Platinum Monolayer Electrocatalysts for Oxygen Reduction Reaction

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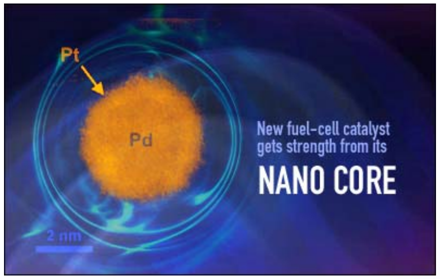
Outline



- Introduction on fuel cells, electrocatalysis, existing developments and remaining obstacles to commercialization

- Platinum monolayer electrocatalysts, the main properties, synthesis, factor affecting the activity and stability- core – shell interactions.

- Tuning the activity and stability by core-shell interactions Several illustrations: Nanowires, Tetrahedral nanoparticles, Hollow Pd nanoparticles, Alloys as cores

- Fuel cell tests, long-term stability, self healing effects

- Conclusions

- Acknowledgements

Fuel Cells for Sustainable Energy Future

Fuel cells, an electrochemical power source that converts directly chemical energy of fuel into electrical energy, have several outstanding properties:

- **High efficiency (theoretical, close to 100%, practical 50-60%)**
- **High power density**
- **Ideal for automotive application**

Main Reactions of Electrochemical Energy Conversion

Cathode: O_2 reduction reaction (ORR) (slow)

$O_2 + 4H^+ + 4e \rightarrow 2H_2O$ $E° = 1.23V$

Anode: H_2 oxidation (HOR) (fast)

$H_2 \rightarrow 2H^+ + 2e^-$ $E° = 0.0V$

Anode: Methanol oxidation (MOR) (slow, CO strongly ads.)

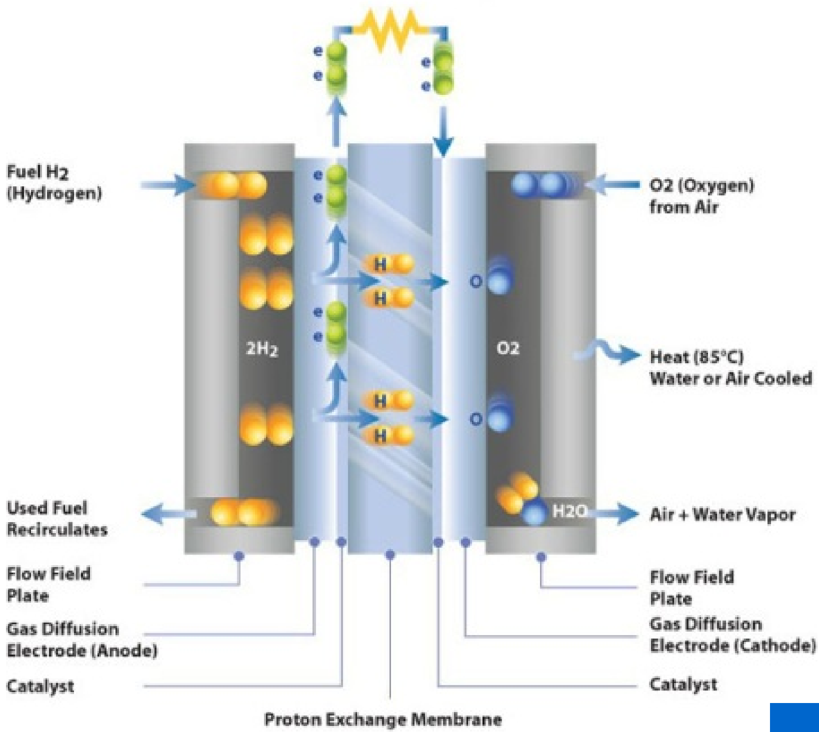
$CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-$ $E° = 0.016V$

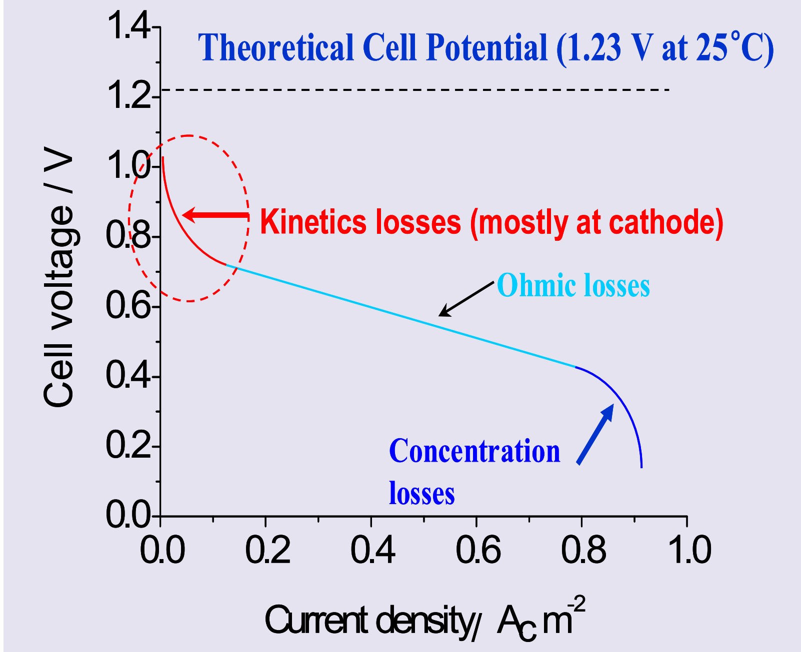
Anode: Ethanol oxidation (EOR) (slow, partial oxidation)

$C_2H_5OH + 3H_2O \rightarrow 2CO_2 + 12H^+ + 12e^-$ $E° = 0.084V$

Fuel Cells for Sustainable Energy Future

Proton exchange membrane fuel cell (PEMFC)





With high efficiency and clean operation (H_2O is the reaction product), fuel cells will prolong the availability of fossil fuels and improve quality of the environment.

Obstacles caused by slow ORR kinetics:

1. Efficiency below theoretical, even for Pt, the best catalyst
2. High Pt content in cathode; in addition to
3. Insufficient stability of Pt

http://www.ballard.com

Fuel Cells for Sustainable Energy Future

The last two decades brought considerable advances in Fuel Cell Electrocatalysts by:

i) increasing activity ii) decreasing loadings and iii) increasing their stability

Some improvements are, however, needed to remove the remaining obstacles to their commercialization.

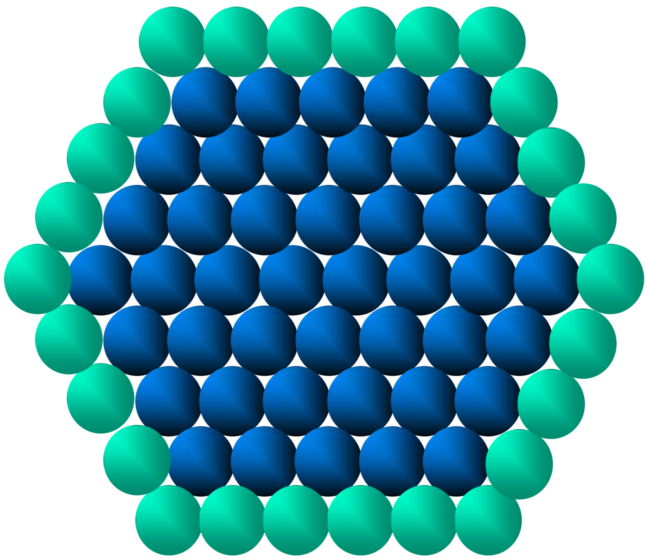
Several promising current approaches to address these problems include:

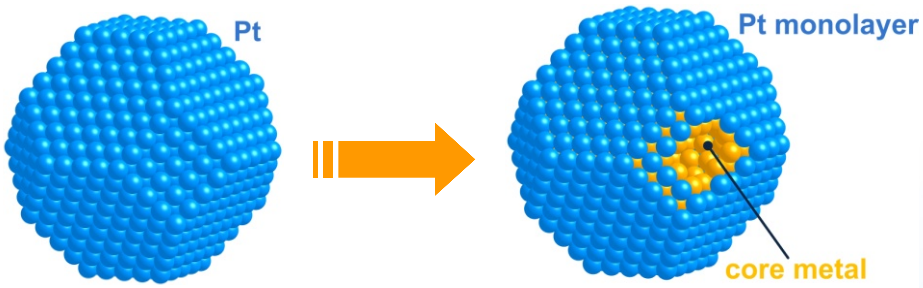
1. **Segregated alloys (Markovic, Stamenkovic)**
2. **Nanostructured Pt films (Debe, Atanasoski)**
3. **Non-noble metal complexes (Zelenay)**
4. **Heat-treated macrocyclics (Dodelet)**

Our approach: Platinum Monolayer Electrocatalysts

Pt Monolayer Electrocatalysts

Pt_{ML}/M





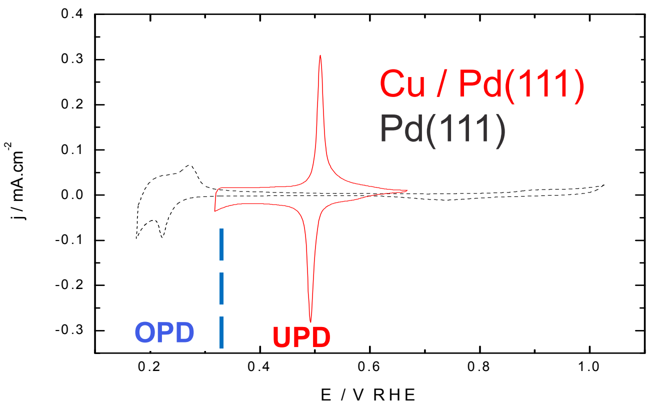
For ~5 nm Pt nanoparticles (NPs), ~25% of atoms are on the surface

- Ultra-low Pt content
- High utilization of Pt
- Tunable activity via strain and/or electronic effects from the interaction between Pt_{ML} and substrates

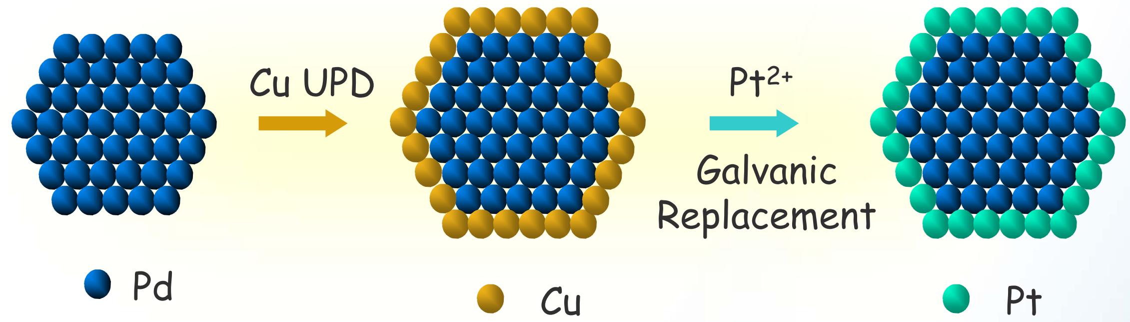
This electrocatalyst is commercially available from N.E. ChemCat Co., based on four patents licensed by BNL to NE CC

