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2016 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

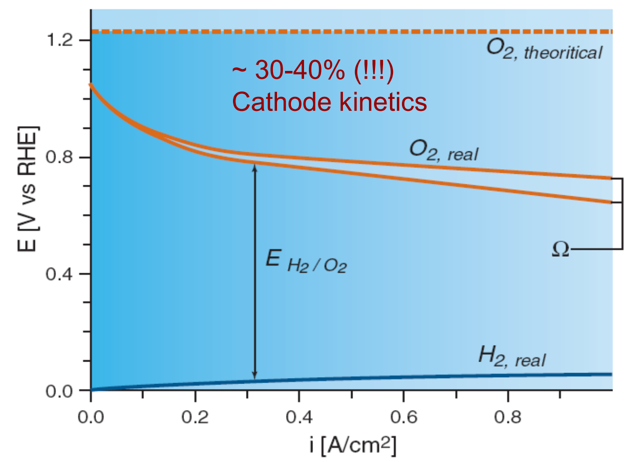
Timeline

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

Budget

- Total Project funding $ 3.6M
- Funding for FY16: $ 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

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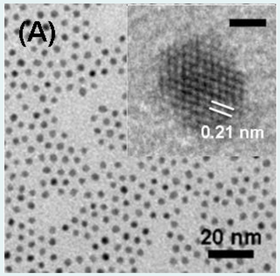
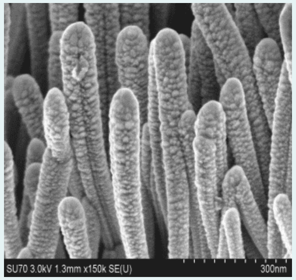
ANL Technical Targets

- 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

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

A N L

PEMFC Cathode Catalysts Development

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

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)

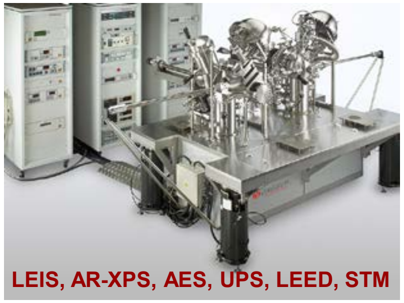
2° synthesis of nano-, meso- and thinfilm- PtMN catalysts:
- shape/size/composition control
- intermetallics; core/interlayer/shell; thin-film systems
(colloidal chemical synthesis, PVD, HRTEM/STEM)

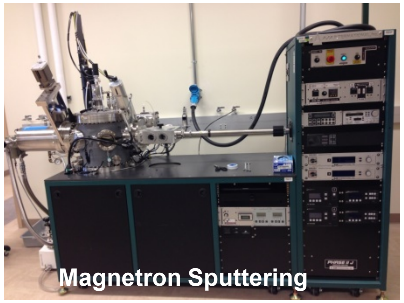
3° electrochemical characterization of catalysts:
- optimization: ionomer/carbon/propanol/catalyst ink
- temperature effect; Ionic Liquid evaluation
- activity/durability in RDE vs. 5-50cm²/MEA; HRTEM

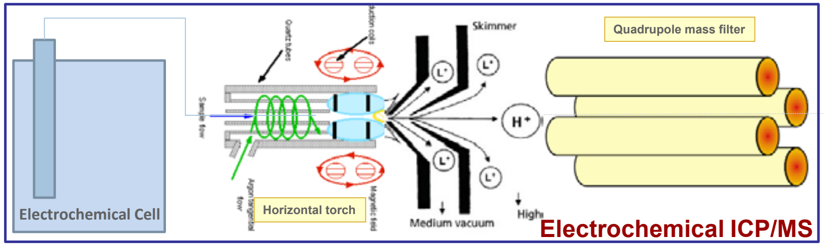
4° fine tuning of performance through catalyst-support:
- Carbon based materials

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

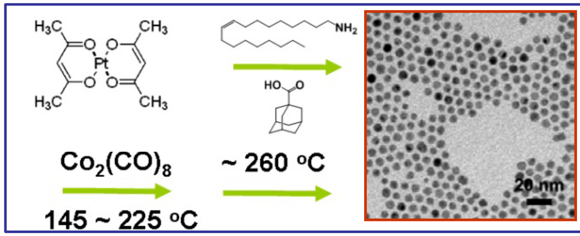
TASK 1







TASK 2&5



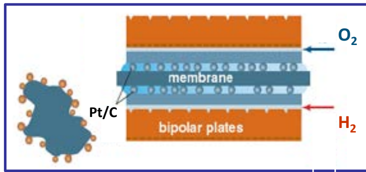
scale-up synthesis of nanomaterials

grams of catalyst

solvo-thermal

advanced supports

TASK 3



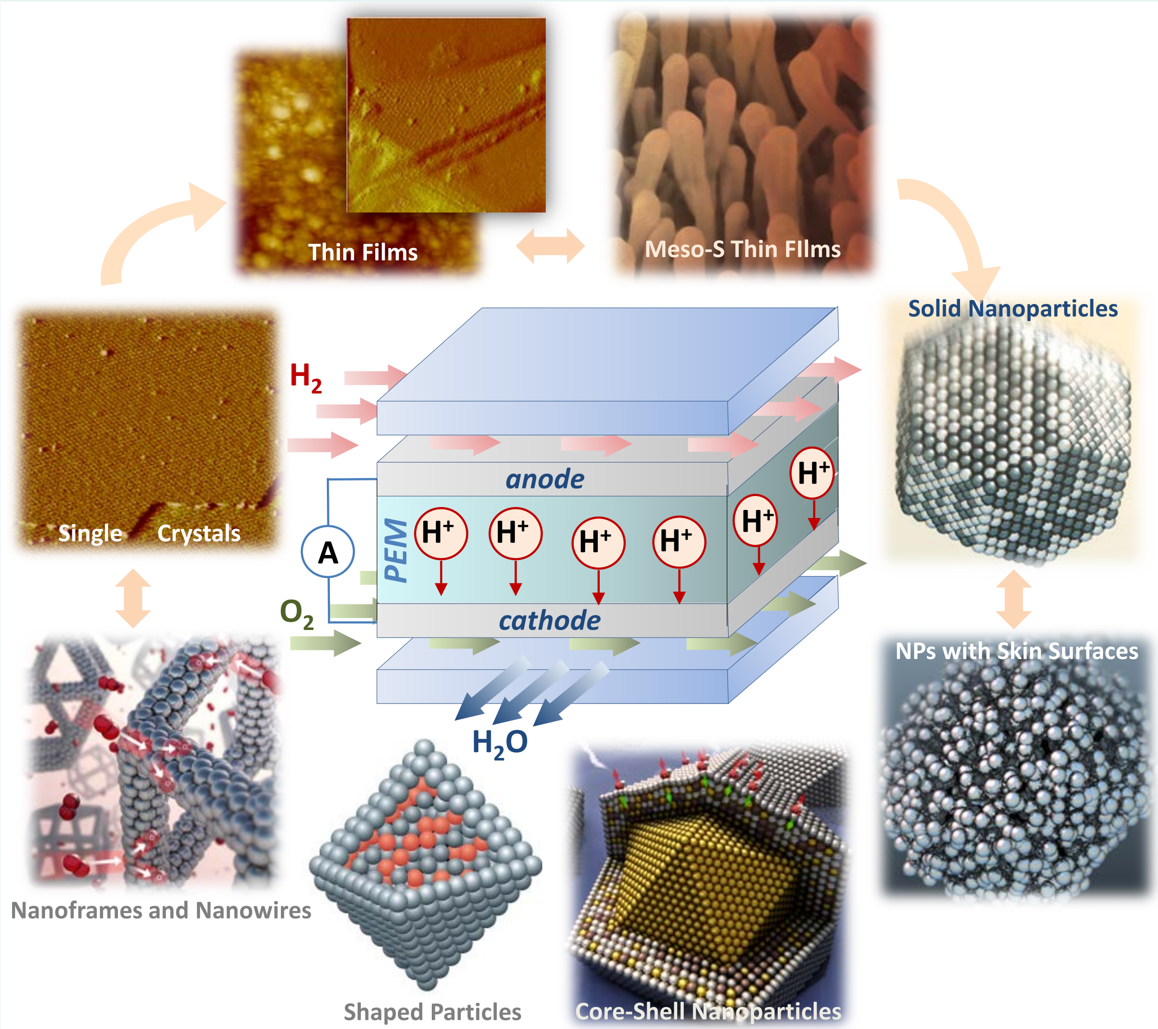
MEA test stand

5 - 25 cm²

RDE vs. MEA

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

Approach



Project Management

Table 1	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**

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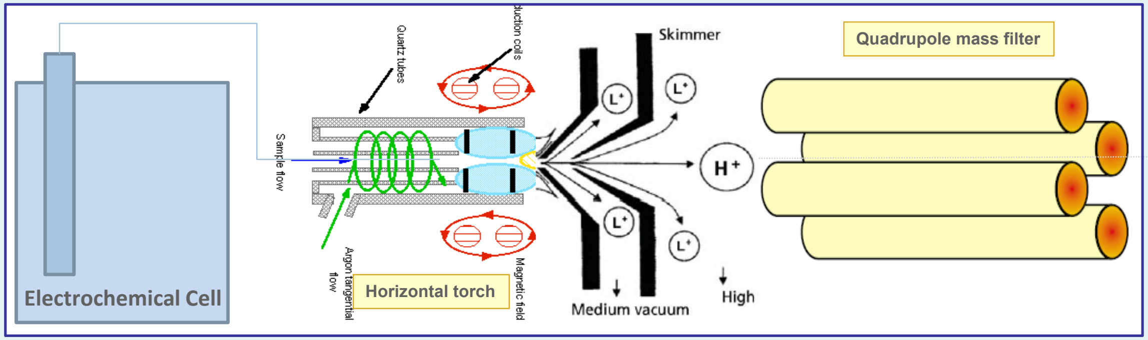
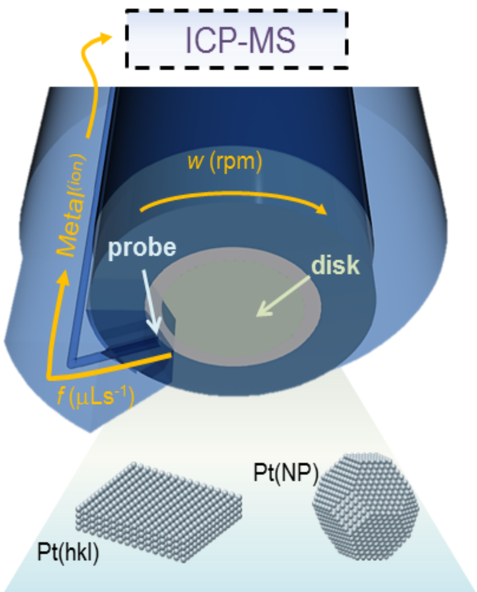
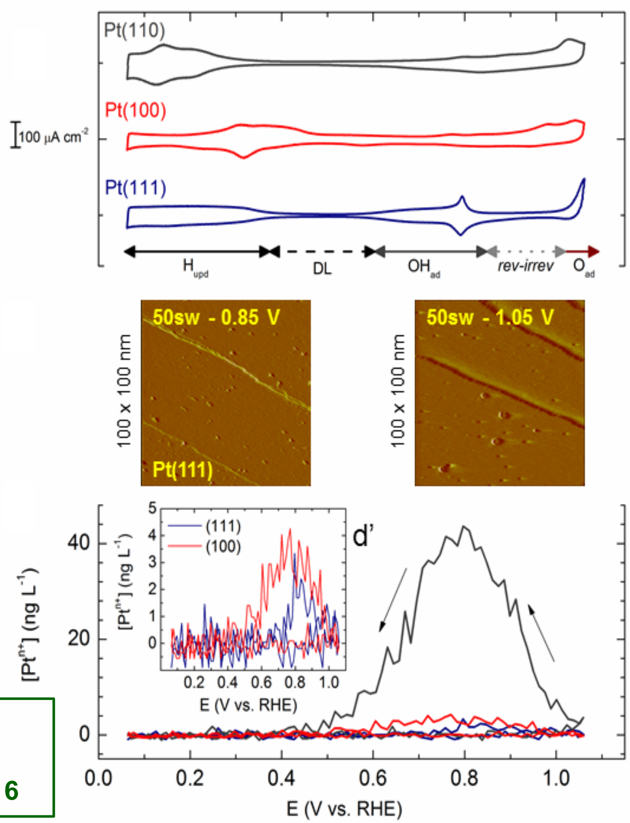
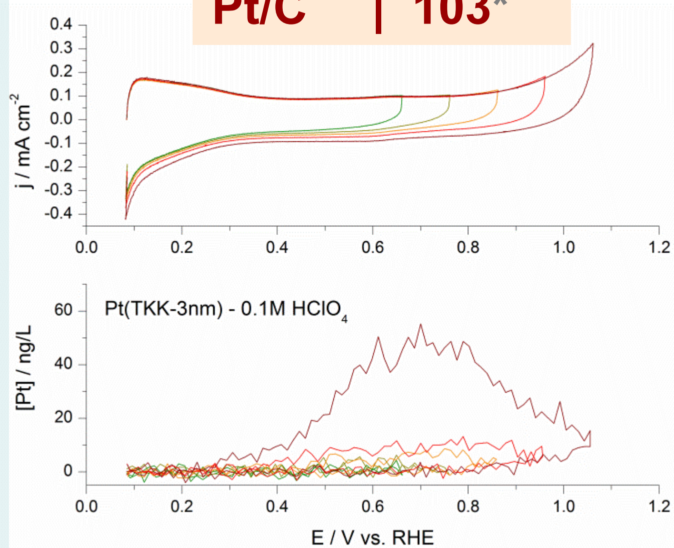


