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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

Project ID#
FC008

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

Overview

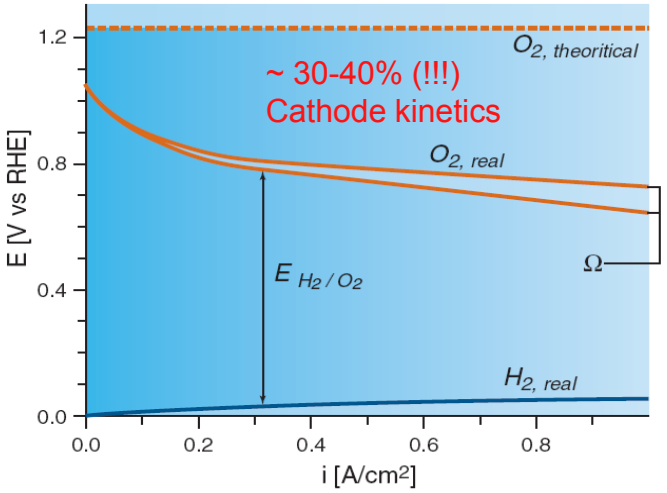
Timeline

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

Budget

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

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

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_1M_2 (M_1=Co,Ni; M_2=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*

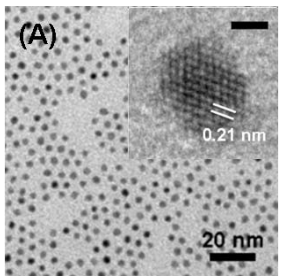
DOE Technical Targets

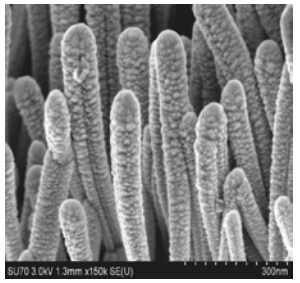
- Specific activity @0.9$V_{iR\text{-}free}$: 720 μA/cm^2
- Mass activity @0.9V: 0.44 A/mg_{Pt}
- Electrochemical area loss: < 40%
- Catalyst support loss: < 30%
- PGM Total content: 0.2 g/kW
- PGM Total loading: 0.2 mg/$cm^2_{electrode}$
- Cost*: $ 30/kW_e
- Durability w/cycling (80°C): 5000 hrs

*based on Pt cost of $450/troy ounce

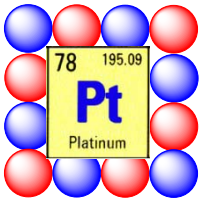
ANLTechnical Targets

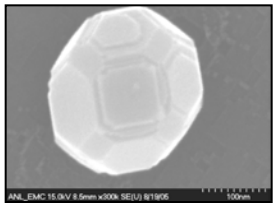
- Specific activity @ 0.9$V_{iR\text{-}free}$
  2015 DOE target x 3
- Mass activity @ 0.9$V_{iR\text{-}free}$
  2015 DOE target x 3
- Electrochemical area loss
  2015 DOE target
- PGM Total content
  < 0.1g/kW

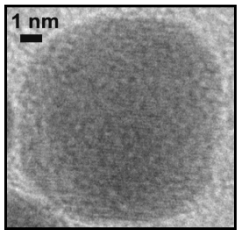




Approach



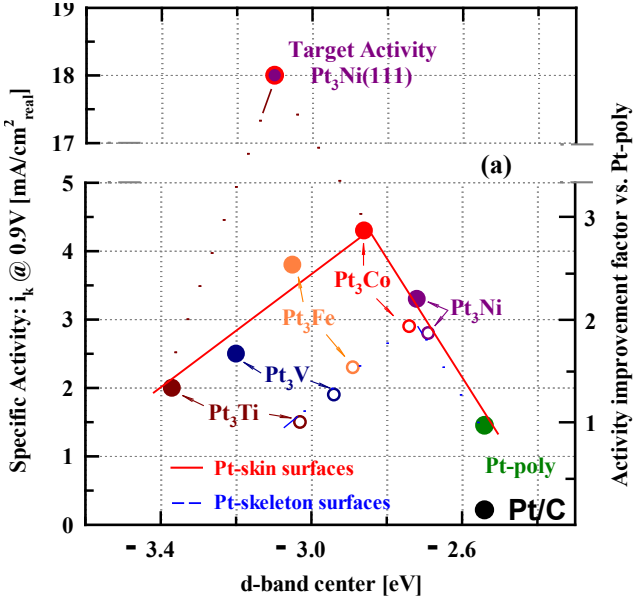




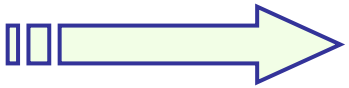
EXTENDED Multi-M SURFACES | MODEL NANOPARTICLES | REAL NANOPARTICLES

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

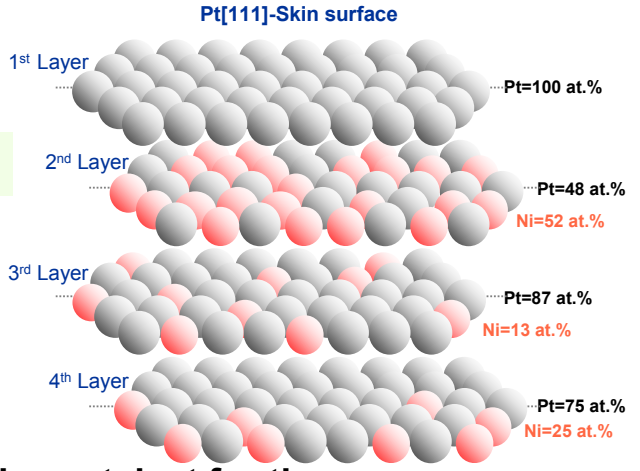
Well-Defined Systems



Advanced Nanoscale Catalyst



Nanosegregated Profile



Pt_3Ni((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%)

