Project FC009

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, Johnson Matthey Fuel Cells

BNL team: Stoyan Bliznakov, David Buceta, Kurian Kuttiyiel, Yu Zhang , Guangyu Chen

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Overview

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

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)

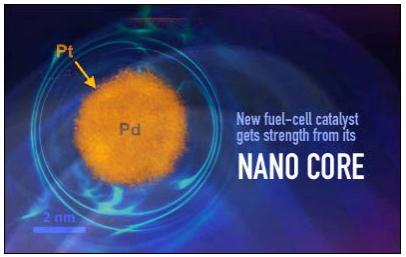
Collaborations

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

Technology transfer

Four patents on Pt ML electrocatalysts licensed to N.E. ChemCat Co.
CRADA with Toyota M.C.

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_9Au_1 alloys obtained by electrodeposition
   - 3.3.1 Delivering a 450 cm^2 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

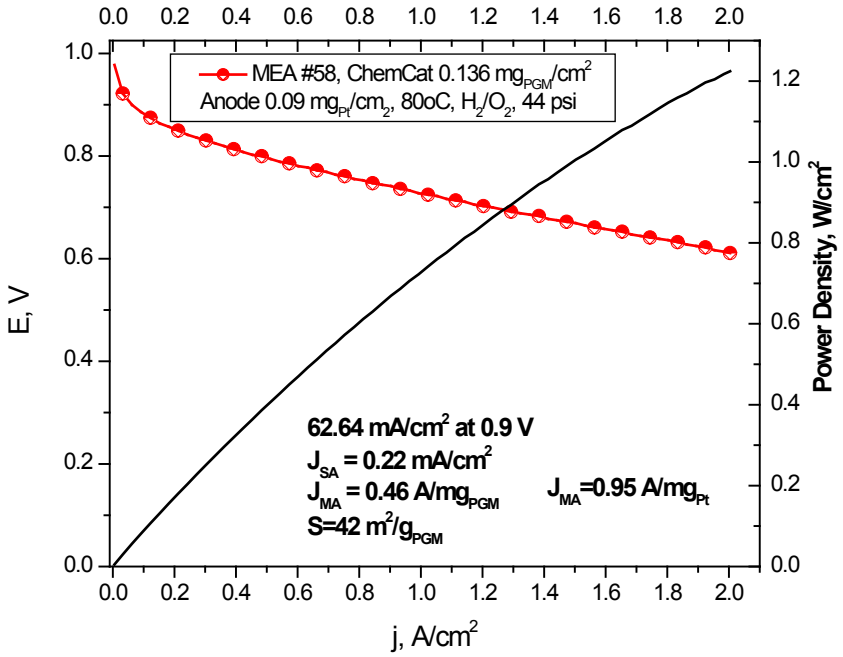
2. Electrodeposition of cores to optimize their shapes and composition and maximize catalyst utilization
   - Metal and alloy- nanoparticles, nanorods, nanowires

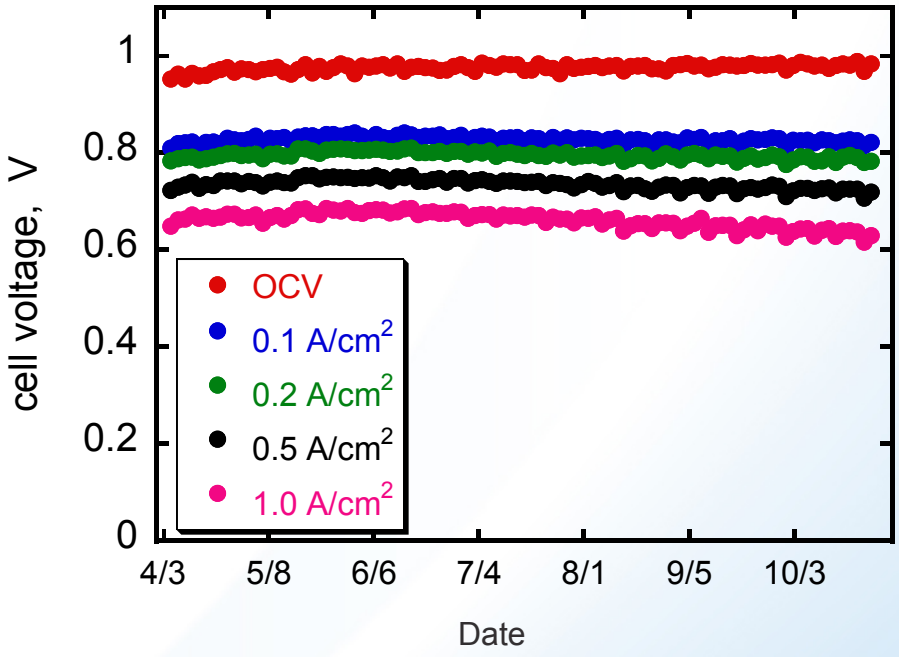
3. Refractory metal alloys used as cores to reduce PGM content
   - Co-deposition of W and Ni cores

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.

Technical Accomplishments and Progress

Behavior of commercial Pt_{ML}/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$_{Pt}$

Cathode loading PGM 136 µg/cm^2

No change in performance over 6 months at OCP and 4 current densities

0.1 mg/cm^2 PGM (Data, Hiroshi Igarashi, NECC)

Technical Accomplishments and Progress

Synthesis of hollow Pd nanoparticles and $Pt_{ML}/Pd_{hollow}/C$ catalyst

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

Ptm@PdM/C

Synthesis in microemulsion; 60 mg catalyst/200 ml sol

Particle size: 5.5-6 nm

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

Ptm@PdH/C

Synthesis in water with citrate:

60 mg of catalyst/300 ml

Particle size: 22 nm

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

Ptm@PdCu/C

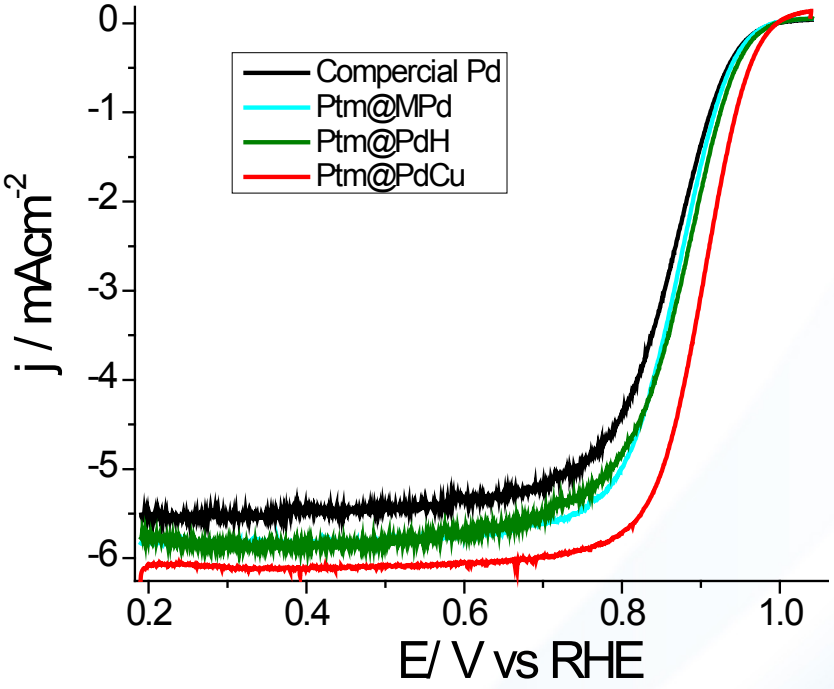
Synthesis in water; no surfactant

150 mg of catalyst/100 ml

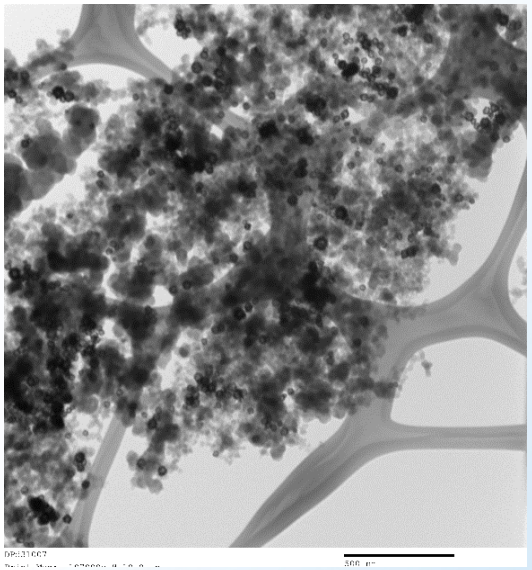
Particle size: 3-5 nm

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

RDE for Pt_{ML} on three hollow Pd and solid Pd NPs



TEM of Pd hollow NPs from water-citrate synthesis



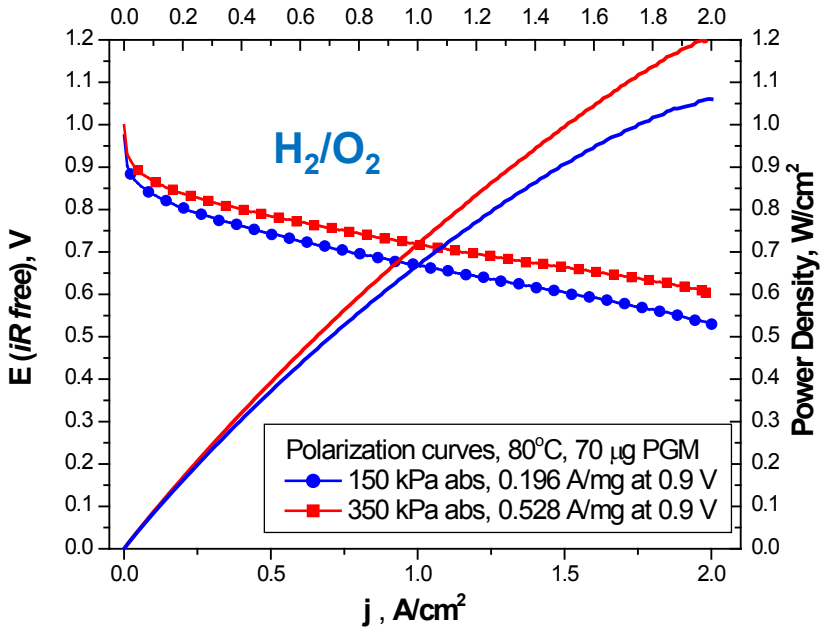
Composition of nanoparticles established using ICP

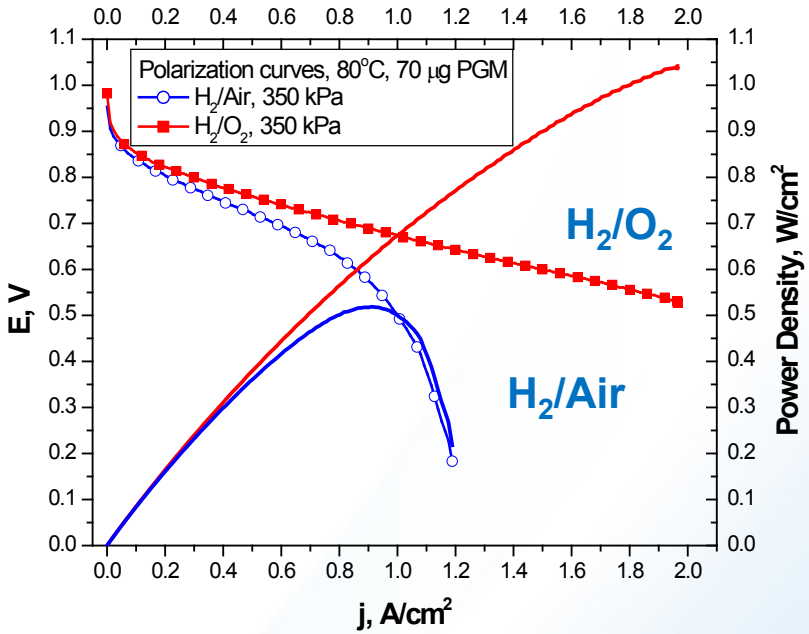
Pt (%wt)	Pd(%wt)	Cu(%wt)
9.67	18.44	1.47

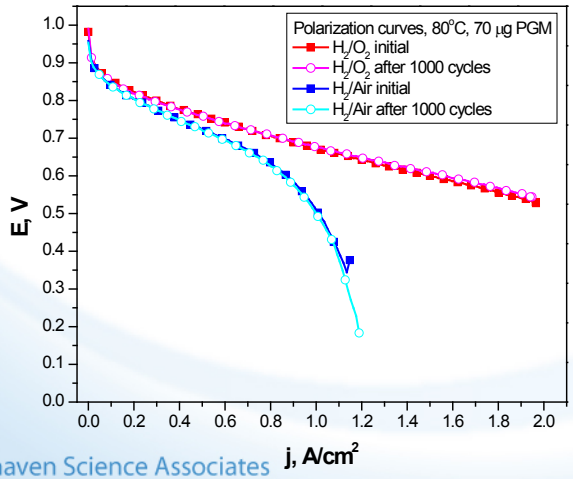
Technical Accomplishments and Progress

MEA test of Pt_{ML}/ Pd_{hollow}/C nanoparticles

Cathode PGM loading: 70 µg/cm²; Anode: 50 µg/cm² Pt ; Electrode area: 5 cm²







High activity for H_2/O_2 operation. Mass transport needs improvement for H_2/AIR operation.

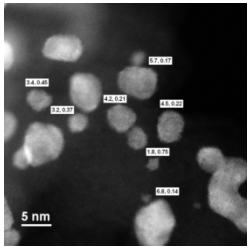
No change in polarization curves with O_2 or AIR in 1000 potential cycles stability test.

