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/cm^3 (2010) and 300 A/cm^3 (2015).
  - Durability at temperatures ≤ 80°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/cm^2 and 2015 activity targets are 300 A/cm^2.
- 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 H$_2$ 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 ~ 130 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.*
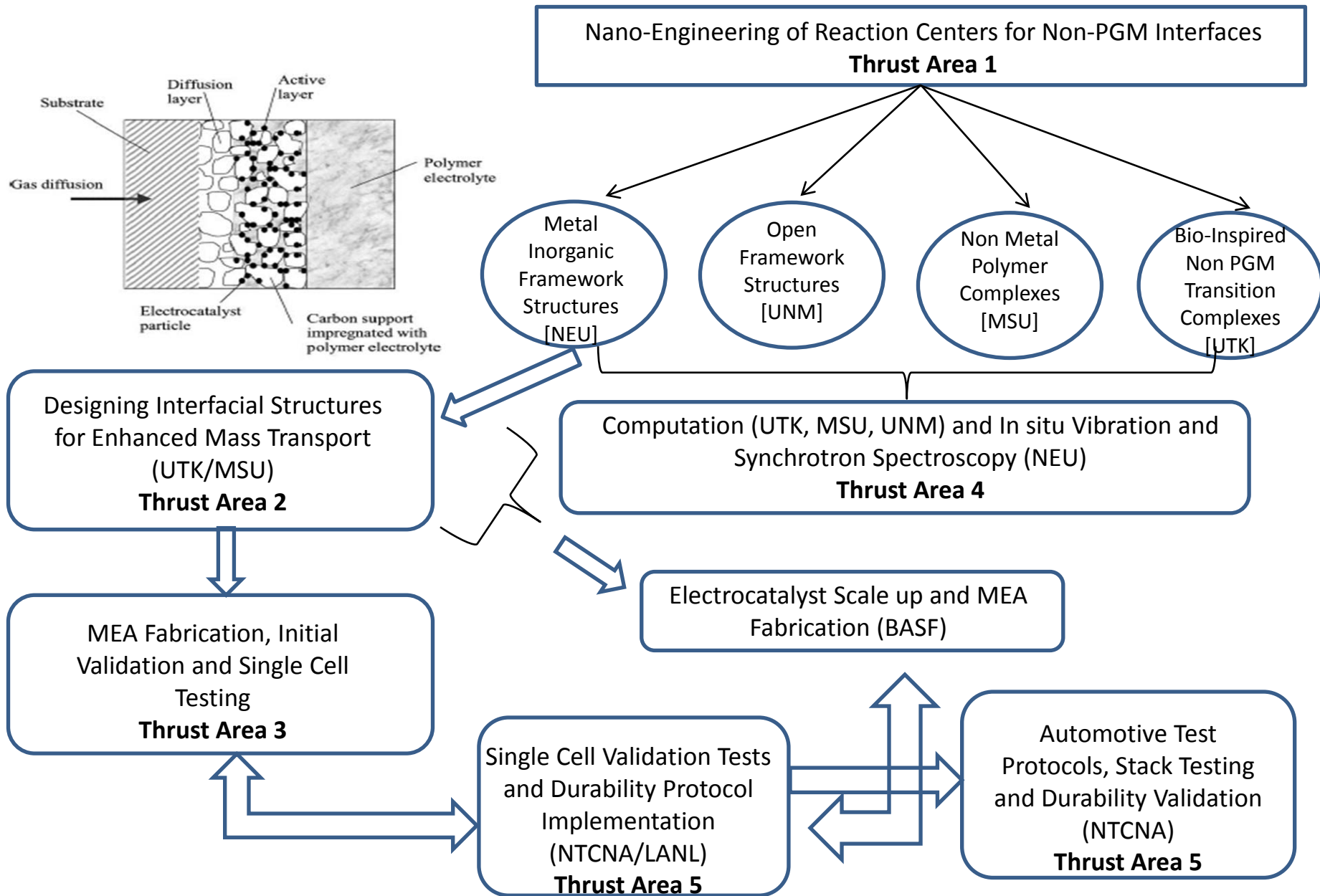
Milestones and Go/No Go Decisions

– **Milestones (2011)**

- Materials Development: RDE measurement of volumetric power density Q 1-4

- Meet ~ 150 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

Nano-Engineering of Reaction Centers for Non-PGM Interfaces
Thrust Area 1

Metal Inorganic Framework Structures [NEU]

Open Framework Structures [UNM]

Non Metal Polymer Complexes [MSU]

Bio-Inspired Non PGM Transition Complexes [UTK]

Designing Interfacial Structures for Enhanced Mass Transport (UTK/MSU)
Thrust Area 2

Computation (UTK, MSU, UNM) and In situ Vibration and Synchrotron Spectroscopy (NEU)
Thrust Area 4

MEA Fabrication, Initial Validation and Single Cell Testing
Thrust Area 3

Electrocatalyst Scale up and MEA Fabrication (BASF)

Single Cell Validation Tests and Durability Protocol Implementation (NTCNA/LANL)
Thrust Area 5

Automotive Test Protocols, Stack Testing and Durability Validation (NTCNA)
Thrust Area 5

Technical Accomplishments

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

CV at 20 mV/s of M-Triazole on GC/Au RRDE in 0.1 M $HClO_4$

Legend:
- $FeCl_2$-Triazole under Ar
- $FeCl_2$-Triazole under O_2
- $CoCl_2$-Triazole under O_2
- $CuSO_4$-Triazole under Ar
- $CuSO_4$-Triazole under O_2

ORR Cathodic Sweep at 20 mV/s on GC/Au RRDE in 0.1 M $HClO_4$

Legend:
- $FeSO_4$-Triazole under O_2
- $FeSO_4$-Triazole pyrolyzed under O_2
- $FeSO_4$-Triazole under Ar

Color codes:
Co-cyan
O-red
N-blue
C-white
Trinuclear Cobalt system with a μ_3-oxo center using triazole ligands.

- Iron and Cobalt showed the best catalytic activity
    - $FeCl_2$ and $FeSO_4$ 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
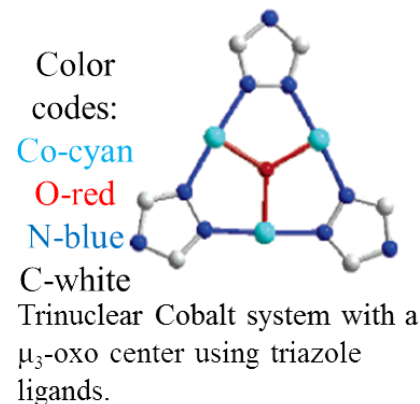
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Task 1. Design and Synthesis of Novel Materials for Oxygen Reduction Reaction (ORR)

- **Development of Metal Organic Framework Catalysts (NEU)**

- Flexible MOF selective for O2 adsorption
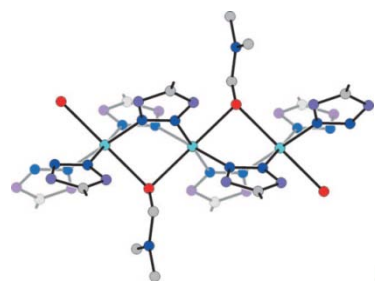
Color Codes:
Cu-light blue
O-red
N-blue
C-gray
N or C triazolate ring-purple
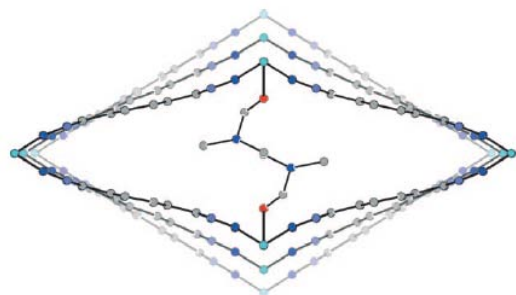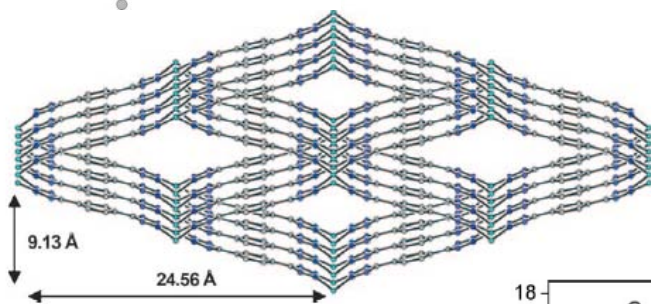
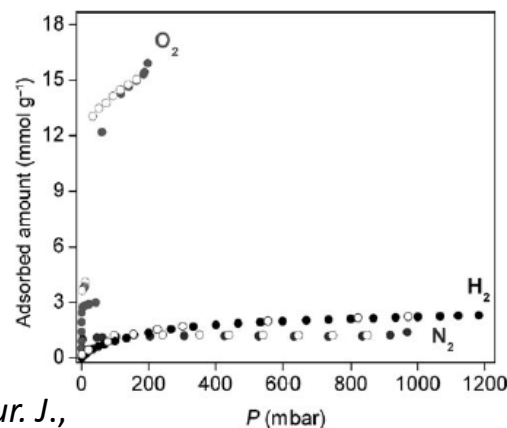- MOFs with entatic metal center that mimics active site of hemoglobin
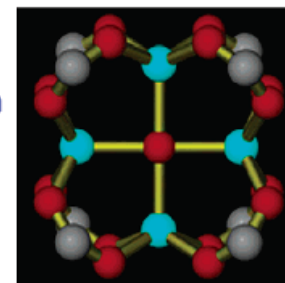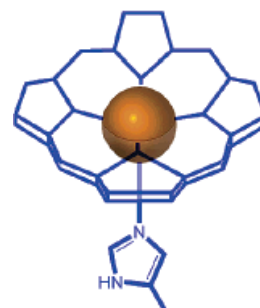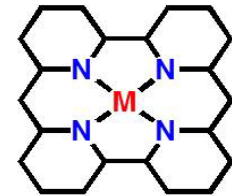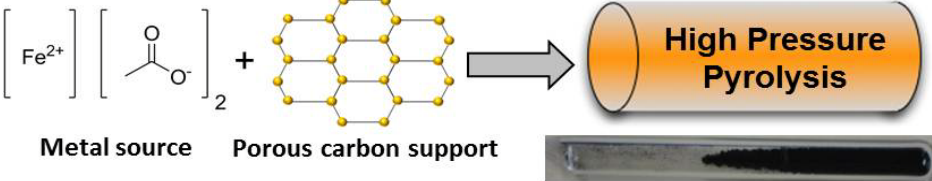
Color Codes:
Co-light blue
O-red
C-gray
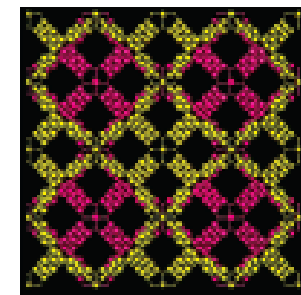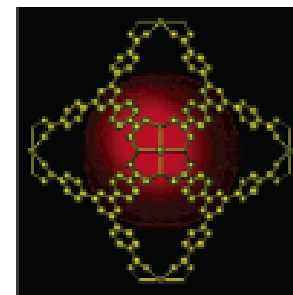
9.13 Å

24.56 Å

A. Demessence and J.R. Long, *Chem. Eur. J.*, **2010,** 16, 5902-5908.

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

– **Development of Novel MNC Catalysts (MSU)**

Approach

$$[Fe^{2+}] \left[\begin{array}{c} O \\ \parallel \\ C-O^- \end{array} \right]_2 +$$

Metal source   **Porous carbon support**   →   **High Pressure Pyrolysis**
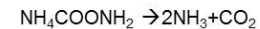
+

Metal-functionalized pyridinic carbon (Proposed catalytic site)
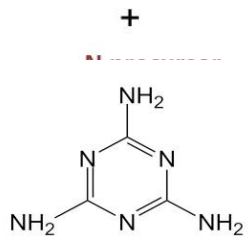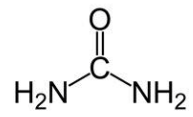
N precursor

Melamine (N/C – 2.0)

Urea
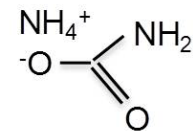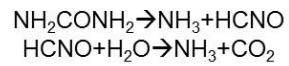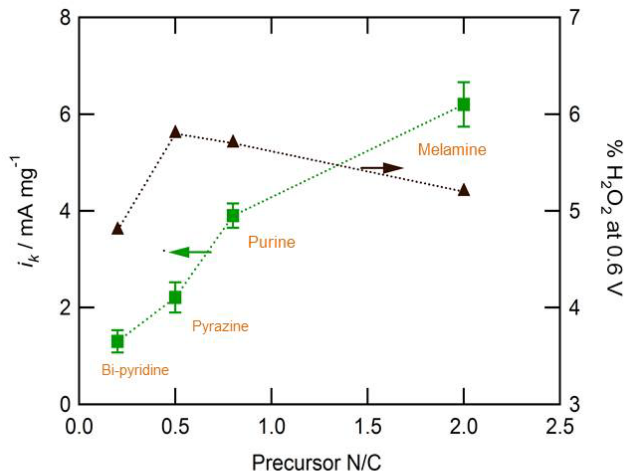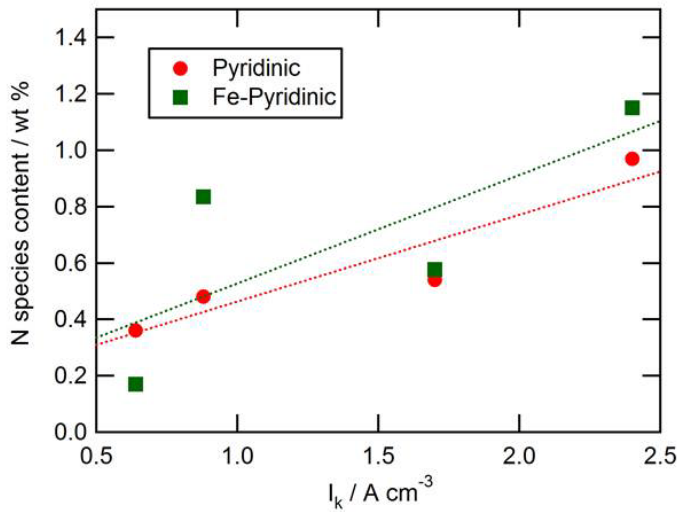
$NH_2CONH_2 \rightarrow NH_3 + HCNO$
$HCNO + H_2O \rightarrow NH_3 + CO_2$

