



## Tailored High Performance Low-PGM Alloy Cathode Catalysts

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**Materials Science Division**

**Argonne National Laboratory**

Project ID#  
FC140

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## Overview

### Timeline

- Project start: 10/2015
- Project end: 10/2018

### Budget

- Total Project funding \$ 3.25M
- Total DOE funds spent: \$ 2.93M
- Funding for FY18: \$ 900K

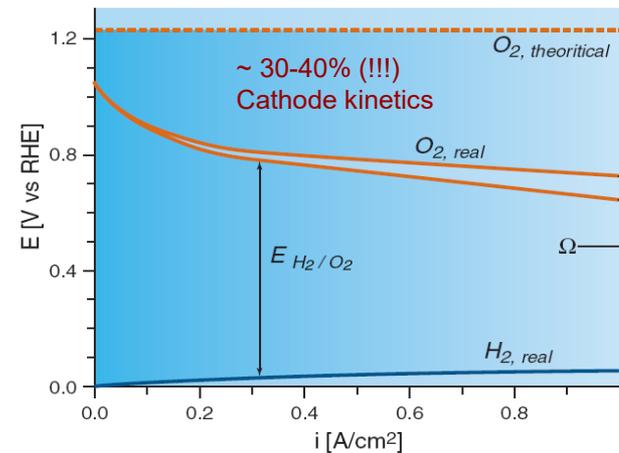
### Partners:

- Argonne National Laboratory – MERF - CSE – Greg Krumdick, Debbie Myers
- Oak Ridge National Laboratory – Karren More
- National Renewable Energy Laboratory – Kenneth Neyerlin

### Project Lead:

- Argonne National Laboratory - MSD – V. Stamenkovic / N. Markovic

### Barriers to be addressed



1) **Durability** of fuel cell stack (<40% activity loss)

2) **Cost** (total loading of PGM  $0.125 \text{ mg}_{\text{PGM}} / \text{cm}^2$ )

3) **Performance** (mass activity @ 0.9V  $0.44 \text{ A/mg}_{\text{Pt}}$ )

# Relevance

**Objectives** The main focus of ongoing DOE Hydrogen & Fuel Cell Program is development of highly-efficient and durable Pt-Alloy *catalysts* for the ORR *with low-Pt content*

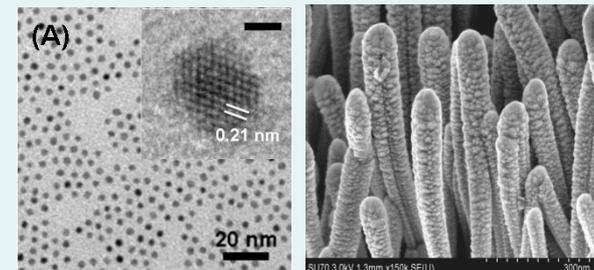
Table 3.4.13 Technical Targets: Electrocatalysts for Transportation Applications<sup>h</sup>

Characteristic	Units	2011 Status	2020 Targets
Platinum group metal total content (both electrodes) <sup>a</sup>	g / kW (rated)	0.19 <sup>b</sup>	0.125
Platinum group metal (pgm) total loading <sup>a</sup>	mg PGM / cm <sup>2</sup> electrode area	0.15 <sup>b</sup>	0.125
Loss in initial catalytic activity <sup>c</sup>	% mass activity loss	48 <sup>b</sup>	<40
Electro catalyst support stability <sup>d</sup>	% mass activity loss	<10 <sup>b</sup>	<10
Mass activity <sup>e</sup>	A / mg Pt @ 900 mV <sub>iR-free</sub>	0.24 <sup>b</sup>	0.44
Non-Pt catalyst activity per volume of supported catalyst <sup>e, f</sup>	A / cm <sup>3</sup> @ 800 mV <sub>iR-free</sub>	60 (measured at 0.8 V) <sup>g</sup> 165 (extrapolated from >0.85 V) <sup>g</sup>	300

Source: Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan

## ANL Technical Targets

- Total PGM loading  
2020 DOE target 0.125 mg<sub>PGM</sub>/cm<sup>2</sup>
- Loss in initial mass activity  
2020 DOE target <40%
- Mass activity @ 0.9V<sub>iR-free</sub>  
2020 DOE target 0.44 A/mg<sub>Pt</sub>



# Approach

Materials-by-design approach - to design, characterize, understand, synthesize/fabricate, test and develop tailored high performance low platinum-alloy nanoscale catalysts

**Project Lead**  
AIO 4A Low-PGM

**Inter Lab Collaborators**

**ANL Catalyst Synthesis**

**ORNL Electron Microscopy**

**NREL 50cm<sup>2</sup> MEA testing**

**ANL - ES Carbon nano/m tubes**

**ANL - ES Support of Scaling-Up**

**ANL**

## PEMFC Cathode Catalysts Development

well-defined systems, fundamental principles, chemical and thin film synthesis, structural and RDE & MEA characterizations

**Task**

**1° WDS** well-defined bulk and thin film surfaces of PtMN:  
-single crystalline and polycrystalline systems  
-structure/composition vs. activity/durability (UHV, PVD, STM vs. RDE, STM, ICP/MS)

**2° SYN** synthesis of nano-, meso- and thinfilm- PtMN catalysts:  
-shape/size/composition control  
-intermetallics; core/interlayer/shell; thin-film systems (colloidal chemical synthesis, PVD, HRTEM/STEM)

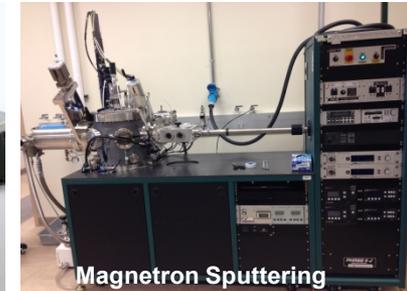
**3° ECC** electrochemical characterization of catalysts:  
-optimization: ionomer/carbon/propanol/catalyst ink  
-temperature effect; Ionic Liquid evaluation  
-activity/durability in RDE vs. 5-50cm<sup>2</sup>/MEA; HRTEM

**4° SUP** fine tuning of performance through catalyst-support:  
-Carbon based materials

**5° SCA** scaling-up of the most promising catalysts:  
-gram scale single batches

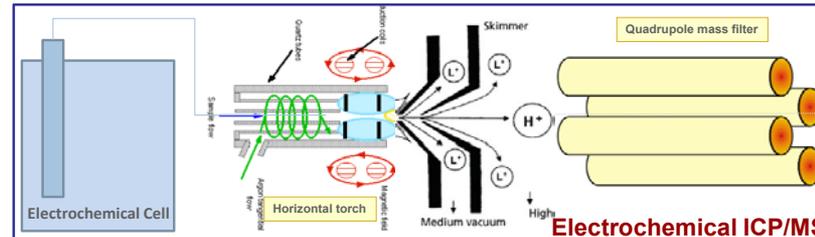


LEIS, AR-XPS, AES, UPS, LEED, STM



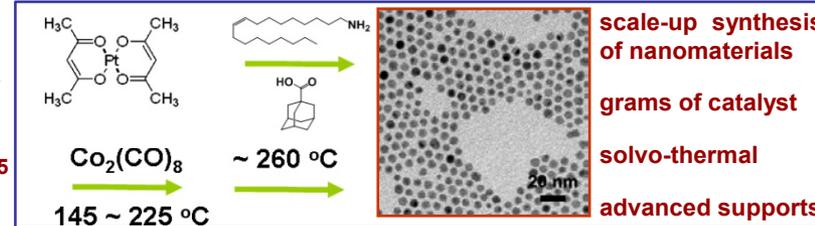
Magnetron Sputtering

TASK 1



Electrochemical ICP/MS

TASK 2&5



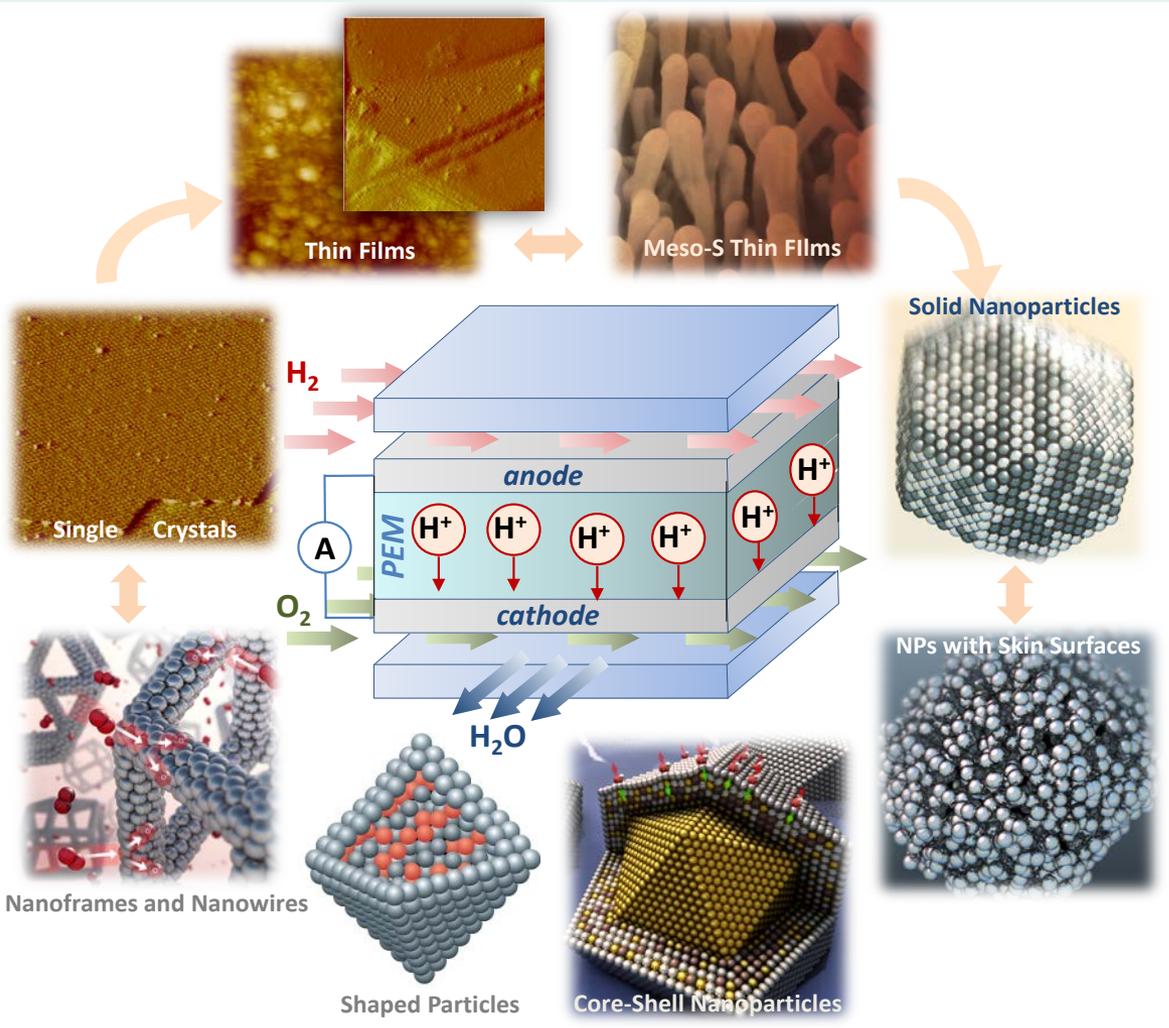
TASK 3



- Rational synthesis based on well-defined systems
- Addition of the elements that hinder Pt dissolution

- Activity boost by lower surface coverage of spectators
- Prevent loss of TM atoms without activity decrease

# Approach



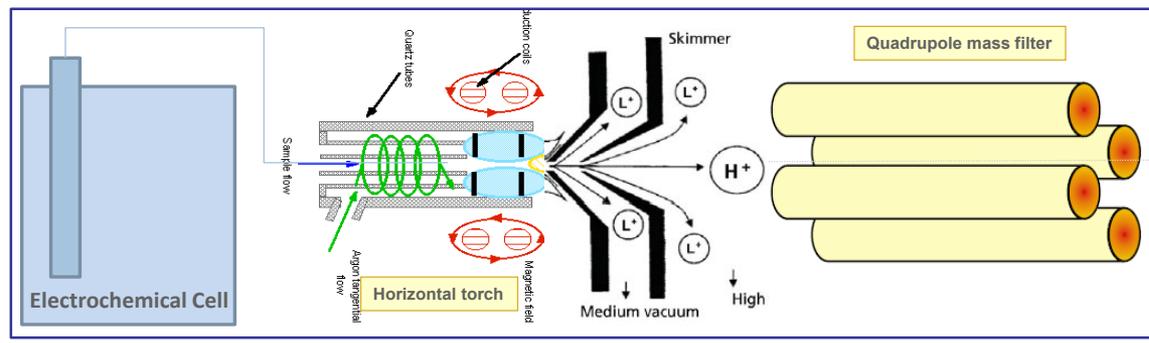
## Project Management

Table 1	FY16   FY17   FY18			
	Q1 Jan	Q2 Apr	Q3 July	Q4 Oct
Active Task				
T1 WDS	↕	↕	↕	↕
T2 SYN	↕	↕	↕	↕
T3 ECC	↕	↕	↕	↕
T4 SUP	↕	↕	↕	↕
T5 SCA	↕	↕	↕	↕

- Task 1 - Well-Defined Systems (WDS)
- Task 2 - Synthesis of Materials (SYN)
- Task 3 - Electrochemical Characterization (ECC)
- Task 4 - Novel Support/Catalyst (SUP)
- Task 5 - Scaling Up of Materials (SCA)

- From fundamentals to real-world materials
- Simultaneous effort in five Tasks
- Go-No Go evaluation
- Progress measures are quarterly evaluated

# Task 1 Accomplishments: RDE-ICP/MS of Pt/C Nanoparticles

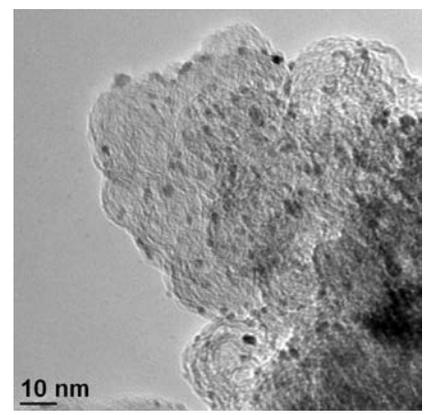
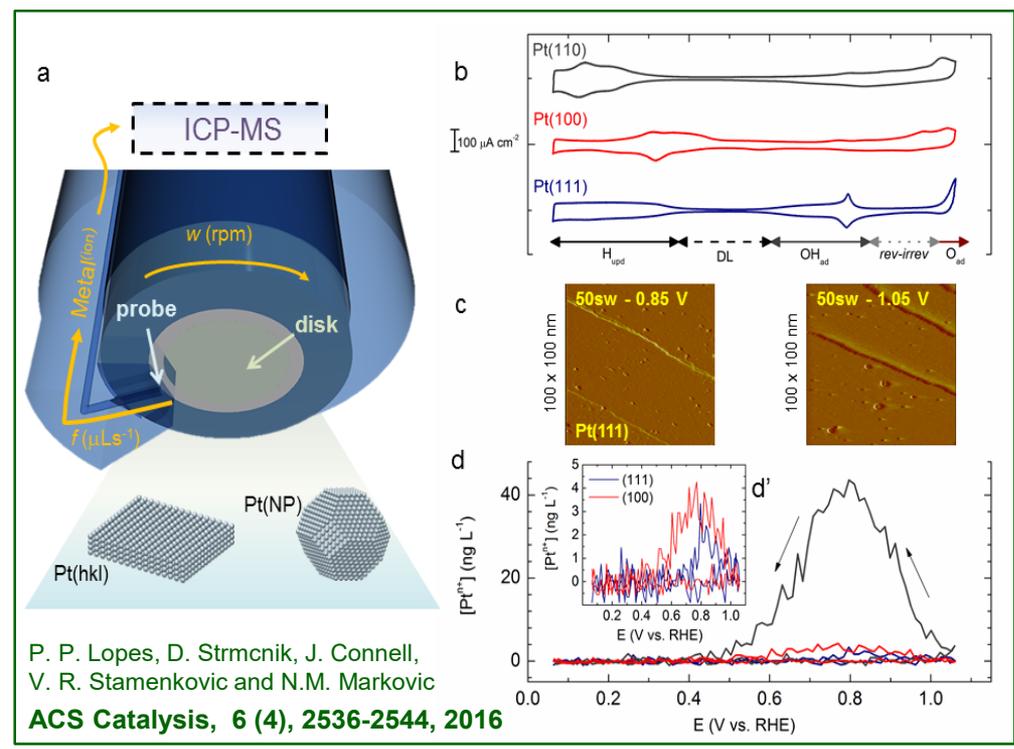


Surface Structure	Pt(111)	Pt(100)	Pt(110)	Pt-poly
Dissolved Pt per cycle [ $\mu\text{ML}$ ]	2	7	83	36

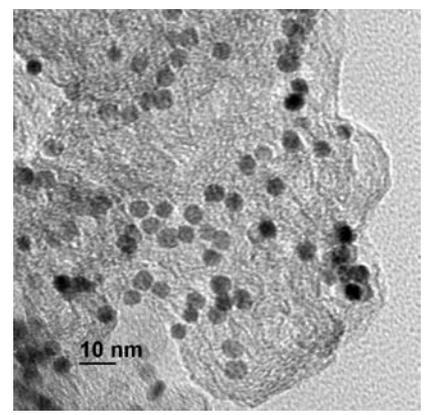
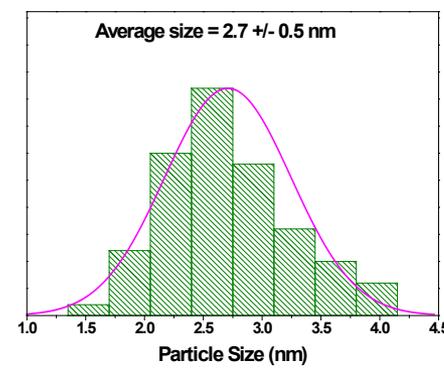
Detection Limit: 0.8  $\mu\text{ML}$  of Pt

