Argonne NATIONAL LABORATORY

2019 DOE Hydrogen and Fuel Cells Program Review

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

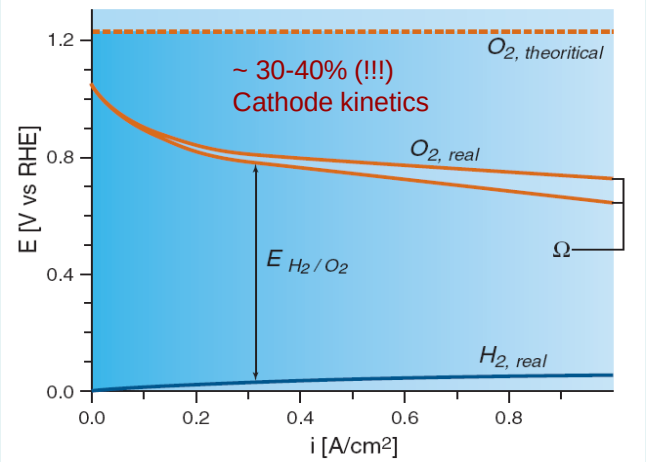
Timeline

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

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} / cm^2)

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***

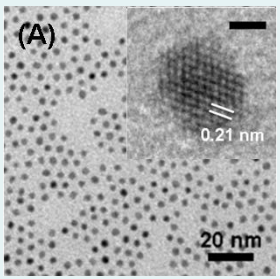
Table 3.4.13 Technical Targets: Electrocatalysts for Transportation Applications[h]

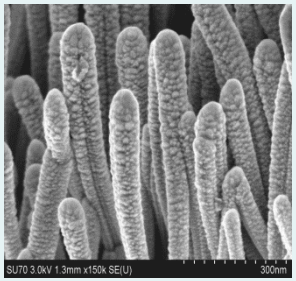
Characteristic	Units	2011 Status	2020 Targets
Platinum group metal total content (both electrodes)[a]	g / kW (rated)	0.19[b]	0.125
Platinum group metal (pgm) total loading[a]	mg PGM / cm^2 electrode area	0.15[b]	0.125
Loss in initial catalytic activity[c]	% mass activity loss	48[b]	<40
Electro catalyst support stability[d]	% mass activity loss	<10[b]	<10
Mass activity[e]	A / mg Pt @ 900 $mV_{iR\text{-}free}$	0.24[b]	0.44
Non-Pt catalyst activity per volume of supported catalyst[e, f]	A / cm^3 @ 800 $mV_{iR\text{-}free}$	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}/cm^2
- Loss in initial mass activity
  2020 DOE target <40%
- Mass activity @ $0.9V_{iR\text{-}free}$
  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

A N L

PEMFC Cathode Catalysts Development

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

Task 1º

EC

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

Task 2º

DM

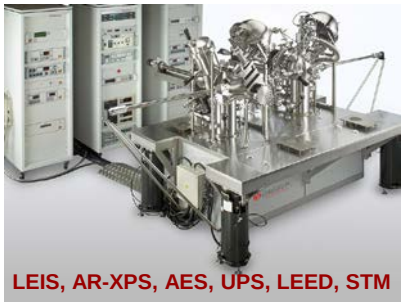
durability evaluations by in-situ EC - ICP/MS:
- Crafted electrochemical AST - E/V protocols
- atomic scale precision to follow dissolution
- nano-, meso- and thinfilm catalysts
- size, shape, composition tuning
- structure: intermetallic, core/interlayer/shell

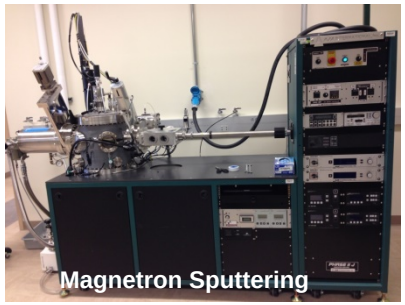
Task 3º

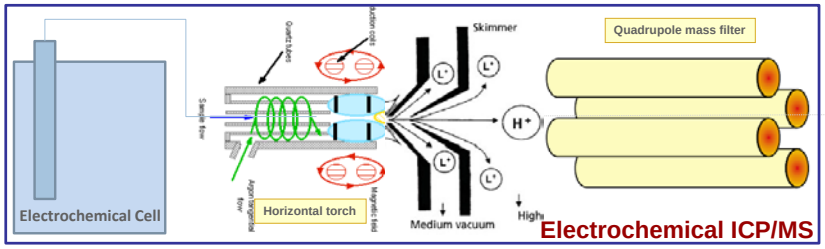
SN

synthesis of advanced catalyst-support systems:
- 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

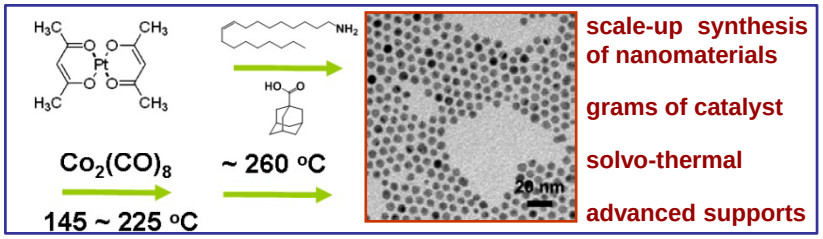
TASK 1&2







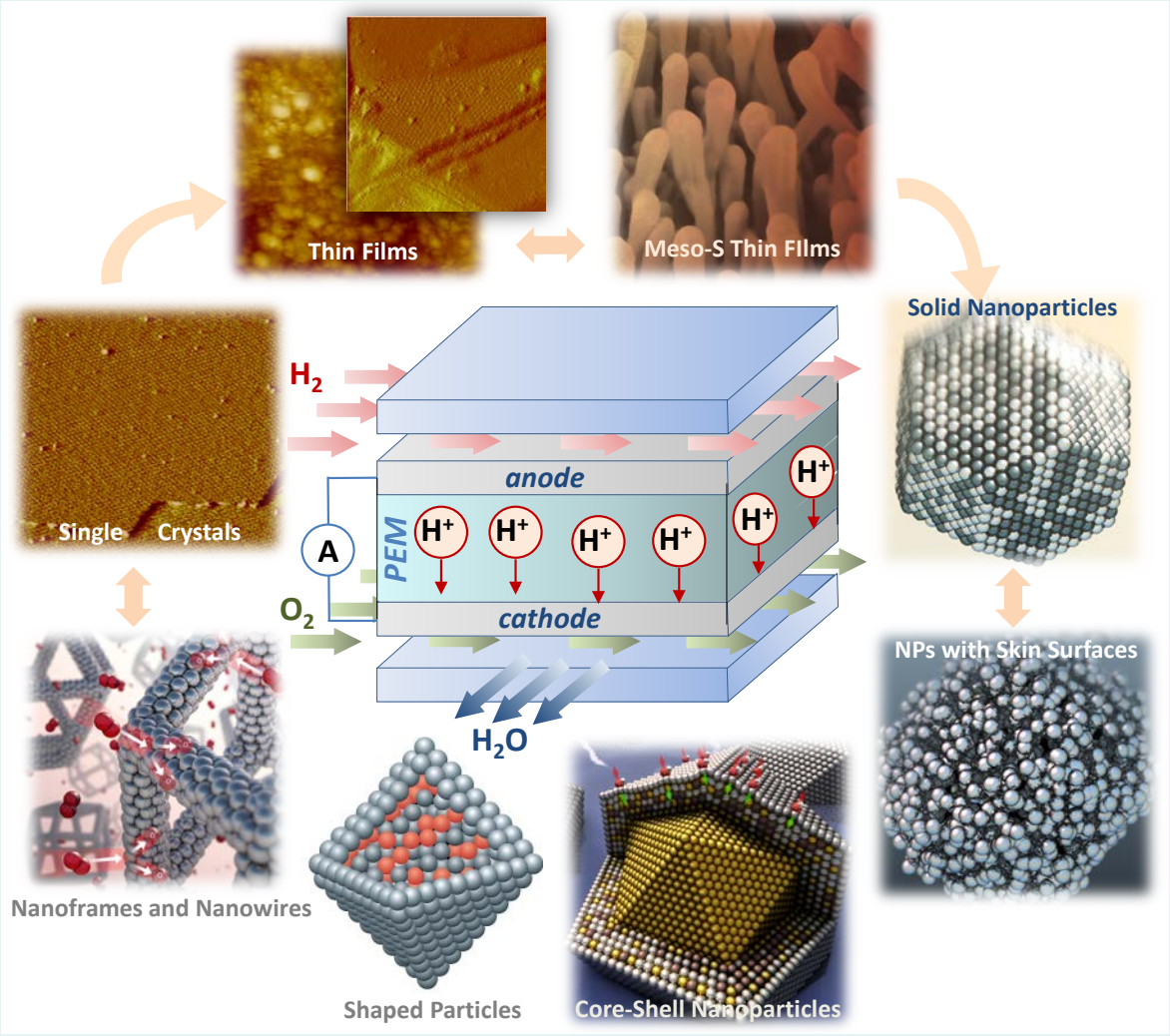
TASK 2&3



TASK 1&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	FY19 | FY20 | FY21			
Active Task	Q1 Jan	Q2 Apr	Q3 July	Q4 Oct
T1 EC				
T2 DM				
T3 SN				

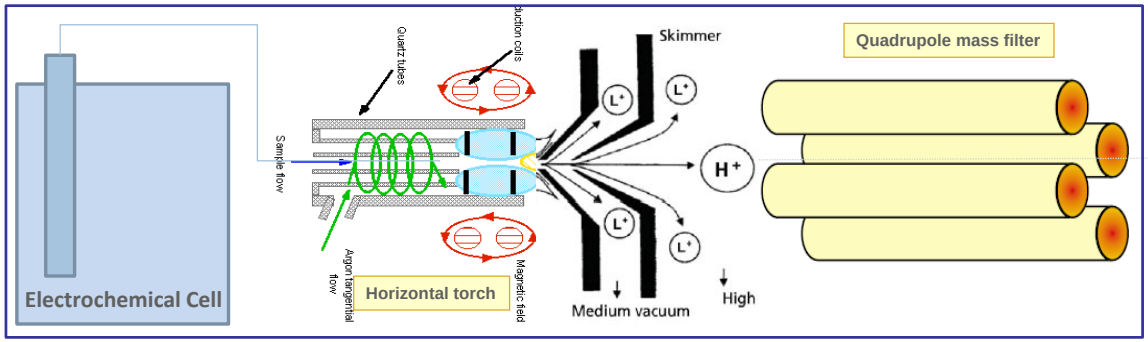
Task 1 - Electrochemical Characterization (EC)

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**

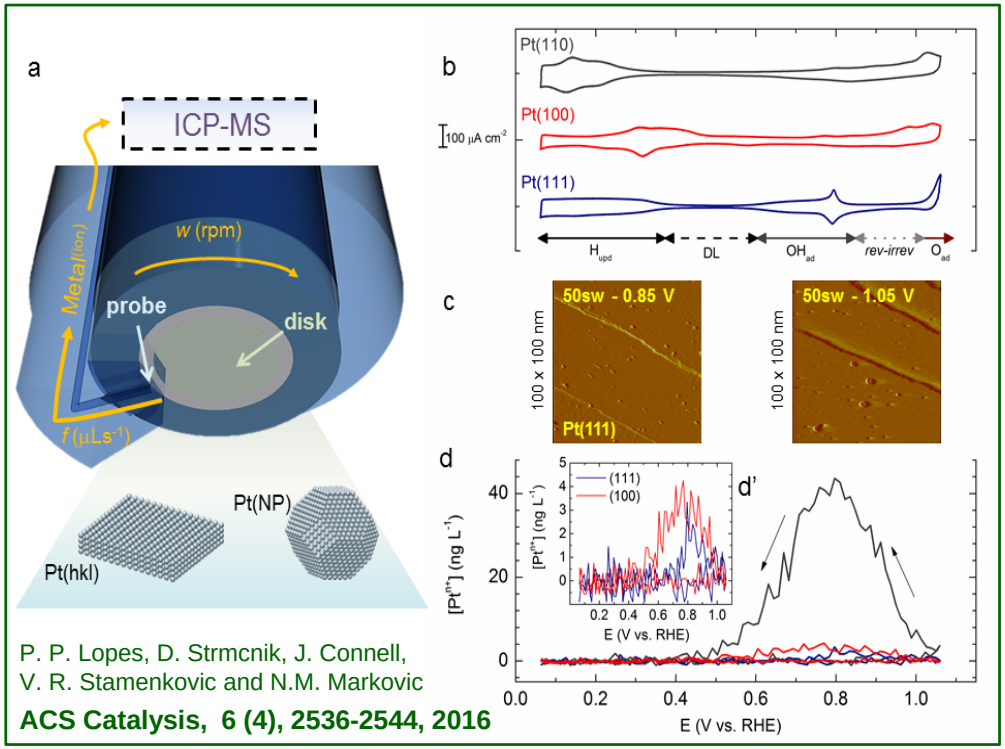
Task 1 Introduction: *RDE-ICP/MS of* Pt/C Nanoparticles



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

In-Situ RDE-ICP/MS

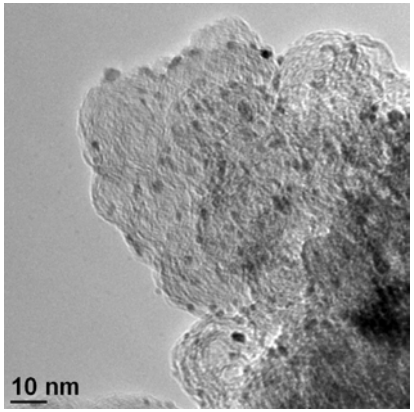


P. P. Lopes, D. Strmcnik, J. Connell, V. R. Stamenkovic and N.M. Markovic

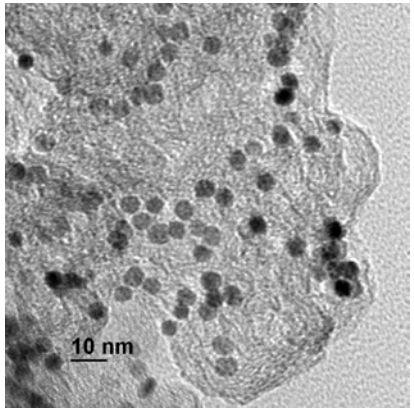
ACS Catalysis, 6 (4), 2536-2544, 2016

Correlation between Surface Structure - Activity – Dissolution

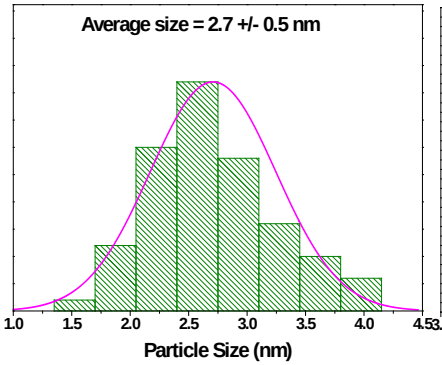
Monodisperse 20% Pt/C NPs 3 and 5nm

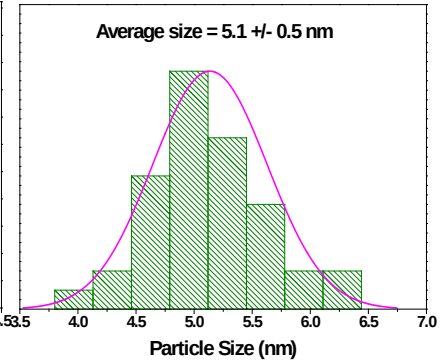


2.7+/-0.5 nm

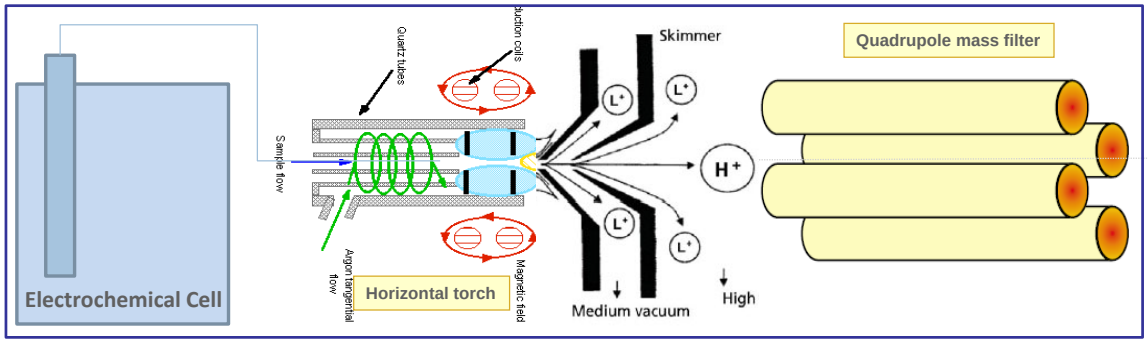


5.1 +/- 0.5nm





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



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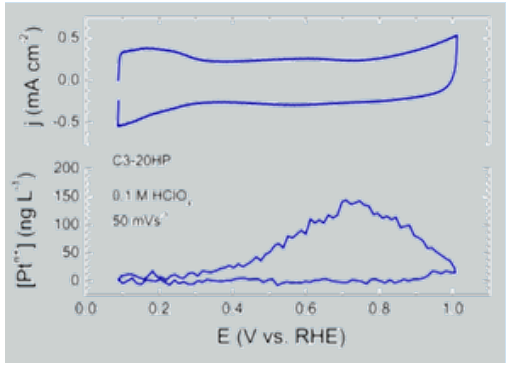
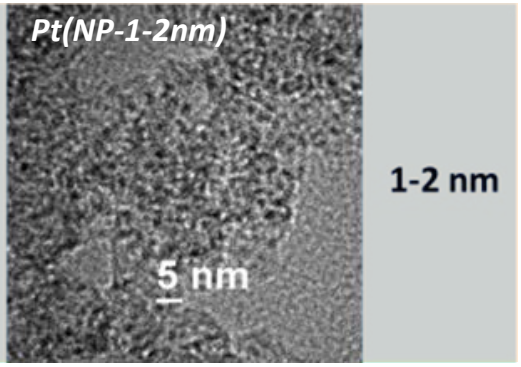
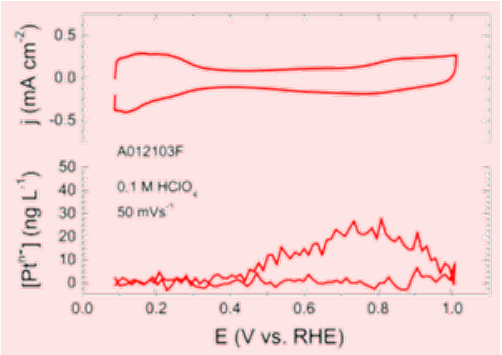
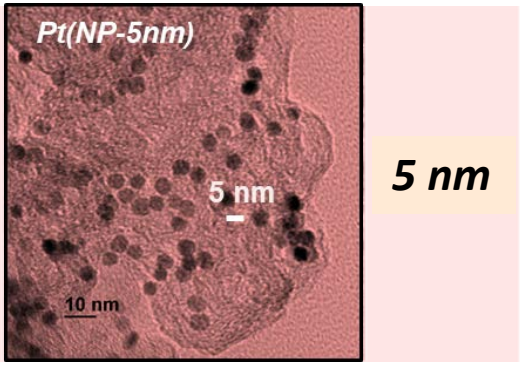


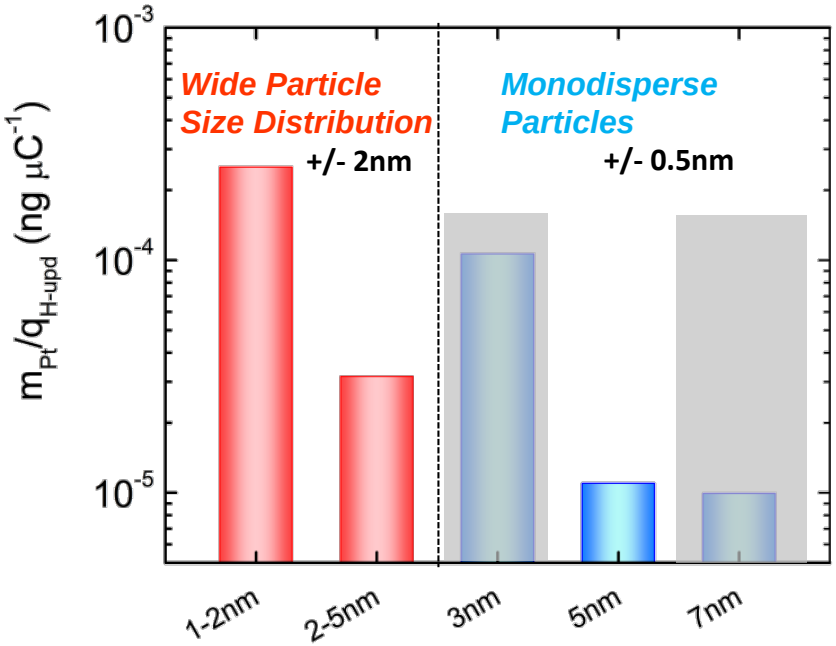






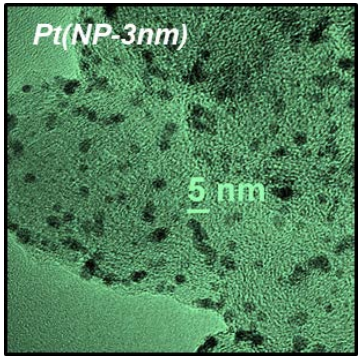
Dissolution Rates

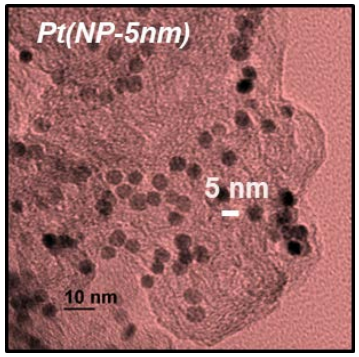
CV up to 1V @ 50m,Vs^{-1}

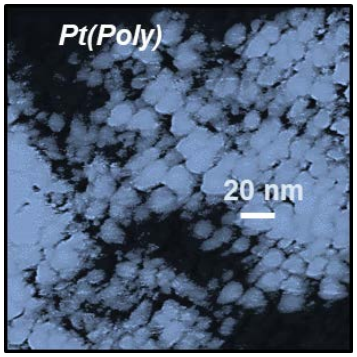


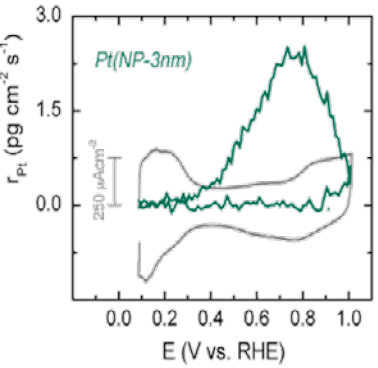
Control of particle size distribution and metal loading have important role for dissolution rate

