NREL
NATIONAL RENEWABLE ENERGY LABORATORY

Novel Approach to Advanced Direct Methanol Fuel Cell Anode Catalysts

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Presenter - Thomas Gennett

National Renewable Energy Laboratory (NREL)

May 13, 2011

2011 DOE Hydrogen and Fuel Cells Program Review

FC041

Overview

Timeline

Start: July 2009
End: September 2011
% complete: ~80%

Budget

DOE Cost Share	Recipient Cost Share	TOTAL
$2.4M	$69,714	$2.47M*

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

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

Barriers

Barrier	2010 Target (consumer electronics)
A: Durability	5,000 h
B: Cost	$3/W
C. Performance	100 W/L, 100 W/kg

Partners (PI)

Colorado School of Mines (CSM)
[Ryan O'Hayre]

Jet Propulsion Laboratory (JPL)
[Charles Hayes]

MTI MicroFuel Cells (MTI)
[Chuck Carlstrom]

BASF Fuel Cells (BASF)
[Emory DeCastro]

Relevance: Catalyst Support Interaction

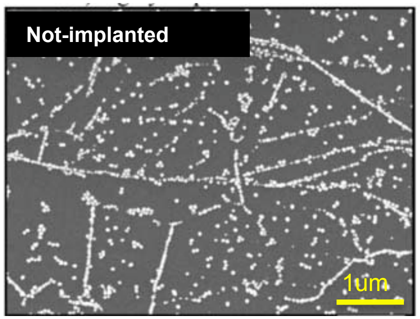
DOE Objective:

Develop and demonstrate direct methanol fuel cell (DMFC) anode catalyst systems that allow DOE's 2010 targets for consumer electronics application t be met.

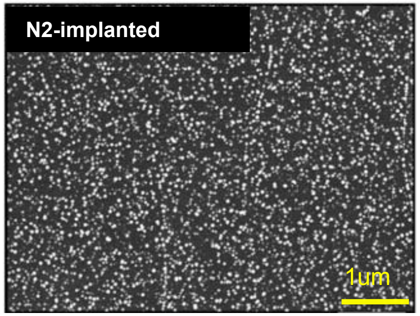
Project Goal:

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

Pt-Ru Nucleation HOPG

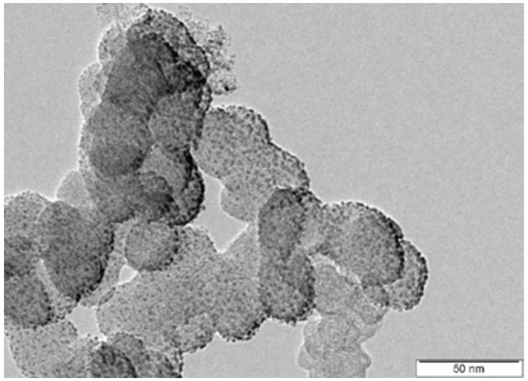


•Preferential nucleation on defect sites, step edges.



Increased nucleation density: preferential nucleation C-N, defect sites

Pt-Ru decorated carbon powder substrates via sputter deposition



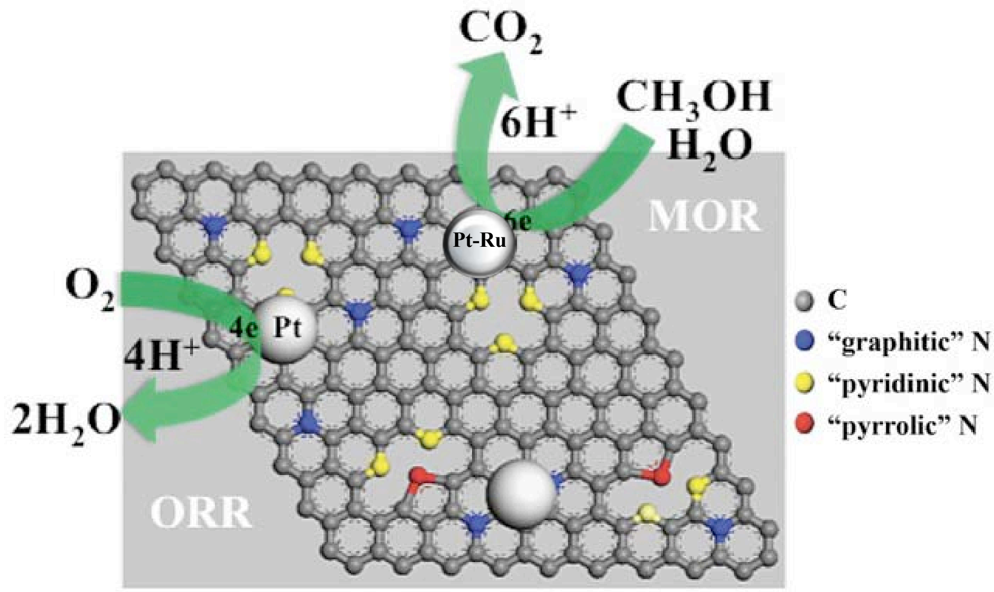
Enhanced catalyst substrate interactions are also advantageous for Oxygen Reduction Reaction (ORR) catalysis.

Relevance – Background Data - Approach

Performance

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

DFT calculations predict tethering of catalyst clusters on carbon next to substitutionally implanted nitrogen.



Durability:

N-implantation improved durability of Pt and Pt/Ru system(s) with minimal aggregation/coarsening of particles.

Cost:

To reduce cost, catalyst activity must be increased by ca. 10X of current state of the art system.

Enhanced mass activity for MOR with Pt/Ru can help reduce cost.

Improving durability, reduce costs with long-lifetime DMFC devices.

Task 1 – HOPG Model System
- Establish implantation effects (nitrogen and other gases)
- Nitrogen-content
- Durability-effects of cycling

Task 2 - Apply info from Task 1 to powder systems

Task 3 – Go/No-go decisions on specific powders

Task 4 – Optimize implantation-sputter conditions for "go" carbon substrate materials via half-cell performance.

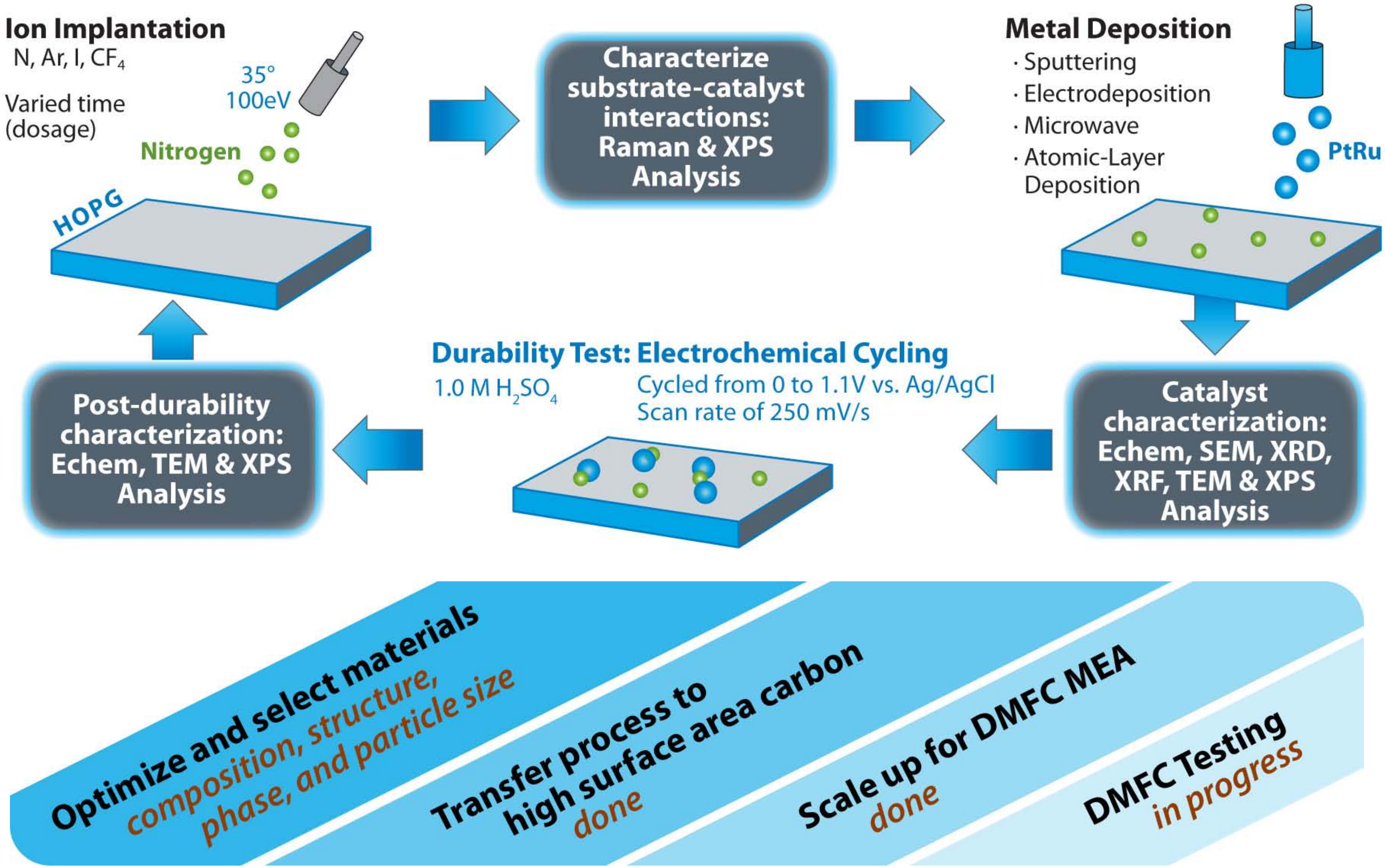
Task 5 – Construct MEAs of best performing materials

