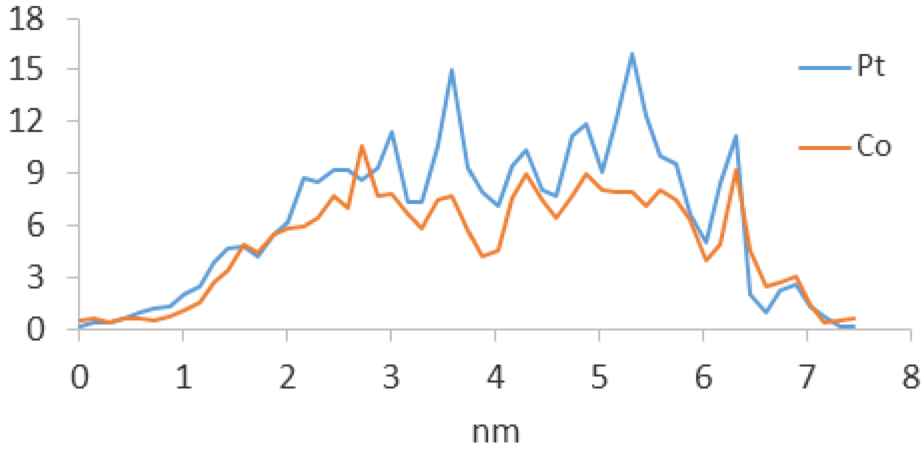
After 30K cycles in MEA

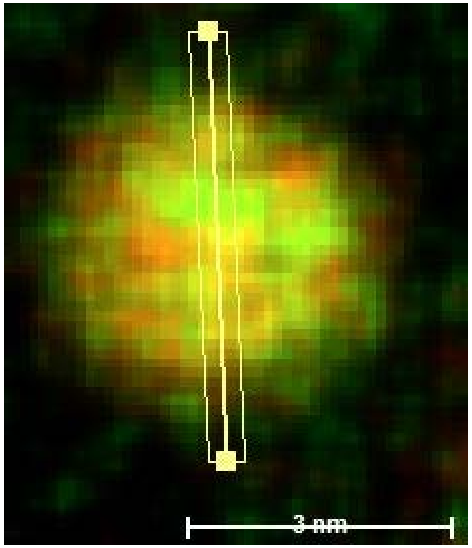


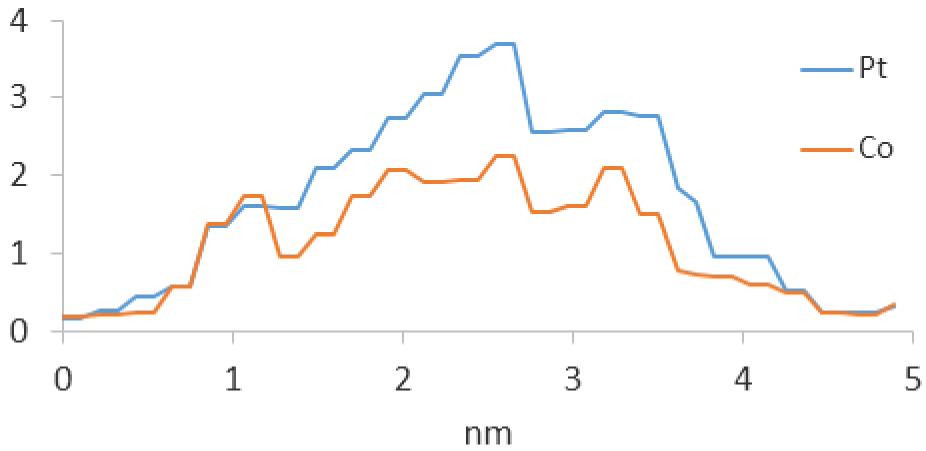
Ordered particles remain after AST

A1-PtCo/Vulcan, BOL









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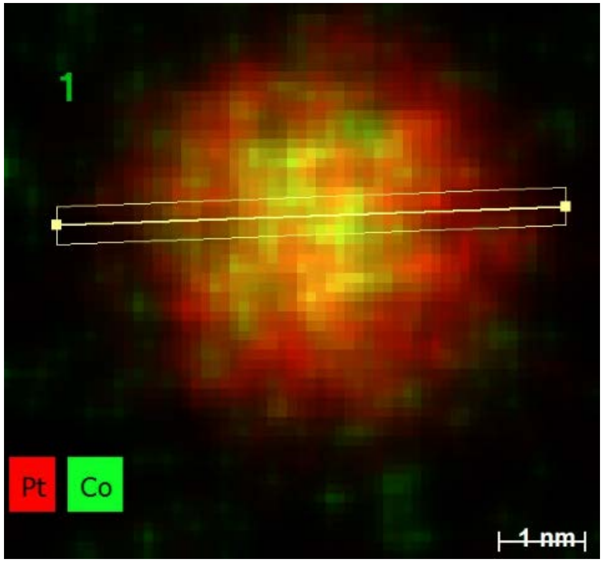
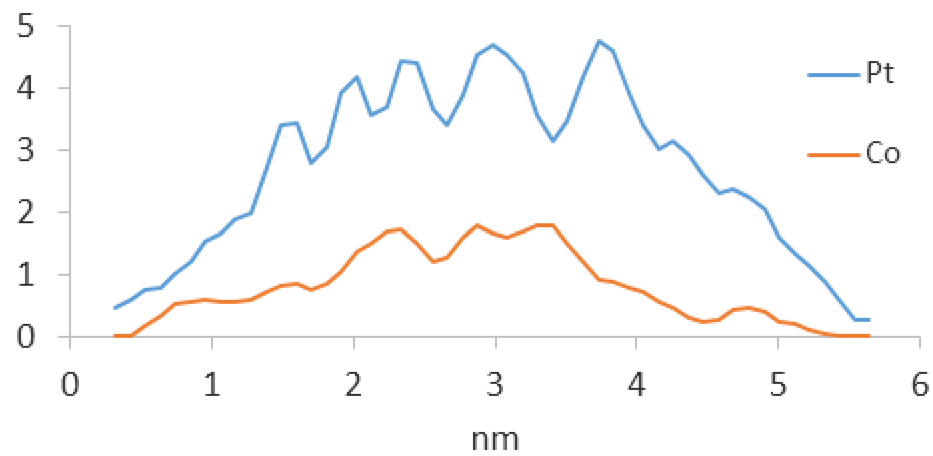
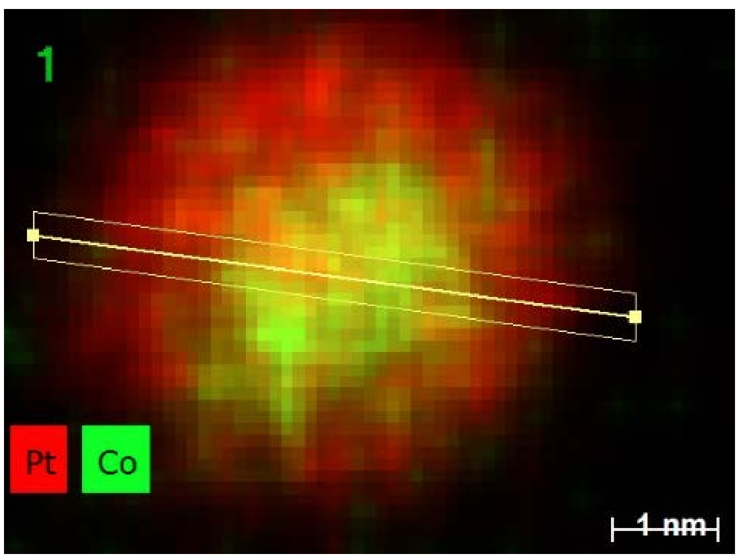
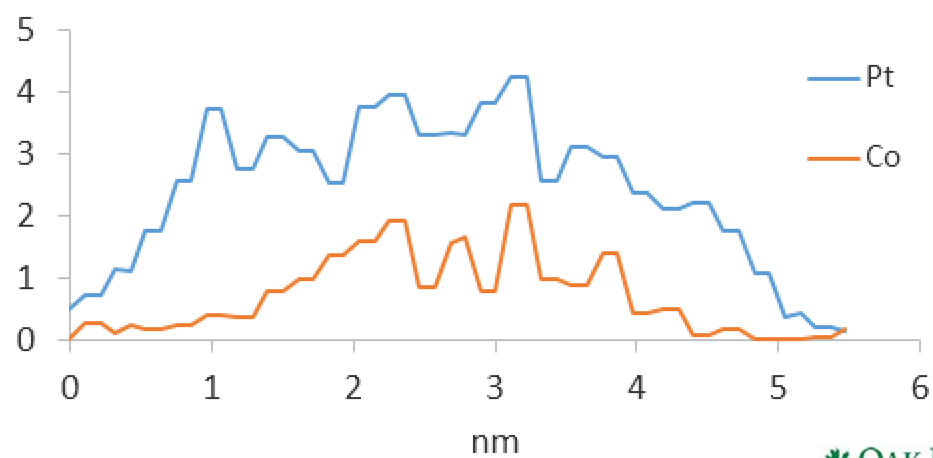
A1-PtCo/Vulcan, EOL









