Advanced Electro-Catalysts through Crystallographic Enhancement

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Los Alamos National Laboratory

June 7, 2017

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: $195K*

  **As of 3/31/2017*

Barriers

A. Durability

B. Cost

C. Performance

Partners

- LANL (J. Spendelow, Y.S. Kim, Y. Pan)
- Brown University (S. Sun, A. Peterson)
- University of Pennsylvania (C. Murray)
- SUNY University at Buffalo (G. Wu)
- EWII Fuel Cells (M. Odgaard)
- Pajarito Powder* (B. Zulevi)
- 3M* (M. Yandrasits)

**No cost partners*

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 Fe, Co, Ni, other base metals
  - Initial catalysts will contain Fe, but project will transition away from Fenton-active metals
  - Catalysts will be supported on Fe-free, highly graphitized N-doped C supports
- **Demonstrate and validate catalysts in high-performance, durable 50 cm^2 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

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

- Synthesize intermetallic nanoparticles (FePt, CoPt, NiPt, ternaries)
  - Prepare fully-ordered cores to stabilize base metal
  - Further protect core with Pt skin
  - Eliminate Fe from system
  - Use theory and computation (DFT, machine-learning techniques) to guide experimental synthesis
- Support nanoparticles on Fe-free, N-doped graphitic carbon
- 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 (ICP-MS, 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 (multi-gram batches)

Approach: Catalyst Structures

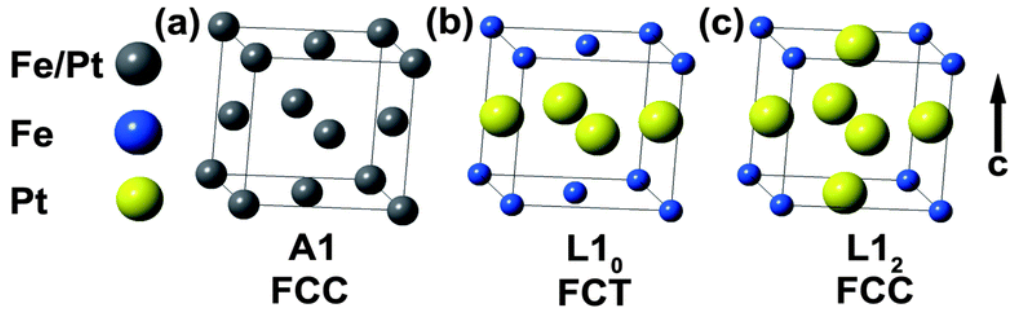
Ordered intermetallic alloy catalysts

Primary material set:

1. fct-FePt (face-centered tetragonal, $L1_0$ structure)
2. fct-CoPt, fct-NiPt
3. fct-M_1M_2Pt (ternaries)

Alternative materials (risk mitigation):

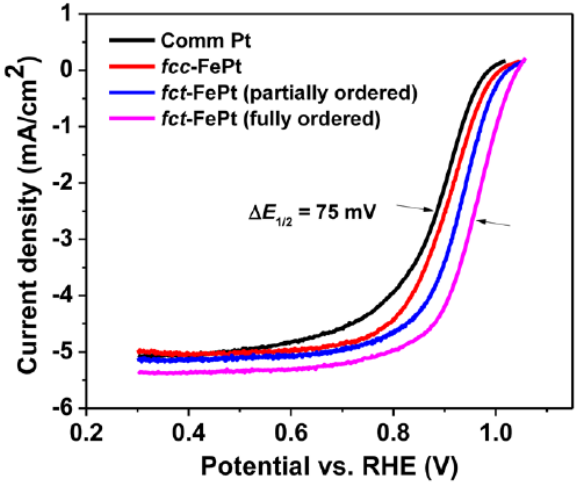
1. $L1_2$ structures (Pt_3M)
2. Doping with other elements
3. Other intermetallics

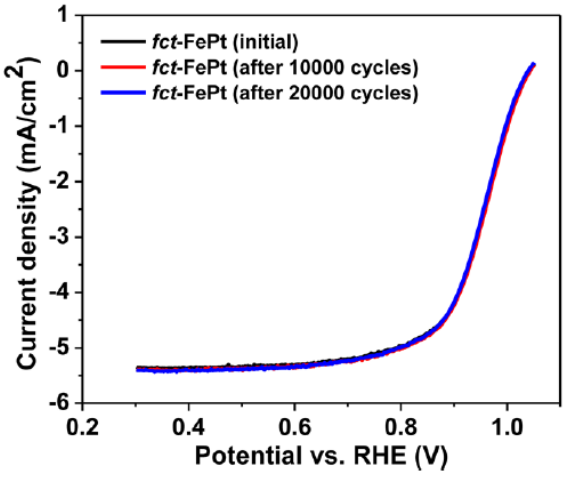


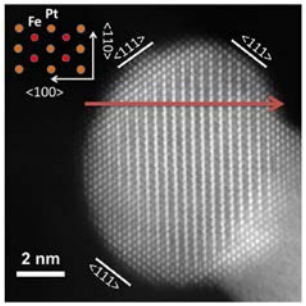
Johnston-Peck et al., *Nanoscale*, 2011, **3**, 4142

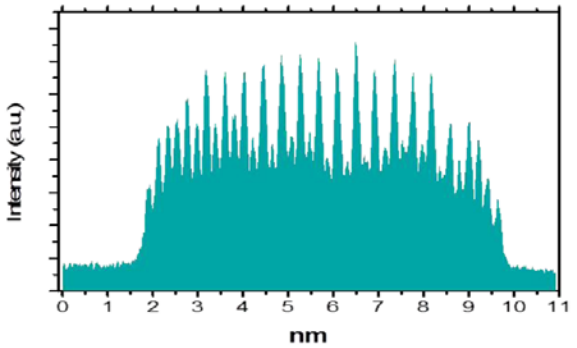
Background: Fully Ordered fct-FePt in RDE

- Higher degree of ordering provides higher ORR activity
- Fully-ordered fct structure and ORR activity maintained during 20,000 potential cycles
- Fe:Pt ratio change during cycling:
  Fully-ordered: 50:50 → 47:53 (20,000 cycles)
  Partially-ordered: 50:50 → 26:74 (300 cycles)









Li et al, *Nano Lett*. 2015, 15, 2468.

