Project FC009

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

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a passion for discovery

2012 DOE Hydrogen Program Annual Merit Review Meeting
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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. 60%

Budget in $K

Total project funding:	3,544
Funding in FY11:	425
Planned Funding in FY 12:	925

Technology transfer

Four patents on Pt ML electrocatalysts licensed to N.E. ChemCat Co.

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

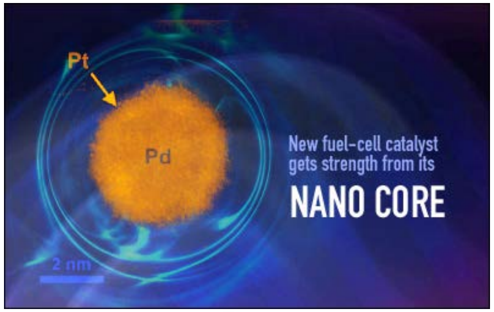
Partners

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

Collaborations

UTC Power, Toyota M. C., U. Wisconsin, U. Stony Brook, 3M Corporation, GM Corporation, CFN-BNL

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 nanostructures.**

2. Increasing activity and stability of Pt monolayer shell and stability of supporting cores, while reducing noble metal contents.

3. **Maximizing utilization of Pt to use every Pt atom.**

4. Scale-up of two syntheses for testing catalysts in fuel cell stacks:

   4.1 Conventional synthesis of ultra thin Pd alloy (refractory metals or Au) NWs or hollow NPs as support for a Pt ML.

   4.2 Synthesis based entirely on electrodeposition of NWs or NRDs (delivering a 500cm^2 MEA for stack- testing at UTC).

Approach

Increasing Pt monolayer activity and stability, and reducing the PGM content

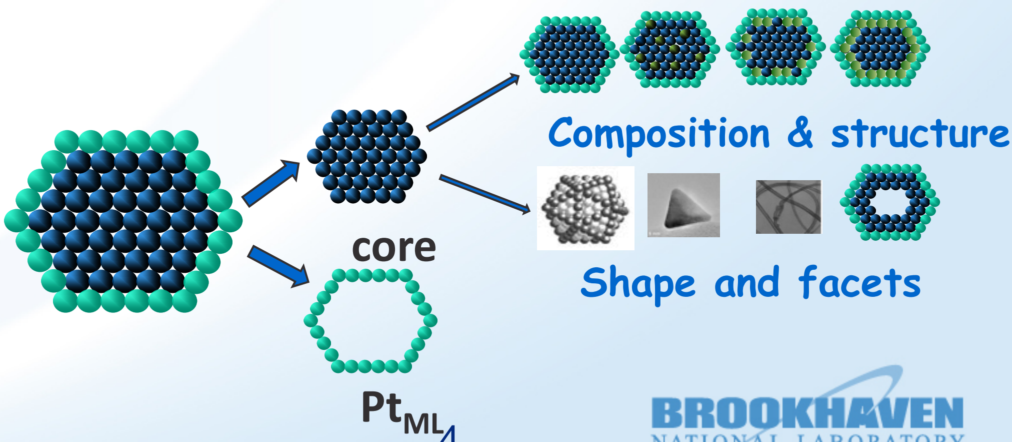
by

- Reducing oxygen binding energy
- Decreasing the number of low-coordination atoms
- Compressing the top layer of atoms
- Forming moderately compressed (111) facets
- Increasing stability of cores

accomplished *via*

- Surface contraction (induced by core, hollow core, subsurface ML, segregation),
- Improving Pt ML deposition process
- Designing the cores with specific structure, composition, shape and distribution
- Electrodeposition of cores and shells to maximize catalyst utilization
- Metal-, alloy- nanowires obtained in conventional syntheses
- Refractory metal alloys used as cores

tests, characterizations

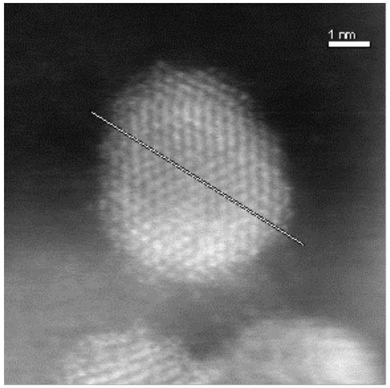


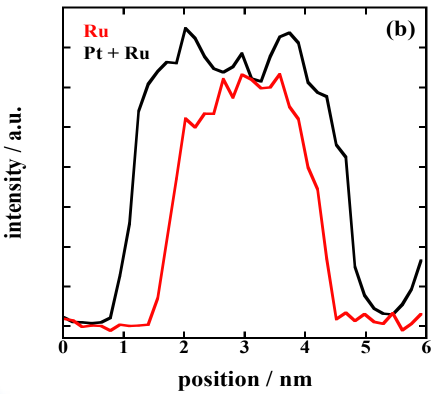
*J.X. Wang, H. Inada, L. Wu, Y. Zhu, Y. Choi, P. Liu, W.P. Zhou, R.R. Adzic, *J. Am. Chem. Soc, 131 (2009) 17298, JACS Select #8*

Technical Accomplishments and Progress

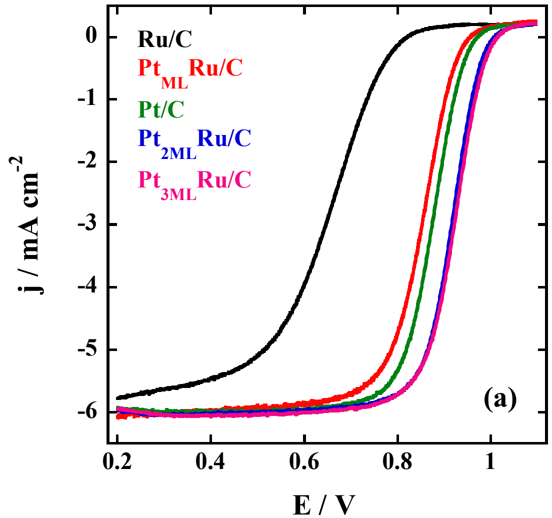
Decreasing the content of Pd in cores

Tuning Pt-Ru interaction to obtain a high-activity Pt/Ru core-shell electrocatalyst for the ORR