**Monodisperse 20% Pt/C NPs 3 and 5nm**

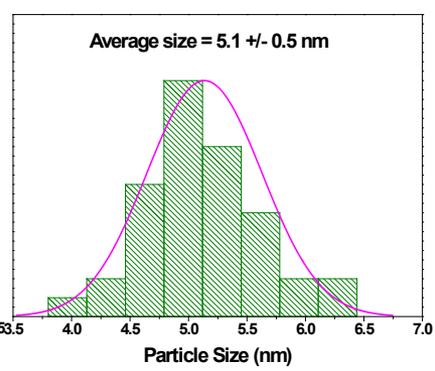
## In-Situ RDE-ICP/MS



2.7 +/- 0.5 nm

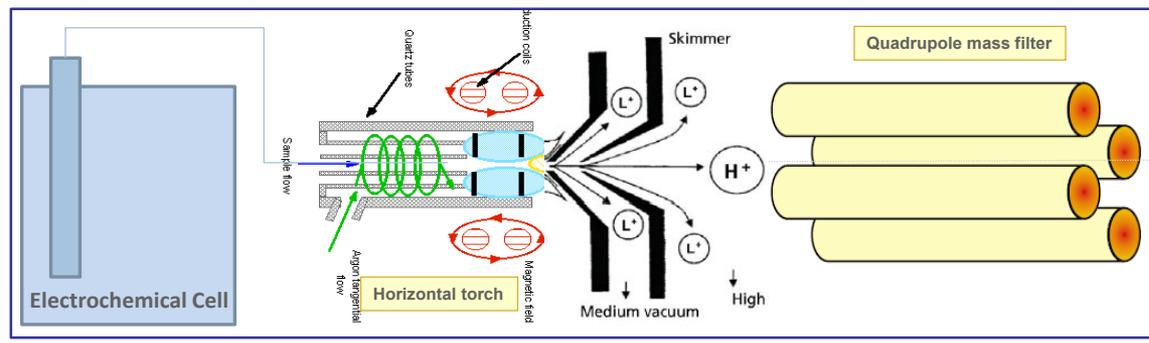


5.1 +/- 0.5 nm



## Correlation between Surface Structure - Activity - Dissolution

# Task 1 Accomplishments and Progress: RDE-ICP/MS of Pt/C Nanoparticles

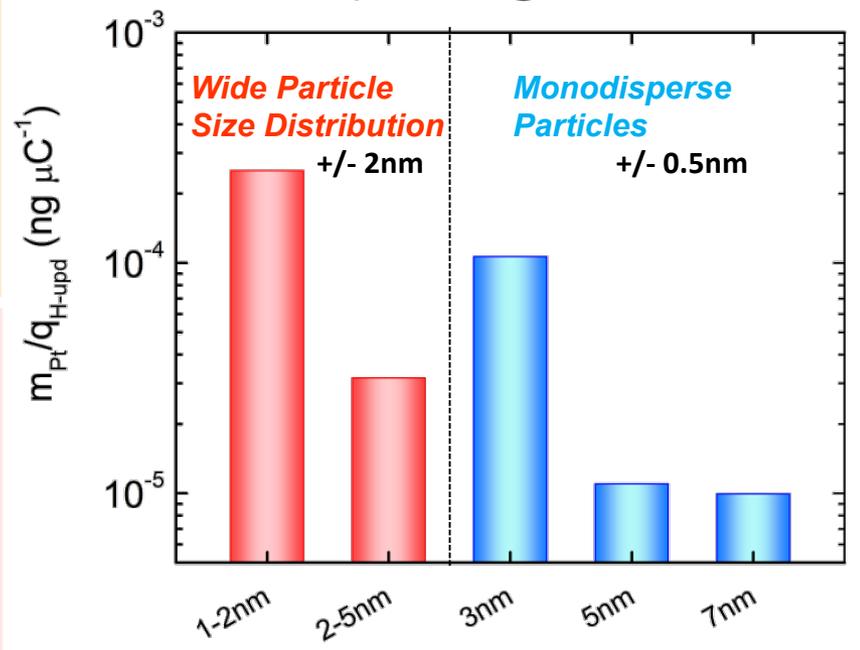
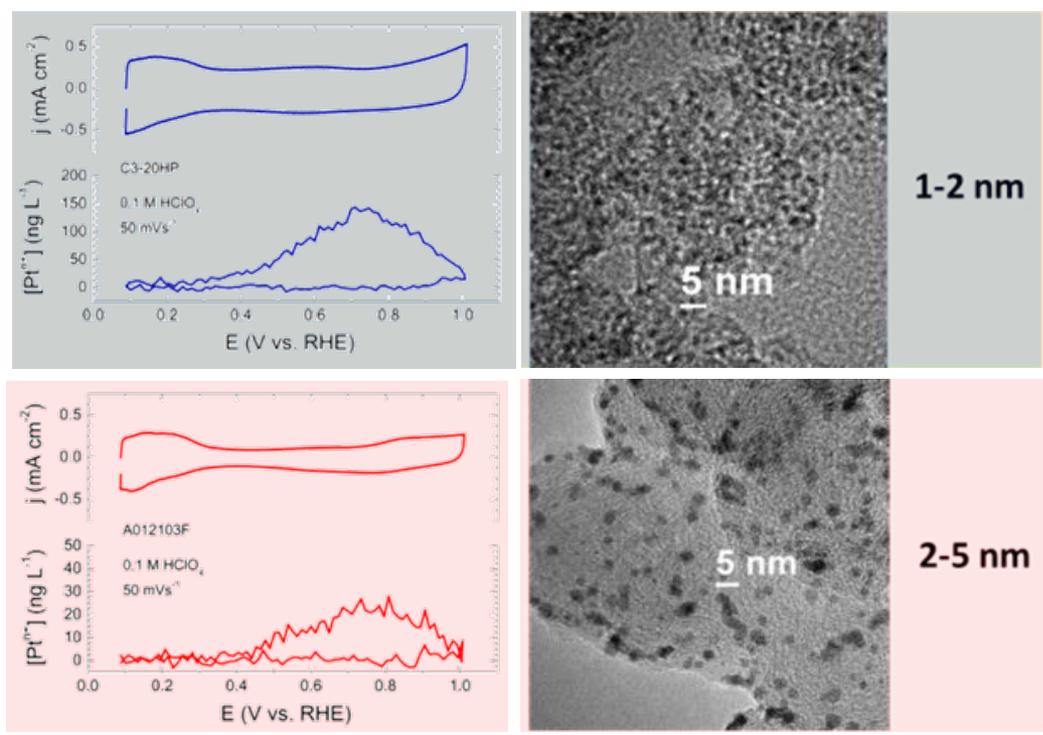


Surface Structure	Pt(111)	Pt(100)	Pt(110)	Pt-poly
Dissolved Pt per cycle [μML]	2	7	83	36

Detection Limit: 0.8 μML of Pt

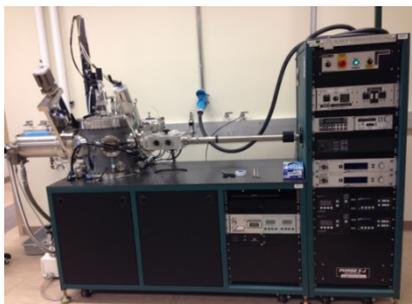
## Dissolution Rates

CV up to 1V @ 50mVs<sup>-1</sup>

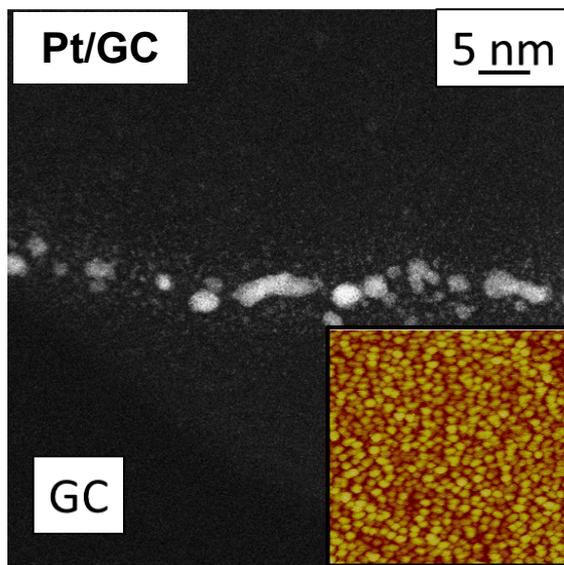
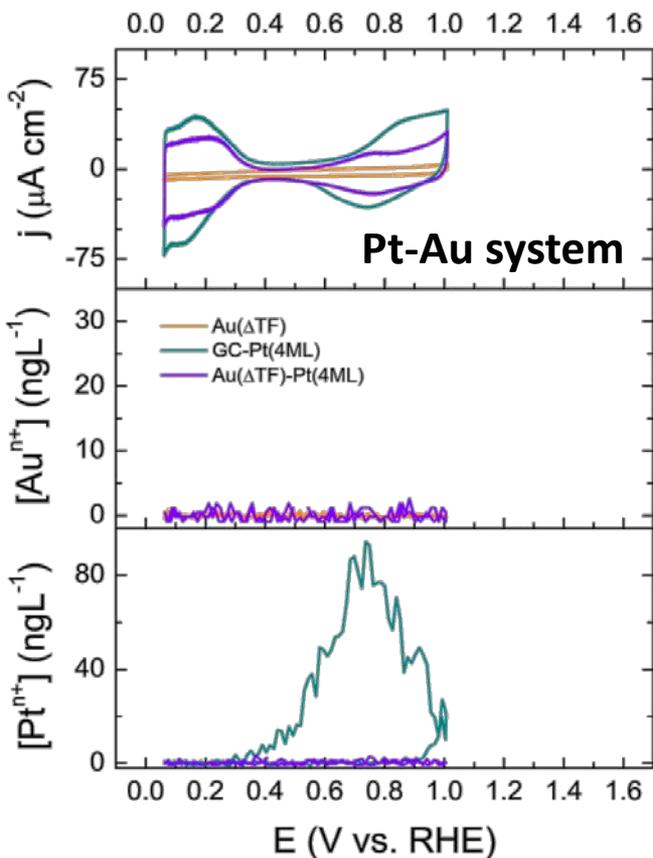
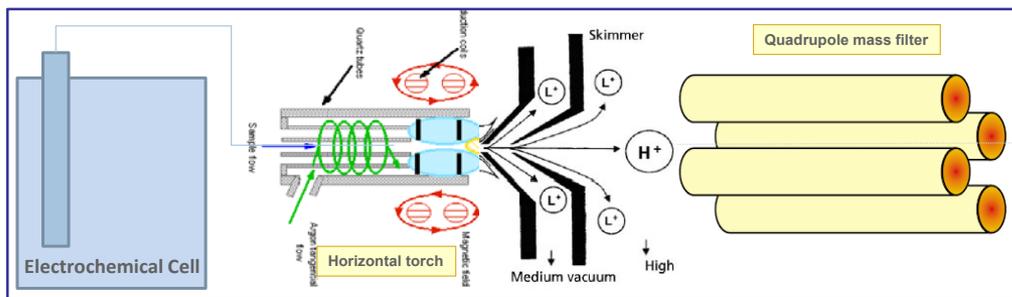


Control of particle size distribution have important role for dissolution rate

# Task 1 Accomplishments and Progress: *EC-ICP-MS* Pt-Surfaces effect of substrate

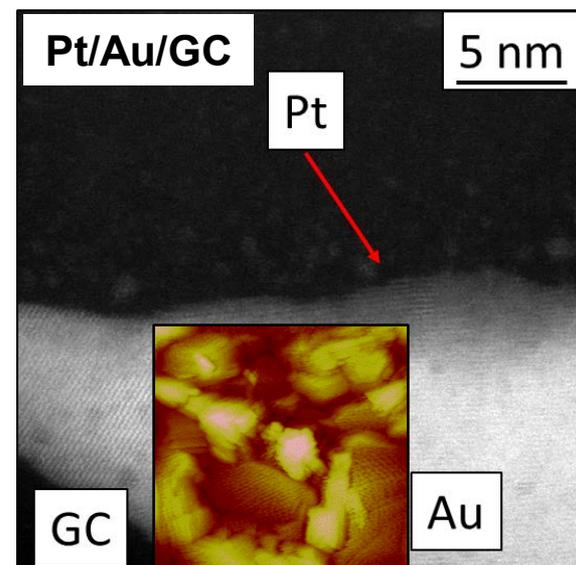


**Au Substrate**



Potential range:  
0.05 to 1.0 V

0.1M HClO<sub>4</sub>



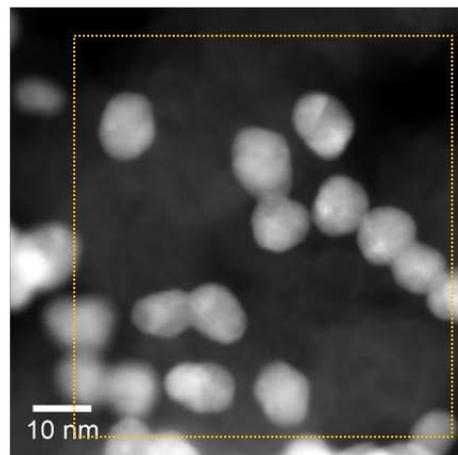
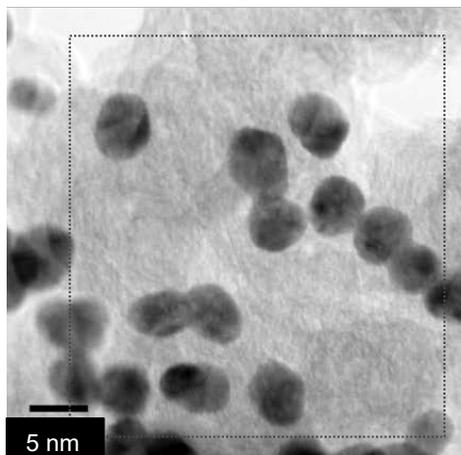
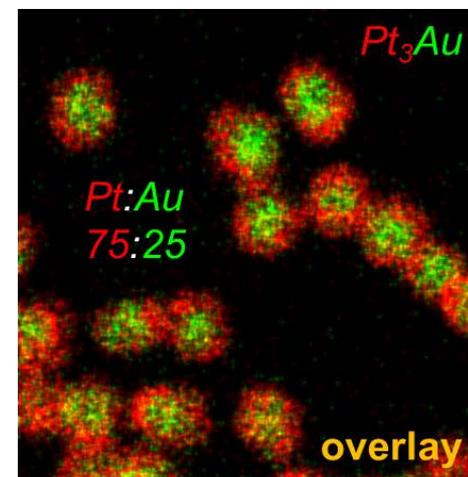
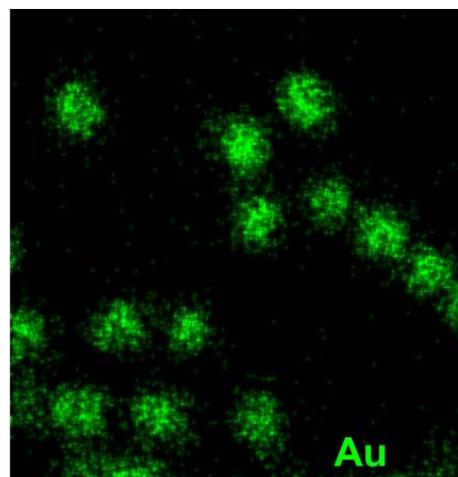
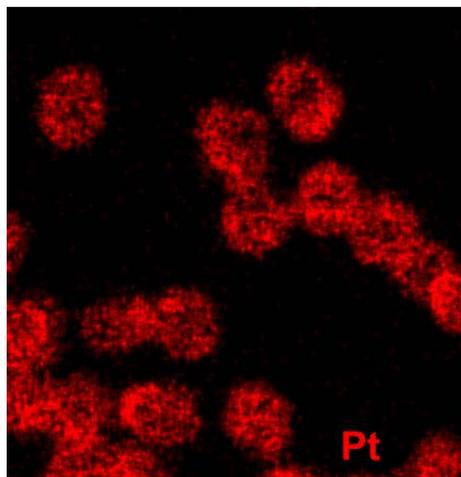
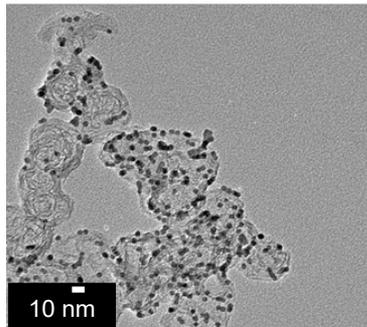
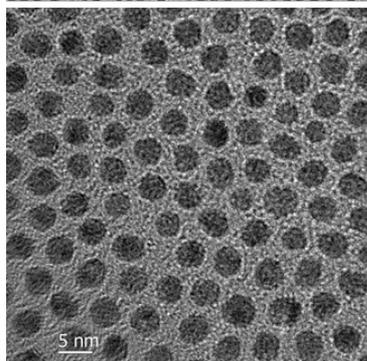
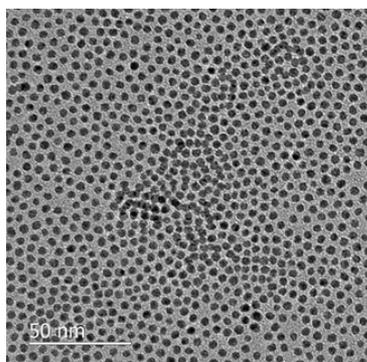
- Pt 4ML over GC forms a non-continuous film, full of small nanoparticles (~2nm)

- Pt 4ML over Au thin layer) shows the Pt with Au structure, favoring (111) surface

