



Tailored High Performance Low-PGM Alloy Cathode Catalysts

PIs: Vojislav R. Stamenkovic
Nenad M. Markovic

Materials Science Division

Argonne National Laboratory

Project ID#
FC140

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Overview

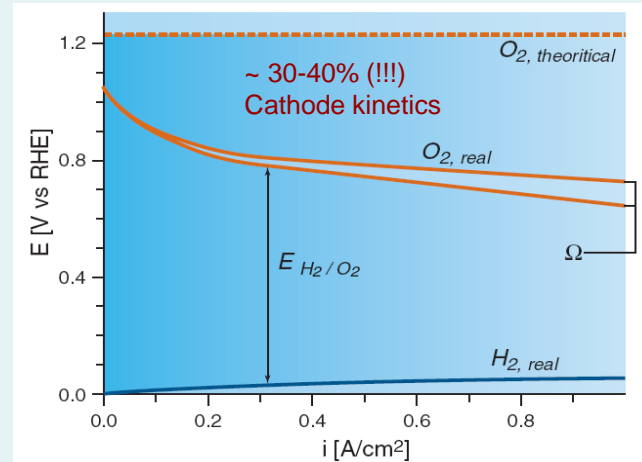
Timeline

- Project start: 10/2015
- Project end: 10/2019

Budget

- Total Project funding \$ 4.0M
- Funding for FY19: \$ 700K

Barriers to be addressed



- 1) **Durability** of fuel cell stack (<40% activity loss)
- 2) **Cost** (total loading of PGM 0.125 mg_{PGM} / cm²)
- 3) **Performance** (mass activity @ 0.9V 0.44 A/mg_{Pt})

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

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*

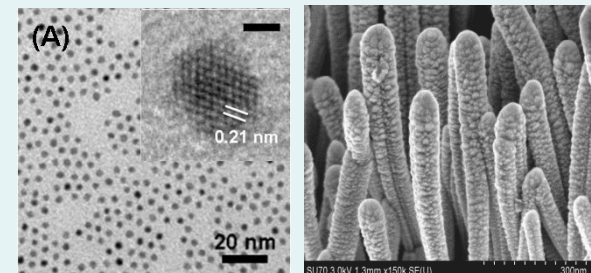
Table 3.4.13 Technical Targets: Electrocatalysts for Transportation Applications^h

Characteristic	Units	2011 Status	2020 Targets
Platinum group metal total content (both electrodes) ^a	g / kW (rated)	0.19 ^b	0.125
Platinum group metal (pgm) total loading ^a	mg PGM / cm ² electrode area	0.15 ^b	0.125
Loss in initial catalytic activity ^c	% mass activity loss	48 ^b	<40
Electro catalyst support stability ^d	% mass activity loss	<10 ^b	<10
Mass activity ^e	A / mg Pt @ 900 mV _{iR-free}	0.24 ^b	0.44
Non-Pt catalyst activity per volume of supported catalyst ^{e, f}	A / cm ³ @ 800 mV _{iR-free}	60 (measured at 0.8 V) ^g 165 (extrapolated from >0.85 V) ^g	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_{PGM}/cm²
- Loss in initial mass activity
2020 DOE target <40%
- Mass activity @ 0.9V_{iR-free}
2020 DOE target 0.44 A/mg_{Pt}



Approach

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

Project Lead
Low-PGM

Inter Lab
Collaborators

NREL / Task 1
50cm² MEA testing

ORNL / Task 1, 2, 3
Electron Microscopy

ANL

PEMFC Cathode Catalysts Development

well-defined systems, fundamental principles, chemical and PVD synthesis, structural and RDE, GDE & MEA characterizations

Task 1°

electrochemical characterization of catalysts:

- EC**
- optimization: ionomer/carbon/propanol/catalyst ink
 - temperature effect; Ionic Liquid evaluation
 - activity/AST in RDE, GDE and 5-50cm²/MEA

Task 2°

durability evaluations by in-situ EC - ICP/MS:

- DM**
- Crafted electrochemical AST - E/V protocols
 - atomic scale precision to follow dissolution
 - nano-, meso- and thinfilm catalysts
 - size, shape, composition tuning
 - structure: intermetallic, core/interlayer/shell

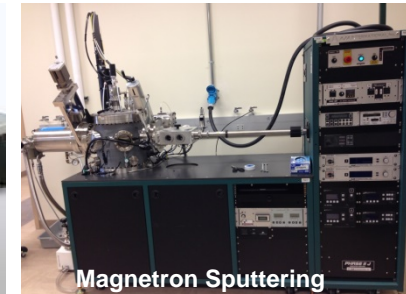
Task 3°

synthesis of advanced catalyst-support systems:

- SN**
- nano-, meso- and thinfilm- PtMN catalysts
 - shape/size/composition control
 - structure control: intermetallics; core/interlayer/skin
 - carbon and non-carbon based materials
 - gram scale synthesis



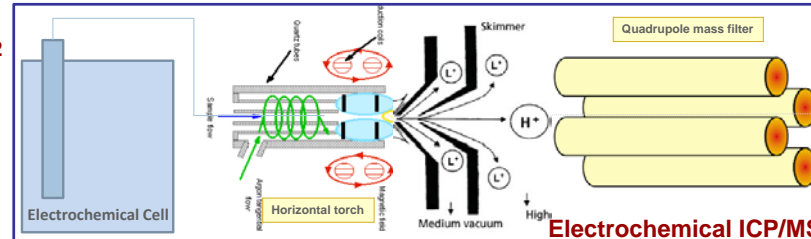
LEIS, AR-XPS, AES, UPS, LEED, STM



Magnetron Sputtering

T
A
S
K

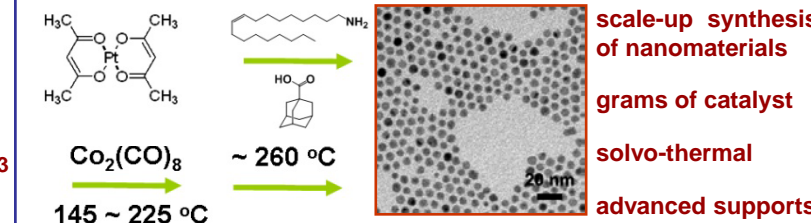
1&2



Electrochemical ICP/MS

T
A
S
K

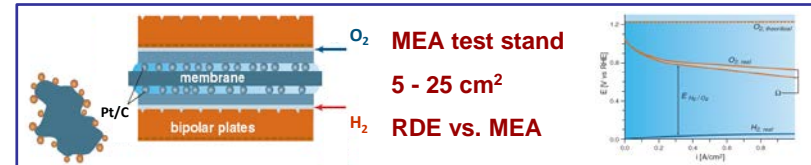
2&3



scale-up synthesis of nanomaterials
grams of catalyst
solvo-thermal
advanced supports

T
A
S
K

1&3



MEA test stand

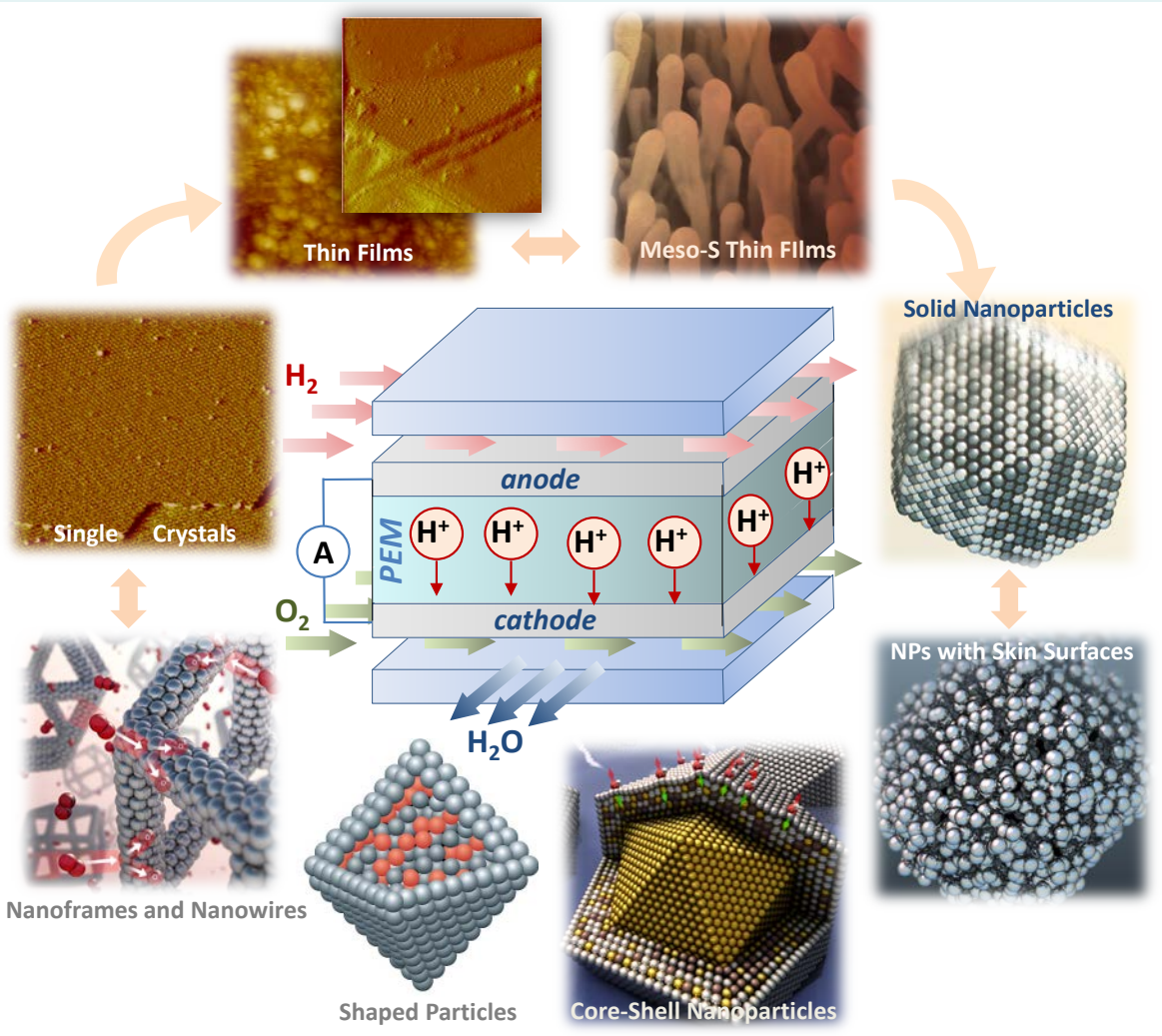
5 - 25 cm²

RDE vs. MEA

- 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



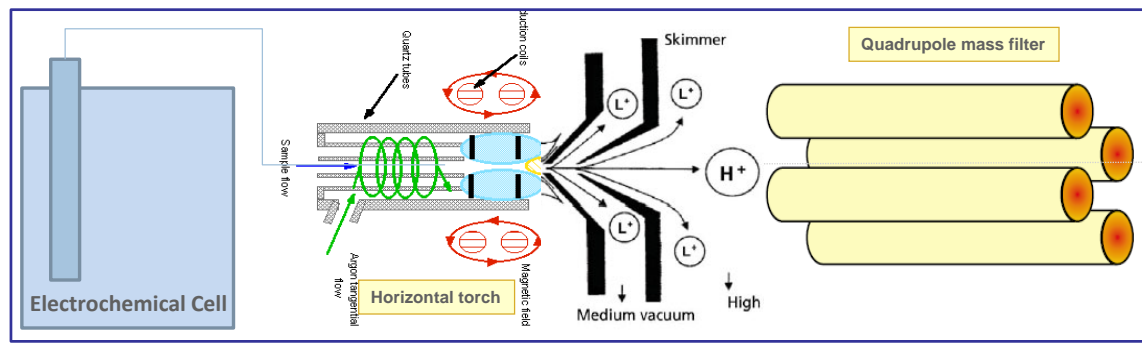
Project Management

Table 1	FY19 FY20 FY21			
	Q1 Jan	Q2 Apr	Q3 July	Q4 Oct
Active Task				
T1 EC	↓	↓	↓	↓
T2 DM	↑	↑	↑	↑
T3 SN	↔	↔	↔	↔

- Task 1 - Electrochemical Characterization (EC)
- Task 2 - Durability Management (DM)
- Task 3 - Synthesis of Nanomaterials (SN)

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

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

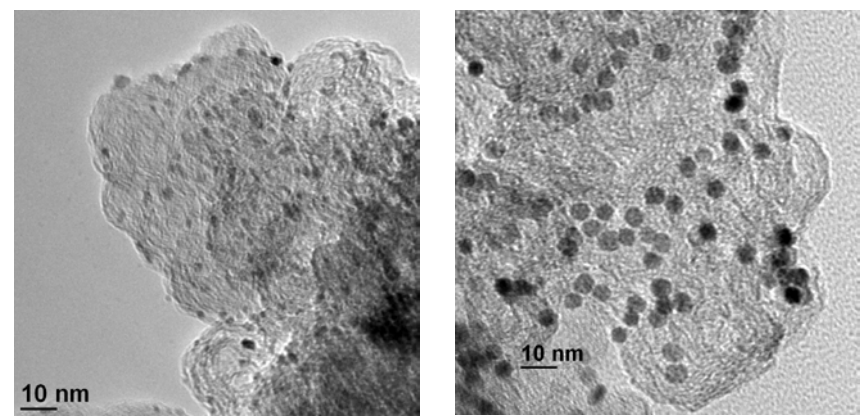
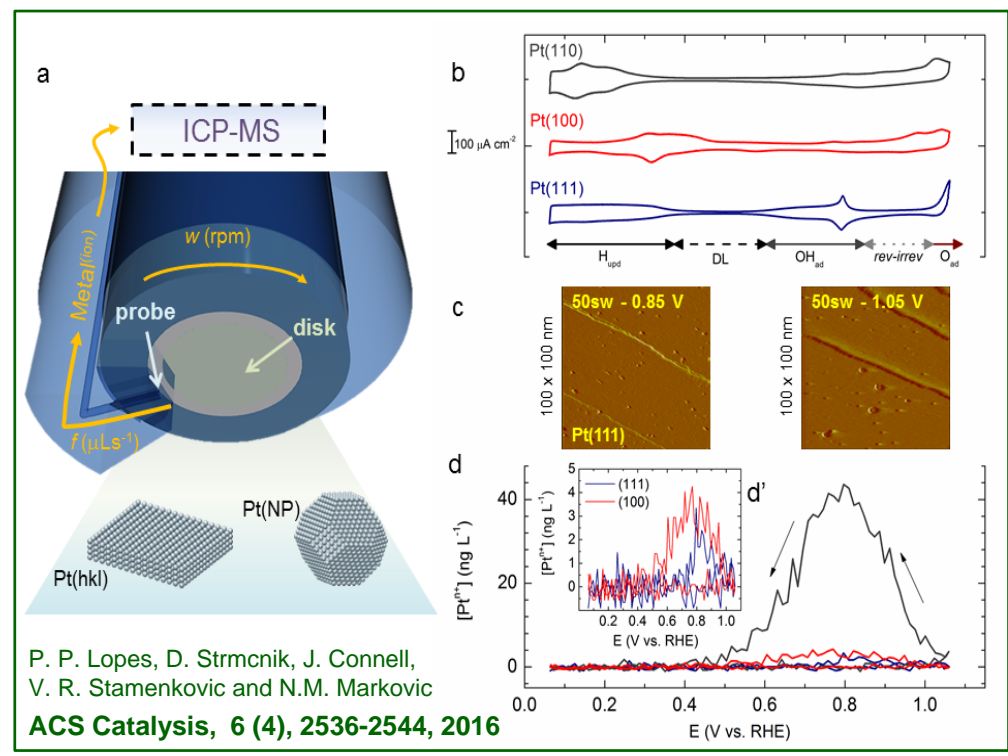


Surface Structure	Pt(111)	Pt(100)	Pt(110)	Pt-poly
Dissolved Pt per cycle [μML]	2	7	83	36

Detection Limit: 0.8 μML of Pt

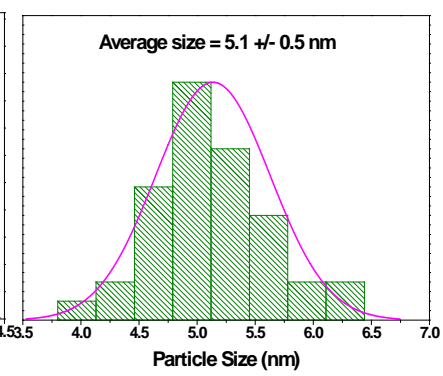
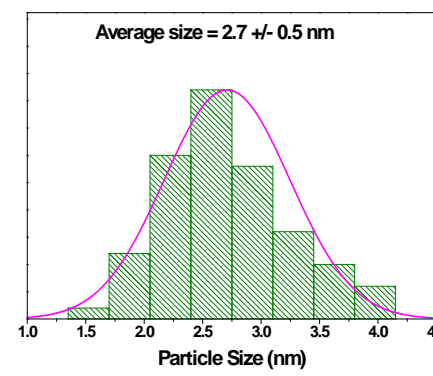
Monodisperse 20% Pt/C NPs 3 and 5nm

In-Situ RDE-ICP/MS



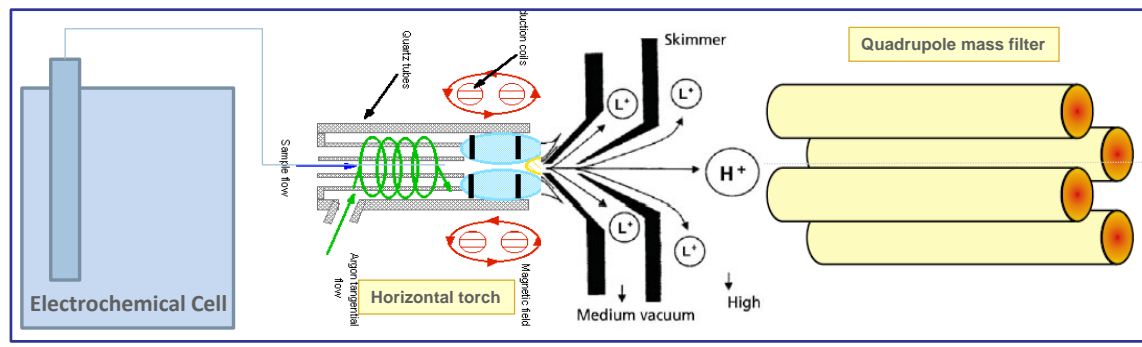
2.7 +/- 0.5 nm

5.1 +/- 0.5 nm



Correlation between Surface Structure - Activity – Dissolution

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

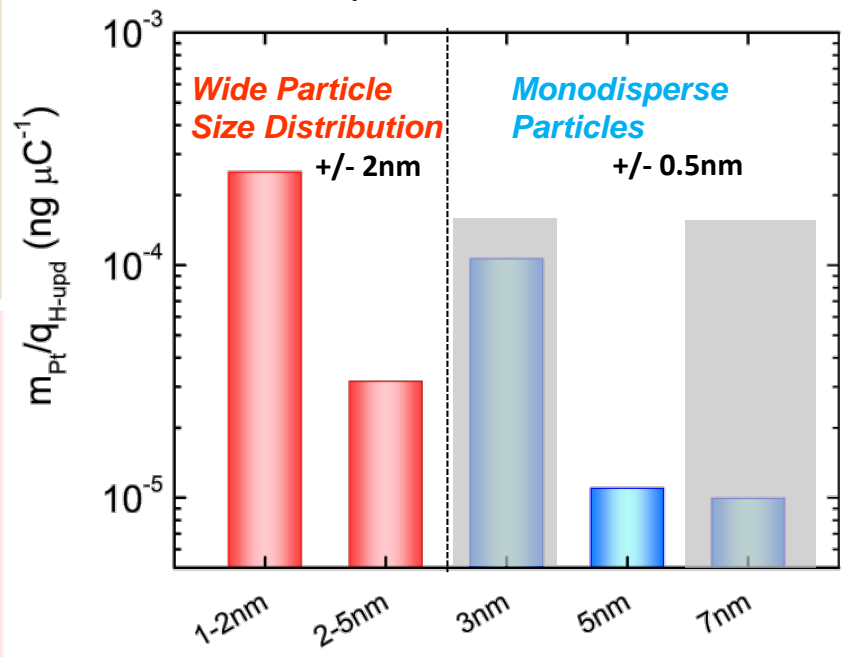
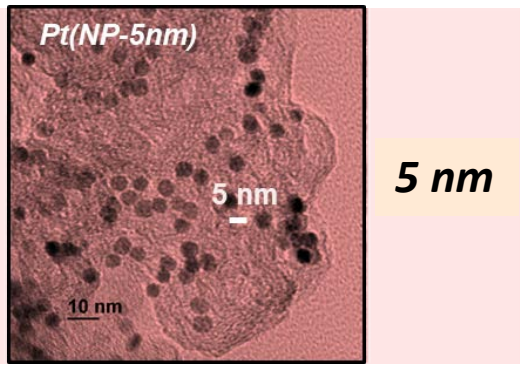
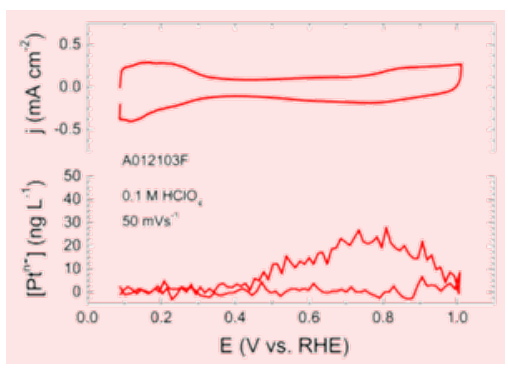
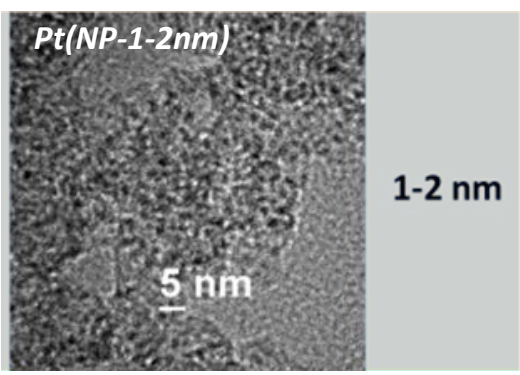
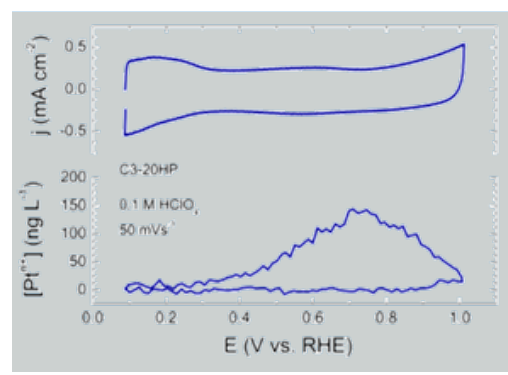


