Argonne NATIONAL LABORATORY

2017 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

Overview

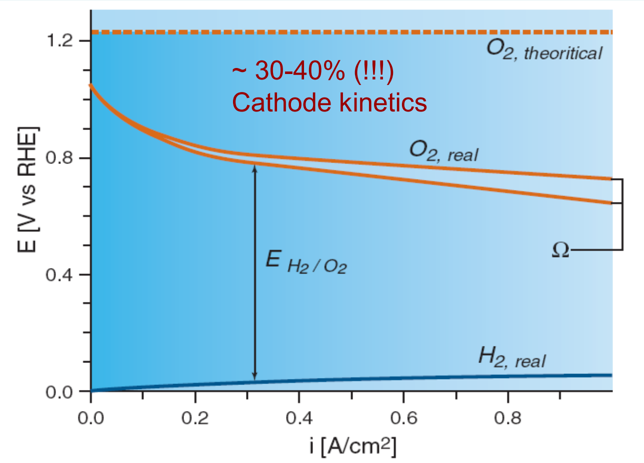
Timeline

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

Budget

- Total Project funding $ 3.6M
- Funding for FY17: $ 1.2M

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
- **Lawrence Berkeley National Laboratory** – Peidong Yang
- **Los Alamos National Laboratory** – Rod Borup, Plamen Atanassov (UNM)
- **Oak Ridge National Laboratory** – Karren More

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***

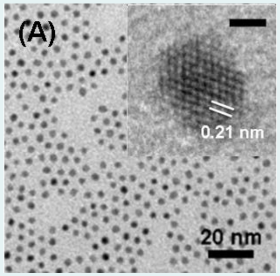
Table 3.4.13 Technical Targets: Electrocatalysts for Transportation Applications[h]

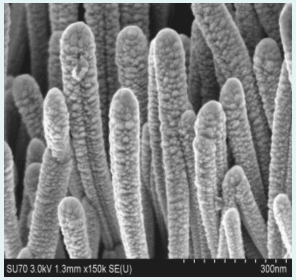
Characteristic	Units	2011 Status	2020 Targets
Platinum group metal total content (both electrodes)[a]	g / kW (rated)	0.19[b]	0.125
Platinum group metal (pgm) total loading[a]	mg PGM / cm^2 electrode area	0.15[b]	0.125
Loss in initial catalytic activity[c]	% mass activity loss	48[b]	<40
Electro catalyst 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 → **A N L**

PEMFC Cathode Catalysts Development

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

Inter Lab Collaborators

- **LBNL $100K** Catalyst Synthesis
- **ORNL $50K** Electron Microscopy
- **LANL $150K** $50cm^2$ MEA testing
- **LANL** Advanced supports
- **ANL/LBNL $200K** Support of Scaling-Up

Task

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

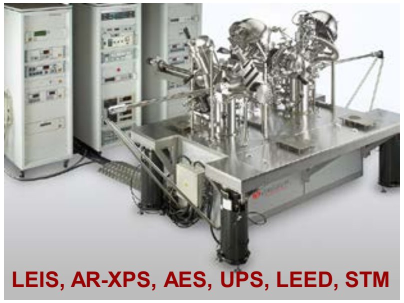
2° synthesis of nano-, meso- and thinfilm- PtMN catalysts:
- -shape/size/composition control
- -intermetallics; core/interlayer/shell; thin-film systems
- (colloidal chemical synthesis, PVD, HRTEM/STEM)

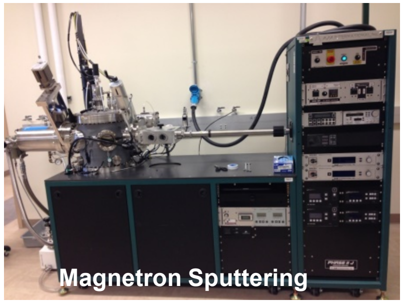
3° electrochemical characterization of catalysts:
- -optimization: ionomer/carbon/propanol/catalyst ink
- -temperature effect; Ionic Liquid evaluation
- -activity/durability in RDE vs. 5-50cm²/MEA; HRTEM

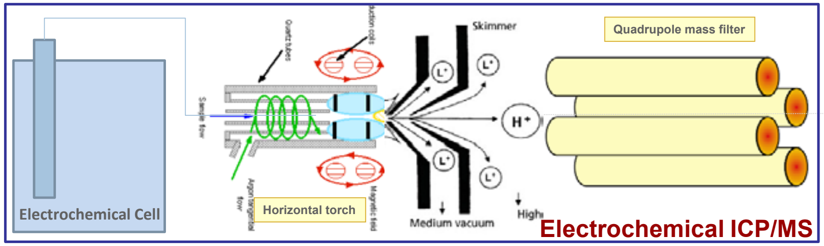
4° fine tuning of performance through catalyst-support:
- -Carbon based materials

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

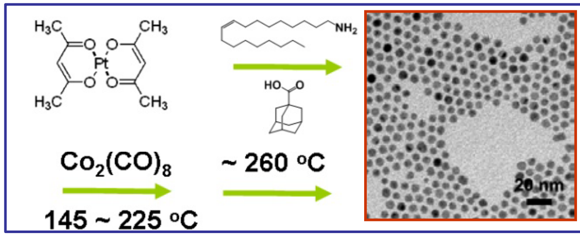
TASK 1







TASK 2&5



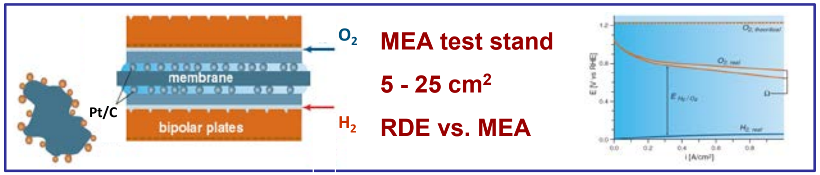
scale-up synthesis of nanomaterials

grams of catalyst

solvo-thermal

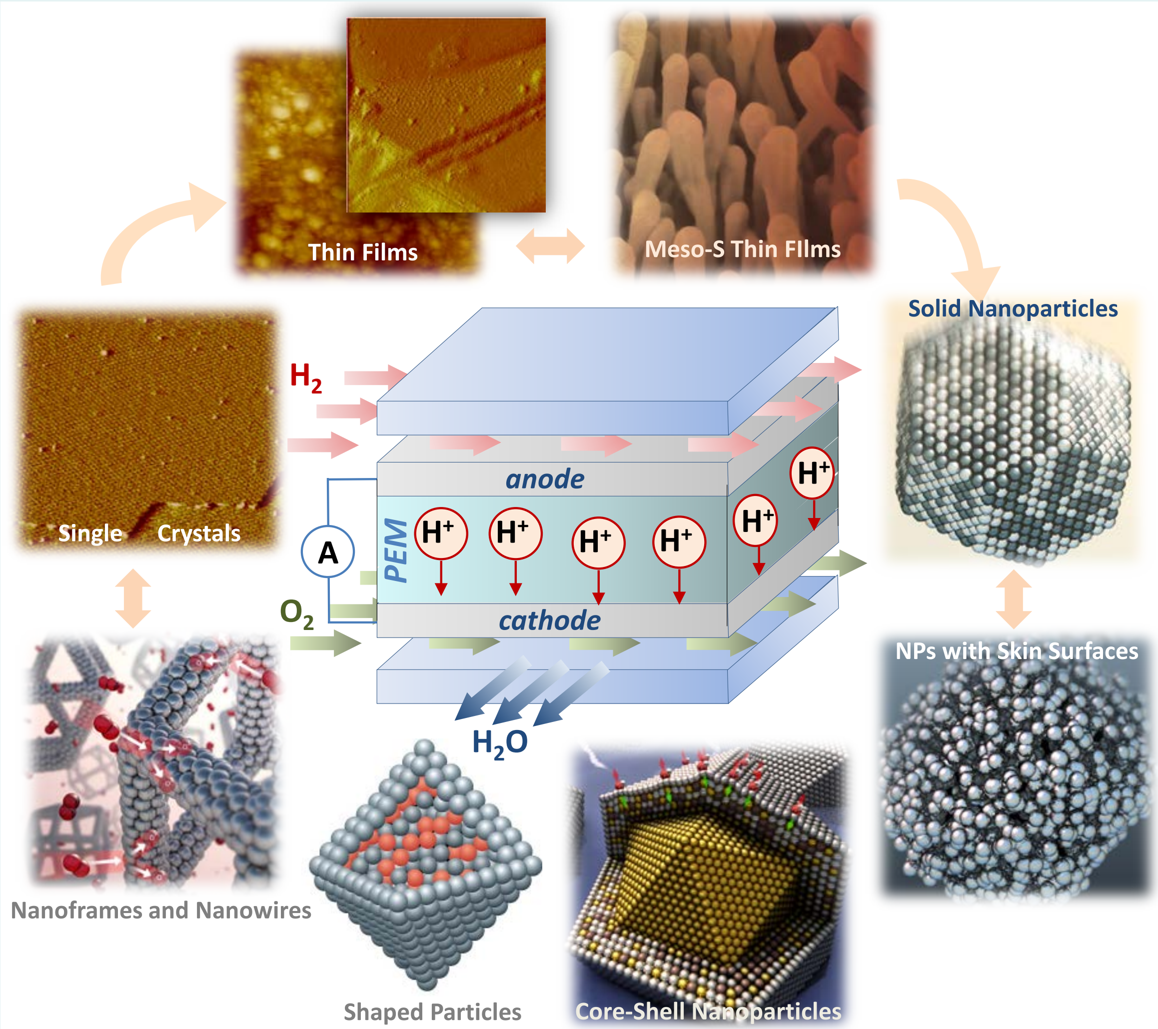
advanced supports

TASK 3



- **Rational synthesis based on well-defined systems**
- **Addition of the elements that hinder Pt dissolution**
- **Activity boost by lower surface coverage of spectators**
- **Prevent loss of TM atoms without activity decrease**

Approach



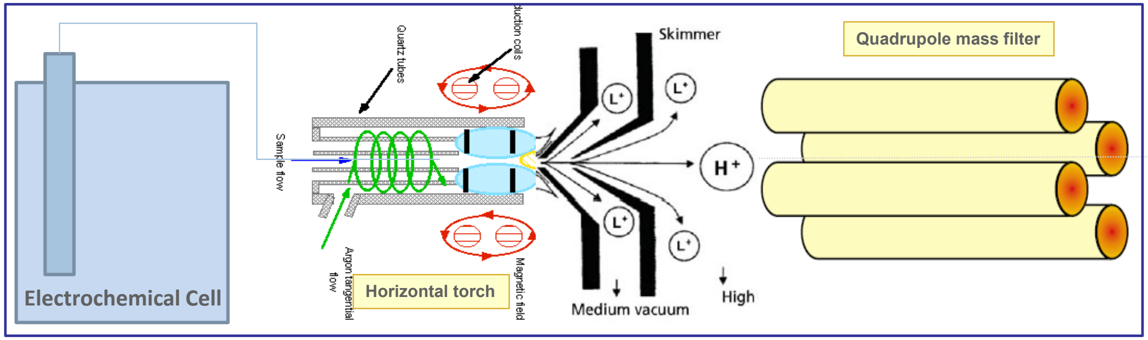
Project Management

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

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

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

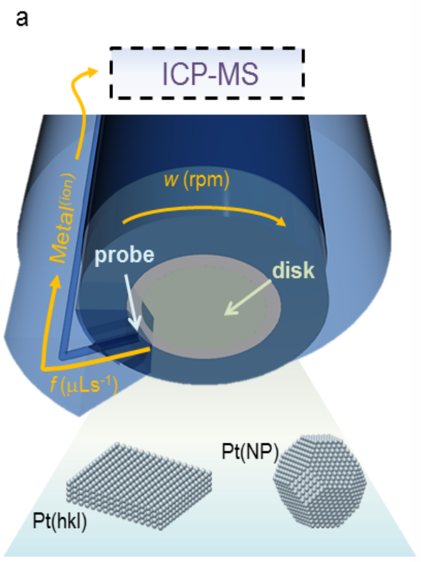
Task 1 Accomplishments and Progress: *RDE-ICP/MS of* Pt/C Nanoparticles

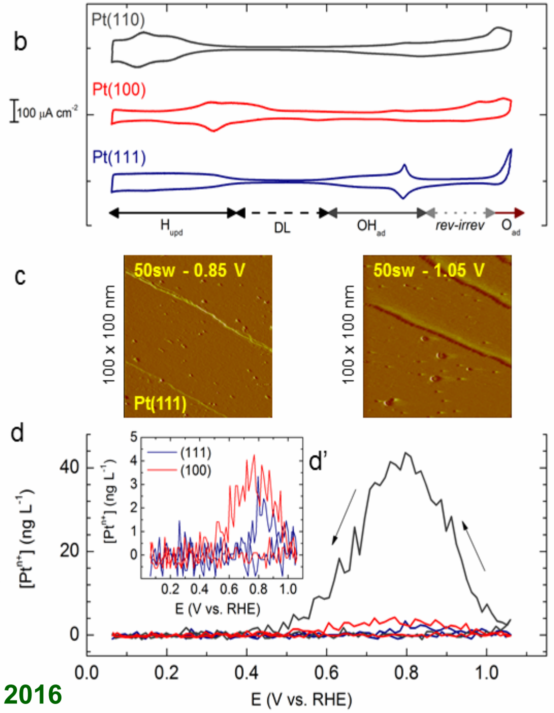


Surface Structure	Pt(111)	Pt(100)	Pt(110)	Pt-poly
Dissolved Pt per cycle [μML]	2	7	83	36

Detection Limit: 0.8 μML of Pt

In-Situ RDE-ICP/MS

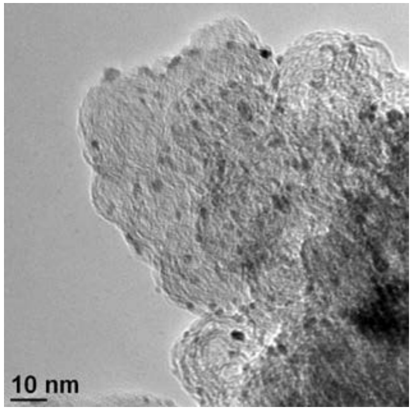


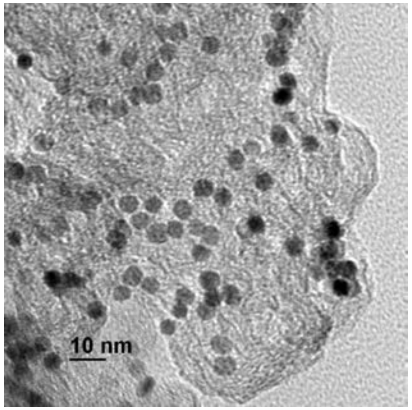


P. P. Lopes, D. Strmcnik, J. Connell,
V. R. Stamenkovic and N.M. Markovic
ACS Catalysis, 6 (4), 2536-2544, 2016

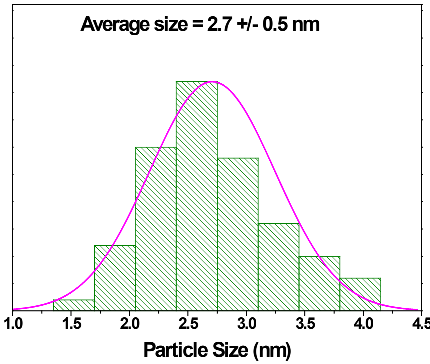
Correlation between Surface Structure - Activity – Dissolution

