

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

Radoslav Adzic

Brookhaven National Laboratory

Co-PIs: Jia Wang, Miomir Vukmirovic, Kotaro Sasaki

Brookhaven National Laboratory

Yang Shao-Horn

Massachusetts Institute of Technology

Rachel O'Malley, David Thompsett, Sarah Ball, Graham Hard

Johnson Matthey Fuel Cells

Project FC009

2010 DOE Hydrogen Program Annual Merit Review Meeting
June 7-11 , 2010



Overview

Timeline

Project start date: July 2009
Project end date: September 2013
Percent complete: Approx. 20%

Budget in \$K

Total project funding:	3,529
Funding in FY09:	615
Funding for FY10:	267

Barriers

Performance:

Catalyst activity; ≥ 0.44 A/mg_{PGM}

Cost:

PGM loading; ≤ 0.3 mg PGM /cm²

Durability:

< 40% loss in activity under potential cycling

Partners

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

Collaborations

UTC Power; **3M** Corporation; U. Wisconsin
U. Stony Brook

Relevance

Objectives:

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

- nanoparticles (NP)
- nanorods,
- nanowires,
- carbon nanotubes (CNT), and
- scale-up syntheses of selected catalysts,
- MEA-testing, stack- testing

Initial studies:

BNL: Pd and Pd-Nb alloy NPs, nanorods and nanowires; Modification of cores: sub-surface MLs and hollow cores; Pd thin layers on CNTs

MIT: Develop uniform L-B-L thin film structures on functionalized CNTs. Preparing a contiguous Pt film. Reveal surface structures and near-surface compositions.

JMFC: Contiguous metal layers on C and CNTs surfaces. Verification of the stability. Scale-up synthesis of selected catalysts.

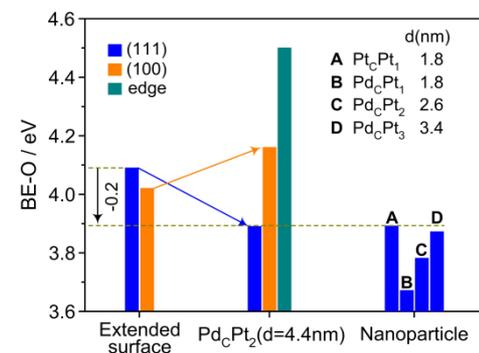
Approach – basis of the research plan -

Fuel cell test of Pt_{ML}/Pd catalyst showed a moderate loss in activity in 100,000 potential cycles

1. Prior work on Pt ML electrocatalysts.

2. Improved understanding of factors affecting ORR activity of Pt monolayer, including* :

- Particle size-induced surface contraction affects the facet-dependent oxygen binding energy
- Coordination-dependent surface atomic contraction
- Low number of low-coordination atoms is needed
- Moderately compressed (111) facet, the most conducive to ORR on NPs



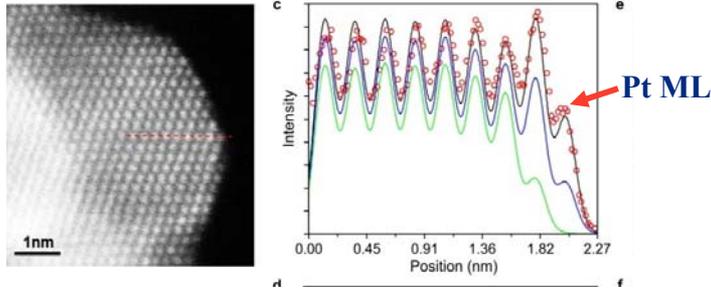
Further improvement with Pt as a contiguous monolayer on smooth surfaces of nanorods, nanowires, NPs or CNTs.

*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*

APPROACH - Methodologies to be used in accomplishing the research plan-

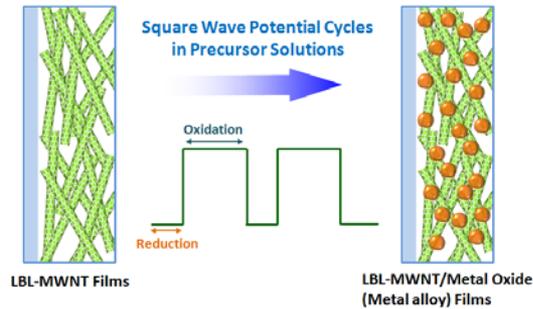
BNL

1. depositing close-packed Pt MLs.

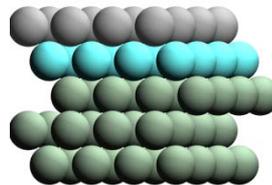


MIT

In-situ NPs Synthesis Using Square-Wave Pulse Potential



Pt₁/Ru₁/M₃



Modeling Pt ML on *ONION* layered NPs Supports with M. Mavrikakis, U. Wisconsin

JMFC

Catalization of Carbon Nanotubes

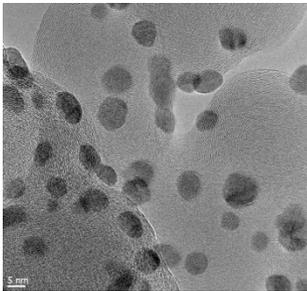
1. An extensive multi-year experience in generating Pt based fuel cell electrocatalysts using CNT, oxides, nitrides as the support will be used. MEAs fabrications and scale-up syntheses