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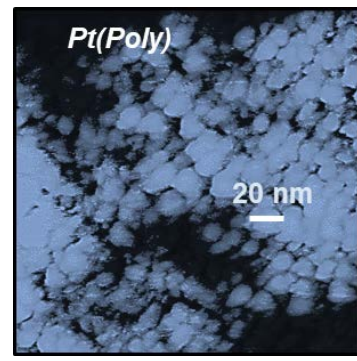
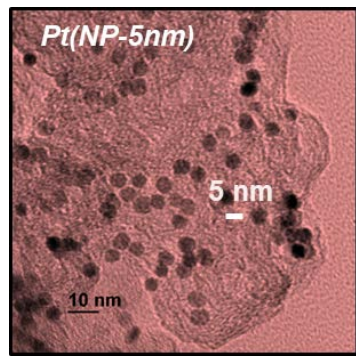
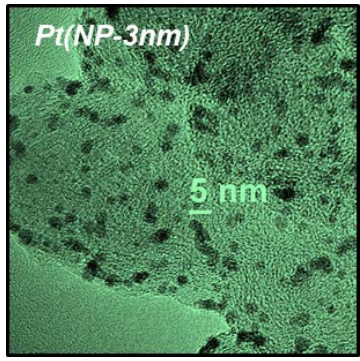
Detection Limit: 0.8 μML of Pt

Dissolution Rates

CV up to 1V @ 50mVs⁻¹



Control of particle size distribution and metal loading have important role for dissolution rate



Dissolution Rates Dependency

(in addition to applied electrode potential)

1) Particle Size:

Smaller particles have higher dissolution rates due to surface atoms with low coordination

2) Metal Loading:

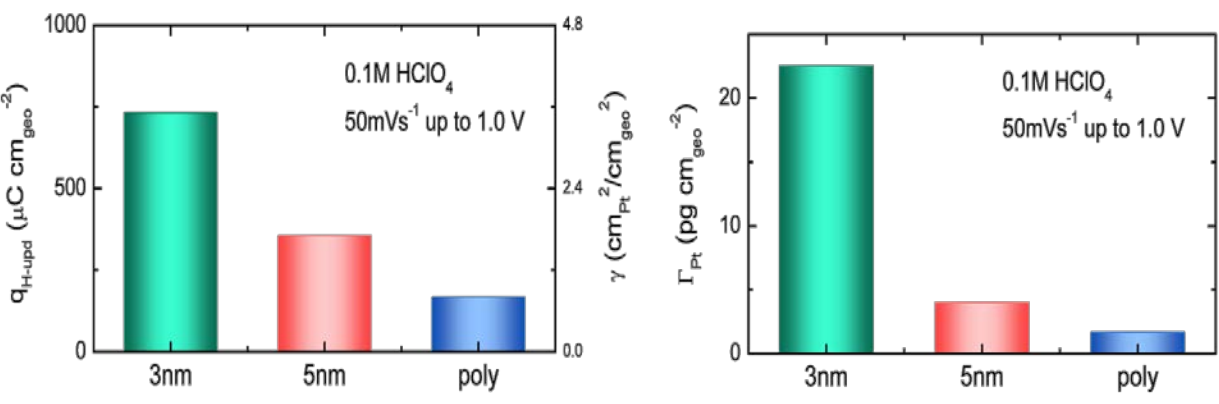
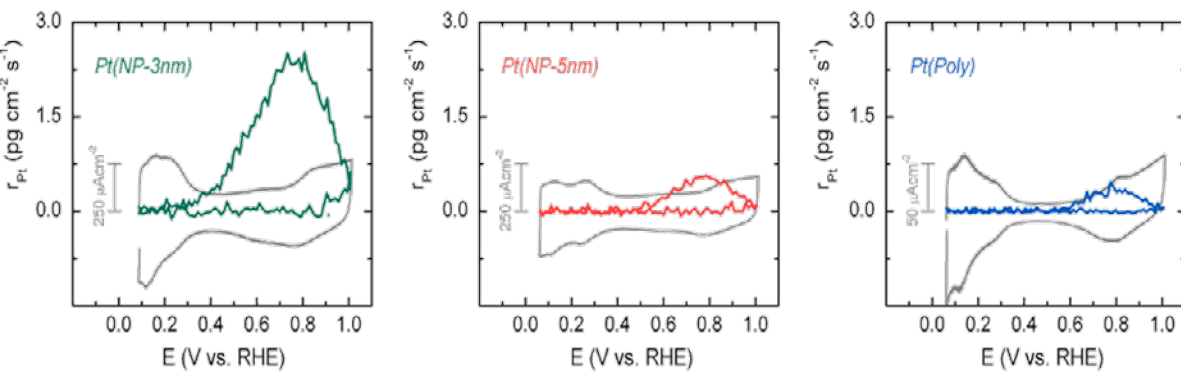
Higher loading of metallic NPs onto carbon support leads to higher dissolution rates

3) Support:

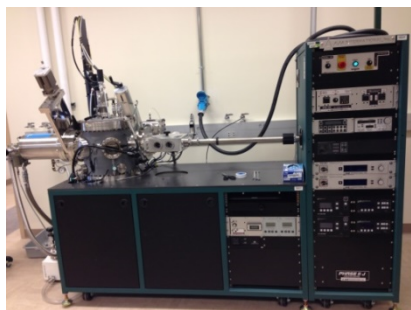
Dissolved Pt atoms can be redeposited in high surface area carbon support

4) Electrolyte:

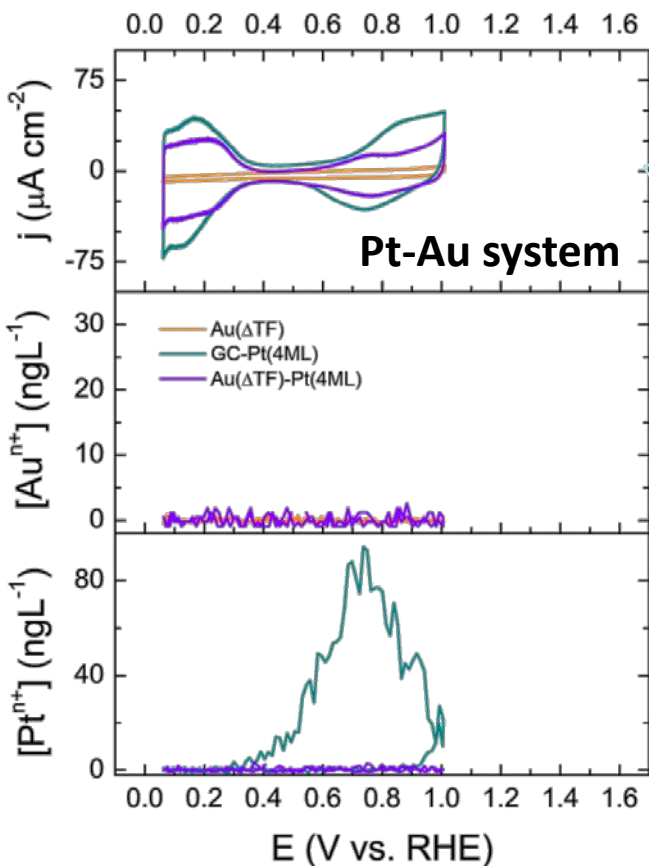
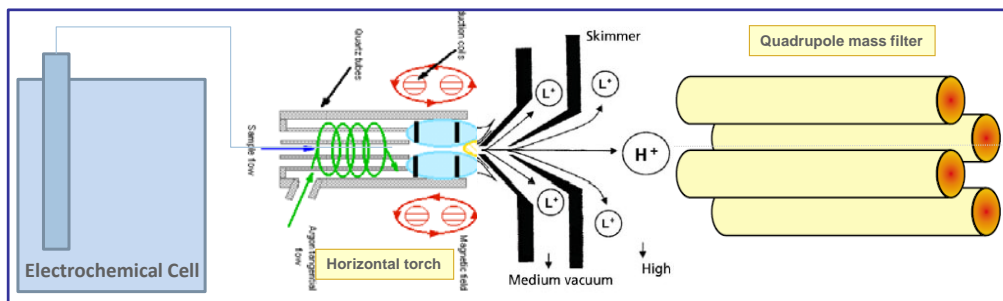
Dissolved amount Pt of atoms varies with electrolyte and presence of different anions



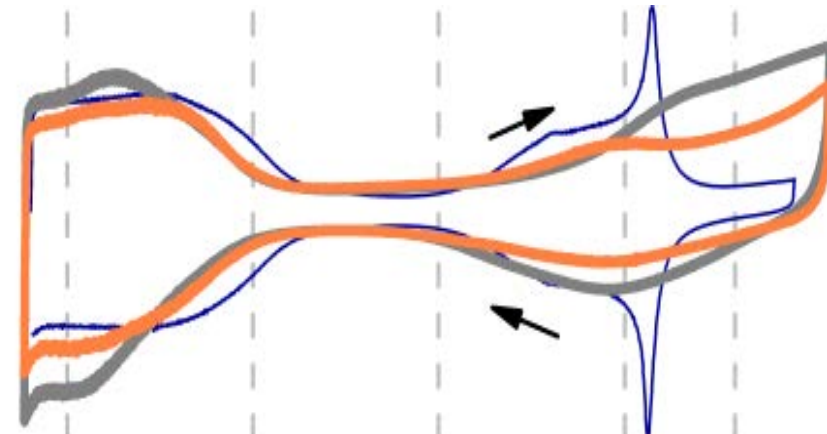
Task 1 Accomplishments and Progress: EC-ICP-MS PtAu Thin Films



Au Substrate



PtAu vs. Pt(111) vs. Pt-4ML



Potential range:
0.05 to 1.0 V

0.1M HClO₄

- Pt 4ML over GC forms a continuous film of interconnected clusters-nanoparticles (~3-5nm)

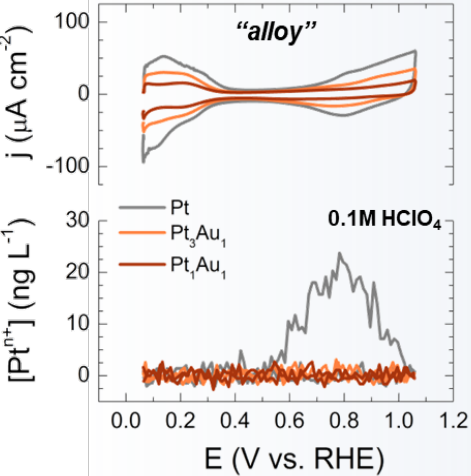
- Pt 4ML over Au thin layer) shows Pt(111)-like voltammetry, indicating ordering of Pt surface

Task 1 Accomplishments and Progress: EC-ICP-MS PtAu Thin Films

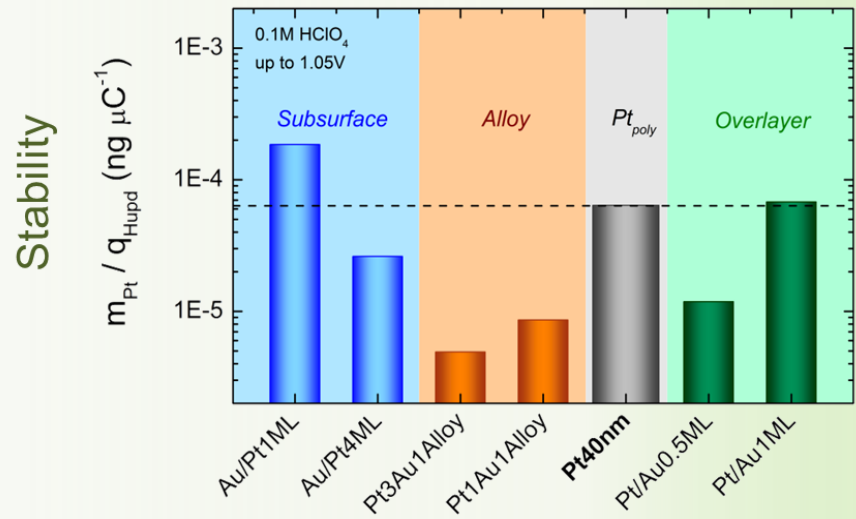
a



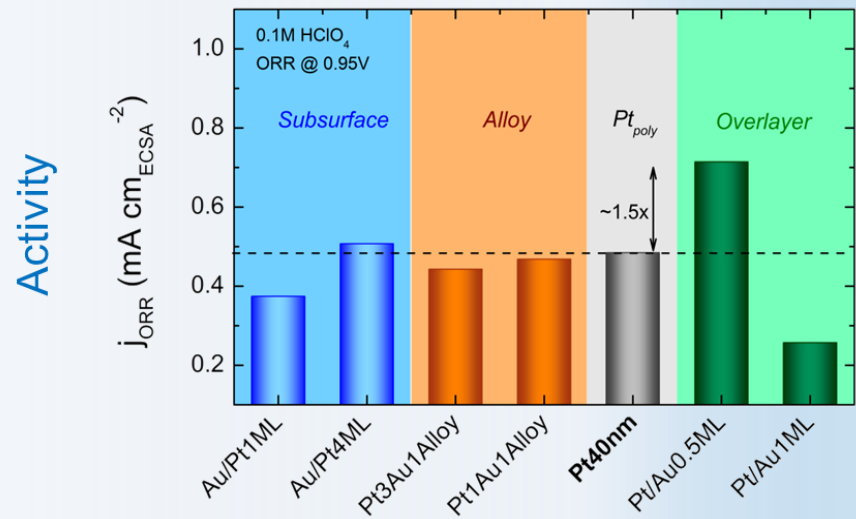
b



c



d



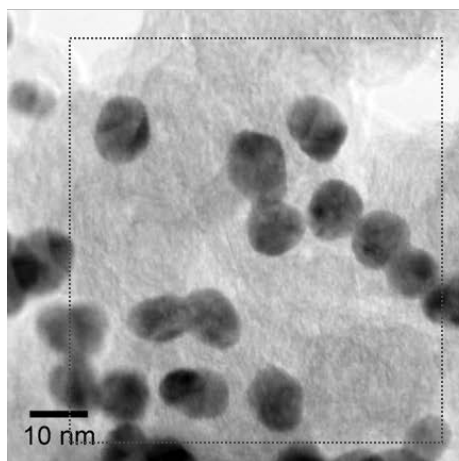
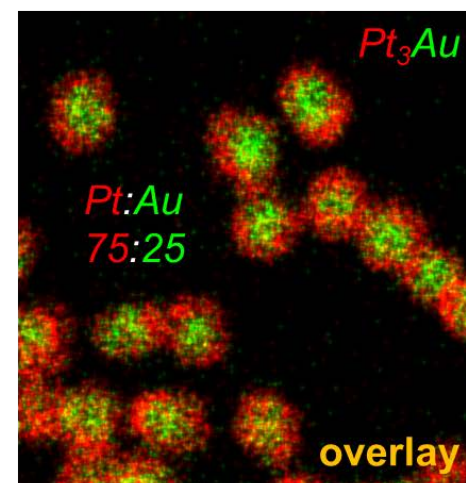
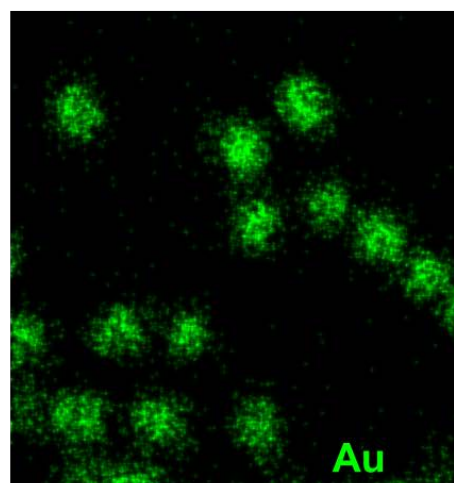
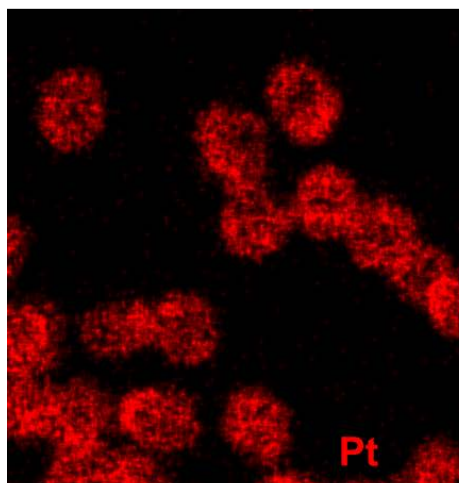
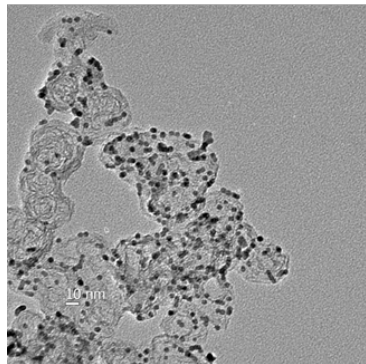
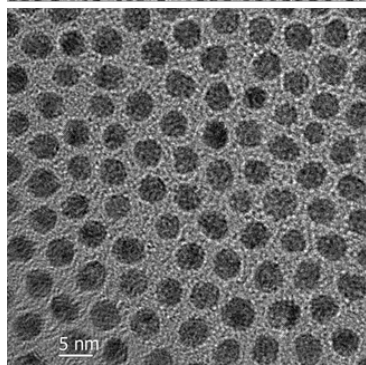
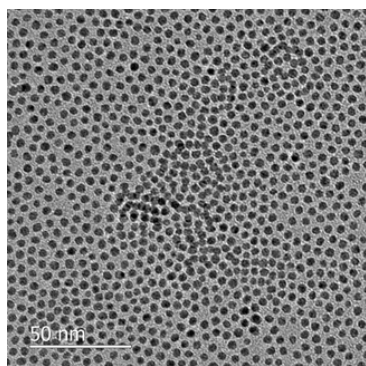
Different arrangements between Pt and Au have been tested for dissolution rates that has been normalized for the actual Hupd from Pt surface atoms

