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2015 DOE Hydrogen and Fuel Cells Program Review

Nanosegregated Cathode Catalysts with Ultra-Low Platinum Loading

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Argonne National Laboratory

Project ID# FC008

U.S. Department of Energy

UChicago Argonne LLC

Office of Science U.S. DEPARTMENT OF ENERGY

A U.S. Department of Energy laboratory managed by UChicago Argonne, LLC

Overview

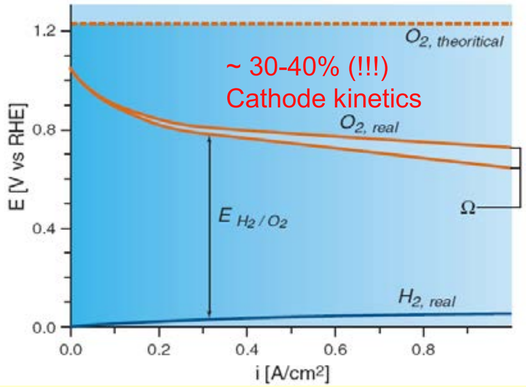
Timeline

- Project start: 9/2009
- Project end: 9/2015

Budget

- Total Project funding $ 5.1M
- Funding for FY14: $ 764K
- Planned FY15 DOE Funding: $764K

Barriers



1) Durability of fuel cell stack

2) Cost (catalyst, membrane, gdl)

3) Performance (losses and activity)

Partners:

- **Oak Ridge National Laboratory** – Karren More
- **Argonne National Laboratory** – Debbie Myers
- **Los Alamos National Laboratory** – Rod Borup

Project Lead:

- **Argonne National Laboratory**

Relevance

Objectives **The main focus of ongoing DOE Hydrogen & Fuel Cell Program is development of highly-efficient and durable multimetallic PtMN (M, N = Co, Ni, Fe, V, T)** ***nanosegregated catalysts*** **for the oxygen reduction reaction** ***with ultra low-Pt content***

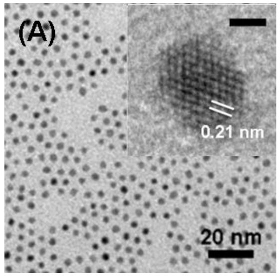
DOE Technical Targets

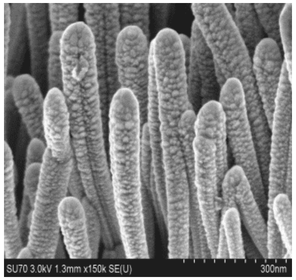
- Specific activity @0.9$V_{iR\text{-free}}$: 720 $\mu A/cm^2$
- Mass activity @0.9V: 0.44 A/mg_{Pt}
- Electrochemical area loss: < 40%
- Catalyst support loss: < 30%
- PGM Total content: 0.2 g/kW
- PGM Total loading: 0.2 $mg/cm^2_{electrode}$
- Cost*: $ 30/kW_e
- Durability w/cycling (80^{o}C): 5000 hrs

*based on Pt cost of $450/troy ounce

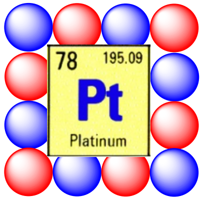
ANL Technical Targets

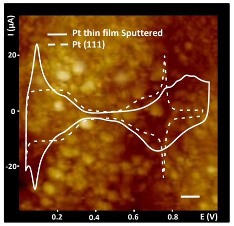
- Specific activity @ 0.9$V_{iR\text{-free}}$
  2015 DOE target x 3
- Mass activity @ 0.9$V_{iR\text{-free}}$
  2015 DOE target x 3
- Electrochemical area loss
  2015 DOE target
- PGM Total content
  < 0.1g/kW

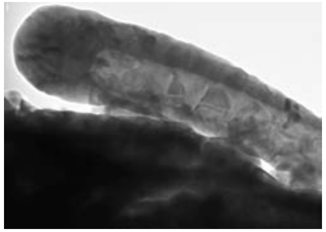


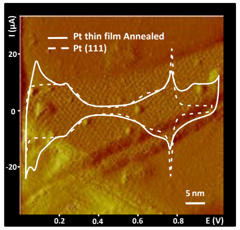


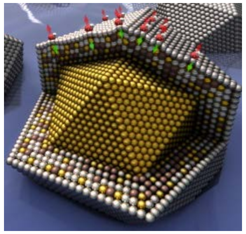
Approach







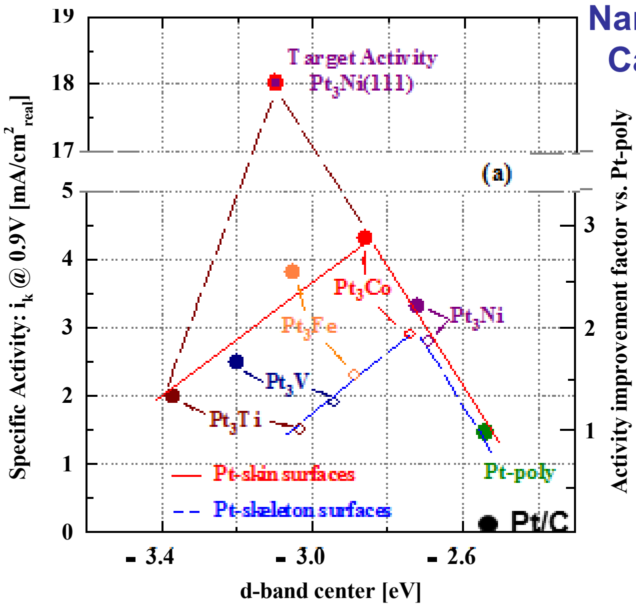




EXTENDED Multi-M SURFACES | **THIN METAL FILMS / MODEL NANOPARTICLES** | **NANOPARTICLES**

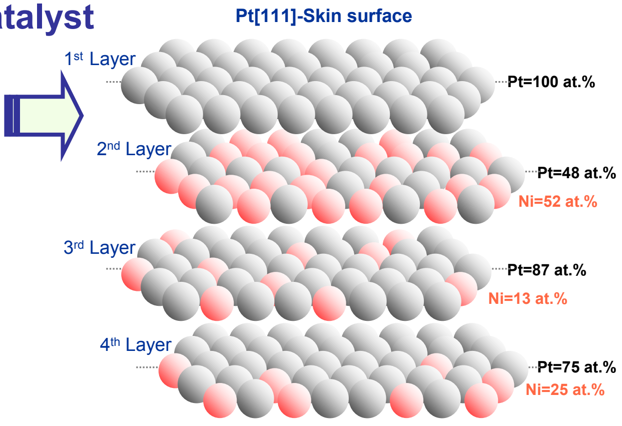
Materials-by-design approach - by ANL to design, characterize, understand, synthesize/fabricate, test and develope advanced nanosegregated multi-metallic nanoparticles and nanostructured thin metal films

Well-Defined Systems



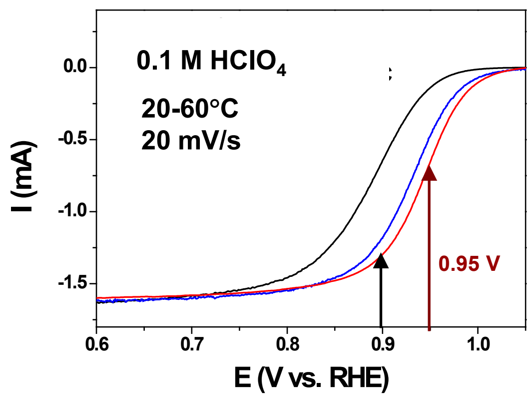
Advanced Nanoscale Catalyst

Nanosegregated Profile



<u>$Pt_3Ni(111)$-Skin</u> ~100 times more active than the state-of-the-art Pt/C catalysts

Intrinsic Activity



RDE:
- ORR activity measured at 0.95V
- iR corrected currents
- Measurements without ionomer

- 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 / Milestone

(Go-No Go Decision Met)

Milestone 1. Fundamental understanding (FY09-13) (Accomplished)

1.1 Resolved electronic/atomic structure and segregation profile (100%)

1.2 Confirmed reaction mechanism of the ORR (100%)

1.3 Improved specific and mass activity (95%)

Milestone 2. Synthesis and characterization (FY10-14)

2.1 Physical methods: TM films (5-10 layers), nanoparticles (5-300 nm) (95%)

2.2 Established chemical methods: colloidal and impregnation synthesis (95%)

2.3 Characterization: Ex-situ (UHV, TEM) and in-situ (EXAFS, EC) (100%)

2.4 Theoretical modeling (DFT, MC) methods (95%)

Milestone 3. Fabrication and testing (FY11-14)

3.1 New PtM_1M_2 catalysts with higher activity and improved durability (95%)

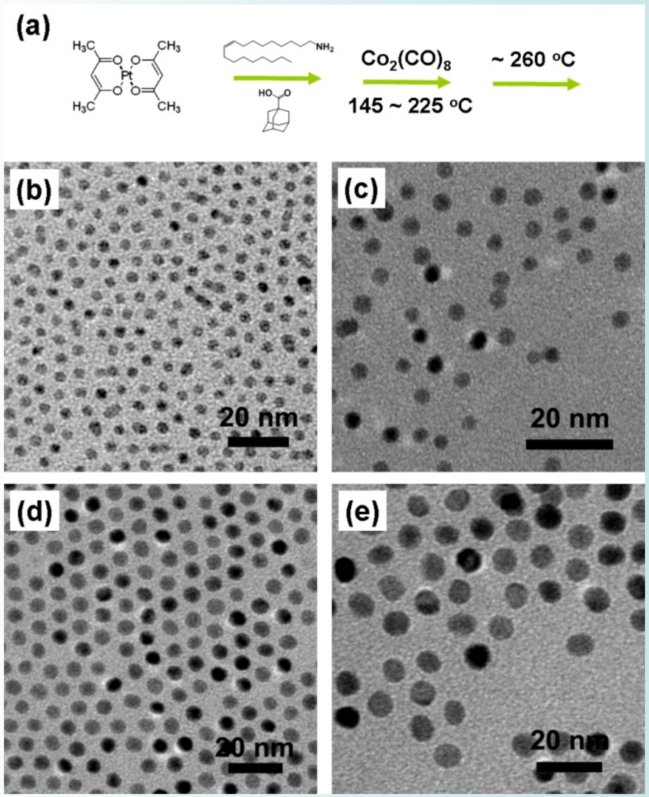
3.2 Carbon support vs. nanostructured thin film catalysts (95%)

3.3 MEA testing (50 cm^2) of the optimized catalysts (85%)

3.4 Scale up of the catalyst fabrication in lab environment (80%)

Technical Accomplishments FY09 -14: *Pt-alloy Nanocatalysts*

Colloidal solvo - thermal approach has been developed for monodispersed PtMN NPs with **controlled size and composition**



Efficient surfactant removal method does not change the catalyst properties

1° Particle size effect applies to Pt-bimetallic NPs

Specific Activity increases with particle size: 3 < 4.5 < 6 < 9nm

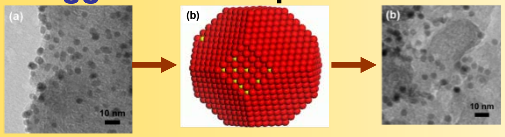
Mass Activity decreases with particle size

Optimal size particle size ~5nm

J. Phys. Chem. C., 113 (2009) 19365

2° Temperature induced segregation in Pt-bimetallic NPs

Agglomeration prevented



Optimized annealing temperature 400-500°C

Phys.Chem.Chem.Phys., 12 (2010) 6933

3° Surface chemistry of homogeneous Pt-bimetallic NPs

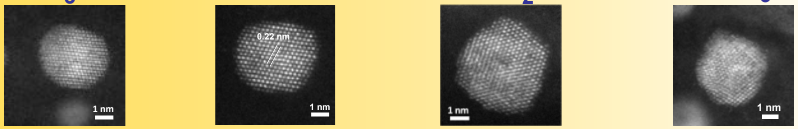
$Pt_xM_{(1-x)}$ NPs

Dissolution of non Pt surface atoms leads to **Pt-skeleton** formation

Adv. Funct. Mat., 21 (2011) 147

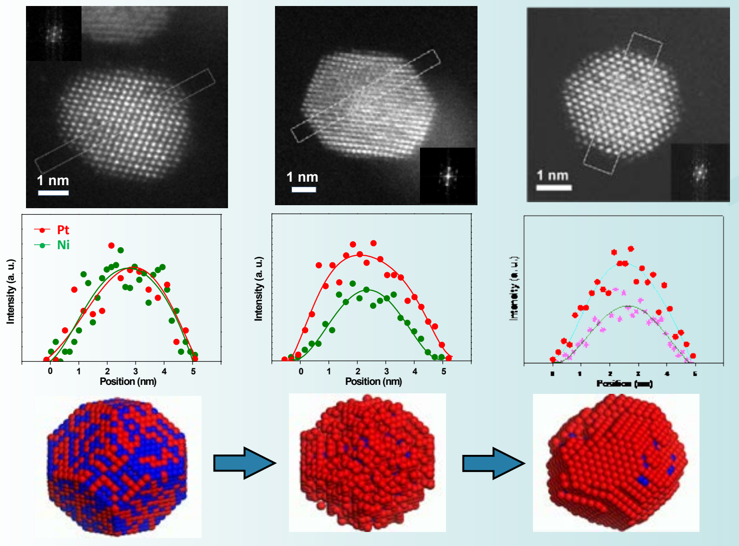
4° Composition effect in Pt-bimetallic NPs