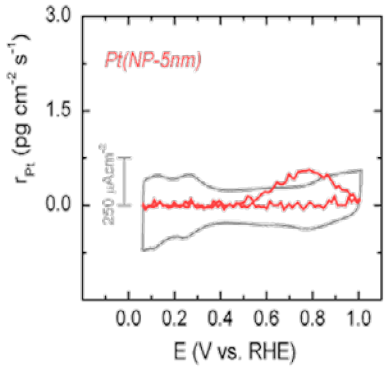
Task 1 Accomplishments and Progress: *RDE-ICP/MS of* Pt/C Nanoparticles

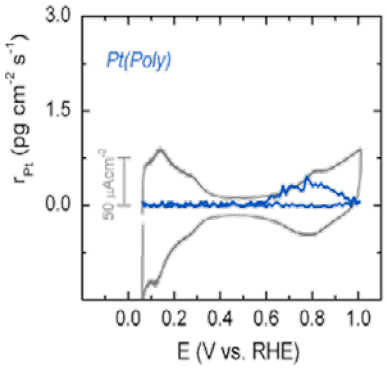


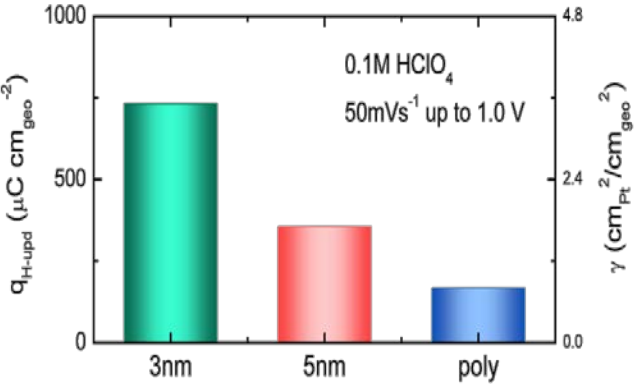


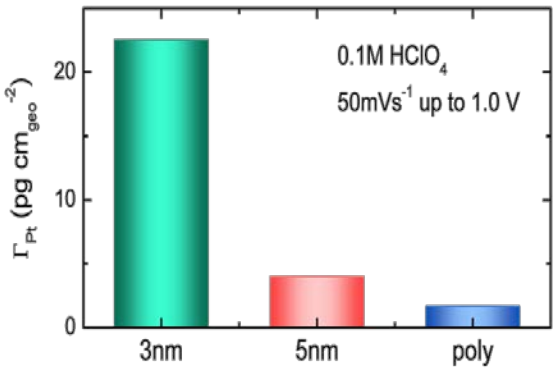












Dissolution Rates Dependency

(in addition to applied electrode potential)

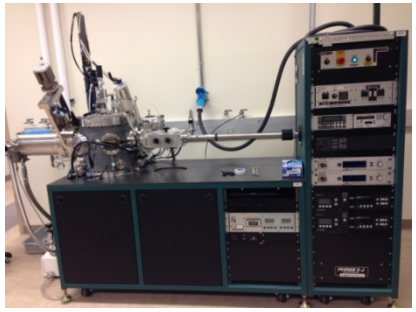
1) Particle Size:
Smaller particles have higher dissolution rates due to surface atoms with low coordination

2) Metal Loading:
Higher loading of metallic NPs onto carbon support leads to higher dissolution rates

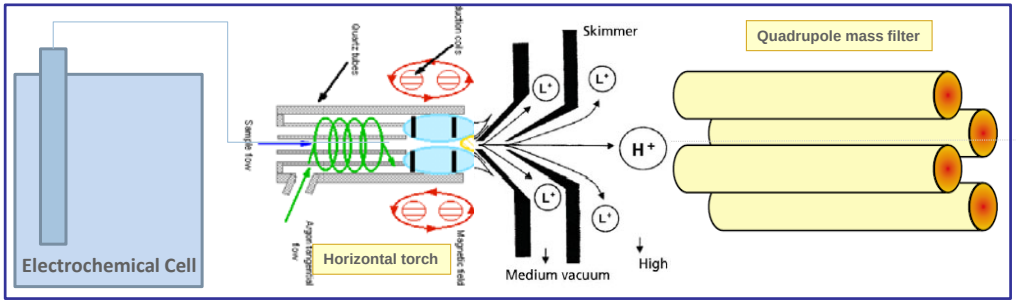
3) Support:
Dissolved Pt atoms can be redeposited in high surface area carbon support

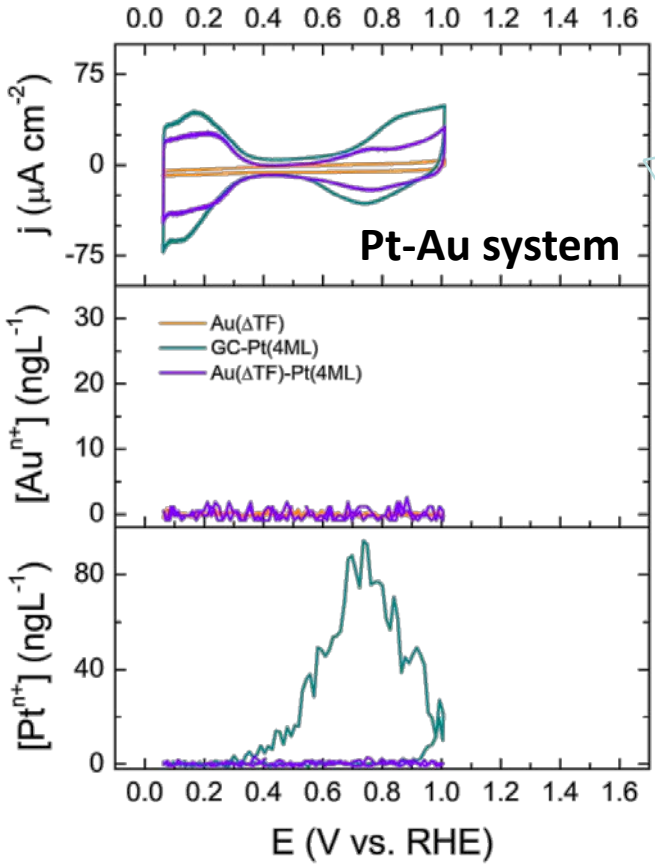
4) Electrolyte:
Dissolved amount Pt of atoms varies with electrolyte and presence of different anions

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

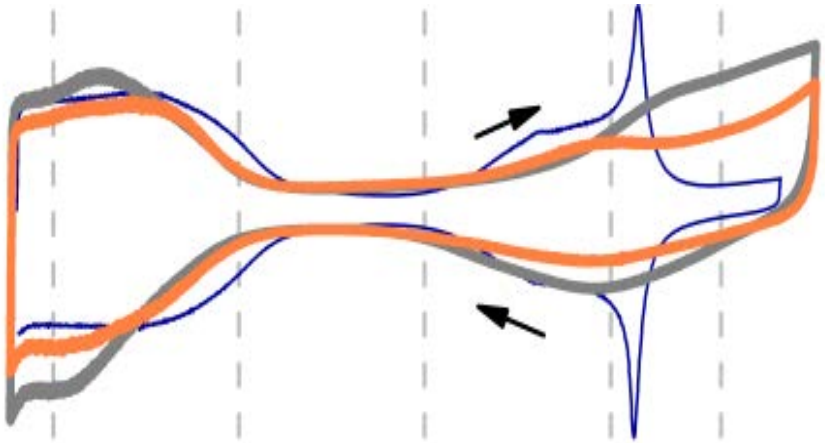


Au Substrate





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



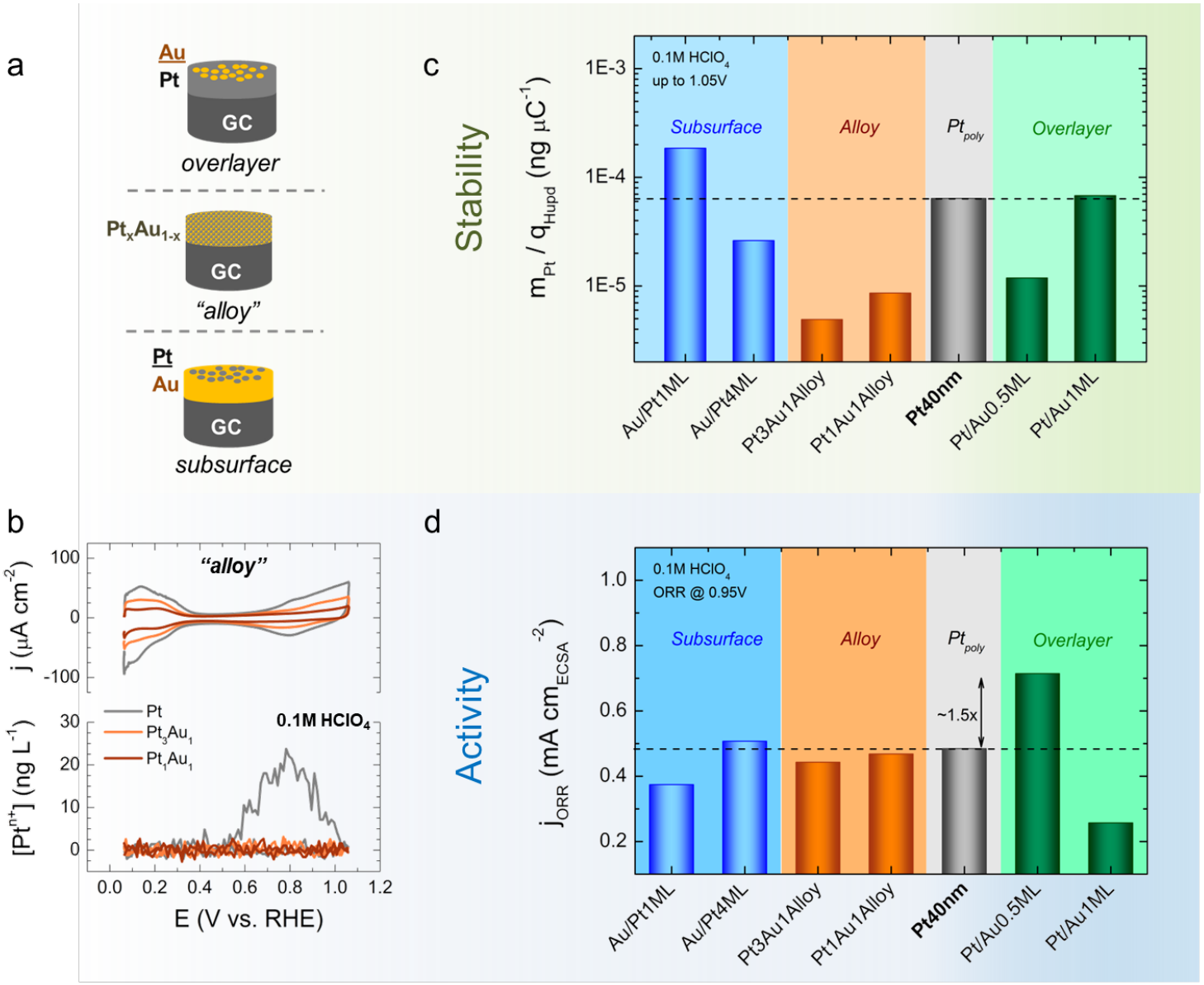
Potential range: 0.05 to 1.0 V

0.1M $HClO_4$

- 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

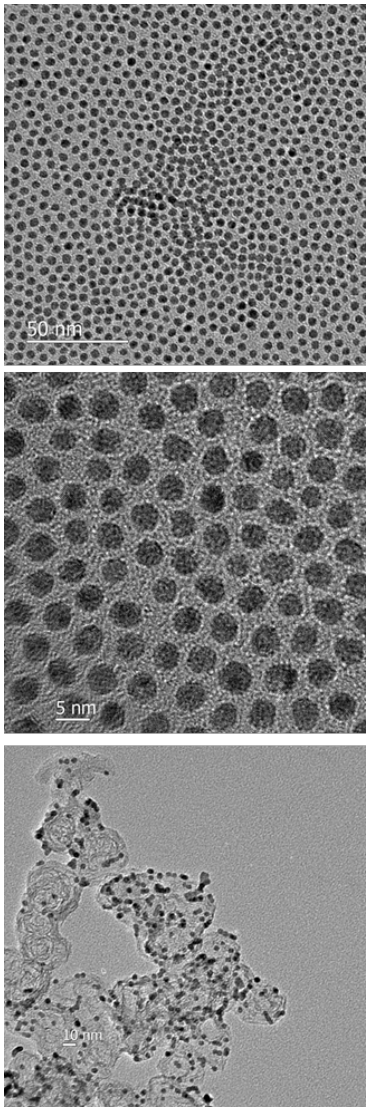


Different arrangements between Pt and Au have been tested for dissolution rates that has been normalized for the actual Hupd from Pt surface atoms

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

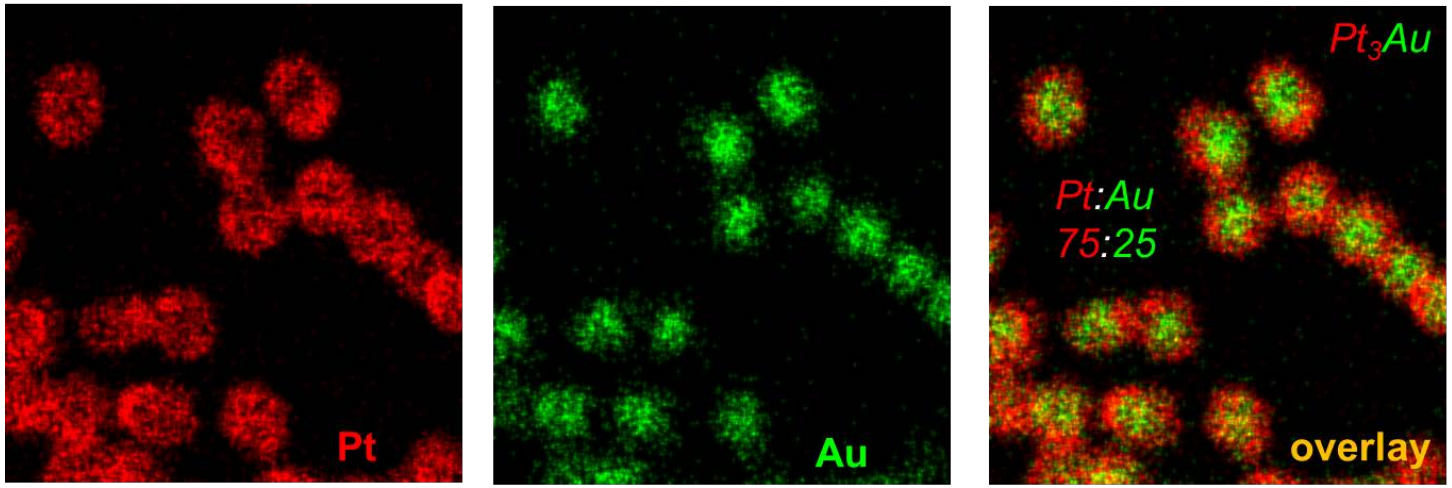
Task 2 Introduction: Pt_3Au synthesis and characterization

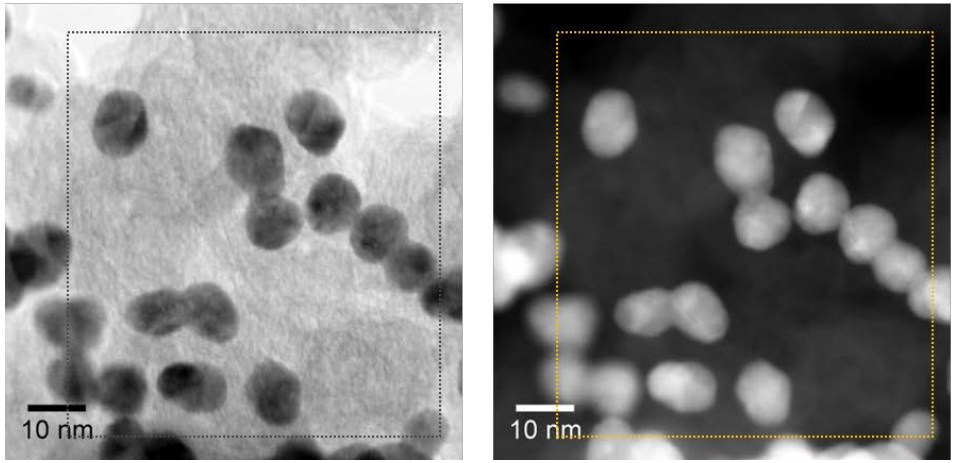
in collaboration with K.L. More, ORNL



High-Precision Synthesis

monodisperse NPs with uniform compositional profile



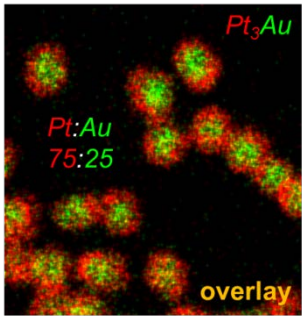


5 nm

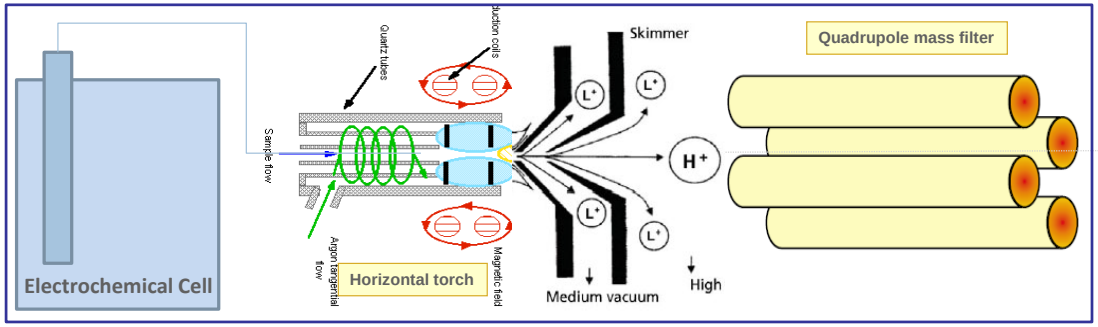
Pt shell Au core nanoparticles:

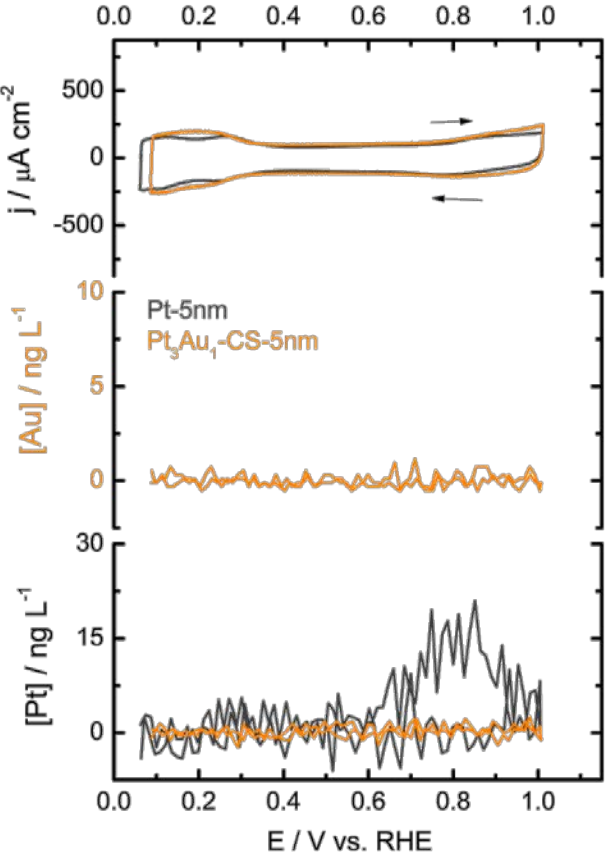
- **Monodisperse ~5nm**
- **Uniform Pt shell**

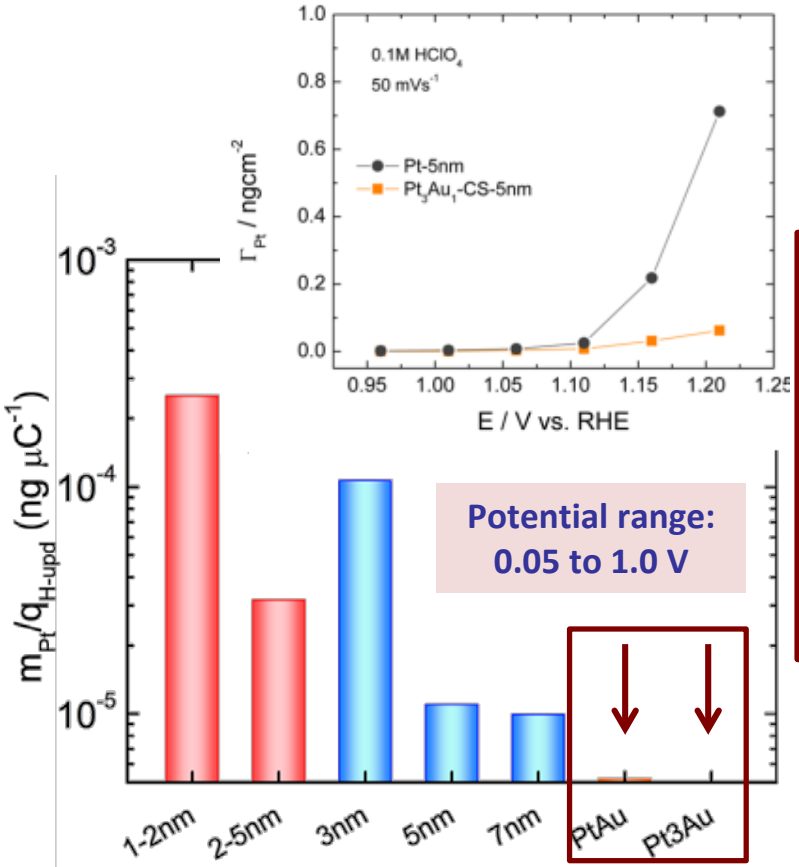
Task 1-2 Accomplishments and Progress: *EC-ICP-MS* Pt_3Au nanoparticles