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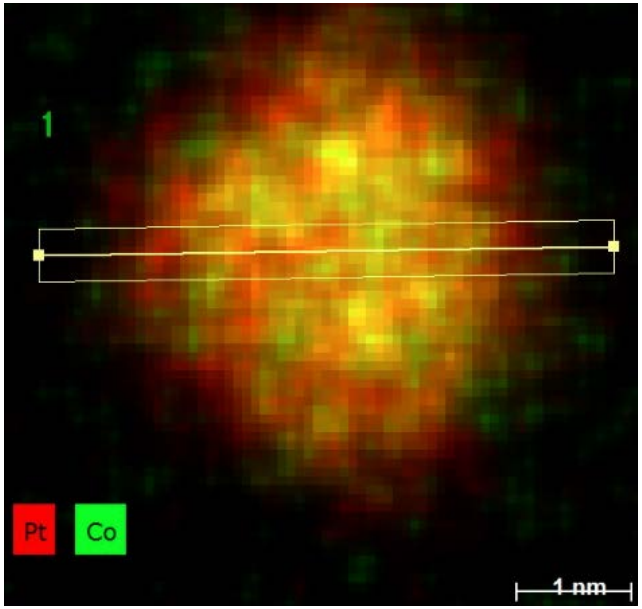
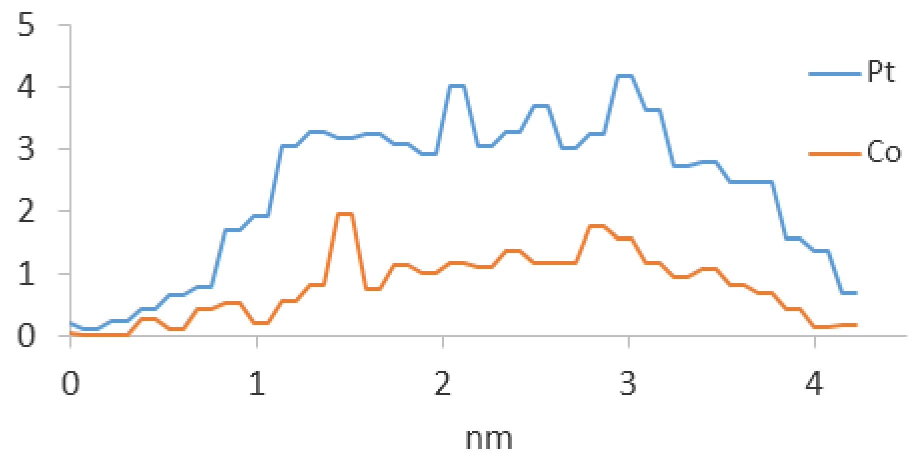
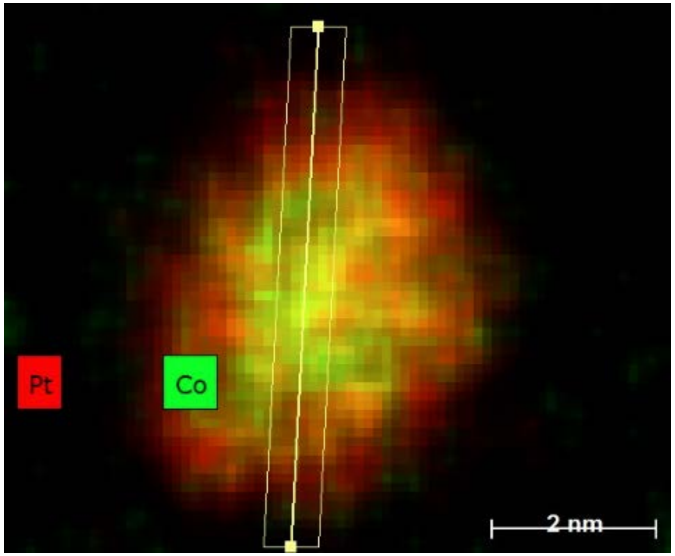
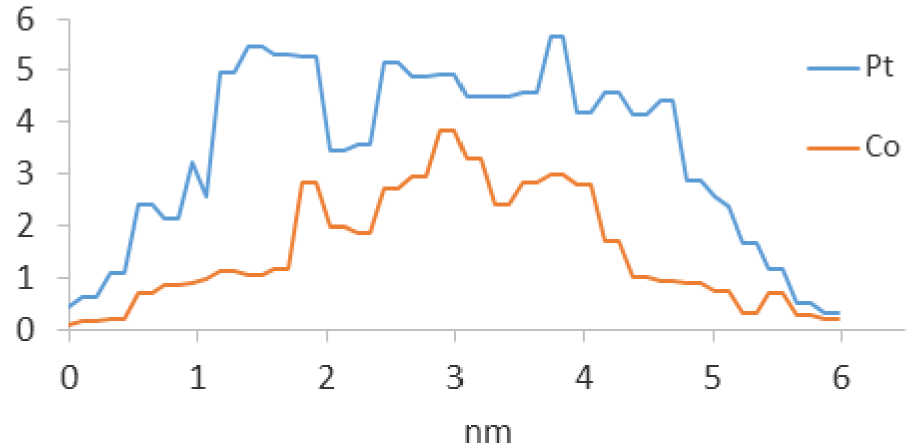
$L1_0$-PtCo@Pt/Vulcan, BOL