Pt_3M | PtM | PtM_2 | PtM_3



Optimal composition of Pt-bimetallic NPs is PtM

Technical Accomplishments FY09-14: *Pt-alloy Nanocatalysts*

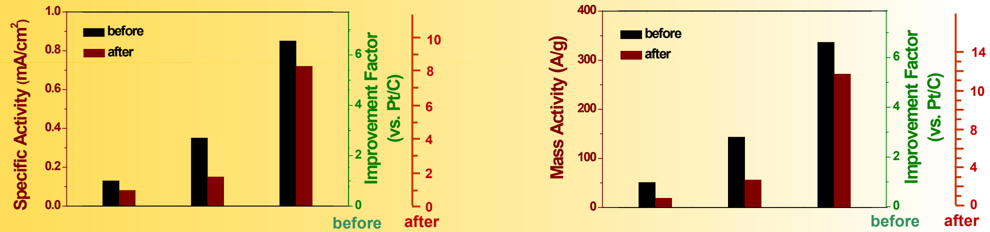


5° Pt-bimetallic catalysts with mutilayered Pt-skin surfaces

Synthesized PtNi NPs have homogeneous distribution of Pt, Ni

3-4ML of Pt-skeleton surfaces for PtNi acid leached NPs

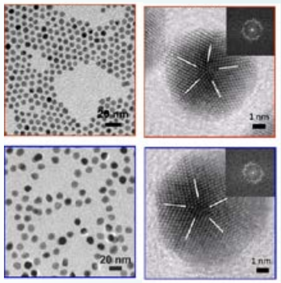
Multilayered Pt-skin surfaces confirmed for PtNi annealed NPs



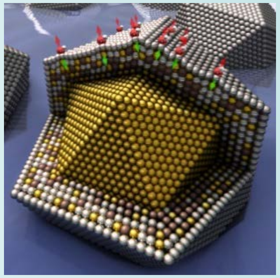
RDE after 4K cycles @60°C (0.6-1.05V vs. RHE):

8-fold specific and 10-fold mass activity improvements over Pt/C

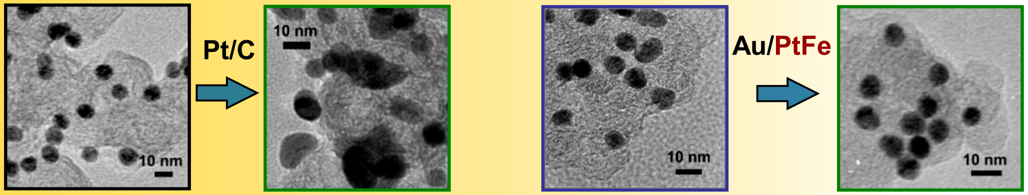
***JACS*, 133 (2011) 14396**



Au core
PtFe shell

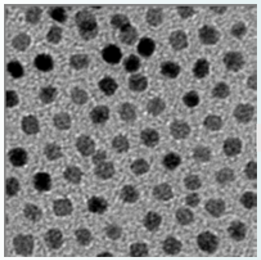


6° Multimetallic NPs can further improve activity and durability

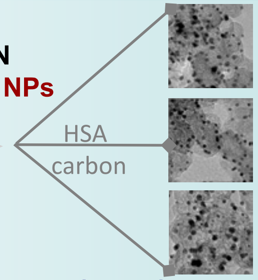


before | After 60K cycles | before | After 60K cycles

***Nano Letters*, 11 (2011) 919**



PtMN
Ternary NPs

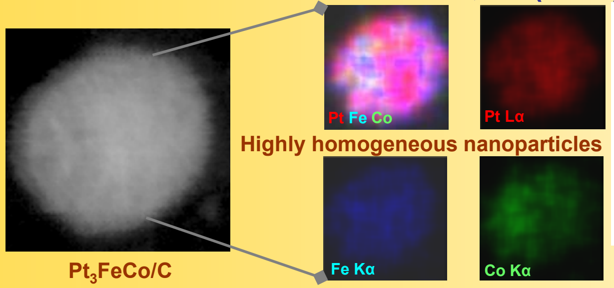


Pt_3FeCo/C

Pt_3CoNi/C

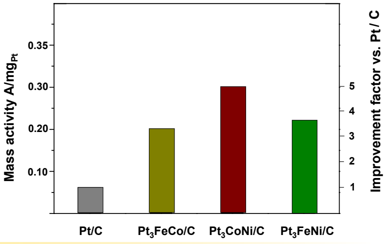
Pt_3FeNi/C

***J. Phys. Chem. Letters*, 3 (2012) 1668**



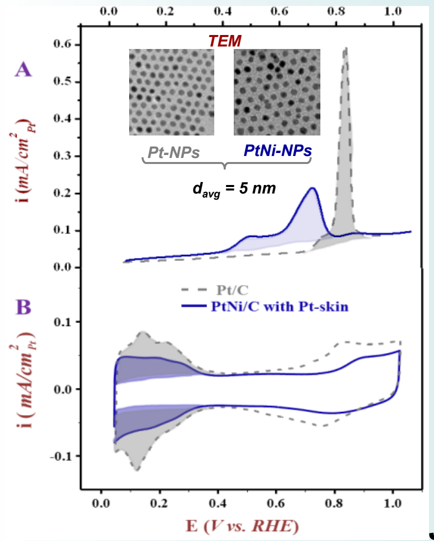
Highly homogeneous nanoparticles

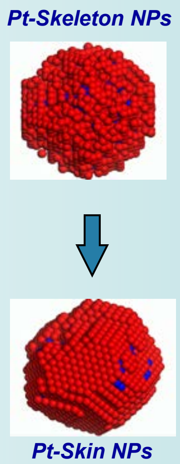
Pt_3FeCo/C



Additional gain in mass and specific activities vs. Pt and Pt_3M alloys

Technical Accomplishments FY09-14: *Pt-alloy Nanocatalysts*





JACS 133 (2011) 14396

7° Electrochemically active surface area of Pt-Skin catalysts

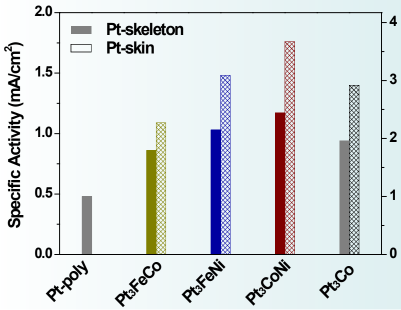
Catalysts with multilayered Pt-skin surfaces exhibit substantially lower coverage by H_{upd} vs. Pt/C
(up to 40% lower H_{upd} region is obtained on Pt-Skin catalyst)

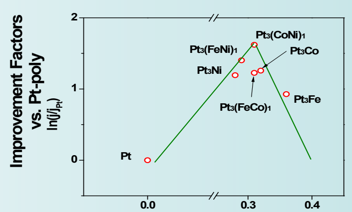
Surface coverage of adsorbed CO is not affected on Pt-skin surfaces

Ratio between Q_{CO}/Q_{Hupd}>1 is indication of Pt-skin formation

Electrochemical oxidation of adsorbed CO should be used for estimation of EAS of Pt-skin catalysts

Benefits: to avoid overestimation of specific activity



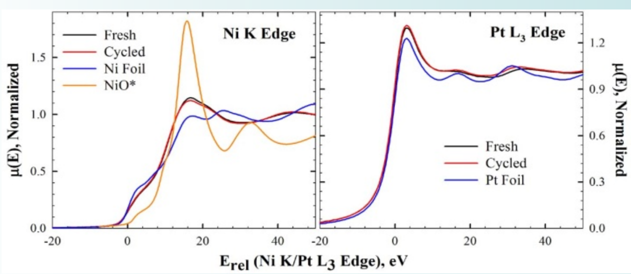


8° Multimetallic Pt_3NM alloys can further improve activity

Similarly to Pt_3M alloys, ternary alloys form Pt-skeleton and Pt-skin surfaces depending on the surface treatment

The most active alloy is Pt_3NiCo, with 4-fold improvement factor in specific activity compared to Pt-poly

J. Phys. Chem. Letters, 3 (2012) 1668



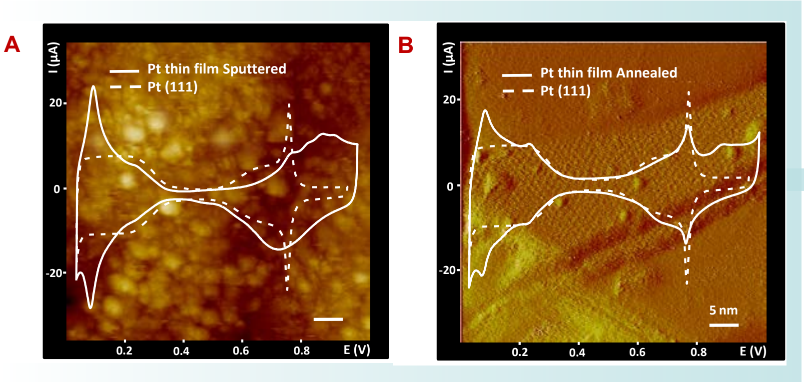
9° MEA: PtNi-MLSkin/NPs 20,000 potential cycles, 0.6 – 0.95 V

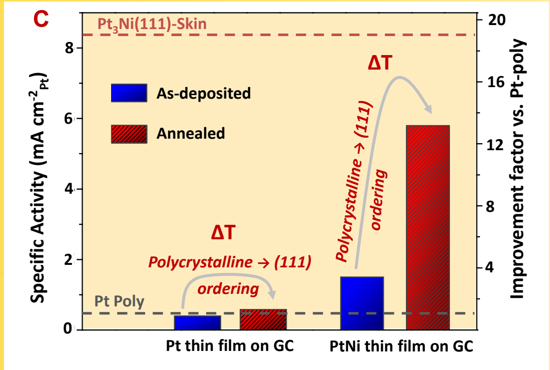
No change in Ni and Pt edges after 20K cycles confirms high stability pf multilayered Pt-Skin under operating conditions

Specific surface area loss was only 12%, while Pt/C catalysts suffer loss of 20-50%

