

Development of Novel Non Pt Group Metal Electrocatalysts for Proton Exchange Membrane Fuel Cell Applications

2011 DOE Hydrogen and Fuel Cell Program Review

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Project ID# FC086

Overview Slide

– Timeline:

- Start date: 8/01/2010
- End date: 01/31/2013 (Budget period 1) and 2/1/2013 to 7/31/2014 (Budget period 2)
- Percent complete: 11% (5 months)

– Budget Data: \$ 4,942,301.00 (Federal), \$ 1,437,714.00 (cost share); Total \$ 6,380,015.00

– Barriers

- Activity Targets for Non PGM catalysts: exceed 130 A/cm³ (2010) and 300 A/cm³ (2015).
- Durability at temperatures $\leq 80^{\circ}\text{C}$, 2000 hrs (2010); 5000 hrs (2015)

– Partners

- Northeastern Univ., (Prime) Boston: S. Mukerjee (P.I) and S. Smotkin
- Univ. of Tennessee, Knoxville: Prof. T. Zawodzinski
- Univ. of New Mexico, Albuquerque: Prof. P. Atanassov
- Michigan State University: Prof. S. Barton
- BASF Fuel Cells, Somerset, NJ: Dr. E. DeCastro
- Nissan Technical Center North America (NTCNA): Dr. K. Adjemian
- Los Alamos National Lab: Dr. P. Zelenay

Relevance

- Objectives: This project will develop new classes of non-PGM electrocatalysts which would meet or exceed DOE 2015 targets for activity and durability. 2010 Activity targets for DOE are 130 A/cm² and 2015 activity targets are 300 A/cm².
- Relevance to DOE Mission: This will enable decoupling PEM technology from Pt resource availability and lower MEA costs to less than or equal to \$ 3/KW. Science of electrocatalysis will be extended from current state of the art supported noble metal catalysts to a wide array of reaction centers.
- Impact
 - Lower MEA cost to less than or equal to \$ 3/KW
 - Independence from Pt and other precious metal global availability
 - Greater independence to poisons which typically effect of Pt & Pt alloys (i.e., sulfur, CO etc.), Hence ability to tolerate H₂ with greater impurity.

Overall Approach

- **Overall technical approach:**

- **Comprehensive materials development strategy encompassing:**
 - **Novel new reaction centers under the broad categories of**
 - Metal organic frameworks
 - Metal polymer composites
 - Metals in controlled ligand environments
 - **Controlling Metal support interactions**
 - For ensuring reaction center dynamics
 - Efficient mass transport of charged and solute species
 - **Ensuring Stability via careful control of reaction center's electronic structure**
- **Computing transport and reaction dynamics**
 - Reaction dynamics at complex reaction layer for oxygen and oxide bonding
 - Transport modeling in multi-layer structures
- **In situ Infrared and Synchrotron X-ray Spectroscopy**
 - For elucidating electrocatalytic pathways in complex reaction centers
 - Quantifying degradation with element specificity under *in situ* operating conditions

- **Program Technical Barriers and Approach to Overcome them:**

- **Current volumetric Power density is $\sim 130 \text{ A/cm}^3$ which is close to 2010 DOE target. 2015 target is 300 A/cm^3 which requires the following approach to materials development**
 - (a) Development of new classes of materials,
 - (b) Redesign of the catalyst support and
 - (c) Understanding at a fundamental level
 - (d) Transport of charged and solutes species and
 - (e) Electrocatalytic and degradation pathways under actual operando conditions.

Our approach addresses all these issues for meeting 2015 DOE target.

Milestones and Go/No Go Decisions

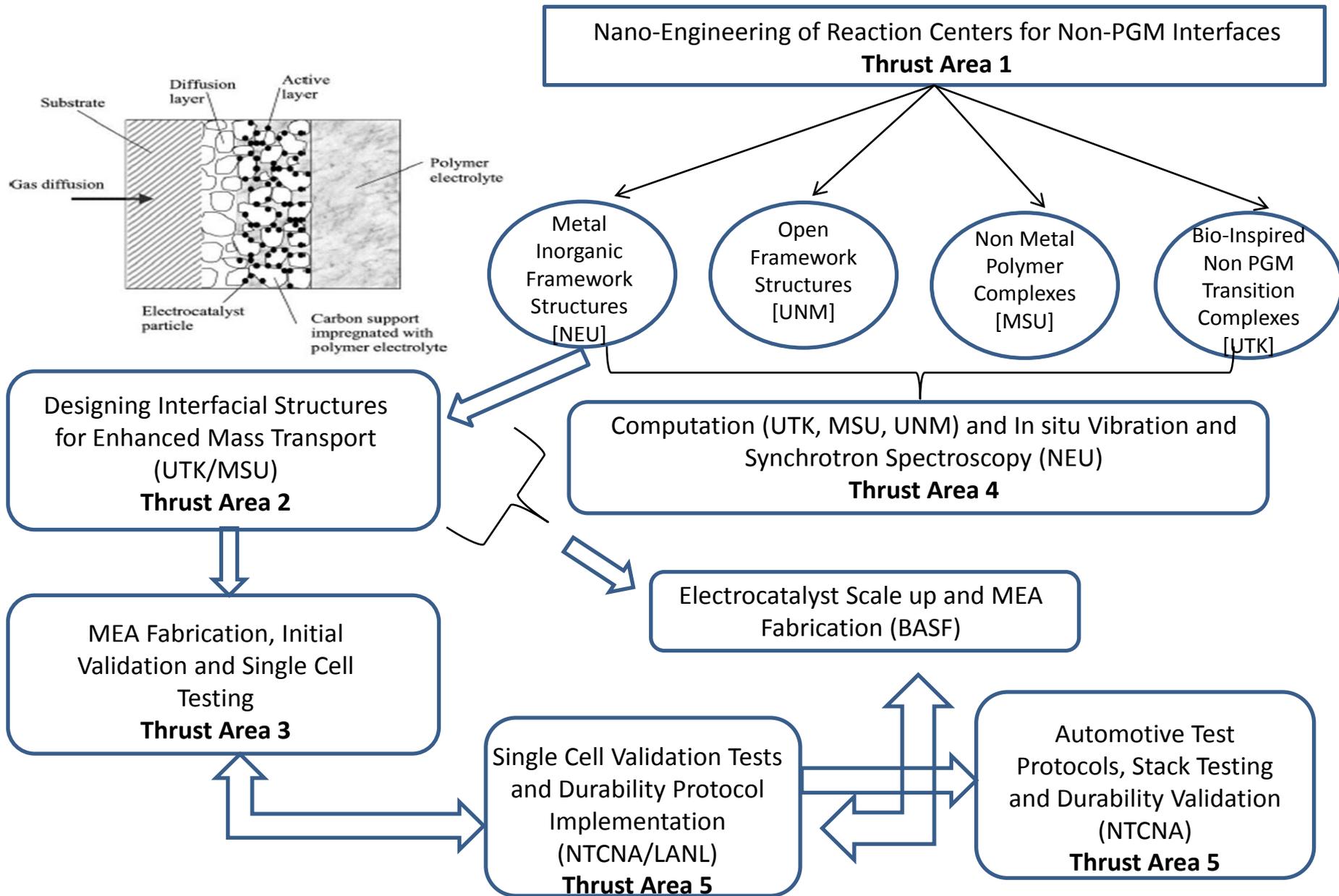
– Milestones (2011)

- Materials Development: RDE measurement of volumetric power density Q 1-4
- Meet $\sim 150 \text{ A/cm}^3$ (iR free) at 0.8 V RHE (80°C or below) Q 1-4
- Durability measurements based on DOE protocols to project stability within DOE specifications in RRDE and single cells (2011) Q 1-4
- Initiation of in situ measurements for degradation and electrocatalytic studies (2011) Q3
- Initiation of Membrane Electrode Fabrication for Single Cell Studies (2011) Q 1-4
- Computational efforts for electrocatalysis and transport measurements Q 2-4
- Set up protocols for computational efforts and generate first set of data for comparison with experiments Q 2.

– Go/No Go Decisions (2011)

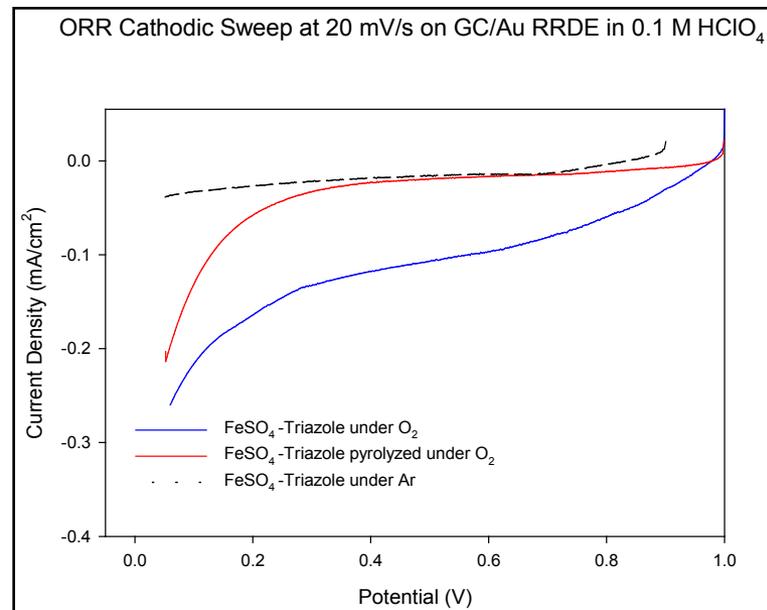
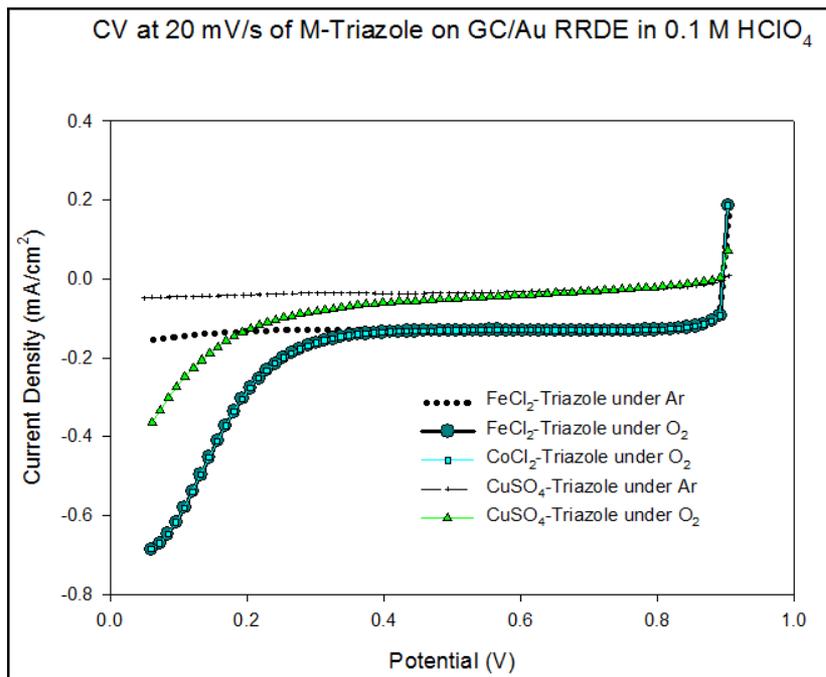
- Materials Screening based on above mentioned benchmark (Q2, 2011) and decision on materials choice for further development will be based on DOE target of 150 A/cm^3 at 0.8 V (iR free).
- Computation approach assessment based on its predictive capabilities and short listing of approaches (2011, Q 4), based on correlating experimental data with predictions.

Program Structure and Management

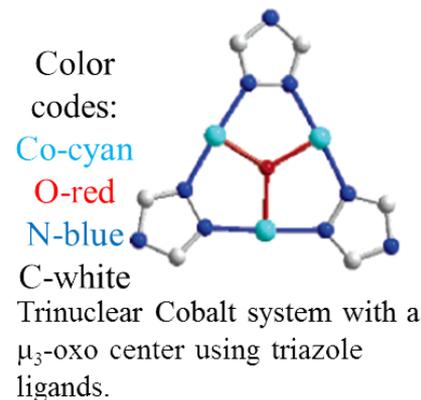


Technical Accomplishments

- **Task 1: Design and Synthesis of Novel Materials for Oxygen Reduction Reaction (ORR)**
 - **Development of Polynuclear Reaction Centers (NEU)**
 - **Triazoles and Triazines on C (as discrete supported molecules)**
 - **Using Graphene and Graphene Oxides as Platforms for Metal coordinated complexes**
 - **Abbreviated Metal Organic Framework Systems**



- Iron and Cobalt showed the best catalytic activity
 - FeCl₂ and FeSO₄ showed the best performance
- Copper had poor catalytic activity and was not stable
- Pyrolysis of M-Triazole complex did not improve catalytic activity
- None of the M-Triazole complexes performed well in acidic media

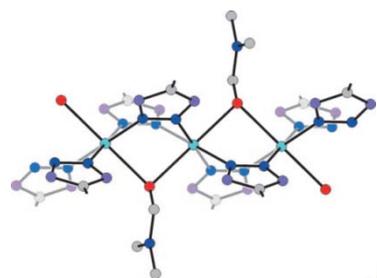


Technical Accomplishment continued....

Task 1. Design and Synthesis of Novel Materials for Oxygen Reduction Reaction (ORR)

– Development of Metal Organic Framework Catalysts (NEU)

- Flexible MOF selective for O₂ adsorption



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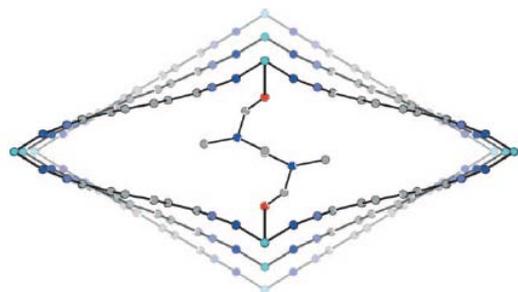
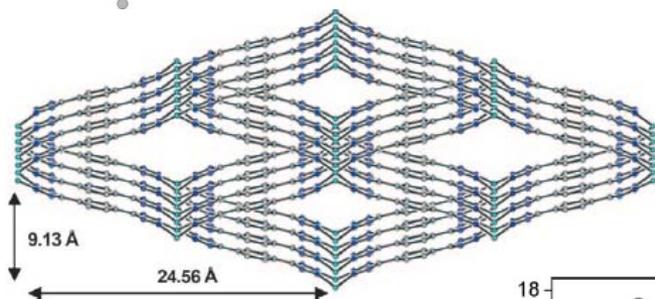
Cu-light blue

O-red

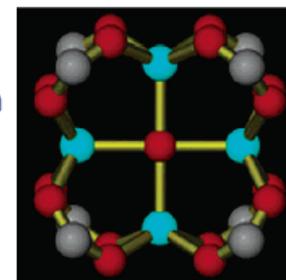
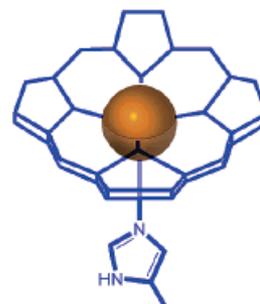
N-blue

C-gray

N or C triazolate ring-purple



- MOFs with entatic metal center that mimics active site of hemoglobin

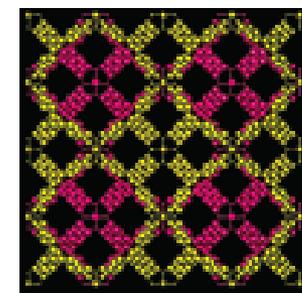
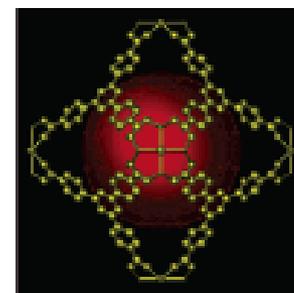
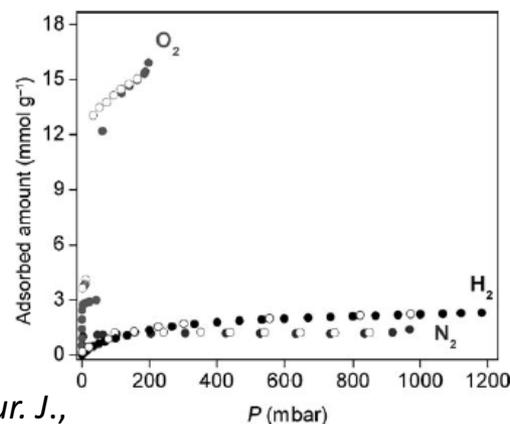


Color Codes:

Co-light blue

O-red

C-gray

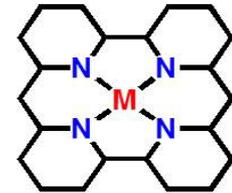
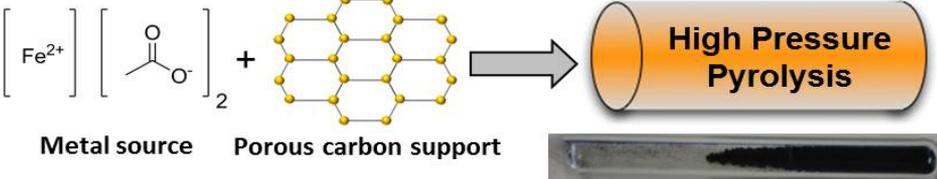


Technical Accomplishment continued....

