



... for a brighter future

# 2010 DOE Annual Merit Review

Announcement No: **DE-PS36-08GO98010**

Topic: **1A**

## **Nanosegregated Cathode Catalysts with Ultra-Low Platinum Loading**

**Argonne National Laboratory  
Materials Science Division**

**PI: Nenad M. Markovic**

**Co-PI: Vojislav R. Stamenkovic**



U.S. Department  
of Energy

UChicago ►  
Argonne<sub>LLC</sub>



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

Project ID#  
FC008

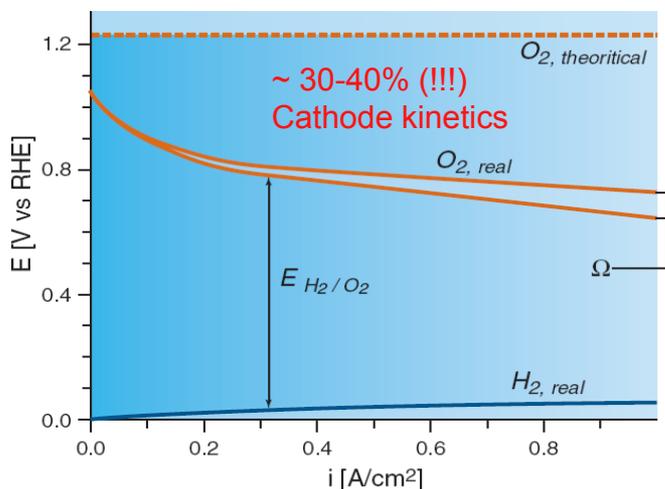
This presentation does not contain any proprietary,  
confidential, or otherwise restricted information

# Overview

## Timeline

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

## Barriers



- The main limitations: CATHODE

1) Durability (Pt dissolves: power loss)

2) High content of Pt = High Cost (\$75/g)

3) Poor activity: Pt/C = Pt-poly/10

## Budget

- Total Project funding \$ 3.6M
  - DOE share: 80 %
  - Contractor share: 20%
- Received in FY09: \$ 300K
- Funding for FY10: \$ 564.4K

## Subcontractors:

- **Oak Ridge National Laboratory** – Karren More
- **Jet Propulsion Laboratory** – S.R. Narayan
- **Brown University** – Shouheng Sun
- **Indiana University Purdue** – Goufeng Wang
- **3M Company** – Radoslav Atanasoski

# Objectives-Relevance

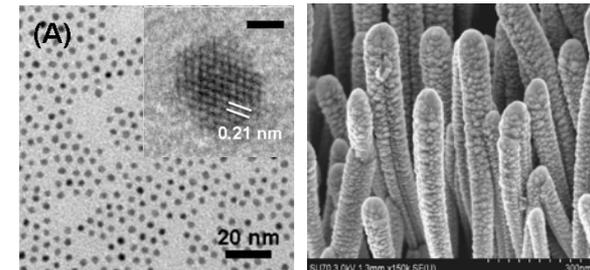
The main focus of ongoing DOE Fuel Cell Hydrogen Program is fundamental understanding of the oxygen reduction reaction on PtM bimetallic and PtM<sub>1</sub>M<sub>2</sub> (M<sub>1</sub>=Co,Ni; M<sub>2</sub>=Fe, Mn, Cr, V, Ti etc) ternary systems that would lead to the development of highly-efficient and durable *real-world nanosegregated Pt-skin catalysts with low-Pt content*

## DOE Technical Targets

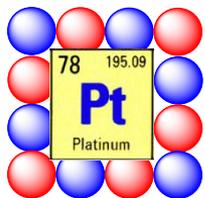
- Specific activity @0.9V<sub>iR-free</sub>: 720 μA/cm<sup>2</sup>
- Mass activity @0.9V: 0.44 A/mg<sub>Pt</sub>
- Electrochemical area loss: < 40%
- Catalyst support loss: < 30%
- PGM Total content: 0.2 g/kW
- PGM Total loading: 0.2 mg/cm<sup>2</sup><sub>electrode</sub>
- Cost\*: \$ 30/kW<sub>e</sub>
- Durability w/cycling (80°C): 5000 hrs  
\*based on Pt cost of \$450/troy ounce

## ANL Technical Targets

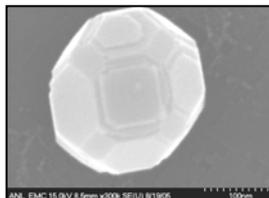
- Specific activity @ 0.9V<sub>iR-free</sub>  
2015 DOE target x 3
- Mass activity @ 0.9V<sub>iR-free</sub>  
2015 DOE target x 3
- Electrochemical area loss  
2015 DOE target
- PGM Total content  
< 0.1g/kW



