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U.S. DEPARTMENT OF ENERGY

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2012 DOE Hydrogen and Fuel Cells Program Review

Nanosegregated Cathode Catalysts with Ultra-Low Platinum Loading

Announcement No: DE-PS36-08GO98010

Topic: 1A

PIs: Nenad M. Markovic
Vojislav R. Stamenkovic

Materials Science Division

Argonne National Laboratory

Project ID#
FC008

Overview

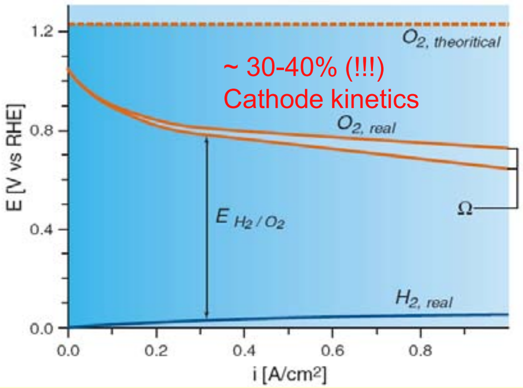
Timeline

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

Budget

- Total Project funding $ 3.6M
  - DOE share: 80 %
  - Cost share: 20%
- Funding for FY11: $ 1.2M
- Planned Funding for FY12: $ 1.2M

Barriers



A) Durability of fuel cell stack

B) Cost (catalyst, membrane, gdl)

C) Performance   (losses and activity)

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

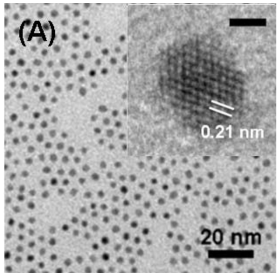
Objectives **The main focus of ongoing DOE Hydrogen and Fuel Cells Program is fundamental understanding of the oxygen reduction reaction on multimetallic systems of PtMN-alloys (M=Co,Ni; N=Fe, Mn, Cr, V, Ti, etc.) that will lead to the development of highly-efficient and durable *real-world nanosegregated Pt-skin catalysts with low-Pt content***

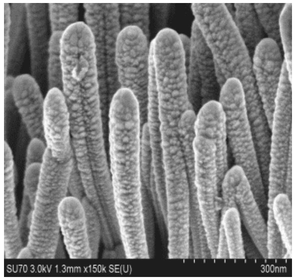
Original DOE Technical Targets

- Specific activity @0.9$V_{\text{iR-free}}$: 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/$cm^2_{\text{electrode}}$
- Cost*: $ 30/kW_e
- Durability w/cycling (80^{o}C): 5000 hrs

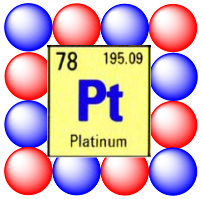
ANL Technical Targets

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

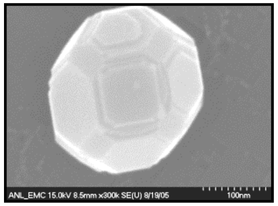




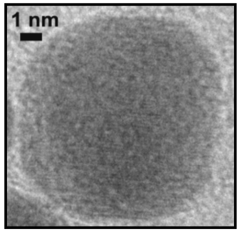
Approach



EXTENDED Multi-M SURFACES



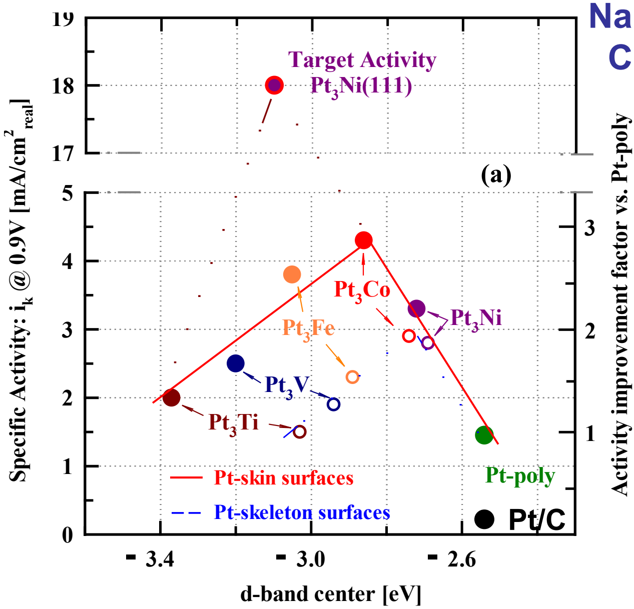
THIN METAL FILMS / MODEL NANOPARTICLES



REAL NANOPARTICLES

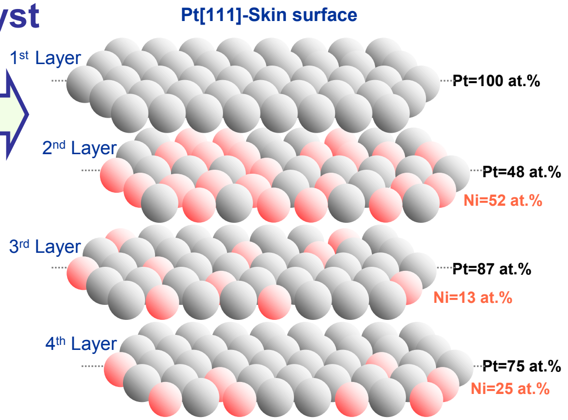
Materials-by-design approach - developed by ANL to design, characterize, understand, synthesize/fabricate and test advanced nanosegregated multi-metallic nanoparticles and nanostructured thin metal films

Well-Defined Systems



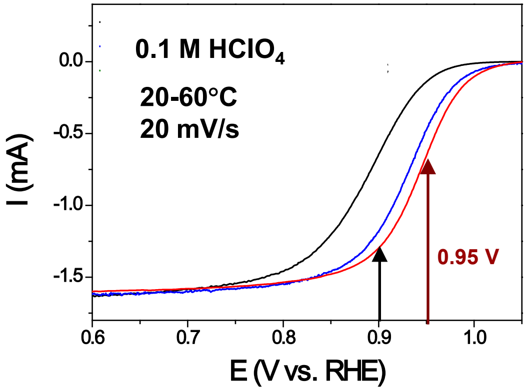
Advanced Nanoscale Catalyst

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. Fundamental understanding (FY09, FY10, FY11, FY12) (Accomplished)

- 1.1 Resolved electronic/atomic structure and segregation profile (85%)
- 1.2 Confirmed reaction mechanism of the ORR (100%)
- 1.3 Improved specific and mass activity (80%)

Milestone 2. Synthesis and characterization (FY10, FY11, FY12)

- 2.1 Physical methods: TM films (5-10 layers), nanoparticles (5-300 nm) (75%)
- 2.2 Established chemical methods: colloidal and impregnation synthesis (80%)
- 2.3 Characterization: Ex-situ (UHV, TEM) and in-situ (EXAFS, EC) (80%)
- 2.4 Theoretical modeling (DFT, MC) methods (85%)

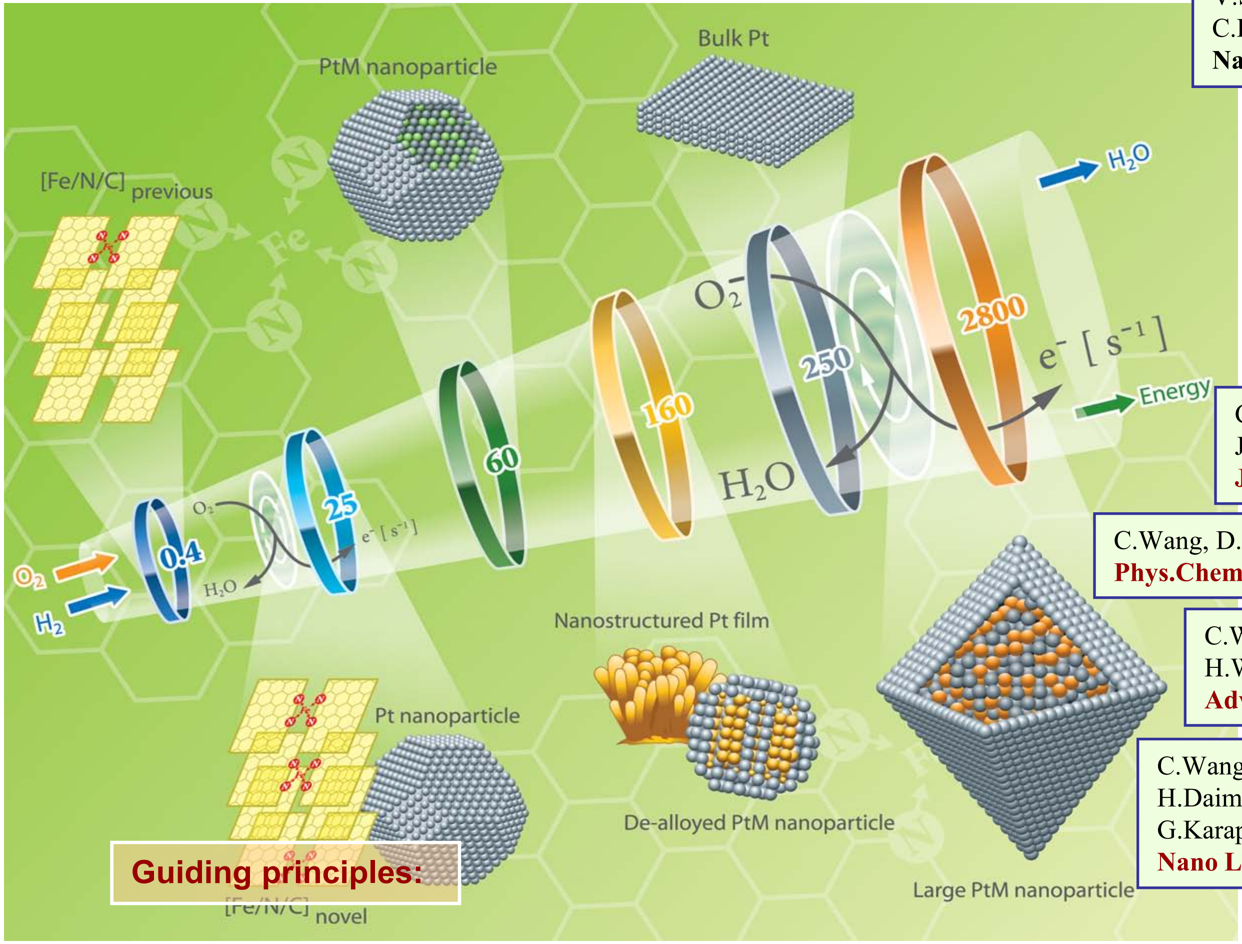
Milestone 3. Fabrication and testing (FY11, FY12)