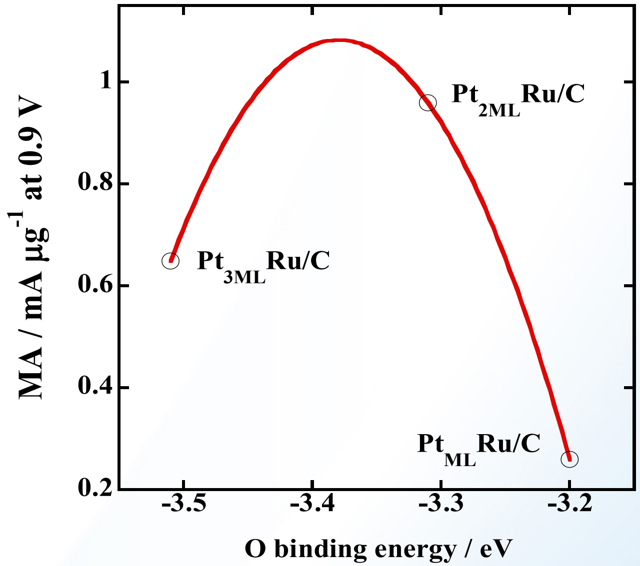


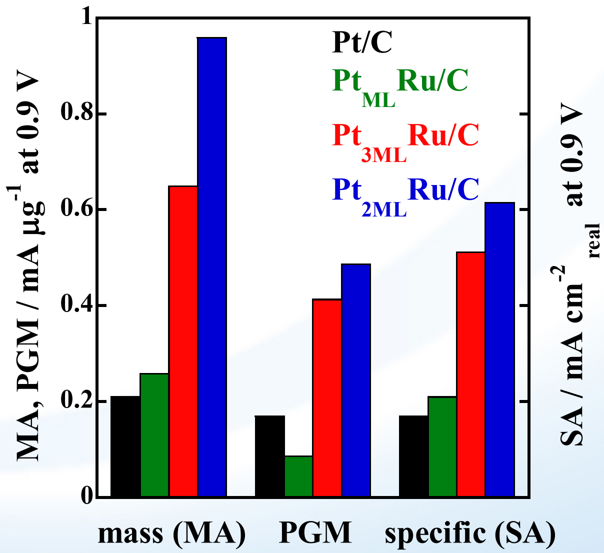


HAADF image of $Pt_{2ML}Ru/C$, element-sensitive EELS indicate the 2MLs Pt shell



RDE of the ORR on $Pt_{xML}Ru/C$, 0.1M$HClO_4$; 20mV/s; 1600rpm





Volcano plot of the ORR activity as a function of calculated BE of O for Pt overlayers on Ru.
Data illustrate the possibility how other substrates can be used to support a Pt_{ML}

Technical Accomplishments and Progress

Decreasing the content of Pd in cores

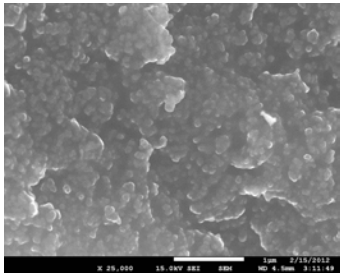
Refractory metal alloys as cores - NiW

Pt_{ML}/Pd/NiW

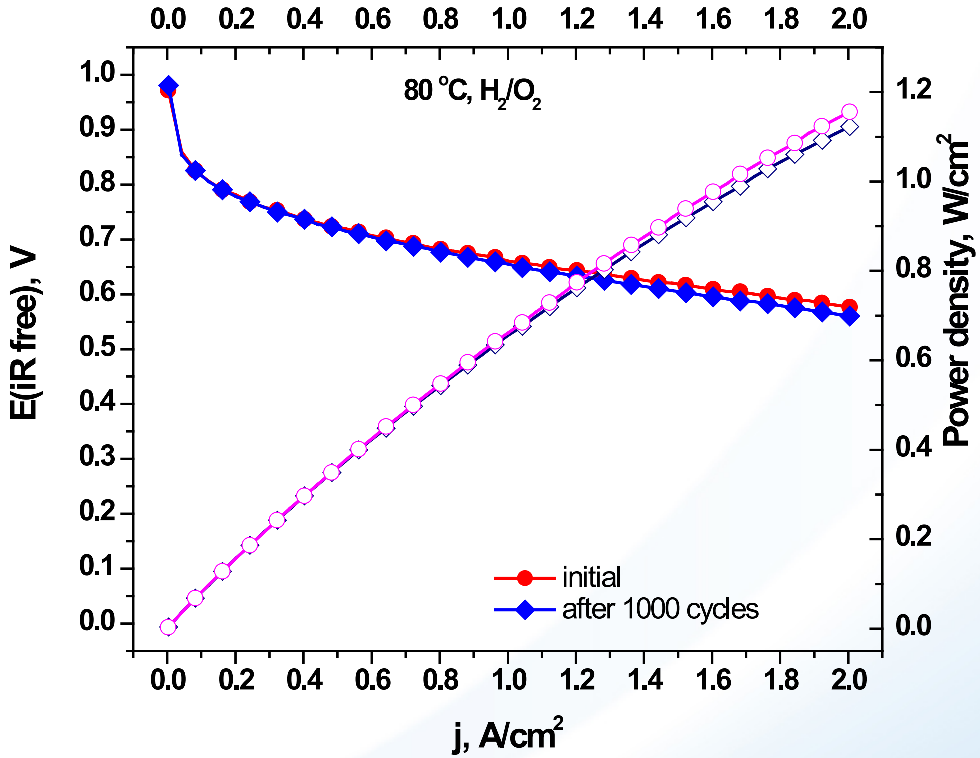
NiW obtained by co-deposition of Ni and W on GDL

Ni is partially displaced by Pd from the top layer of NiW. Electrode : 5cm²

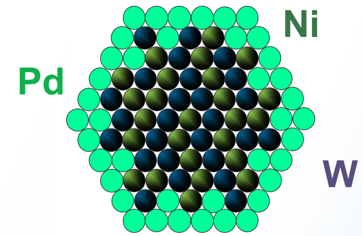
SEM image after NiW deposition on GDL.



1:1 Ni:W ratio verified using EDS
W max conc. 50%



< 40 μg_{Pt} /cm²



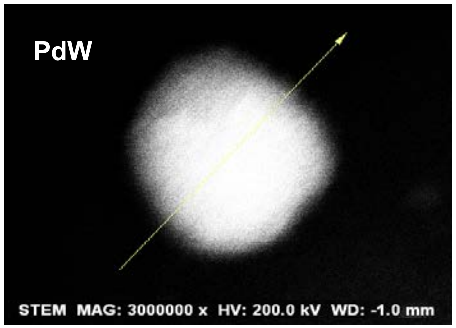
Model of NiW core with a partially displaced Ni by Pd