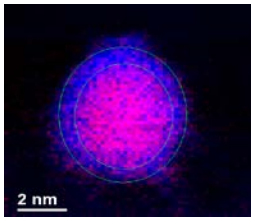
PGM Mass activity: 0.53 A/mg at 0.9V

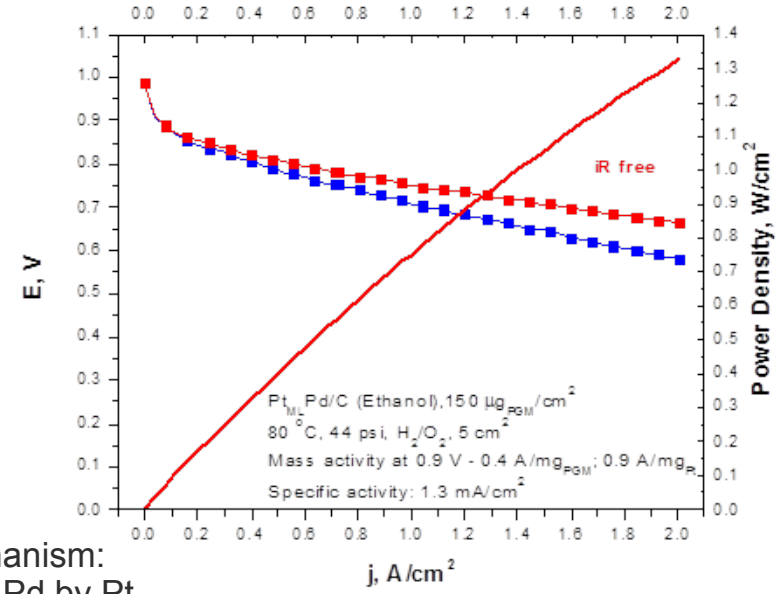
Technical Accomplishments and Progress

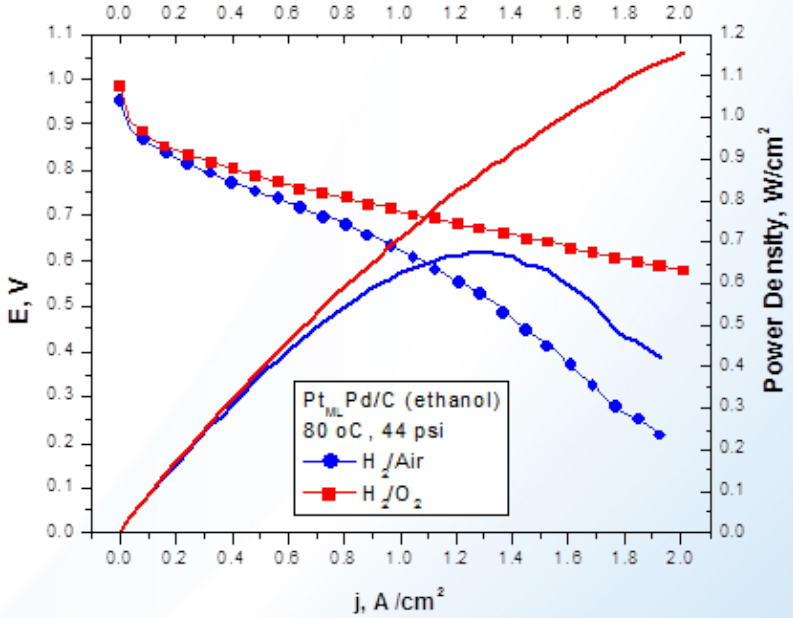
MEA tests of Pt_{ML}/Pd/C catalyst synthesized in ethanol

Cathode: Pt_{ML}Pd/C: 150 $\mu g_{PGM}/cm^2$ (70 $\mu g_{Pt}/cm^2$);
Anode: Pt/C: 90 $\mu g_{Pt}/cm^2$
Nafion® XL100; Catalysts sprayed on 5 cm^2 GDL (Sigracet® 25BC)









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

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

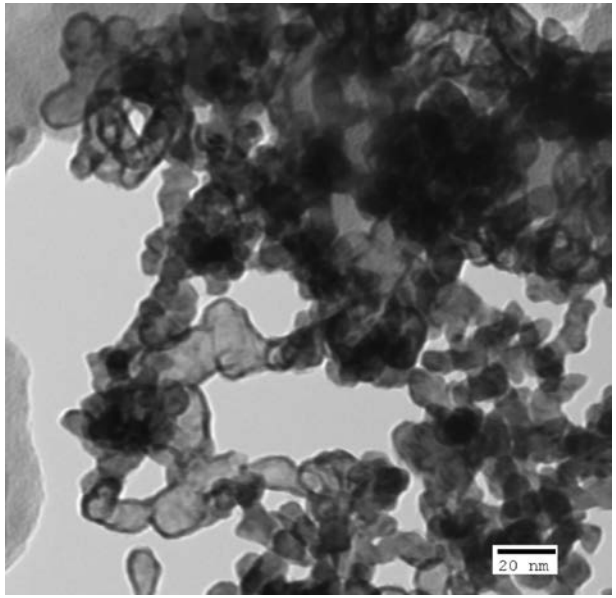
PGM activity : 0.4 A/mg_{PGM}
Pt mass activity: 0.9 A/mg_{Pt}
Specific activity: 1.3 mA/cm^2

No change in polarization curves with O_2 or AIR in 2000 potential cycles.

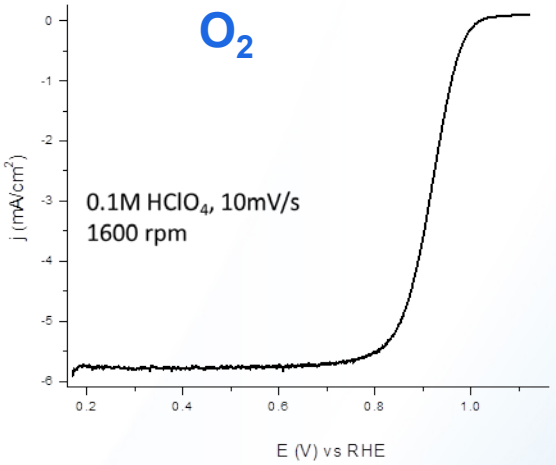
Technical Accomplishments and Progress

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

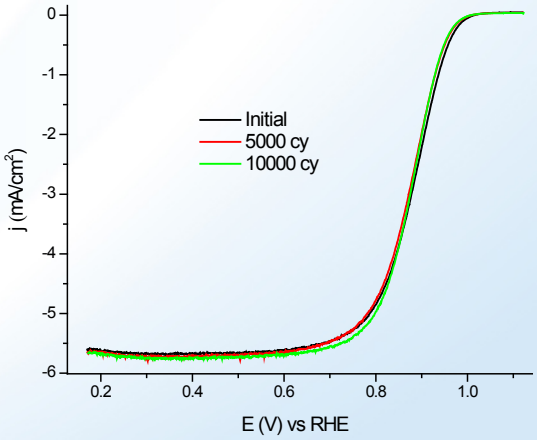
Hollow Pt prepared with Cu as a sacrificial metal



MA= 0.32 A/mg
SA = 2.06 mA/cm^2



The procedure allows for maximizing Pt hollow, i.e. making the thinnest Pt shell. Less than 30μg$_{Pt}$/cm^2

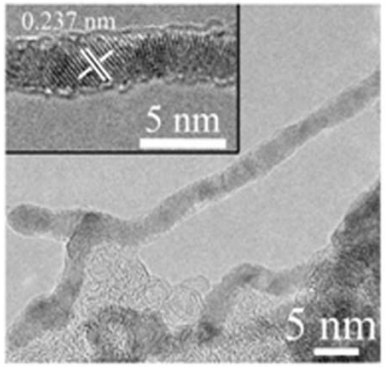


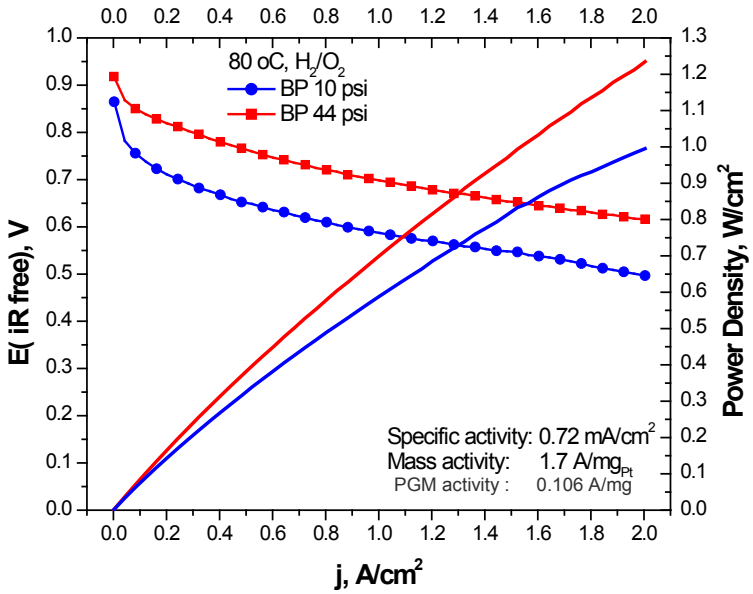
The stability of this type of Pt hollow electrocatalyst is high; no change can be observed after 10,000 potential cycles.

