# 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: $1.85M*

  **As of 3/01/2019*

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 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 $cm^2$**

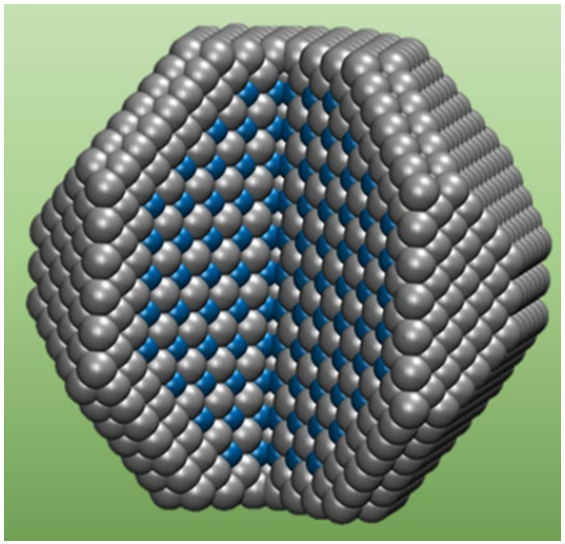
## Project Targets:

- 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: 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: Catalyst Structures

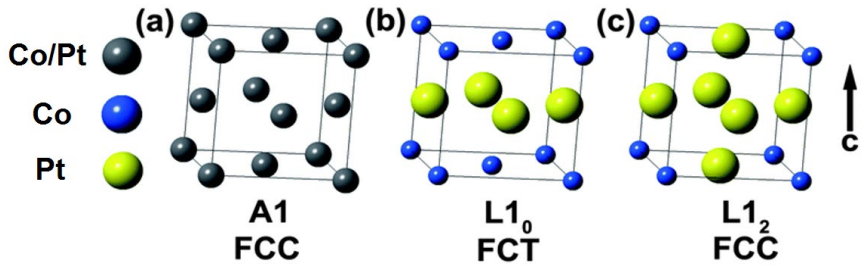
**Ordered intermetallic catalysts**

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

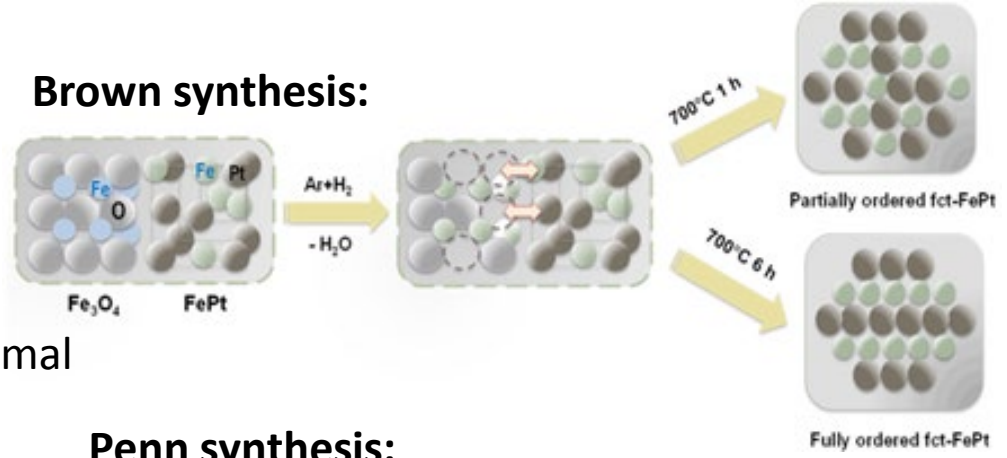



Adapted from Johnston-Peck et al., *Nanoscale*, 2011, **3**, 4142

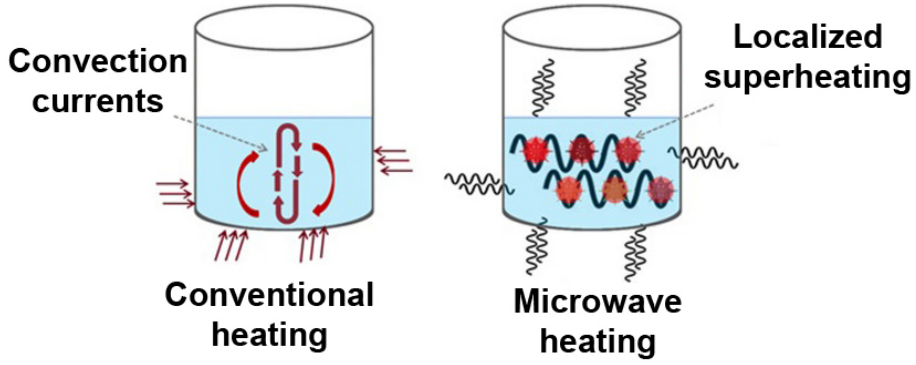
# Approach: $L1_0$-MPt Synthesis

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)

