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

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Project FC009

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BROOKHAVEN NATIONAL LABORATORY
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Office of Science
U.S. DEPARTMENT OF ENERGY

Overview

Timeline

Project start date: July 2009
Project end date: September 2013
Percent complete: Approx. 40%

Barriers

Performance:
Catalyst activity; ≥ 0.44 A/mg_{PGM}
Cost:
PGM loading; ≤ 0.3 mg PGM /cm^2
Durability:
< 40% loss in activity under potential cycling

Budget in $K

Total project funding:	3,529
Funding in FY10:	267
Funding in FY 11:	860

Partners

Massachusetts Institute of Technology (MIT)
Johnson Matthey Fuel Cells (JMFC)

Collaborations

UTC Power; Toyota M. C.,3M Corporation; U. Wisconsin, U. Stony Brook, U. Santiago de Compostela, CFN-BNL

BNL coworkers: Yun Cai, Stoyan Bliznakov, Kuanping Gong, Kurian Kuttiyiel

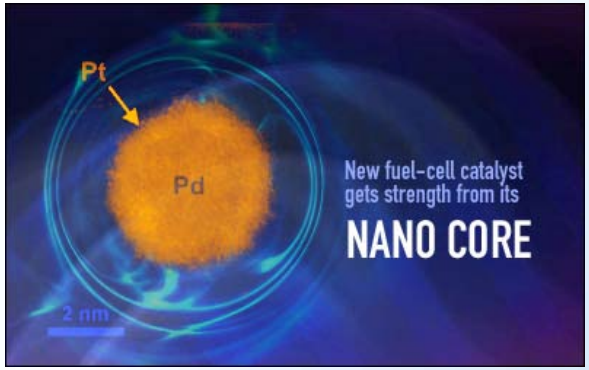
Relevance

Objectives:

1. Developing high performance fuel cell electrocatalysts for the oxygen reduction reaction (ORR) comprising contiguous Pt monolayer (ML) on stable, inexpensive metal or alloy:

   - nanoparticles (NPs)
   - nanowires (NWs), nanorods (NRs),
   - hollow NPs
   - carbon nanotubes (CNT),

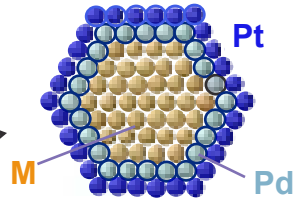
2. Increasing stability of cores and supports
3. Scale-up syntheses of selected catalysts,
4. MEA-testing, stack- testing

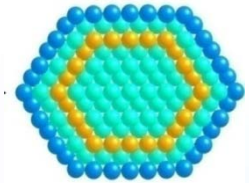


Approach

Our approach is based on improved understanding of factors affecting the ORR from the studies of:

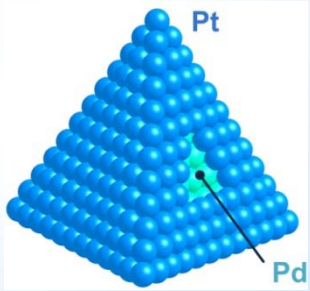
1. **Oxygen binding energy**
2. **Surface contraction effects (size-induced, hollow NPs),**
3. **Surface segregation effects;**
4. **Core-shell structures - 2nd generation (interlayer; core sub-surface layer)**
5. **Computations and modeling**





High activity and stable Pt –based ORR catalysts require:

- **Reduced Oxygen binding energy**
- **Low number of low-coordination atoms**
- **Compressed top layer of atoms**
- **Moderately compressed (111) facets**



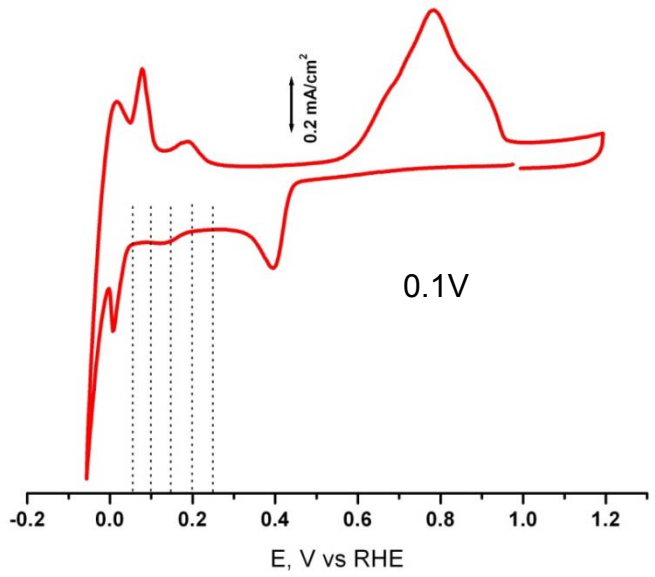
Cores have a key role in achieving these requirements

Additional improvements with Pt as a contiguous monolayer

*J.X. Wang, H. Inada, L.Wu, Y. Zhu, Y. Choi, P. Liu, W.P. Zhou, R.R. Adzic, *J. Am. Chem. Soc, 131 (2009) 17298, JACS Select #8*

Technical Accomplishments and Progress

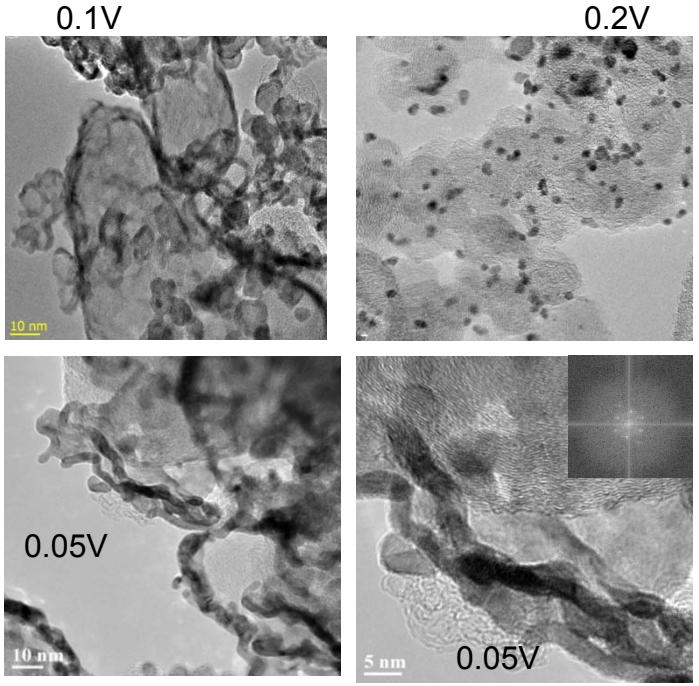
Synthesis of Pd nanowires and nanorods by electrodeposition on carbon



Deposition of Pd on carbon surfaces in 0.1M $HClO_4$ with 1mM Pd^{2+}.

