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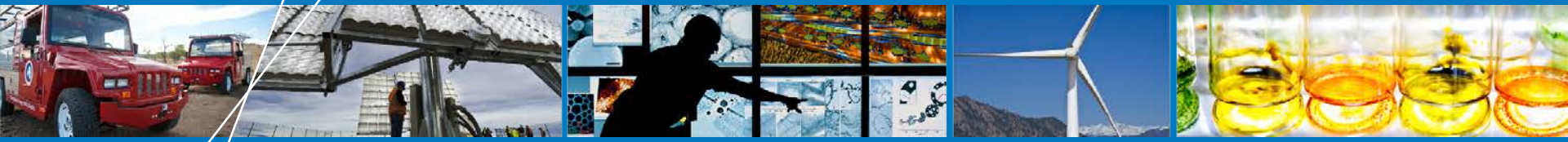
Novel Approach to Advanced Direct Methanol Fuel Cell Anode Catalysts



Venue: 2012 DOE Hydrogen and Fuel Cells Program Review

Presenter: Huyen Dinh (PI)

Thomas Gennett (co-PI)

National Renewable Energy Laboratory

Date: May 16, 2012

FC041

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

NREL is a national laboratory of the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, operated by the Alliance for Sustainable Energy, LLC.

Overview

Timeline

Start: July 2009
End: September 2011
% complete: 100%

Budget

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

FY 2011 DOE share = $834K which completed project

Barriers

Barrier	2015 Target[+] (consumer electronics)
A: Durability	5,000 h
C. Performance	13 W/L, 10 W/kg (< 2 W) 55 W/L, 45 W/kg (10-50 W)

Partners (PI)

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

Jet Propulsion Laboratory (JPL)
[Charles Hayes]

MTI MicroFuel Cells (MTI)
[Chuck Carlstrom]

[+] Revised DOE Portable Power Fuel Cell Targets, July 18, 2011

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)
- 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), Joghee Prabhuram (postdoc), April Corpuz (graduate student), Kevin Wood (graduate student), Prof. Ryan Richards**

JPL: ***Staff:*** **Charles Hays, Sri R. Narayan (now at University of Southern California)**

Collaborators: - Stanford University, Timothy Holmes, DFT Studies

- **Oak Ridge Laboratory, Albina Borisevich, Karren More, under SHaRE program**
- **SLAC National Accelerator Laboratory Facilities, Dennis Nordlund, Michael Toney, and John Poppel: Recently funded, 2 proposals for use of (June 2011): Soft X-ray and Hard X-ray scattering studies in-situ during electrochemical analysis to determine the sites for PtRu attachment and study the degradation of PtRu during cycling.**

[#]Independent MEA performance evaluation

Relevance: Catalyst Support Interaction

Project Goal:

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

Performance

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

Durability:

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

Impact:

Improve the durability and performance of direct methanol fuel cell (DMFC) anode catalyst for consumer electronics application..

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

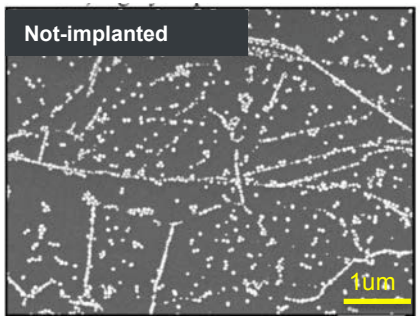
- Durability,
- Catalytic activity
- Dispersion of Pt alloys on carbon substrates

Approach:
Ion Implantation to Improve Catalyst Support Interaction

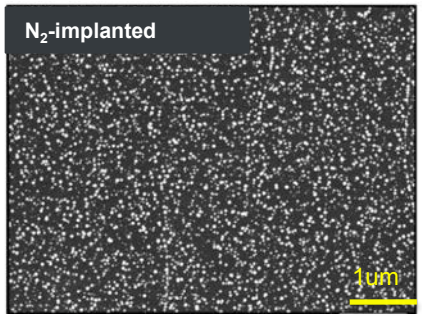
Potential benefits of ion implantation:

- Alter **nucleation** and growth of metal nanophase to improve utilization of precious metal
- Enhance binding between metal and support to improve **durability**
- Alter electronic structure of the catalyst to improve catalytic **activity**

PtRu Nucleation on HOPG

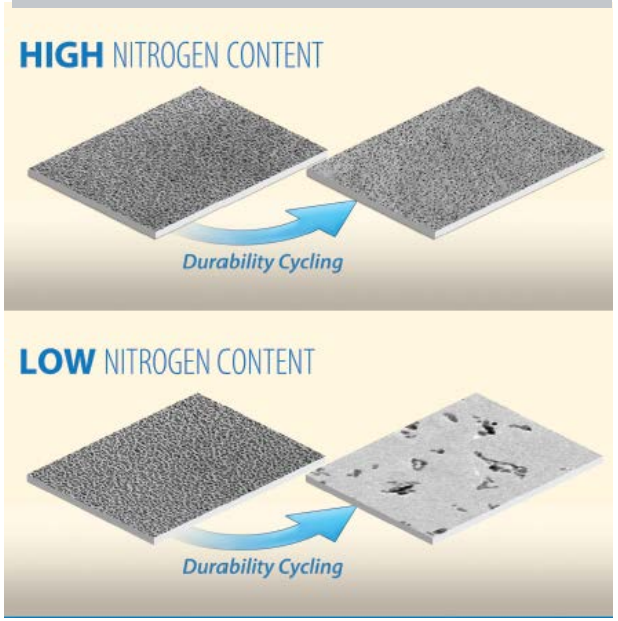


Preferential nucleation on defect sites, step edges.



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

Durability of PtRu on HOPG



S. Pylypenko, et al., *J Phys Chem C*, *115* (28), 13676, **2011**, ***cover of July issue***.

Approach

Task 1 – HOPG Model System

- Establish N-implantation effects on PtRu
  - Optimize nitrogen content
  - Determine durability and activity effects
- Explore alternate dopants to nitrogen (Ar, I, F)

Task 2 – Apply info learned from Task 1 to powder systems

- Explore different carbon powders and different PtRu deposition methods

Go/No-go decisions on specific carbon powders and PtRu deposition method

- Select Vulcan carbon and sputtering of PtRu

Task 3 – Optimize implantation-sputter conditions for "go" carbon substrate materials via half-cell performance.

- Optimize for PtRu composition, particle size, phase, structure and nitrogen content

Task 4 – Scale up and construct membrane electrode assemblies (MEAs) of best performing materials

Task 5 – DMFC testing (activity & durability)

Approach – FY10-11 Milestones

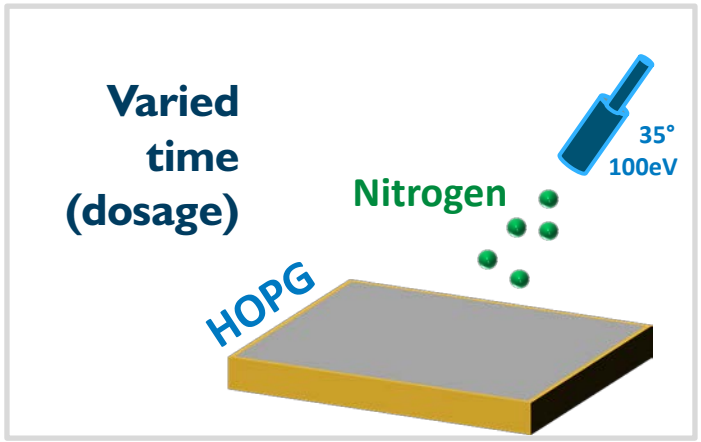
2010	1	Perform sputter deposition of PtRu on HOPG surface to establish optimal deposition parameters.	12/2009	100% complete
	2	Develop a processing system for nitrogen doping of applicable carbon materials.	04/2010	100% complete
	3	Perform 5 cm2 fuel cell testing of MEAs fabricated with novel catalysts 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	100% complete
	4	Submit final report on N-doping for DMFC catalysts to DOE.	09/2011	100% complete

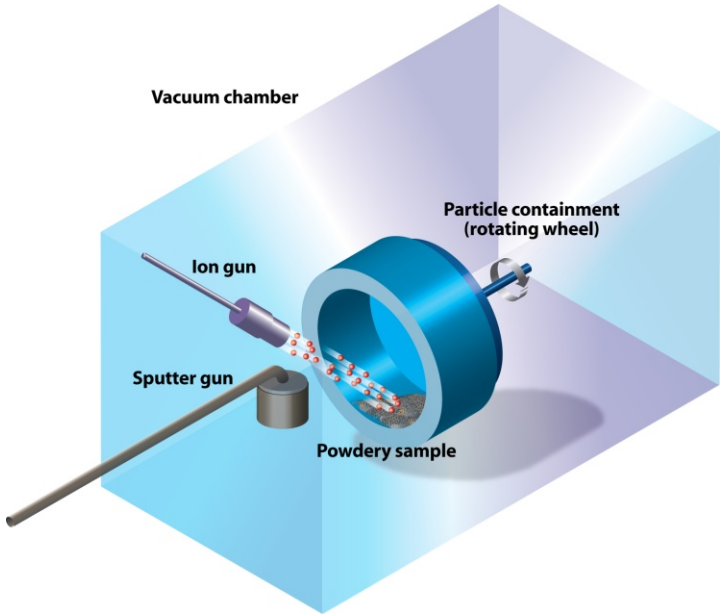
Technical Accomplishments: Outline

1. Model studies

Ion Implantation of HOPG



2. High surface area catalyst



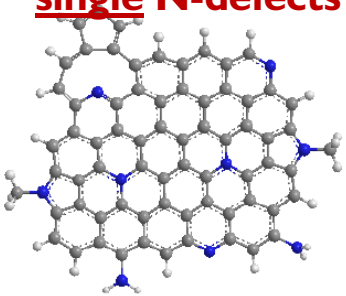
Ion Implantation and PtRu Deposition

3. Design of N-doped materials: applications and future directions

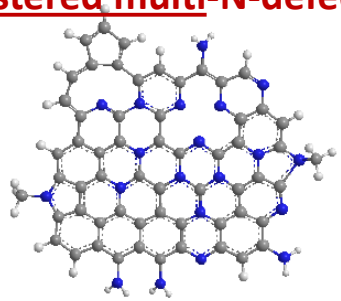
Technical Accomplishments: HOPG, Effect of N_2 dosage on durability:

Undoped HOPG

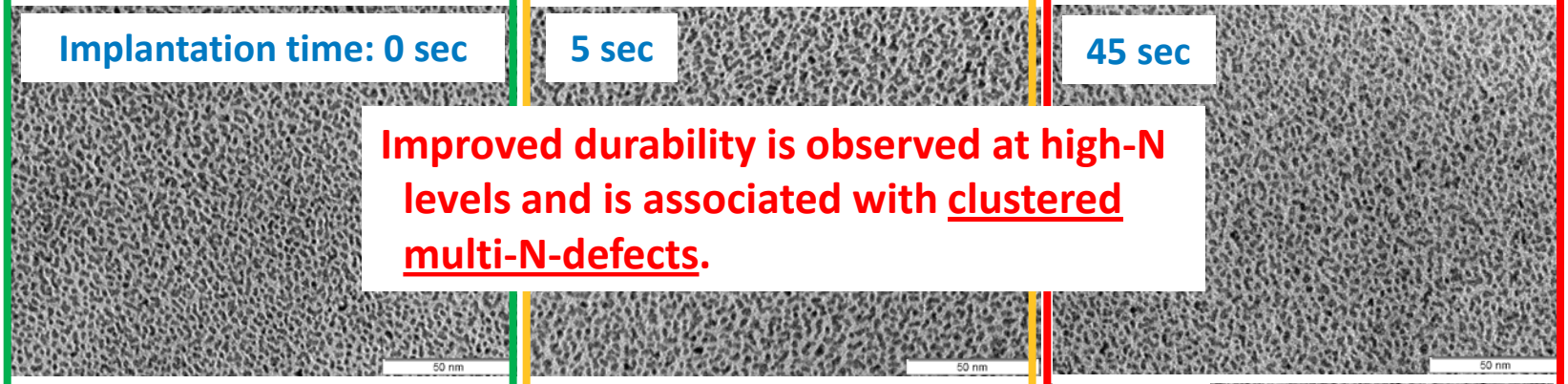
Low implantation dose: single N-defects



High implantation dose: clustered multi-N-defects

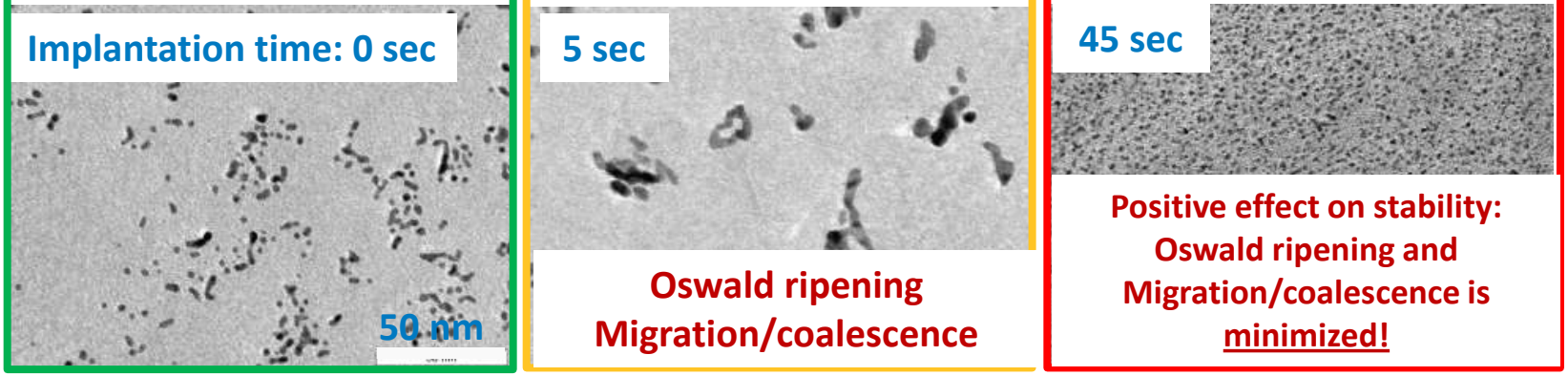


Before Cycling



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

After 300 Cycles



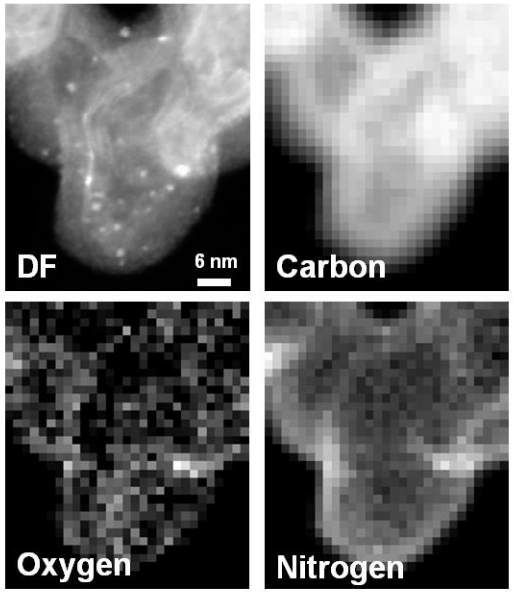
Oswald ripening Migration/coalescence

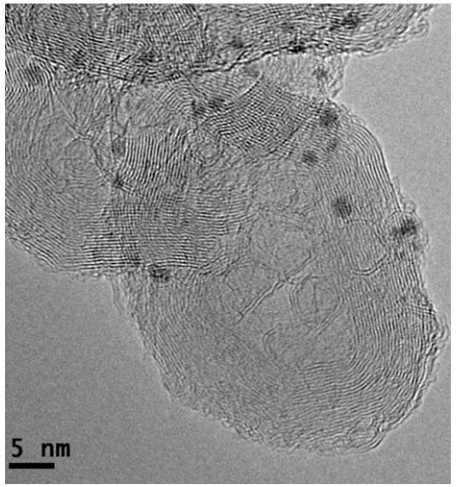
Positive effect on stability: Oswald ripening and Migration/coalescence is minimized!

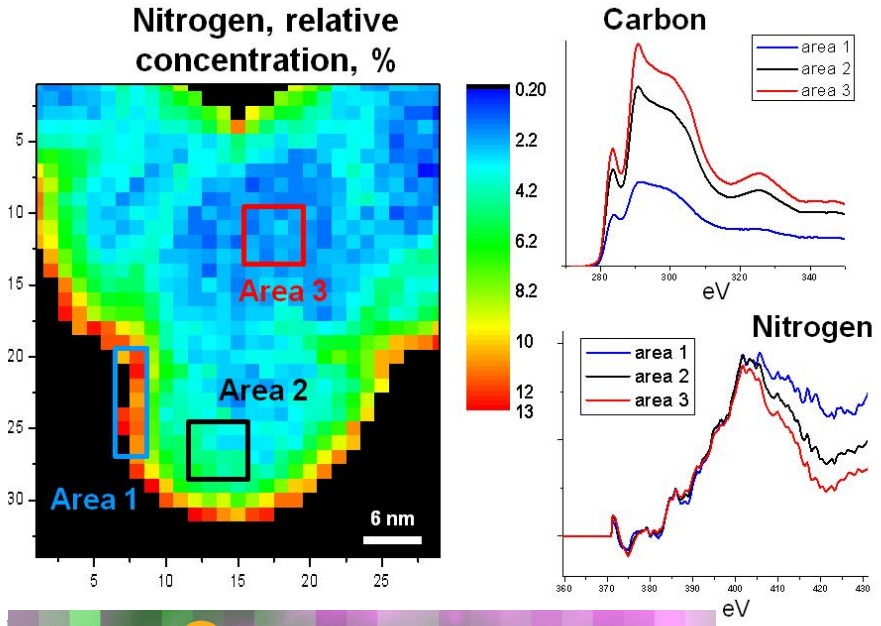
Potential cycling:
1.0 M H_2SO_4,
from 0.2 V to 1.3 V vs. RHE, scan rate of 250 mV/s, 300 cycles

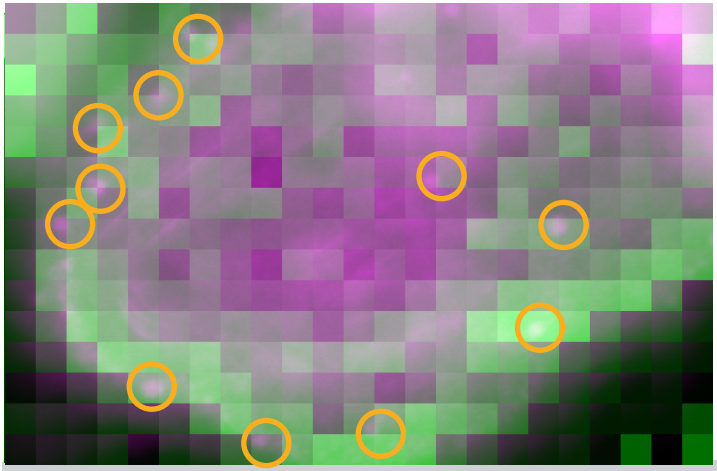
Technical Accomplishments:
N-doped powders, spatial correlation between N sites and Pt nanoparticles