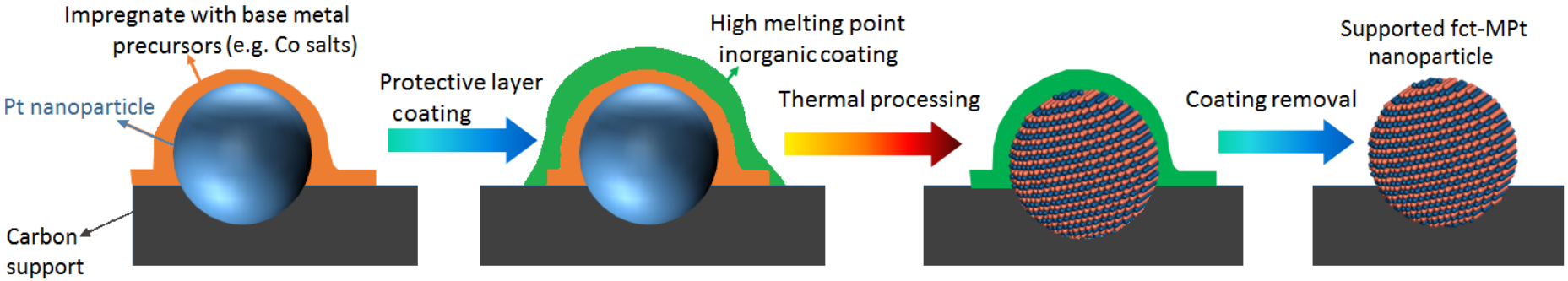
**Brown synthesis:**



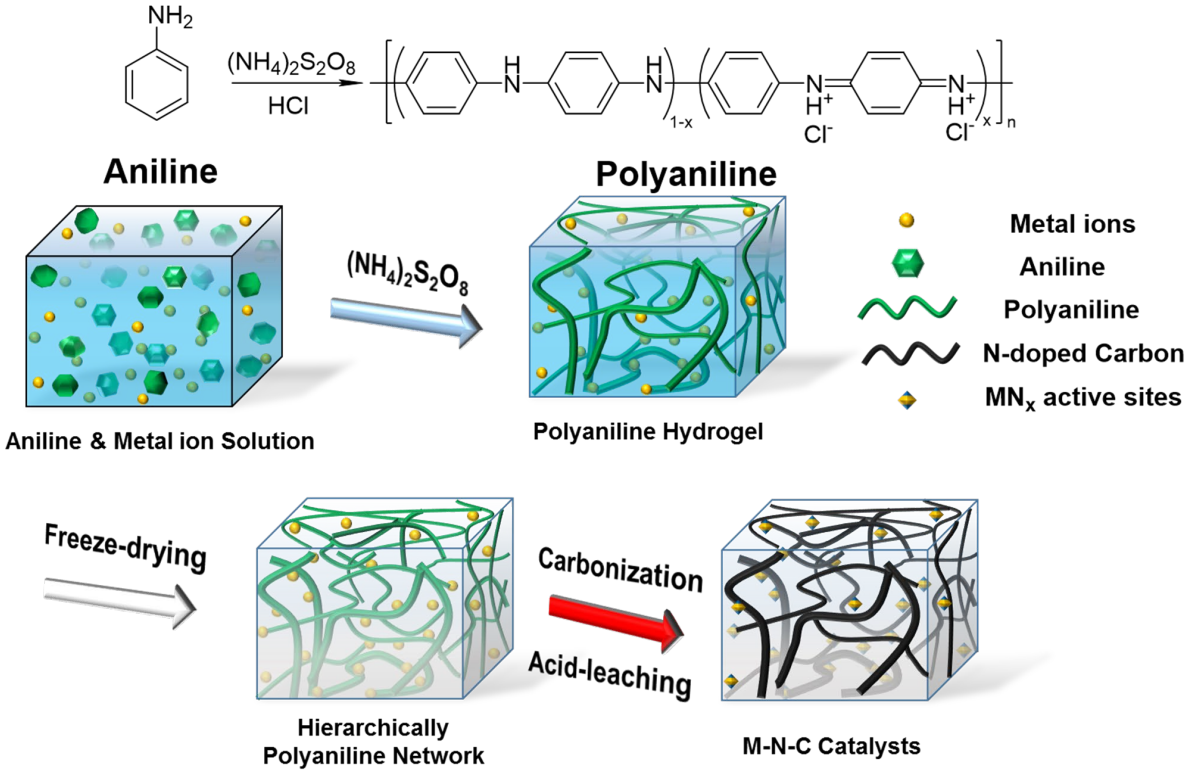

**Penn synthesis:**

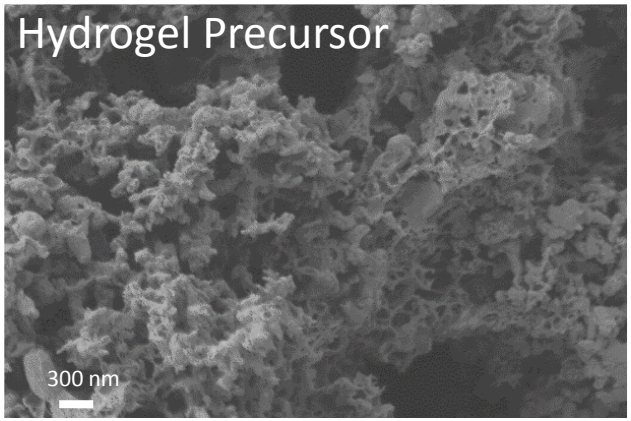


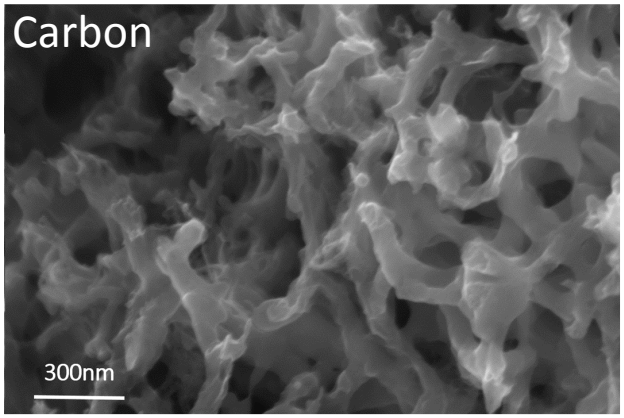

**LANL synthesis:**



# Approach: N-doped Carbon Supports



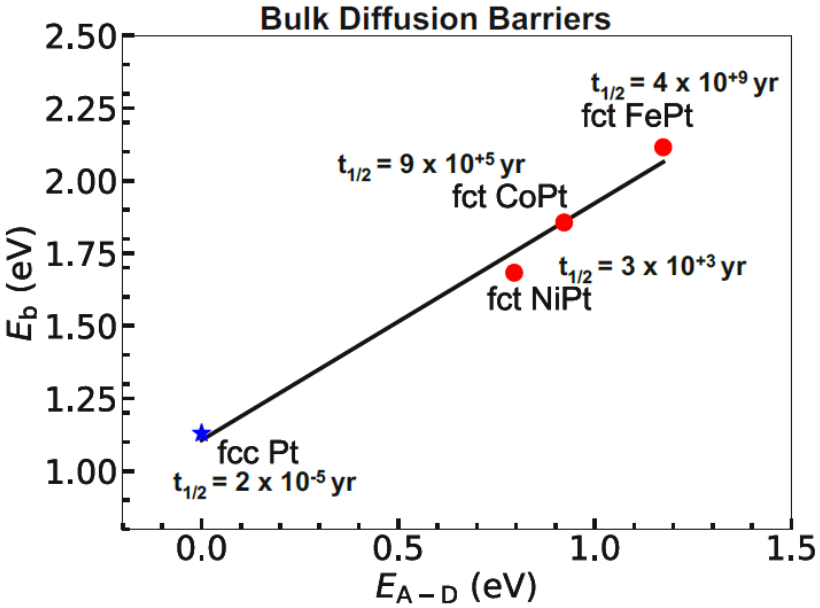

Key attributes:

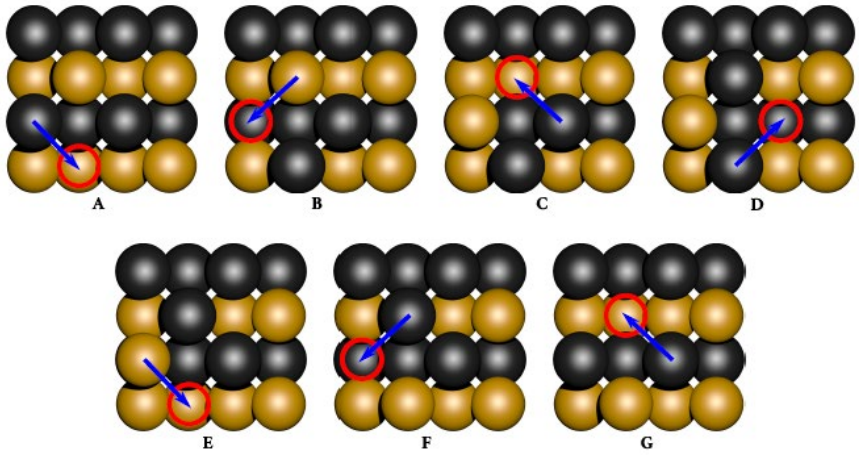
- **N-doped** - improved dispersion and stabilization of nanoparticle catalysts
- **Highly graphitized** - improved durability
- **Fe-free** - avoids Fenton degradation

# Milestones

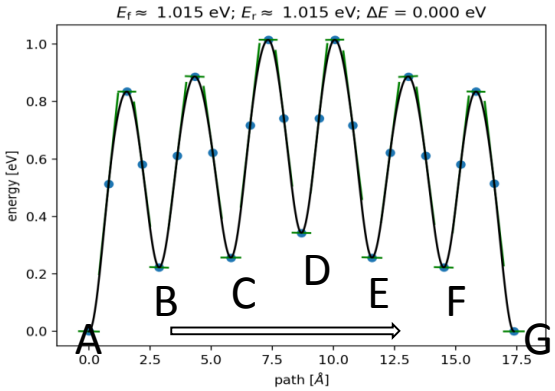
| | | |
|---|---|---|
| **12/16** | Synthesize fully ordered fct-FePt nanoparticles from FePt-$Fe_3O_4$ precursors and perform initial electrochemical characterization | ☑ |
| **3/17** | Incorporate at least two distinct ordered intermetallic catalysts into MEAs and perform fuel cell testing including mass activity and high-current performance | ☑ |
| **6/17** | Perform initial durability testing (square-wave AST) on ordered intermetallic catalysts in MEA | ☑ |
| **9/17** | Demonstrate 5-7 nm fct-MPt with durability in electrocatalyst AST superior to baseline Pt/C | ☑ |
| **12/17** | Synthesize at least two distinct N-doped supports and compare their properties as catalyst supports | ☑ |
| **3/18** | **GO/NO-GO:** Demonstrate 0.44 A/$mg_{PGM}$ mass activity on an Fe-free system under operating conditions specified for DOE mass activity target | ☑ |
| **6/18** | Develop alternative fct-CoPt synthetic pathway using deposition on Pt nanoparticle seeds | ☑ |
| **9/18** | Develop atomistic models that attribute reactivity changes to strain, ligand, and crystal structure for fct-CoPt system | ☑ |
| **12/18** | Demonstrate ordered intermetallic nanoparticle catalyst meeting mass activity and 30,000 cycle AST durability targets in 5 $cm^2$ MEA | ☑ |
| **3/19** | Demonstrate supported catalyst meeting 5,000 cycle support AST durability targets in 5 $cm^2$ MEA | ☑ |
| **6/19** | Demonstrate ordered intermetallic nanoparticle catalyst meeting mass activity and 30,000 cycle AST durability targets in 50 $cm^2$ MEA | |
| **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 | |