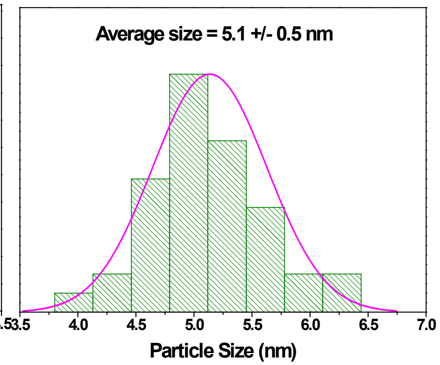
Monodisperse 20% Pt/C NPs 3 and 5nm



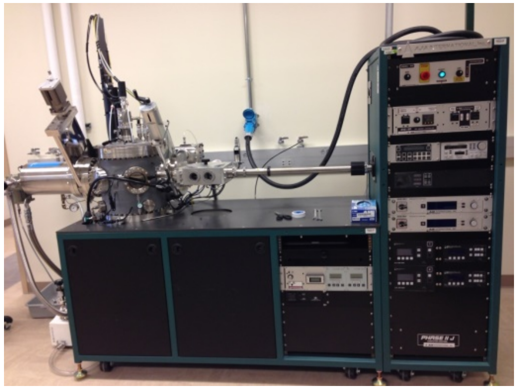


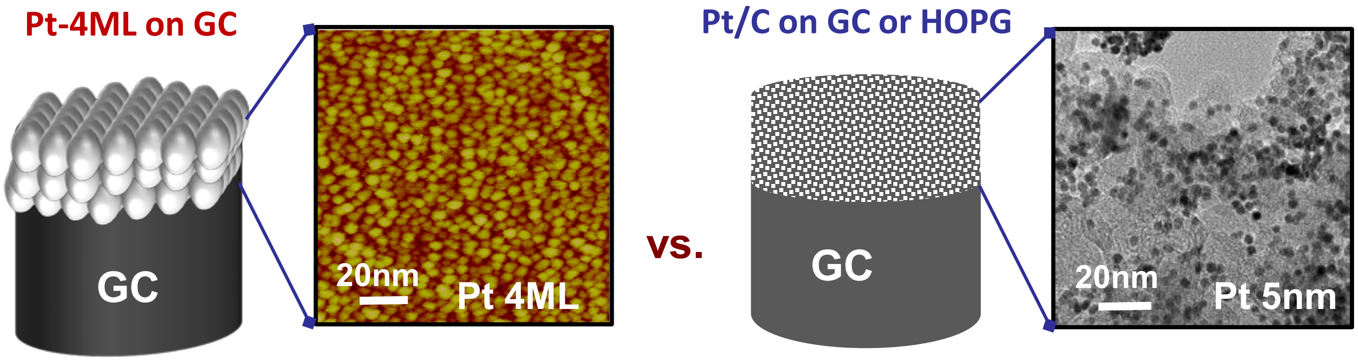
2.7+/-0.5 nm **5.1 +/- 0.5nm**



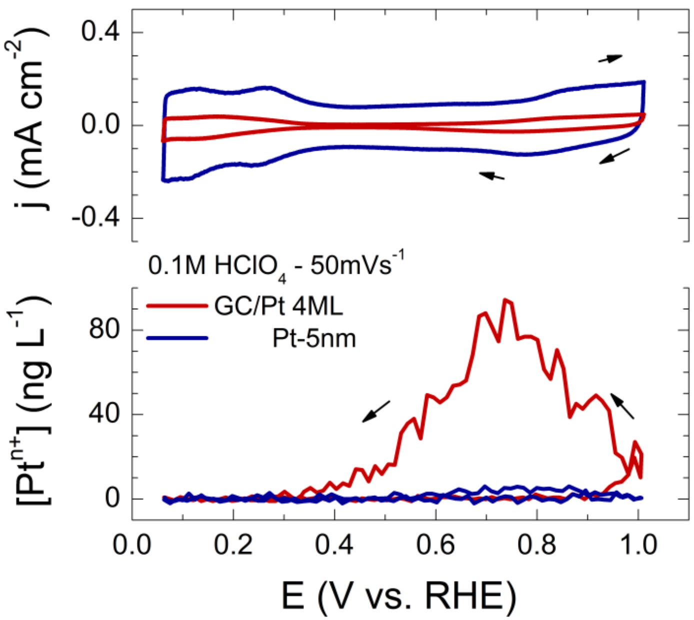


Accomplishments and Progress: *In-Situ EC-ICP-MS* Pt-Surfaces





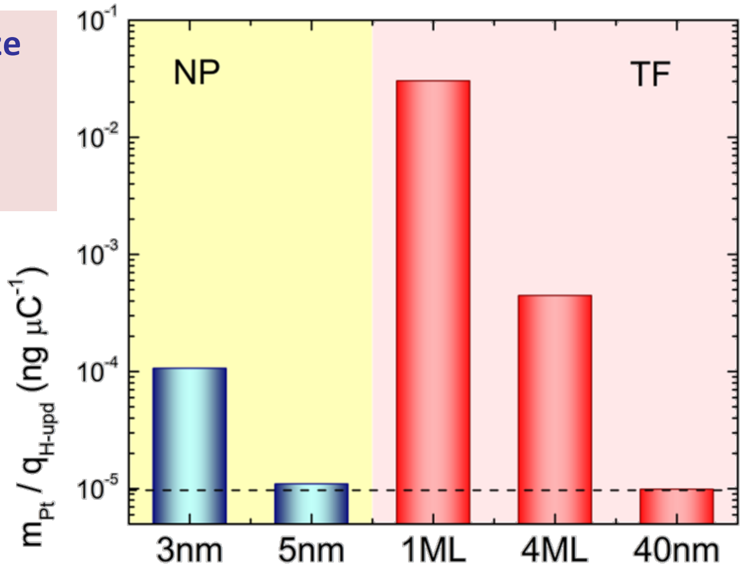
Electrode morphology ("2D" vs. 3D)



- Similar cluster/particle size
- Normalization by H_{upd} : *specific dissolution rate*

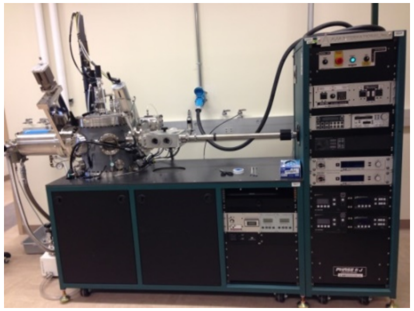
Potential range: 0.05 to 1.0 V

T = 25°C

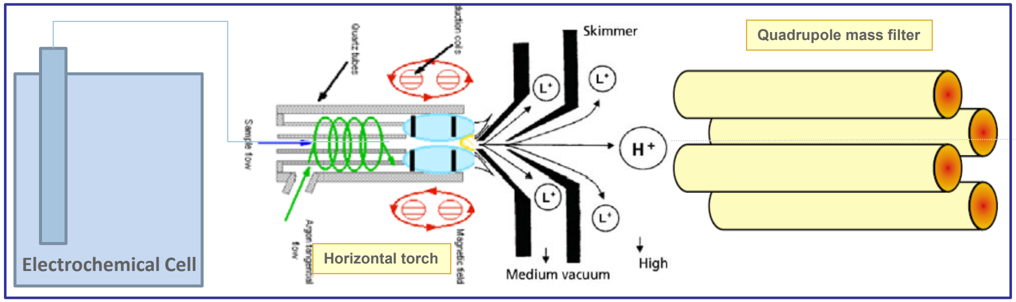


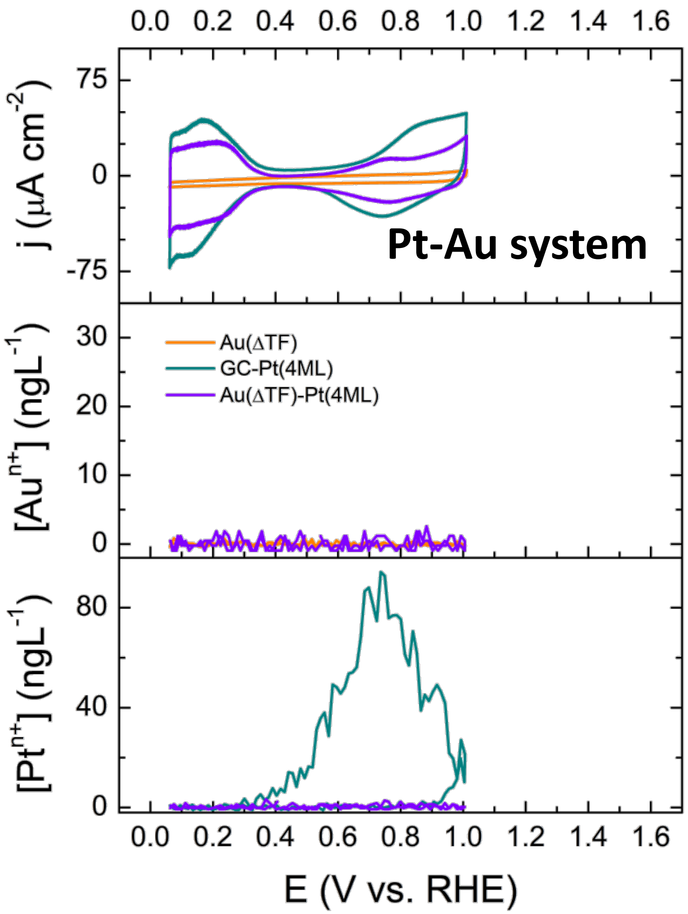
3D morphology of Pt/C layer over GC enables redeposition of Pt and attenuates dissolution

Redeposition of Pt leads to the coarsening of particles as opposed to dissolution



GC vs. Au vs. Pd

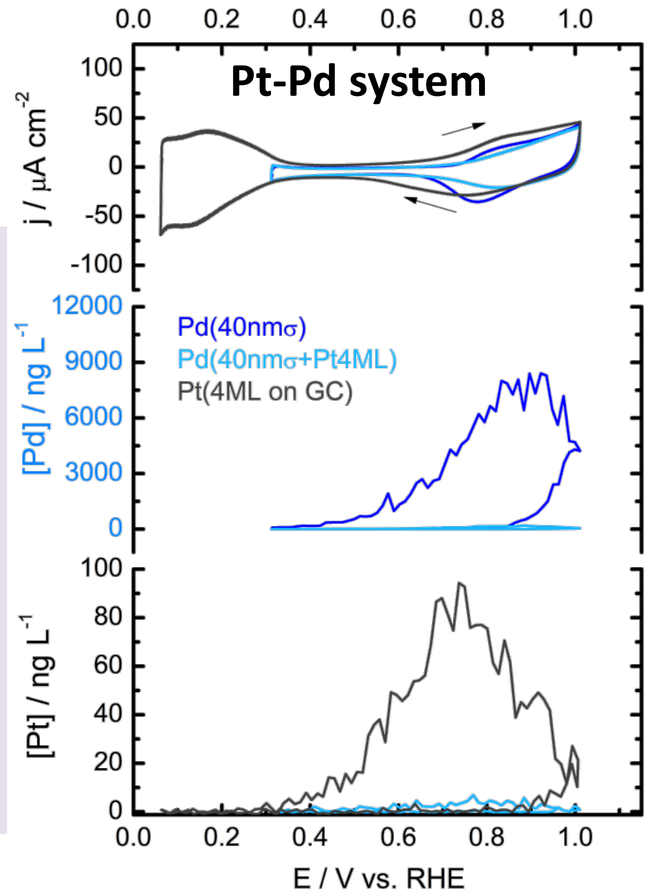




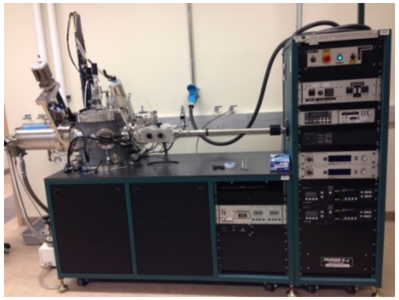
Potential range: 0.05 to 1.0 V

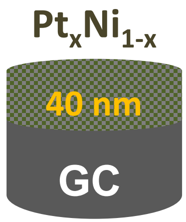
T = 25°C

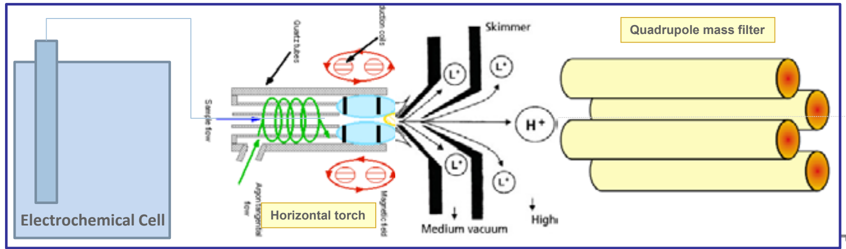
- **Adding Pt on top of Pd decreases significantly Pd dissolution**
- **Subsurface of Pd improves Pt stability as compared to GC as substrate**
- **Improved stability for both metals**
- **Pd subsurface still dissolves through pinholes**



