Novel Approach to Advanced Direct Methanol Fuel Cell Anode Catalysts

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National Renewable Energy Laboratory

June 11, 2010

2010 Annual Merit Review and Peer Evaluation Meeting

Washington, D.C.

NREL/PR-560-48063

FC041

This presentation does not contain any proprietary, confidential, or otherwise restricted information

Overview

Timeline

Start: July 2009
End: September 2011
% complete: ≈ 40%

Barriers

Barrier	2010 Target (consumer electronics)
A: Durability	5000 h
B: Cost	$3/W
C. Performance	100 W/L, 100 W/kg

Budget

DOE Cost Share	Contractor Cost Share	TOTAL
$2.4M	$69,714	$2.47M*
97%	3%	100%

	DOE Budget ($K)
FY 2009	610
FY 2010	950
FY 2011	840

*Final award amounts are subject to appropriations and award negotiations.

Partners [date under contract]

Colorado School of Mines (CSM) [9/2009]
Jet Propulsion Laboratory (JPL) [12/2009]
MTI MicroFuel Cells (MTI) [N/A]
BASF Fuel Cells (BASF) [N/A]

Kickoff meeting 12/10/2009 at NREL.

Relevance: Catalyst Support Interaction

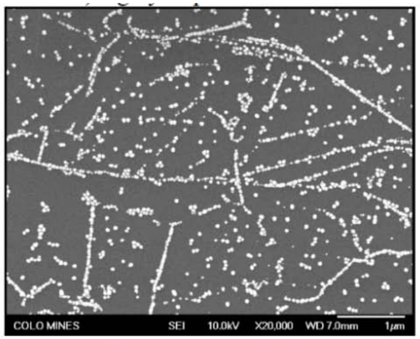
DOE Objective:

Develop and demonstrate direct methanol fuel cell (DMFC) anode catalyst systems that meet or exceed DOE's 2010 targets for consumer electronics application.

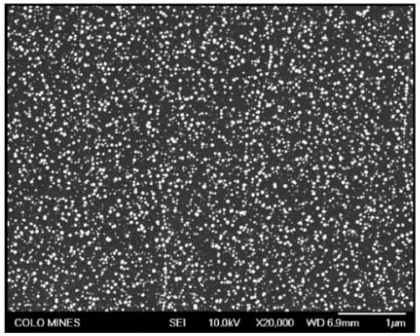
Project Goal:

Improve the catalytic activity and durability of the PtRu for the methanol oxidation reaction (MOR) via optimized catalyst-support interactions.

PtRu on highly oriented pyrolytic graphite (HOPG)



(a) PtRu on undoped-HOPG



(b) PtRu on N-doped HO

Similar approach for ORR catalysis advantageous for both DMFC and hydrogen fuel cells.

Relevance – Background Data

Performance

Methanol oxidation reaction (MOR) on the anode limits the performance of DMFCs. Hence, focus on improving MOR catalytic activity on the anode.

Previous results for Pt/N-doped HOPG showed 52X higher in mass activity for MOR compared to Pt/undoped-HOPG.

Durability:

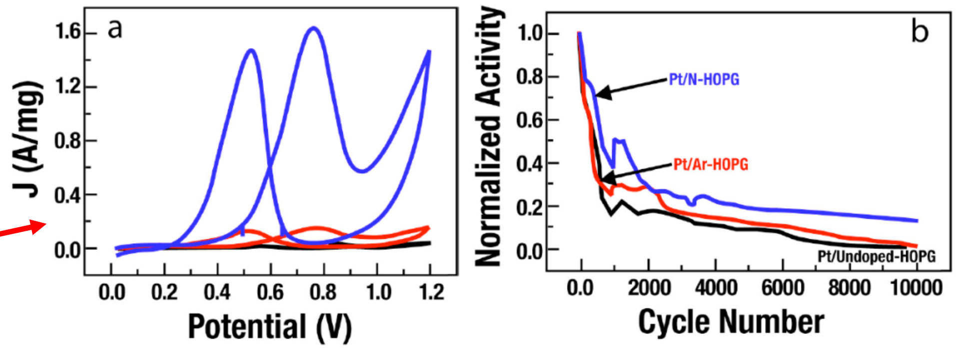
Expect the unique stabilization of Pt nanocatalyst observed in the Pt/N-doped HOPG system will translate to the PtRu system and improve DMFC's durability.

N-doping improved durability of system with minimal aggregation/coarsening of particles.

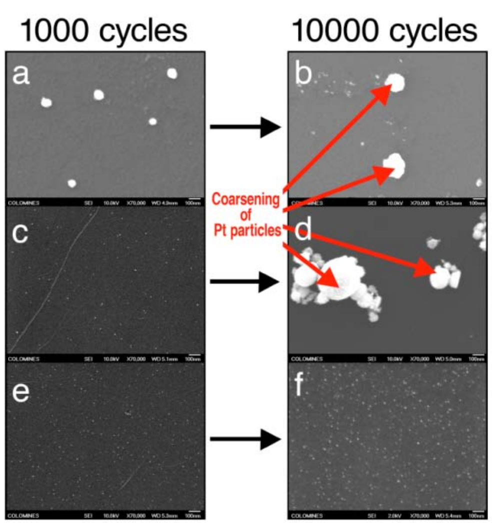
Cost:

To reduce cost, catalyst activity must be increased by ca. 10X of current state of the art (SOA) system with lower catalyst loading.

Translating the enhanced mass activity for MOR to PtRu can help reduce cost.

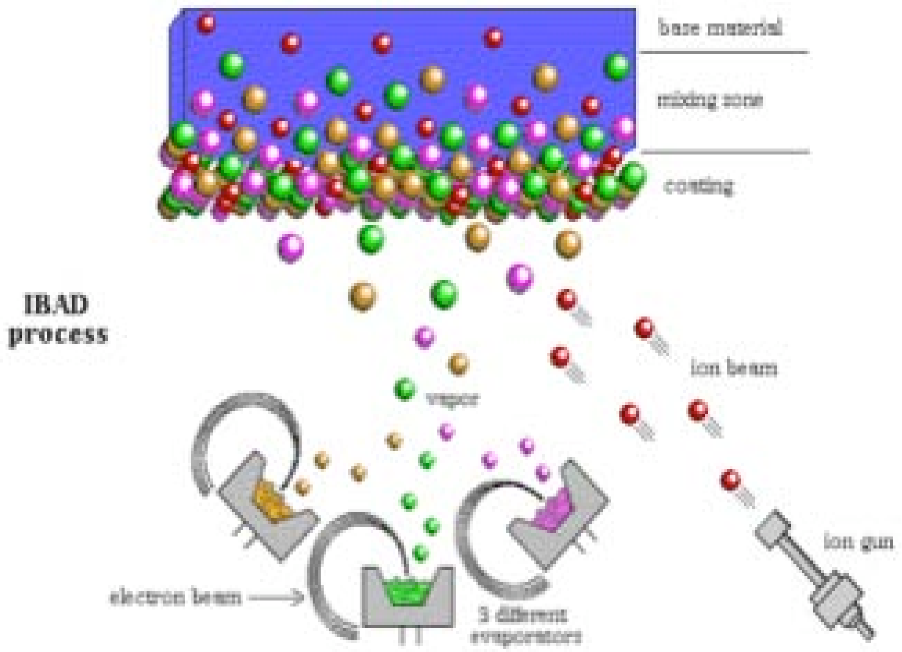


(a) Mass activity (A/mg) of methanol oxidation (MOR) on Pt/undoped, Pt/Ar-, and Pt/N-HOPG, at room temperature (scan rate = 50 mV/s; Reference electrode = Ag/AgCl); (b) MOR peak current density (activity) normalized against first cycle activity as a function of cycle number These data show that N-doped Pt has enhanced catalytic activity and durability for MOR.



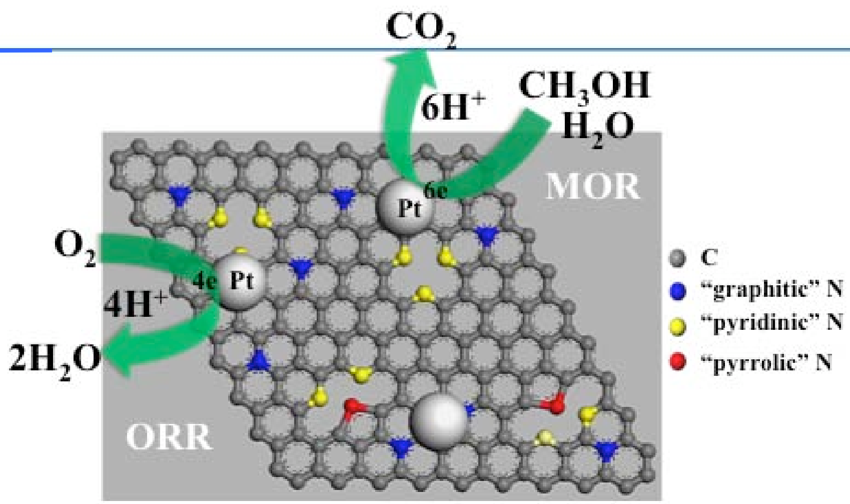
Yingke Zhou, Robert Pasquarelli, Timothy Holme, Joe Berry, David Ginley and Ryan O'Hayre, *J Mater. Chem.*, **2009,** 19, 7830-7838.

Approach - Ion implantation



- Ion gun is at a 35 degree angle from the sample plane
- Base chamber pressure is 10^{-7} torr or lower
- Ion source gas is maintained at 10^{-4} torr
- Deposition is performed at room temperature
- Current setup can use N_2, Ar, other gases
- Time varies from 1 - 125 seconds of exposure
- Low beam energies used for implanting ions, typically 100 eV, into HOPG
- Ion dosing levels of 1×10^{12} cm^{-2} to 1×10^{16} cm^{-2} can be controllably obtained

Density functional theory calculations predict tethering of catalyst clusters on carbon next to substitutionally implanted nitrogen.