2. Modeling Pt Wetting of Non-Carbon Supports

Three efforts are directed to one goal, helped by theory

Cu UPD-mediated deposition of Pt ML

2. removing low-coordination Pd atoms



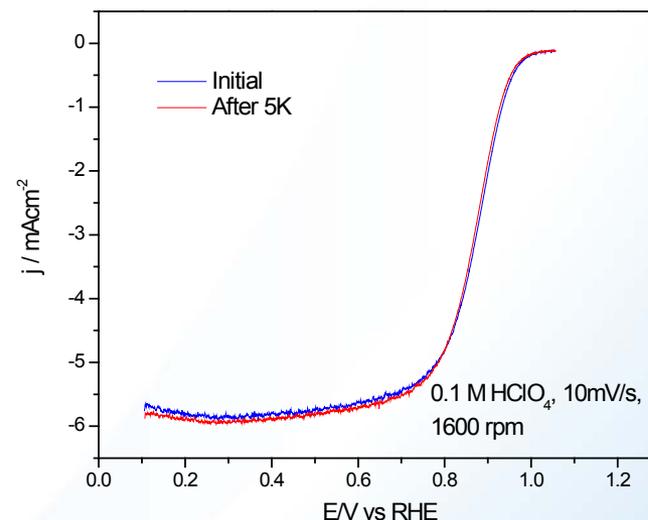
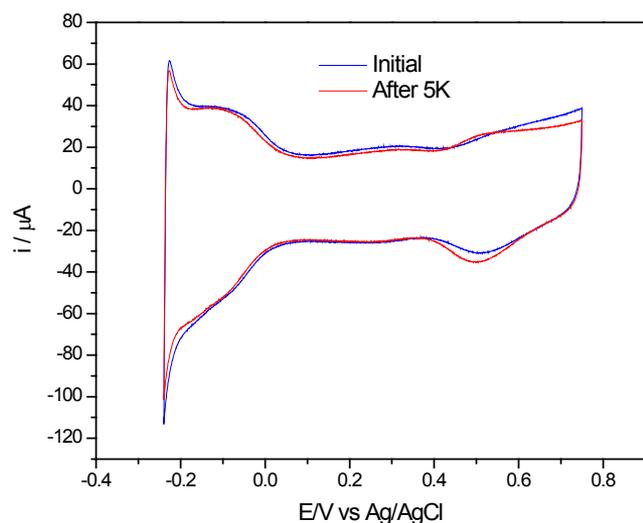
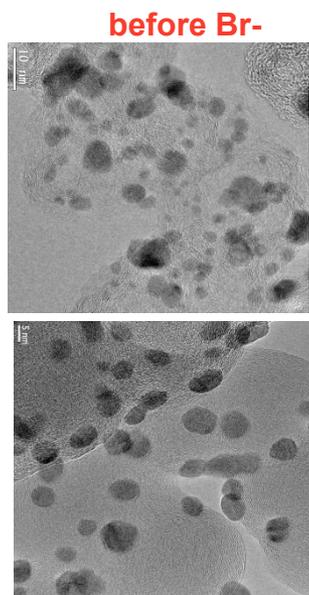
Pd/C after Br-

3. syntheses of hollow NPs of Pt and Pd;
4. cation adsorption/reduction, adatom displacement method for oxidized surfaces

Technical Accomplishments and Progress

Enhanced ORR Kinetics on Smooth Surfaces: Pt_{ML}/ Br-treated_Pd/C

Improving stability of Pd and Pt_{ML}/Pd by removing low- coordination atoms



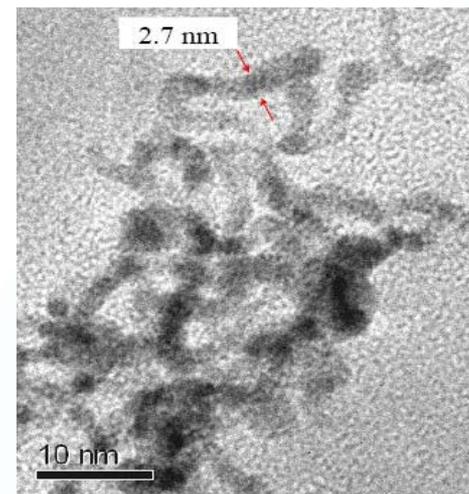
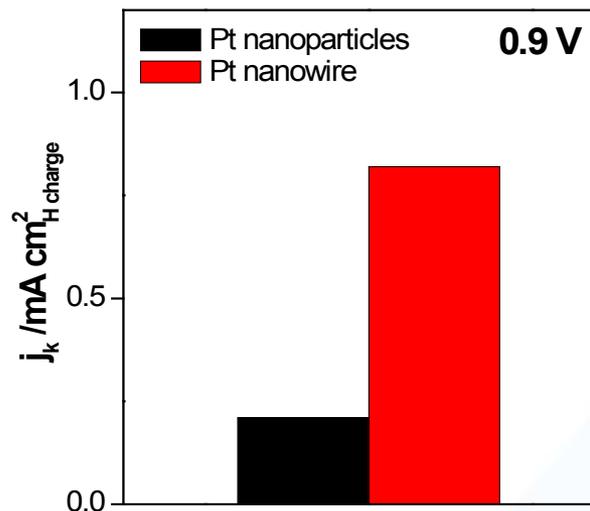
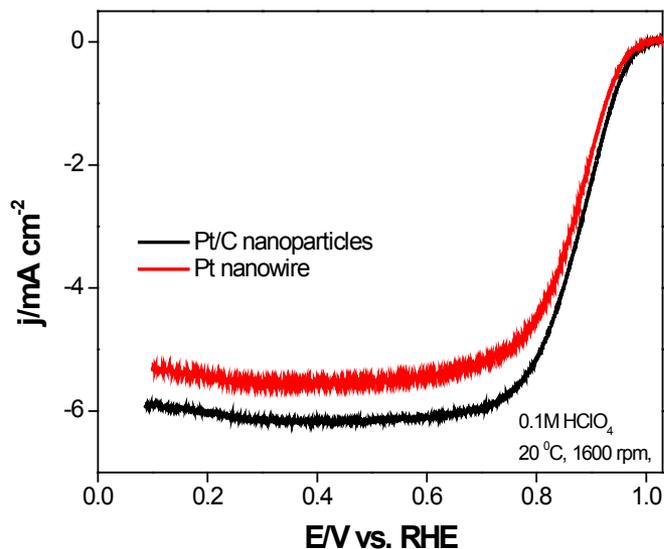
6 mV shift of $E_{1/2}$ and 5% lost in H_{des} after 5K potential cycles

Br- oxidatively chemisorbed and reductively desorbed removes low-coordinated Pd atoms

*Stability test was carried out in air applying potentials between 0.6 and 1.0 V (vs RHE).