Au/Pt4ML and Pt-Au alloys have comparable beneficial properties

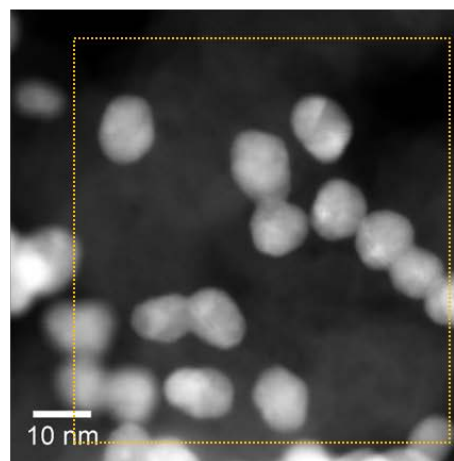
Task 2 Introduction: Pt₃Au synthesis and characterization

in collaboration with K.L. More, ORNL

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



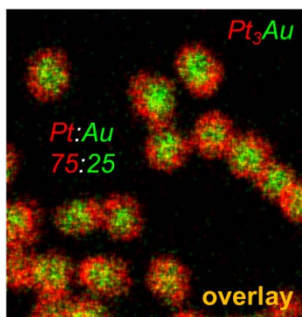
5 nm



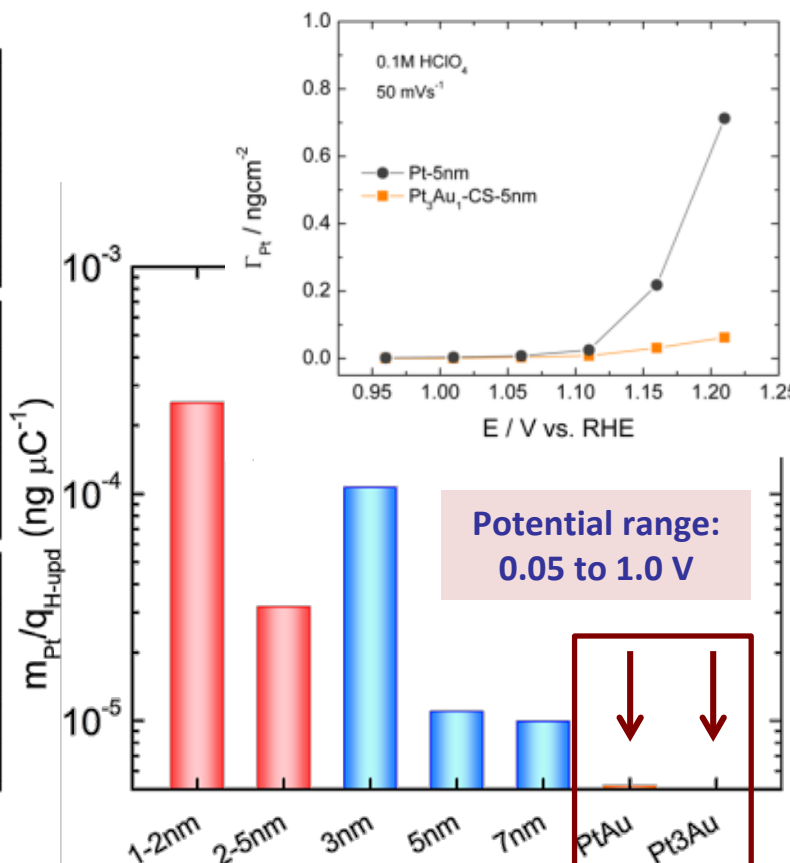
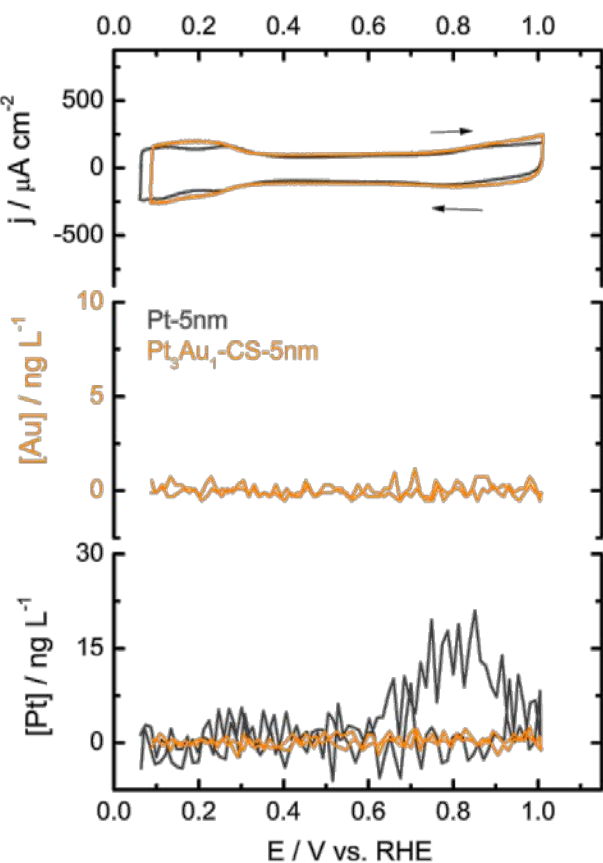
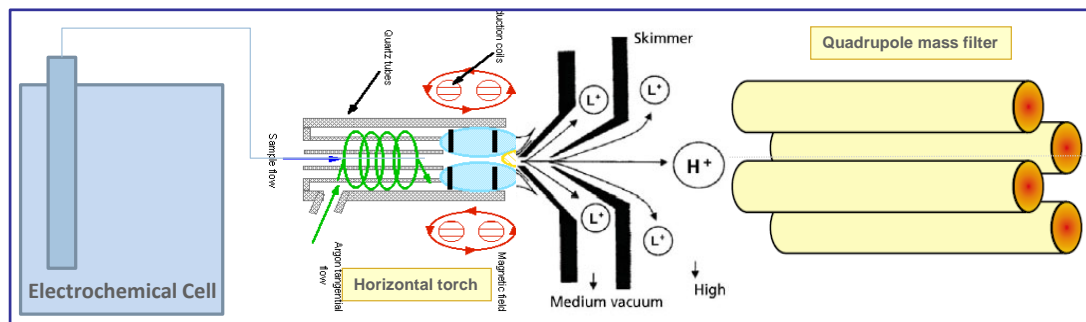
Pt shell Au core nanoparticles:

- Monodisperse ~5nm
- Uniform Pt shell

Task 1-2 Accomplishments and Progress: EC-ICP-MS Pt₃Au nanoparticles



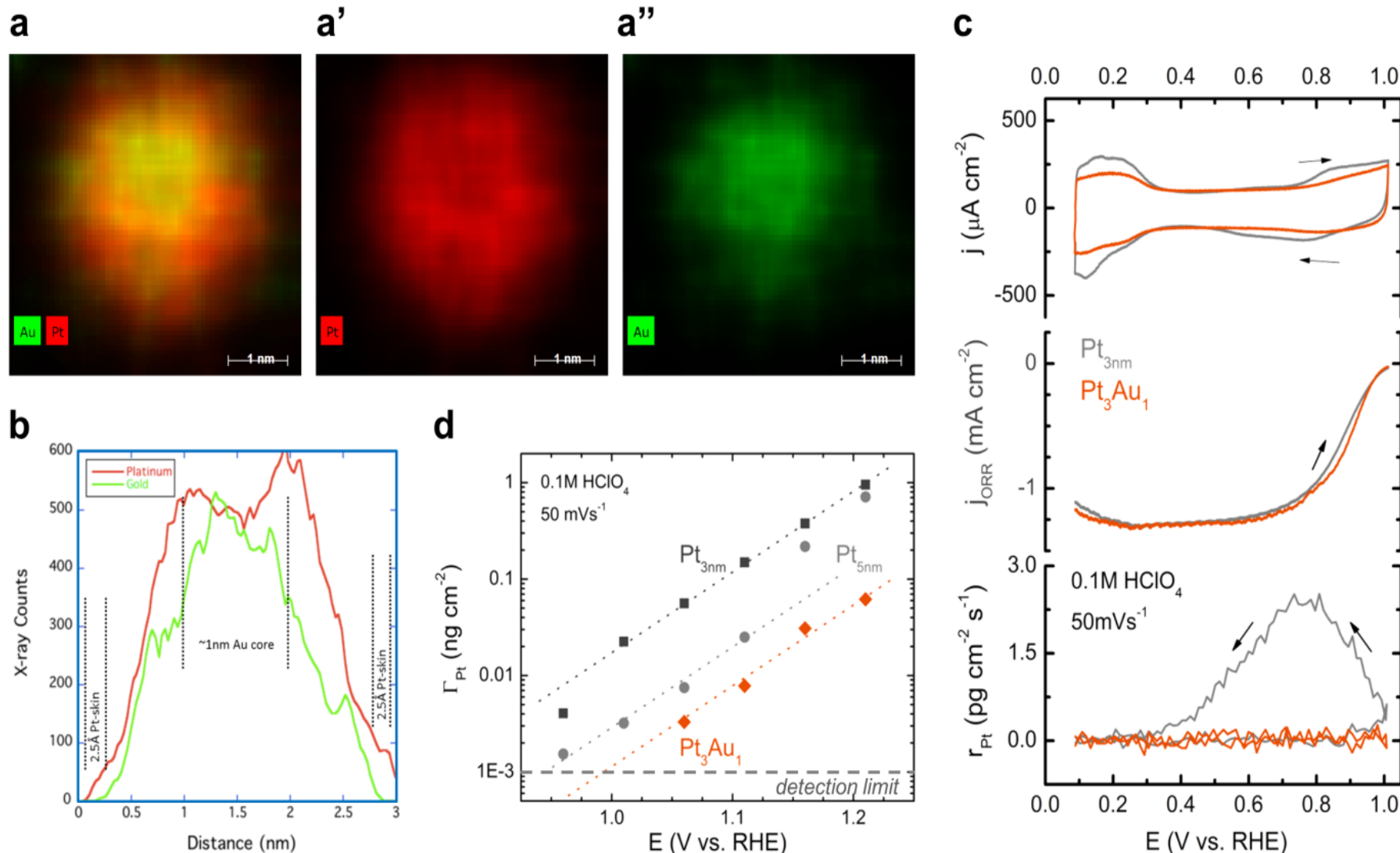
Pt₃Au/C - GC



Pt₃Au/C

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

Task 2 Accomplishments and Progress: Pt₃Au/C 3nm vs Pt/C 3 and 5 nm



PtAu 3nm have been synthesized with the same success as bigger 5nm NPs, which was confirmed by TEM studies and electrochemical evaluations of dissolution rates with over one order of magnitude improvement

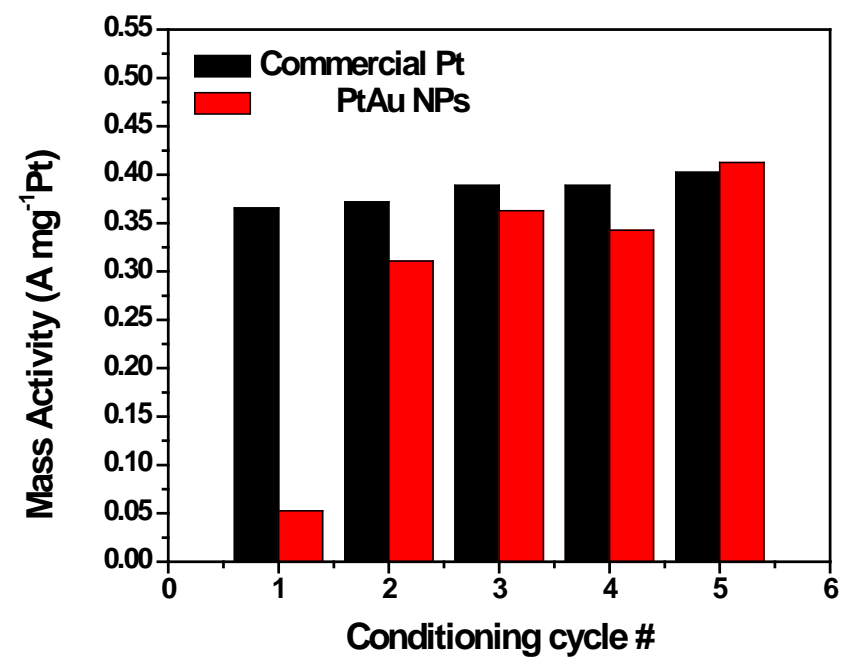
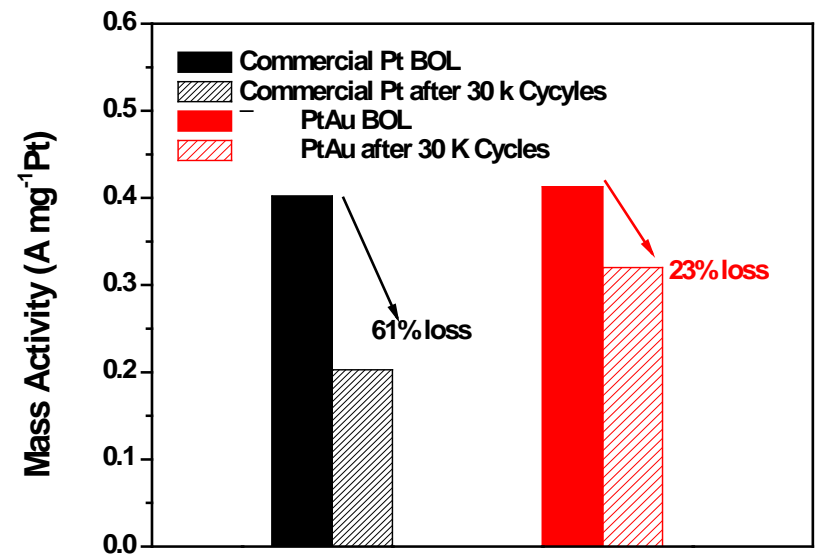
in collaboration with Kenneth Neyerlin, NREL

- 150 kPa, 100% RH, 80°C H₂/O₂, 50 cm², N211
- Ultrasonic spray coated 0.9 I:C (D2020 ionomer)
- Cathode loading 0.075 mgPt/cm²

Developed PtAu/HSC: $i_m^{0.9V} \sim 420 \text{ mA/mg}_{Pt}$

- 150 kPa, 100% RH, 80°C H₂/Air, 50 cm²

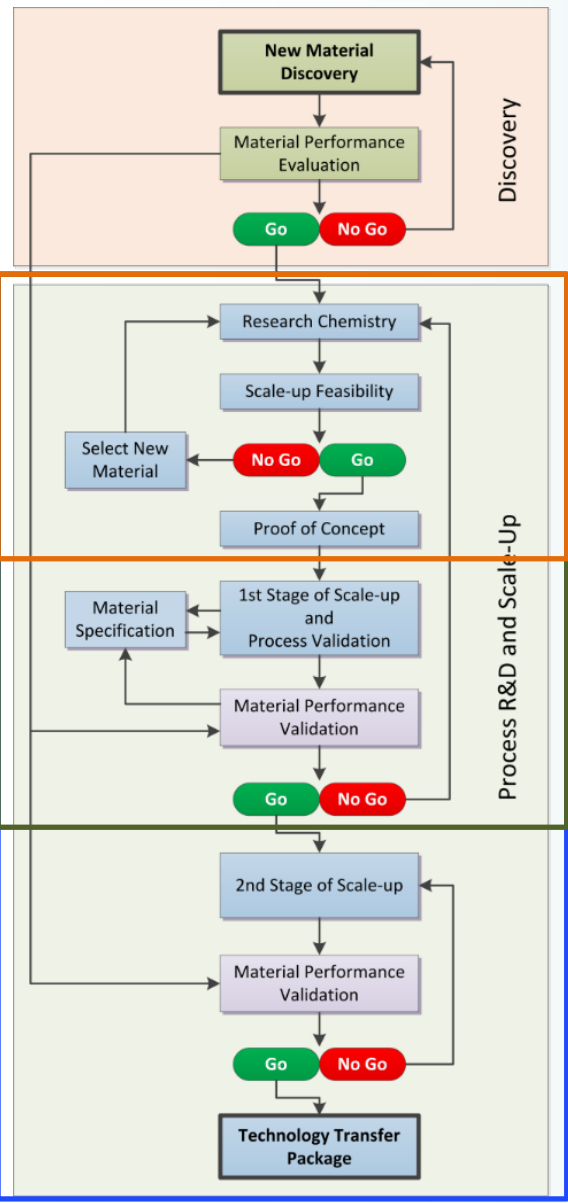
PtAu/C losses only 17% of ECSA and 23% of MA after 30K cycles of AST - FCPAD protocol meeting the DOE target



	ECSA (m ² /g)
Before AST	31.8
After AST	26.3

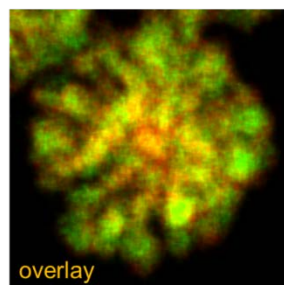
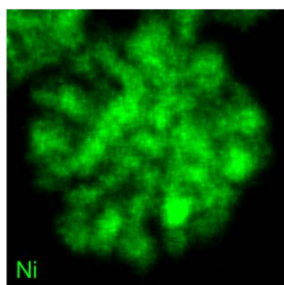
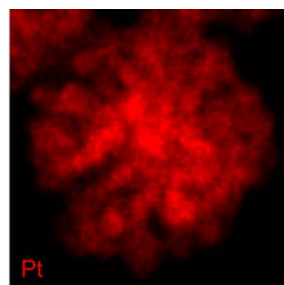
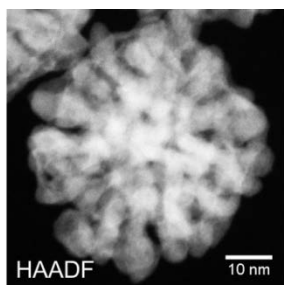
Task 3 Introduction: Process R&D and Scale Up

collab. with Greg Krumdick, ANL -MERF

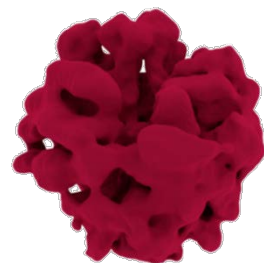


Timeline & Milestones		
Research Chemistry	M 1-2	1) Hot-injection was avoid using one-pot synthesis . 2) Benzyl ether as solvent. No Go
	M 3	3) Phenyl ether as solvent. 4) Best synthesis condition was established. 5) Reproducibility was confirmed. Go
1 st stage scale up	M 4	6) 1 st stage scale up (1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

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

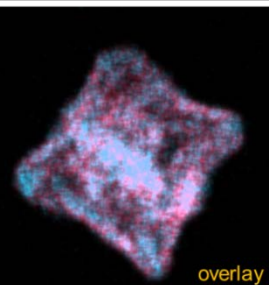
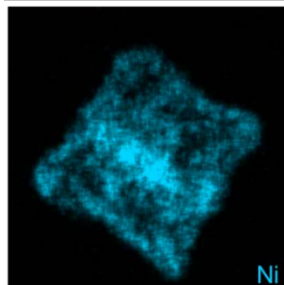
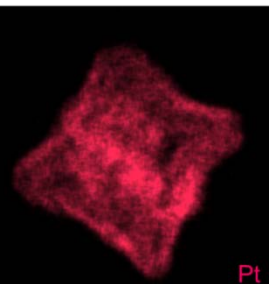
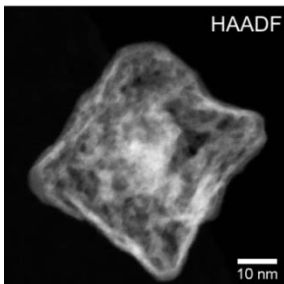
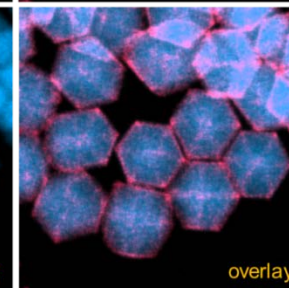
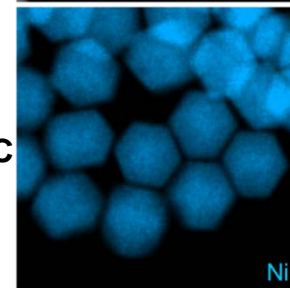
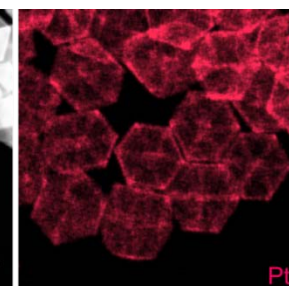
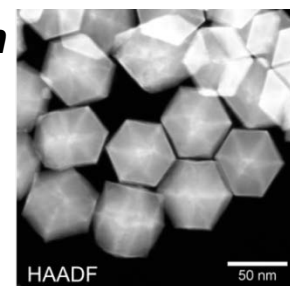
Nano Multi Skin



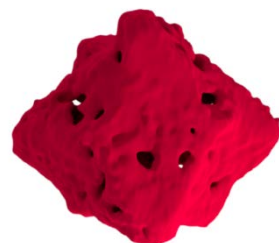
ANL, ORNL

Improvement vs. Pt/C
RDE @ 0.95V

SA: 7
MA: 4



Nanocages

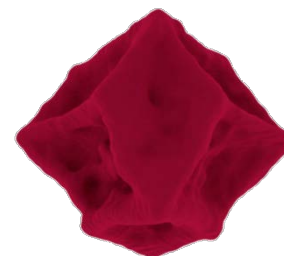


ANL, ORNL

Improvement vs. Pt/C
RDE @ 0.95V

SA: 9
MA: 6

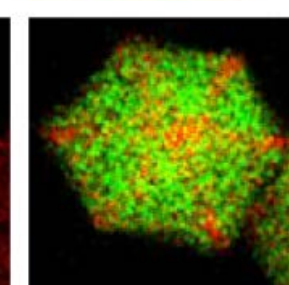
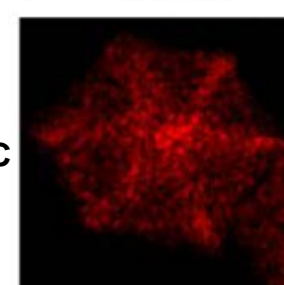
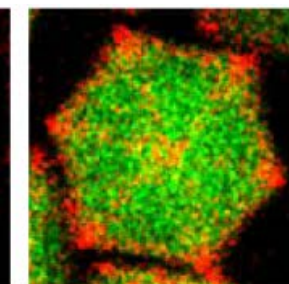
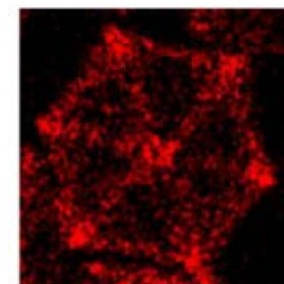
Excavated Nanoframes



LBNL, ANL, ORNL

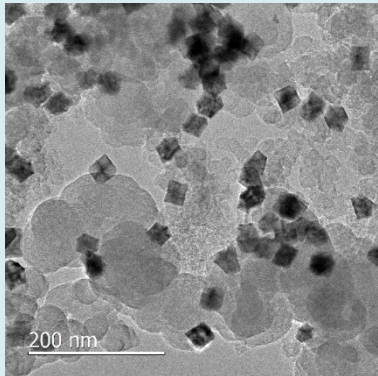
Improvement vs. Pt/C
RDE @ 0.95V

SA: 13
MA: 7

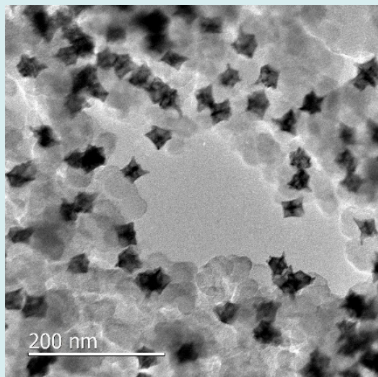
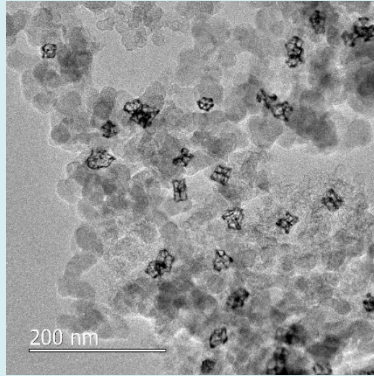