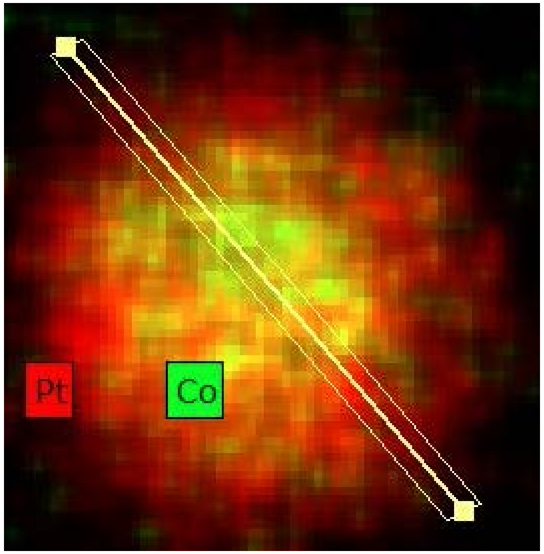


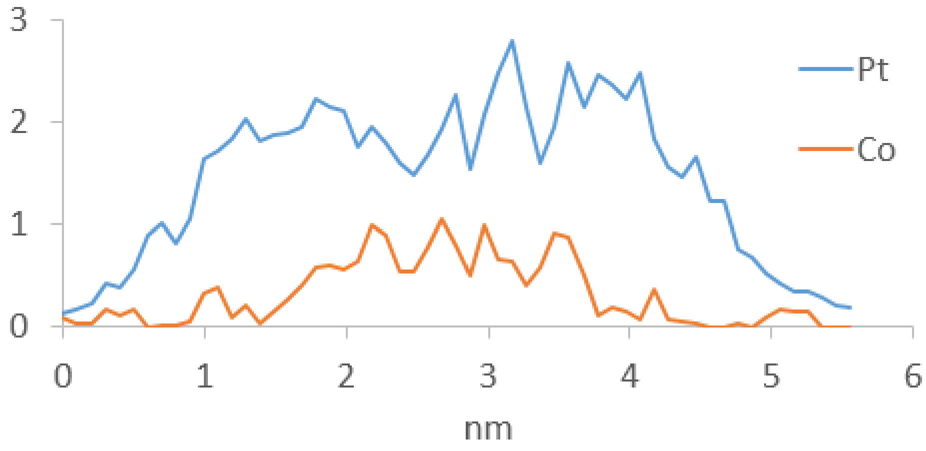


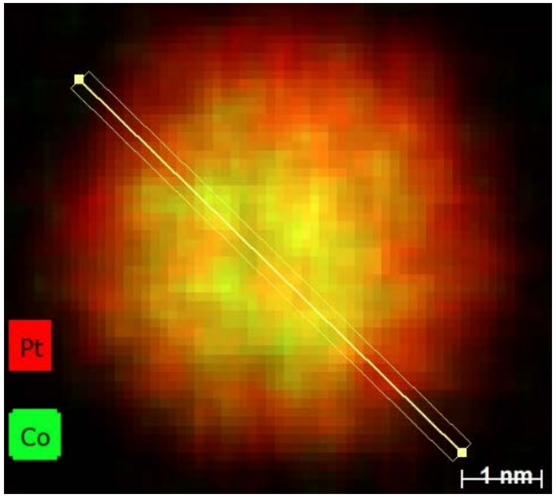


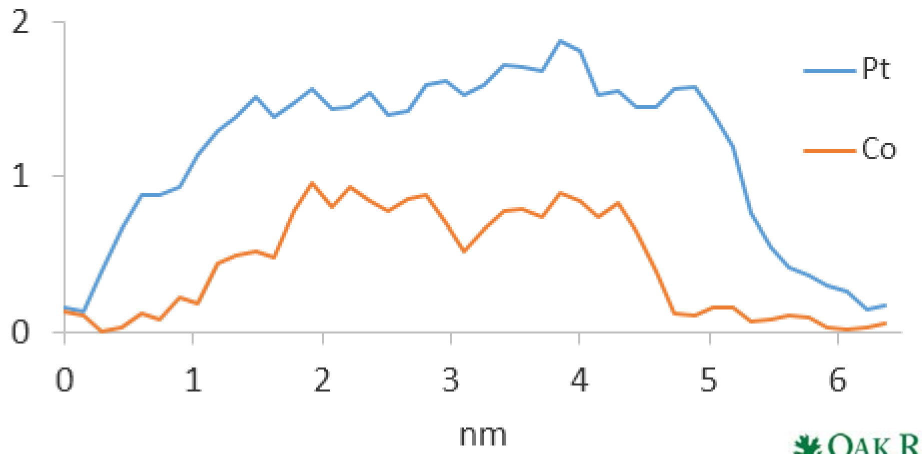


$L1_0$-PtCo@Pt/Vulcan, EOL



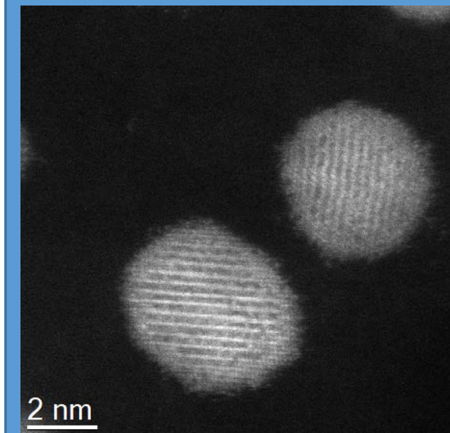


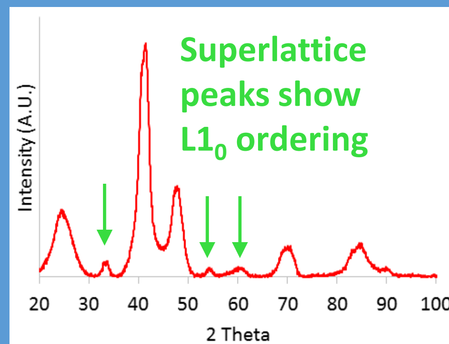


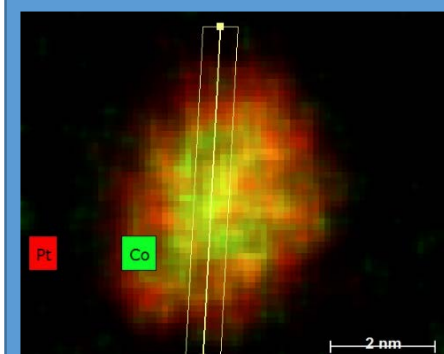


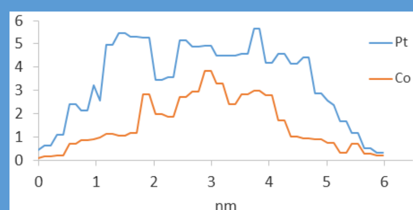
Accomplishment: Small $L1_0$-PtCo Particles

BOL Catalyst

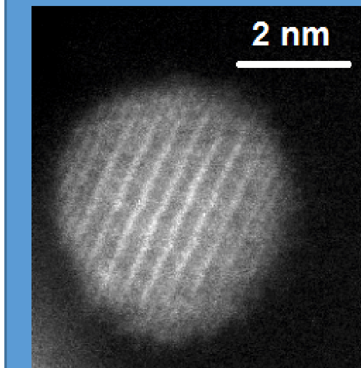


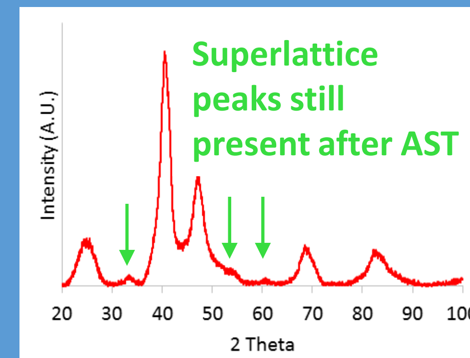


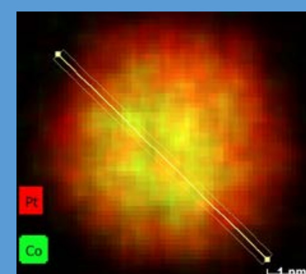


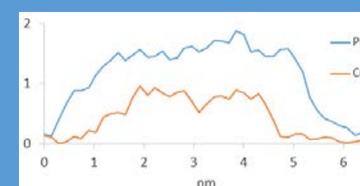


After 30K cycles in MEA









Particle structure is similar before and after AST: Pt shell around $L1_0$-PtCo core

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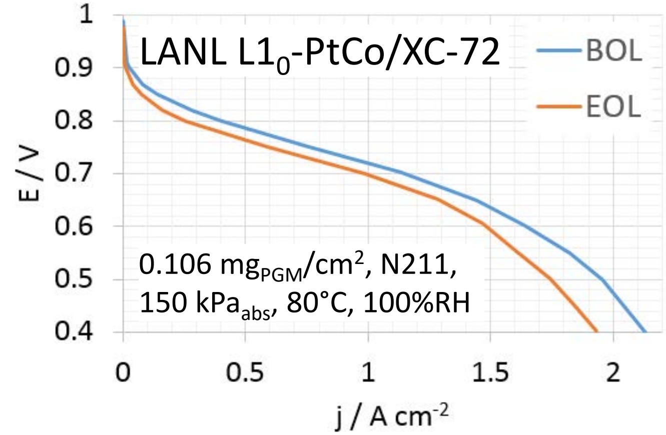
$L1_0$-PtCo/Vulcan: Fuel Cell Testing