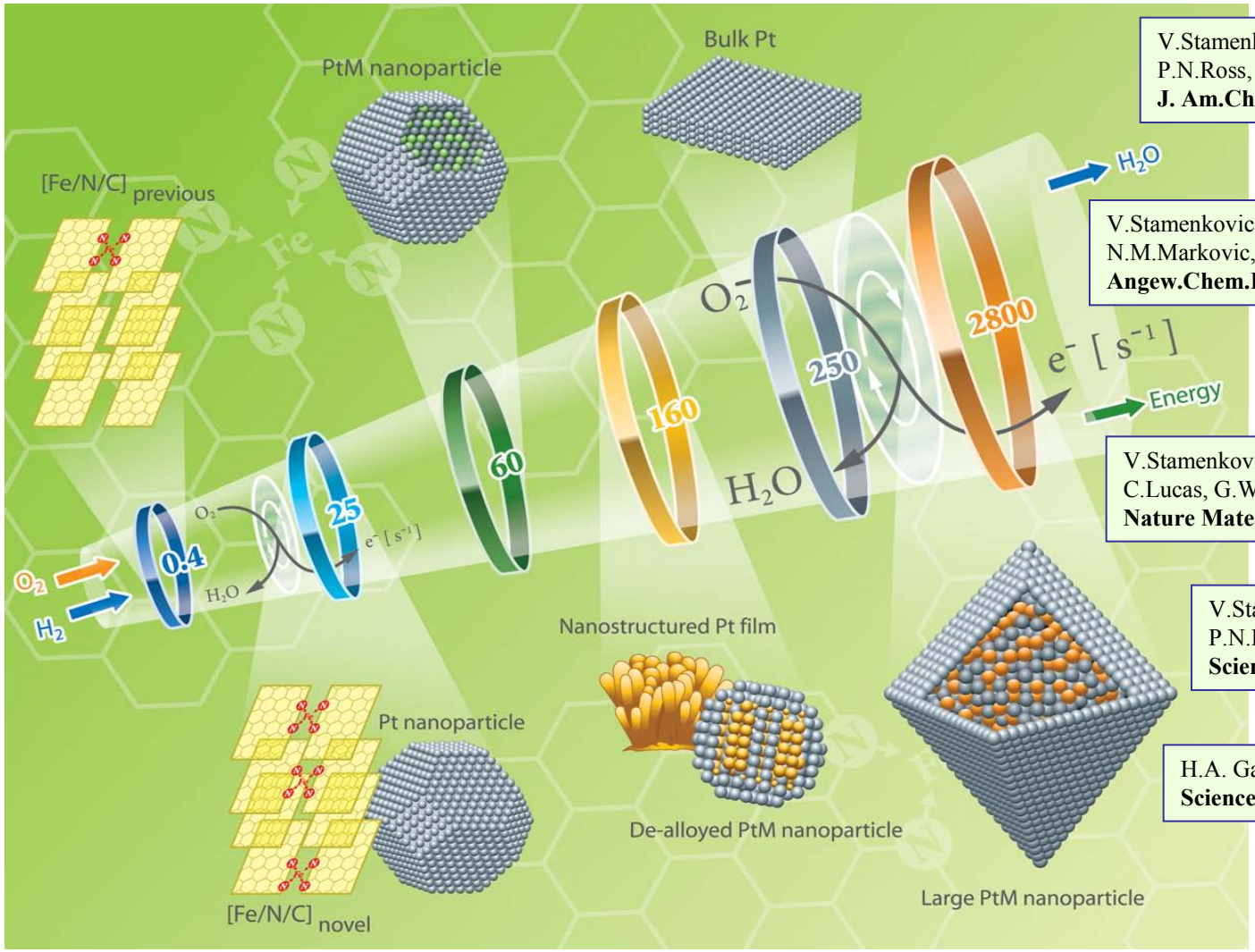
Milestone 2. Synthesis and characterization (2009/10)

- 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_1M_2 catalyst to increase catalytic activity and decrease dissolution
- 3.2 Carbon support vs. nanostructured thin film catalysts
- 3.3 MEA testing (50 cm^2)
- 3.4 Short stack testing verification (>300cm^2)

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
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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

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Science, 315(2007)493

H.A. Gasteiger, N.M.Markovic
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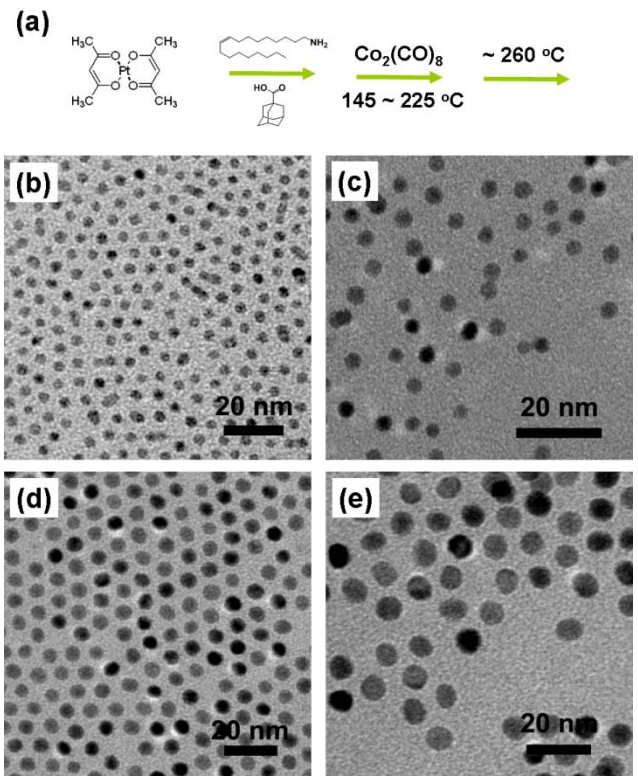
Nanosegregated particle would be the best catalysts for the ORR

