2011 DOE Hydrogen and Fuel Cells Program Review

Nanosegregated Cathode Catalysts with Ultra-Low Platinum Loading

Announcement No: DE-PS36-08GO98010

Topic: 1A

PI: Nenad M. Markovic

Co-PI: Vojislav R. Stamenkovic

Materials Science Division

Argonne National Laboratory

Project ID# FC008

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U.S. Department of Energy

UChicago Argonne LLC

Office of Science U.S. DEPARTMENT OF ENERGY

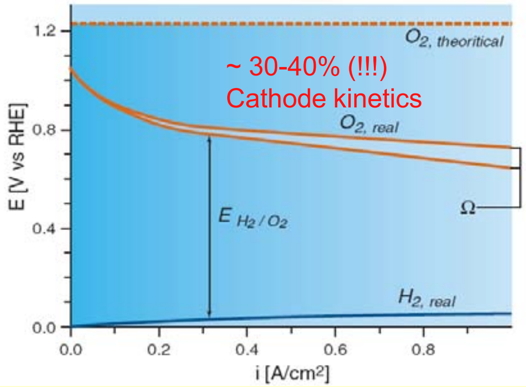
A U.S. Department of Energy laboratory managed by UChicago Argonne, LLC

Overview

Timeline

- Project start: 9/2009
- Project end: 9/2012

Barriers



1) Durability of fuel cell stack

2) Cost (catalyst, membrane, gdl)

3) Performance   (losses and activity)

Budget

- Total Project funding $ 3.6M
  - DOE share: 80 %
  - Contractor share: 20%
- Received in FY09: $ 300K
- Funding for FY10: $ 1.2M
- Funding for FY11: $ 1.2M

Partners:

- **Oak Ridge National Laboratory** – Karren More
- **Jet Propulsion Laboratory** – C. Hays
- **Brown University** – Shouheng Sun
- **University of Pittsburgh** – Goufeng Wang
- **3M Company** – Radoslav Atanasoski

Project Lead:

- **Argonne National Laboratory**

Relevance

Objectives **The main focus of ongoing DOE Fuel Cell Hydrogen Program is related to the ORR evaluation on PtM bimetallic and PtM_1M_2 (M_1=Co,Ni; M_2=Fe, Mn, Cr, V, Ti etc) ternary systems that will lead to the development of highly-efficient and durable *real-world nanosegregated Pt-skin catalysts with low-Pt content***

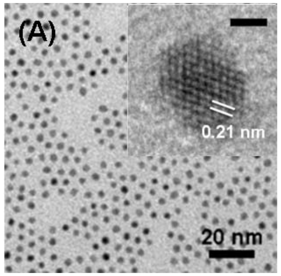
DOE Technical Targets

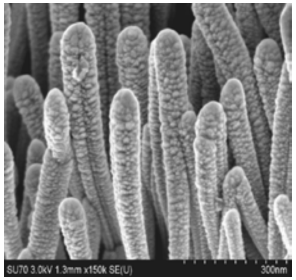
- Specific activity @0.9$V_{iR\text{-}free}$: 720 μA/cm^2
- Mass activity @0.9V: 0.44 A/mg_{Pt}
- Electrochemical area loss: < 40%
- Catalyst support loss: < 30%
- PGM Total content: 0.2 g/kW
- PGM Total loading: 0.2 mg/$cm^2_{electrode}$
- Cost*: $ 30/kW_e
- Durability w/cycling (80°C): 5000 hrs

*based on Pt cost of $450/troy ounce

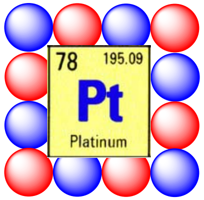
ANL Technical Targets

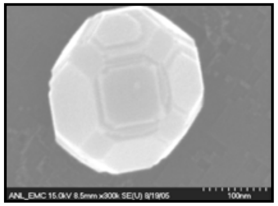
- Specific activity @ 0.9$V_{iR\text{-}free}$
  2015 DOE target x 3
- Mass activity @ 0.9$V_{iR\text{-}free}$
  2015 DOE target x 3
- Electrochemical area loss
  2015 DOE target
- PGM Total content
  < 0.1g/kW

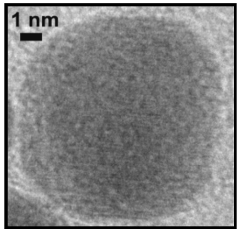




Approach



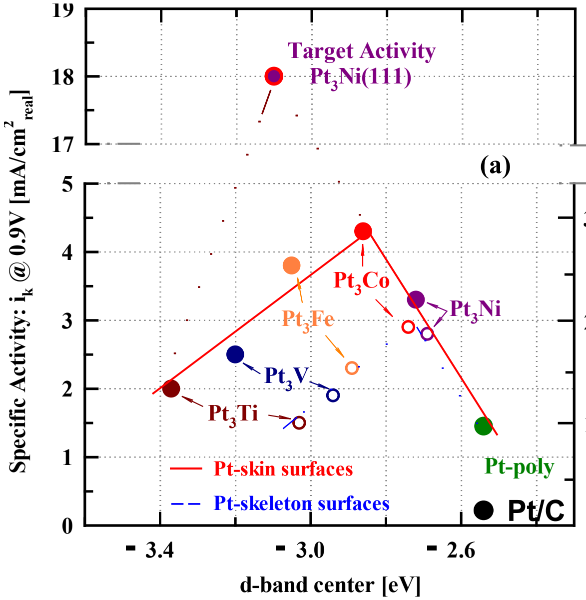




EXTENDED Multi-M SURFACES — **THIN METAL FILMS / MODEL NANOPARTICLES** — **REAL NANOPARTICLES**

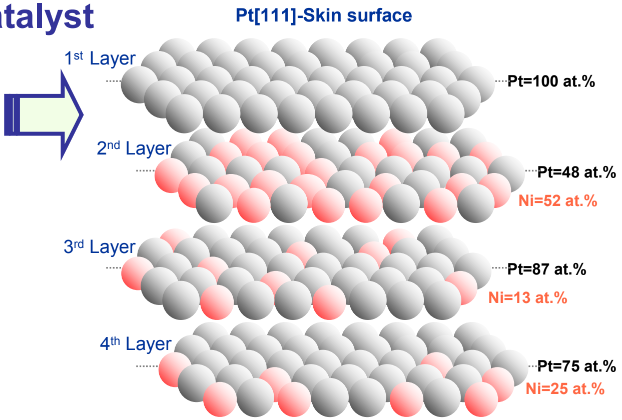
Materials-by-design approach - developed by ANL to design, characterize, understand, synthesize/fabricate and test advanced nanosegregated multi-metallic nanoparticles and nanostructured thin metal films

Well-Defined Systems



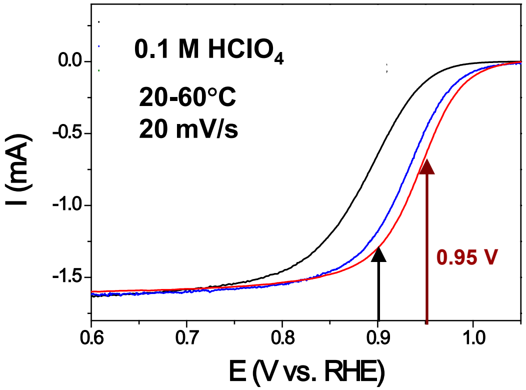
Advanced Nanoscale Catalyst

Nanosegregated Profile



$Pt_3Ni(111)$-Skin ~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

Approach / Milestone

(Go-No Go Decision Met)

Milestone 1. Composition – function relationship (FY11) (Accomplished)

1.1 Resolved electronic/atomic structure and segregation profile (50%)

1.2 Confirmed reaction mechanism of the ORR (40%)

1.3 Improved specific and mass activity (50%)

Milestone 2. Synthesis and characterization (FY11)