Approach – FY10-11 Milestones

2010	1	Perform sputter deposition of PtRu on HOPG surface to establish optimal deposition parameters.	12/2009	100% complete
	2	Develop a processing system for nitrogen doping of applicable carbon materials.	04/2010	100% complete
	3	Perform 5 cm2 fuel cell testing of MEAs fabricated with novel catalysts with highest performance.	09/2010	100% complete

2011	1	Identify promising dopant system(s) (>3 uA/cm^2 metal at 550 mV) for further optimization using high-throughput electrochemical screening. (CF_4 implantation)	12/2010	100% complete
	2	Deliver at least 2 MEAs to MTI for independent fuel cell benchmarking. (pending NDA)	02/2011	100% complete
	3	Demonstrate 50% improvement in methanol oxidation reaction performance of PtRu/doped carbon powders compared to an undoped system.	08/2011	20% complete
	4	Submit final report on N-doping for DMFC catalysts to DOE.	09/2011	

Approach: Highly-Oriented Pyrolytic Graphite, HOPG

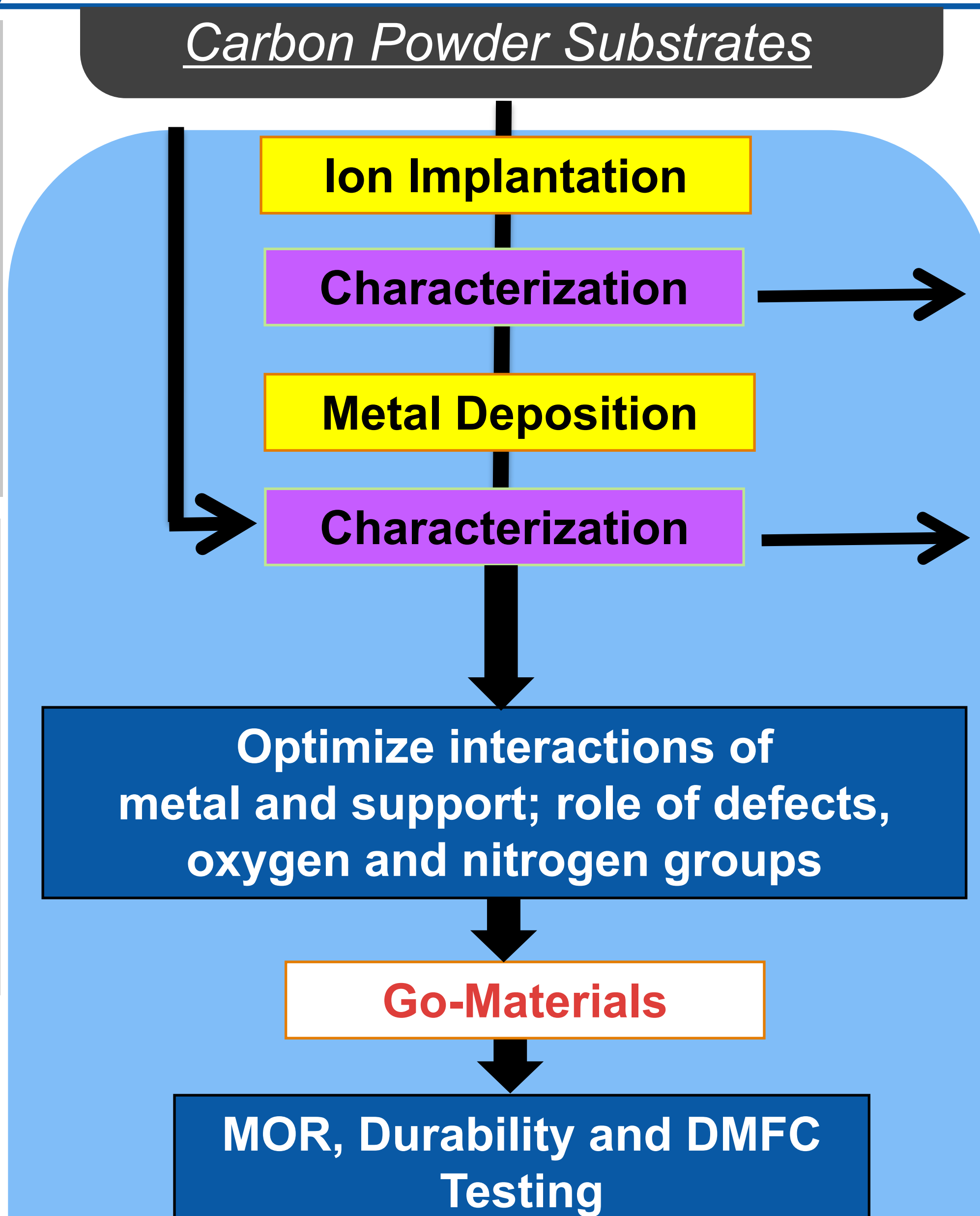


Approach: Powders

Materials Synthesis and Characterization

Carbon:
- **Vulcan (Go)**
- Ketjen
- Black pearl
- Pyrolyzed PEEK
- Carbon Nanotubes
- Graphitic nanofibers

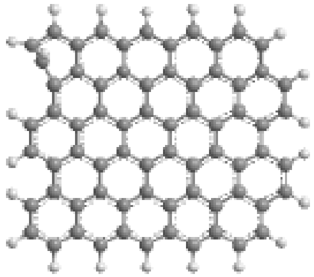
Metal Deposition
- **Magnetron Sputtering (Go)**
- Atomic layer deposition (ALD)
- Electrodeposition
- Microwave
- Incipient wetness



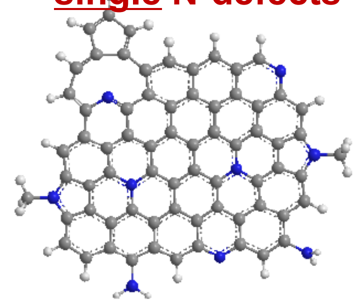
Characterization
- Electrochemical (half-cell)
  - CO Stripping
  - Methanol oxidation
- Microscopic (TEM, SEM, AFM)
- Temperature Programmed Desorption (TPD)
- Thermogravimetric Analysis (TGA)
- X-Ray Photoelectron Spectroscopy (XPS)
- X-Ray Diffraction (XRD)
- X-Ray Fluorescence (XRF)

Technical Accomplishments: HOPG, Effect of N_2 dosage on durability:

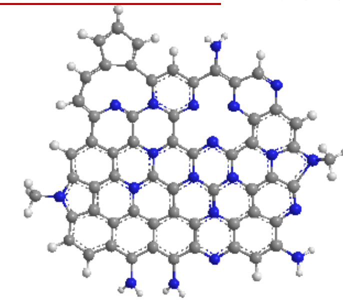
Undoped HOPG



Low implantation dose: single N-defects

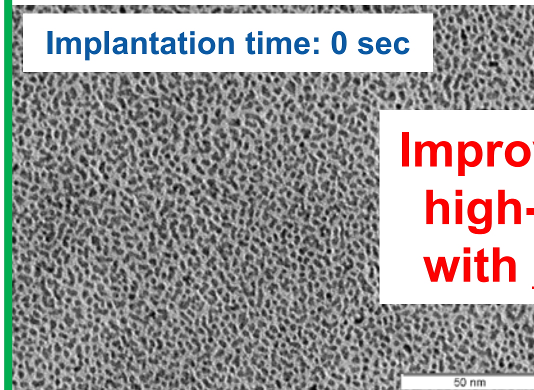


High implantation dose: clustered multi-N-defects

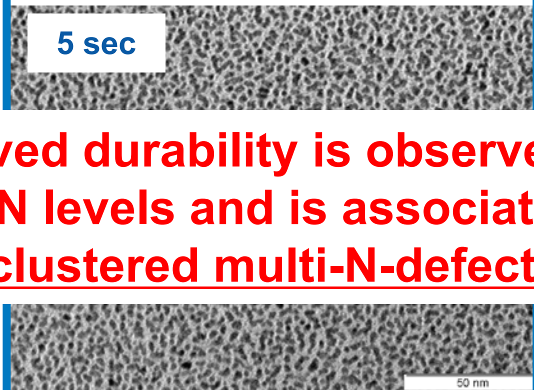


Before Cycling

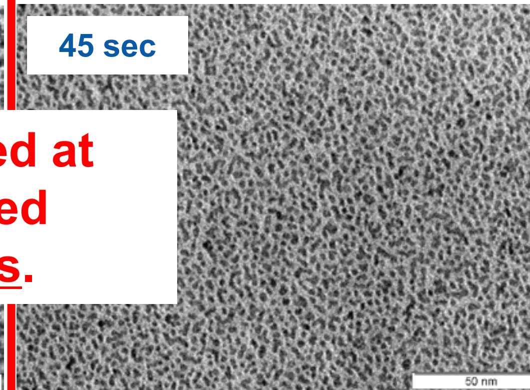
Implantation time: 0 sec



5 sec



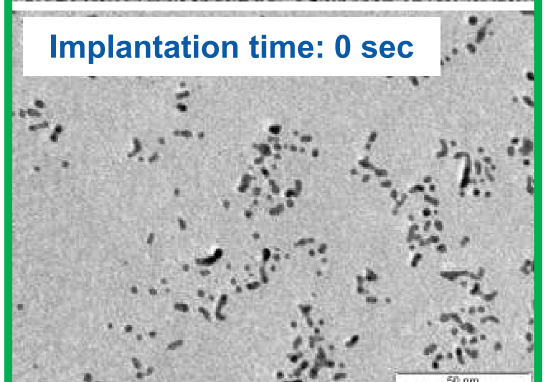
45 sec



Improved durability is observed at high-N levels and is associated with clustered multi-N-defects.

After 300 Cycles

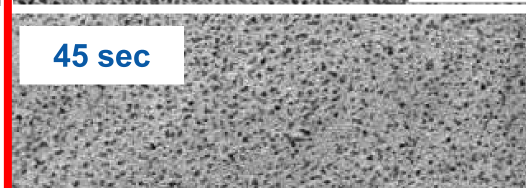
Implantation time: 0 sec



5 sec

Oswald ripening
Migration/coalescence

45 sec



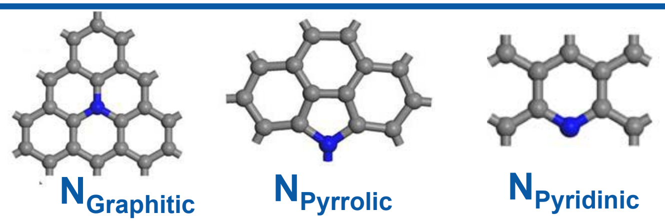
Positive effect on stability: Oswald ripening and Migration/coalescence is minimized!

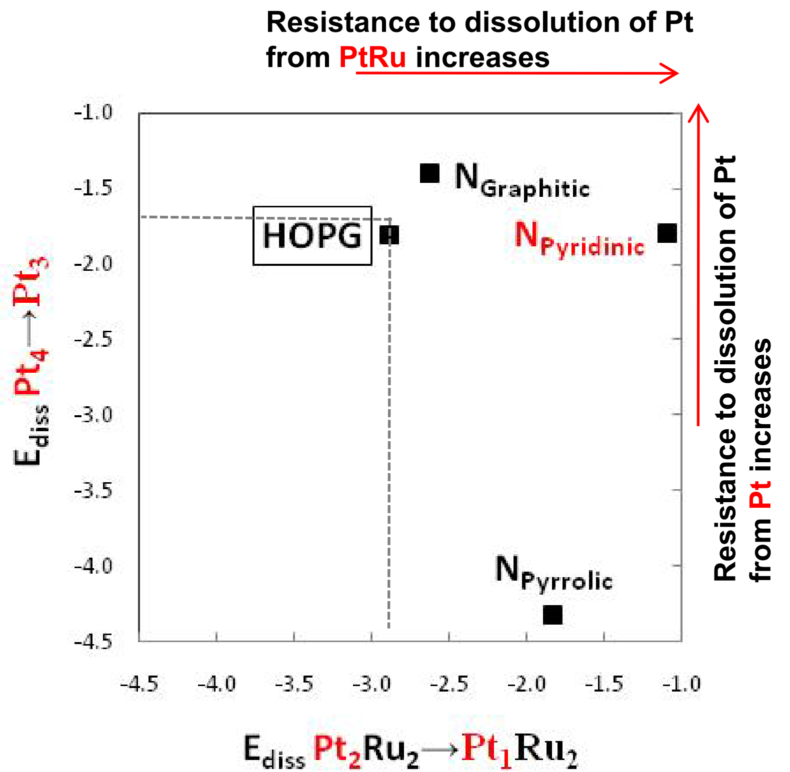
50 nm

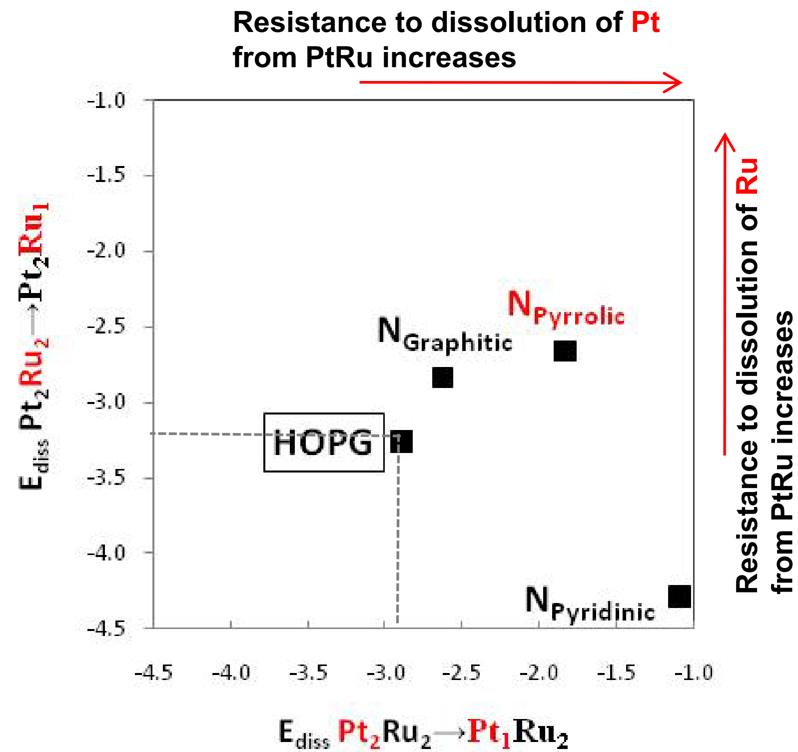
Potential cycling:
1.0 M H_2SO_4,
from 0.2 V to 1.3 V vs. RHE, scan rate of 250 mV/s

Technical Accomplishments: HOPG; Effect of nitrogen functionalities and nitrogen concentration on durability.