STEM-EEL spectral imaging









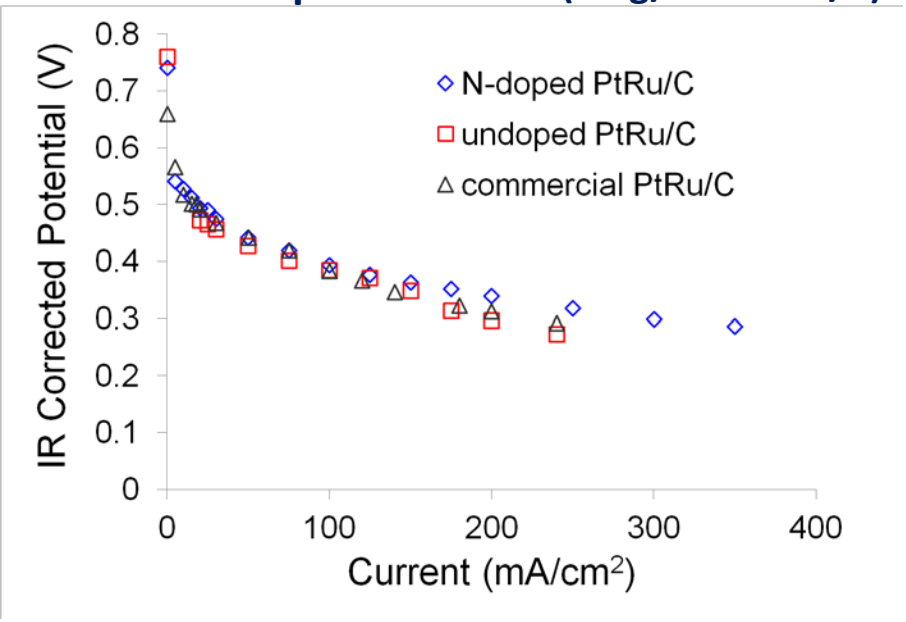
Purple: ADF signal;
Green: N K integrated intensity

There is a spatial correlation between Pt nucleation sites and nitrogen sites

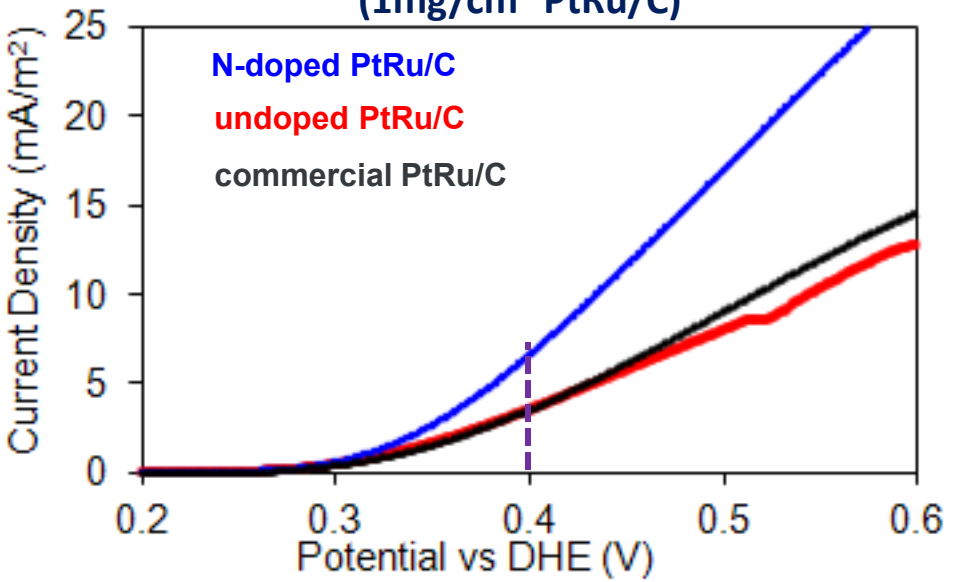
A.Borisevich, K.More, @ ORL under SHaRE program

Technical Accomplishments: Initial DMFC MEA performance

DMFC performance (1mg/cm² PtRu/C)



Methanol anode polarization (1mg/cm² PtRu/C)



In-house N-doped and undoped materials show similar DMFC performance (despite their lower ECSA) to the commercial benchmark catalyst.

In-house N-doped material outperforms undoped and commercial benchmark catalyst.

Membrane: Nafion® 117; Cell temperature: 80°C

Anode: 30wt% PtRu/Carbon, metal loading: 1 mg cm^{-2} or Commercial catalyst: JM HiSPEC™ 5000 (1:1 PtRu, 30wt% PtRu/C)

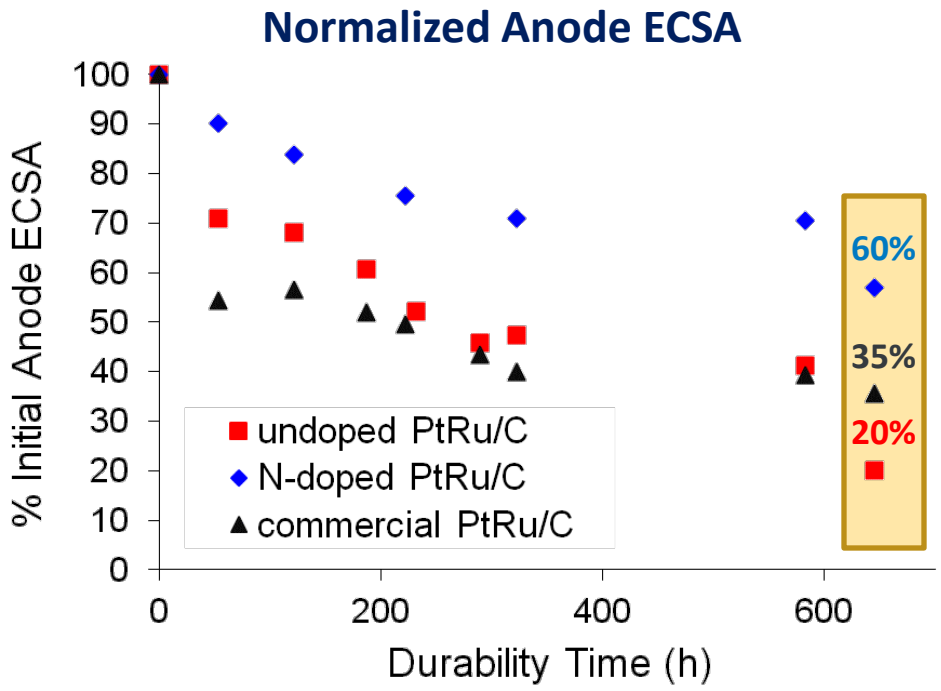
1M MeOH, 1 ml min^{-1} ;

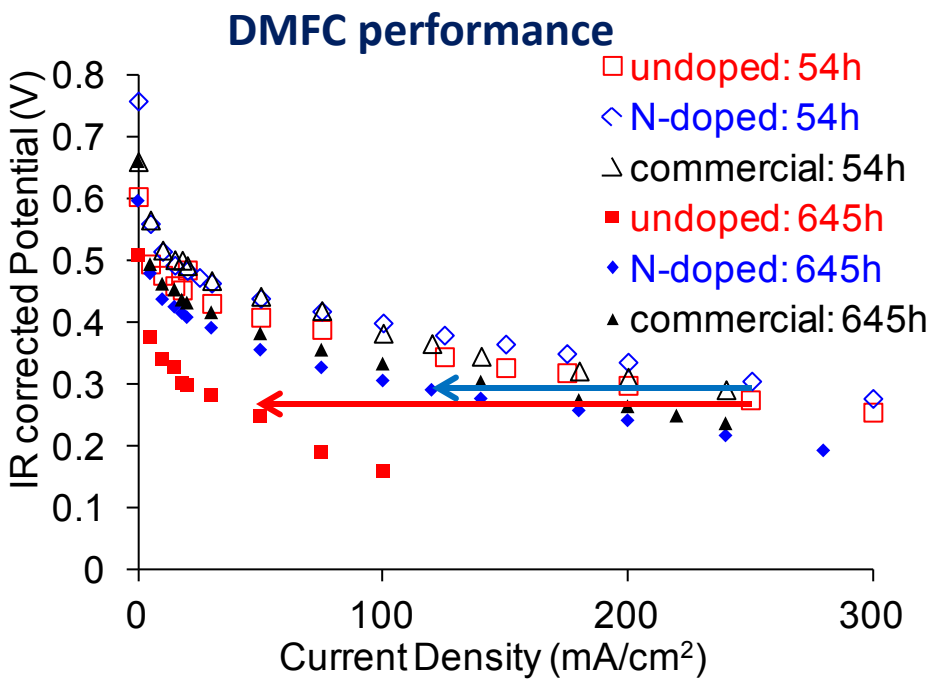
Cathode: Johnson Matthey GDE, Pt loading: 0.4 mg cm^{-2};

Polarization curve: Air, 100% RH, 3.3 stoich;

Anode polarization curve: Hydrogen, 100% RH, 50 sccm, scan rate = 2 mV/s

Technical Accomplishments: DMFC MEA durability





In-house N-doped material retains more anode ECSA compared to the undoped and commercial benchmark catalyst →N-doping decreases metal dissolution

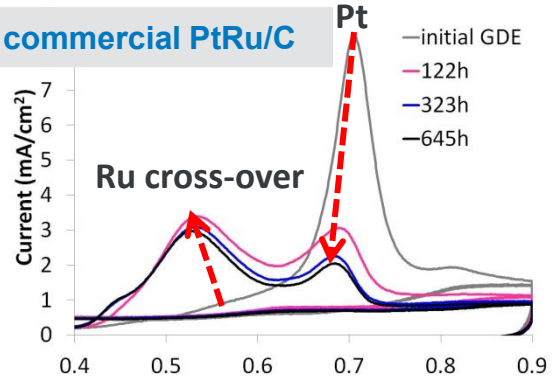
- **In-house N-doped material is more durable than undoped catalysts**
- **XPS data shows that the commercial catalyst has more metallic Ru and the in-house sputtered catalyst has more hydrous Ru oxide, making it more difficult to compare their durability.**