Accomplishments and Progress: *In-Situ EC-ICP-MS* Pt_xNi_{1-x} Alloys



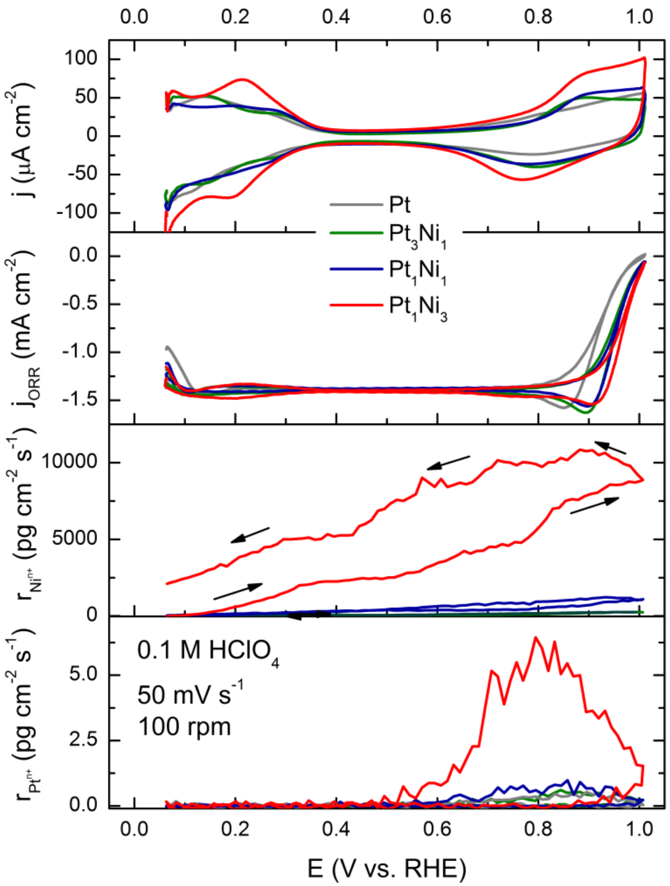




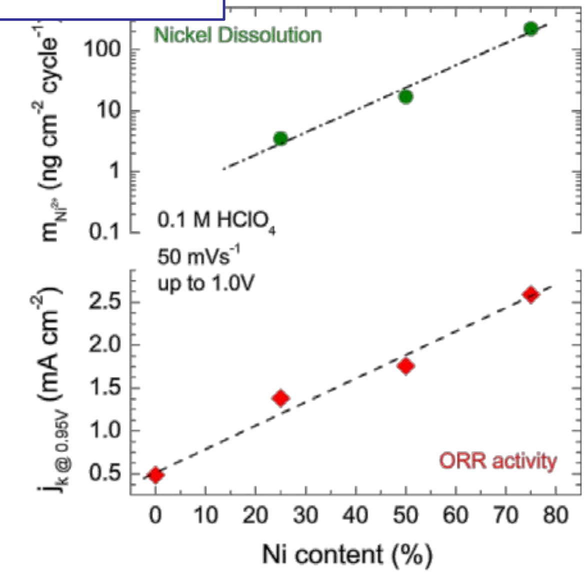
Tuning the alloy composition to explore activity-stability relationships

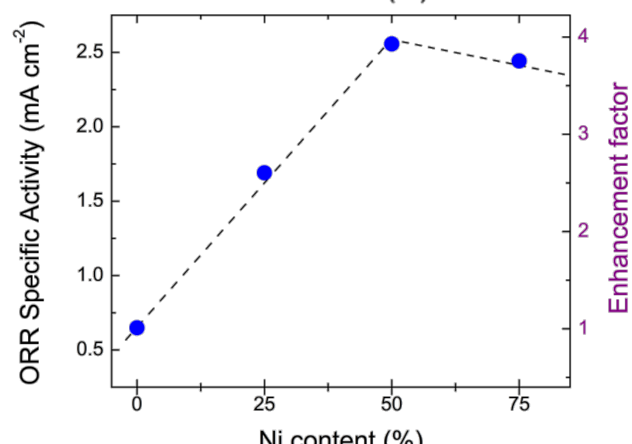
Potential range: 0.05 to 1.0 V

T = 25°C



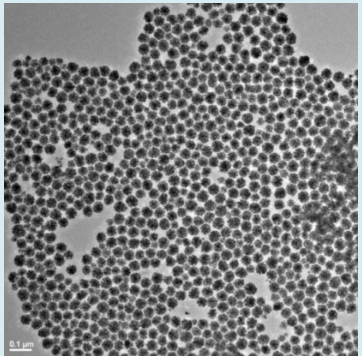
- **Presence of Pt promotes Ni stability**
- **Increasing Ni content enhances ORR activity**
- **Stability of Pt decreases with Ni content**
- **Optimal Ni conc. is 1:1**

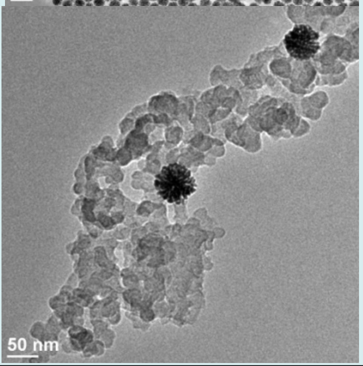


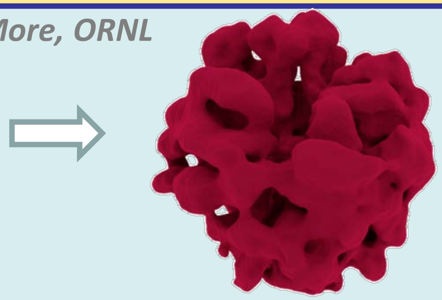


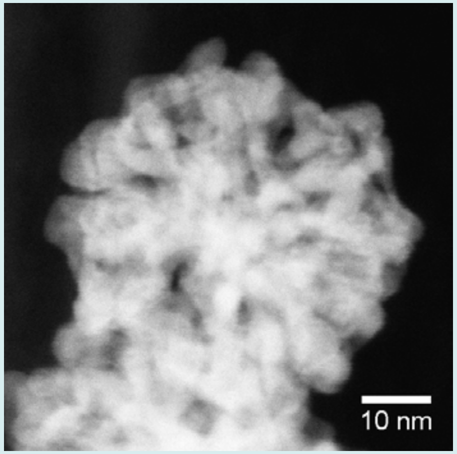
Accomplishments and Progress: *PtNi Nanopinwheels / C*

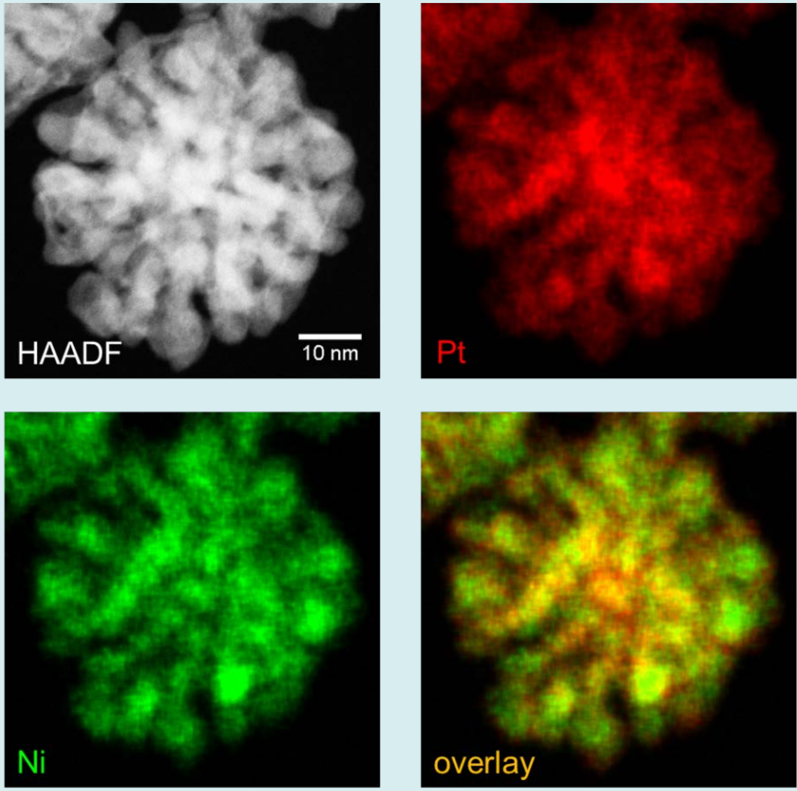
in collaboration with K.L. More, ORNL

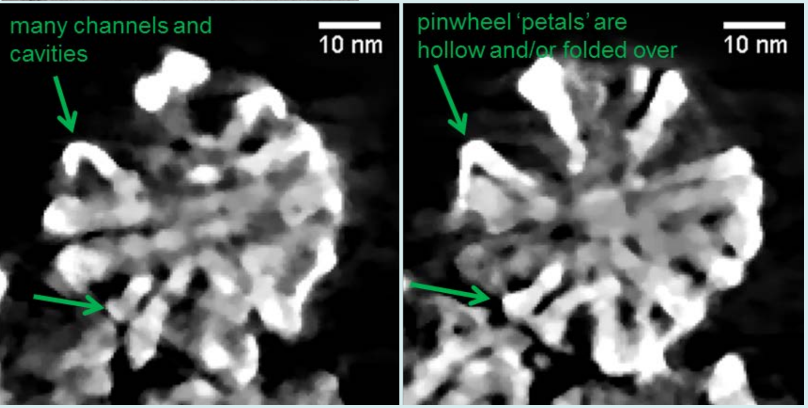


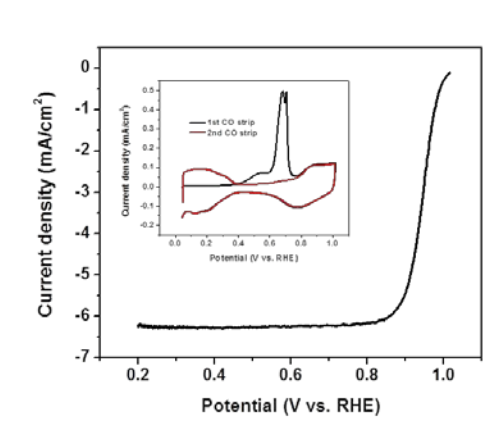


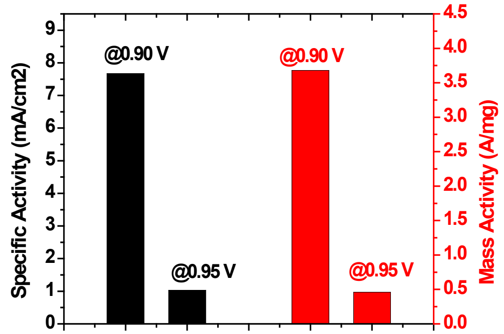






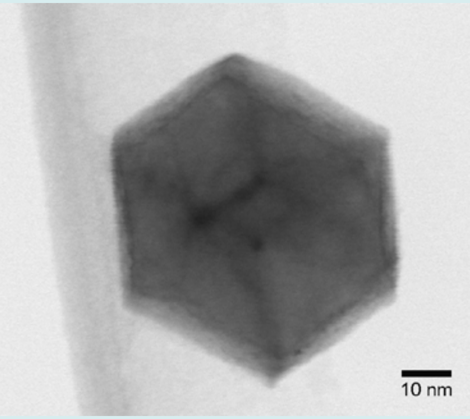


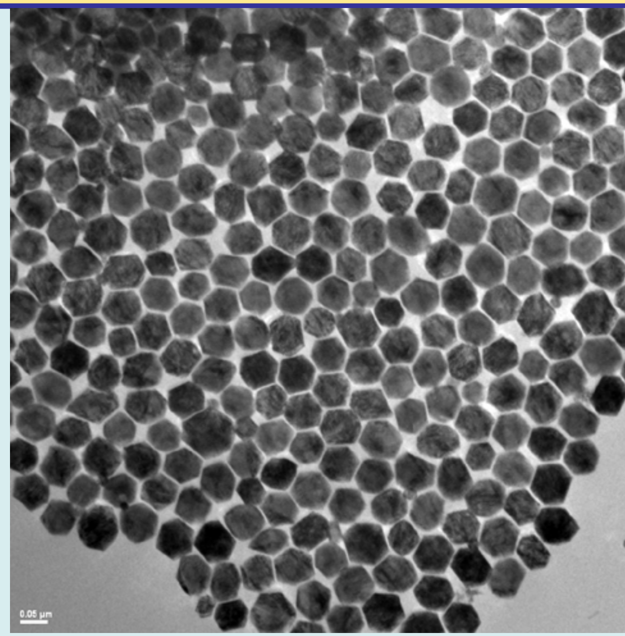


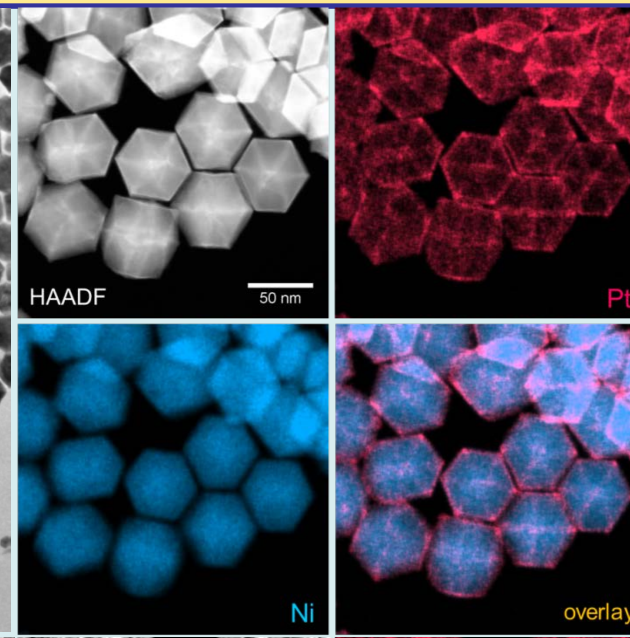


Accomplishments and Progress: *PtNi Nanocage Structure*

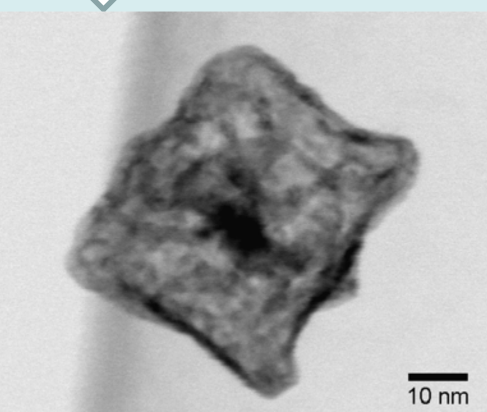
in collaboration with K.L. More, ORNL

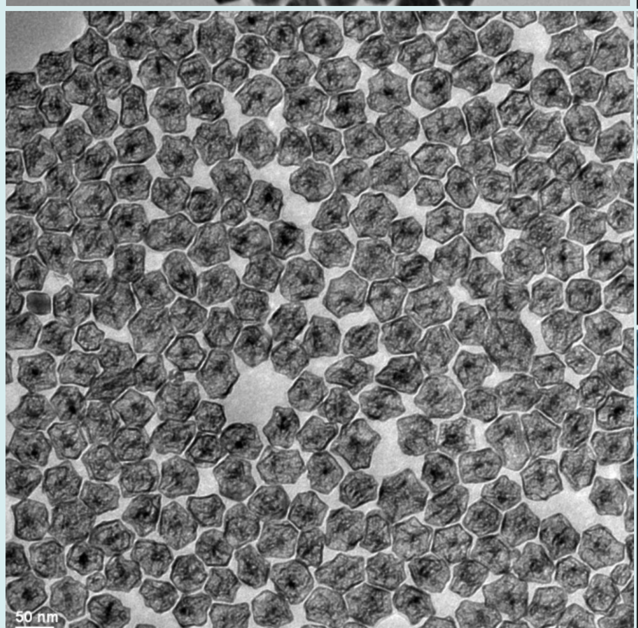


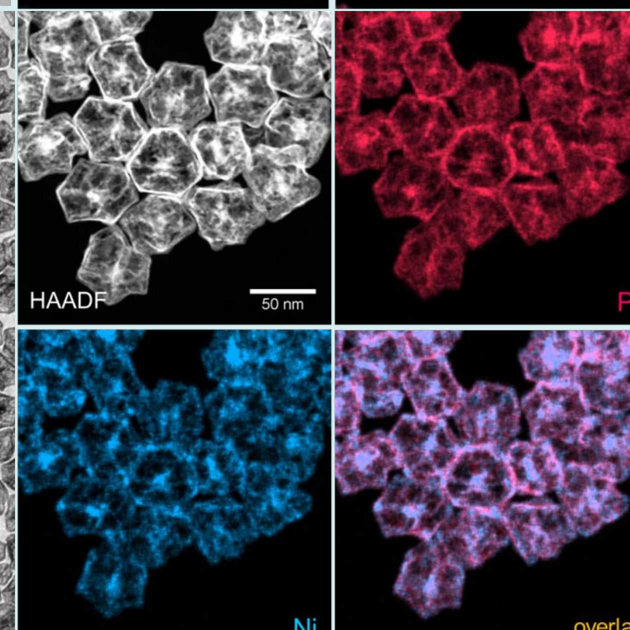




PtNi solid polyhedra are converted into hollow nanocages after evolution treatment



