

Platinum Monolayer Electrocatalysts

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Brookhaven National Laboratory

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Overview

Timeline

Start: July 2009
End: Project continuation and direction determined annually by DOE
% completed N/A

Budget

Funding received in
FY2016: \$900,000

Barriers

Catalysts' Performance:

Catalyst activity; $\geq 0.44 \text{ A/mg}_{\text{PGM}}$

Catalysts' Cost:

PGM loading; $\leq 0.125 \text{ mg PGM /cm}^2$

Catalysts' Durability:

< 40% loss in activity under potential cycling

Partners

Los Alamos National Laboratory

PI: Piotr Zelenay;

Coworker: Ulises Martinez

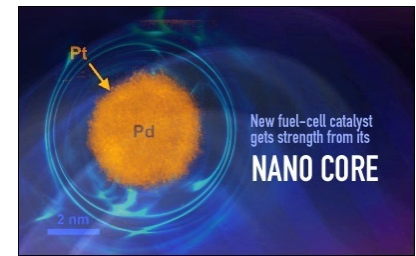
Collaborations

U. Wisconsin, U. Connecticut, BNL,

Toyota M.C., General Motors,

Korean Institute for Energy Research

Relevance



Project objectives:

Synthesizing high performance Pt monolayer (ML) electrocatalysts for the oxygen reduction reaction (ORR) consisting of a Pt ML shell on stable, inexpensive metal, alloy, metal oxide, nitride or carbide nanoparticle cores. Three catalysts will be developed that that will meet the DOE technical targets for 2020 with the ultimately low Pt contents.

This reporting period:

Further improvement of performance of Pt monolayer catalysts while reducing their PGM contents by the following strategies:

- Exploring synthesis of new non-noble metal cores
- Modifying core components by nitriding, alloying, electrodeposition of specific structures, and using reactive spray deposition (RSDT) without oxide formation.
- Electrodeposition of rare earths alloys from ionic liquids and non-aqueous solvents
- Improving catalysts response at high current densities

Approach

Synthesis of new non-noble metal cores

- ❖ Developing nitrided refractory metal cores
- ❖ Developing refractory metal alloy cores
- ❖ Nitriding non-noble metal core components

Milestone 1: Develop Pt ML catalysts on non-noble metal core that meet the 2020 targets

Exploring new alloys, new structures, new deposition methods

- ❖ Developing catalysts based on alloys with Mo.
- ❖ Developing a new class of core-shell catalysts with oxidized species segregated to edges and vertices of nanoparticles.
- ❖ Electrodeposition of yttrium, alloys of Y and Pt, Pd from ionic liquids and non-aqueous solvents to increase the ORR activity.
- ❖ Electrodeposition of nanoparticles with 3D porosity for enhanced mass transport and response at high current densities.
- ❖ Achieve better proton penetration into the catalyst layer by functionalizing CNT. Fabricate gas diffusion electrodes for fast screening of catalysts before MEA tests. Use Graphene as support.

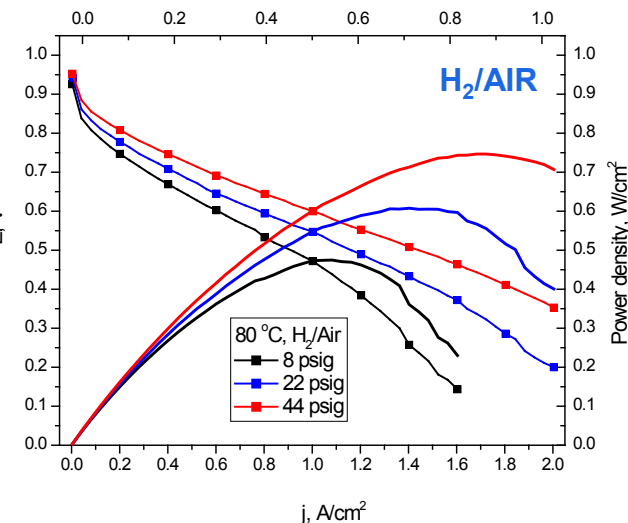
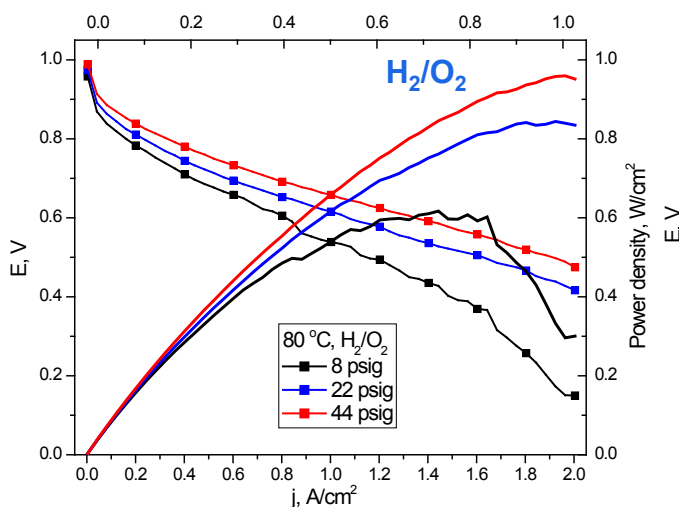
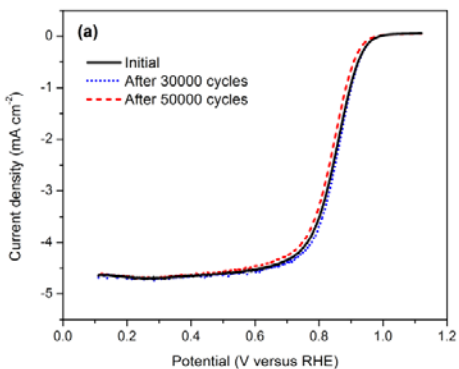
Milestone 2: Improve catalysts response at high current density by 80%

Accomplishments and Progress: Nitride-stabilized non-noble core components

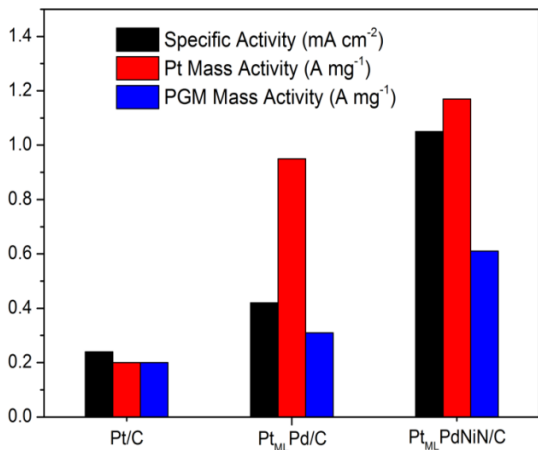
Pt_{ML} on nitride-stabilized PdNi core catalysts

NiPd calcined at 250 ° C in N₂ and 510 ° C in NH₃
 XAS, Ni nitride formation stabilizes Ni.

MEA performance as a function of back pressures

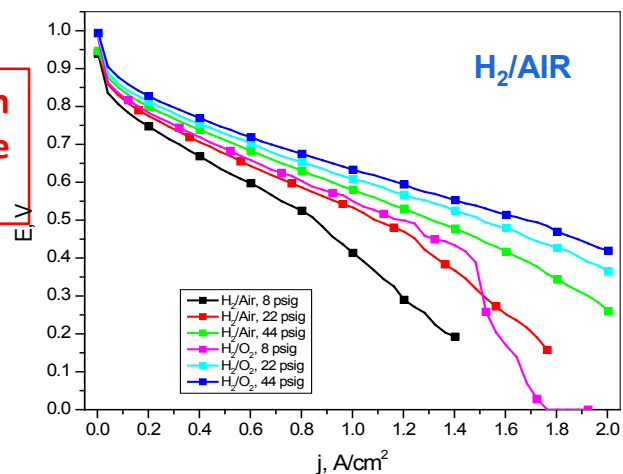


Anode- Pt (TKK 46%) 0.1 mgPt/cm²
 Cathode – PtPdNiN/C (17 %) 0.2 mgPt/cm², 0.2mgPdcm²



Pd content is reduced by 50% in comparison with Pt/Pd/C catalyst, while stability and activity are enhanced

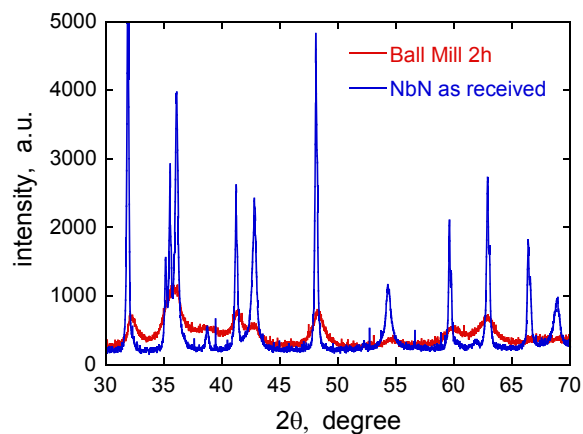
Anode- Pt (TKK 46% 0.1 mgPt/cm²):
 Cathode – PtPdNiN/C (17 % Pt) 0.1 mgPt/cm².
 0.1mgPd/cm²



