

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

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# Overview

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## Timeline

Project start date: July 2009

Project end date: September 2013

Percent complete: Approx. 80%

## Budget in \$K

Total project funding: 3,594

Funding in FY12: 975

Planned Funding in FY 13: 625

## Technology transfer

Four patents on Pt ML electrocatalysts

licensed to N.E. ChemCat Co.

CRADA with Toyota M.C.

## Barriers

### Performance:

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

### Cost:

PGM loading;  $\leq 0.3 \text{ mg PGM /cm}^2$

### Durability:

< 40% loss in activity under potential cycling

## Partners

Massachusetts Institute of Technology (MIT)

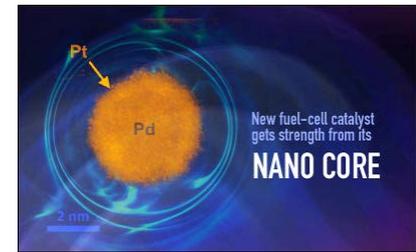
Johnson Matthey Fuel Cells (JMFC)

## Collaborations

UTC Power, Toyota M. C., U. Wisconsin, U.

Stony Brook, 3M Corporation, GM Corporation, CFN-BNL

# Relevance



## Objectives:

### General:

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.

### Specific (recent):

3. Scale-up of syntheses to produce multi-gram quantities of three catalysts:
  - 3.1 Pt ML on Pd hollow NPs using a microemulsion or similar method
  - 3.2 Pt ML on ultra thin Pd alloy nanowires
  - 3.3 Pt ML on WNi and Pd<sub>9</sub>Au<sub>1</sub> alloys obtained by electrodeposition
    - 3.3.1 Delivering a 450 cm<sup>2</sup> MEA for testing at UTC.
    - 3.3.2 Achieving a 100% utilization of Pt

# Approach

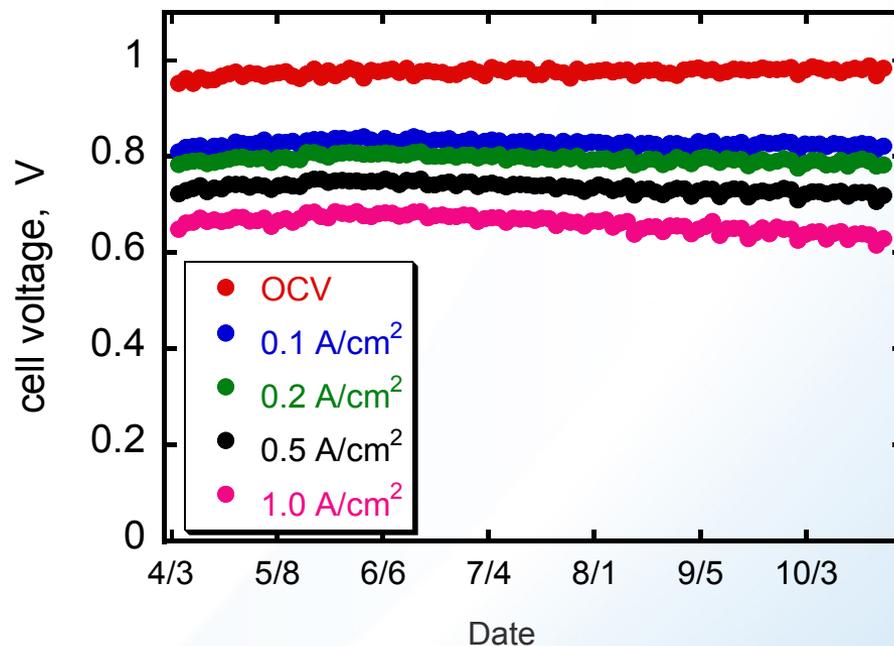
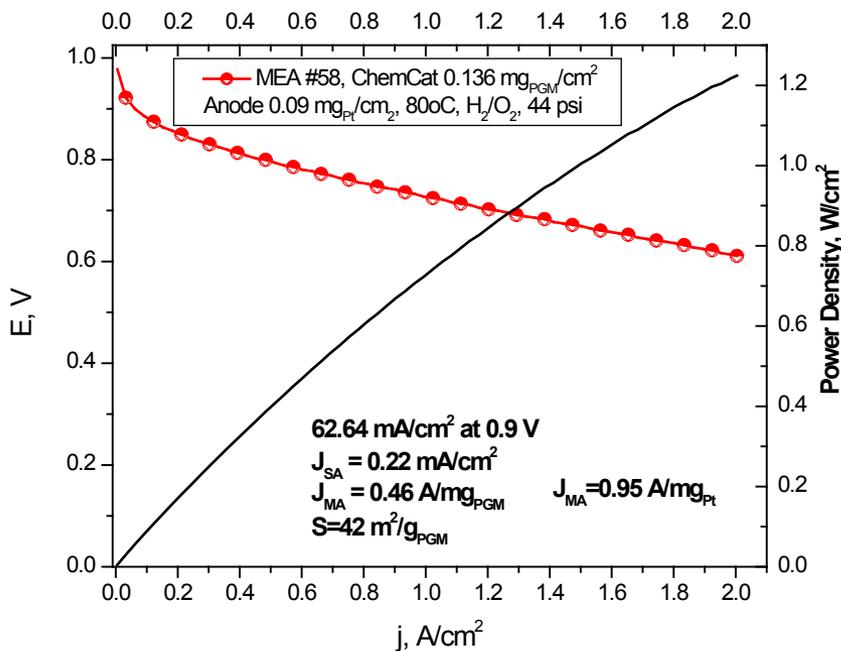
## Research Strategies

1. Improving the Pt monolayer properties using core-shell interaction:
  - 1.1. Reducing oxygen binding energy by:
    - Compression of Pt ML atoms induced by core, hollow core, subsurface ML
    - Electronic effects of cores
    - Decreasing the number of low-coordination atoms
    - Increasing stability of cores with specific structure, composition and shape
2. Electrodeposition of cores to optimize their shapes and composition and maximize catalyst utilization
  - Metal and alloy- nanoparticles, nanorods, nanowires
3. Refractory metal alloys used as cores to reduce PGM content
  - Co-deposition of W and Ni cores

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*

L. Yang, M. Vukmirovic, D. Su, K. Sasaki, J. A. Herron, M. Mavrikakis, S. Liao, R.R. Adzic, *J. Phys. Chem.*, 2013, 117, 1748-1753.

## Behavior of commercial Pt<sub>ML</sub>/Pd/C catalyst (N.E. ChemCat) as a baseline



at 0.9 V

PGM Mass Activity: 0.46 A/mg;

Pt Mass Activity: 0.95 A/mg<sub>Pt</sub>

Cathode loading PGM 136 μg/cm<sup>2</sup>

No change in performance over 6 months at  
OCP and 4 current densities  
0.1 mg/cm<sup>2</sup> PGM (Data, Hiroshi Igarashi, NECC)

# Technical Accomplishments and Progress

## Synthesis of hollow Pd nanoparticles and Pt<sub>ML</sub>/Pd<sub>hollow</sub>/C catalyst

Three different syntheses of hollow Pd NPs developed, all scalable to multi-gram quantities

### Pt<sub>m</sub>@PdM/C

Synthesis in microemulsion; 60 mg catalyst/200 ml sol

Particle size: 5.5-6 nm

$J_{0.9V} = -1.59 \text{ mAcm}^{-2}$ ;  $E_{1/2} = 0.867 \text{ V}$

### Pt<sub>m</sub>@PdH/C

Synthesis in water with citrate:

60 mg of catalyst/300 ml

Particle size: 22 nm

$J_{0.9V} = -1.90 \text{ mAcm}^{-2}$ ;  $E_{1/2} = 0.874 \text{ V}$

### Pt<sub>m</sub>@PdCu/C

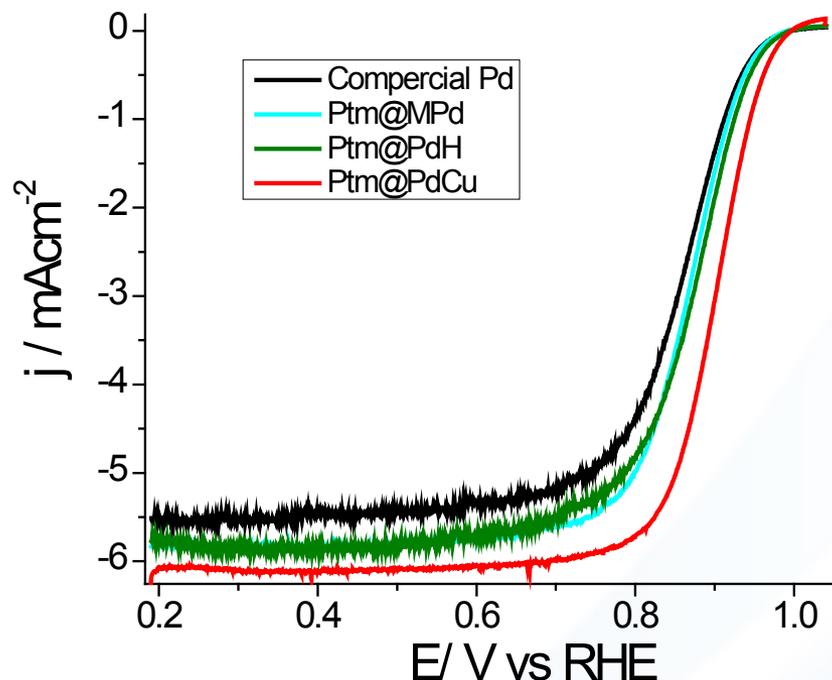
Synthesis in water; no surfactant

150 mg of catalyst/100 ml

Particle size: 3-5 nm

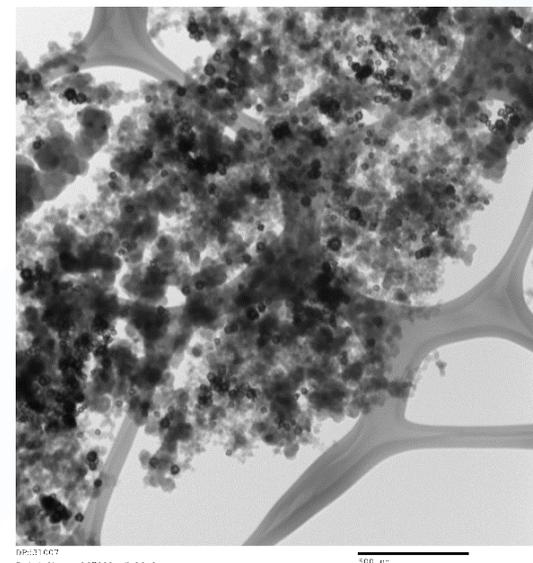
$J_{0.9V} = -3.04 \text{ mAcm}^{-2}$ ;  $E_{1/2} = 0.90 \text{ V}$

RDE for Pt<sub>ML</sub> on three hollow Pd and solid Pd NPs



Composition of nanoparticles established using ICP

TEM of Pd hollow NPs from water-citrate synthesis

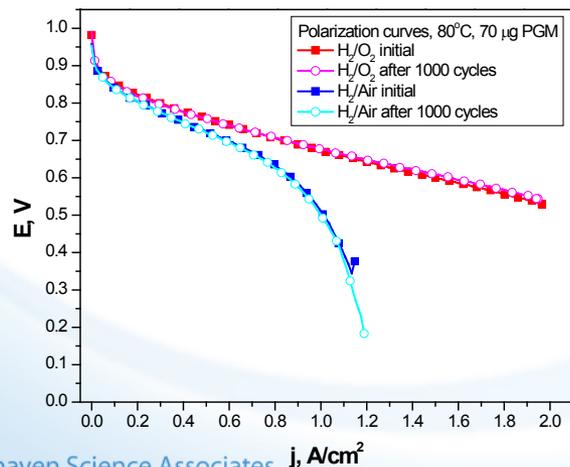
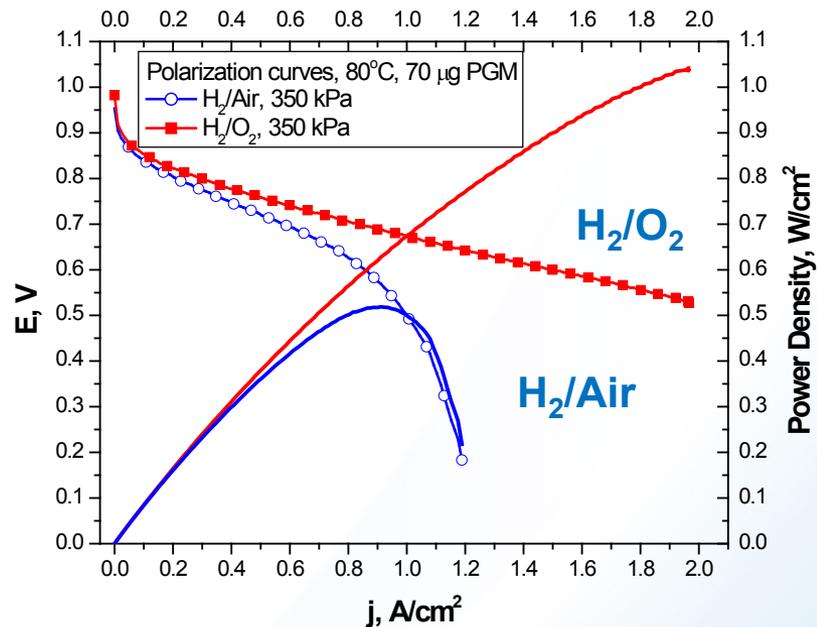
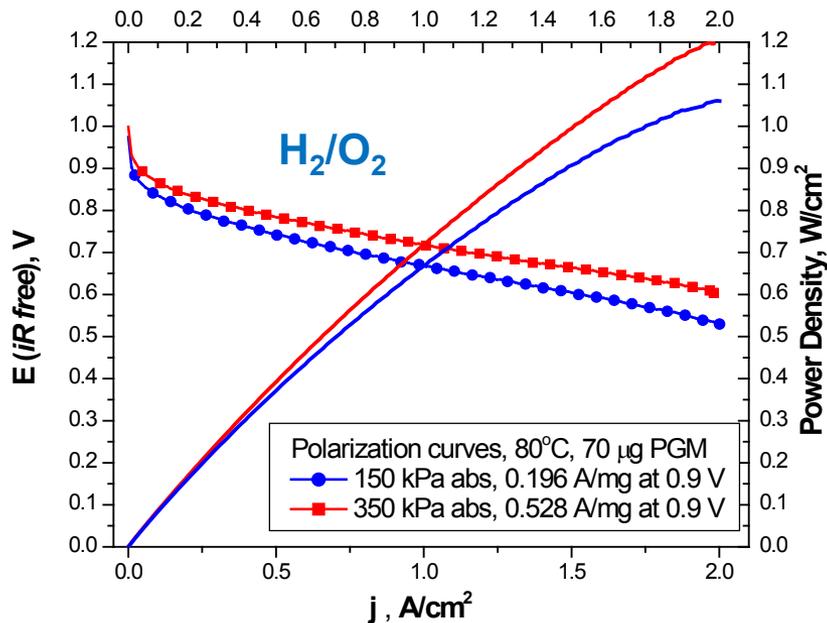


Pt (%wt)	Pd (%wt)	Cu (%wt)
9.67	18.44	1.47

# Technical Accomplishments and Progress

## MEA test of Pt<sub>ML</sub>/Pd<sub>hollow</sub>/C nanoparticles

Cathode PGM loading: 70  $\mu\text{g}/\text{cm}^2$ ; Anode: 50  $\mu\text{g}/\text{cm}^2$  Pt ; Electrode area: 5  $\text{cm}^2$



High activity for H<sub>2</sub>/O<sub>2</sub> operation. Mass transport needs improvement for H<sub>2</sub>/AIR operation.

No change in polarization curves with O<sub>2</sub> or AIR in 1000 potential cycles stability test.