Pre-project data shows fully-ordered fct-FePt structure has improved activity and durability in RDE

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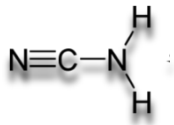
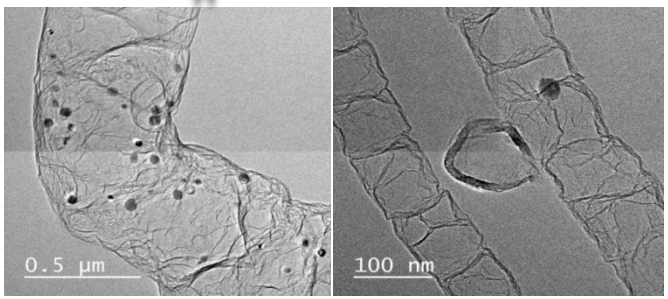
Approach: N-doped Carbon Supports

We are developing several classes of advanced carbon supports:

N-doped graphene tube supports

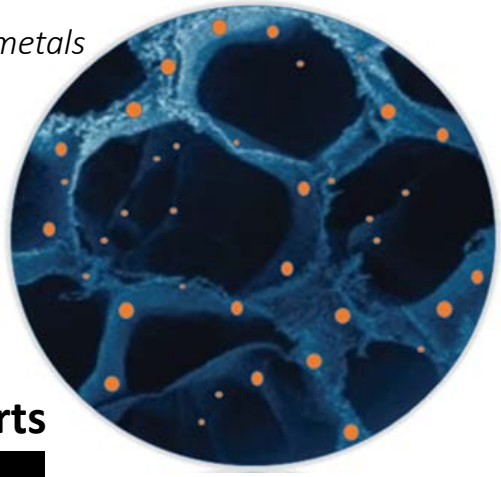


Dicyanamide + metals



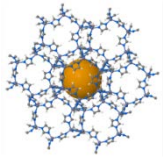
Hydrogel-based nanocarbon supports

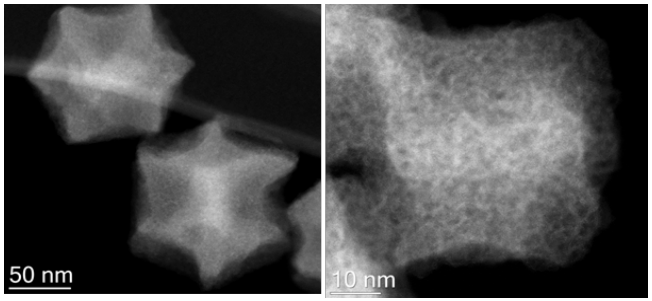
Polyaniline + metals



MOF-derived nanocarbon supports

ZIF-8 + metals





Key attributes:

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

Approach: Testing and Characterization

MEA testing procedure:

- MEA conditioning/break-in
- Performance characterization
  - H_2 crossover
  - CV (ECSA)
  - ORR mass activity
  - H_2/air polarization
- Durability testing (30,000 square wave cycles)

Additional MEA diagnostics:

- H_2/air impedance
- H_2/N_2 impedance (electrode protonic resistance)
- O_2 limiting current techniques (transport loss breakdown, local O_2 resistance)

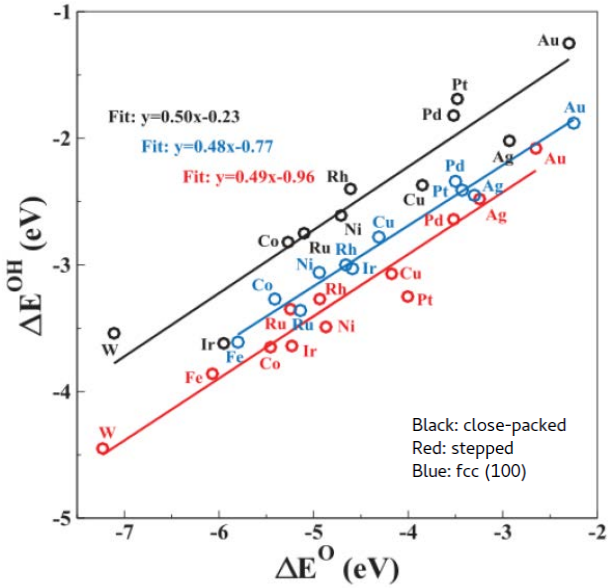
Catalyst/MEA characterization:

- ICP-MS (alloy composition)
- XRD (alloy structure, before and after test)
- XRF (composition/loading)
- SEM-EDS (component thickness, interfaces, metal content in membrane)
- TEM, HAADF-STEM, STEM-EDS (particle size, structure, composition)
- XAS (chemical and structural information)

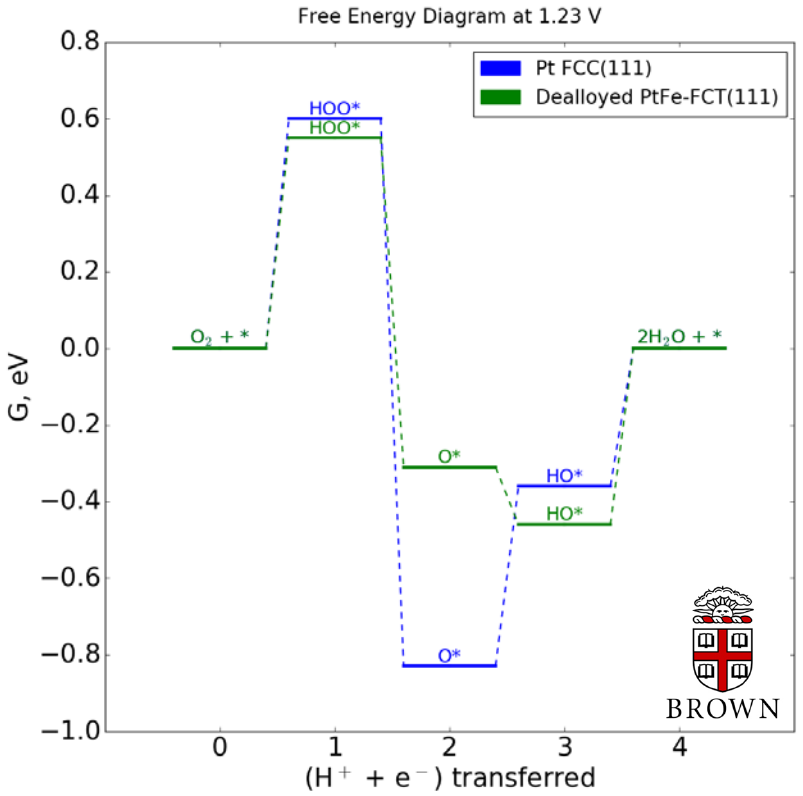
Milestones

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 <40% loss in mass activity following square-wave AST	
12/17	Synthesize at least two distinct N-doped supports and compare their properties as catalyst supports	
3/18	Demonstrate Fe-free intermetallic catalyst that meets DOE mass activity target (0.44 A/mg_{PGM} at 0.9 V) **(GO/NO-GO)**	
6/18	Synthesize 1.0 g of size controlled fct-M_1M_2Pt nanoparticles	
9/18	Develop theoretical coverage-dependent mechanisms for the most promising systems to provide further insights and continued design improvement	
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: ORR Intermediate Adsorption Strengths