# Accomplishments and Progress: DFT Computation

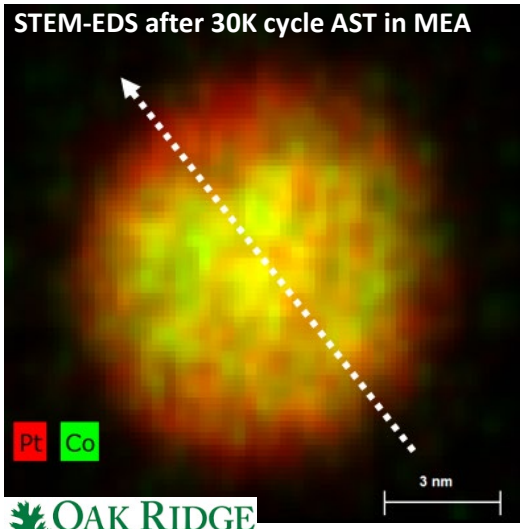


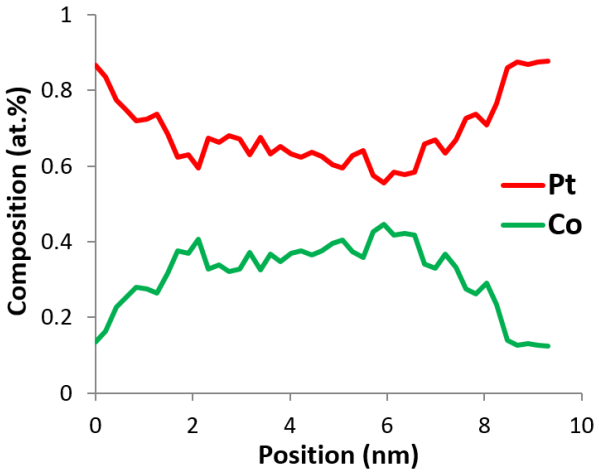




- Bulk diffusion barrier correlates strongly with potential energy difference between states A and D
- $L1_0$ intermetallics show much larger diffusion barriers than fcc Pt
- Results suggest that **alternative mechanisms (e.g., oxygen place exchange) are more important in controlling base metal leaching**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



# Previous Year: 9 nm $L1_0$-CoPt




- 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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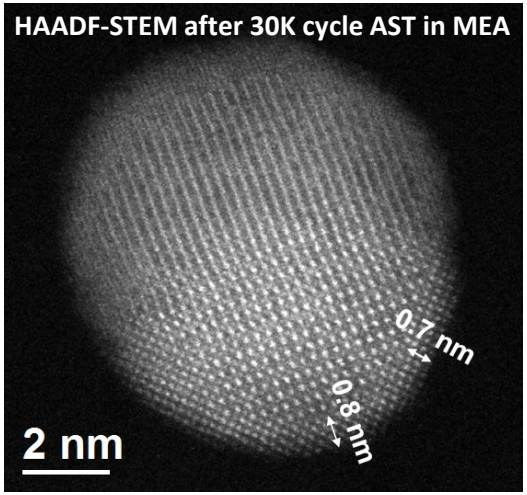


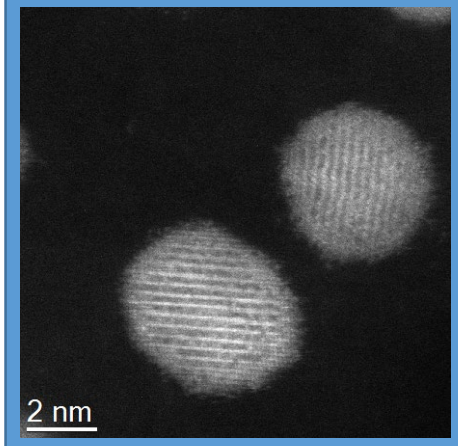

**Key conclusions:**

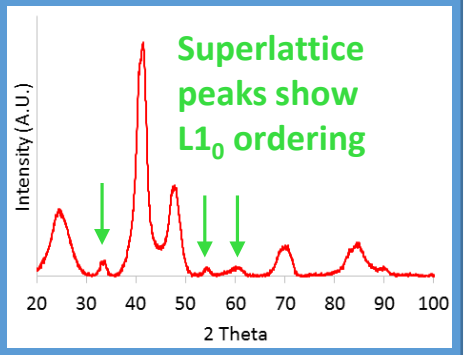
- Ordered core remains intact even after AST
- Co leaching occurs only from surface, forming Pt shell that protects particle interior from further leaching
- Pt shell is too thick for significant ligand enhancement after AST, but **kinetic enhancement due to strain remains**
- High mass activity (0.56 A/$mg_{PGM}$) and durability (20% loss in mass activity after 30K cycles), but poor high-current performance due to large particle size

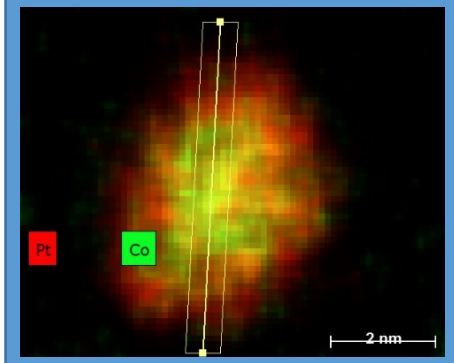
**Best FY18 catalyst met mass activity and durability targets. Key goal for FY19: meeting these targets while also reducing particle size, increasing ECSA, and meeting power density targets.**

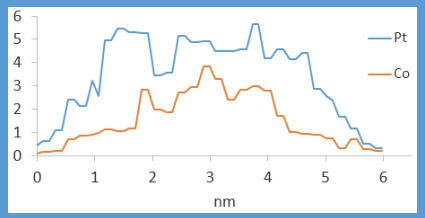
# Accomplishment: Small $L1_0$-PtCo Particles