Technical Accomplishments and Progress

Enhanced ORR Kinetics on Smooth Surfaces: Pt nanowires



Similar synthesis of Pt nanowires by JMFC; RDE studies ongoing.

Pt NPs on C: 46.4 wt.%; particle size 3.3 nm

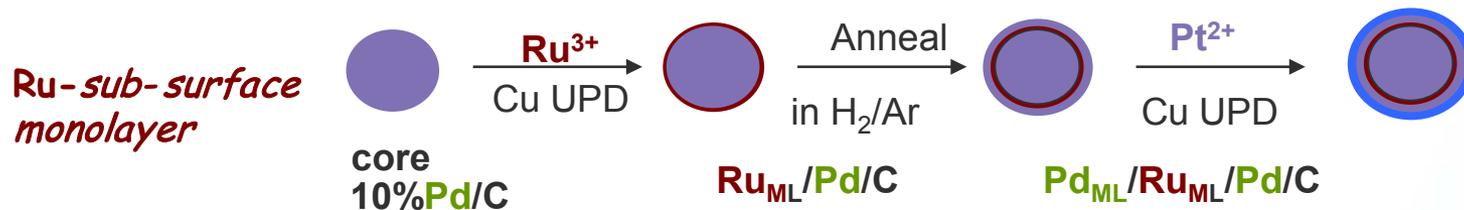
Pt nanowires: average wire diameter: = 1.65 nm

Specific activity (ECA, H UPD charge) = **0.8 mA/cm²**

with Koenigsmann and Wong

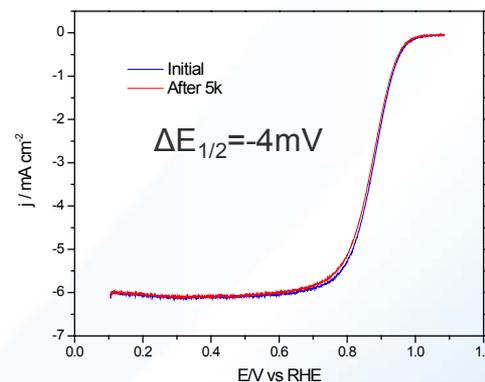
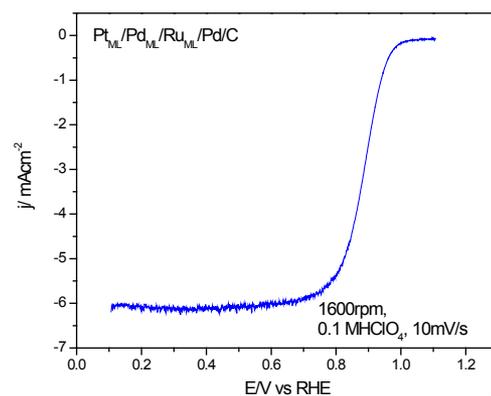
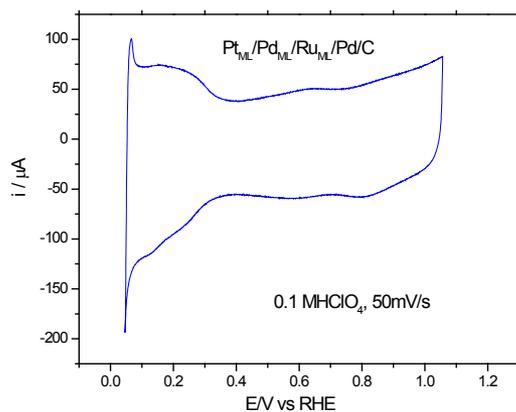
Technical Accomplishments and Progress

Sub-surface modification of cores to tune the interaction with a Pt ML



Smaller Ru \rightarrow contraction of Pd and Pt shells \rightarrow enhancement of activity and stability

$\text{Pt}_{\text{ML}}/\text{Pd}_{\text{ML}}/\text{Ru}_{\text{ML}}/\text{Pd/C}$



Very high stability,
after 5K cycles
0.6-0.9 V, 4mV lost

$E_{1/2} = 886\text{mV}$; Loading: Pd: $6.7\mu\text{g}/\text{cm}^2$; Ru: $0.38\mu\text{g}/\text{cm}^2$

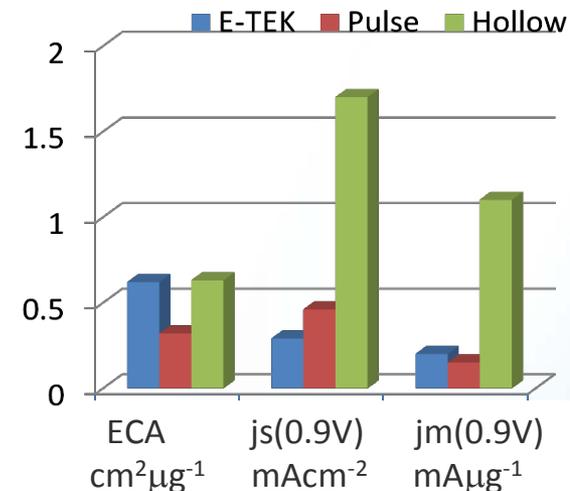
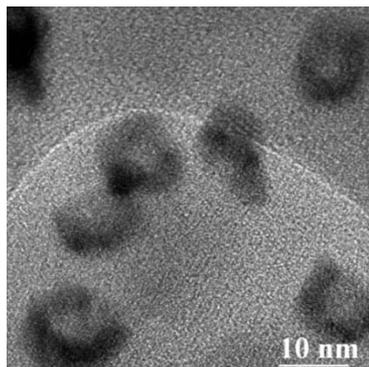
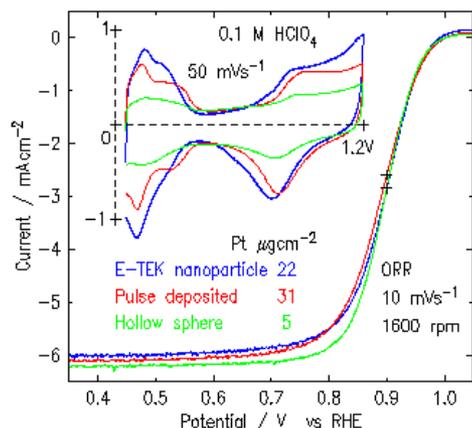
$i_m(0.9\text{V}) = 1.8\text{mA}/\mu\text{g}_{\text{Pt}}$; $i_s(0.9\text{V}) = 1.1\text{mA}/\text{cm}^2$;