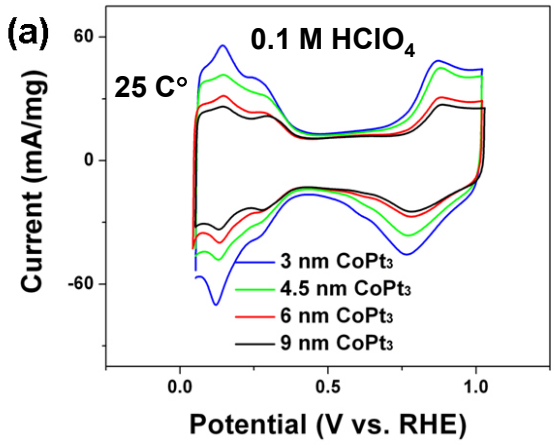
Technical Accomplishments: *Particle Size Effect*

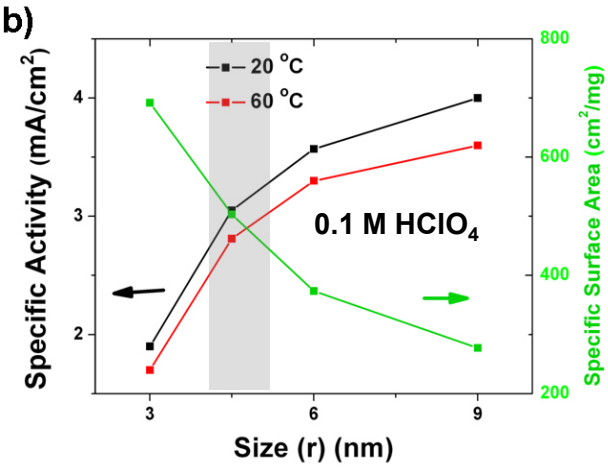
Colloidal deposition approach is used to synthesize (a) monodispersed Pt_3Co bimetallic NPs with diameter of 3, 4.5, 6 and 9nm

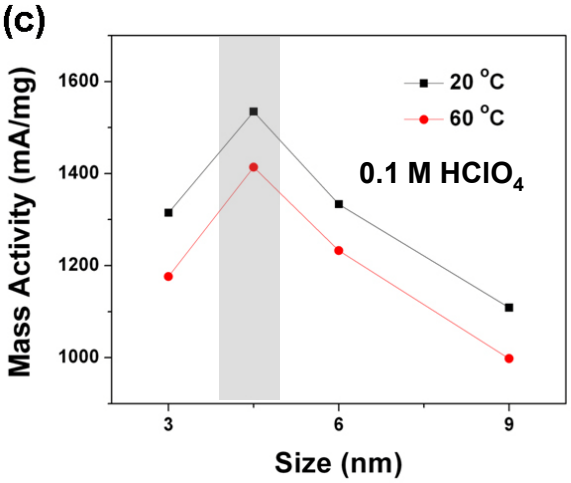


Particle size is determined by analyzing TEM images (b-e)

Particle size effect applies to bimetallic NPs





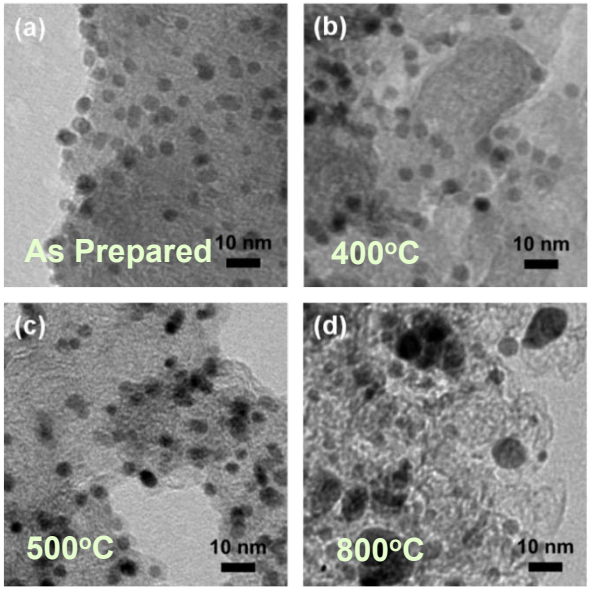


Specific surface area is determined from Θ_{Hupd}

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

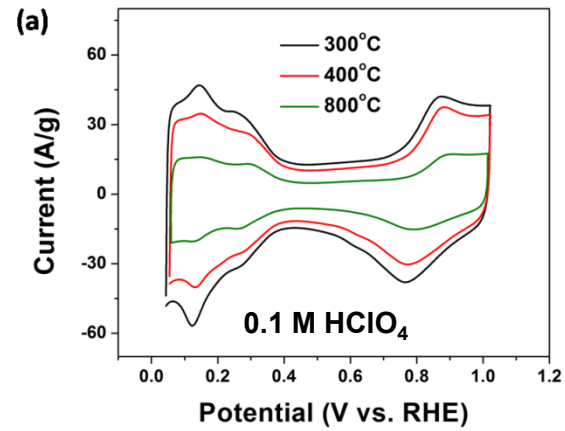
Mass Activity decreases with particle size: optimal size ~5nm

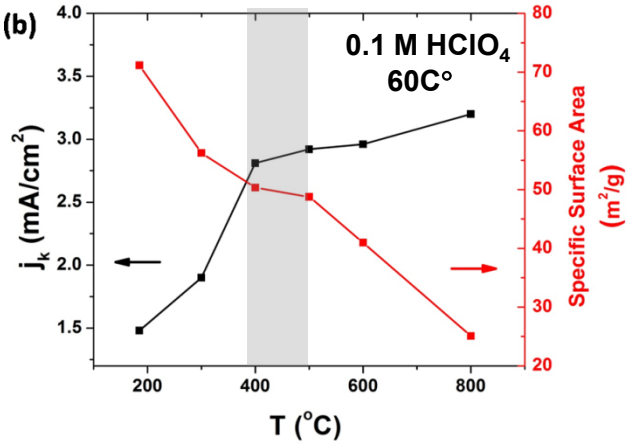
Technical Accomplishments: *Temperature-induced Segregation*