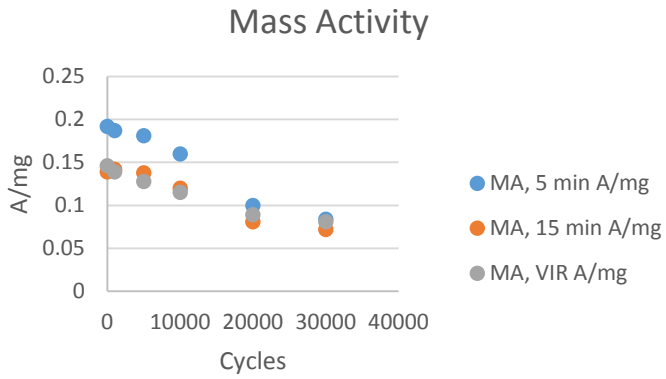


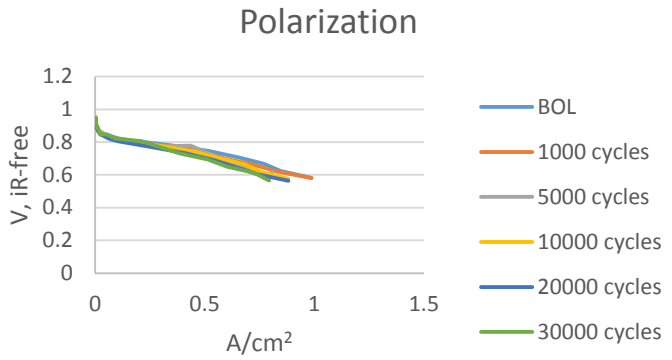
Abild-Pedersen et al., Phys Rev Lett 99:16105 (2007).

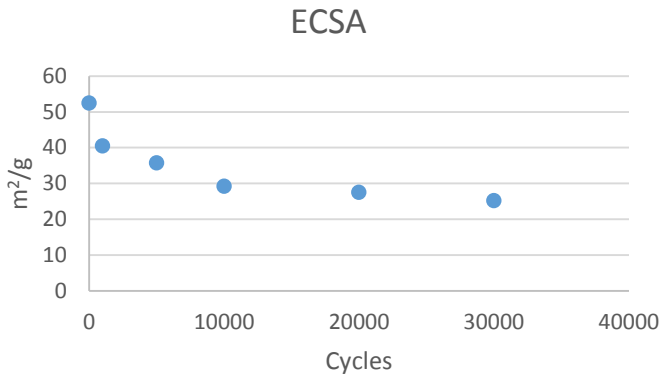


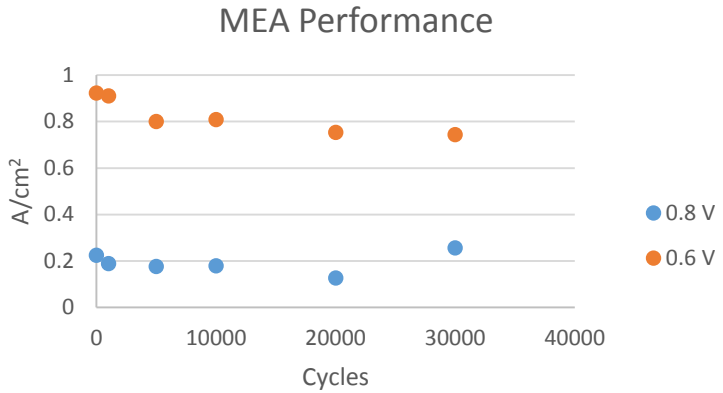
- Strong correlation between adsorption strength of different oxygen-containing species makes it difficult to strengthen OOH while weakening O
- Initial calculations indicate that dealloyed fct-PtFe(111) surface has stronger OOH adsorption and weaker O adsorption than Pt(111) – **unique fct structure breaks the adsorption strength scaling relationship, enabling faster kinetics**

Accomplishments: Pt/C Baseline MEA





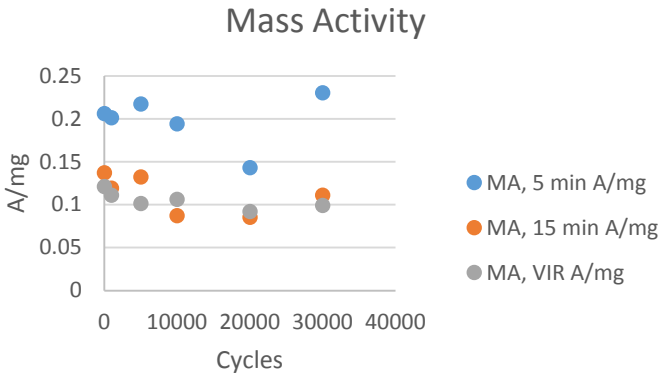


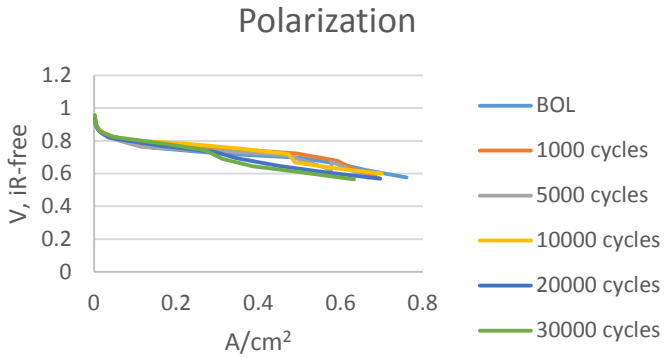


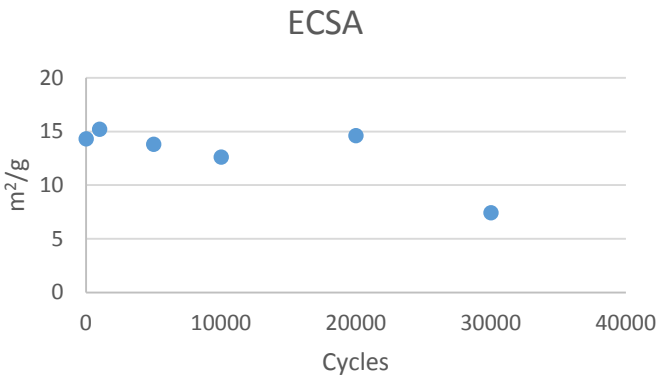
- TKK TEC10E20E (20%Pt/C) catalyst used as a baseline for comparison
- Nominal composition: 20% Pt
- Cathode loading: 0.122 mg_{Pt}/cm^2

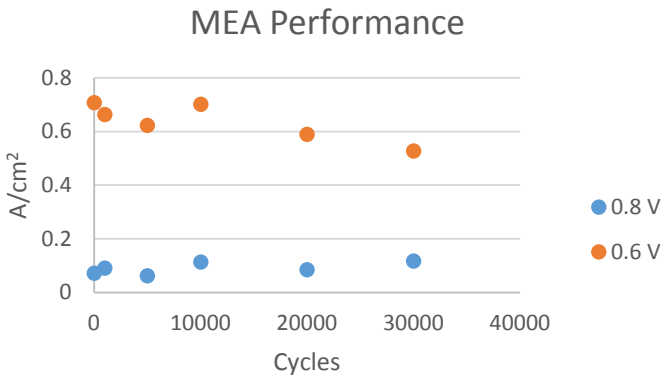
100/200 sccm H_2/air
N212, 5 cm^2
100%RH, 150 kPa_{abs}
Anode 0.1 mg_{Pt}/cm^2