Total Pt loss over one potential cycle up to 1.05 V for distinct Pt surface morphologies, indicating the stability trend follows the coordination number of the surface sites

Pt Surface	Dissolved Pt per cycle [μML]
Pt(111)	2
Pt(100)	7
Pt(110)	83
Pt-poly	36
Pt/C	**103***

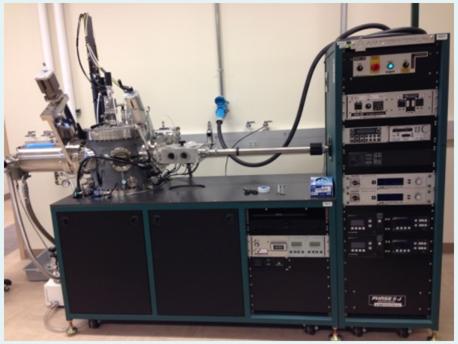




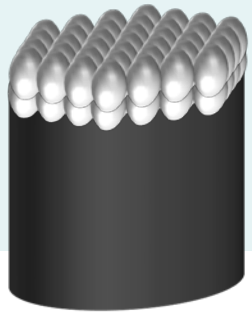


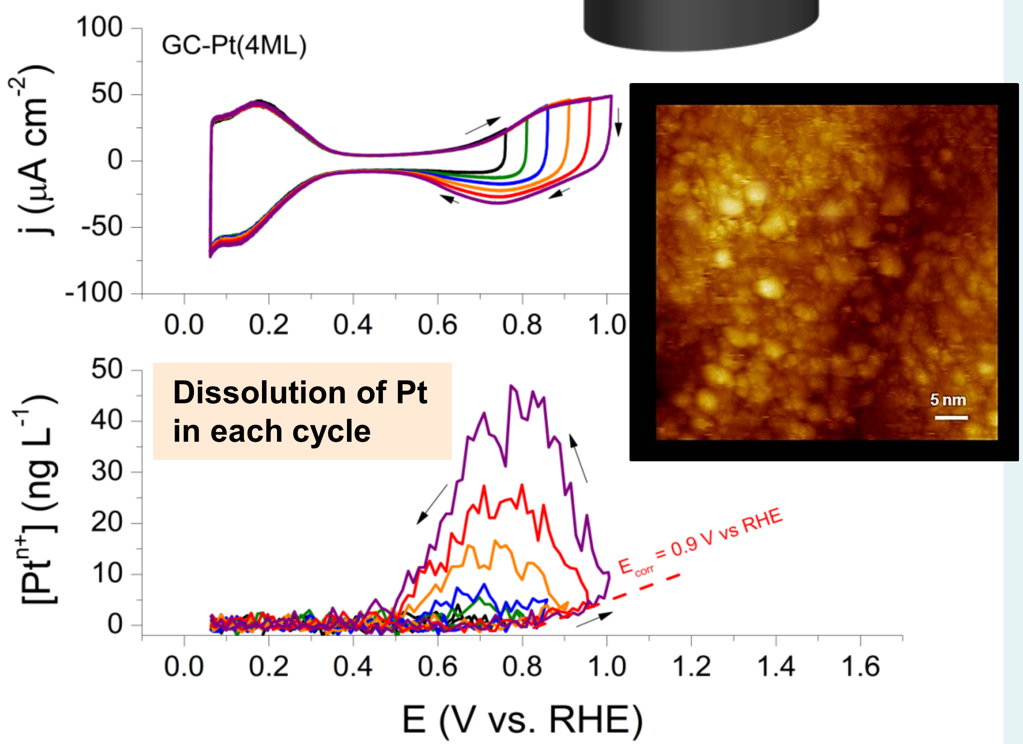
P. P. Lopes, D. Strmcnik, J. Connell,
V. R. Stamenkovic and N.M. Markovic
ACS Catalysis, 6 (4), 2536-2544, 2016

1º Accomplishments and Progress: *In-Situ EC-ICP-MS* Pt-Surface/Au Subsurface

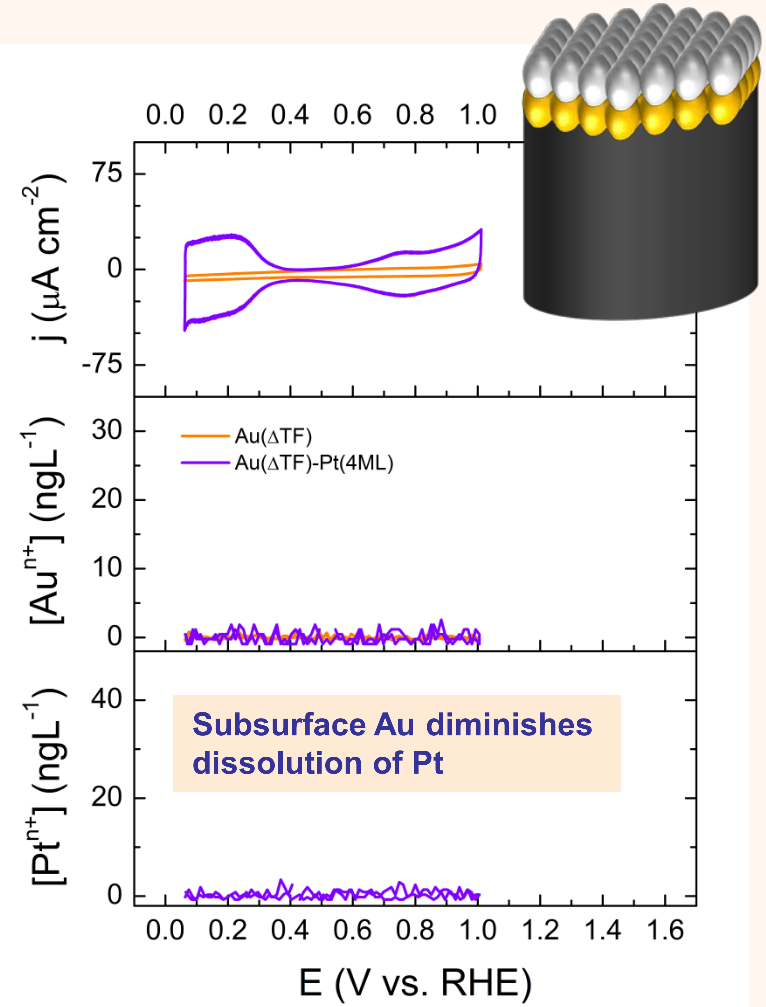


GC-Pt(4ML)

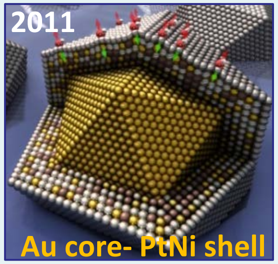


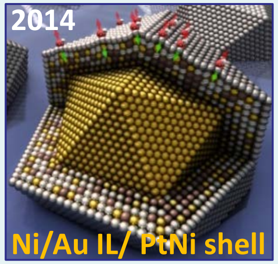


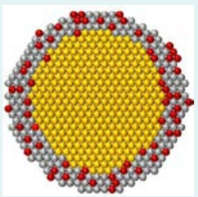
GC-Au-Pt(4ML)

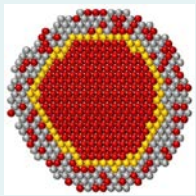


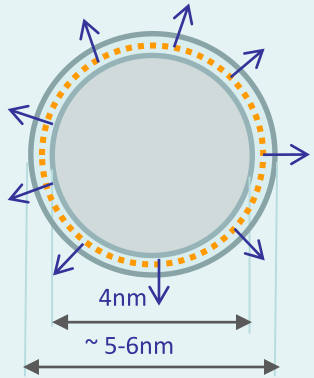
2º Accomplishments and Progress: *Catalysts Structures with Subsurface Au*