## BOL Catalyst

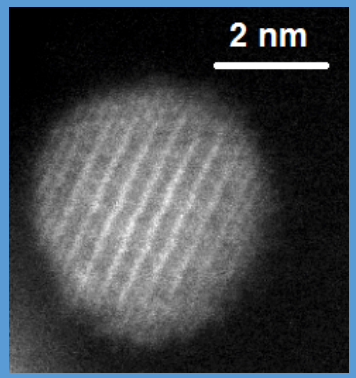


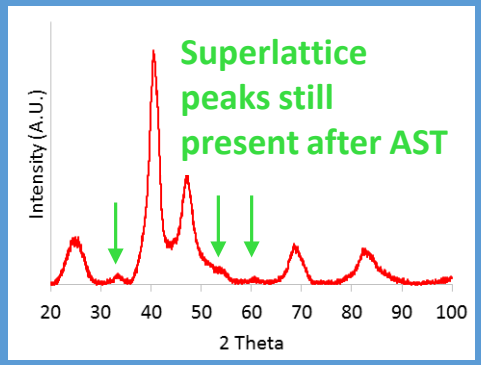



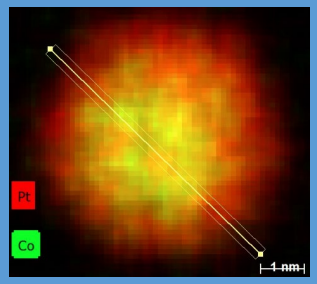



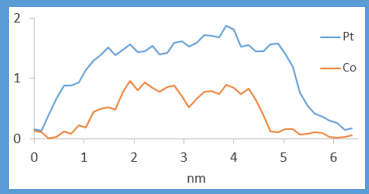




## After 30K cycles in MEA




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

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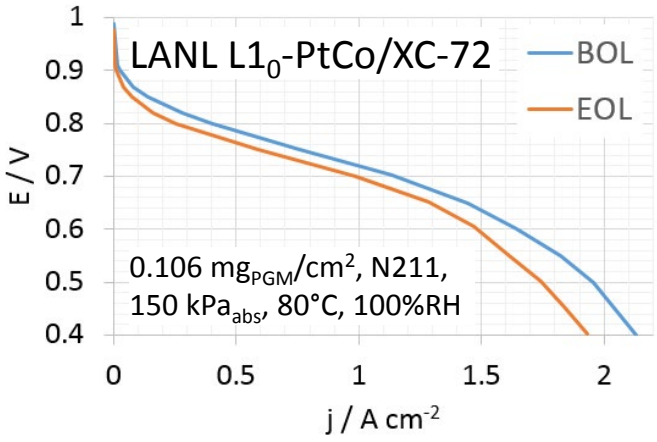
# Small Particle $L1_0$-PtCo/XC-72: Fuel Cell Testing

| | 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



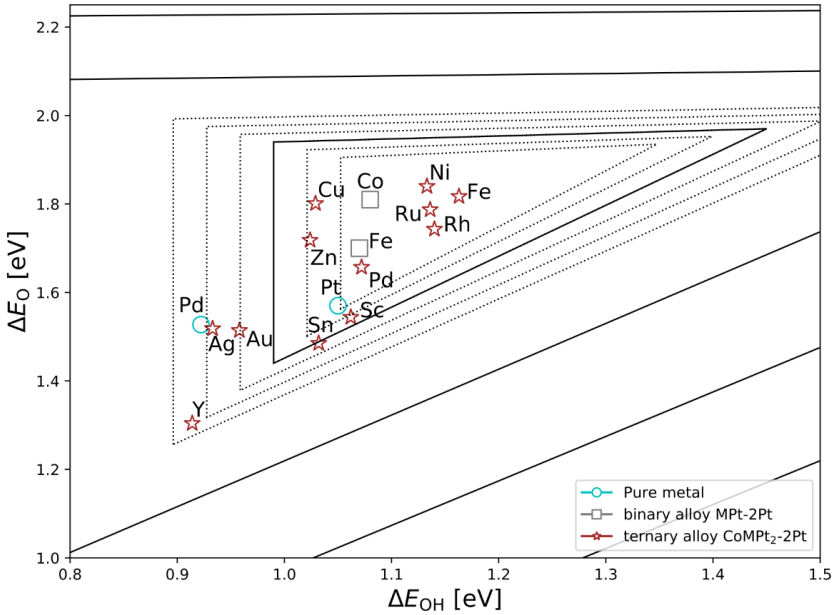

ECSA (CO stripping):
62 m$^2$/g (BOL)
40 m$^2$/g (after 30K cycles)

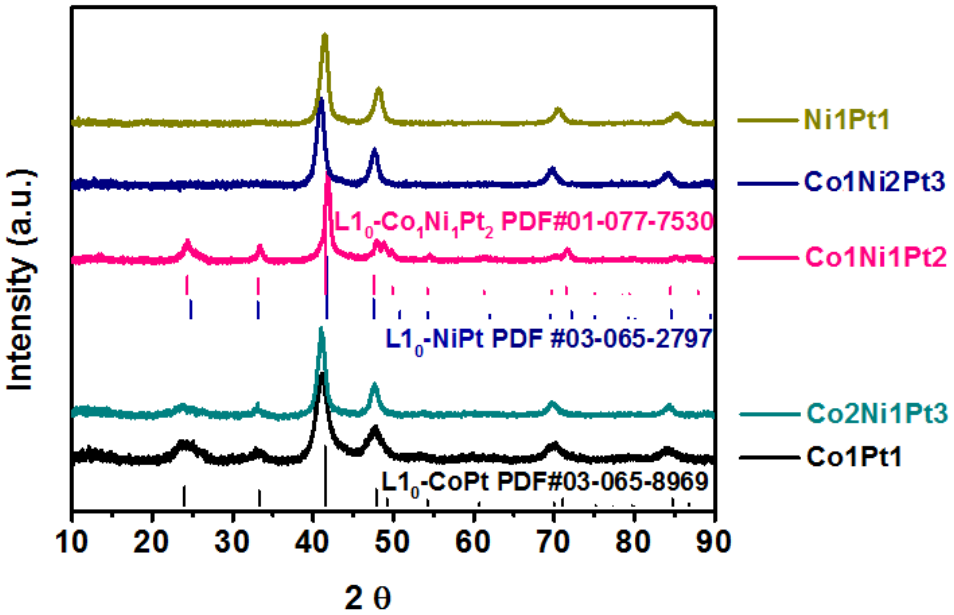
**$L1_0$-PtCo@Pt/XC-72 catalyst meets or approaches DOE catalyst and MEA targets**