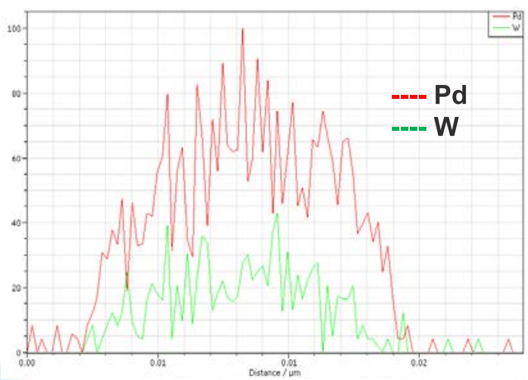
Technical Accomplishments and Progress

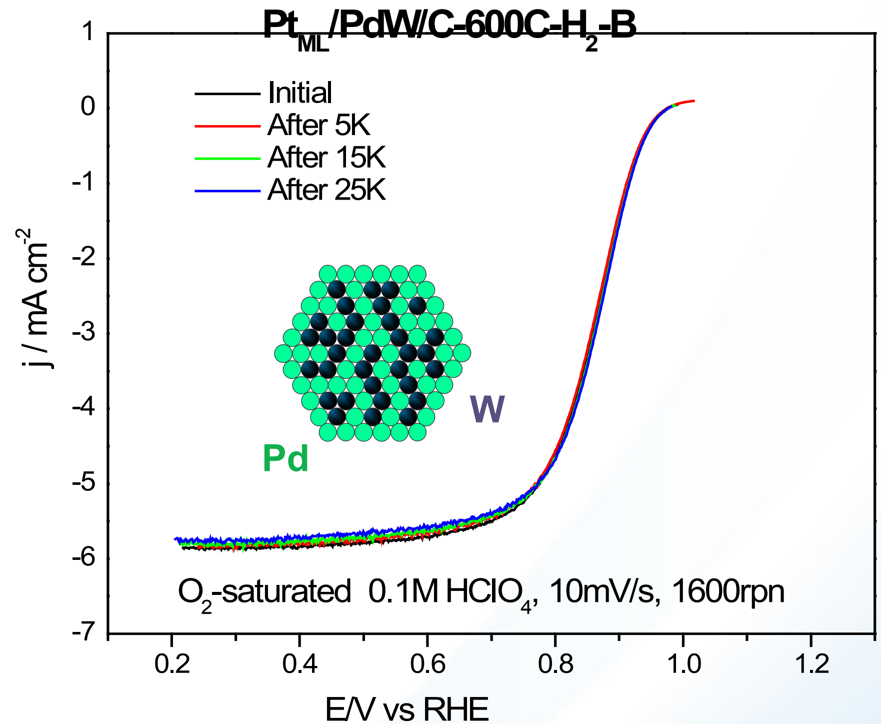
Decreasing the content of Pd in cores

Refractory metal alloys as cores – PdW obtained in H_2 600° C Pd:W = 1:1

STEM-EDX of PdW/C







Structure: Pd-rich shell on a Pd-W alloy core

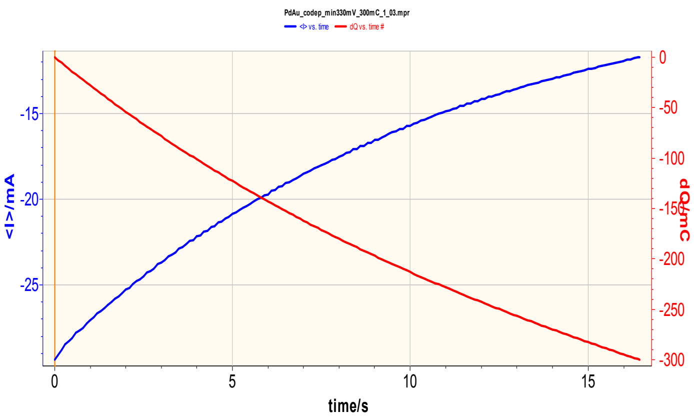
	J_m (A mg^{-1})	J_{PGM} (A mg^{-1})	J_s (A Ptcm^{-2})	$E_{1/2}$ V(RHE)
Pt/PdW 600° C	0.81	0.22	0.58	0.867

High stability induced by W: No change after 25K cycles

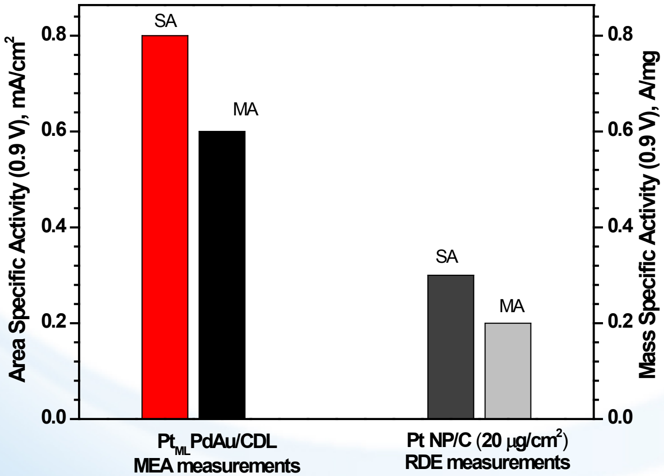
Technical Accomplishments and Progress

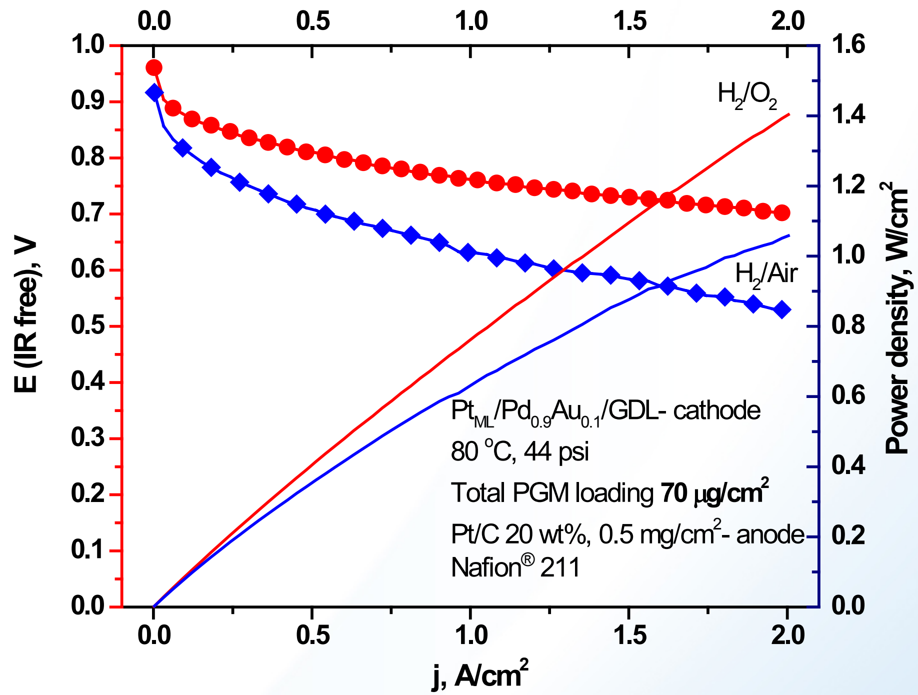
Electrochemical deposition of PdAu NRs $Pt_{ML}/Pd_{0.9}Au_{0.1}/GDL$