$i_m(0.9\text{V}) = 0.44\text{A}/\text{mg}_{\text{PGM}}$; $i_m(0.9\text{V}) = 1.07\text{A}/\text{mg}_{\text{PGM}}$ (price adjusted)

(ICP) Pd: 4.4%; Ru: 0.25%;

Technical Accomplishments and Progress

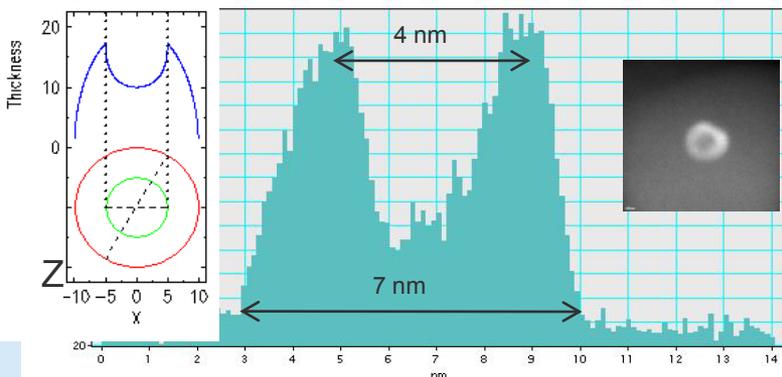
Hollow-induced lattice contraction enhances ORR activity



A loss of 33% after 3000 cycles. No changes after 10000 cycles 0.65 to 1.05 V; Six-fold enhancement in activity

Pt hollow spheres (6 nm on average) made using Ni as template have 5-fold Pt mass activity or those of solid nanoparticles

After the test, 4 – 8 nm hollow spheres with 1-2 nm Pt shell. Lattice contraction ranging 1 to 2 %. Smooth sphere have least low-coordinated sites and thus are least prone to dissolution.



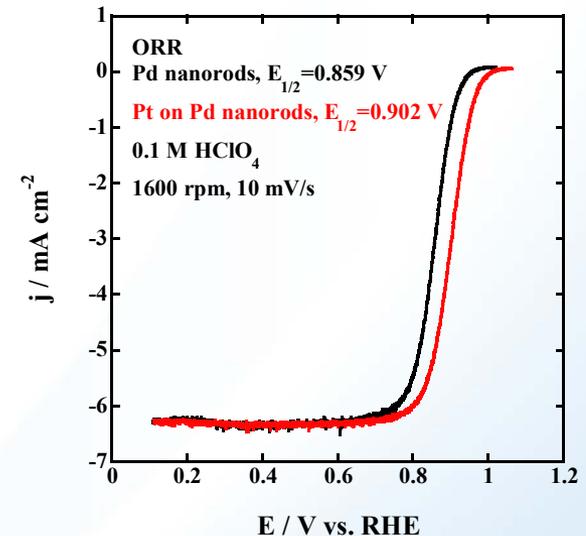
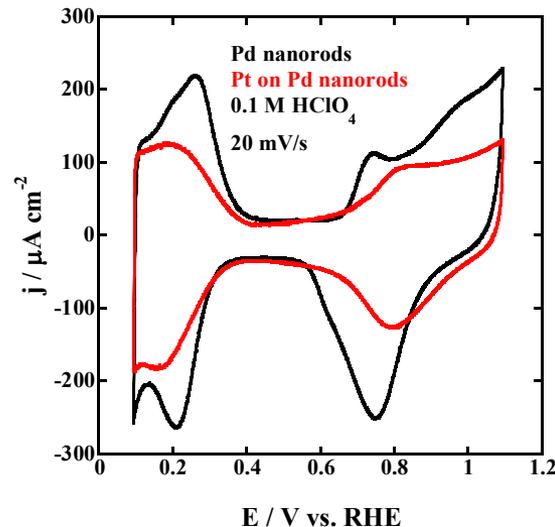
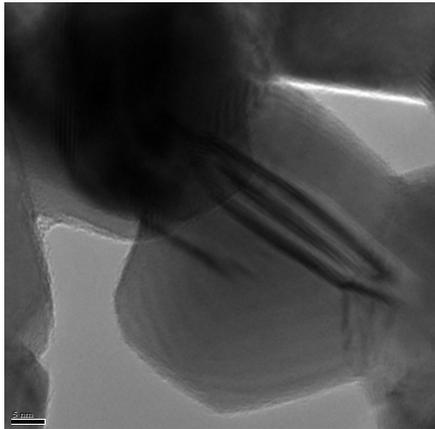
Pd hollow nanoparticles have been synthesized and activated by a Pt_{ML}. Pt mass activity is = 1.67 A /mg.

