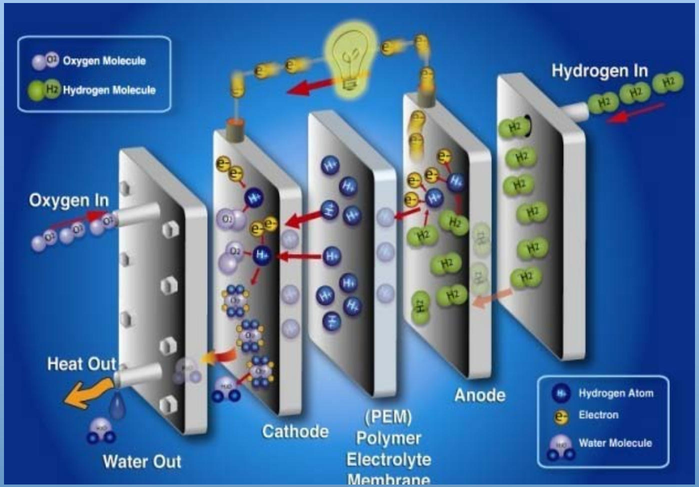
U.S. Department of Energy
Fuel Cell Technologies Program

U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

DOE’s fuel cell catalyst R&D activities

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Kick-off Catalyst Working Group
Arlington, VA
May 14, 2012

Department of Energy

Key Challenges

DOE's Hydrogen & Fuel Cells Program addresses the key challenges facing the widespread commercialization of fuel cells.

Technology Barriers*

Fuel Cell Cost & Durability

Targets*:

Stationary **(1–10 kW_e Residential CHP + DG with NG):**

$1,000-$1,700/kW depending on scale, 60,000-hr durability by 2020

Vehicles: **$30/kW, 5,000-hr durability**

Hydrogen Threshold Cost

$2 – 4 /gge, (dispensed and untaxed)

Hydrogen Storage Capacity

Target: > 300-mile range for vehicles—without compromising interior space or performance

Technology Validation:

Technologies must be demonstrated under real-world conditions.

Economic & Institutional Barriers

Safety, Codes & Standards Development

Domestic Manufacturing & Supplier Base

Public Awareness & Acceptance

Hydrogen Supply & Delivery Infrastructure

Market Transformation

Assisting the growth of early markets will help to overcome many barriers, including achieving significant cost reductions through economies of scale.

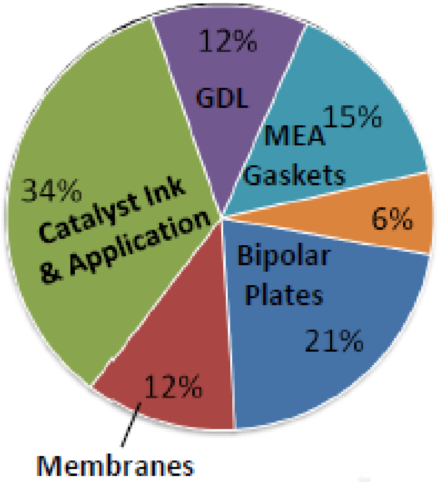
*** Targets and metrics are being updated**

Source: US DOE 10/2011

Catalysts dominate FC issues

- Catalyst is highest stack cost at high production volumes.

500,000 systems/year (2010)



- Learning Demonstration project indicates durability needs to be increased.
- Catalyst degradation is a key aspect of performance loss.

DOE is investigating

- **Cost reduction by decreasing Pt loading:**
  - Extended Pt surfaces
  - Platinum alloy catalysts, including core-shell concepts
  - Non-PGM catalysts
  - Hybrid catalysts
- **Durability improvement by:**
  - More stable structured alloys
  - Addition of catalyst functionality to reduce the severity of conditions at the electrodes during start-up/shut-down cycles
  - More stable catalyst supports

Evaluation of catalyst approaches

Approach	Extended Surfaces	Core-shell particles	Dealloyed Particles	Non-PGM Catalysts
Activity	+	+	+	Needs improvement
Durability	+	??	??	Needs improvement
Mass transport	-	+	+	?
Other		Activities in MEAs not as high as those in RDE experiments	Activities in MEAs not as high as those in RDE experiments	

Catalyst Targets (from MYRD&D Plan)

Characteristic	Units	Target 2017
Platinum group metal total content [a]	g / kW rated	≤ 0.125
Platinum group metal total loading [a]	mg PGM / cm^2 electrode area	≤ 0.125
Loss in catalytic (mass) activity [b]	% mass activity loss	< 40%
Catalyst support stability [c]	% mass activity loss	< 10%
Mass activity [d]	A / mg PGM @ 900 $mV_{iR\text{-free}}$	≥ 0.44
Non-Pt catalyst activity per volume of supported catalyst [d, e]	A / cm^3 @ 800 $mV_{iR\text{-free}}$	≥ 300

[a] PGM content and loading targets may have to be lower to achieve system cost targets.

[b] Durability measured in a 25-50 cm^2 MEA during triangle sweep cycles at 50 mV/s between 0.6 V and 1.0 V at 80°C, atmospheric pressure, 100% relative humidity, H_2 at 200 sccm and N_2 at 75 sccm for a 50 cm^2 cell. Based on U.S. DRIVE Fuel Cell Tech Team Cell Component Accelerated Stress Test and Polarization Curve Protocols

[c] Durability measured in a 25-50 cm^2 MEA during a hold at 1.2 V in H_2/N_2 at 80°C, 150 kPa, 100% relative humidity. Based on U.S. DRIVE Fuel Cell Tech Team Cell Component Accelerated Stress Test and Polarization Curve Protocols (http://www.uscar.org/commands/files_download.php?files_id=267), Catalyst Support Cycle and Metrics (Table 2). Activity loss is based on loss of mass activity, using initial catalyst mass, at end of test.

[d] Test at 80°C H_2/O_2 in MEA; fully humidified with total outlet pressure of 150 kPa; anode stoichiometry 2; cathode stoichiometry 9.5. (as per Gasteiger et al. Applied Catalysis B: Environmental, 56 (2005) 9-35) .

[e] Volume = active area * catalyst layer thickness

Current Fuel Cell Activities (from MYRD&D Plan)

Task	Approach	Activities
Catalysts/ Electrodes	• Develop electrocatalysts with reduced precious metal loading, increased activity, improved durability /	**3M:** Advanced Cathode Catalysts and Electrodes
	stability, and increased tolerance to air, fuel, and system-derived impurities	**3M:** Durable Catalysts for Fuel Cell Protection During Transient Conditions
	• Develop supports with reduced corrosion, lower cost, and increased non-PGM catalyst loading	**ANL**: Polymer Electrolyte Fuel Cell Lifetime Limitations: The Role of Electrocatalyst Degradation
	• Optimize electrode design and assembly	**Argonne National Laboratory:** Nanosegregated Cathode Catalysts with Ultra-Low Platinum Loading
	• Develop anodes for fuel cells operating on non-hydrogen fuels	**BNL:** Contiguous Platinum Monolayer Oxygen Reduction Electrocatalysts on High-Stability Low-Cost Supports
		GM: High-Activity Dealloyed Catalysts
		IIT: Synthesis and Characterization of Mixed-Conducting Corrosion Resistant Oxide Supports
		Los Alamos National Laboratory: The Science and Engineering of Durable Ultralow PGM Catalysts
		Los Alamos National Laboratory: Engineered Nano-scale Ceramic Supports for PEM Fuel Cells
		Northeastern University: Development of Novel Non-Pt Group Metal Electrocatalysts for PEMFC Applications
		NREL: Extended, Continuous Pt Nanostructures in Thick, Dispersed Electrodes
		NREL: WO_3 and HPA Based System for Ultra-High Activity and Stability of Pt Catalysts in PEMFC Cathodes
		University of South Carolina: Development of Ultra-Low Platinum Alloy Cathode Catalyst for PEM Fuel Cells