Accomplishments and Progress: Non-noble metal cores

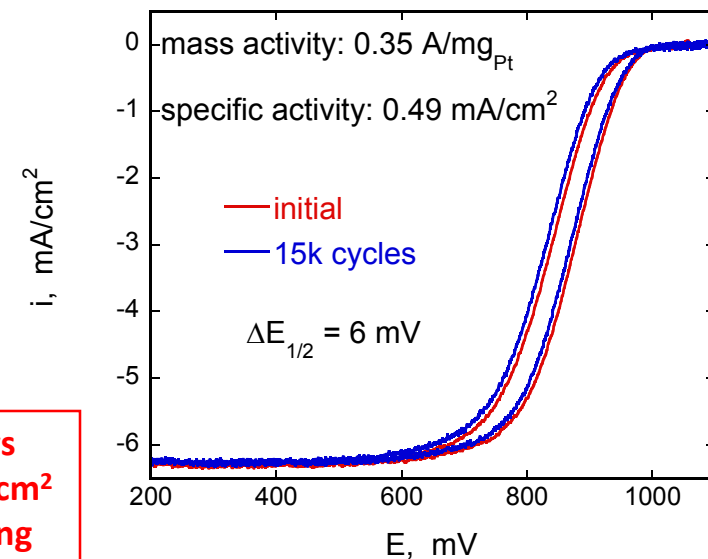
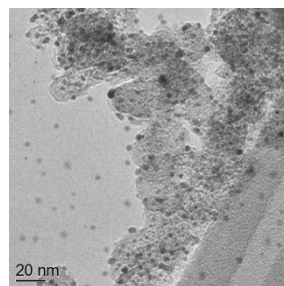
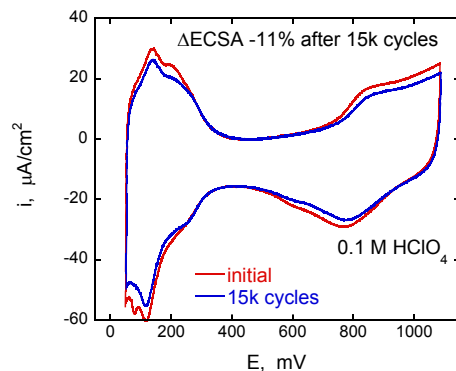
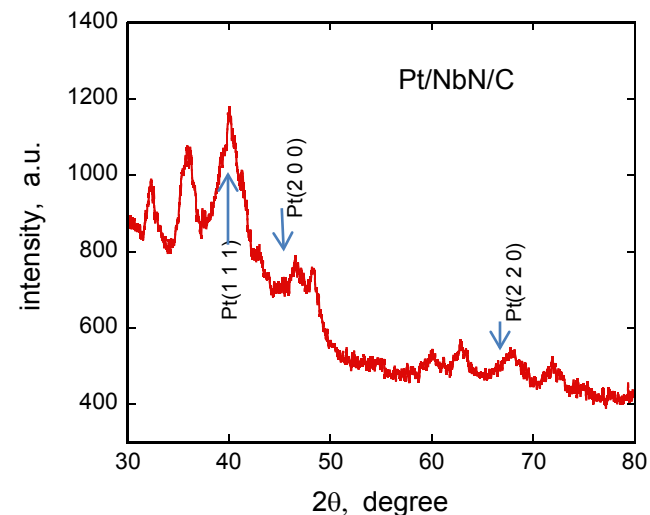
NbN, Niobium nitride as a core

Pt 13%, reduced by NaBH_4



NbN particle size
initial: 500 nm
after ball milling:
50 nm

NbN Resistivity:
150 $\mu\Omega\text{cm}$

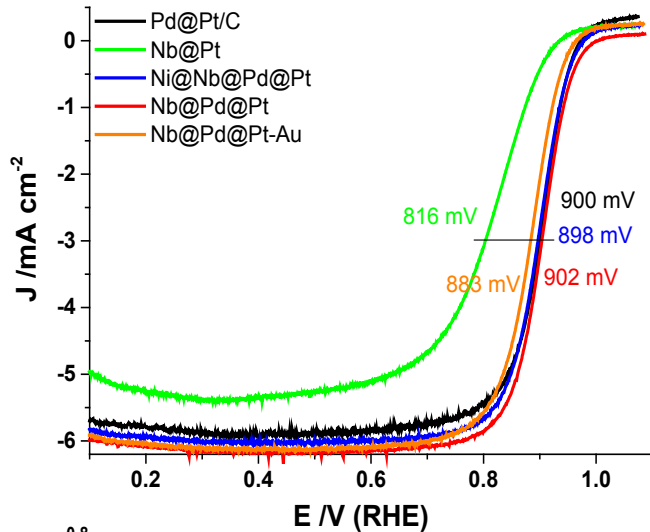


Preliminary results show NbN is a very attractive core material.

Far from optimized, Pt/NbN/C shows
MA = 0.35 $\text{mA}/\text{mg}_{\text{Pt}}$; SA = 0.49 mA/cm^2
Future studies will focus on improving
synthesis and durability.

Accomplishments and Progress: Non-noble metal based cores

Performance of several catalysts based on Nb cores

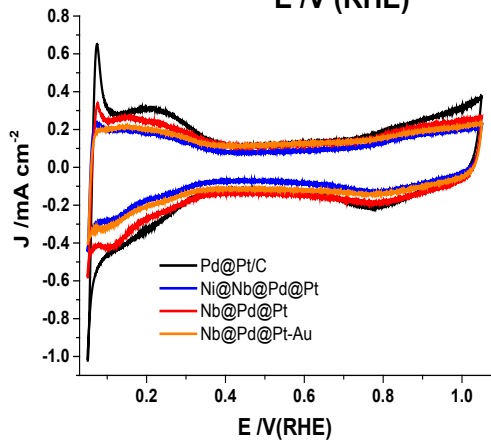
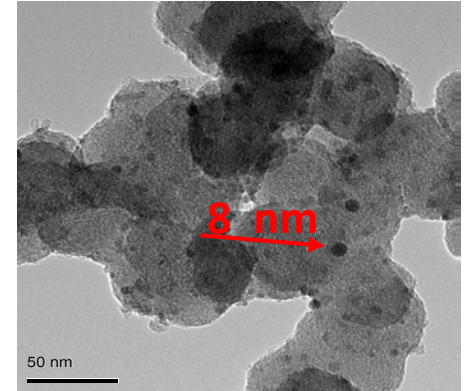


Synthesis:

Salts $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, NbCl_5 and Vulcan-X72 mixed in ethanol and dried.

Annealed the mixture at 650 or 700 °C for 1 h in H_2 .

Immersed in solution of PdCl_2 in Ar to deposit approximately 2 ML of Pd.

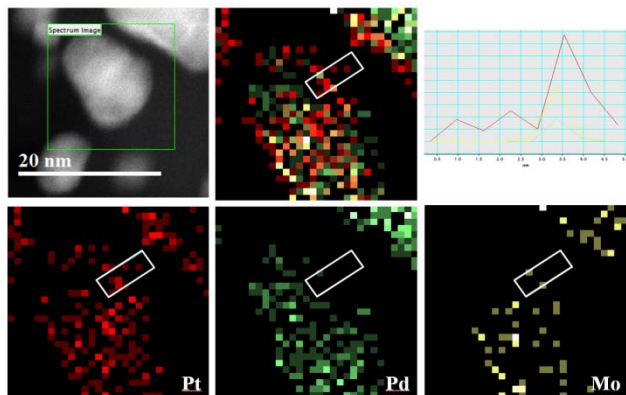


Catalysts	MA_{Pt} A/mg _{Pt}	MA_{PGM} A/mg _{PGM}	$E_{1/2}$ mV	$E_{1/2}$ shift mV
Pd@Pt	1.38	0.23	900	19
Nb@Pt	0.03	-	816	-
Ni@Nb@Pd@Pt	3.1	0.4	898	28
Nb@Pd@Pt	3	0.38	900	32
Nb@Pd@Pt@Au	~1.6	~0.15	883	29

Nb cores: Promising PGM mass activity. Improvements are expected with optimized synthesis.