Unpublished

Technical Accomplishments FY09-14: *Pt-alloy Nanocatalysts*



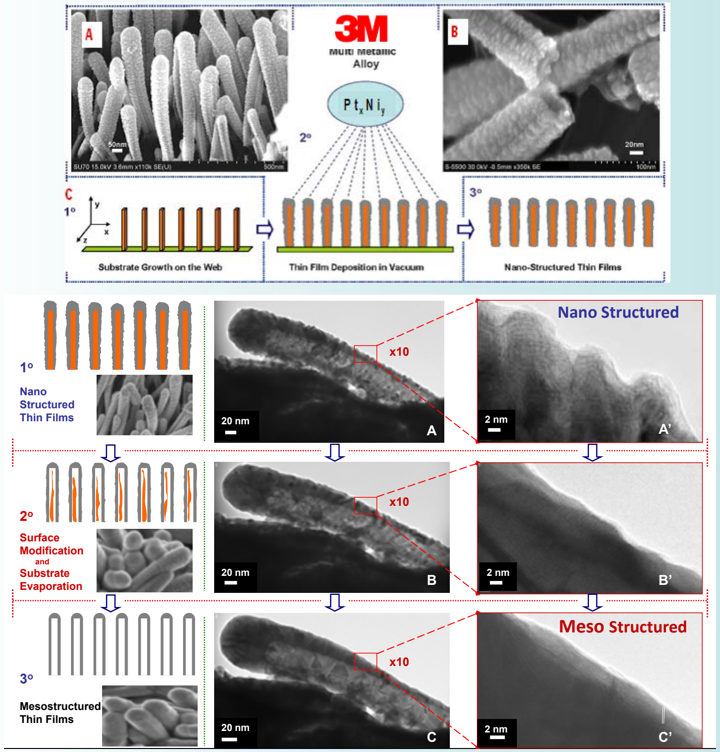


Scientific Achievement

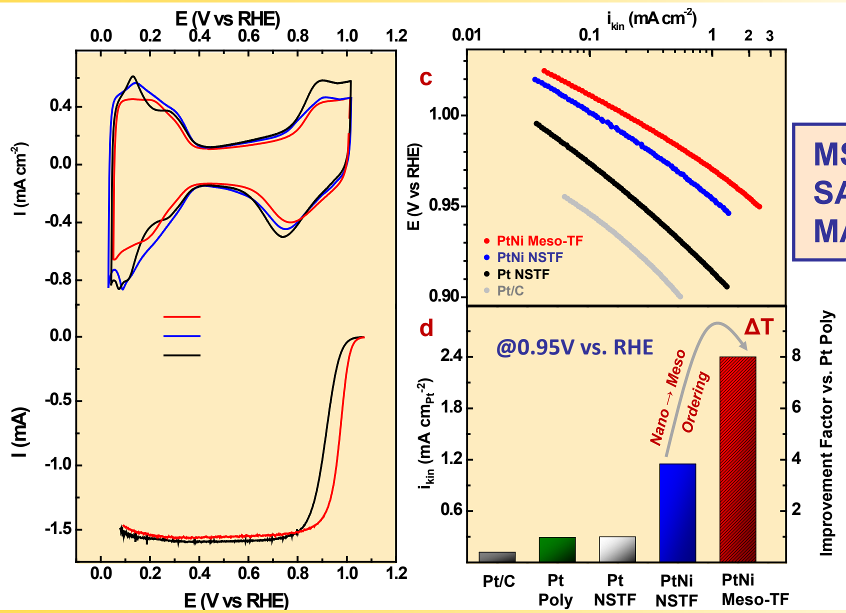
Control of surface structure and morphology of multimetallic thin films without use of templates for epitaxial growth

Significance and Impact

Enables electrocatalytic properties of Pt-alloy single crystals in thin film materials



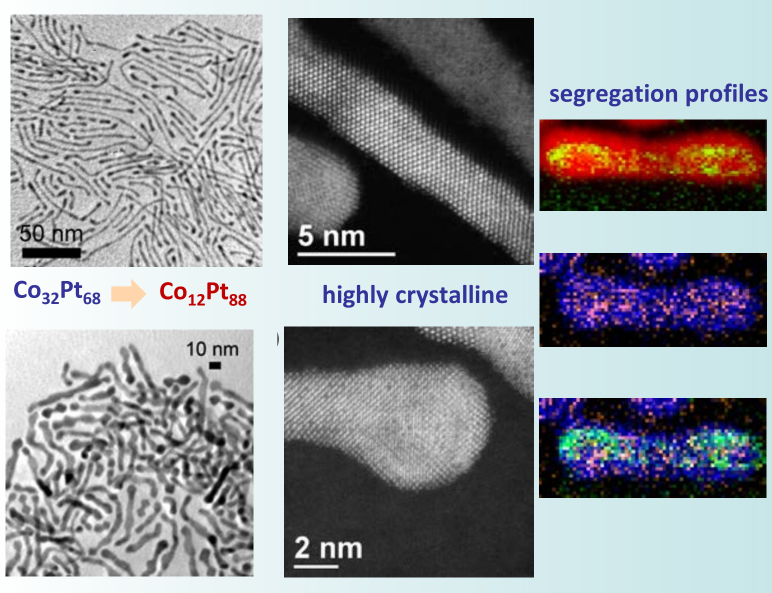
10° Mesostructured Thin Films with Tunable Morphology



MSTF vs. Pt/C:
SA 20-fold
MA 6-fold

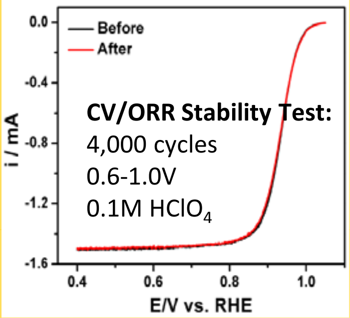
Nature Materials, 11 (2012) 1051

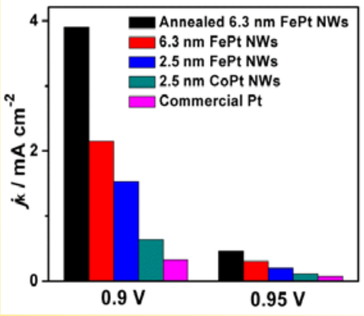
Technical Accomplishments FY09-14: *Pt-alloy Nanocatalysts*



width 5.5 nm

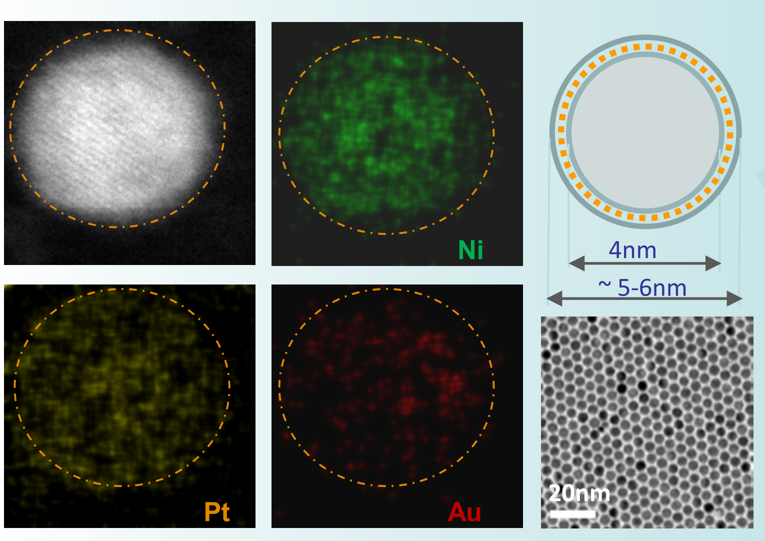
11° Highly active and durable multimetallic NWs



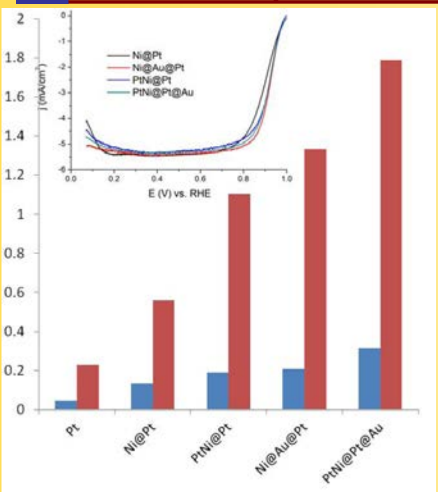


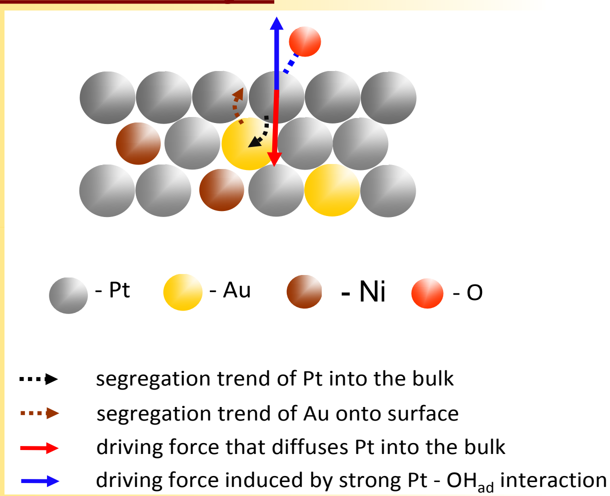
Pt Alloy NWs are active and durable catalyst with no change in activity after 4,000 cycles
Specific activity depends on the composition and width of NWs
Annealing of NWs induces formation of nanosegregated profile with Pt-Skin type of surface
Pt-Skin confirmed by suppressed H_{upd}, Pt-OH shift, CO_{ad}/Hupd ratio, and high ORR activity

***Angew. Chem. Int.Ed.*, 52 (2013) 3465**



12° Core-Shell particles with Au interlayer





***Nano Letters*, 14 (2014) 6361**

Technical Accomplishments FY09-14: *Pt-alloy Nanocatalysts*

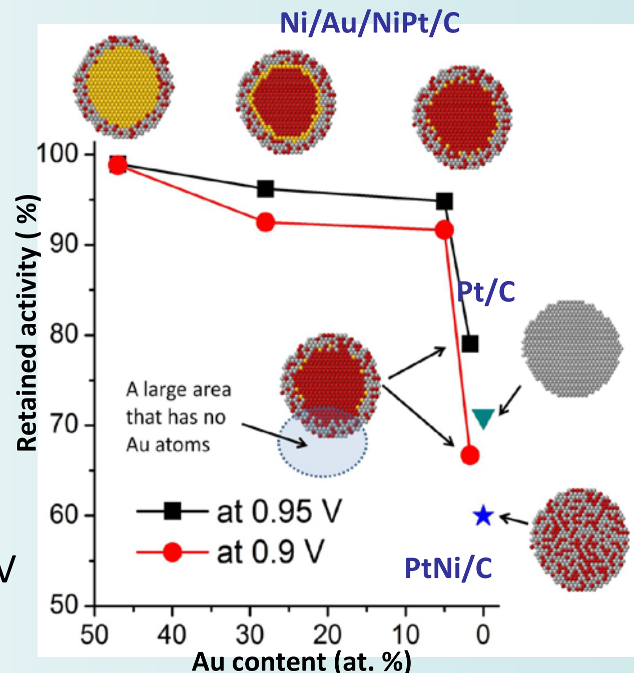
Non-PGM core /Au interlayer/PtM shell

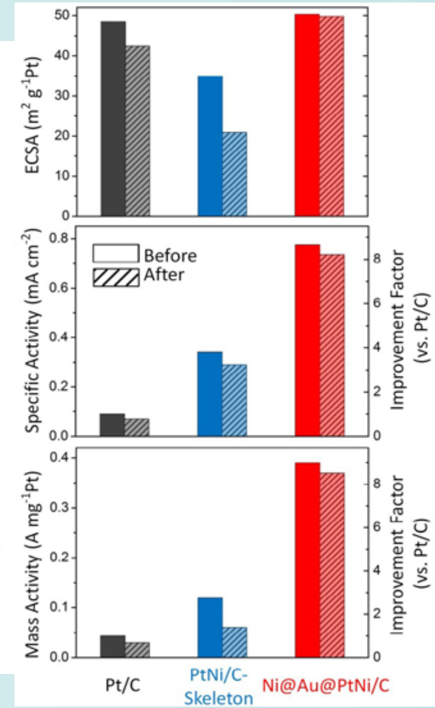
Scientific Achievement

Nanoparticles with tuned size, surface and subsurface compositional profile based on Ni core coated with Au interlayer which is covered by PtNi shell enable advanced electrocatlytic properties for the ORR

Significance and Impact

ORR specific and mass activities of NP with core/interlayer/shell are 8-fold more active than Pt/C catalyst after less than 10% of loss in activity in 10K cycles between 0.6 and 1.1V





Research Details

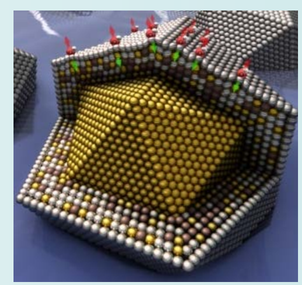
–Monodisperse 3nm Ni NPs were synthesized as core

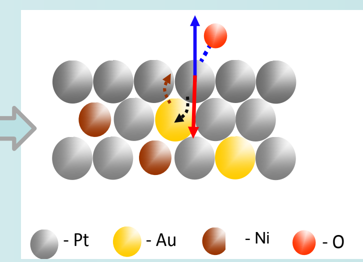
–Thickness of the Au interlayer was tuned for durability