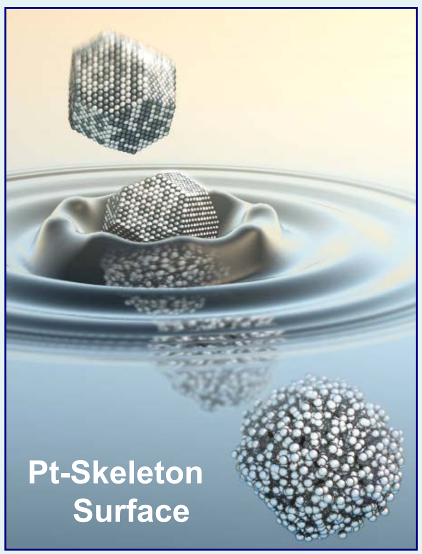


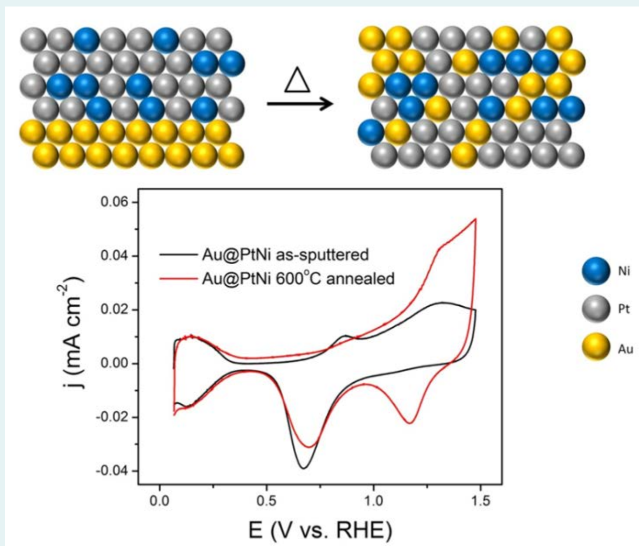




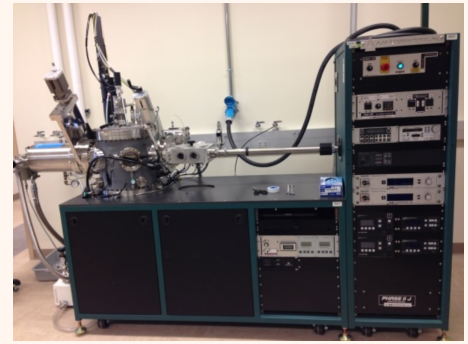


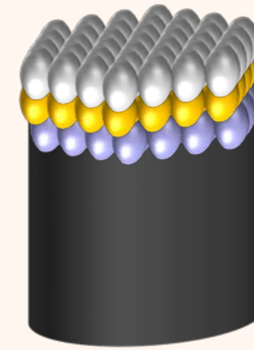
Subsurface Au does not alter catalytic properties of NPs

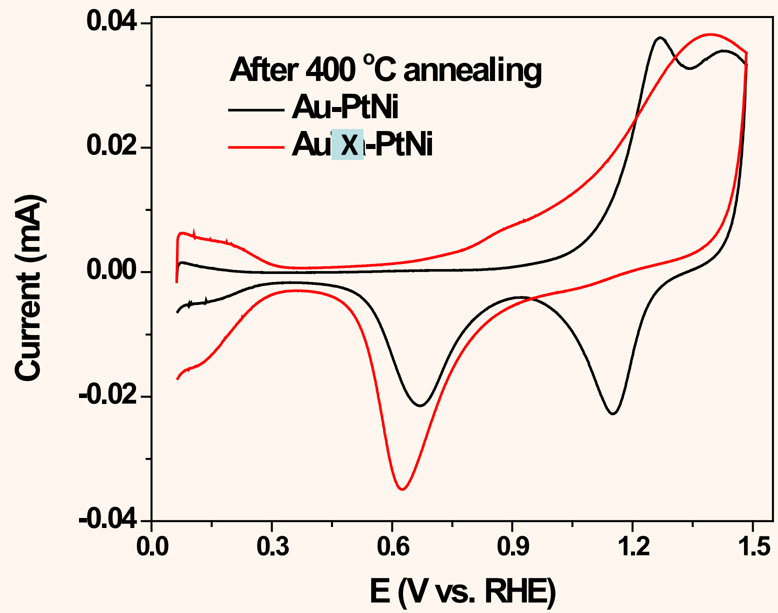




Existence of Au surface atoms lowers the number of Pt active sites for adsorption of O_2





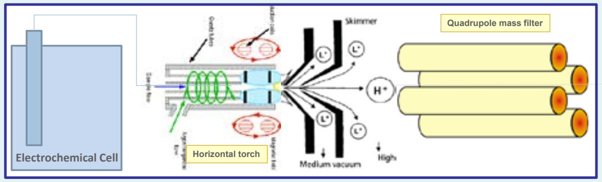


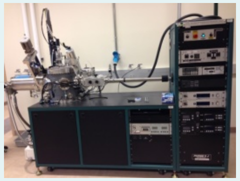
Addition of element in the core prevents segregation of Au over Pt after annealing

Annealing induces formation of Pt-Skin structure

Au remains in the subsurface

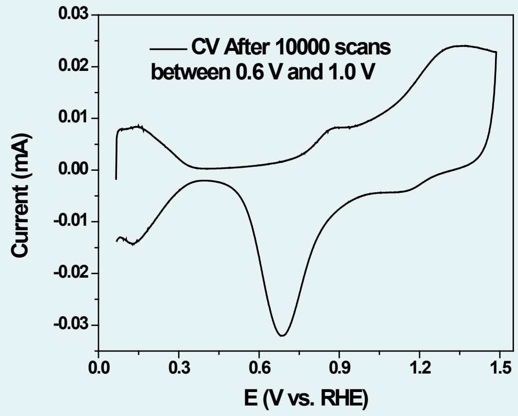
2º Accomplishments and Progress: *Catalysts Structures with Subsurface Au*

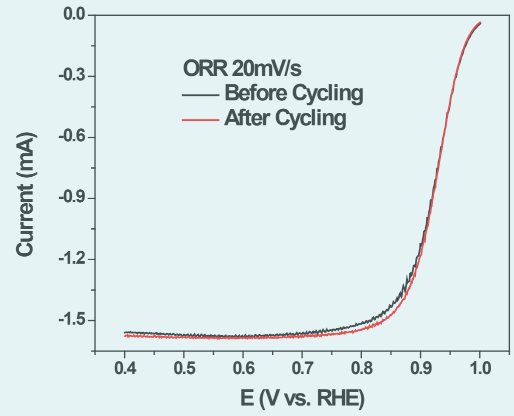


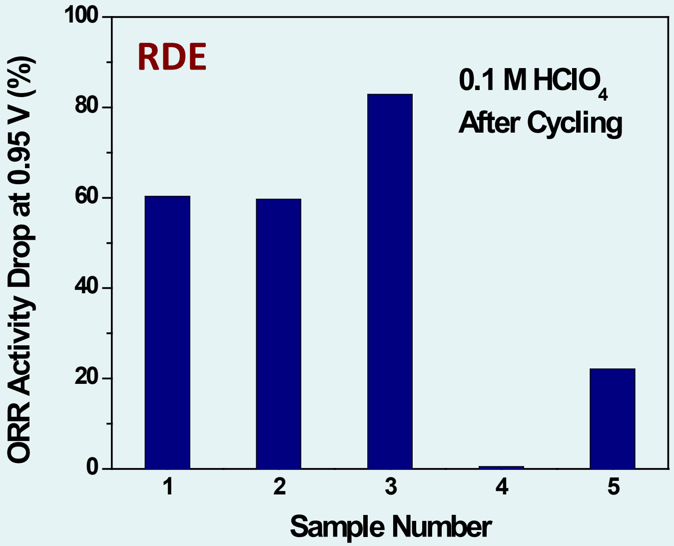


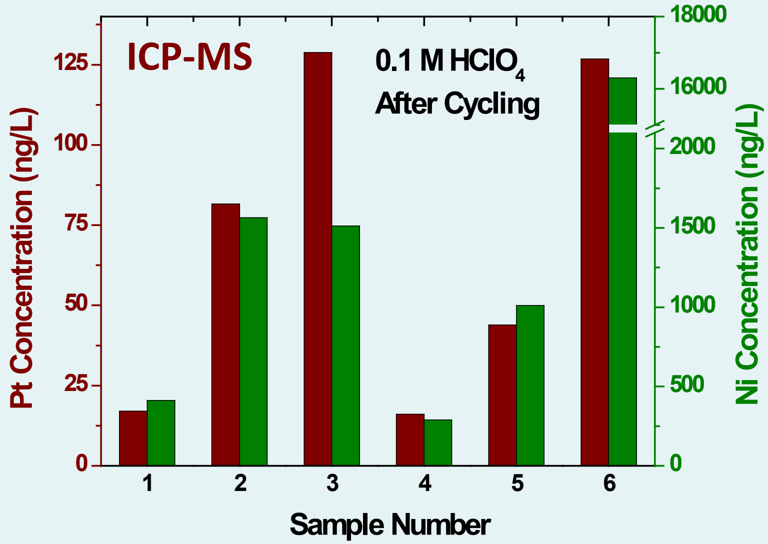
Au-X / NiPt-Skin Thin Film Structures

- Fine tuning of activity & durability
- Thickness of the PtNi shell
- Thickness/composition of Au-X subsurface
- Annealing temperature







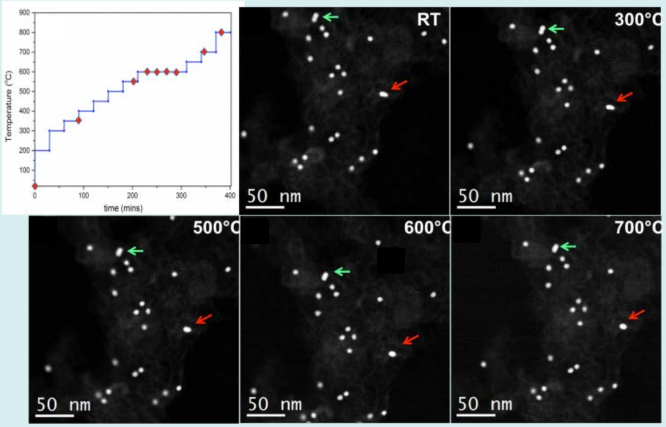


Sample 4 of AuX/NiPt-Skin after 10K cycles to OCP shows the best activity-stability at room temperature