As synthesized

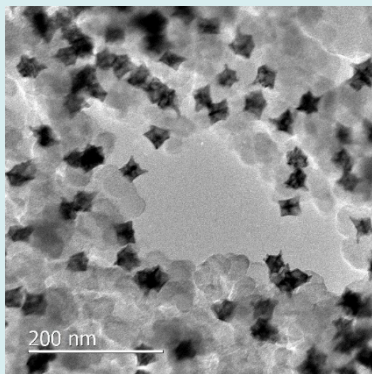
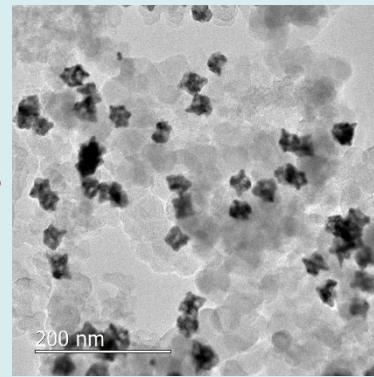
Acid treated



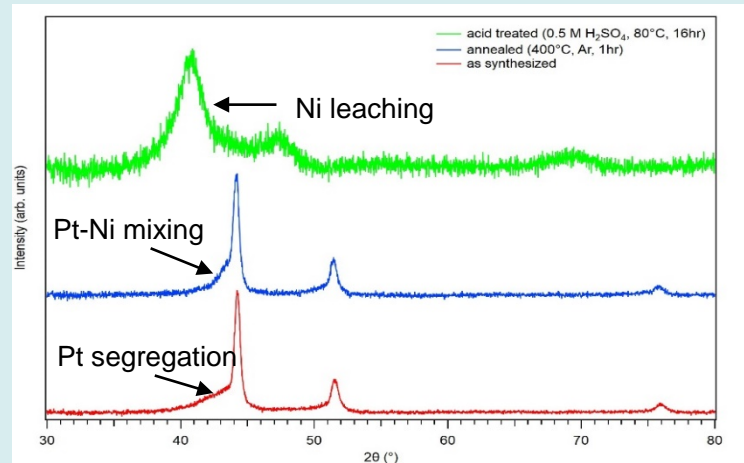
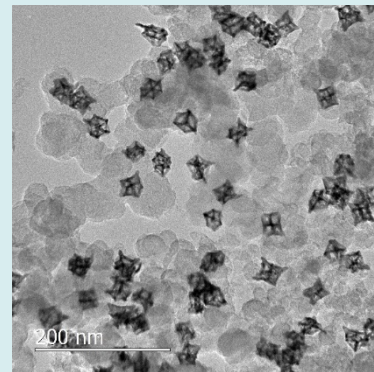
Pt-Ni h-NFs



Pt-Ni rd-NFs



Pt-Ni e-NFs



- NF structures synthesized at ~1g batch scale
- High temperature annealing preserves hollow structure
- Durable after harsh acid treatment (0.5 M H₂SO₄, 80°C) before MEA

Tasks 2-3 Accomplishments and Progress: PtNi NanoFrames 1g batch in 50 cm² MEA

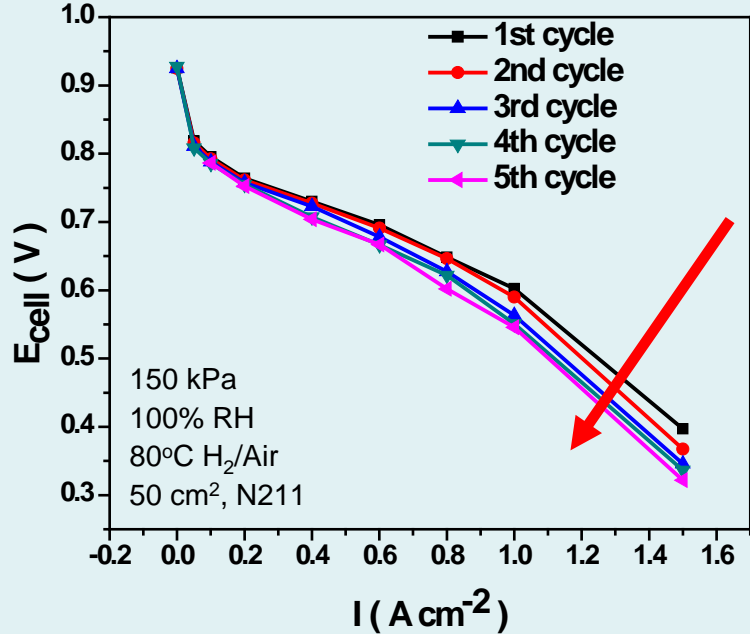
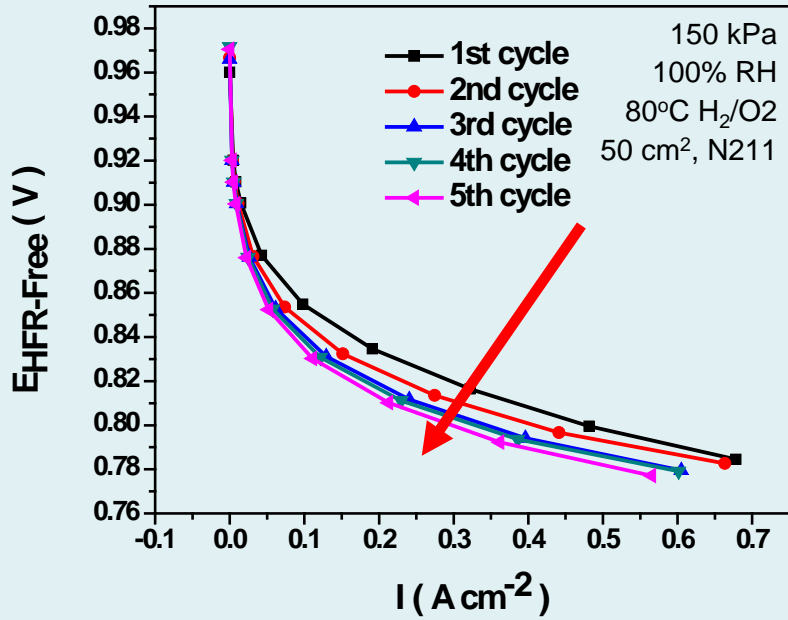
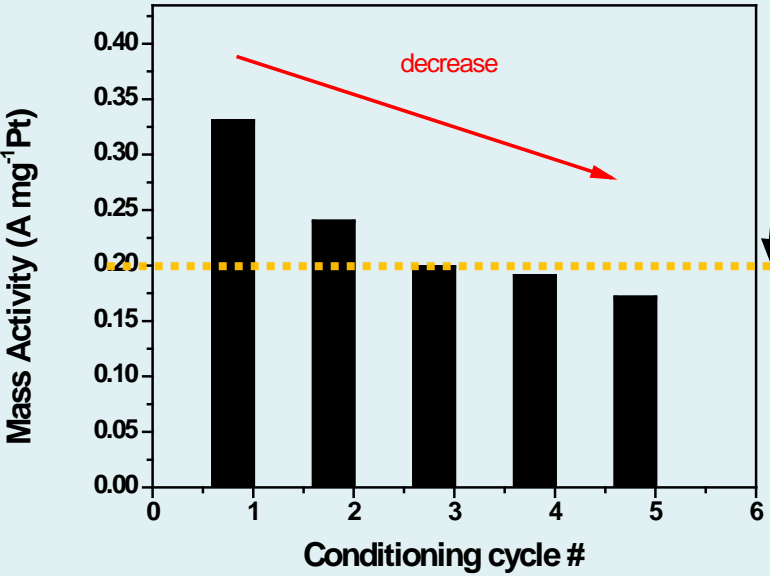
in collaboration with Kenneth Neyerlin, NREL

- 150 kPa, 100% RH, 80°C H₂/O₂, 50 cm², N211
- Ultrasonic spray 0.5 I:C (D2020 ionomer)
- Cathode loading 0.055mgPt/cm²

Developed PtNi NanoFrames/Vulcan:

$i_m^{0.9V} \sim 330 \text{ mA/mg}_{Pt}$
vs. $\sim 200 \text{ mA/mg}_{Pt}$ for 30 wt% Pt/Vulcan

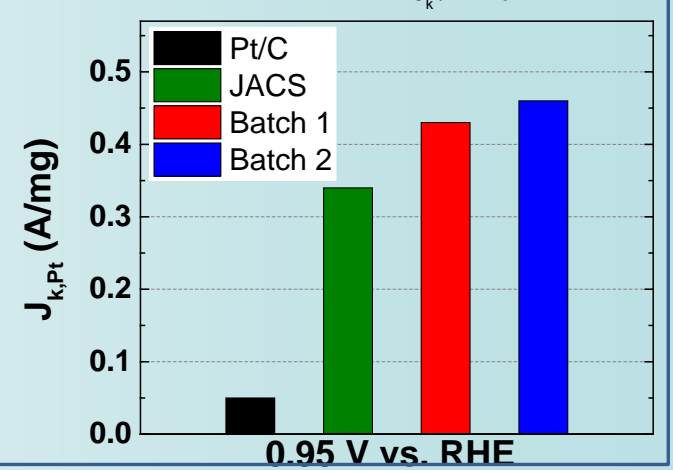
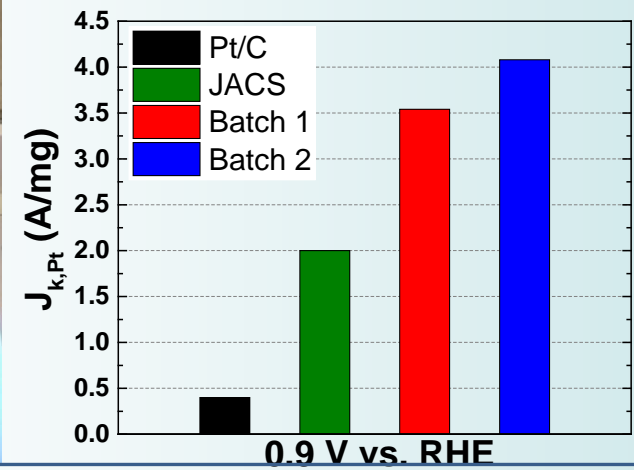
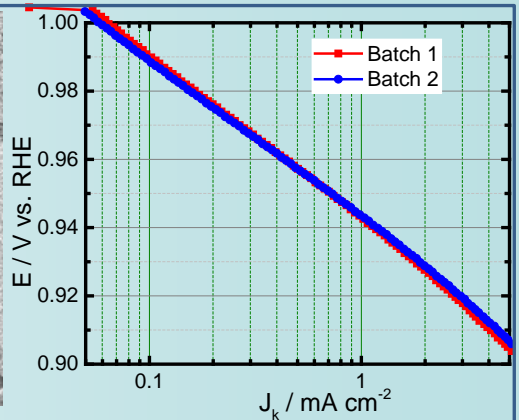
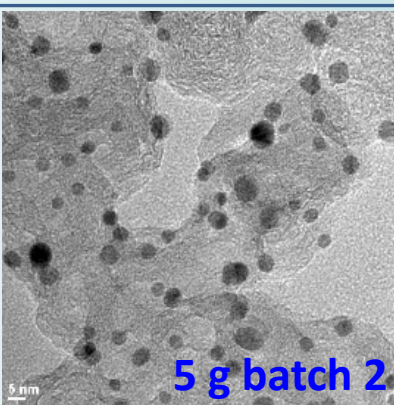
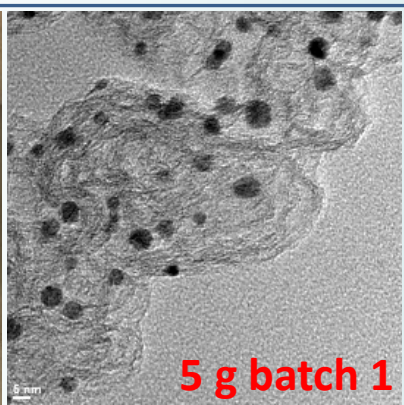
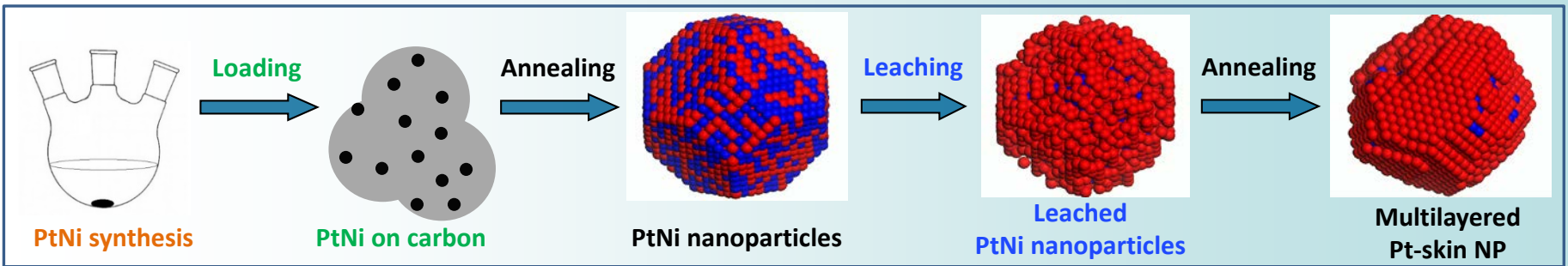
Pt/Vulcan shows about 0.2 A/mg_{Pt} mass activity at 0.9 V

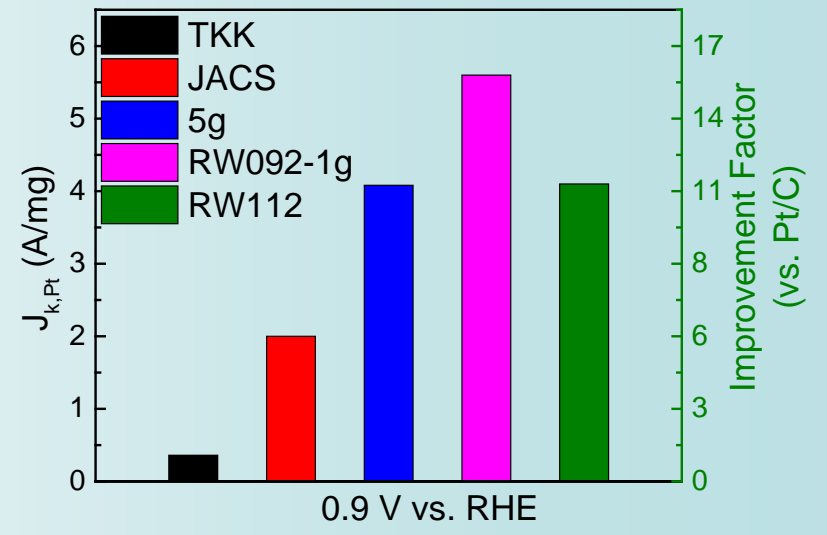
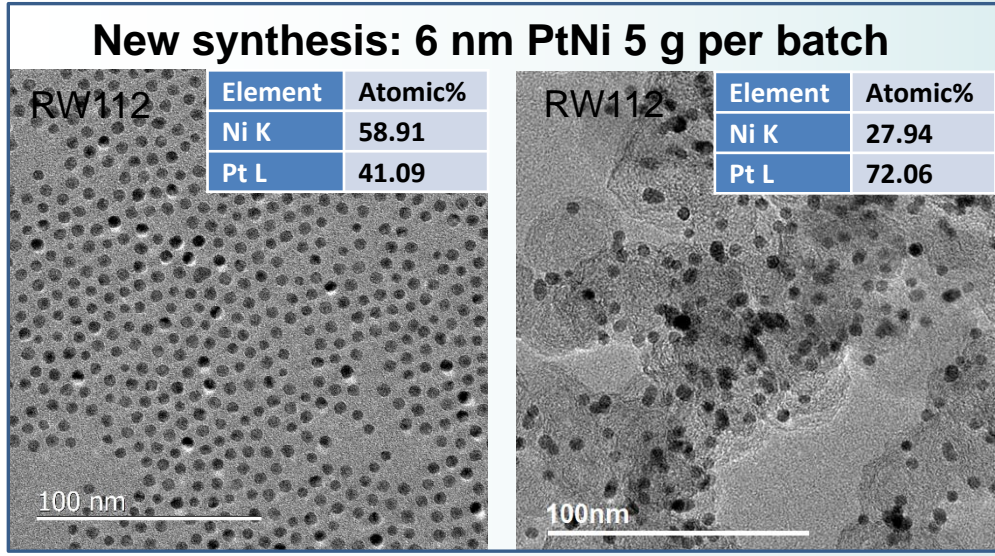
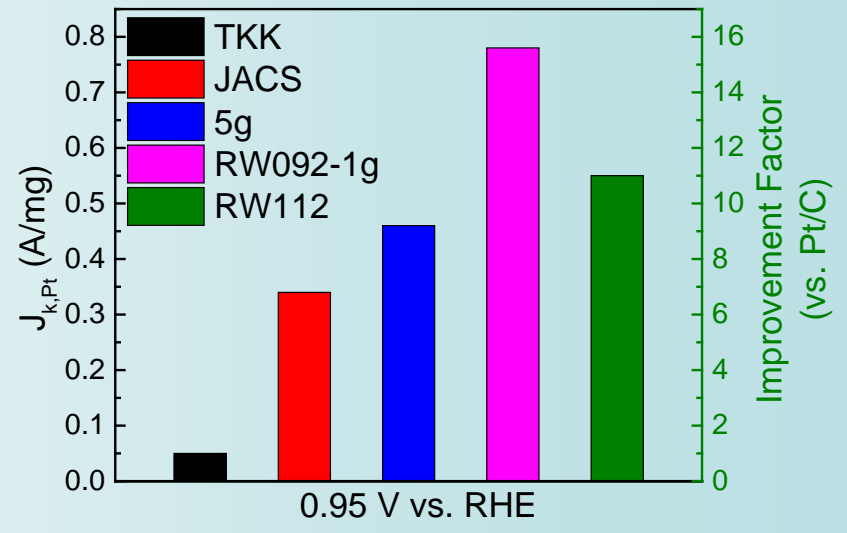
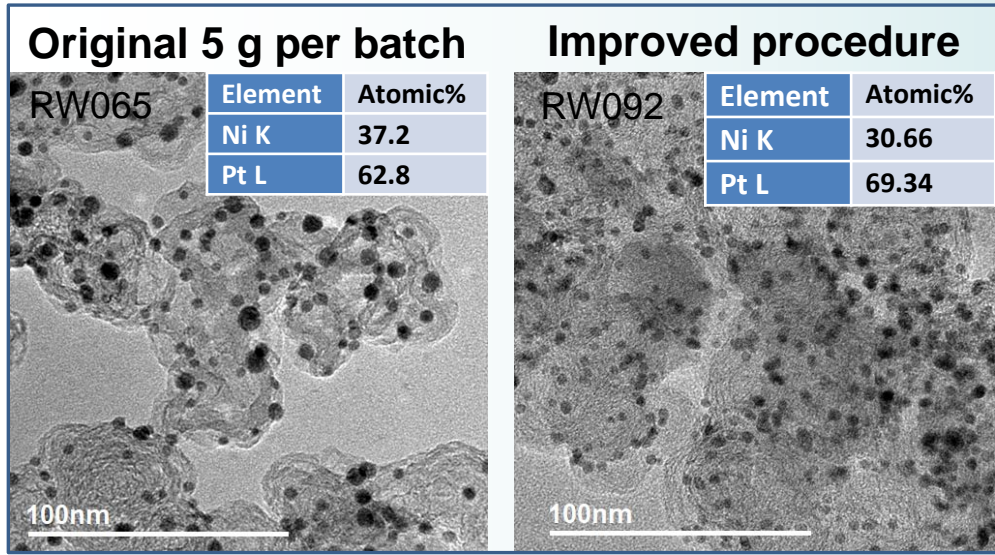


Task 3 Accomplishments and Progress: Process Scale Up | RDE Evaluations

collab. with Greg Krumdick, ANL -MERF

From 0.1 g to 5 g per batch





➤ Sintering during high temperature annealing is limited.