Accomplishments: Initial fct-FePt/C MEA Testing





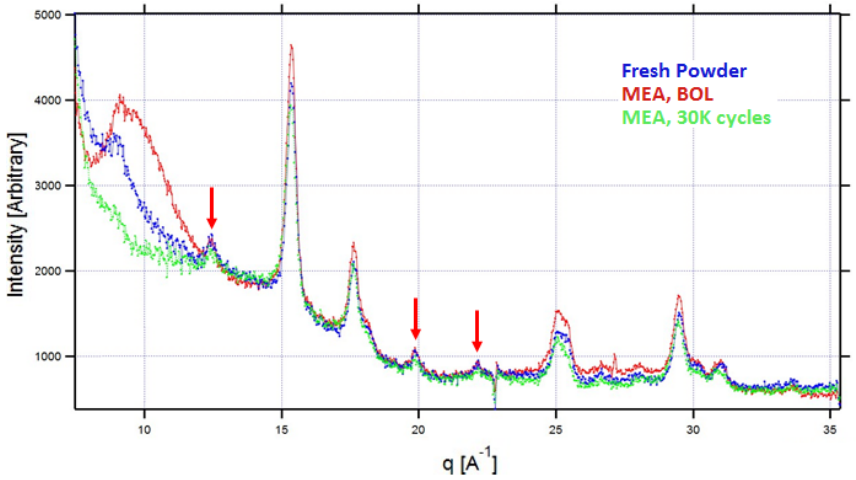




- fct-FePt/C, 15% metal, 0.112 mg/cm^2 Pt
- Mass activity below RDE results (~0.2 A/mgPt vs. ~0.7 A/mgPt), but excellent durability
- Better durability than Pt/C baseline, but worse high-current performance

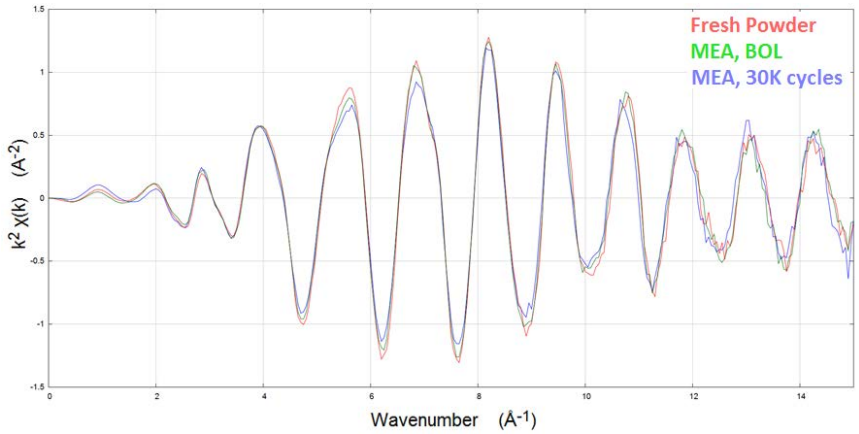
100/200 sccm H_2/air
N212, 5 cm^2
100%RH, 150 kPa_{abs}
Anode 0.1 mg_{Pt}/cm^2

Accomplishments: Synchrotron fct-FePt/C Studies

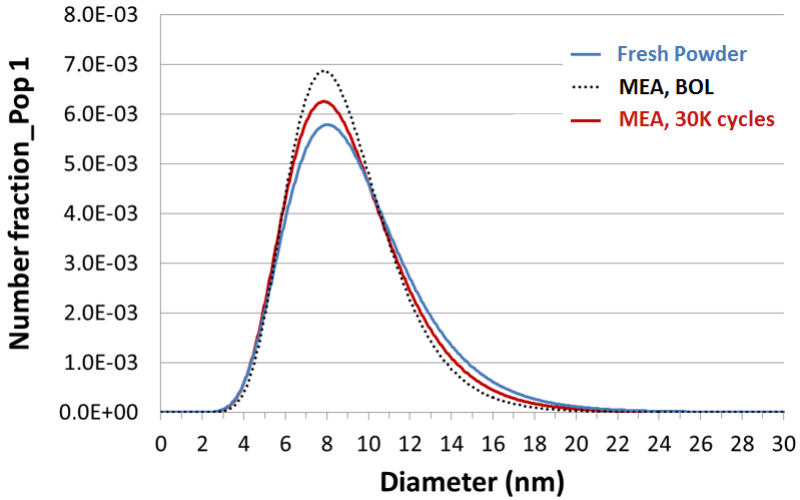


N.N. Kariuki, A.J. Kropf, D.J. Myers (ANL)

- Superlattice peaks in WAXS (red arrows) show intermetallic fct structure
- Little change in ordering peaks after 30K cycle AST – **fct structure is durable**

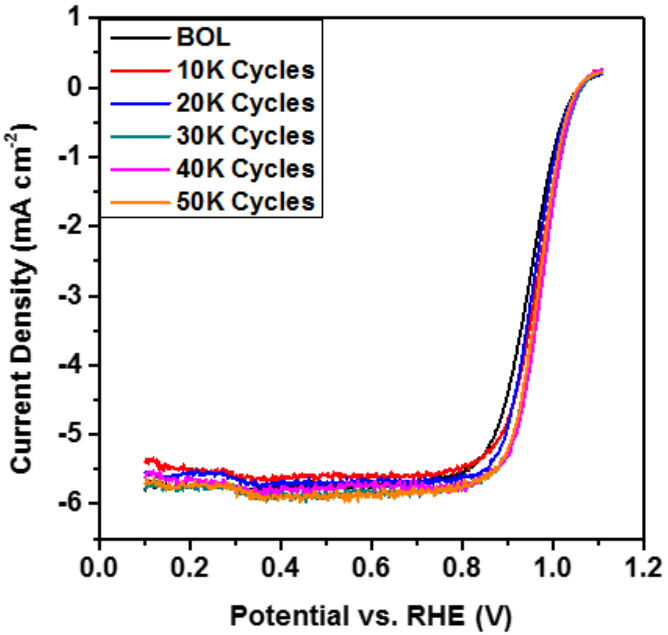


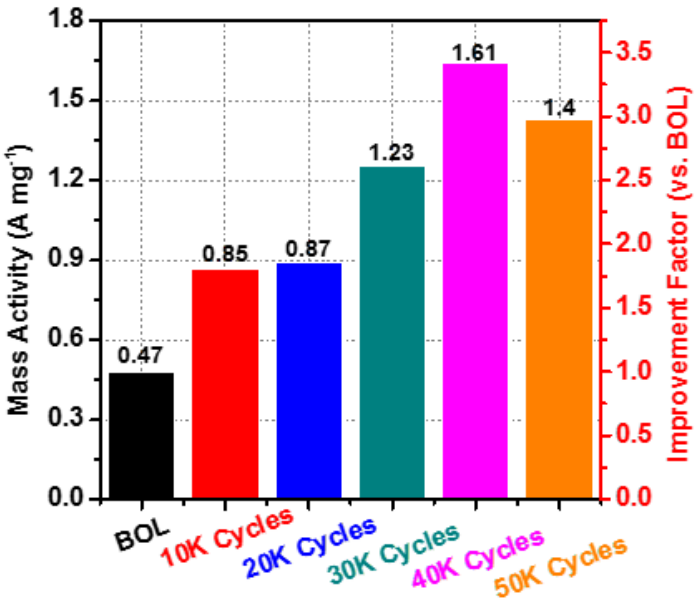
Preliminary Pt L3 EXAFS data indicates similar bond length before and after AST

