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

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DOE Projects Kickoff Meeting

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BROOKHAVEN NATIONAL LABORATORY

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Office of Science U.S. DEPARTMENT OF ENERGY

Project Overview

1. Objectives: Developing high performance fuel cell electrocatalysts for the oxygen reduction reaction (ORR) comprising contiguous *Pt monolayer* on stable, inexpensive metal or alloy nanorods, nanowires, nanobars and carbon nanotubes (CNT)

2. Barriers:
Durability (cathode electrocatalyst)
Costs (cathode electrocatalyst)
Electrode Performance (cathode electrocatalyst, ORR kinetics)

3. Technical targets:

- **Platinum group metal loading: 0.2 mg_{PGM} /cm^2 (cathode) (0.3 mg_{PGM} /cm^2 both electrodes)**
- **Activity (PGM catalysts): 0.44 A/mg_{Pt} at 0.90 $V_{iR\text{-}free}$ 720 μA/cm^2 at 0.90 $V_{iR\text{-}free}$**
- **Durability with cycling: 5,000 hours at T ≤ 80°C, 2,000 hours at T > 80°C**
- **ESA loss:** < **40%;** **Cost:** < **5 $/kW**

4. Timeline: Start date: **July 2009** End date: **September 2013**

5. Budget:

	FY09	FY10	FY11	FY12	FY13	Total
in $K	615	267	882	882	882	3,529

APPROACH

1. **Prior work**

   Pt monolayers on metal or alloy nanoparticles (NPs) are verified as the very high-activity, high durability and the lowest Pt content ORR electrocatalysts.

2. **Our experimental and DFT data**

   Pt atoms with high coordination are less susceptible to PtOH formation. They are, thus, more active for the ORR than low-coordination ones.

3. **Further improvement**

   Improvements are likely with Pt as a contiguous monolayer on smooth surfaces of nanorods, nanowires, nanobars or NPs of selected metals, alloys, or CNTs.

4. **Methods**

   We have developed: i) the method for depositing uniform, close-packed Pt MLs.

   ii) the method for removing low-coordination atoms without changing the size of nanoparticles used as support for Pt.

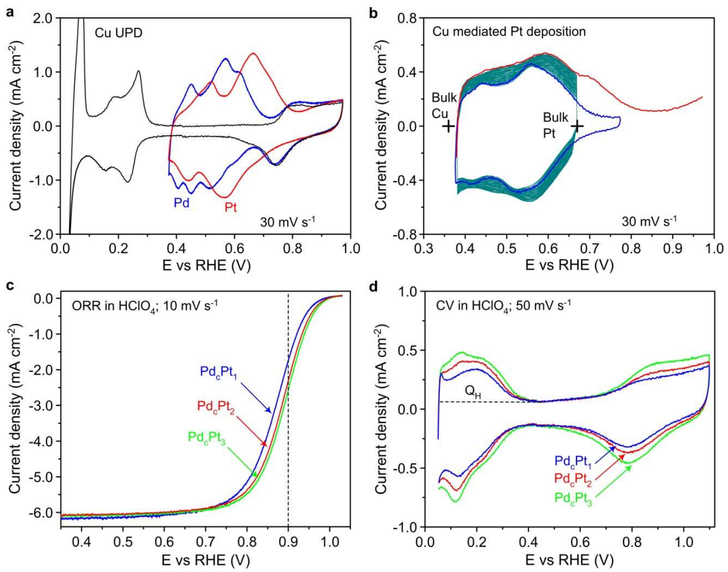
   iii) cation adsorption/reduction/adatom replacement method

   Techniques for extensive catalyst characterization exist at BNL, JMFC, MIT.

   Several synthetic approaches are explored, such as BNL's sonolysis of refractory metal salts.