2.1 Physical methods: TM films (5-10 layers), nanoparticles (5-300 nm) (50%)

2.2 Established chemical methods: colloidal and impregnation synthesis (40%)

2.3 Characterization: Ex-situ (UHV, TEM) and in-situ (EXAFS, EC) (40%)

2.4 Theoretical modeling (DFT, MC) methods (50%)

Milestone 3. Fabrication and testing (FY11)

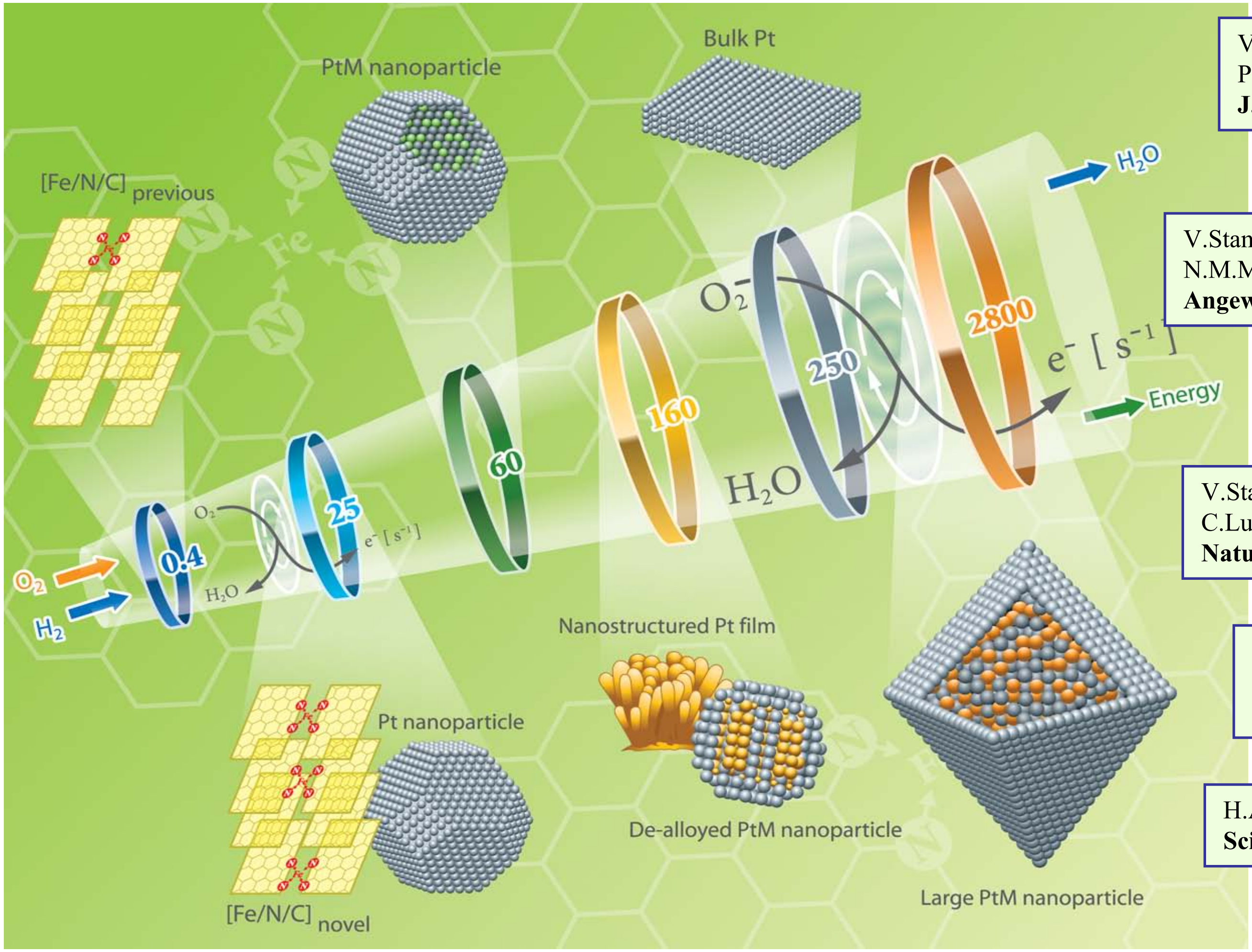
3.1 New PtM_1M_2 catalysts with higher activity and improved durability (40%)

3.2 Carbon support vs. nanostructured thin film catalysts (30%)

3.3 MEA testing (50 cm^2) of the optimized catalysts (15%)

3.4 Scale up of the catalyst fabrication in lab environment (15%)

Relevant Prior Work



V.Stamenkovic, B.S.Mun, K.J.J.Mayrhofer, P.N.Ross, N.M.Markovic
J. Am.Chem.Soc., 128(2006)8813

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Angew.Chem.Int.Ed., 45(2006)2897

V.Stamenkovic, B.S.Mun, M. Arenz, K.J.J.Mayerhofer, C.Lucas, G.Wang, P.N.Ross, N.M.Markovic
Nature Materials, 6(2007)241

V.Stamenkovic, B.Flower, B.S.Mun, G.Wang, P.N.Ross, C.Lucas, N.M.Markovic
Science, 315(2007)493

H.A. Gasteiger, N.M.Markovic
Science, 3124(2009)48

Nanosegregated particles should be the best catalysts for the ORR

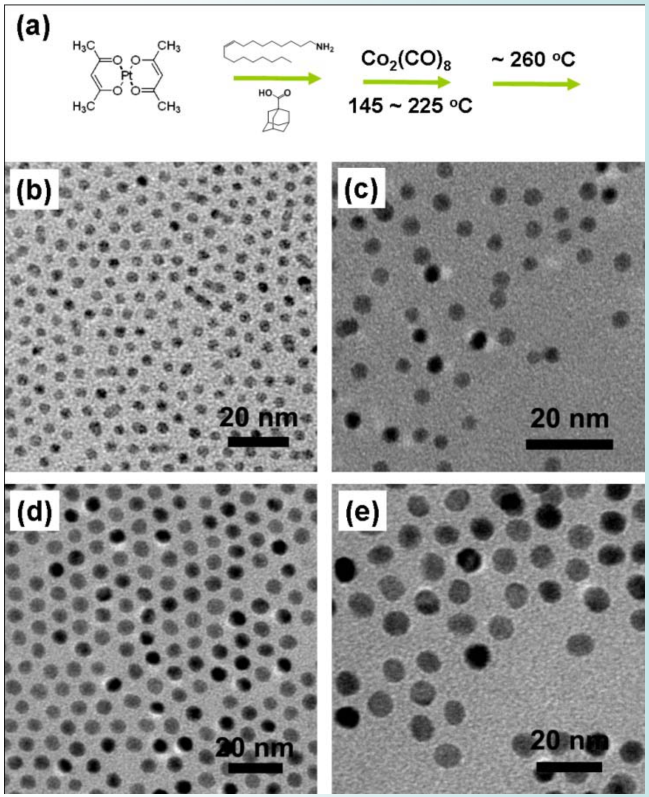
Guiding principles:

maximize activity by minimizing surface coverage of spectators

without compromising activity protect 3d elements by additional Pt layer

Technical Accomplishments FY09, FY10: *Bimetallic Nanocatalysts*

Colloidal solvo - thermal approach has been developed for monodispersed PtM 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

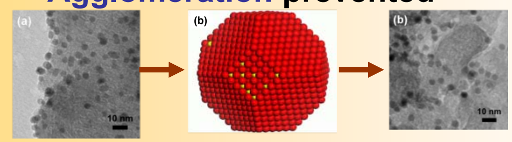
Specific Activity increases with particle size: 3 < 4.5 < 6 < 9nm