- A variety of N functionalities are formed during implantation
- Implantation of HOPG results in $N_{Pyrrolic}/N_{Pyridinic} = 1.2$
- DFT was used to infer on the effect of specific N functionalities on stability of Pt-Ru







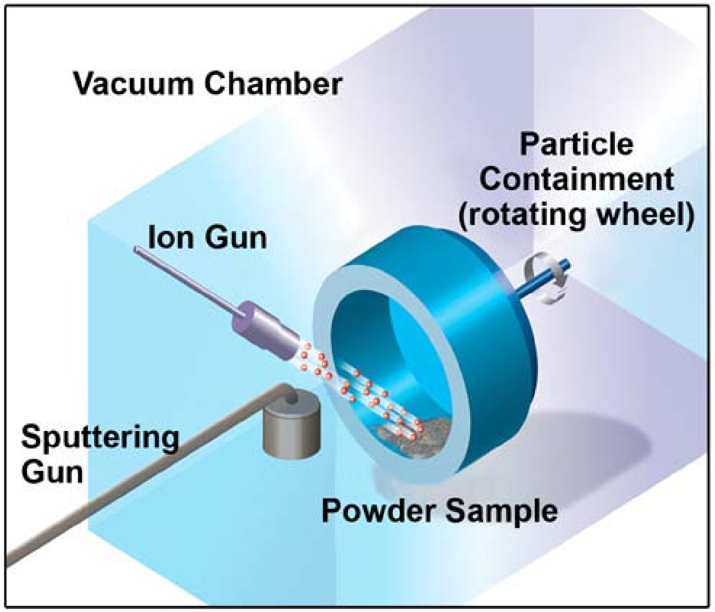
- In the presence of Ru, dissolution of Pt becomes more prevalent than in case of pure Pt
- N defects increase stability of Pt in PtRu

- Dissolution of Pt and Ru are equally important
- Pyrrolic N improves stability of Pt-Ru by stabilizing both Pt and Ru

Tim Holme, Stanford University

Technical Accomplishments and Progress: Powders
Powder ion implantation/Sputter chamber (FY 10 Milestone)

Ion Implantation

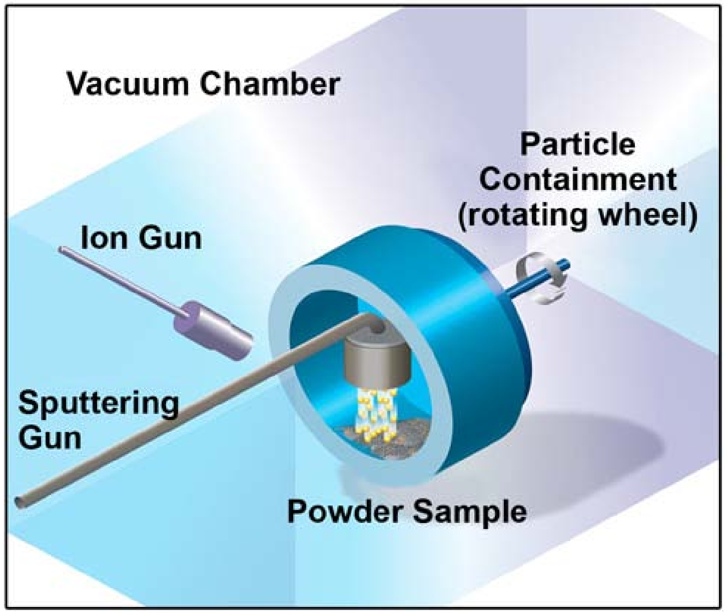


Control Parameters:

- •Gas type for ionization
  - •N_2, CF_4, H_2, Ar, O_2
- •Beam current
  - •Controls Ion flux (10 - 50 milliamps)
- •Acceleration Voltage
  - •Depth of ion penetration (20-100 Volts)

These are Interdependent parameters as we optimize catalyst: dispersion, composition, particle size and electroactive surface area

Sputtering PtRu



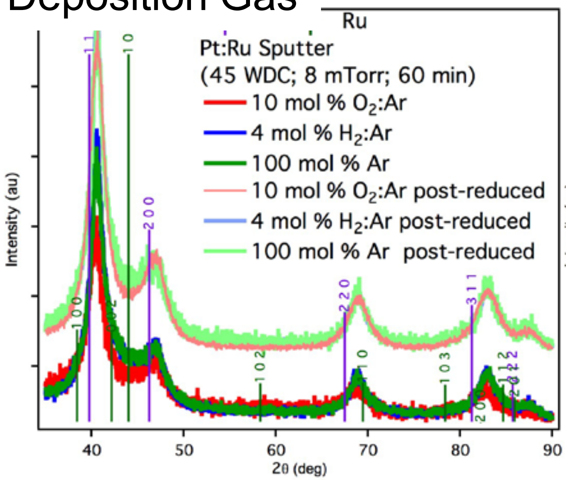
Control Parameters:

- •Material (Pt, Pt-Ru 50:50 and 70:30)
- •RF or DC Power
  - •15-45 W (on 2” target)
- •Gas Composition and concentration (mol%)
  - •Ar (100%), H_2 (4%), O_2 (5–50%)
- • Chamber Pressure
  - •8-25 mtorr
- •Wheel Rotation Speed
  - •0-40 RPM

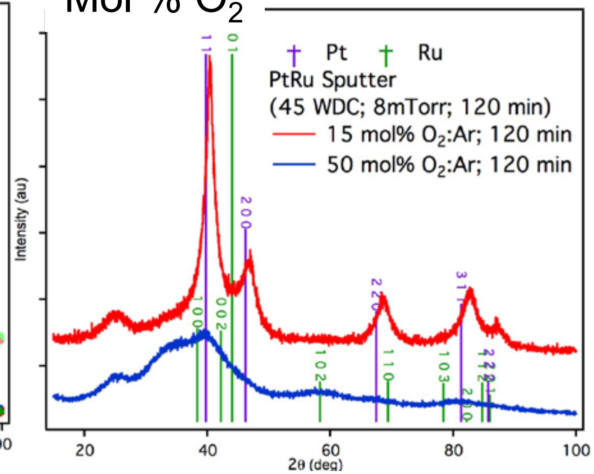
Technical Accomplishments: Powders

XRD evaluation of process parameters for catalyst deposition.

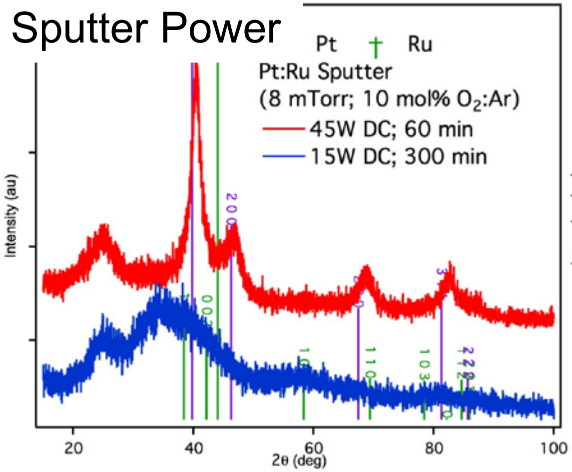
Deposition Gas



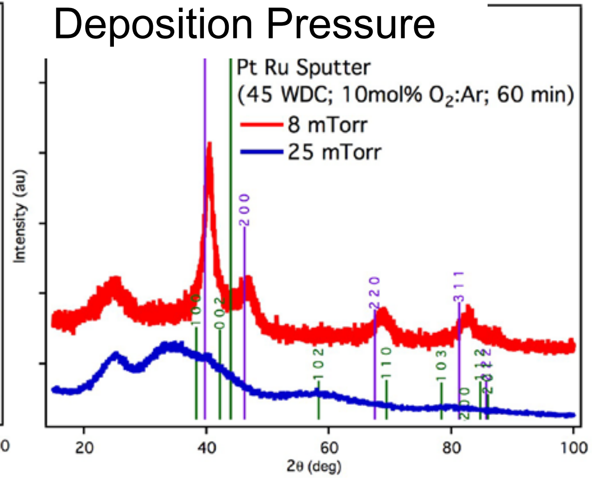
Mol % O_2



Sputter Power



Deposition Pressure

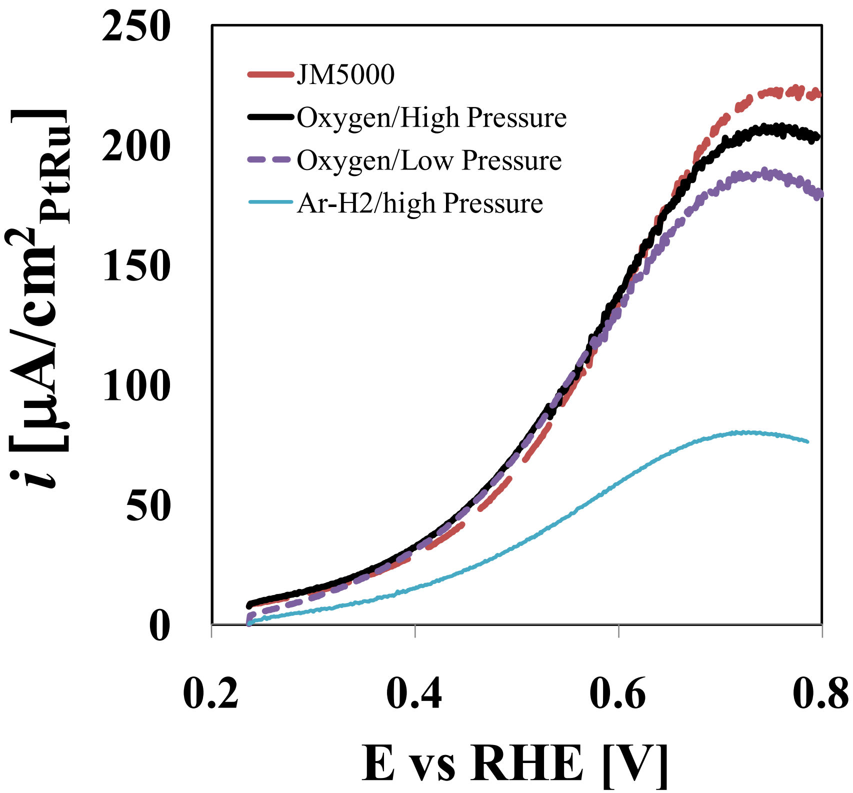


X-ray Diffraction (XRD) one tool used to evaluate powders.