DMFC durability experiment: constant cell voltage (0.4 V) for a total of 645 h
Anode ECSA was determined from CO stripping on the anode (1% CO in Ar: 300 sccm, 100% RH for 30 minutes at 0.1 V vs. DHE, then N_2 at 300 sccm for 30 minutes); cathode: H_2, 50 sccm, 100% RH; cycle between 0.1 and 0.9 V vs. DHE at 20 mV/s)

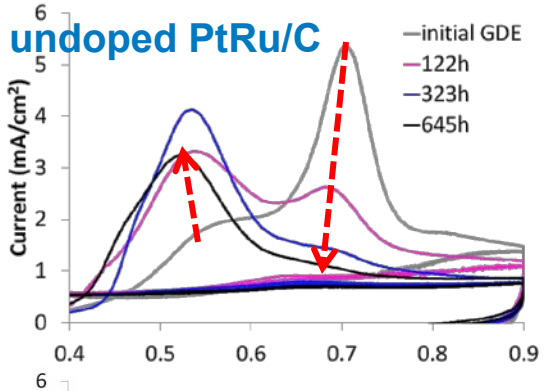
Technical Accomplishments:
DMFC MEA durability: Ruthenium crossover in DMFC MEA

CO stripping on cathode

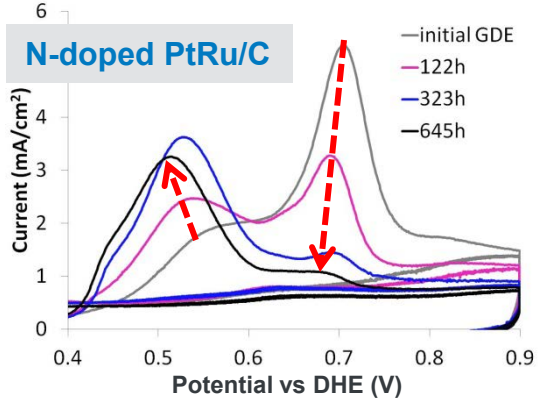
commercial PtRu/C



undoped PtRu/C



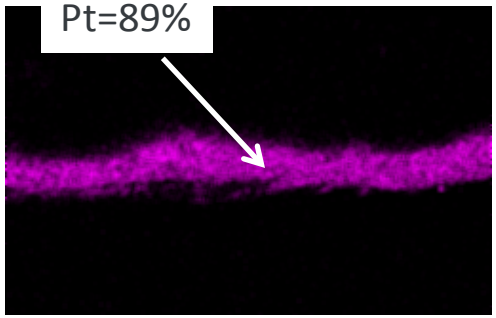
N-doped PtRu/C

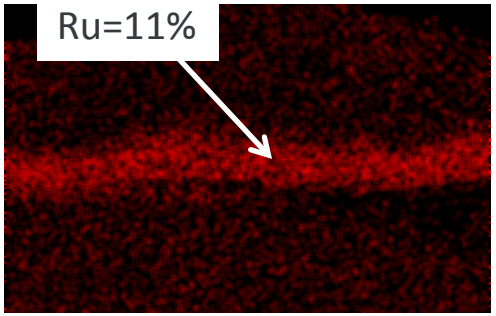


N-doping decreases metal dissolution and Ru cross-over, resulting in more durable MEA during long-term operation compared to undoped PtRu/C.

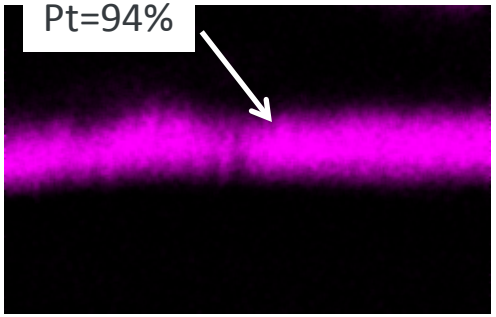
EDS elemental mapping on the cathode post-durability (after 645 hours)

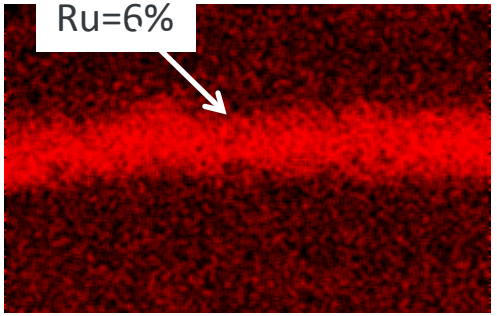
undoped PtRu/C





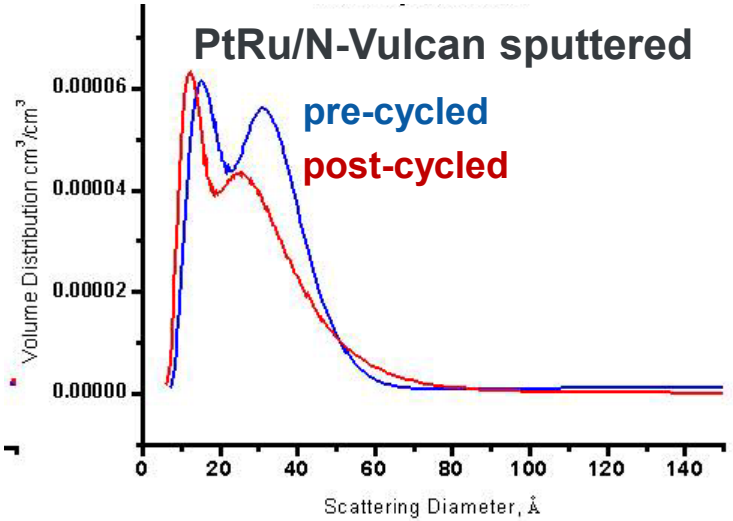
N-doped PtRu/C: less Ru crossed over to the cathode

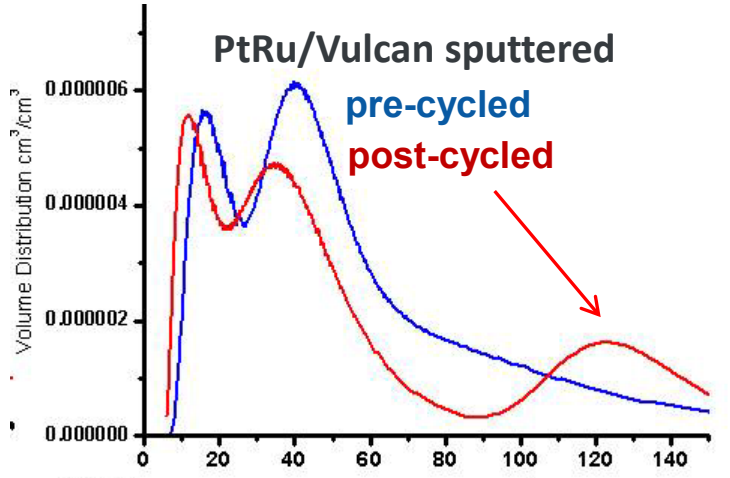




Technical Accomplishments: Durability of PtRu/Vulcan in-situ studies to elucidate loss mechanism