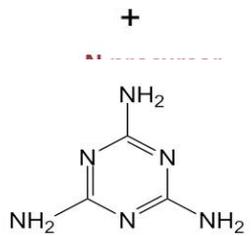
Task 1. Design and Synthesis of Novel Materials for Oxygen Reduction Reaction (ORR)

– Development of Novel MNC Catalysts (MSU)

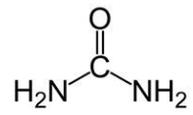
Approach



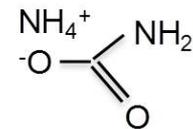
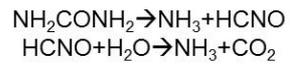
Metal-functionalized pyridinic carbon (Proposed catalytic site)



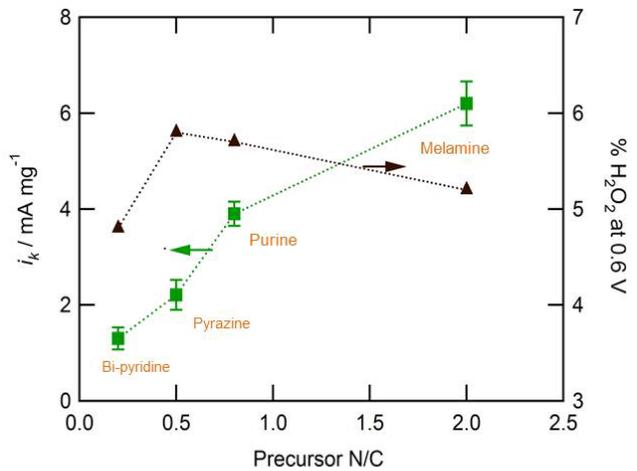
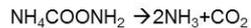
Melamine (N/C – 2.0)



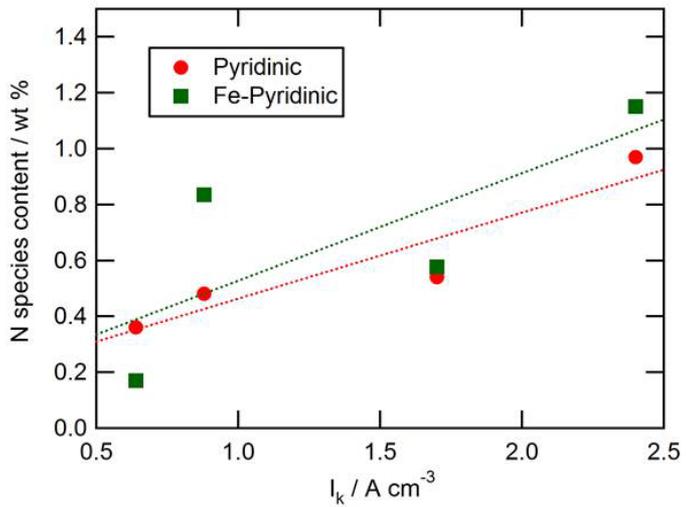
Urea



Ammonium carbamate



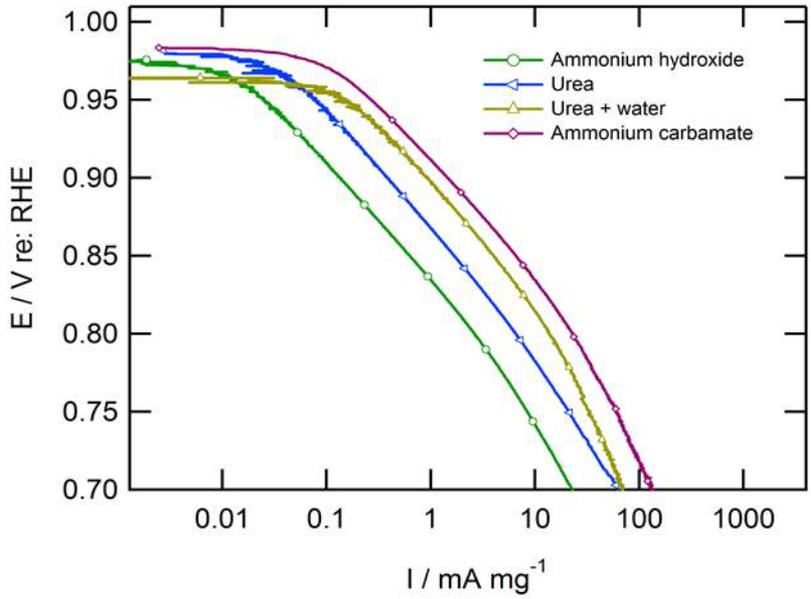
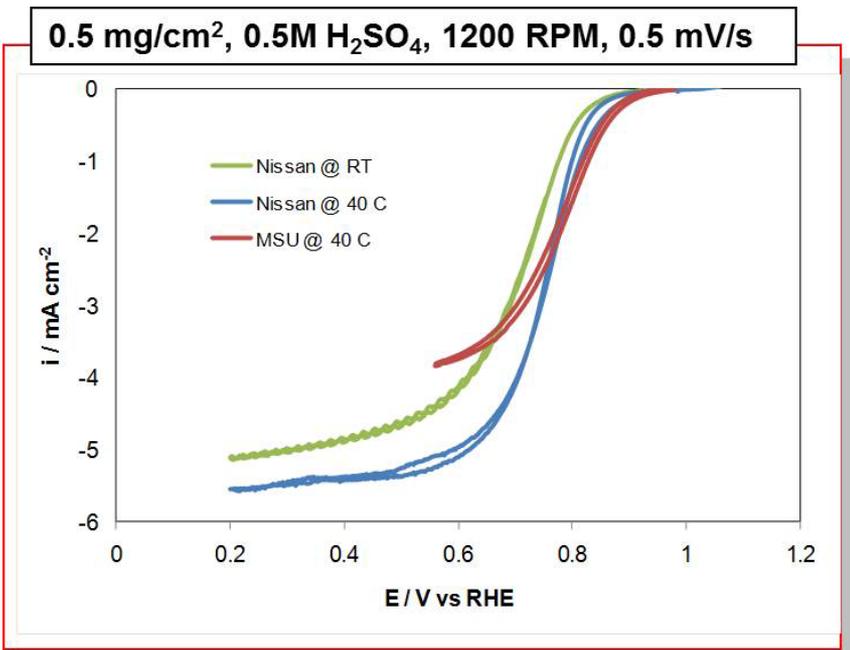
RDE - 1200 rpm, 40°C, 0.5 mV s⁻¹, 0.5M H₂SO₄



Technical Accomplishment continued....

Task 1. Design and Synthesis of Novel Materials for Oxygen Reduction Reaction (ORR)

– Development of Novel MNC Catalysts (MSU) continued...



RDE - 1200 rpm, 40°C, 0.5 mV s⁻¹, 0.5M H₂SO₄

Test	Tafel slope mV/decade	Volumetric Activity (A/cm ³)
MSU @ 40 C	80	2.11

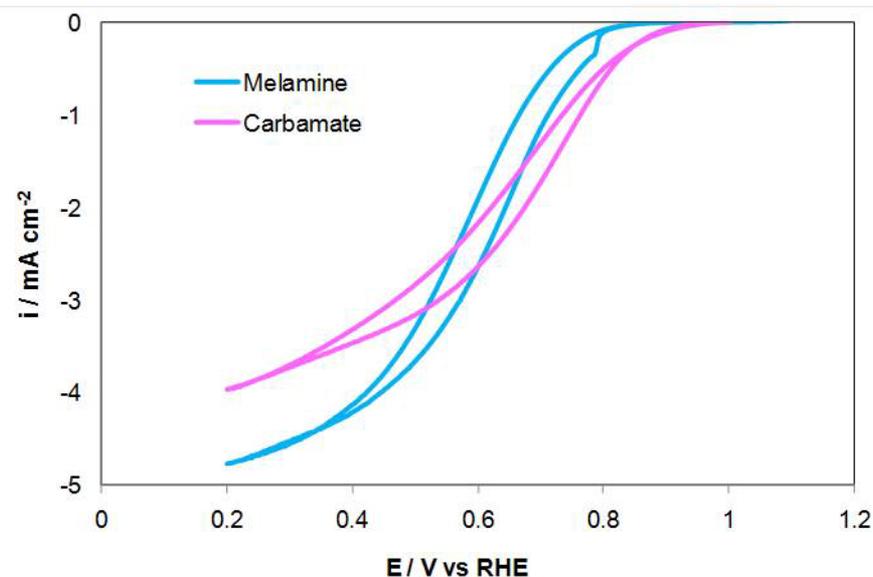
- Higher limiting currents were obtained using NTCNA RDE setup.
- Lower activity values for NTCNA data than MSU are due to hydrophobic nature of catalyst
 - Surface treatment is needed to make the catalyst surface hydrophilic. Differences between NTCNA and MSU results are being addressed with personnel exchange and close collaboration.

Technical Accomplishment continued....

Task 1. Design and Synthesis of Novel Materials for Oxygen Reduction Reaction (ORR)

- Development of Novel MNC Catalysts (MSU/NTCNA)

0.1 mg/cm², 0.1 M HClO₄, 1200 RPM, 0.5 mV/s, RT



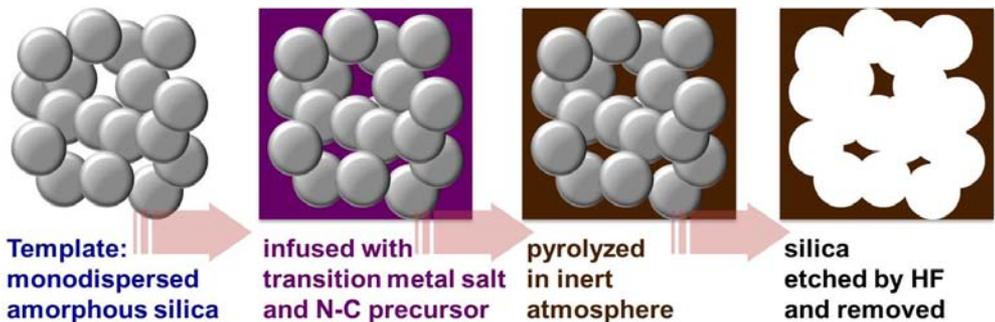
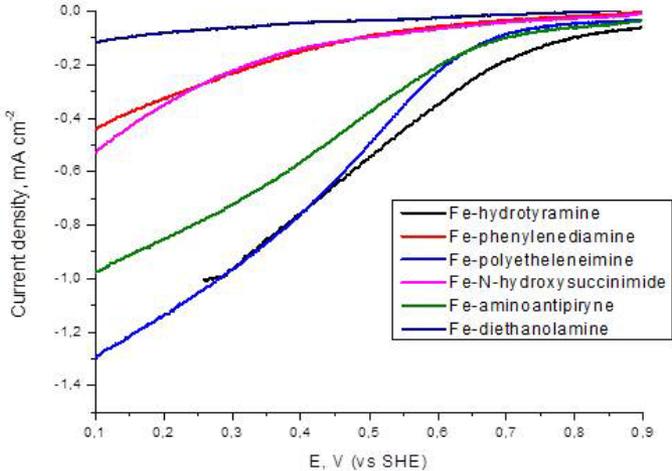
Catalyst based on precursor	Tafel slope mV/decade	Volumetric Activity (A/cm ³)
Melamine	80	0.43
Ammonium Carbamate	77	2.92

- Ammonium carbamate based catalyst showed higher volumetric activity than Melamine based catalyst under these test conditions

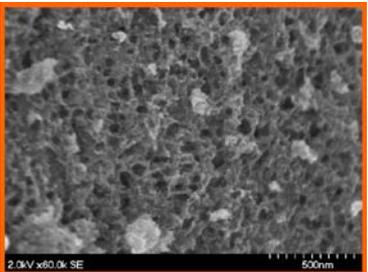
- Melamine based catalyst showed poor results in perchloric acid as compared to sulfuric

Task 1. Design and Synthesis of Novel Materials for Oxygen Reduction Reaction (ORR)

Development of Novel Open Framework Templated Structures (UNM)

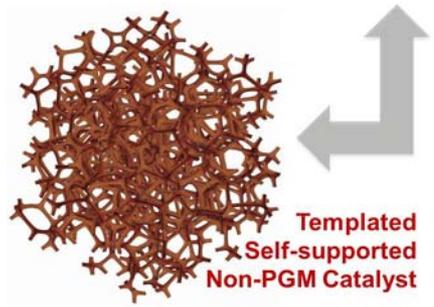


RDE of Fe-different-N-source catalysts in 0.5 M H₂SO₄, 1600 RPM. Loading 40.5 mg cm²



Fumed Silica:
BET-SA 380 m²/g

N-C Precursor:
1,4-Phenylenediamine
3-Hydroxytyramine
4-Aminoantipyrine
Diethanolamine
N-Hydroxysuccinimide
Poly(ethyleneimine)
Phenanthroline



Average pore size 40-50 nm

Metals: Ce, Zr, V, Ti, Ta, Nb, W, Mo, Fe, Ru, Co, Ni, Cu

Task 2. Development of Novel Reaction Layer Formulations, Design of Gas Diffusion Layers and Fabrication of MEAs (NTCNA)

GDE Fabrication

Catalyst ink recipe

Water/Carbon	13.6/1
Ethanol/Carbon	27.2/1
Ionomer/Carbon	28.6/1



Mixing with stir bar for 10 min



Mixing with homogenizer for 3 hrs



Spray on to GDL (25BCH)

MEA Preparation

Pre-pressing MSU GDE under 1,200 lb and room temperature for 10 min



Sandwiching MSU and JM GDEs
JM GDE (A) + NRE 211 + MSU GDE (C)