Technical Accomplishments and Progress

MEA test of Pt_{ML} on ultrathin bimetallic PdAu nanowires

Nanowires Pt_{ML}/Pd



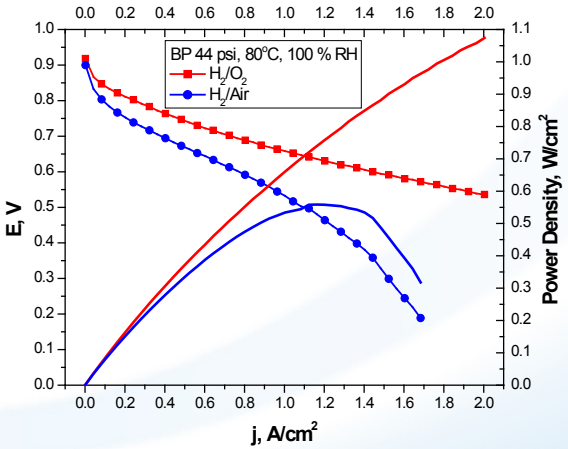


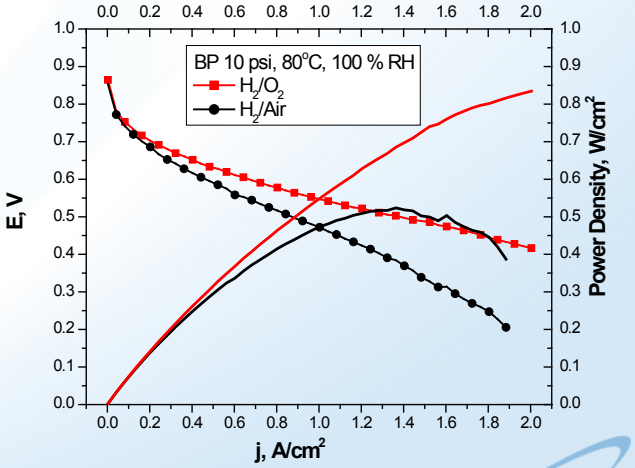
Pt mass activity: 1.7 A/mg_{Pt}

Specific activity: 0.72 mA/cm^2

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 $NaBH_4$ into both the aqueous and organic phases.





Electrodeposition of cores

Further improvement of Pt_{ML} 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^2
- 100% utilization of Pt in Pt_{ML} electrodeposited catalysts

Total utilization of Pt in MEA

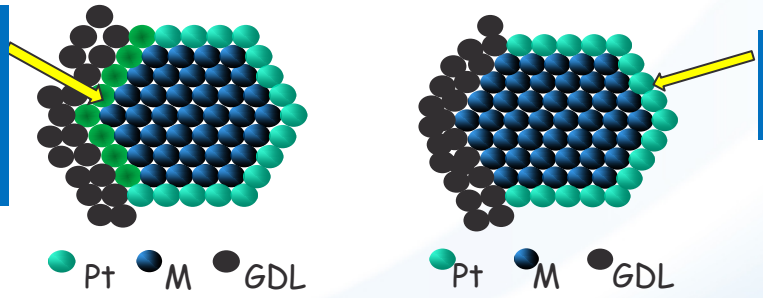
Standard catalysts
Pt/C 4-5 nm = 15-20%

Pt ML standard MEA prep
Pt_{ML}/Pd/C 4-5 nm = 50%

Pt ML on electrodeposited core
$Pt_{ML}/Pd_{electrodeposited}$/C = 100%

100% utilization of Pt

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

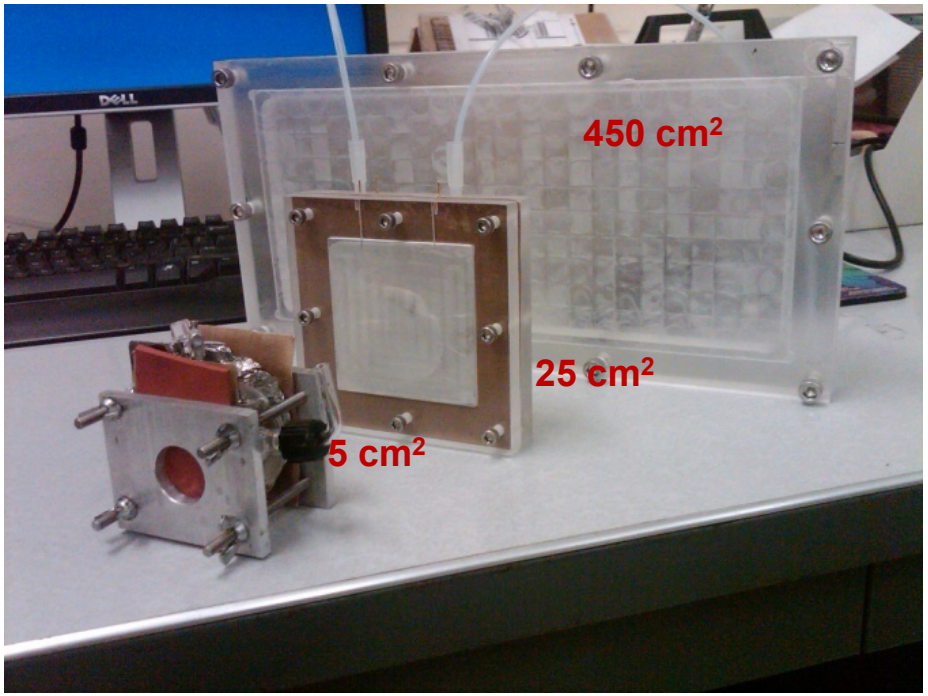


All Pt atoms are accessible for electrons and protons

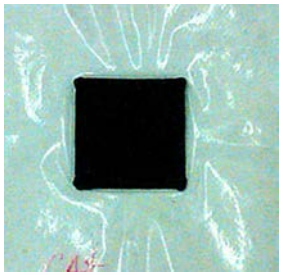
Technical Accomplishments and Progress

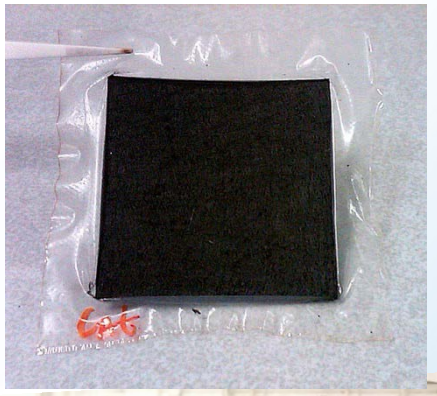
Scale-up in electrodeposition of catalysts directly on GDLs

Electrochemical cells for processing of electrodes with area of 5, 25 and 450 cm^2



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





Advantages of electrodeposition:

- All particles accessible to electrons and protons
- Short production time per MEA

