Project FC009

Contiguous Platinum Monolayer Oxygen Reduction Electrocatalysts on High-Stability-Low-Cost Supports

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BROOKHAVEN NATIONAL LABORATORY

a passion for discovery

Office of Science U.S. DEPARTMENT OF ENERGY

Overview

Timeline

Project start date: July 2009
Project end date: September 2013
Percent complete: Approx. 90%

Budget in $K

Total project funding:	4244
Funding in FY13:	625
Planned Funding in FY14:	650

Barriers

Performance:
Catalyst activity; ≥ 0.44 A/mg_{PGM}
Cost:
PGM loading; ≤ 0.125 mg PGM /cm^2
Durability:
< 40% loss in activity under potential cycling

Collaborations

Massachusetts Institute of Technology (MIT)

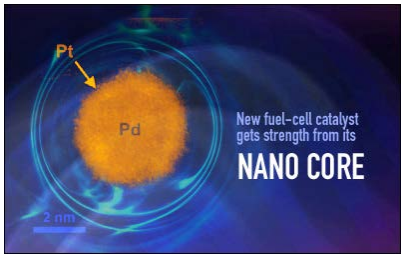
Johnson Matthey Fuel Cells (JMFC)

Toyota M. C., U. Wisconsin, U. Stony Brook, 3M Corporation, GM Corporation, CFN-BNL, IRD-Fuel Cells

Technology transfer

Four patents licensed to N.E. ChemCat Co.
CRADA with Toyota M.C. and
WFO with Korean Institute for Energy Research

Relevance



Overall project objectives:

1. Synthesizing high performance Pt monolayer (ML) on stable, inexpensive metal or alloy nanostructures fuel cell electrocatalysts for the oxygen reduction reaction (ORR);
2. Increasing activity and stability of Pt monolayer shell and stability of supporting cores, while reducing noble metal contents.

Recent project objectives:

3. Scale-up of syntheses of three catalysts including:
   - 3.1 Pt ML on Pd hollow NPs
   - 3.2 Pt ML on WNi nanoparticles
   - 3.3 Pt ML on Pd_9Au_1 alloy nanoparticles
4. Obtaining perfect Pt ML deposition and achieving 100% utilization of Pt
5. New methods for increasing stability of core-shell nanoparticles, while reducing PGM contents
6. Delivering a 300 cm^2 MEA for testing at GM.

Approach

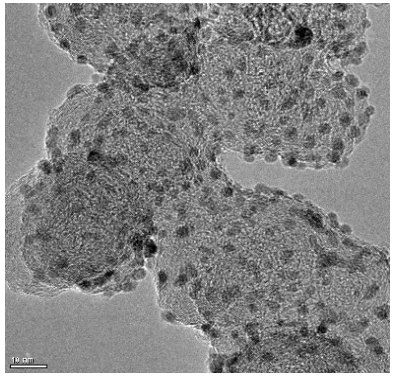
Improving Pt ML and core properties, novel core compositions, new synthetic methods

- Depositing nearly perfect Pt MLs on various cores
- Ordering core-monolayer shell interface structure
- Synthesizing monodisperse, smooth cores, hollow cores
- Nitriding non-noble metal core components for increased stability
- Electrodeposition and underpotential deposition of cores (refractory metal alloys) to optimize their composition and maximize catalyst utilization
- Ordered intermetallic compounds with high activity without Pt
- Reactive spray deposition method to synthesize novel low cost cores

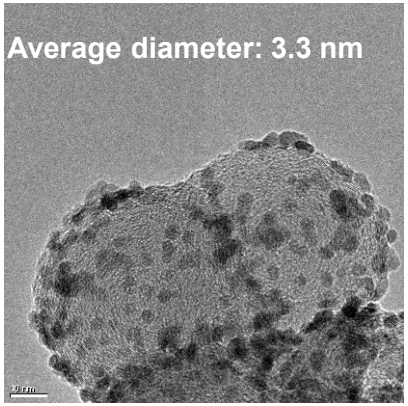
Date	Milestones
March 2014	Electrodeposition of Pd alloys and Pd thin layer on co-deposited Ni-W alloy will be carried out and tested on 5 and 25 cm2 GDL supports. Completed
June 2014	Synthesis of 2 grams of an electrocatalyst consisting of a Pt monolayer on hollow Pd, and Pd-W or Pd/Ni-W alloy cores to meet the 2017 target
June 2014	Pulse – potential deposition of cores on GDL carbon will be applied to obtain 302 cm^2 CCDM to be delivered to GM for stack testing;
September 2014	Underpotential deposition on reactive metals for unprecedented combinations of core-shell structures using non-aqueous solvents
September 2014	Electrodeposition and chemical codeposition of Ni-W alloy cores will be developed. The resulting Pt ML catalysts will meet the 2017 DOE targets. 100% Pt utilization.

Technical Accomplishments and Progress

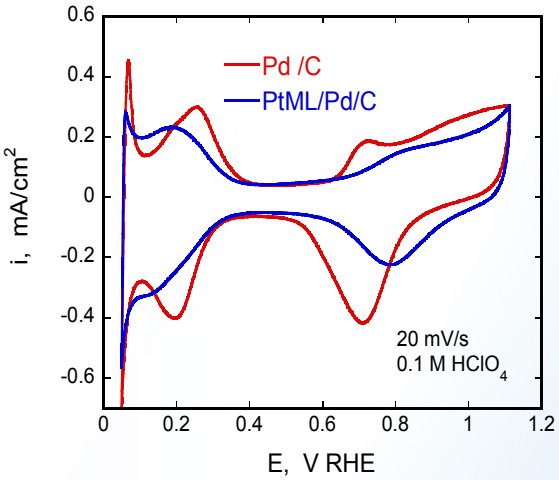
Synthesis of monodisperse Pd cores for improved properties of Pt ML catalysts

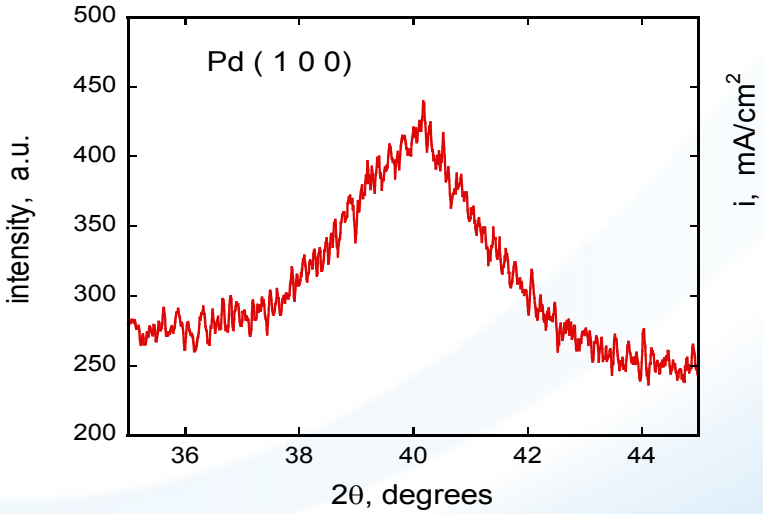


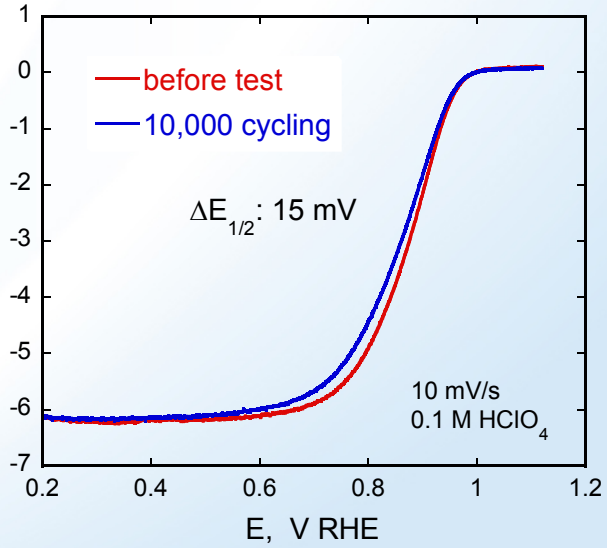
Monodisperse Pd nanoparticles obtained by decreasing Pd nucleation rate in reduction of $PdCl_2$ by $NaBH_4$ with surfactants on Vulcan XC72