Smoothing and/or broadening is a convolution of the particle size decreasing, introduction of defects, introduction of oxide phases and possibly strain effects. Most “crystalline” PtRu has not been best performing catalyst.

- **Best performing Pt-Ru-carbon powder the XRD spectra are broadened significantly possibly due to small particle size and oxide formation**
- **Illustrates affect of sputter process parameters on catalyst properties**

Technical Accomplishments: Powders
PtRu, undoped Carbon, effect of sputter parameters.



Effect of Deposition Parameters— pressure, gas composition.

Oxygen presence during deposition was found to correlate to surface normalized MOR. Materials from reducing atmosphere have diminished performance.

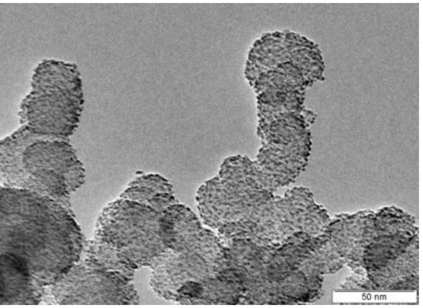
Increases in pressure (8 to 25 mtorr) with same concentration of oxygen, 10 mol%, results in:

- **Increased electrochemical surface area (ECA)**
- **Decreased metal deposition rate- i.e. smaller particles.**
- **Increased dispersion.**
- **Maintained surface specific activity.**

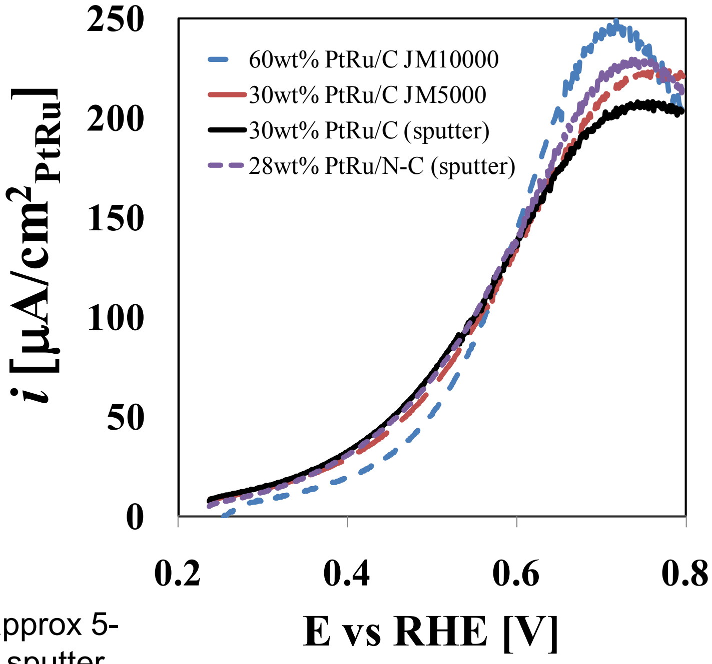
Catalyst	Pt-Ru (wt%)	PtRu Composition	ECA (m^2/g)	Specific Activity @ 0.4V (A/cm^2_{metal})	Mass Activity @ 0.4V (A/g_{metal})
O_2/25 mtorr	**30**	**1 : 0.9**	**73**	**3.3×10^{-5}**	**24**
O_2/8 mtorr	42	1 : 1.1	42	3.2×10^{-5}	13
Ar-H_2/25 mtorr	19	1 : 1	23	1.5×10^{-5}	8.5
JM 5000 (as received)	**30**	**1 : 1**	**69**	**2.9×10^{-5}**	**20**

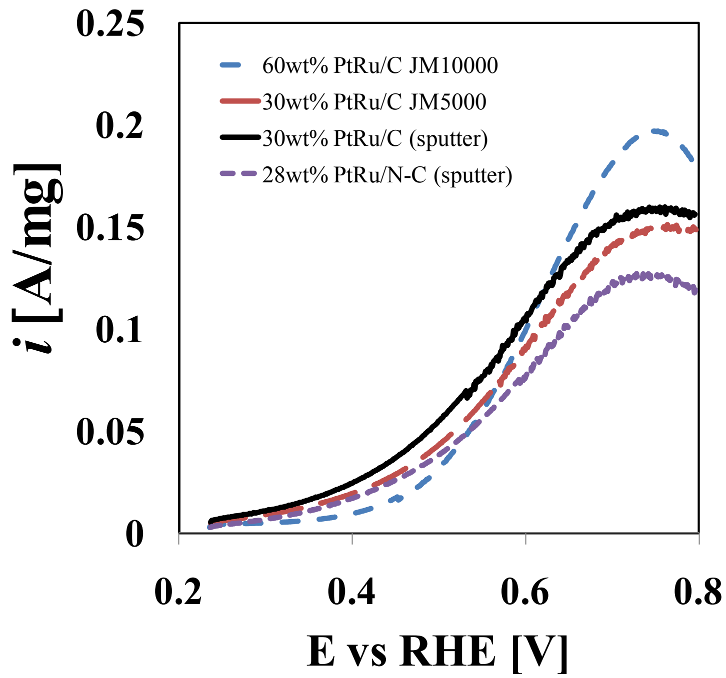
JM 5000 is 30%w/w Pt-Ru carbon purchased from Johnson-Matthey.

Technical Accomplishments: Powders
Implanted carbon -sputter Pt-Ru performance



Representative TEM of Sputter Deposition materials





PtRu/C – sputter only
PtRu/N-C – Nitrogen implant (approx 5-6% N-incorporation followed by sputter deposition) (JM 10000 60%w/w Pt-Ru)

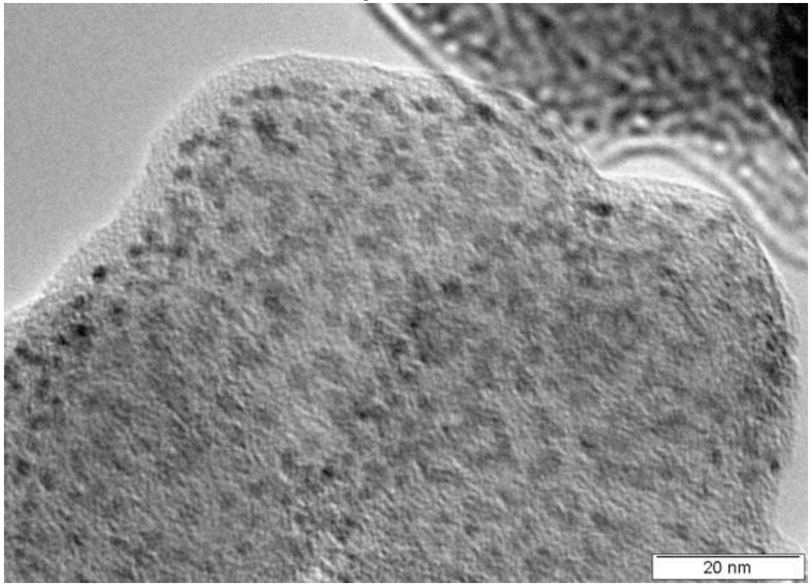
Catalyst	ECA (m^2/g)	Specific Activity @ 0.4V (A/cm^2_{metal})	Mass Activity @ 0.4V (A/mg_{metal}) X 10^3
30wt% PtRu/C (sputter)	73	3.3×10^{-5}	24
28wt% PtRu/N-C (sputter not optimized)	55	3.0×10^{-5}	17
30wt% PtRu/C JM 5000	69	2.9×10^{-5}	20
60wt% PtRu/C JM 10000	55	1.9×10^{-5}	9

In-house catalyst has better dispersion and coverage on the carbon substrate.

Consistent 20-30% improvement in MOR half-cell activity as compared to commercial materials

Technical Accomplishments: Powders
Durability of PtRu/Vulcan carbon catalyst

In-house sputter deposited catalyst after 5,000 cycles in half-cell.