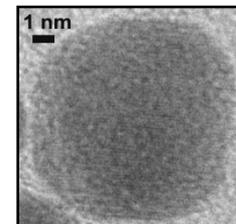
# Approach



EXTENDED Multi-M SURFACES



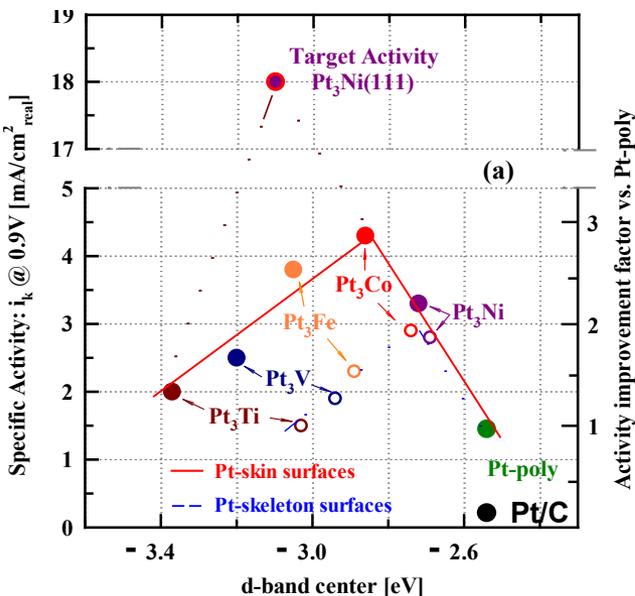
MODEL NANOPARTICLES



REAL NANOPARTICLES

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

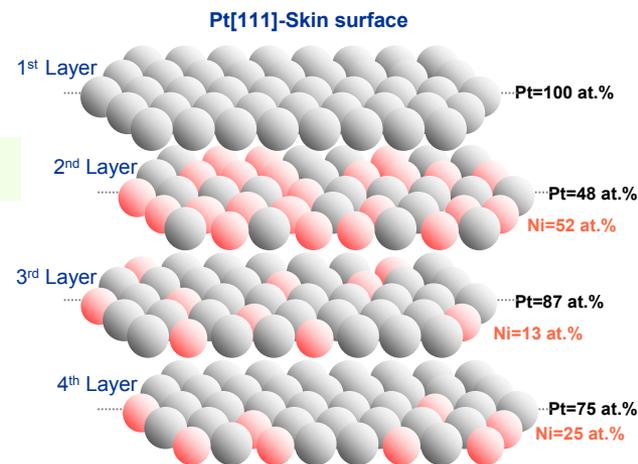
## Well-Defined Systems



## Advanced Nanoscale Catalyst



## Nanosegregated Profile



**Pt<sub>3</sub>Ni((111)-Skin** is the most active catalyst for the oxygen reduction reaction, and it is ~100 times more active than the state-of-the-art Pt/C catalysts. Design of real-world bi-/multi-metallic catalysts with this activity is our goal.

## Approach / Milestone

(Go-No Go Decision Met)

### **Milestone 1.** Fundamental understanding (2009/10)

(Accomplished)

- 1.1 Resolved electronic/atomic structure and segregation profile (85%)
- 1.2 Confirmed reaction mechanism of the ORR (95%)
- 1.3 Improved specific and mass activity (95%)

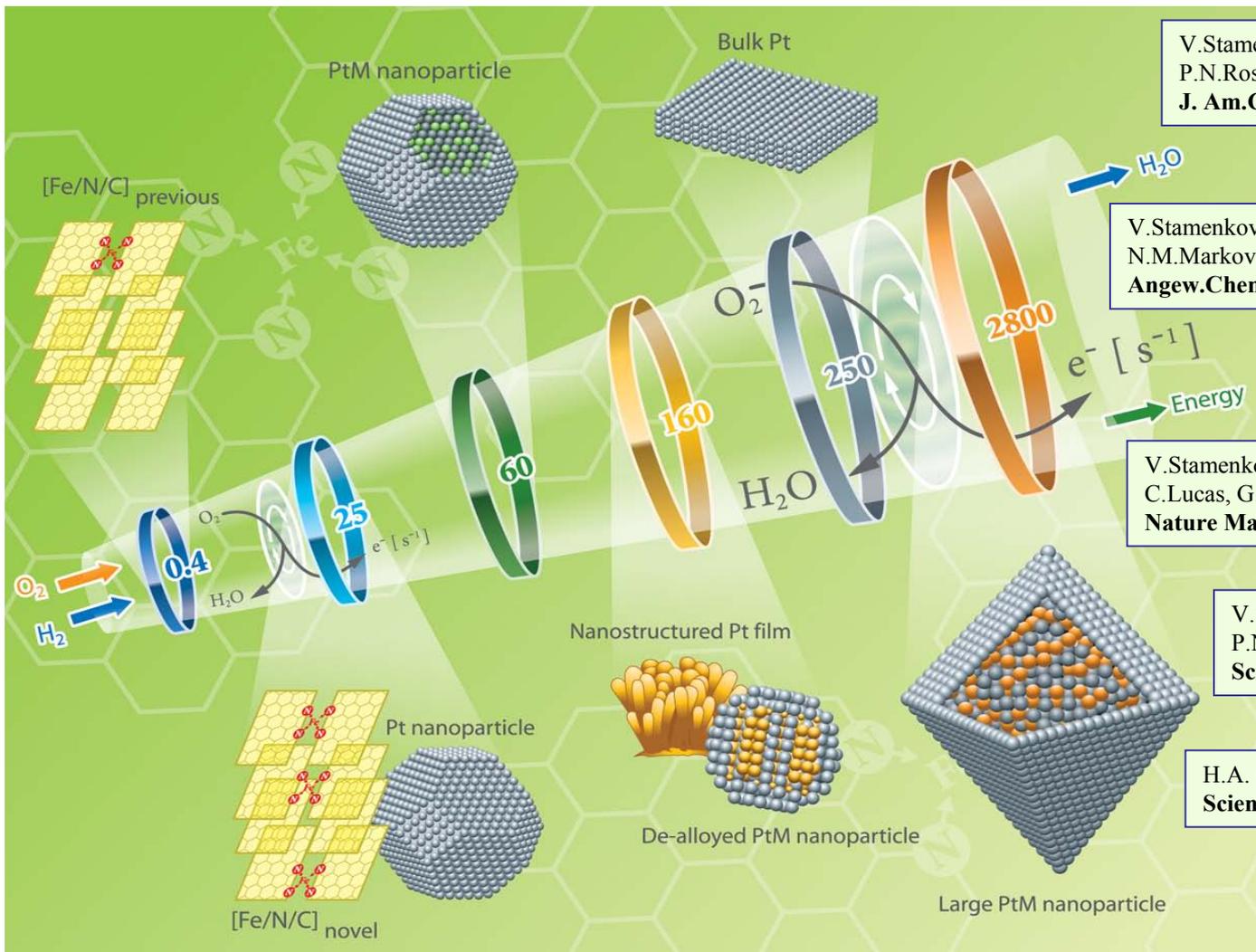
### **Milestone 2.** Synthesis and characterization (2009/10)

- 2.1 Physical methods: TM films (5-10 layers), nanoparticles (5-300 nm) (90%)
- 2.2 Established chemical methods: colloidal and impregnation synthesis (90%)
- 2.3 Characterization: Ex-situ (UHV, TEM) and in-situ (SXS, EC) (90%)
- 2.4 Theoretical modeling (DFT, MC) methods (90%)

### **Future Milestone 3.** Fabrication and testing

- 3.1 New PtM<sub>1</sub>M<sub>2</sub> catalyst to increase catalytic activity and decrease dissolution
- 3.2 Carbon support vs. nanostructured thin film catalysts
- 3.3 MEA testing (50 cm<sup>2</sup>)
- 3.4 Short stack testing verification (>300cm<sup>2</sup>)

# 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**

V.Stamenkovic, B.S.Mun, K.J.J.Mayrhofer, P.N.Ross, N.M.Markovic, J.Rossmeisl, J.Greeley, J.K. Norskov  
**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**