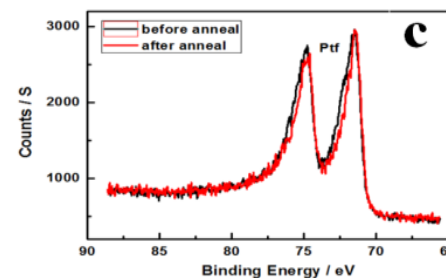
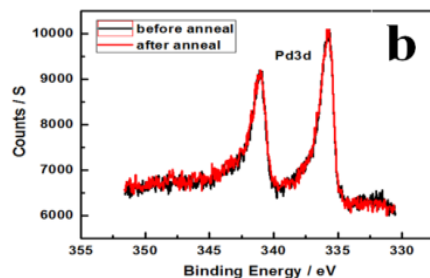
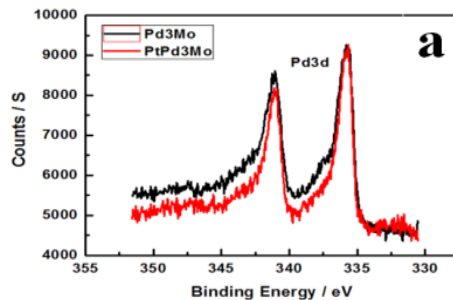
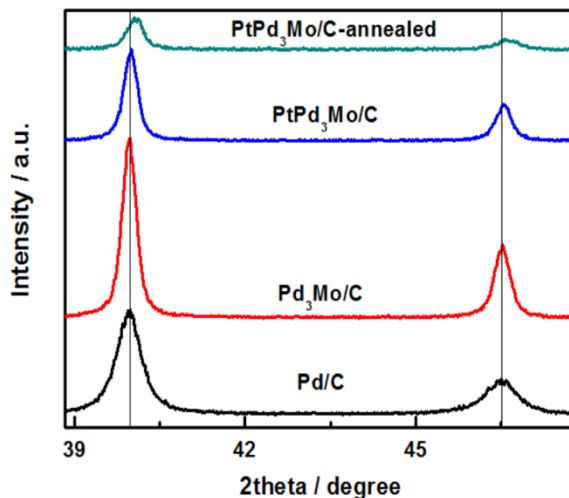
Accomplishments and Progress: New core modifiers

1. Mo-modified cores: Pt_{ML} on Pd-Mo core



EDS mapping of Pt@Pd₃Mo/C catalyst.

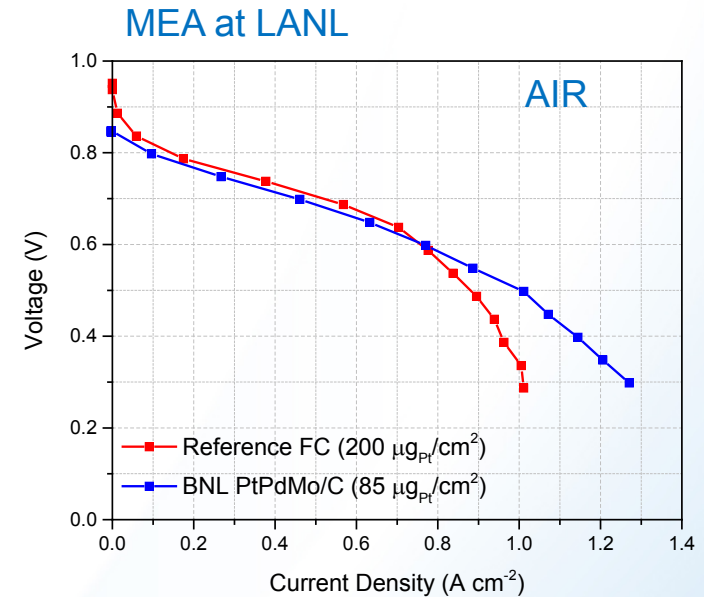
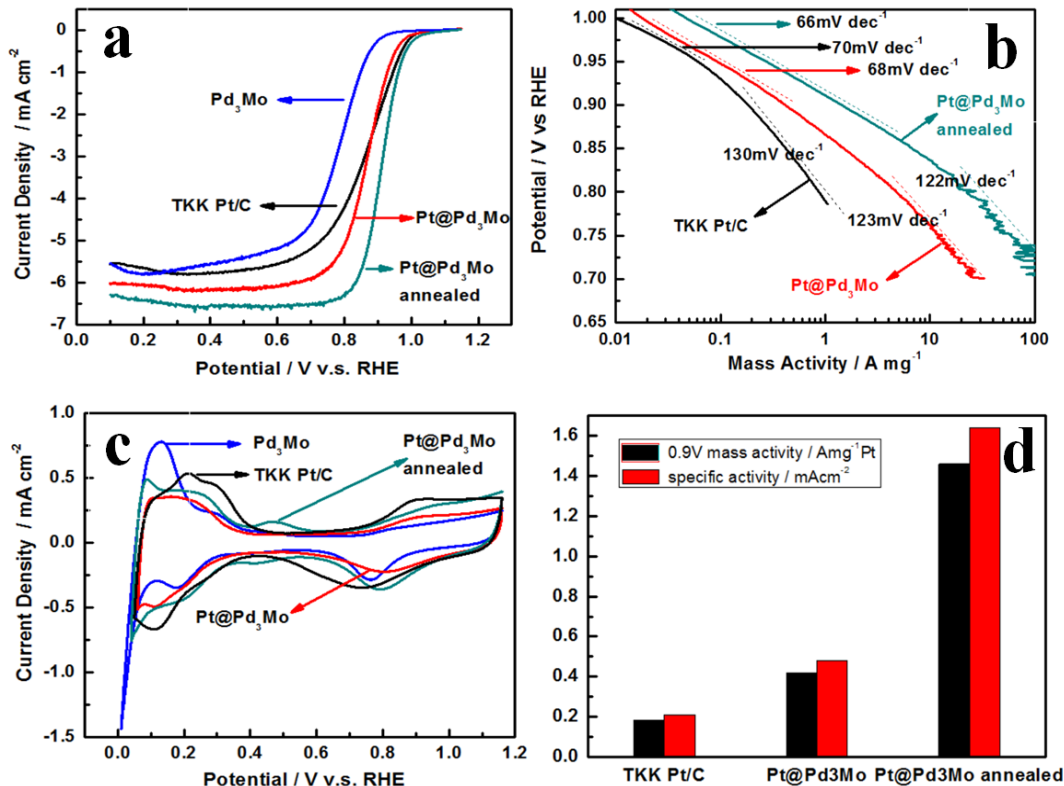
Synthesis



XPS of Pd in modified cores

Mo in the Pd₃Mo core is segregated to the surface after annealing, where Mo is oxidized. Mo reduced in H₂ forms strong bond with Pt and stabilizes Pt atoms. That interaction improves activity and stability of Pt for the ORR.

2. Mo-modified cores: Pt_{ML} on Pd-Mo core



Cathode: BNL PtPdMo/C ca. 85 μg_{Pt}cm⁻², 13 μg_{Pd}cm⁻², air, 200 sccm, 1.0 bar air;
Anode: Commercial GDE ca. 0.2 mg_{Pt}cm⁻²;
Membrane: Nafion®·211; Cell: 80°C;
Reference Fuel Cell: 0.1 mg cm⁻² anode; 0.2 mg cm⁻² cathode; 47 wt.% Pt/C (TKK).

The Pt monolayer on Pd₃Mo has 7 and 8 times higher mass and specific activities than commercial catalyst, respectively.
 PGM mass activity is expected to increase with improved synthesis.
 Similar synthesis of **PtRuMo** catalysts produced smaller effects

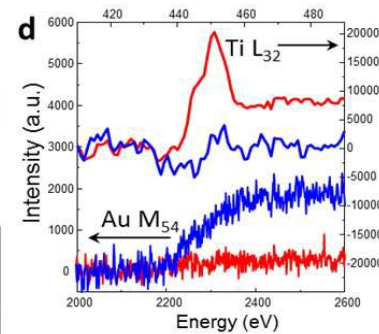
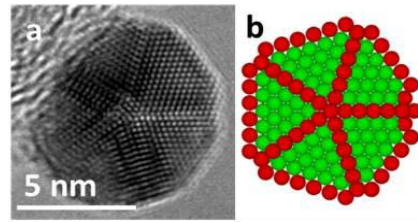
Accomplishments and Progress: New class of core-shell catalysts

Catalysts with oxidized component preferentially segregated to edges and vertexes

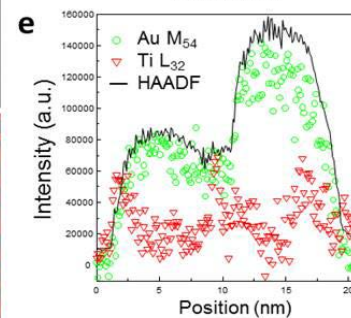
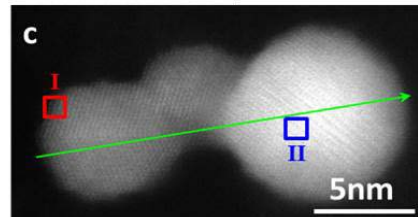
Pt monolayer on TiO_x decorated Au cores

Au and Ti co-deposited by reduction of solution of their salts

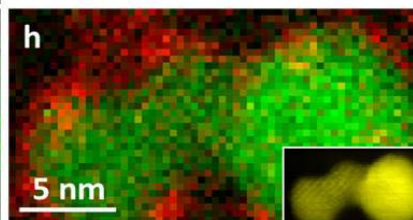
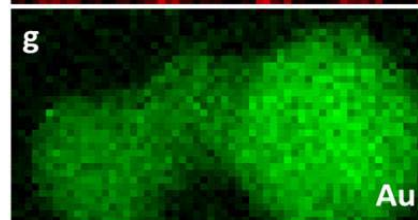
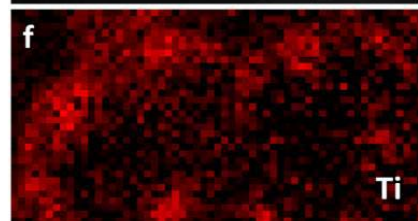
HRTEM of a Ti-Au nanoparticle viewed along five-fold axis ($[110]$ direction) in fcc lattice), showing five twins and truncated decahedral shape.