Current and charge transients



MEA test vs. RDE





PGM content approx. 70μg/cm²

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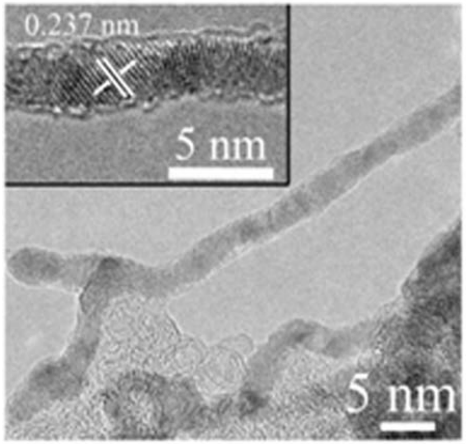
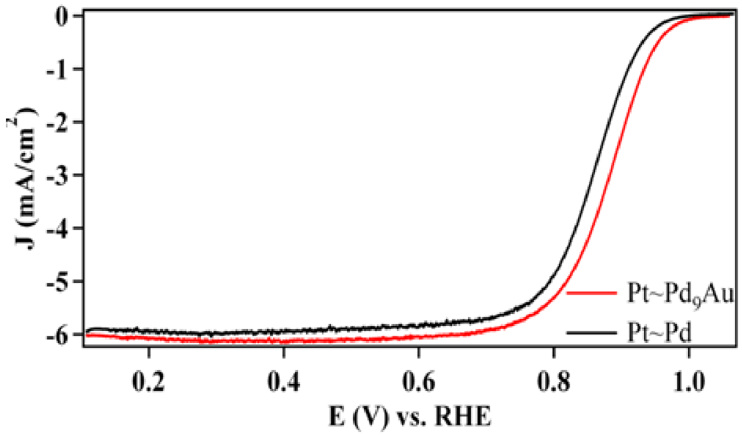
Electrochemical deposition of NRDs and NWs cores with Pt_{ML} deposition using galvanic displacement of Cu ML facilitates close to 100% utilization of Pt.

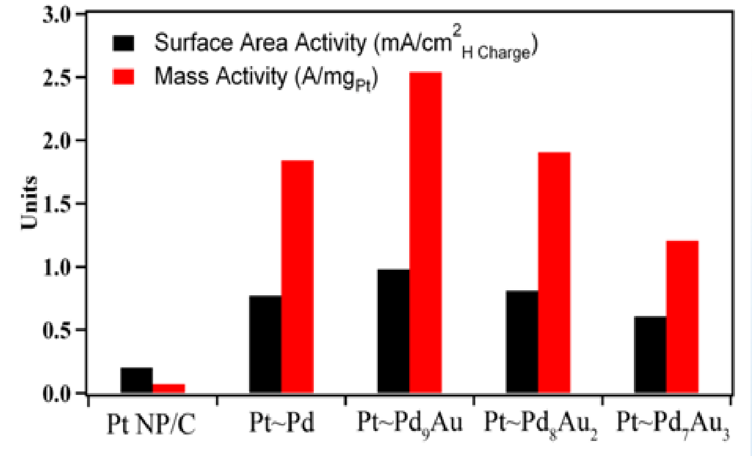
Technical Accomplishments and Progress

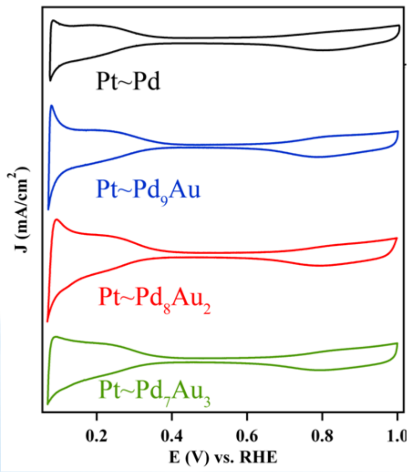
Synthesis of the ultrathin bimetallic PdAu nanowires





Pd and Au precursors are combined with octadecylamine and a phase transfer catalyst in an organic solvent system.





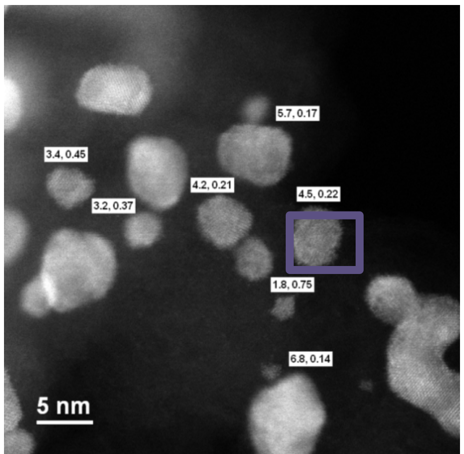
The phase transfer catalyst dodecyltrimethyl ammonium bromide (DTAB) is used to allow for co-solubilization of $NaBH_4$ into both the aqueous and organic phases.

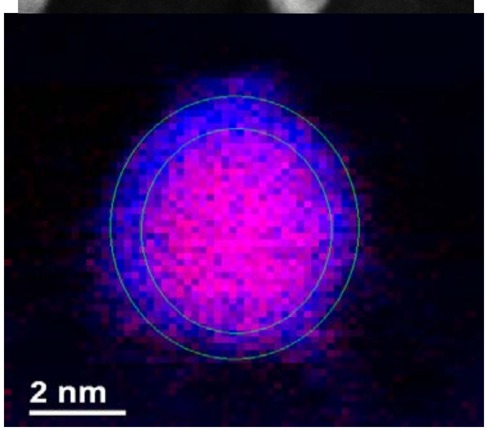
With Koenigsmann and Wong

Improving deposition of Pt monolayer on Pd nanoparticles

Smooth coating of Pt on Pd nanoparticles from ethanol solution

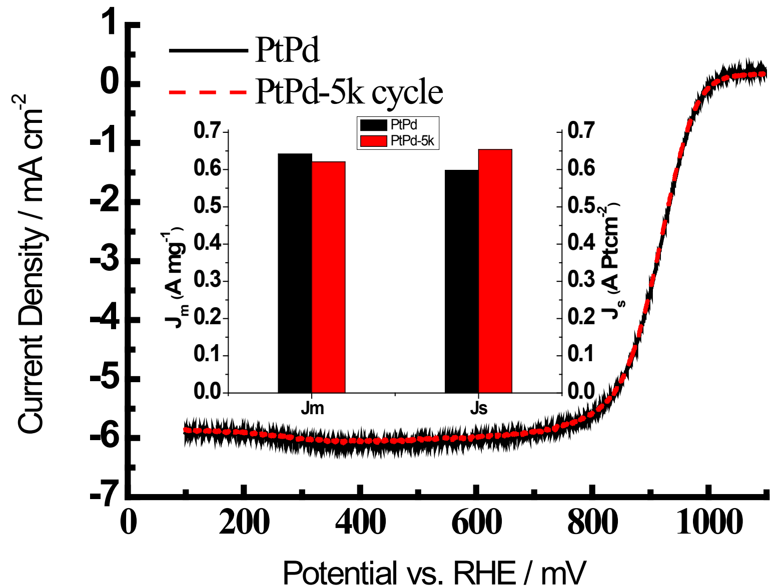
Pt/(Pt+Pd) ratio for individual particles by EDX





Deposition mechanism: Displacement of Pd by Pt and reduction of Pd^{2+} by ethanol at elevated temperatures.