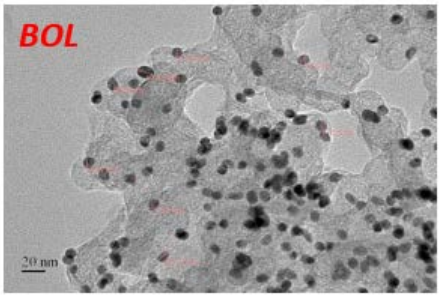


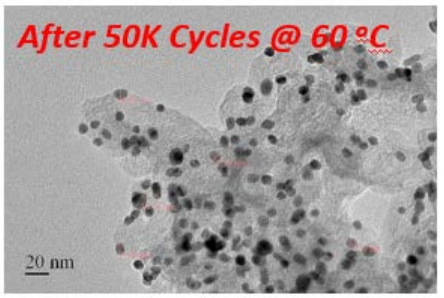
USAXS indicates average particle size of 9 nm does not change during AST

Accomplishments: fct-CoPt Initial Synthesis

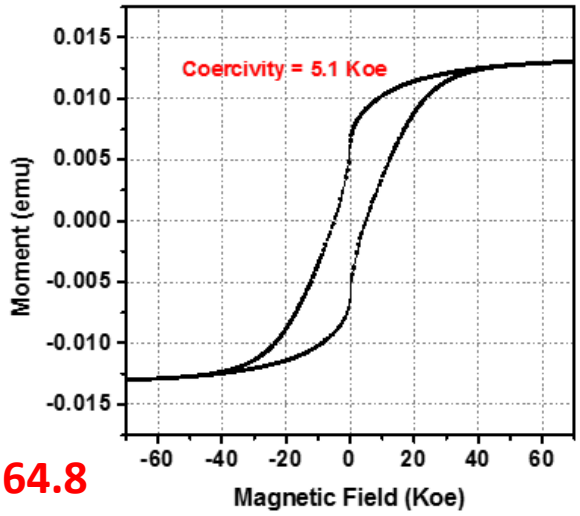


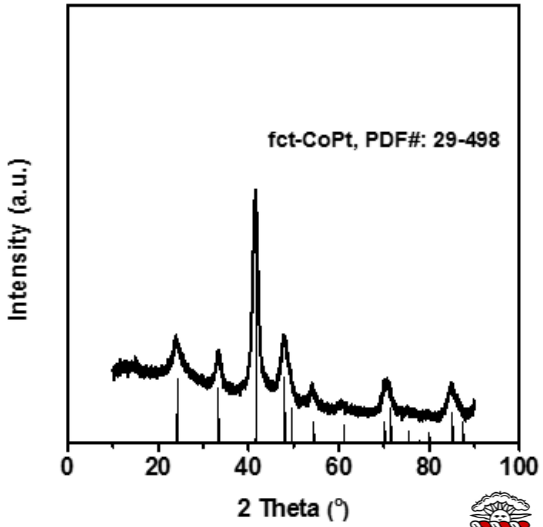






- **Initial synthesis demonstrated partially-ordered fct-CoPt with high ORR activity**
- **Improved ordering needed to provide Co stability**
- **BOL Co : Pt = 50.9 : 49.1**
- **50K Cycles @ 60°C Co : Pt = 35.2 : 64.8**





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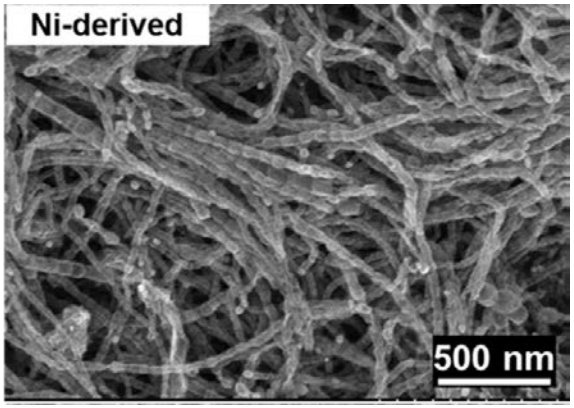
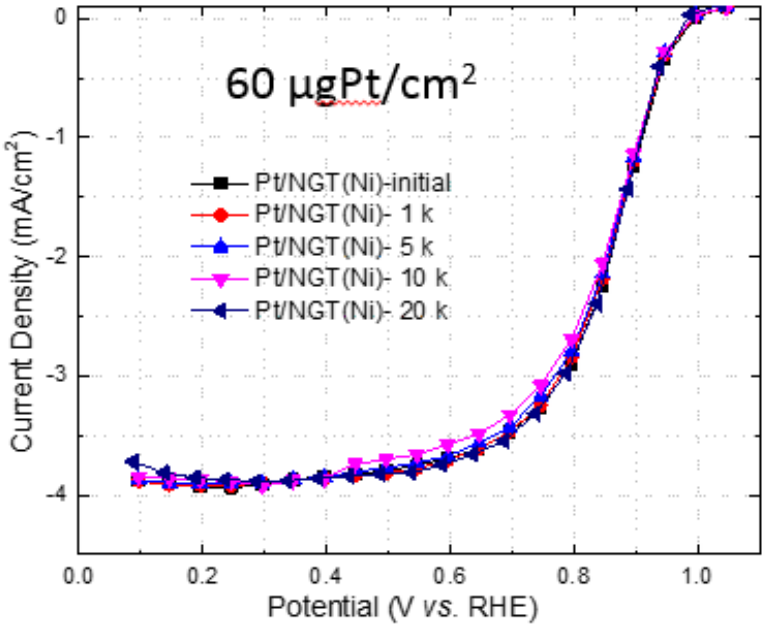
Accomplishments: N-doped Graphene Tube Supports

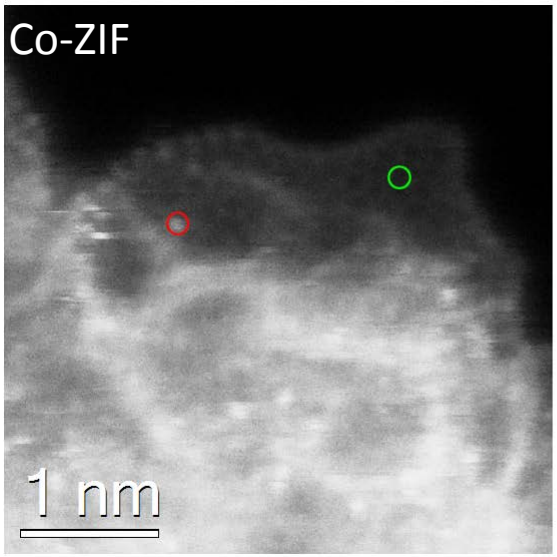
20wt% Pt/N-GT(Ni) **Iron-free carbon supports**