	SA mA cm^{-2})	MA (A mg^{-1})	PGM (A mg^{-1})
Pt_{ML}/Pd/C	0.46	1.15	0.40
Pt/C	0.24	0.20	0.20





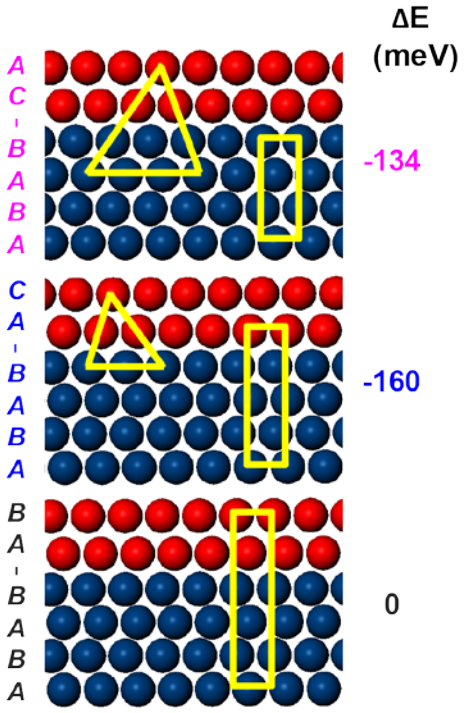


Pt loading: 4.2 μg/cm²

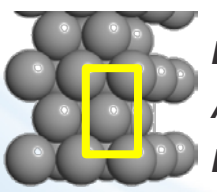
- 10,000 potential cycles between 0.6 V and 1.0 V

Technical Accomplishments and Progress

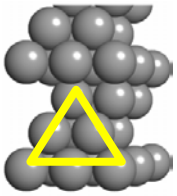
Atomically ordered, sharp core-shell interface for enhancing catalysts' activity and durability



3D crystal structures



(HCP) Hexagonal Close-Packed
AB-AB-AB...

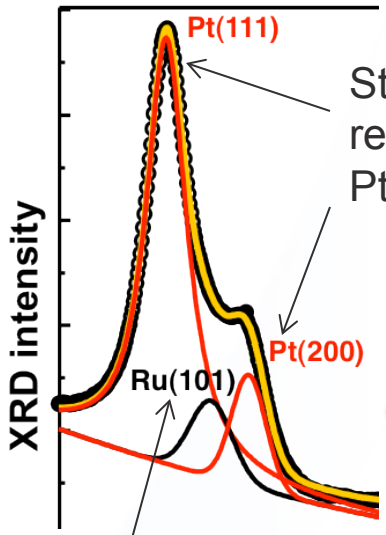


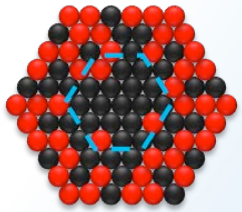
(FCC) Face-Centered Cubic
ABC-ABC

Disordered Ru Pt core-shell particles are common.

DFT shows that ordered hcp-fcc structural transition is energetically favorable for Pt bilayer on Ru.

Two favorable stacking sequences in the Pt bilayer identified: AC or CA, no B.



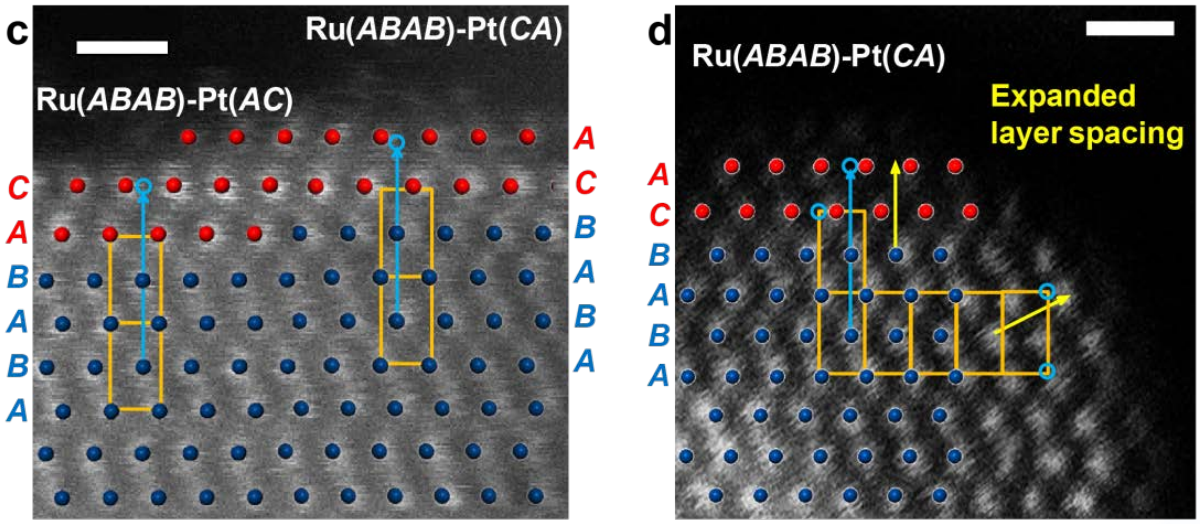


Weak hcp Ru peak with 1.3% lattice expansion due to 22% Pt in the Ru-rich cores.

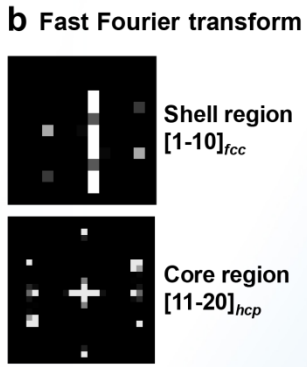
Ru-Pt inter-diffusion causes structural disordering.
Reducing lattice defects before forming Pt shell can prevent partial alloy.

Technical Accomplishments and Progress

Ordered Ru-Pt core-shell interface observed by STEM



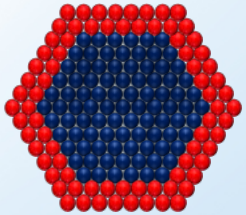
Scale bar 0.5 nm



Distinct fcc (Pt shell) and hcp (Ru core) diffraction patterns

Superimposed DFT-optimized Ru-Pt interfaces (blue-red dots) match well with observed STEM images (white dots).

Pt (red dots) atoms shift from the hcp lattice sites (blue circles) showing a switch from hcp to fcc structure. The yellow arrows show lattice expansion at the edges since Pt is larger than Ru. Z-contrast intensity profiles also support a Pt bilayer shell.



Sharp, ordered Ru-Pt core-shell interface verified.

Y. Hsieh et al., Nat. Commun. 4:2466, 2013

GM-tested Pt(ML)/Pd/NiW from BNL

Anu Kongkanand, Yun Cai

	BOL	After 30k cycles
Pt Surface Area [m^2_{-Pt}/g_{-Pt}]	100	94
Mass Activity [A/mg_{-Pt}]	0.45	0.41
Mass Activity [$A/mg_{-Pt\text{-}equiv}$]	0.37	0.34
Specific Activity [mA/cm^2_{-Pt}]	450	440

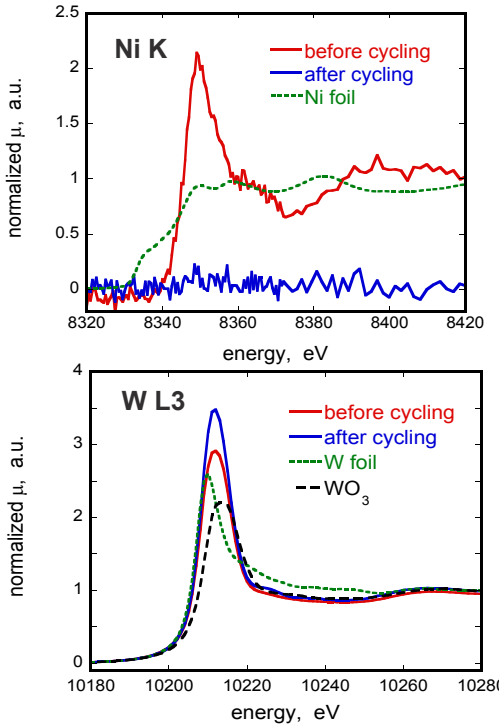
Cycling:
0.6-1.0V
50 mV/s, H_2/N_2, 80°C, 100% RH
Cathode loadings:
0.030 mg_{Pt}/cm^2

- Promising preliminary data on cheap cores from BNL.
- Very low Pt loading.
- Negligible Pt surface area loss.
- H_2/Air performance needs improvement. May benefit from higher Pt loading and improved ionomer distribution.