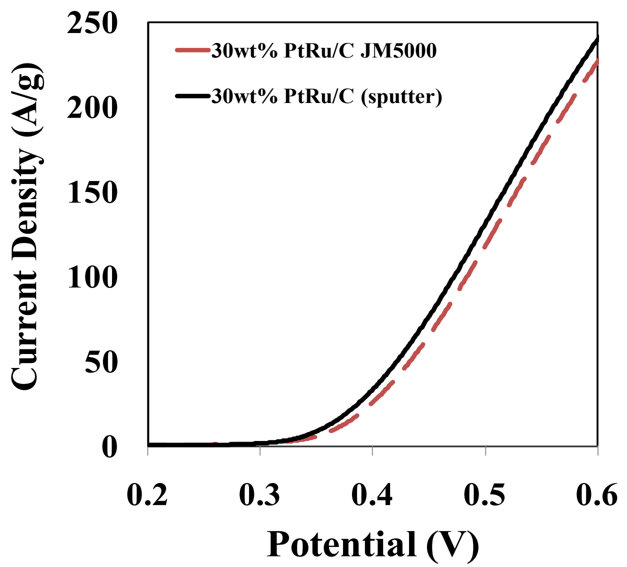


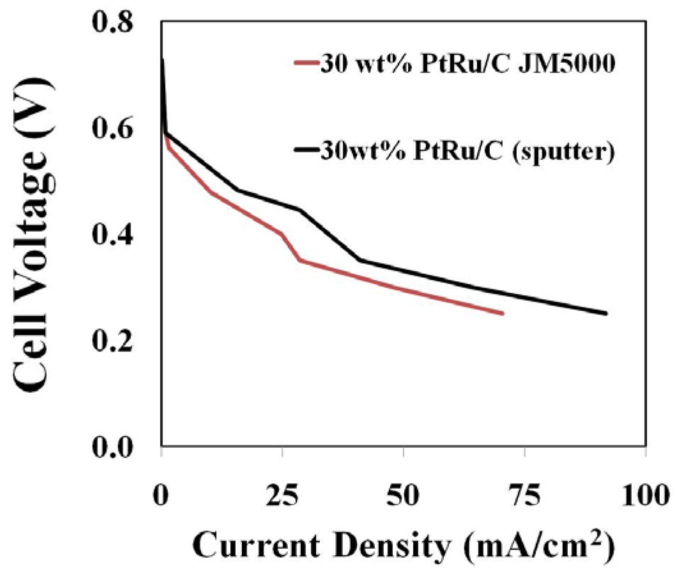
- *In-house* catalyst is durable, resulting in highly dispersed, nanoparticles even after 5000 cycles to high potentials.
- PtRu on N-doped carbon is more durable than un-doped catalyst and commercial catalysts.

Pt-Ru deposition technique/description	Deposition parameter	Pt-Ru (wt%)	PtRu Composition	% of ECA after 100x durability cycles	% of ECA after 5000x durability cycles
Sputter / Vulcan	O2; high Pressure	30	1 : 0.9	51	10
Sputter/ N-modified Vulcan	O2; low Pressure	30	1 : 1.2	60	40
Sputter/ N-modified Vulcan	O2; high Pressure	40	1 : 1	70	24
Colloidal / JM 5000	-	30	1 : 1	48	17

1M H_2SO_4, 1M CH_3OH, 25 °C, cycle 0-0.80 V vs RHE, @ 20 mv/sec

Technical Accomplishments: Powders
DMFC MEA Data





Anode polarization: in-house catalyst out-performs (A/g and μA/cm²) the commercial catalysts JM5000.

- **In-house sputter catalyst outperforms DMFC commercial catalyst JM5000 with same catalyst loading (1 mg/cm²)**

1M methanol/Air feed, 50 °C, 100% humidification, 5 cm^2 MEA			DMFC Current Density @ 0.4 V			Anode Polarization @ 0.4 V	
Catalyst	Catalyst loading (mg/cm^2)	PtRu ECA* (m^2/g)	(mA/cm^2) Geometric SA	(uA/cm^2)	(mA/mg)	(uA/cm^2)	(mA/mg)
JM5000	1	55	25	45	25	48	26
Sputtered PtRu/C	1	41	30	73	30	83	34

Collaborations & Project Participants

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

Team Members:

NREL: *Staff*; Huyen Dinh, Thomas Gennett, Arrelaine Dameron, David Ginley, Bryan Pivovar, Kevin O'Neill, Katherine Hurst.
PostDocs:, Tim Olson, KC Neyerlin, Jennifer Leisch, Steve Christensen.

CSM: Prof. Ryan O'Hayre, Svitlana Pylypenko (postdoc), April Corpuz (graduate student)

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

Collaborators: Stanford University, Timothy Holmes, DFT Studies
Oak Ridge Laboratory, Albina Borisevich, Karen Moore, under SHaRE program

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

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:** Model Systems: HOPG used to better understand the effect of catalyst-support interaction on enhanced catalyst activity and stability of PtRu catalyst nanoparticles. HOPG surface modified via ion implantation to evaluate performance and durability. Apply this controlled materials engineering approach to develop advanced PtRu anode catalyst systems by ion-implanting high surface area carbon supports followed by catalyst deposition via gas and solution phase processes. Evaluate and optimize to improve catalyst utilization, activity, and durability at lower catalyst loading.

- **Technical Accomplishments and Progress:** We have met all project milestones. We developed a processing system for ion implantation of high surface area carbon materials We have selected, developed, and are optimizing PtRu sputter deposition methods, established new materials processing techniques with resultant catalyst matrix which match/outperform standard commercial materials , demonstrated that nitrogen implantation on enhances the methanol oxidation activity and durability of PtRu catalyst, and initiated study of where and how the Pt-Ru catalyst is attached to the 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:** Optimize the implantation and sputter deposition parameters to further develop performance and durability of unique materials. Establish catalyst degradation mechanisms, i.e. extent of ruthenium dissolution and catalyst coarsening.

Proposed Future Work

- Establish surface structure of current high performance Pt/Ru – implanted vulcan materials (Amorphous-Crystalline).
- Optimization of catalyst utilization through sputter-implantation parameter control.
- Construct MEAs from industrial standard PtRu catalyst and in-house PtRu/implanted carbon.
- Evaluate the DMFC performance and durability of PtRu/implanted carbon catalyst materials.
- Establish catalyst degradation mechanisms, e.g.. extent of ruthenium dissolution and catalyst coarsening.

Recently funded, *2 p*roposals for use of SLAC National Accelerator Laboratory Facilities (June 2011):

Soft X-ray and Hard X-ray scattering studies *in-situ* during electrochemical analysis to determine the sites for Pt-Ru attachment and study the degradation of Pt-Ru during cycling.

Technical Back-Up Slides

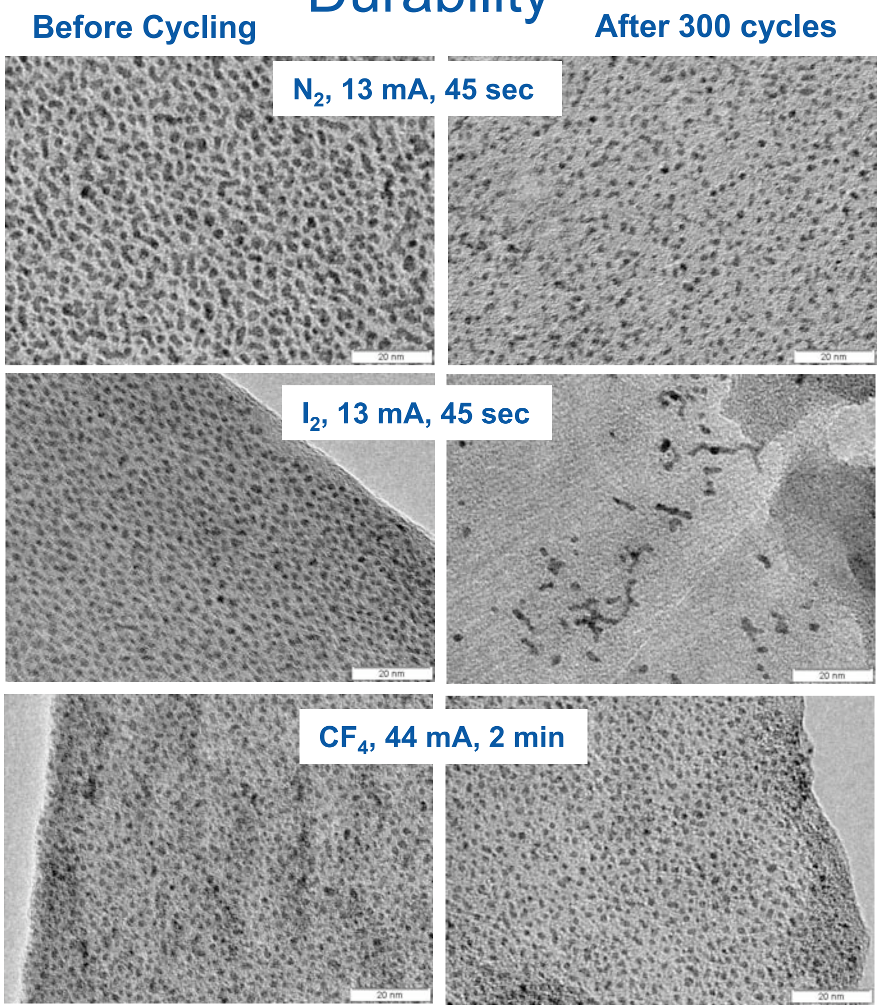
Technical Accomplishments: HOPG, Effect of different dopants on performance and durability