Ammonium carbamate

$NH_4COONH_2 \rightarrow 2NH_3 + CO_2$

Melamine

Purine

Pyrazine

Bi-pyridine

RDE - 1200 rpm, 40°C, 0.5 mV s^{-1}, 0.5M H$_2$SO$_4$

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

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

0.5 mg/cm^2, 0.5M H$_2$SO$_4$, 1200 RPM, 0.5 mV/s

Legend:
- Nissan @ RT
- Nissan @ 40 C
- MSU @ 40 C

(Axes: i / mA cm^{-2} vs E / V vs RHE)

Legend:
- Ammonium hydroxide
- Urea
- Urea + water
- Ammonium carbamate

(Axes: E / V re: RHE vs I / mA mg^{-1})
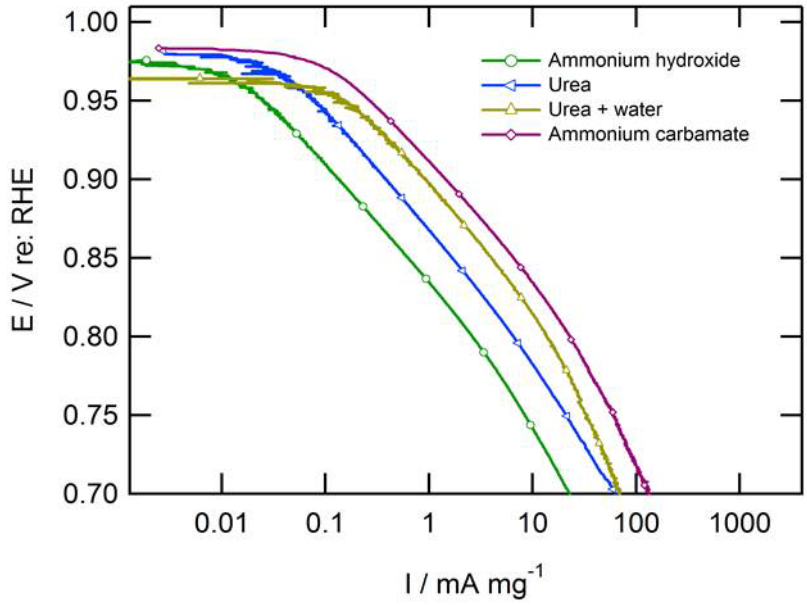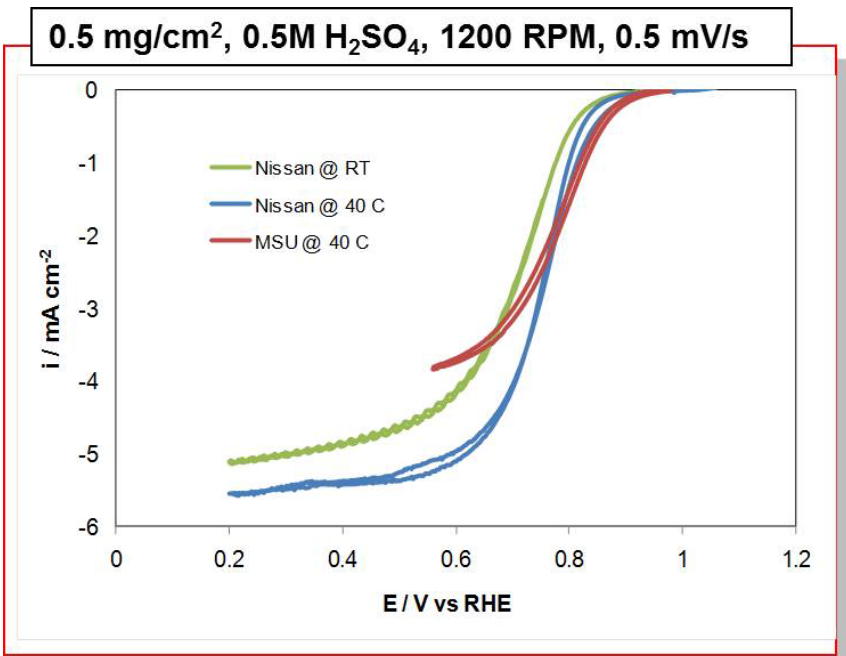
RDE - 1200 rpm, 40°C, 0.5 mV s^{-1}, 0.5M H$_2$SO$_4$

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.**

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
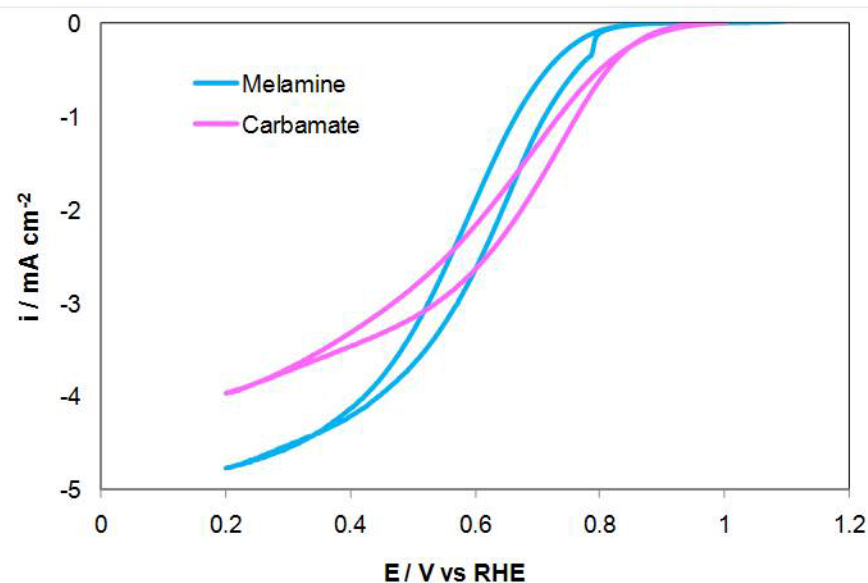
Catalyst based on precursor	Tafel slope mV/decade	Volumetric Activity (A/cm³)
Melamine	80	0.43
Ammonium Carbamate	77	2.92

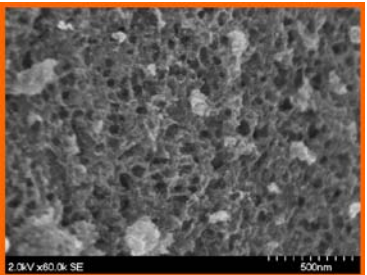- **Ammonium carbamate based catalyst showed higher volumetric activity than Melamine based catalyst under these test conditions**
  - Melamine based catalyst showed poor results in perchloric acid as compared to sulfuric

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

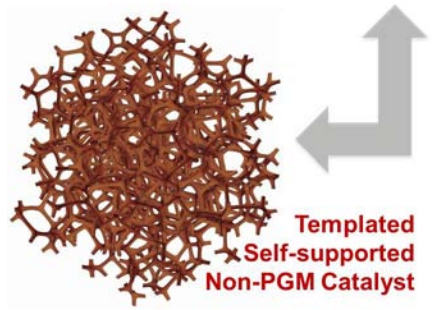### Development of Novel Open Framework Templated Structures (UNM)
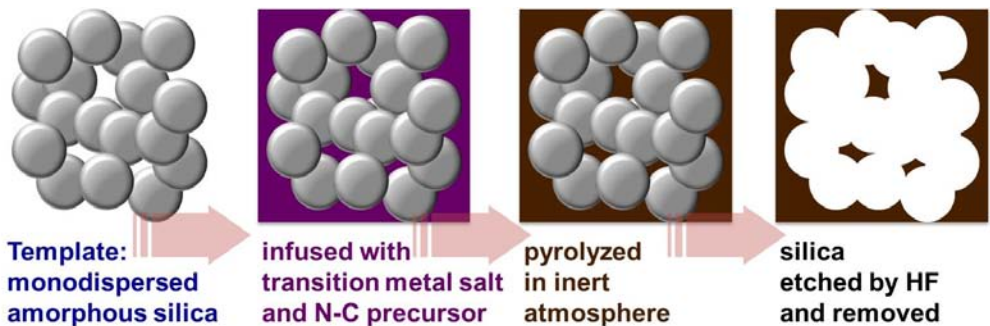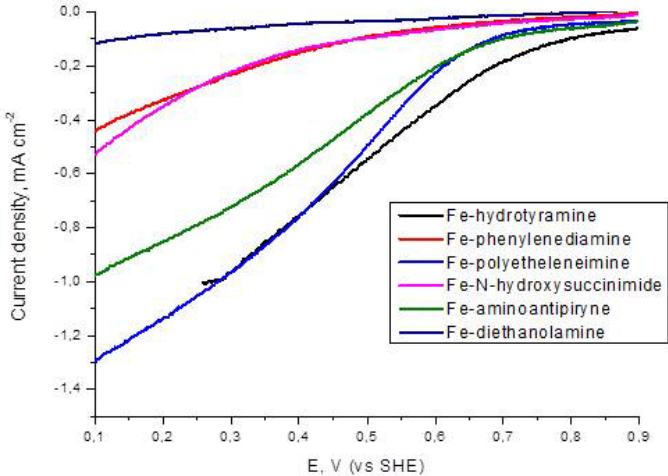
RDE of Fe-different-N-source catalysts
in 0.5 M H_2SO_4, 1600 RPM. Loading 40.5 mg cm^2

Average pore size 40-50 nm

Fumed Silica:
BET-SA 380 m^2/g

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

Template: monodispersed amorphous silica → infused with transition metal salt and N-C precursor → pyrolyzed in inert atmosphere → silica etched by HF and removed