# Task 2 Accomplishments and Progress: Pt<sub>3</sub>Au synthesis and characterization

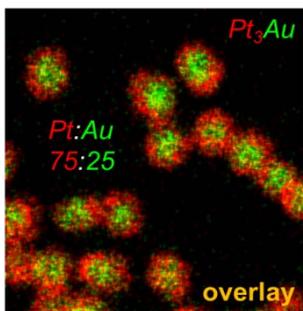
in collaboration with K.L. More, ORNL

## High-Precision Synthesis *monodisperse NPs with uniform compositional profile*

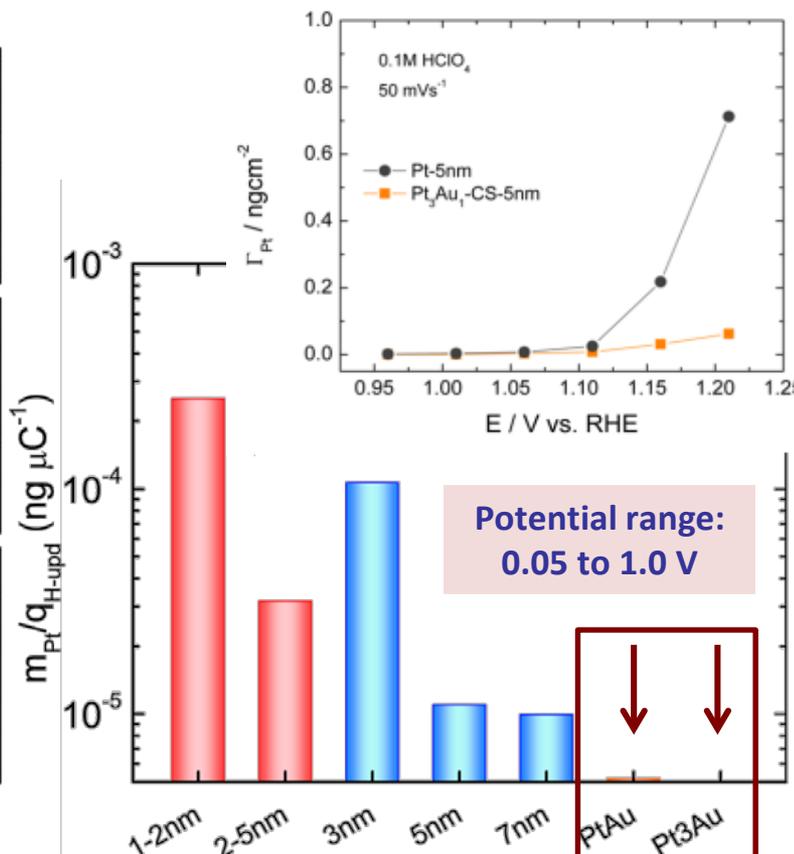
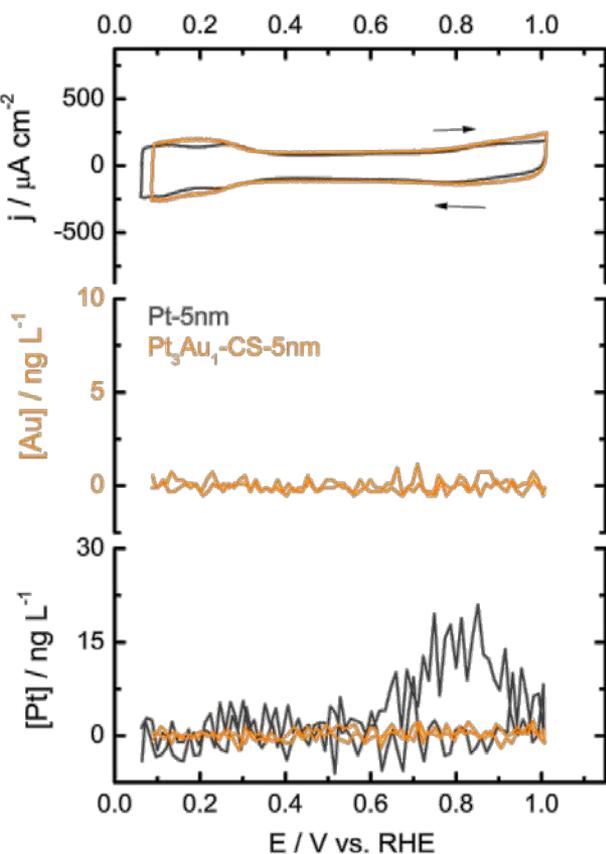
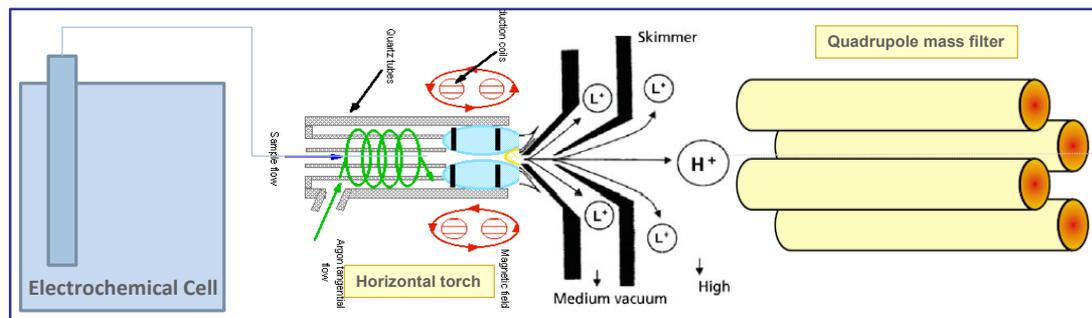


- Pt shell Au core nanoparticles:
- Monodisperse ~5 nm
  - Uniform Pt shell

# Task 1-2 Accomplishments and Progress: EC-ICP-MS Pt<sub>3</sub>Au nanoparticles



Pt<sub>3</sub>Au/C - GC

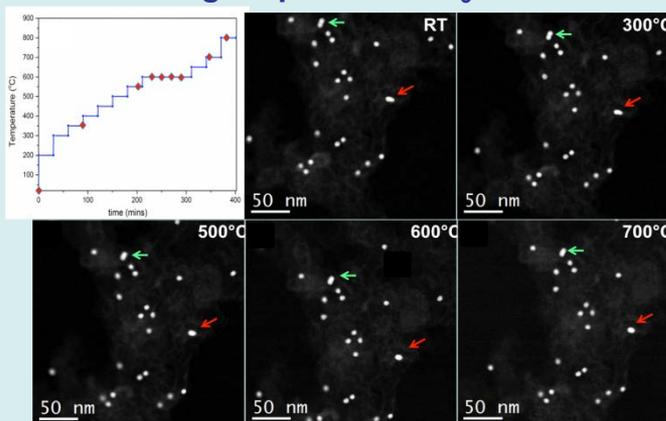


Pt<sub>3</sub>Au/C

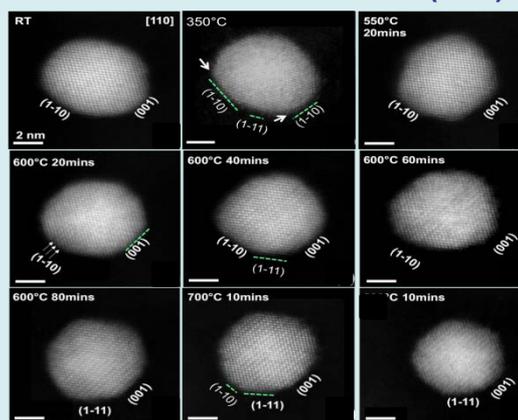
- Dissolution of Pt completely diminished up to 1.0 V
- Stability improvement retains at higher electrode potentials
- Up to 10 times more stable above 1.2V

in collaboration with K.L. More, ORNL

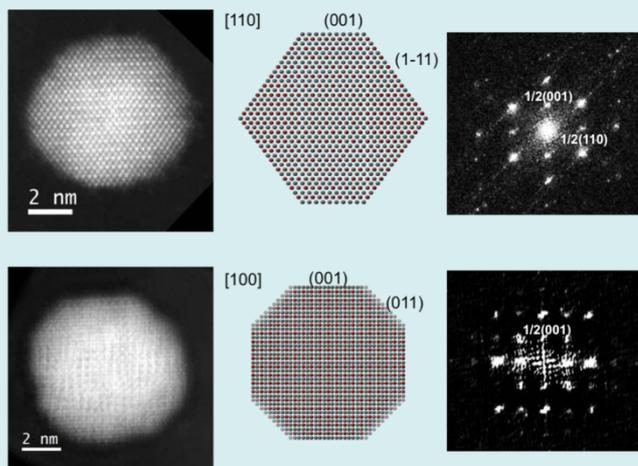
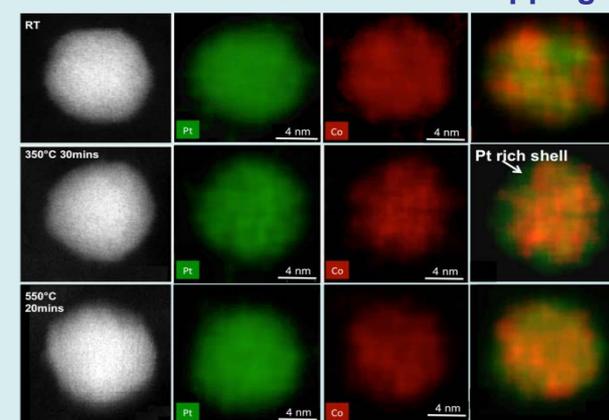
## Annealing sequence of Pt<sub>3</sub>Co NP



## HAADF at different T and t(min)



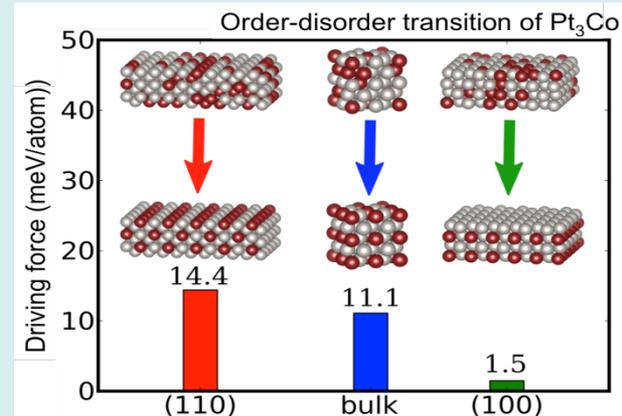
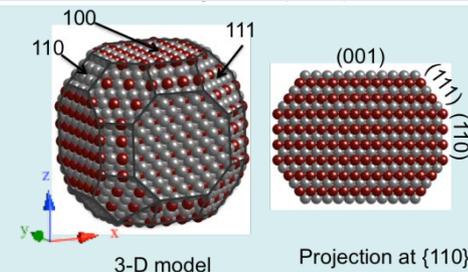
## HAADF and EDS elemental mapping



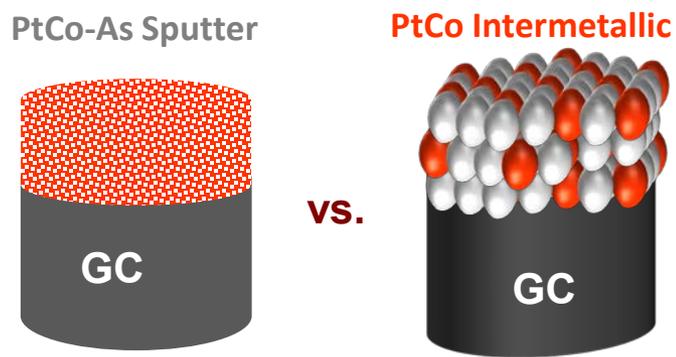
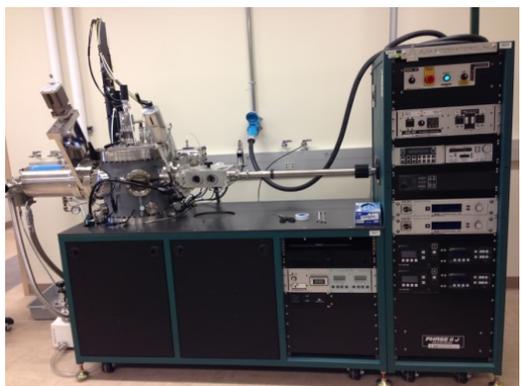
**Dynamic of structural and chemical evolution at the atomic scale of Pt<sub>3</sub>Co NPs during in-situ annealing**  
distinct behavior at critical stages:

- {111}, {110}, {100} facets play different roles during the evolution of structure
- formation of a Pt-Skin shell with an alloyed disordered core;
- the nucleation of ordered domains;
- the establishment of an ordered L<sub>12</sub> phase followed by pre-melting

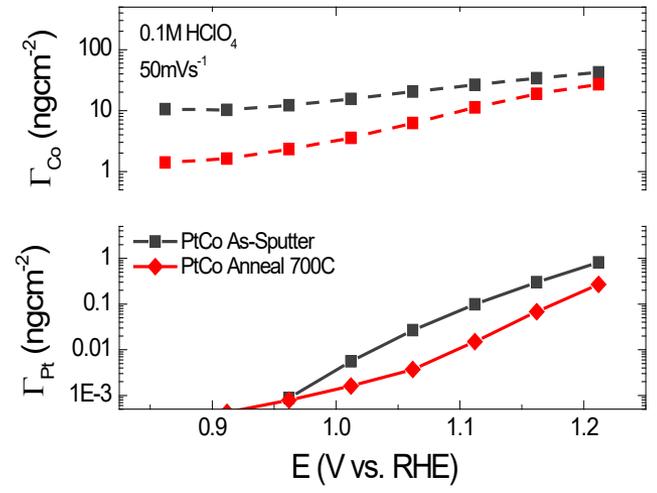
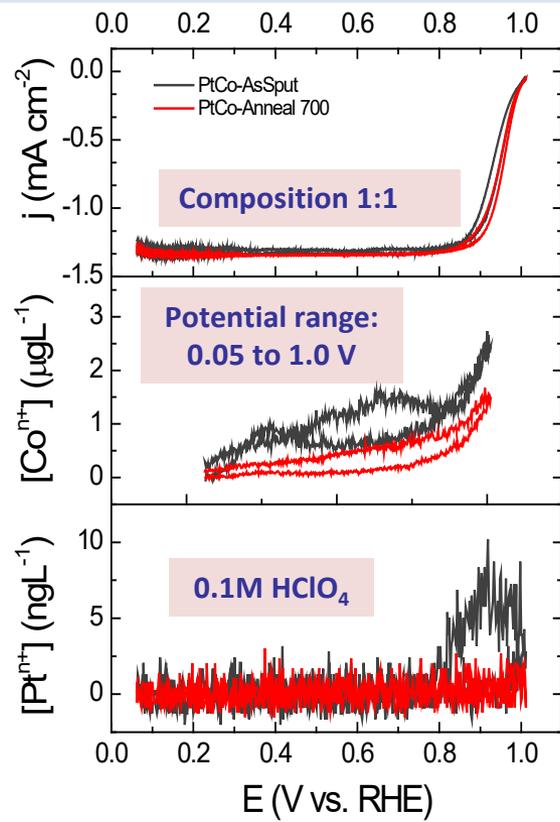
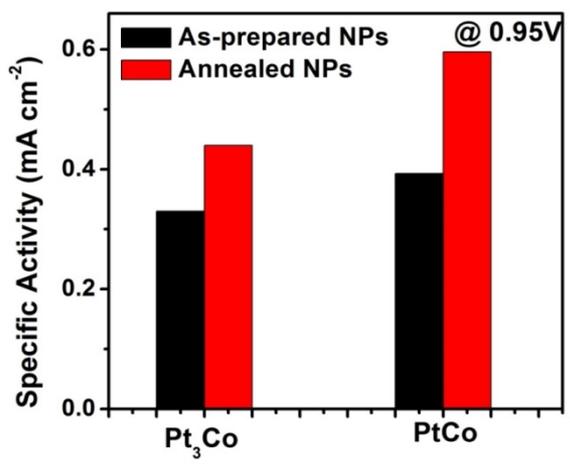
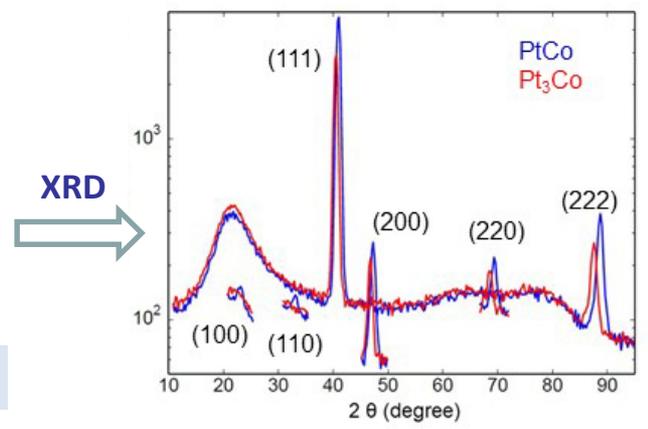
M. Chi, C. Wang, Y. Lei, G. Wang, K.L. More, A. Lupini, L.F. Allard, N.M. Markovic, and V.R. Stamenkovic  
**Nature Communications 6 (2015) No. 8925**



# Task 1 Accomplishments and Progress: *In-Situ* EC-ICP-MS Pt-Alloys Intermetallic



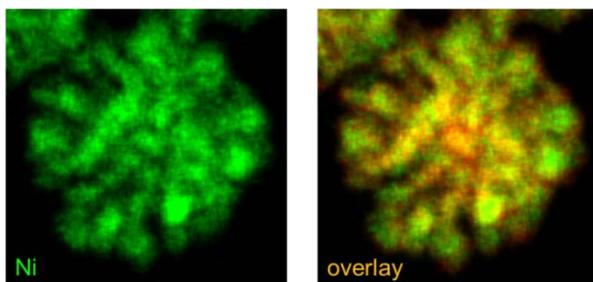
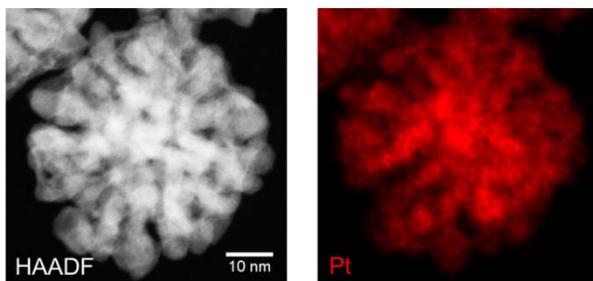
Annealing at 700°C = Intermetallic Phase