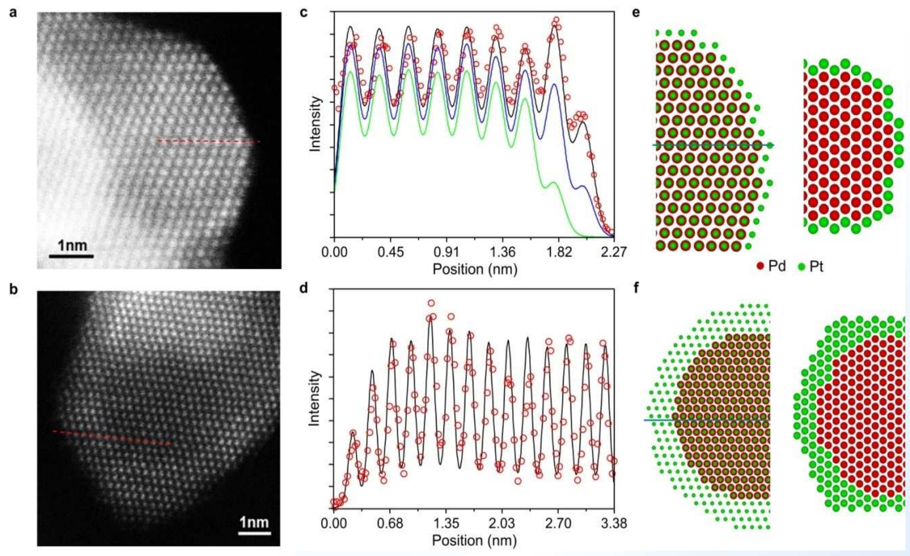
APPROACH - Method for depositing smooth, uniform Pt MLs

Cu UPD-mediated deposition of Pt Monolayers



Controllable deposition of uniform 1, 2, 3 Pt MLs using Cu UPD-mediated method

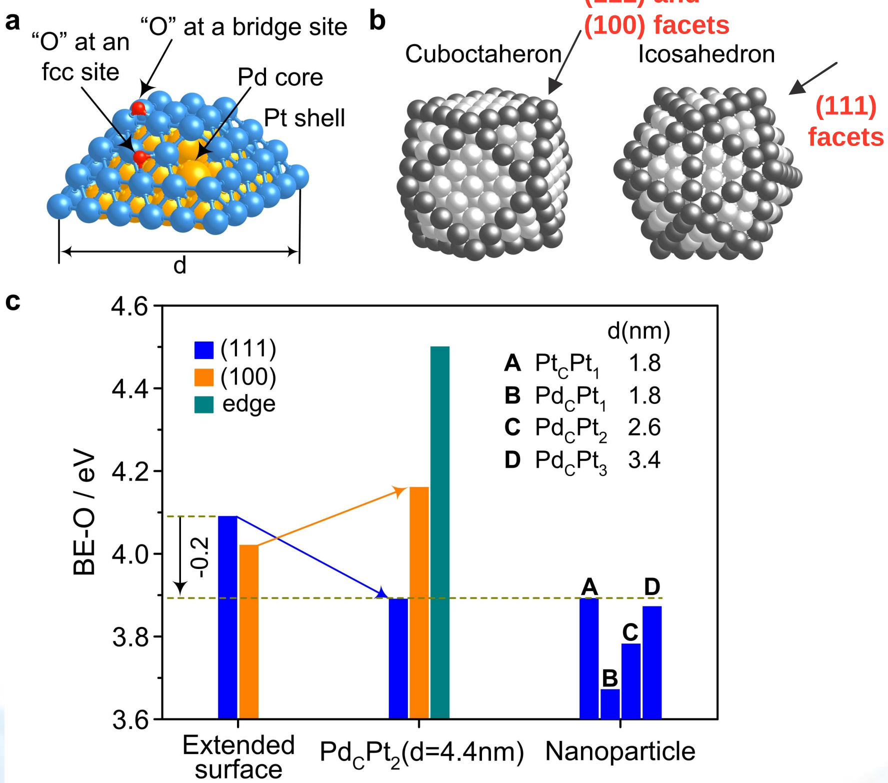
HAADF-STEM images of the Pd(core)-Pt(shell) NPs having 1 ML and 4MLs of Pt on Pd/C



Intensity profiles from the scan lines in (a) and (b) (open circles), and the best fits (black lines), based on the structure models shown in (e) and (f)

