2018 DOE Hydrogen and Fuel Cells Program Review

Tailored High Performance Low-PGM Alloy Cathode Catalysts

PIs: Vojislav R. Stamenkovic
Nenad M. Markovic

Materials Science Division

Argonne National Laboratory

Project ID# FC140

Overview

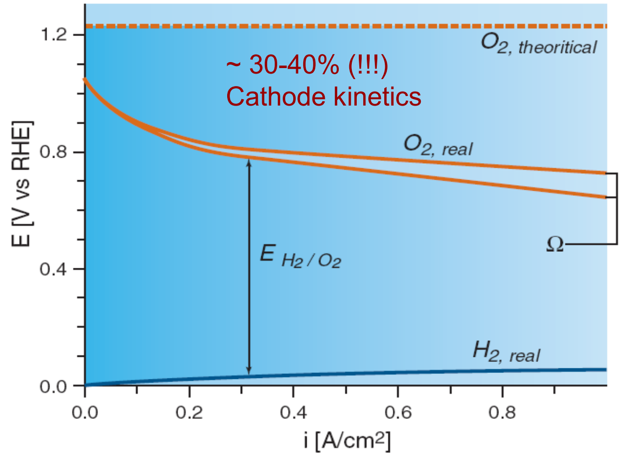
Timeline

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

Budget

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

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***

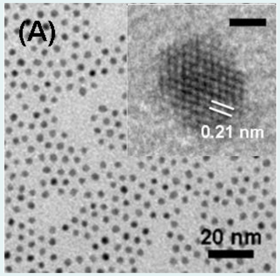
Table 3.4.13 Technical Targets: Electrocatalysts for Transportation Applications[h]

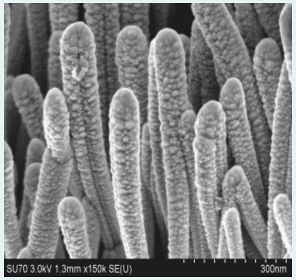
Characteristic	Units	2011 Status	2020 Targets
Platinum group metal total content (both electrodes)[a]	g / kW (rated)	0.19[b]	0.125
Platinum group metal (pgm) total loading[a]	mg PGM / cm^2 electrode area	0.15[b]	0.125
Loss in initial catalytic activity[c]	% mass activity loss	48[b]	<40
Electro catalyst 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
AIO 4A Low-PGM

Inter Lab Collaborators

ANL
Catalyst Synthesis

ORNL
Electron Microscopy

NREL
$50cm^2$ MEA testing

ANL - ES
Carbon nano/m tubes

ANL - ES
Support of Scaling-Up

A N L

PEMFC Cathode Catalysts Development

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

Task

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

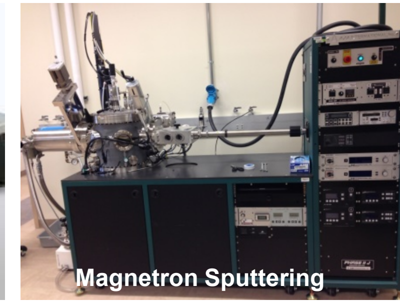
2° S YN synthesis of nano-, meso- and thinfilm- PtMN catalysts:
- -shape/size/composition control
- -intermetallics; core/interlayer/shell; thin-film systems
- (colloidal chemical synthesis, PVD, HRTEM/STEM)

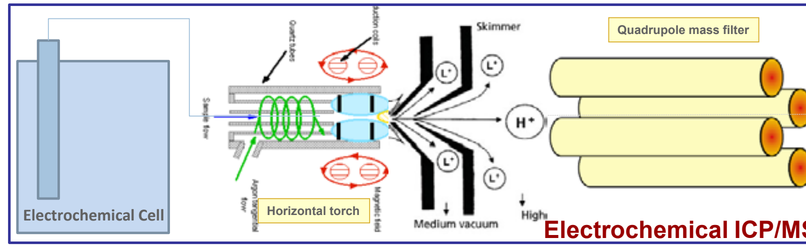
3° ECC electrochemical characterization of catalysts:
- -optimization: ionomer/carbon/propanol/catalyst ink
- -temperature effect; Ionic Liquid evaluation
- -activity/durability in RDE vs. 5-50cm²/MEA; HRTEM

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

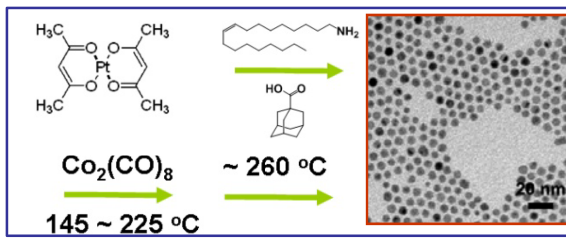
5° SCA scaling-up of the most promising catalysts:
- -gram scale single batches

TASK 1





TASK 2&5



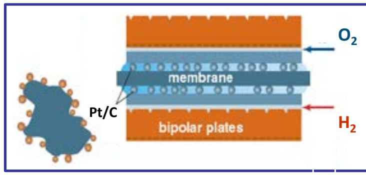
scale-up synthesis of nanomaterials

grams of catalyst

solvo-thermal

advanced supports

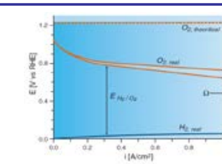
TASK 3



MEA test stand

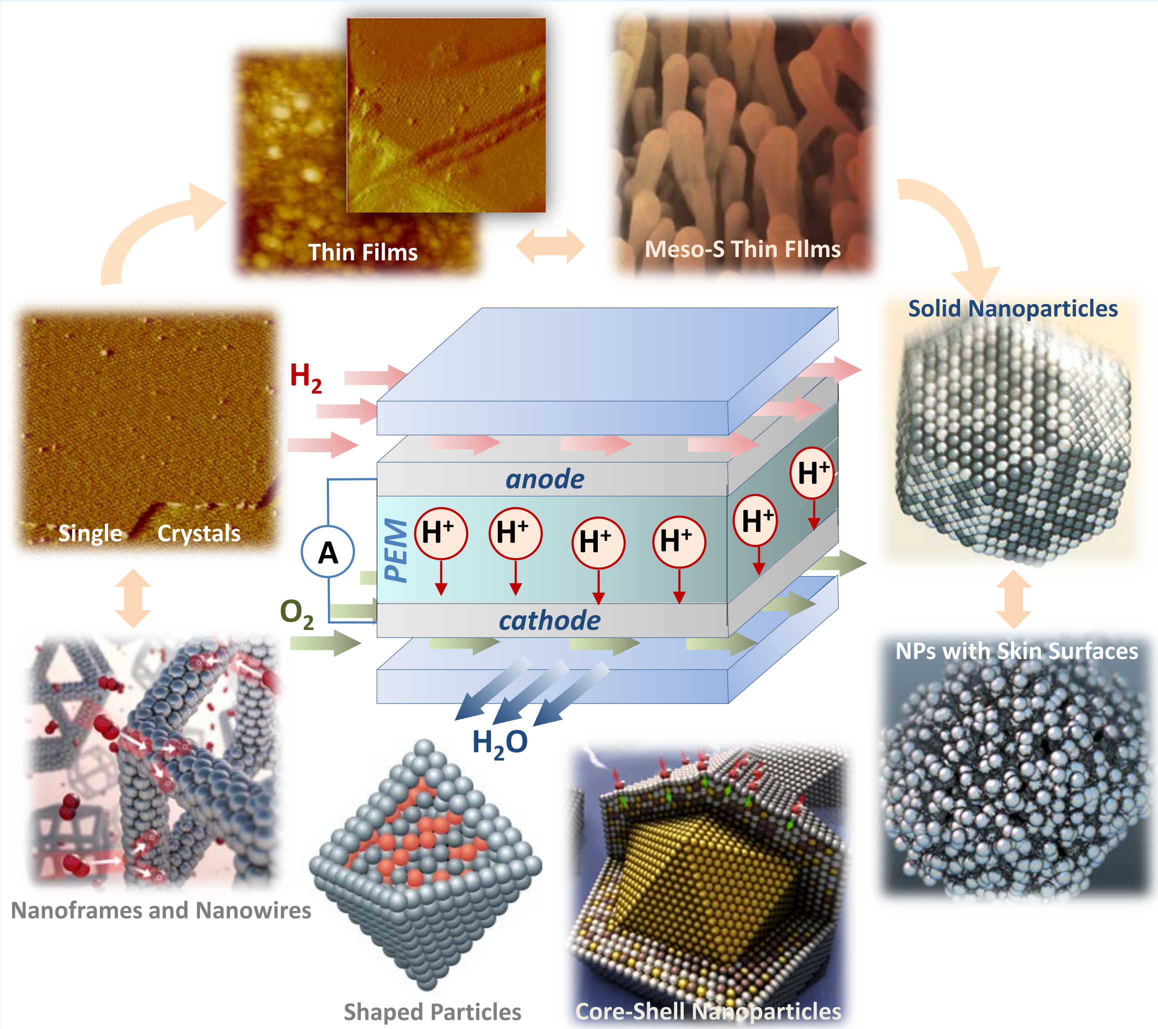
5 - 25 cm^2

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



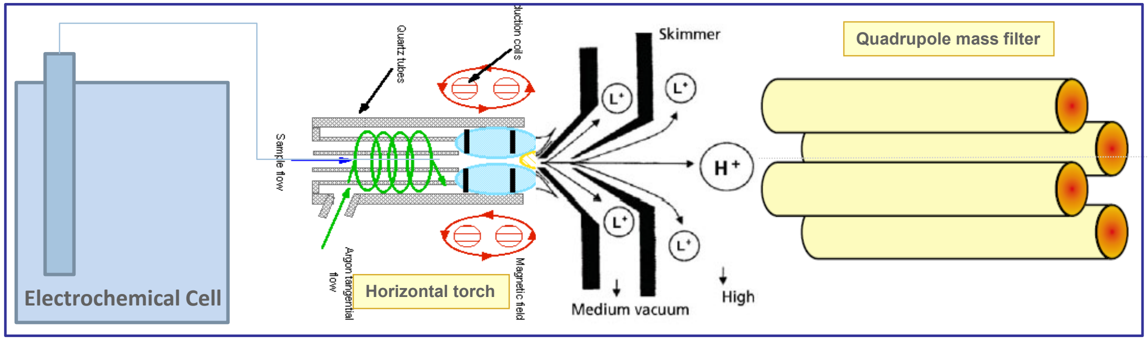
Project Management

Table 1	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

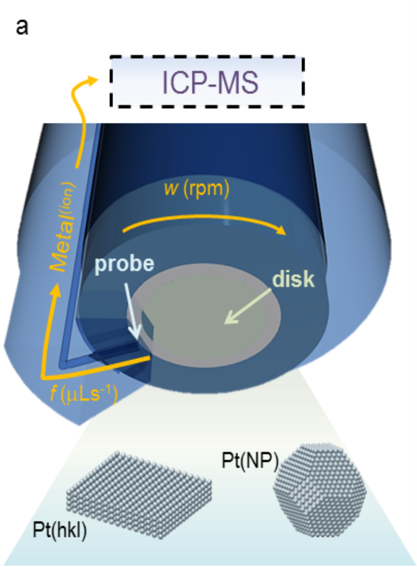
Task 1 Accomplishments: *RDE-ICP/MS of* Pt/C Nanoparticles

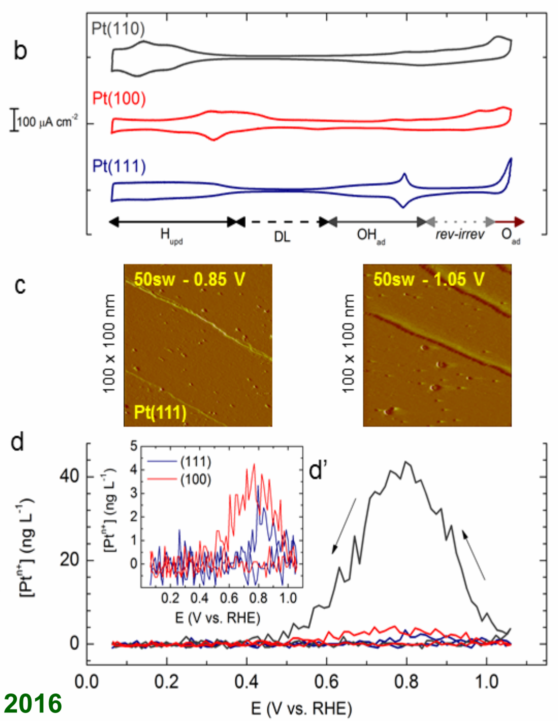


Surface Structure	Pt(111)	Pt(100)	Pt(110)	Pt-poly
Dissolved Pt per cycle [μML]	2	7	83	36

Detection Limit: 0.8 μML of Pt

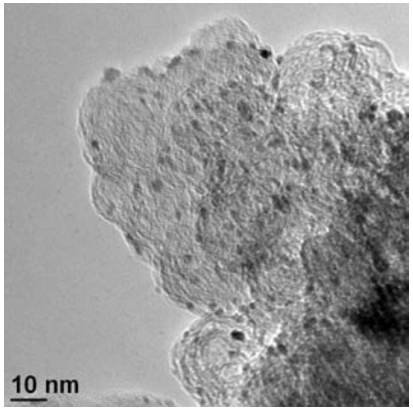
In-Situ RDE-ICP/MS

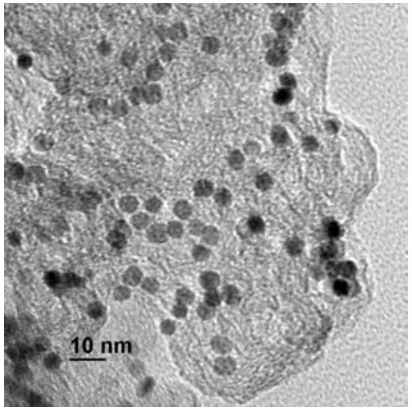




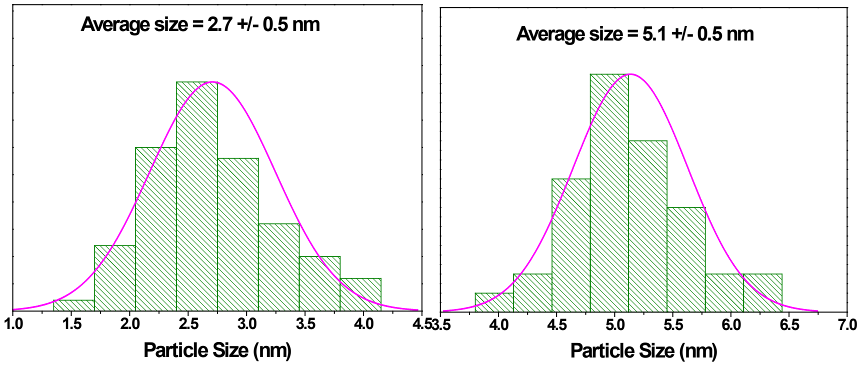
P. P. Lopes, D. Strmcnik, J. Connell, V. R. Stamenkovic and N.M. Markovic
ACS Catalysis, 6 (4), 2536-2544, 2016

<u>Monodisperse</u> 20% Pt/C NPs 3 and 5nm



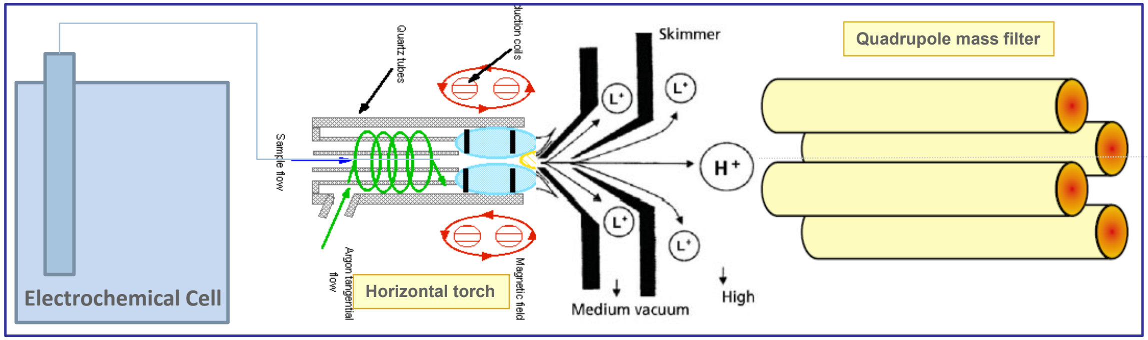


2.7+/-0.5 nm **5.1 +/- 0.5nm**



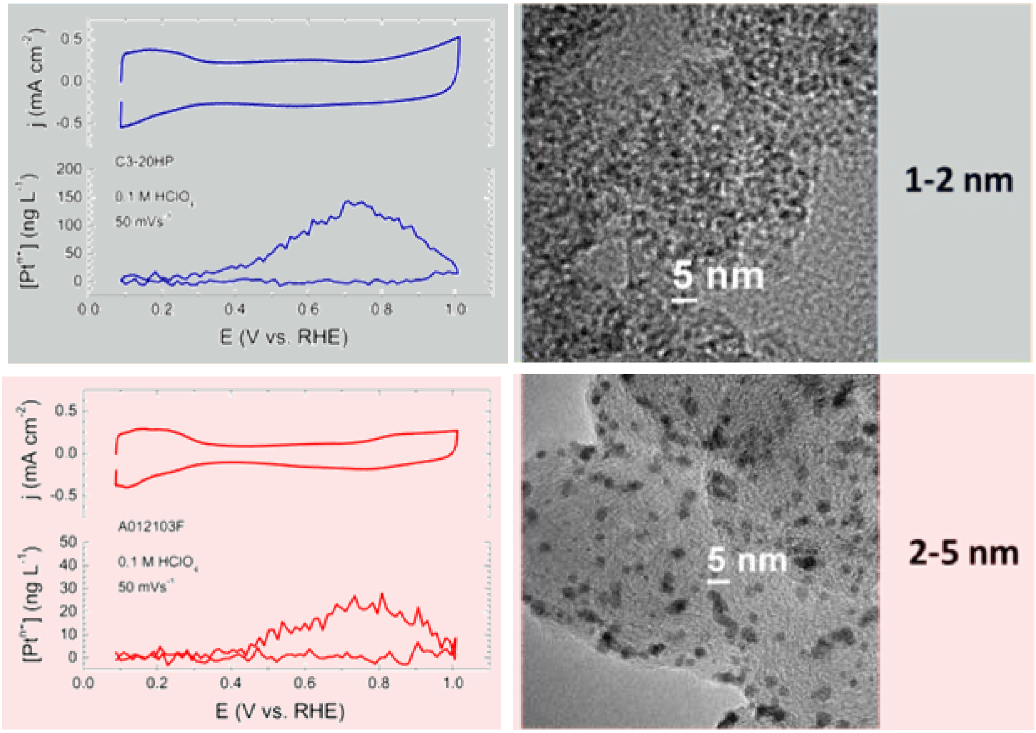
Correlation between Surface Structure - Activity – Dissolution