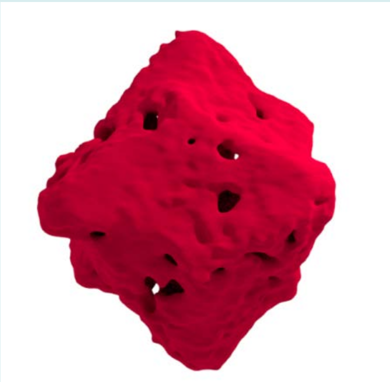


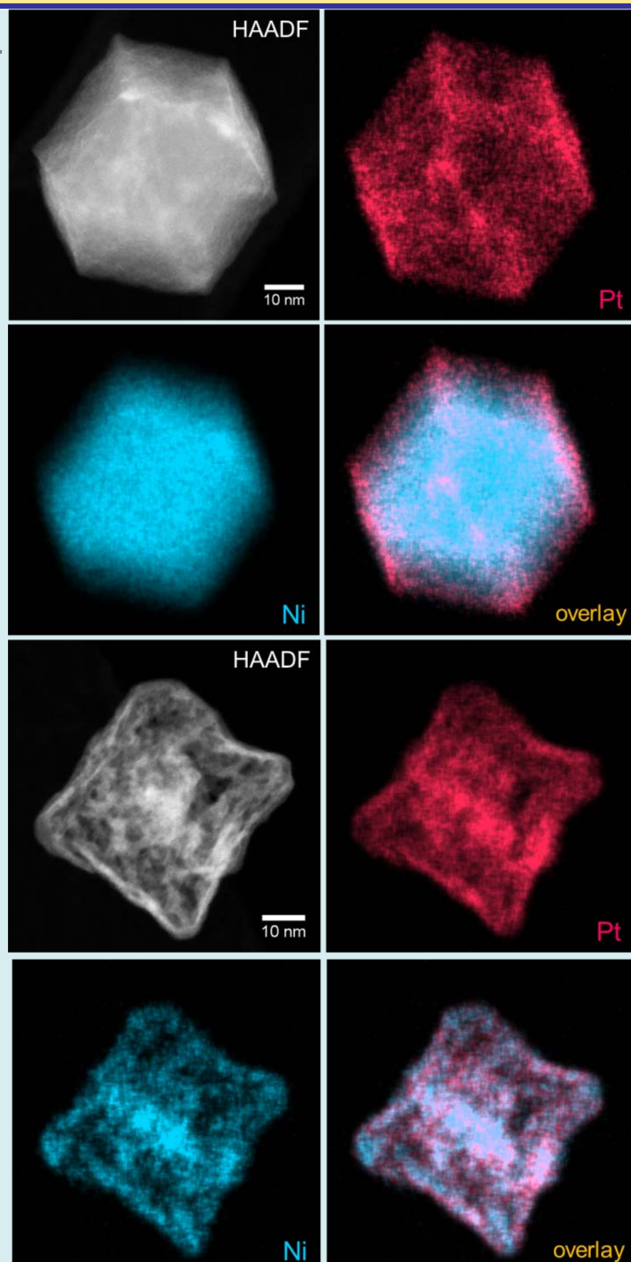


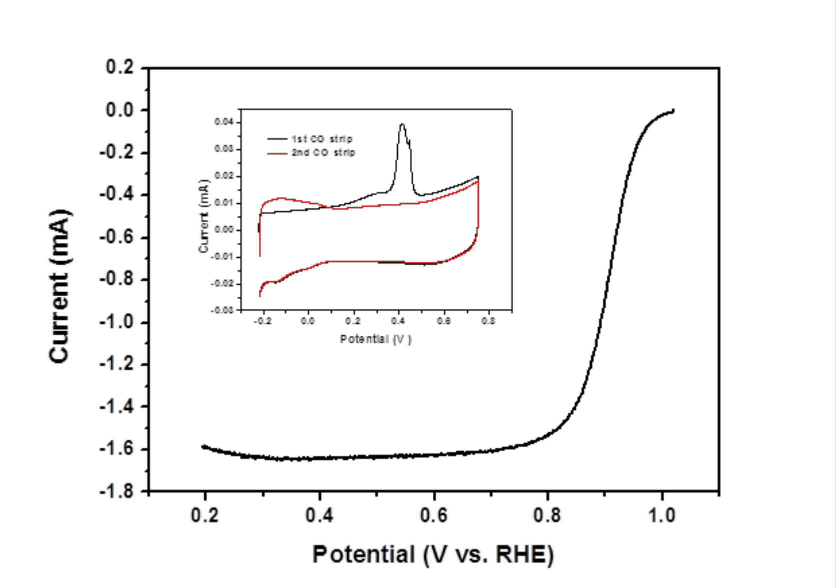
Task 2-3 Accomplishments and Progress: *PtNi Nanocage Properties*

Collab. with K.L. More, ORNL

Evolution treatment







	Specific Aactivity (mA/cm2)		Mass Activity (A/mgPt)	
	0.95 V	0.90 V	0.95 V	0.90 V
PtNi Nanocages	**0.73**	**5.89**	**0.44**	**2.8**
Pure Pt Nanocages (1)	**NA**	**1.98**	**NA**	**0.75**

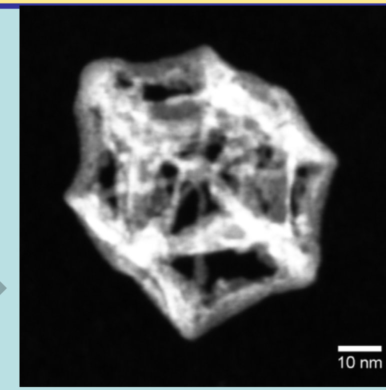
The PtNi Nanocages show high ORR activity in RDE experiments

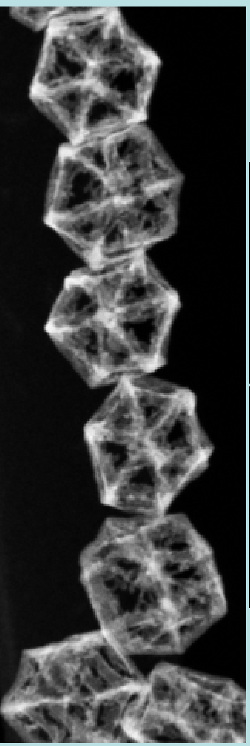
Task 2 Accomplishments and Progress: *PtNi Nanoframes with Radial Joists*

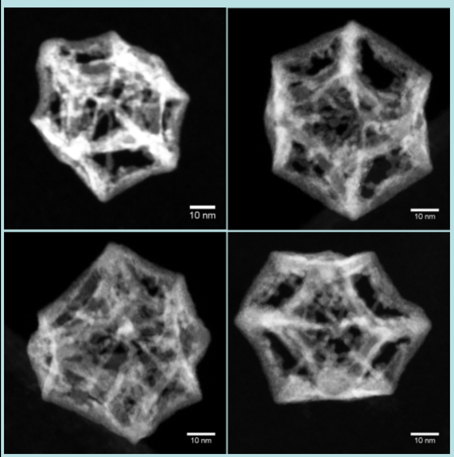
in collaboration with K.L. More, ORNL

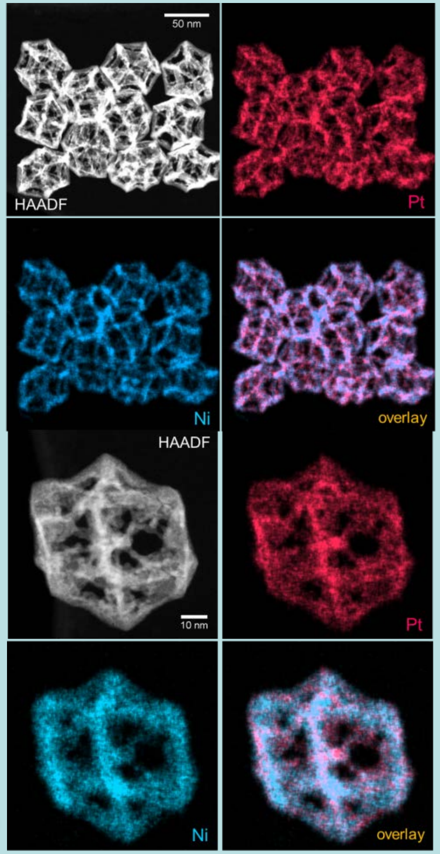
Different than the NFs
A new PtNi NFs with the radial joists

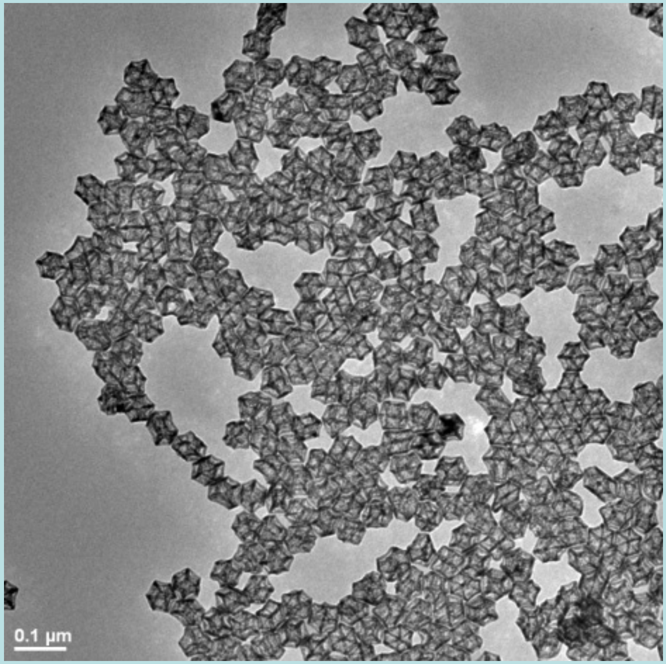
HAADF







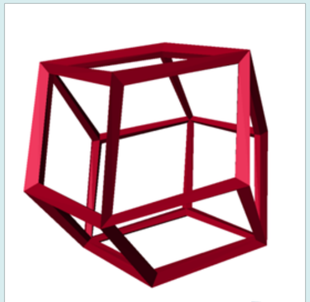




in collaboration with K.L. More, ORNL

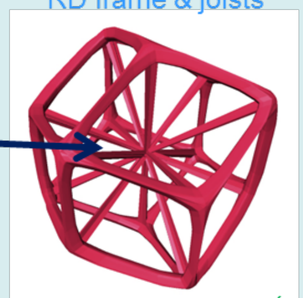
Structure analysis

blender models: RD frame



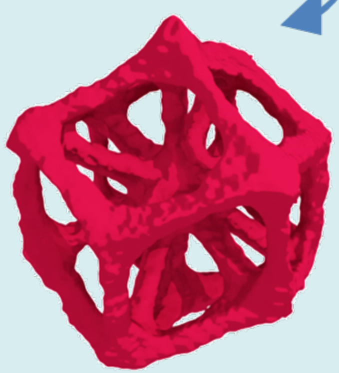
*structure is slightly deformed (concave/excavated facets with wire frame) and contains additional linkages in the interior… connecting surface vertices to central point

RD frame & joists



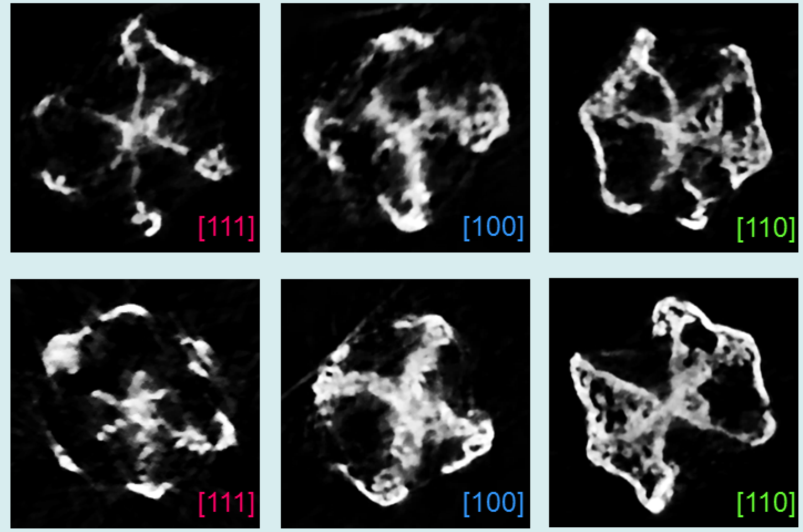
radial joists to each vertex

…& deformation added:



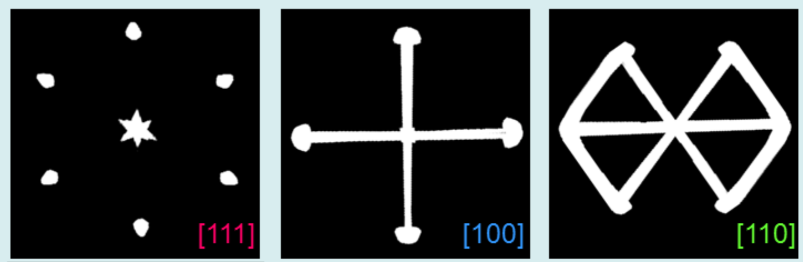
slices through volume center at different orientations:

(electron tomography)



slices through volume center of blender RD frame model with joists from each vertex to center (for reference):

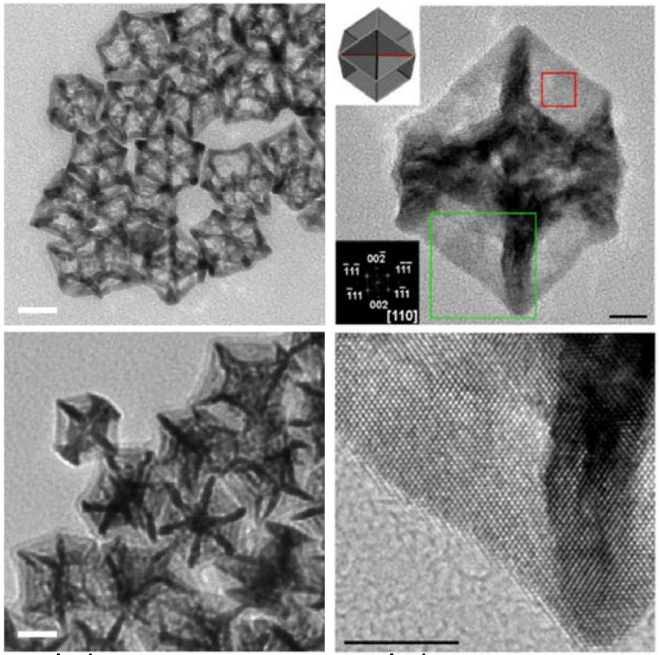
(model)