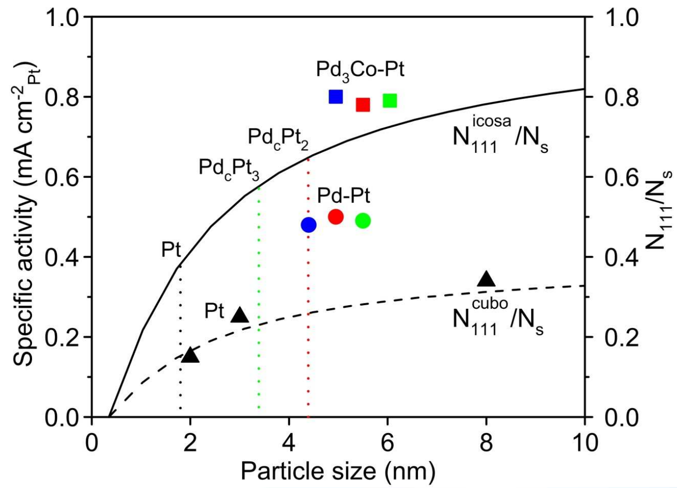
APPROACH - The (111)-oriented, slightly contracted Pt best for the ORR

DFT calculation: Size-induced surface contraction and Pd core effects
out-of-plane contraction at edges, in-plane contraction at the (111) facets



Facet-dependent binding energy of oxygen on core-shell nanoparticles

Activity and surface fraction of atoms on the (111) facets as a function of particle size.



N	Specific [mA cm^{-2}]	Pt mass [mA μg^{-1}]	PGM mass [mA μg^{-1}]
4.0-nm Pd/C (10% wt)			
1	0.50	**0.96**	0.25
2	0.52	0.59	0.27
3	0.51	0.43	0.25
3-nm Pt/C (20% wt)			
0	0.25	0.17	0.17

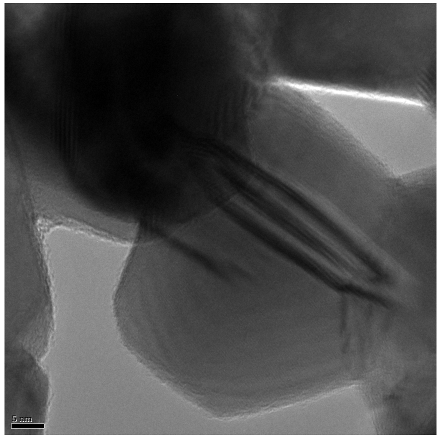
DFT: the in-plane spacing on the (111) terraces compared to the extended Pt(111) surface (–4.2%).

Preliminary results: Enhanced ORR Kinetics on Smooth Surfaces

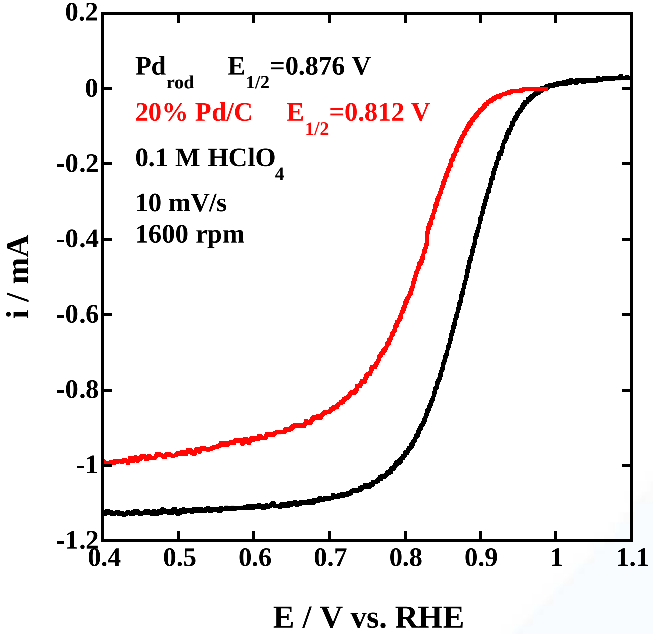
Pt ML on Pd nanorods with smooth surfaces