Thank you

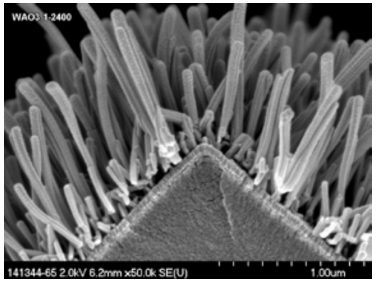
http://www.eere.energy.gov/hydrogenandfuelcells

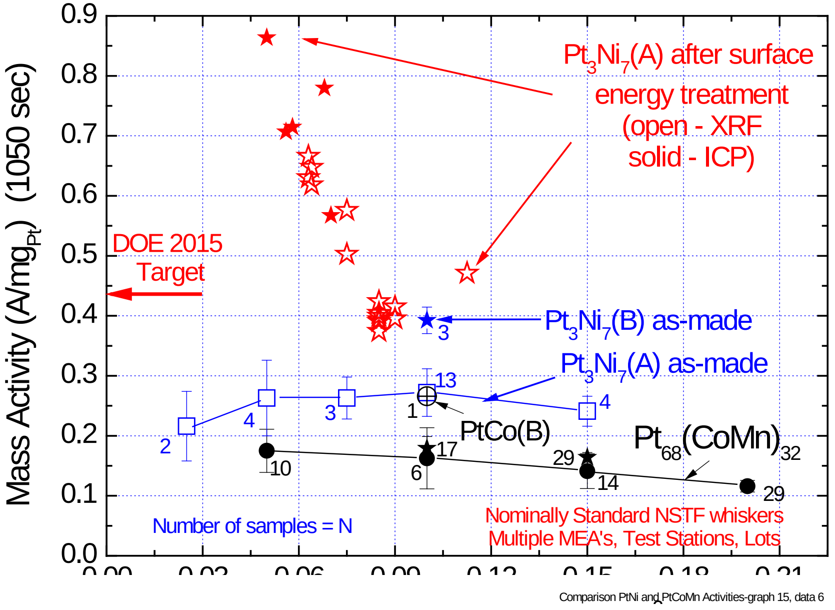
Extended Surface Catalysts : Nanostructured thin film (NSTF) catalysts

3M has developed NSTF Pt and Pt alloy catalysts on crystalline organic supports:

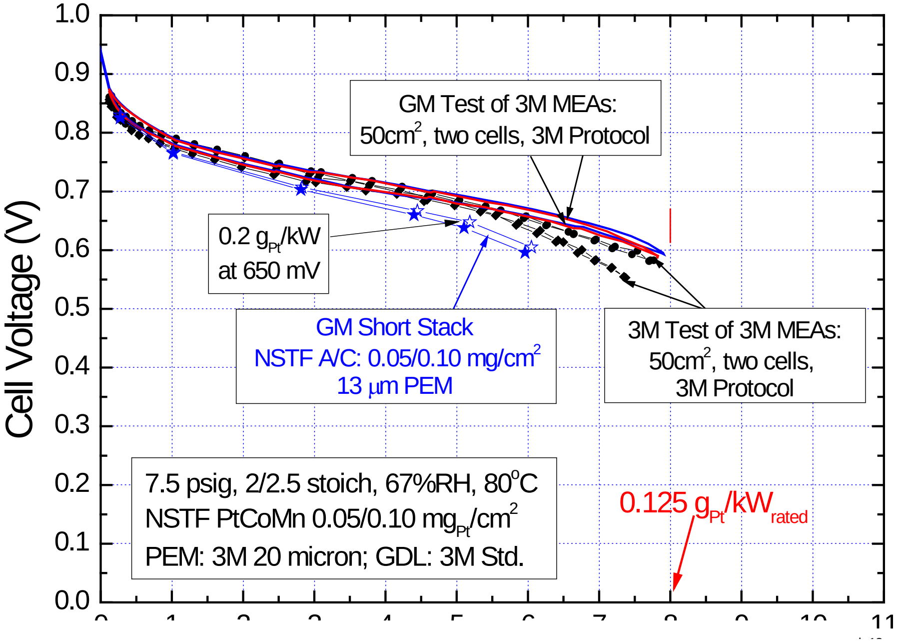
3M

- Eliminates carbon corrosion issues, demonstrates higher resistance to Pt dissolution, and reduces rates of degradation of the membrane by chemical attack
- ORR mass activities > 0.43 A/mg$_{PGM}$ for surface-energy-treated Pt_3Ni_7 alloy catalyst
- Ultra-thin catalyst layer enables higher J(A/cm^2) below 0.2 mg/cm^2
- Requires different water management under cool/wet conditions
- High volume roll-to-roll production scale-able with standard technology





Comparison PtNi and PtCoMn Activities-graph 15, data 6



805 Nanostructured Thin Film Electrocatalysts - Current Status and Future Potential, T 9:00

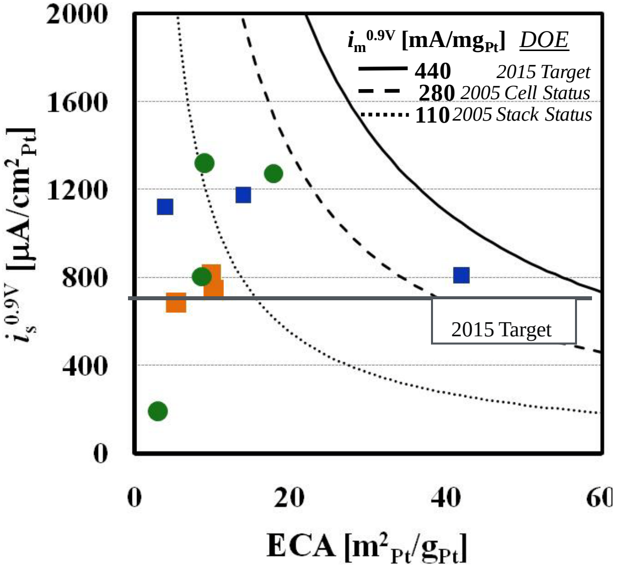
NREL is developing extended thin film structures

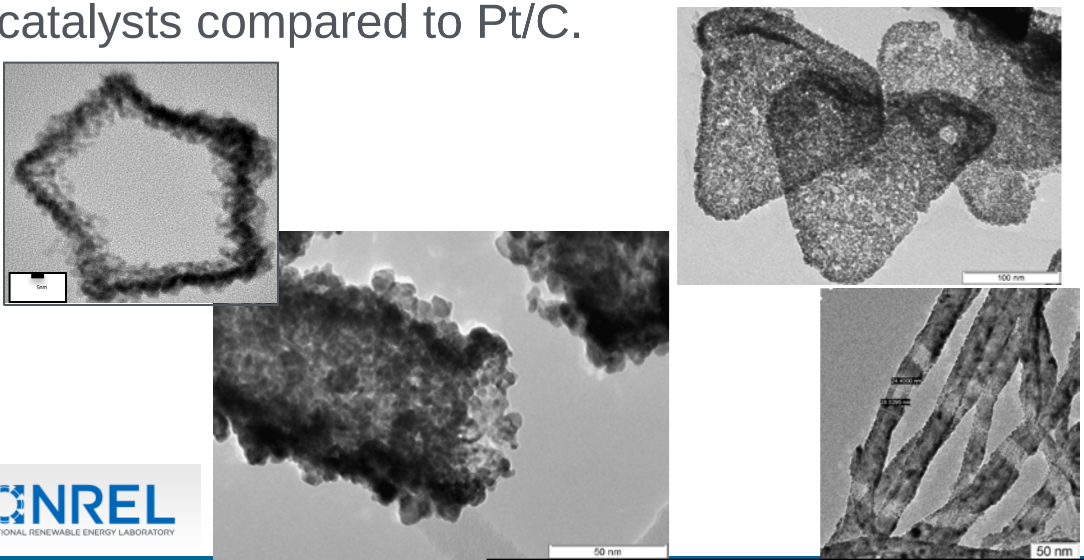
Synthesized novel, extended-Pt catalysts and incorporated them into thick, dispersed electrodes for improved mass transport/water management