Hot pressing MEA under 1,000 lb, 266 °F for 5 min

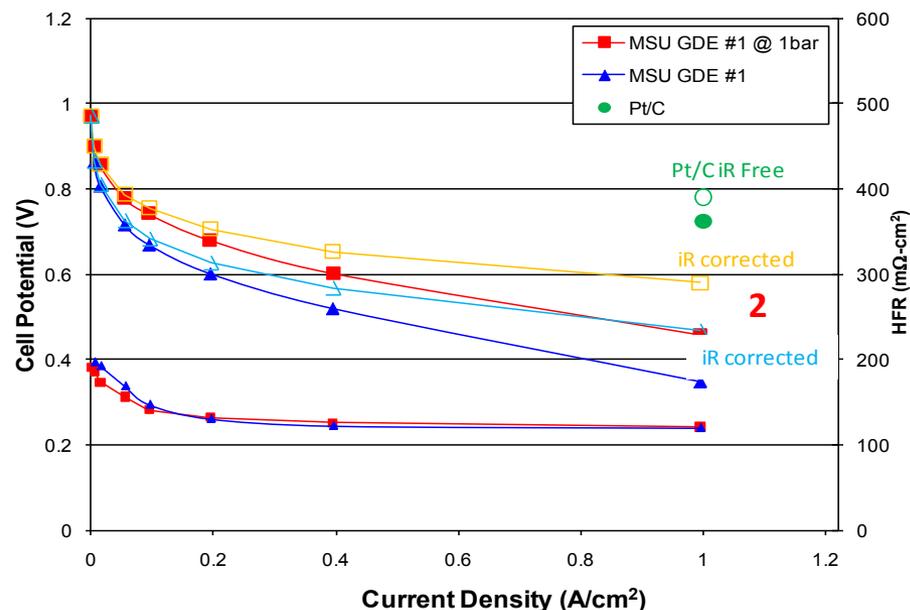
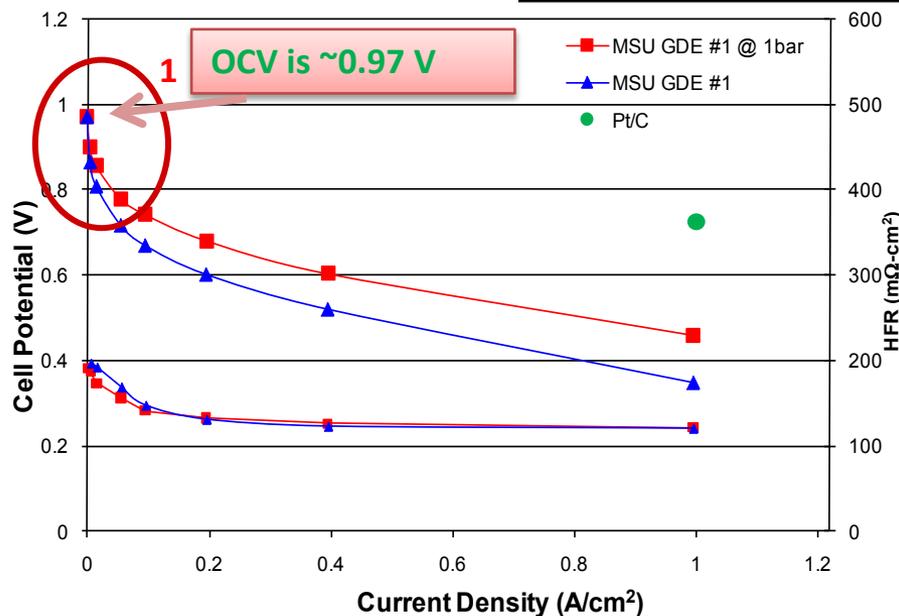


Cooling under room temperature

iV performance

MSU's MNC - ORR

H_2/O_2 , 100% RH, 80°C, 0.42 / 0.84 NLPM

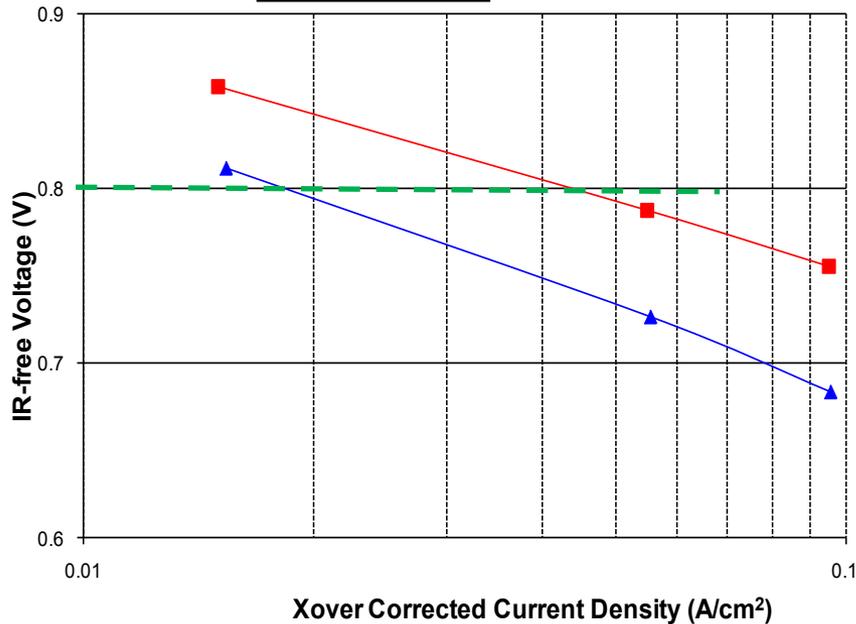


- Higher OCV values were obtained at NTCNA than MSU Lab data
- 1. Similar high OCV values were observed with/without back pressure due to the presence of pressure in the cell caused by high flow rate and serpentine channel
- 2. Since HFR values are high due very thick catalyst layer (**thicker than the membrane!**), iR correction shows significant improvement

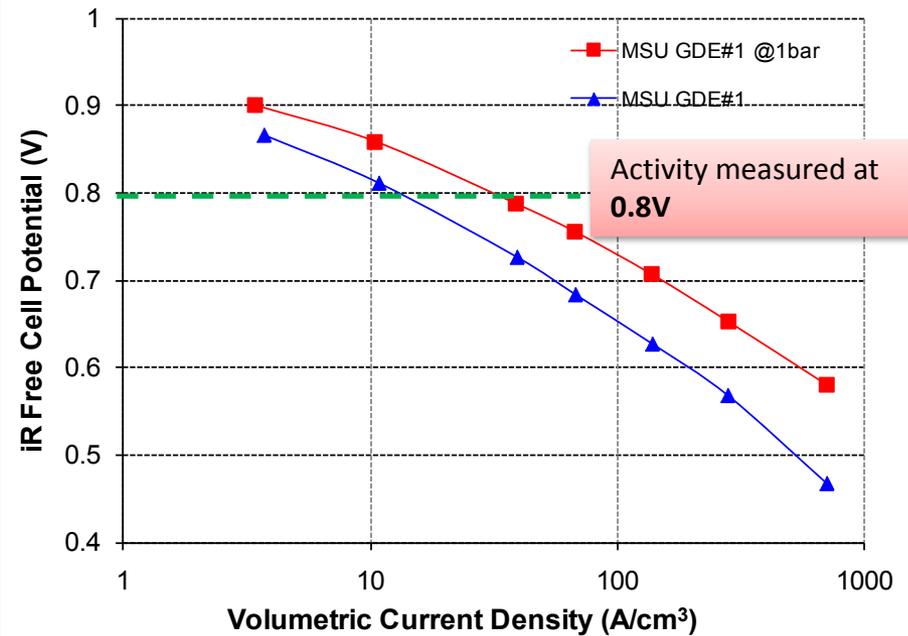
iV performance

MSU's MNC – Tafel and Activity plot

Tafel Plot



Volumetric Activity Plot



Cathode Loading: $4 \text{ mg}_{(\text{Total catalyst+ionomer})} / \text{cm}^2$

$0.565 \text{ mg}_{(\text{Cat})} / \text{cm}^2$

Without back pressure	13 A/cm ³
With back pressure	31 A/cm ³

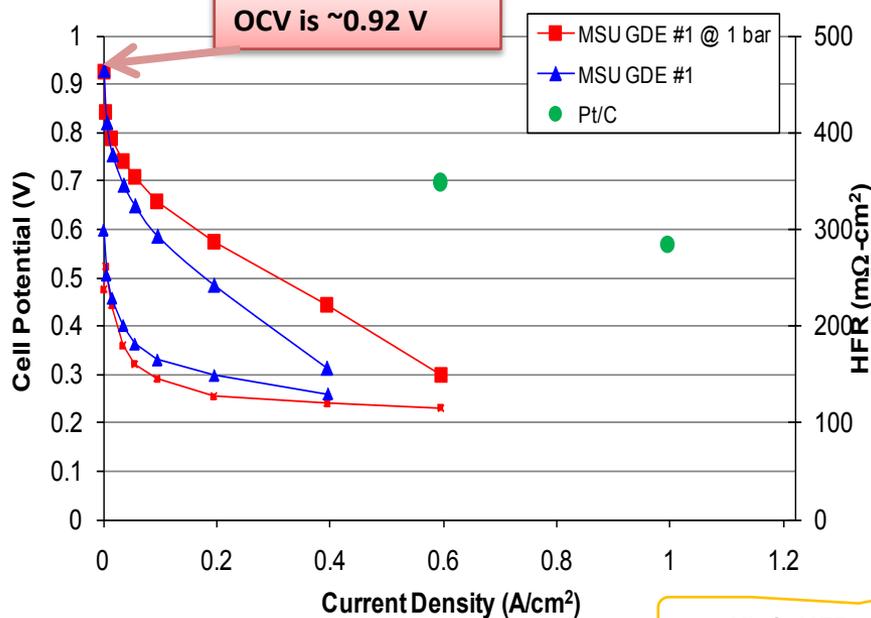
2010 DOE Target is 130 A/cm³

- Activity calculations are done using effective carbon density of 0.4 g/cm³ and 0.565 mg/cm² catalyst loading

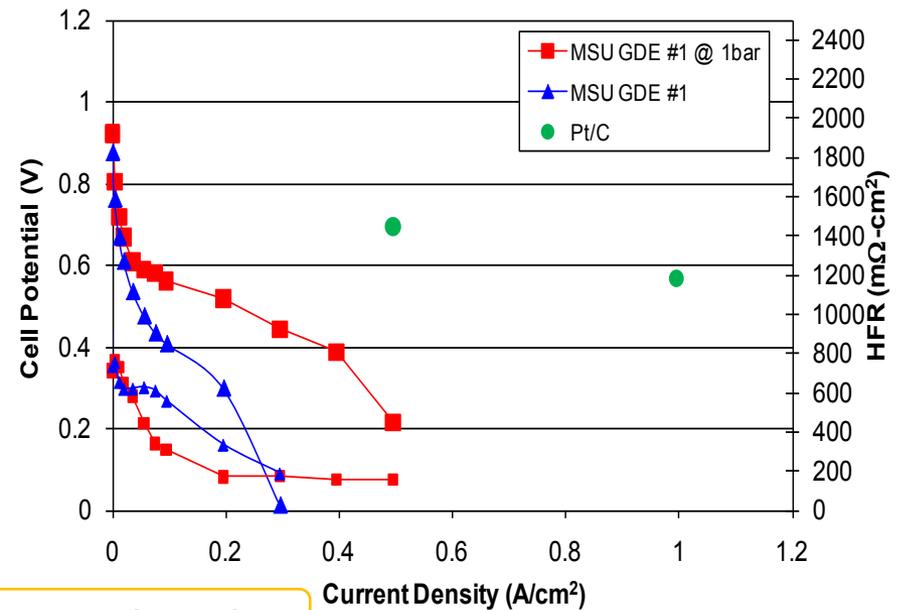
I. iV performance

MSU's MNC – H₂/Air iV

H₂/Air, 100% RH, 80°C, 0.31 / 1.05 NLPM



H₂/Air, 50% RH, 80°C



- Under H₂/Air conditions, iV performance was significantly lower than oxygen – 1 A cm² could not be pulled.
- Performance drop is significant in kinetic as well as in mass transport region

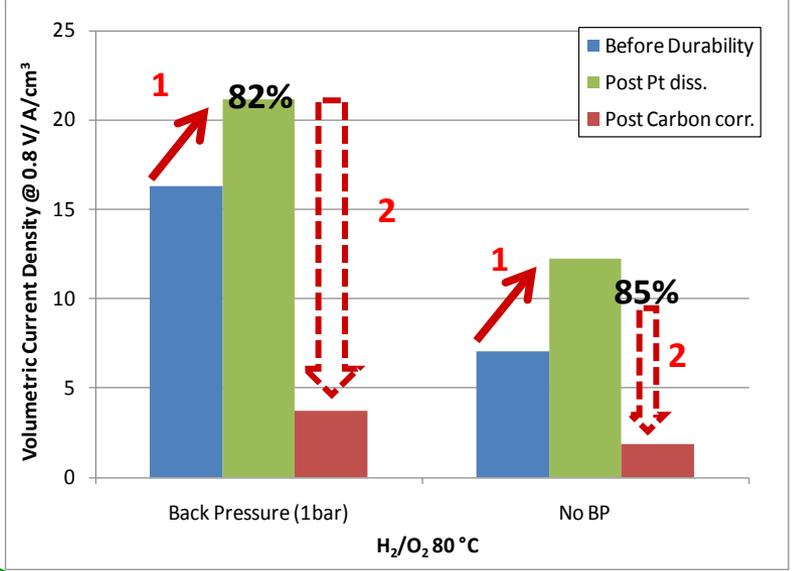
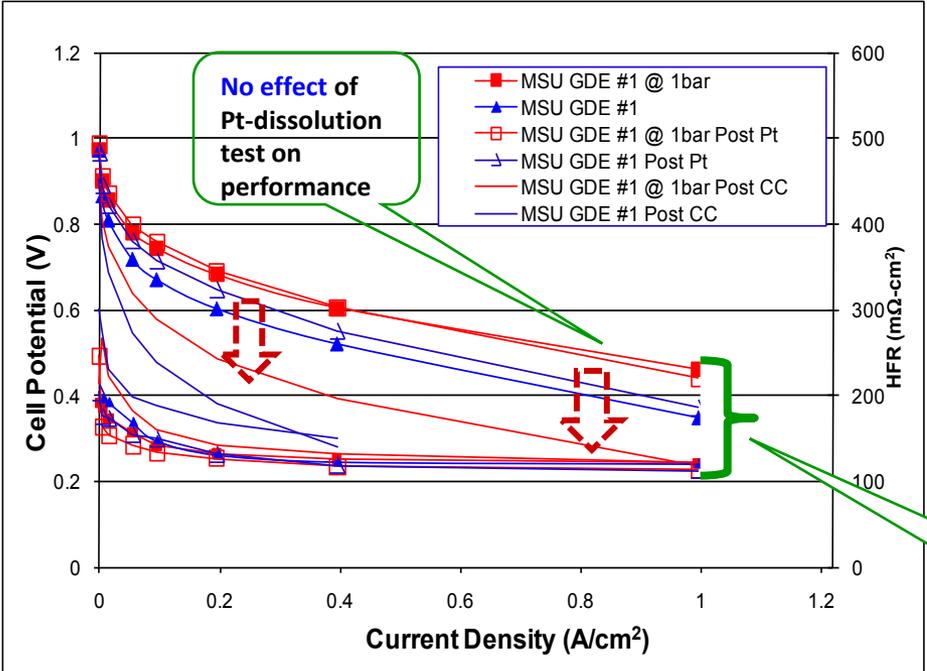
Task 2. Testing and Durability Measurements (MSU/NTCNA)

- Same MEA as iV performance was used for durability tests
- **Load Cycling: Pt Dissolution test (Protocol) applied to Non PGM electrode**
 - MEA tested was composed of NRE 211, JM GDE (anode), and MSU catalyst coated GDL (25BCH).
 - OCV and CV were measured during cycling.
 - iV performance of MEAs was evaluated in the beginning and at the end of 10,000 load cycles to obtain the effect of catalyst degradation
 - To verify the effect of this protocol for Pt based catalyst, this test was performed with expectation of no effect on this non Pt catalyst
- **Start-Stop cycling: Carbon corrosion**
 - Same MEA used for Pt diss. was used for Carbon corr. after verifying the minimal effects on performance.
 - Potential was cycled for simulate start-stop cycle from 1 to 1.5 V for maximum of 1,000 cycles
 - iV performance test of MEAs was evaluated in the beginning and at the end of 1,000 start-stop cycles to obtain the effect of carbon support corrosion
 - OCV and CV were measured during cycling.