Finishes HOPG System Milestones

CO Stripping and MOR on HOPG

Sample	ESA(cm^2)	J ($\mu A/cm^2_{PtRu}$) @ 0.55V vs RHE
CF_4 (44 mA, 2 min)	7.3	39
I_2 (13 mA, 45 s)	4.2	16
N_2 (13 mA, 45 s)	4.8	17
N_2/H_2	2.64	14

Durability

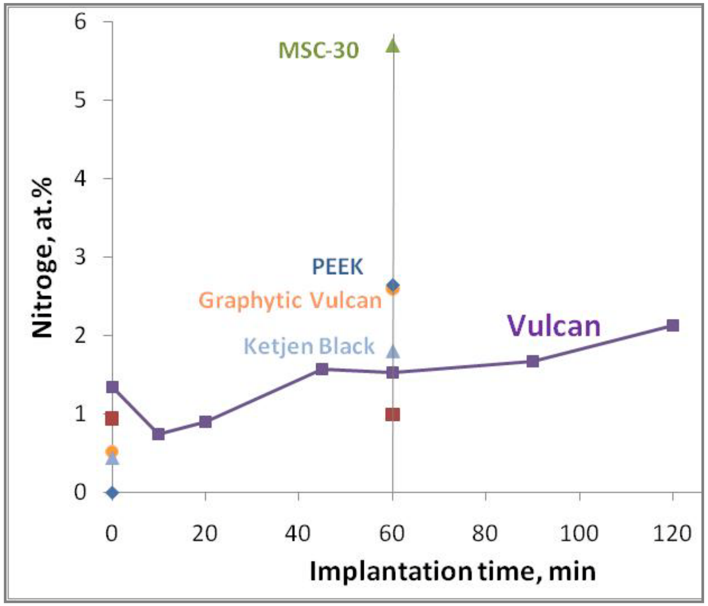


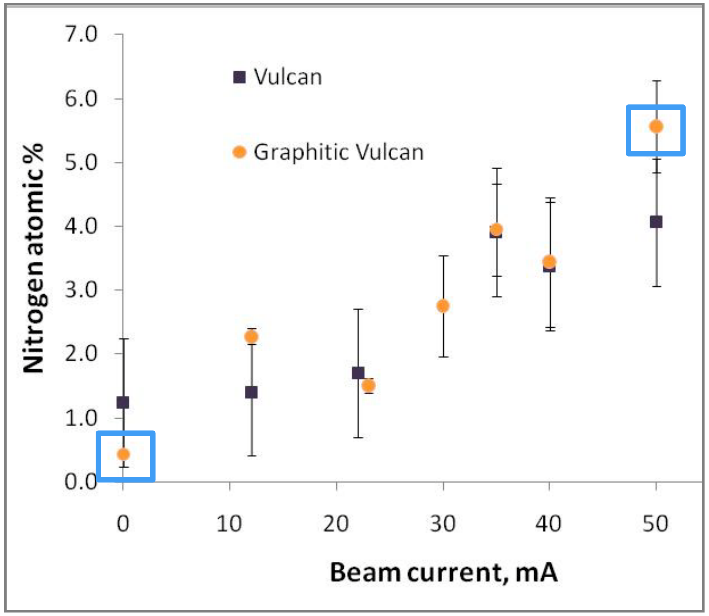
1.0 M H_2SO_4, 300 cycles from 0 to 1.1 V vs. Ag/AgCl , 250 mV/s

Durability is affected by the nature of the dopant and its dose level

JPL

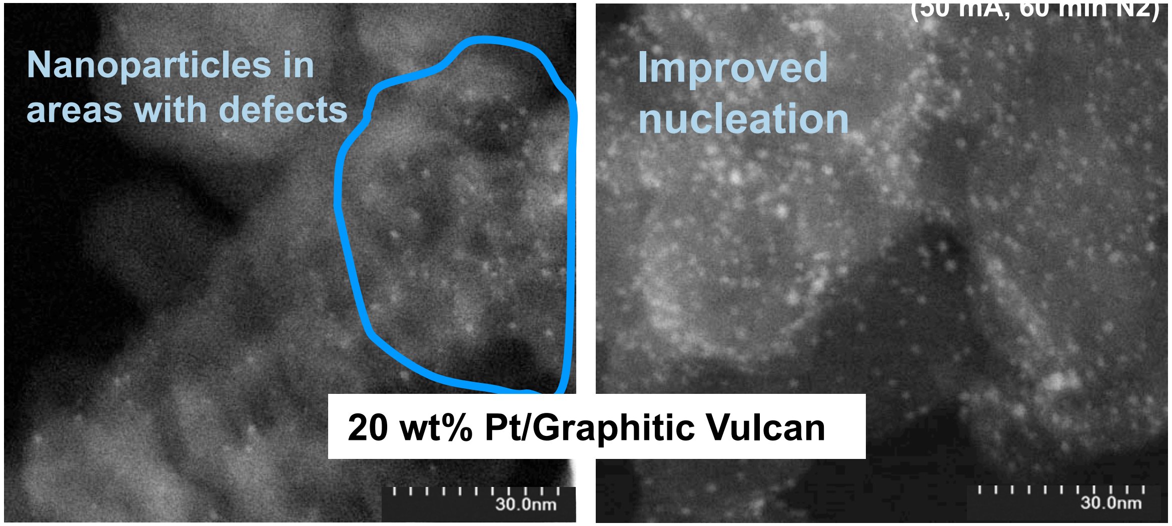
Technical Accomplishments – Evaluating structural and chemical modification of ion implanted powders