Technical Accomplishments and Progress

Stability of WNi on GDL as a core of Pt_{ML}/Pd/WNi

Co-deposition of $W_{0.5}Ni_{0.5}$ alloys on GDL

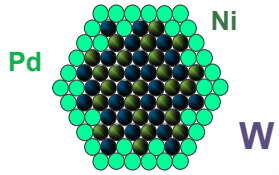


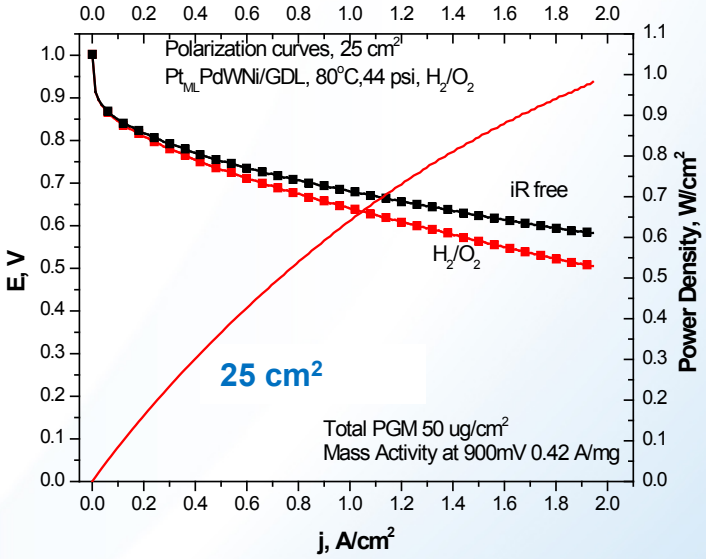
Very low Ni intensity due to low Ni concentration. Higher *white line* than that of Ni foil is due to Ni oxidation. Ni may form NiO or $Ni(OH)_2$.

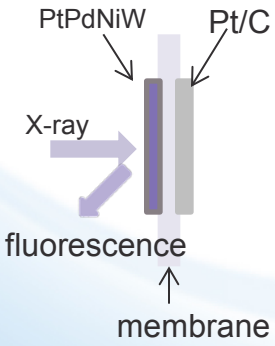
No peak for Ni after test indicates almost complete dissolution of Ni.

Higher W *white line* intensity after test indicates oxidation of W. *White line* is lower than that of WO_3 - the oxidation state is less than +6.

Model of NiW core with a partially displaced Ni by Pd







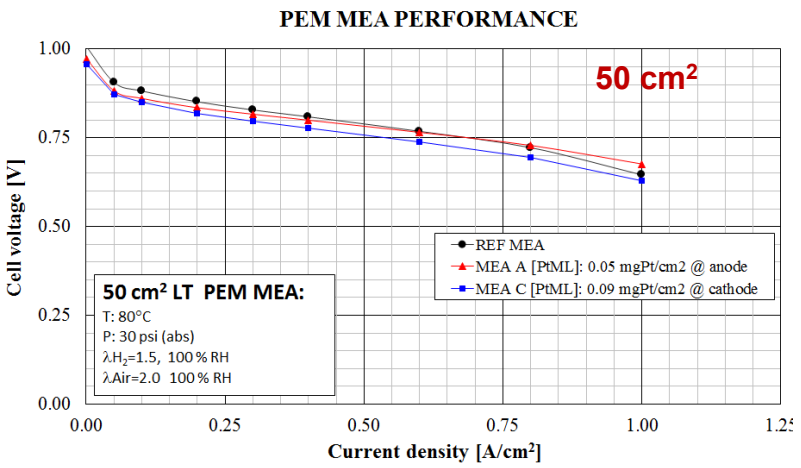
Performance increased after 5000 (5 cm^2) and 15,000 (25 cm^2) potential cycles from 0.6 to 1.0 V, 50 mV/s ;

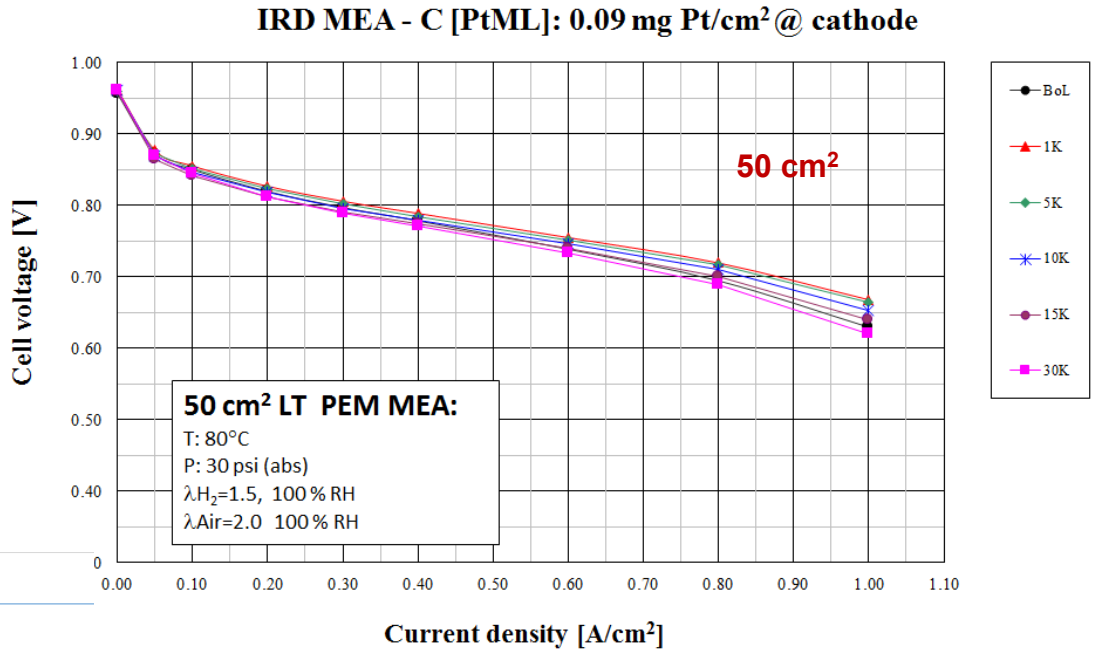
MEA 25 cm^2 PGM: 50 μg/cm^2 MA_{Pt} = 1.1 A/mg ; MA_{PGM} = 0.42 A/mg