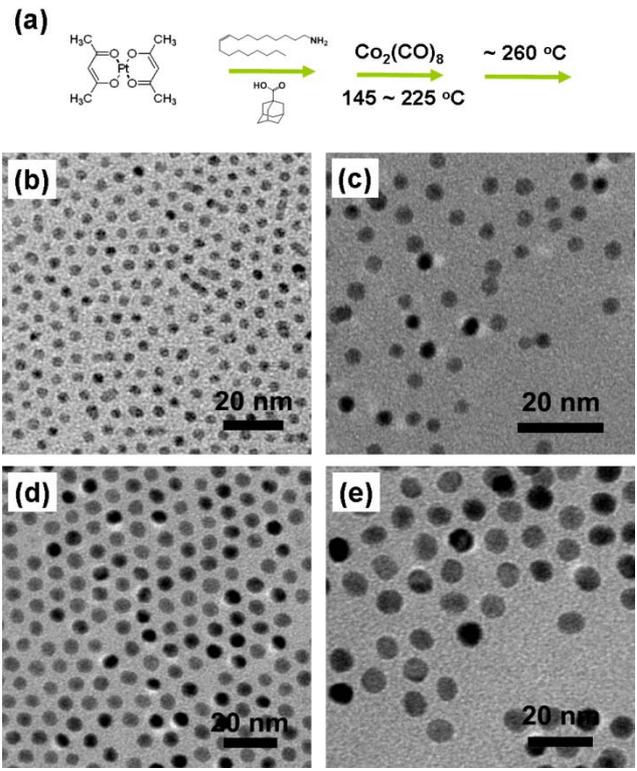
V.Stamenkovic, B.Flower, B.S.Mun, G.Wang, P.N.Ross, C.Lucas, N.M.Markovic  
**Science, 315(2007)493**

H.A. Gasteiger, N.M.Markovic  
**Science, 312(2009)48**

**Nanosegregated particle would be the best catalysts for the ORR**

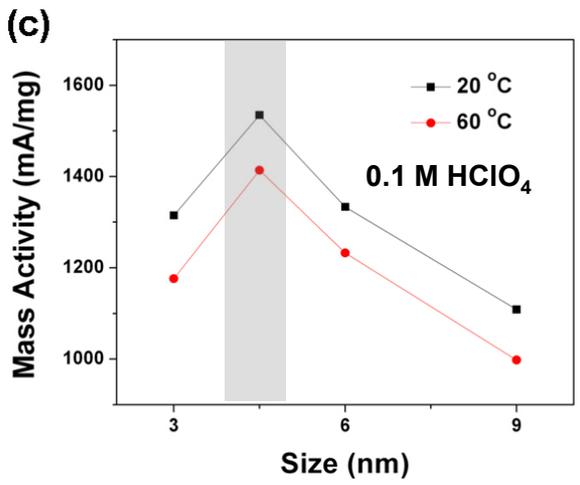
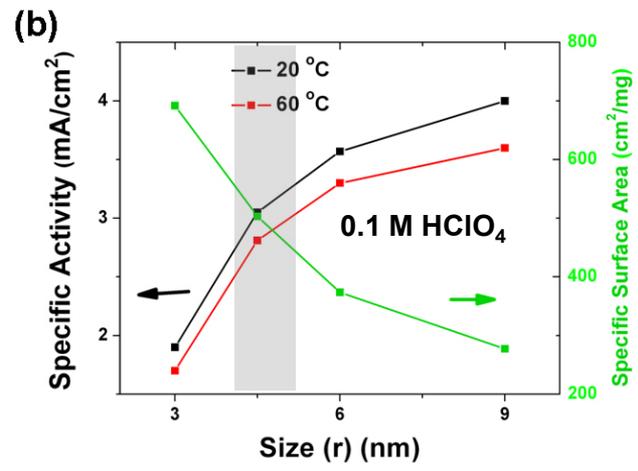
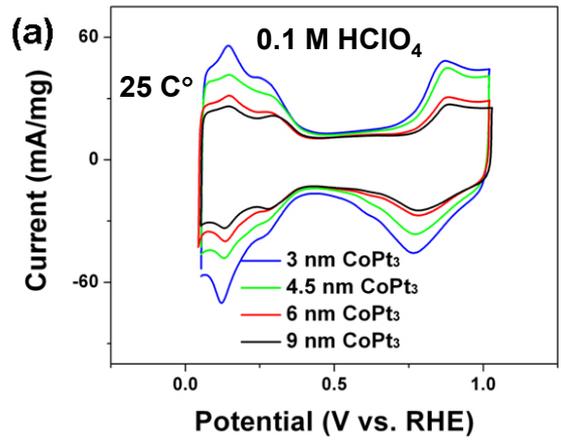
# Technical Accomplishments: Particle Size Effect

**Colloidal deposition approach** is used to synthesize (a) monodispersed Pt<sub>3</sub>Co bimetallic NPs with diameter of 3, 4.5, 6 and 9nm