- 3.1 New PtM_1M_2 catalysts with higher activity and improved durability (85%)
- 3.2 Carbon support vs. nanostructured thin film catalysts (80%)
- 3.3 MEA testing (50 cm^2) of the optimized catalysts (35%)
- 3.4 Scale up of the catalyst fabrication in lab environment (40%)

Relevant Prior Work

Pt-alloy catalysts with nanosegregated concentration profile exhibit the superior performance for the ORR

- **Maximization of activity by lowering the surface coverage of spectators**
- **Prevent leaching of TM by addition of Pt layers without activity loss**
- **Addition of the elements that may hinder Pt disolution**



Guiding principles:

Selected publications from our group

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, 3124(2009)48

Selected publications from FY09-11

C.Wang, D.vanderVliet, K.C.Chang, H.You, D.Strmcnik, J.A.Schlueter, N.M.Markovic, V.R.Stamenkovic
J. Phys. Chem. C., 113(2009)19365

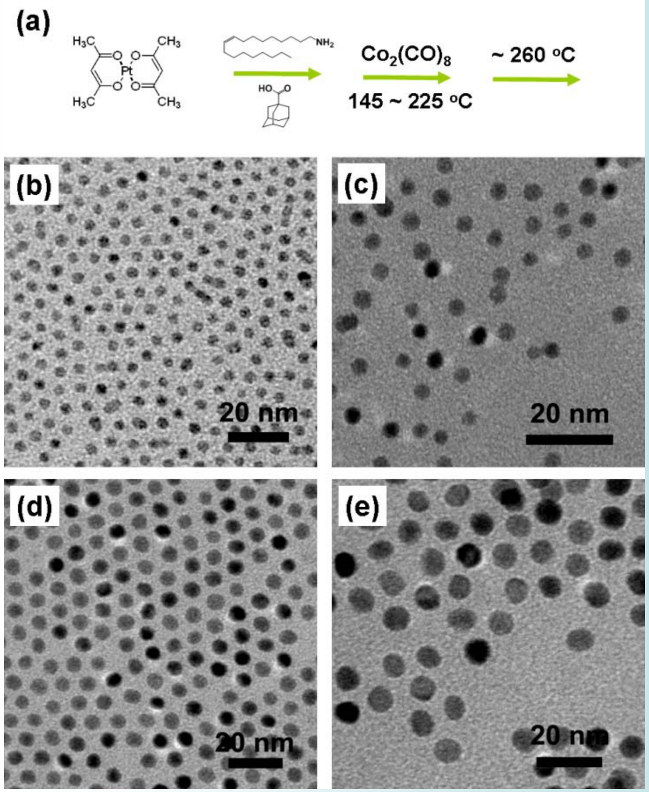
C.Wang, D.vanderVliet, K.C.Chang, N.M.Markovic, V.R.Stamenkovic
Phys.Chem.Chem.Phys., 12(2010)6933, COVER PAGE Article

C.Wang, M.Chi, G.Wang, D.vanderVliet, D.Li, K.L.More, H.Wang, J.A.Schluter, N.M.Markovic, V.R.Stamenkovic
Adv. Funct. Mater. 21(2011)147, COVER PAGE Article

C.Wang, D.vanderVliet, K.L.More, N.J.Zaluzec, S.Peng, S.Sun, H.Daimon, G.Wang, J.Greeley, J.Pearson, A.P.Paulikas, G.Karapetrov, D.Strmcnik, N.M.Markovic, V.R.Stamenkovic
Nano Letters, 11(2011)919-928, COVER PAGE Article

Technical Accomplishments FY09, FY10 and FY11: *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

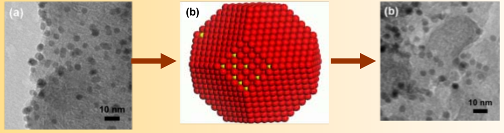
Specific Activity increases with particle size: 3 < 4.5 < 6 < 9nm

Mass Activity decreases with particle size

Optimal size particle size ~5nm

2° Temperature induced segregation in Pt-bimetallic NPs

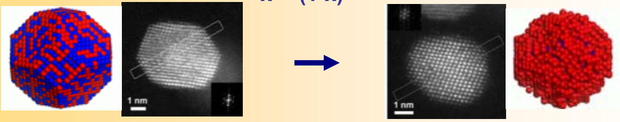
Agglomeration prevented



Optimized annealing temperature 400-500°C

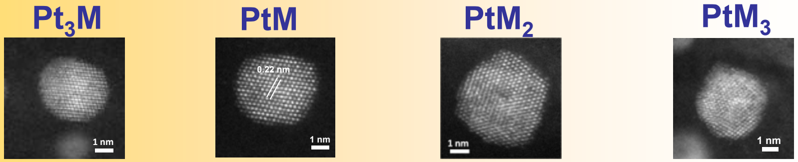
3° Surface chemistry of homogeneous Pt-bimetallic NPs

$Pt_xM_{(1-x)}$ NPs



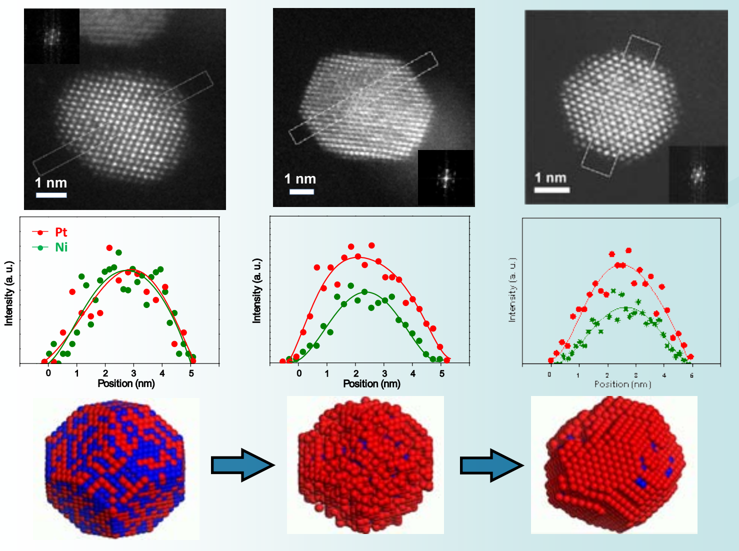
Dissolution of non Pt surface atoms leads to **Pt-skeleton** formation

4° Composition effect in Pt-bimetallic NPs



Optimal composition of Pt-bimetallic NPs is PtM

Technical Accomplishments FY09, FY10 and FY11: *Pt-alloy Nanocatalysts*

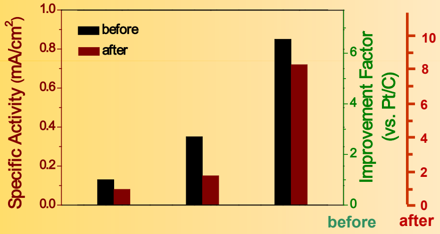


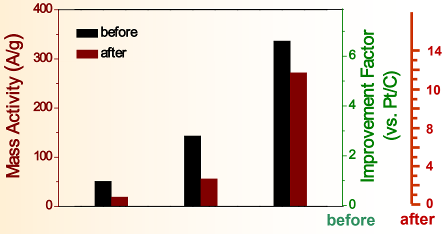
5º Pt-bimetallic catalysts with mutilayered Pt-skin surfaces

Synthesized PtNi NPs have homogeneous distribution of Pt, Ni

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

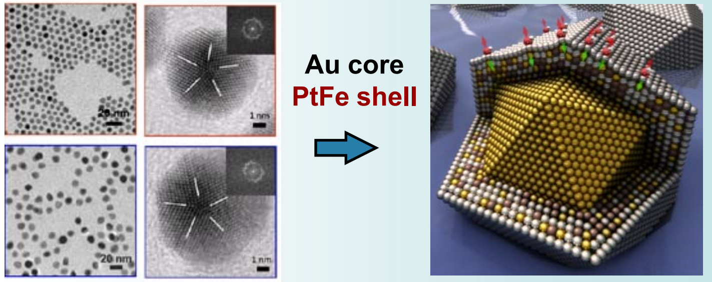
Multilayered Pt-skin surfaces confirmed for PtNi annealed NPs