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

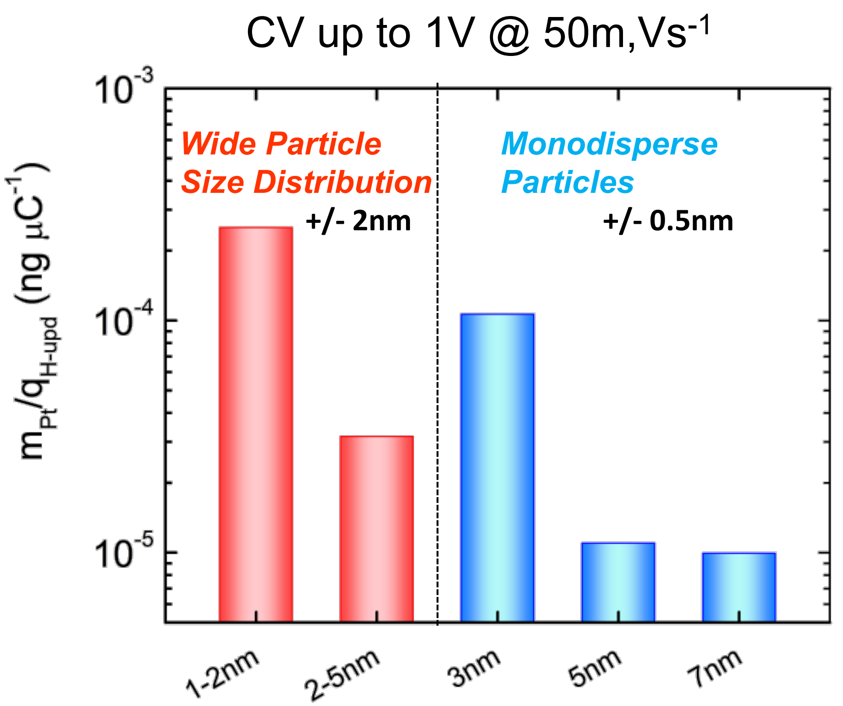


Surface Structure	Pt(111)	Pt(100)	Pt(110)	Pt-poly
Dissolved Pt per cycle [μML]	2	7	83	36

Detection Limit: 0.8 μML of Pt

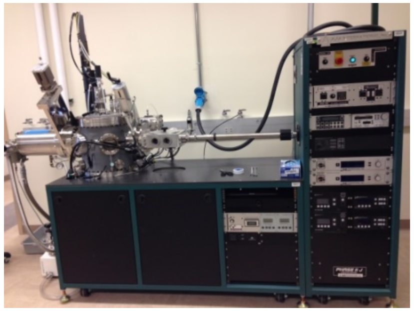


Dissolution Rates

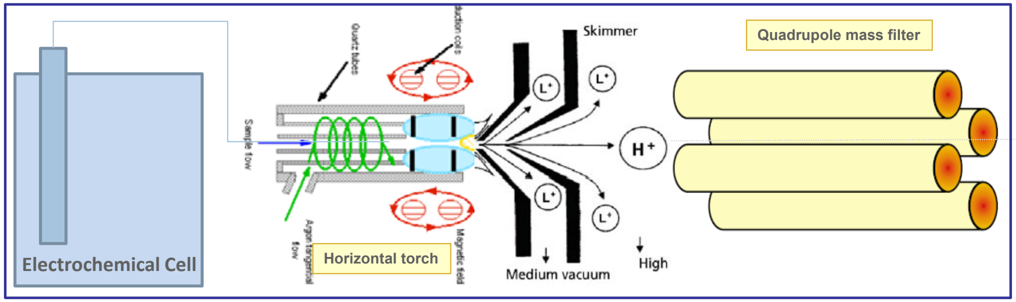


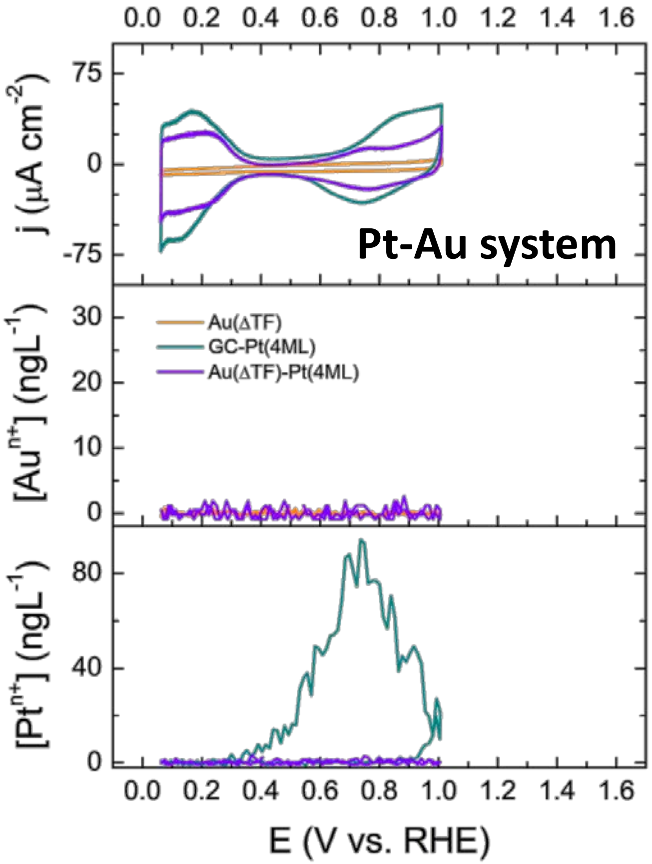
Control of particle size distribution have important role for dissolution rate

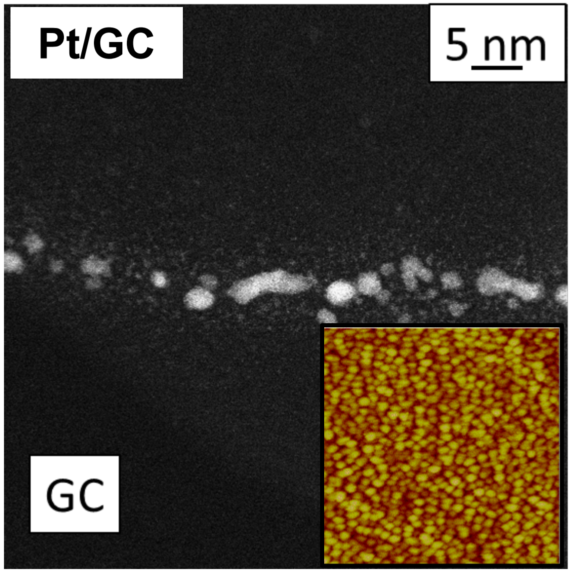
Accomplishments and Progress: *EC-ICP-MS* Pt-Surfaces *effect of substrate*

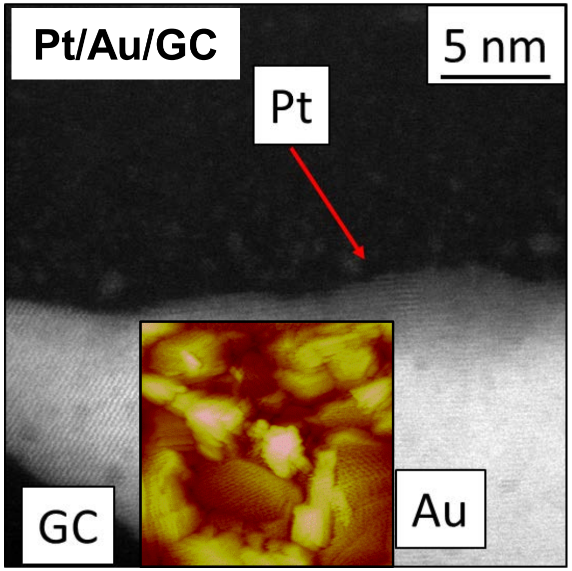


Au Substrate









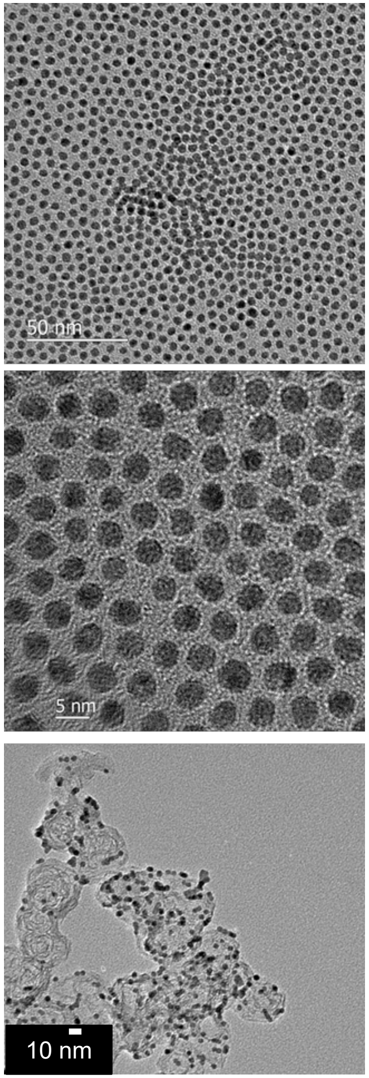
Potential range:
0.05 to 1.0 V

0.1M $HClO_4$

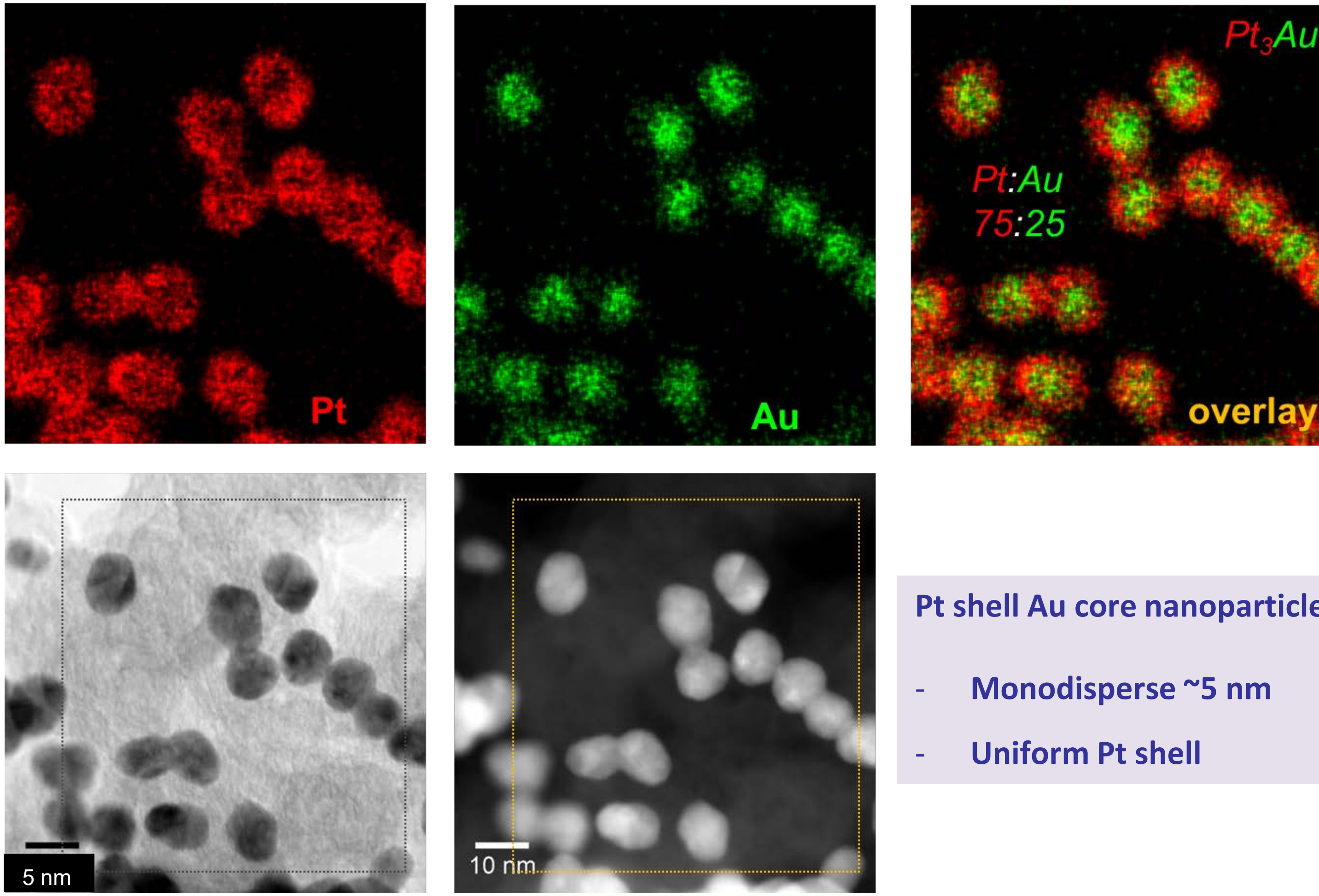
- Pt 4ML over GC forms a non-continuous film, full of small nanoparticles (~2nm)
- Pt 4ML over Au thin layer) shows the Pt with Au structure, favoring (111) surface

Task 2 Accomplishments and Progress: Pt_3Au synthesis and characterization

in collaboration with K.L. More, ORNL



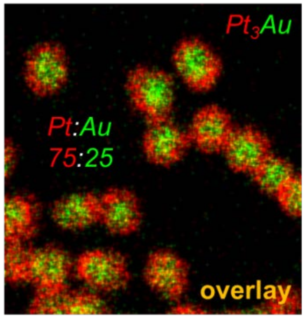
High-Precision Synthesis *monodisperse NPs with uniform compositional profile*



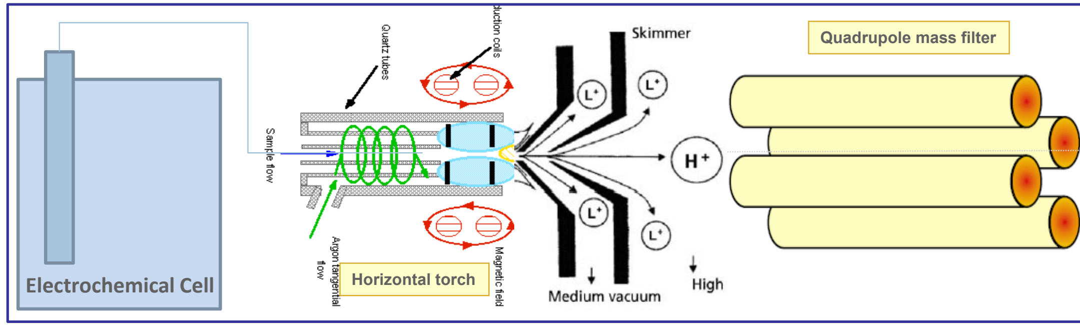
Pt shell Au core nanoparticles:

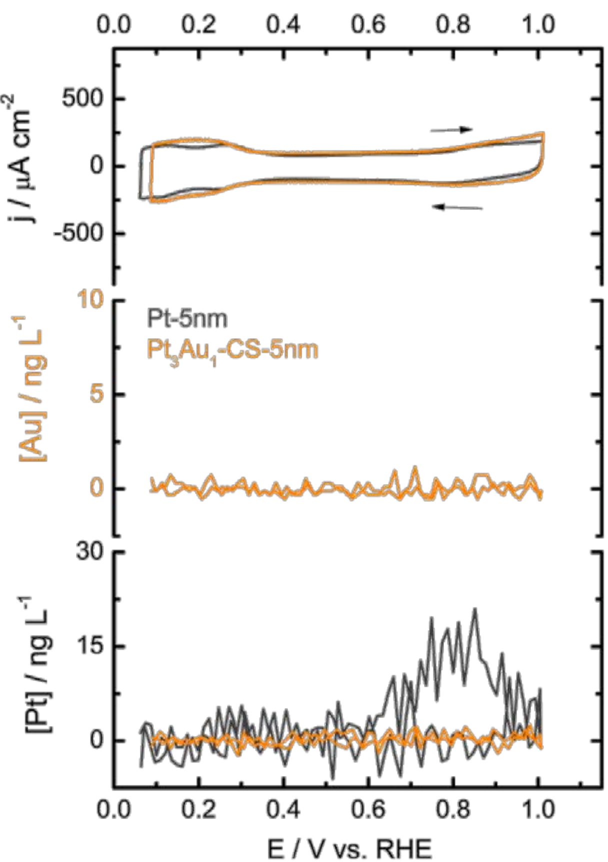
- **Monodisperse ~5 nm**
- **Uniform Pt shell**