The growth mechanism: Hupd in Pd acts as reducing promotor at terraces, while chlorides adsorb at low-coordination sites and block growth in that direction.

The type of deposit: NPs, NWs or NRs, depend on the potential and Pd ion concentration

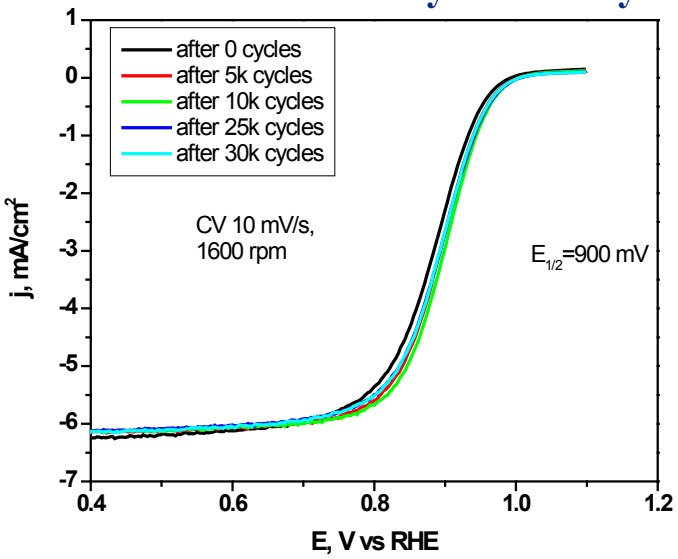


FFT of the TEM image showing (111) pattern of Pd(111)

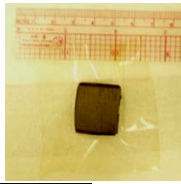
Scale-up: Cell for 5 cm^2 electrode was constructed. It appears that a uniform deposition of NWs at electrodes of any practical surface area will be possible. Thus, this synthesis will be compatible with MEA fabrication.

Technical Accomplishments and Progress

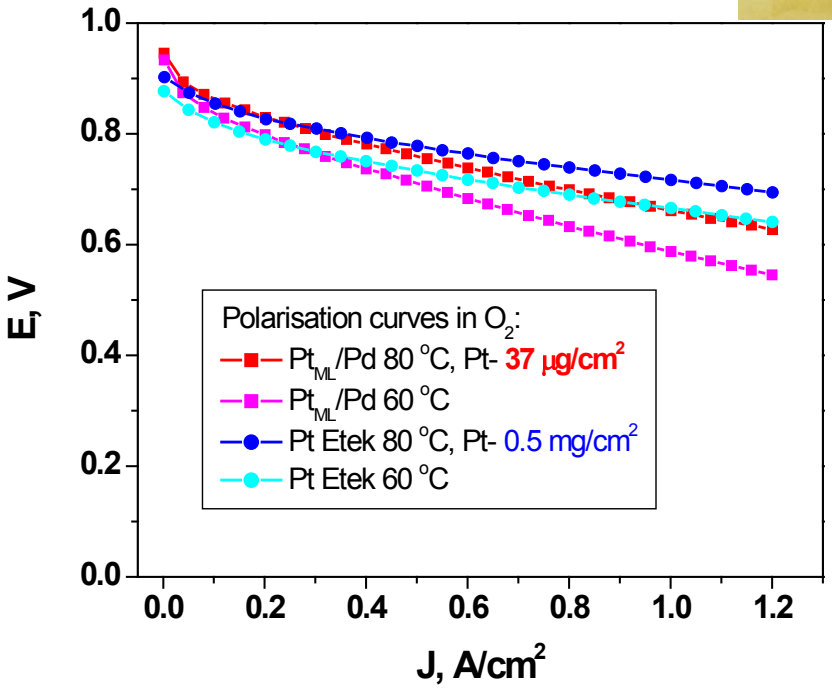
Electrocatalytic activity of Pt_{ML} on Pd NWs, NRs and PdAu NWs for the ORR



Pt/PdAu Mass activity: **3.5 A/mg$_{Pt}$**
Specific activity: **1.5mAcm^{-2}**

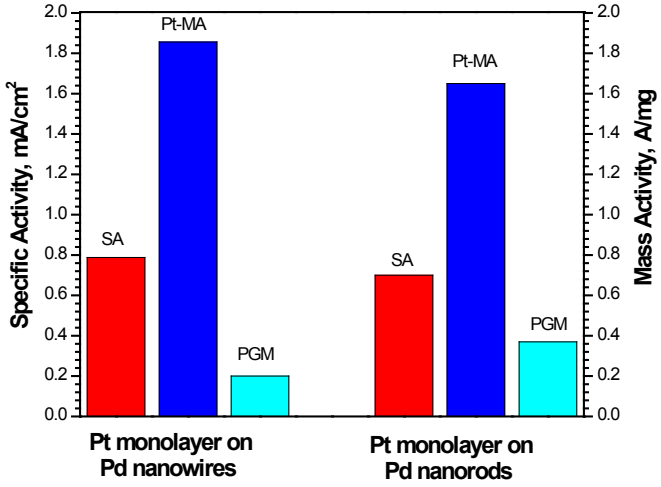


First MEA test of 5 cm^2 electrode (Toray paper)