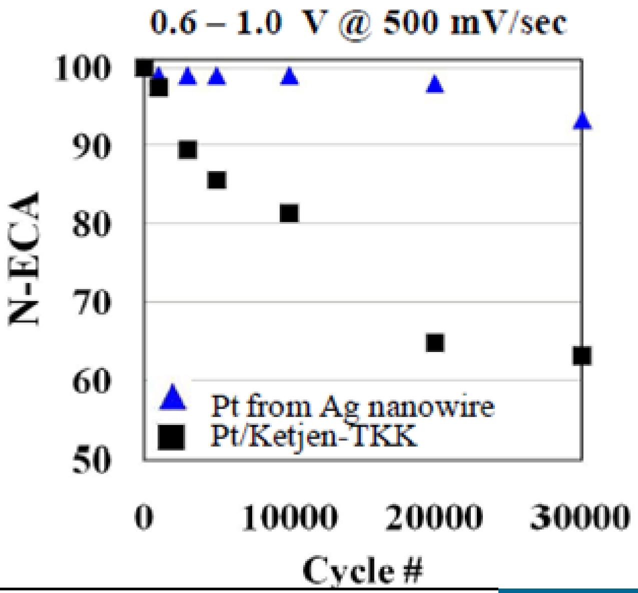
Deposited Pt on multiple substrates: carbon nanotubes, TiO_2-coated Si nanowires, Cu nanowires, Ag nanowires and nanoplates

NREL has demonstrated:

- Pt deposited on Ag nanowires by spontaneous galvanic displacement (SGD) displays activity as high as 1,300 µA/cm^2 Pt.
- Improved stability for SGD-deposited Pt nanowire catalysts compared to Pt/C.



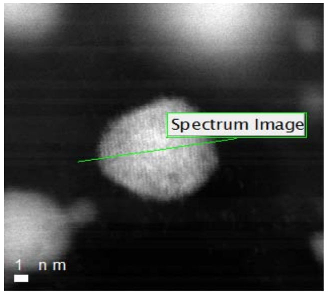




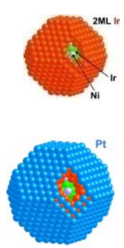
808 Electrochemically Available Surface Area and Mass and Specific Activities of Extended Surface Pt Nanostructures T 10:00

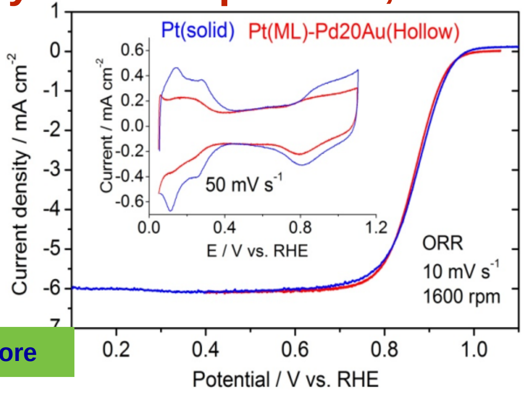
Improving Pt monolayer electrocatalysts for the ORR

Lowering noble metal content, increasing activity and stability by smooth surface morphology, mass-saving geometry and composition, induced lattice contraction in cores

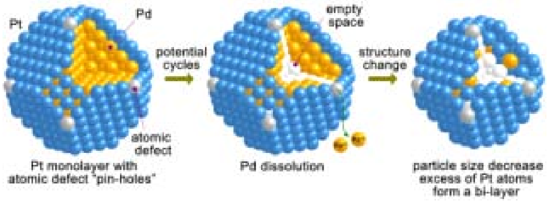


2ML Ir around Ni

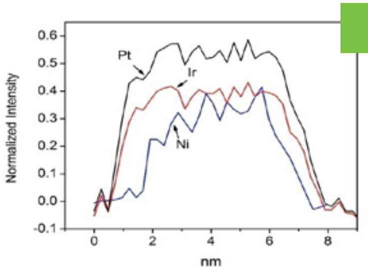


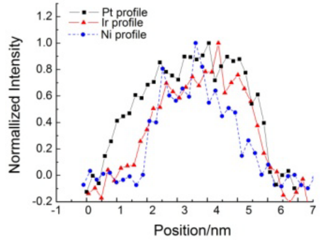


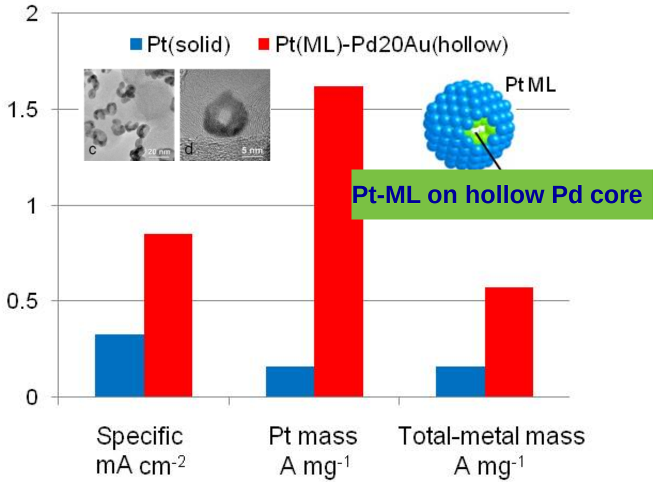
Pt-ML on bimetallic core



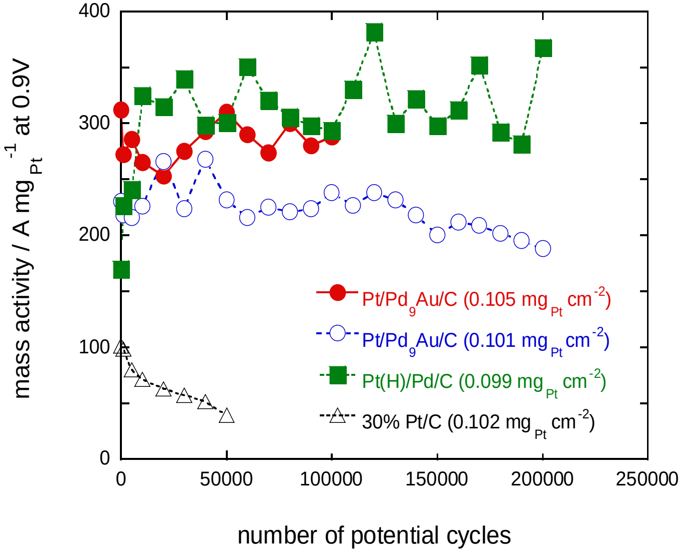
Pt shell protected by the core; No dissolution of Pt ML; Loss of Pd induces contraction of Pt ML thus increasing stability and activity







Pt-ML on hollow Pd core



STEM image

EELS intensities for Pt, Ir, and Ni before (middle) and after 50K cycles (lower panel)