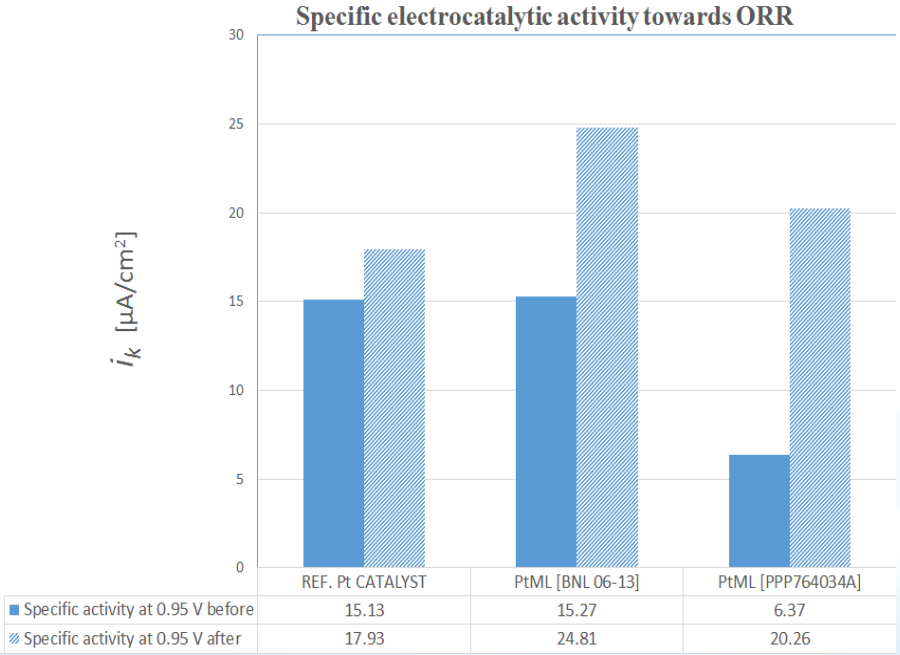
Technical Accomplishments and Progress

Tests of Pt_{ML}/Pd/C in H_2-Air at IRD Fuel Cells, LLC

Madeleine Odgaard







PtML polarization curves after 1, 5, 10, 15, and 30K cycles

Polarization curves for 60wt% Pt/C and PtML at cathode and anode

Reference: 60wt%Pt/C catalyst.

Cycling 0.7-0.9 $V_{IR\text{-}free}$ with step change of 30 s in H_2-Air.

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Technical Accomplishments and Progress

Nitride-stabilized Pt-M core-shell catalysts in acid media

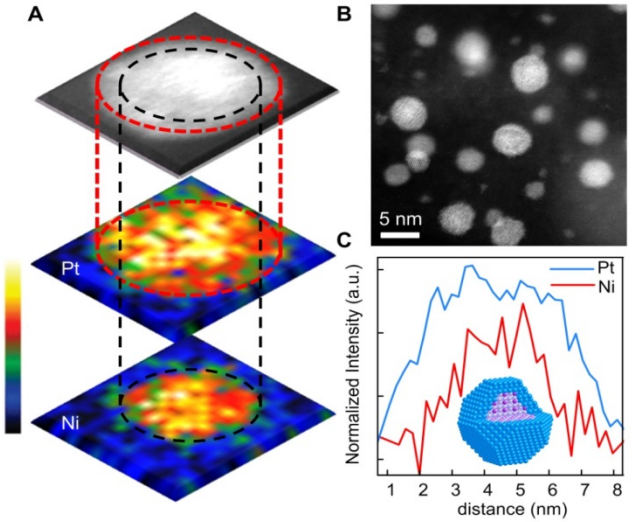
Synthesis:

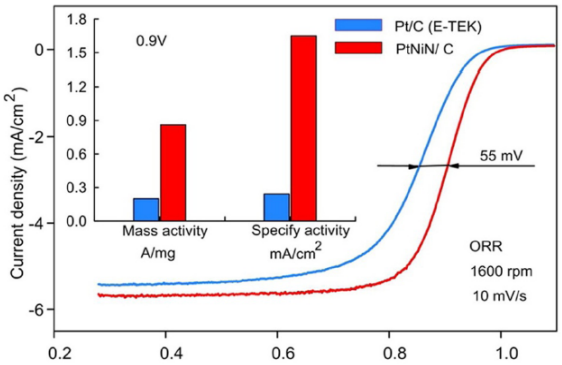
K_2PtCl_4 + $Ni(HCO_2)2H_2O$ + Vulcan XC72R

↓ NH_3, 500°C

$PtNiN_x$ nanoparticles

XAS: Ni_4N cores are stable at elevated potentials

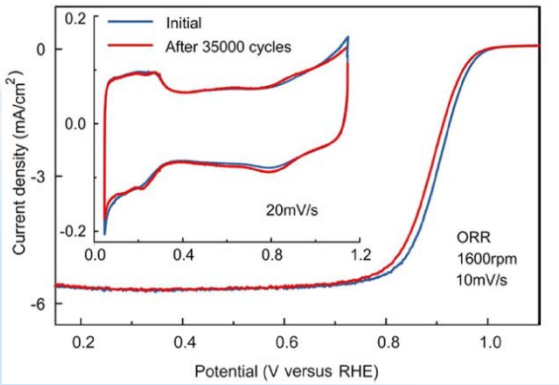




The order of activity:

PtNiN/C > PtFeNN > PtCoN/C > Pt/C

SA= 1.64 $mAcm^{-2}$, MA= 0.84Amg^{-1}



- ❑ High stability - little change in ECSA & small decrease in $E_{1/2}$ after 35k potential cycles
- ❑ High ORR Activity

Kuttiyiel, Sasaki, Adzic, et al., *Nano Lett.*, 2012, 12, 6266
Patent: BSA 13-25

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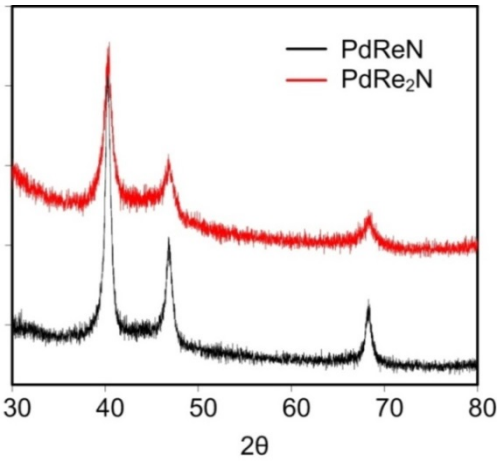
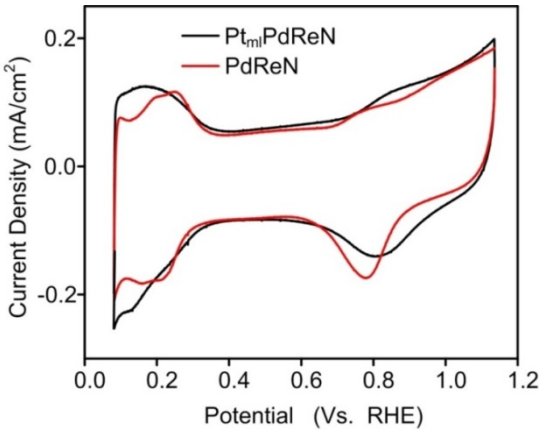
Technical Accomplishments and Progress

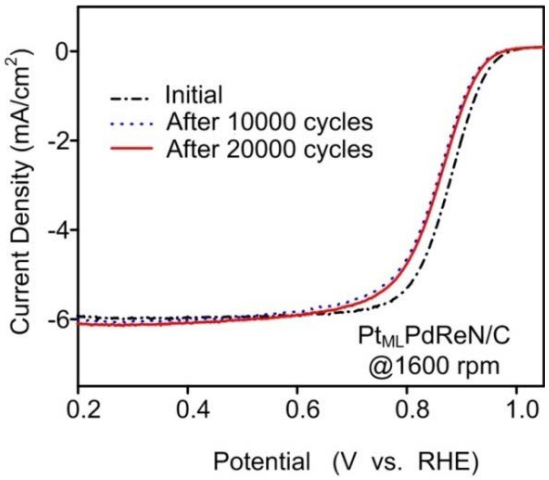
Nitriding Re to improve its stability and make it reliable core constituent



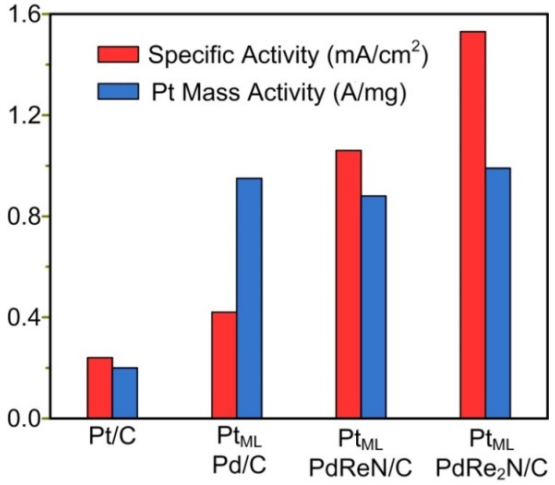
PdReN Synthesis
NH_3 at 350ºC

XRD:
PdReN - 10 nm
$PdRe_2N$ - 7.5 nm.