Mass activity: **1.07 A/mg$_{Pt}$** Spec activity: **0.45mAcm^{-2}**

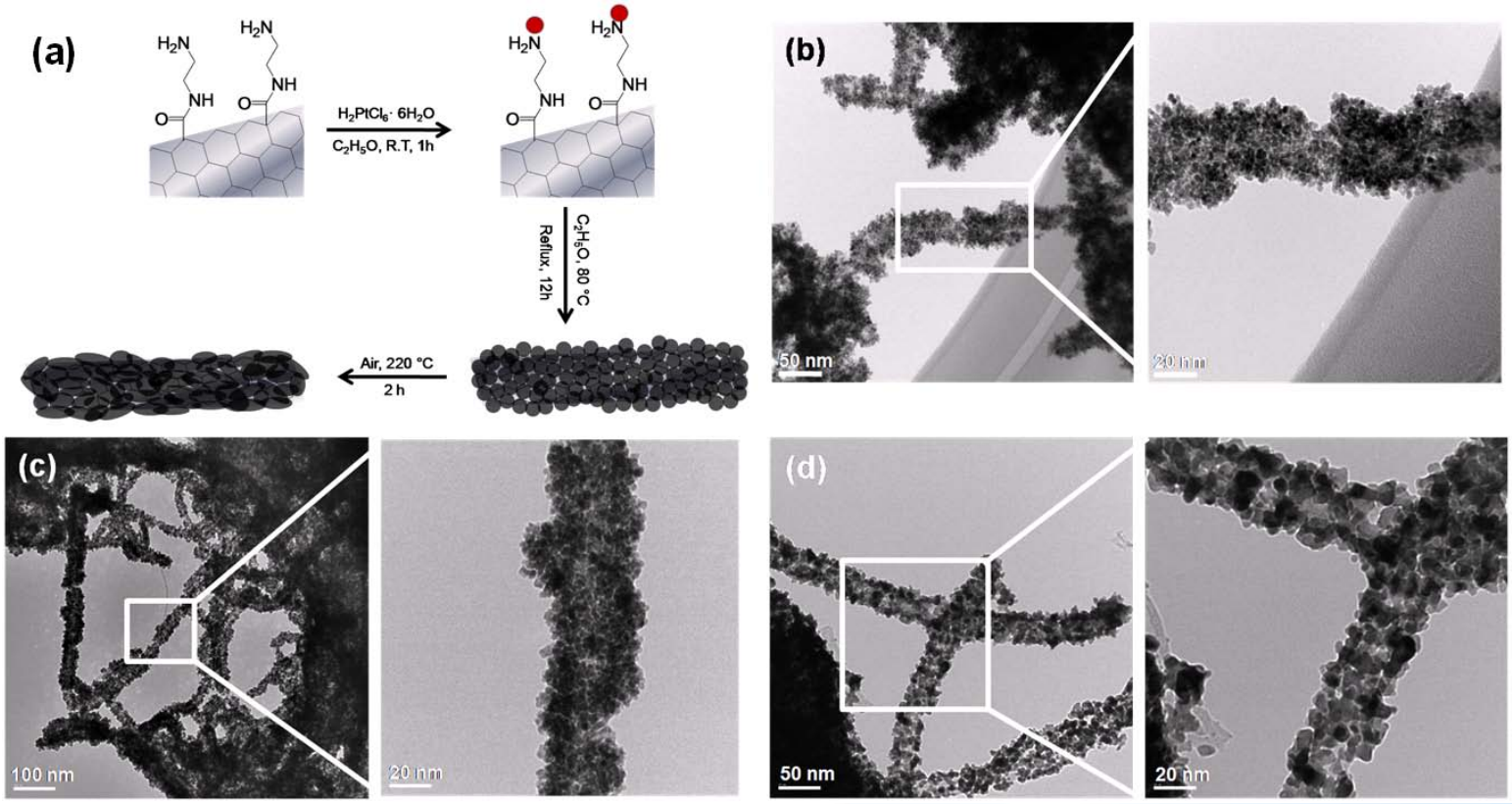
High activity and excellent stability due to:
(i) the smooth surface; (ii) the reduced number of defects
(iii) low number of low-coordinated sites.



Additional Pd NWs from surfactant-based synthesis have similar activities (with S, Wong, C. Koenigsmann)

Technical Accomplishments and Progress

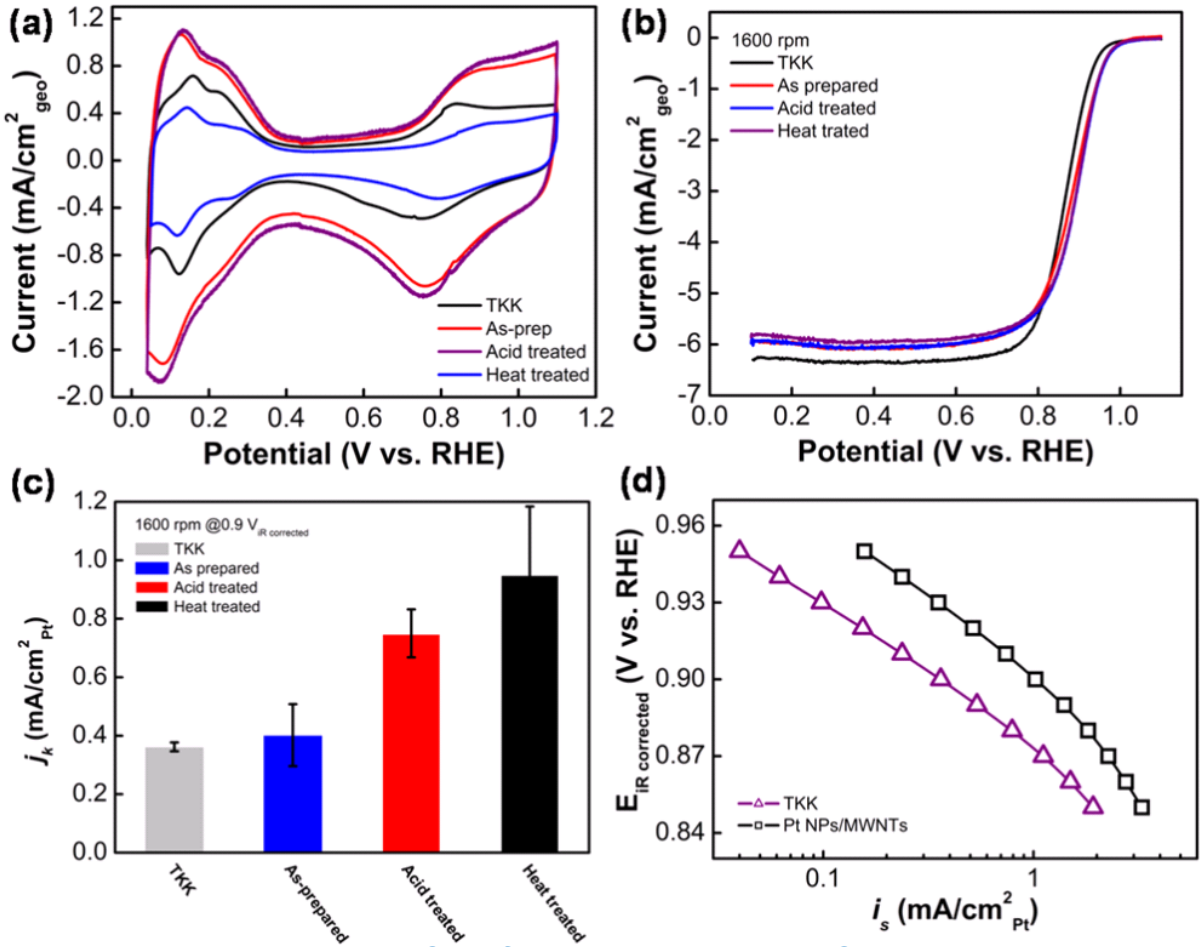
1-Dimensional Interconnected Pt NPs on Amine-Functionalized MWCNTs for the ORR



(a) Polyol synthesis of 1-D Pt NPs/MWNTs, TEM image of (b) as prepared 1-D sample (c) after 6 M HCl treated (b) as prepared Pt NPs/MWNTs and (d) after heat at 220 °C.