**Benefit of intermetallic phase:**

- Decreases dissolution of both Pt and Co
- Improvement in ORR activity

# Task 2-3 Selected Nanostructures: Pt-Alloys, Solid, Porous and Hollow Structures



## Nanopinwheels

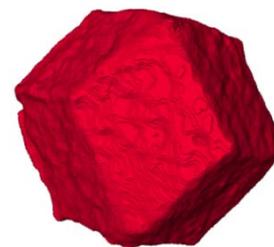


ANL, ORNL

Improvement vs. Pt/C  
RDE @ 0.95V

SA: 10  
MA: 5

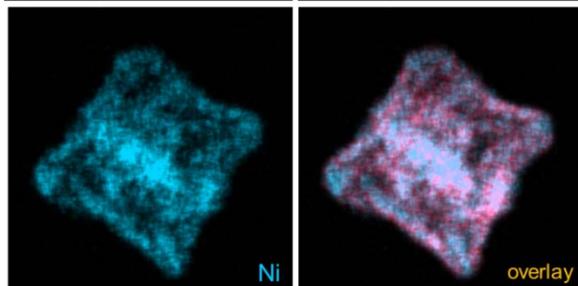
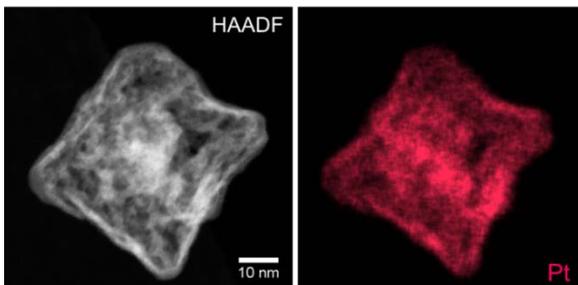
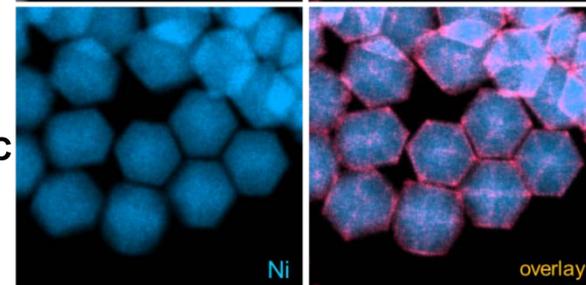
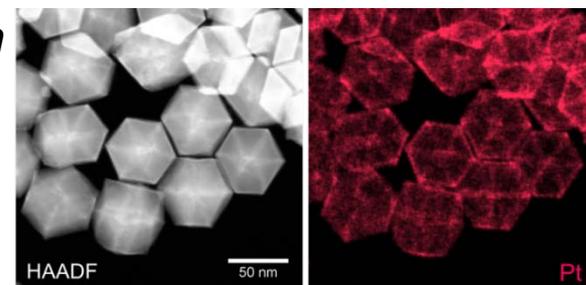
## Nano Multi Skin



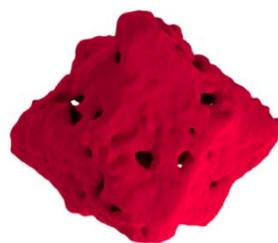
ANL, ORNL

Improvement vs. Pt/C  
RDE @ 0.95V

SA: 7  
MA: 4



## Nanocages



ANL, ORNL

Improvement vs. Pt/C  
RDE @ 0.95V

SA: 9  
MA: 6

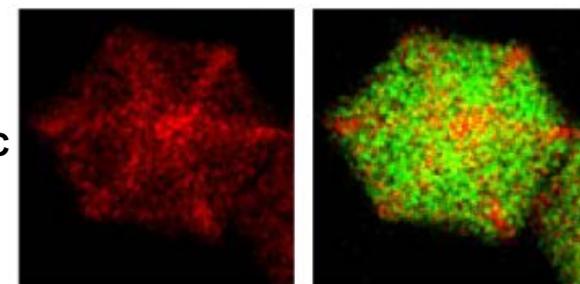
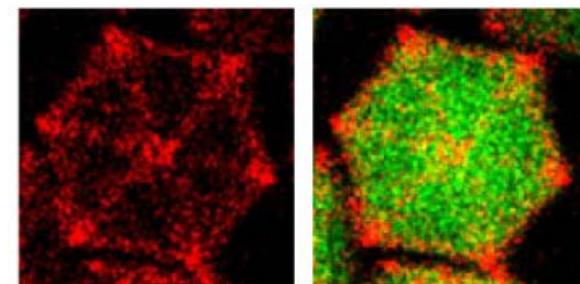
## Excavated Nanoframes



LBNL, ANL, ORNL

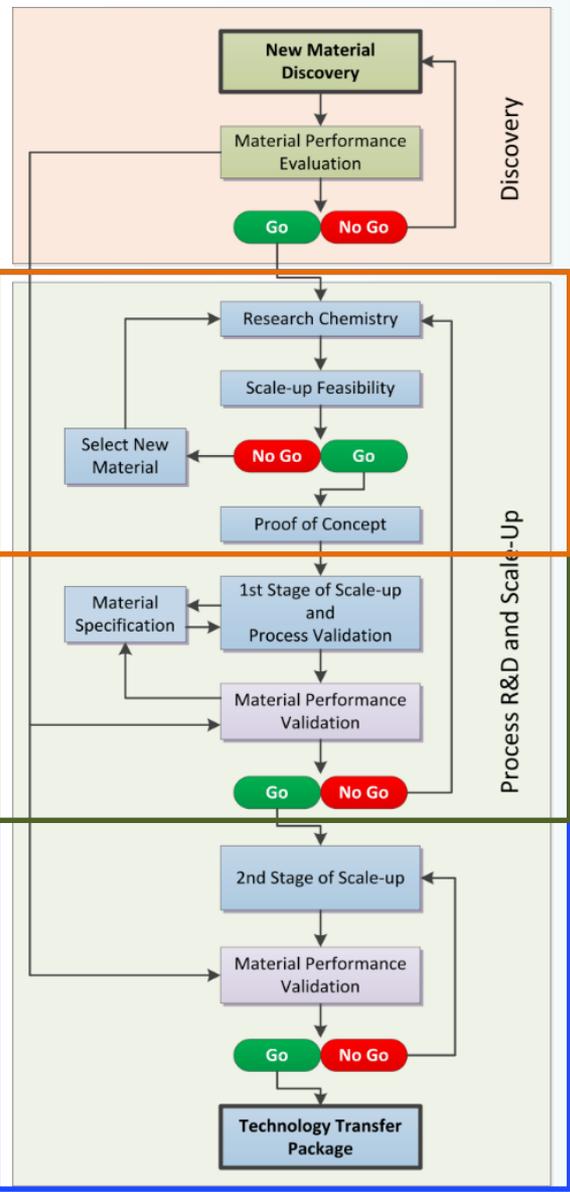
Improvement vs. Pt/C  
RDE @ 0.95V

SA: 13  
MA: 7

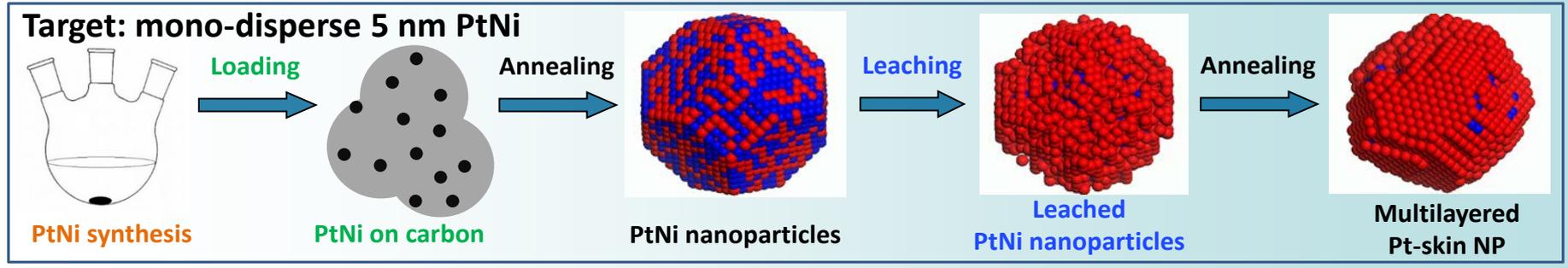


# Task 5 Accomplishments: Process R&D and Scale Up

collab. with Greg Krumdick, ANL -MERF



Timeline & Milestones		
Research Chemistry	M 1-2	1) <b>Hot-injection</b> was avoid using <b>one-pot synthesis</b> . 2) Benzyl ether as solvent. <b>No Go</b>
	M 3	3) <b>Phenyl ether</b> as solvent. 4) <b>Best synthesis condition</b> was established. 5) <b>Reproducibility</b> was confirmed. <b>Go</b>
1 <sup>st</sup> stage scale up	M 4	6) 1 <sup>st</sup> stage scale up ( <b>1 g / batch</b> ) was <b>successful</b> . 7) <b>New method</b> to load PtNi nanoparticles on carbon and its separation from solvent was developed.
	M 5-6	8) <b>Reproducibility</b> of 1 <sup>st</sup> stage scale up was confirmed. 9) Pre-annealing process applied.
	M 6-7	10) <b>Acid leaching process</b> was modified. <b>Go</b>
2 <sup>nd</sup> stage scale up	M 8-9	11) The 2 <sup>nd</sup> stage scale up ( <b>5 g / batch</b> ) was <b>successful</b> . 12) <b>Acid leaching process</b> was established.
	M 10	13) The 2 <sup>nd</sup> stage scale up is <b>reproducible</b> . <b>Go</b>
	M 11-12	14) MEA performance; <b>New IP application</b> ; Sample send out; Manuscript submitted.



**PtNi synthesis: 0.1 g Scale**

- Pre-heat mixture to 200 °C.**  
 Nickel acetate tetrahydrate (0.1667 g)  
 1,2-Tetradecanediol (0.085 g)  
 Oleic acid (0.4 ml) & Oleylamine (0.4 ml)  
 Diphenyl ether (20 ml) or Dibenzyl ether (20 ml) **X**
- Inject preheated Pt solution (~80 °C). X**  
 Platinum(II) acetylacetonate (0.13 g)  
 In 1,2-Dichlorobenzene (1.5 ml)
- Hold T at 200 °C for 1 h.**

**Loading on carbon:**

**0.1 g Scale**

- Mix and sonicate in Hexane or Chloroform.
- Evaporation of solvent. X**

**5 g Scale**

- Mix and sonicate with pre-dispersed carbon in Chloroform
- Precipitate PtNi/C with Hexane.
- Filtration.



↓ **Safer > Easier > Scalable > Reproducible**

One-pot	5 g Scale
200 °C 30 min	Nickel acetate tetrahydrate (2.5 g)
	1,2-Tetradecanediol (1.28 g)
	Oleic acid (7.5 ml) & Oleylamine (7.5 ml)
	Diphenyl ether (300 ml)
	Platinum(II) acetylacetonate (1.95 g)
	1,2-Dichlorobenzene (45 ml)

**Acid leaching:**

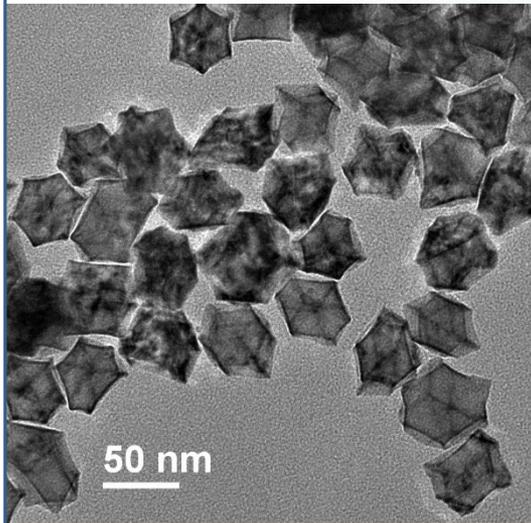
**0.1 g Scale**

- Sonicate and soak PtNi/C in 0.1 M HClO<sub>4</sub>. X**
- Centrifuge.

**5 g Scale**

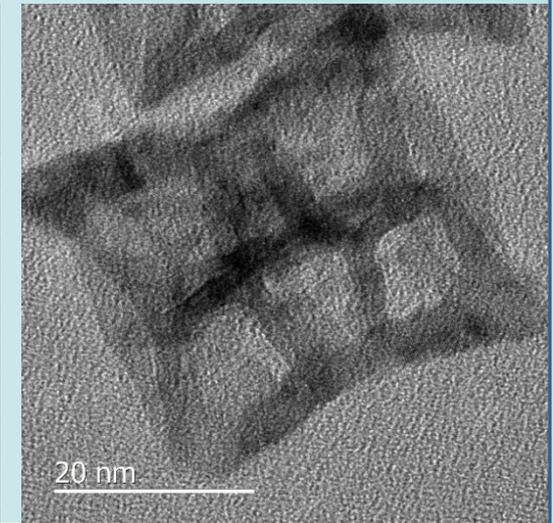
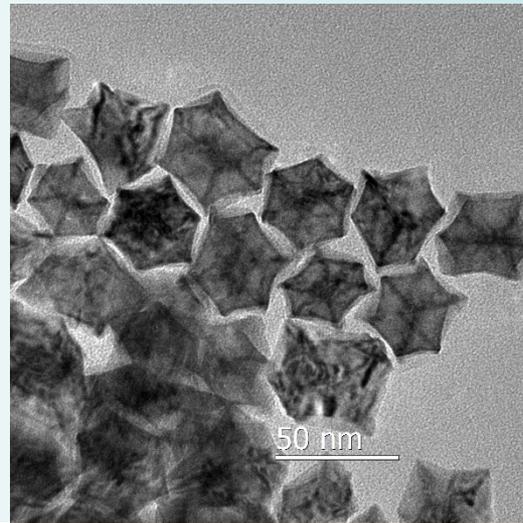
- Sonicate PtNi/C in H<sub>2</sub>O.
- Mix with 0.1 M HClO<sub>4</sub> and soak.
- Filtration.

Nanoframe

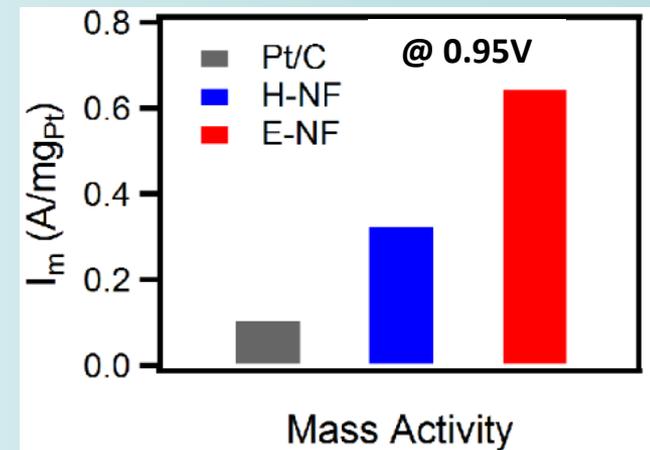
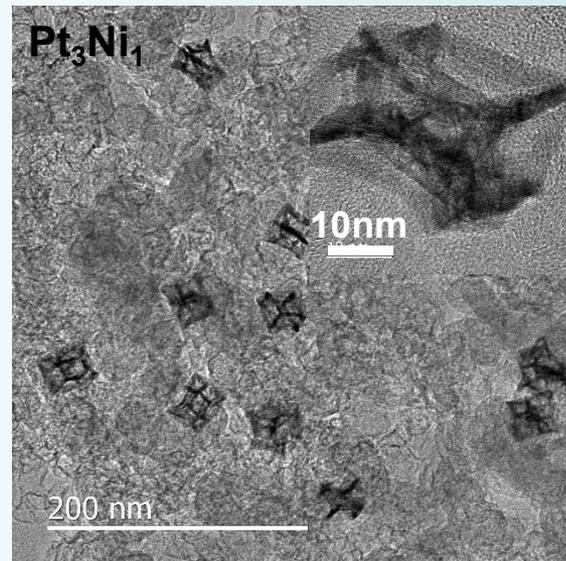
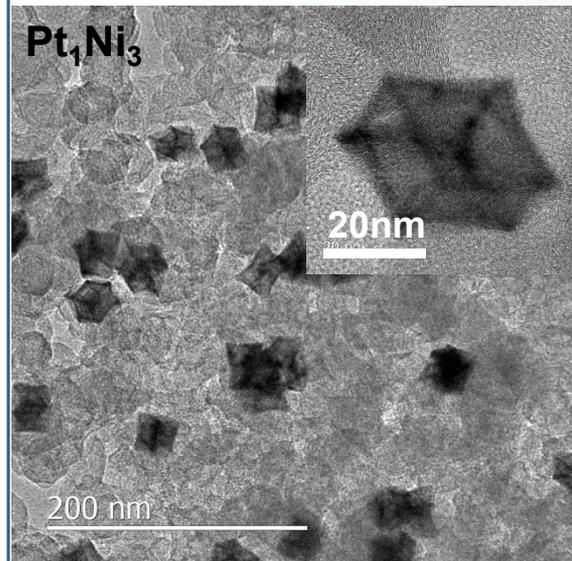


Particle  
larger  
↔  
than  
small  
scale

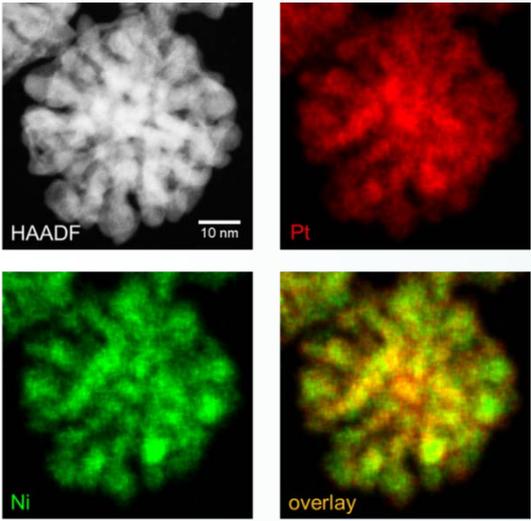
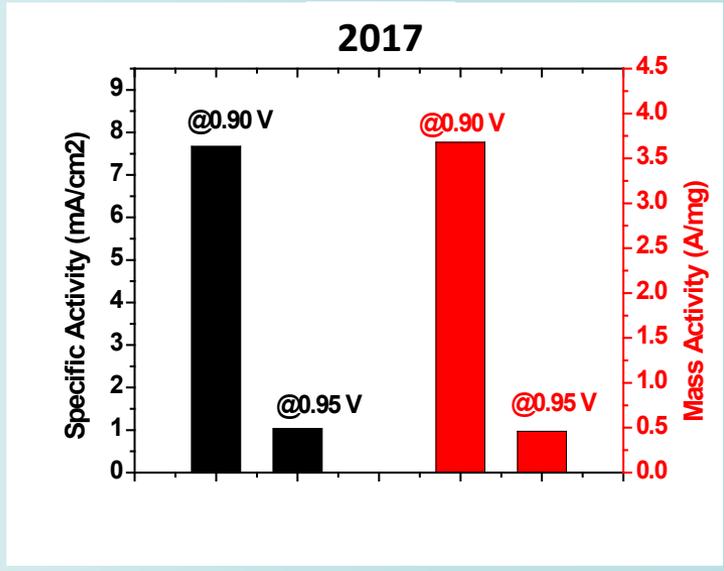
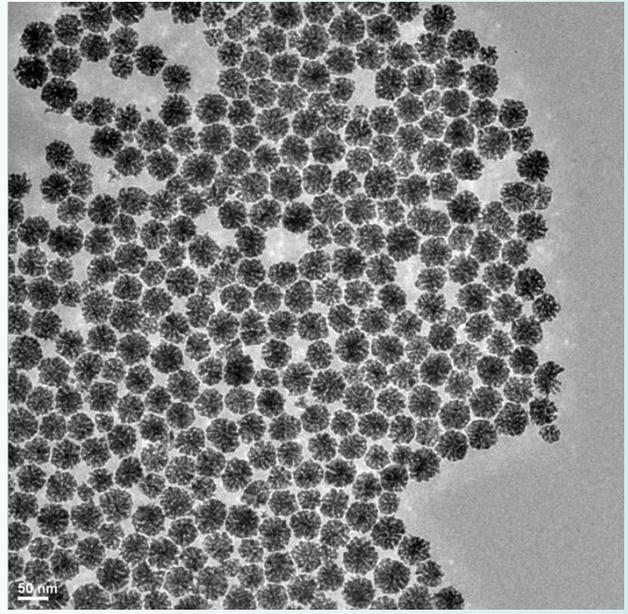
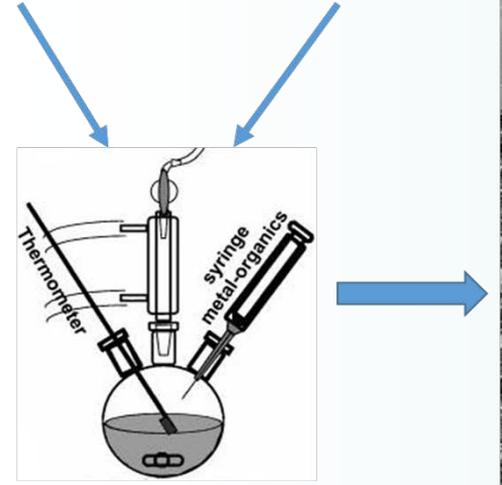
Excavated nanoframe