Technical Accomplishments and Progress

Pd nanorods as support for a Pt ML

Enhanced ORR Kinetics on Smooth Surfaces

Pd nanorods obtained by electrochemical deposition



Pd nanorods electrodeposited on C NPs

2 μg of Pd; 0.45 μg of Pt

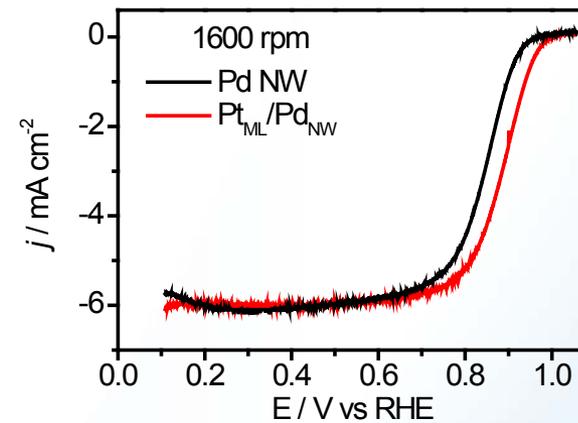
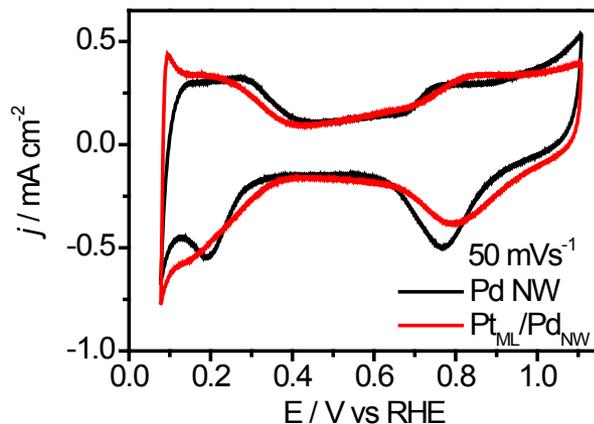
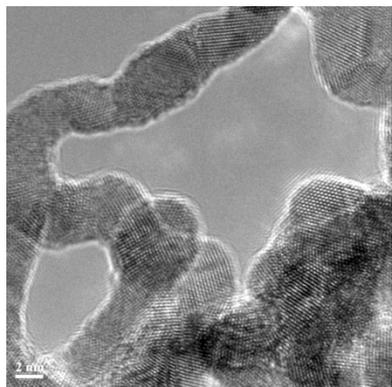
Pt mass activity = 2.3 A/mg (average of 3 samples)

Specific activity = 1.1 mA cm^{-2}

These data confirm the suitability of smooth Pd surfaces as support of a Pt ML.

Technical Accomplishments and Progress

Pd nanowires as support for a Pt ML



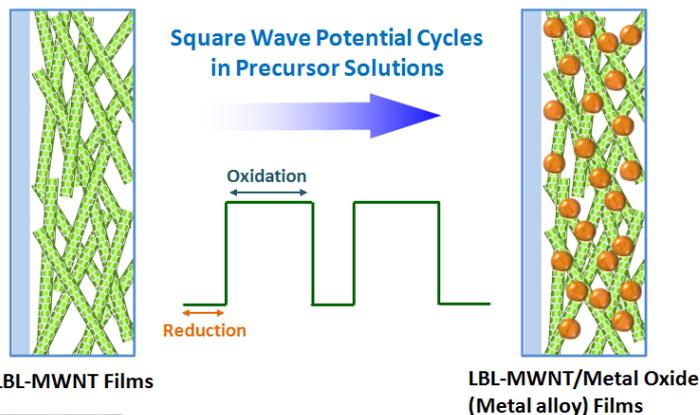
Price-adjusted PGM mass activity = **0.45 A/mg_{Pt,Pd}**

	$E_{1/2}$ (V vs RHE)	Surface Activity (A/cm ²)	Mass activity ¹ (A/mg _{Pt})	Mass activity ² (A/mg _{Pt,Pd})
Pt _{ML} /Pd _{NW} /C	885	6.41×10^{-4}	1.02	0.13
Pt/C	852	2.21×10^{-4}	0.19	0.19

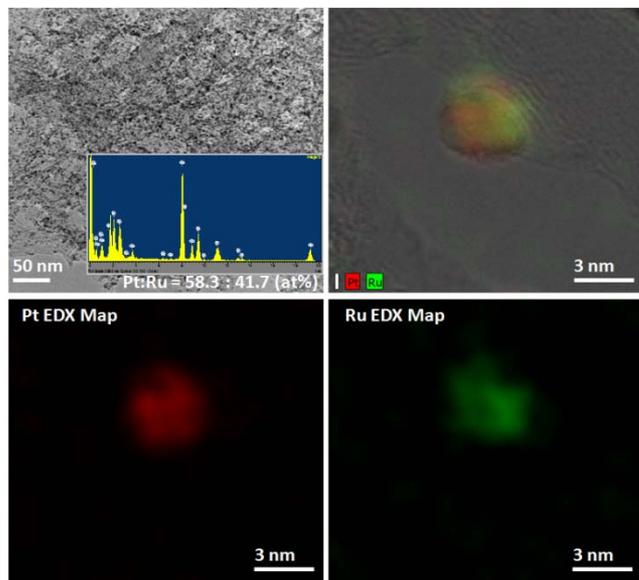
Preparation of Pd NWs. Pd(NO₃)₃, octadecylamine, and dodecyltrimethylammonium bromide dispersed in toluene NaBH₄ solution in water was added, Pd NWs, collected by centrifugation and cleaned with ethanol