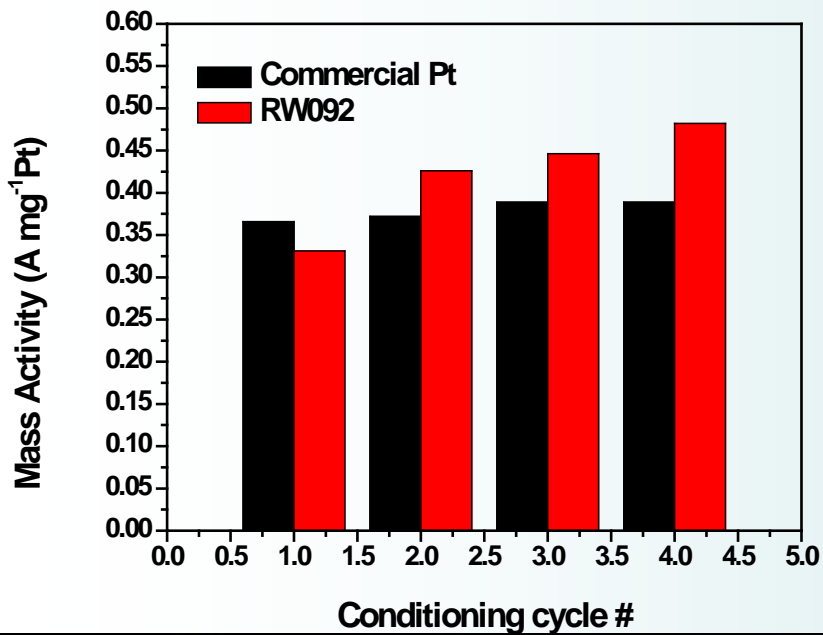
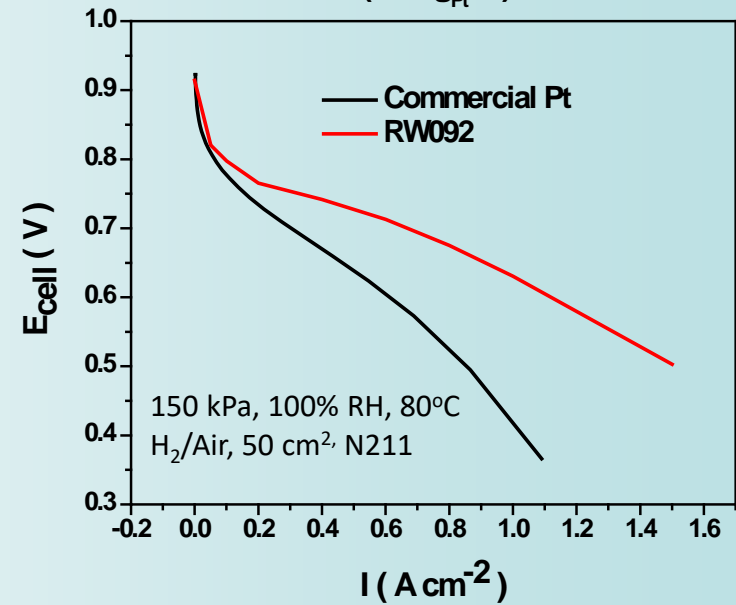
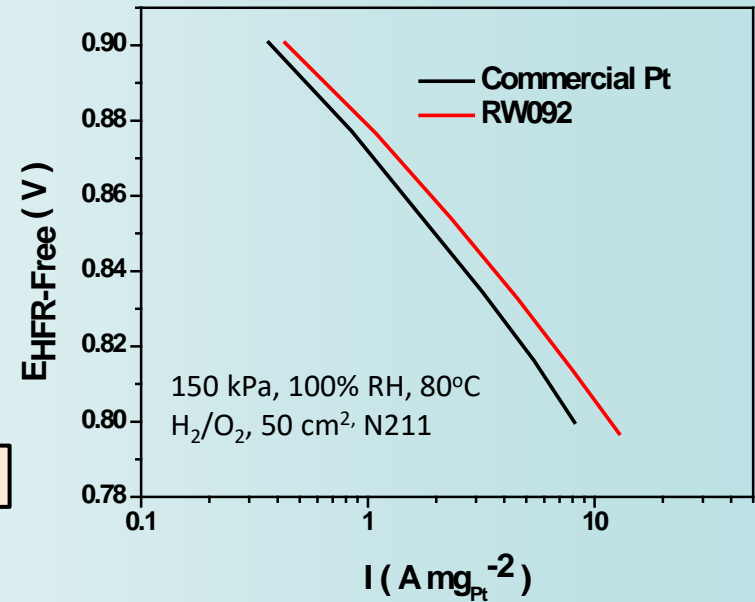
Task 2-3 Accomplishments and Progress: PtNi NPs 5g batch in 50 cm² MEA

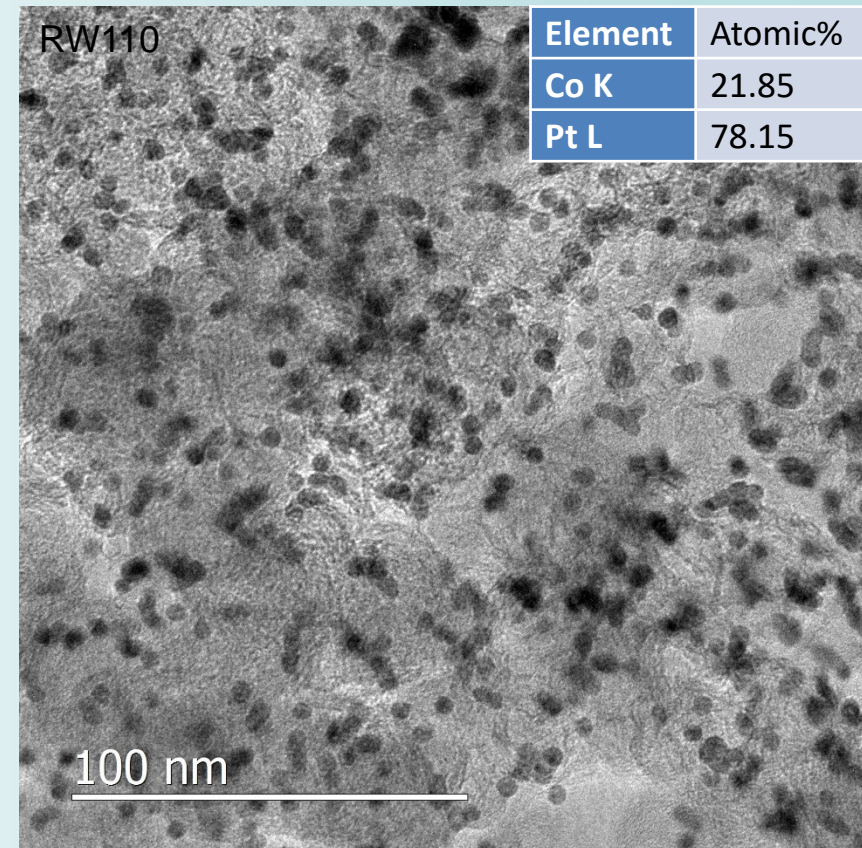
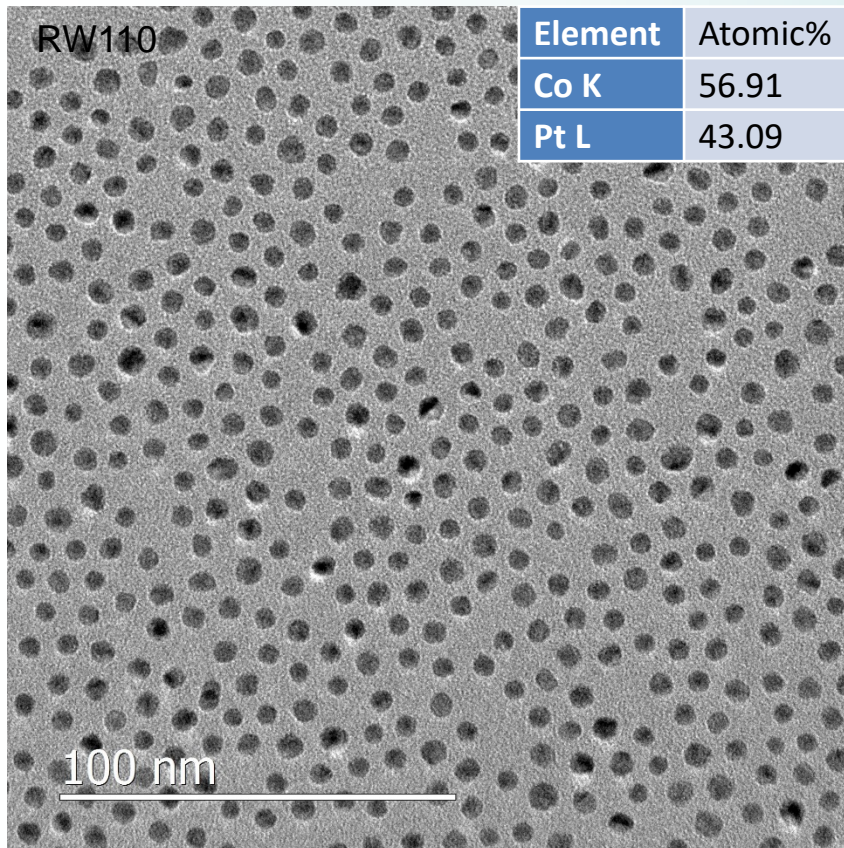
in collaboration with Kenneth Neyerlin, NREL

150 kPa, 100% RH, 80°C H₂/O₂, 50 cm², N211
 Ultrasonic spray coated 0.9 I:C (D2020 ionomer)
 Cathode loading 0.04mgPt/cm²

Developed RW092 PtNi/HSC: $i_m^{0.9V} \sim 500 \text{ mA/mg}_{Pt}$

PtNi/C shows MA that meets the DOE target in 50 cm² MEA



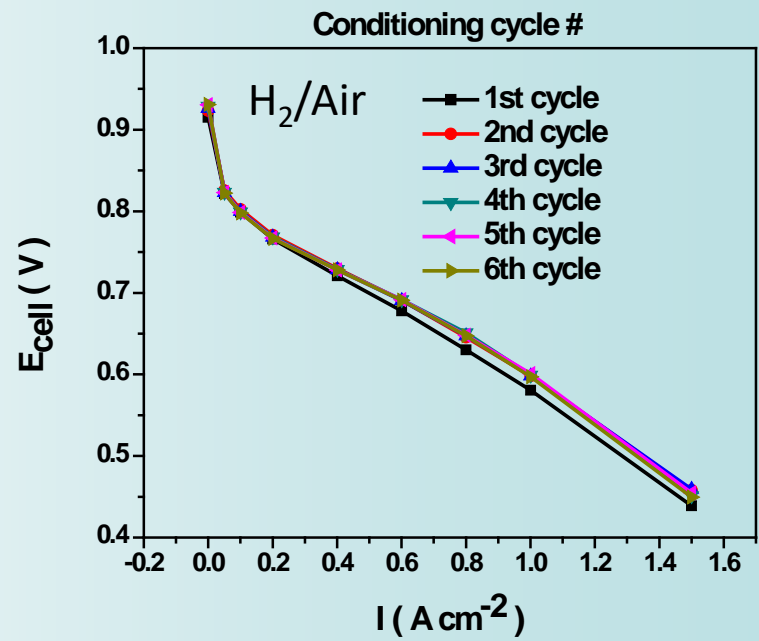
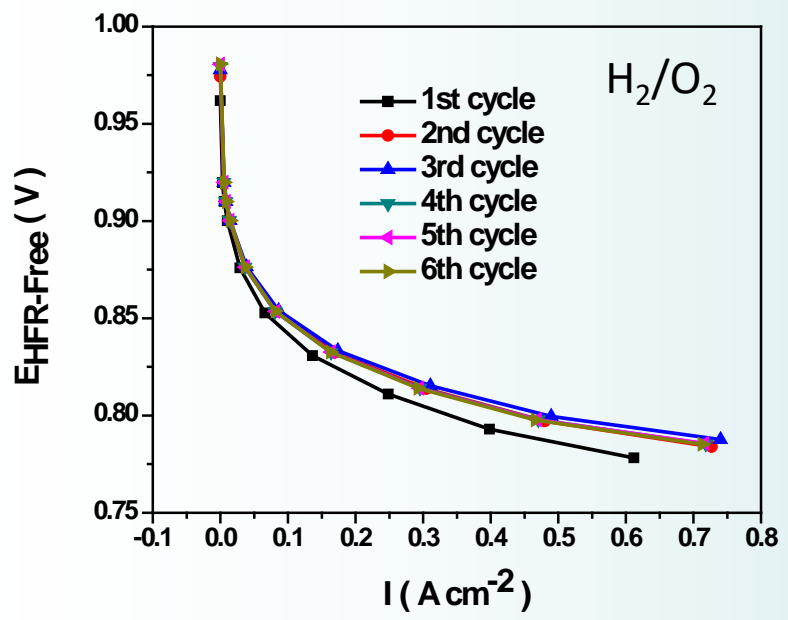
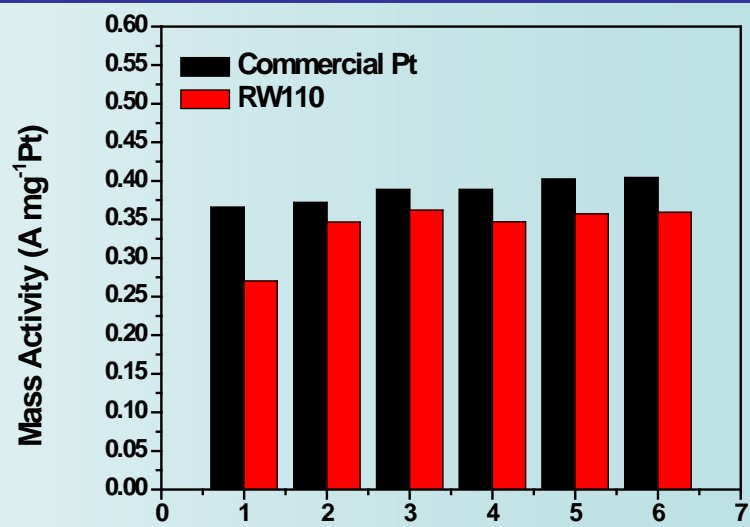
5 nm Pt₃Co-1 g catalyst per batch

- Developed one-pot scalable synthesis of 6 nm PtCo nanoparticle.
- Post-treatment needs to be optimized for better performance.

in collaboration with Kenneth Neyerlin, NREL

- 150 kPa, 100% RH, 80°C H₂/O₂, 50 cm², N211
- Ultrasonic spray coated at NREL 0.9 I:C (D2020 ionomer)
- Cathode loading 0.055 mg Pt/cm²

Developed PtCo/_{HSA}C: $i_m^{0.9V} \sim 350 \text{ mA/mg}_{Pt}$

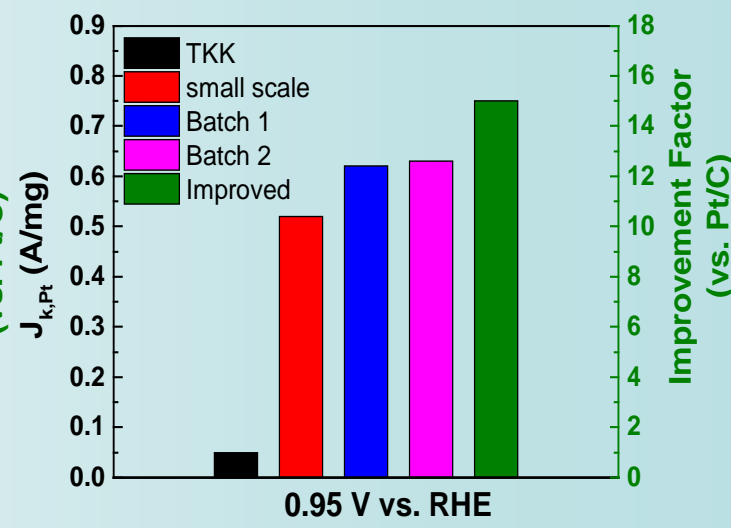
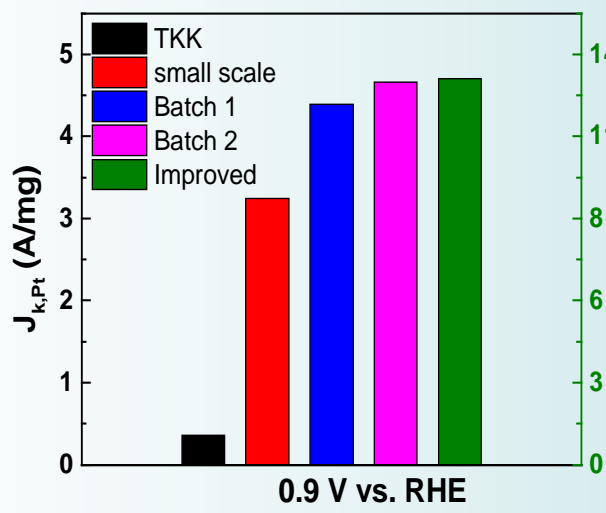


One-pot synthesis and structural optimization of Nanocages

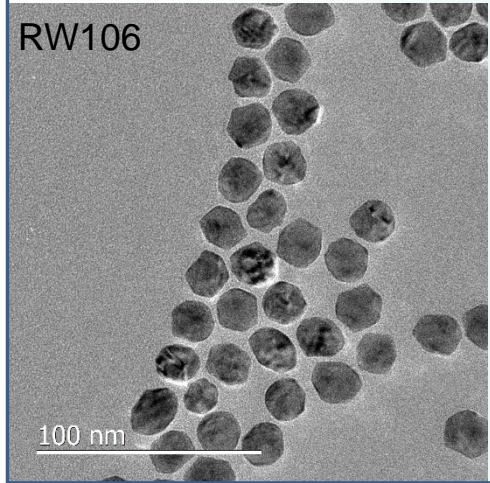
0.1 g per batch

RW096

Element	Atomic%
Ni K	60.0
Pt L	40.0



0.6 g per batch modified acid leaching procedure



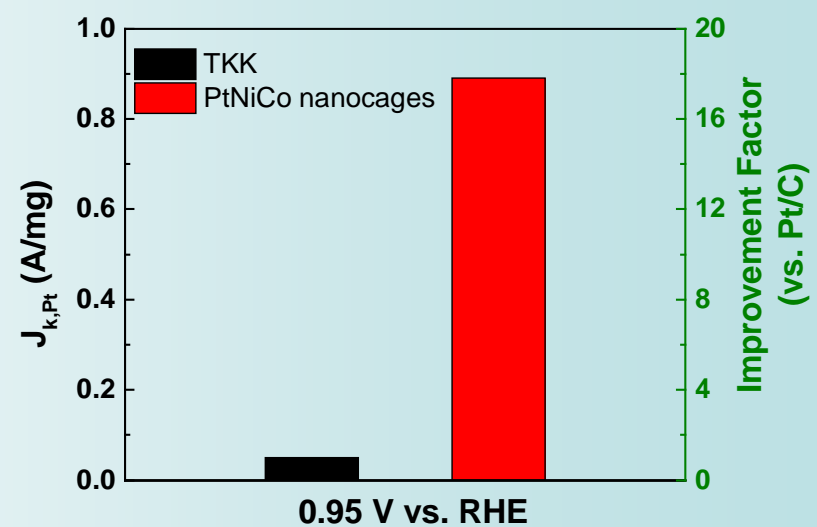
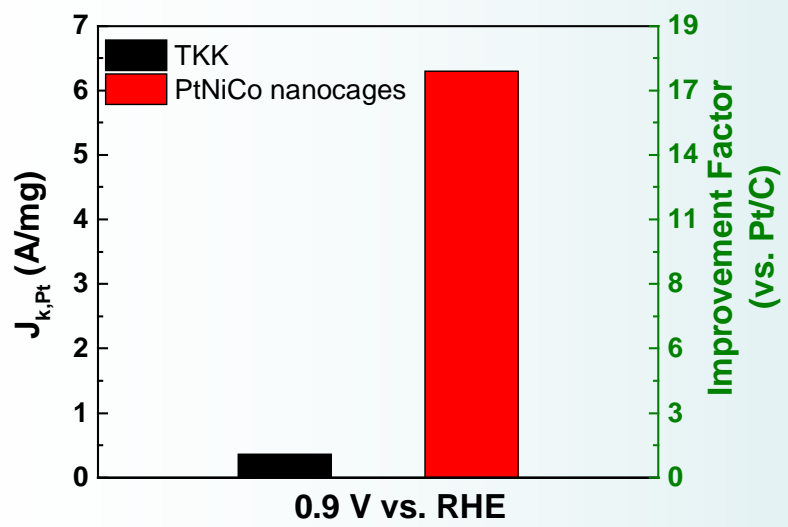
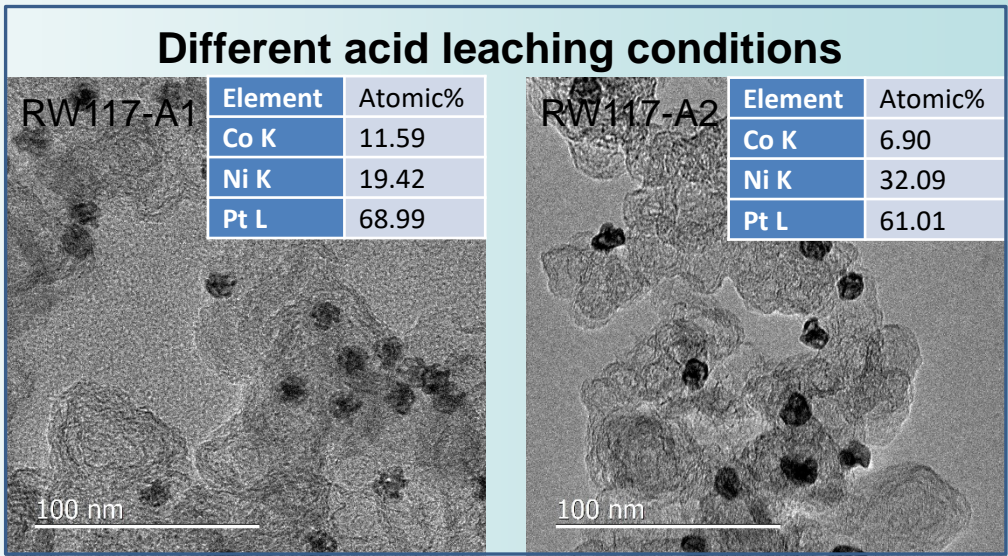
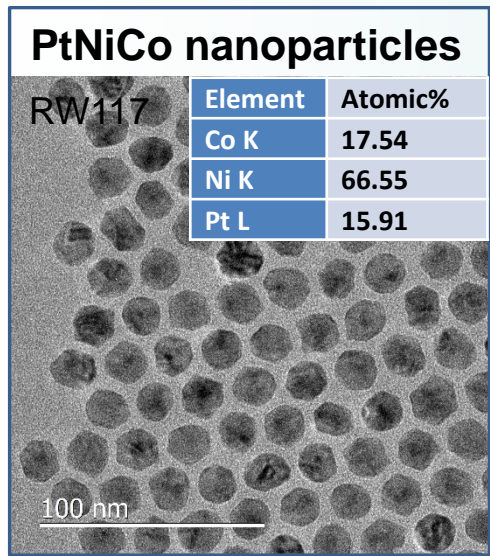
RW106-A1