Excavated nanoframe-Further reducing Ni precursor amount

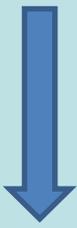


5X Precursor      5X Solvent



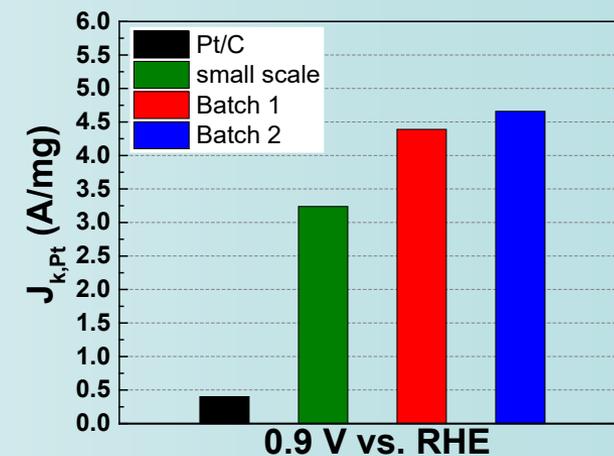
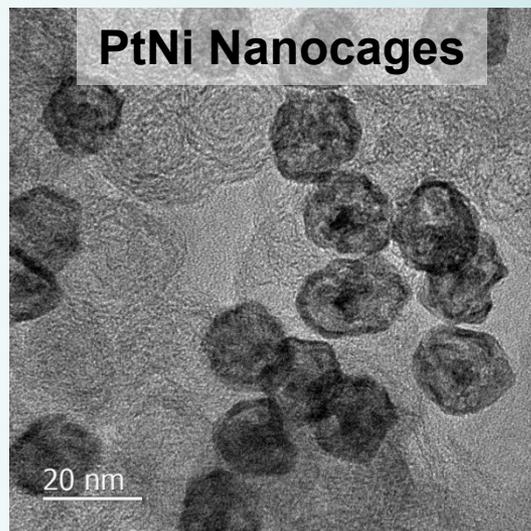
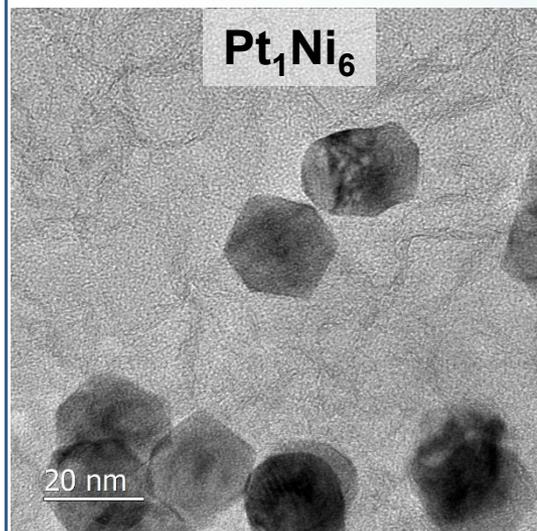
5X scaled up PtNi Nanopinwheels keep the same morphology

5X scaled up PtNi Nanopinwheels maintain high performance

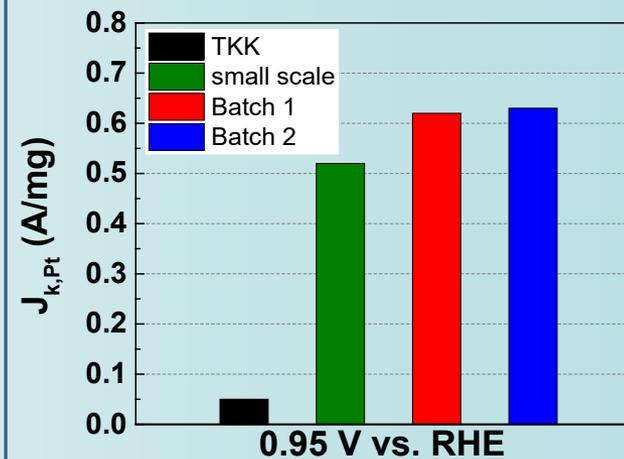
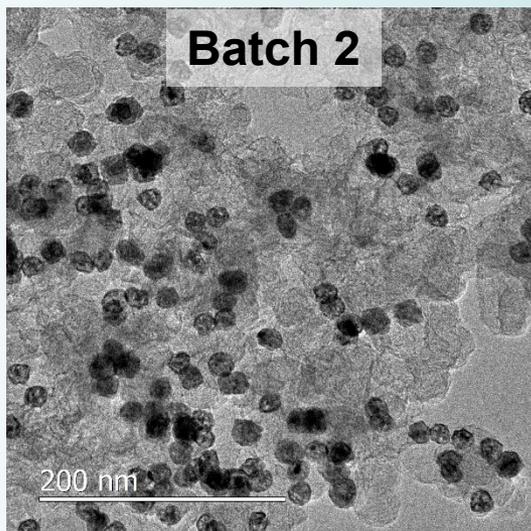
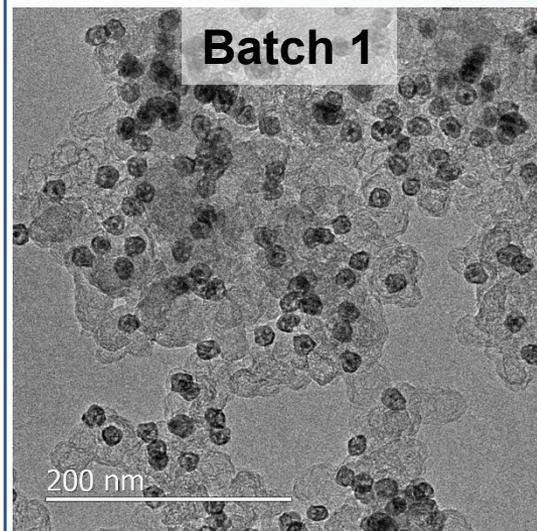


	2018	
	0.90 V	0.95 V
5X scale up	8.2	1.14
Nanopinwheels	<b>8.8</b>	<b>1.3</b>

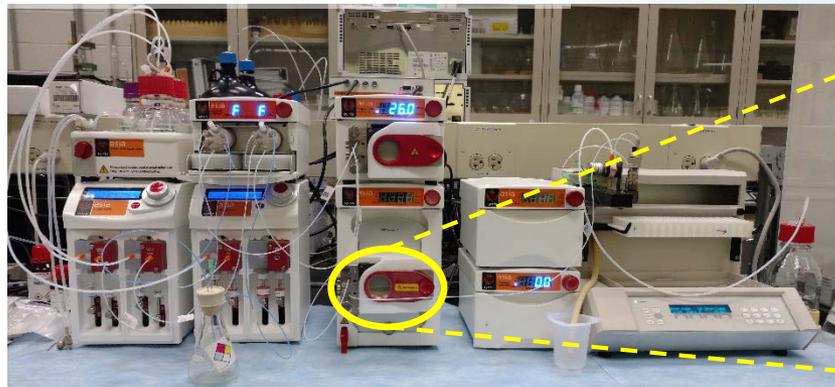
One-pot synthesis-0.1 g / batch



Scale up-0.6 g / batch

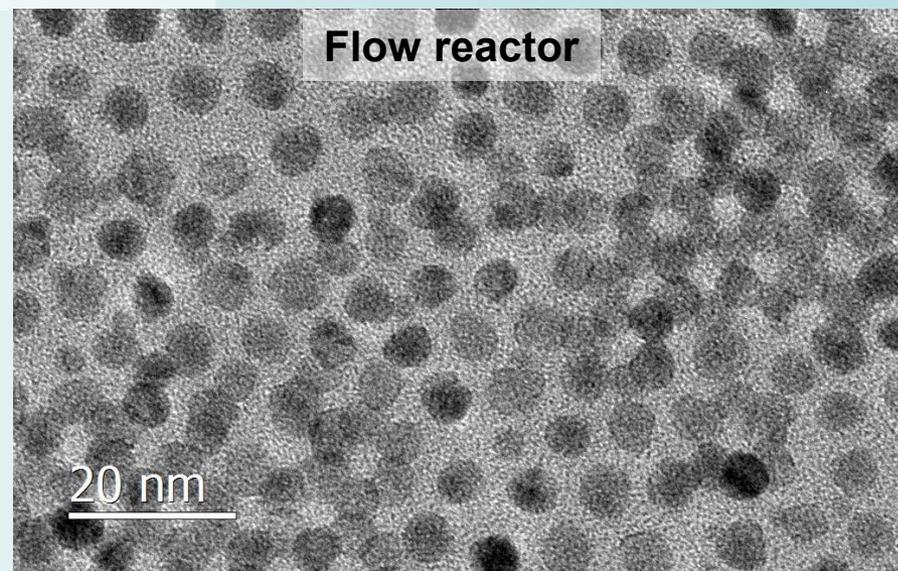
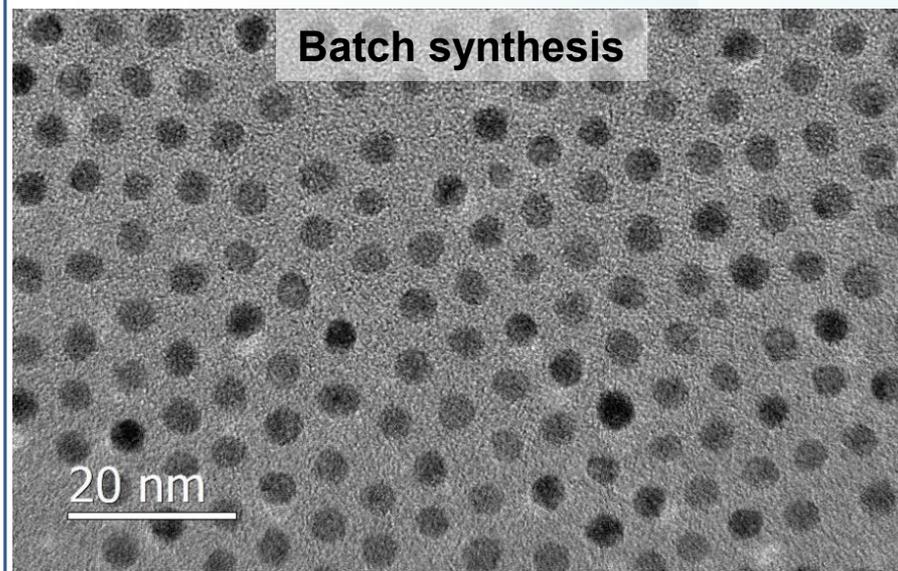


**Flow reactor at MERF, ANL**

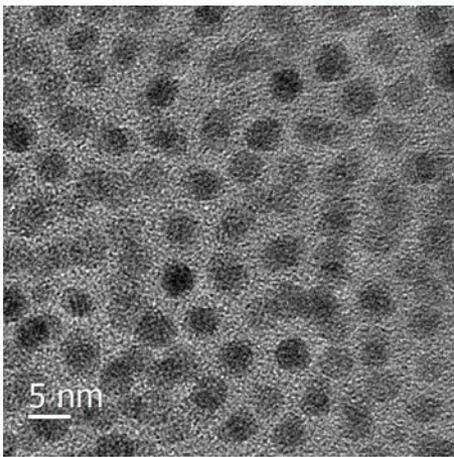


- > Fast mass and heat transfer.
- > Rapid optimization of reaction parameters.
- > Easy scalability.
- > Accurate control of reaction temperature and duration.
- > Low usage of reagents in the optimization process.
- > Capability for online monitoring.