PGM Mass activity: 0.53 A/mg at 0.9V

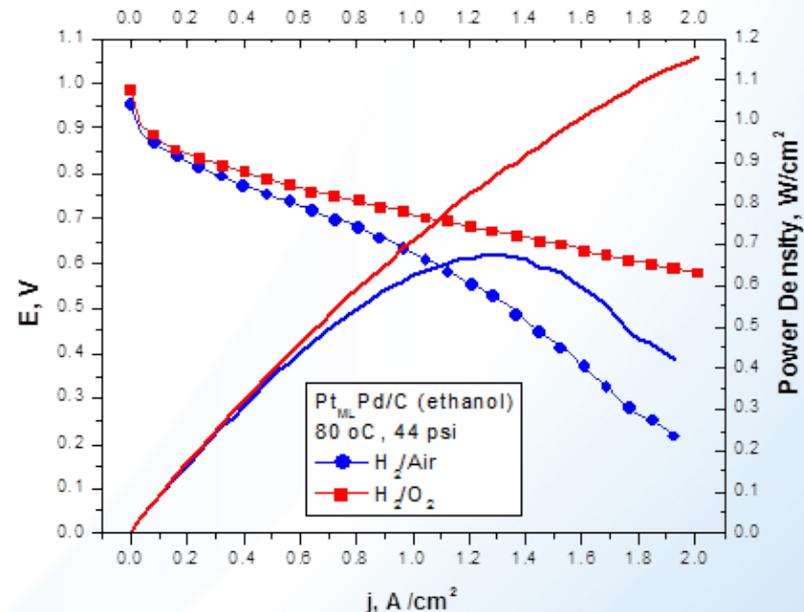
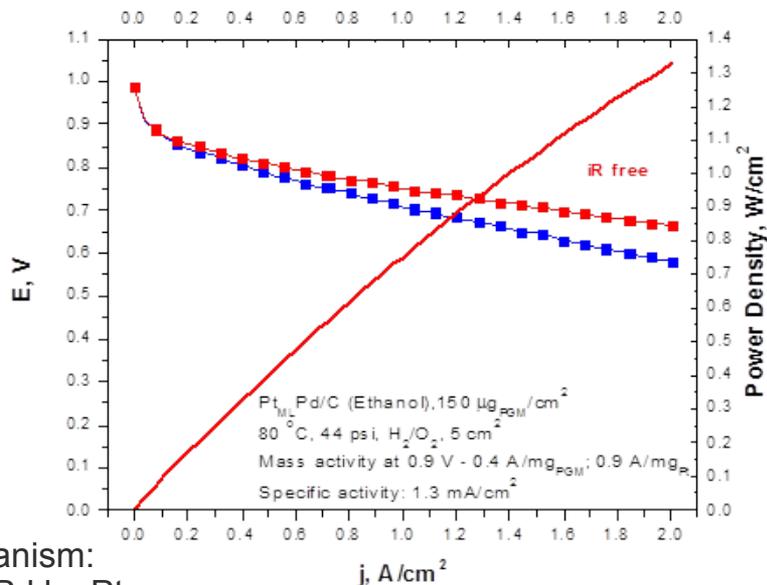
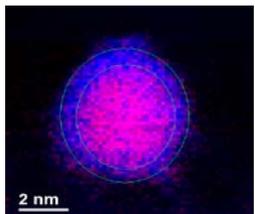
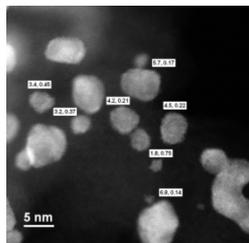
# Technical Accomplishments and Progress

## MEA tests of Pt<sub>ML</sub>/Pd/C catalyst synthesized in ethanol

Cathode: Pt<sub>ML</sub>Pd/C: 150 μg<sub>PGM</sub>/cm<sup>2</sup> (70 μg<sub>Pt</sub>/cm<sup>2</sup>);

Anode: Pt/C: 90 μg<sub>Pt</sub>/cm<sup>2</sup>

Nafion® XL100; Catalysts sprayed on 5 cm<sup>2</sup> GDL (Sigracet® 25BC)



Deposition mechanism:  
Displacement of Pd by Pt  
and reduction of Pd<sup>2+</sup> by  
ethanol at elevated  
temperatures.

HAADF image (blue) and  
Pd-EELS signal (red)  
overlaid for a  
representative Pd@Pt  
core-shell nanoparticle

**PGM activity : 0.4 A/mg<sub>PGM</sub>**

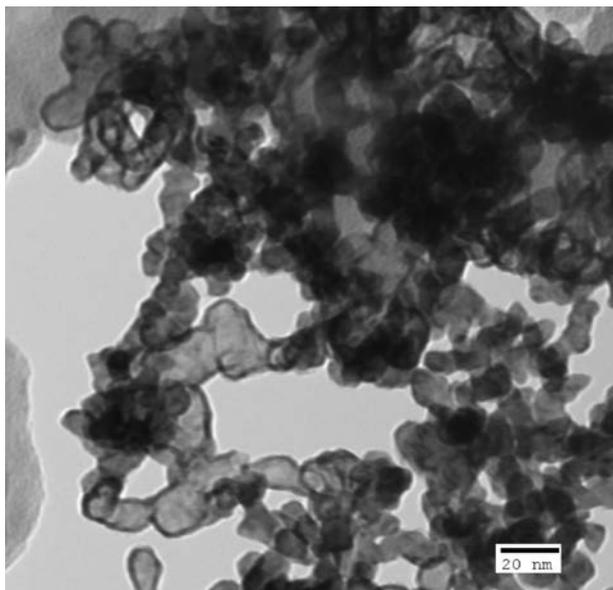
**Pt mass activity: 0.9 A/mg<sub>Pt</sub>**

**Specific activity: 1.3 mA/cm<sup>2</sup>**

**No change in polarization curves with  
O<sub>2</sub> or AIR in 2000 potential cycles.**

## New scale – up syntheses of Pt hollow nanoparticles - maximizing Pt hollow

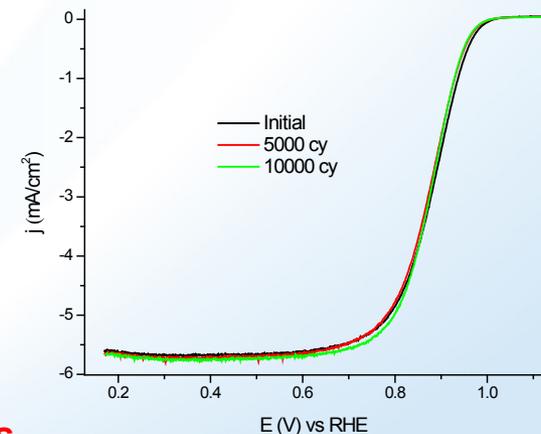
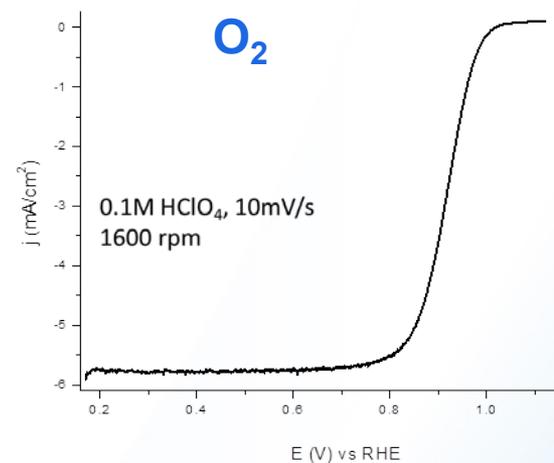
Hollow Pt prepared with Cu as a sacrificial metal



**MA = 0.32 A/mg**  
**SA = 2.06 mA/cm<sup>2</sup>**

**The procedure allows for maximizing Pt hollow, i.e. making the thinnest Pt shell. Less than 30 μg<sub>Pt</sub>/cm<sup>2</sup>**

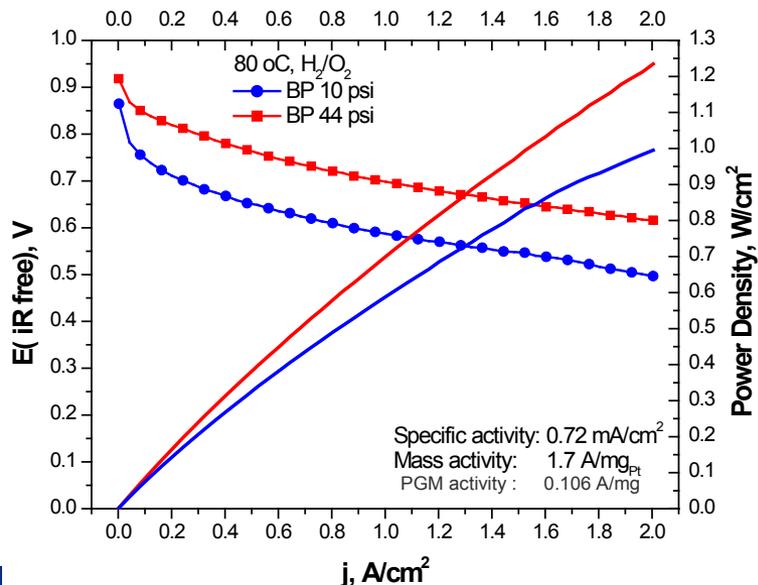
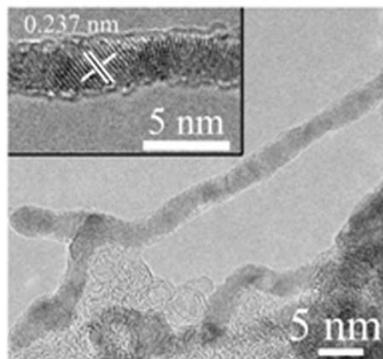
**The stability of this type of Pt hollow electrocatalyst is high; no change can be observed after 10,000 potential cycles.**