Pd detected by EELS (red) is in the core of a Pd-Pt(2ML) particle (blue).



Comparable Pt mass activity with those fabricated using Cu upd.

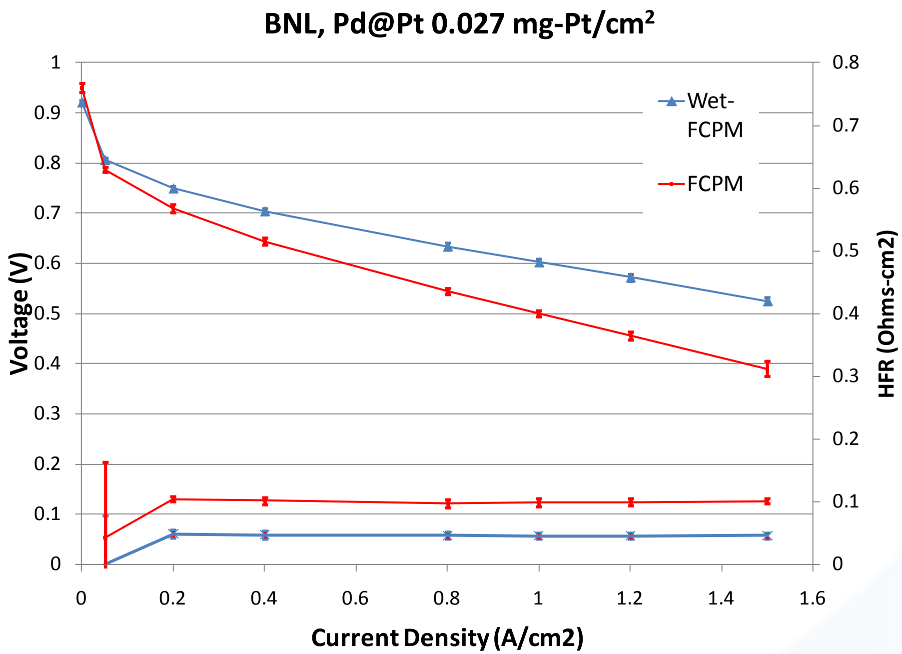
Better PGM mass activity with hollow Pd core.

Smaller ECSA caused by vacancy-induced lattice contraction.

Activity/ composition	EtOH $PtPd_{2.7}$	EtOH $PtPd_2$
Pt /(Pt+Pd) atom	0.27	0.33
Pt (wt%)	17.1	18.1
Pd (wt%)	24.9	19.7
MA_Pt (A mg^{-1})	**0.64**	**0.62**
MA_PGM (A mg^{-1})	0.26	0.30
SA (mA cm^{-2})	0.58	0.70
ECSA (m^2 g^{-1})	110	89

Preliminary testing of Pt monolayer catalysts in MEA and RDE at GM

H_2/air fuel cell polarization curves of Pt/Pd/C

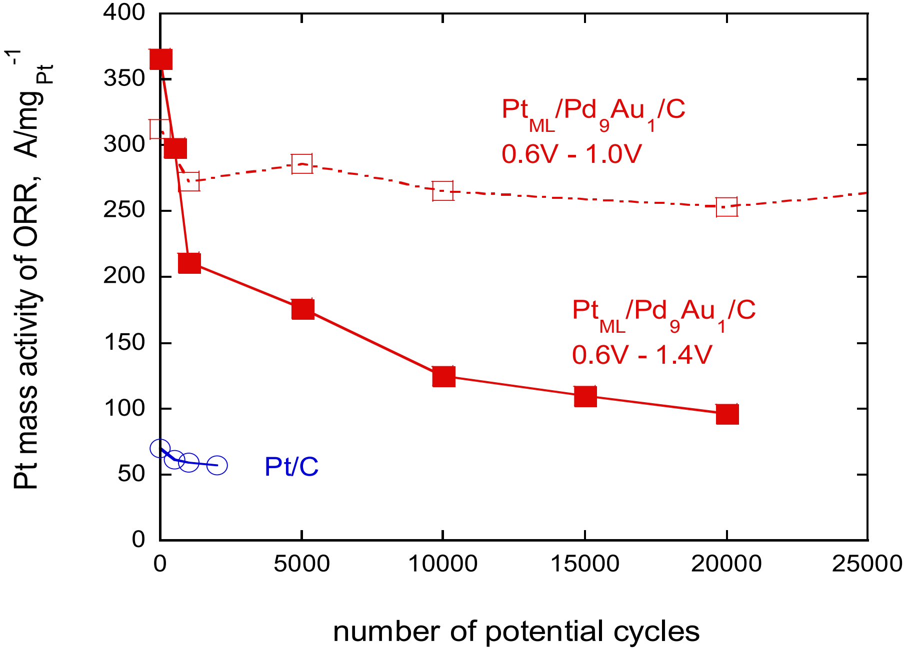


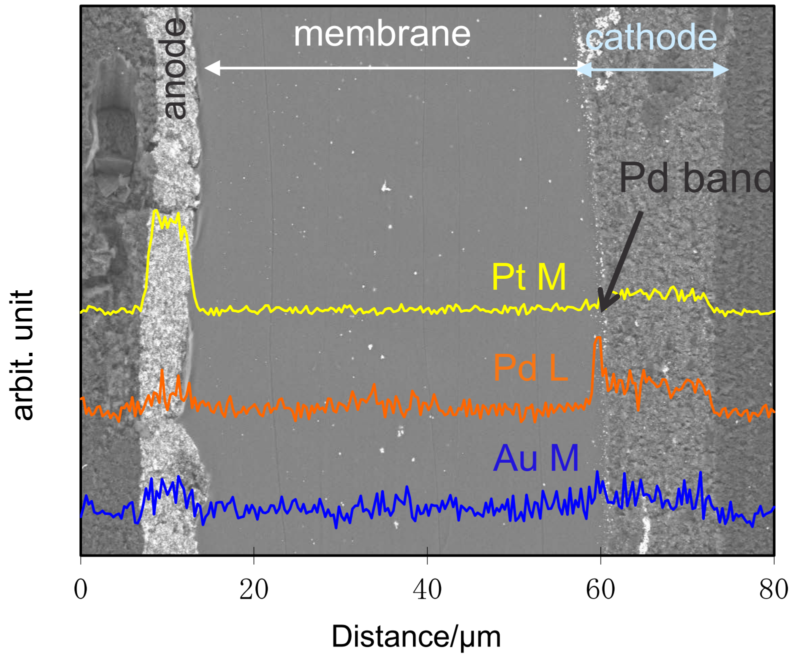
- The ORR activities comparable to literature were reproduced in MEA and RDE.
- Very impressive fuel cell performance with low Pt loading was observed on (at least) Pt/Pd/C.
- Poor performance of two other catalysts are most likely due to their thick cathodes.
- Future tests with higher metal contents preferred