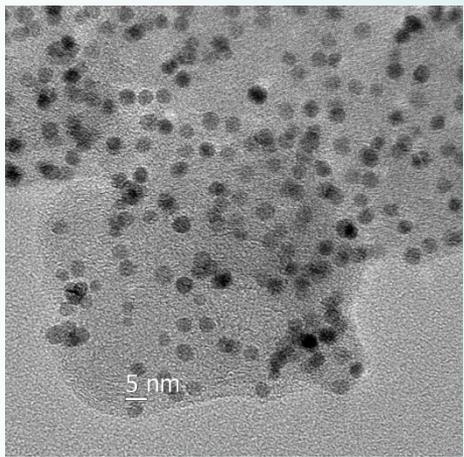
**PtNi Nanoparticles**



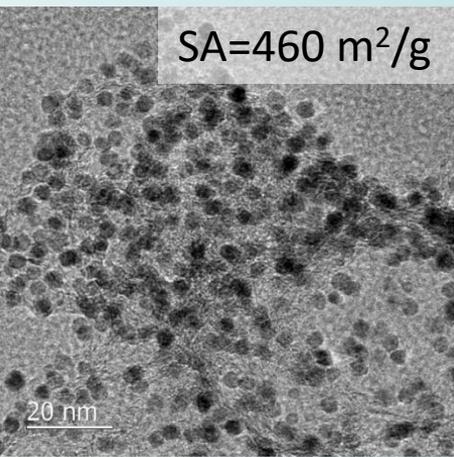
**As synthesized**



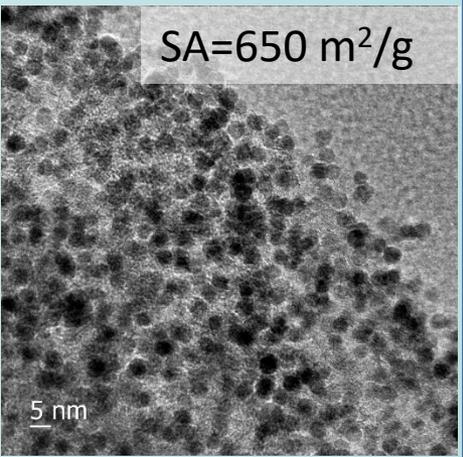
**On Vulcan xc-72**



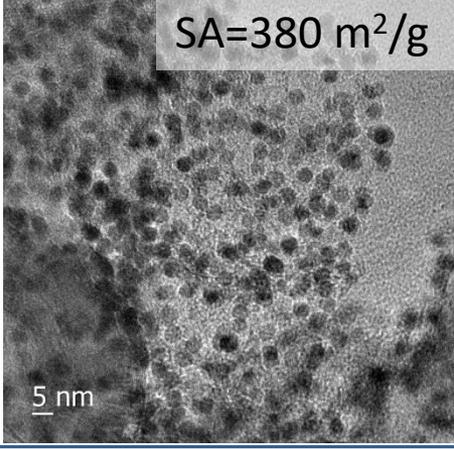
**On C2**



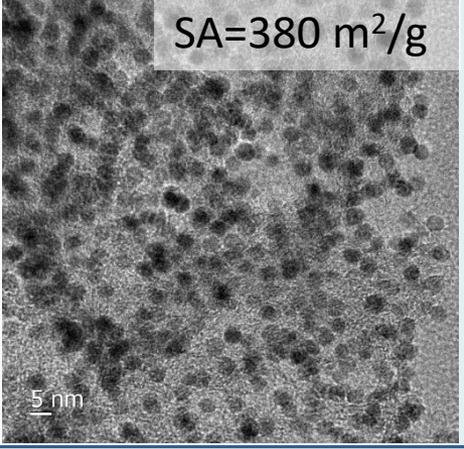
**On C3**



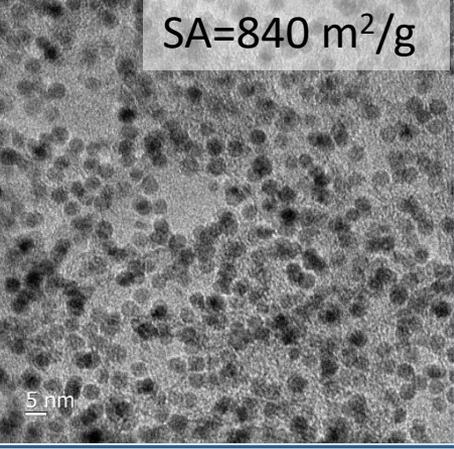
**On C4**



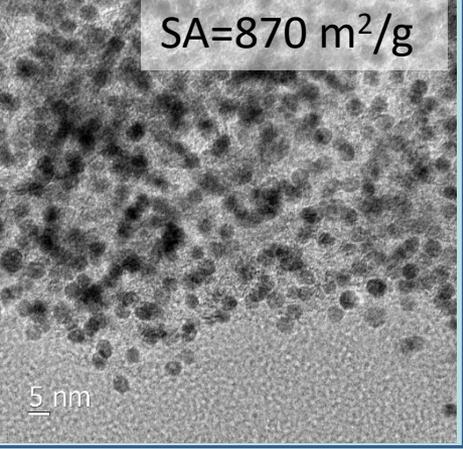
**On C5**



**On C6**

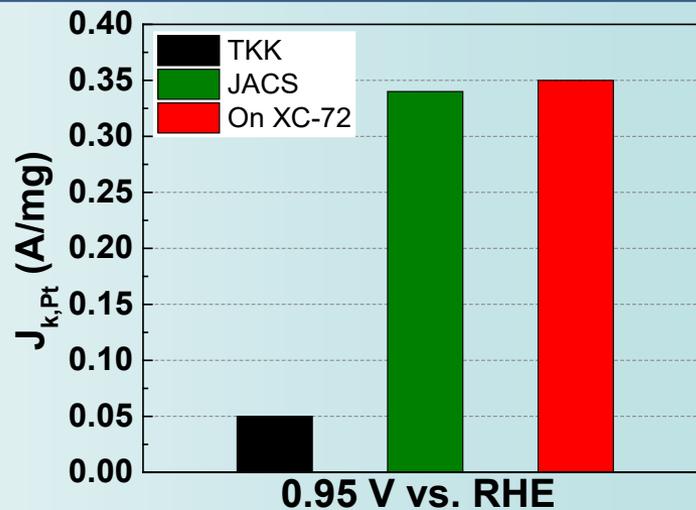
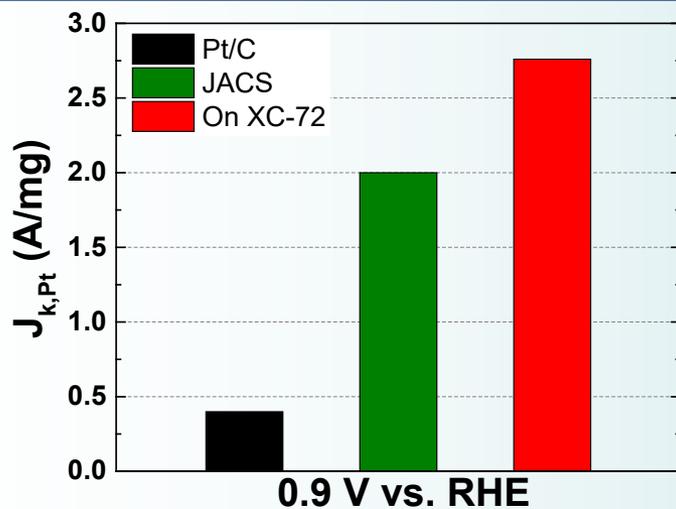
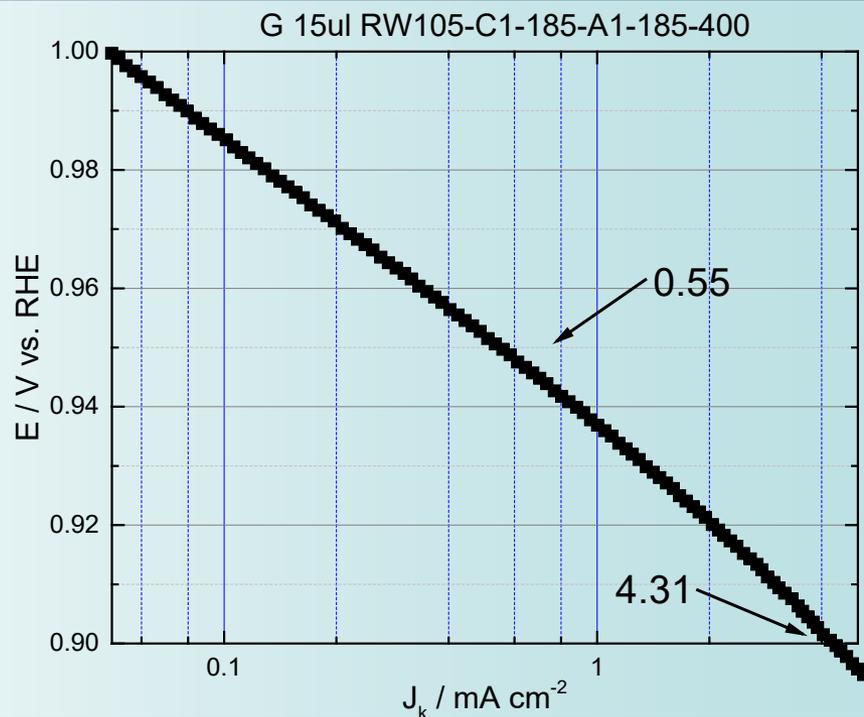
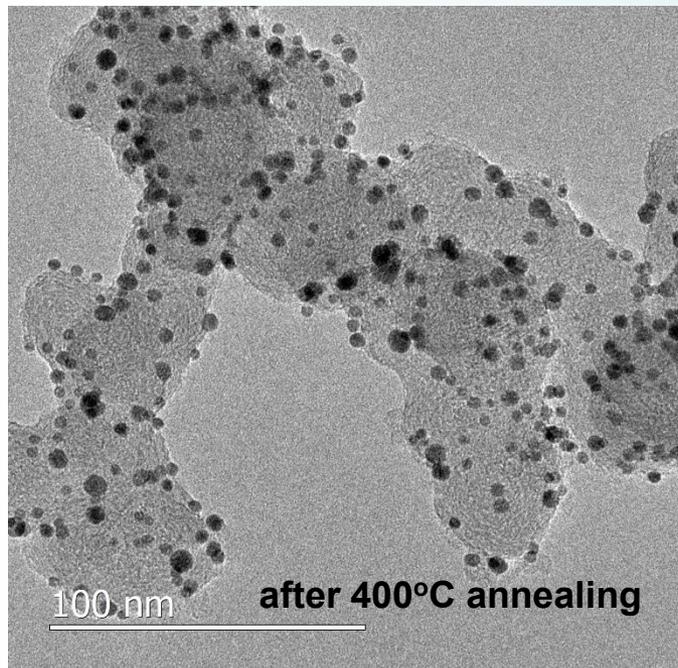


**On C7**



Same loading but different particle densities ↔ Different accessible carbon surface areas

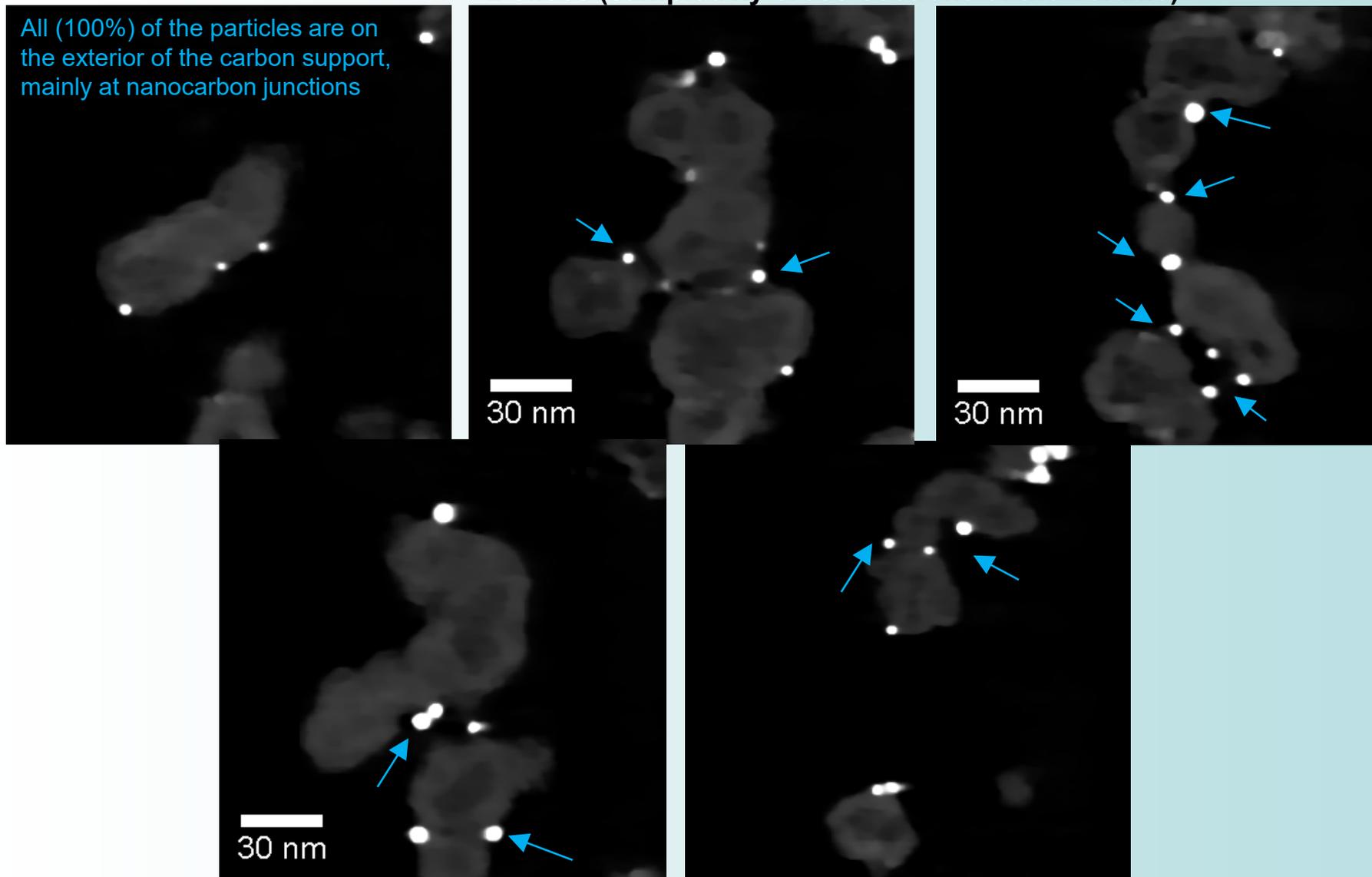
On XC-72



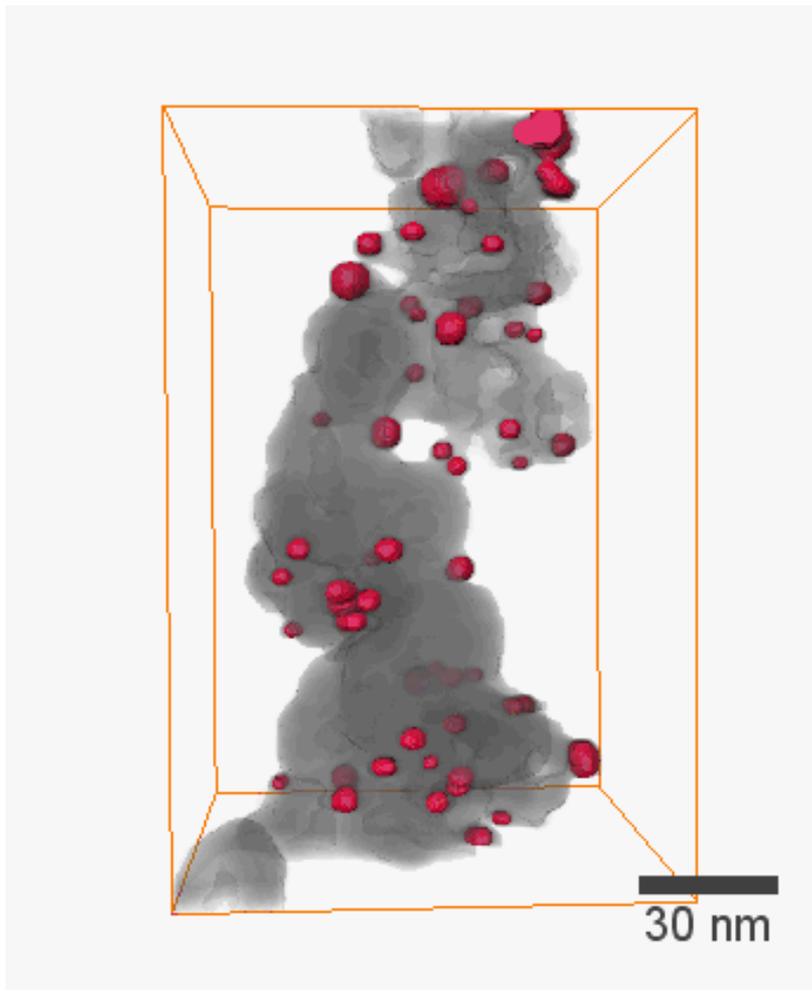
# Task 4-5 Accomplishments and Progress: Particle deposition on carbon support

in collaboration with K.L. More, ORNL

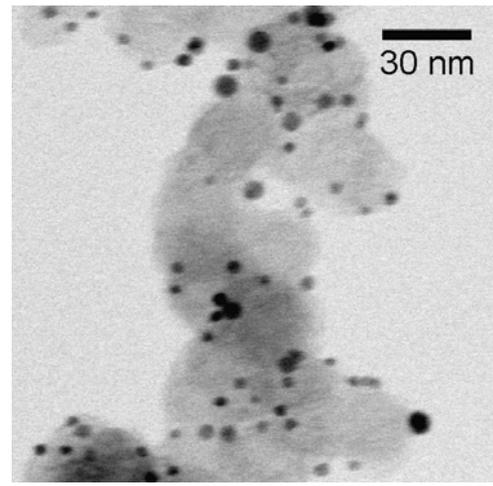
z-slices (sampled xy cross-sections of the volume)



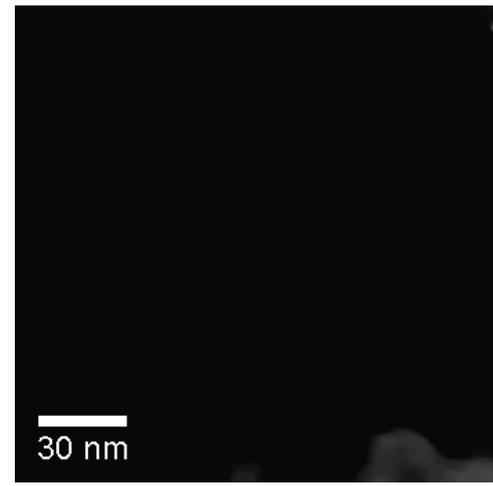
*in collaboration with K.L. More, ORNL*



Tilt series



z-stack (cross-sections)

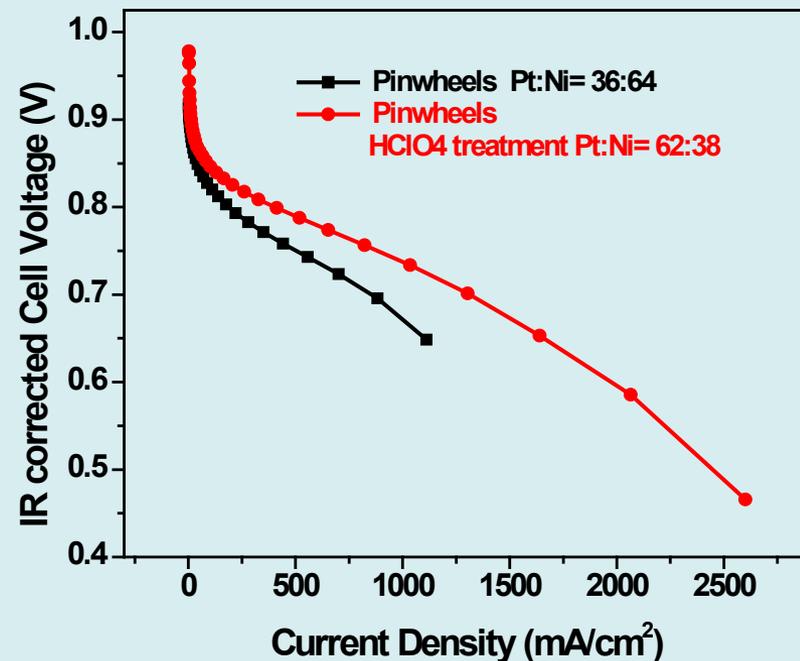
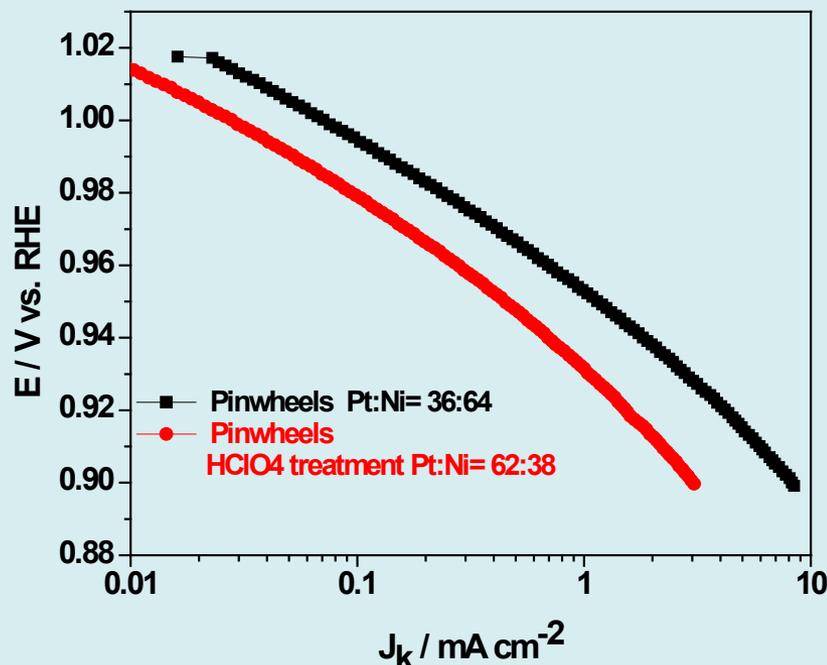
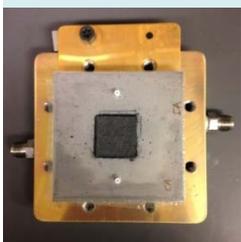


clipping  
animation



# Task 3-5 Accomplishments and Progress: *scaled Nanopinwheels in 5cm<sup>2</sup> MEA*

in collaboration with Debbie Myers, ANL /CSE and Karren More, ORNL



Cathode Loading:  
0.03 mg-Pt/cm<sup>2</sup>  
I/C = 0.8,  
H<sub>2</sub>/O<sub>2</sub> (or Air),  
80°C, 150 kPa(abs)  
100%RH

After acid treatment an increase on the MEA performance  
Activation condition, held certain constant voltage for more 12 hours  
until reach the best performance