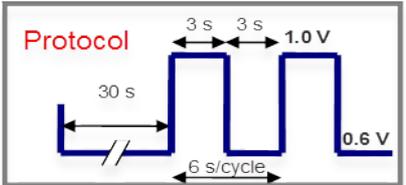
Catalyst Durability

Effect of Durability Tests (Pt Diss. & CC): Oxygen

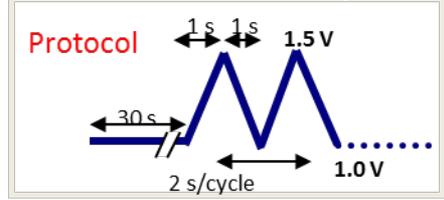
H₂/O₂, 100% RH, 80°C, 0.42 / 0.84 NLPM



Pt dissolution test protocol

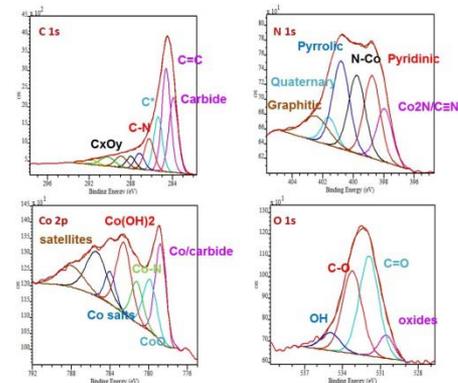


Carbon corrosion test protocol



- Activity was increased after Pt dissolution test protocol. This may be due to more conditioning. ✓ Same MEA was used for both Pt dissolution test and carbon corrosion.
- Loss of electronic contact and electrode integrity can be attributed to such loss in activities

Task 3. Mechanistic Studies and Spectroscopy



Participating Institutions:

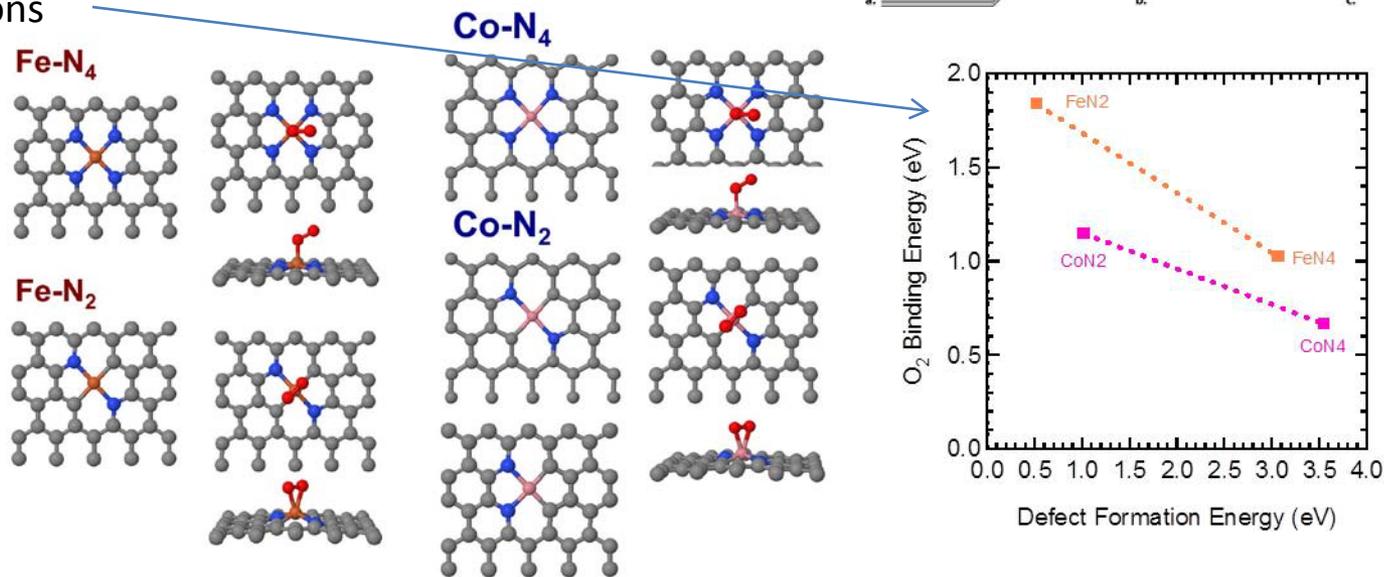
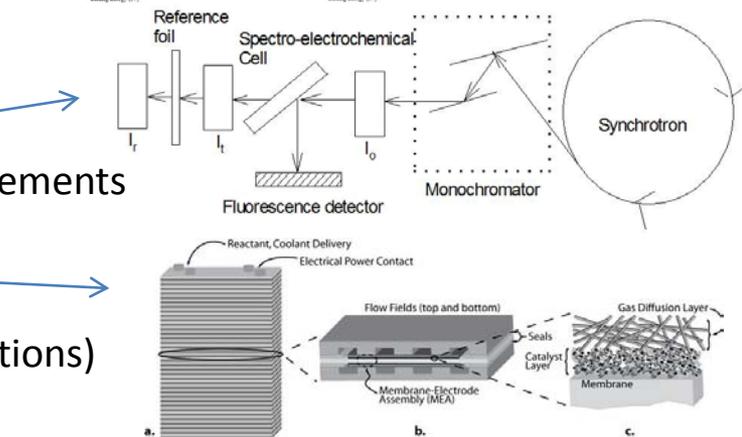
UNM- Ex situ Studies with XPS and PCA analysis

NEU- In situ Spectroscopy with Synchrotron and FTIR Measurements

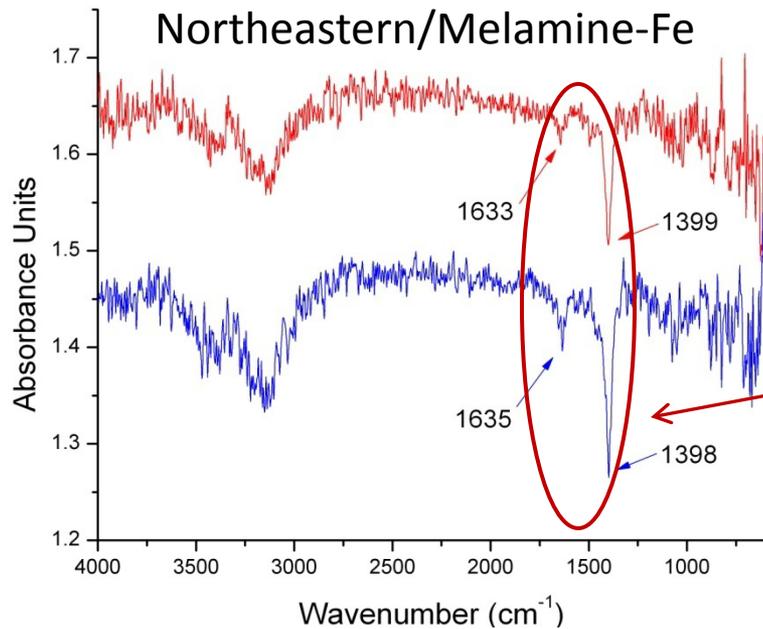
SMU- Macroscopic Modeling

UTK- Molecular Level Computation (Ab-Initio and MD Simulations)

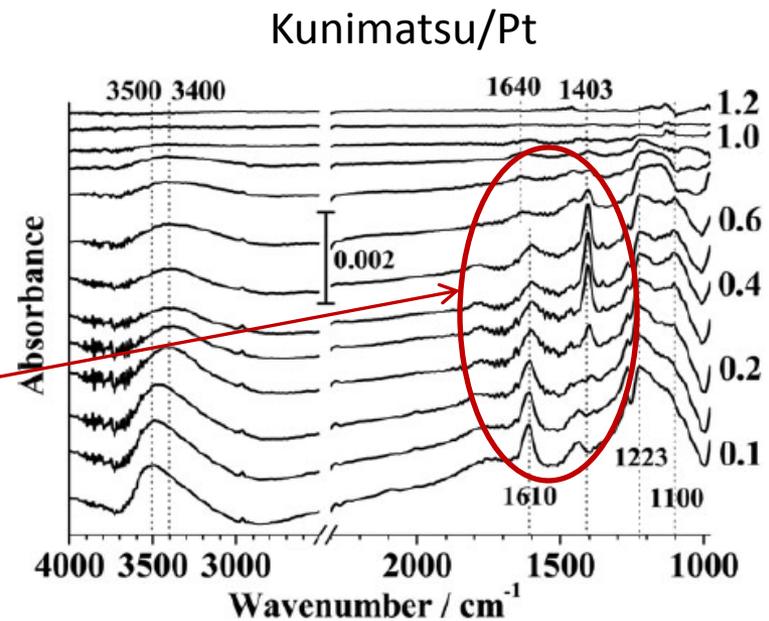
UNM- DFT Calculations



Infrared Spectra of O₂ adsorbed on melamine



O₂ adsorption on Melamine/Fe. Red: Air. Blue: Air/CO for 30 min.



O₂ adsorbed on Pt referenced to 1.2V spectrum (Kunimatsu et al. *Phys. Chem. Chem. Phys.* **2010**, *12*, 621)

First time direct detection of oxygen adsorption on Fe in Fe-N systems

Future Work

- Operando IR spectroscopy of fuel cell electrodes
 - Stark tuning of CO
 - Stark tuning of O₂

Kendrick et al. *J. Am. Chem. Soc.* **2010**, *132*, 17611

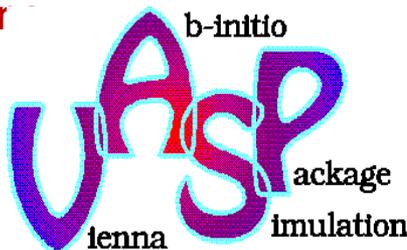
Mukerjee et al., manuscript in preparation



Task 4 Computation and Transport Modeling

Density-Functional-Theory:

- Generalized Gradient Approximation (PBE).
- 3-d periodic boundary condition
- Plane-waves.
- Spin polarized: Co.
- PAW-potentials.
- Fermi-smearing ($\sigma=0.025$ eV)



Surfaces:

- Graphene (32 atoms).
- 14 Å vacuum.
- Molecule(s) pre-optimized.
- Dipole correction.

Approach: *Universal* solid, liquid and gas.

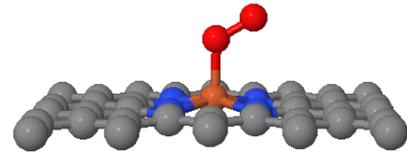
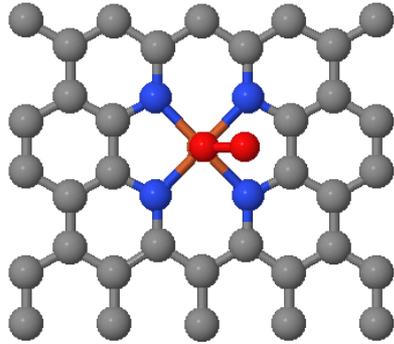
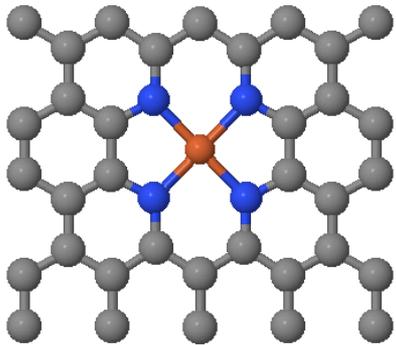
- Ionic, covalent and metallic bonding.
- Predictive power:
 - independent.
 - synergy with experiment.
- Periodic boundary conditions → extended structure.
Eliminates edge effects from molecular/cluster approach.
- Flexibility to engineer defect composition, chemistry, and geometry.

Objective:

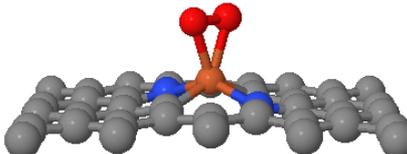
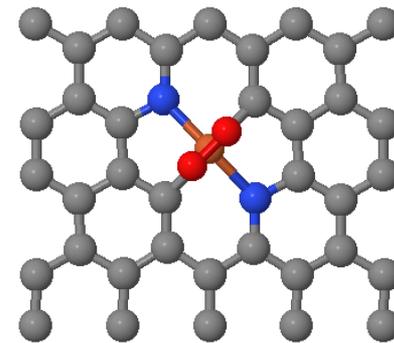
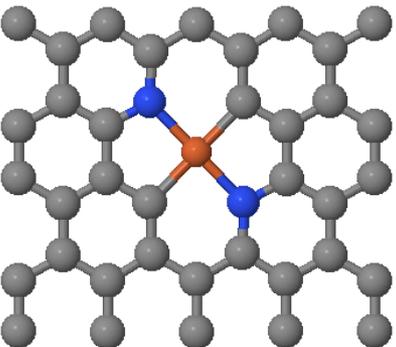
- Determine defect formation energies of pyridinic Fe/Co-N_{2,4}-graphene.
- Determine O₂ (ORR intermediate) adsorption energies.
- Evaluate correlation between energies.

Fe – N_x/Graphene System (UNM)

Fe-N₄



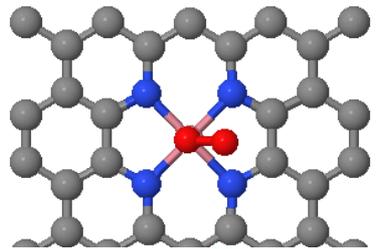
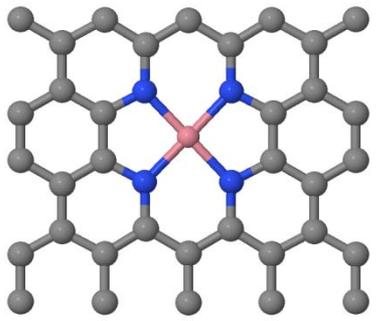
Fe-N₂



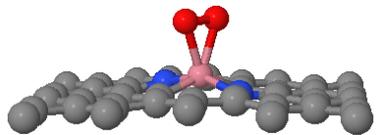
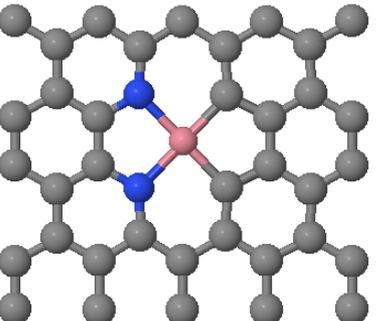
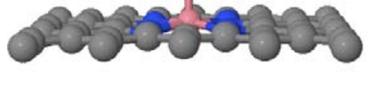
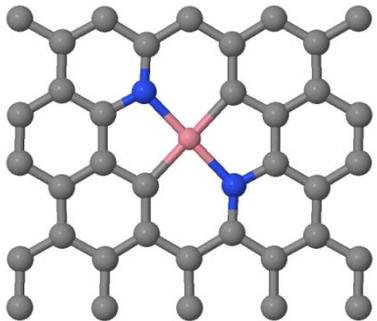
- Defects only stable in the presence of Fe.
- $E_{\text{for}}(\text{Fe-N}_2/\text{C}) > E_{\text{for}}(\text{Fe-N}_4/\text{C})$
 - ➔ Fe-N₄/C: low temperature.
 - ➔ Fe-N₂/C more abundant at high temperature.
- O₂, Fe-N_x geometry depend on nitrogen content:
 - ➔ FeN₄/C: high angle.
 - ➔ FeN₂/C: parallel to sheet.
- $E_{\text{B}}(\text{O}_2)$: depends on N content.