Adzic, Zhang, Sasaki, Vukmirovic, Shao, Wang, Nilekar, Mavrikakis, Valerio, Uribe, Top. Catal. 46 (2007), 249

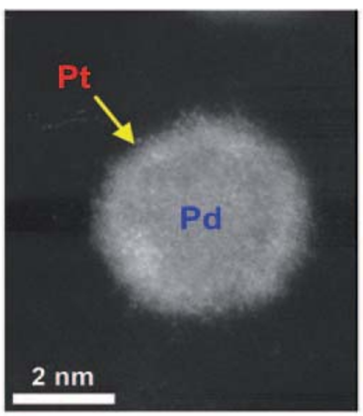
Structure-controlled syntheses of Pt Monolayer Electrocatalysts

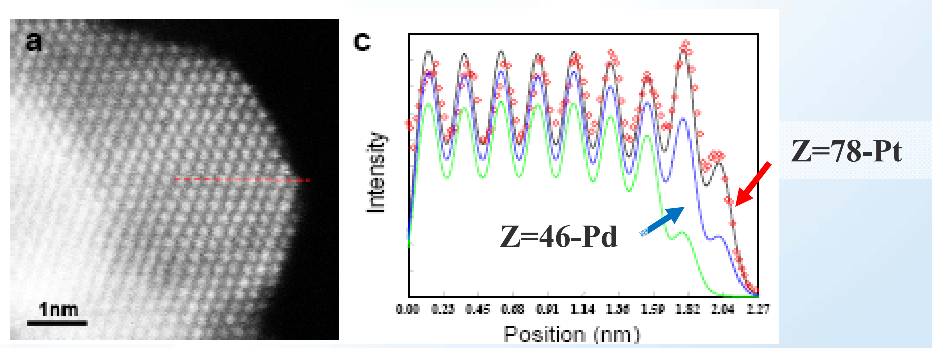


Brankovic et al. Surf. Sci., 477, L173 (2001)



Galvanic displacement of Cu ML deposited at underpotentials (UPD) - a ML-limited process)

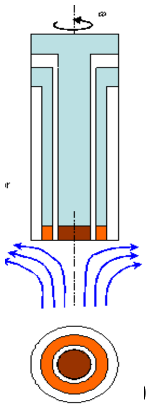




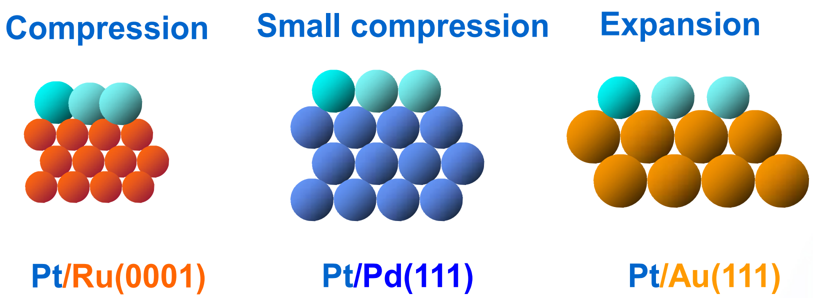
STEM, EELS evidence of a Pt ML shell

Adzic, Zhang, Sasaki, Vukmirovic, Shao, Wang, Nilekar, Mavrikakis, Valerio, Uribe, Top. Catal. 46 (2007), 249

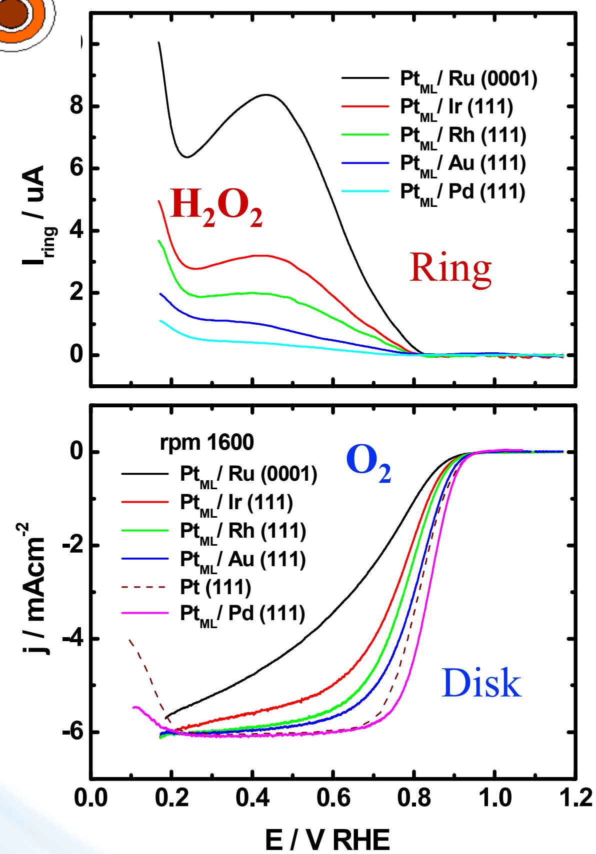
Factors affecting Pt_{ML} ORR Activity

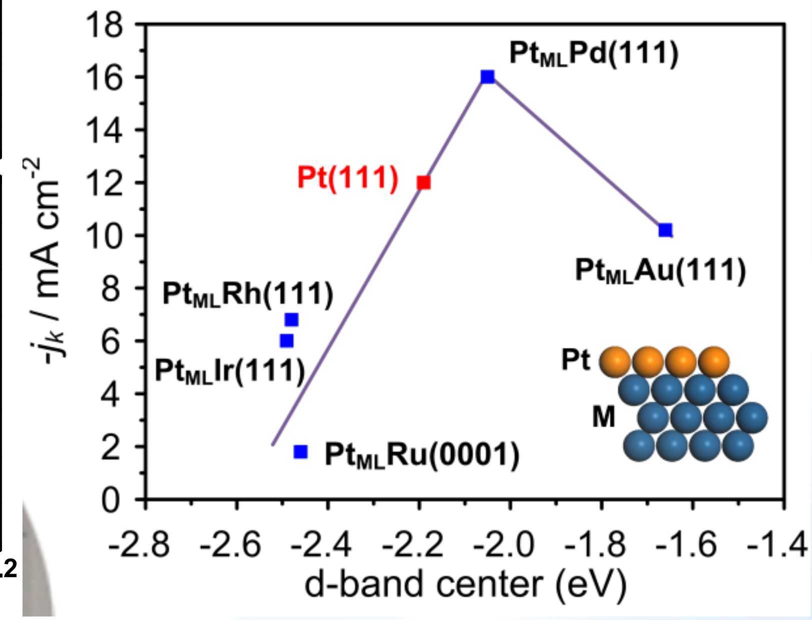


Core-induced surface strain



strain
↓
d-band center shift
↓
E_{OH}





Trends in surface reactivity can be described by the position of d-band center (εd)

Small contraction of a Pt lattice (*decreased reactivity)* makes it more active for the ORR.

Adzic, Zhang, Sasaki, Vukmirovic, Shao, Wang, Nilekar, Mavrikakis, Valerio, Uribe, Top. Catal. 46 (2007), 249
Zhang, Vukmirovic, Xu, Mavrikakis, Adzic, Angew. Chem. Int. Ed. 44 (2005), 2132

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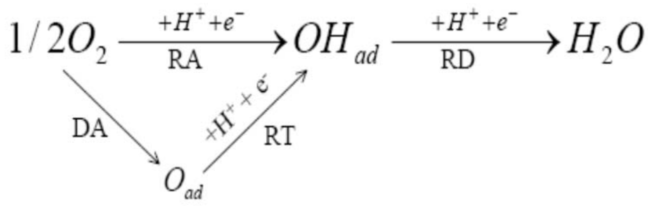
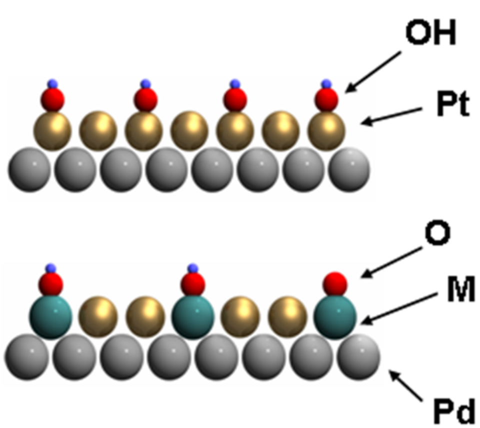
Decreasing the OH_{ads} at Pt ML electrocatalysts

The concept of the OH –OH repulsion

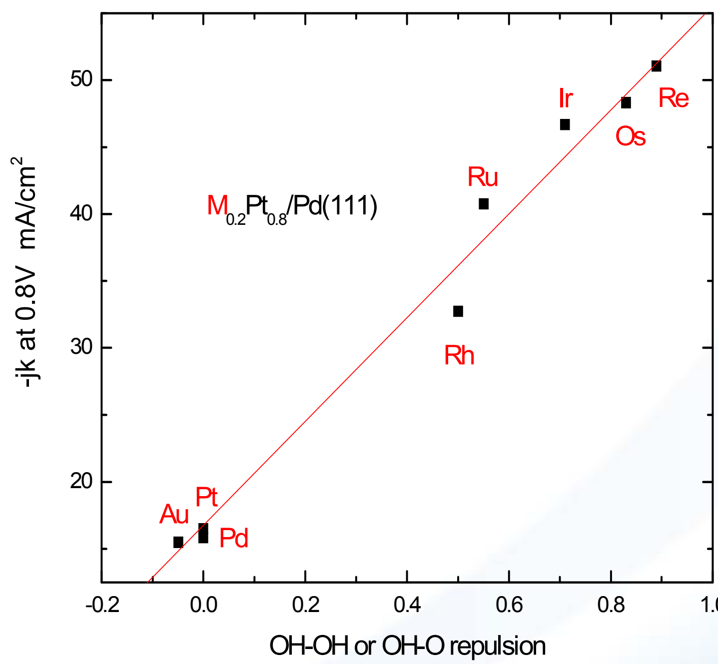


A consensus: High OH_{ads} coverage from H_2O reduces the ORR rate : **Tarasevich 1977, Adzic 1989, Gottesfeld 1989**