Templated Self-supported Non-PGM Catalyst

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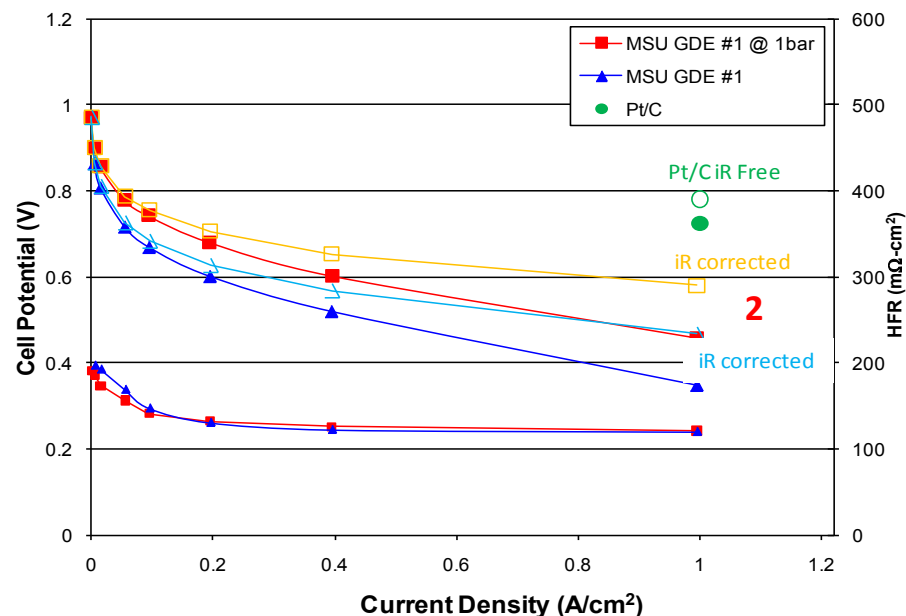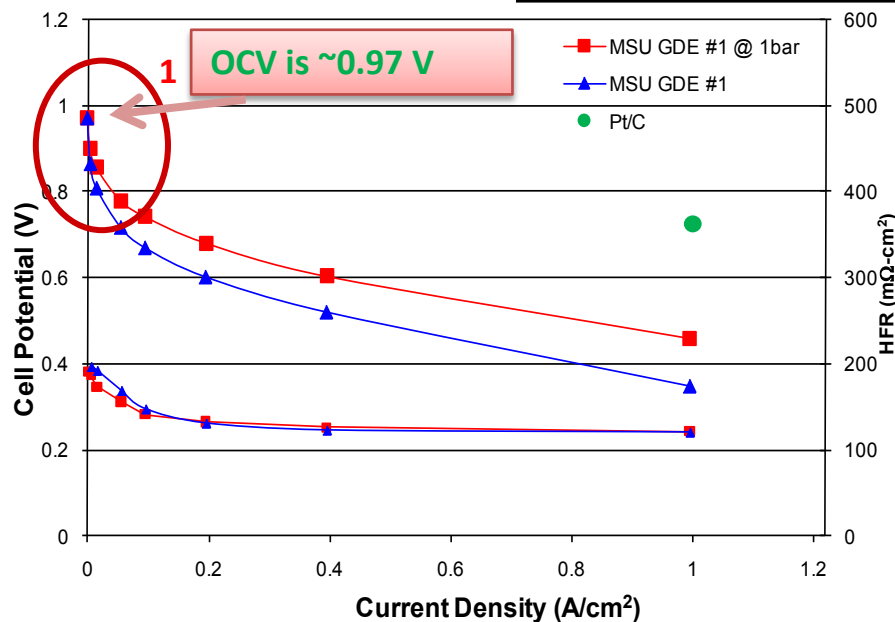
- **Higher OCV values were obtained at NTCNA than MSU Lab data**
1. **Similar high OCV values were observed with/without back pressure due to the presence of pressure in the cell caused by high flow rate and serpentine channel**
2. **Since HFR values are high due very thick catalyst layer (thicker than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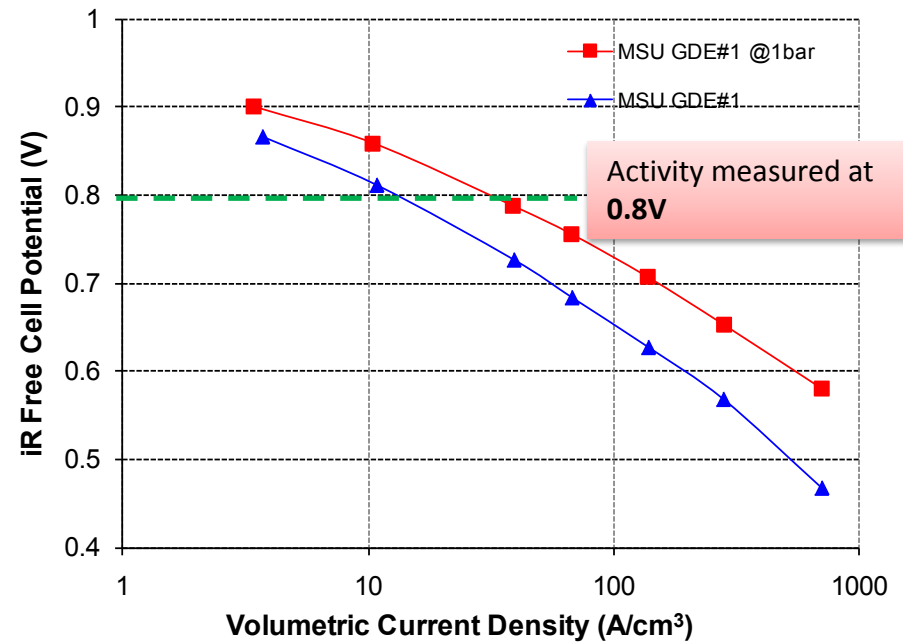
NTCNA-FH
Fuel Cell Laboratory

iV performance
MSU's MNC – Tafel and Activity plot

Tafel Plot — IR-free Voltage (V) vs Xover Corrected Current Density (A/cm²)

Volumetric Activity Plot — iR Free Cell Potential (V) vs Volumetric Current Density (A/cm³)

Legend: MSU GDE#1 @1bar; MSU GDE#1

Activity measured at **0.8V**
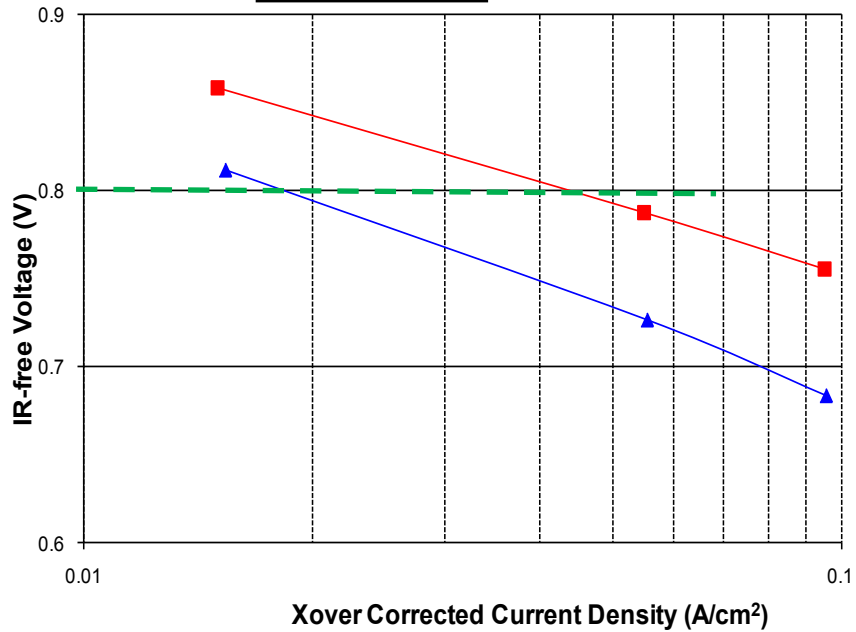
Cathode Loading: 4 mg$_{(Total\ catalyst+ionomer)}$ / cm²

0.565 mg$_{(Cat)}$/cm²

Without back pressure	**13 A/cm³**
With back pressure	**31 A/cm³**

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**

NTCNA-FH
Fuel Cell Laboratory

I. iV performance
MSU's MNC – H_2/Air iV

H_2/Air, 100% RH, 80°C, 0.31 / 1.05 NLPM

H_2/Air, 50% RH, 80°C

OCV is ~0.92 V

High HFR values were observed
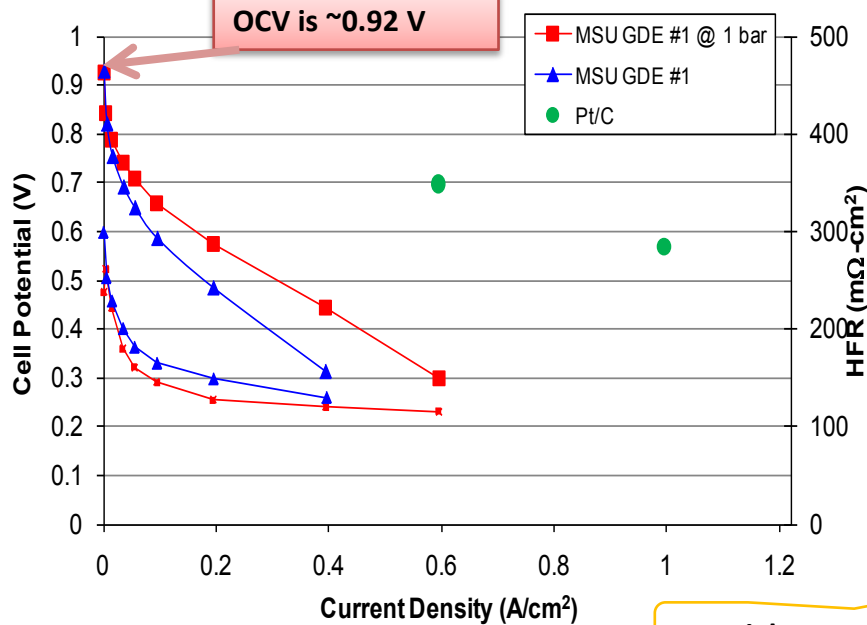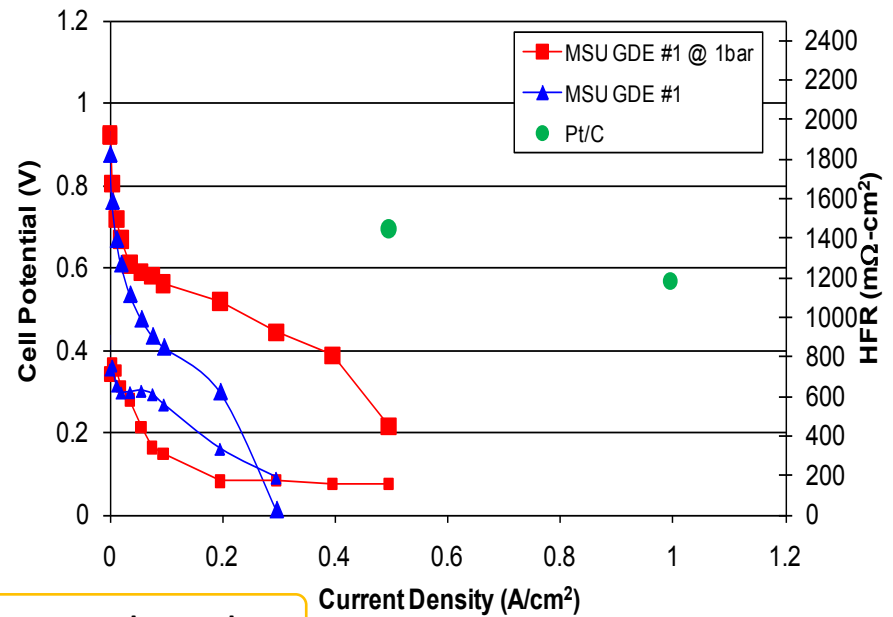
- **Under H_2/Air conditions, iV performance was significantly lower than oxygen – 1 A cm² could not be pulled.**
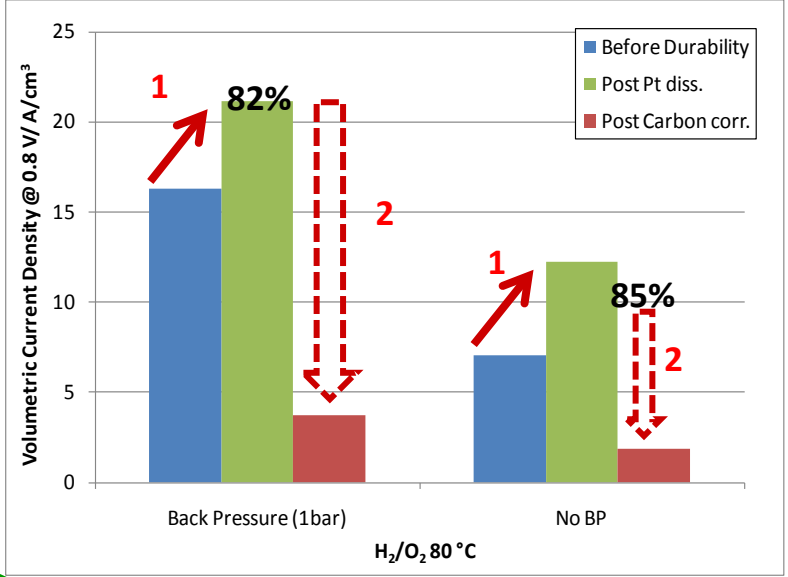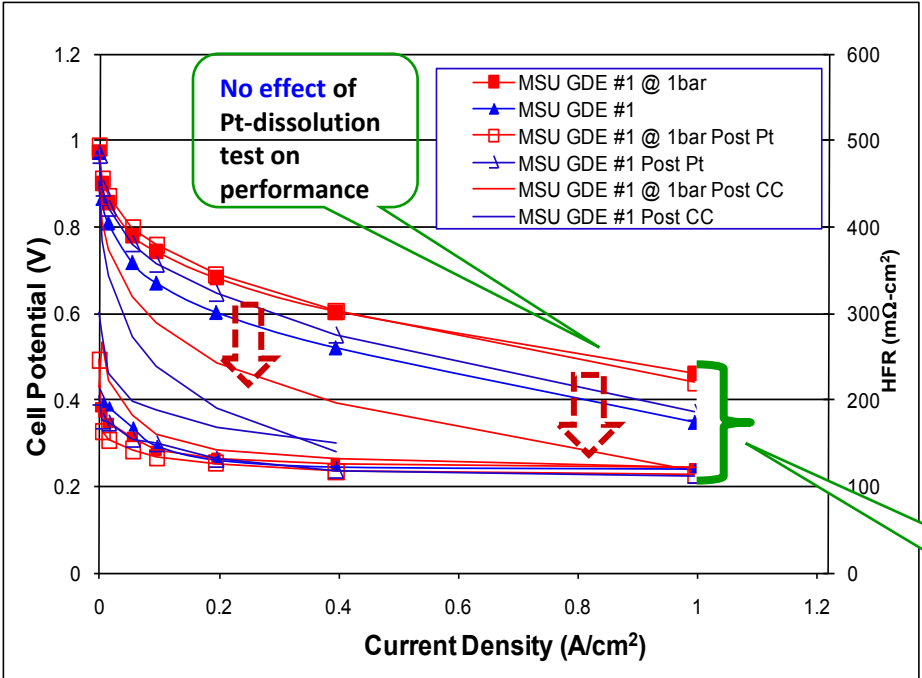- **Performance drop is significant in kinetic as well as in mass transport region**

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
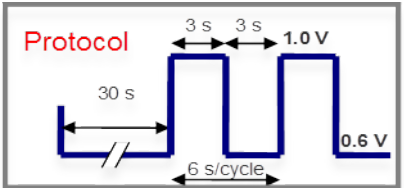 - OCV and CV were measured during cycling.