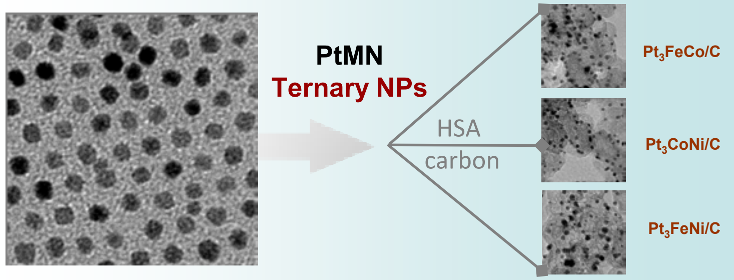




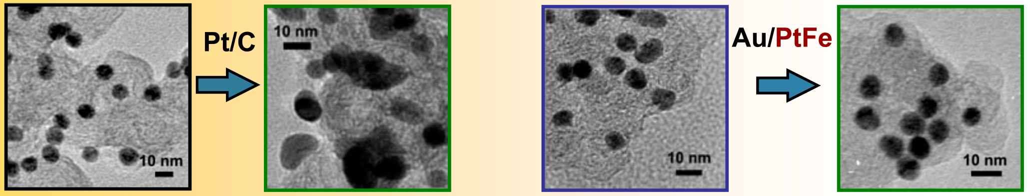
RDE after 4K cycles @60°C (0.6-1.05V vs. RHE):

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

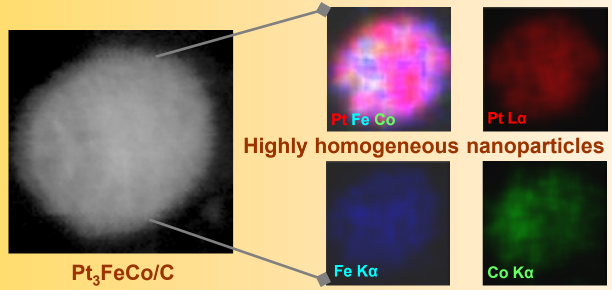




6º Multimetallic NPs can further improve activity and durability

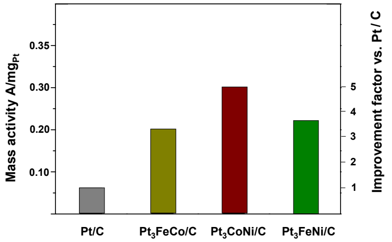


before **After 60K cycles** **before** **After 60K cycles**



Highly homogeneous nanoparticles

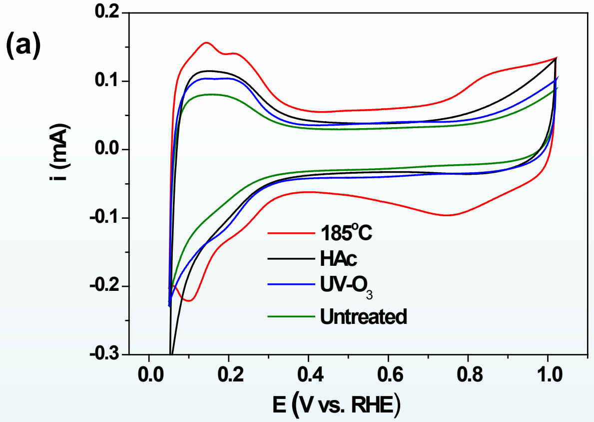
Pt_3FeCo/C

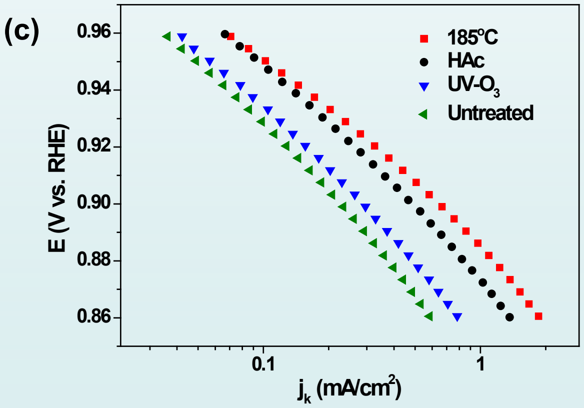


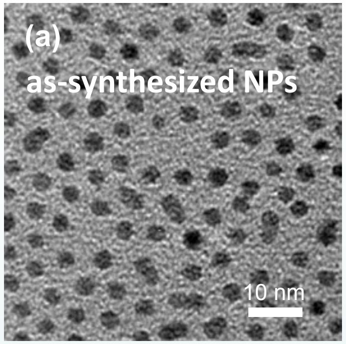
Additional gain in mass and specific activities vs. Pt and Pt_3M alloys

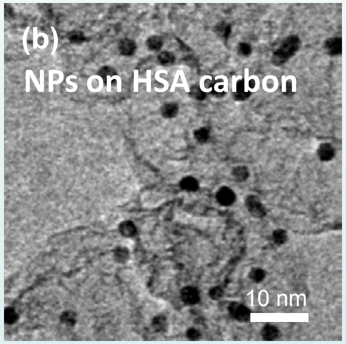
Technical Accomplishments: *Surfactant Removal from NPs*

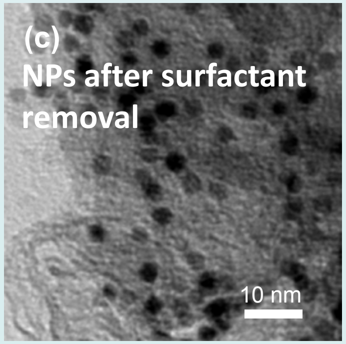
Effectiveness of Surfactant Removal by Different Treatments

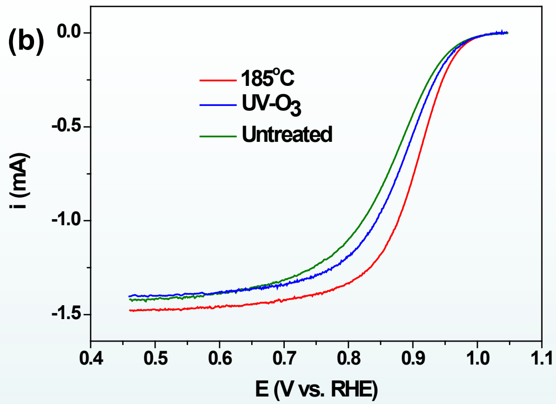


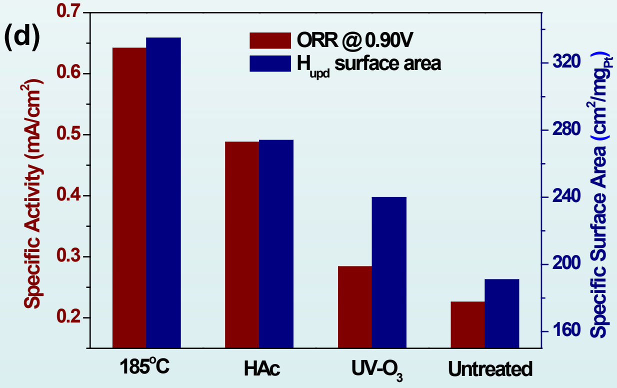












Annealing in oxygen atmosphere is the most efficient procedure for the capping agent removal

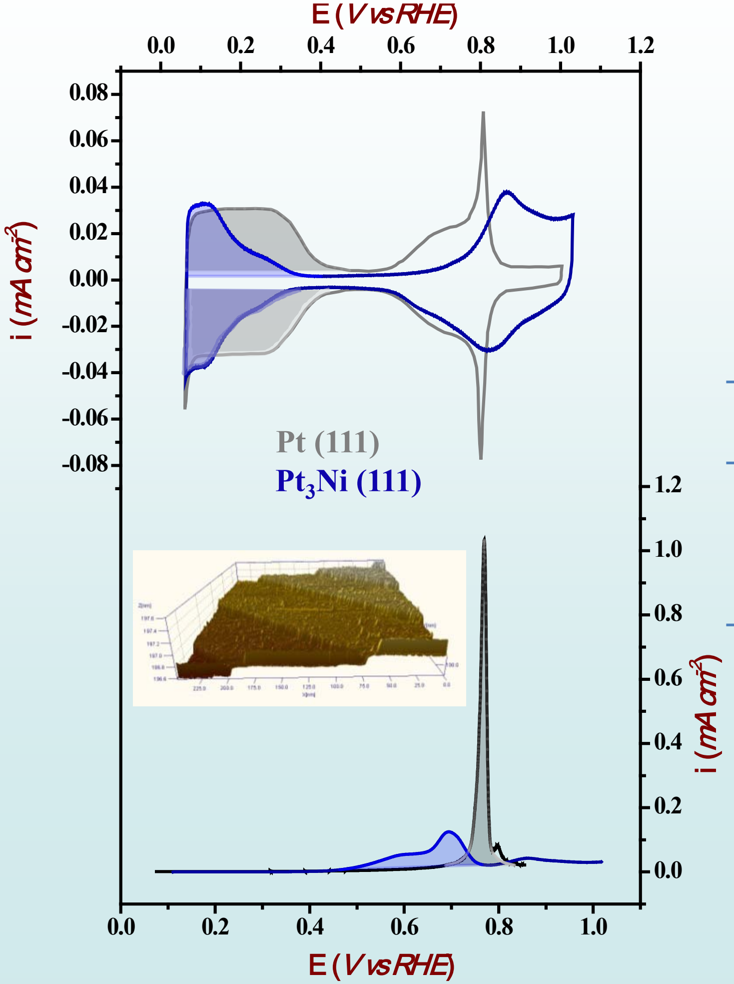
Annealing in oxygen atmosphere does not induce agglomeration and/or sintering of NPs

In Press ACS Catalysis, 2012

Technical Accomplishments: *Adsorption properties of Pt-skin surfaces*

Pt-skin surfaces: ***Important*** to perform evaluation of electrochemically active surface area