Mass Activity decreases with particle size

Optimal size particle size ~5nm

2° Temperature induced segregation in Pt-bimetallic NPs

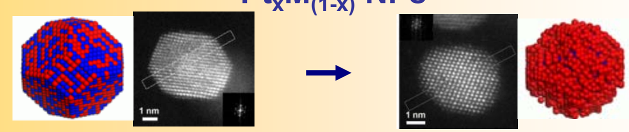
Agglomeration prevented



Optimized annealing temperature 400-500°C

3° Surface chemistry of homogeneous Pt-bimetallic NPs

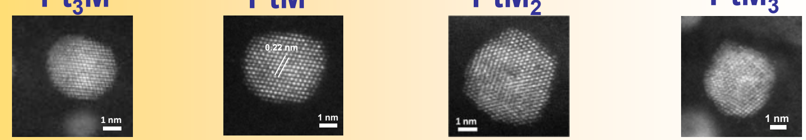
$Pt_xM_{(1-x)}$ NPs



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

4° Composition effect in Pt-bimetallic NPs

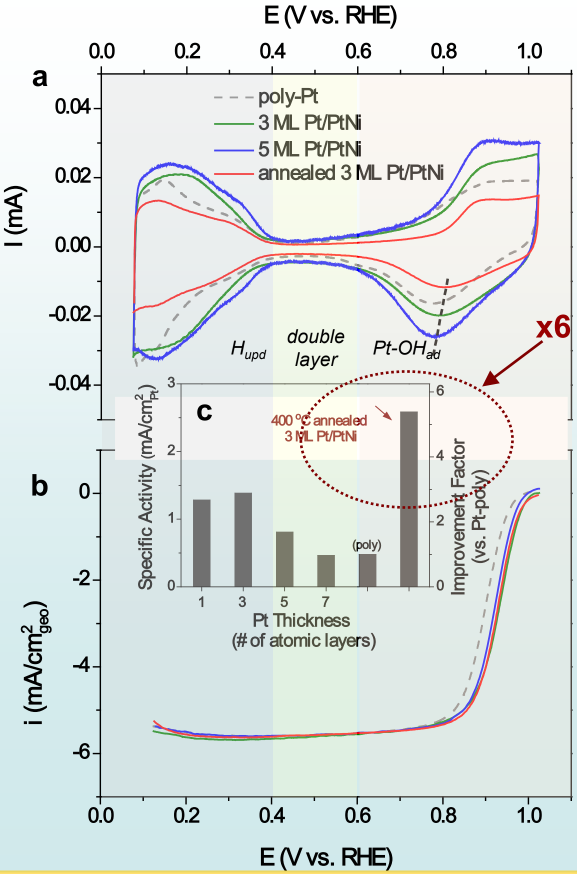
Pt_3M | PtM | PtM_2 | PtM_3



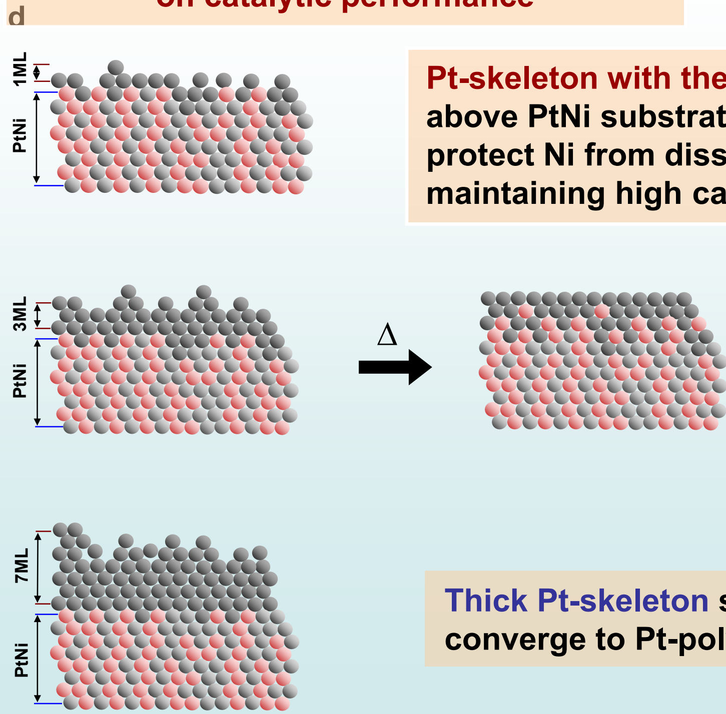
Optimal composition of Pt-bimetallic NPs is PtM

Technical Accomplishments: *Optimization of Pt-skeleton thickness*

Thin Pt bi/multi metallic film studies: **Physical vapor deposition over the substrates with adjustable compositions**



Pt-skeleton thickness has direct influence on catalytic performance



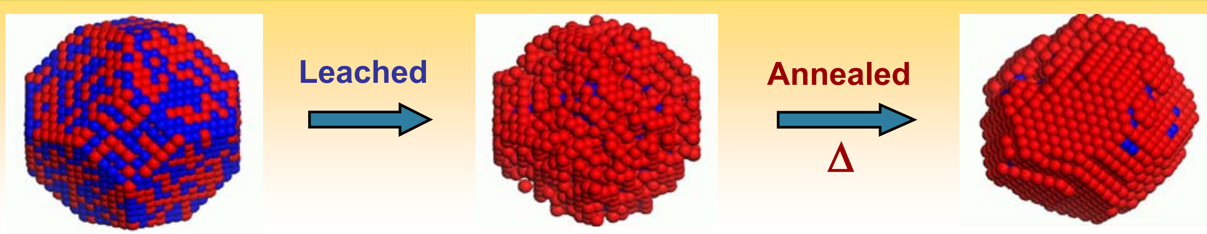
Pt-skeleton with the thickness of 3ML above PtNi substrate can effectively protect Ni from dissolution, while maintaining high catalytic activity

Annealed Pt-skeleton surface forms multilayered skin type of surface with superior catalytic properties (x6 vs. Pt-poly)