Catalyst Durability

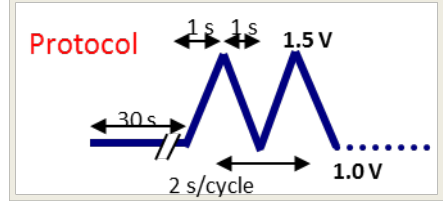## Effect of Durability Tests (Pt Diss. & CC): Oxygen

H$_2$/O$_2$, 100% RH, 80°C, 0.42 / 0.84 NLPM

No effect of Pt-dissolution test on performance

Legend:
- MSU GDE #1 @ 1bar
- MSU GDE #1
- MSU GDE #1 @ 1bar Post Pt
- MSU GDE #1 Post Pt
- MSU GDE #1 @ 1bar Post CC
- MSU GDE #1 Post CC

Significant effect of Carbon corrosion on performance

82%

85%

- Before Durability
- Post Pt diss.
- Post Carbon corr.

H$_2$/O$_2$ 80 °C

Back Pressure (1bar) | No BP

Pt dissolution test protocol

Protocol — 3 s, 3 s, 1.0 V, 30 s, 6 s/cycle, 0.6 V

Carbon corrosion test protocol

Protocol — 1 s, 1 s, 1.5 V, 30 s, 2 s/cycle, 1.0 V

1. **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.**
2. **Loss of electronic contact and electrode integrity can be attributed to such loss in activities**

Technical Accomplishment continued….

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 O_2 adsorbed on melamine

Northeastern/Melamine-Fe

1633   1399

1635   1398

Absorbance Units

Wavenumber (cm^{-1})

Kunimatsu/Pt

3500 3400   1640 1403   1.2
                                      1.0
                                      0.6
0.002   0.4
                                      0.2
                            1223   0.1
              1610   1100

Absorbance

Wavenumber / cm^{-1}
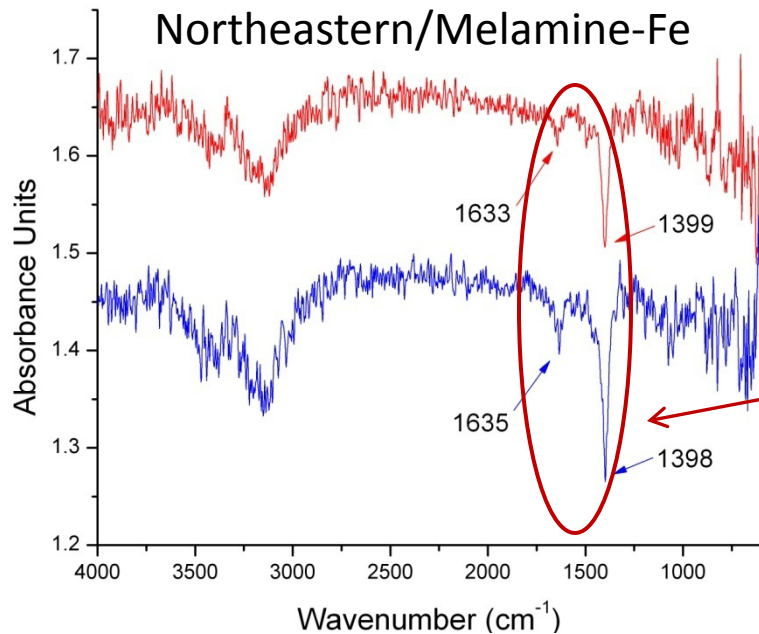
O_2 adsorption on Melamine/Fe. Red: Air. Blue: Air/CO for 30 min.
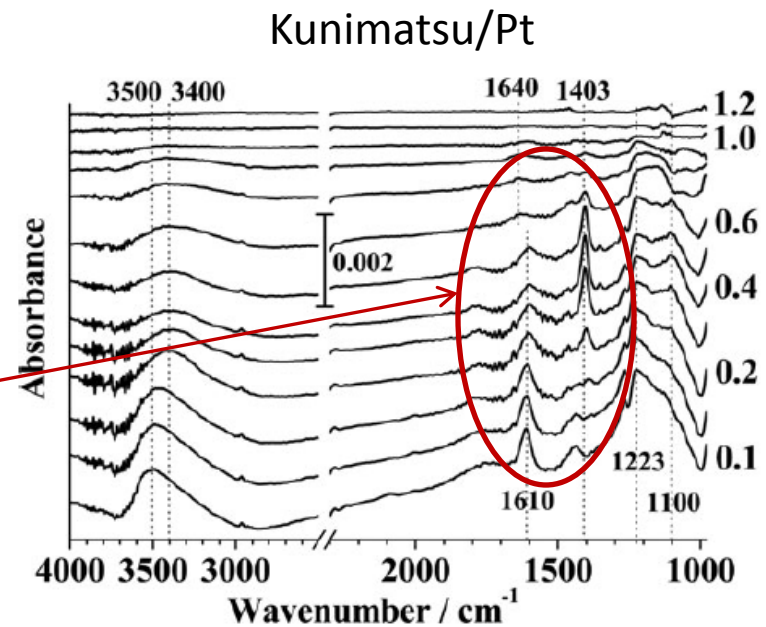
O_2 adsorbed on Pt referenced to 1.2V spectrum (Kunimatsu et al. *Phys. Chem. Chem. Phys.* **2010,** *12,* 621)

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 O_2

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 (σ=0.025 eV)**

b-initio
VASP
ackage
ienna imulation

Surfaces:
- **Graphene (32 atoms).**
- **14 A 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 O_2 (ORR intermediate) adsorption energies.
- Evaluate correlation between energies.

Fe – N_x/Graphene System (UNM)

Fe-N_4
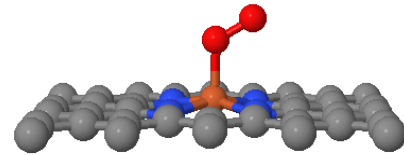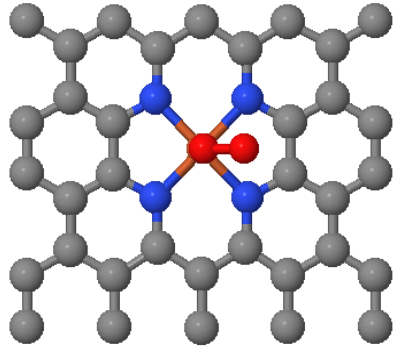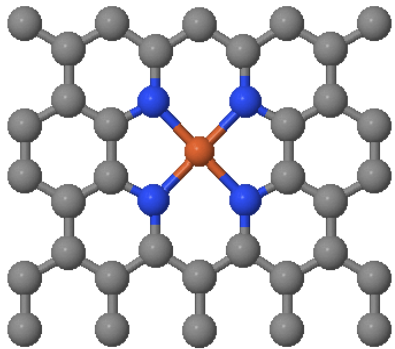
Fe-N_2
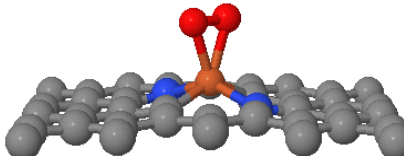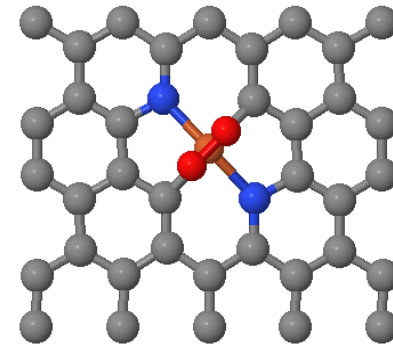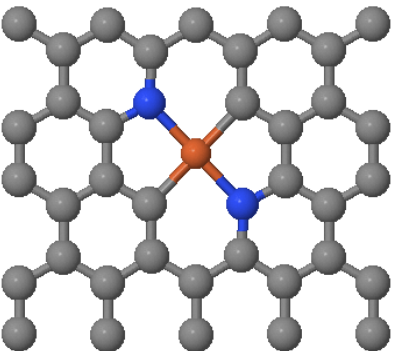
- Defects only stable in the presence of Fe.

- E_{for}(Fe-N_2/C) > E_{for}(Fe-N_4/C)
  - ➔ Fe-N_4/C: low temperature.
  - ➔ Fe-N_2/C more abundant at high temperature.

- O_2, Fe-N_x geometry depend on nitrogen content:
  - ➔ FeN_4/C: high angle.
  - ➔ FeN_2/C: parallel to sheet.

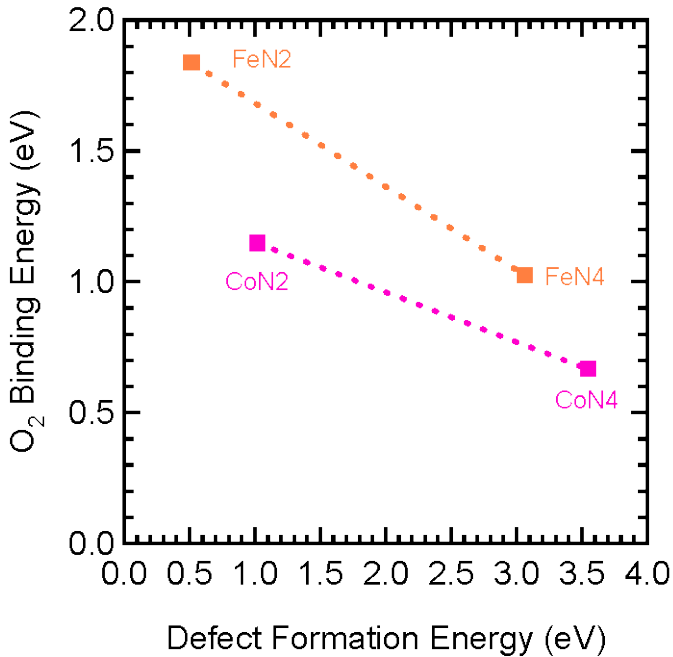- E_B(O_2): depends on N content.

Co – N$_x$/Graphene System (UNM)

Co-N$_4$
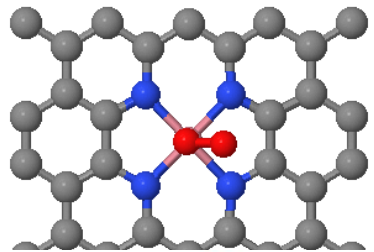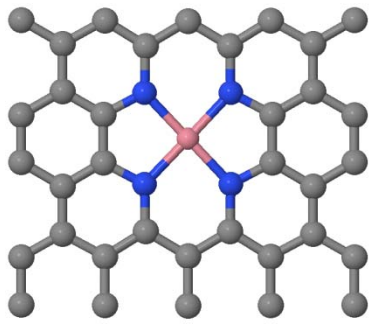
Co-N$_2$
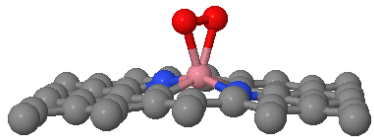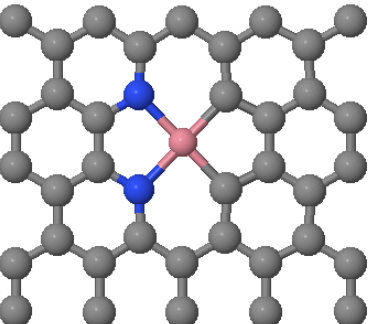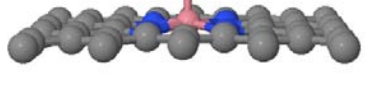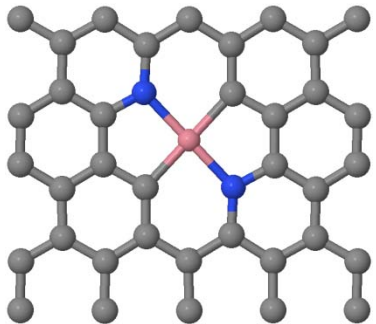
- Defects only stable in the presence of Co.
- Very similar trends to Fe defect.