Pt-skin surfaces on well-defined single crystal surfaces



Pt(111)-skin surfaces exhibit substantially lower coverage by H_{upd} vs. Pt(111)
(up to 50% lower H_{upd} region is obtained on Pt(111)-Skin)

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

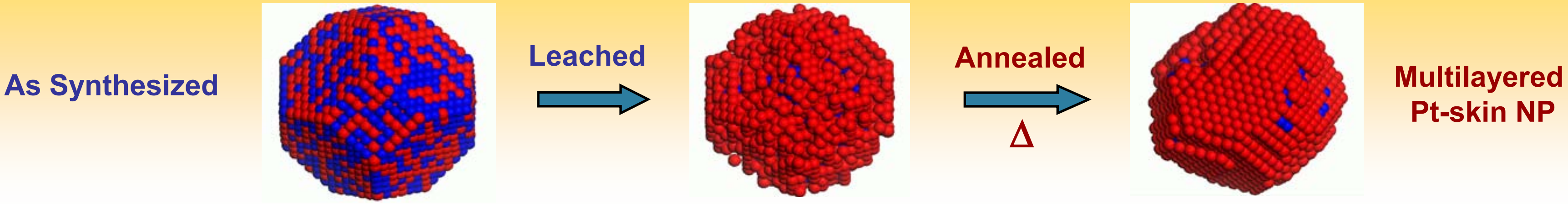
Surface	Q_H (μC/cm²)	Q_{CO} (μC/cm²)	Q_{CO} / $2Q_H$
Pt (111)	152	315	1.04
Pt_3Ni (111)	98	304	1.55
Pt (poly)	190	386	1.02

Electrooxidation of adsorbed CO (CO stripping) has to be performed for Pt-skin surfaces in order to avoid underestimation of electrochemically active surface area and overestimation of specific activity

Same effect was confirmed on Pt-skin thin film surfaces

Technical Accomplishments: *Adsorption properties of Pt-skin surfaces*

Transfer to nanoscale PtM catalysts with Pt-skin surfaces



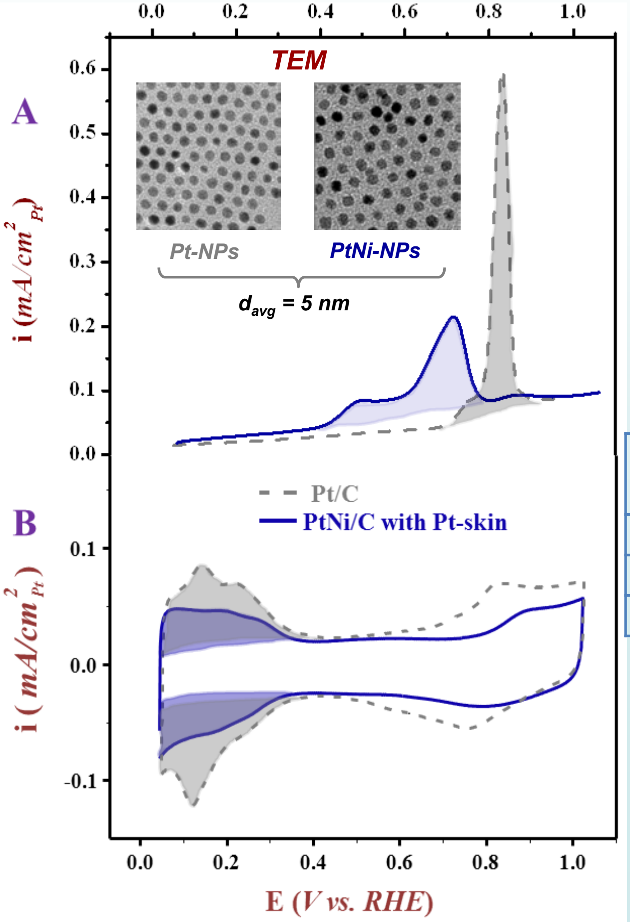
As Synthesized

Leached

Annealed

Δ

Multilayered Pt-skin NP



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

Catalyst	Q_H (μC)	$ECSA_H$ (cm^2)	Q_{CO} (μC)	$ECSA_{CO}$ (cm^2)	$Q_{CO}/2Q_H$
Pt/C	279	1.47	545	1.41	0.98
PtNi/C	292	1.54	615	1.60	1.05
PtNi-skin/C	210	1.10	595	1.54	1.42

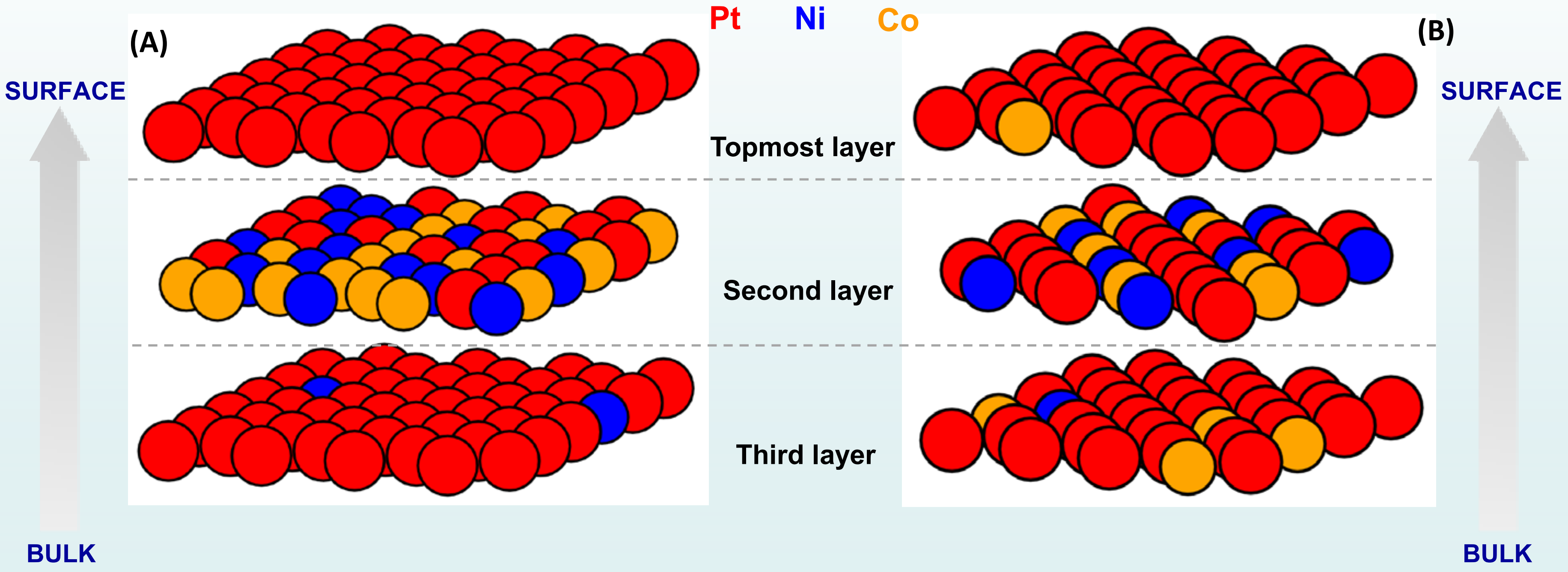
Electrooxidation of adsorbed CO (CO stripping) has to be performed for Pt-alloy catalysts in order to avoid underestimation electrochemically active surface area and overestimation of specific and mass activities

JACS *133(2011)14396*

Technical Accomplishments: *Fine Tuning of PtMN catalytic properties*

Feasibility studies of nanosegregated profile in ternary alloys

Monte Carlo Simulation for Segregation on Pt_3MN Extended Surfaces



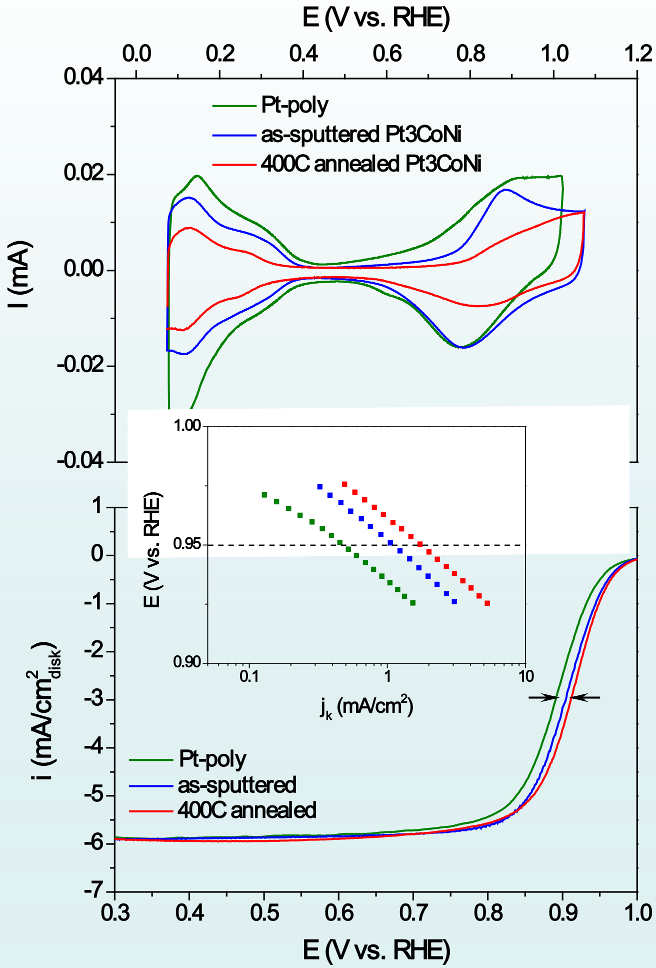
Equilibrium structures of the outermost three layers of the extended (a) (111) and (b) (100) surfaces of $Pt_{75}Ni_{12.5}Co_{12.5}$ alloy after annealing at 500^{o}C