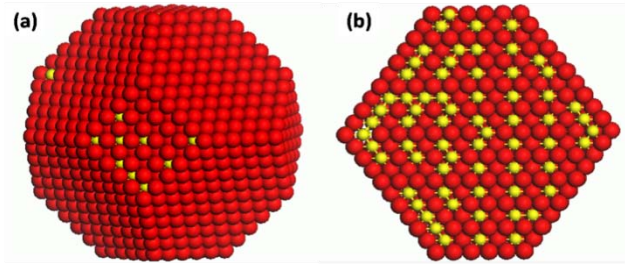


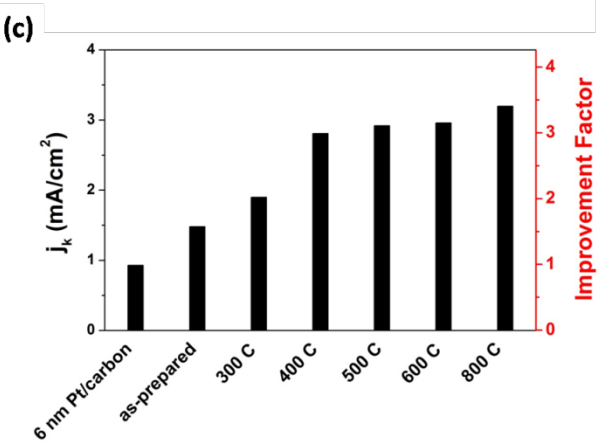
TEM: no agglomeration below 500°C

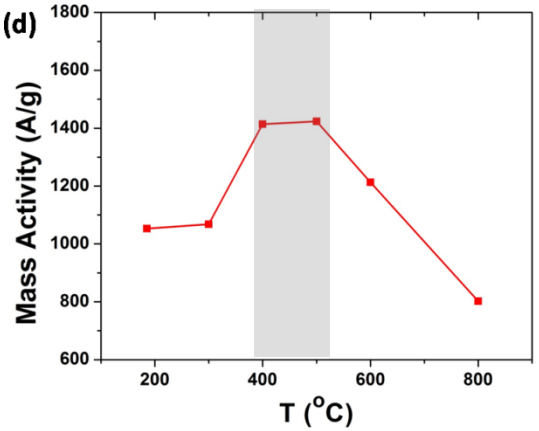
Temperature Induced Segregation: apply 400 to 500°C to optimize catalytic activity of the ORR on PtCo bimetallic NPs









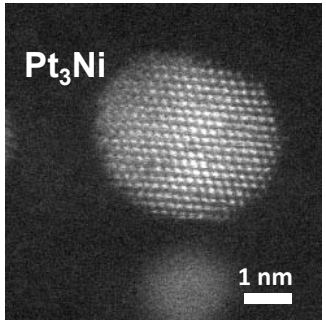


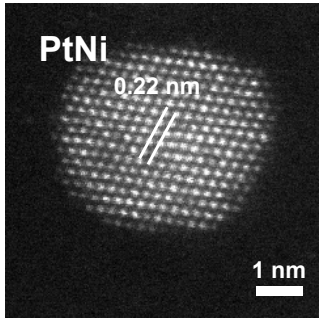
MC simulations at 400°C confirmed segregation profile of Pt_3Co NPs, which was experimentally observed for extended surfaces

Annealing above 500°C provides small increase in specific activity but significant decrease in mass activity of Pt_3Co NPs

Technical Accomplishments: *Composition Effect*

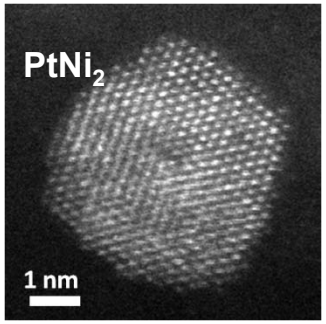
Colloidal method is used to synthesize Pt_xNi_y NPs with 3:1, 1:1, 1:2 and 1:3 atomic ratio