Very high activity of Pd nanorods

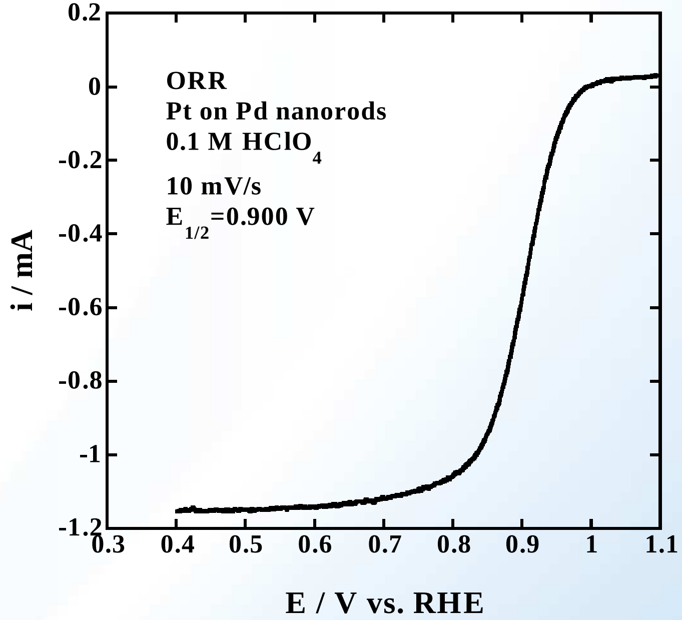
Pd



Pd/C



Pt_{ML}/Pd/C

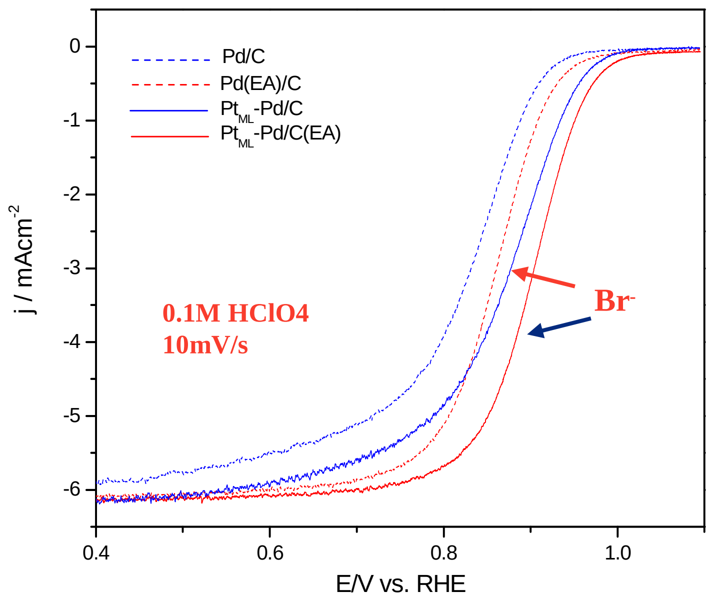


Pt mass activity = 1.03 A/mg

Synthesis of Pd wires is underway; success with Pt – wires with diameters bellow 2 nm

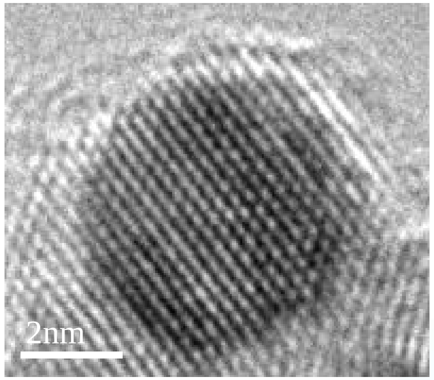
Preliminary results: Enhanced ORR Kinetics on Smooth Surfaces

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

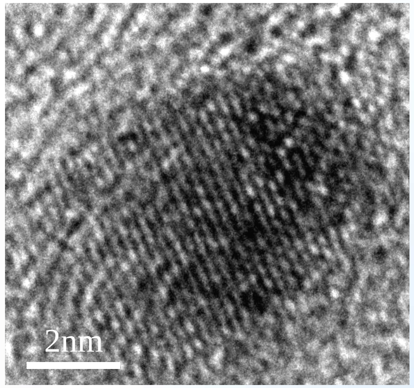


Polarization curves for the ORR on Br^- -treated and untreated Pd/C, and Pt_{ML}-Pd/C

Adsorbing Br- on Pd nanoparticles and desorbing the adsorbate removes low-coordination atoms.