Pt_3Au/C - GC



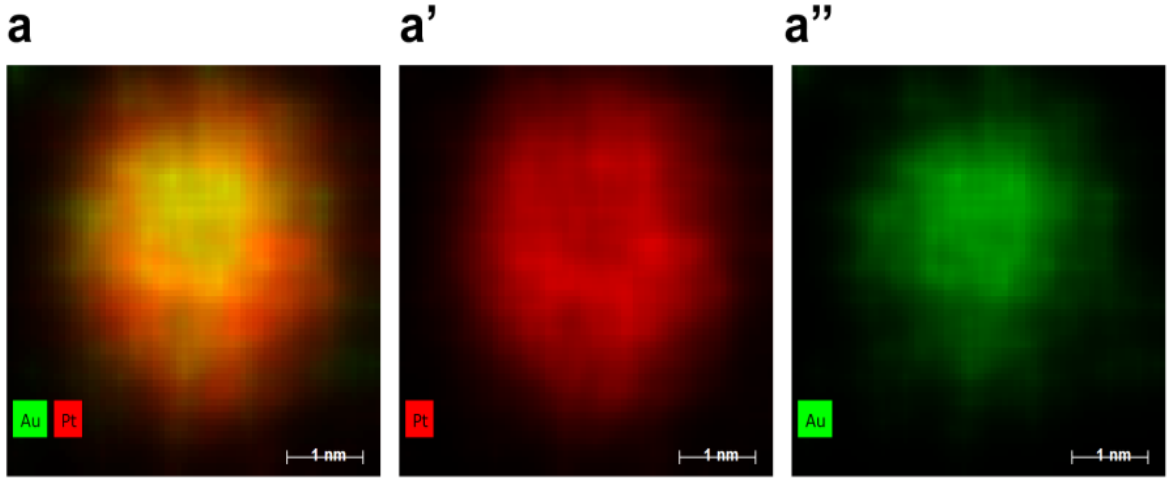


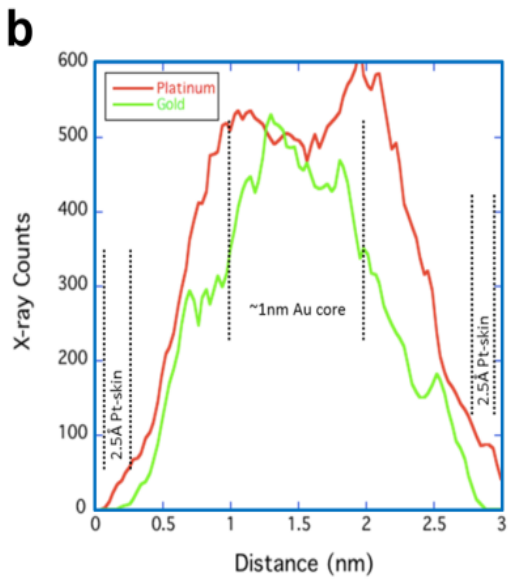


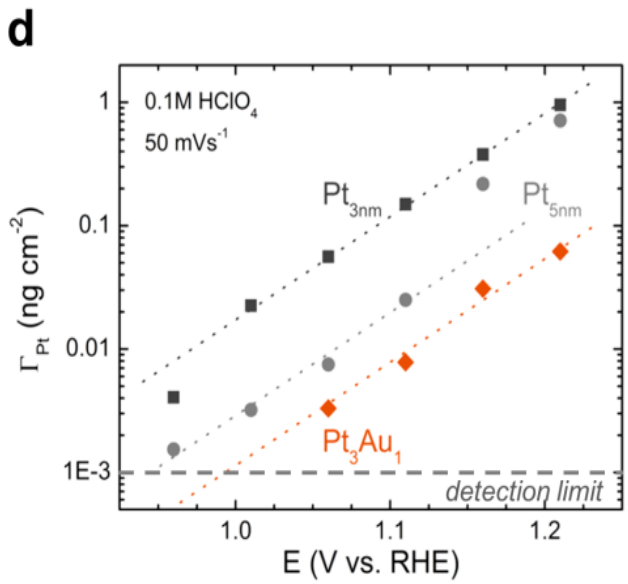
Pt_3Au/C

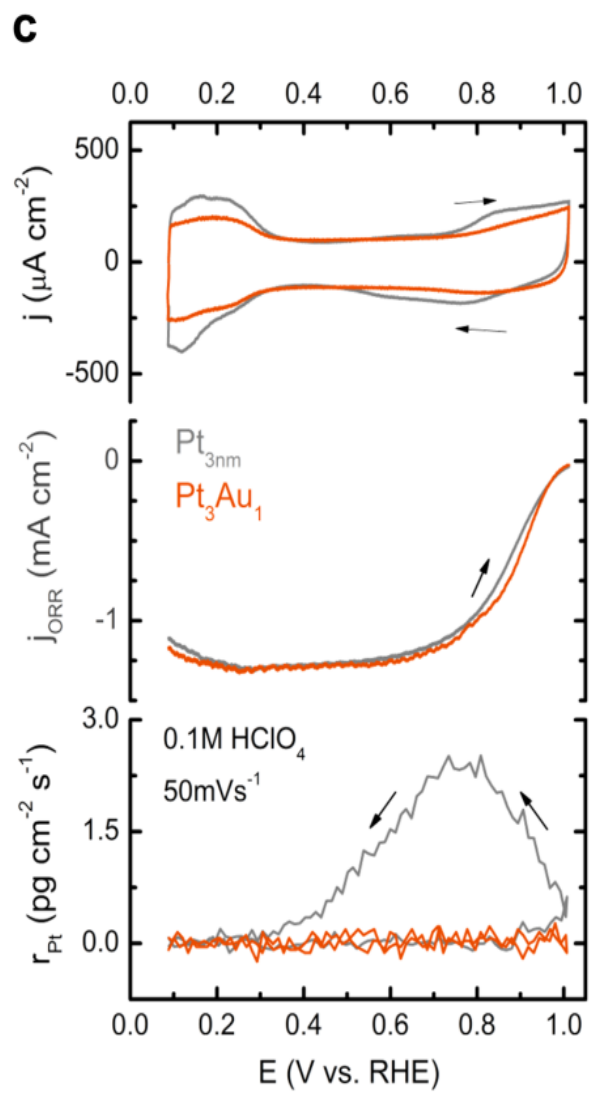
- Dissolution of Pt completely diminished up to 1.0V
- Stability improvement retains at higher electrode potentials
- Up to 10 times more stable above 1.2V

Task 2 Accomplishments and Progress: Pt_3Au/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

Task 3 Accomplishments and Progress: *Scaled PtAu > 5nm in 50 cm² MEA*

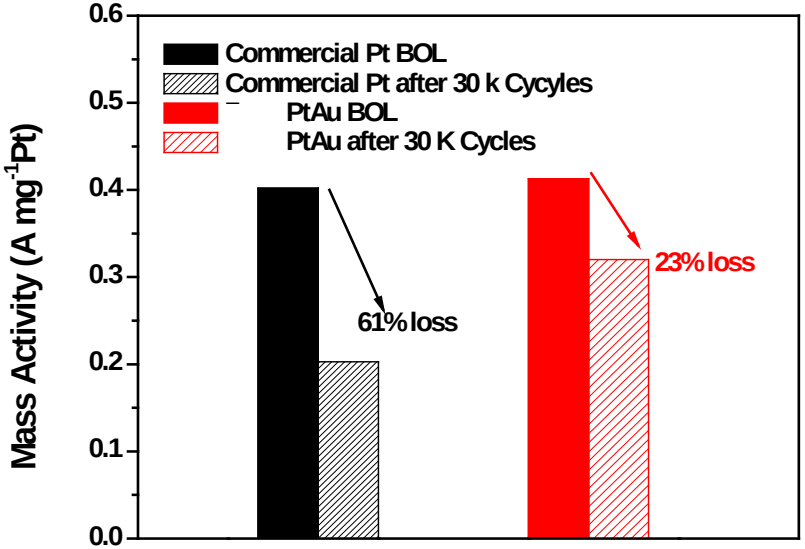
in collaboration with Kenneth Neyerlin, NREL

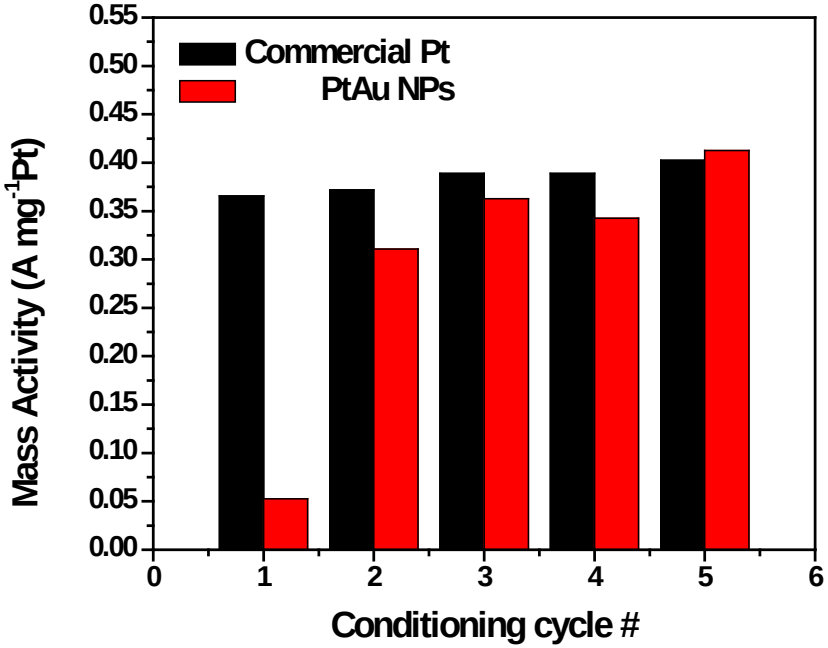
- 150 kPa, 100% RH, 80°C H_2/O_2, 50 cm², N211
- Ultrasonic spray coated 0.9 I:C (D2020 ionomer)
- Cathode loading 0.075 mgPt/cm2

Developed PtAu/HSC: **$i_m^{0.9V}$ ~ 420 mA/mg_{Pt}**

- 150 kPa, 100% RH, 80°C H_2/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

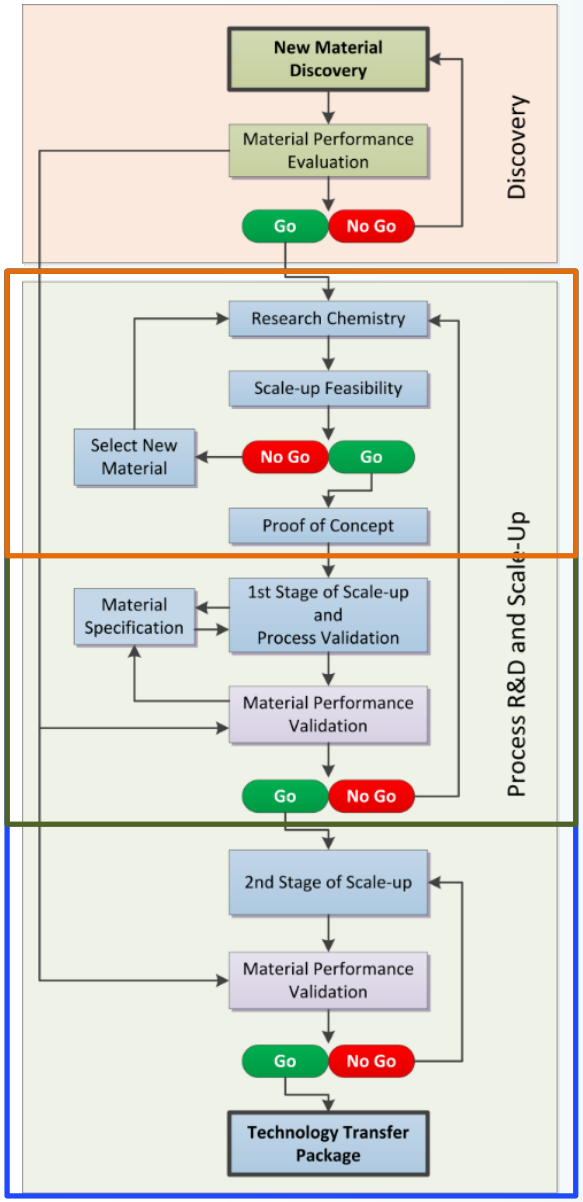




	ECSA (m2/g)
Before AST	31.8
After AST	26.3

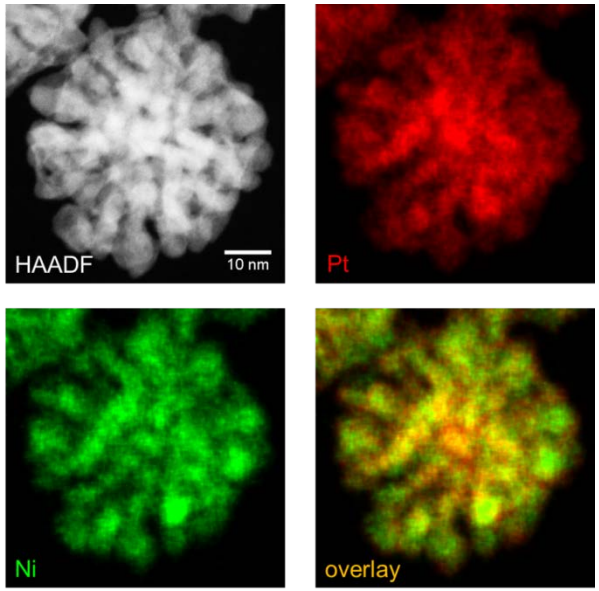
Task 3 Introduction: *Process R&D and Scale Up*

collab. with Greg Krumdick, ANL -MERF

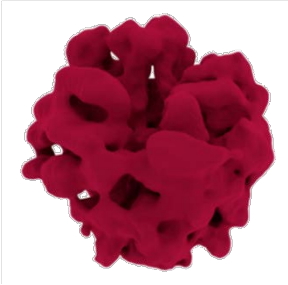


	Timeline & Milestones	
Research Chemistry	M 1-2	1) **Hot-injection** was avoid using **one-pot synthesis.** 2) Benzyl ether as solvent. No Go
	M 3	3) **Phenyl ether** as solvent. 4) **Best synthesis condition** was established. 5) **Reproducibility** was confirmed. Go
1st stage scale up	M 4	6) 1st stage 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 1st stage scale up was confirmed. 9) Pre-annealing process applied.
	M 6-7	**10) Acid leaching process was modified. Go**
2nd stage scale up	M 8-9	11) The 2nd stage scale up (**5 g / batch**) **was successful**. 12) **Acid leaching process** was established.
	M 10	13) The 2nd 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

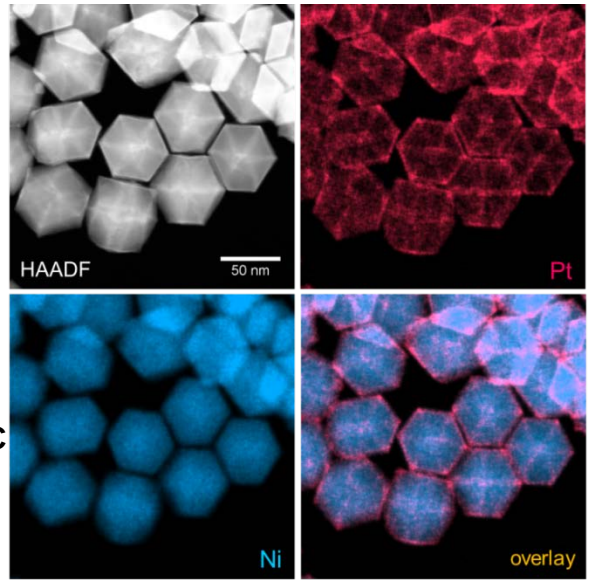
SA: 10
MA: 5

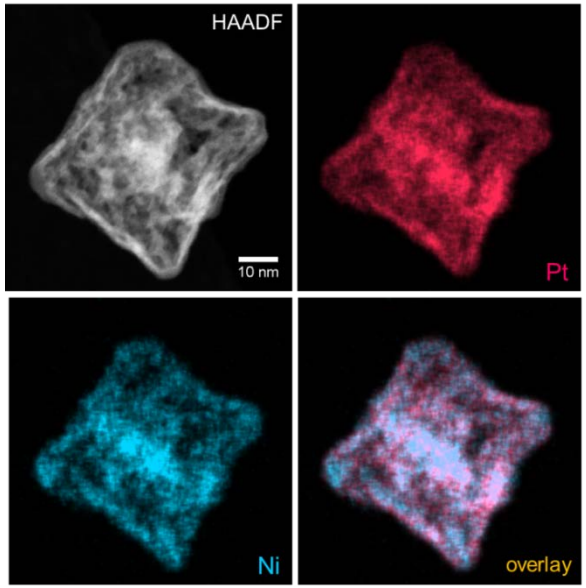
Nano Multi Skin

ANL, ORNL

Improvement vs. Pt/C
RDE @ 0.95V

SA: 7
MA: 4





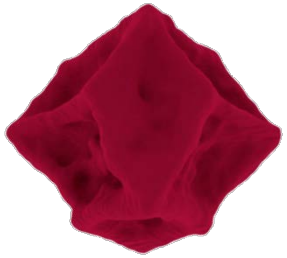
Nanocages

ANL, ORNL

Improvement vs. Pt/C
RDE @ 0.95V

SA: 9
MA: 6

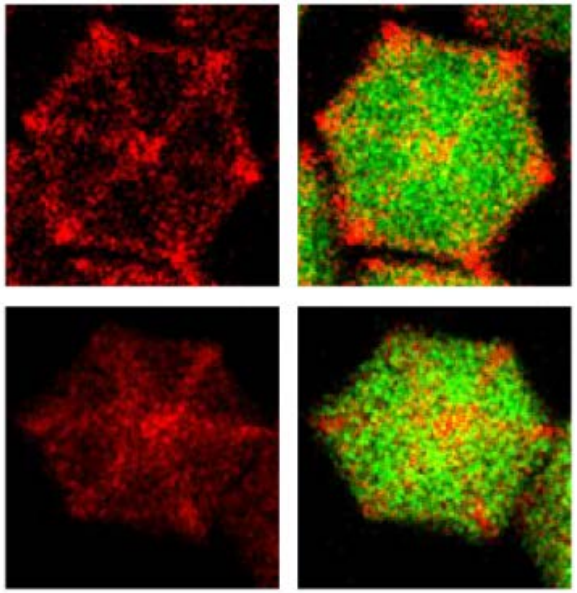
Excavated Nanoframes



LBNL, ANL, ORNL

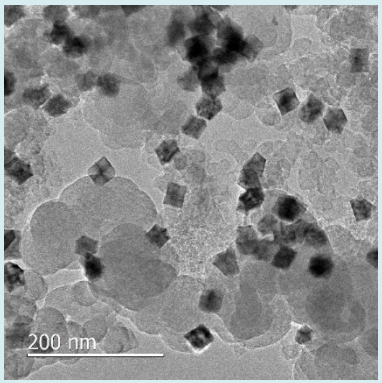
Improvement vs. Pt/C
RDE @ 0.95V

SA: 13
MA: 7

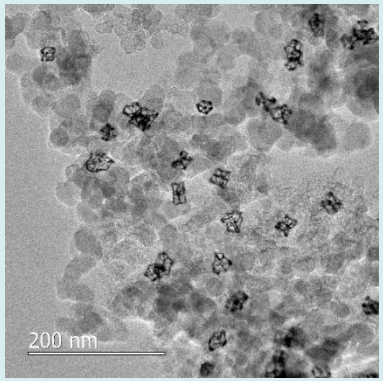


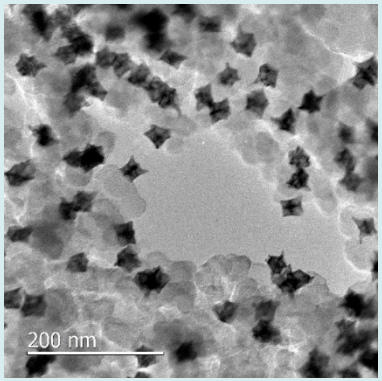
Accomplishments and Progress: *PtNi NanoFrames ~ 1g*