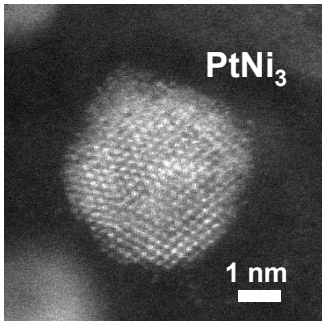


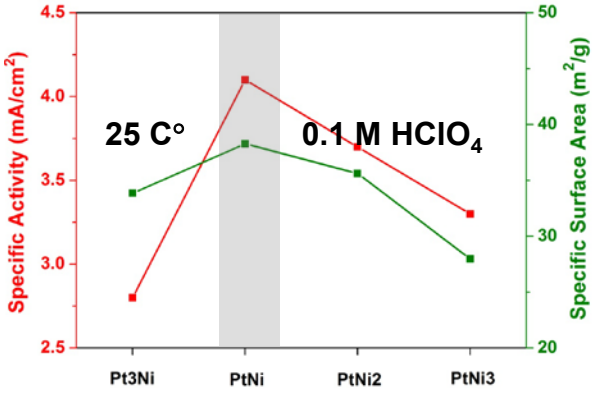


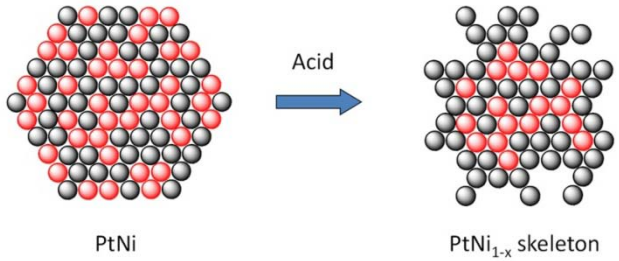
~5nm Pt_xNi_y

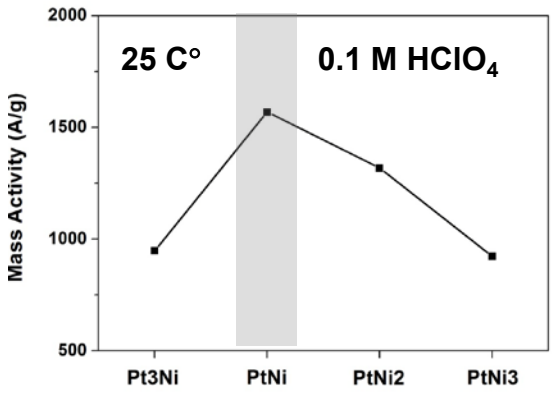
Last step annealing at 400°C











Maximum activity obtained for as-synthetized 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

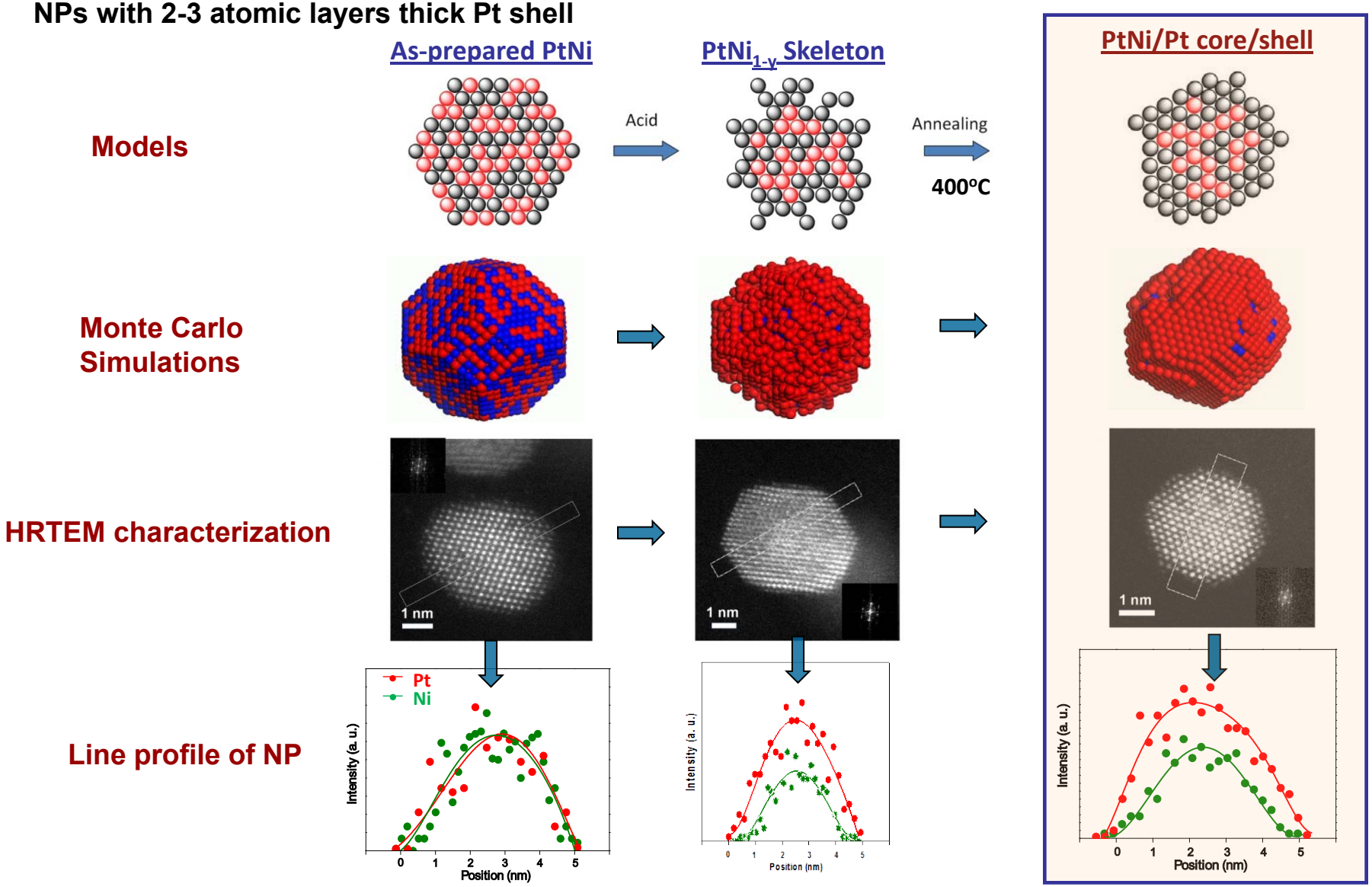
$Pt_3Ni \Rightarrow Pt_{85}Ni_{15}$ $PtNi \Rightarrow Pt_{75}Ni_{25}$ $PtNi_2 \Rightarrow Pt_{80}Ni_{20}$ $PtNi_3 \Rightarrow Pt_{90}Ni_{10}$

PtNi transforms into Pt_3Ni skeleton

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

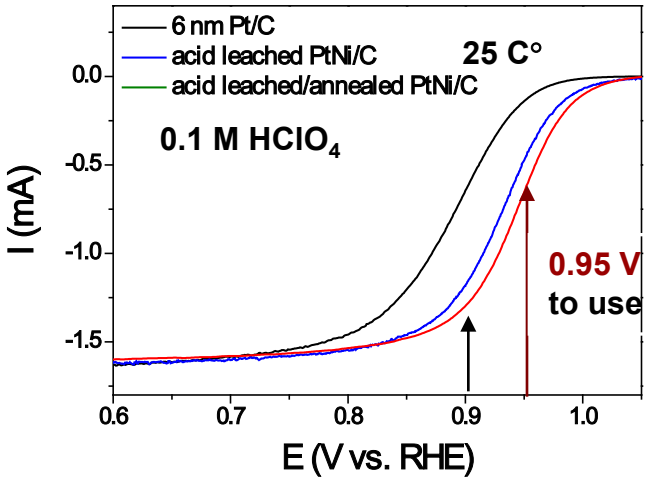
Technical Accomplishments: *Tailoring of Nanosegregated Layers*