Defect Engineering;
- **Higher formation energy ➜ lower O$_2$ 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 Anlaysis 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
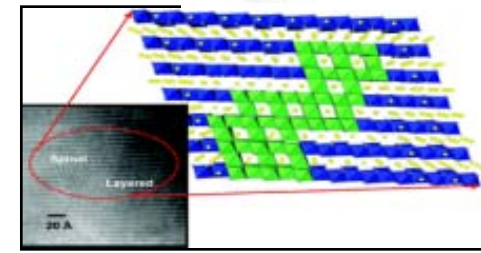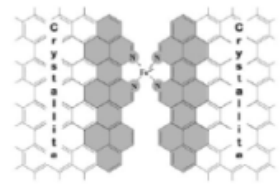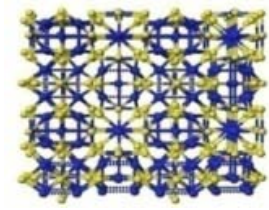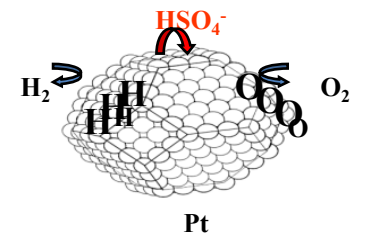
Brief Background on Current State of the Art in Non PGM Catalysis

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

Obtained by heat treatment of organic and transition metal precursors
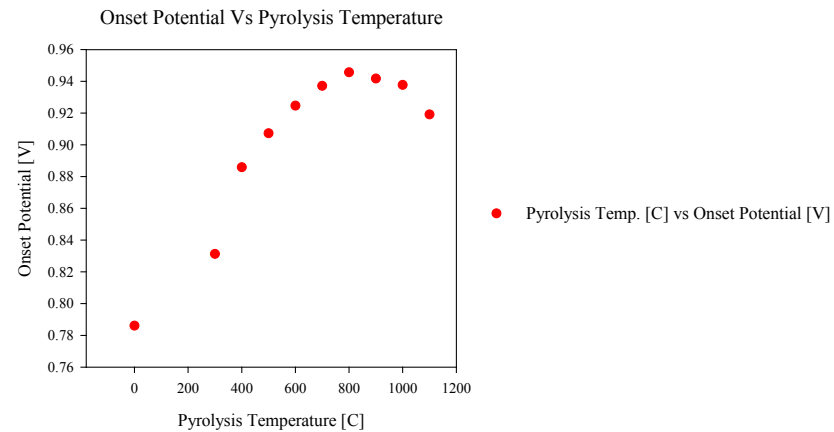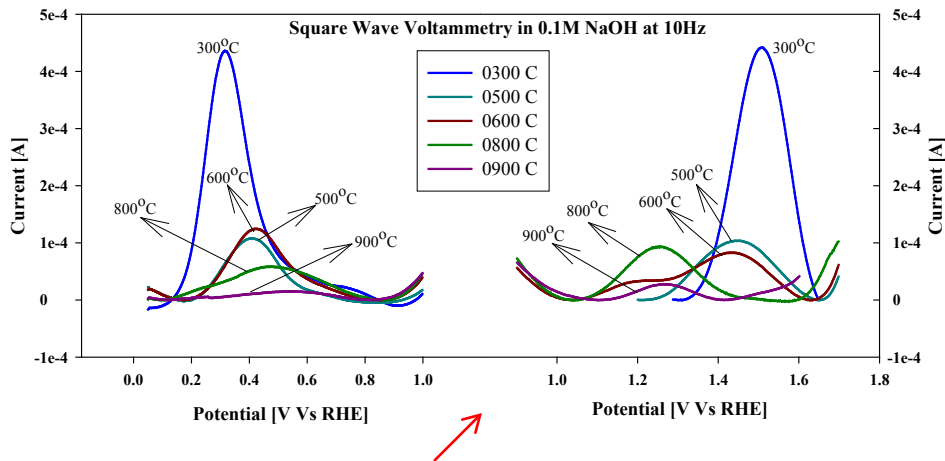
shift of oxidation potential towards higher towards higher values

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 (CNx)
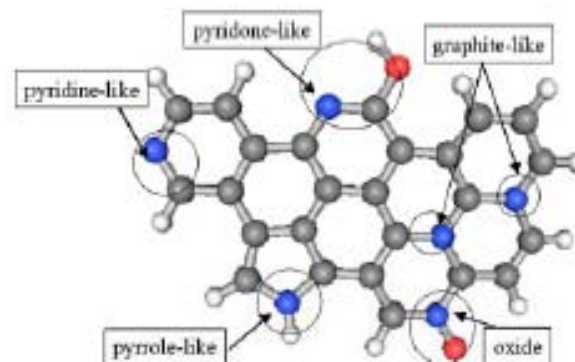
- Two types of micropore-hosted active sites proposed:
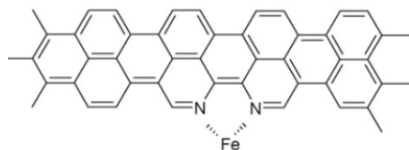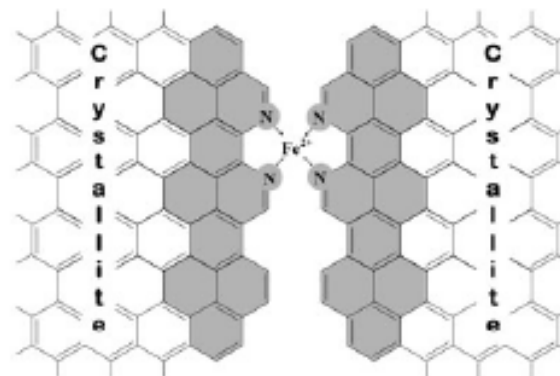
 Metal-N2+2/C   Metal-N4/C
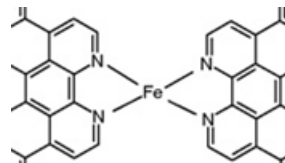
Metal Organic systems

ORR active site concept:

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

- planetary ball-milling
- 2-step pyrolyzis: 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)

Lefèvre *et al, Science,* 324, 71, 2009
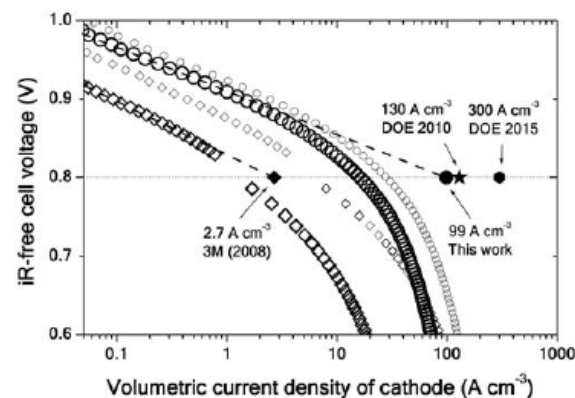
Metal Organic systems:
Fe-Cyanamide/C

- 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)
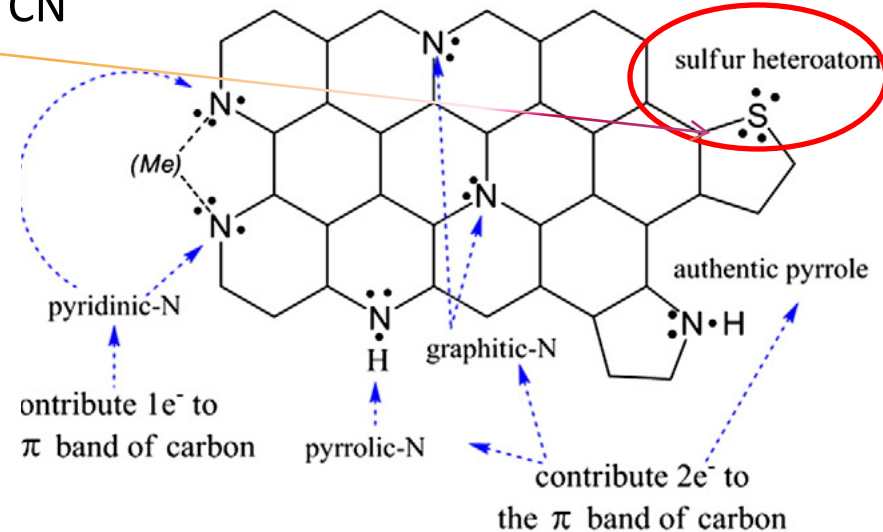
- Stability problem

Chung et al. ECS Transactions, 25 (1) 485-492 (2009)
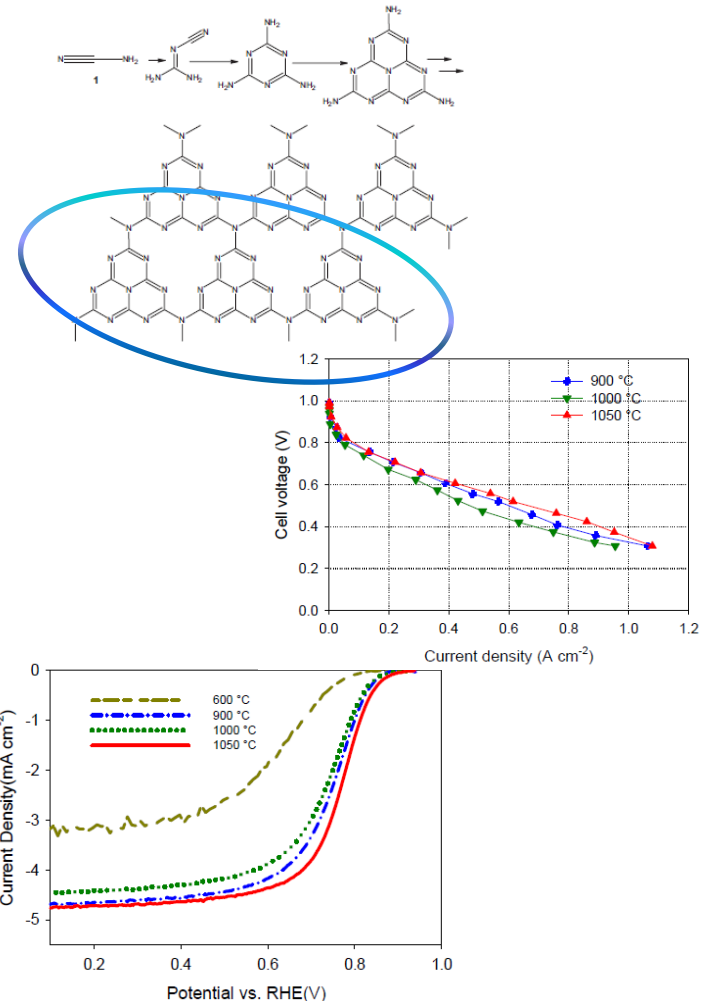
Cyanamide-based M/N/C catalysts Zelenay 2009-2010

- 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

sulfur heteroatom

authentic pyrrole

pyridinic-N

graphitic-N

contribute 1e⁻ to π band of carbon

pyrrolic-N

contribute 2e⁻ to the π band of carbon

Chung et al. Electrochem. Comm., 12 (2010) 1792-1795

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


- C
- H
- N
- Co^{δ} ($0 \leq \delta \leq +2$)

Wu et al. ECS Transactions, 25 (1) 1299-1311 (2009)
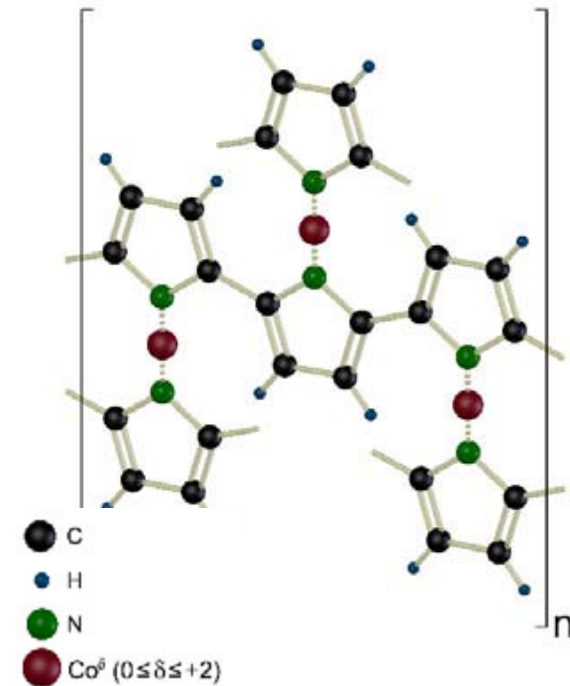
Fe(Co)-PANI-C composites
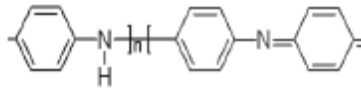
Polyaniline(PANI)

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

Wu et al. ECS Transactions, 25 (1) 1299-1311 (2009)
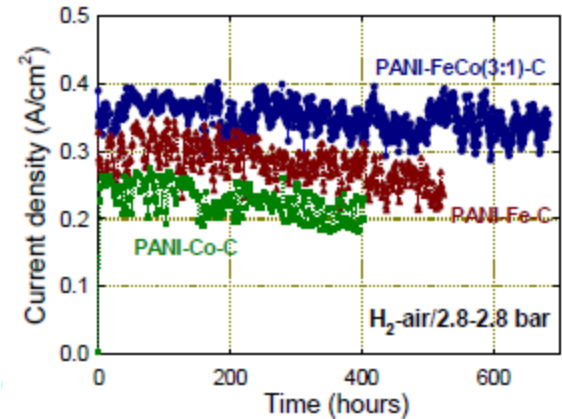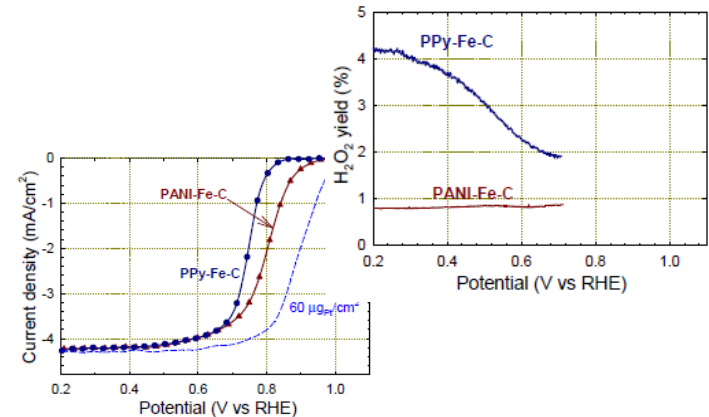
Transition Metal Chalcogenide