| | 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**

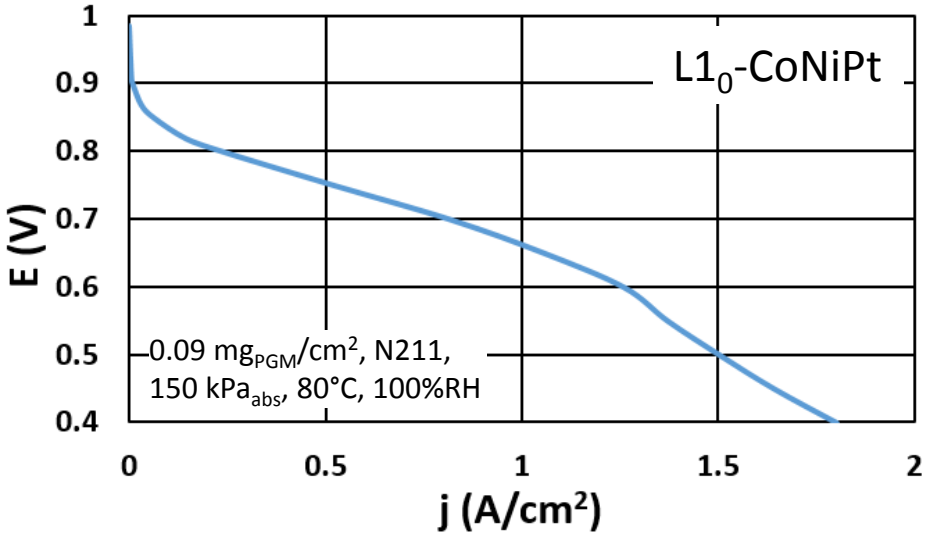
# Accomplishment: Ternary $L1_0$ Development

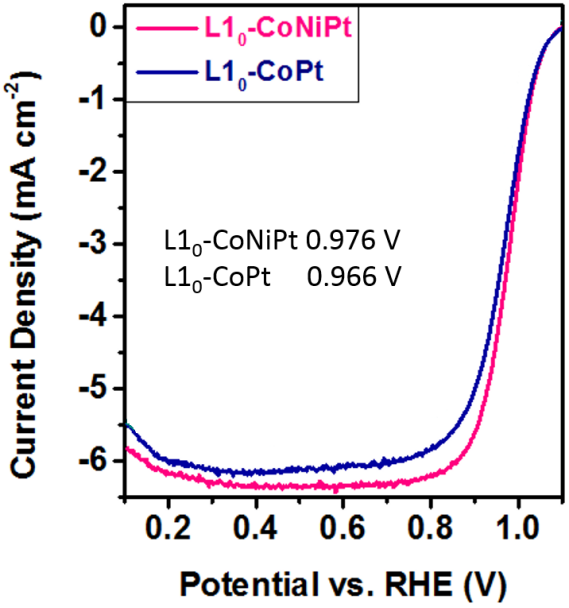



- DFT results suggest adding a 3rd component (e.g. Ni) to $L1_0$-PtCo could provide near-optimal O/OH binding energy
- XRD shows Co:Ni:Pt = 1:1:2 gives good ordering
- **Based on DFT and XRD, ternary $L1_0$-CoNiPt looks promising**

# $L1_0$-CoNiPt: MEA Testing



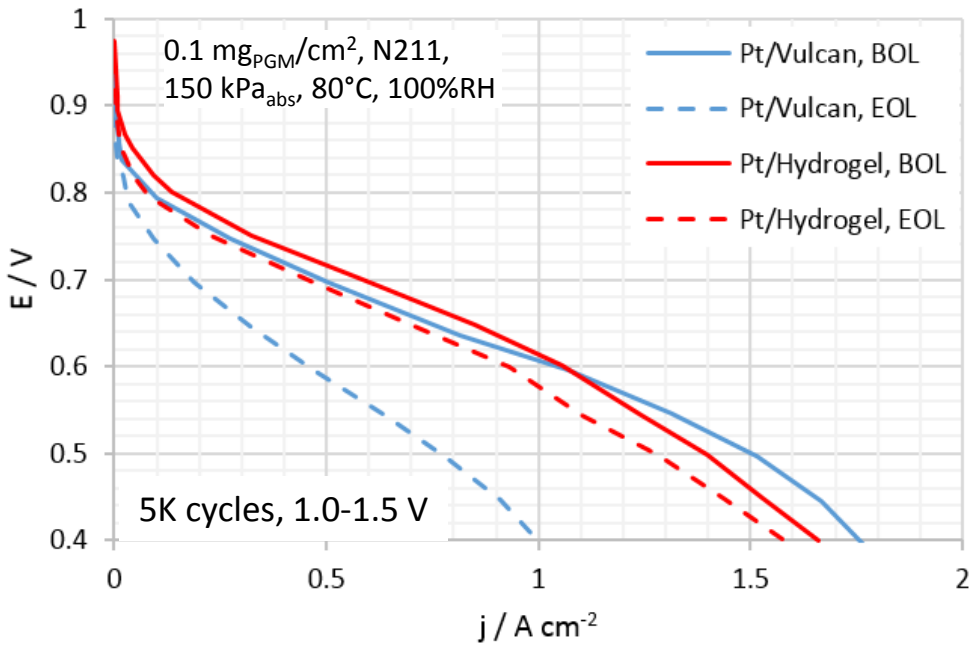

| | Units | Measured | Target |
|---|---|---|---|
| Mass Activity | A/mgPGM | **0.33** | **0.44** |
| Mass Activity Loss [1] | % | | **40** |
| Degradation at 0.8 A/cm² [1] | mV | | **30** |
| Current Density at 0.8 V | A/cm² | **0.23** | **0.3** |
| Power at 0.67 V, 150 $kPa_{abs}$ | W/cm² | **0.64** | **1** |
| Power at 0.67 V, 250 $kPa_{abs}$ | W/cm² | | **1** |
| PGM Loading [2] | mg/cm² | **0.091** | **0.125** |