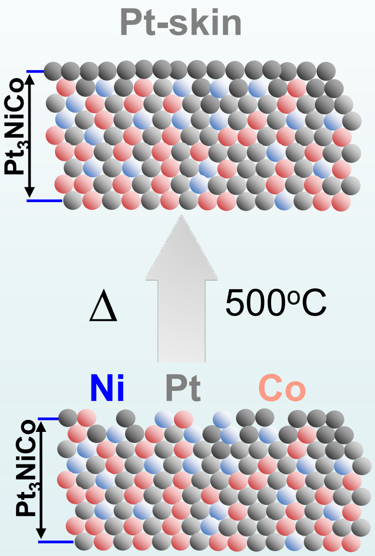
To be published in 2012

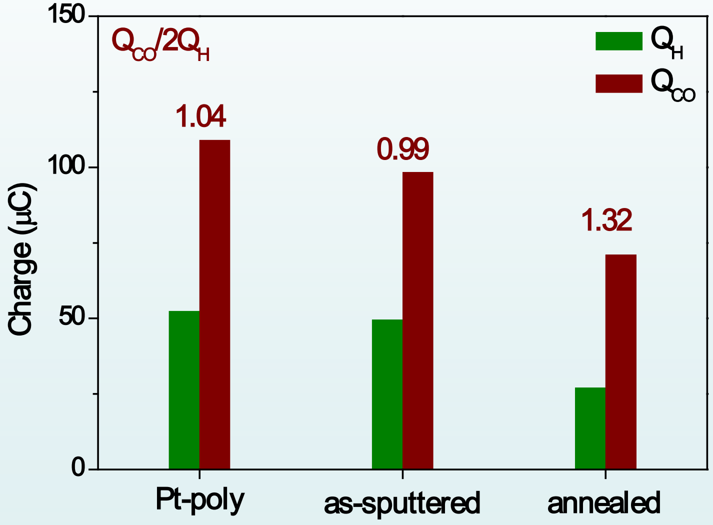
Technical Accomplishments: *Fine Tuning of PtMN catalytic properties*

Feasibility studies to induce nanosegregated profile in ternary alloys

Surface Segregation on Pt_3MN Thin Film Extended Surfaces







Ternary alloys do form nanosegregated concentration profile with Pt-skin topmost surface layer

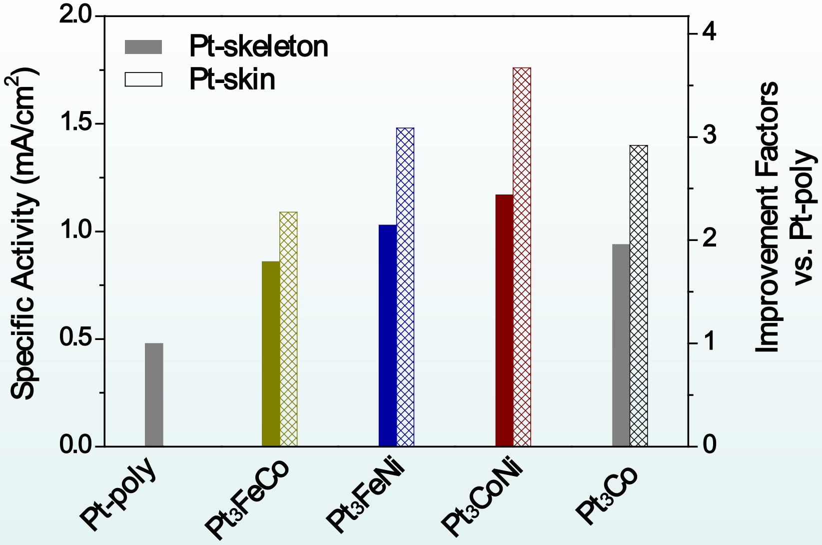
(Ratio between Q_{CO}/Q_{hupd} > 1 confirms formation of Pt-Skin over ternary alloy)

To be published in 2012

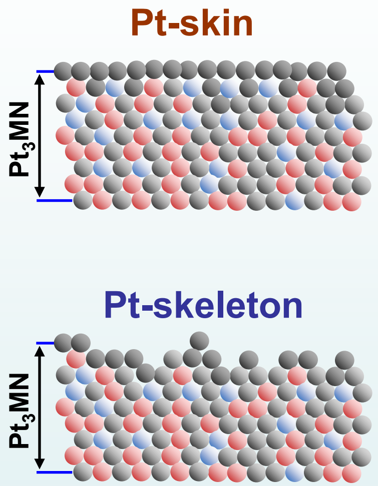
Technical Accomplishments: *Fine Tuning of PtMN catalytic properties*

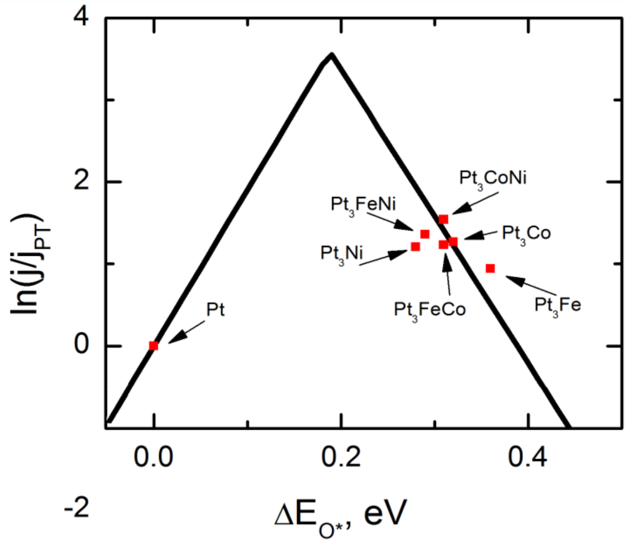
ORR Activity Evaluation in Ternary Alloys

ORR Activity Trends on Pt_3MN Thin Film Extended Surfaces

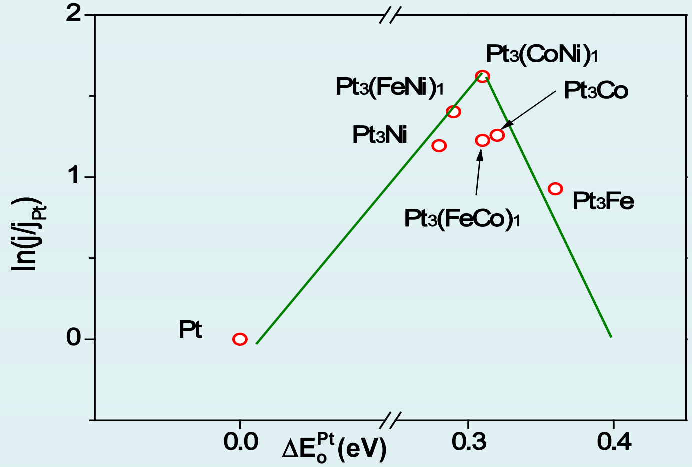


RDE in 0.1M $HClO_4$: ORR @ 0.95V vs. RHE





DFT predictions



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

Polycrystalline Pt_3MN alloys can deliver additional gain of 25% in specific activity over Pt-binary alloys if nanosegregated concentration profile is induced

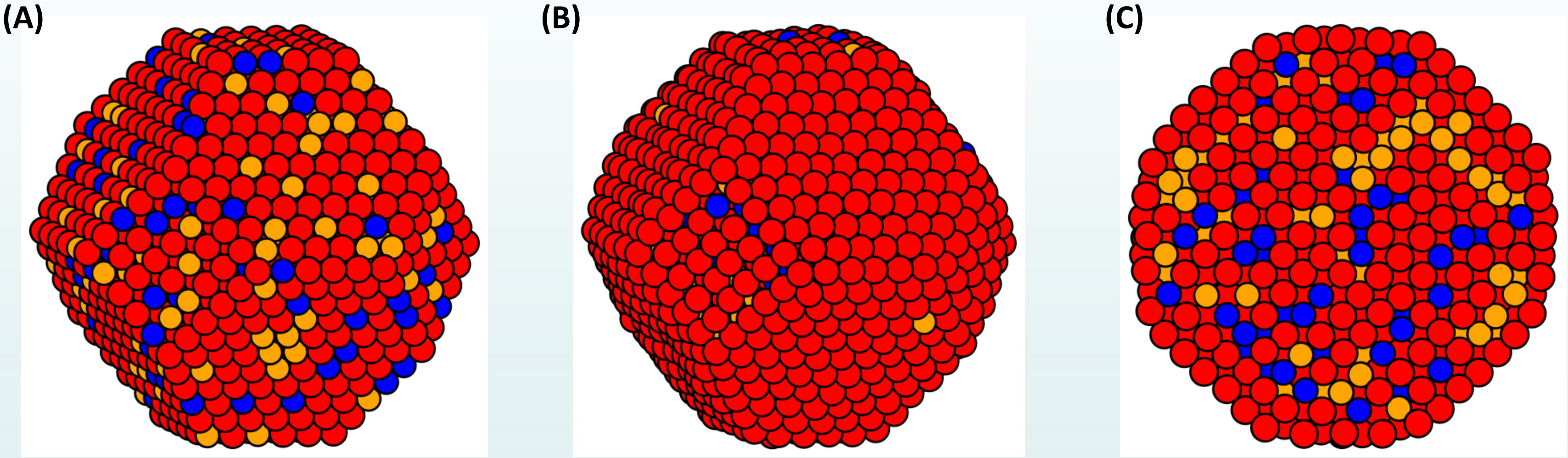
The most active alloy is Pt_3NiCo, with 4-fold improvement factor in specific activity compared to Pt-poly