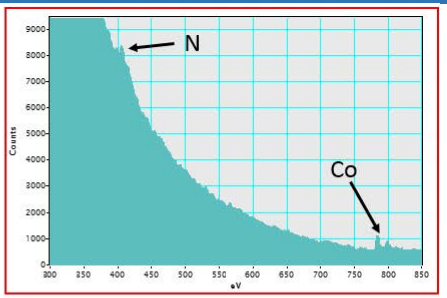


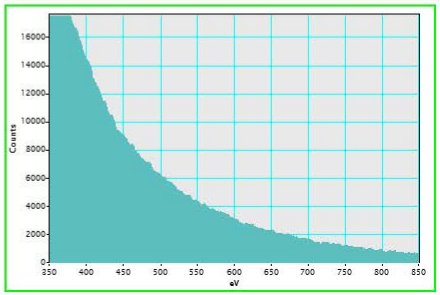


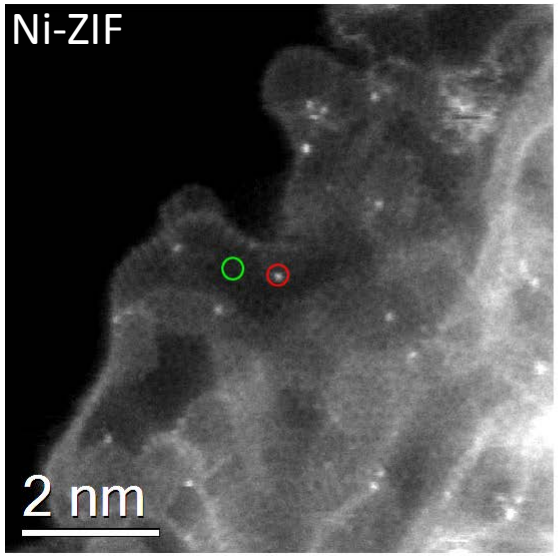
- Mixing and pyrolysis of inexpensive precursors generates Fe-free N-doped graphene tube support (N-GT)
- Pt/N-GT showed **no loss after 20,000 cycles** during 1.0 to 1.5 V potential cycling in N_2 sat. 0.5 M H_2SO_4 (MEA testing now underway)
- Further optimization of support synthesis and Pt deposition is ongoing

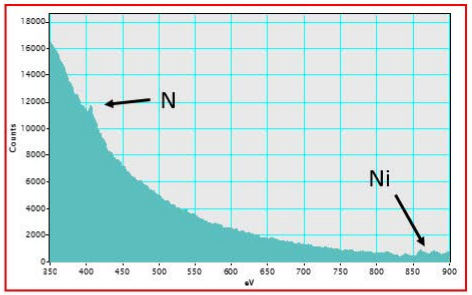
Accomplishments: Co and Ni ZIF-based Supports

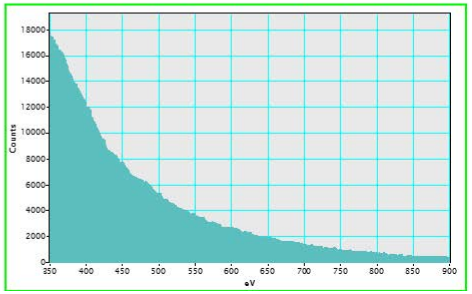












D.A. Cullen, K.L. More (ORNL)

- Supports based on pyrolyzed Co and Ni ZIF precursors were prepared. Supports exhibit graphitic character, with residual Co and Ni atoms dispersed throughout.
- STEM-EELS spectra acquired with beam on a Co or Ni atom show presence of N, while spectra acquired in metal-free areas show no N, indicating that **N is co-located with transition metal (Co, Ni).**
- Next step: low-loaded platinum on ZIF-based supports will be examined to study co-location of Pt with N.

Response to Previous Year Reviewer Comments

This project was not reviewed last year.

Collaborations: Team Member Roles

LANL

- Coordinate project
- Synthesize catalysts
- Produce and test MEAs

Brown

- Synthesize and characterize catalysts; supply to partners
- Provide theory-based design principles

Penn

- Synthesize and characterize catalysts; supply to partners

Buffalo

- Synthesize and characterize supports; supply to partners

EWII

- Scale up MEA production
- Catalyst/MEA validation

No-cost partners:

- **Pajarito Powders** (catalyst scale-up)
- **3M** (SOA low EW membranes and ionomers)

Other collaborators:

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

Remaining Challenges and Barriers

- Produce fct-CoPt and fct-NiPt with similar degree of ordering to current fct-FePt
- Decrease fct-MPt particle size from current levels (8-10 nm) to 3-7 nm while maintaining degree of ordering
- Scale up synthesis to multi-gram batches using cost-effective chemistry
- Incorporate N-doped graphitized supports into high-performance electrodes
- Demonstrate simultaneous achievement of high activity (mass activity > 0.44 A/mg_{PGM}) and high durability (satisfying catalyst and support ASTs)
- Develop optimized electrode structures with effective transport properties to enable >1 W/cm^2 operation

Future Work

FY17:

- Perform initial synthesis of Fe-free fct-PtM/C and fct-PtM_1M_2/C catalysts
- Test Fe-free catalysts in RDE (initial screening) and MEA and compare to fct-FePt/C and baseline Pt/C, including 30,000 cycle AST
- Deposit fct-MPt catalysts on N-doped graphitized supports and compare with baseline Pt/C and fct-MPt/C
- Scale up successful synthetic chemistries to gram scale
- Begin MEA scale-up and validation
- Perform computational studies to guide synthetic work and interpret experimental findings

FY18:

- Key milestone: demonstrate 0.44 A/mg mass activity at 0.9 V in MEA during FY18Q2. If mass activity target cannot be met with fct-intermetallics, switch to other PtM intermetallic formulations (such as Pt_3M)
- Continue catalyst and support development using feedback from MEA testing and characterization

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

Tech Transfer Activities

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

Summary

Objective: Design active and durable ORR catalysts based on fully-ordered intermetallic alloys on highly 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: Fully-ordered intermetallic Pt alloy catalysts supported on highly-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: Project has just begun, but fct-FePt/C catalysts have already demonstrated promising durability. New N-doped graphitized supports also show promising durability.