"Green" properties

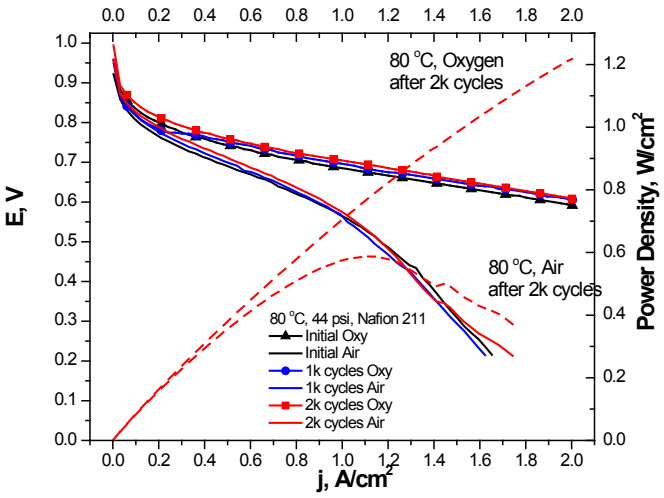
- No free nanoparticle generation
- No ink preparation and placing on electrode

Technical Accomplishments and Progress

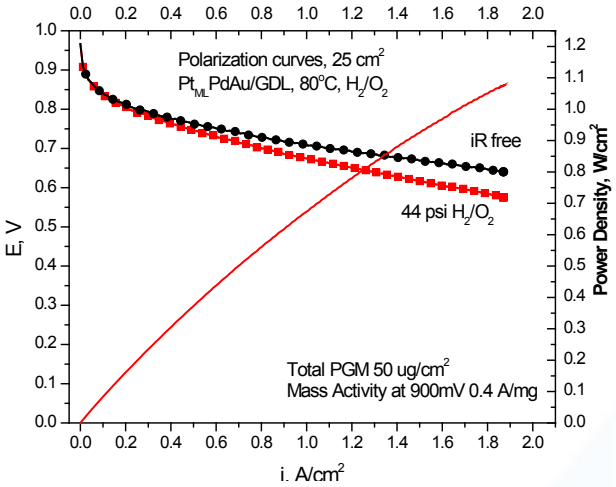
MEA test of Pt_{ML}/Pd_9Au_1/GDL at 80ºC and 60ºC

Activities as a function of the electrode size

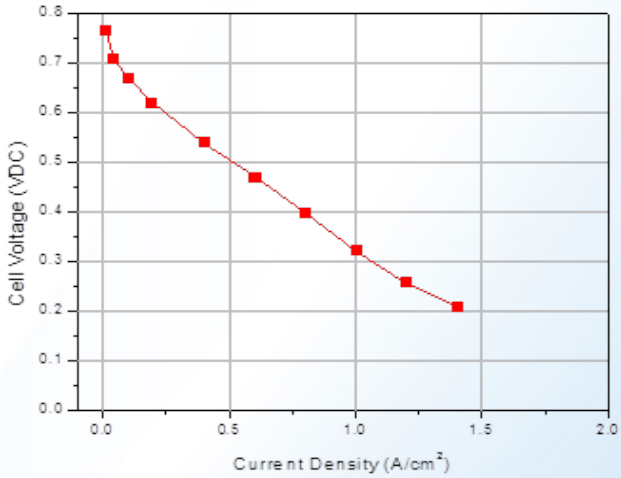
5 cm²



25 cm²



450 cm²



After 2000 potential cycles, the activity increased. PGM ~ 70 µg/cm²

MA_{PGM}= 0.4 A/mg_{PGM}
PGM = 50 µg/cm²

	SA, mA/cm²	Pt MA, A/mg_{Pt}	PGM activity, A/mg_{PGM}
Pt_{ML}PdAu/GDL 5 cm²(at 0.9V)	0.4	1.2	0.5
Pt_{ML}PdAu/GDL 25 cm² (at 0.9V)	0.2	1.1	0.4
Pt_{ML}PdAu/GDL 450 cm²(at 0.75V)	-	1	0.4

Similar activity for 5 and 25 cm² electrodes.
Lower activity for 450 cm² electrode is caused by the ambient pressure applied and low OCP indicating inadequate state of the surface. Both can be corrected.

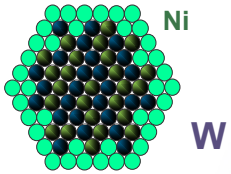
Electrode-BNL, ; MEA, measurements – UTC Power

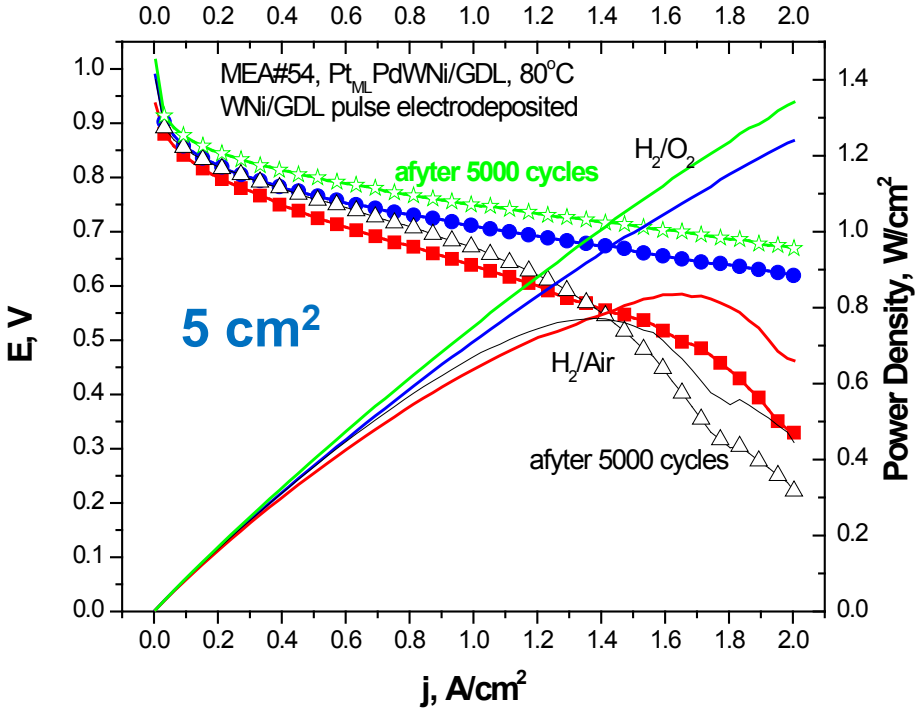
Technical Accomplishments and Progress

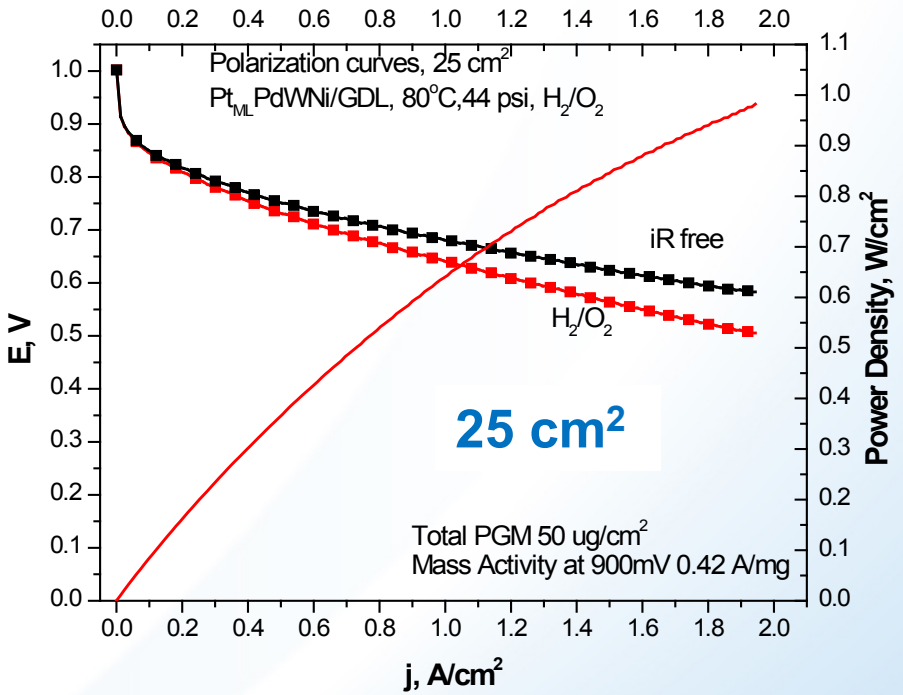
Co-deposition of W – Ni as a core of Pt_{ML}/Pd/WNi/GDL – MEA test