EELS of Ti L_{32} and Au M_{54} edges from area I (red) and area II (blue) in c



Maps of Ti L_{32} (f) and Au M_{54} (g) edges from the 2D EELS spectrum image, and overlap f and g

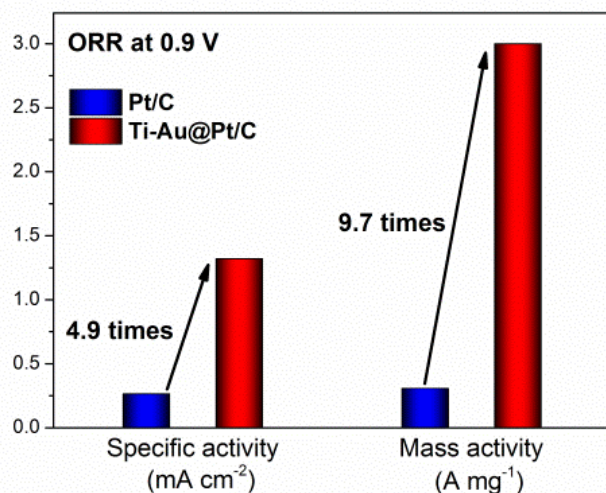
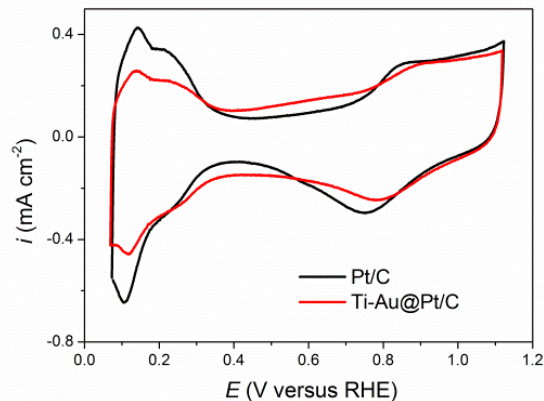


Au is at core, **Ti** distributes at the surface of the particles, mainly at the sharp corners

Accomplishments and Progress: New class of core-shell catalysts

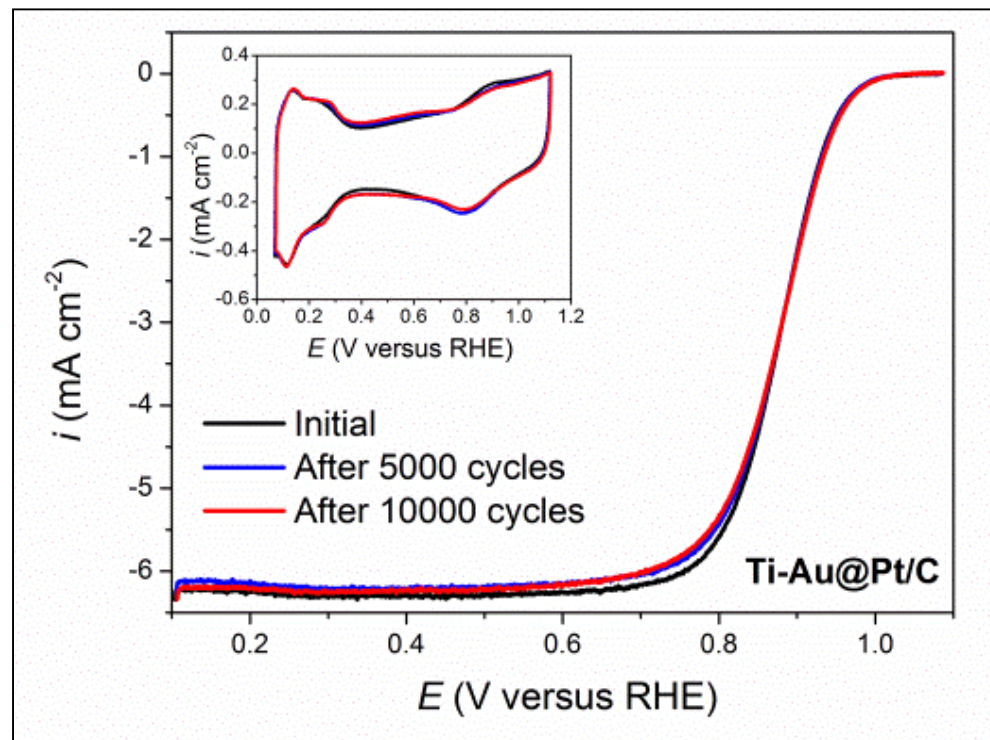
Pt monolayer on TiO_x decorated Au cores

ORR activity and durability



$$\text{MA(Pt)} = 3\text{A/mg}_{\text{Pt}}$$

$$\text{MA(Pt + Au)} = 0.34\text{A/mg}_{\text{(Pt + Au)}}$$



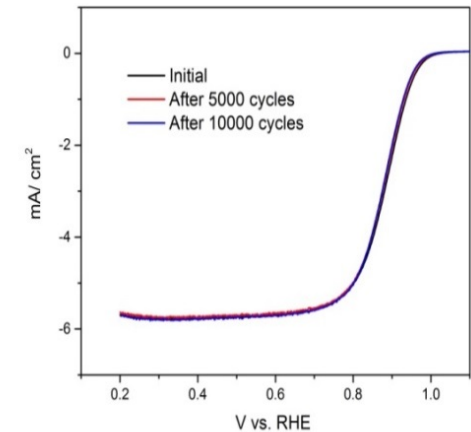
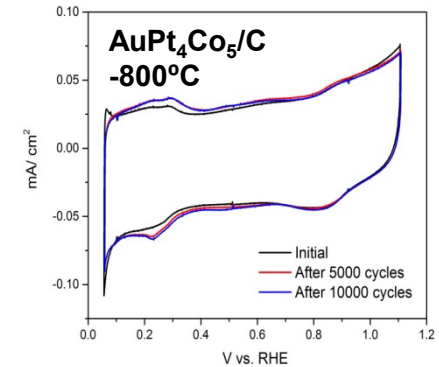
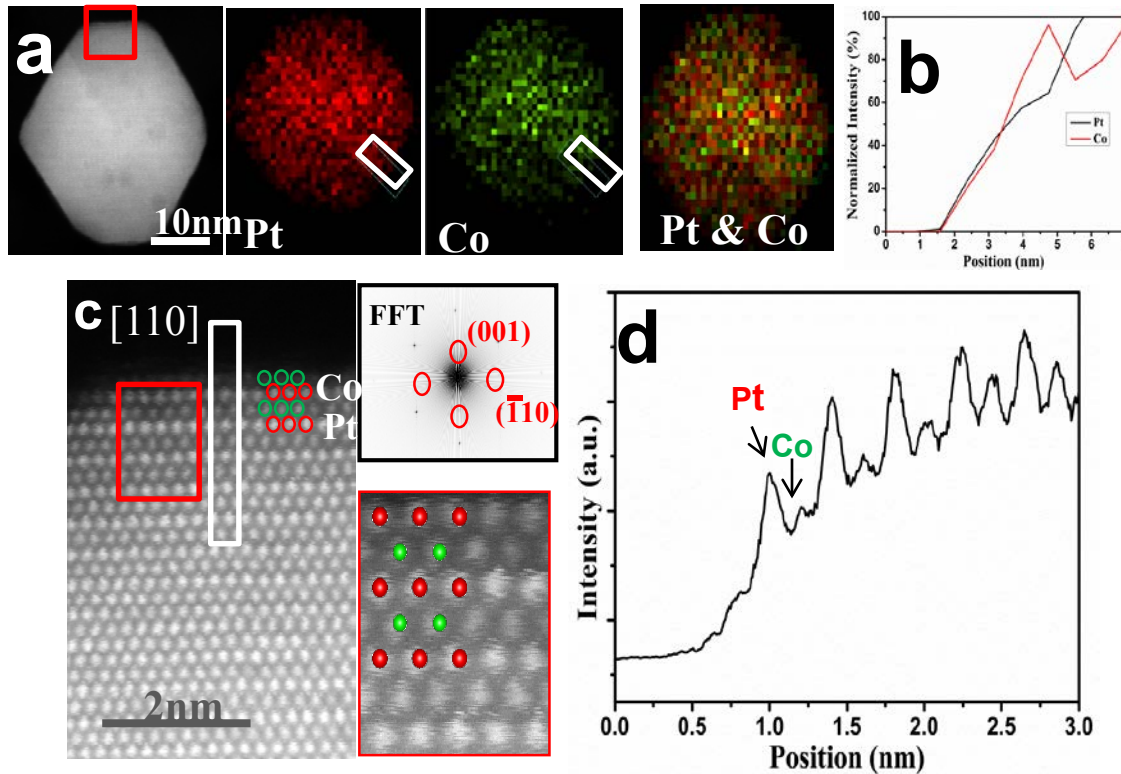
Ti-oxide:

- Controls the amount of Au atoms that segregate on the Pt surface
- destabilizes OH_{ad} on Pt . High durability is expected.