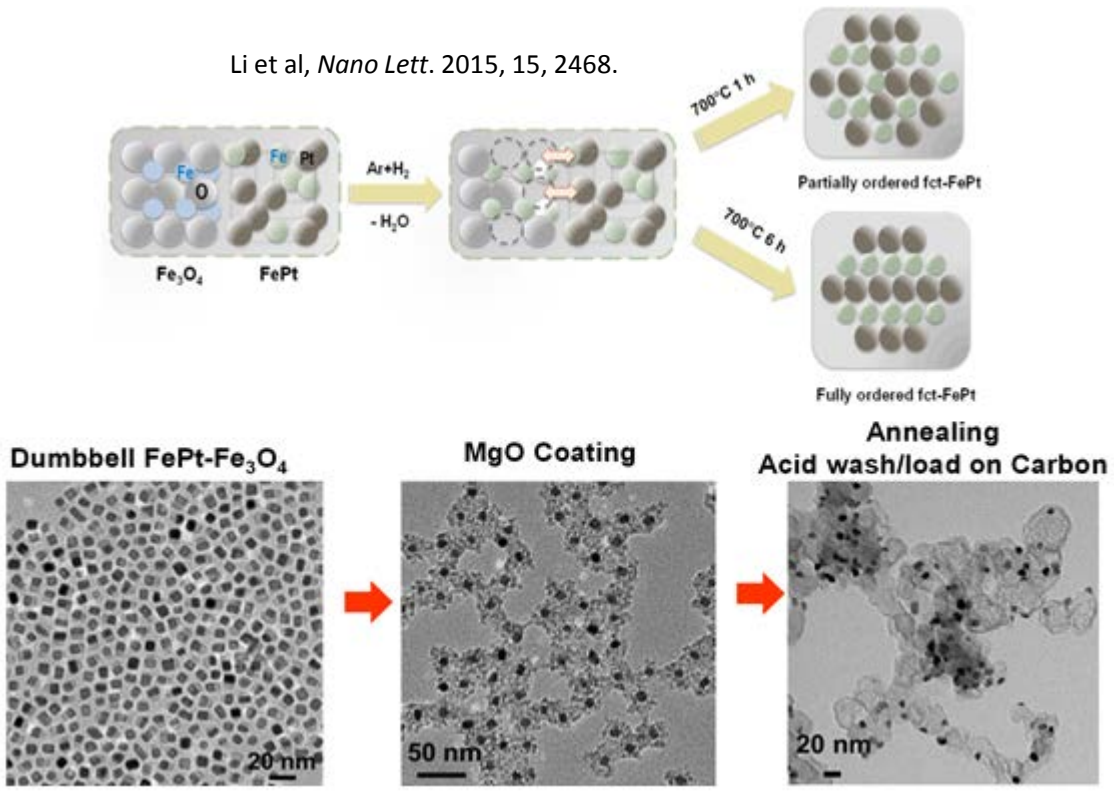
Collaborations: Strong team consists of a national lab with extensive catalyst synthesis, MEA testing, and characterization capabilities, three universities with excellent synthetic and computational capabilities, and an industrial partner with experience in MEA validation and scale-up. No-cost partners and external collaborators provide additional industrial perspective, materials, and characterization techniques.

Technical Backup Slides

Preparation of Fully Ordered fct-FePt

Preparation procedure:

1. Thermal decomposition of metal precursors to FePt-Fe_3O_4 nanoparticles
2. Formation of protective MgO coating
3. Annealing (700°C, 6 h) to produce fully-ordered fct structure
4. Removal of MgO and deposition on carbon support

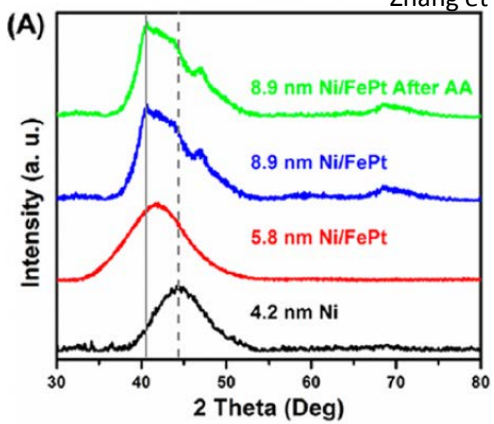


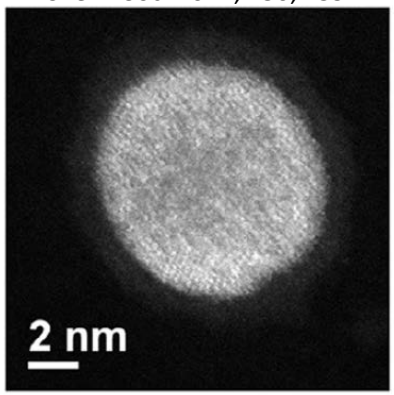
MgO protection enables annealing to fully-ordered fct structure without particle growth

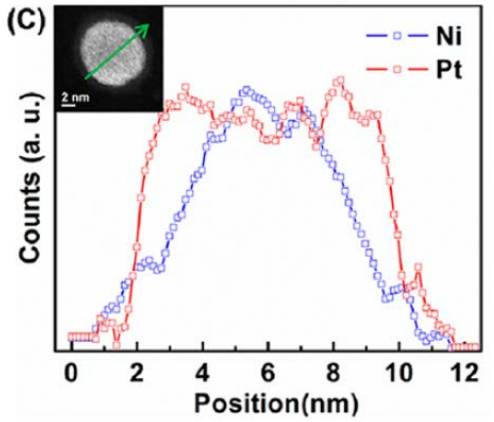
Preparation of Structured Particles

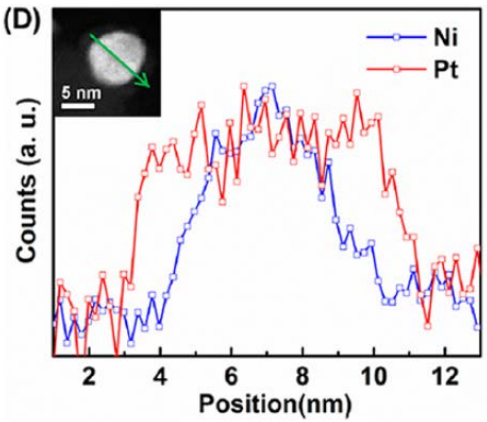
- Seed-mediated growth can produce monodisperse particles with thin Pt shell on non-Pt core
- Technique will be used to prepare monodisperse fct-PtM, fct-PtM_1M_2, and fct-alloy core/Pt shell particles

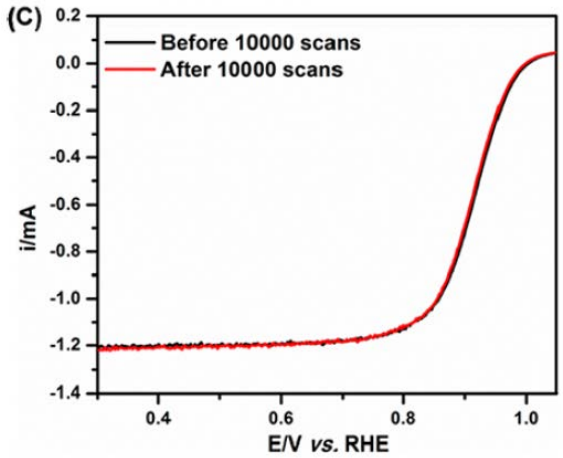
Zhang et al., J. Am. Chem. Soc. 2014, 136, 15921−15924