–Threshold content of Au was found to be 5 at. %

–PtNi shell was deposited over Ni/Au core/shell particles

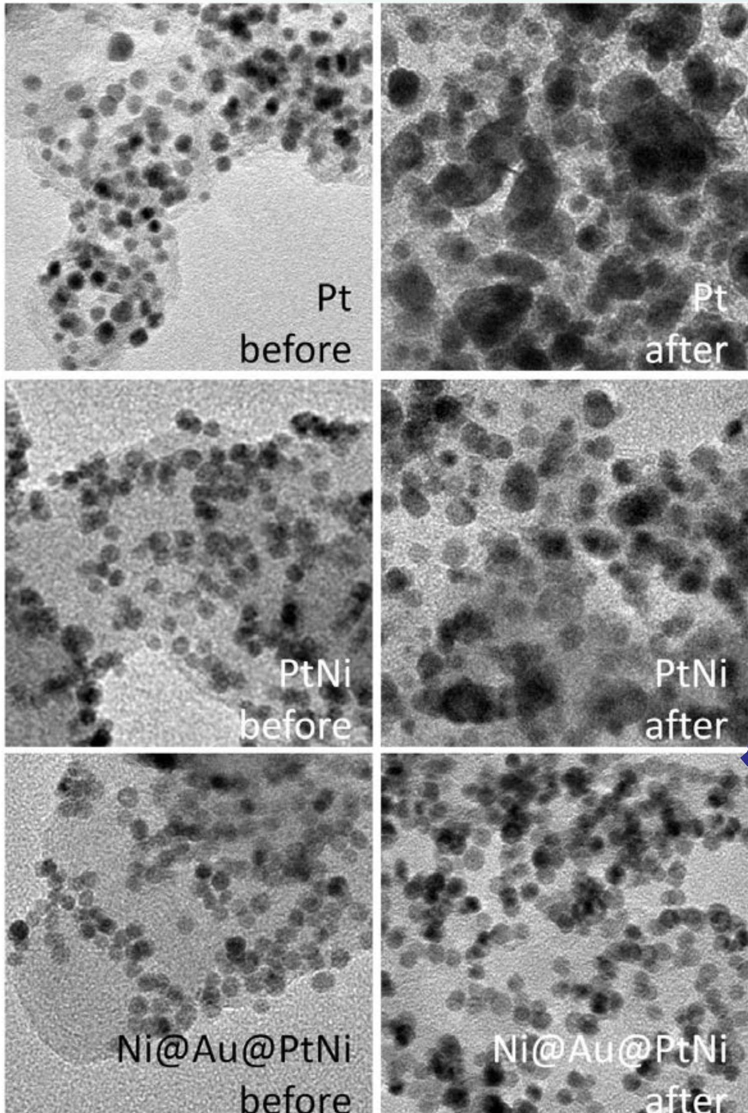
–Synergy between electronic effect and Au surface energy defines advanced electrocatalytic properties

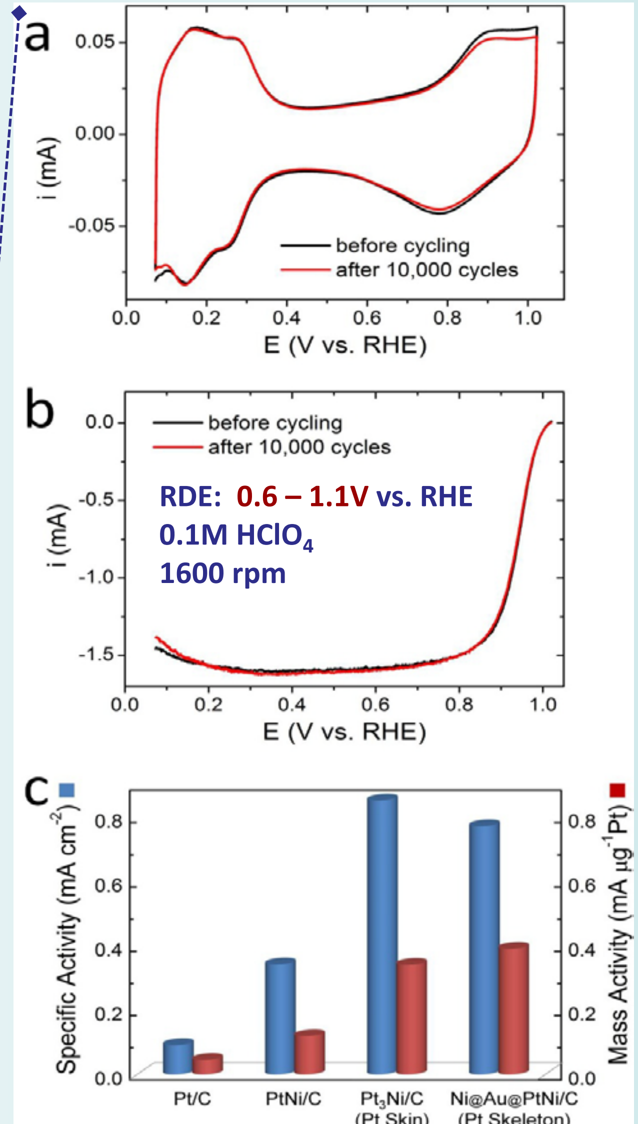




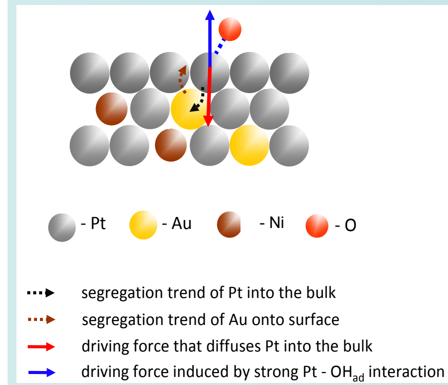
Technical Accomplishments FY09-14: *Pt-alloy Nanocatalysts*

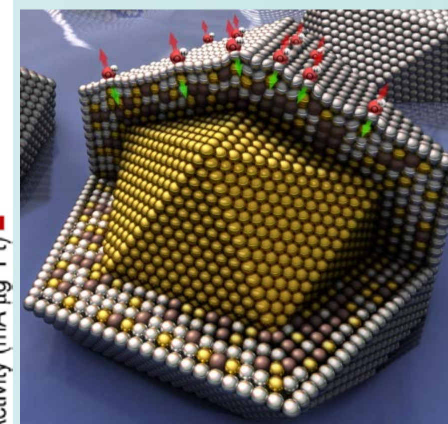
Non-PGM core /Au interlayer/PtM shell





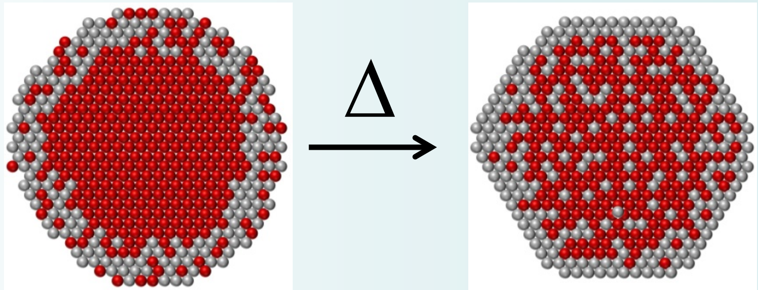
Stabilization mechanism





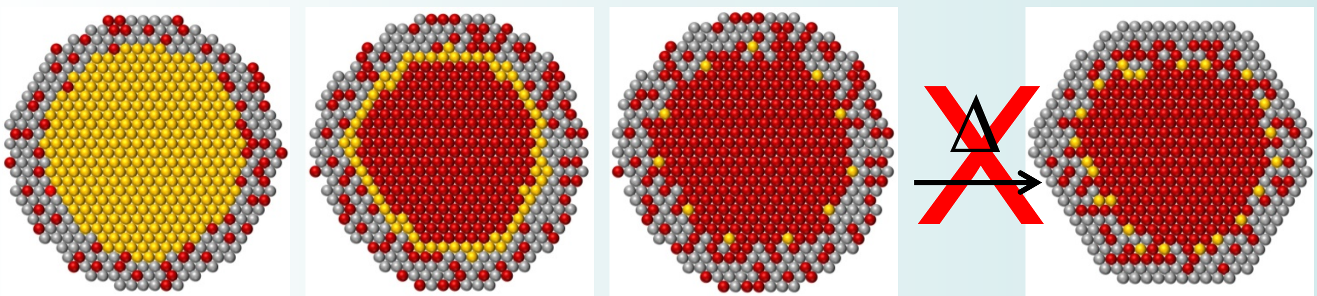
Accomplishments and Progress: *Core/Shell NPs with Au interlayer*

Synthesis, Structural and Electrochemical evaluation of core shell NPs



Pt-Skin

high activity Pt_3M



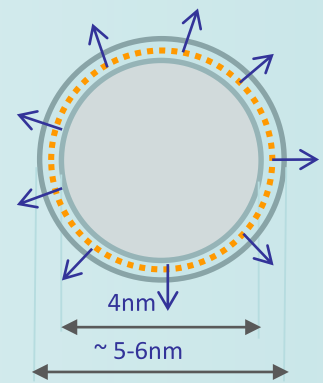
underlayered Au

high durability

Au core / PtNi shell NPs have the same catalytic activity as PtNi NPs

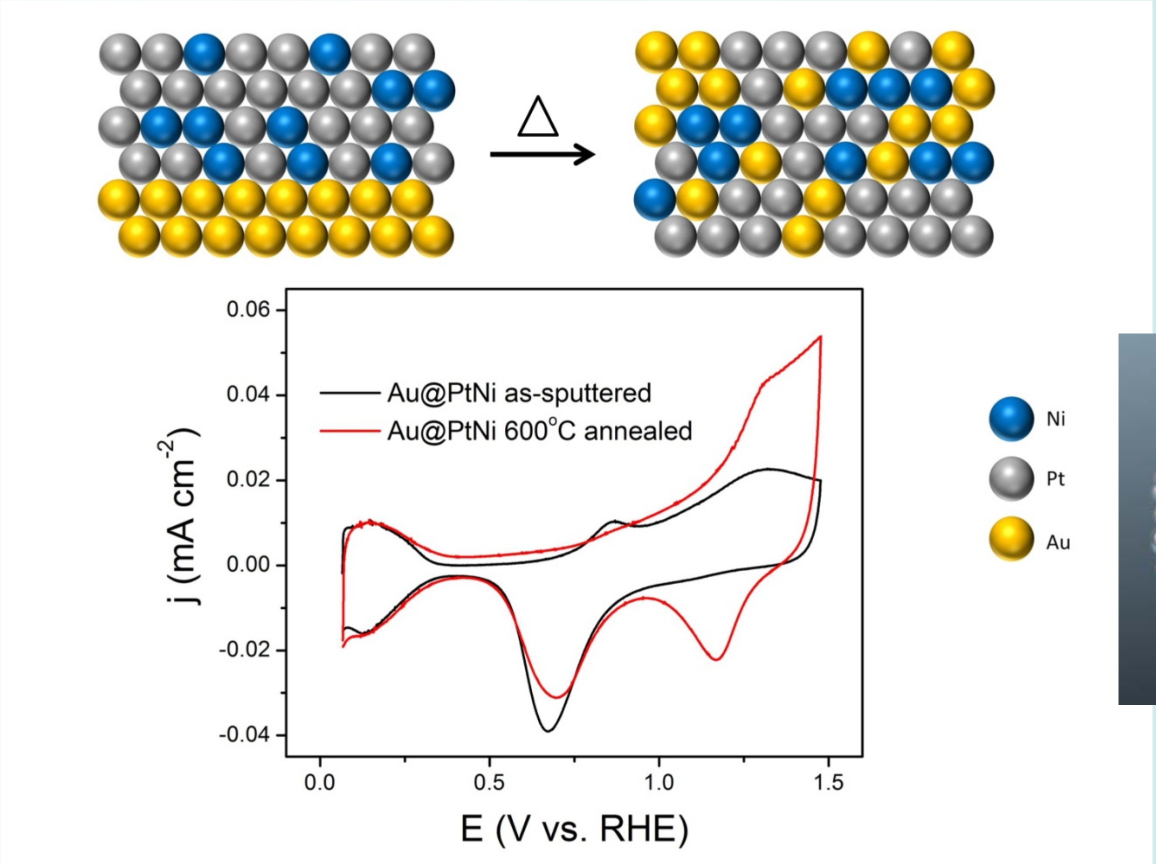
Subsurface Au does not alter catalytic properties of NPs