	Units	Measured	Target
Mass Activity	A/mgPGM	**0.60**	**0.44**
Mass Activity Loss [1]	%	**40**	**40**
Degradation at 0.8 A/cm^2 [1]	mV	**26**	**30**
Current Density at 0.8 V	A/cm^2	**0.41**	**0.3**
Power at 0.67 V, 150 kPa_{abs}	W/cm^2	**0.89**	**1**
Power at 0.67 V, 250 kPa_{abs}	W/cm^2	**1.10**	**1**
PGM Loading [2]	mg/cm^2	**0.106**	**0.125**
Robustness (cold)		**0.94**	**0.7**
Robustness (cold transient)		**0.91**	**0.7**
Robustness (hot)		**0.92**	**0.7**

[1] 30K square wave cycles, 0.6-0.95 V [2] Cathode



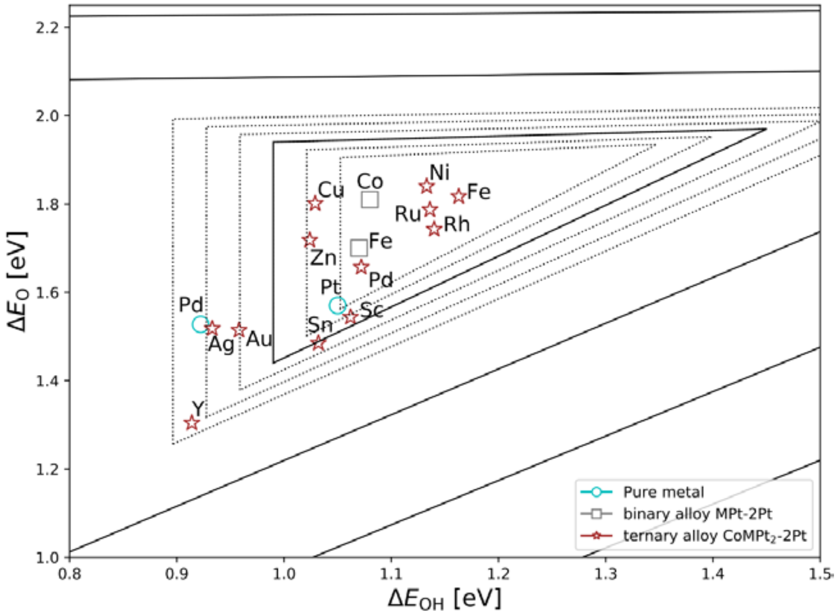
ECSA (CO stripping):
62 m^2/g (BOL)
40 m^2/g (after 30K cycles)

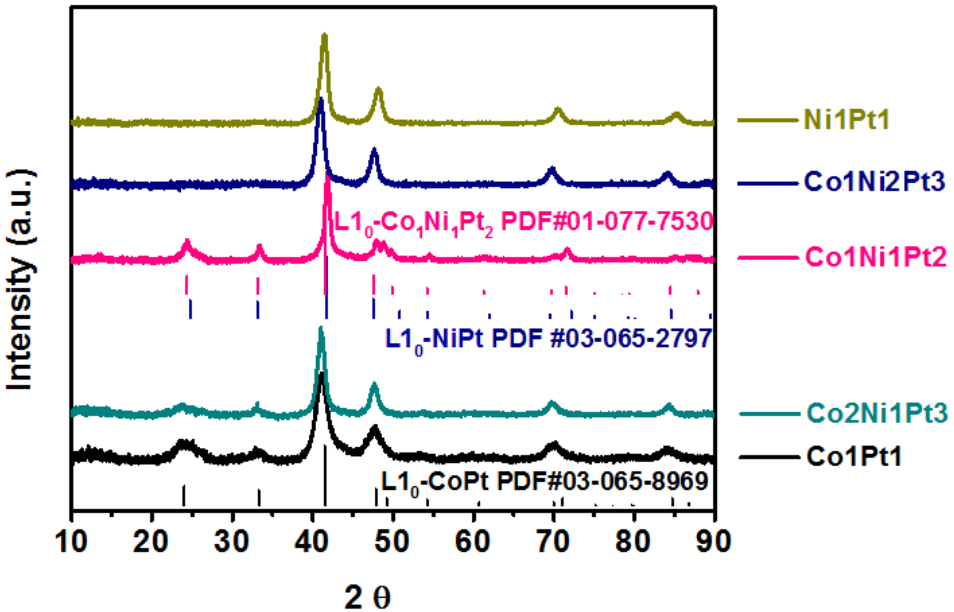
$L1_0$-PtCo@Pt/XC-72 catalyst meets or approaches DOE catalyst and MEA targets

	LANL FCC-PtCo	Commercial FCC-PtCo	LANL $L1_0$-PtCo
BOL Co%	48%	22%	**27%**
EOL Co%	12%	7%	**17%**

High durability of $L1_0$ ordered PtCo is due to decreased Co leaching – $L1_0$-PtCo has higher Co content than FCC-PtCo after 30K cycle AST

Accomplishment: Ternary $L1_0$ Development

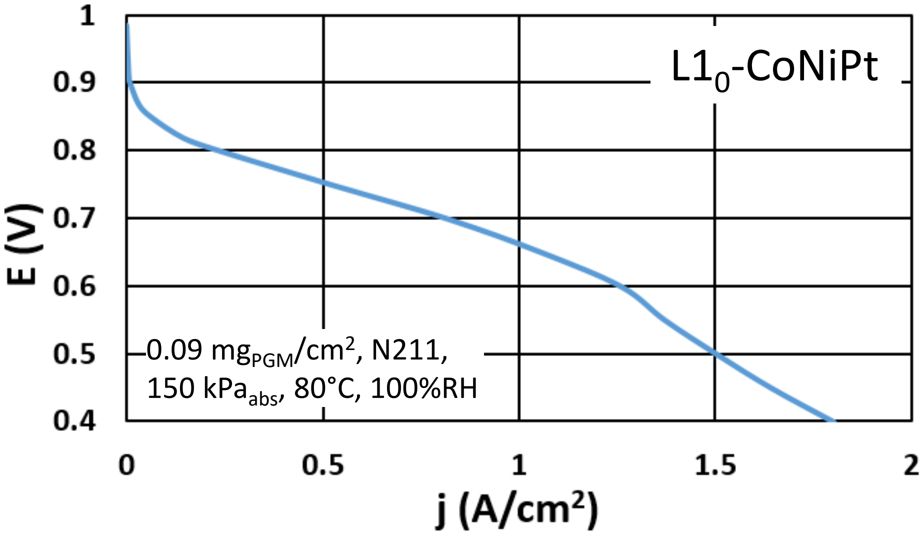


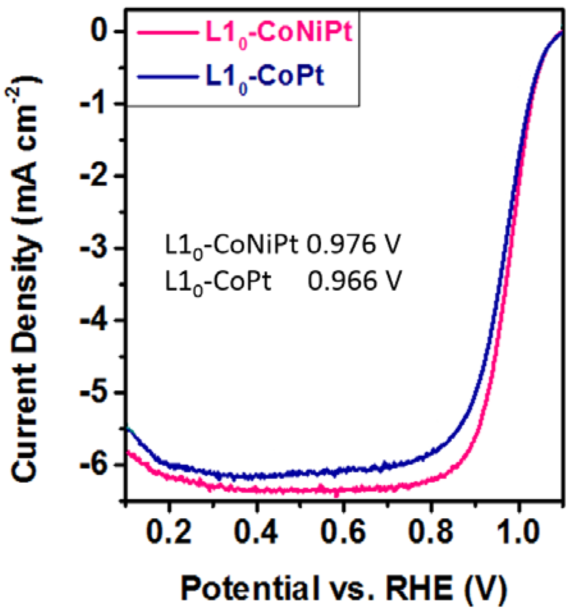


- DFT results suggest adding a 3rd component (e.g. Ni) to $L1_0$-PtCo could provide near-optimal O/OH binding energy
- XRD shows Co:Ni:Pt = 1:1:2 gives good ordering
- **Based on DFT and XRD, ternary $L1_0$-CoNiPt looks promising**