(a)



(b)

Pd: $E_{1/2}$ =831mV $E'_{1/2}$ =859mV

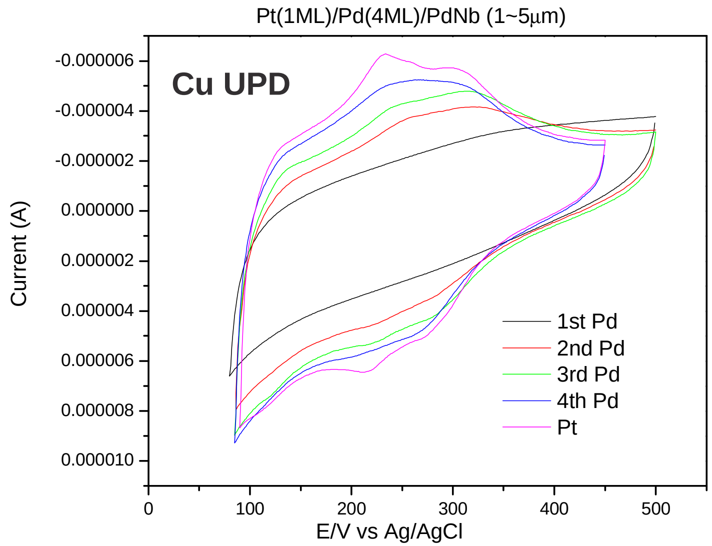
Pt/Pd: $E_{1/2}$= 876mV; $E'_{1/2}$=903mV

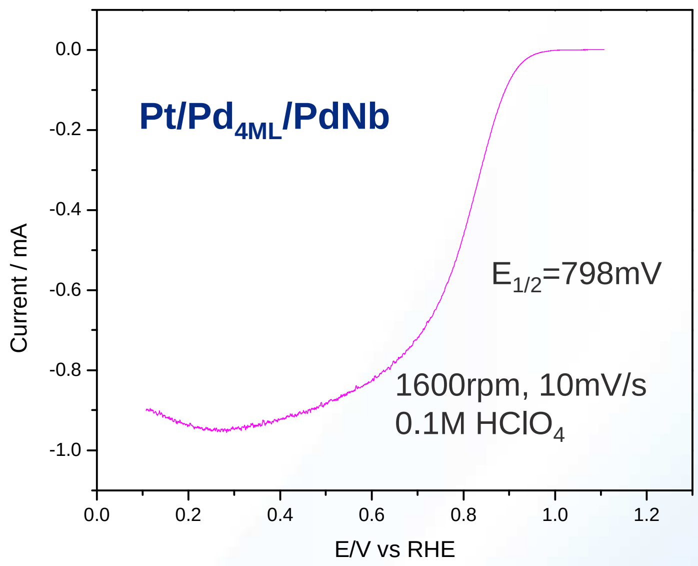
Low-coordination Pt atoms are susceptible to formation of PtOH species (ORR inhibitor) and are points of attack in dissolution of electrocatalysts