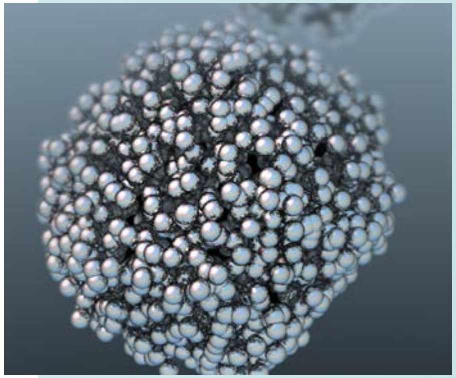
Subsurface Au decreases total number of Pt active sites for adsorption of O_2



non-PGM core / Au interlayer / PtNi shell

Synthesis, Structural and Electrochemical evaluation of core shell NPs

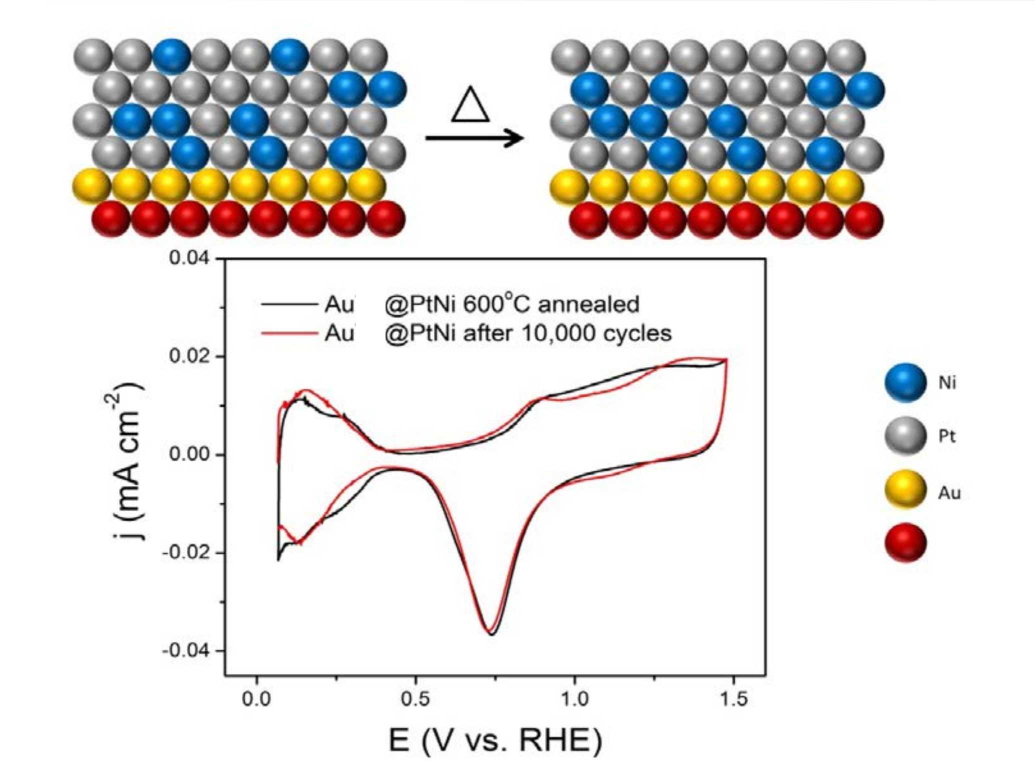


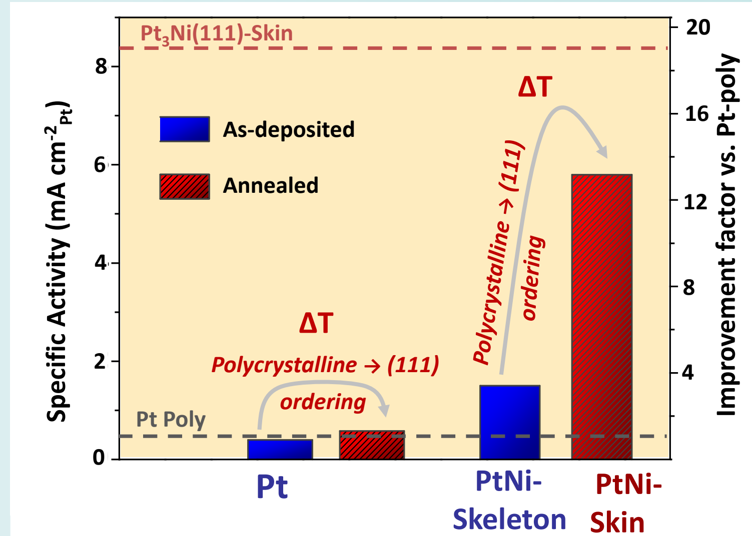


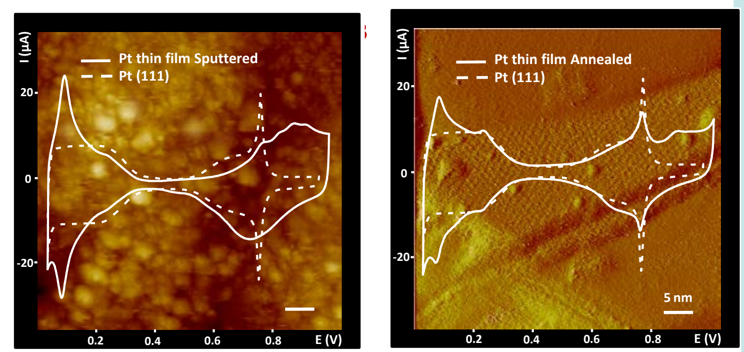
Subsurface Au segregates over Pt after thermal annealing which diminish number of Pt active sites for adsorption of O_2

Accomplishments and Progress: *Core/Shell NPs with Au interlayer*

Synthesis, Structural and Electrochemical evaluation of core shell NPs





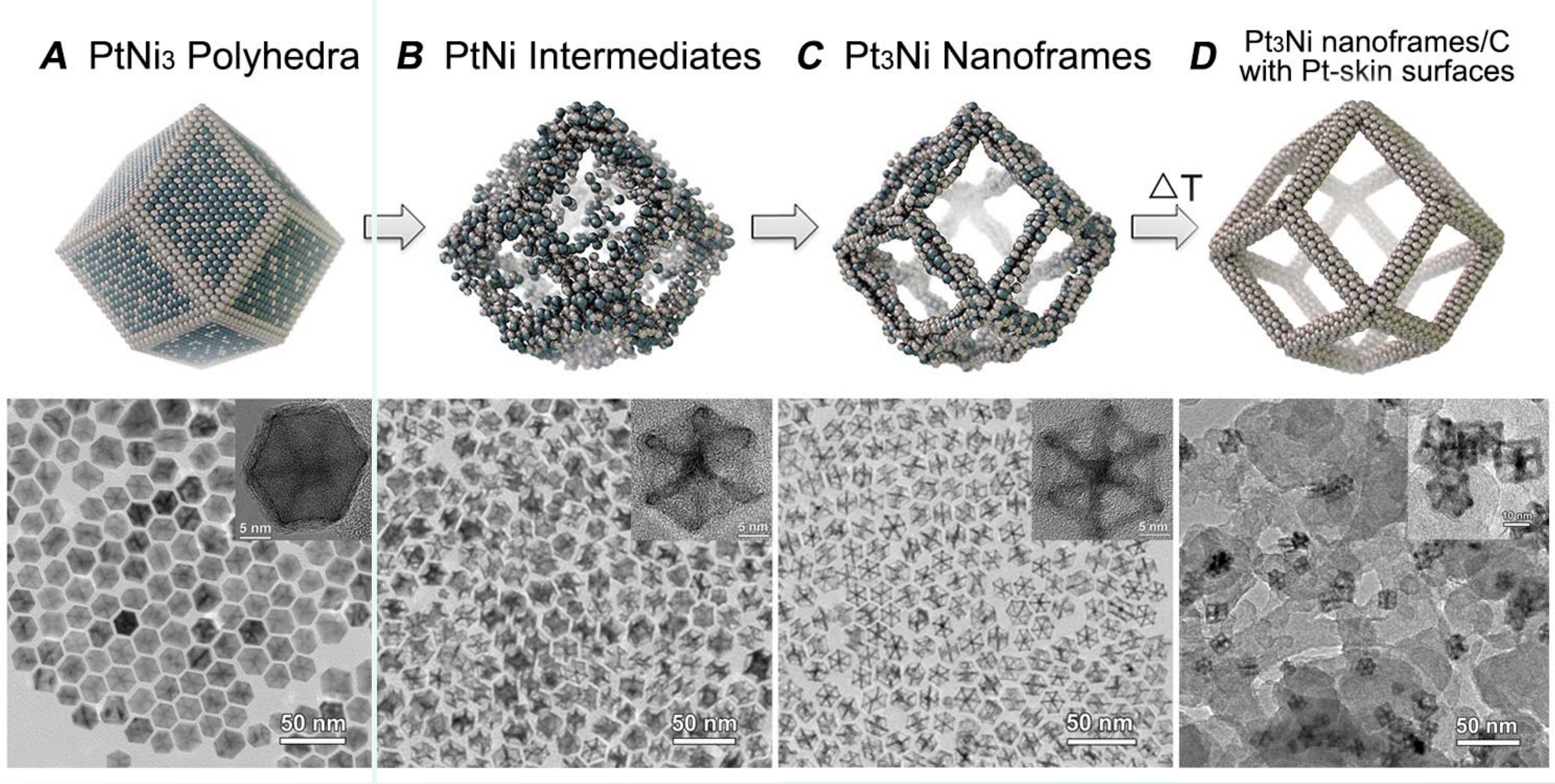


Subsurface Au does not segregate over Pt after thermal annealing, preserves number of Pt active sites and forms Pt-Skin overlayer with high ORR activity

Dissolution of Pt surface and Ni near-surface is diminished by 2-3 order of magnitude

Technical Accomplishments FY14: *PtNi Nanoframes*

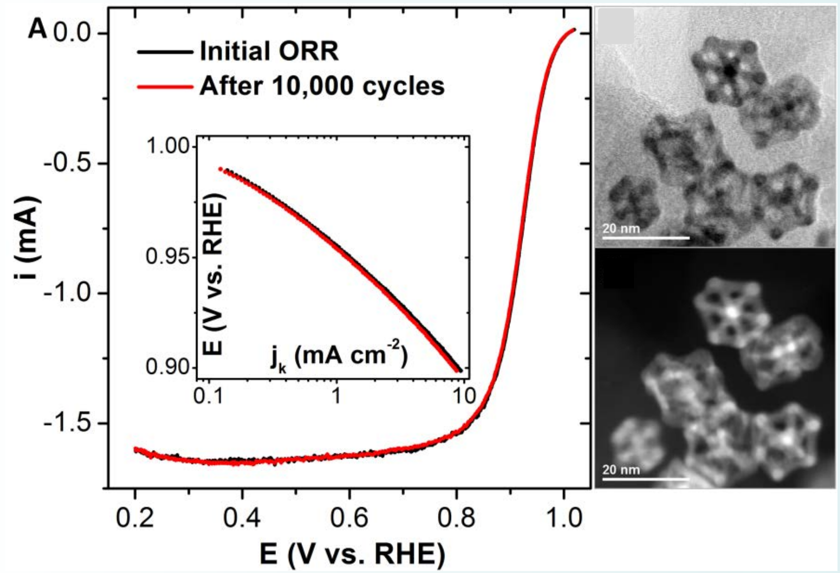
Synthesis, Structural and Electrochemical evaluation of Nanoframes