Accomplishments and Progress: New intermetallic cores

Cores: AuPt₄Co₅/C-800C intermetallic nanoparticle

HAADF and EDS mapping; STEM-HAADF PtCo intermetallic



Nanoparticles heat treated at 800° C attain a full PtCo intermetallic structure; 700°C not sufficient.

Promising RDE. MEA tests at LANL are in progress

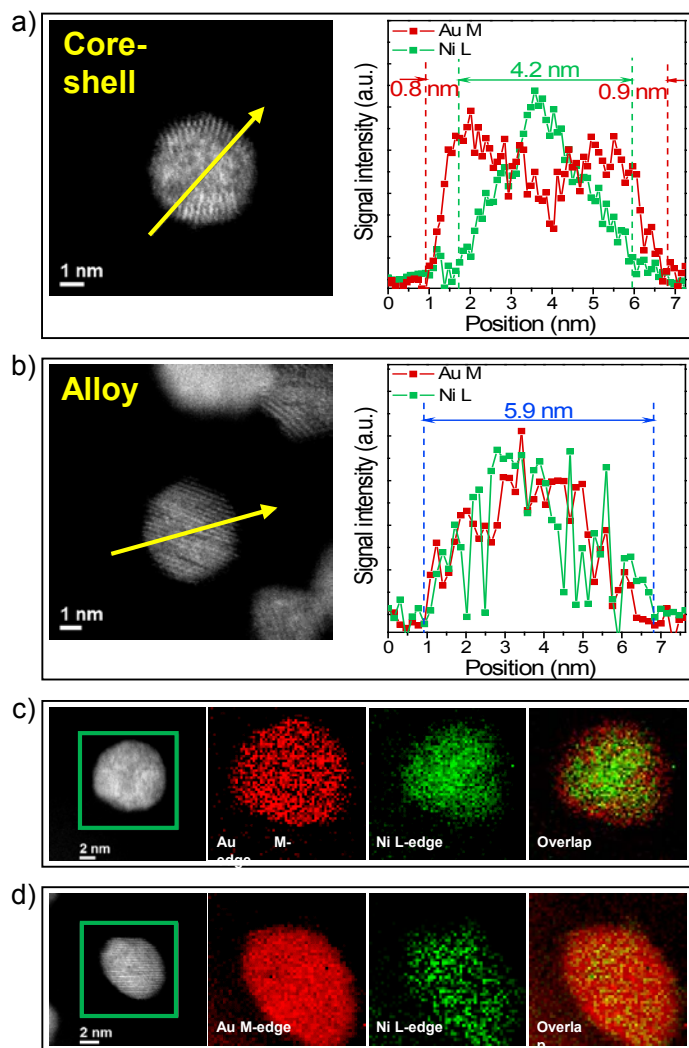
Half wave potentials (mV)		A/mg _{Pt}
AuPt ₄ Co ₅ /C-700°C	900	0.58
AuPt ₄ Co ₅ /C-800°C	885	0.50

Accomplishments and Progress: New insights in core-shell catalysis

Strong effect of the structure of bimetallic AuNi cores on the activity of Pt shell

Core-shell vs. alloyed AuNi cores

Interaction of alloyed AuNi with a Pt shell makes it more active for the ORR than that with AuNi core-shell nanoparticles.



HAADF-STEM images and EELS line-scan profiles of Au (red) and Ni (green)

Coordination numbers and alloying extent for AuNi nanoparticles

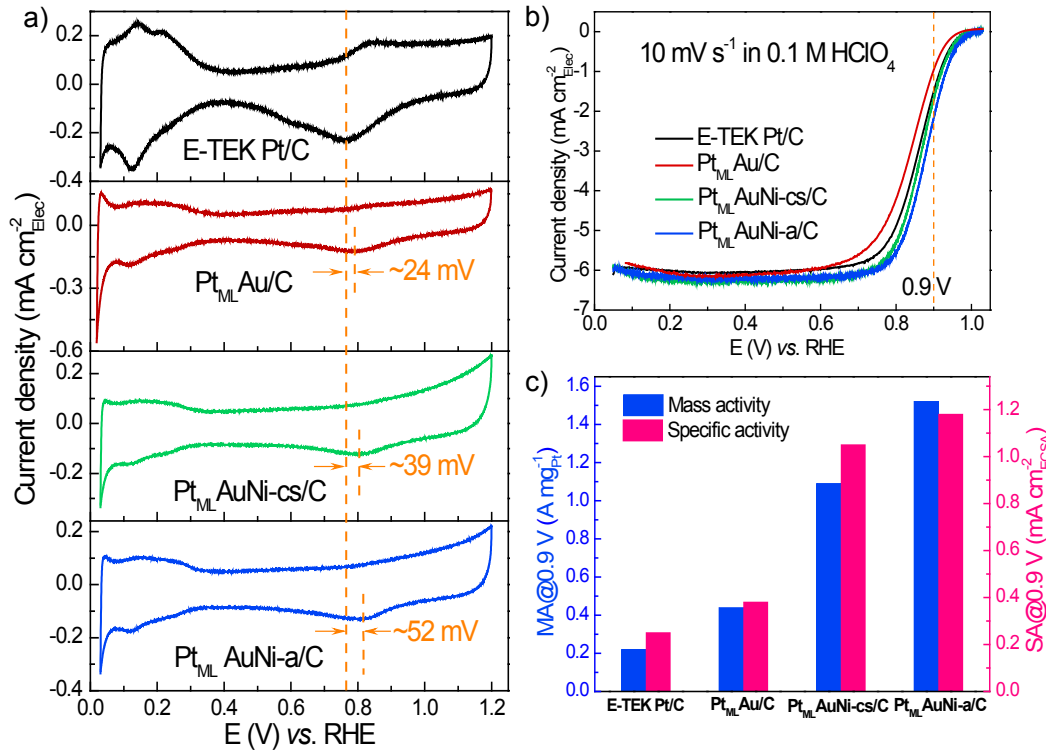
	$N_{\text{Au-Au}}$	$N_{\text{Au-Ni}}$	$N_{\text{Ni-Ni}}$	$N_{\text{Ni-Au}}$	P_{observed}	R_{observed}	$J_{\text{Au}}(\%)$	$J_{\text{Ni}}(\%)$
AuNi-cs/C	6.7	3.8	8.1	3.8	0.36	0.32	72	63
AuNi-a/C	5.4	4.7	5.7	4.7	0.47	0.45	93	91

HAADF-STEM images and EELS line-scan profiles of Au (red) and Ni (green)
 Che

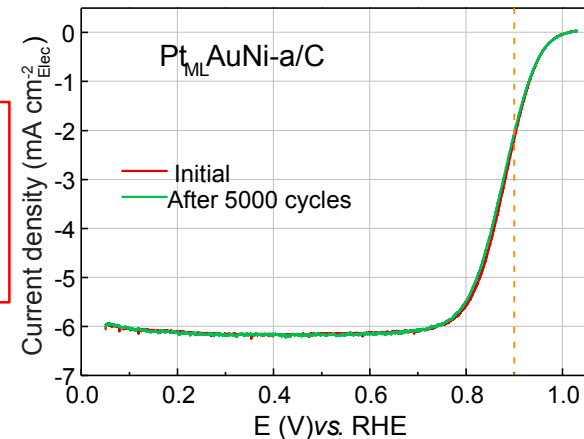
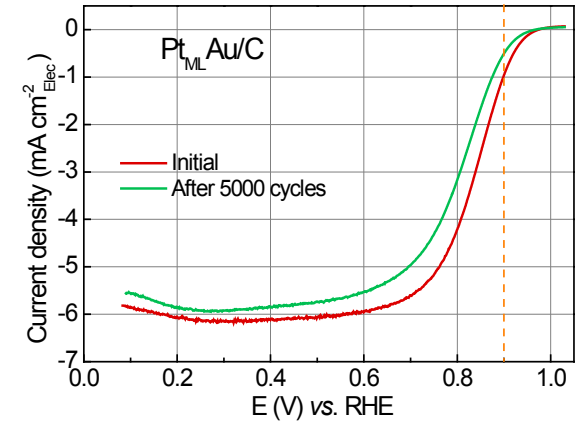
Hu et al., Chemistry of Materials, accepted

Accomplishments and Progress: New insights in core shell catalysts

Strong effect of the structure of bimetallic AuNi cores on the activity of Pt shell



Electronic effects of the alloy change the O₂ and H₂O interaction with the Pt shell and facilitate increased ORR kinetics.