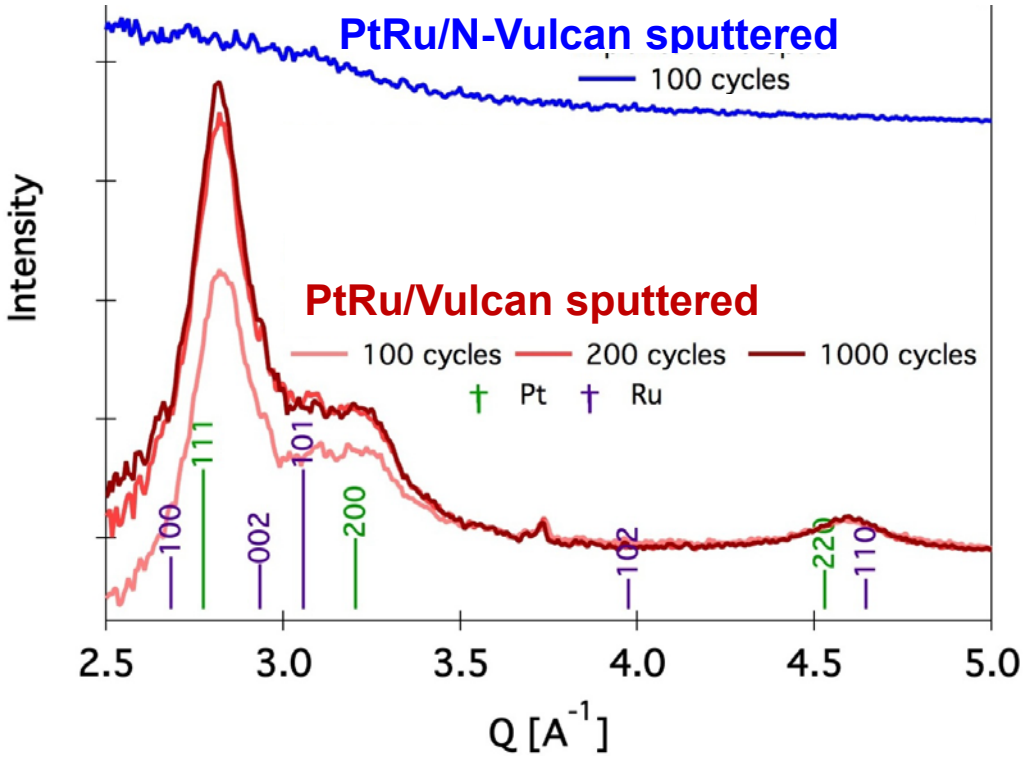
SAXS





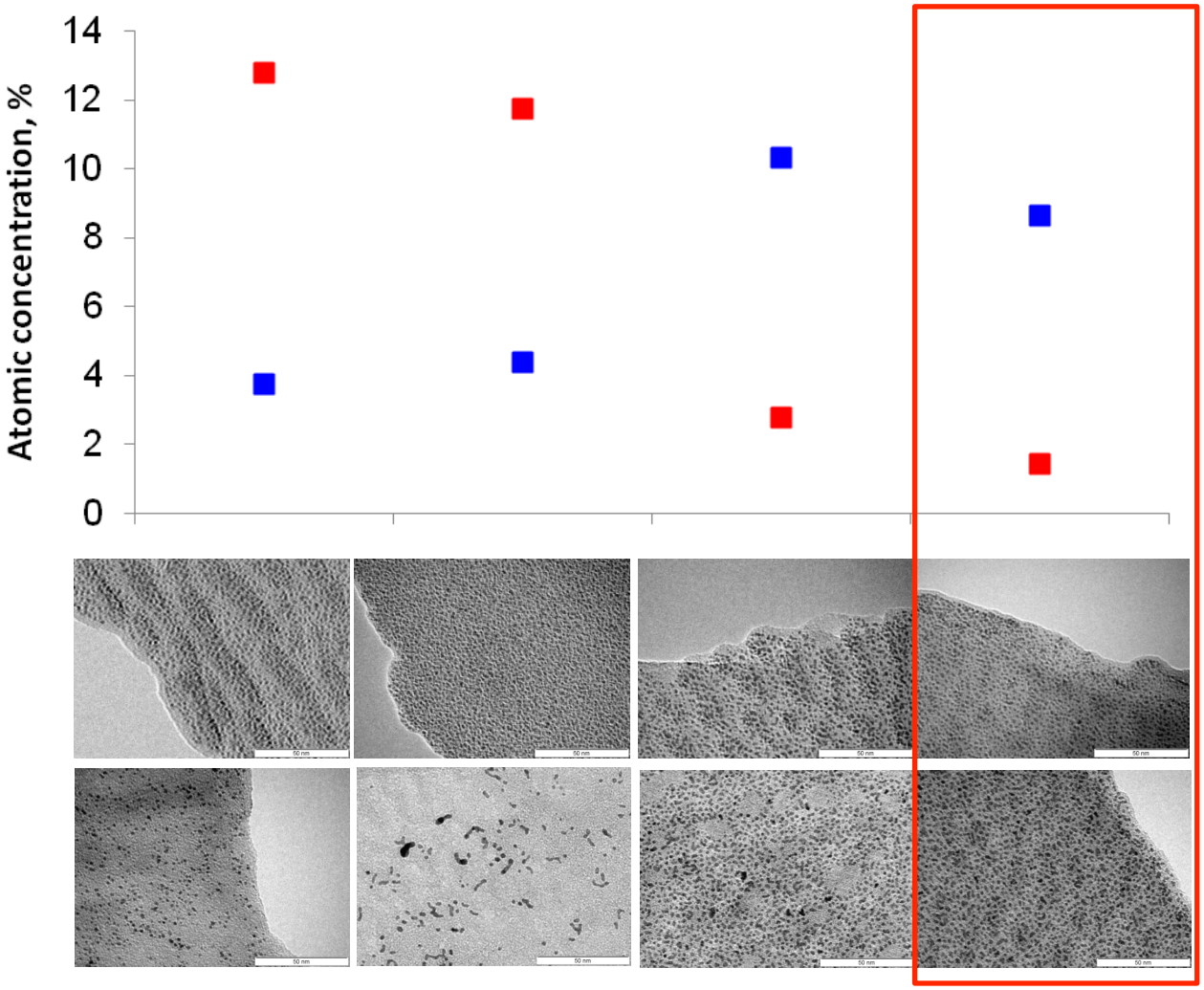
XRD:

difference between post- and pre-cycled



Coarsening of particles and appearance of crystalline phase are only observed for undoped material

Technical Accomplishments: HOPG, Durability of N-F-codoped system



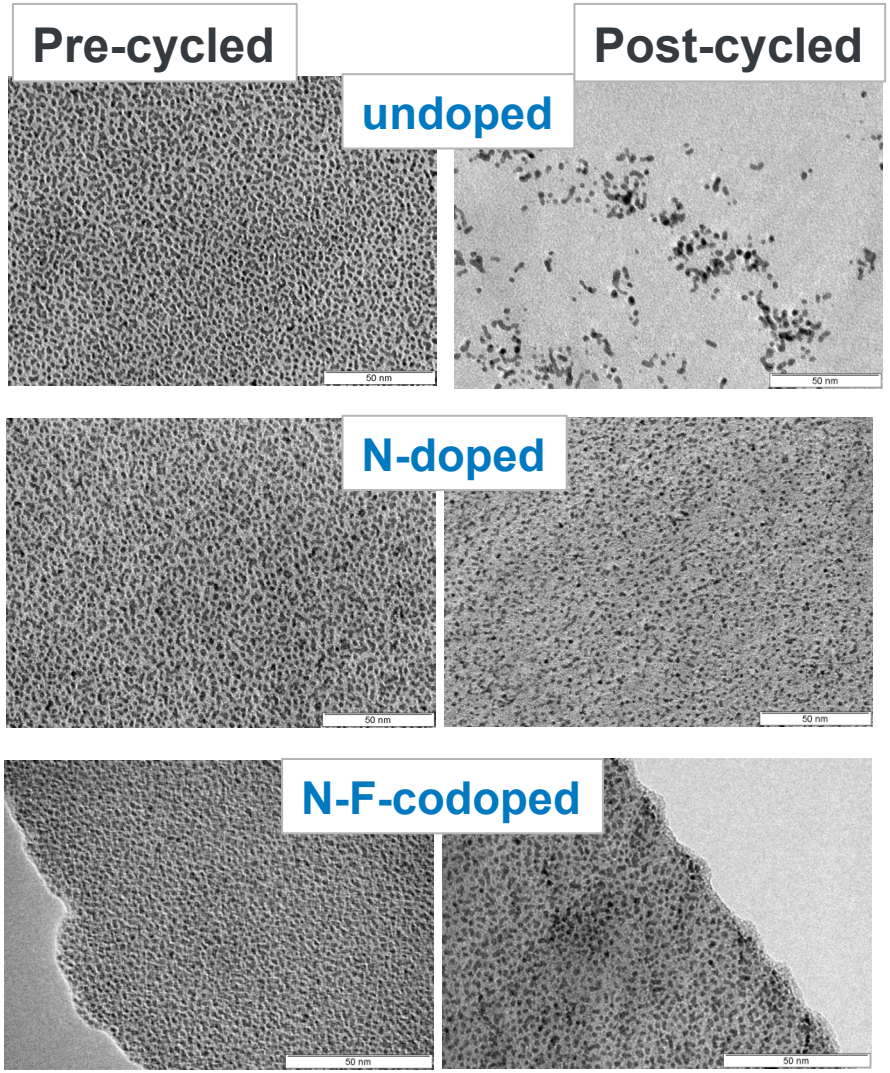
Best durability:
High N content with F incorporated as C-F, without presence of CF_4 precursor fragments (CF_2, CF_3)

Pre-cycled

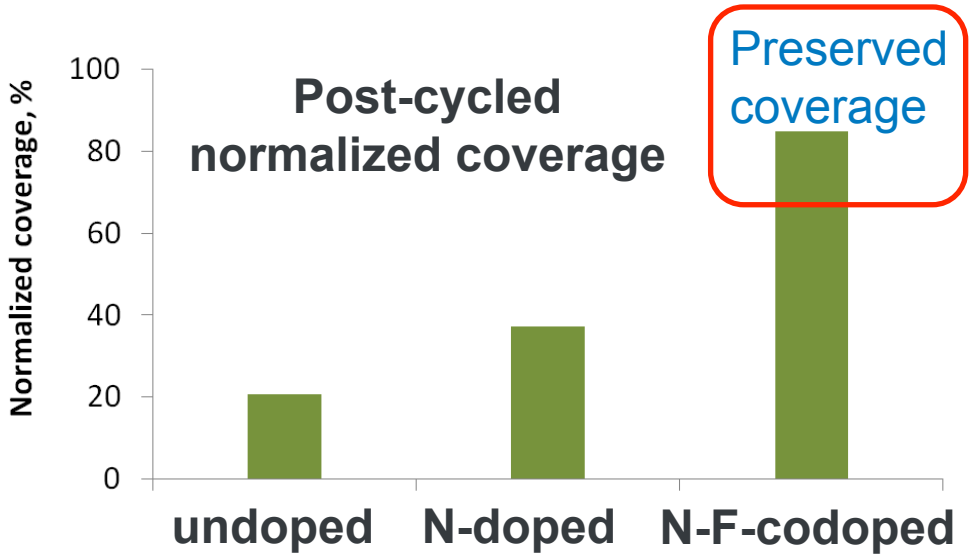
Post-cycled

Potential cycling: 1.0 M H_2SO_4, from 0.2 V to 1.3 V vs. RHE, scan rate of 250 mV/s, 300 cycles

Technical Accomplishments: HOPG, Durability of N-F-codoped system

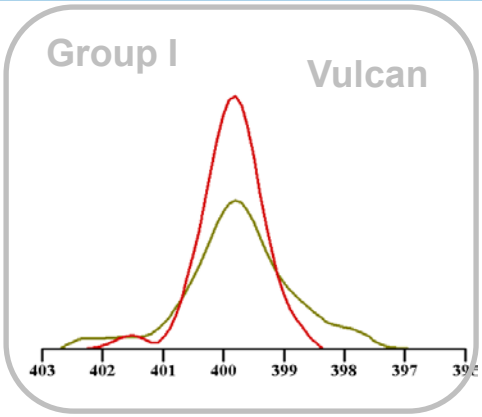


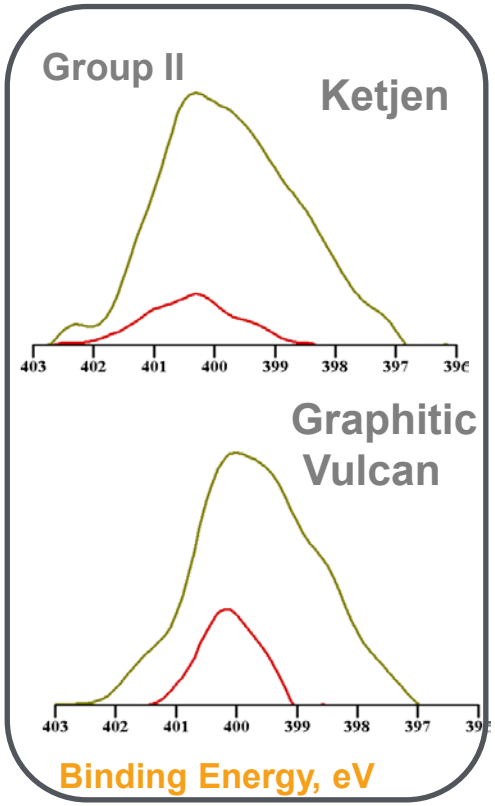
N-F-codoped system offers benefits exceeding those of N-doped system