Junhyung Kim, Seung Woo Lee, Christopher Carlton and Yang Shao-Horn, MIT

1-D Interconnected Pt Nanoparticles on Amine-Functionalized MWCNTs

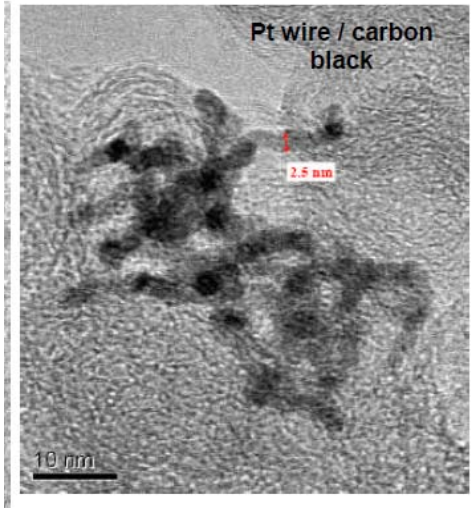


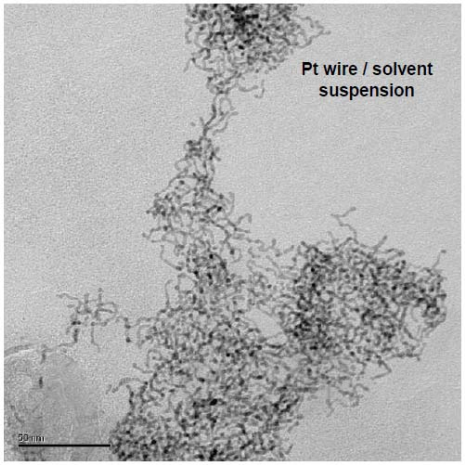
PGM mass activity is 1.4 times that of 40% TKK

Intrinsic ORR activity comparison. (a) CVs from 4 samples, (b) ORR at RDE at 1600 rpm ; 10 mV/s, (c) specific activities at 0.9 V, iR corrected and (d) specific activity of TKK and heat treated Pt NPs/MWNTs.

Technical Accomplishments and Progress

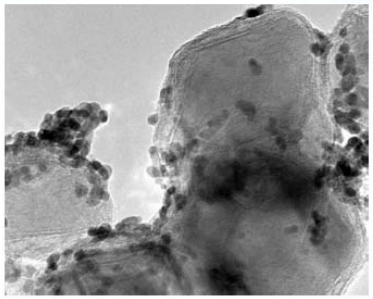
Syntheses of Pt wires, tests of TiC and WC supports





Pt wires synthesized and transferred to CNPs successively

- further optimization required
- Pt was blocked by strong surfactant

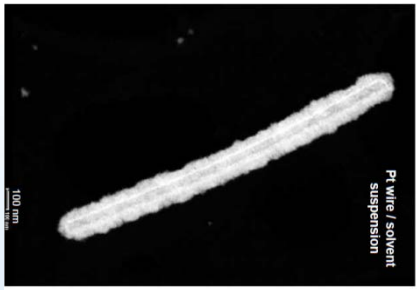


40w% Pt (5nm) on Commercial TiC (100nm)

New supporting materials developed:

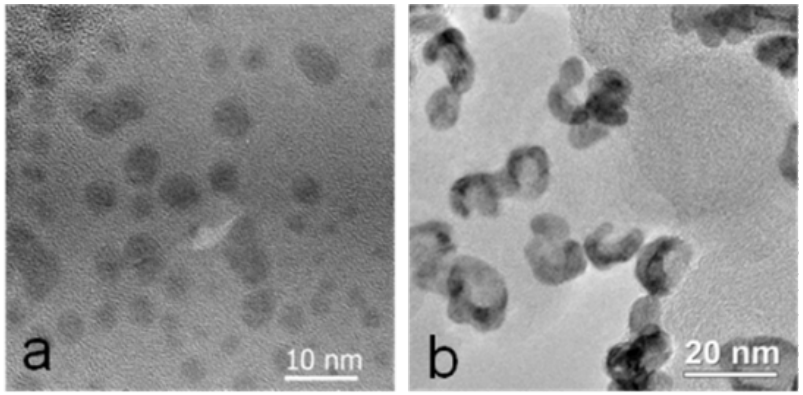
1.TiC
2.WC
3.Pt wires on cores to thrift PGM

Initial tests are being conducted



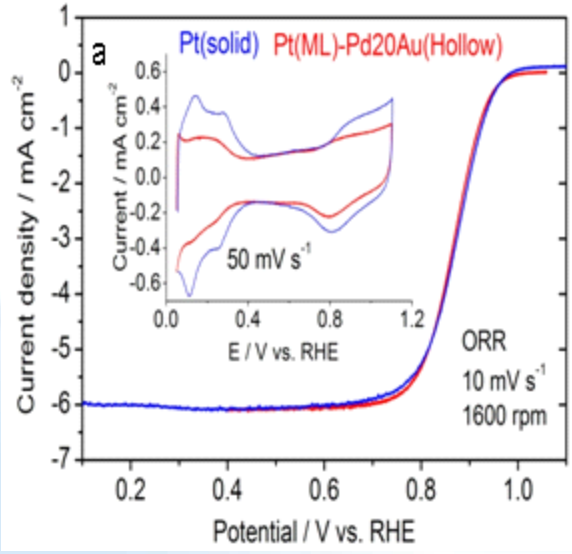
Technical Accomplishments and Progress

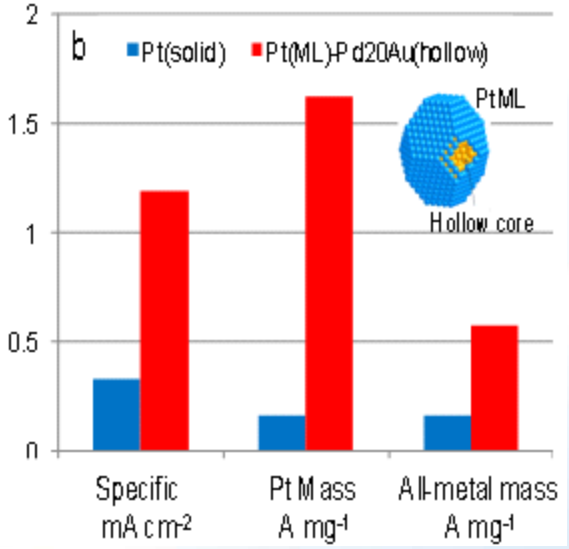
Pt monolayer on hollow Pd nanoparticles



TEM images of pulse-deposited Ni nanoparticles (**a**), Pt(ML)-$Pd_{20}Au$ hollow particles fabricated using Ni nanoparticles as templates (**b**).