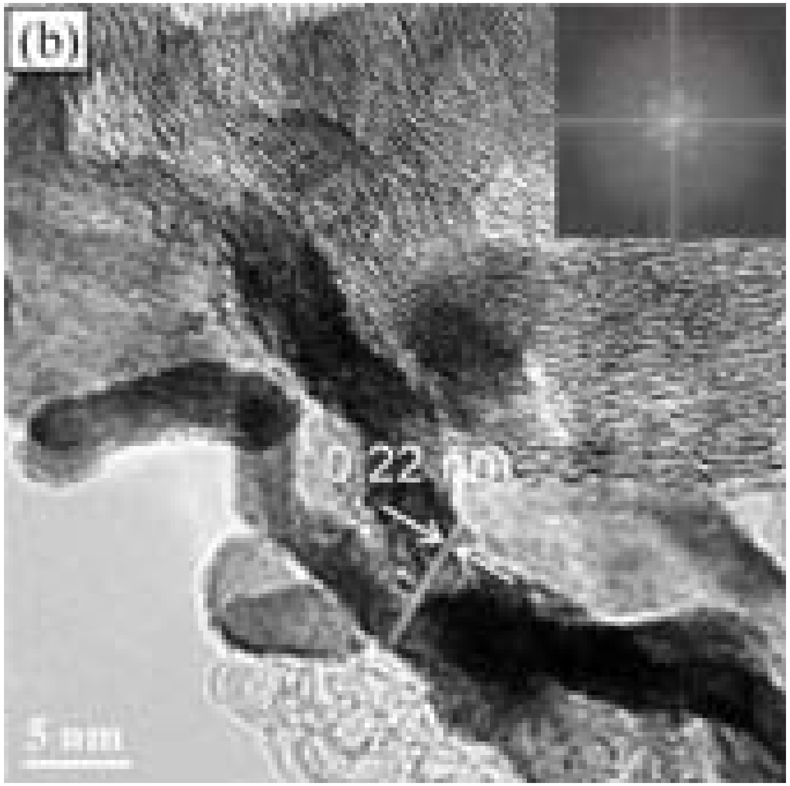
PGM MA: 0.76 A/mg

SA: 0.80 mA/cm^2
PGM MA: 0.57 A/mg

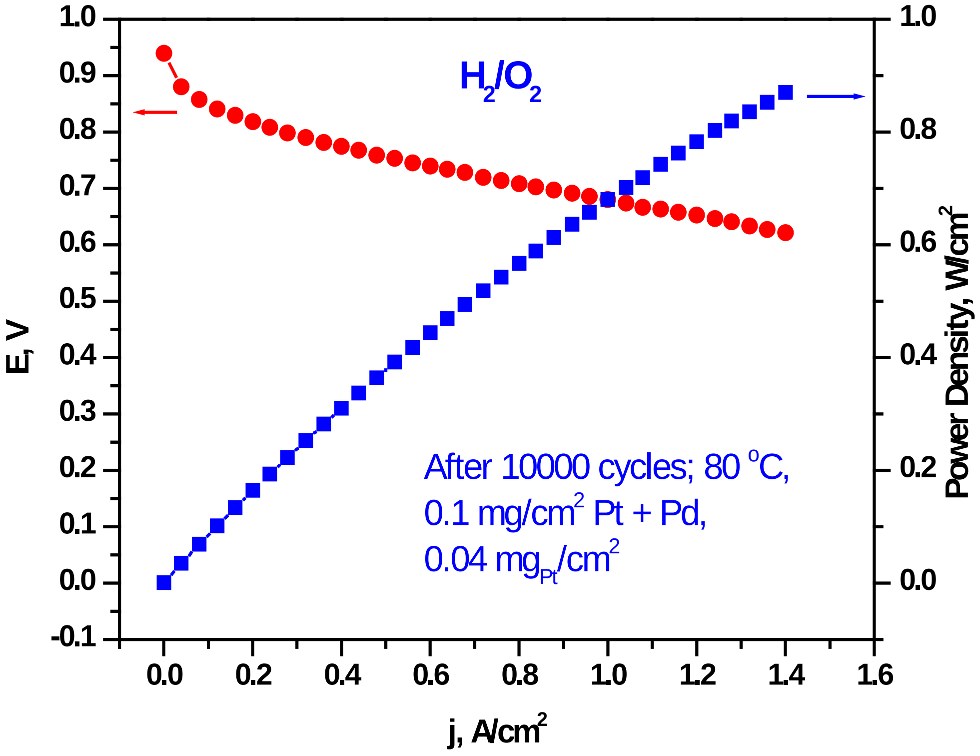
Complete stability of improved Pt ML/Pd/C in 200,000 cycles 0.6-1.0 V at Toyota Motor Company

1057 Bimetallic Core-Protected Platinum Monolayer Shell Electrocatalysts for Fuel-Cell Cathode W 16:40

Improving Pt Monolayer Electrocatalysts for the ORR



Electrodeposited Pd NWs on carbon NPs. FFT indicates (111) facets



Pt-ML on Pd wires electrodeposited on C

Pt MA: 1.74 A/mg Pt
SA: 0.76 mA/cm^2
PGM MA: 0.39 A/mg

BROOKHAVEN NATIONAL LABORATORY

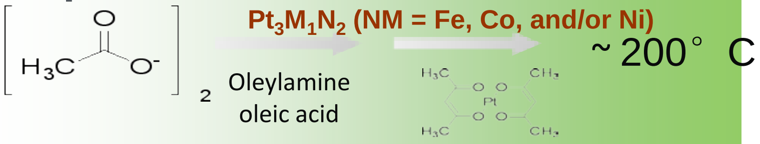
MEA 5 cm^2
Cathode total metal loading 0.1 mg/cm^2 on Toray paper
PGM MA: 1.2 A/mg at 0.85 V

1058 Pt Monolayer on Electrodeposited Pd Nanostructures-Advanced Cathode Catalysts for PEM Fuel Cells W 17:00

Nanosegregated catalysts: binary and ternary systems

Colloidal solvo - thermal approach

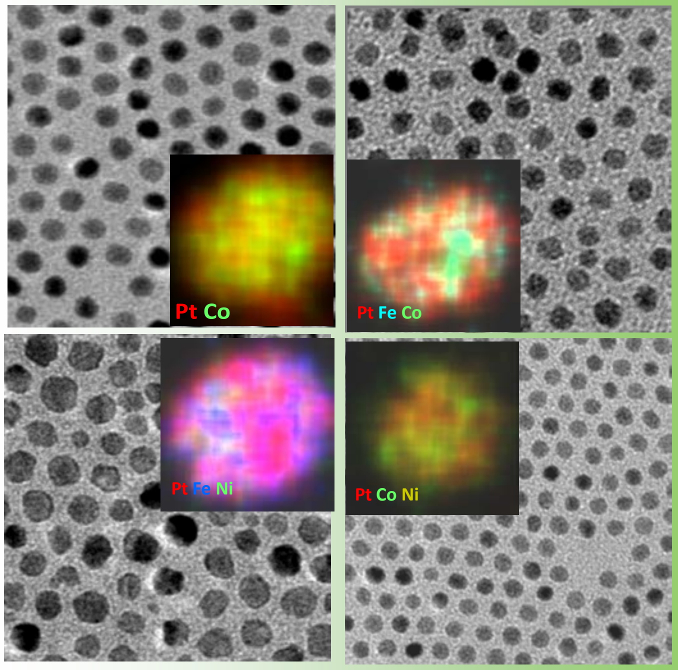
for monodispersed PtM and PtMN NPs with controlled size and composition



$Pt_3M_1N_2$ (NM = Fe, Co, and/or Ni)

Oleylamine
oleic acid

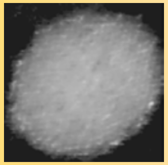
~ 200° C



Efficient surfactant removal

~ 150° C

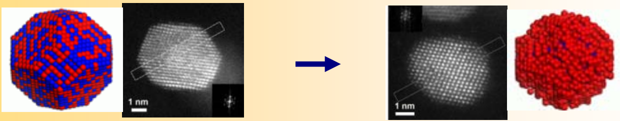
1. Particle size effect



Optimal particle size ~ 6 nm

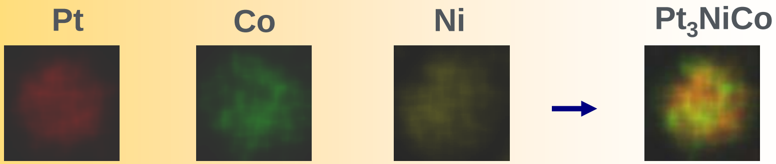
2. Surface chemistry

$Pt_xM_{(1-x)}N$



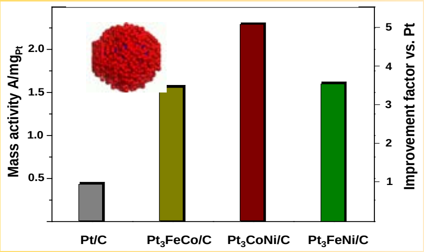
Dissolution of 3d elements leads to Pt-skeleton