Approach – AOP Milestones

FY09 Milestones

1	Establish the optimal nitrogen doping level on a model HOPG substrate for DMFC catalysis. – established that 45 seconds implantation of N on HOPG is optimal	09/09 100% complete
2	Conduct preliminary combinatorial electrochemical evaluation of prospective materials and refine the analytical methods for combinatorial library. – extended until 04/10 due to delayed in JPL funding	09/09 50% complete

FY10 Milestones

1	Perform sputter deposition of PtRu on HOPG surface to establish optimal deposition parameters. – can control PtRu phase and composition with power and pressure	12/09 100% complete
2	Develop a processing system for nitrogen doping of applicable carbon materials. – built a system for ion implantation of carbon powders and PtRu deposition	04/10 100% complete
3	Perform 5 cm^2 fuel cell testing of MEAs fabricated with novel catalysts with highest performance. – initiated benchmarking with commercial catalyst materials	09/10 10% complete

Approach - Modify support via ion implantation

Optimize surface-catalyst interactions:
Ion implantation of HOPG with N, Ar, CF_4, I, S, B

Deposit PtRu catalyst:
sputtering, electrochemical deposition, microwave deposition

Catalyst characterization:
Microscopy (particle size, dispersion, composition), XPS (composition)
XRD (structure/phase, degree of alloying)

Measure methanol oxidation activity and durability:
High throughput electrochemical analysis

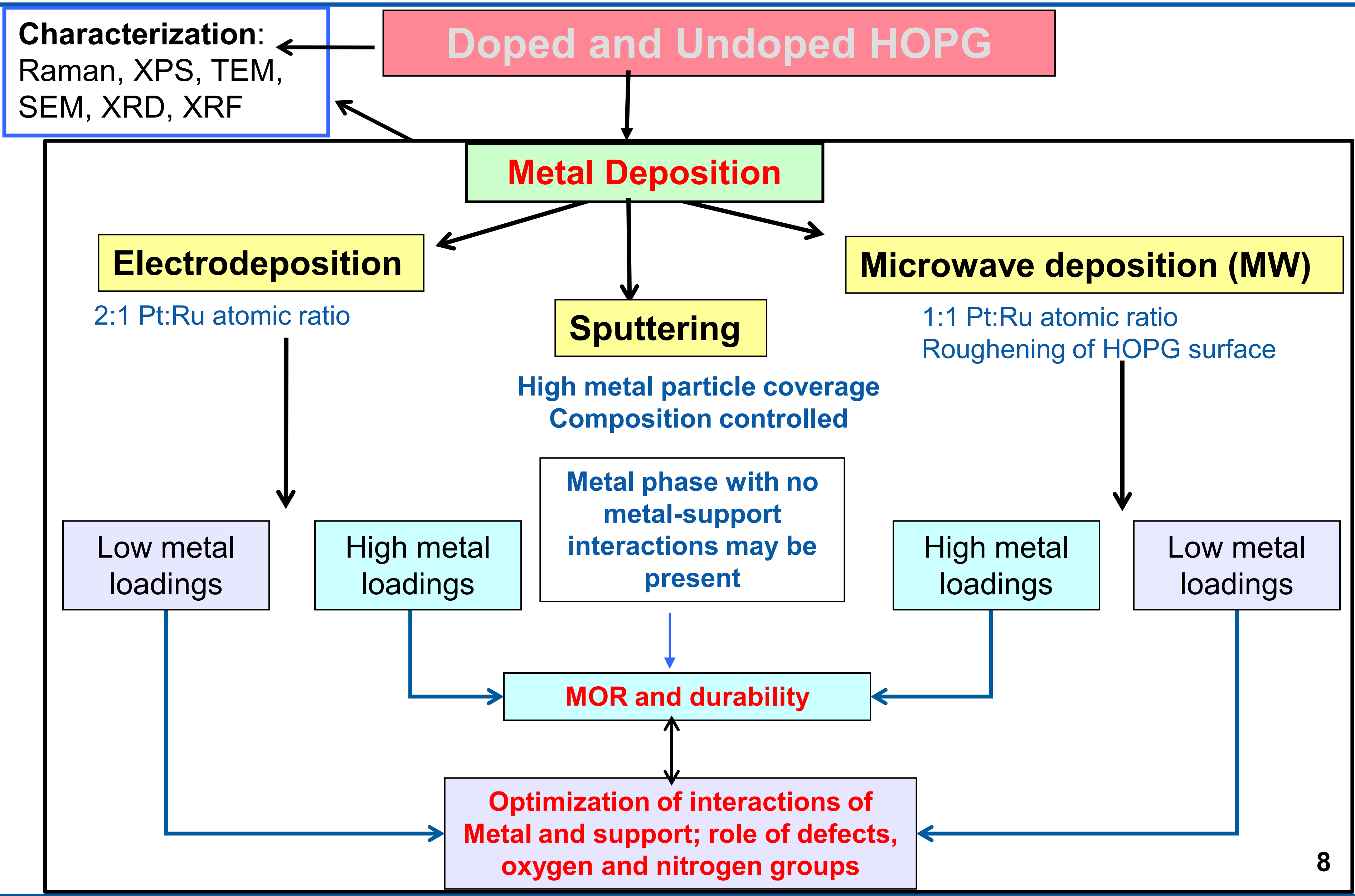
Optimize and down-select materials
composition, structure, phase, and particle size

Transfer process to high surface area carbon

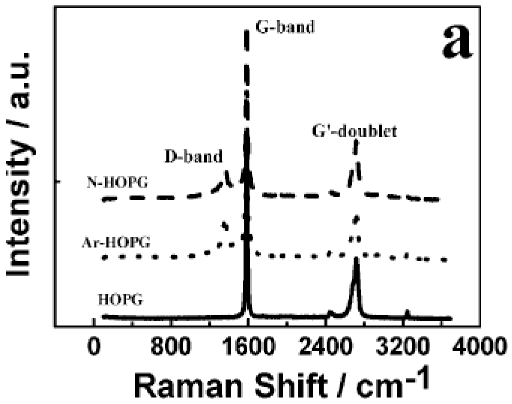
Scale up for DMFC MEA

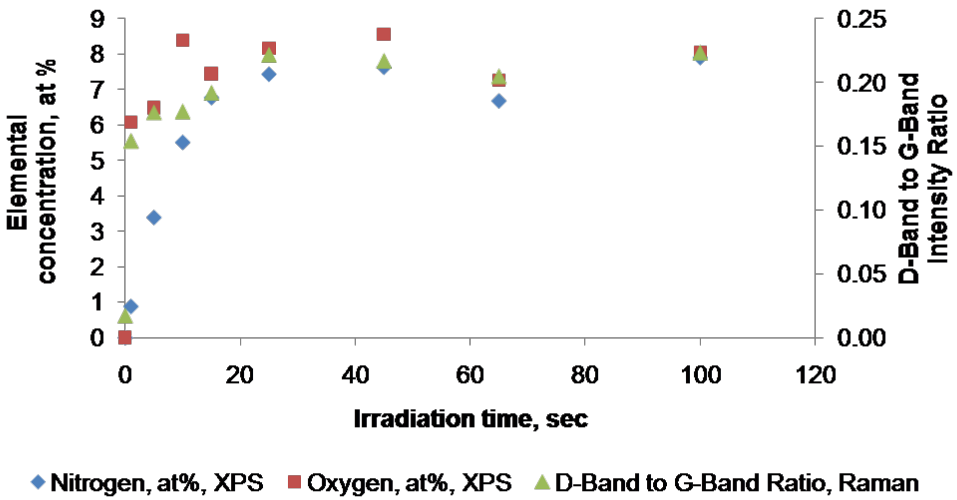
DMFC Testing

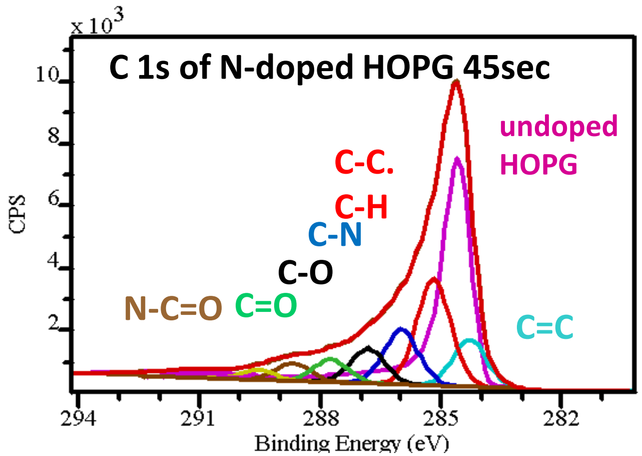
Approach – First 7 months roadmap



Technical Accomplishments – Understanding structural & chemical modification of N-HOPG via ion implantation







- Nitrogen is incorporated in the carbon network, resulting in formation of sp^3-sp^2 bonding instead of sp^2-sp^2 in graphitic structure and C-O, C=O and N-C=O.

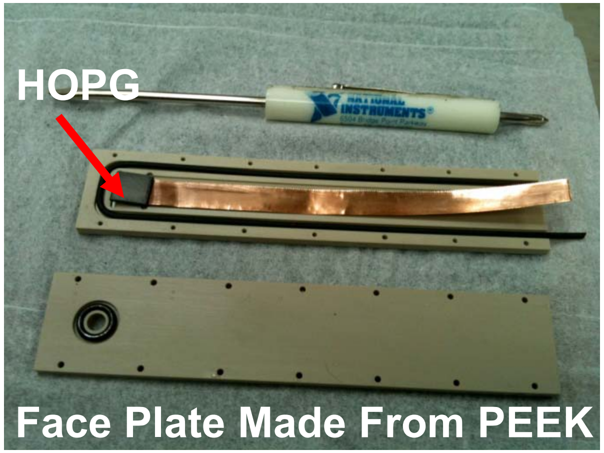
- Ion implantation of N_2 longer than 45 seconds results in no additional structural disorder. Increase in the surface defects detected by Raman correlates with increase in both nitrogen and oxygen surface groups.
- The relative amount of nitrogen (7%, via XPS) introduced into the carbon substrate also saturates after 45 seconds.

Optimum N-doping conditions are achieved at 45 sec.