A. Kongkanand, J. Zhang, F. Wagner

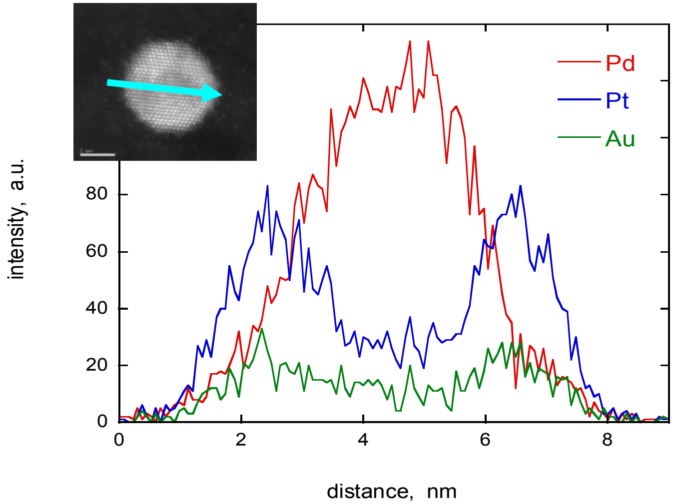
H_2/Air, 80° C, 65%RH, 150kPa; 100%RH, 170kPa; **27µgPt/cm²**

MEA tests of $Pt_{ML}/Pd_9Au_1/C$: potential cycles 0.6 V – 1.4 V





EDS/STEM line scan analysis of components



- The Pt MA decreased *ca* 60% of that under 0.6 V - 1.4 V after 20k cycle test.
- Pd band is formed at the interface between membrane and cathode.
- The core-shell structure is seen and the Pt shell is thickened (thereby inhibits Pd dissolution).
- The intensity of Pd is decreased. Insignificant dissolution of Pt and Au can take place.

With Hideo Naohara

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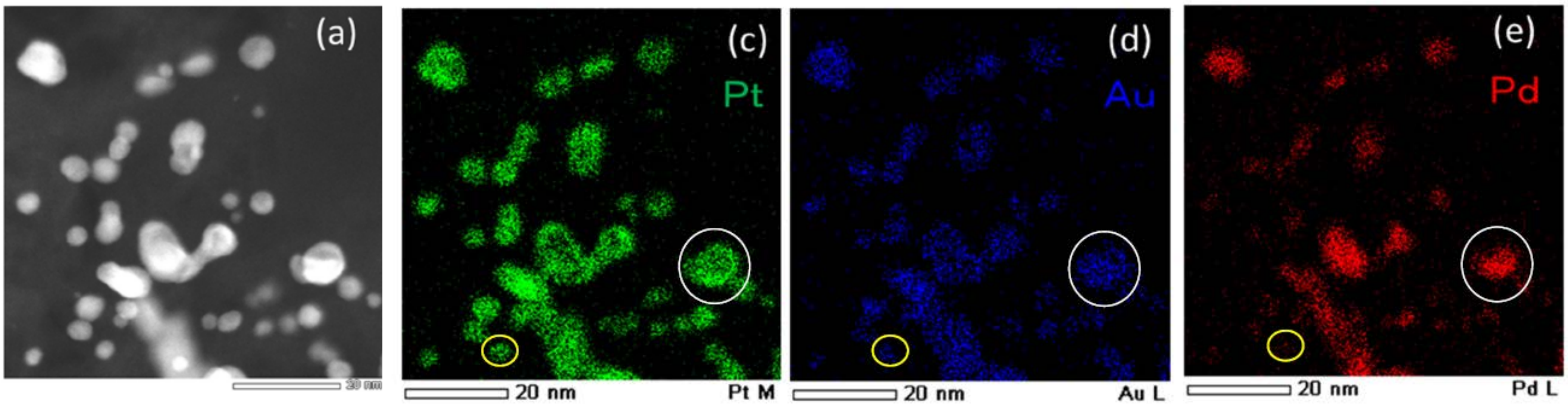
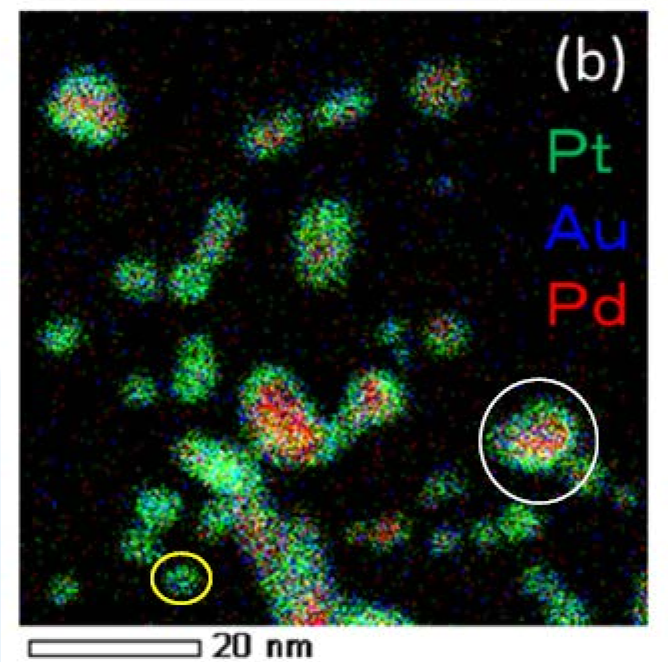
MEA tests of $Pt_{ML}/Pd_9Au_1/C$ electrocatalysts: 0.6 V – 1.4 V

STEM/EDS elemental maps after 20,000 cycles between 0.6V-1.4V





For relatively large particles, the core-shell structure is clearly retained under the hash condition.

Origins of high stability:

- ❖ Increase in Pd oxidation/dissolution potential by Au
- ❖ Surface segregation and mobility of Au
- ❖ Cathodic protection of Pt by sacrificial Pd
- ❖ Thickening Pt shells
- ❖ (Generation of smooth & high-coordinated surfaces)