Core metals	SA [mA cm^{-2}]	Pt mass [A mg^{-1}]	Pt+Pd+Au mass [A mg^{-1}]
$Pd_{20}Au$	0.85	1.62	0.57
Pd solid	0.50	0.96	0.25
Pt solid	0.33	0.16	0.16



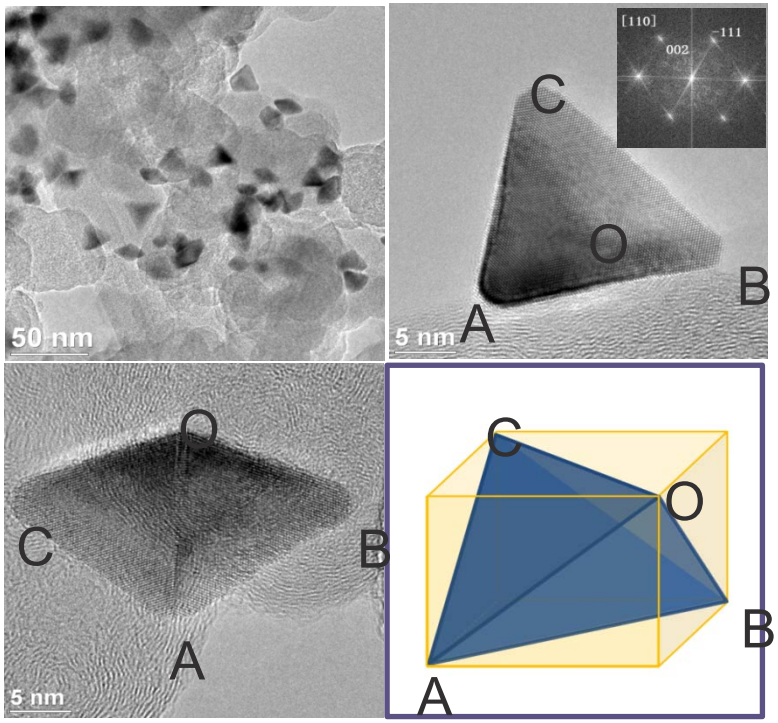


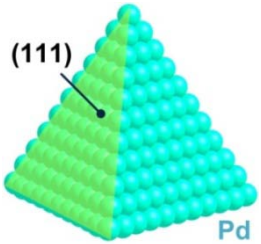
High activity is due to smooth surface morphology, and hollow-induced lattice contraction.

Scale-up synthesis is being developed using:

1. **The cell for electrodeposition of Pd NWs**
2. **The microemulsion method.**

Pt monolayer on Pd tetrahedral nanoparticles: Synthesis

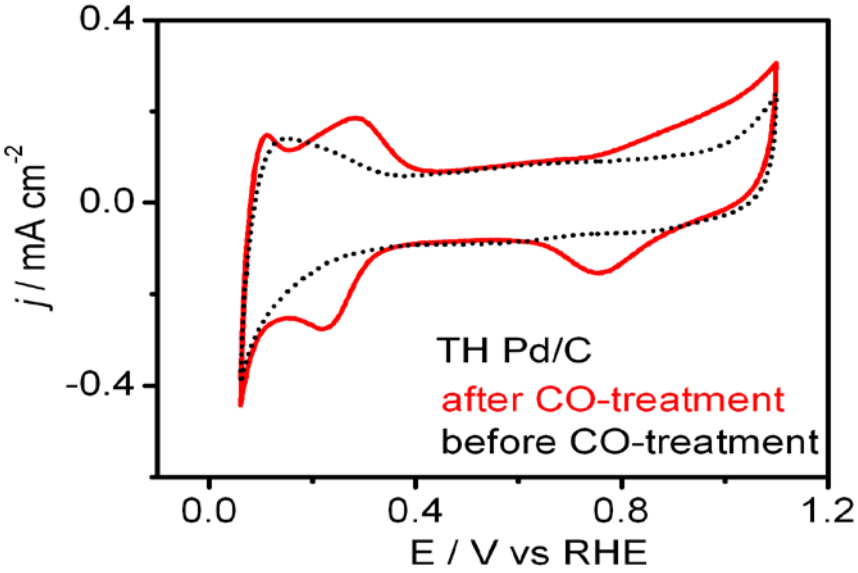




Tetrahedral (TH) Pd NPs were prepared using a hydrothermal route using PVP as surfactant. PVP was removed from the NPs by CO adsorption-induced desorption.

CO adsorption-induced surfactants desorption

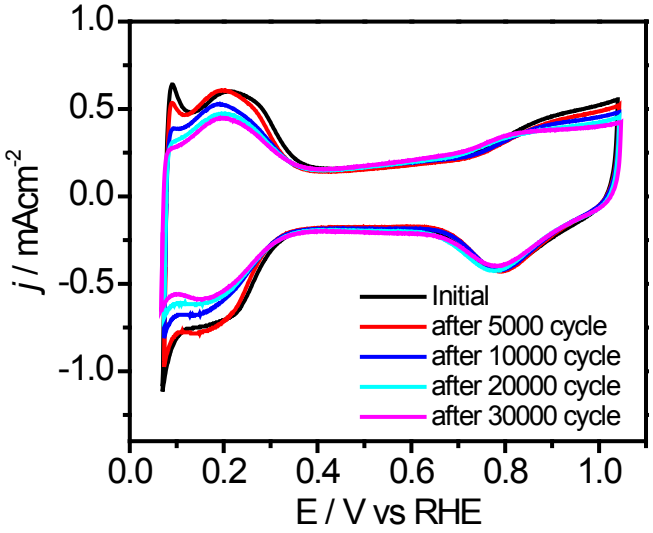
A versatile, noninvasive method for removing surfactants - from NPs surfaces

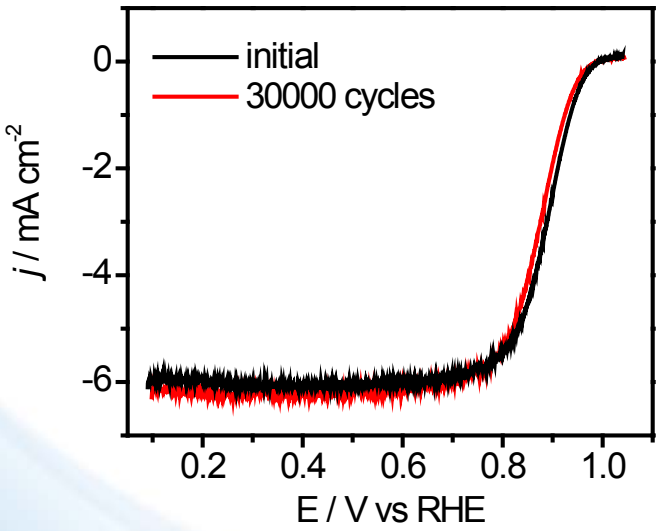


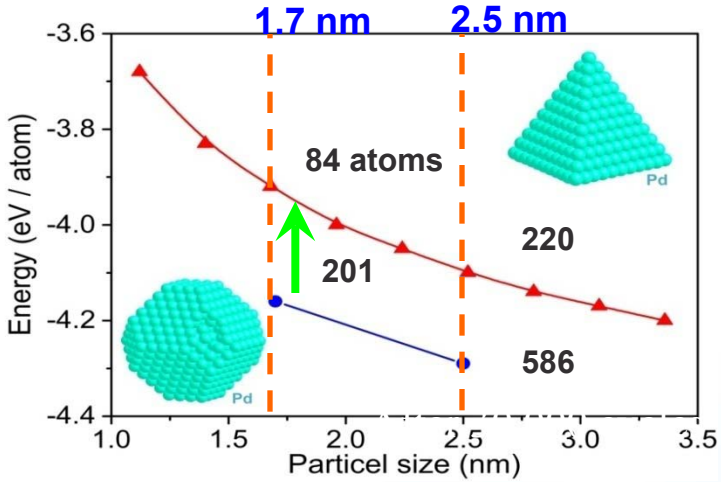
Synthesis of particles of smaller size and scale-up is underway