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



Technical Accomplishments: *Tailoring the Catalytic Activity*

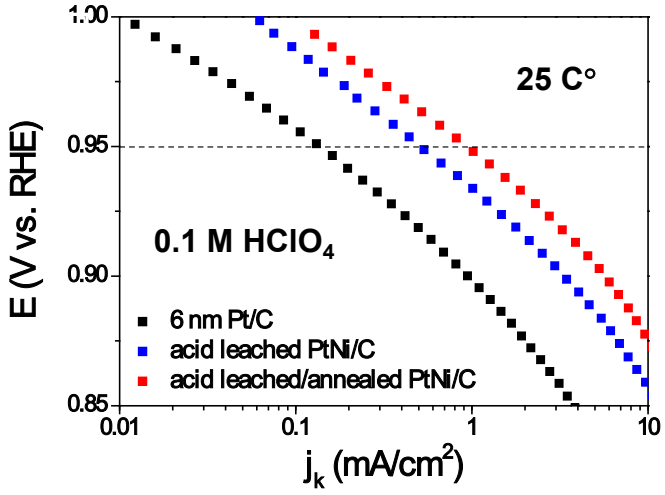
PtNi/Pt core/shell catalyst has 7 fold improved activity over corresponding (similar size) Pt/C

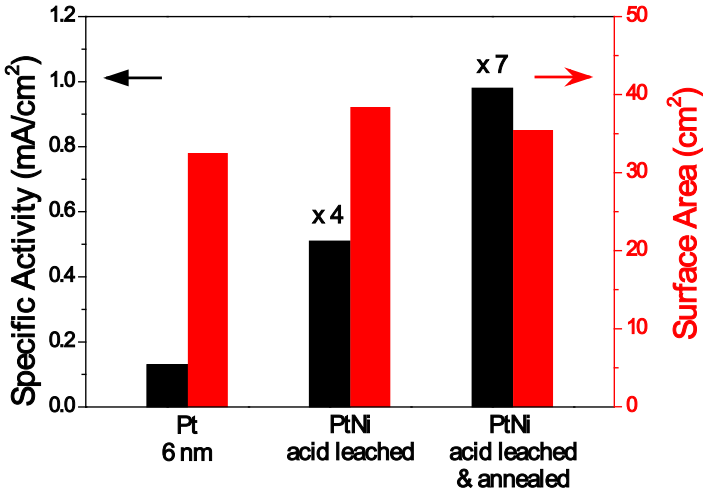


Pt and PtNi NPs

The same Tafel slope

0.95 V is more accurate to use for i_k (mA/cm^2)



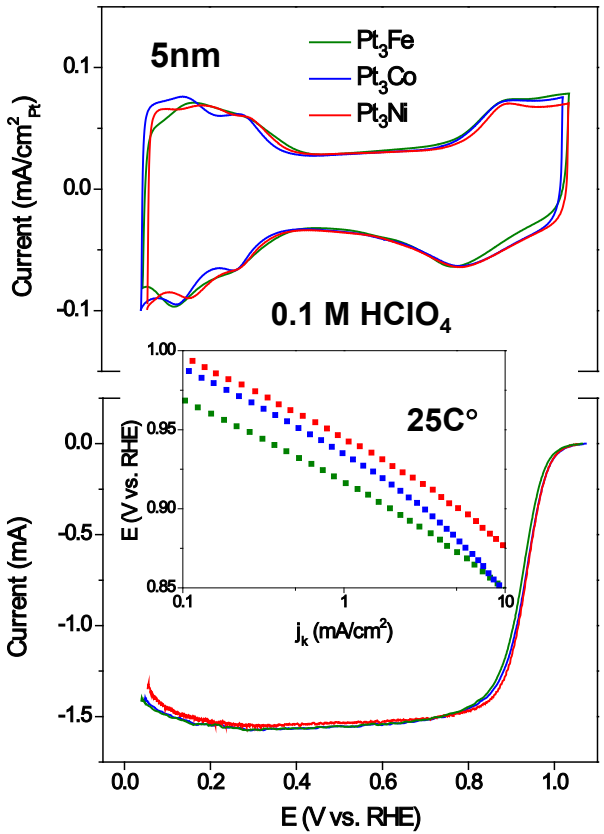


Activity/Stability trend is controlled by surface coverage of spectator OH_{ad} species formed from dissociation of water:

Pt < Pt_3Ni (skeleton) < Pt_3Ni/Pt core/shell

Multi-layered Pt-shell protects Ni in the core: Pt_3Ni/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_{upd} coverage