- ## CoSe/C
  - Prepared by microwave-assisted polyol method
  - 20% loading
  - Poor stability in acidic media
  - Tolerant to alcohol and formic acid
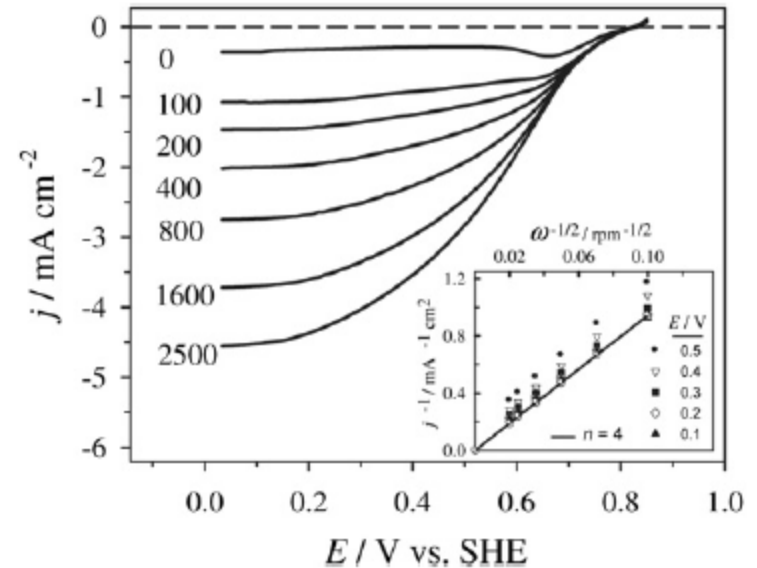
Most work in this area is with Pt group metals so I did not include it

Parisa Nekooi, Int J of Hydrogen Energy, **2010**, *35, 6392-6398.*

EXAFS analysis – study of catalytic site structure
A Representative Study using Co(II) TPP Pyrolyzed Catalyst

Co(II)TPP

● **Co**

● **N**

● **C**
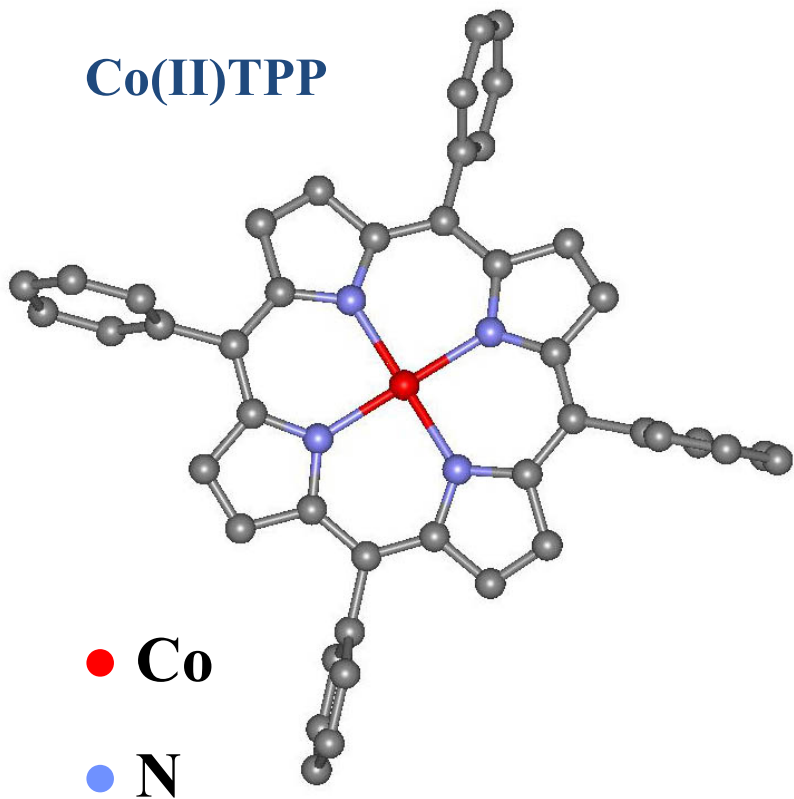
➢ Metal porphyrins – similar to heme groups present in proteins systems

M-N4 planar structure – very selective 4e ORR

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

➢ Pyrolized 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
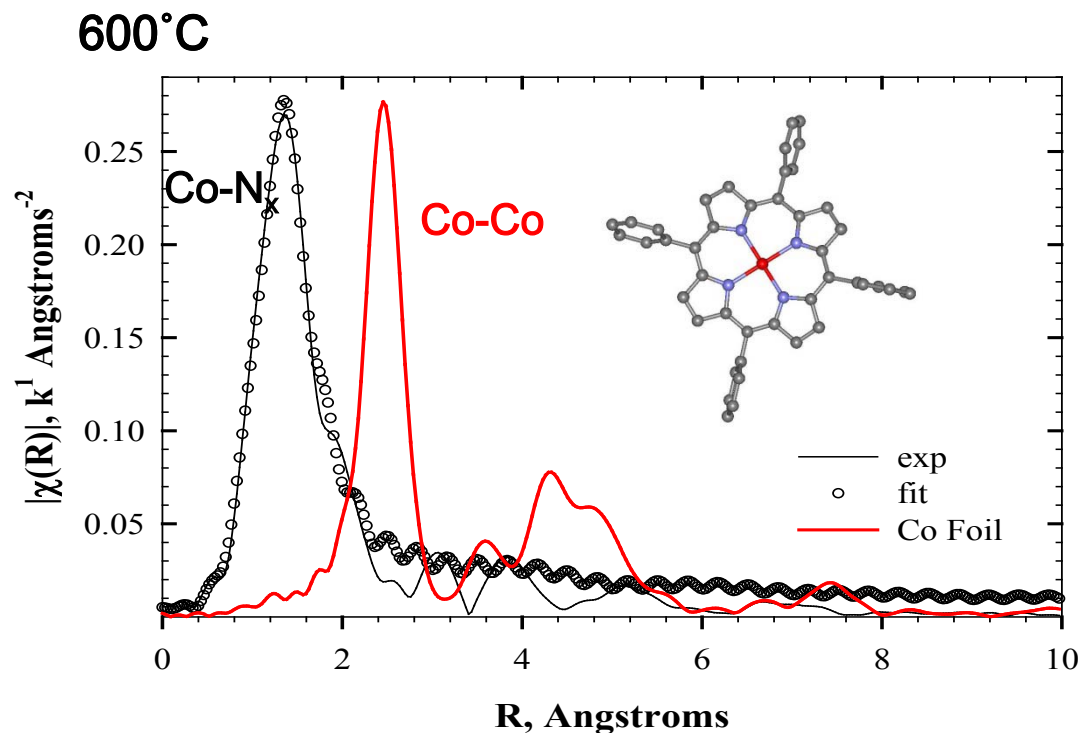
600°C

0.40 V FT Fitting – no adsorbates on the surface

Material	N_{Co-N}	N_{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/**

J. Ziegelbauer, T. Olson, S. Plylypenko, F. Alamgir, C. Jaye, P. Atanassov, and S. Mukerjee, *J. Phys. Chem.,* C **112**, 8839 (2008)

$$\Delta\mu = \mu(CoN_xC_yO) - \mu(CoN_xC_y)$$

N-coordination	Clean	"axial" O_{ads}	"equatorial" O_{ads}

N=4

N/A

N=3

N=2

● Co   ● N   ● O   ● C

J. Ziegelbauer, T. Olson, S. Plylypenko, F. Alamgir, C. Jaye, P. Atanassov, and S. Mukerjee, *J. Phys. Chem.,*C **112**, 8839 (2008)
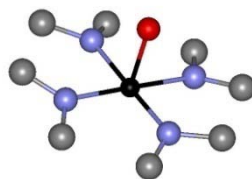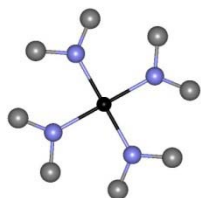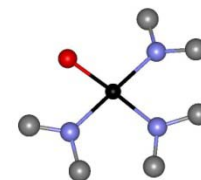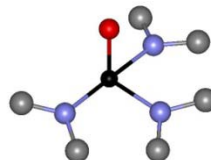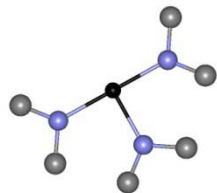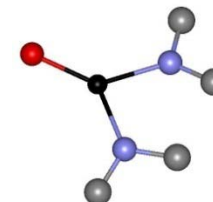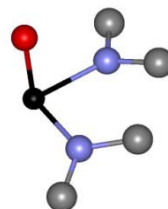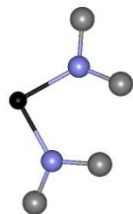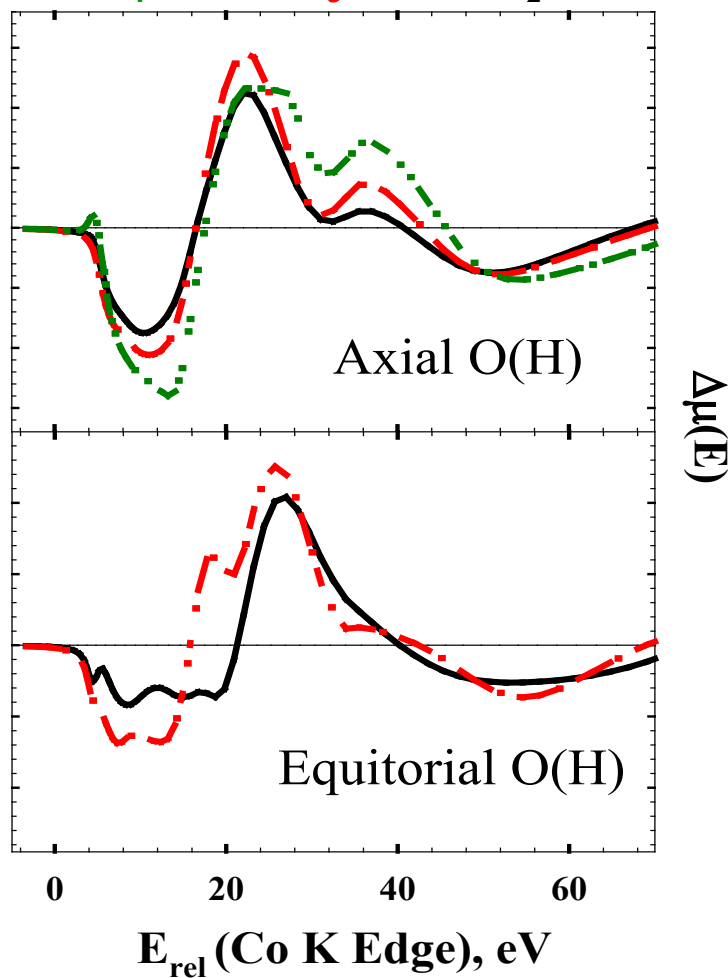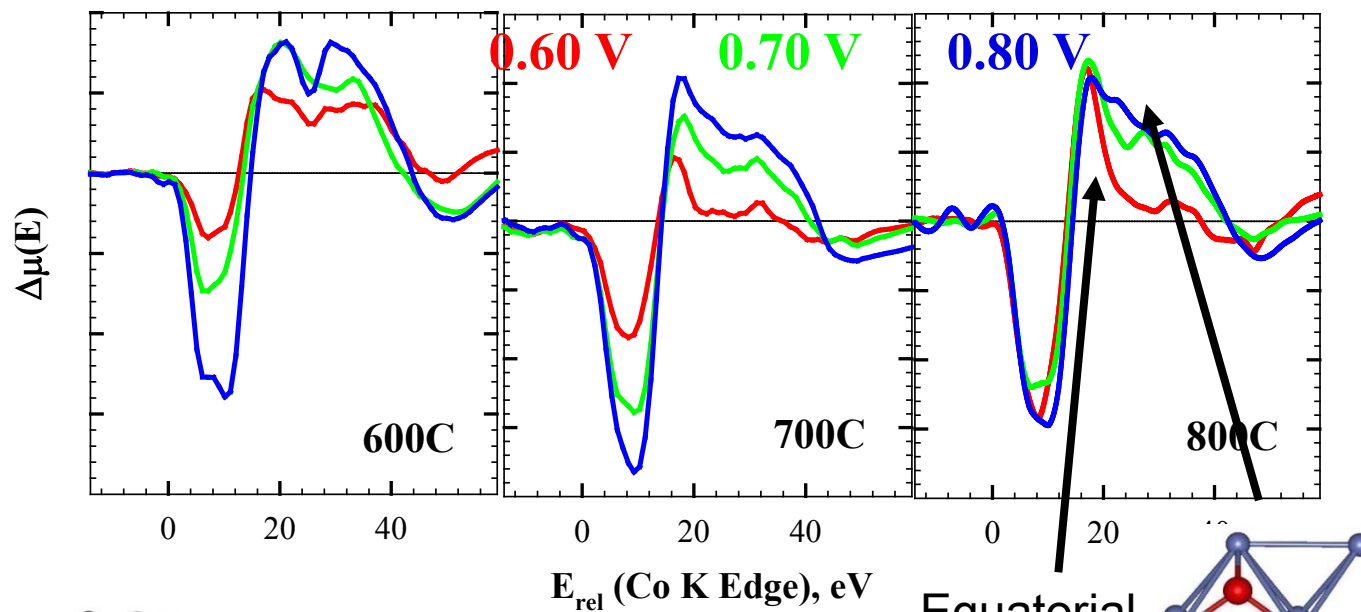
FEFF Results

Axial-O

- Double peak after minimum

- Difference increases with loss of N

Equitorial-O

- N=2: Broad minimum, tailing maximum

- N=3: Reversed (from axial) double peaks
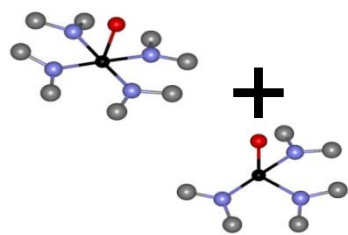
- Both: "Flattened" minimum

J. Ziegelbauer, T. Olson, S. Plylypenko, F. Alamgir, C. Jaye, P. Atanassov, and S. Mukerjee, *J. Phys. Chem.,*C **112**, 8839 (2008)