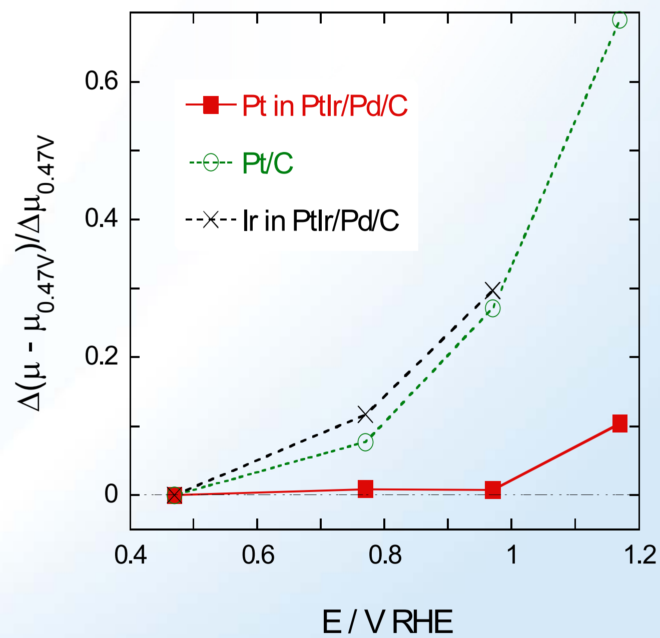
Sketch of the OH-OH or OH – O repulsion



OH-OH, or OH-O repulsion from DFT



XANES evidence that Pt is stabilized against oxidation

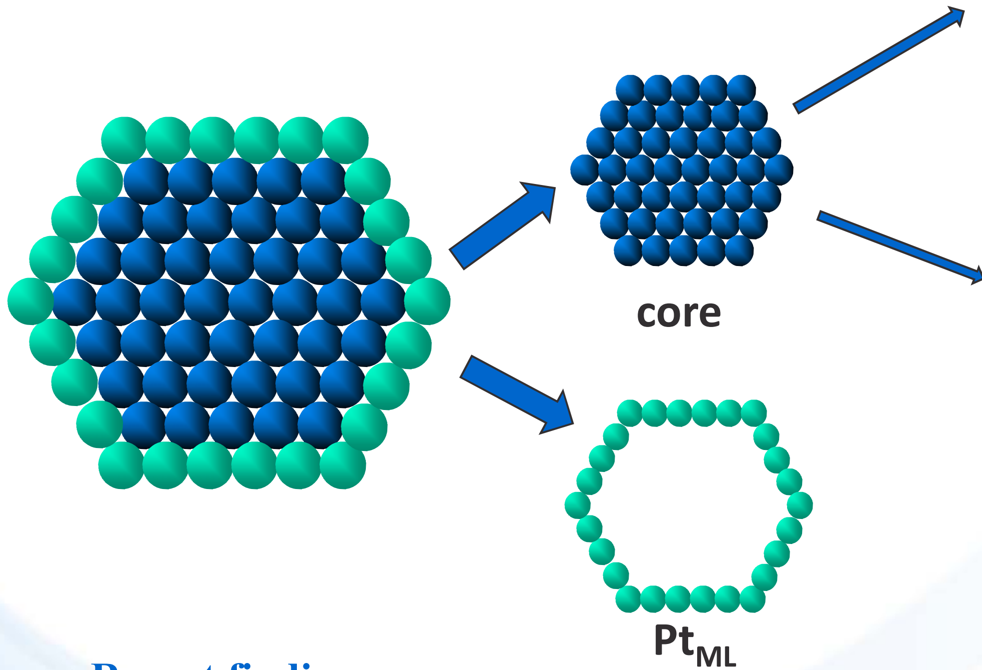


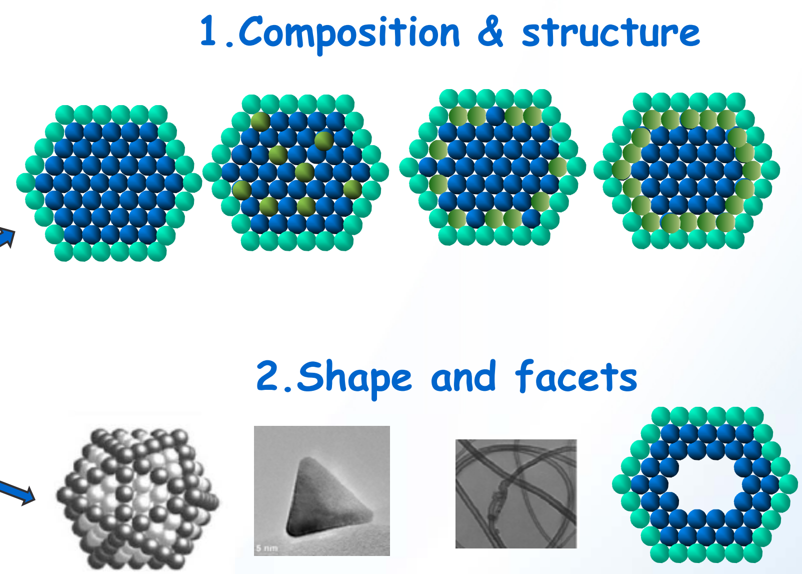
J. Am. Chem. Soc. Comm. 127 (2005) 12481

Activity vs. OH-OH, or OH-O repulsion for Pt-M mixed-monolayer ($Pt_{0.2}$-$M_{0.8}$).

Tuning the activity of Pt_{ML} electrocatalysts by core - shell interaction

Geometric and electronic effects:
- to induce a small contraction in PtML;
- small number of low-coordination sites
- smooth core surfaces (111) oriented
- weak bonding of OH



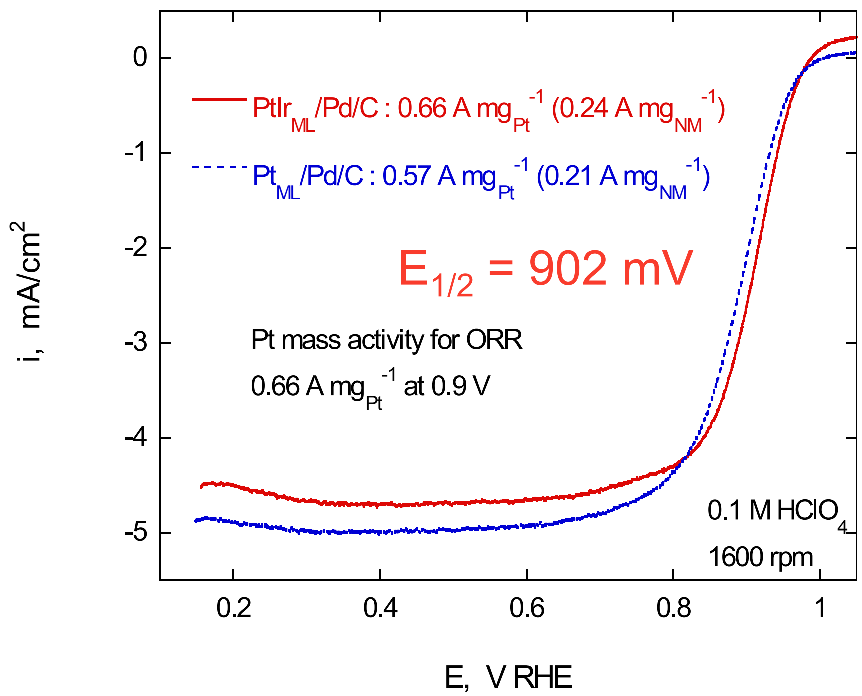


Recent findings:
- **Particle size-induced surface contraction of a top ML (affects the BE_O; facet – dependent)**
- **Coordination-dependent surface atomic contraction**

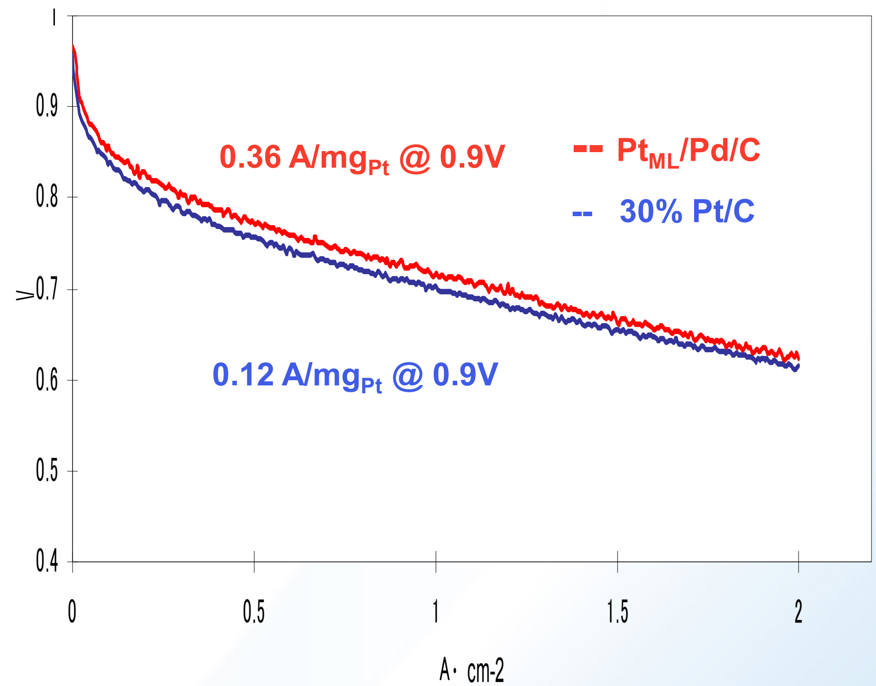
Wang, J. X., H. Inada, L. Wu, Y. Zhu, Y. Choi, P. Liu, W-P. Zhou, and R. R. Adzic, J. Am. Chem. Soc., 131, 17298 (2009).

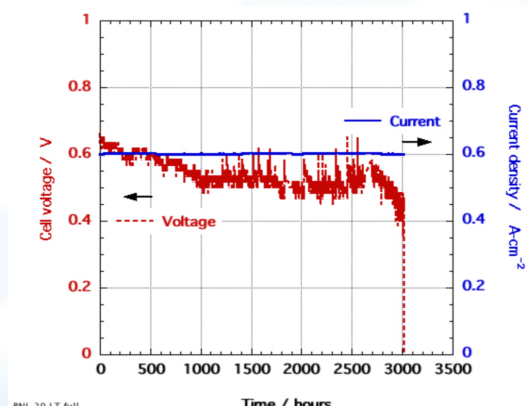
High Activity and Stability of Pt ML Electrocatalysts

Pt_{ML}/ Pd/C   Pt-Ir $_{(4:1)ML}$/ Pd/C



Fuel Cell Tests

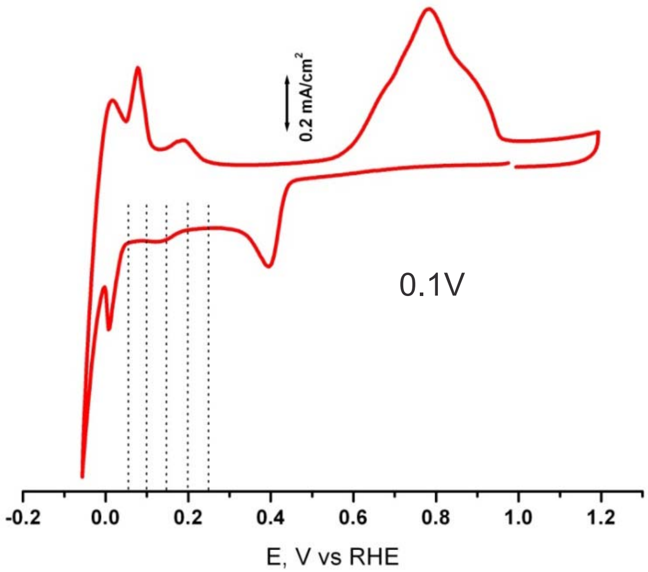




Current density of 2 A/cm² at 0.63 V; 0.36 A/mg_{Pt} at 0.9V; commercial catalyst, Pt/C has 0.12 A/mg_{Pt} @ 0.9V
60,000 potential cycles - small loss of activity

3000 hour fuel cell test; H_2/Air 0.6A/cm², 80C membrane failure; 18% performance loss at LANL