To be published in 2012

Technical Accomplishments: *Fine Tuning of PtMN catalytic properties*

Feasibility studies of nanosegregated profile in ternary alloy NPs

Monte Carlo Simulation for Segregation on Pt_3MN Nanoscale Surfaces



(A) Surface composition of the as-synthesized ternary alloy cubo-octahedral NP

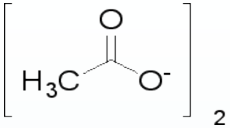
(B) External view and (C) Cross-section of the equilibrium structure of the annealed cubo-octahedral

To be published in 2012

Technical Accomplishments: *Synthesis of Pt Ternary Alloy NPs*

$Pt_3M_1N_2$ (NM = Fe, Co, and/or Ni)

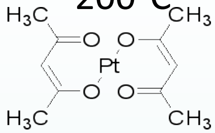
TM^{2+}

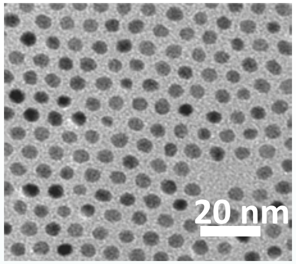


TM = Fe, Co, Ni

Oleylamine
oleic acid

~ 200°C

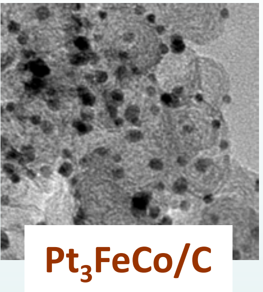


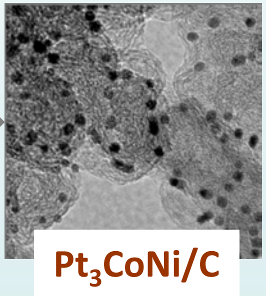


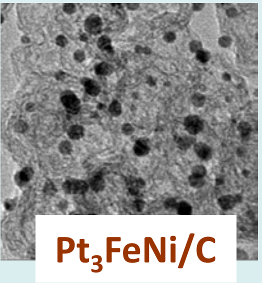
~ 150°C

Surfactant
removal

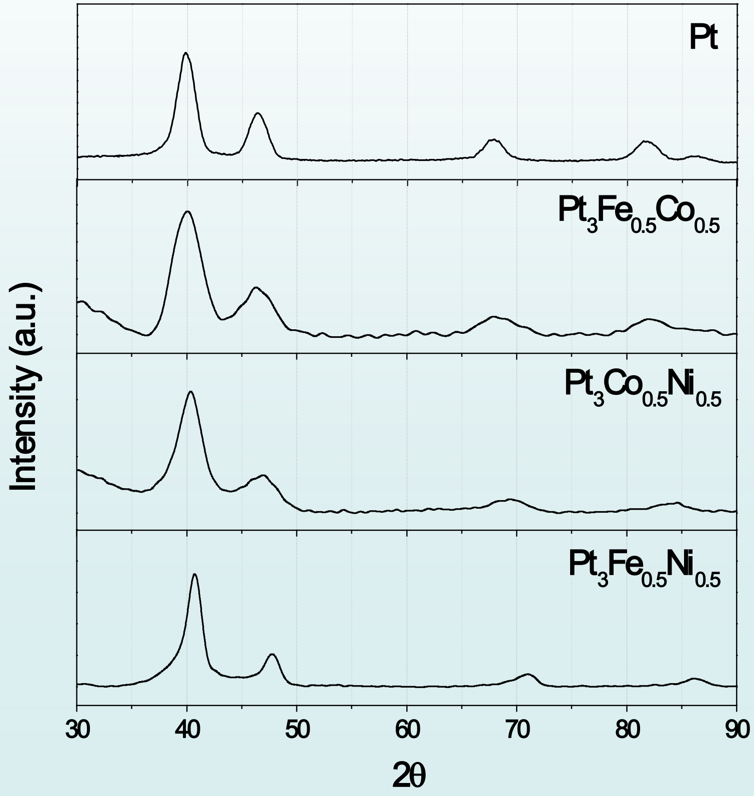
HSA
carbon







XRPD

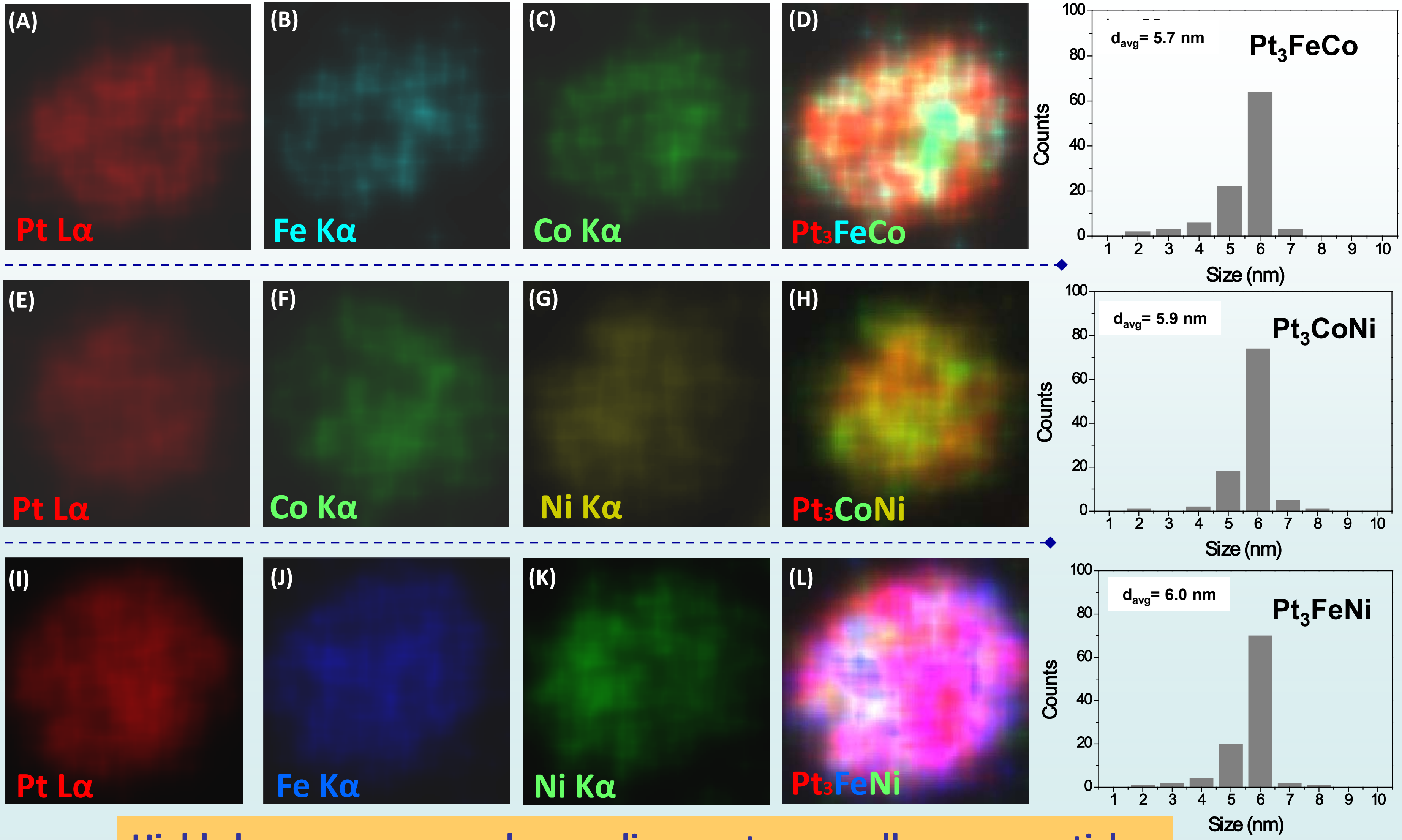


Synthesis of homogeneous and monodisperse ternary alloy nanoparticles has been accomplished