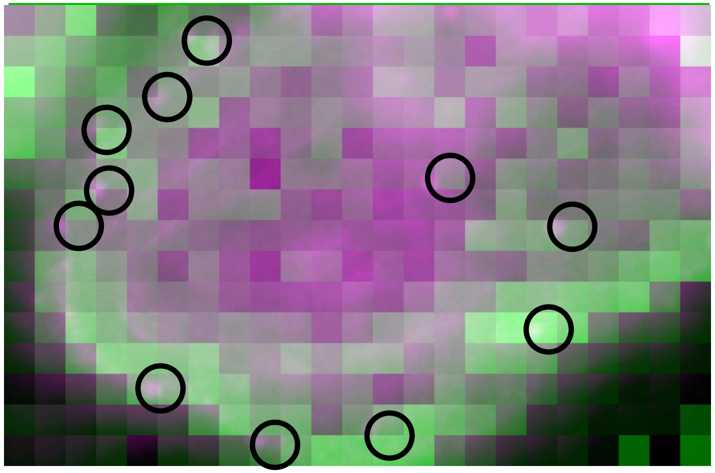


Undoped Graphitic Vulcan

N-doped Graphitic Vulcan



EELS Spectral imaging

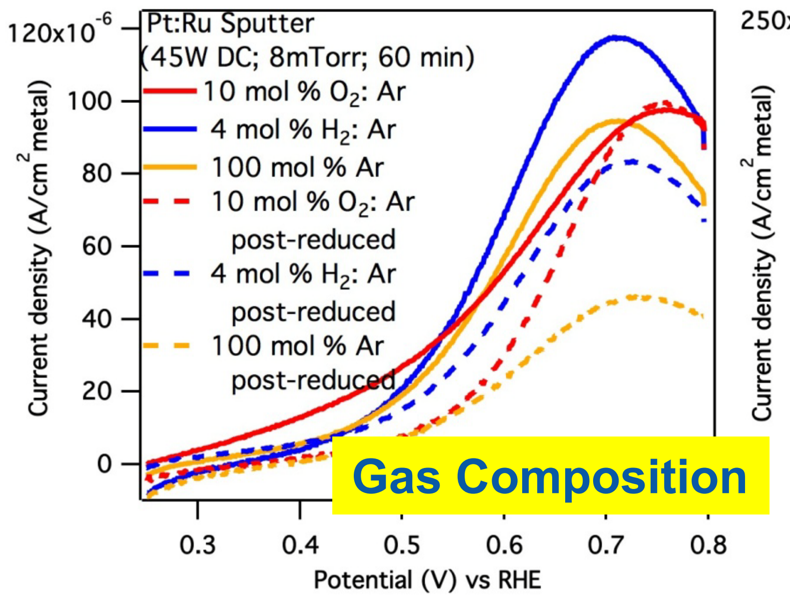


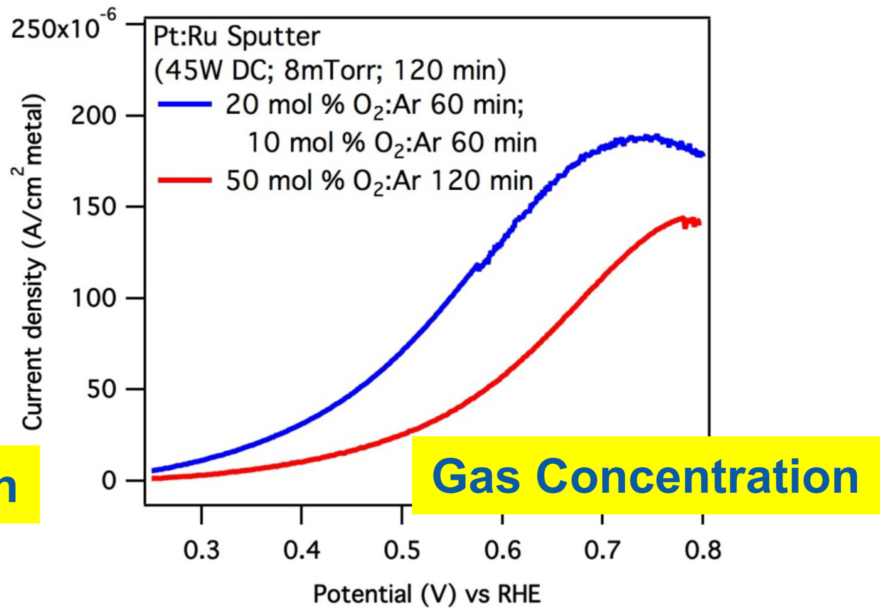
Purple: ADF signal; Green: N K integrated intensity

Correlation between Pt nucleation sites and nitrogen rich sites

A.Borisevich, K.Moore, @ ORL under SHaRE program

Technical Accomplishments: Effects of Sputter Parameters





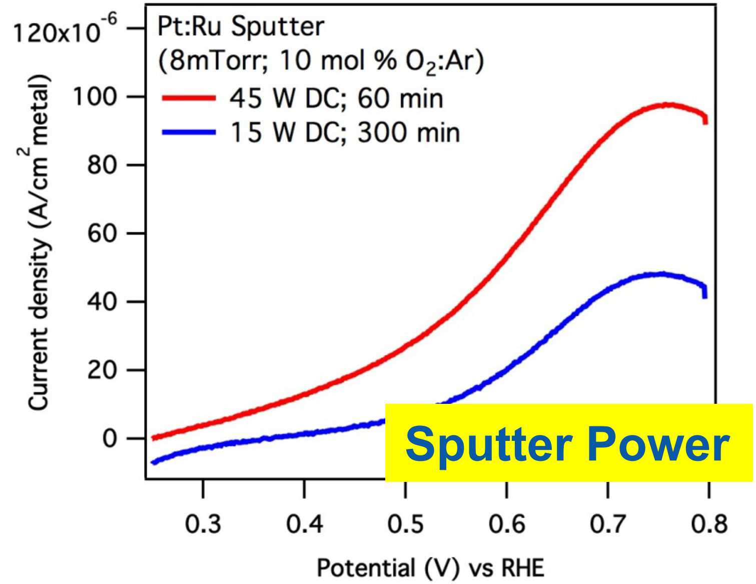
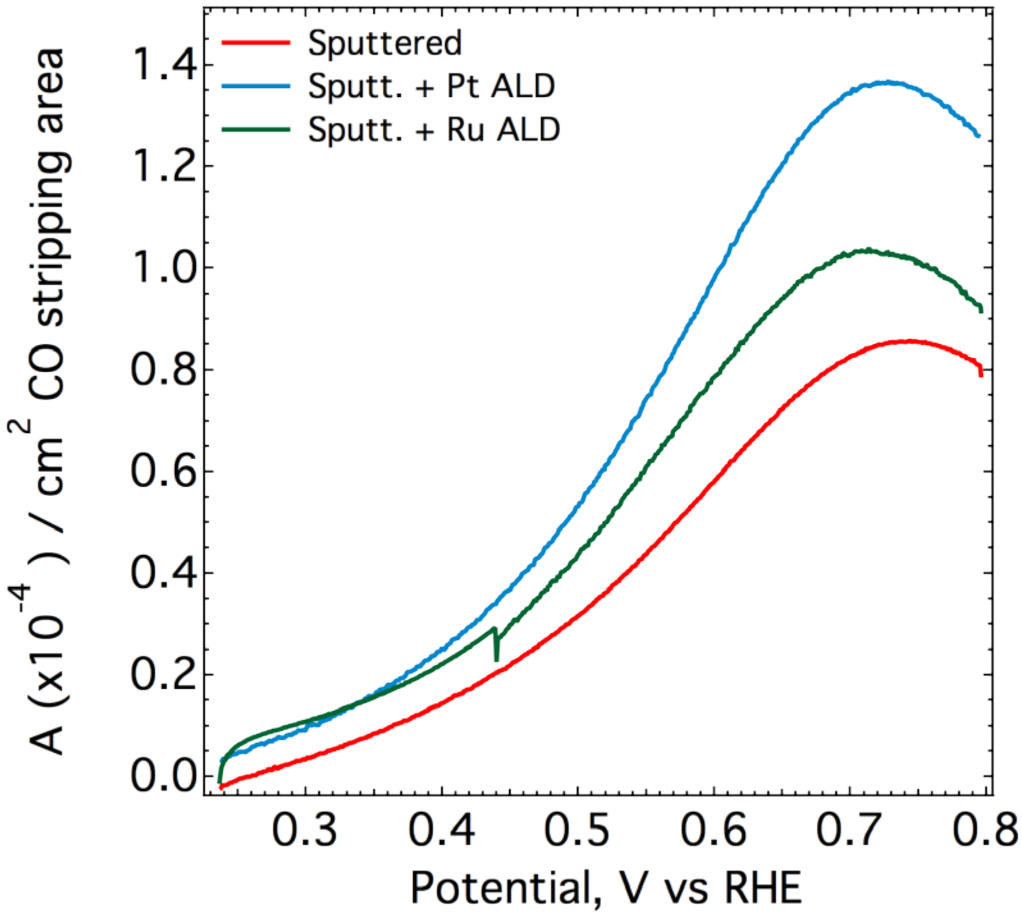


Illustration of sputter parameter effects on electrochemical MOR performance.

Technical Accomplishments: Powders
ALD modification of sputtered Pt:Ru catalysts

- Limited sputter deposition to nucleate, followed by ALD multi-cycle growth of Pt/Ru catalyst.
- Electrochemical oxidation peak and 'kinetic' region (~0.4 V) depend heavily on the surface Pt:Ru composition
- Pt ALD modification dramatically improves the performance
- Ru ALD modification demonstrates the ability to tune performance



- Methanol oxidation for a sputtered catalyst
- Same sputtered catalyst w/4 Pt ALD cycles
- Same sputtered catalyst w/4 Ru ALD cycles

Technical Accomplishment: Powders ORR Studies:

Catalyst	Pt wt% by TGA	ECSA $[m^2_{Pt}/g_{Pt}]$	$i_m^{0.9V}$ $[mA/mg_{Pt}]$	$i_s^{0.9V}$ $[\mu A/cm^2_{Pt}]$	Crystallite size by XRD (nm)
Pt Poly		-	-	2300 ± 90	
TKK Pt on Vulcan	45	63 ± 3	340 ± 25	540 ± 40	5.0
Pt on Undoped Vulcan C	25	63 ± 3	360 ± 10	570 ± 50	5.0
Pt on N-Doped Vulcan C (13 mA, 60 min)	40	27 ± 2	195 ± 20	705 ± 10	5.1

Deposition of platinum catalyst on commercial carbon support.

Observed enhanced performance. Process may be applicable to preparation of ORR catalysts with further optimization