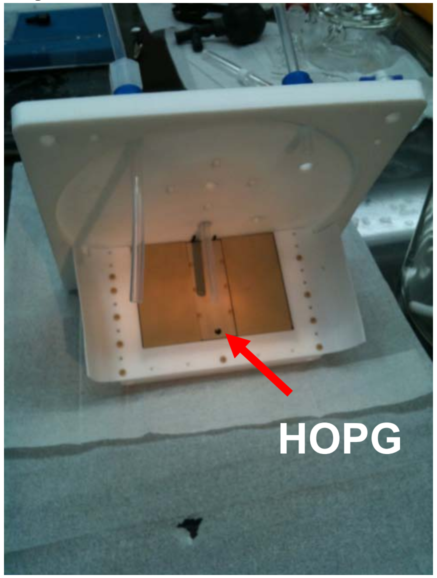
Technical Accomplishments
High-throughput electrochemical screening

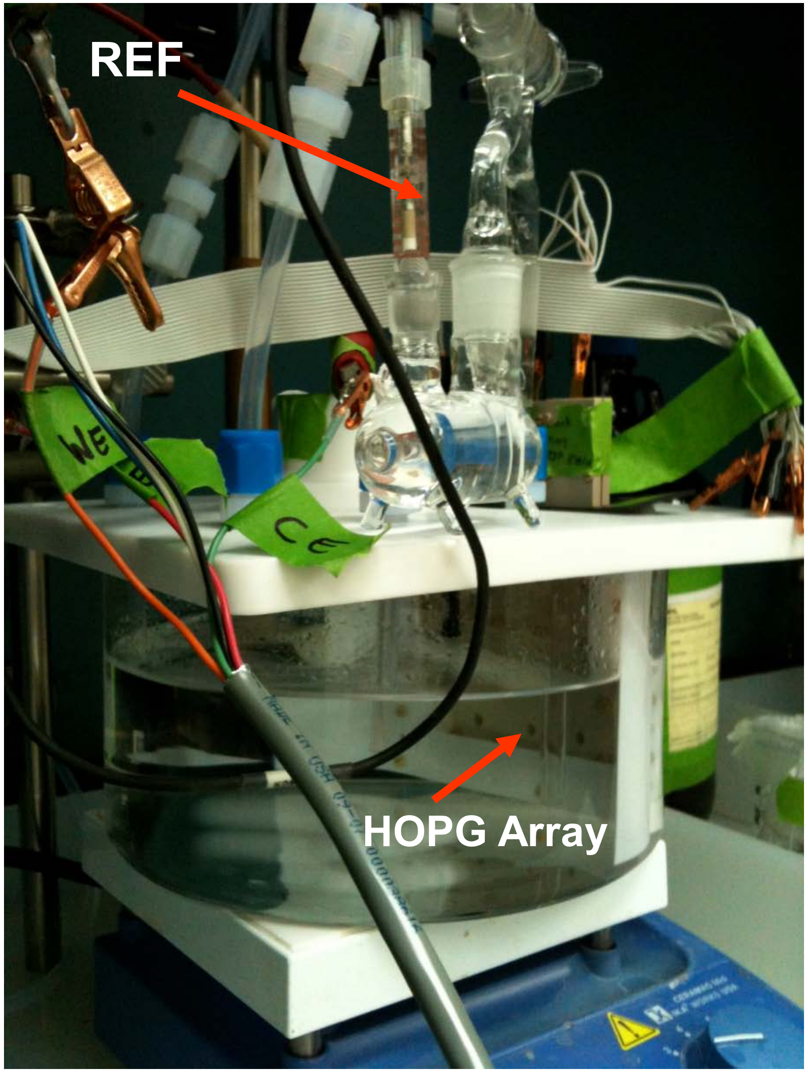
- Designed and fabricated multi-electrode cell for electrochemical tests on an array of ion-implanted HOPG substrates;
- Conducted tests on cartridge-style HOPG electrode holder
- Custom-built multi-electrode half cell enables simultaneous electrochemical measurements on a multi-electrode array

Cartridge-style electrode holder



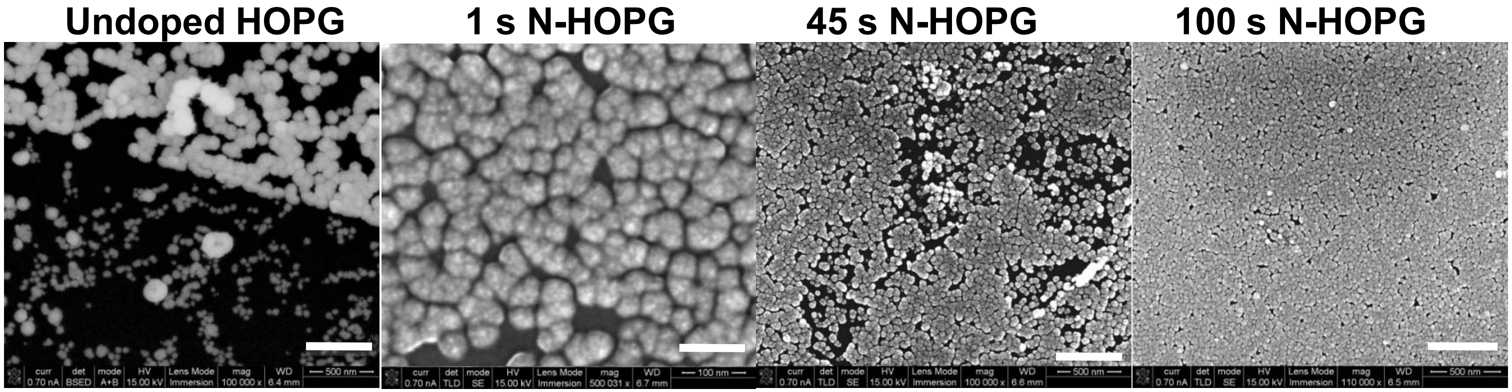
Single electrode cartridge shown on a 5 cartridge-style electrode holder.





Jet Propulsion Laboratory
California Institute of Technology
Pasadena, California

Technical Accomplishments and Progress
High-throughput electrochemical screening



Mag: 100 kX
Scale Bar = 500 nm

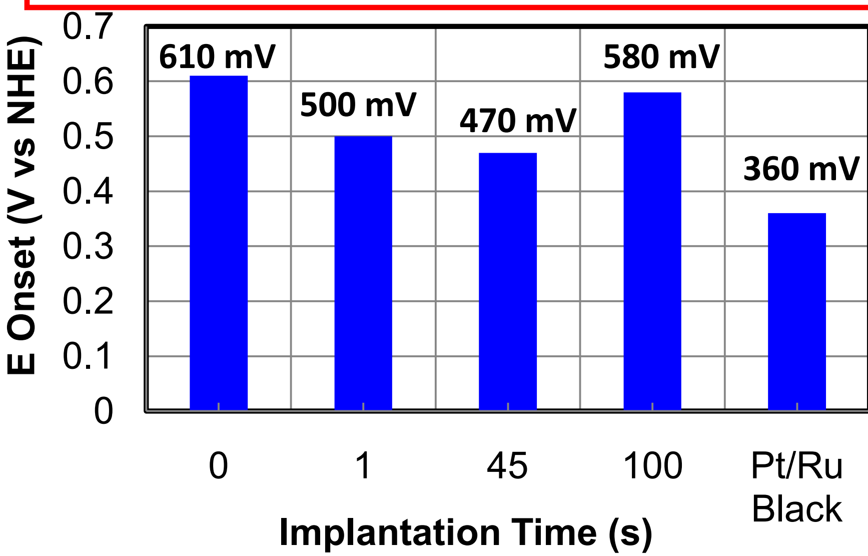
Mag: 500 kX
Scale Bar = 100 nm

Mag: 110 kX
Scale Bar = 500 nm

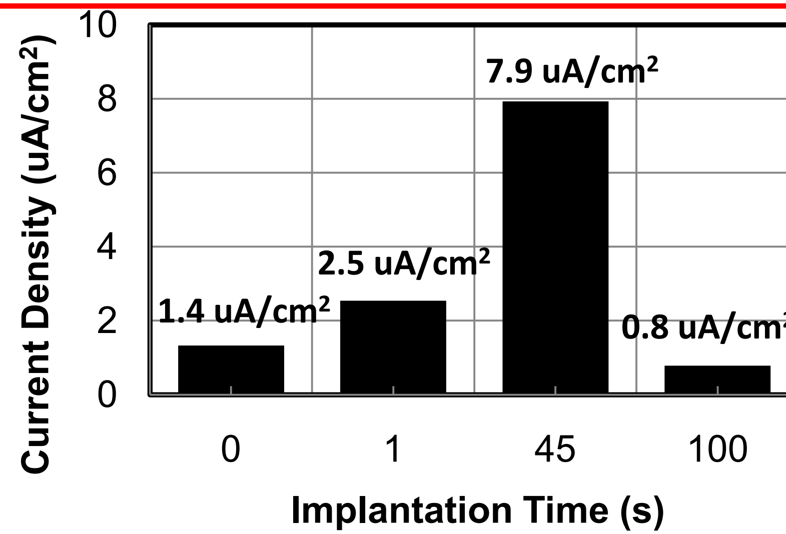
Mag: 100 kX
Scale Bar = 500 nm

20 potential pulses, applied at -0.3 V vs. RHE for 0.4 sec each on HOPG substrate [Pt(IV) and Ru(III) salts]

Electrochemical data confirms 45 s N-HOPG is optimum for methanol oxidation activity

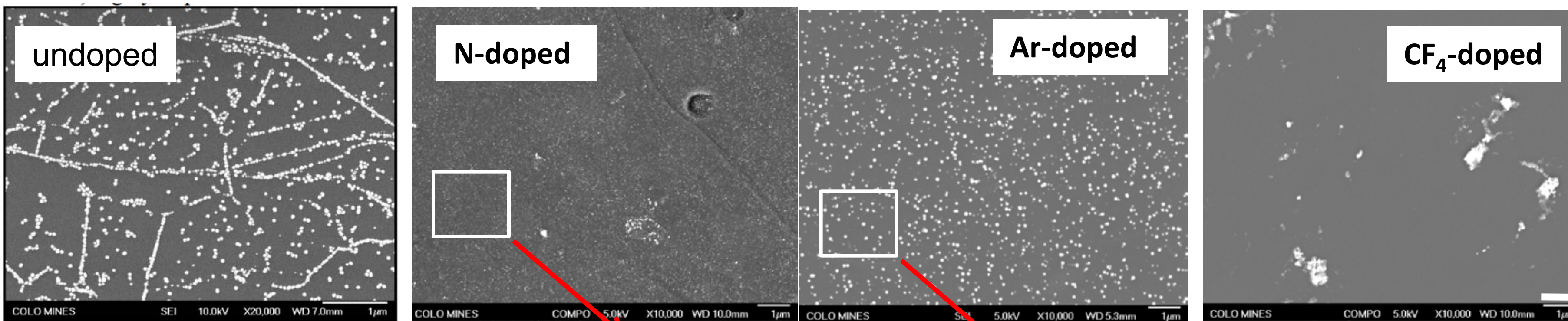


MOR Onset Potential vs. Implantation Time



Methanol oxidation current density at 0.65 V vs. NHE

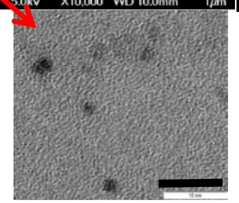
Technical Accomplishments – Effect of different dopants (electrodeposition of “low loading” PtRu on HOPG)