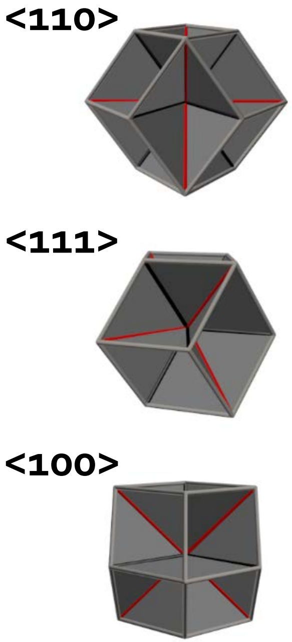
the similarity between the 3D cross-sections and cross sections of the modeled frame with radial joists suggests the majority of vertices are joined with the core, no major preference toward 100 (6x) or 111 vertices (8x)

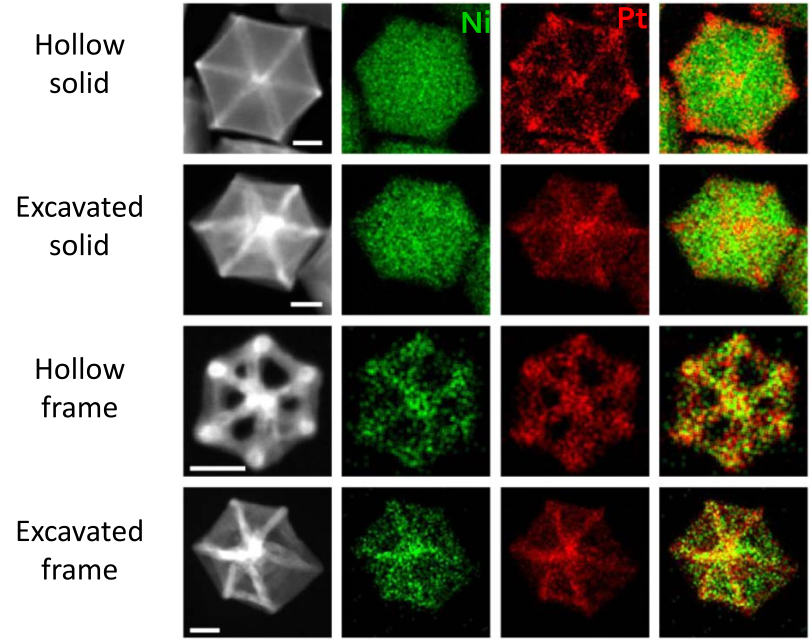
Accomplishments and Progress: *PtNi Excavated Nanoframes*

in collaboration with Peidong Yang, LBNL

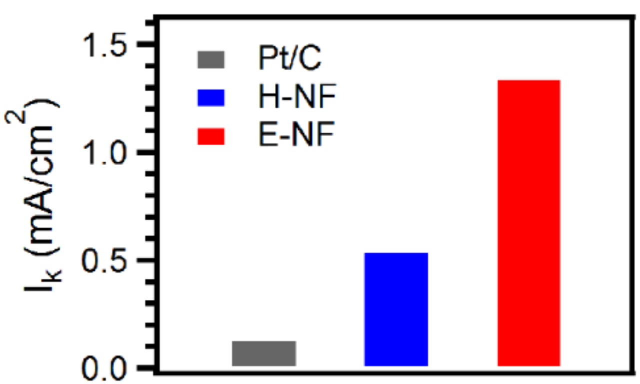


Scale bar = 20 nm   Scale bar = 5 nm

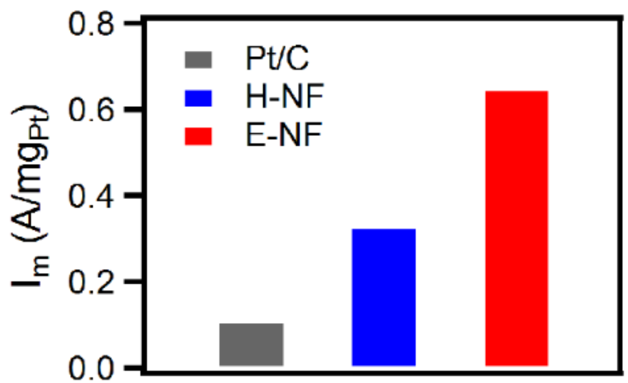




Scale bars = 10 nm

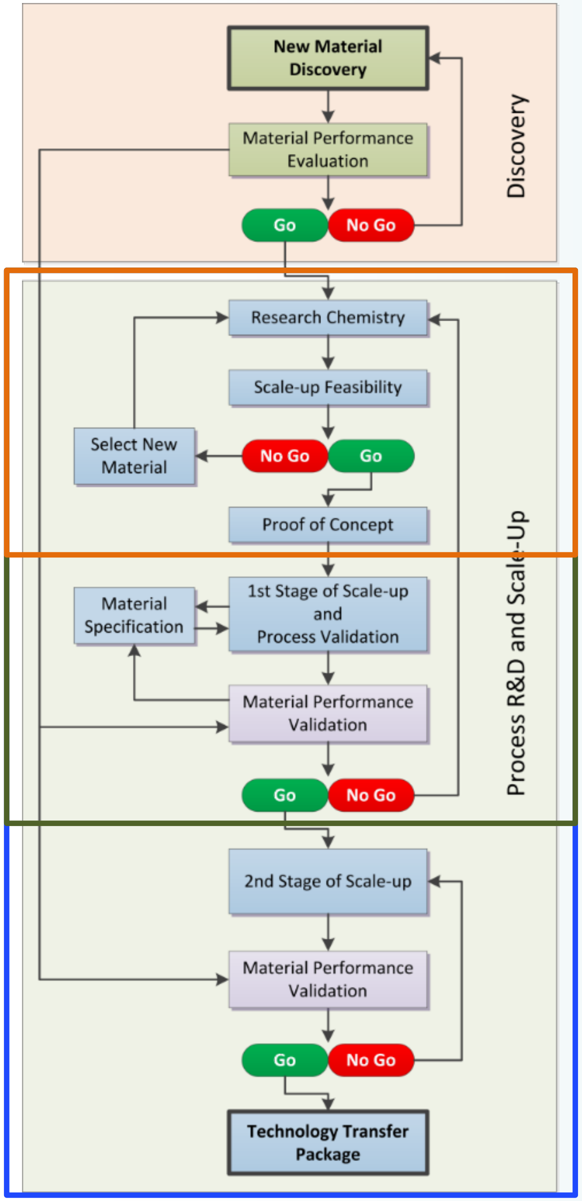


Specific Activity



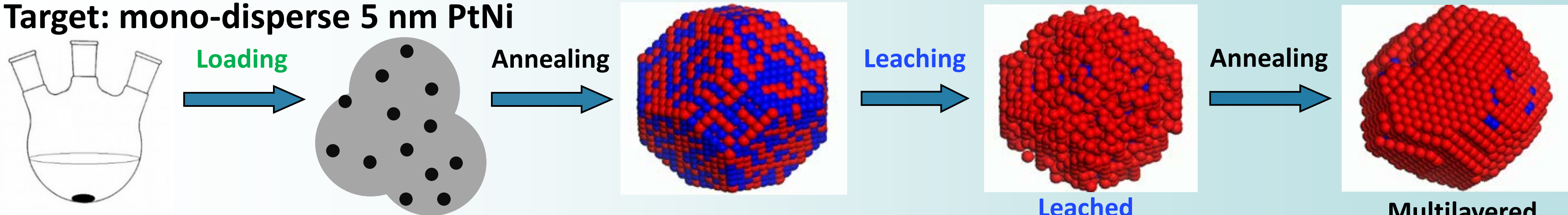
Mass Activity

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 was investigated.
	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 further investigated.
	M 10	13) The 2nd stage scale up is **reproducible**. Go
	M 11-12	14) MEA performance; New **IP application**; Sample send out; Manuscript preparation.

Target: mono-disperse 5 nm PtNi



PtNi synthesis — PtNi on carbon — PtNi nanoparticles — Leached PtNi nanoparticles — Multilayered Pt-skin NP

PtNi synthesis: 0.1 g Scale

1. Pre-heat mixture to 200 °C.
Nickel acetate tetrahydrate (0.1667 g)
1,2-Tetradecanediol (0.085 g)
Oleic acid (0.4 ml) & Oleylamine (0.4 ml)
Diphenyl ether (20 ml) or Dibenzyl ether (20 ml) X

2. Inject preheated Pt solution (~80 °C). X
Platinum(II) acetylacetonate (0.13 g)
In 1,2-Dichlorobenzene (1.5 ml)

3. Hold T at 200 °C for 1 h.

⇩ ➢ Safer ➢ Easier ➢ Scalable ➢ Reproducible

One-pot 5 g Scale

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

Loading on carbon:

0.1 g Scale

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

5 g Scale

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

Acid leaching:

0.1 g Scale

1. Sonicate and soak PtNi/C in 0.1 M $HClO_4$. **X**
2. Centrifuge.

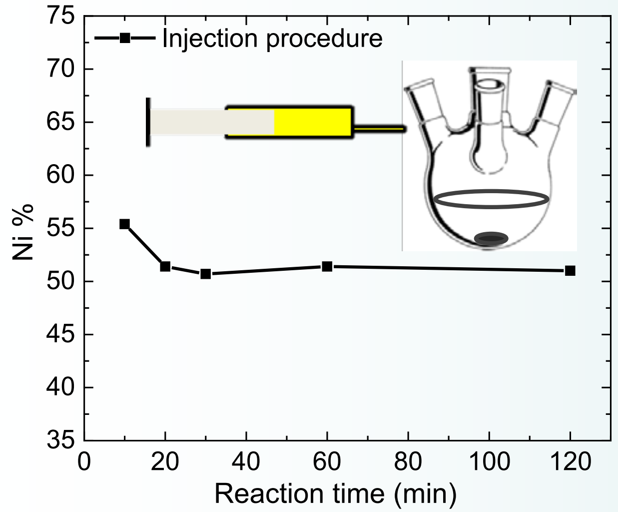
5 g Scale

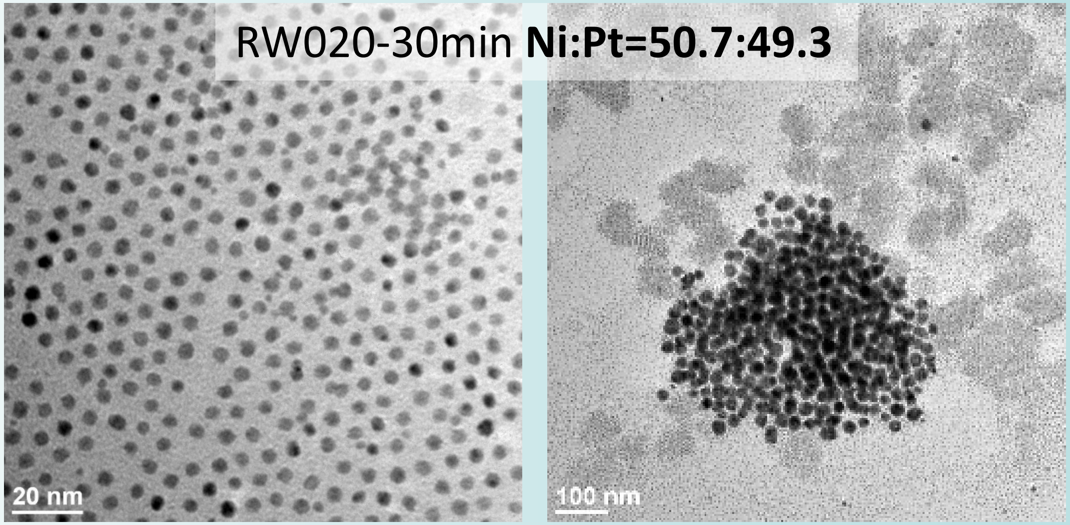
1. Sonicate PtNi/C in H_2O.
2. Mix with 0.1 M $HClO_4$ and soak.
3. Filtration.

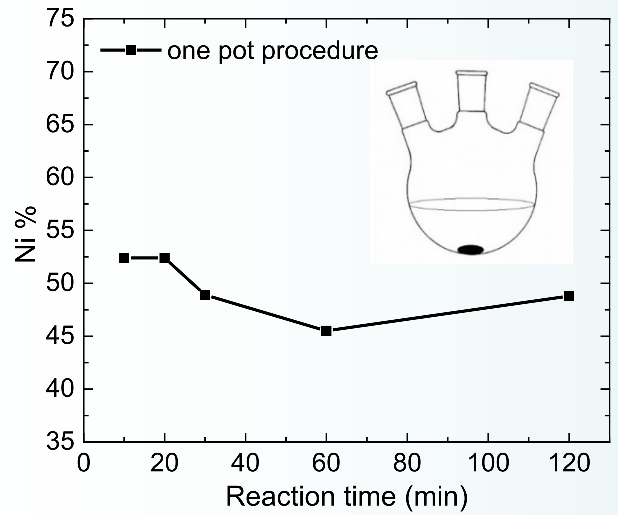
5 g scale

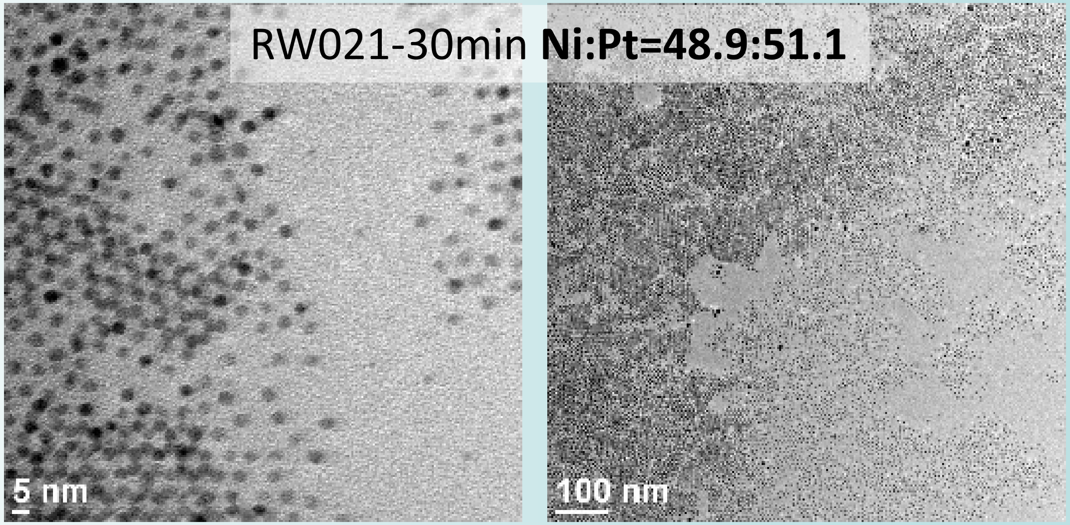
Accomplishments and Progress: *One pot vs. Injection Diphenyl ether*