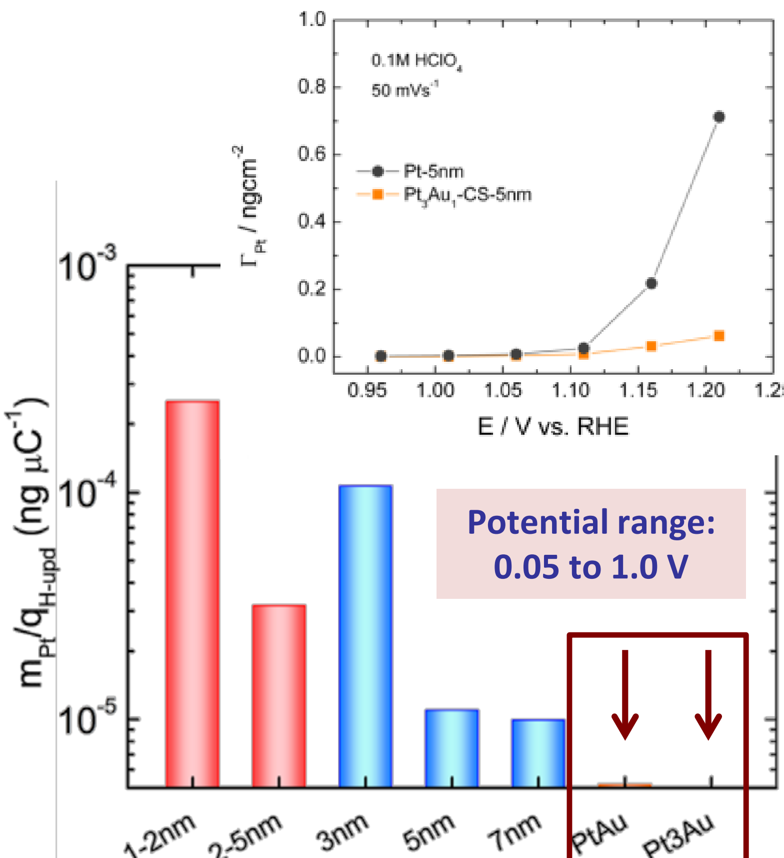
 Accomplishments and Progress: *EC-ICP-MS* **Pt_3Au nanoparticles**



Pt_3Au/C - GC





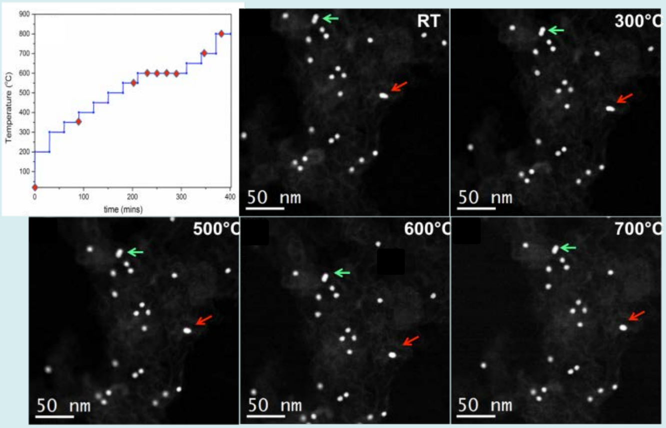


Pt_3Au/C

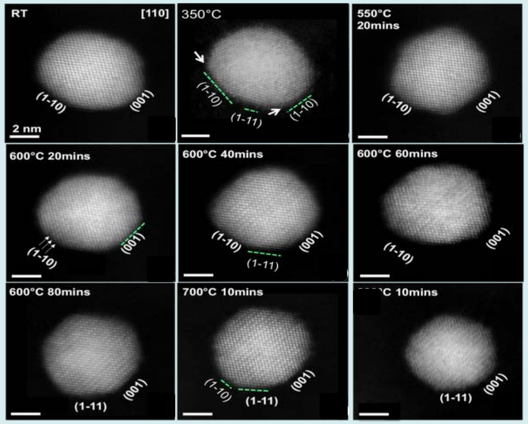
- **Dissolution of Pt completely diminished up to 1.0 V**
- **Stability improvement retains at higher electrode potentials**
- **Up to 10 times more stable above 1.2V**

in collaboration with K.L. More, ORNL

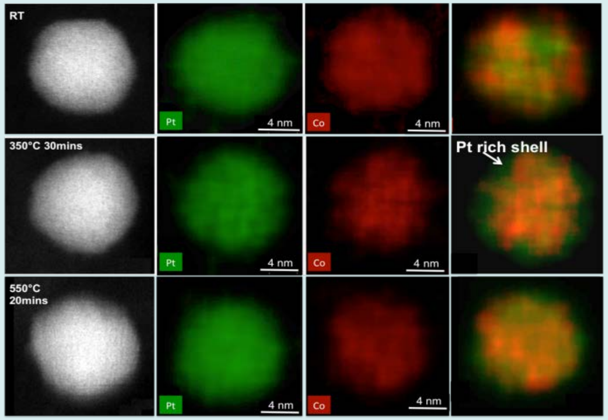
Annealing sequence of Pt_3Co NP

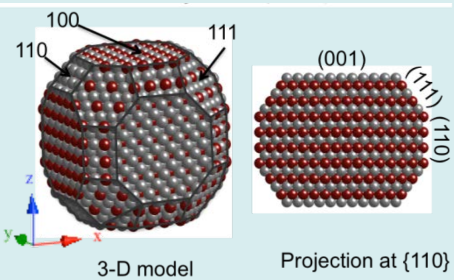


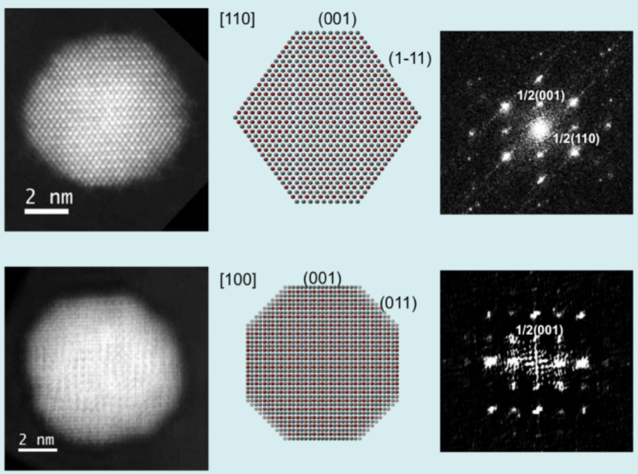
HAADF at different T and t(min)



HAADF and EDS elemental mapping







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

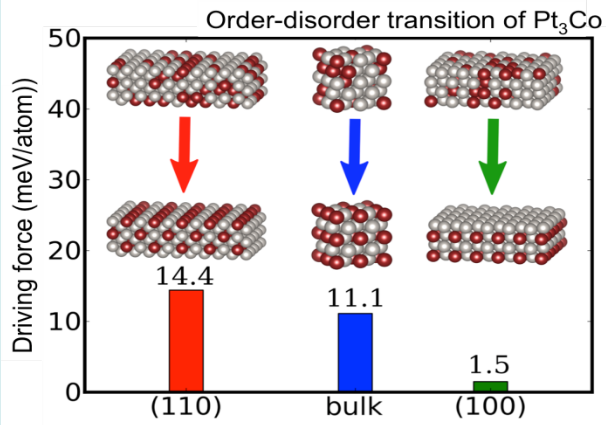
distinct behavior at critical stages:

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

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

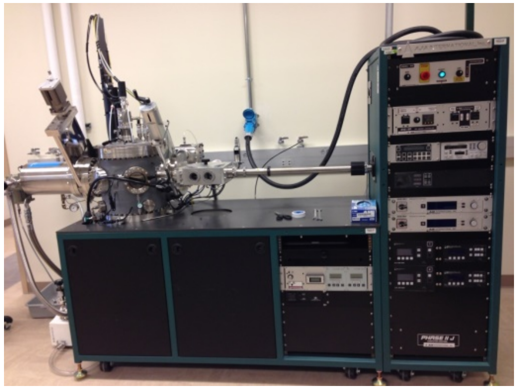
the nucleation of ordered domains;

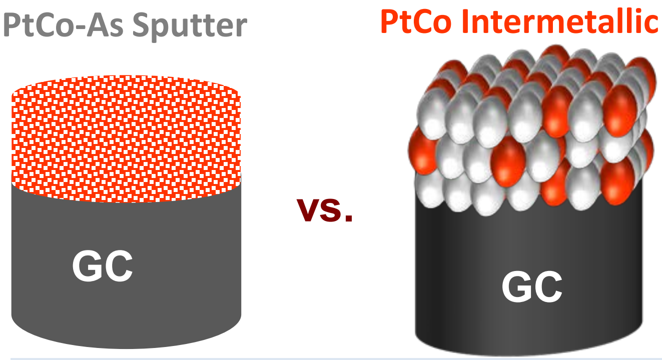
the establishment of an ordered $L1_2$ phase followed by pre-melting

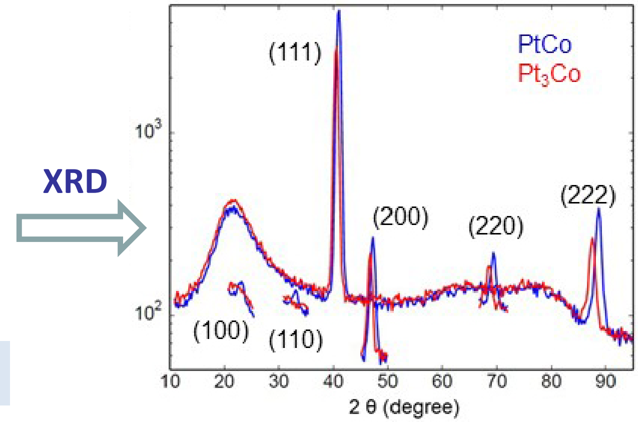


M. Chi, C. Wang, Y. Lei, G. Wang, K.L. More, A. Lupini, L.F. Allard, N.M. Markovic, and V.R. Stamenkovic
Nature Communications 6 (2015) *No.* 8925

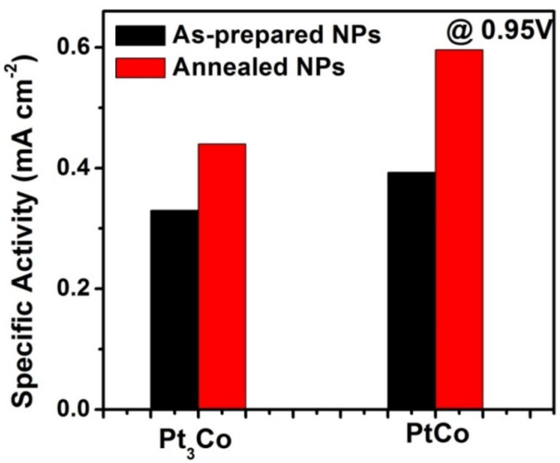
Accomplishments and Progress: *In-Situ EC-ICP-MS* Pt-Alloys Intermetallic

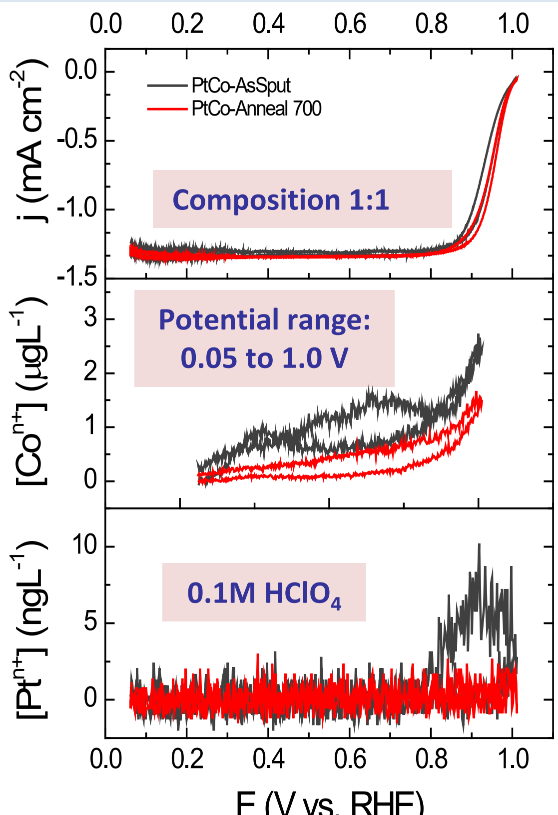


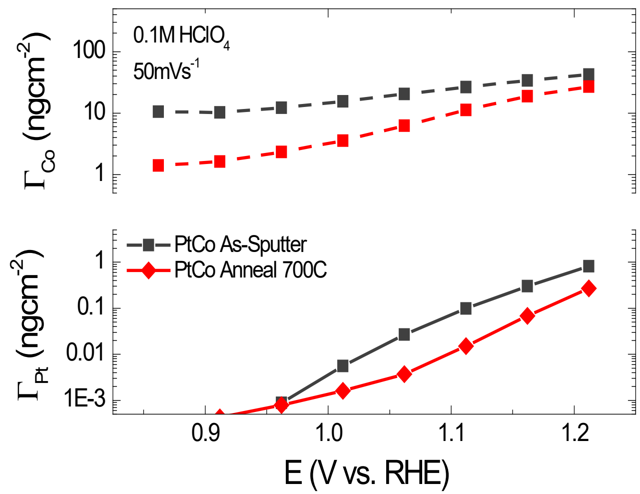




Annealing at 700°C= Intermetallic Phase



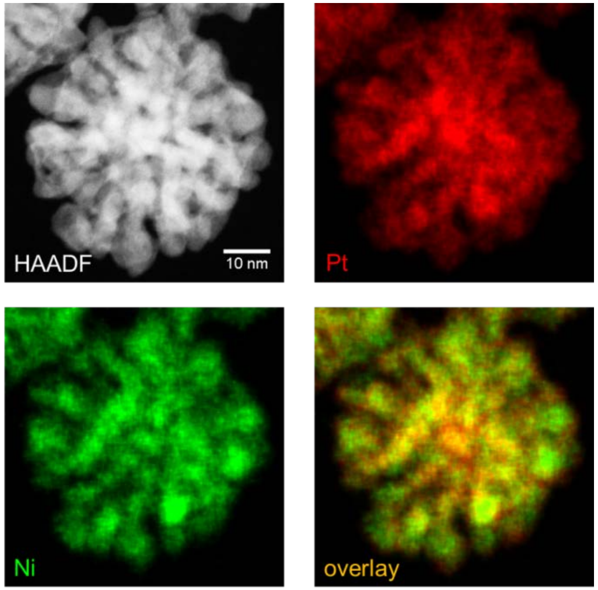




Benefit of intermetallic phase:

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

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



Nanopinwheels

ANL, ORNL

Improvement vs. Pt/C
RDE @ 0.95V

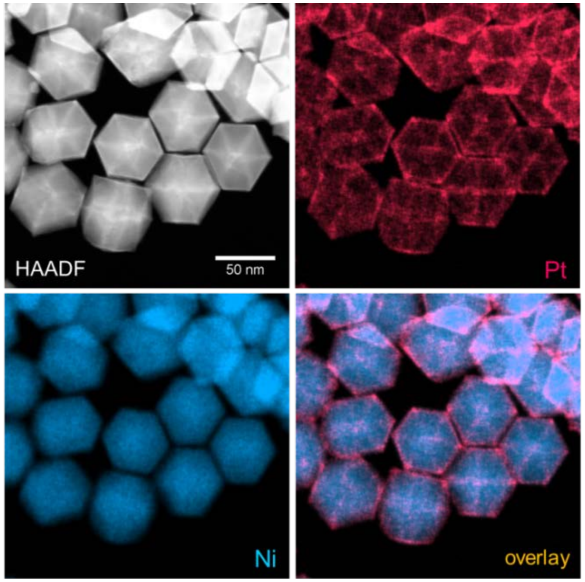
SA: 10
MA: 5

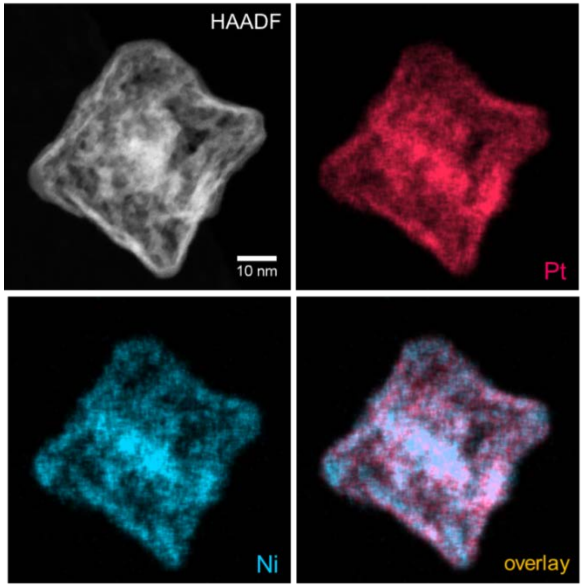
Nano Multi Skin

ANL, ORNL

Improvement vs. Pt/C
RDE @ 0.95V

SA: 7
MA: 4





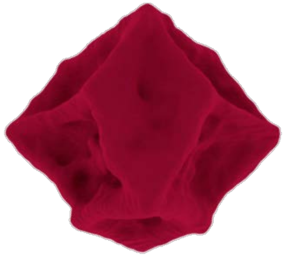
Nanocages

ANL, ORNL

Improvement vs. Pt/C
RDE @ 0.95V

SA: 9
MA: 6

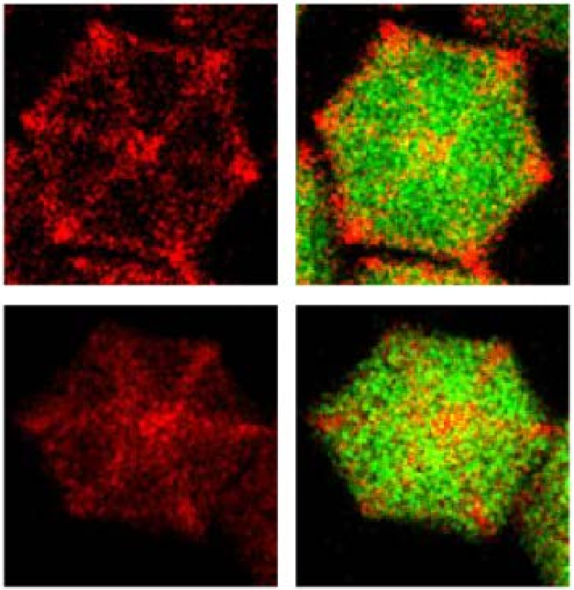
Excavated Nanoframes



LBNL, ANL, ORNL

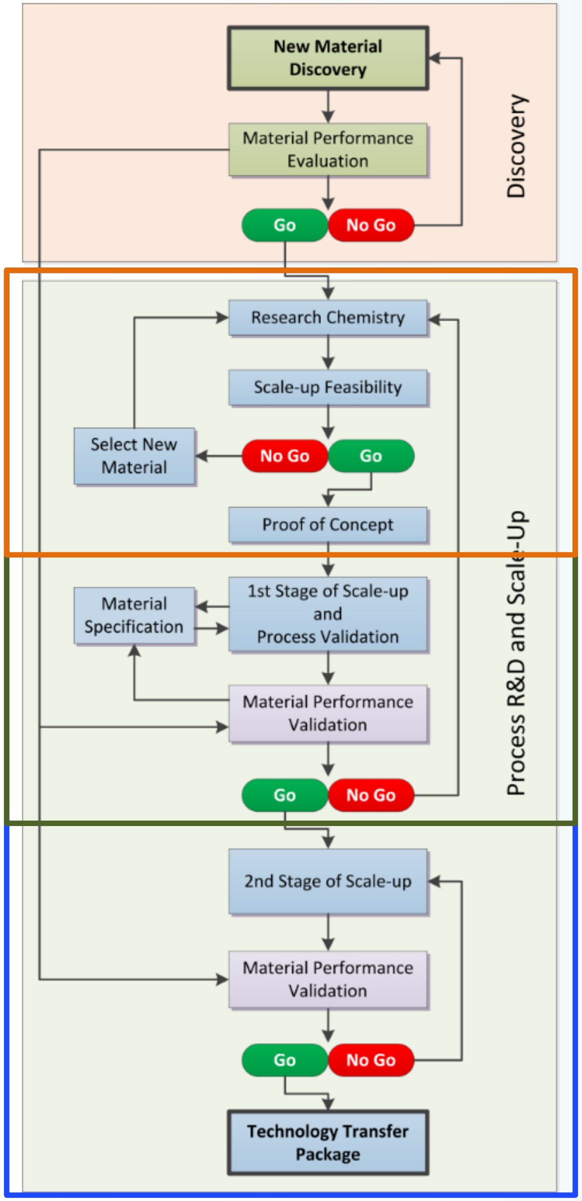
Improvement vs. Pt/C
RDE @ 0.95V

SA: 13
MA: 7



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

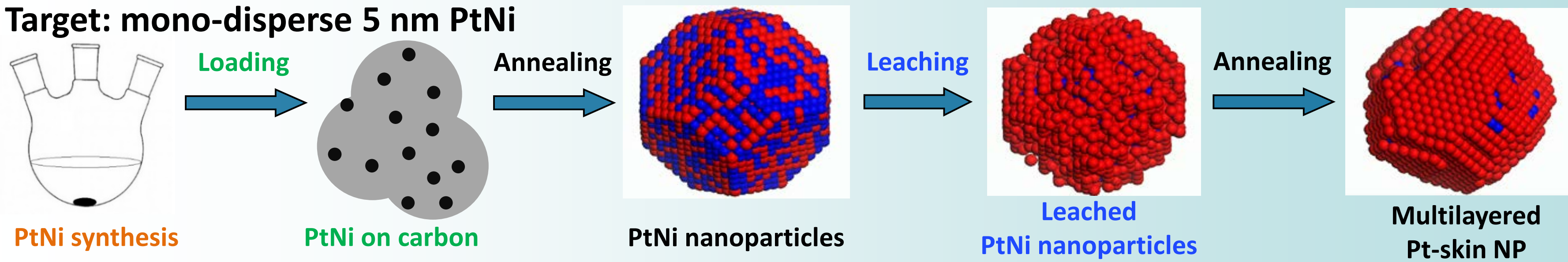
collab. with Greg Krumdick, ANL -MERF



		Timeline & Milestones
Research Chemistry	M 1-2	1) **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.

 Accomplishments: ***Process overview: 0.1 g vs. 5 g***

Target: mono-disperse 5 nm PtNi



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:

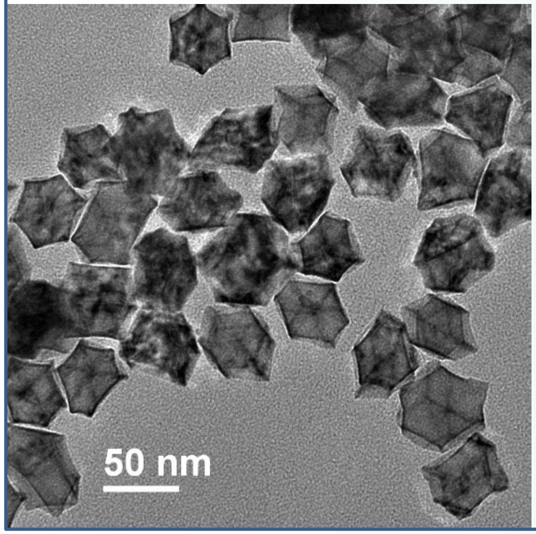
0.1 g Scale
1. Sonicate and soak PtNi/C in 0.1 M $HClO_4$. **X**
2. Centrifuge.

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

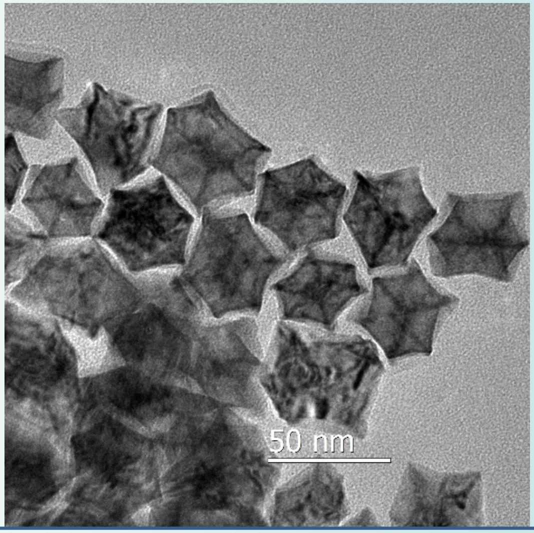
 Accomplishments and Progress: *Scale-up of Excavated Nanoframes 0.3g*

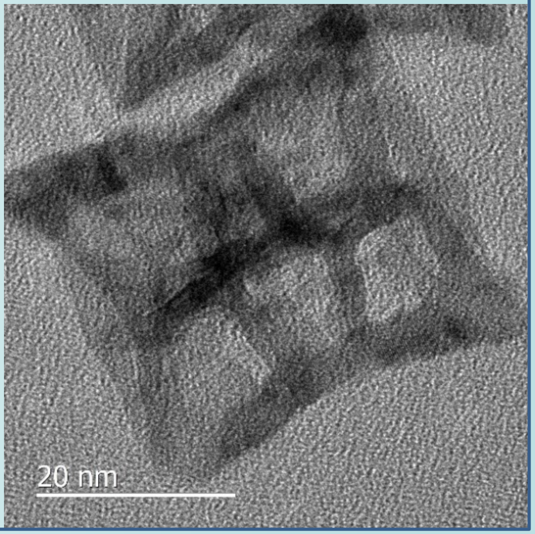
Nanoframe



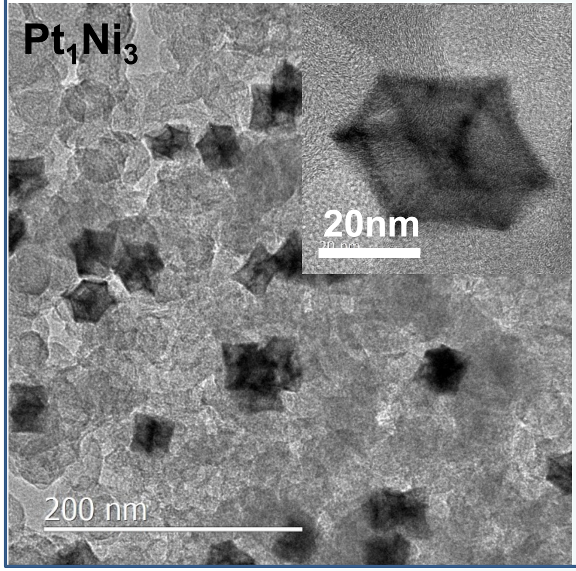
Particle larger ⟺ than small scale

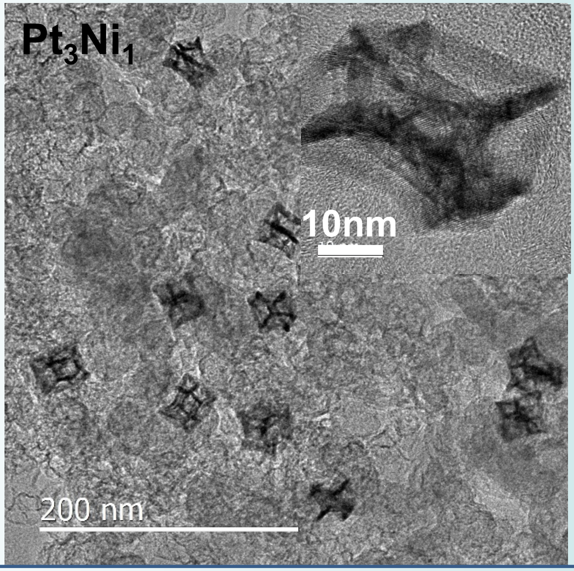
Excavated nanoframe

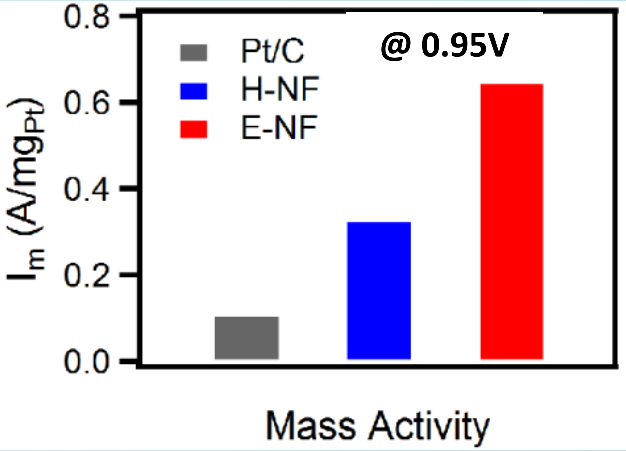


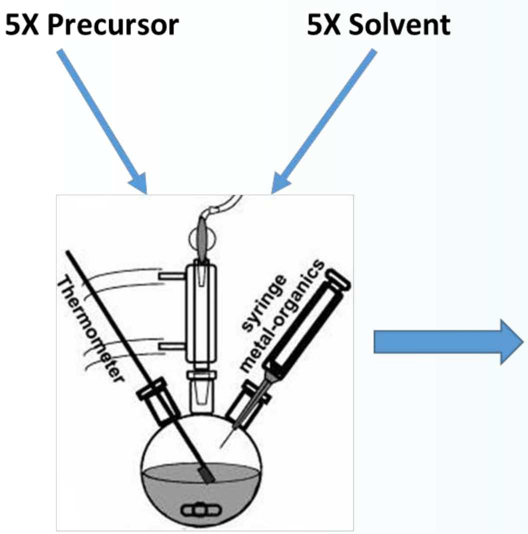


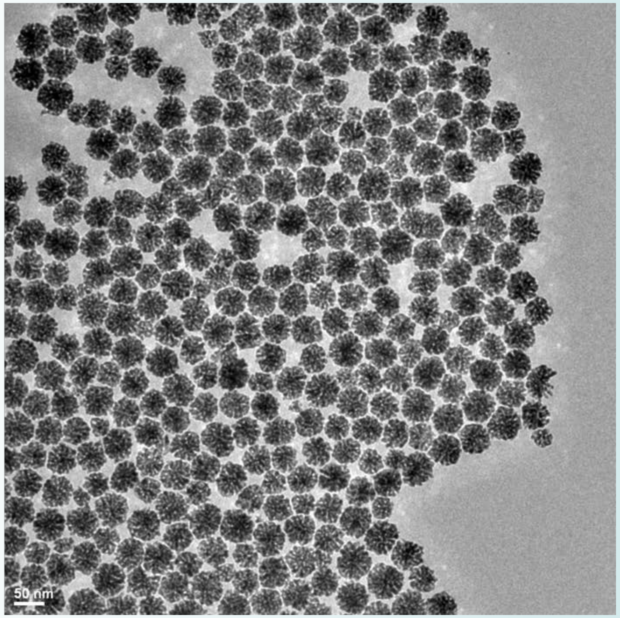
Excavated nanoframe-Further reducing Ni precursor amount

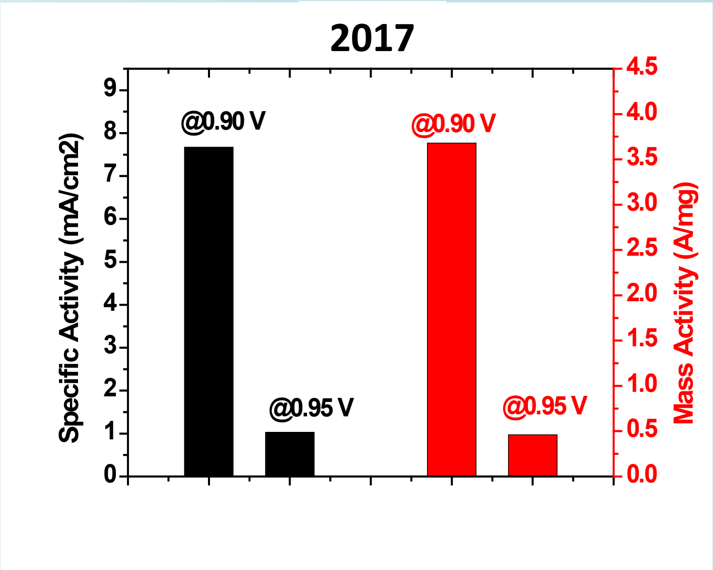


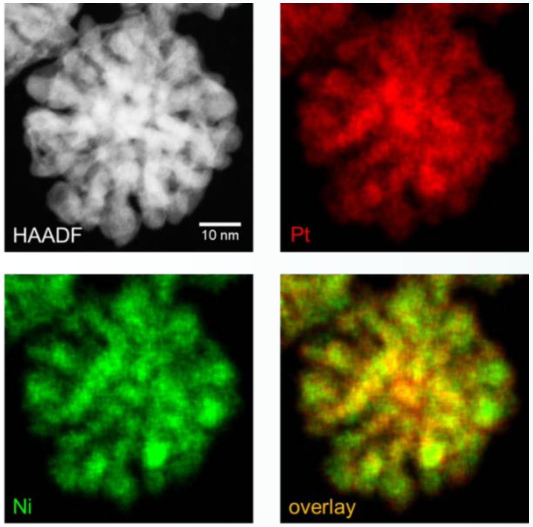










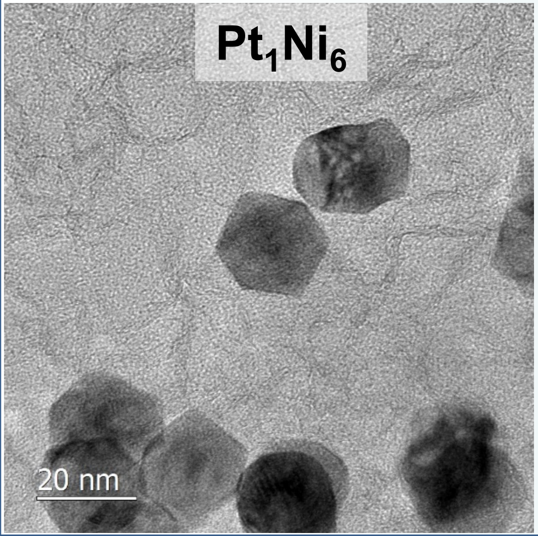


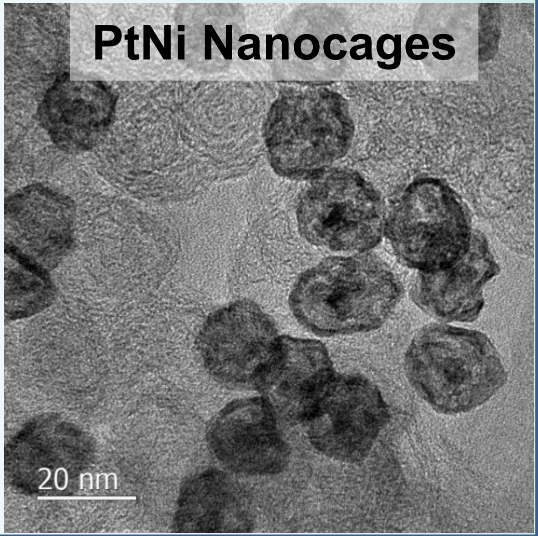
5X scaled up PtNi Nanopinwheels keep the same morphology