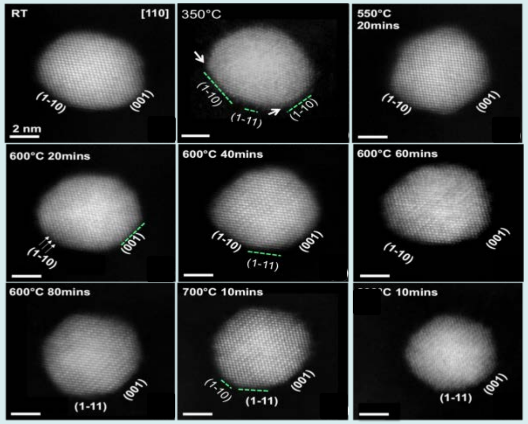
Input to nanoscale synthesis about the structure/compostiion of the core-shell catalyst

in collaboration with M. Chi and K.L. More, ORNL

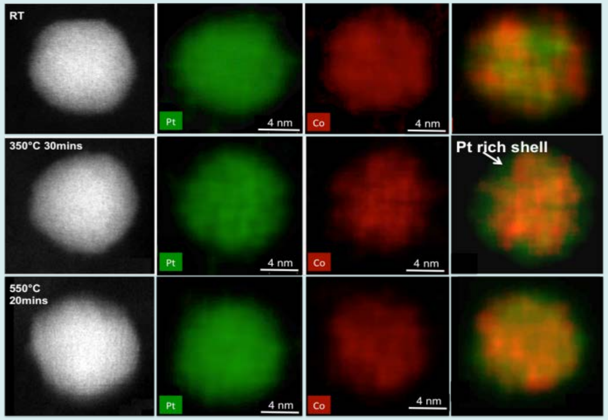
Annealing sequence of Pt_3Co NP

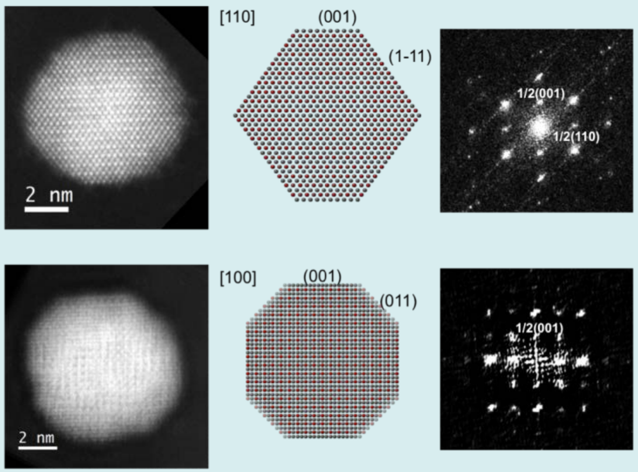


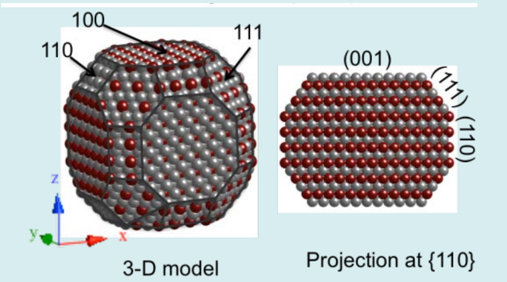
HAADF at different T and t(min)



HAADF and EDS elemental mapping







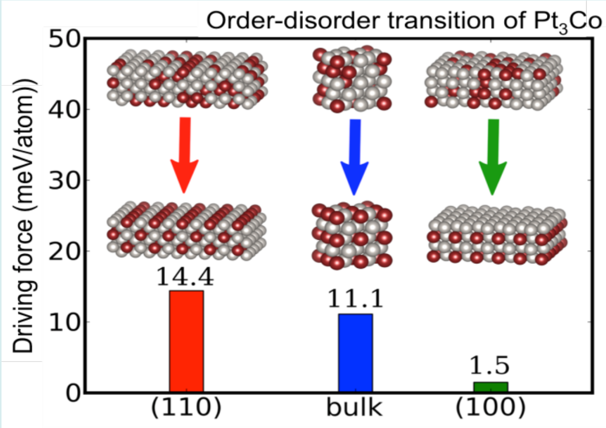
Dynamic of structural and chemical evolution at the atomic scale of Pt_3Co NPs during in-situ annealing
distinct behavior at critical stages:

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

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

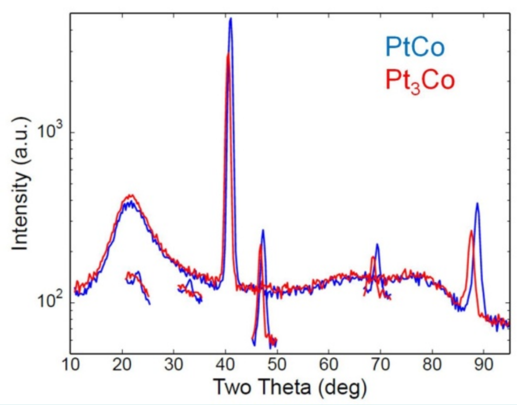
the nucleation of ordered domains;

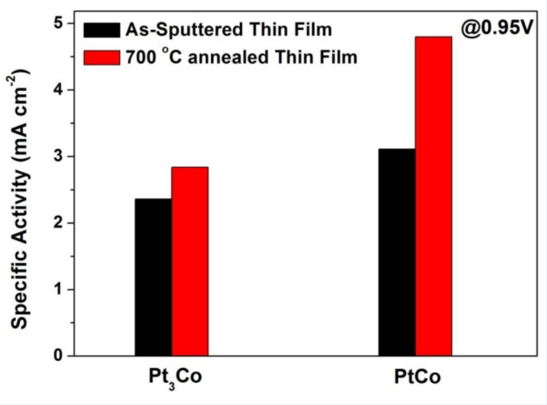
the establishment of an ordered $L1_2$ phase followed by pre-melting

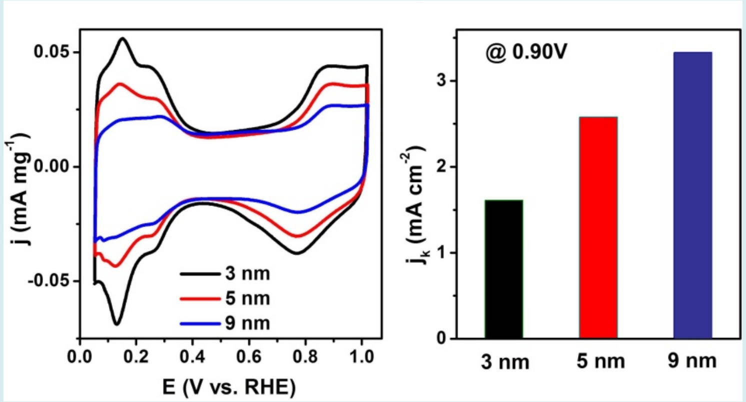


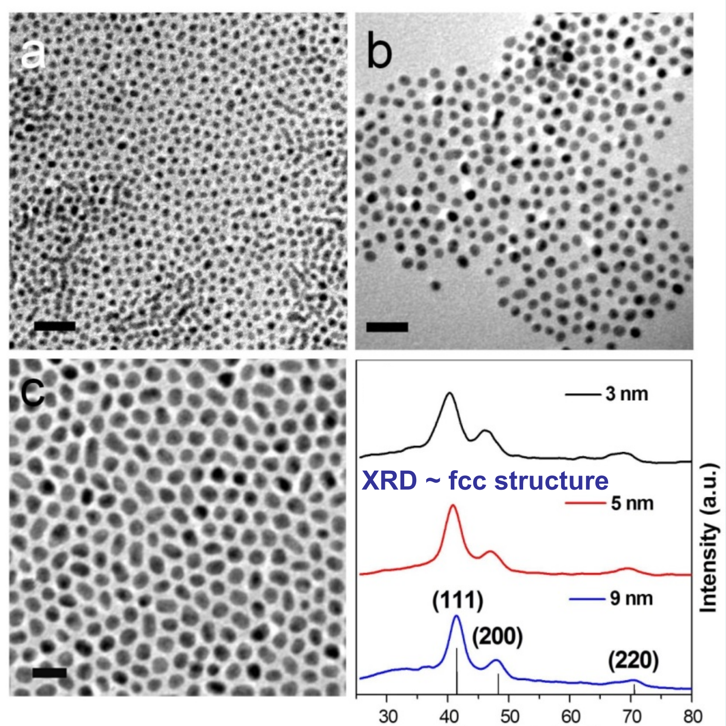
M. Chi, C. Wang, Y. Lei, G. Wang, K.L. More, A. Lupini, L.F. Allard, N.M. Markovic, and V.R. Stamenkovic
Nature Communications 6 (2015) *No.* 8925

3º Accomplishments and Progress: *PtCo Structures Towards Intermetallics*

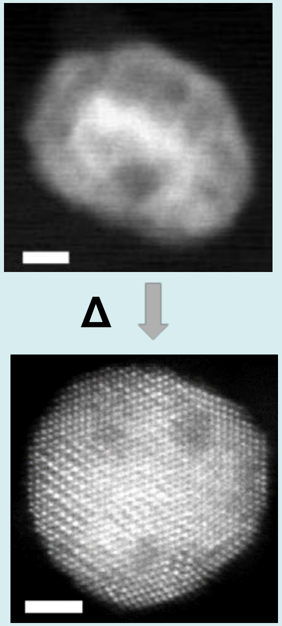


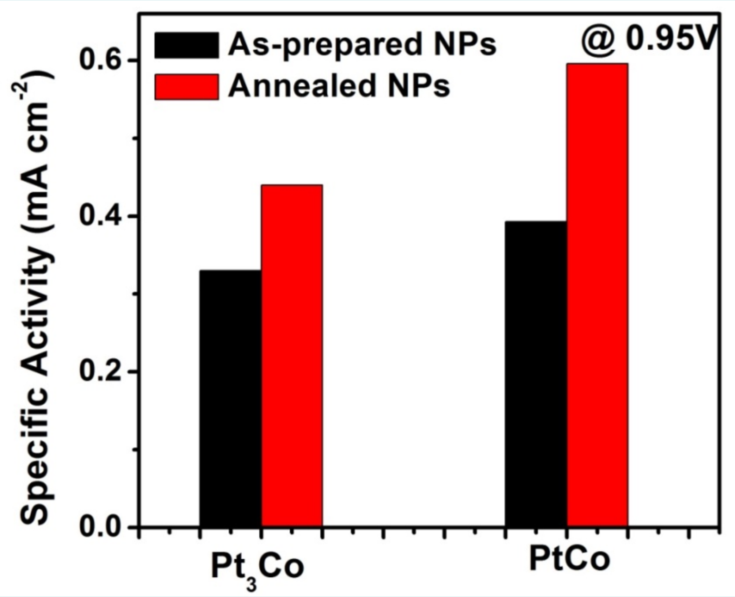






a-c) 3, 5, 9 nm PtCo NPs





It is expected that PtCo ($L1_0$) has even better performance than the intermetallic Pt_3Co ($L1_2$)* *Nat. Mat. 12, 81–87 (2013)*

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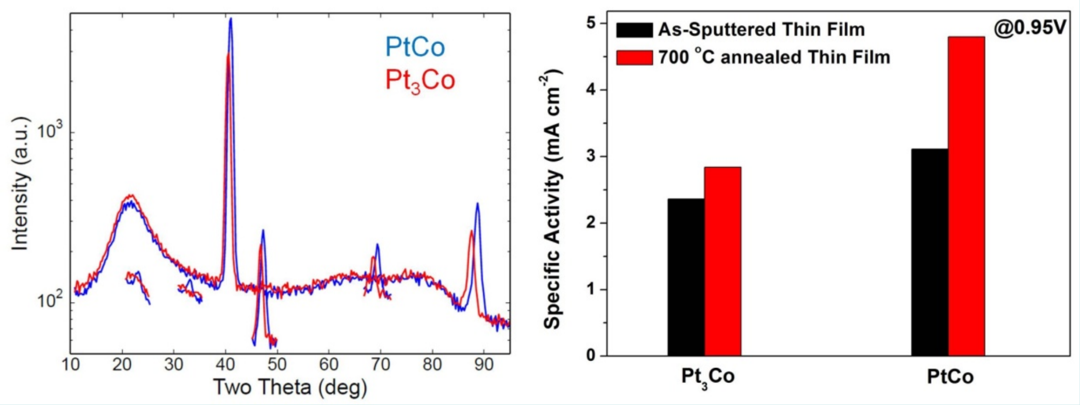