# Technical Accomplishments and Progress

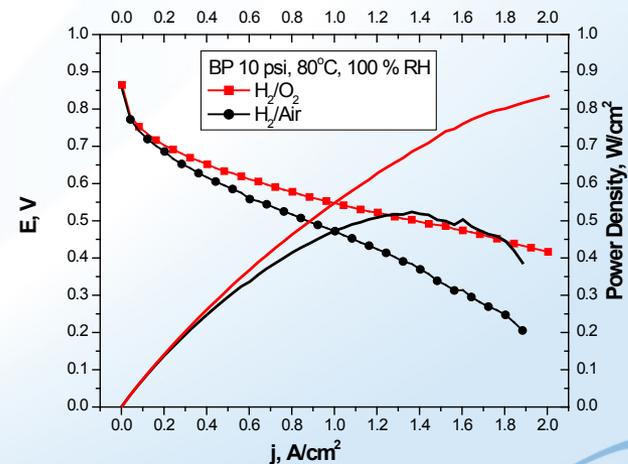
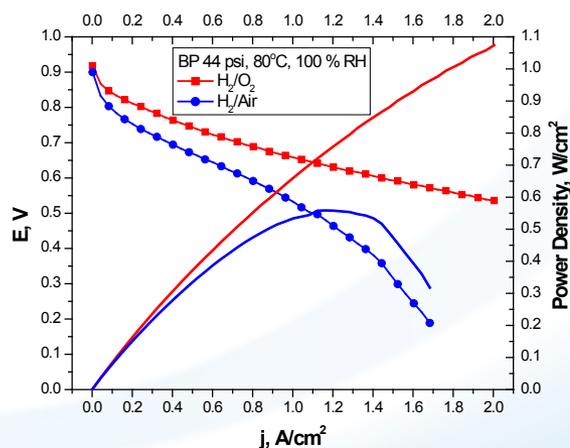
## MEA test of Pt<sub>ML</sub> on ultrathin bimetallic PdAu nanowires

Nanowires Pt<sub>ML</sub>/Pd



**Pt mass activity: 1.7 A/mg<sub>Pt</sub>**  
**Specific activity: 0.72 mA/cm<sup>2</sup>**  
**PGM activity: 0.106 A/mg**

Pd and Au precursors are combined with octadecylamine and a phase transfer catalyst catalyst dodecyltrimethyl ammonium bromide (DTAB) is used to allow for co-solubilization of NaBH<sub>4</sub> into both the aqueous and organic phases.



## Electrodeposition of cores

### Further improvement of Pt<sub>ML</sub> electrocatalysts

- ❑ Alloy cores and cores obtained by co-deposition of refractory and alloying metal, e.g. W-Ni
- ❑ Scale-up in electrodeposition at electrodes from 5 and 25 to 450 cm<sup>2</sup>
- ❑ 100% utilization of Pt in Pt<sub>ML</sub> electrodeposited catalysts

### Total utilization of Pt in MEA

Standard catalysts

Pt/C 4-5 nm = **15-20%**

Pt ML standard MEA prep

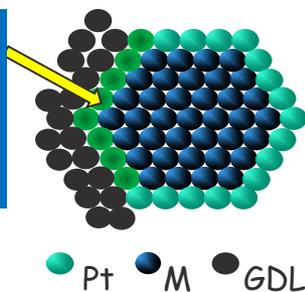
Pt<sub>ML</sub>/Pd/C 4-5 nm = **50%**

Pt ML on electrodeposited core

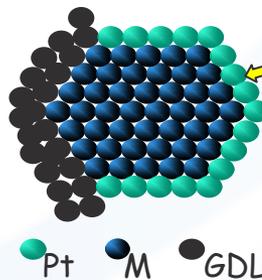
Pt<sub>ML</sub>/Pd<sub>electrodeposited</sub>/C = **100%**

## 100% utilization of Pt

Avoiding loss of Pt atoms in contact with carbon that are not accessible to protons



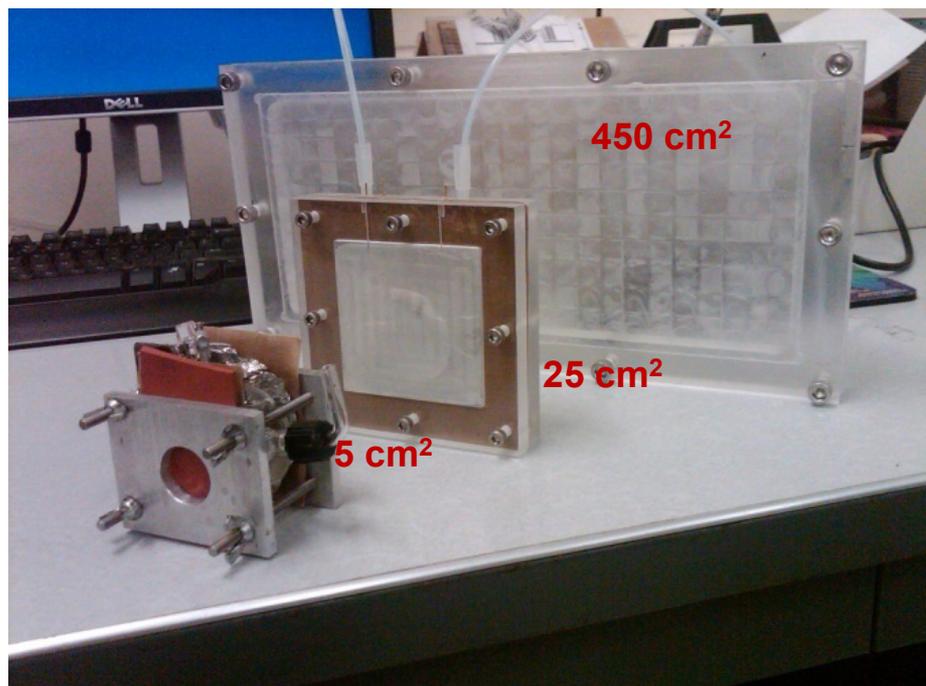
All Pt atoms are accessible for electrons and protons



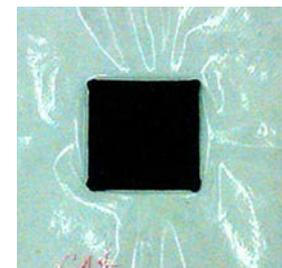
# Technical Accomplishments and Progress

## Scale-up in electrodeposition of catalysts directly on GDLs

Electrochemical cells for processing of electrodes with area of 5, 25 and 450 cm<sup>2</sup>



Potential pulse deposition protocol tailored to optimize the deposition process for GDL



5 cm<sup>2</sup>



25 cm<sup>2</sup>



450 cm<sup>2</sup>

Advantages of electrodeposition:

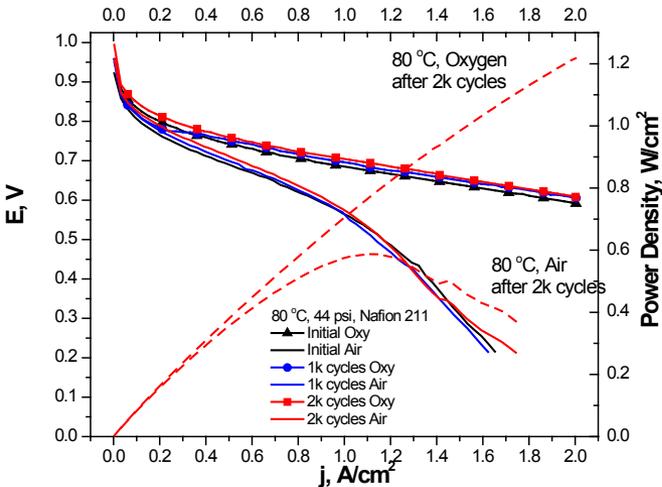
- All particles accessible to electrons and protons
- Short production time per MEA
- “Green” properties
- No free nanoparticle generation
- No ink preparation and placing on electrode