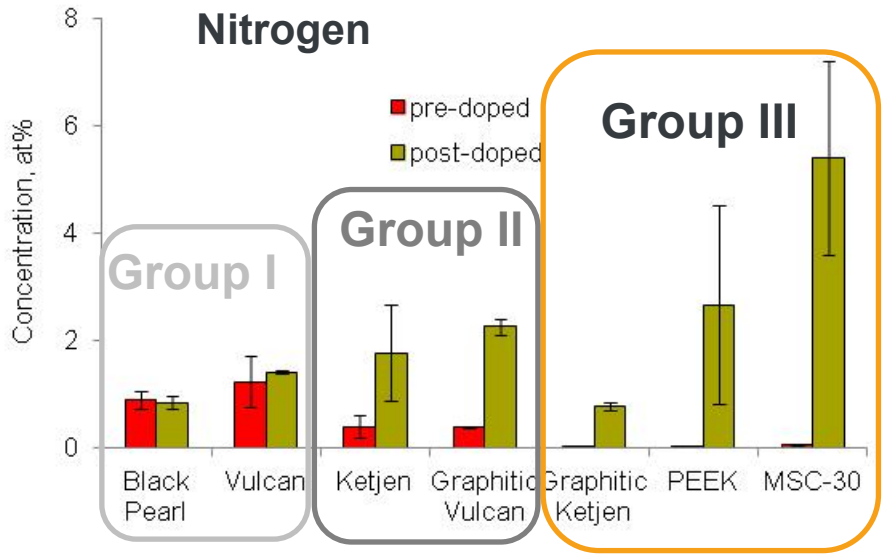


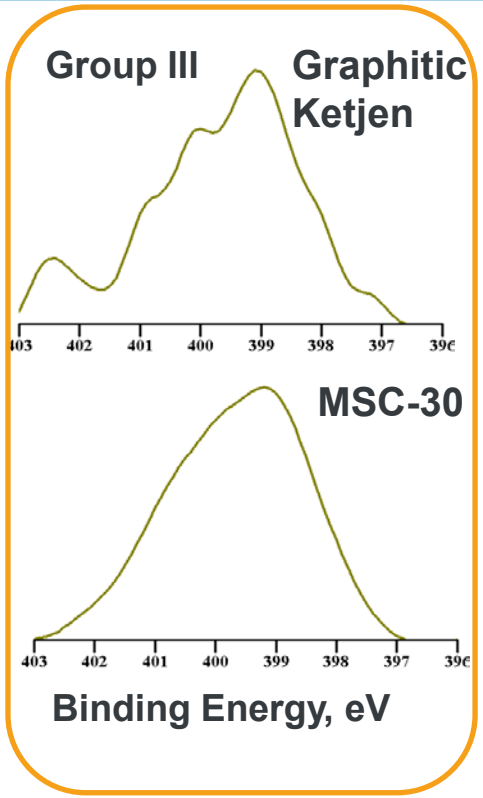
Potential cycling: 1.0 M H_2SO_4, from 0.2 V to 1.3 V vs. RHE, scan rate of 250 mV/s, 300 cycles

Technical Accomplishments:
Nitrogen incorporation into powders and potential applications.



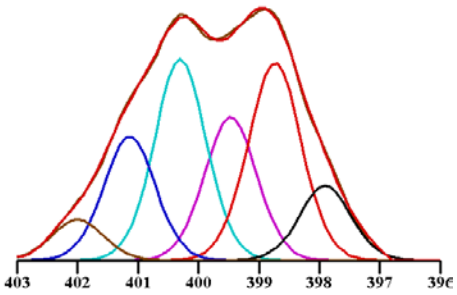




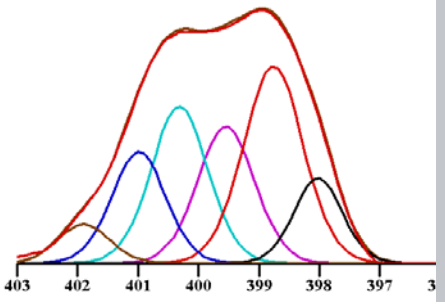


Controlled functionalization

Vulcan, 50 mA; N=4.8%



Graphitic Vulcan, 50 mA; N=4.8%



Potential applications of N-doped materials:
- ORR;
- Non-Pt catalysts;
- Hydrogen storage;
- Batteries

Summary

Model HOPG substrate:

- **We demonstrated that nitrogen implantation has an inherent beneficial effect on MOR activity and durability and that nitrogen dosage and functionalities play a role on these effects.**
- **We screened several different chemical dopants and determined that dopant type and dopant level of interaction with carbon matrix affect MOR activity and durability.**
- **We showed that N-F-codoped system offers benefits exceeding those of N-doped system**

High surface area carbon system:

- **We showed that Pt and PtRu nanoparticles deposit in proximity to N-defect sites**
- **We demonstrated that PtRu on N-doped Vulcan carbon catalysts are more durable than PtRu on undoped carbon and commercial catalysts.**
  - Limit PtRu particle coarsening/dissolution and Ru cross-over to cathode
- **We showed controlled nitrogen functionalization of carbon powders, allowing one to design catalyst for specific applications, such as ORR in PEMFC, hydrogen storage, batteries, etc.**

Impact:

- **Affecting the catalyst-substrate interaction via the ion implantation is a viable approach to producing durable anode catalysts for direct methanol fuel cells**

Future Research Needs

- **Determine the performance and durability of PtRu/co-doped N-F high surface area carbon system**
- **Determine and optimize ORR performance and durability of Pt/doped-carbon system**
- **Improve catalyst activity by achieving nitrogen doping without decreasing ECSA.**
- **Establish catalyst degradation mechanisms, e.g. extent of ruthenium dissolution and cross-over to cathode, type of ruthenium and catalyst coarsening.**

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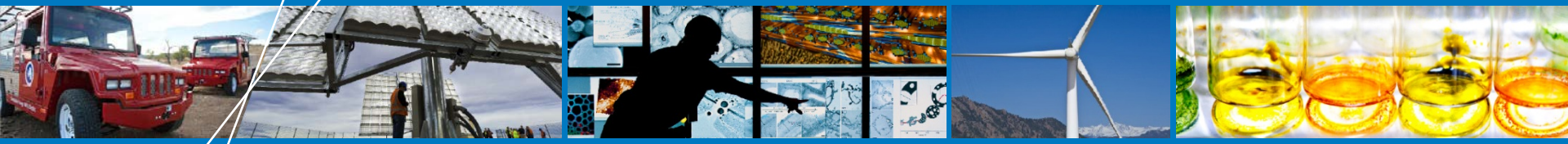