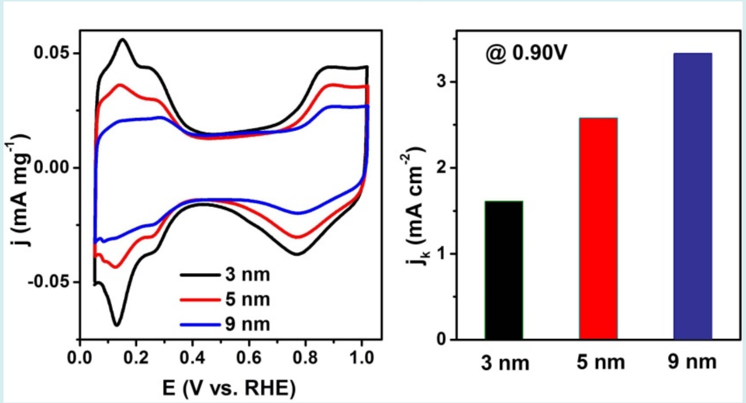

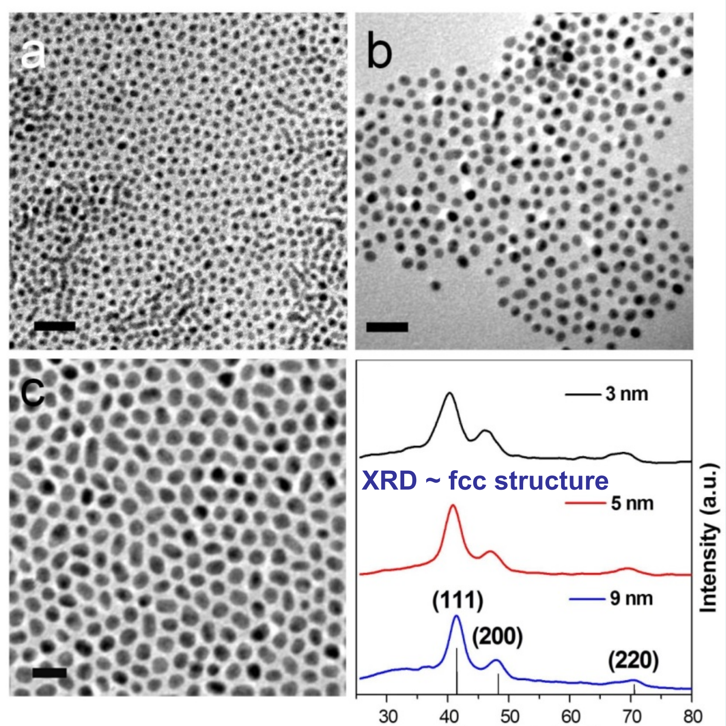

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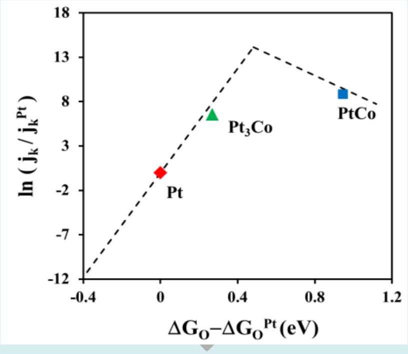

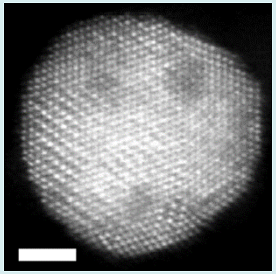

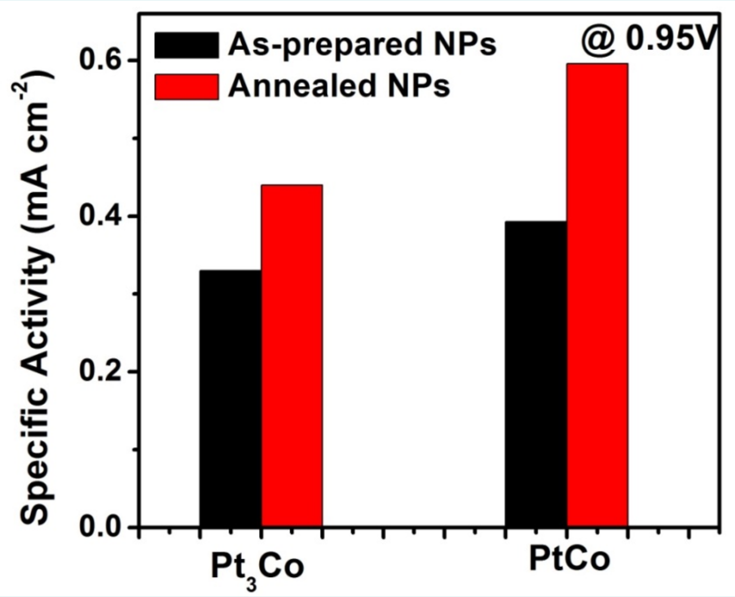

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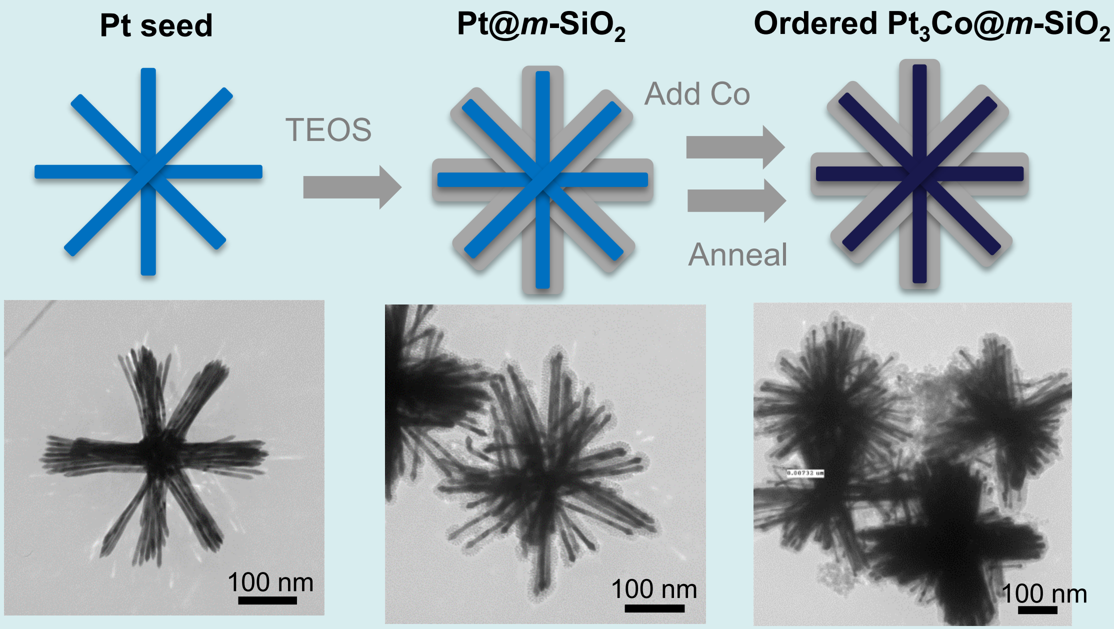
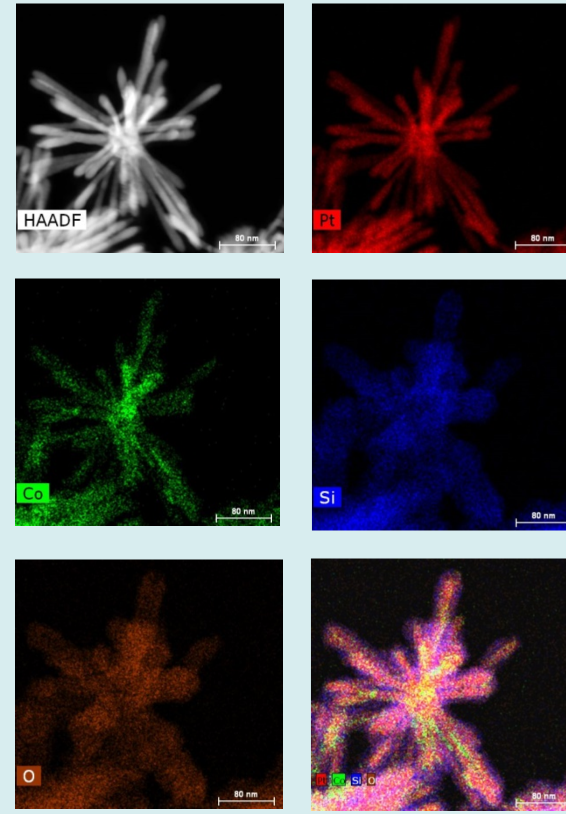
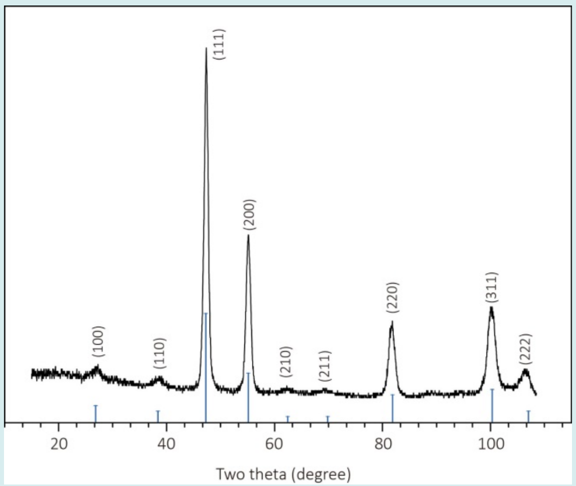
in collaboration with Peidong Yang, LBNL

3-D Intermetallic Nanostructures for Enhanced ORR Stability



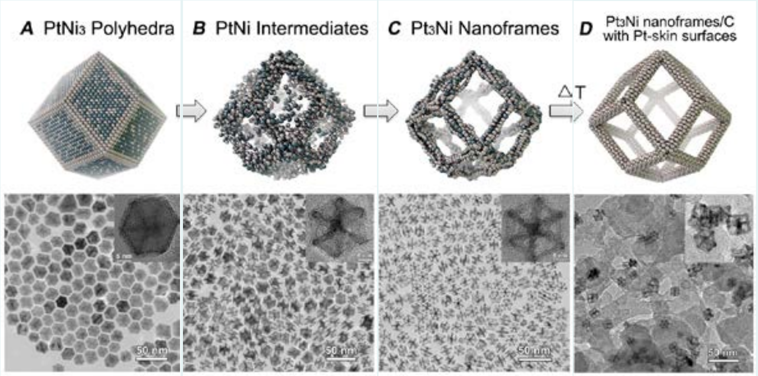


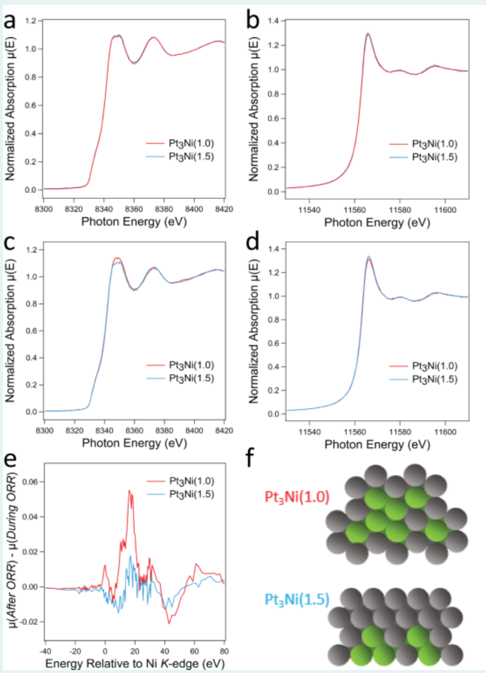


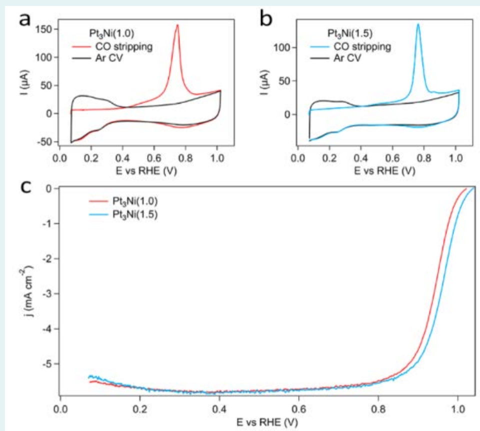
XRD: Converted to intermetallic Pt_3Co after annealing treatment