Theory-based Design Principles

Associative mechanism

$O_2 + (H^+ + e^-) + * \rightarrow *OOH$

$*OOH + (H^+ + e^-) \rightarrow *O + H_2O_{(l)}$

$*O + (H^+ + e^-) \rightarrow *OH$

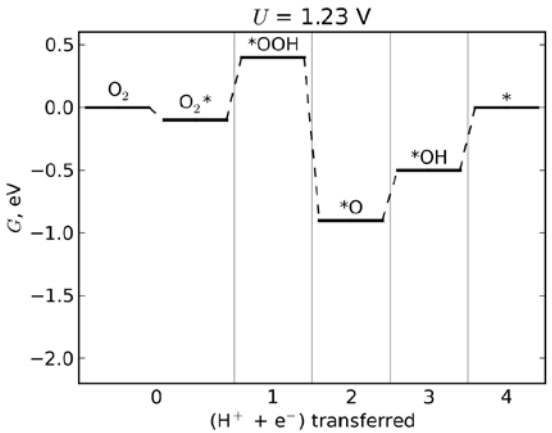
$*OH + (H^+ + e^-) \rightarrow * + H_2O_{(l)}$

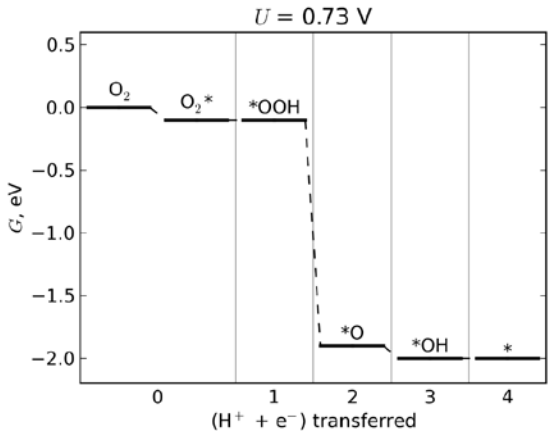
Dissociative mechanism

$O_2 + 2 * \rightarrow 2\,O*$

$2\,O* + 2\,(H^+ + e^-) \rightarrow 2\,*OH$

$2\,*OH + 2\,(H^+ + e^-) \rightarrow 2\,* + 2\,H_2O_{(l)}$



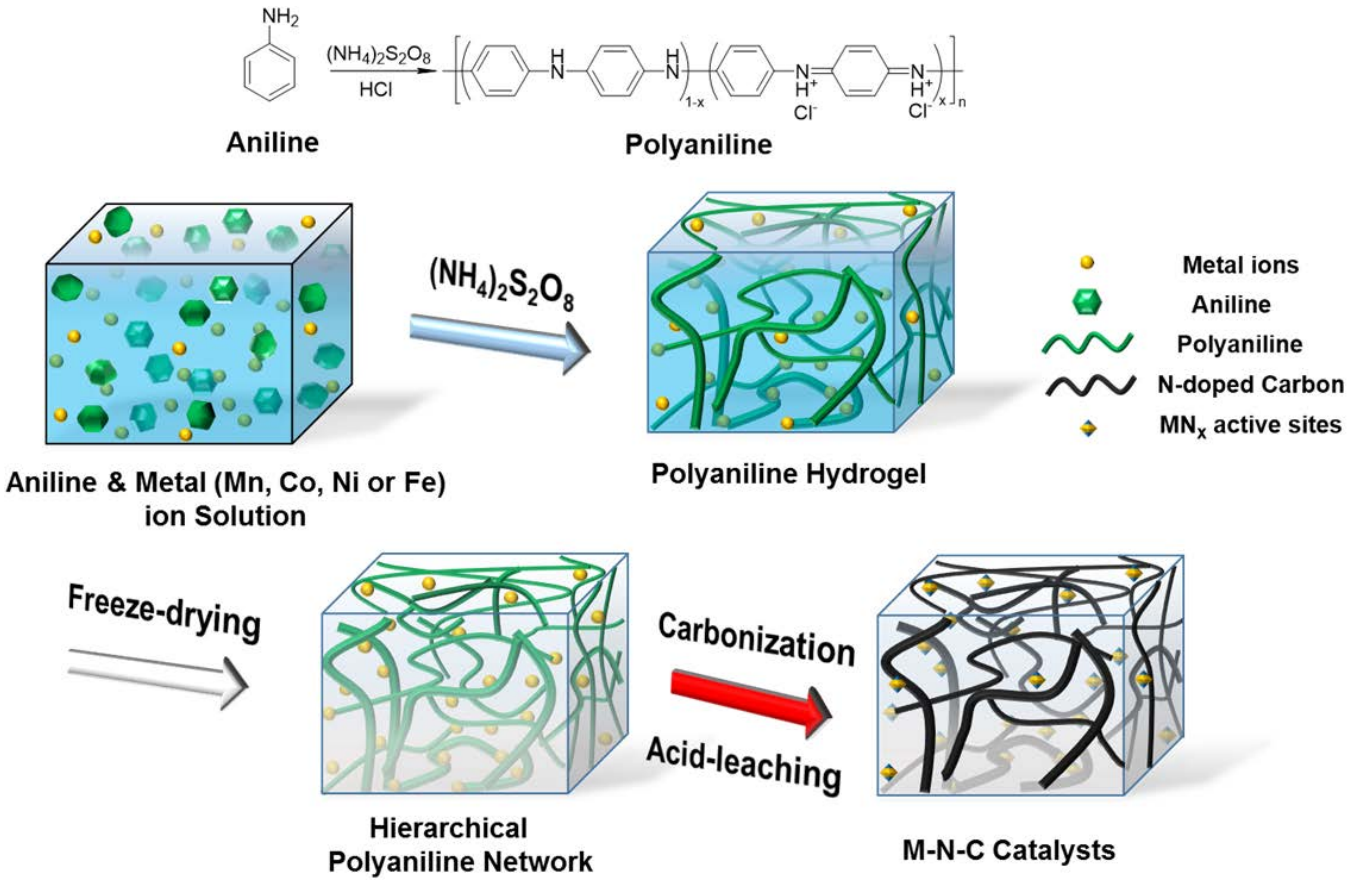


- Non-optimal adsorption strength for reaction intermediates leads to sluggish ORR kinetics on Pt
- 500 mV overpotential required before all steps become spontaneous

BROWN

New Hydrogel-based N-doped C Synthesis Method

- Able to tune material properties by controlling synthetic chemistry:
  - Surface area
  - Particle size
  - Graphitization degree
  - Porosity
  - Dopant
- No additional carbon support required



Mn-Based Carbon from Hydrogel Method

- Hydrogel method can produce ORR active Mn-derived carbon
- Activity approaches state of the art PGM-free catalysts (i.e. Fe-N-C)
- Initial samples have low stability in 1.0-1.5 V AST; optimization is ongoing