Preliminary results: ORR on a Pt ML on Pd deposits on Nb particles

Learning about Pd deposition on Nb

Deposition of Pd on Nb particles (1-4 μm) has been accomplished





Synthesis of Nb nanoparticles is underway

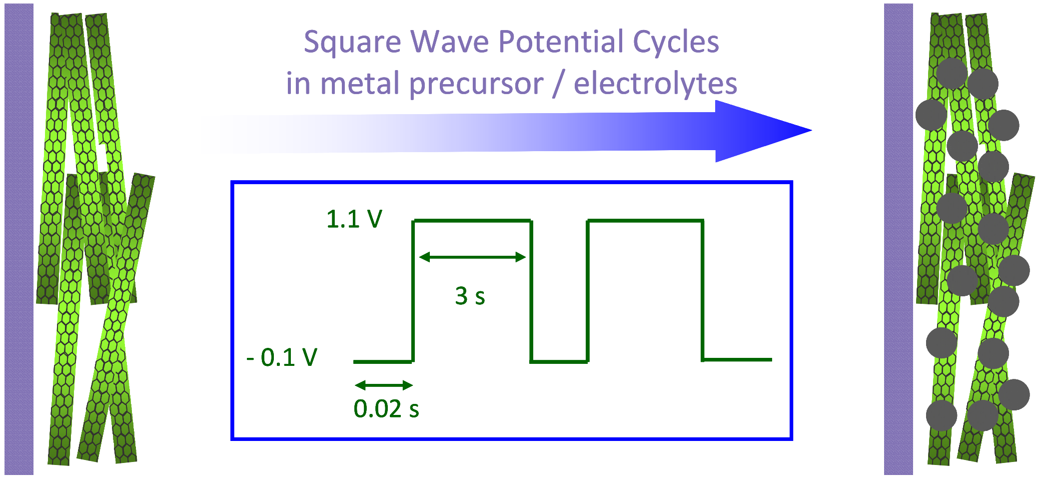
I_s (0.9V)=0.23mA/cm^2

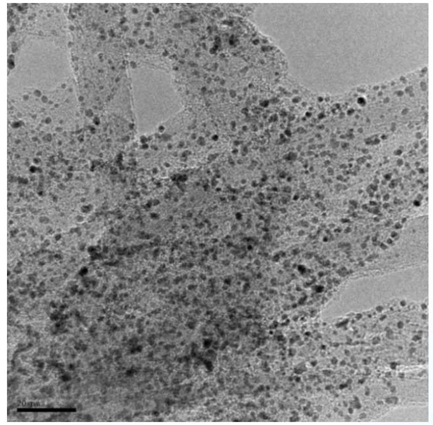
I_m (0.9V)=0.5mA/μgPt

I_s (0.85V)=0.88mA/cm^2

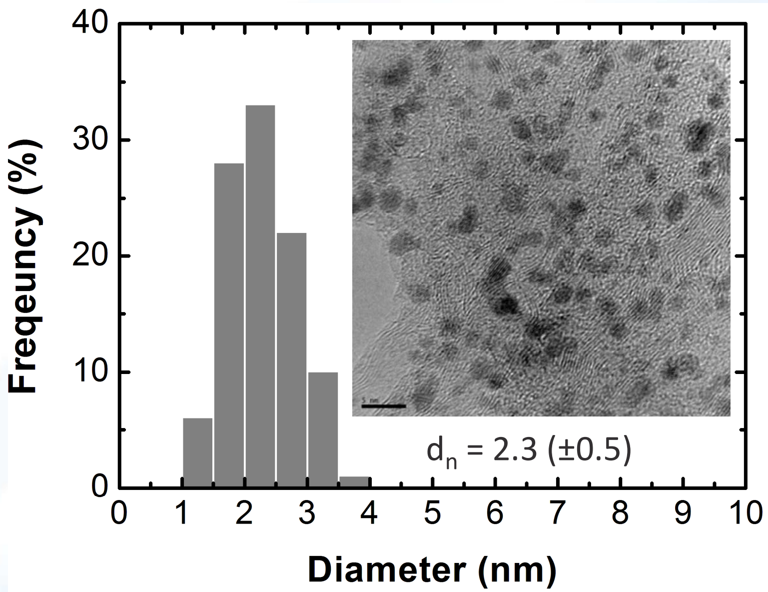
I_m (0.85V)=2.07mA/μgPt

Preliminary results: In-situ NPs Synthesis Using Square-Wave Pulse Potential





MWCNTs deposited using
LBL assembly

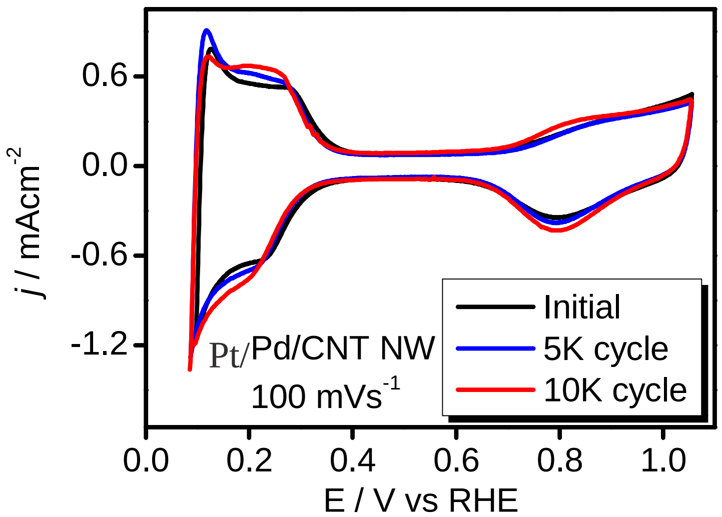


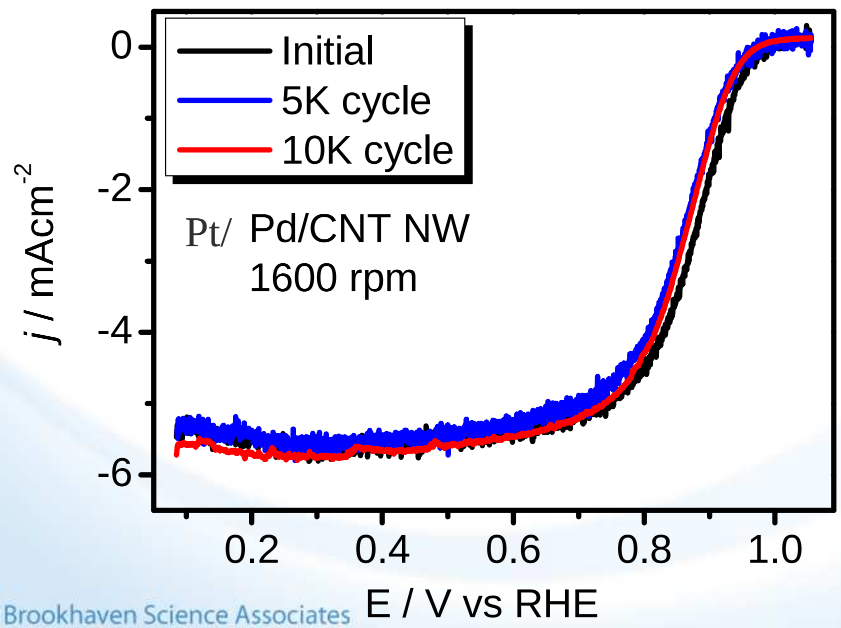
- HRTEM Images (400 Cycles in 50mM K_2PtCl_4 / 0.1M $HClO_4$ + Annealing at 200°C in N_2)

PtRu deposit has a good activity for MOR

S.W.Lee, J. Kim, Chen, P.T. Hammond, Y.Shao-Horn, Manuscript in Preparation

Preliminary results: **ORR on a Pt ML on Pd deposits on CNTs**





Initial:

Pt loading: 2.3 μg/cm^2
Pt mass activity: 1.13 mA/ μg_{Pt} at 900 mV
Specific activity: 0.54 mA/cm$^2_{ESA}$
$E'_{1/2}$ = 874 mV vs RHE

After 10K cycles:

E.S.A, No observable loss

Pt mass activity: 0.72 mA/ μg_{Pt} at 900 mV
Specific activity: 0.34 mA/cm$^2_{ESA}$