Co-deposition of $W_{0.5}Ni_{0.5}$ alloys on GDL
small nanoparticles with composite (amorphous-nanocrystalline) structure

Model of NiW core with a partially displaced Ni by Pd







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

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

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

	Specific activity, mA/cm^2 (at 0.9V)	Pt mass activity, A/mg_{Pt} (at 0.9V)	PGM mass activity, A/mg_{PGM} (at 0.9V)
$Pt_{ML}PdAu$ 5 cm^2	0.4	1.2	0.5
$Pt_{ML}Pd_{hollow}$ 5 cm^2	1.4	1.2	0.5
$Pt_{ML}Pd_{nanowires}$ 5 cm^2	0.7	1.7	0.1
$Pt_{ML}Pd_{nanowires}$ 5 cm^2, electrodeposition	0.2	1.2	0.5
$Pt_{ML}PdWNi$ 5 cm^2	0.3	1.3	0.5
Pt_{ML}/Pd Ethanol medium	1.3	0.9	0.4
Pt/C Commercial	0.15-0.2	0.1-0.12	0.1-0.12

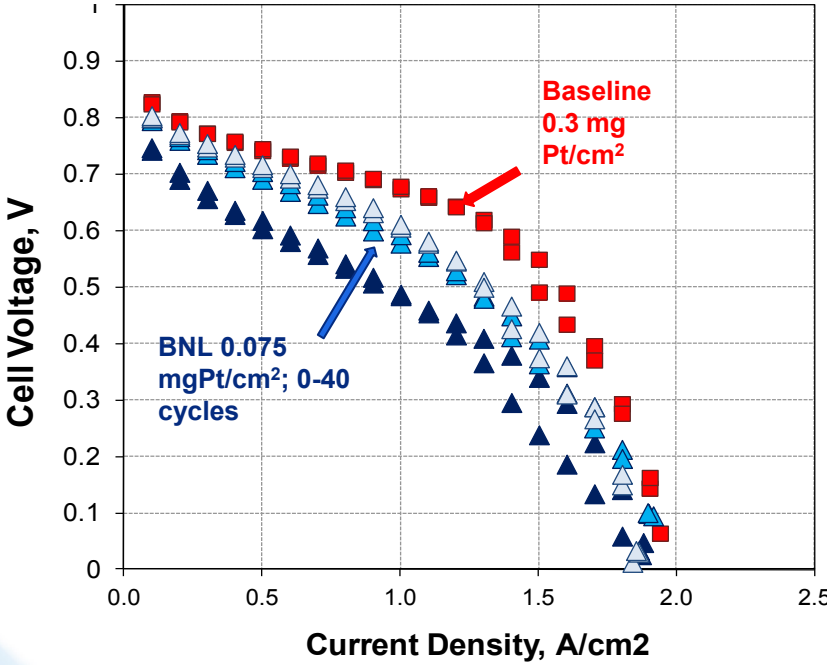
All above Pt_{ML} catalysts have the PGM activity 3-5 times higher than commercial catalysts, while their Pt mass activity is one order of magnitude higher. The only exception is lower PGM activity of Pt_{ML}/Pd NW caused by the mass of Pd wire.

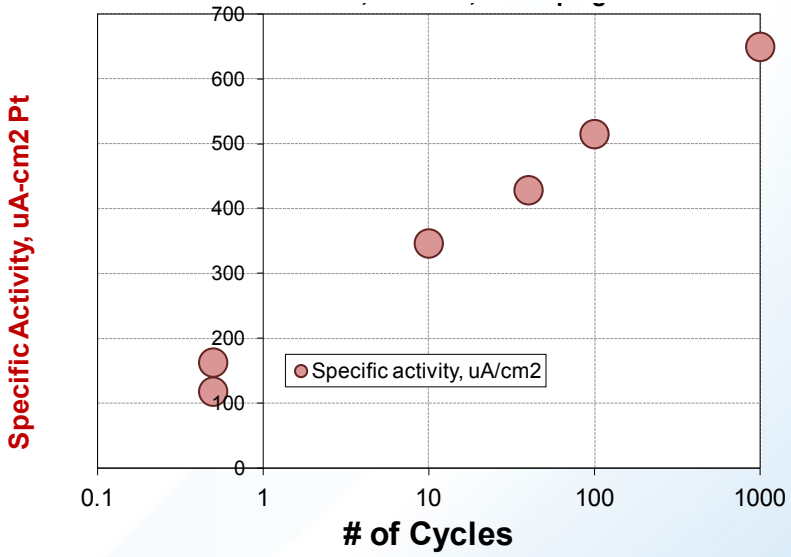
Technical Accomplishments and Progress

New tests of Pt_{ML}/Pd/C at 3M

Potential cycling 0.6 to 1.2V, 20 mV/s;70C, 100% RH
New ink formulatic..
Electrode size 50cm²
Loadings from 0.06 to 0.10 mg Pt/cm²

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 μA/cm²
Core shell reaches 650 μA/cm²
Self-healing mechanism supported by these data.

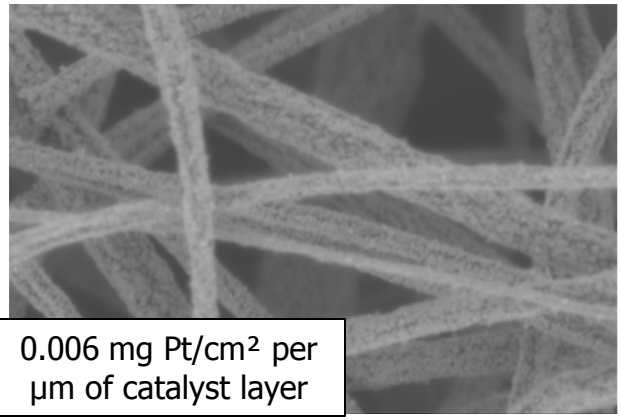
3M recommendations / conclusions
Mass transport region looks very good; High current capability at low loadings.
Add Au to slow or stop metal dissolution
The 3M carbon might improve mass and specific activity
Continue testing; making CCMs