PGM activity:
PtPdReN = 0.23 A/mg
$PtPdRe_2N$ = 0.26 A/mg.



Initial $E_{1/2}$ = 880mV; 860mV after 10K cycles
0.6-1.05 V 50mV/s, stable thereafter.
ECSA loss 7% after 20K cycles;
$Pt_{ML}PdRe_2N/C$ is **less stable in acid**

Re is an inexpensive PGM, not readily used as elemental catalyst. It can be an excellent core component if made more stable by nitriding

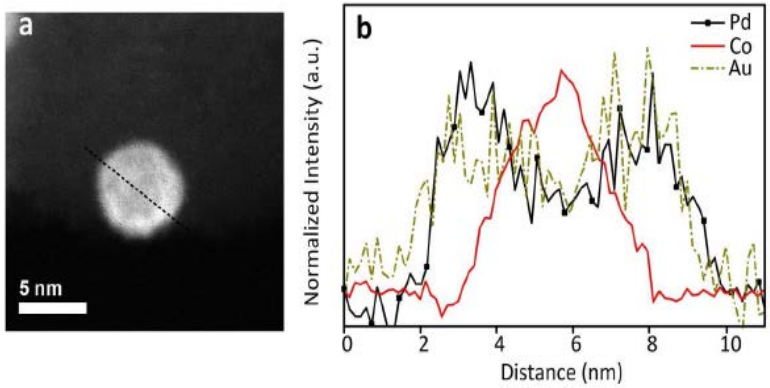
Technical Accomplishments and Progress

Au–Promoted Formation of Structurally Ordered Intermetallic PdCo Nanoparticles

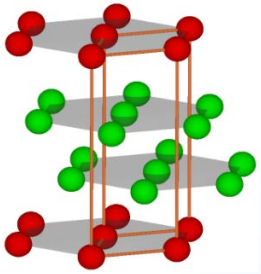
$Au_{10}Pd_{40}Co_{50}$ catalyst

Core-shell (AuPd shell & Co core) nanoparticles

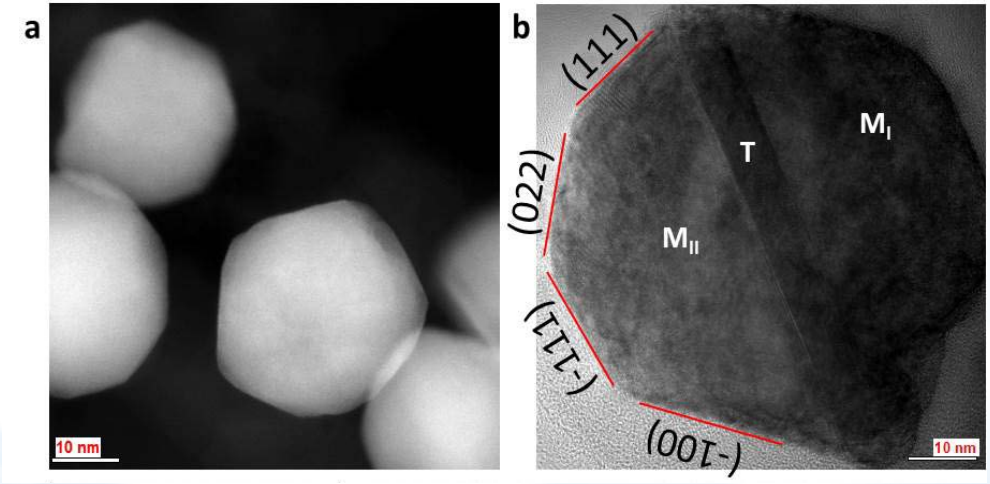
- Comparable activity to Pt in acid/alkaline
- Better stability than Pt in alkaline media



800°C



Ordered intermetallic



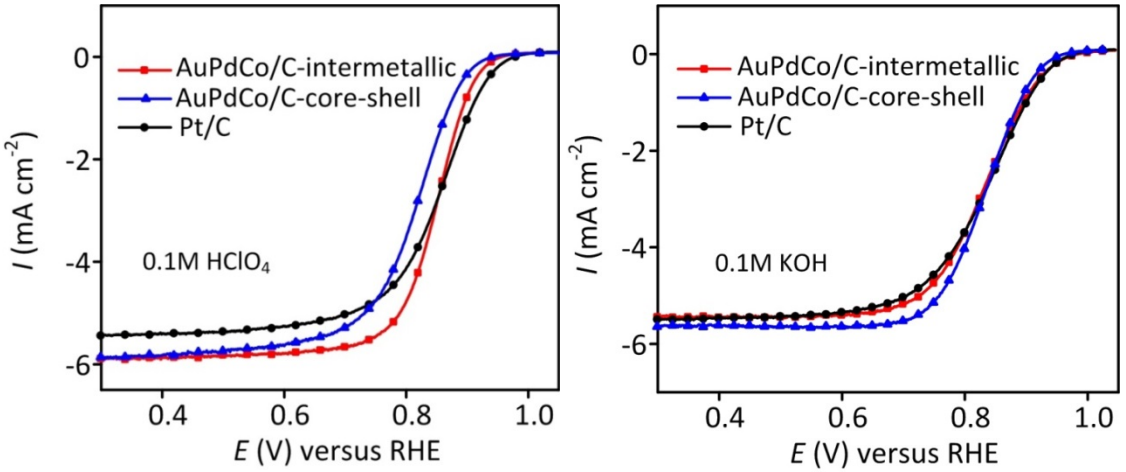
Upon addition of Au, PdCo forms a rare ordered structure with twin boundaries with stable {111}, {110}, {100} facets

STEM and HRTEM image of AuPdCo-intermetallic nanoparticles showing multiple facets

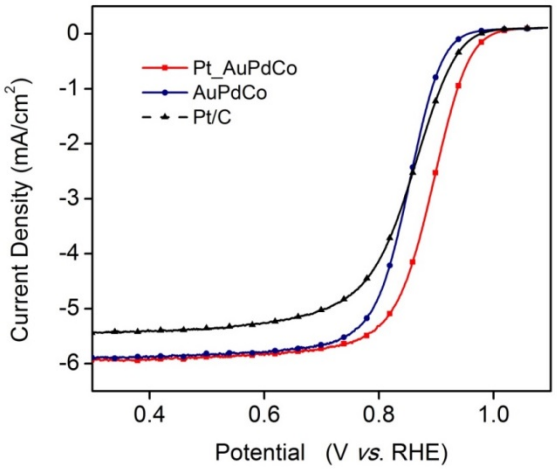
Technical Accomplishments and Progress

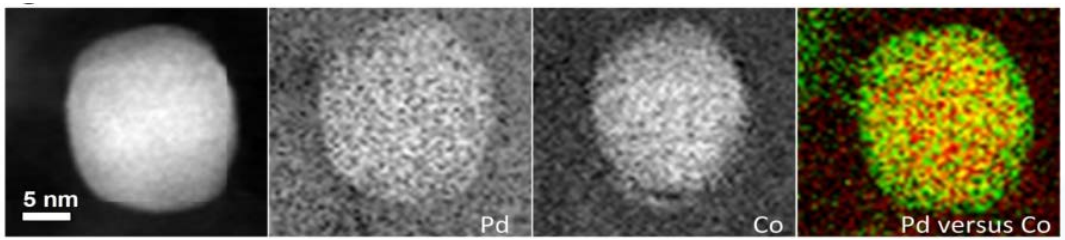
AuPdCo: Non-Pt Catalysts in Acid and Alkaline Media

Precious metal loading was 7.65 μg cm^{-2} for AuPdCo catalysts and 6.0 μg cm^{-2} for Pt catalyst.