**Particle size** is determined by analyzing TEM images (b-e)

## Particle size effect applies to bimetallic NPs

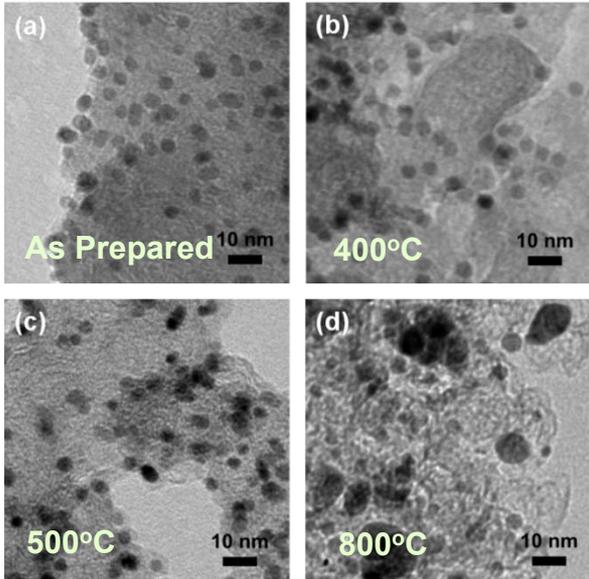


**Specific surface area** is determined from  $\Theta_{Hupd}$

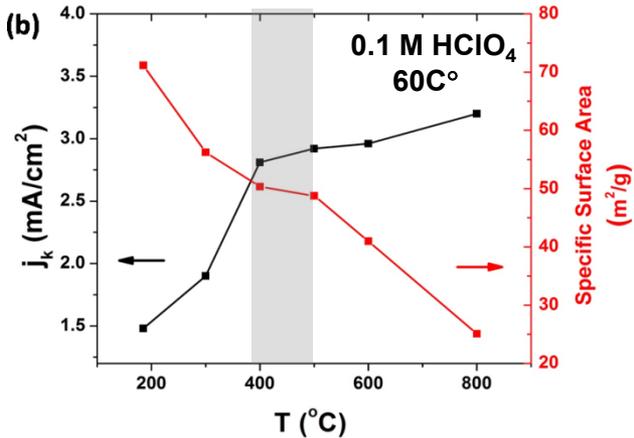
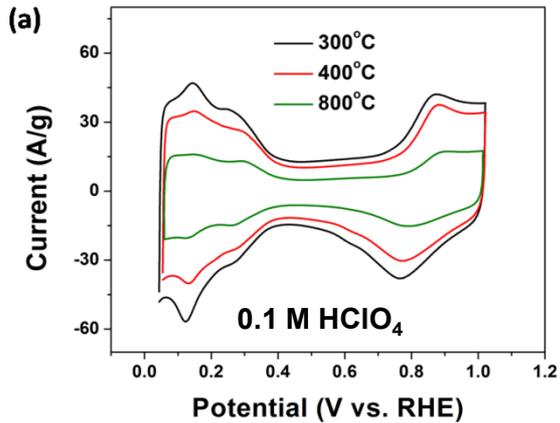
**Specific Activity** increases with particle size: 3 < 4.5 < 6 < 9nm

**Mass Activity** decreases with particle size: optimal size ~5nm

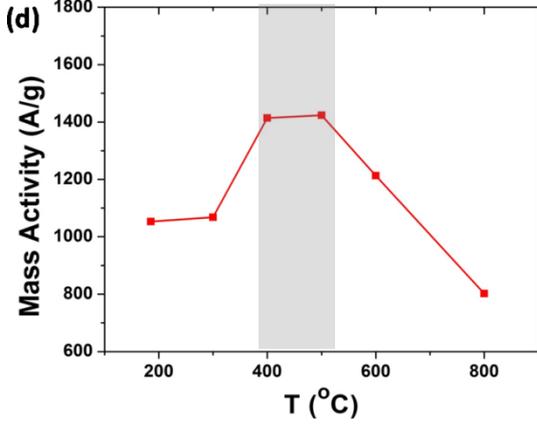
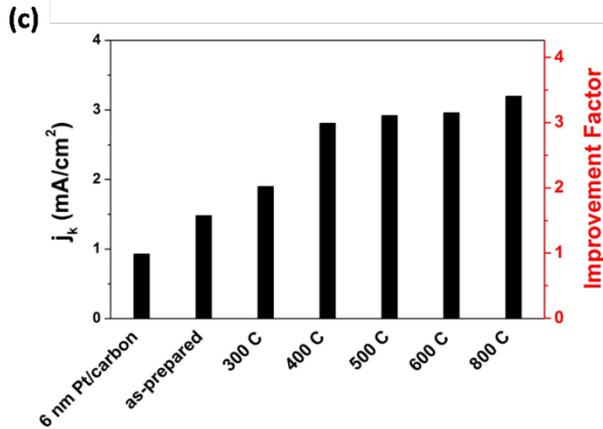
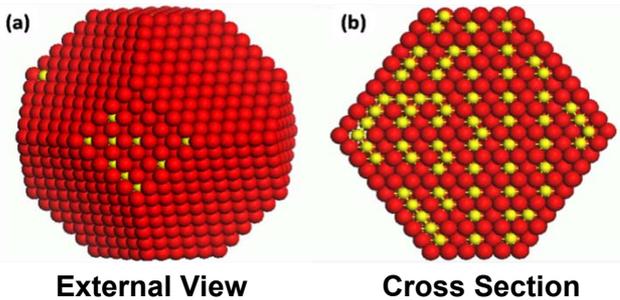
# Technical Accomplishments: *Temperature-induced Segregation*



**Temperature Induced Segregation:** apply 400 to 500°C to optimize catalytic activity of the ORR on PtCo bimetallic NPs



**TEM:** no agglomeration below 500°C

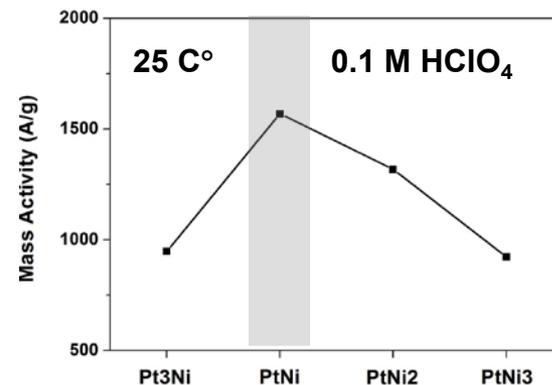
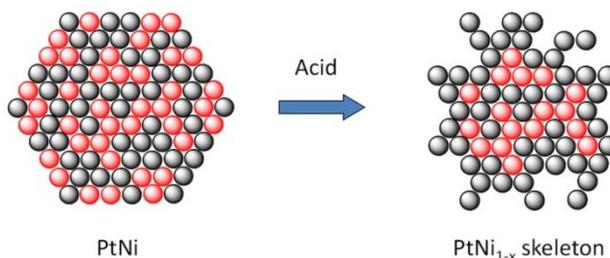
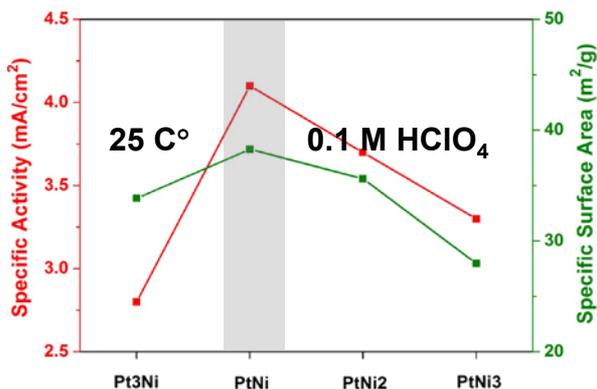
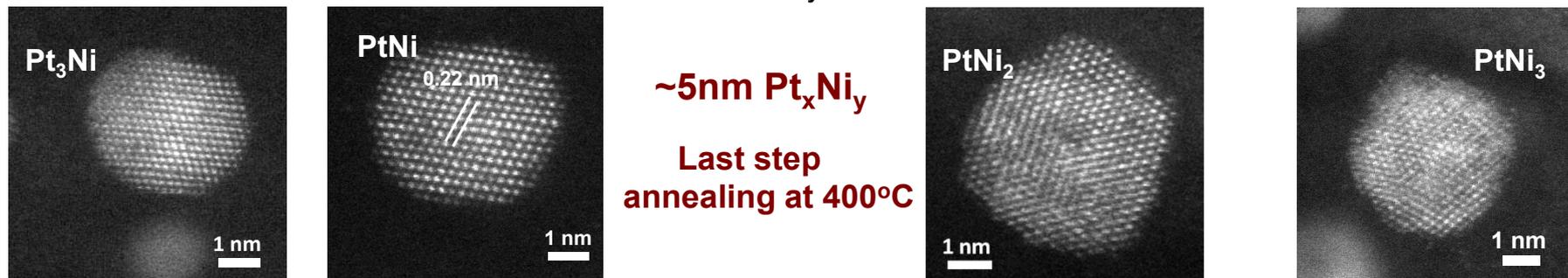