Element	Atomic%
Ni K	32.7
Pt L	67.3

RW106-A2

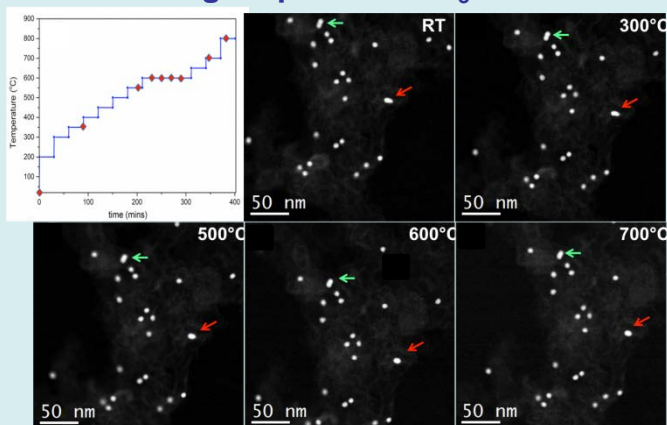
Element	Atomic%
Ni K	64.7
Pt L	35.3

One-pot synthesis-1 g per batch of PtNiCo Nanocages

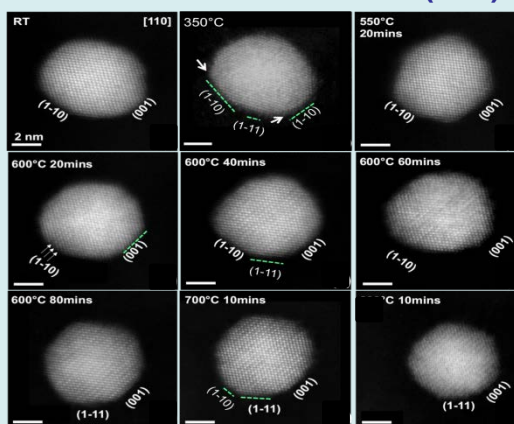


in collaboration with K.L. More, ORNL

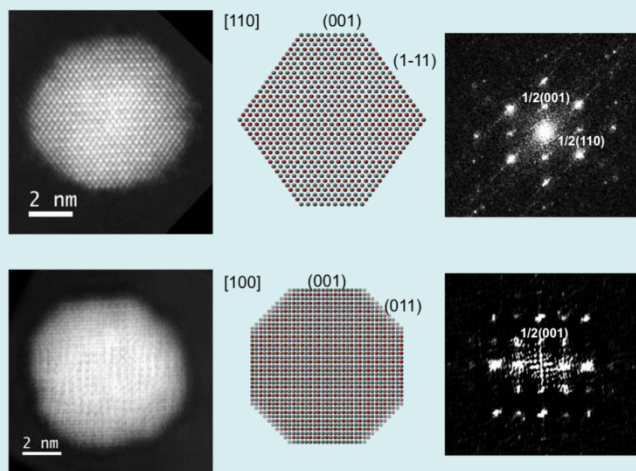
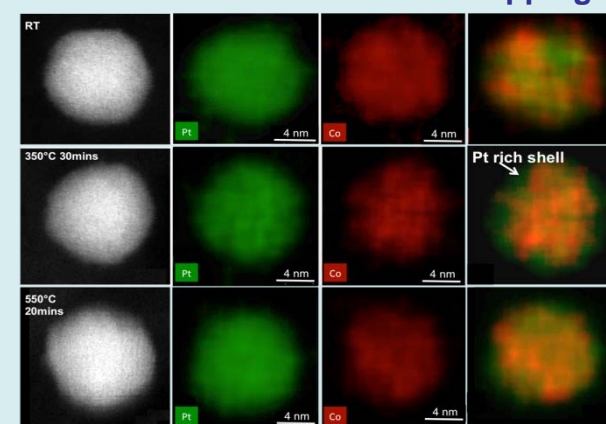
Annealing sequence of Pt₃Co NP



HAADF at different T and t(min)



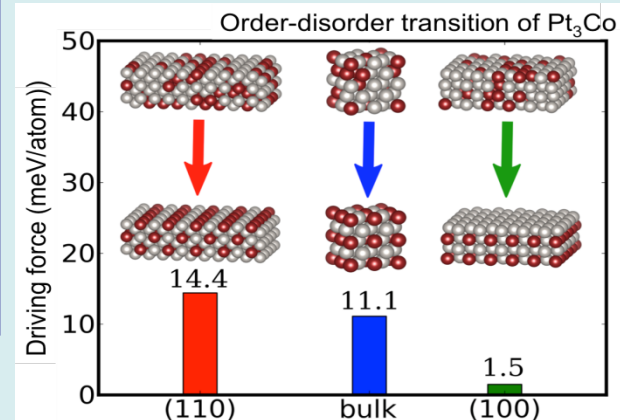
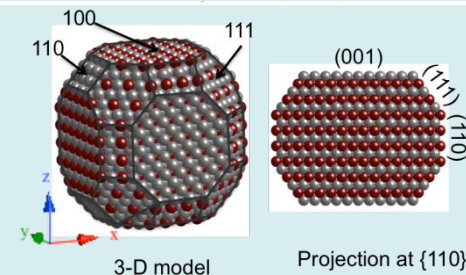
HAADF and EDS elemental mapping



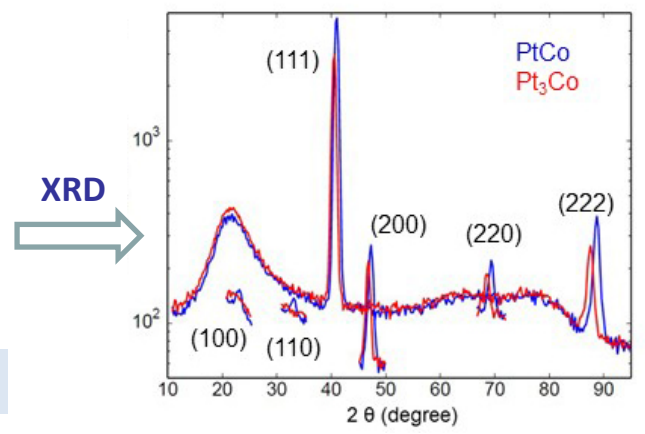
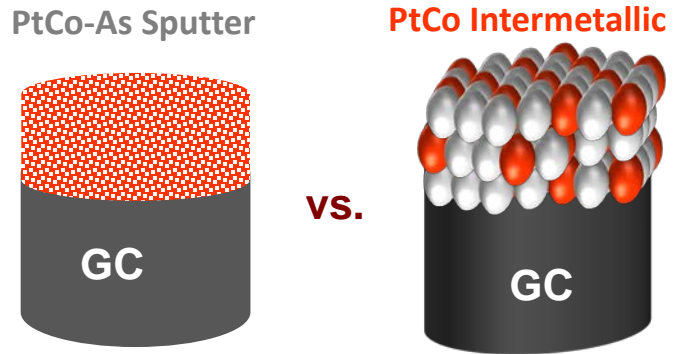
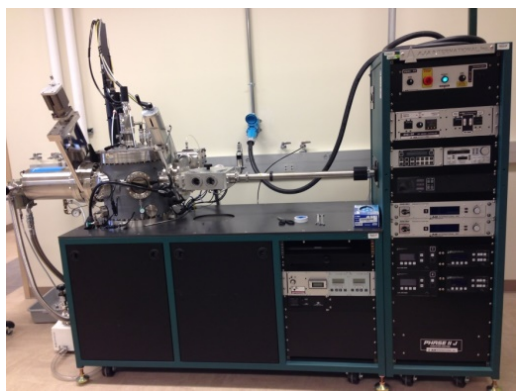
Dynamic of structural and chemical evolution at the atomic scale of Pt₃Co NPs during in-situ annealing
distinct behavior at critical stages:

- {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 L₁₂ phase followed by pre-melting

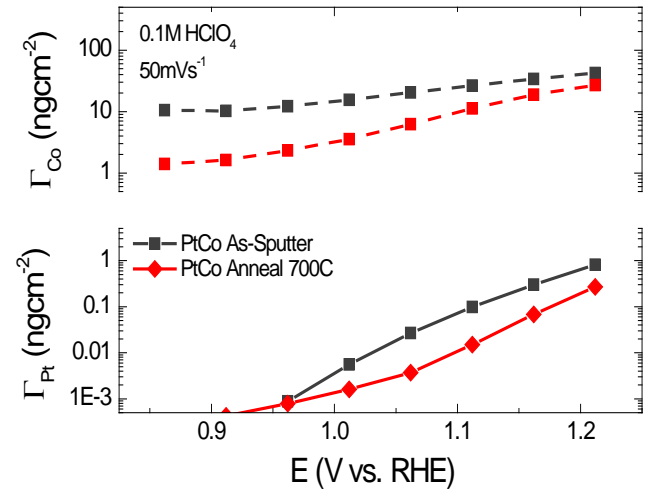
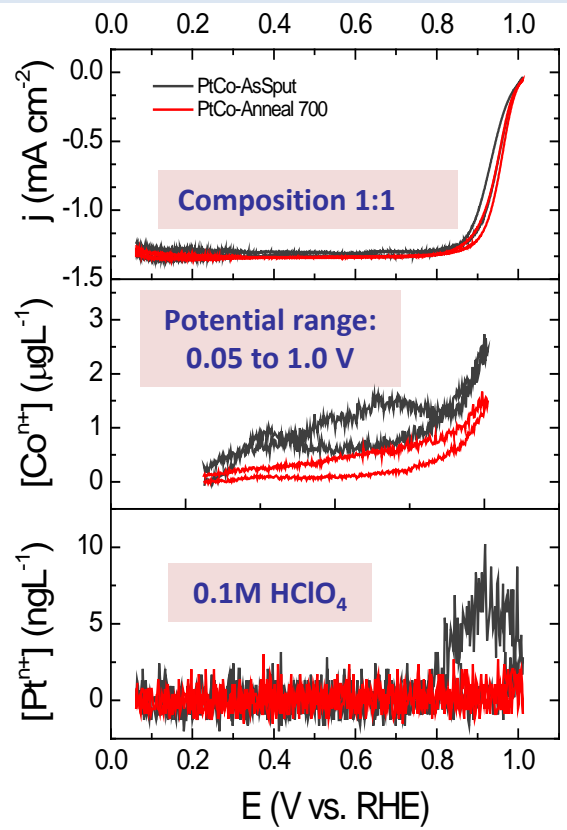
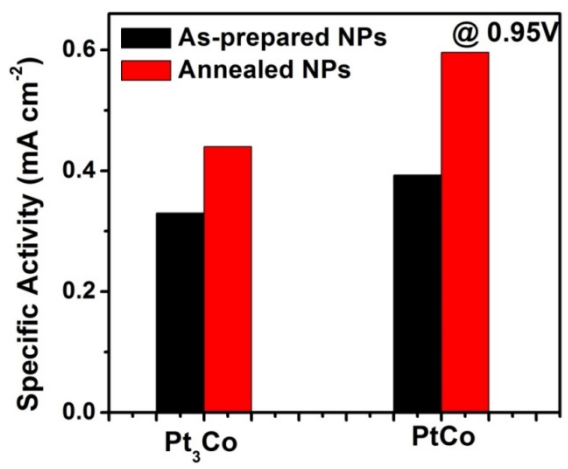
M. Chi, C. Wang, Y. Lei, G. Wang, K.L. More, A. Lupini, L.F. Allard, N.M. Markovic, and V.R. Stamenkovic
Nature Communications 6 (2015) No. 8925



Task 1 Introduction: *In-Situ* EC-ICP-MS Pt-Alloys Intermetallic

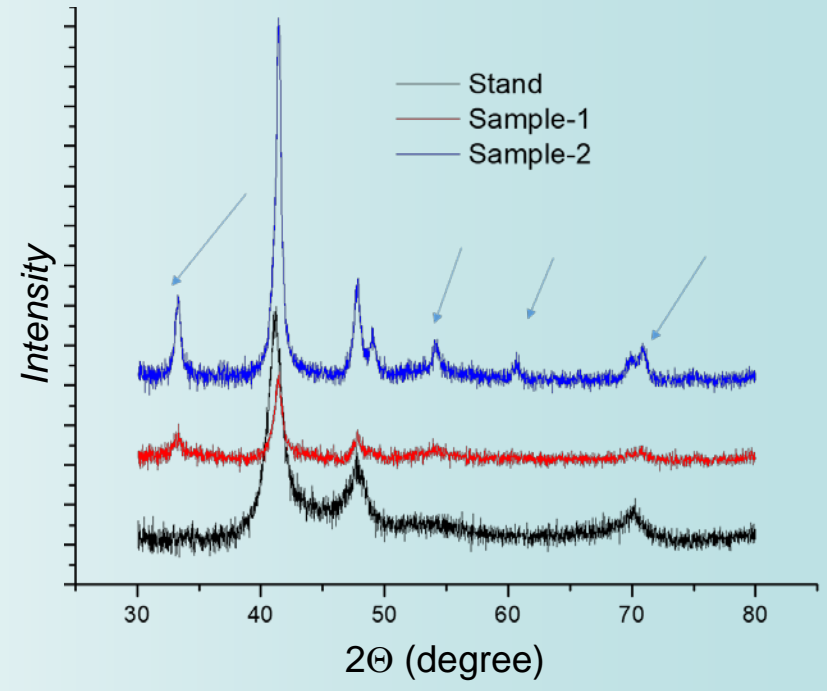
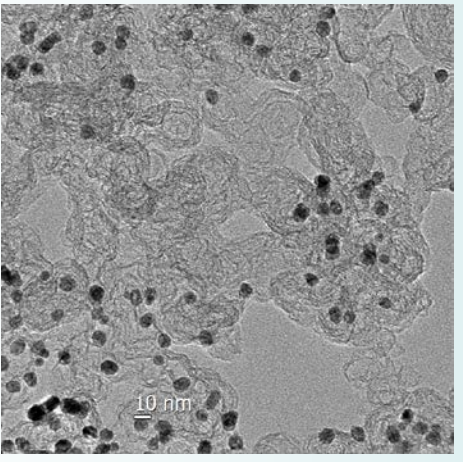
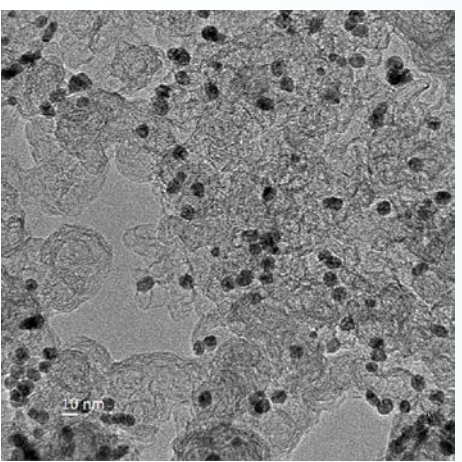
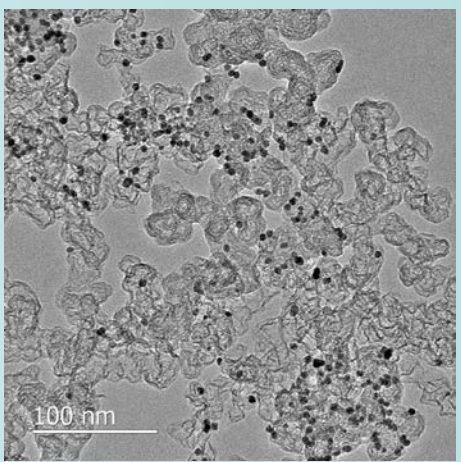
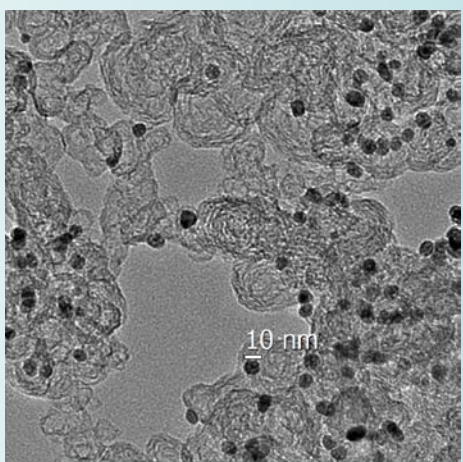
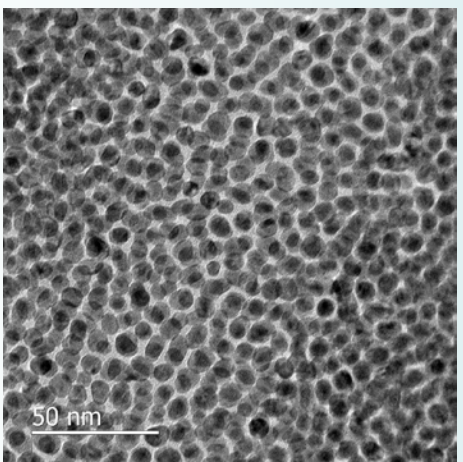
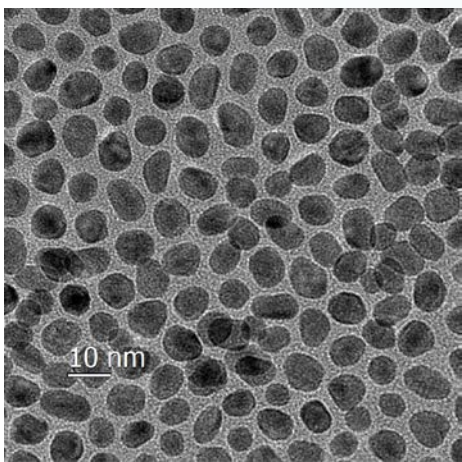


Annealing at 700°C = Intermetallic Phase

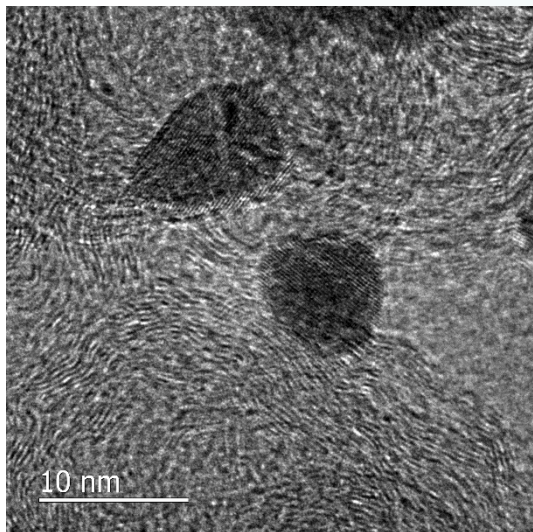


Benefit of intermetallic phase:

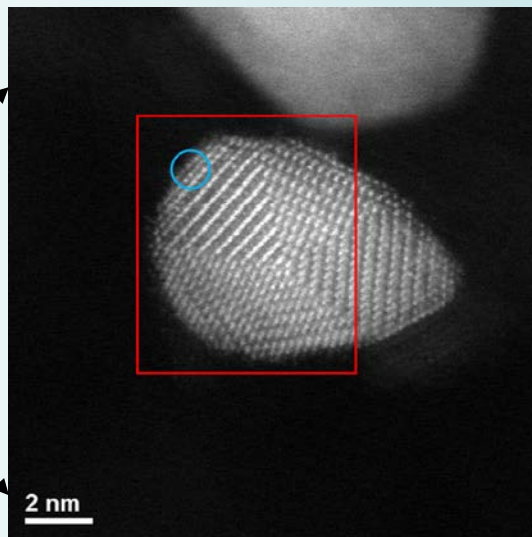
- Decreases dissolution of both Pt and Co
- Improvement in ORR activity