BROWN

$L1_0$-CoNiPt: MEA Testing





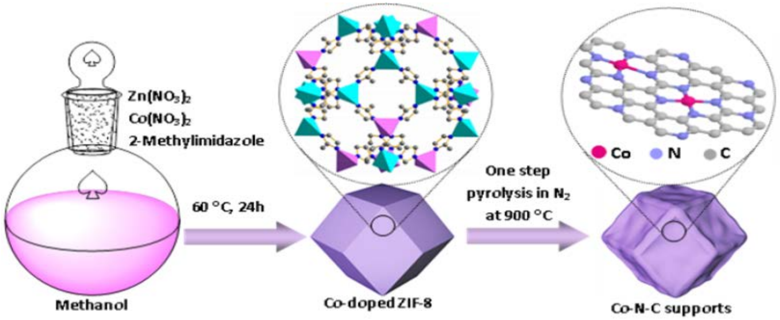
	Units	Measured	Target
Mass Activity	A/mgPGM	0.33	0.44
Mass Activity Loss [1]	%		40
Degradation at 0.8 A/cm^2 [1]	mV		30
Current Density at 0.8 V	A/cm^2	0.23	0.3
Power at 0.67 V, 150 kPa$_{abs}$	W/cm^2	0.64	1
Power at 0.67 V, 250 kPa$_{abs}$	W/cm^2		1
PGM Loading [2]	mg/cm^2	0.091	0.125

[1] 30K square wave cycles, 0.6-0.95 V

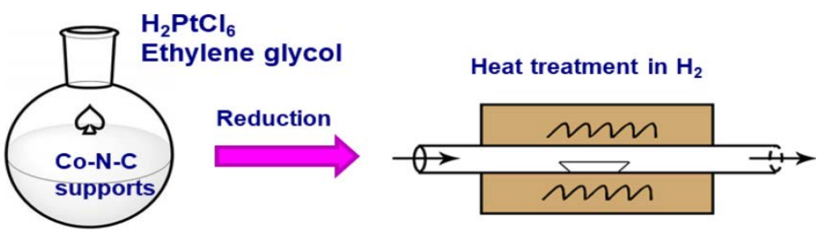
[2] Cathode

- RDE performance promising, but initial MEA results lower than expected
- Ternary $L1_0$ development still a work in progress

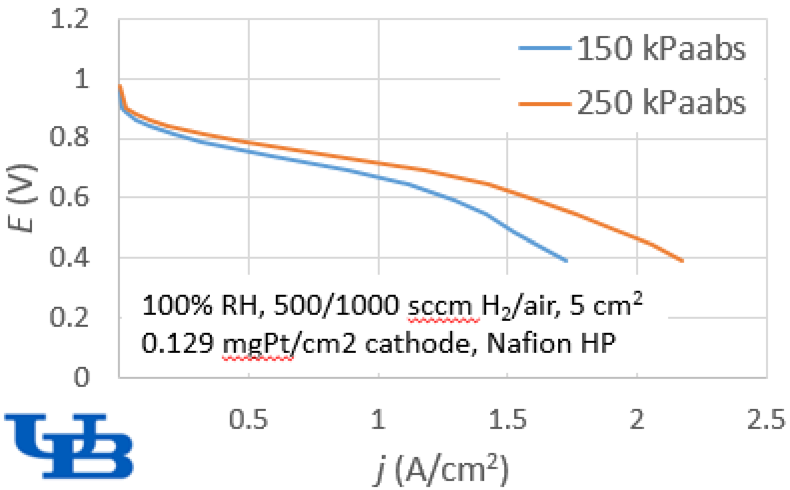
Buffalo $L1_2$-CoPt

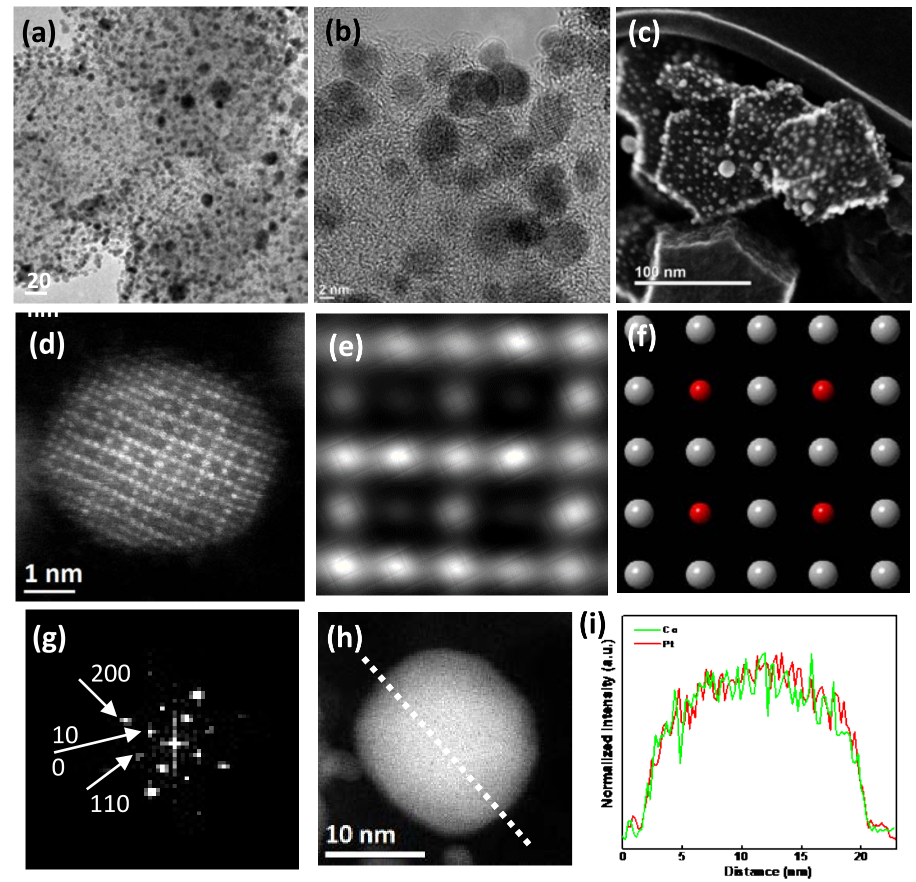


Preparation of ZIF derived carbon supports



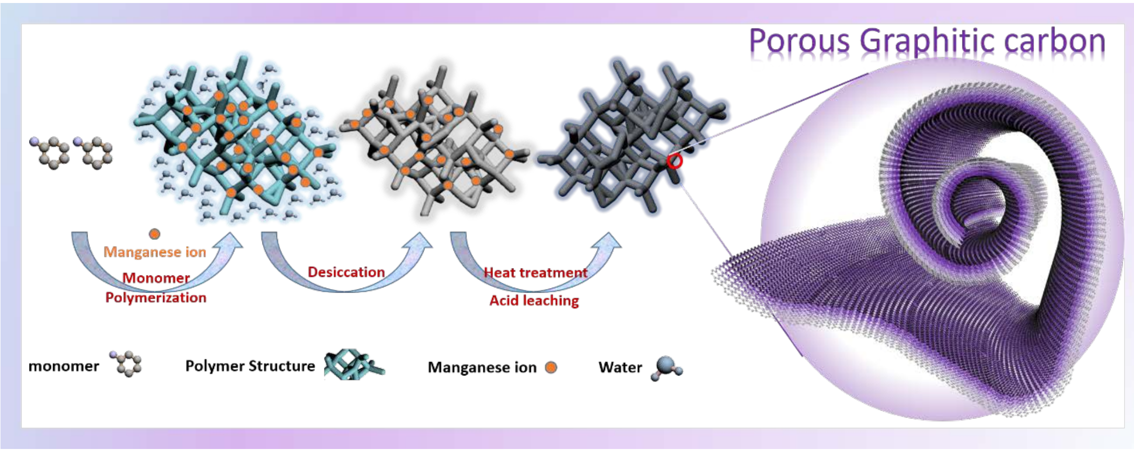
Preparation of Pt-Co intermetallic catalysts