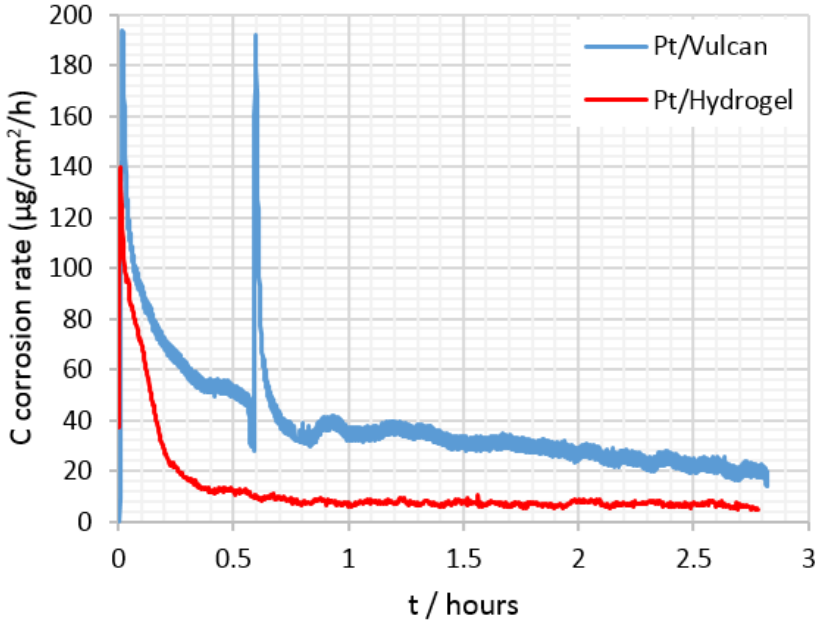
[1] 30K square wave cycles, 0.6-0.95 V

[2] Cathode

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

# Accomplishment: Mn-Hydrogel Supports



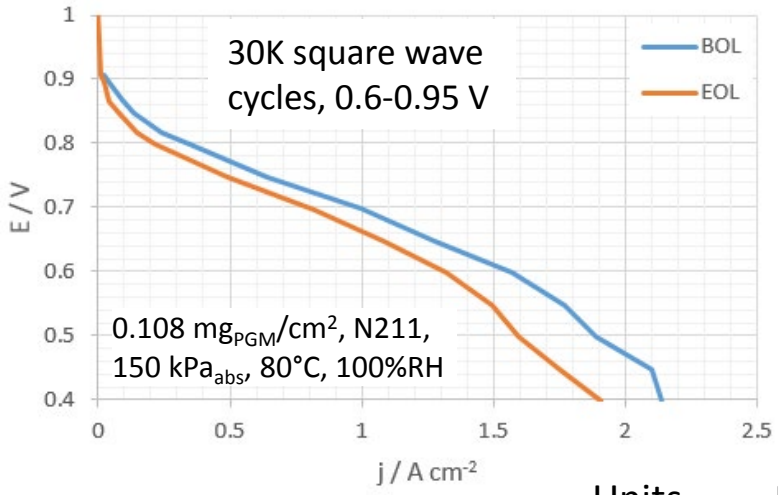

| | Units | Measured | Target |
|---|---|---|---|
| Mass Activity | A/mgPGM | **0.18** | **0.44** |
| Mass Activity Loss [1] | % | **39** | **40** |
| Degradation at 1.5 A/cm$^2$ [1] | mV | **31** | **30** |
| Current Density at 0.8 V | A/cm$^2$ | **0.14** | **0.3** |
| Power at 0.67 V, 150 kPa$_{abs}$ | 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** |