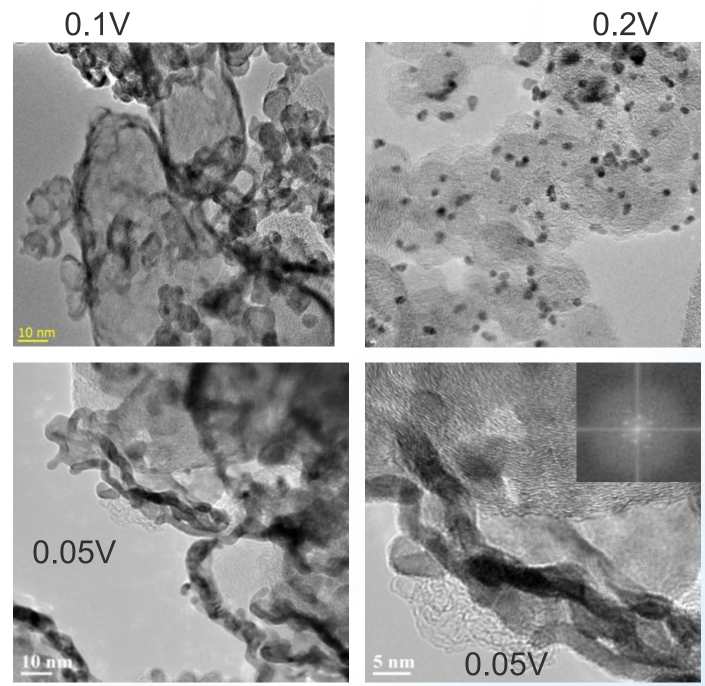
Nanowires and nanorods as support
Electrodeposition of Pd nanowires and nanorods on carbon



Deposition of Pd on carbon surfaces in 0.1M $HClO_4$ with 1mM Pd^{2+}.

The growth mechanism: H_{upd} in Pd acts as reducing promotor at terraces, while chlorides adsorb at low-coordination sites and block growth in that direction.

Nanowires have smoother surface, less low-coordination sites, edges, more (111) facets.



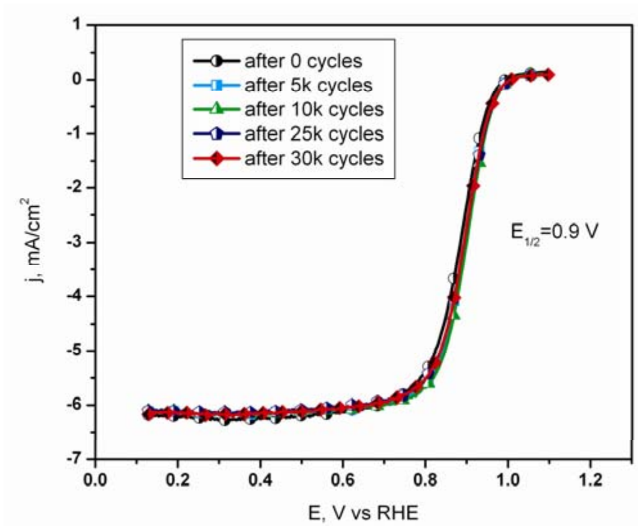
FFT of the TEM image showing (111) pattern of Pd(111)

The type of deposit: NPs, NWs or NRs, depend on the potential and Pd ion concentration

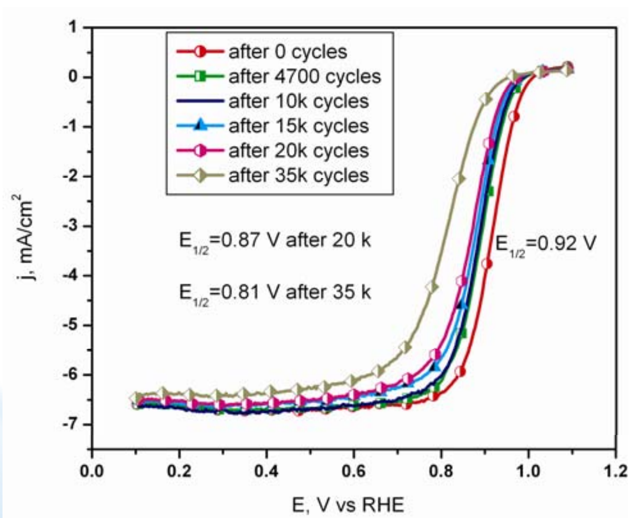
Scale-up is simple: Cell for 25 cm^2 electrode was constructed.

Bliznakov et al. JES, in press

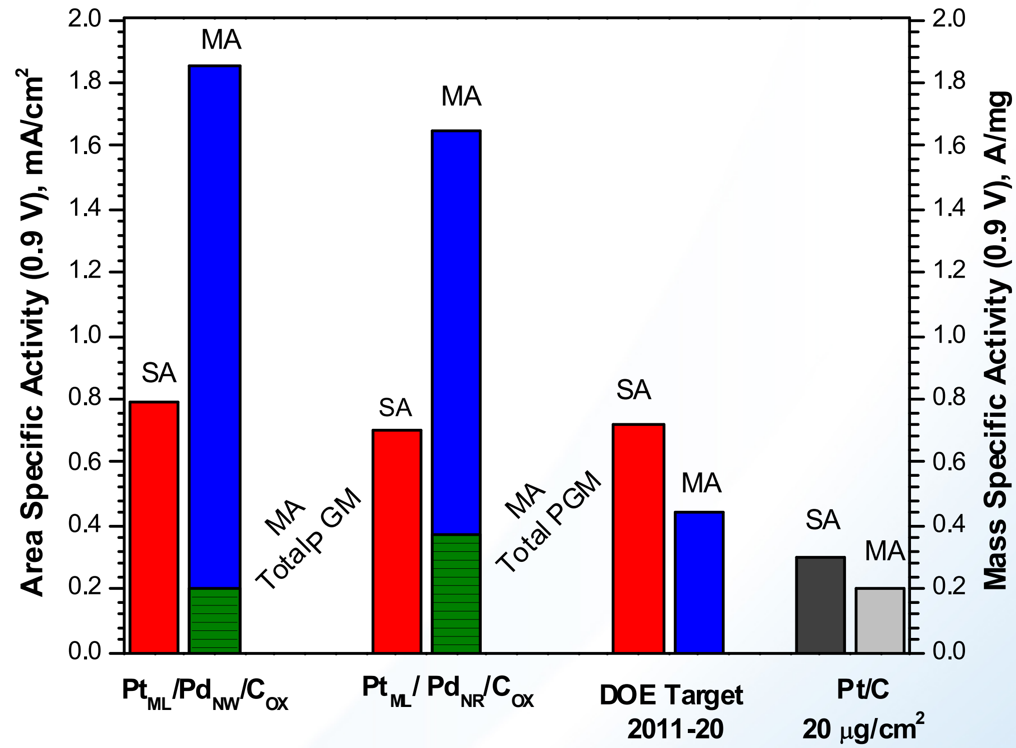
Polarization ORR curves measured on $Pt_{ML}Pd_{NW}/C$ and $Pt_{ML}Pd_{NR}/C$



Polarization ORR curves measured on $Pt_{ML}Pd_{NW}/C$



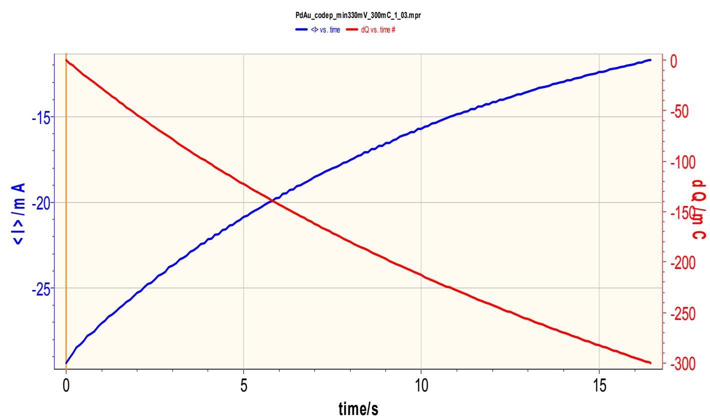
Polarization ORR curves measured on $Pt_{ML}Pd_{NR}/C$



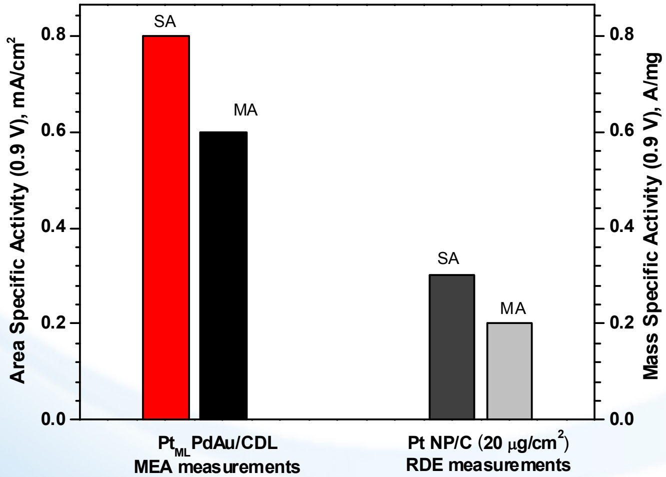
Comparison of the mass and specific activities

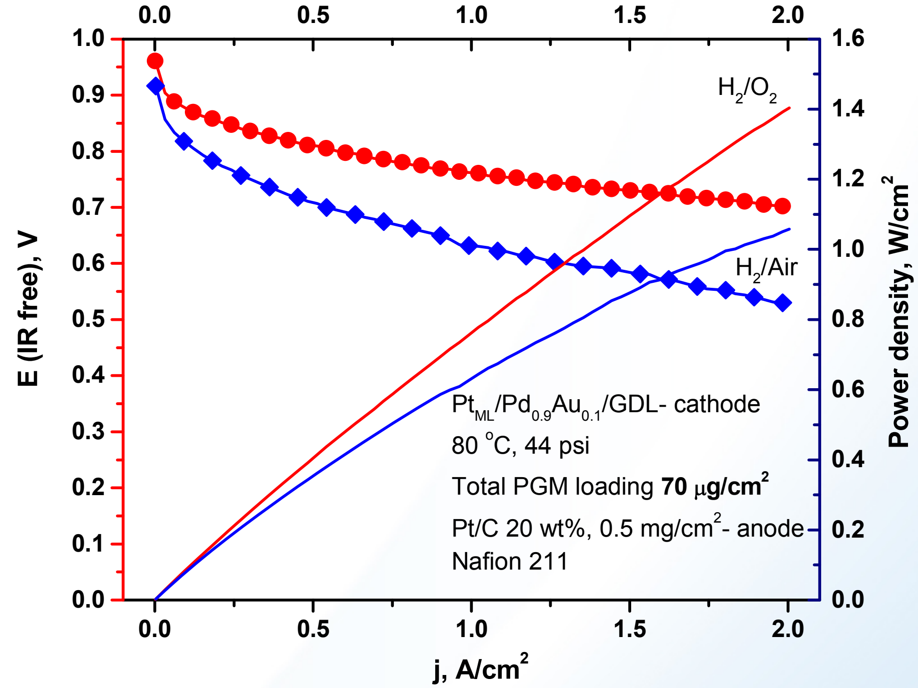
Electrochemical deposition of PdAu NRs, $Pt_{ML}/Pd_{0.9}Au_{0.1}/GDL$