**MC simulations at 400°C** confirmed segregation profile of Pt<sub>3</sub>Co NPs, which was experimentally observed for extended surfaces

**Annealing above 500°C** provides small increase in specific activity but significant decrease in mass activity of Pt<sub>3</sub>Co NPs

# Technical Accomplishments: *Composition Effect*

Colloidal method is used to synthesize  $Pt_xNi_y$  NPs with 3:1, 1:1, 1:2 and 1:3 atomic ratio



Maximum activity obtained for as-synthesized NPs with 1:1 Pt to Ni atomic ratio

In acidic environment, atomic % of Ni in  $Pt_xNi_y$  NPs decreases due to dissolution of Ni surface atoms



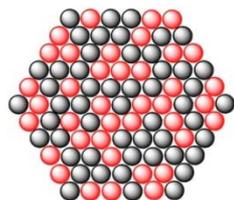
Segregation of Pt at 400°C is not complete in  $Pt_xNi_y$  NPs, which induces dissolution of Ni

# Technical Accomplishments: *Tailoring of Nanosegregated Layers*

Temperature annealing protocol used to transform  $\text{PtNi}_{1-x}$  skeletons to  $\text{PtNi/Pt}$  core/shell NPs with 2-3 atomic layers thick Pt shell

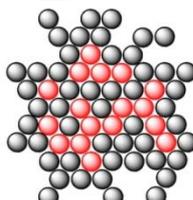
Models

As-prepared PtNi



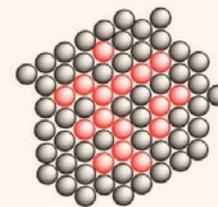
Acid

$\text{PtNi}_{1-y}$  Skeleton

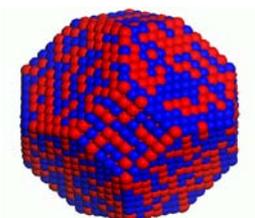


Annealing  
400°C

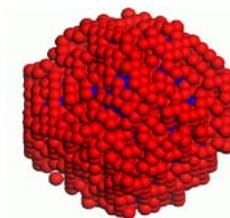
PtNi/Pt core/shell



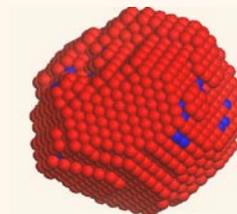
Monte Carlo Simulations



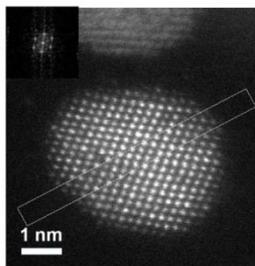
→



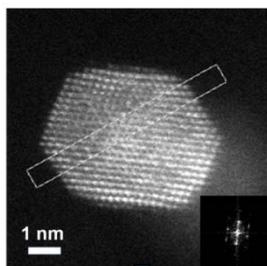
→



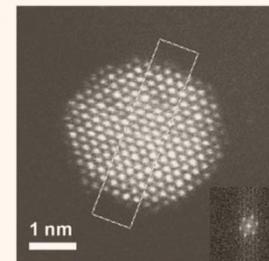
HRTEM characterization



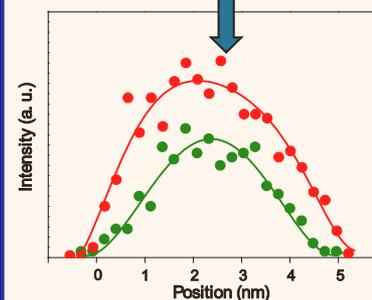
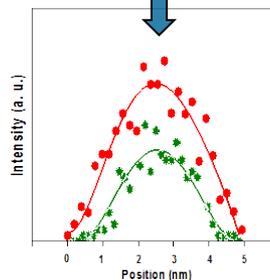
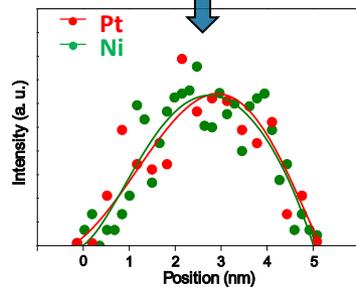
→