⇩

Similar active surface area

ORR Activity Trend

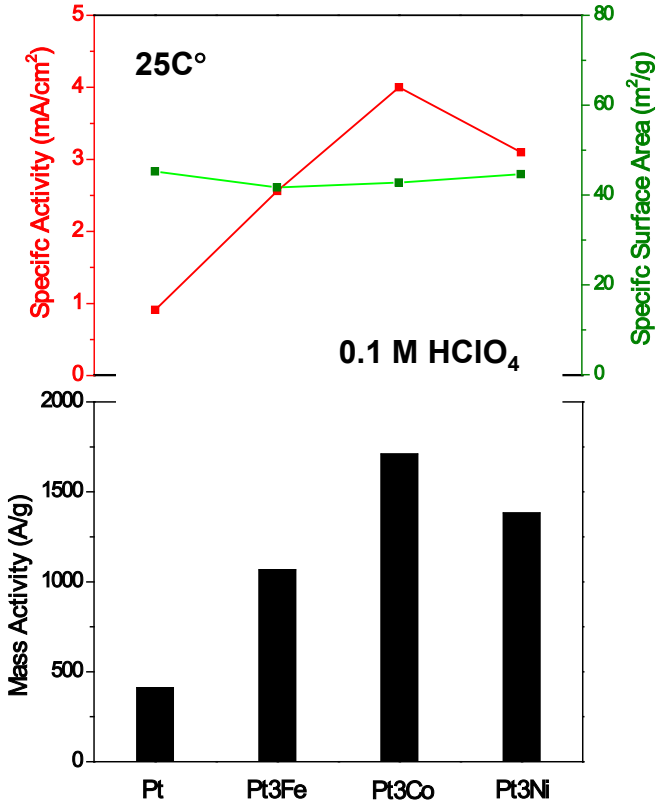
Pt < Pt_3Fe < Pt_3Ni < Pt_3Co

⇩

The same Tafel slope

⇩

The same mechanism

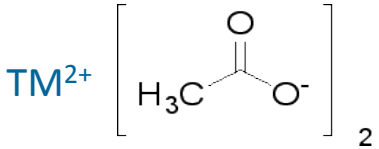


Specific and Mass Activity trends for the ORR of Pt-bimetallic NPs is the same as electrocatalytic trends established on extended Pt_3M well-defined surfaces

Reaction mechanism for the ORR is the same on extended and real-world nanosegregated Pt_3M catalysts; the $4e^-$ serial pathway

Activity is determined by electronic properties of the Pt surface atoms, i.e., by surface coverage of blocking non-reactive OH_{ad} species – not by the energetics of reaction intermediates

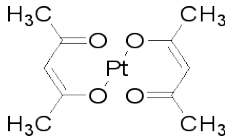
Technical Accomplishments: *Ternary Alloy Catalysts*