PGM Activity:

$$\text{AuNi}_{\text{alloy}} = 1.52 \text{ A mg}^{-1}$$

$$\text{AuNi}_{\text{core-shell}} = 1.18 \text{ mA cm}^{-2}$$

Stability (5000 potential cycles):

AuNi_{alloy}: almost no loss

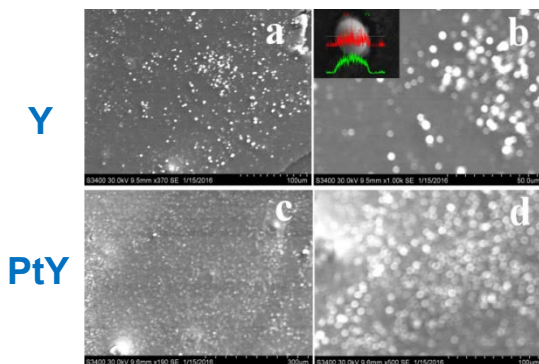
AuNi_{core-shell}: 25mV loss in E_{1/2}

Bimetallic cores are promising for Pt_{ML} core-shell catalysts

Accomplishments and Progress: New syntheses from ionic liquids

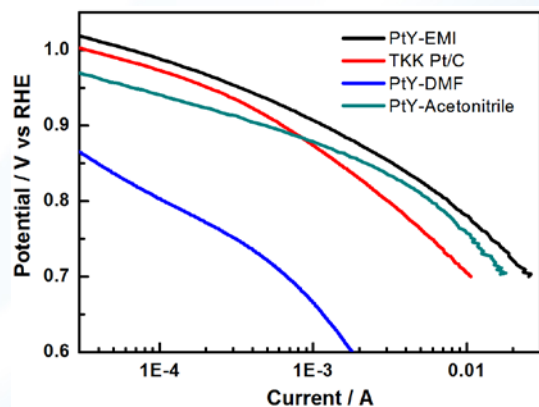
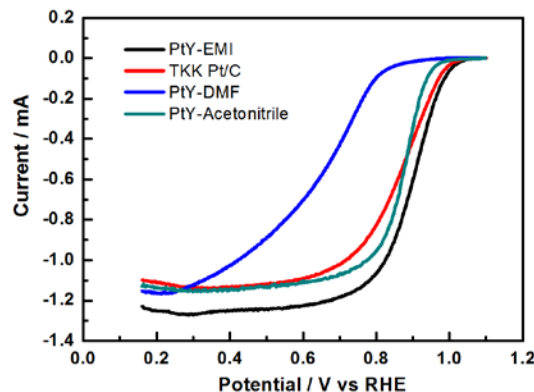
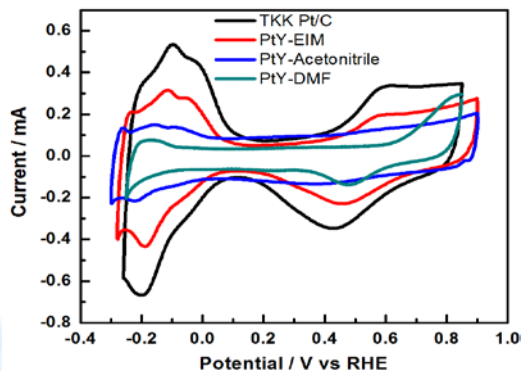
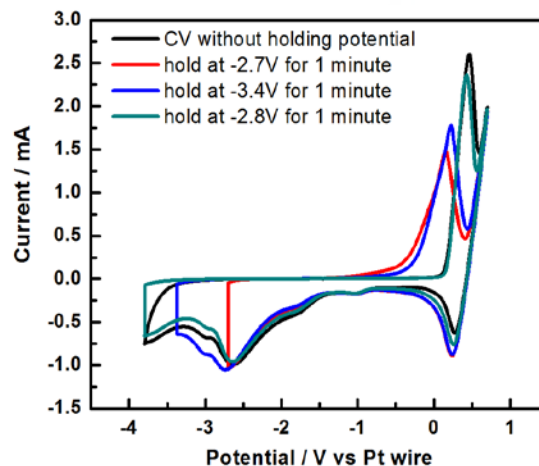
Electrodeposition of Yttrium and Y-Pt alloys from ionic liquids and non-aqueous solvents

High activity of Pt-Y alloys shown by DFT calculations and sputter deposition catalysts. Norskov et al. Electrodeposition from ionic liquids offers a promising possibility for nanoparticle synthesis.



The highest activity found for PtY – EMI catalyst, larger than for PtY-AN; PtY-DMF or Pt/C TKK.

SEM pictures of electrodeposited Y (a,b) and PtY (c,d). Insert is EDS of an Y particle



CV in Ar saturated 0.1M HClO₄ solution. PtY electrodeposited in 1-Ethyl-3-methylimidazolium tetrafluoroborate (EMI), acetonitrile (AN) and dimethylformamide (DMF).

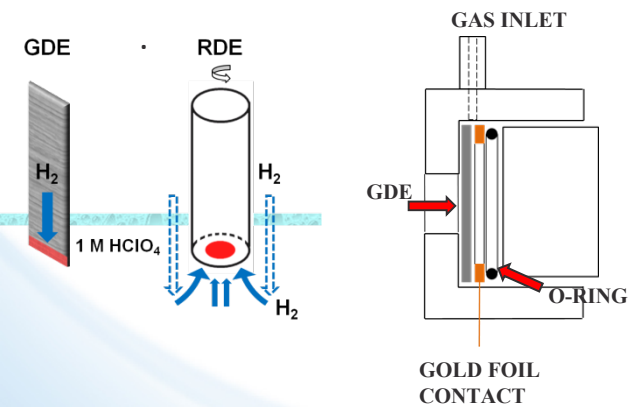
Accomplishments and Progress: Improving performance at high CD

Factors limiting the high CD ORR : i) thin catalyst layer, ii) low proton transport into it

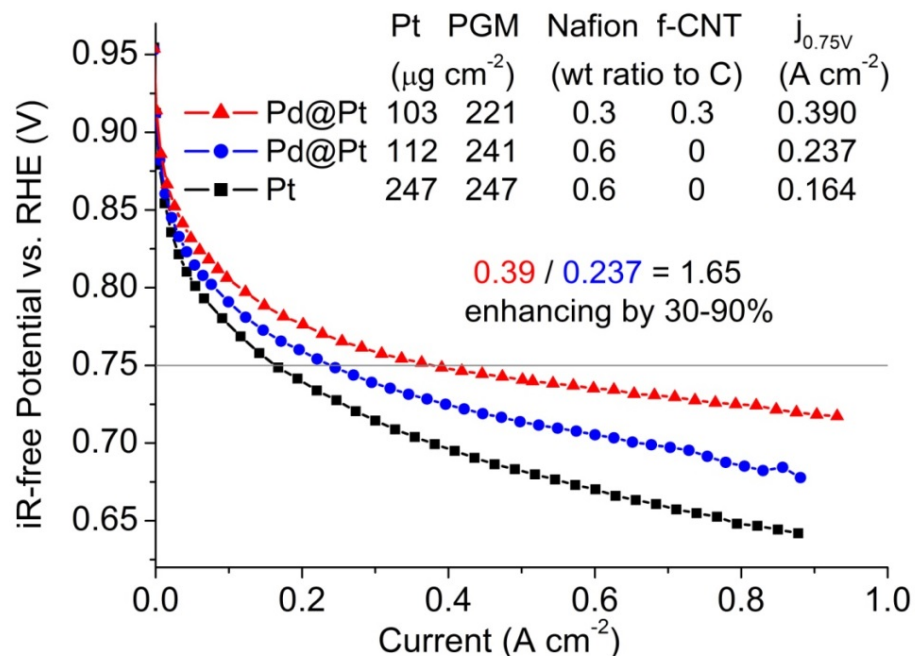
Remedies: (1) Stimulate proton transport into the catalyst layer (by attached anions),
 (2) more conductive carbon network, (3) reducing the amount of Nafion to improve gas access.

Measuring high CD performance using gas diffusion electrodes for fast screening before MEA tests

	RDE	GDE	MEA
Oxygen	O ₂	O ₂	Air, O ₂
Temperature (°C)	23	23	60 - 80
Pt Loading (μg cm ⁻²)	< 20	< 300	< 300
Current (mA cm ⁻²)	6	800	2000
Catalyst layer	2D/solution	3D/solution	3D/Membrane
Electrode area (cm ²)	0.2	1	5 - 50
Catalyst needed (mg)	5	20	200



Partially replacing Nafion with acid-treated CNT



The enhancement factor normalized to the Pt surface area is 80%.
MEA tests are being planned at GM.

These measurements helped elucidating slower HOR-HER Kinetics in base than in acid. It is caused by switch from the Tafel RDS in acid to the Volmer RDS in base.

Summary

New results show possibility of developing high-performance, low cost Pt ML catalysts with non-noble metal cores. Nitriding cores components can help achieving that. NbN core is very promising.

New class of core-shell catalysts include oxidized component segregated to edges and vortexes causing stability and improved activity. Complex synthesis may be an obstacle.