Pt_{ML}/AuPdCo





EELS mapping and overlapped mapping (Pd (green) and Co (red)) showing the intermetallic structure of PdCo atoms after potential cycling

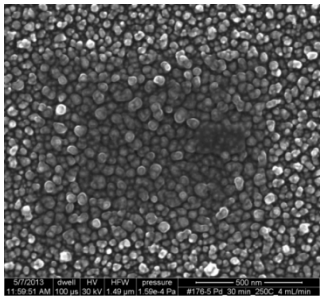
Electrocatalyst	$Pt_{3.5nm}$	AuPdCo intermetallic	Pt_{ML}/AuPdCo intermetallic
ECSA (m^2/g_{Pt})	85		124
Pt specific activity (mA/cm^2)	0.24		0.92
Pt mass activity (A/mg)	0.20		1.14
Precious Metal mass activity (A/mg)	0.20	0.14	0.37

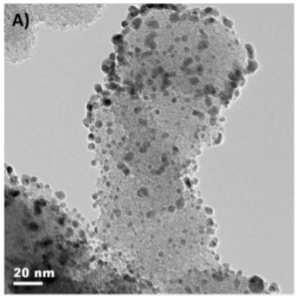
The superior stability is attributed to the atomic structural order of PdCo nanoparticles along with protective clusters of Au atoms on the surface.

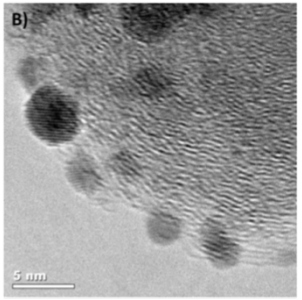
Reactive Spray Deposition Technology

Flame-Based Synthesis of Core-Shell Structures : Pd, Pd-Ru and Pd-Y Cores

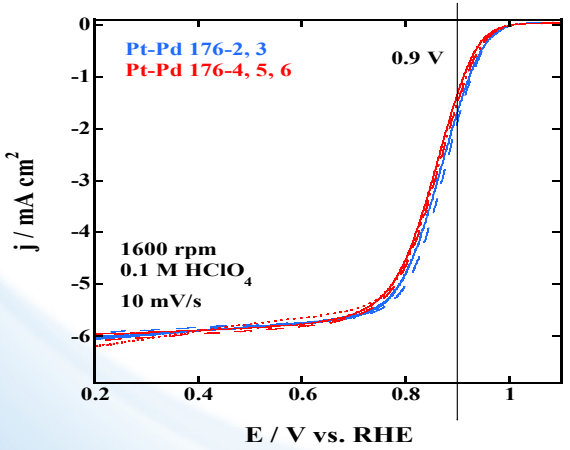
Collaboration with Radenka Maric, UCONN



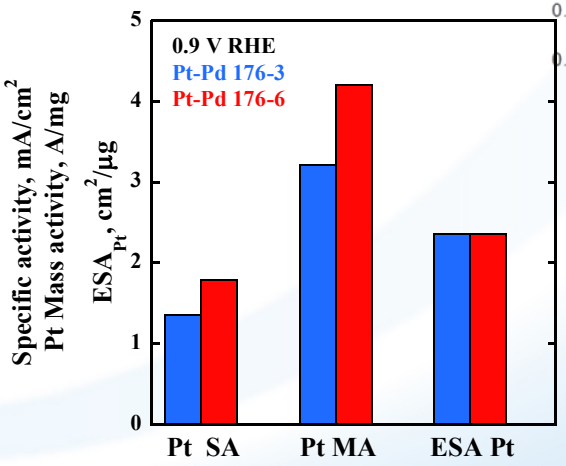


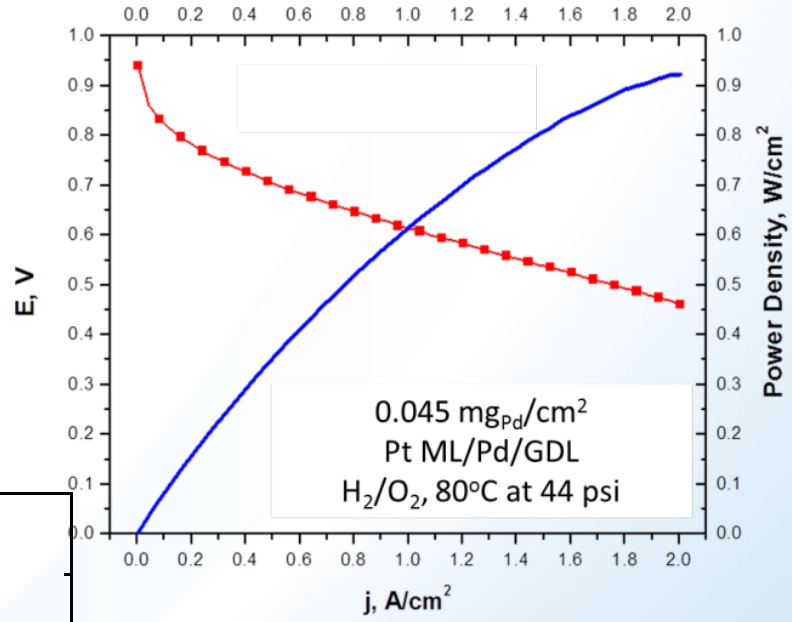


Pd on GC left, on C NPs right



Pd 4,5,6 (250 ºC) smoother than
Pd 1,2,3 (150 ºC) Higher ORR activity





1.2 A/mg$_{Pt}$ at 0.9V
0.357 A/mg$_{PGM}$ at 0.9 V

Reactive Spray Deposition opens possibilities for synthesis of metal, alloy, oxide core-shell nanoparticles unattainable by other methods.

Responses to the Previous Year's Reviewers' Comments

Q1 **Several comments were made on the necessity of more MEA tests with selected catalysts.**

A1 We performed the MEA testing with a recently acquired FC test station, in collaboration with Industry and National Laboratory teams. We increased that activity and such tests are conducted at GM, 3M, IRD, Toyota, BNL. Some tests were delayed for regulation and legal matters, equipment and system failure.

Q2 **More H_2/Air tests, effect of contaminants, mediocre activity observed with Air compared with O_2.**

A2 More H_2/Air tests were carried out. Of note, the "mediocre activity observed with Air compared with O_2" was seen for only one catalyst in the last review.

Q3 ***Post mortem* analysis of the catalysts should be conducted.**

A3 XAS of the Pt/Pd/W-Ni/C catalyst has been carried out.

Q4 **Several comments questioned the usefulness of the electrodeposition of catalysts approach. "Leave electrodeposition out unless there is a plan to be more aggressive," "The team should perform a more thorough cost–benefit analysis."**

A4 There is a plan from BNL to undertake a serious effort in developing the electrodeposition technology. A number of indicators of cost saving, time saving, and simplifications of MEA manufacturing process are easily seen.

Q5 **The PI should place a greater emphasis on core stability.**

A5 We are very much concerned about the long term core stability and often warn about Kirkendall effects on alloys with Ni, Co, Fe, and Cu whose cations cannot be reduced by H_2 (unlike the noble metal cations) and will damage the Nafion® membrane. We show that ordered intermetallics and nitrated non-noble metal core components can provide excellent cores.