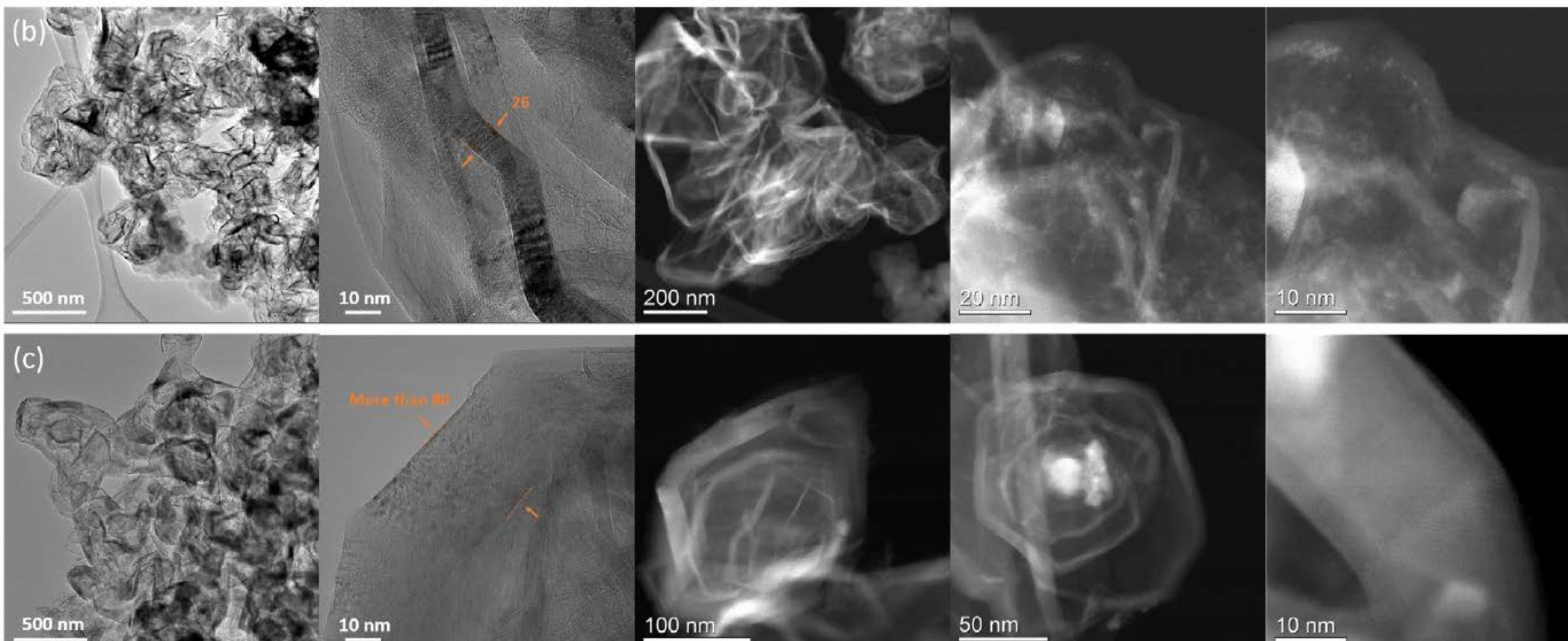


- Heat treatment of Co ZIF, followed by Pt impregnation and additional heat treatment, produces ordered PtCo on N-doped carbon
- High fuel cell performance in unoptimized MEA

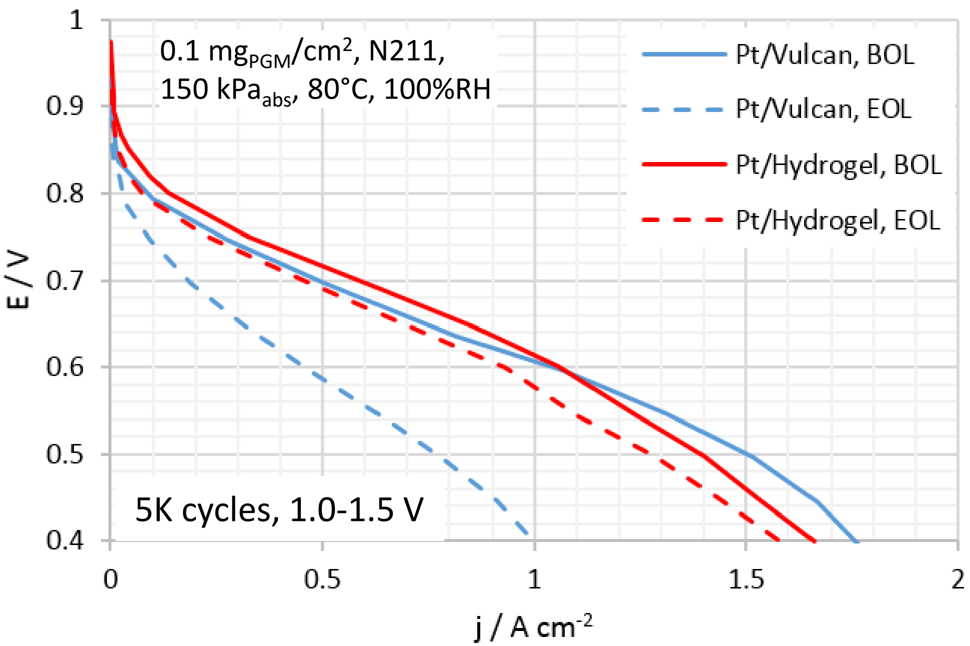
Buffalo Mn-Hydrogel Supports

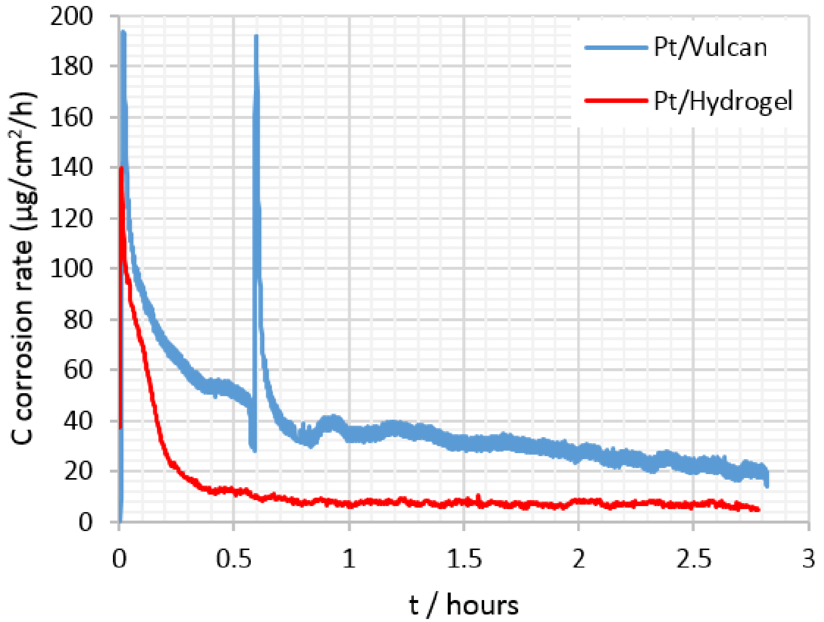


- Polymer hydrogels carbonized in presence of Mn have highly graphitic structure
- Graphitic structure prevents C corrosion, enhancing fuel cell stability