Co – N_x/Graphene System (UNM)

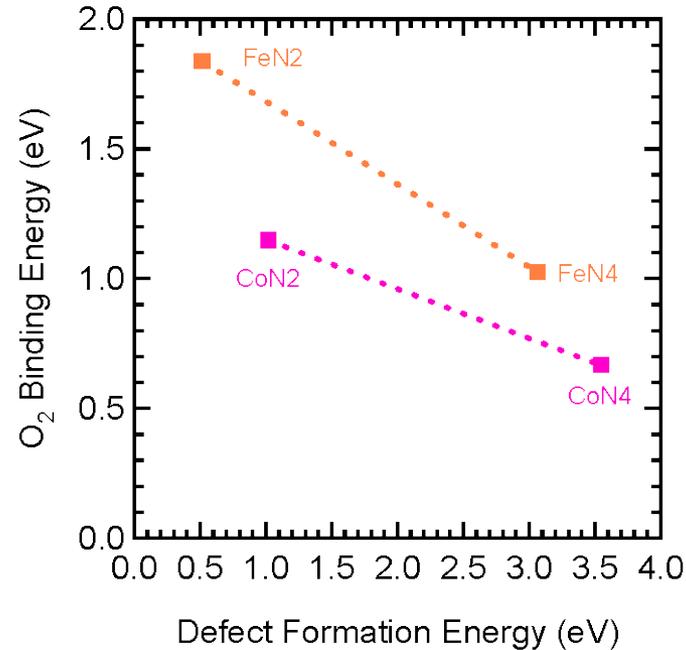
Co-N₄



Co-N₂



- Defects only stable in the presence of Co.
- Very similar trends to Fe defect.



Defect Engineering;

- Higher formation energy → lower O₂ binding energy.

Structure to the left most stable but for consistency with Fe we look at the same geometry $\Delta E = 1.33$ eV, small compared to other energy differences.

Collaborations

Partners (this project)

- Northeastern Univ., (Prime) Boston: S. Mukerjee (P.I) and S. Smotkin
- Univ. of Tennessee, Knoxville: Prof. T. Zawodzinski (Univ., subcontractor)
- Univ. of New Mexico, Albuquerque: Prof. P. Atanassov (Univ., subcontractor)
- Michigan State University: Prof. S. Barton (Univ., subcontractor)
- BASF Fuel Cells, Somerset, NJ: Dr. E. DeCastro (Industry, subcontractor)
- Nissan Technical Center North America: Dr. K. Adjemian (Industry, subcontractor)
- Los Alamos National Lab: Dr. P. Zelenay (Federal Lab., subcontractor)

Other collaborators:

- (1) Jean Paul Dodelet: CNRS, Canada (Non funded collaborator)

Proposed Future Work (2011-12)

- Screening of initial tranche of materials using RRDE & array fuel cells and single cell polarization measurements for down-selected electrocatalysts (Q1-Q4, 2011).
- Initial attempts to improve mass transport in gas diffusion medium. Novel approaches to electrode preparation, additives for improved oxygen solubility and fabrication of MEAs (Q2-Q4, 2011)
- Modeling of mass transport in electrode layers to be in sync with design of electrode structures (layer by layer approach) (Q3-Q4, 2011)
- First set of in situ synchrotron measurements taken in NSLS (March 2011). Data Analysis along with PCA analysis of the ex situ XPS data in progress. More runs planned (Q2-Q4, 2011).
- First set of DFT calculations on metal oxides and development of approaches to simulate M-N coordinated structures (Q1, 2011). Detailed DFT calculations (NEU and UNM) and MD simulations (UTK)planned (Q2-Q4, 2011)

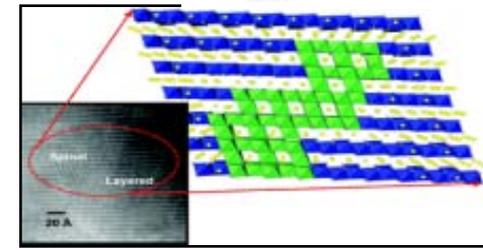
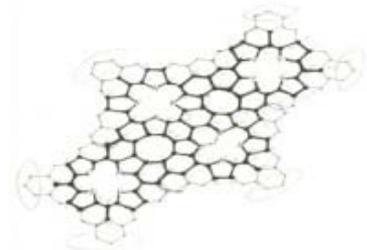
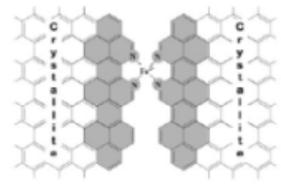
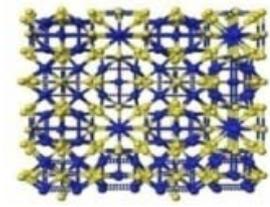
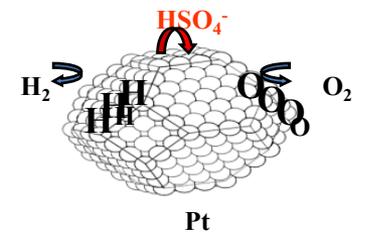
Summary Slide

- Current efforts focus on liganding non PGM metals onto carbon supports for effecting improved ORR performance and stability. Such as those shown by LANL group.
- Our effort encompasses development of novel bi-dentate and tetra-dentate complexes where tandem electron transfer to oxygen can be facilitated using two or three transition metals with different oxidation states.
- Current status of the non PGM field puts the volumetric power density at 130 A/cm^3 this however needs to be translated to actual fuel cell performance levels. Which requires redesign of electrode structures.
- In situ determination of charge transfer at the reaction center is expected to yield important leads for improved design of reaction centers.

Supplemental Slides

Non PGM Catalysts: Summary of Classes of Materials

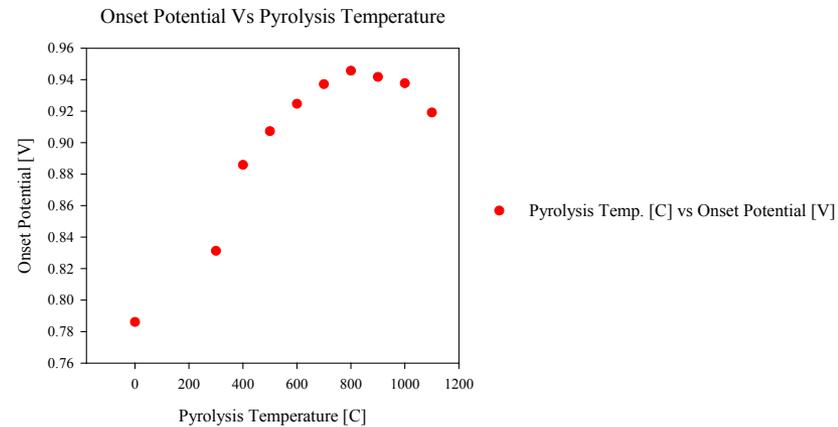
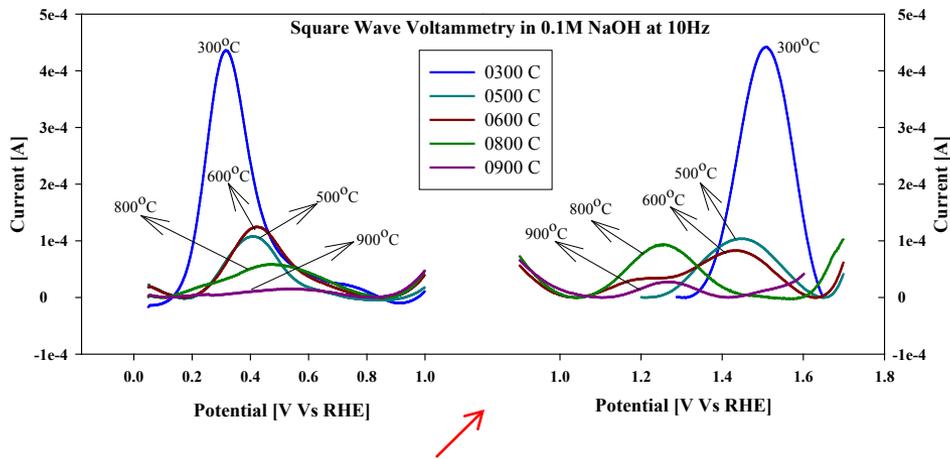
- Chalcogenides (limited success)
- Metal Oxides (possible candidates for anode electrode)
- Inorganic Framework structures
- Metal-N/C
- Metal Organic Framework systems
- Metal Polymer Composites



Brief Background on Current State of the Art in Non PGM Catalysis

Metal-nitrogen-carbon (M/N/C) catalysts

Obtained by heat treatment of organic and transition metal precursors



shift of oxidation potential towards higher towards higher values

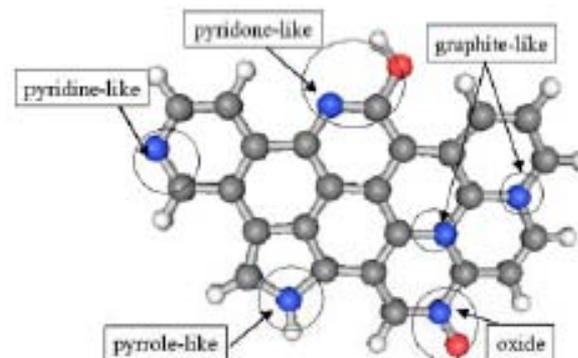
Three precursors are required for making well-performing ORR catalysts: transition metal (often salts), nitrogen source, carbon source

Metal-nitrogen-carbon (M/N/C) catalysts

Form of catalytic sites still under investigation

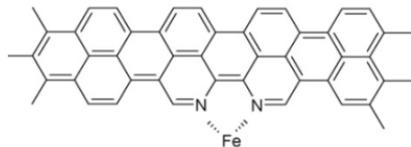
Catalytic sites suggestions:

- Nanostcured carbon doped with nitrogen often viewed as ORR active site (CN_x)

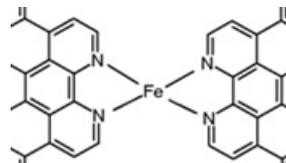


- Two types of micropore-hosted active sites proposed:

Metal-N₂₊₂/C



Metal-N₄/C

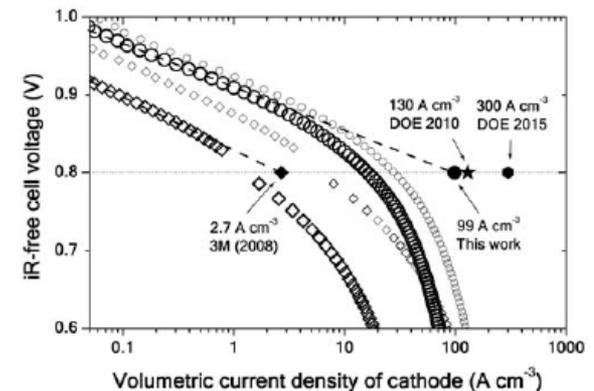
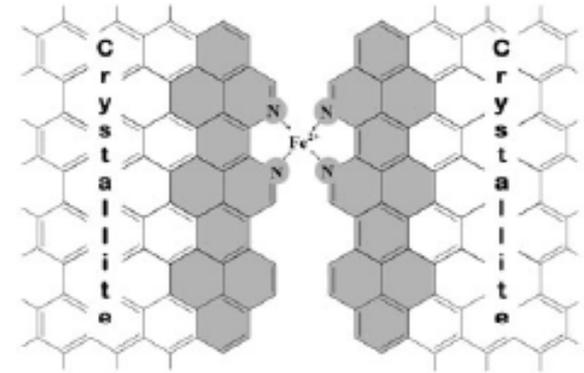


Metal Organic systems

ORR active site concept:

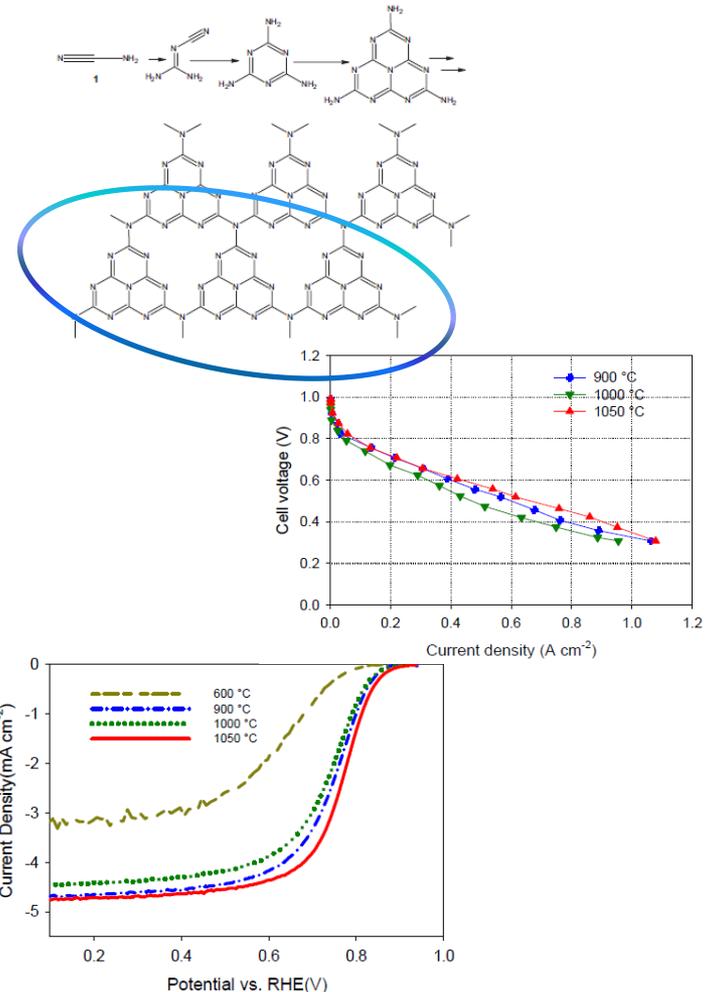
MeN₄/C (Me: Co or Fe) species embedded in carbon micropores

- planetary ball-milling
- 2-step pyrolysis: first with Ar at 1050°C; 2nd step with NH₃ at 950°C
- **99 A/cm³ at 0.8V** (DOE 2010 goal - 130 A/cm³)
- **50% performance loss after 40 hours** (DOE goal – min. 5000 hrs)



Metal Organic systems: Fe-Cyanamide/C

- Cyanamide pyrolysis at certain temp. forms graphitic C_3N_4
- High content of pyridinic nitrogen, often associated with activity in non-precious metal catalysts
- One of the highest ORR activity among non-PGM obtained so far
155 A/cm³ at 0.8V (130A/cm³ - DOE goal)
- Stability problem



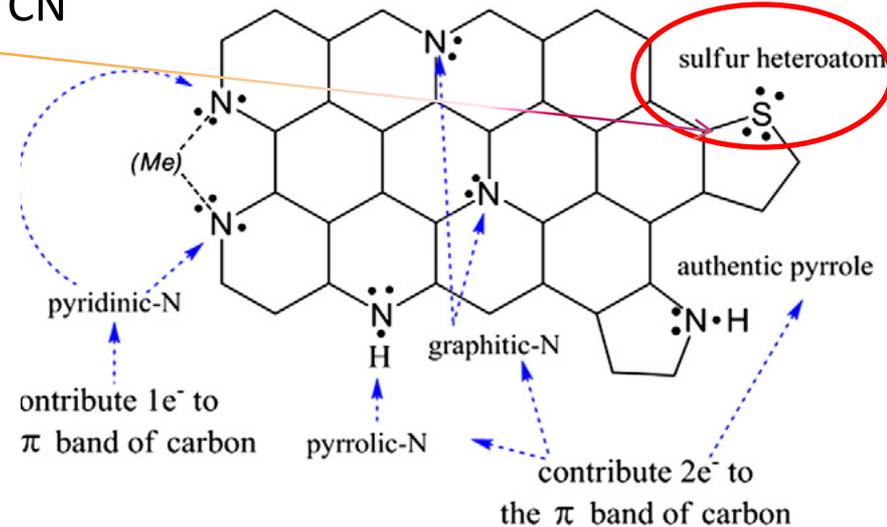
Cyanamide-based M/N/C catalysts

Zelenay 2009-2010

- Second step Pyrolysis at 1050C results in significant ORR activity explained with incorporation thiophene-like S-atoms into the CN structure