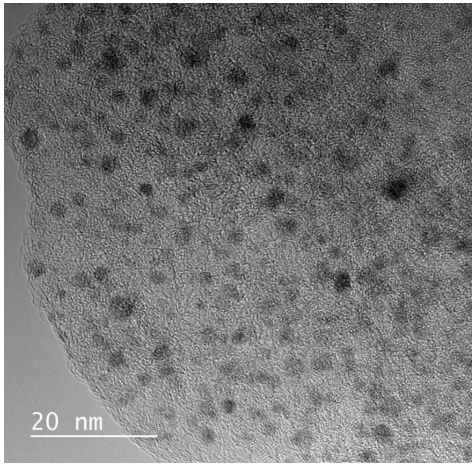
[1] 5K triangle wave cycles, 1.0-1.5 V

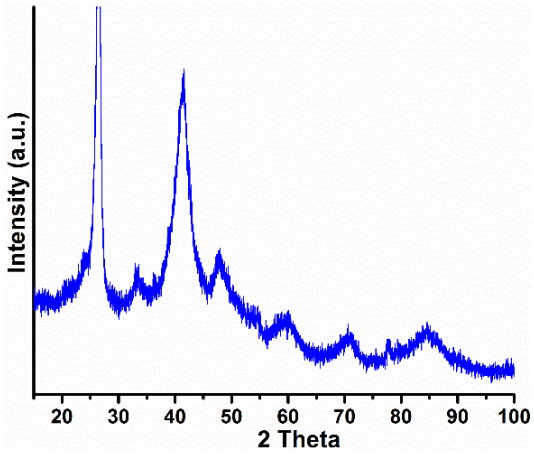
[2] Cathode

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

# $L1_0$-PtCo/Hydrogel



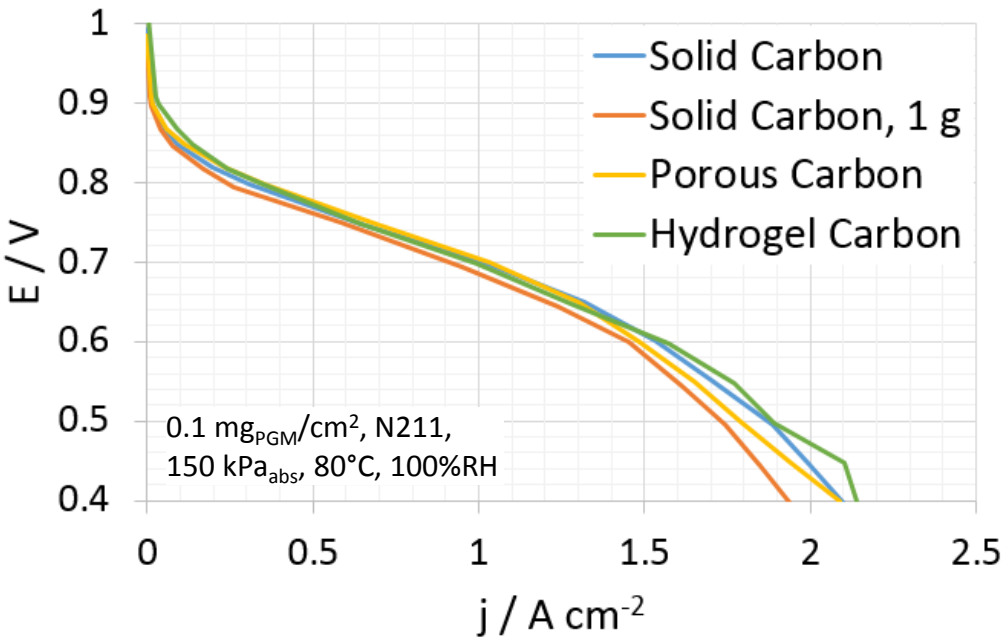

| | Units | Measured | Target |
|---|---|---|---|
| Mass Activity | A/mgPGM | **0.79** | **0.44** |
| Mass Activity Loss [1] | % | **37** | **40** |
| Degradation at 0.8 A/cm$^2$ [1] | mV | **31** | **30** |
| Current Density at 0.8 V | A/cm$^2$ | **0.34** | **0.3** |
| Power at 0.67 V, 150 kPa$_{abs}$ | 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.**

# Accomplishment: Catalyst 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

# Response to Reviewer Comments

While some catalysts in this project have shown promising mass activity, they all show quite low ECSA. The participants need to clearly demonstrate they have a path to achieve performance targets at > 1.5 A/cm$^2$. This can be by increasing ECSA, mass activity, or reducing local $O_2$ transport losses.

**This was true as of last year, but we have made substantial progress in this area. Our best intermetallic catalysts developed in the past year have ECSA >60 $m^2/g_{Pt}$. This high ECSA is competitive with state-of-the-art catalysts. Our high current performance (0.64 V at 1.5 A/cm$^2$ in 150 $kPa_{abs}$ $H_2$/air) is competitive with state-of-the-art MEAs.**

Support work seems less valuable than catalytic development. There is concern this will dilute from the strong catalytic developments.

**Catalyst/support interactions are critical for good catalyst performance and durability. Support development is only ~10% of project budget. This low level investment has yielded highly promising supports that have resulted in improved mass activity and durability.**

Promising results for certain metrics or catalysts, yet their scale up need to be demonstrated.

**Agreed. We have made significant progress on scale-up, demonstrating gram-scale batches with good performance. Further work is underway to improve scaled-up synthesis and progress to multi-gram batches that match performance of small batches.**

# 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

**EWII**

- Scale up MEA production
- Catalyst/MEA validation

Other collaborators in FY19:

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

# Remaining Challenges and Barriers

- Extend gram-scale synthesis to multi-gram batches that match performance of small batches
- Increase high-current performance of N-doped supports
- Develop optimized electrode structures with effective transport properties to enable consistent achievement of >1 W/cm$^2$ operation

# 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
- 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)
- Continue development of ternary $L1_0$-CoNiPt and verify whether promising RDE results can be extended to high MEA performance
- Scale up MEA testing from 5 $cm^2$ to 50 $cm^2$
- Continue computational studies to guide synthetic work and interpret experimental findings

*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.

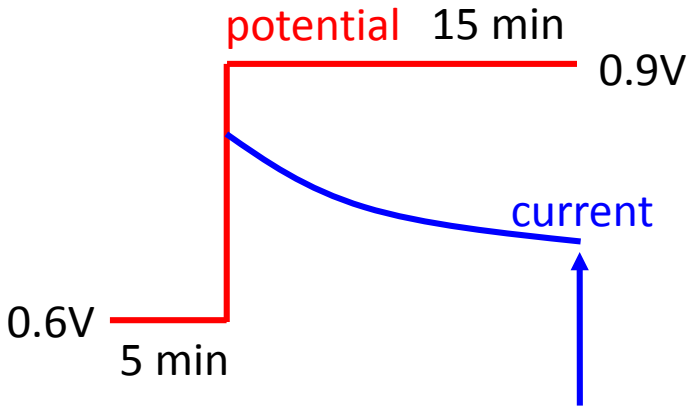
**Accomplishments:** Intermetallic $L1_0$-CoPt catalyst meets mass activity and durability targets. New N-doped supports enable high mass activity and meet support durability targets. Ordered $L1_0$ structure was demonstrated to decrease Co leaching, improving durability.

**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

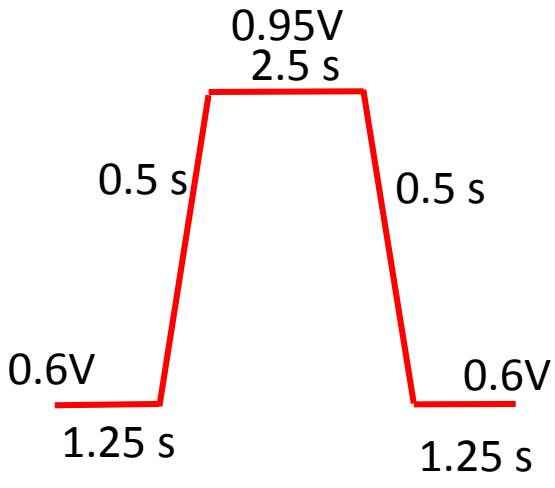
**Mass Activity: 15 min hold at 0.9 V**



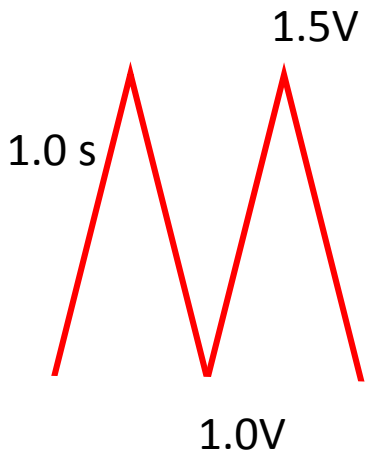

**Mass activity measured during last 1 min of 15 min hold**

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

**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**




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

# 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**