Accomplishment: 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	31	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

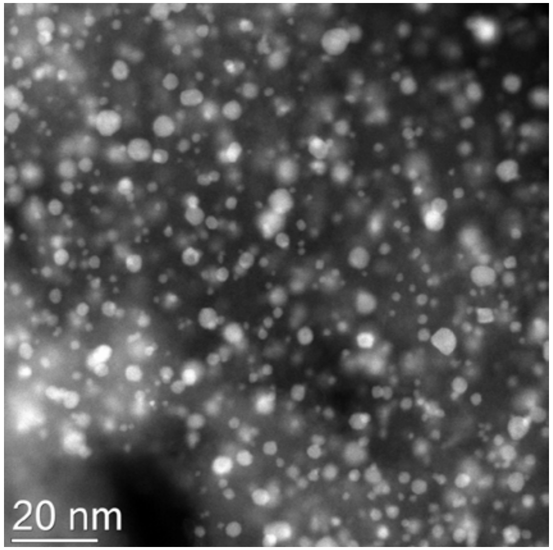
[1] 5K triangle wave cycles, 1.0-1.5 V

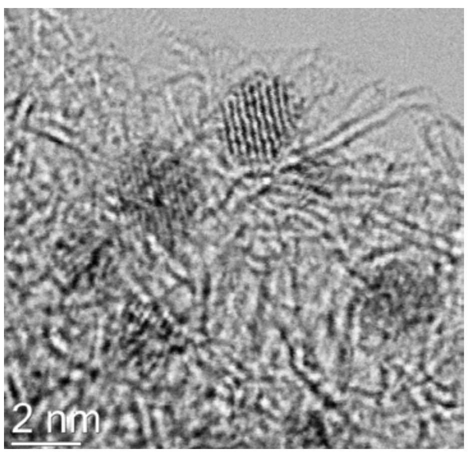
[2] Cathode

- Graphitic structure reduces corrosion
- **Hydrogel supports meet or approach durability targets with pure Pt**
- Need more active catalyst for performance targets

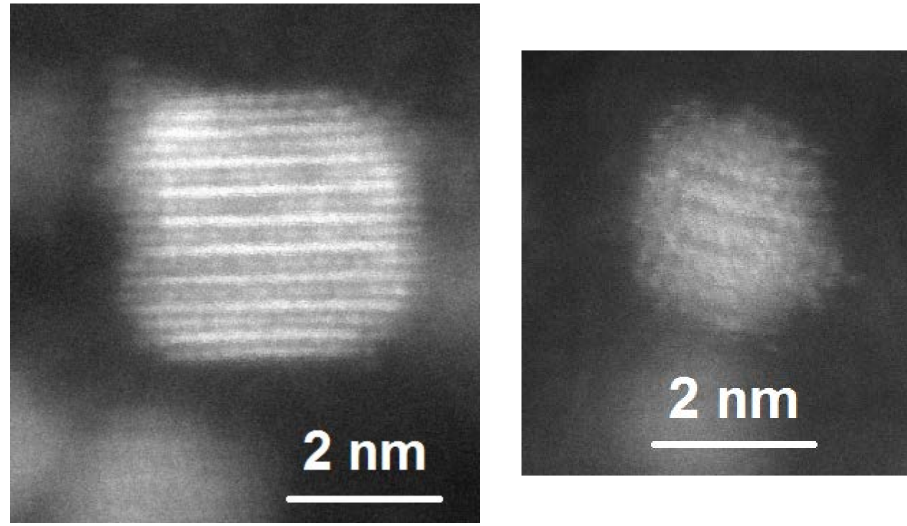
Qiao et al., Energy Environ. Sci., 2019, Accepted

$L1_0$-PtCo/Hydrogel





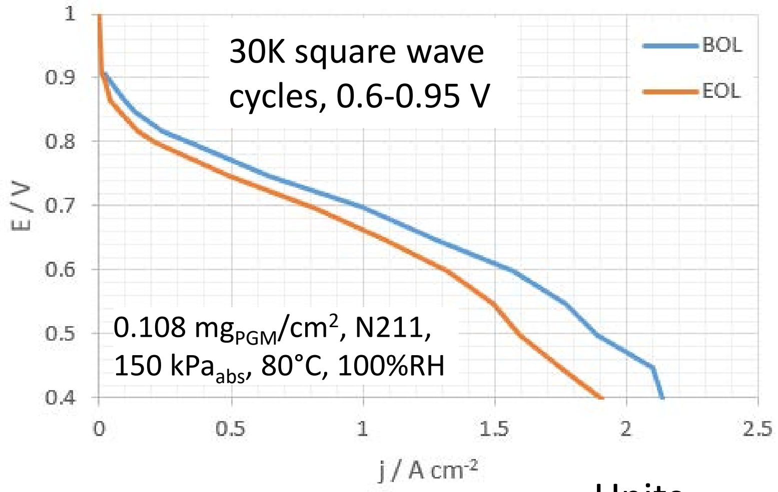
PtCo particles on folded graphene sheets