→

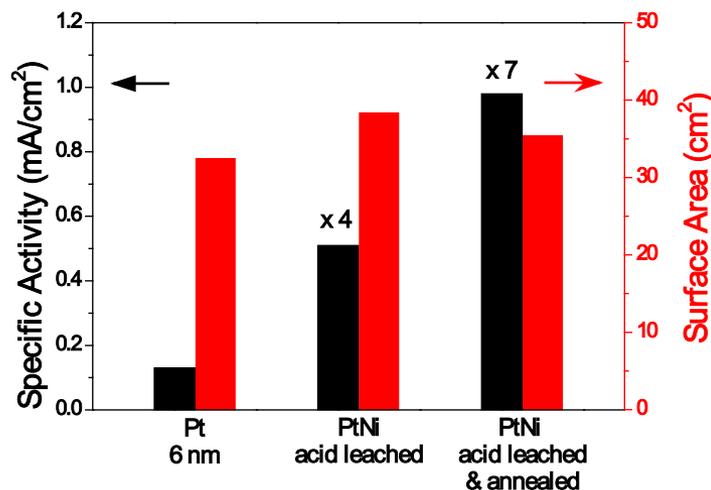
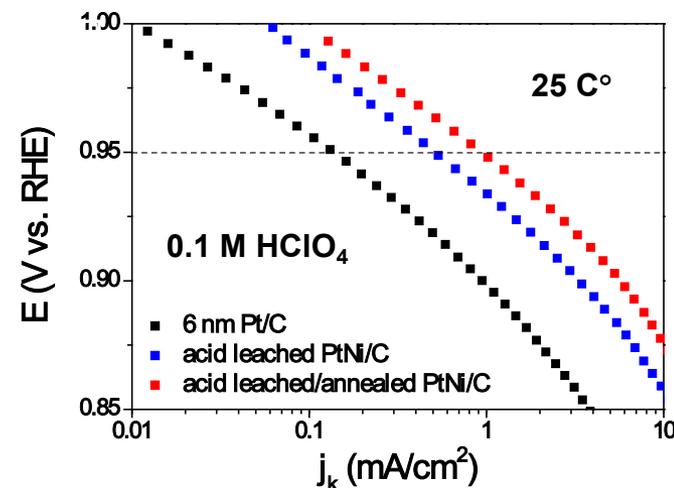
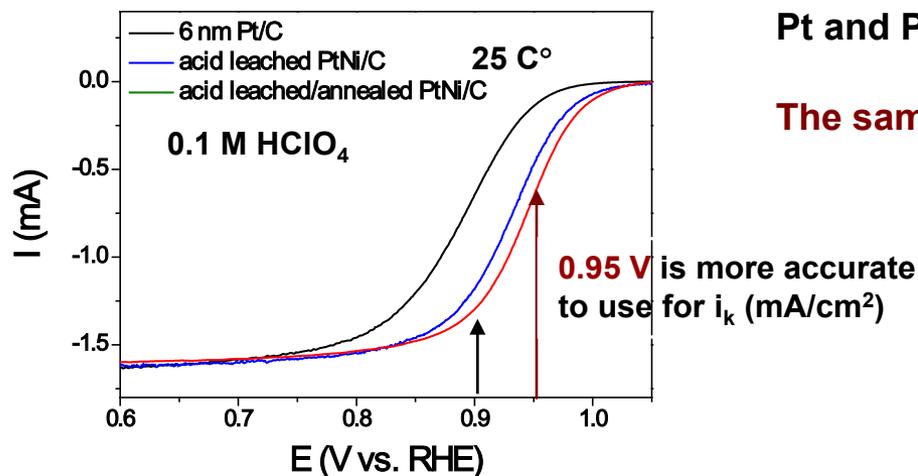


Line profile of NP



# Technical Accomplishments: Tailoring the Catalytic Activity

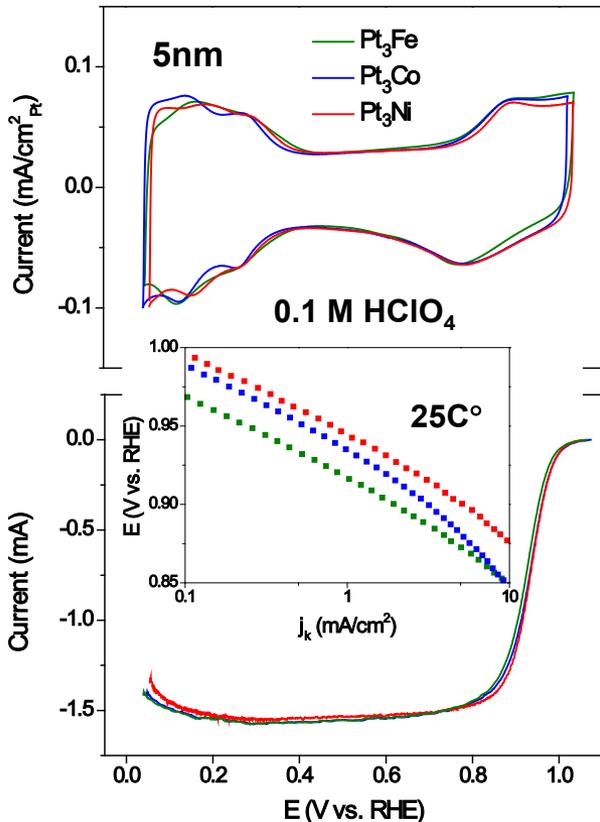
PtNi/Pt core/shell catalyst has **7 fold** improved activity over corresponding (similar size) Pt/C



**Activity/Stability trend** is controlled by surface coverage of spectator  $\text{OH}_{\text{ad}}$  species formed from dissociation of water:  
 $\text{Pt} < \text{Pt}_3\text{Ni (skeleton)} < \text{Pt}_3\text{Ni/Pt core/shell}$

**Multi-layered Pt-shell protects Ni in the core:  $\text{Pt}_3\text{Ni/Pt}$  NPs do not suffer from the decay in activity or surface area after 30,000 cycles between 0.5 to 1.1V**

# Technical Accomplishments: Catalytic Trends



## Adsorption Trend

The same particle size



Similar H<sub>upd</sub> coverage



Similar active surface area

## ORR Activity Trend

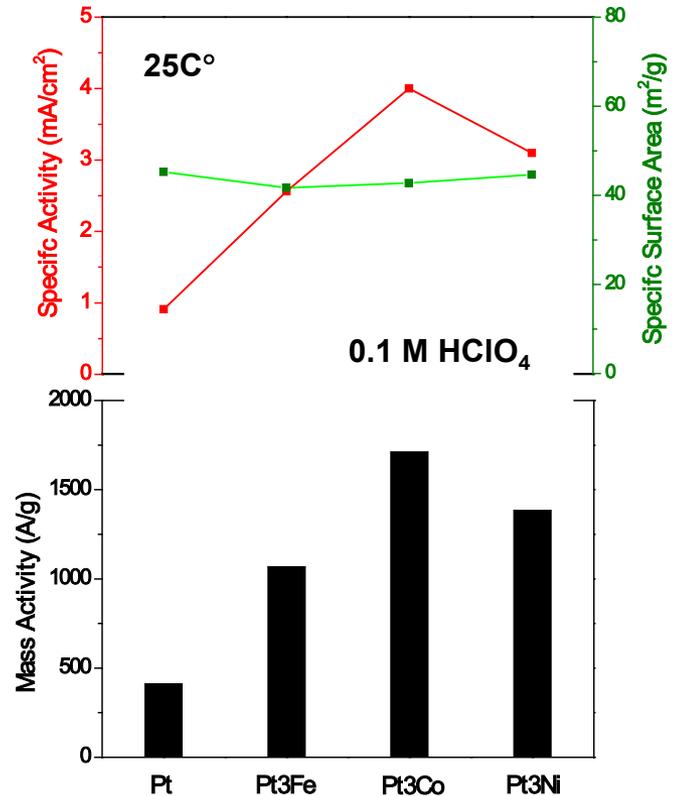
Pt < Pt<sub>3</sub>Fe < Pt<sub>3</sub>Ni < Pt<sub>3</sub>Co