As synthesized | **Acid treated**

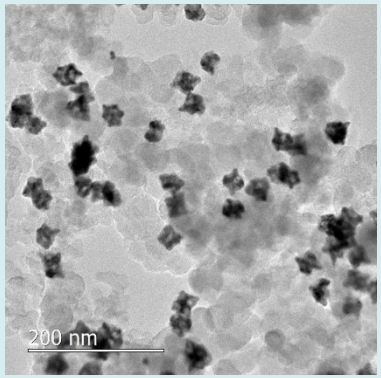


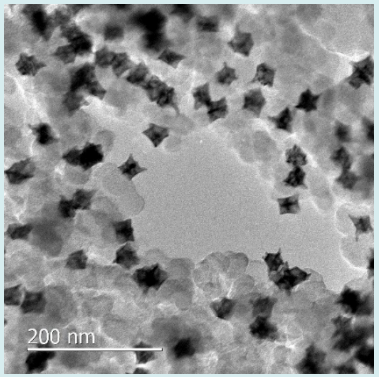
Pt-Ni h-NFs



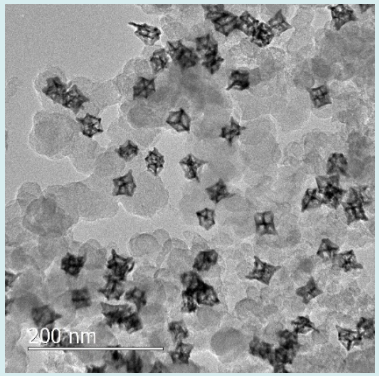


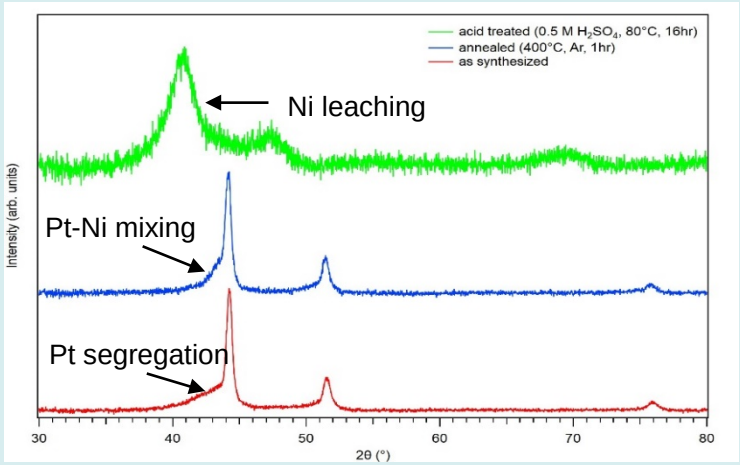
Pt-Ni rd-NFs





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 H_2SO_4, 80°C) before MEA**

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

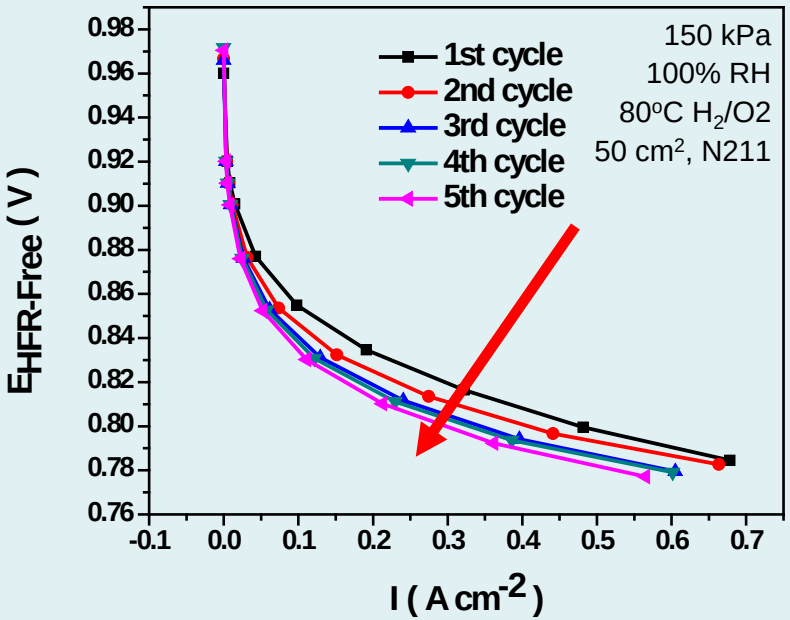
in collaboration with Kenneth Neyerlin, NREL

- 150 kPa, 100% RH, 80°C H_2/O_2, 50 cm^2, N211
- Ultrasonic spray 0.5 I:C (D2020 ionomer)
- Cathode loading 0.055mgPt/cm2

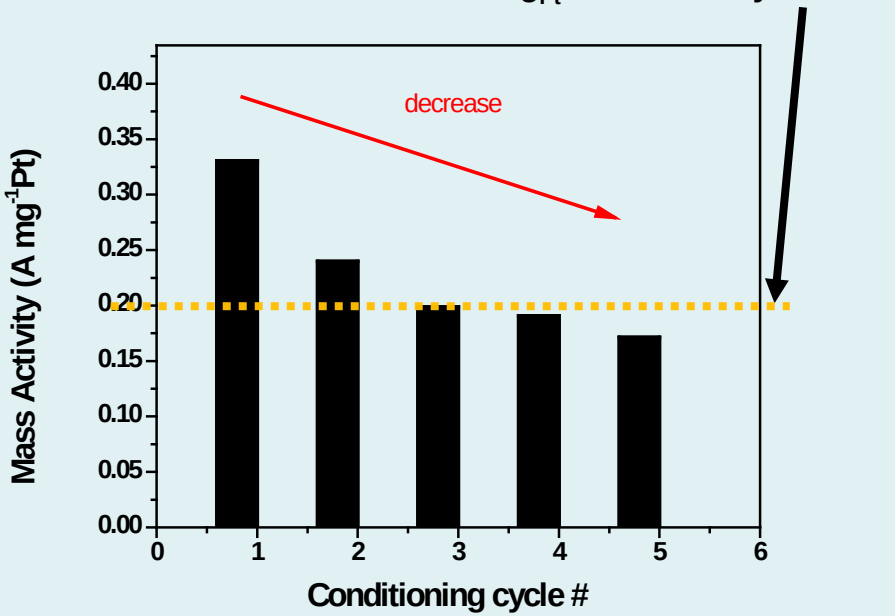
Developed PtNi NanoFrames/Vulcan:

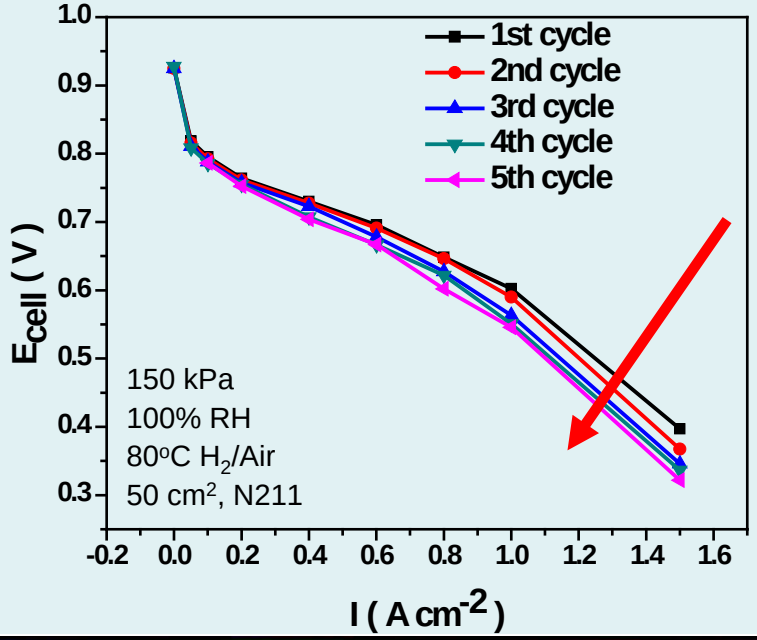
$i_m^{0.9V}$ ~ 330 mA/mg_{Pt}

vs. ~200 mA/mg_{Pt} for 30 wt% Pt/Vulcan



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

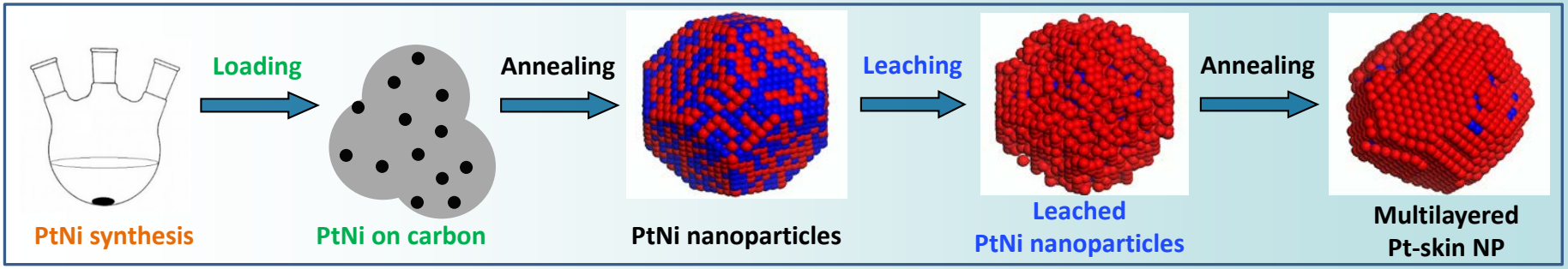


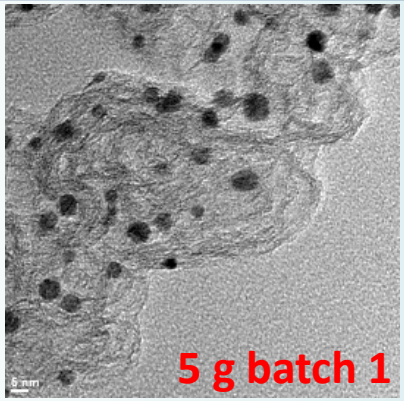


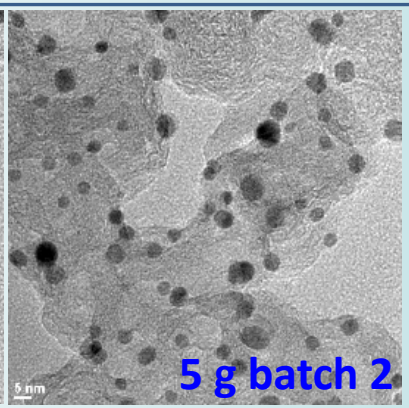
Task 3 Accomplishments and Progress: *Process Scale Up* | *RDE Evaluations*

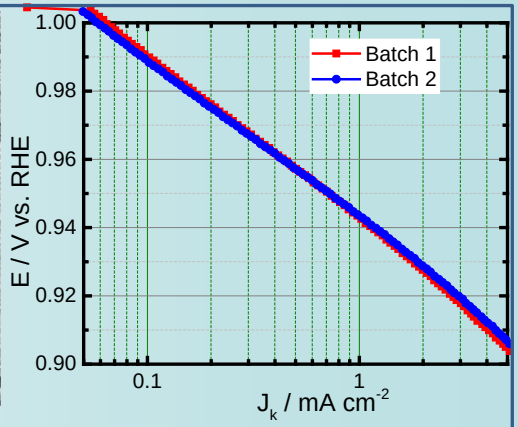
collab. with Greg Krumdick, ANL -MERF

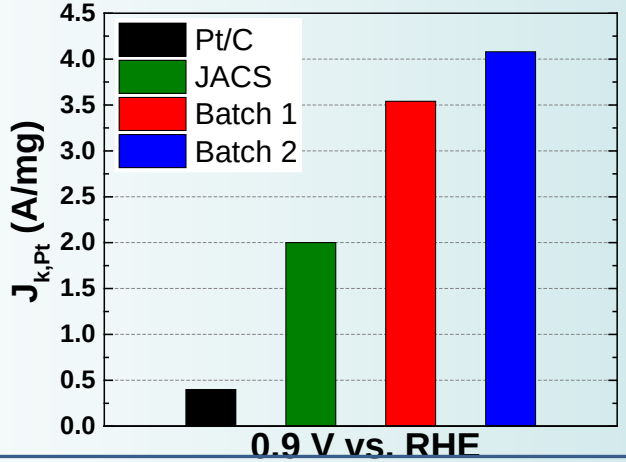
From 0.1 g to 5 g per batch

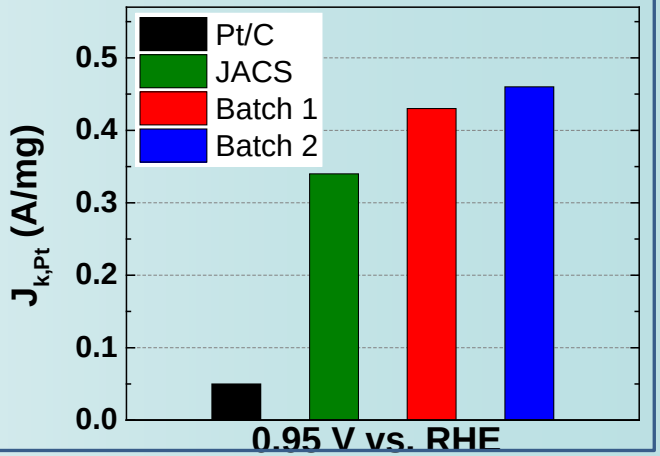




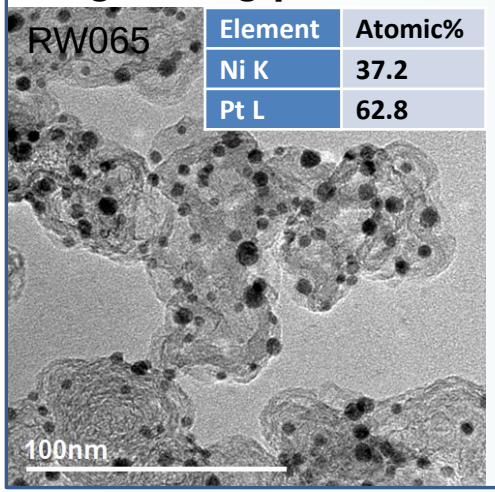






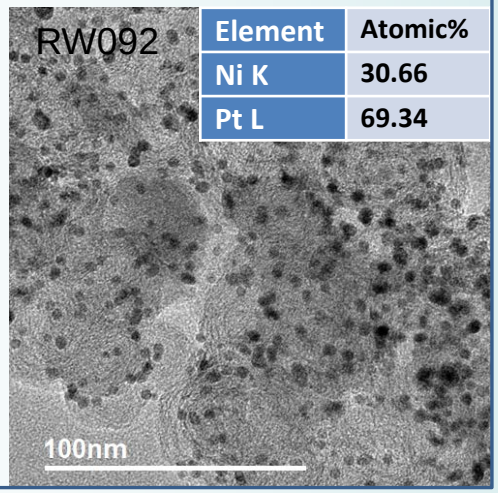


Original 5 g per batch



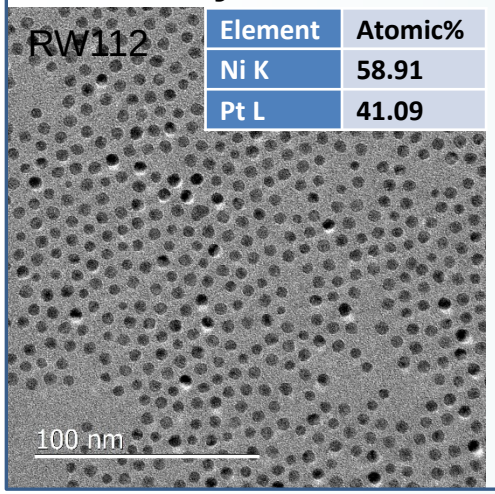
Element	Atomic%
Ni K	37.2
Pt L	62.8

Improved procedure

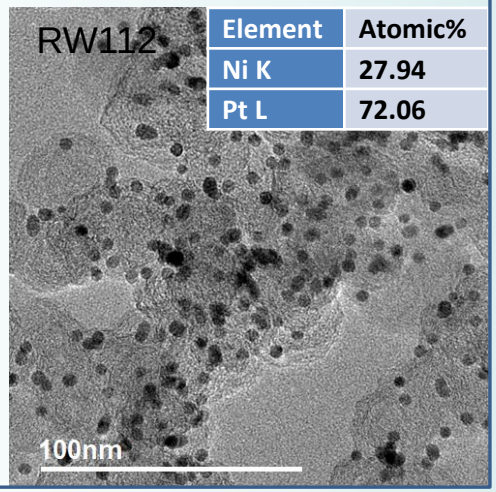


Element	Atomic%
Ni K	30.66
Pt L	69.34

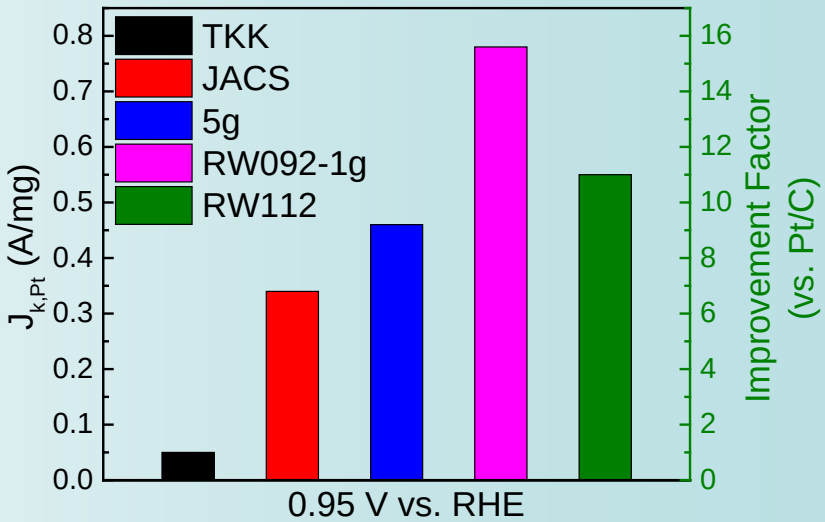
New synthesis: 6 nm PtNi 5 g per batch

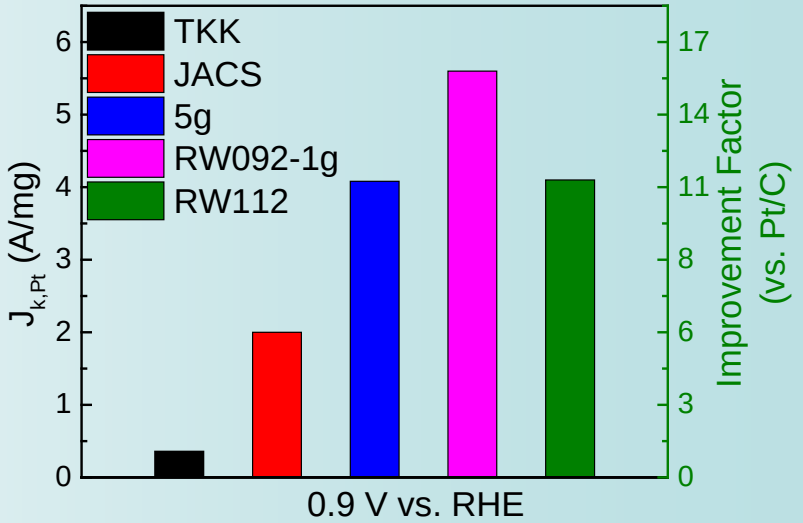


Element	Atomic%
Ni K	58.91
Pt L	41.09



Element	Atomic%
Ni K	27.94
Pt L	72.06





- **Sintering during high temperature annealing is limited.**

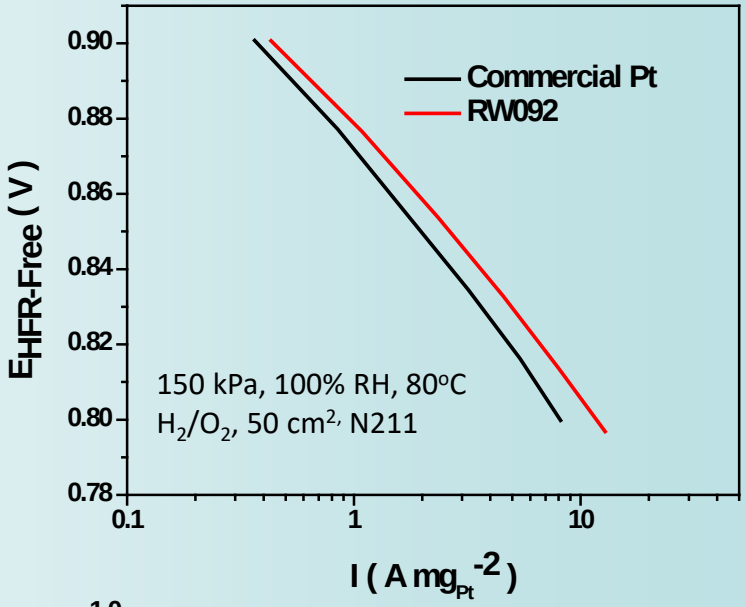
Task 2-3 Accomplishments and Progress: *PtNi NPs 5g batch in 50 cm² MEA*

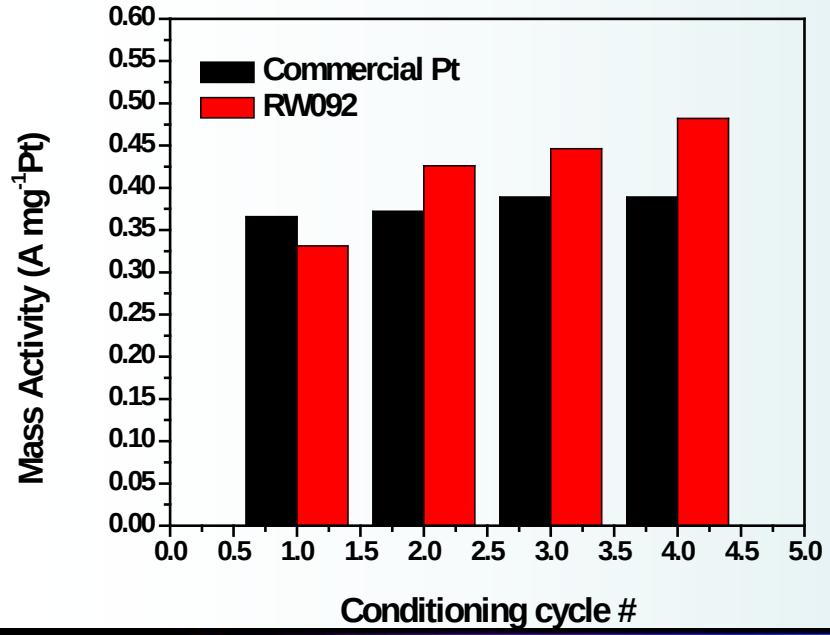
in collaboration with Kenneth Neyerlin, NREL