$E'_{1/2}$ = 859 mV vs RHE

Almost all the loss occurred within the first 5K cycles

Project Timeline

START July 2009 — Sept 2010 — Sept 2011 — Sept 2012 — **END** Sept 2013

TASK 1
Syntheses: Pt ML on Nanorods, Nanowires of selected metals, alloys, CNT; refractory metal NPs
Tests: RDE, MEA activity, stability (preliminary)
Scale-up: Synthesis 20g of selected catalyst (JMFC delivers) $50 cm^2$ single-cell tests
Go/No Go
scale-up not successful – return to start
BNL, MIT, JMFC

TASK 1
Scale-up: Improved scale-up, single-cell tests $50 cm^2$,

Catalyst, MEAs delivered to UTC for durability testing
Go/No Go
activity < 0.44 A/mg_{Pt}, - return to start
BNL, JMFC, MIT, UTC

TASK 2
Syntheses: Metalized refractory metal nanorods and CNT, tests, scale up, single-cell tests
BNL, MIT, JMFC

TASK 3
MEAs: Catalyst selection from 1 and 2**;** scale up to 50-100g , catalyst layer optimization, MEA fabrication, tests cell >$50 cm^2$. H_2/AIR testing
JMFC delivers optimized MEAs to UTC
Go/No Go
activity < 0.44A/mg_{Pt} or durability low - end project
JMFC, BNL,UTC, MIT

TASK 4
Stacks: MEAs for Stacks delivered to UTC
Ex situ MEA testing

Stack built

Stack testing

UTC, JMFC, BNL, MIT