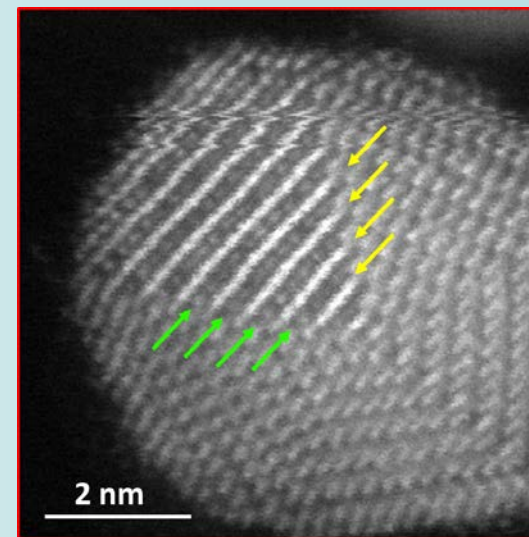
in collaboration with K.L. More, ORNL



Majority of NPs have L10 ordering
Pt:Co in powder 45:55



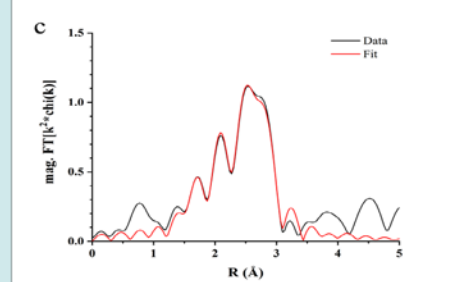
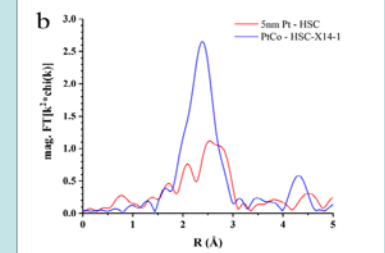
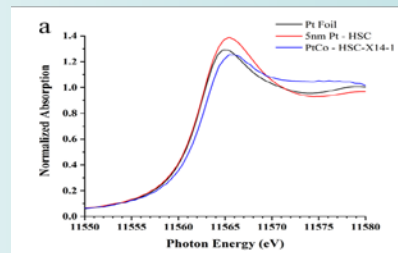
Surface facets demonstrate alternating Pt and Co (100) planes
Pt atoms – yellow arrows; Co atoms – green arrows



in collaboration with Debbie Myers, ANL - CSE

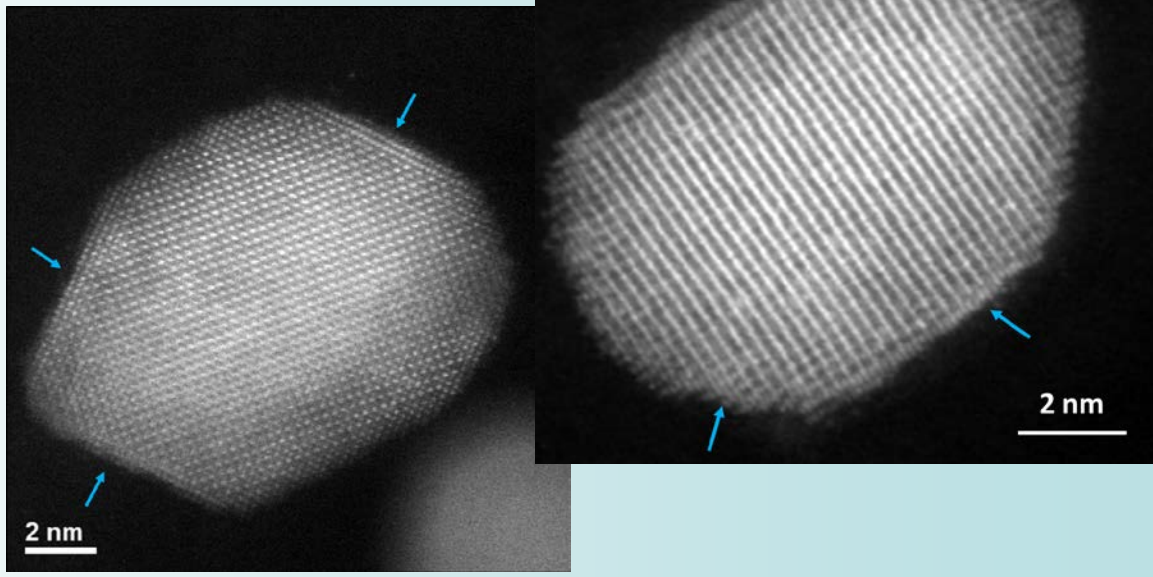
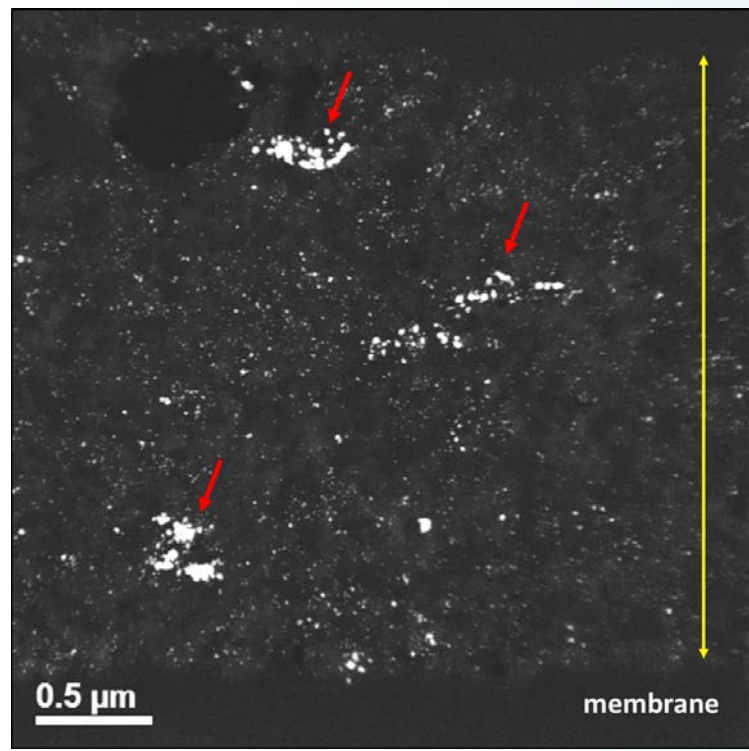
The annealed and carbon-supported intermetallic PtCo NPs were analyzed using Pt L3 edge X-ray absorption spectroscopy

Sample	Edge Energy (eV)	S_0^2	CN (Scattering Path)	R (Å)	σ^2 ($\times 10^3 \text{ \AA}^2$)	E_0 (eV)	R factor ($\times 10^2$)
Pt	11563.0	0.79	8.4 ± 0.6 (Pt-Pt)	2.76 ± 0.003	5.7 ± 0.04	6.1 ± 0.7	k ¹ : 0.3
			0.9 ± 0.3 (Pt-O)	2.01 ± 0.04	4.7 ± 4.9	6.9 ± 4.3	k ² : 0.2
							k ³ : 0.1
PtCo	11563.3	0.79	4.9 ± 1.1 (Pt-Pt)	2.69 ± 0.01	3.3 ± 1.0	5.2 ± 0.8	k ¹ : 0.08
			5.2 ± 0.7 (Pt-Co)	2.64 ± 0.01	4.6 ± 0.9	5.2 ± 0.8	k ² : 0.04
							k ³ : 0.08



in collaboration with Kenneth Neyerlin NREL and Karren More ORNL

Ultrasonic spray coated 0.9 I:C (D2020 ionomer)
Cathode loading 0.056mgPt/cm²



Pt-Skin shell formation (2-3 layers) obvious in CCL of fresh MEA
Loss of Co facilitates Pt-Skin formation on NP surfaces
Surface oxides less prevalent

CCL thickness ~2.5 mm
Wide cluster size distribution in CCL
loss of Co in ink/MEA preparation
Pt:Co 60:40

Task 2-3 Accomplishments and Progress: Scaled 8nm PtCo/HSC in 50 cm² MEA

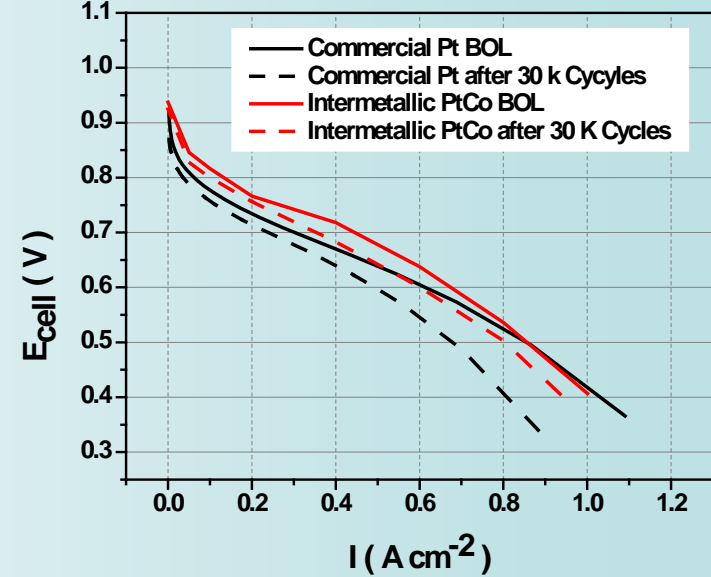
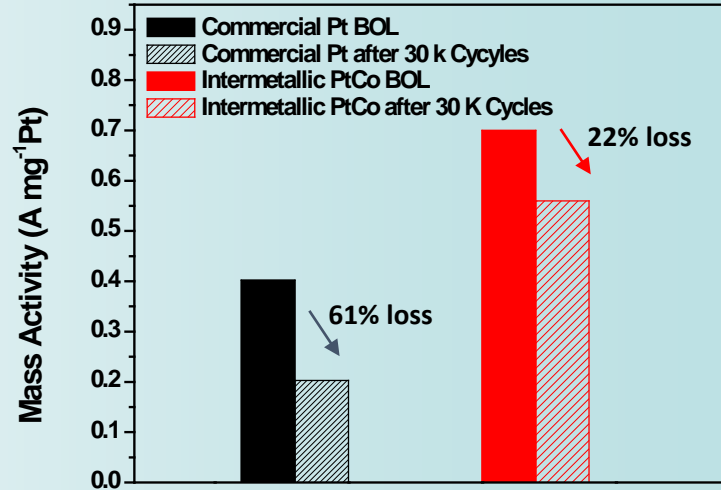
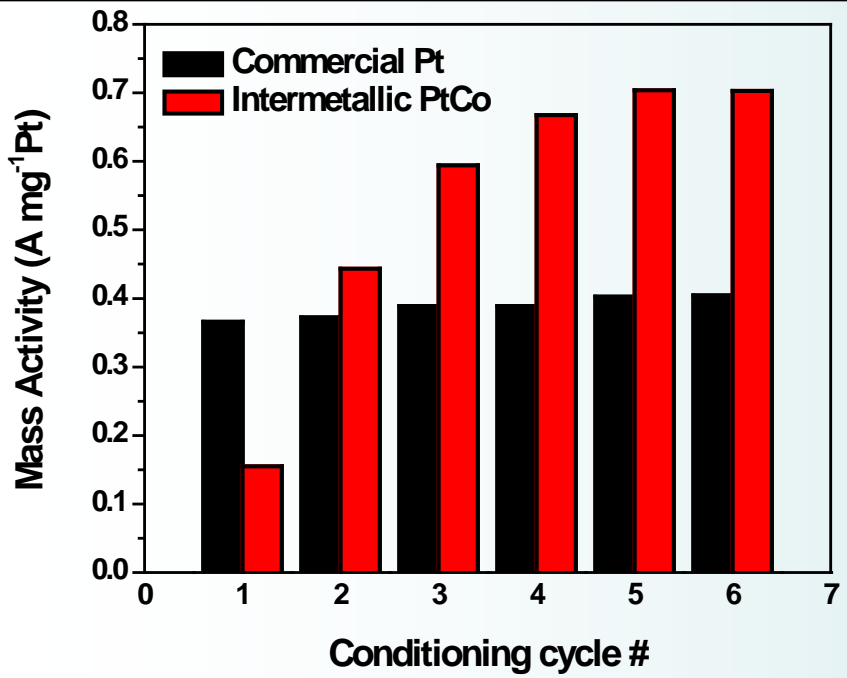
in collaboration with Kenneth Neyerlin, NREL

150 kPa, 100% RH, 80°C H₂/O₂, 50 cm², N211
 Ultrasonic spray coated 0.9 I:C (D2020 ionomer)
 Cathode loading 0.056mgPt/cm²

Developed intermetallic PtCo/HSC: $i_m^{0.9V} \sim 700 \text{ mA/mg}_{Pt}$

ECSA	(m ² /g)
before AST	34.5
after AST	28.6

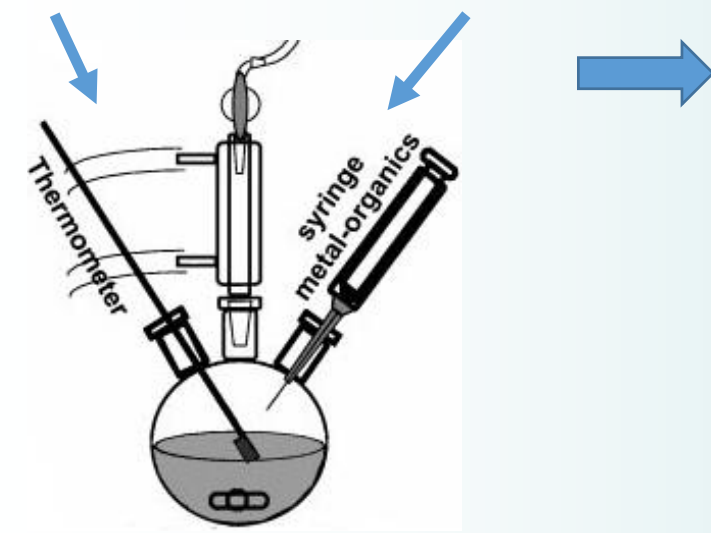
PtCo/C shows MA and ECSA that meets the DOE targets



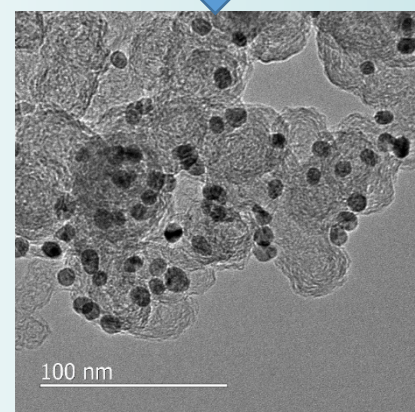
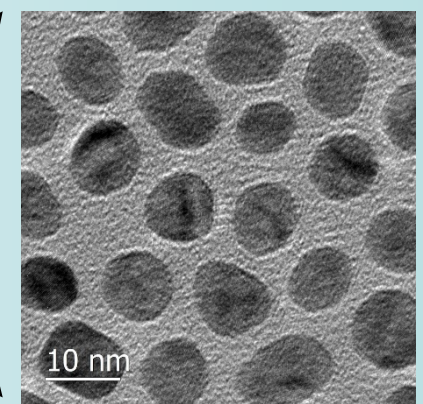
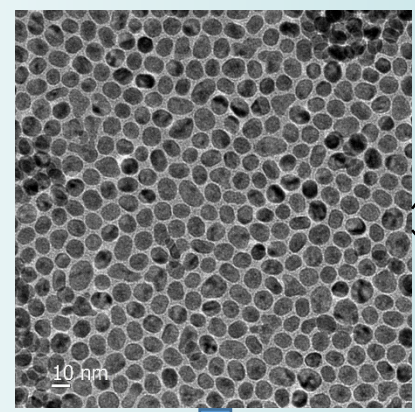
PtCo/C losses only 17% of ECSA and 22% of MA 30K cycles of AST - FCPAD protocol

5X Precursor

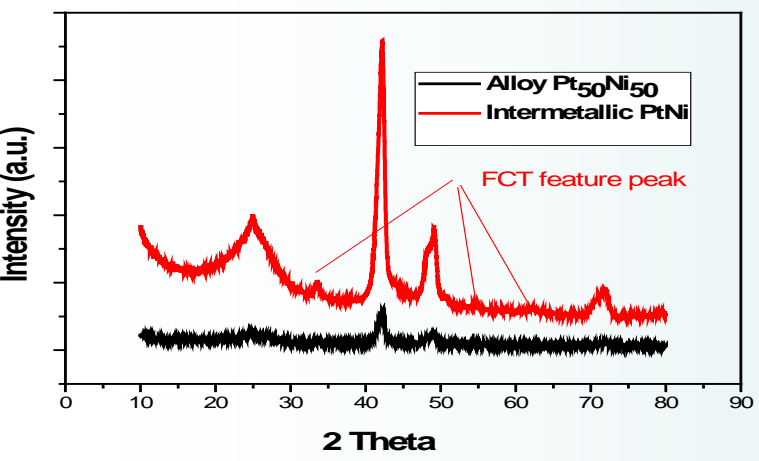
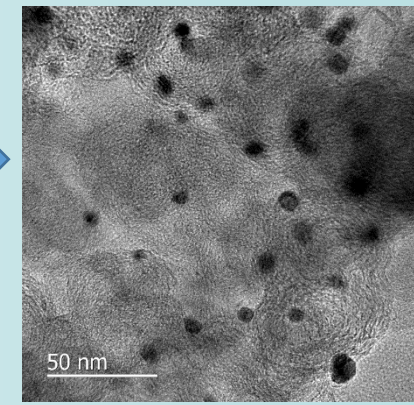
5X Solvent



PtNi/_{HSA}C



Δ High T



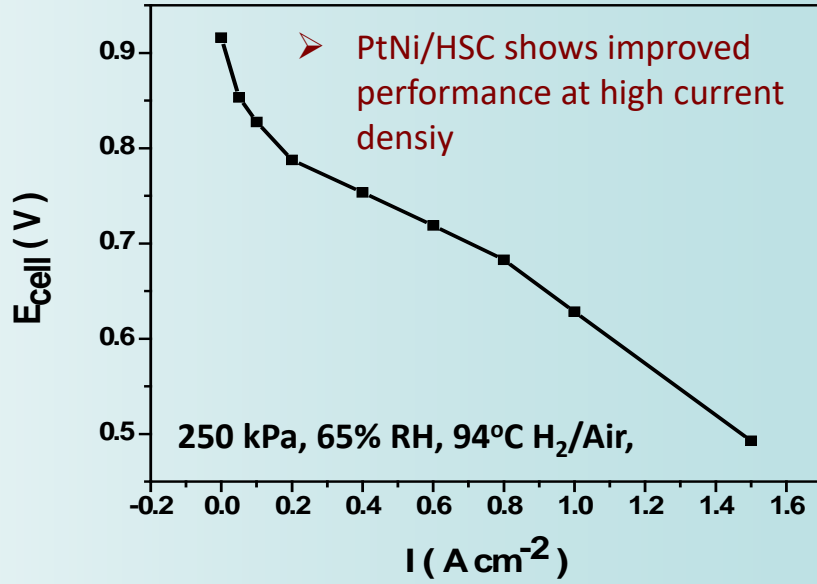
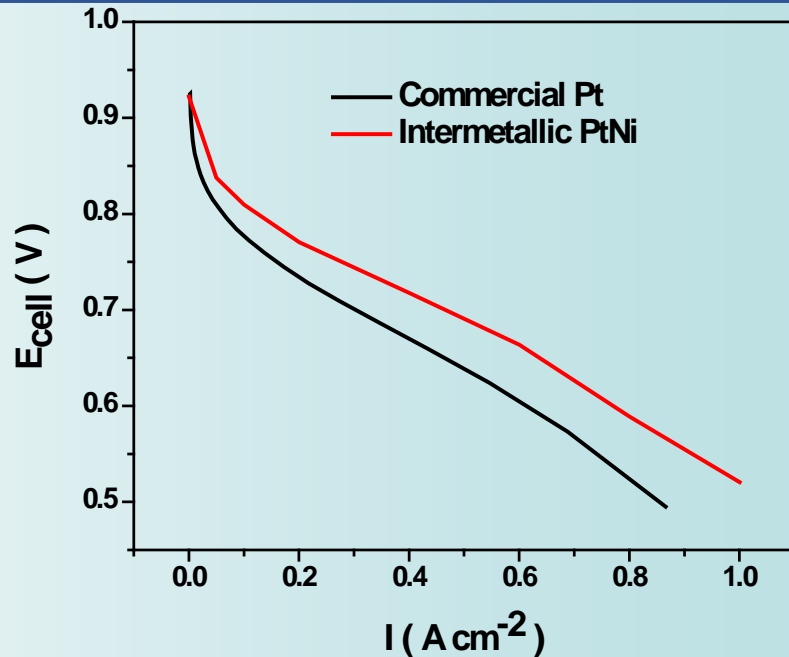
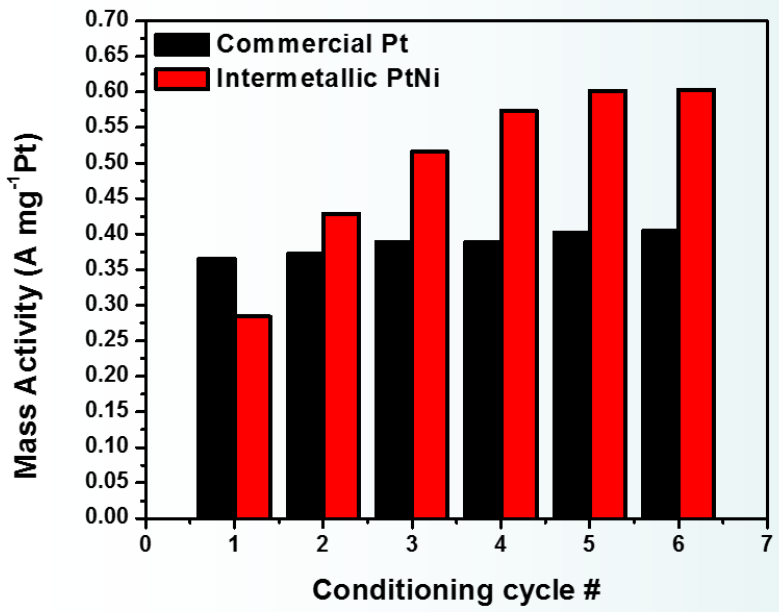
- PtNi NPs keep the same morphology fater annealing
- PtNi NPs no sintering after annealing
- PtNi NPs converted to intermetallic structure

in collaboration with Kenneth Neyerlin, NREL

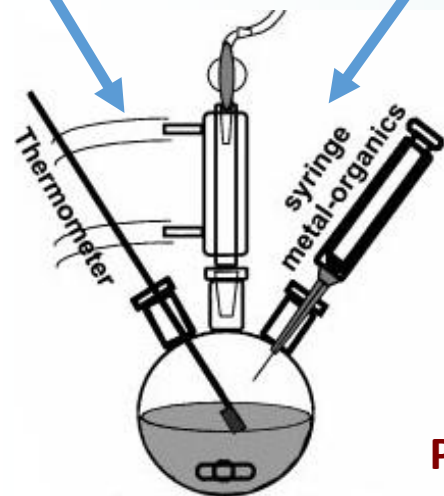
- 150 kPa, 100% RH, 80°C H₂/O₂, 50 cm², N211
- Ultrasonic spray coated 0.9 I:C (D2020 ionomer)
- Cathode loading 0.07 mgPt/cm²