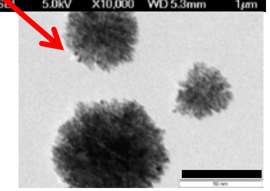
1 µm

Potential pulses are applied at -0.3 V vs. RHE for 0.4 sec each

- 3-5 pulses for small particles
- 20-40 pulses for increased surface coverage



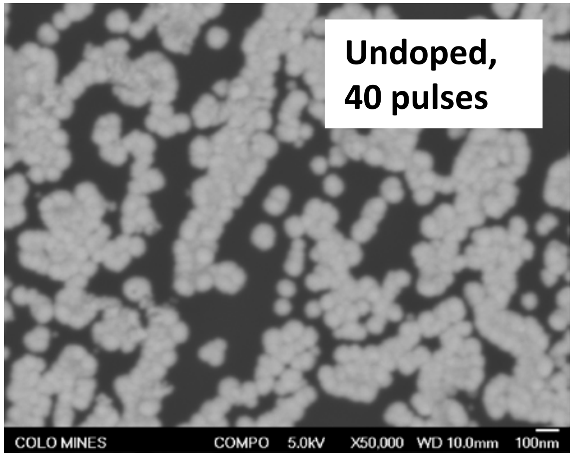
10 nm

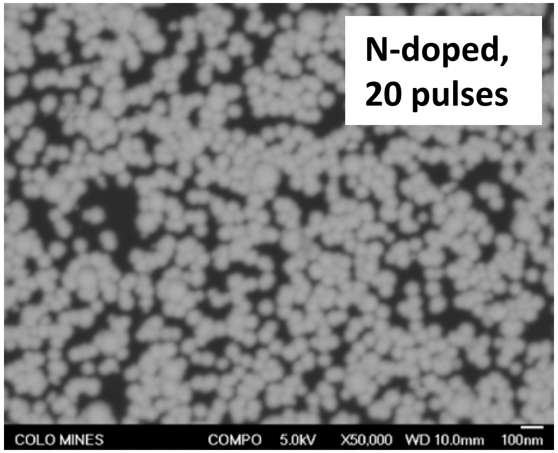


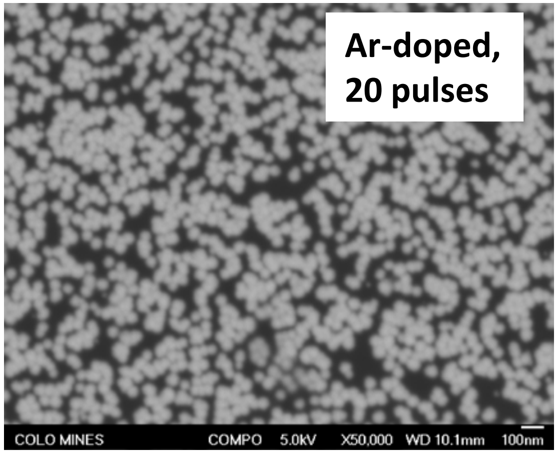
50 nm

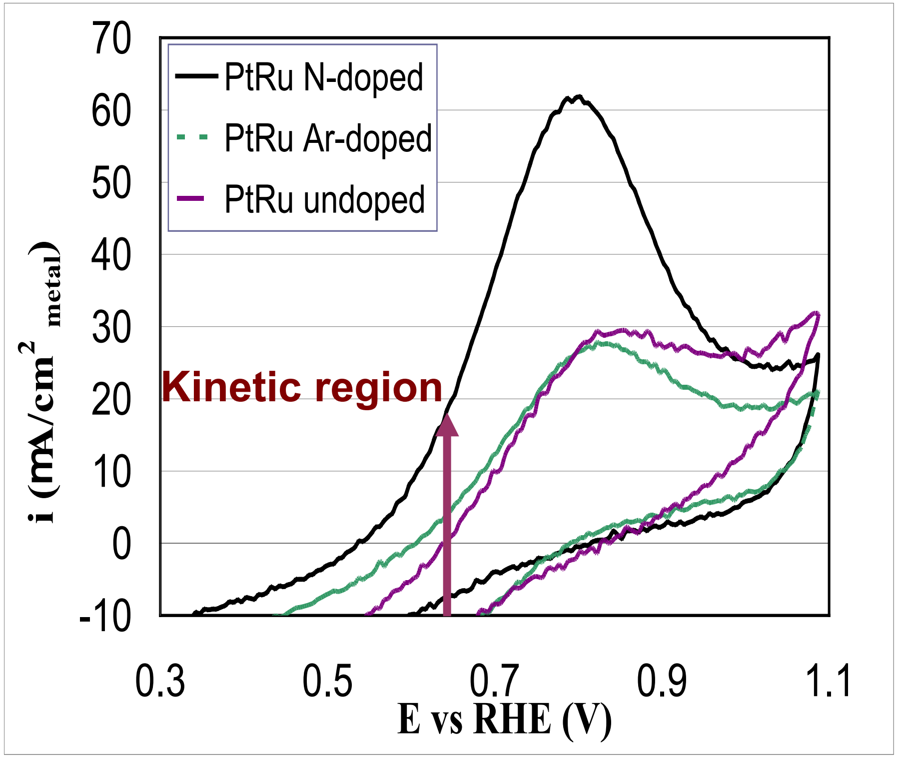
- **The best dispersion of PtRu catalyst is obtained on N-doped sample.**
- Ar-doping improved dispersion compared to undoped sample but resulted in a more pronounced agglomeration compared to N-doping.
- CF_4-doping possibly inhibits metal deposition
- Doping leads to expected decrease in the contact angle, N_2,Ar, CF_4<undoped
- Investigation of structure and composition of the doped HOPG samples is necessary to elucidate the differences in the metal deposition.

Technical Accomplishments and Progress
Electrodeposition of "high" loading PtRu on HOPG









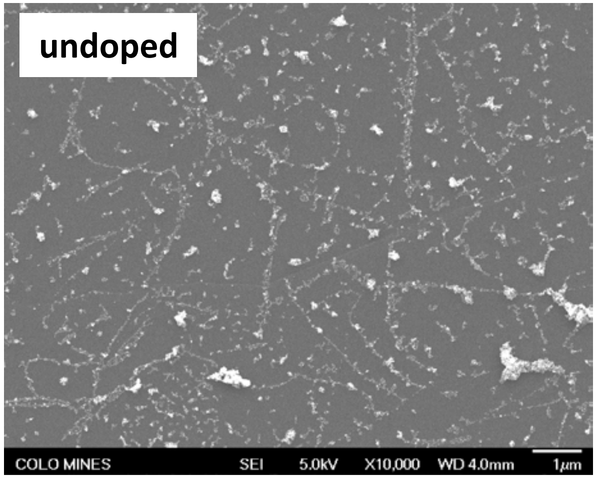
N-doped: highest activity & best onset potential

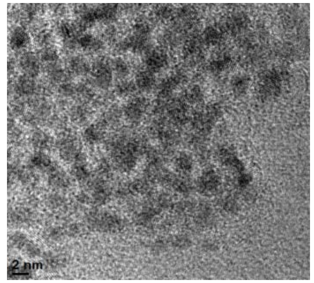
	Roughness Factor cm^2_{metal} / $cm^2_{electrode}$	i @ 650 mV $\mu A/cm^2_{metal}$
PtRu/HOPG	0.24	1.5
PtRu/N-HOPG	1.47	20.7
PtRu/Ar-HOPG	1.09	5.4

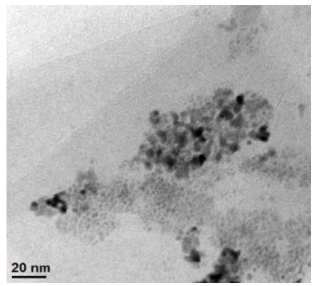
cm^2_{metal} = area determined from CO stripping voltammetry

$cm^2_{electrode}$ = geometric area

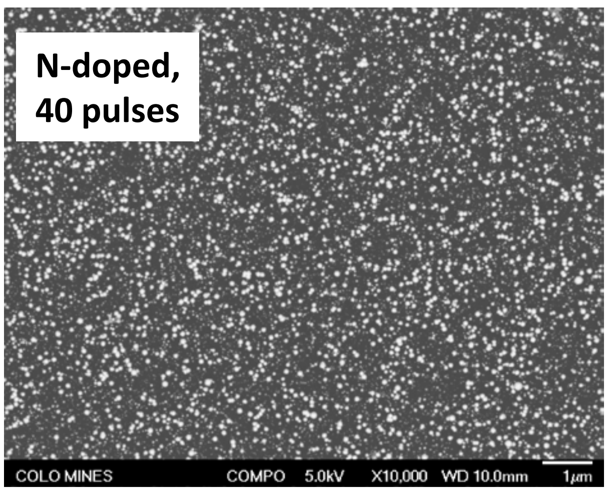
Technical Accomplishments and Progress
Microwave deposition of PtRu