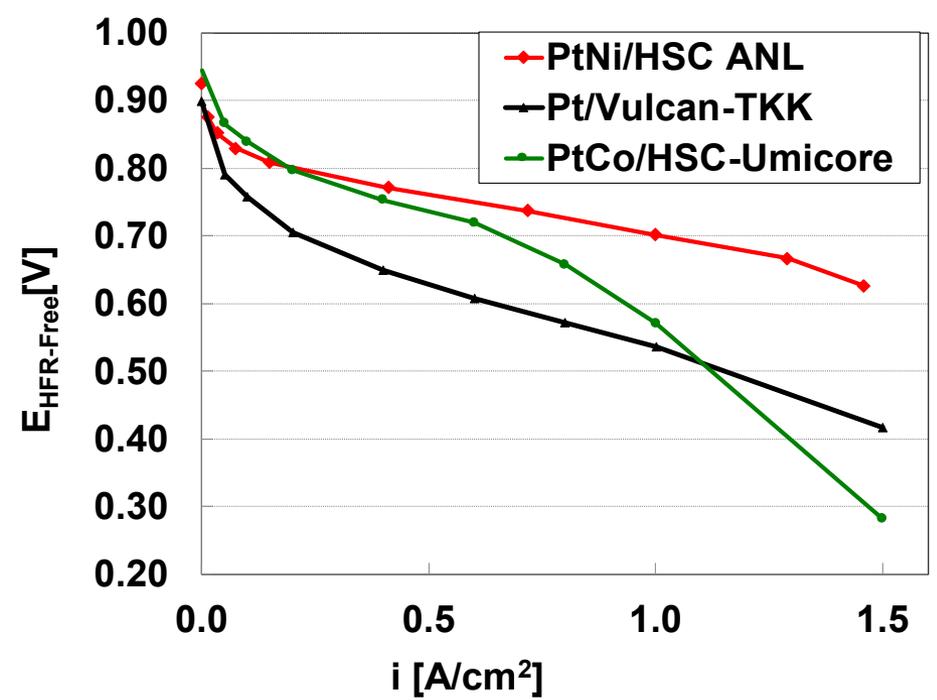
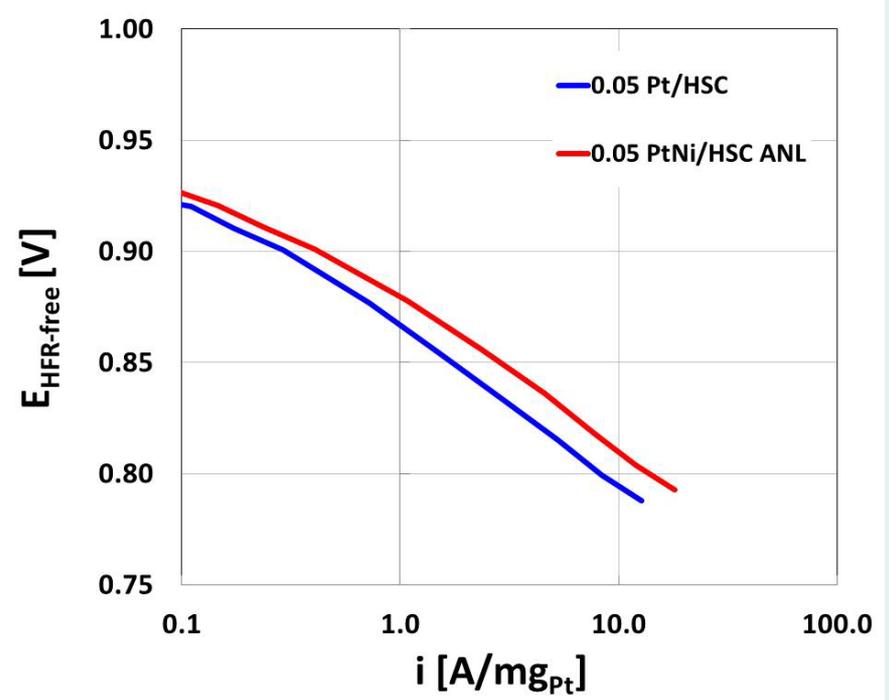
(H<sub>2</sub>-O<sub>2</sub>, 80C, 100%RH, 150kPa<sub>(abs)</sub>) from high-low current

Mass activity at 0.9V: ~0.5 A/mg with 0.03 mg/cm<sup>2</sup> Pt loading

*in collaboration with Kenneth Neyerlin, NREL*

- 150 kPa, 100% RH, 80°C H<sub>2</sub>/O<sub>2</sub>, 50 cm<sup>2</sup>, N211
- Ultrasonic spray coated at NREL 0.9 I:C
- Cathode loading 0.046 mgPt/cm<sup>2</sup>

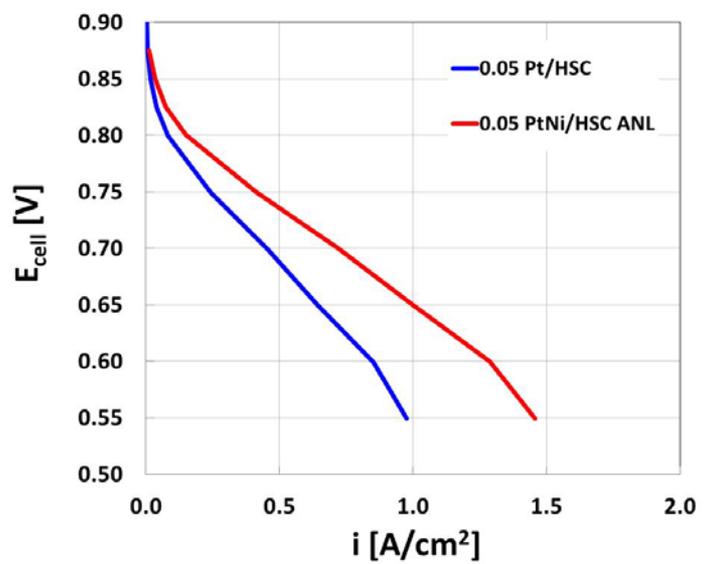
- 150 kPa, 100% RH, 80°C H<sub>2</sub>/Air, 50 cm<sup>2</sup>,



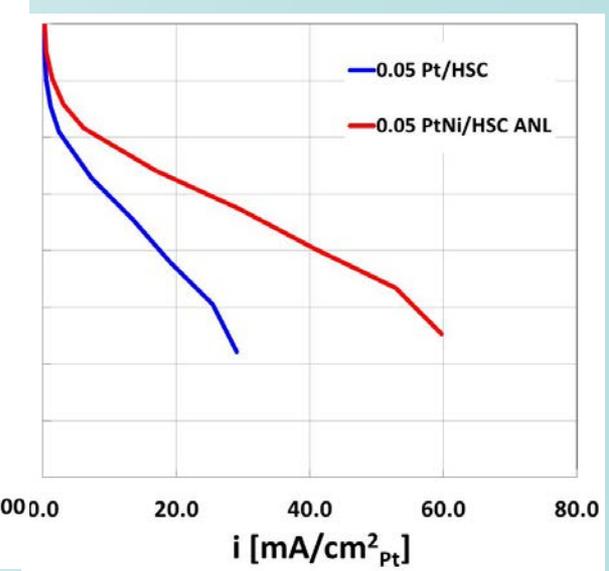
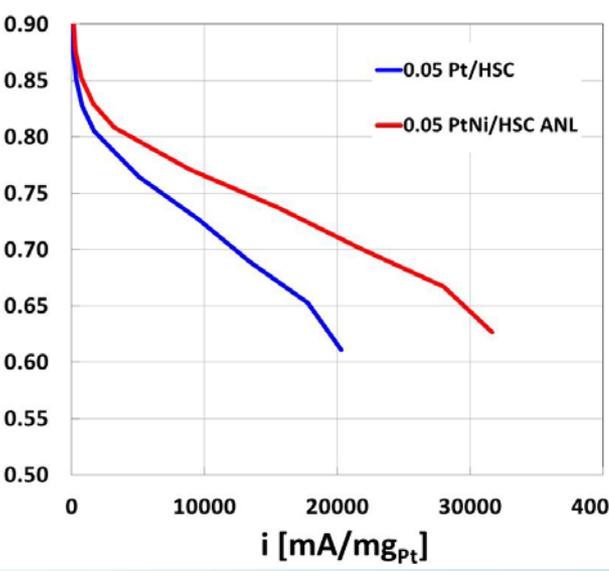
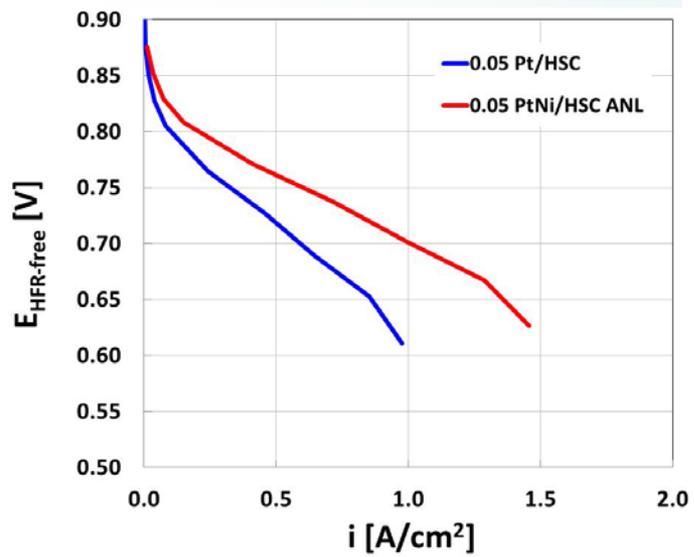
- Developed PtNi/HSC:  $i_m^{0.9V} \sim 500 \text{ mA/mg}_{Pt}$  vs. to  $\sim 300 \text{ mA/mg}_{Pt}$  for 50 wt% Pt/HSC (TKK)
- PtNi/HSC:  $i_s^{0.9V} 920 \mu\text{A/cm}^2_{Pt}$  vs.  $480 \mu\text{A/cm}^2_{Pt}$  for Pt/HSC (TKK)
- PtNi/HSC shows improved performance at high current density / Improved non-Fickian transport

*in collaboration Neyerlin, NREL*

- 150 kPa, 100% RH, 80°C H<sub>2</sub>/Air, 50 cm<sup>2</sup>, N211



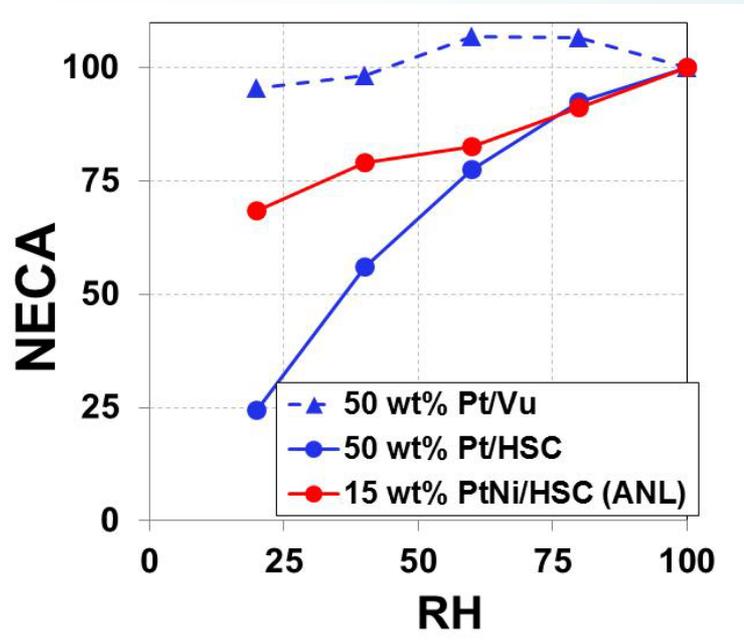
- PtNi/HSC shows improved performance
  - Both at high and low potential
  - For both raw cell voltage and HFR-corrected cell voltage
- Performance improvement is significant at low potential (transport limited regime) when normalized to ECSA
  - Suspect improved non-fickian transport



*in collaboration with Kenneth Neyerlin, NREL*

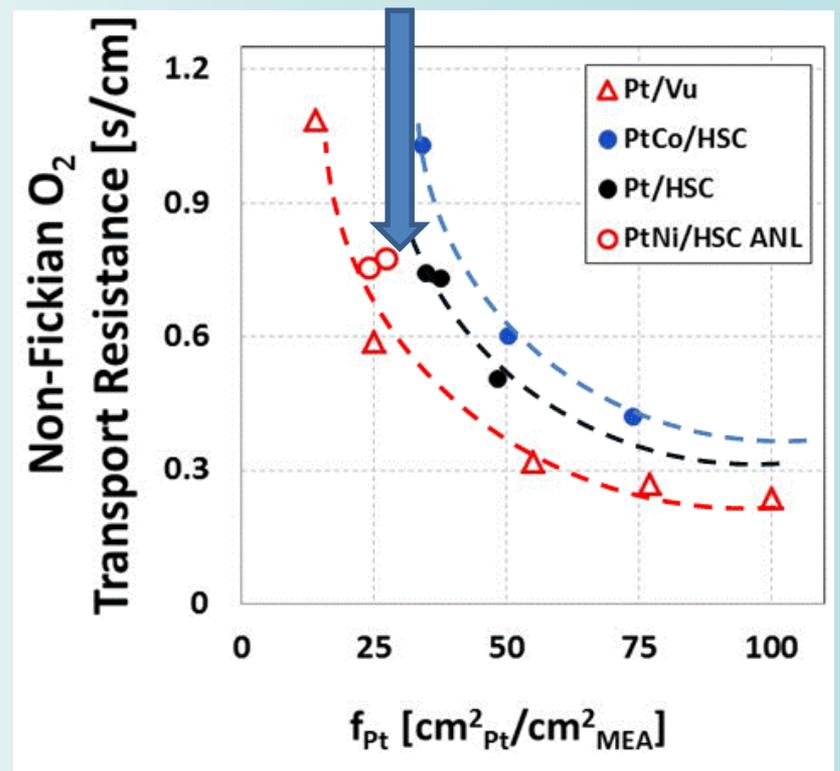
**Improved Non-Fickian Transport Resistance**

- By first synthesizing the nanoparticles then supporting them on HSC, the particles are preferentially located on the surface of the carbon



CO stripping as a function of RH reveals that the majority of Pt sites are located on the carbon surface

- Reduced non-Fickian transport resistance

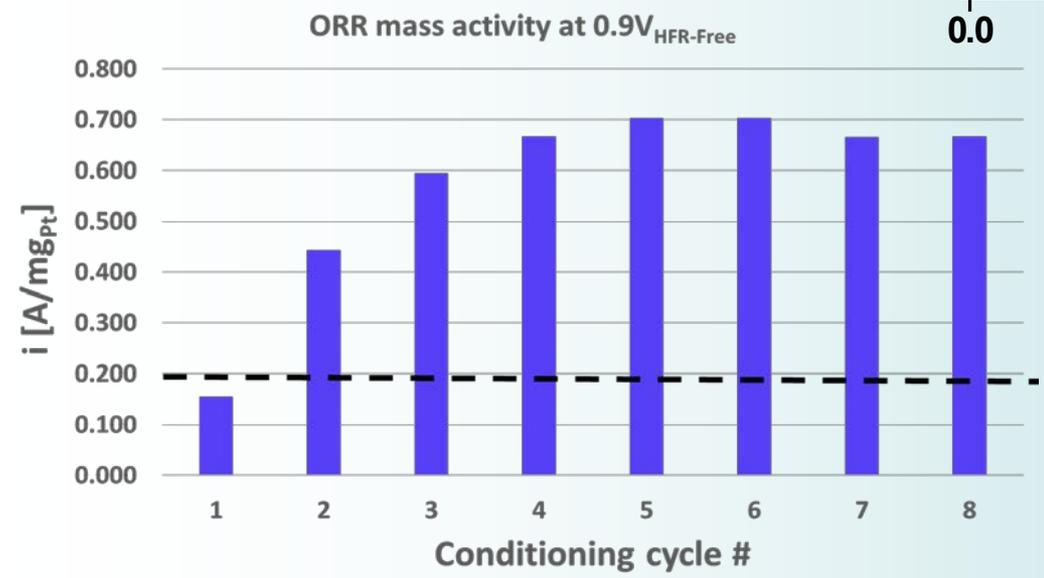
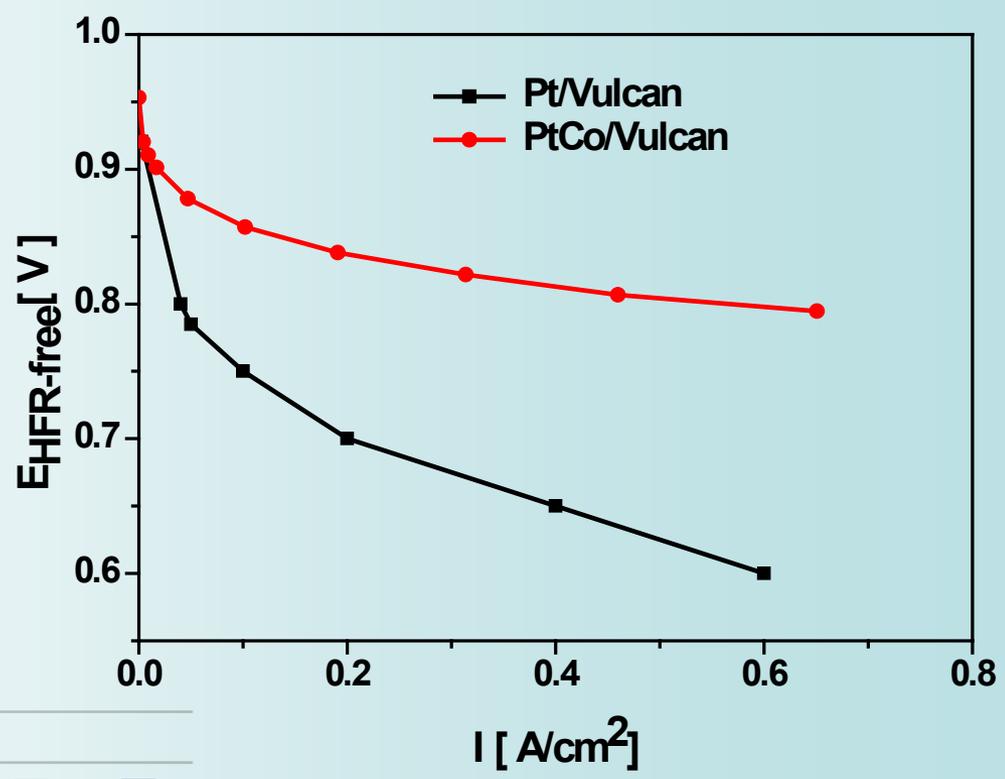