# Technical Accomplishments and Progress

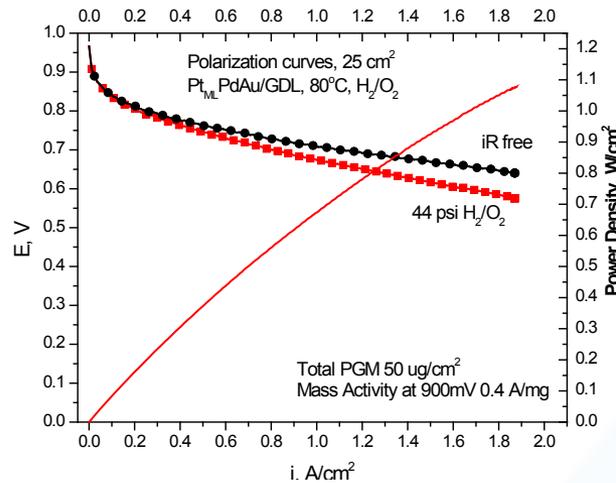
## MEA test of Pt<sub>ML</sub>/Pd<sub>9</sub>Au<sub>1</sub>/GDL at 80°C and 60°C

### Activities as a function of the electrode size

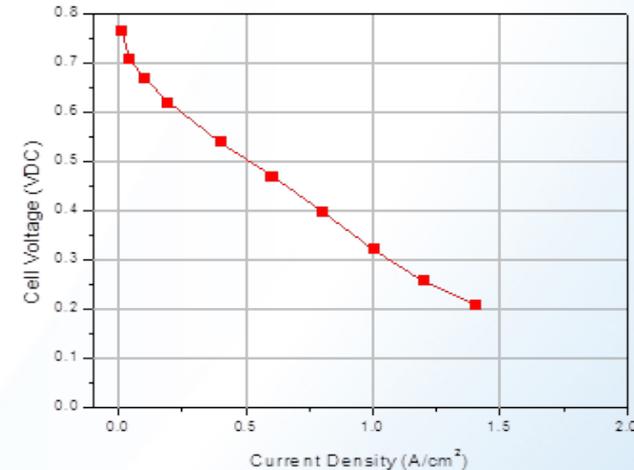
5 cm<sup>2</sup>



25 cm<sup>2</sup>



450 cm<sup>2</sup>



After 2000 potential cycles, the activity increased. PGM ~ 70 µg/cm<sup>2</sup>

MA<sub>PGM</sub> = 0.4 A/mg<sub>PGM</sub>  
PGM = 50 µg/cm<sup>2</sup>

Similar activity for 5 and 25 cm<sup>2</sup> electrodes. Lower activity for 450 cm<sup>2</sup> electrode is caused by the ambient pressure applied and low OCP indicating inadequate state of the surface. Both can be corrected.

Electrode-BNL, ; MEA, measurements – UTC Power

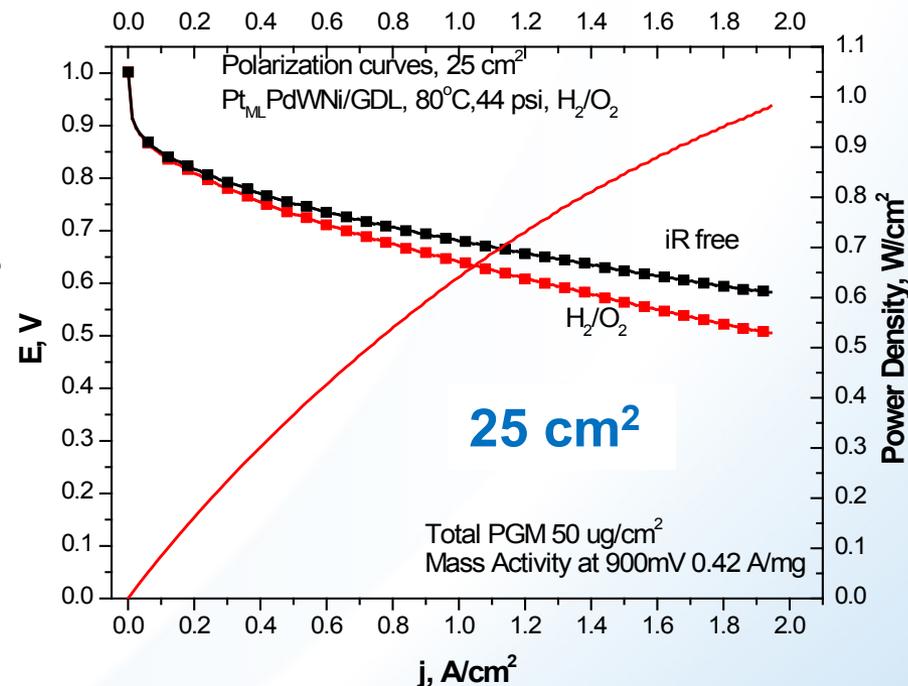
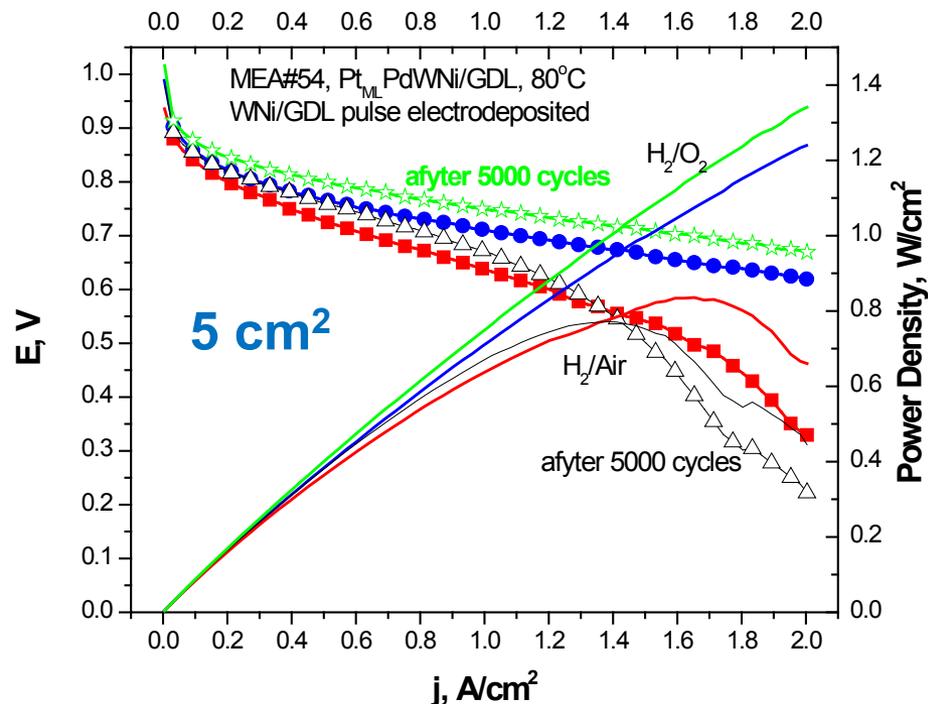
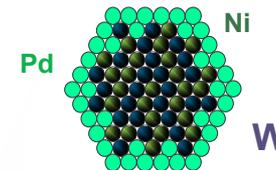
	SA, mA/cm <sup>2</sup>	Pt MA, A/mg <sub>Pt</sub>	PGM activity, A/mg <sub>PGM</sub>
Pt <sub>ML</sub> PdAu/GDL 5 cm <sup>2</sup> (at 0.9V)	0.4	1.2	0.5
Pt <sub>ML</sub> PdAu/GDL 25 cm <sup>2</sup> (at 0.9V)	0.2	1.1	0.4
Pt <sub>ML</sub> PdAu/GDL 450 cm <sup>2</sup> (at 0.75V)	-	1	0.4

# Technical Accomplishments and Progress

## Co-deposition of W – Ni as a core of Pt<sub>ML</sub>/Pd/WNi/GDL – MEA test

Co-deposition of W<sub>0.5</sub>Ni<sub>0.5</sub> alloys on GDL  
small nanoparticles with composite  
(amorphous-nanocrystalline) structure

Model of NiW core with a  
partially displaced Ni by Pd



MEA 25 cm<sup>2</sup> PGM: 50 µg/cm<sup>2</sup> MA<sub>Pt</sub> = 1.1 A/mg ; MA<sub>PGM</sub> = 0.42 A/mg