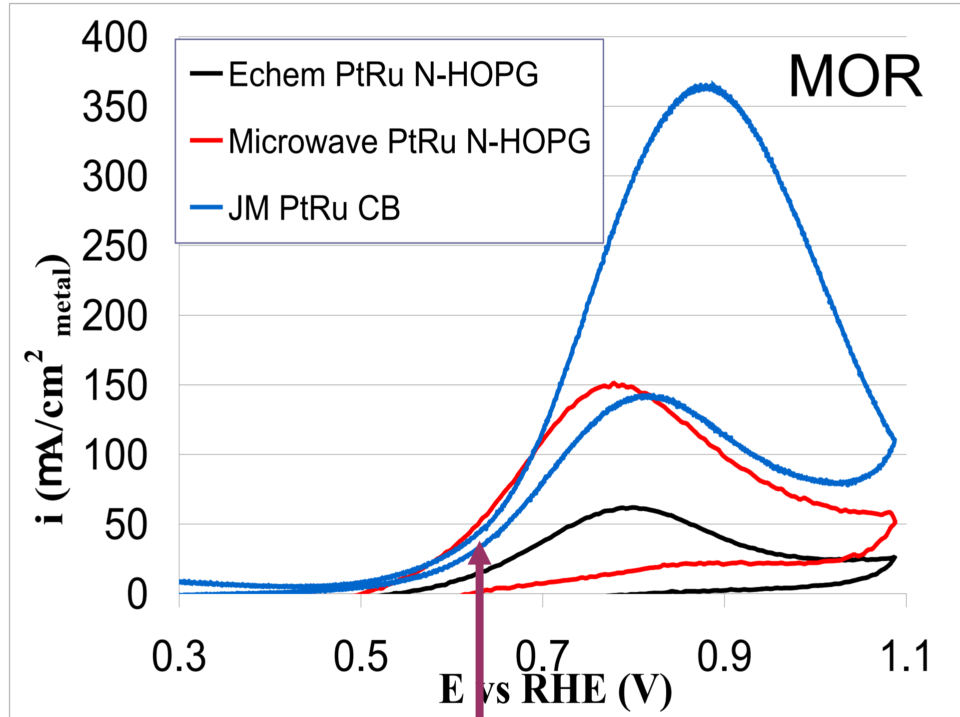






Microwave-250 W - pulsed





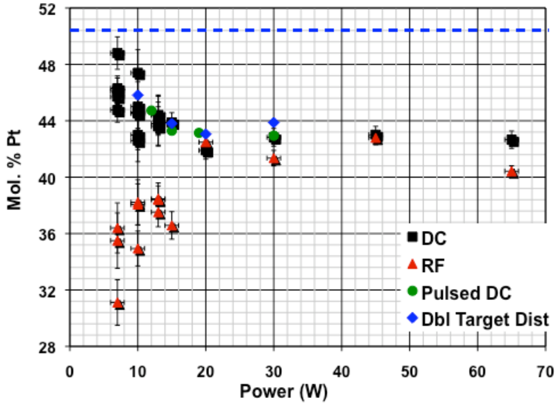
Kinetic region

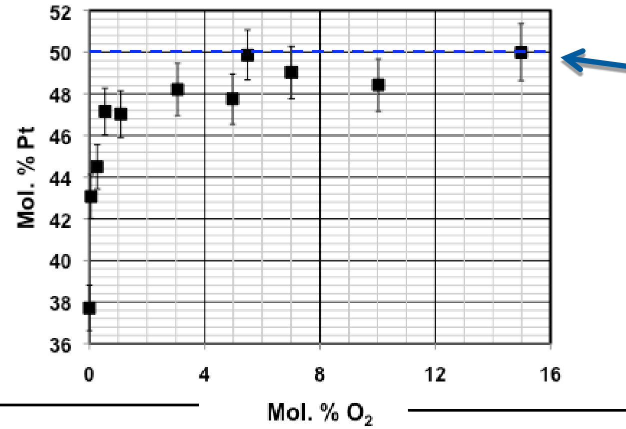
	Roughness Factor cm^2_{metal} / $cm^2_{electrode}$	i @ 650 mV $\mu A/cm^2_{metal}$
E-chem PtRu N-HOPG	1.5	20.7
Microwave PtRu N-HOPG	1.1	72.0
JM HiSPEC 10000 PtRu/C	22.5	58.0

Comparable performance to commercial catalyst (durability underway)

Technical Accomplishments and Progress
Sputtered $Pt_{1-x}Ru_x$ Thin Films from single target

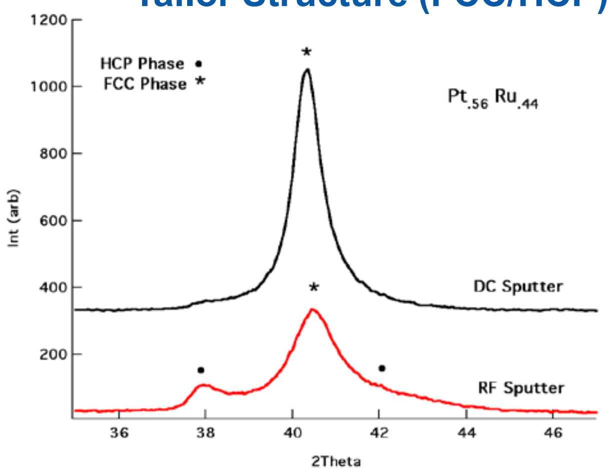
Pt composition after sputter from 50:50 Pt-Ru alloy target.



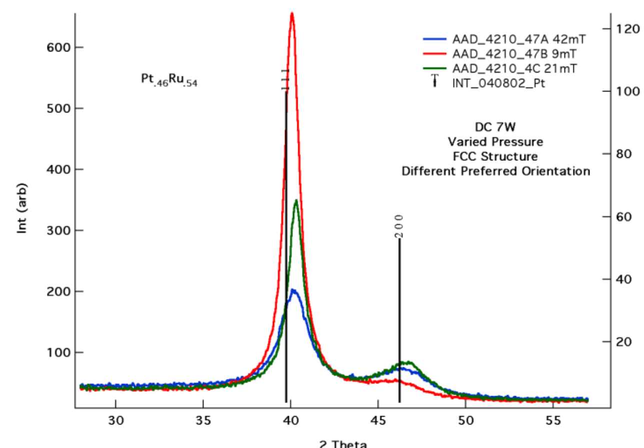


Target composition; expected equilibrium composition

Tailor Structure (FCC/HCP)



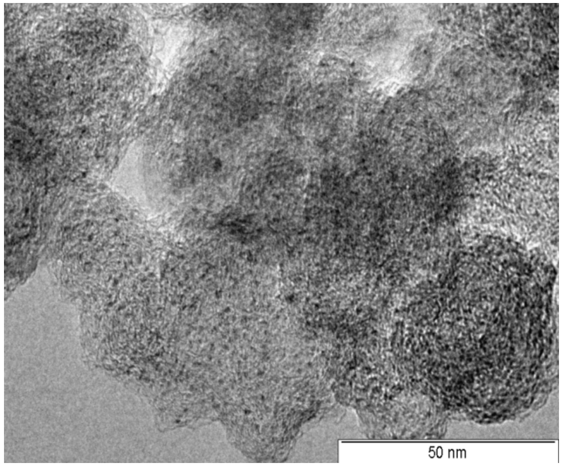
Tailor Orientation via Pressure

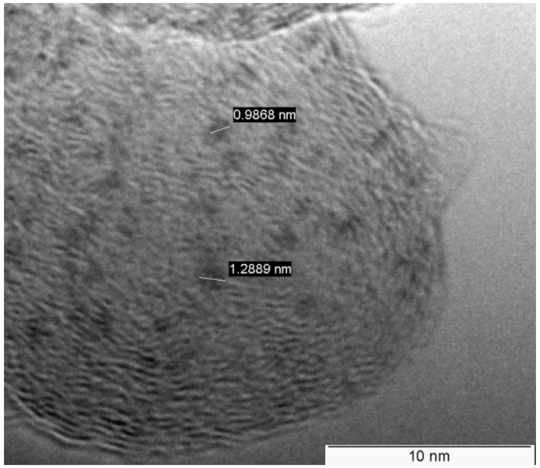


- The film/particle compositions can be effectively controlled with sputtering power
- Can deposit PtRu alloy or amorphous oxides, as thin films or particles
- Changing the chamber O_2 concentration impacts the Pt:Ru ratio of the films
- Experimentally can control composition, preferred orientation and phases

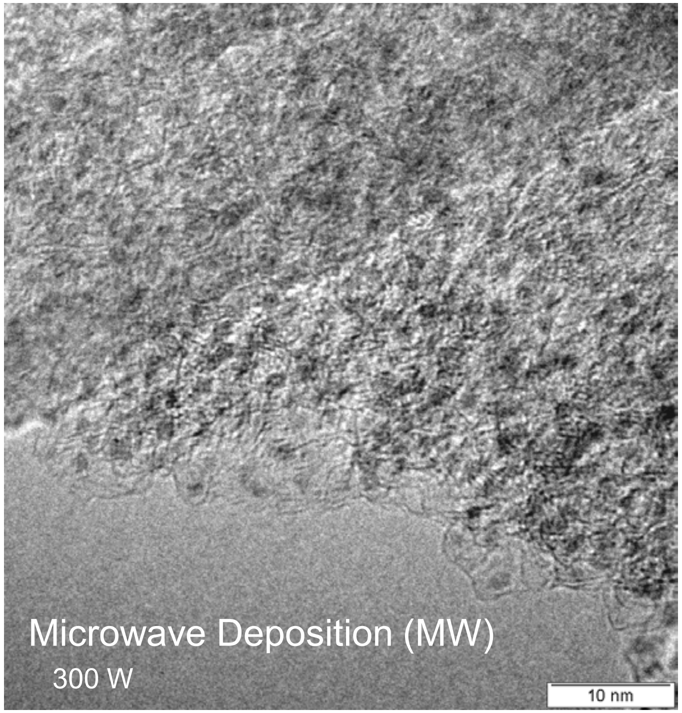
Technical Accomplishments and Progress
Synthesis capabilities for high surface area carbon

PtRu particle dispersion on Black Pearl carbon (1200 m^2/g) via MW (70% Pt, 30% Ru by XRF)





MW Ruthenium particle deposition on chemical vapor deposition (CVD) synthesized B-doped carbon substrate (1100 m^2/g)