Collaborations

Toyota Motor Company (Industry) **Toshihiko Yoshida** MEA test, catalysts scale-up

U. Wisconsin (University) **Manos Mavrikakis,** collaboration on theoretical calculations

Center for Functional Nanomaterials, BNL Ping Liu, DFT calculations;
Eli Sutter, Dong Su and Yimei Zhu, TEM, STEM

3M Corporation (Industry) **Radoslav Atanasoski, Andrew Haug, Daniel Peppin**

GM (Industry) **Anu Kongkanand, Yun Cai**

IRD Fuel Cells, (Industry) **Madeleine Odgaard**

Korean Institute for Energy Research

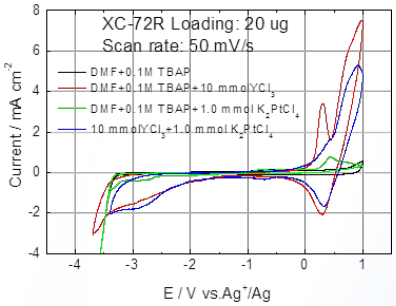
Technology Transfer
N.E. Chemcat Co. (Industry) **Catalysts synthesis. Licensing agreement for four patents.**

Future Studies

MEA and STACK TESTS

Three catalysts *viz*., $Pt/Pd_{hollow}/C$; Pt/PdAu/C; $Pt_{ML}/Pd/WNi/C$ will be tested.

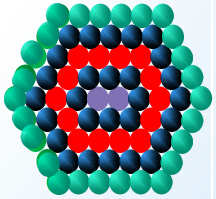
(Tests of $Pt_{ML}/Pd/WNi$ catalyst are underway at GM)



ELECTRODEPOSITION

New core materials made by deposition of Yttrium and other refractory metals from non-aqueous solvents to increase Pt ML activity and stability, and to reduce the costs.

ONION-STRUCTURED NANOPARTICLES with new cores of multiple metal layers



Supporting DFT calculations have been completed (Mavrikakis).

REACTIVE SPRAY DEPOSITION TECHNOLOGY (with Radenka Maric, UCONN)

Syntheses of alloy cores of Yttrium or other refractory metals with Pd and Re. Syntheses of nanoparticles with oxide inner cores, metal outer cores to induce compressive strain in Pt ML, increase stability, and reduce the costs of catalysts.

APPROACHING 1.23V – The Grand Challenge in Electrocatalysis

Pt MLs on new cores obtained using the above techniques will be studied. The possibility of the "Dry Cave" effect causing reduction of water activity while facilitating faster O_2 adsorption and the O –O bond splitting will be explored.

Summary

Further testing and additional improvements of Pt monolayer electrocatalysts that demonstrate their attractive features, their application readiness, and the versatility of the core shell approach for designing catalysts are discussed in this report.

New methodologies for improving activity and stability of these catalysts:

- Synthesis of monodisperse cores.
- Forming atomically ordered, sharp core-shell interfaces.
- Gold promoting the formation of ordered intermetallic compounds.
  (The AuPdCo compound is a Pt-free catalyst with activity approaching that of Pt. It can serve as an excellent core supporting Pt ML.)
- Nitriding non–noble metal cores constituents.
  (Both ordered intermetallic compounds and nitrided alloys **provide better and more stable cores than common alloys.)**

Summary

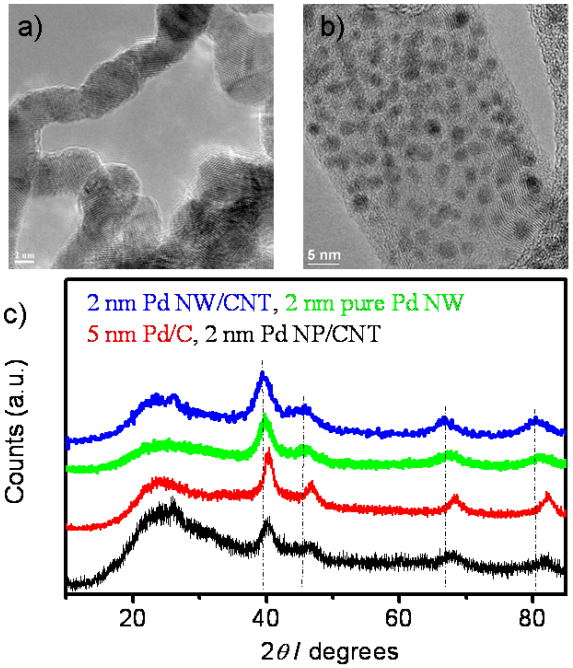
Further Research

Addressing the efficiency barrier that involves approaching Eº of H_2/O_2 cell of 1.23 V.

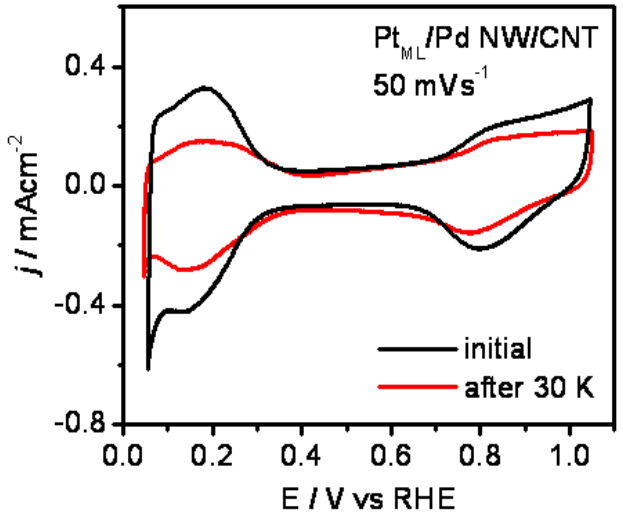
- The tunability of Pt ML properties through core-shell interactions provides a promising route.
- Novel types of core-shell interactions.
- Electrodeposition from non-aqueous solvents to obtain new cores.
- Reactive spray deposition technology is another method to obtain cores unattainable so far with conventional syntheses.
- Revisiting the “Dry Cave” concept to modify Pt-water interactions and enhance the ORR efficiency.

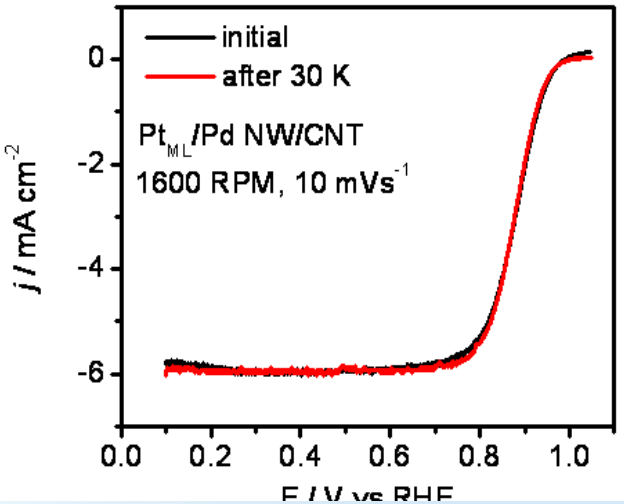
Technical back-up slides

Metallizing Carbon Nanotubes with Pd-Pt Core-Shell Nanowires



TEM images of the freestanding Pd NWs (a) and Pd_{NP}/MWNTs (b). c) XRD patterns for Pd_{NP}/MWNTs, the freestanding Pd NWs, the Pd/C and Pd $_{NP}$/MWNTs (from top to bottom).