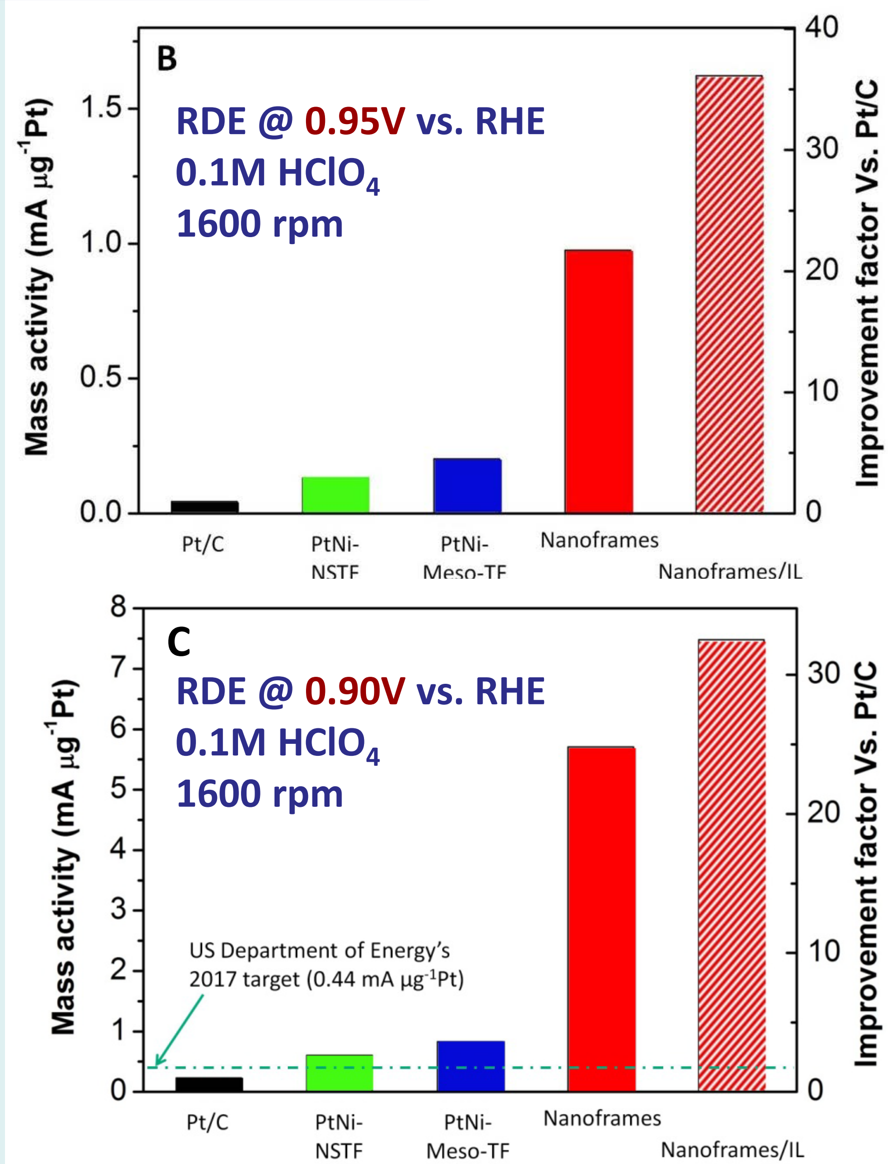


- H_2PtCl_6 and $Ni(NO_3)_2$ react in oleylamine at 270°C for 3 min forming solid $PtNi_3$ polyhedral NPs
- Reacting solution is exposed to O_2 that induces spontaneous corrosion of Ni
- Ni rich NPs are converted into Pt_3Ni nanoframes with Pt-skeleton type of surfaces
- Controlled annealing induces Pt-Skin formation on nanoframe surfaces

Technical Accomplishments FY14: *PtNi Nanoframes*

Incorporation of Ionic Liquid Into the Nanoframes

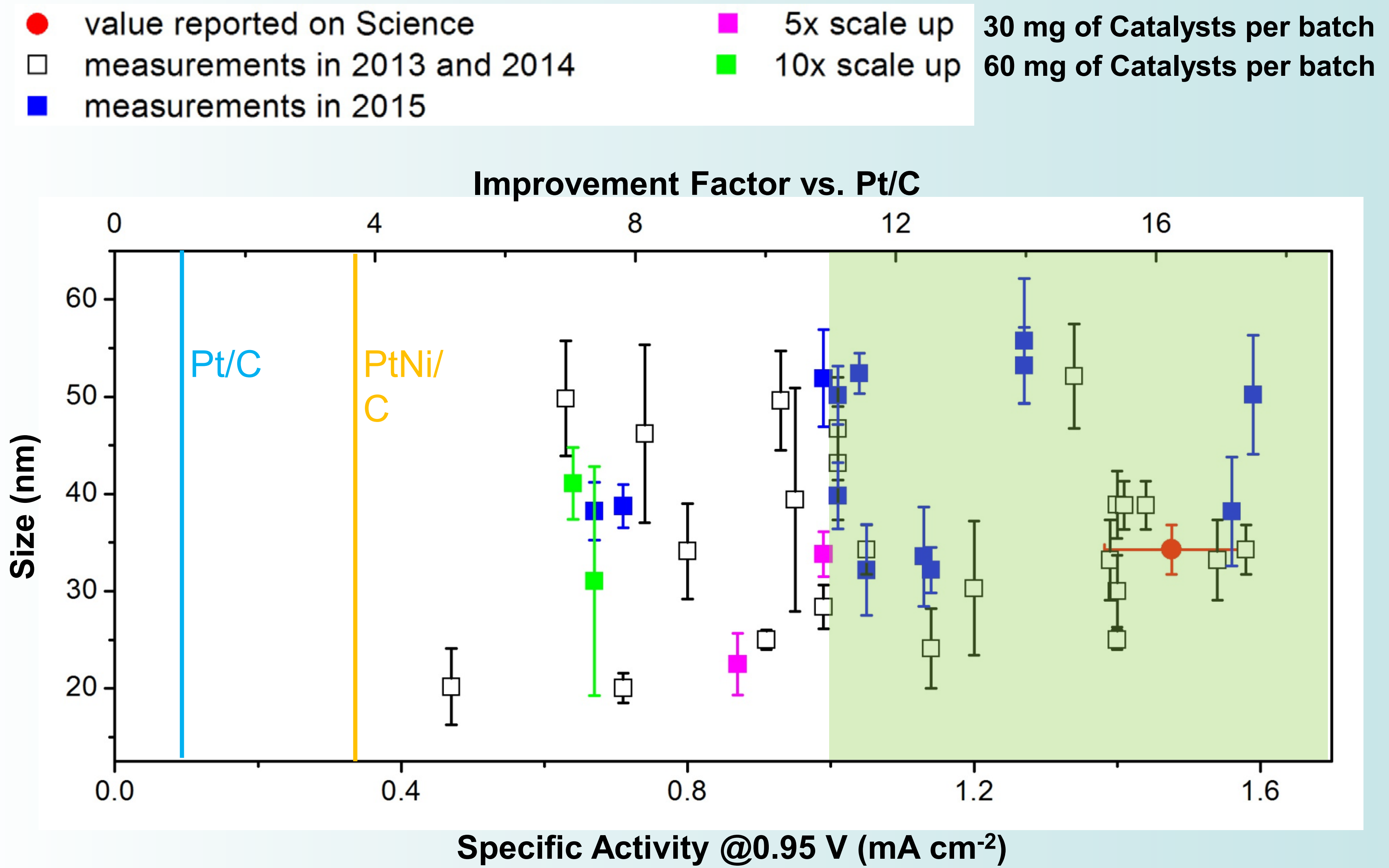




- No change in activity after 10K cycles 0.6 – 1.0 V
- Specific activity increase over 20-fold vs. Pt/C
- Mass activity increase over 35-fold vs. Pt/C
- Increase in mass activity over 15-fold vs. DOE target

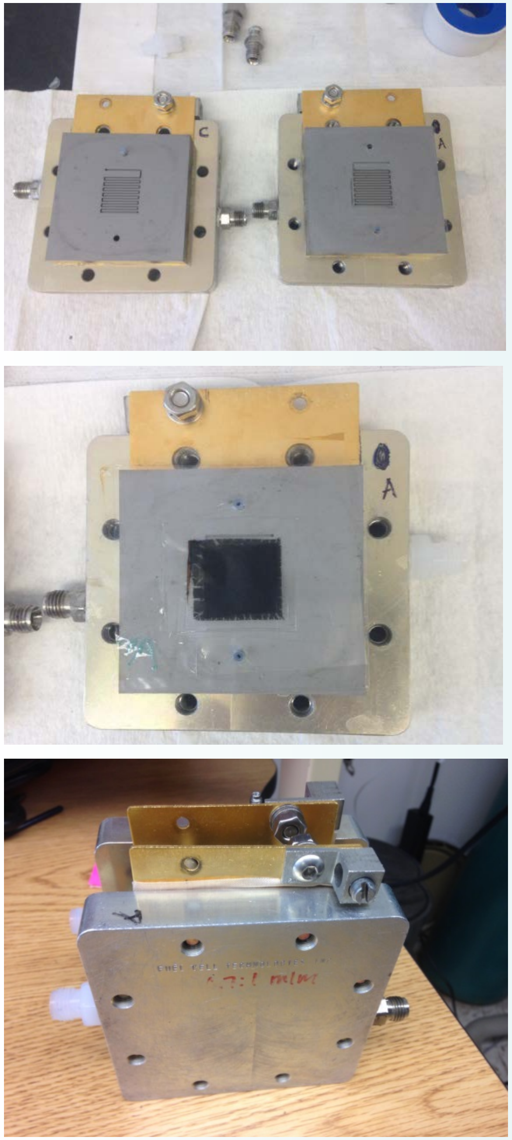
Accomplishments and Progress: *PtNi Nanoframes*

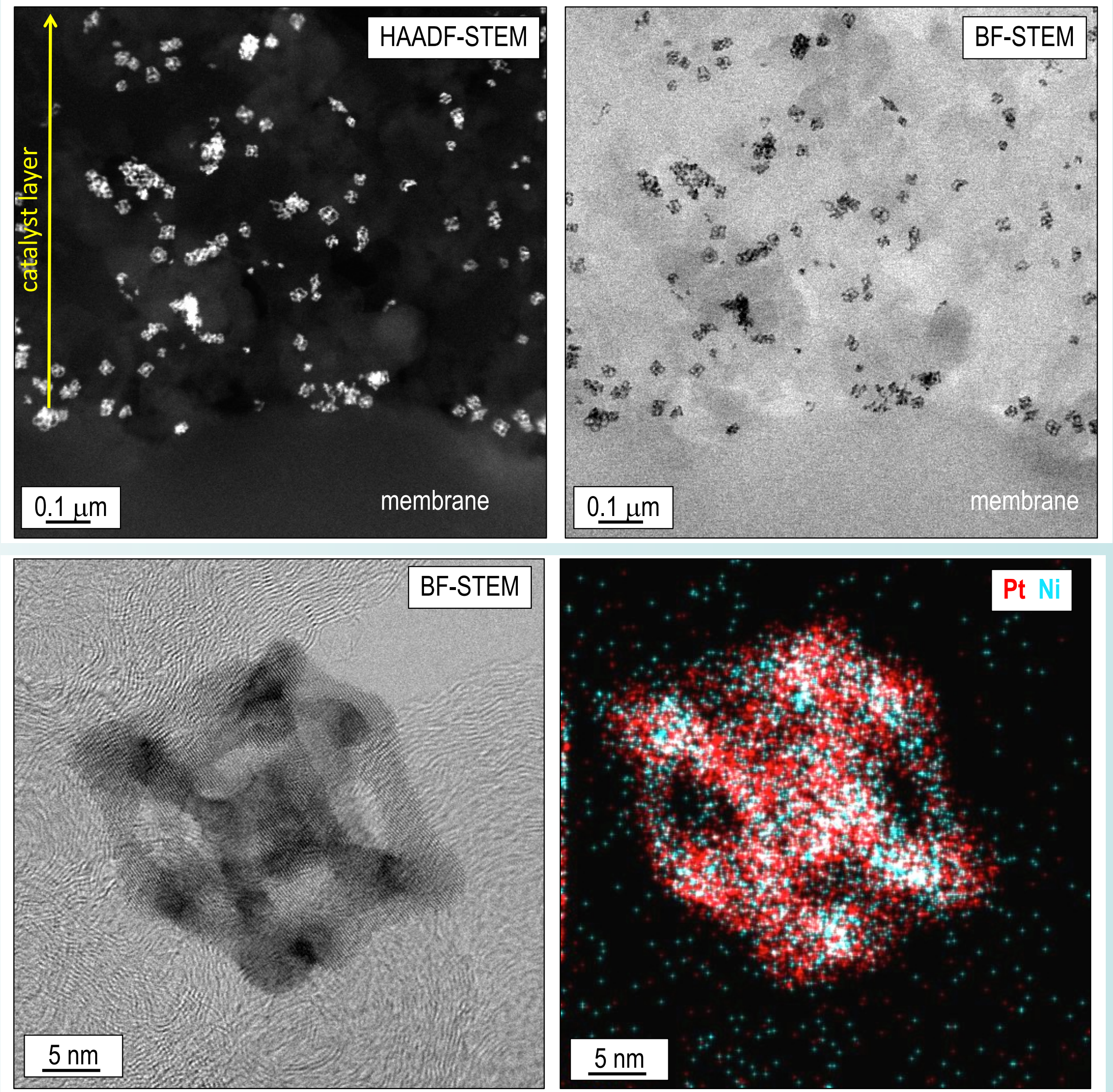
Lab Scale Synthesis, Structural and Electrochemical Evaluations