Andrew Haug, Daniel Peppin, Radoslav Atanasoski

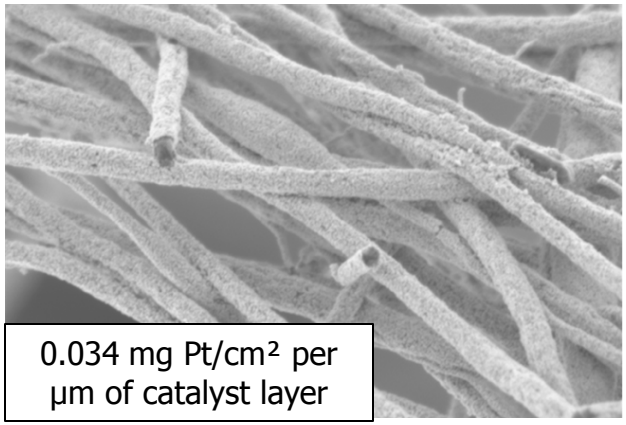
Thin Film Pt on Fibrous Supports

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

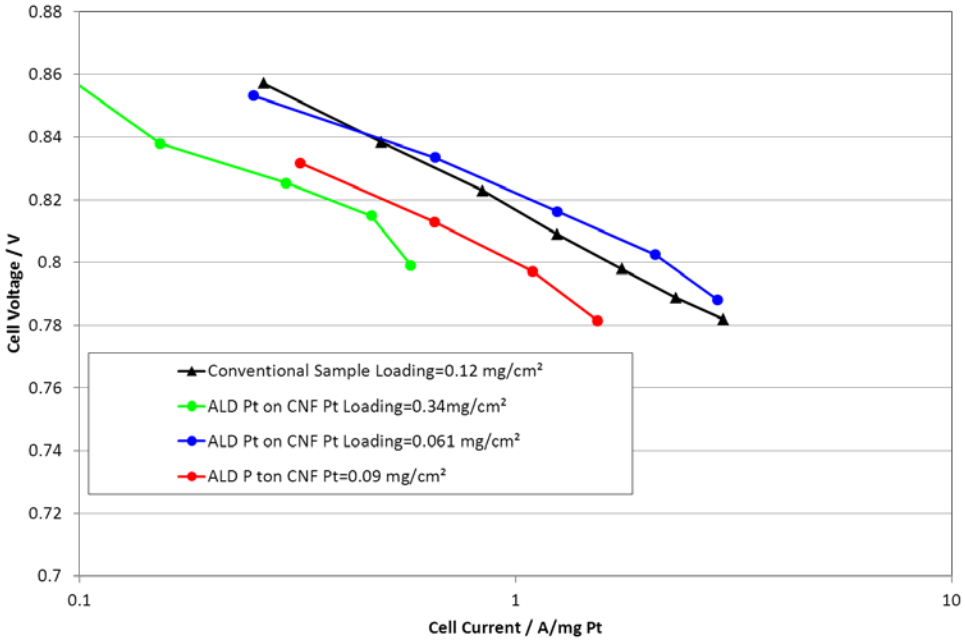
Investigation of materials for interface layers that help Pt 'wetting' of the fibrous substrates.

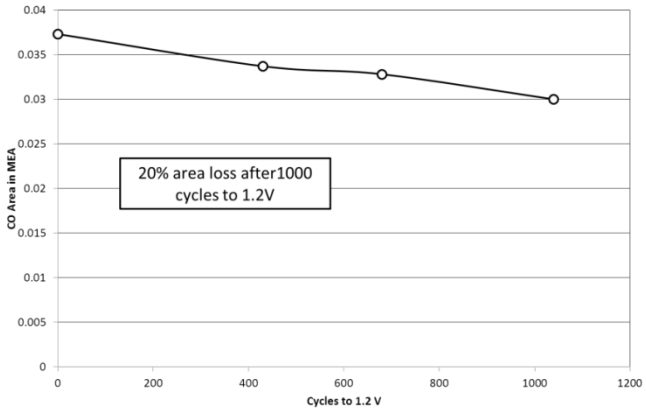


0.006 mg Pt/cm² per µm of catalyst layer



0.034 mg Pt/cm² per µm of catalyst layer





Further work:

Reduce layer porosity.

Improve film-formation of Pt during deposition.

After oxygen, develop layer structure for air.

Johnson Matthey Fuel Cells

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_{ML}/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 $Pt_{ML}/Pd_{hollow}/C$ catalyst and MEA fabrication and tests (BNL, JMFC).

2. Optimize electrodeposition of the Pt_{ML}/Pd/WNi catalyst, fabrication of 450 cm^2 electrodes and tests of 25 cm^2 segments of this electrode (BNL).

3. Optimize the synthesis of Pt_{ML}/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_{ML}/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_9Au_1 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 3**M**.

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

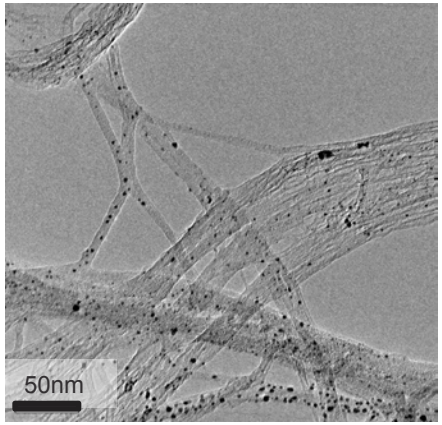
Pt_{ML} electrocatalysts for ORR --- On the road to application and can be further improved!

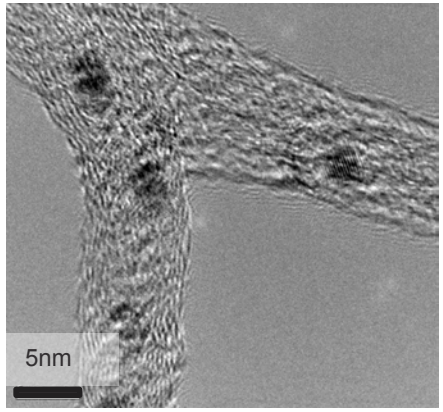
Technical back-up slides

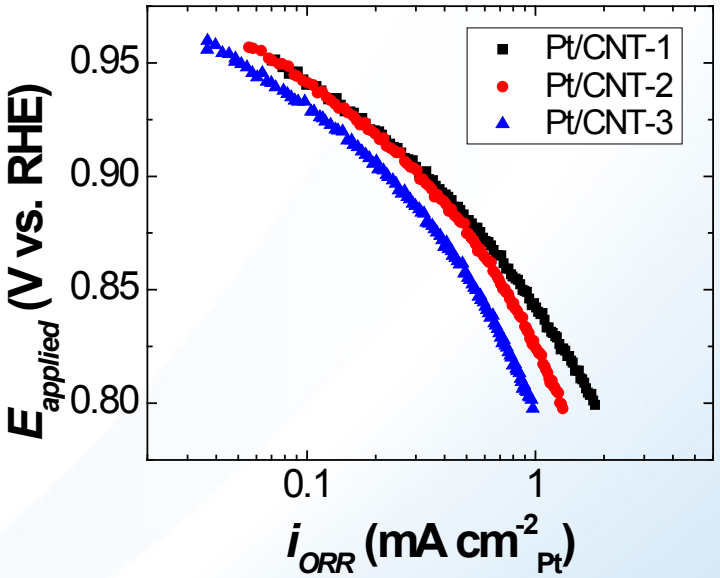
Pt nanoparticles on CNTs

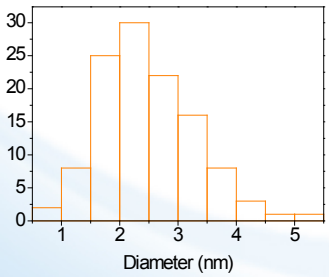
Limiting current part is not well-defined probably caused by poor CNT distribution on disk surface.