The same Tafel slope



The same mechanism

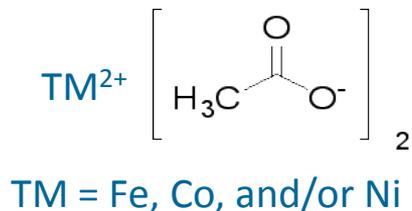


**Specific and Mass Activity trends for the ORR** of Pt-bimetallic NPs is the same as electrocatalytic trends established on extended Pt<sub>3</sub>M well-defined surfaces

**Reaction mechanism for the ORR** is the same on extended and real-world nanosegregated Pt<sub>3</sub>M catalysts; the 4e<sup>-</sup> serial pathway

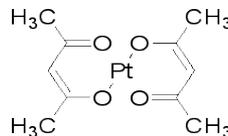
**Activity** is determined by electronic properties of the Pt surface atoms, i.e., by surface coverage of blocking non-reactive OH<sub>ad</sub> species - not by the energetics of reaction intermediates

# Technical Accomplishments: Ternary Alloy Catalysts

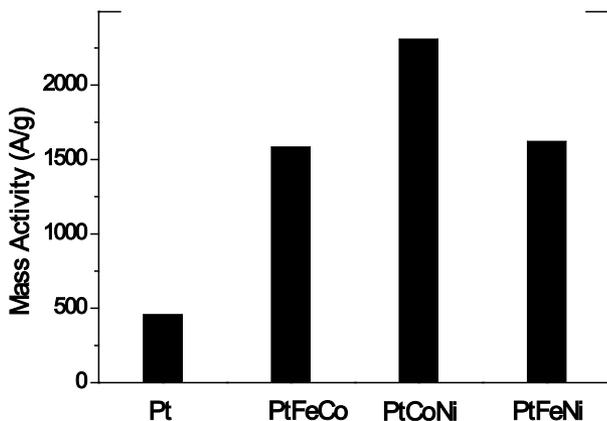
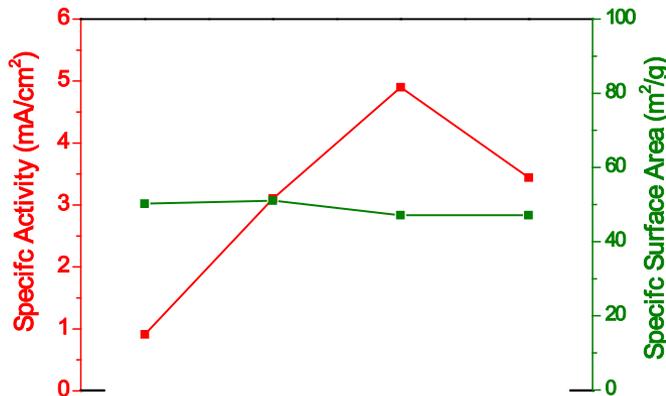
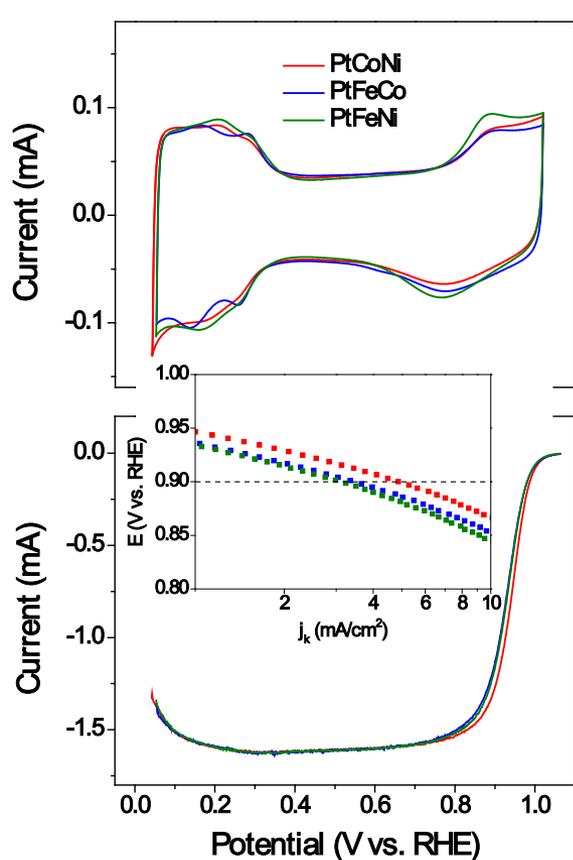


Oleylamine  
oleic acid

~ 200°C



Synthesis of  
PtM<sub>1</sub>N<sub>2</sub> (NM = Fe, Co, and/or Ni)



## Activity

Specific and Mass Activities for ORR of ternary alloys confirmed potential of utilizing TM in further reducing of Pt content

Ternary alloys could provide additional tunability towards activity and stability  
PtNiCo the most active catalyst

Segregation trends in ternary alloys are still under investigation

# 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 2010

- **Fundamental understanding of ternary alloy catalysts**
- **Resolving electronic and atomic structures**
- **Composition screening**
- **Characterization and evaluation of activity and stability trends**
- **Syntheses, characterization and laboratory testing**

### FY 2011

- **Fabrication and testing in MEA**
- **Composition validation**
- **Characterization and evaluation of activity and stability trends**
- **Syntheses, characterization and laboratory testing**