Developed PtNi/HSC: $i_m^{0.9V} \sim 600 \text{ mA/mg}_{Pt}$

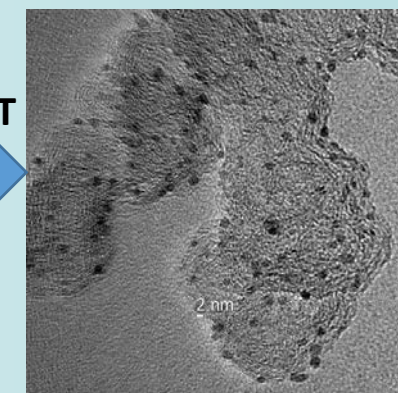
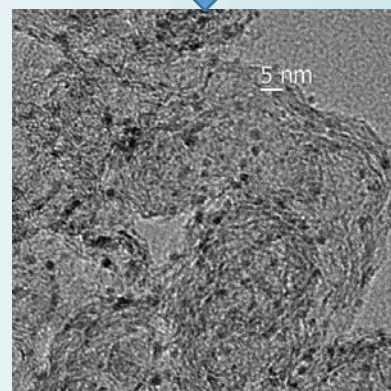
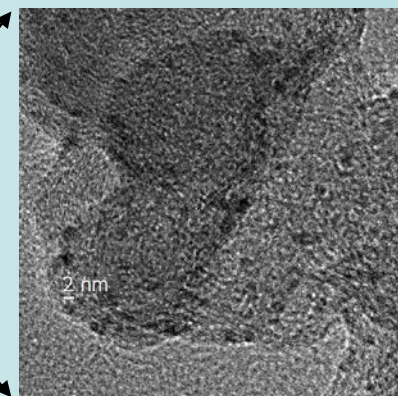
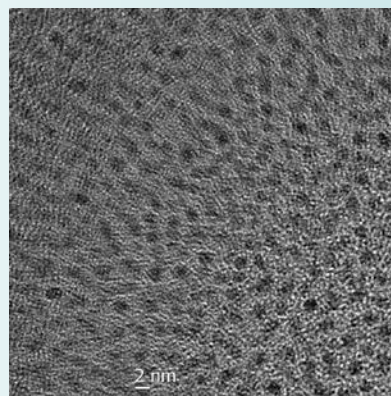
	(m ² /g)
ECSA	35.0



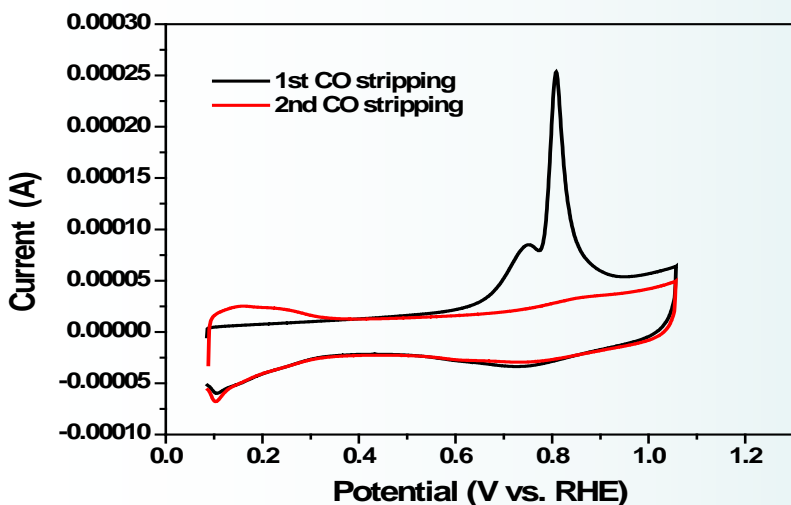
5X Precursor 5X Solvent



Pt₃Co/HSA C



Δ High T



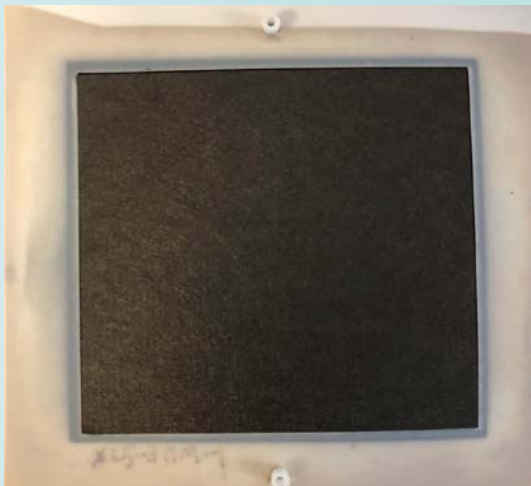
ECSA	(m ² /g)
before annealing	110
after annealing	98

- PtNi NPs keep the same morphology after annealing
- Minimum sintering after annealing

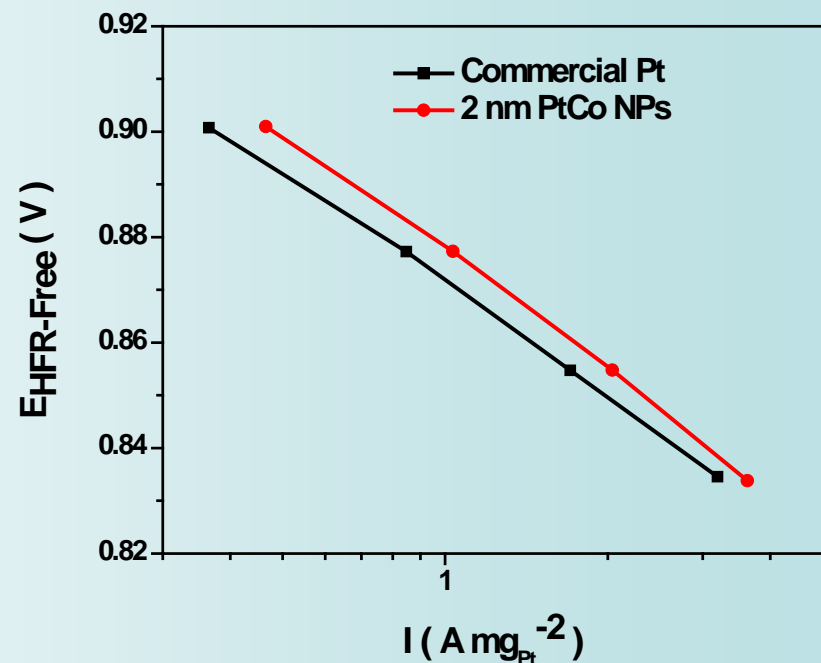
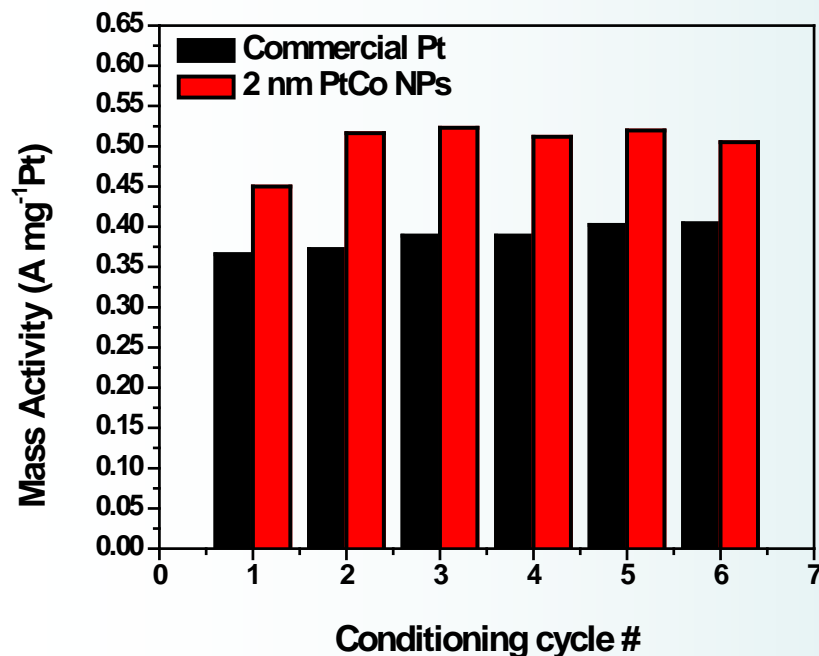
in collaboration with Kenneth Neyerlin, NREL

- 150 kPa, 100% RH, 80°C H₂/O₂, 50 cm², N211
- Ultrasonic spray coated at NREL 0.9 I:C (D2020 ionomer)
- Cathode loading 0.06 mgPt/cm²

Developed Pt₃Co/_{HSA}C: $i_m^{0.9V} \sim 520 \text{ mA/mg}_{Pt}$



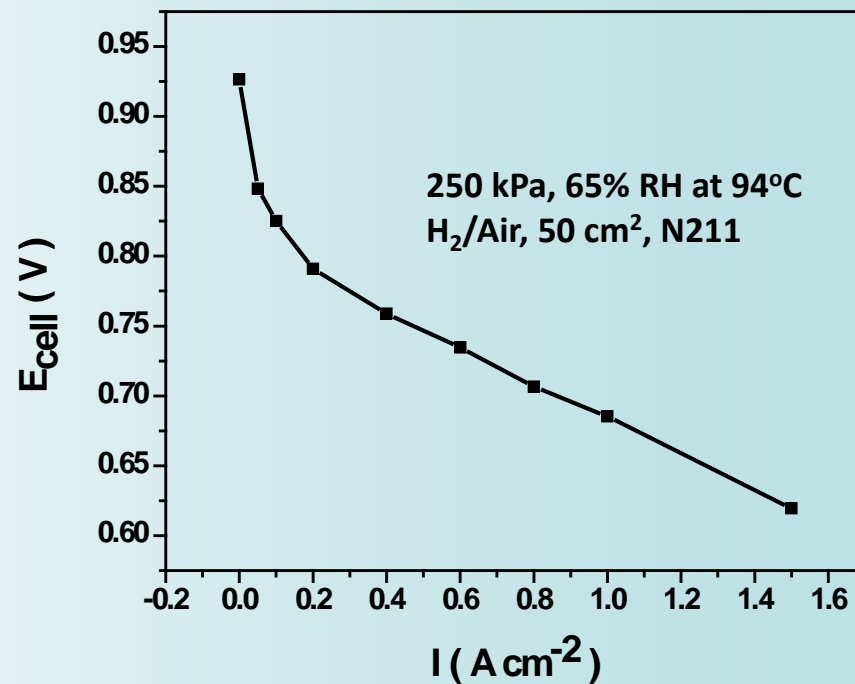
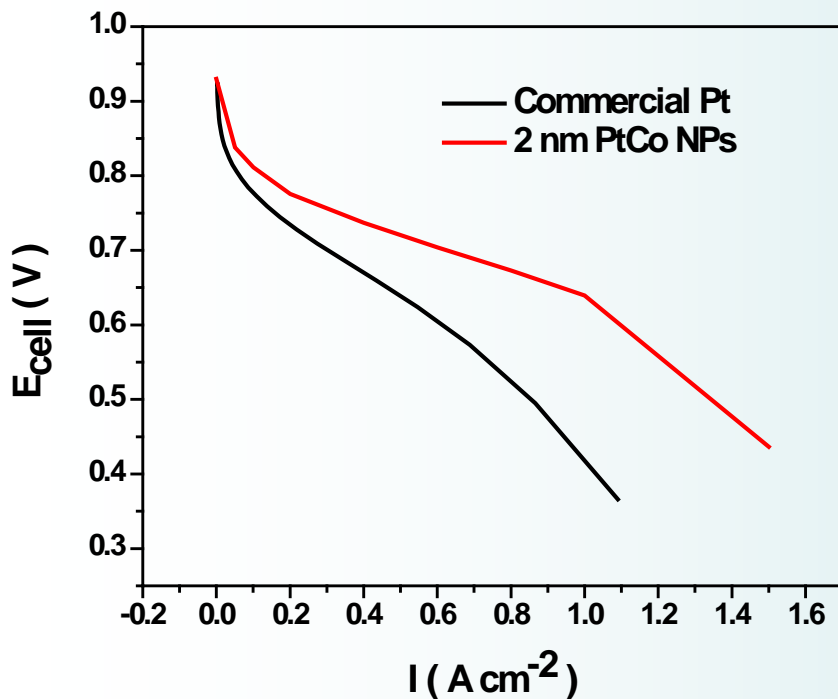
PtCo/C 2nm shows MA that meets the DOE target in 50 cm² MEA



in collaboration with Kenneth Neyerlin, NREL

- 150 kPa, 100% RH, 80°C H₂/Air, 50 cm², N211, 0.055 mg_{Pt}/cm²

	(m ² /g)
ECSA	56.0



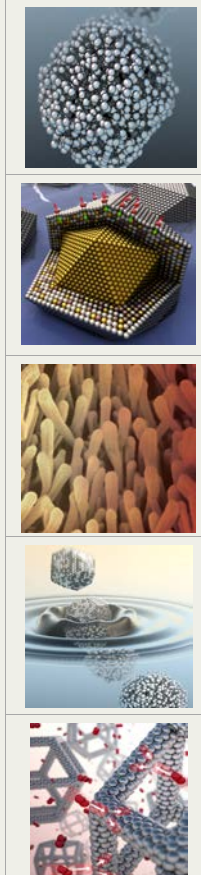
➤ **2nm Pt₃Co/HSC also shows improved performance at high current density**

Collaborations and Coordination

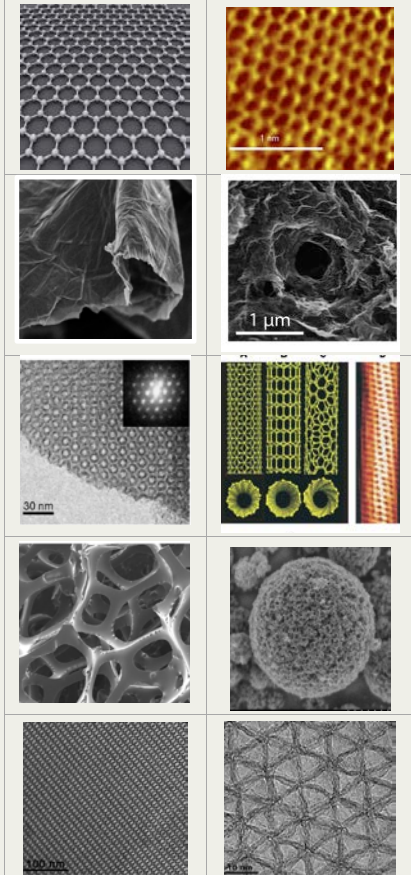
Argonne NATIONAL LABORATORY **Lead: design, synthesis, evaluation**

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

Low-PGM Alloys

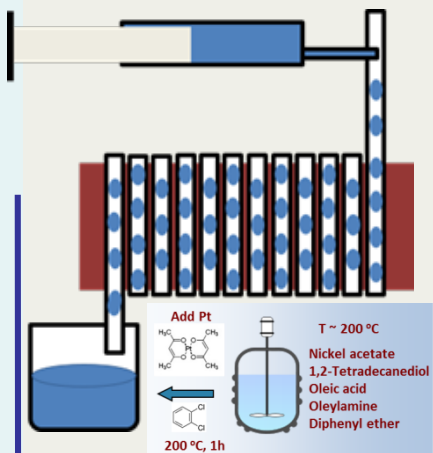


Advanced Catalyst Supports



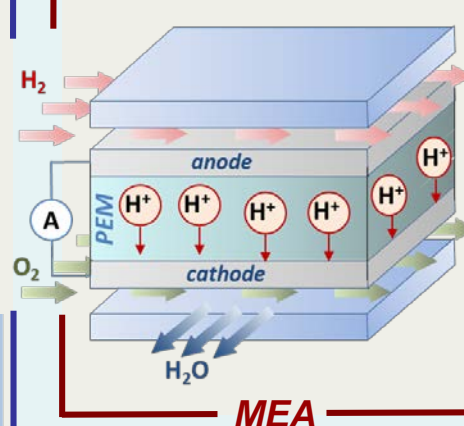
Low-PGM Alloy Catalysts

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



Catalysts Scale Up

Argonne NATIONAL LABORATORY **5 / 25cm² MEA**
 NREL NATIONAL RENEWABLE ENERGY LABORATORY **50cm² 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
- **Improved** ECSA by introduction of catalyst particles with small size

- **High Durability, High Duty, High ECSA** systems

Future work will depend on appropriations

Technology Transfer Activities

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) **NANOSEGREGATED SURFACES AS CATALYSTS FOR FUEL CELLS**

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

Paulus 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, U.S.A.

Paulus et al., "Oxygen Reduction on High Surface Area Pt-based Alloy Catalysts in Comparison to Well Defined Smooth Bulk Alloy Electrodes", *Electrochimica Acta*, 2002, pp. 3787-3798, vol. 47.

US 20110077147A1

(19) **United States**
(12) **Patent Application Publication**
Stamenkovic et al.

(10) Pub. No.: **US 2011/0077147 A1**
(43) Pub. Date: **Mar. 31, 2011**

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

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

Publication Classification

(51) Int. Cl. **H01M 4/88** (2006.01)
B01J 25/42 (2006.01)

(52) U.S. Cl. **502/191; 502/330; 502/326; 502/313**

US009179463B2

(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, Naperville, 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. **502/184; 502/185; 420/466; 420/507; 420/510; 420/512; 420/548; 420/570; 420/615; 420/603; 420/524; 420/527; 977/773; 977/810; 977/948**

(58) Field of Classification Search **502/184**

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**

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

C22C 5/02 (2006.01)
C22C 5/04 (2006.01)

(52) U.S. Cl. **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**

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

US009246177B2

(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 Stamenkovic, Naperville, IL (US); Chao Wang, Aurora, IL (US); Nenad M. Markovic, Hinsdale, IL (US)**

References Cited

U.S. PATENT DOCUMENTS

5,879,827 A 3,1990 Debe et al.
7,522,217 B2 11,2009 Debe et al.
7,471,770 B2 12,011 Stamenkovic et al.
2009/0247420 A1* 10,2009 Stamenkovic et al. 502/185

US10099207B2

(12) **United States Patent**
Stamenkovic et al.

(10) Patent No.: **US 10,099,207 B2**
(45) Date of Patent: **Oct. 16, 2018**

(54) **MULTIMETALLIC CORE/INTERLAYER/SHELL NANOPARTICLES**

(71) Applicant: **UChicago Argonne, LLC, Chicago, IL (US)**

(72) Inventors: **Vojislav Stamenkovic, Naperville, IL (US); Nenad Markovic, Hinsdale, IL (US)**

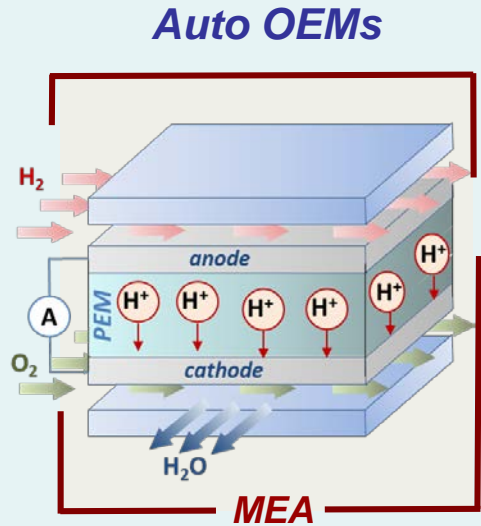
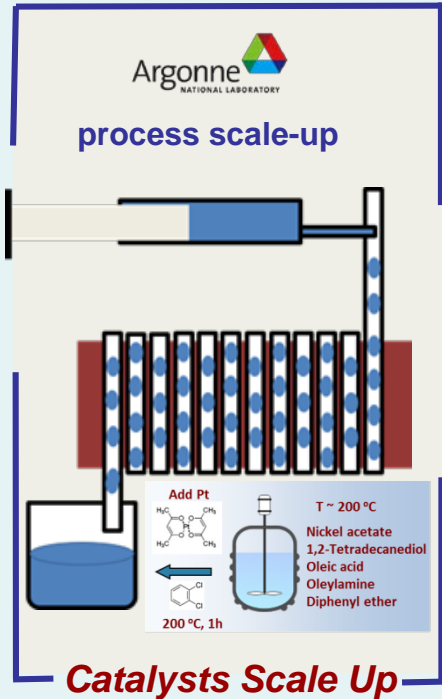
(52) U.S. Cl. **CPC 502/184; 502/185; 428/403; 428/548; 428/570; 420/524; 420/527; 420/466; 420/507; 420/510; 420/512**

(54) **MULTIMETALLIC CORE/INTERLAYER/SHELL NANOPARTICLES**

(71) Applicant: **UChicago Argonne, LLC, Chicago, IL (US)**

(72) Inventors: **Vojislav Stamenkovic, Naperville, IL (US); Nenad Markovic, Hinsdale, IL (US)**

(52) U.S. Cl. **CPC 502/184; 502/185; 428/403; 428/548; 428/570; 420/524; 420/527; 420/466; 420/507; 420/510; 420/512**



FY19

1 NDA signed

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

SUMMARY

Approach

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

Accomplishments

- Established dissolution rates of Pt for different particle size and loadings of Pt on carbon
- Resolved the mechanism of diminished Pt dissolution for Au subsurface
- Designed 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 Pt₃Au/C NPs
- Well-Defined Pt-Alloy intermetallic systems are more active and durable vs. solid-solution Pt-Alloys
- Scaled several nanoarchitectures at the gram level quantities
- Compared HSA carbon vs. Vulcan
- Approached highly durable systems with low NP diameter ~2nm
- PtAu, PtCo 5nm, PtCo 2nm, PtNi 5nm, PtNi/PtCo intermetallic exceeded DOE 2020 Technical Target in 50 cm² MEA
- Two patent applications in FY19, 3 articles submitted and 3 presentations at conferences

Collaborations

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

Full time postdocs:

Dr. Haifeng Lv (RDE, scale up 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)

***Publications and
Presentations***

***3 Presentations
1 Patent Issued
3 Patent Applications***