5X scaled up PtNi Nanopinwheels maintain high performance

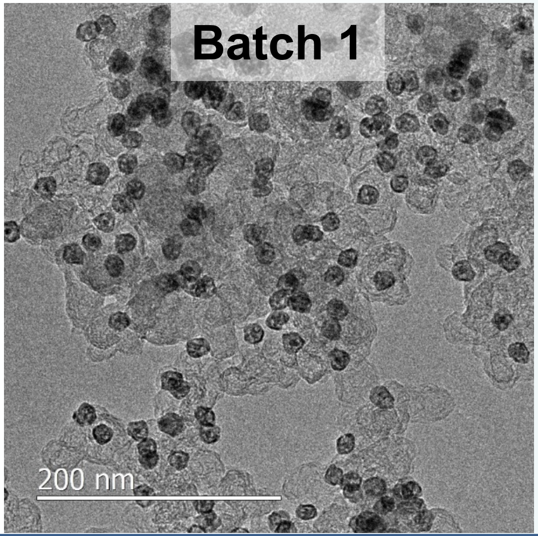
2018	0.90 V	0.95 V
5X scale up	8.2	1.14
Nanopinwheels	8.8	1.3

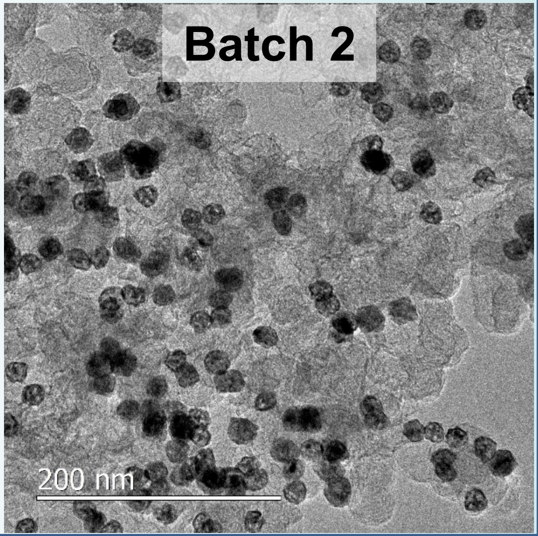
One-pot synthesis-0.1 g / batch

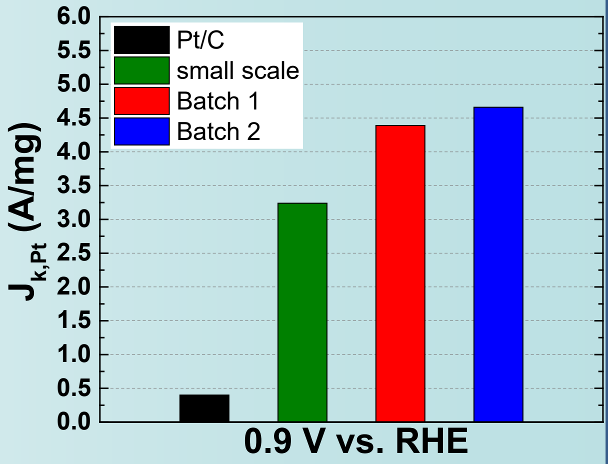


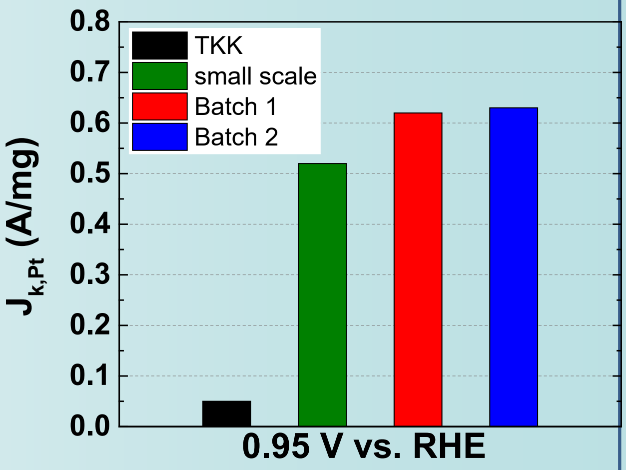


Scale up-0.6 g / batch

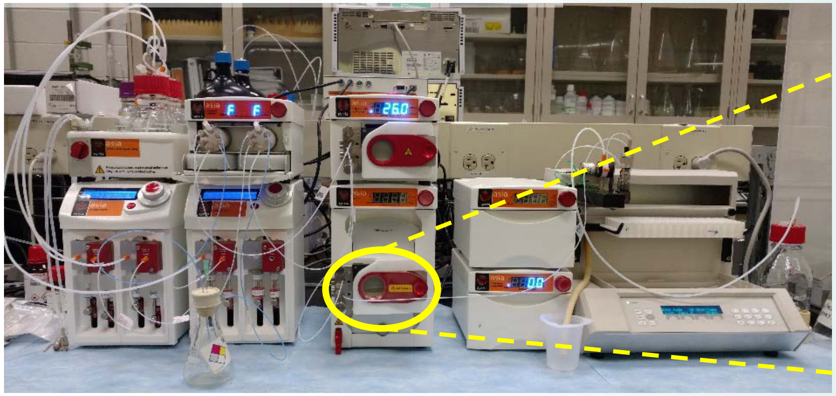


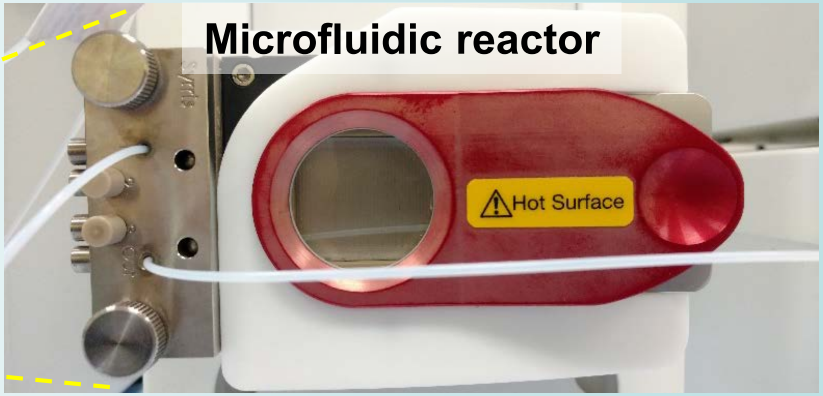






Flow reactor at MERF, ANL

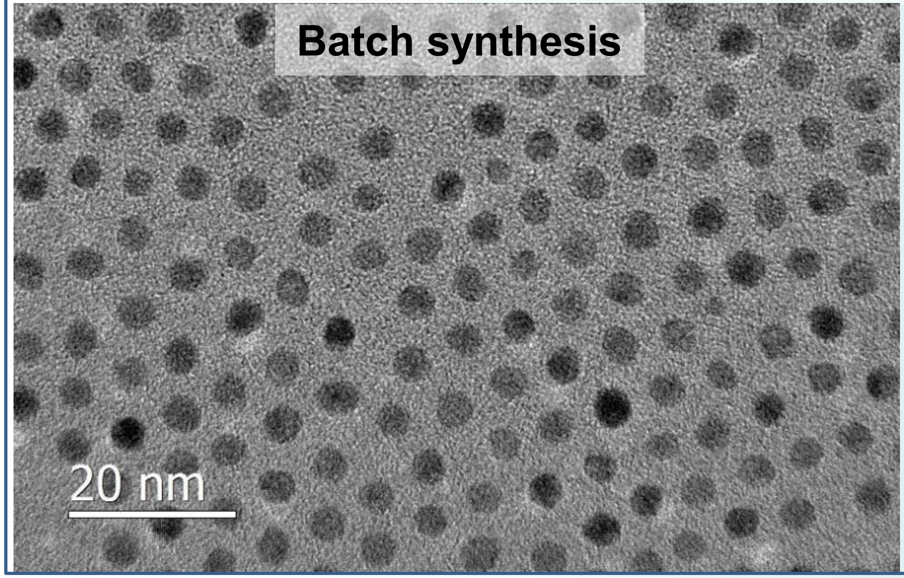


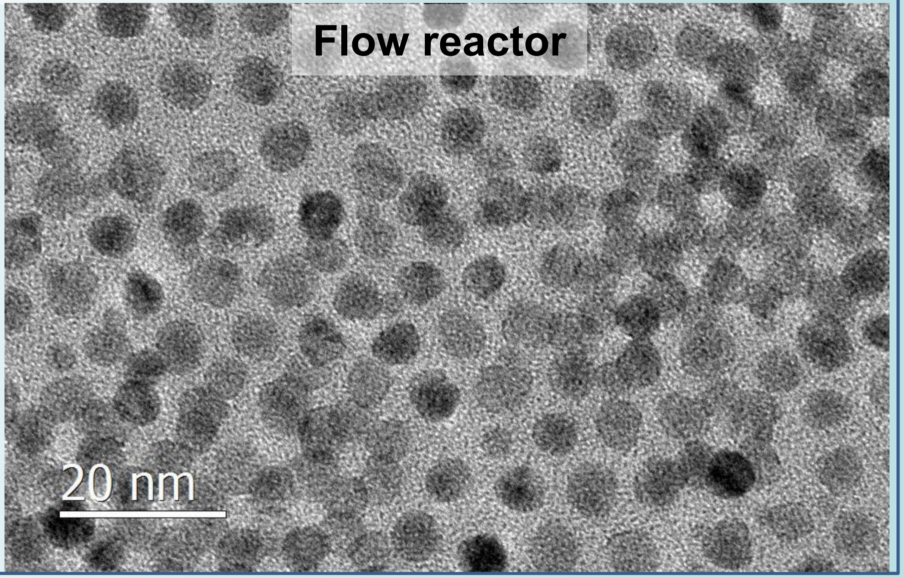


> Fast mass and heat transfer.
> Rapid optimization of reaction parameters.
> Easy scalability.

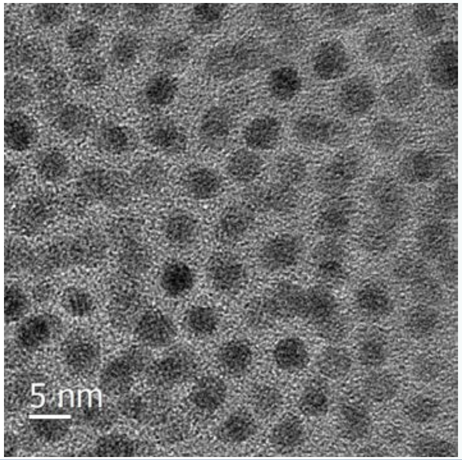
> Accurate control of reaction temperature and duration.
> Low usage of reagents in the optimization process.
> Capability for online monitoring.