3. Composition effect



Optimal composition of Pt-ternary NPs is Pt_3MN

4. ORR activity



Pt-ternary (IF~5) vs. Pt/C

Pt-bimetallic NPs (IF~2.5) vs. Pt/C

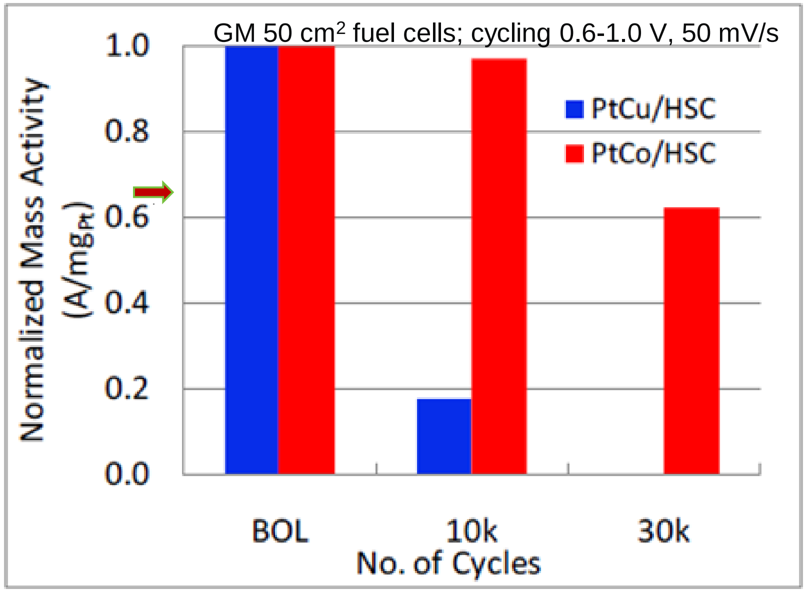
Pt< Pt_3FeCo < Pt_3FeNi < Pt_3Co < Pt_3CoNi

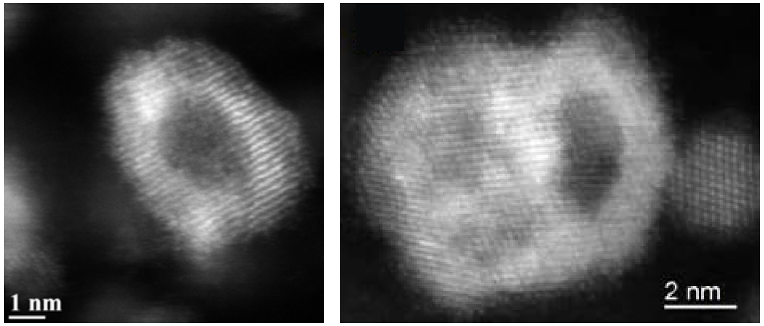
1005 Rational Design and Synthesis of Pt-Bimetallic Electrocatalysts, W 8:40

De-alloyed Nanoparticles

General Motors is developing dealloyed catalysts [$PtM_3 \rightarrow \sim Pt_2M$, M= Cu,Co,Ni,Fe,V] to increase ORR activity above that of Pt or standard Pt-alloy particles

- Dealloyed $PtCu_3$ catalysts have greater initial ORR activity (0.69 A/mg_{Pt}) than dealloyed $PtCo_3$ (0.37 A/mg_{Pt}), but dealloyed $PtCo_3$ shows better stability against voltage cycling
- Detailed characterization (electron microscopy and x-ray absorption spectroscopy) are providing insights towards combining the attributes of activity and durability in a single catalyst. The roles of different particle morphologies are being investigated
- Dealloying conditions are being modified to improve manufacturability and to mitigate negative effects of excess alloying-element ions, which leach to the membrane



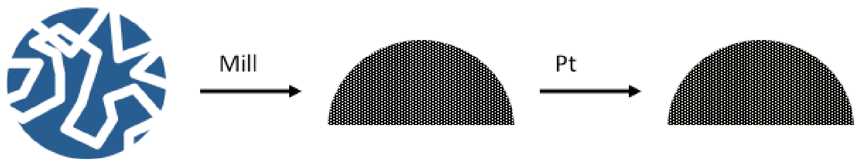


HAADF STEM images of (left) single-alloy-core particle in D-$PtCu_3$ and (right) multiple-alloy-core particle in D-$PtCo_3$. Both show Pt-only shells.

1110 X-ray Absorption Spectroscopy Investigation on Activity and Durability of De-Alloyed Pt_3Co Cathodic Catalysts. Th 12:00

LANL - Durable Ultralow PGM Catalysts

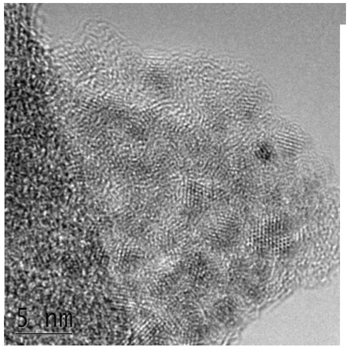
Synthesis of 2-nm ceria supports on carbon

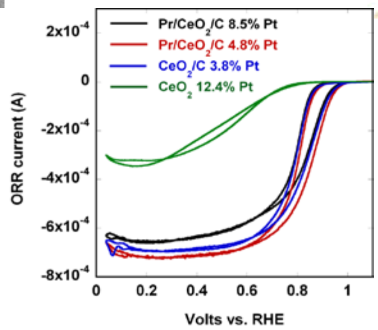


Ceria/Carbon Bead
SA ~ 60 - 75 m²/g

Ce/C Powder
SA ~ 70 - 90 m²/g

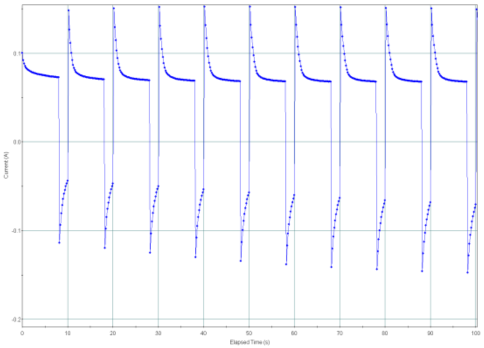
Pt-Ce/C Powder
~ 4 - 9 wt% Pt

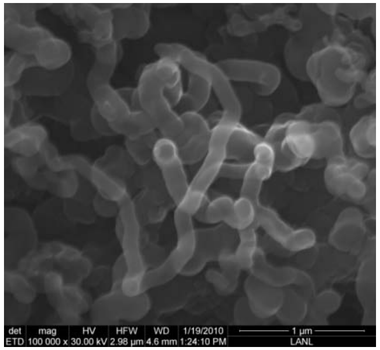




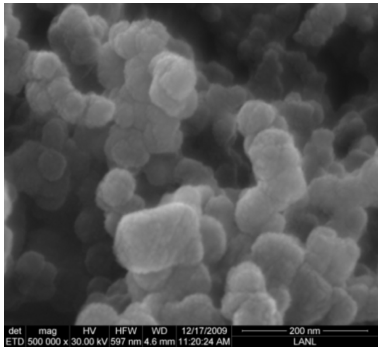
Synthesis of Pt/PPY nanowires using multi-potential steps and Pt sputter deposition