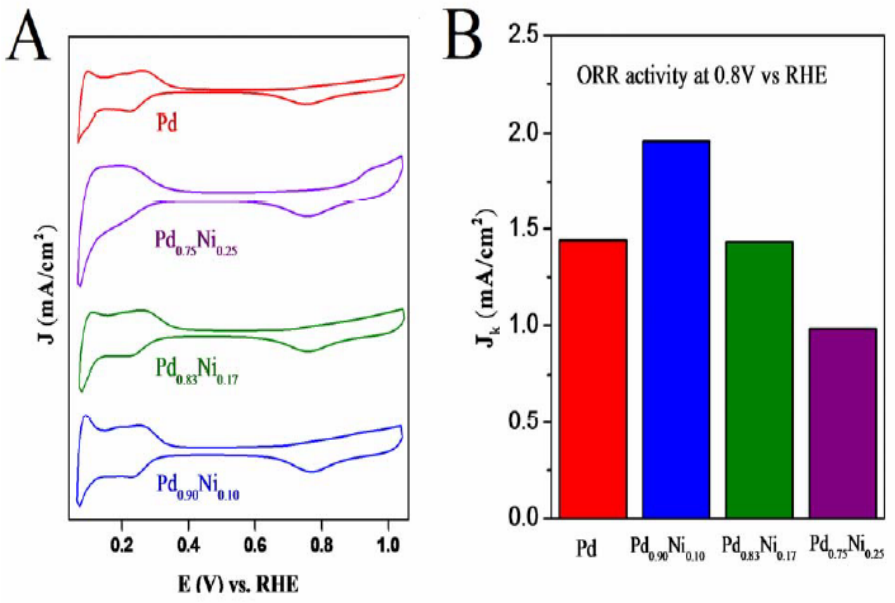


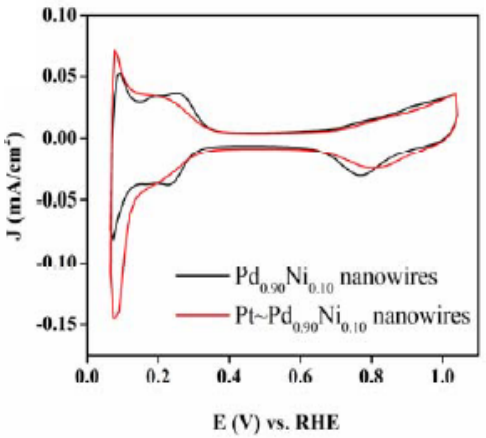


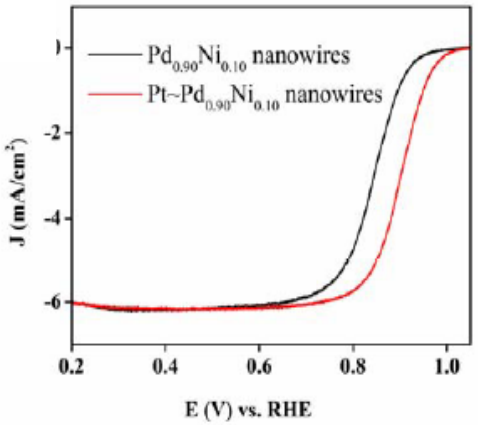
	$E_{1/2}$ (mV)	specific activity (mA/cm)	mass activity[b] (A/mg $_{Pt}$)	mass activity[c] (A/mg $_{Pt,Pd}$)
Pt/C (20 wt%)	850	0.24	0.22	0.22
Pt_{ML}/Pd_{NP}/C	881	0.52	0.97	0.35
Pt_{ML}/Pd_{NW}/MWNT	885	0.65	1.45	0.58

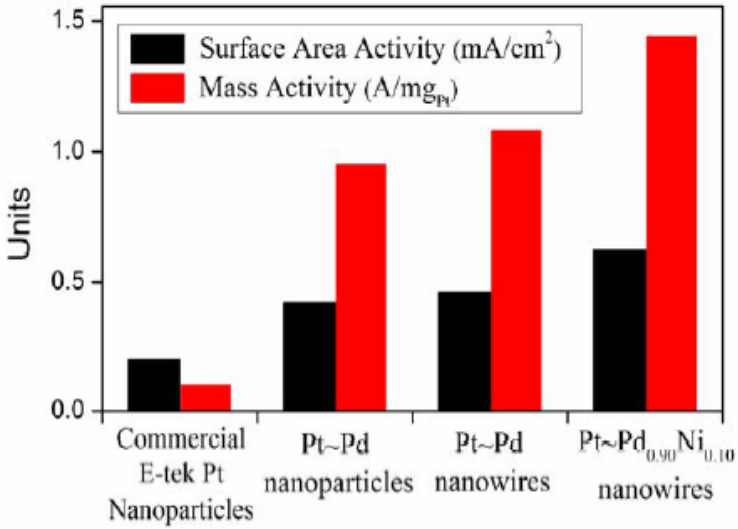
PdNi nanowires as electrocatalysts for the ORR

With Liu and Wong







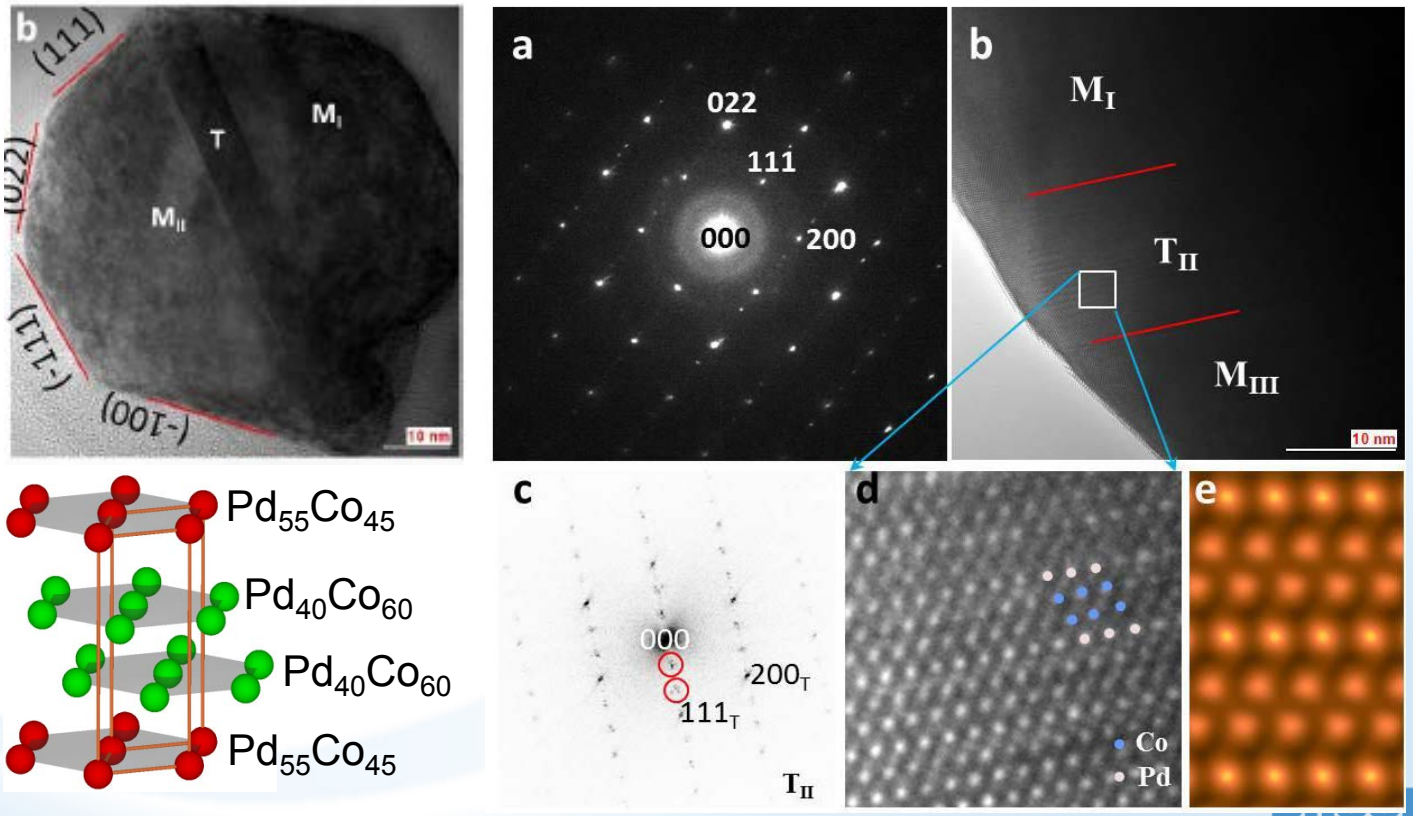


Surfactant-based synthesis octadecylamine (ODA); Removal of ODA by CO adsorption.

Ordered Intermetallic AuPdCo Catalysts

The core-shell nanoparticles transform to an ordered intermetallic structure by annealing at 800°C for 30 min

- Smooth low-indexed facets
- No transformation without Au



(with L. Wu & Y. Zhu, BNL)