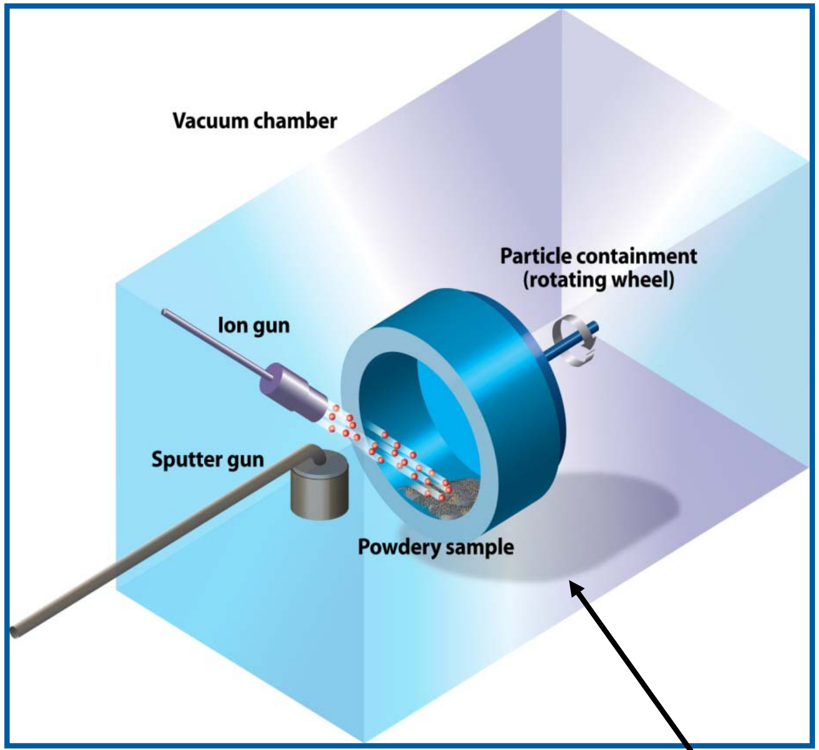


Excellent dispersion of catalyst particles, similar to commercial grade.
(Electrochemistry characterization underway)

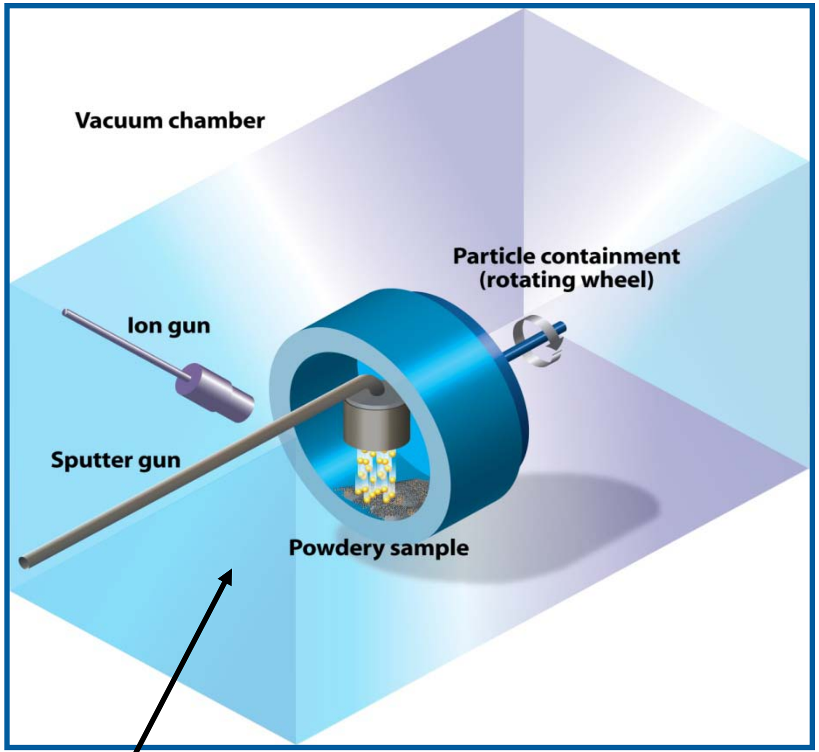
Technical Accomplishments and Progress
Powder ion implantation/Sputter chamber

Chamber is built for implanting ions and sputtering catalyst on high surface area carbon materials

Ion Implantation



Sputtering PtRu



Vacuum chamber

Technical Accomplishments and Progress

Focus: Enhance performance of methanol fuel cells with novel catalyst-substrate matrix.

1. Established an optimal N-implantation parameter set for HOPG
   - Demonstrated enhanced PtRu catalytic activity for methanol oxidation by achieving smaller particle size and higher dispersion of PtRu catalyst on N-doped carbon substrate.
   - **Comparable performance to SOA catalyst (either electrochemical or microwave deposition).**
   - Preliminary results suggest an apparent increase in durability of PtRu on N-doped HOPG as compared to undoped.
2. Sputter deposition of alloy with controlled composition from single alloy target.
   - **Experimentally can control composition (%), preferred orientation (crystal face) and phases (hcp/fcc)**
3. Established protocol for deposition of uniform PtRu catalysts particles on commercial and CVD synthesized B-doped and N-doped powders
   - **Commercial grade dispersion on powders, evaluation underway.**
4. Developed a process and built the chamber to implant ion and sputter PtRu onto carbon powders

Collaborations & Project Participants

- **Develop novel catalyst-doped supports** (NREL, CSM)
- **Combinatorial electrode studies** (JPL, NREL)
- **Generate down-selected novel catalysts for DMFC membrane electrode assembly (MEA)** (NREL, CSM, BASF*)
- **MEA Evaluation** (NREL,CSM, MTI#)

Accelerated built-up of team to accelerate progress:

NREL: *Staff*; Huyen Dinh, Thomas Gennett, David Ginley, Bryan Pivovar, Kevin O'Neill, Katherine Hurst,

PostDocs: Arrelaine Dameron, Jennifer Leisch, Tim Olson, KC Neyerlin.

CSM: Prof. Ryan O'Hayre, Svitlana Pylypenko (postdoc) & graduate students

JPL: *Staff:* Charles Hays, Sri R. Narayan

#Independent MEA performance evaluation
*Provide state of the art catalyst for benchmarking

Proposed Future Work

- Initiate implantation of other dopants into HOPG (B, S, I)
- Continue combinatorial electrochemical investigation of various implanted HOPG substrates (type and extent of dopant) (JPL)
- Investigate different methods to dope high surface area carbon (in situ and ex situ)
  - ion implantation, chemical vapor deposition, pyrolysis
- Investigate the effect of different high surface area carbon supports
- Characterize and measure methanol oxidation performance of PtRu/ doped high surface area carbon
- Select optimal materials, methods
- Construct MEAs from industrial standard PtRu catalyst and early generation tethered catalysts (PtRu/doped carbon)
- Measure DMFC performance and durability of tethered catalysts

Summary

Relevance: Focus on developing next generation DMFC anode catalyst materials that meet or exceed DOE's 2010 performance, durability and cost targets for consumer electronics application to enable and accelerate the commercialization of DMFCs.

Approach: Modify HOPG surface with different dopants, via ion implantation, to better understand the effect of catalyst-support interaction on enhanced catalyst activity and stability of PtRu catalyst nanoparticles. Apply this dopant-engineering approach to develop advanced PtRu anode catalyst systems by doping high surface area carbon supports. This will improve catalyst utilization, activity, and durability at lower catalyst loading.

Technical Accomplishments and Progress: We have achieved significant progress to-date, including assembling the team and establishing capability quickly. We have met all project milestones (deadline extended for one FY'09 milestone). All subcontracts and funding are in place We have established different PtRu deposition methods, optimized N-doping level (45 s) on HOPG via ion implantation, demonstrated that nitrogen implantation on HOPG enhanced the methanol oxidation activity and durability on PtRu catalyst, developed a processing system for ion implantation of high surface area carbon materials, and initiated study of high surface area carbon.

Collaborations: We have a diverse team of researchers with relevant expertise in materials synthesis and characterization and fuel cells, from several institutions including 2 national labs, a university, and 2 industry partners.

Proposed Future Research: We will study other dopants and transition from model HOPG substrate to real catalyst systems using high surface area carbon.

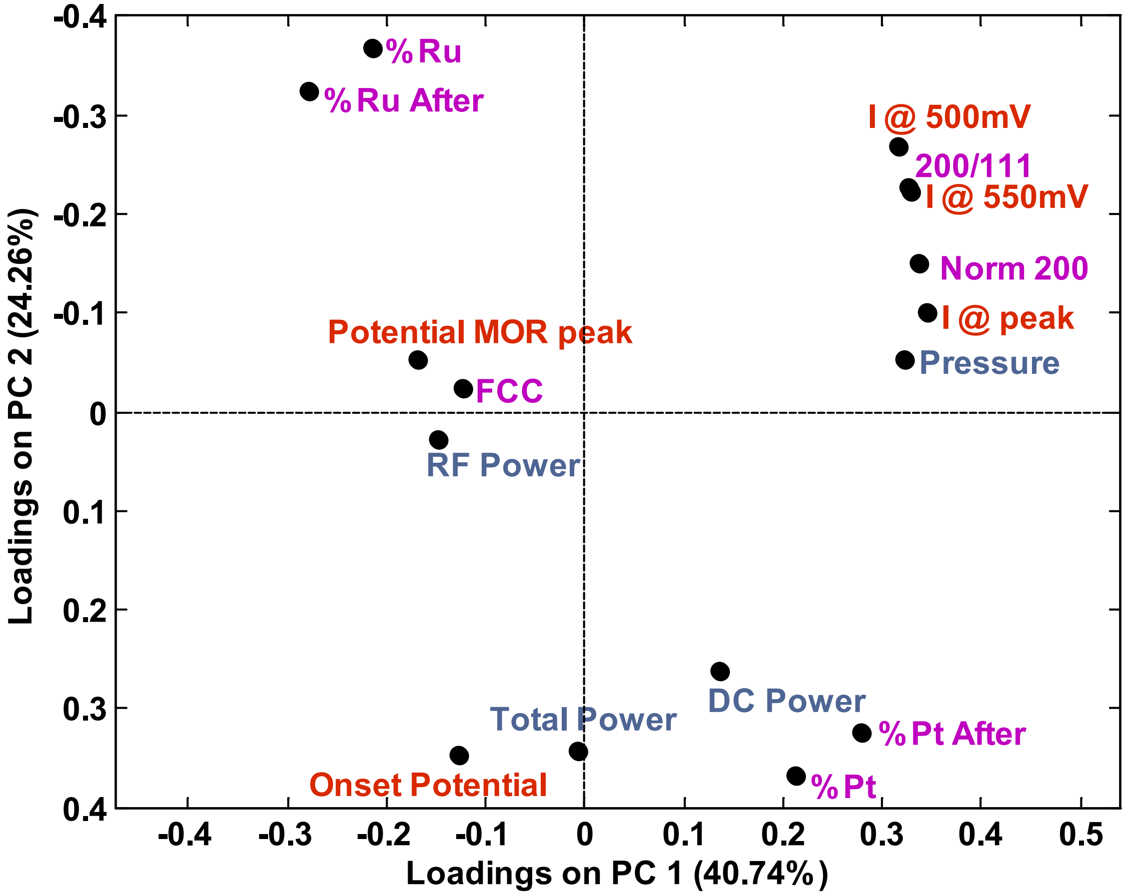
Supplemental Slides

Presentations & Publications

1. A. Dameron, S. Pylypenko, S. Studer, J. Leisch, K. Neyerlin, T. Olson, K. O'Neill, A. Queen, R. O'Hayre, H.N. Dinh, T. Gennett "Sputtering $Pt_{1-x}Ru_x$ Alloyed Particles for Direct Methanol Fuel Cell Catalysts", American Chemical Society Spring 2010 Meeting, March, 2010
2. S. Studer, "Electrochemical Analysis of Single Source Sputtered PtRu", Case Study Defense Presentation, Colorado School of Mines, March 2010.
3. Y. Zhou,K.C Neyerlin, T. Olson, S. Pylypenko, J. Bult, H.N. Dinh, T. Gennett, Z. Shao, R. O'Hayre, "Enhancement of Pt and Pt-Alloy Fuel Cell Catalyst Activity and Durability via Nitrogen-Modified Carbon Supports", Review paper for Energy & Environmental Science, submitted Jan 2010.