Pyrolyzed Co-based Porphyrins:

0.60 V **0.70 V** **0.80 V**

$\Delta\mu(E)$

600C   700C   800C

E_{rel} (Co K Edge), eV

Equatorial

All axial

Axial +
Equatorial

Co
Oxides

Key points:

Co-N$_4$ = axial O$_{ads}$

Axial O$_{ads}$
↓
efficient 4e$^-$ ORR

J. Ziegelbauer, T. Olson, S. Plylypenko, F. Alamgir, C. Jaye, P. Atanassov, and S. Mukerjee, *J. Phys. Chem.,*C 112, 8839 (2008)
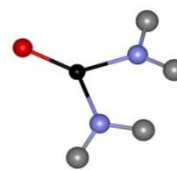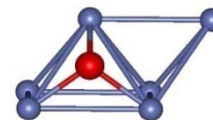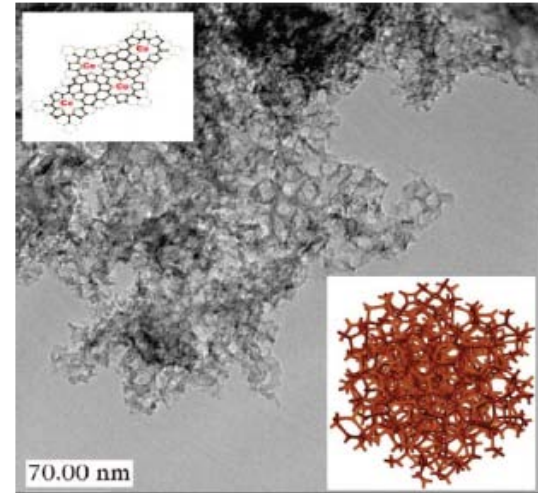
Support Materials

- 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

- Graphene Sheets
  - High surface area
  - Many edge sites an 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

Joseph M. Ziegelbauer. , J. Phys Chem C **2008**, *112, 8839-8849.*
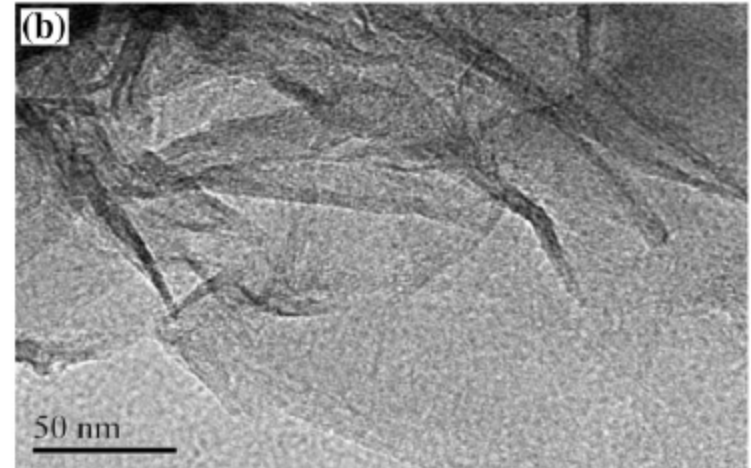
Ki Rak Lee. Electrochemistry Communications, **2010**, *12, 1052-1055.*

Effect of Pore Formation in C-Supports
MNC catalysts based on ammonia precursors (MSU)
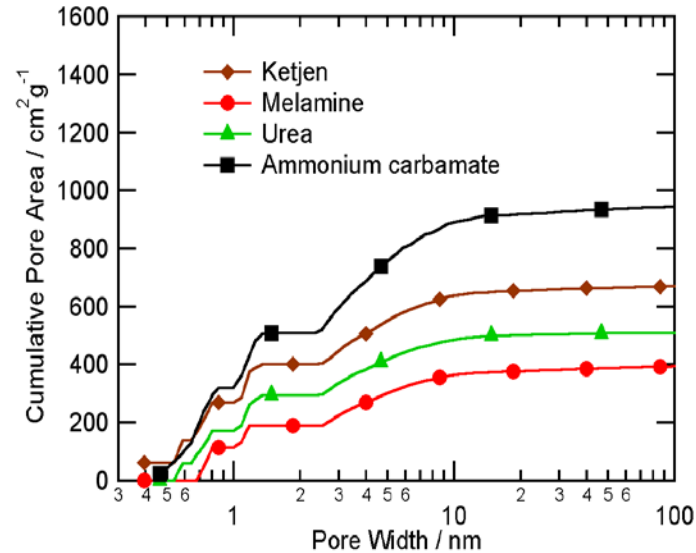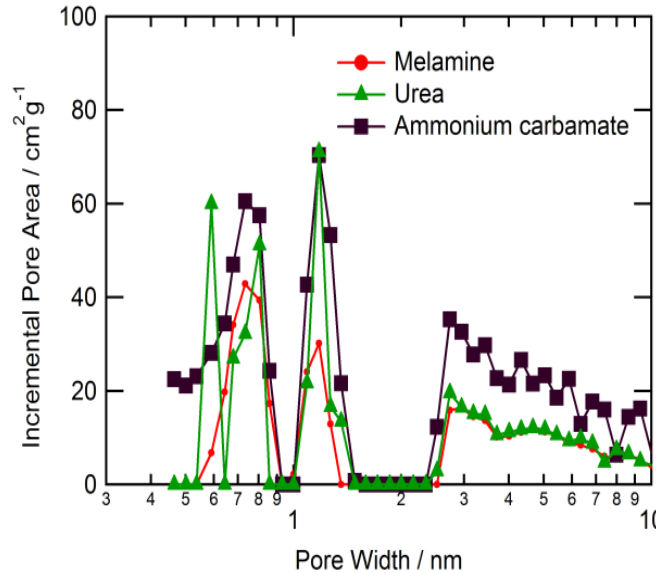
- Increase in surface area was observed for ammonia based precursors due to carbon etching resulting in increase of porosity

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.
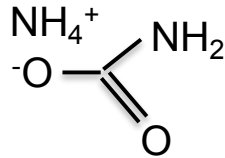- MEAs were prepared with NRE211as the electrolyte and JMFC GDE anodes.

Precursors

Melamine ($C_3H_6N_6$)
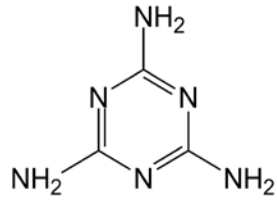
N/C ratio – 2.0

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_2SO_4
Temperature	Room Temp	40 C
Rotation speed	2500, 1600, 900, 400	1200
Loading	37.75 $\mu g_{(cat)}/cm^2$	0.5 $mg_{(cat)}/cm^2$
Scan rate	10 mV/s	0.5 mV/s

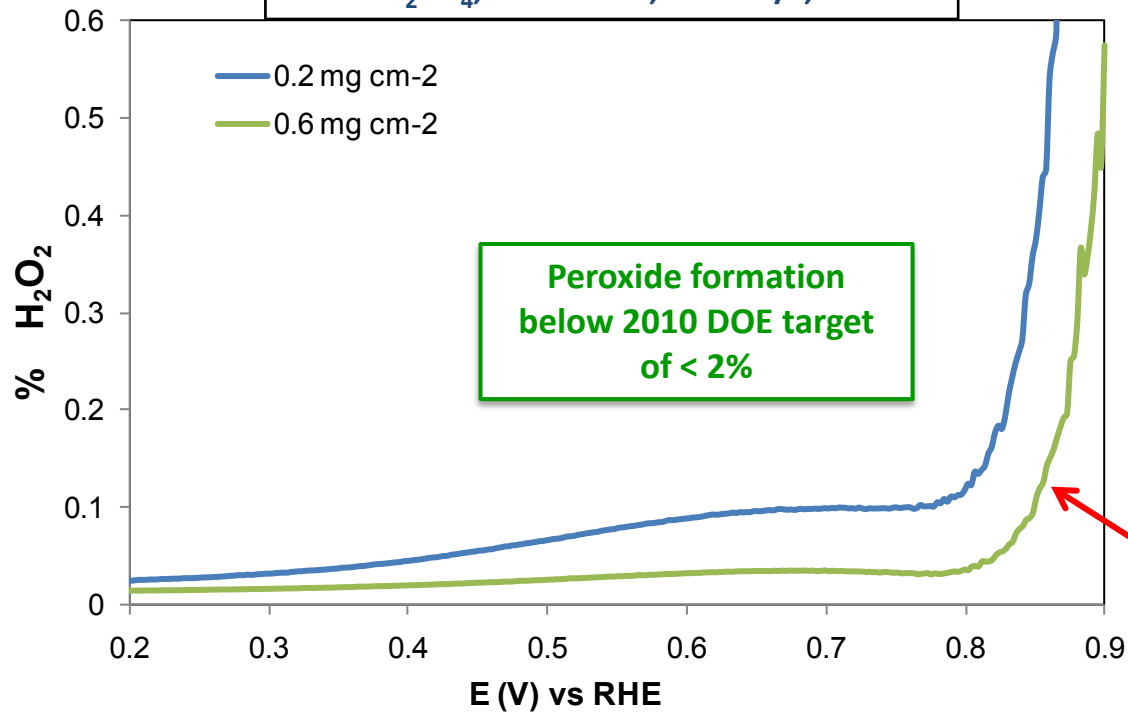**DOE Technical targets for non-precious metal catalysts** [*]

- Activity toward oxygen reduction reaction – **130 A/cm³** at $0.8V_{iR-free}$ vs. RHE (2010)

  300 A/cm³ at $0.8V_{iR-free}$ vs. RHE (2015)

- Selectivity towards water formation – < 2% H_2O_2 generation

- Durability – 2000 hr lifetime

[*] http://www1.eere.energy.gov/hydrogenandfuelcells/fuelcells/

45

NTCNA-FH
Fuel Cell Laboratory

II.RRDE
Melamine based Catalyst

0.5 M H_2SO_4, 1200 RPM, 0.5 mV/s, RT

— 0.2 mg cm-2
— 0.6 mg cm-2

Peroxide formation below 2010 DOE target of < 2%

Y-axis: **% H_2O_2** (0 to 0.6)
X-axis: **E (V) vs RHE** (0.2 to 0.9)

Equations used

$$n = 4I_D/\left(I_D + \left(I_R/N\right)\right)$$

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

Where,
N= collection Efficiency = 25.6%

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

Pathways for O_2 reduction

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$$
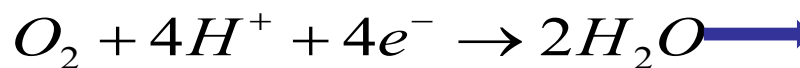
This path is favorable →Low peroxide formation

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \rightarrow 2H^+ + 2e^- \rightarrow 2H_2O$$
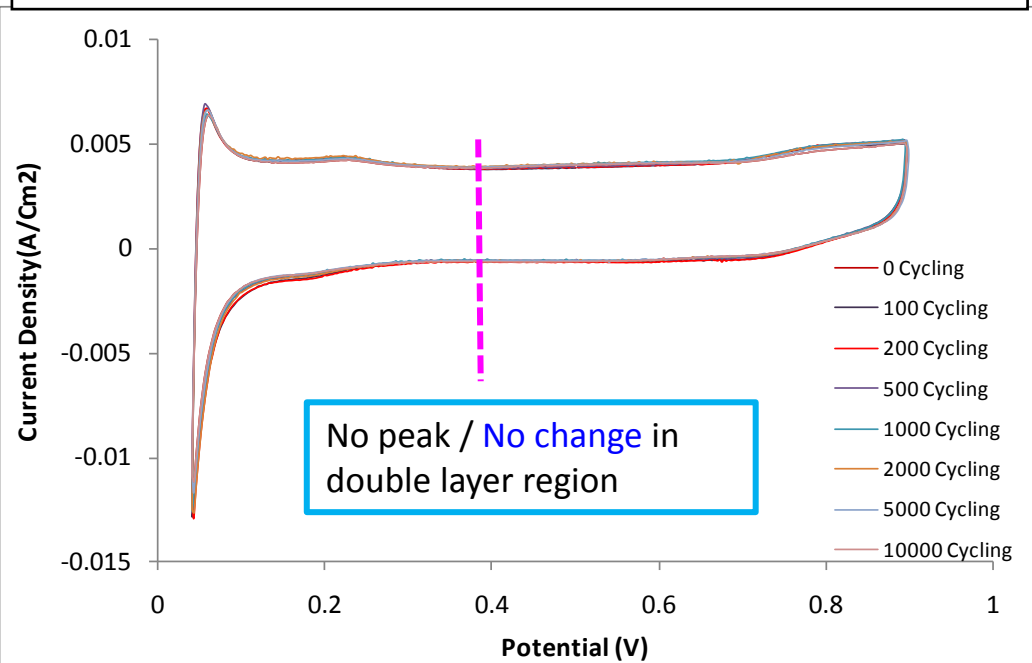
II. Catalyst Durability

- 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
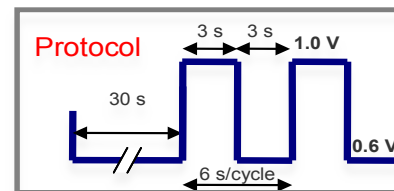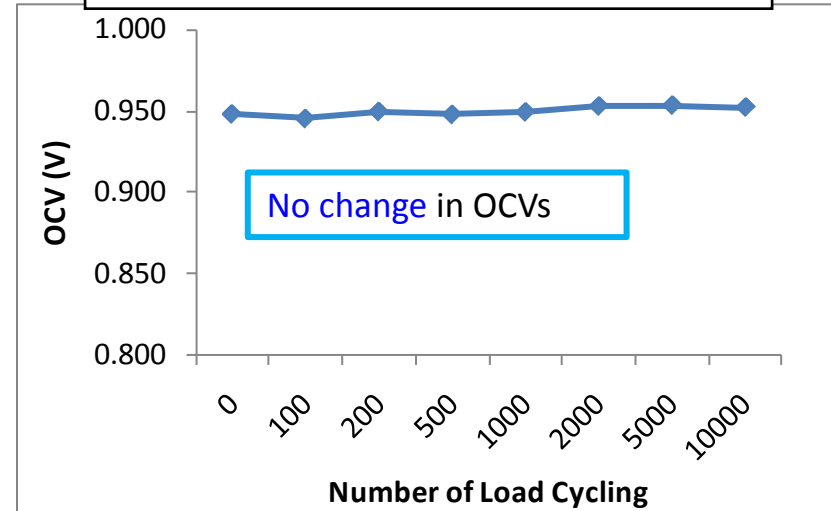 - OCV and CV were measured during cycling.