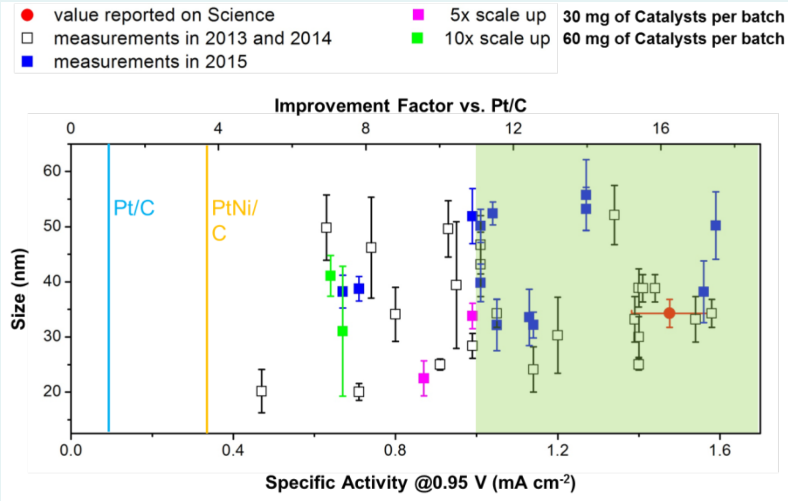
- **SiO_2 coating allows high T annealing w/o agglomeration**
- **High surface to volume ratio**
- **1-D branches protruding from the core**
- **Elongated highly crystalline surfaces with Pt-Skin topmost layer**
- **Tunable composition and structure, including intermetallics**

in collaboration with Peidong Yang, LBNL









$Pt_3Ni(1.0)$ = Q_{CO}/Q_{Hupd} = 1.0

$Pt_3Ni(1.5)$ = Q_{CO}/Q_{Hupd} = 1.5

ORR rate: $Pt_3Ni(1.0)$ < $Pt_3Ni(1.5)$

N. Becknell, Y. Kang, Chen Chen, J. Resasco, N. Kornienko, J. Guo, N.M. Markovic, G.A. Somorjai, V.R. Stamenkovic, P. Yang
JACS 137 (2015) 15817

In situ EXAFS:

$Pt_3Ni(1.0)$ has a larger extent of alloying vs. Pt3Ni(1.5), including surface Ni that becomes NiO

$Pt_3Ni(1.5)$ has significant segregation of Pt with smoother morphology and the thickness of at least two atomic layers

$Pt_3Ni(1.0)$ has a thinner, rougher Pt surface caused by insufficient segregation of Pt to the surface

$Pt_3Ni(1.5)$ exhibits extremely high ORR activity due to its significant segregation of Pt, forming of a Pt-skin

The activity of a given nanoframe sample is primarily pre-determined by the level of platinum surface enrichment

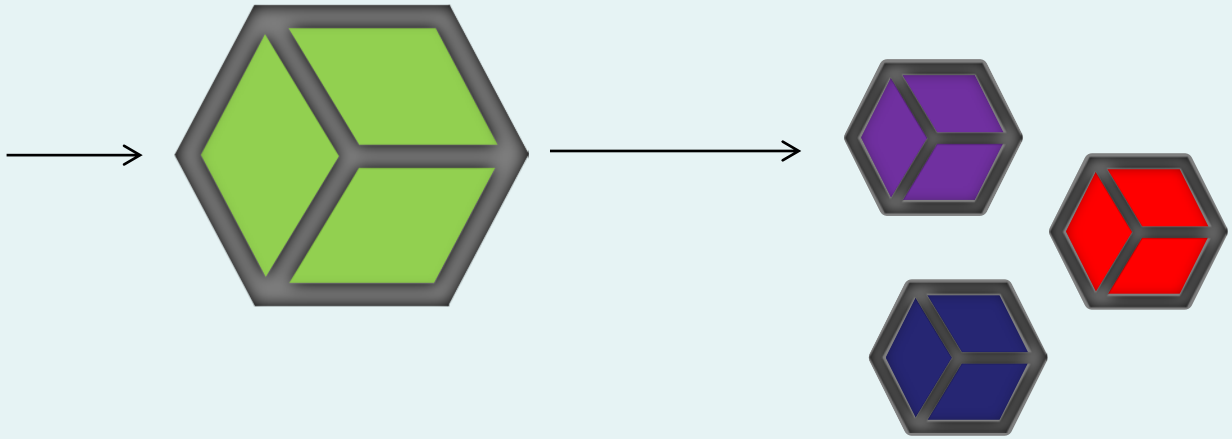
in collaboration with Peidong Yang, LBNL

Ternary Metal Nanoframes

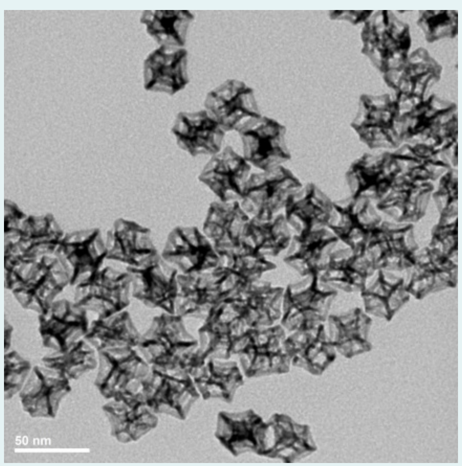
Metal precursors

Solid Pt-Ni dodecahedra

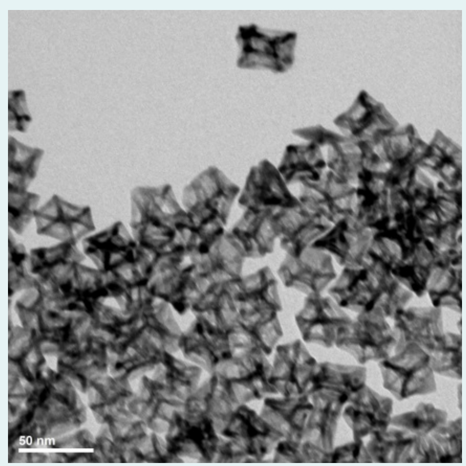
Composition tuning to Pt-Ni-Fe, Pt-Ni-Rh, Pt-Ni-Mo etc.