Thick Pt-skeleton surfaces converge to Pt-poly properties

Transfer to nanoscale systems

As Synthesized

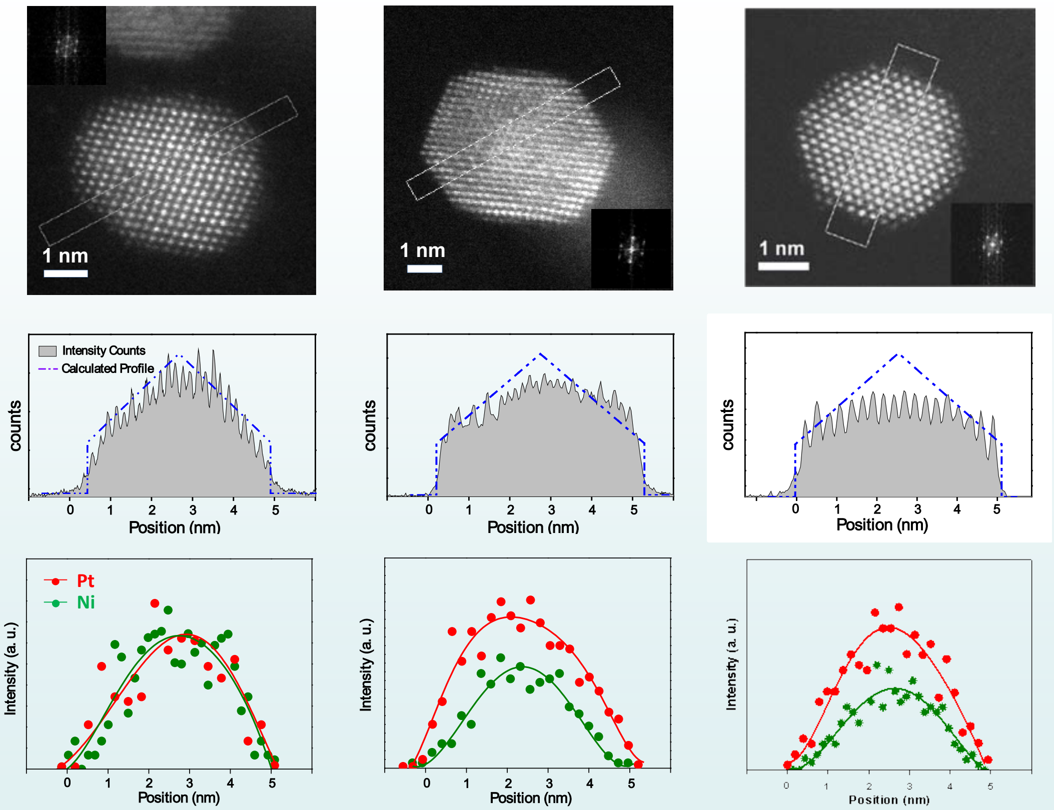


Multilayered Pt-skin NP

To be published in 2011

Technical Accomplishments: *Fine Tuning of PtM catalytic properties*

HRTEM | HAADF – STEM | EDX

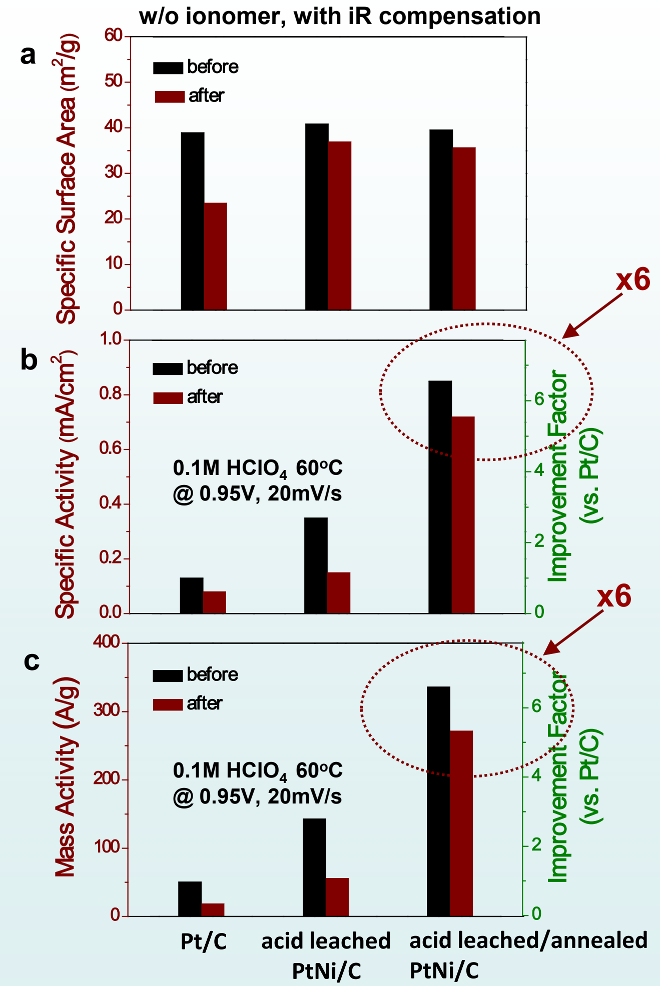


Synthesized PtNi NPs have homogeneous distribution of Pt, Ni

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

Multilayered Pt-skin surfaces confirmed for PtNi annealed NPs

Electrochemical Characterization



RDE: PtNi NPs with multilayered skin have ~x6 higher specific and mass activities than Pt/C after 20K cycles (0.6 - 1.05V)

To be published in 2011

Technical Accomplishments: *RDE and MEA Testing of PtNi NPs*

General Motors R & D
Electrochemical Energy Research Lab

RDE

0.1M $HClO_4$, 60°C, @ 0.90V, 1600 rpm, 20 mV/s, w/o ionomer w/o iR compensation

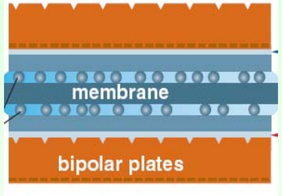
RDE: PtNi/C NPs with multilayered skin have ~10 times specific ~4 times mass activities of Pt/C catalyst in the initial cycle SA~2 mA/cm^2_{Pt}, MA~0.8 A/mg_{Pt}

RDE: Specific activity drops from sweep to sweep by 20%
Lower values for SA are obtained for sweep rate of 5 mV/s ~ 1.2 mA/cm^2_{Pt}

RDE: Specific activity was recovered to initial value of ~2mA/cm^2_{Pt}

Deactivation due to degradation of the catalyst was ruled out, and it depends on the presence of spectator/blocking species (ions, oxides, impurities)

MEA



50 cm^2, 25μ DuPont NRE membrane, 80°C, 32% RH, 150kPa_{abs}, @ 0.90V, H_2 - Air 20K cycles from 0.6-0.925V

MEA: PtNi/C NPs with multilayered skin have ~3 times higher specific and mass activities than benchmark Pt/C catalyst: SA~0.8mA/cm^2_{Pt}, MA~0.35A/mg_{Pt}

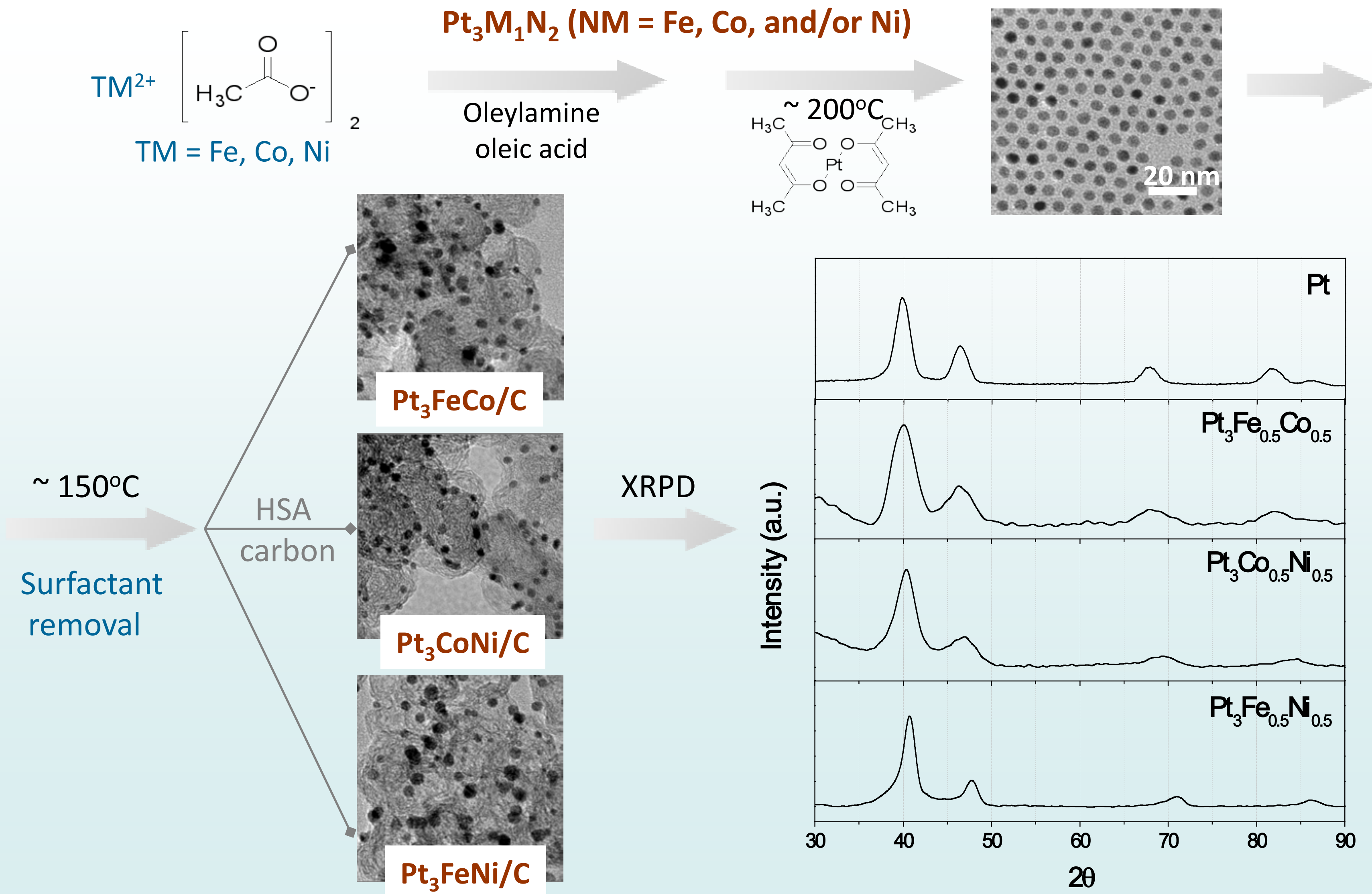
MEA: After 20K cycles activity loss was only 12% (~ 0.7 mA/cm^2_{Pt}), while commercially available Pt/C and PtM/C catalysts suffer loss of 20-50%