Y-Pt alloy deposition from ionic liquids and AN produced catalysts with activity high enough to continue this work. This opens new synthesis possibilities unachievable by conventional methods.

Improvements of the GDE response at the high CDs has been obtained using functionalized CNTs and reducing the Nafion content in the catalyst ink.

Efforts not covered on the slides:

- Electrodeposited WNi cores with high PGM MA are being tested by industry collaborators.
- The Pt/Pd/C catalyst is now commercially available based on the BNL license; It is being tested in several industrial laboratories. Recent industry results (Kongkanand et al. ACS Catalysis, Jan. 2016) indicate that 2g of Pt is necessary for a 80kW FC car battery.
- BNL publications on PtML catalysts have been cited over 2000 times last year.

Proposed Future Work

FY 16 and beyond

1. Synthesis and MEA tests of selected catalysts

- Nb-based non-noble metal cores will be synthesized using thermal routes and RFDT.
- New synthesis of hollow Pd cores with a simple scale up will be completed.
- Other refractory metals will be tested, given their attractive stability. Deactivation induced by their low-filled *d*-band has to be resolved.
- Electrodeposited Pt_{ML}/Pd/WNi will be improved for high CD.

Milestone 1 Pt ML catalysts on non-noble metal core to meet the 2020 targets *Completed 20%*

2. Novel strategies to synthesize high performance, Pt monolayer electrocatalysts

- Electrodeposition of refractory metal alloys and earth metals using aqueous, ionic liquids and/or non-aqueous solvents.
- Nitriding will be used at ambient and high pressure to stabilize non-noble metal cores.
- Reactive spray deposition of non-noble metal alloys without oxidation of components.

3. Approaching 1.23V

Onion-structured nanoparticles with new cores of multiple metal layers to tune Pt monolayer properties and shift E° closer to 1.23 V. Supporting DFT calculations have been completed.

4. Improving catalysts response at high CD

Functionalized CNTs and reducing the Nafion content in the catalyst ink will be used and combined with 3D deposited catalysts layers.

Milestone 2 Improve catalysts response at high CD regions by 80%

Completed 10%

Collaborations

Partners

Los Alamos National Laboratory, Piotr Zelenay PI, Ulises Martinez, co-worker; Catalysts characterization, MEA tests, results discussion and future work.

Collaborators

U. Wisconsin (University) Manos Mavrikakis, DFT studies

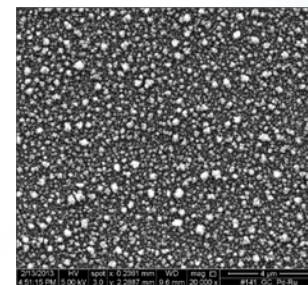
U. Connecticut, Radenka Maric, reactive spray catalysts deposition (RSD);
Finishing equipment construction to avoid any oxidation of refractory metal cores

BNL, Dong Su, Lijun Wu and Yimei Zhu, TEM, STEM,

Ping Liu, DFT calculations

GM (Industry) Anu Kongkanand, Yun Cai, MEA tests

Toyota Motor Company (Industry), Makoto Adachi, MEA tests.



**Pt/Pd/Ru/C
by RSDT**

Korean Institute for Energy Research, Gu-Gon Park, Catalysts design

Technology Transfer

N.E. Chemcat Co. (Industry) Catalysts synthesis. Licensing agreement for four patents.

Responses to the Previous Year's Reviewers' Comments

Q1 Industry needs to be more involved in order to help the team with optimization of catalyst layers.

A1 We agree with this comment. Our collaboration with industrial teams is focused, *inter alia*, exactly on the optimization topic. It is very important that a partner on the project is Dr. P. Zelenay from LANL, who is an expert on this topic. Separate industrially-funded CRADA efforts are in place with GM and Toyota.

Q2 The project covers too many novel systems instead of focusing on the full optimization of just a few of them.

A2 Our previous development of Pd@Pt core-shell catalysts started with screening of cores, then focused on optimization of Pd cores. Those are now licensed and in commercial pilot scale production. We are now completing screening of several strategies for low-PGM and non-PGM cores. We are beginning to focus efforts on the most promising strategies to optimize.

Q3 It is questionable whether the strategies here are viable in mass production

Q4 It was not clear if the complex chemistries used here will ever translate to industrial-scale implementation.

A3 A4 We are trying to simplify synthesis procedures as much as possible. Based on that approach, one of our previous core-shell catalysts (Pd@Pt) is in pilot scale production. It is offered commercially without specified limits, indicating an industrial scale production.

Publications

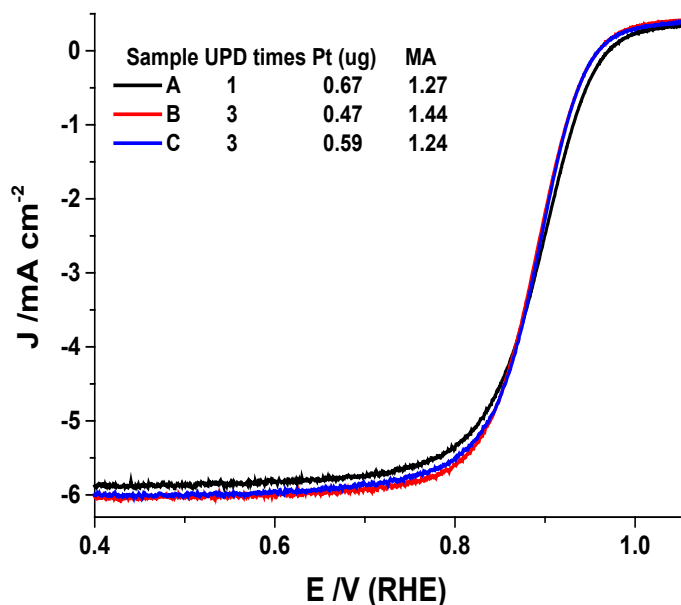
1. Katherine Elbert, Jue Hu, Zhong Ma, Yu Zhang, Guangyu Chen, Wei An, Ping Liu, Hugh S. Isaacs, Radoslav R. Adzic, and Jia X. Wang, “Elucidating Hydrogen Oxidation/Evolution Kinetics in Alkaline and Acid Solutions via Optimizing Pt-Shell Thickness on Ru Core”, *ACS Catalysis*, 5 (2015) 6764.
2. G. Chen, M. Li, K. A. Kuttiyiel, K. Sasaki, F. Kong, C. Du, Y. Gao, G. Yin, R. R. Adzic, “Evaluation of Oxygen Reduction Activity by the Thin-Film Rotating Disk Electrode Methodology: The Effects of Potentiodynamic Parameters”, *Electrocatalysis*, accepted.
3. K. Sasaki, N. Marinkovic, H. S. Isaacs, R. R. Adzic, “Synchrotron-Based *In Situ* Characterization of Carbon-Supported Platinum and Platinum Monolayer Electrocatalysts”, *ACS Catalysis*, 6 (1) (2016) 69–76.
4. J. Hu, K.A. Kuttiyiel, K. Sasaki, D. Su, G.-G. Park, C. Zhang, G. Chen, R.R. Adzic, “Pt Monolayer Shell on Nitride Alloy Core – A Path to Highly Stable Oxygen Reduction Catalyst”, *Catalysts*, 5 (2015) 1321-1332.
5. H. Liu, W. An, Y. Li, A. Frenkel, K. Sasaki, C. Koenigsmann, D. Su, R. Anderson, R.M. Crooks, R.R. Adzic, P. Liu, S.S. Wong, “Combining Theory and Experiment to Deduce the Active Structure Geometry of Ultrathin Nanowires Analyzed *In Situ* for the Oxygen Reduction Reaction”, *Journal of American Chemical Society*, 137(39) (2015) 12597–12609.
6. K.A. Kuttiyiel, Y.M. Choi, S.-M. Hwang, G.-G. Park, T.-H. Yang, D. Su, K. Sasaki, P. Liu, R.R. Adzic, “Enhancement of the oxygen reduction on nitride stabilized Pt-M (M=Fe, Co, and Ni) core-shell nanoparticle electrocatalysts”, *Nano Energy* 13 (2015) 442–449.
7. David Buceta, Concha Tojo, Miomir B. Vukmirovic, Francis Leonard Deepak, and M. Arturo López-Quintela, Controlling Bimetallic Nanostructures by the Microemulsion Method with Subnanometer Resolution Using a Prediction Model, *Langmuir* 31 (2015) 7435-7439.
8. Guangyu Chen, Kurian A. Kuttiyiel, Dong Su, Meng Li, Chiu-Hui Wang, David Buceta, Chunyu Du, Yunzhi Gao, Geping Yin, Kotaro Sasaki, Miomir B. Vukmirovic, Radoslav R. Adzic, Oxygen Reduction Kinetics on Pt Monolayer Shell Highly Affected by the Structure of Bimetallic AuNi Cores, *Chemistry of Materials*, accepted

Book chapter:

1. K. Sasaki, N. Marinkovic, “X-ray Absorption Spectroscopic Characterization of Nanomaterial Catalysts in Electrochemistry and Fuel Cells”, the 5th volume of SPRINGER book series on "X-ray and Neutron Techniques for Nanomaterials Characterization " (Challa S.S.R. Kumer (Ed.)), in print.