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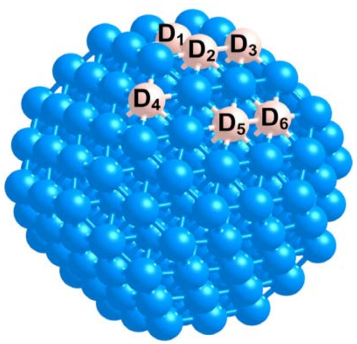
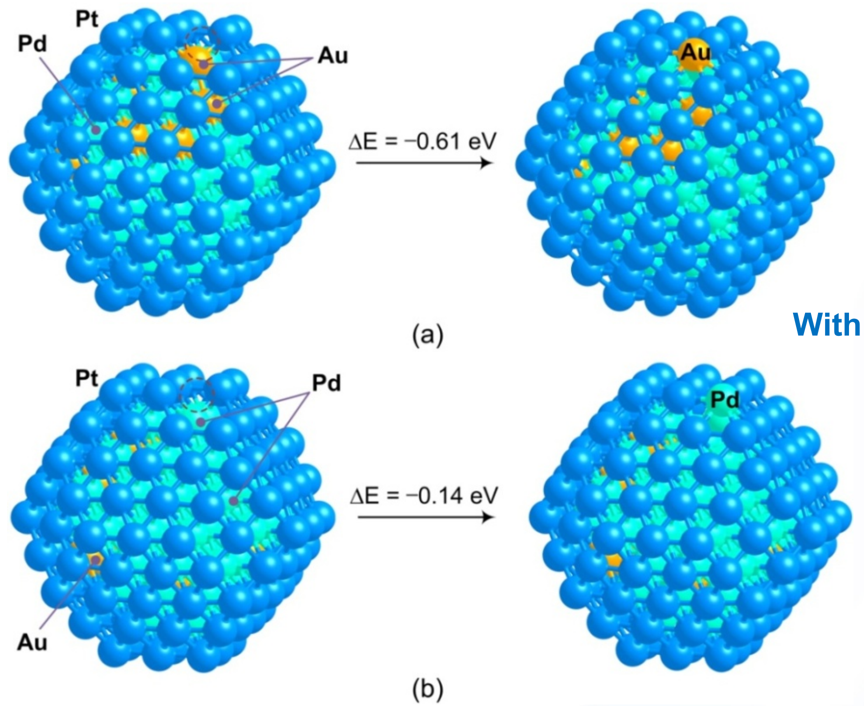
Stability of Pt_{ML}/Pd_9Au_1 from DFT calculations





With Choi and Liu

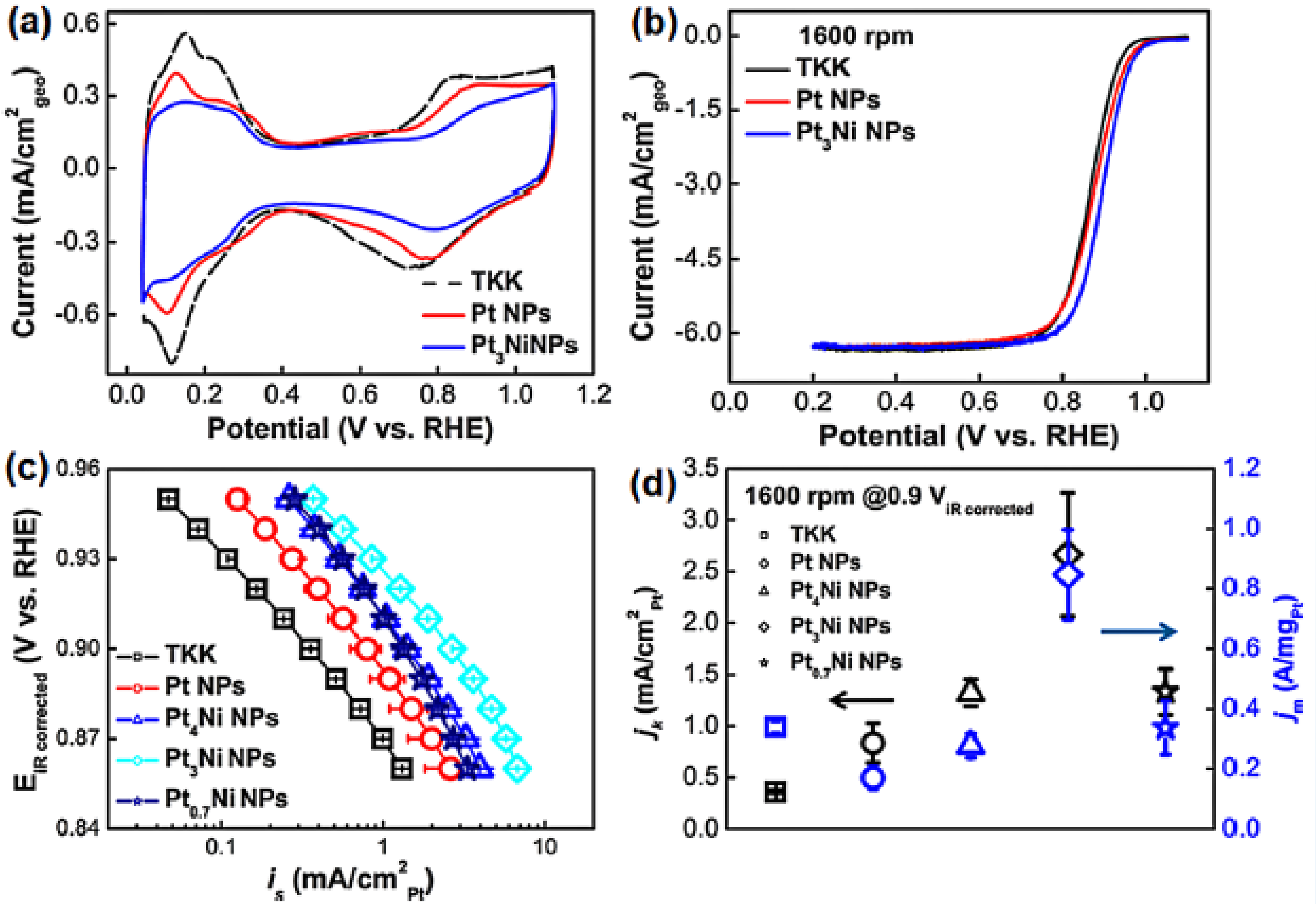
1. Model a sphere-like Pt ML on Pd_9Au_1 random alloy core (*ca* ϕ1.7 nm)
2. Introduce a defect (vacancy) in the Pt ML at vertex (D_3)
3. Calculate energy changes (ΔE) when Au or Pd atom diffuses from core to the defect site (ΔE_{Au} = -0.61 eV, ΔE_{Pd} = -0.14 eV)

Au preferentially segregates on the surface → inhibit further dissolution of Pd

The notion is similar to our previous study (Zhang et al., Science, 315 (2007) 220)

ORR Activities on $Pt_{1-x}Ni_x$ Nanoparticles on MWNTs (MIT)

Remarkable activities are observed for MWNTs covered with very small catalyst particles