PPY electrodeposition





PPY nanowires



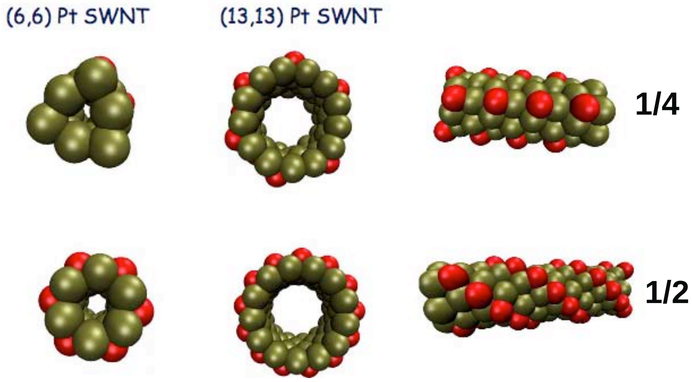
Pt-coated PPY nanowires

Theoretical Modeling of Novel Pt Nanoparticles

- DFT modeling show that smaller Pt nanotubes are stable only for larger coverage and symmetric structures
- (6,6) Pt nanotube binds O more strongly than Pt(111)
- (13,13) Pt nanotube binds O similar or slightly more weakly than Pt(111)

adsorption energies in eV of atomic oxygen for fcc site

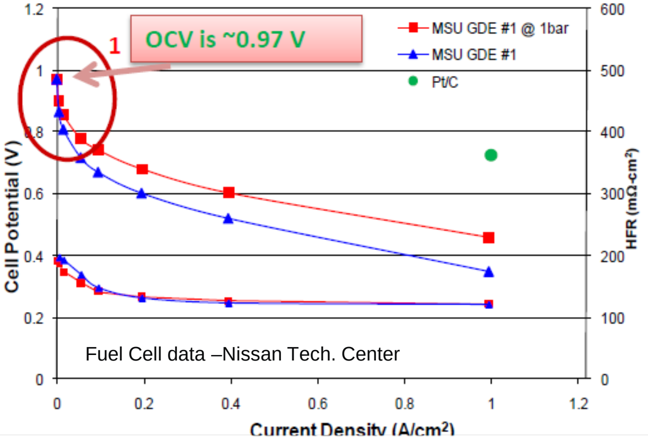
	Pt(111)	(6,6) SWNT	(13,13) SWNT
1/4	-4.42	-4.72	-4.57
1/3	-4.25	-4.44	-4.11
1/2	-4.07	-4.24	-4.06
2/3	-3.79	-4.28	



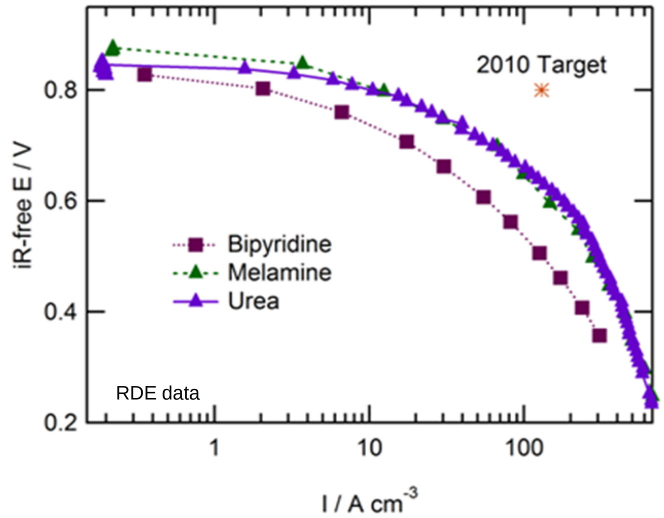
1213 Ultra-Low Pt Load Catalysts Based on Electrochemically Synthesized Polypyrrole Nanowires F 14:00

NE - Non-PGM Catalysts

Non-PGM ORR catalyst based on melamine precursors prepared at MSU showed good activity and durability under catalyst durability protocol, however poor durability under C-corrosion conditions



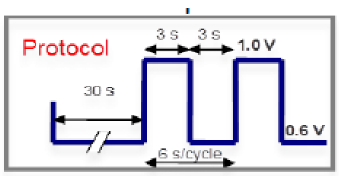
Fuel Cell data –Nissan Tech. Center



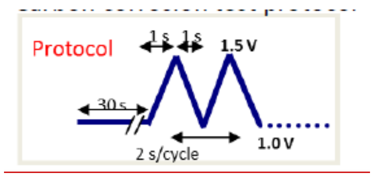
RDE data

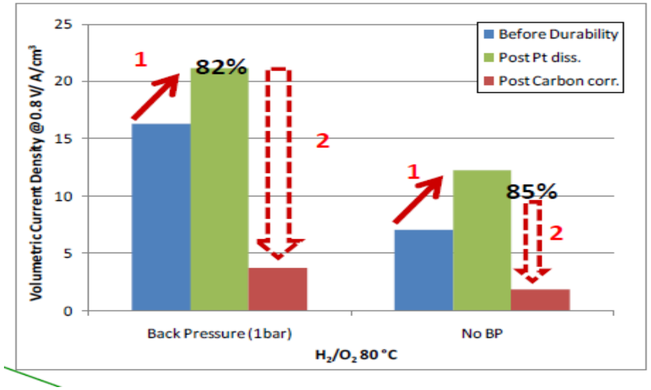
- **GDEs were prepared for melamine-based catalyst using NTCNA's spray system.**
- **MEAs were prepared with NRE211 as the electrolyte and JMFC GDE anodes.**