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







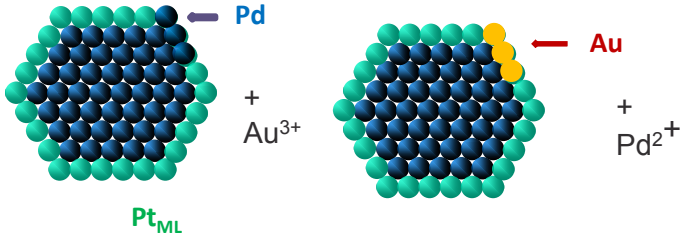


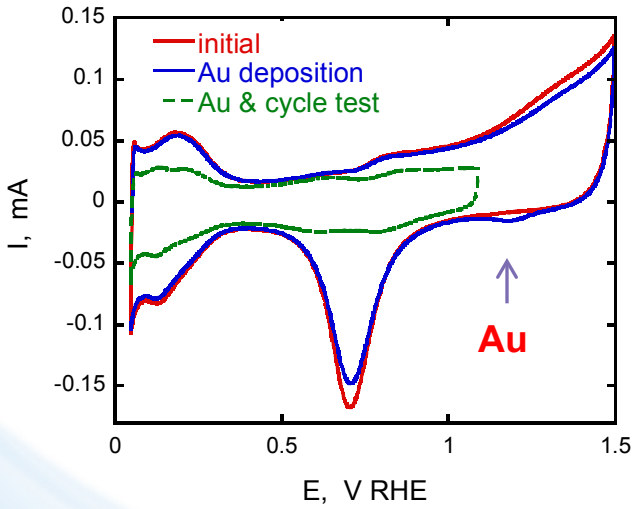
Average particle size: 2.5 nm

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

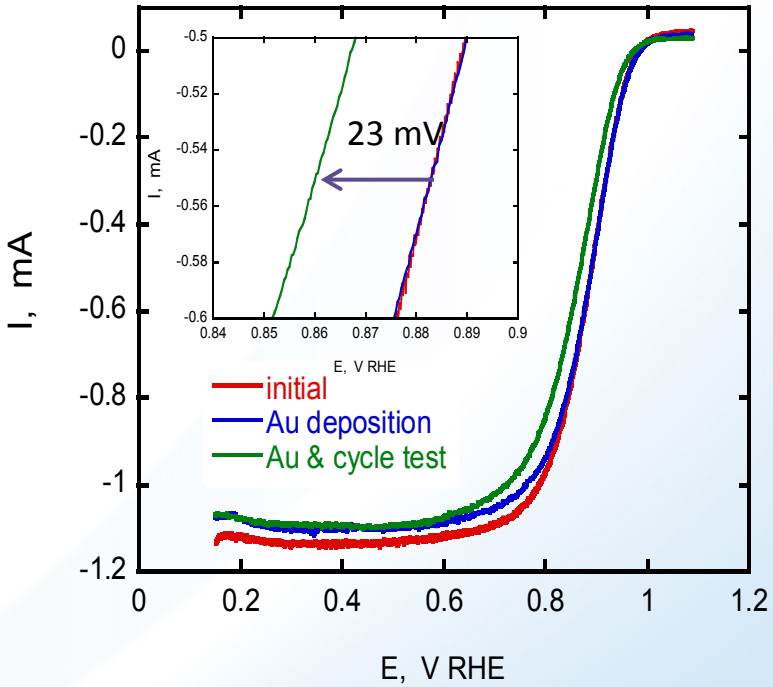
Au deposition by galvanic replacement

Completing partial Pt monolayer to promote activity and stability





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



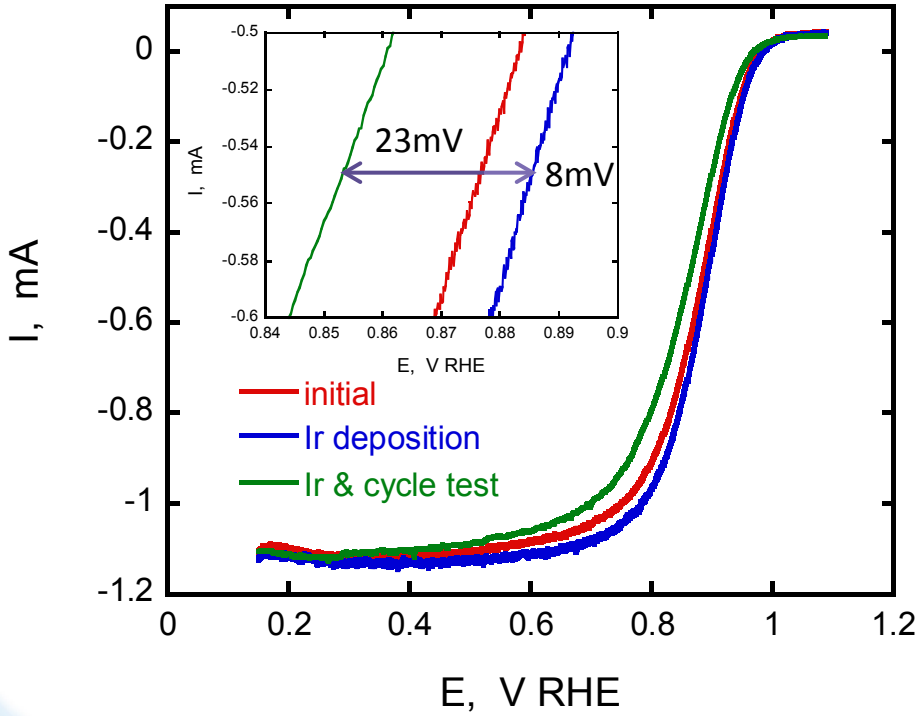
ECSA : 57% decrease after cycle test

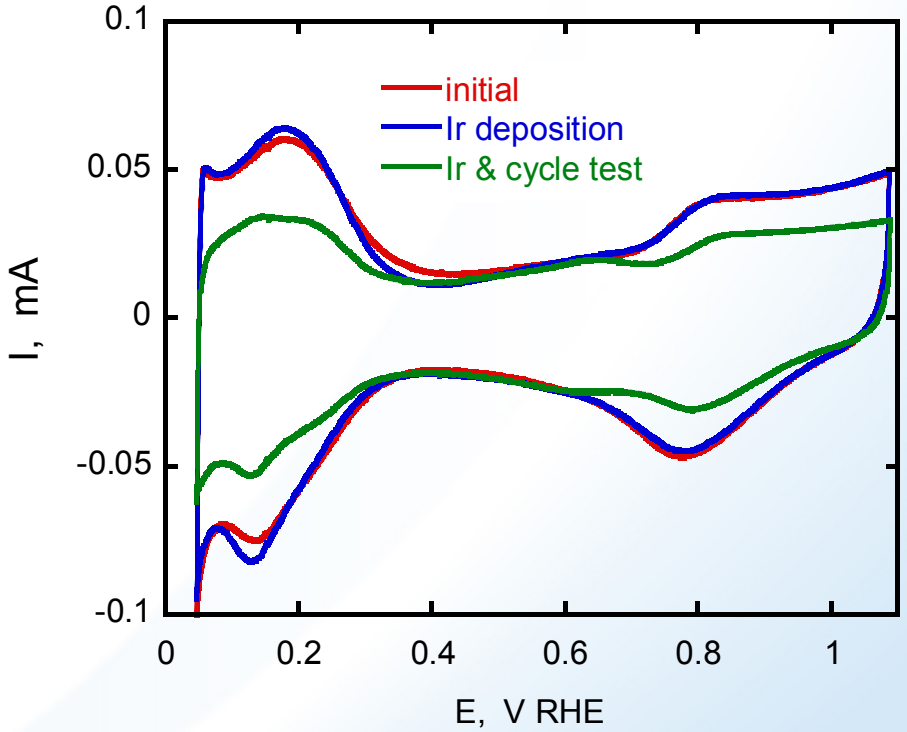
$E_{1/2}$: 23 mV decrease by cycle test. Miniscule Au coverage has an effect (arrow). (31 mV decrease for Pt_{ML}/Pd/C)

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 $Pt_{ML}/Pd/C$)

ECSA :54% decrease after cycle test
(from initial area)
(same as that of $Pt_{ML}/Pd/C$)