MEA/EXAFS: Before and after 20K cycles in MEA Pt-Pt and Pt-Ni distances remain stable indicating no change in catalyst morphology

PtNi/C is highly durable catalyst, which meets DOE 2015 targets for specific activities and exceeds anticipated targets for stability

To be published in 2011

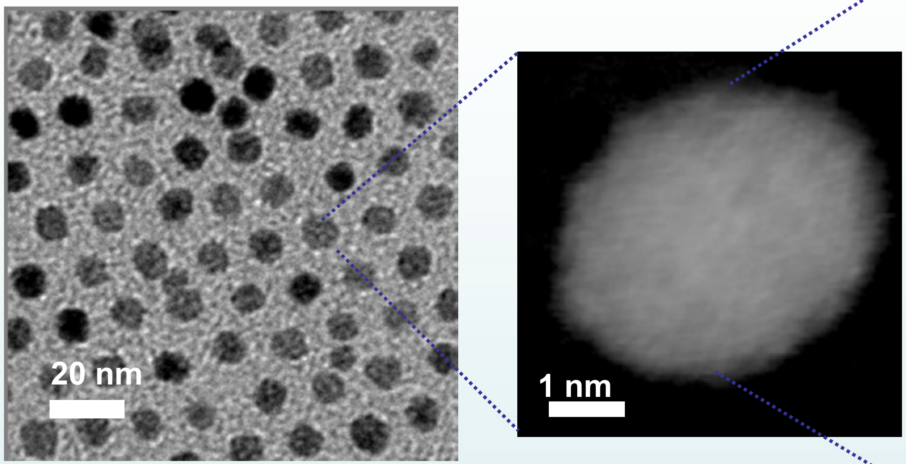
Technical Accomplishments: *Synthesis of Pt Ternary Alloy NPs*

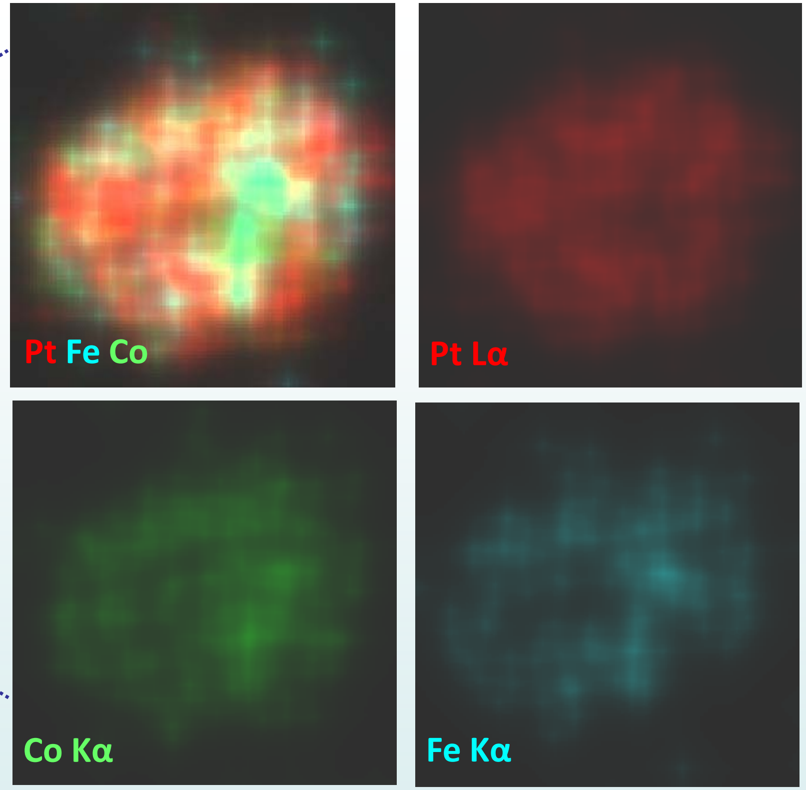


Synthesis of homogeneous and monodisperse ternary alloy nanoparticles has been accomplished

Pt_3FeCo

TEM | HAADF – STEM | EDX





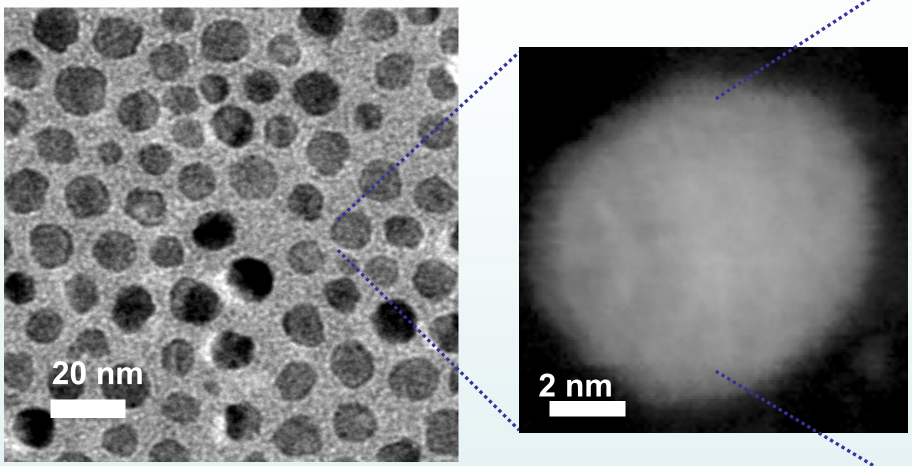
TEM: uniform particle size distribution. The average particle size is about 6 nm

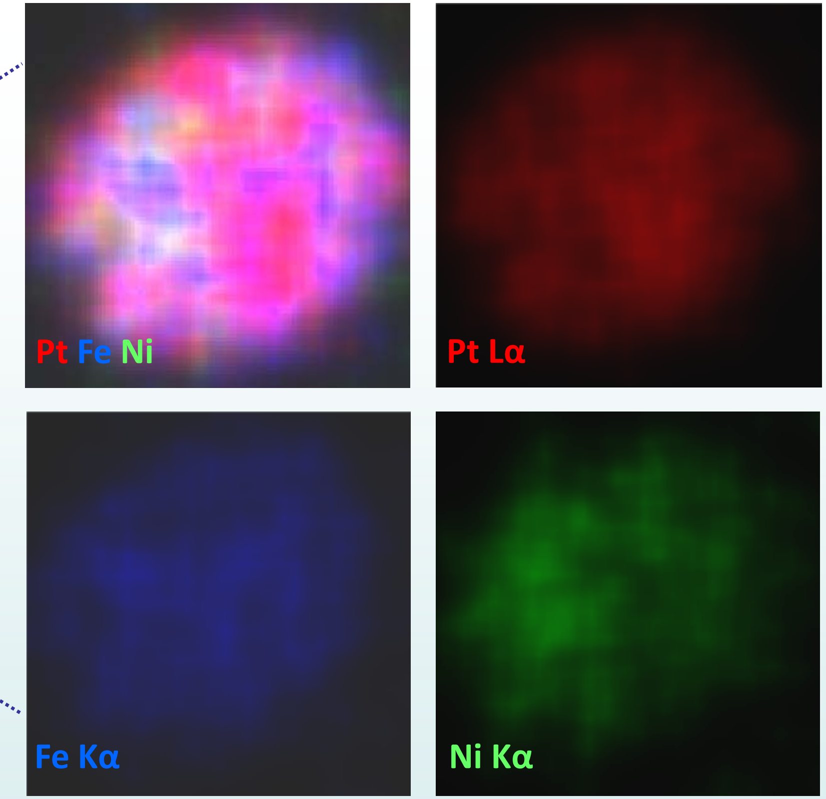
HAADF-STEM elemental mapping: homogeneous distribution of alloying elements