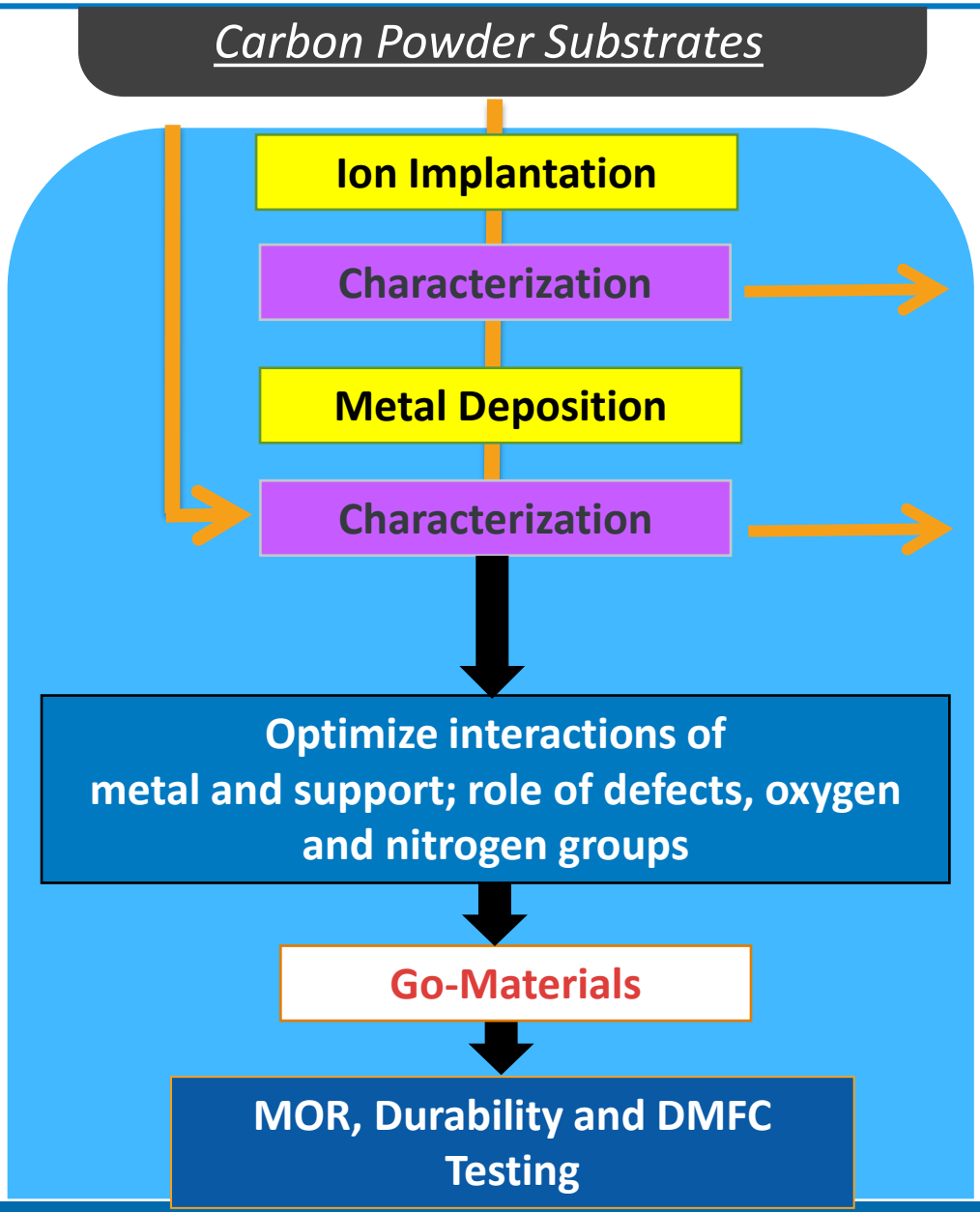
Back-up Slides

Approach: Powders

Materials Synthesis and Characterization

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

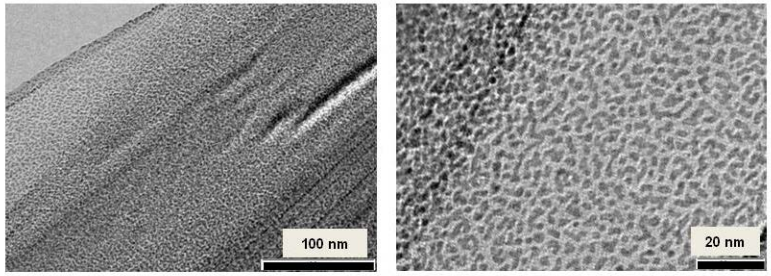
Metal Deposition
- **Magnetron Sputtering (Go)**
- Atomic layer deposition (ALD)
- Electrodeposition
- Microwave
- Incipient wetness



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)

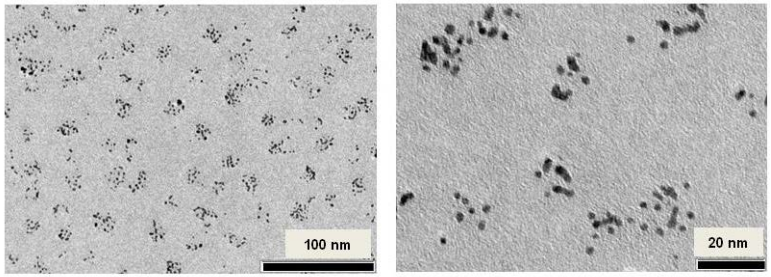
Technical Accomplishments:
HOPG, Effect of N-doping on durability, nanoscale chemical imaging

Pre-cycled PtRu/N-HOPG



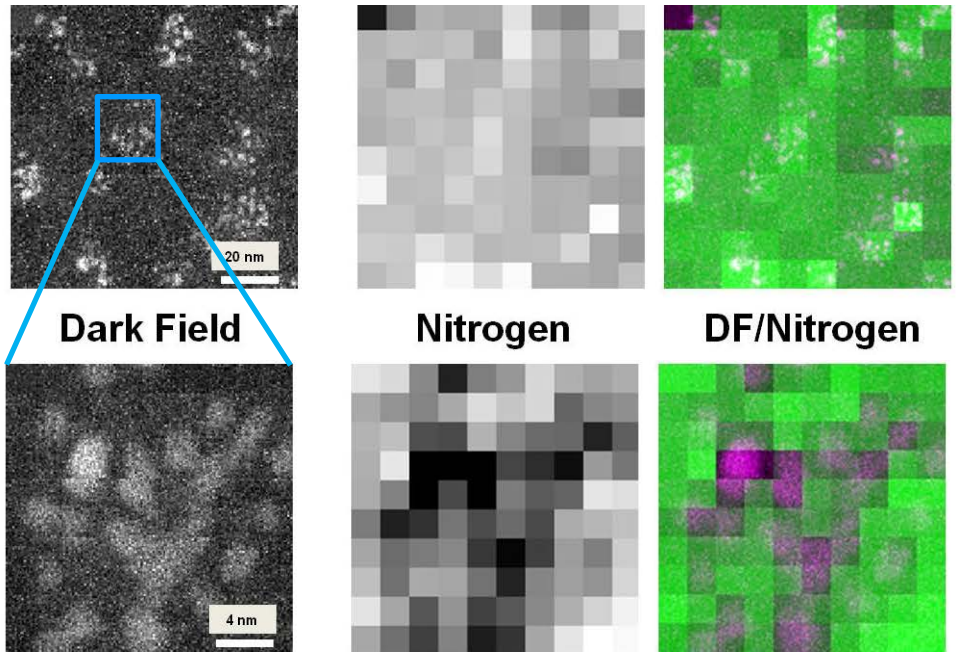
1,000 cycles

Post-cycled PtRu/N-HOPG



Formation of clusters

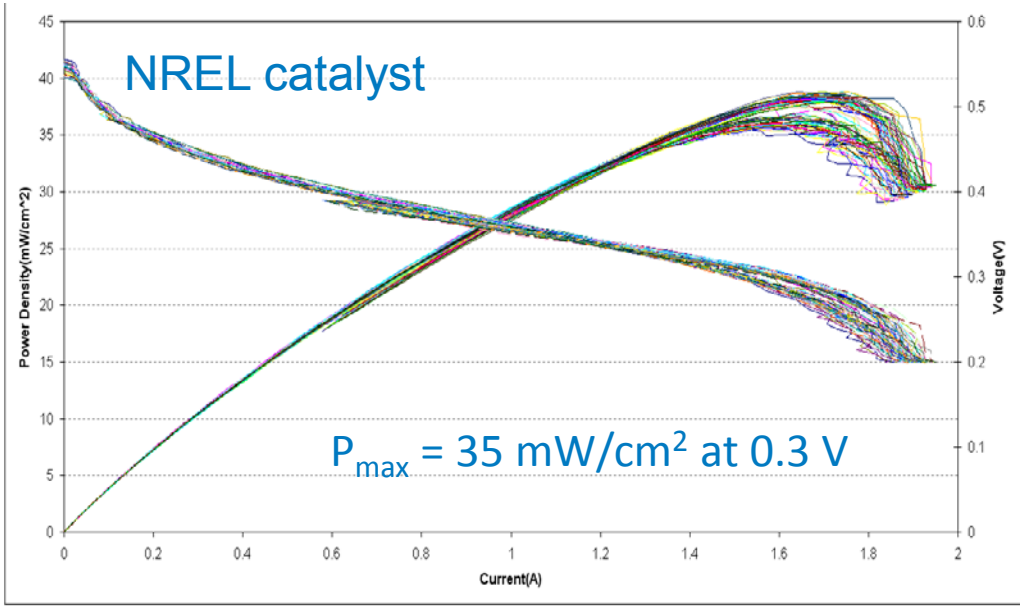
STEM-EEL spectral imaging

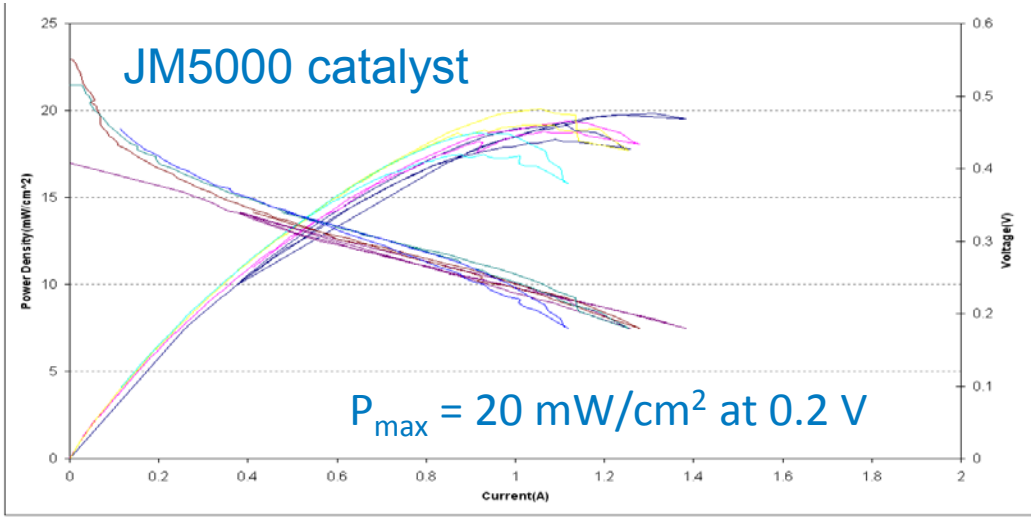


PtRu nanoparticles are in proximity to nitrogen rich sites, rather than deposit on top of nitrogen sites.