Accomplishments and Progress: *PtNi Nanoframes*

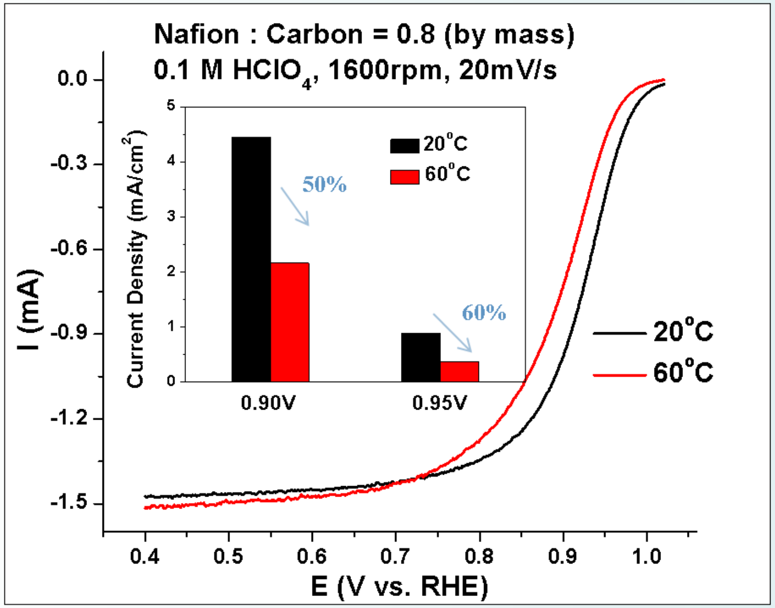
Nanoframes in 5 cm^2 MEA ANL and ORNL





Accomplishments and Progress: *PtNi Nanoframes*

Nanoframes in RDE with Ionomer and T



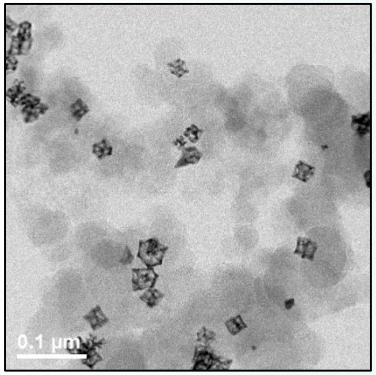
- 2x decrease in specific activity of with addition of ionomer to nanoframes
- Nanoframes have >10x higher activity than 20 wt% Pt/C

	20°C Specific Activity [mA/cm²] No Ionomer	20°C Specific Activity [mA/cm²] I/C = 0.8	60°C Specific Activity [mA/cm²] No Ionomer	60°C Specific Activity [mA/cm²] I/C = 0.8
0.95V	1.25	0.92	0.659	0.372
0.90V	7.35	4.87	4.14	2.16

Specific Activity of Pt/C TKK 20 wt%
I/C=0.8, 60°C,
0.9 V: **0.2 mA/cm²**

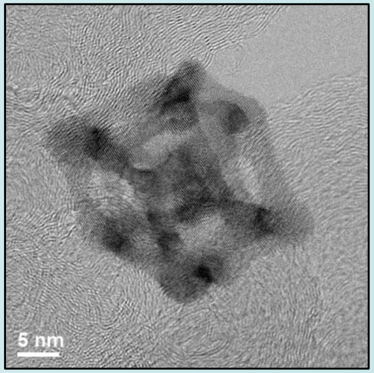
Accomplishments and Progress: *PtNi Nanoframes*

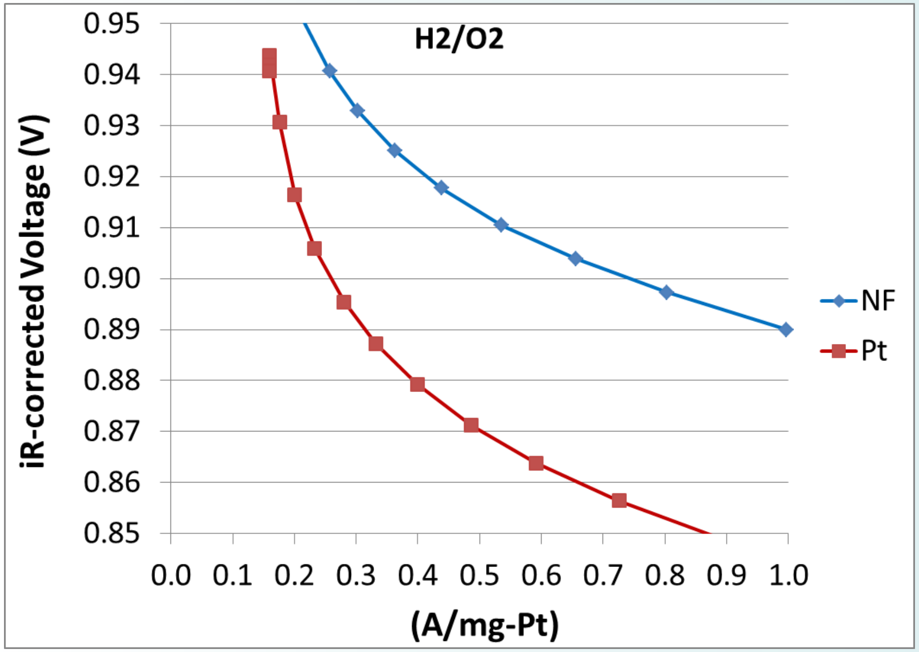
Nanoframes in 5 cm^2 MEA   ANL and ORNL

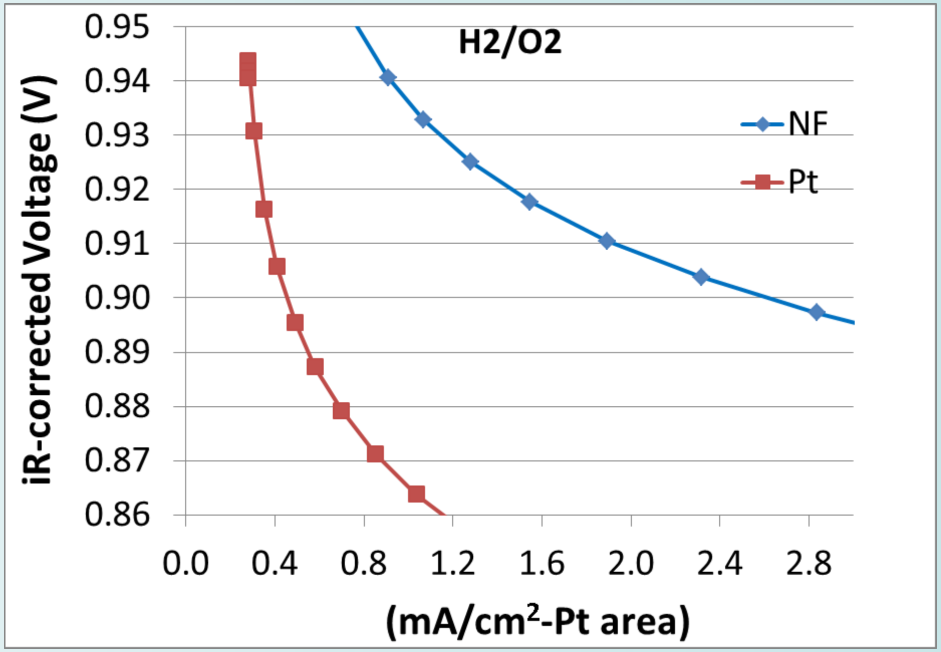


Cathode Loading: 0.035 mg-Pt/cm^2, I/C = 0.8
H_2/O_2, 80°C, 150 kPa(abs), 100%RH

ORR Activity @ 0.9 V:	**Mass Activity**	**Specific Activity**
TKK 20 wt%Pt/C:	0.24 A/mg-Pt	0.45 mA/cm^2-Pt
PtNi Nanoframes:	**0.76 A/mg-Pt**	**2.60 mA/cm^2-Pt**

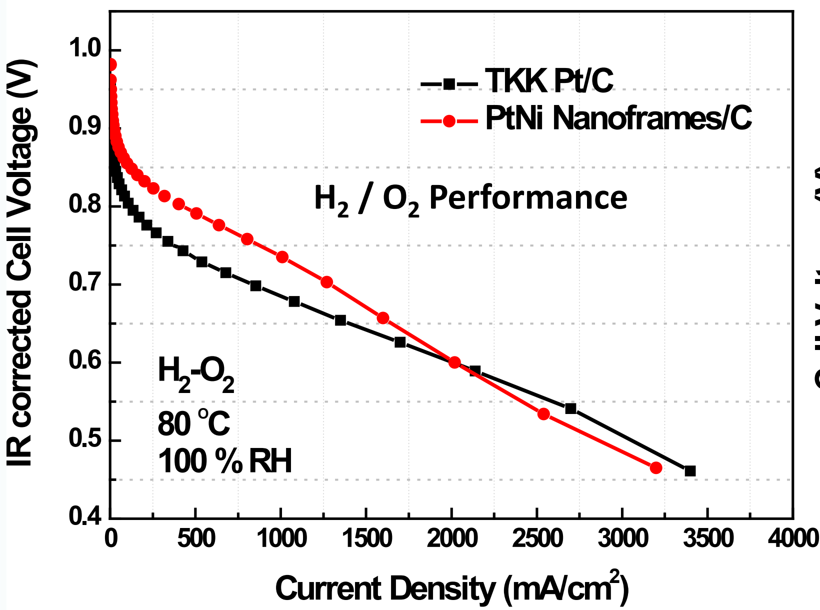


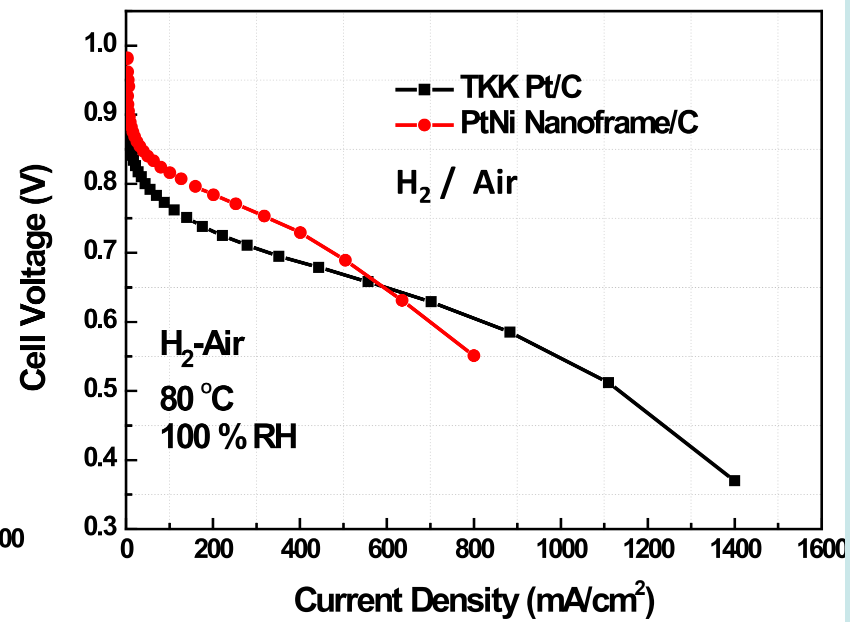




Accomplishments and Progress: *PtNi Nanoframes*

Nanoframes in 5 cm² MEA ANL and LANL



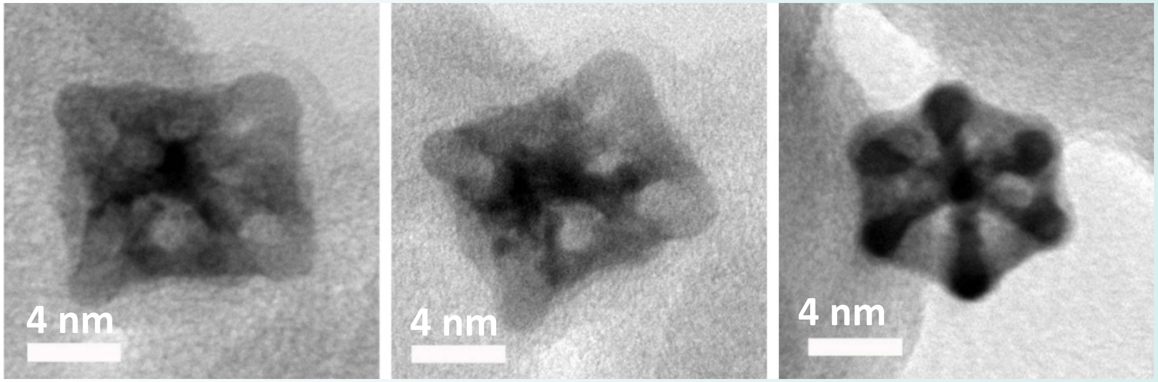


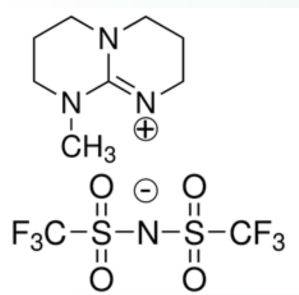
Metric	Units	DOE 2020 Target	PtNi Nanoframe	TKK Pt/C
Pt total loading	mg-PGM/cm$^2_{geo}$	≤0.125	**0.035**	**0.035**
Mass activity	A/mg$_{PGM}$@0.9mV$_{iR\text{-}free}$	≥0.44	**0.76**	**0.22**
MEA performance	mA/cm$^2_{geo}$ @ 800 mV	≥300	**148**	**44.3**