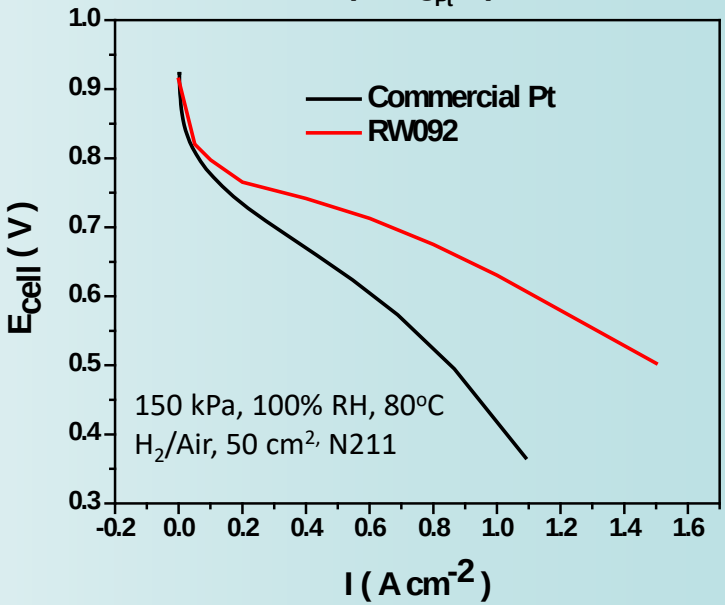
150 kPa, 100% RH, 80°C H_2/O_2, 50 cm², N211
Ultrasonic spray coated 0.9 I:C (D2020 ionomer)
Cathode loading 0.04mgPt/cm2

Developed **RW092** PtNi/HSC: **$i_m^{0.9V}$ ~ 500 mA/mg_{Pt}**

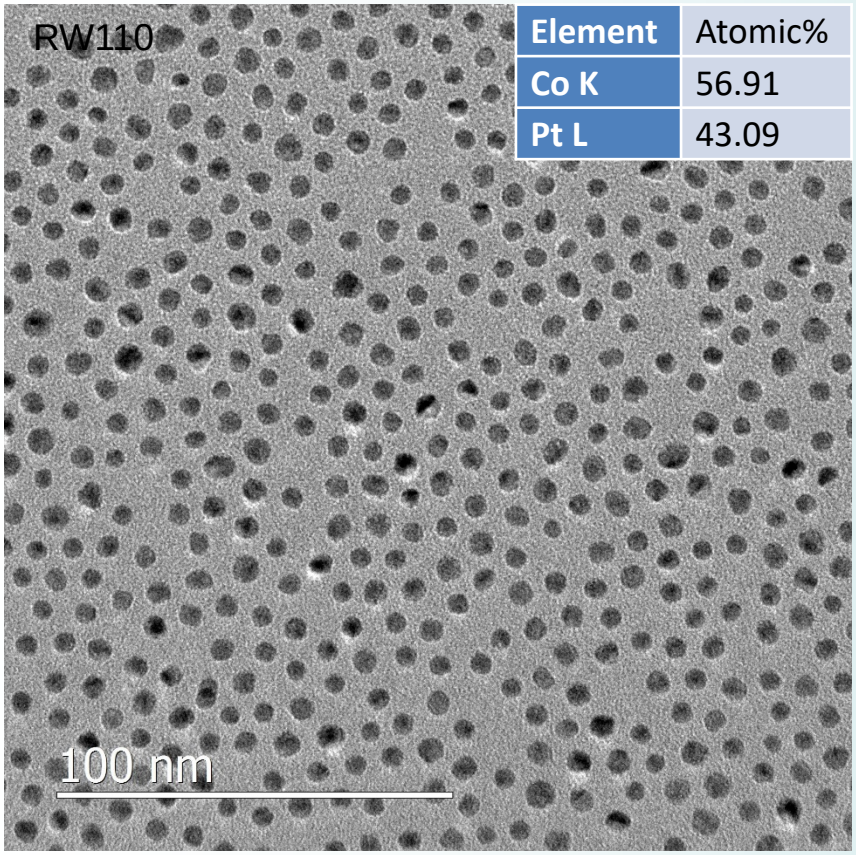
PtNi/C shows MA that meets the DOE target in 50 cm² MEA



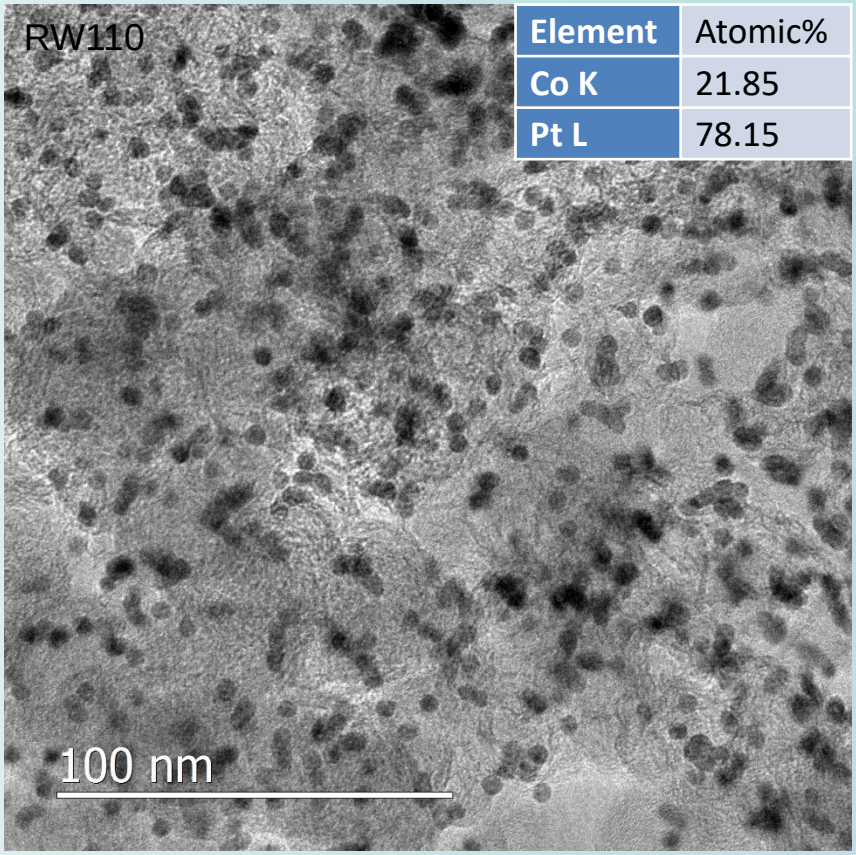




5 nm Pt_3Co-1 g catalyst per batch



Element	Atomic%
Co K	56.91
Pt L	43.09



Element	Atomic%
Co K	21.85
Pt L	78.15

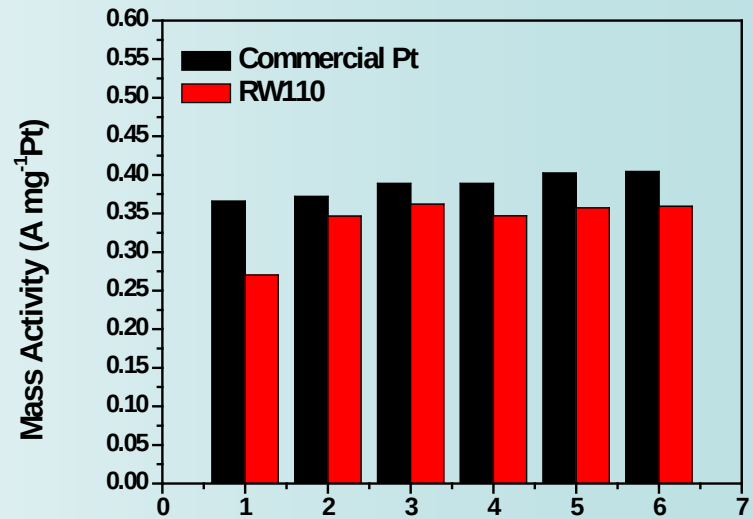
- **Developed one-pot scalable synthesis of 6 nm PtCo nanoparticle.**
- **Post-treatment needs to be optimized for better performance.**

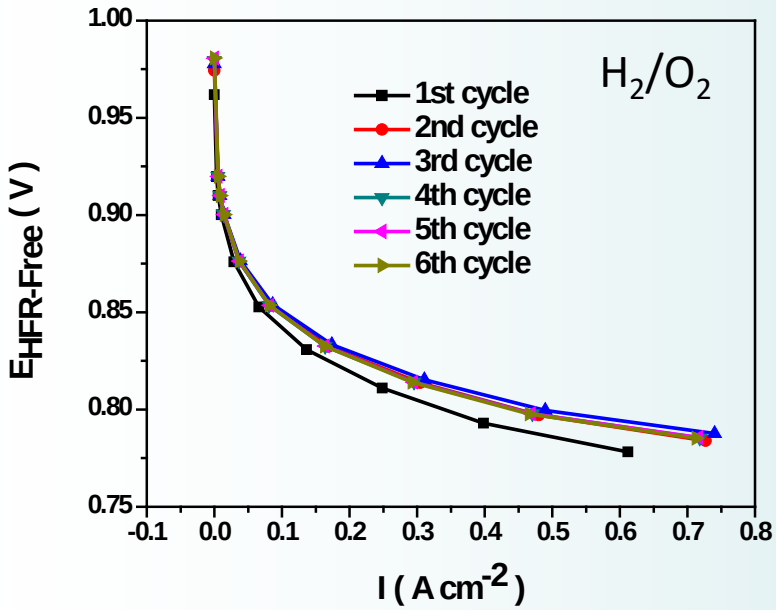
Task 2-3 Accomplishments and Progress: *scaled 5nm PtCo in 50 cm² MEA*

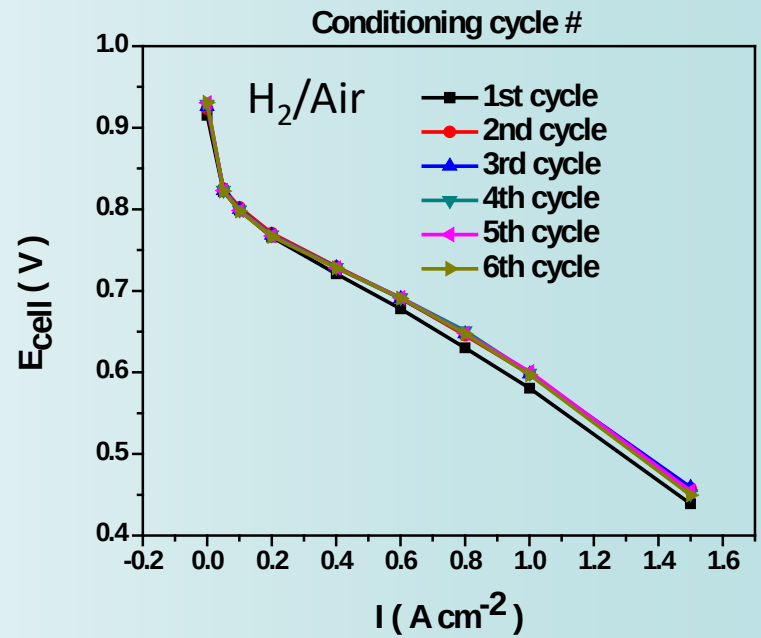
in collaboration with Kenneth Neyerlin, NREL

- 150 kPa, 100% RH, 80°C H_2/O_2, 50 cm^2, N211
- Ultrasonic spray coated at NREL 0.9 I:C (D2020 ionomer)
- Cathode loading 0.055 mg Pt/cm^2

Developed PtCo/$_{HSA}$C: **$i_m^{0.9V}$ ~ 350 mA/mg_{Pt}**

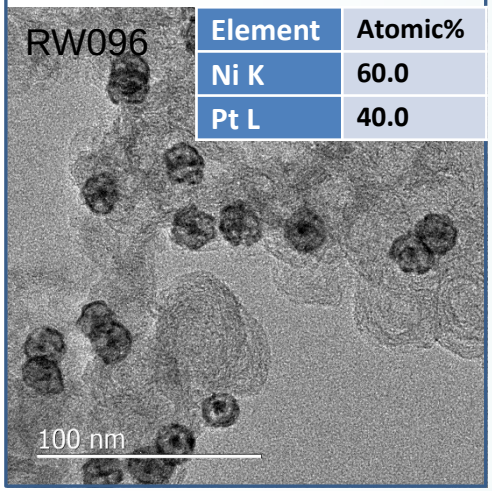




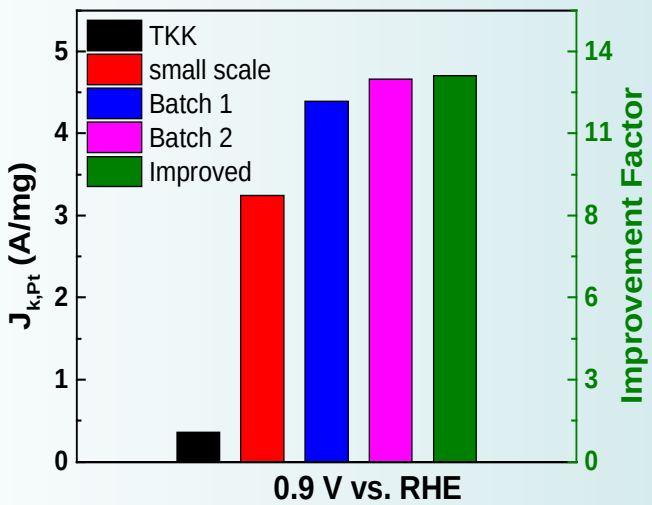


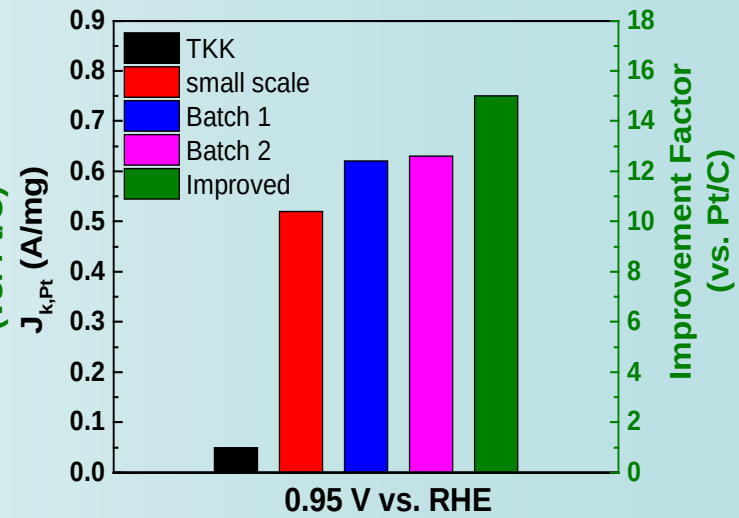
One-pot synthesis and structural optimization of Nanocages

0.1 g per batch

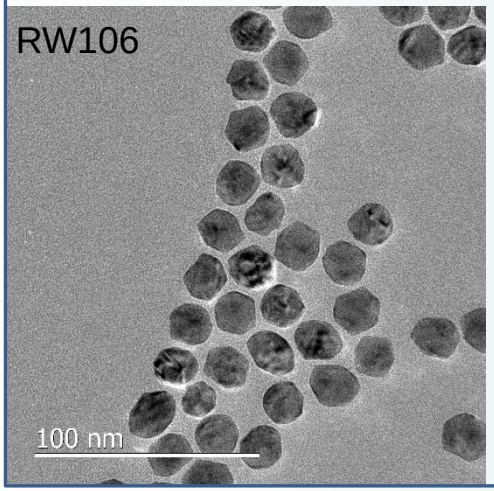


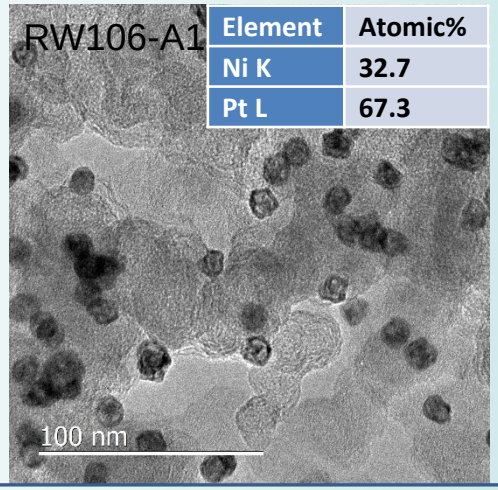
Element	Atomic%
Ni K	60.0
Pt L	40.0



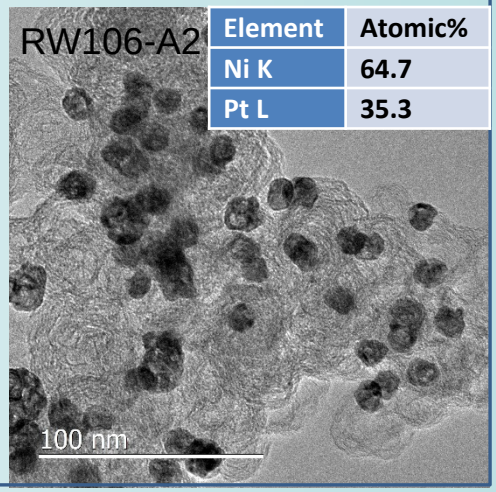


0.6 g per batch modified acid leaching procedure





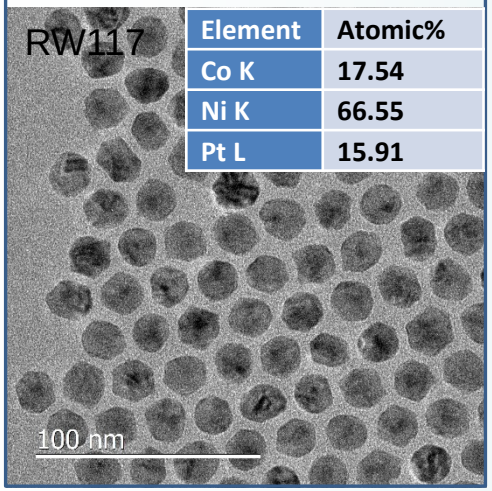
Element	Atomic%
Ni K	32.7
Pt L	67.3



Element	Atomic%
Ni K	64.7
Pt L	35.3

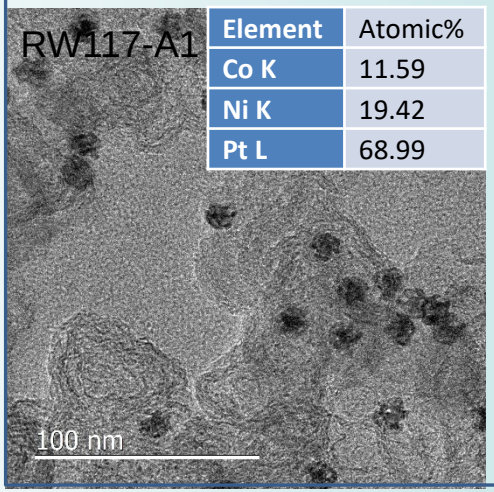
One-pot synthesis-1 g per batch of PtNiCo Nanocages