PCA Analysis of Relationships

We use Principal Component Analysis (PCA) to elucidate the relationships between sputtering parameters, composition and structure, and electrochemical performance.



PC1:

- Higher pressure → increase in [200] phase = largest effect on MOR Peak Current
- Higher %Pt → higher Currents

PC2:

- Higher DC Power and Total Power → higher %Pt → more positive onset potential
- Lower DC Power and Total power → higher %Ru and higher ratio of [200]/[111] → more negative Onset Potential and higher Currents

PC3:

- Lower RF Power and lower Total Power, as well as lower Pressure result in more FCC structure and more positive MOR peak potential

PCA Analysis of Relationships

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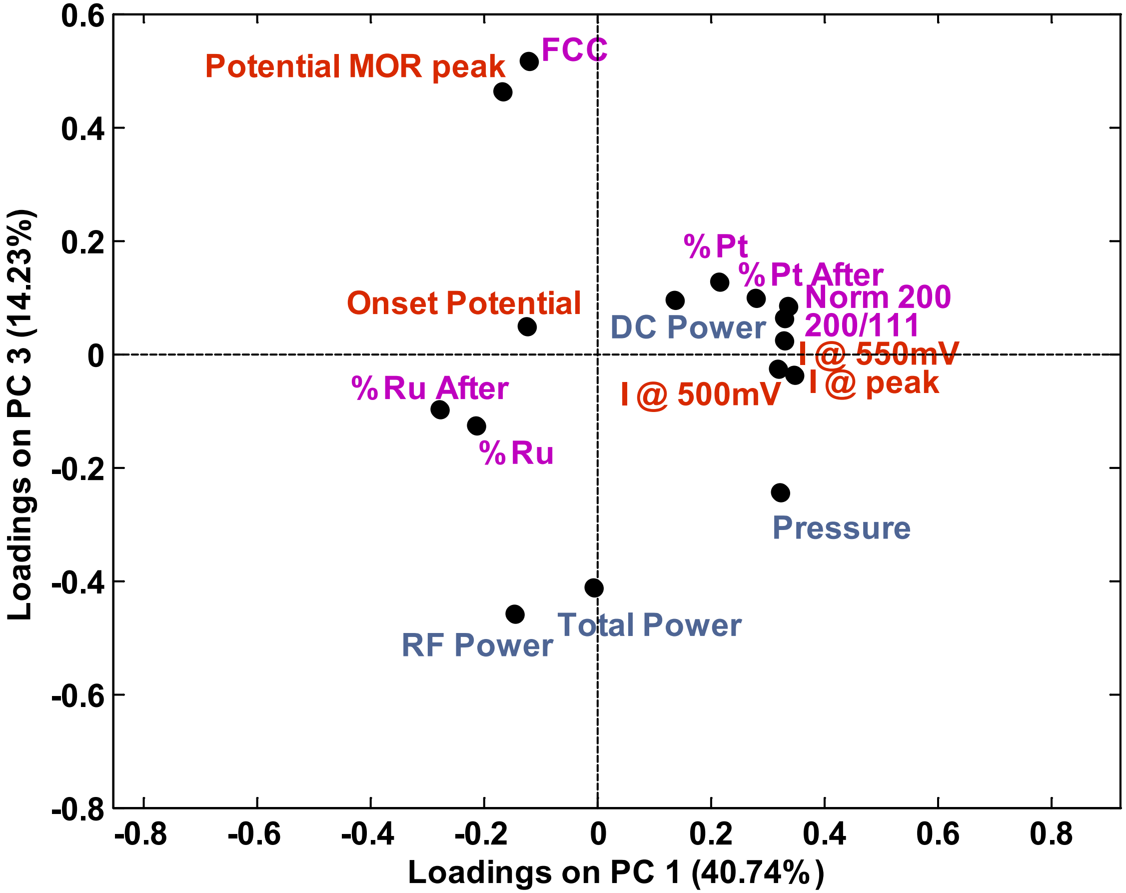

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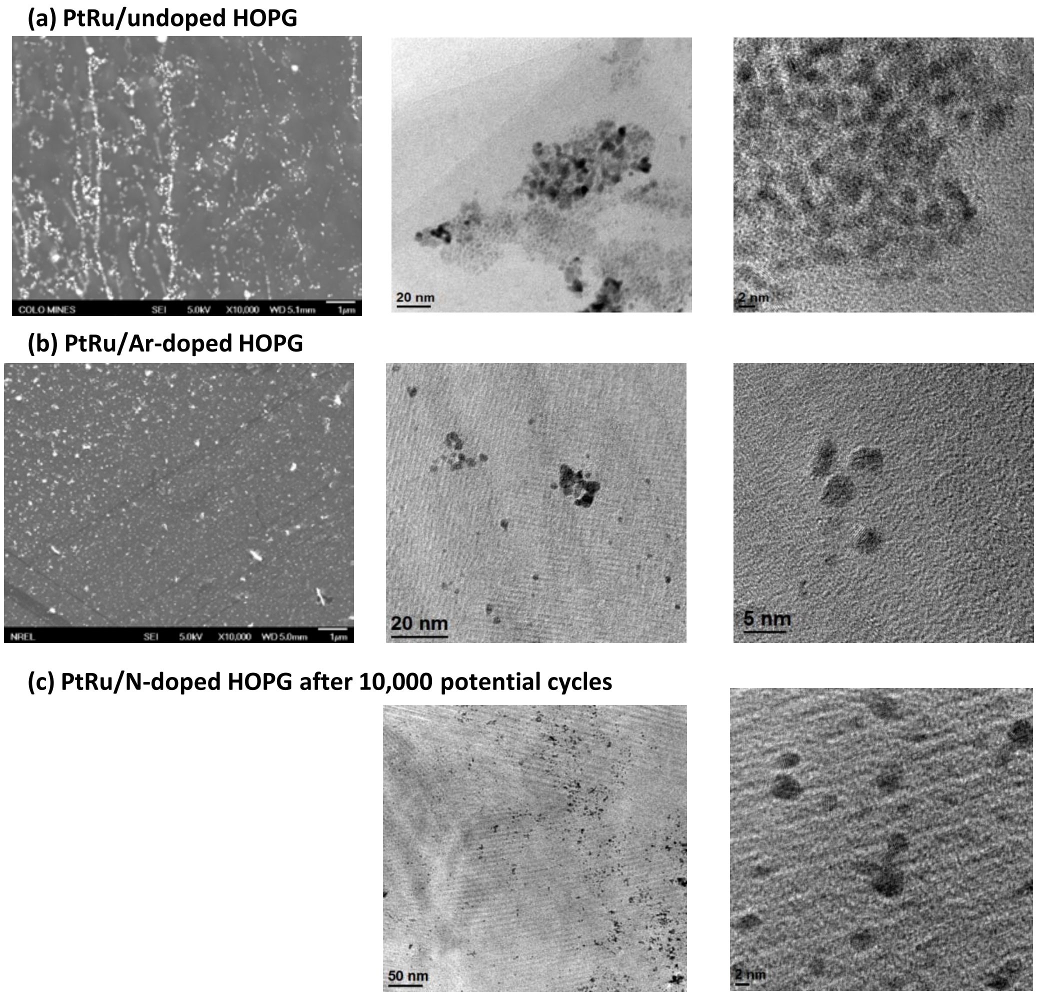
PC2:

- Higher DC Power and Total Power → higher %Pt → more positive onset potential
- Lower DC Power and Total power → higher %Ru and higher ratio of [200]/[111]→ more negative Onset Potential and higher Currents

PC3:

- Lower RF Power and lower Total Power, as well as lower Pressure result in more FCC structure and more positive MOR peak potential

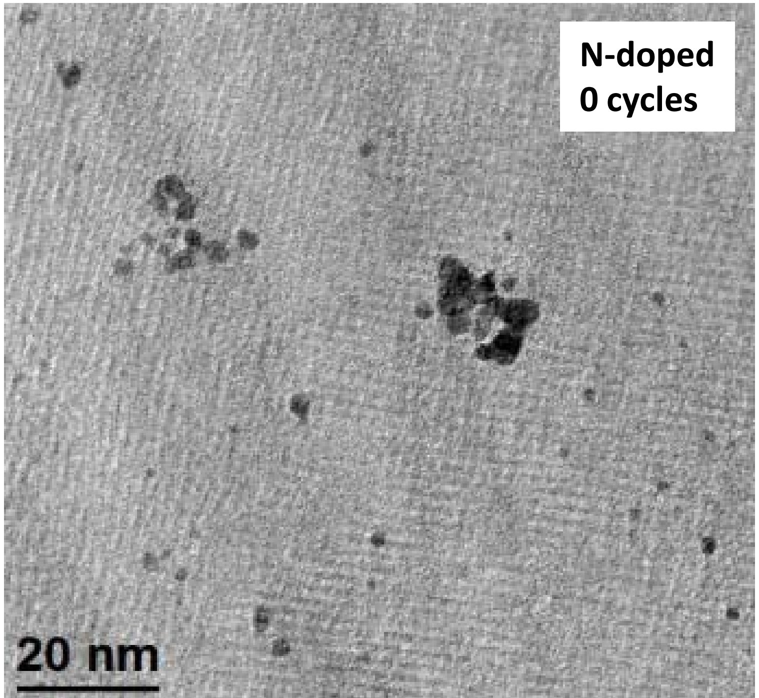
Preliminary durability of microwave deposited PtRu catalysts on N-doped HOPG

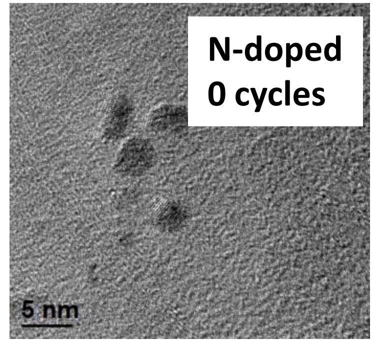


PtRu nanoparticles deposited on N-doped HOPG, via a **microwave**, are highly dispersed compared to PtRu catalysts deposited on undoped HOPG.