Technical Accomplishments and Progress

Pt monolayer on Pd tetrahedral nanoparticles







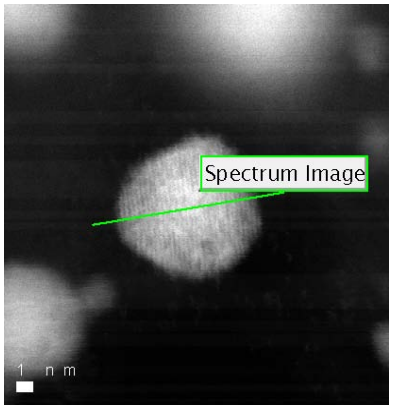
TH consists of much smaller number of atoms than a sphere-like (SP) model → Lower Pd, Pt loading

	Pt_{ML}/TH Pd/C
Half-wave potential (V)	891
ECSA (m^2/mg_{Pt})	19
Pt specific activity (mA/cm^2_{Pt})	0.64
Pt mass activity (A/mg_{Pt})	0.92
PGM mass act. ($A/mg_{Pt, Pd}$)	0.14

The weaker BE-O of TH Pt_{ML}Pd may cause its higher activity than that of Pt_{ML}Pd.

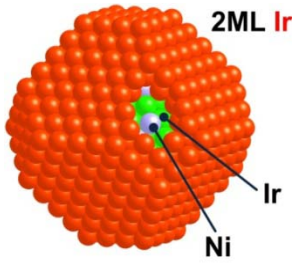
Technical Accomplishments and Progress

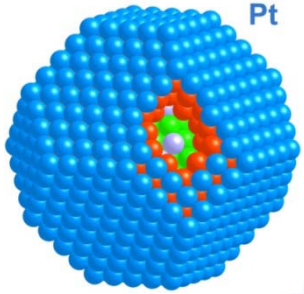
Improving cores by alloying: Pt/IrNi/C



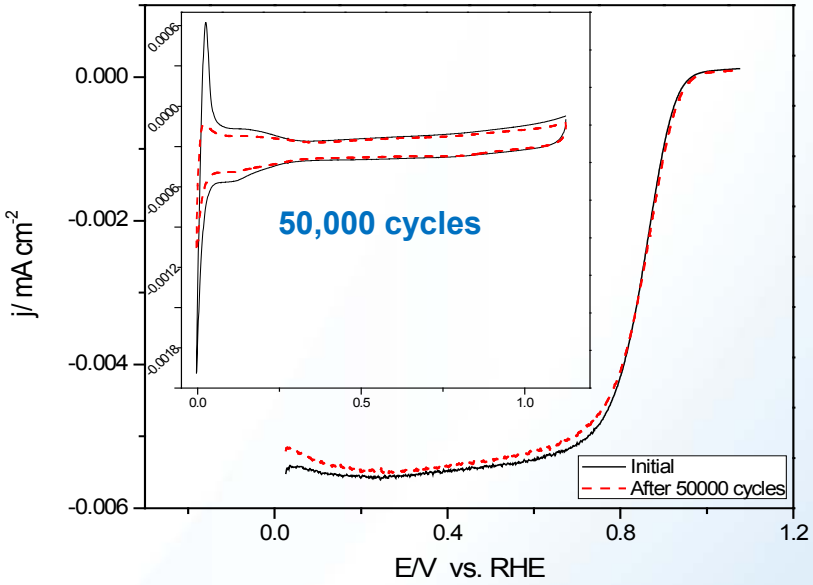
HAADF-STEM image of a PtIrNi nanoparticle

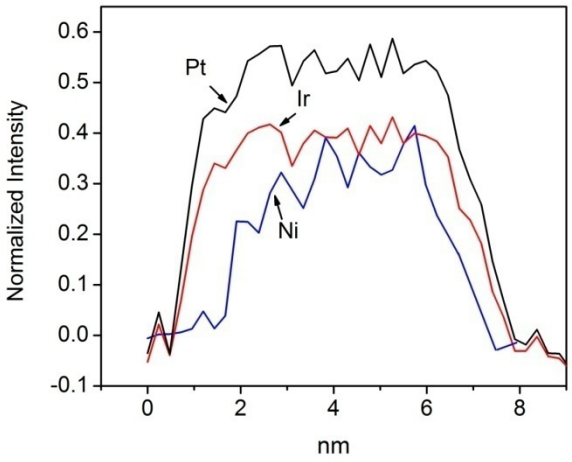
Thermal treatment induces Ir segregation to surfaces





Exceptional stability of cores alloys of Ir with non-noble metals: e.g. IrNi, IrFe





EELS intensities for the Pt and Ir M-edge and Ni L-edge along the scanned line

Pt Mass Activity:
1.4 A/mg$_{Pt}$
Spec. Activity:
0.60 mA/cm^2
PGM Mass Activity:
0.78 A/mg$_{Pt+Ir}$