Technical Accomplishments and Progress

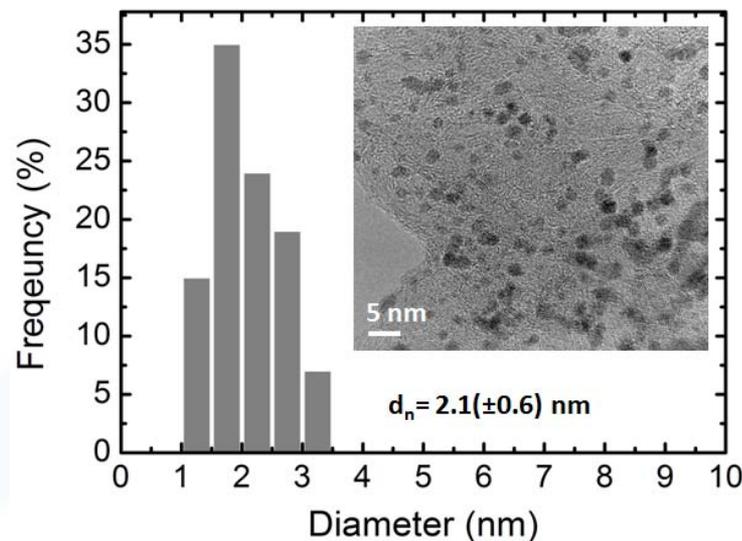
In-situ NPs Synthesis Using Square-Wave Pulse Potential



Energy Dispersive X-ray (EDX) Spectroscopy of Pt/Ru Nanoparticles



Pt/Ru NPs within LbL-MWNT Electrodes

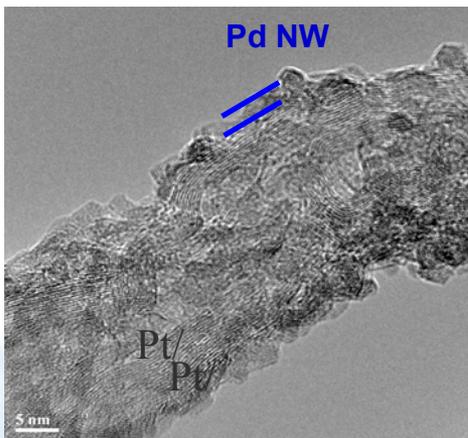
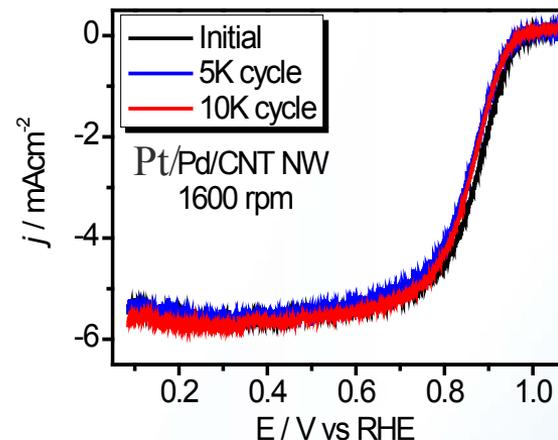
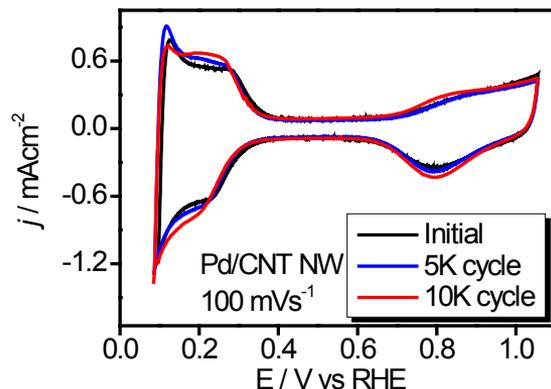
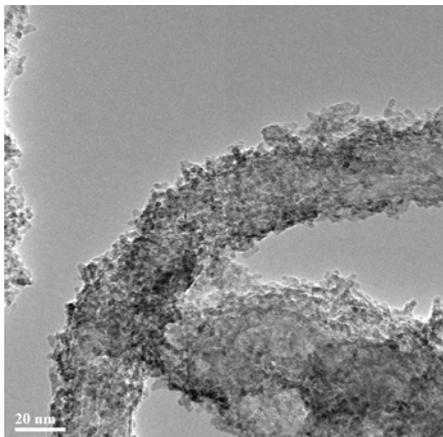


✓ Homogenous distribution of both Pt and Ru atoms throughout the particle

✓ Introduction of Size-controlled NPs into LbL MWNT electrodes

Technical Accomplishments and Progress

Metallization of CNTs



Synthesis of Pd NPs on CNTs
Pd NPs obtained by reducing Pd(NO₃)₂ with hydrogen in 0.05 M H₂SO₄ containing 0.01 wt. % Nafion®.

E.S.A, No observable loss
Pt mass activity: 0.72 mA/μg_{Pt} at 0.9V
Specific activity: 0.34 mA/cm²_{ESA}
 $E'_{1/2} = 859$ mV vs RHE