in collaboration with Greg Krumdick, ANL -MERF









Better result from one-pot procedure

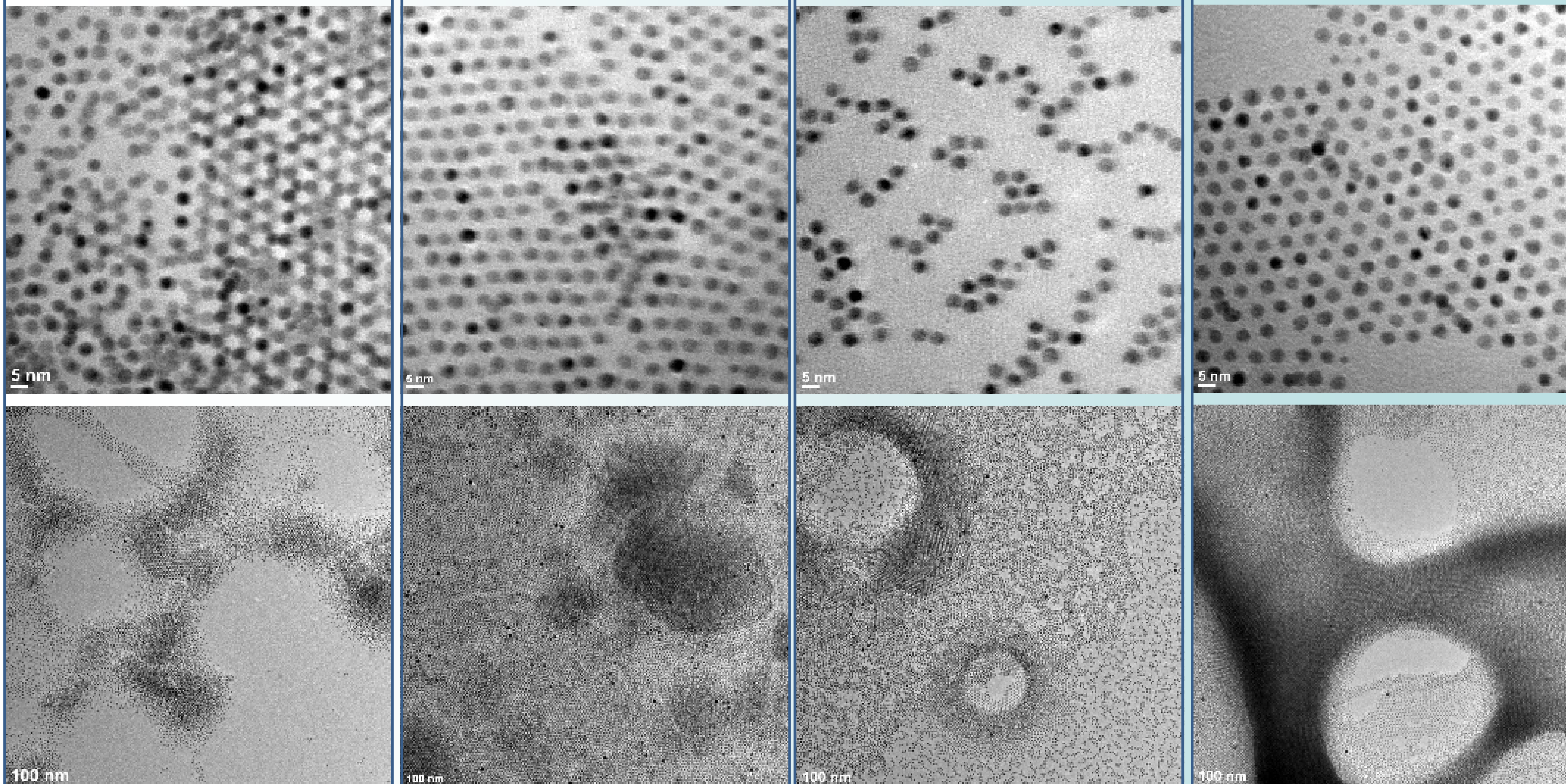
Particle sizes keep constant after 10 min reaction **Good for scale up**

Task 5 Accomplishments and Progress: *Reproducibility-one pot*

in collaboration with Greg Krumdick, ANL -MERF

Best reaction condition established by investigating surfactant amount

RW022-30min Ni:Pt=49.5:50.5	RW025-30min Ni:Pt=50.3:49.7	RW026-30min Ni:Pt=50.8:49.2	RW027-30min Ni:Pt=48.3:51.7

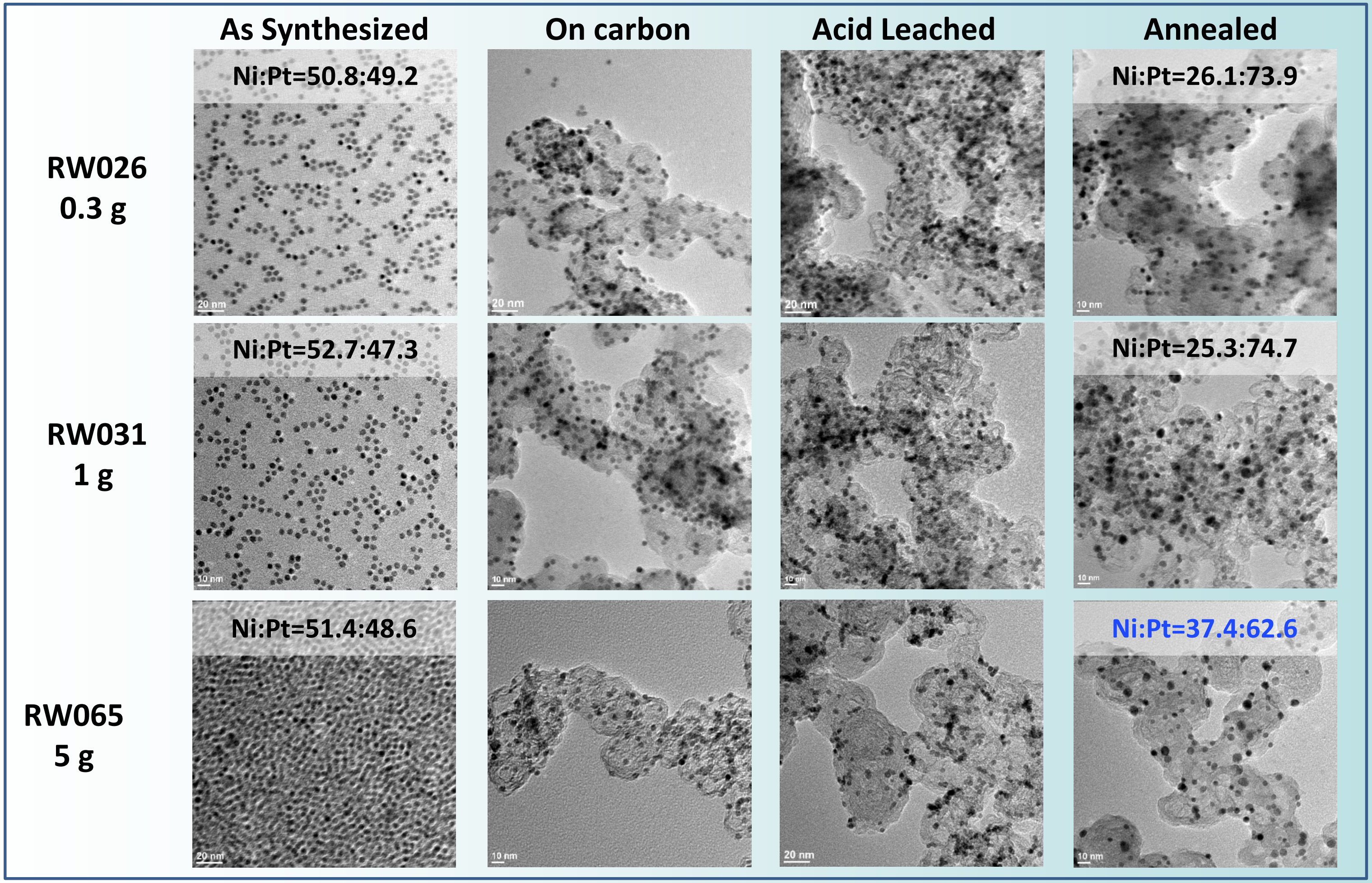


Desirable mono-dispersed 5 nm PtNi nanoparticles are obtained reproducibly

Go

Task 5 Accomplishments and Progress: *TEM/EDX of different stage catalysts*

in collaboration with Greg Krumdick, ANL -MERF



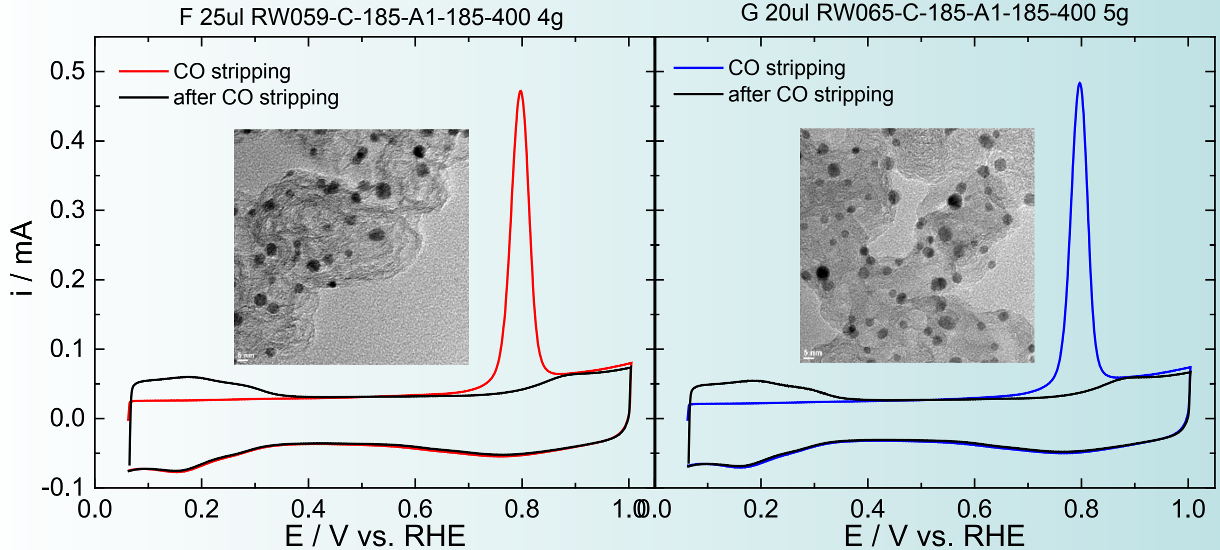
- **Uniform distribution of PtNi nanoparticles on carbon was achieved using newly developed loading method.**
- **More Ni left in PtNi nanoparticles with modified leaching process.**

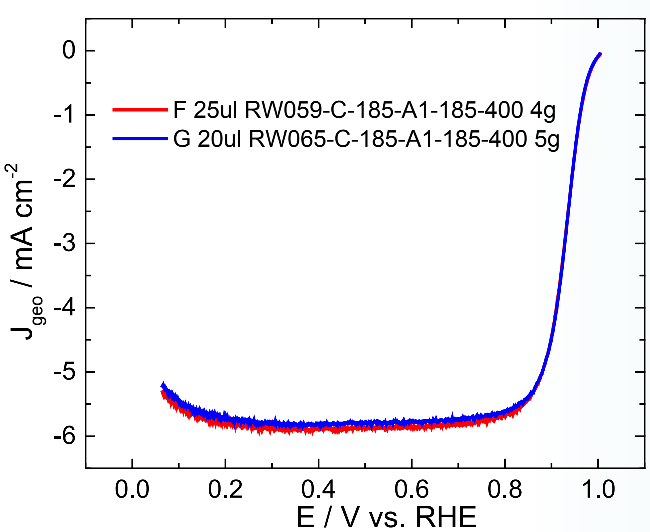
Task 5 Accomplishments and Progress: *5 g Reproducibility-RDE/ECSA*

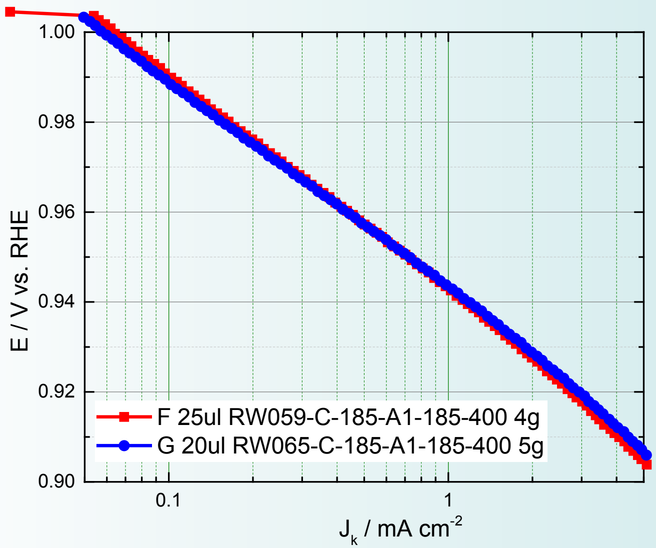
in collaboration with Greg Krumdick, ANL -MERF

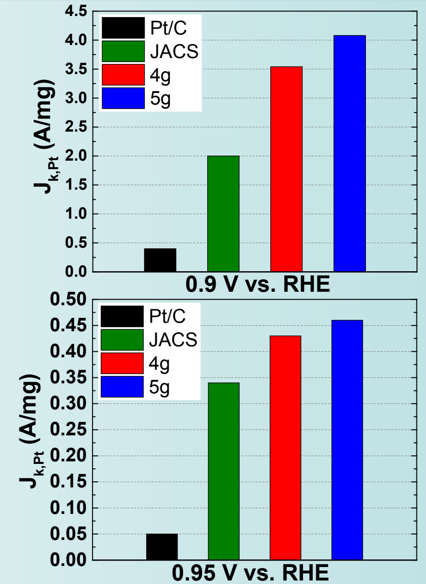
	$ECSA_{HUPD}$ (cm^2)	$ECSA_{CO}$ (cm^2)	$ECSA_{CO}$ / $ECSA_{HUPD}$
4 g	0.684	0.946	**1.38**
5 g	0.672	0.923	**1.37**

	Pt loading (%)	SSA_{CO} (m^2/g)	Pt:Ni (atomic)
4 g	12.66	**60**	1.37:1
5 g	14.53	**63.5**	1.35:1