Current and charge transients



MEA test vs. RDE

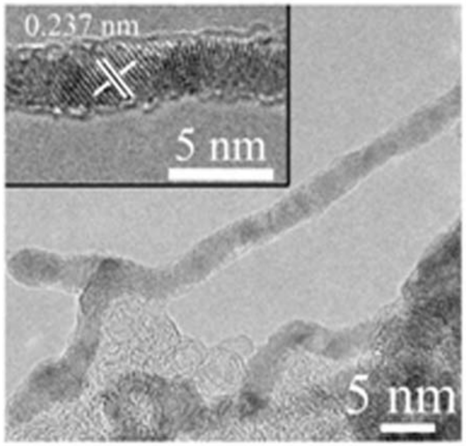




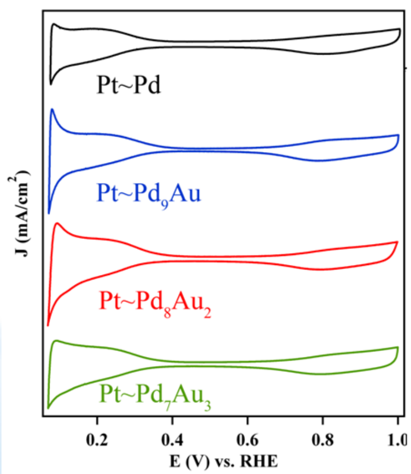
PGM content approx. 70µg/cm²

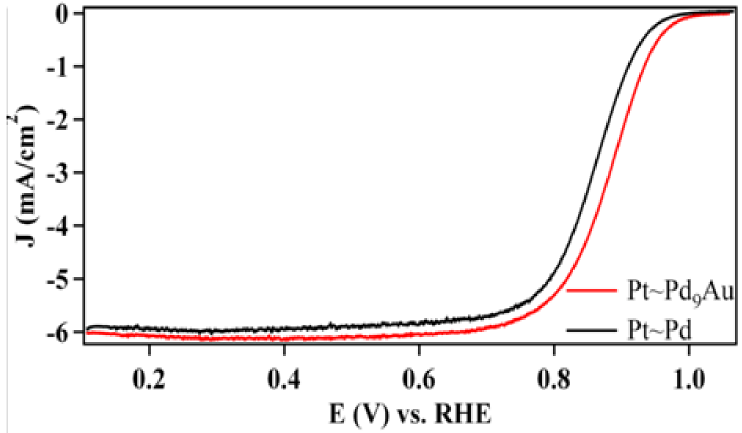
Electrochemical deposition of NRDs and NWs cores with Pt_{ML} deposition using galvanic displacement of Cu ML facilitates close to 100% utilization of Pt.

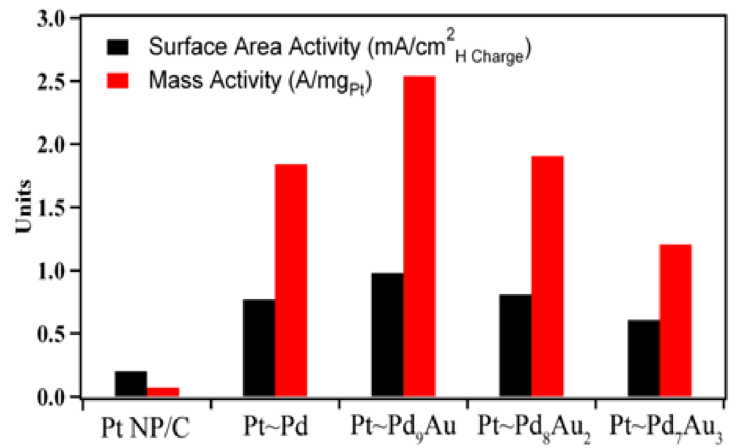
Synthesis of the ultrathin bimetallic PdAu nanowires



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



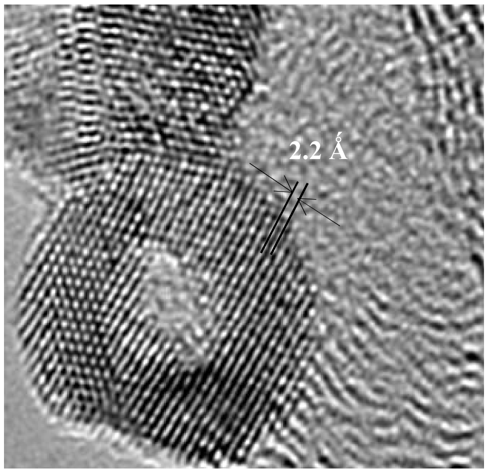




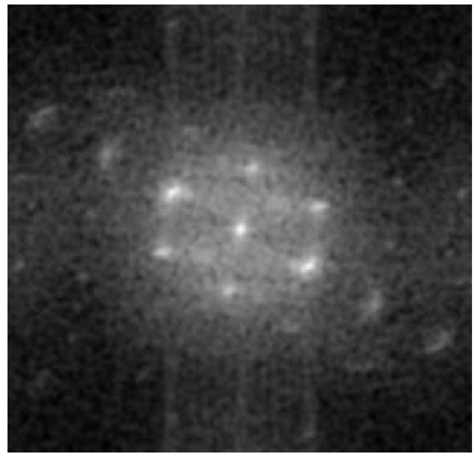
The phase transfer catalyst dodecyltrimethyl ammonium bromide (DTAB) is used to allow for co-solubilization of $NaBH_4$ into both the aqueous and organic phases.

With Koenigsmann and Wong

Enhanced ORR kinetics on electrodeposited Pt / Pd nanowires



TEM image of toroidal particle formed by connecting wires' ends. 2.2 Å is the interplanar distance of Pd(111).

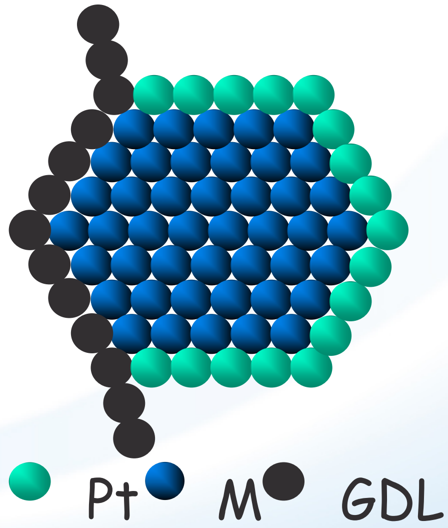


FFT of the TEM image left showing the (111) pattern of Pd(111).

A very high activity of Pt ML on Pd nanowires is due to:

1. The dominant (111) pattern of Pd
2. Very high utilization of Pt

This result confirms the (111) facets of Pd are the best surface for the ORR.



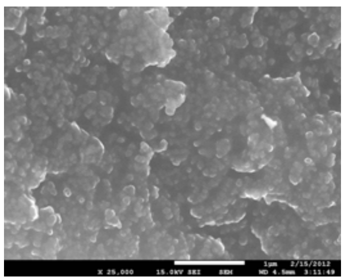
Model for 100% utilization of Pt in Pt_{ML} catalysts with cores electrodeposited on GDL

Decreasing the content of Pd in cores
Refractory metal alloys as cores - NiW

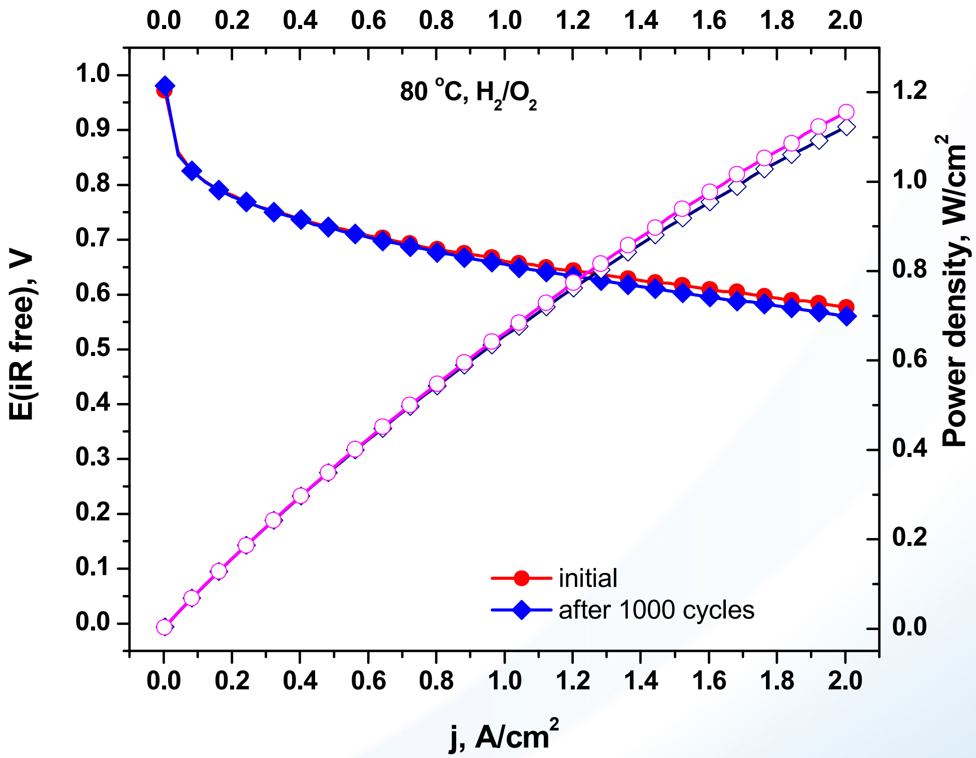
Pt_{ML}/Pd/NiW
NiW obtained by co-deposition of Ni and W on gas diffusion layer (GDL)

Ni is partially displaced by Pd from the top layer of NiW. Electrode : $5cm^2$

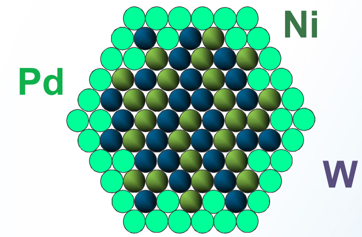
SEM image after NiW deposition on GDL.