PtNi Nanoparticles

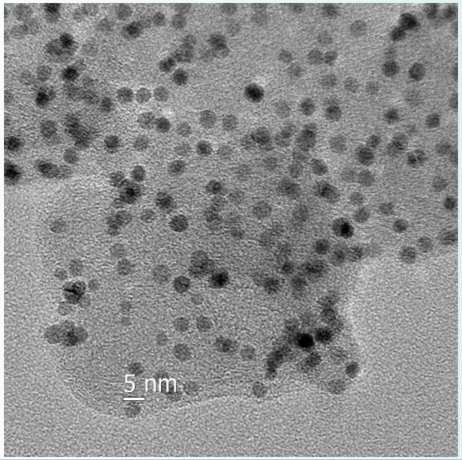




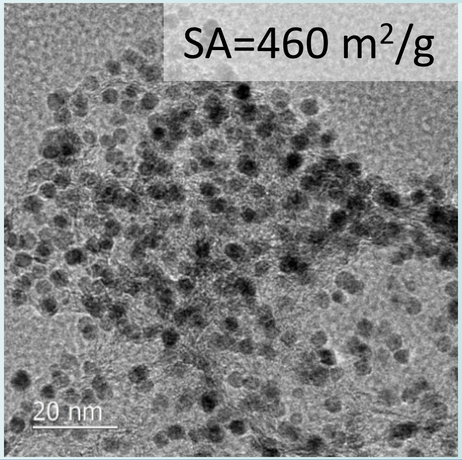
As synthesized



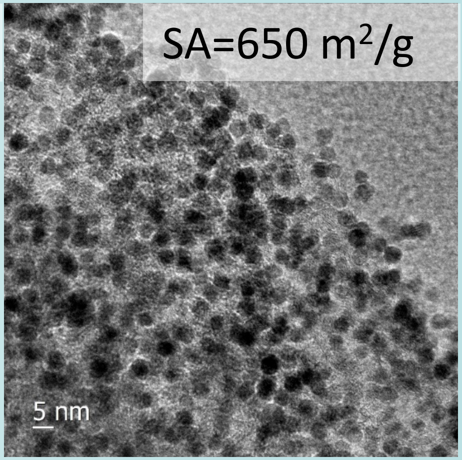
On Vulcan xc-72



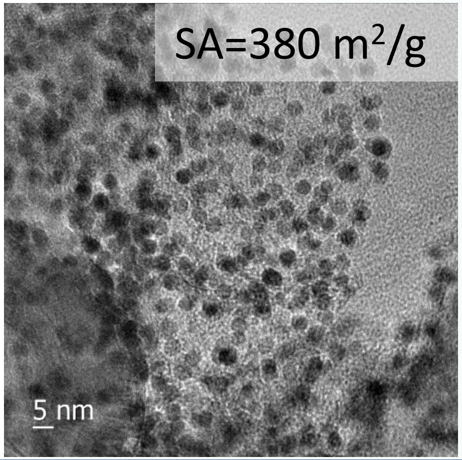
On C2



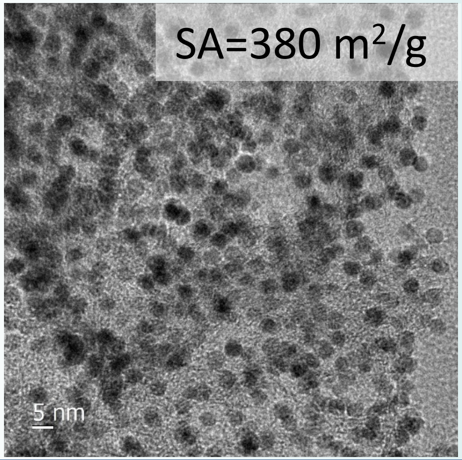
On C3



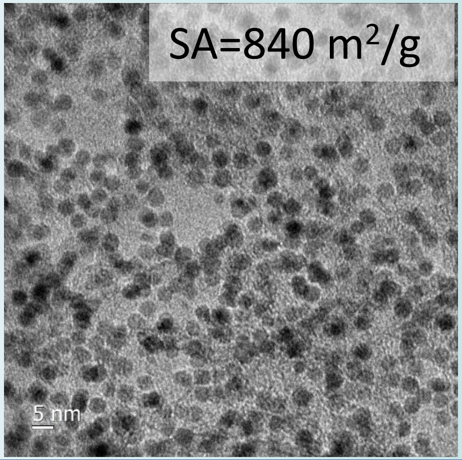
On C4



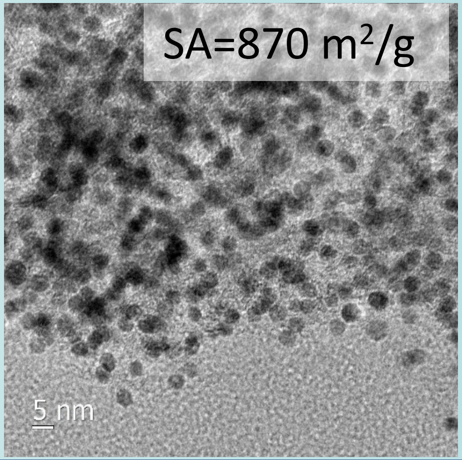
On C5



On C6



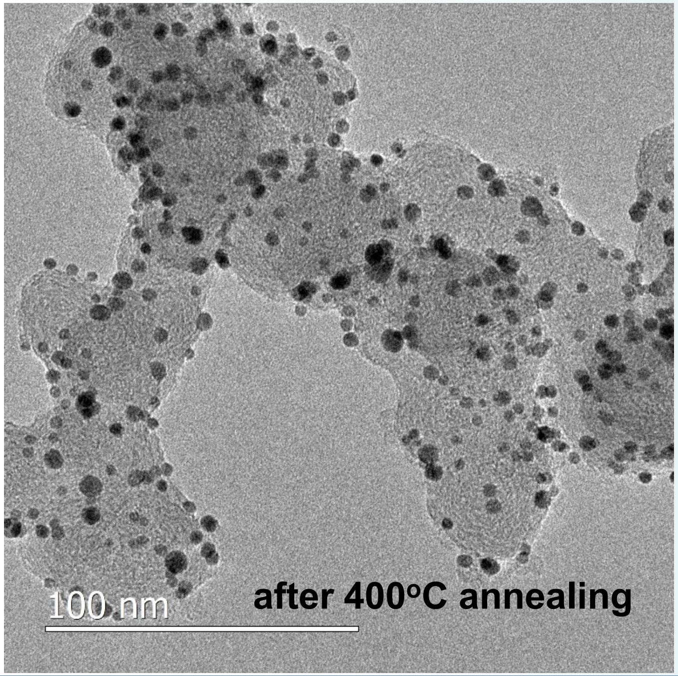
On C7

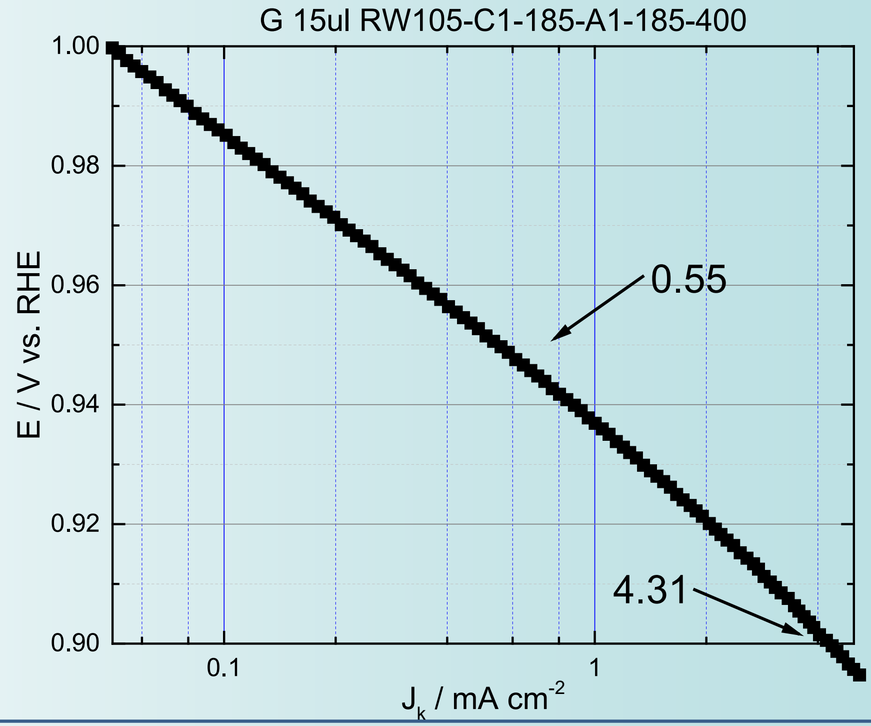


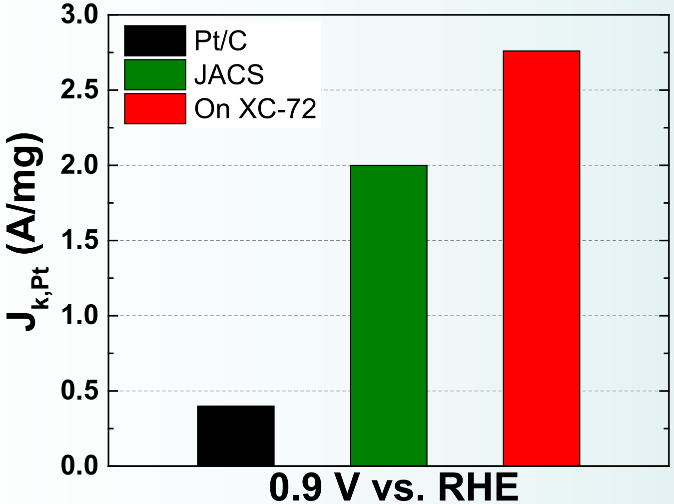
Same loading but different particle densities ⟺ Different accessible carbon surface areas

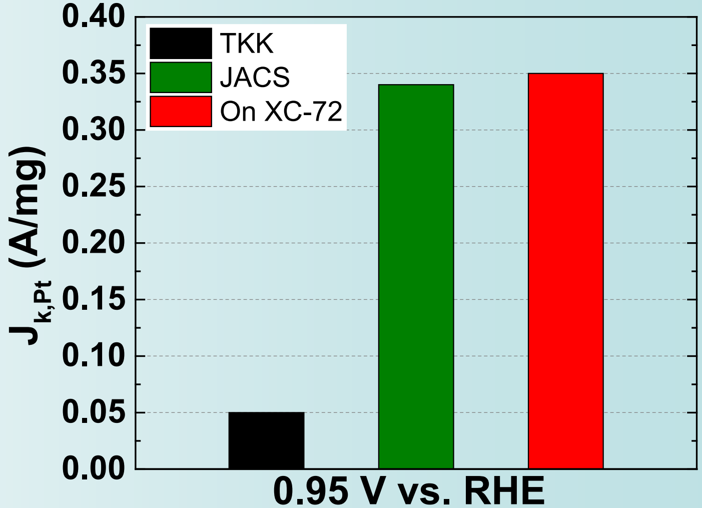
Accomplishments and Progress: *Different Supports & Loadings*

On XC-72





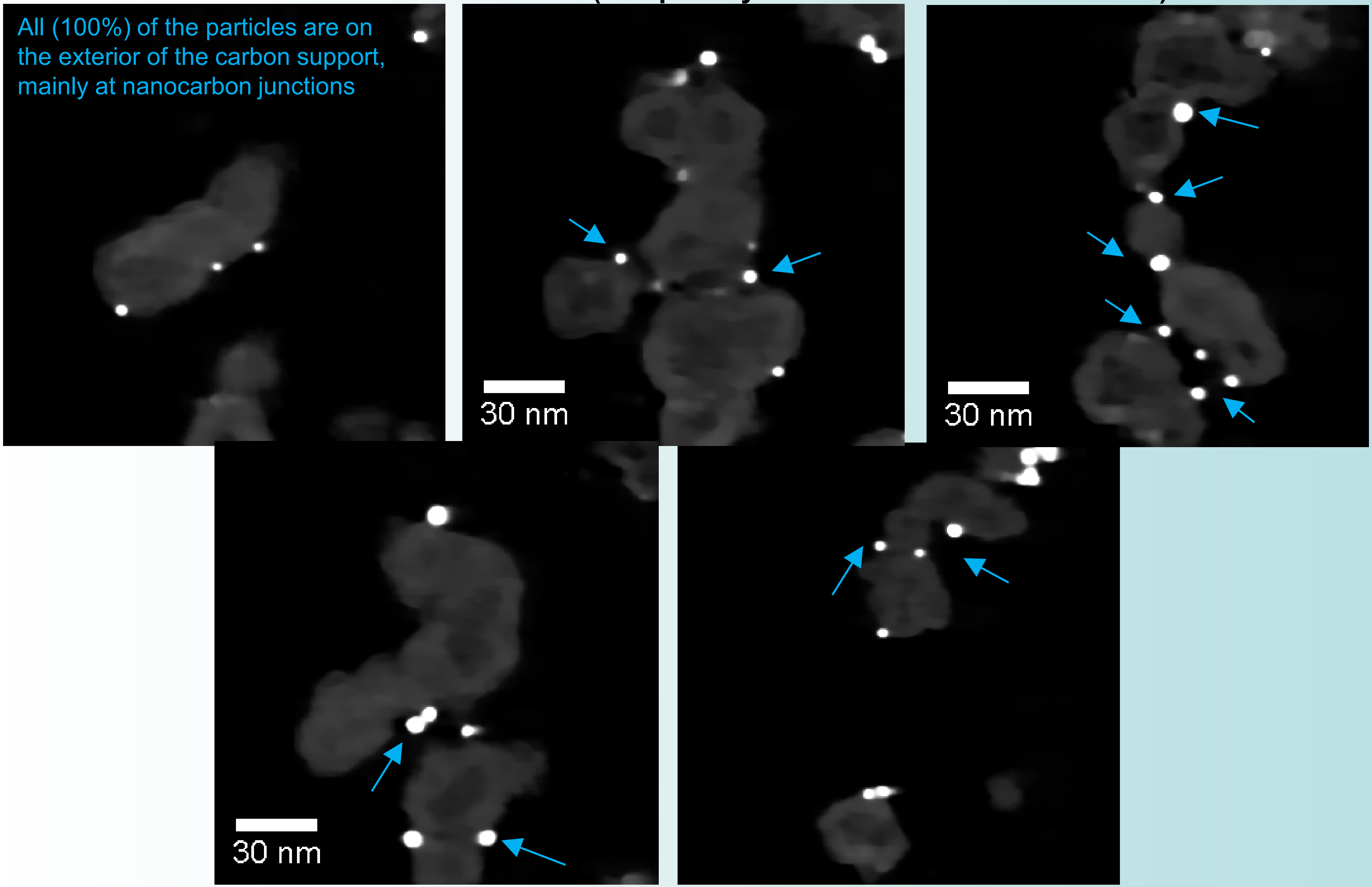




 Accomplishments and Progress: ***Particle deposition on carbon support***

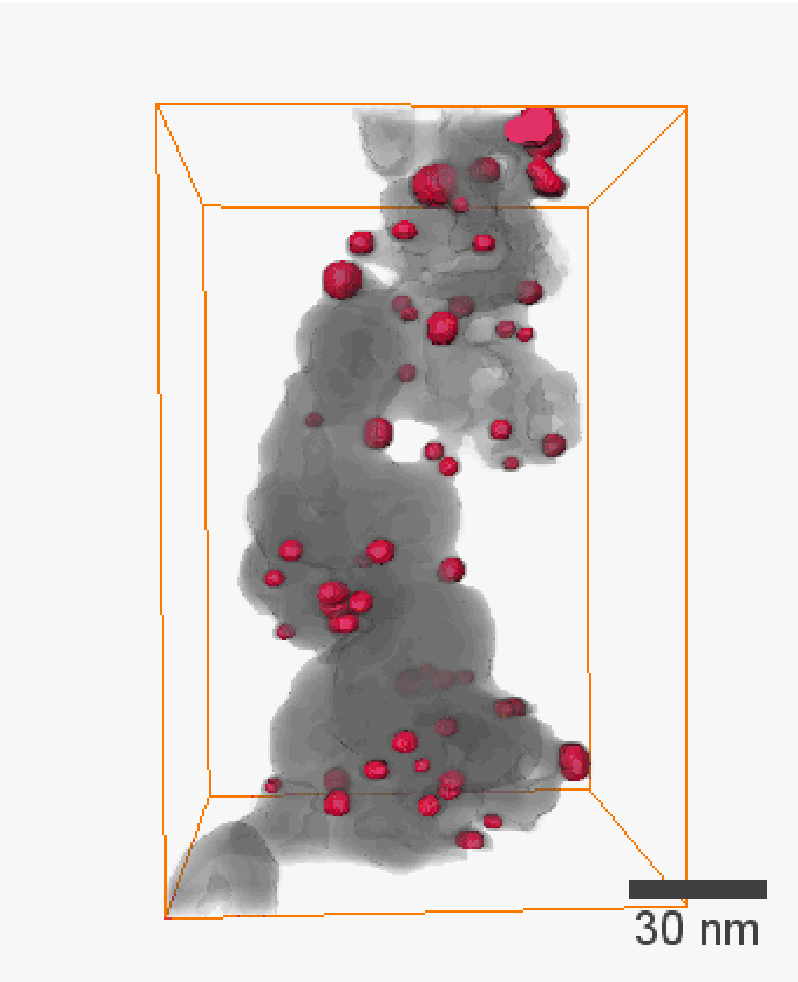
in collaboration with K.L. More, ORNL

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

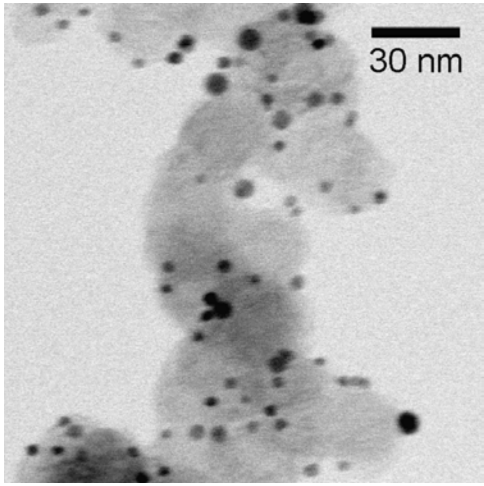


Accomplishments and Progress: *scaled PtNi in 50 cm² MEA*

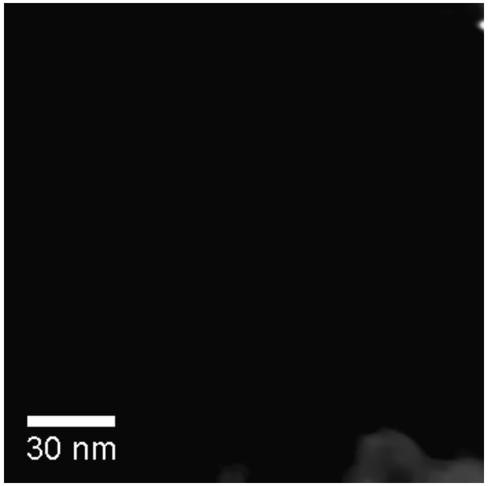
in collaboration with K.L. More, ORNL



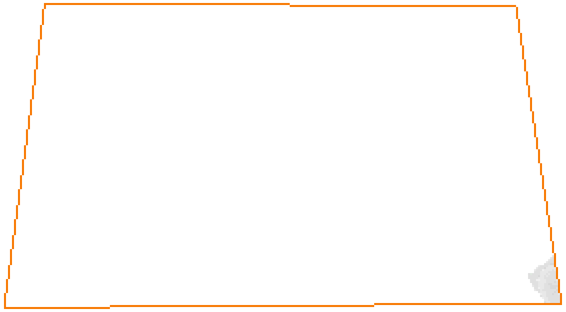
Tilt series



z-stack (cross-sections)

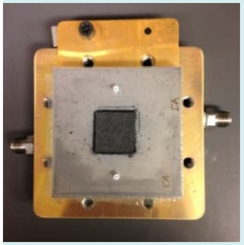


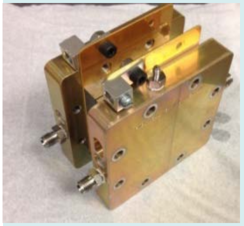
clipping
animation

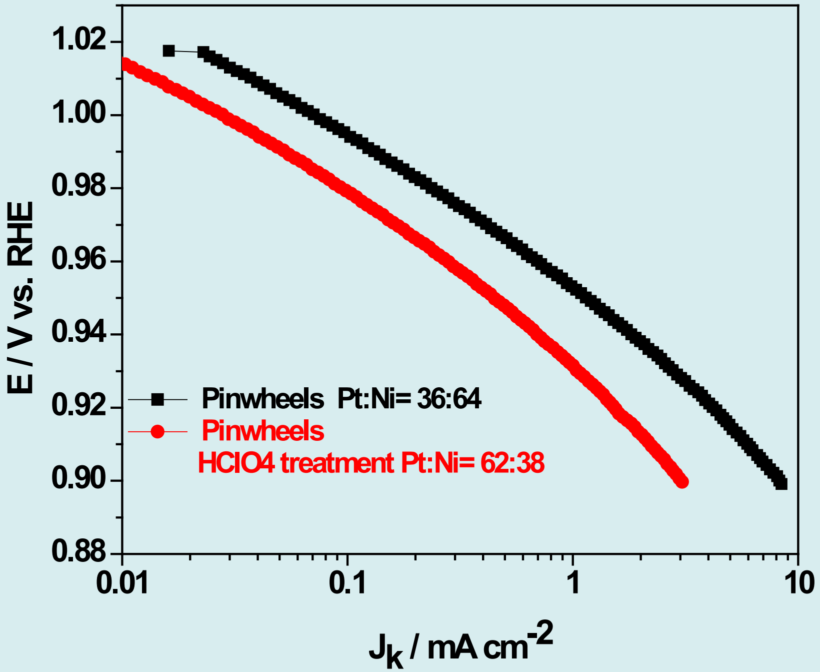


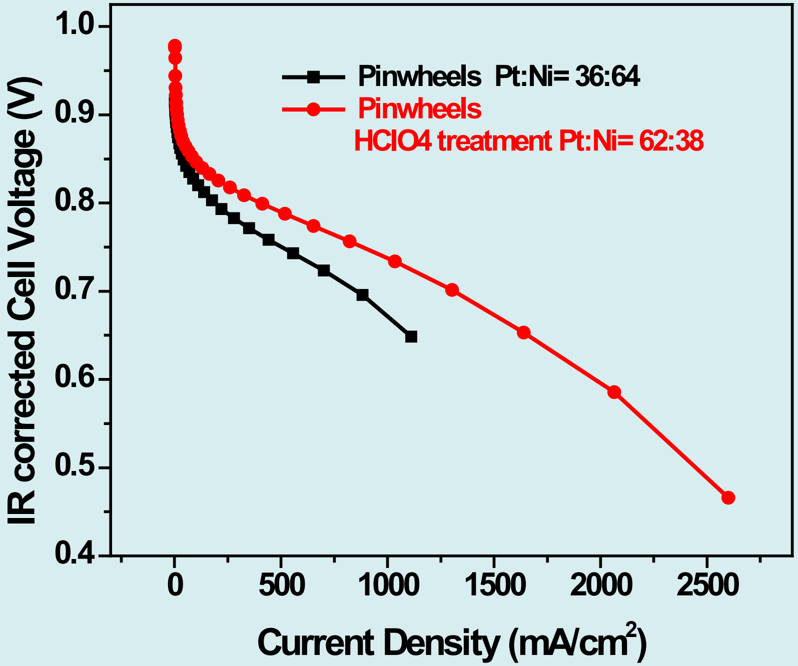
Accomplishments and Progress: *scaled Nanopinwheels in 5cm² MEA*