II. Catalyst Durability
MSU's MNC –Pt Dissolution test

H₂ = 0.5 L/min, N₂ = 0.5 L/min , 80 ºC, 0.6V – 1 V vs. RHE

H₂ = 0.5 L/min, O₂ = 0.5 L/min , 80 ºC

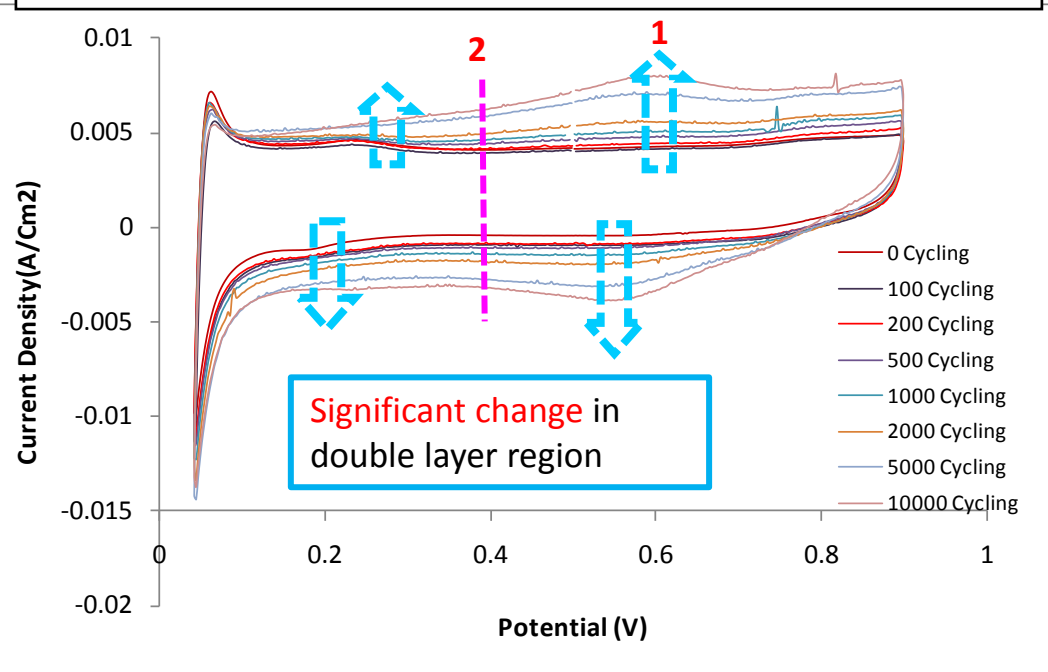No peak / No change in double layer region

No change in OCVs

Protocol

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

II. Catalyst Durability
MSU's MNC –Carbon Corrosion

H₂ = 0.5 L/min, N₂ = 0.5 L/min , 80 ºC, 1 V – 1.5 V vs. RHE

$H_2 = 0.5$ L/min, $N_2 = 0.5$ L/min , 80 ºC, 1 V – 1.5 V vs. RHE

H₂ = 0.5 L/min, O₂ = 0.5 L/min , 80 ºC

Significant change in double layer region

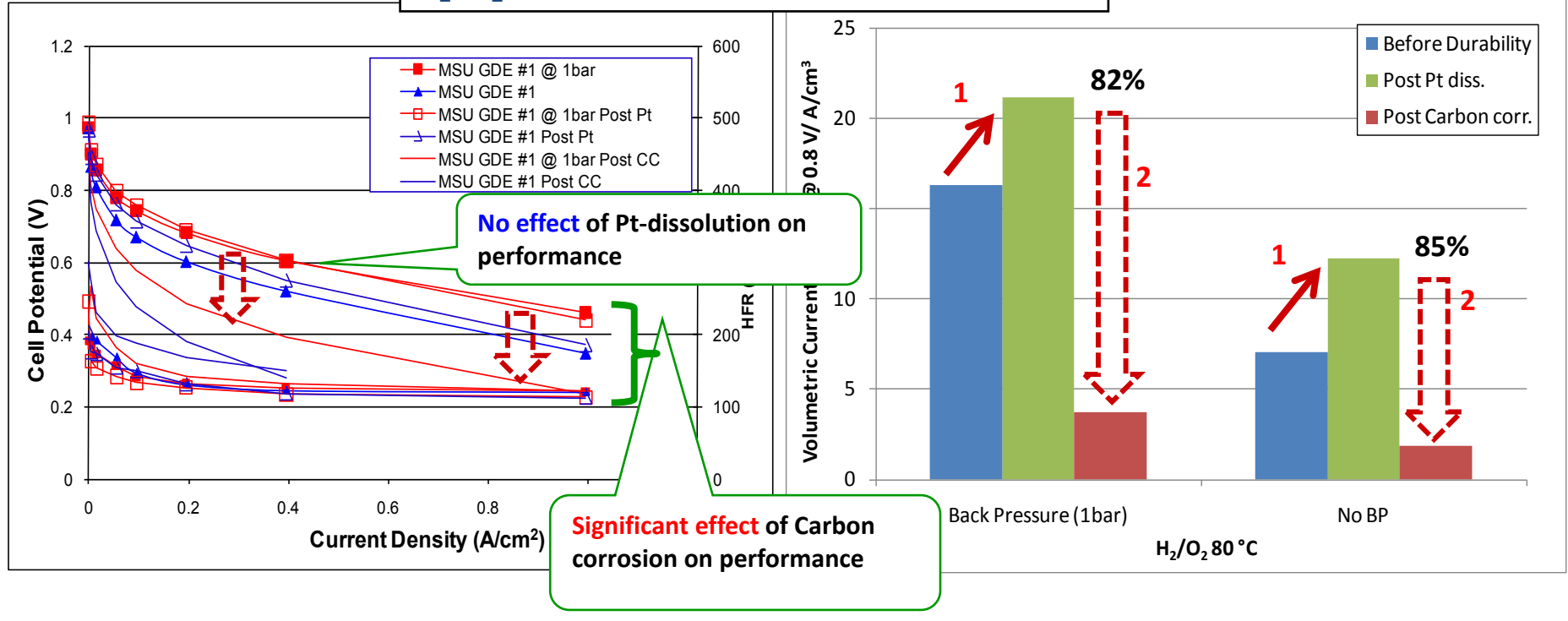Significant OCV drop after 200 cycles

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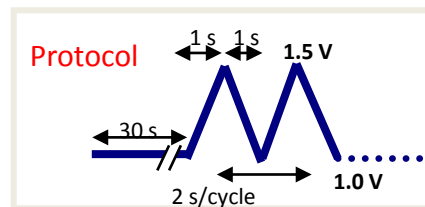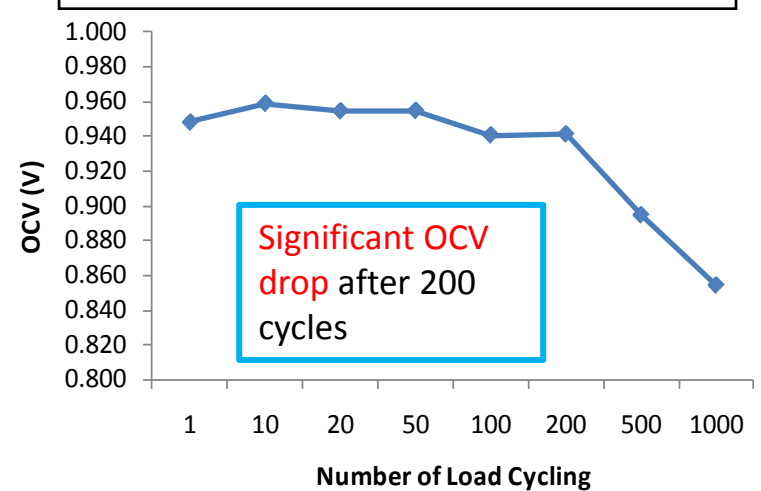
1. **Oxidation peak appears at 0.6 V. Similar phenomena was observed in Pt/C catalyst (HSAC) with Start/Stop cycling.**
2. **Double layer capacitance (Cdl) increases as number of potential cycling increases.**
   - This increase in DL can be attributed due to formation of electro-active surface oxides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

No effect of Pt-dissolution on performance

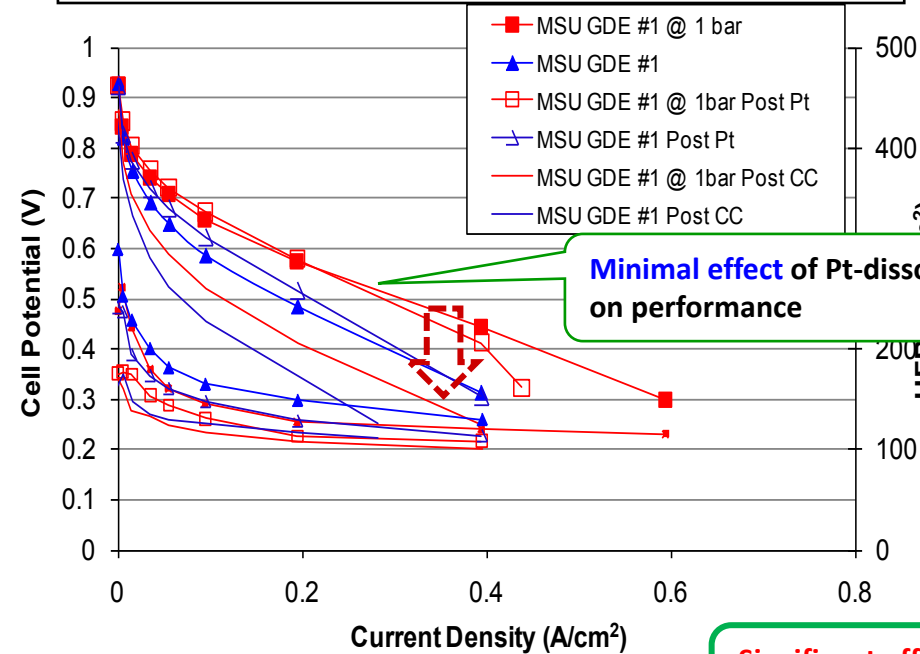**Significant effect** of Carbon corrosion on performance

1. **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.**
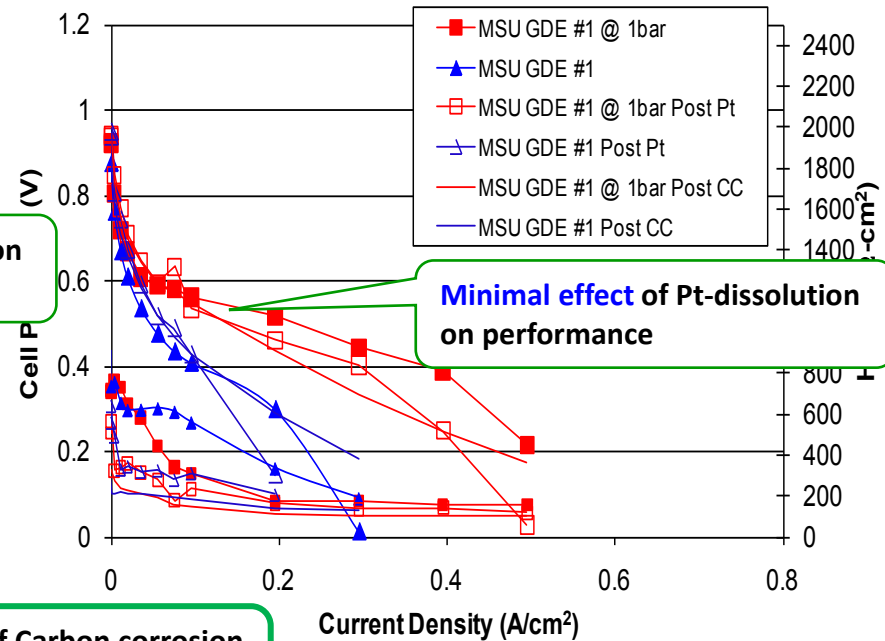2. **Loss of electronic contact and electrode integrity can be attributed to such loss in activities**

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II. Catalyst Durability

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

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

H₂/Air, 50% RH, 80°C

Minimal effect of Pt-dissolution on performance

Significant effect of Carbon corrosion on iV performance

- **Carbon corrosion severely deteriorates the iV performance at all current densities 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 (~0.97 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**