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



< 40 μg_{Pt} /cm^2

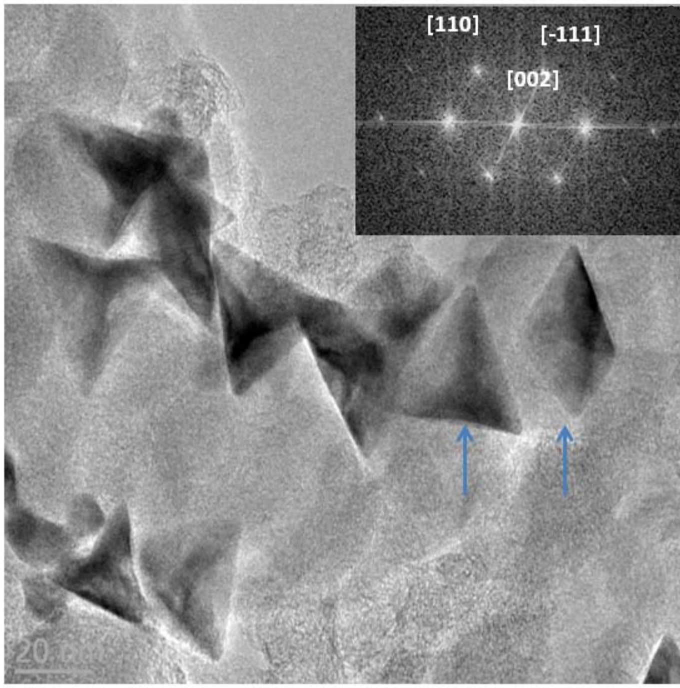


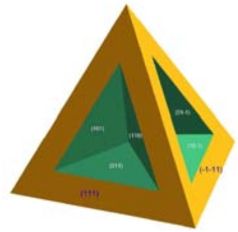
Model of NiW core with a partially displaced Ni by Pd

Concave Tetrahedral Pd Nanocrystals

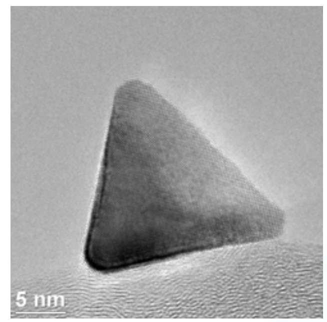
HRTEM

SAED

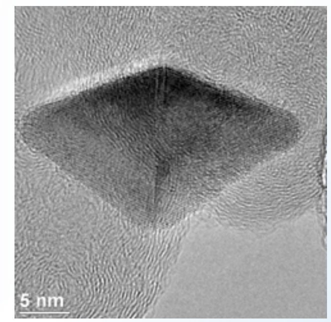




Dominant (111) and (110) facets



tetrahedral



octahedral

~ 30nm

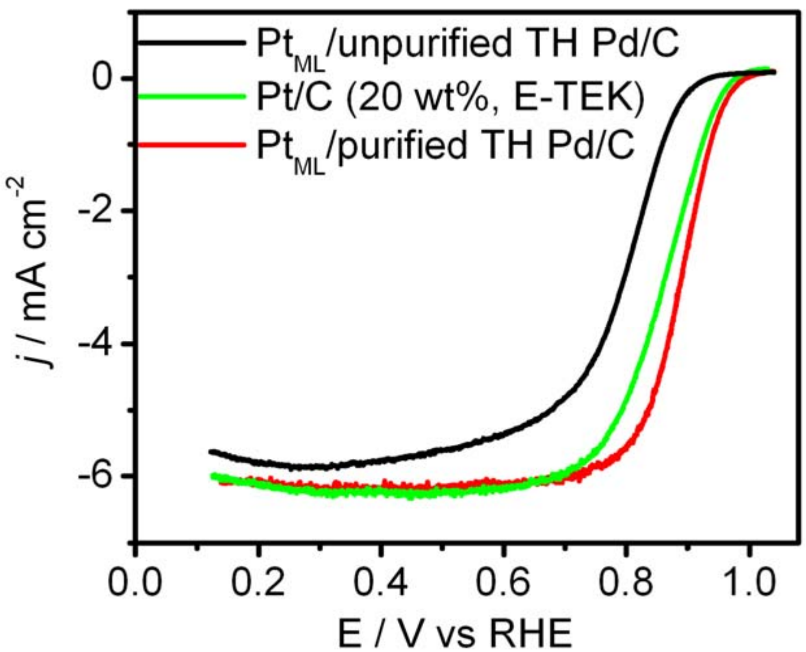
Hydrothermal preparation

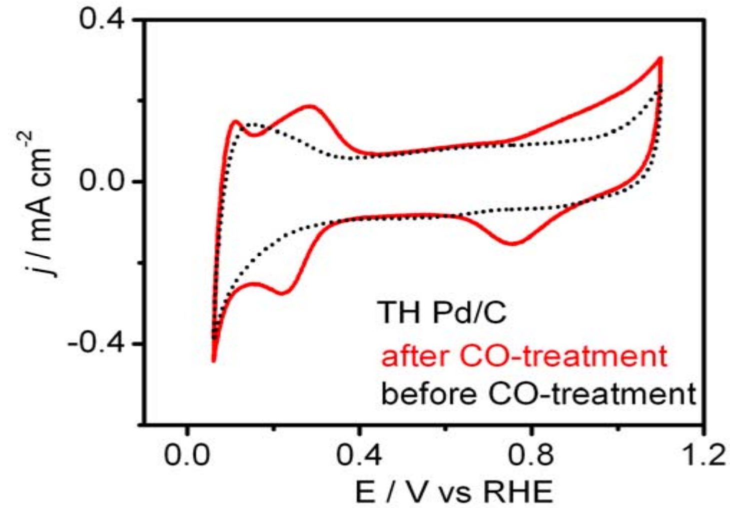
$Pd(acac)_2$ + Formaldehyde + PVP
(Pd salt) (Capping (100)) (Surfactant)

Surfactant: poly(vinyl pyrrolidone) (PVP)

J. Electroanal. Chem. (2011) In press

Concave Tetrahedral Pd Nanocrystals

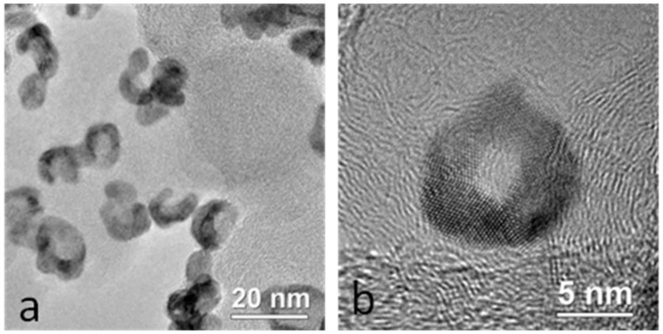




	Pt(111)	Pt$_{ML}$/TH Pd/C
Half-wave potential (V)	803	888
ECSA (m^2/mg_{Pt})	205	15
Pt specific activity (mA/cm^2_{Pt})	0.8	0.53
Pt mass activity (A/mg_{Pt})	1.6	0.82

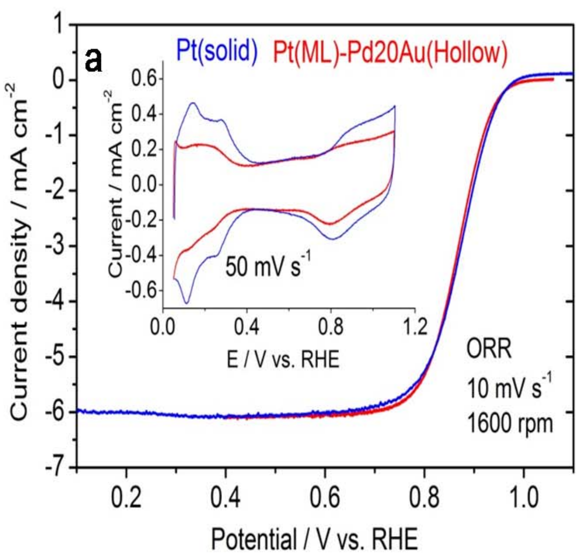
J. Electroanal. Chem. (2011) In press

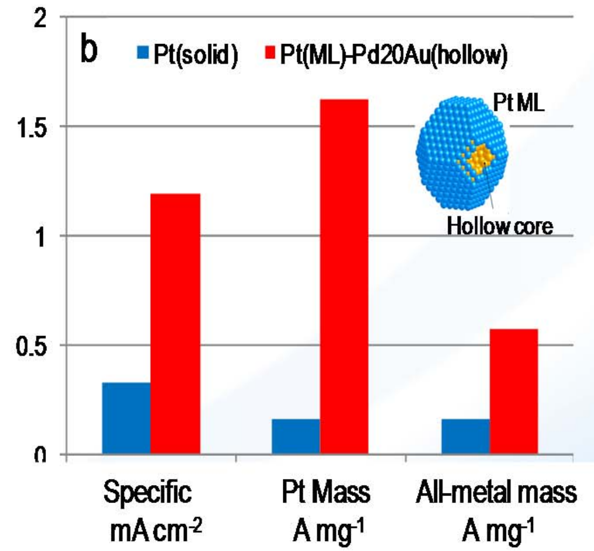
Pt monolayer on hollow Pd nanoparticles



TEM images of Pt(ML)-$Pd_{20}Au$ hollow particles fabricated using Ni nanoparticles as templates.

Core metals	SA [mA cm^{-2}]	Pt mass [A mg^{-1}]	Pt+Pd+Au mass [A mg^{-1}]
$Pd_{20}Au$	0.85	1.62	0.57
Pd solid	0.50	0.96	0.25
Pt solid	0.33	0.16	0.16





High activity is due to smooth surface morphology, and hollow-induced lattice contraction.

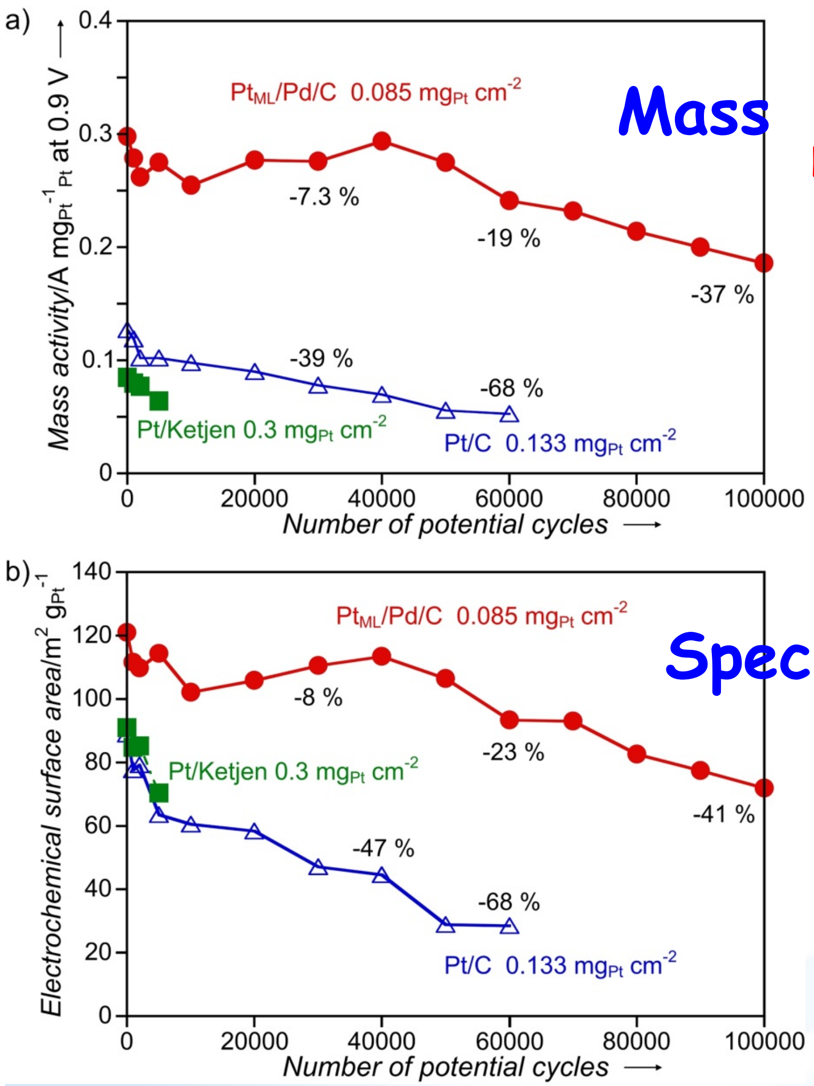
Scale-up synthesis is being developed using:

1. **The cell for electrodeposition of Pd NWs**
2. **The microemulsion method.**

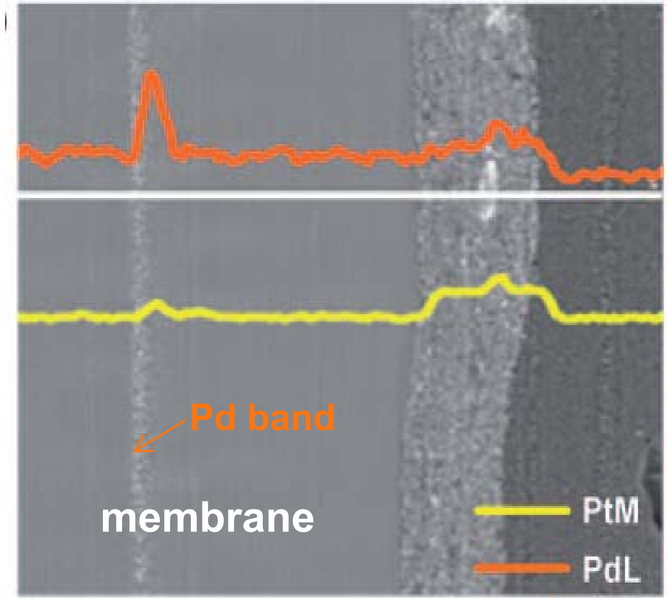
Zhang et al. Catalysis Today, htpp://dx.doi.org/10.1016/j.cattod.2012.03.040

Fuel Cell Stability Tests of $Pt_{ML}/Pd/C$

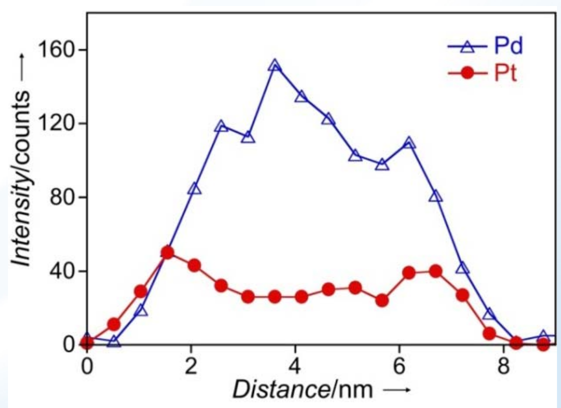
Stability after **100,000** potential cycles



DOE target 2015: <40% loss after 30,000 cycles



SEM image and EELS line scan analysis



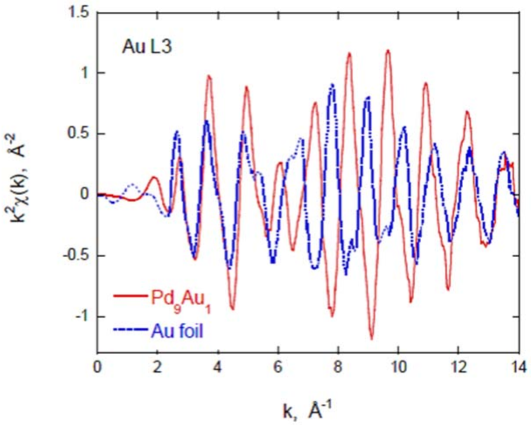
Angewandte Chemie International Edition, 49 (2010) 8602

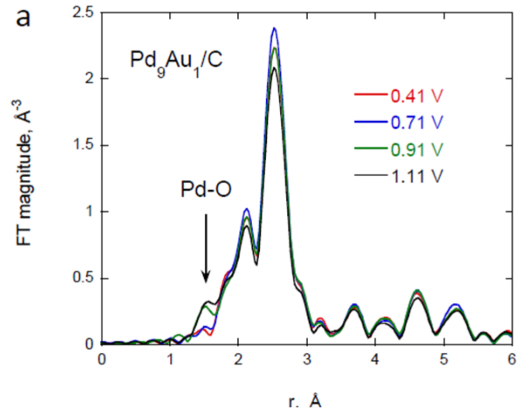
Stability: 30 s at 0.7 and 0.9 V

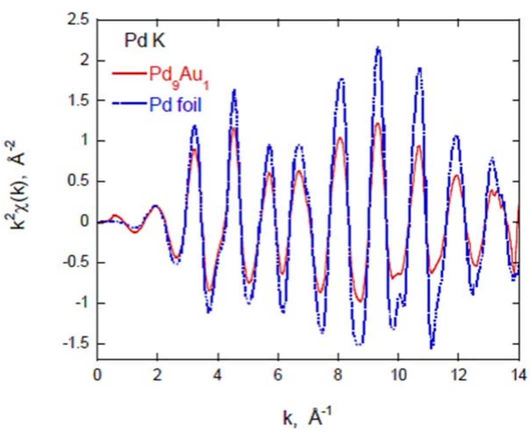
BROOKHAVEN NATIONAL LABORATORY

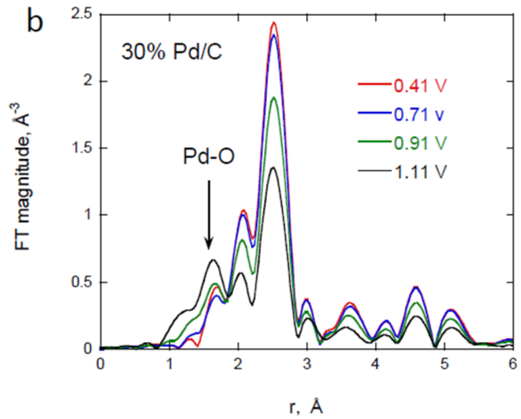
Pd_9Au/C nanoparticle cores for Pt monolayer

In-situ XAS









Fitting

$N_{Au\text{-}Au}$	2.4 (±1.6)
$N_{Au\text{-}Pd}$	8.0 (±1.1)
$N_{Pd\text{-}Pd}$	9.2 (±0.4)
$N_{Pd\text{-}Au}$	0.9 (±0.13)

Au-Au	2.771 Å
Au-Pd (= Pd-Au)	2.760 Å
Pd-Pd	2.756 Å

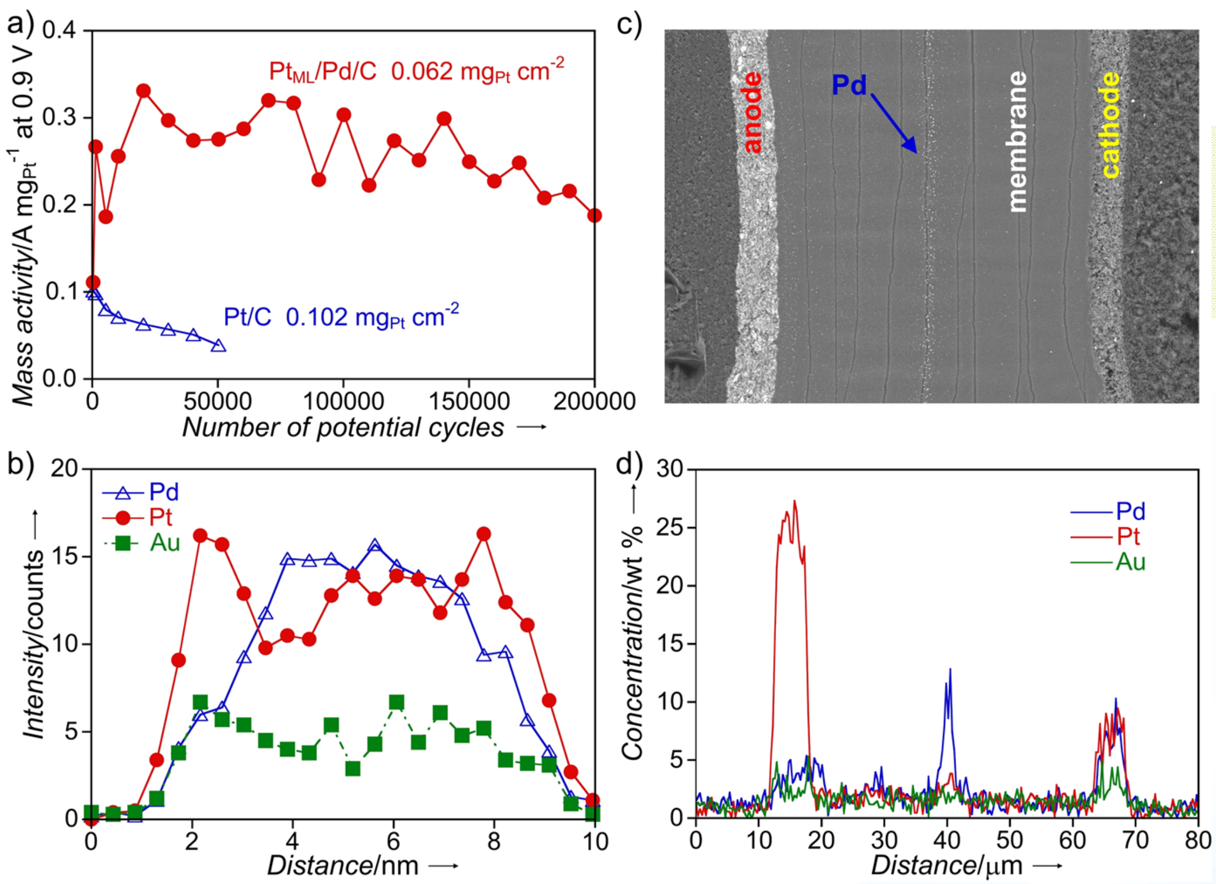
The fitting result indicates the Pd-Au (pseudo) solid-solution

Based on the inhibition effect of Au on Pt (Science, 315 2007, 220), we synthesized PdAu (9:1) nanoparticles for Pt ML cores.

Significant retardation of Pd oxidation for Pd_9Au/C compared with Pd/C.