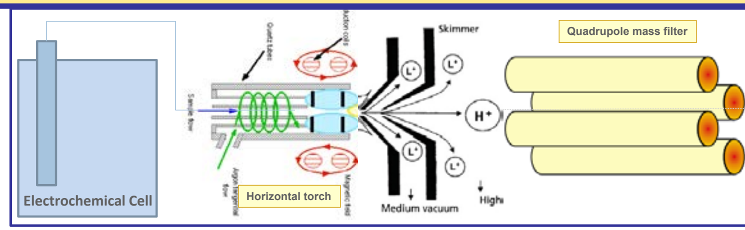




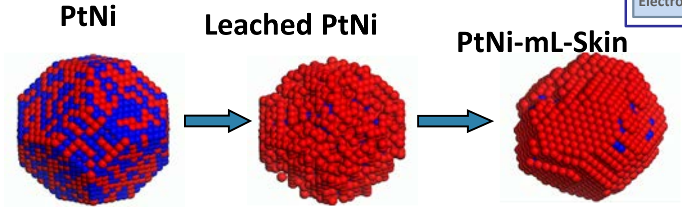


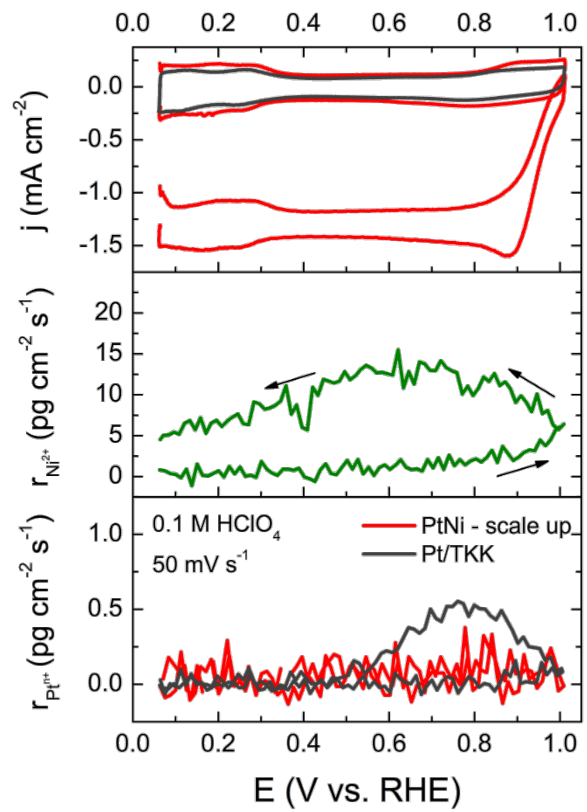


Accomplishments and Progress: *In-Situ EC-ICP-MS* Pt-Alloy NPs



Scaled PtNi with mL Pt-Skin





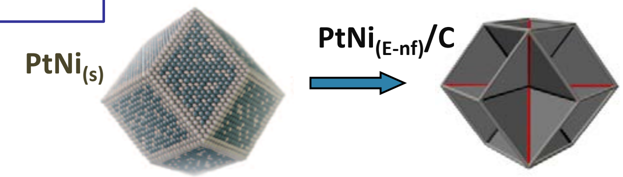
Electrochemical stability of PtNi particles

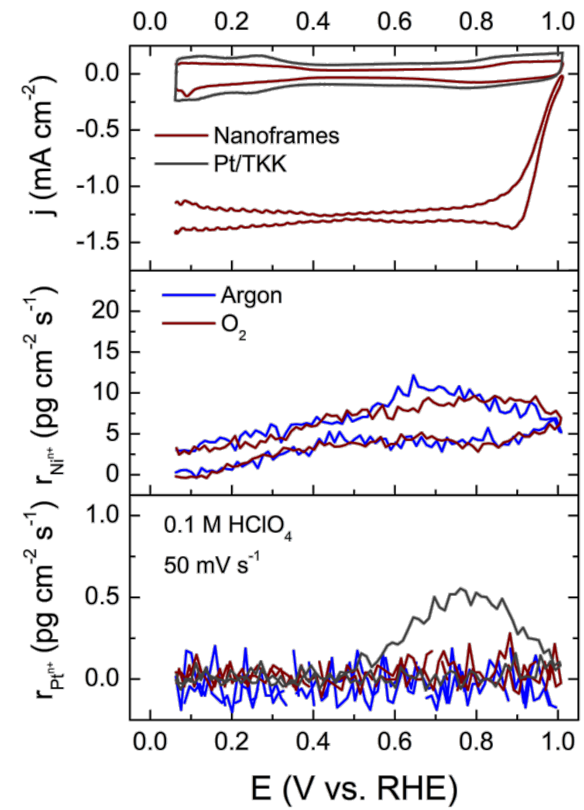
Potential range: 0.05 to 1.0 V

T = 25°C

- Similar Ni dissolution profiles for both nanoframes and scale-up particles
- No dissolution increase due presence of O_2
- Pt dissolution on detection limit – favoring multilayered Pt surfaces

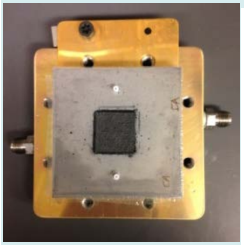
Excavated Nanoframes

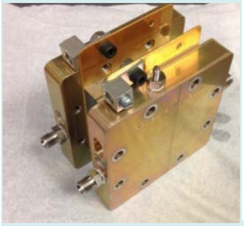


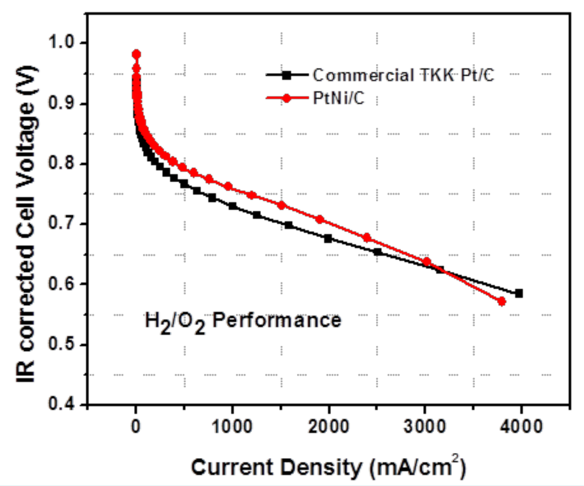


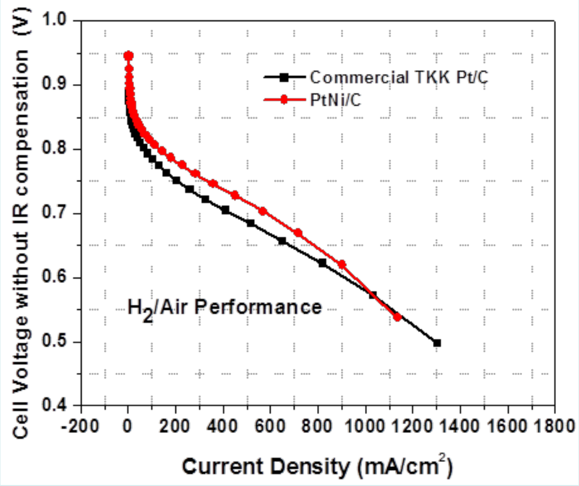
Accomplishments and Progress: *scaled PtNi in 5cm² MEA*

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

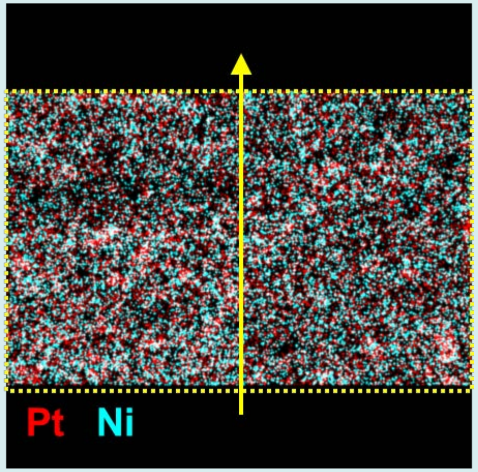


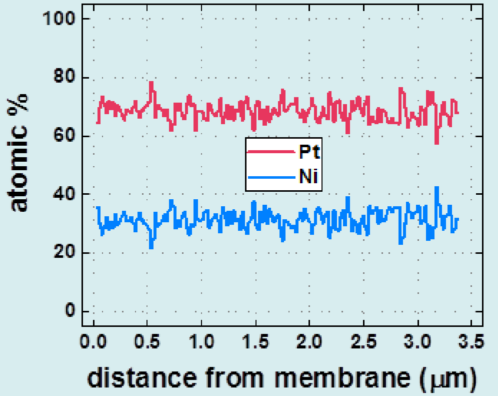






line profile





TKK 20 wt%Pt/C

PtNi 12.66 wt%Pt/C

Cathode Loading:
0.04 mg-Pt/cm²
I/C = 0.8,
H_2/O_2 (or Air),
80°C, 150 kPa(abs)
100%RH

	Units	PtNi Cathode	TKK Pt Cathode
Pt total loading	mg_{Pt}/cm^2_{geo}	~0.04	~0.04
Mass activity (H2-O2)	A/mg_{PGM} @0.9 $V_{iR\text{-}free}$	0.5	0.22
Specific activity (H2-O2)	mA/cm^2_{PGM} @0.9 V	1.01	0.39
MEA performance (H2-Air)	mA/cm^2 @0.8 V	131.34	64.3
ECSA	m^2/g_{PGM}	50	52.5