Technical back-up slides

Ru@Pd@Pt double-shell ORR catalysts for enhancing cost-equivalent-Pt mass activity



Motivation:

- Lowering metal cost - The price ratio for Ru:Pt is about 1:10:20 . Improving core stability - Ru binds carbon exceptionally strong and can induce a lattice contraction of the Pd shell to stabilize Pd.

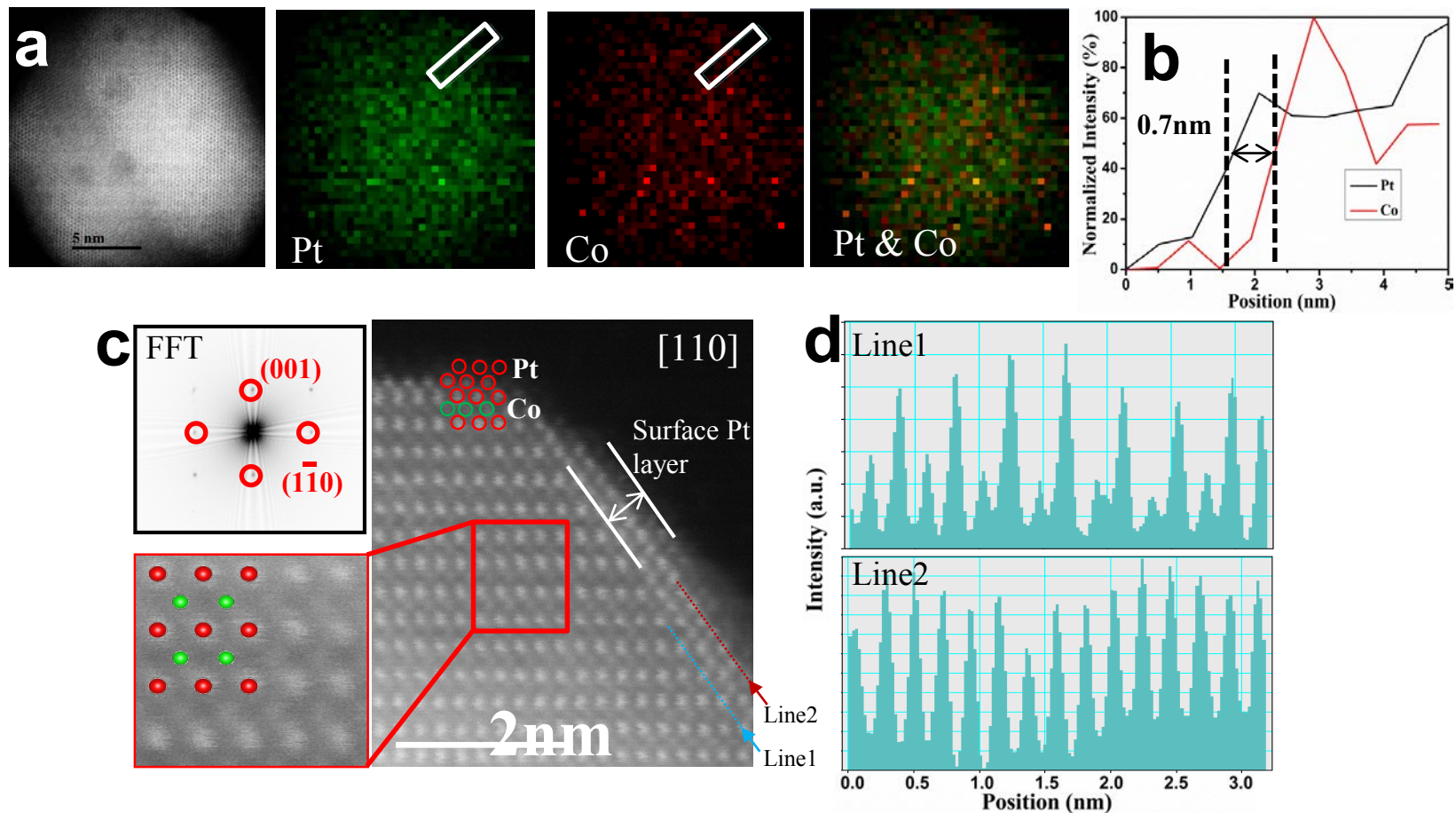
Preparation methods:

- Ru core on carbon support was synthesized from ethanol solution containing RuCl_3 .
- Pd coating of Ru was made in ethanol solution containing Na_2PdCl_4 .
- Pt shell was added via replacing Cu UPD layers.

Catalyst	Ru	Pd	Pt	MA_{Pt}	MA_{PG}	$\text{MA}_{\text{Pt-eq}}$
	ug	ug	ug	A/ mg	A/ mg	A /mg
Pd@Pt A	0	3	0.67	1.25	0.23	0.39
Ru@Pd@Pt B	1.5	2	0.47	1.44	0.27	0.44
Ru@Pd@Pt C	1.5	2	0.59	1.24	0.28	0.44

$E_{1/2}$ (mV)	BOL	5K	10K	$dE_{1/2}$	Size (nm)
Ru@Pd@Pt	874	874	875	+1	3
Pd@Pt	900	881	886	-14	6

AuPt₄Co₅/C-700C Core-Shell intermetallic nanoparticle



Nanoparticles heat treated at 700° C attain a core-shell structure with a PtCo intermetallic core covered by 2-3 layers of Pt on the surface

Comparison of the Pd catalyst film before and after cleaning procedure

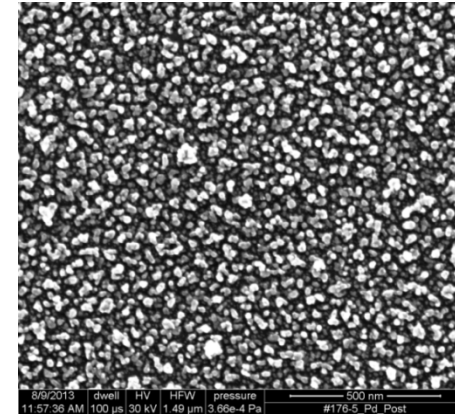
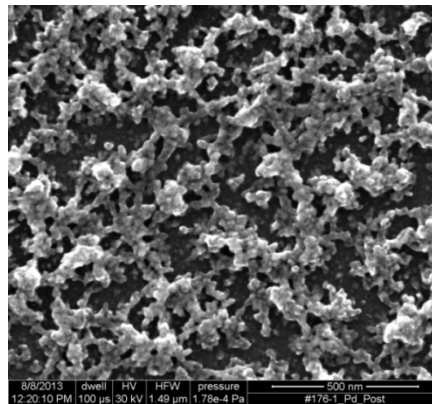
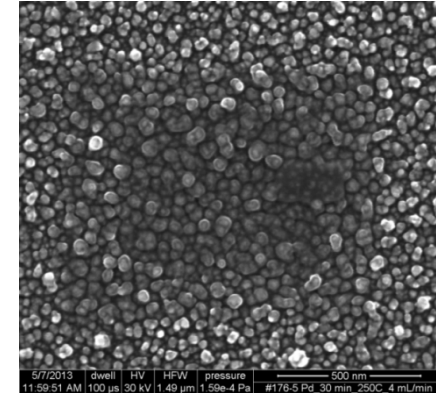
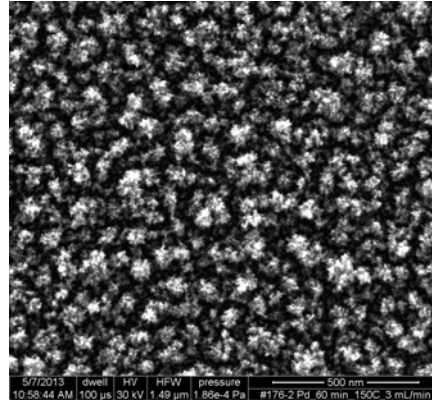
(in collaboration with Prof. Radenka Maric from Un. of Conn. Addition to the instrument is being constructed to avoid oxidation of metals being melted in a flame)

1,2,3; 150 °C
nodes with sharp features

4,5,6; 250 °C
rounded nodes

Before cycling

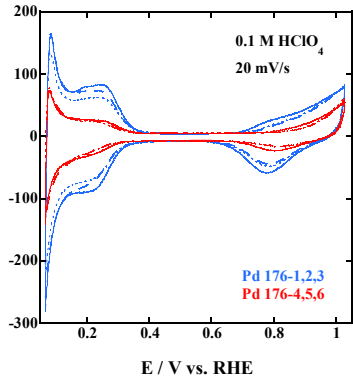
Sharper edges on film particles
consistent with lower
temperature deposition



With Pt_{ML}

Microstructure changes from nodes with sharp features to interconnected morphology.

No distinct change in morphology before and after



After cycling