Limiting current measurements indicate that PtNi/HSC has significantly reduced non-Fickian transport resistance relative to other highly active electrocatalysts (PtCo/HSC)

*in collaboration with Kenneth Neyerlin, NREL*

150 kPa, 100% RH, 80°C H<sub>2</sub>/O<sub>2</sub>, 50 cm<sup>2</sup>  
 Ultrasonic spray coated at NREL 0.5 l:C  
 Cathode loading 0.035 mgPt/cm<sup>2</sup>

PtCo/Vulcan:  $i_m^{0.9V} \sim 700 \text{ mA/mg}_{Pt}$   
 Pt/Vulcan:  $i_m^{0.9V} \sim 200 \text{ mA/mg}_{Pt}$

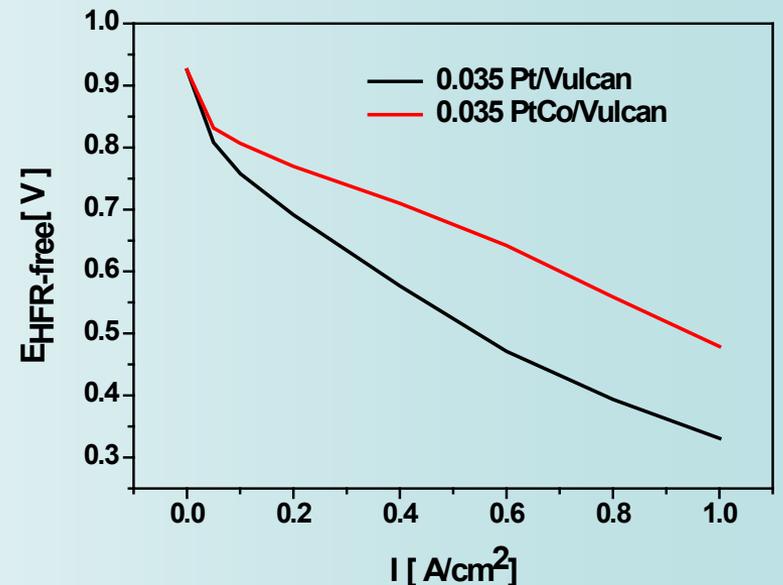
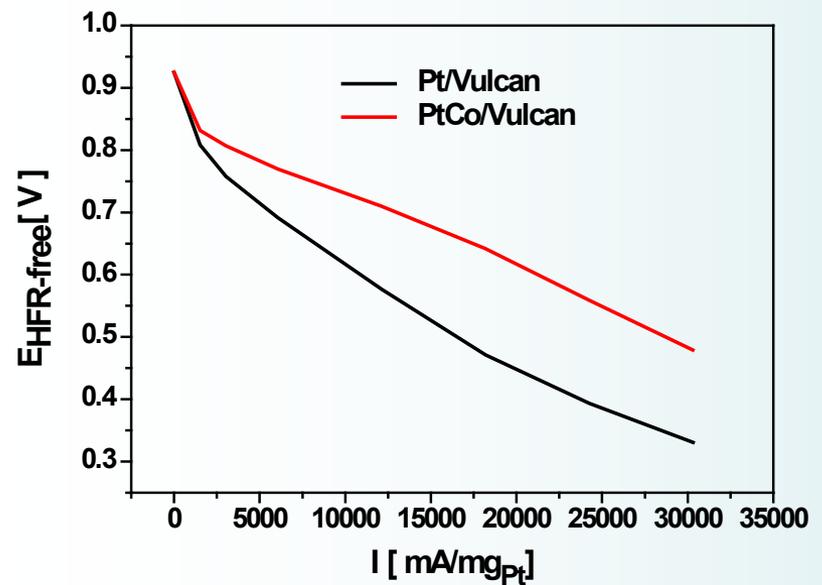
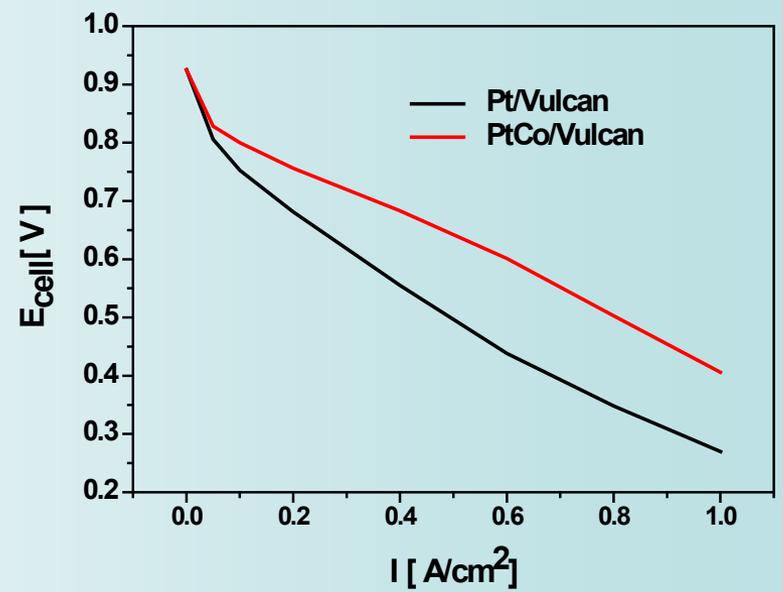


Pt/Vulcan only shows about 0.2 A/mg mass activity at 0.9 V

*in collaboration with Kenneth Neyerlin, NREL*

**150 kPa, 100% RH, 80°C H<sub>2</sub>/Air, 50 cm<sup>2</sup>  
 Ultrasonic spray coated at NREL 0.5 I:C  
 Cathode loading 0.035 mgPt/cm<sup>2</sup>**

- PtCo/Vulcan shows improved performance
- Both at high and low potential region
- For both raw cell voltage and HFR-corrected cell voltage
- Performance improvement is significant at low potential (transport limited regime)



# Responses to some reviewers comments

## Question 1: Approach to performing the work

- The approach is both aggressive (multiple tasks in parallel) and well designed, since it strives to address many potential risks (in a highly complex system) at early stages.
- The project team uses world-leading resources and capabilities to design catalysts from a fundamental point of view.

## Question 2: Accomplishments and progress toward DOE goals

- This project had impressive results in the past year in all key areas. (1) Fundamentals: The previous development of the RDE-inductively coupled plasma mass spectrometry (ICP-MS) was a great contribution, and it is great to see the group using this tool effectively on these new catalysts, with interesting results. (2) Synthesis: The core team has continued to make excellent progress in developing new nanostructures. (3) Scale-up: The progress here is especially impressive. It is unclear whether this new one-pot process can be used to make nanoframes as well as nanoparticles. (4) MEA performance: It is also great to see MEA results, which are impressive when one considers how challenging it is to make a good MEA with a new catalyst.
- A year later, they have even more new catalysts, more evidence of their potential, and more poor fuel cell performance. More effort should have been put into demonstrating that RDE results can translate into MEA results, and if not, why not.

**Much more has been accomplished over the last year in testing of our catalysts in 50cm<sup>2</sup> MEAs. All of them exceeded DOE technical target and labeling our performance with “poor” has more to do with the reviewer’s ability to perform an unbiased review.**

## Question 3: Collaboration and coordination with other institutions

- The collaboration with the Fuel Cell Consortium for Performance and Durability to obtain the MEA results is especially commendable. The catalyst community position should simply be that RDE is a good screening tool and that they would welcome improved methods to translate this into MEA performance projections by those who can contribute to this challenging task.

**The project has constant interaction among the participants including the OEMs, which does not necessarily mean that all results can be disclosed. During the TechTeam meetings much more has been shared.**

## Project weakness

- Activity of the catalyst in MEAs is approximately 10 times below RDE activity. Apparently, there is limited work on MEA-level testing and characterization. MEA testing was a project weakness.

**We are making constant progress in MEA testing and understanding similarities and differences between RDE and MEA.**

## Recommendations for additions/deletions to project scope

- More MEA work should be planned. - The project should look for new collaboration at the international level

**Additional MEA testing are confirming improvement in performance and more international collaborations are being launched.**

# Collaborations

**Argonne NATIONAL LABORATORY** **Lead: design, synthesis, evaluation**

**BERKELEY LAB** **Sub: synthesis, scale-up support**

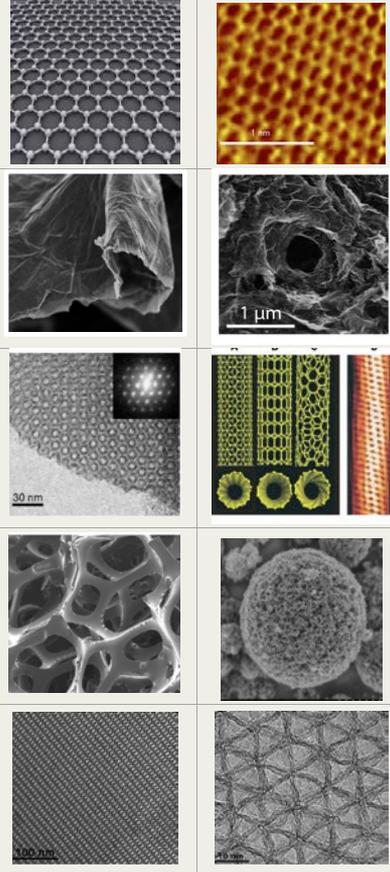
**OAK RIDGE National Laboratory** **Sub: structural characterization**

**Los Alamos NATIONAL LABORATORY** **Sub: catalyst supports**

## Low-PGM Alloys



## Advanced Catalyst Supports



## Low-PGM Alloy Catalysts

**Argonne NATIONAL LABORATORY** **Lead: process R&D and scale-up**

**BERKELEY LAB** **Sub: process support**

**Catalysts Scale Up**

**Argonne NATIONAL LABORATORY** **Lead: 5 and 25cm<sup>2</sup> MEA**

**Los Alamos NATIONAL LABORATORY** **Sub: 25 and 50cm<sup>2</sup> MEA**

**ONREL NATIONAL RENEWABLE ENERGY LABORATORY**

**MEA**

**OEMs**  
**T2M**

# Challenges and Barriers

- **Differences** between RDE and MEA, surface chemistry, ionomer catalyst interactions
- **Temperature** effect on performance activity/durability
- **High current density** region needs improvements for MEA
- **Support** – catalyst interactions
- **Scale-up** process (one pot and flow reactor) for the most advanced structures

1) **Durability** of fuel cell stack (<40% activity loss)

2) **Cost** (total loading of PGM  $0.125 \text{ mg}_{\text{PGM}} / \text{cm}^2$ )

3) **Performance** (mass activity @ 0.9V  $0.44 \text{ A/mg}_{\text{Pt}}$ )

- **Alternative** approaches towards highly active and stable catalysts with low PGM content
- **Tailoring** of the structure/composition that can optimize durability/performance in Pt-alloys
- **Synthesis** of tailored low-PGM practical catalysts with alternative supports
- **Structural** characterization (in-situ XAS, HRTEM, XRD)
- **Resolving** the surface chemistry in MEA
- **Electrochemical** evaluation of performance (RDE, MEA)
- **In-situ** durability studies for novel catalyst-support structures (RDE-ICP/MS)
- **Scale-up** of chemical processes to produce gram quantities of the most promising catalysts

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

**T2M**

US007871738B2

(12) **United States Patent**  
Stamenkovic et al. (10) Patent No.: **US 7,871,738 B2**  
(45) Date of Patent: **Jan. 18, 2011**

(54) **NANOSSEGREGATED SURFACES AS CATALYSTS FOR FUEL CELLS**

(75) Inventors: **Vojislav Stamenkovic, Niperville, IL (US); Nenad M. Markovic, Hinsdale, IL (US)**

Palau et al., "Oxygen Reduction on Carbon-Supported Pt-Ni and Pt-Co Alloy Catalysts", *J. Phys. Chem. B*, 2002, pp. 4181-4191, vol. 106, American Chemical Society, USA.

Palau et al., "Oxygen Reduction on High Surface Area Pt-IrOx Alloy Catalysts: a Comparison to Well-Defined Smooth Bulk Alloy Electrodes", *Electrochimica Acta*, 2002, pp. 3787-3798, vol. 47, (US)

US 20110077147A1

(12) **United States Patent Application Publication**  
Stamenkovic et al. (10) Pub. No.: **US 2011/0077147 A1**  
(43) Pub. Date: **Mar. 31, 2011**

(54) **NANOSSEGREGATED SURFACES AS CATALYSTS FOR FUEL CELLS**

(75) Inventors: **Vojislav Stamenkovic, Niperville, IL (US); Nenad M. Markovic, Hinsdale, IL (US)**

Publication Classification

(51) Int. Cl. **H01M 4/88** (2006.01)  
**B01J 23/42** (2006.01)

(52) U.S. Cl. **502/101; 502/336; 502/326; 502/313**

US008178463B2

(12) **United States Patent**  
Stamenkovic et al. (10) Patent No.: **US 8,178,463 B2**  
(45) Date of Patent: **May 15, 2012**

(54) **HIGHLY DURABLE NANOSCALE ELECTROCATALYST BASED ON CORE SHELL PARTICLES**

(75) Inventors: **Vojislav Stamenkovic, Niperville, IL (US); Nenad M. Markovic, Hinsdale, IL (US); Chao Wang, Chicago, IL (US); Hideo Daimon, Osaka (JP); Shouheng Sun, Providence, RI (US)**

(52) U.S. Cl. **502/101; 502/184; 502/185; 420/466; 420/507; 420/510; 420/512; 420/546; 420/570; 428/615; 428/603; 420/524; 420/527; 977/773; 977/774**

US008685878B2

(12) **United States Patent**  
Stamenkovic et al. (10) Patent No.: **US 8,685,878 B2**  
(45) Date of Patent: **Apr. 1, 2014**

(54) **HIGHLY DURABLE NANOSCALE ELECTROCATALYST BASED ON CORE SHELL PARTICLES**

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**C22C 5/04** (2006.01)

(58) Field of Classification Search  
USPC **502/101; 502/184; 502/185; 428/403; 428/548; 428/570; 428/615; 420/524; 420/527; 420/466; 420/507; 420/510; 420/512**

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(12) **United States Patent**  
Stamenkovic et al. (10) Patent No.: **US 9,246,177 B2**  
(45) Date of Patent: **Jan. 26, 2016**

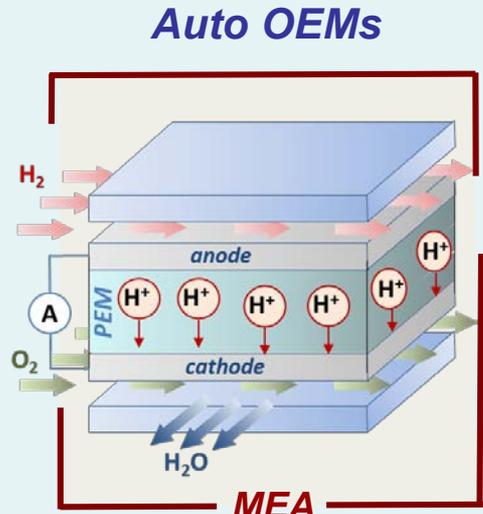
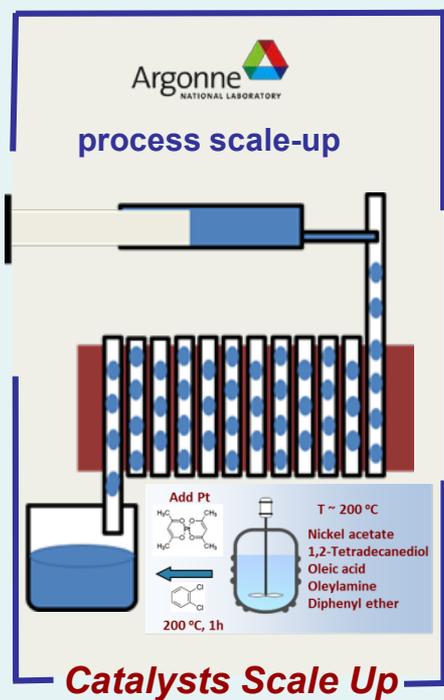
(54) **BIMETALLIC ALLOY ELECTROCATALYSTS WITH MULTILAYERED PLATINUM-SKIN SURFACES**

(75) Inventors: **Vojislav R. Stamenkovic, Niperville, IL (US); Chao Wang, Aurora, IL (US); Nenad M. Markovic, Hinsdale, IL (US)**

(73) Assignee: **Chicago Argonne, LLC, Chicago, IL (US)**

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FY18

2 NDA signed

- **Constant build up of IP portfolio**  
**6 issued patents, 5 pending**

# SUMMARY

## Approach

- From fundamentals to real-world materials
- Focus on addressing DOE Technical Targets
- Link between the performance measured in RDE vs. MEA
- Rational design and synthesis of advanced materials with low content of precious metals

## Accomplishments

- Dissolution of Pt for different particle size distributions of Pt/C: the advantage of monodisperse
- Resolved the mechanism of diminished Pt dissolution for Au subsurface
- Designed of highly durable NPs: Applied the knowledge from well-defined surfaces to nanoparticles
- “No-Dissolution” Proof of Concept in Highly Durable NPs: Synthesis and Characterization of Pt<sub>3</sub>Au/C NPs
- Well-Defined Pt-Alloy intermetallic systems are more active and durable vs. solid-solution Pt-Alloys
- Scaled four nanoarchitectures at the gram level quantities
- Applied different carbon supports
- Effective placement of particles exclusively on the high surface area carbon surface – no buried particles
- PtNi with multilayered Pt-Skin and Nanopinwheels exceeded DOE 2020 Technical Target for mass activity in MEA
- Two patent application in FY18, 2 articles submitted and 6 presentations at conferences

## Collaborations

- Collaborative effort among the teams from four national laboratories is executed simultaneously in five tasks
- Ongoing exchange with Auto-OEMs and stake holders
- Numerous contacts and collaborative exchanges with academia and other national laboratories

***Full time postdocs:***

Dr. Dongguo Li (RDE, synthesis, thin films)  
Dr. Haifeng Lv (RDE, synthesis, MEA)  
Dr. Nigel Becknell (Synthesis, RDE)  
Dr. Rongyue Wang (scale up synthesis, RDE, MEA)

***Partial time Staff:***

Dr. Pietro Papa Lopes (RDE-ICP-MS), Krzysztof Pupek

## ***Publications and Presentations***

***3 Publications  
3 Presentations  
2 patent applications***