Nature Chemistry, submitted

Fuel cell test of $Pt_{ML}/Pd_9Au/C$ electrocatalyst



Stability after **200,000** potential cycles

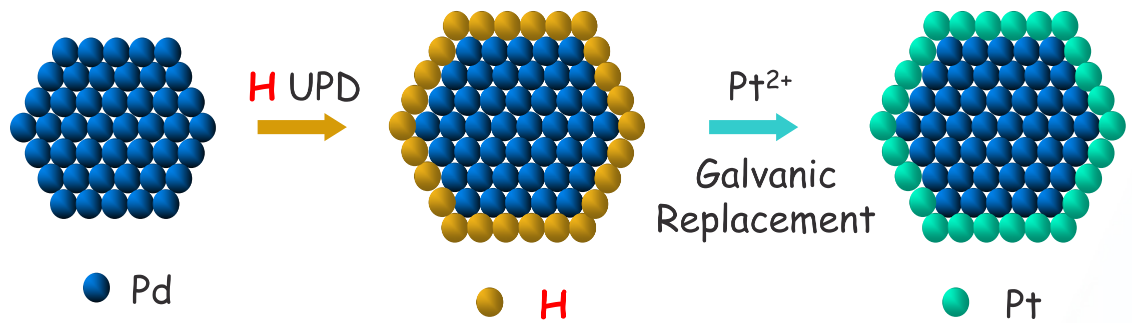
Core-protected core-shell electrocatalysts

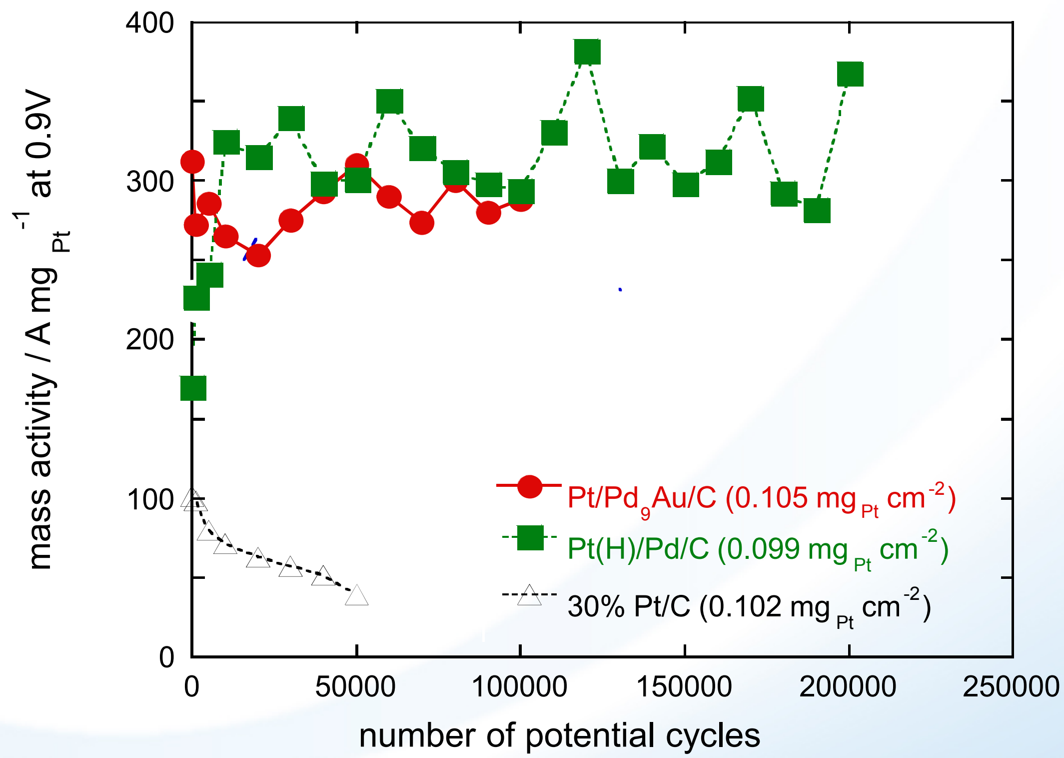
$Pt_{ML}/Pd_9Au/C$ contains 0.062 mgPt cm^{-2}
Pt/C 0.102 mgPt cm^{-2}

The potential limits were 0.6 and 1.0 V; sweep rate of 50 mV s^{-1}. 80°C.

DOE target: Pt mass activity : < 40% loss of for 30,000 cycles;
$Pt_{ML}/Pd_9Au/C$: 30% loss after 200,000 cycles;
Pt/C: a terminal loss before 50, 000 cycles.

Pt Monolayer deposition via H_{upd}

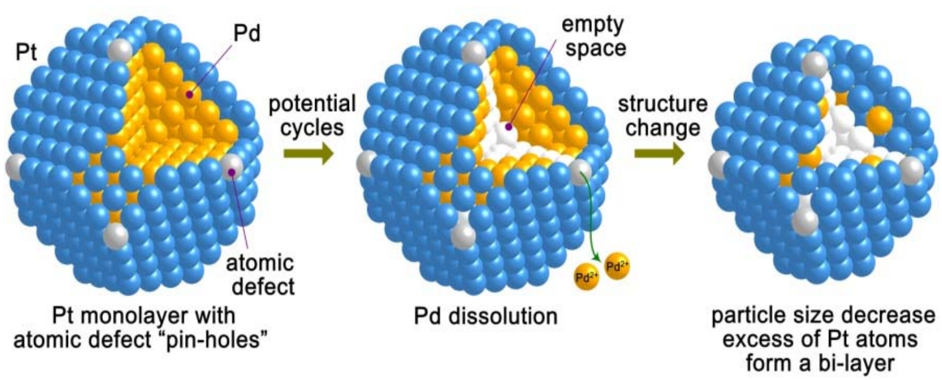


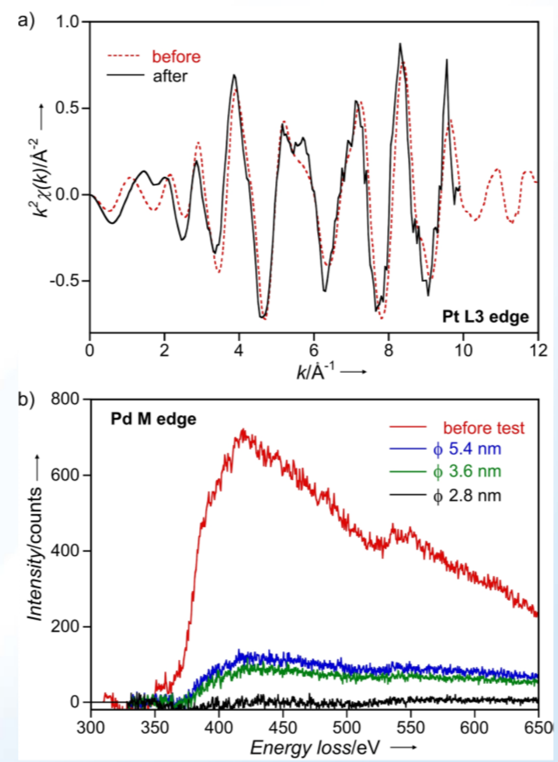


New mechanism of stability of core-shell electrocatalysts: Shell protected by the core and self-healing effect

1. **PtOH formation shifted positively.**
2. **Contraction of Pt and Pd lattices induced by loss of Pd - self-healing effect; hollow may form**
3. **Cathodic protection effect.**

Data supported by EXAFS, XANES, EELS, EDS, RDE, DFT results.



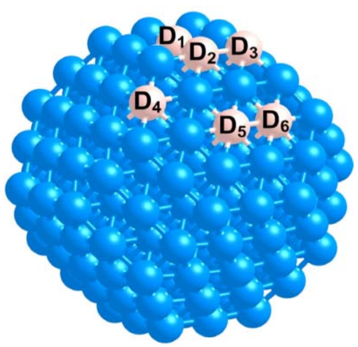


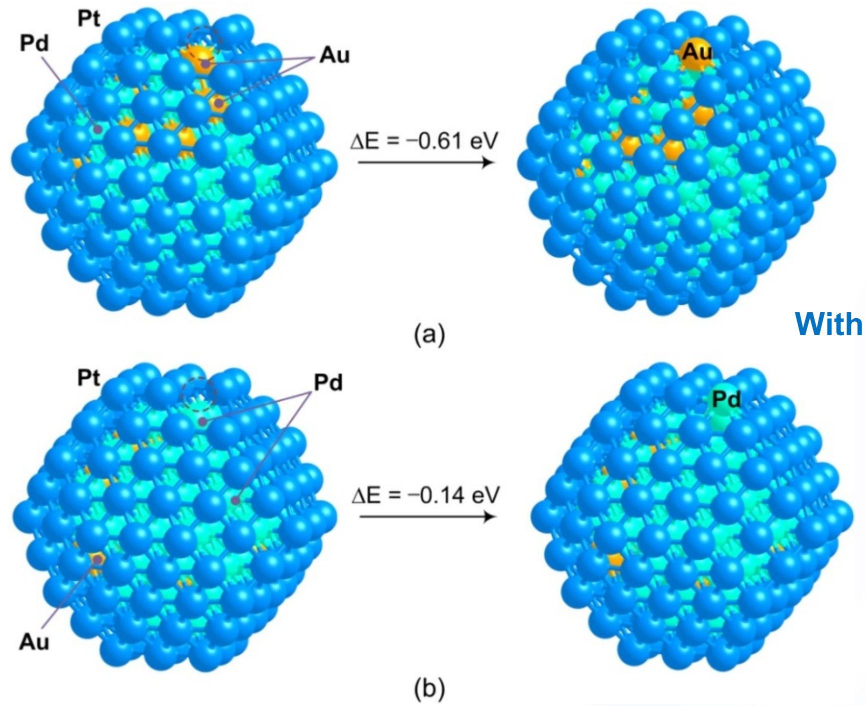
Pd dissolution precludes dissolution of Pt, which would readily occur and a Pt ML would disappear.

The structure of Pt shells was almost retained after the tests

25

Stability of Pt_{ML}/Pd_9Au_1 from DFT calculations



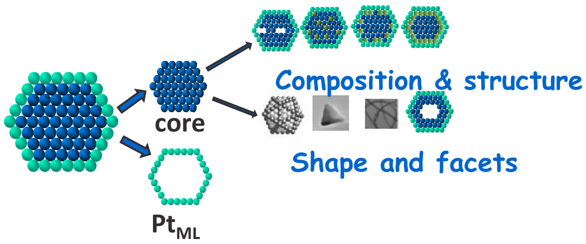


With Choi and Liu

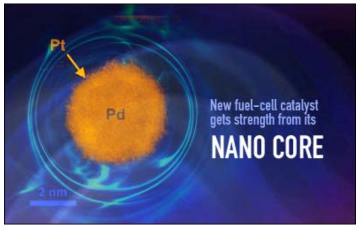
1. **Model a sphere-like Pt ML on Pd_9Au_1 random alloy core (*ca* ϕ1.7 nm)**
2. **Introduce a defect (vacancy) in the Pt ML at vertex (D_3)**
3. **Calculate energy changes (ΔE) when Au or Pd atom diffuses from core to the defect site (ΔE_{Au} = -0.61 eV, ΔE_{Pd} = -0.14 eV)**

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

This is in agreement with (Zhang, Sasaki, Sutter, Adzic et al., Science, 315 (2007) 220)



Conclusions



- $Pt_{ML}/Pd_9Au/C$ and $Pt_{ML}/Pd/C$ are practical electrocatalysts.
- Self-healing-mechanism helps in providing stability of these catalysts.
- Pd alloys with refractory metals provide stable and inexpensive cores.
- Several new efficient syntheses include: electrochemical deposition of NWs, deposition of Pd NWs using simple surfactant, using ethanol as a medium and reactant, using UPD H.

- E_{OH} plays an vital important role in the activity and stability of Pt_{ML} for ORR and can be tuned via the interaction between Pt_{ML} and various substrates.
- Significant improvement of activity and stability over those of Pt/C.
- Flexibility of the core-shell structure enables the possibility of the further improvement.

Current Pt/C used in the laboratory tests: 400 μgPt/cm^2;

Pt_{ML} electrocatalysts: 40-80 μgPt/cm^2, 60-100 μgPd/cm^2;

For a 100-kW fuel-cell car, 1W/cm^2: 4-8g Pt + 10g Pd; current catalyst converter per car: ~ 5g Pt.

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

Acknowledgements

Collaborators

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