Technical Accomplishments: *Characterization of Pt_3FeNi NPs*

Pt_3FeNi

TEM | HAADF – STEM | EDX





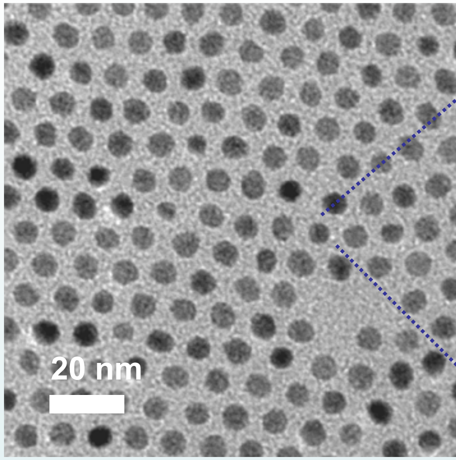
TEM: Less uniform particle size distribution. The particle size is about 2-7 nm

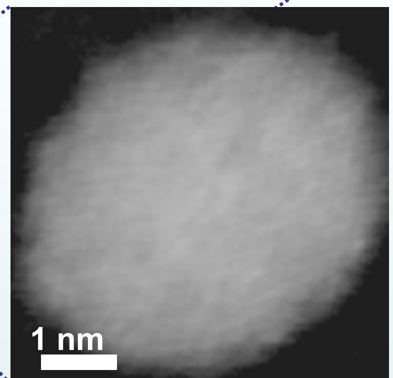
HAADF-STEM elemental mapping: Homogeneous distribution of alloying elements

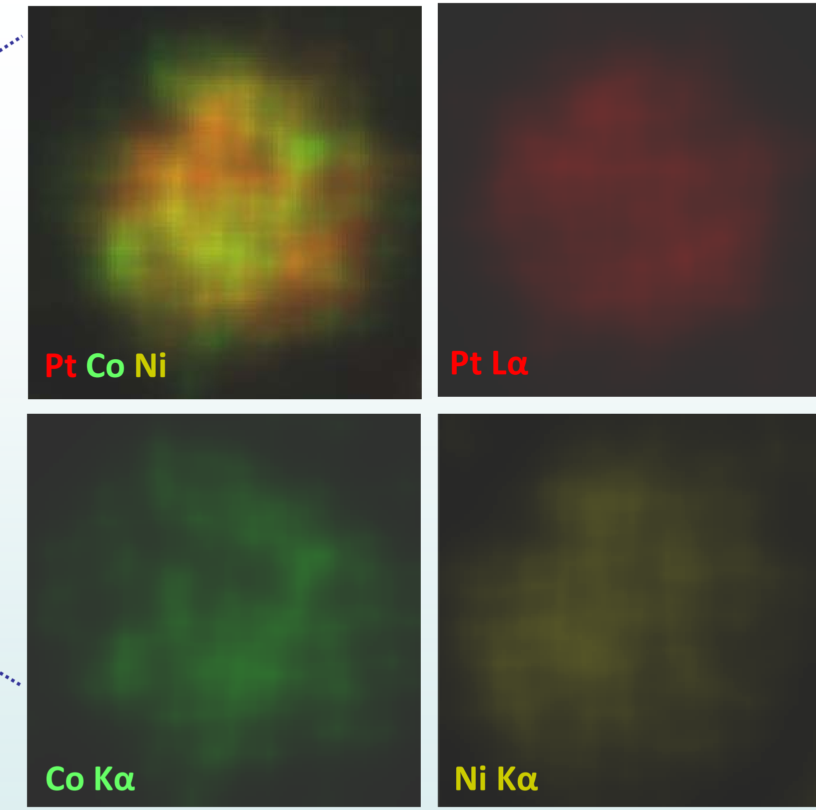
Technical Accomplishments: *Characterization of Pt_3CoNi NPs*

Pt_3CoNi

TEM | HAADF – STEM | EDX





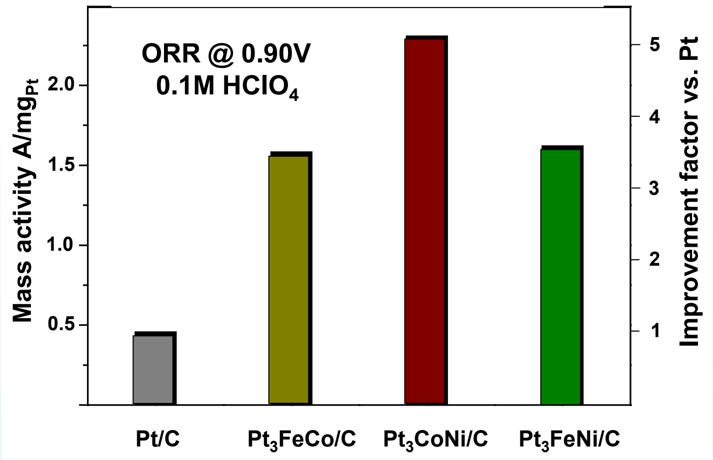


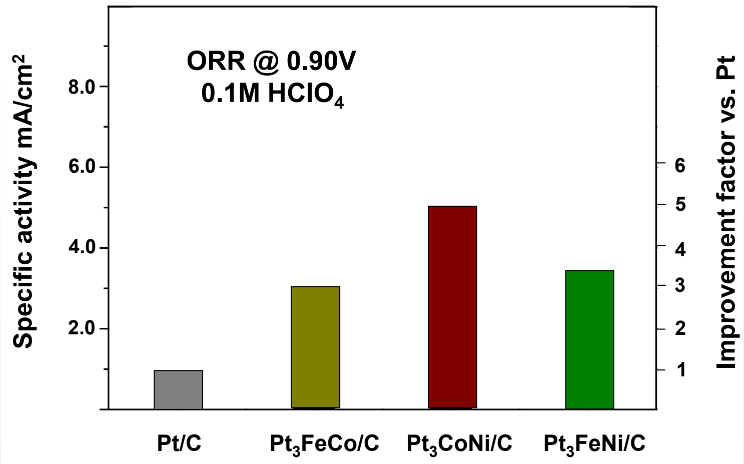
TEM: Highly uniform particle size. The average particle size is 6 nm

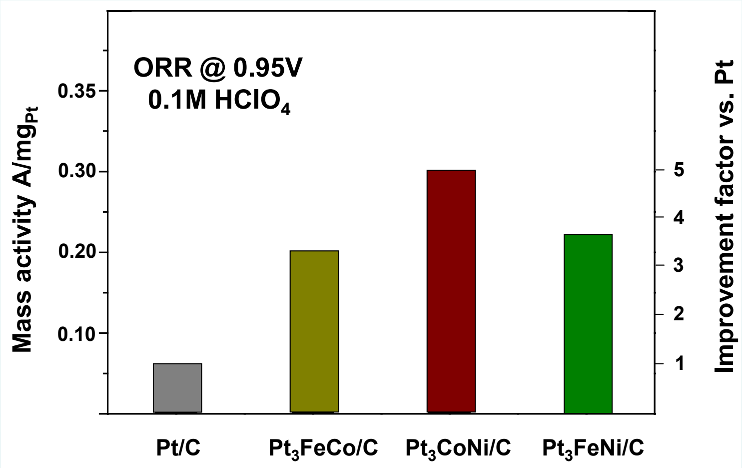
HAADF-STEM elemental mapping: homogeneous distribution of alloying elements