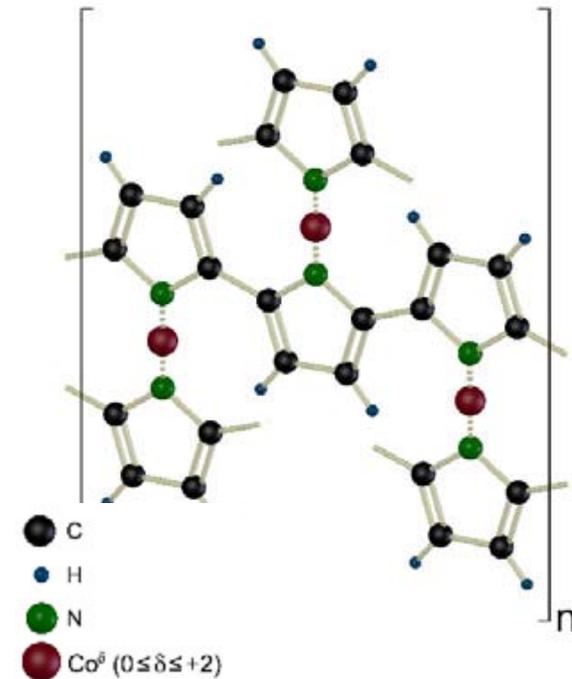
- Formation of the thiophene-S believes to be promoted by presence of cyanamide

- S-atom as another electron donating Heteroatom – potential binding site for transition metal

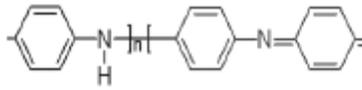


Metal-polymer composites

- non-precious metal(Co, Fe)/ heteroatomic polymer (polypyrrole, polyaniline) nanocomposite catalysts
- a dual role of the heteroatomic polymer
 - formation of the active ORR site
 - stabilization of the non-precious metal center via the formation of a bond with the heteroatom
- good ORR activity and unique performance durability (for a non-precious metal catalyst) operating at low pH



Fe(Co)-PANI-C composites



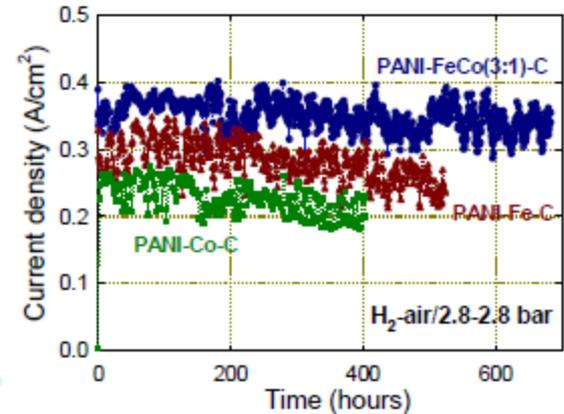
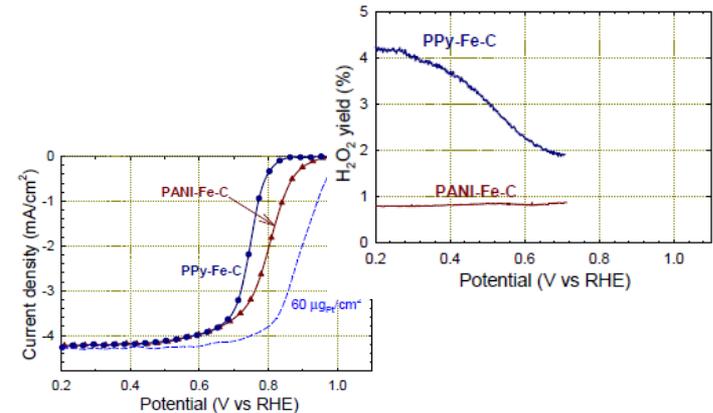
Polyaniline(PANI)

High onset potential

Good 4e ORR selectivity, only $<1\%$ H_2O_2

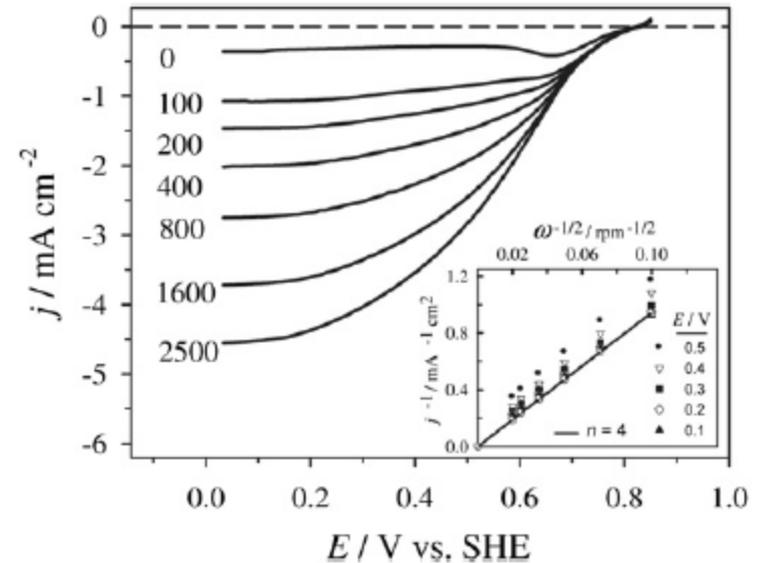
PANI-FeCo(3:1)-C exhibiting the best fuel cell activity (among metal-polymer composites) and performance stability

Very little performance loss at ~ 700 hours of operation at 0.4 V



Transition Metal Chalcogenide

- CoSe/C
 - Prepared by microwave-assisted polyol method
 - 20% loading
 - Poor stability in acidic media
 - Tolerant to alcohol and formic acid

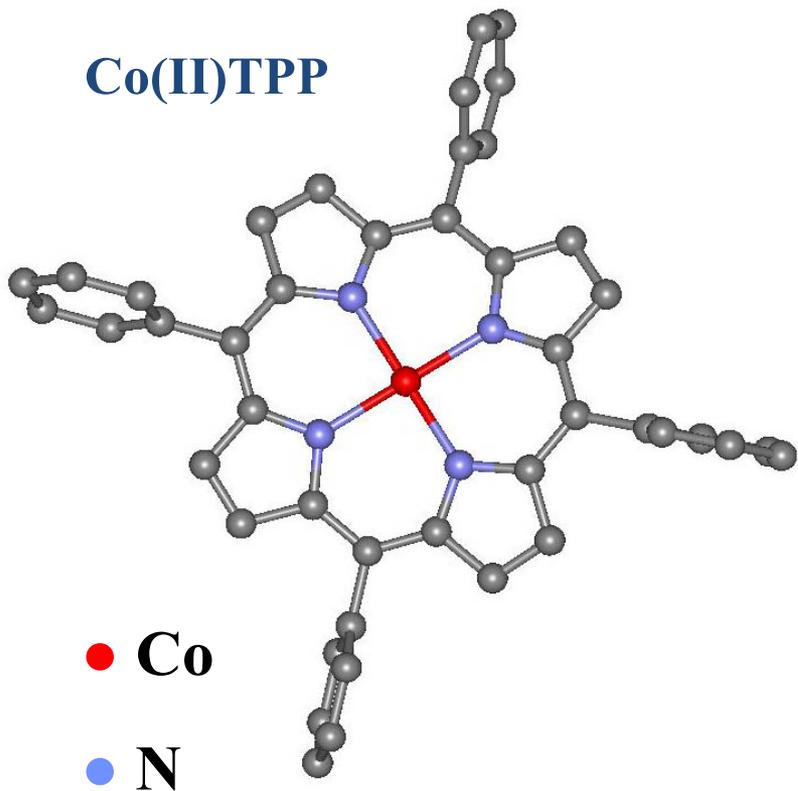


Most work in this area is with Pt group metals so I did not include it

EXAFS analysis – study of catalytic site structure

A Representative Study using Co(II) TPP Pyrolyzed Catalyst

Co(II)TPP



➤ Metal porphyrins – similar to heme groups present in proteins systems

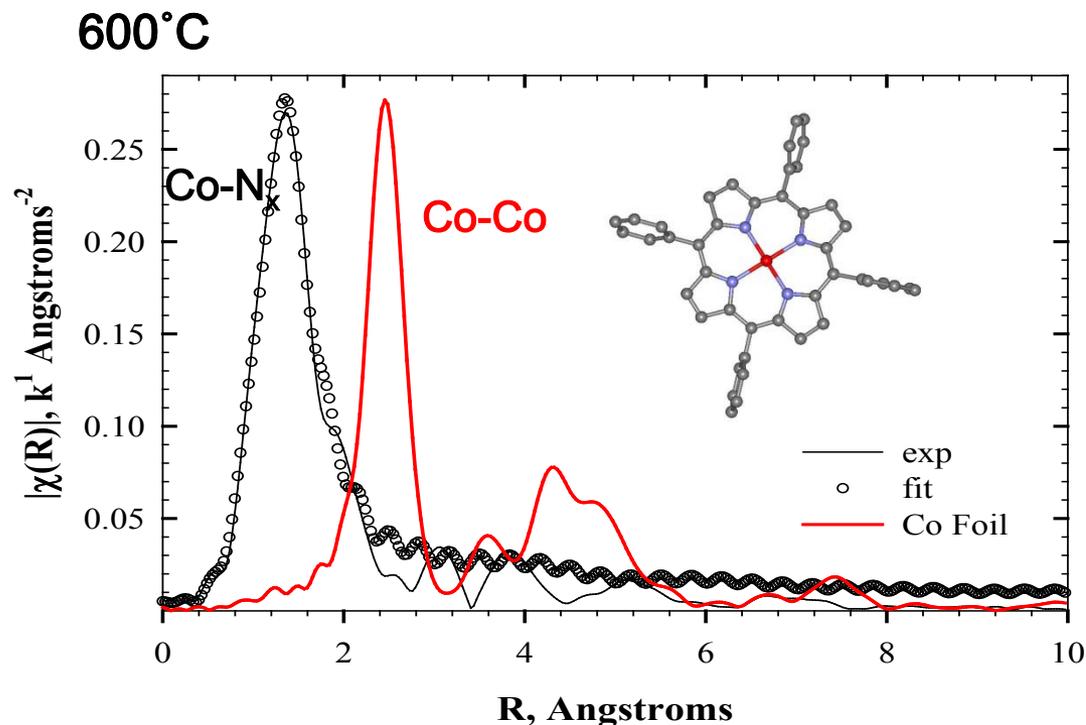
M-N4 planar structure – very selective 4e ORR

➤ Out of the protein environment, porphyrins, unstable and exhibit high formation of peroxide, H_2O_2

➤ Pyrolyzed porphyrins show similar properties as the biocatalysts depending on the temperature

In Situ EXAFS – study of catalyst active sites structure and correlation with the H_2O_2 formation

In Situ EXAFS



0.40 V FT Fitting – no adsorbates on the surface

Material	$N_{\text{Co-N}}$	$N_{\text{Co-O}}$
600°C	3.1	1.2
700°C	2.8	1.2
800°C	1.4	1.1

Co-N coordination correlates well with (*ex situ*, as-synthesized) XPS results

Beyond the first shell – FT XAS fitting is limited by inherent uncertainty

ALL fitting and analysis via the IFEFFIT suite: <http://cars9.uchicago.edu/ifeffit/>

$$\Delta\mu = \mu(\text{CoN}_x\text{C}_y\text{O}) - \mu(\text{CoN}_x\text{C}_y)$$

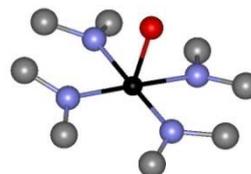
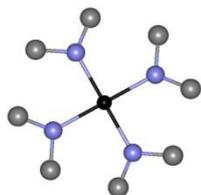
N-coordination

Clean

“axial” O_{ads}

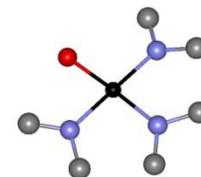
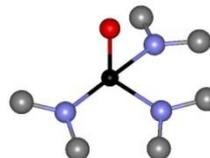
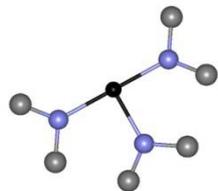
“equatorial” O_{ads}

N=4

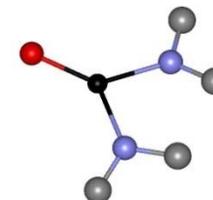
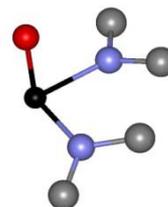
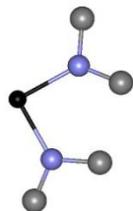


N/A

N=3



N=2



● Co

● N

● O

● C

FEFF Results

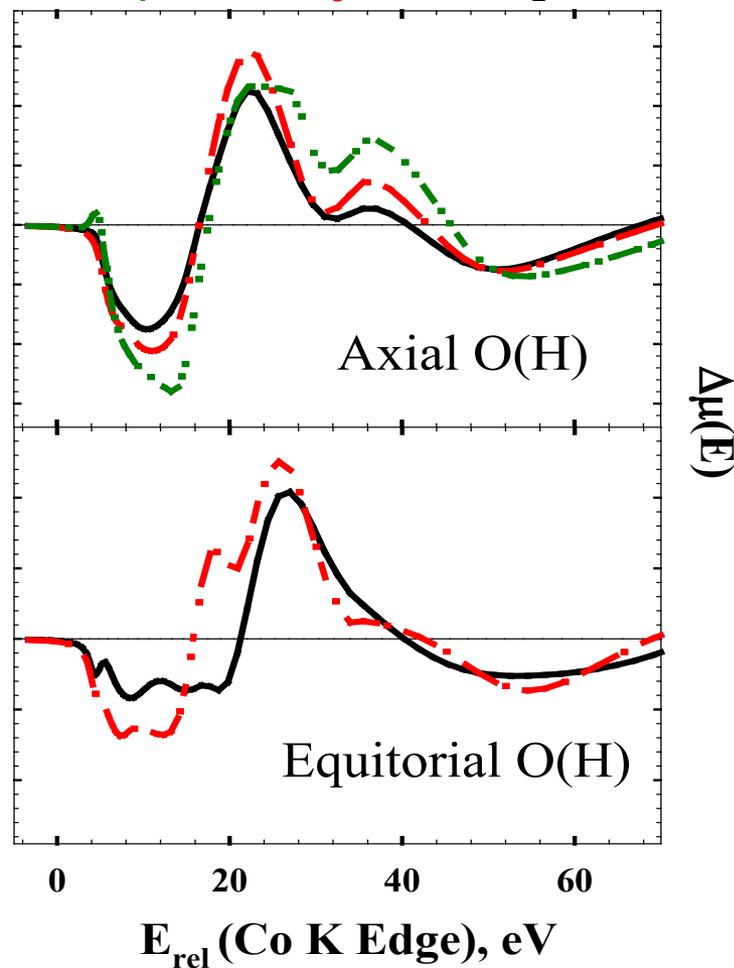
CoN₄-O CoN₃-O CoN₂-O

Axial-O

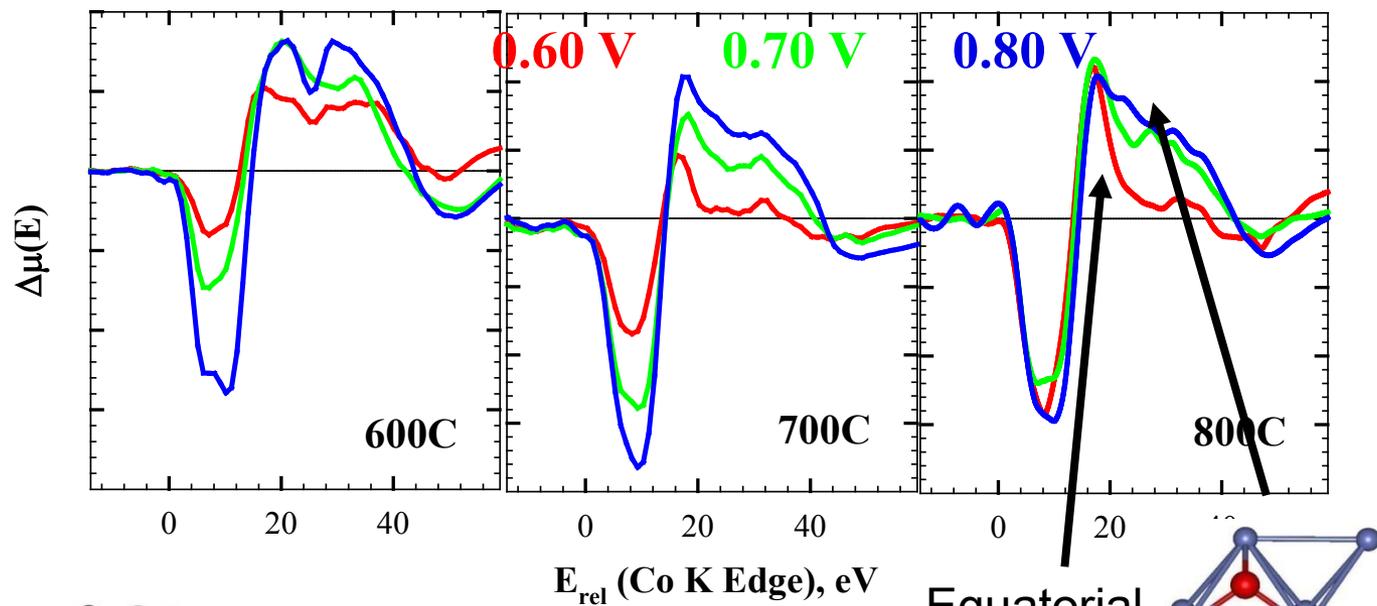
- Double peak after minimum
- Difference increases with loss of N