PtNiCo nanoparticles

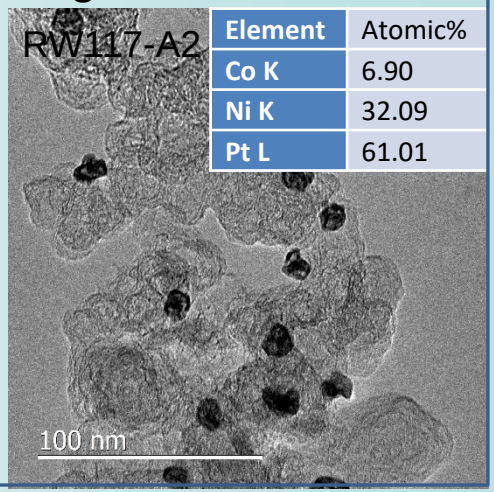


Element	Atomic%
Co K	17.54
Ni K	66.55
Pt L	15.91

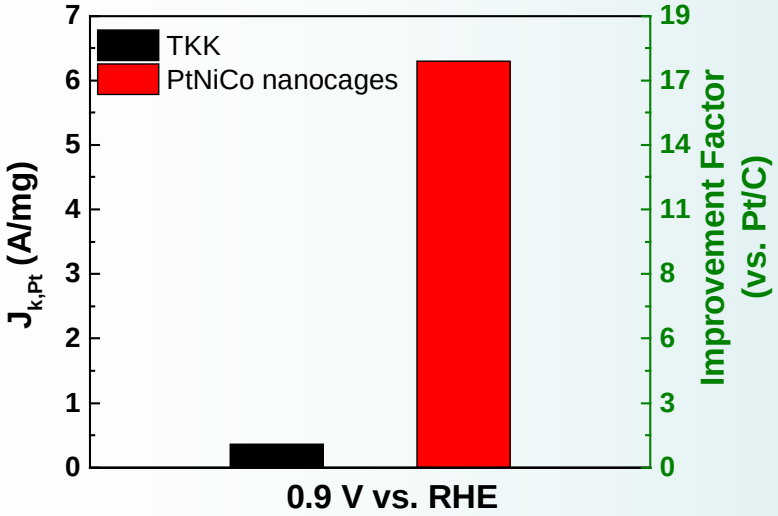
Different acid leaching conditions

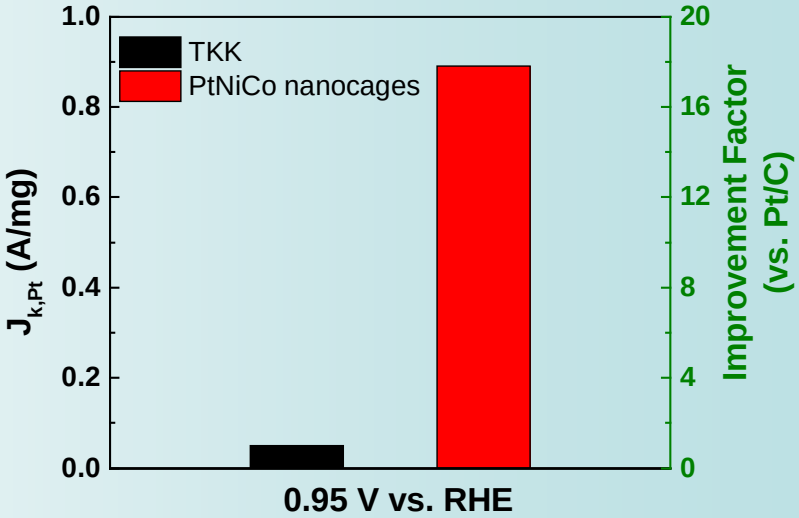


Element	Atomic%
Co K	11.59
Ni K	19.42
Pt L	68.99



Element	Atomic%
Co K	6.90
Ni K	32.09
Pt L	61.01

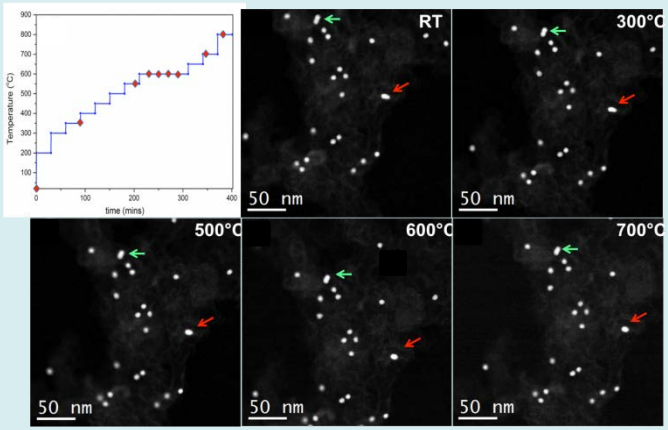




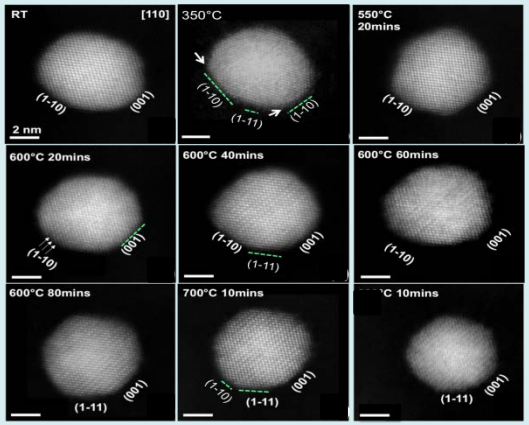
Introduction: Pt_3Co Catalysts Structures

in collaboration with K.L. More, ORNL

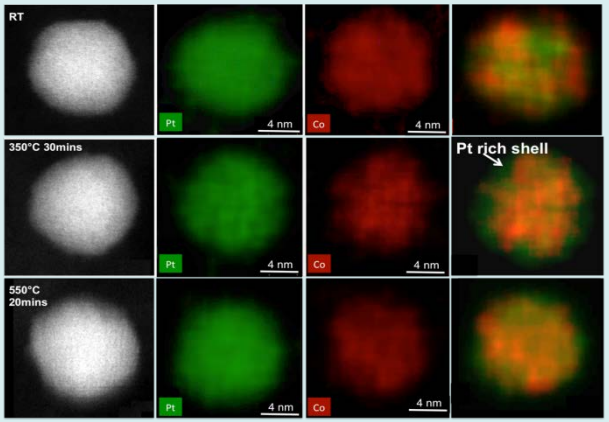
Annealing sequence of Pt_3Co NP

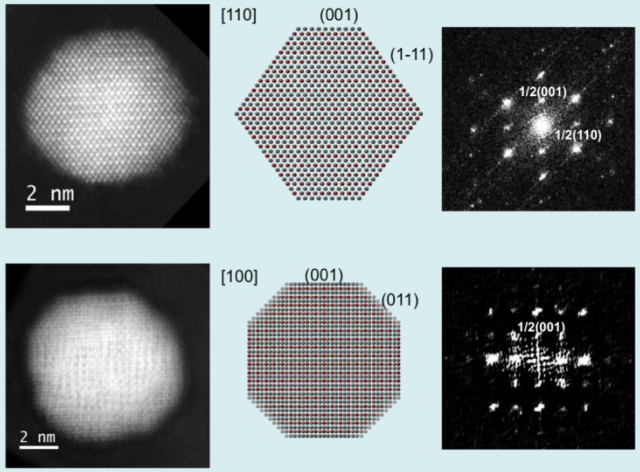


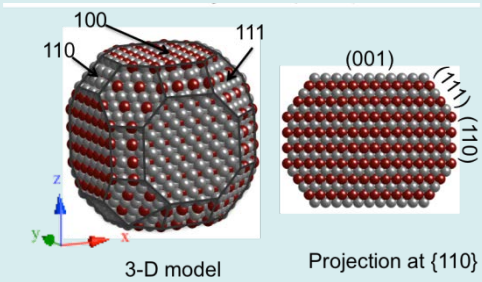
HAADF at different T and t(min)



HAADF and EDS elemental mapping







Dynamic of structural and chemical evolution at the atomic scale of Pt_3Co NPs during in-situ annealing

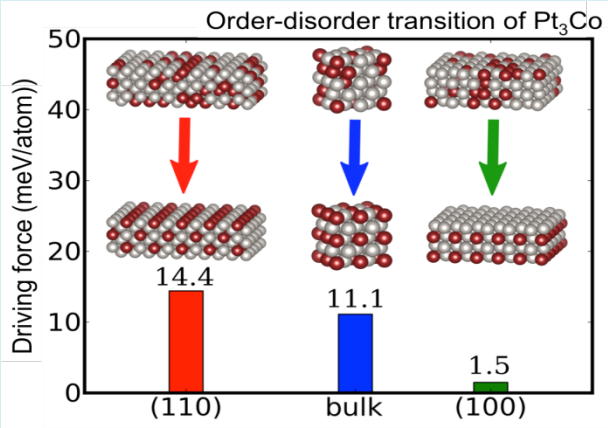
distinct behavior at critical stages:

{111}, {110}, {100} facets play different roles during the evolution of structure

formation of a Pt-Skin shell with an alloyed disordered core;

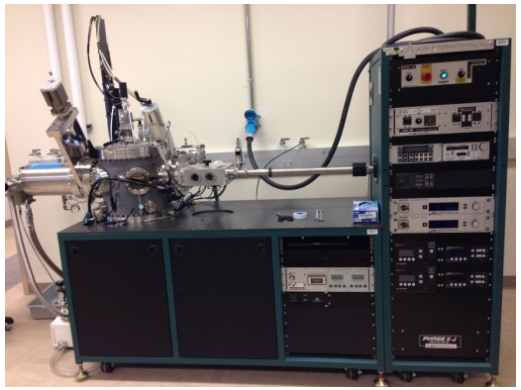
the nucleation of ordered domains;

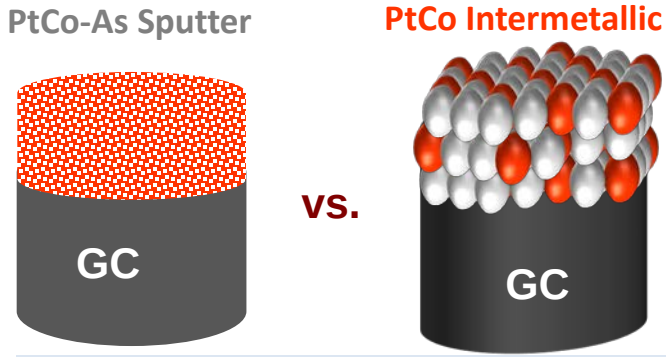
the establishment of an ordered $L1_2$ phase followed by pre-melting

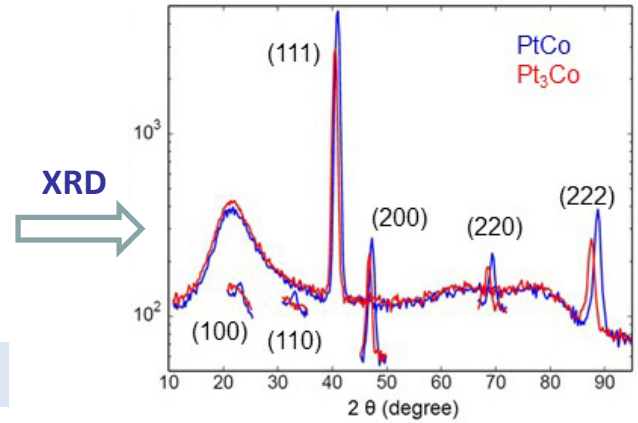


M. Chi, C. Wang, Y. Lei, G. Wang, K.L. More, A. Lupini, L.F. Allard, N.M. Markovic, and V.R. Stamenkovic
Nature Communications 6 (2015) *No.* 8925

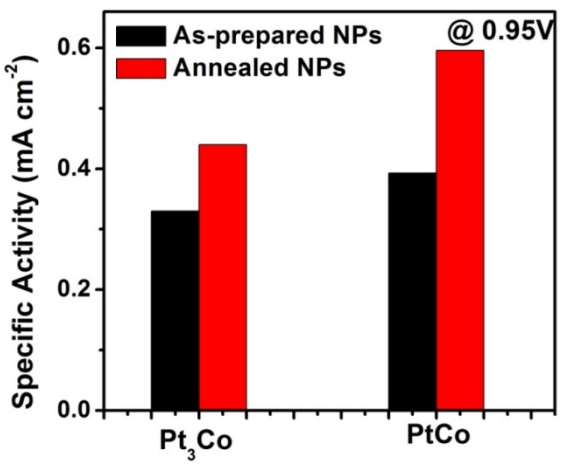
Task 1 Introduction: *In-Situ EC-ICP-MS* Pt-Alloys Intermetallic

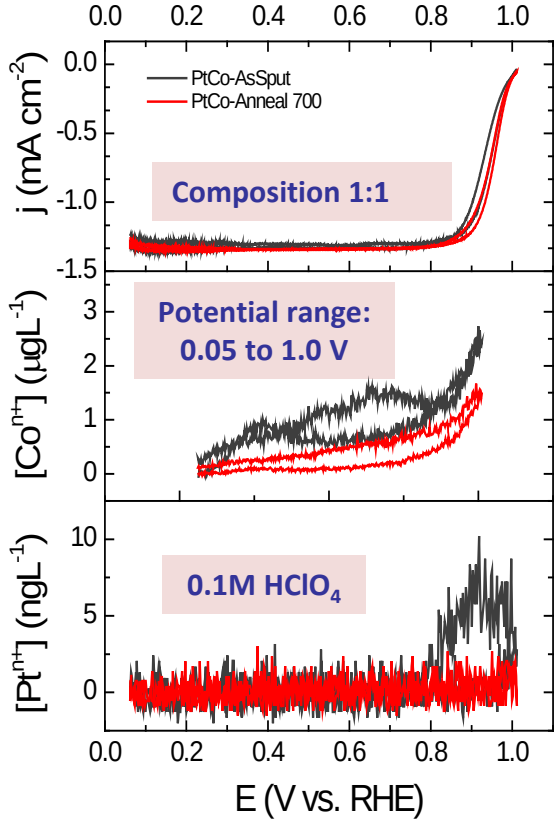


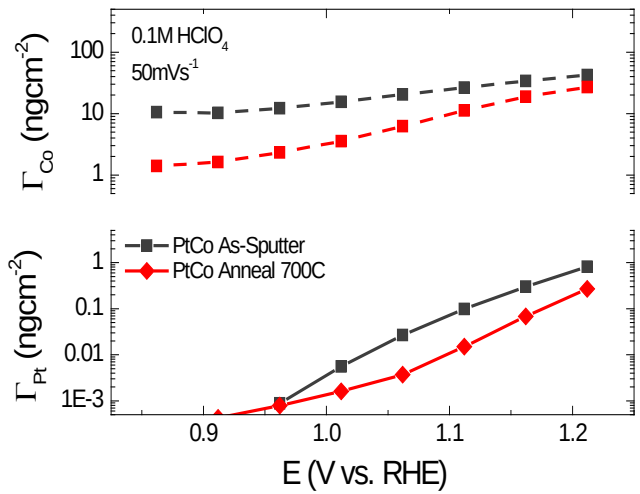




Annealing at 700°C= Intermetallic Phase

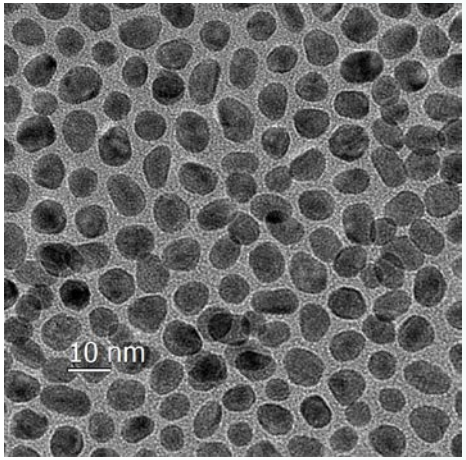


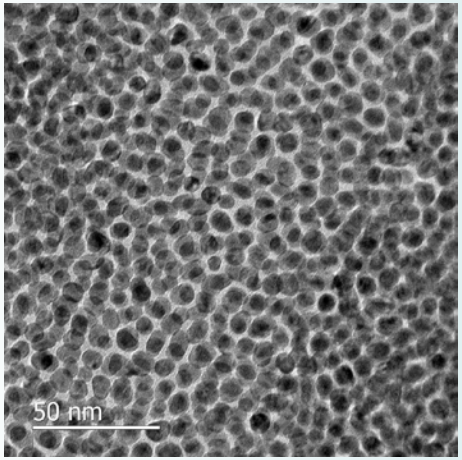


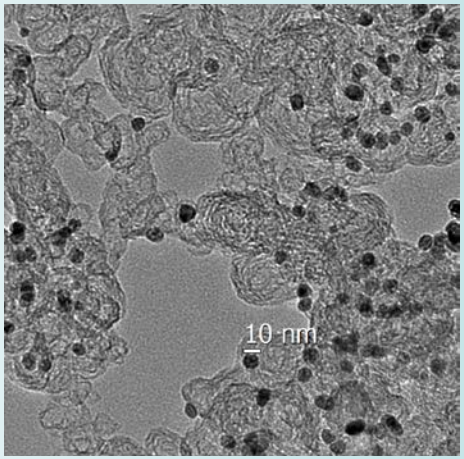


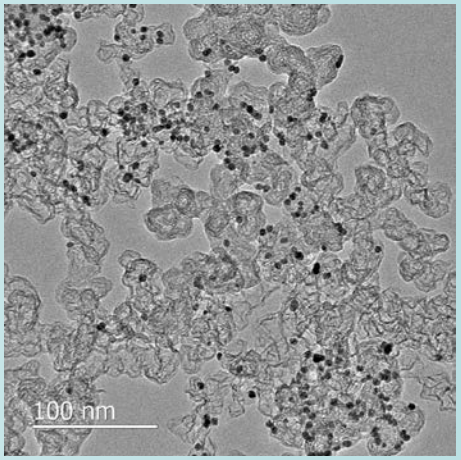
Benefit of intermetallic phase:
- **Decreases dissolution of both Pt and Co**
- **Improvement in ORR activity**

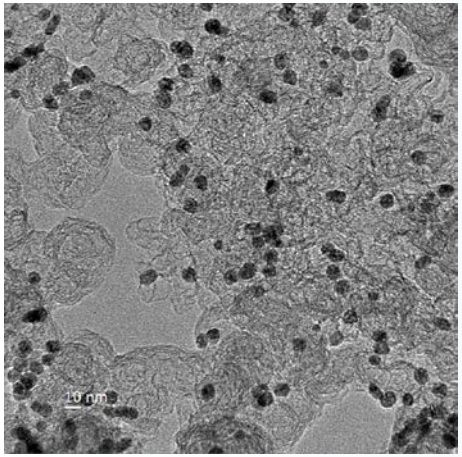
Task 1 Accomplishments and Progress: *As-Synthesized* $PtCo_{IM}/C$ 8nm NPs

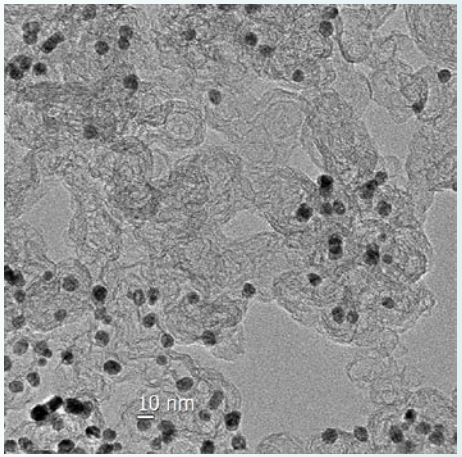


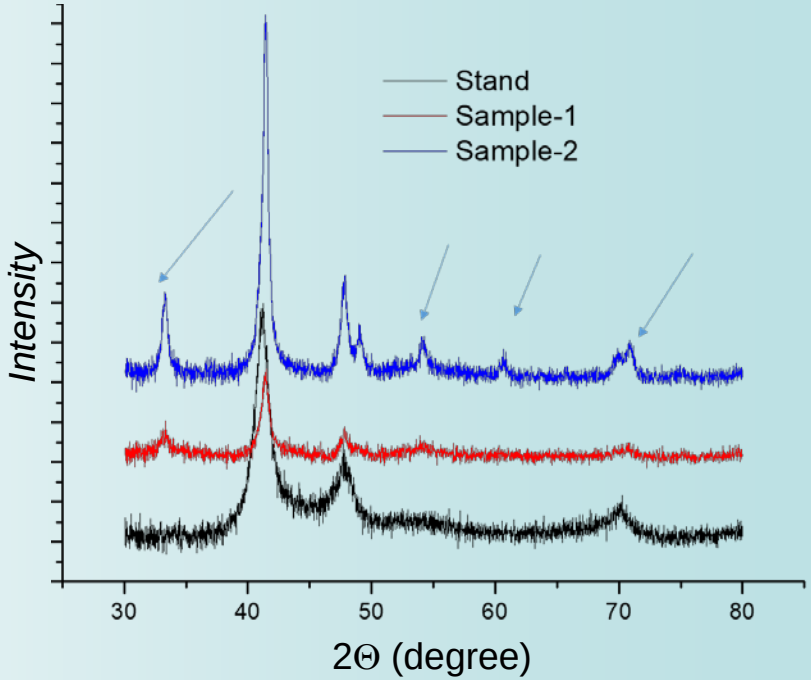




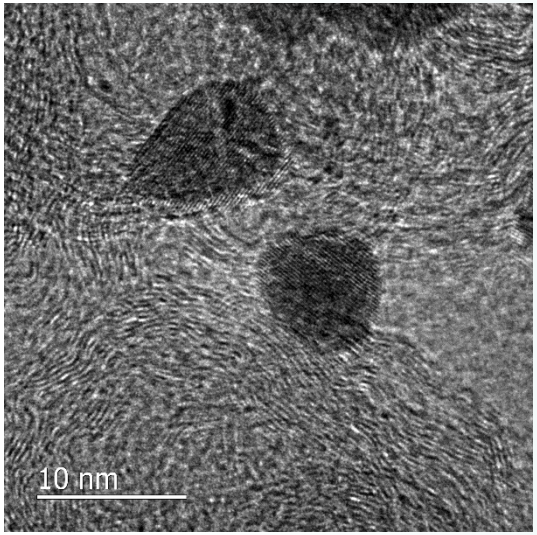


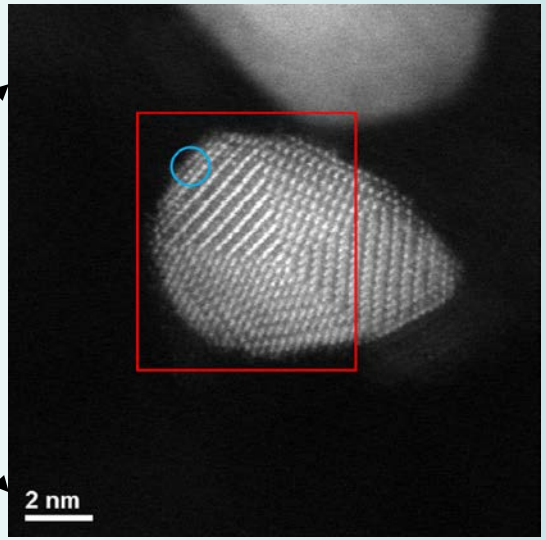


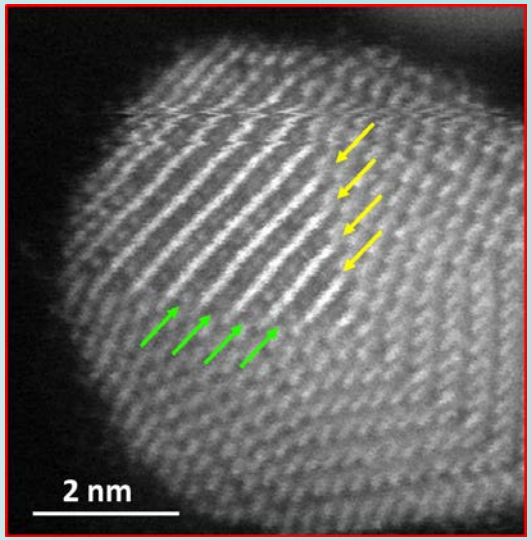




in collaboration with K.L. More, ORNL







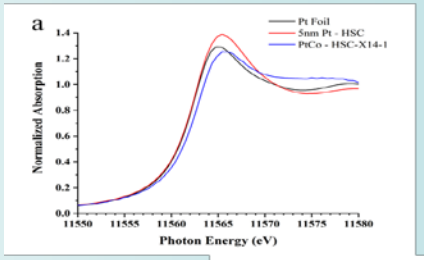
Majority of NPs have L10 ordering
Pt:Co in powder 45:55