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

# Technical Accomplishments and Progress

## Comparison of MEA activities of the catalysts from scale-up syntheses

	Specific activity, mA/cm <sup>2</sup> (at 0.9V)	Pt mass activity, A/mg <sub>Pt</sub> (at 0.9V)	PGM mass activity, A/mg <sub>PGM</sub> (at 0.9V)
Pt <sub>ML</sub> PdAu 5 cm <sup>2</sup>	0.4	1.2	0.5
Pt <sub>ML</sub> Pd <sub>hollow</sub> 5 cm <sup>2</sup>	1.4	1.2	0.5
Pt <sub>ML</sub> Pd <sub>nanowires</sub> 5 cm <sup>2</sup>	0.7	1.7	0.1
Pt <sub>ML</sub> Pd <sub>nanowires</sub> 5 cm <sup>2</sup> , electrodeposition	0.2	1.2	0.5
Pt <sub>ML</sub> PdWNI 5 cm <sup>2</sup>	0.3	1.3	0.5
Pt <sub>ML</sub> /Pd Ethanol medium	1.3	0.9	0.4
Pt/C Commercial	0.15-0.2	0.1-0.12	0.1-0.12

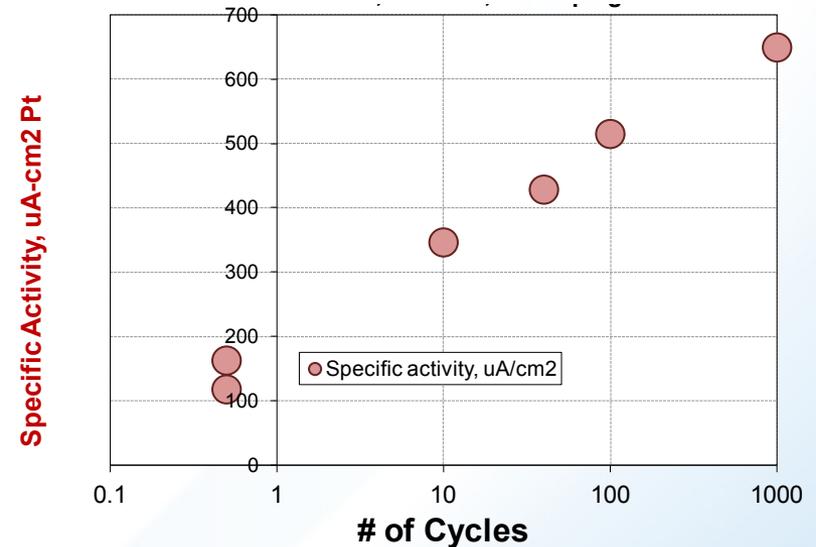
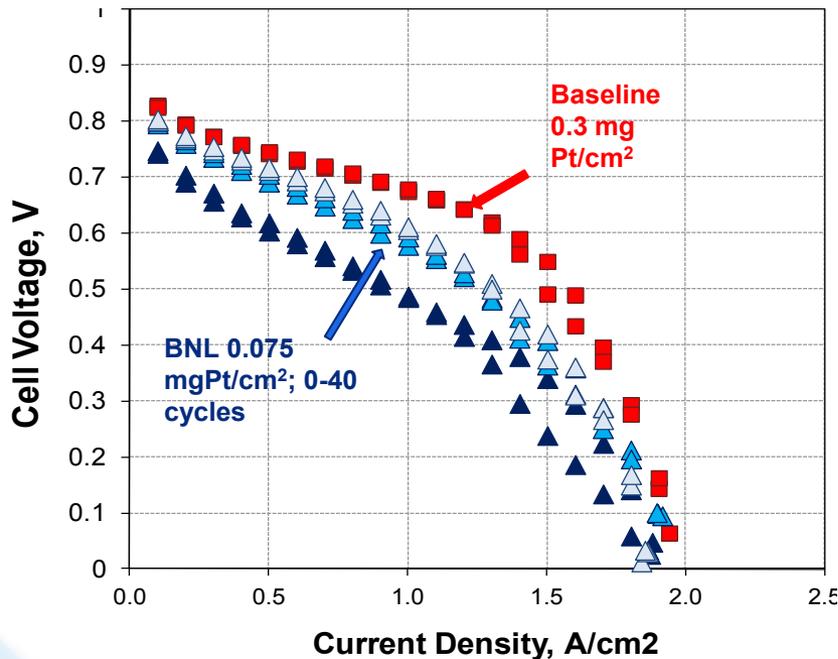
All above Pt<sub>ML</sub> catalysts have the PGM activity 3-5 times higher than commercial catalysts, while their Pt mass activity is one order of magnitude higher. The only exception is lower PGM activity of Pt<sub>ML</sub>/Pd NW caused by the mass of Pd wire.

# Technical Accomplishments and Progress

## New tests of Pt<sub>ML</sub>/Pd/C at 3M

Potential cycling 0.6 to 1.2V, 20 mV/s; 70C, 100% RH  
New ink formulati...  
Electrode size 50cm<sup>2</sup>  
Loadings from 0.06 to 0.10 mg Pt/cm<sup>2</sup>

Significant surface area loss with cycling, slower for baseline. Significant performance gains after 10 cycles



MA doubles; SA 3-4X improvement  
Baselines = 0.15 A/mg Pt; = 150  $\mu$ A/cm<sup>2</sup>  
Core shell reaches 650  $\mu$ A/cm<sup>2</sup>  
Self-healing mechanism supported by these data.

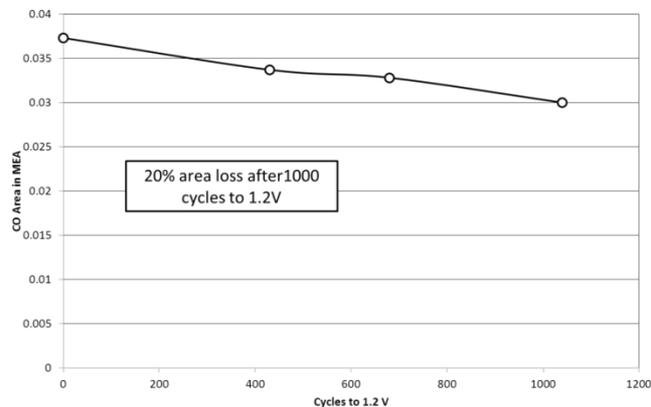
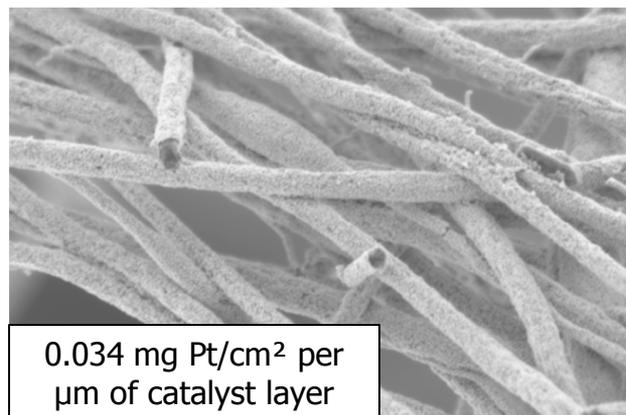
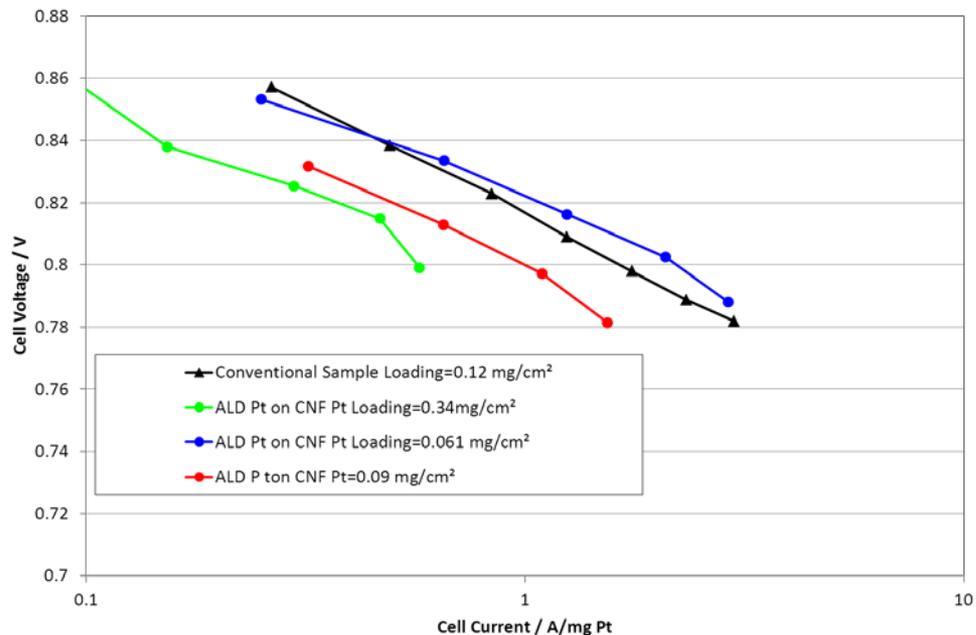
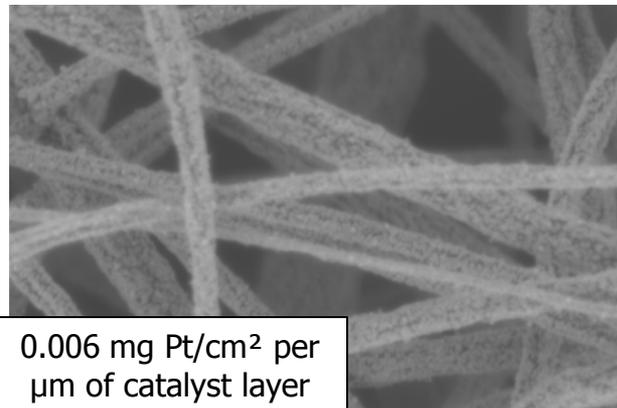
### 3M recommendations / conclusions