Electrochemical and Solid-State Letters, **14** (10) B110-B113 (2011)
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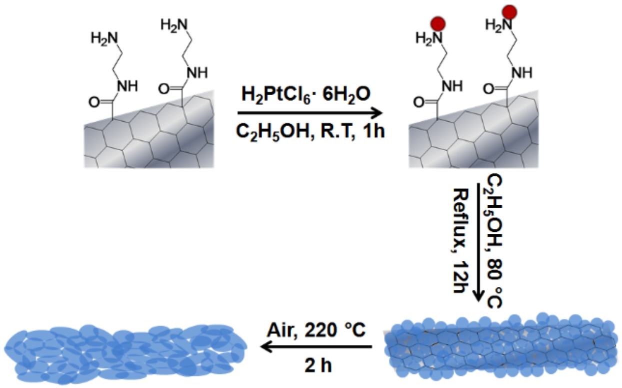
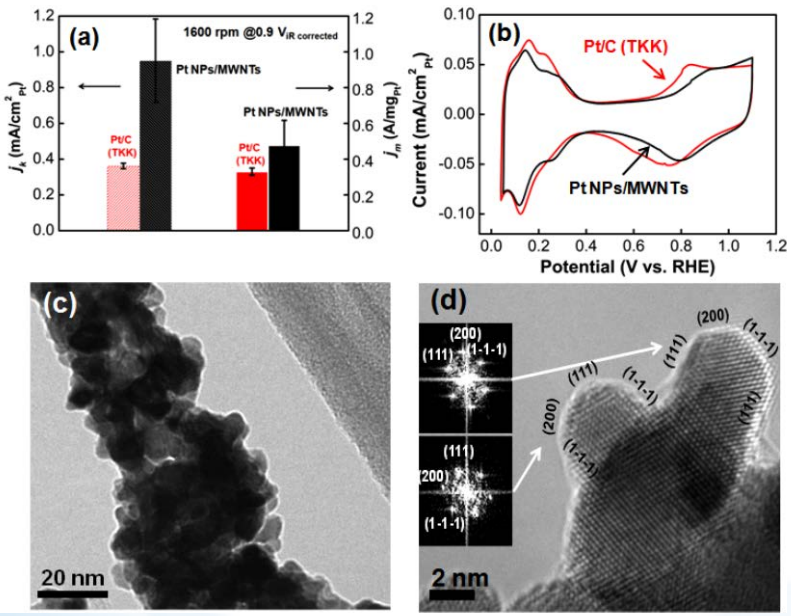
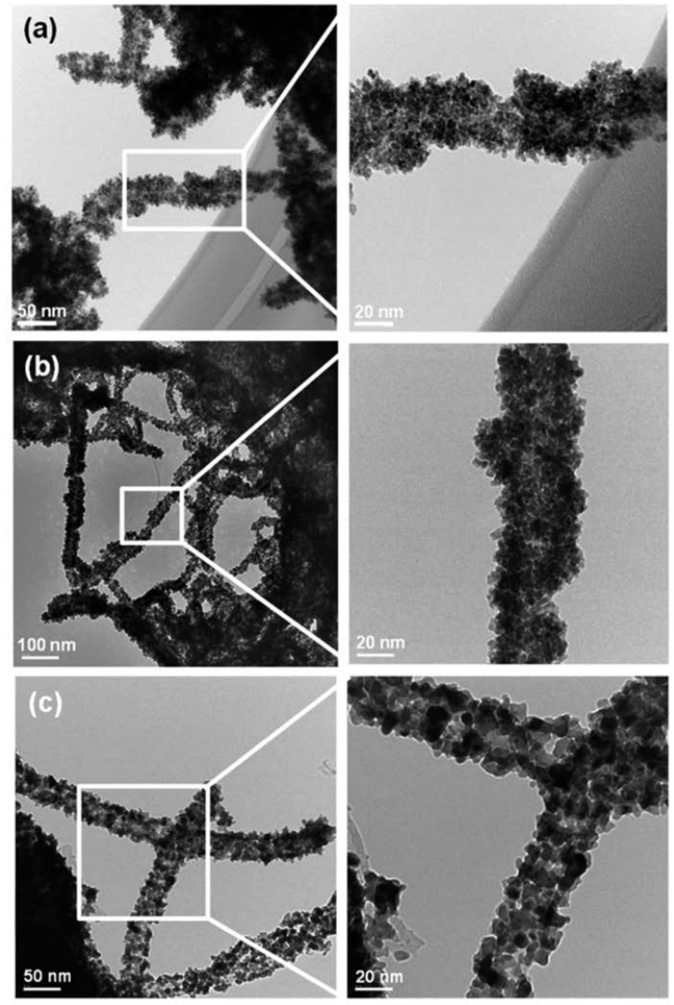
Pt-Covered MWNTs for ORR







dx.doi.org/10.1021/jz200531z | J. Phys. Chem. Lett. 2011, 2, 1332–1336

Collaborations

Partners:

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

2. **Johnson Matthey Fuel Cells (JMFC)** (Industry) **Rachel O'Malley Co-PI**

3. **UTC Power (Industry) Minhua Shao, Lesia Protsailo, CRADA**
   Collaboration on MEAs making, stack building and testing.

Technology Transfer

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

Other Collaborations

6. **Toyota Motor Company** (Industry) **Hideo Naohara, Toshihiko Yoshida** MEA test, catalysts scale-up
7. **U. Wisconsin** (University) **Manos Mavrikakis,** collaboration on theoretical calculations-
8. **Center for Functional Nanomaterials, BNL Ping Liu, YongMan Choi**, DFT calculations;
   Eli Sutter ad Yimei Zhu, TEM, STEM
9. **3M Corporation (Industry) Radoslav Atanasoski, Andrew Haug, Greg Haugen**
10. **GM (Industry) Fred Wagner, Anu Kongkanand, Junliang Zhang**

Proposed Future Work

FY12

1. **Scale-up synthesis of Pd alloy NWs by electrodeposition electrodes of 25 and 500 cm^2 (BNL).**

2. **Scale-up of synthesis to produce 20 grams of ultra thin NWs using weak surfactants (JMFC).**

3. **Developing the microemulsion method to synthesize hollow Pd nanoparticles (BNL).**

4. **Improve metallization and catalyzation of CNTs (JMFC, MIT).**

5. **Further work on the Pd-refractory metal alloy cores (BNL).**

FY13

1. **MEA fabrication and tests. Go/No go based on MEA tests. (BNL, JMFC, UTC).**

2. **Scale-up syntheses to produce the catalyst amounts for fuel cell stack. (BNL, JMFC)**

3. **Manufacturing and tests of fuel cell stacks (UTC).**

Summary

$Pt_{ML}/Pd_9Au/C$ and $Pt_{ML}/Pd/C$ are practical electrocatalysts. Stability under potential cycling to 1.4V is high. Self-healing-mechanism confirmed in this test.

Four patents on their technology have been licensed to N.E. ChemCat Co. by BNL.

Pd alloys with refractory metals provide stable and inexpensive cores, reduced PGM content.

An efficient method for Pt_{ML} electrocatalysts syntheses involving electrochemical deposition on GDL has been developed. High activity, high stability electrocatalysts are obtained, Pt utilization close to 100%; Scale-up is simple.

Synthesis of ultra-thin Pd alloy nanowires using simple surfactant has been developed to provide an excellent support for a Pt_{ML}.

An efficient method for Pt_{ML} deposition on Pd nanoparticles using ethanol as a medium and reactant has been developed.

The mechanism of stability of core-shell electrocatalysts, in which shell is protected by the core, and the self-healing mechanism have been verified in tests involving potential cycling to 1.4V.

Pt_{ML} electrocatalysts for ORR --- On the road to application and could be further improved!