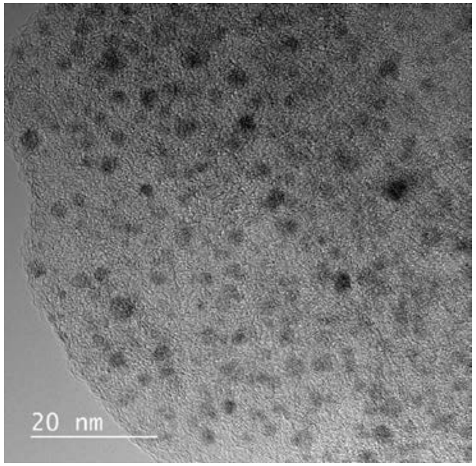


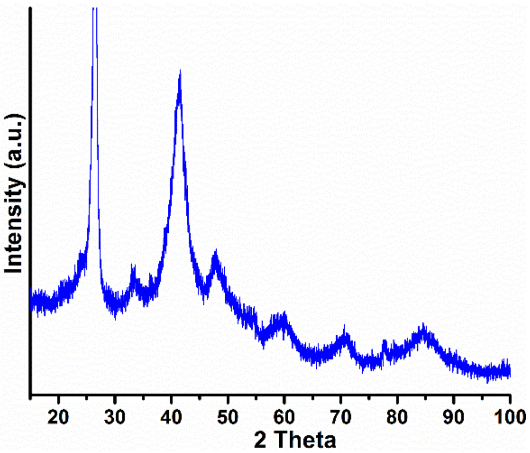
Small $L1_0$ ordered PtCo

Hydrogel-based support enables improved dispersion of 2-4 nm $L1_0$-PtCo

$L1_0$-PtCo/Hydrogel







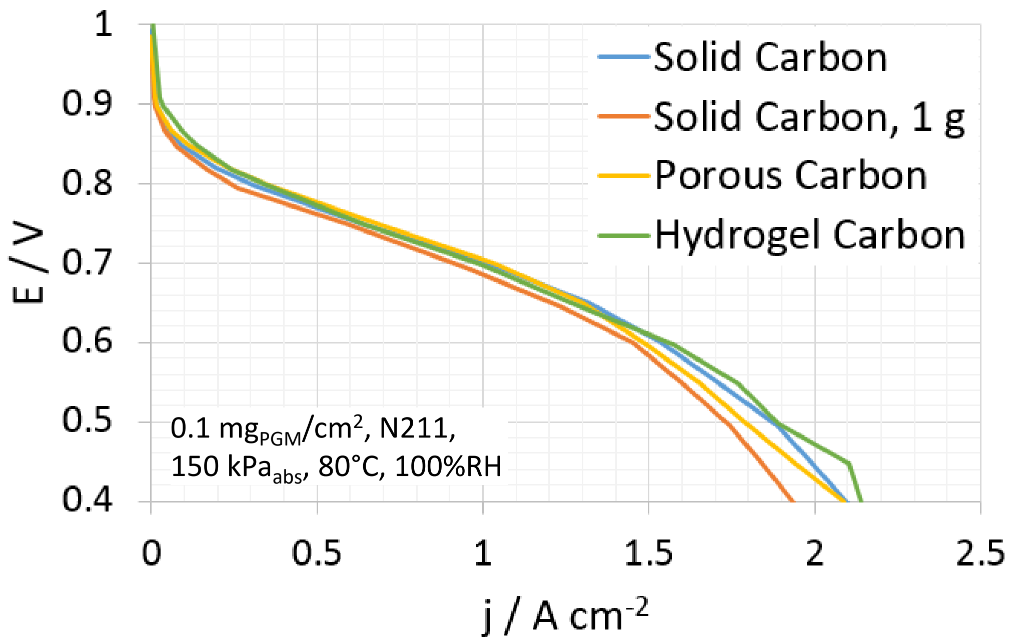
	Units	Measured	Target
Mass Activity	A/mgPGM	**0.79**	**0.44**
Mass Activity Loss [1]	%	**37**	**40**
Degradation at 0.8 A/cm^2 [1]	mV	**31**	**30**
Current Density at 0.8 V	A/cm^2	**0.34**	**0.3**
Power at 0.67 V, 150 kPa_{abs}	W/cm^2	**0.77**	**1**
Power at 0.67 V, 250 kPa_{abs}	W/cm^2		**1**
PGM Loading [2]	mg/cm^2	**0.108**	**0.125**
ECSA	m^2/gPt	**72**	
ECSA after Catalyst AST	m^2/gPt	**37**	

[1] 30K square wave cycles, 0.6-0.95 V [2] Cathode

- Combination of **LANL PtCo technology** and **Buffalo support technology** produces **extremely high mass activity and good durability**
- $L1_0$-PtCo on hydrogel support: small, monodisperse, ordered
- MEA optimization needed to improve power density

Primary goal of support work is to improve performance and durability through better dispersion of intermetallic nanoparticles. Meeting support durability targets is secondary goal.

L1$_0$-PtCo Scaleup



- Initial synthesis: 100-200 mg batches
- Gram-scale synthesis began Jan 2019
- Initial gram-scale synthesis shows similar performance (slightly lower)
- Further optimization of scaled-up synthesis underway

Intermetallic L1$_0$-CoPt developed in this project is compatible with multiple carbon supports (XC-72, Ketjen, and hydrogel-based carbons) and has high performance in large and small batches

Project Status

	Units	$L1_0$-PtCo/ XC-72	$L1_0$-PtCo/ Hydrogel	Target
Mass Activity	A/mgPGM	**0.60**	**0.79**	**0.44**
Mass Activity Loss [1]	%	**40**	**37**	**40**
Degradation at 0.8 A/cm^2 [1]	mV	**26**	**31**	**30**
Current Density at 0.8 V	A/cm^2	**0.41**	**0.34**	**0.3**
Power at 0.67 V, 150 kPa_{abs}	W/cm^2	**0.89**	**0.77**	**1**
Power at 0.67 V, 250 kPa_{abs}	W/cm^2	**1.10**		**1**
PGM Loading [2]	mg/cm^2	**0.106**	**0.108**	**0.125**
Robustness (cold)		**0.94**		**0.7**
Robustness (cold transient)		**0.91**		**0.7**
Robustness (hot)		**0.92**		**0.7**

[1] 30K square wave cycles, 0.6-0.95 V [2] Cathode

- $L1_0$-PtCo/XC-72 meets most DOE catalyst and durability targets; further work on power density underway
- $L1_0$-PtCo/Hydrogel provides path to higher mass activity
- $L1_0$ ordering improves durability by decreasing Co leaching; ordering is retained even after 30K cycle AST in MEA

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
- Extend gram-scale synthesis to multi-gram batches that match performance of small batches
- Perform MEA optimization on the two most promising catalysts (small particle $L1_0$-CoPt/XC-72 and $L1_0$-CoPt/Hydrogel Carbon)
- Scale up MEA testing from 5 cm^2 to 50 cm^2

Summary

- 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
- **MEA testing is critical to evaluate ORR catalysts!**
- We collaborate to test promising catalysts – contact me at **spendelow@lanl.gov**

Acknowledgements

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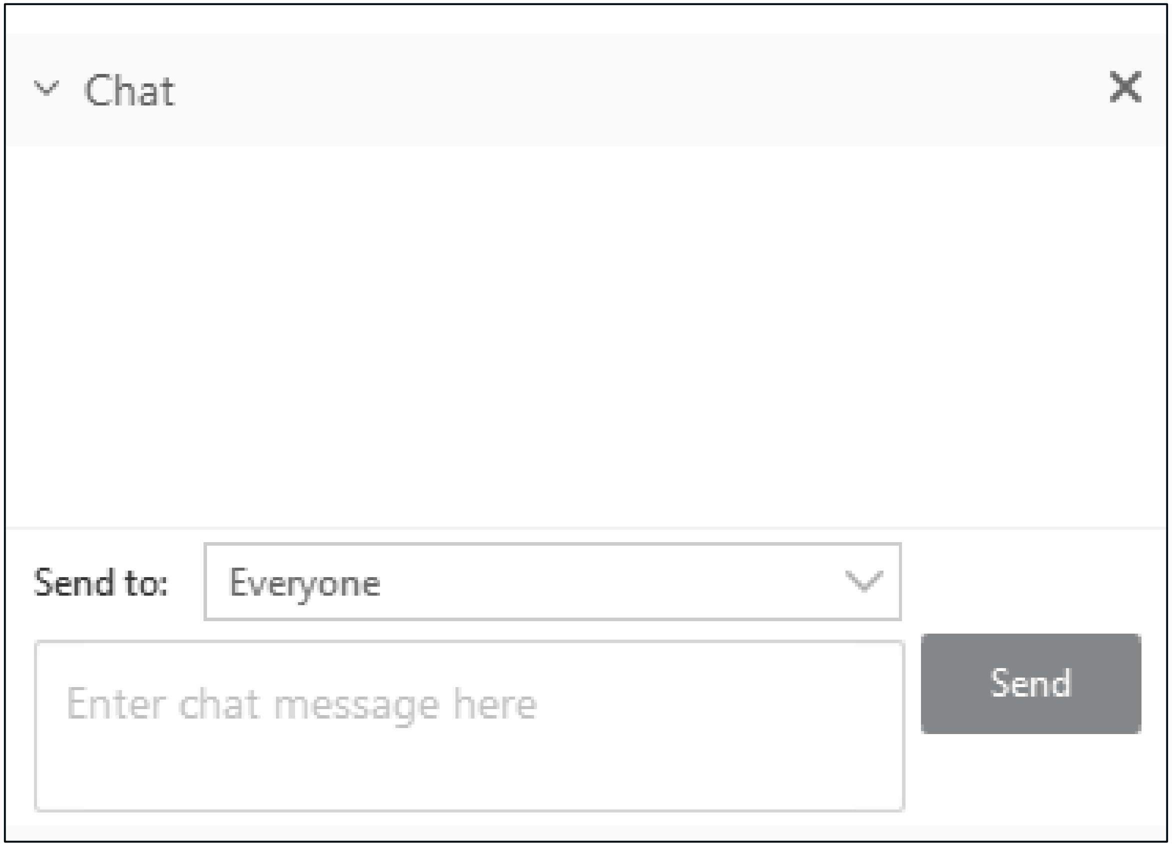
Question and Answer

- Please type your questions to the chat box. **Send to: (HOST)**



Thank you

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