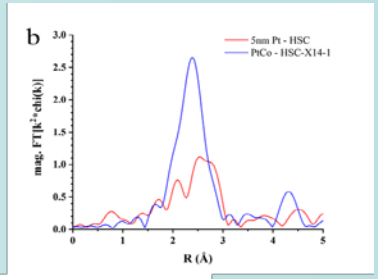
Surface facets demonstrate alternating Pt and Co (100) planes
Pt atoms – yellow arrows; Co atoms – green arrows

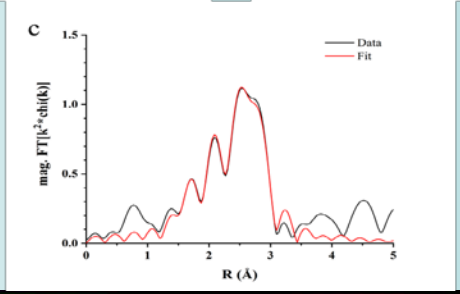
in collaboration with Debbie Myers, ANL - CSE

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 (*10^3 Å^2)	E_0 (eV)	R factor (*10^2)
Pt	11563.0	0.79	8.4 ± 0.6 (Pt-Pt) 0.9 ± 0.3 (Pt-O)	2.76 ± 0.003 2.01 ± 0.04	5.7 ± 0.04 4.7 ± 4.9	6.1 ± 0.7 6.9 ± 4.3	k^1: 0.3 k^2: 0.2 k^3: 0.1
PtCo	11563.3	0.79	4.9 ± 1.1 (Pt-Pt) 5.2 ± 0.7 (Pt-Co)	2.69 ± 0.01 2.64 ± 0.01	3.3 ± 1.0 4.6 ± 0.9	5.2 ± 0.8 5.2 ± 0.8	k^1: 0.08 k^2: 0.04 k^3: 0.08



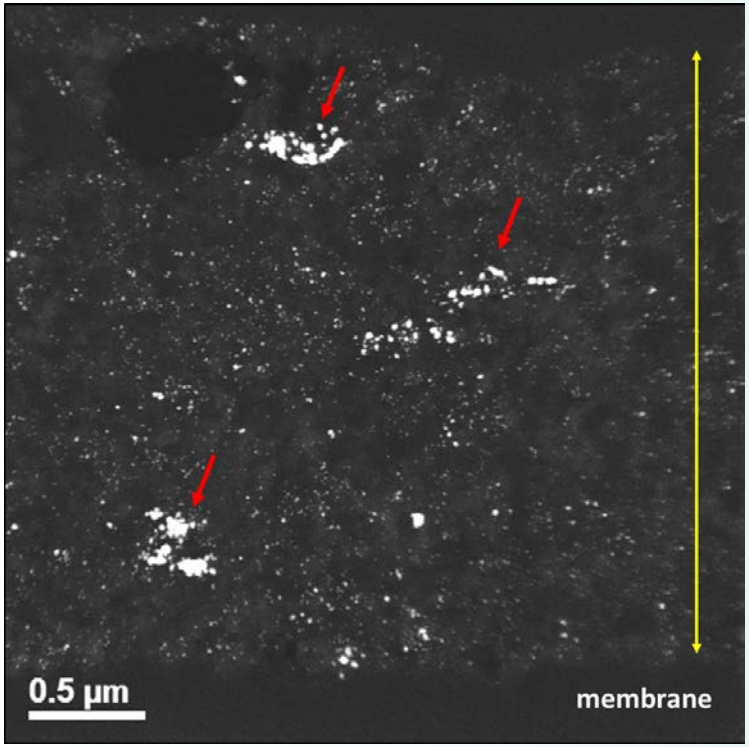


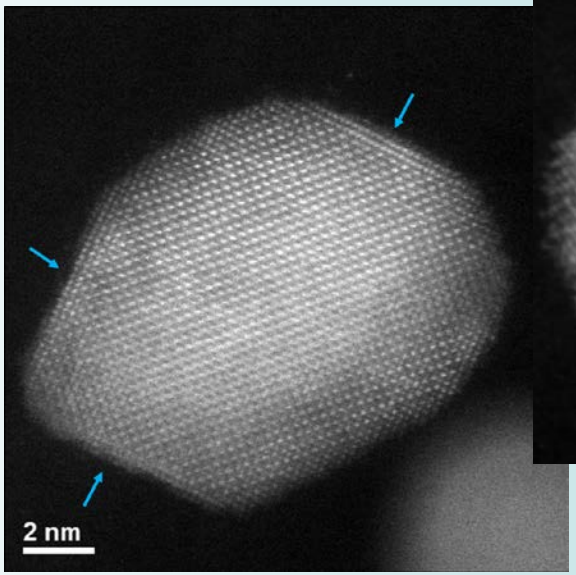


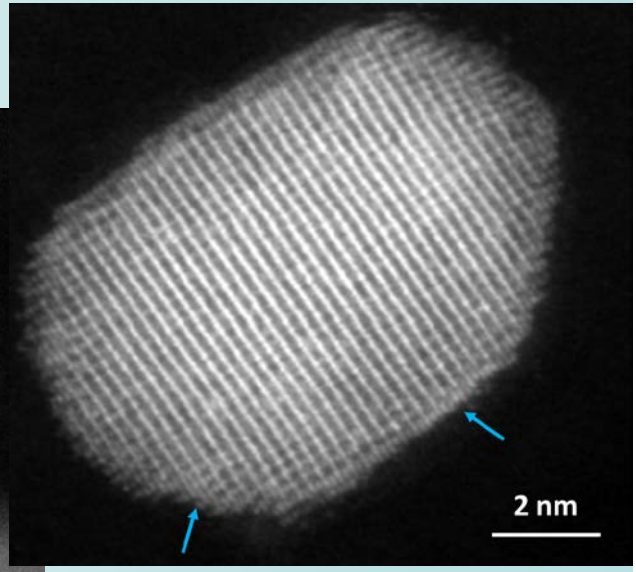
Task 2 Accomplishments and Progress: *Scaled PtCo/HSC in 50 cm^2 MEA*

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*

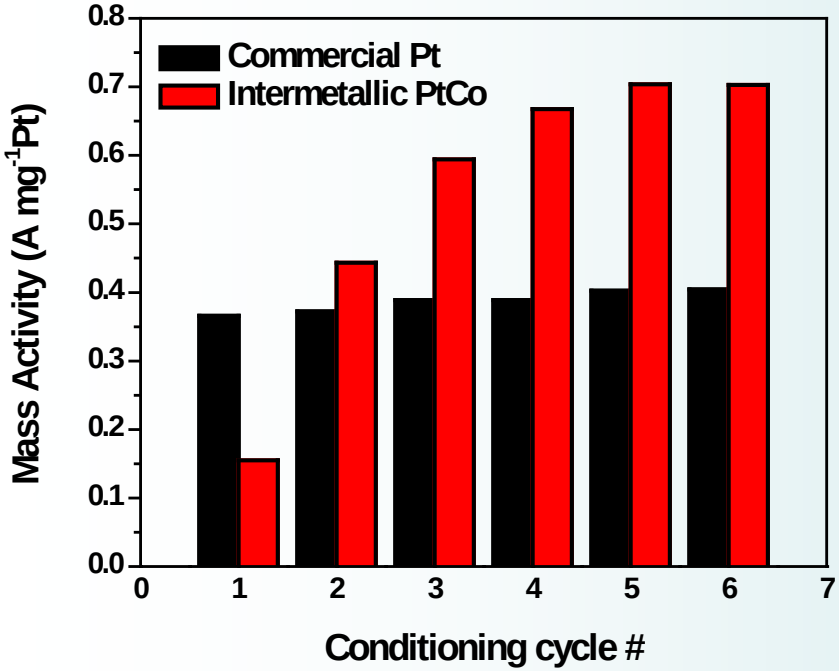
in collaboration with Kenneth Neyerlin, NREL

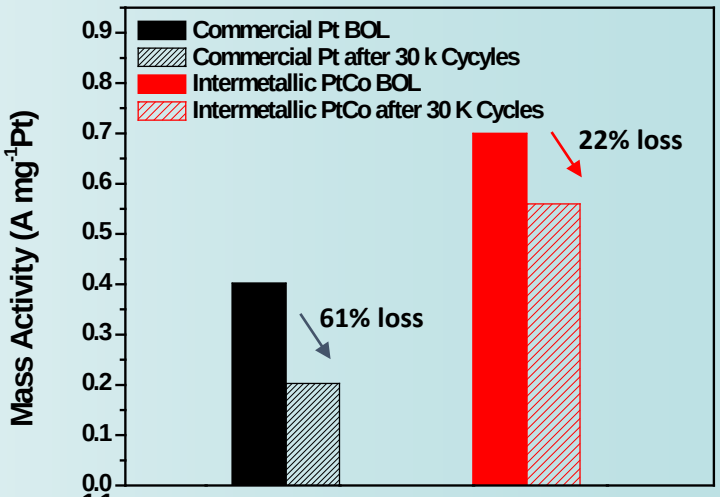
150 kPa, 100% RH, 80°C H_2/O_2, 50 cm², N211
Ultrasonic spray coated 0.9 I:C (D2020 ionomer)
Cathode loading 0.056mgPt/cm2

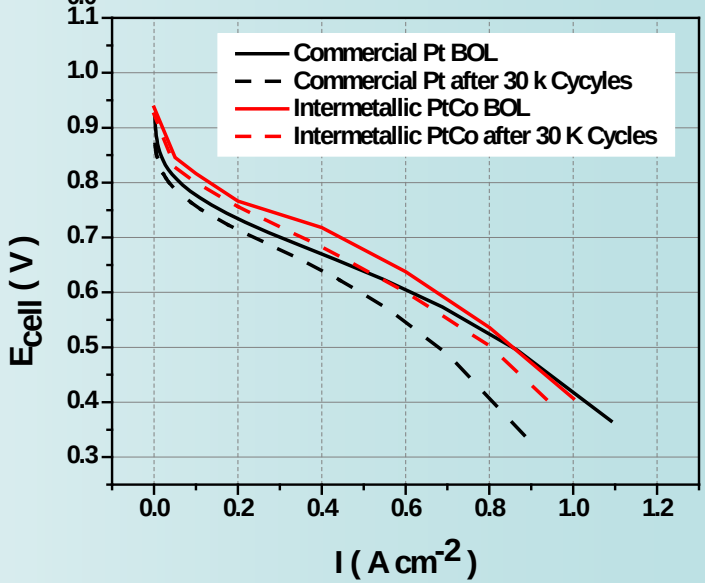
Developed intermetallic PtCo/HSC: $i_m^{0.9V}$ ~ **700 mA/mg$_{Pt}$**

ECSA	(m²/g)
before AST	34.5
after AST	28.6

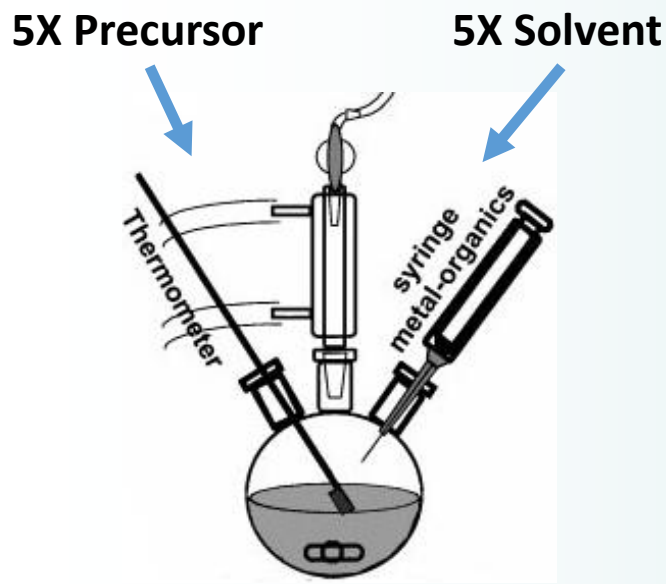
PtCo/C shows MA and ECSA that meets the DOE targets



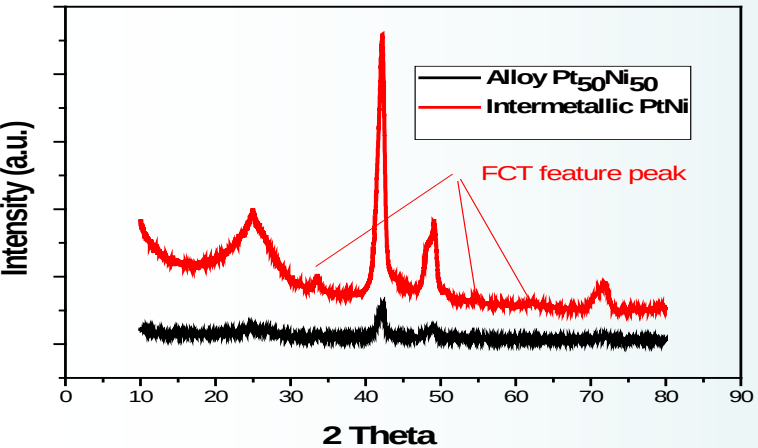


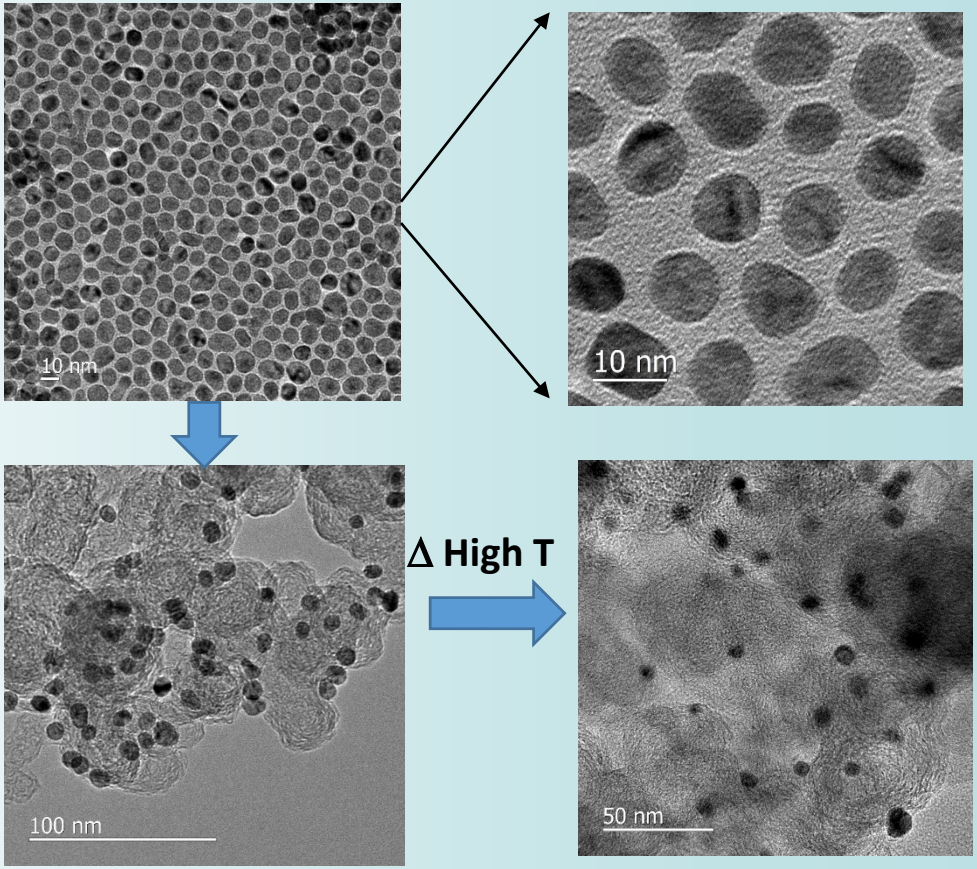


PtCo/C losses only 17% of ECSA and 22% of MA 30K cycles of AST - FCPAD protocol



PtNi/$_{HSA}$C





PtNi NPs keep the same morphology fater annealing

PtNi NPs no sintering after annealing

PtNi NPs converted to intermetallic structure

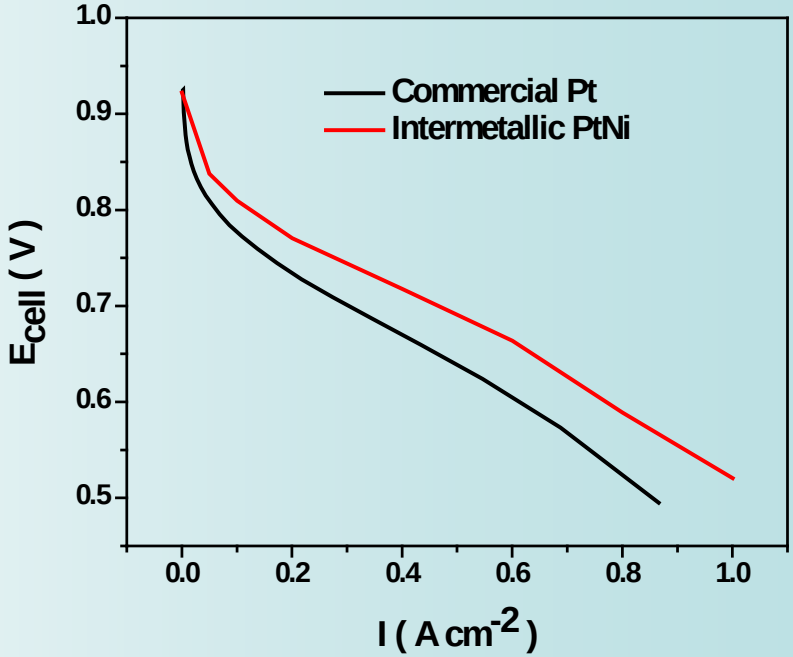
Task 2 Accomplishments: *PtNi 9nm Intermetallic Structures in MEA*

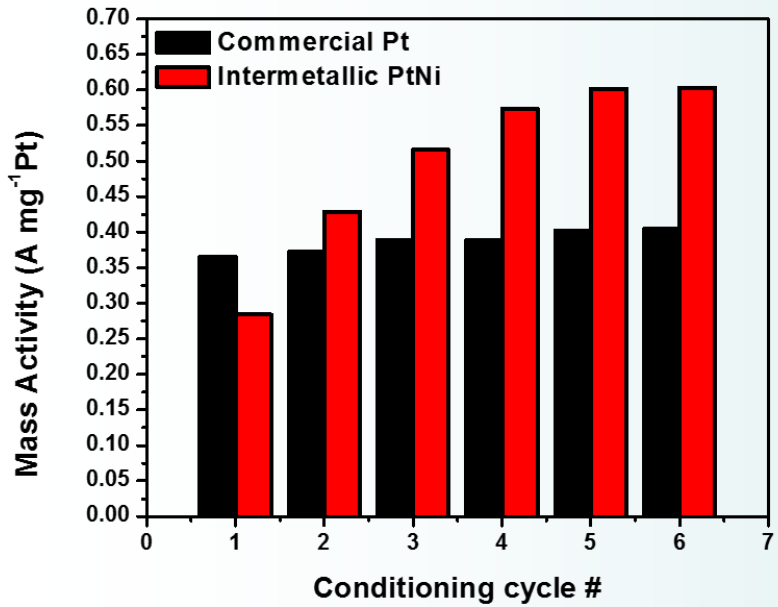
in collaboration with Kenneth Neyerlin, NREL

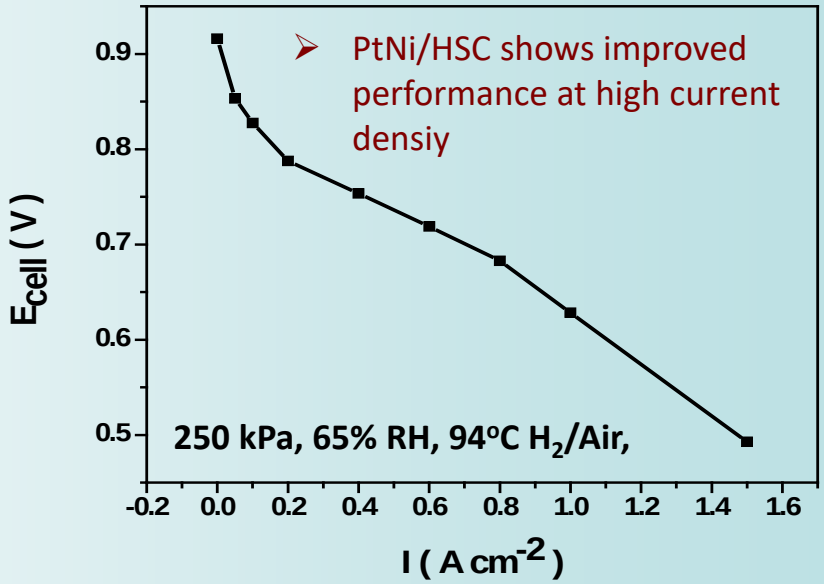
- 150 kPa, 100% RH, 80°C H_2/O_2, 50 cm^2, N211
- Ultrasonic spray coated 0.9 I:C (D2020 ionomer)
- Cathode loading 0.07 mgPt/cm2