PtRu nanoparticles on the N-doped HOPGs are stable after 10,000 cycles between 0 and 1.2 V vs. Ag/Ag/Cl.

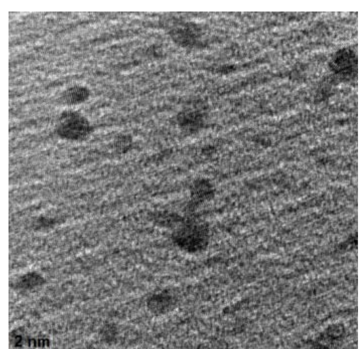
Technical Accomplishments - Durability of MW deposited PtRu catalysts on N-doped HOPG

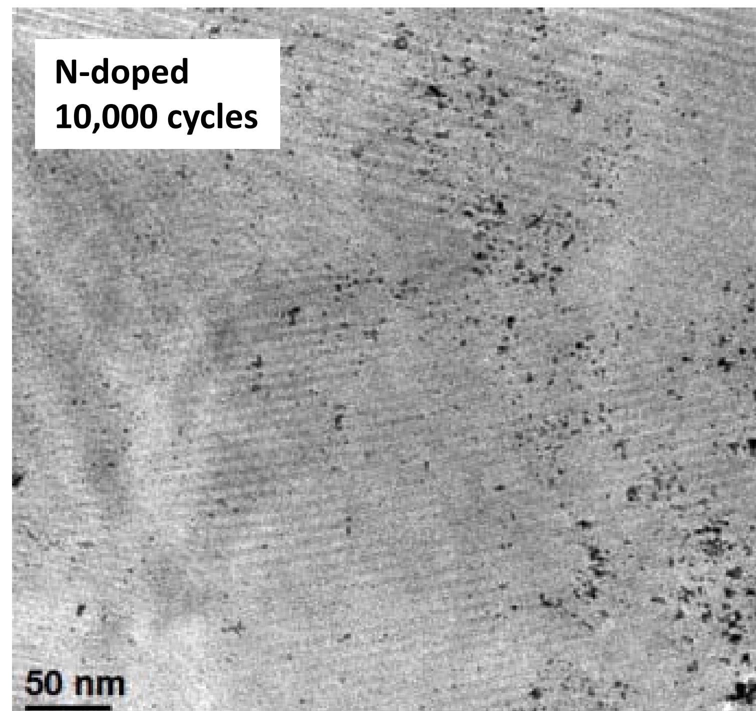


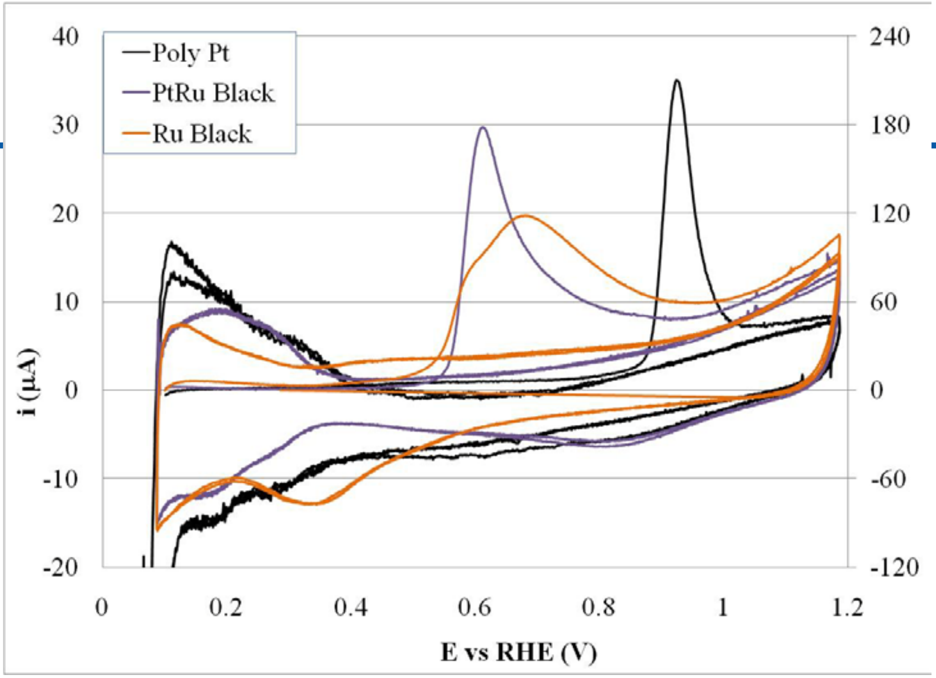


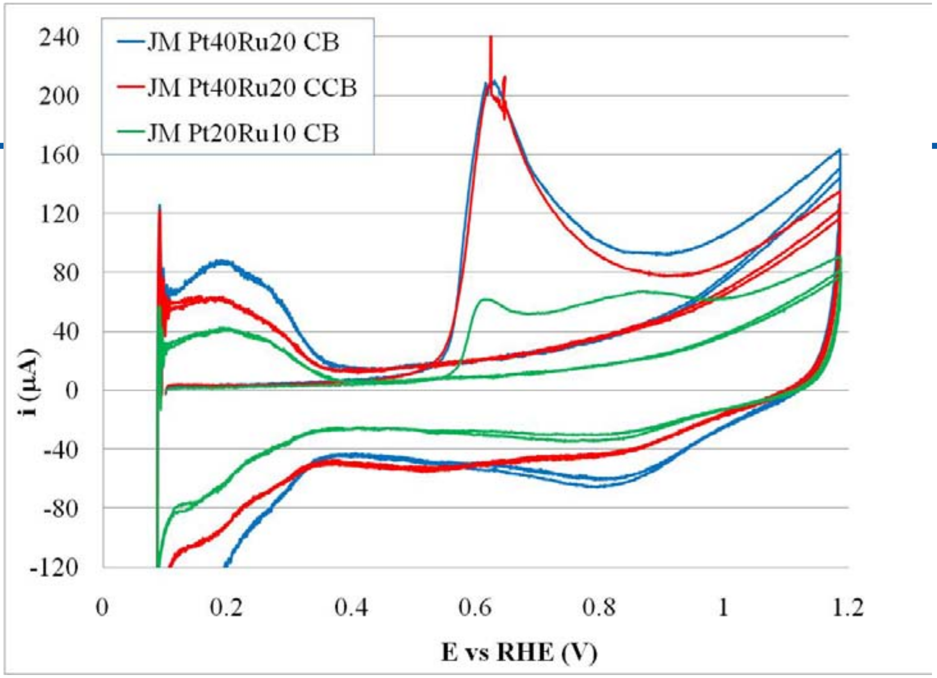
PtRu nanoparticles on the N-doped HOPGs are stable after 10,000 cycles (Low mass Loading)

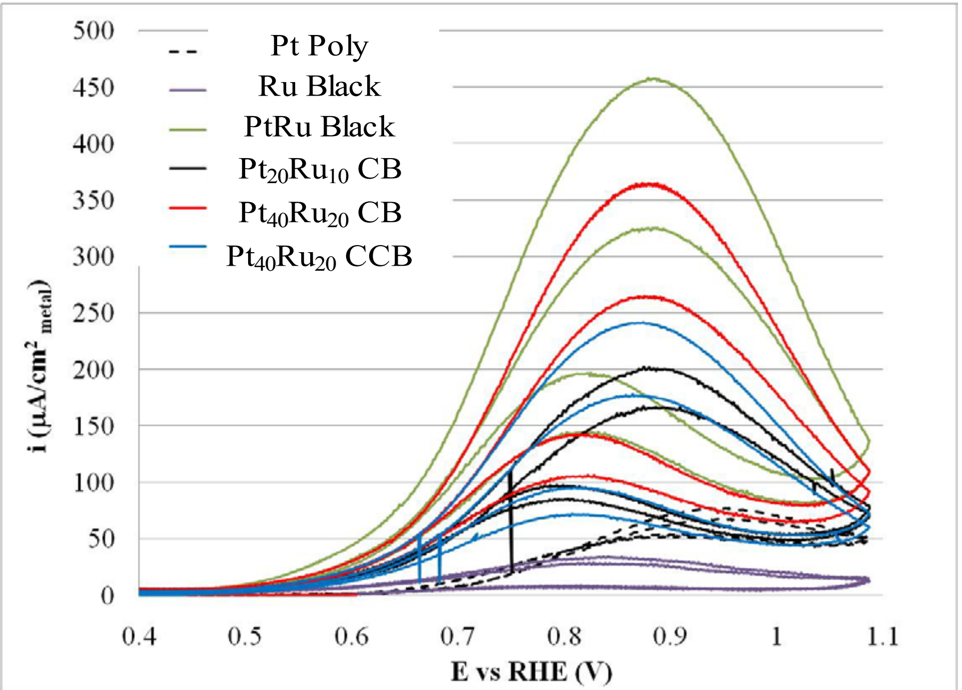
10,000 cycles between 0 and 1.2 V vs. Ag/Ag/Cl.











	CO stripping	RF	i @ 650 mV
	μW	$cm^2_{metal}/cm^2_{electrode}$	$\mu A/cm^2_{metal}$
Pt Poly	2.2	1.3	3.9
Ru Black	22.9	13.9	11.9
PtRu Black	23.0	14.0	83.3
$Pt_{20}Ru_{10}$ CB	16.0	9.7	34.5
$Pt_{40}Ru_{20}$ CB	37.0	22.5	58.0
$Pt_{40}Ru_{20}$ CCB	33.0	20.0	45.7

XPS: Structural & chemical modification of HOPG