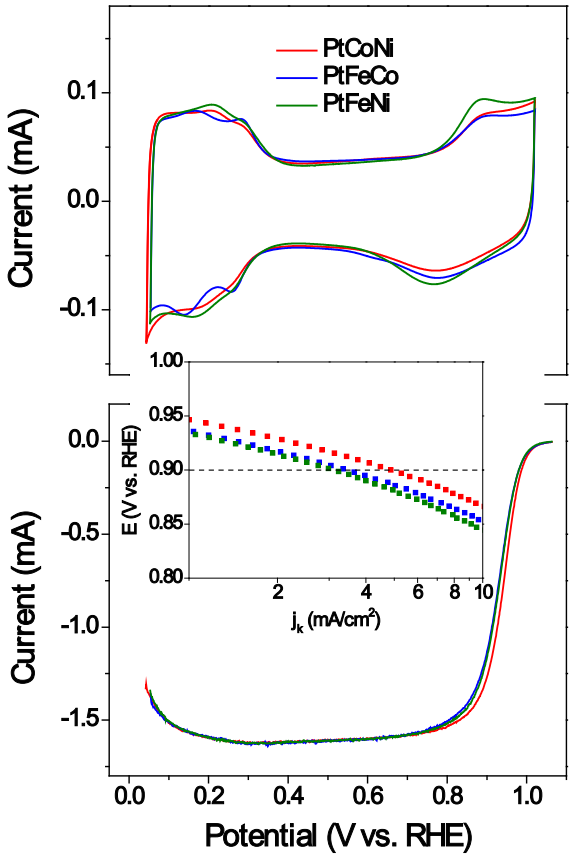
TM = Fe, Co, and/or Ni

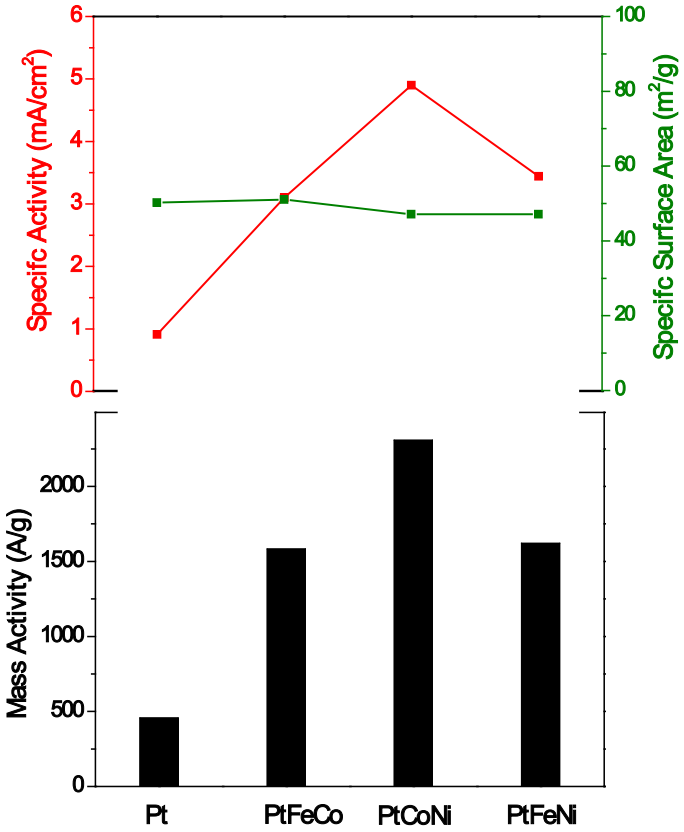
Oleylamine
oleic acid

~ 200°C



Synthesis of
PtM_1N_2 (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

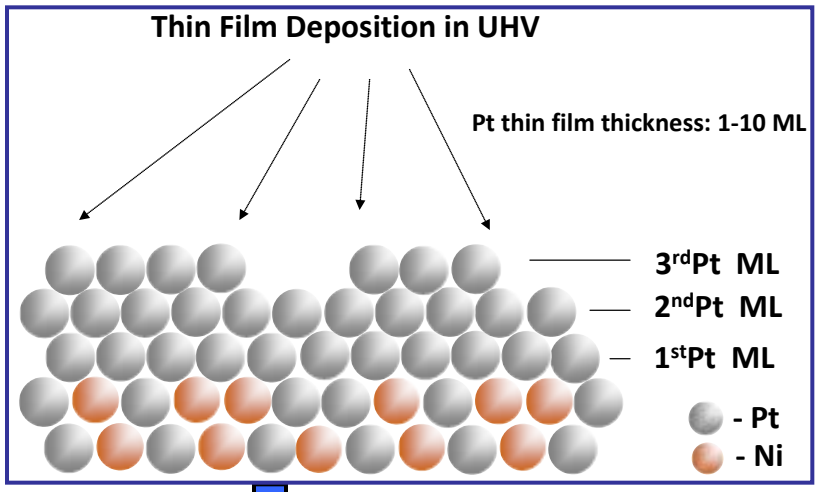
2.3 Characterization: Ex-situ (UHV, TEM) and in-situ (EC, Combinatorial)

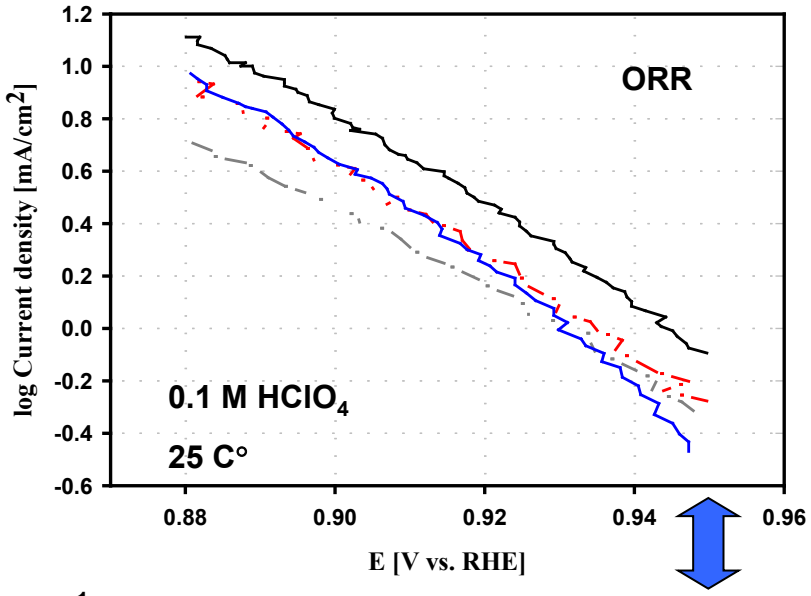
2.4 Theoretical modeling (DFT, MC) methods

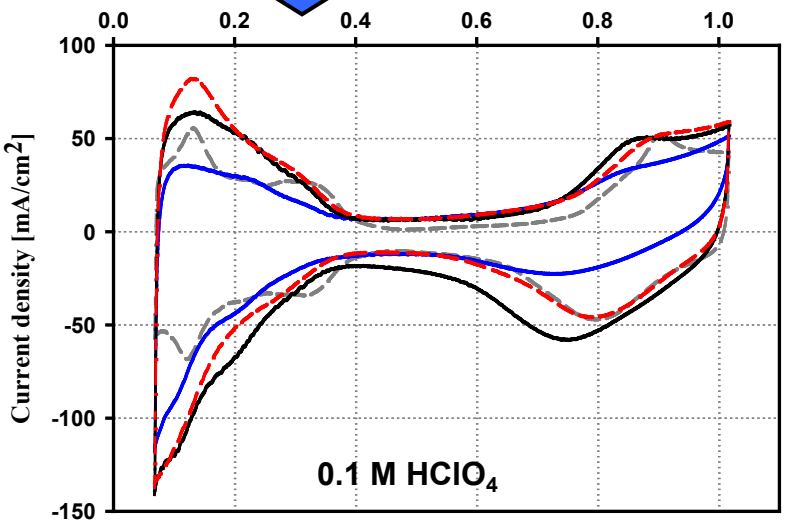
2.5 Novel multimetallic catalyst with Pt increased activity and improved stability

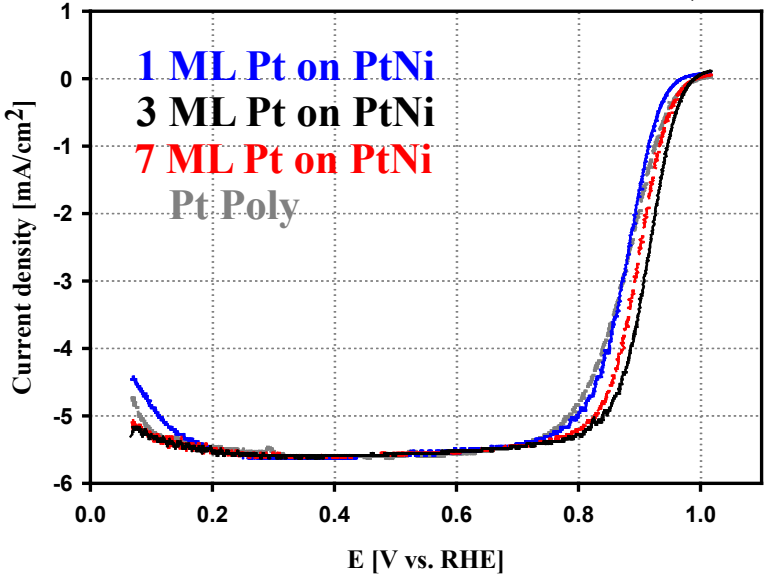
Supplemental Slides

Thin Films of Pt over PtNi substrate









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