Developed PtNi/HSC: $i_m^{0.9V}$ ~ **600 mA/mg_{Pt}**

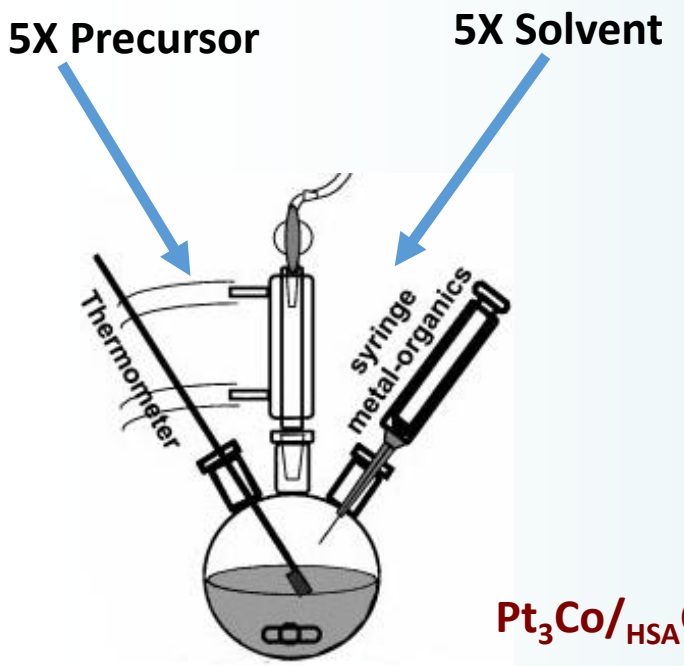
	(m^2/g)
ECSA	35.0



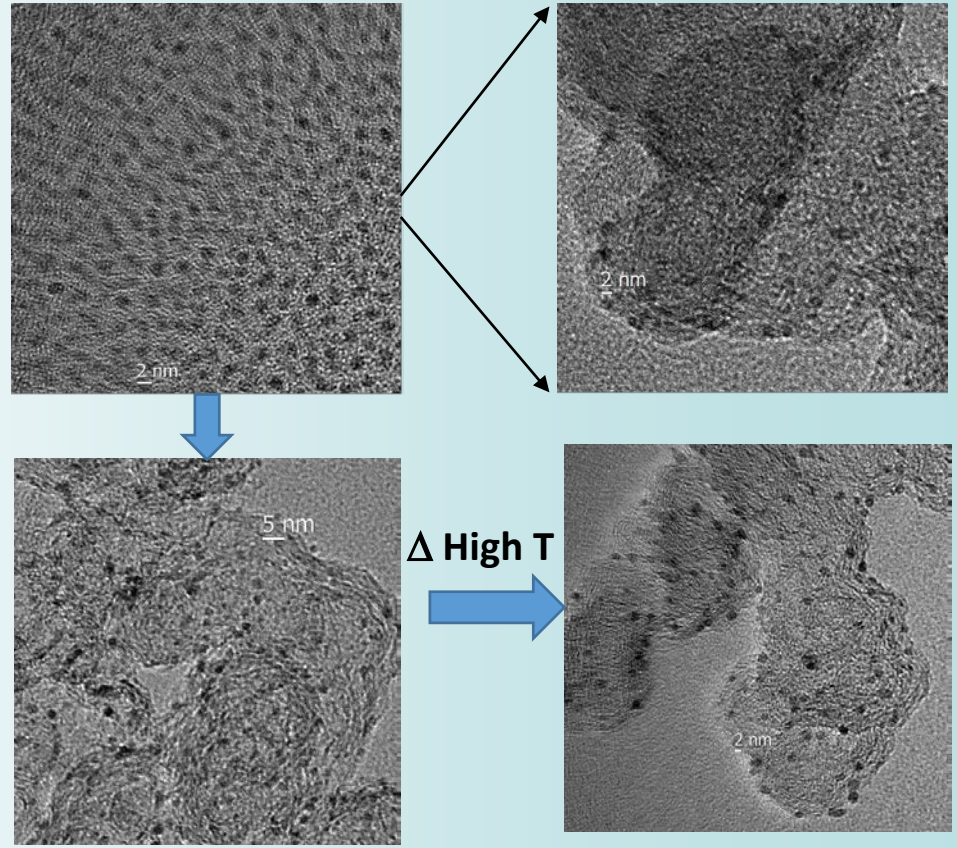


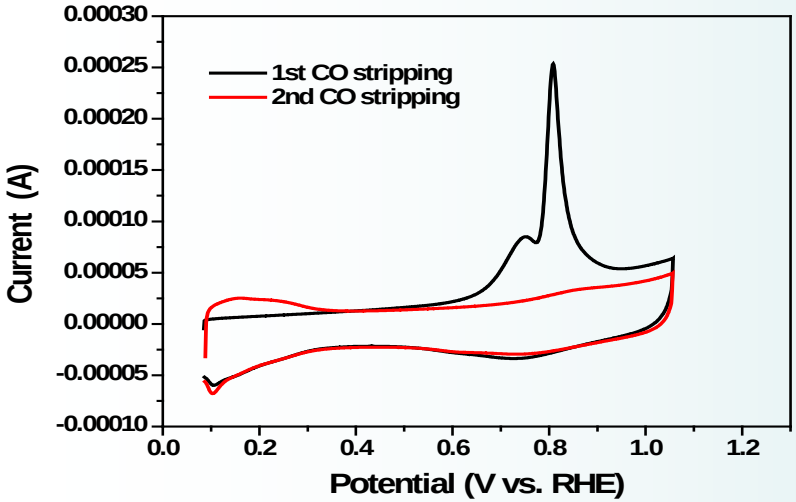


Accomplishments: *Pt_3Co 2nm Annealed Structures*



$Pt_3Co/_{HSA}C$





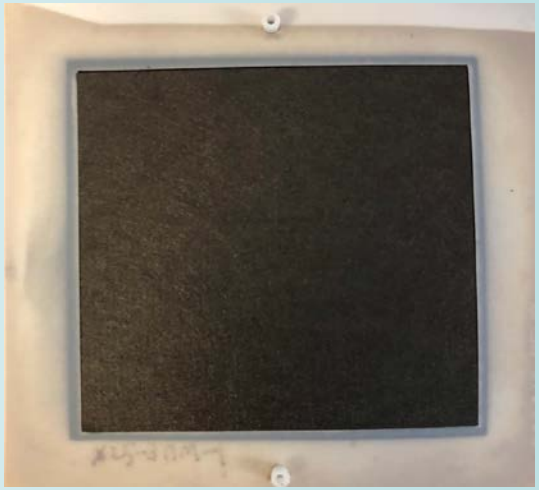
ECSA	(m^2/g)
before annealing	110
after annealing	98

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

Task 2 Accomplishments: *Pt_3Co 2nm Annealed Structures in MEA*

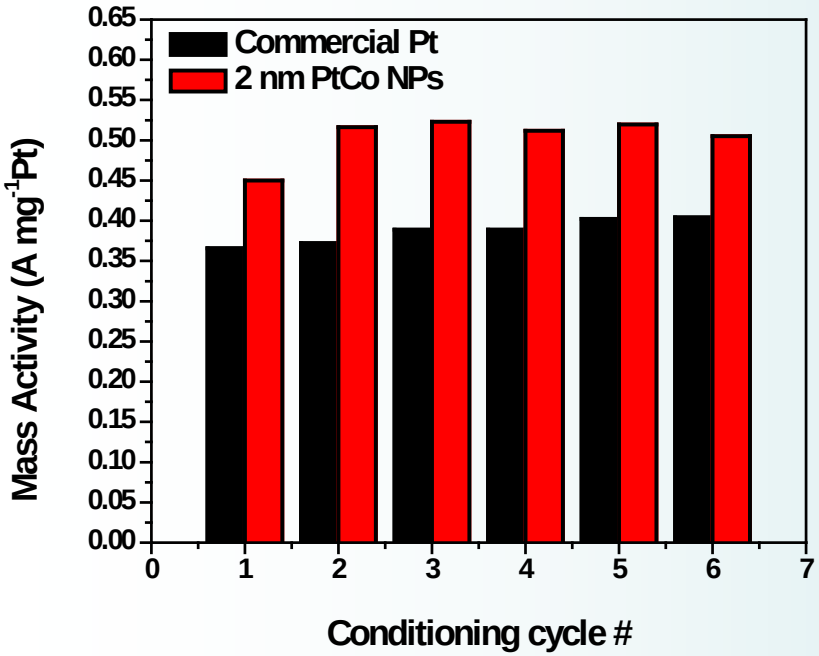
in collaboration with Kenneth Neyerlin, NREL

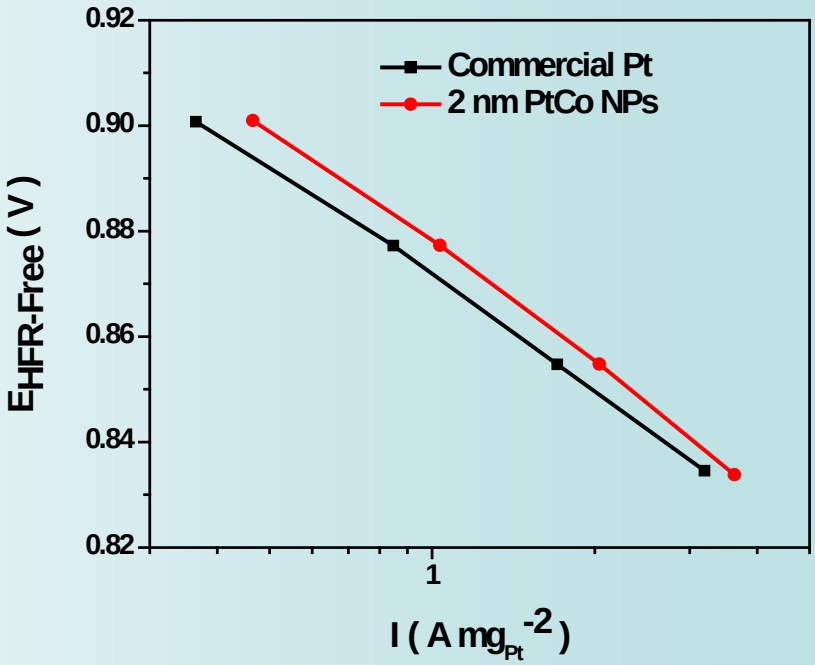
- 150 kPa, 100% RH, 80°C H_2/O_2, 50 cm^2, N211
- Ultrasonic spray coated at NREL 0.9 I:C (D2020 ionomer)
- Cathode loading 0.06 mgPt/cm2



Developed $Pt_3Co/_{HSA}C$: **$i_m^{0.9V}$ ~ 520 mA/mg_{Pt}**

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

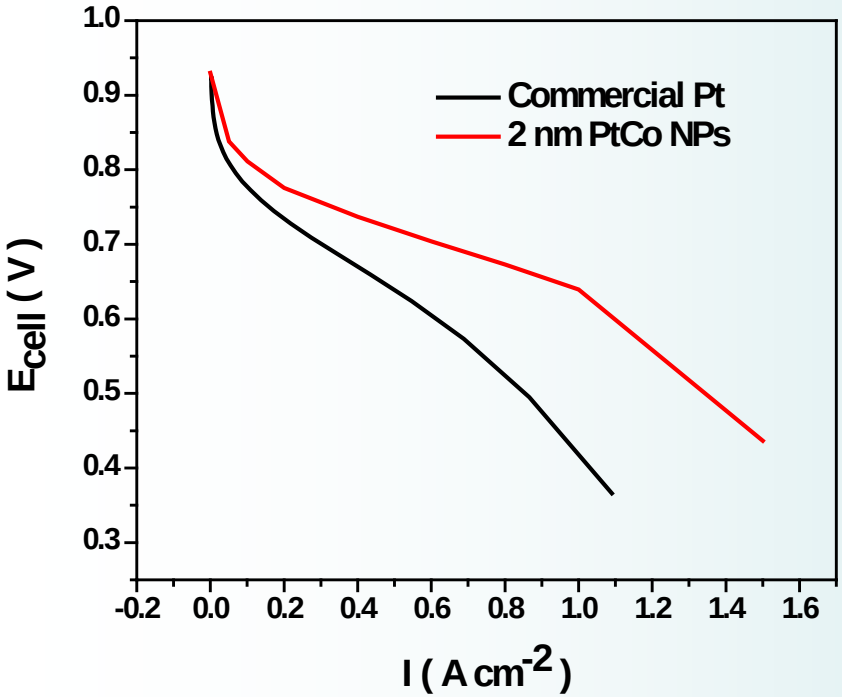


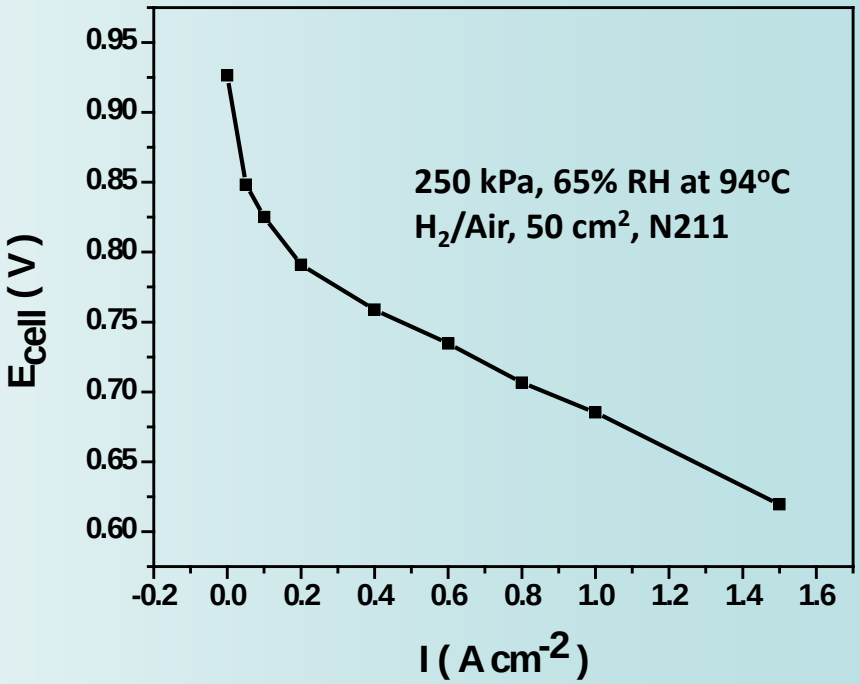


in collaboration with Kenneth Neyerlin, NREL

- 150 kPa, 100% RH, 80°C H_2/Air, 50 cm^2, N211, 0.055 mg_{Pt}/cm^2

	(m^2/g)
ECSA	56.0



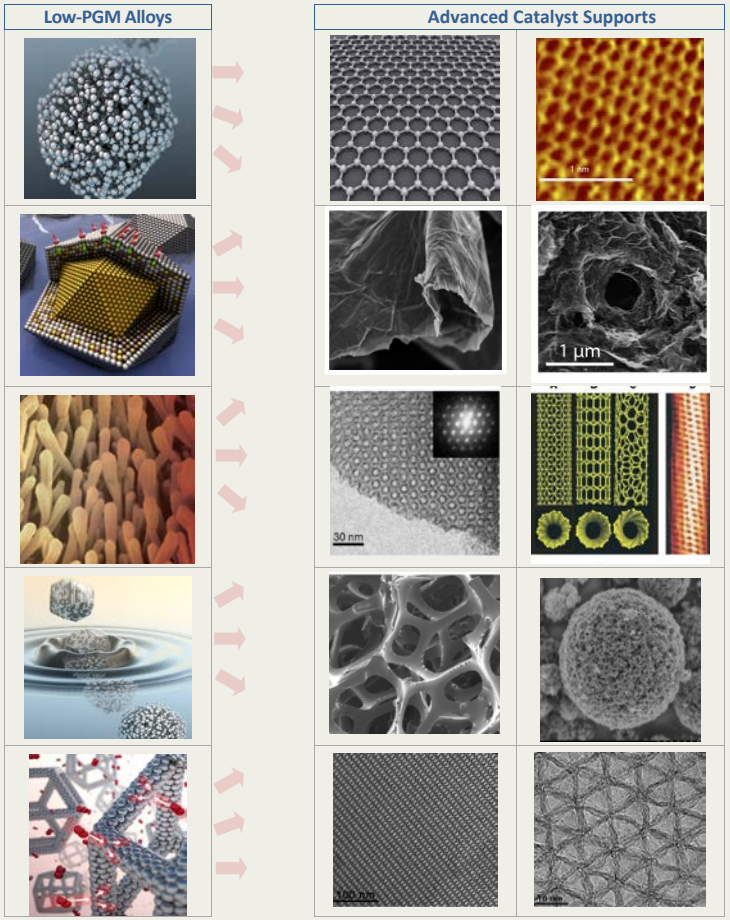


➢ **2nm Pt_3Co/HSC also shows improved performance at high current density**

Collaborations and Coordination

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

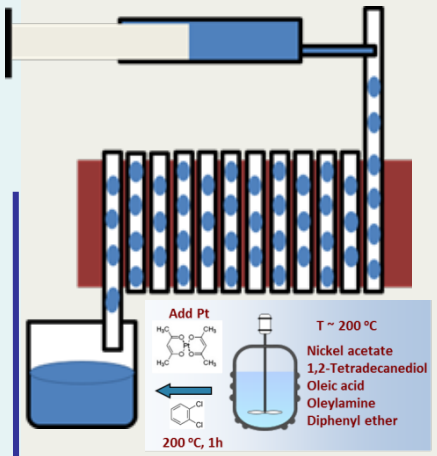
OAK RIDGE National Laboratory **Sub:** structural characterization



Low-PGM Alloy Catalysts

Argonne NATIONAL LABORATORY

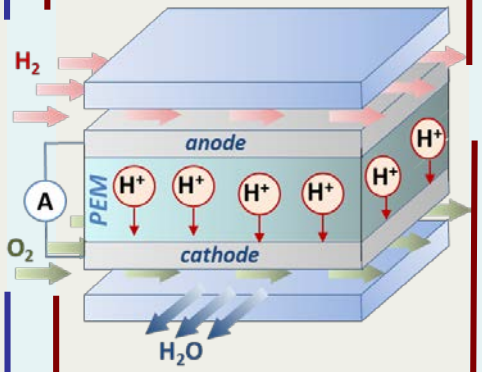
process R&D and scale-up



Catalysts Scale Up

Argonne NATIONAL LABORATORY **5 / 25cm² MEA**

NREL **50cm² MEA**



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 mg_{PGM} / cm^2)

3) Performance (mass activity @ 0.9V 0.44 A/mg_{Pt})

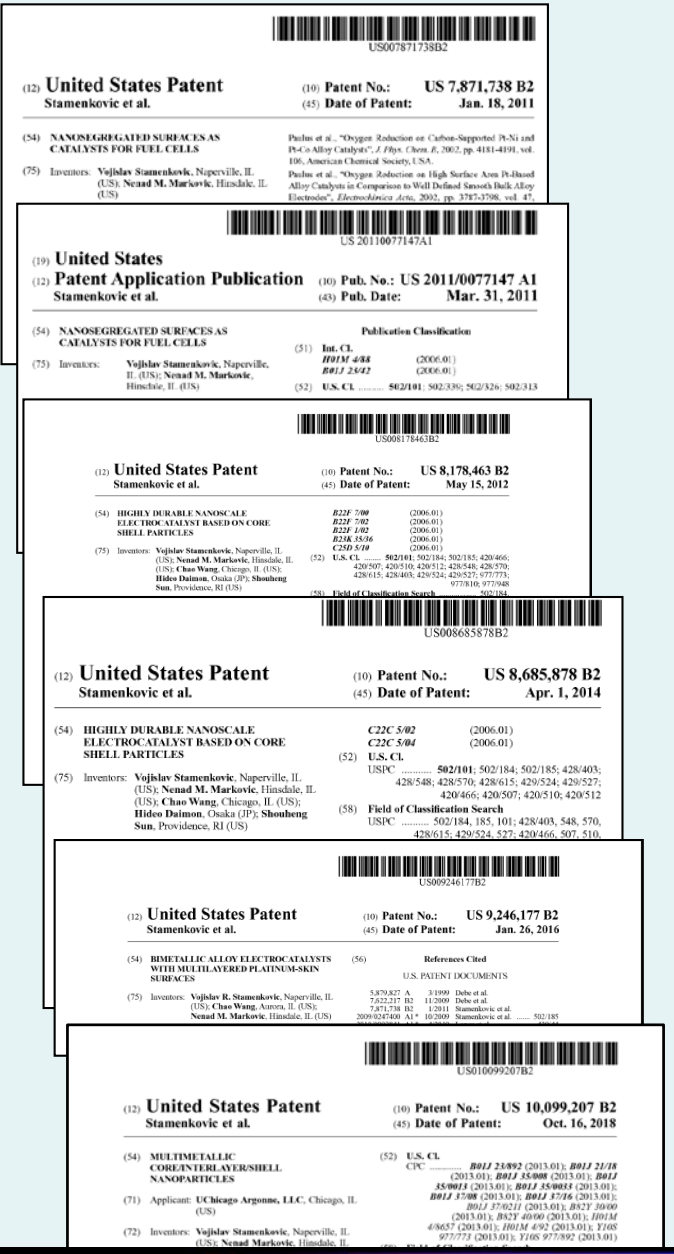
Future Work

- **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

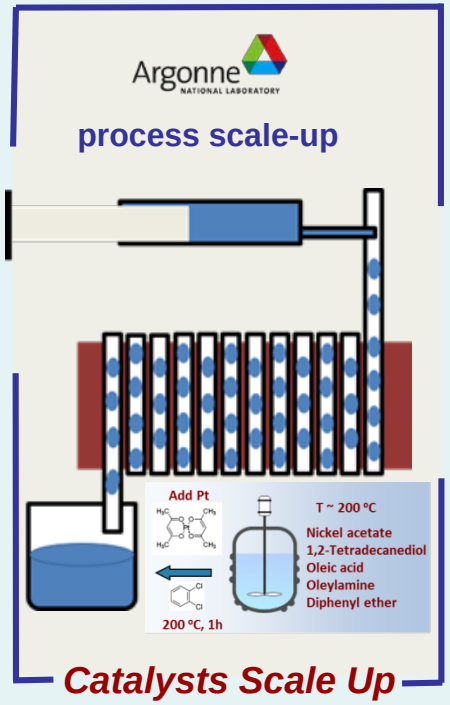
- **High Durability, High Duty, High ECSA** systems

Future work will depend on appropriations

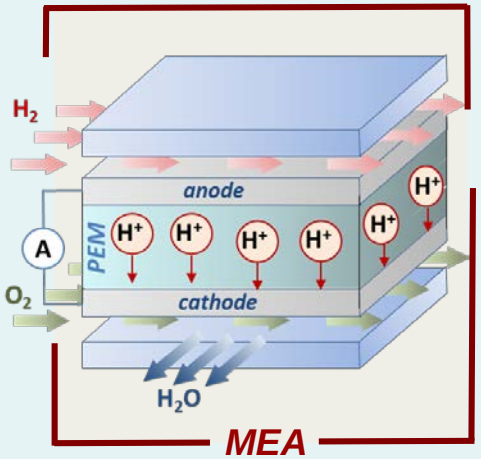
Technology Transfer Activities



T2M



Auto OEMs



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 Pt_3Au/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 cm^2 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