# Summary

## Task 1. Fundamental understanding

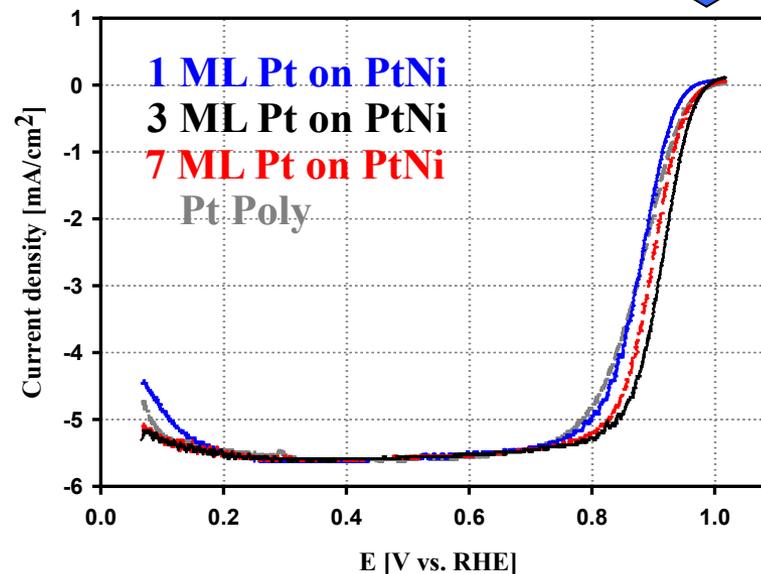
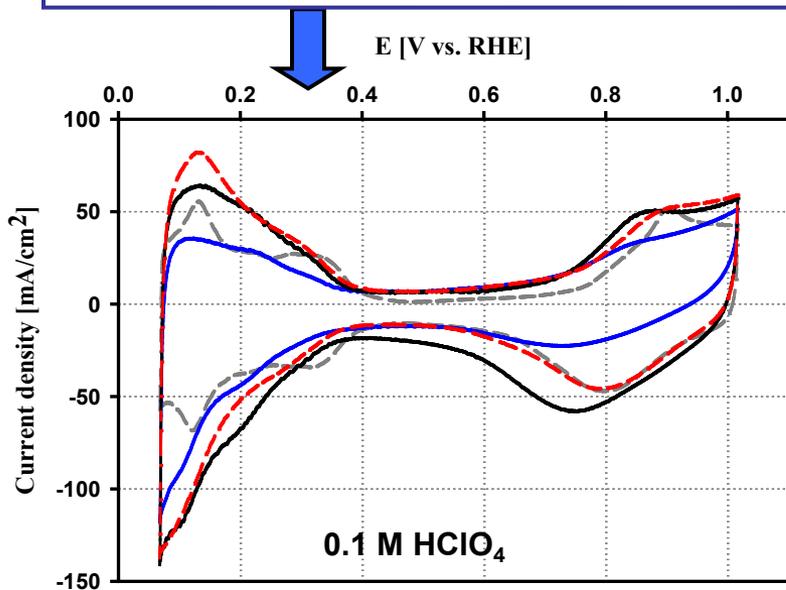
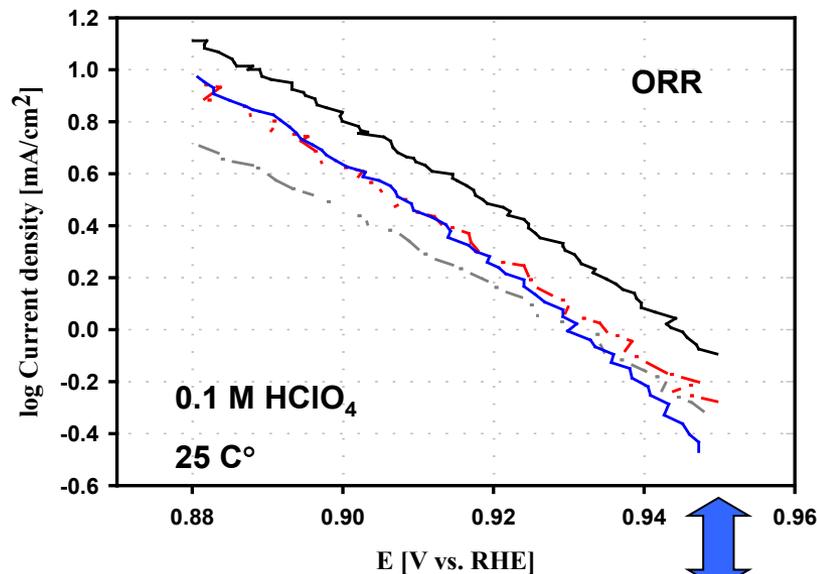
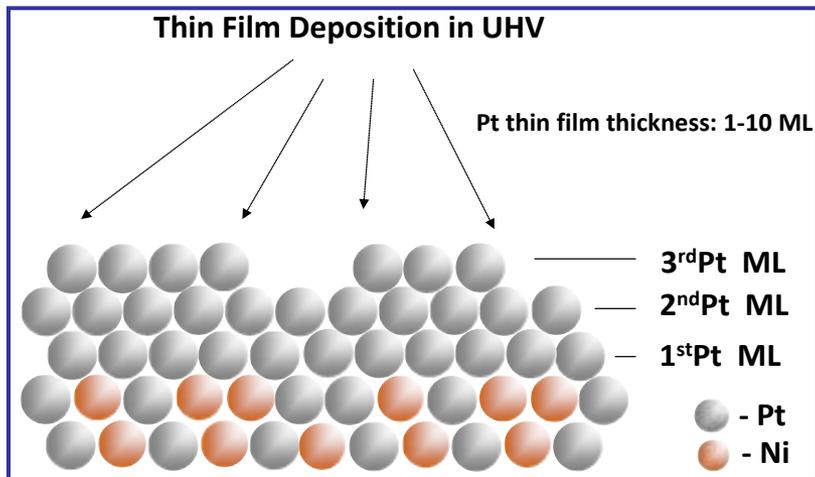
- 1.1 Resolved electronic/atomic structure and segregation profile
- 1.2 Confirmed the reaction mechanism of the ORR
- 1.3 Mass activity and durability improvement are obtained for Pt-alloy NPs

## Task 2. Synthesis and characterization

- 2.1 Physical methods: TM films (5-10 layers) were used to confirm EC properties
- 2.2 Chemical methods: colloidal solvo-thermal approach in NPs synthesis
- 2.3 Characterization: Ex-situ (UHV, TEM) and in-situ (EC, Combinatorial)
- 2.4 Theoretical modeling (DFT, MC) methods
- 2.5 Novel multimetallic catalyst with Pt increased activity and improved stability

## ***Supplemental Slides***

# Thin Films of Pt over PtNi substrate



The most active surface is PtNi/Pt-3ML  
which corresponds to core/shell PtNi/Pt