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









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

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

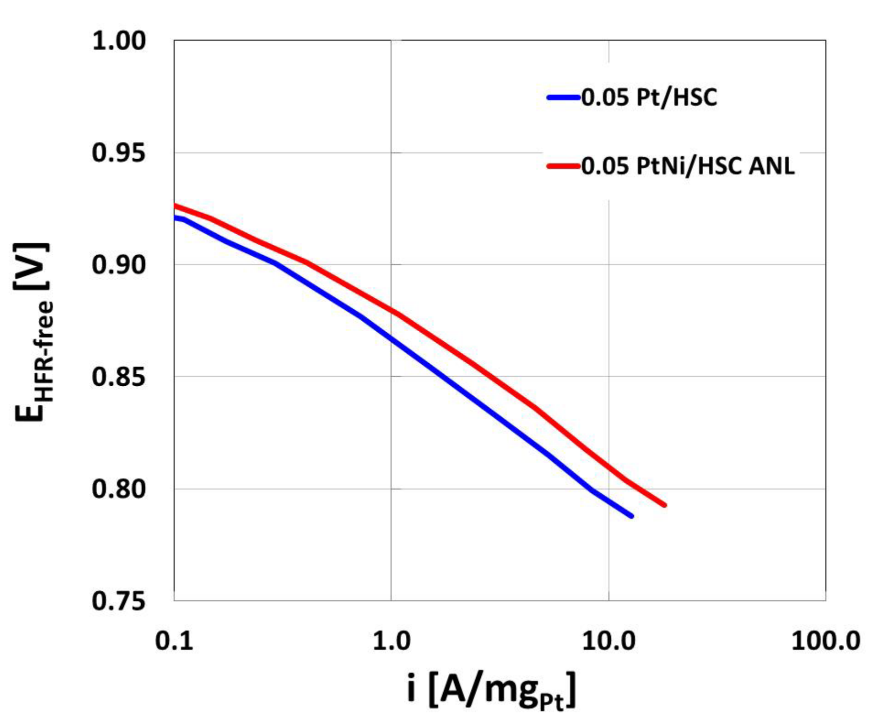
(H_2-O_2, 80C, 100%RH, 150kPa$_{(abs)}$) from high-low current

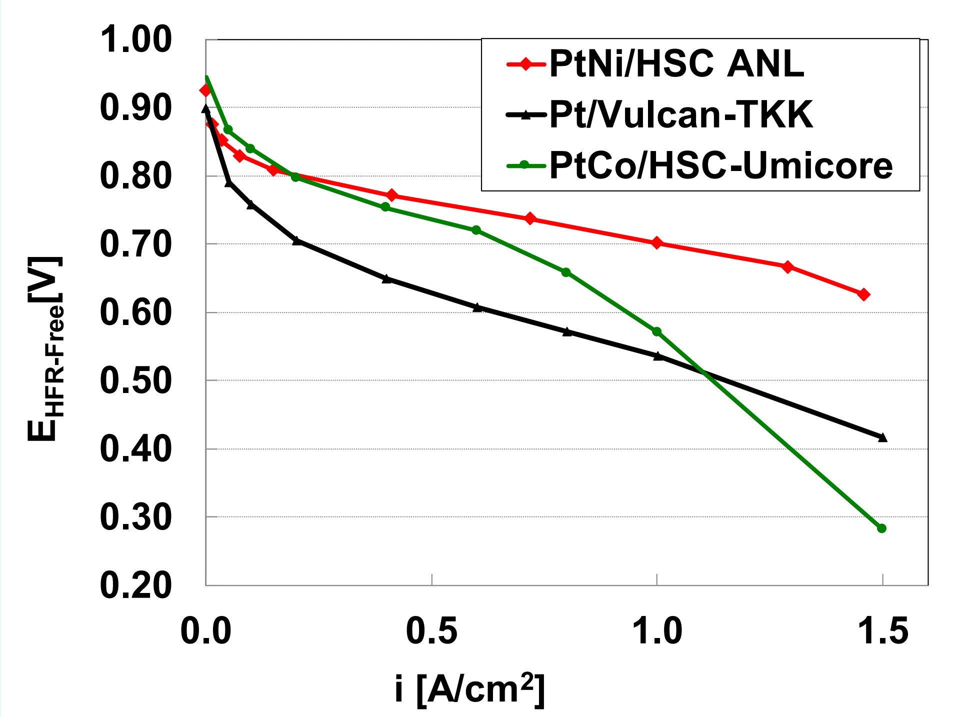
Mass activity at 0.9V: ~0.5 A/mg with 0.03 mg/cm² Pt loading

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
- Cathode loading 0.046 $mgPt/cm^2$

- 150 kPa, 100% RH, 80°C H_2/Air, 50 cm^2,

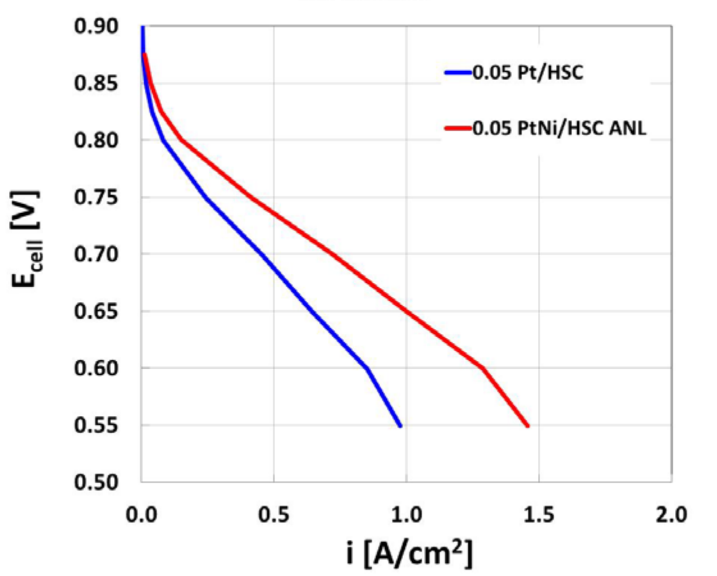




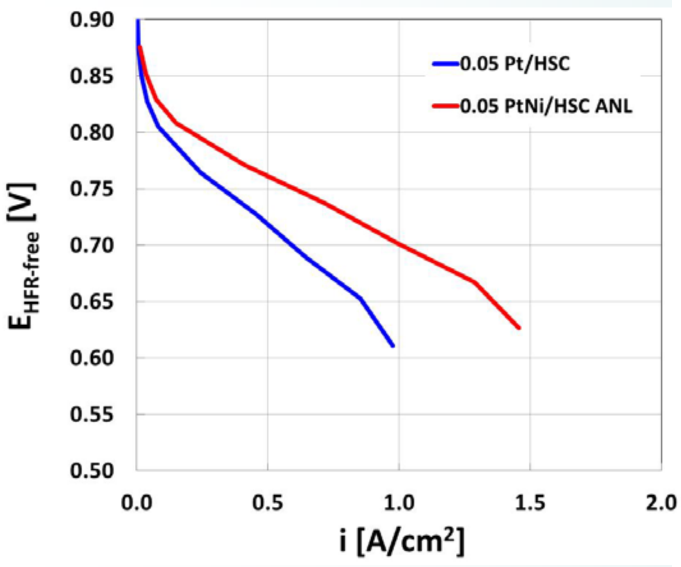
- Developed PtNi/HSC: **$i_m^{0.9V}$ ~ 500 mA/mg_{Pt}** vs. to ~300 mA/mg_{Pt} for 50 wt% Pt/HSC (TKK)
- PtNi/HSC: **$i_s^{0.9V}$ 920 $\mu A/cm^2_{Pt}$** vs. 480 $\mu A/cm^2_{Pt}$ for Pt/HSC (TKK)
- PtNi/HSC shows improved performance at high current density / Improved non-Fickian transport

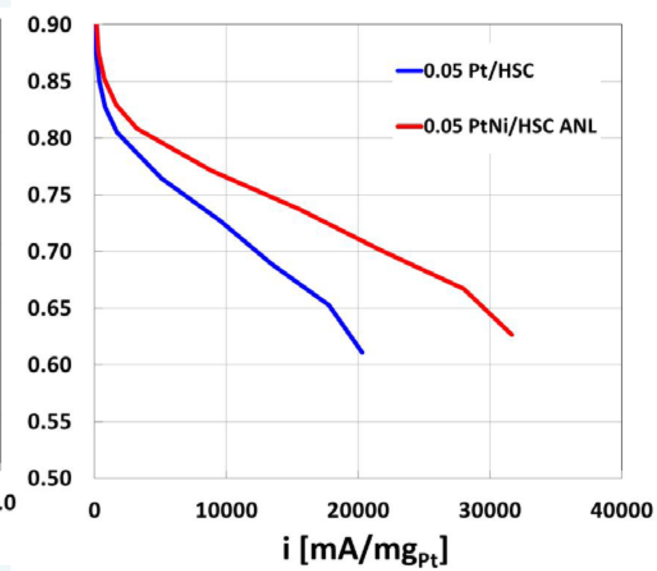
in collaboration Neyerlin, NREL

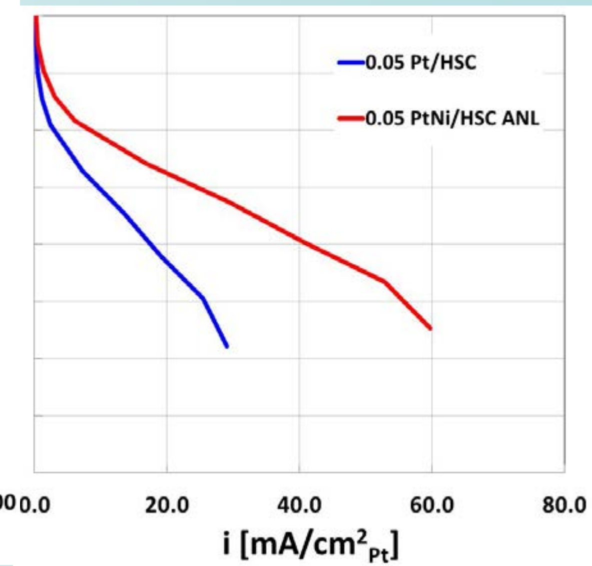
- 150 kPa, 100% RH, 80°C H_2/Air, 50 cm^2, N211



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





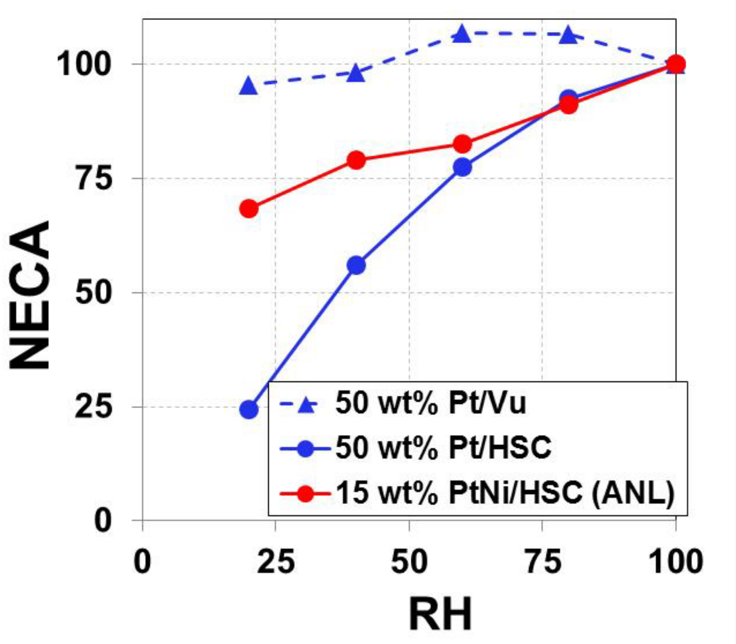


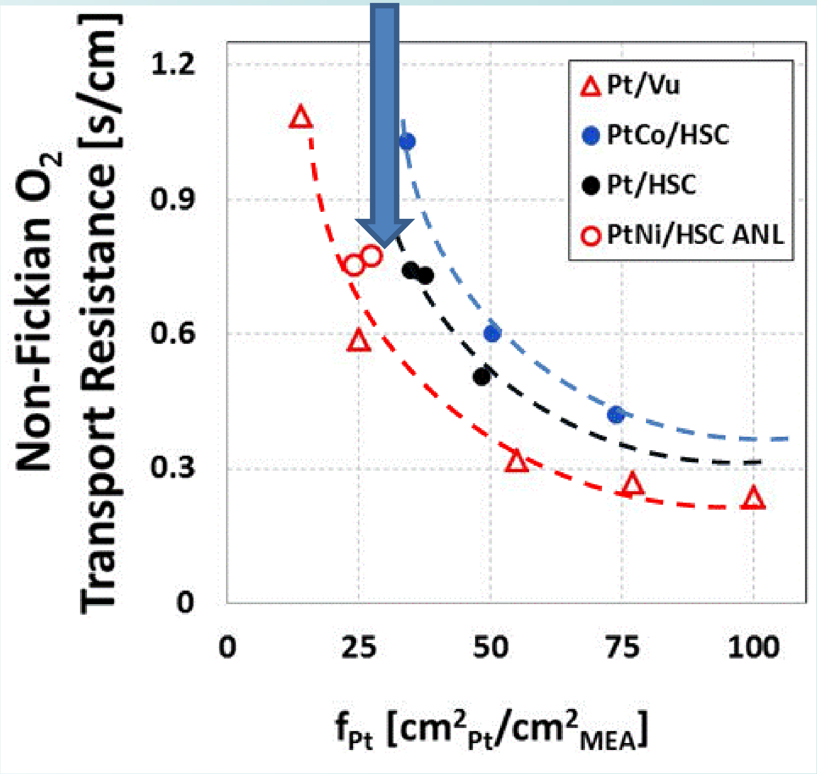
in collaboration with Kenneth Neyerlin, NREL

Improved Non-Fickian Transport Resistance

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

- Reduced non-Fickian transport resistance



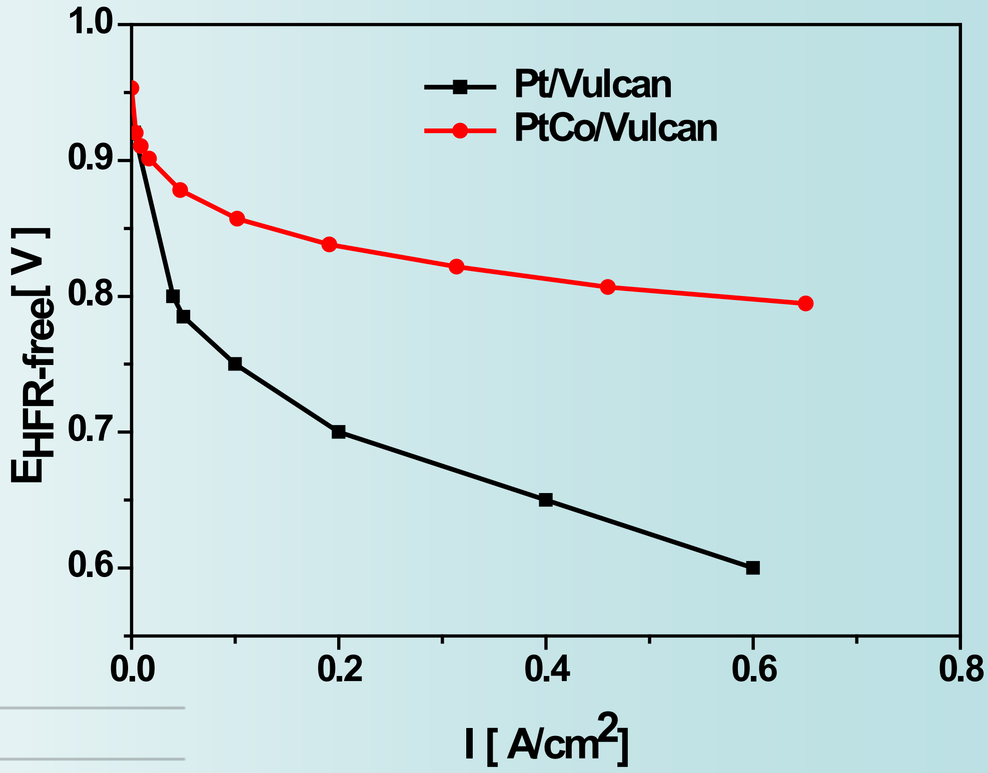


Limiting current measurements indicate that PtNi/HSC has significantly reduced non-Fickian transport resistance relative to other highly active electrocatalysts (PtCo/HSC)