Equatorial-O

- N=2: Broad minimum, tailing maximum
- N=3: Reversed (from axial) double peaks
- Both: “Flattened” minimum



Pyrolyzed Co-based Porphyrins:

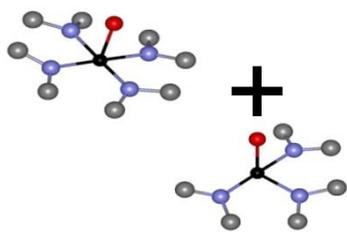


Key points:

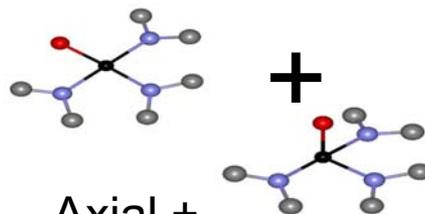
Co-N₄ = axial O_{ads}

Axial O_{ads}

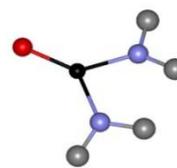
↓
efficient 4e⁻ ORR



All axial



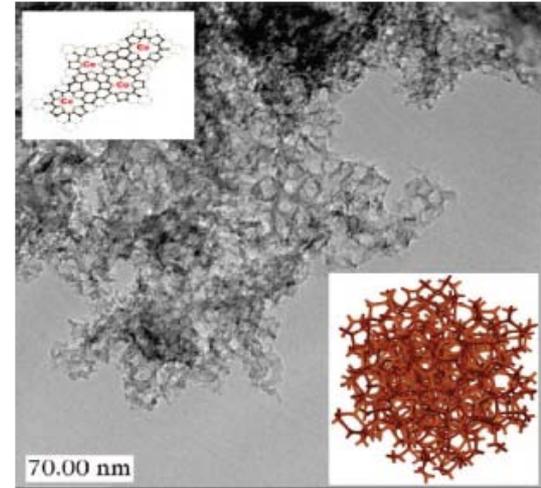
Axial +
Equatorial



Co
Oxides

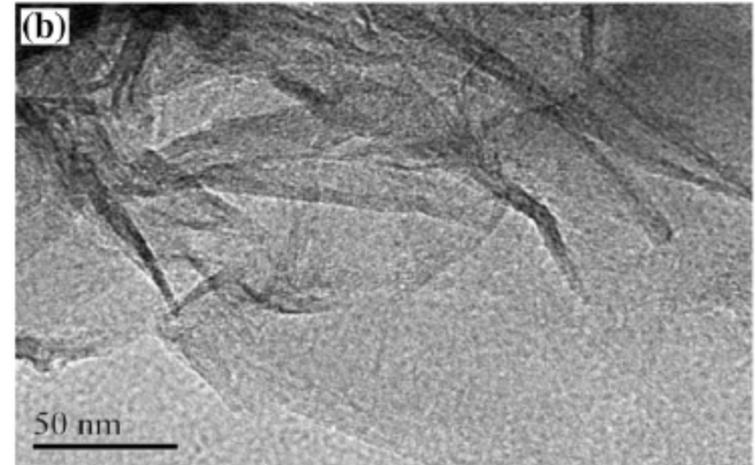
Support Materials

- Self-Templating
 - Precursor is deposited on a non-carbon carrier
 - Compound is pyrolyzed and then carrier is removed
 - Material is porous with graphite like domains
 - Pore size is optimized and transport is enhanced



Joseph M. Ziegelbauer, *J. Phys Chem C* **2008**, *112*, 8839-8849.

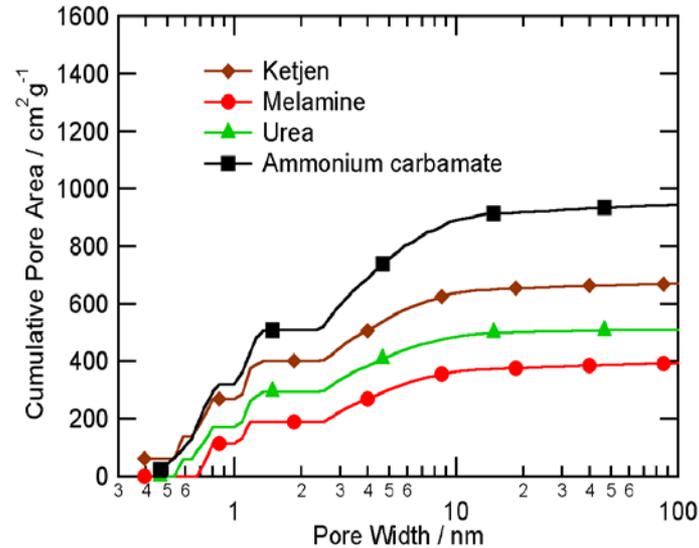
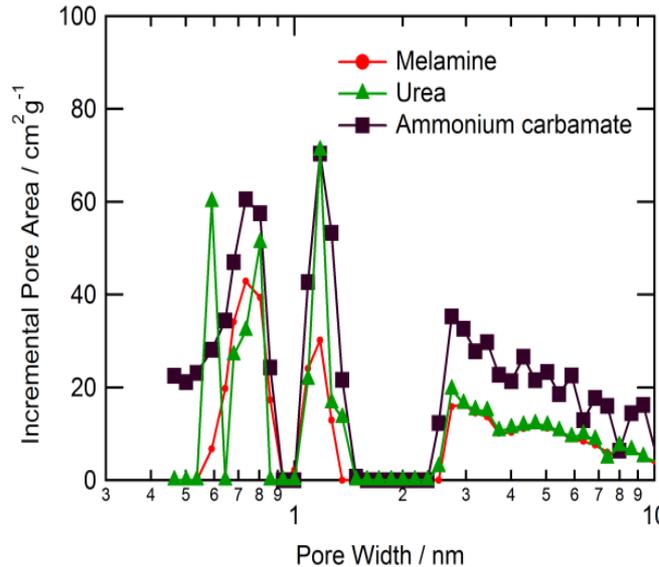
- Graphene Sheets
 - High surface area
 - Many edge sites and pyridinic N sites
 - 35 times more mass activity than Vulcan carbon
 - 50% lower ORR activity than Pt
 - More active in acidic media
 - 7% H₂O₂ produced at 0.70 V
 - Highly selective for four-electron pathway



Ki Rak Lee, *Electrochemistry Communications*, **2010**, *12*, 1052-1055.

Effect of Pore Formation in C-Supports

MNC catalysts based on ammonia precursors (MSU)



- Increase in surface area was observed for ammonia based precursors due to carbon etching resulting in increase of porosity

Background

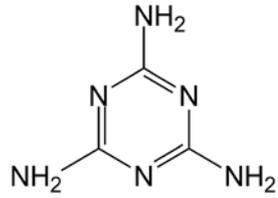
MSU's MNC catalyst

Summary:

- Ex-situ RDE and RRDE experiments were conducted for the non-precious metal (PGM) oxygen reduction reaction (ORR) catalyst based on Melamine and Ammonium Carbamate precursors prepared at MSU
- GDEs were prepared for Melamine based catalyst using NTCNA spray system.
- MEAs were prepared with NRE211 as the electrolyte and JMFC GDE anodes.

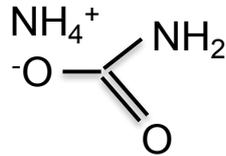
Precursors

Melamine ($C_3H_6N_6$)



N/C ratio – 2.0

Ammonium Carbamate



RDE conditions	Typical Nissan protocol for Pt based catalyst	Typical MSU protocol for non- PGM catalyst
Electrolyte	0.1 M HClO ₄	0.5 M H ₂ SO ₄
Temperature	Room Temp	40 C
Rotation speed	2500, 1600, 900, 400	1200
Loading	37.75 μg _(cat) /cm ²	0.5 mg _(cat) /cm ²
Scan rate	10 mV/s	0.5 mV/s

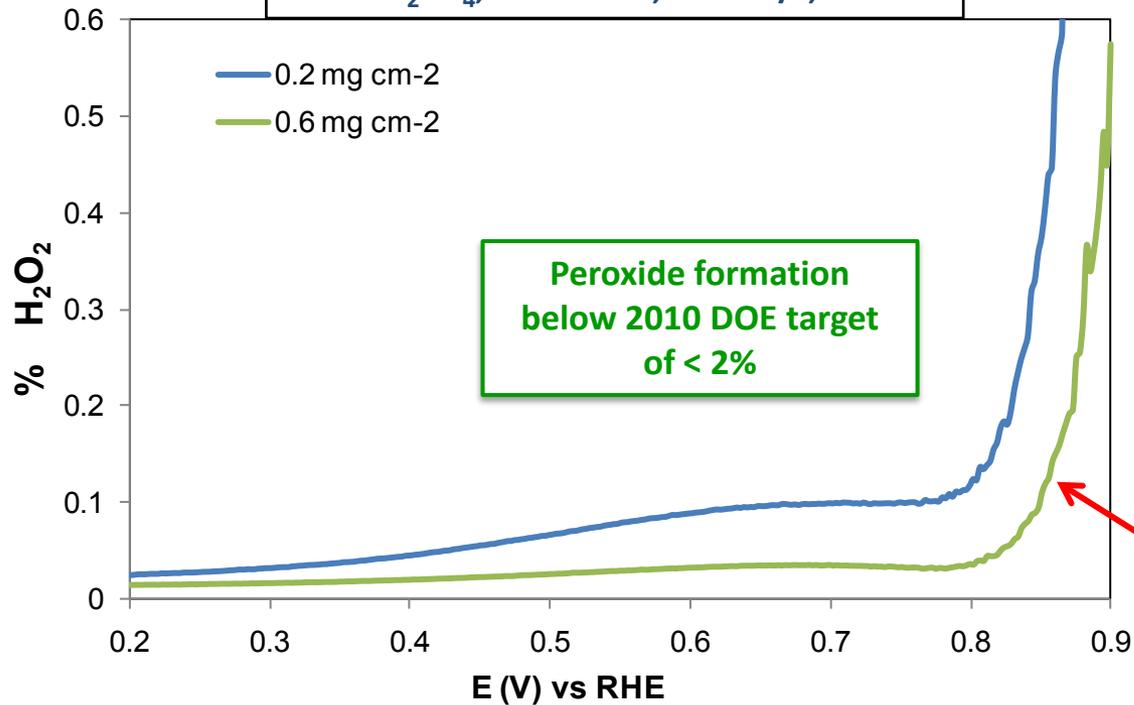
DOE Technical targets for non-precious metal catalysts *

- Activity toward oxygen reduction reaction – **130 A/cm²** at 0.8V_{ir-free} vs. RHE (2010)
300 A/cm² at 0.8V_{ir-free} vs. RHE (2015)
- Selectivity towards water formation – < 2% H₂O₂ generation
- Durability – 2000 hr lifetime

* <http://www1.eere.energy.gov/hydrogenandfuelcells/fuelcells/>

II.RRDE

Melamine based Catalyst

0.5 M H₂SO₄, 1200 RPM, 0.5 mV/s, RT

Equations used

$$n = 4I_D / (I_D + (I_R/N))$$

$$\%H_2O_2 = 100(4 - n)/2 = 100 \frac{2I_R/N}{I_D + I_R/N}$$

Where,

N= collection Efficiency = 25.6%

Increase in peroxide formation at higher potential is contrary to Pt based catalysts

Pathways for O₂ reduction

This path is favorable → Low peroxide formation



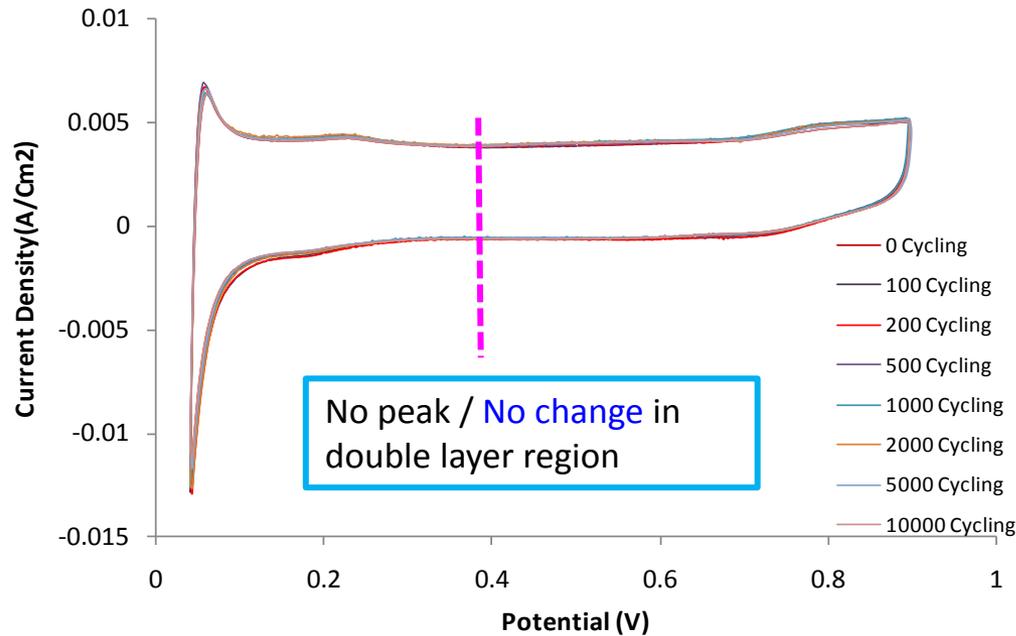
II. Catalyst Durability

- Same MEA as iV performance was used for durability tests
 - Due to small amount of catalyst sample provided by MSU and required high loading for electrode, only few GDEs were prepared
- **Load Cycling: Pt Dissolution**
 - MEA tested was composed of NRE 211, JM GDE (anode), and MSU catalyst coated GDL (25BCH).
 - OCV and CV were measured during cycling.
 - iV performance of MEAs was evaluated in the beginning and at the end of 10,000 load cycles to obtain the effect of catalyst degradation
 - To verify the effect of this protocol for Pt based catalyst, this test was performed with expectation of no effect on this non Pt catalyst
- **Start-Stop cycling: Carbon corrosion**
 - Same MEA used for Pt diss. was used for Carbon corr. after verifying the minimal effects on performance.
 - Potential was cycled for simulate start-stop cycle from 1 to 1.5 V for maximum of 1,000 cycles
 - iV performance test of MEAs was evaluated in the beginning and at the end of 1,000 start-stop cycles to obtain the effect of carbon support corrosion
 - OCV and CV were measured during cycling.