In 10K cycles small loss occurred within the first 5K

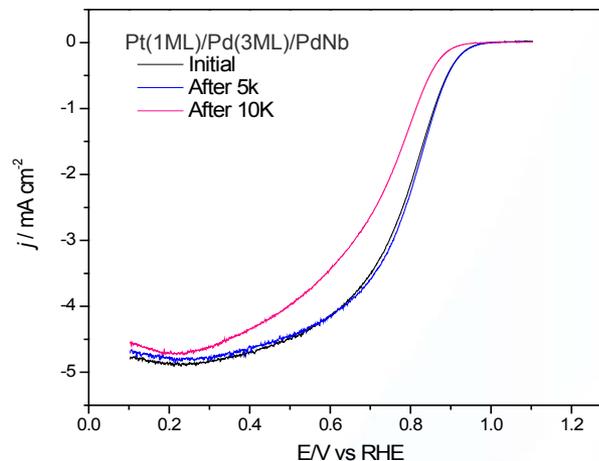
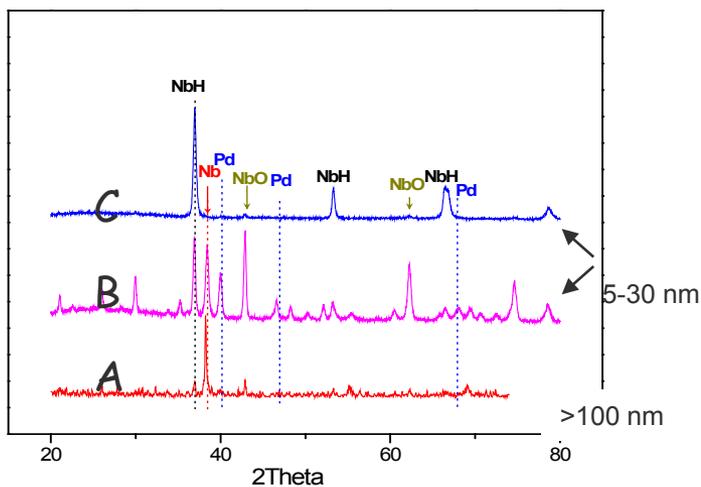
Indication for formation of Pd NWs on CNTs
By self-assembling of Pd NPs

Smooth metal deposits on CNTs are not easily obtained. Initial results are, however, encouraging considering the activity and stability of Pt/Pd/CNT

Technical Accomplishments and Progress

Refractory metal alloys as cores: Pt_{ML}/Pd_xNb

- A: Pd10Nb90 - Anneal Pd salt and Nb in H_2/Ar ;
- B: Anneal Pd salt and ball-milled-Nb in H_2/Ar ;
- C: Impregnate H_2 -annealed Nb in $PdCl_2$.



Almost no loss of activity after 5k and 20% of H_{des} lost after 10k

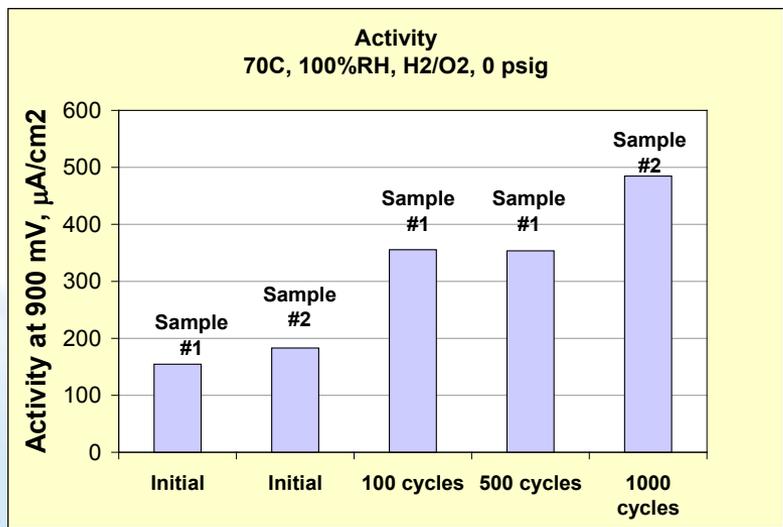
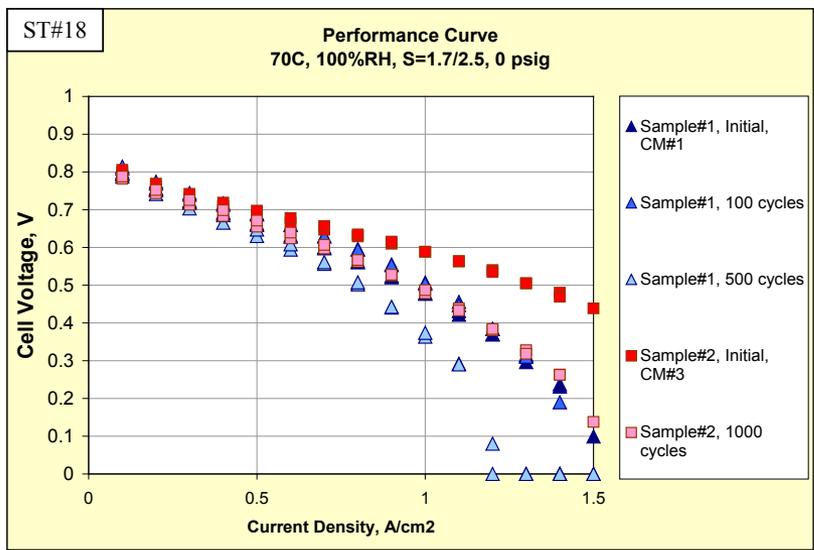
Sample	$E_{1/2}$ (mV)	$j_k(0.85V)$ (mA)	$j_k(0.9V)$ (mA)	$I_s(0.85V)$ (mA/cm ²)	$I_s(0.9V)$ (mA/cm ²)	$im(0.85V)$ (mA/ugPt)	$im(0.9V)$ (mA/ugPt)
Pt _M L/Pd(3ML)/Pd _x Nb	791	1.65	0.43	1.21	0.32	1.72	0.45

The data are encouraging; smaller W NPs are needed.

Comparable with Pt/C!

Technical Accomplishments and Progress

Stability Testing of Pt_{ML}/Pd/C Catalyst with potential cycling to 1.2V at 3M Corporation



1 cycle = 0.6 to 1.2 V to 0.6V, 20 mV/s @ 70^lC, 100% RH, H₂/N₂

~ 76% surface area loss after 1000 cycles

Specific activity increases during cycling

~185 mA/cm² to nearly ~490 mA/cm²

Both samples showed only modest performance losses after cycling

Initial testing indicates a path to improve performance and perhaps activity

Initial testing shows that performance is stable after repeatedly cycling to 1.2V in H₂/N₂.