Mass transport region looks very good; High current capability at low loadings.  
Add Au to slow or stop metal dissolution  
The 3M carbon might improve mass and specific activity  
Continue testing; making CCMs

# Thin Film Pt on Fibrous Supports

Atomic Layer Deposition (ALD) to create continuous Pt thin films on a range of nano-fibrous supports  
Preparation and scale-up of electro-spun carbonisable and oxide fibrous supports

Investigation of materials for interface layers that help Pt 'wetting' of the fibrous substrates.



Further work:  
Reduce layer porosity.  
Improve film-formation of Pt during deposition.  
After oxygen, develop layer structure for air.

# 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**  
Collaboration on MEA making, stack building and testing. This collaboration ended in Feb. 2013 due to the organizational changes in the company.

## Technology Transfer

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

**Pt<sub>ML</sub>/Pd/C catalyst is available from NE ChemCat Co.**

## Other Collaborations

6. **Toyota Motor Company (Industry) 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**, DFT calculations; **Eli Sutter and Yimei Zhu**, TEM, STEM
9. **3M Corporation (Industry) Radoslav Atanasoski, Andrew Haug, Daniel Peppin**
10. **GM (Industry) Anu Kongkanand**

# Proposed Future Work

## FY13

1. Optimize the synthesis of the Pt<sub>ML</sub>/Pd<sub>hollow</sub>/C catalyst and MEA fabrication and tests (BNL, JMFC).
2. Optimize electrodeposition of the Pt<sub>ML</sub>/Pd/WNi catalyst, fabrication of 450 cm<sup>2</sup> electrodes and tests of 25 cm<sup>2</sup> segments of this electrode (BNL).
3. Optimize the synthesis of Pt<sub>ML</sub>/Pd/C in ethanol and MEA tests (BNL and 3M).
4. For stack testing the agreement with GM is proposed. GM is conducting the tests of Pt<sub>ML</sub>/Pd/WNi catalyst.

## FY 14

1. Syntheses of hollow Pd and Pt to maximize the hollow and to optimize the particle size in relation to the degree of atom's contraction and activity.
2. Tuning the effect of core on a Pt monolayer shell by hetero-layered core structure. Graphene oxide as support.
3. Electrodeposition of selected alloys as stable, inexpensive cores with known segregation properties. Optimization of the cores shapes.
4. Using non-aqueous solvents for electrodeposition of reactive metal cores, UPD of various MLs for Pt ML deposition on reactive metals and alloys.

# Summary

Further improvements of Pt ML catalyst aimed at reducing the cost of the Pd core, increasing stability and improving syntheses efficiency have been achieved in 2012.

These include several syntheses of hollow Pd cores, Pd alloys with refractory metals, Pd<sub>9</sub>Au<sub>1</sub> alloy, Pt monolayer on ultrathin Pd nanowires and electrodeposited Pd nanostructures, verified in scale-up syntheses and the MEA tests.

Pt utilization of 100%, the unique feature of Pt ML catalysts with electrodeposited cores. Technology based on electrodeposition of catalysts on GDLs appears promising.

The mechanism of stability of core-shell electrocatalysts\*, including the self-healing mechanism, have been verified in tests involving potential cycling to 1.2V at 3M.

\*K. Sasaki, H. Naohara, Y.M. Choi, et al., *Nature Communications*, 2012, 3, 1115.

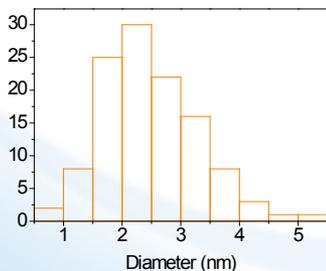
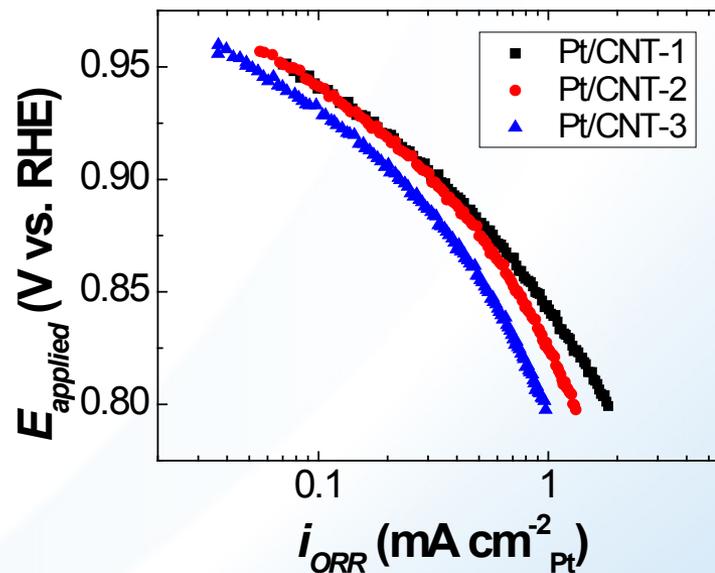
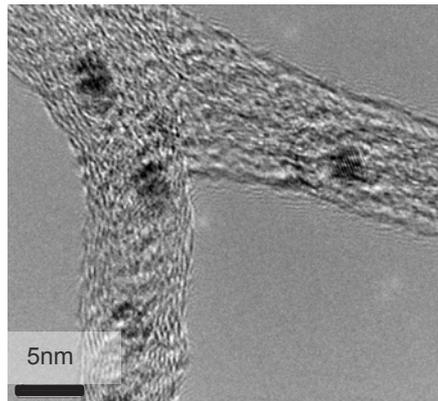
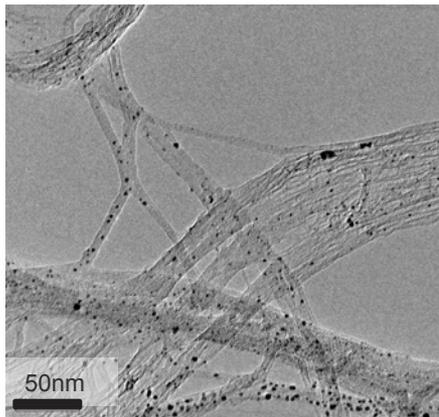
**Pt<sub>ML</sub> electrocatalysts for ORR --- On the road to application and can be further improved!**

# Technical back-up slides

# Pt nanoparticles on CNTs

Limiting current part is not well-defined probably caused by poor CNT distribution on disk surface.

The activity is  $\sim 0.3 \text{ mA/cm}^2_{\text{Pt}}$ , better than that of commercial Pt/C ( $0.22 \text{ mA/cm}^2_{\text{Pt}}$ ).