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

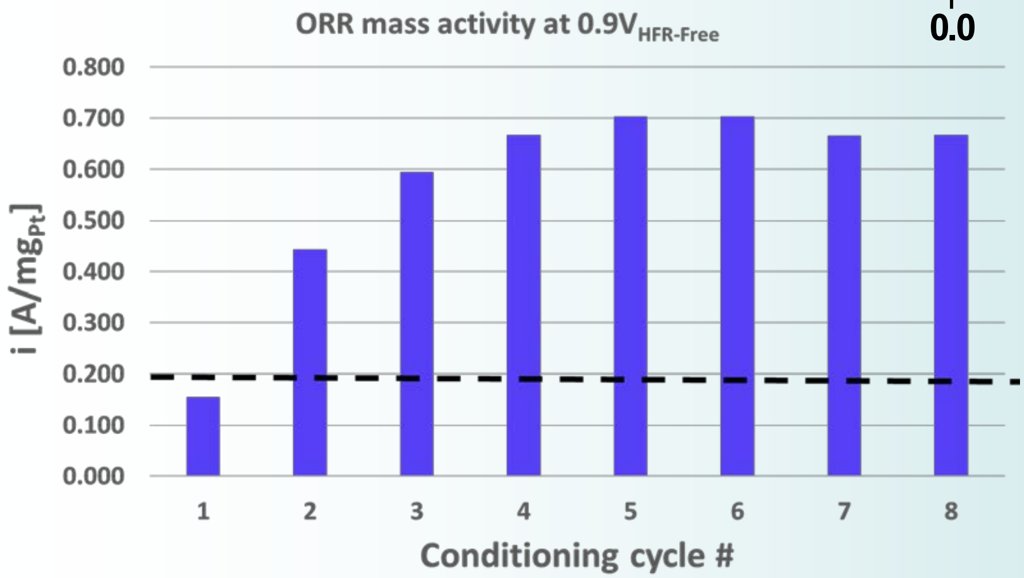
in collaboration with Kenneth Neyerlin, NREL

150 kPa, 100% RH, 80°C H_2/O_2, 50 cm²
Ultrasonic spray coated at NREL 0.5 I:C
Cathode loading 0.035 mgPt/cm²



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

Pt/Vulcan: $i_m^{0.9V}$ **~200 mA/mg$_{Pt}$**

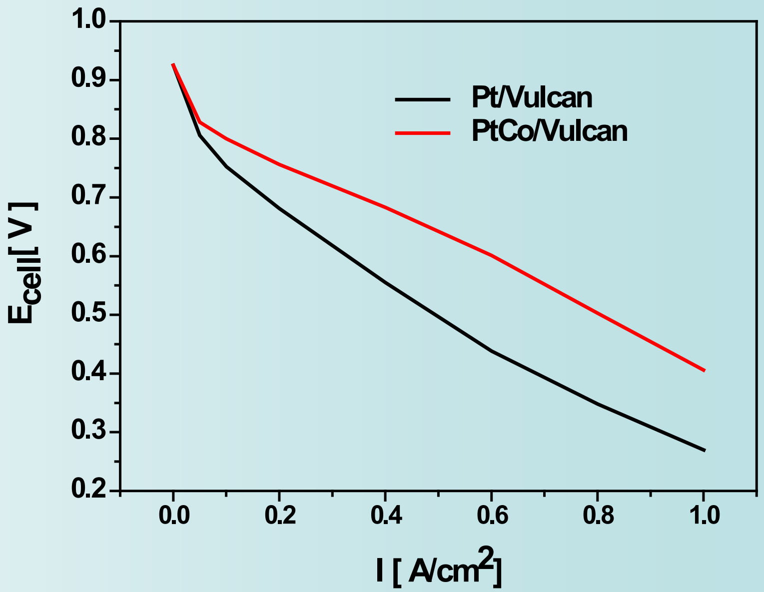


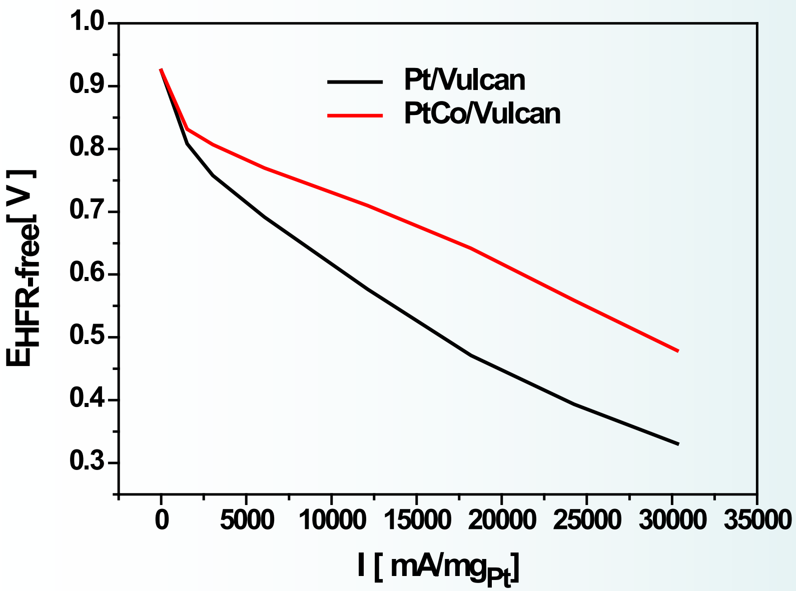
Pt/Vulcan only shows about 0.2 A/mg mass activity at 0.9 V

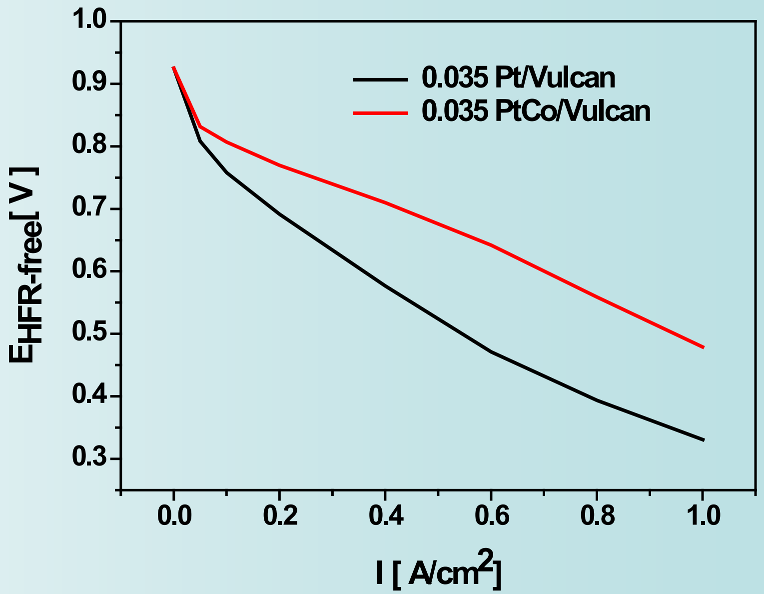
in collaboration with Kenneth Neyerlin, NREL

150 kPa, 100% RH, 80ºC H_2/Air, 50 cm²
Ultrasonic spray coated at NREL 0.5 I:C
Cathode loading 0.035 mgPt/cm2

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







Responses to some reviewers comments

Question 1: Approach to performing the work

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

Question 2: Accomplishments and progress toward DOE goals

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

Much more has been accomplished over the last year in testing of our catalysts in 50cm^2 MEAs. All of them exceeded DOE technical target and labeling our performance with "poor" has more to do with the reviewer's ability to perform an unbiased review.

Question 3: Collaboration and coordination with other institutions

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

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

Project weakness

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

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

Recommendations for additions/deletions to project scope

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

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

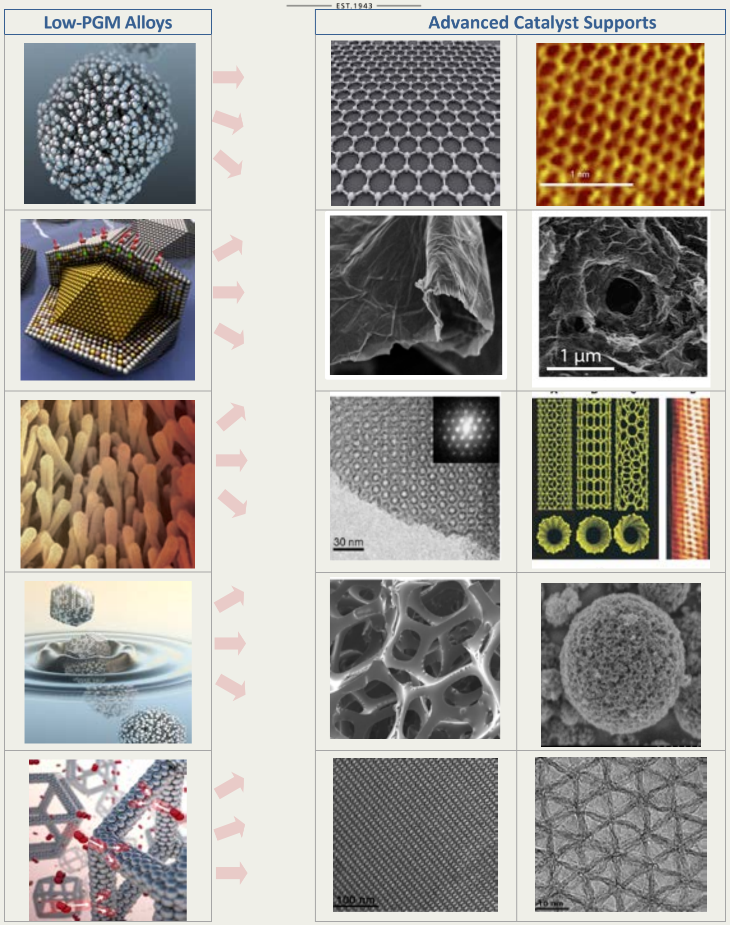
Collaborations

Argonne National Laboratory — **Lead: design, synthesis, evaluation**

Berkeley Lab — **Sub: synthesis, scale-up support**

Oak Ridge National Laboratory — **Sub: structural characterization**

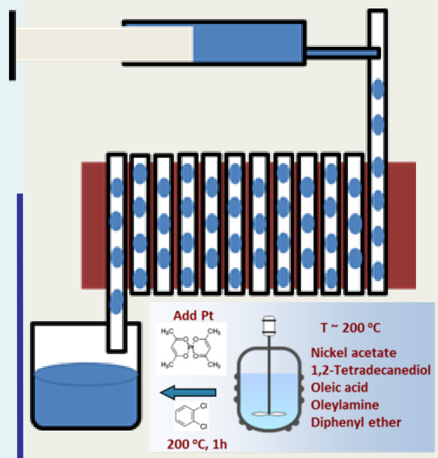
Los Alamos National Laboratory — **Sub: catalyst supports**



Low-PGM Alloy Catalysts

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

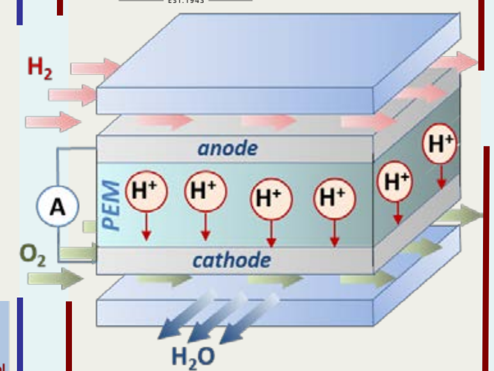
Berkeley Lab — **Sub: process support**



Catalysts Scale Up

Argonne National Laboratory — **Lead: 5 and 25cm² MEA**

NREL — Los Alamos National Laboratory — **Sub: 25 and 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)

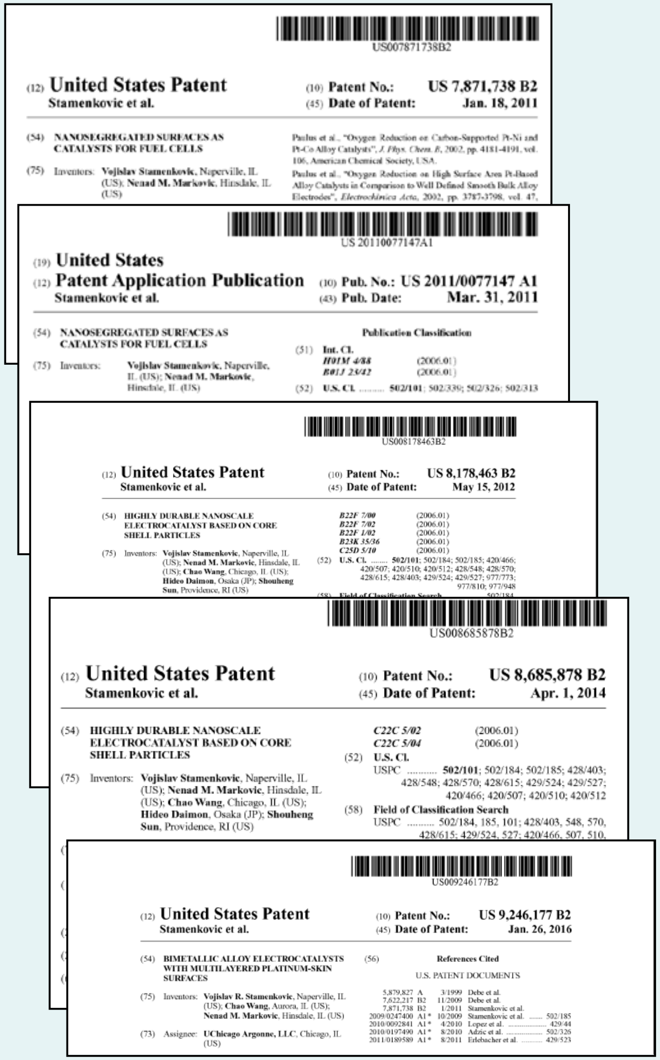
2) Cost (total loading of PGM 0.125 mg_{PGM} / cm^2)

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

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


(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)

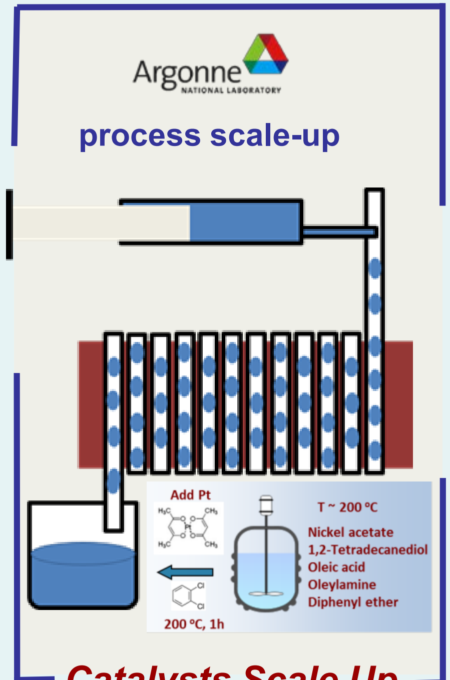
(19) United States (12) Patent Application Publication — Stamenkovic et al. — (10) Pub. No.: US 2011/0077147 A1 — (43) Pub. Date: Mar. 31, 2011
(54) NANOSEGREGATED SURFACES AS CATALYSTS FOR FUEL CELLS

(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

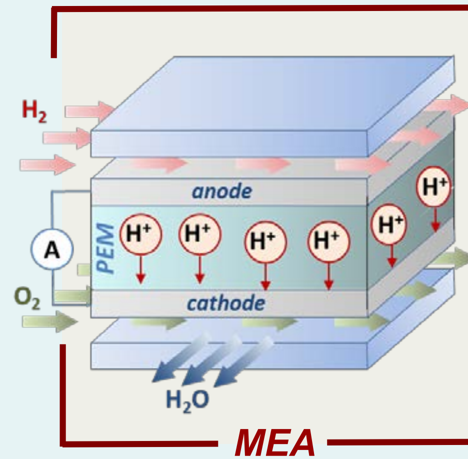
(12) United States Patent — Stamenkovic et al. — (10) Patent No.: US 8,685,878 B2 — (45) Date of Patent: Apr. 1, 2014
(54) HIGHLY DURABLE NANOSCALE ELECTROCATALYST BASED ON CORE SHELL PARTICLES
(75) Inventors: Vojislav Stamenkovic, Naperville, IL (US); Nenad M. Markovic, Hinsdale, IL (US); Chao Wang, 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
(73) Assignee: UChicago Argonne, LLC, Chicago, IL (US)

T2M



Auto OEMs



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

FY18

2 NDA signed

SUMMARY

Approach

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

Accomplishments

- Dissolution of Pt for different particle size distributions of Pt/C: the advantage of monodisperse
- Resolved the mechanism of diminished Pt dissolution for Au subsurface
- Designed of highly durable NPs: Applied the knowledge from well-defined surfaces to nanoparticles
- "No-Dissolution" Proof of Concept in Highly Durable NPs: Synthesis and Characterization of Pt_3Au/C NPs
- Well-Defined Pt-Alloy intermetallic systems are more active and durable vs. solid-solution Pt-Alloys
- Scaled four nanoarchitectures at the gram level quantities
- Applied different carbon supports
- Effective placement of particles exclusively on the high surface area carbon surface – no buried particles
- PtNi with multilayered Pt-Skin and Nanopinwheels exceeded DOE 2020 Technical Target for mass activity in MEA
- Two patent application in FY18, 2 articles submitted and 6 presentations at conferences

Collaborations

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

Full time postdocs:

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

Partial time Staff:

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

Publications and Presentations

3 Publications
3 Presentations
2 patent applications