STEM-EEL = Scanning transmission electron microscope-electron energy loss

Technical Accomplishments:
DMFC MEA Performance, Tested by MTI MicroFuel Cells



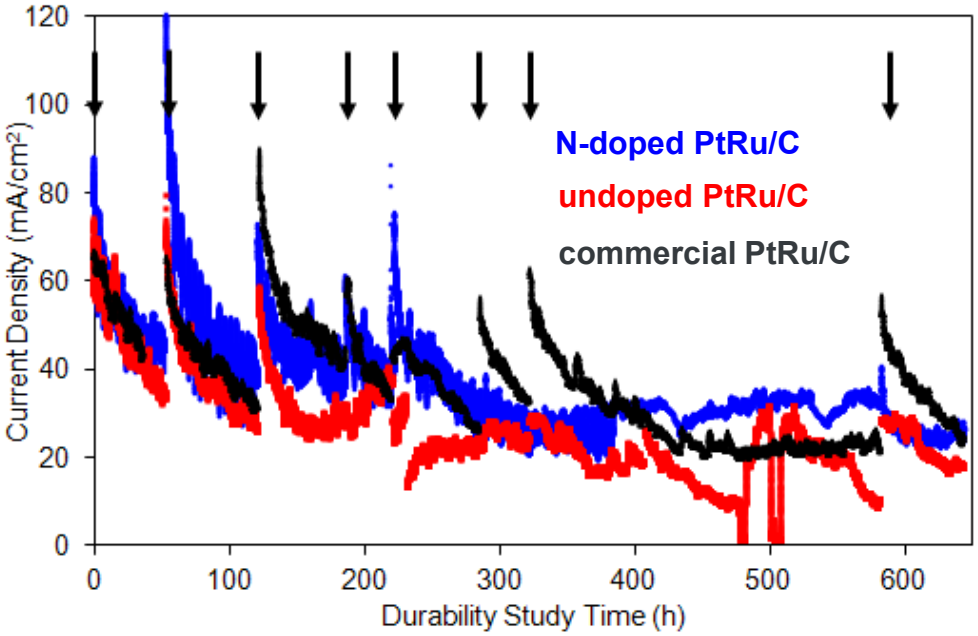


MTI's testing showed that our in-house PtRu/Vulcan performed better than the commercial catalyst, with the same catalyst loading

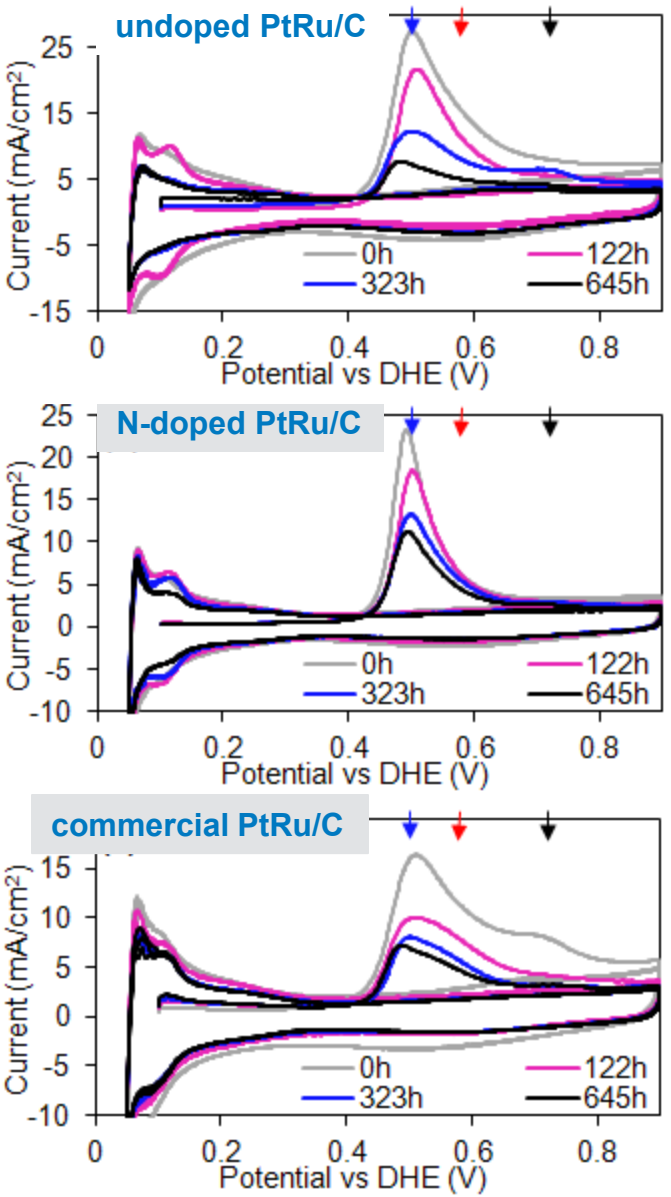
Anode: 30wt% PtRu/C; 2 mg/cm^2

Technical Accomplishments: DMFC MEA durability

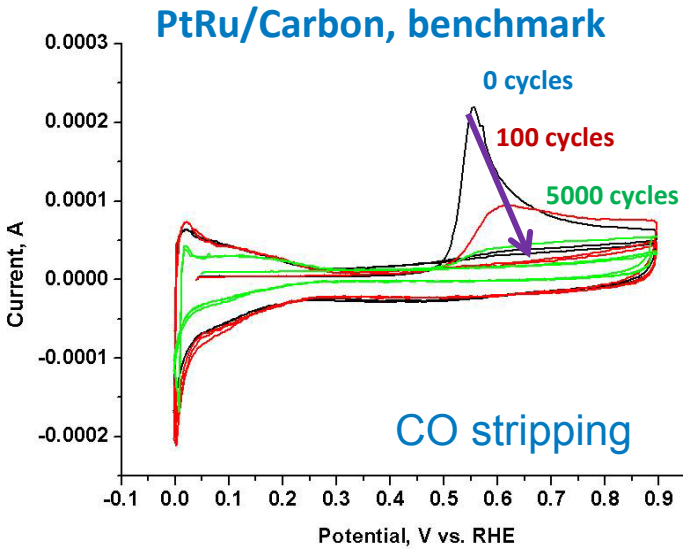
CO stripping on anode

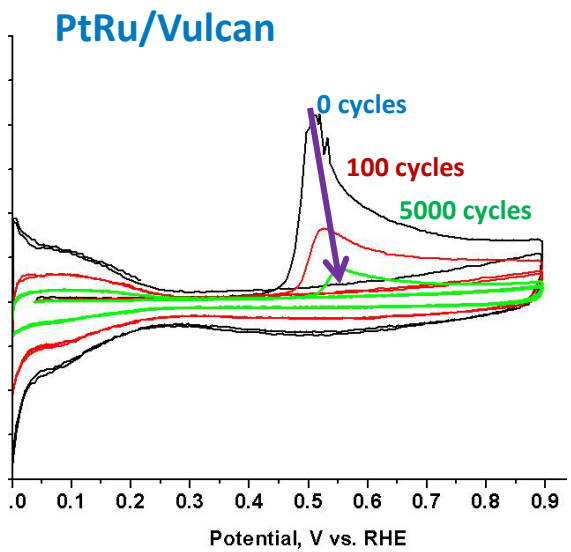


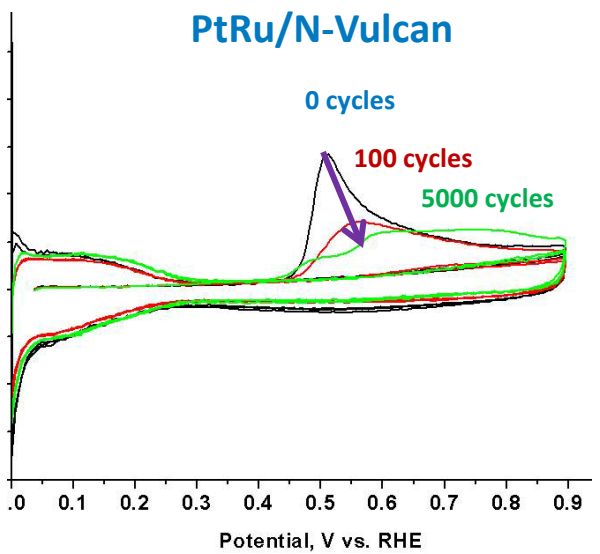
Durability: constant cell voltage (0.4 V) for a total of 645 h

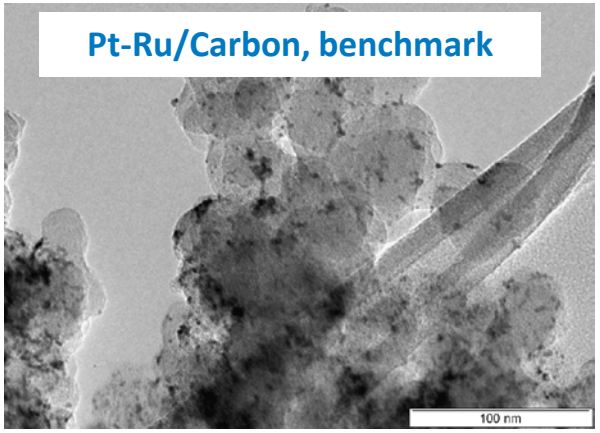


Technical Accomplishments: Durability of PtRu/Vulcan (RDE)

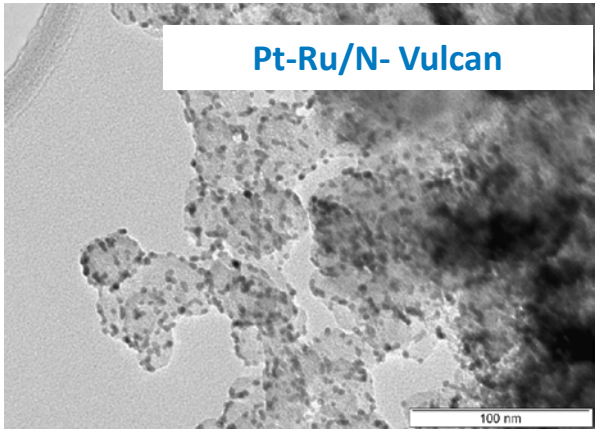








Catalyst	% of ECSA after 100 durability cycles	% of ECSA after 5000 durability cycles
PtRu/C JM 5000	48	17
PtRu/C (sputter)	51	10
PtRu/N-C (sputter)	70	47



N-doped sample outperforms undoped in-house and commercial benchmark catalysts

Durability cycling conditions: 0-0.9 V vs. RHE, scan rate 500mV/s, 1 M H_2SO_4
ECSA = electrochemical surface area, determined from CO stripping experiment