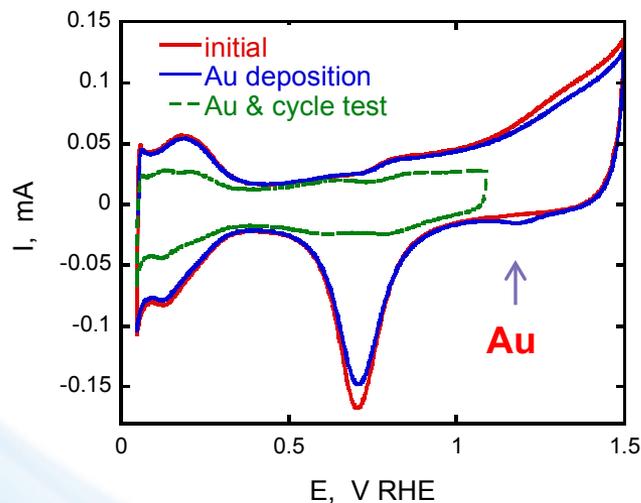
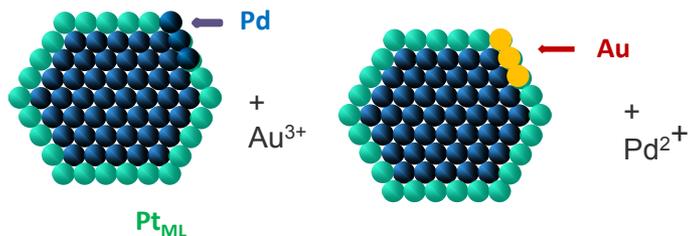


Average particle size: 2.5 nm

# Simultaneous stability and activity improvements by selective removal of inactive, low stability sites

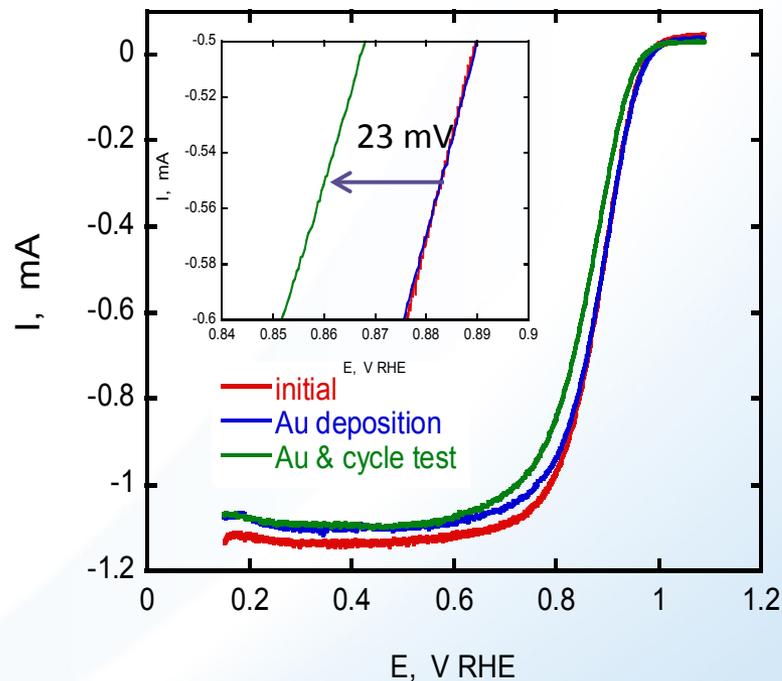
## Au deposition by galvanic replacement

Completing partial Pt monolayer to promote activity and stability



$E_{1/2}$ : 23 mV decrease by cycle test. Miniscule Au coverage has an effect (arrow). (31 mV decrease for  $\text{Pt}_{\text{ML}}/\text{Pd}/\text{C}$ )

Cycle test: 1000 cycles between 0.6 – 1.4 V at 50 mV/s

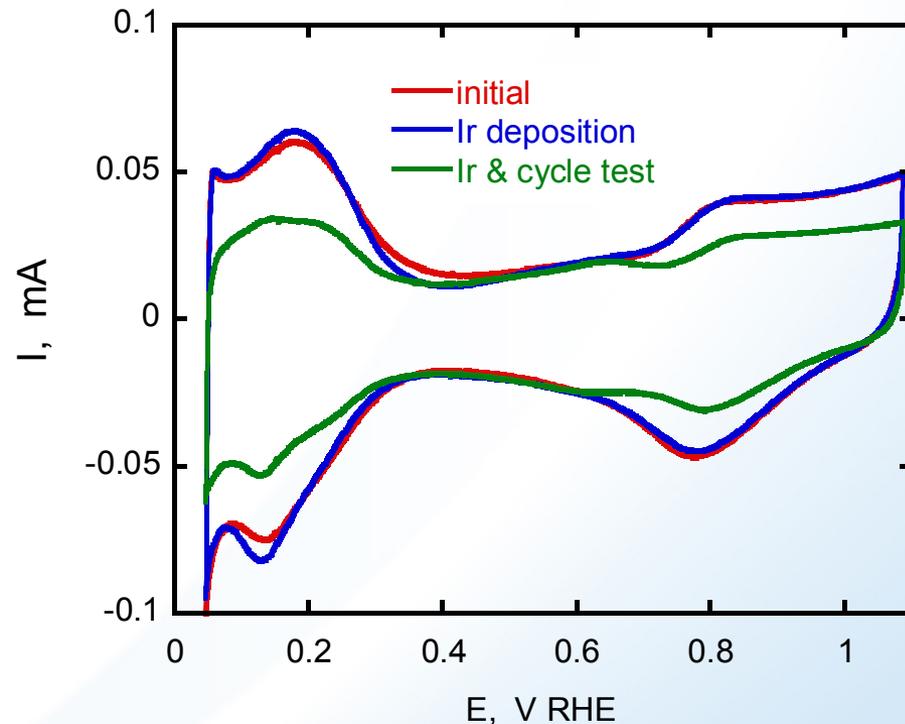
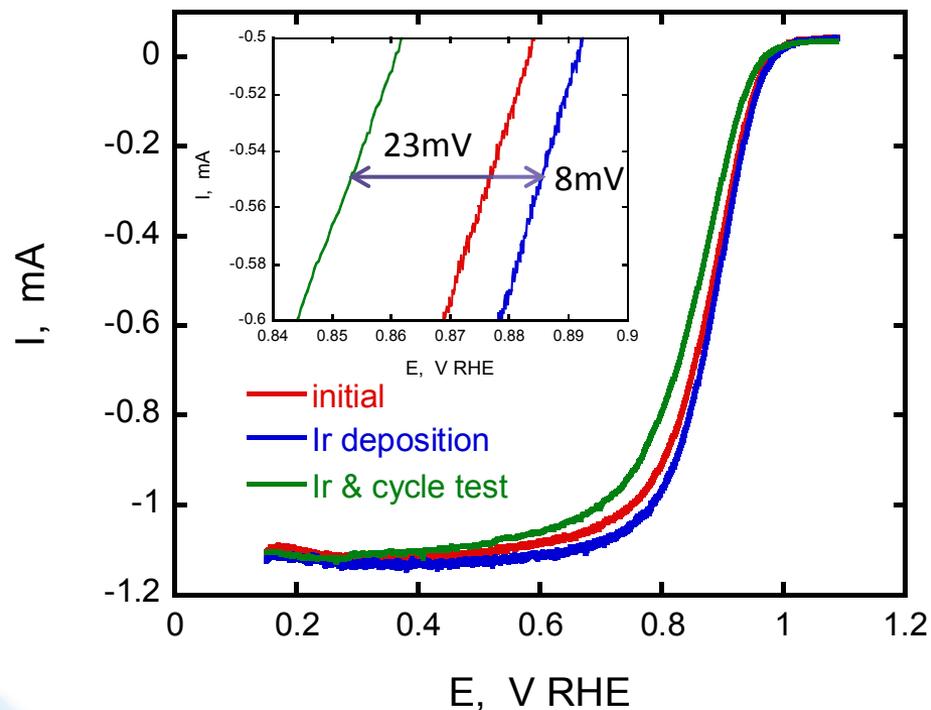


ECSA : 57% decrease after cycle test

# Simultaneous stability and activity improvements by selective removal of inactive, low stability sites

## Ir deposition by galvanic replacement

Cycle test: 1000 cycles between 0.6 – 1.4 V at 50 mV/s



$E_{1/2}$  :  
 8 mV increase by Ir deposition  
 23 mV decrease by cycle test  
 (31 mV decrease for Pt<sub>ML</sub>/Pd/C)

ECSA :54% decrease after cycle test  
 (from initial area)  
 (same as that of Pt<sub>ML</sub>/Pd/C)