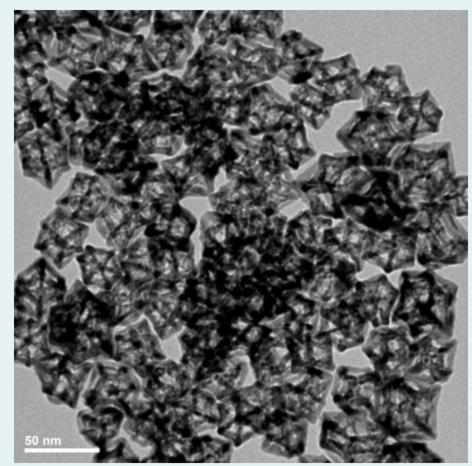
1% Fe



3% Fe

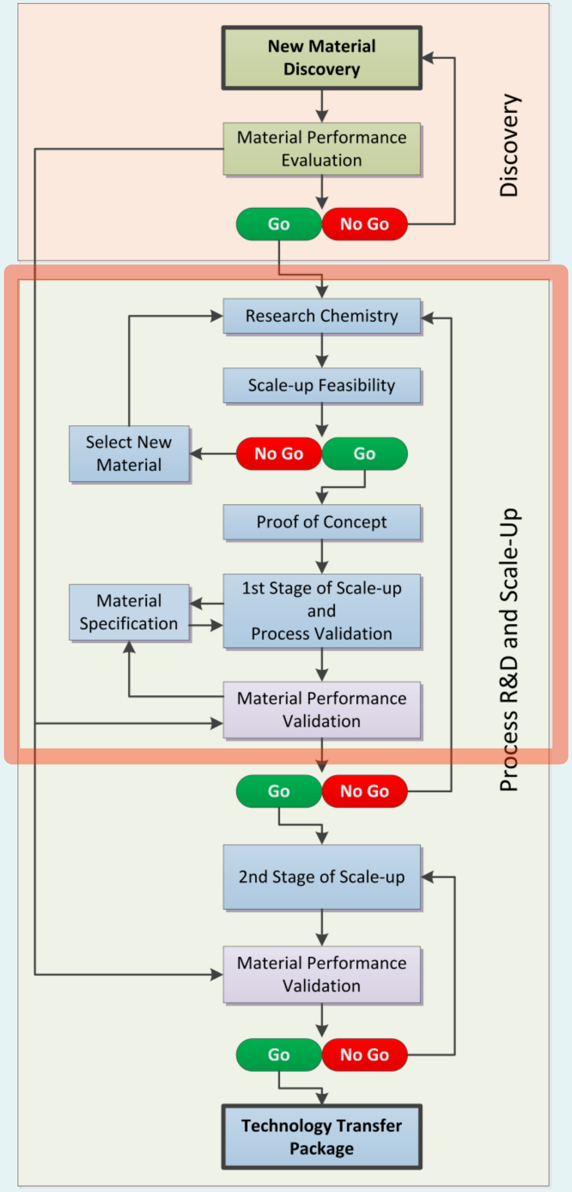


5% Fe



5º Accomplishments and Progress: *Process R&D and Scale Up*

in collaboration with Greg Krumdick, ANL -MERF

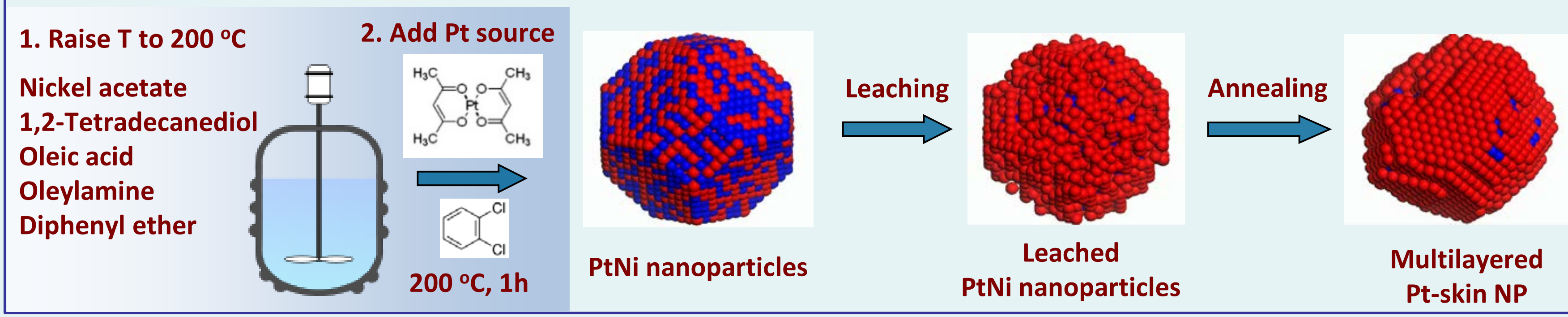


- **Argonne's Material Engineering Research Facility (MERF) was tasked with scaling up the new materials.**
- **The current process used in the discovery laboratory will be reviewed and scrutinized for scale up utility.**
- **MERF will conduct process R&D and develop scalable process for producing the material.**
- **The materials will be validated on each stage of scale up process and performance compared with the original sample.**
- **Detailed procedures for synthetizing, characterizing, and evaluating will be compiled into Technology Transfer Package.**
- **The materials will be available for both basic researches and industrial evaluators.**

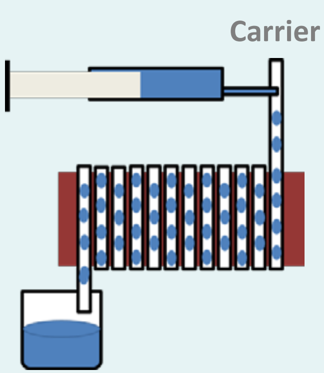
5º Accomplishments and Progress: *Process R&D and Scale Up*

in collaboration with Greg Krumdick, ANL -MERF

- Initial process R&D will focus on batch NP synthesis.
  - Investigate temperature and rate of addition on NP characteristic.
  - Nucleation rate vs. addition rate.
  - Improve safety of the process.
- Material selected for scale up is multilayered Pt-skin NP (Lab scale—0.1 g catalyst).
- 1^{st} stage of scale up—1 g catalyst.
- 2^{nd} stage of scale up—5 g catalyst.

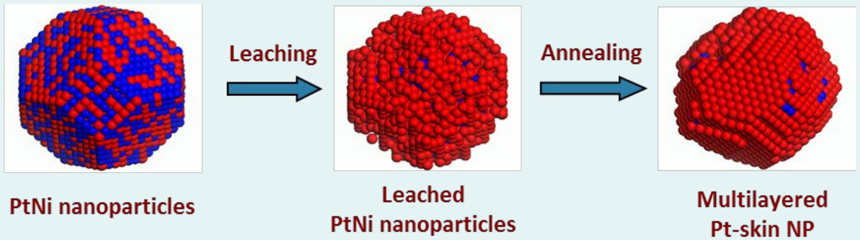


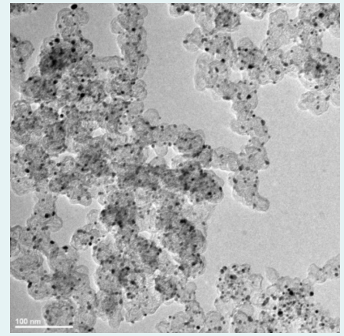
- Future target is to develop continuous process (flow reactor).



- Fast mass and heat transfer.
- Accurate control of reaction temperature and duration.
- Allow rapid optimization of reaction parameters.
- Low usage of reagents in the optimization process.
- Easy scalability by duplicating.
- Capability for online quality monitoring.

Pt_3Ni Nanoframes/C with Pt-skin surfaces

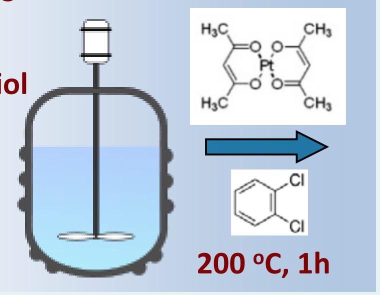




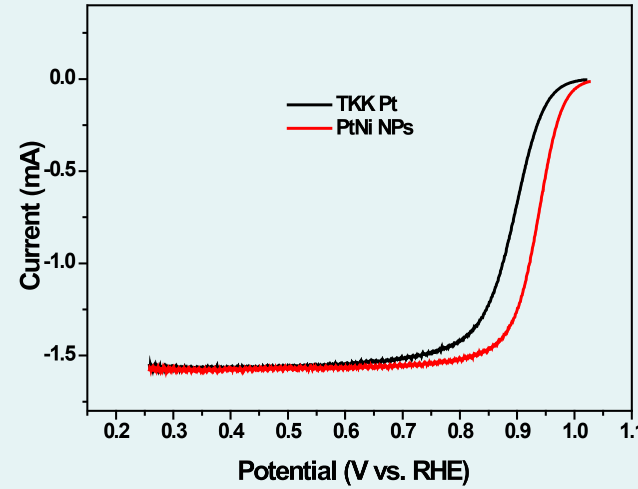
1. Raise T to 200 °C

Nickel acetate
1,2-Tetradecanediol
Oleic acid
Oleylamine
Diphenyl ether

2. Add Pt source



200 °C, 1h



Multiple Batches
200mg each

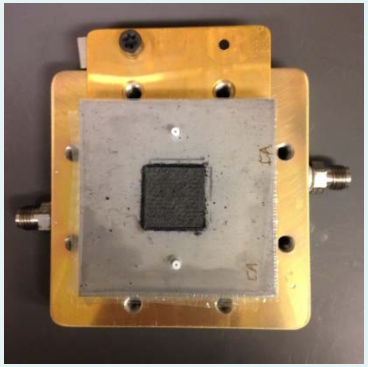
1 g of catalyst / 2 days
quality/performance matches small scale synthesis

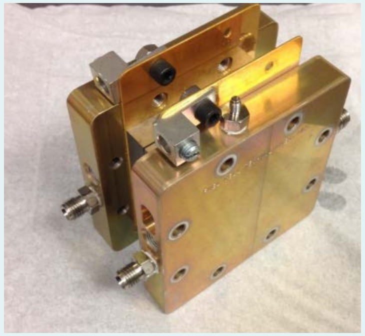
RDE: PtNi with multilayered Skin in >7 more active than Pt/C

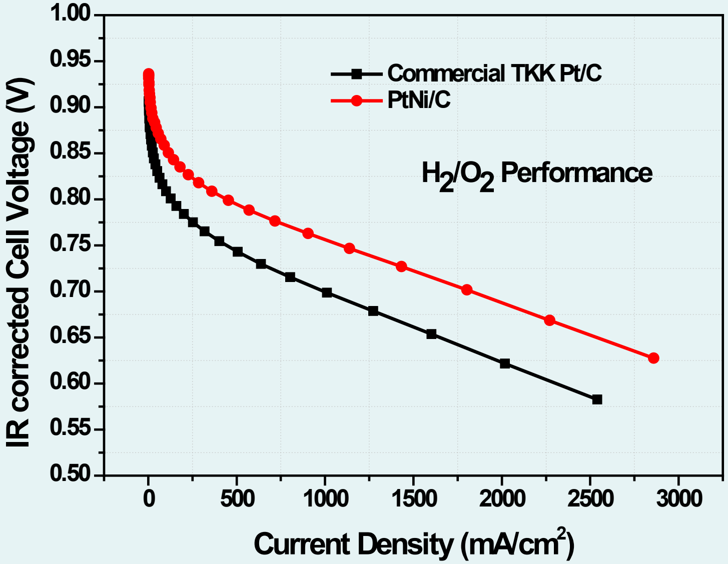
Performance	PtNi	TKK Pt
Specific Activity 0.9V/0.95V (mA/cm^2)	**5.30/0.68**	**0.78/0.11**
Mass Activity 0.9V/0.95V (A/mg)	**3.5/0.49**	**0.56/0.11**

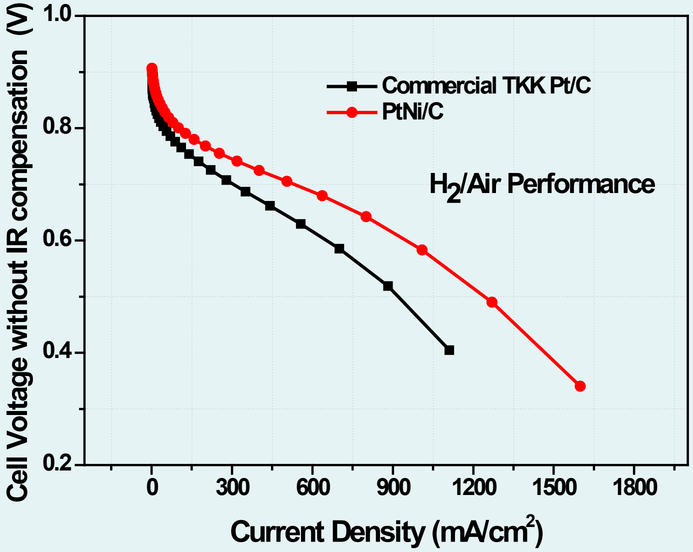
6º Accomplishments and Progress: *PtNi MEA Characterization*

in collaboration with Debbie Myers, ANL - CSE









Cathode Loading: 0.046 mg-Pt/cm²
I/C = 1, H_2/O_2 (or Air),
80°C, 150 kPa(abs), 100%RH

TKK 20 wt%Pt/C

PtNi 16.7 wt%Pt/C

	Units	PtNi	TKK Pt
Pt loading	mg_{PGM}/cm^2_{geo}	**0.045**	**0.045**
Mass Activity (H_2-O_2)	A/mg_{PGM} @ 0.9 $V_{iR\text{-}free}$	**0.60**	**0.27**
Specific Activity (H_2-O_2)	mA/cm^2_{PGM} @ 0.9 $V_{iR\text{-}free}$	**1.85**	**0.39**
MEA performance (H_2-Air)	mA/cm^2 @ 0.8 V	**101**	**47**
ECSA	m^2/g_{PGM}	**35.10**	**52.5**