To be published 2012

Technical Accomplishments: *Characterization of Pt Ternary Alloy NPs*

EDS/STEM: *Elemental mapping and particle size distribution*

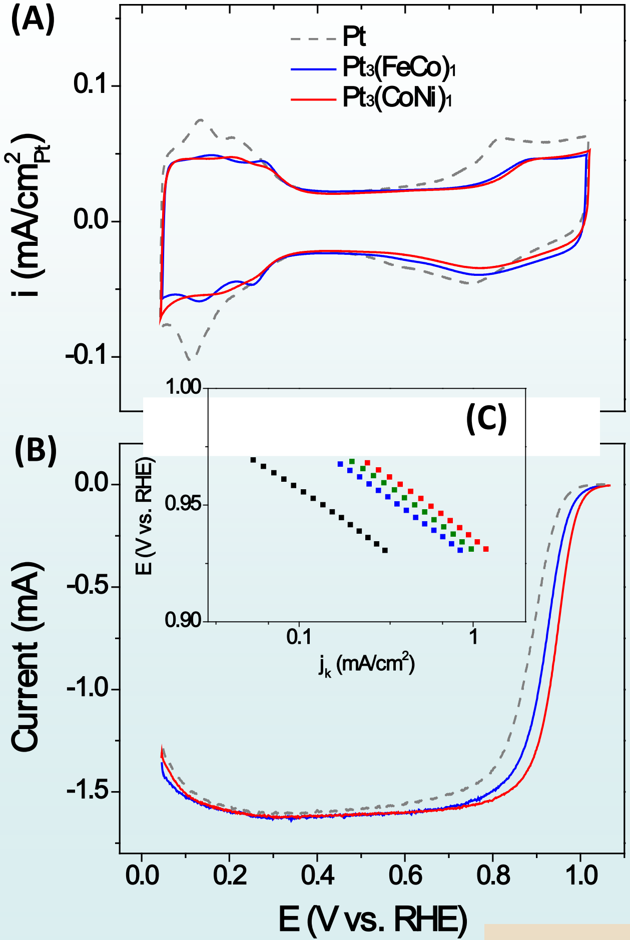


Highly homogeneous and monodisperse ternary alloy nanoparticles

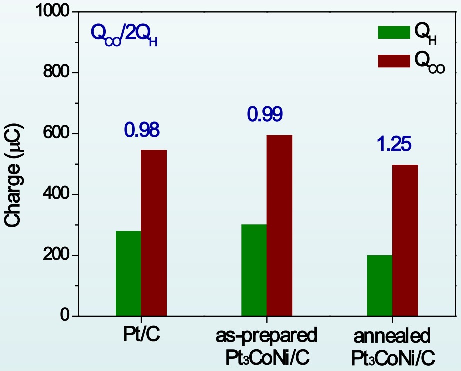
To be published 2012

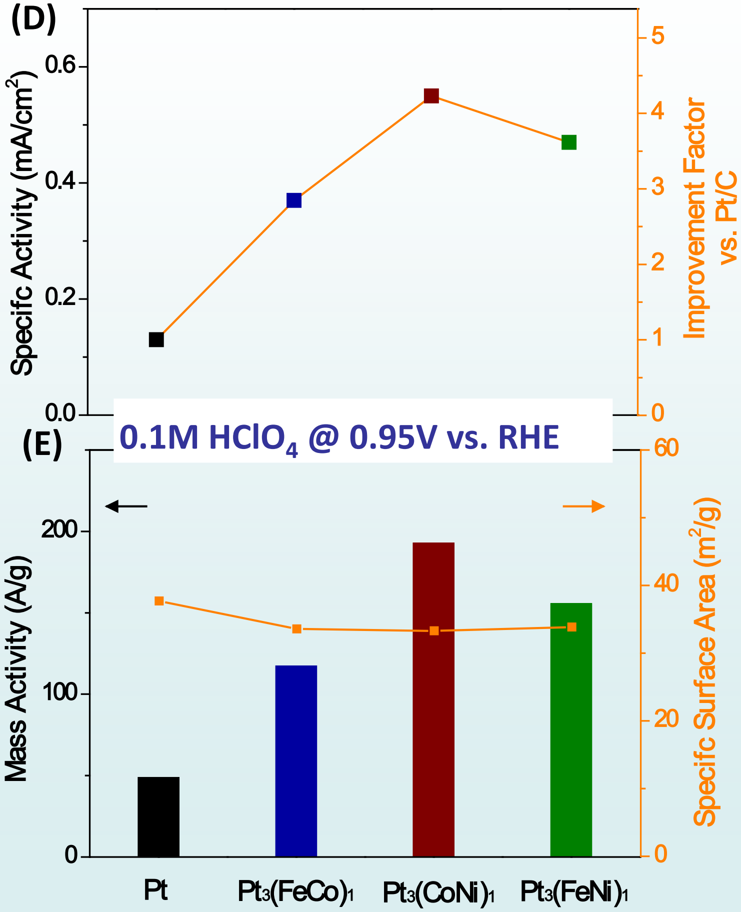
Technical Accomplishments: *Characterization of Pt Ternary Alloy NPs*

Electrochemical evaluation of Pt_3MN NPs by RDE



Existence of Pt-skin surface over Pt_3MN NPs was proved by the difference in integrated H_{upd} vs. CO stripping charge





Pt/C catalyst with same total metal loading, particle size prepared by solvothermal synthesis was used for comparison to ternary alloy catalysts

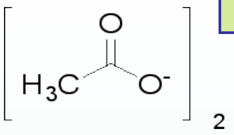
Improvement factor > 4 was achieved for specific and mass activities of Pt_3NiCo/C

To be published 2012

Technical Accomplishments: *PtMN Ternary Alloy NPs*

Synthesis and characterization of PtMN [Ongoing effort]

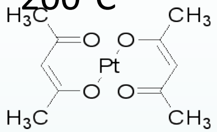
TM^{2+}

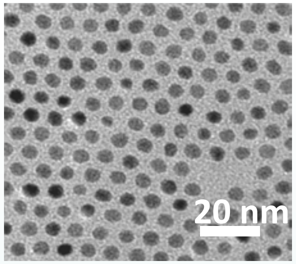


TM = Fe, Co, Ni

Oleylamine
oleic acid

~ 200°C

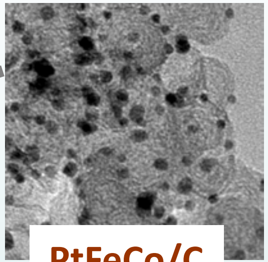




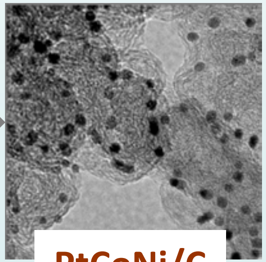
~ 150°C

Surfactant removal

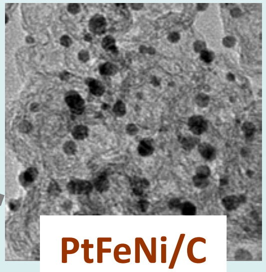
HSA carbon



PtFeCo/C



PtCoNi/C



PtFeNi/C

RDE

Ternary alloy NPs with higher content of Ni, Co and Fe were not stable during electrochemical characterizations. Attempts to stabilize these materials have not been accomplished yet

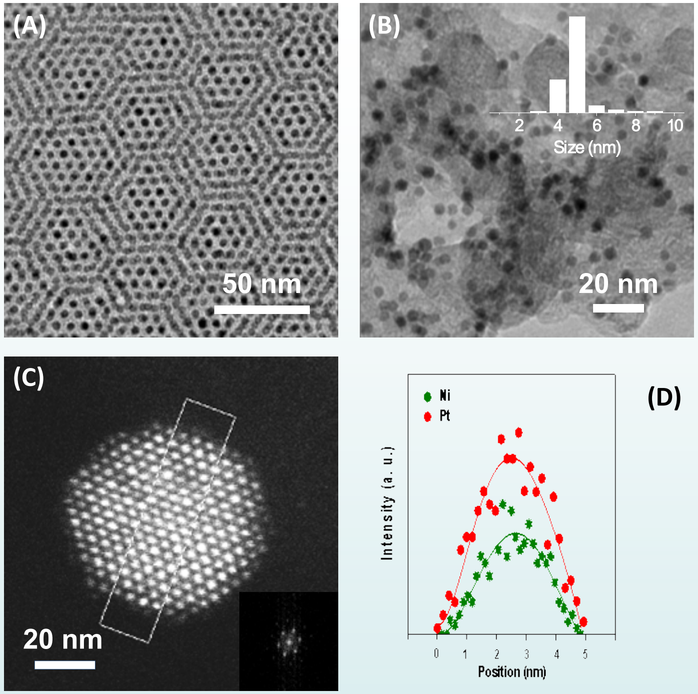
TEM

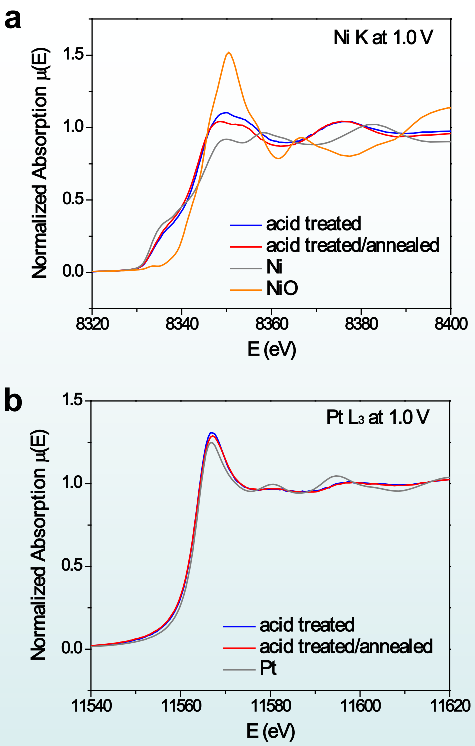
Nucleation growth of Pt is much faster than Co, Ni and Fe, which induces formation of separate Pt NPs, Pt-rich core and inhomogeneous distribution elements across in nanoparticles

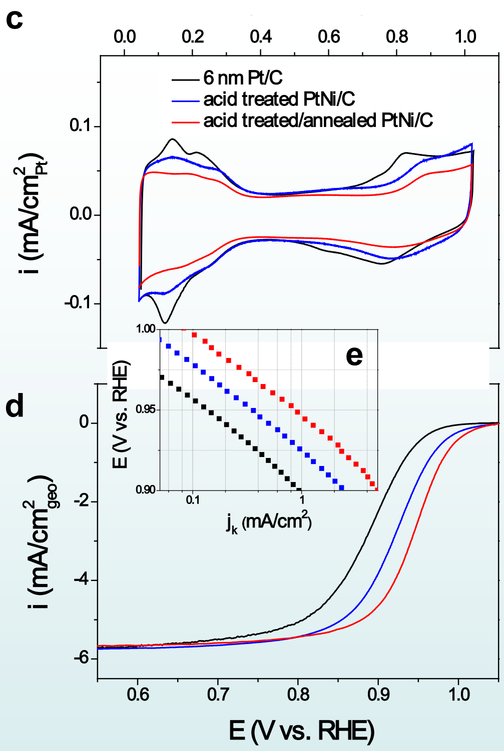
To be published 2012

Technical Accomplishments: *Catalyst of Choice*

PtNi Catalyst with Multilayered Pt-skin Surfaces







TEM: PtNi-Skin NPs have uniform particle size distribution with unique nanosegregated concentration profile