LANL obtained mass activity of 0.3 A/mg$_{Pt}$ @ 80ºC and 3x higher Pt loading on the cathode in an unoptimized 5cm² MEA

Accomplishments and Progress: *PtNi Nanoframes*

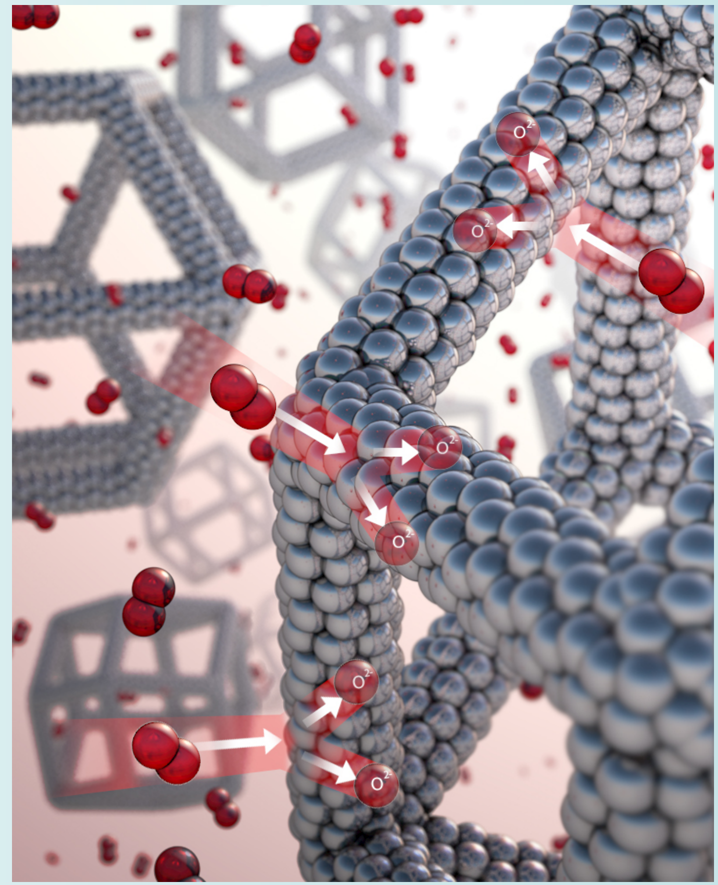
Incorporation of Ionic Liquid Into the Nanoframes in MEA





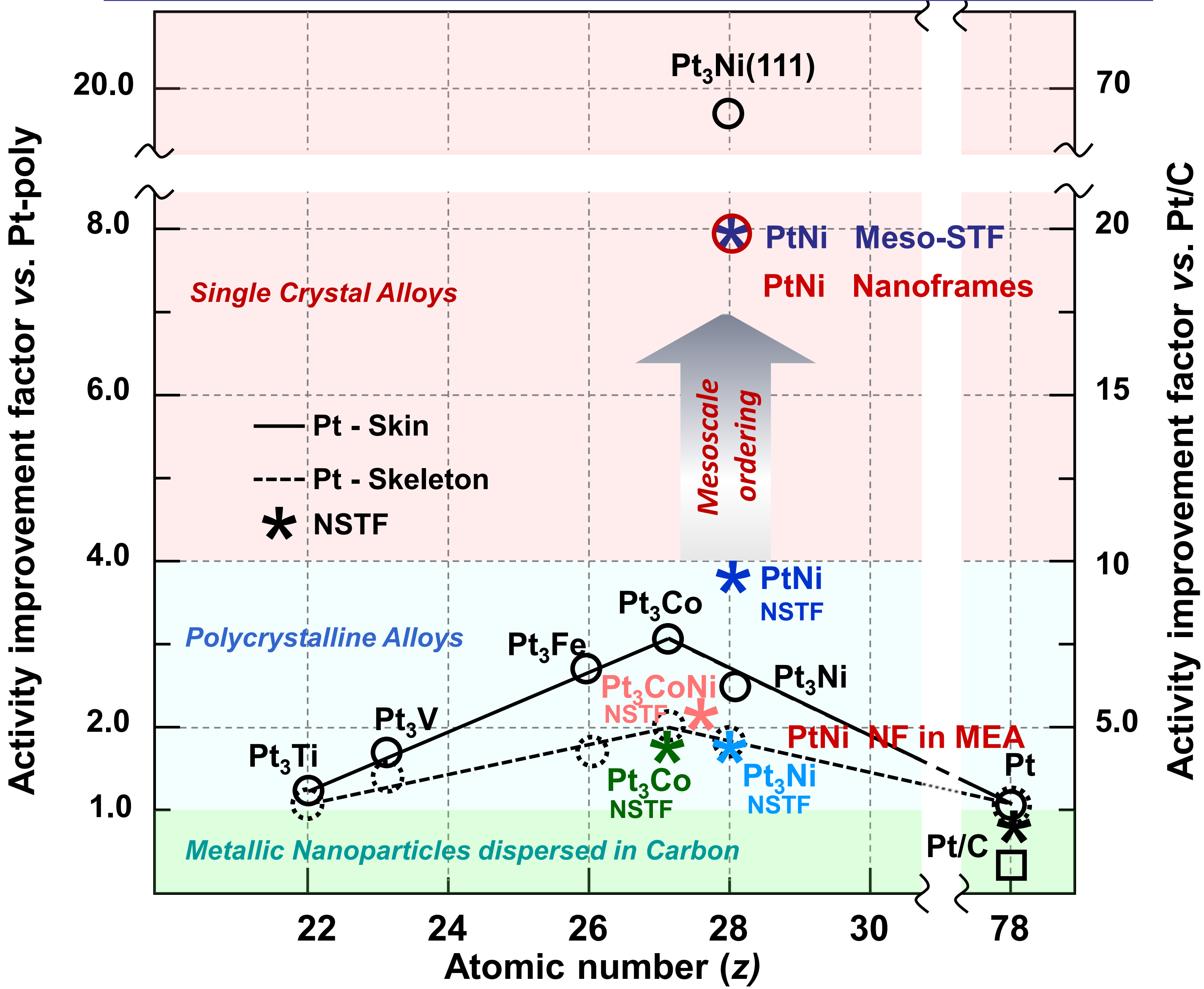
- **Initial measurements with nanoframes and IL in MEA justifies this approach**
- **Nanoframes with IL exhibit 30% improved activity**

7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene [MTBD]



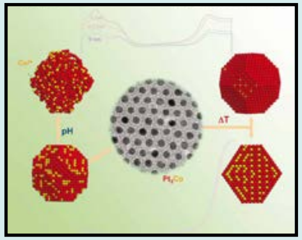
Accomplishments and Progress: *ORR on Pt-alloys*

Electrochemical Activity Map for the ORR RDE and MEA



Summary

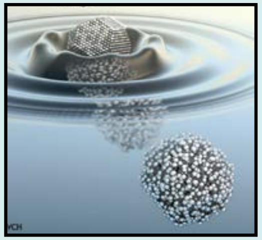
Electrocatalysts based on nanosegregated Pt alloy NPs, NWs, MSTFs and Nanoframes



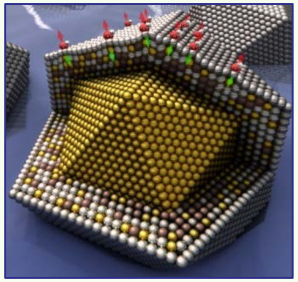
Efficient implantation of fundamental principles to the practical systems in the form of NPs, NWs, and nanoframes with adjustable compositional profile and structure

Established methodology that is capable to form and determine the nanosegregated Pt-skin surfaces for different classes of electrocatalysts

Established scalable synthetic protocols to produce larger amounts of materials

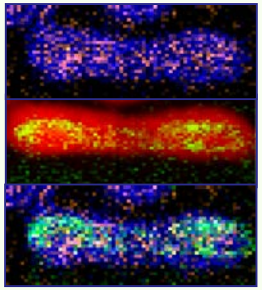


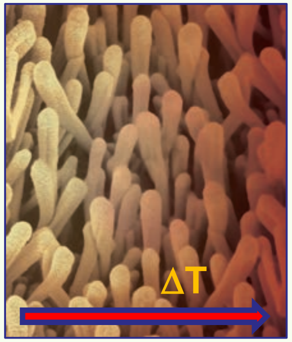
Evaluation of multimetallic Pt-alloy electrocatalysts



Different classes of materials have been synthesized in the form of NPs, NWs, nanoframes and characterized by TEM, HRSEM, in-situ HRTEM, XRD, RDE, MEA

Specific activity of Pt-alloy vs. Pt/C electrocatalysts can be improved by **20-fold for Nanoframes** and MSTF, 10-fold for core/shell NPs and 7-fold for NWs.
Mass activities improvements vs. Pt/C are **36-fold for nanoframes**, 7-fold for core/shell, 6-fold for MSTF and 4-fold for NWs (RDE in 0.1M $HClO_4$ @ 0.95V *vs.* RHE)

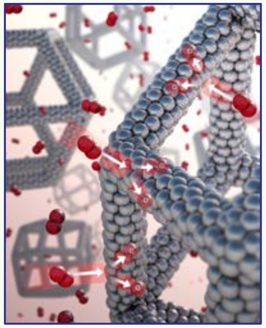




Stability of Nanoframes, MSTF, core/shell NPs and NWs is superior compared to Pt/C

Two fold power of annealing facilitates the formation of an energetically more favorable surface state rich in (111) facets and distinct oscillatory segregation profile in core/shell NPs, NWs, mesostructured thin films and Nanoframes

Nanoframes are the first nanoscale catalyst with ORR bulk single crystal activity



Future Work

FY 2015

- Activity/stability evaluation and optimization of MEA protocols at ANL and LANL
- Achieving full lab scale capacity for scaling up of chemical synthesis of nanoframe catalysts
- Alternative approaches towards highly active and stable catalysts with low PGM content

FY 2016 (new funding period)

- Tailoring of the composition that can improve/optimize durability/performance in Pt-alloys
- Synthesis of tailored low-PGM practical catalysts (Meso-TF | Core/Interayer/Shell | Nanoframes)
- Characterization Structural and Electrochemical (RDE, MEA, HRTEM)
- Support – Catalyst interactions / Tuning of the performance
- Scaling-up of synthesis to produce gram scale quantities of the most promising catalysts

Collaborations

SUB-CONTRACTORS

- **Oak Ridge National Laboratory** – HRTEM

COLLABORATORS

- **Argonne National Laboratory** – Nanoscale fabrication and DFT (CNM)
- **Argonne National Laboratory** – MEA Testing D. Myers (CSE)
- **Los Alamos National Laboratory** – MEA Testing R. Borup / T. Rockward

Publications and Presentations FY09-15

15 Publications
36 Presentations
over 1200 Citations
3 issued US patents
5 patent applications

US 7,871,738 B2
Jan. 18, 2011

(54) NANOSEGREGATED SURFACES AS CATALYSTS FOR FUEL CELLS

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

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

US 8,178,463 B2
May 15, 2012

US 8,685,878 B2
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)

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