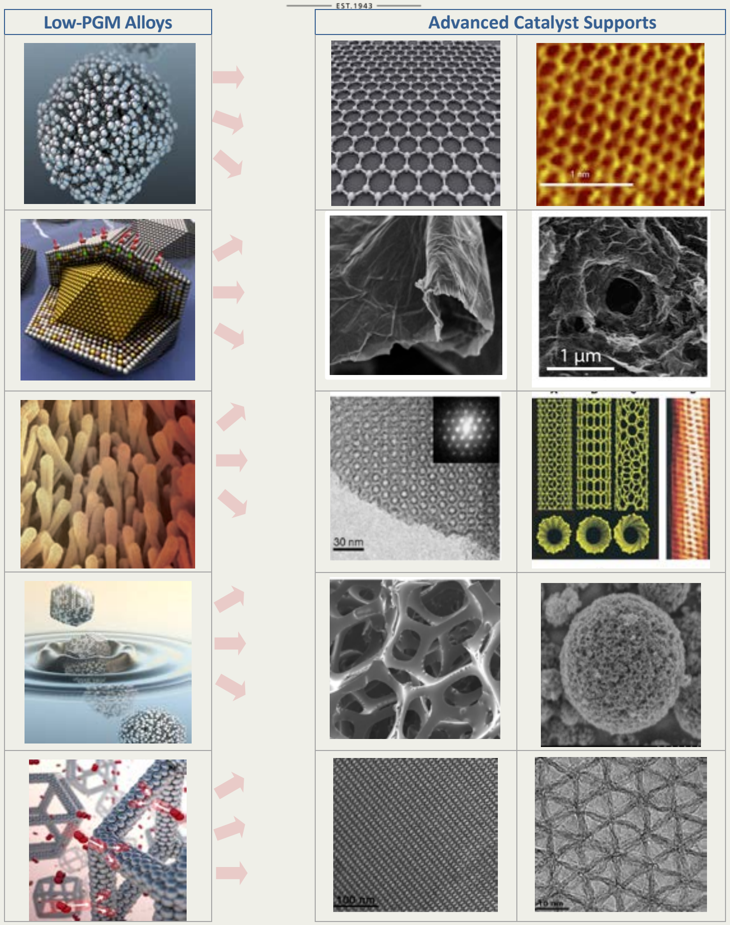
Collaborations

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

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

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

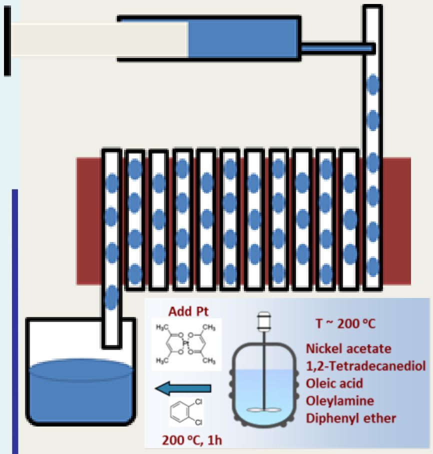
Los Alamos National Laboratory — **Sub:** catalyst supports



Low-PGM Alloy Catalysts

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

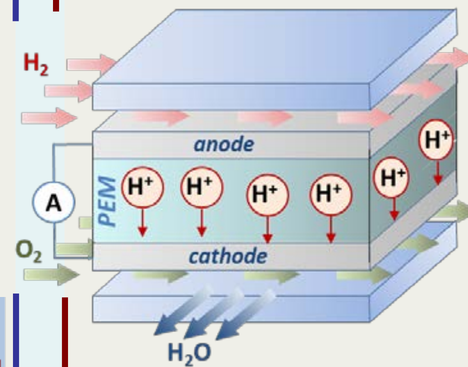
Berkeley Lab — **Sub:** process support



Catalysts Scale Up

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

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



MEA

OEMs

T2M

Remaining Challenges and Barriers

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

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

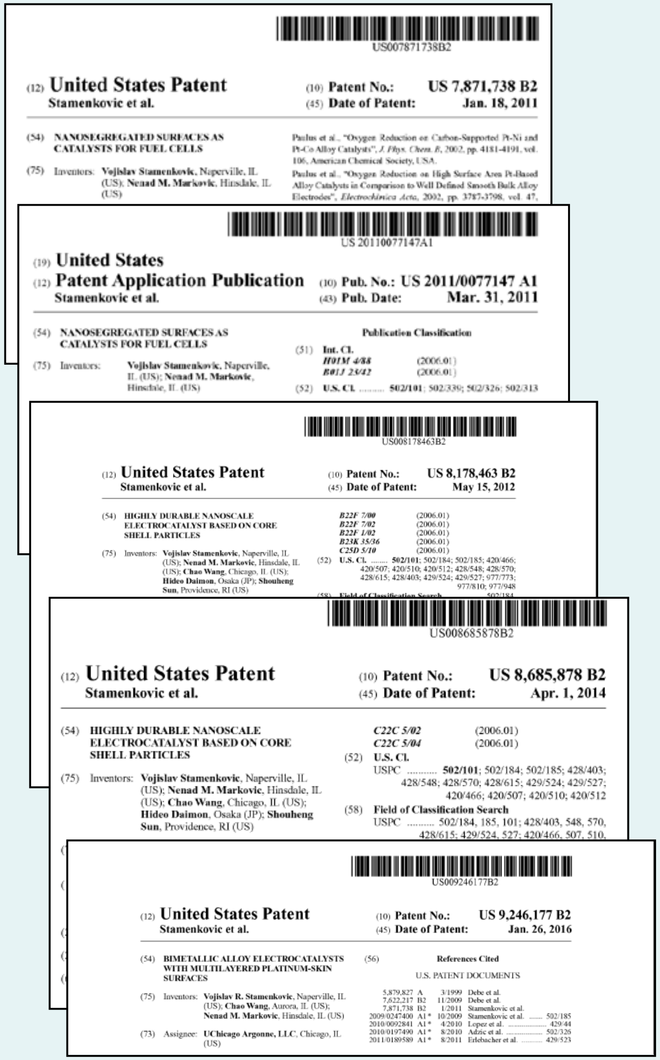
3) Performance (mass activity @ 0.9V 0.44 A/mg_{Pt})

- **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**

Proposed Future Work

- **Evaluation** of activity/durability and optimization of MEA protocols at ANL and LANL
- **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



US007871738B2

(12) United States Patent
Stamenkovic et al.

(10) Patent No.: US 7,871,738 B2
(45) Date of Patent: Jan. 18, 2011

(54) NANOSEGREGATED SURFACES AS CATALYSTS FOR FUEL CELLS

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

Paulus et al., "Oxygen Reduction on Carbon-Supported Pt-Ni and Pt-Co Alloy Catalysts", J. Phys. Chem. B, 2002, pp. 4181-4191, vol. 106, American Chemical Society, USA.
Paulus et al., "Oxygen Reduction on High Surface Area Pt-Based Alloy Catalysts in Comparison to Well Defined Smooth Bulk Alloy Electrodes", Electrochimica Acta, 2002, pp. 3787-3798, vol. 47,

US 20110077147A1

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

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

(54) NANOSEGREGATED SURFACES AS CATALYSTS FOR FUEL CELLS

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

Publication Classification
(51) Int. Cl.
H01M 4/88 (2006.01)
B01J 23/42 (2006.01)
(52) U.S. Cl. 502/101; 502/339; 502/326; 502/313

US008178463B2

(12) United States Patent
Stamenkovic et al.

(10) Patent No.: US 8,178,463 B2
(45) Date of Patent: May 15, 2012

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

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

B22F 7/00 (2006.01)
B22F 7/02 (2006.01)
B22F 1/02 (2006.01)
B23K 35/36 (2006.01)
C25D 5/10 (2006.01)
(52) U.S. Cl. 502/101; 502/184; 502/185; 420/466; 420/507; 420/510; 420/512; 428/548; 428/570; 428/615; 428/403; 429/524; 429/527; 977/773; 977/810; 977/948

US008685878B2

(12) United States Patent
Stamenkovic et al.

(10) Patent No.: US 8,685,878 B2
(45) Date of Patent: Apr. 1, 2014

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

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

C22C 5/02 (2006.01)
C22C 5/04 (2006.01)
(52) U.S. Cl.
USPC 502/101; 502/184; 502/185; 428/403; 428/548; 428/570; 428/615; 429/524; 429/527; 420/466; 420/507; 420/510; 420/512
(58) Field of Classification Search
USPC 502/184, 185, 101; 428/403, 548, 570, 428/615; 429/524, 527; 420/466, 507, 510,

US009246177B2

(12) United States Patent
Stamenkovic et al.

(10) Patent No.: US 9,246,177 B2
(45) Date of Patent: Jan. 26, 2016

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

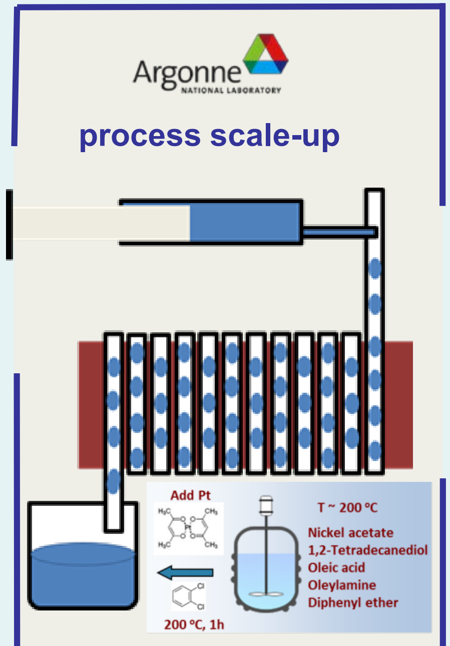
(75) Inventors: Vojislav R. Stamenkovic, Naperville, IL (US); Chao Wang, Aurora, IL (US); Nenad M. Markovic, Hinsdale, IL (US)

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

(56) References Cited
U.S. PATENT DOCUMENTS

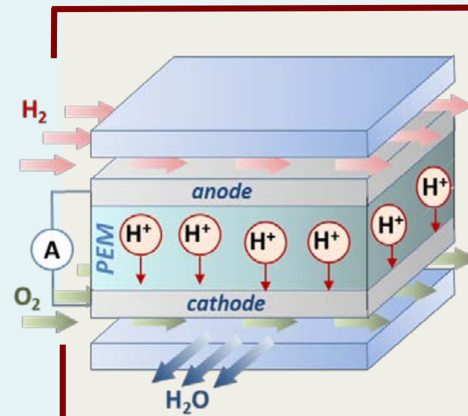
- Constant build up of IP portfolio
  5 issued patents, 4 pending

T2M



Catalysts Scale Up

Auto OEMs



MEA

Auto OEMs in FY16

Four OEM visits
3 NDA signed

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 three new labs since 10/2015: EC-ICP/MS, MEA and Scale-Up process Lab
- Quantified durability, atom-by atom on different Pt surfaces
- Surfaces with highly corrugated morphology are less stable (Pt-Skeleton)
- Addition of subsurface Au diminishes Pt dissolution
- Novel Au core structures allow annealing of Pt-alloy shell w/o segregation Au while Pt-skin is formed
- In-situ annealing of Pt-alloy NP reveal transition from disordered alloy, Pt overlayer (Pt-Skin) to intermetallics
- Novel intermetallic structures with promising electrochemical properties have been synthesized
- In-situ EXAFS revealed the real surface structure of highly active PtNi nanoframe catalysts
- PtNi with multilayered Pt-Skin exceeded DOE 2020 Technical Target for mass activity and durability in MEA
- One patent issued in 2016, 5 articles published and 4 presentations at conferences

Collaborations

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

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)

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

Publications and Presentations FY16

5 Publications
4 Presentations
1 issued US patent
3 patent applications