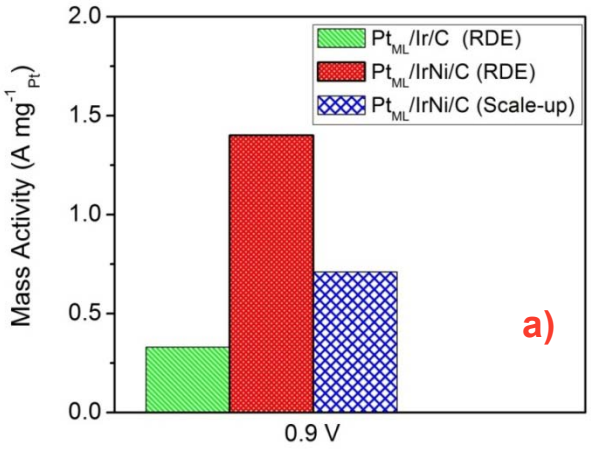
Technical Accomplishments and Progress

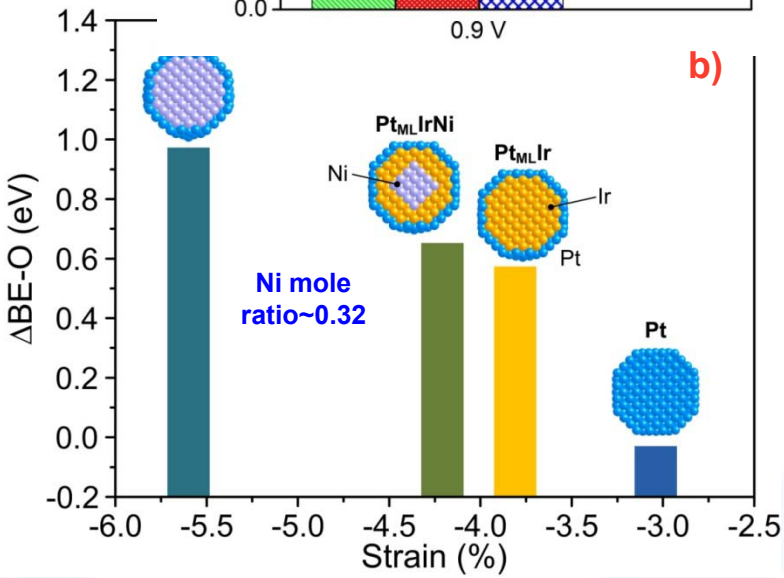
Improving cores by alloying: Pt/IrNi/C

Correlating activities and BE-O:

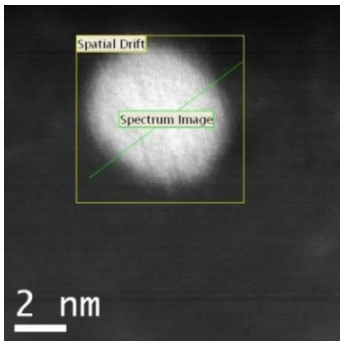
RDE data (a);

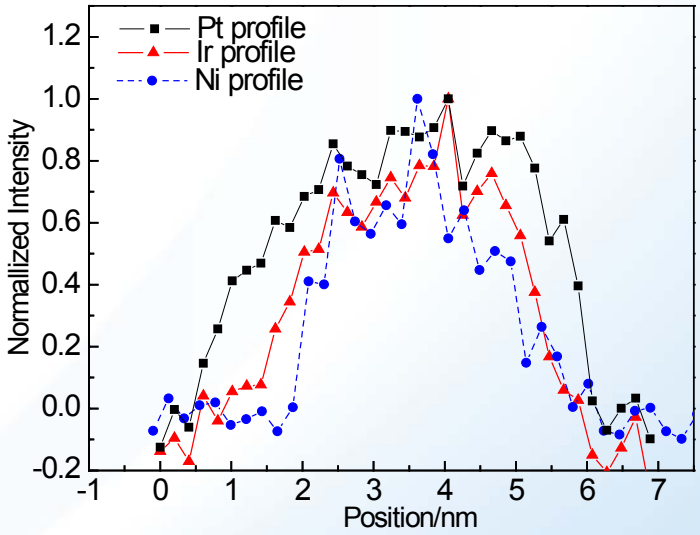
DFT results (b)





DFT: Adding Ni to Ir makes BE-O weaker as a function of strain → Higher activity

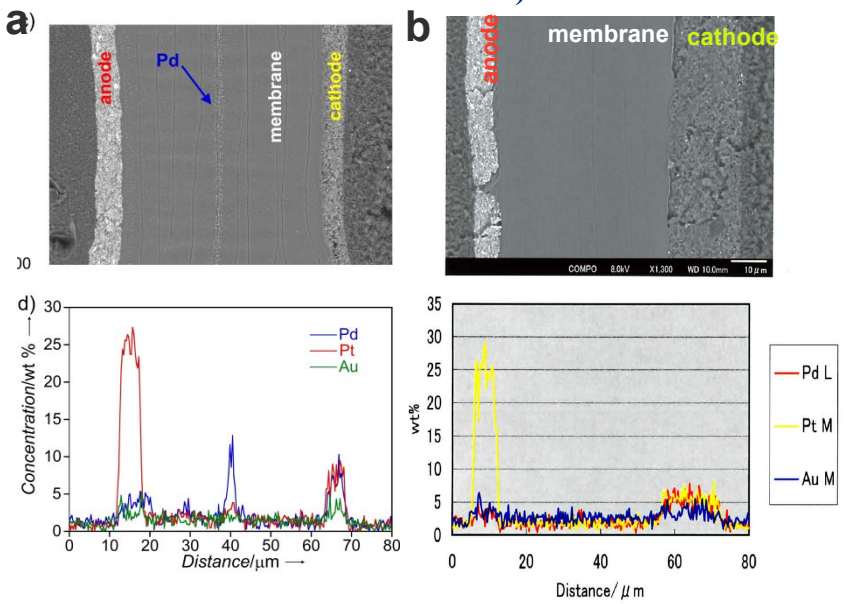




EELS intensities after 50,000 cycles; Ni is clearly observed

Technical Accomplishments and Progress

Fuel cell test of $Pt_{ML}/Pd_9Au/C$ (a) and its improved version (b) Stability tests: potential cycling (0.6 -1.0 V; 50 mV/s, 80°C)



SEM image and EDS line analysis of Pt/Pd_9Au after 200K (a) and 100K cycles (b).

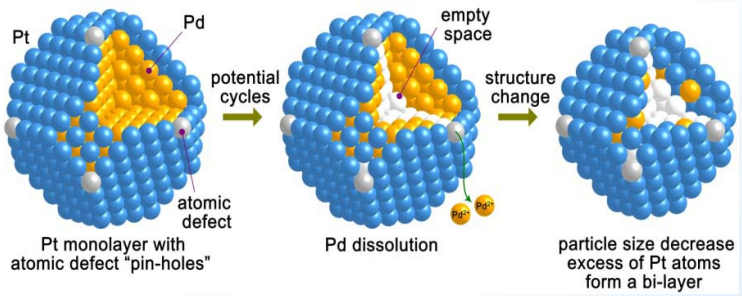
Pd "band" forms from dissolved Pd (a) sample, but not for a more stable Pd_9Au_1 (b).

No Pt dissolution is observed

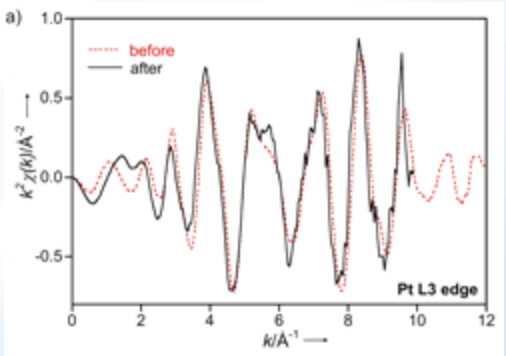
MEA tests at Toyota MC

New mechanism of stability of core-shell electrocatalysts: shell protected by the core

1. PtOH formation shifted positively.
2. Contraction of Pt and Pd lattices induced by some loss of Pd (hollow may form).
3. Cathodic protection effect.



Data supported by EXAFS, XANES, EELS, EDS, RDE, DFT results.



The structure of Pt shells was almost retained after the tests

Sasaki et al. Angew. Chem. Int. Ed., 49 (2010) 8602.