Catalyst durability test protocol

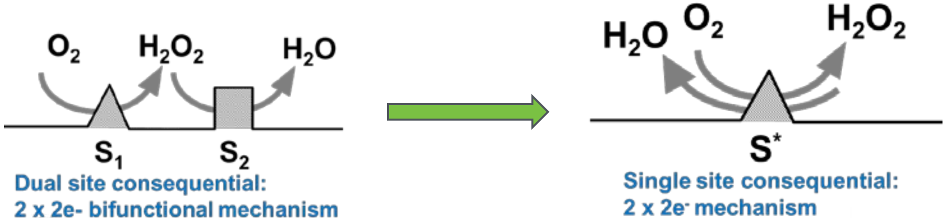


Carbon corrosion test protocol



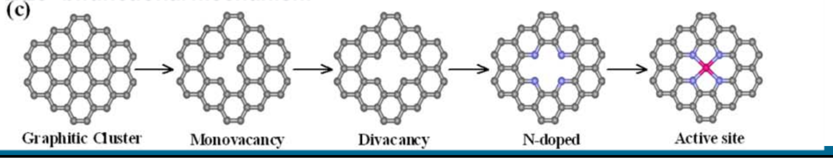


Mechanistic Studies



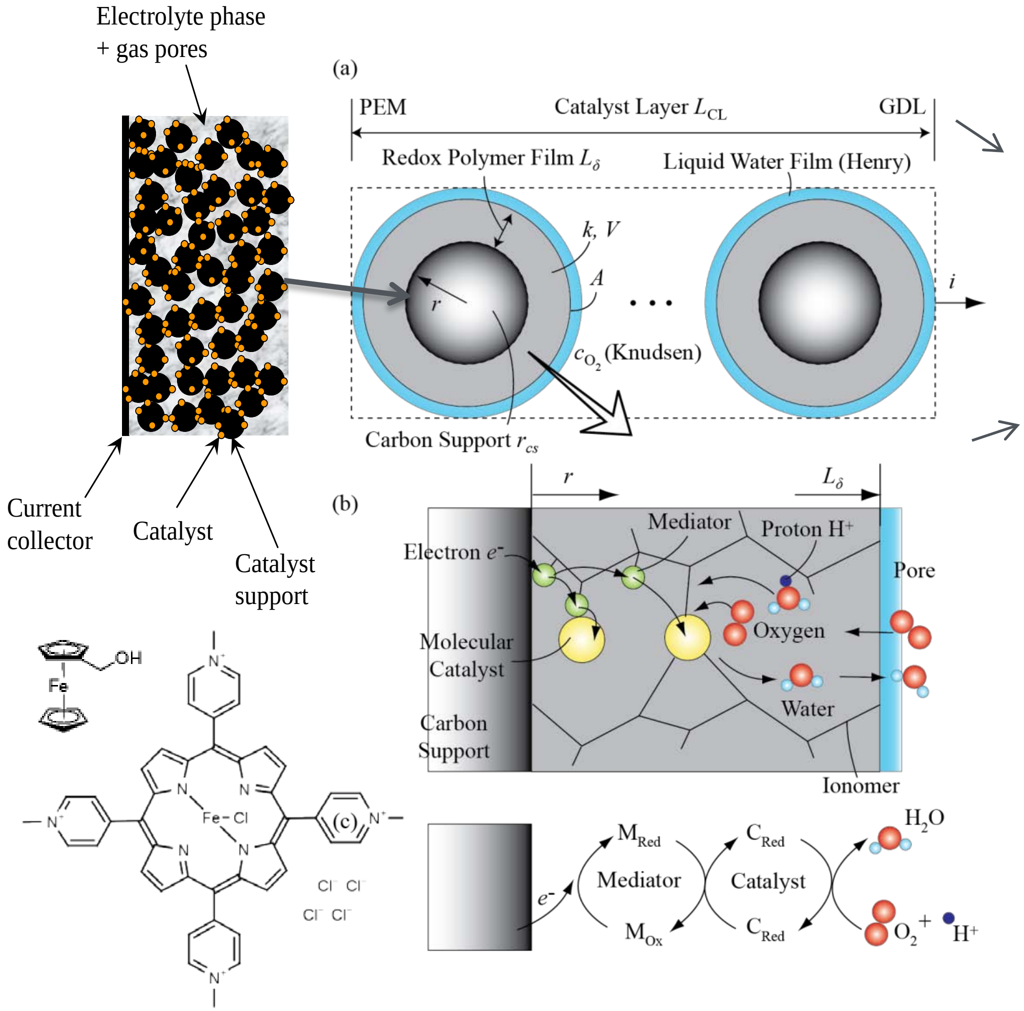
Dual site consequential: 2 x 2e- bifunctional mechanism

Single site consequential: 2 x 2e- mechanism

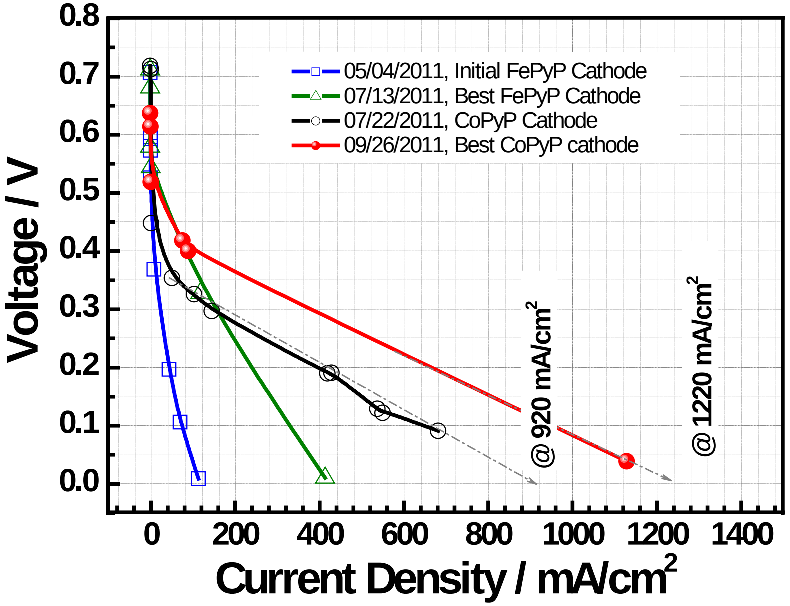


LBNL - 3D Non-PGM Catalyst

Molecular catalysts dispersed in ionomer film over carbon particles



Schematic of oxygen, proton, electron, and water transport in the thin redox polymer and the catalyst layer.



- High activity and turnover within the catalyst layer
- Decent initial (>20 hr) stability
- Changing inks, metal center, loading and mediator leads to better performance

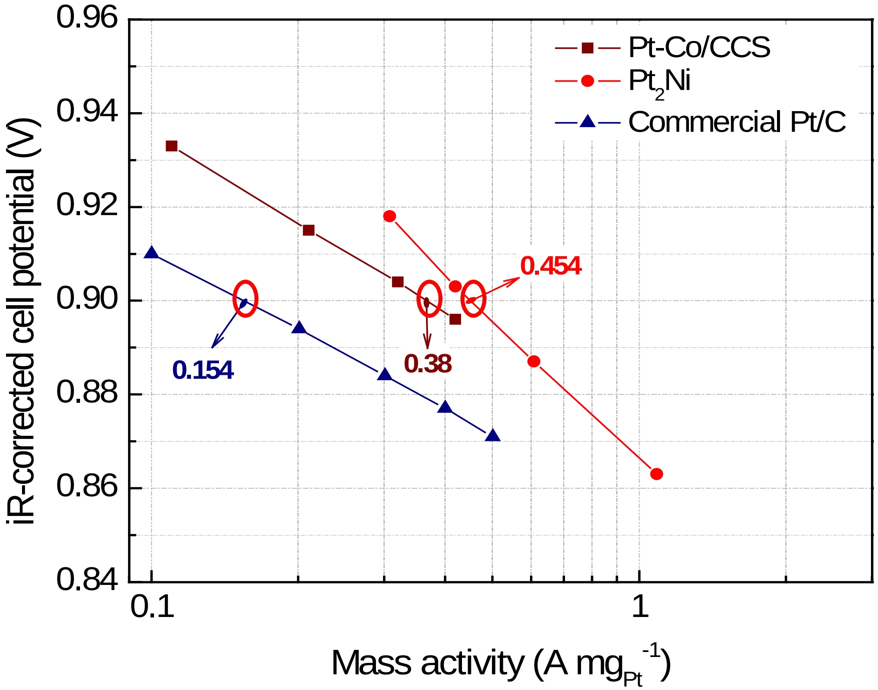
USC - Hybrid Catalysts

The University of South Carolina, in collaboration with Yonsei University (S. Korea) is developing two types of ultra-low loading Pt catalysts:

(i) Hybrid cathode catalyst (HCC) combines a non-PGM carbon composite catalyst (CCC) as a support for a PGM-based catalyst to obtain ultra-low Pt loading.

(ii) Pt and Pt-M alloy catalysts are deposited on activated graphitic carbon support, Pt-M/AGC.

The Pt-Co HCC catalyst and Pt-M/AGC catalyst had mass activities in the range of 0.38 to 0.44 A/mg$_{PGM}$ at loadings of 0.1 mg$_{PGM}$/cm^2 approaching the DOE target.