TEM/XRD: Content of Ni is maximized and allows formation of the multilayered Pt-skin by leaching/annealing

RDE: PtNi-Skin catalyst exhibits superior catalytic performance for the ORR and is highly durable system

***In-Situ* XANES:** Subsurface Ni is well protected by less oxophilic multilayered Pt-skin during potential cycling

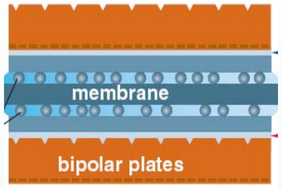
JACS *133(2011)14396*

Technical Accomplishments: *Catalyst of Choice*

MEA Studies: PtNi Catalyst with Multilayered Pt-skin Surfaces

Durability Studies of PtNi-skin Catalysts with GM: F. Wagner, E. Thompson and J. Ziegelbauer

MEA

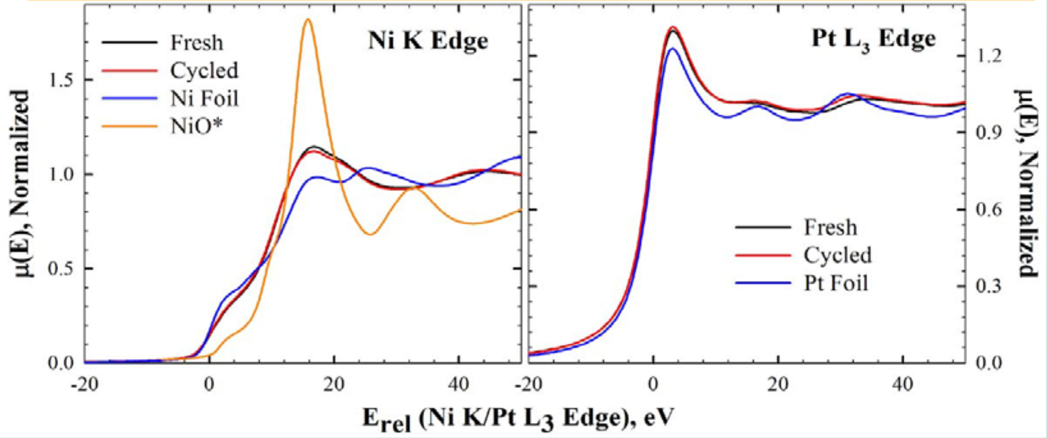


50 cm^2, 25μ DuPont NRE membrane, 80°C, 32% RH, 150kPa$_{abs}$, H_2 – Air, 20K cycles from 0.6-0.95V

MEA: 20,000 potential cycles, 0.6 – 0.95 V vs. RHE, at 80°C

Sample	ECSA (m^2/g_{Pt})	r.f. (cm_{Pt}^2/cm_{geo}^2)	M.A. (A/mg_{Pt})	S.A. ($\mu A/mg_{Pt}$)	% loss in M.A.
PtNi/C (1)	41	53.3	0.327	794	12%
PtNi/C (2)	39	–	0.287	700	

Ex-Situ EXAFS: Before and after 20,000 cycles in MEA



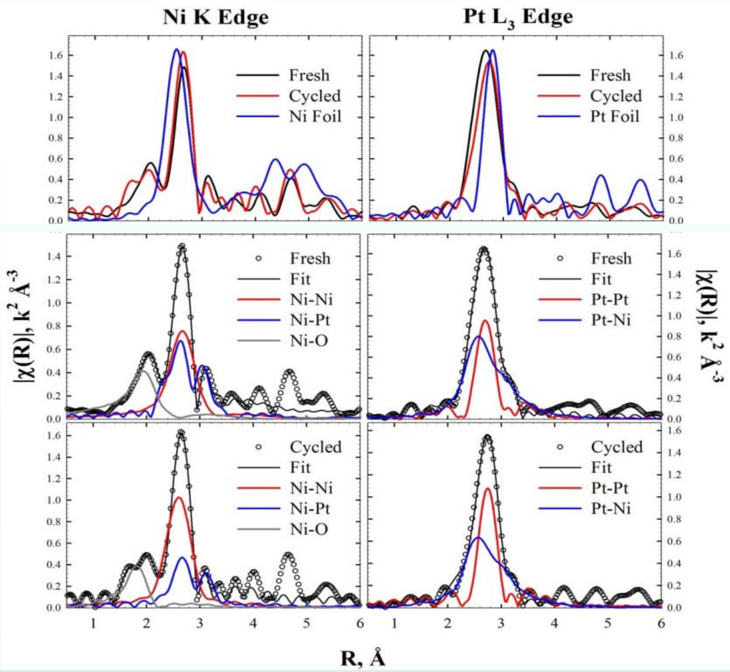
***Ex-Situ* EXAFS in MEA:** From both Ni and Pt edges negligible change occurred to the PtNi/C catalyst after 20K cycles, which confirms high stability of the multilayered Pt-skin near-surface formation that is capable of preserving the nanostructure during the electrochemical reactions

To be published in 2012

Technical Accomplishments: ***Catalyst of Choice***

MEA Studies: PtNi Catalyst with Multilayered Pt-skin Surfaces

Durability Studies of PtNi-skin Catalysts with GM: F. Wagner, E. Thompson and J. Ziegelbauer



Fresh **Edge**	**M-N**	**R (Å)[a]**	**N[b]**	**E_0 (eV)**	**σ^2 (Å^2)[c]**	**r-factor**
Ni K	Ni-Ni	2.602	3.6	7.52	0.012	0.006
	Ni-Pt	2.630	3.3	4.36	0.007	
	Ni-O	2.026	1.2	5.32	0.0015	
Pt L_3	Pt-Pt	2.678	6.8	5.16	0.008	0.009
	Pt-Ni	2.631	3.5	7.83	0.008	
Cycled						
Ni K	Ni-Ni	2.569	3.9	3.88	0.012	0.009
	Ni-Pt	2.633	1.8	7.20	0.007	
	Ni-O	2.012	0.8	4.61	0.0015	
Pt L_3	Pt-Pt	2.715	6.0	7.50	0.008	0.010
	Pt-Ni	2.632	3.2	9.34	0.008	

***Ex-Situ* EXAFS in MEA:** particles posses a Ni concentration gradient; most Ni is concentrated in the center of the particle and gradually depletes within the Pt-skin region (2 ~ 3 atomic layers)

The shift in the Ni-Ni interatomic distances arises because of the bulk-averaging nature of XAFS

Initially, the Ni-rich centers of the particles (with $R_{Ni\text{-}Ni} <$ 2.602 Å) are averaged with the $R_{Ni\text{-}Ni}$ values from Ni atoms closer to the surface

The “outer layer” Ni atoms are in a Pt-rich PtNi alloy environment where the interatomic distances are longer due to the presence of larger diameter Pt atoms in the lattice

After extensive voltage cycling, the remaining outermost Ni (within ~3 atomic layers from the surface) is removed, revealing the Ni-rich PtNi core in the center

The compositions of the “cores” of the particles are relatively resistant to change, due to the protection by the Pt-skin surface

The altered surface electronic and adsorption properties were preserved after the cycling

To be published in 2012

Summary

Pt-alloy NPs supported on HSA carbon:

Efficient removal of the capping agents from Pt-alloy NPs synthesized by colloidal solvo-thermal approach

Established methodology for determination of the electrochemically active surface area ECSA for nanosegregated catalysts with Pt-skin surfaces:

Ratio >1 between integrated charge from CO stripping curve and H_{upd} region can be used as indication for the formation of Pt-skin surfaces

Evaluation of PtMN systems

Nanosegregated concentration profile can be induced in Pt_3MN systems (TEM, RDE, EXAFS, XRD, DFT, MC)

Specific and mass activity of ternary alloy NPs can be improved by 4-fold for Pt_3NiCo system (RDE in 0.1M $HClO_4$ @ 0.95V *vs.* RHE: SA~ 0.6mA/cm^2 and MA~0.2A/mg$_{Pt}$, which is exceeds DOE target by factor of 3)

Pt_3MN are more active than Pt_3M catalysts

Stability of Pt_3M and Pt_3MN is comparable and it leads to ~30% of losses in electrochemical active surface area

PtNi with multilayered skin is the catalyst of choice with superior activity and durability properties. After potential cycling the improvements factors in specific and mass activities are 8 and 10 respectively over Pt/C.

EXAFS confirmed that structural parameters did not change by potential cycling

Surface area loss is ~12%, which was revealed from both RDE and MEA studies

Future Work

FY 2012

- **Final tailoring of the compositional properties that are controlling catalytic activity of PtMN systems**
- **Synthesis and characterization of nanosegregated PtNiCo system with higher content of TM**
- **Optimization of the nanosegregated catalyst of choice**
- **Evaluation of nanosegregated PtMN thin film nanoscale catalysts with tailored structure (!!!)**
- **Electrochemical evaluation in RDE and MEA (ANL, 3M)**
- **Scaling up of solvo-thermal approach to produce larger quantities of the catalyst of choice**

FY 2013

- **Activity/stability evaluation and optimization of MEA protocols in 3M, GM, ANL**
- **Achieving full capacity for scaling up of chemical synthesis of NPs supported on HSA carbon**
- **Alternative approaches for fabrication of thin-film nanoscale catalysts with ultra low PM content**

Collaborations

SUB-CONTRACTORS

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

COLLABORATORS

- **Argonne National Laboratory** – Nanoscale fabrication and DFT (CNM)
- **GM** – Technology transfer