Initial activity 1A/cm² at 0.6V. Optimization of electrode to increase the activity.

Andrew Haug, Greg Haugen, Radoslav Atanasoski
3M Corporation; Fuel Cells Division

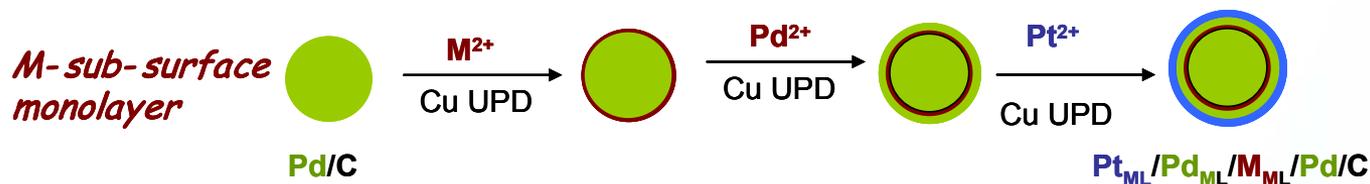
Collaborations

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, David Thompsett, Sarah Ball, Graham Hard, Co-PIs of the project
3. **UTC Power** (Industry)
Collaboration on MEAs making, stack building and testing.
4. **U. Wisconsin** (University)
Manos Mavrikakis, collaboration on theoretical calculations- long-term, extensive
5. **3M Corporation** (Industry)
Radoslav Atanasoski, Andrew Haug, Greg Haugen

Proposed Future Work

FY10

1. Fast screening of the sub-surface layers effects on the activity of a Pt MLs to select the best system, avoid annealing and answer the question whether annealing keeps the “onion” shape or the ML gets distributed uniformly into the NP.



2. Improve synthesis of Pd nanorods, nanowires, and Pd hollow NPs. (BNL, MIT, JMFC)
3. Improve metallization and catalysation of CNTs, oxides, nitrides. (JMFC, MIT, BNL)

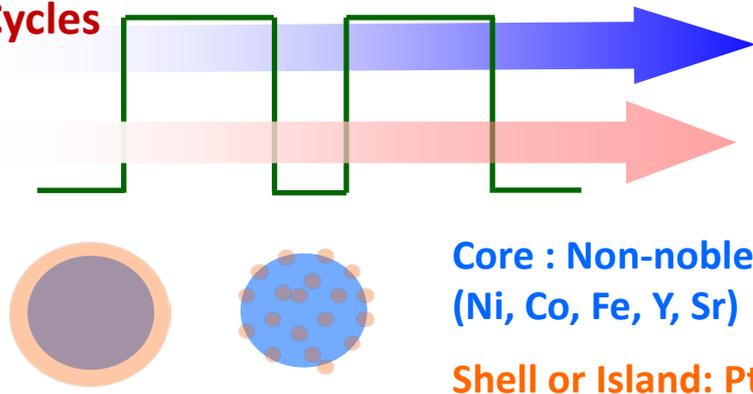
FY11

4. Pd-Nb alloy NPs; start the work on Pd-W NPs and Pd-V. (BNL, MIT)
5. Scale-up of selected catalysts up to 20 grams. (JMFC, BNL)
6. MEA fabrication and tests. Go/No go for these catalysts based on MEA tests. (JMFC, UTC)

Proposed Future Work

MIT in FY10 and FY11: Design of Highly Active Alloy NPs on MWNT Matrix

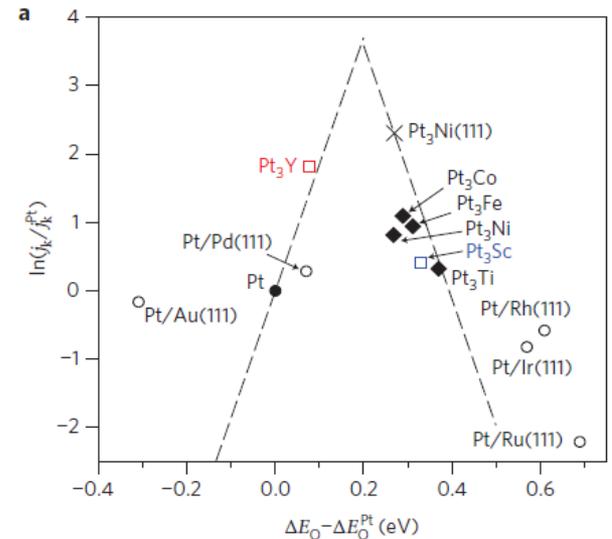
Sequential Square Wave Potential Cycles



Core : Non-noble Metal
(Ni, Co, Fe, Y, Sr)

Shell or Island: Pt

Volcano Plot for ORR activity



J. Greeley et al., Nature Chemistry, 2009

Electrodeposition in Ionic liquid to reduce non-noble metals

Ionic liquid

Aqueous Electrolyte Region



Milestones and Deliverables

Synthesis of a Pt ML on Pd-Nb alloy nanoparticles high-activity catalyst

September 2010

High coverage of Pt 2D island deposit achieved with carbon nanotubes

September 2010

Synthesis of a Pt ML on Pd nano[Pt] catalyst that meets the DOE 2010 target.

September 2010

Summary

The results obtained show:

1. Smooth surfaces, with highly-coordinated atoms, are suitable to support a Pt ML that yields very active catalysts.
2. Pd nanowires were synthesized. Their thickness needs to be reduced and removal of surfactants simplified to obtain an excellent catalyst with a Pt ML. (Synthesis of Pt NWs is easier)
3. Sub-surface ML modification of cores is very promising; it opens up numerous possibilities for design of catalysts.
4. Hollow Pd and Pt nanoparticles are very attractive for further studies.
5. Initial difficulties with refractory metal alloys and metallization of CNTs are being resolved; the results are encouraging.