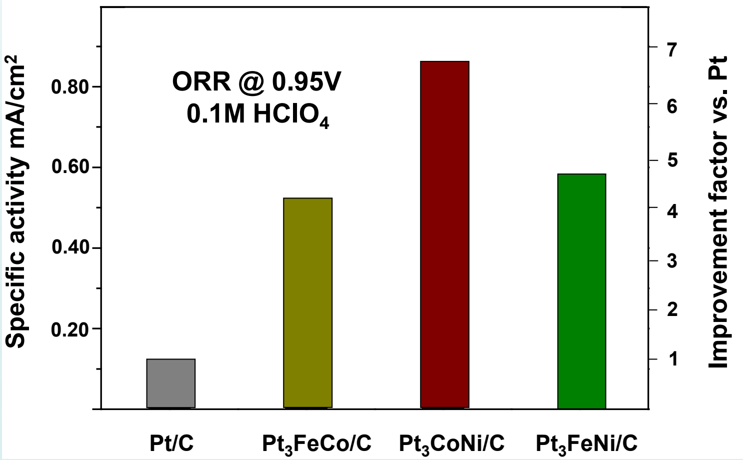
Technical Accomplishments: *ORR Activity of Pt Ternary Alloy NPs*

Electrochemical RDE characterization: 60ºC, 1600rpm, 20mV/s







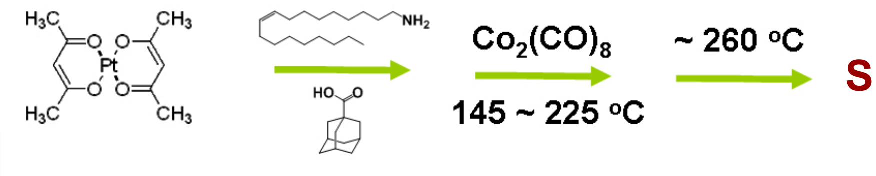


RDE: As-prepared Pt-ternary alloys with Pt-skeleton surfaces exhibit higher activity (IF~5) for ORR than corresponding Pt-bimetallic NPs (IF~2.5) vs. Pt/C

ORR Activity Trend: $Pt < Pt_3Fe < Pt_3Ni < Pt_3FeCo < Pt_3FeNi < Pt_3Co < Pt_3NiCo$

To be published 2011

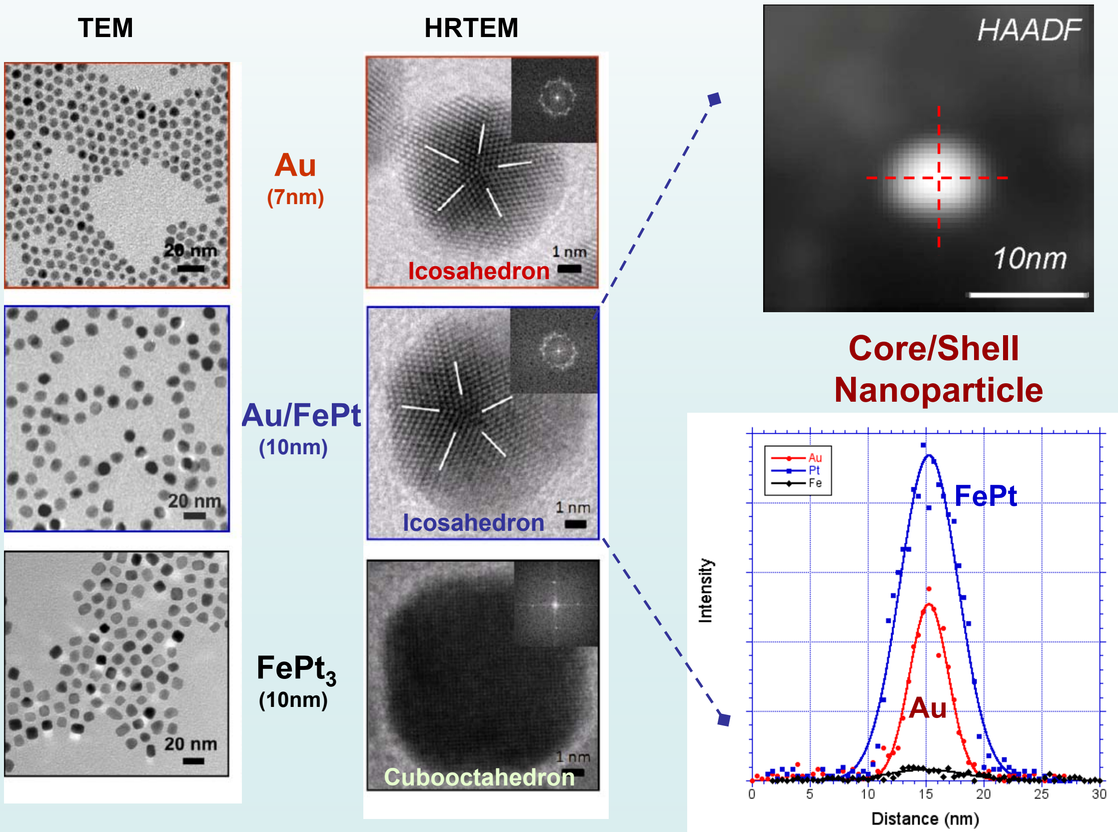
Technical Accomplishments: *Pt Ternary System Au/$FePt_3$*