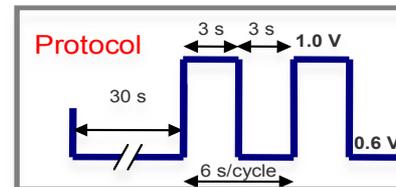
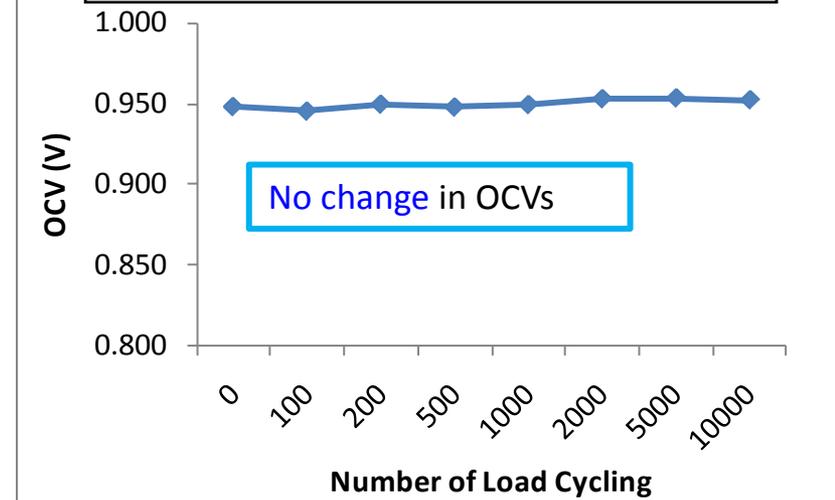
II. Catalyst Durability

MSU's MNC –Pt Dissolution test

$H_2 = 0.5 \text{ L/min}$, $N_2 = 0.5 \text{ L/min}$, $80 \text{ }^\circ\text{C}$, $0.6\text{V} - 1 \text{ V vs. RHE}$



$H_2 = 0.5 \text{ L/min}$, $O_2 = 0.5 \text{ L/min}$, $80 \text{ }^\circ\text{C}$

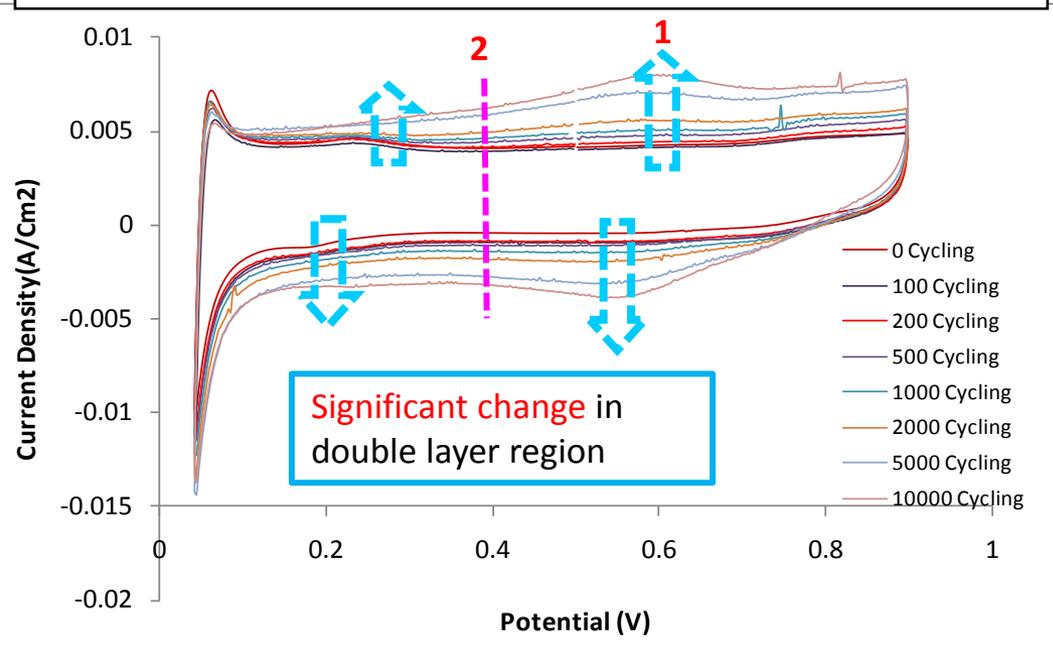


- As expected, no change in double layer capacitance (Cdl) and OCVs were observed after load cycling

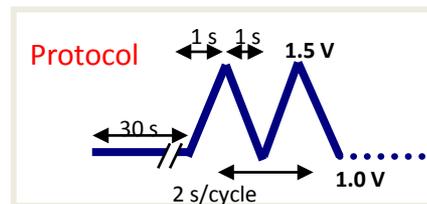
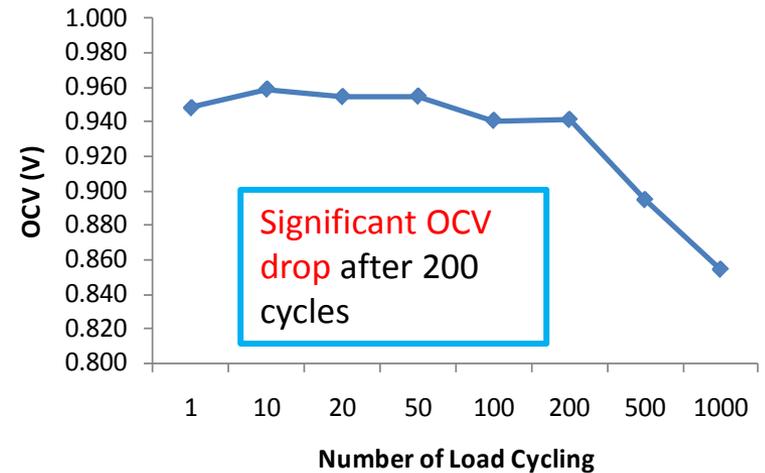
II. Catalyst Durability

MSU's MNC – Carbon Corrosion

$H_2 = 0.5 \text{ L/min}$, $N_2 = 0.5 \text{ L/min}$, $80 \text{ }^\circ\text{C}$, $1 \text{ V} - 1.5 \text{ V vs. RHE}$



$H_2 = 0.5 \text{ L/min}$, $O_2 = 0.5 \text{ L/min}$, $80 \text{ }^\circ\text{C}$

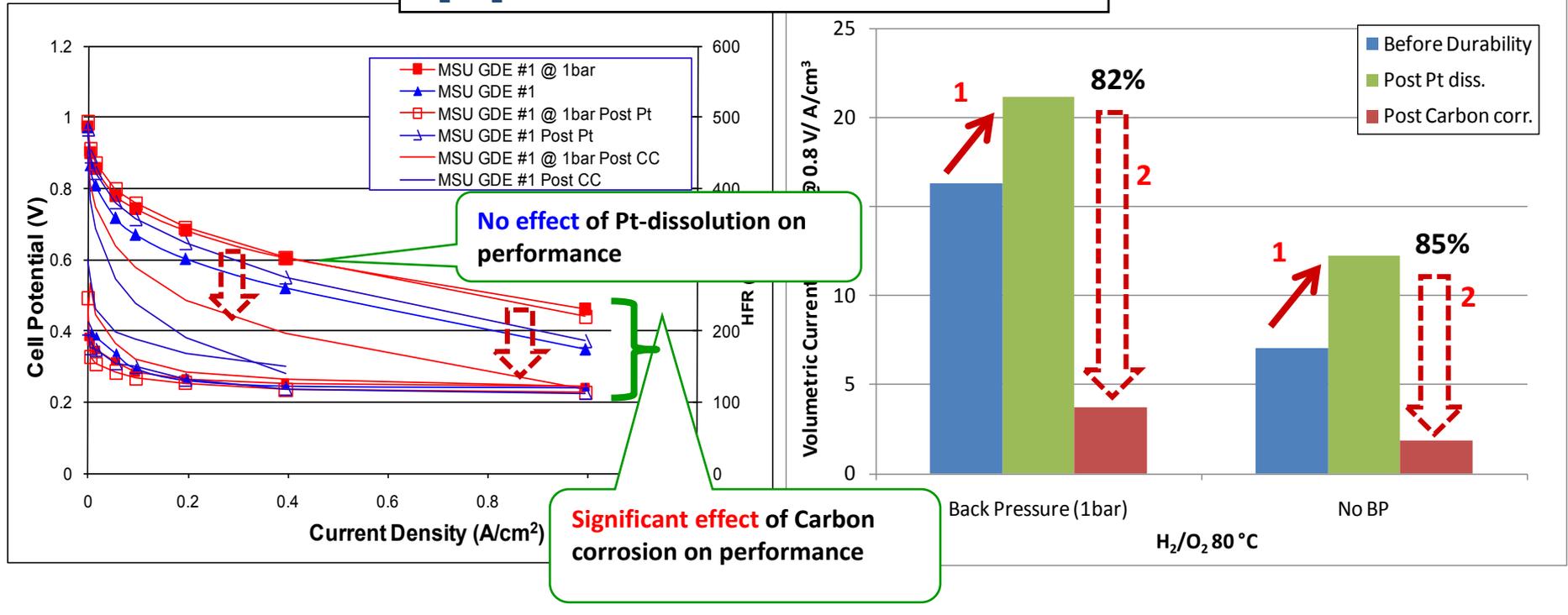


1. Oxidation peak appears at 0.6 V. Similar phenomena was observed in Pt/C catalyst (HSAC) with Start/Stop cycling.
2. Double layer capacitance (Cdl) **increases** as number of potential cycling **increases**.
 - This increase in DL can be attributed due to formation of electro-active surface oxides and redox couples such as quinone and hydro-quinone

II. Catalyst Durability

Effect of Durability Tests (Pt Diss. & CC): Oxygen

H_2/O_2 , 100% RH, 80°C, 0.42 / 0.84 NLPM

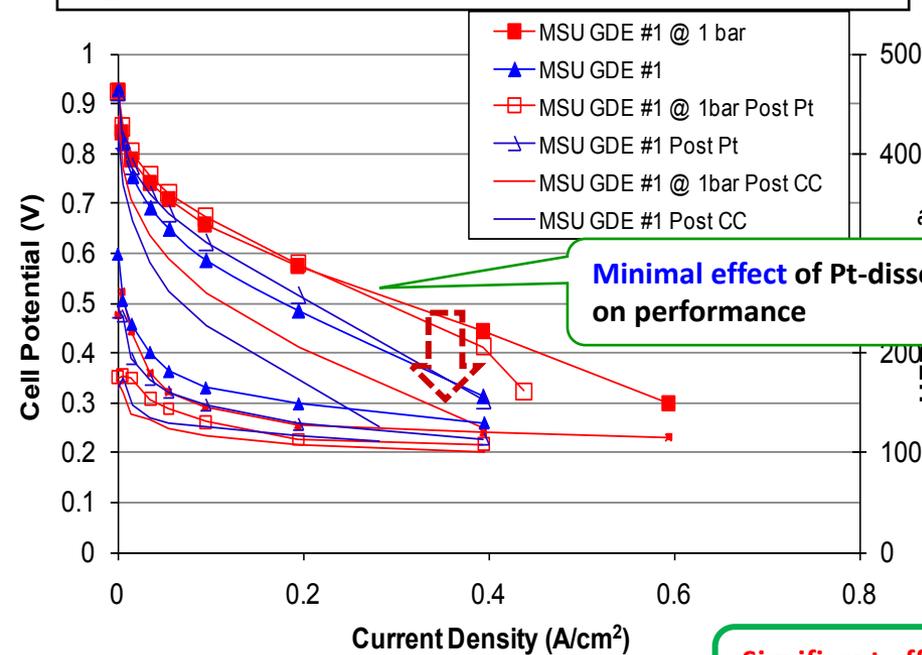


- Activity was increased after Pt dissolution test. This may be due to more conditioning.
 - ✓ Same MEA was used for both Pt dissolution and carbon corrosion tests.
- Loss of electronic contact and electrode integrity can be attributed to such loss in activities

II. Catalyst Durability

Effect of Durability Tests (Pt Diss. & CC): Air & low RH

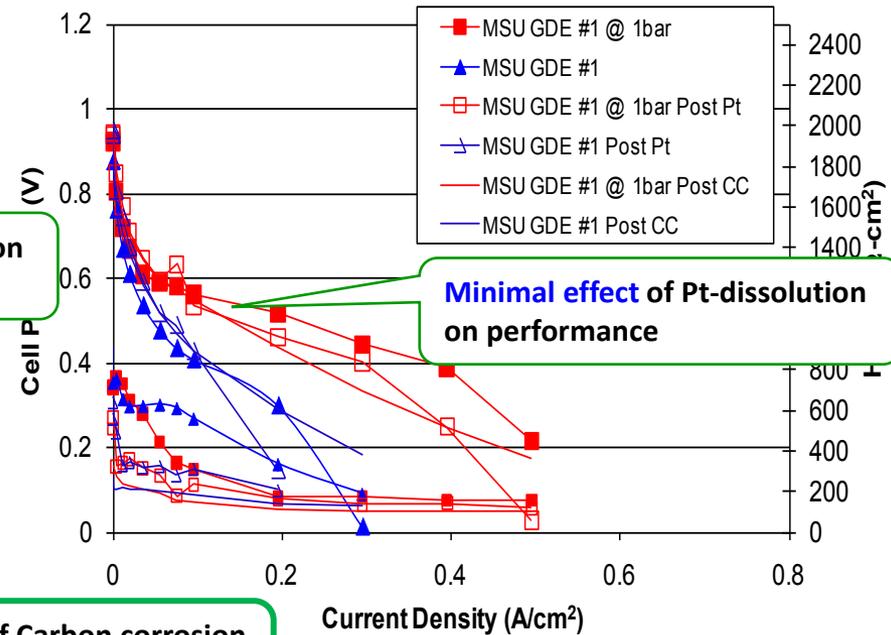
H₂/Air, 100% RH, 80°C, 0.31 / 1.05 NLPM



Minimal effect of Pt-dissolution on performance

Significant effect of Carbon corrosion on iV performance

H₂/Air, 50% RH, 80°C



Minimal effect of Pt-dissolution on performance

- Carbon corrosion severely deteriorates the iV performance at all current density conditions due to structural change in electrode when compared to the effect of platinum dissolution.

MSU's MNC Catalyst Summary

First catalyst under this DOE project tested at NTCNA FC Lab

Ex-situ:

- RDE ORR results are comparable between NTCNA and MSU Lab
- These non-PGM catalyst results are electrolyte specific
 - Carbamate based catalyst performed better in HClO_4
 - Melamine based catalyst showed better results in H_2SO_4
- RRDE experiment showed low peroxide formation indicating its selectivity towards four electron ORR

In-situ:

- OCV was high ($\sim 0.97 \text{ V}$) but iV performance was poor v. Pt based catalyst
- As expected, no effect of Pt dissolution test was observed for this catalyst
- Carbon corrosion test showed increase in DL due to formation of surface oxides and significant effect was observed on iV performance
- **More joint testing in future and technical discussions between NTCNA and University research groups would help greatly for the progress of the DOE project**