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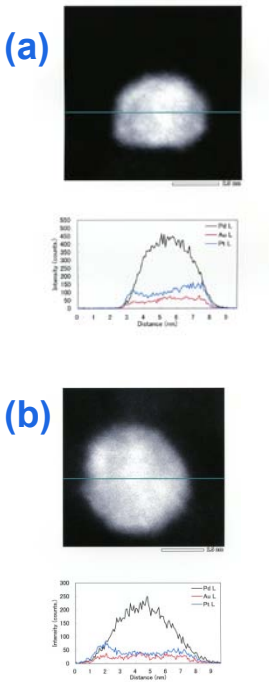
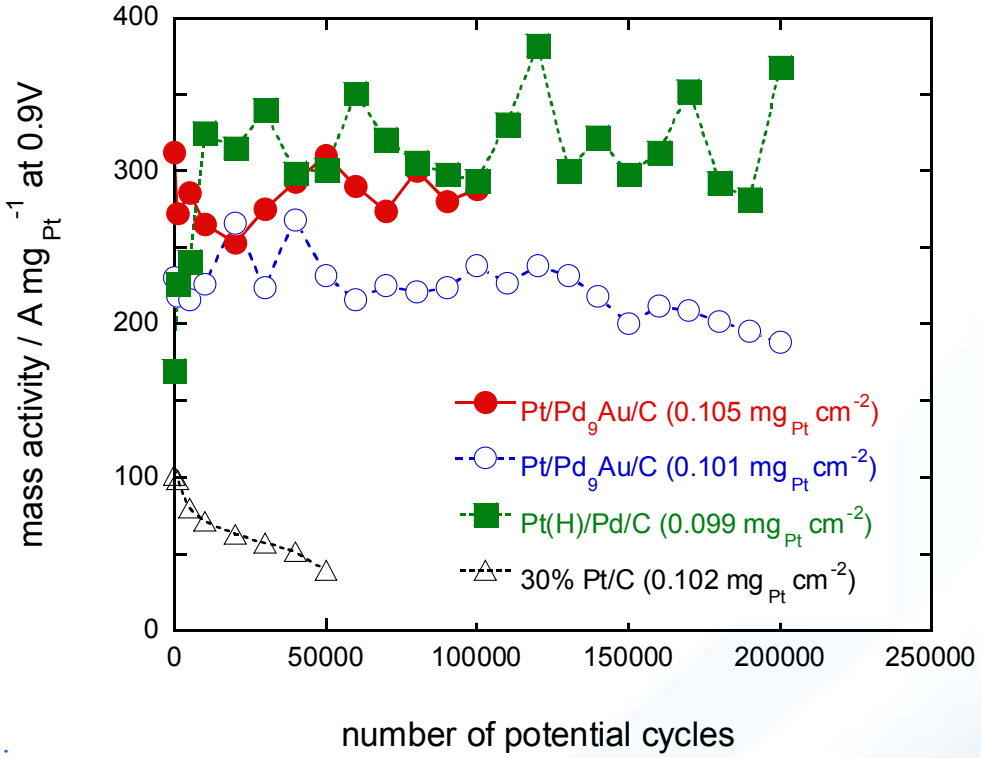
Technical Accomplishments and Progress

Fuel cell performance stability test of $Pt_{ML}/Pd_9Au/C$ and $Pt_{ML}/Pd/C$ electrocatalysts

No change in performance in 200,000 potential cycles with $Pt_{ML}/Pd/C$



TEM images and EDS line analysis of Pt/PdAu/C catalyst, before (a) and after (b) cycling test



For $Pt_{ML}/Pd/C$
Potential cycles:
Rectangular pulse
0.6V (10 sec)-1.0V (10 sec)
Temp. 80C; RH = 100%
Back Pressure: Ambient

Cycling to 1.2 and 1.4V (at **3M Company**) caused a significant loss of Pd but Pt was preserved and its specific activity increased by 6-fold.

Collaborations

1. **Massachusetts Institute of Technology (MIT)** (University)
   Yang Shao-Horn, Co-PI of the project

2. **Johnson Matthey Fuel Cells (JMFC)** (Industry)
   Rachel O'Malley, Co-PI of the project, Sarah Ball, Graham Hard

3. **Toyota Motor Company**
   Hideo Naohara, MEA test, catalysts scale-up

4. **UTC Power (Industry)**
   Collaboration on MEAs making, stack building and testing.

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

6. **Center for Functional Nanomaterials, BNL**
   Ping Liu, YongMan Choi, DFT calculations; **Eli Sutter ad Yimei Zhu**, TEM, STEM

7. **3M Corporation** (Industry)
   Radoslav Atanasoski, Andrew Haug, Greg Haugen

8. **University Santiago de Compostela, Spain**
   David Bucheta, microemulsions-based syntheses of core-shell nanoparticles

Proposed Future Work

FY11

1. Scale-up synthesis of Pd nanowires by electrodeposition at electrodes of 5 cm^2 and 25 cm^2. Further study of the synthesis involving chemical route with surfactants. (BNL)

2. Further studies of hollow Pd and PdAu nanoparticles with a scale-up using:

i) Electrodeposited Ni templates that are galvanically displaced by Pd

ii) Developing the microemulsion method to synthesize hollow Pd nanoparticles. (BNL, JMFC, MIT)

Scale-up of selected synthesis to produce 20 grams of the catalyst (JMFC), or the electrodes of 25 cm^2 compatible with MEA manufacturing.

FY12

1. Improving synthesis of Pd tetrahedra, scale-up to 5 grams
2. Improving synthesis of Pt/Ir-Ni/C ; Pt/Pd/Ru/C. (BNL, MIT, JMFC)
3. Improve metallization and catalyzation of CNTs, oxides, nitrides. (JMFC, MIT, BNL)
4. Further the work on Pd-W, Pd-N and Pd-V NPs. (BNL, MIT)
5. MEA fabrication and tests. Go/No go for these catalysts based on MEA tests. (JMFC, UTC)

Summary

Pt monolayer electrocatalysts supported on several types of cores, which can have several shapes, are ready for scale-up syntheses and MEA testing.

Nanowires, nanorods, hollow NPs and tetrahedral NPs provide excellent supports-cores.

Pd, Pd alloys, Ir - non-noble metal alloys provide excellent cores.

Using refractory metal alloys in cores and metallization of CNTs require further studies.

Sub-surface ML modification of cores opens up possibilities for additional improvements.

New mechanism of stability of core-shell electrocatalysts, in which shell is protected by the core, has been proposed.

$Pt_{ML}/Pd_9Au/C$ and $Pt_{ML}/Pd/C$ are practical electrocatalysts.
Only 10 grams of Pt, and about 15-20 grams of Pd is needed for a FC of 100 KW.
Currently, catalytic converters use 5-10 g of Pt per vehicle. No new Pt is needed for converting to fuel cells.