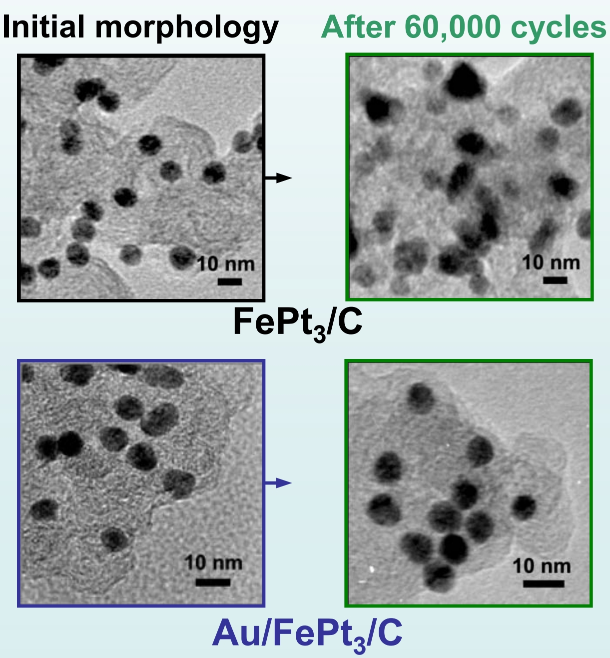


Shape Controlled Core/Shell Particles Au/$FePt_3$

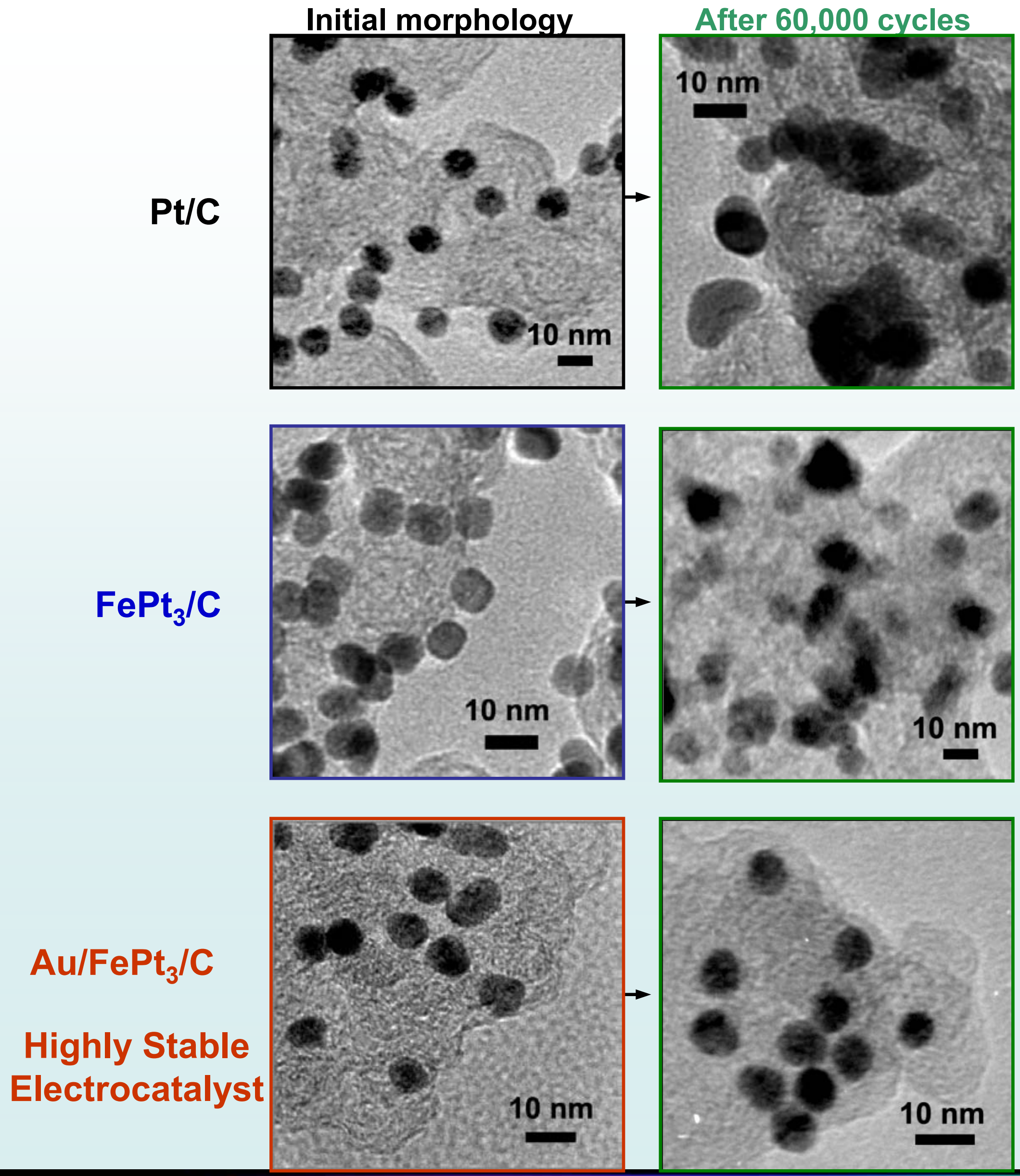
Icosahderal Au core (7nm) is synthesized chemically and coated with 1.5nm Pt-bimetallic shell

Multimetallic Electrocatalyst :
Maintain high activity of bimetallic catalysts while enhancing stability





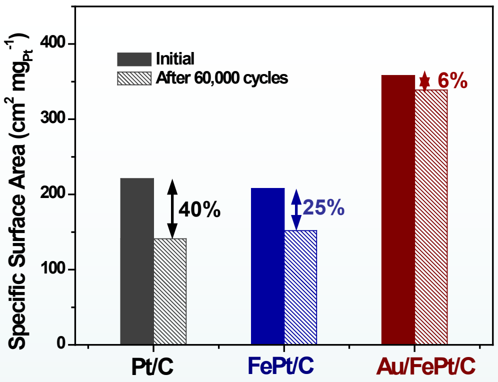
Technical Accomplishments: *Pt Ternary System Au/FePt₃*



Au/$FePt_3$/C

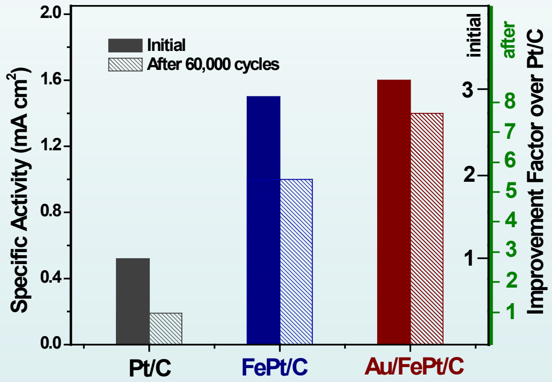
Surface Area Loss

<10%



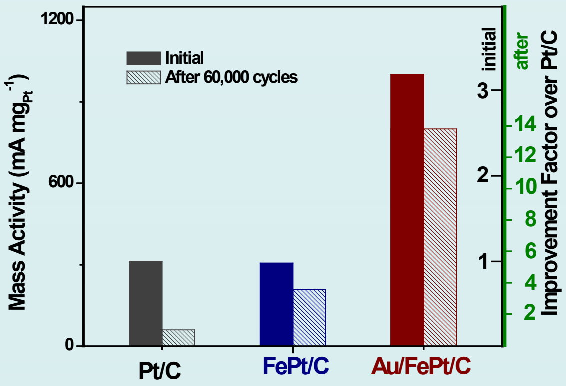
Spec. Activity

>7 times



Mass. Activity

>10 times



Collaborations

PARTNERS

- **Oak Ridge National Laboratory** – HRTEM
- **Jet Propulsion Laboratory** – Alloying and Combinatorial Approach
- **Brown University** – Chemical Synthesis
- **Indiana University Purdue** – Theoretical Modeling
- **3M** – Testing

TECHNOLOGY TRANSFER

- **GM** – Collaboration to utilize highly active Pt-alloy catalysts
- **Argonne National Laboratory** – Nanoscale fabrication (CNM)

Future Work

FY 2011

- **Composition – function relationship for PtM_1M_2 systems**
- **Synthesis and characterization of new nanosegregated PtM_1M_2 alloys and thin films**
- **Activity/stability evaluation of nanosegregated PtM_1M_2 alloys and TM films catalysts**
- **Activity/stability optimization of the most promising nanosegregated systems**
- **Fabrication of the best PtM_1M_2 catalysts and testing in MEA**

FY 2012

- **Continuous activity/stability evaluation and optimization of MEA tested catalysts**
- **Scaling up synthesis methods for larger production of PtM_1M_2 catalysts**
- **Laboratory and MEA activity/stability evaluation of the most promising catalysts**

Summary

Bimetallic PtM systems:

RDE: PtNi NPs with multilayered skin have ~x6 higher specific and mass activities than Pt/C after 20K cycles (0.6 - 1.05V)

MEA: PtNi/C NPs with multilayered skin have ~3 times higher specific and mass activities than benchmark Pt/C catalyst: SA~0.8mA/cm^2_{Pt}, MA~0.35A/mg_{Pt}

MEA/EXAFS: Before and after 20K cycles in MEA Pt-Pt and Pt-Ni distances remain stable indicating no change in catalyst morphology

PtNi/C is highly durable catalyst, which meets DOE 2015 targets for specific activities and exceeds anticipated targets for stability (~12% loss)

Ternary PtM_1M_2 systems:

TEM: Highly uniform particle size. The average particle size is 6 nm

HAADF-STEM elemental mapping: homogeneous distribution of alloying elements

RDE: As-prepared Pt-ternary alloys with Pt-skeleton surfaces exhibit higher activity (IF~5) for ORR than corresponding Pt-bimetallic NPs (IF~2.5) vs. Pt/C

Revealed the importance of nanosegregated concentration profiles of PtM_1M_2 catalysts for high specific and mass activities