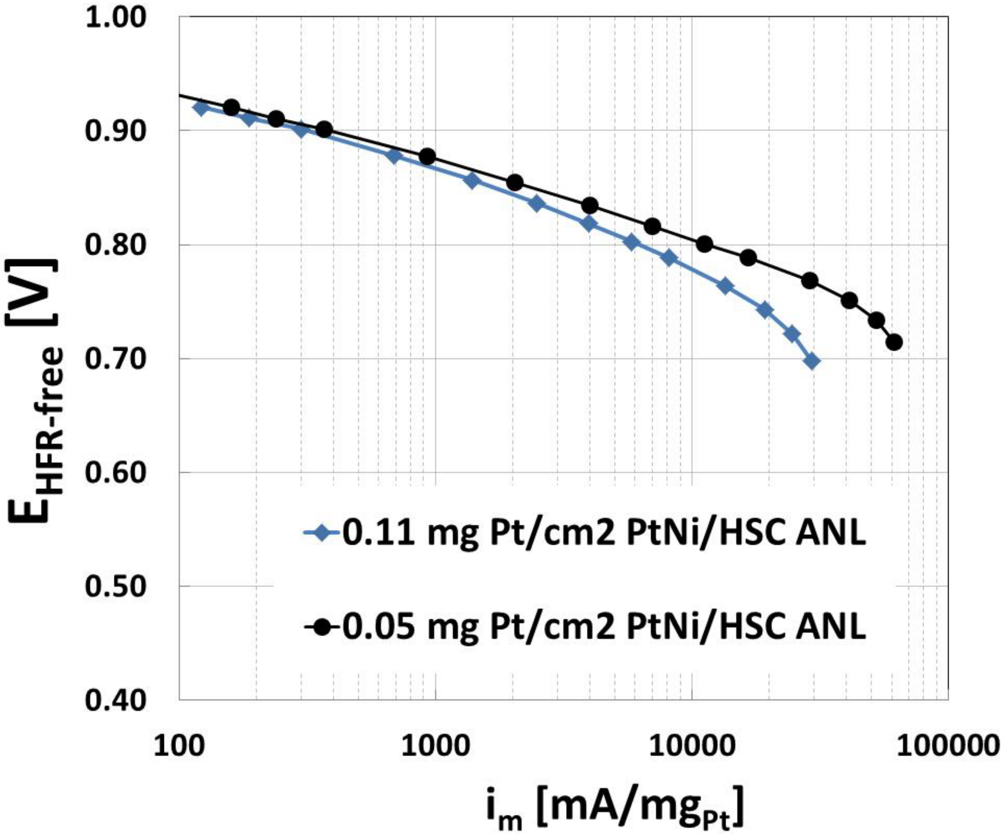
Fresh:
Pt at.% = 72%
Ni at.% = 28%

Tested:
Pt at.% = 80%
Ni at.% = 20%

in collaboration with Shyam Kocha and Kenneth Neyerlin, NREL

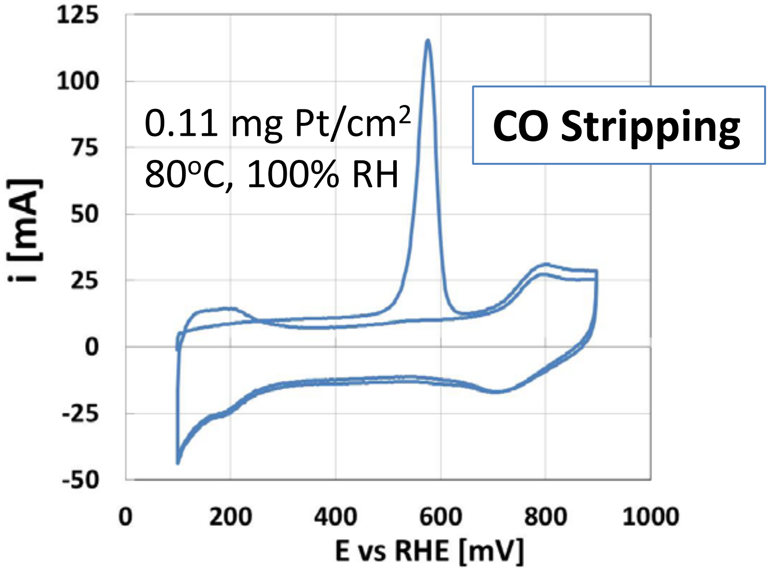
PtNi/HSC 5cm² MEA Kinetics

ORR Mass Activity
150 kPa, (100 kPa $_{P}O_2$), 100%RH, 80°C



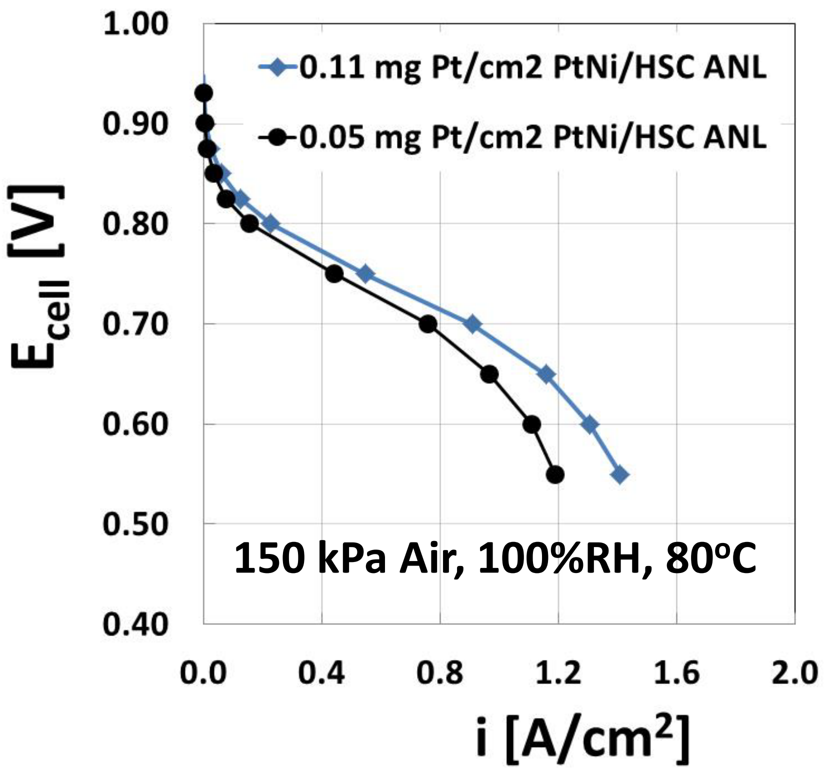
Electrochemical Analysis

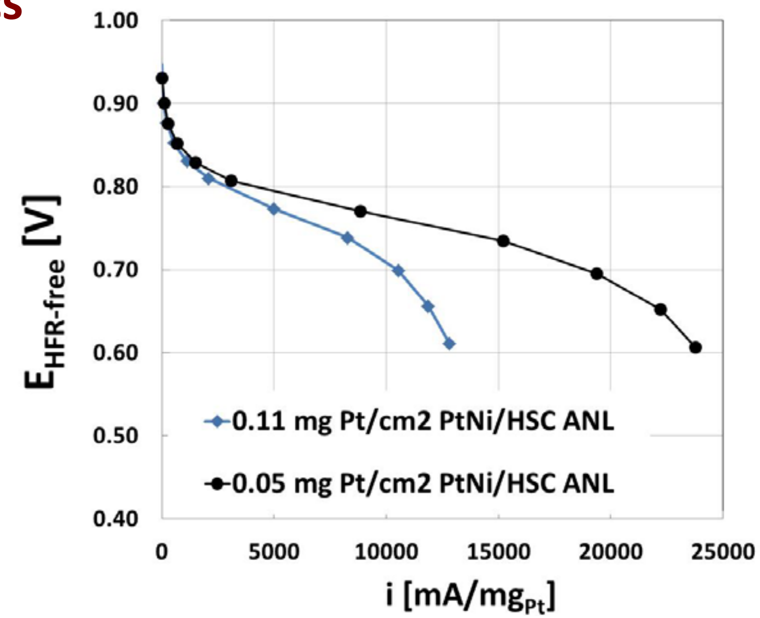
Pt Loading (mg/cm^2_{Pt})	0.05	0.11
I_m (mA/mg_{Pt})	390	290
I_s ($\mu A/cm^2_{Pt}$)	640	610
ECA (m^2/g_{Pt})	60	48
ECA CO (m^2/g_{Pt})	53	43
HFR ($m\Omega\text{-}cm^2$)	45	43

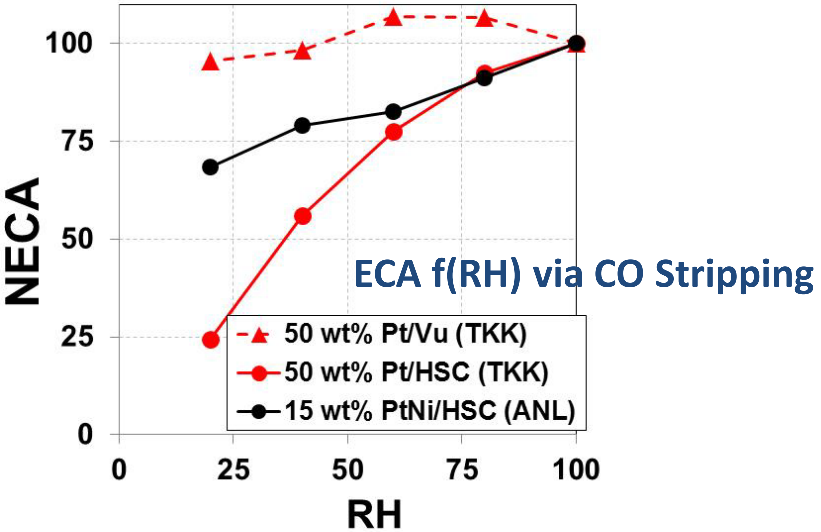


in collaboration with Shyam Kocha and Kenneth Neyerlin, NREL

PtNi/HSC 5cm² MEA Kinetics







- **Synthesis technique results in the majority of Pt sites available at lower RH**
  - —May have positive implications on RO_2^{Pt}
- **Further studies in progress**

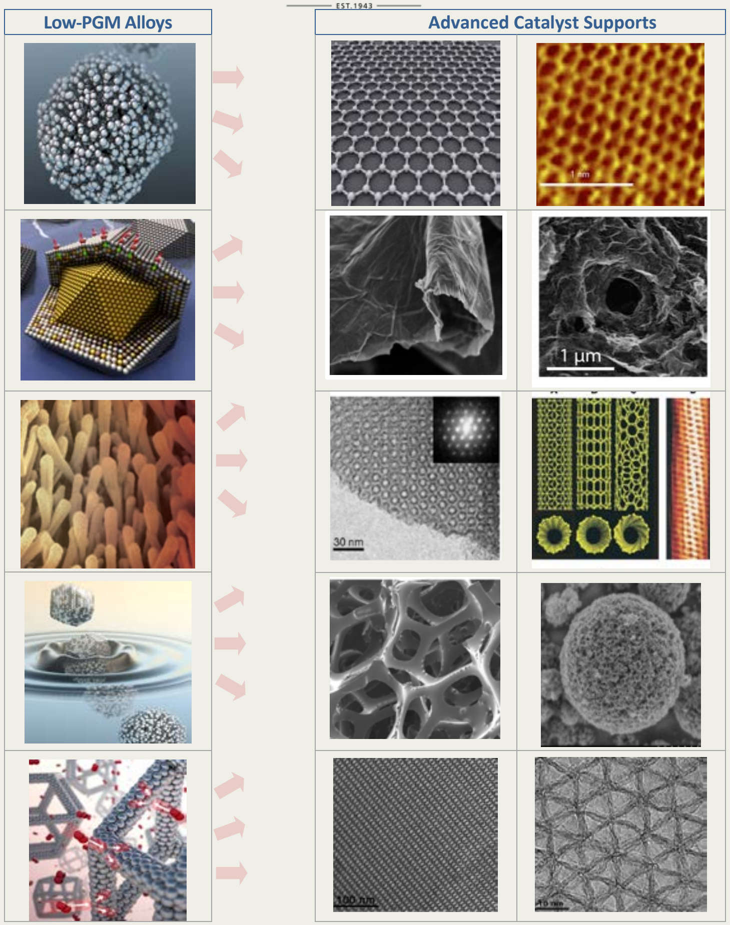
Collaborations

Argonne National Laboratory — Lead: design, synthesis, evaluation

Berkeley Lab — Sub: synthesis, scale-up support

Oak Ridge National Laboratory — Sub: structural characterization

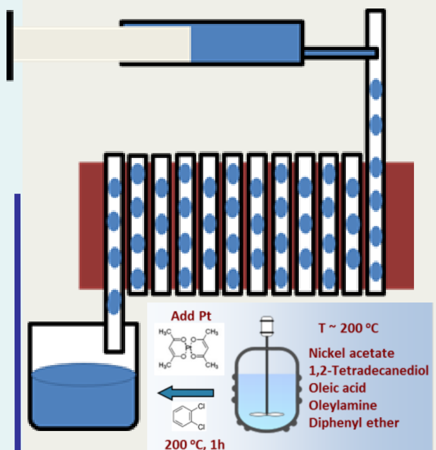
Los Alamos National Laboratory — Sub: catalyst supports



Low-PGM Alloy Catalysts

Argonne National Laboratory — Lead: process R&D and scale-up

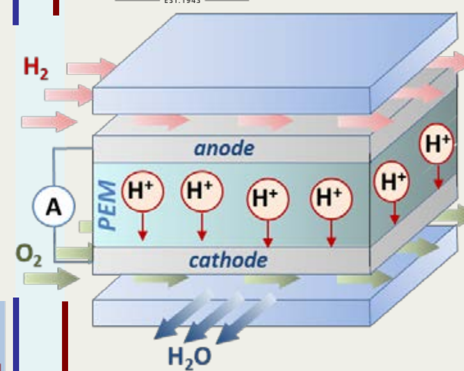
Berkeley Lab — Sub: process support



Catalysts Scale Up

Argonne National Laboratory — Lead: 5 and 25cm^2 MEA

NREL, Los Alamos National Laboratory — Sub: 25 and 50cm^2 MEA



MEA

OEMs

T2M

Remaining 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 for the most advanced structures

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

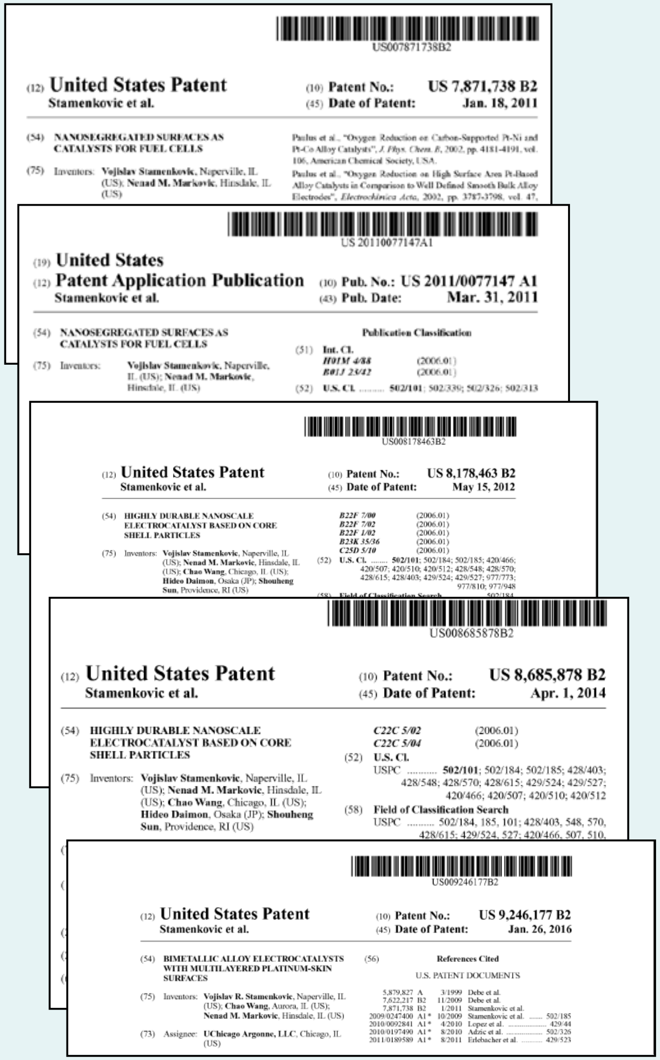
2) Cost (total loading of PGM 0.125 mg_{PGM} / cm^2)

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

Proposed 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

Technology Transfer Activities


(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)

(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

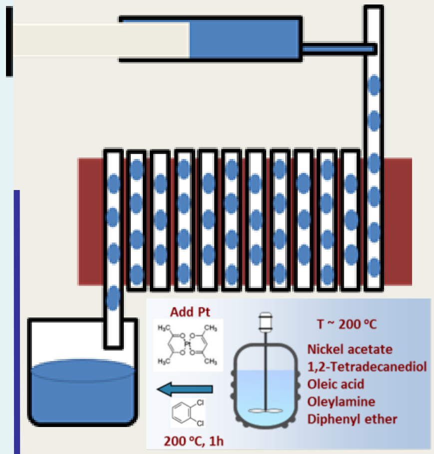
(12) United States Patent
Stamenkovic et al.
(10) Patent No.: US 8,178,463 B2
(45) Date of Patent: May 15, 2012
(54) HIGHLY DURABLE NANOSCALE ELECTROCATALYST BASED ON CORE SHELL PARTICLES

(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)

(12) United States Patent
Stamenkovic et al.
(10) Patent No.: US 9,246,177 B2
(45) Date of Patent: Jan. 26, 2016
(54) BIMETALLIC ALLOY ELECTROCATALYSTS WITH MULTILAYERED PLATINUM-SKIN SURFACES
(75) Inventors: Vojislav R. Stamenkovic, Naperville, IL (US); Chao Wang, Aurora, IL (US); Nenad M. Markovic, Hinsdale, IL (US)
(73) Assignee: UChicago Argonne, LLC, Chicago, IL (US)

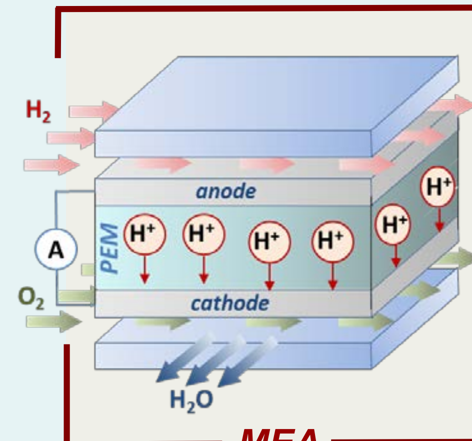
T2M

process scale-up



Catalysts Scale Up

Auto OEMs



FY17

3 NDA signed

- **Constant build up of IP portfolio**
  5 issued patents, 3 pending

SUMMARY

Approach

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

Accomplishments

- Established routine operations in a new Scale-Up process Lab and new RDE-ICP/MS
- Dissolution of Pt from 2D thin film surfaces vs. 3D Pt/C catalyst layers
- Addition of both subsurface Au or Pd diminishes Pt dissolution
- Established stability trend for Pt_xNi_{1-x} and particle size dependence for Pt/C
- Novel nanoscale structures with superior electrochemical properties have been synthesized
- In-situ RDE-ICP/MS revealed stability of highly active PtNi catalysts with multilayered Pt-Skin surfaces
- Scaled reproducible synthesis process of 5 grams per batch for PtNi/C with multilayered Pt-Skin surfaces
- Scaled catalyst is monodisperse with advanced catalytic properties in both RDE and MEA
- PtNi with multilayered Pt-Skin exceeded DOE 2020 Technical Target for mass activity and durability in MEA
- One patent application in FY17, 2 articles published and 6 presentations at conferences

Collaborations

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

Full time postdocs:
Dr. Dongguo Li (RDE, synthesis, thin films)
Dr. Haifeng Lv (RDE, synthesis, MEA)
Dr. Rongyue Wang (scale up syntehsis, RDE, MEA)

Partial time postdocs: Dr. Pietro Papa Lopes (RDE-ICP-MS)

Partial time Staff: Paul Paulikas (UHV, thin films), Krzysztof Pupek

Grad student: Nigel Becknell (synthesis, RDE, EXAFS)

Publications and Presentations FY17

2 Publications
6 Presentations
2 patent applications