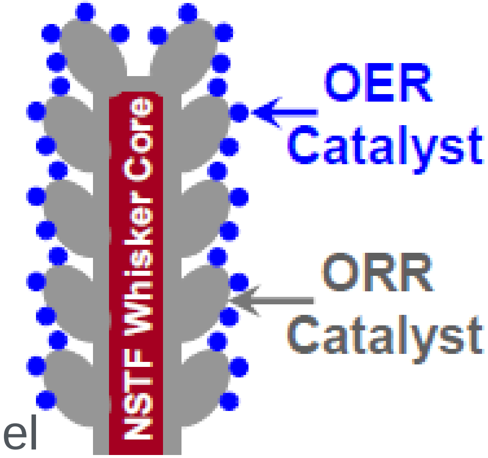


Durability of Mass Activity of Pt$_3$M Catalyst

	After 30,000 cycles	
	Mass activity at 0.9 V	**ECSA in MEA**
DOE target	**≤ 40% loss**	**≤ 40% loss**
Pt$_3$M/AGC	**34% loss (from 0.41 to 0.27 A/mg$_{Pt}$)**	**30% loss (from 29.5 to 20.8 m^2/g)**

3M – Protect catalysts during transient conditions

Absence of hydrogen and simultaneous **presence of oxygen** in **separate** regions of the anode results in **cathode potential > 1.23 V during transients and startup/shutdown.**

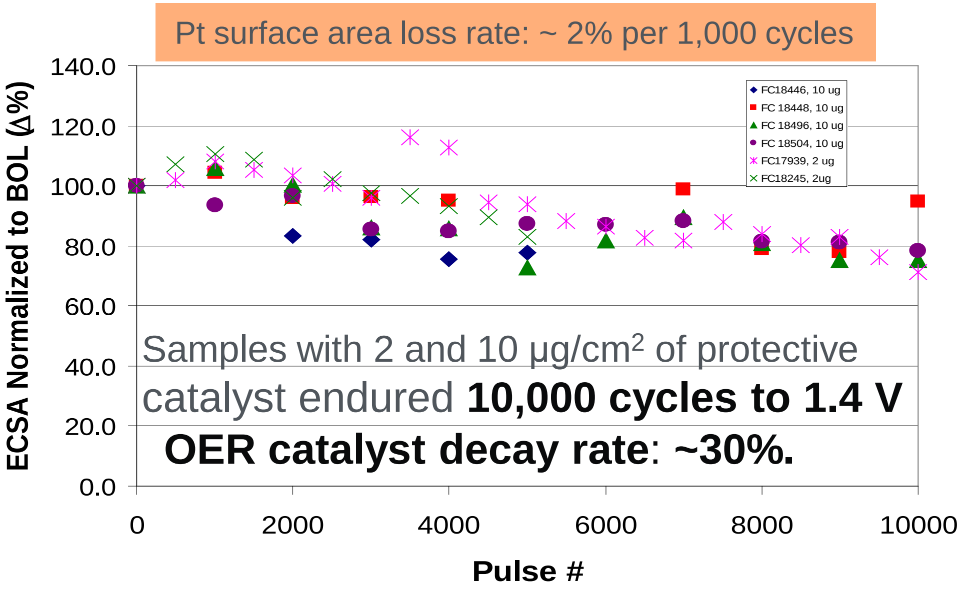


3M approach: **modify both anode and cathode catalysts** to enable PEM fuel cell systems to weather the conditions in the fuel cell at **voltages beyond the thermodynamic stability of water** during the transient periods.

3M

To achieve this goal 3M will develop **two major concepts**:

1. **Cathode catalysts with high oxygen evolution reaction (OER) activity**
2. **Anode catalysts with low oxygen reduction (ORR) reaction activity**



Pt surface area loss rate: ~ 2% per 1,000 cycles

Samples with 2 and 10 μg/cm^2 of protective catalyst endured **10,000 cycles to 1.4 V**

OER catalyst decay rate: **~30%.**

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• 3M Company	R. Atanasoski, M. Debe
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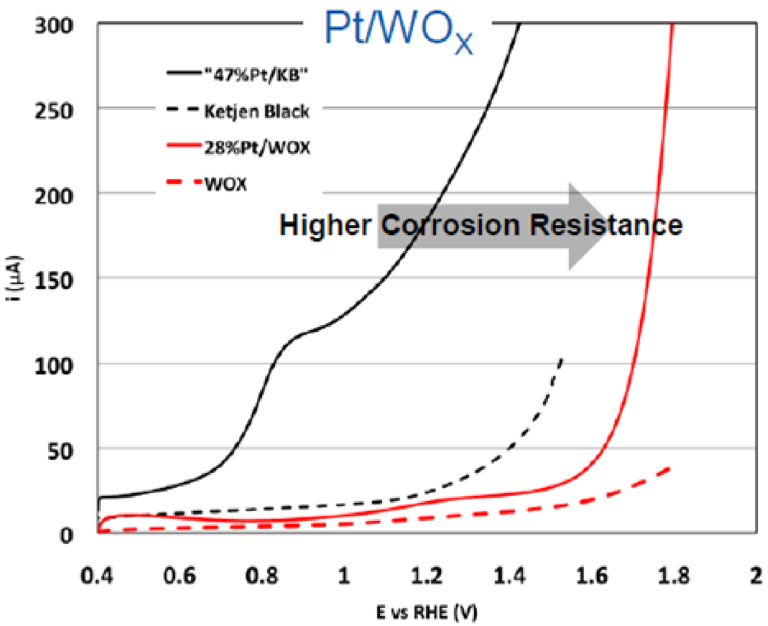
• University of South Carolina	B. Popov

Carbon catalyst support degradation affects durability

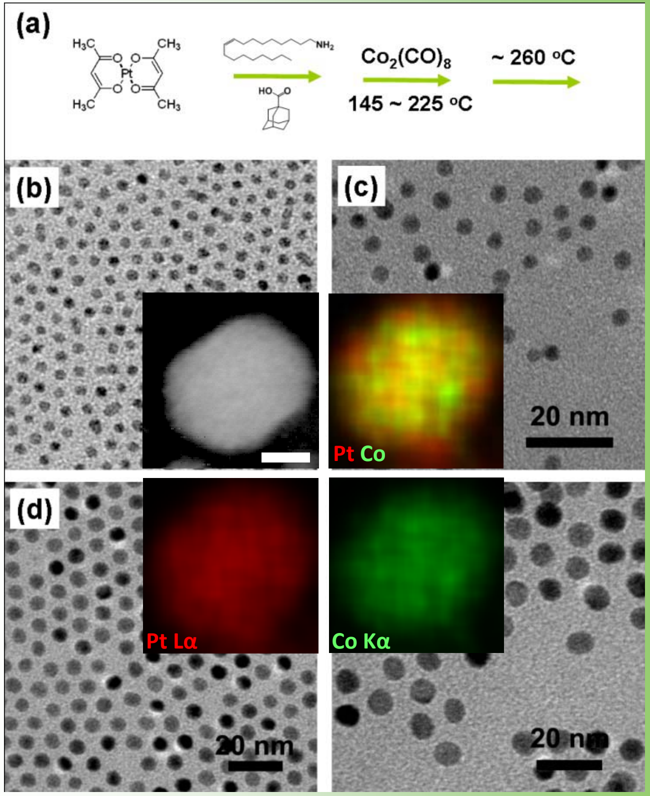
NREL team is investigating heteropolyacids and tungsten oxide catalyst supports to increase stability and activity of Pt catalysts.

- Expected to increase stability due to their higher corrosion resistance and the strong catalyst -support interaction.
- Initial tests indicate the Pt/WO_X catalysts are more corrosion resistant than Pt/C, with corrosion not occurring until above 1.6V



ANL Nanosegregated Catalysts for ORR

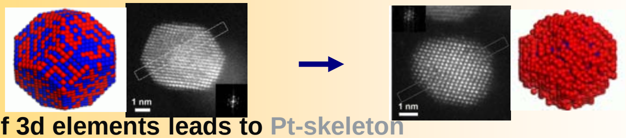
Colloidal solvo - thermal approach for monodispersed PtM NPs with controlled size and composition



Efficient surfactant removal

Surface chemistry

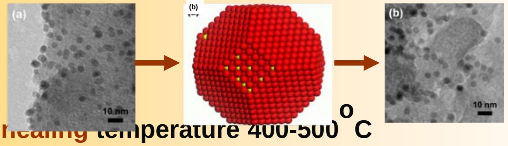
PtxM(1-x) NPs



Dissolution of 3d elements leads to Pt-skeleton

Temperature induced segregation

Agglomeration prevented



Optimized annealing temperature 400-500 °C

Activity